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# Synthesis of 2-Nitroglycals from Glycals Using the Tetrabutylammonium Nitrate–Trifluoroacetic Anhydride–Triethylamine Reagent System and Base-Catalyzed Ferrier Rearrangement of Acetylated 2-Nitroglycals

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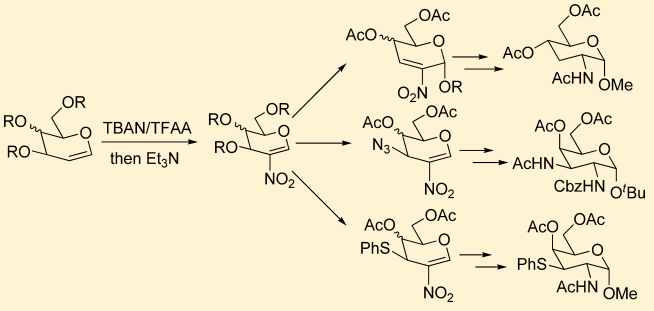
Supporting Information

**ABSTRACT:** A reagent system comprising tetrabutylammonium nitrate–trifluoroacetic anhydride–triethylamine has been developed for the synthesis of 2-nitroglycals from various protected glycals. The base-catalyzed Ferrier rearrangement on tri-*O*-acetylated 2-nitroglycals has been reported for the first time. Reactivity of these nitroacetates and associated selectivity has been examined, and some of the products have been converted into 2,3-diamino-2,3-dideoxyglycosides and methyl *N*-acetyl-D-lividosaminide.



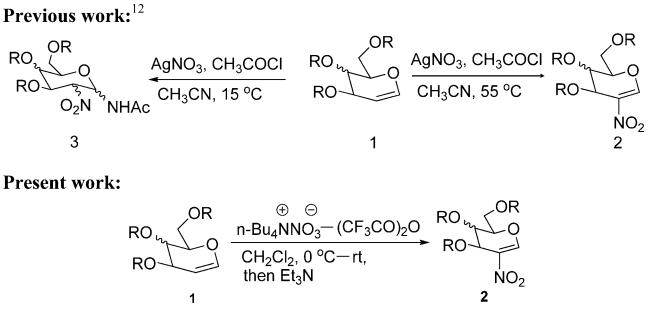

## INTRODUCTION

The 2-nitroglycals have been recognized as important synthons in carbohydrate chemistry in the recent past.[1] This is because of the presence of a conjugated nitroolefin and an enol ether moiety that offer many possibilities of synthetic manipulations. For example, such a combination makes these substrates useful for the Michael addition, Diels–Alder reactions, (2 + 3) cycloadditions etc.[1,2] In addition, the nitro group can be converted into many other useful functionalities such as a carbonyl and an amino group, apart from it being reductively removed.[2] As a result, the 2-nitroglycals have been utilized as excellent glycosyl donors[1,3] in the synthesis of glycoproteins,[4] glycosyl amino acids,[5] and aminosugars.[6] They are also used in the synthesis of bicyclic hybrid molecules,[5b,7] fused heterocycles,[8] C-glycosides,[9] 2C-branched sugars,[10] etc. While a number of methods have been reported[2] for the preparation of conjugated nitroalkenes, the synthesis of 2-nitroglycals is not well-reported in the literature. Most of the reported reactions[3a,11] either employ harsh conditions or the reagents are expensive, and hence, there is a need for developing better alternatives given the synthetic potential of 2-nitroglycals.

## RESULTS AND DISCUSSION

We have recently reported a reagent system comprising of acetyl chloride–silver nitrate–acetonitrile[12] which allows conversion of glycals into the corresponding 2-nitroglycals as well as 2-nitro-1-acetamides depending on the experimental conditions. As we are mainly interested in the synthesis of 2-nitroglycals and thus avoid the formation of nitroacetamide byproducts occurring via acetonitrile attack at the carbocation, we considered using other organic solvents. The change of nitronium ion source thus became necessary since silver nitrate is only soluble in acetonitrile. Therefore, we decided to use tetrabutylammonium nitrate (TBAN), as a precursor for nitronium ion, which is soluble in many organic solvents. In this paper, we report our results on the development of a reagent system TBAN–trifluoroacetic anhydride (TFAA)–$Et_3N$, which gives exclusively 2-nitroglycals from glycals (Scheme 1), thus avoiding the formation of nitroacetamides.[12]

**Scheme 1. Methods for Conversion of Glycals to 2-Nitroglycals**




It is assumed that in the present reagent system, nitronium trifluoroacetate species **D** is generated in situ which reacts with an olefin to form nitro trifluoroacetate **F** via a carbocation **E** as shown in Scheme 2. Thus, treatment of an olefin with TBAN–TFAA[13] only and monitoring the progress of the reaction by thin-layer chromatography indicated formation of more than

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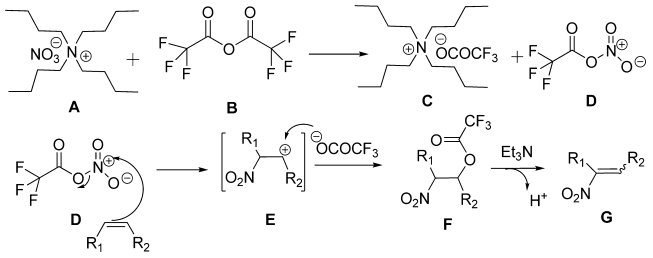
**Scheme 2. Tentative Mechanism for the Formation of Nitroolefins**



two products, and we assumed these to be a mixture of nitro trifluoroacetates. Attempts to isolate these products led to substantial decomposition. Hence, once the starting material was completely consumed, based on TLC monitoring, 1.0 equiv of $Et_3N$ was added into the same pot to cause elimination of the trifluoroacetate moieties to form nitroolefin **G** as a single product.

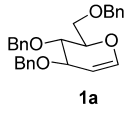
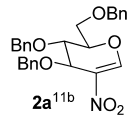
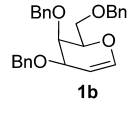
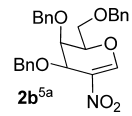
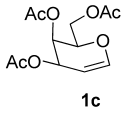
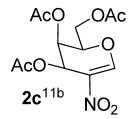
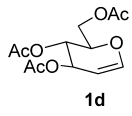
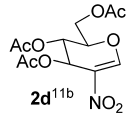
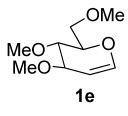
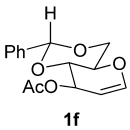
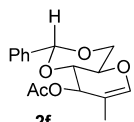
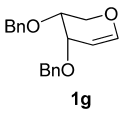
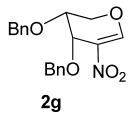
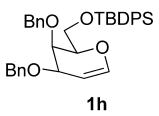
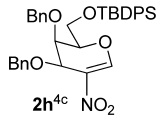
The standardized experimental conditions require the use of 1.1 equiv of TBAN, 1.1 equiv of TFAA, followed by addition of 1.0 equiv of $Et_3N$ per 1.0 equiv of the olefin. Several glycals were successfully converted to the corresponding 2-nitroglycals in moderate to fairly good yields. Our results are summarized in Table 1. 3,4,6-Tri-*O*-benzyl and 3,4,6-tri-*O*-acetyl glycals viz. **1a**, **1b**, **1c**, and **1d** were converted to the corresponding 2-nitroglycals **2a**, **2b**, **2c**, and **2d**, and their spectral data were in agreement with the reported data.[5a,11b]

In addition, we also performed the reaction of 3,4,6-tri-*O*-methyl-D-glucal **1e**, 4,6-*O*-benzylidene-D-glucal **1f**, and 3,4-di-*O*-benzyl-D-arabinal **1g** to obtain the 2-nitroglycals **2e**, **2f**, and **2g**, respectively. The structures of these products were confirmed from their spectral data. Thus, typically, in their $^1$H NMR spectra the presence of a singlet for the C-1 olefin proton at $\delta$ 8.12−8.17 was observed. The IR spectra showed a strong peak at 1501−1509 cm$^{-1}$, which is characteristic of an unsaturated nitro group. Likewise, the −OTBDPS-protected galactal **1h** was subjected to these reaction conditions to obtain the corresponding 2-nitroglycal **2h** in fairly good yield. These examples clearly show that the acid-sensitive groups were not affected in these reactions, and thus, this reagent system is more mild and efficient as compared to previously reported methods.

