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Synthesis of 5a,5a′-dicarba-D-glucobioses from conformationally restricted carbaglucosyl triflates using S_N2-type inversion with carbaglucosyl nucleophiles

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ABSTRACT

Novel carbohydrate mimics were designed which contain two 5a-carba-D-glucose residues, one each at reducing and nonreducing end, and thus these mimics are 5a,5a′-dicarba-D-glucobioses. Dicarbadisaccharides have attractive features such as stability against endogenous degradative enzymes and being resistant to glycation reactions such as the Maillard reaction. For the synthesis of dicarba-β-D-isomaltose derivatives, the carbaglucosyl triflate locked in $^4C_1$ conformation was synthesized by protecting with butane-2,3-diacetal group or benzylidene group. Then, 5a,5a′-dicarba-β-D-maltose and 5a,5a′-dicarba-α,β-D-trehalose were synthesized by the S_N2-type inversion reaction using 4,6-*O*-benzylidene carbaglucosyl triflate with 4-OH and 1-OH carba-β-D-glucose derivatives, respectively, and similarly 5a,5a′-dicarba-α-D-isomaltose with 6-OH carba-α-D-glucose derivative.

1. Introduction

Carbohydrates play important roles as glycoconjugates in a variety of biological processes such as cell-cell recognition, fertilization, cell growth, viral and bacterial infection, and tumor cell metastasis.[1–4] Glycoconjugates are poly- or oligosaccharides linked to proteins, lipids, and other molecules. Oligosaccharides and their analogues are potential therapeutic agents[5–10] because they can act as regulators of biological processes.

Much research has focused on developing carbohydrate mimics such as azasugars, thiosugars, carbasugars, and phosphasugars, where the ring oxygen has been replaced by nitrogen, sulfur, carbon, and phosphorus, respectively. In particular, azasugars have been reported to be potent inhibitors of several glycosidases.[11,12] Also, nucleotide analogues containing thiosugar or carbasugar have been reported to be glycosyltransferase inhibitors.[13–16] Carbasugars with a cyclohexane ring are expected to be the most stable of carbohydrate mimics towards endogenous degradative enzymes. In addition, carbasugars do not undergo glycation *in vivo*. For example, carbasugars do not undergo the Maillard reaction[17] due to the absence of an acetal moiety. Carbasugars are useful as carbohydrate mimics in glycobiology because they are recognized by the corresponding enzymes or lectins.[18–20]

A number of synthetic strategies for carbasugars have been reported[21] since the first synthesis of 5a-carba-α-DL-talopyranose by McCasland.[22] For example, Ogawa and co-workers reported the synthesis of various carbasugars using an optically active Diels-Alder adduct.[23] In addition, Yu and Chung synthesized the entire D-series of 16 carbasugar stereoisomers by systematically altering the hydroxyl stereochemistry of a carba-β-D-altropyranose derivative.[24] However, carbasugar synthesis on the preparative scale remains challenging due to the multiple steps required.

The synthesis of disaccharide mimics with a carbasugar at the nonreducing or reducing end has recently been reported.[25] The 5a-carbadisaccharides should be stable against glycation *in vivo*. The 5a-carbadisaccharides are easily synthesized in excellent yield using either conventional glycosylation or enzyme-catalyzed glycosylation[26,27] but are easily hydrolyzed chemically or enzymatically. On the other hand, carbadisaccharides with a carbasugar at the nonreducing end (5a′-carbadisaccharides) are resistant against enzymatic cleavage by glycosidases. 5a′-Carbadisaccharides have been synthesized by two approaches: (i) S_N2-type inversion between 5a-carbasugar C-1 alcohols and carbohydrate triflates, and (ii) epoxide opening under basic conditions. However, these synthetic methods afforded the 5a′-carbadisaccharides in poor yield, except for the S_N2-type inversion using the C-4 triflate of the 1,6-anhydrogalactose derivative[28] or the epoxide opening of 1,2-anhydro-5a-carbasugar derivatives.[29,30] There are therefore no general methods available for the preparation of 5a′-carbadisaccharides.

The purpose of the present study was to establish the process to synthesize 5a,5a′-dicarba-D-glucobioses (**1–4**) containing a 5a-carba-D-

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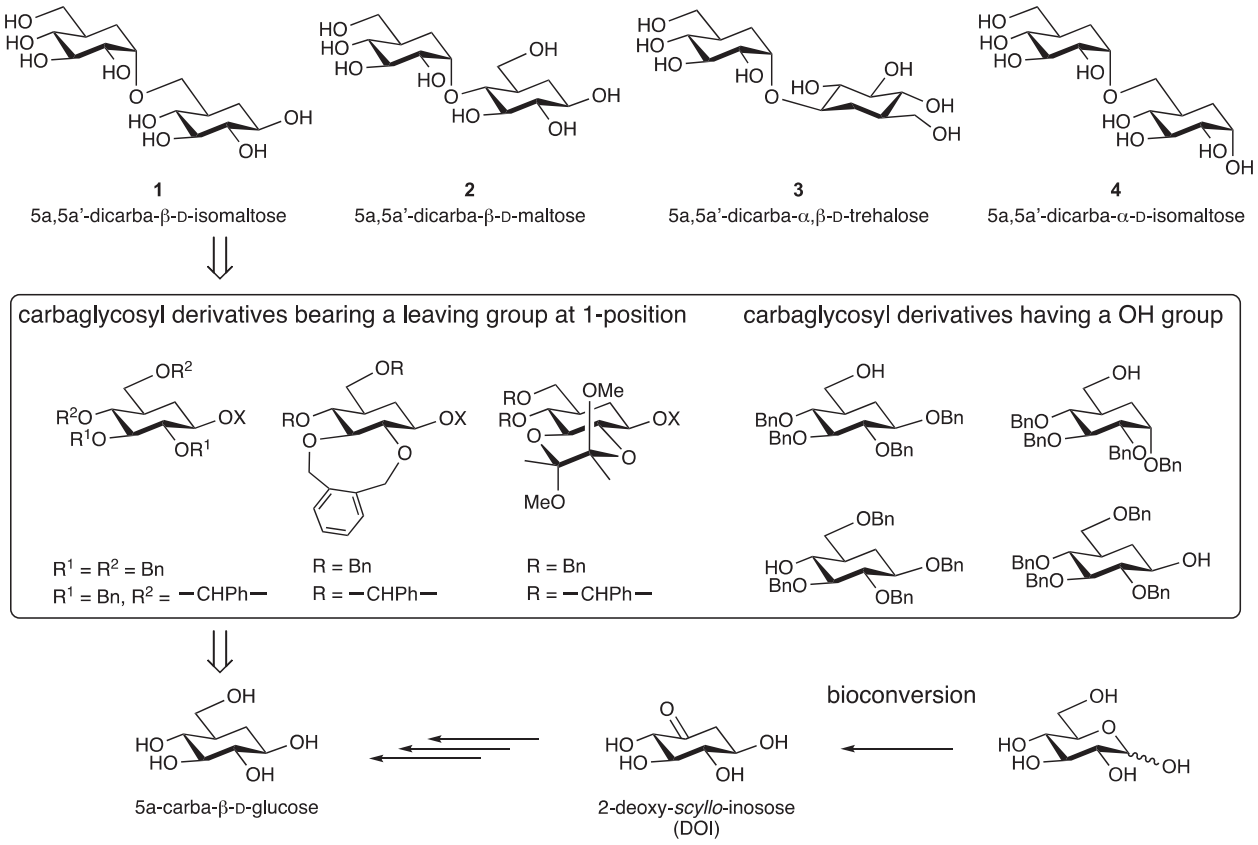


Scheme 1. Retrosynthetic analysis of four kinds of 5a,5a′-dicarba-D-glucobioses.

glucose residue linked at both the reducing and the nonreducing end (Scheme 1). As a starting material, 2-deoxy-*scyllo*-inosose (DOI) was prepared from the culture medium of metabolically engineered *Escherichia coli*.[31] Then the obtained DOI was changed to 5a-carba-β-D-glucose according to the literature[32] in large scale. A benzyl protected or conformationally restricted 5a-carba-β-D-glucose derivative bearing a leaving group at the 1-position and carbaglucosyl derivatives having an OH group are provided from the 5a-carba-β-D-glucose. The optimum conditions for the synthesis of 5a,5a′-dicarba-D-glucobioses of various linkage by the S_N2-type inversion were examined using the upper carbaglucosyl derivatives. Thus, obtained 5a,5a′-dicarba-D-glucobioses are expected to be used as the new sources in the medicinal screening.

2. Results and discussion

2.1. Synthesis of dicarba-β-D-isomaltose derivative via S_N2-type inversion reaction by use of carbaglucosyl sulfonates.

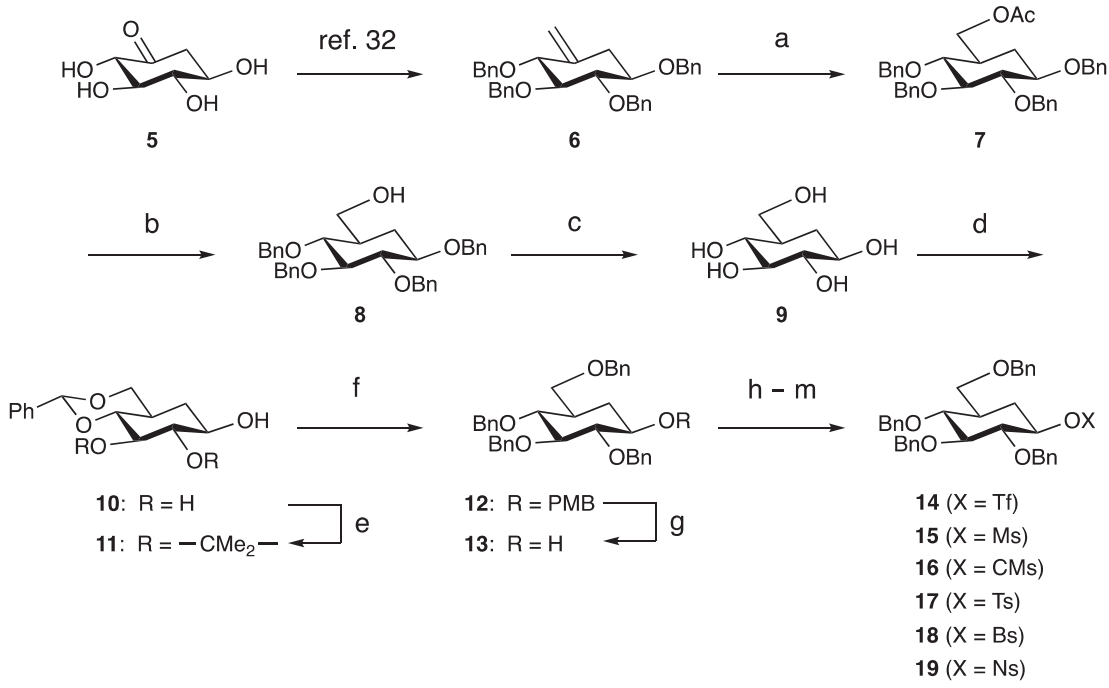
*2.1.1. Synthesis of the reducing-end moiety **8** and 5a-carba-β-D-glucose derivatives having various leaving groups at the 1-position **14–19***

The carbaglucosyl derivatives bearing a leaving group at the 1-position were synthesized by preparing 5a-carba-β-D-glucose from 2-deoxy-*scyllo*-inosose (DOI), which in turn was derived from D-glucose through bioconversion (Scheme 2). We established a facile purification method for DOI from the culture solution. Culture solution containing DOI was filtered through a membrane filter to provide the cell-free solution. DOI is unstable under basic conditions and thus the filtrate was desalted using strong cation–exchange column chromatography (H^+ form) and weak anion–exchange column chromatography (AcO^- form). DOI was isolated by crystallization from methanol and ethanol in 67% yield based on the amount of D-glucose used in the fermentation.

