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Article

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Glycosylations of Glycals Using *N*-Iodosuccinimide (NIS) and Phosphorus Compounds for Syntheses of 2-Iodo- and 2-Deoxyglycosides

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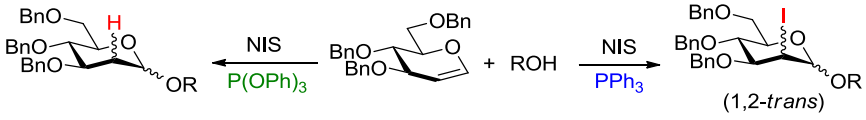


ABSTRACT: The glycosylations of glycals and alcohols using *N*-iodosuccinimide (NIS) and a catalytic amount of PPh_3 effectively proceeded under mild conditions to provide the corresponding 2-deoxy-2-iodoglycosides in high yields. The reactivity of the iodoglycosylations with PPh_3 significantly increased compared to that using NIS alone as an activator. In addition, the glycosylations of glycals and alcohols using catalytic amounts of NIS and $P(OPh)_3$ were effectively realized to give the corresponding 2-deoxyglycosides in high yields.

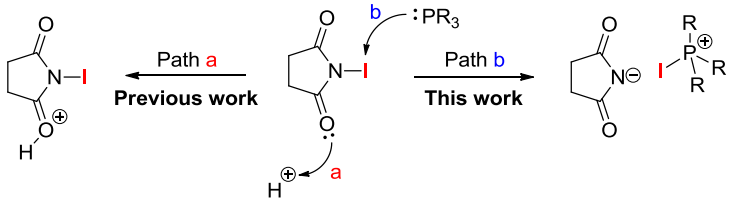
Introduction

Many kinds of natural products including mono- and oligosaccharides, such as proteoglycans, glycoproteins, glycolipids, and antibiotics, are now recognized as important biological substances. A large

number of recent biological studies on these glycomolecules at the molecular level have shed light on the biological significance of their carbohydrate parts (glycons) in molecular recognition for the transmission of biological information,[1] and it was found that carbohydrates play very important roles in many biological events. Additionally, some glycomolecules are being used as new functional materials.[2] For example, there is great hope that certain alkyl glycosides can be employed as biodegradable surfactants. Therefore, glycomolecules are worth developing in chemistry, biology, and material science. With this stimulating background, the efficient synthesis of not only the carbohydrate itself, but also carbohydrate-containing products, is of particular interest both in academia and in industry. In this context, glycosylation, which is a crucial organic synthetic method to attach a sugar to other sugar moieties or other molecules (aglycons), is becoming more and more important in synthetic organic chemistry and carbohydrate chemistry, and considerable attention has been directed towards the development and efficiency of glycosylation methods.[3] In this study, we focused on the iodoglycosylation[4] of glycals[5] using *N*-iodosuccinimide (NIS). 2-Iodoglycosides produced by iodoglycosylation can be converted to 2-deoxysugars, and thus this method widely applies to natural product[6] or oligosaccharide synthesis.[7] Additionally, 2-iodoglycosides can be used to label glycosides in biology.[8] Although iodoglycosylation is known as an efficient glycosylation methodology, it sometimes needs a reaction accelerator such as TfOH, which is a strong acid,[9] to improve the efficiency of the glycosylation reaction (Figure 1, path a).

Consequently, it cannot be applied to acid-sensitive substrates. Herein, we report an efficient iodoglycosylation utilizing PPh_3 as a novel and neutral reaction accelerator. Along with this reaction, we disclose a novel glycosylation of glycals using NIS and $P(OPh)_3$ as a combined activator to directly give 2-deoxyglycosides.[10] To realize such an efficient iodoglycosylation, we built upon Ishihara's iodocyclization reaction,[11] in which NIS could be activated by a phosphorus compound as a nucleophilic promoter. In this study, the high reactivity of a phosphonium iodide cation intermediate generated from NIS and a phosphorus compound was well demonstrated (Figure 1, path b). In this context, we expected that use of a phosphorus compound combined with NIS would realize an effective iodoglycosylation of glycals under mild and neutral conditions.

Figure 1. Activation of NIS by a protic acid (a) and a phosphorus compound (b).



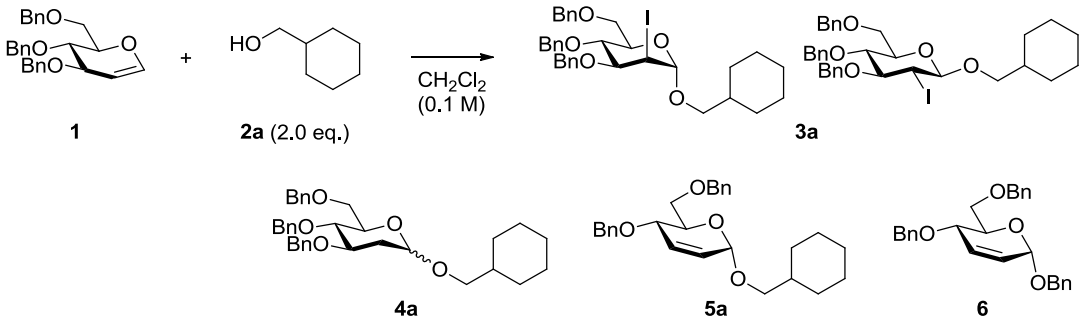
Results and discussion

To investigate our hypothesis, we first selected tri-*O*-benzyl-D-glucal (**1**) and NIS as the glycosyl donor and activator, respectively. We then investigated the iodoglycosylation reaction of **1** with alcohol **2a** using NIS and several phosphorus compounds under several conditions. These results are summarized in Table 1.

It was found that the use of PBu_3, $P(OMe)_3$ or $P(OPh)_3$ as an additive gave the corresponding glycoside **3a** in moderate yields to a similar degree as the reaction with no phosphorus compound (entries 1-4). In addition, when $P(OMe)_3$ and $P(OPh)_3$ were employed as the reaction additive, non-negligible amounts of the Ferrier-type[12] rearranged by-products **5a** and **6**[13] were produced (entries 3 and 4). In contrast, when PPh_3 was used as the reaction additive, the reactivity of the reaction and the yield of **3a** were dramatically increased. Thus, we found that the use of PPh_3 significantly promoted the iodoglycosylation using NIS just as well as the use of TfOH, and the corresponding 2-deoxy-2-iodoglycosides were obtained in excellent yields (82%, α/β = 75/25) (entries 5 and 6). It was also confirmed that the α/β-stereoselectivity of the glycosylation using NIS and PPh_3 was quite similar to that using NIS and TfOH. Based on these results, we next examined the amounts of PPh_3. When 0.1 equiv. PPh_3 was employed as the reaction accelerator, the yield of **3a** was only moderate (entry 7). It was found that the use of 0.2 or 0.4 equiv. PPh_3 gave the best results (entries 5 and 8). Surprisingly, when 0.1 equiv. NIS and 0.2 equiv. $P(OPh)_3$ were employed as an activator and an additive, respectively, 2-deoxyglycoside **4a**[14] was directly produced in 39% yield (entry 9). Although the reaction mechanism is different from the present glycosylation, the glycosylation using PPh_3-HBr to give 2-deoxyglycoside was reported by Mioskowski *et al.*[15] In the reaction using 0.1 equiv. NIS and 0.2 equiv. PPh_3, the glycosylation did not proceed at all (entry 10). Moreover, the glycosylation of **1** and **2a** using 0.1 equiv. NIS and 0.2 equiv. $P(OPh)_3$ at warmer reaction temperatures afforded **4a** in

excellent yields (entries 11-13). Interestingly, 2-deoxyglycoside **4a** was not obtained by the glycosylation reaction using 0.15 equiv. NIS and 0.15 equiv. $P(OPh)_3$ or by using 0.2 equiv. NIS and 0.1 equiv. $P(OPh)_3$, and only the rearranged by-products **5a** and **6** were produced as principal products in those cases (entries 14 and 15).

Table 1. Glycosylations of 1 and 2a using NIS and several phosphorus compounds under several conditions.



1 **2a** (2.0 eq.) **3a** **4a** **5a** **6**

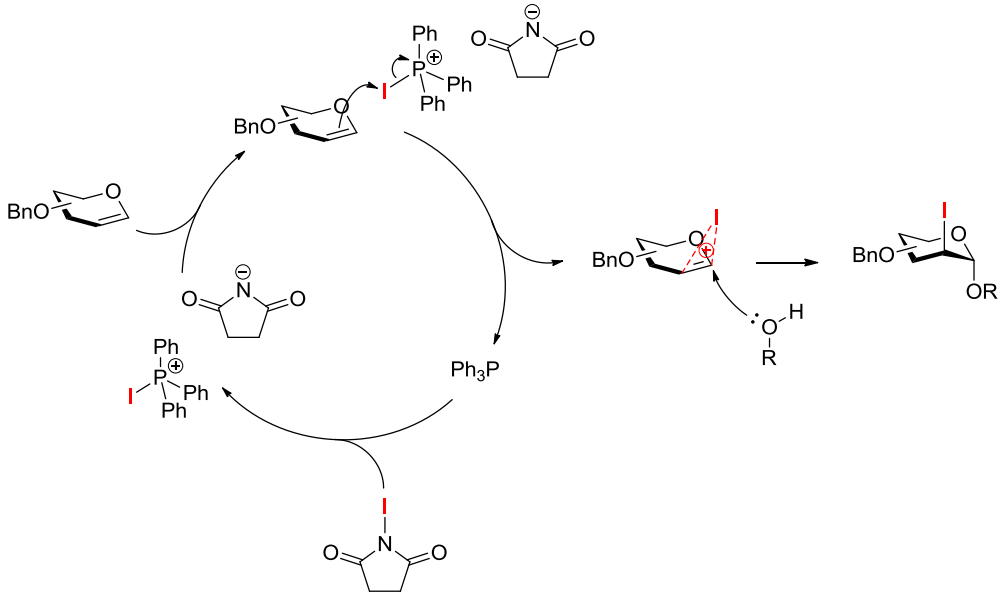
Entr	Temp. (^{o}C)	Time (h)	Conditions	Yields(%)[a]				
				3a	**4a**	**5a**	**6**	**1**
1	-40	12	NIS (2.0 eq.)	45 (α/β = 48/52)	-	-	-	37
2	-40	12	NIS (2.0 eq.), PBu_3 (0.2 eq.)	53 (α/β = 71/29)	-	-	-	40
3	-40	12	NIS (2.0 eq.), $P(OMe)_3$ (0.2 eq.)	42 (α/β = 70/30)	-	8	8	25
4	-40	12	NIS (2.0 eq.), $P(OPh)_3$ (0.2 eq.)	49 (α/β = 65/35)	-	10	8	20
5	-40	12	NIS (2.0 eq.), PPh_3 (0.2 eq.)	82 (α/β = 75/25)	-	-	-	-
6	-40	12	NIS (2.0 eq.), TfOH (0.2 eq.)	86 (α/β = 72/28)	-	-	-	-
7	-40	12	NIS (2.0 eq.), PPh_3 (0.1 eq.)	58 (α/β = 68/32)	-	-	-	31
8	-40	12	NIS (2.0 eq.), PPh_3 (0.4 eq.)	83 (α/β = 72/28)	-	-	-	-
9	-40	12	NIS (0.1 eq.), $P(OPh)_3$ (0.2 eq.)	-	39 (α/β = 39/61)	-	-	52
10	-40	12	NIS (0.1 eq.), PPh_3 (0.2 eq.)	-	-	-	-	89
11	-20	12	NIS (0.1 eq.), $P(OPh)_3$ (0.2 eq.)	-	84 (α/β = 45/55)	-	-	-
12	0	12	NIS (0.1 eq.), $P(OPh)_3$ (0.2 eq.)	-	88 (α/β = 48/52)	-	-	-
13	rt	3	NIS (0.1 eq.), $P(OPh)_3$ (0.2 eq.)	-	89 (α/β = 65/35)	-	-	-

14	rt	3	NIS (0.15 eq.), $P(OPh)_3$ (0.15 eq.)	-	-	58	31	-
15	rt	3	NIS (0.2 eq.), $P(OPh)_3$ (0.1 eq.)	-	-	54	30	-

[a] α/β Ratios were determined by ^{1}H NMR analysis.

With these interesting and favorable results in hand, we propose the reaction mechanism of the present iodoglycosylation reaction using NIS and PPh_3 as shown in Figure 2. First, a reactive phosphonium iodide cation is generated from NIS and PPh_3 by nucleophilic activation of PPh_3, which then continuously reacts with glycal, the glycosyl donor. As a result, a glycosyl iodonium cation intermediate is generated. Finally, the corresponding 2-deoxy-2-iodoglycoside is produced by nucleophilic addition of the alcohol to the cation intermediate. Additionally, PPh_3 behaves catalytically and is recycled during the reaction.