This reagent system was also used to examine the reactivity of some non-carbohydrate olefins. Thus, cyclohexene **3a**, 2,3-dihydropyran **3b**, styrene **3c**, and *trans*-stilbene **3d** were successfully converted to the corresponding conjugated nitroolefins **4a**, **4b**, **4c**, and **4d** in moderate to fairly good yields whose spectral data matched with the literature reported data[14a−c,9b] (Table 2). Interestingly, when *trans*-stilbene was treated with this reagent system, the product obtained was *cis*-$\alpha$-nitrostilbene **4d**. This was confirmed from its $^1$H NMR spectrum and literature comparison, where olefinic proton appears at $\delta$ 8.2 ppm for the *cis*-$\alpha$-nitrostilbene but in the case of *trans*-$\alpha$-nitrostilbene it appears at $\delta$ 6.8 ppm.[14d,e]

Although the chemistry of benzyl-protected 2-nitroglycals has been extensively studied by others as well as by us,[1,3−5,6b,7−10] the chemistry of acetylated nitroglycals is surprisingly not very well known in the literature. In continuation of our interest in exploring the chemistry of 2-nitroglycals, and with the present results in hand, we wanted to study the nucleophilic additions on acetylated 2-nitroglycals. As the Ferrier rearrangement[15] is an important method to obtain *O*-glycosides from glycals, it was of interest to us to investigate

**Table 1. Reactions of Various Glycals Using the Reagent System TBAN−TFAA−$Et_3N$**

| Entry | Substrate | Product | % Yield |
|---|---|---|---|
| 1 |  **1a** |  **2a**[11b] | 62 |
| 2 |  **1b** |  **2b**[5a] | 72 |
| 3 |  **1c** |  **2c**[11b] | 68 |
| 4 |  **1d** |  **2d**[11b] | 56 |
| 5 |  **1e** |  **2e**[11b] | 61 |
| 6[a] |  **1f** |  **2f** | 52 |
| 7 |  **1g** |  **2g** | 72 |
| 8 |  **1h** |  **2h**[4c] | 74 |

[a]Triethylamine was not used.

the hitherto unknown Ferrier rearrangement on tri-*O*-acetylated 2-nitroglycals and examine the reactivity of these nitro acetates and study the associated selectivity.

First, we treated 3,4,6-tri-*O*-acetyl-2-nitrogalactal with cyclohexanol in the presence of a Lewis acid catalyst such as TMSOTf or $BF_3{\cdot}OEt_2$, but the desired rearranged product was not formed. Next, we attempted the reaction using *t*-BuOK as a base expecting that cyclohexanol might add to the nitroolefin in a Michael addition fashion followed by the loss of the acetate group to give the Ferrier type rearranged product. Unfortunately, however, the reaction was very slow and did not improve even after stirring for 24 h. It is known in the literature that alcohols readily add to 3,4,6-tri-*O*-benzylated 2-nitrogalactal in presence of DMAP[3b] as a catalyst to give the corresponding Michael adducts. Following this protocol, addition of 0.1 equiv of DMAP to the reaction mixture gave the desired Ferrier product **6d** in 78% yield, whose structure was confirmed from $^1$H NMR and IR spectral analysis. Thus, typically a peak at $\delta$ 7.23 corresponding to C-3 olefin proton was found to appear as a doublet in its $^1$H NMR spectrum. It


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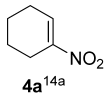
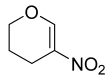
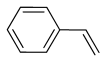
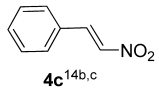
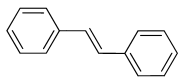
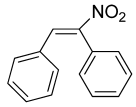
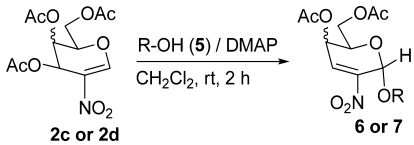
**Table 2. Reactions of Non-carbohydrate Olefins Using TBAN−TFAA−$Et_3N$ Reagent System**

| Entry | Substrate | Product | % Yield |
|---|---|---|---|
| 1 |  **3a** |  **4a**[14a] | 62 |
| 2 |  **3b** |  **4b**[9b] | 56 |
| 3 |  **3c** |  **4c**[14b,c] | 68 |
| 4 |  **3d** |  **4d**[14d] | 72 |

also showed a strong peak at 1537 $cm^{-1}$ in the IR spectrum corresponding to the stretching frequency of an unsaturated nitro group. In order to confirm the role of DMAP, we performed the reaction only in the presence of DMAP without adding an extra base, and this also led to the rearranged product in good yields. Finally, after exploring various conditions for the addition of different alcohols to acetylated 2-nitroglycals, it was found that DMAP alone was a suitable catalyst for the Ferrier rearrangement. To the best of our knowledge, this is the first base-catalyzed Ferrier rearrangement reported. Optimization studies were carried out to conclude that 10 mol % of DMAP and 1.1 equiv of an alcohol were sufficient to carry out this transformation (Scheme 3).

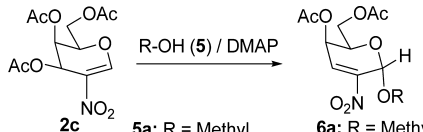
**Scheme 3. Reaction of Acetylated 2-Nitroglycals with Various Alcohols in the Presence of DMAP**




**2c or 2d** **6 or 7**

Having the reaction conditions optimized, we then examined the addition of different alcohols viz. **5a**, **5b**, **5c**, and **5e** to tri-*O*-acetyl-2-nitro-D-galactal **2c** which successfully gave the corresponding rearranged products **6a**, **6b**, **6c**, and **6e**, respectively, in moderate to fairly good yields (Scheme 4).

**Scheme 4. Addition of Various Alcohols to Tri-*O*-acetyl-2-nitrogalactal 2c**



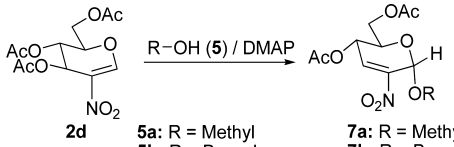

**2c**

**5a:** R = Methyl
**5b:** R = Benzyl
**5c:** R = *p*-OMeBenzyl
**5d:** R = Cyclohexyl
**5e:** R = allyl

**6a:** R = Methyl, 75%
**6b:** R = Benzyl, 68%
**6c:** R = *p*-OMeBenzyl, 84%
**6d:** R = Cyclohexyl, 78%
**6e:** R = allyl, 67%

Under the same reaction conditions, the same alcohols (**5a**−**e**) were found to add on to tri-*O*-acetyl-2-nitro-D-glucal **2d** also, and again the products (**7a**−**e**) were obtained in moderate to fairly good yields (Scheme 5).

**Scheme 5. Addition of Various Alcohols to Tri-*O*-acetyl-2-nitroglucal 2d**




**2d**

**5a:** R = Methyl
**5b:** R = Benzyl
**5c:** R = *p*-OMeBenzyl
**5d:** R = Cyclohexyl
**5e:** R = allyl

**7a:** R = Methyl, 69%
**7b:** R = Benzyl, 56%
**7c:** R = *p*-OMeBenzyl, 74%
**7d:** R = Cyclohexyl, 62%
**7e:** R = allyl, 63%

The stereochemistry of the newly generated stereocenter at the anomeric carbon in galactal series was proved by the single-crystal X-ray studies of the reference compound **6d**.[16] On the other hand, in the glucal series the stereochemistry was established by the spectral analysis, including NOE studies, of compounds **17** and **18** (Scheme 9) obtained from **7a**. The $\alpha$ selectivity observed in the alcohol addition to both glucal as well as galactal derivatives is interesting and can be explained by using a transition-state model as shown in Scheme 6.

