Effective and chemoselective glycosylations using 2,3-unsaturated sugars†

Shunichi Kusumi, Kaname Sasaki, Sainan Wang, Tatsuya Watanabe, Daisuke Takahashi and Kazunobu Toshima*

Received 16th March 2010, Accepted 12th May 2010
First published as an Advance Article on the web 26th May 2010
DOI: 10.1039/c004204h

Glycosyl donors containing a double bond between C2 and C3 were designed by mimicking the reaction mechanism of lysozyme-initiated hydrolysis of mucopolysaccharides. It was found that, under various glycosylation conditions, the reactivities of 2,3-unsaturated glycosyl acetates were significantly higher, while those of the corresponding 2,3-unsaturated-4-keto glycosyl acetates were much lower than those of the corresponding 2,3-dideoxy (2,3-saturated) glycosyl acetates. Based on these results, chemoselective glycosylations were effectively realized *via* combinatorial techniques in short-steps using three types of glycosyl donors to construct several types of deoxyoligosaccharides. Furthermore, the highly reactive 2,3-unsaturated glycosyl acetates were found to be useful in the synthesis of the *O*-glycosides of low reactive tertiary alcohols.

Introduction

Oligosaccharides play very important roles in many biological events, and accordingly, the development of novel and effective synthetic methods has attracted much attention in the field of synthetic carbohydrate chemistry.[1] One of the most attractive strategy for this purpose is chemoselective glycosylation.[2] The "armed-disarmed" concept introduced by Fraser-Reid and co-workers has been one of the most influential ideas in this field.[3] Thus, the reactivity of glycosyl donors that possess the same leaving group at the anomeric position can be controlled by the combinational use of electron-withdrawing and -donating protecting groups at the C2-position. Unfortunately, this approach cannot be directly applied to 2-deoxy glycosyl donors, which lack a C2-substituent, and therefore, an alternative strategy is required for the chemoselective glycosylation of 2-deoxy sugars.[4] Interestingly, although 2,3-dideoxyglycosides frequently appear in biologically important natural products, such as vineomycin B_2,[5] lactonamycin,[6] or PI-080,[7] only a few attempts at constructing the structure, including that of Sulikowski and coworkers,[8] have been reported to date. The total synthesis of these natural products has yet to be reported due to the difficulty in the construction of the highly deoxygenated oligosaccharides. The purpose of this study is to develop a novel glycosylation method inspired by an enzymatic reaction as a new strategy in armed/disarmed methodology, and as a powerful protocol for constructing glycosidic linkages between highly deoxygenated sugars (represented by 2,3-dideoxyglycosides) and alcohols with low nucleophilicity.

Our strategy involves mimicking the features of lysozyme, which is known to recognize the six hexose residues of mucopolysaccharides (A to F sugars). Furthermore, as shown in Fig. 1(a), lysozyme can regioselectively hydrolyze hexasaccharides between the D and E-sugars,[9] due to two factors, both which increase the hydrolytic cleavage rate of oligosaccharides: 1) conformational distortion by the lysozyme forces the D-sugar to adopt an unusual half-chair conformation ($^4H_5$), which is very similar to the conformation of the oxocarbenium intermediate,[10] and 2) stabilization of the resulting oxocarbenium cation *via* electrostatic interactions with the carboxylate anion of Asp 52 of lysozyme.[11] These factors prompted us to design a novel class of glycosyl donors that possess an *endo* double bond between the C2- and C3-positions, as shown in Fig. 1(b). First, the introduction of an unsaturated bond would cause distortion of the glycosyl donor into the half-chair conformation (in its ground state) that is similar to the distorted conformation of the mucopolysaccharide D-sugar induced by lysozyme. Secondly, such glycosyl donors would allow for the similar stabilization of the oxocarbenium intermediate during the glycosylation reactions due to the location of the cationic charge at the allylic position of the double bond. Therefore, we anticipated that such 2,3-unsaturated glycosyl donors would exhibit high reactivities under relatively mild chemical glycosylation conditions. In contrast, 2,3-unsaturated-4-keto glycosyl donors[12] possessing an α,β-unsaturated keto structure should be significantly less reactive than the corresponding 2,3-unsaturated glycosyl donors because the corresponding oxocarbenium intermediate, generated by the activation of the 2,3-unsaturated-4-keto glycosyl donor, would be highly unstable due to the resonance effect of the α,β-unsaturated keto system adjacent to the C1 cation, as shown in Fig. 1(c). In this paper, we report effective and chemoselective glycosylations using 2,3-unsaturated and 2,3-unsaturated-4-keto sugars as novel armed and disarmed glycosyl donors, respectively.[13]

Results and discussion

Synthesis of 2,3-unsaturated, 2,3-dideoxy, and 2,3-unsaturated-4-keto glycosyl donors

As shown in Scheme 1, benzoyl (Bz)-protected 2,3-unsaturated glycosyl acetate **1**, 2,3-dideoxy glycosyl acetate **2**, and

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, 223-8522, Japan. E-mail: toshima@applc.keio.ac.jp; Fax: +81-45-566-1576; Tel: +81-45-566-1576

† Electronic Supplementary Information (ESI) available: Effective and chemoselective glycosylations using 2,3-unsaturated sugars. See DOI: 10.1039/c004204h/

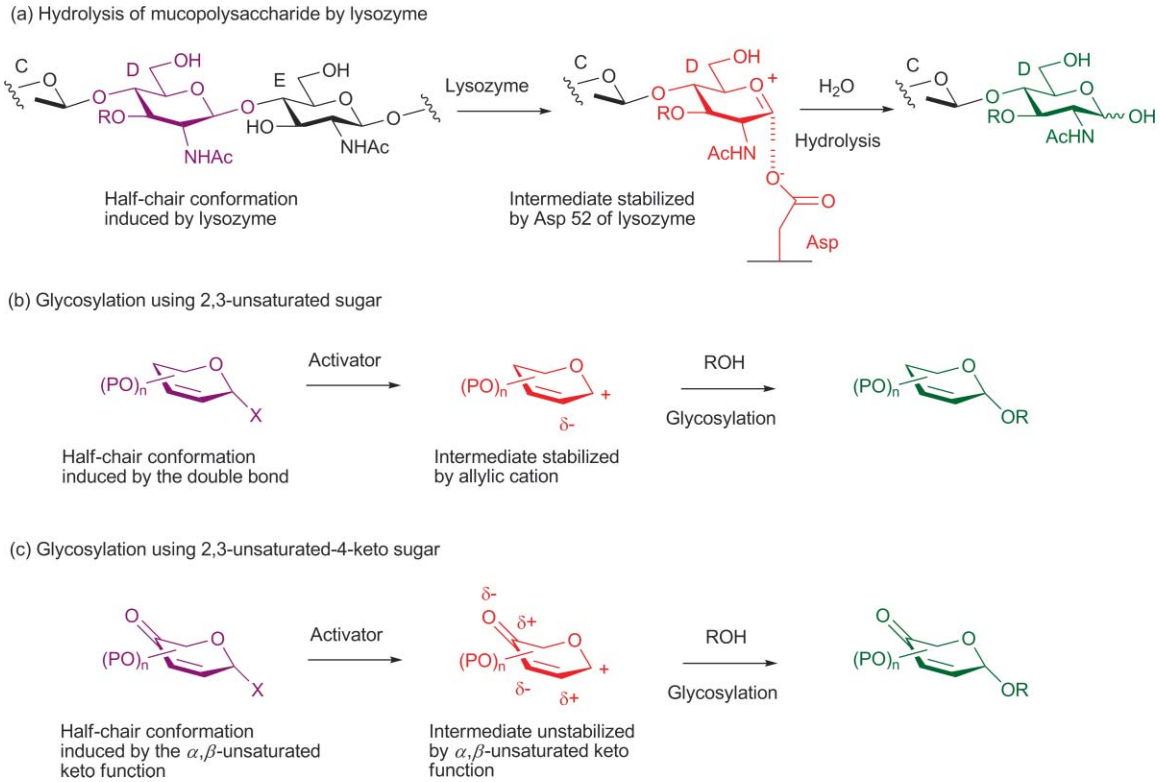
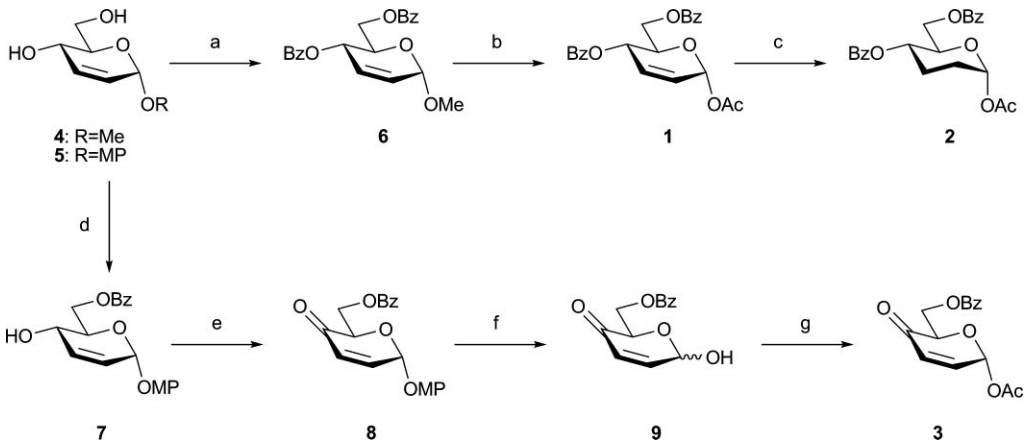


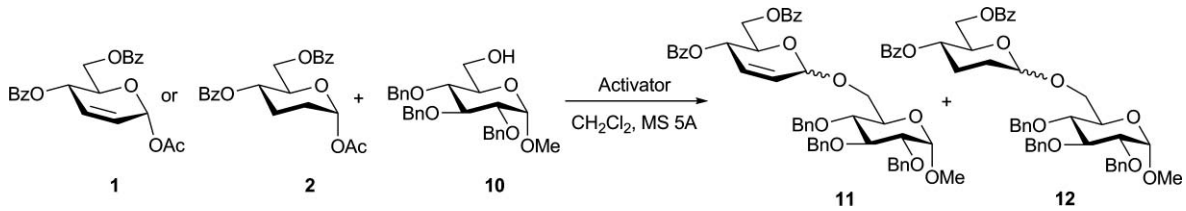
Fig. 1 (a) Reaction mechanism of regioselective hydrolysis of mucopolysaccharide by lysozyme, and the concept of (b) glycosylation using 2,3-unsaturated sugar and (c) glycosylation using 2,3-unsaturated-4-keto sugar.



Scheme 1 Synthesis of 2,3-unsaturated glycosyl acetate **1**, 2,3-dideoxy glycosyl acetate **2**, and 2,3-unsaturated-4-keto glycosyl acetate **3**[a a] *Reagents and conditions*: (a) BzCl, Py, 0 °C, 0.5 h, 100%; (b) Ac_2O, H_2SO_4, –40 °C, 0.5 h, 70%; (c) H_2, cat. Rh/Al_2O_3, EtOAc–PhMe (9/1), 0 °C, 1 h, 86%; (d) BzCl, Py, CH_2Cl_2, –78 °C, 2 h, 85%; (e) PDC, CH_2Cl_2, 25 °C, 18 h, 84%; (f) CAN, MeCN–H_2O (9/1), 25 °C, 1.5 h, 94%; (g) AcCl, Py, CH_2Cl_2, 25 °C, 1.5 h, 73% ($\alpha : \beta = 89 : 11$).

2,3-unsaturated-4-keto glycosyl acetate **3** were effectively synthesized from 2,3-unsaturated glycosides **4**[14] and **5**,[15] which were readily prepared from glucal *via* Ferrier-rearrangement reactions.[16] Thus, **4** was protected with benzoyl groups using benzoyl chloride in pyridine, then subjected to acetolysis using acetic anhydride and H_2SO_4 (conc.) to give 2,3-unsaturated glycosyl acetate **1** *via* **6** in a high overall yield. At this stage, ^{1}H-NMR analysis confirmed that **1** adopts a half-chair conformation based on coupling constants between H1 and H2 (2.1 Hz), H2 and H3 (10.2 Hz), and H3 and H4 (1.5 Hz). Benzoyl-protected 2,3-dideoxy glycosyl acetate **2** was effectively prepared by hydrogenation of **1** using Rh/Al_2O_3 as a catalyst.[17] In contrast, the acetolysis of methyl glycosides that possess a 2,3-unsaturated-4-keto skeleton was ineffective, and therefore, 2,3-unsaturated-4-keto glycosyl acetate **3** was synthesized from 2,3-unsaturated glycoside **5** in four steps: 1) regioselective benzoylation of the C6 hydroxy group of **5**, 2) oxidation of the C4 hydroxy group of **7** using PDC, 3) deprotection of the *p*-methoxyphenyl (MP) group at the C1-position of **8** using CAN, and 4) acetylation at the C1-position of **9** using AcCl in pyridine.

Table 1 Competitive glycosylations using **1** and **2**



Entry[a]	Donor	Activator (equiv.)	Temp./°C	Time/h	Glycoside yield (%) [b] (α : β ratio)[b]	Recovery yield of donor (%)[b]
1	**1**	TMSOTf (0.3)	–78	3	**11**: 89 (69 : 31)	**1**: 0
2	**1**	TBSOTf (0.3)	–70	3	**11**: 91 (68 : 32)	**1**: 0
3	**1**	BF_3-OEt_2 (1.0)	–60	24	**11**: 72 (80 : 20)	**1**: 13
4	**1**	TfOH (0.5)	–70	24	**11**: 85 (80 : 20)	**1**: 5
5	**1**	MK-10[c]	0	96	**11**: 80 (56 : 44)	**1**: 9
6	**2**	TMSOTf (0.3)	–78	3	**12**: 5 (60 : 40)	**2**: 89
7	**2**	TBSOTf (0.3)	–70	3	**12**: 4 (58 : 42)	**2**: 91
8	**2**	BF_3-OEt_2 (1.0)	–60	24	**12**: 3 (67 : 33)	**2**: 90
9	**2**	TfOH (0.5)	–70	24	**12**: 10 (60 : 40)	**2**: 85
10	**2**	MK-10[c]	0	96	**12**: 4 (35 : 65)	**2**: 87

[a] The ratio between glycosyl donor and glycosyl acceptor was 1.0 : 0.9. [b] Yields and α : β ratios were determined by HPLC analysis. [c] 100 wt% of MK-10 (relative to donor) to donor was used.

Reactivities and chemoselectivities for the glycosylations of 1–3

To confirm our hypothesis, competitive glycosylations were carried out using either 2,3-unsaturated glycosyl donor **1** (1.0 equiv.) or 2,3-dideoxy glycosyl donor **2** (1.0 equiv.) and glycosyl acceptor **10** (0.9 equiv.) under several conditions. As listed in Table 1, the glycosylations were carried out using TMSOTf, TBSOTf, $BF_3{\cdot}OEt_2$, TfOH, or montmorillonite K-10 (MK-10) as activators. As expected, the activation of **1** afforded disaccharide **11** in high yields (entries 1–5). Under similar conditions, however, the activation of **2** did not provide disaccharide **12** (entries 6–10) – in fact, unreacted glycosyl donor **2** was recovered in high yields. These results clearly show that the 2,3-unsaturated glycosyl donors, which mimic the mechanism of the lysozyme hydrolysis reaction, are much more reactive than the corresponding 2,3-dideoxy glycosyl donors. This tendency was essentially independent of the glycosylation activator. Furthermore, a one-flask competitive glycosylation using both donors (**1**, 1.0 equiv.; **2**, 1.0 equiv.) and acceptor (**10**, 0.9 equiv.) (TMSOTf, MS 5A, CH_2Cl_2, –78 °C, 3 h) resulted in the preferential formation of **11** (91%, $\alpha : \beta = 70 : 30$) over **12** (0%). Similarly, as shown in Fig. 2, the glycosylations of **10** and of 2,3-unsaturated glycosyl acetate **13** and 2,3-dideoxy glycosyl acetate **14**, which are the C4-epimers of **1** and **2**, respectively, resulted in the preferential formation of disaccharide **15** over **16**. Based on these results, the chemoselective phenomenon was shown to be independent of the configuration of the hydroxyl group of the glycosyl donors. Furthermore, it was confirmed that these chemoselectivities were highly independent of the examined solvents, such as CH_2Cl_2, PhMe, THF, and ether. Thus, the chemoselective activations of the 2,3-unsaturated glycosyl donors were effectively realized in these solvents by controlling the reaction temperature appropriately.

