Heterocyclic Letters
Vol. 13| No.3|467-475|May-July|2023
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

STEREOSPECIFIC GLYCOSYLATION: A CARBOHYDRATE CHIRON FOR OPTICAL RESOLUTION

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Abstract

The stereospecific glycosylation of the 3-(1-hydroxyethyl)-4-phenyl-2-azetidine moiety of the thienamycin side chain is achieved using Bismuth triflate as the catalyst, employing D-glycal. This reaction results in the formation of two distinguishable diastereomeric mixtures of α-glycosides. Subsequently, the sugar residue of these diastereomers is cleaved by mild acid-mediated de-glycosylation, leading to the generation of two optically active β-lactam alcohols, which serve as precursors to thienamycin.

Keywords: Ferrier glycosylation, glycosylation, 2-azetidine, glycosides, glycal

Introduction

The discovery of penicillin in 1928 by Alexander Fleming, derived from the Penicillium notatum mold, marked the advent of β-lactam antibiotics. Subsequently, the pioneering efforts of H. Florey and E. Chain showcased the potential of penicillin as a bactericidal agent capable of combating various infectious diseases caused by diverse bacterial strains. Their work demonstrated the efficacy of penicillin against a wide range of bacterial classes, thereby paving the way for the use of β-lactam antibiotics in the treatment of infectious diseases.[i–iii].

In continued scientific research, substantial resources have been dedicated to the analysis of penicillin's chemical structure. In 1957,

J.C. Sheehan's milestone achievement of the total synthesis of penicillin introduced a new dimension to the field of physiological medicine. This groundbreaking accomplishment expanded our understanding of penicillin's composition and opened up possibilities for further advancements in developing and applying this vital class of antibiotics [iv, v].

Penicillin is analogous to a carbapenem antibiotic based on its chemical structure. Carbapenems are a distinct class of antibiotics

that possess a different chemical structure and a broader spectrum of activity compared to penicillin. However, in the realm of antibiotic research, the total synthesis of cephalosporin by R.B. Woodward introduced a new class of antibiotics. This synthesis involved the ring expansion of natural penicillin, leading to the development of cephalosporins. Cephalosporins belong to the β-lactam class of antibiotics and have demonstrated enhanced activity against bacterial infections, particularly those caused by organisms producing β-lactamase enzymes. The addition of cephalosporins expanded the repertoire of β-lactam antibiotics, providing more effective options for combating bacterial infections that possess β-lactamase activity [vi,vii].

In the late 1970s, a remarkable discovery was made when a new compound belonging to the naturally occurring carbapenem family was isolated from the culture broth of Streptomyces cattleya. This compound was subsequently identified as thienamycin [viii, ix]. The establishment of the central carbapenem ring of thienamycin through de novo synthesis required significant dedication and effort from researchers. Thienamycin has garnered substantial attention worldwide within the scientific community due to its outstanding bactericidal activities against both gram-positive and gram-negative bacteria, as well as its ability to resist bacterial β-lactamases [X]. This unique class of antibiotics sparked widespread exploration among researchers to develop synthetic protocols for the synthesis of thienamycin, further highlighting its significance in the field of antibiotic research.

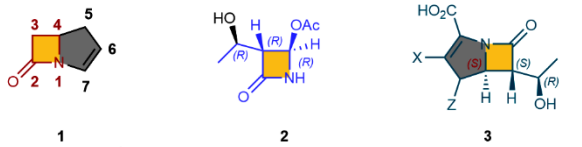
Thienamycin's exceptional bactericidal activities against both gram-positive and gram-negative bacteria, as well as its resistance to bacterial β-lactamases, garnered immense attention from the global scientific community. This led to extensive exploration of potential synthetic protocols to produce this unique class of antibiotics. The differentiating structural feature of thienamycin, setting it apart from natural penicillin and cephalosporins, is the presence of a hydroxymethyl side chain at the C-6 position with a β-configuration. In contrast, penicillin and cephalosporin traditionally exhibit a cis-configuration at the C5(α)-C6(α) position of the azetidine nucleus. Additionally, thienamycin features a trans-configuration at the C6(β)-C5(α) position on the β-lactam ring, further distinguishing it from penicillin and cephalosporins [xi].

