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Ceric Ammonium Nitrate-Catalyzed Azidation of 1,2-Anhydro Sugars: Application in the Synthesis of Structurally Diverse Sugar-Derived Morpholine 1,2,3-Triazoles and 1,4-Oxazin-2-ones

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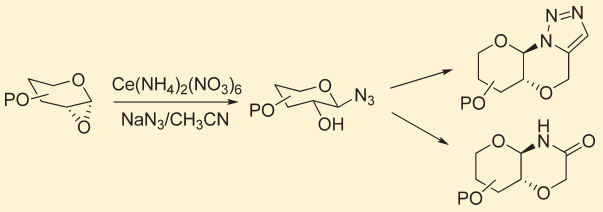
Supporting Information

ABSTRACT: Azidation of 1,2-anhydro sugars with NaN_3 in CH_3CN by using a catalytic amount of ceric ammonium nitrate has been accomplished in a regio- and stereoselective manner. Various 1,2-anhydro sugars produced 2-hydroxy-1-azido sugars in good yields which, in turn, were converted to structurally diverse sugar-derived morpholine triazoles and sugar oxazin-2-ones. These sugar derivatives were tested against various commercially available glycosidases, and two of them were found to be active in the micromolar range.



INTRODUCTION

The importance of 1,2,3-triazole derivatives as biologically important molecules having activities such as antibacterial,[1] anti-HIV,[2] herbicidal,[3] antitumor,[4] tuberculosis inhibition,[5] tyrosinase inhibition,[6] antiallergic,[7] and glycosidase inhibition[8] has been well documented in the literature in recent years. As a result, several reports have appeared[9] dealing with the synthesis of a variety of triazole derivatives including carbohydrate-fused triazoles.[10] Likewise, the morpholine moiety has been found to be an excellent pharmacophore in medicinal chemistry[11] and it has been a part of a number of important drugs currently on the market.[11a,g−j] Therefore, many new approaches toward the synthesis of morpholine derivatives have been reported in the literature.[12] The preparation of 1,2,3-triazoles is conveniently performed by using the well-known[13] "click chemistry" whereby an acetylene and an azide moiety are readily fused under a modified protocol.[14] It would thus be interesting to synthesize molecules possessing these moieties fused with carbohydrates and evaluate their biological properties.

For this purpose, D-glycosyl azides could act as useful entities which are also known to be powerful building blocks in organic as well as in medicinal chemistry.[15] Nitrogen atom attached to the anomeric carbon in the form of an azide group can be used for the synthesis of *N*-glycopeptides,[16a,b] and amino sugars.[16c] Further, the nitrogen atom attached to the anomeric carbon could play a predominant role in the synthesis of monocyclic[17a−c] and bicyclic iminosugars[17d,e] as useful glycosidase inhibitors. D-Glycopyranosyl azides can be obtained from direct nucleophilic displacement by an azide group using Me_3SiN_3 or metal azides (lithium, sodium, or silver) as nucleophilic azide sources[18] and leaving groups such as an acetate or a halide moiety (chloride or bromide) at the anomeric center of a carbohydrate molecule. We have recently developed a novel reagent system comprising Me_3SiN_3 and Me_3SiONO_2 to convert glycals to 1-azido-2-deoxy sugars.[16a] Further, the Ferrier type of rearrangement, using Me_3SiN_3 along with a Lewis acid-like $Yb(OTf)_3$,[19a] $Sc(OTf)_3$,[19b] and $InBr_3$[19c] has been reported to obtain enopyranosyl azides. Azidation of 1,2-anhydro sugars using lithium azide and THF in the presence of DIBAL as a Lewis acid catalyst has been reported by Chung et al.[20a] Ceric ammonium nitrate (CAN) is a versatile reagent and is used for a variety of functional group transformations.[20b] Among them, regioselective azidolysis of noncarbohydrate epoxides by using NaN_3 in *t*-BuOH and CAN as a catalyst under refluxing conditions, as reported by Iranpoor and Kazemi,[20c] caught our attention for the present study. Although the reagent system works well with a variety of epoxides, the solvent as *t*-BuOH and the refluxing conditions did not seem to be compatible for use on 1,2-anhydro sugars in the present study. Hence, we have used a modified solvent system, viz., acetonitrile and water, that works well with a number of 1,2-anyhdro sugars.

In conjunction with our continued interest toward the functionalization of glycals[16a,c,21] for possible application toward the synthesis of *N*-glycopetides,[16a] and other useful synthons,[16c] and the synthesis of glycosidase inhibitors[17a,b,e,22] we hereby report an extremely simple and mild method using ceric ammonium nitrate (CAN)-catalyzed opening of 1,2-anyhdro sugars to form vicinal *trans*-azido alcohols. Further, we also report the utility of these azido alcohols in the synthesis of carbohydrate-fused morpholine triazoles and carbohydrate-fused 1,4-oxazin-2-ones and report their glycosidase inhibition activity.

RESULTS AND DISCUSSION

Preparation of 1,2-anhydro sugars was carried out from the corresponding glycals by reaction with the in situ-generated dimethyl dioxirane (DMDO) by following a procedure developed

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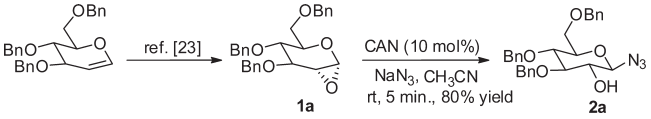
Scheme 1. Reaction of 1,2-Anhydroglucopyranose 1a with NaN_3 in the Presence of CAN

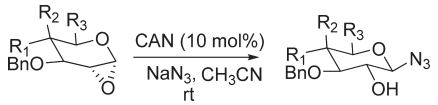


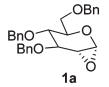
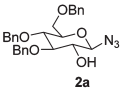
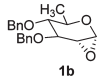
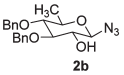
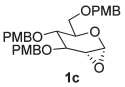
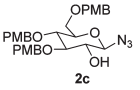
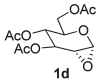
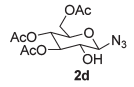
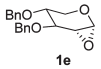
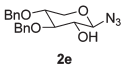
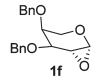
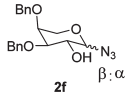
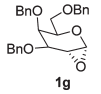
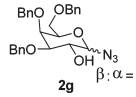
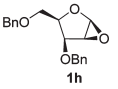
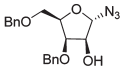
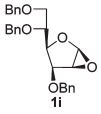
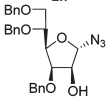
by Dondoni et al.[23] (Scheme 1). In initially attempted experiments, treatment of l,2-anhydro-3,4,6-tri-*O*- benzyl-D-glucopyranose **1a** with the reagent system comprising 10 mol % of CAN and 3 equiv of sodium azide in acetonitrile for a long time led to no reaction. However, addition of a drop of water allowed the reaction to be completed within 5 min, and 3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl azide **2a**[24] was obtained in 80% yield as the only product.

The spectral data of this compound was an absolute match with the literature data.[24] The stereochemistry of the product was found to be trans with the anomeric proton appearing as a doublet at *δ* 4.51 with *J* = 8.8 Hz, which indicated that this reaction proceeded through a regio- and stereoselective oxirane ring-opening via an S_N2 mechanism. The reaction was compatible with other protecting groups such as *p*-methoxy benzyl ethers and acetates. Thus, examination of the other glycal-derived 1,2-anhydro sugars (Table 1) such as 1,2-anhydro-3,4-di-*O*-benzyl-6-deoxy-D-glucopyranose **1b**,[25] 1,2-anhydro-3,4,6-tri-*O*-(p-methoxy)benzyl-D-glucopyranose **1c**,[26] 1,2-anhydro-3,4,6-tri-*O*-acetyl-D-glucopyranose **1d**,[23] and 1,2-anhydro-3,4-di-*O*-benzyl-D-xylopyranose **1e**[27] led to the formation of the corresponding glycopyranosyl azido alcohols in moderate to good yields (Table 1) with *β*-selectivity.[25] Consequently, the azido alcohols were also converted into morpholine triazoles (vide infra) whose structural elucidation also confirmed that these are *trans*-azido alcohols. The reaction was then extended to other 1,2-anhydropyranoses, such as 1,2-anhydro-3,4-di-*O*-benzyl-L-arabinopyranose[28] **1f** which afforded compound **2f** in good yield (83%), however, as a mixture of diastereomers in a 8:2 ratio with α-anomer **2f-α** having formed as the minor product. The stereochemistry of the major product was found to be trans with the anomeric proton appearing as a doublet at *δ* 4.44 with *J* = 8.3 Hz, whereas for the minor product (α-isomer) the anomeric proton appeared as a doublet at *δ* 5.41 with *J* = 3.6 Hz. We then studied the reaction of the galacto derivative **1g**[23] under similar conditions, which afforded a mixture of diastereomers **2g** again in 8:2 ratio but in excellent yield.

Further, 1,2-anhydro-3,5-di-*O*-benzyl-D-lyxofuranose **1h** and 1,2-anhydro-3,5,6-tri-*O*-benzyl-D-glucofuranose **1i** were also synthesized by using a known literature procedure[29] and were converted into the corresponding azido alcohols **2h** and **2i**, respectively, in moderate yields (Table 1).[25] The coupling constant of the anomeric proton (H-2) at *δ* 4.53 being 2.4 Hz indicated[15b] the trans relationship between H-2 and H-3 in compound **2h** which ascertains that the reaction proceeded through a regio- and stereoselective oxirane ring-opening mostly via an S_N2 mechanism. Besides, the stereochemical outcome was also confirmed from the $^1H-^1H$ COSY and NOE (Figure 1) spectral data. In an NOE experiment, irradiation of the signal for H-6 and H-6′ led to the enhancement of the signal for H-2, and there was no enhancement of the signals for H-3 and H-4. Likewise, irradiation of the signal for H-3 led to the enhancement of the signal for H-5 and there was no enhancement of the signal for H-6 and H-6′. This indicated that the carbon side chain, benzyloxy group at C-4, and hydroxyl group at C-3 are in cis

Table 1. Conversion of 1,2-Anhydro Sugars to 1,2-Azido Alcohols



entry	glycal epoxide 1a-i	1- azido sugar 2 a-i	% yield [a]
1	 1a	 2a	80
2	 1b	 2b	74
3	 1c	 2c	83
4	 1d	 2d	65
5	 1e	 2e	77
6	 1f	 2f β:α = 8 : 2	83[b]
7	 1g	 2g β:α = 8 : 2	89[b]
8	 1h	 2h	64
9	 1i	 2i	61

[a] Yields of chromatographically pure compounds. [b] Combined yields of both anomers after column chromatography.

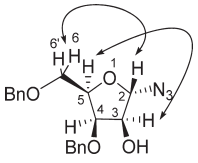


Figure 1. ^1H NOE correlations of compound **2h**.

relationship with each other. Thus, it was concluded that the azide group at the anomeric carbon is α-oriented and consequently the absolute stereochemistry at the anomeric center (i.e., C-2) and at C-3 being 2*S* and 3*S*, respectively.

A tentative mechanism for this transformation is shown in Scheme 2. The reaction is presumably initiated by the electron transfer from oxirane ring to the CAN, and regio- and stereoselective concomitant opening by sodium azide, through an S_N2 mechanism, could lead to the product formation. It was observed that glucal derivatives gave better selectivity than the galactal

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derivatives which in turn gave a mixture of the α and β glycosyl azides (Table 1). This is not surprising, as the lack of stereoselectivity in ring-opening of galacto-1,2-anhydropyranosugars has been previously observed by Danishefsky and co-workers.[30]

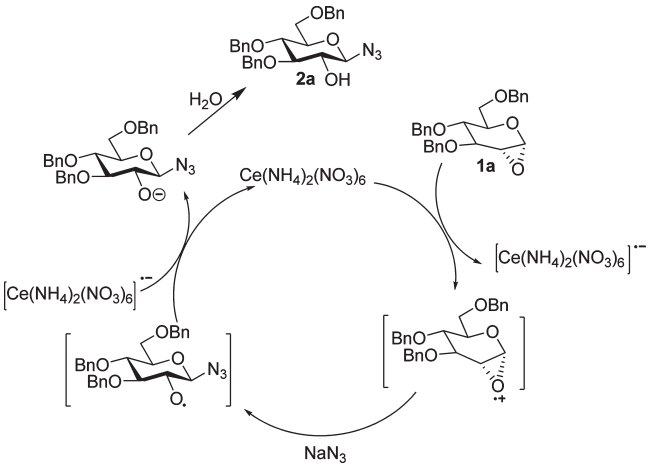
After the development of an improved protocol for Huisgen 1,3-dipolar cycloaddition between azides and alkynes by Sharpless,[13,14] the reaction has witnessed a renewed interest to procure a variety of biologically important 1,2,3-triazoles. Because we were able to prepare stereoselectively the 1,2-azido alcohols from 1,2-anhydro sugars easily, we have explored the conversion of D-glycopyranosyl azido alcohols into tricyclic [1,2,3]triazolo[1,5-*d*][1,4]oxazines upon sequential alkylation with propargyl bromide followed by intramolecular thermal cycloaddition reaction (Scheme 3). These molecules were prepared with a view to assess their glycosidase inhibition activities, as 1,2,3-triazole derivatives have been reported[8] to be glycosidase inhibitors.