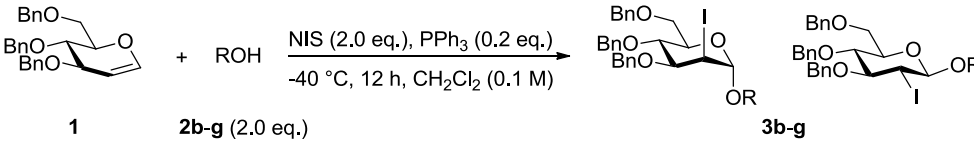
Figure 2. Proposed mechanism of the iodoglycosylation of glycal using NIS and PPh_3.



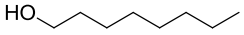
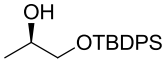
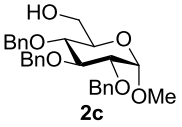
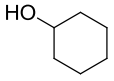
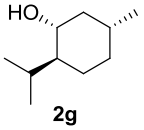
Accordingly, we next examined the generality of the present iodoglycosylation method using primary alcohols **2b** and **2c**, secondary chain alcohols **2d** and **2e**, and cyclic secondary alcohols **2f** and **2g** as

glycosyl acceptors. These results are summarized in Table 2. In all cases, we found that the corresponding glycosides **3b**-**3g** as well as **3a** were obtained in high yields with α-stereoselectivities by the glycosylations using NIS and PPh_3 as a reaction accelerator at low temperature, -40 °C.

Table 2. Iodoglycosylations of 1 and several alcohols using NIS and PPh_3.



1 **2b-g** (2.0 eq.) **3b-g**

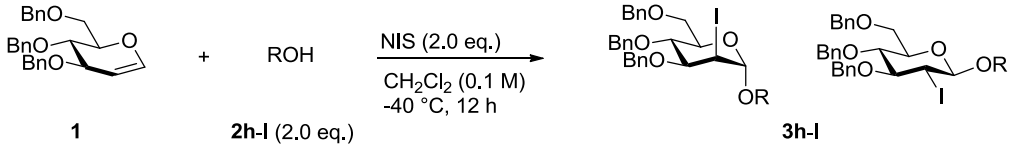
Entry	ROH	Yield (%)[a]	Entry	ROH	Yield (%)[a]
1	 **2b**	**3b**; 89 (α/β = 68/32)	4	 **2e**	**3e**; 91 (α/β = 76/24)
2	 **2c**	**3c**; 81 (α/β = 91/9)	5	 **2f**	**3f**; 90 (α/β = 74/26)
3	 **2d**	**3d**; 90 (α/β = 68/32)	6	 **2g**	**3g**; 83 (α/β = 78/22)

[a] α/β Ratios were determined by ^1H NMR analysis.

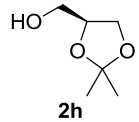
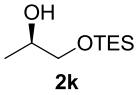
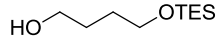
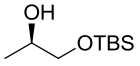
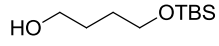
Furthermore, we investigated the iodoglycosylation of **1** with acid-sensitive alcohols, **2h-l**, by utilizing TfOH or PPh_3 as a reaction accelerator, and compared these results (Table 3). Although iodoglycosylation of **2h**, **2i** and **2k** with TfOH gave only a complex mixture, it was found that the use of PPh_3 promoted iodoglycosylations effectively to give the corresponding 2-deoxy-2-iodoglycosides **3h**, **3i** and **3k** in good yields (entries 1-4, 7 and 8). Similarly, when **2j** and **2l** were employed as glycosyl acceptors, the product

yields significantly increased by using PPh_3 as a reaction accelerator compared with the additive of TfOH (entries 5, 6, 9 and 10). These results clearly indicated that the iodoglycosylation using PPh_3 effectively proceeded under mild conditions, and demonstrated the usefulness of PPh_3 as a reaction accelerator for iodoglycosylation using NIS.

Table 3. Iodoglycosylations of 1 and acid-sensitive alcohols using NIS and TfOH or PPh_3.



1 **2h-l** (2.0 eq.) **3h-l**

Entry	ROH	Additive (0.2 eq.)	Yield (%)[a]	Entry	ROH	Additive (0.2 eq.)	Yield (%)[a]
1	 **2h**	TfOH	Many spots	7	 **2k**	TfOH	Many spots
2	**2h**	PPh_3	**3h**; 86 (α/β = 70/30)	8	**2k**	PPh_3	**3k**; 69 (α/β = 71/29)
3	 **2i**	TfOH	Many spots				
4	**2i**	PPh_3	**3i**; 77 (α/β = 64/36)	9	 **2l**	TfOH	**3l**; 60 (α/β = 63/37)
5	 **2j**	TfOH	**3j**; 68 (α/β = 65/35)				
6	**2j**	PPh_3	**3j**; 85 (α/β = 63/37)	10	**2l**	PPh_3	**3l**; 74 (α/β = 68/32)

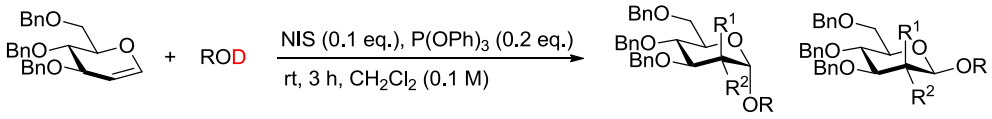
[a] α/β Ratios were determined by ^1H NMR analysis.

We performed a mechanistic study on the glycosylation reaction using NIS and $P(OPh)_3$, which directly produced 2-deoxyglycoside in Table 1 (Figure 3a). When deuterated alcohol **7** was employed as a glycosyl acceptor, 2-deoxyglycosides **8**, **9**, **11** and **12**, which were deuterated at the C-2 position, were produced in

high yields. These results clearly indicated that glycosyl donor **1** was protonated by the glycosyl acceptor, alcohol **7**, at the C-2 position. Based on these experimental results, we propose the reaction mechanism for the glycosylation as shown in Figure 3b. First, a phosphonium iodide cation is generated from NIS and $P(OPh)_3$ by nucleophilic addition of $P(OPh)_3$. The unoccupied electron orbital of the phosphorus atom is activated by the electron withdrawing effect of the phenoxy groups to accept two electrons from the alcohol, the glycosyl acceptor. After the coordination of the glycosyl acceptor to the phosphorus atom, the proton of the glycosyl acceptor activates the glycosyl donor. As a result of the reaction, an oxonium cation intermediate is generated. Finally, a glycosidic bond is formed due to the nucleophilic addition of the aglycon portion to the oxonium cation intermediate. Additionally, the phosphonium iodide cation intermediate behaves catalytically and is recycled during the reaction. Furthermore, an excess amount of $P(OPh)_3$ to NIS decreases the Lewis acidity of the phosphonium iodide cation intermediate to prevent the production of the rearranged by-products **5a** and **6**.

Figure 3. Mechanistic study (a) and proposed mechanism (b) of the glycosylation using NIS and $P(OPh)_3$.

a)



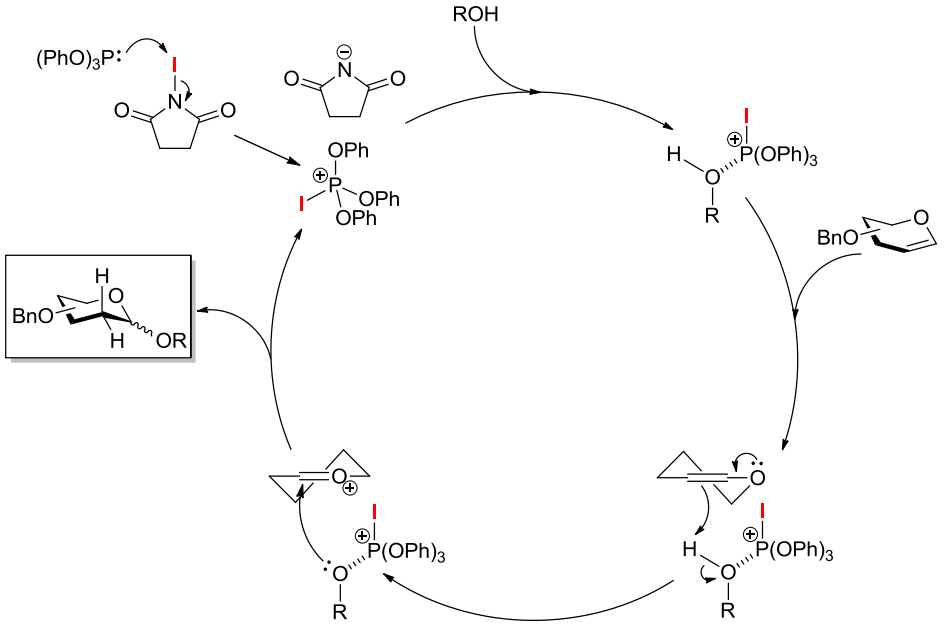
1 **7** (2.0 eq.)

8; R^1 = D, R^2 = H **11**; R^1 = D, R^2 = H
9; R^1 = H, R^2 = D **12**; R^1 = H, R^2 = D
10; R^1 = H, R^2 = H **13**; R^1 = H, R^2 = H

ROD	Yield (%)	
	8+**9**+**10** (ratio[a])	**11**+**12**+**13** (ratio[a])
Cyclohexanol-d_{12} (**7**)	68 (**8**/**9**/**10** = 11/71/18)	16 (**11**/**12**/**13** = 15/69/16)

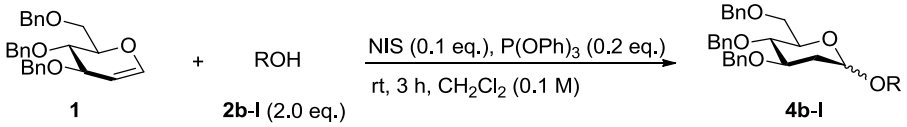
[a] Ratios were determined by ^{1}H NMR analysis.

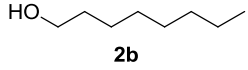
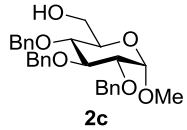
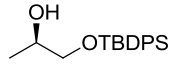
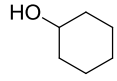
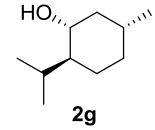
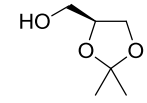
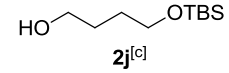
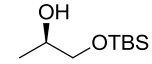
b)



Next, we examined the generality of the glycosylation method by catalytic amounts of NIS and $P(OPh)_3$ using several alcohols. These results are summarized in Table 4. It was found that all glycosylations of **2b**-**h**, **j** and **l** as well as **2a** with **1** using NIS and $P(OPh)_3$ proceeded smoothly to give the corresponding 2-deoxyglycosides **4b**-**d**,[14] **e**, **f**,[14] **g**-**h**, **j** and **l** directly in high yields with α-stereoselectivities.

Table 4. Glycosylation reaction of 1 and several alcohols using NIS and $P(OPh)_3$.



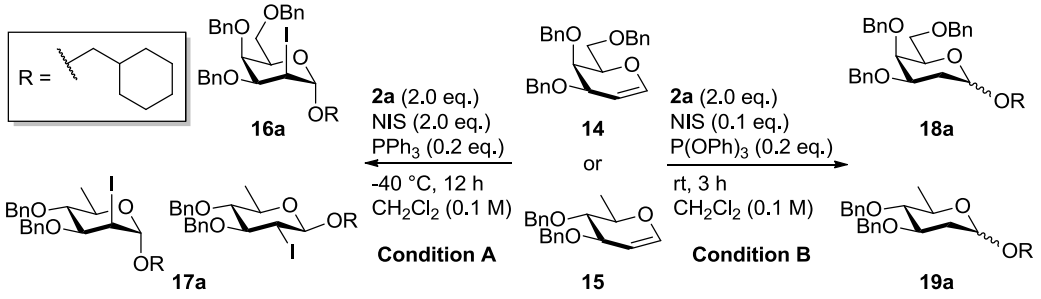
Entry	ROH	Yield (%)[a]
1	 **2b**	**4b**; 84 (α/β = 70/30)
2	 **2c**	**4c**; 88 (α/β = 72/28)
3	 **2d**	**4d**; 83 (α/β = 67/33)
4	 **2e**	**4e**; 81 (α/β = 75/25)
5	 **2f**	**4f**; 87 (α/β = 83/17)
6	 **2g**	**4g**; 82 (α/β = 71/29)
7[b]	 **2h**	**4h**; 88 (α/β = 63/37)
8	 **2j**[c]	**4j**; 79 (α/β = 71/29)
9	 **2l**[c]	**4l**; 78 (α/β = 68/32)

[a]α/β Ratios were determined by ^{1}H NMR analysis. [b]This reaction was performed at 40 ^{o}C. [c]0.5 equiv. of alcohol was used.

