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Note

Reaction of D-glycals with azidotrimethylsilane

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Abstract

The treatment of 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol with azidotrimethylsilane by the aid of a catalytic amount of $Yb(OTf)_3$ afforded 2,4,6-tri-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl azide in high yield.

Keywords: Glycosyl azide; Glucal; Azidotrimethylsilane

Glycosyl azides have been used as precursors for the synthesis of glycosyl amines (*N*-glycosides),[1] *N*-glycopeptides and *N*-glycoproteins.[2] Furthermore, they have been utilized as chiral templates for α- and β-amino acid,[3] α-aminophosphonic acid derivatives,[4] and α-aminonitrile synthesis.[5] Therefore, the development of a highly effective and stereoselective synthesis of glycosyl azides is desired.[6]

Several methods have been reported for the formation of the glycosyl azide bond. These can be classified in two categories: One method is by nucleophilic substitution reactions, and the other is by the addition reaction to the double bond in glycals. The former methods are based on the reaction of glycosyl donors with metal azides such as sodium or silver azide or azidotrimethylsilane. As glycosyl donors, glycosyl halides are often used for metal azides[7] and 1-*O*-acyl sugars or alkyl thio-glycosides for azidotrimethylsilane.[8] Lewis acids such as $BF_3{\cdot}OEt_2$, $SnCl_4$–$AgClO_4$, and $Yb(OTf)_3$ are often used as the promoters for the reaction of 1-*O*-acyl sugars to generate the oxocarbenium species that should be captured by azidotrimethylsilane. 1,1,3,3,-Tetramethylguanidinium azide has also been used for the reaction of glycosyl halides.[9,10] The alternative methods include the addition of phenylselenyl azide to protected glycals. For examples, Giuliano et al., reported the addition reaction of phenylselenyl azide to protected glycals which afforded 2-phenylselenoglycosyl azides.[11]

We recently reported the reaction of protected and unprotected D-glycal with cyanotrimethylsilane[12] and aromatic compounds,[13] which led to the facile synthesis of 2,3-unsaturated glycosyl cyanides and aryl glycosides, respectively. During the course of this study, we have focused in the reaction of some D-glycals with azidotrimethylsilane. Herein, we would like to report the reaction of azidotrimethylsilane with D-glycals.

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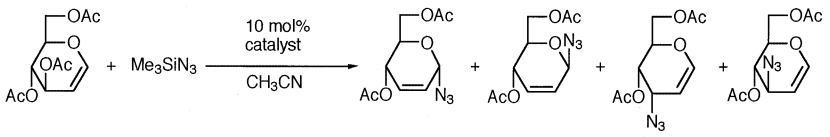
In 1978, Heyns and Hohlweg reported the reaction of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) with sodium azide in the presence of 3 equiv of $BF_3{\cdot}OEt_2$. They also reported sigmatropic rearrangement of the products between glycosyl azides and 3-azido-3-deoxy sugars.[14] However, from the viewpoint of the preparative utility of glycosyl azides, this rearrangement is not desirable. We found that when we used 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol, the above rearrangement was suppressed. The details of these studies will be discussed.

