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Environmentally benign β-stereoselective glycosidations of glycosyl phosphites using a reusable heterogeneous solid acid, montmorillonite K-10☆

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Abstract—Environmentally benign and stereoselective β-glycosidations of glycopyranosyl phosphites and alcohols using a reusable heterogeneous solid acid, montmorillonite K-10, as an activator have been developed. By these glycosidations, β-gluco-, 2-deoxy-β-gluco-, and β-mannopyranosides were selectively produced in good to high yields.

Keywords: Glycosidation; Glycosyl phosphite; Heterogeneous solid acid; Montmorillonite K-10

1. Introduction

Carbohydrates are a naturally abundant and renewable feedstock. Various glycoconjugates and oligosaccharides are found in many bioactive or functional molecules. Such glycosubstances including, glycoconjugates and oligosaccharides, continue to be a central focus of research in chemistry, biology, and material science.[1] One of the most important reactions of carbohydrates is chemical glycosidation,[2] for preparing both natural and unnatural glycosides. Consequently, a highly effective, simple, and environmentally benign glycosidation method is urgently needed in both academia and industry. In this context, the 'greening' of chemical glycosidation could include the use of a heterogeneous and reusable solid acid as an activator. In previous studies, we have demonstrated several stereoselective *O*-glycosidation methods using glycals,[3] glycosyl fluorides,[4] glycosyl sulfoxides,[5] and 1-hydroxy sugars[6] as glycosyl donors, and montmorillonite K-10, sulfated zirconia (SO_4/ZrO_2) or Nafion-H as environmentally friendly heterogeneous activators. Glycosyl phosphites have also attracted considerable attention as effective glycosyl donors.[7–11] However, heterogeneous solid acid-mediated glycosidation involving glycosyl phosphite has never been reported. We report here the novel and environmentally benign glycosidations of glycosyl phosphites with alcohols, using a heterogeneous and reusable solid acid, montmorillonite K-10, for the highly stereoselective syntheses of β-gluco-, 2-deoxy-β-gluco-, and β-manno-pyranosides (Fig. 1).[12]

2. Results and discussion

2.1. β-Glucosidation

Stereoselective β-glucosidation[13] is a very attractive goal in the field of carbohydrate chemistry because of the wide distribution of β-glucosides in nature. In this context, Wong,[8c] Watanabe,[9a] and Hashimoto[10a] have independently demonstrated the highly stereoselective 1,2-*trans*-β-glucosidations of glucopyranosyl phosphites, using a Lewis acid as a homogeneous promoter. With these results in mind, we first examined the

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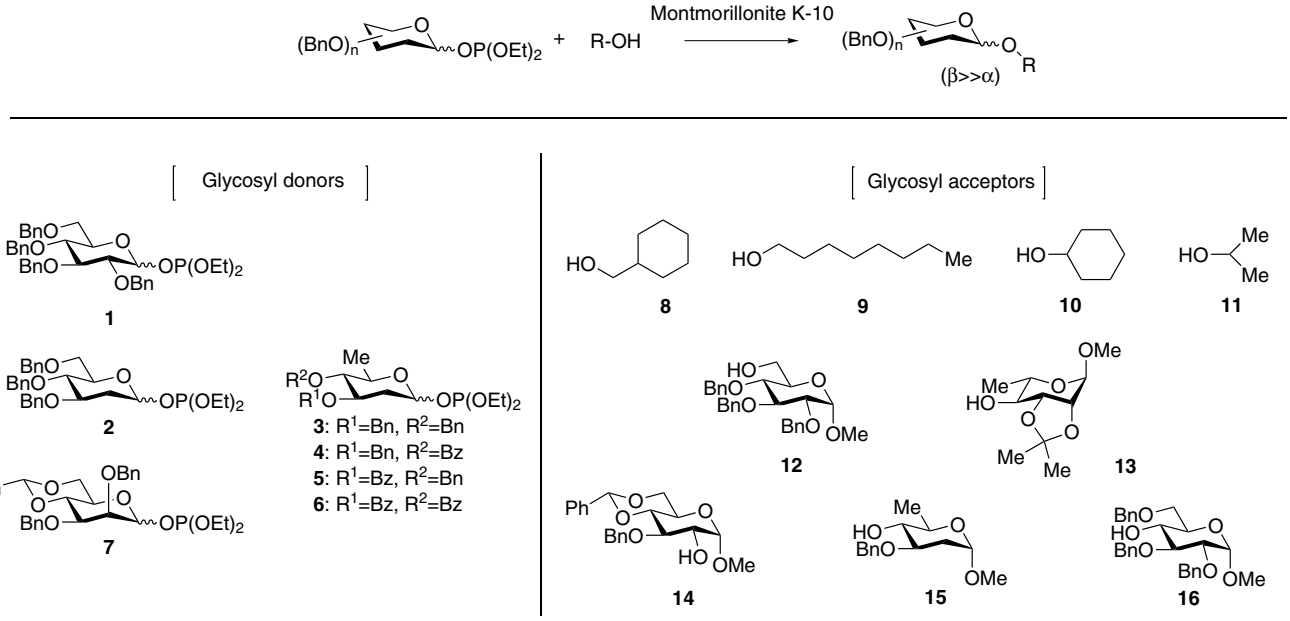
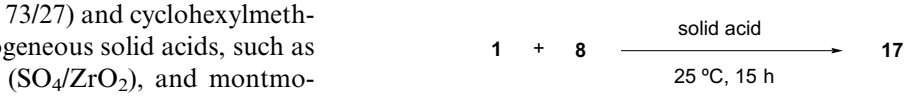


Figure 1. β-Stereoselective glycosidations of glycopyranosyl diethyl phosphites using a heterogeneous solid acid, montmorillonite K-10.

glycosidations of the totally benzylated glucopyranosyl diethyl phosphite **1**[10a] (α/β = 73/27) and cyclohexylmethanol (**8**), using several heterogeneous solid acids, such as Nafion-H, sulfated zirconia (SO_4/ZrO_2), and montmorillonite K-10. These heterogeneous solid acids are well known as environmentally benign catalysts for organic synthesis; they are easily handled because of their nonvolatile, noncorrosive, and odorless properties, and they can be recovered from the reaction mixture by simple filtration and then be reused. Neutralization of the reaction mixture is not required after the reaction is complete. Consequently, extraction of the product from the reaction mixture by an organic solvent is not needed in the work-up process. The results of such glycosidation are summarized in Table 1. It was found, for the first time, that the glucopyranosyl diethyl phosphite **1** was effectively activated by these heterogeneous solid acids in CH_2Cl_2 under mild conditions, and underwent smooth coupling with the alcohol **8** to give the corresponding glucopyranosides **17** in high yield. Among these, montmorillonite K-10 was found to be superior to the other solid acids with respect to both the chemical yield and β-stereoselectivity (entry 3 in Table 1). It is noteworthy that the stereoselective tendency of the present glycosidation is similar to those in Wong's, Watanabe's, and Hashimoto's glycosidations, all of which use benzyl-protected glucopyranosyl phosphite and a homogeneous promoter. Our attention turned next to solvent effects on this glycosidation using montmorillonite K-10 as the activator. The glycosidation of **1** and **8**, using montmorillonite K-10 in several solvents such as Et_2O, MeCN, and PhMe was tested and compared to that in

Table 1. Glycosidations of **1** and **8** by several solid acids in CH_2Cl_2[a]



Entry	Solid acid (wt %)	Solvent (0.1 M)	Yield[b] (%)	α/β Ratio[c]
1	Nafion-H (100)	CH_2Cl_2	83	28/72
2	SO_4/ZrO_2 (100)	CH_2Cl_2	73	55/45
3	Montmorillonite K-10 (100)	CH_2Cl_2	90	27/73

[a] All reactions were carried out using of 2.0 equiv of **8** to **1**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by HPLC analysis (column, CrestPak C18S®, 4.6 × 150 mm; eluent, 10% H_2O in MeCN; flow rate, 1.0 mL/min, 40 °C; detection, UV 250 nm).

CH_2Cl_2 (Table 2). The highest yield was obtained in CH_2Cl_2 (entry 3 in Table 1), while the highest β-stereoselectivity was observed in MeCN (entry 2 in Table 2). The glycosidation proceeded effectively, even at 0 °C for 30 min in both cases, and the β-stereoselectivity gradually increased as the reaction temperature decreased (entries 5 and 8 in Table 2). The addition of 100 wt % montmorillonite K-10 to the glycosyl donor **1** gave the best results, and the use of a smaller or larger amount of montmorillonite K-10 was less effective in both cases (entries 4–9 in Table 2). When larger amounts of montmorillonite K-10 were used, considerable amounts of the corresponding 1-OH sugar were produced because of the hydrolysis of **1** by water originally contained in the montmorillonite K-10. We further examined the glycosidations of **1** and **8** using 100 wt % montmorillonite

Table 2. Glycosidations of **1** and **8** by montmorillonite K-10 under various conditions[a]

1 + **8** —Montmorillonite K-10→ **17**

Entry	wt % of K-10	Solvent (0.1 M)	Temp (°C)	Time (h)	Yield[b] (%)	α/β Ratio[c]
1	100	Et_2O	25	15	62	56/44
2	100	MeCN	25	15	75	18/82
3	100	PhMe	25	15	80	26/74
4	50	CH_2Cl_2	0	0.5	89	23/77
5	100	CH_2Cl_2	0	0.5	93	23/77
6	200	CH_2Cl_2	0	0.5	92	24/76
7	50	MeCN	0	0.5	83	11/89
8	100	MeCN	0	0.5	86	11/89
9	200	MeCN	0	0.5	84	14/86
10	100	CH_2Cl_2–MeCN (5:1)[d]	−20	0.5	82	6/94
11	100	CH_2Cl_2–MeCN (10:1)[d]	−20	0.5	94	6/94
12	100	CH_2Cl_2–MeCN (15:1)[d]	−20	0.5	87	10/90

[a] All reactions were carried out using 2.0 equiv of **8** to **1**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by HPLC analysis (column, CrestPak C18S®, 4.6 × 150 mm; eluent, 10% H_2O in MeCN; flow rate, 1.0 mL/min, 40 °C; detection, UV 250 nm).
[d] 0.05 M solvent was used.

K-10 in mixed solvents of CH_2Cl_2 and MeCN. After several attempts, we finally found that the glycosidation of **1** and **8** using 100 wt % montmorillonite K-10 in 10:1 CH_2Cl_2–MeCN (0.05 M for **1**) at −20 °C for 30 min was the best combination, affording the corresponding glucopyranosides **17** in 94% yield with 6:94 α/β-stereoselectivity (entry 11 in Table 2). With the optimized conditions in hand, the glycosidations using other primary and secondary alcohols (**9**–**14**), and including sugar derivatives **12**,[14] **13**,[15] and **14**[16] were next carried out to enhance the synthetic utility of the procedure. Based on the results (summarized in Table 3), the glycosidations of **1** and **9**–**11** using 100 wt % montmorillonite K-10 in 10:1 CH_2Cl_2–MeCN at −20 °C for 30 min, as well as that of **8**, proceeded effectively to give the corresponding β-glucopyranosides **18β**–**20β** in high yields (entries 2–4 in Table 3). When the sugar derivatives **12**–**14** were employed as glycosyl acceptors, a longer reaction time (2 h) was required, and 3.0 equiv of the glycosyl acceptor was needed for such low-reactive glycosyl acceptors as **13** to obtain good yields of the corresponding β-glucopyranosides **21β**–**23β** (entries 5–7 in Table 3). It was confirmed that the glycosidic bond at the anomeric position of the glycoside obtained was not epimerized under the glycosidation conditions. Therefore, the predominant β-stereoselectivity must arise from kinetic control. Such acid-sensitive protecting groups such as benzylidene and isopropylidene acetals were not cleaved under these conditions. Finally, we tested the solid acid, montmorillonite K-10, for recycling in the glycosidation reaction. After filtration followed by washing with chloroform and methanol and drying at 100 °C/1 mmHg for 12 h, the recycled montmorillonite K-10 was reused in the glycosidation of **1** and **8** for at least three times and showed good to high yields and high β-stereoselectivities, as described in Table 4. No further addition of the fresh montmorillonite K-10 was needed to perform the glycosidation repeatedly.

Table 3. β-Stereoselective glycosidations of **1** and several alcohols[a]

1 + **8-14** —Montmorillonite K-10 (100 wt%), 10:1 CH_2Cl_2-MeCN, -20 °C→ **17-23**

Entry	Alcohol[a]	Time (h)	Product	Yield[b] (%)	α/β Ratio[c]
1	**8**	0.5	**17**	94	6/94
2	**9**	0.5	**18**	88	6/94
3	**10**	0.5	**19**	88	7/93
4	**11**	0.5	**20**	86	8/92
5	**12**	2	**21**	77	7/93
6	**13**[d]	2	**22**	74	16/84
7	**14**	2	**23**	73	13/87

[a] All reactions were carried out using 2.0 equiv of the alcohol to **1**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by HPLC analysis (column, CrestPak C18S®, 4.6 × 150 mm; eluent, 10% H_2O in MeCN for entries 1–4 and 6, 12.5% H_2O in MeCN for entry 5; flow rate, 1.0 mL/min, 40 °C; detection, UV 250 nm).
[d] 3.0 equiv of alcohol was used.