It was envisioned that the hydroxy functionality of thienamycin is believed to bind to bacterial cell wall enzymes, like how the 6b-amino group of penicillin and cephalosporin, as well as the 6a-methoxy group in cephamycin (cephem), confer resistance to β-lactamase [xii]. However, despite its structural complexity and high potency against various bacterial infections, the stereoselective synthesis of thienamycin poses a formidable challenge, especially in constructing the unusual trans-ring configuration of the azetidine nucleus for the stereocontrolled installation of the hydroxymethyl side chain [xiii]. In 1978, B.G. Christensen and his colleagues at Merck's research laboratory accomplished the first total synthesis of racemic- (+/-)-thienamycin. They employed the [2ps+2ps] cycloaddition of 1-acetoxybutadiene and chlorosulfonyl isocyanate as a vital reaction [xiv]. The compound (+)-4-acetoxy-3-hydroxyethyl-2-azetidinone **2** was identified as a potential synthetic precursor for the stereocontrolled total synthesis of (+)-thienamycin and other related carbapenem antibiotics [xv, xvi]. The Sankyo group initiated the synthesis of intermediate 2, which was later developed into a practical approach by Japanese pharmaceutical companies based on the Noyori-Murahashi asymmetric protocol [xvii]. Thus, the synthesis of the intermediate establishes the formal total synthesis of (+)-thienamycin [xviii].

In 2000, Tatsuta et al. published a novel synthesis of (+)-thienamycin using carbohydrates as a chiral auxiliary. This approach involved a combination of skeletal rearrangement and epimerization strategies

[xix]. Since then, several remarkable works have contributed to the total synthesis of thienamycin, resulting in the development of various thienamycin analogs with distinct central motifs (Figure 1) [xx-xxiii].

Herein, we present a facile strategy utilizing



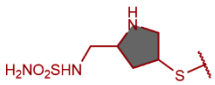
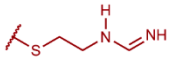
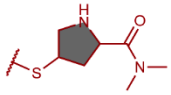
	Z	X
Doripenem	Me	
Thienamycine	H	
Imepeneme	H	
Meopenem	Me	

Figure 1. Thienamycine group antibiotics and their analogs

bismuth triflate as a catalyst to produce enantiomeric forms of the 1-hydroxyethyl side chain found in thienamycin antibiotics. This is achieved through the Ferrier rearrangement of a racemic β-lactam alcohol and glycal, allowing for the generation of both enantiomers of the side chain.