Based on these favorable results, we turned our attention to investigate the relative reactivities of 2,3-unsaturated *versus* 2,3-unsaturated-4-keto glycosyl donors. Accordingly, competitive glycosylations were carried out using 2,3-unsaturated glycosyl donor **1** (1.0 equiv.) or 2,3-unsaturated-4-keto glycosyl donor **3** (1.0 equiv.) and glycosyl acceptor **10** (1.0 equiv.) under several conditions. As shown in Table 2, disaccharide **11** was generated from **1** and **10** in high yields using TMSOTf, TBSOTf, $BF_3{\cdot}OEt_2$, TfOH, or montmorillonite K-10 (MK-10) as the activator (entries 1–5). In contrast, the formation of disaccharide **17** using **3** and **10** (entries 6–10), under similar conditions, was unsuccessful; again, the starting material **3** was recovered in high yield. These results

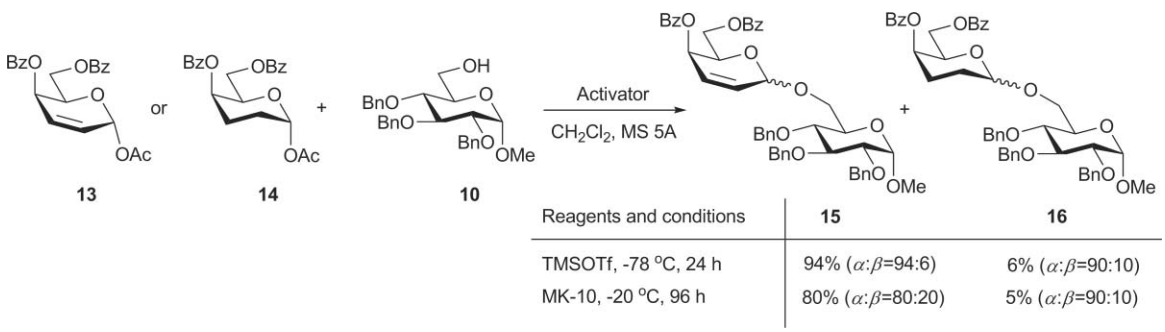
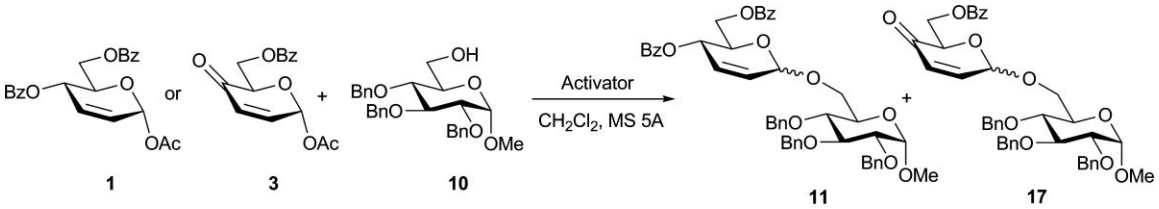


Fig. 2 Competitive glycosylations using **13** and **14**.

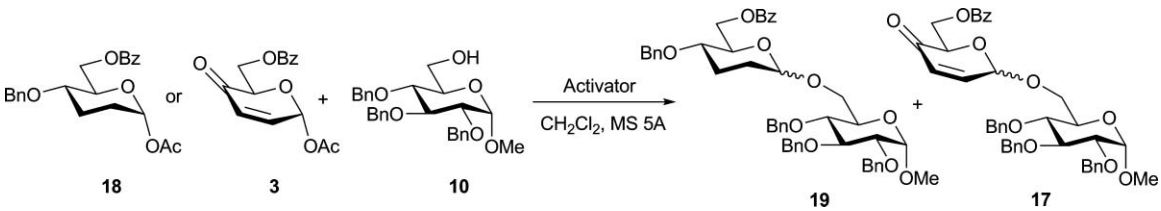
Table 2 Competitive glycosylations using **1** and **3**



Entry[a]	Donor	Activator (equiv.)	Temp/°C	Time/h	Glycoside yield (%) [b] (α : β ratio)[c]	Recovery yield of donor (%)[b]
1	**1**	TMSOTf (0.3)	–60	1	**11**: 100 (66 : 34)	**1**: 0
2	**1**	TBSOTf (0.3)	–50	1	**11**: 92 (70 : 30)	**1**: 0
3	**1**	BF_3-OEt_2 (2.0)	–60	48	**11**: 83 (76 : 24)	**1**: 8
4	**1**	TfOH (0.3)	–50	0.75	**11**: 92 (69 : 31)	**1**: 0
5	**1**	MK-10[d]	0	8	**11**: 95 (64 : 36)	**1**: 0
6	**3**	TMSOTf (0.3)	–60	1	**17**: 0	**3**: 95
7	**3**	TBSOTf (0.3)	–50	1	**17**: 8 (63 : 37)	**3**: 83
8	**3**	BF_3-OEt_2 (2.0)	–60	48	**17**: 2 (77 : 23)	**3**: 95
9	**3**	TfOH (0.3)	–50	0.75	**17**: 5 (76 : 24)	**3**: 94
10	**3**	MK-10[d]	0	8	**17**: 8 (74 : 26)	**3**: 87

[a] The ratio of glycosyl donor to glycosyl acceptor was 1.0 : 1.0. [b] Isolated yields. [c] α : β ratios were determined by ^{1}H-NMR analysis. [d] 100 wt% of MK-10 (relative to donor) was used.

Table 3 Competitive glycosylations using **18** and **3**



Entry[a]	Donor	Activator (equiv.)	Temp/°C	Time/h	Glycoside yield (%) [b] (α : β ratio)[c]	Recovery yield of donor (%)[b]
1	**18**	TMSOTf (0.3)	–50	1	**19**: 99 (68 : 32)	**18**:0
2	**18**	TBSOTf (0.3)	–45	1	**19**: 98 (68 : 32)	**18**:0
3	**18**	BF_3-OEt_2 (2.0)	–50	36	**19**: 94 (69 : 31)	**18**:0
4	**18**	TfOH (0.3)	–45	1	**19**: 96 (73 : 27)	**18**:0
5	**18**	MK-10[d]	25	25	**19**: 84 (68 : 32)	**18**:9
6	**3**	TMSOTf (0.3)	–50	1	**17**: 0	**3**: 91
7	**3**	TBSOTf (0.3)	–45	1	**17**: 4 (66 : 34)	**3**: 96
8	**3**	BF_3-OEt_2 (2.0)	–50	36	**17**: 6 (81 : 19)	**3**: 93
9	**3**	TfOH (0.3)	–45	1	**17**: 4 (84 : 16)	**3**: 91
10	**3**	MK-10[d]	25	25	**17**: 0	**3**: 91

[a] The ratio between glycosyl donor and glycosyl acceptor was 1.0 : 1.0. [b] Isolated yields. [c] α : β ratios were determined by ^{1}H-NMR analysis. [d] 100 wt% of MK-10 (relative to donor) was used.

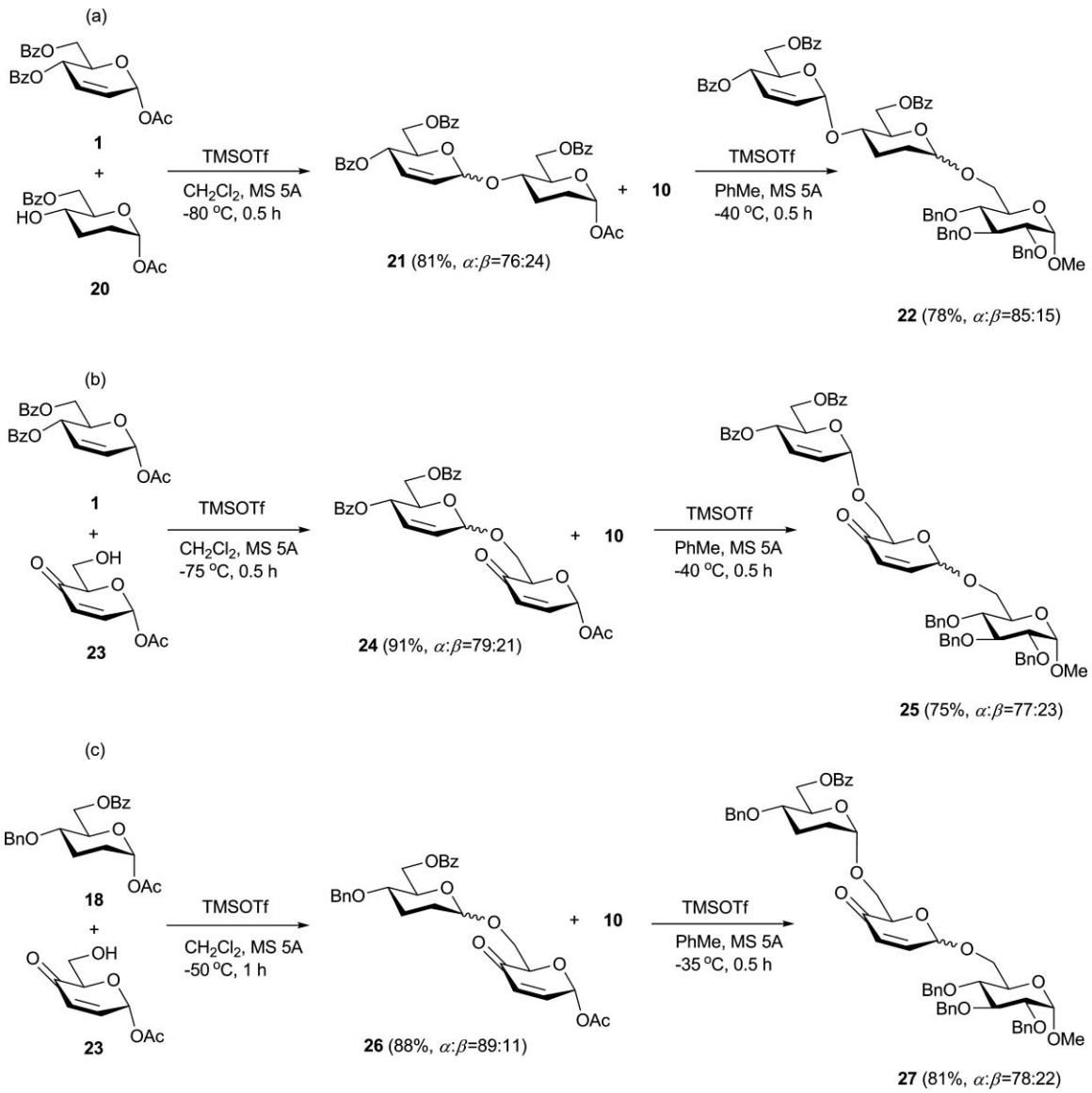
clearly indicate that the 2,3-unsaturated glycosyl donor is more reactive than the corresponding 2,3-unsaturated-4-keto glycosyl donor. Similarly, a one-flask competitive glycosylation using **1** (1.0 equiv.), **3** (1.0 equiv.), and **10** (1.0 equiv.) (TMSOTf, MS 5A, CH_2Cl_2, –60 °C, 1 h) resulted in the preferential formation of **11** (93%, α : β = 67 : 33) over **17** (3%, α : β = 64 : 36).

Next, the comparative reactivities between 2,3-dideoxy and 2,3-unsaturated-4-keto glycosyl donors, both which can serve as the disarmed analog of 2,3-unsaturated glycosyl donors, were investigated. Because the conformations and the electronic characteristics of the glycosyl donors differ significantly, it was difficult to predict which donor would exhibit higher reactivity. We therefore first conducted competitive glycosylations using 2,3-dideoxy glycosyl donor **2** (1.0 equiv.), 2,3-unsaturated-4-keto glycosyl donor **3** (1.0 equiv.), and glycosyl acceptor **10** (1.0 equiv.) under various conditions. Although the reactivity of **2** was found to be slightly higher than that of **3**, the difference was insignificant in terms of chemoselective glycosylation. It has been reported that protection using an acyl group generally decreases the reactivity of the glycosyl donor.[18] Accordingly, to improve the reactivity, competitive glycosylation was carried out using 2,3-dideoxy glycosyl donor **18** (1.0 equiv.), which, instead of benzoyl, has a benzyl protecting group at the C4-position. As shown in Table 3, disaccharide **19** was formed from **18** and **10** in high yields using TMSOTf, TBSOTf, BF_3·OEt_2, TfOH, or montmorillonite K-10 (MK-10) as the activator (entries 1–5). Under similar conditions, insignificant amounts of disaccharide **17** were generated from **3** and **10** (entries 6–10), in which **3** was recovered in high yield. These

results clearly indicate that the 2,3-dideoxy glycosyl donor is more reactive than the corresponding 2,3-unsaturated-4-keto glycosyl donor, and that the difference in reactivity between these glycosyl donors can be enhanced by choosing the optimal protecting group at the C4-position of the 2,3-dideoxy glycosyl donor. Finally, the one-flask competitive glycosylation between **18** (1.0 equiv.) and **3** (1.0 equiv.) with **10** (1.0 equiv.) (TMSOTf, MS 5A, CH_2Cl_2, −50 °C, 1 h) demonstrated a preference toward **19** (99%, $\alpha:\beta =$ 71 : 29) over **17** (0%).

Chemoselective glycosylations for the synthesis of deoxyoligosaccharides

Consequently, chemoselective glycosylations were investigated using 2,3-unsaturated, 2,3-unsaturated-4-keto, and 2,3-dideoxy sugars. First, the glycosylation between 2,3-unsaturated glycosyl acetate **1** (glycosyl donor) and 2,3-dideoxy glycosyl acetate **20** (glycosyl acceptor) was carried out. Hex-2-enosyl-hexose disaccharides are found, for example, in the angucycline group of antibiotics as acurose-rhodinose disaccharides.[19] As shown in Scheme 2(a), desired disaccharide **21** was obtained in a high yield with α-stereoselectivity *via* chemoselective glycosylation using TMSOTf at −80 °C for 0.5 h. In contrast, oligosaccharide(s) that would result from the undesirable activation of **20** (which would lead to self-condensation) was not detected. Disaccharide **21** possesses an acetate leaving group at the C1-position, without epimerization. Furthermore, the reaction between disaccharide **21** and acceptor **10** proceeded smoothly using TMSOTf at −40 °C for 0.5 h in PhMe to afford trisaccharide **22** in a high yield with α-stereoselectivity. The use of PhMe as the solvent in the second glycosylation reaction was found to be highly effective in preventing the cleavage of the first glycosidic bond, and in increasing the α-stereoselectivity. Based on these results, the combination of the 2,3-unsaturated and the corresponding 2,3-dideoxy glycosyl donors can define a new family of armed and disarmed glycosyl donors, respectively.



Scheme 2 Synthesis of trisaccharides by chemoselective glycosylations using 2,3-unsaturated, 2,3-dideoxy, and 2,3-unsaturated-4-keto sugars

Next, as shown in Scheme 2(b), chemoselective glycosylation between 2,3-unsaturated glycosyl acetate **1** (glycosyl donor) and 2,3-unsaturated-4-keto glycosyl acetate **23** (glycosyl acceptor) proceeded smoothly using TMSOTf at −75 °C for 0.5 h to give desired disaccharide **24** in a high yield with α-stereoselectivity. Furthermore, disaccharide **24**, which possesses an acetate leaving group at the C1-position, reacted with glycosyl acceptor **10** using TMSOTf at −40 °C for 0.5 h to afford trisaccharide **25** in a high yield with α-stereoselectivity. In this case, 2,3-unsaturated and the corresponding 2,3-unsaturated-4-keto glycosyl donors can define another new family of armed and disarmed glycosyl donors, respectively.

As shown in Scheme 2(c), chemoselective glycosylation between 2,3-dideoxy glycosyl acetate **18** (glycosyl donor) and 2,3-unsaturated-4-keto glycosyl acetate **23** (glycosyl acceptor) using TMSOTf at −50 °C for 1 h afforded disaccharide **26** in a high yield with α-stereoselectivity; the disaccharide further gave tirsaccharide **27** *via* glycosylation with **10** using TMSOTf at −35 °C for 0.5 h. In this case, 2,3-dideoxy and the corresponding 2,3-unsaturated-4-keto glycosyl donors function as the armed and disarmed glycosyl donors, respectively.

Efficient glycosylations of 2,3-unsaturated glycosyl acetates with tertiary alcohols

Finally, we examined the reaction between highly reactive 2,3-unsaturated glycosyl donors and unreactive alcohols, such as tertiary alcohols, towards the construction of glycosides. The formation of *O*-glycosidic linkages between tertiary alcohols and highly deoxygenated sugars remains challenging for two reasons: 1) tertiary alcohols have a tendency to generate carbocations, along with elimination of a hydroxyl group under acidic conditions; and 2) because of the low nucleophilicity of tertiary alcohols, the active species—an oxocarbenium intermediate generated from a glycosyl donor—is easily converted to the corresponding glycal *via* deprotonation at the C2-position. Our glycosylation method, in contrast, succeeds in overcoming these problems because 2,3-unsaturated glycosyl donors can be activated under much milder acidic conditions than that for the corresponding 2,3-dideoxy glycosyl donors. Furthermore, the absence of a β-proton at the cationic center of the oxocarbenium ion prevents the side reaction mentioned above.

Accordingly, as shown in Fig. 3(a), the glycosylations of adamantan-1-ol (**28**) and *tert*-butanol (**29**) with an almost equal amount of 2,3-unsaturated glycosyl acetate **30** proceeded effectively in the presence of a very mild Lewis acid, $Yb(OTf)_3$,[20] at 0 °C to give glycosides **31** and **32**, respectively, in high yields. For the glycosylations using **33**, whose α-glycosides can readily be converted into naturally occurring L-rhodinosides, L-acurosides, L-cinerulosides, and L-rhamnosides by appropriate reduction and/or oxidation,[12c] the corresponding glycosides **34** and **35** were also obtained in good to high yields with excellent α-stereoselectivities. In contrast, when glycal **36**, which is the synthetic equivalent of **30** and can be converted into **31** and **32** by Ferrier rearrangement, was used as the glycosyl donor for the glycosylation of **28**, the reaction did not proceed, under identical conditions as those for **30**. Likewise, as shown in Fig. 3(b), the glycosylation between 2,3-dideoxy glycosyl donor **18** and **28**, under the same conditions as used for **30**, did not proceed. When 2,3,6-trideoxy glycosyl donor **37** was used instead of **33** for the glycosylation of **28**, activation of the donor was not observed below 0 °C in the presence of $Yb(OTf)_3$. When the reaction was carried out at 0 to 25 °C, as shown in Fig. 3(c), the corresponding glycoside **38** was obtained in a yield of merely 22%, accompanied by considerable amounts of by-products. These results clearly indicate that glycosylations involving 2,3-unsaturated glycosyl donors proceed under conditions that are considerably milder than usual, and can be used in the effective construction of *O*-glycosidic linkages, even for tertiary alcohols with low nucleophilicity.