Table 4. Recycling of montmorillonite K-10 in glycosidation of **1** and **8**

Recycling number	0	1st	2nd	3rd
Yield (%)	94	90	86	70
α/β Ratio	6/94	5/95	5/95	7/93

2.2. β-2-Deoxyglycosidation

Deoxy sugars frequently feature in the glycosidic components of bioactive substances.[17,18] Among them,

2-deoxyglycosides, including 2,6-dideoxyglycosides, are some of the most common and important, and are found in many biologically interesting natural products, especially in antitumor antibiotics. However, direct and stereoselective β-glycosidation of a 2-deoxy sugar is quite difficult because of the anomeric effect and the lack of stereodirecting anchimeric assistance from the C-2 position.[2c,19] Therefore, the development of direct and stereoselective β-glycosidations of 2-deoxy sugar[20,21] in an environmentally compatible manner is of particular interest. In our studies just mentioned, we have observed β-stereoselective glycosidation of the benzyl-protected glucopyranosyl diethyl phosphite **1** with several alcohols, using montmorillonite K-10 with a nonparticipating group. Hashimoto and co-workers reported an efficient β-stereoselective glycosidation of 2-deoxyglycopyranosyl diethyl phosphite using a homogeneous promoter, trimethysilyl trifluoromethanesulfonate (Me_3SiOTf).[10b] Therefore, based on these results, we next examined the glycosidations of the totally benzylated 2-deoxyglucopyranosyl diethyl phosphite **2**[10b] and the sugar derivative alcohol **12**, using montmorillonite K-10 under various conditions. The results are summarized in Table 5. Unfortunately, we found that glycosidation of **2** (α/β = 80/20) and **12**, under conditions similar to the optimized conditions for the benzylated glucopyranosyl diethyl phosphite **1**, gave the 2-deoxyglucopyranosides **24** in low yield and with low stereoselectivity (entry 1 in Table 5). However, both the chemical yield and stereoselectivity increased as the reaction temperature decreased, and when the glycosidation was performed at low temperature, −78 °C, a better chemical yield and β-stereoselectivity were obtained (entry 2 in Table 5). In addition, it was found that the glycosidations of **2** and **12** in Et_2O at −78 °C proceeded effectively to afford **24** in high yield (87%) with good β-stereoselectivity (α/β = 19/81) (entry 7 in Table 5). Diethyl ether was shown to be superior to such other solvents as CH_2Cl_2, EtCN, PhMe, and THF (entries 3–7 in Table 5) with respect to both the chemical yield and unusual β-stereoselectivity. Moreover, it was confirmed that the chemical yield and β-stereoselectivity were highly dependent on the amount of montmorillonite K-10 and the reaction temperature. The highest chemical yield and β-stereoselectivity were achieved when 100 wt % montmorillonite K-10 was used in Et_2O at −78 °C for 1 h (entries 7–12 in Table 5). The optimized conditions for selectively obtaining the 2-deoxy-β-glucopyranoside differed significantly from that for the previously mentioned β-stereoselective glucosidation. This difference came from the higher reactivity of the 2-deoxyglycosyl donor **2** as compared to that of the glucosyl donor **1**. With these favorable new results, next our attention turned to the glycosidations of a typical 2,6-dideoxy sugar, olivose, because β-olivosides are very common and important 2,6-dideoxyglycosides related to antitumor antibiotics.[17,18] Therefore, we examined the glycosidation with **12** of the olivosyl diethyl phosphites **3** (α/β = 86/14), **4** (α/β = 72/28), **5** (α/β = 89/11), and **6** (α/β = 79/21), which have different protecting groups at the C-3 and C-4. The results are outlined in Table 6. In this case, it was found that the chemical yield and stereoselectivity were highly dependent on the protecting groups at C-3 and 4 of the donors, and the C-4 acyl protecting group significantly assisted the β-stereoselectivity by the participating effect, as shown in Figure 2.[5,22] Thus, the glycosidations of **4** and **12** using 100 wt % montmorillonite K-10 in Et_2O at −78 °C for 1 h effectively gave the corresponding olivosides **26** in 92% yield with 10:90 α/β-stereoselectivity (entry 2 in Table 6). Armed with these results, the glycosidations of **2** and **4**

Table 5. Glycosidations of **2** and **12** by montmorillonite K-10 under various conditions[a]

2 + **12** —Montmorillonite K-10→ **24**

Entry	Wt % of K-10	Solvent (0.1 M)	Temp (°C)	Yield[b] (%)	α/β Ratio[c]
1	100	CH_2Cl_2–MeCN (10:1)[d]	−20	58	43/57
2	100	CH_2Cl_2–MeCN (10:1)[d]	−78	78	26/74
3	100	CH_2Cl_2	−78	87	23/77
4	100	EtCN	−78	81	32/68
5	100	PhMe	−78	69	25/75
6	100	THF	−78	84	47/53
7	100	Et_2O	−78	87	19/81
8	200	Et_2O	−78	82	24/76
9	50	Et_2O	−78	80	21/79
10	20	Et_2O	−78	63	21/79
11	100	Et_2O	−50	80	31/69
12	100	Et_2O	−20	77	44/56

[a] All reactions were carried out using 2.0 equiv of **12** to **2**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by HPLC analysis (column, CrestPak C18S®, 4.6 × 150 mm; eluent, 10% H_2O in MeCN; flow rate, 0.5 mL/min, 40 °C; detection, UV 250 nm).
[d] 0.05 M solvent was used.

Table 6. Glycosidations of **3**–**6** and **12** by montmorillonite K-10[a]

3-6 + **12** —Montmorillonite K-10 (100 wt%), Et_2O, -78 °C, 1 h→ **25-28**

Entry	Donor	Product	Yield[b] (%)	α/β Ratio[c]
1	**3**	**25**	76	20/80
2	**4**	**26**	92	10/90
3	**5**	**27**	72	22/78
4	**6**	**28**	68	16/84

[a] All reactions were carried out using 2.0 equiv of **12** to the glycosyl donors **3**–**6**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by HPLC analysis (column, CrestPak C18S®, 4.6 × 150 mm; eluent, 10% H_2O in MeCN; flow rate, 0.5 mL/min, 40 °C; detection, UV 250 nm).

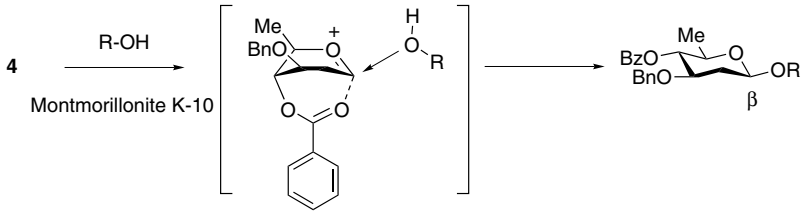


Figure 2. C-4 participation in the glycosidation of **4**.

Table 7. β-Stereoselective glycosidations of **2** and **4** with and several alcohols[a]

2 or **4** + **8-13**, **15** —Montmorillonite K-10 (100 wt%), Et_2O, -78 °C, 1 h→ **24**, **26**, **29-40**

Entry	Donor	Alcohol	Product	Yield[b] (%)	α/β Ratio[c]
1	**2**	**12**	**24**	87	19/81
2		**8**	**29**	93	17/83
3		**9**	**30**	94	14/86
4		**10**	**31**	97	22/78
5		**11**	**32**	96	23/77
6		**13**	**33**	88	21/79
7		**15**	**34**	70	29/71
8	**4**	**12**	**26**	92	10/90
9		**8**	**35**	86	14/86
10		**9**	**36**	90	10/90
11		**10**	**37**	95	19/81
12		**11**	**38**	86	17/83
13		**13**	**39**	89	17/83
14		**15**	**40**	82	15/85

[a] All reactions were carried out using 2.0 equiv of the alcohol to **2** or **4**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by HPLC analysis (column, CrestPak C18S®, 4.6 × 150 mm; eluent, 10% H_2O in MeCN; flow rate, 0.5 mL/min, 40 °C; detection, UV 250 nm).

using other primary and secondary alcohols (**8**–**11**, **13**, and **15**)[23] were next examined. The results summarized in Table 7 show that the glycosidations of **2** and **4** with **8**–**11**, **13**, and **15**, using 100 wt % montmorillonite K-10 in Et_2O at −78 °C for 1 h, as well as that of **12**, proceeded effectively to give the corresponding 2-deoxy-β-glucopyranosides **29β**–**34β** and β-olivosides **35β**–**40β**, respectively, in good to high yields and with good stereoselectivities. Although it is well known that epimerization of 2-deoxyglycosides occurs readily under strong acidic conditions, no epimerization of the glycosidic bond was observed during the present glycosidation. We examined the recycling of the activator in the glycosidations of **2** and **8**. After treating the used montmorillonite K-10 as described in the glycosidation of **1**, the recovered montmorillonite K-10 could be reused for at least three times and showed high yields and good β-stereoselectivities, as described in Table 8.

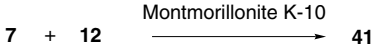
Table 8. Recycling of montmorillonite K-10 in glycosidation of **2** and **8**

Recycling number	0	1st	2nd	3rd
Yield (%)	93	89	89	87
α/β Ratio	17/83	17/83	17/83	17/83

2.3. β-Mannosidation

Since β-mannopyranosides feature in many natural bioactive substances, such as asparagine-linked glycoproteins and certain antibiotics, the stereocontrolled formation of β-mannopyranosides is of considerable importance.[24] The stereoselective and direct construction of β-mannopyranosides is particularly difficult, because the axial β-hydroxy group at C-2 and the anomeric effect block access to the β face. A direct and stereoselective construction of β-mannopyranosidic linkages[25,26] in a practical and environmentally friendly manner is thus of particular interest. β-Stereoselective mannosidation using mannopyranosyl diethyl phosphite and Me_3SiOTf was very recently announced by Hashimoto's group.[10e] As another challenging extension of our studies, we next examined the glycosidation of 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl diethyl phosphite (**7**)[10e] and the sugar alcohol **12**, using montmorillonite K-10 as a heterogeneous activator,[27] under various conditions. These results are summarized in Table 9. The glycosidation of **7** and **12** proceeded smoothly in CH_2Cl_2 to give the disaccharides **41** in high yield with good β-stereoselectivity. The other solvents examined such as PhMe, Et_2O, and MeCN were less effective than CH_2Cl_2 with respect to both the chemical yield and β-stereoselectivity (entries 1–4 in Table 9). Lower reaction temperatures, <−30 °C, significantly decreased the chemical yield, while the stereoselectivity was not changed (entries 5 and 6 in Table 9). The use of 200 wt % montmorillonite K-10 increased the chemical yield, with good β-stereoselectivity (entries 5, 7–9 in Table 9). Thus, the glycosidation of **7** and **12** was best effected by using 200 wt % montmorillonite K-10 in CH_2Cl_2 at −10 °C for 1 h, giving **41** in 93% yield with α/β ratio of 15/85. The optimized conditions for obtaining the β-mannopyranoside stereoselectively differed significantly from those for the previously mentioned β-stereoselective glycosidations of glucopyranosyl and 2-deoxyglucopyranosyl diethyl phosphites **1** and **2**. The chemical yields in the glycosidations of **7** and **12**, using a homogeneous Lewis

Table 9. Glycosidations of **7** and **12** by montmorillonite K-10 under various conditions[a]

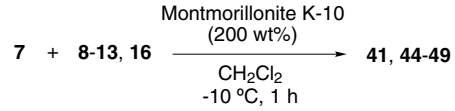


Entry	Activator	Amount of activator	Solvent (0.1 M)	Temp (°C)	Time (h)	Yield[b] (%)	α/β Ratio[c]
1	Montmorillonite K-10	150 wt %	CH_2Cl_2	0	1	89	16/84
2	Montmorillonite K-10	150 wt %	PhMe	0	1	85	38/62
3	Montmorillonite K-10	150 wt %	Et_2O	0	1	74	37/63
4	Montmorillonite K-10	150 wt %	MeCN	0	1	12	42/58
5	Montmorillonite K-10	100 wt %	CH_2Cl_2	−10	1	84	16/84
6	Montmorillonite K-10	100 wt %	CH_2Cl_2	−30	1	74	17/83
7	Montmorillonite K-10	50 wt %	CH_2Cl_2	−10	1	61	19/81
8	Montmorillonite K-10	150 wt %	CH_2Cl_2	−10	1	91	16/84
9	Montmorillonite K-10	200 wt %	CH_2Cl_2	−10	1	93	15/85
10	Me_3SiOTf	0.3 mol %	CH_2Cl_2	−10	1	50	17/83
11	TfOH	0.3 mol %	CH_2Cl_2	−10	1	60	18/82

[a] All reactions were carried out using 2.0 equiv of **12** to **7**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by 300 MHz ^{1}H NMR analysis.

acid, Me_3SiOTf, and a homogeneous protic acid, TfOH, under similar conditions were much lower than that with montmorillonite K-10 because of partial hydrolysis[28] of the benzylidene acetal group of **7** (entries 10 and 11 in Table 9). Moreover, although the mannopyranosyl triflate, which is the key intermediate for obtaining high β-stereoselectivity in Crich's method,[26] was not present in this case, the 4,6-*O*-benzylidene functionality of **7** was found to be very helpful[29] for achieving good β-stereoselectivity. Indeed, a modest α/β ratio of 31/69 was observed in the glycosidation of 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl diethyl phosphite (**42**) and **12** under similar conditions (Fig. 3). These results strongly suggest that the montmorillonite K-10 anion coordinate with the oxonium intermediate came from **42**. With these favorable results, our attention then turned to the scope and limitation of this glycosidation reaction. Glycosidations of **7** with other primary and secondary alcohols **8**–**11**, **13**, and **16** were next carried out. From the results summarized in Table 10, it is clear glycosidations of **8**–**11**, **13**, and **16**[30] using 200 wt % montmorillonite K-10 in CH_2Cl_2 at −10 °C for 1 h, as well as **12**, produces the corresponding β-mannopyranosides **44β**–**49β** in good to high yields with good β-stereoselectivities. Furthermore, the acid-sensitive isopropylidene acetal group, is not cleaved under these conditions. The montmorillonite K-10 recovered by washing followed by drying could be reused for at least three times, and showed similar high yields and good stereoselectivities in the glycosidations of **7** and **8** (Table 11).

Table 10. β-Stereoselective glycosidations of **7** and several alcohols[a]



Entry	Alcohol[a]	Product	Yield (%)[b]	α/β Ratio[c]
1	**12**	**41**	93	15/85
2	**8**	**44**	92	11/89
3	**9**	**45**	84	13/87
4	**10**	**46**	85	12/88
5	**11**	**47**	86	10/90
6	**13**	**48**	92	15/85
7	**16**	**49**	78	13/87

[a] All reactions were carried out using 2.0 equiv of the alcohol to **7**.
[b] Isolated yields after purification by column chromatography.
[c] α/β Ratios were determined by 300 MHz ^{1}H NMR analysis.

Table 11. Recycling of montmorillonite K-10 in glycosidation of **7** and **8**

Recycling number	0	1st	2nd	3rd
Yield (%)	92	91	86	82
α/β Ratio	11/89	12/88	10/90	9/91

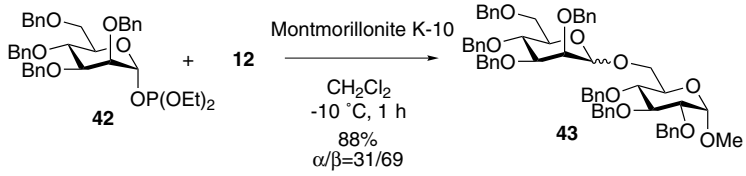


Figure 3. Glycosidation of mannopyranosyl diethyl phosphite **42** and **2**.

3. Conclusion

We have presented a stereoselective strategy for the direct syntheses of β-gluco-, 2-deoxy-β-gluco-, and β-mannopyranosides from appropriate glycopyranosyl diethyl phosphites and alcohols, using a reusable heterogeneous solid acid, montomorillonite K-10. The results, showing a simple protocol and stereoselectivity, should stimulate further research on heterogeneous solid acids in glycosidation reactions. The present protocols should find wide application for the synthesis of biologically important natural products.