Finally, we examined the generality of the glycosylation method using **2a** and other glycals, tri-*O*-benzyl-D-galactal (**14**) and di-*O*-benzyl-6-deoxy-D-glucal (**15**) (Table 5). In condition A, which employs NIS and PPh_3, the corresponding 2-deoxy-2-iodoglycosides **16a** and **17a** were obtained from **14** and **15**, respectively, in high yields (entries 1 and 2). In addition, it was found that the iodoglycosylation reaction of **2a** and acceptor **14** gave only the α isomer of **16a** with complete α-stereoselectivity. In contrast,

under condition B, which uses NIS and $P(OPh)_3$, the corresponding 2-deoxyglycosides **18a** and **19a** were obtained from **14** and **15**, respectively, in high yields (entries 3 and 4).

Table 5. Glycosylations using 2a and 14 or 15 under conditions A and B.



Entry	Donor	Condition	Product	Yield (%)[a]
1	**14**	**A**	**16a**	88 (α only)
2	**15**	**A**	**17a**	89 (α/β = 72/28)
3	**14**	**B**	**18a**	91 (α/β = 71/29)
4	**15**	**B**	**19a**	86 (α/β = 59/41)

[a] α/β Ratios were determined by ^{1}H NMR analysis.

Conclusion

In conclusion, we have developed novel glycosylation reactions using NIS and PPh_3 or $P(OPh)_3$. We found that the use of NIS and PPh_3 as a reaction accelerator realized effective iodoglycosylations under mild conditions to provide 2-deoxy-2-iodoglycosides in high yields. On the other hand, the use of NIS and $P(OPh)_3$ was proven to be effective for the glycosylation to directly afford 2-deoxysugars in high yields. These reactions, which can produce both 2-iodo- and 2-deoxyglycosides individually by changing the phosphorus compound additive, are very attractive and provide new insights into the glycosylation reaction.

Furthermore, although the present glycosylation methods could not simply be applied to glycals bearing acetate protecting groups, they should find wide application in the synthesis of 2-iodo- and 2-deoxyglycosides, which frequently appear as biologically important glycons.

Experimental Section

General procedure for iodoglycosylations of glucal 1 and alcohols 2 using NIS and PPh_3

To a solution of glycosyl donor **1** (25.0 mg, 60.0 μmol) in dry CH_2Cl_2 (0.600 mL) were added glycosyl acceptor **2** (2.0 eq., 120 μmol) and PPh_3 (0.2 eq., 12.0 μmol) at room temperature under Ar atmosphere. After stirring at the same temperature for 20 min, the reaction mixture was cooled to −40 °C, and then NIS (2.0 eq., 120 μmol) was added to the reaction mixture. After the reaction mixture was stirred for 12 h, the reaction was quenched by addition of a mixture of 50 wt% $Na_2S_2O_3$ and sat. $NaHCO_3$ aq. (1/1, 2 ml) at −40 °C. The resulting mixture was extracted with $CHCl_3$ (2 mL × 3). The combined organic layer was washed with brine (2 mL), dried over Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash column chromatography (10 g) gave the corresponding glycosides as a α/β mixture.

General procedure for glycosylations of glucal 1 and alcohols 2 using NIS and $P(OPh)_3$

To a solution of glycosyl acceptor **2** (2.0 eq., 120 μmol) in dry CH_2Cl_2 (0.600 mL) were added NIS (0.1 eq., 6.0 μmol) and $P(OPh)_3$ (0.2 eq., 12.0 μmol) at room temperature under Ar atmosphere. After stirring at the same temperature for 20 min, glycosyl donor **1** (25.0 mg, 60.0 μmol) was added to the reaction mixture.

After the reaction mixture was stirred for 3 h, the reaction was quenched by addition of a mixture of 50 wt% $Na_2S_2O_3$ aq. and sat. $NaHCO_3$ aq. (1/1, 2 ml). The resulting mixture was extracted with $CHCl_3$ (2 mL × 3). The combined organic layer was washed with brine (2 mL), dried over Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash column chromatography (10 g) gave the corresponding glycosides as a α/β mixture.

Cyclohexylmethyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-α-D-glucopyranoside (3aα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3aα** (23.5 mg, 60%). Colorless syrup; R_f 0.48 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +14.8º (*c* 0.91, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.24 (13H, m), 7.17-7.15 (2H, m), 5.17 (1H, br s), 4.85 and 4.49 (2H, ABq, *J* = 10.6 Hz), 4.71 and 4.53 (2H, ABq, *J* = 12.4 Hz), 4.70 and 4.53 (2H, ABq, *J* = 12.4 Hz), 4.48 (1H, dd, *J* = 1.2 and 4.3 Hz), 3.90 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.84 (1H, ddd, *J* = 1.5, 4.3 and 9.8 Hz), 3.78 (1H, dd, *J* = 4.3 and 10.9 Hz), 3.69 (1H, dd, *J* = 1.5 and 10.9 Hz), 3.45 (1H, dd, *J* = 6.6 and 9.5 Hz), 3.31 (1H, dd, *J* = 4.3 and 8.6 Hz), 3.18 (1H, dd, *J* = 6.1 and 9.2 Hz), 1.71-1.65 (6H, m), 1.26-1.10 (3H, m), 0.93-0.84 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.7, 128.4, 128.3×2, 128.1×2, 127.8, 127.7, 127.6, 127.4, 101.5, 76.0, 75.3, 73.6, 73.3, 72.1, 71.0, 68.9, 37.8, 33.8, 30.0, 29.8, 26.5, 25.8, 25.7, 22.6, 14.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{34}H_{41}IO_5Na$ 679.1896; found 679.1900.

Cyclohexylmethyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-β-D-glucopyranoside (3aβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3aβ** (9.2 mg, 23%). White solid; R_f 0.42 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +25.4º (*c* 1.33, $CHCl_3$); mp 66-67 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.41 (2H, m), 7.34-7.27 (11H, m), 7.20-7.17 (2H, m), 4.98 and 4.85 (2H, ABq, *J* = 10.1 Hz), 4.79 and 4.57 (2H, ABq, *J* = 10.9 Hz), 4.61 and 4.55 (2H, ABq, *J* = 12.0 Hz), 4.50 (1H, d, *J* = 8.9 Hz), 3.92 (1H, dd, *J* = 8.9 and 10.9 Hz), 3.76-3.68 (4H, m), 3.60 (1H, dd, *J* = 8.6 and 9.7 Hz), 3.49 (1H, ddd, *J* = 2.3, 4.6 and 9.7 Hz), 3.29 (1H, dd, *J* = 7.2 and 9.2 Hz), 1.92-1.61 (6H, m), 1.29-1.13 (3H, m), 1.02-0.93 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 137.7, 128.5, 128.4×2, 128.1, 127.9, 127.7, 127.6, 103.3, 85.9, 79.7, 76.0, 75.5, 75.2, 74.9, 73.5, 68.6, 37.8, 33.1, 30.1, 29.8, 26.6, 25.8×2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{34}H_{41}IO_5Na$ 679.1896; found 679.1888.

***n*-Octyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-α-D-glucopyranoside (3bα):** The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3bα** (24.4 mg, 61%). Colorless syrup; R_f 0.43 (8/1 *n*-hexane/EtOAc); $[\alpha]^{28}_D$ +11.6º (*c* 1.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.24 (13H, m), 7.17-7.14 (2H, m), 5.21 (1H, br s), 4.85 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.72 and 4.53 (2H, ABq, *J* = 12.0 Hz), 4.70 and 4.52 (2H, ABq, *J* = 11.5 Hz), 4.49 (1H, dd, *J* = 1.4 and 4.0 Hz), 3.90 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.85 (1H, ddd, *J* = 1.8, 4.6 and 9.8 Hz), 3.79 (1H, dd, *J* = 4.6 and 10.9 Hz), 3.70 (1H, dd, *J* = 1.8 and 10.9 Hz), 3.64 (1H, dt, *J* = 6.9 and 9.4 Hz), 3.38 (1H, dt, *J* = 6.6 and 9.8

Hz), 3.32 (1H, dd, *J* = 4.0 and 8.6 Hz), 1.53-1.50 (2H, m), 1.30-1.24 (10H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.8, 128.4, 128.3×2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 101.3, 75.9, 75.3, 73.3, 72.1, 70.9, 68.9, 68.1, 33.8, 31.8, 29.4, 29.3, 29.2, 26.1, 22.6, 14.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{45}IO_5Na$ 695.2209; found 695.2206.

***n*-Octyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-β-D-glucopyranoside (3bβ):** The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3bβ** (11.5 mg, 28%). White solid; R_f 0.38 (8/1 *n*-hexane/EtOAc); $[\alpha]^{29}_D$ +26.4º (*c* 1.38, $CHCl_3$); mp 60-61 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.42 (2H, m), 7.36-7.26 (11H, m), 7.19-7.17 (2H, m), 4.98 and 4.85 (2H, ABq, *J* = 10.3 Hz), 4.80 and 4.56 (2H, ABq, *J* = 10.9 Hz), 4.61 and 4.55 (2H, ABq, *J* = 12.3 Hz), 4.52 (1H, d, *J* = 8.9 Hz), 3.92 (1H, dd, *J* = 8.9 and 10.9 Hz), 3.89 (1H, dt, *J* = 6.6 and 9.5 Hz), 3.76-3.68 (3H, m), 3.60 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.55-3.48 (2H, m), 1.69-1.59 (2H, m), 1.33-1.25 (10H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.7, 128.5, 128.4×2, 128.1, 127.9, 127.8, 127.6, 103.2, 85.9, 79.7, 75.5, 75.2, 74.9, 73.5, 70.4, 68.6, 33.2, 31.8, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{45}IO_5Na$ 695.2209; found 695.2216.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranosyl)-α-D-glucopyranoside (3cα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 3/1) to give compound **3cα** (44.5 mg, 74%). Colorless syrup; R_f 0.41 (3/1

n-hexane/EtOAc); $[\alpha]^{27}_{D}$ +36.4º (*c* 2.13, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.18 (28H, m), 7.13-7.11 (2H, m), 5.27 (1H, br s), 4.99 and 4.80 (2H, ABq, *J* = 10.6 Hz), 4.87 and 4.45 (2H, ABq, *J* = 10.9 Hz), 4.85 and 4.47 (2H, ABq, *J* = 10.6 Hz), 4.79 and 4.69 (2H, ABq, *J* = 12.3 Hz), 4.69 and 4.49 (2H, ABq, *J* = 12.3 Hz), 4.64 and 4.41 (2H, ABq, *J* = 12.0 Hz), 4.59 (1H, d, *J* = 3.4 Hz), 4.49 (1H, dd, *J* = 1.2 and 4.3 Hz), 3.98 (1H, dd, *J* = 9.2 and 9.2 Hz), 3.89 (1H, dd, *J* = 9.2 and 9.5 Hz), 3.83 (1H, dd, *J* = 4.3 and 11.5 Hz), 3.75 (1H, ddd, *J* = 1.5, 4.3 and 9.5 Hz), 3.69 (1H, ddd, *J* = 1.8, 4.3 and 9.8 Hz), 3.64 (1H, dd, *J* = 4.3 and 10.9 Hz), 3.58 (1H, dd, *J* = 1.5 and 11.5 Hz), 3.54 (1H, dd, *J* = 1.8 and 10.9 Hz), 3.50 (1H, dd, *J* = 3.4 and 9.2 Hz), 3.41 (1H, dd, *J* = 9.2 and 9.8 Hz), 3.32 (3H, s), 3.24 (1H, dd, *J* = 4.3 and 9.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.4, 138.3, 138.1, 138.0, 137.4, 128.5, 128.4×2, 128.3, 128.2, 128.1, 128.0×2, 127.9×2, 127.8, 127.6×3, 127.5, 127.4×2, 101.7, 97.9, 82.1, 79.9, 77.4, 76.2, 75.8, 75.1, 74.9, 73.3, 73.2, 72.2, 70.7, 69.6, 68.6, 66.1, 55.1, 33.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{55}H_{59}IO_{10}Na$ 1029.3051; found 1029.3060.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-β-D-glucopyranosyl)-α-D-glucopyranoside (3cβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 3/1) to give compound **3cβ** (4.4 mg, 7%). White solid; R_f 0.38 (3/1 *n*-hexane/EtOAc); $[\alpha]^{25}_{D}$ +46.3º (*c* 0.84, $CHCl_3$); mp 121-122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.40 (2H, m), 7.37-7.22 (26H, m), 7.20-7.17 (2H, m), 4.99 and 4.82 (2H, ABq, *J* = 10.6 Hz), 4.96 and 4.82 (2H, ABq, *J* = 10.6 Hz),

4.96 and 4.89 (2H, ABq, *J* = 10.9 Hz), 4.78 and 4.56 (2H, ABq, *J* = 11.2 Hz), 4.64 (1H, d, *J* = 3.5 Hz), 4.57 and 4.52 (2H, ABq, *J* = 12.1 Hz), 4.53 (1H, d, *J* = 8.9 Hz), 4.12-4.10 (1H, m), 4.02-3.99 (1H, m), 3.96 (1H, dd, *J* = 8.9 and 10.6 Hz), 3.78-3.65 (6H, m), 3.58 (1H, dd, *J* = 3.5 and 9.2 Hz), 3.49 (1H, ddd, *J* = 1.5, 4.3 and 9.8 Hz), 3.39 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.6, 138.2, 138.0, 137.6, 128.5, 128.4×2, 128.3, 128.1×3, 127.9×2, 127.7, 127.6, 103.0, 98.2, 85.7, 82.3, 79.7, 79.6, 75.8, 75.5, 75.4, 75.1, 74.9, 73.4×2, 69.5, 68.6, 68.0, 55.3, 32.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{55}H_{59}IO_{10}Na$ 1029.3051; found 1029.3045.

Isopropyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-α-D-glucopyranoside (3dα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3dα** (22.1 mg, 61%). Colorless syrup; R_f 0.49 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +13.5° (*c* 1.50, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.41 (2H, m), 7.38-7.26 (11H, m), 7.16-7.14 (2H, m), 5.32 (1H, br s), 4.84 and 4.47 (2H, ABq, *J* = 10.6 Hz), 4.72 and 4.52 (2H, ABq, *J* = 12.0 Hz), 4.70 and 4.52 (2H, ABq, *J* = 10.6 Hz), 4.48 (1H, dd, *J* = 1.4 and 4.0 Hz), 3.93-3.88 (4H, m), 3.80 (1H, dd, *J* = 4.9 and 10.9 Hz), 3.69 (1H, dd, *J* = 2.0 and 10.9 Hz), 3.34 (1H, m), 1.17 (3H, d, *J* = 6.3 Hz), 1.12 (3H, d, *J* = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7×2, 127.6, 127.4, 99.5, 76.0, 75.3, 73.3, 72.1, 70.8, 69.9, 68.9, 34.5, 23.2, 21.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{35}IO_5Na$ 625.1427; found 625.1439.

Isopropyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-β-D-glucopyranoside (3dβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3dβ** (10.4 mg, 29%). White solid; R_f 0.46 (8/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ +32.1º (*c* 1.06, $CHCl_3$); mp 91-92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (2H, m), 7.36-7.26 (11H, m), 7.20-7.18 (2H, m), 4.98 and 4.85 (2H, ABq, *J* = 10.3 Hz), 4.80 and 4.60 (2H, ABq, *J* = 10.6 Hz), 4.61 and 4.55 (2H, ABq, *J* = 12.3 Hz), 4.59 (1H, d, *J* = 8.9 Hz), 3.98 (1H, m), 3.90 (1H, dd, *J* = 8.9 and 10.9 Hz), 3.75-3.71 (2H, m), 3.68 (1H, dd, *J* = 4.9 and 10.9 Hz), 3.58 (1H, dd, *J* = 8.6 and 9.7 Hz), 3.50 (1H, ddd, *J* = 2.1, 4.9 and 9.7 Hz), 1.28 (3H, d, *J* = 6.3 Hz), 1.26 (3H, d, *J* = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 137.7, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 102.0, 86.1, 79.7, 75.4, 75.2, 74.9, 73.4, 72.9, 68.7, 34.1, 23.4, 21.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{35}IO_5Na$ 625.1427; found 625.1435.

1-((*tert*-Butyldiphenylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranoside (3eα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3eα** (35.5 mg, 69%). Colorless syrup; R_f 0.40 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +23.7º (*c* 1.12, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.64 (4H, m), 7.45-7.27 (19H, m), 7.17-7.14 (2H, m), 5.53 (1H, br s), 4.85 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.73 and 4.53 (2H, ABq, *J* = 12.0 Hz), 4.65 and 4.46 (2H, ABq, *J* = 11.5 Hz), 4.46 (1H, dd, *J* = 1.1 and 4.3 Hz), 3.98 (1H, ddd, *J* = 1.7, 4.6 and 10.0 Hz), 3.95-3.90 (2H, m), 3.81 (1H, dd, *J* = 4.6 and 10.9 Hz), 3.71 (1H, dd, *J*

= 1.7 and 10.9 Hz), 3.57 (1H, dd, *J* = 6.9 and 10.9 Hz), 3.53 (1H, dd, *J* = 4.0 and 10.9 Hz), 3.32 (1H, dd, *J* = 4.3 and 8.6 Hz), 1.10 (3H, d, *J* = 6.6 Hz), 1.06 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.8, 135.5, 133.4, 133.3, 129.7, 128.4, 128.3×2, 128.1, 127.9, 127.7×3, 127.6, 127.4, 101.9, 76.1, 75.4, 75.3, 73.4, 72.3, 70.7, 68.9, 67.9, 33.9, 26.8, 19.2, 17.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{46}H_{53}IO_6SiNa$ 879.2552; found 879.2546.

1-((*tert*-Butyldiphenylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-β-D-glucopyranoside (3eβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3eβ** (11.2 mg, 22%). Colorless syrup; R_f 0.38 (8/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ +24.1° (*c* 1.32, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.66 (5H, m), 7.42-7.22 (18H, m), 7.18-7.16 (2H, m), 4.96 and 4.85 (2H, ABq, *J* = 10.3 Hz), 4.77 and 4.56 (2H, ABq, *J* = 10.6 Hz), 4.54 (1H, d, *J* = 8.9 Hz), 4.50 and 4.39 (2H, ABq, *J* = 12.3 Hz), 3.93-3.87 (2H, m), 3.84 (1H, dd, *J* = 8.9 and 10.6 Hz), 3.68 (1H, dd, *J* = 8.6 and 10.6 Hz), 3.64 (1H, dd, *J* = 4.3 and 10.9 Hz), 3.60-3.55 (2H, m), 3.53 (1H, dd, *J* = 1.8 and 10.9 Hz), 3.38 (1H, ddd, *J* = 1.8, 4.3 and 11.5 Hz), 1.32 (3H, d, *J* = 6.0 Hz), 1.05 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 137.8×2, 135.7, 135.6, 133.8, 133.6, 129.6, 128.4×2, 128.3, 128.1, 127.9, 127.7×2, 127.6, 127.5, 102.0, 86.0, 79.5, 76.5, 75.5, 75.1, 74.9, 73.5, 68.5, 67.3, 33.8, 26.9, 19.3, 16.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{46}H_{53}IO_6SiNa$ 879.2552; found 879.2549.

Cyclohexyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-α-D-glucopyranoside (3fα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3fα** (25.7 mg, 67%). Colorless syrup; R_f 0.47 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +20.3º (*c* 1.95, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.41 (2H, m), 7.38-7.24 (11H, m), 7.18-7.15 (2H, m), 5.35 (1H, br s), 4.85 and 4.47 (2H, ABq, *J* = 10.6 Hz), 4.72 and 4.52 (2H, ABq, *J* = 11.7 Hz), 4.70 and 4.52 (2H, ABq, *J* = 10.4 Hz), 4.47 (1H, dd, *J* = 1.7 and 4.3 Hz), 3.96 (1H, ddd, *J* = 1.7, 4.3 and 10.0 Hz), 3.91 (1H, dd, *J* = 8.3 and 10.0 Hz), 3.80 (1H, dd, *J* = 4.3 and 10.9 Hz), 3.70 (1H, dd, *J* = 1.7 and 10.9 Hz), 3.59 (1H, m), 3.35 (1H, dd, *J* = 4.3 and 8.3 Hz), 1.82 (2H, br s), 1.68 (2H, br s), 1.50 (1H, br s), 1.37-1.17 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7×2, 127.6, 127.4, 99.4, 76.1, 75.7, 75.3, 73.3, 72.1, 70.9, 69.0, 34.7, 33.2, 31.5, 25.5. 24.0, 23.8, 76.1, 75.7, 75.3, 73.3, 72.1, 70.9, 69.0, 34.7, 33.2, 31.5, 25.5, 24.0, 23.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{39}IO_5Na$ 665.1740; found 665.1730.

Cyclohexyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-β-D-glucopyranoside (3fβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3fβ** (9.0 mg, 23%). White solid; R_f 0.43 (8/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +15.2º (*c* 1.15, $CHCl_3$); mp 83-85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (2H, m), 7.36-7.25 (11H, m), 7.21-7.19 (2H, m), 4.98 and 4.85 (2H, ABq, *J* = 10.0 Hz), 4.80 and 4.58 (2H, ABq, *J* = 10.6 Hz), 4.64 (1H, d, *J* = 8.9 Hz), 4.61 and 4.56 (2H, ABq, *J* = 12.3 Hz), 3.92 (1H, dd, *J* = 8.9 and 10.6 Hz), 3.75-3.65 (4H, m), 3.58 (1H, dd, *J* = 8.9 and 9.8 Hz), 3.50

(1H, ddd, *J* = 2.0, 4.9 and 9.8 Hz), 1.95 (2H, br s), 1.83-1.76 (2H, m), 1.53-1.21 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 137.8×2, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 101.7, 86.1, 79.7, 78.1, 75.4, 75.2, 74.9, 73.4, 68.7, 34.1, 33.4, 31.4, 25.6, 24.0, 23.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{39}IO_5Na$ 665.1740; found 665.1737.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranoside (3gα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3gα** (27.1 mg, 65%). Colorless syrup; R_f 0.42 (8/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +15.2° (*c* 1.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.22 (13H, m), 7.18-7.16 (2H, m), 5.26 (1H, br s), 4.86 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.71 and 4.51 (2H, ABq, *J* = 12.1 Hz), 4.70 and 4.57 (2H, ABq, *J* = 11.5 Hz), 4.40 (1H, dd, *J* = 1.5 and 4.1 Hz), 4.03 (1H, ddd, *J* = 2.0, 4.9 and 9.7 Hz), 3.89 (1H, dd, *J* = 8.9 and 9.7 Hz), 3.79 (1H, dd, *J* = 4.9 and 10.9 Hz), 3.68 (1H, dd, *J* = 2.0 and 10.9 Hz), 3.30 (2H, m), 2.17 (1H, br d), 1.95-1.89 (1H, m), 1.36-1.26 (2H, m), 1.19-1.12 (1H, m), 0.88 (3H, d, *J* = 7.2 Hz), 0.82 (3H, d, *J* = 6.6 Hz), 0.72 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.9, 137.8, 128.5, 128.4, 128.0×2, 127.9, 127.8, 127.7, 127.6, 100.4, 86.2, 79.7, 77.9, 75.3, 75.1, 75.0, 47.7, 40.3, 34.3, 34.1, 31.5, 25.0, 23.1, 22.3, 21.0, 15.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{47}IO_5Na$ 721.2366; found 721.2365.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-β-D-glucopyranoside (3gβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3gβ** (7.7 mg, 18%). White solid; R_f 0.39 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +15.2° (*c* 1.15, $CHCl_3$); mp 98-99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (2H, m), 7.36-7.26 (11H, m), 7.22-7.20 (2H, m), 4.98 and 4.86 (2H, ABq, *J* = 10.4 Hz), 4.80 and 4.61 (2H, ABq, *J* = 10.9 Hz), 4.60 and 4.53 (2H, ABq, *J* = 12.0 Hz), 4.61 (1H, d, *J* = 8.9 Hz), 3.88 (1H, dd, *J* = 8.9 and 10.9 Hz), 3.75-3.71 (2H, m), 3.69 (1H, dd, *J* = 1.7 and 10.9 Hz), 3.62 (1H, dd, *J* = 8.9 and 9.7 Hz), 3.52-3.45 (2H, m), 2.32-2.27 (1H, m), 2.15 (1H, br d), 1.65 (2H, br d), 0.95 (3H, d, *J* = 6.6 Hz), 0.89 (3H, d, *J* = 6.9 Hz), 0.79 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.7, 128.4, 128.3, 128.2, 128.1×2, 127.8, 127.7, 127.6, 127.4, 103.1, 81.9, 76.2, 75.3, 73.3, 72.2, 71.1, 69.0, 48.4, 42.5, 34.5, 34.2, 31.5, 25.8, 23.2, 22.2×2, 21.0, 16.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{47}IO_5Na$ 721.2366; found 721.2374.