We first examined the reaction of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) with azidotrimethylsilane in the presence of a catalytic amount (10 mol%) of Lewis acids such as Me_3SiOTf and $Yb(OTf)_3$. The reactions were carried out in acetonitrile at room temperature using 10 mol% of Lewis acid and 1.2 equiv of azidotrimethylsilane per **1**. The results that were obtained are summarized in Table 1. The products of the reaction were α- and β-glycosyl azides (**2a** and **2b**) and α- and β-3-azido-3-deoxy sugars (**3a** and **3b**). The ratio of the products, α-1-N_3 (**2a**):β-1-N_3 (**2b**):α-3-N_3 (**3a**):β-3-N_3 (**3b**) was changed depending on the reaction time, which suggests that the ratio obtained was a thermodynamic effect. The stereospecific rearrangement between glycosyl azides and 3-azido-3-deoxy sugars was observed. The stereospecificity and equilibrium ratio (**2a**:**2b**:**3a**:**3b** = 32:3:55:10) was confirmed by following the development of the products of the reaction by ^{1}H NMR spectroscopy. In order to suppress the rearrangement between the glycosyl azide and 3-azido-3-deoxy sugar, we undertook the use of 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**4**) as a substrate. A variety of Lewis acids including rare-earth metal triflates (10 mol% per substrate) were employed in the reaction of **4** with azidotrimethylsilane (Table 2). In most cases we examined, 2,4,6-tri-*O*-acetyl-2,3-dideoxy-D-hex-2-enopyranosyl azide (Ferrier type-product **5**[15]) was obtained in high yield as a mixture of α (**5a**) and β anomers (**5b**), in which **5a** was produced predominantly (α:β = 67:33–83:17). The formation of the rearranged product, the 3-azido-3-deoxy sugar, was not observed. On the other hand, in the case of trimethylsilyl triflate (Me_3SiOTf) and $Sc(OTf)_3$, not only Ferrier type product **5**, but also 3,4-dideoxy-3-eno-2-ulopyranosyl azide **6** was obtained in almost the same amounts.

Then we examined the reaction of disaccharide, 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**7**) with azidotrimethylsilane (Table 3). Also, in this case, rearrangement between the glycosyl azide and 3-azido-3-deoxy sugar was not observed. In this disaccharide reaction, the α-selectivity was increased in up to α:β = 86:14.

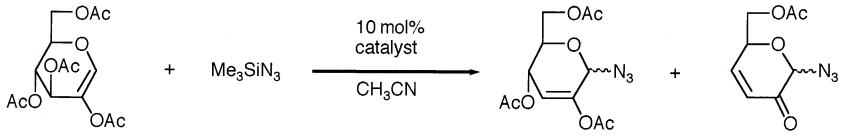
Table 1
Reaction of 3,4,6-tri-*O*-acetyl-D-glucal with azidotrimethylsilane [a]



Entry	Catalyst	Conditions		Product		
		T (°C)	*t* (h)	% yield (**2a**:**2b**:**3a**:**3b**) [b]	α:β [c]	1-N_3:3-N_3 [d]
1	Me_3SiOTf	20	1	89 (37:5:40:18)	77:23	42:58
2	Me_3SiOTf	23	21	90 (24:7:41:28)	65:35	31:69
3	$Yb(OTf)_3$	21	1	92 (31:5:43:21)	74:26	36:74

[a] All reactions were carried out in CH_3CN using 10 mol% of catalyst and 1.2 equiv of azidotrimethylsilane per **1**.
[b] Isolated yield after silica-gel column chromatography. The ratio was determined by ^{1}H NMR analyses.
[c] α:β = (**2a** + **3a**):(**2b** + **3b**).
[d] 1-N_3:3-N_3 = (**2a** + **2b**):(**3a** + **3b**).

Table 2
Reaction of 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**4**) with azidotrimethylsilane [a]

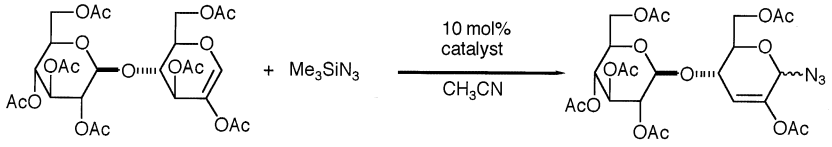


4 5 6

Entry	Catalyst	Conditions		% yield of product [b]	
		T (°C)	*t* (h)	**5** (α:β) [c]	**6** (α:β) [c]
1	Me_3SiOTf	16	20	9 (83:17)	66 (64:36)
2	$BF_3{\cdot}OEt_2$	27	25	76 (67:33)	2
3	$Yb(OTf)_3$	26	33	95 (69:31)	
4	$Sm(OTf)_3$	26	62	71 (69:31)	3
5	$Sc(OTf)_3$	24	64	51 (83:17)	34 (58:42)
6	$Y(OTf)_3$	24	54	61 (67:33) [d]	

[a] All reactions were carried out in CH_3CN using 10 mol% of catalyst and 1.2 equiv of azidotrimethylsilane per **4**.
[b] Isolated yield after silica-gel column chromatography.
[c] Determined by ^1H NMR analyses.
[d] Starting material **4** was recovered in 37% yield.