4. Experimental

4.1. General methods

Melting points were determined on a micro hot-stage Yanako MP-S3 and were uncorrected. Optical rotations were measured on a Jasco DIP-360 photoelectric polarimeter in chloroform unless otherwise noted. ^{1}H NMR spectra were recorded on a Jeol GSX 270 (270 MHz) or a Lambda 300 (300 MHz) spectrometer in $CDCl_3$ using Me_4Si as the internal standard, unless otherwise noted. Thin-layer and column chromatography was performed on Merck 60F-254 (0.25 mm) TLC plates and Kanto Chemical Co., Inc Silica Gel 60 N (spherical, neutral), respectively. Nafion-H was purchased from Wako Pure Chemical Industries, Ltd. as Nafion® NR-50 and was dried at 25 °C/1 mmHg for 2 h before using. SO_4/ZrO_2 was purchased from Wako Pure Chemical Industries, Ltd. and dried at 200 °C/1 mmHg for 12 h before using. Montmorillonite K-10 was purchased from Aldrich Chemical Company, Inc. and dried at 200 °C/1 mmHg for 12 h before using. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon with oven-dried glassware. In general, organic solvents were purified and dried by appropriate procedures, and evaporations and concentrations were carried out under diminished pressure below 30 °C, unless otherwise noted.

4.2. Glycosidation protocol for the preparation of the β-glucopyranosides

To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl diethyl phosphite (**1**, α/β = 73/27, 0.1 mmol) and an alcohol (0.2 mmol) in dry 10:1 CH_2Cl_2–MeCN (2 mL) was added montmorillonite K-10 (100 wt % to the glycosyl donor **1**). After stirring at −20 °C for 30 min, the mixture was filtered and the filtrate was concentrated in vacuo. Purification of the residue by flash column chromatography gave the corresponding glucopyranosides, which contained predominately the β anomers.

4.2.1. Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (17α). Colorless syrup, R_f 0.35 (4:1 *n*-hexane–EtOAc); $[\alpha]_D^{27}$ +43.1 (*c* 1.03, $CHCl_3$); ^{1}H NMR δ 0.83–1.02 (2H, m), 1.07–1.35 (3H, m), 1.58–1.90 (6H, m), 3.19 (1H, dd, *J* 9.6 and 6.0 Hz), 3.42 (1H, dd, *J* 9.6 and 7.2 Hz), 3.55 (1H, dd, *J* 9.6 and 3.6 Hz), 3.58–3.82 (4H, m), 3.97 (1H, dd, *J* 9.0 and 9.0 Hz), 4.47 (2H, d, *J* 11.6 Hz), 4.61 (1H, d, *J* 11.6 Hz), 4.63 (1H, d, *J* 12.4 Hz), 4.73 (1H, d, *J* 3.6 Hz), 4.77 (1H, d, *J* 12.4 Hz), 4.81 (1H, d, *J* 11.0 Hz), 4.82 (1H, d, *J* 10.4 Hz), 5.00 (1H, d, *J* 11.0 Hz), 7.10–7.16 (2H, m), 7.22–7.40 (18H, m). Anal. Calcd for $C_{41}H_{48}O_6$: C, 77.33; H, 7.60. Found: C, 77.31; H, 7.55.

4.2.2. Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (17β). White solid, mp 97.0–98.5 °C; R_f 0.40 (4:1 *n*-hexane–EtOAc); $[\alpha]_D^{26}$ +4.5 (*c* 1.05, $CHCl_3$); ^{1}H NMR δ 1.11–1.34 (3H, m), 1.58–1.92 (6H, m), 3.32 (1H, dd, *J* 9.6 and 7.0 Hz), 3.40–3.49 (2H, m), 3.52–3.78 (4H, m), 3.79 (1H, dd, *J* 9.6 and 6.0 Hz), 4.37 (1H, d, *J* 7.4 Hz), 4.52 (1H, d, *J* 11.6 Hz), 4.56 (1H, d, *J* 10.4 Hz), 4.63 (1H, d, *J* 11.6 Hz), 4.72 (1H, d, *J* 10.8 Hz), 4.78 (1H, d, *J* 10.8 Hz), 4.82 (1H, d, *J* 10.4 Hz), 4.92 (1H, d, *J* 10.8 Hz), 4.97 (1H, d, *J* 10.8 Hz), 7.12–7.18 (2H, m), 7.22–7.38 (18H, m). Anal. Calcd for $C_{41}H_{48}O_6$: C, 77.33; H, 7.60. Found: C, 77.20; H, 7.51.

4.2.3. *n*-Octyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (18α). Colorless syrup, R_f 0.45 (6/1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +39.5 (*c* 1.38, $CHCl_3$); ^{1}H NMR δ 0.82–0.93 (3H, m), 1.18–1.40 (10H, m), 1.50–1.68 (2H, m), 3.41 (1H, dt, *J* 10.4 and 6.4 Hz), 3.55 (1H, dd, *J* 9.2 and 3.6 Hz), 3.55–3.68 (1H, m), 3.62 (1H, dd, *J* 10.4 and 3.6 Hz), 3.63 (1H, dd, *J* 9.2 and 4.8 Hz), 3.72 (1H, dd, *J* 10.4 and 4.8 Hz), 3.78 (1H, ddd, *J* 10.4, 4.8, and 3.6 Hz), 3.98 (1H, dd, *J* 9.2 and 9.2 Hz), 4.47 (2H, d, *J* 11.0 Hz), 4.61 (1H, d, *J* 11.0 Hz), 4.64 (1H, d, *J* 11.0 Hz), 4.75 (1H, d, *J* 3.2 Hz), 4.78 (1H, d, *J* 11.0 Hz), 4.81 (1H, d, *J* 11.0 Hz), 4.82 (1H, d, *J* 11.0 Hz), 4.89 (1H, d, *J* 11.0 Hz), 7.09–7.18 (2H, m), 7.20–7.40 (18H, m). Anal. Calcd for $C_{42}H_{52}O_6$: C, 77.27; H, 8.03. Found: C, 77.29; H, 7.84.

4.2.4. *n*-Octyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (18β). White solid, mp 32.2–33.0 °C; R_f 0.50 (6:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +5.8 (*c* 1.38, $CHCl_3$); ^{1}H NMR δ 0.82–0.93 (3H, m), 1.19–1.46 (10H, m), 1.58–1.74 (2H, m), 3.44 (1H, dd, *J* 9.0 and 7.6 Hz), 3.42–3.55 (2H, m), 3.57 (1H, dd, *J* 9.0 and 9.0 Hz), 3.63–3.71 (1H, m), 3.64 (1H, dd, *J* 9.0 and 9.0 Hz), 3.75 (1H, dd, *J* 10.4 and 2.2 Hz), 3.96 (1H, dt, *J* 9.6 and 6.6 Hz), 4.39 (1H, d, *J* 7.6 Hz), 4.52 (1H, d, *J* 11.0 Hz), 4.56 (1H, d, *J* 12.4 Hz), 4.62 (1H, d, *J* 12.4 Hz), 4.72 (1H, d, *J* 11.0 Hz), 4.78 (1H, d, *J* 10.2 Hz), 4.82 (1H, d, *J* 10.2 Hz), 4.93 (1H, d, *J* 11.0 Hz), 4.96 (1H,

d, *J* 11.0 Hz), 7.13–7.18 (2H, m), 7.22–7.39 (18H, m). Anal. Calcd for $C_{42}H_{52}O_6$: C, 77.27; H, 8.03. Found: C, 77.32; H, 7.96.

4.2.5. Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (19α). Colorless syrup, R_f 0.64 (60:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +56.0 (*c* 0.74, $CHCl_3$); ^{1}H NMR δ 1.10–1.62 (6H, m), 1.66–1.96 (4H, m), 3.48–3.69 (1H, m), 3.55 (1H, dd, *J* 9.6 and 3.6 Hz), 3.62 (1H, dd, *J* 11.2 and 2.0 Hz), 3.63 (1H, dd, *J* 9.8 and 9.2 Hz), 3.74 (1H, dd, *J* 11.2 and 3.6 Hz), 3.88 (1H, ddd, *J* 9.8, 3.6 and 2.0 Hz), 4.00 (1H, dd, *J* 9.2 and 9.2 Hz), 4.47 (2H, d, *J* 11.2 Hz), 4.62 (1H, d, *J* 11.2 Hz), 4.65 (1H, d, *J* 10.6 Hz), 4.75 (1H, d, *J* 11.2 Hz), 4.80 (1H, d, *J* 10.6 Hz), 4.82 (1H, d, *J* 10.6 Hz), 4.95 (1H, d, *J* 3.6 Hz), 5.00 (1H, d, *J* 10.6 Hz), 7.09–7.16 (2H, m), 7.20–7.38 (18H, m). Anal. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.44. Found: C, 76.97; H, 7.21.

4.2.6. Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (19β). White solid, mp 103.5–105.0 °C; R_f 0.48 (60:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +9.2 (*c* 1.01, $CHCl_3$); ^{1}H NMR δ 1.16–1.62 (6H, m), 1.68–1.84 (2H, m), 1.88–2.08 (2H, m), 3.44 (1H, dd, *J* 8.2 and 8.2 Hz), 3.45 (1H, ddd, *J* 9.2, 5.0, and 2.0 Hz), 3.59–3.79 (2H, m), 3.65 (1H, dd, *J* 8.2 and 7.2 Hz), 3.74 (1H, dd, *J* 9.2 and 2.0 Hz), 4.50 (1H, d, *J* 7.2 Hz), 4.53 (1H, d, *J* 11.0 Hz), 4.56 (1H, d, *J* 12.0 Hz), 4.61 (1H, d, *J* 12.0 Hz), 4.71 (1H, d, *J* 11.0 Hz), 4.77 (1H, d, *J* 11.0 Hz), 4.82 (1H, d, *J* 11.0 Hz), 4.92 (1H, d, *J* 11.0 Hz), 4.99 (1H, d, *J* 11.0 Hz), 7.14–7.19 (2H, m), 7.22–7.38 (18H, m). Anal. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.44. Found: C, 77.18; H, 7.26.

4.2.7. Isopropyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (20α). Colorless syrup, R_f 0.60 (60:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +38.4 (*c* 1.32, $CHCl_3$); ^{1}H NMR δ 1.11 and 1.15 (each 3H, each d, *J* 6.0 Hz), 3.48 (1H, dd, *J* 9.2 and 3.2 Hz), 3.54 (1H, dd, *J* 10.4 and 2.0 Hz), 3.57 (1H, dd, *J* 9.8 and 9.2 Hz), 3.67 (1H, dd, *J* 10.4 and 3.2 Hz), 3.77 (1H, ddd, *J* 9.8, 3.2, and 2.0 Hz), 3.82 (1H, septet, *J* 6.0 Hz), 3.92 (1H, dd, *J* 9.2 and 9.2 Hz), 4.39 (2H, d, *J* 12.0 Hz), 4.54 (1H, d, *J* 12.0 Hz), 4.58 (1H, d, *J* 11.2 Hz), 4.71 (1H, d, *J* 12.0 Hz), 4.74 (1H, d, *J* 11.2 Hz), 4.76 (1H, d, *J* 11.2 Hz), 4.80 (1H, d, *J* 3.2 Hz), 4.93 (1H, d, *J* 10.6 Hz), 7.02–7.08 (2H, m), 7.14–7.33 (18H, m). Anal. Calcd for $C_{37}H_{42}O_6$: C, 76.26; H, 7.26. Found: C, 76.35; H, 6.99.

4.2.8. Isopropyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (20β). White solid, mp 109.0–110.5 °C; R_f 0.38 (60:1 chloroform–EtOAc); $[\alpha]_D^{27}$ +12.0 (*c* 1.12, $CHCl_3$); ^{1}H NMR δ 1.24 and 1.32 (each 3H, each d, *J* 6.0 Hz), 3.43 (1H, dd, *J* 8.8 and 8.8 Hz), 3.44 (1H, ddd, *J* 8.8, 4.2, and 1.6 Hz), 3.54 (1H, dd, *J* 8.8 and 8.8 Hz), 3.63 (1H, dd, *J* 8.8 and 7.6 Hz), 3.65 (1H, dd, *J* 10.4 and 4.2 Hz), 3.74 (1H, dd, *J* 10.4 and 1.6 Hz), 4.02 (1H, septet, *J* 6.0 Hz), 4.46 (1H, d, *J* 7.6 Hz), 4.53 (1H, d, *J* 10.8 Hz), 4.56 (1H, d, *J* 11.6 Hz), 4.61 (1H, d, *J* 11.6 Hz), 4.70 (1H, d, *J* 10.8 Hz), 4.78 (1H, d, *J* 10.8 Hz), 4.82 (1H, d, *J* 10.8 Hz), 4.92 (1H, d, *J* 10.8 Hz), 4.97 (1H, d, *J* 10.8 Hz), 7.13–7.19 (2H, m), 7.23–7.39 (18H, m). Anal. Calcd for $C_{37}H_{42}O_6$: C, 76.26; H, 7.26. Found: C, 76.25; H, 7.11.

4.2.9. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside (21α). White solid, mp 101.8–102.8 °C;R_f 0.35 (3:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +145 (*c* 0.71, $CHCl_3$); ^{1}H NMR δ 3.35 (3H, s), 3.44 (1H, dd, *J* 9.6 and 3.6 Hz), 3.49–3.86 (9H, m), 3.90–4.03 (2H, m), 4.37–4.48 (2H, m), 4.53–4.67 (5H, m), 4.55 (1H, d, *J* 3.4 Hz), 4.71 (1H, d, *J* 12.0 Hz), 4.77 (1H, d, *J* 10.6 Hz), 4.81 (1H, d, *J* 10.6 Hz), 4.82 (1H, d, *J* 11.4 Hz), 4.92 (1H, d, *J* 11.4 Hz), 4.93 (1H, d, *J* 10.6 Hz), 4.96 (1H, d, *J* 11.4 Hz), 4.98 (1H, d, *J* 3.8 Hz), 7.08–7.13 (2H, m), 7.20–7.36 (33H, m). Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74. Found: C, 75.34; H, 6.49.

4.2.10. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (21β). White solid, mp 136.5–138.0 °C; R_f 0.35 (3:1 *n*-hexane–EtOAc); $[\alpha]_D^{27}$ +19.5 (*c* 1.31, $CHCl_3$); ^{1}H NMR δ 3.32 (3H, s), 3.38–3.75 (9H, m), 3.82 (1H, dd, *J* 10.6 and 3.6 Hz), 3.99 (1H, dd, *J* 9.4 and 9.4 Hz), 4.18 (1H, dd, *J* 10.6 and 2.0 Hz), 4.34 (1H, d, *J* 8.0 Hz), 4.47–4.60 (5H, m), 4.61 (1H, d, *J* 3.6 Hz), 4.65 (1H, d, *J* 12.0 Hz), 4.71 (1H, d, *J* 11.0 Hz), 4.74–4.82 (3H, m) 4.80 (1H, d, *J* 10.6 Hz), 4.90 (1H, d, *J* 11.0 Hz), 4.96 (1H, d, *J* 11.0 Hz), 4.97 (1H, d, *J* 11.0 Hz), 7.13–7.37 (35H, m). Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74. Found: C, 75.36; H, 6.49.