(3*S*)-2,2-Dimethyl-1,3-dioxolane-4-methyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranoside (3hα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 3/1) to give compound **3hα** (24.4 mg, 60%). Colorless syrup; R_f 0.40 (3/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +13.4° (*c* 1.81, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.24 (13H, m), 7.16-7.14 (2H, m), 5.28 (1H, br s), 4.85 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.70 and 4.50 (2H, ABq, *J* = 12.1

Hz), 4.69 and 4.53 (2H, ABq, *J* = 12.3 Hz), 4.58 (1H, dd, *J* = 1.4 and 4.3 Hz), 4.24 (1H, m), 4.01 (1H, dd, *J* = 6.6 and 8.3 Hz), 3.89 (1H, dd, *J* = 8.3 and 9.8 Hz), 3.85 (1H, ddd, *J* = 1.7, 4.6 and 9.8 Hz), 3.77 (1H, dd, *J* = 4.6 and 10.9 Hz), 3.70 (1H, dd, *J* = 1.7 and 10.9 Hz), 3.66 (1H, dd, *J* = 4.6 and 10.9 Hz), 3.62 (1H, dd, *J* = 6.6 and 8.3 Hz), 3.49 (1H, dd, *J* = 6.3 and 10.3 Hz), 3.31 (1H, dd, *J* = 4.3 and 8.3 Hz), 1.39 (3H, s), 1.35 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 138.2, 137.7, 128.4, 128.3×2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 109.7, 101.8, 75.8, 75.2, 74.5, 73.4, 72.3, 70.9, 68.9, 68.8, 66.4, 33.0, 26.7, 25.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{39}IO_7Na$ 697.1638; found 697.1642.

(3*S*)-2,2-Dimethyl-1,3-dioxolane-4-methyl 3',4',6'-tri-*O*-benzyl-2-deoxy-2-iodo-β-D-glucopyranoside (3hβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 3/1) to give compound **3hβ** (10.4 mg, 26%). Colorless syrup; R_f 0.40 (3/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ +32.5° (*c* 0.86, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.41 (2H, m), 7.37-7.27 (11H, m), 7.19-7.17 (2H, m), 4.97 and 4.85 (2H, ABq, *J* = 10.1 Hz), 4.80 and 4.56 (2H, ABq, *J* = 10.6 Hz), 4.61 and 4.53 (2H, ABq, *J* = 12.0 Hz), 4.57 (1H, d, *J* = 8.9 Hz), 4.32 (1H, m), 4.10 (1H, dd, *J* = 6.3 and 8.3 Hz), 3.97 (2H, m), 3.90 (1H, dd, *J* = 8.9 and 10.9 Hz), 3.71 (3H, m), 3.62 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.53 (1H, dd, *J* = 7.2 and 9.8 Hz), 3.50 (1H, ddd, *J* = 2.3, 4.0 and 9.8 Hz), 1.44 (3H, s), 1.36 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.7, 128.5, 128.4×2, 128.1, 127.9×2, 127.8×2, 127.7, 109.4,

103.4, 85.7, 79.5, 75.6, 75.2, 75.0, 74.0, 73.5, 70.6, 68.4, 67.1, 32.5, 27.0, 25.3; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{33}H_{39}IO_7Na$ 697.1638; found 697.1632.

1-((Triethylsilyl)oxy)-4-buthyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranoside (3iα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3iα** (22.0 mg, 49%). Colorless syrup; R_f 0.39 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +9.27º (*c* 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.24 (13H, m), 7.16-7.14 (2H, m), 5.21 (1H, br s), 4.84 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.72 and 4.52 (2H, ABq, *J* = 11.9 Hz), 4.69 and 4.51 (2H, ABq, *J* = 11.6 Hz), 4.50 (1H, dd, *J* = 1.2 and 4.3 Hz), 3.90 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.84 (1H, ddd, *J* = 1.8, 4.6 and 9.8 Hz), 3.79 (1H, dd, *J* = 4.6 and 10.9 Hz), 3.70-3.65 (2H, m), 3.60 (2H, t, *J* = 6.0 Hz), 3.41 (1H, dt, *J* = 6.6 and 9.5 Hz), 3.32 (1H, dd, *J* = 4.3 and 8.6 Hz), 1.62-1.51 (4H, m), 0.95 (9H, t, *J* = 7.8 Hz), 0.59 (6H, q, *J* = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.4, 128.4, 128.3×2, 128.1, 128.0, 127.8, 127.6×2, 127.4, 101.4, 75.9, 75.2, 73.4, 72.1, 70.9, 68.9, 67.9, 62.4, 33.7, 29.5, 26.0, 6.79, 4.37; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{37}H_{51}IO_6SiNa$ 769.2397; found 769.2374.

1-((Triethylsilyl)oxy)-4-buthyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-β-D-glucopyranoside (3iβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3iβ** (12.4 mg, 28%). Colorless syrup; R_f 0.35 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +24.5º (*c* 0.88, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (2H, m), 7.37-7.25 (11H, m), 7.19-7.17 (2H, m), 4.98 and

4.86 (2H, ABq, *J* = 10.3 Hz), 4.80 and 4.56 (2H, ABq, *J* = 10.9 Hz), 4.61 and 4.54 (2H, ABq, *J* = 12.3 Hz), 4.53 (1H, d, *J* = 8.9 Hz), 3.95-3.89 (2H, m), 3.75-3.65 (5H, m), 3.61 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.55 (1H, dt, *J* = 6.6 and 9.8 Hz), 3.49 (1H, ddd, *J* = 2.3, 4.3 and 9.8 Hz), 1.71-1.60 (4H, m), 0.96 (9H, t, *J* = 7.8 Hz), 0.60 (6H, q, *J* = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.7, 128.5, 128.4×2, 128.3, 127.9×3, 127.8, 127.6, 103.1, 85.9, 79.6, 75.5, 75.2, 74.9, 73.5, 70.1, 68.6, 62.5, 33.1, 29.4, 25.9, 6.83, 4.41; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{51}IO_6SiNa$ 769.2397; found 769.2377.

1-((*tert*-Butyldimethylsilyl)oxy)-4-buthyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranoside (3jα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3jα** (24.0 mg, 54%). Colorless syrup; R_f 0.42 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +8.80º (*c* 1.90, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.25 (13H, m), 7.16-7.14 (2H, m), 5.21 (1H, br s), 4.85 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.72 and 4.52 (2H, ABq, *J* = 12.0 Hz), 4.70 and 4.51 (2H, ABq, *J* = 11.2 Hz), 4.49 (1H, dd, *J* = 1.2 and 4.0 Hz), 3.91 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.84 (1H, ddd, *J* = 1.8, 4.6 and 9.8 Hz), 3.79 (1H, dd, *J* = 4.6 and 10.9 Hz), 3.70-3.65 (2H, m), 3.60 (2H, t, *J* = 6.3 Hz), 3.41 (1H, dt, *J* = 6.6 and 9.8 Hz), 3.32 (1H, dd, *J* = 4.0 and 8.6 Hz), 1.62-1.50 (4H, m), 0.89 (9H, s), 0.04 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.7, 128.4, 128.3×2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 101.4, 75.9, 75.3, 73.4, 72.1, 70.9, 68.9, 67.9, 62.8, 33.7, 29.4, 26.0, 18.3, -5.30; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{51}IO_6SiNa$ 769.2397; found 769.2385.

1-((*tert*-Butyldimethylsilyl)oxy)-4-buthyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-β-D-glucopyranoside (3jβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3jβ** (14.1 mg, 31%). White solid; R_f 0.38 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +23.3º (*c* 1.15, $CHCl_3$); mp 38-39 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (2H, m), 7.36-7.26 (11H, m), 7.19-7.17 (2H, m), 4.98 and 4.86 (2H, ABq, *J* = 10.3 Hz), 4.80 and 4.56 (2H, ABq, *J* = 10.9 Hz), 4.61 and 4.54 (2H, ABq, *J* = 12.3 Hz), 4.53 (1H, d, *J* = 8.9 Hz), 3.95-3.90 (2H, m), 3.75-3.64 (5H, m), 3.61 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.55 (1H, dt, *J* = 6.6 and 9.8 Hz), 3.49 (1H, ddd, *J* = 2.3, 4.3 and 9.8 Hz), 1.73-1.62 (4H, m), 0.89 (9H, s), 0.05 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.7, 128.5, 128.4×2, 128.1, 127.9×2, 127.8×2, 127.6, 103.1, 85.9, 79.6, 75.5, 75.2, 74.9, 70.1, 68.5, 62.8, 33.2, 29.3, 25.9, 18.3, -5.25; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{51}IO_6SiNa$ 769.2397; found 769.2401.

1-((Triethylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranoside (3kα)

: The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3kα** (21.6 mg, 49%). Colorless syrup; R_f 0.47 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +12.5º (*c* 1.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.25 (13H, m), 7.16-7.15 (2H, m), 5.52 (1H, br s), 4.85 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.73 and 4.50 (2H, ABq, *J* = 12.0 Hz), 4.70 and 4.53 (2H, ABq, *J* = 11.5 Hz), 4.58 (1H, br d, *J* = 4.0 Hz), 3.97 (1H, ddd, *J* = 1.5, 4.0 and 9.8 Hz), 3.93 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.85 (1H, m), 3.81 (1H, dd, *J* = 4.0 and 10.6 Hz), 3.70 (1H, br d, *J* = 10.6 Hz), 3.50 (1H, br d, *J* = 5.5 Hz), 3.33

(1H, dd, *J* = 4.0 and 8.6 Hz), 1.10 (3H, d, *J* = 6.6 Hz), 0.96 (9H, t, *J* = 8.1 Hz), 0.60 (6H, q, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.9, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7×3, 127.4, 101.9, 76.1, 75.4, 75.3, 73.3, 72.2, 70.7, 68.9, 67.1, 34.0, 17.7, 6.83, 4.36; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{49}IO_6SiNa$ 755.2241; found 755.2227.

1-((Triethylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-β-D-glucopyranoside (3kβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3kβ** (8.8 mg, 20%). Colorless syrup; R_f 0.42 (8/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ +27.9º (*c* 0.74, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.42 (2H, m), 7.37-7.25 (11H, m), 7.20-7.17 (2H, m), 4.97 and 4.86 (2H, ABq, *J* = 10.3 Hz), 4.80 and 4.59 (2H, ABq, *J* = 10.6 Hz), 4.63 (1H, d, *J* = 9.2 Hz), 4.61 and 4.53 (2H, ABq, *J* = 10.9 Hz), 3.90-3.82 (3H, m), 3.74-3.69 (3H, m), 3.62 (1H, dd, *J* = 8.9 and 9.8 Hz), 3.50-3.46 (2H, m), 1.27 (3H, d, *J* = 6.0 Hz), 0.95 (9H, t, *J* = 8.0 Hz), 0.60 (6H, q, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.8, 137.7, 128.5, 128.4×2, 128.1, 127.9×2, 127.7, 127.6, 102.1, 86.0, 79.6, 75.5, 75.2, 74.9, 73.6, 68.6, 66.5, 33.8, 16.8, 6.77, 4.39; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{49}IO_6SiNa$ 755.2241; found 755.2251.

1-((*tert*-Butyldimethylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-α-D-glucopyranoside (3lα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3lα** (22.1 mg, 50%). Colorless syrup; R_f 0.46 (8/1

n-hexane/EtOAc); $[\alpha]^{25}_{D}$ +12.8º (*c* 1.57, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.25 (13H, m), 7.16-7.14 (2H, m), 5.51 (1H, br s), 4.85 and 4.48 (2H, ABq, *J* = 10.6 Hz), 4.73 and 4.51 (2H, ABq, *J* = 12.4 Hz), 4.70 and 4.53 (2H, ABq, *J* = 11.5 Hz), 4.54 (1H, dd, *J* = 1.1 and 4.3 Hz), 3.97 (1H, ddd, *J* = 1.7, 4.3 and 10.1 Hz), 3.92 (1H, dd, *J* = 8.6 and 10.1 Hz), 3.85 (1H, m), 3.81 (1H, dd, *J* = 4.3 and 10.9 Hz), 3.70 (1H, dd, *J* = 1.7 and 10.9 Hz), 3.49 (1H, br d, *J* = 5.8 Hz), 3.32 (1H, dd, *J* = 4.3 and 8.6 Hz), 1.09 (3H, d, *J* = 6.6 Hz), 0.90 (9H, s), 0.05×2 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 137.9, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7×2, 127.6, 127.4, 101.8, 76.1, 75.3×2, 73.3, 72.2, 70.8, 68.9, 67.4, 34.0, 25.9, 18.2, 17.7, -5.35, -5.41; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{49}IO_6SiNa$ 755.2241; found 755.2261.

