

**SYNTHESIS OF KETOSYL SPIRO-ISOXAZOLIDINE BY
1,3-DIPOLAR CYCLOADDITION OF 1-METHYLENE-
SUGARS WITH NITRONES
—A NEW ACCESS TO C-GLYCOSYL AMINO ACIDS[#]**

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Abstract - The 1,3-dipolar cycloaddition reactions of 1-methylenesugars (**1a~c**) with nitrones (**2** and **5**) were carried out diastereoselectively under the catalysis of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at low temperature and afforded the α -stereoselective spiro ketosyl isoxazolidines in good to excellent yields. The reductive isoxazolidine ring-opening of the spiro moiety with the treatment of zinc and acetic acid resulted in a new kind of C-glycosyl amino acid possessing a ketose form, providing an access to C-glycosyl amino acids. The structures of the synthesized compounds were confirmed by the spectroscopic analyses.

INTRODUCTION

Spiro-glycoside ring substructures, such as spiro-nucleoside, spiro-orthoesters, and spiro-ketal have been found in many biologically active natural products.¹⁻³ The strong biological activity of these compounds have triggered great interest in building such substructures.⁴⁻⁶ Of the conventional method, cyclo-glycosidation reactions were used for the syntheses of the spiro-glycosides, especially for that of spiro-ketal. However, recent studies revealed that the rigid spiro system of a spiro-ketodisaccharide made the stereoselectivity of cyclo-ketosylation different from that of linear ketosylation.^{5e,6,7} While the ketosylations of ketopyranoses could provide the thermodynamic stable α -ketodisaccharides exclusively,^{6b,6c,7} the cyclo-ketosylation of forming the spiro-ketodisaccharide preferred the α,β -stereoselectivity to the α,α -selectivity in the two spiro anomeric carbons, affording the mixture of α,α - and α,β -isomers.^{6b,6d} The stereoselective and efficient formation of a spiro-anomeric center is still a great challenge.

[#]*Dedicated to Professor Yuichi Kanaoka on the occasion of his 75th birthday.*

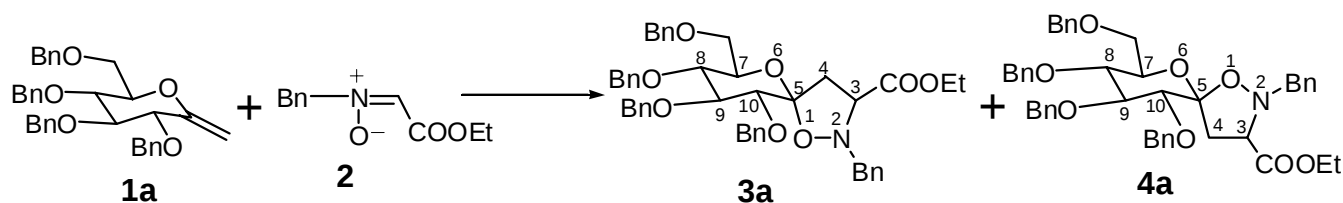
1,3-Dipolar cycloadditions of nitrones with alkenes, as one of the most important methods of cyclization reactions, have been widely used in organic synthesis.⁸ With this reaction up to three new contiguous chiral centers could be created in one step. A stereoselective cycloaddition could be achieved by choosing an appropriate nitron or alkene which contains either an electron-donating or electron-withdrawing substituent. Moreover, the use of Lewis acid could also control the stereoselectivity by forming metallic complexes with the nitrones or alkenes.^{8c,8d,8g,9}

Although the utility of the 1,3-dipolar cycloaddition in the synthesis of carbohydrate derivatives has been recently reported,^{8e-h,10} very few of the application of this methodology in the formation of spiro-glycoside has been briefly studied so far.¹¹ As an extension of our recent work on the syntheses of ketosyl glycosides and spiro-ketodisaccharides using 1-methylenesugars as the precursor,^{6b,7d,7e} we describe in this article the stereoselective synthesis of glycosyl spiro-isoxazolidine by the 1,3-dipolar cycloaddition of nitron to 1-methylenesugar and the further exploration of converting the spiro isoxazolidine to new C-glycosyl amino acids.

RESULTS AND DISCUSSION

Most of nitrones are relatively stable and easily accessible compounds and they have been successfully used in organic synthesis.^{8,12} The nitrones (**2**) and (**5**) were readily prepared according to the Dondoni's procedure¹³ by the reaction of ethyl glyoxalate with the corresponding *N*-benzylhydroxylamine and *N*-methylhydroxylamine, respectively.

Considering the achievements of the stereoselective 1,3-dipolar cycloadditions of nitrones to alkenes^{8,9} and the stereoselective glycosidations of 1-methylenesugars (**1**)^{6b,7d,7e} catalysed by Lewis acids, we firstly examined the cycloaddition of the 1-methylenesugar (**1a**) with the nitron (**2**) under various conditions (Scheme 1). The results are listed in Table 1.



Scheme 1

It should be noted that the 1,3-dipolar cycloaddition of **1a** with **2** proceeded diastereoselectively and gave only two anomeric isomers (**3a**) and (**4a**) possessing R-configuration on C-3, although the 1,3-dipolar cycloadditions of the 1-methylenesugars (**1a**) with the nitrones (**2**) should be supposed to afford four diastereomers, that is, two anomeric isomers having R-configuration on C-3 (**3a** and **4a**) and their diastereomers with S-configuration on C-3 (**3s** and **4s**) (as shown in Figure 2). The reaction did not

produce the other two anomeric isomers (**3s**) and (**4s**).

Table 1 1,3-Dipolar cycloaddition of the methylenesugar (**1a**) with nitrone (**2**)^a

Entry	Conditions	3a (%) (α -isomer)	4a (%) (β -isomer)	$\alpha : \beta$
1	BF ₃ ·OEt ₂ (0.3 eq.), CH ₂ Cl ₂ , -78°C, 4 h	33.2	2.2	15.1 : 1.0
2	BF ₃ ·OEt ₂ (1.3 eq.), CH ₂ Cl ₂ , -78°C, 4 h	56.8	3.8	14.9 : 1.0
3	BF ₃ ·OEt ₂ (0.5 eq.), CH ₂ Cl ₂ , rt, 3 h	57.2	11.2	5.1 : 1.0
4	BF₃·OEt₂ (1.3 eq.), CH₂Cl₂, -78°C, 4 h→0°C	71.9	6.4	11.3 : 1.0
5 ^b	BF ₃ ·OEt ₂ (1.3 eq.), CH ₂ Cl ₂ , -78°C, 4 h→0°C	87.5	8.0	10.9 : 1.0
6	BF ₃ ·OEt ₂ (1.5 eq.), Et ₂ O, -78°C, 4 h→rt	67.8	5.6	12.1 : 1.0
7	ZnBr ₂ (1.5 eq.), CH ₂ Cl ₂ , rt, 24 h	28.1	35.9	1.0 : 1.3
8	ZnBr ₂ (1.5 eq.), Et ₂ O, rt, 24 h	18.2	13.2	1.5 : 1.0
9	ZnCl ₂ (1.5 eq.), CH ₂ Cl ₂ , rt, 24 h	18.4	29.5	1.0 : 1.6
10	Et ₂ AlCl (1.5 eq.), CH ₂ Cl ₂ , rt, 4 h	22.1	18.4	1.2 : 1.0
11	AlCl ₃ (1.5 eq.), CH ₂ Cl ₂ , rt, 4 h	16.3	14.8	1.1 : 1.0
12	TiCl ₄ (1.0 eq.), CH ₂ Cl ₂ , rt, 4 h	12.7	10.5	1.2 : 1.0
13	benzene, reflux, 24 h	43.4	52.3	1.0 : 1.2

a: **1a** (0.2 mmol) and **2** (0.25 mmol) were used.

b: 2.0 equiv. of **2** was used.

As shown in Table 1, the cycloaddition reaction of the 1-methylenesugar (**1a**) with the nitrone (**2**) under the catalysis of BF₃·Et₂O provided a mixture of the α - and β -anomeric isomers, ketosyl spiro-isoxazolidines (**3a**) and (**4a**) with the α -isomer (**3a**) as the predominant (Entries 1~6). In the presence of a catalytic amount of BF₃·Et₂O (0.3 equiv.), the reaction of **1a** with **2** (1.25 equiv.) at -78°C gave the adducts (**3a**) and (**4a**) in low yield (35.4%) and in a α,β -stereoselective ratio of 15.1 : 1 with the nearly 58% recovery of the starting material (**1a**) (Entry 1), indicating that the stoichiometric amounts of the Lewis acid might be necessary for the reaction. In fact, the use of BF₃·Et₂O in 1.3 equiv. afforded the products (**3a**) and (**4a**) in the overall yield of 60.6% without the remarkable change of the α -stereoselectivity (Entry 2). Moreover, increasing the reaction temperature up to 0°C after reacting at -78°C for 4 h resulted in a good yield (78.3%) of the adducts (**3a**) and (**4a**) with a satisfying α -stereoselectivity (Entry 4, this condition is called as **Procedure A**). Under this condition, an excessive use of the nitrone (**2**) (2.0 equiv.) provided an excellent yield (95.5%) of the products with a similar stereoselectivity (Entry 5).

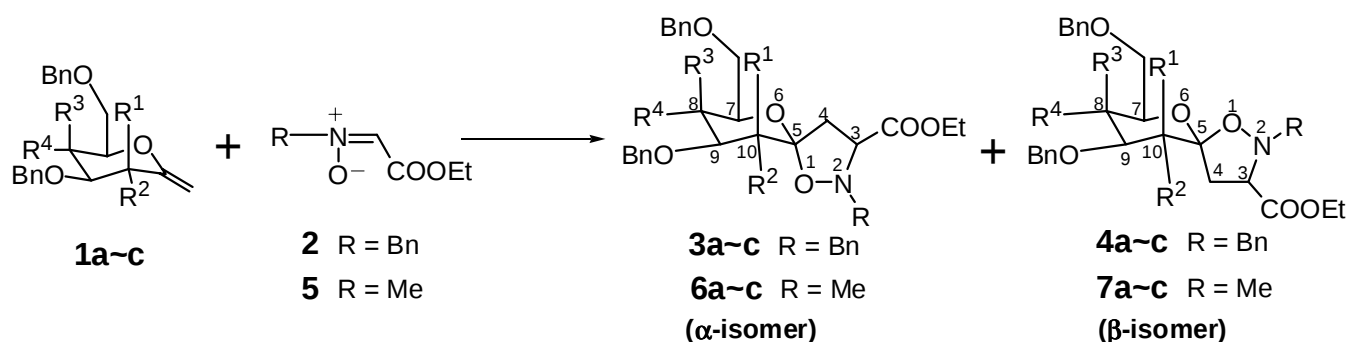
However, other Lewis acids, such as ZnBr₂, ZnCl₂, Et₂AlCl, AlCl₃, and TiCl₄, were found not to be efficient to this reaction and gave a poor stereoselectivity (Entries 7~12), although it has been recently

observed that the Lewis acids, such as ZnBr_2 and Et_2AlCl could induce the 1,3-dipolar cycloaddition of some nitron and enolic compounds to proceed in contrary stereoselective way.⁹

Further experiments showed that the reaction temperature could remarkably influence the reaction stereoselectivity and reactivity (Entries 2, 3, 4, and 13). A considerable decrease of the stereoselectivity was observed when the reaction was performed at room temperature with 0.5 equiv. of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyst (Entry 3). Moreover, while the cycloaddition could not complete at -78°C in the presence of 1.3 equiv. of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (Entry 2), the reaction could efficiently proceed in benzene at reflux to afford the mixture of **3a** and **4a** in excellent overall yield of 95.7% without using any Lewis acid catalyst (Entry 13, this condition is called as **Procedure B**). Unfortunately, the stereoselectivity of the reaction was not satisfied. The reaction stereoselectivities observed above were identical with those in the cycloglycosylations of forming spiro-ketodisaccharides.^{6b}

The reaction stereoselectivity was slightly affected by the nature of the solvent due to the anomeric effects.¹⁴ For example, the use of Et_2O instead of CH_2Cl_2 was of benefit to the α -stereoselectivity in the reaction (Entries 6, 8).

The 1,3-dipolar cycloaddition reactions of **1b~c** to **2** and **1a~c** to **5** were also carried out according to **Procedure A** and **Procedure B**, respectively (Scheme 2), and the similar stereoselectivity as in the reaction of **1a** to **2** was obtained. The results are summarized in Table 2. In the case of mannose derivative (**1c**) possessing an axial 2-benzyloxy group, the reaction exhibited an increase of β -stereoselectivity under each condition of **Procedure A** and **B** in comparison with the cases of glucose derivative (**1a**) and galactose derivative (**1b**).