DOI was converted to 5a-carba-β-D-glucose **9** using the methods described by Kakinuma and co-workers,[32] with modifications. Wittig reaction on the 6-oxo moiety afforded the *exo* methylene derivative **6** in 72% yield in three steps. Hydroboration of the exocyclic olefin **6** with 9-BBN under reflux in THF gave a mixture of two diastereomeric alcohols (*gluco*:*ido* = 2.7:1). After acetylation of the diastereomeric mixture, the desired carba-β-D-glucose derivative **7** was isolated by recrystallization from diisopropyl ether in 60% yield. Additionally, the two isomers in the filtrate were separated by silica gel column chromatography to provide a 6% yield of carba-β-D-glucose derivative **7** and a 20% yield of carba-α-L-idose. Saponification of the acetyl group to provide compound **8** and subsequent removal of the benzyl groups provided the 5a-carba-β-D-glucose **9** as a key synthetic intermediate. 5a-Carba-β-D-glucose **9** was converted to compound **11** via compound **10** by the reported method.[33] The hydroxyl group of compound **11** was protected as a *p*-methoxybenzyl group, then the acetal groups were removed using 60% aqueous acetic acid. Subsequent benzylation provided compound **12** in 78% yield from compound **11**. The *p*-methoxybenzyl group of **12** was oxidatively removed using CAN in a solution of aqueous acetonitrile to give compound **13** in 82% yield. Treatment of compound **13** with trifluoromethanesulfonic anhydride (Tf_2O) and utilization of the less nucleophilic base di-*tert*-butyl-4-methylpyridine (DTBMP) led to the desired carbaglucosyl triflate **14** in 92% yield. Compound **13** was converted to mesylate **15** and chloromesylate **16** in 94% and 87% yield by treatment with methanesulfonyl chloride and chloromethanesulfonyl chloride, respectively. Compound **13** was reacted with *p*-toluenesulfonyl chloride at 50 °C to give tosylate **17** in 96% yield. Brosylate **18** and nosylate **19** were obtained in 87% and 88% yield, respectively, at this raised temperature.

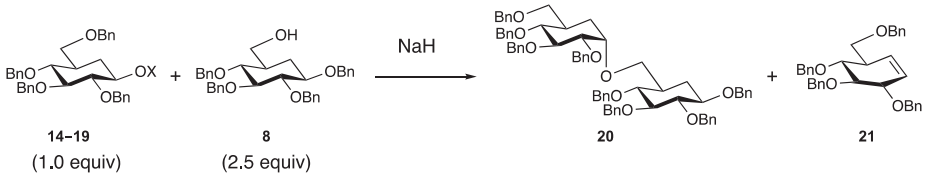
*2.1.2. Optimization of reaction condition in S_N2-type reaction by use of carbaglucosyl sulfonates **14–19***

The results of S_N2-type inversion between the carbaglucosyl sulfonates **14–19** and 1,2,3,4-*O*-Bn-carba-β-D-glucoside **8** are summarized in Table 1. Treatment of compound **8** (2.5 equiv. based on triflate **14**) with



Scheme 2. Synthesis of the reducing-end moiety **8** and the carbaglucosyl sulfonates **14–19**. Reagents and conditions: (a) 1. 9-BBN, THF, reflux, 2 h then 30% H_2O_2, 3 N NaOH, 0 °C, 3 h, (*gluco*:*ido* = 2.7:1); 2. Ac_2O, pyridine, rt, 2 h, 65%, two steps; (b) NaOMe, MeOH, rt, quant; (c) H_2, 10% Pd/C, MeOH, AcOH, quant; (d) benzaldehyde dimethylacetal, CSA, DMF, 60 °C, 3 h, 80%; (e) 2,2-dimethoxypropane, CSA, DMF, 60 °C, 20 min, 53%; (f) 1. 4-methoxybenzyl chloride, NaH, DMF, 0 °C, 1 h; 2. 60% AcOH, 60 °C, 1.5 h; 3. BnBr, NaH, DMF, 0 °C, 10 min, 78%, three steps; (g) CAN, MeCN, H_2O, rt, 82%; (h) Tf_2O, DTBMP, CH_2Cl_2, −10 °C, 15 min, 92% (i) methanesulfonyl chloride, pyridine, 0 °C, overnight, 94%; (j) chloromethanesulfonyl chloride, pyridine, 0 °C, 10 min, 87%; (k) *p*-toluenesulfonyl chloride, DMAP, pyridine, 50 °C, overnight, 96%; (l) 4-bromobenzenesulfonyl chloride, DMAP, pyridine, 40 °C, 5 h, 87%; (m) 4-nitorobenzenesulfonyl chloride, DMAP, 50 °C, 4 h, 88%. 9-BBN = 9-borabicyclo[3.3.1]nonane, CAN = cerium ammonium nitrate, DTBMP = di-*tert*-butyl-4-methylpyridine, CMs = chloromethanesulfonyl, Bs = 4-bromobenzensulfonyl, Ns = 4-nitrobenzensulfonyl.

Table 1
Optimization of S_N2-type inversion between the carbaglucosyl sulfonates **14–19** and 1,2,3,4-tetra-*O*-Bn-carba-β-D-glucopyranoside **8**.



Entry	Sulfonate	X	Conc. (M) **14–19**	Conc. (M) **8**	Solvent	NaH (equiv.)	15-Crown-5 (equiv.)	Temp. (°C)	Product (%) **20**	Olefin (%) **21**	Recovered (%) **8**
1	**14**	Tf	0.08	0.20	THF	2.5	2.5	rt	6	79	86
2	**14**	Tf	0.34	0.85	Neat	2.5	14.8	rt	10	40	66
3	**14**	Tf	0.68	1.70	Neat	2.5	7.4	rt	21	47	67
4	**14**	Tf	1.36	3.40	Neat	2.5	3.7	rt	22	49	73
5	**14**	Tf	0.68	1.68	THF	2.5	–	rt	11	52	68
6[a]	**15**	Ms	0.68	1.68	Neat	2.5	7.5	50	–	41	73
7[b]	**16**	CMs	0.68	1.68	Neat	2.5	7.5	rt	–	16	92
8	**17**	Ts	0.68	1.68	Neat	2.5	7.4	rt	–	10	77
9[c]	**18**	Bs	0.68	1.68	Neat	2.5	7.4	rt	–	–	91
10[d]	**19**	Ns	0.68	1.68	Neat	2.5	7.3	rt	–	–	59
11	**14**	Tf	0.68	1.68	Neat	7.3	7.3	0	37	26	88
12	**14**	Tf	0.68	1.68	Neat	2.5	7.3	50	24	70	84
13	**14**	Tf	0.68	1.68	THF	2.5	3.7	0	47	33	76
14	**14**	Tf	0.68	1.68	MeCN	2.5	3.7	0	33	33	85
15	**14**	Tf	0.68	1.68	HMPA	2.5	3.7	0	28	37	95
16	**14**	Tf	0.68	1.68	DMI	2.5	3.7	0	46	28	74

[a] Compound **13** was obtained in 29%.
[b] Mesylate **15** was obtained in 18%.
[c] Compound **22** was obtained in 24%.
[d] Compound **22** was obtained in 19%.

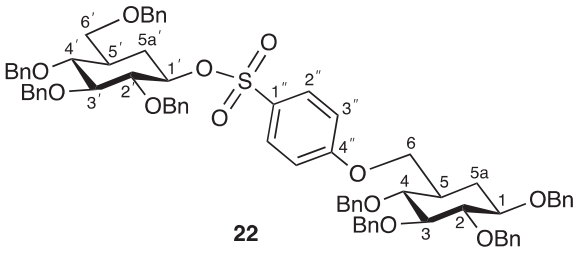


Fig. 1. Structure of compound **22**.

sodium hydride in THF in the presence of 15-crown-5 ether, and then reaction with triflate **14** (0.08 M) at room temperature (entry 1), gave the desired 5a,5a′-dicarba-β-D-isomaltose **20** in low yield (6%). This reaction preferred β-elimination of triflate **14**, to give olefin **21** in 79% yield. Conducting the reaction at higher substrate concentration (0.34 M, 0.68 M and 1.38 M) under neat reaction conditions increased the yield of coupling product **20** to 10%, 21% and 22% yield, respectively (entries 2–4). The reaction without 15-crown-5 ether provided compound **20** in 11% yield, showing that 15-crown-5 ether is an effective additive to improve the yield (entry 5).

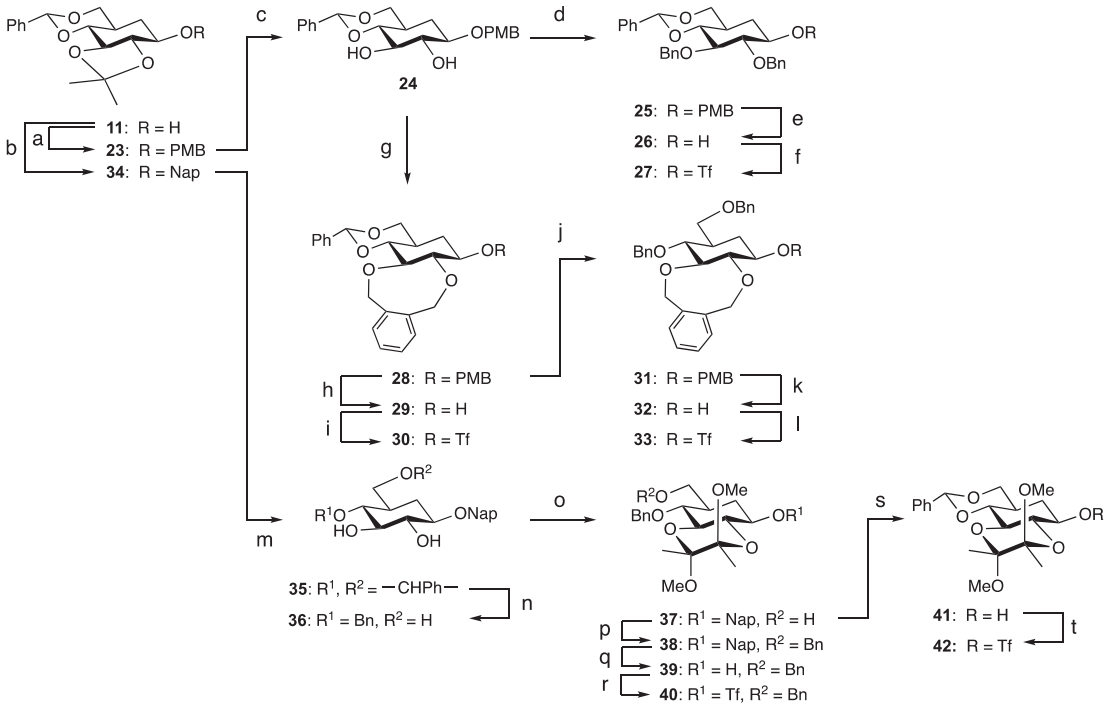
The reaction of mesylate **15** under the same conditions as entry 3 gave only the recovered material **15**. Reaction at a higher temperature (50 °C) gave the olefin **21** in 41% yield and the hydrolyzed compound **13** in 29% yield (entry 6). The reaction of chloromesylate **16** and compound **8** gave the olefin **21** and the mesylate **15**, which may be derived from reductive nucleophilic attack on the chloromesylate group (entry 7). Although the reaction of tosylate **17** at room temperature led only to olefin **21** (entry 8), the reaction of brosylate **18** or nosylate **19** with compound **8** unexpectedly yielded the coupled product **22** in 24% and 19% yield, respectively (entries 9 and 10), (Fig. 1). The HMBC experiment on compound **22** showed a correlation between C-4″ of the phenyl group and H-6. Unfortunately, no dicarbadisaccharide **20** was formed under these reaction conditions utilizing the sulfonates **15–19**.