1-((*tert*-Butyldimethylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-2'-iodo-β-D-glucopyranoside (3lβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **3lβ** (10.4 mg, 24%). White solid; R_f 0.40 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_{D}$ +26.8º (*c* 0.77, $CHCl_3$); mp 54-55 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.25 (13H, m), 7.20-7.18 (2H, m), 4.97 and 4.86 (2H, ABq, *J* = 10.3 Hz), 4.80 and 4.60 (2H, ABq, *J* = 10.6 Hz), 4.63 (1H, d, *J* = 8.9 Hz), 4.56 and 4.54 (2H, ABq, *J* = 10.9 Hz), 3.90-3.81 (3H, m), 3.74-3.70 (3H, m), 3.61 (1H, dd, *J* = 8.9 and 9.8 Hz), 3.50-3.45 (2H, m), 1.26 (3H, d, *J* = 6.6 Hz), 0.89 (9H, s), 0.06 (3H, s), 0.04 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.8, 137.7, 128.5, 128.4×2, 128.1, 127.9×2, 127.7, 127.6, 101.9, 86.0, 79.6, 76.6,

75.5, 75.2, 74.9, 68.6, 66.8, 33.8, 25.9, 18.3, 16.7, -5.25, -5.30; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{49}IO_6SiNa$ 755.2241; found 755.2253.

1-((*tert*-Butyldiphenylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-α-D-glucopyranoside (4eα): The anomeric mixture was purified by flash column chromatography (10g, $CHCl_3$) to give compound **4eα** (26.7 mg, 61%). Colorless syrup; R_f 0.48 ($CHCl_3$); $[\alpha]^{25}_D$ +49.6º (*c* 1.46, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.69-7.65 (4H, m), 7.44-7.26 (19H, m), 7.18-7.16 (2H, m), 5.22 (1H, br d, *J* = 2.9 Hz), 4.89 and 4.51 (2H, ABq, *J* = 10.6 Hz), 4.66 and 4.52 (2H, ABq, *J* = 12.3 Hz), 4.66 and 4.62 (2H, ABq, *J* = 12.3 Hz), 4.01 (1H, ddd, *J* = 5.2, 8.9 and 11.5 Hz), 3.94-3.86 (2H, m), 3.80 (1H, dd, *J* = 3.7 and 10.6 Hz), 3.67 (1H, dd, *J* = 1.7 and 10.6 Hz), 3.62 (1H, dd, *J* = 8.9 and 9.8 Hz), 3.60 (1H, dd, *J* = 6.9 and 10.6 Hz), 3.52 (1H, dd, *J* = 4.3 and 10.6 Hz), 2.28 (1H, dd, *J* = 5.2 and 12.6 Hz), 1.68 (1H, ddd, *J* = 3.7, 11.5 and 12.6 Hz), 1.10 (3H, d, *J* = 6.3 Hz), 1.04 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.5, 138.2, 135.6, 133.5, 129.6×2, 128.4, 128.3, 127.7, 127.6, 127.5×2, 97.9, 78.4, 77.8, 75.0, 74.2, 73.5, 71.7, 70.9, 68.9, 67.8, 35.6, 26.8, 19.2, 18.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{46}H_{54}O_6SiNa$ 753.3587; found 753.3578.

1-((*tert*-Butyldiphenylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-β-D-glucopyranoside (4eβ): The anomeric mixture was purified by flash column chromatography (10g, $CHCl_3$) to give compound **4eβ** (8.9 mg, 20%). Colorless syrup; R_f 0.53 ($CHCl_3$); $[\alpha]^{27}_D$ +2.31º (*c* 1.60, $CHCl_3$); ^1H

NMR (500 MHz, $CDCl_3$) δ 7.68-7.65 (4H, m), 7.41-7.19 (21H, m), 4.87 and 4.55 (2H, ABq, *J* = 10.9 Hz), 4.67 and 4.59 (2H, ABq, *J* = 11.8 Hz), 4.52 and 4.41 (2H, ABq, *J* = 12.3 Hz), 4.48 (1H, dd, *J* = 1.8 and 9.8 Hz), 3.95-3.89 (2H, m), 3.66 (1H, dd, *J* = 4.6 and 10.9 Hz,), 3.62 (1H, ddd, *J* = 5.2, 8.9 and 11.8 Hz), 3.57 (1H, dd, *J* = 1.7 and 10.9 Hz), 3.54-3.47 (2H, m), 3.30 (1H, ddd, *J* = 1.7, 4.6 and 9.7 Hz), 2.27 (1H, ddd, *J* = 1.8, 5.2 and 12.4 Hz), 1.60 (1H, ddd, *J* = 9.8, 11.8 and 12.4 Hz), 1.24 (3H, d, *J* = 6.1 Hz), 1.05 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4×2, 135.7, 135.6, 133.8, 133.7, 129.5, 128.4, 128.3×2, 128.0, 127.7, 127.6×3, 127.4, 98.1, 79.5, 78.1, 75.1, 74.9, 74.7, 73.5, 71.3, 69.2, 67.5, 37.0, 26.9, 19.3, 17.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{46}H_{54}O_6SiNa$ 753.3587; found 753.3583.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-α-D-glucopyranoside(4gα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **4gα** (20.0 mg, 58%). Colorless syrup; R_f 0.41 (8/1 *n*-hexane/EtOAc); $[\alpha]^{28}_D$ +49.3° (*c* 1.02, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.24 (13H, m), 7.18-7.16 (2H, m), 5.01 (1H, br d, *J* = 2.9 Hz), 4.89 and 4.49 (2H, ABq, *J* = 10.6 Hz), 4.68 and 4.64 (2H, ABq, *J* = 11.5 Hz), 4.65 and 4.49 (2H, ABq, *J* = 12.6 Hz), 3.99 (1H, ddd, *J* = 4.9, 8.9 and 11.8 Hz), 3.94 (1H, ddd, *J* = 2.0, 4.0 and 9.8 Hz), 3.79 (1H, dd, *J* = 4.0 and 10.6 Hz), 3.66 (1H, dd, *J* = 2.0 and 10.6 Hz), 3.59 (1H, dd, *J* = 8.9 and 9.8 Hz), 3.30 (1H, ddd, *J* = 4.0, 10.6 and 10.6 Hz), 2.25 (1H, dd, *J* = 4.9 and 12.6 Hz), 2.11-2.09 (1H, m), 2.04-1.98 (1H, m), 1.68 (1H, ddd, *J* = 3.8, 11.8 and 12.6 Hz), 1.39-1.32 (1H, m),

1.19-1.13 (1H, m), 0.90 (3H, d, *J* = 7.2 Hz), 0.83 (3H, d, *J* = 6.6 Hz), 0.74 (3H, d, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 128.4, 128.3×2, 128.1, 127.6, 127.6, 127.5, 127.4, 96.3, 79.7, 78.2, 76.2, 75.1, 75.0, 73.6, 71.2, 69.7, 47.8, 40.7, 37.3, 34.4, 31.4, 25.2, 23.1, 22.3, 21.0, 15.8; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{37}H_{48}O_5Na$ 595.3399; found 595.3405.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-β-D-glucopyranoside (4gβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **4gβ** (8.2 mg, 24%). White solid; R_f 0.48 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ -51.5º (*c* 1.28, $CHCl_3$); mp 97-98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (15H, m), 4.90 and 4.61 (2H, ABq, *J* = 10.9 Hz), 4.68 and 4.55 (2H, ABq, *J* = 11.8 Hz), 4.62 and 4.59 (2H, ABq, *J* = 11.8 Hz), 4.54 (1H, dd, *J* = 1.8 and 9.8 Hz), 3.72 (1H, br d, *J* = 3.5 Hz), 3.67 (1H, ddd, *J* = 4.9, 8.6 and 11.5 Hz), 3.53 (1H, ddd, *J* = 4.3, 11.8 and 11.8 Hz), 3.52 (1H, dd, *J* = 8.6 and 9.8 Hz), 3.38 (1H, ddd, *J* = 3.2, 3.2 and 9.8 Hz), 2.34-2.28 (1H, m), 2.27 (1H, ddd, *J* = 1.8, 4.9 and 12.3 Hz), 2.00-1.97 (1H, m), 1.66-1.61 (3H, m), 1.39-1.31 (1H, m), 1.23-1.18 (1H, m), 0.91 (3H, d, *J* = 6.6 Hz), 0.90 (3H, d, *J* = 6.9 Hz), 0.82 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.6, 138.2, 128.3×3, 127.9, 127.8, 127.7, 127.5×2, 99.5, 80.5, 78.5, 77.7, 74.9, 73.4, 71.7, 70.8, 69.0, 48.8, 43.0, 36.0, 34.3, 31.6, 25.8, 23.3, 22.2, 21.1, 16.4; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{37}H_{48}O_5Na$ 595.3399; found 595.3390.

(3*S*)-2,2-Dimethyl-1,3-dioxolane-4-methyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-α-D-glucopyranoside (4hα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 3/1) to give compound **4hα** (18.2 mg, 55%). Colorless syrup; R_f 0.45 (3/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +71.9º (*c* 1.27, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (13H, m), 7.18-7.17 (2H, m), 4.99 (1H, br d, *J* = 2.9 Hz), 4.88 and 4.52 (2H, ABq, *J* = 10.9 Hz), 4.63 and 4.51 (2H, ABq, *J* = 12.3 Hz), 4.66 and 4.62 (2H, ABq, *J* = 11.8 Hz), 4.26 (1H, m), 4.03 (1H, dd, *J* = 6.6 and 8.3 Hz), 3.98 (1H, ddd, *J* = 5.2, 8.9 and 11.5 Hz), 3.78-3.58 (6H, m), 3.46 (1H, dd, *J* = 6.3 and 10.3 Hz), 2.35 (1H, dd, *J* = 5.2 and 12.4 Hz), 1.73 (1H, ddd, *J* = 3.7, 11.5 and 12.4 Hz), 1.40 (3H, s), 1.36 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.5, 138.1, 128.4, 128.3, 127.9, 127.8, 127.6×2, 127.5, 109.6, 97.8, 78.2, 77.5, 75.0, 74.7, 73.5, 71.8, 70.9, 68.9, 66.8, 35.3, 26.7, 25.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{40}O_7Na$ 571.2672; found 571.2668.

(3*S*)-2,2-Dimethyl-1,3-dioxolane-4-methyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-β-D-glucopyranoside (4hβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 3/1) to give compound **4hβ** (10.7 mg, 33%). Colorless syrup; R_f 0.43 (3/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ -5.86º (*c* 0.71, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (13H, m), 7.21-7.20 (2H, m), 4.89 and 4.55 (2H, ABq, *J* = 10.6 Hz), 4.67 and 4.59 (2H, ABq, *J* = 11.8 Hz), 4.62 and 4.55 (2H, ABq, *J* = 10.3 Hz), 4.48 (1H, dd, *J* = 1.8 and 9.8 Hz), 4.28 (1H, m), 4.04 (1H, dd, *J* = 6.3 and 8.3

Hz), 3.93 (1H, dd, *J* = 4.9 and 10.6 Hz), 3.83 (1H, dd, *J* = 6.0 and 8.3 Hz), 3.74 (1H, dd, *J* = 2.0 and 10.9 Hz), 3.70 (1H, dd, *J* = 4.9 and 10.9 Hz), 3.65 (1H, ddd, *J* = 4.9, 8.9 and 11.5 Hz), 3.54 (1H, dd, *J* = 5.7 and 10.3 Hz), 3.50 (1H, dd, *J* = 8.9 and 9.8 Hz), 3.40 (1H, ddd, *J* = 2.0, 4.9 and 9.8 Hz), 2.34 (1H, ddd, *J* = 1.8, 4.9 and 12.6 Hz), 1.65 (1H, ddd, *J* = 9.8, 11.5 and 12.6 Hz), 1.41 (3H, s, CH_3), 1.36 (3H, s, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 138.2, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 109.3, 100.2, 79.3, 78.0, 75.2, 75.0, 73.5, 71.4, 69.3, 69.2, 66.6, 36.5, 26.7, 25.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{40}O_7Na$ 571.2672; found 571.2679.