	R^1	R^2	R^3	R^4
a (Glc)	H	BnO	H	BnO
b (Gal)	H	BnO	BnO	H
c (Man)	BnO	H	H	BnO

Scheme 2

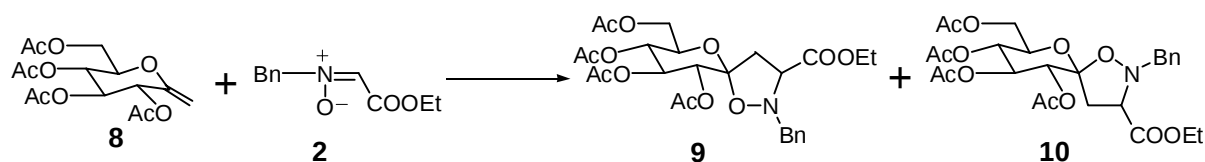
Table 2 1,3-Dipolar cycloadditions of the methylenesugar (**1a~c**) with nitrones (**2**) and (**5**)

Entry	1	Nitrones	Conditions (Procedure)	Products (Yield %)		$\alpha : \beta$
1	1a	2	A	3a (71.9)	4a (6.4)	11.3 : 1.0
2	1b	2	A	3b (72.6)	4b (4.9)	14.8 : 1.0
3	1c	2	A	3c (58.0)	4c (10.8)	5.4 : 1.0
4	1a	2	B	3a (43.4)	4a (52.3)	1.0 : 1.2
5	1b	2	B	3b (31.0)	4b (31.5)	1.0 : 1.0
6	1c	2	B	3c (23.4)	4c (42.1)	1.0 : 1.8
7	1a	5	A	6a (70.1)	7a (7.7)	9.1 : 1.0
8	1b	5	A	6b (68.6)	7b (7.8)	8.8 : 1.0
9	1c	5	A	6c (53.7)	7c (28.6)	1.9 : 1.0
10	1a	5	B	6a (41.0)	7a (41.4)	1.0 : 1.0
11	1b	5	B	6b (37.5)	7b (41.3)	1.0 : 1.1
12	1c	5	B	6c (12.3)	7c (38.2)	1.0 : 3.1

Procedure A: 1-Methylenesugar (0.2 mmol), nitrone (0.25 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (1.3 eq.), CH_2Cl_2 , -78°C , 4 h $\rightarrow 0^\circ\text{C}$.

Procedure B: 1-Methylenesugar (0.2 mmol), nitrone (0.25 mmol), benzene, reflux, 24 h.

In order to study the effect of the protecting groups on the reaction stereoselectivity, the 1,3-dipolar cycloaddition of the acetyl-protected 1-methylenesugar (**8**) with the nitrone (**2**) was examined under the similar conditions as in the **Procedure A** using 1.5 equiv. of $\text{BF}_3 \cdot \text{OEt}_2$ (Scheme 3), and a similar result, except a decreased reactivity, was obtained as shown in the Table 3. Interestingly, a substantial decrease of the α -stereoselectivity was not observed, although the existence of the equatorial 2-*O*-acetyl group usually caused a remarkable increase of the β -stereoselectivity in a common glycosylation reaction due to its neighboring group participation effect.¹⁴

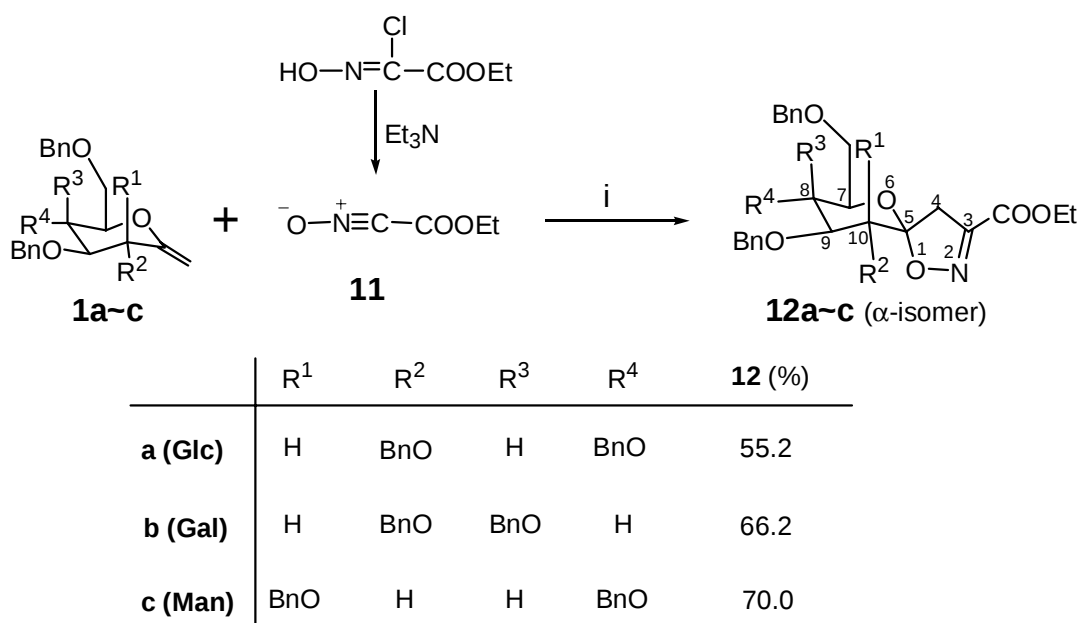


Scheme 3

Table 3 1,3-Dipolar cycloaddition of the 2,3,4,5-tetra-*O*-acetyl-1-methylenesugar (**8**) with nitrone (**2**)

Entry	Conditions	9 (α)	10 (β)	$\alpha : \beta$
1	$\text{BF}_3 \cdot \text{OEt}_2$ (1.5 eq.), CH_2Cl_2 , -78°C , 1 h	No reaction		
2	$\text{BF}_3 \cdot \text{OEt}_2$ (1.5 eq.), CH_2Cl_2 , -78°C , 1 h $\rightarrow$ rt, 4 h	72.6%	7.3%	9.9 : 1.0

The 1,3-dipolar cycloaddition reactions of **1a~c** with the nitrile oxide (**11**) which was generated *in situ* from the corresponding ethyl chlorooximidoacetate under a basic condition were also studied. The reaction proceeded stereospecifically at room temperature and provided the ketosyl spiro-isoxazoline (**12**) as the sole product (Scheme 4). This stereospecific result was consistent with the RajanBau's observation.¹⁵



Scheme 4 Reaction conditions: (i) CH₂Cl₂, rt

The structures and configurations of the synthesized spiro-isoxazolidines and spiro-isoxazolines were determined by the analyses of their spectral data of ¹H NMR, ¹³C NMR and 2D-COSY, and by the NOESY experiments. It has been shown that in the ¹³C NMR spectra of C-glycosides¹⁶ and ketosyl spiro-disaccharides^{6b} the signals of the anomeric carbon in the α-isomers appeared in higher field than those in the β-isomers. From this point of view, the anomeric configurations of the products were assigned by the comparison of the anomeric ¹³C NMR spectral data between each two anomeric isomers. Careful examination of vicinal proton-coupling constants unambiguously suggested a chair conformation for the six membered sugar rings (See the **EXPERIMENTAL** for the proton assignments). Accordingly, the configuration of the anomeric carbon and the relative orientation of the isoxazolidine ring substituents were further established from the NOE observations between H³ and H⁴, H⁴ and H¹⁰ as exemplified by the analyses of compounds (**3a**) and (**4a**) in Figure 1 (Also see Table 4).

The respective irradiations of H^{4a} and H^{4b} in **3a** resulted in the enhancements of the signals for H¹⁰ and H³. The enhancements on H¹⁰ and H³ caused by H^{4a} were bigger than those resulted from H^{4b}. When H¹⁰ was irradiated, the similar results that the interaction between H^{4a} and H¹⁰ was stronger than H^{4b} and H¹⁰ were observed, indicating that H¹⁰ to H^{4a} and H^{4a} to H³ should be in *cis*-orientation as shown in Figure 1. Comparatively, in compound (**4a**) stronger effects of H^{4b} to H³ and H¹⁰ were observed, supporting the

conformation shown in Figure 1.

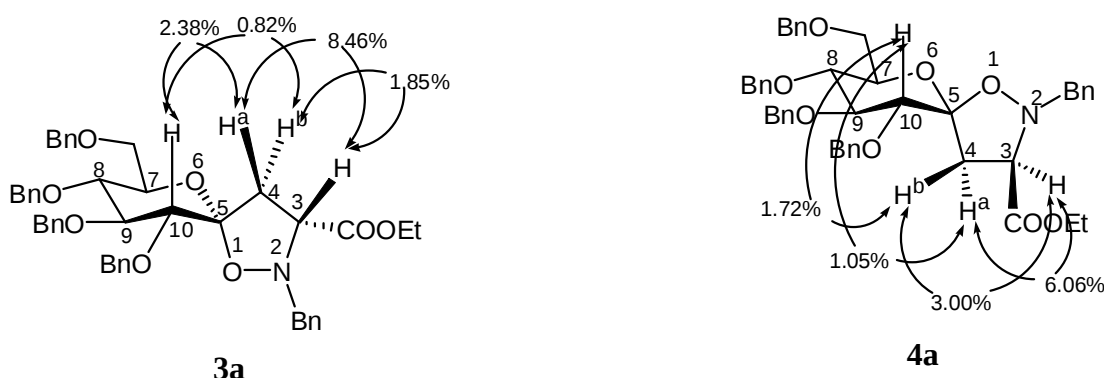


Figure 1 NOE analyses of compounds (**3a**) and (**4a**)

Table 4 Selected NOE data of the ketosyl spiro-isoxazolidines **3a~c**, **4a~c**, **9** and **10**

	3a (%)	4a (%)	4b (%)	3c (%)	4c (%)	9 (%)	10 (%)
H ^{4a} → H ¹⁰	2.38	1.05	1.85	1.51	1.71	5.59	0.86
H ^{4a} → H ^{4b}	13.71	19.17	12.66	6.52	15.07	26.82	17.82
H ^{4a} → H ³	8.46	6.06	7.01	2.73	5.83	9.46	6.87
H ^{4b} → H ¹⁰	0.82	1.72	4.12	0	5.11	0.95	4.96
H ^{4b} → H ^{4a}	7.57	15.20	13.21	2.87	16.27	18.05	16.76
H ^{4b} → H ³	1.85	3.00	1.69	2.62	1.87	2.62	2.02
H ¹⁰ → H ^{4a}	2.31	0.70	-	-	-	-	-
H ¹⁰ → H ^{4b}	0.70	1.00	-	-	-	-	-

Similarly, the configurations of the other isooxazolidine compounds except **3b** were established on the basis of their NOE experiments (See Table 4). As for the compound (**3b**), since the signals of the H^{4a} and H^{4b} were overlapped, it was difficult to distinguish the NOE effects resulted from H^{4a} or H^{4b}. The structure was deduced by the comparison of the signals of the anomeric carbons with its diastereomer (**4b**) whose configuration were assigned by NOE experiment. In addition, the configurations obtained from the NOE experiments as above were also supported by the molecular modeling calculation results using MacroModel program¹⁷ as shown in Figure 2.

The conformations and their corresponding energies (ΔE) of the compounds (**3a**) and (**4a**), and their diastereomers (**3s**) and (**4s**) were calculated¹⁷ using MacroModel 6.0 with the MM2* force field¹⁸ with LOMD (Low Mode) conformational search technique.¹⁹ The most stable conformations of the diastereomers and the corresponding minimized energies are shown in Figure 2. It was found that in all

cases the pyranoid rings took the energetically favoured chair form. In the cases of **3a** and **4a** being anomeric isomers with the *R*-configuration on C-3, the stable conformers from the most stable one to the 20th were in the almost same conformations, but in the cases of **3s** and **4s** having *S*-configuration on C-3, there were a variety of conformations among the stable conformers from the first one to the 20th. Moreover, the calculated energies corresponding the most stable conformers of **3a** and **4a** were much lower than those of **3s** and **4s**, that is, the *R*-diastereomer (C-3) of **3a** and **4a** were more thermodynamically stable than the *S*-diastereomer (C-3) of **3s** and **4s**. With the calculation results it was reasonable to understand the reaction stereoselectivity that the 1,3-dipolar cycloadditions of 1-methylenesugars (**1a~c**) with nitrones (**2**) and (**5**) afforded only two of the four diastereomers in each case.