Thus, compound **2a** upon treatment with propargyl bromide in the presence of NaH in DMF gave the propargylated azido compound **3** which was not isolated, and the crude reaction mixture was further quenched with water and stirred at room temperature for a further 15 min to afford the triazole-fused tricyclic molecule **4** in 96% yield. The ^{1}H NMR spectrum of **4** showed a sharp singlet at δ 7.52 near the aromatic region, typical for the 1,2,3-triazole hydrogen. In addition, the absence of the azide peak in the IR spectrum and HRMS $[M + H]^+$ peak at 514.2344 (calculated 514.2342) in the mass spectrum confirmed the structure assigned to it. A few more azido alcohols, viz., **2b**, **2e**, **2f** (β-isomer), **2g** (β-isomer), **2h**, and **2i**, were also subjected to the sequential alkynylation and cyclization. In the case of galacto-configured azides **2f**, **2g**, **2h**, and **2i**, the reaction mixture required heating to effect cycloaddition to form the triazole-fused tricyclic compounds **7** (88%), **8** (90%), **9** (90%), and **10** (92%) respectively.

In order to increase structural diversity, compound **4** was subjected to global deprotection with 20% $Pd(OH)_2/C$ in methanol at 5 atm H_2 for 30 h, which resulted in the removal of all the benzyl protecting groups to form product **11** in 93% yield. The tricyclic compound **11** represents a combination of D-glucose, morpholine, and triazole whose structure and stereochemical outcome was deduced from ^{1}H−^{1}H COSY and ^{1}H−^{1}H NOESY experiments along with mass spectral data of its peracetylated derivative **18**. Compound **11** was acetylated using the standard conditions (Ac_2O/Py) to get the triacetate **18** in 88% yield. Two-dimensional ^{1}H NMR spectral studies of compound **18** showed cross-peaks (Figure 2) between H-9a, H-6, and H-8 in the ^{1}H−^{1}H NOESY spectrum, and no cross-peaks were observed between H-7 and H-9a. This indicated that H-9a, H-6, and H-8 are in cis relationship.

An interaction between H-5a and H-7 proton signals was also observed. No interaction signals were observed between H-5a and H-8, indicating that H-5a, H-7, and the hydroxylmethyl moiety are in cis relationship. Therefore it was concluded that the orientation of the nitrogen at the anomeric center (i.e., C-9a) and oxygen at C-5a are β and α, respectively. These ^{1}H−^{1}H NOESY data confirm the absolute stereochemistry at the anomeric center (i.e., C-9a) and at C-5a of the carbohydrate moiety to be 9a*R* and 5a*R*, respectively (Figure 2). Likewise, rhamno **12**, xylo **13**, arabino **14**, galacto **15**, lyxo **16**, and furanogluco **17** derived tricyclic compounds were made and their structures and stereochemical outcome deduced from ^{1}H−^{1}H COSY and ^{1}H−^{1}H NOESY experiments along with mass spectrometry (Table 2).[25]

Scheme 2. Tentative Mechanism for CAN-Catalyzed Opening of Epoxide



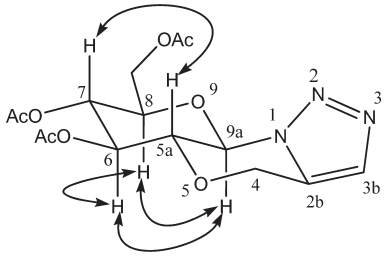


Figure 2. ^{1}H−^{1}H NOESY contacts recorded for compounds **18**.

Scheme 3. Synthesis of Sugar-Derived Morpholine Triazoles from Azido Alcohols

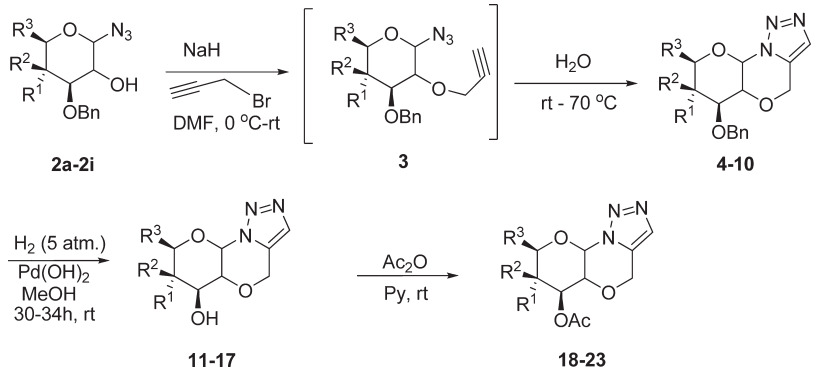


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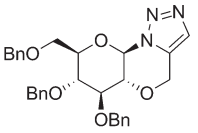
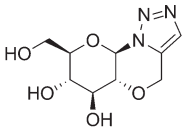
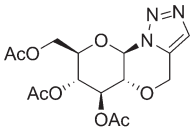
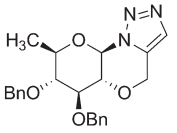
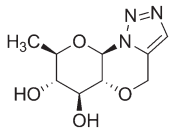
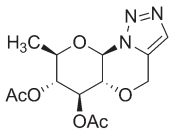
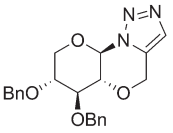
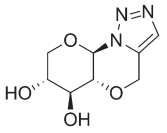
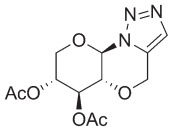
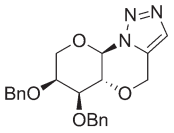
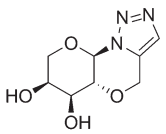
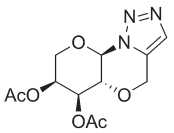
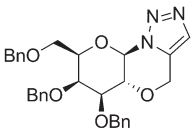
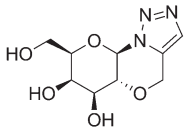
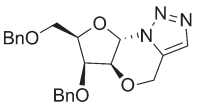
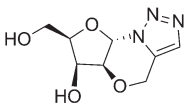
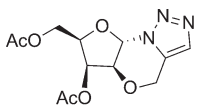
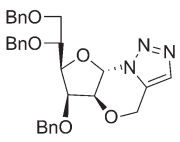
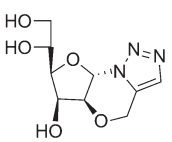
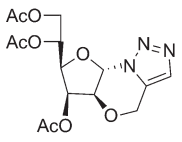
Table 2. Conversion of 1,2-Azido Alcohols to 1,2,3-Triazole Derivatives

entry	1-Aazido sugar	Fully protected 1,2,3-triazole derivative	Fully deprotected 1,2,3-triazole derivative	Acetylated 1,2,3-triazole derivative
1	**2a**	 **4** (96%)	 **11** (93%)	 **18** (88%)
2	**2b**	 **5** (92%)	 **12** (87%)	 **19** (83%)
3	**2e**	 **6** (95%)	 **13** (83%)	 **20** (77%)
4	**2f**	 **7** (88%)	 **14** (88%)	 **21** (83%)
5	**2g**	 **8** (90%)	 **15** (88%)	—
6	**2h**	 **9** (90%)	 **16** (86%)	 **22** (80%)
7	**2i**	 **10** (92%)	 **17** (88%)	 **23** (93%)

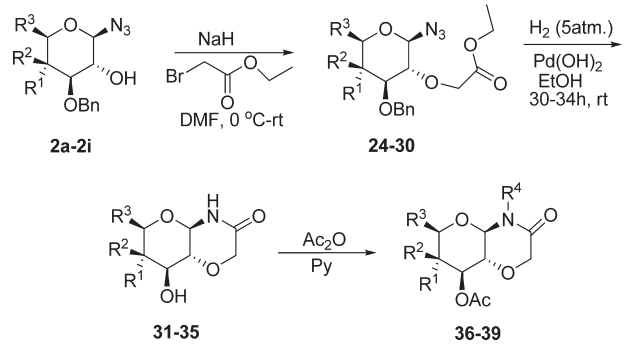
Interestingly, in case of compound **8**, the deprotection of the benzyl groups afforded the sugar-fused morpholine triazole derivative **15** as a crystalline compound, and thus its stereochemistry was confirmed by X-ray crystallographic analysis.[25]

We have further exploited the azido alcohols in synthesizing the sugar-fused oxazin-2-ones. Thus, D-glycopyranosyl azides, when subjected to sequential alkylation with ethyl bromoacetate, azide reduction followed by cyclization, and deprotection of the benzyl groups led to the sugar-fused oxazin-2-ones (Scheme 4).

The reaction of azido alcohol **2a** with ethyl bromoacetate and sodium hydride in DMF gave the azido ester **24** in good yield. Treatment of the azido ester **24** with 20% $Pd(OH)_2/C$ in ethanol under 5 atm of hydrogen for 35 h resulted in the reduction of azide followed by cyclization and deprotection of the benzyl groups in one pot to provide compound **31** in 93% yield. The structure and stereochemical outcome of the sugar oxazin-2-one **31** was deduced from $^1H-^1H$ COSY and $^1H-^1H$ NOESY experiments along with mass spectrometry of its triacetate derivative **36** obtained in 68% yield from **31** using the standard conditions

dx.doi.org/10.1021/jo200260w |*J. Org. Chem.* 2011, 76, 5972–5984

Scheme 4. Synthesis of Sugar-Derived Oxazin-2-ones from Azido Alcohols



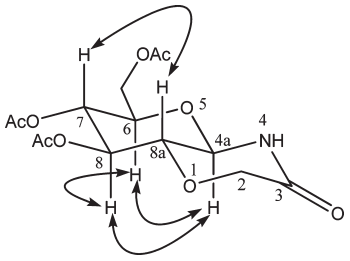


Figure 3. $^1H-^1H$ NOESY contacts recorded for compound **36**.

(Ac_2O/Py, 2 h). The appearance of a peak in ^1H NMR spectrum at δ 6.74 corresponding to the NH proton and the absence of the peak at δ 2.5 corresponding to NAc suggested compound **36** to be a tri-*O*-acetyl-oxazin-2-one. However, acetylation for a longer reaction time (15 h) led to the formation of the tetraacetate **37** in 64% yield. Two-dimensional ^1H NMR spectral studies of compound **36** (Figure 3) showed cross-peaks between H-4a, H-6, and H-8 in the $^1H-^1H$ NOESY spectrum and no cross-peaks were observed between H-7 and H-4a, indicating that H-4a, H-6, and H-8 are in cis relationship. An interaction between H-8a and H-7 proton signals was also observed; however, no interaction signals were observed between H-8a and H-6 which suggested that H-8a and the hydroxyl methyl are in cis relationship.

Thus, it was concluded that the orientation of the nitrogen at the anomeric center (i.e., C-4a) and oxygen at the C-8a are β and α, respectively, and the absolute stereochemistry at the anomeric center (C-4a) and C-8a of the carbohydrate moiety to be 4a*R* and 8a*R*, respectively (Figure 3). Likewise, rhamno **32**, xylo **33**, arabino **34**, and galacto **35** derived oxazin-2-ones were made from azido alcohols **2b**, **2e**, **2f**, and **2g**, and their structures and stereochemical outcome were established from $^1H-^1H$ COSY and $^1H-^1H$ NOESY experiments along with mass spectrometry of their peracetylated derivatives (Table 3).[25] Interestingly, irrespective of the geometry of the anomeric azide, the geometry of the final coupled product was β at the anomeric center. Thus, the minor α-isomeric azido alcohols **2f-α** and **2g-α** were converted into corresponding azido esters **40** and **41** (Scheme 5), and their reductions and deprotections were carried out by using hydrogenolysis to form **34** and **35**, respectively. In continuation, the azido alcohols **2h** and **2i** were also converted into their corresponding azido esters **29** and **30**, respectively, but subsequent reduction under hydrogenation conditions led to a complex mixture of products in both the cases.

