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Glycosyl 2-Pyridinecarboxylate as an Effective Glycosyl Donor: Glycosidation of Mannose, 2-Azidosugar, and 2-Deoxysugar into Disaccharides

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Glycosylation reactions using a glycosyl 2-pyridinecarboxylate as a glycosyl donor were performed. Glycosyl 2-pyridinecarboxylate was designed based on a variation of the Remote Activation Concept and is activated through bidentate coordination to mild Lewis acids such as copper triflate and tin triflate. This method was effective for the glycosidation of not only glucose, but several other sugars such as the mannose-type, 2-azidosugar-type, and 2-deoxysugar-type. Various disaccharides were obtained in excellent yield by this reaction.

Key words glycosylation; glycosyl 2-pyridinecarboxylate; glycosyl donor; disaccharide; copper triflate; tin triflate

The biologically important role of oligosaccharides has been clarified, and their synthesis is an important theme in synthetic organic chemistry. Despite the fact that a number of glycosylation methods have been developed,[1] it is still very difficult to form a glycoside bond stereoselectively and in high yield. For example, 2-deoxyglycosides are very prone to acid hydrolysis due to the lack of an electron-withdrawing C2-substituent, and efficient glycosidation of a 2-deoxysugar is therefore difficult. There are few methods to provide α- or β-mannosides stereoselectively without modifying the substrate. Previously, we reported a glycosylation method using glucopyranosyl 2-pyridinecarboxylate (A) as a novel glycosyl donor (Chart 1).[2] This glycosylation proceeded smoothly with copper(II) triflate ($Cu(OTf)_2$) or tin(II) triflate ($Sn(OTf)_2$) to give α-glucosides or β-glucosides (D), respectively. Other activators such as boron trifluoride etherate and trimethylsilyl triflate were ineffective. It was also found that the isomeric glycosyl 4-pyridinecarboxylate was unreactive when treated with $Cu(OTf)_2$ and a glycosyl acceptor. These results clearly suggest that the glycosyl 2-pyridinecarboxylate is activated through bidentate coordination to a Lewis acid (B) resulting in generation of a reactive oxonium species (C). Initial activation thus takes place at a site remote from the anomeric carbon, and we proposed that the present methodology was based on the remote activation concept.[3] Characteristic features of our methodology are as follows: (1) the glycosyl donor can be prepared very easily and is stable, (2) the activators required are non-toxic, and other additives, such as silver perchlorate, are not necessary. This paper describes an extension of this methodology for the glycosidation of mannose, 2-azidosugar, and 2-deoxysugar derivatives.

We prepared several glycosyl 2-pyridinecarboxylates according to our reported procedure.[2] Namely, esterification of the anomeric hydroxyl group of 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose[4] with commercially available picolinoyl chloride in the presence of triethylamine gave mannosyl 2-pyridinecarboxylate **1** in 96% yield as a mixture (*ca.* 9 : 1) of α- and β-anomers (Chart 2). Analogously, 2-azidoglucopyranoside **2** (79%), tri-*O*-benzyl-2-deoxy-*arabino*-hexopyranoside **3** (85%), and tri-*O*-acetyl-2-