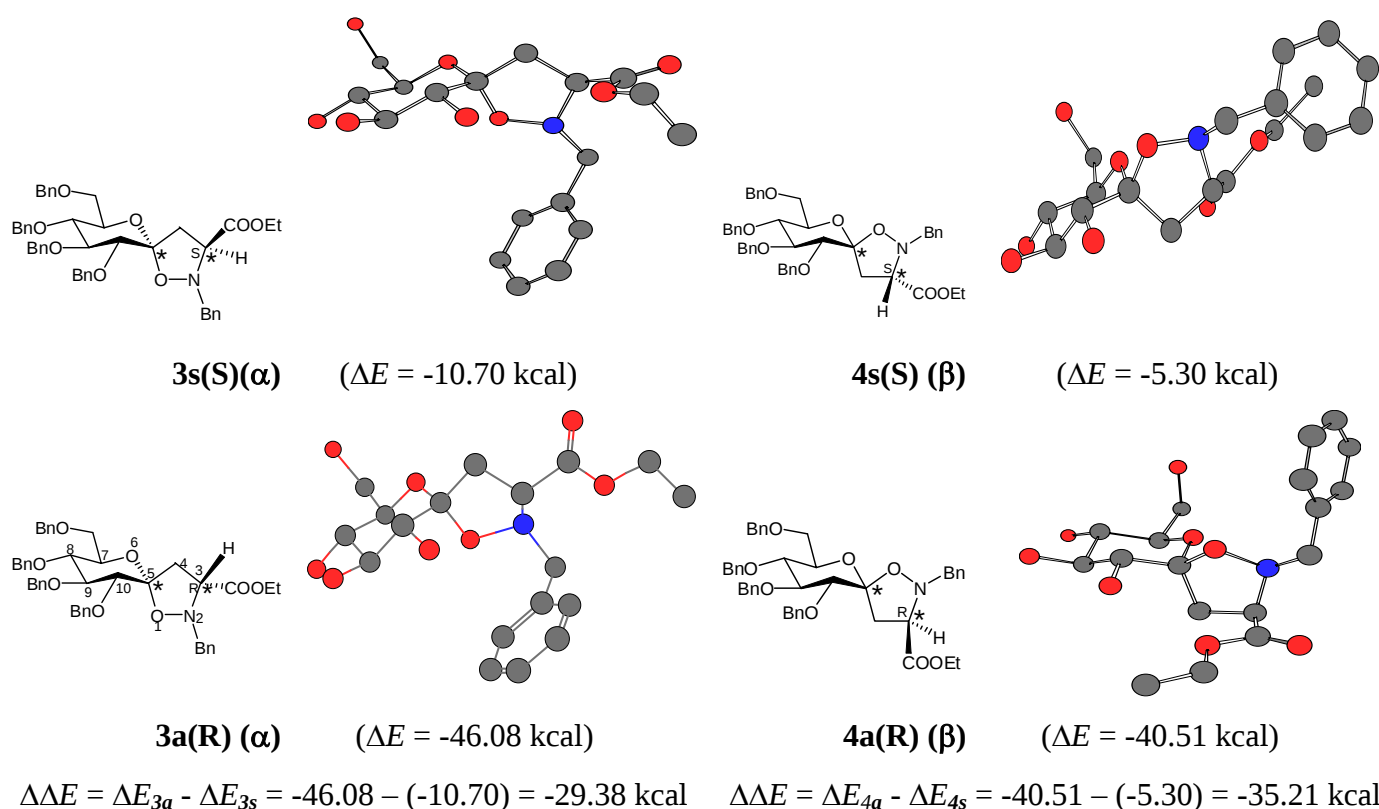


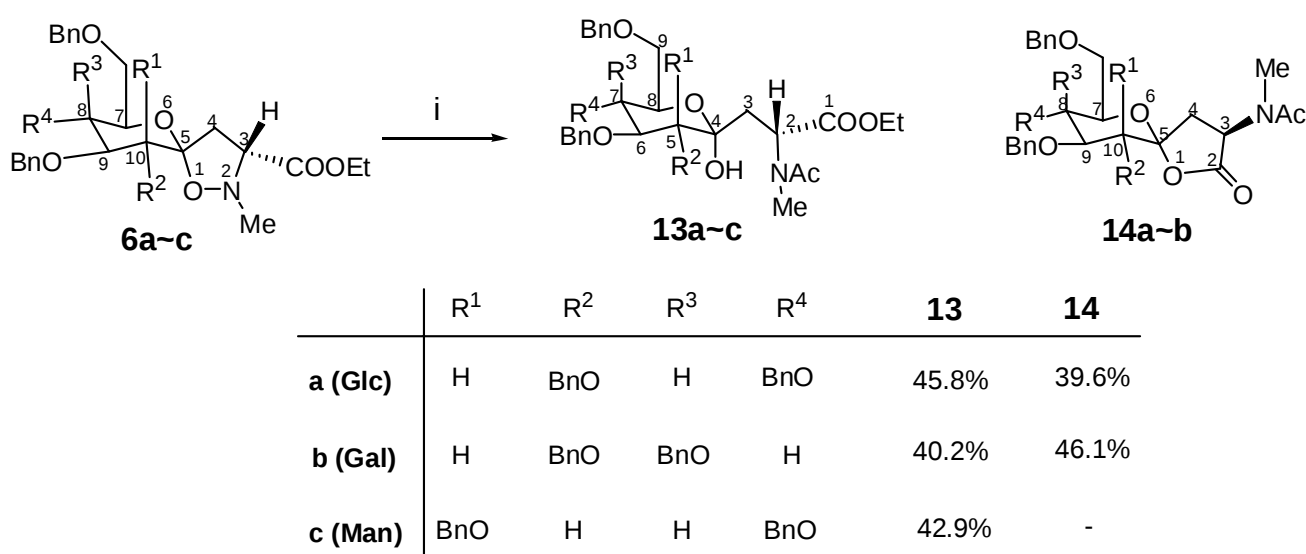
Figure 2 Energy minimized conformations of **3a** and **4a** and their two diastereomers (**3s**) and (**4s**)

(The benzyls on pyranoid rings and all protons were omitted after minimization for clarity)

It has been revealed that the carbohydrate-protein interaction played very important roles in carbohydrate biology,²⁰ and great attentions have recently been attracted on the syntheses of glycopeptides and glycosyl amino acids, and their analogues.^{21,22} With the convenient preparation of the ketosyl spiro-isoxazolidine in hands, we extended our study by approaching a new access to C-glycosyl amino acids from the ketosyl spiro-isoxazolidines in virtue of the reductive cleavage of the N-O bond.

A variety of the reductive isoxazolidine ring-opening methods which generated β -amino alcohol have been developed.^{8a,8b} For example, the catalytic hydrogenation with palladium or Raney nickel and the

treatment of the isoxazolidine with zinc and acid were commonly used. The hydrogenation catalyzed by $\text{Pd}(\text{OH})_2/\text{C}$ (20%) of the spiro-isoxazolidine (**6a**) was firstly tried in hope that the cleavage of the O-N bond and debenzoylation would be finished by using this one step reaction. However, the reaction was found not to proceed efficiently and produced an inseparable mixture most likely due to the inactivation of the catalyst by the generated amino group. After careful examination, the best result of reductively cleaving the N-O bond was obtained. The treatment of ketosyl spiro-isoxazolidines (**6a~c**) with activated zinc powder in $\text{AcOH}/\text{Ac}_2\text{O}$ solution at room temperature afforded the ring-opened products (**13a~c**) (C-glycosyl amino acids) and the recycled products (**14a~b**) (Scheme 5)



Scheme 5 Reaction conditions: (i) Zn, AcOH, Ac₂O, rt

In the reaction, the chiral carbons in the products (**13a~c**) (C*-2) and (**14a~b**) (C*-3) conserved the configurations on the corresponding chiral carbons (C*-3) in compounds (**6a~c**). The *R*-configuration on this carbon was further confirmed by the analyses of NOE experiments with **14a~b** as shown in Figure 3.

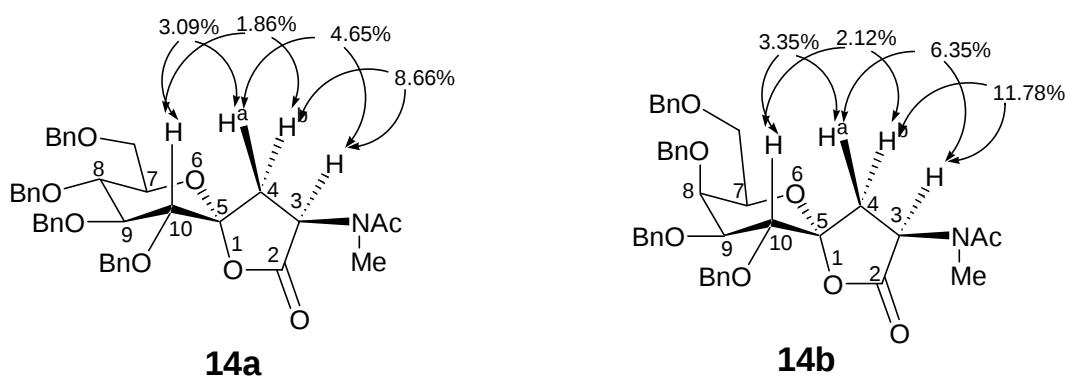
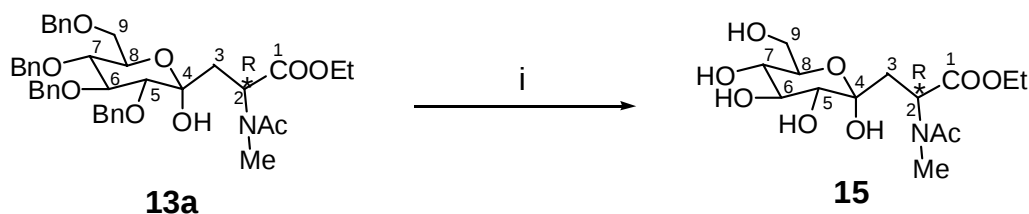


Figure 3 The NOE analyses of compounds (**14a**) and (**14b**)

Finally, the debenzoylation of the C-glycosyl amino acid (**13a**) was completed by the catalytic hydrogenation on Pd(OH)₂/C and afforded the corresponding C-glycosyl amino acid (**15**) as shown in Scheme 6. The spectral properties of **15** were identical with the structure shown.



Scheme 6 Reaction conditions: (i) Pd(OH)₂/C, H₂, MeOH.

In summary, stereoselective formation of glycosyl spiro-isoxazolidine was achieved by the 1,3-dipolar cycloaddition of 1-methylenesugar with nitron and provided two anomeric isomers. While the reaction showed low stereoselectivity under thermodynamic conditions (**Procedure B**), the cycloaddition promoted by BF₃•Et₂O at -78°C (**Procedure A**) gave the α-isomer predominantly. The stereoselectivity was similar to that in the cycloketosylation in our previous report.^{6b} The treatment of the spiro-isoxazolidine (**6a**) with Zn in AcOH and Ac₂O solution resulted in the reductive cleavage of O-N bond with the retention of the configuration at the chiral carbon (C*-3), and followed by debenzoylation using the catalytic hydrogenation the C-glycosyl amino acid with a ketose-like structure was obtained, providing a new access to the C-glycosyl amino acids.

EXPERIMENTAL

General methods. — Melting points were measured on a YANACO Micro Melting Point Apparatus and were uncorrected. IR spectra were recorded on a Jasco FT/IR-800 Fourier-transform infrared spectrophotometer. ¹HNMR, ¹³CNMR and COSY spectra were measured on a JEOL ECP 600 (600 MHz) NMR spectrometers using tetramethylsilane (Me₄Si) as an internal standard. MS spectra and HRMS spectra were carried out on a JEOL JMS-SX102A mass spectrometer with FAB (Fast Atomic Bombardment) using 3-Nitrobenzyl alcohol (NBA) as the matrix. Optical rotations were measured with a Jasco DIP-370 digital polarimeter. TLC was performed on precoated plates (Merck TLC aluminum sheets silica 60 F₂₅₄) with detection by UV light or with phosphomolybdic acid in EtOH/H₂O followed by heating. Column chromatography was performed using SiO₂ (Wakogel C-200, Wako).

Calculations. — Low-mode searches (LOMD)¹⁹ for compounds (**3a**) and (**4a**), and their diastereomers (**3s**) and (**4s**) were performed using MacroModel ver. 6.0¹⁸ with the MM2* derivative of MM2 force field on a Silicon Graphics IRIS-Indigo workstation. LOMD for each compound was continued until around 5,000 conformers were generated.

General procedure of 1,3-dipolar cycloadditions of the 1-methylenesugars (**1**) with nitrones (**2**).

Procedure A: Under the catalysis of a Lewis acid: — To a solution of **1a** (107 mg, 0.2 mmol), **2** (52 mg, 0.25 mmol) and Molecular sieves 4A (MS 4A, 300 mg) in 4 mL of CH₂Cl₂ was added BF₃•Et₂O (32 μL, 0.25 mmol, 1.3 equiv.) under Argon atmosphere at –78°C. The solution was stirred at the same temperature for 4 h, then the reaction temperature was gradually increased up to 0°C, then, triethylamine (0.1 mL) was added to quench the reaction. The solvent was removed under reduced pressure, and the residue was applied on silica gel column chromatography using AcOEt : Hexane (1 : 5) as the eluent to afford 107.6 mg (71.9%) of **3a** and 9.5 mg (6.4%) of **4a**. With the same procedure, different conditions with various Lewis acids were examined and the results are summarized in Table 1.

Procedure B: In the absence of Lewis acid: — A solution of **1a** (107 mg, 0.2 mmol) and **2** (52 mg, 0.25 mmol) in 5 mL of benzene was refluxed under Argon for 24 h. The reaction was monitored by TLC (AcOEt : Hexane = 1 : 2). After the completion of the reaction, the solvent was removed under reduced pressure. The residue was submitted to silica gel column chromatography using AcOEt : Hexane (1 : 5) as the eluent to afford **3a** (64.5 mg, 43.4%) and **4a** (77.8 mg, 52.3%).

Following the procedures of **A** and **B**, the 1,3-dipolar cycloadditions of **1b**, **1c** with **2**, and **1a~c** with **5** were carried out and afforded the corresponding products. Similarly, the reaction of **8** with **2** under the conditions in **Procedure A** provided the products (**9**) and (**10**). The results are listed in Table 2 and Table 3, respectively.

Ethyl (3*R*,5*R*,8*R*,9*S*,10*R*)-2-benzyl-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (**3a**)

Colorless syrup, $[\alpha]_D^{25}$: +68.80° (*c* 1.0, CHCl₃); IR (neat) 3063.33, 3030.54, 2907.80, 2866.57, 1954.13, 1871.18, 1811.38, 1743.86, 1604.97, 1541.31, 1496.94, 1450.50, 1363.84, 1288.61, 1209.51, 1157.43, 1072.55, 906.65, 871.93, 736.90, 698.32 cm⁻¹; ¹HNMR (CDCl₃): δ (ppm) 1.23 (t, 3H, *J* = 7.15 Hz, CH₃), 2.49 (dd, 1H, *J* = 13.20 Hz, *J* = 8.25 Hz, 4-H), 2.59 (dd, 1H, *J* = 12.65 Hz, *J* = 7.15 Hz, 4-H), 3.57 (d, 1H, *J* = 9.90 Hz, 10-H), 3.60 (t, 1H, *J* = 7.70 Hz, 3-H), 3.65 (dd, 1H, *J* = 10.99 Hz, *J* = 2.20 Hz, 7-CH₂), 3.76 (dd, 1H, *J* = 11.00 Hz, *J* = 2.65 Hz, 7-CH₂), 3.78 (t, 1H, *J* = 9.35 Hz, 8-H), 3.88 (br d, 1H, *J* = 8.80 Hz, 7-H), 3.89 (t, 1H, *J* = 9.35 Hz, 9-H), 4.06~4.18 (m, 3H, two OCH₂- and one NCH₂Ph), 4.19 (d, 1H, *J* = 13.75 Hz, one NCH₂Ph), 4.49 (d, 1H, *J* = 12.09 Hz, CH₂Ph), 4.58 (d, 1H, *J* = 10.45 Hz, CH₂Ph), 4.62 (d, 1H, *J* = 12.05 Hz, CH₂Ph), 4.70 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 4.82 (d, 1H, *J* = 10.44 Hz, CH₂Ph), 4.88 (d, 1H, *J* = 11.00 Hz, CH₂Ph), 4.90 (d, 1H, *J* = 10.99 Hz, CH₂Ph), 5.03 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 7.17~7.18 (m, 2H, ArH), 7.25~7.39 (m, 23H, ArH); ¹³CNMR (CDCl₃): δ (ppm) 14.07 (CH₃), 41.24 (4-C), 61.13 (OCH₂), 61.38 (NCH₂Ph), 65.65 (3-C), 68.22 (7-CH₂), 72.19 (7-C), 73.42 (CH₂Ph), 74.83 (CH₂Ph), 75.40 (CH₂Ph), 75.45 (CH₂Ph), 78.03 (8-C), 79.57 (10-C), 83.90 (9-C), 105.41 (5-C), 127.35 (Ar), 127.56 (Ar), 127.59 (Ar), 127.71 (Ar), 127.77 (Ar), 127.78 (Ar), 127.81 (Ar), 127.91 (Ar), 128.18 (Ar), 128.30

(Ar), 128.31 (Ar), 128.38 (Ar), 128.46 (Ar), 129.36 (Ar), 136.21 (Ar), 138.07 (Ar), 138.12 (Ar), 138.27 (Ar), 138.51 (Ar), 169.59 (C=O); HRMS (FAB) calcd for $C_{46}H_{49}NO_8Na$ 766.3356, Found: 766.3353.