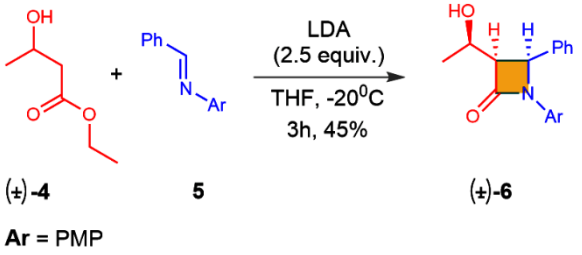
Result and Discussion

The glycosylation of alcohols represents a challenging and highly relevant research area due to the complexity and broad applications of the process [xxiv]. Among the various methods discovered, the Ferrier rearrangement stands out as a highly effective approach for synthesizing stereoselective glycosides using glycal as the glycosyl donor [xxv, xxvi]. In certain cases, Lewis's acids and acidic supports have been employed as glycosyl activators [xxvii, xxviii]. This reaction typically leads to the formation of 2,3-unsaturated glycosides, wherein the glycosidic linkage between the oxygen and the anomeric position of the sugar ring can adopt either an axial or equatorial configuration [xxix]. Predicting the stereochemistry of the glycosidic bond is challenging as it depends on multiple factors, such as the nature of the protecting group on the glycal, the nucleophilicity of the alcohol, the reaction temperature, the mode of reagent addition, and the choice of solvents [xxx]. Consequently, this reaction often yields a mixture of α- and β-glycosides. However, a few intriguing methods have been discovered to selectively obtain α- or β-isomers. For example, the indium-induced reaction has been developed for the stereoselective synthesis of glycosides by reacting alcohols with bromo-sugars. Additionally, stereospecific glycosylation of alcohols through iodine-catalyzed Ferrier rearrangement has also been reported.

Thienamycin, PS-5, and carpetimycin are antibiotics of significant importance, and synthetic routes have been developed for their preparation [xxxi]. To synthesize these antibiotics, optically pure 3-(1-hydroxyethyl)-4-acetoxy-2-azetidine **6** is required. It is necessary to obtain optically active forms of this compound to obtain isomeric forms of these antibiotics. One approach that was envisioned is the use of racemic β-lactam alcohol, which can undergo Ferrier rearrangement to produce optically active versions of the thienamycin side chain [xxxii]. In our previous publications, we described the synthesis of all four isomers in their enantiomeric forms of racemic monocyclic 3-hydroxyl β-lactam through an efficient Ferrier glycosylation process catalyzed by iodine, using D-glycal as the glycosyl donor [xxxiii]. This method allowed for the selective preparation of the desired enantiomers, providing a valuable strategy for obtaining the optically active forms of the thienamycin side chain and facilitating the synthesis of these important antibiotics.

Based on our extensive expertise in the optical resolution of enantiopure β-lactam compounds through Ferrier glycosylation, we have now shifted our focus towards synthesizing the hydroxyethyl side chain at the C-6 position of thienamycin. Our vision is to utilize rac-*cis*-3-(1-hydroxyethyl)-4-

phenyl-N-*p*-anisyl-azetidinone **6** as a key component in the synthesis of thienamycin. To achieve this goal, we conducted a reaction between *rac*-(±)-ethyl-3-hydroxy-butyrate **4**



Scheme 1 Synthesis of *racemic cis*-3-(1-hydroxyethyl)-4-phenyl-N-*p*-anisyl-azetidinone **6**

dianion of ester-enolate, generated at -20°C using 2.5 equivalents of lithium isopropyl amide (LDA) in a 1 M THF solution, reacted with one equivalent of p-anisylaldimine **5** to afford *cis*-β-lactam **6** as an exclusive diastereoisomer in a 45% yield (Scheme 1).

Extensive studies in the field of β-lactam chemistry have revealed that the stereochemical outcome of cis and trans β-lactams at the **C3** and **C4** positions is highly dependent on the configuration of the lithium enolate (Z/E structure) and the spatial arrangement of the substituents on the aldimine in the transition state of the ester-imine enolate intermediate. According to reports in the literature, the formation of the cis stereochemistry is attributed to the presence of the E-enolate configuration, which subsequently leads to the formation of a transition state favoring the *cis* arrangement of the substituents (Figure 2)[xxxv].

The transition state model corresponding to the E-enolate leads to the formation of the cis-β-lactam (3R, 4S) **6**. The driving force for the specific transition state is the stabilization achieved through remote hydrogen bonding between the hydroxyl group of the hydroxyethyl moiety and the ester functionality of the butyrate. This interaction promotes a faster reaction rate and results in the exclusive formation of the desired product. The cis-β-lactam **6** has been successfully isolated through column and anisylaldimine **5** in anhydrous THF at temperatures ranging from -20°C to room temperature [xxxiv, xxxv]. During our investigations, we observed that the lithium chromatography and characterized through NMR spectral analysis of the pure sample.