Conclusions

In the present studies, we have designed 2,3-unsaturated glycosyl donors that mimic the distinctive features of the regioselective hydrolysis reaction of lysozyme. We found that 2,3-unsaturated glycosyl donors exhibit high reactivity, while the corresponding 2,3-unsaturated-4-keto glycosyl donors show low reactivity, under several glycosylation conditions. Our results have helped establish 2,3-unsaturated and 2,3-unsaturated-4-keto glycosyl donors as a new family of armed and disarmed glycosyl donors, respectively. Furthermore, chemoselective glycosylations *via* combinatorial uses of 2,3-unsaturated, 2,3-unsaturated-4-keto, and 2,3-dideoxy glcosyl donors can effectively provide various types of deoxyoligosaccharides in short-steps. We have further shown that 2,3-unsaturated glycosyl donors can be employed in the challenging construction of *O*-glycosides of unreactive alcohols. Our novel glycosylation methodology, therefore, can be widely applicable towards the efficient synthesis of biologically important natural products, including several antitumor antibiotics that possess 2,3-dideoxy, 2,3-unsaturated, and/or 2,3-unsaturated-4-keto sugar(s).[21] Investigations to widen the applicability of our glycosylation method are currently underway in our laboratories.[22]

Experimental section

General method for chemical synthesis

Melting points were determined on a micro hot-stage (Yanako MP-S3) and were uncorrected. Optical rotations were measured on a JASCO DIP-370 photo-electric polarimeter. NMR spectra were recorded on a Varian MVX-300 (300 or 75 MHz) spectrometer using tetramethylsilane as internal standard unless otherwise noted. ESI-TOF Mass spectra were measured on a Waters LCT premier XE. Silica gel TLC and column chromatography were performed on Merck TLC 60F-254 (0.25 mm) and Silica Gel 60 N (spherical, neutral) (Kanto Chemical Co., Inc.), respectively. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon using oven-dried glassware. In general, organic solvents were purified and dried using an appropriate procedure, and evaporation and concentration were carried out under reduced pressure below 30 °C, unless otherwise noted. The configurations at the anomeric positions of the 2,3-unsaturated glycosides were determined by the ^{1}H-NMR analyses of the corresponding 2,3-dideoxy glycosides which were obtained by standard hydrogenations of the double bond in the 2,3-unsaturated glycosides using H_2 and 10% Pd/C. On the other hand, the configurations at the anomeric positions of the 2,3-unsaturated-4-keto glycosides were determined by the ^{1}H-NMR analyses

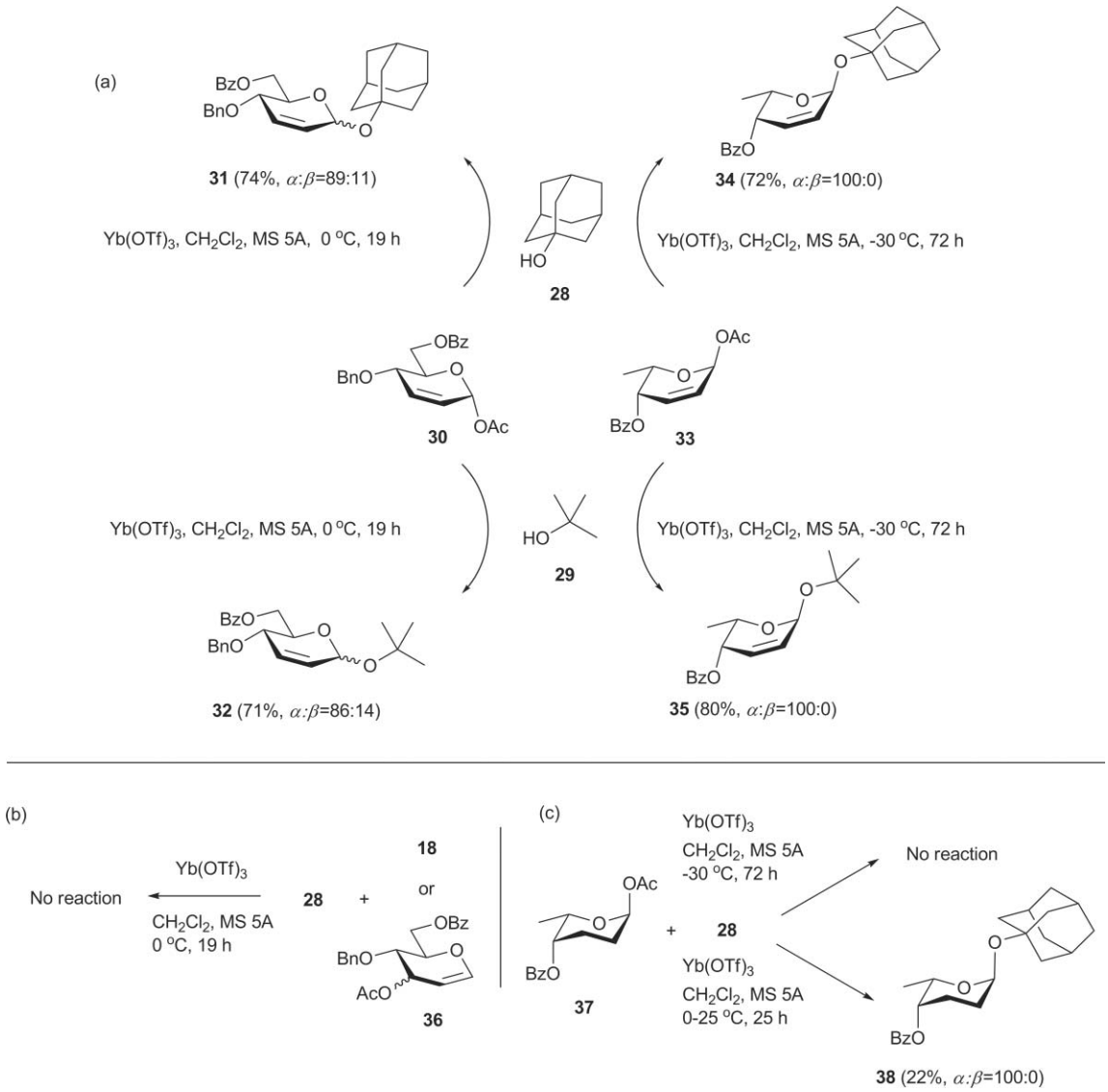


Fig. 3 Glycosylations of 2,3-unsaturated glycosyl acetates and tertiary alcohols.

of the corresponding 2,3-dideoxy glycosides which were obtained by standard hydrogenations of the double bond in the 2,3-unsaturated-4-keto glycosides using H_2 and 10% Pd/C, followed by stereoselective reductions of the ketone group in the resulting 2,3-dideoxy-4-keto glycosides using $NaBH_4$.[12c]

Methyl 4,6-di-*O*-benzoyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (6)

To a solution of methyl 2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (**4**) (5.00 g, 31.2 mmol) in dry pyridine (50.0 ml) was added benzoyl chloride (11.5 mL, 93.6 mmol) under ice-bath cooling. After the mixture was stirred at 0 °C for 30 min, the reaction was quenched by addition of water (100 mL). The resulting mixture was extracted with EtOAc (100 mL × 3). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by silica-gel column chromatography (hexane–EtOAc = 5/1) gave **6** (11.5 g, quant.). White needles; m.p. 73.2 – 73.9 °C (Et_2O–hexane); R_f 0.37 (3/1 hexane–EtOAc); $[\alpha]_D^{22}$ +193.2 (*c* 1.27, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS) δ 8.07-7.99 (4H, m, ArH), 7.61-7.51 (2H, m, ArH), 7.47-7.37 (4H, m, ArH), 6.05 (1H, br-ddd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 1.5 Hz, H-3), 5.92 (1H, ddd, $J_{2,3}$ = 10.0 Hz, $J_{2,4}$ = 2.0 Hz, $J_{1,2}$ = 2.0 Hz, H-2), 5.70 (1H, ddd, $J_{4,5}$ = 9.0 Hz, $J_{2,4}$ = 2.0 Hz, $J_{3,4}$ = 1.5 Hz, H-4), 5.00 (1H, br-dd, $J_{1,2}$ = 2.0 Hz, H-1), 4.59 (1H, dd, $J_{6,6}$ = 11.7 Hz, $J_{5,6}$ = 2.4 Hz, H-6), 4.47 (1H, dd, $J_{6,6}$ = 11.7 Hz, $J_{5,6}$ = 5.7 Hz, H-6), 4.43 (1H, ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 5.7 Hz, $J_{5,6}$ = 2.4 Hz, H-5), 3.49 (3H, s, OMe); Anal. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47. Found: C, 68.51; H, 5.62.

4,6-Di-*O*-benzoyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranosyl acetate (1)

To a solution of **6** (3.00 g, 8.14 mmol) in Ac_2O (60.0 ml) was dropwisely added concd H_2SO_4 (0.434 mL, 8.14 mmol) at –40 °C. After the mixture was stirred at the temperature for 30 min, NaOAc (1.34 g, 16.3 mmol) was added. The mixture

was poured into water (100 mL), and the resulting mixture was extracted with EtOAc (100 mL × 3). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by silica-gel column chromatography (chloroform–EtOAc/TEA = 98/2/5) gave **1** (2.26 g, 70%). Colorless syrup; R_f 0.63 (1/1 hexane–EtOAc); $[\alpha]_D^{29}$ +120.1 (*c* 2.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.06-7.96 (4H, m, ArH), 7.62-7.49 (2H, m, ArH), 7.47-7.34 (4H, m, ArH), 6.39 (1H, d, $J_{1,2}$ = 2.1 Hz, H-1), 6.19 (1H, ddd, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 1.5 Hz, H-3), 5.94 (1H, ddd, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 2.7 Hz, $J_{1,2}$ = 2.1 Hz, H-2), 5.75 (1H, ddd, $J_{4,5}$ = 9.3 Hz, $J_{2,4}$ = 2.7 Hz, $J_{3,4}$ = 1.5 Hz, H-4), 4.62 (1H, dd, $J_{6,6}$ = 11.1 Hz, $J_{5,6}$ = 2.7 Hz, H-6), 4.46 (1H, dd, $J_{6,6}$ = 11.1 Hz, $J_{5,6}$ = 5.7 Hz, H-6), 4.43 (1H, ddd, $J_{4,5}$ = 9.3 Hz, $J_{5,6}$ = 5.7 Hz, $J_{5,6}$ = 2.7 Hz, H-5), 2.11 (3H, s, OAc); Anal. Calcd for $C_{22}H_{20}O_7$: C, 66.66; H, 5.09. Found: C, 66.73; H, 5.14.

4,6-Di-*O*-benzoyl-2,3-dideoxy-*α*-D-*erythro*-hexopyranosyl acetate (2)

A suspension of **1** (20.0 mg) and 5% Rh/Al_2O_3 (2.0 mg) in EtOAc–toluene (9/1, v/v, 1.00 mL) was stirred under H_2 atmosphere (balloon). After the suspension was stirred at 0 °C for 1 h, it was filtered through celite pad. The filtrate was concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane/acetone = 3/1) gave **2** (17.2 mg, 86%). White needles; m.p. 102.5–102.9 °C; R_f 0.43 (2/1 hexane–EtOAc); $[\alpha]_D^{30}$ +138.5 (*c* 1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.06-7.97 (4H, m, ArH), 7.60-7.50 (2H, m, ArH), 7.47-7.36 (4H, m, ArH), 6.21 (1H, br-dd, H-1), 5.18 (1H, ddd, $J_{4,5}$ = $J_{3,4}$ = 10.2 Hz, $J_{3,4}$ = 4.8 Hz, H-4), 458 (1H, dd, $J_{6,6}$ = 11.7 Hz, $J_{5,6}$ = 2.7 Hz, H-6), 4.40 (1H, dd, $J_{6,6}$ = 11.7 Hz, $J_{5,6}$ = 5.1 Hz, H-6), 4.32 (1H, ddd, $J_{4,5}$ = 10.2 Hz, $J_{5,6}$ = 5.1 Hz, $J_{5,6}$ = 2.7 Hz, H-5), 2.34-2.23 (1H, m), 2.15 (3H, s, OAc), 2.10-1.90 (3H, m); Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.25; H, 5.55.

p-Methoxyphenyl 6-*O*-benzoyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (7)

To a solution of *p*-methoxyphenyl 2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (**5**) (152 mg, 0.602 mmol) in dry CH_2Cl_2 (3.04 mL) was added pyridine (107 μL, 1.33 mmol) and benzoyl chloride (76.3 μL, 0.663 mmol) at −78 °C under Ar atmosphere. After the mixture was stirred at the temperature for 2 h, the mixture was poured into water (4 mL), and extracted with EtOAc (3 mL × 4). The combined organic layer was washed with brine (4 mL), dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by silica-gel column chromatography (0→50% EtOAc in hexane) gave **7** (182 mg, 85%). White solids; m.p. 96.3–96.9 °C; R_f 0.45 (1/1 hexane–EtOAc); $[\alpha]_D^{32}$ +71.9 (*c* 0.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 7.96 (2H, dd, $J_{o,m}$ = 8.1 Hz, $J_{o,p}$ = 0.9 Hz, H_o of Bz), 7.56 (1H, tt, $J_{m,p}$ = 7.5 Hz, $J_{o,p}$ = 0.9 Hz, H_p of Bz), 7.40 (2H, dd, $J_{o,m}$ = 8.1 Hz, $J_{m,p}$ = 7.5 Hz, H_m of Bz), 7.05 & 6.76 (4H, m, ArH), 6.12 (1H, br-d, *J* = 9.9 Hz, H-3), 5.95 (1H, ddd, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = $J_{2,4}$ = 2.1 Hz, H-2), 5.58 (1H, m, H-1), 4.73 (1H, dd, $J_{6,6}$ = 12.0 Hz, $J_{5,6}$ = 5.4 Hz, H-6), 4.52 (1H, dd, $J_{6,6}$ = 12.0 Hz, $J_{5,6}$ = 2.1 Hz, H-6), 4.22-4.10 (2H, m, H-4 & H-5), 3.75 (3H, s, OMe), 2.33 (1H, d, $J_{4,OH}$ = 6.9 Hz, OH); Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.18; H, 5.70.

p-Methoxyphenyl 6-*O*-benzoyl-2,3-dideoxy-*α*-D-*glycelo*-hex-2-enopyranos-4-uloside (8)

To a solution of **7** (518 mg, 1.46 mmol) in dry CH_2Cl_2 (10.4 mL) was added pyridinium dichromate (2.74 g, 7.27 mmol) under Ar atmosphere. After the mixture was stirred at room temperature (25 °C) for 18 h, the mixture was filtrated through celite pad. The filtrate was concentrated in *vacuo*. Purification of the residue by silica-gel column chromatography (0→50% EtOAc in hexane) gave **8** (430 mg, 84%). Pale yellow solids; m.p. 98.6–99.0 °C; R_f 0.40 (2/1 hexane–EtOAc); $[\alpha]_D^{33}$ +63.9 (*c* 0.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 7.94 (2H, dd, $J_{o,m}$ = 8.1 Hz, $J_{o,p}$ = 1.2 Hz, H_o of Bz), 7.56 (1H, tt, $J_{m,p}$ = 7.5 Hz, $J_{o,p}$ = 1.2 Hz, H_p of Bz), 7.41 (2H, dd, $J_{o,m}$ = 8.1 Hz, $J_{m,p}$ = 7.5 Hz, H_m of Bz), 7.07 & 6.75 (4H, m, ArH), 7.07 (1H, dd, $J_{2,3}$ = 10.2 Hz, $J_{1,2}$ = 3.6 Hz, H-2), 6.29 (1H, d, $J_{2,3}$ = 10.2 Hz, H-3), 5.54 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 4.99 (1H, dd, $J_{5,6}$ = 6.6 Hz, $J_{5,6}$ = 3.0 Hz, H-5), 4.84 (1H, dd, $J_{6,6}$ = 12.3 Hz, $J_{5,6}$ = 3.0 Hz, H-6), 4.68 (1H, dd, $J_{6,6}$ = 12.3 Hz, $J_{5,6}$ = 6.6 Hz, H-6), 3.75 (3H, s, OMe); Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.58; H, 5.20.