Ethyl (3*R*,5*S*,8*R*,9*S*,10*R*)-2-benzyl-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (4a)

White solid, mp 104~105°C; $[\alpha]_D^{25}$: +22.40° (*c* 1.0, $CHCl_3$); IR (KBr): 3088.41, 3063.33, 3030.54, 2976.52, 2916.72, 2870.43, 1954.13, 1880.82, 1817.17, 1740.00, 1604.97, 1496.94, 1454.50, 1394.70, 1358.05, 1188.30, 1172.86, 1078.34, 1062.91, 1030.11, 995.39, 891.22, 752.33, 698.32; 1H NMR ($CDCl_3$): δ (ppm) 1.10 (t, 3H, *J* = 7.15 Hz, CH_3), 2.51 (dd, 1H, *J* = 12.65 Hz, *J* = 8.25 Hz, 4-H), 2.83 (dd, 1H, *J* = 13.19 Hz, *J* = 8.24 Hz, 4-H), 3.57 (d, 1H, *J* = 9.90 Hz, 10-H), 3.65 (t, 1H, *J* = 9.90 Hz, 8-H), 3.67 (dd, 1H, *J* = 10.99 Hz, *J* = 1.65 Hz, 7- CH_2), 3.73 (dd, 1H, *J* = 10.99 Hz, *J* = 4.40 Hz, 7- CH_2), 3.86 (t, 1H, *J* = 8.24 Hz, 3-H), 3.91 (qd, 2H, *J* = 7.15 Hz, *J* = 1.10 Hz, OCH_2 -), 3.98 (t, 1H, *J* = 9.35 Hz, 9-H), 3.99~4.01 (m, 1H, 7-H, overlapped with 9-H), 4.16 (d, 1H, *J* = 12.65 Hz, NCH_2Ph), 4.49 (d, 1H, *J* = 12.64 Hz, NCH_2Ph), 4.53 (d, 1H, *J* = 12.65 Hz, CH_2Ph), 4.54 (d, 1H, *J* = 9.90 Hz, CH_2Ph), 4.63 (d, 1H, *J* = 12.09 Hz, CH_2Ph), 4.71 (d, 1H, *J* = 11.55 Hz, CH_2Ph), 4.84 (d, 1H, *J* = 11.00 Hz, CH_2Ph), 4.85 (d, 1H, *J* = 11.45 Hz, CH_2Ph), 4.88 (d, 1H, *J* = 11.00 Hz, CH_2Ph), 4.96 (d, 1H, *J* = 11.55 Hz, CH_2Ph), 7.17~7.18 (m, 2H, ArH), 7.25~7.38 (m, 23H, ArH); ^{13}C NMR ($CDCl_3$): δ (ppm) 13.95 (CH_3), 41.18 (4-C), 61.08 (OCH_2), 64.80 (NCH_2Ph), 65.52 (3-C), 68.77 (7- CH_2), 72.09 (7-C), 73.47 (CH_2Ph), 74.98 (CH_2Ph), 75.19 (CH_2Ph), 75.53 (CH_2Ph), 78.25 (8-C), 78.37 (10-C), 83.81 (9-C), 107.96 (5-C), 127.50 (Ar), 127.59 (Ar), 127.67 (Ar), 127.73 (Ar), 127.79 (Ar), 127.83 (Ar), 127.84 (Ar), 127.85 (Ar), 128.23 (Ar), 128.25 (Ar), 128.30 (Ar), 128.38 (Ar), 129.28 (Ar), 136.29 (Ar), 137.73 (Ar), 137.97 (Ar), 138.04 (Ar), 138.41 (Ar), 170.64 (C=O); HRMS (FAB) calcd for $C_{46}H_{49}NO_8Na$ 766.3356, Found: 766.3359.

Ethyl (3*R*,5*R*,8*S*,9*S*,10*R*)-2-benzyl-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (3b)

Colorless syrup, $[\alpha]_D^{25}$ = +66.00° (*c* 1.0, $CHCl_3$); IR (neat): ν 3063.33, 3030.54, 2912.87, 2870.43, 1741.93, 1496.94, 1454.50, 1367.70, 1273.17, 1207.59, 1103.42, 1060.98, 736.90, 698.32 cm^{-1} ; 1H NMR ($CDCl_3$): δ 1.20 (t, 3H, *J* = 7.15 Hz, CH_3), 2.56 (d, 2H, *J* = 7.70 Hz, 4-H), 3.51 (dd, 1H, *J* = 8.80 Hz, *J* = 4.95 Hz, 7- CH_2), 3.61 (br t, 2H, *J* = 8.80 Hz, 3-H and 7- CH_2), 3.87 (dd, 1H, *J* = 9.89 Hz, *J* = 2.75 Hz, 9-H), 4.05~4.11 (m, 6H, 7-H, 10-H, 8-H, two H of OCH_2 and one H of NCH_2Ph), 4.17 (d, 1H, *J* = 13.75 Hz, NCH_2Ph), 4.42 (d, 1H, *J* = 11.54 Hz, CH_2Ph), 4.46 (d, 1H, *J* = 11.55 Hz, CH_2Ph), 4.63 (d, 1H, *J* = 11.54 Hz, CH_2Ph), 4.69 (d, 1H, *J* = 12.09 Hz, CH_2Ph), 4.71 (d, 1H, *J* = 12.65 Hz, CH_2Ph), 4.74 (d, 1H, *J* = 11.55 Hz, CH_2Ph), 4.93 (d, 1H, *J* = 11.55 Hz, CH_2Ph), 5.07 (d, 1H, *J* = 11.55 Hz, CH_2Ph), 7.26~7.37 (m, 25H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.06 (CH_3), 41.07 (4-C), 61.15 (NCH_2Ph), 61.44(OCH_2), 65.73 (3-C), 67.97 (7- CH_2), 70.76 (7-C), 72.27 (CH_2Ph), 73.27 (CH_2Ph), 74.28 (10-C), 74.80 (CH_2Ph), 75.46 (CH_2Ph), 76.06 (8-C), 81.21 (9-C), 106.20 (5-C), 127.49 (Ar), 127.54 (Ar), 127.65 (Ar), 127.70 (Ar), 127.91 (Ar), 128.09 (Ar), 128.14 (Ar), 128.16 (Ar), 128.18 (Ar), 128.36 (Ar), 128.40 (Ar), 129.32 (Ar), 136.46 (Ar),

138.07 (Ar), 138.36 (Ar), 138.77 (Ar), 169.69 (C=O); HRMS (FAB) calcd for C₄₆H₄₉NO₈Na 766.3356, Found: 766.3365.

Ethyl (3*R*,5*S*,8*S*,9*S*,10*R*)-2-benzyl-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (4b)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +36.50^{\circ}$ (*c* 1.0, CHCl₃); IR (neat): ν 3063.33, 3030.54, 2932.80, 2880.52, 1742.02, 1604.97, 1496.94, 1454.50, 1365.51, 1278.22, 1208.60, 1110.02, 1061.58, 906.28, 736.90, 698.32 cm⁻¹; ¹H NMR (CDCl₃): δ 1.12 (t, 3H, *J* = 7.15 Hz, CH₃), 2.55 (dd, 1H, *J* = 12.65 Hz, *J* = 8.80 Hz, 4-H), 2.88 (dd, 1H, *J* = 12.65 Hz, *J* = 7.15 Hz, 4-H), 3.52 (dd, 1H, *J* = 9.35 Hz, *J* = 7.15 Hz, 7-CH₂), 3.56 (dd, 1H, *J* = 9.35 Hz, *J* = 6.60 Hz, 7-CH₂), 3.83 (t, 1H, *J* = 7.70 Hz, 3-H), 3.92 (q, 2H, *J* = 7.15 Hz, OCH₂), 3.93 (dd, 1H, *J* = 9.90 Hz, *J* = 2.75 Hz, 9-H), 3.96 (dd, 1H, *J* = 2.75 Hz, *J* = 1.65 Hz, 8-H), 4.03~4.09 (m, 2H, 7-H and 10-H), 4.16 (d, 1H, *J* = 13.75 Hz, NCH₂Ph), 4.46 (d, 1H, *J* = 13.75 Hz, NCH₂Ph, overlapped), 4.46 (d, 1H, *J* = 11.55 Hz, CH₂Ph, overlapped), 4.51 (d, 1H, *J* = 12.10 Hz, CH₂Ph), 4.62 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 4.69~4.74 (m, 3H, CH₂Ph), 4.97 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 4.97 (d, 1H, *J* = 10.99 Hz, CH₂Ph), 7.23~7.36 (m, 25H, ArH); ¹³C NMR (CDCl₃): δ 13.98 (CH₃), 41.07 (4-C), 61.11 (NCH₂Ph), 61.45 (OCH₂), 65.61 (3-C), 68.14 (7-CH₂), 71.22 (7-C), 72.14 (CH₂Ph), 72.88 (CH₂Ph), 73.28 (10-C), 73.51 (CH₂Ph), 74.65 (CH₂Ph), 74.99 (8-C), 81.23 (9-C), 108.91 (5-C), 127.31 (Ar), 127.36 (Ar), 127.58 (Ar), 127.68 (Ar), 127.72 (Ar), 127.74 (Ar), 128.14 (Ar), 128.18 (Ar), 128.25 (Ar), 128.29 (Ar), 128.33 (Ar), 128.38 (Ar), 128.78 (Ar), 129.17 (Ar), 136.69 (Ar), 137.96 (Ar), 138.32 (Ar), 138.55 (Ar), 169.68 (C=O); HRMS (FAB) calcd for C₄₆H₄₉NO₈Na 766.3358, Found: 766.3349.

Ethyl (3*R*,5*R*,8*R*,9*S*,10*S*)-2-benzyl-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (3c)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +71.60^{\circ}$ (*c* 1.0, CHCl₃); IR (neat) ν 3063.33, 3030.54, 2903.22, 2866.57, 1741.93, 1496.94, 1450.50, 1367.70, 1207.59, 1095.70, 1028.18, 912.44, 736.90, 698.32 cm⁻¹; ¹H NMR (CDCl₃): δ 1.21 (t, 3H, *J* = 7.15 Hz, CH₃), 2.41 (br s, 1H, 4-H), 2.69 (dd, 1H, *J* = 13.47 Hz, *J* = 6.87 Hz, 4-H), 3.48 (br t, 1H, *J* = 7.15 Hz, 3-H), 3.63 (br s, 1H, 10-H), 3.68 (dd, 1H, *J* = 11.27 Hz, *J* = 1.65 Hz, 7-CH₂), 3.79 (dd, 1H, *J* = 11.28 Hz, *J* = 3.85 Hz, 7-CH₂), 3.83~3.86 (m, 2H, 9-H and 8-H), 4.04 (br d, 1H, *J* = 13.47 Hz, NCH₂Ph), 4.06~4.15 (m, 4H, 7-H, OCH₂ and one of NCH₂Ph), 4.48 (d, 1H, *J* = 11.82 Hz, CH₂Ph), 4.55 (br d, 1H, *J* = 10.99 Hz, CH₂Ph), 4.64 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 4.68 (d, 1H, *J* = 11.82 Hz, CH₂Ph), 4.72 (d, 1H, *J* = 11.82 Hz, CH₂Ph), 4.77 (d, 2H, *J* = 11.82 Hz, CH₂Ph), 4.99 (br d, 1H, *J* = 10.73 Hz, CH₂Ph), 7.17~7.19 (m, 2H, ArH), 7.23~7.39 (m, 23H, ArH); ¹³C NMR (CDCl₃): δ 14.05 (CH₃), 42.21 (4-C), 61.30 (NCH₂Ph), 61.43 (OCH₂), 64.94 (3-C), 68.84 (7-CH₂), 72.99 (CH₂Ph), 73.31 (CH₂Ph), 73.71 (8-C), 74.32 (CH₂Ph), 74.73 (7-C), 74.82 (CH₂Ph), 77.45 (10-C), 81.42 (9-C), 105.86 (5-C), 126.96 (Ar), 127.30 (Ar), 127.52 (Ar), 127.62 (Ar), 127.66 (Ar), 127.68 (Ar), 127.70 (Ar), 127.93 (Ar), 127.95 (Ar), 128.07 (Ar), 128.17 (Ar), 128.26 (Ar), 128.30 (Ar), 128.31 (Ar), 128.43 (Ar), 128.54 (Ar), 129.60 (Ar), 138.25 (Ar), 138.44 (two C, Ar), 138.63 (Ar), 169.17 (C=O); HRMS (FAB) calcd for C₄₆H₄₉NO₈Na

766.3356, Found: 766.3360.