Interestingly, the oxazin-2-one derivatives **33** and **35** were obtained as crystalline compounds whose X-ray crystallographic analysis[25] unequivocally established their structures as shown.

Enzyme Inhibition Studies. Enzyme inhibition activity of these tricyclic molecules has been studied with five commercially available glycosidases. These results revealed that one of the tricyclic compounds, viz., **11** exhibited selectivity toward α-glucosidase (yeast) and the IC_{50} value was found to be 34.9 μM, but it showed no inhibition of β-glucosidase (almonds), β-galactosidase (bovine liver), α-galactosidase (coffee beans), and α-mannosidase (jack beans). The tricyclic compound **12** showed no inhibition of β-glucosidase, α-mannosidase, and β-galactosidase, but it inhibited α-galactosidase and α-glucosidase at 37.6 μM and 72.2 μM concentrations, respectively. On the other hand, tricyclic molecules derived from xylose, arabinose, and galactose, viz., **13**, **14**, **15**, **16**, and **17** did not show any activity against all tested enzymes. Clearly, there is a change in terms of specificity as well as the inhibition constant values as a result of the combination of the structural features. This further suggests that structural variations of these hybrid molecules could promote better and specific glycosidase inhibition. The sugar oxazin-2-ones also were tested against the same glycosidases, as discussed above, however, the inhibitions were rather poor.

CONCLUSIONS

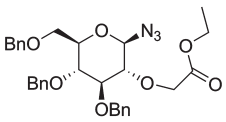
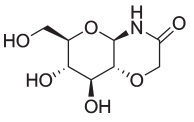
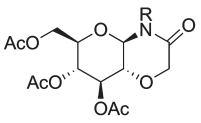
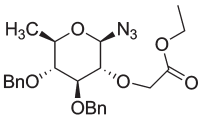
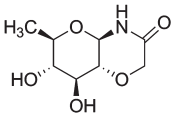
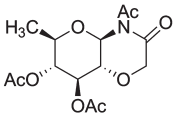
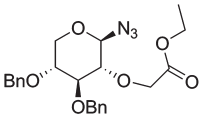
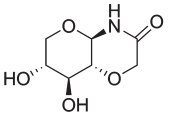
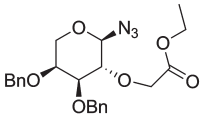
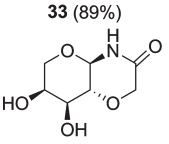
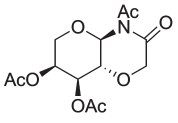
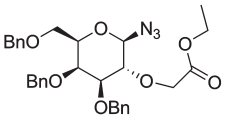
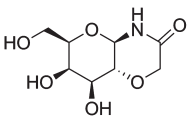
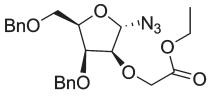
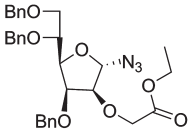
In summary, we have reported that NaN_3/CAN/H_2O is a useful reagent system to prepare sugar-derived vicinal azido alcohols from 1,2-anhydro sugars. These sugar-derived vicinal azido alcohols are converted into structurally diverse sugar-derived morpholine triazoles and sugar oxazin-2-ones and some of which have been found to be moderate to good inhibitors against some glycosidases. It is especially worth mentioning that compound **11** is a selective α-glucosidase inhibitor and showed fairly good activity in the micromolar range. Further work to extend the scope of the present study is in progress.

EXPERIMENTAL SECTION

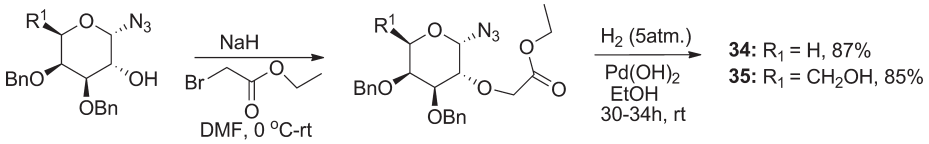
General Experimental Methods. IR spectra were recorded with FTIR as a thin film or using KBr pellets and are expressed in cm^{-1}. ^1H (400 or 500 MHz) and ^{13}C (100 or 125 MHz) NMR spectra were recorded using $CDCl_3$, D_2O, or CD_3OD as solvents. The absolute configurations of the new compounds are assigned with the help of NOE and $^1H-^1H$ NOESY experiments. 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), q (quartet), m (multiplet). Optical rotations were measured using polarimeter at 28 °C. All reactions were carried out using freshly distilled and dried 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.

General Procedure for Inhibition Assay. The enzymes and all the corresponding substrate were purchased from Sigma Aldrich Chemical Co. Inhibition studies of the tricyclic and bicyclic molecules **11**, **12**, **13**, **14**, **15**, **16**, **17**, **31**, **32**, **33**, **34**, and **35** were determined by measuring the residual hydrolytic activities of the glycosidases. The substrate concentration (3 mM) was prepared in 0.025 M citrate buffer with pH 4.0, and test compounds were preincubated with the enzymes for 1 h at 37 °C. The enzyme reaction was initiated by the addition of 100 μL substrate, and the controls were run simultaneously in the

Table 3. Conversion of 1,2-Azido Alcohols to Sugar-Fused Oxazin-2-ones

entry	1-Azido sugar	Azido ester	sugar oxazin-2-one	Acetylated derivative
1	**2a**	 **24** (88%)	 **31** (94%)	 **36,** R= H, (68%) **37**, R=Ac, (70%)
2	**2b**	 **25** (82%)	 **32** (86%)	 **38** (74%)
3	**2e**	 **26** (84%)	 **33** (89%)	–
4	**2f**	 **27** (78%)	 **34** (87%)	 **39** (76%)
5	**2g**	 **28** (83%)	 **35** (85%)	–
6	**2h**	 **29** (70%)	Complex mixture	–
7	**2i**	 **30** (72%)	Complex mixture	–

Scheme 5. Conversion of the α-Azido Alcohols into Their Corresponding α-Azido Esters



2f-α: R_1=H

2g-α: R_1= CH_2OBn

40: R_1 = H, 80%

41: R_1= CH_2OBn, 85%

absence of the test compound. The reaction was terminated at the end of the 10 min by the addition of 0.05 M borate buffer (pH 9.8), and the absorbance of the liberated *p*-nitrophenol was measured at 405 nm using Schimadzu spectrophotometer UV-160A. One unit of glycosidase activity is defined as the amount of enzyme that hydrolyzed 1 μM of *p*-nitrophenyl pyranoside per min at 25 °C.[31]

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General Procedure A for the Synthesis of Azido Alcohols. To a stirred solution of requisite 1,2-anhydro sugar (100 mg, 0.23 mmol) in dry acetonitrile (6 mL) were added sodium azide (45 mg, 0.69 mmol) and CAN (12 mg, 0.02 mmol). Then water (100 μL) was introduced into the reaction mixture. After completion of the reaction (TLC monitoring, approximately 5 min), the reaction was quenched with aq saturated sodium bicarbonate (4 mL) and extracted with ethyl acetate (3 × 4 mL). The combined organic extracts were washed with brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered and the solvent removed in vacuo. Purification of the azido alcohols was accomplished by column chromatography.

General Procedure B for the Synthesis of Fused Tricyclic of Sugar Morpholine Triazoles. To a solution of azido alcohol (80 mg, 0.17 mmol) in DMF (3 mL) at 0 °C were added sodium hydride (5 mg, 0.20 mmol) and propargyl bromide (19 mg, 0.16 mmol), and the mixture was stirred until the complete consumption of azido alcohol (TLC monitoring, approximately 5 min). The reaction mixture was quenched with water (1 mL) and stirring continued at rt to 70 °C for the required amount of time. DMF was evaporated under vacuum, and the resultant slurry was extracted with ethyl acetate (3 × 3 mL). The combined organic extracts were washed with brine (10 mL) and filtered through anhydrous Na_2SO_4. Evaporation of the solvent gave a crude product which was purified by column chromatography on silica gel (hexane/ethyl acetate as eluents) to obtain the triazole-fused compounds.

General Procedure C: Deprotection of Benzyl Groups. The cyclized product (100 mg, 0.19 mmol) was dissolved in 4 mL of MeOH, 20% $Pd(OH)_2/C$ (100 mg) was added, and the mixture was stirred under 5 atm of H_2 for 30−34 h at room temperature. The catalyst was filtered through Celite and concentrated in vacuo to obtain the tricyclic molecules, which were purified by column chromatography.

General Procedure D for the O-Alkylation of Azido Alcohols. To a stirred solution of an alcohol (100 mg, 0.21 mmol) in DMF (4 mL) at 0 °C was added a 60% suspension of NaH in paraffin oil (8 mg, 0.33 mmol). After 30 min, ethyl bromoacetate (42 mg, 0.25 mmol) was added dropwise at 0 °C and the reaction mixture stirred for 30 min at room temperature. Excess NaH was quenched by pouring the reaction mixture into ice, and then the mixture was extracted with diethyl ether (3 × 10 mL) followed by washing with water (3 × 10 mL). The organic layer was dried with $MgSO_4$ and concentrated in vacuo and the crude product purified by column chromatography to get the azido ester.

General Procedure E: Reduction of Azide, Cyclization, and Deprotection of Benzyl Groups. The azido ester (100 mg, 0.19 mmol) was dissolved in 4 mL of EtOH and treated with 20% $Pd(OH)_2/C$ (100 mg), and the resultant mixture was stirred under 5 atm H_2 for 30−34 h at room temperature. The catalyst was filtered through Celite, and the filtrate was concentrated in vacuo to obtain a bicyclic molecule which was subjected to column chromatography to obtain pure bicyclic sugar oxazin-2-one.

General Procedure F: Acetylation of Alcohols. Bicyclic and tricyclic molecules were subjected to acetylation with excess of pyridine and Ac_2O (1:1, 2 mL) at room temperature for 2−15 h. Removal of the solvent under reduced pressure gave a residue that was purified by column chromatography to obtain an acetylated product.

*(2R,3R,4R,5R,6R)-2-Azido-4,5-bis(benzyloxy)-6-methyltetrahydro-2H-pyran-3-ol (**2b**).* The corresponding glycal (100 mg, 0.32 mmol) was dissolved in an ice-cooled biphasic solution of CH_2Cl_2 (0.85 mL), acetone (0.09 mL), and saturated aqueous $NaHCO_3$ (1.4 mL). The mixture was vigorously stirred, and a solution of Oxone (102 mg, 0.65 mmol) in H_2O (0.8 mL) was added dropwise. The crude reaction was vigorously stirred at 0 °C for 30 min and was then allowed to warm to room temperature until TLC indicated complete consumption of the glycal (~2 h). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 × 4 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated to afford the 1,2-anhydropyranoses (94 mg, yield: 99%) as a white syrup. The crude product could not be purified because of decomposition of the 1,2-anhydro sugar. This crude 1,2 anhydro sugar **1b** (75 mg, 0.23 mmol) was subjected to azidolysis by using general procedure A to give **2b** (63 mg, Yield 74%) as a white solid. Mp: 139−141 °C. R_f = 0.55 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −5.0 (*c* 0.6, CH_2Cl_2). IR (CH_2Cl_2) ν_{max}: 3444, 3031, 2921, 2852, 2113, 1731, 1597, 1495, 1454, 1360, 1316, 1247, 1117, 1071, 916, 736, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44−7.25 (m, 10H, Ar-H), 4.90−4.83 (m, 3H, 3 × OC*H*Ph), 4.66 (d, *J* = 10.9 Hz, 1H, OC*H*Ph), 4.49 (d, *J* = 8.6 Hz, 1H), 3.53−3.48 (m, 2H), 3.42 (t, *J* = 8.8 Hz, 1H), 3.20 (t, *J* = 9.15 Hz, 1H), 2.30 (s, 1H), 1.34 (d, *J* = 5.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 137.8, 128.7−128.0 (m, Ar-C), 90.1, 84.4, 82.9, 75.5, 75.4, 74.3, 73.8, 17.9. HRMS calcd for $C_{20}H_{23}N_3O_4Na$ $[M + Na]^+$ 392.1586, Found: 392.1585.