The yields of compound **20** and olefin **21** at 50 °C were 24% and 70%, respectively, and the yield of compound **20** improved to up to 37% and that of olefin **21** was suppressed to 26% when the reaction was conducted at 0 °C (entries 11 and 12). The effect of solvent (THF, acetonitrile, hexamethylphosphoramide (HMPA) and 1,3-dimethyl-2-imidazolidine (DMI) on the reaction was investigated at 0 °C. As shown in entries 13–16, THF and DMI improved the yields of desired compound **20**, up to 47% and 46%, respectively, whereas acetonitrile and HMPA did not improve the yield. The improved yield might be due to the sodium alkoxide generated from compound **8** dissolving well in THF and DMI. The structure of the obtained dicarbadisaccharide **20** was confirmed from its NMR spectra: 1) the ^{1}H NMR spectrum showed the coupling constants for $J_{1',2'}$, $J_{1',5'aax}$ and $J_{1',5'aeq}$ as 2.7, 1.3 and 3.7 Hz, respectively; and 2) the chemical shift of C-6 (δ 70.23) was shifted downfield in comparison to that of the C-6 signal in **8** (δ 64.60); 3) in the HMBC spectrum, indicating the correlation between C-1′ and H-6. These results confirmed that compound **20** has the α1 → 6 linkage.

2.2. Synthesis of dicarbaglucobioses derivatives via S_N2-type inversion reaction by use of conformationally restricted carbaglucosyl triflates *27*, *30*, *33*, *40* and *42*

2.2.1. Synthesis of the conformationally restricted carbaglucosyl triflates *27*, *30*, *33*, *40* and *42*

In the synthesis of 5a,5a′-dicarba-β-D-isomaltose derivative **20**, we selected the synthetic strategy using 1-*O*-Tf-carba-β-D-glucose derivative as electrophile. Although we also tried another synthetic strategy using a 1-OH-carba-α-D-glucosyl derivative as a nucleophile, the



Scheme 3. Synthesis of conformationally restricted carbaglucosyl triflates **27**, **30**, **33**, **40** and **42**. Reagents and conditions: (a) 4-methoxybenzyl chloride, NaH, DMF, 0 °C, 1 h, 90%; (b) 2-(Bromomethyl)naphthalene, NaH, DMF, 0 °C, 1 h, 92%; (c) 60% AcOH, MeOH, 60 °C, 1.5 h, 77%; (d) BnBr, NaH, DMF, rt, 30 min, 93%; (e) DDQ, CH_2Cl_2, H_2O, rt, 1 h, 85%; (f) Tf_2O, DTBMP, CH_2Cl_2, −15 °C, 15 min, 80%; (g) α,α′-dibromo-*o*-xylene, NaH, DMF, rt, overnight, 56%; (h) DDQ, CH_2Cl_2, H_2O, rt, 40 min, 97%; (i) Tf_2O, pyridine, CH_2Cl_2, −10 °C, 2 h, 85%; (j) 1. 60% AcOH, 60 °C, 10 h; 2. BnBr, NaH, DMF, 0 °C, 30 min, 80%; (k) DDQ, CH_2Cl_2, H_2O, rt, 1.5 h, 91%; (l) Tf_2O, pyridine, CH_2Cl_2, −10 °C, 2 h, 83%; (m) 60% AcOH, MeOH, 60 °C, 2 h, 85%; (n) BH_3·THF, $CoCl_2$, rt, 5 h, 89%; (o) 2,3-butanedione, trimethyl orthoformate, CSA, MeOH, 60 °C, 4.5 h, 95%; (p) BnBr, NaH, DMF, rt, 2 h, 96%; (q) DDQ, CH_2Cl_2, H_2O, rt, 1 h, 81%; (r) Tf_2O, pyridine, CH_2Cl_2, −10 °C, 2.5 h, 87%; (s) 1. H_2, 10% Pd/C, MeOH, AcOH, rt, overnight; 2. benzaldehyde dimethylacetal, CSA, DMF, 60 °C, 15 min, 78%, two steps; (t) Tf_2O, pyridine, CH_2Cl_2, −10 °C, 2 h, 92%. Nap = 2-naphthylmethyl.

required 6-*O*-Tf-carba-β-D-glucose derivative could not be synthesized in typical triflation conditions due to the instability of 6-*O*-Tf-product. Furthermore, a low reactivity of the 1-OH carba-α-D-glucose derivative led us to select the carba-β-D-glucose derivative bearing a triflate at the 1-position for the electrophile in the following experiments. Since β-elimination of the triflate **14** should occur in the axial form, the triflates were synthesized in the conformationally fixed form locked in the $^4C_1$ conformation (Scheme 3). Compound **11** was protected as a *p*-methoxybenzyl ether, followed by chemoselective removal of the isopropylidene group using acetic acid at 60 °C to give the 2,3-diol **24**. Benzylation of **24** followed by removal of the *p*-methoxybenzyl group using DDQ and subsequent triflation provided triflate **27** in 63% yield over three steps.

Triflate with the *o*-xylylene group at the 2,3-positions was prepared from compound **11**. Compound **11** was treated with α,α′-dibromo-*o*-xylene and NaH in DMF to provide compound **28** in 56% yield. The *p*-methoxybenzyl group was removed and the resulting hydroxyl group was converted into the Tf group to give triflate **30**. Then, acidic cleavage of the benzylidene of compound **28**, followed by benzylation, provided compound **31** in 80% yield. After DDQ oxidation of the obtained compound **31**, triflation gave the desired triflate **33** in 83% yield.

Triflate with butane-2,3-diacetal (BDA) group at the 2,3-positions was prepared from compound **11**. Compound **11** was treated with 2-(bromomethyl)naphthalene and NaH in DMF to afford compound **34**. Removal of the isopropylidene group with acetic acid at 60 °C gave the 2,3-diol **35** in 85% yield. Installation of a BDA group was attempted using 1,1,2,2-tetramethoxydiacetal, generated *in situ* from 2,3-butanedione and trimethoxy orthoformate.[34] However, the desired compound was obtained only in 23% yield because the benzylidene group was deprotected under this condition. Therefore, selective ring-opening reduction of compound **35** was attempted by the use of BH_3·THF and $CoCl_2$ to give compound **36** in 89% yield, followed by installation of the BDA group, yielding compound **37** in 95% yield. Benzylation of **37** and subsequent oxidative cleavage of the 2-methylnaphtyl group, then triflation, gave the desired triflate **40**. Hydrogenolysis of compound **37** over Pd/C removed the 2-methylnaphtyl and benzyl groups simultaneously. Introduction of the benzylidene group yielded compound **41** in 78% yield in two steps. Finally, triflation of compound **41** gave the triflate **42** in 92% yield. Large coupling constants in ^{1}H NMR, $J_{1,2} = 8.7$ Hz, $J_{1,5aax} = 11.8$ Hz, $J_{2,3} = 8.8$ Hz, $J_{3,4} = 9.0$ Hz, $J_{4,5} = 9.3$ Hz, and $J_{5,5aax} = 11.8$ Hz, indicate a $^4C_1$ conformation for the triflate **27**. Triflates **30**, **33**, **40** and **42** also show similar large coupling constants, indicating the $^4C_1$ conformation for these compounds.

2.2.2. Optimization of reaction condition for the 5a,5a′-dicarba-β-D-isomaltose

The five conformationally restricted triflates **27**, **30**, **33**, **40**, and **42** were reacted with carbaglucosyl derivative **8** under optimized reaction conditions in the presence of NaH and 15-crown-5 ether at 0 °C in THF (0.68 M). The results are summarized in Table 2. The S_N2-type inversion of triflate **27** bearing only the benzylidene group and compound **8** gave the desired dicarbadisaccharide **43** in 55% yield (entry 2). The restricted triflate gave better yield than per-*O*-Bn-triflate, and the yield of the olefin was decreased to 19%. In a similar manner, triflate **33** bearing only the *o*-xylylene group was reacted with carbaglucosyl derivative **8** to afford the corresponding dicarbadisaccharide **45** in 32% yield (entry 3). The use of triflate **30** having both the benzylidene and *o*-xylylene groups gave dicarbadisaccharide **47** in 35% yield (entry 4). On the other hand, S_N2-type inversion of the triflate **40** bearing the BDA group by the carbaglucosyl derivative **8** gave the dicarbadisaccharide **48** in 57% yield and reduced the degree of β-elimination, giving the olefin **49** in 9% yield (entry 5). The use of triflate **42** bearing the benzylidene and BDA groups resulted in the dicarbadisaccharide **50** in 53% yield (entry 6). These results suggested that using a triflate with either 4,6-*O*-benzylidene or 2,3-*O*-BDA groups efficiently provides the desired dicarba-β-D-isomaltose derivatives and synthesis of the undesired olefins is suppressed. Finally, deprotection of compounds **20**, **43**, **45**, **47**, **48**, and **50** gave the desired 5a,5a′-dicarba-β-D-isomaltose **1** in quantitative yield (Scheme 4).

2.2.3. Synthesis of 5a,5a′-dicarba-β-D-maltose 2 and 5a,5a′-dicarba-α,β-D-trehalose 3

We evaluated substrate specificity under the optimized reaction conditions using the carbaglucosyl derivatives **52** and **13**, which have a secondary alcohol (Scheme 5). The carbaglucosyl derivative **52** with a hydroxyl group at the 4-position was prepared from compound **10**. Benzylation of the hydroxyl group, followed by selective ring-opening of the benzylidene group using trimethylamine borane and $AlCl_3$ in THF, provided compound **52** in 79% yield in two steps. The S_N2-type inversion reaction of the per-*O*-Bn-triflate **14** and compound **52** gave dicarba-β-D-maltose **53** in only 3% yield. On the other hand, the use of triflate **27** bearing the benzyliden group increased the yield of compound **54** up to 20%. Deprotection of both **53** and **54** gave the desired 5a,5a′-dicarba-β-D-maltose **2** in quantitative yield.