Table 3
Reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**7**) with azidotrimethylsilane [a]



7 8

Entry	Catalyst	Conditions		Product [b]	
		T (°C)	*t* (h)	% yield	α:β [c]
1	Me_3SiOTf	26	2.5	100	86:14
2	$Yb(OTf)_3$	26	69	98	76:24

[a] All reactions were carried out in CH_3CN using 10 mol% of catalyst and 1.2 equiv of azidotrimethylsilane per **7**.
[b] Isolated yield after silica-gel column chromatography.
[c] Determined by ^1H NMR analyses.

In conclusion, the reaction of glucals possessing a 2-acetoxy group with azidotrimethylsilane with the aid of a catalytic amount of $Yb(OTf)_3$ provided Ferrier type 2,3-unsaturated glycopyranosyl azides that led to a new approach to the synthesis of glycosyl azides. These compounds do not undergo rearrangement into 3-azido-hex-1-enopyranosose, which is quite in contrast with the case of 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl azide.

1. Experimental

General methods.—All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400S (400 and 100.6 MHz, respectively) using Me_4Si as the internal standard in $CDCl_3$. IR spectra were measured on a Nicolet Impact 410. Optical rotations were measured by a Sepa-300 (Horiba) in solution in a 1-dm cell. Elemental analyses were performed on a Perkin–Elmer

2400II CHNS/O. Preparative-column chromatography was carried out on Fuji–Davison BW-820 or Daisogel IR-60-W media (40–63 μm). Thin-layer chromatography (TLC) was carried out on foil plates, Silica Gel 60 F_{254} (E. Merck; layer thickness 0.2 mm). Acetonitrile was distilled from P_4O_{10}.

General procedure (Entry 3 in Table 2).—In a dry Schlenk tube equipped with a magnetic stirring bar were placed 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**4**) (158.8 mg, 0.48 mmol) and CH_3CN (1.5 mL) under an Ar atmosphere. After the addition of azidotrimethylsilane (0.08 mL, 0.58 mmol) and $Yb(OTf)_3$ (29.8 mg, 0.05 mmol), the mixture was stirred for 33 h at 26 °C. After confirmation of the completion of the reaction by TLC, the mixture was poured into satd aq $NaHCO_3$ (20 mL). Extractive workup with EtOAc, followed by silica-gel column chromatography, afforded 2,4,6-tri-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl azide (**5**) (143.4 mg, 95%) as a pale-yellow oil as a mixture of α isomer **5a** and β isomer **5b** (**5a**:**5b** = 69:31).

2,4,6-Tri-O-*acetyl-3-deoxy*-α-D-erythro-*hex-2-enopyranosyl azide* (**5a**).—R_f 0.39 (3:1 hexane–EtOAc); $[\alpha]_D = +168.9°$ (*c* 1.0, $CHCl_3$); IR (neat): ν_{max} (cm^{-1}) 2960, 2110 (N_3), 1745, 1695, 1437, 1375, 1240, 1165, 1100, 1050; ^1H NMR ($CDCl_3$): δ 2.10 (s, 3 H, $COCH_3$), 2.12 (s, 3 H, $COCH_3$), 2.20 (s, 3 H, $COCH_3$), 4.16 (dt, 1 H, $J_{5,4}$ 9.4, $J_{5,6}$ 4.1 Hz, H-5), 4.26 (d, 2 H, $J_{6,5}$ 4.1 Hz, H-6), 5.46 (dd, 1 H, $J_{4,5}$ 9.4, $J_{4,3}$ 2.2 Hz, H-4), 5.57 (s, 1 H, H-1), 5.81 (d, 1 H, $J_{3,4}$ 2.2 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ 20.7, 20.9, 21.0 ($COCH_3 \times 3$), 62.2 (C-6), 64.8 (C-4), 69.2 (C-5), 83.9 (C-1), 115.8 (C-3), 144.9 (C-2), 167.9, 170.0, 170.7 ($COCH_3 \times 3$). Anal. Calcd for $C_{12}H_{15}N_3O_7$: C, 46.01; H, 4.83; N, 13.41. Found: C, 45.96; H, 4.90; N, 13.48.