4.2.11. Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (22α). Colorless syrup, R_f 0.40 (3:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +37.7 (*c* 0.77, $CHCl_3$); ^{1}H NMR δ 1.31 (3H, d, *J* 6.0 Hz), 1.25 and 1.43 (each 3H, each s), 3.32 (1H, dd, *J* 10.0 and 7.0 Hz), 3.33 (3H, s), 3.59 (1H, dd, *J* 9.2 and 3.0 Hz), 3.63 (1H, dd, *J* 10.0 and 1.2 Hz), 3.74 (1H, dq, *J* 10.0 and 6.0 Hz), 3.78 (1H, dd, *J* 9.0 and 9.0 Hz), 3.80 (1H, br d, *J* 10.0 Hz), 3.97 (1H, dd, *J* 9.2 and 9.0 Hz), 4.02–4.12 (1H, m), 4.05 (1H, d, *J* 5.2 Hz), 4.09 (1H, dd, *J* 7.0 and 5.2 Hz), 4.49 (1H, d, *J* 11.8 Hz), 4.52 (1H, d, *J* 10.0 Hz), 4.62 (1H, d, *J* 11.8 Hz), 4.71 (1H, d, *J* 11.4 Hz), 4.79 (1H, d, *J* 11.4 Hz), 4.82 (1H, br s), 4.83 (1H, d, *J* 10.0 Hz), 4.86 (1H, d, *J* 10.4 Hz), 4.95 (1H, d, *J* 10.4 Hz), 4.97 (1H, d, *J* 3.0 Hz), 7.14–7.19 (2H, m), 7.21–7.37 (18H, m). Anal. Calcd for $C_{44}H_{52}O_{10}$: C, 71.33; H, 7.07. Found: C, 71.33; H, 6.72.

4.2.12. Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (22β). Colorless syrup, R_f 0.54 (3:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ −15.6 (*c* 1.23, $CHCl_3$); ^1H NMR δ 1.34 (3H, d, *J* 5.6 Hz), 1.32 and 1.46 (each 3H, each s), 3.34–3.46 (2H, m), 3.39 (3H, s), 3.58–3.76 (6H, m), 4.09 (1H, d, *J* 5.2 Hz), 4.21 (1H, dd, *J* 6.8 and 5.2 Hz), 4.55 (1H, d, *J* 11.8 Hz), 4.61 (1H, d, *J* 11.8 Hz), 4.69 (1H, d, *J* 10.8 Hz), 4.77 (1H, d, *J* 10.6 Hz), 4.82 (1H, d, *J* 10.6 Hz), 4.86 (1H, br s), 4.89 (1H, d, *J* 10.8 Hz), 4.91 (1H, d, *J* 10.8 Hz), 4.93 (1H, d, *J* 10.8 Hz), 4.94 (1H, d, *J* 5.0 Hz), 7.16–7.22 (2H, m), 7.22–7.40 (18H, m). Anal. Calcd for $C_{44}H_{52}O_{10}$: C, 71.33; H, 7.07. Found: C, 71.40; H, 6.82.

4.2.13. Methyl 3-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-4,6-*O*-benzylidene-α-D-glucopyranoside (23α). White solid, mp 88.0–89.5 °C; R_f 0.25 (10:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +38.4 (*c* 0.66, $CHCl_3$); ^1H NMR δ 3.34–3.50 (2H, m), 3.46 (3H, s), 3.58 (1H, dd, *J* 9.0 and 3.2 Hz), 3.60 (1H, dd, *J* 9.0 and 9.0 Hz), 3.67 (1H, dd, *J* 9.2 and 9.2 Hz), 3.73 (1H, dd, *J* 10.0 and 9.8 Hz), 3.79–3.91 (2H, m), 4.04–4.18 (3H, m), 4.28 (1H, d, *J* 12.0 Hz), 4.31 (1H, dd, *J* 9.0 and 4.4 Hz), 4.44 (1H, d, *J* 10.8 Hz), 4.52 (1H, d, *J* 12.0 Hz), 4.71 (1H, d, *J* 11.8 Hz), 4.78 (1H, d, *J* 10.2 Hz), 4.78–4.93 (4H, m), 4.84 (1H, d, *J* 3.6 Hz), 4.90 (1H, d, *J* 3.2 Hz), 5.01 (1H, d, *J* 10.6 Hz), 5.56 (1H, s), 6.97–7.05 (2H, m), 7.06–7.16 (2H, m), 7.17–7.43 (34H, m), 7.46–7.53 (2H, m). Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found: C, 73.74; H, 6.33.

4.2.14. Methyl 3-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-α-D-glucopyranoside (23β). White solid, mp 175.0–176.0 °C; R_f 0.57 (10:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +20.1 (*c* 1.05, $CHCl_3$); ^1H NMR δ 3.36–3.49 (1H, m), 3.44 (3H, s), 3.49–3.70 (6H, m), 3.75 (1H, dd, *J* 10.0 and 10.0 Hz), 3.86 (1H, dd, *J* 9.0 and 3.2 Hz), 3.92 (1H, dd, *J* 9.8 and 4.4 Hz), 4.10 (1H, dd, *J* 9.0 and 9.0 Hz), 4.32 (1H, dd, *J* 10.0 and 4.6 Hz), 4.52 (1H, d, *J* 10.6 Hz), 4.50 and 4.57 (each 1H, ABq, *J* 11.8 Hz), 4.66 (1H, d, *J* 10.6 Hz), 4.76 (1H, d, *J* 11.2 Hz), 4.77 (1H, d, *J* 10.6 Hz), 4.78 (1H, d, *J* 10.6 Hz), 4.80 (1H, d, *J* 4.0 Hz), 4.81 (1H, d, *J* 10.6 Hz), 4.92 (1H, d, *J* 10.6 Hz), 4.96 (1H, d, *J* 3.2 Hz), 5.05 (1H, d, *J* 11.2 Hz), 5.56 (1H, s), 7.15–7.41 (28H, m), 7.42–7.50 (2H, m). Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found: C, 73.79; H, 6.29.

4.3. Glycosidation protocol for the preparations of 2-deoxy- and 2,6-dideoxy-β-glucopyranosides

To a stirred solution of the glycosyl phosphite **2** (α/β = 80/20, 0.1 mmol) or **4** (α/β = 72:28, 0.1 mmol) and an alcohol (0.2 mmol) in dry Et_2O (1 mL) was added montmorillonite K-10 (100 wt % to the glycosyl donor **2** or **4**). After stirring for 1 h at −78 °C, the mixture was filtered and the filtrate was concentrated in vacuo. Purification of the residue by flash column chromatography gave the corresponding 2-deoxyglucopyranosides or the olivosides, both of which selectively included the β-anomers.

4.3.1. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (24α). Colorless syrup, R_f 0.24 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +65.4 (*c* 0.60, $CHCl_3$); ^1H NMR δ 1.69 (1H, ddd, *J* 12.4, 12.4, and 4.0 Hz), 2.30 (1H, br dd, *J* 12.4 and 5.2 Hz), 3.34 (3H, s), 3.44–3.69 (7H, m), 3.70–3.75 (1H, m), 3.78–3.84 (1H, m), 3.89–4.02 (2H, m), 4.36–4.70 (8H, m), 4.77–5.01 (6H, m), 7.12–7.38 (30H, m). Anal. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98; H, 6.86. Found: C, 74.92; H, 6.66.

4.3.2. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (24β). White solid, mp 130.5–132.0 °C; R_f 0.36 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{27}$ +23.5 (*c* 1.33, $CHCl_3$); ^1H NMR δ 1.53–1.68 (1H, m), 2.15 (1H, ddd, *J* 12.4, 4.8, and 1.6 Hz), 3.36 (3H, s), 3.30–3.78 (9H, m), 3.56–3.75 (4H, m), 3.99 (1H, dd, *J* 9.6 and 9.6 Hz), 4.07 (1H, dd, *J* 10.8 and 2.0 Hz), 4.16 (1H, dd, *J* 10.0 and 1.6 Hz), 4.49–4.68 (8H, m), 4.77–4.89 (4H, m), 5.00 (1H, d, *J* 10.8 Hz), 7.18–7.38 (30H, m). Anal. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98; H, 6.86. Found: C, 74.97; H, 6.68.

4.3.3. Cyclohexylmethyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (29α). Colorless syrup, R_f 0.36 (5:2 *n*-hexane–ether); $[\alpha]_D^{29}$ +67.0 (*c* 0.88, $CHCl_3$); ^1H NMR δ 0.81–1.02 (2H, m), 1.05–1.35 (3H, m), 1.46–1.81 (7H, m), 2.27 (1H, br dd, *J* 12.4 and 4.8 Hz), 3.15 (1H, dd, *J* 9.2 and 6.0 Hz), 3.41 (1H, dd, *J* 9.2 and 6.8 Hz), 3.56–3.83 (4H, m), 3.98 (1H, ddd, *J* 11.2, 8.4, and 4.8 Hz), 4.51 (2H, d, *J* 11.0 Hz), 4.64 (1H, d, *J* 11.0 Hz), 4.65 (1H, d, *J* 11.0 Hz), 4.68 (1H, d, *J* 11.0 Hz), 4.89 (1H, d, *J* 11.0 Hz), 4.91 (1H, br d, *J* 3.2 Hz), 7.14–7.20 (2H, m), 7.22–7.39 (13H, m). Anal. Calcd for $C_{34}H_{42}O_5$: C, 76.95; H, 7.98. Found: C, 76.93; H, 7.97.

4.3.4. Cyclohexylmethyl 3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranoside (29β). White solid, mp 72.0–73.0 °C; R_f 0.45 (5:2 *n*-hexane–ether); $[\alpha]_D^{28}$ −18.5 (*c* 1.32, $CHCl_3$); ^1H NMR δ 0.82–1.02 (2H, m), 1.07–1.34 (3H, m), 1.50–1.84 (7H, m), 2.35 (1H, ddd, *J* 12.4, 4.8, and 1.6 Hz), 3.22 (1H, dd, *J* 9.0 and 6.4 Hz), 3.40 (1H, ddd, *J* 9.2, 4.4, and 1.6 Hz), 3.49 (1H, dd, *J* 9.2 and 8.0 Hz), 3.65 (1H, dd, *J* 11.0 and 4.4 Hz), 3.69 (1H, ddd, *J* 12.0, 8.0, and 4.8 Hz), 3.73 (1H, dd, *J* 9.0 and 6.0 Hz), 3.77 (1H, dd, *J* 11.0 and 1.6 Hz), 4.40 (1H, dd, *J* 9.6 and 1.6 Hz), 4.55 (1H, d, *J* 10.8 Hz), 4.57 (1H, d, *J* 11.6 Hz), 4.59 (1H, d, *J* 12.4 Hz), 4.63 (1H,

d, *J* 12.4 Hz), 4.69 (1H, d, *J* 11.6 Hz), 4.90 (1H, d, *J* 10.8 Hz), 7.17–7.23 (2H, m), 7.23–7.38 (13H, m). Anal. Calcd for $C_{34}H_{42}O_5$: C, 76.95; H, 7.98. Found: C, 76.97; H, 7.62.

4.3.5. *n*-Octyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (30α). Colorless syrup, R_f 0.36 (5:2 *n*-hexane–ether); $[\alpha]_D^{29}$ +64.6 (*c* 1.40, $CHCl_3$); ^1H NMR δ 0.84–0.93 (3H, m), 1.20–1.37 (10H, m), 1.44–1.62 (2H, m), 1.72 (1H, ddd, *J* 12.8, 11.6, and 3.6 Hz), 2.28 (1H, br dd, *J* 12.8 and 6.4 Hz), 3.34 (1H, dt, *J* 9.6 and 6.8 Hz), 3.55–3.82 (5H, m), 4.00 (1H, ddd, *J* 11.6, 8.8, and 6.4 Hz), 4.43–4.60 (2H, m), 4.63 (1H, d, *J* 11.6 Hz), 4.65 (1H, d, *J* 12.0 Hz), 4.69 (1H, d, *J* 11.6 Hz), 4.89 (1H, d, *J* 10.4 Hz), 4.94 (1H, br d, *J* 3.6 Hz), 7.14–7.38 (15H, m). Anal. Calcd for $C_{35}H_{46}O_5$: C, 76.89; H, 8.48. Found: C, 76.90; H, 8.16.

4.3.6. *n*-Octyl 3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranoside (30β). Colorless syrup, R_f 0.47 (5:2 *n*-hexane–ether); $[\alpha]_D^{28}$ −16.7 (*c* 0.98, $CHCl_3$); ^1H NMR δ 0.84–0.92 (3H, m), 1.19–1.40 (10H, m), 1.53–1.71 (3H, m), 2.34 (1H, ddd, *J* 12.8, 4.8, and 1.6 Hz), 3.36–3.53 (3H, m), 3.61–3.79 (3H, m), 3.89 (1H, dt, *J* 9.2 and 7.2 Hz), 4.42 (1H, dd, *J* 10.0 and 1.6 Hz), 4.53–4.65 (4H, m) 4.68 (1H, d, *J* 11.6 Hz), 4.90 (1H, d, *J* 10.0 Hz), 7.16–7.37 (15H, m). Anal. Calcd for $C_{35}H_{46}O_5$: C, 76.89; H, 8.48. Found: C, 76.92; H, 8.10.

4.3.7. Cyclohexyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (31α). Colorless syrup, R_f 0.46 (30:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +80.6 (*c* 0.82, $CHCl_3$); ^1H NMR δ 1.11–1.91 (11H, m), 2.24 (1H, br dd, *J* 12.8 and 5.2 Hz), 3.49–3.69 (3H, m), 3.72–3.89 (2H, m), 4.02 (1H, ddd, *J* 11.6, 8.8, and 5.2 Hz), 4.47–4.54 (2H, m), 4.64 (1H, d, *J* 10.8 Hz), 4.65 (1H, d, *J* 12.0 Hz), 4.68 (1H, d, *J* 10.8 Hz), 4.89 (1H, d, *J* 10.8 Hz), 5.12 (1H, br d, *J* 4.8 Hz), 7.14–7.39 (15H, m). Anal. Calcd for $C_{33}H_{40}O_5$: C, 76.71; H, 7.80. Found: C, 76.75; H, 7.49.