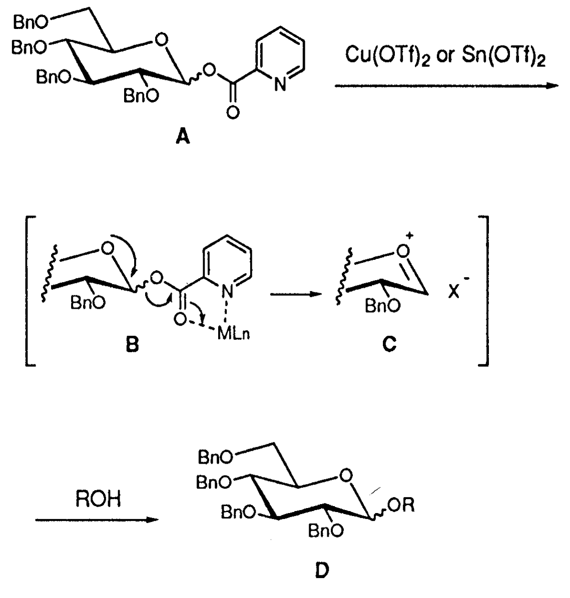

Chart 1

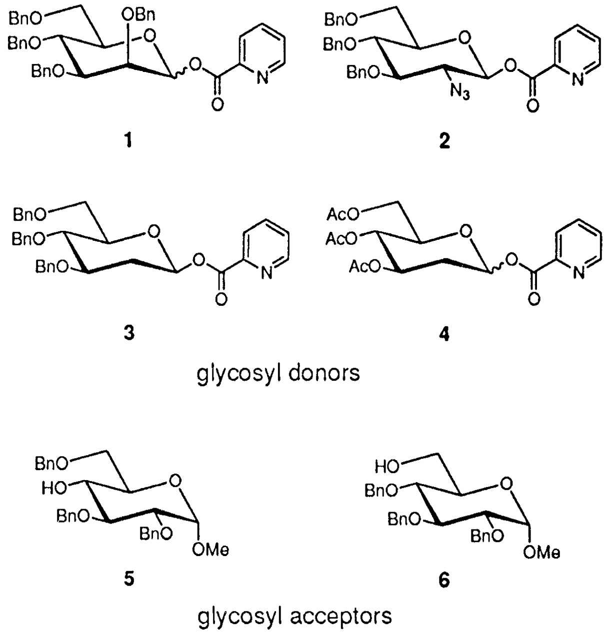

Chart 2

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Table 1. Glycosidation of Glycosyl 2-Pyridinecarboxylates **1**—**4** with **5** and **6**

Run	Donor	Acceptor (1.1 eq)	Activator (2.4 eq)	Solvent	Temp. (°C)	Product[a]	Yield[b] (%)	α:β
1	**1**	**5**	$Cu(OTf)_2$	CH_2Cl_2	−50 to rt	**7**	83	91:9[c]
2	**1**	**5**	$Sn(OTf)_2$	CH_2Cl_2	−70 to rt	**7**	94	90:10[c]
3	**1**	**6**	$Cu(OTf)_2$	CH_2Cl_2	−50 to rt	**8**	93	59:41[d]
4	**1**	**6**	$Sn(OTf)_2$	CH_2Cl_2	−70 to rt	**8**	90	53:47[d]
5	**2**	**5**	$Cu(OTf)_2$	THF/CH_2Cl_2 (6/1)	−30 to rt	**9**	71	78:22[d]
6	**2**	**5**	$Sn(OTf)_2$	CH_3CN	−30 to rt	**9**	76	30:70[d]
7	**2**	**6**	$Cu(OTf)_2$	THF/CH_2Cl_2 (6/1)	−30 to rt	**10**	89	50:50[d]
8	**2**	**6**	$Sn(OTf)_2$	CH_3CN	−30 to rt	**10**	62	17:83[d]
9	**3**	**5**	$Cu(OTf)_2$	CH_2Cl_2	−78 to rt	**11**	48	92:8[c]
10	**3**	**5**	$Sn(OTf)_2$	CH_3CN	−30 to rt	**11**	81	92:8[c]
11	**3**	**6**	$Cu(OTf)_2$	CH_2Cl_2	−78 to −40	**12**	57	47:53[c]
12	**3**	**6**	$Sn(OTf)_2$	CH_3CN	−30 to rt	**12**	99	80:20[c]
13	**4**	**5**	$Cu(OTf)_2$	CH_2Cl_2	−78 to rt	**13**	68	91:9[c]
14	**4**	**5**	$Sn(OTf)_2$	CH_2Cl_2	−78 to rt	**13**	64	90:10[c]
15	**4**	**6**	$Cu(OTf)_2$	CH_2Cl_2	−78 to rt	**14**	87	64:36[c]
16	**4**	**6**	$Sn(OTf)_2$	CH_2Cl_2	−78 to rt	**14**	79	59:41[c]

a) Products 7, 8, 11—14 have been previously reported, see ref. 5—7), and references therein. *b*) Isolated yields. *c*) Determined by individual isomer separation. *d*) Determined by ^{1}H-NMR (270 MHz) analysis.