Next, we studied the reactivity of nitrogen and sulfur nucleophiles onto **2c** and **2d**. For this purpose, $TMSN_3$ and thiophenol were used as nucleophiles. To our surprise, the azide and the thiophenol moieties were found to add at C-3, instead of forming the expected Ferrier products by nucleophilic attack at C-1. The structures of the products were confirmed from spectral studies. Thus, in the $^1H$ NMR spectrum of **9a**, the peak of C-1 olefinic proton appeared at $\delta$ 8.30, characteristic of an unsaturated nitroolefin. Further, in the IR spectrum of **9a**, a peak appeared at 2112 $cm^{-1}$ corresponding to the azide group, along with a strong peak at 1508 $cm^{-1}$, again characteristic of an unsaturated nitro group. The products of azide and thiophenol addition were obtained in fairly good yields, as summarized in Table 3. However, addition of PhSH to **2d** gave a mixture of products, as was evident from the crude $^1H$ NMR spectrum, which could not be purified as they were unstable during column chromatographic purification. The azide and SPh groups were equatorially oriented at C-3 position which was confirmed at later stages by analyzing the spectral details of some of the advanced intermediates as shown in Schemes 7 and 8.

**Proposed Mechanism.** The selectivity in this Ferrier rearrangement is believed to be entirely based on the role of DMAP, which directs the attack of nucleophiles such as alcohols, azide, and thiophenol moieties. Accordingly, the addition of DMAP should occur preferably from the $\beta$-side in a pseudo axial manner to replace the allylic acetate via $S_N2'$ mechanism resulting in the transition state **H** (Scheme 6). The oxygen nucleophiles then attack at C-1 in an $S_N2$ fashion to release DMAP to give axially oriented compounds **K** and **L**. However, in the case of $TMSN_3$ or PhSH, the attack takes place at the C-3 position through $S_N2'$ mechanism to give equatorially oriented compounds **I** and **J**. The difference in the regioselectivity can be explained on the basis of HSAB concept,[17] where oxygen nucleophiles being hard bases add on to the hard acid center C-1. On the other hand, azide and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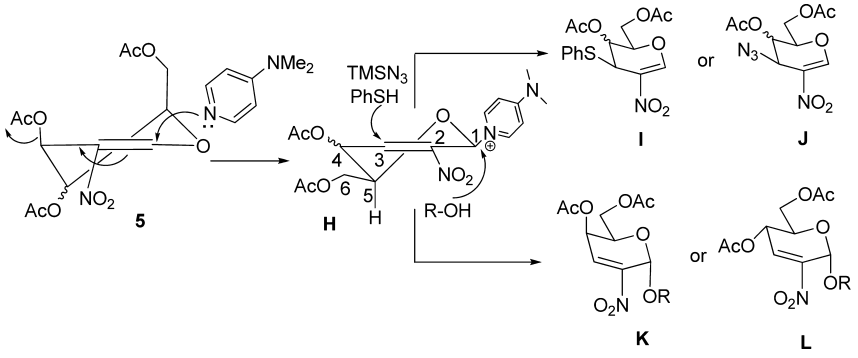
**Scheme 6. Proposed Mechanism for the Formation of C-1,C-3-Substituted Products**



**Scheme 7. Synthesis of Differentially Protected 2,3-Diamino-2,3-dideoxy Galactosides**

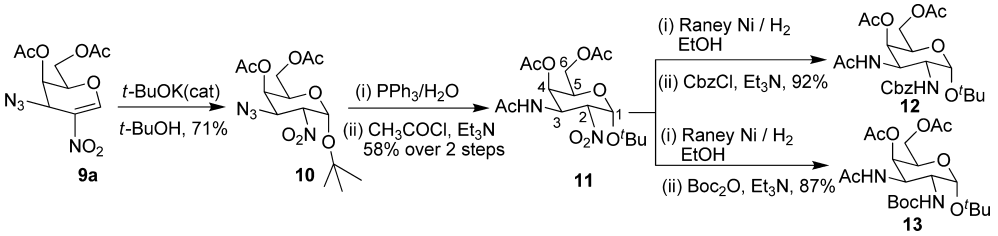
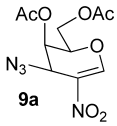
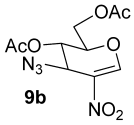
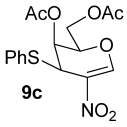


**Table 3. Addition of $TMSN_3$, PhSH to 3,4,6-tri-*O*-acetyl-2-nitroglycals 2c and 2d**

| Entry | R = -$N_3$, -SPh | Product | % Yield |
|---|---|---|---|
| 1 | $TMSN_3$ **8a** |  **9a** | 78 |
| 2 | $TMSN_3$ **8a** |  **9b** | 65 |
| 3 | PhSH **8b** |  **9c** | 86 |

thiophenol moieties are soft bases and thus prefer to add on soft acid center C-3 (Scheme 6).

**Synthesis of Differentially Protected 2,3-Diamines.** 2,3-Diamino-2,3-dideoxy sugars are integral parts of lipopolysachharides which are found in Gram-negative bacteria.[18] In the present study, it was envisaged that compound **9a** (cf. Table 3) could be a good precursor to obtain 2,3-diamino sugars. With this view in consideration, addition of *tert*-butyl alcohol to nitroolefin **9a** was carried out in the presence of a catalytic amount of *t*-BuOK. It is expected that the resulting O-glycoside could serve as a glycosyl donor, after selective deprotection[19] of the $-O^tBu$ group to a free $-OH$ at the anomeric center, followed by its activation. The desired Michael adduct **10** was obtained in 71% yield, the azido group was selectively reduced using $PPh_3/H_2O$, and the resulting amine was protected with acetyl chloride and $Et_3N$ to form the *N*-acetyl derivative **11**. The stereochemistry of the newly formed stereocenters in **11** was confirmed from the $^1H$ NMR spectral analysis ($J_{1,2}$ = 4.0 Hz and $J_{2,3}$ = 11.6 Hz), and NOE analysis (H-3/H-5, H-3/H-4, H-1/H-2) as shown in Figure 1. Reduction of the $NO_2$ group with Raney Ni followed

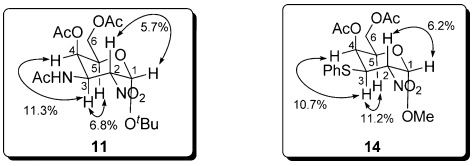


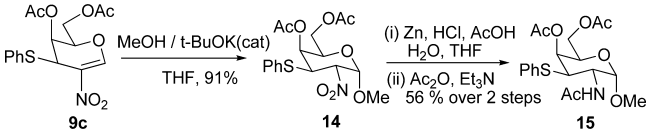
**Figure 1.** NOE analysis of compounds **11** and **14**.

by protection of the crude amine as Cbz and Boc amines using appropriate reagents as shown in Scheme 7 led to the formation of differentially protected 2,3-diamino derivatives **12** and **13**.

Likewise, compound **9c** was treated with MeOH/*t*-BuOK to give a single compound **14** in 91% yield. The stereochemistry of the newly formed centers was established with the help of $^1H$ NMR ($J_{1,2}$ = 3.9 Hz and $J_{2,3}$ = 12.5 Hz) and 2D NMR experiments, including NOE analysis (H-3/H-2, H-3/H-4, H-1/H-2) as shown in Figure 1. The final compound **15** was obtained by reducing the nitro group to amine with Zn/HCl/AcOH, followed by acetylation using $Ac_2O$ and $Et_3N$ (Scheme 8). The use of Raney Ni to reduce the nitro group was avoided as it was anticipated that the $-SPh$ group at C-3 might undergo reductive desulfurization.