*(2R,3R,4R,5R,6R)-2-Azido-4,5-bis(4-methoxybenzyloxy)-6-((4-methoxybenzyloxy)methyl)tetrahydro-2H-pyran-3-ol (**2c**).* 1,2-Anhydropyranose **1c**[26] was subjected to azidolysis using general procedure A to give **2c** (yield: 83%) as a yellow liquid. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = +6.0 (*c* 1.0, CH_2Cl_2). IR (neat) ν_{max}: 3432, 2922, 2852, 2113, 1611, 1586, 1513, 1462, 1420, 1361, 1301, 1248, 1174, 1114, 1033, 819, 681, 518 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.24 (m, 4H, Ar-H), 7.07 (m, 2H, Ar-H), 6.90−6.81 (m, 6H, Ar-H), 4.82 (d, *J* = 10.9 Hz, 1H, OC*H*Ph), 4.72 (dd, *J* = 11.0 Hz, 10.5 Hz, 2H, 2 × OC*H*Ph), 4.61 (br s, 2H, 2 × OC*H*Ph), 4.56 (d, *J* = 11.9 Hz, 1H, OC*H*Ph), 4.48 (dd, *J* = 8.5 Hz, 7.5 Hz, 2H), 3.79 (br s, 9H, OMe), 3.69−3.67 (m, 1H), 3.58 (t, *J* = 9.2 Hz, 1H), 3.51−3.46 (m, 2H), 3.39 (t, *J* = 8.8 Hz, 1H), 2.30 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 159.4, 159.3, 133.1, 130.5−128.7 (m, Ar-C), 114.1−113.9 (m, Ar-C), 90.2, 84.2, 76.0, 75.0, 74.7, 73.9, 73.2, 67.9, 65.1, 55.3. HRMS calcd for $C_{30}H_{35}N_3O_8Na$ $[M + Na]^+$ 588.2322, Found: 588.2321.

*(2R,3R,4R,5R)-2-Azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-ol (**2e**).* 1,2-Anhydropyranose **1e**[27] was subjected to azidolysis using general procedure A to give **2e** (yield: 77%) as a yellow oil. R_f = 0.65 (hexane/EtOAc, 1:1).$[\alpha]^{28}_D$ = −28.8 (*c* 1.25, CH_2Cl_2). IR (neat) ν_{max}: 3328, 3064, 3030, 2984, 2927, 2873, 2115, 1603, 1494, 1372, 1312, 1240, 1091, 1061, 1025, 1002, 897, 736, 696, 646, 604 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.24 (m, 10H, Ar-H), 4.84 (d, *J* = 11.4 Hz, 1H, OC*H*Ph), 4.76 (d, *J* = 11.4 Hz, 1H, OC*H*Ph), 4.68−4.63 (m, 3H), 4.06 (dd, *J* = 11.7 Hz, 11.6 Hz, 1H), 3.58 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 3.53−3.51 (m, 1H), 3.45−3.39 (m, 2H), 2.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.5, 128.5−127.8 (m, Ar-C), 90.5, 80.8, 76.3, 74.4, 72.8, 71.1, 64.2. HRMS calcd for $C_{19}H_{21}N_3O_4Na$ $[M + Na]^+$ 378.1430, Found: 378.1430.

*(3R,4R,5S)-2-Azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-ol (**2f**).* 1,2-Anhydropyranose **1f**[28] was subjected to azidolysis by using general procedure A to give chromatographically separable diastereomeric mixture of **2f** and **2f-α** in 8:2 ratio, respectively (combined yield: 83%).

*Major Diastereomer: (2R,3R,4R,5S)-2-Azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-ol (**2f**).* (β-Anomer, yield: 67%): colorless thick liquid. R_f = 0.55 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = +110.0 (*c* 1.0, CH_2Cl_2). IR (neat) ν_{max}: 3328, 3032, 2863, 2120, 1453, 1365, 1313, 1243, 1125, 1072, 1022, 932, 768, 734, 696, 595 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.25 (m, 10H, Ar-H), 4.73 (d, *J* = 12.2 Hz, 1H, OC*H*Ph), 4.61 (t, *J* = 11.9 Hz, 2H, 2 × OC*H*Ph), 4.50 (d, *J* = 11.9 Hz, 1H, OC*H*Ph), 4.44 (d, *J* = 8.3 Hz, 1H), 4.14 (dd, *J* = 13.1 Hz, 12.9 Hz, 1H), 3.90 (t, *J* = 8.9 Hz, 1H), 3.74 (br s, 1H), 3.41−3.37 (m, 2H), 2.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 137.5, 128.5−127.7 (m, Ar-C), 90.8, 80.3, 71.6, 71.4, 71.3, 70.2, 65.4. HRMS calcd for $C_{19}H_{21}N_3O_4Na$ $[M + Na]^+$ 378.1430, Found: 378.1433.

*Minor Diastereomer: (2S,3R,4R,5S)-2-Azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-ol (**2f-α**).* (α-Anomer, yield: 16%): colorless thick liquid. R_f = 0.55 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = +24.0 (*c* 1.25, CH_2Cl_2). IR (neat) ν_{max}: 3334, 3090, 3065, 3031, 2902, 2867, 2120, 1639, 1494, 1454, 1406, 1349, 1333, 1312, 1242, 1122, 1081, 1047, 1017, 988, 920,

883, 834, 766, 739, 698, 667, 592, 565 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.25 (m, 10H, Ar-H), 5.41 (d, J = 3.6 Hz, 1H), 4.63 (dd, J = 12.4 Hz, 12.7 Hz, 3H, 3 × OC*H*Ph), 4.53 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.18 (br d, J = 8.3 Hz, 1H), 3.90−3.87 (m, 1H), 3.78 (d, J = 12.2 Hz, 2H), 3.65 (dd, J = 2.4 Hz, 8.8 Hz, 1H), 2.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 137.7, 128.5−127.7 (m, Ar-C), 89.5, 72.3, 71.9, 71.7, 68.1, 68.0, 62.44. HRMS calcd for $C_{19}H_{21}N_3O_4Na$ $[M + Na]^+$ 378.1430, Found: 378.1432.

*(3R,4R,5S,6R)-2-Azido-4,5-bis(benzyloxy)-6-(benzyloxymethyl)-tetrahydro-2H-pyran-3-ol (**2g**).* 1,2-Anhydropyranose **1g**[23] was subjected to azidolysis using general procedure A to give chromatographically separable diastereomeric mixture of **2g** and **2g-α** in 8:2 ratio, respectively (combined yield 89%).

*Major Diastereomer: (2R,3R,4R,5S,6R)-2-Azido-4,5-bis(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-3-ol (**2g**).* (β-Anomer, yield: 71%): colorless thick liquid. R_f = 0.5 (hexane/EtOAc, 9:1). $[\alpha]^{28}_D$ = −9.1 (*c* 1.1, CH_2Cl_2). IR (neat) ν_{max}: 3439, 3063, 3031, 2919, 2871, 2116, 1605, 1496, 1453, 1334, 1249, 1209, 1094, 1027, 930, 736, 698, 606, 464. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37−7.23 (m, 15H, Ar-H), 4.85 (d, J = 11.4 Hz, 1H, OC*H*Ph), 4.71 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.58 (d, J = 11.7 Hz, 2H, 2 × OC*H*Ph), 4.51−4.42 (m, 3H), 3.95 (d, J = 2.2 Hz, 1H), 3.87 (t, J = 8.9 Hz, 1H), 3.68−3.59 (m, 3H), 3.40 (dd, J = 9.5 Hz, 9.7 Hz, 1H), 2.48 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.6, 128.5−127.6 (m, Ar-C), 90.4, 82.0, 75.7, 74.5, 73.5, 72.4, 72.3, 70.5, 68.2. HRMS calcd for $C_{27}H_{29}N_3O_5Na$ $[M + Na]^+$ 498.2005, Found: 498.2006.

*Minor Diastereomer: (2S,3R,4R,5S,6R)-2-Azido-4,5-bis(benzyloxy)-6-benzyloxymethyl)tetrahydro-2H-pyran-3-ol (**2g-α**).* (α-Anomer, yield: 18%): yellow liquid. R_f = 0.6 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = +5.33 (*c* 1.5, CH_2Cl_2). IR (neat) ν_{max}: 3438, 3063, 3030, 2921, 2855, 2116, 1592, 1495, 1453, 1336, 1248, 1210, 1094, 1026, 928, 736, 698, 604 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.24 (m, 15H, Ar-H), 5.46 (d, J = 4.4 Hz, 1H), 4.84 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.71 (d, J = 11.4 Hz, 1H, OC*H*Ph), 4.58 (d, J = 11.4 Hz, 1H, OC*H*Ph), 4.53 (t, J = 11.1 Hz, 2H, 2 × OC*H*Ph), 4.43 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.25 (dd, J = 10.0 Hz, 9.7 Hz, 1H), 4.08−4.04 (m, 1H), 4.00 (br s, 1H), 3.63−3.56 (m, 3H), 2.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.6, 128.5−127.7 (m, Ar-C), 89.8, 79.1, 74.6, 73.5, 73.3, 72.2, 71.8, 68.3, 68.1. HRMS calcd for $C_{27}H_{29}N_3O_5Na$ $[M + Na]^+$ 498.2005, Found: 498.2002.

*(2S,3S,4R,5R)-2-Azido-4-(benzyloxy)-5-(benzyloxymethyl)tetrahydrofuran-3-ol (**2h**).* 1,2-Anhydropyranose **1h**[29] was subjected to azidolysis using general procedure A to give **2h** (yield: 64%) as a colorless thick liquid. R_f = 0.6 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = +16.0 (*c* 0.5, CH_2Cl_2). IR (neat) ν_{max}: 3378, 3064, 3031, 2919, 2869, 2109, 1496, 1453, 1361, 1241, 1146, 1068, 1027, 909, 737, 698. cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33−7.26 (m, 10H, Ar-H), 5.35 (s, 1H, −OH), 4.67 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.60 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.53 (d, J = 2.4 Hz, 1H, H-2), 4.51 (s, 1H), 4.44 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.42−4.38 (m, 1H, H-5), 4.36−4.32 (m, 1H, H-4), 3.93 (dd, J = 4.8, 10.4 Hz, 1H, H-3), 3.66−3.57 (m, 2H, H-6, H-6′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 136.9, 128.4−127.8 (m, Ar-C), 96.0, 78.6, 76.8, 73.9, 72.6, 72.4, 67.4. HRMS calcd for $C_{19}H_{21}N_3O_4Na$ $[M + Na]^+$ 378.1430, Found: 378.1437.

*(2S,3S,4R,5R)-2-Azido-4-(benzyloxy)-5-((R)-1,2-bis(benzyloxy)ethyl)-tetrahydrofuran-3-ol (**2i**).* 1,2-Anhydropyranose **1i**[29] was subjected to azidolysis using general procedure A to give **2i** (yield: 61%) as a colorless thick liquid. R_f = 0.65 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = +60.00 (*c* 1.1, CH_2Cl_2). IR (neat) ν_{max}: 3437, 3062, 3030, 2925, 2863, 2110, 1602, 1495, 1453, 1360, 1317, 1243, 1065, 1028, 902, 737, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.24 (m, 15H, Ar-H), 5.30 (d, J = 15.3 Hz, 1H, −OH), 4.83 (d, J = 11.3 Hz, 1H, OC*H*Ph), 4.61 (dd, J = 11.3 Hz, 11.3 Hz, 2H, 2 × OC*H*Ph), 4.54−4.46 (m, 3H), 4.44−4.42 (m, 1H), 4.34−4.32 (m, 1H), 4.04−4.00 (m, 2H), 3.95−3.92 (m, 1H), 3.81 (dd, J = 10.4 Hz, 10.7 Hz, 1H), 3.73 (dd, J = 10.7 Hz, 10.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 137.8, 137.3, 128.6−127.2 (m, Ar-C), 96.3, 79.3, 78.3, 78.0, 73.9, 73.4, 73.4, 73.3, 69.7. HRMS calcd for $C_{27}H_{30}N_3O_5$ $[M + H]^+$ 476.2185, Found: 476.2184.