2,4,6-Tri-O-*acetyl-2,3-dideoxy*-β-D-erythro-*hex-2-enopyranosyl azide* (**5b**).—R_f 0.36 (3:1 hexane–EtOAc); $[\alpha]_D = +97.7°$ (*c* 1.0, $CHCl_3$); IR (neat): ν_{max} (cm^{-1}) 2965, 2115 (N_3), 1745, 1690, 1435, 1370, 1235, 1200, 1170, 1050; ^1H NMR ($CDCl_3$): δ 2.09 (s, 3 H, $COCH_3$), 2.12 (s, 3 H, $COCH_3$), 2.20 (s, 3 H, $COCH_3$), 4.12 (ddd, 1 H, $J_{5,4}$ 5.7, $J_{5,6}$ 6.3, $J_{5,6'}$ 4.6 Hz, H-5), 4.26 (dd, 1 H, $J_{6,5}$ 6.3, $J_{6,6'}$ 12.0 Hz, H-6), 4.31 (dd, 1 H, $J_{6',5}$ 4.6, $J_{6',6}$ 12.0 Hz, H-6′), 5.37 (ddd, 1 H, $J_{4,5}$ 5.7, $J_{4,3}$ 3.8, $J_{4,1}$ 1.4 Hz, H-4), 5.54 (d, 1 H, $J_{1,3}$ 1.3, $J_{1,4}$ 1.4 Hz, H-1), 5.84 (dd, 1 H, $J_{3,4}$ 3.8, $J_{3,1}$ 1.3 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ 20.7, 20.8, 20.9 ($COCH_3 \times 3$), 62.5 (C-6), 64.8 (C-4), 73.7 (C-5), 83.3 (C-1), 114.4 (C-3), 146.1 (C-2), 168.0, 170.0, 170.6 ($COCH_3 \times 3$). Anal. Calcd for $C_{12}H_{15}N_3O_7$: C, 46.01; H, 4.83; N, 13.41. Found: C, 46.01; H, 4.87; N, 13.29.

6-O-*Acetyl-3,4-dideoxy*-α-D-glycero-*hex-3-en-2-ulopyranosyl azide* (**6a**).—R_f 0.68 (2:1 hexane–EtOAc); $[\alpha]_D = -13.0°$ (*c* 1.0, $CHCl_3$); IR (neat): ν_{max} (cm^{-1}) 2960, 2116 (N_3), 1745, 1695, 1385, 1370, 1230, 1165, 1130, 1095, 1045; ^1H NMR ($CDCl_3$): δ 2.12 (s, 3 H, $COCH_3$), 4.29 (dd, 1 H, $J_{6,5}$ 4.3, $J_{6,6'}$ 11.8 Hz, H-6), 4.38 (dd, 1 H, $J_{6',5}$ 5.5, $J_{6',6}$ 11.8 Hz, H-6′), 4.90 (dddd, 1 H, $J_{5,6}$ 4.3, $J_{5,6'}$ 5.5, $J_{5,3}$ 2.4, $J_{5,4}$ 1.7 Hz, H-5), 5.41 (s, 1 H, H-1), 6.21 (dd, 1 H, $J_{3,4}$ 10.7, $J_{3,5}$ 2.4, H-3), 7.01 (d, 1 H, $J_{4,3}$ 10.7, $J_{4,5}$ 1.7 Hz, H-4); ^{13}C NMR ($CDCl_3$): δ 20.5, ($COCH_3 \times 3$), 64.0 (C-6), 68.0 (C-5), 87.3 (C-1), 125.7 (C-3), 147.3 (C-4), 170.4 ($COCH_3$). 186.5 (C-2). Anal. Calcd for $C_8H_9N_3O_4$: C, 45.50; H, 4.30; N, 19.90. Found: C, 45.62; H, 4.51; N, 19.59.