6-*O*-Benzoyl-2,3-dideoxy-D-*glycelo*-hex-2-enopyranos-4-ulose (9)

To a solution of **8** (392 mg, 1.11 mmol) in aq. acetonitrile (acetonitrile–water = 9/1, 3.92 mL) was added cerium(IV) ammonium nitrate (1.51 g, 2.76 mmol). After the mixture was stirred at room temperature (25 °C) for 1 h, the mixture was poured into water (3 mL), and extracted with EtOAc (3 mL × 4). After the combined organic layer was washed with brine (3 mL), dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by silica-gel column chromatography (0→60% EtOAc in hexane) gave **9** as a mixture of anomers (259 mg, 94%, α : β = 75 : 25). Yellow solids; R_f 0.36 (1/1 hexane–EtOAc); ^{1}H NMR ($CDCl_3$, TMS), α isomer (**9**α): δ 8.05-7.98 (2H, m, ArH), 7.58-7.53 (1H, m, ArH), 7.46-7.39 (2H, m, ArH), 6.96 (1H, dd, $J_{2,3}$ = 10.5 Hz, $J_{1,2}$ = 0.7 Hz, H-2), 6.23 (1H, d, $J_{2,3}$ = 10.5 Hz, H-3), 5.73 (1H, br-d, *J* = 3.2 Hz, H-1), 4.96 (1H, dd, $J_{5,6}$ = 5.1 Hz, $J_{5,6}$ = 2.6 Hz, H-5), 4.83 (1H, dd, $J_{6,6}$ = 11.9 Hz, $J_{5,6}$ = 2.6 Hz, H-6), 4.71 (1H, dd, $J_{6,6}$ = 11.9 Hz, $J_{5,6}$ = 5.1 Hz, H-6), 3.15 (1H, m, OH); β isomer (**9**β): 8.05-7.98 (2H, m, ArH), 7.58-7.53 (1H, m, ArH), 7.46-7.39 (2H, m, ArH), 7.01 (1H, dd, $J_{2,3}$ = 10.5 Hz, $J_{1,2}$ = 2.0 Hz, H-2), 6.26 (1H, m, H-1), 6.23 (1H, d, $J_{2,3}$ = 10.5 Hz, H-3), 4.81 (1H, dd, $J_{6,6}$ = 11.9 Hz, $J_{5,6}$ = 1.7 Hz, H-6), 4.74 (1H, dd, $J_{6,6}$ = 11.9 Hz, $J_{5,6}$ = 3.2 Hz, H-6), 4.56 (1H, m, H-5), 3.15 (1H, m, OH); Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.69; H, 4.94.

6-*O*-Benzoyl-2,3-dideoxy-*α*-D-*glycelo*-hex-2-enopyranos-4-ulosyl acetate (3)

To a solution of **9** (1.186 g, 4.78 mmol) in dry CH_2Cl_2 (23.7 mL) was added pyridine (850 μL, 10.5 mmol) and acetyl chloride (510 μL, 7.17 mmol) under Ar atmosphere and ice-bath cooling. After the mixture was stirred for 1.5 h at room temperature (25 °C), the mixture was poured into water (150 mL), and extracted with EtOAc (100 mL × 4). The combined organic layer was washed with brine (150 mL), dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (chloroform/acetone = 50/1) gave **3**α (0.89 g, 65%) and **3**β (0.11 g, 8%). α isomer (**3**α): Pale yellow syrup; R_f

0.28 (2/1 hexane–EtOAc); $[\alpha]_D^{32}$ −148.4 (*c* 0.87, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS) δ 7.98 (2H, dd, $J_{o,m} = 8.5$ Hz, $J_{o,p} = 1.5$ Hz, H_o of Bz), 7.56 (1H, tt, $J_{m,p} = 7.3$ Hz, $J_{o,p} = 1.5$ Hz, H_p of Bz), 7.42 (2H, dd, $J_{o,m} = 8.5$ Hz, $J_{m,p} = 7.3$ Hz, H_m of Bz), 6.99 (1H, dd, $J_{2,3} = 10.2$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 6.59 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 6.32 (1H, d, $J_{2,3} = 10.2$ Hz, H-3), 4.86 (1H, dd, $J_{5,6} = 4.8$ Hz, $J_{5,6} = 3.0$ Hz, H-5), 4.80 (1H, dd, $J_{6,6} = 12.0$ Hz, $J_{5,6} = 3.0$ Hz, H-6), 4.71 (1H, dd, $J_{6,6} = 12.0$ Hz, $J_{5,6} = 4.8$ Hz, H-6), 2.15 (3H, s, OAc); Anal. Calcd for $C_{15}H_{14}O_6$: C, 62.07; H, 4.86. Found: C, 61.77; H, 4.95. β isomer (**3***β*): Pale yellow syrup; R_f 0.28 (2/1 hexane–EtOAc); $[\alpha]_D^{32}$ +49.5 (*c* 1.61, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS) δ 8.01 (2H, dd, $J_{o,m} = 8.7$ Hz, $J_{o,p} = 0.9$ Hz, H_o of Bz), 7.57 (1H, tt, $J_{m,p} = 7.5$ Hz, $J_{o,p} = 0.9$ Hz, H_p of Bz), 7.43 (2H, dd, $J_{o,m} = 8.7$ Hz, $J_{m,p} = 7.5$ Hz, H_m of Bz), 6.94 (1H, dd, $J_{2,3} = 10.5$ Hz, $J_{1,2} = 3.0$ Hz, H-2), 6.61 (1H, dd, $J_{1,2} = 3.0$ Hz, $J_{1,3} = 1.2$ Hz, H-1), 6.37 (1H, dd, $J_{2,3} = 10.2$ Hz, $J_{1,3} = 1.2$ Hz, H-3), 4.75-4.66 (3H, m, H-5 & H-6 × 2), 1.99 (3H, s, OAc); Anal. Calcd for $C_{15}H_{14}O_6$: C, 62.07; H, 4.86. Found: C, 61.90; H, 4.91.

General glycosylation procedure in Table 1 and Fig. 2

A suspension of glycosyl donor (2,3-unsaturated glycosyl acatate **1** or **13** (0.05 mmol) or 2,3-dideoxy glycosyl acetate **2** or **14** (0.05 mmol)), methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**10**) (0.045 mmol) and MS 5A (100 wt% to glycosyl donor) in dry CH_2Cl_2 (40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added an activator as listed in Table 1 and Fig. 2. After the suspension was stirred at the temperature for the period as listed in Table 1 or Fig. 2, triethylamine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into saturated $NaHCO_3$ aq., and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The yields of the glycosides and their $\alpha:\beta$ ratios were determined by HPLC analysis (column, Develosil ODS-HG-5^{TM}, (4.6 × 250 mm) × 2; eluent, 11.1% (v/v) H_2O in MeOH; flow rate, 0.5 mL min^{-1}, 40 °C; detection, UV 250 nm).

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*α*-D-*erythro*-hex-2-nopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (11*α*)

Colorless syrup; R_f 0.73 (1/1 hexane–EtOAc); $[\alpha]_D^{30}$ +84.1 (*c* 1.57, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS) δ 8.02-7.95 (4H, m, ArH), 7.66-7.52 (2H, m, ArH), 7.52-7.22 (19H, m, ArH), 6.02 (1H, ddd, $J_{2',3'} = 10.2$ Hz, $J_{1',3'} = 0.9$ Hz, $J_{3',4'} = 0.9$ Hz, H-3′), 5.91 (1H, ddd, $J_{2',3'} = 10.2$ Hz, $J_{1',2'} = 2.4$ Hz, $J_{2',4'} = 2.1$ Hz, H-2′), 5.68 (1H, ddd, $J_{4',5'} = 7.2$ Hz, $J_{2',4'} = 2.1$ Hz, $J_{3',4'} = 0.9$ Hz, H-4′), 5.16 (1H, dd, $J_{1',2'} = 2.4$ Hz, $J_{1',3'} = 0.9$ Hz, H-1′), 4.99 & 4.80 (2H, ABq, $J = 10.8$ Hz, $ArCH_2$), 4.91 & 4.64 (2H, ABq, $J = 11.4$ Hz, $ArCH_2$), 4.78 & 4.67 (2H, ABq, $J = 12.0$ Hz, $ArCH_2$), 4.61 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.46 (1H, dd, $J_{6',6'} = 8.7$ Hz, $J_{5',6'} = 4.5$ Hz, H-6′), 4.37 (1H, ddd, $J_{4',5'} = 7.2$ Hz, $J_{5',6'} = 5.1$ Hz, $J_{5',6'} = 4.5$ Hz, H-5′), 4.34 (1H, dd, $J_{6',6'} = 8.7$ Hz, $J_{5',6'} = 5.1$ Hz, H-6′), 4.01 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 4.8$ Hz, H-6), 4.00 (1H, dd, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 3.82-3.72 (2H, m, H-5 & H-6), 3.53 (1H, dd, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.49 (1H, dd, $J_{2,3} = 9.3$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.38 (3H, s, OMe); Anal. Calcd for $C_{48}H_{48}O_{11}$: C, 71.98; H, 6.04. Found: C, 71.83; H, 5.90.

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*β*-D-*erythro*-hex-2-nopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (11*β*)

Colorless syrup; R_f 0.73 (1/1 hexane–EtOAc); $[\alpha]_D^{30}$ +104.5 (*c* 1.95, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS) δ 8.04-7.96 (4H, m, ArH), 7.61-7.46 (2H, m, ArH), 7.46-7.22 (19H, m, ArH), 6.10 (1H, ddd, $J_{2',3'} = 10.2$ Hz, $J_{3',4'} = 3.6$ Hz, $J_{1',3'} = 1.5$ Hz, H-3′), 5.92 (1H, ddd, $J_{2',3'} = 10.2$ Hz, $J_{1',2'} = 1.5$ Hz, $J_{2',4'} = 1.5$ Hz, H-2′), 5.55 (1H, ddd, $J_{4',5'} = 11.4$ Hz, $J_{3',4'} = 3.6$ Hz, $J_{1',3'} = 1.5$ Hz, H-4′), 5.16 (1H, dd, $J_{1',2'} = 1.5$ Hz, $J_{1',3'} = 1.5$ Hz, H-1′), 4.98 & 4.80 (2H, ABq, $J = 11.1$ Hz, $ArCH_2$), 4.87 & 4.61 (2H, ABq, $J = 11.1$ Hz, $ArCH_2$), 4.78 & 4.66 (2H, ABq, $J = 12.0$ Hz, $ArCH_2$), 4.59 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.54 (1H, dd, $J_{6',6'} = 11.7$ Hz, $J_{5',6'} = 6.0$ Hz, H-6′), 4.49 (1H, dd, $J_{6',6'} = 11.7$ Hz, $J_{5',6'} = 5.4$ Hz, H-6′), 4.31 (1H, ddd, $J_{4',5'} = 11.4$ Hz, $J_{5',6'} = 6.0$ Hz, $J_{5',6'} = 5.4$ Hz, H-5′), 4.08-4.01 (1H, m, H-6), 3.97 (1H, dd, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 3.79-3.71 (2H, m, H-5 & H-6), 3.57 (1H, dd, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.53 (1H, dd, $J_{2,3} = 9.3$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.30 (3H, s, OMe); Anal. Calcd for $C_{48}H_{48}O_{11}$: C, 71.98; H, 6.04. Found: C, 71.71; H, 6.15.

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*α*-D-*erythro*-hexopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (12*α*)

Colorless syrup; R_f 0.40 (2/1 hexane–EtOAc); $[\alpha]_D^{29}$ +81.5 (*c* 2.26, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS) δ 8.02-7.95 (2H, m, ArH), 7.93-7.88 (2H, m, ArH), 7.58-7.48 (2H, m, ArH), 7.42-7.22 (19H, m, ArH), 5.11-5.01 (1H, m, H-4′), 5.00 & 4.80 (2H, ABq, $J = 10.8$ Hz, $ArCH_2$), 4.98 & 4.68 (2H, ABq, $J = 10.8$ Hz, $ArCH_2$), 4.73 (1H, br-dd, H-1′), 4.78 & 4.68 (2H, ABq, $J = 12.0$ Hz, $ArCH_2$), 4.63 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.46 (1H, dd, $J_{6',6'} = 9.9$ Hz, $J_{5',6'} = 2.1$ Hz, H-6′), 4.26 (1H, dd, $J_{6',6'} = 9.9$ Hz, $J_{5',6'} = 6.0$ Hz, H-6′), 4.22 (1H, ddd, $J_{4',5'} = 9.3$ Hz, $J_{5',6'} = 6.0$ Hz, $J_{5',6'} = 2.1$ Hz, H-5′), 4.01 (1H, dd, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 3.96 (1H, dd, $J_{6,6} = 11.1$ Hz, $J_{5,6} = 4.8$ Hz, H-6), 3.81 (1H, ddd, $J_{4,5} = 10.2$ Hz, $J_{5,6} = 4.8$ Hz, $J_{5,6} = 1.2$ Hz, H-5), 3.68 (1H, dd, $J_{6,6} = 11.1$ Hz, $J_{5,6} = 1.2$ Hz, H-6), 3.53 (1H, dd, $J_{4,5} = 10.2$ Hz, $J_{3,4} = 9.3$ Hz, H-4), 3.48 (1H, dd, $J_{2,3} = 9.3$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.40 (3H, s, OMe), 2.21-2.11 (1H, m, H-3′), 2.05-1.80 (3H, m, H-2′ × 2, H-3′). Anal. Calcd for $C_{48}H_{50}O_{11}$: C, 71.80; H, 6.28. Found: C, 71.68; H, 6.31.

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*β*-D-*erythro*-hexopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (12*β*)

Colorless syrup; R_f 0.38 (2/1 hexane–EtOAc); $[\alpha]_D^{30}$ +32.6 (*c* 1.69, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS) δ 8.02-7.95 (4H, m, ArH), 7.61-7.47 (2H, m, ArH), 7.44-7.22 (19H, m, ArH), 5.02 (1H, ddd, $J_{3',4'} = 9.3$ Hz, $J_{4',5'} = 9.0$ Hz, $J_{3',4'} = 5.1$ Hz, H-4′), 4.98 & 4.80 (2H, ABq, $J = 10.5$ Hz, $ArCH_2$), 4.88 & 4.59 (2H, ABq, $J = 11.1$ Hz, $ArCH_2$), 4.78 & 4.65 (2H, ABq, $J = 12.3$ Hz, $ArCH_2$), 4.60 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.56 (1H, dd, $J_{6',6'} = 12.0$ Hz, $J_{5',6'} = 3.9$ Hz, H-6′), 4.43 (1H, br-dd, $J_{1',2'} = 9.0$ Hz, H-1′), 4.40 (1H, dd, $J_{6',6'} = 12.0$ Hz, $J_{5',6'} = 6.0$ Hz, H-6′), 4.09 (1H, br-dd, $J_{6,6} = 10.5$ Hz, H-6), 3.98 (1H, dd, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 3.93 (1H, ddd, $J_{4',5'} = 9.0$ Hz, $J_{5',6'} = 6.0$ Hz, $J_{5',6'} = 3.9$ Hz, H-5′), 3.75 (1H, br-ddd, $J_{4,5} = 9.6$ Hz, $J_{5,6} = 3.9$ Hz, H-5), 3.64 (1H, dd, $J_{6,6} = 10.5$ Hz, $J_{5,6} = 3.9$ Hz, H-6), 3.56 (1H, dd, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 3.54 (1H, dd, $J_{2,3} = 9.6$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.33 (3H, s, OMe), 2.40-2.30 (1H, m), 1.92-1.57 (3H, m). Anal. Calcd for $C_{48}H_{50}O_{11}$: C, 71.80; H, 6.28. Found: C, 71.70; H, 6.03.

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*α*-D-*threo*-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (15*α*)

Colorless viscous syrup; R_f 0.68 (1/1 hexane–EtOAc); $[\alpha]_D^{29}$ −80.9 (*c* 1.22, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.07-8.01 (2H, m, ArH), 7.99-7.92 (2H, m, ArH), 7.60-7.47 (2H, m, ArH), 7.47-7.17 (19H, m, ArH), 6.25 (1H, ddd, $J_{2',3'} = 10.2$ Hz, $J_{3',4'} = 5.4$ Hz, $J_{1',3'} = 0.9$ Hz, H-3′), 6.09 (1H, dd, $J_{2',3'} = 10.2$ Hz, $J_{1',2'} = 3.0$ Hz, H-2′), 5.32 (1H, dd, $J_{3',4'} = 5.4$ Hz, $J_{4',5'} = 1.8$ Hz, H-4′), 5.21 (1H, dd, $J_{1',2'} = 3.0$ Hz, $J_{1',3'} = 0.9$ Hz, H-1′), 4.97 & 4.80 (2H, ABq, $J =$ 10.5 Hz, $ArCH_2$), 4.87 & 4.58 (2H, ABq, $J = 11.1$ Hz, $ArCH_2$), 4.76 & 4.65 (2H, ABq, $J = 12.3$ Hz, $ArCH_2$), 4.62-4.40 (3H, m), 4.58 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 3.98 (1H, dd, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 3.96 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 4.8$ Hz, H-6), 3.79 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 1.8$ Hz, H-6), 3.76 (1H, ddd, $J_{4,5} = 9.3$ Hz, $J_{5,6} = 4.8$ Hz, $J_{5,6} = 1.8$ Hz, H-5), 3.45 (1H, dd, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.44 (1H, dd, $J_{2,3} = 9.3$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.36 (3H, s, OMe). Anal. Calcd for $C_{48}H_{48}O_{11}$: C, 71.98; H, 6.04. Found: C, 71.80; H, 6.14.