*(5aR,6S,7R,8R,9aR)-6,7-Bis(benzyloxy)-8-(benzyloxymethyl)-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine (**4**).* Azido alcohol **2a** (80 mg, 0.16 mmol) was converted into tricyclic molecule by using general procedure B to give **4** (83 mg, yield 96%) as a light yellow thick liquid. R_f = 0.3 (hexane/EtOAc, 6:4). $[\alpha]^{28}_D$ = −36.66 (*c* 1.20, CH_2Cl_2). IR (neat) ν_{max}: 3062, 3030, 2921, 2868, 1716, 1595, 1553, 1495, 1453, 1352, 1317, 1249, 1208, 1096, 1027, 984, 913, 822, 738, 698, 643 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52(s, 1H), 7.39−7.14 (m, 15H, Ar-H), 5.27 (d, J = 8.5 Hz, 1H), 5.11 (d, J = 14.9 Hz, 1H), 4.99 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.90−4.80 (m, 3H), 4.64 (d, J = 11.9 Hz, 1H, OC*H*Ph), 4.52 (t, J = 11.9 Hz, 2H, 2 × OC*H*Ph), 3.99−3.83 (m, 5H), 3.61 (t, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.7, 131.8, 128.4−127.7 (m, Ar-C), 83.1, 81.7, 79.8, 78.6, 76.7, 75.4, 75.0, 73.6, 67.6, 62.8. HRMS calcd for $C_{30}H_{32}N_3O_5$ $[M + H]^+$ 514.2342, Found: 514.2344.

*(5aR,6S,7R,8R,9aR)-6,7-Bis(benzyloxy)-8-methyl-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine (**5**).* Azido alcohol **2b** was converted into tricyclic molecule by using general procedure B to give **5** (yield 92%) as a colorless thick liquid. R_f = 0.35 (hexane/EtOAc, 6:4). $[\alpha]^{28}_D$ = −68.66 (*c* 1.5, CH_2Cl_2). IR (neat) ν_{max}: 3062, 3031, 2979, 2897, 1602, 1496, 1453, 1353, 1316, 1250, 1209, 1155, 1097, 1009, 986, 904, 827, 740, 698, 636, 559 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.39−7.25 (m, 10H, Ar-H), 5.27 (d, J = 8.5 Hz, 1H), 5.12 (d, J = 14.8 Hz, 1H), 4.99 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.95 (d, J = 10.7 Hz, 1H, OC*H*Ph), 4.90 (d, J = 14.8 Hz, 1H), 4.82 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.68 (d, J = 11.0 Hz, 1H, OC*H*Ph), 3.89−3.82 (m, 2H), 3.62−3.57 (m, 1H), 3.36 (t, J = 8.8 Hz, 1H), 1.48 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.7, 131.7−127.9 (m, Ar-C), 83.0, 82.9, 81.6, 80.2, 75.7, 75.4, 75.1, 62.8, 18.0. HRMS calcd for $C_{23}H_{26}N_3O_4$ $[M + H]^+$ 408.1923, Found: 408.1922.

*(5aR,6S,7R,9aR)-6,7-Bis(benzyloxy)-8-(benzyloxymethyl)-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine (**6**).* Azido alcohol **2e** was converted into tricyclic molecule by using general procedure B to give **6** (yield: 95%) as a thick liquid. R_f = 0.40 (hexane/EtOAc, 6:4). $[\alpha]^{28}_D$ = −54.0 (*c* 1.5, CH_2Cl_2). IR (neat) ν_{max}: 3030, 2867, 1642, 1496, 1453, 1370, 1247, 1204, 1098, 1010, 985, 826, 740, 698, 643 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51(s, 1H), 7.40−7.25 (m, 10H, Ar-H), 5.19 (d, J = 8.8 Hz, 1H), 5.11 (d, J = 15.1 Hz, 1H), 4.95 (d, J = 11.4 Hz, 1H−OC*H*Ph), 4.90−4.78 (m, 3H), 4.66 (d, J = 11.4 Hz, 1H, OC*H*Ph), 4.25 (dd, J = 12.6 Hz, 11.4 Hz, 1H), 3.82−3.73 (m, 2H), 3.63−3.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.5, 131.7, 128.5−127.8 (m, Ar-C), 83.7, 80.8, 79.5, 75.0, 73.9, 67.5, 62.8. HRMS calcd for $C_{22}H_{24}N_3O_4$ $[M + H]^+$ 394.1767, Found: 394.1767.

*(5aR,6S,7S,9aR)-6,7-Bis(benzyloxy)-8-(benzyloxymethyl)-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine (**7**).* Azido alcohol **2f** was converted into tricyclic molecule by using general procedure B to give **7** (yield: 88%) as a yellow liquid. R_f = 0.45 (hexane/EtOAc, 6:4). $[\alpha]^{28}_D$ = −18.6 (*c* 1.5, CH_2Cl_2). IR (neat) ν_{max}: 3031, 2865, 1657, 1496, 1453, 1376, 1350, 1292, 1243, 1214, 1179, 1094, 1060, 1026, 987, 940, 826, 738, 699, 652, 596 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51(s, 1H), 7.39−7.26 (m, 10H, Ar-H), 5.15−5.09 (m, 2H), 4.96 (d, J = 15.1 Hz, 1H), 4.81−4.68 (m, 4H), 4.34 (br d, J = 13.2 Hz, 1H), 4.17−4.13 (m, 1H), 3.86 (br s, 1H), 3.75−3.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 137.5, 131.9, 128.4−127.5 (m, Ar-C), 84.6, 77.1, 73.3, 72.5, 72.4, 72.0, 67.3, 62.8. HRMS calcd for $C_{22}H_{24}N_3O_4$ $[M + H]^+$ 394.1767, Found: 394.1764.

*(5aR,6S,7S,8R,9aR)-6,7-Bis(benzyloxy)-8-(benzyloxymethyl)-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine (**8**).* Azido alcohol **2g** was converted into tricyclic molecule by using general procedure B to give **8** (yield 90%) as a colorless thick liquid. R_f = 0.3 (hexane/EtOAc, 6:4). $[\alpha]^{28}_D$ = −38.00 (*c* 1.0, CH_2Cl_2). IR (neat) ν_{max}:

3030, 2869, 1725, 1601, 1495, 1452, 1355, 1271, 1210, 1101, 987, 825, 738, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49(s, 1H), 7.38−7.29 (m, 15H, Ar-H), 5.21 (d, J = 8.5 Hz, 1H), 5.09 (d, J = 15.1 Hz, 1H), 4.97 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.93 (d, J = 14.8 Hz, 1H), 4.86 (d, J = 12.2 Hz, 1H, OC*H*Ph), 4.75 (d, J = 12.2 Hz, 1H, OC*H*Ph), 4.62 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.51−4.48 (m, 3H), 4.12 (dd, J = 10.0 Hz, 10.0 Hz, 2H), 3.98−3.95 (m, 1H), 3.79−3.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.8, 137.4, 131.9, 128.4−127.4 (m, Ar-C), 84.2, 78.6, 77.2, 76.8, 75.4, 74.4, 73.6, 72.9, 67.2, 62.8. HRMS calcd for $C_{30}H_{32}N_3O_5$ $[M + H]^+$ 514.2342, Found: 514.2347.

*(5aS,6S,7R,8aS)-6-Benzyloxy)-7-(benzyloxymethyl)-5a,6,7,8a-tetrahydro-4H-furo[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine (**9**).* Azido alcohol **2h** was converted into tricyclic molecule by using general procedure B to give **9** (yield 90%) as a light yellow thick liquid. R_f = 0.45 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = +11.6 (c 2.0, CH_2Cl_2). IR (neat) ν_{max}: 3062, 3030, 2919, 2863, 1721, 1636, 1496, 1453, 1384, 1357, 1251, 1203, 1139, 1078, 1046, 1026, 1005, 790, 737, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.53(s, 1H), 7.33−7.24 (m, 10H, Ar-H), 5.79 (d, J = 8.6 Hz, 1H), 5.23 (d, J = 14.9 Hz, 1H), 5.04 (d, J = 15.75 Hz, 1H), 4.90 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.73−4.69 (m, 2H), 4.67 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.58 (dd, J = 11.7 Hz, 11.7 Hz, 2H, 2 × OC*H*Ph), 3.94−3.90 (m, 1H), 3.85−3.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 137.5, 131.1, 128.5−127.6 (m, Ar-C), 83.3, 82.8, 82.4, 73.7, 73.7, 73.2, 67.8, 64.7. HRMS calcd for $C_{22}H_{24}N_3O_4$ $[M + H]^+$ 394.1767, Found: 394.1765.

*(5aS,6S,7R,8aS)-6-(Benzyloxy)-7-((R)-1,2-bis(benzyloxy)ethyl)-5a,6,7,8a-tetrahydro-4H-furo[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine (**10**).* Azido alcohol **2i** was converted into tricyclic molecule by using general procedure B to give **10** (yield 92%) as a light yellow thick liquid. R_f = 0.4 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −13.20 (c 2.0, CH_2Cl_2). IR (neat) ν_{max}: 3030, 2923, 2855, 1646, 1496, 1453, 1357, 1304, 1249, 1208, 1124, 1092, 1049, 1027, 984, 737, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.55(s, 1H), 7.36−7.23 (m, 15H, Ar-H), 5.86 (d, J = 8.6 Hz, 1H), 5.23 (d, J = 15.1 Hz, 1H), 5.04 (d, J = 15.1 Hz, 1H), 4.97 (d, J = 10.8 Hz, 1H, OC*H*Ph), 4.77 (d, J = 11.4 Hz, 1H, OC*H*Ph), 4.66−4.63 (m, 2H), 4.61−4.58 (m, 2H), 4.55−4.52 (m, 1H), 4.48 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.15−4.12 (m, 1H), 3.97−3.91 (m, 2H), 3.78 (dd, J = 4.9 Hz, 10.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6, 138.4, 137.6, 131.1, 128.8−127.6 (m, Ar-C), 83.8, 82.7, 81.9, 75.5, 74.1, 73.5, 73.4, 72.5, 69.6, 64.7. HRMS calcd for $C_{30}H_{32}N_3O_5$ $[M + H]^+$ 514.2342, Found: 514.2343.

*(5aR,6S,7R,8R,9aR)-8-(Hydroxymethyl)-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diol (**11**).* Compound **4** (52 mg, 0.1 mmol) was subjected to global deprotection by using general procedure C to give **11** (23 mg, Yield: 93%) as a white solid. Mp: 286−288 °C. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −17.00 (c 1.0, MeOH). ^1H NMR (400 MHz, D_2O): δ 7.53 (s, 1H), 5.39 (d, J = 8.5 Hz, 1H), 5.07 (d, J = 15.4 Hz, 1H), 4.84 (d, J = 15.6 Hz, 1H), 3.88 (d, J = 10.4 Hz, 1H), 3.78−3.67 (m, 3H), 3.49−3.40 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ 134.2, 129.8, 83.3, 80.3, 78.5, 73.5, 70.7, 63.4, 61.3. HRMS calcd for $C_9H_{13}N_3O_5Na$ $[M + Na]^+$ 266.0753, Found: 266.0754.

*(5aR,6S,7R,8R,9aR)-8-Methyl-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diol (**12**).* Compound **5** was subjected to global deprotection by using general procedure C to give **12** (yield: 87%) as a thick liquid. R_f = 0.5 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −29.00 (c 1.0, MeOH). ^1H NMR (400 MHz, D_2O): δ 7.58 (s, 1H), 5.41 (d, J = 8.5 Hz, 1H), 5.12 (d, J = 15.4 Hz, 1H), 4.89 (d, J = 15.6 Hz, 1H), 3.82−3.72 (m, 2H), 3.49−3.45 (m, 1H), 3.26 (t, J = 9.0 Hz, 1H), 1.34 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, D_2O): δ 135.9, 131.6, 85.0, 80.5, 78.5, 78.0, 75.0, 65.1, 19.3. HRMS calcd for $C_9H_{14}N_3O_4$ $[M + H]^+$ 228.0984, Found: 228.0980.

*(5aR,6S,7R,9aR)-4,5a,6,7,8,9a-Hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diol (**13**).* Compound **6** was subjected to global deprotection by using general procedure C to give **13** (yield: 83%) as a colorless liquid. R_f = 0.55 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −10.66 (c 0.75, MeOH). ^1H NMR (400 MHz, D_2O): δ 7.52 (s, 1H), 5.29 (d, J = 8.5 Hz, 1H), 5.07 (d, J = 15.3 Hz, 1H), 4.83 (d, J = 15.4 Hz, 1H), 4.14 (d, J = 11.7 Hz, 1H), 3.68 (d, J = 7.5 Hz, 1H), 3.57−3.52 (m, 2H), 3.41−3.37 (m, 1H). ^{13}C NMR (100 MHz, D_2O): δ 134.2, 129.8, 84.1, 78.5, 73.6, 70.4, 69.1, 63.4. HRMS calcd for $C_8H_{12}N_3O_4$ $[M + H]^+$ 214.0828, Found: 214.0827.