6-O-*Acetyl-3,4-dideoxy*-β-D-glycero-*hex-3-en-2-ulopyranosyl azide* (**6b**).—R_f 0.32 (2:1 hexane–EtOAc); $[\alpha]_D = -121.8°$ (*c* 1.0, $CHCl_3$); IR (neat): ν_{max} (cm^{-1}) 2955, 2115 (N_3), 1740, 1705, 1445, 1370, 1230, 1085, 1045; ^1H NMR ($CDCl_3$): δ 2.13 (s, 3 H, $COCH_3$), 4.34 (dd, 1 H, $J_{6,5}$ 5.0, $J_{6,6'}$ 11.7 Hz, H-6), 4.41 (dd, 1 H, $J_{6',5}$ 6.4, $J_{6',6}$ 11.7 Hz, H-6′), 4.80 (dddd, 1 H, $J_{5,6}$ 5.0, $J_{5,6'}$ 6.4, $J_{5,3}$ 2.4, $J_{5,4}$ 2.5 Hz, H-5), 5.24 (s, 1 H, H-1), 6.27 (dd, 1 H, $J_{3,4}$ 10.6, $J_{3,5}$ 2.4 Hz, H-3), 7.01 (d, 1 H, $J_{4,3}$ 10.6, $J_{4,5}$ 2.5 Hz, H-4); ^{13}C NMR ($CDCl_3$): δ 20.5, ($COCH_3$), 64.6 (C-6), 72.3 (C-5), 87.3 (C-1), 126.7 (C-3), 147.2 (C-4), 170.6 ($COCH_3 \times 3$), 187.4 (C-2). Anal. Calcd for $C_8H_9N_3O_4$: C, 45.50; H, 4.30; N, 19.90. Found: C, 45.61; H, 4.38; N, 19.55.

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl-(1→4)-2,6-di*-O-*acetyl-3-deoxy*-α-D-glycero-*hex-2-enopyranosyl azide* (**8a**).—R_f 0.42 (1:1 hexane–EtOAc); mp 101.9 °C; $[\alpha]_D = +63.4°$ (*c* 0.5, $CHCl_3$); IR (neat): ν_{max} (KBr) (cm^{-1}) 2960, 2110 (N_3), 1755, 1430, 1370, 1235, 1175, 1095, 1065, 1045, 1015; ^1H NMR ($CDCl_3$): δ 2.00, 2.03, 2.06, 2.09, 2.12, 2.21 (each s, 3 H,

$COCH_3 \times 6$), 3.72 (ddd, 1 H, $J_{5',4'}$ 9.9, $J_{5',6a'}$ 5.0, $J_{5',6b'}$ 2.8 Hz, H-5′), 4.05 (ddd, 1 H, $J_{5,4}$ 9.3, $J_{5,6a'}$ 2.0, $J_{5,6b}$ 5.5 Hz, H-5), 4.17 (dd, 1 H, $J_{6a',6b'}$ 12.3, $J_{6a',5'}$ 2.8 Hz, H-6a′), 4.19 (dd, 1 H, $J_{6b,6a}$ 12.0, $J_{6b,5}$ 5.5 Hz, H-6b), 4.22 (dd, 1 H, $J_{6b',6a'}$ 12.3, $J_{6b',5'}$ 5.0 Hz, H-6b′), 4.34 (dd, 1 H, $J_{6a,6b}$ 12.0, $J_{6a,5}$ 2.0 Hz, H-6a), 4.35 (dd, 1 H, $J_{4,5}$ 9.3, $J_{4,3}$ 1.8 Hz, H-4), 4.64 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.98 (dd, 1 H, $J_{2',3'}$ 9.6, $J_{2',1'}$ 8.0 Hz, H-2′), 5.05 (dd, 1 H, $J_{4',5'}$ 9.9, $J_{4',3'}$ 9.5 Hz, H-4′), 5.20 (dd, 1 H, $J_{3',2'}$ 9.6, $J_{3',4'}$ 9.5 Hz, H-3′), 5.52 (s, 1 H, H-1), 5.94 (d, 1 H, $J_{3,4}$ 1.8 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ 20.3, 20.4, 20.5, 20.6 ($COCH_3 \times 6$), 61.7 (C-6′), 61.9 (C-6), 68.0 (C-4′), 69.4 (C-5), 71.0 (C-2′), 71.7 (C-5′), 72.4 (C-3′), 72.5 (C-4), 83.5 (C-1), 101.2 (C-1′), 118 (C-3), 143.7 (C-2), 168.0, 169.0, 169.1, 169.9, 170.3 ($COCH_3 \times 6$). Anal. Calcd for $C_{24}H_{31}N_3O_{15}$: C, 47.92; H, 5.19; N, 6.99. Found: C, 48.20; H, 5.17; N, 6.94.