4.3.8. Cyclohexyl 3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranoside (31β). White solid, mp 48.0–50.0 °C; R_f 0.35 (30:1 chloroform–EtOAc); $[\alpha]_D^{28}$ −26.6 (*c* 1.00, $CHCl_3$); ^1H NMR δ 1.13–2.05 (11H, m), 2.31 (1H, ddd, *J* 12.4, 5.2, and 1.6 Hz), 3.47–3.51 (2H, m), 3.61–3.80 (4H, m), 4.53–4.65 (5H, m), 4.69 (1H, d, *J* 12.0 Hz), 4.90 (1H, d, *J* 10.8 Hz), 7.19–7.47 (15H, m). Anal. Calcd for $C_{33}H_{40}O_5$: C, 76.71; H, 7.80. Found: C, 76.74; H, 7.64.

4.3.9. Isopropyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (32α). Colorless syrup, R_f 0.38 (30:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +76.6 (*c* 1.88, $CHCl_3$); ^1H NMR δ 1.12 (3H, d, *J* 6.0 Hz), 1.16 (3H, d, *J* 6.0 Hz), 1.74 (1H, ddd, *J* 12.8, 11.6, and 3.6 Hz), 2.24 (1H, br dd, *J* 12.8 and 5.2 Hz), 3.58–3.69 (2H, m), 3.77–3.86 (2H, m), 3.88 (1H, septet, *J* 6.0 Hz), 4.01 (1H, ddd, *J* 11.6, 8.8, and 5.2 Hz), 4.48–4.53 (2H, m), 4.63 (1H, d, *J* 11.6 Hz), 4.66 (1H, d, *J* 12.4 Hz), 4.68 (1H, d, *J* 11.6 Hz), 4.89 (1H, d, *J* 10.8 Hz), 5.08 (1H, br d, *J* 3.6 Hz), 7.14–7.38 (15H, m). Anal. Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.63; H, 7.41.

4.3.10. Isopropyl 3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranoside (32β). Colorless syrup, R_f 0.27 (30:1 chloroform–EtOAc); $[\alpha]_D^{29}$ −25.9 (*c* 1.58, $CHCl_3$); ^1H NMR δ 1.15 (3H, d, *J* 6.0 Hz), 1.26 (3H, d, *J* 6.0 Hz), 1.65 (1H, ddd, *J* 12.8, 12.2, and 10.0 Hz), 2.30 (1H, ddd, *J* 12.8, 5.6, and 1.6 Hz), 3.36–3.51 (2H, m), 3.61–3.71 (3H, m), 4.01 (1H, septet, *J* 6.0 Hz), 4.49–4.65 (5H, m), 4.68 (1H, d, *J* 12.0 Hz), 4.89 (1H, d, *J* 10.8 Hz), 7.14–7.38 (15H, m). Anal. Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.65; H, 7.42.

4.3.11. Methyl 4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (33α). Colorless syrup, R_f 0.28 (8:1 toluene–EtOAc); $[\alpha]_D^{28}$ +63.0 (*c* 1.29, $CHCl_3$); ^1H NMR δ 1.24 (3H, d, *J* 6.0 Hz), 1.25 and 1.44 (each 3H, each s), 1.73 (1H, ddd, *J* 12.4, 11.0, and 3.2 Hz), 2.26 (1H, dd, *J* 12.4 and 4.6 Hz), 3.33 (1H, dd, *J* 10.0 and 6.4 Hz), 3.35 (3H, s), 3.60 (1H, dq, *J* 10.0 and 6.0 Hzz), 3.63 (1H, dd, *J* 10.2 and 1.4 Hz), 3.76 (1H, dd, *J* 9.0 and 9.0 Hz), 3.85 (1H, dd, *J* 10.2 and 1.6 Hz), 3.95 (1H, ddd, *J* 11.0, 9.0, and 4.6 Hz), 3.97–4.07 (3H, m), 4.52 and 4.64 (each 1H, ABq, *J* 12.0 Hz), 4.56 and 4.90 (each 1H, ABq, *J* 10.6 Hz), 5.06 (1H, br d, *J* 3.2 Hz), 7.17–7.39 (15H, m). Anal. Calcd for $C_{37}H_{46}O_9$: C, 70.01; H, 7.30. Found: C, 69.99; H, 7.13.

4.3.12. Methyl 4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (33β). Colorless syrup, R_f 0.44 (8:1 toluene–EtOAc); $[\alpha]_D^{28}$ −34.1 (*c* 1.91, $CHCl_3$); ^1H NMR δ 1.33 (3H, d, *J* 5.2 Hz), 1.33 and 1.46 (each 3H, each s), 1.59 (1H, ddd, *J* 12.0, 11.6, and 10.0 Hz), 2.39 (1H, ddd, *J* 12.0, 4.8, and 1.2 Hz), 3.31–3.41 (1H, m), 3.37 (3H, s), 3.58 (1H, dd, *J* 9.0 and 9.0 Hz), 3.58–3.73 (4H, m), 3.77 (1H, d, *J* 10.6 and 4.0 Hz), 4.08 (1H, d, *J* 5.2 Hz), 4.17 (1H, dd, *J* 7.0 and 5.2 Hz), 4.57 and 4.63 (each 1H, ABq, *J* 10.2 Hz), 4.60 and 4.69 (each 1H, ABq, *J* 11.0 Hz), 4.60 and 4.90 (each 1H, ABq, *J* 10.2 Hz), 4.91 (1H, dd, *J* 10.0 and 1.2 Hz), 7.21–7.38 (15H, m). Anal. Calcd for $C_{37}H_{46}O_9$: C, 70.01; H, 7.30. Found: C, 70.05; H, 7.02.

4.3.13. Methyl 3-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-2,6-dideoxy-α-D-*arabino*-hexopyranoside (34α). Colorless syrup, R_f 0.43 (6:1 toluene–EtOAc); $[\alpha]_D^{28}$ +67.1 (*c* 1.08, $CHCl_3$); ^1H NMR δ 1.27 (3H, d, *J* 5.8 Hz), 1.61 (1H, ddd, *J* 12.8,

11.6, and 3.8 Hz), 1.65 (1H, ddd, *J* 12.8, 11.0, and 4.0 Hz), 2.16 (1H, dd, *J* 12.8 and 4.6 Hz), 2.27 (1H, dd, *J* 12.8 and 4.8 Hz), 3.31 (3H, s), 3.34 (1H, dd, *J* 9.0 and 9.0 Hz), 3.55–3.69 (1H, m), 3.60 (1H, dd, *J* 9.4 and 9.0 Hz), 3.63 (1H, br d, *J* 10.0 Hz), 3.75–3.95 (2H, m), 3.80 (1H, dd, *J* 10.0 and 3.2 Hz), 3.89 (1H, ddd, *J* 11.6, 9.0, and 4.6 Hz), 4.43 (1H, d, *J* 11.2 Hz), 4.49 (1H, d, *J* 12.0 Hz), 4.50 (1H, d, *J* 10.2 Hz), 4.60 (2H, s, $ArCH_2$ and 1H, d, *J* 11.6 Hz), 4.64 (1H, d, *J* 12.0 Hz), 4.73 (1H, br d, *J* 3.8 Hz), 4.86 (1H, d, *J* 12.0 Hz), 5.53 (1H, br d, *J* 4.8 Hz), 7.14–7.37 (20H, m). Anal. Calcd for $C_{41}H_{48}O_8$: C, 73.63; H, 7.23. Found: C, 73.72; H, 7.21.

4.3.14. Methyl 3-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-α-D-*arabino*-hexopyranoside (34β). Colorless syrup, R_f 0.30 (6:1 toluene–EtOAc); $[\alpha]_D^{27}$ +62.1 (*c* 1.51, $CHCl_3$); ^1H NMR δ 1.27 (3H, d, *J* 6.2 Hz), 1.61 (1H, ddd, *J* 13.0, 11.0, and 10.8 Hz), 1.68 (1H, ddd, *J* 12.4, 11.0, and 3.2 Hz), 2.20 (1H, ddd, *J* 13.0, 4.8, and 1.2 Hz), 2.34 (1H, dd, *J* 12.4 and 4.4 Hz), 3.28 (3H, s), 3.23–3.38 (2H, m), 3.54 (1H, dd, *J* 8.6 and 8.6 Hz), 3.61 (1H, ddd, *J* 11.0, 8.6, and 4.4 Hz), 3.63–3.67 (2H, m), 3.70 (1H, dq, *J* 9.2 and 6.2 Hz), 3.87 (1H, ddd, *J* 10.8, 8.0, and 4.8 Hz), 4.47 (1H, d, *J* 11.8 Hz), 4.52 (1H, d, *J* 11.8 Hz), 4.56 (1H, d, *J* 10.4 Hz), 4.59 (1H, d, *J* 11.4 Hz), 4.59 (1H, dd, *J* 11.0 and 1.2 Hz), 4.60 (1H, d, *J* 11.0 Hz), 4.66 (1H, d, *J* 11.0 Hz), 4.71 (1H, br d), 4.77 (1H, d, *J* 11.4 Hz), 4.87 (1H, d, *J* 10.4 Hz), 7.16–7.36 (20H, m). Anal. Calcd for $C_{41}H_{48}O_8$: C, 73.63; H, 7.23. Found: C, 73.27; H, 6.90.

4.3.15. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (26α). White solid, mp 92.0–94.0 °C; R_f 0.37 (4:1 toluene–EtOAc); $[\alpha]_D^{29}$ +58.6 (*c* 0.56, $CHCl_3$); ^1H NMR δ 1.09 (3H, d, *J* 6.0 Hz), 1.77 (1H, ddd, *J* 12.6, 11.0, and 3.2 Hz), 2.35 (1H, dd, *J* 12.6 and 4.8 Hz), 3.37 (3H, s), 3.49–3.64 (3H, m), 3.71–3.91 (3H, m), 3.91 (1H, ddd, *J* 11.0, 9.0, and 4.8 Hz), 4.02 (1H, dd, *J* 9.0 and 9.0 Hz), 4.43 (1H, d, *J* 11.8 Hz), 4.53–4.62 (2H, m), 4.65 (1H, d, *J* 3.2 Hz), 4.71 (1H, d, *J* 11.2 Hz), 4.82 (1H, d, *J* 12.2 Hz), 4.83 (1H, br d, *J* 3.2 Hz), 4.94 (1H, d, *J* 10.2 Hz), 4.99 (1H, dd, *J* 9.2 and 9.0 Hz), 5.00 (1H, d, *J* 11.2 Hz), 5.02 (1H, d, *J* 10.2 Hz), 7.08–7.15 (5H, m), 7.21–7.47 (17H, m), 7.52–7.62 (1H, m), 7.88–7.97 (2H, m). Anal. Calcd for $C_{48}H_{52}O_{10}$: C, 73.08; H, 6.64. Found: C, 73.04; H, 6.67.

4.3.16. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (26β). White solid, mp 154–156 °C; R_f 0.49 (4:1 toluene–EtOAc); $[\alpha]_D^{28}$ −9.0 (*c* 1.07, $CHCl_3$); ^1H NMR δ 1.22 (3H, d, *J* 6.0 Hz), 1.75 (1H, ddd, *J* 12.4, 11.6, and 9.4 Hz), 2.21 (1H, ddd, *J* 12.4, 4.8, and 1.2 Hz), 3.37 (3H, s), 3.41 (1H, dq, *J* 9.4 and 6.0 Hz), 3.48–3.59 (3H, m), 3.59 (1H, ddd, *J* 11.6, 9.2, and 4.8 Hz), 3.77 (1H, ddd, *J* 10.0, 2.2, and 1.2 Hz), 4.00 (1H, dd, *J* 9.0 and 8.8 Hz), 4.06 (1H, dd, *J* 10.0 and 1.2 Hz), 4.25 (1H, dd, *J* 9.4 and 1.2 Hz), 4.44 (1H, d, *J* 12.0 Hz), 4.59 (1H, d, *J* 12.0 Hz), 4.59 (1H, d, *J* 11.2 Hz), 4.61 (1H, d, *J* 3.2 Hz), 4.66 (1H, d, *J* 12.0 Hz), 4.79 (1H, d, *J* 12.0 Hz), 4.81 (1H, d, *J* 10.6 Hz), 4.89 (1H, d, *J* 11.2 Hz), 4.98 (1H, dd, *J* 9.4 and 9.2 Hz), 5.00 (1H, d, *J* 10.6 Hz), 7.11–7.20 (5H, m), 7.22–7.40 (15H, m), 7.41–7.51 (2H, m), 7.55–7.64 (1H, m), 7.97–8.06 (2H, m). Anal. Calcd for $C_{48}H_{52}O_{10}$: C, 73.08; H, 6.64. Found: C, 73.02; H, 6.42.

4.3.17. Cyclohexylmethyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (35α). Colorless syrup, R_f 0.38 (3:1 *n*-hexane–ether); $[\alpha]_D^{28}$ +37.2 (*c* 0.91, $CHCl_3$); ^1H NMR δ 0.85–1.05 (2H, m), 1.10–1.37 (3H, m), 1.20 (3H, d, *J* 6.0 Hz), 1.51–1.87 (6H, m), 1.80 (1H, ddd, *J* 13.0, 11.0, and 3.2 Hz), 2.32 (1H, dd, *J* 13.0 and 4.8 Hz), 3.18 (1H, dd, *J* 9.2 and 6.0 Hz), 3.43 (1H, dd, *J* 9.2 and 6.8 Hz), 3.87 (1H, dq, *J* 9.2 and 6.0 Hz), 3.99 (1H, ddd, *J* 11.0, 9.0, and 4.8 Hz), 4.48 and 4.60 (each 1H, ABq, *J* 11.6 Hz), 4.88 (1H, br d, *J* 3.2 Hz), 5.03 (1H, dd, *J* 9.2 and 9.0 Hz), 7.12–7.18 (5H, m), 7.41–7.50 (2H, m), 7.53–7.63 (1H, m), 8.00–8.09 (2H, m). Anal. Calcd for $C_{27}H_{34}O_5$: C, 73.94; H, 7.81. Found: C, 73.93; H, 7.85.