Ethyl (3*R*,5*S*,8*R*,9*S*,10*S*)-2-benzyl-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxaspiro[4.5]decane-3-carboxylate (4c)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +19.40^{\circ}$ (*c* 1.0, CHCl₃); IR (neat) ν 3063.33, 3030.54, 2909.01, 2868.50, 1740.00, 1496.94, 1450.50, 1369.63, 1205.66, 1095.70, 1028.18, 912.44, 736.90, 698.32 cm⁻¹; ¹H NMR (CDCl₃): δ 1.14 (t, 3H, *J* = 7.15 Hz, CH₃), 2.52 (dd, 1H, *J* = 12.65 Hz, *J* = 9.34 Hz, 4-H), 2.78 (dd, 1H, *J* = 13.20 Hz, *J* = 7.42 Hz, 4-H), 3.72~3.77 (m, 2H, 7-CH₂), 3.85 (dd, 1H, *J* = 9.07 Hz, *J* = 2.75 Hz, 9-H), 3.91~3.94 (m, 3H, 10-H, 8-H and 3-H), 3.98 (ddd, 1H, *J* = 9.90 Hz, *J* = 5.50 Hz, *J* = 2.47 Hz, 7-H), 4.03 (q, 2H, *J* = 7.15 Hz, OCH₂), 4.17 (d, 1H, *J* = 12.92 Hz, NCH₂Ph), 4.43 (d, 1H, *J* = 12.92 Hz, NCH₂Ph), 4.53 (d, 1H, *J* = 10.72 Hz, CH₂Ph), 4.56 (d, 1H, *J* = 12.10 Hz, CH₂Ph), 4.64 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 4.68 (d, 1H, *J* = 11.27 Hz, CH₂Ph), 4.71 (d, 2H, *J* = 11.27 Hz, CH₂Ph), 4.85 (d, 1H, *J* = 10.73 Hz, CH₂Ph), 4.97 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 7.17~7.19 (m, 2H, ArH), 7.24~7.36 (m, 23H, ArH); ¹³C NMR (CDCl₃): δ 13.98 (CH₃), 43.30 (4-C), 61.40 (OCH₂), 65.07 (NCH₂Ph), 66.00 (3-C), 69.59 (7-CH₂), 72.62 (CH₂Ph), 73.38 (CH₂Ph), 73.44 (7-C), 74.58 (CH₂Ph), 74.83 (8-C), 75.08 (CH₂Ph), 77.22 (10-C), 82.06 (9-C), 108.23 (5-C), 126.95 (Ar), 127.47 (Ar), 127.53 (Ar), 127.61 (Ar), 127.62 (Ar), 127.65 (Ar), 127.67 (Ar), 127.70 (Ar), 128.08 (Ar), 128.13 (Ar), 128.27 (Ar), 128.30 (Ar), 128.33 (Ar), 128.36 (Ar), 128.41 (Ar), 128.54 (Ar), 129.31 (Ar), 135.94 (Ar), 138.19 (Ar), 138.22 (Ar), 138.28 (Ar), 138.41 (Ar), 170.48 (C=O); HRMS (FAB) calcd for C₄₆H₄₉NO₈Na 766.3356, Found: 766.3352.

Ethyl (3*R*,5*R*,8*R*,9*S*,10*R*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-2-methyl-1,6-dioxaspiro[4.5]decane-3-carboxylate (6a)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +43.70^{\circ}$ (*c* 1.0, CHCl₃); IR (neat): ν 3063.33, 3030.54, 2897.43, 2870.43, 1952.20, 1869.25, 1745.79, 1496.94, 1454.50, 1363.84, 1294.39, 1209.51, 1070.62, 1028.18, 902.80, 736.90, 698.32 cm⁻¹; ¹H NMR (CDCl₃): δ 1.26 (t, 3H, *J* = 7.15 Hz, CH₃), 2.45 (dd, 1H, *J* = 13.20 Hz, *J* = 8.25 Hz, 4-H), 2.54 (dd, 1H, *J* = 13.20 Hz, *J* = 8.25 Hz, 4-H), 2.82 (s, 3H, NCH₃), 3.34 (br t, 1H, *J* = 8.30 Hz, 3-H), 3.54 (d, 1H, *J* = 9.89 Hz, 10-H), 3.68 (dd, 1H, *J* = 11.00 Hz, *J* = 1.65 Hz, 7-CH₂), 3.78 (dd, 1H, *J* = 11.00 Hz, *J* = 2.75 Hz, 7-CH₂), 3.80 (t, 1H, *J* = 9.90 Hz, 9-H), 3.90 (t, 1H, *J* = 9.35 Hz, 8-H), 3.96 (dt, 1H, *J* = 9.90 Hz, *J* = 2.20 Hz, 7-H), 4.15~4.20 (m, 2H, OCH₂), 4.48 (d, 1H, *J* = 12.64 Hz, CH₂Ph), 4.57 (d, 1H, *J* = 10.45 Hz, CH₂Ph), 4.61 (d, 1H, *J* = 12.10 Hz, CH₂Ph), 4.69 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 4.81 (d, 1H, *J* = 11.00 Hz, CH₂Ph), 4.87 (d, 1H, *J* = 11.00 Hz, CH₂Ph), 4.89 (d, 1H, *J* = 11.00 Hz, CH₂Ph), 5.00 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 7.15~7.16 (m, 2H, ArH), 7.23~7.36 (m, 18H, ArH); ¹³C NMR (CDCl₃): δ 12.75 (CH₃), 40.94 (4-C), 43.81 (NCH₃), 60.01 (OCH₂), 66.90 (7-CH₂), 68.14 (3-C), 70.89 (7-C), 72.17 (CH₂Ph), 73.54 (CH₂Ph), 74.04 (CH₂Ph), 74.16 (CH₂Ph), 76.66 (9-C), 78.07 (10-C), 82.63 (8-C), 103.78 (5-C), 126.26 (Ar), 126.28 (Ar), 126.40 (Ar), 126.43 (Ar), 126.45 (Ar), 126.58 (Ar), 126.60 (Ar), 126.71 (Ar), 126.98 (Ar), 127.01 (Ar), 127.04 (Ar), 127.07 (Ar), 127.17 (Ar), 136.68 (Ar), 136.77 (Ar), 136.96 (Ar), 137.21 (Ar), 167.88 (C=O); HRMS (FAB) calcd for C₄₀H₄₅NO₈Na 690.3043, Found: 690.3040.

Ethyl (3*R*,5*S*,8*R*,9*S*,10*R*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-2-methyl-1,6-dioxaspiro[4.5]decane-3-carboxylate (7a)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +22.38^{\circ}$ (*c* 1.0, CHCl₃); IR (neat): ν 3063.33, 3030.54, 2918.22, 2887.80, 1951.70, 1866.89, 1744.98, 1496.94, 1454.50, 1394.66, 1359.88, 1210.56, 1076.26, 1028.38, 743.88, 698.32 cm⁻¹; ¹H NMR (CDCl₃): δ 1.23 (t, 3H, *J* = 7.08 Hz, CH₃), 2.42 (dd, 1H, *J* = 13.18 Hz, *J* = 7.81 Hz, 4-H), 2.82 (dd, 1H, *J* = 13.18 Hz, *J* = 8.24 Hz, 4-H), 2.94 (s, 3H, NCH₃), 3.53 (d, 1H, *J* = 9.77 Hz, 10-H), 3.62 (dd, 1H, *J* = 10.50 Hz, *J* = 1.46 Hz, 7-CH₂), 3.67 (t, 1H, *J* = 8.90 Hz, 3-H), 3.71 (t, 1H, *J* = 9.52 Hz, 8-H), 3.73 (dd, 1H, *J* = 10.50 Hz, *J* = 3.47 Hz, 7-CH₂), 3.92~4.01 (m, 2H, 9-H and 7-H), 4.06~4.15 (m, 2H, OCH₂), 4.49 (d, 1H, *J* = 12.21 Hz, CH₂Ph), 4.52 (d, 1H, *J* = 11.96 Hz, CH₂Ph), 4.60 (d, 1H, *J* = 12.45 Hz, CH₂Ph), 4.68 (d, 1H, *J* = 11.48 Hz, CH₂Ph), 4.83 (d, 2H, *J* = 10.74 Hz, CH₂Ph), 4.80 (d, 1H, *J* = 10.98 Hz, CH₂Ph), 4.93 (d, 1H, *J* = 11.72 Hz, CH₂Ph), 7.14~7.17 (m, 2H, ArH), 7.26~7.36 (m, 18H, ArH); ¹³C NMR (CDCl₃): δ 14.23 (CH₃), 40.92 (4-C), 45.24 (NCH₃), 61.33 (OCH₂), 67.90 (3-C), 68.60 (7-CH₂), 71.73 (7-C), 73.43 (CH₂Ph), 74.95 (CH₂Ph), 74.15 (CH₂Ph), 75.52 (CH₂Ph), 78.15 (10-C), 78.24 (9-C), 83.76 (8-C), 107.18 (5-C), 127.52 (Ar), 127.55 (Ar), 127.61 (Ar), 127.63 (Ar), 127.70 (Ar), 127.75 (Ar), 127.77 (Ar), 127.88 (Ar), 128.09 (Ar), 128.13 (Ar), 128.18 (Ar), 128.21 (Ar), 128.24 (Ar), 137.58 (Ar), 137.80 (Ar), 137.95 (Ar), 138.26 (Ar), 169.84 (C=O); HRMS (FAB) calcd for C₄₀H₄₅NO₈Na 690.3043, Found: 690.3040.

Ethyl (3*R*,5*R*,8*S*,9*S*,10*R*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-2-methyl-1,6-dioxaspiro[4.5]decane-3-carboxylate (6b)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +46.30^{\circ}$ (*c* 1.0, CHCl₃); IR (neat): ν 3063.33, 3030.54, 2914.80, 2872.36, 1745.79, 1496.94, 1454.50, 1209.51, 1136.21, 1101.49, 1059.05, 736.90, 698.32 cm⁻¹; ¹H NMR (CDCl₃): δ 1.23 (t, 3H, *J* = 7.15 Hz, CH₃), 2.51 (dd, 2H, *J* = 8.24 Hz, *J* = 4.40 Hz, 4-H), 2.81 (s, 3H, NCH₃), 3.34 (br t, 1H, *J* = 7.70 Hz, 3-H), 3.54 (dd, 1H, *J* = 8.52 Hz, *J* = 4.95 Hz, 7-CH₂), 3.62 (t, 1H, *J* = 8.80 Hz, 7-CH₂), 3.88 (dd, 1H, *J* = 10.18 Hz, *J* = 2.75 Hz, 9-H), 4.03 (d, 1H, *J* = 10.17 Hz, 10-H), 4.08 (dd, 1H, *J* = 2.75 Hz, *J* = 1.38 Hz, 8-H), 4.12~4.16 (m, 3H, 7-H and OCH₂), 4.10 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 4.45 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 4.60 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 4.67~4.73 (m, 3H, CH₂Ph), 4.91 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 5.03 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 7.25~7.35 (m, 20H, ArH); ¹³C NMR (CDCl₃): δ 14.02 (CH₃), 42.30 (4-C), 45.18 (NCH₃), 61.20 (OCH₂), 67.81 (7-CH₂), 69.33 (3-C), 70.67 (8-C), 72.25 (CH₂Ph), 73.33 (CH₂Ph), 74.18 (7-C), 74.80 (CH₂Ph), 75.31 (CH₂Ph), 75.92 (10-C), 81.33 (9-C), 105.62 (5-C), 127.36 (Ar), 127.46 (Ar), 127.51 (Ar), 127.57 (Ar), 127.59 (Ar), 127.64 (Ar), 127.66 (Ar), 127.91 (Ar), 128.04 (Ar), 128.07 (Ar), 128.10 (Ar), 128.13 (Ar), 128.14 (Ar), 128.17 (Ar), 128.26 (Ar), 128.30 (Ar), 128.32 (Ar), 128.33 (Ar), 137.90 (Ar), 138.20 (Ar), 138.31 (Ar), 138.72 (Ar), 169.35 (C=O); HRMS (FAB) calcd for C₄₀H₄₅NO₈Na 690.3043, Found: 690.3038.