2′,3′,4′,6′-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1→4)-2,6-di*-O-*acetyl-3-deoxy-β*-D-glycero-*hex-2-enopyranosyl azide* (**8b**).—R_f 0.47 (1:1 hexane–EtOAc); mp 112.0 °C; $[\alpha]_D = +57.2°$ (*c* 1.0, $CHCl_3$); IR (neat): ν_{max} (cm^{-1}) 2965, 2110 (N_3), 1760, 1695, 1435, 1370, 1305, 1255, 1210, 1175, 1140, 1090, 1050, 1030, 1015; ^{1}H NMR ($CDCl_3$): δ 2.00, 2.03, 2.06, 2.10, 2.12, 2.20 (each s, 3 H, $COCH_3$), 3.72 (ddd, 1 H, $J_{5',4'}$ 9.9, $J_{5',6a'}$ 5.3, $J_{5',6b'}$ 2.6 Hz, H-5′), 3.94 (ddd, 1 H, $J_{5,4}$ 8.0, $J_{5,6a'}$ 6.1, $J_{5,6b}$ 2.6 Hz, H-5), 4.13 (dd, 1 H, $J_{6a,6b}$ 12.0, $J_{6a,5}$ 6.1 Hz, H-6a), 4.17 (dd, 1 H, $J_{6a',6b'}$ 12.2, $J_{6a',5'}$ 2.6 Hz, H-6a′), 4.23 (dd, 1 H, $J_{6b',6a'}$ 12.2, $J_{6b',5'}$ 5.3 Hz, H-6b′), 4.33 (ddd, 1 H, $J_{4,5}$ 8.0, $J_{4,3}$ 2.4 Hz, $J_{4,1}$ 1.9 Hz, H-4), 4.37 (dd, 1 H, $J_{6b,6a}$ 12.0, $J_{6b,5}$ 2.6 Hz, H-6b), 4.64 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.97 (dd, 1 H, $J_{2',3'}$ 9.6, $J_{2',1'}$ 8.0 Hz, H-2′), 5.05 (dd, 1 H, $J_{4',5'}$ 9.9, $J_{4',3'}$ 9.6 Hz, H-4′), 5.20 (dd, 1 H, $J_{3',2'}$ 9.6, $J_{3',4'}$ 9.5 Hz, H-3′), 5.89 (dd, 1 H, $J_{1,4}$ 1.9, $J_{1,3}$ 1.4 Hz, H-1), 5.96 (dd, 1 H, $J_{3,4}$ 2.4, $J_{3,1}$ 1.4 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ 20.3, 20.4, 20.5, 20.6, 20.7 ($COCH_3 \times 6$), 61.9 (C-6′), 62.4 (C-6), 68.3 (C-4′), 71.2 (C-2′), 72.0 (C-5′), 72.6 (C-3′), 74.7 (C-5), 83.9 (C-1), 101.5 (C-1′), 118.2 (C-3), 144.7 (C-2), 168.1, 169.3, 169.4, 170.2, 170.6 ($COCH_3 \times 6$). Anal. Calcd for $C_{24}H_{31}N_3O_{15}$: C, 47.92; H, 5.19; N, 6.99. Found: C, 48.16; H, 5.26; N, 7.01.

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