Next, we reacted carbaglucosyl derivative **13** bearing a hydroxyl group at the 1-position with the per-*O*-Bn-triflate **14** to afford dicarba-α,β-D-trehalose derivative **55** in 37% yield. In contrast, the use of triflate **27** increased the yield of compound **56** up to 64%. Deprotection of compounds **55** and **56** gave the desired 5a,5a′-dicarba-α,β-D-trehalose **3** in quantitative yield. Application of the optimized reaction conditions to the two carbaglucosyl derivatives with a secondary alcohol resulted in moderate yields. The higher reactivity of compound **13** is likely due to less steric hindrance between the hydroxy group and the adjacent deoxy moiety at the 5a-position.

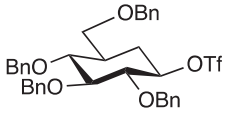
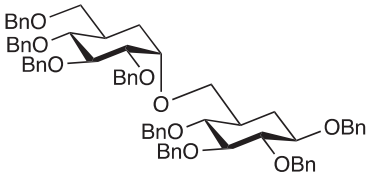
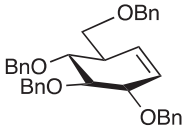
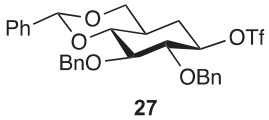
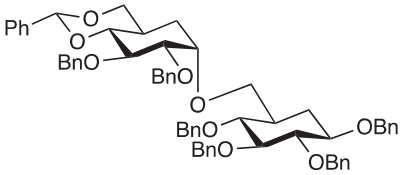
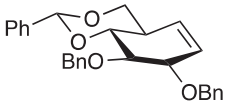
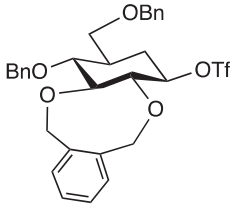
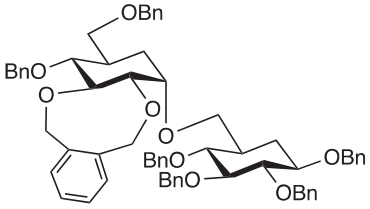
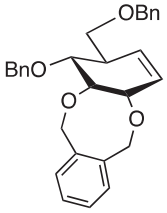
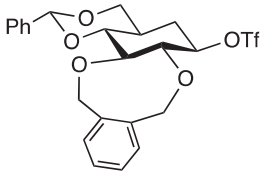
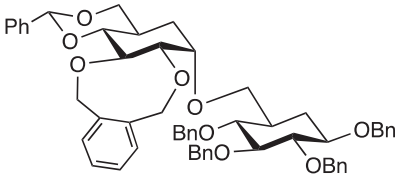
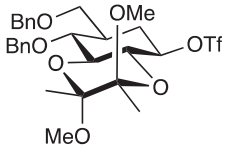
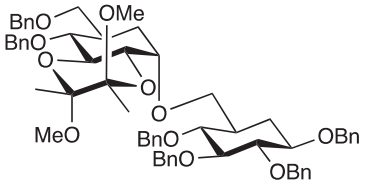
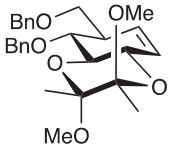
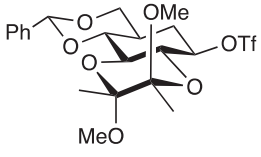
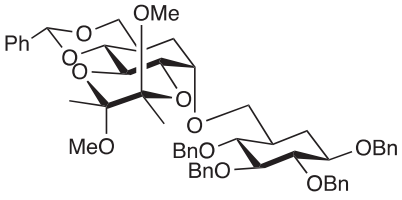
2.2.4. Synthesis of 5a,5a′-dicarba-α-D-isomaltose 4

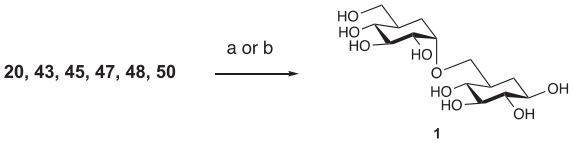
An α-form of 5a,5a′-dicarba-α-D-isomaltose **4** was also synthesized to compare the isomaltose and the corresponding dicarbadisaccharide (Scheme 6). Triflation of compound **26**, followed by the inversion reaction with CsOAc, afforded the carba-α-glucose derivative **57** in 94% yield. After deacetylation, the resulting product was protected with the benzyl group, and subsequent selective ring-opening reduction provided the compound **59**. In a similar manner, the S_N2-type inversion reaction of triflate **14** by compound **59** proceeded to furnish dicarba-α-D-isomaltose **60** in 17% yield. As expected, the use of triflate **27** increased desired compound **61** to up to 37% yield. Deprotection of compounds **60** and **61** gave 5a,5a′-dicarba-α-D-isomaltose **4** in quantitative yield.

3. Conclusion

In the present study, a novel approach was investigated for the synthesis of 5a,5a′-dicarba-D-glucobioses having α1 → 6, α1 → 4, and α1 → β1 linkages by S_N2-type inversion reaction. The 5a-carba-D-glucose residue was introduced with α-linkage by the S_N2 inversion using of 5a-carba-β-D-glucosyl triflate **14** and 6-OH carbaglucose derivatives **8**, the 5a,5a′-dicarba-β-D-isomaltose derivative **20** was obtained in the yield of 47% at 0 °C under high concentration. As a next step, the carbaglucosyl triflate **14** was changed to a conformationally restricted carbaglucosyl triflate bearing with 4,6-*O*-benzylidene **27** or 2,3-*O*-BDA groups **40**, the yield of 5a,5a′-dicarba-β-D-isomaltose derivative **43** and **48** increased to 55% and 57%. By the similar reactions using conformationally restricted carbaglucosyl triflate **27**, 5a,5a′-dicarba-β-D-maltose derivative **54**, 5a,5a′-dicarba-α,β-D-trehalose derivative **56**, and 5a,5a′-dicarba-α-D-isomaltose derivative **61** were obtained in yield of 20%, 64%, and 37%, respectively. The conformationally restricted structure of carbaglucosyl triflate was revealed to be critical in this S_N2-type inversion reaction. The present approach is expected as a new tool for the synthesis of 5a,5a′-dicarba-D-glucobioses of various linkages or pseudo-oligosaccharides as new chemical sources for medical uses. The dicarbadisaccharide are expected to be stable against glucosidases and

Table 2
S_N2-type inversion by use of the conformationally restricted carbaglucosyl triflates **27**, **30**, **33**, **40** and **42**.

Entry	Triflates	Dicarbadisaccharide product (%)	Yield of olefin (%)
1	 **14**	 **20** (47%)	 **21** (33%)
2	 **27**	 **43** (55%)	 **44** (19%)
3	 **33**	 **45** (36%)	 **46** (16%)
4	 **30**	 **47** (42%)	–
5	 **40**	 **48** (57%)	 **49** (9%)
6	 **42**	 **50** (53%)	–



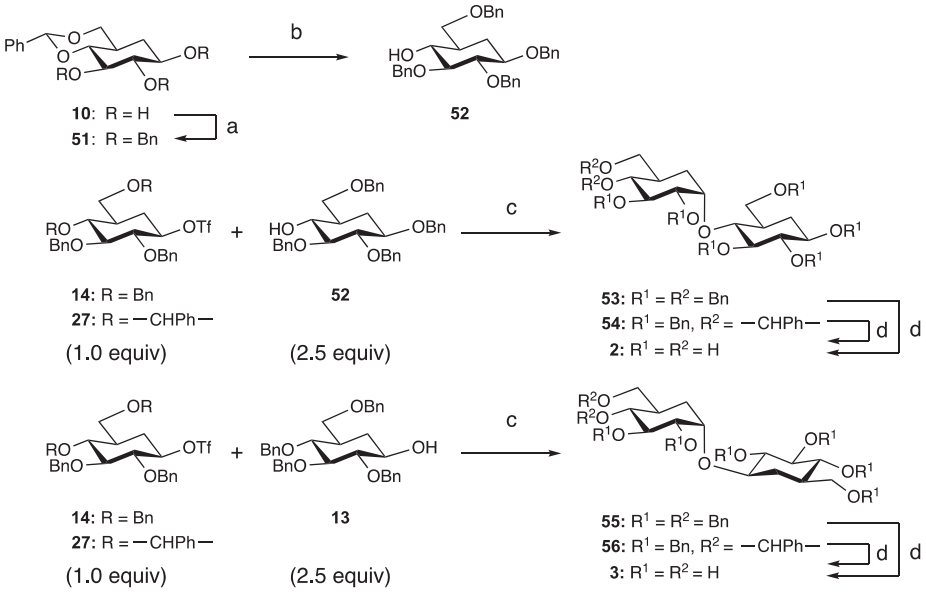
Scheme 4. Synthesis of 5a,5a′-dicarba-β-D-isomaltose **1**. Reagents and conditions: (a) H_2, Pd Black, MeOH, AcOH, rt, quant; (b) 1. 60% AcOH, 60 °C; 2. H_2, Pd Black, MeOH, AcOH, rt, quant, two steps.

the Maillard reaction. Thus, a preliminary test against hydrolases such as α-glucosidases showed a good stability of these carba-analogs of the disaccharides with little inhibitory activity. A further investigation on their biological properties is in due course.

4. Experimental section

4.1. General methods

All reagents and anhydrous solvents were obtained from



Scheme 5. Synthesis of 5a,5a′-dicarba-β-D-maltose **2** and 5a,5a′-dicarba-α,β-D-trehalose **3**. Reagents and conditions: (a) BnBr, NaH, DMF, rt, overnight, 94%; (b) trimethylamine borane, $AlCl_3$, THF, rt, overnight, 84%; (c) NaH, 15-crown-5, THF, 0 °C, **53**: 5%, **54** : 20%, **55** : 37%, **56**: 64%; (d) H_2, Pd Black, MeOH, AcOH, rt, quant.

commercial suppliers and were used as supplied without further purification. Non-aqueous reactions were performed under an atmosphere of argon. Thin layer chromatography (TLC) was carried out on plates precoated with silica gel 60 F-254 (E. Merck). Compounds ware visualized by UV-light at 254 nm and by dipping the plates in a cerium sulfate ammonium molybdate solution followed by heating. Column chromatography was carried out on Silica gel 60N (63–210 μm, spherical, neutral, Kanto Chemical Co.) and Silica gel 60N (40–50 μm, spherical, neutral, Kanto Chemical Co.). Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a Bruker AVANCE II 400 (400 MHz) and are reported in parts per million (δ) relative to the resonance of the solvent. Dates are represented as follows: chemical shift, integration, multiplicity (s, singlet; d, doublet; m, multiplet; br, broad), coupling constant in hertz (Hz), and assignment. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a Bruker AVANCE II 400 (100 MHz) and are reported in parts per million (δ) relative to the resonance of the solvent. Infrared spectra were measured on a *Perkin-Elmer* Ultra II FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Optical rotations were measured on a JASCO P-2300 Polarimeter with a path length of 1 dm; concentrations are given in g/100 mL. Melting points (mp) were recorded using an apparatus and not corrected. High-resolution mass spectra (HRMS) were recorded with a Bruker micrOTOF II.