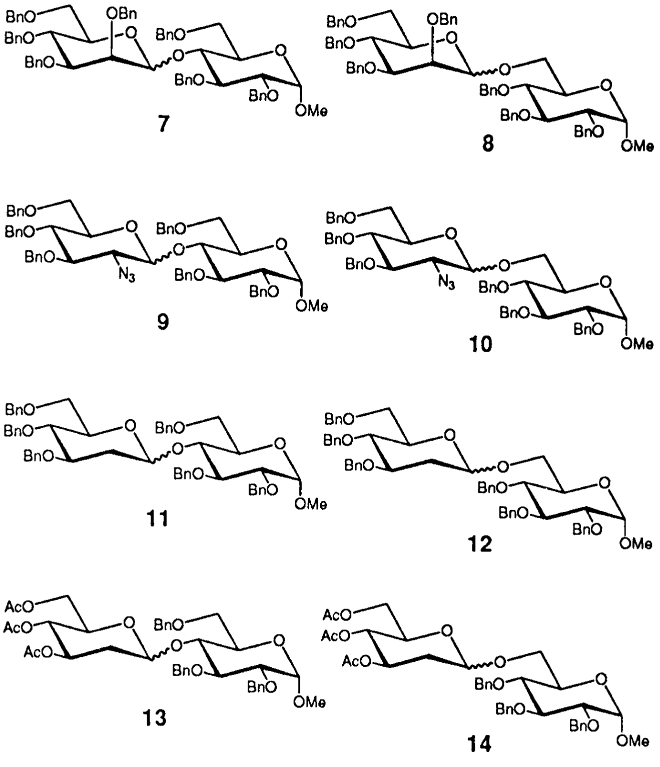

Chart 3

deoxy-*arabino*-hexopyranoside **4** (84%) were prepared.[4] Tri-*O*-acetyl-2-deoxysugar derivative **4** was obtained as an anomeric mixture (α:β=*ca.* 1:2), but α-anomers of the 2-azidosugar-type and tri-*O*-benzyl-2-deoxysugar-type could not be detected. It was difficult to separate the α- and β-anomers (**1**α and **1**β; **4**α and **4**β), and the anomeric mixture was used for glycosidation without separation. We have previously observed that α- and β-glucopyranosyl 2-pyridinecarboxylate (A) showed almost the same selectivity and reactivity in the $Cu(OTf)_2$- and $Sn(OTf)_2$-mediated glycosidation.[2]

The glycosylation reaction using these donors and two acceptors, the 4-*O*- and 6-*O*-unprotected glucose derivatives **5** and **6**, was then examined. The activators we used for these studies were $Cu(OTf)_2$ and $Sn(OTf)_2$, since these Lewis acids were the most successful in activating glycosyl 2-pyridinecarboxylate. We investigated various solvent systems, and representative results are shown in Table 1. All reactions were carried out in the presence of molecular sieves (3A or 4A depending on the solvent used) in order to prevent competitive hydrolysis caused by a trace amount of water present in the reaction mixture. It was found that the glycosidation reaction proceeded above −30 °C, and that isomerization of the resultant glycosides was not observed in the present reaction. Therefore, the reaction mixture was gradually warmed to room temperature for convenience.

As expected, mannose-type **1** reacted smoothly with acceptors **5** and **6** to give disaccharides **7** and **8**[5] in high yield (runs 1 to 4). A highly α-selective glycosidation of **1** with secondary alcohol sugar **5** was observed when the reaction was carried out in dichloromethane with $Cu(OTf)_2$ (run 1). Our previous experiments revealed that the stereoselectivity with $Sn(OTf)_2$ differed from that with $Cu(OTf)_2$, but similar selectivity was observed in this case (run 2). For the mannose-type donor, primary alcohol sugar **6** was a much less stereoselective acceptor (runs 3, 4). In all reactions using **1**, β-selectivity was not observed.