Ethyl (3*R*,5*S*,8*S*,9*S*,10*R*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-2-methyl-1,6-dioxaspiro[4.5]decane-3-carboxylate (7b)

Colorless syrup, $[\alpha]_D^{25} = +35.15^\circ$ (c 1.0, CHCl_3); IR (neat): ν 3063.33, 3030.54, 2910.84, 2891.64, 2870.32, 1745.79, 1604.97, 1496.94, 1454.50, 1359.86, 1210.68, 1098.35, 1039.80, 743.50, 698.32 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.20 (t, 3H, $J = 7.15$ Hz, CH_3), 2.45 (dd, 1H, $J = 12.65$ Hz, $J = 7.70$ Hz, 4-H), 2.84 (dd, 1H, $J = 12.65$ Hz, $J = 8.80$ Hz, 4-H), 2.93 (s, 3H, NCH_3), 3.50 (dd, 1H, $J = 8.45$ Hz, $J = 6.90$ Hz, 7- CH_2), 3.51 (t, 1H, $J = 8.45$ Hz, 7- CH_2), 3.68 (br t, 1H, $J = 7.70$ Hz, 3-H), 3.92 (dd, 1H, $J = 10.17$ Hz, $J = 2.75$ Hz, 9-H), 3.97 (dd, 1H, $J = 2.75$ Hz, $J = 1.35$ Hz 8-H), 4.03 (d, 1H, $J = 10.17$ Hz, 10-H), 4.11~4.15 (m, 3H, 7-H and OCH_2), 4.42 (d, 1H, $J = 11.82$ Hz, CH_2Ph), 4.47 (d, 1H, $J = 11.82$ Hz, CH_2Ph), 4.59 (d, 1H, $J = 11.27$ Hz, CH_2Ph), 4.68~4.73 (m, 3H, CH_2Ph), 4.94 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 4.95 (d, 1H, $J = 11.28$ Hz, CH_2Ph), 7.24~7.36 (m, 20H, ArH); ^{13}C NMR (CDCl_3): δ 14.20 (CH_3), 40.91 (4-C), 48.50 (NCH_3), 60.29 (OCH_2), 67.92 (7- CH_2), 68.84 (3-C), 70.62 (8-C), 72.71 (CH_2Ph), 73.38 (CH_2Ph), 74.64 (7-C), 74.84 (CH_2Ph), 74.86 (10-C), 74.99 (CH_2Ph), 81.10 (9-C), 108.08 (5-C), 127.46 (Ar), 127.51 (Ar), 127.57 (Ar), 127.59 (Ar), 127.66 (Ar), 127.91 (Ar), 128.10 (Ar), 128.12 (Ar), 128.15 (Ar), 128.16 (Ar), 128.27 (Ar), 128.29 (Ar), 128.31 (Ar), 137.87 (Ar), 138.00 (Ar), 138.30 (Ar), 138.54 (Ar), 170.30 (C=O); HRMS (FAB) calcd for $\text{C}_{40}\text{H}_{45}\text{NO}_8\text{Na}$ 690.3043, Found: 690.3038.

Ethyl (3*R*,5*R*,8*R*,9*S*,10*S*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-2-methyl-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (6c)

Colorless syrup, $[\alpha]_D^{25} = +80.80^\circ$ (c 1.0, CHCl_3); IR (neat): ν 3063.33, 3030.54, 2903.22, 2868.50, 1745.79, 1496.94, 1450.50, 1367.70, 1207.59, 1095.70, 1028.18, 968.38, 736.90, 698.32 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.28 (t, 3H, $J = 7.15$ Hz, CH_3), 2.60~2.65 (m, 1H, 4-H), 2.73 (dd, 1H, $J = 13.75$ Hz, $J = 8.25$ Hz, 4-H), 2.77 (s, 3H, NCH_3), 3.24 (br t, 1H, $J = 8.25$ Hz, 3-H), 3.73 (d, 1H, $J = 2.48$ Hz, 10-H), 3.75 (dd, 1H, $J = 11.28$ Hz, $J = 1.93$ Hz, 7- CH_2), 3.86 (dd, 1H, $J = 11.27$ Hz, $J = 3.57$ Hz, 7- CH_2), 3.93 (dd, 1H, $J = 9.08$ Hz, $J = 2.48$ Hz, 9-H), 3.94~3.97 (m, 1H, 7-H), 4.19 (t, 1H, $J = 9.62$ Hz, 8-H), 4.20 (q, 2H, $J = 7.15$ Hz, OCH_2), 4.52 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.60 (d, 1H, $J = 10.72$ Hz, CH_2Ph), 4.73 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.75 (d, 1H, $J = 12.37$ Hz, CH_2Ph), 4.79 (d, 1H, $J = 11.74$ Hz, CH_2Ph), 4.82 (d, 1H, $J = 11.83$ Hz, CH_2Ph), 4.84 (d, 1H, $J = 11.72$ Hz, CH_2Ph), 5.09 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 7.20~7.22 (m, 2H, ArH), 7.26~7.42 (m, 18H, ArH); ^{13}C NMR (CDCl_3): δ 14.06 (CH_3), 43.12 (4-C), 45.31 (NCH_3), 61.36 (OCH_2), 68.80 (7- CH_2), 69.03 (3-C), 72.95 (CH_2Ph), 73.38 (CH_2Ph), 73.53 (7-C), 74.31 (CH_2Ph), 74.69 (CH_2Ph), 74.80 (8-C), 77.54 (10-C), 81.64 (9-C), 105.26 (5-C), 127.27 (Ar), 127.46 (Ar), 127.53 (Ar), 127.58 (Ar), 127.59 (Ar), 127.87 (Ar), 127.90 (Ar), 127.93 (Ar), 128.14 (Ar), 128.20 (Ar), 128.26 (Ar), 128.37 (Ar), 138.31 (Ar), 138.46 (Ar), 138.50 (Ar), 138.59 (Ar), 169.15 (C=O); HRMS (FAB) calcd for $\text{C}_{40}\text{H}_{45}\text{NO}_8\text{Na}$ 690.3043, Found: 690.3041.

Ethyl (3*R*,5*S*,8*R*,9*S*,10*S*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-2-methyl-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (7c)

Colorless syrup, $[\alpha]_D^{25} = +35.00^\circ$ (c 1.0, CHCl_3); IR (neat): ν 3063.33, 3030.54, 2905.15, 2866.57, 1741.93, 1496.94, 1450.50, 1369.63, 1205.66, 1093.77, 1028.18, 910.51, 736.90, 698.32 cm^{-1} ; ^1H NMR

(CDCl₃): δ 1.29 (t, 3H, J = 7.15 Hz, CH₃), 2.50 (dd, 1H, J = 12.92 Hz, J = 9.07 Hz, 4-H), 2.79 (dd, 1H, J = 12.92 Hz, J = 7.43 Hz, 4-H), 2.97 (s, 3H, NCH₃), 3.73 (br d, 1H, J = 10.45 Hz, 7-CH₂), 3.76~3.79 (m, 2H, 3-H and 7-CH₂), 3.88 (d, 1H, J = 2.48 Hz, 10-H), 3.91~3.93 (m, 1H, 9-H), 3.98~4.00 (m, 2H, 8-H and 7-H), 4.17~4.22 (m, 2H, OCH₂), 4.54 (d, 1H, J = 12.37 Hz, CH₂Ph), 4.55 (d, 1H, J = 10.72 Hz, CH₂Ph), 4.66 (d, 1H, J = 12.06 Hz, CH₂Ph), 4.71~4.76 (m, 3H, CH₂Ph), 4.89 (d, 1H, J = 10.73 Hz, CH₂Ph), 5.01 (d, 1H, J = 11.82 Hz, CH₂Ph), 7.19~7.20 (m, 2H, ArH), 7.27~7.39 (m, 18H, ArH); ¹³C NMR (CDCl₃): δ 14.06 (CH₃), 43.42 (4-C), 48.74 (NCH₃), 61.42 (OCH₂), 68.11 (3-C), 69.32 (7-CH₂), 72.57 (CH₂Ph), 73.03 (7-C), 73.24 (CH₂Ph), 74.41 (CH₂Ph), 74.77 (8-C), 75.01 (CH₂Ph), 76.71 (10-C), 81.96 (9-C), 107.73 (5-C), 127.40 (Ar), 127.54 (Ar), 127.56 (Ar), 127.59 (Ar), 127.63 (Ar), 127.92 (Ar), 128.22 (Ar), 128.26 (Ar), 128.39 (Ar), 138.23 (Ar), 138.26 (two C, Ar), 138.36 (Ar), 170.43 (C=O); HRMS (FAB) calcd for C₄₀H₄₅NO₈Na 690.3043, Found: 690.3045.

Ethyl (3*R*,5*R*,8*R*,9*S*,10*R*)-8,9,10-tris(acetyloxy)-7-(acetyloxymethyl)-2-benzyl-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (9)

Colorless syrup, $[\alpha]_D^{25} = + 115.09^\circ$ (c 1.0, CHCl₃); IR (neat): ν 2958.12, 2879.65, 1755.51, 1605.28, 1496.94, 1450.50, 1371.35, 1221.18, 1090.56, 978.20 cm⁻¹; ¹H NMR (CDCl₃) δ (ppm): 1.25 (t, 3H, J = 7.15 Hz, CH₃), 1.99 (s, 3H, COCH₃), 2.00 (s, 3H, COCH₃), 2.01 (s, 3H, COCH₃), 2.09 (s, 3H, COCH₃), 2.51 (dd, 1H, J = 13.75 Hz, J = 8.80 Hz, 4-H), 2.74 (dd, 1H, J = 13.75 Hz, J = 7.70 Hz, 4-H), 3.51 (t, 1H, J = 8.25 Hz, 3-H), 4.05 (dd, 1H, J = 12.65 Hz, J = 2.20 Hz, 7-CH₂), 4.10~4.17 (m, 3H, 7-H and OCH₂), 4.17 (d, 1H, J = 13.75 Hz, NCH₂Ph), 4.22 (d, 1H, J = 13.75 Hz, NCH₂Ph), 4.28 (dd, 1H, J = 12.65 Hz, J = 3.85 Hz, 7-CH₂), 5.11 (t, 1H, J = 9.90 Hz, 8-H), 5.17 (d, 1H, J = 10.44 Hz, 10-H), 5.30 (t, 1H, J = 9.89 Hz, 9-H), 7.31 (br d, 1H, J = 7.15 Hz, ArH), 7.35 (t, 2H, J = 7.15 Hz, ArH), 7.41 (d, 2H, J = 7.15 Hz, ArH); ¹³C NMR (CDCl₃) δ (ppm): 14.06 (CH₃), 20.59 (CH₃), 20.61 (two C, CH₃), 20.74 (CH₃), 41.19 (4-C), 60.98 (NCH₂Ph), 61.52 (7-CH₂ and OCH₂), 64.67 (3-C), 67.97 (8-C), 69.16 (7-C), 69.76 (10-C), 71.70 (9-C), 103.69 (5-C), 127.73 (Ar), 128.30 (two C, Ar), 129.81 (two C, Ar), 135.08 (Ar), 168.74 (C=O), 169.53 (C=O), 169.92 (C=O), 170.01 (C=O), 170.71 (C=O); HRMS (FAB) calcd for C₂₆H₃₃NO₁₂Na 534.1901, Found: 534.1905.

Ethyl (3*R*,5*S*,8*R*,9*S*,10*R*)-8,9,10-tris(acetyloxy)-7-[acetyloxymethyl]-2-benzyl-1,6-dioxo-2-azaspiro-[4.5]decane-3-carboxylate (10)

Colorless syrup, $[\alpha]_D^{25} = + 57.20^\circ$ (c 1.0, CHCl₃); IR (neat): ν 2960.10, 2877.58, 1749.85, 1602.88, 1496.94, 1450.50, 1369.89, 1093.16, 978.09, 798.62 cm⁻¹; ¹H NMR (CDCl₃) δ (ppm): 1.20 (t, 3H, J = 7.15 Hz, CH₃), 1.99 (s, 3H, COCH₃), 2.04 (s, 6H, COCH₃), 2.13 (s, 3H, COCH₃), 2.80 (dd, 1H, J = 13.20 Hz, J = 8.25 Hz, 4-H), 2.74 (dd, 1H, J = 13.20 Hz, J = 7.15 Hz, 4-H), 3.79 (ddd, 1H, J = 9.90 Hz, J = 5.50 Hz, J = 2.75 Hz, 7-H), 3.90 (t, 1H, J = 7.70 Hz, 3-H), 4.09~4.23 (m, 4H, NCH₂Ph and OCH₂ overlapped), 4.46 (d, 1H, J = 12.65 Hz, 7-CH₂), 5.07 (t, 1H, J = 9.35 Hz, 8-H), 5.11~5.16 (m, 2H, 7-CH₂ and 9-H), 5.25 (d, 1H, J = 9.35 Hz, 10-H), 7.29~7.37 (m, 5H, ArH); ¹³C NMR (CDCl₃) δ (ppm): 14.03 (CH₃), 20.55 (CH₃),

20.58 (CH₃), 20.63 (CH₃), 20.81 (CH₃), 36.95 (4-C), 61.49 (NCH₂Ph), 61.78 (OCH₂), 62.50 (7-CH₂), 65.42 (3-C), 68.36 (8-C), 68.46 (7-C), 71.30 (10-C), 72.51 (9-C), 108.17 (5-C), 128.25 (Ar), 128.36 (two C, Ar), 129.53 (two C, Ar), 135.80 (Ar), 168.68 (C=O), 168.82 (C=O), 169.30 (C=O), 169.72 (C=O), 170.16 (C=O); HRMS (FAB) calcd for C₂₆H₃₃NO₁₂Na 534.1901, Found: 534.1909.

1,3-Dipolar cycloadditions of the 1-methylenesugars (1a~c) with the nitrile oxide (11): — 107 mg (0.2 mmol) of **1a** and 38 mg (0.25 mmol) of ethyl chlorooximidoacetate were dissolved in 2 mL of dry Et₂O under Argon atmosphere. To the solution was added 20 μ L (0.14 mmol) of Et₃N at rt. After stirring for 10 min, other 15 μ L (0.11 mmol) of Et₃N was added. The forming suspension was stirred at rt for 3 h. The reaction mixture was diluted by Et₂O and washed with H₂O. The organic solution was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was applied on silica gel column chromatography eluted by AcOEt : Hexane (1 : 8 and then 1 : 5) to afford the adduct (**12a**) (72 mg, yield 55.2 %) and the reactant (**1a**) (35 mg, 32.7 %). The reactions of **1b~c** with ethyl chlorooximidoacetate were carried out with the same procedure and the results are shown in Scheme 4.