To initiate the optical resolution of the 1-hydroxyethyl side chain of thienamycin, we utilized the glycosyl acceptor, cis-3-(1-

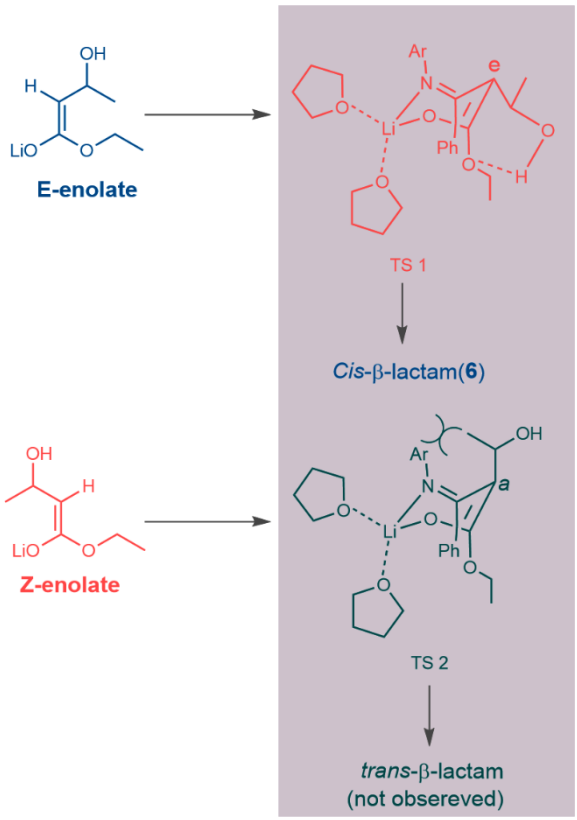
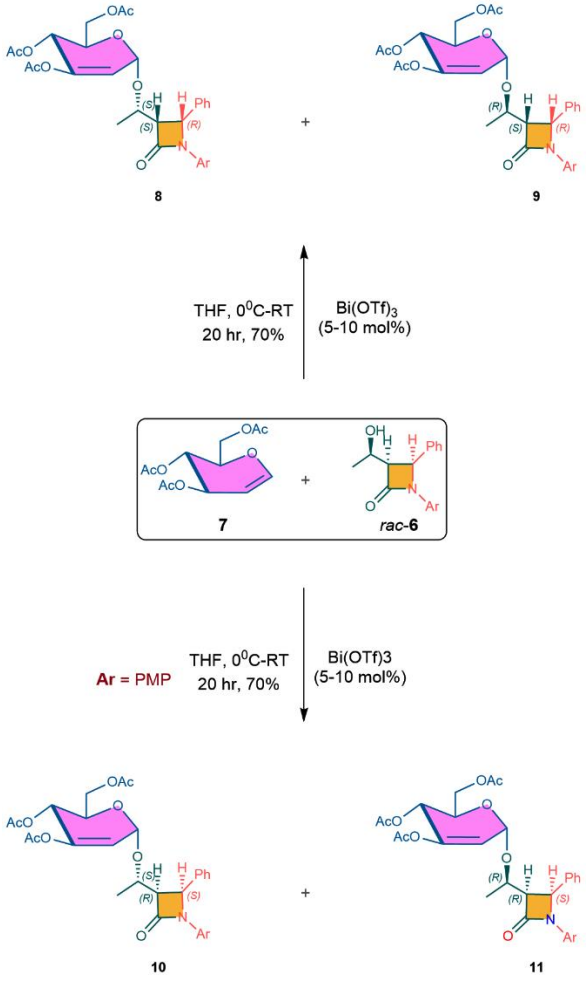