The stereoselectivities of glycosylation with 2-azido-sugar-type **2** were reminiscent of the results with the glucose derivative (A). The isolated chemical yields of **9** and **10** were fairly high, considering the unstability of an azido group (runs 5 to 8). α-Selectivity was obtained with $Cu(OTf)_2$ in tetrahydrofuran (THF)-dichloromethane (run 5) and β-selectivity was obtained with $Sn(OTf)_2$ in acetonitrile (runs 6, 8). α-Glycosides and β-glycosides could be selectively obtained from the same glycosyl donor by proper choice of the metal salt and solvent. Again, α-selectivity with $Cu(OTf)_2$ decreased in the sterically less hindered acceptor **6**, albeit the chemical yield was slightly higher (run 7).

We then turned out attention to glycosylation with one of the most challenging substrates, a 2-deoxysugar. The glycosidation of tri-*O*-benzyl-2-deoxysugar-type **3** with $Cu(OTf)_2$ was less efficient than the reactions of the other substrates (runs 9, 11). By-product in these reactions was a hydrolyzed 2-deoxypyranose. Fortunately, we found that **3** reacted with **5** and **6** in acetonitrile in the presence of $Sn(OTf)_2$ to provide **11** and **12**[6] in high yield as well as good α-selectivity (runs 10, 12). The glycosidation of tri-*O*-acetyl-2-deoxysugar-type **4** also proceeded to give disaccharides **13** and **14**[7] (runs 13 to 16). In this case, yields and stereoselectivities were not influenced by the kind of Lewis acid used.

In summary, we have demonstrated that glycosyl 2-pyridinecarboxylate can serve as a useful glycosyl donor for the glycosidation of various sugars such as the mannose-type, 2-azidosugar-type, and 2-deoxysugar-type. The stability of all the glycosyl 2-pyridinecarboxylates we prepared is noteworthy. This method can potentially be applied to the synthesis of other oligosaccharides and glycosylated biologically interesting compounds.

Experimental

Optical rotations were measured with a JASCO DIP-360 digital polarimeter. Infrared (IR) spectra were recorded on a Horiba FT-210 spectrometer. ^{1}H-NMR spectra were measured with a JEOL JNM-EX 270 (270 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane, using tetramethylsilane ($\delta=0$) as an internal standard. ^{13}C-NMR spectra were measured with a JEOL JNM-EX 270 (68 MHz) spectrometer and are reported in ppm using the solvent resonance as an internal standard (77.0 for $CDCl_3$). Mass spectra were taken with a JEOL JMS-SX102A mass spectrometer. Unless otherwise noted, all experiments were carried out under an atmosphere of dry argon using anhydrous solvents. For thin-layer chromatographic (TLC) analyses, Merck precoated TLC plates (Silica gel 60 F254, 0.25 mm, Art 5715) were used.