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*β*-D-*threo*-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (15*β*)

White needles; m.p. 88.2-89.6 °C; R_f 0.83 (1/1 hexane–EtOAc); $[\alpha]_D^{30}$ −85.6 (*c* 0.27, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.04-7.99 (2H, m, ArH), 7.98-7.93 (2H, m, ArH), 7.60-7.49 (2H, m, ArH), 7.45-7.22 (19H, m, ArH), 6.24 (1H, ddd, $J_{2',3'} = 10.2$ Hz, $J_{3',4'} =$ 4.5 Hz, $J_{1',3'} = 1.2$ Hz, H-3′), 5.99 (1H, d, $J_{2',3'} = 10.2$ Hz, H-2′), 5.45 (1H, dd, $J_{3',4'} = 4.5$ Hz, $J_{4',5'} = 3.0$ Hz, H-4′), 5.20 (1H, d, $J_{1',2'} = 1.2$ Hz, H-1′), 4.98 & 4.82 (2H, ABq, $J = 10.5$ Hz, $ArCH_2$), 4.88 & 4.69 (2H, ABq, $J = 11.1$ Hz, $ArCH_2$), 4.80 & 4.66 (2H, ABq, $J = 12.0$ Hz, $ArCH_2$), 4.59 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.58 (1H, dd, $J_{6',6'} = 11.4$ Hz, $J_{5',6'} = 7.2$ Hz, H-6′), 4.47 (1H, dd, $J_{6',6'} =$ 11.4 Hz, $J_{5',6'} = 5.4$ Hz, H-6′), 4.18 (1H, ddd, $J_{5',6'} = 7.2$ Hz, $J_{5',6'} =$ 5.4 Hz, $J_{4',5'} = 3.0$ Hz, H-5′), 4.00 (1H, dd, $J_{6,6} = 10.5$ Hz, $J_{5,6} =$ 2.1 Hz, H-6), 3.99 (1H, dd, $J_{2,3} = 9.6$ Hz, $J_{3,4} = 9.3$ Hz, H-3), 3.89 (1H, dd, $J_{6,6} = 10.5$ Hz, $J_{5,6} = 3.6$ Hz, H-6), 3.79 (1H, ddd, $J_{4,5} =$ 9.6 Hz, $J_{5,6} = 3.6$ Hz, $J_{5,6} = 2.1$ Hz, H-5), 3.61 (1H, dd, $J_{4,5} =$ 9.6 Hz, $J_{3,4} = 9.3$ Hz, H-4), 3.55 (1H, dd, $J_{2,3} = 9.6$ Hz, $J_{1,2} =$ 3.6 Hz, H-2), 3.33 (3H, s, OMe). Anal. Calcd for $C_{48}H_{48}O_{11}$: C, 71.98; H, 6.04. Found: C, 71.90; H, 6.09.

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*α*-D-*threo*-hexopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (16*α*)

Colorless syrup; R_f 0.80 (1/1 hexane–EtOAc); $[\alpha]_D^{30}$ +34.8 (*c* 0.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.11-8.06 (2H, m, ArH), 7.98-7.93 (2H, m, ArH), 7.61-7.49 (2H, m, ArH), 7.48-7.41 (2H, m, ArH), 7.40-7.20 (17H, m, ArH), 5.22 (1H, br-dd, H-1′), 5.02 (1H, br-ddd, H-4′), 4.98 & 4.80 (2H, ABq, $J = 10.8$ Hz, $ArCH_2$), 4.92 & 4.58 (2H, ABq, $J = 11.4$ Hz, $ArCH_2$), 4.76 & 4.65 (2H, ABq, $J = 12.0$ Hz, $ArCH_2$), 4.61 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.40 (1H, dd, $J_{6',6'} = 12.9$ Hz, $J_{5',6'} = 9.9$ Hz, H-6′), 4.30 (1H, br-ddd, $J_{5',6'} =$ 9.9 Hz, $J_{5',6'} = 4.2$ Hz, H-5′), 4.28 (1H, dd, $J_{6',6'} = 12.9$ Hz, $J_{5',6'} =$ 4.2 Hz, H-6′), 3.99 (1H, dd, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 3.89 (1H, dd, $J_{6,6} = 11.1$ Hz, $J_{5,6} = 5.1$ Hz, H-6), 3.78 (1H, ddd, $J_{4,5} = 9.3$ Hz, $J_{5,6} = 5.1$ Hz, $J_{5,6} = 1.5$ Hz, H-5), 3.71 (1H, dd, $J_{6,6} = 11.1$ Hz, $J_{5,6} = 1.5$ Hz, H-6), 3.43 (1H, dd, $J_{2,3} = 9.3$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.42 (1H, dd, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.38 (3H, s, OMe), 2.22-1.94 (3H, m, H-2′ × 2, H-3′), 1.72-1.62 (1H, m, H-3′). Anal. Calcd for $C_{48}H_{50}O_{11}$: C, 71.80; H, 6.28. Found: C, 71.50; H, 6.12.

Methyl 6-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-*β*-D-*threo*-hexopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (16*β*)

Colorless syrup; R_f 0.78 (1/1 hexane–EtOAc); $[\alpha]_D^{31}$ −15.5 (*c* 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.11-8.05 (2H, m, ArH), 8.01-7.96 (2H, m, ArH), 7.61-7.49 (2H, m, ArH), 7.47-7.22 (19H, m, ArH), 5.20 (1H, br-ddd, H-4′), 4.99 & 4.80 (2H, ABq, $J = 11.1$ Hz, $ArCH_2$), 4.88 & 4.58 (2H, ABq, $J = 11.1$ Hz, $ArCH_2$), 4.80 & 4.66 (2H, ABq, $J = 11.7$ Hz, $ArCH_2$), 4.63 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.52 (1H, dd, $J_{6',6'} = 11.1$ Hz, $J_{5',6'} = 6.0$ Hz, H-6′), 4.39 (1H, br-dd, $J_{1',2'} = 6.6$ Hz, H-1′), 4.37 (1H, dd, $J_{6',6'} = 11.1$ Hz, $J_{5',6'} = 6.0$ Hz, H-6′), 4.16 (1H, dd, $J_{6,6} = 10.8$ Hz, $J_{5,6} = 1.5$ Hz, H-6), 4.00 (1H, br-ddd, $J_{5',6'} = 6.9$ Hz, $J_{5',6'} = 6.0$ Hz, H-5′), 4.00 (1H, dd, $J_{2,3} =$ $J_{3,4} = 9.6$ Hz, H-3), 3.81 (1H, ddd, $J_{4,5} = 9.6$ Hz, $J_{5,6} = 4.5$ Hz, $J_{5,6} = 1.5$ Hz, H-5), 3.66 (1H, dd, $J_{6,6} = 10.8$ Hz, $J_{5,6} = 4.5$ Hz, H-6), 3.55 (1H, dd, $J_{2,3} = 9.6$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.55 (1H, dd, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 3.37 (3H, s, OMe), 2.25-2.15 (1H, m, H-3′), 2.03-1.71 (2H, m), 1.67-1.55 (1H, m). Anal. Calcd for $C_{48}H_{50}O_{11}$: C, 71.80; H, 6.28. Found: C, 71.61; H, 6.34.

General glycosylation procedure in Table 3

A suspension of glycosyl donor (2,3-dideoxy glycosyl acatate **18** (0.05 mmol) or 2,3-unsaturated-4-keto glycosyl acetate **3** (0.05 mmol)), methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**10**) (0.05 mmol) and MS 5A (100 wt% to glycosyl donor) in dry CH_2Cl_2 (40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added an activator as listed in Table 3. After the suspension was stirred at the temperature for the period as listed in Table 3, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane/ether = 1/1 (for the glycosylation using **18**) or hexane–EtOAc = 1/1 (for the glycosylation using **3**) afforded disaccharide **19** and recovered **18** or disaccharide **17** and recovered **3** as indicated in Table 3. The $\alpha:\beta$ ratios were determined by ^{1}H NMR analysis.

Methyl 6-*O*-(6′-*O*-benzoyl-4′-*O*-benzyl-2′,3′-dideoxy-*α*-D-*erythro*-hexopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (19*α*)

Colorless syrup; R_f 0.38 (9/1 toluene–EtOAc); $[\alpha]_D^{32}$ +65.3 (*c* 3.63, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 7.95 (2H, dd, $J_{o,m} = 8.5$ Hz, $J_{o,p} = 1.2$ Hz, H_o of Bz), 7.52 (1H, tt, $J_{m,p} = 7.4$ Hz, $J_{o,p} = 1.2$ Hz, H_p of Bz), 7.39-7.19 (23H, m, ArH), 4.99 & 4.81 (2H, ABq, $J =$ 12.0 Hz, $ArCH_2$), 4.95 & 4.62 (2H, ABq, $J = 11.4$ Hz, $ArCH_2$), 4.85 (1H, br-s, H-1′), 4.77 & 4.67 (2H, ABq, $J = 12.0$ Hz, $ArCH_2$), 4.63 & 4.43 (2H, ABq, $J = 11.7$ Hz, $ArCH_2$), 4.61 (1H, d, $J_{1,2} =$ 3.5 Hz, H-1′), 4.48-4.37 (2H, m, H-6′ × 2), 4.01 (1H, dd, $J_{2,3} = J_{3,4} =$ 9.0 Hz, H-3), 3.99-3.94 (1H, m, H-5′), 3.89 (1H, dd, $J_{6,6} = 11.0$ Hz, $J_{5,6} = 5.0$ Hz, H-6), 3.77 (1H, ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 5.0$ Hz, $J_{5,6} = 1.5$ Hz, H-5), 3.62 (1H, dd, $J_{6,6} = 11.0$ Hz, $J_{5,6} = 1.5$ Hz, H-6), 3.52 (1H, dd, $J_{3,4} = J_{4,5} = 9.0$ Hz, H-4), 3.51 (1H, dd, $J_{2,3} =$ 9.0 Hz, $J_{1,2} = 3.5$ Hz, H-2), 3.46 (1H, ddd, $J_{3',4'} = J_{4',5'} = 10.2$ Hz, $J_{3',4'} = 4.5$ Hz, H-4′), 3.37 (3H, s, OMe), 2.11-2.06 (1H, m, H-3′),

1.93-1.67 (3H, m, H-2′ × 2 & H-3); Anal. Calcd for $C_{48}H_{52}O_{10}$: C, 73.08; H, 6.64. Found: C, 72.78; H, 6.69; HRMS (ESI-TOF) *m/z* 811.3450 (811.3458 calcd for $C_{48}H_{52}O_{10}Na$, $[M+Na]^+$).

Methyl 6-*O*-(6′-*O*-benzoyl-4′-*O*-benzyl-2′,3′-dideoxy-*α*-D-*erythro*-hexopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (19*β*)

Colorless syrup; R_f 0.27 (9/1 toluene–EtOAc); $[\alpha]_D^{32}$ +30.1 (*c* 2.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 7.99 (2H, dd, $J_{o,m} = 8.3$ Hz, $J_{o,p} = 1.2$ Hz, H_o of Bz), 7.53 (1H, tt, $J_{m,p} = 7.3$ Hz, $J_{o,p} = 1.2$ Hz, H_p of Bz), 7.41-7.21 (23H, m, ArH), 4.97 & 4.79 (2H, ABq, J = 11.0 Hz, $ArCH_2$), 4.85 & 4.55 (2H, ABq, J = 11.2 Hz, $ArCH_2$), 4.78 & 4.64 (2H, ABq, J = 11.9 Hz, $ArCH_2$), 4.60 & 4.43 (2H, ABq, J = 11.5 Hz, $ArCH_2$), 4.59 (1H, d, $J_{1,2} = 3.7$ Hz, H-1), 4.59-4.53 (1H, m, H-6′), 4.47 (1H, $J_{6',6'} = 11.7$ Hz, $J_{5',6'} = 5.6$ Hz, H-6′), 4.35 (1H, dd, $J_{1',2'} = 9.3$ Hz, $J_{1',2'} = 2.1$ Hz, H-1′), 4.05 (1H, dd, $J_{6',6'} = 11.7$ Hz, $J_{5',6'} = 2.0$ Hz, H-6′), 4.00 (1H, dd, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 3.73 (1H, m, H-5), 3.68-3.57 (2H, m, H-6 & H-5′), 3.61 (1H, dd, $J_{6,6} = 10.5$ Hz, $J_{5,6} = 10.0$ Hz, H-6), 3.54 (1H, dd, $J_{3,4} = J_{4,5} = 9.0$ Hz, H-4), 3.52 (1H, dd, $J_{2,3} = 9.2$ Hz, $J_{1,2} = 3.7$ Hz, H-2), 3.41 (1H, ddd, $J_{3',4'} = J_{4',5'} = 9.2$ Hz, $J_{3',4'} = 5.3$ Hz, H-4′), 3.31 (3H, s, OMe), 2.29-2.24 (1H, m, H-3′), 1.83-1.42 (3H, m, H-2′ × 2 & H-3); HRMS (ESI-TOF) *m/z* 811.3448 (811.3458 calcd for $C_{48}H_{52}O_{10}Na$, $[M+Na]^+$).

6-*O*-Benzoyl-4-*O*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-D-*erythro*-hex-2-enopyranosyl)-2,3- dideoxy-*α*-D-*erythro*-hexopyranosyl Acetate (21)

A suspension of 2,3-unsaturated glycosyl acatate **1** (13.4 mg, 0.0338 mmol), 2,3-dideoxy glycosyl acetate **20** (19.8 mg, 0.0677 mmol) and MS 5A (13.4 mg, 100 wt% to glycosyl donor) in dry CH_2Cl_2 (0.536 mL, 40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (3.7 μL, 0.020 mmol) at −80 °C. After the suspension was stirred at −80 °C for 30 min, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by preparative TLC (chloroform–EtOAc = 9/1) afforded disaccharide **21** (17.8 mg, 81%, $\alpha:\beta$ = 76:24). **21***α*: Colorless syrup; R_f 0.61 (1/1 hexane–EtOAc); $[\alpha]_D^{32}$ +115.6 (*c* 5.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.06-7.97 (6H, m, ArH), 7.57-7.48 (3H, m, ArH), 7.44-7.34 (6H, m, ArH), 6.13 (1H, m, H-1), 6.06 (1H, dd, br-d, $J_{2',3'} = 10.6$ Hz, H-3′), 5.84 (1H, ddd, $J_{2',3'} = 10.6$ Hz, $J_{1',2'} = 2.4$ Hz, $J_{2',4'} = 2.2$ Hz, H-2′), 5.68 (1H, br-dd, J = 9.2 Hz, J = 2.2 Hz, H-4′), 5.33 (1H, m, H-1′), 4.67 (1H, dd, $J_{6,6} = 11.7$ Hz, $J_{5,6} = 2.4$ Hz, H-6), 4.52 (1H, dd, $J_{6,6} = 11.7$ Hz, $J_{5,6} = 5.1$ Hz, H-6), 4.38-4.28 (3H, m, H-5′ & H-6′ × 2), 4.08 (1H, ddd, $J_{4,5} = 9.7$ Hz, $J_{5,6} = 5.1$ Hz, $J_{5,6} = 2.4$ Hz, H-5), 3.98 (1H, ddd, $J_{3,4} = J_{4,5} = 9.9$ Hz, $J_{3,4} = 4.6$ Hz, H-4), 2.22 (1H, m, H-3), 2.11 (3H, s, OAc), 1.95 (1H, m, H-3), 1.80 (2H, m, H-2 × 2); Anal Calcd for $C_{35}H_{34}O_{11}$: C, 66.66; H, 5.43. Found: C, 66.60; H, 5.52.; HRMS (ESI-TOF) *m/z* 653.1996 (653.1999 calcd for $C_{35}H_{34}O_{11}Na$, $[M+Na]^+$). **21***β*: Colorless syrup; R_f 0.58 (1/1 hexane–EtOAc); $[\alpha]_D^{33}$ +150.5 (*c* 0.73, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.07-7.99 (6H, m, ArH), 7.60-7.53 (3H, m, ArH), 7.48-7.38 (6H, m, ArH), 6.13-6.08 (2H, m, H-1 & H-3′), 5.99 (1H, ddd, $J_{2',3'} = 10.2$ Hz, $J_{1',2'} = J_{2',4'} = 1.7$ Hz, H-2′), 5.61 (1H, m, H-4′), 5.26 (1H, d, $J_{1',2'} = 1.7$ Hz, H-1′), 4.62 (1H, dd, $J_{6,6} = 11.9$ Hz, $J_{5,6} = 4.1$ Hz, H-6), 4.57-4.51 (2H, m, H-6′ × 2), 4.44 (1H, dd, $J_{6,6} = 11.9$ Hz, $J_{5,6} = 2.4$ Hz, H-6), 4.30 (1H, ddd, $J_{5',6'} = 5.9$ Hz, $J_{4',5'} = J_{5',6'} = 5.6$ Hz, H-5′), 3.99 (1H, ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 4.1$ Hz, $J_{5,6} = 2.4$ Hz, H-5), 3.79 (1H, ddd, $J_{3,4} = 9.9$ Hz, $J_{4,5} = 9.0$ Hz, $J_{3,4} = 4.1$ Hz, H-4), 2.30 (1H, m, H-3), 2.09 (3H, s, OAc), 1.99 (1H, m, H-3), 1.86 (2H, m, H-2 × 2); HRMS (ESI-TOF) *m/z* 653.1977 (653.1999 calcd for $C_{35}H_{34}O_{11}Na$, $[M+Na]^+$).