1-((*tert*-Butyldimethylsilyl)oxy)-4-buthyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-α-D-glucopyranoside (4jα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **4jα** (20.9 mg, 56%). Colorless syrup; R_f 0.39 (8/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ -3.45° (*c* 1.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.25 (13H, m), 7.18-7.16 (2H, m), 4.94 (1H, br d, *J* = 2.6 Hz), 4.89 and 4.51 (2H, ABq, *J* = 10.6 Hz), 4.67 and 4.63 (2H, ABq, *J* = 11.8 Hz), 4.64 and 4.51 (2H, ABq, *J* = 10.9 Hz), 3.99 (1H, ddd, *J* = 4.9, 8.9 and 11.5 Hz), 3.79-3.73 (2H, m), 3.66 (1H, dd, *J* = 1.5 and 10.1 Hz), 3.64-3.60 (4H, m), 3.37 (1H, dt, *J* = 6.1 and 9.7 Hz), 2.27 (1H, dd, *J* = 4.9 and 12.6 Hz), 1.71 (1H, ddd, *J* = 3.7, 11.5 and 12.6 Hz), 1.62-1.52 (4H, m), 0.89 (9H, s), 0.04 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.5, 138.2, 128.3×2, 127.9×2, 127.6, 127.5, 97.3,

78.3, 77.8, 75.0, 73.4, 71.8, 70.7, 68.9, 67.1, 62.9, 35.5, 31.6, 26.0, 18.3, -5.30; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{37}H_{52}O_6SiNa$ 643.3431; found 643.3436.

1-((*tert*-Butyldimethylsilyl)oxy)-4-buthyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-β-D-glucopyranoside (4jβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **4jβ** (8.5 mg, 23%). Colorless syrup; R_f 0.42 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +59.1° (*c* 1.74, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (13H, m), 7.21-7.20 (2H, m), 4.89 and 4.55 (2H, ABq, *J* = 10.9 Hz), 4.68 and 4.56 (2H, ABq, *J* = 11.7 Hz), 4.62 and 4.59 (2H, ABq, *J* = 12.3 Hz), 4.43 (1H, dd, *J* = 1.8 and 9.8 Hz), 3.92 (1H, dt, *J* = 6.6 and 9.5 Hz), 3.76 (1H, dd, *J* = 2.0 and 10.9 Hz), 3.71 (1H, dd, *J* = 4.9 and 10.9 Hz), 3.66 (1H, ddd, *J* = 4.9, 8.6 and 11.5 Hz), 3.62 (1H, t, *J* = 6.0 Hz), 3.50 (1H, dd, *J* = 8.6 and 9.7 Hz), 3.46 (1H, dt, *J* = 6.9 and 9.5 Hz), 3.41 (1H, ddd, *J* = 2.0, 4.9 and 9.7 Hz), 2.34 (1H, ddd, *J* = 1.8, 4.9 and 12.6 Hz), 1.67-1.54 (5H, m), 0.89 (9H, s), 0.04 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.3, 128.4, 128.3×2, 128.0, 127.8, 127.7, 127.6, 127.5, 99.8, 79.5, 78.2, 75.2, 75.0, 73.4, 71.4, 69.4, 69.2, 62.9, 36.7, 29.4, 26.0, 18.3, -5.30; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{37}H_{52}O_6SiNa$ 643.3431; found 643.3440.

1-((*tert*-Butyldimethylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-α-D-glucopyranoside (4lα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **4lα** (19.3 mg, 53%). Colorless syrup; R_f 0.41 (8/1

n-hexane/EtOAc); $[\alpha]^{27}_{D}$ +52.4º (*c* 1.61, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.24 (13H, m), 7.18-7.16 (2H, m), 5.21 (1H, br d, *J* = 3.2 Hz), 4.89 and 4.51 (2H, ABq, *J* = 10.9 Hz), 4.67 and 4.63 (2H, ABq, *J* = 11.5 Hz), 4.66 and 4.51 (2H, ABq, *J* = 12.1 Hz), 4.00 (1H, ddd, *J* = 5.2, 9.2 and 11.8 Hz), 3.86 (1H, ddd, *J* = 2.1, 3.4 and 9.7 Hz), 3.83-3.78 (2H, m), 3.66 (1H, dd, *J* = 2.1 and 10.4 Hz), 3.62 (1H, dd, *J* = 9.2 and 9.7 Hz), 3.53 (1H, dd, *J* = 6.9 and 10.6 Hz), 3.48 (1H, dd, *J* = 4.6 and 10.6 Hz), 2.30 (1H, ddd, *J* = 1.2, 5.2 and 12.9 Hz), 1.70 (1H, ddd, *J* = 3.8, 11.8 and 12.9 Hz), 1.09 (3H, d, *J* = 6.3 Hz), 0.88 (9H, s), 0.04 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.5, 138.2, 128.3×2, 128.0, 127.9, 127.6, 127.5×2, 97.8, 78.5, 77.8, 75.0, 74.2, 73.5, 71.7, 70.9, 68.9, 67.2, 35.7, 25.9, 18.2, 17.9, -5.33, -5.40; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{50}O_6SiNa$ 629.3274; found 629.3260.

1-((*tert*-Butyldimethylsilyl)oxy)-(2*R*)-2-propyl 3',4',6'-tri-*O*-benzyl-2'-deoxy-β-D-glucopyranoside (4lβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **4lα** (9.1 mg, 25%). Colorless syrup; R_f 0.40 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_{D}$ -2.27º (*c* 1.53, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (13H, m), 7.22-7.20 (2H, m), 4.89 and 4.56 (2H, ABq, *J* = 10.9 Hz), 4.68 and 4.62 (2H, ABq, *J* = 11.5 Hz), 4.62 and 4.57 (2H, ABq, *J* = 11.5 Hz), 4.54 (1H, dd, *J* = 1.7 and 9.8 Hz), 3.89-3.83 (2H, m), 3.74-3.70 (2H, m), 3.66 (1H, ddd, *J* = 5.2, 8.9 and 11.8 Hz), 3.51 (1H, dd, *J* = 8.9 and 9.5 Hz), 3.45-3.37 (2H, m), 2.31 (1H, ddd, *J* = 1.7, 5.2 and 12.6 Hz), 1.64 (1H, ddd, *J* = 9.7, 11.8 and 12.6 Hz), 1.17 (3H, d, *J* = 6.0 Hz), 0.88 (9H, s),

0.05 (3H, s), 0.04 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4×2, 128.4, 128.3×2, 128.0, 127.7×2, 127.6, 127.5, 98.1, 79.5, 78.1, 75.2, 75.0, 74.7, 73.5, 71.3, 69.4, 66.9, 37.1, 25.9, 18.3, 17.1, -5.28, -5.32; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{50}O_6SiNa$ 629.3274; found 629.3279.

Cyclohexylmethyl 4,6-di-*O*-benzyl-2,3-dideoxy-D-erythro-hex-2-enopyranoside (5a): The residue was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **5α** (14.7 mg, 58%). Colorless syrup; R_f 0.45 (8/1 *n*-hexane/EtOAc); $[\alpha]^{28}_D$ +76.3° (*c* 1.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.23 (10H, m), 6.06 (1H, br d, *J* = 10.3 Hz), 5.77 (1H, dt, *J* = 2.0 and 10.3 Hz), 4.71 (1H, br s), 4.65 and 4.51 (2H, ABq, *J* = 12.0 Hz), 4.60 and 4.43 (2H, ABq, *J* = 11.5 Hz), 4.16 (1H, dd, *J* = 1.2 and 9.2 Hz), 3.96 (1H, ddd, *J* = 2.0, 4.0 and 9.2 Hz), 3.74 (1H, dd, *J* = 4.0 and 10.6 Hz), 3.70 (1H, dd, *J* = 2.0 and 10.6 Hz), 3.59 (1H, dd, *J* = 6.9 and 9.5 Hz), 3.29 (1H, dd, *J* = 6.3 and 9.5 Hz), 1.77-1.54 (6H, m), 1.26-1.09 (3H, m), 0.95-0.88 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 138.1, 128.3×2, 127.8×2, 127.7, 127.5, 126.7, 94.6, 74.3, 73.3, 71.0, 70.4, 69.1, 68.9, 38.0, 30.1, 30.0, 26.6, 25.8, 25.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{34}O_4Na$ 445.2355; found 445.2346.

Mixture of compounds 8, 9 and 10: The residue was purified by flash column chromatography (10g, $CHCl_3$/EtOAc = 30/1) to give the mixture of **8**, **9** and **10** (21.1 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.25 (13H, m), 7.18-7.16 (2H, m), 5.11 (1H, d, *J* = 4.0 Hz), 4.89 and 4.51 (2H, ABq, *J* = 10.6 Hz), 4.65 and 4.50 (2H, ABq, *J* = 12.6 Hz), 4.68 and 4.64 (2H, ABq, *J* = 11.5 Hz), 4.02 (1H, dd, *J* = 9.2 and

11.4 Hz), 3.85 (1H, ddd, *J* = 2.0, 4.0 and 9.8 Hz), 3.79 (1H, dd, *J* = 4.0 and 10.6 Hz), 3.67 (1H, dd, *J* = 2.0 and 10.6 Hz), 3.61 (1H, dd, *J* = 9.2 and 9.8 Hz), 2.24 (0.29H, ddd, *J* = 1.2, 4.0 and 12.9 Hz), 1.76-1.70 (0.89H, m); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{29}D_{11}O_5Na$ 550.3464; found 550.3466 and $[M + Na]^+$ calcd for $C_{33}H_{28}D_{12}O_5Na$ 551.3527; found 551.3538.

Mixture of compounds 11, 12 and 13: The residue was purified by flash column chromatography (10g, $CHCl_3$/EtOAc = 30/1) to give the mixture of **11**, **12** and **13** (4.9 mg, 16%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.25 (13H, m), 7.23-7.21 (2H, m), 4.90 and 4.56 (2H, ABq, *J* = 10.9 Hz), 4.68 and 4.59 (2H, ABq, *J* = 11.5 Hz), 4.62 and 4.57 (2H, ABq, *J* = 12.4 Hz), 4.56 (1H, d, *J* = 7.8 Hz), 3.77 (1H, dd, *J* = 2.0 and 10.6 Hz), 3.68 (1H, dd, *J* = 5.2 and 10.6 Hz), 3.66 (1H, dd, *J* = 8.3 and 11.5 Hz), 3.47 (1H, dd, *J* = 8.3 and 9.8 Hz), 3.41 (1H, ddd, *J* = 2.0, 5.2 and 9.8 Hz), 2.31 (0.31H, ddd, *J* = 1.8, 4.9 and 12.4 Hz), 1.70-1.63 (0.85H, m); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{29}D_{11}O_5Na$ 550.3464; found 550.3456 and $[M + Na]^+$ calcd for $C_{33}H_{28}D_{12}O_5Na$ 551.3527; found 551.3531.

Cyclohexylmethyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-α-D-galactopyranoside (16aα): The residue was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **16aα** (34.7 mg, 88%). Colorless syrup; R_f 0.41 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +75.7º (*c* 0.79, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.43 (2H, m), 7.38-7.22 (13H, m), 4.91 (1H, br s), 4.89 and 4.52 (2H, ABq, *J* = 11.2 Hz), 4.77 and 4.72 (2H, ABq, *J* = 11.2 Hz), 4.49 and 4.42 (2H, ABq, *J* = 11.8 Hz), 4.48 (1H, dd, *J* = 1.2 and 4.3

Hz), 4.01 (1H, dd, *J* = 6.6 and 6.9 Hz), 3.95-3.91 (2H, m), 3.56 (1H, dd, *J* = 6.9 and 9.5 Hz), 3.53 (1H, dd, *J* = 6.6 and 9.5 Hz), 3.47 (1H, dd, *J* = 6.6 and 9.5 Hz), 3.25 (1H, dd, *J* = 6.3 and 9.5 Hz), 1.80-1.60 (6H, m), 1.30-1.12 (3H, m), 1.01-0.87 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.9×2, 128.4×2, 128.2×2, 128.0, 127.8, 127.7×2, 98.9, 79.0, 75.2, 74.9, 74.2, 73.5, 73.2, 69.6, 68.8, 50.9, 37.6, 30.0, 29.9, 26.6, 25.8×2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{34}H_{41}IO_5Na$ 679.1896; found 679.1891.