2,3,4,6-Tetra-2*O*-benzyl-D-mannopyranosyl 2-Pyridinecarboxylate (1) To a cold (0 °C) stirred solution of picolinoyl chloride hydrochloride (1.75 g, 9.84 mmol) and triethylamine (2.49 g, 24.6 mmol) in CH_2Cl_2 (50 ml) was added a solution of 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose[4a] (2.66 g, 4.92 mmol) in CH_2Cl_2 (10 ml). After being stirred at room temperature for 15 h, the reaction was quenched with MeOH (5 ml), and the mixture was diluted with EtOAc (300 ml). The whole was washed with saturated aqueous $NaHCO_3$ (100 ml) and brine (100 ml). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1 : 3) to give 3.04 g (96%) of an inseparable anomeric mixture ($\alpha:\beta=$ *ca.* 9 : 1) of **1** as a colorless oil: IR (neat) 3030, 2868, 1740, 1585, 1497, 1454 cm^{-1}; ^{1}H-NMR ($CDCl_3$) for major α-isomer δ 3.67—3.81 (m, 4 H), 4.06 (t, 1H, $J=9.1$ Hz, H-4), 4.12 (dd, 1H, $J=1.0$, 3.0 Hz, H-2), 4.53 (d, 1H, $J=12.2$ Hz, $\mathrm{C\underline{H}HPh}$), 4.57 (d, 1H, $J=10.9$ Hz, $\mathrm{C\underline{H}HPh}$), 4.60 (d, 1H, $J=11.9$ Hz, $\mathrm{C\underline{H}HPh}$), 4.63 (d, 1H, $J=12.2$ Hz, $\mathrm{CH\underline{H}Ph}$), 4.66 (d, 1H, $J=11.9$ Hz, $\mathrm{CH\underline{H}Ph}$), 4.88 (d, 1H, $J=10.9$ Hz, $\mathrm{CH\underline{H}Ph}$), 4.94 (s, 2H, $\mathrm{C\underline{H}_2Ph}$), 5.95 (d, 1H, $J=1.0$ Hz, H-1), 7.17—7.46 (m, 20H, $\mathrm{CH_2\underline{Ph}}\times 4$), 7.47 (ddd, 1H, $J=1.0$, 4.6, 7.6 Hz, H-5 of Py), 7.76 (ddd, 1H, $J=1.7$, 7.6, 7.9 Hz, H-4 of Py), 8.03 (td, 1H, $J=1.0$, 7.9 Hz, H-3 of Py), 8.79 (ddd, 1H, $J=1.0$, 1.7, 4.6 Hz, H-6 of Py). HR-MS (FAB) Calcd for $C_{40}H_{40}NO_7$ $(M^+ + H)$ *m/z* 646.2805, Found 646.2786.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl 2-Pyridinecarboxylate (2) Analogously, 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose[4b] (1.98 g, 4.16 mmol) was converted to 1.90 g (79%) of **2**. Compound **2** was obtained as a colorless oil: $[\alpha]_D^{25}$ $-52.6°$ ($c=2.30$, $CHCl_3$); IR (neat) 3032, 2868, 2112, 1740, 1585, 1497, 1454 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.58—3.85 (m, 6 H), 4.47 (d, 1H, $J=11.9$ Hz, $\mathrm{C\underline{H}HPh}$), 4.59 (d, 1H, $J=10.9$ Hz, $\mathrm{C\underline{H}HPh}$), 4.60 (d, 1H, $J=11.9$ Hz, $\mathrm{CH\underline{H}Ph}$), 4.82 (d, 1H, $J=10.9$ Hz, $\mathrm{CH\underline{H}Ph}$), 4.86 (d, 1H, $J=11.2$ Hz, $\mathrm{C\underline{H}HPh}$), 4.92 (d, 1H, $J=11.2$ Hz, $\mathrm{CH\underline{H}Ph}$), 5.79 (d, 1H, $J=8.3$ Hz, H-1), 7.16—7.52 (m, 15H, $\mathrm{CH_2\underline{Ph}}\times 3$), 7.49 (ddd, 1H, $J=1.0$, 4.6, 7.6 Hz, H-5 of Py), 7.85 (ddd, 1H, $J=1.7$, 7.6, 7.9 Hz, H-4 of Py), 8.17 (td, 1H, $J=1.0$, 7.9 Hz, H-3 of Py), 8.81 (ddd, 1H, $J=1.0$, 1.7, 4.6 Hz, H-6 of Py). HR-MS (FAB) Calcd for $C_{33}H_{33}N_4O_6$ $(M^+ + H)$ *m/z* 581.2401, Found 581.2401.