4.3.18. Cyclohexylmethyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranoside (35β). White solid, mp 64.5–66.5 °C; R_f 0.51 (3:1 *n*-hexane–ether); $[\alpha]_D^{27}$ −71.4 (*c* 0.67, $CHCl_3$); ^1H NMR δ 0.82–1.03 (2H, m), 1.12–1.34 (3H, m), 1.26 (3H, d, *J* 6.0 Hz), 1.50–1.85 (6H, m), 1.76 (1H, ddd, *J* 12.4, 11.6, and 9.6 Hz), 2.38 (1H, ddd, *J* 12.4, 4.8, and 1.6 Hz), 3.22 (1H, dd, *J* 9.2 and 6.8 Hz), 3.49 (1H, dq, *J* 9.2 and 6.0 Hz), 3.68 (1H, ddd, *J* 11.6, 9.0, and 4.8 Hz), 3.71 (1H, dd, *J* 9.2 and 6.2 Hz), 4.46 (1H, dd, *J* 9.6 and 1.6 Hz), 4.46 and 4.62 (each 1H, ABq, *J* 12.0 Hz), 5.02 (1H, dd, *J* 9.2 and 9.0 Hz), 7.12–7.21 (5H, m), 7.41–7.52 (2H, m), 7.54–7.63 (1H, m), 7.97–8.07 (2H, m). Anal. Calcd for $C_{27}H_{34}O_5$: C, 73.94; H, 7.81. Found: C, 73.86; H, 7.82.

4.3.19. *n*-Octyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (36α). Colorless syrup, R_f 0.37 (3:1 *n*-hexane–ether); $[\alpha]_D^{29}$ +32.0 (*c* 1.38, $CHCl_3$); ^1H NMR δ 0.90 (3H, t, *J* 6.2 Hz), 1.21 (3H, d, *J* 6.0 Hz), 1.24–1.42 (10H, m), 1.51–1.67 (2H, m), 1.81 (1H, ddd, *J* 12.6, 11.0, and 3.2 Hz), 2.32 (1H, dd, *J* 12.6 and 4.8 Hz), 3.38 (1H, dt, *J* 9.5 and 6.2 Hz), 3.63 (1H, dt, *J* 9.5 and 6.2 Hz), 3.89 (1H, dq, *J* 9.2 and 6.0 Hz), 4.00 (1H, ddd, *J* 11.0, 9.0, and 4.8 Hz), 4.48 and 4.60 (each 1H, ABq, *J* 12.0 Hz), 4.91 (1H, br d, *J* 3.2 Hz), 5.03 (1H, dd, *J* 9.2 and 9.0 Hz), 7.13–7.18 (5H, m), 7.40–7.50 (2H, m), 7.53–7.63 (1H, m), 8.01–8.09 (2H,

m). Anal. Calcd for $C_{28}H_{38}O_5$: C, 73.98; H, 8.43. Found: C, 74.05; H, 8.44.

4.3.20. *n*-Octyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranoside (36β). Colorless syrup, R_f 0.51 (3:1 *n*-hexane–ether); $[\alpha]_D^{29}$ −64.6 (*c* 1.30, $CHCl_3$); ^1H NMR δ 0.88 (3H, t, *J* 6.2 Hz), 1.20–1.40 (10H, m), 1.26 (3H, d, *J* 6.0 Hz), 1.52–1.68 (2H, m), 1.77 (1H, ddd, *J* 12.4, 12.0, and 9.6 Hz), 2.38 (1H, ddd, *J* 12.4, 4.8, and 1.4 Hz), 3.44 (1H, dt, *J* 9.0 and 6.2 Hz), 3.50 (1H, dq, *J* 9.2 and 6.0 Hz), 3.68 (1H, ddd, *J* 12.0, 9.0, and 4.8 Hz), 3.89 (1H, dt, *J* 9.0 and 6.2 Hz), 4.48 (1H, dd, *J* 9.6 and 1.4 Hz), 4.46 and 4.61 (each 1H, ABq, *J* 12.0 Hz), 5.02 (1H, dd, *J* 9.2 and 9.0 Hz), 7.12–7.21 (5H, m), 7.41–7.51 (2H, m), 7.55–7.64 (1H, m), 7.98–8.07 (2H, m). Anal. Calcd for $C_{28}H_{38}O_5$: C, 73.98; H, 8.43. Found: C, 74.04; H, 8.46.

4.3.21. Cyclohexyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (37α). Colorless syrup, R_f 0.34 (30:1 chloroform–EtOAc); $[\alpha]_D^{29}$ +46.6 (*c* 1.98, $CHCl_3$); ^1H NMR δ 1.14–1.48 (5H, m), 1.20 (3H, d, *J* 6.0 Hz), 1.48–1.63 (1H, m), 1.65–1.96 (5H, m), 2.28 (1H, dd, *J* 12.6 and 4.8 Hz), 3.47–3.63 (1H, m), 3.97 (1H, dq, *J* 9.2 and 6.0 Hz), 4.02 (1H, ddd, *J* 11.0, 9.0, and 4.8 Hz), 4.48 and 4.60 (each 1H, ABq, *J* 12.0 Hz), 5.03 (1H, dd, *J* 9.2 and 9.0 Hz), 5.08 (1H, br d, *J* 3.2 Hz), 7.12–7.18 (5H, m), 7.40–7.50 (2H, m), 7.53–7.62 (1H, m), 8.01–8.09 (2H, m). Anal. Calcd for $C_{26}H_{32}O_5$: C, 73.56; H, 7.60. Found: C, 73.58; H, 7.70.

4.3.22. Cyclohexyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranoside (37β). White solid, mp 74.5–76.0 °C; R_f 0.24 (30:1 chloroform–EtOAc); $[\alpha]_D^{29}$ −77.9 (*c* 1.55, $CHCl_3$); ^1H NMR δ 1.12–1.49 (5H, m), 1.26 (3H, d, *J* 6.0 Hz), 1.49–1.63 (1H, m), 1.66–2.04 (5H, m), 2.34 (1H, ddd, *J* 12.4, 4.8, and 1.6 Hz), 3.50 (1H, dq, *J* 9.2 and 6.0 Hz), 3.60–3.76 (1H, m), 3.68 (1H, ddd, *J* 11.0, 9.0, and 4.8 Hz), 4.45 and 4.62 (each 1H, ABq, *J* 12.0 Hz), 4.63 (1H, dd, *J* 9.6 and 1.6 Hz), 5.03 (1H, dd, *J* 9.2 and 9.0 Hz), 7.13–7.21 (5H, m), 7.42–7.52 (2H, m), 7.54–7.64 (1H, m), 7.99–8.07 (2H, m). Anal. Calcd for $C_{26}H_{32}O_5$: C, 73.56; H, 7.60. Found: C, 73.59; H, 7.61.

4.3.23. Isopropyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (38α). Colorless syrup, R_f 0.29 (30:1 chloroform–EtOAc); $[\alpha]_D^{28}$ +36.7 (*c* 1.20, $CHCl_3$); ^1H NMR δ 1.16 (3H, d, *J* 6.0 Hz), 1.20 (3H, d, *J* 6.0 Hz), 1.22 (3H, d, *J* 6.0 Hz), 1.82 (1H, ddd, *J* 12.6, 11.0, and 3.2 Hz), 2.27 (1H, dd, *J* 12.6 and 4.8 Hz), 3.89 (1H, septet, *J* 6.0 Hz), 3.97 (1H, dq, *J* 9.2 and 6.0 Hz), 4.01 (1H, ddd, *J* 11.0, 9.0, and 4.8 Hz), 4.47 and 4.60 (each 1H, ABq, *J* 12.0 Hz), 5.03 (1H, dd, *J* 9.2 and 9.0 Hz), 5.04 (1H, br d, *J* 3.2 Hz), 7.12–7.18 (5H, m), 7.40–7.50 (2H, m), 7.53–7.63 (1H, m), 8.01–8.10 (2H, m). Anal. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.80; H, 7.38.

4.3.24. Isopropyl 3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranoside (38β). Colorless syrup, R_f 0.19 (30:1 chloroform–EtOAc); $[\alpha]_D^{28}$ −86.1 (*c* 1.51, $CHCl_3$); ^1H NMR δ 1.17 (3H, d, *J* 6.0 Hz), 1.26 (3H, d, *J* 6.0 Hz), 1.26 (3H, d, *J* 6.0 Hz), 1.78 (1H, ddd, *J* 12.2, 11.0, and 9.6 Hz), 2.34 (1H, ddd, *J* 12.2, 5.0, and 1.4 Hz), 3.51 (1H, dq, *J* 9.2 and 6.0 Hz), 3.69 (1H, ddd, *J* 11.0, 9.0, and 5.0 Hz), 4.02 (1H, septet, *J* 6.0 Hz), 4.46 and 4.62 (each 1H, ABq, *J* 12.0 Hz), 4.59 (1H, dd, *J* 9.6 and 1.4 Hz), 5.03 (1H, dd, *J* 9.2 and 9.0 Hz), 7.13–7.21 (5H, m), 7.42–7.52 (2H, m), 7.55–7.63 (1H, m), 7.99–8.05 (2H, m). Anal. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.77; H, 7.35.

4.3.25. Methyl 4-*O*-(3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (39α). Colorless syrup, R_f 0.38 (5:2 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +49.5 (*c* 0.79, $CHCl_3$); ^1H NMR δ 1.20 (3H, d, *J* 6.0 Hz), 1.27 (3H, d, *J* 6.0 Hz), 1.34 and 1.54 (each 3H, each s), 1.82 (1H, ddd, *J* 12.6, 11.0, and 3.4 Hz), 2.31 (1H, ddd, *J* 12.6, 4.8, and 1.0 Hz), 3.38 (3H, s), 3.35–3.43 (1H, m), 3.65 (1H, dq, *J* 9.4 and 6.0 Hz), 3.96 (1H, ddd, *J* 11.0, 9.2, and 4.8 Hz), 4.07–4.13 (2H, m), 4.20 (1H, d, *J* 11.6 Hz), 4.46 (1H, d, *J* 11.6 Hz), 4.59 (1H, d, *J* 11.6 Hz), 4.86 (1H, br s), 5.04 (1H, dd, *J* 3.4 and 1.0 Hz), 5.04 (1H, dd, *J* 9.4 and 9.2 Hz), 7.11–7.20 (5H, m), 7.41–7.52 (2H, m), 7.54–7.63 (1H, m), 8.03–8.12 (2H, m). Anal. Calcd for $C_{30}H_{38}O_9$: C, 66.40; H, 7.06. Found: C, 66.30; H, 7.09.

4.3.26. Methyl 4-*O*-(3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (39β). Colorless syrup, R_f 0.47 (5:2 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ −77.4 (*c* 0.98, $CHCl_3$); ^1H NMR δ 1.24 (3H, d, *J* 6.0 Hz), 1.30 (3H, d, *J* 6.0 Hz), 1.36 and 1.52 (each 3H, each s), 1.67 (1H, ddd, *J* 12.0, 11.8, and 9.4 Hz), 2.42 (1H, ddd, *J* 12.0, 5.0, and 1.6 Hz), 3.37 (3H, s), 3.47 (1H, dq, *J* 9.2 and 6.0 Hz), 3.61 (1H, dq, *J* 9.6 and 5.6 Hz), 3.68 (1H, dd, *J* 9.6 and 6.8 Hz), 3.70 (1H, ddd, *J* 11.8, 9.0, and 5.0 Hz), 4.09 (1H, d, *J* 5.6 Hz), 4.17 (1H, d, *J* 6.8 and 5.6 Hz), 4.45 and 4.61 (each 1H, ABq, *J* 12.0 Hz), 4.86 (1H, br s), 4.95 (1H, dd, *J* 9.6 and 1.6 Hz), 5.02 (1H, dd, *J* 9.2 and 9.0 Hz), 7.12–7.21 (5H, m), 7.41–7.52 (2H, m), 7.54–7.63 (1H, m), 8.03–8.12 (2H, m). Anal. Calcd for $C_{30}H_{38}O_9$: C, 66.40; H, 7.06. Found: C, 66.23; H, 6.91.

4.3.27. Methyl 3-*O*-benzyl-6-*O*-(3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-2,6-dideoxy-α-D-*arabino*-hexopyranoside (40α). Colorless syrup, R_f 0.47 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +37.3 (*c* 2.10, $CHCl_3$); ^1H NMR δ 1.19 (3H, d, *J* 6.0 Hz), 1.32 (3H, d, *J* 6.0 Hz),

1.64 (1H, ddd, *J* 12.6, 11.0, and 3.2 Hz), 1.74 (1H, ddd, *J* 12.6, 11.0, and 3.6 Hz), 2.22 (1H, ddd, *J* 12.6, 4.8, and 1.2 Hz), 2.30 (1H, ddd, *J* 12.6, 4.8, and 1.2 Hz), 3.33 (3H, s), 3.34 (1H, dd, *J* 9.0 and 9.0 Hz), 3.70 (1H, dq, *J* 9.0 and 6.0 Hz), 3.86 (1H, ddd, *J* 9.0, 9.0, and 4.8 Hz), 3.91 (1H, ddd, *J* 9.0, 9.0, and 4.8 Hz), 4.00 (1H, dq, *J* 9.0 and 6.0 Hz), 4.43 and 4.55 (each 1H, ABq, *J* 11.6 Hz), 4.45 and 4.62 (each 1H, ABq, *J* 11.4 Hz), 4.76 (1H, dd, *J* 3.2 and 1.2 Hz), 5.00 (1H, dd, *J* 9.0 and 9.0 Hz), 5.46 (1H, dd, *J* 3.2 and 1.2 Hz), 7.11–7.19 (5H, m), 7.28–7.36 (5H, m), 7.42–7.49 (2H, m), 7.55–7.62 (2H, m), 8.02–8.07 (2H, m). Anal. Calcd for $C_{34}H_{40}O_8$: C, 70.81; H, 6.99. Found: C, 70.68; H, 6.88.

4.3.28. Methyl 3-*O*-benzyl-6-*O*-(3-*O*-benzyl-4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-α-D-*arabino*-hexopyranoside (40β). Colorless syrup, R_f 0.36 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +31.7 (*c* 1.58, $CHCl_3$); ^{1}H NMR δ 1.19 (3H, d, *J* 6.0 Hz), 1.29 (3H, d, *J* 6.0 Hz), 1.69 (1H, ddd, *J* 13.0, 11.0, and 3.2 Hz), 1.74 (1H, ddd, *J* 12.4, 11.4, and 9.6 Hz), 2.24 (1H, ddd, *J* 13.0, 4.8, and 1.2 Hz), 2.39 (1H, ddd, *J* 12.4, 4.8, and 1.6 Hz), 3.31 (3H, s), 3.32 (1H, dd, *J* 9.0 and 8.4 Hz), 3.41 (1H, dq, *J* 9.0 and 6.0 Hz), 3.64 (1H, ddd, *J* 11.4, 8.8, and 4.8 Hz), 3.72 (1H, dq, *J* 9.0 and 6.0 Hz), 3.88 (1H, ddd, *J* 11.0, 8.4, and 4.8 Hz), 4.45 and 4.60 (each 1H, ABq, *J* 12.0 Hz), 4.62 and 4.76 (each 1H, ABq, *J* 11.4 Hz), 4.71–4.75 (1H, m), 4.75 (1H, dd, *J* 9.6 and 1.6 Hz), 5.01 (1H, dd, *J* 9.0 and 8.8 Hz), 7.12–7.21 (5H, m), 7.21–7.40 (5H, m), 7.42–7.50 (2H, m), 7.56–7.63 (2H, m), 7.99–8.04 (2H, m). Anal. Calcd for $C_{34}H_{40}O_8$: C, 70.81; H, 6.99. Found: C, 70.72; H, 6.85.