**Synthesis of Methyl *N*-Acetyl-4,6-di-*O*-acetyl-α-D-lividosaminide (18).** Lividosamine is a 2-amino-2,3-dideoxyglucoside that is present in the core structure of aminoglycoside antibiotics lividomycin A and 3′-deoxykanamycin C.[20] Hence,

**Scheme 8. Synthesis of 2-Amino-3-phenylthio-2,3-dideoxy-*O*-methyl Galactoside**





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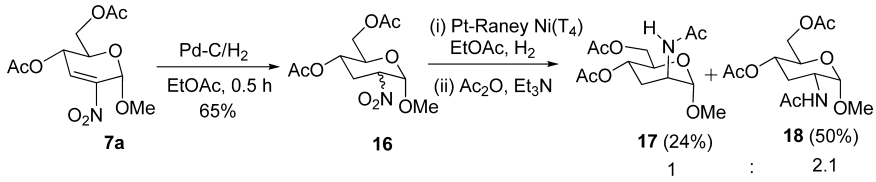
**Scheme 9. Synthesis of Methyl *N*-Acetyl-α-D-lividosaminide**




the synthesis of methyl *N*-acetyl-α-D-lividosaminide has assumed importance in recent years.[6b,21] Application of the above-described Ferrier rearrangement has been demonstrated by utilizing the product **7a** (cf. Scheme 5) for the synthesis of methyl *N*-acetyl-α-D-lividosaminide as shown in Scheme 9. Reduction of the double bond and the $NO_2$ group in one pot is a challenging task as the substrate **7a** contains acetate groups. Our initial attempts for one-pot reduction of nitroolefin with reagents such as $NaBH_4$, $BH_3{\cdot}SMe_2$,[22] and Raney Ni/$H_2$ failed to give the corresponding desired amine. However, reduction of the double bond using Pd/C−$H_2$, followed by the reduction of the nitro group with the freshly prepared platinized Raney Ni ($T_4$),[6b] gave the desired amine. The crude amine, obtained upon filtration of the catalyst, was acetylated using $Ac_2O$ and $Et_3N$. The diastereomeric mixture so obtained was separated using a chromatotron (sold by Harrison Research, USA) to give compounds **17** and **18** in a ratio of 1:2.1. The spectral data of the major isomer viz. methyl *N*-acetyl-α-D-lividosaminide **18** was identical with the literature data reported for it.[21a] The structure of the minor isomer **17** was confirmed by $^1$H NMR studies where the signal at δ 5.88 as a doublet corresponds to N−H proton. The stereochemistry of newly generated stereocenter was confirmed from NOE experiments.[16] The optical rotation value of compound **17** matches with the reported data.[21c]

Thus, methyl *N*-acetyl-α-D-lividosaminide was synthesized from 3,4,6-tri-*O*-acetyl-2-nitroglucal via base-catalyzed Ferrier rearrangement using methanol followed by simple synthetic manipulations in only four steps. To the best of our knowledge, this is the shortest and the most efficient method for the synthesis of **18** so far.

## CONCLUSIONS

A reagent system comprising tetrabutylammonium nitrate−trifluoroacetic anhydride−triethylamine (TBAN−TFAA−$Et_3N$) has been developed for efficient synthesis of 2-nitroglycals from glycals using mild reaction conditions. The first example of base-catalyzed Ferrier rearrangement in glycals with different alcohols has been reported using DMAP as a catalyst. Under the same reaction conditions, azide and thiophenol were added at C-3 position. Using this strategy, products obtained were successfully converted to differentially protected 2,3-diamino-2,3-dideoxy glycosides. Finally, a short synthesis of methyl *N*-acetyl-D-lividosaminide has been carried out in four steps.

## EXPERIMENTAL SECTION

**General Experimental Methods.** IR spectra were recorded with FT-IR as a thin film or using KBr pellets and are expressed in cm$^{-1}$. $^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra were recorded using $CDCl_3$ as a solvent. Chemical shifts are reported in ppm downfield to tetramethylsilane. Coupling constants are reported and expressed in hertz; splitting patterns are designated as br (broad), s (singlet), d (doublet), dd (double doublet), m (multiplet). Optical rotations were measured using a polarimeter at 28 °C. All reactions were carried out using freshly distilled and dry solvents. The visualization of spots on TLC plates was effected by exposure to iodine or spraying with 10% $H_2SO_4$ and charring. Column chromatography was performed over silica gel (100−200 mesh) using hexane and ethyl acetate as eluents. Mass spectra were obtained from high-resolution ESI mass spectrometer using a Q-TOF analyzer.

**General Procedure (A) for Synthesis of Nitroolefins.** To a stirred solution of olefins (0.240 mmol) and tetrabutylammonium nitrate (TBAN) (0.264 mmol) in dry $CH_2Cl_2$ (2 mL) at 0 °C under $N_2$ atmosphere was added dropwise trifluoroacetic anhydride (TFAA) (0.264 mmol). After the addition was completed, the reaction was brought to room temperature slowly and stirred for 1 h. On consumption of starting material (TLC monitoring) the reaction vessel was again cooled to 0 °C, $Et_3N$ (0.240 mmol) was slowly added and the reaction mixture stirred for 15 min. After completion of the reaction (single spot in TLC), the reaction mixture was quenched with 10 mL of ice−water. Extraction was done with $CH_2Cl_2$ (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over $Na_2SO_4$. Concentration in vacuo gave a crude residue which was purified by column chromatography to obtain pure nitroolefins.

*(2R,4aR,8S,8aS)-7-Nitro-2-phenyl-4,4a,8,8a-tetrahydropyrano-[3,2-d][1,3]dioxin-8-yl Acetate (**2f**).* Using general procedure A, compound **2f** was isolated as a white solid: mp 171−175 °C; yield 52%; $R_f$ 0.30 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +170.0 (*c* 0.20, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2921, 2851, 1753, 1636, 1509, 1374, 1350, 1264, 1226, 1092 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.47−7.36 (m, 5H), 6.38 (d, *J* = 7.6 Hz, 1H), 5.55 (s, 1H), 4.51 (dd, *J* = 5.2, 10.7 Hz, 1H), 4.12 (dd, *J* = 5.2, 10.4 Hz, 1H), 4.05−4.02 (m, 1H), 3.92 (t, *J* = 10.4, 1H), 2.10 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.5, 156.0, 136.0, 129.5, 128.4, 126.1, 101.7, 71.0, 67.3, 64.5, 20.8; HRMS calcd for $C_{15}H_{15}NNaO_7$ $[M + Na]^+$ 344.0746, found 344.0746.

*(3S,4S)-3,4-Bis(benzyloxy)-5-nitro-3,4-dihydro-2H-pyran (**2g**).* Using general procedure A, compound **2g** was isolated as a colorless oil: yield 72%; $R_f$ 0.45 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +200.0 (*c* 0.95, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2924, 2870, 1635, 1501, 1455, 1343, 1279, 1225, 1090 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.39−7.27 (m, 10H), 5.00−4.99 (m, 1H), 4.93 (d, *J* = 10.6 Hz, 1H), 4.82 (d, *J* = 10.6 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.23−4.15 (m, 2H), 3.81−3.77 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 156.6, 138.0, 137.1, 131.9−127.7 (Ar-C), 74.6, 72.3, 71.8, 67.2, 64.3; HRMS calcd for $C_{19}H_{19}NNaO_5$ $[M + Na]^+$ 364.1161, found 364.1167.

**General Procedure (B) for Base-Catalyzed Ferrier Rearrangement.** To a stirred solution of an acetylated 2-nitroglycal (0.315 mmol) and an alcohol (0.347 mmol) in dry $CH_2Cl_2$ (2 mL) at room temperature under $N_2$ atmosphere was added DMAP (0.031 mmol), and the reaction mixture was stirred for 2 h. After consumption of starting material (TLC monitoring), evaporation of solvents in vacuo gave a crude residue which was purified by column chromatography to obtain pure product.

*Methyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-threo-hex-2-eno-pyranoside (**6a**).* Using general procedure B, compound **6a** was isolated as a colorless oil: yield 75%; $R_f$ 0.60 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = −70.0 (*c* 0.30, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2925, 2853, 1746, 1643, 1537, 1371, 1218, 1110, 1069 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 5.5 Hz, 1H), 5.54 (s, 1H), 5.38 (dd, *J* = 3.0, 5.8 Hz, 1H), 4.38−4.36 (m, 1H), 4.27−4.25 (m, 2H), 3.52 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.5, 169.8,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150.4, 127.8, 92.9, 66.2, 62.4, 61.8, 56.6, 20.8, 20.5; HRMS calcd for $C_{11}H_{16}NO_8$ $[M + H]^+$ 290.0876, found 290.0878.

*Benzyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-threo-hex-2-enopyranoside (**6b**).* Using general procedure B, compound **6b** was isolated as a colorless oil: yield: 68%; $R_f$ 0.40 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = −90.0 (*c* 0.40, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2927, 1748, 1537, 1371, 1353, 1222, 1061, 1026 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.38−7.31(m, 5H, Ar−*H*), 7.28 (d, *J* = 5.7 Hz, 1H, H-3), 5.77 (s, 1H, H-1), 5.38 (dd, *J* = 2.8, 5.7 Hz, 1H, H-4), 4.83 (d, *J* = 11.2 Hz, 1H, OC*H*Ph), 4.72 (d, *J* = 11.2 Hz, 1H, OC*H*Ph), 4.48−4.45 (m, 1H, H-5), 4.29−4.20 (m, 2H, H-6, H-6′), 2.12 (s, 3H, COC$H_3$), 2.09 (s, 3H, COC$H_3$); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.4, 169.7, 150.3, 136.1, 128.5−127.9 (Ar-C), 91.2, 71.3, 66.3, 62.4, 61.7, 20.7, 20.5; HRMS calcd for $C_{17}H_{19}NNaO_8$ $[M + Na]^+$ 388.1008, found 388.1007.

*(4′-Methoxyphenyl)methyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-threo-hex-2-enopyranoside (**6c**).* Using general procedure B, compound **6c** was isolated as a colorless oil: yield 84%; $R_f$ 0.35 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = −64.0 (*c* 0.50, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2937, 1748, 1612, 1536, 1515, 1370, 1354, 1248, 1223, 1060, 1029 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.28−7.25 (m, 3H), 6.90−6.88 (m, 2H), 5.74 (s, 1H), 5.37 (dd, *J* = 2.7, 5.4 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.64 (d, *J* = 10.9 Hz, 1H), 4.47−4.44 (m, 1H), 4.28−4.24 (m, 2H), 3.79 (s, 3H), 2.10 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.2, 169.8, 159.8, 150.5, 130.2, 128.2, 127.9, 114.0, 90.9, 71.0, 66.4, 62.5, 61.8, 55.3, 20.8, 20.5; HRMS calcd for $C_{18}H_{21}NNaO_9$ $[M + Na]^+$ 418.1114, found 418.1111.

*Cyclohexyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-threo-hex-2-enopyranoside (**6d**).* Using general procedure B, compound **6d** was isolated as a colorless crystalline solid: mp 101− 104 °C yield 78%; $R_f$ 0.50 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = −49.3 (*c* 0.75, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2936, 2859, 1747, 1537, 1370, 1224, 1063, 1031 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.23 (d, *J* = 5.7 Hz, 1H), 5.77 (s, 1H), 5.38 (dd, *J* = 2.9, 5.7 Hz, 1H), 4.49−4.46 (m, 1H), 4.28−4.21 (m, 2H), 3.78−3.74 (m, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 1.93−1.91 (m, 2H), 1.73−1.70 (m, 2H), 1.53−1.19 (m, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.5, 169.8, 151.0, 127.4, 90.7, 78.2, 66.2, 62.7, 61.9, 33.4, 31.5, 25.5, 24.0, 23.8, 20.7, 20.6; HRMS calcd for $C_{16}H_{23}NNaO_8$ $[M + Na]^+$ 380.1321, found 380.1321.

*Allyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-threo-hex-2-enopyranoside (**6e**).* Using general procedure B, compound **6e** was isolated as a colorless oil: yield 67%; $R_f$ 0.40 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = −54.0 (*c* 1.00, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2937, 1748, 1645, 1537, 1371, 1352, 1221, 1106, 1063, 1028 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.27 (d, *J* = 5.5 Hz, 1H), 5.97−5.89 (m, 1H), 5.71 (s, 1H), 5.39 (dd, *J* = 2.7, 5.5 Hz, 1H), 5.31 (dd, *J* = 1.2, 17.1 Hz, 1H), 5.25 (dd, *J* = 1.2, 10.4 Hz, 1H), 4.44−4.41 (m, 1H), 4.30−4.18 (m, 4H), 2.10 (s, 3H), 2.08 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.5, 169.8, 150.4, 133.1, 127.9, 118.8, 90.9, 70.1, 66.3, 62.5, 61.8, 20.8, 20.6; HRMS calcd for $C_{13}H_{18}NO_8$ $[M + H]^+$ 316.1032, found 316.1030.

*Methyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-erythro-hex-2-enopyranoside (**7a**).* Using general procedure B, compound **7a** was isolated as a colorless oil: yield 69%; $R_f$ 0.50 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +117.0 (*c* 0.35, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2938, 1745, 1612, 1534, 1370, 1231, 1109, 1029 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.17 (d, *J* = 2.1 Hz, 1H), 5.57−5.55 (m, 1H), 5.46 (s, 1H), 4.28−4.18 (m, 3H), 3.54 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 169.8, 148.1, 132.7, 128.1, 93.4, 66.3, 64.4, 62.03, 57.08, 20.79; HRMS calcd for $C_{11}H_{16}NO_8$ $[M + H]^+$ 290.0876, found 290.0876

*Benzyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-erythro-hex-2-enopyranoside (**7b**).* Using general procedure B, compound **7b** was isolated as a colorless oil: yield 56%; $R_f$ 0.45 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +128.0 (*c* 0.45, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2936, 1745, 1535, 1370, 1350, 1221, 1082, 1025 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.36−7.33 (m, 5H), 7.19 (d, *J* = 2.1 Hz, 1H), 5.70 (s, 1H), 5.58 (d, *J* = 9.4 Hz, 1H), 4.83 (d, *J* = 11.3 Hz, 1H), 4.75 (d, *J* = 11.3 Hz, 1H), 4.28−4.16 (m, 3H), 2.12 (s, 3H), 2.10 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 169.8, 148.1, 136.4, 132.9−128.4 (Ar−*C*), 91.9, 71.9, 66.5, 64.4, 61.9, 20.8, 20.7; HRMS calcd for $C_{17}H_{19}NaNO_8$ $[M + Na]^+$ 388.1008, found 388.1008.

*(4′-Methoxyphenyl)methyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-erythro-hex-2-enopyranoside (**7c**).* Using general procedure B, compound **7c** was isolated as a colorless oil: yield 74%; $R_f$ 0.30 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +165.0 (*c* 0.80, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2939, 2838, 1746, 1536, 1371, 1354, 1227, 1113, 1070 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.28−7.25 (m, 2H), 7.17 (d, *J* = 2.0 Hz, 1H), 6.89−6.87 (m, 2H), 5.66 (s, 1H), 5.57 (d, *J* = 10.6 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.66 (d, *J* = 10.9 Hz, 1H), 4.29−4.18 (m, 3H), 3.79 (s, 3H), 2.11 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 169.8, 159.7, 148.2, 132.8, 130.1, 128.4, 114.0, 91.6, 71.5, 66.5, 64.5, 62.0, 55.3, 20.8, 20.7. HRMS calcd for $C_{18}H_{21}NNaO_9$ $[M + Na]^+$ 418.1114, found 418.1110.

*Cyclohexyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-erythro-hex-2-enopyranoside (**7d**).* Using general procedure B, compound **7d** was isolated as a colorless oil: yield 62%; $R_f$ 0.50 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = −62.5 (*c* 0.25, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2936, 2859, 1747, 1682, 1536, 1369, 1350, 1222, 1109, 1059 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.14 (d, *J* = 2.3 Hz, 1H, H-3), 5.69 (s, 1H, H-1), 5.53 (dd, *J* = 2.3, 9.6 Hz, 1H, H-4), 4.30−4.27 (m, 2H, H-6, H-6′), 4.23−4.22 (m, 1H, H-5), 3.76−3.74 (m, 1H, cyclohex-*H*), 2.13 (s, 3H, COC$H_3$), 2.08 (s, 3H, COC$H_3$), 1.93−1.87 (m, 2H, cyclohex-*H*), 1.73−1.70 (m, 2H, cyclohex-*H*), 1.52−1.26 (m, 6H, cyclohex-*H*); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 169.9, 148.7, 132.2, 91.1, 78.6, 66.3, 64.6, 62.2, 33.4, 31.6, 25.5, 24.0 23.7, 20.8, 20.7; HRMS calcd for $C_{16}H_{23}NNaO_8$ $[M + Na]^+$ 380.1321, found 380.1324.

*Allyl 4,6-Di-O-acetyl-2,3-dideoxy2-nitro-α-D-erythro-hex-2-enopyranoside (**7e**).* Using general procedure B, compound **7e** was isolated as a colorless oil: yield 63%; $R_f$ 0.50 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +210.0 (*c* 0.50, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2936, 2874, 1746, 1649, 1537, 1428, 1371, 1352, 1109, 1058 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.18 (d, *J* = 2.1 Hz, 1H), 5.97−5.91 (m, 1H), 5.62 (s, 1H), 5.56 (dd, *J* = 2.1, 6.7 Hz, 1H), 5.33 (dd, *J* = 0.9, 17.4 Hz, 1H), 5.25 (dd, *J* = 0.9, 10.3 Hz, 1H), 4.32−4.20 (m, 5H), 2.13 (s, 3H), 2.10 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 169.8, 148.2, 133.1, 132.8, 118.7, 91.4, 70.6, 66.4, 64.4, 62.0, 20.7; HRMS calcd for $C_{13}H_{17}NaNO_8$ $[M + Na]^+$ 338.0852, found 338.0855.

**General Procedure (C) for the Synthesis of 9a, 9b, and 9c.** To a stirred solution of an acetylated 2-nitroglycal (0.630 mmol) and $TMSN_3$ (0.694 mmol) or PhSH (0.694 mmol) in dry $CH_2Cl_2$ (2 mL) was added DMAP (3.8 mg, 0.063 mmol) under $N_2$ atmosphere at room temperature, and the reaction mixture was stirred for 10−15 min. After the consumption of starting material (TLC monitoring), concentration in vacuo gave a crude residue which was purified by short column chromatography to obtain pure product (compounds were not very stable in column).

*((2R,3R,4R)-3-Acetoxy-4-azido-5-nitro-3,4-dihydro-2H-pyran-2-yl)methyl Acetate (**9a**).* Using general procedure C, compound **9a** was isolated as a colorless oil: yield 78%; $R_f$ 0.60 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +180.0 (*c* 0.35, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2924, 2853, 2112, 1750, 1640, 1508, 1372, 1349, 1212, 1126, 1052 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.30 (s, 1H), 5.10 (d, *J* = 1.7 Hz, 1H), 4.78 (d, *J* = 2.8 Hz, 1H), 4.34−4.28 (m, 3H), 2.11 (s, 6H) $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.3, 169.3, 155.5, 129.2, 72.9, 65.2, 61.0, 52.9, 20.7, 20.6. HRMS calcd for $C_{10}H_{12}NaN_4O_7$ $[M + Na]^+$ 323.0604, found 323.0604.

*((2R,3S,4R)-3-Acetoxy-4-azido-5-nitro-3,4-dihydro-2H-pyran-2-yl)methyl Acetate (**9b**).* Using general procedure C, compound **9b** was isolated as a colorless oil: yield 65%; $R_f$ 0.60 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +215.0 (*c* 0.40, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2923, 2111, 1748, 1641, 1509, 1369, 1349, 1211, 1158, 1050 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.17 (s, 1H), 5.18 (d, *J* = 4.2 Hz, 1H), 5.10 (dd, *J* = 4.2, 10.5 Hz, 1H), 4.46−4.4.37 (m, 3H), 2.19 (s, 3H), 2.11 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.3, 169.3, 155.5, 129.2, 72.8, 65.3, 60.4, 53.4, 20.6, 20.4. HRMS calcd for $C_{10}H_{16}N_5O_7$ $[M + NH_4]^+$ 318.1050, found 318.1051.

*((2R,3S,4R)-3-Acetoxy-5-nitro-4-(phenylthio)-3,4-dihydro-2H-pyran-2-yl)methyl Acetate (**9c**).* Using general procedure C, compound **9c** was isolated as a colorless oil: yield 86%; $R_f$ 0.55 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +95.0 (*c* 0.20, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2964, 2850, 1749, 1638, 1508, 1371, 1344, 1211, 1026 $cm^{-1}$; $^1H$


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NMR (500 MHz, $CDCl_3$) $\delta$ 8.23 (s, 1H), 7.60−7.57 (m, 2H), 7.38−7.31 (m, 3H), 5.23 (d, $J$ = 1.2 Hz, 1H), 4.77−4.74 (m, 1H), 4.39 (*br* s, 1H), 4.34−4.27 (m, 2H), 2.11 (s, 3H), 2.01 (s, 3H); $^{13}$CNMR (125 MHz, $CDCl_3$) $\delta$ 170.4, 169.5, 154.4, 133.0−129.0 (Ar-*C*), 72.9, 66.9, 61.9, 43.2, 20.7; HRMS calcd for $C_{16}H_{18}NO_7S$ $[M + H]^+$ 368.0804, found 368.0803.

*tert-Butyl 4,6-Di-O-acetyl-3-azido-2,3-dideoxy-2-nitro-α-D-galactopyranoside (**10**).* To a stirred solution of compound **9a** (100 mg, 0.333 mmol) dissolved in *t*-BuOH (3 mL) was added *t*-BuOK (0.33 mg, 0.033 mmol), and the reaction mixture was stirred for 7 h. After the consumption of starting material (TLC monitoring), *t*-BuOH was evaporated to give a crude product which was dissolved in EtOAC (20 mL), washed with water (2 × 20 mL) and brine (2 × 10 mL), and then dried over $Na_2SO_4$. Concentration in vacuo gave a crude residue which was purified by column chromatography to obtain pure compound **10**: yield 102 mg (71%), colorless oil: $R_f$ 0.70 (hexane/ethyl acetate, 4:1); $[\alpha]_D^{28}$ = +80.0 (*c* 0.30, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2980, 2920, 2850, 2117, 1750, 1640, 1561, 1372, 1226, 1122, 1016 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.62 (d, $J$ = 3.6 Hz, 1H), 5.51−5.50 (m, 1H), 4.61 (dd, $J$ = 4.0, 11.0 Hz, 1H), 4.56 (dd, $J$ = 3.3, 11.0 Hz, 1H), 4.39−4.37 (m, 1H), 4.09−4.01 (m, 2H), 2.13 (s, 3H), 2.04 (s, 3H), 1.19 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.4, 169.8, 91.0, 82.8, 67.6, 66.7, 61.8, 56.9, 28.5, 27.9, 20.7, 20.6; HRMS calcd for $C_{14}H_{26}N_5O_8$ $[M + NH_4]^+$ 392.1781, found 392.1781.