Cyclohexylmethyl 3,4-di-*O*-benzyl-2,6-dideoxy-2-iodo-α-D-glucopyranoside (17aα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **17aα** (28.4 mg, 64%). Colorless syrup; R_f 0.43 (8/1 *n*-hexane/EtOAc); $[\alpha]^{28}_D$ +1.28º (*c* 1.78, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.41 (2H, m), 7.36-7.25 (8H, m), 5.07 (1H, br s), 4.91 and 4.61 (2H, ABq, *J* = 10.9 Hz), 4.69 and 4.52 (2H, ABq, *J* = 11.2 Hz), 4.48 (1H, dd, *J* = 1.1 and 4.3 Hz), 3.79 (1H, dq, *J* = 6.4 and 9.5 Hz), 3.47 (1H, dd, *J* = 8.9 and 9.5 Hz), 3.40 (1H, dd, *J* = 6.6 and 9.2 Hz), 3.24 (1H, dd, *J* = 4.3 and 8.9 Hz), 3.15 (1H, dd, *J* = 6.3 and 9.5 Hz), 1.71-1.65 (5H, m), 1.55-1.47 (1H, m), 1.31 (3H, d, *J* = 6.4 Hz), 1.27-1.10 (3H, m), 0.93-0.86 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.8, 128.4, 128.2, 128.0, 127.7, 101.4, 81.6, 75.5, 73.5, 70.9, 68.2, 37.8, 34.6, 29.9, 29.8, 26.5, 25.8, 25.7, 18.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{35}IO_4Na$ 573.1478; found 573.1467.

Cyclohexylmethyl 3,4-di-*O*-benzyl-2,6-dideoxy-2-iodo-β-D-glucopyranoside (17aβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound

17aβ (11.0 mg, 25%). White solid; R_f 0.40 (8/1 *n*-hexane/EtOAc); $[\alpha]^{28}_D$ +29.8º (*c* 1.25, $CHCl_3$); mp 110-111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (2H, m), 7.37-7.28 (8H, m), 4.98 and 4.85 (2H, ABq, *J* = 10.3 Hz), 4.86 and 4.65 (2H, ABq, *J* = 10.8 Hz), 4.49 (1H, d, *J* = 8.9 Hz), 3.91 (1H, dd, *J* = 8.9 and 10.8 Hz), 3.71-3.66 (2H, m), 3.43 (1H, dq, *J* = 6.2 and 9.2 Hz), 3.27 (1H, dd, *J* = 7.1 and 9.2 Hz), 3.20 (1H, dd, *J* = 8.9 and 9.2 Hz), 1.92-1.89 (1H, m), 1.79-1.59 (5H, m), 1.31 (3H, d, *J* = 6.2 Hz), 1.28-1.11 (3H, m), 1.01-0.92 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 128.5, 128.4, 128.1, 128.0, 127.9, 103.1, 85.8, 85.1, 76.1, 75.5, 75.3, 71.4, 37.8, 33.6, 30.1, 29.8, 26.6, 25.8, 25.7, 17.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{35}IO_4Na$ 573.1478; found 573.1475.

Cyclohexylmethyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranoside (18aα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **18aα** (20.5 mg, 65%). Colorless syrup; R_f 0.43 (8/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +43.1º (*c* 1.71, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.24 (15H, m), 4.94 (1H, br d, *J* = 3.2 Hz), 4.93 and 4.62 (2H, ABq, *J* = 11.8 Hz), 4.62 and 4.62 (2H, ABq, *J* = 12.6 Hz), 4.51 and 4.43 (2H, ABq, *J* = 11.7 Hz), 3.95-3.92 (2H, m), 3.89 (1H, dd, *J* = 6.6 and 6.9 Hz), 3.60 (1H, dd, *J* = 6.9 and 9.5 Hz), 3.56 (1H, dd, *J* = 6.6 and 9.5 Hz), 3.41 (1H, dd, *J* = 7.2 and 9.5 Hz), 3.16 (1H, dd, *J* = 6.1 and 9.5 Hz), 2.21 (1H, ddd, *J* = 3.8, 12.6 and 12.6 Hz), 1.98 (1H, dd, *J* = 4.6 and 12.6 Hz), 1.74-1.65 (5H, m), 1.58-1.51 (1H, m), 1.26-1.11 (3H, m), 0.95-0.86 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 138.5, 138.2, 128.3×2, 128.2×2, 127.7, 127.6, 127.5, 127.3, 97.8, 74.9,

74.2, 73.4, 73.0×2, 70.4, 69.8, 69.6, 37.8, 31.2, 30.1, 30.0, 26.6, 25.8×2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{34}H_{42}O_5Na$ 553.2930; found 553.2922.

Cyclohexylmethyl 3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranoside (18aβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **18aβ** (8.4 mg, 26%). Colorless syrup; R_f 0.47 (8/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ -26.5° (*c* 1.04, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.24 (15H, m), 4.92 and 4.64 (2H, ABq, *J* = 11.8 Hz), 4.59 and 4.56 (2H, ABq, *J* = 12.3 Hz), 4.47 and 4.43 (2H, ABq, *J* = 11.8 Hz), 4.37 (1H, dd, *J* = 3.2 and 9.2 Hz), 3.82 (1H, br s), 3.70 (1H, dd, *J* = 6.3 and 9.5 Hz), 3.64 (1H, dd, *J* = 7.2 and 9.5 Hz), 3.60 (1H, dd, *J* = 6.9 and 9.5 Hz), 3.54 (1H, ddd, *J* = 2.6, 5.8 and 11.5 Hz), 3.46 (1H, ddd, *J* = 1.2, 6.9 and 7.2 Hz), 3.18 (1H, dd, *J* = 7.2 and 9.5 Hz), 2.12-2.04 (2H, m), 1.78-1.52 (6H, m), 1.27-1.09 (3H, m), 0.93-0.84 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 138.3, 138.1, 128.4×2, 128.3, 128.1, 127.8, 127.7, 127.6, 127.4, 127.3, 100.8, 77.5, 75.1, 74.4×2, 73.5, 71.7, 70.1, 69.3, 37.9, 32.8, 30.1, 29.9, 26.6, 25.8×2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{34}H_{42}O_5Na$ 553.2930; found 553.2925.

Cyclohexylmethyl 3,4-di-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside (19aα): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **19aα** (17.4 mg, 51%). Colorless syrup; R_f 0.45 (8/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ +61.3° (*c* 0.99, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.27 (10H, m), 4.94 and 4.66 (2H, ABq, *J* = 10.9 Hz), 4.81 (1H, br d, *J* = 2.6 Hz),

4.68 and 4.64 (2H, ABq, *J* = 11.5 Hz), 3.95-3.92 (2H, m), 3.72 (1H, dq, *J* = 6.3 and 9.5 Hz), 3.38 (1H, dd, *J* = 7.2 and 9.4 Hz), 3.12 (1H, dd, *J* = 8.6 and 9.5 Hz), 3.13 (1H, dd, *J* = 6.0 and 9.5 Hz), 2.28 (1H, ddd, *J* = 1.5, 5.2 and 12.9 Hz), 1.78-1.64 (6H, m), 1.58-1.50 (1H, m), 1.28 (3H, d, *J* = 6.3 Hz), 1.25-1.11 (3H, m), 0.96-0.87 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.8, 128.4, 128.2, 128.0, 127.7, 101.4, 81.6, 75.5, 73.5, 70.9, 68.2, 37.8, 34.6, 29.9, 29.8, 26.5, 25.8, 25.7, 18.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{36}O_4Na$ 447.2511; found 447.2513.

Cyclohexylmethyl 3,4-di-*O*-benzyl-2,6-dideoxy-β-D-glucopyranoside (19aβ): The anomeric mixture was purified by flash column chromatography (10g, *n*-hexane/EtOAc = 8/1) to give compound **19aβ** (12.1 mg, 35%). White solid; R_f 0.41 (8/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ -20.7º (*c* 1.32, $CHCl_3$); mp 72-73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.27 (10H, m), 4.95 and 4.65 (2H, ABq, *J* = 10.9 Hz), 4.69 and 4.60 (2H, ABq, *J* = 11.7 Hz), 4.38 (1H, dd, *J* = 2.0 and 9.7 Hz), 3.68 (1H, dd, *J* = 6.3 and 9.5 Hz), 3.62 (1H, ddd, *J* = 5.2, 8.6 and 11.8 Hz), 3.32 (1H, dq, *J* = 6.3 and 9.3 Hz), 3.19 (1H, dd, *J* = 7.2 and 9.5 Hz), 3.14 (1H, dd, *J* = 8.6 and 9.3 Hz), 2.35 (1H, ddd, *J* = 2.0, 5.2 and 12.6 Hz), 1.79-1.53 (7H, m), 1.33 (3H, d, *J* = 6.3 Hz), 1.30-1.11 (3H, m), 0.96-0.84 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 128.5, 128.4, 128.1, 128.0, 127.9, 103.0, 85.8, 85.1, 76.1, 75.5, 75.3, 71.4, 37.8, 33.6, 30.1, 29.8, 26.6, 25.8, 25.7, 17.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{36}O_4Na$ 447.2511; found 447.2518.

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Notes

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Associated Content

Supporting Information

NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ernst, B.; Hart, G. W.; Sinaÿ, P., Eds.; *Carbohydrates in Chemistry and Biology*; Wiley-VCH: Weinheim, Germany, 2000; Vols. 1-4. (b) Fraser-Reid, B. O.; Tatsuta, K.; Thiem, J., Eds.; *Glycoscience, Chemistry and Chemical Biology;* Springer: Berlin, Germany, 2001; Vols. 1-3.

(2) Biriaderis, C. G.; Izydorczyck, M. S., Eds.; *Functional Carbohydrates*; CPC Press: Boca Raton, FL, 2006.

(3) Demchenko, A. V. In Handbook of Chemical Glycosylation: Advances in Stereoselectivity and Therapeutic Relevance; Demchenko, A. V., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 1-27.

(4) (a) Lemieux, R. U.; Levine, S. *Can. J. Chem.* **1964**, *42*, 1473. (b) Thiem, J.; Karl, H.; Scwentner, J. *Synthesis* **1978**, *696*. (c) De Castro, M.; Marzabadi, C. H. *Tetrahedron* **2010**, *66*, 3395.

(5) Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem. Int. Ed. Engl*. **1996**, *35*, 1380.

(6) (a) Suzuki, K.; Sulikowski, G. A.; Friesen, R. W.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 8895. (b) Sebesta, D. P.; Roush, W. R. *J. Org. Chem.* **1992**, *57*, 4799.

(7) (a) Friesen, R. W.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6656. (b) Wang, H.; Tao, J.; Cai, X.; Chen, W.; Zhao, Y.; Xu, Y.; Yao, W.; Zheng, J.; Wan, Q. *Chem. Eur. J.* **2014**, *20*, 17319.

(8) Perret, P.; Slimani, L.; Briat, A.; Villemain, D.; Halimi, S.; Demongeot, J.; Fagret, D.; Ghezzi, C. *Eur. J. Nucl. Med. Mol. Imaging* **2007**, *34*, 734.

(9) (a) Tanaka, H.; Takahashi, D.; Takahashi, T. *Angew. Chem. Int. Ed*. **2006**, *45*, 770. (b) Pradhan, T. K.; Lin, C. C.; Mong, K.-K. T. *Org. Lett*. **2014**, *16*, 1474.

(10) For selected and recent references for direct synthesis of 2-deoxygycosides by glycosylation, see: (a) Issa, J. P.; Lloyd, D.; Steliotes, E.; Bennett, C. S. *Org. Lett*. **2013**, *15*, 4170. (b) Zhu, D.; Baryal, K. N.; Adhikari, S.; Zhu, J. *J. Am. Chem. Soc.* **2014**, *136*, 3172. (c) Beale, T. M.; Moon, P. J.; Taylor, M. S. *Org. Lett.* **2014**, *16*, 3604. (d) Kaneko, M.; Herzon, S. B. *Org. Lett*. **2014**, *16*, 2776.

(11) Sakakura, A.; Ukai, A.; Ishihara, K. *Nature* **2007**, *445*, 900.

(12) Ferrier, R. J.; Prasad, N. *J. Chem. Soc. C* **1969**, 570.

(13) Kumar, B.; Aga, M. A.; Rouf, A.; Shah, B. A.; Taneja, S. C. *J. Org. Chem.* **2011**, *76*, 3506.

(14) Toshima, K.; Nagai, H.; Kasumi, K.; Kawahara, K.; Matsumura, S. *Tetrahedron* **2004**, *60*, 5331.

(15) Bolitt, V.; Mioskowski, C.; Lee, S.-G.; Falck, J. R. *J. Org. Chem.* **1990**, *55*, 5812.