*(5aR,6S,7S,9aR)-4,5a,6,7,8,9a-Hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diol (**14**).* Compound **7** was subjected to global deprotection by using general procedure C to give **14** (yield: 88%) as a liquid. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −5.0 (c 0.6, MeOH). ^1H NMR (400 MHz, D_2O): δ 7.53 (s, 1H), 5.26 (d, J = 8.3 Hz, 1H), 5.07 (d, J = 15.6 Hz, 1H), 4.86 (d, J = 15.4 Hz, 1H), 4.10 (d, J = 13.1 Hz, 1H), 4.00 (br s, 1H), 3.96−3.92 (m, 2H), 3.74−3.69 (m, 1H). ^{13}C NMR (100 MHz, D_2O): δ 134.2, 129.9, 84.6, 76.5, 70.9, 70.2, 69.4, 63.4. HRMS calcd for $C_8H_{12}N_3O_4$ $[M + H]^+$ 214.0828, Found: 214.0829.

*(5aR,6S,7R,8R,9aR)-8-(Hydroxymethyl)-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diol (**15**).* Compound **8** was subjected to global deprotection by using general procedure C to give **15** (yield: 88%) as a white crystalline compound. Mp: 273−275 °C. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −6.0 (c 1.0, MeOH). ^1H NMR (400 MHz, D_2O): δ 7.55 (s, 1H, H-2b), 5.35 (d, J = 8.4 Hz, 1H, H-9a), 5.09 (d, J = 15.3 Hz, 1H, H-4), 4.87 (d, J = 15.6 Hz, 1H, H-4′), 4.01−3.93 (m, 3H, H-7, H-10, H-10′), 3.81−3.67 (m, 3H, H-5a, H-8, H-6). ^{13}C NMR (125 MHz, D_2O): δ 133.5, 129.3, 83.4, 79.1, 75.8, 69.8, 68.9, 62.8, 61.0. HRMS calcd for $C_9H_{14}N_3O_5$ $[M + H]^+$ 244.0933, Found: 244.0936.

*(5aS,6S,7R,8aS)-7-(Hydroxymethyl)-5a,6,7,8a-tetrahydro-4H-furo-[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazin-6-ol (**16**).* Compound **9** was subjected to global deprotection by using general procedure C to give **16** (yield: 86%) as a colorless oil. R_f = 0.45 (MeOH/EtOAc, 2:8). $[\alpha]^{28}_D$ = +56.0 (c 0.25, MeOH). ^1H NMR (500 MHz, CD_3OD): δ 7.60(s, 1H), 5.70 (d, J = 8.6 Hz, 1H), 5.24 (d, J = 15.1 Hz, 1H), 5.08 (d, J = 15.2 Hz, 1H), 4.60−4.54 (m, 2H), 3.92−3.86 (m, 3H). ^{13}C NMR (125 MHz, CD_3OD): δ 134.0, 129.7, 86.8, 84.7, 82.7, 68.6, 65.2, 61.7. HRMS calcd for $C_8H_{11}N_3O_4Na$ $[M + Na]^+$ 236.0647, Found: 236.0640.

*(R)-1-((5aS,6S,7R,8aS)-6-Hydroxy-5a,6,7,8a-tetrahydro-4H-furo-[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazin-7-yl)ethane-1,2-diol (**17**).* Compound **10** was subjected to global deprotection by using general procedure C to give **17** (yield: 88%) as a colorless oil. R_f = 0.45 (MeOH/EtOAc, 2:8). $[\alpha]^{28}_D$ = +55.7 (c 0.70, MeOH). ^1H NMR (500 MHz, D_2O): δ 7.54(s, 1H), 5.64 (d, J = 8.5 Hz, 1H), 5.15 (d, J = 15.4 Hz, 1H), 5.02 (d, J = 15.4 Hz, 1H), 4.63 (t, J = 3.7 Hz, 1H), 4.38 (dd, J = 9.1 Hz, 3.4 Hz, 1H), 3.98−3.94 (m, 2H), 3.76 (dd, J = 12.3 Hz, 12.0 Hz, 1H), 3.63 (dd, J = 5.4 Hz, 5.4 Hz, 1H). ^{13}C NMR (125 MHz, D_2O): δ 132.8, 129.3, 83.6, 83.3, 80.1, 68.6, 67.0, 64.2, 62.7. HRMS calcd for $C_9H_{13}N_3O_5Na$ $[M + Na]^+$ 266.0753, Found: 266.0760.

*(5aR,6S,7R,8R,9aR)-8-(Acetoxymethyl)-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diyl Diacetate (**18**).* Compound **11** (15 mg, 0.06 mmol) was acetylated by using general procedure F to give **18** (20 mg, Yield: 88%) as a white amorphous solid. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −16.42 (c 0.7, CH_2Cl_2). IR (neat) ν_{max}: 2919, 1737, 1434, 1377, 1226, 1175, 1142, 1115, 1075, 1044, 1014, 983, 965, 924, 822, 757, 636, 602, 564, 480, 436 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H, H-2b), 5.44 (t, J = 8.3 Hz, 2H, H-9a, H-6), 5.26 (t, J = 9.6 Hz, 1H, H-7), 5.13 (d, J = 15.1 Hz, 1H, H-4), 4.90 (d, J = 15.1 Hz, 1H, H-4′), 4.42 (d, J = 12.6 Hz, 1H, H-10), 4.41 (d, J = 12.6 Hz, 1H, H-10′), 4.14−4.11 (m, 1H, H-8), 3.68 (t, J = 9.2 Hz, 1H, H-5a), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 169.4, 131.7, 128.5, 83.0, 75.5, 71.4, 68.0, 63.0, 61.3, 21.0−20.5 (OAc). HRMS calcd for $C_{15}H_{19}N_3O_8Na$ $[M + Na]^+$ 392.1070, Found: 392.1063.

*(5aR,6S,7R,8R,9aR)-8-Methyl-4,5a,6,7,8,9a-hexahydropyrano[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diyl Diacetate (**19**).* Compound **12** was acetylated by using general procedure F for 2 h to give **19** (yield: 83%) as a colorless oil. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ =

−32.00 (*c* 0.5, CH_2Cl_2). IR (neat) ν_{max}: 2922, 1748, 1591, 1452, 1376, 1238, 1156, 1097, 1045, 986, 925 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H, H-2b), 5.37−5.33 (m, 2H, H-9a, H-6), 5.09 (d, *J* = 15.1 Hz, 1H, H-4′), 4.94 (t, *J* = 9.2 Hz, 1H, H-7), 4.86 (d, *J* = 15.1 Hz, 1H, H-4′), 3.99−3.96 (m, 1H, H-8), 3.63−3.59 (m, 1H, H-5a), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 1.39 (d, *J* = 6.3 Hz, 3H, H-10). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 169.7, 131.6, 128.5, 83.0, 74.1, 73.3, 71.4, 63.0, 20.7, 20.6, 17.4. HRMS calcd for $C_{13}H_{18}N_3O_6$ $[M + H]^+$ 312.1196, Found: 312.1198.

*(5aR,6S,7R,9aR)-4,5a,6,7,8,9a-Hexahydropyrano[3,2-b][1,2,3]triazolo-[1,5-d][1,4]oxazine-6,7-diyl Diacetate (**20**).* Compound **13** was acetylated using general procedure F for 2 h to give **20** (yield: 77%) as a colorless oil. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −88.0 (*c* 0.5, CH_2Cl_2). IR (neat) ν_{max}: 2919, 1634, 1360, 1222, 1049, 829, 750, 683, 639, 598, 472 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H, H-2b), 5.42 (t, *J* = 9.6 Hz, 1H, H-6), 5.33 (d, *J* = 8.5 Hz, 1H, H-9a), 5.18−5.10 (m, 2H, H-7, H-4), 4.89 (d, *J* = 15.1 Hz, 1H, H-4′), 4.44 (dd, *J* = 11.7 Hz, 11.7 Hz, 1H, H-8), 3.74−3.68 (m, 1H, H-8′), 3.63−3.58 (m, 1H, H-5a), 2.14 (s, 3H, OAc), 2.08 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 169.7, 131.6, 128.4, 83.7, 76.8, 70.9, 68.7, 66.1, 63.0, 20.7, 20.6. HRMS calcd for $C_{12}H_{16}N_3O_6$ $[M + H]^+$ 298.1039, Found: 298.1039.

*(5aR,6S,7S,9aR)-4,5a,6,7,8,9a-Hexahydropyrano[3,2-b]-[1,2,3]triazolo[1,5-d][1,4]oxazine-6,7-diyl Diacetate (**21**).* Compound **14** was acetylated by using general procedure F for 2 h to give **21** (yield: 83%) as a colorless oil. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −13.0 (*c* 0.75, CH_2Cl_2). IR (neat) ν_{max}: 2923, 1745, 1635, 1453, 1374, 1238, 1124, 1091, 1039, 961, 926, 530 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H, H-2b), 5.42 (br s, 1H, H-7), 5.31−5.29 (m, 2H, H-9a, H-6). 5.09 (d, *J* = 15.3 Hz, 1H, H-4), 4.92 (d, *J* = 14.9 Hz, 1H, H-4′), 4.30 (br d, *J* = 13.7 Hz, 1H, H-8), 4.05 (br d, *J* = 13.7 Hz, 1H, H-8′), 3.97 (dd, *J* = 8.4 Hz, 8.8 Hz, 1H, H-5a), 2.13 (s, 3H, OAc), 2.09 (s, 3H, OAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.8, 131.6, 128.4, 84.4, 74.1, 69.2, 68.1, 68.0, 62.9, 20.7, 20.6. HRMS calcd for $C_{12}H_{16}N_3O_6$ $[M + H]^+$ 298.1039, Found: 298.1039.

*((5aS,6S,7R,8aS)-6-Acetoxy-5a,6,7,8a-tetrahydro-4H-furo[3,2-b]-[1,2,3]triazolo[1,5-d][1,4]oxazin-7-yl)methyl Acetate (**22**).* Compound **16** was acetylated by using general procedure F to give **22** (yield: 80%) as a light yellow oil. R_f = 0.5 (hexane/EtOAc, 1:4). $[\alpha]^{28}_D$ = +37.14 (*c* 0.35, CH_2Cl_2). IR (neat) ν_{max}: 2922, 2851, 1746, 1594, 1372, 1224, 1079, 1027 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 1H, H-2b), 5.84 (t, *J* = 4.0 Hz, 1H, H-6), 5.71 (d, *J* = 8.5 Hz, 1H, H-8a), 5.20 (d, *J* = 14.9 Hz, 1H, H-4), 5.07 (d, *J* = 15.2 Hz, 1H, H-4′), 4.91−4.88 (m, 1H, H-7), 4.38−4.34 (m, 2H, H-9, H-9′), 3.92 (dd, *J* = 4.0 Hz, 8.5 Hz, 1H, H-5a), 2.16 (s, 3H, OAc), 2.08 (s, 3H, OAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 169.3, 130.9, 128.8, 83.1, 80.8, 79.7, 67.9, 64.6, 61.3, 20.7, 20.5. HRMS calcd for $C_{12}H_{15}N_3O_6Na$ $[M + Na]^+$ 320.0859, Found: 320.0857.

*(R)-1-((5aS,6S,7R,8aS)-6-Acetoxy-5a,6,7,8a-tetrahydro-4H-furo-[3,2-b][1,2,3]triazolo[1,5-d][1,4]oxazin-7-yl)ethane-1,2-diyl Diacetate (**23**).* Compound **17** was acetylated by using general procedure F to give **23** (yield: 93%) as a yellow oil. R_f = 0.5 (hexane/EtOAc, 1:4). $[\alpha]^{28}_D$ = +36.0 (*c* 0.5, CH_2Cl_2). IR (neat) ν_{max}: 2924, 2853, 1747, 1641, 1446, 1374, 1227, 1143, 1124, 1074, 1049, 1020, 954, 692 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 1H, H-2b), 5.87 (t, *J* = 4.0 Hz, 1H, H-6), 5.74 (d, *J* = 8.6 Hz, 1H, H-8a), 5.40−5.37 (m, 1H, H-1), 5.20 (d, *J* = 15.1 Hz, 1H, H-4), 5.07 (d, *J* = 15.2 Hz, 1H, H-4′), 4.84 (dd, *J* = 10.0 Hz, 10.0 Hz, 1H, H-7), 4.72 (dd, *J* = 12.3 Hz, 12.6 Hz, 1H, H-2), 4.24 (dd, *J* = 12.3 Hz, 12.6 Hz, 1H, H-2′), 3.95 (dd, *J* = 8.3 Hz, 4.0 Hz, 1H, H-5a), 2.11 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.00 (s, 3H, OAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.4, 169.3, 131.0, 128.9, 83.7, 79.6, 77.2, 67.3, 67.3, 64.6, 62.2, 20.7−20.5 (OAc). HRMS calcd for $C_{15}H_{20}N_3O_8$ $[M + H]^+$ 370.1250, Found: 370.1255.