4.1.1. Purification of DOI **5** from the culture solution

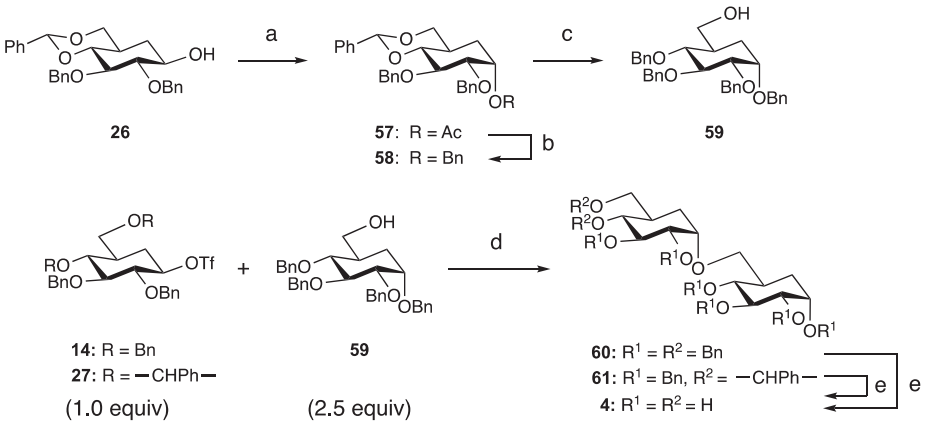
The culture solution[31] 10.5 L (DOI 39.2 g / L) was filtered through a membrane filter (Mixed cellulose ester, pore size 0.45, 2.0, 5.0 μm, diameter 293 mm, ADVANTEC Co. Ltd.) under pressure to give the cell-free solution. The filtrate was subsequently desalted by strong cation-exchange column chromatography (Amberlite 200CT, H^+ form, 5 L, ϕ14 cm × 32 cm, ORGANO Co. Ltd.) and the weak anion-exchange column chromatography (Amberlite IRA96SB, AcO^- form, 7.5 L, ϕ13 cm × 56 cm, ORGANO Co. Ltd.). Then, the eluted solution including DOI was evaporated. After the residue (422 g) was dissolved in MeOH (505 mL), then EtOH (3.5 L) was added with dropwise to crystalize the DOI. The obtained DOI was dried in desiccator with P_2O_5. The yield was 67% (283 g) based on utilizing the D-glucose (473 g) in fermentation. The physical data were identical to the reported data.[32]

Keto form: ^{1}H NMR (400 MHz, D_2O) δ 4.37(d, 1H, $J_{3,4}$ = 10.2 Hz, H-4), 3.82(dd, 1H, $J_{1,2}$ = 9.6 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 3.75(ddd, 1H, H-1), 3.47(dd, 1H, H-3), 2.83–2.74(m, 2H, H-5aeq, H-5aax); ^{13}C NMR (100 MHz, D_2O) δ 206.92(C-5), 77.84(C-4), 76.06(C-2), 73.87(C-3), 68.20(C-1), 44.16(C-5a).

Hydrate form: ^{1}H NMR (400 MHz, D_2O) δ 3.67(ddd, 1H, $J_{1,2}$ = 9.0 Hz, $J_{1,5aeq}$ = 5.0 Hz, $J_{1,5aax}$ = 11.9 Hz, H-1), 3.49(d, 1H, $J_{3,4}$ = 9.1 Hz, H-4), 3.43(dd, 1H, $J_{2,3}$ = 9.1 Hz, H-3), 3.38(dd, 1H, H-2), 2.25(dd, 1H, J_{gem} = 13.3 Hz, H-5aeq), 1.73(dd, 1H, H-5aax); ^{13}C NMR (100 MHz, D_2O) δ 93.27(C-5), 77.01(C-2), 76.27(C-4), 73.54(C-3), 68.47(C-1), 40.68(C-5a).

4.1.2. 2,4/3,5–2,3,4,5-Tetrabenzyloxy-1-methylenecyclohexane (**6**)

To a stirred suspension of methyltriphenylphosphonium bromide



Scheme 6. Synthesis of 5a,5a′-dicarba-α-D-isomaltose **4**. Reagents and conditions: (a) 1. Tf_2O, DTBMP, CH_2Cl_2, −10 °C, 10 min; 2. CsOAc, 18-crown-6, Toluene, rt, 1 h, 96%, two steps; (b) 1. NaOMe, MeOH, rt, 7 h; 2. BnBr, NaH, DMF, 0 °C, 30 min, 90%, two steps; (c) THF·BH_3, $CoCl_2$, THF, rt, 2 h, 93%; (d) NaH, 15-crown-5, THF, 0 °C, **60**: 17%, **61**: 37%; (e) H_2, Pd Black, MeOH, AcOH, rt, quant.

(69.0 g, 192.9 mmol) in THF (200 mL) was added dropwise a solution of *n*-BuLi (55 mL, 2.64 M in hexane, 144.6 mmol) at −60 °C. After the addition, the suspension was stirred at room temperature. The suspension was added a solution of 3,4,5,6-*O*-benzyl-2-deoxy-*scyllo*-inosose (25.20 g, 48.2 mmol) in THF (50 mL) dropwise at −60 °C. After being stirred at room temperature for 40 min, the solution was diluted with EtOAc and washed subsequently with 1 M HCl, saturated $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 9:1) to give compound **6** (24.4820 g, 98%) as a white amorphous solid. R_f = 0.36 (Hex/EtOAc, 10:1); [α] = −25.8° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.25(m, 20H), 5.24(m, 1H, H-6a), 4.97(m, 1H, H-6b), 4.92(d, 1H, *J* = 10.7 Hz), 4.91(d, 1H, *J* = 10.8 Hz), 4.86(d, 1H, *J* = 10.8 Hz), 4.82(d, 1H, *J* = 10.7 Hz), 4.74(d, 1H, *J* = 11.4 Hz), 4.68(s, 2H), 4.68(d, 1H, *J* = 11.4 Hz), 3.92(d, 1H, $J_{3,4}$ = 9.2 Hz, H-4), 3.62(dd, 1H, $J_{1,2}$ = 9.0 Hz, $J_{2,3}$ = 9.1 Hz, H-2), 3.43(ddd, 1H, $J_{1,5aeq}$ = 5.1 Hz, $J_{1,5aax}$ = 11.9 Hz, H-1), 3.39(dd, 1H, H-3), 2.72(dd, 1H, J_{gem} = 12.9 Hz, H-5aeq), 2.04(dd, 1H, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.16(C-5), 138.87, 138.83, 138.53, 138.35, 128.38, 128.30, 128.29, 127.97, 127.96, 127.75, 127.69, 127.61, 127.48, 110.34(C-6), 85.81(C-3), 85.09(C-2), 83.10(C-4), 80.44(C-1), 75.86, 75.84, 73.54, 72.56, 36.39(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{36}O_4Na$ 543.2506, found 543.2508.

4.1.3. 6-O-Acetyl-1,2,3,4-tetra-O-benzyl-5a-carba-β-D-glucopyranose (7)

A solution of 2,4/3,5–2,3,4,5-tetrabenzyloxy-1-methylenecyclohexane **6** (25.00 g, 48.2 mmol) in 9-BBN (193 mL, 0.5 M in THF, 96.4 mmol) was stirred for 2 h at reflux. To the solution cooled to 0 °C was added H_2O (35 mL), 3 N NaOH (30 mL), and 30% H_2O_2 (30 mL). After being stirred for 3 h at room temperature, the solution was diluted with EtOAc and washed subsequently with 1 M HCl, saturated $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to give a mixture of two diastereomeric alcohols (25.6130 g, 99%) as a colorless syrup. To a solution of the mixture (47.13 g, 87.5 mmol) in pyridine (40 mL) was added Ac_2O (21 mL, 219 mmol). After being stirred for overnight, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed subsequently with 1 M HCl, saturated $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was crystallized from diisopropyl ether to give compound **7** (30.5998 g, 60%) as a white solid. The residue was purified by column chromatography (toluene/EtOAc, 20:1) to give compound **7** (3.0154 g, 6%) as a white amorphous solid and isomer (10.3459 g, 20%) as a colorless syrup. R_f = 0.40 (Hex/EtOAc, 2:1); [α] = +32.3° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.26(m, 20H), 4.95(d, 2H, *J* = 10.8 Hz), 4.90(d, 1H, *J* = 10.8 Hz), 4.85(d, 1H, *J* = 10.8 Hz), 4.84(d, 1H, *J* = 10.8 Hz), 4.68(s, 2H), 4.55(d, 1H, *J* = 10.8 Hz), 4.19(dd, 1H, $J_{5,6a}$ = 3.1 Hz, J_{gem} = 10.9 Hz, H-6a), 4.15(dd, 1H, $J_{5,6b}$ = 4.8 Hz, H-6b), 3.55–3.51(m, 3H, H-1, H-2, H-3), 3.40(dd, 1H, $J_{3,4}$ = 8.5 Hz, $J_{4,5}$ = 10.6 Hz, H-4), 2.06(ddd, 1H, $J_{1,5aeq}$ = 3.6 Hz, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 13.3 Hz, H-5aeq), 2.00(s, 3H), 1.74(m, 1H, H-5), 1.34(ddd, 1H, $J_{1,5aax}$ = 11.0 Hz, $J_{5,5aax}$ = 11.0 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.88, 138.71, 138.63, 138.47, 138.14, 128.44, 128.39, 128.34, 128.11, 127.98, 127.80, 127.76, 127.68, 127.62, 127.56, 86.20(C-3), 85.83(C-2), 80.14(C-4), 79.90(C-1), 75.83, 75.23, 72.55, 64.18(C-6), 37.71(C-5), 30.13(C-5a), 20.80(CH_3); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{37}H_{40}O_6Na$ 603.2717, found 603.2717.

4.1.4. 1,2,3,4-Tetra-O-benzyl-5a-carba-β-D-glucopyranose (8)

To a solution of 6-*O*-acetyl-1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **7** (44.90 g, 77.43 mmol) in MeOH (250 mL) was added NaOMe (4.18 g, 77.43 mmol). After being stirred for overnight, the solution was neutralized with Amberlite 200CT (H^+), and the resin was filtered off. The filtrate was concentrated *in vacuo* to give compound **8** (43.78 g, quant) as a white amorphous solid. R_f = 0.24 (Hex/EtOAc, 3:1); [α] = +29.7° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25(m, 20H), 4.96(d, 1H, *J* = 10.8 Hz), 4.95(d, 2H, *J* = 10.8 Hz), 4.83(d, 2H, *J* = 10.8 Hz), 4.68(d, 1H, *J* = 11.5 Hz), 4.65(d, 1H, *J* = 10.8 Hz), 4.64(d, 1H, *J* = 11.5 Hz), 3.66–3.55(m, 2H, H-6a, H-6b), 3.57(dd, 1H, $J_{2,3}$ = 8.8 Hz, $J_{3,4}$ = 8.8 Hz, H-3), 3.54(m, 1H, H-1), 3.51(dd, 1H, $J_{1,2}$ = 8.7 Hz, H-2), 3.42(dd, 1H, $J_{4,5}$ = 10.4 Hz, H-4), 2.03(ddd, 1H, $J_{1,5aeq}$ = 3.8 Hz, $J_{5,5aeq}$ = 3.8 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.81(br, 1H, OH), 1.62(m, 1H, H-5), 1.26(ddd, 1H, $J_{1,5aax}$ = 11.0 Hz, $J_{5,5aax}$ = 11.0 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.77, 138.64, 138.54, 138.12, 128.58, 128.39, 128.37, 128.33, 128.24, 127.96, 127.76, 127.68, 127.59, 127.56, 127.53, 86.28(C-3), 85.93(C-2), 82.09(C-4), 80.10(C-1), 75.79, 75.75, 75.10, 72.36, 64.60(C-6), 40.16(C-5), 29.89(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{38}O_5Na$ 561.2611, found561.2613.