Ethyl (5*R*,8*R*,9*S*,10*R*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxo-2-azaspiro[4.5]dec-2-ene-3-carboxylate (12a**)**

Colorless syrup, [α]_D²⁵: +9.40° (*c* 1.0, CHCl₃); IR (neat) 3063.33, 3030.54, 2982.31, 2924.44, 2868.50, 1956.06, 1875.04, 1811.38, 1722.64, 1593.40, 1496.94, 1450.50, 1408.21, 1363.84, 1278.96, 1219.16, 1122.71, 1089.91, 1028.18, 912.44, 856.50, 829.49, 738.83, 698.32 cm⁻¹; ¹HNMR (CDCl₃): δ (ppm) 1.35 (t, 3H, *J* = 7.15 Hz, CH₃), 2.97 (d, 1H, *J* = 18.14 Hz, 4-H), 3.04 (d, 1H, *J* = 18.14 Hz, 4-H), 3.58 (br d, 1H, *J* = 11.00 Hz, 7-CH₂), 3.68 (d, 1H, *J* = 9.90 Hz, 10-H), 3.76 (dd, 1H, *J* = 11.00 Hz, *J* = 2.75 Hz, 7-CH₂), 3.82 (t, 1H, *J* = 9.89 Hz, 8-H), 4.03 (br d, 1H, *J* = 10.45 Hz, 7-H), 4.11 (t, 1H, *J* = 9.35 Hz, 9-H), 4.31 (q, 2H, *J* = 7.15 Hz, OCH₂), 4.45 (d, 1H, *J* = 12.15 Hz, CH₂Ph), 4.56 (d, 1H, *J* = 10.45 Hz, CH₂Ph), 4.57 (d, 1H, *J* = 12.10 Hz, CH₂Ph), 4.68 (d, 1H, *J* = 12.10 Hz, CH₂Ph), 4.84 (d, 1H, *J* = 10.45 Hz, CH₂Ph), 4.89 (d, 1H, *J* = 11.00 Hz, CH₂Ph), 4.93 (d, 1H, *J* = 11.00 Hz, CH₂Ph), 4.97 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 7.16~7.17 (m, 2H, ArH), 7.25~7.33 (m, 18H, ArH); ¹³CNMR (CDCl₃): δ (ppm) 14.05 (CH₃), 41.62 (4-C), 62.06 (OCH₂), 67.94 (7-CH₂), 72.86 (7-C), 73.46 (CH₂Ph), 74.88 (CH₂Ph), 74.97 (CH₂Ph), 75.65 (CH₂Ph), 77.48 (8-C), 78.39 (10-C), 83.64 (9-C), 110.90 (5-C), 127.70 (Ar), 127.74 (Ar), 127.78 (Ar), 127.82 (Ar), 127.90 (Ar), 127.97 (Ar), 128.01 (Ar), 128.37 (Ar), 128.43 (Ar), 128.52 (Ar), 137.55 (Ar), 137.76 (Ar), 138.01 (Ar), 138.23 (Ar), 152.50 (3-C), 160.09 (C=O); HRMS (FAB) calcd for C₃₉H₄₁NO₈Na 674.2730, Found: 674.2736.

Ethyl (5*R*,8*S*,9*S*,10*R*)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxo-2-azaspiro[4.5]dec-2-ene-3-carboxylate (12b**)**

Colorless syrup, [α]_D²⁵: +11.60° (*c* 1.0, CHCl₃); IR (neat) ν 3063.33, 3030.54, 2982.31, 2912.87, 2872.36, 1956.06, 1880.82, 1811.38, 1720.71, 1593.40, 1496.94, 1450.50, 1408.21, 1371.55, 1286.68, 1265.46,

1205.66, 1101.49, 1059.05, 1028.18, 914.37, 862.29, 740.76, 698.32 cm^{-1} ; ^1H NMR (CDCl_3) δ (ppm): 1.34 (t, 3H, $J = 7.15$ Hz, CH_3), 2.93 (d, 1H, $J = 18.15$ Hz, 4-C), 3.08 (d, 1H, $J = 18.15$ Hz, 4-C), 3.46 (dd, 1H, $J = 8.79$ Hz, $J = 5.50$ Hz, 7- CH_2), 3.55 (dd, 1H, $J = 9.35$ Hz, $J = 7.70$ Hz, 7- CH_2), 4.09~4.11 (m, 2H, 9-H and 8-H), 4.17 (d, 1H, $J = 9.90$ Hz, 10-H), 4.22 (br d, 1H, $J = 7.60$ Hz, 7-H), 4.31 (qd, 2H, $J = 7.15$ Hz, $J = 1.10$ Hz, OCH_2), 4.41 (d, 1H, $J = 11.54$ Hz, CH_2Ph), 4.44 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.61 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 4.71 (d, 1H, $J = 12.00$ Hz, CH_2Ph), 4.73 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 4.77 (d, 1H, $J = 11.54$ Hz, CH_2Ph), 4.94 (d, 1H, $J = 11.45$ Hz, CH_2Ph), 5.00 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 7.24~7.37 (m, 20H, ArH); ^{13}C NMR (CDCl_3) δ (ppm): 13.98 (CH_3), 41.64 (4-C), 61.90 (OCH_2), 67.89 (7- CH_2), 71.59 (7-C), 72.51 (CH_2Ph), 73.28 (9- or 8-C), 74.17 (CH_2Ph), 74.80 (CH_2Ph), 74.86 (CH_2Ph), 75.08 (10-C), 80.93 (8- or 9-C), 111.55 (5-C), 127.50 (Ar), 127.65 (Ar), 127.70 (Ar), 127.76 (Ar), 127.99 (Ar), 128.07 (Ar), 128.21 (Ar), 128.33 (Ar), 128.35 (Ar), 128.38 (Ar), 137.69 (Ar), 137.75 (Ar), 137.97 (Ar), 138.38 (Ar), 152.28 (3-C), 160.10 ($\text{C}=\text{O}$); HRMS (FAB) calcd for $\text{C}_{39}\text{H}_{41}\text{NO}_8\text{Na}$ 674.2730, Found: 674.2733.

Ethyl (5*R*,8*R*,9*S*,10*S*)-8,9,10-tris(benzyloxy)-7-[benzyloxymethyl]-1,6-dioxaspiro[4.5]dec-2-ene-3-carboxylate (12c)

White solid, mp 96~97°C; $[\alpha]_D^{25}$: +63.10° (c 1.0, CHCl_3); IR (KBr) ν 3063.33, 3030.54, 2905.15, 2868.50, 1956.06, 1869.25, 1811.38, 1722.64, 1593.40, 1496.94, 1450.50, 1371.55, 1315.61, 1230.73, 1099.56, 1026.25, 912.44, 864.21, 740.76, 698.32 cm^{-1} ; ^1H NMR (CDCl_3) δ (ppm): 1.34 (t, 3H, $J = 7.15$ Hz, CH_3), 3.04 (br d, 1H, $J = 17.59$ Hz, 4-C), 3.18 (d, 1H, $J = 18.69$ Hz, 4-C), 3.63 (dd, 1H, $J = 11.55$ Hz, $J = 1.65$ Hz, 7- CH_2), 3.76 (dd, 1H, $J = 11.55$ Hz, $J = 4.40$ Hz, 7- CH_2), 3.91 (d, 1H, $J = 2.20$ Hz, 10-H), 3.98 (ddd, 1H, $J = 9.90$ Hz, $J = 4.40$ Hz, $J = 2.20$ Hz, 7-H), 4.03 (dd, 1H, $J = 8.80$ Hz, $J = 2.20$ Hz, 8-H), 4.10 (br t, 1H, $J = 9.35$ Hz, 9-H), 4.31 (qd, 2H, $J = 7.15$ Hz, $J = 4.40$ Hz, OCH_2), 4.47 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.53 (br d, 1H, $J = 10.45$ Hz, CH_2Ph), 4.63 (d, 1H, $J = 12.09$ Hz, CH_2Ph), 4.68 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 4.76 (d, 1H, $J = 12.09$ Hz, CH_2Ph), 4.80 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 4.81 (br d, 1H, $J = 11.00$ Hz, CH_2Ph), 5.01 (br d, 1H, $J = 11.51$ Hz, CH_2Ph), 7.16~7.17 (m, 2H, ArH), 7.25~7.34 (m, 18H, ArH); ^{13}C NMR (CDCl_3) δ (ppm): 14.05 (CH_3), 43.48 (4-C), 62.14 (OCH_2), 68.69 (7- CH_2), 73.20 (CH_2Ph), 73.32 (CH_2Ph), 73.98 (CH_2Ph), 74.31 (7-C), 74.36 (CH_2Ph), 74.76 (8-C), 76.09 (10-C), 80.92 (9-C), 111.35 (5-C), 127.49 (Ar), 127.65 (Ar), 127.78 (Ar), 127.82 (Ar), 127.89 (Ar), 127.93 (Ar), 128.14 (Ar), 128.26 (Ar), 128.31 (Ar), 128.43 (Ar), 128.49 (Ar), 137.81 (Ar), 138.14 (Ar), 138.23 (Ar), 153.15 (3-C), 160.05 ($\text{C}=\text{O}$); HRMS (FAB) calcd for $\text{C}_{39}\text{H}_{41}\text{NO}_8\text{Na}$ 674.2730, Found: 674.2729.

Reductive cleavage of the O-N bond: — Activated zinc powder (230 mg, 4.0 mmol) was added to the solution of **6a** (67 mg, 0.1 mmol) in 2 mL of AcOH and 1.5 mL of Ac_2O . The solution was stirred under argon atmosphere at rt for 24 h, and the reaction was monitored by TLC (AcOEt : Hexane = 1:1). After completion of the reaction, 30 mL of AcOEt were added. The solution was washed with H_2O and saturated aq. NaHCO_3 , and dried over MgSO_4 . After removing the solvent under reduced pressure, the residue was applied on silica gel column chromatography (AcOEt : Hexane = 1 : 2.5) to afford products

(**13a**) (32.6 mg, 45.8%) and (**14a**) (25.6 mg, 39.6%). Compounds (**6b**) and (**6c**) were treated following the same procedure and the results are shown in Scheme 5.

Ethyl 2-[acetyl(methyl)amino]-5,6,7,9-tetra-O-benzyl-2,3-dideoxy-D-glycero- α -D-gulo-non-4-ulo-pyranosonate (13a**)**

Colorless syrup, $[\alpha]_{\text{D}}^{25} = -7.62^{\circ}$ (c 0.42, CHCl_3); IR (neat): ν 3267.81, 3063.33, 3030.54, 2930.23, 2866.57, 1738.07, 1651.27, 1620.40, 1495.01, 1454.50, 1406.28, 1365.77, 1209.51, 1143.93, 1070.62, 1028.18, 738.83, 700.25 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.24 (t, 3H, $J = 7.15$ Hz, CH_3), 1.73 (dd, 1H, $J = 14.29$ Hz, $J = 11.00$ Hz, 3-H), 1.84 (s, 3H, COCH_3), 2.47 (dd, 1H, $J = 14.29$ Hz, $J = 3.85$ Hz, 3-H), 2.77 (s, 3H, NCH_3), 3.26 (d, 1H, $J = 9.35$ Hz, 5-H), 3.39 (dd, 1H, $J = 10.44$ Hz, $J = 2.20$ Hz, 9-H), 3.36 (t, 1H, $J = 9.35$ Hz, 6-H), 3.59 (dd, 1H, $J = 10.44$ Hz, $J = 4.39$ Hz, 9-H), 3.85 (ddd, 1H, $J = 9.90$ Hz, $J = 4.40$ Hz, $J = 2.20$ Hz, 8-H), 4.11~4.20 (m, 3H, OCH_2 and 7-H), 4.38 (d, 1H, $J = 12.65$ Hz, CH_2Ph), 4.51 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.57 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 4.69 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 4.84 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 4.89 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 4.92 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 4.96 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 5.35 (dd, 1H, $J = 11.00$ Hz, $J = 3.85$ Hz, 2-H), 7.19~7.21 (m, 2H, ArH), 7.26~7.35 (m, 18H, ArH); ^{13}C NMR (CDCl_3): δ 14.11 (CH_3), 21.42 (COCH_3), 32.95 (NCH_3), 34.92 (3-C), 52.64 (2-C), 61.53 (OCH_2), 68.87 (9-C), 70.54 (8-C), 73.29 (CH_2Ph), 74.70 (CH_2Ph), 75.50 (CH_2Ph), 75.53 (CH_2Ph), 78.52 (6-C), 82.23 (5-C), 83.46 (7-C), 97.56 (4-C), 127.53 (Ar), 127.59 (Ar), 127.72 (Ar), 127.81 (Ar), 127.85 (Ar), 128.22 (Ar), 128.31 (Ar), 128.33 (Ar), 128.38 (Ar), 128.62 (Ar), 137.83 (Ar), 137.92 (Ar), 138.39 (Ar), 138.70 (Ar), 170.83 ($\text{C}=\text{O}$), 173.33 ($\text{C}=\text{O}$); HRMS (FAB) calcd for $\text{C}_{42}\text{H}_{49}\text{NO}_9\text{Na}$ 734.3305, Found: 734.3300.