*tert-Butyl 3-Acetamido-4,6-di-O-acetyl-2,3-dideoxy-2-nitro-α-D-galactopyranoside (**11**).* To a stirred solution of azido compound **10** (50 mg, 0.133 mmol) dissolved in THF (1 mL) were added $PPh_3$ (52 mg, 0.200 mmol) and $H_2O$ (4 μL, 0.200 mmol) at room temperature, and the reaction mixture was stirred for 8 h. After consumption of the starting material (TLC monitoring), the reaction mixture was quenched with 2 mL of $H_2O$, extracted with EtOAc (2 × 10 mL), washed with water (1 × 10 mL) and brine (1 × 10 mL), and then dried over $Na_2SO_4$. Concentration under vacuum gave a crude residue which was passed through a short silica gel column using 1% $Et_3N$ in hexane/ethyl acetate (4:1) as eluent. Solvent was evaporated, and the residue was dissolved in dry $CH_2Cl_2$ and cooled to 0 °C. To this were added dry $Et_3N$ (0.022 mL) and acetyl chloride (0.011 mL) followed by DMAP (1.6 mg) and the mixture stirred for 15 min. After completion of reaction (TLC monitoring), the reaction mixture was quenched with $H_2O$ (10 mL), extracted with $CH_2Cl_2$ (2 × 10 mL), washed with brine (1 × 10 mL), and then dried over $Na_2SO_4$. Concentration in vacuo gave a crude residue which was purified by column chromatography to obtain pure compound **11** as a semisolid: yield 30 mg (58% over two steps); $R_f$ = 0.30 (hexane/ethyl acetate, 2:3), $[\alpha]_D^{28}$ = +117.0 (*c* 0.40, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 3379, 2976, 2923, 1748, 1656, 1557, 1371, 1226, 1060, 1015 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.77 (d, $J$ = 8.6 Hz, N−*H*), 5.63 (d, $J$ = 4.0 Hz, 1H, H-1), 5.39 (d, $J$ = 3.5 Hz, 1H, H-4), 5.18−5.14 (m, 1H, H-3), 4.77 (dd, $J$ = 4.0, 11.7 Hz, 1H, H-2), 4.46−4.43 (m, 1H, H-5), 4.03−4.01 (m, 2H, H-6, H-6′), 2.14 (s, 3H, COC$H_3$), 2.03 (s, 3H, COC$H_3$), 1.92 (s, 3H, NCOC$H_3$), 1.19 (s, 9H, *t*-Bu−*H*); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.5, 169.9, 169.7, 90.9, 82.7, 69.0, 67.0, 61.9, 45.6, 28.0, 23.1, 20.7; HRMS calcd for $C_{16}H_{26}N_2NaO_9$ $[M + Na]^+$ 413.1536, found 413.1536.

**General Procedure (D) for Raney Ni Hydrogenation.** The nitroacetamide **11** (50 mg, 0.128 mmol) was added to a stirred solution of freshly prepared Raney nickel catalyst (100 mg) in EtOH, and the reaction mixture was stirred under $H_2$ atmosphere for 14 h at room temperature. After completion of reaction (TLC monitoring), the reaction mixture was filtered and the solvent was evaporated under vacuum to give the crude amine. To this amine, dissolved in $CH_2Cl_2$ (1 mL), was added $Et_3N$ (0.021 mL, 0.153 mmol) and 50% CbzCl (0.044 mL, 0.153 mmol) added to obtain product **12** or $Boc_2O$ (0.036 mL, 0.153 mmol) to obtain product **13**. After 4 h of stirring at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), extracted with $CH_2Cl_2$ (3 × 10 mL), washed with brine (1 × 10 mL), and then dried over $Na_2SO_4$. The solvent was evaporated and the crude product was purified by column chromatography to obtain pure products.

*tert-Butyl 3-Acetamido-4,6-di-O-acetyl-2-(benzyloxycarbonylamino)-2,3-dideoxy-α-D-galactopyranoside (**12**).* Using general procedure D, compound **12** was isolated in 92% yield (over two steps) as a colorless oil: $R_f$ 0.60 (hexane/ethyl acetate, 1:2); $[\alpha]_D^{28}$ = +33.3 (*c* 0.15, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 3314, 2955, 2925, 2854, 1747, 1707, 1659, 1457, 1227, 1057 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.36−7.29 (m, 5H), 5.91 (d, $J$ = 7.5 Hz, 1H), 5.31 (d, $J$ = 2.5 Hz, 1H), 5.16 (d, $J$ = 12.0 Hz, 1H), 5.14 (*br* s, 1H), 4.99 (d, $J$ = 12.0 Hz, 1H), 4.91 (d, $J$ = 9.7 Hz, 1H), 4.37−4.30 (m, 2H), 4.05−3.97 (m, 3H), 2.14 (s, 3H), 2.00 (s, 3H), 1.74 (s, 3H), 1.24 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.7, 170.5, 170.2, 157.3, 136.2, 128.6−128.1 (Ar−*C*), 92.0, 76.2, 68.9, 67.2, 66.9, 62.4, 49.8, 49.5, 37.1, 32.0, 29.7, 28.5, 23.0, 22.7, 20.8; HRMS calcd for $C_{24}H_{34}N_2NaO_9$ $[M + Na]^+$ 517.2162, found 517.2162.

*tert-Butyl 3-Acetamido-4,6-di-O-acetyl-2-(tert-butoxycarbonylamino)-2,3-dideoxy-α-D-galactopyranoside (**13**).* Using general procedure D, compound **13** was isolated in 87% yield (over two steps) as a colorless oil: $R_f$ 0.75 (hexane/ethyl acetate, 1:2), $[\alpha]_D^{28}$ = +128.0 (*c* 0.25, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 3346, 2977, 1748, 1695, 1454, 1392, 1299, 1171, 1051 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.12 (*br* s, 1H), 5.32 (*br* s, 1H), 5.12 (*br* s, 1H), 4.64 (*br* s, 1H), 4.39−4.31 (m, 2H), 3.99−3.98 (m, 3H), 2.13 (s, 3H), 2.06 (s, 3H), 1.94 (s, 3H), 1.25 (s, 9H), 1.19 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.7, 170.5, 170.2, 157.0, 92.1, 80.4, 78.2, 78.0, 76.0, 68.9, 66.9, 62.5, 50.3, 48.7, 28.6, 28.3, 23.1, 20.8; HRMS calcd for $C_{21}H_{36}N_2NaO_9$ $[M + Na]^+$ 483.2319, Found 483.2311.

*Methyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-3-phenythio-α-D-galactopyranoside (**14**).* To a stirred solution of compound **9c** (100 mg, 0.272 mmol), dissolved in MeOH (3 mL), was added *t*-BuOK (3.1 mg, 0.027 mmol), and the reaction mixture was stirred for 24 h. The solvent MeOH was evaporated to give a crude product which was dissolved in EtOAc (1 × 20 mL), washed with water (2 × 10 mL) and brine (1 × 10 mL), and then dried over $Na_2SO_4$. Concentration in vacuo gave a crude residue which was purified by column chromatography to obtain 102 mg (91%) of pure compound **14** as a colorless oil: $R_f$ 0.55 (hexane/ethyl acetate, 4:1), $[\alpha]_D^{28}$ = +192.0 (*c* 0.55, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 2924, 2851, 1748, 1561, 1373, 1220, 1065 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.60−7.57 (m, 2H, Ar-*H*), 7.38−7.33 (m, 3H, Ar-*H*), 5.42 (d, $J$ = 3.1 Hz, 1H, H-4), 5.20 (d, $J$ = 3.9 Hz, 1H, H-1), 4.79 (dd, $J$ = 3.9, 12.5 Hz, 1H, H-2), 4.12−4.08 (m, 2H, H-6, H-6′), 4.02−3.99 (m, 1H, H-5), 3.88 (dd, $J$ = 3.3, 12.5 Hz, 1H, H-3), 3.36 (s, 3H, OC$H_3$), 2.21 (s, 3H, COC$H_3$), 2.06 (s, 3H, COC$H_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.5, 169.9, 134.5−129.1 (Ar-*C*), 96.6, 83.4, 68.1, 67.7, 62.5, 55.7, 48.8, 20.8; HRMS calcd for $C_{17}H_{21}NaNO_8S$ $[M + Na]^+$ 422.0886, found 422.0882.