3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl 2-Pyridinecarboxylate (3) Analogously, 3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hexopyranose[4c] (2.52 g, 5.80 mmol) was converted to 2.67 g (85%) of **3**. Compound **3** was obtained as a colorless oil: $[\alpha]_D^{25}$ $+6.0°$ ($c=1.91$, $CHCl_3$); IR (neat) 3030, 2868, 1736, 1585, 1497, 1454 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.99 (ddd, 1H, $J=9.9$, 10.9, 12.5 Hz, H-2ax), 2.54 (ddd, 1H, $J=2.3$, 5.0, 12.5 Hz, H-2eq), 3.61—3.85 (m, 5 H), 4.50 (d, 1H, $J=12.0$ Hz, $\mathrm{C\underline{H}HPh}$), 4.58 (d, 1H, $J=12.0$ Hz, $\mathrm{CH\underline{H}Ph}$), 4.62 (d, 1H, $J=10.9$ Hz, $\mathrm{C\underline{H}HPh}$), 4.63 (d, 1H, $J=11.6$ Hz, $\mathrm{C\underline{H}HPh}$), 4.71 (d, 1H, $J=11.6$ Hz, $\mathrm{CH\underline{H}Ph}$), 4.91 (d, 1H, $J=10.9$ Hz, $\mathrm{CH\underline{H}Ph}$), 6.00 (dd, 1H, $J=2.3$, 9.9 Hz, H-1), 7.19—7.36 (m, 15H, $\mathrm{CH_2\underline{Ph}}\times 3$), 7.48 (ddd, 1H $J=1.3$, 4.6, 7.6 Hz, H-5 of Py), 7.83 (ddd, 1H, $J=1.7$, 7.6, 7.9 Hz, H-4 of Py), 8.15 (ddd, 1H, $J=1.0$, 1.3, 7.9 Hz, H-3 of Py), 8.79 (ddd, 1H, $J=1.0$, 1.7, 4.6 Hz, H-6 of Py). HR-MS (FAB) Calcd for $C_{33}H_{34}NO_6$ $(M^+ + H)$ *m/z* 540.2386, Found 540.2374.

3,4,6-Tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranosyl 2-Pyridinecarboxylate (4) Analogously, 3,4,6-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranose[4d] (2.50 g, 8.61 mmol) was converted to 2.87 g (84%) of an inseparable anomeric mixture ($\alpha:\beta=$ *ca.* 1 : 2) of **4**. Compound **4** was obtained as a colorless oil: IR (neat) 3022, 1743, 1632, 1585, 1439 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.05, 2.07, 2.08 (3s, each 3H × 1/3, $COCH_3\times 3$), 2.06, 2.07, 2.07 (3s, each 3H × 2/3, $COCH_3\times 3$), 2.11—2.19 (m, 1H H-2ax), 2.45—2.52 (m, 1H × 1/3, H-2eq), 2.54 (ddd, 1H × 2/3, $J=2.3$, 4.9, 12.5 Hz, H-2eq), 3.86 (ddd, 1H × 2/3, $J=2.3$, 4.6, 9.2 Hz, H-5), 4.07 (dd, 1H × 1/3, $J=2.0$, 12.4 Hz, H-6), 4.15 (dd, 1H × 2/3, $J=2.3$, 12.5 Hz, H-6), 4.24 (ddd, 1H × 1/3, $J=2.0$, 4.0, 10.2 Hz, H-5), 4.33 (dd, 1H × 2/3, $J=4.6$, 12.5 Hz, H-6′), 4.36 (dd, 1H × 1/3, $J=4.0$, 12.4 Hz, H-6′), 5.09 (t, 1H × 2/3, $J=9.2$ Hz, H-4), 5.16 (t, 1H × 1/3, $J=9.6$ Hz, H-4), 5.16 (ddd, 1H × 2/3, $J=4.9$, 9.2, 10.9 Hz, H-3), 5.50 (ddd, 1H × 1/3, $J=5.3$, 9.6, 11.6 Hz, H-3), 6.13 (dd, 1H × 2/3, $J=2.3$, 9.9 Hz, H-1), 6.57 (br d, 1H × 1/3, $J=2.3$ Hz, H-1), 7.52 (ddd, 1H × 2/3, $J=1.3$, 4.6, 7.6 Hz, H-5 of Py), 7.53 (ddd, 1H × 1/3, $J=1.3$, 4.6, 7.6 Hz, H-5 of Py), 7.87 (ddd, 1H × 2/3, $J=1.7$, 7.6, 7.9 Hz, H-4 of Py), 7.88 (ddd, 1H × 1/3, $J=1.7$, 7.6, 7.9 Hz, H-4 of Py), 8.13 (ddd, 1H × 1/3, $J=1.0$, 1.3, 7.9 Hz, H-3 of Py), 8.16 (ddd, 1H × 2/3, $J=1.0$, 1.3, 7.9 Hz, H-3 of Py), 8.80 (ddd, 1H, $J=1.0$, 1.7, 4.6 Hz, H-6 of Py). HR-MS (FAB) Calcd for $C_{18}H_{22}NO_9$ $(M^+ + H)$ *m/z* 396.1295, Found 396.1291.