Methyl 6-*O*-(6′-*O*-benzoyl-4′-*O*-(4″,6″-di-*O*-benzoyl-2″,3″-dideoxy-*α*-D-*erythro*-hex-2- enopyranosyl)-D-*erythro*-hexopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (22)

A suspension of disaccharide **21***α* (33.4 mg, 0.0530 mmol), methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**10**) (12.3 mg, 0.0265 mmol) and MS 5A (33.4 mg, 100 wt% to glycosyl donor) in dry toluene (1.34 mL, 40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (3.0 μL, 0.015 mmol) at −40 °C. After the suspension was stirred at −40 °C for 30 min, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane–EtOAc = 1/1) afforded trisaccharide **22** (21.4 mg, 78%, $\alpha:\beta$ = 85:15). **22***α*: Colorless syrup; R_f 0.56 (1/1 hexane–EtOAc); $[\alpha]_D^{32}$ +114.7 (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.02-7.98 (6H, m, ArH), 7.57-7.22 (24H, m, ArH), 6.04 (1H, br-d, J = 10.2 Hz, H-3″), 5.81 (1H, ddd, $J_{2'',3''} = 10.2$ Hz, $J_{1'',2''} = J_{2'',4''} = 2.7$ Hz, H-2″), 5.68 (1H, ddd, $J_{4'',5''} = 10.2$ Hz, $J_{2'',4''} = 2.7$ Hz, $J_{3'',4''} = 1.2$ Hz, H-4″), 5.29 (1H, br-s, H-1″), 4.99 & 4.80 (2H, ABq, J = 10.7 Hz, $ArCH_2$), 4.96 & 4.60 (2H, ABq, J = 11.0 Hz, $ArCH_2$), 4.86 (1H, br-d, $J_{1',2'} = 2.4$ Hz, H-1′), 4.77 & 4.67 (2H, ABq, J = 12.2 Hz, $ArCH_2$), 4.62 (1H, br-d, H-1), 4.55 (1H, dd, $J_{6',6'} = 11.7$ Hz, $J_{5',6'} = 2.1$ Hz, H-6′), 4.44-4.37 (3H, m, H-6′ & H-6″ × 2), 4.34 –4.26 (1H, m, H-5″), 4.04-3.96 (2H, m, H-3 & H-5′), 3.93-3.82 (2H, m, H-6 & H-4′), 3.79-3.75 (1H, m, H-5), 3.64 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 1.2$ Hz, H-6), 3.51 (1H, dd, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.48 (1H, dd, $J_{2,3} = 9.3$ Hz, $J_{1,2} = 3.6$ Hz, H-2), 3.38 (3H, s, OMe), 2.12-2.07 (1H, m, H-3′), 1.92-1.59 (3H, m, H-2′ × 2 & H-3′); ^{13}C NMR ($CDCl_3$) δ 166.42, 166.14, 165.80, 138.74, 138.31, 138.21, 133.39, 132.95, 130.18, 129.85, 129.80, 129.62, 129.46, 128.39, 128.14, 127.96, 127.91, 127.65, 97.89, 96.31, 89.96, 82.23, 80.16, 78.02, 75.78, 75.01, 73.25, 69.99, 69.83, 67.39, 66.08, 65.54, 64.43, 63.59, 55.09, 28.59, 23.08; HRMS (ESI-TOF) *m/z* 1057.3982 (1057.3986 calcd for $C_{61}H_{62}O_{15}Na$, $[M+Na]^+$). **22***β*: Colorless syrup; R_f 0.56 (1/1 hexane–EtOAc); $[\alpha]_D^{31}$ +70.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.04-7.97 (6H, m, ArH), 7.59-7.23 (24H, m, ArH), 6.05 (1H, d, $J_{2'',3''} = 10.2$ Hz, H-3″), 5.82 (1H, ddd, $J_{2'',3''} = 10.2$ Hz, $J_{1'',2''} = J_{2'',4''} = 2.7$ Hz, H-2″), 5.67 (1H, m, H-4″), 5.25 (1H, br-s, H-1″), 4.98 & 4.79 (2H, ABq, J = 10.7 Hz, $ArCH_2$), 4.86 & 4.56 (2H, ABq, J = 11.0 Hz, $ArCH_2$), 4.78 & 4.65 (2H, ABq, J = 12.0 Hz, $ArCH_2$), 4.67 (1H, dd, $J_{6',6'} = 12.0$ Hz, $J_{5',6'} = 3.4$ Hz, H-6′), 4.60 (1H, d, $J_{1,2} = 3.3$ Hz, H-1), 4.47 (1H, m, H-6′), 4.38 (1H, br-dd, $J_{1',2'} = 9.3$ Hz, H-1′), 4.39-4.32 (3H, m, H-5″ & H-6″ × 2), 4.06 (1H, dd, $J_{6,6} = 11.0$ Hz, $J_{5,6} = 1.2$ Hz, H-6), 3.97 (1H, dd, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 3.91-3.81 (1H, m, H-4′), 3.79-3.54 (4H, m, H-4, H-5, H-6 & H-5′), 3.53 (1H, dd, $J_{2,3} = 9.6$ Hz, $J_{1,2} = 3.3$ Hz, H-2), 3.33 (3H, s, OMe), 2.33-3.23 (1H, m, H-3′), 1.88-1.78 & 1.70-1.42 (3H, m, H-2′ × 2 & H-3′); ^{13}C NMR ($CDCl_3$)

δ 166.39, 166.16, 166.78, 165.78, 138.84, 138.44, 138.19, 133.37, 132.96, 129.85, 129.71, 129.67, 128.42, 128.37, 128.32, 128.14, 128.01, 127.91, 127.81, 127.77, 127.60, 101.89, 98.02, 90.82, 82.22, 79.91, 77.63, 76.01, 75.75, 74.86, 73.33, 70.16, 69.76, 67.54, 67.44, 66.01, 64.71, 63.63, 55.11, 29.30, 26.17; HRMS (ESI-TOF) *m/z* 1057.3977 (1057.3986 calcd for $C_{61}H_{62}O_{15}Na$, $[M+Na]^+$).

6-*O*-(4′,6′-Di-*O*-benzoyl-2′,3′-dideoxy-D-*erythro*-hex-2-enopyranosyl)-2,3-dideoxy-*α*-D-*glycelo*-hex-2-enopyranos-4-ulosyl Acetate (24)

A suspension of 2,3-unsaturated glycosyl acatate **1** (23.2 mg, 0.0585 mmol), 2,3-unsaturated-4-keto glycosyl acetate **23** (22.0 mg, 0.118 mmol) and MS 5A (23.2 mg, 100 wt% to glycosyl donor) in dry CH_2Cl_2 (0.928 mL, 40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (3.2 μL 0.017 mmol) at −75 °C. After the suspension was stirred at −75 °C for 30 min, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by preparative TLC (chloroform–EtOAc = 9/1) afforded disaccharide **24** (27.9 mg, 91%, $\alpha:\beta$ = 79 : 21). **24***α*: Colorless syrup; R_f 0.59 (9/1 chloroform–EtOAc); $[\alpha]_D^{32}$ +12.1 (*c* 2.68, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.09-7.99 (4H, m, ArH), 7.60-7.49 (2H, m, ArH), 7.46-7.36 (4H, m, ArH), 6.91 (1H, dd, $J_{2,3}$ = 10.2 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 6.56 (1H, d, $J_{1,2}$ = 3.7 Hz, H-1), 6.27 (1H, d, $J_{2,3}$ = 10.2 Hz, H-3), 6.05 (1H, br-d, J = 10.5 Hz, H-3′), 5.90 (1H, ddd, $J_{2',3'}$ = 10.2 Hz, $J_{2',4'}$ = 2.0 Hz, $J_{1',2'}$ = 2.7 Hz, H-2′), 5.70 (1H, ddd, $J_{4',5'}$ = 9.5 Hz, $J_{3',4'}$ = 3.2 Hz, $J_{2',4'}$ = 2.0 Hz, H-4′), 5.13 (1H, br-s, H-1′), 4.68 (1H, dd, $J_{5,6}$ = 4.2 Hz, $J_{5,6}$ = 2.7 Hz, H-5), 4.65 (1H, dd, $J_{6',6'}$ = 10.5 Hz, $J_{5',6'}$ = 2.7 Hz, H-6′), 4.48 (1H, dd, $J_{6',6'}$ = 10.5 Hz, $J_{5',6'}$ = 5.4 Hz, H-6′), 4.40 (1H, m, H-5′), 4.38 (1H, dd, $J_{6,6}$ = 11.0 Hz, $J_{5,6}$ = 4.2 Hz, H-6), 3.90 (1H, dd, $J_{6,6}$ = 11.0 Hz, $J_{5,6}$ = 2.7 Hz, H-6), 2.14 (3H, s, OAc); Anal. Calcd for $C_{28}H_{26}O_{10}$: C, 64.36; H, 5.02. Found: C, 64.59; H, 5.20; HRMS (ESI-TOF) *m/z* 545.1406 (545.1424 calcd for $C_{28}H_{26}O_{10}Na$, $[M+Na]^+$). **24***β*:Colorless syrup; R_f 0.52 (9/1 chloroform–EtOAc); $[\alpha]_D^{32}$ +57.5 (*c* 0.93, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.06-8.01 (4H, m, ArH), 7.60-7.52 (2H, m, ArH), 7.45-7.40 (4H, m, ArH), 6.93 (1H, dd, $J_{2,3}$ = 10.2 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 6.57 (1H, d, $J_{1,2}$ = 3.7 Hz, H-1), 6.21 (1H, d, $J_{2,3}$ = 10.2 Hz, H-3), 6.04 (1H, br-d, H-3′), 5.91 (1H, ddd, $J_{2',3'}$ = 10.2 Hz, $J_{2',4'}$ = 2.2 Hz, $J_{1',3'}$ = 1.2 Hz, H-2′), 5.70 (1H, ddd, $J_{4',5'}$ = 9.5 Hz, $J_{3',4'}$ = 3.8 Hz, $J_{2',4'}$ = 1.2 Hz, H-4′), 5.26 (1H, m, H-1′), 4.68 (1H, m, H-5), 4.65 (1H, dd, $J_{6',6'}$ = 11.0 Hz, $J_{5',6'}$ = 2.7 Hz, H-6′), 4.48 (1H, dd, $J_{6',6'}$ = 11.0 Hz, $J_{5',6'}$ = 5.4 Hz, H-6′), 4.40 (1H, m, H-5′), 4.38 (1H, dd, $J_{6,6}$ = 10.7 Hz, $J_{5,6}$ = 4.1 Hz, H-6), 3.90 (1H, dd, $J_{6,6}$ = 10.7 Hz, $J_{5,6}$ = 2.7 Hz, H-6), 2.10 (3H, s, OAc); HRMS (ESI-TOF) *m/z* 545.1425 (545.1424 calcd for $C_{28}H_{26}O_{10}Na$, $[M+Na]^+$).

Methyl 6-*O*-(6′-*O*-Benzoyl-6′-*O*-(4″,6″-di-*O*-benzoyl-2″,3″-dideoxy-*α*-D-*erythro*-hex-2- enopyranosyl)-2′,3′-dideoxy-D-*glycelo*-hex-2-enopyranos-4-ulosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (25)

A suspension of disaccharide **24***α* (22.7 mg, 0.0434 mmol), methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**10**) (10.1 mg, 0.0217 mmol) and MS 5A (22.7 mg, 100 wt% to glycosyl donor) in dry toluene (0.908 mL, 40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (2.5 μL 0.013 mmol) at −40 °C. After the suspension was stirred at −40 °C for 30 min, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane–EtOAc = 1/1) afforded trisaccharide **25** (22.2 mg, 75%, $\alpha:\beta$ = 79 : 21). **25***α*: Colorless syrup; R_f 0.70 (1/1 hexane–EtOAc); $[\alpha]_D^{32}$ +28.3 (*c* 1.42, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.08-8.00 (4H, m, ArH), 7.59-7.23 (21H, m, ArH), 6.85 (1H, dd, $J_{2',3'}$ = 10.2 Hz, $J_{1',2'}$ = 3.7 Hz, H-2′), 6.11 (1H, d, $J_{2',3'}$ = 10.2 Hz, H-3′), 5.98 (1H, br-d, $J_{2'',3''}$ = 10.0 Hz, $J_{3'',4''}$ = 2.7 Hz, H-3″), 5.83 (1H, ddd, $J_{2'',3''}$ = 10.0 Hz, $J_{1'',2''}$ = 2.7 Hz, $J_{2'',4''}$ = 2.2 Hz, H-2″), 5.68 (1H, ddd, $J_{4'',5''}$ = 8.9 Hz, $J_{3'',4''}$ = 2.7 Hz, $J_{2'',4''}$ = 2.2 Hz, H-4″), 5.34 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1′), 5.07 (1H, d, $J_{1'',2''}$ = 2.7 Hz, H-1″), 5.00 & 4.80 (2H, ABq, J = 10.7 Hz, $ArCH_2$), 4.91 & 4.57 (2H, ABq, J = 11.0 Hz, $ArCH_2$), 4.79 & 4.66 (2H, ABq, J = 12.2 Hz, $ArCH_2$), 4.64 (1H, dd, $J_{6'',6''}$ = 11.9 Hz, $J_{5'',6''}$ = 2.4 Hz, H-6″), 4.59 (1H, d, $J_{1,2}$ = 3.7 Hz, H-1), 4.51 (1H, m, H-5′), 4.47 (1H, dd, $J_{6'',6''}$ = 11.9 Hz, $J_{5'',6''}$ = 5.6 Hz, H-6″), 4.36 (1H, m, H-5″), 4.30 (1H, dd, $J_{6',6'}$ = 11.0 Hz, $J_{5',6'}$ = 3.9 Hz, H-6′), 4.03 (1H, dd, $J_{6,6}$ = 11.2 Hz, $J_{5,6}$ = 4.4 Hz, H-6), 4.00 (1H, dd, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3), 3.82 (1H, m, H-6), 3.79 (1H, m, H-5), 3.71 (1H, dd, $J_{6',6'}$ = 11.0 Hz, $J_{5',6'}$ = 2.4 Hz, H-6′), 3.53 (1H, dd, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 6.8 Hz, H-4), 3.51 (1H, dd, $J_{2,3}$ = 9.3 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 3.35 (3H, s, OMe); ^{13}C NMR ($CDCl_3$) δ 193.69, 166.34, 165.78, 143.51, 138.62, 138.19, 138.08, 133.32, 132.88, 129.98, 129.75, 129.51, 128.45, 128.42, 128.39, 128.26, 128.03, 127.93, 127.83, 127.73, 127.63, 127.55, 127.47, 98.07, 94.09, 93.56, 81.98, 79.99, 77.67, 75.72, 74.88, 74.09, 73.33, 69.98, 67.61, 67.13, 66.13, 66.06, 63.66, 55.22; HRMS (ESI-TOF) *m/z* 949.3407 (949.3411 calcd for $C_{54}H_{54}O_{14}Na$, $[M+Na]^+$). **25***β*: Colorless syrup; R_f 0.67 (1/1 hexane–EtOAc); $[\alpha]_D^{32}$ +110.6 (*c* 0.64, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.06-7.98 (4H, m, ArH), 7.59-7.22 (21H, m, ArH), 6.75 (1H, dd, $J_{2',3'}$ = 10.5 Hz, $J_{1',2'}$ = 1.7 Hz, H-2′), 6.12 (1H, dd, $J_{2',3'}$ = 10.5 Hz, $J_{1',3'}$ = 1.4 Hz, H-3′), 5.99 (1H, br-d, $J_{2'',3''}$ = 10.2 Hz, H-3″), 5.85 (1H, ddd, $J_{2'',3''}$ = 10.0 Hz, $J_{1'',2''}$ = $J_{2'',4''}$ = 2.2 Hz, H-2″), 5.68 (1H, m, H-4″), 5.17 (1H, br-d, $J_{1',2'}$ = 1.7 Hz, H-1′), 5.10 (1H, m, H-1″), 4.99 & 4.80 (2H, ABq, J = 10.7 Hz, $ArCH_2$), 4.88 & 4.60 (2H, ABq, J = 11.2 Hz, $ArCH_2$), 4.76 & 4.64 (2H, ABq, J = 11.4 Hz, $ArCH_2$), 4.58-4.52 (1H, m, H-6″), 4.57 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 4.48-4.39 (2H, m, H-5″ & H-6″), 4.27 (1H, m, H-5′), 4.21 (1H, dd, $J_{6',6'}$ = 11.0 Hz, $J_{5',6'}$ = 4.9 Hz, H-6′), 4.06 (1H, m, H-6), 3.99 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.96 (1H, dd, $J_{6',6'}$ = 11.0 Hz, $J_{5',6'}$ = 3.2 Hz, H-6′), 3.78-3.71 (2H, m, H-5& H-6), 3.52 (1H, dd, $J_{4,5}$ = 9.7 Hz, $J_{3,4}$ = 9.0 Hz, H-4), 3.49 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{1,2}$ = 3.4 Hz, H-2), 3.31 (3H, s, OMe); ^{13}C NMR ($CDCl_3$) δ 193.63, 166.32, 165.80, 146.68, 138.72, 138.38, 138.11, 133.39, 132.95, 129.94, 129.79, 129.54, 129.38, 128.98, 128.49, 128.42, 128.32, 128.11, 128.01, 127.95, 127.90, 127.85, 127.81, 127.65, 98.07, 95.90, 94.59, 82.15, 79.90, 78.24, 75.77, 74.80, 73.32, 69.70, 67.54, 67.35, 67.25, 66.16, 63.76, 55.21; HRMS (ESI-TOF) *m/z* 949.3402 (949.3411 calcd for $C_{54}H_{54}O_{14}Na$, $[M+Na]^+$).