*Ethyl 2-((2R,3R,4S,5R,6R)-2-Azido-4,5-bis(benzyloxy)-6-(benzyloxymethyl)-tetrahydro-2H-pyran-3-yloxy)acetate (**24**).* Azido alcohol **2a** (80 mg, 0.16 mmol) was subjected to alkylation by using general procedure D to give **24** (83 mg, yield: 88%). R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = −20.0 (*c* 1.5, CH_2Cl_2). IR (neat) ν_{max}: 3008, 3063, 3031, 2981, 2916, 2868, 2115, 1754, 1603, 1496, 1453, 1363, 1251, 1209, 1099, 1028, 736, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33−7.13 (m, 15H, Ar-H), 4.94 (d, *J* = 11.0 Hz, 1H, OC*H*Ph), 4.81 (t, *J* = 10.3 Hz, 2H, 2 × OC*H*Ph), 4.67 (d, *J* = 8.5 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H, OC*H*Ph), 4.52 (d, *J* = 11.0 Hz, 1H, OC*H*Ph), 4.43 (d, *J* = 15.6 Hz, 1H), 4.28 (d, *J* = 15.6 Hz, 1H), 4.21−4.16 (m, 3H), 3.74−3.64 (m, 3H), 3.60 (d, *J* = 9.0 Hz, 1H), 3.52−3.50 (m, 1H), 3.22 (t, *J* = 8.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 138.3, 137.92, 128.3−127.6 (m, Ar-C), 89.7, 89.6, 84.4, 83.0, 77.3, 75.6, 75.0, 73.5, 70.0, 68.3, 60.8, 14.1. HRMS calcd for $C_{31}H_{35}N_3O_7Na$ $[M + Na]^+$ 584.2373, Found: 584.2372.

*Ethyl 2-((2R,3R,4S,5R,6R)-2-Azido-4,5-bis(benzyloxy)-6-methyltetrahydro-2H-pyran-3-yloxy)acetate (**25**).* Azido alcohol **2b** was subjected to esterification by using general procedure D to give **25** (yield: 82%) as a liquid. R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = −13.0 (*c* 1.5, CH_2Cl_2). IR (neat) ν_{max}: 3068, 3031, 2980, 2914, 2870, 2113, 1748, 1598, 1496, 1444, 1386, 1359, 1256, 1211, 1149, 1114, 1090, 1052, 1031, 1006, 941, 910, 859, 834, 753, 699, 641 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33−7.25 (m, 10H, Ar-H), 4.94 (d, *J* = 11.0 Hz, 1H, OC*H*Ph), 4.84 (dd, *J* = 10.9 Hz, 11.0 Hz, 2H, 2 × OC*H*Ph), 4.66−4.61 (m, 2H), 4.43 (dd, *J* = 15.6 Hz, 11.0 Hz, 1H), 4.28 (d, *J* = 15.8 Hz, 1H), 4.24−4.16 (m, 2H), 3.66 (t, *J* = 9.0 Hz, 1H), 3.50−3.43 (m, 1H), 3.21−3.14 (m, 2H), 1.31 (d, *J* = 6.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 138.3, 137.8, 128.4−127.0 (m, Ar-C), 89.5, 84.2, 83.3, 82.7, 75.6, 75.3, 73.4, 70.0, 60.9, 17.7, 14.1. HRMS calcd for $C_{24}H_{30}N_3O_6$ $[M + H]^+$ 456.2135, Found: 456.2136.

*Ethyl 2-((2R,3R,4S,5R)-2-Azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-yloxy)acetate (**26**).* Azido alcohol **2e** was subjected to esterification by using general procedure D to give **26** (yield: 84%) as a liquid. R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = −13.0 (*c* 1.0, CH_2Cl_2). IR (neat) ν_{max}: 3064, 3032, 2982, 2923, 2117, 1753, 1624, 1496, 1455, 1369, 1242, 1207, 1100, 1028, 738, 699, 463 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.34−7.25 (m, 10H, Ar-H), 4.87 (s, 2H), 4.70 (d, *J* = 11.7 Hz, 1H, OC*H*Ph), 4.60 (dd, *J* = 8.3 Hz, 11.7 Hz, 2H), 4.33 (dd, *J* = 16.0 Hz, 15.7 Hz, 2H), 4.20−4.14 (m, 2H), 3.87 (dd, *J* = 11.7 Hz, 11.7 Hz, 1H), 3.66−3.52 (m, 2H), 3.26 (dd, *J* = 10.3 Hz, 10.0 Hz, 1H), 3.13 (t, *J* = 8.5 Hz, 1H), 1.24 (t, *J* = 7.15 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 138.3, 137.8, 128.4−127.8 (m, Ar-C), 90.3, 83.4, 82.5, 77.2, 75.5, 73.4, 70.0, 65.7, 60.9, 14.1. HRMS calcd for $C_{23}H_{28}N_3O_6$ $[M + H]^+$ 442.1978, Found: 442.1982.

*Ethyl 2-((2R,3R,4S,5S)-2-Azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-yloxy)acetate (**27**).* Azido alcohol **2f** was subjected to esterification by using general procedure D to give **27** (yield: 78%) as a colorless oil. R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = +10.0 (*c* 0.6, CH_2Cl_2). IR (neat) ν_{max}: 2918, 2113, 1752, 1587, 1452, 1366, 1253, 1207, 1143, 1094, 1055, 1025, 930, 737, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.25 (m, 10H, Ar-H), 4.72 (d, *J* = 12.6 Hz, 1H, OC*H*Ph), 4.64−4.61 (m, 4H), 4.38 (dd, *J* = 16.1 Hz, 15.8 Hz, 2H), 4.20−4.07 (m, 3H), 3.70 (br s, 1H), 3.64−3.56 (m, 2H), 3.35 (br d, *J* = 12.9 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 137.9, 137.8, 128.4−127.5 (m, Ar-C), 90.0, 79.8, 79.4, 72.1, 71.8, 71.3, 70.1, 64.7, 60.8, 14.1. HRMS calcd for $C_{23}H_{27}N_3O_6Na$ $[M + Na]^+$ 464.1798, Found: 464.1797.

*Ethyl 2-((2R,3R,4S,5S,6R)-2-Azido-4,5-bis(benzyloxy)-6-(benzyloxymethyl)-tetrahydro-2H-pyran-3-yloxy)acetate (**28**).* Azido alcohol **1g** was subjected to esterification by using general procedure D to give **28** (yield: 83%). R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = +4.0 (*c* 0.5, CH_2Cl_2). IR (neat) ν_{max}: 3063, 3030, 2918, 2869, 2115, 1755, 1605, 1496, 1453, 1365, 1254, 1208, 1147, 1111, 1027, 737, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.34−7.23 (m, 15H, Ar-H), 4.88 (d, *J* = 11.0 Hz, 1H, OC*H*Ph), 4.71 (s, 2H), 4.66 (d, *J* = 7.7 Hz, 1H), 4.56 (d, *J* = 11.0 Hz, 1H, OC*H*Ph), 4.46−4.33 (m, 4H), 4.19−4.09 (m, 2H), 3.91

(br s, 1H), 3.63−3.53 (m, 5H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 138.3, 138.1, 137.7, 128.3−127.5 (m, Ar-C), 90.0, 82.0, 80.1, 75.5, 74.7, 73.7, 73.0, 72.8, 70.5, 68.4, 60.9, 14.2. HRMS calcd for $C_{31}H_{35}N_3O_7Na$ $[M + Na]^+$ 584.2373, Found: 584.2371.

*Ethyl 2-((2S,3S,4S,5R)-2-Azido-4-(benzyloxy)-5-(benzyloxymethyl)-tetrahydrofuran-3-yloxy)acetate (**29**).* Azido alcohol **2h** was subjected to alkylation by using general procedure D to give **29** (yield: 70%). R_f: 0.6 (hexane:ethyl acetate, 4:1). $[\alpha]^{28}_D$ = +73.75 (c 0.8, CH_2Cl_2). IR (neat) ν_{max}: 2928, 2109, 1750, 1600, 1453, 1372, 1302, 1238, 1209, 1152, 1048, 863, 782, 737, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.26 (m, 10H, Ar-H), 5.50 (d, J = 3.1 Hz, 1H), 4.80 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.60 (d, J = 12.0 Hz, 2H, 2 × OC*H*Ph), 4.48 (d, J = 12.0 Hz, 1H, OC*H*Ph), 4.42 (dd, J = 11.4 Hz, 11.7 Hz, 1H), 4.23−4.17 (m, 5H), 3.84 (t, J = 3.4 Hz, 1H), 3.73−3.72 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 138.1, 137.8, 128.5−127.7 (m, Ar-C), 93.4, 84.0, 79.5, 77.2, 73.5, 73.5, 69.2, 67.9, 61.2, 14.2. HRMS calcd for $C_{23}H_{27}N_3O_6Na$ $[M + Na]^+$ 464.1798, Found: 464.1795.

*Ethyl 2-((2S,3S,4S,5R)-2-Azido-4-(benzyloxy)-5-((R)-1,2-bis(benzyloxy)-ethyl)tetrahydrofuran-3-yloxy)acetate (**30**).* Azido alcohol **2i** was subjected to alkylation by using general procedure D to give **30** (yield: 72%). R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = +46.66 (c 1.35, CH_2Cl_2). IR (neat) ν_{max}: 3030, 2982, 2929, 2109, 1752, 1599, 1496, 1453, 1423, 1380, 1302, 1208, 1152, 1114, 1094, 1056, 1028, 737, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.25 (m, 15H, Ar-H), 5.43 (d, J = 5.4 Hz, 1H), 4.94 (d, J = 10.9 Hz, 1H, OC*H*Ph), 4.74 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.57−4.43 (m, 4H), 4.30−4.04 (m, 7H), 3.89−3.83 (m, 2H), 3.64 (dd, J = 5.1 Hz, 4.6 Hz, 1H), 1.28 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 138.6, 138.5, 138.4, 128.4−127.5 (m, Ar-C), 93.8, 86.3, 79.3, 77.5, 75.8, 73.9, 73.5, 72.2, 69.7, 68.1, 61.2, 14.2. HRMS calcd for $C_{31}H_{35}N_3O_7Na$ $[M + Na]^+$ 584.2373, Found: 584.2377.

*(4aR,6R,7S,8S,8aR)-7,8-Dihydroxy-6-(hydroxymethyl)hexahydropyrano-[3,2-b][1,4]oxazin-3(2H)-one (**31**).* Compound **24** (80 mg, 0.14 mmol) was subjected to global deprotection by using general procedure E to give **31** (29 mg, Yield: 94%) as a colorless liquid. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −5.71 (c 0.35, MeOH). ^{1}H NMR (500 MHz, D_2O): δ 4.56 (d, J = 8.0 Hz, 1H) 4.18 (d, J = 17.2 Hz, 1H), 4.10 (d, J = 17.2 Hz, 1H), 3.75 (d, J = 12.6 Hz, 1H), 3.58 (dd, J = 13.0 Hz, 10.3 Hz, 2H), 3.44−3.41 (m, 1H), 3.32 (t, J = 9.1 Hz, 1H), 3.14 (dd, J = 8.0 Hz, 9.2 Hz, 1H). ^{13}C NMR (125 MHz, D_2O): δ 171.7, 79.8, 78.5, 76.8, 72.9, 70.2, 67.0, 60.5. HRMS calcd for $C_8H_{14}NO_6$ $[M + H]^+$ 220.0821, Found: 220.0825.

*(4aR,6R,7S,8S,8aR)-7,8-Dihydroxy-6-methylhexahydropyrano[3,2-b][1,4]oxazin-3(2H)-one (**32**).* Compound **25** was subjected to global deprotection by using general procedure E to give **32** (yield: 86%) as a liquid. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −14.00 (c 1.0, MeOH). ^{1}H NMR (400 MHz, D_2O): δ 4.54 (d, J = 8.2 Hz, 1H), 4.13 (dd, J = 17.0 Hz, 16.8 Hz, 2H), 3.54−3.42 (m, 2H), 3.16−3.07 (m, 2H), 1.16 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, D_2O): δ 172.4, 80.4, 77.8, 76.4, 75.3, 73.3, 67.6, 17.4. HRMS calcd for $C_8H_{14}NO_5$ $[M + H]^+$ 204.0872, Found: 204.0874.