Typical Procedure for Glycosylation Using Glycosyl 2-Pyridinecarboxylate To a cold (−50 °C) stirred suspension of $Cu(OTf)_2$ (135 mg, 0.372 mmol), powdered molecular sieves 4A (300 mg) and methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**5**) (79.4 mg, 0.171 mmol) in CH_2Cl_2 (5 ml) was added a solution of **1** (100 mg, 0.155 mmol) in CH_2Cl_2 (3 ml). The reaction mixture was warmed gradually to room temperature over 2.5 h with stirring, then quenched with triethylamine (0.2 ml) and saturated aqueous $NaHCO_3$ (20 ml). The mixture was filtered through a Celite-pad and washed with CH_2Cl_2. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (10 ml × 2). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1 : 5) to give 115 mg (75%) of **7**α and 11.3 mg (7.4%) of **7**β.[5]

Methyl 4-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α and β-D-Glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (9) Compound **9** was obtained as a colorless oil: IR (neat) 3030, 2868, 2110, 1497, 1454 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.377 (s, 3H, OMe of β-isomer), 3.383 (s, 3H, OMe of α-isomer), 3.25—4.22 (m, 12H), 4.27—4.88 (m, 12H, $\mathrm{C\underline{H}_2Ph}\times 5+\mathrm{C\underline{H}HPh}$, H-1), 5.03 (d, 1H, $J=11.2$ Hz, $\mathrm{CH\underline{H}Ph}$ of β-isomer), 5.11 (d, 1H, $J=10.9$ Hz, $\mathrm{CH\underline{H}Ph}$ of α-isomer), 5.74 (d, 1H, $J=4.0$ Hz, H-1′ of α-isomer), 7.09—7.36 (m, 30H, $\mathrm{CH_2\underline{Ph}}\times 6$), H-1′ of β-isomer could not be identified; ^{13}C-NMR ($CDCl_3$) δ 97.7 (C1′ of α-isomer), 98.3 (C1 of α- and β-isomer), 100.9 (C1′ of β-isomer). HR-MS (FAB) Calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M^+ + Na)$ *m/z* 944.4098, Found 944.4116.

Methyl 6-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α and β-D-Glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (10) Compound **10** was obtained as white crystals: IR (neat) 3032, 2912, 2118, 1497, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 3H, OMe of α-isomer), 3.38 (s, 3H, OMe of β-isomer), 3.30—4.18 (m, 12H), 4.40—4.67 (m, 4H, $\mathrm{C\underline{H}_2Ph}\times 2$), 4.63 (d, 1H, $J=7.3$ Hz, H-1′ of β-isomer), 4.67 (d, 1H, $J=3.6$ Hz, H-1 of β-isomer), 4.77—5.01 (m, 8H, $\mathrm{C\underline{H}_2Ph}\times 4$), 7.15—7.36 (m, 30H, $\mathrm{CH_2\underline{Ph}}\times 6$), H-1 and H-1′ of α-isomer could not be identified; ^{13}C-NMR ($CDCl_3$) δ 97.9, 98.0 (C1 and C1′ of α-isomer), 98.1 (C1 of β-isomer), 102.0 (C1′ of β-isomer). HR-MS (FAB) Calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M^+ + Na)$ *m/z* 944.4098, Found 944.4120.

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