(3R,5R,8R,9S,10R)-3-(N-Methylacetylamido)-8,9,10-tris(benzyloxy)-7-(benzyloxymethyl)-1,6-dioxaspiro[4.5]decane-2-one (14a**)**

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +56.15^{\circ}$ (c 0.80, CHCl_3); IR (neat): ν 3063.33, 3030.54, 2945.57, 2903.26, 1754.22, 1654.62, 1603.30, 1495.05, 1454.50, 1385.60, 1213.58, 1068.66, 738.85 cm^{-1} ; ^1H NMR (CDCl_3): δ 2.09 (s, 3H, COCH_3), 2.22 (d, 2H, $J = 10.45$ Hz, 4-H), 2.68 (s, 3H, NCH_3), 3.53 (d, 1H, $J = 10.34$ Hz, 10-H), 3.61 (br d, 1H, $J = 11.00$ Hz, 7- CH_2), 3.77 (dd, 1H, $J = 11.00$ Hz, $J = 1.85$ Hz, 7- CH_2), 3.82~3.86 (m, 2H, 8-H and 9-H), 4.05~4.08 (m, 1H, 7-H), 4.47 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.59 (d, 1H, $J = 10.45$ Hz, CH_2Ph), 4.60 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.64 (d, 1H, $J = 12.10$ Hz, CH_2Ph), 4.84 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 4.87 (d, 1H, $J = 11.00$ Hz, CH_2Ph), 4.92 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 5.02 (d, 1H, $J = 11.55$ Hz, CH_2Ph), 5.74 (t, 1H, $J = 10.45$ Hz, 3-H), 7.16~7.18 (m, 2H, ArH), 7.26~7.33 (m, 18H, ArH); ^{13}C NMR (CDCl_3): δ 21.50 (COCH_3), 31.89 (NCH_3), 32.08 (4-C), 52.47 (3-C), 67.80 (7- CH_2), 73.53 (CH_2Ph), 73.66 (7-C), 74.87 (CH_2Ph), 75.65 (CH_2Ph), 75.67 (CH_2Ph), 77.28 (8-C), 82.23 (10-C), 83.46 (9-C), 105.64 (5-C), 127.57 (Ar), 127.68 (Ar), 127.72 (Ar), 127.77 (Ar), 127.88 (Ar), 127.91 (Ar), 128.12 (Ar), 128.35 (Ar), 128.41 (Ar), 128.43 (Ar), 128.52 (Ar), 137.51 (Ar), 137.71 (Ar), 138.03 (Ar), 138.15 (Ar), 171.33 ($\text{C}=\text{O}$), 172.80 ($\text{C}=\text{O}$); HRMS (FAB) calcd for $\text{C}_{40}\text{H}_{43}\text{NO}_8\text{Na}$ 668.2887, Found: 668.2881.

Ethyl 2-[acetyl(methyl)amino]-5,6,7,9-tetra-*O*-benzyl-2,3-dideoxy-*D*-glycero- β -*L*-manno-non-4-ulo-pyranosonate (13b)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = -4.20^{\circ}$ (*c* 1.0, CHCl₃); IR (neat): ν 3258.80, 3063.33, 3030.54, 2926.65, 2898.08, 1729.11, 1653.28, 1615.10, 1494.97, 1454.50, 1398.89, 1368.12, 1219.28, 1069.20, 1009.86, 743.24 cm⁻¹; ¹H NMR (CDCl₃): δ 1.24 (t, 3H, *J* = 7.15 Hz, CH₃), 1.80 (dd, 1H, *J* = 14.57 Hz, *J* = 11.00 Hz, 3-H), 1.91 (s, 3H, COCH₃), 2.62 (dd, 1H, *J* = 14.58 Hz, *J* = 4.85 Hz, 3-H), 2.79 (s, 3H, NCH₃), 3.34 (dd, 1H, *J* = 9.08 Hz, *J* = 6.05 Hz, 9-H), 3.41 (dd, 1H, *J* = 9.35 Hz, *J* = 6.88 Hz, 9-H), 3.74 (d, 1H, *J* = 9.89 Hz, 5-H), 3.93~3.94 (m, 1H, 7-H), 4.00 (td, 1H, *J* = 6.46 Hz, *J* = 1.37 Hz, 8-H), 4.09 (dd, 1H, *J* = 9.63 Hz, *J* = 2.75 Hz, 6-H), 4.11~4.20 (m, 2H, OCH₂), 4.37 (d, 1H, *J* = 11.82 Hz, CH₂Ph), 4.42 (d, 1H, *J* = 12.10 Hz, CH₂Ph), 4.59 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 4.71 (d, 1H, *J* = 11.27 Hz, CH₂Ph), 4.76 (s, 2H, CH₂Ph), 4.94 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 4.98 (d, 1H, *J* = 11.27 Hz, CH₂Ph), 5.33 (dd, 1H, *J* = 11.00 Hz, *J* = 3.85 Hz, 2-H), 7.26~7.38 (m, 20H, ArH); ¹³C NMR (CDCl₃): δ 14.11 (CH₃), 21.48 (COCH₃), 33.21 (NCH₃), 35.03 (3-C), 52.81 (2-C), 61.46 (OCH₂), 69.22 (9-C), 69.37 (8-C), 72.64 (CH₂Ph), 73.23 (CH₂Ph), 74.59 (CH₂Ph), 75.02 (7-C), 75.54 (CH₂Ph), 78.53 (5-C), 80.67 (6-C), 98.02 (4-C), 127.52 (Ar), 127.55 (Ar), 127.57 (Ar), 127.61 (Ar), 127.75 (Ar), 127.81 (Ar), 127.90 (Ar), 128.19 (Ar), 128.20 (Ar), 128.22 (Ar), 128.38 (Ar), 128.77 (Ar), 137.80 (Ar), 138.17 (Ar), 138.57 (Ar), 138.86 (Ar), 170.92 (C=O), 173.30 (C=O); HRMS (FAB) calcd for C₄₂H₄₉NO₉Na 734.3305, Found: 734.3302.

(3*R*,5*S*,8*S*,9*S*,10*R*)-8,9,10-Tris(benzyloxy)-7-(benzyloxymethyl)-3-(methylacetylamido)-1,6-dioxaspiro[4.5]decane-2-one (14b)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = +34.00^{\circ}$ (*c* 0.6, CHCl₃); IR (neat): ν 3063.33, 3030.54, 2936.80, 2988.61, 1758.16, 1653.90, 1606.02, 1495.03, 1454.50, 1381.75, 1210.56, 1039.81, 978.22, 739.57 cm⁻¹; ¹H NMR (CDCl₃): δ 2.08 (s, 3H, COCH₃), 2.21 (dd, 1H, *J* = 12.92 Hz, *J* = 9.34 Hz, 4-H), 2.26 (dd, 1H, *J* = 12.92 Hz, *J* = 10.72 Hz, 4-H), 2.66 (s, 3H, NCH₃), 3.48 (dd, 1H, *J* = 9.08 Hz, *J* = 5.50 Hz, 7-CH₂), 3.59 (dd, 1H, *J* = 9.07 Hz, *J* = 8.25 Hz, 7-CH₂), 3.75~3.80 (m, 2H, 8-H and 9-H), 3.91~3.94 (m, 1H, 7-H), 4.00 (d, 1H, *J* = 9.89 Hz, 10-H), 4.43 (d, 1H, *J* = 11.82 Hz, CH₂Ph), 4.47 (d, 1H, *J* = 11.82 Hz, CH₂Ph), 4.61 (d, 1H, *J* = 11.28 Hz, CH₂Ph), 4.65 (d, 1H, *J* = 11.55 Hz, CH₂Ph), 4.70 (d, 1H, *J* = 11.45 Hz, CH₂Ph), 4.75 (d, 1H, *J* = 11.45 Hz, CH₂Ph), 4.93 (d, 1H, *J* = 11.00 Hz, CH₂Ph), 5.06 (d, 1H, *J* = 11.54 Hz, CH₂Ph), 5.72 (dd, 1H, *J* = 10.73 Hz, *J* = 9.62 Hz, 3-H), 7.27~7.37 (m, 20H, ArH); ¹³C NMR (CDCl₃): δ 21.50 (COCH₃), 31.97 (NCH₃), 32.00 (4-C), 52.46 (3-C), 67.72 (7-CH₂), 72.32 (6-C), 72.57 (CH₂Ph), 73.48 (CH₂Ph), 74.05 (8-C), 74.96 (CH₂Ph), 75.69 (CH₂Ph), 76.58 (10-C), 80.46 (9-C), 106.41 (5-C), 127.59 (Ar), 127.62 (Ar), 127.75 (Ar), 127.78 (Ar), 127.85 (Ar), 127.88 (Ar), 127.94 (Ar), 128.14 (Ar), 128.31 (Ar), 128.43 (Ar), 128.45 (Ar), 128.49 (Ar), 137.64 (Ar), 137.79 (Ar), 137.93 (Ar), 138.40 (Ar), 171.31 (C=O), 173.13 (C=O); HRMS (FAB) calcd for C₄₀H₄₃NO₈Na 668.2887, Found: 668.2885.

Ethyl (2*R*)-2-[acetyl(methyl)amino]-5,6,7,9-tetra-*O*-benzyl-2,3-dideoxy-*D*-glycero- α -*D*-galacto-non-

4-ulopyranosonate (13c)

Colorless syrup, $[\alpha]_{\text{D}}^{25} = -6.58^{\circ}$ (c 1.0, CHCl_3); IR (neat): ν 3280.10, 3063.33, 3030.54, 2918.83, 2890.26, 1736.84, 1653.08, 1621.12, 1494.90, 1454.50, 1381.28, 1212.67, 1143.93, 1075.10, 986.20, 736.86, 698.32 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.25 (t, 3H, $J = 7.15\text{ Hz}$, CH_3), 1.90 (dd, 1H, $J = 14.50\text{ Hz}$, $J = 3.42\text{ Hz}$, 3-H), 1.88 (s, 3H, COCH_3), 2.41 (dd, 1H, $J = 14.50\text{ Hz}$, $J = 11.96\text{ Hz}$, 3-H), 2.74 (s, 3H, NCH_3), 3.49 (br d, 1H, $J = 10.50\text{ Hz}$, 9-H), 3.59 (dd, 1H, $J = 10.74\text{ Hz}$, $J = 4.88\text{ Hz}$, 9-H), 3.69 (d, 1H, $J = 2.44\text{ Hz}$, 5-H), 3.82 (dd, 1H, $J = 9.15\text{ Hz}$, $J = 2.44\text{ Hz}$, 6-H), 3.90 (t, 1H, $J = 9.13\text{ Hz}$, 7-H), 4.11~4.21 (m, 3H, 8-H and OCH_2), 4.54 (d, 1H, $J = 10.98\text{ Hz}$, CH_2Ph), 4.56 (d, 1H, $J = 10.75\text{ Hz}$, CH_2Ph), 4.68~4.74 (m, 3H, CH_2Ph), 4.87 (d, 1H, $J = 11.23\text{ Hz}$, CH_2Ph), 4.99 (d, 1H, $J = 11.48\text{ Hz}$, CH_2Ph), 5.05 (d, 1H, $J = 11.64\text{ Hz}$, CH_2Ph), 5.34 (dd, 1H, $J = 11.96\text{ Hz}$, $J = 3.42\text{ Hz}$, 2-H), 7.17~7.39 (m, 20H, ArH); ^{13}C NMR (CDCl_3): δ 14.33 (CH_3), 21.58 (COCH_3), 33.06 (NCH_3), 35.45 (3-C), 52.42 (2-C), 61.46 (OCH_2), 68.87 (9-C), 69.96 (8-C), 72.80 (CH_2Ph), 73.58 (CH_2Ph), 74.37 (CH_2Ph), 74.74 (CH_2Ph), 75.19 (8-C), 77.59 (5-C), 79.17 (6-C), 97.61 (4-C), 127.42 (Ar), 127.45 (Ar), 127.48 (Ar), 127.51 (Ar), 127.75 (Ar), 127.78 (Ar), 127.81 (Ar), 127.85 (Ar), 128.05 (Ar), 128.11 (Ar), 128.17 (Ar), 128.28 (Ar), 137.90 (Ar), 138.27 (Ar), 138.41 (Ar), 138.49 (Ar), 170.62 ($\text{C}=\text{O}$), 173.85 ($\text{C}=\text{O}$); HRMS (FAB) calcd for $\text{C}_{42}\text{H}_{49}\text{NO}_9\text{Na}$ 734.3305, Found: 734.3308.

Ethyl 2-[acetyl(methyl)amino]-2,3-dideoxy-D-glycero- α -D-gulo-non-4-ulopyranosonate (15)

13a (71.1 mg, 0.1 mmol) was dissolved in 2 mL of methanol. To the solution was added 20 mg of $\text{Pd}(\text{OH})_2/\text{C}$ (20 wt%), and the mixture was stirred vigorously under H_2 atmosphere at rt for 12 h. After the reaction completed, the catalyst was removed by filtration through a Celite pad and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography ($\text{AcOEt} : \text{MeOH} : \text{H}_2\text{O} = 4 : 2 : 1$) to afford 23.1 mg (65.8%) of the debenzylated product (**15**). Colorless amorphous solid, $[\alpha]_{\text{D}}^{25} = +69.11^{\circ}$ (c 1.58, CH_3OH); ^1H NMR (CD_3OD): δ 1.25 (t, 3H, $J = 7.15\text{ Hz}$, CH_3), 2.11 (s 3H, COCH_3), 2.15 (dd, 1H, $J = 14.85\text{ Hz}$, $J = 9.35\text{ Hz}$, 3-H), 2.59 (dd, 1H, $J = 14.85\text{ Hz}$, $J = 4.12\text{ Hz}$, 3-H), 3.03 (s, 3H, NCH_3), 3.08 (d, 1H, $J = 9.35\text{ Hz}$, 5-H), 3.27 (t, 1H, $J = 9.34\text{ Hz}$, 7-H), 3.61~3.76 (m, 4H, 6-H, 8-H and two 9-H), 4.15~4.22 (m, 2H, OCH_2), 5.20 (dd, 1H, $J = 9.34\text{ Hz}$, $J = 3.85\text{ Hz}$, 2-H); ^{13}C NMR (CDCl_3): δ 14.44 (CH_3), 21.86 (COCH_3), 31.88 (NCH_3), 37.16 (3-C), 55.59 (2-C), 62.66 (OCH_2), 62.78 (9-C), 71.62 (7-C), 74.11 (8-C), 75.75 (6-C), 76.15 (5-C), 98.27 (4-C), 172.90 ($\text{C}=\text{O}$), 174.64 ($\text{C}=\text{O}$); HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_9\text{Na}$ 374.1427, Found: 374.1425.

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