Figure 2 Plausible T.S for the formation *Cis*-β-lactam

hydroxyethyl)-4-phenyl-N-p-anisyl-2 azetidinone **6**, in bismuth triflate-catalyzed Ferrier glycosylation reactions. As a model glycosyl donor, Tri-*O*-acetyl-D-glucal **7** was employed in the presence of Bi $(OTf)_3$ (5-10 mol%) as the catalyst. The reactions were conducted in anhydrous THF at temperatures ranging from 0°C to 25°C for 20 hours. The progression of the reaction was monitored using thin-layer chromatography (TLC) with an ethyl acetate-hexane solvent system (20:80). Two major new spots were observed on the TLC plate, indicating the formation of new products. After performing work-up

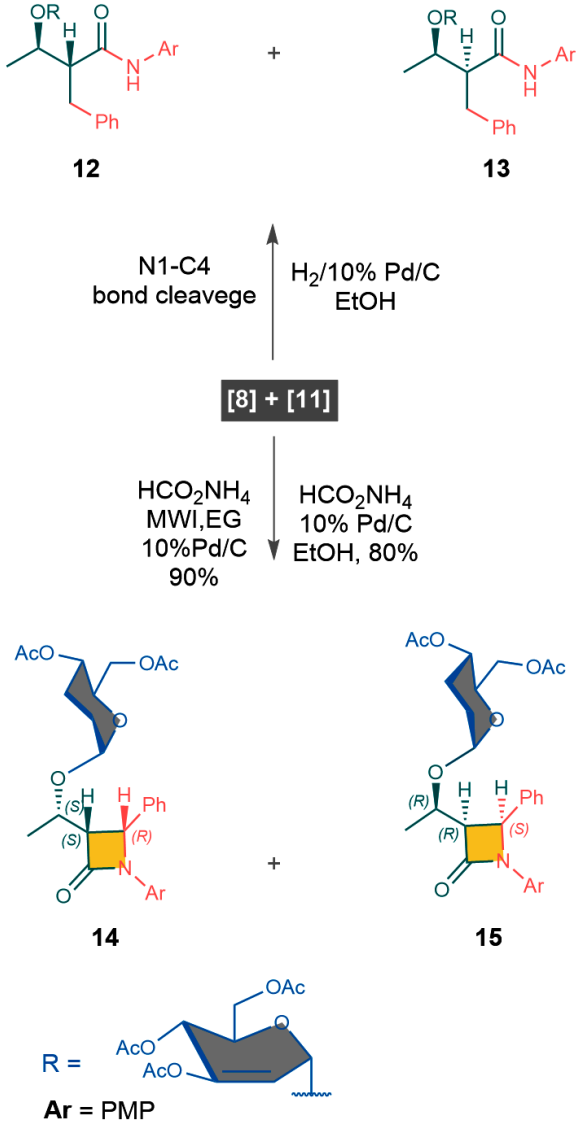
procedures and subsequent column chromatography purification of the crude materials, we obtained two isolated products corresponding to compounds **8-9** and **10-11** in a 70% yield (Scheme 2) [xxxvi]. It was observed that an increase in reaction time did not significantly alter the distribution of the products. However, when the amount of bismuth triflate was increased to 30 mol%, the consumption of glycal **7** was observed, but



Scheme 2 Bismuthtriflate induced streospecific Ferrier-O-glycosylation of rac-cis-3-(1-hydroxyethyl)-4-phenyl-N-p-anisyl-2-azetidinone (**6**)

the yield of compounds **8-9** and **10-11** decreased. It is noteworthy to mention that the glycosylation reaction using 3, 4, 5-tri-O-acetyl D-galactal as the glycosyl donor, along with the racemic β-lactam alcohol 6 in the presence of bismuth triflate under identical conditions, did not result in the formation of any glycosides. Additionally, when 3, 4, 5-tri-O-benzyl D-glucose was utilized, no reaction occurred with the alcohol **6**. These observations emphasize the critical role played by the protecting group in D-glycal derivatives in the success of the Ferrier rearrangement reaction [xxxvii]