4.1.5. 5a-Carba-β-D-glucopyranose (9)

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (41.71 g, 77.43 mmol) in MeOH (300 mL), THF (50 mL), and AcOH (20 mL) was added 10% Pd/C (4.12 g, 3.87 mmol). The resulting suspension was hydrogenated at 1 atm. After 10.5 h, further portion of 10% Pd/C (4.12 g, 3.87 mmol) was added to the mixture. After being stirred for total 36.5 h, the solution was filtered through of Celite, and the solvent was evaporated. The residue was chromatographed on a column of Amberlite 200CT ion-exchange resin (H^+ form) and IRA 96SB ion-exchange resin (OH^-) to give compound **9** (14.3957 g, quant) as a colorless syrup. R_f = 0.30 ($CHCl_3$/MeOH/H_2O, 10:5:1); [α] = +16.1° (*c* 1.00, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 3.81(dd, 1H, $J_{5,6a}$ = 3.6 Hz, J_{gem} = 11.2 Hz, H-6a), 3.68(dd, 1H, $J_{5,6b}$ = 6.1 Hz, H-6b), 3.61(ddd, 1H, $J_{1,2}$ = 8.9 Hz, $J_{1,5aeq}$ = 4.7 Hz, $J_{1,5aax}$ = 11.6 Hz, H-1), 3.34(m, 1H, H-4), 3.32(m, 1H, H-3), 3.28(dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 2.05(ddd, 1H, $J_{5,5aeq}$ = 3.8 Hz, J_{gem} = 12.9 Hz, H-5aeq), 1.68(m, 1H, H-5), 1.31(ddd, 1H, $J_{5,5aax}$ = 11.8 Hz, H-5aax); ^{13}C NMR (100 MHz, D_2O) δ 76.93(C-2), 76.77(C-3), 72.59(C-4), 71.06(C-1), 62.14(C-6), 40.06(C-5), 31.64(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_7H_{14}O_5Na$ 201.0733, found 201.0735.

4.1.6. 4,6-O-Benzylidene-5a-carba-β-D-glucopyranose (10)

To a solution of 5a-carba-β-D-glucopyranose **9** (7.43 g, 41.7 mmol) in DMF (100 mL) at 60 °C was added benzaldehyde dimethyl acetal (9.3 mL, 62.5 mmol) and CSA (4.8 g, 20.9 mmol). After being stirred for 3 h, the solution was cooled to 0 °C and neutralized with Et_3N. The solution was concentrated *in vacuo*, and the residue was crystallized from EtOH–H_2O to give compound **10** (7.00 g, 63%) as a white solid. The residue was purified by column chromatography ($CHCl_3$/MeOH, 10:1) to give compound **10** (1.8731 g, 17%) as a white amorphous solid. R_f = 0.21 ($CHCl_3$/MeOH, 10:1); [α] = −50.0° (*c* 1.00, MeOH); ^{1}H NMR (400 MHz, MeOD) δ 7.52–7.32(m, 5H), 5.56(s, 1H, PhCH), 4.13(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 10.9 Hz, H-6a), 3.66(dd, 1H, $J_{5,6b}$ = 10.9, H-6b), 3.52(ddd, 1H, $J_{1,5aeq}$ = 4.8 Hz, $J_{1,2}$ = 9.0 Hz, $J_{1,5aax}$ = 11.4 Hz, H-1), 3.47(dd, 1H, $J_{2,3}$ = 8.9 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.43(dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.24(dd, 1H, H-2), 1.79(m, 1H, H-5), 1.74(ddd, 1H, $J_{5,5aeq}$ = 3.3 Hz, J_{gem} = 12.6 Hz, H-5aeq), 1.11(ddd, 1H, $J_{5,5aax}$ = 11.4 Hz, H-5aax); ^{13}C NMR (100 MHz, MeOD) δ 139.88, 129.77, 129.00, 127.51, 102.88(PhCH), 84.07(C-4), 79.61(C-2), 75.85(C-3), 72.87(C-1), 71.97(C-6), 35.53(C-5), 31.77(C-5a); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{18}O_5Na$ 266.1046, found 266.1046.

4.1.7. 4,6-O-Benzylidene-2,3-O-isopropylidene-5a-carba-β-D-glucopyranose (11)

To a solution of 4,6-*O*-benzylidene-5a-carba-β-D-glucopyranose **10** (8.00 g, 30.04 mmol) in DMF (150 mL) at 60 °C was added 2,2-dimethoxypropane (18.6 mL, 150.2 mmol) and CSA (698 mg, 3.00 mmol). After being stirred for 20 min, the solution was cooled to 0 °C and neutralized with Et_3N. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (hexane/acetone, 4:1) to give 4,6-*O*-benzylidene-2,3-*O*-isopropylidene-5a-carba-β-D-

glucopyranose **11** (4.8818 g, 53%) as a white amorphous solid and 4,6-*O*-benzylidene-1,2-*O*-isopropylidene-5a-carba-β-D-glucopyranose (4.1501 g, 45%) as a white amorphous solid. R_f = 0.24 (hexane/acetone, 3:1); [α] = −33.3° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.30(m, 5H), 5.58(s, 1H, PhCH), 4.19(dd, 1H, $J_{5,6a}$ = 4.1 Hz, J_{gem} = 11.0 Hz, H-6a), 3.99(ddd, 1H, $J_{1,5aeq}$ = 4.5 Hz, $J_{1,2}$ = 9.5 Hz, $J_{1,5aax}$ = 9.9 Hz, H-1), 3.81(dd, 1H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.74(dd, 1H, $J_{5,6b}$ = 11.0 Hz, H-6b), 3.65(dd, 1H, $J_{2,3}$ = 9.3 Hz, H-3), 3.44(dd, 1H, H-2), 2.46(br, 1H, OH), 1.94(m, 1H, H-5), 1.88(ddd, 1H, $J_{5,5aeq}$ = 4.3 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.48(s, 3H, CH_3), 1.46(s, 3H, CH_3), 1.16(ddd, 1H, $J_{5,5aax}$ = 10.3 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.55, 129.01, 128.16, 126.40, 111.79, 101.67(PhCH), 82.71(C-2), 80.54(C-4), 77.80(C-3), 70.85(C-6), 69.61(C-1), 36.55(C-5), 31.90(C-5a), 26.78(CH_3), 26.77(CH_3); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{18}O_5Na$ 329.1359, found 329.1360.

4.1.8. 2,3,4,6-Tetra-O-Benzyl-1-O-(p-methoxybenzyl)-5a-carba-β-D-glucopyranose (12)

To a solution of 4,6-*O*-benzylidene-2,3-*O*-isopropylidene-5a-carba-β-D-glucopyranose **11** (183 mg, 0.597 mmol) in DMF (3 mL) and NaH (60 mg, 1.49 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 4-methoxybenzyl chloride (202 μL, 1.49 mmol). After being stirred for 45 min, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with Et_2O, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. To a solution of the residue was dissolved in AcOH (1.5 mL) and H_2O (1 mL) at 60 °C, and the mixture was stirred for 1.5 h. The solvent was concentrated *in vacuo*. To a solution of the residue was dissolved in DMF (3 mL) was added NaH (191 mg, 4.78 mmol), and the mixture was stirred for 30 min. After being cooled to 0 °C, to the solution was added BnBr (568 μL, 4.78 mmol). After being stirred for 10 min, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with Et_2O, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 5:1) to give compound **12** (308 mg, 78%) as a white amorphous solid. R_f = 0.33 (hexane/EtOAc, 5:1); [α] = +16.0° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.18(m, 22H), 6.86–6.83(m, 2H), 4.94(d, 1H, *J* = 10.7 Hz), 4.92(d, 1H, *J* = 10.7 Hz), 4.86(d, 1H, *J* = 11.0 Hz), 4.82(d, 1H, *J* = 10.7 Hz), 4.82(d, 1H, *J* = 10.7 Hz), 4.62(d, 1H, *J* = 11.0 Hz), 4.57(d, 1H, *J* = 11.0 Hz), 4.50(d, 1H, *J* = 11.0 Hz), 4.45(s, 2H), 3.79(s, 3H), 3.56(dd, 1H, $J_{5,6a}$ = 5.3 Hz, J_{gem} = 8.9 Hz, H-6a), 3.54–3.47(m, 2H, H-2, H-3), 3.53(dd, 1H, $J_{5,6b}$ = 3.1 Hz, H-6b), 3.50(m, 1H, H-1), 3.46(dd, 1H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 8.9 Hz, H-4), 2.16(ddd, 1H, $J_{1,5aeq}$ = 3.7 Hz, $J_{5,5aeq}$ = 3.7 Hz, J_{gem} = 13.2 Hz, H-5aeq), 1.69(m, 1H, H-5), 1.45(ddd, 1H, $J_{1,5aax}$ = 11.0 Hz, $J_{5,5aax}$ = 11.0 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.13, 138.93, 138.83, 138.58, 138.41, 130.85, 129.28, 128.36, 128.35, 128.31, 128.00, 127.96, 127.80, 127.60, 127.53, 127.51, 127.47, 113.78, 86.34(C-3), 85.96(C-2), 80.87(C-4), 80.03(C-1), 75.80, 75.76, 75.24, 73.11, 72.05, 70.19(C-6), 55.26(OCH_3), 39.03(C-5), 30.59(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{43}H_{46}O_6Na$ 681.3187, found 681.3187.

4.1.9. 2,3,4,6-Tetra-O-benzyl-5a-carba-β-D-glucopyranose (13)

To a solution of 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*p*-methoxybenzyl)-5a-carba-β-D-glucopyranose **12** (4.70 g, 7.13 mmol) in MeCN–H_2O (9:1, 100 mL) was added CAN (7.8 g, 14.27 mmol). After being stirred for 2.5 h, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 4:1) to give compound **13** (3.1556 g, 82%) as a white amorphous solid. R_f = 0.16 (hexane/EtOAc, 4:1); [α] = +9.2° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.20(m, 20H), 4.99(d, 1H, *J* = 11.3 Hz), 4.92(d, 1H, *J* = 11.1 Hz), 4.88(d, 1H, *J* = 11.1 Hz), 4.87(d, 1H, *J* = 11.1 Hz), 4.69(d, 1H, *J* = 11.3 Hz), 4.54(d, 1H, *J* = 10.8 Hz), 4.45(s, 2H), 3.61(dd, 1H, $J_{5,6a}$ = 5.0 Hz, J_{gem} = 8.9 Hz, H-6a), 3.56(ddd, 1H, $J_{1,5aeq}$ = 4.2 Hz, $J_{1,2}$ = 9.2 Hz, $J_{1,5aax}$ = 11.9 Hz , H-1), 3.56–3.52(m, 2H, H-3, H-4), 3.49(dd, 1H, $J_{5,6b}$ = 2.7 Hz, H-6b), 3.31(dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 2.28(br, 1H, OH), 2.02(ddd, 1H, $J_{5,5aeq}$ = 4.2 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.75(m, 1H, H-5), 1.52(ddd, 1H, $J_{5,5aax}$ = 11.9 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.58, 138.52, 138.48, 138.37, 128.64, 128.42, 128.39, 128.33, 127.921, 27.90, 127.70, 127.65, 127.58, 127.52, 127.51, 86.42(C-3), 86.38(C-2), 81.12(C-4), 75.52, 75.48, 75.29, 73.06, 71.28(C-1), 69.79(C-6), 39.29(C-5), 31.85(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{38}O_5Na$ 561.2611, found 561.2618.