*(4aR,7R,8S,8aR)-7,8-Dihydroxyhexahydropyrano[3,2-b][1,4]oxazin-3(2H)-one (**33**).* Compound **26** was subjected to global deprotection by using general procedure E to give **33** (yield: 89%) as a white crystalline compound. Mp: 207−209 °C. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −12.00 (c 1.0, MeOH). ^{1}H NMR (500 MHz, D_2O): δ 4.47 (d, J = 8.4 Hz, 1H), 4.12 (dd, J = 16.8 Hz, 17.2 Hz, 2H), 3.88 (dd, J = 11.4 Hz, 11.8 Hz, 1H), 3.57−3.48 (m, 2H), 3.28−3.23 (m, 1H), 3.12 (t, J = 8.7 Hz, 1H). ^{13}C NMR (125 MHz, D_2O): δ 171.7, 80.6, 76.8, 72.9, 69.8, 67.4, 66.9. HRMS calcd for $C_7H_{11}NO_5Na$ $[M + Na]^+$ 212.0535, Found: 212.0536.

*(4aR,7S,8S,8aR)-7,8-Dihydroxyhexahydropyrano[3,2-b][1,4]oxazin-3(2H)-one (**34**).* Compounds **27** and **40** were subjected to global deprotection by using general procedure E to give **34** (yield: 87%) as a liquid. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = +4.00 (c 0.5, MeOH). ^{1}H NMR (400 MHz, D_2O): δ 4.39 (d, J = 8.2 Hz, 1H), 4.13 (dd, J = 17.1 Hz, 17.1 Hz, 2H), 3.85−3.80 (m, 2H), 3.72 (dd, J = 10.0 Hz, 10.3 Hz, 1H), 3.60 (br d, J = 13.1 Hz, 1H), 3.39 (dd, J = 8.5 Hz, 8.5 Hz, 1H). ^{13}C NMR (125 MHz, D_2O): δ 171.7, 80.9, 74.9, 69.5, 68.9, 68.8, 67.3. HRMS calcd for $C_7H_{12}NO_5$ $[M + H]^+$ 190.0715, Found: 190.0717.

*(4aR,6R,7R,8S,8aR)-7,8-Dihydroxy-6-(hydroxymethyl)hexahydropyrano-[3,2-b][1,4]oxazin-3(2H)-one (**35**).* Compounds **28** and **41** were subjected to global deprotection by using general procedure E to give **35** (yield: 85%) as a white solid. Mp: 238−240 °C. R_f = 0.45 (MeOH/EtOAc, 1:9). $[\alpha]^{28}_D$ = −10.0 (c 0.4, MeOH). ^{1}H NMR (500 MHz, D_2O): δ 4.54 (d, J = 8.4 Hz, 1H, H-4a). 4.20 (dd, J = 17.2 Hz, 16.8 Hz, 2H, H-2, H-2′), 3.90 (s, 1H, H-7), 3.76 (dd, J = 10.3 Hz, 10.3 Hz, 1H, H-8), 3.71−3.62 (m, 3H, H-6, H-9, H-9′), 3.45 (dd, J = 8.4 Hz, 8.4 Hz, 1H, H-8a). ^{13}C NMR (125 MHz, D_2O): δ 171.8, 80.6, 78.0, 75.2, 70.0, 69.2, 67.4, 61.0. HRMS calcd for $C_8H_{14}NO_6$ $[M + H]^+$ 220.0821, Found: 220.0825.

*(4aR,6R,7R,8S,8aR)-6-(Acetoxymethyl)-3-oxooctahydropyrano-[3,2-b][1,4]oxazine-7,8-diyl Diacetate (**36**).* Compound **31** was acetylated by using general procedure F for 2 h to give **36** (yield: 68%) as a colorless oil. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −5.0 (c 0.4, CH_2Cl_2). IR (neat) ν_{max}: 3457, 2920, 2851, 1745, 1681, 1431, 1370, 1229, 1086, 1048 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (br s, 1H, H-4), 5.28 (t, 1H, J = 9.4 Hz, H-8), 5.11 (t, 1H, J = 9.6 Hz, H-7), 4.68 (d, 1H, J = 8.0 Hz, H-4a), 4.34−4.14 (m, 4H, H-9, H-9′, H-2, H-2′), 3.84−3.82 (m, 1H, H-6), 3.42 (t, 1H, J = 9.0 Hz, H-8a), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 170.1, 169.4, 168.0, 80.9, 75.7, 74.3, 71.6, 68.4, 68.0, 61.6, 20.7−20.5. HRMS calcd for $C_{14}H_{19}NO_9Na$ $[M + Na]^+$ 368.0958, Found: 368.0959.

*(4aR,6R,7R,8S,8aR)-6-(Acetoxymethyl)-4-acetyl-3-oxooctahydropyrano[3,2-b][1,4]oxazine-7,8-diyl Diacetate (**37**).* Compound **31** was acetylated by using general procedure F for 15 h to give **37** (yield: 70%) as a colorless oil. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −35.83 (c 1.2, CH_2Cl_2). IR (neat) ν_{max}: 2924, 1748, 1643, 1419, 1370, 1305, 1234, 1093, 1049, 614 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.32 (t, J = 9.3 Hz, 1H, H-8). 5.12 (m, 2H, H-4a, H-7), 4.42 (d, J = 17.1 Hz, 1H, H-2), 4.29 (dd, J = 12.6 Hz, 12.6 Hz, 1H, H-9), 4.22 (d, J = 17.1 Hz, 1H, H-2′), 4.05 (dd, J = 12.6 Hz, 12.6 Hz, 1H, H-9′), 3.89−3.86 (m, 1H, H-6), 3.56 (t, J = 9.7 Hz, 1H, H-8a), 2.54 (s, 3H, N−Ac), 2.07 (s, 6H, OAc), 2.03 (s, 3H, OAc), 1.21 (d, J = 5.1 Hz, 3H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 170.6, 170.1, 169.6, 168.3, 81.3, 75.6, 74.7, 72.4, 70.0, 68.5, 61.5, 28.0, 20.8, 20.6. HRMS calcd for $C_{16}H_{21}NO_{10}Na$ $[M + Na]^+$ 410.1063, Found: 410.1067.

*(4aR,6R,7R,8S,8aR)-4-Acetyl-6-methyl-3-oxooctahydropyrano[3,2-b][1,4]oxazine-7,8-diyl Diacetate (**38**).* Compound **32** was acetylated by using general procedure F for 10 h to give **38** (yield: 74%) as a colorless oil. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −30.0 (c 0.6, CH_2Cl_2). IR (neat) ν_{max}: 2986, 2943, 1750, 1721, 1584, 1418, 1371, 1332, 1305, 1237, 1214, 1177, 1128, 1111, 1087, 1059, 618, 577, 539 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.26 (t, J = 9.1 Hz, 1H, H-8), 5.12 (d, J = 9.1 Hz, 1H, H-4a), 4.82 (t, J = 8.8 Hz, 1H, H-7), 4.41 (d, J = 16.6 Hz, 1H, H-2), 4.21 (d, J = 16.6 Hz, 1H, H-2′), 3.74 (br s, 1H, H-6), 3.51 (t, J = 9.15 Hz, 1H, H-8a), 2.54 (s, 3H, N−Ac), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.21 (d, J = 5.1 Hz, 3H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 170.1, 169.8, 168.4, 81.0, 75.9, 73.9, 72.9, 72.7, 69.9, 28.0, 20.7, 20.6, 17.5. HRMS calcd for $C_{14}H_{20}NO_8$ $[M + H]^+$ 330.1189, Found: 330.1189.

*(4aR,7S,8S,8aR)-4-Acetyl-3-oxooctahydropyrano[3,2-b][1,4]oxazine-7,8-diyl Diacetate (**39**).* Compound **34** was acetylated by using general procedure F for 10 h to give **39** (yield: 76%) as a colorless oil. R_f = 0.5 (hexane/EtOAc, 1:1). $[\alpha]^{28}_D$ = −11.66 (c 0.6, CH_2Cl_2). IR (neat) ν_{max}: 2922, 2853, 1745, 1648, 1370, 1311, 1237, 1125, 1100, 1060, 605 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.36 (br s, 1H, H-7), 5.17 (dd, J = 10.3 Hz, 3.8 Hz, 1H, H-8), 5.04 (d, J = 9.1 Hz, 1H, H-4a), 4.43 (d, J = 17.2 Hz, 1H, H-2), 4.28 (d, J = 17.5 Hz, 1H, H-2′), 4.00 (d, J = 13.8 Hz, 1H, H-6),

3.87−3.83 (m, 2H, H-8a, H-6′), 2.55 (s, 3H, N−Ac), 2.14 (s, 3H, OAc), 2.06 (s, 3H, OAc). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 169.9, 169.8, 168.5, 82.5, 73.2, 70.0, 70.0, 68.4, 67.4, 28.0, 20.8, 20.6. HRMS calcd for $C_{13}H_{17}NO_8Na$ $[M+Na]^+$ 338.0852, Found: 338.0856.

*Ethyl 2-((2S,3R,4S,5S)-2-Azido-4,5-bis(benzyloxy)tetrahydro-2H-pyran-3-yloxy)acetate (**40**).* Azido alcohol **1fα** was subjected to esterification by using general procedure D to give **40** (yield: 80%). R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = +103.57 (*c* 0.7, CH_2Cl_2). IR (neat) ν_{max}: 3031, 2925, 2115, 1746, 1632, 1495, 1454, 1379, 1261, 1211, 1103, 1052, 878, 739, 697, 463 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.25 (m, 10H, Ar-H), 5.63 (d, *J* = 5.8 Hz, 1H), 4.69−4.60 (m, 4H), 4.37 (s, 2H), 4.18 (dd, *J* = 14.4 Hz, 14.4 Hz, 2H), 3.92 (dd, *J* = 3.8 Hz, 3.9 Hz, 1H), 3.84−3.73 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 138.0, 137.8, 128.4−127.5 (m, Ar-C), 88.9, 77.5, 76.5, 72.8, 72.2, 71.5, 69.7, 62.0, 60.9, 14.1. HRMS calcd for $C_{23}H_{28}N_3O_6$ $[M+H]^+$ 442.1978, Found: 442.1974.

*Ethyl 2-((2S,3R,4S,5S,6R)-2-Azido-4,5-bis(benzyloxy)-6-(benzyloxymethyl)-tetrahydro-2H-pyran-3-yloxy)acetate (**41**).* Azido alcohol **1g-α** was subjected to esterification by using general procedure D to give **41** (yield: 85%) as a light yellow oil. R_f: 0.34 (hexane:ethyl acetate, 4:2). $[\alpha]^{28}_D$ = +31.42 (*c* 0.7, CH_2Cl_2). IR (neat) ν_{max}: 3063, 3030, 2981, 2922, 2871, 2116, 1747, 1731, 1604, 1496, 1453, 1372, 1344, 1306, 1276, 1210, 1181, 1145, 1108, 1057, 1028, 737, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36−7.25 (m, 15H, Ar-H), 5.74 (d, *J* = 4.2 Hz, 1H) 4.87 (d, *J* = 11.4 Hz, 1H, OC*H*Ph), 4.69 (s, 2H), 4.51 (dd, *J* = 11.4 Hz, 11.8 Hz, 2H, 2 × OC*H*Ph), 4.42−4.31 (m, 3H), 4.18−4.14 (m, 2H), 4.03 (t, *J* = 6.5 Hz, 1H), 3.97 (d, *J* = 9.9 Hz, 2H), 3.78 (d, *J* = 9.9 Hz, 1H), 3.54 (d, *J* = 6.1 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 138.3, 138.2, 137.8, 128.6−127.5 (m, Ar-C), 89.1, 79.3, 77.6, 74.9, 74.1, 73.6, 72.2, 71.5, 70.0, 68.4, 61.1, 14.2. HRMS calcd for $C_{31}H_{36}N_3O_7$ $[M+H]^+$ 562.2553, Found: 562.2555.

■ ASSOCIATED CONTENT

Supporting Information. General experimental procedures and characterization data for all new compounds, copies of ^{1}H NMR, ^{13}C NMR, ^{1}H−^{1}H COSY, and ^{1}H−^{1}H NOESY spectra, and single X-ray crystallographic data for compounds **15**, **33**, **35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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