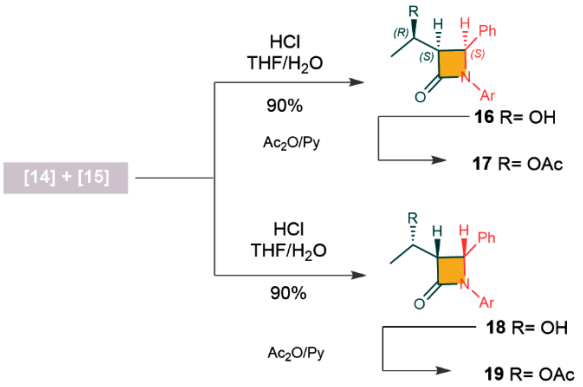
The stereochemistry of the anomeric center in unsaturated pyranose sugars can be challenging to establish. However, in the case of saturated sugars, it is comparatively easier



Scheme 3 Catalytic hydrogenation of β-lactam-*O*-glycosides under controlled experiments to determine the anomeric configuration of glycosides.

to determine the nature of the bond at the anomeric carbon. To this end, the alkenyl

bonds in compounds **8** and **11** were reduced using catalytic transfer hydrogenation with ammonium formate and a 10% Pd-C catalyst in ethanol [xxxviii]. Other attempts using various reducing conditions such as cyclohexene, hydrazine, formic acid, cyclohexadiene, and sodium hypophosphite did not yield satisfactory results. However, microwave-induced hydrogenation using ethylene glycol and ammonium formate as hydrogen donors in the presence of a 10% Pd C catalyst proceeded successfully, leading to the formation of saturated products **14** and **15**. In catalytic transfer hydrogenation, when applied to a less sterically hindered β-lactam system, it often results in the formation of amide derivatives **12** and **13** due to the cleavage of the N1-C4 bond. The proton NMR spectra of the 2,3-dideoxy compounds **14** and **15** exhibited small couplings (1-2 Hz) for the anomeric hydrogen, indicating an axial linkage of the glycoside bonds. In contrast, a much higher coupling constant (8-10 Hz) was observed for a β-glycoside, which can be attributed to the axial-axial interaction of the hydrogens (Scheme 3).



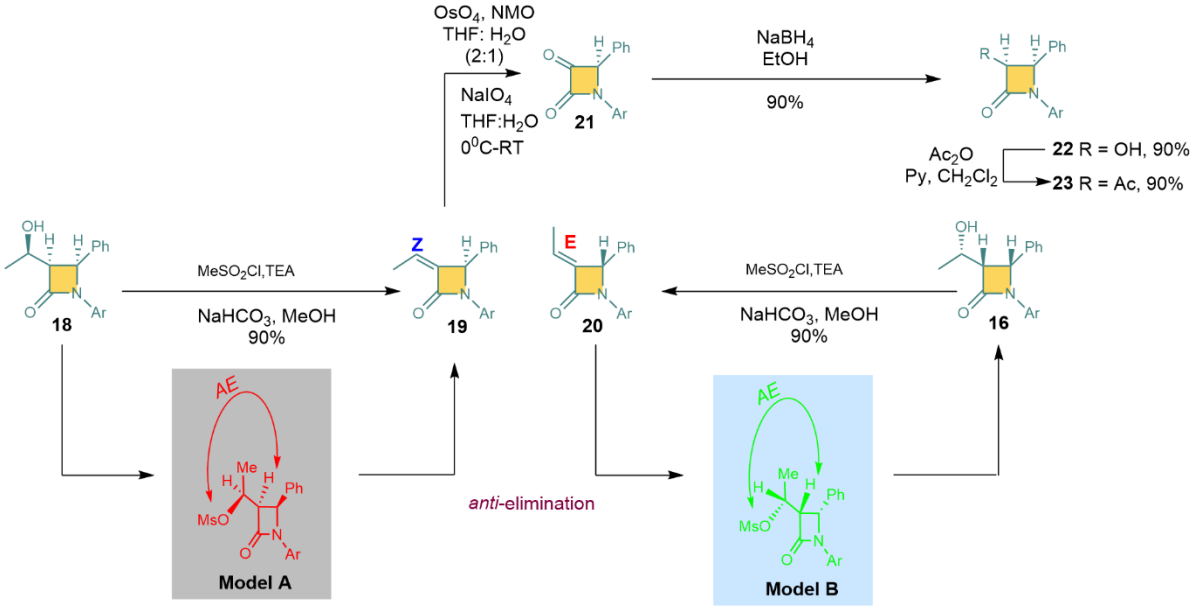
Scheme 4 Acid mediated de-glycosylation in the preparation of enantiopure *cis*-3-hydroxymethyl-b-lactam **16** and **18** and their transformation to its corresponding acetates (**17** and **19**)