4.1.10. 2,3,4,6-Tetra-O-benzyl-1-O-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose (14)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (464 mg, 0.861 mmol) in CH_2Cl_2 (15 mL) at −10 °C was added 2,6-di-*t*-butyl-4-methylpyridine (248 mg, 1.20 mmol) and Tf_2O (435 μL, 2.58 mmol). After being stirred for 15 min, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Toluene) to give compound **14** (532 mg, 92%) as a white amorphous solid. R_f = 0.51 (Toluene); [α] = +0.51° (*c* 0.955, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.16(m, 20H), 4.86(s, 2H), 4.85(d, 1H, *J* = 10.7 Hz), 4.83(m, 1H, H-1), 4.82(s, 2H), 4.52(d, 1H, *J* = 10.7 Hz), 4.46(d, 1H, *J* = 12.0 Hz), 4.42(d, 1H, *J* = 12.0 Hz), 3.67(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 9.0 Hz, H-6a), 3.61(dd, 1H, $J_{2,3}$ = 9.1 Hz, $J_{1,2}$ = 9.3 Hz, H-2), 3.57(dd, 1H, $J_{4,5}$ = 6.3 Hz, $J_{3,4}$ = 8.8 Hz, H-4), 3.54(dd, 1H, H-3), 3.45(dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 2.23(ddd, 1H, $J_{1,5aeq}$ = 3.8 Hz, $J_{5,5aeq}$ = 5.1 Hz, J_{gem} = 12.9 Hz, H-5aeq), 1.93(ddd, 1H, $J_{1,5aax}$ = 12.4 Hz, $J_{5,5aax}$ = 12.4 Hz, H-5aax), 1.72(m, 1H, H-5); ^{13}C NMR (100 MHz, CDC_{l3}) δ 138.18, 138.12, 127.97, 127.39, 128.44, 128.35, 128.10, 127.91, 127.82, 127.80, 127.79, 127.67, 127.55, 88.14(C-1), 85.83(C-3), 82.45(C-2), 79.59(C-4), 75.91, 75.88, 75.42, 73.22, 68.76(C-6), 38.48(C-5), 30.73(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{37}O_7NaSF_3$ 693.2104 found 693.2098.

4.1.11. 2,3,4,6-Tetra-O-Benzyl-1-O-methanesulfonyl-5a-carba-β-D-glucopyranose (15)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (21 mg, 0.039 mmol) in pyridine (500 μL) was added methanesulfonyl chloride (15 μL, 0.195 mmol) at 0 °C, and the solution was stirred overnight. To the solution was added MeOH, and the solvents were evaporated. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 4:1) to give compound **15** (23 mg, 94%) as a white amorphous solid. R_f = 0.44 (Toluene/EtOAc, 10:1); [α] = +23.6° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.18(m, 20H), 4.93(d, 1H, *J* = 11.0 Hz), 4.90(d, 1H, *J* = 10.7 Hz), 4.87(d, 1H, *J* = 10.7 Hz), 4.85(dd, 1H, *J* = 10.8 Hz), 4.73(d, 1H, *J* = 11.0 Hz), 4.54(d, 1H, *J* = 10.8 Hz), 4.47(ddd, 1H, $J_{1,5aeq}$ = 5.1 Hz, $J_{1,2}$ = 8.4 Hz, $J_{1,5aax}$ = 12.0 Hz, H-1), 4.44(s, 2H), 3.69(dd, 1H, $J_{5,6a}$ = 4.1 Hz, J_{gem} = 9.0 Hz, H-6a), 3.58–3.55(m, 3H, H-2, H-3, H-4), 3.44(dd, 1H, $J_{5,6b}$ = 2.4 Hz, H-6b), 2.82(s, 3H, CH_3), 2.25(ddd, 1H, $J_{5,5aeq}$ = 3.3 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.86(ddd, 1H, $J_{5,5aax}$ = 11.9 Hz, H-5aax), 1.74(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.27, 138.26, 138.12, 137.94, 128.45, 128.42, 128.38, 127.91, 127.81, 127.74, 127.65, 127.63, 127.60, 86.19(C-3), 83.21(C-2), 81.87(C-1), 79.97(C-4), 75.83, 75.80, 75.38, 73.17, 68.94(C-6), 38.71(C-5), 38.11(CH_3), 31.56(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{40}O_7NaS$ 639.2387, found 639.2388.

4.1.12. 2,3,4,6-Tetra-O-benzyl-1-O-chloromethanesulfonyl-5a-carba-β-D-glucopyranose (16)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (22 mg, 0.041 mmol) in pyridine (500 μL) was added

chloromethanesulfonyl chloride (19 μL, 0.200 mmol) at 0 °C, and the solution was stirred 10 min. To the solution was added MeOH, and the solvents were evaporated. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Toluene/EtOAc, 20:1) to give compound **16** (23 mg, 87%) as a colorless syrup. R_f = 0.59 (Toluene/EtOAc, 10:1); [α] = +22.1° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36–7.17(m, 20H), 4.93(d, 1H, *J* = 10.8 Hz), 4.90(d, 1H, *J* = 11.0 Hz), 4.85(d, 1H, *J* = 11.0 Hz), 4.85(d, 1H, *J* = 10.8 Hz), 4.79(d, 1H, *J* = 10.8 Hz), 4.64(ddd, 1H, $J_{1,5aeq}$ = 5.1 Hz, $J_{1,2}$ = 8.8 Hz, $J_{1,5aax}$ = 11.9 Hz, H-1), 4.53(d, 1H, *J* = 10.8 Hz), 4.44(s, 2H), 4.43(d, 1H, *J* = 12.4 Hz), 4.38(d, 1H, *J* = 12.4 Hz), 3.68(dd, 1H, $J_{5,6a}$ = 4.2 Hz, J_{gem} = 9.0 Hz, H-6a), 3.59(m, 1H, H-2), 3.57(m, 2H, H-3, H-4), 3.45(dd, 1H, $J_{5,6b}$ = 2.4 Hz, H-6b), 2.27(ddd, 1H, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.89(ddd, 1H, $J_{5,5aax}$ = 12.1 Hz, H-5aax), 1.74(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.18, 138.06, 137.81, 128.43, 128.41, 127.91, 127.84, 127.77, 127.70, 127.67, 127.62, 86.14(C-3), 83.98(C-1), 82.90(C-2), 79.87(C-4), 75.84, 75.78, 75.39, 73.17, 68.87(C-6), 54.12, 38.60(C-5), 31.39(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{39}O_7NaSCl$ 673.1997, found 673.1999.

4.1.13. 2,3,4,6-Tetra-O-benzyl-1-O-(4-toluenesulfonyl)-5a-carba-β-D-glucopyranose (17)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (164 mg, 0.304 mmol) in pyridine (2 mL) was added 4-toluenesulfonyl chloride (580 mg, 3.04 mmol) and DMAP (4 mg, 0.030 mmol) at 50 °C, and the solution was stirred overnight. To the solution was added MeOH, and the solvents were evaporated. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Toluene → Toluene/EtOAc, 20:1) to give compound **17** (203 mg, 96%) as a white amorphous solid. R_f = 0.31 (Toluene/EtOAc, 20:1); [α] = +14.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.75–7.73(m, 2H), 7.35–7.09(m, 22H), 4.83(d, 1H, *J* = 10.8 Hz), 4.80(d, 1H, *J* = 10.7 Hz), 4.77(d, 1H, *J* = 10.7 Hz), 4.68(d, 1H, *J* = 10.7 Hz), 4.63(d, 1H, *J* = 10.7 Hz), 4.52(ddd, 1H, $J_{1,5aeq}$ = 5.1 Hz, $J_{1,2}$ = 8.3 Hz, $J_{1,5aeq}$ = 12.0 Hz, H-1), 4.50(d, 1H, *J* = 10.8 Hz), 4.43(d, 1H, *J* = 12.0 Hz), 4.40(d, 1H, *J* = 12.0 Hz), 3.64(dd, 1H, $J_{5,6a}$ = 4.3 Hz, J_{gem} = 8.9 Hz, H-6a), 3.53–3.47(m, 3H, H-2, H-3, H-4), 3.42(dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 2.34(s, 3H, CH_3), 2.22(ddd, 1H, $J_{5,5aeq}$ = 3.2 Hz, J_{gem} = 12.8 Hz, H-5aeq), 1.80(ddd, 1H, $J_{1,5aax}$ = 12.0 Hz, H-5aax), 1.68(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.44, 138.37, 138.20, 138.10, 134.18, 129.68, 128.38, 128.36, 128.33, 128.10, 127.88, 127.69, 127.66, 127.60, 127.54, 127.53, 127.35, 85.93(C-3), 83.14(C-2), 82.13(C-1), 79.92(C-4), 75.85, 75.37, 75.30, 73.11, 69.12(C-6), 38.66(C-5), 31.36(C-5a), 21.60(CH_3); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{42}H_{44}O_7NaS$ 715.2700, found 715.2705.

4.1.14. 2,3,4,6-Tetra-O-benzyl-1-O-(p-bromobenzenesulfonyl)-5a-carba-β-D-glucopyranose (18)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (14 mg, 0.026 mmol) in pyridine (500 μL) was added 4-bromobenzenesulfonyl chloride (66 mg, 0.26 mmol) and DMAP (1.0 mg, 0.008 mmol). After being stirred at 40 °C for 5 h, the solution was cooled to 0 °C and MeOH was added to the solution. The solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 7:1) to give compound **18** (17 mg, 87%) as a white amorphous solid. R_f = 0.54 (hexane/EtOAc, 3:1); [α] = +11.4° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.69–7.66(m, 2H), 7.43–7.40(m, 2H), 7.36–7.06(m, 20H), 4.83(d, 1H, *J* = 10.8 Hz), 4.80(s, 2H), 4.76(d, 1H, *J* = 10.9 Hz), 4.58(d, 1H, *J* = 10.9 Hz), 4.51(d, 1H, *J* = 10.8 Hz), 4.50(ddd, 1H, $J_{1,5aeq}$ = 5.2 Hz, $J_{1,2}$ = 8.4 Hz, $J_{1,5aax}$ = 11.8 Hz, H-1), 4.44(d, 1H, *J* = 12.0 Hz), 4.41(d, 1H, *J* = 12.0 Hz), 3.65(dd, 1H, $J_{5,6a}$ = 4.2 Hz, J_{gem} = 9.0 Hz, H-6a), 3.52(dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.51(dd, 1H, $J_{2,3}$ = 8.0 Hz, H-2), 3.47(dd, 1H, H-3), 3.43(dd, 1H, $J_{5,6b}$ = 2.4 Hz, H-6b), 2.25(ddd, 1H, $J_{5,5aeq}$ = 3.4 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.83(ddd, 1H, $J_{5,5aax}$ = 12.0 Hz, H-5aax), 1.73–1.65(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.30, 138.26, 138.13, 137.91, 136.02, 132.36, 129.13, 128.70, 128.40, 128.37, 128.29, 127.89, 127.71, 127.70, 127.67, 127.62, 127.59, 127.56, 127.31, 85.98(C-3), 82.98(C-2), 82.67(C-1), 79.87(C-4), 75.89, 75.40, 75.34, 73.16, 69.02(C-6), 38.67(C-5), 31.41(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{41}H_{41}O_7NaBr$ 779.1649, found 779.1650.