4.3.29. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4-di-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (25α). White solid, mp 95.5–97.0 °C; R_f 0.46 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{29}$ +59.1 (*c* 1.31, $CHCl_3$); ^{1}H NMR δ 1.17 (3H, d, *J* 6.0 Hz), 1.64 (1H, ddd, *J* 12.8, 11.2, and 3.2 Hz), 2.31 (1H, dd, *J* 12.8 and 3.8 Hz), 3.09 (1H, dd, *J* 9.0 and 8.8 Hz), 3.35 (3H, s), 3.46–3.61 (3H, m), 3.68 (1H, dq, *J* 9.0 and 6.0 Hz), 3.74 (1H, br d, *J* 11.0 Hz), 3.81 (1H, dd, *J* 11.0 and 3.6 Hz), 3.90 (1H, ddd, *J* 11.0, 8.4, and 4.8 Hz), 4.00 (1H, dd, *J* 9.0 and 8.8 Hz), 4.57 (1H, d, *J* 10.4 Hz), 4.59–4.66 (4H, m), 4.68 (1H, d, *J* 11.8 Hz), 4.80 (1H, d, *J* 11.8 Hz), 4.81 (1H, d, *J* 10.2 Hz), 4.87–4.97 (3H, m), 5.00 (1H, d, *J* 10.2 Hz), 7.19–7.41 (25H, m). Anal. Calcd for $C_{48}H_{54}O_9$: C, 74.39; H, 7.02. Found: C, 74.30; H, 6.83.

4.3.30. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4-di-*O*-benzyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (25β). White solid, mp 140.5–142.5 °C; R_f 0.59 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +14.5 (*c* 0.41, $CHCl_3$); ^{1}H NMR δ 1.28 (3H, d, *J* 6.0 Hz), 1.60 (1H, ddd, *J* 12.2, 11.2, and 9.4 Hz), 2.16 (1H, ddd, *J* 12.2, 4.6, and 1.2 Hz), 3.09 (1H, dd, *J* 8.8 and 8.6 Hz), 3.24 (1H, dq, *J* 8.8 and 5.8 Hz), 3.36 (3H, s), 3.47–3.60 (4H, m), 3.68–3.78 (1H, m), 3.99 (1H, dd, *J* 9.0 and 9.0 Hz), 4.03 (1H, dd, *J* 10.0 and 1.4 Hz), 4.15 (1H, dd, *J* 9.4 and 1.2 Hz), 4.57 (1H, d, *J* 11.2 Hz), 4.58 (1H, d, *J* 12.0 Hz), 4.57–4.59 (4H, m), 4.79 (1H, d, *J* 12.0 Hz), 4.81 (1H, d, *J* 10.4 Hz), 4.87 (1H, d, *J* 11.0 Hz), 4.92 (1H, d, *J* 10.8 Hz), 4.99 (1H, d, *J* 10.4 Hz), 7.21–7.39 (25H, m). Anal. Calcd for $C_{48}H_{54}O_9$: C, 74.39; H, 7.02. Found: C, 74.38; H, 6.80.

4.3.31. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(4-*O*-benzyl-3-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (27α). White solid, mp 132.8–135.5 °C; R_f 0.50 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{29}$ +44.0 (*c* 1.50, $CHCl_3$); ^{1}H NMR δ 1.23 (3H, d, *J* 6.0 Hz), 1.80 (1H, ddd, *J* 12.2, 11.0, and 3.2 Hz), 2.46 (1H, dd, *J* 12.2 and 5.0 Hz), 3.33 (1H, dd, *J* 9.0 and 9.0 Hz), 3.38 (3H, s), 3.52–3.67 (3H, m), 3.72–3.80 (3H, m), 4.00 (1H, dd, *J* 9.2 and 9.0 Hz), 4.59 (1H, d, *J* 3.6 Hz), 4.60 (1H, d, *J* 11.0 Hz), 4.64 (1H, d, *J* 11.0 Hz), 4.67 (1H, d, *J* 12.0 Hz), 4.72 (1H, d, *J* 11.0 Hz), 4.80 (1H, d, *J* 12.0 Hz), 4.82 (1H, d, *J* 11.0 Hz), 4.94 (1H, br d, *J* 3.2 Hz), 4.97 (1H, d, *J* 11.0 Hz), 5.00 (1H, d, *J* 11.0 Hz), 5.54 (1H, ddd, *J* 11.0, 9.0, and 5.0 Hz), 7.14–7.40 (20H, m), 7.40–7.49 (2H, m), 7.52–7.61 (1H, m), 7.98–8.07 (2H, m). Anal. Calcd for $C_{48}H_{52}O_{10}$: C, 73.08; H, 6.64. Found: C, 73.00; H, 6.49.

4.3.32. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(4-*O*-benzyl-3-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (27β). White solid, mp 140.5–143 °C; R_f 0.50 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ −4.9 (*c* 0.42, $CHCl_3$); ^{1}H NMR δ 1.34 (3H, d, *J* 5.6 Hz), 1.72 (1H, ddd, *J* 12.0, 11.8, and 9.6 Hz), 2.32 (1H, ddd, *J* 12.0, 5.0, and 1.2 Hz), 3.31 (1H, dd, *J* 9.0 and 8.4 Hz), 3.35 (3H, s), 3.39 (1H, dq, *J* 9.0 and 5.6 Hz), 3.45–3.60 (3H, m), 3.68–3.77 (1H, m), 3.98 (1H, dd, *J* 9.2 and 8.8 Hz), 4.03 (1H, dd, *J* 12.4 and 1.4 Hz), 4.28 (1H, dd, *J* 9.6 and 1.2 Hz), 4.57 (1H, d, *J* 11.0 Hz), 4.58 (1H, d, *J* 3.0 Hz), 4.59 (1H, d, *J* 10.6 Hz), 4.64 (1H, d, *J* 11.6 Hz), 4.70 (1H, d, *J* 10.6 Hz), 4.78 (1H, d, *J* 11.6 Hz), 4.81 (1H, d, *J* 11.0 Hz), 4.87 (1H, d, *J* 11.0 Hz), 4.99 (1H, d, *J* 11.0 Hz), 5.19 (1H, ddd, *J* 11.8, 8.2, and 5.0 Hz), 7.14–7.40 (20H, m), 7.53–7.62 (1H, m), 7.98–8.06 (2H, m). Anal. Calcd for $C_{48}H_{52}O_{10}$: C, 73.08; H, 6.64. Found: C, 72.92; H, 6.49.

4.3.33. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (28α). Colorless syrup, R_f 0.47 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ +42.8 (*c* 0.78, $CHCl_3$); ^{1}H NMR δ 1.16 (3H, d, *J* 6.0 Hz), 1.93 (1H, ddd, *J* 12.4, 11.0, and 3.2 Hz), 2.53 (1H, dd, *J* 12.4 and 4.8 Hz), 3.42 (3H, s), 3.61 (1H, dq, *J* 9.0 and 6.0 Hz), 3.56–3.70 (2H, m), 3.77–3.86 (1H, m), 3.91 (1H, dd, *J* 11.0 and 3.8 Hz),

4.02 (1H, dd, *J* 9.0 and 3.2 Hz), 4.03 (1H, dd, *J* 9.0 and 9.0 Hz), 4.63 (1H, d, *J* 3.2 Hz), 4.69 and 4.82 (each 1H, ABq, *J* 12.0 Hz), 4.83 and 5.02 (each 1H, ABq, *J* 10.4 Hz), 4.72 and 5.05 (each 1H, ABq, *J* 11.0 Hz), 5.03 (1H, br d,, *J* 3.2 Hz), 5.18 (1H, dd, *J* 9.2 and 9.0 Hz), 5.61 (1H, ddd, *J* 11.0, 9.2, and 4.8 Hz), 7.21–7.43 (19H, m), 7.43–7.53 (2H, m), 7.85–7.96 (4H, m). Anal. Calcd for $C_{48}H_{50}O_{11}$: C, 71.80; H, 6.28. Found: C, 71.72; H, 6.34.

4.3.34. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4-di-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-α-D-glucopyranoside (28β). White solid, mp 126.5–128 °C; R_f 0.47 (2:1 *n*-hexane–EtOAc); $[\alpha]_D^{28}$ −24.2 (*c* 0.97, $CHCl_3$); ^1H NMR δ 1.28 (3H, d, *J* 6.0 Hz), 1.88 (1H, ddd, *J* 12.0, 11.0, and 9.4 Hz), 2.40 (1H, dd, *J* 12.0, 4.4 Hz), 3.37 (3H, s), 3.48–3.68 (4H, m), 3.72–3.82 (1H, m), 4.00 (1H, dd, *J* 9.0 and 8.8 Hz), 4.08 (1H, br d, *J* 10.6 Hz), 4.41 (1H, br d, *J* 9.4 Hz), 4.62 (1H, d, *J* 3.2 Hz), 4.60 and 4.90 (each 1H, ABq, *J* 11.2 Hz), 4.65 and 4.79 (each 1H, ABq, *J* 12.0 Hz), 4.83 and 5.00 (each 1H, ABq, *J* 10.8 Hz), 5.17 (1H, dd, *J* 9.2 and 9.2 Hz), 5.28 (1H, ddd, *J* 11.0, 9.2, and 4.4 Hz), 7.23–7.45 (19H, m), 7.45–7.56 (2H, m), 7.88–7.99 (4H, m). Anal. Calcd for $C_{48}H_{50}O_{11}$: C, 71.80; H, 6.28. Found: C, 71.67; H, 5.96.

4.4. Glycosidation protocol for the preparation of the β-mannopyranosides

To a stirred solution of 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl diethyl phosphite (**7**) (α/β = >99/1, 0.1 mmol) and an alcohol (0.2 mmol) in dry CH_2Cl_2 (1 mL) was added montmorillonite K-10 (200 wt % to the glycosyl donor **7**). After stirring for 1 h at −10 °C, the mixture was filtered and the filtrate was concentrated in *vacuo*. Purification of the residue by flash column chromatography gave the mannopyranosides in which β-anomers are major components.

4.4.1. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-α-D-glucopyranoside (41α). White solid, mp 93.7–95.0 °C; R_f 0.22 (6:1 toluene–EtOAc); $[\alpha]_D^{27}$ +54.2 (*c* 0.94, $CHCl_3$); ^1H NMR δ 3.28 (3H, s), 3.34 (1H, dd, *J* 9.0 and 9.0 Hz), 3.44 (1H, dd, *J* 9.0 and 3.2 Hz), 3.59 (1H, dd, *J* 11.0 and 1.2 Hz), 3.67 (1H, ddd, *J* 9.0, 4.4, and 1.2 Hz), 3.72–3.85 (3H, m), 3.76 (1H, dd, *J* 11.0 and 4.4 Hz), 3.89 (1H, dd, *J* 9.4 and 2.6 Hz), 3.97 (1H, dd, *J* 9.0 and 9.0 Hz), 4.12–4.29 (1H, m), 4.23 (1H, dd, *J* 9.4 and 9.0 Hz), 4.48 (1H, d, *J* 10.2 Hz), 4.55 (1H, d, *J* 3.2 Hz), 4.65 (1H, d, *J* 12.0 Hz), 4.67 (1H, d, *J* 11.8 Hz), 4.69 (1H, d, *J* 12.8 Hz), 4.74–4.83 (4H, m), 4.85 (1H, d, *J* 1.2 Hz), 4.86 (1H, d, *J* 12.8 Hz), 4.99 (1H, d, *J* 10.2 Hz), 5.62 (1H, s), 7.18–7.40 (28H, m), 7.44–7.50 (2H, m). Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found: C, 73.75; H, 6.39.

4.4.2. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-α-D-glucopyranoside (41β). White solid, mp 158.5–160 °C; R_f 0.42 (6:1 toluene–EtOAc); $[\alpha]_D^{27}$ −5.8 (*c* 0.94, $CHCl_3$); ^1H NMR δ 3.22 (1H, ddd, *J* 10.0, 9.2, and 4.6 Hz), 3.33 (3H, s), 3.39–3.54 (4H, m), 3.69 (1H, d, *J* 2.6 Hz), 3.75 (1H, ddd, *J* 9.6, 4.6, and 1.6 Hz), 3.90 (1H, dd, *J* 10.0 and 10.0 Hz), 4.01 (1H, dd, *J* 9.0 and 9.0 Hz), 4.08 (1H, br s), 4.08 (1H, dd, *J* 10.0 and 1.6 Hz), 4.18 (1H, dd, *J* 9.2 and 9.2 Hz), 4.25 (1H, dd, *J* 10.0 and 4.6 Hz), 4.50 (1H, d, *J* 11.2 Hz), 4.58 (1H, d, *J* 3.2 Hz), 4.60 (1H, d, *J* 12.0 Hz), 4.67 (1H, d, *J* 12.0 Hz), 4.71 (1H, d, *J* 12.0 Hz), 4.75–4.87 (4H, m), 4.92 (1H, d, *J* 12.0 Hz), 5.03 (1H, d, *J* 10.8 Hz), 5.59 (1H, s), 7.12–7.44 (28H, m), 7.45–7.53 (2H, m). Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found: C, 73.75; H, 6.39.

4.4.3. Cyclohexylmethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (44α). Colorless syrup, R_f 0.44 (20:1 toluene–EtOAc); $[\alpha]_D^{28}$ +48.3 (*c* 0.94, $CHCl_3$); ^1H NMR δ 0.80–0.98 (2H, m), 1.04–1.32 (3H, m), 1.42–1.78 (6H, m), 3.14 (1H, dd, *J* 9.0 and 6.0 Hz), 3.43 (1H, dd, *J* 9.0 and 6.4 Hz), 3.77 (1H, ddd, *J* 9.6, 9.4, and 4.2 Hz), 3.81 (1H, dd, *J* 3.0 and 1.2 Hz), 3.88 (1H, dd, *J* 10.0 and 9.6 Hz), 3.96 (1H, dd, *J* 9.4 and 3.0 Hz), 4.24 (1H, dd, *J* 9.4 and 9.4 Hz), 4.25 (1H, dd, *J* 10.0 and 4.2 Hz), 4.67 and 4.86 (each 1H, ABq, *J* 11.6 Hz), 4.73 and 4.83 (each 1H, ABq, *J* 12.0 Hz), 4.74 (1H, d, *J* 1.2 Hz), 5.65 (1H, s), 7.23–7.43 (13H, m), 7.47–7.55 (2H, m). Anal. Calcd for $C_{34}H_{40}O_6$: C, 74.97; H, 7.40. Found: C, 74.95; H, 7.03.