6-*O*-(6′-*O*-Benzoyl-4′-*O*-benzyl-2′,3′-dideoxy- D -*erythro*-hexopyranosyl)-2,3-dideoxy-*α*-D-*glycelo*-hex-2-enopyranos-4-ulosyl acetate (26)

A suspension of 2,3-dideoxy glycosyl acatate **18** (41.3 mg, 0.107 mmol), 2,3-unsaturated-4-keto glycosyl acetate **23** (10.0 mg, 0.0537 mmol) and MS 5A (41.3 mg, 100 wt% to glycosyl donor) in dry CH_2Cl_2 (1.65 mL, 40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (3.1 μL 0.016 mmol) at -50 °C. After the suspension was stirred at -50 °C for 1 h, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane–EtOAc = 1/1) afforded disaccharide **26** (24.1 mg, 88%, $\alpha:\beta$ = 89 : 11). **26***α*: Colorless syrup; R_f 0.40 (3/5/3 hexane–chloroform/ether); $[\alpha]_D^{32}$ +2.7 (*c* 6.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.03 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{o,p}$ = 1.2 Hz, H_o of Bz), 7.58 (1H, tt, $J_{m,p}$ = 7.3 Hz, $J_{o,p}$ = 1.2 Hz, H_p of Bz), 7.41 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{m,p}$ = 7.3 Hz, H_m of Bz), 7.32-7.17 (5H, m, ArH), 6.96 (1H, dd, $J_{2,3}$ = 10.2 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 6.57 (1H, d, $J_{1,2}$ = 3.7 Hz, H-1), 6.26 (1H, d, $J_{2,3}$ = 10.2 Hz, H-3), 4.82 (1H, br-s, H-1′), 4.64 (1H, dd, $J_{5,6}$ = 3.9 Hz, $J_{5,6}$ = 2.7 Hz, H-5), 4.63 & 4.46 (2H, ABq, J = 11.9 Hz, $ArCH_2$), 4.61 (1H, dd, $J_{6',6'}$ = 11.7 Hz, $J_{5',6'}$ = 2.5 Hz, H-6′), 4.55 (1H, dd, $J_{6',6'}$ = 11.7 Hz, $J_{5',6'}$ = 4.9 Hz, H-6′), 4.23 (1H, dd, $J_{6,6}$ = 11.0 Hz, $J_{5,6}$ = 3.9 Hz, H-6), 4.00 (1H, ddd, $J_{4',5'}$ = 10.0 Hz, $J_{5',6'}$ = 4.9 Hz, $J_{5',6'}$ = 2.5 Hz, H-5′), 3.76 (1H, dd, $J_{6,6}$ = 11.0 Hz, $J_{5,6}$ = 2.7 Hz, H-6), 3.47 (1H, ddd, $J_{3',4'} = J_{4',5'}$ = 10.0 Hz, $J_{3',4'}$ = 4.4 Hz, H-4′), 2.13 (3H, s, OAc), 2.10-2.03 (1H, m, H-3′), 1.91-1.85 (1H, m, H-2′), 1.77-1.68 (2H, m, H-2′ & H-3′); Anal. Calcd for $C_{28}H_{30}O_9$: C, 65.87; H, 5.92. Found: C, 65.88; H, 6.09; HRMS (ESI-TOF) *m*/*z* 533.1783 (533.1788 calcd for $C_{28}H_{30}O_9Na$, $[M+Na]^+$). **26***β*: Colorless syrup; R_f 0.37 (3/5/3 hexane–chloroform/ether); ^{1}H NMR ($CDCl_3$, TMS) δ 8.01 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{o,p}$ = 1.5 Hz, H_o of Bz), 7.55 (1H, tt, $J_{m,p}$ = 6.6 Hz, $J_{o,p}$ = 1.5 Hz, H_p of Bz), 7.42 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{m,p}$ = 6.6 Hz, H_m of Bz), 7.29-7.19 (5H, m, ArH), 6.90 (1H, dd, $J_{2,3}$ = 10.2 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 6.54 (1H, d, $J_{1,2}$ = 3.7 Hz, H-1), 6.19 (1H, d, $J_{2,3}$ = 10.2 Hz, H-3), 4.71 (1H, dd, $J_{5,6}$ = 5.6 Hz, $J_{5,6}$ = 2.2 Hz, H-5), 4.66-4.53 (1H, m, H-6′), 4.61 & 4.45 (2H, ABq, J = 11.5 Hz, $ArCH_2$), 4.57 (1H, dd, $J_{1,2}$ = 9.2 Hz, $J_{1,2}$ = 2.4 Hz, H-1′), 4.51-4.44 (1H, m, H-6′), 4.30 (1H, dd, $J_{6,6}$ = 11.7 Hz, $J_{5,6}$ = 2.2 Hz, H-6), 3.92 (1H, dd, $J_{6,6}$ = 11.7 Hz, $J_{5,6}$ = 5.6 Hz, H-6), 3.73 (1H, ddd, $J_{4',5'}$ = 9.0 Hz, $J_{5',6'}$ = 6.0 Hz, $J_{5',6'}$ = 3.0 Hz, H-5′), 3.45 (1H, m, H-4′), 2.08 (3H, s, OAc), 2.35-2.25 (1H, m, H-3′), 1.95-1.91 (1H, m, H-2′), 1.65-1.51 (2H, m, H-2′ & H-3′). This compound was found to be too unstable to precisely measure other data, and easily epimerized to the corresponding α anomer.

Methyl 6-*O*-(6′-*O*-benzoyl-6′-*O*-(6″-*O*-benzoyl-4″-benzyl-2″,3″-dideoxy-*α*-D-*erythro*-hex-2-enopyranosyl)-2′,3′-dideoxy-D-*glycelo*-hex-2′-enopyranos-4′-ulosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (27)

A suspension of disaccharide **26***α* (22.6 mg, 0.0443 mmol), methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**10**) (10.3 mg, 0.0222 mmol) and MS 5A (22.6 mg, 100 wt% to glycosyl donor) in dry toluene (0.904 mL, 40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (2.6 μL 0.013 mmol) at -35 °C. After the suspension was stirred at -35 °C for 30 min, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane–EtOAc = 1/1) afforded trisaccharide **27** (16.4 mg, 81%, $\alpha:\beta$ = 78 : 22). **27***α*: Colorless syrup; R_f 0.43 (3/5/3 hexane–chloroform/ether); $[\alpha]_D^{31}$ +28.6 (*c* 5.05, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.02 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{o,p}$ = 1.2 Hz, H_o of Bz), 7.52 (1H, tt, $J_{m,p}$ = 6.6 Hz, $J_{o,p}$ = 1.2 Hz, H_p of Bz), 7.39 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{m,p}$ = 6.6 Hz, H_m of Bz), 7.36-7.16 (20H, m, ArH), 6.84 (1H, dd, $J_{2',3'}$ = 10.2 Hz, $J_{1',2'}$ = 3.7 Hz, H-2′), 6.09 (1H, d, $J_{2',3'}$ = 10.2 Hz, H-3′), 5.34 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.98 & 4.80 (2H, ABq, J = 11.0 Hz, $ArCH_2$), 4.89 & 4.57 (2H, ABq, J = 11.2 Hz, $ArCH_2$), 4.79 & 4.66 (2H, ABq, J = 12.2 Hz, $ArCH_2$), 4.77 (1H, br-s, H-1″), 4.63-4.49 (3H, m, H-5′, H-6″ × 2), 4.61 & 4.43 (2H, ABq, J = 11.9 Hz, $ArCH_2$), 4.59 (1H, br, H-1), 4.10 (1H, dd, $J_{6',6'}$ = 10.7 Hz, $J_{5',6'}$ = 4.9 Hz, H-6′), 4.05-4.00 (2H, m, H-6, H-5″), 4.00 (1H, dd, $J_{2,3} = J_{3,4}$ = 9.8 Hz, H-3), 3.82-3.75 (2H, m, H-5, H-6), 3.67 (1H, dd, $J_{6',6'}$ = 10.7 Hz, $J_{5',6'}$ = 2.7 Hz, H-6′), 3.52 (1H, dd, $J_{3,4} = J_{4,5}$ = 9.8 Hz, H-4), 3.51 (1H, dd, $J_{2,3}$ = 9.8 Hz, $J_{1,2}$ = 3.4 Hz, H-2), 3.43 (1H, ddd, $J_{3'',4''} = J_{4'',5''}$ = 9.5 Hz, $J_{3'',4''}$ = 5.4 Hz, H-4″), 3.34 (3H, s, OMe), 2.04-1.97 (1H, m, H-3″), 1.84-1.62 (3H, m, H-2″ × 2, H-3″); ^{13}C NMR ($CDCl_3$) δ 193.76, 166.40, 143.51, 138.60, 138.16, 138.05, 132.70, 130.31, 129.62, 128.41, 128.34, 128.31, 128.18, 127.98, 127.88, 127.76, 127.70, 127.65, 127.62, 127.57, 127.45, 97.97, 95.83, 93.40, 81.95, 79.88, 77.67, 75.67, 74.86, 73.92, 73.23, 72.61, 70.35, 70.17, 69.94, 67.44, 64.79, 64.28, 55.14, 28.69, 23.67; HRMS (ESI-TOF) *m*/*z* 937.3779 (937.3775 calcd for $C_{54}H_{54}O_{14}Na$, $[M+Na]^+$). **27***β*: Colorless syrup; R_f 0.38 (3/5/3 hexane–chloroform/ether); $[\alpha]_D^{31}$ +86.6 (*c* 0.56, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.00 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{o,p}$ = 1.2 Hz, H_o of Bz), 7.53 (1H, tt, $J_{m,p}$ = 7.3 Hz, $J_{o,p}$ = 1.2 Hz, H_p of Bz), 7.41 (2H, dd, $J_{o,m}$ = 8.3 Hz, $J_{m,p}$ = 7.3 Hz, H_m of Bz), 7.36-7.19 (20H, m, ArH), 6.73 (1H, dd, $J_{2',3'}$ = 10.5 Hz, $J_{1',2'}$ = 1.5 Hz, H-2′), 6.11 (1H, dd, $J_{2',3'}$ = 10.5 Hz, $J_{1',3'}$ = 1.5 Hz, H-3′), 5.13 (1H, br-s, H-1′), 4.99 & 4.80 (2H, ABq, J = 10.7 Hz, $ArCH_2$), 4.88 & 4.60 (2H, ABq, J = 11.2 Hz, $ArCH_2$), 4.79 (1H, dd, $J_{1'',2''}$ = 8.8 Hz, $J_{1'',2''}$ = 2.7 Hz, H-1″), 4.76 & 4.64 (2H, ABq, J = 11.9 Hz, $ArCH_2$), 4.63-4.57 (1H, m, H-6′), 4.62 (1H, d, $J_{1,2}$ = 3.4 Hz, H-1), 4.60 & 4.22 (2H, ABq, J = 11.5 Hz, $ArCH_2$), 4.23 (1H, dd, $J_{5'',6''}$ = 5.6 Hz, $J_{5'',6''}$ = 3.2 Hz, H-5″), 4.07 (1H, dd, $J_{6'',6''}$ = 11.0 Hz, $J_{5'',6''}$ = 5.6 Hz, H-6″), 4.09-3.99 (2H, m, H-6 & H-5′), 3.99 (1H, dd, $J_{2,3} = J_{3,4}$ = 9.2 Hz, H-3), 3.82 (1H, dd, $J_{6'',6''}$ = 11.0 Hz, $J_{5'',6''}$ = 3.2 Hz, H-6″), 3.77-3.73 (2H, m, H-5, H-6), 3.55 (1H, dd, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4), 3.51-3.41 (3H, m, H-2, H-4′ & H-6′), 3.31 (3H, s, OMe), 2.02 (1H, m, H-3″), 1.88-1.63 (3H, m, H-2″ × 2 & H-3″); ^{13}C NMR ($CDCl_3$) δ 193.71, 166.45, 146.60, 138.70, 138.39, 138.09, 132.76, 130.30, 129.71, 128.93, 128.45, 128.37, 128.24, 128.11, 128.01, 127.88, 127.76, 127.68, 127.63, 98.01, 96.16, 95.87, 82.17, 79.80, 78.12, 77.15, 75.75, 74.76, 73.27, 72.59, 70.37, 70.26, 69.60, 67.26, 66.00, 64.32, 55.19, 28.72, 23.70; HRMS (ESI-TOF) *m*/*z* 937.3763 (937.3775 calcd for $C_{54}H_{54}O_{14}Na$, $[M+Na]^+$).

General glycosylation procedure in Fig. 3

A suspension of 2,3-unsaturated glycosyl donor **30** or **33** (0.10 mmol), an alcohol **28** or **29** (0.09 mmol) and MS 5A (100 wt% to glycosyl donor) in dry CH_2Cl_2 (40 μL mg^{-1} to glycosyl donor) was stirred for 30 min at 25 °C, then to the suspension was added $Yb(OTf)_3$ (68.2 mg, 0.110 mmol) at the temperature listed in Fig. 3. After the suspension was stirred for the period listed in Fig. 3, to the mixture was added triethylamine (27.9 μL, 0.200 mmol), followed by warming to 25 °C. The resulting mixture was poured into saturated $NaHCO_3$ aq., and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography gave the corresponding glycosides.

1-Adamantyl 4-*O*-benzyl-6-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (31)

31*α*:. White solids; m.p. 89.3–90.3 °C ($CHCl_3$–hexane); R_f 0.75 (2/1 hexane–EtOAc); $[\alpha]_D^{30}$ +95.4 (*c* 2.57, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.02 (2H, dd, $J_{o,m} = 7.8$ Hz, $J_{o,p} = 1.5$ Hz, H_o of Bz), 7.54 (1H, tt, $J_{m,p} = 7.8$ Hz, $J_{o,p} = 1.5$ Hz, H_p of Bz), 7.40 (2H, dd, $J_{o,m} = 7.8$ Hz, $J_{m,p} = 7.8$ Hz, H_m of Bz), 7.35-7.18 (5H, m, ArH of Bn), 6.10 (1H, ddd, $J_{2,3} = 9.9$ Hz, $J_{3,4} = 3.0$ Hz, $J_{1,3} = 0.6$ Hz, H-3), 5.74 (1H, ddd, $J_{2,3} = 9.9$ Hz, $J_{1,2} = 2.7$ Hz, $J_{2,4} = 1.5$ Hz, H-2), 5.40 (1H, dd, $J_{1,2} = 2.7$ Hz, $J_{1,3} = 0.6$ Hz, H-1), 4.70 & 4.53 (2H, ABq, $J = 11.7$ Hz, $ArCH_2$), 4.57 (1H, dd, $J_{6,6} = 11.7$ Hz, $J_{5,6} = 2.1$ Hz, H-6), 4.47 (1H, dd, $J_{6,6} = 11.7$ Hz, $J_{5,6} = 6.6$ Hz, H-6), 4.31 (1H, ddd, $J_{4,5} = 9.6$ Hz, $J_{5,6} = 6.6$ Hz, $J_{5,6} = 2.1$ Hz, H-5), 4.01 (1H, ddd, $J_{4,5} = 9.6$ Hz, $J_{3,4} = 3.0$ Hz, $J_{2,4} = 1.5$ Hz, H-4), 2.08-1.98 (3H, m, CH of adamantyl), 1.89-1.74 (6H, m, $CH_2 \times 3$ of adamantyl), 1.62-1.46 (6H, m, $CH_2 \times 3$ of adamantyl). Anal. Calcd for $C_{30}H_{34}O_5$: C, 75.92; H, 7.22. Found: C, 75.97; H, 7.01. **31*β***: Colorless syrup; R_f 0.45 (4/1 hexane/acetone); $[\alpha]_D^{29}$ +86.0 (*c* 0.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.02 (2H, dd, $J_{o,m} = 7.5$ Hz, $J_{o,p} = 1.2$ Hz, H_o of Bz), 7.55 (1H, tt, $J_{m,p} = 7.5$ Hz, $J_{o,p} = 1.2$ Hz, H_p of Bz), 7.42 (2H, dd, $J_{o,m} = 7.5$ Hz, $J_{m,p} = 7.5$ Hz, H_m of Bz), 7.35-7.21 (5H, m, ArH of Bn), 6.06 (1H, ddd, $J_{2,3} = 10.2$ Hz, $J_{3,4} = 2.4$ Hz, $J_{1,3} = 1.8$ Hz, H-3), 5.78 (1H, ddd, $J_{2,3} = 10.2$ Hz, $J_{1,2} = 1.8$ Hz, $J_{2},4 = 1.2$ Hz, H-2), 5.48 (1H, dd, $J_{1,2} = 1.8$ Hz, $J_{1,3} = 1.8$ Hz, H-1), 4.66 & 4.56 (2H, ABq, $J = 11.7$ Hz, $ArCH_2$), 4.54 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 3.9$ Hz, H-6), 4.48 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 6.3$ Hz, H-6), 4.08 (1H, ddd, $J_{4,5} = 6.3$ Hz, $J_{5,6} = 6.3$ Hz, $J_{5,6} = 3.9$ Hz, H-5), 4.02 (1H, ddd, $J_{4,5} = 6.3$ Hz, $J_{3,4} = 2.4$ Hz, $J_{2,4} = 1.2$ Hz, H-4), 2.14-2.04 (3H, m, CH of adamantyl), 1.91-1.74 (6H, m, $CH_2 \times 3$ of adamantyl), 1.66-1.50 (6H, m, $CH_2 \times 3$ of adamantyl). Anal. Calcd for $C_{30}H_{34}O_5$: C, 75.92; H, 7.22. Found: C, 75.94; H, 7.21.