The saturated glycosides **14** and **15** were purified using column chromatography with silica gel as the stationary phase. Subsequently, the sugar residue in these compounds was removed by performing deglycosylation in the presence of aqueous hydrochloric acid. This process yielded the enantiomeric hydroxy β-lactams **16** and **18**. The hydroxy β-lactams were further converted into their acetate derivatives, resulting in the formation of compounds **17** and **19**. The enantiomeric purity of β-lactam **17** was determined through ^{1}H NMR spectroscopy, utilizing an optically active shift reagent [xxxiii]. This analysis confirmed that compound **17** is enantiomerically pure. Furthermore, the same NMR study provided additional evidence supporting the enantiomeric relationship between molecules **17** and **19** (Scheme 4).

To determine the absolute stereochemistry of the optically active compounds, the hydroxy-β-lactams **16** and **18** were converted into the corresponding alkenes **19** and **20** through mesylation followed by elimination reactions [xxxix]. The formation of the Z-olefin β-lactam **19** provided information about the stereochemistry of the hydroxy group and the hydrogen at the C3 position of the ring (referred to as model A, Scheme 5). Next, the olefinic functionality of β-lactam **19** underwent oxidation through osmium tetraoxide-mediated dihydroxylation, followed by oxidative cleavage of the resulting vic-diol in situ using $NaIO_4$ in THF: H_2O (3:1) to yield the 3-oxo-β-lactam **21**. The keto group of compounds **21** was then reduced to generate the cis-hydroxy β-lactam with a defined absolute stereochemistry, corresponding to compound **18**. The optical rotation of the cis-hydroxy β-lactam **18** was compared with that of a known compound to establish its absolute stereochemistry (as depicted in Scheme 5). Additionally, the hydroxy β-lactam **22** was transformed into its corresponding acetate **23** with quantitative yield. The absolute stereochemistry of compound **18** was also confirmed using acetate **23**. An NMR study utilizing a chiral shift reagent further supported the stereochemistry determination of compound **18**, as illustrated in Scheme 5. A similar approach was employed to ascertain the stereochemical outcome of the diastereoisomer of β-lactam **16**.

Conclusion

The reaction between (±)-3-hydroxyethyl-4-p-methoxyphenyl-2-azetidinone **6** and glycal **7** in the presence of bismuth triflate results in the formation of α-glycosides **8-9** and **10-11**. This method offers several advantages, including mild reaction conditions and high product yields. The absolute stereochemistry of the glycosides is determined through physicochemical correlation studies, which involve comparing their properties with known compounds with established



Scheme 5 Determination of absolute configuration in streochemical outcomes of glycosylated product

stereochemistry. The hydroxy β-lactams derived from this process serve as chiral precursors for the synthesis of the potent antibacterial antibiotic thienamycin **2**. Currently, our research group is actively working on the total synthesis of a potential precursor for the formal total synthesis of thienamycin.

Acknowledgment

BKB gratefully acknowledges the funding support from the NIH. RNY and AKS thanks the Department of Chemistry and Mathematics at VBS Purvanchal University and TEQIP-III for providing necessary technical help during the preparation of the manuscript.

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Received on February 12, 2022.