4.4.4. Cyclohexylmethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (44β). Colorless syrup, R_f 0.40 (20:1 toluene–EtOAc); $[\alpha]_D^{28}$ −66.4 (*c* 0.94, $CHCl_3$); ^1H NMR δ 0.88–1.06 (2H, m), 1.08–1.36 (3H, m), 1.50–1.83 (6H, m), 3.21 (1H, dd, *J* 9.0 and 6.4 Hz), 3.31 (1H, ddd, *J* 9.6, 9.2, and 4.6 Hz), 3.57 (1H, dd, *J* 9.4 and 2.8 Hz), 3.78 (1H, dd, *J* 9.0 and 6.0 Hz), 3.93 (1H, d, *J* 2.8 Hz), 3.95 (1H, dd, *J* 10.0 and 9.6 Hz), 4.22 (1H, dd, *J* 9.4 and 9.2 Hz), 4.31 (1H, dd, *J* 10.0 and 4.6 Hz), 4.42 (1H, br s), 4.58 and 4.68 (each 1H, ABq, *J* 12.2 Hz), 4.88 and 5.00 (each 1H, ABq, *J* 12.0 Hz), 5.61 (1H, s), 7.23–7.42 (11H, m), 7.44–7.54 (4H, m). Anal. Calcd for $C_{34}H_{40}O_6$: C, 74.97; H, 7.40. Found: C, 74.91; H, 7.24.

4.4.5. *n*-Octyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (45α). Colorless syrup, R_f 0.46 (20:1 toluene–EtOAc); $[\alpha]_D^{28}$ +116 (*c* 0.94, $CHCl_3$); ^1H NMR δ 0.89 (1H, t, *J* 6.4 Hz), 1.22–1.35 (10H, m), 1.47–1.60 (2H, m), 3.34 (1H, dd, *J* 9.2 and 6.4 Hz), 3.62 (1H, dd, *J* 9.2 and 6.4 Hz), 3.79 (1H, ddd, *J* 10.2, 9.4, and 4.2 Hz), 3.82 (1H, dd, *J* 3.0 and 1.2 Hz), 3.88 (1H, dd, *J* 10.2 and 9.4 Hz), 3.97 (1H, dd, *J* 9.6 and 3.0 Hz), 4.24 (1H, dd, *J* 9.4 and 9.6 Hz), 4.25 (1H, dd, *J* 9.4

and 4.2 Hz), 4.66 and 4.84 (each 1H, ABq, *J* 11.6 Hz), 4.73 and 4.83 (each 1H, ABq, *J* 12.0 Hz), 4.77 (1H, d, *J* 1.2 Hz), 5.65 (1H, s), 7.23–7.43 (13H, m), 7.48–7.55 (2H, m). Anal. Calcd for $C_{35}H_{44}O_6$: C, 74.97; H, 7.91. Found: C, 74.92; H, 7.62.

4.4.6. *n*-Octyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (45β). White solid, mp 43.0–44.5 °C; R_f 0.42 (20:1 toluene–EtOAc); $[\alpha]_D^{27}$ −70.5 (*c* 0.84, $CHCl_3$), ^{1}H NMR δ 0.89 (1H, t, *J* 6.4 Hz), 1.24–1.43 (10H, m), 1.57–1.69 (2H, m), 3.32 (1H, ddd, *J* 9.6, 9.2, and 4.6 Hz), 3.42 (1H, dd, *J* 9.0 and 6.4 Hz), 3.58 (1H, dd, *J* 9.4 and 2.8 Hz), 3.72 (1H, d, *J* 2.8 Hz), 3.94 (1H, dd, *J* 9.0 and 6.0 Hz), 3.94 (1H, dd, *J* 10.0 and 9.6 Hz), 4.21 (1H, dd, *J* 9.4 and 9.2 Hz), 4.31 (1H, dd, *J* 10.0 and 4.6 Hz), 4.94 (1H, br s), 4.58 and 4.68 (each 1H, ABq, *J* 12.2 Hz), 4.88 and 5.00 (each 1H, ABq, *J* 12.0 Hz), 5.62 (1H, s), 7.24–7.42 (11H, m), 7.44–7.54 (4H, m). Anal. Calcd for $C_{35}H_{44}O_6$: C, 74.97; H, 7.91. Found: C, 74.94; H, 7.63.

4.4.7. Cyclohexyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (46α). Colorless syrup, R_f 0.42 (20:1 toluene–EtOAc); $[\alpha]_D^{28}$ +54.6 (*c* 1.88, $CHCl_3$); ^{1}H NMR δ 1.09–1.43 (5H, m), 1.43–1.60 (1H, m), 1.60–1.87 (2H, m), 3.47–3.58 (1H, m), 3.78 (1H, dd, *J* 2.8 and 1.2 Hz), 3.81–3.93 (2H, m), 4.00 (1H, dd, *J* 9.6 and 2.8 Hz), 4.18–4.32 (2H, m), 4.67 and 4.86 (each 1H, ABq, *J* 11.8 Hz), 4.71 and 4.84 (each 1H, ABq, *J* 12.4 Hz), 4.90 (1H, d, *J* 1.2 Hz), 5.65 (1H, s), 7.23–7.43 (13H, m), 7.48–7.55 (2H, m). Anal. Calcd for $C_{33}H_{38}O_6$: C, 74.69; H, 7.22. Found: C, 74.57; H, 6.95.

4.4.8. Cyclohexyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (46β). Colorless syrup, R_f 0.35 (20:1 toluene–EtOAc); $[\alpha]_D^{28}$ −70.6 (*c* 0.41, $CHCl_3$); ^{1}H NMR δ 1.20–1.42 (4H, m), 1.43–1.59 (2H, m), 1.63–1.86 (3H, m), 1.86–1.98 (1H, m), 3.31 (1H, ddd, *J* 9.6, 9.0, and 4.6 Hz), 3.58 (1H, dd, *J* 9.4 and 2.8 Hz), 3.65–3.75 (1H, m), 3.87 (1H, d, *J* 2.8 Hz), 3.94 (1H, dd, *J* 10.0 and 9.6 Hz), 4.22 (1H, dd, *J* 9.4 and 9.0 Hz), 4.30 (1H, dd, *J* 10.0 and 4.6 Hz), 4.59 and 4.67 (each 1H, ABq, *J* 12.4 Hz), 4.60 (1H, br s), 4.91 and 5.02 (each 1H, ABq, *J* 12.2 Hz), 5.62 (1H, s), 7.22–7.42 (11H, m), 7.45–7.54 (4H, m). Anal. Calcd for $C_{33}H_{38}O_6$: C, 74.69; H, 7.22. Found: C, 74.39; H, 7.28.

4.4.9. Isopropyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (47α). Colorless syrup, R_f 0.38 (20:1 toluene–EtOAc); $[\alpha]_D^{28}$ +47.5 (*c* 1.33, $CHCl_3$); ^{1}H NMR δ 1.05 (3H, d, *J* 5.6 Hz), 1.17 (3H, d, *J* 6.0 Hz), 3.79 (1H, dd, *J* 2.8 and 1.2 Hz), 3.80–3.92 (3H, m), 3.98 (1H, dd, *J* 9.6 and 2.8 Hz), 4.17–4.29 (2H, m), 4.67 and 4.85 (each 1H, ABq, *J* 12.0 Hz), 4.72 and 4.85 (each 1H, ABq, *J* 12.0 Hz), 4.86 (1H, d, *J* 1.2 Hz), 5.65 (1H, s), 7.23–7.43 (13H, m), 7.47–7.55 (2H, m). Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.73; H, 6.94.

4.4.10. Isopropyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (47β). Colorless syrup, R_f 0.30 (20:1 toluene–EtOAc); $[\alpha]_D^{28}$ −76.1 (*c* 0.45, $CHCl_3$); ^{1}H NMR δ 1.16 (3H, d, *J* 5.6 Hz), 1.28 (3H, d, *J* 6.0 Hz), 3.32 (1H, ddd, *J* 9.6, 9.2, and 4.6 Hz), 3.58 (1H, dd, *J* 9.4 and 2.8 Hz), 3.86 (1H, d, *J* 2.8 Hz), 3.94 (1H, dd, *J* 10.0 and 9.6 Hz), 3.98 (1H, septet, *J* 6.0 Hz), 4.21 (1H, dd, *J* 9.4 and 9.2 Hz), 4.39 (1H, dd, *J* 10.0 and 4.6 Hz), 4.54 (1H, br s), 4.58 and 4.67 (each 1H, ABq, *J* 12.4 Hz), 4.89 and 5.00 (each 1H, ABq, *J* 12.2 Hz), 5.62 (1H, s), 7.22–7.42 (11H, m), 7.45–7.54 (4H, m). Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.16; H, 6.73.

4.4.11. Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (48α). White solid, mp 131.0–133.0 °C; R_f 0.48 (3:1 *n*-hexane–EtOAc); $[\alpha]_D^{27}$ +62.8 (*c* 0.71, $CHCl_3$), ^{1}H NMR δ 0.96 (3H, d, *J* 6.2 Hz), 1.31 and 1.49 (each 3H, each s), 3.25 (1H, dd, *J* 10.0 and 7.0 Hz), 3.33 (3H, s), 3.51 (1H, dq, *J* 10.0 and 6.2 Hz), 3.78 (1H, d, *J* 3.0 Hz), 3.84 (1H, dd, *J* 10.0 and 9.8 Hz), 3.92 (1H, dd, *J* 9.4 and 3.0 Hz), 3.97–4.12 (1H, m), 4.00 (1H, dd, *J* 7.0 and 5.4 Hz), 4.06 (1H, d, *J* 5.4 Hz), 4.24 (1H, dd, *J* 9.8 and 5.0 Hz), 4.25 (1H, dd, *J* 9.4 and 9.0 Hz), 4.67 and 4.87 (each 1H, ABq, *J* 12.0 Hz), 4.70 and 4.85 (each 1H, ABq, *J* 12.4 Hz), 4.75 (1H, br s), 4.81 (1H, br s), 5.65 (1H, s), 7.24–7.43 (13H, m), 7.49–7.57 (2H, m). Anal. Calcd for $C_{37}H_{44}O_{10}$: C, 68.50; H, 6.84. Found: C, 68.18; H, 6.62.

4.4.12. Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (48β). Colorless syrup, R_f 0.48 (3:1 *n*-hexane–EtOAc); $[\alpha]_D^{27}$ −84.8 (*c* 0.65, $CHCl_3$); ^{1}H NMR δ 1.33 (3H, d, *J* 5.0 Hz), 1.32 and 1.49 (each 3H, each s), 3.32 (1H, ddd, *J* 9.6, 9.2, and 4.6 Hz), 3.39 (3H, s), 3.57–3.73 (2H, m), 3.63 (1H, dd, *J* 9.6 and 2.8 Hz), 3.95 (1H, dd, *J* 10.2 and 9.6 Hz), 3.96 (1H, d, *J* 2.8 Hz), 4.28 (1H, d, *J* 5.2 Hz), 4.32 (1H, dd, *J* 6.0 and 5.2 Hz), 4.39 (1H, dd, *J* 9.6 and 9.2 Hz), 3.97–4.12 (1H, m), 4.00 (1H, dd, *J* 7.0 and 5.4 Hz), 4.06 (1H, d, *J* 5.4 Hz), 4.24 (1H, dd, *J* 9.8 and 5.0 Hz), 4.25 (1H, dd, *J* 9.4 and 9.0 Hz), 4.27 (1H, dd, *J* 10.2 and 4.6 Hz), 4.60 and 4.68 (each 1H, ABq, *J* 12.0 Hz), 4.80 and 4.92 (each 1H, ABq, *J* 11.8 Hz), 4.86 (1H, br s), 4.99 (1H, br s), 5.62 (1H, s), 7.22–7.55 (15H, m). Anal. Calcd for $C_{37}H_{44}O_{10}$: C, 68.50; H, 6.84. Found: C, 68.59; H, 6.86.

4.4.13. Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-α-D-glucopyranoside (49α). Colorless syrup, R_f 0.27 (8:1 toluene–EtOAc); $[\alpha]_D^{28}$ +13.3 (*c* 1.15, $CHCl_3$); ^{1}H NMR δ 3.39

(3H, s), 3.55 (1H, dd, *J* 8.4 and 3.0 Hz), 3.44 (1H, dd, *J* 9.0 and 3.2 Hz), 3.59 (1H, dd, *J* 11.0 and 1.2 Hz), 3.67–3.89 (6H, m), 3.78 (1H, dd, *J* 2.8 and 1.2 Hz), 3.83 (1H, dd, *J* 8.4 and 8.4 Hz), 3.92 (1H, dd, *J* 9.2 and 2.8 Hz), 4.06–4.13 (1H, m), 4.20 (1H, d, *J* 11.2 Hz), 4.22 (1H, dd, *J* 9.2 and 8.8 Hz), 4.31 (1H, d, *J* 11.2 Hz), 4.34–4.64 (5H, m), 4.42 (1H, d, *J* 11.2 Hz), 4.68 (1H, d, *J* 11.6 Hz), 4.80 (1H, d, *J* 12.0 Hz), 5.09 (1H, d, *J* 11.2 Hz), 5.30 (1H, d, *J* 1.2 Hz), 5.60 (1H, s), 7.10–7.17 (2H, m), 7.17–7.41 (26H, m), 7.45–7.53 (2H, m). Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found: C, 73.73; H, 6.33.

4.4.14. Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-α-D-glucopyranoside (49β). Colorless syrup, R_f 0.43 (8:1 toluene–EtOAc); $[\alpha]_D^{28}$ −26.4 (*c* 1.50, $CHCl_3$); ^1H NMR δ 3.04 (1H, ddd, *J* 9.2, 9.0, and 4.6 Hz), 3.32 (1H, dd, *J* 9.2 and 2.6 Hz), 3.40 (3H, s), 3.42–3.66 (4H, m), 3.45 (1H, dd, *J* 10.0 and 2.6 Hz), 3.63 (1H, d, *J* 2.6 Hz), 3.81–3.93 (2H, m), 3.75 (1H, ddd, *J* 9.6, 4.6, and 1.6 Hz), 4.04 (1H, dd, *J* 10.0 and 4.6 Hz), 4.07 (1H, dd, *J* 9.2 and 9.0 Hz), 4.28 (1H, d, *J* 11.6 Hz), 4.37 (1H, br s), 4.54–4.67 (4H, m), 4.70–4.86 (5H, m) 5.05 (1H, d, *J* 10.4 Hz), 5.51 (1H, s), 7.15–7.42 (28H, m), 7.44–7.51 (2H, m). Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found: C, 73.76; H, 6.44.

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