***tert*-Butyl 4-*O*-benzyl-6-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (32)**

32*α*:. Colorless syrup; R_f 0.63 (4/1 hexane/acetone); $[\alpha]_D^{28}$ +105.3 (*c* 1.78, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.00 (2H, dd, $J_{o,m} = 7.2$ Hz, $J_{o,p} = 1.5$ Hz, H_o of Bz), 7.55 (1H, tt, $J_{m,p} = 7.2$ Hz, $J_{o,p} = 1.5$ Hz, H_p of Bz), 7.41 (2H, dd, $J_{o,m} = 7.2$ Hz, $J_{m,p} = 7.2$ Hz, H_m of Bz), 7.35-7.17 (5H, m, ArH of Bn), 6.10 (1H, ddd, $J_{2,3} = 9.9$ Hz, $J_{3,4} = 3.0$ Hz, $J_{1,3} = 0.3$ Hz, H-3), 5.74 (1H, ddd, $J_{2,3} = 9.9$ Hz, $J_{1,2} = 3.0$ Hz, $J_{2,4} = 1.5$ Hz, H-2), 5.29 (1H, dd, $J_{1,2} = 3.0$ Hz, $J_{1,3} = 0.3$ Hz, H-1), 4.70 & 4.53 (2H, ABq, $J = 12.0$ Hz, $ArCH_2$), 4.57 (1H, dd, $J_{6,6} = 12.0$ Hz, $J_{5,6} = 2.1$ Hz, H-6), 4.48 (1H, dd, $J_{6,6} = 12.0$ Hz, $J_{5,6} = 5.4$ Hz, H-6), 4.26 (1H, ddd, $J_{4,5} = 9.3$ Hz, $J_{5,6} = 5.4$ Hz, $J_{5,6} = 2.1$ Hz, H-5), 4.06 (1H, ddd, $J_{4,5} = 9.3$ Hz, $J_{3,4} = 3.0$ Hz, $J_{2,4} = 1.5$ Hz, H-4), 1.26 (9H, s, *t*-Bu). Anal. Calcd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12. Found: C, 72.53; H, 6.90. **32*β***: Colorless syrup; R_f 0.55 (4/1 hexane/acetone); $[\alpha]_D^{28}$ +123.5 (*c* 0.20, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.01 (2H, dd, $J_{o,m} = 7.5$ Hz, $J_{o,p} = 1.2$ Hz, H_o of Bz), 7.57 (1H, tt, $J_{m,p} = 7.5$ Hz, $J_{o,p} = 1.2$ Hz, H_p of Bz), 7.42 (2H, dd, $J_{o,m} = 7.5$ Hz, $J_{m,p} = 7.5$ Hz, H_m of Bz), 7.35-7.20 (5H, m, ArH of Bn), 6.06 (1H, ddd, $J_{2,3} = 10.2$ Hz, $J_{1,3} = 2.1$ Hz, $J_{3,4} = 2.1$ Hz, H-3), 5.77 (1H, ddd, $J_{2,3} = 10.2$ Hz, $J_{1,2} = 1.5$ Hz, $J_{2,4} = 0.9$ Hz, H-2), 5.36 (1H, dd, $J_{1,3} = 2.1$ Hz, $J_{1,2} = 1.5$ Hz, H-1), 4.66 & 4.56 (2H, ABq, $J = 11.7$ Hz, $ArCH_2$), 4.55 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 4.2$ Hz, H-6), 4.48 (1H, dd, $J_{6,6} = 11.4$ Hz, $J_{5,6} = 5.7$ Hz, H-6), 4.07 (1H, ddd, $J_{4,5} = 6.9$ Hz, $J_{5,6} = 5.7$ Hz, $J_{5,6} = 4.2$ Hz, H-5), 4.03 (1H, ddd, $J_{4,5} = 6.9$ Hz, $J_{3,4} = 2.1$ Hz, $J_{2,4} = 0.9$ Hz, H-4), 1.27 (9H, s, *t*-Bu). Anal. Calcd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12. Found: C, 72.44; H, 7.15.

1-Adamantyl 4-*O*-benzoyl-2,3,6-trideoxy-*α*-L-*threo*-hex-2-enopyranoside (34)

Colorless syrup; R_f 0.73 (2/1 hexane–EtOAc); $[\alpha]_D^{28}$ +183.0 (*c* 1.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.08 (2H, dd, $J_{o,m} = 7.5$ Hz, $J_{o,p} = 1.2$ Hz, H_o of Bz), 7.56 (1H, tt, $J_{m,p} = 7.5$ Hz, $J_{o,p} = 1.2$ Hz, H_p of Bz), 7.43 (2H, dd, $J_{o,m} = 7.5$ Hz, $J_{m,p} = 7.5$ Hz, H_m of Bz), 6.17 (1H, ddd, $J_{2,3} = 9.9$ Hz, $J_{3,4} = 5.4$ Hz, $J_{1,3} = 0.6$ Hz, H-3), 5.97 (1H, ddd, $J_{2,3} = 9.9$ Hz, $J_{1,2} = 3.3$ Hz, $J_{2,4} = 0.6$ Hz, H-2), 5.52 (1H, dd, $J_{1,2} = 3.3$ Hz, $J_{1,3} = 0.6$ Hz, H-1), 5.15 (1H, ddd, $J_{3,4} = 5.4$ Hz, $J_{4,5} = 2.4$ Hz, $J_{2,4} = 0.6$ Hz, H-4), 4.46 (1H, qd, $J_{5,6} = 6.6$ Hz, $J_{4,5} = 2.4$ Hz, H-5), 2.21-2.12 (3H, m, CH of adamantyl), 1.95-1.81 (6H, m, $CH_2 \times 3$ of adamantyl), 1.71-1.59 (6H, m, $CH_2 \times 3$ of adamantyl), 1.28 (3H, d, $J_{5,6} = 6.6$ Hz, H-6). Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.75; H, 7.62.

***tert*-Butyl 4-*O*-benzoyl-2,3,6-trideoxy-*α*-L-*threo*-hex-2-enopyranoside (35)**

Colorless syrup; R_f 0.83 (2/1 hexane–EtOAc); $[\alpha]_D^{28}$ +196.7 (*c* 1.26, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.09 (2H, dd, $J_{o,m} = 7.2$ Hz, $J_{o,p} = 1.5$ Hz, H_o of Bz), 7.56 (1H, tt, $J_{m},p = 7.2$ Hz, $J_{o,p} = 1.5$ Hz, H_p of Bz), 7.43 (2H, dd, $J_{o,m} = 7.2$ Hz, $J_{m,p} = 7.2$ Hz, H_m of Bz), 6.17 (1H, ddd, $J_{2,3} = 9.9$ Hz, $J_{3,4} = 5.4$ Hz, $J_{1,3} = 0.6$ Hz, H-3), 5.98 (1H, dd, $J_{2,3} = 9.9$ Hz, $J_{1,2} = 3.3$ Hz, H-2), 5.39 (1H, dd, $J_{1,2} = 3.3$ Hz, $J_{1,3} = 0.6$ Hz, H-1), 5.16 (1H, dd, $J_{3,4} = 5.4$ Hz, $J_{4,5} = 2.7$ Hz, H-4), 4.44 (1H, qd, $J_{5,6} = 6.6$ Hz, $J_{4,5} = 2.7$ Hz, H-5), 1.32 (9H, s, *t*-Bu), 1.28 (3H, d, $J_{5,6} = 6.6$ Hz, H-6). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.20; H, 7.57.

1-Adamantyl 4-*O*-benzoyl-2,3,6-trideoxy-*α*-L-*threo*-hexopyranoside (38)

Colorless syrup; R_f 0.83 (2/1 hexane–EtOAc); $[\alpha]_D^{30}$ −38.5 (*c* 0.74, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS) δ 8.12 (2H, dd, $J_{o,m} = 7.2$ Hz, $J_{o,p} = 1.5$ Hz, H_o of Bz), 7.57 (1H, tt, $J_{m,p} = 7.5$ Hz, $J_{o,p} = 1.5$ Hz, H_p of Bz), 7.44 (2H, dd, $J_{m,p} = 7.5$ Hz, $J_{o,m} = 7.2$ Hz, H_m of Bz), 5.37 (1H, br-ddd, $J_{3ax,4} = 3.9$ Hz, $J_{4,5} = 1.5$ Hz, H-4), 5.04 (1H, br-dd, $J_{1,2ax} = 2.7$ Hz, H-1), 4.33 (1H, qd, $J_{5,6} = 6.6$ Hz, $J_{4,5} = 1.5$ Hz, H-5), 2.23 (1H, dddd, $J_{2ax,3ax} = 13.5$ Hz, $J_{2ax,2eq} = 13.5$ Hz,

$J_{2ax,3eq}$ = 4.2 Hz, $J_{1,2ax}$ = 2.7 Hz, H-2ax), 2.19-2.11 (3H, m, CH of adamantyl), 2.03 (1H, dddd, $J_{2ax,3ax}$ = 13.5 Hz, $J_{3ax,3eq}$ = 13.5 Hz, $J_{2eq,3ax}$ = 3.9 Hz, $J_{3ax,4}$ = 3.9 Hz, H-3ax), 1.91-1.77 (6H, m, CH_2 × 3 of adamantyl), 1.89 (1H, br-dddd, $J_{2ax,2eq}$ = 13.5 Hz, $J_{2eq,3eq}$ = 6.6 Hz, $J_{2eq,3ax}$ = 3.9 Hz, H-2eq), 1.71-1.57 (6H, m, CH_2 × 3 of adamantyl), 1.46(1H, br-dddd, $J_{3ax,3eq}$ = 13.5 Hz, $J_{2eq,3eq}$ = 6.6 Hz, $J_{2ax,3eq}$ = 4.2 Hz, H-3eq), 1.15 (3H, d, J5,6 = 6.6 Hz, H-6). Anal. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.24; H, 8.24.

Acknowledgements

This research was supported in part by a Grant-in-Aid for the 21st Century Center of Excellence (COE) Program 'KEIO Life Conjugated Chemistry', for the Scientific Research on Priority Areas 18032068, for the JSPS Fellows 18·6013, and for the High-Tech Research Center Project for Private Universities: Matching Fund Subsidy, 2006-2011, from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (MEXT).

References

1 For selected reviews on synthesis of oligosaccharides, see: (*a*) J. P. Kamerling, G.-J. Boons, Y. C. Lee, A. Suzuki, N. Taniguchi and A. G. J. Voragen, *Comprehensive Glycoscience*, Elsevier, Oxford, 2007; (*b*) B. O. Fraser-Reid, K. Tatsuta, and J. Thiem, *Glycosience*, Springer, Berlin, 1st ed. 2001 and 2nd ed. 2008; (*c*) B. Ernst, G. W. Hart and P. Sinäy, *Carbohydrates in Chemistry and Biology*, Wiley-VCH, Weinheim, 2000.
2 For selected reviews on chemoselective glycosylation, see: (*a*) A. V. Demchenko, *Handbook of Chemical Glycosylation: Advances in Stereochemistry and Therapeutic Relevance*, Wiley-VCH, Weinheim, 2008; (*b*) H. Tanaka, H. Yamada and T. Takahashi, *Trends Glycosci. Glycotechnol.*, 2007, **19**, 183; (*c*) G. A. van der Marel, L. J. van den Bos, H. S. Overkleeft, R. E. J. N. Litjens and J. D. C. Codee, *ACS Symp. Ser.*, 2007, **960**, 190; (*d*) B. Fraser-Reid, K. N. Jayaprakash, J. C. Lopez, A. M. Gomez and C. Uriel, *ACS Symp. Ser.*, 2007, **960**, 91.
3 D. R. Mootoo, P. Konradsson, U. Udodong and B. Fraser-Reid, *J. Am. Chem. Soc.*, 1988, **110**, 5583.
4 For a selected review on chemoselective glycosylations for 2-deoxy sugars, see: K. Toshima and K. Tatsuta, *Chem. Rev.*, 1993, **93**, 1503.
5 (*a*) S. Omura, H. Tanaka, R. Oiwa, J. Awaya, R. Masuma and K. Tanaka, *J. Antibiot.*, 1977, **30**, 908; (*b*) N. Imamura, K. Kakinuma, N. Ikekawa, H. Tanaka and S. Omura, *J. Antibiot.*, 1981, **34**, 1517.
6 (*a*) N. Matsumoto, T. Tsuchida, M. Maruyama, R. Sawa, N. Kinoshita, Y. Homma, Y. Takahashi, H. Iinuma, H. Naganawa, T. Sawa, M. Hamada and T. Takeuchi, *J. Antibiot.*, 1996, **49**, 953; (*b*) N. Matsumoto, T. Tsuchida, M. Maruyama, N. Kinoshita, Y. Homma, H. Iinuma, T. Sawa, M. Hamada, T. Takeuchi, N. Heida and T. Yoshioka, *J. Antibiot.*, 1999, **52**, 269; (*c*) N. Matsumoto, T. Tsuchida, H. Nakamura, R. Sawa, Y. Takahashi, H. Naganawa, H. Iinuma, T. Sawa, T. Takeuchi and M. Shiro, *J. Antibiot.*, 1999, **52**, 276.
7 A. Kawashima, Y. Kishimura, M. Tamai and K. Hanada, *Chem. Pharm. Bull.*, 1989, **37**, 3429.
8 A. Sobti, K. Kim and G. A. Sulikowski, *J. Org. Chem.*, 1996, **61**, 6.
9 (*a*) W. P. Jencks, In *Catalysis in Chemistry and Enzymology*, Dover Publishers, Inc., New York, 1987, pp. 302–305; (*b*) N. C. J. Strynadka and M. N. G. James, *J. Mol. Biol.*, 1991, **220**, 401.
10 (*a*) L. O. Ford, L. N. Johnson, P. A. Machin, D. C. Phillips and R. Tjian, *J. Mol. Biol.*, 1974, **88**, 349; (*b*) C. M. Chipman and N. Sharon, *Science*, 1969, **165**, 454; (*c*) D. M. Chipman, *Biochemistry*, 1971, **10**, 1714; (*d*) J. A. Rupley, *Proc. R. Soc. London, Ser. B*, 1967, **167**, 416; (*e*) I. Imoto, L. N. Johnson, A. C. T. North, D. C. Phillips and J. A. Rupley, In *The Enzymes*, ed. P. Boyer, Academic Press, New York, 1972, 3rd ed., vol. 7, pp. 665–868.
11 (*a*) F. W. Dahlquist, T. Rand-Meir and M. A. Raftery, *Biochemistry*, 1969, **8**, 4214; (*b*) L. E. H. Smith, L. H. Mohr and M. A. Raftery, *J. Am. Chem. Soc.*, 1973, **95**, 7497; (*c*) S. Rosenberg and J. F. Kirsh, *Biochemistry*, 1981, **20**, 3196.
12 6-Acyl-2*H*-pyran-3(6*H*)-one system was effectively used in palladium-catalyzed glycosylation, see: (*a*) A. C. Comely, R. Eelkema, A. J. Minnaard and B. L. Feringa, *J. Am. Chem. Soc.*, 2003, **125**, 8714; (*b*) R. S. Babu and G. A. O'Doherty, *J. Am. Chem. Soc.*, 2003, **125**, 12406; (*c*) R. S. Babu, M. Zhou and G. A. O'Doherty, *J. Am. Chem. Soc.*, 2004, **126**, 3428; (*d*) S. R. Guppi, M. Zhou and G. A. O'Doherty, *Org. Lett.*, 2006, **8**, 293; (*e*) R. S. Babu, S. R. Guppi and G. A. O'Doherty, *Org. Lett.*, 2006, **8**, 1605; (*f*) M. Zhou and G. A. O'Doherty, *Org. Lett.*, 2008, **10**, 2283; (*g*) X. Yu and G. A. O'Doherty, *Org. Lett.*, 2008, **10**, 4529; (*h*) M. Shan, Y. Xing and G. A. O'Doherty, *J. Org. Chem.*, 2009, **74**, 5961.
13 For our preliminary communication on this work, see: (*a*) K. Sasaki, S. Matsumura and K. Toshima, *Tetrahedron Lett.*, 2006, **47**, 9039; (*b*) S. Kusumi, S. Wang, T. Watanabe, K. Sasaki, D. Takahashi and K. Toshima, *Org. Biomol. Chem.*, 2010, **8**, 988.
14 B. Fraser-Reid and B. Boctor, *Can. J. Chem.*, 1969, **47**, 393.
15 B. Shanmugasundaram, A. K. Bose and K. K. Balasubramanian, *Tetrahedron Lett.*, 2002, **43**, 6795.
16 (*a*) R. J. Ferrier and N. Prasad, *J. Chem. Soc.*, 1969, **C**, 570; (*b*) R. J. Ferrier, *Top. Curr. Chem.*, 2001, **215**, 153.
17 (*a*) K. Sasaki, T. Wakamatsu, S. Matsumura and K. Toshima, *Tetrahedron Lett.*, 2006, **47**, 8271; (*b*) M. H. Haukaas and G. A. O'Doherty, *Org. Lett.*, 2002, **4**, 1771.
18 For a typical example, see: K. Toshima, G. Matsuo and M. Nakata, *J. Chem. Soc., Chem. Commun.*, 1994, 997.
19 (*a*) For reviews of angucycline group of antibiotics, see: J. Rohr and R. Thiericke, *Nat. Prod. Rep.*, 1992, **9**, 103; (*b*) M. C. Carreño and A. Urbano, *Synlett*, 2005, 1–25.
20 N. Hashizume and S. Kobayashi, *Carbohydr. Lett.*, 1996, **2**, 157.
21 B. W. Bycroft, *Dictionary of Antibiotics and Related Substances*, Chapman and Hall, New York, 1988.
22 For our preliminary communication on that work, see: K. Sasaki, S. Matsumura and K. Toshima, *Tetrahedron Lett.*, 2007, **48**, 6982.