*Methyl 2-Acetamido-4,6-di-O-acetyl-2,3-dideoxy-3-phenythio-α-D-galactopyranoside (**15**).* Compound **14** (60 mg, 0.150 mmol) was dissolved in a mixture of THF (7 mL), concentrated HCl (0.3 mL), acetic acid (1.6 mL), and $H_2O$ (3.0 mL) and cooled to 0 °C. Zn dust (195 mg, 3.00 mmol) was added to it portionwise. After 1 h of stirring at 0 °C, the residue was filtered, and the reaction mixture was diluted with $CH_2Cl_2$ (20 mL), washed with water (1 × 10 mL), saturated aqueous $NaHCO_3$ (1 × 10 mL), and brine (1 × 10 mL), and dried over anhydrous $Na_2SO_4$. After evaporation of the solvents, the crude amine was dissolved in dry $CH_2Cl_2$ at 0 °C, treated with $Et_3N$ (0.025 mL, 0.180 mmol) and acetic anhydride (0.017 mL, 0.180 mmol) followed by DMAP (2.0 mg, 0.014 mmol), and stirred for 15 min. After completion of reaction (TLC monitoring), the reaction mixture was quenched with $H_2O$ (5 mL), extracted with $CH_2Cl_2$ (3 × 10 mL), washed with brine (1 × 10 mL), and then dried over $Na_2SO_4$. Concentration in vacuo gave a crude residue which was purified by column chromatography to obtain 34 mg (56% over 2 steps) of compound **15** as a colorless oil: $R_f$ 0.3 (hexane/ethyl acetate, 1:2), $[\alpha]_D^{28}$ = +40.0 (*c* 0.40, $CH_2Cl_2$); IR (neat) $\nu_{max}$ 3285, 2924, 2854, 1746, 1660, 1440, 1226, 1127, 1054 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.43−7.41 (m, 2H), 7.31−7.27 (m, 3H), 5.54 (d, $J$ = 9.4 Hz, 1H), 5.32 (*br* s, 1H), 4.73 (d, $J$ = 3.4 Hz, 1H), 4.55−4.50 (m, 1H), 4.11 (dd, $J$ = 4.6, 11.2, 1H), 4.05−4.02 (m, 1H), 3.95 (dd, $J$ = 7.4, 11.1 Hz, 1H), 3.44−3.36 (m, 1H), 3.35 (s, 3H), 2.17 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 170.4, 170.0, 134.1−


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128.0 (Ar-C), 98.3, 68.6, 67.9, 63.1, 55.2, 51.5, 48.2, 23.4, 20.8; HRMS calcd for $C_{19}H_{25}NaNO_7S$ $[M + Na]^+$ 434.1249, found 434.1250.

*Methyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-arabino-hexapyronoside and Methyl 4,6-Di-O-acetyl-2,3-dideoxy-2-nitro-α-D-ribo-hexapyronoside (**16**).* To a solution of compound **7a** (300 mg, 1.0 mmol) in EtOAc (5 mL) was added 10% Pd/C (30 mg). The suspension was stirred under an atmosphere of $H_2$ for 0.5 h at room temperature. After consumption of the starting material (TLC monitoring), the insoluble material was filtered off. The filtrate was concentrated under reduced pressure to give a residue, which was purified by silica gel column chromatography to afford compound 197 mg of **16** (65%) as a colorless oil: $R_f$ 0.45 (hexane/ethyl acetate, 4:1); IR (neat) $\nu_{max}$ 2924, 2851, 1744, 1556, 1372, 1236, 1047 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$, 2.1:1 mixture of isomers) $\delta$ 5.25−5.24 (m, 1H, both isomer), 4.83−4.77 (m, 1H, both isomer), 4.59−4.55 (m, 1H, both isomer), 4.27−4.13 (m, 2H, both isomer), 3.96−3.92 (m, 1H, both isomer), 3.46 (s, 3H, minor isomer), 3.42 (s, 3H, major isomer), 2.83−2.75 (m, 1H, minor isomer), 2.63−2.59 (m, 1H, major isomer), 2.40−2.33 (m, 1H, major isomer), 2.10−2.07 (m, 1H, minor isomer), 2.07−2.03 (s, 6H, both isomer); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.7, 169.7, 97.0, 96.2, 82.0, 79.6, 75.1, 68.5, 68.0, 65.6, 63.4, 62.7, 62.1, 62.0, 55.8, 55.6, 27.0, 26.8, 20.9, 20.8; HRMS calcd for $C_{11}H_{17}NaNO_8$ $[M + Na]^+$ 314.0852, found 314.0853

**Procedure for Synthesis of Methyl *N*-Acetyl-α-D-lividosaminide (18) and Its Isomer (17).** To a solution of compound **16** (200 mg, 0.686 mmol) in 2 mL of EtOAc was added freshly prepared platinised Raney Ni ($T_4$) (400 mg) in ethanol, and the reaction mixture was stirred for 12 h under $H_2$ atmosphere at room temperature. After completion of the reaction, the mixture was filtered through a Celite pad and washed with MeOH, and the filtrate was evaporated to give the corresponding crude amine. The crude amine was dissolved in dry $CH_2Cl_2$ cooled to 0 °C, to it were added $Et_3N$ (0.11 mL) and acetic anhydride (0.076 mL) followed by DMAP (8 mg), and the mixture was stirred for 0.5 h. The reaction mixture was quenched with $H_2O$ (15 mL), extracted with $CH_2Cl_2$ (2 × 20 mL), washed with brine (1 × 20 mL), and then dried over $Na_2SO_4$. Concentration in vacuo gave a crude mixture of diastereomers which were separated by using chromatotron to obtain **17** and **18** in 24% and 50% yields, respectively.

*Methyl 2-acetamido-4,6-di-O-acetyl-2,3-dideoxy-α-D-arabino-hexapyronoside (**17**):* yield 24%; $R_f$ = 0.1 (hexane/ethyl acetate, 1:4); $[\alpha]_D^{25}$ = +68.0 (*c* 0.25, $CH_2Cl_2$) [lit.[21c] $[\alpha]_D^{25}$= +67.3 (*c* 1.0, $CHCl_3$)]; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 5.88 (d, *J* = 8.0 Hz, N−*H*), 4.83 (dt, *J* = 5.1, 10.8 Hz, H-4), 4.52 (*br* s, 1H, H-1), 4.26−4.24 (m, 1H, H-6′), 4.22−4.20 (m, 1H, H-2), 4.10 (dd, *J* = 2.3, 12.0 Hz, H-6), 3.94 (ddd, *J* = 2.3, 5.7, 8.0 Hz, H-5), 3.38 (s, 3H, $OCH_3$), 2.12−1.96 (m, 2H, H-3, H-3′), 2.09 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.01 (s, 3H, $NCOCH_3$); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.8, 170.1, 169.6, 99.2, 68.2, 64.4, 63.0, 55.1, 47.8, 29.7, 23.5, 21.0; HRMS calcd for $C_{13}H_{22}NO_7$ $[M + H]^+$ 304.1396, found 304.1390.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Details on general experimental methods, structural characterization of compounds **2f**−**17**, copies of $^1H$ NMR and $^{13}C$ NMR spectra of all the new compounds, COSY and NOE spectra of the compounds **11**, **14**, and **17**, and crystallographic details for compound **6d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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