4.1.15. 2,3,4,6-Tetra-O-benzyl-1-O-(4-nitrobenzenesulfonyl)-5a-carba-β-D-glucopyranose (19)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (150 mg, 0.278 mmol) in pyridine (5 mL) was added 4-nitrobenzenesulfonyl chloride (370 mg, 1.67 mmol) and DMAP (3.0 mg, 0.028 mmol). After being stirred at 50 °C for 4 h, the solution was cooled to 0 °C and MeOH was added to the solution. The solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 7:1) to give compound **19** (177 mg, 88%) as a white amorphous solid. R_f = 0.48 (hexane/EtOAc, 7:1); [α] = +2.9° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98–7.92(m, 4H), 7.36–7.14(m, 18H), 7.02–6.99(m, 2H), 4.84(d, 1H, *J* = 10.8 Hz), 4.82(d, 1H, *J* = 10.7 Hz), 4.80(d, 1H, *J* = 11.8 Hz), 4.77(d, 1H, *J* = 10.7 Hz), 4.53(ddd, 1H, $J_{1,5aeq}$ = 5.0 Hz, $J_{1,2}$ = 9.1 Hz, $J_{1,5aax}$ = 11.9 Hz, H-1), 4.51(d, 1H, *J* = 10.8 Hz), 4.44(s, 2H), 4.42(d, 1H, *J* = 11.8 Hz), 3.67(dd, 1H, $J_{5,6a}$ = 4.2 Hz, J_{gem} = 8.9 Hz, H-6a), 3.55(dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.50(m, 2H, H-2, H-3), 3.45(dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 2.29(ddd, 1H, $J_{5,5aeq}$ = 3.5 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.89(ddd, 1H, $J_{5,5aax}$ = 12.1 Hz, H-5aax), 1.73(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 150.24, 142.33, 138.22, 138.06, 138.02, 137.74, 128.82, 128.43, 128.42, 128.40, 128.19, 127.87, 127.77, 127.68, 127.62, 126.62, 124.08, 86.05(C-3), 83.56(C-1), 82.69(C-2), 79.82(C-4), 75.95, 75.37, 75.04, 73.21, 68.93(C-6), 38.69(C-5), 31.60(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{41}H_{41}O_9NNa$ 746.2394, found 746.2399.

4.1.16. Experimental for Table 2

4.1.16.1. Entry 1. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (60 mg, 0.112 mmol) in 15-crown-5 ether (132 μL, 0.667 mmol) was added NaH (4 mg, 0.112 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (30 mg, 0.045 mmol). After being stirred for 5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 6:1) to give compound **20** (3 mg, 6%) as a colorless syrup and olefin **21** (18 mg, 79%) as a colorless syrup and recovered **8** (52 mg, 86%). Date for 2,3,4,6-tetra-*O*-benzyl-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-*O*- benzyl-5a-carba-β-D-glucopyranoside (**20**): R_f = 0.20 (hexane/EtOAc, 6:1); [α] = +46.3° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.35–7.23(m, 40H), 4.95(d, 1H, *J* = 10.9 Hz), 4.95(d, 1H, *J* = 10.9 Hz), 4.94(d, 1H, *J* = 10.8 Hz), 4.92(d, 1H, *J* = 10.7 Hz), 4.90(d, 1H, *J* = 10.8 Hz), 4.83(d, 1H, *J* = 10.8 Hz), 4.82(d, 1H, *J* = 10.9 Hz), 4.82(d, 1H, *J* = 10.9 Hz), 4.67(s, 2H), 4.66(d, 1H, *J* = 11.2 Hz), 4.61(d, 1H, *J* = 11.2 Hz), 4.54(d, 1H, *J* = 10.7 Hz), 4.52(d, 1H, *J* = 10.8 Hz), 4.38(s, 2H), 3.92(dd, 1H, $J_{2',3'}$ = 9.6 Hz, $J_{3',4'}$ = 9.4 Hz, H-3′), 3.72(ddd, 1H, $J_{1',2'}$ = 2.7 Hz, $J_{1',5a'ax}$ = 1.3 Hz, $J_{1',5a'eq}$ = 3.7 Hz, H-1′), 3.70–3.67(m, 2H, H-6), 3.64(dd, 1H, $J_{5',6'a}$ = 4.3 Hz, J_{gem} = 8.9 Hz, H-6′a), 3.55–3.50(m, 3H, H-1, H-2, H-3), 3.47(dd, 1H, $J_{4',5'}$ = 9.0 Hz, H-4′), 3.46(dd, 1H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 9.0 Hz, H-4), 3.38(dd, 1H, H-2′),

3.34(dd, 1H, $J_{5',6'b}$ = 2.5 Hz, H-6′b), 2.16(ddd, 1H, $J_{1,5aeq}$ = 3.5 Hz, $J_{5,5aeq}$ = 3.5 Hz, J_{gem} = 13.0 Hz, H-5aeq), 2.07(m, 1H, H-5′), 1.85(ddd, 1H, $J_{5',5a'eq}$ = 3.7 Hz, J_{gem} = 14.3 Hz, H-5a′eq), 1.67(m, 1H, H-5), 1.52(ddd, 1H, $J_{1,5aax}$ = 10.9 Hz, $J_{5,5aax}$ = 10.9 Hz, H-5aax), 1.39(ddd, 1H, $J_{5',5a'ax}$ = 13.1 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.12, 138.94, 138.91, 138.83, 138.78, 138.76, 138.57, 128.36, 128.33, 128.31, 128.30, 128.27, 128.04, 128.01, 127.87, 127.79, 127.65, 127.64, 127.59, 127.52, 127.44, 127.42, 127.36, 86.40(C-3), 86.01(C-2), 83.88(C-3′), 83.83(C-2′), 80.96(C-4′), 80.71(C-4), 80.34(C-1), 75.79, 75.68, 75.22, 75.13, 74.87(C-1′), 72.93, 72.46, 72.26, 70.23(C-6), 69.95(C-6′), 39.19(C-5), 37.35(C-5′), 30.48(C-5a), 29.28(C-5′a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{70}H_{74}O_9Na$ 1081.5225, found 1081.5225.

Date for olefin **21**: R_f = 0.50 (hexane/EtOAc, 6:1); [α] = +105.1° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.18(m, 20H), 5.72(ddd, 1H, $J_{1,2}$ = 2.2 Hz, $J_{1,5}$ = 2.2 Hz, $J_{1,5a}$ = 10.2 Hz, H-1), 5.67(ddd, 1H, $J_{5,5a}$ = 1.6 Hz, $^4J_{2,5a}$ = 1.6 Hz, H-5a), 4.91(s, 2H), 4.91(d, 1H, *J* = 10.9 Hz), 4.69(s, 2H), 4.46(d, 1H, *J* = 12.2 Hz), 4.45(d, 1H, *J* = 10.9 Hz), 4.40(d, 1H, *J* = 12.2 Hz), 4.25(m, 1H, H-2), 3.81(dd, 1H, $J_{2,3}$ = 7.7 Hz, $J_{3,4}$ = 10.0 Hz, H-3), 3.67(dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 3.54(dd, 1H, $J_{5,6a}$ = 3.5 Hz, J_{gem} = 9.0 Hz, H-6a), 3.51(dd, 1H, $J_{5,6b}$ = 4.7 Hz, H-6b), 1.26(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.92, 138.60, 138.53, 138.24, 129.19(C-5a), 128.38, 128.35, 128.33, 128.06, 127.89, 127.85, 127.76, 127.62, 127.59, 127.49, 126.84(C-1), 85.35(C-3), 80.89(C-2), 78.42(C-4), 75.28, 75.27, 73.10, 72.05, 69.20(C-6), 44.39(C-5); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{36}O_4Na$ 543.2506, found 543.2502.

4.1.16.2. Entry 2. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (60 mg, 0.112 mmol) in 15-crown-5 ether (132 μL, 0.667 mmol) was added NaH (4 mg, 0.112 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (30 mg, 0.045 mmol). After being stirred for 7 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 6:1) to give compound **20** (5 mg, 10%) as a colorless syrup and olefin **21** (9 mg, 40%) as a colorless syrup and recovered **8** (40 mg, 66%).

4.1.16.3. Entry 3. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (60 mg, 0.112 mmol) in 15-crown-5 ether (66 μL, 0.335 mmol) was added NaH (4 mg, 0.112 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (30 mg, 0.045 mmol). After being stirred for 11 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 6:1) to give compound **20** (10 mg, 21%) as a colorless syrup and olefin **21** (11 mg, 47%) as a colorless syrup and recovered **8** (40 mg, 67%).

4.1.16.4. Entry 4. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (60 mg, 0.112 mmol) in 15-crown-5 ether (33 μL, 0.167 mmol) was added NaH (4 mg, 0.112 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (30 mg, 0.045 mmol). After being stirred for 9 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 6:1) to give compound **20** (10 mg, 22%) as a colorless syrup and olefin **21** (11 mg, 49%) as a colorless syrup and recovered **8** (44 mg, 73%).

4.1.16.5. Entry 5. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (40 mg, 0.074 mmol) in THF (44 μL) was added NaH (3 mg, 0.074 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (20 mg, 0.030 mmol). After being stirred for 10 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Hexane/EtOAc, 6:1) to give compound **20** (3 mg, 11%) as a colorless syrup and olefin **21** (8 mg, 52%) as a colorless syrup and recovered **8** (27 mg, 68%).

4.1.16.6. Entry 6. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (37 mg, 0.069 mmol) in 15-crown-5 ether (41 μL, 0.207 mmol) was added NaH (3 mg, 0.069 mmol), and the mixture was stirred for 30 min under Ar. After being stirred for 30 min, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-methanesulfonyl-5a-carba-β-D-glucopyranose **15** (17 mg, 0.028 mmol). After being stirred for 6 h, to the solution was added, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Hexane/EtOAc, 10:1) to give olefin **21** (6 mg, 41%) as a colorless syrup and compound **13** (4 mg, 29%) and recovered **8** (27 mg, 73%).

4.1.16.7. Entry 7. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (62 mg, 0.115 mmol) in 15-crown-5 ether (68 μL, 0.345 mmol) was added NaH (4 mg, 0.115 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-chloromethanesulfonyl-5a-carba-β-D-glucopyranose **16** (30 mg, 0.046 mmol). After being stirred for 8 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Toluene/EtOAc, 20:1) to give olefin **21** (4 mg, 16%) as a colorless syrup and recovered mesylate **15** (5 mg, 18%) and recovered **8** (57 mg, 92%).

4.1.16.8. Entry 8. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (58 mg, 0.108 mmol) in 15-crown-5 ether (63 μL, 0.319 mmol) was added NaH (4 mg, 0.108 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-(4-toluenesulfonyl)-5a-carba-β-D-glucopyranose **17** (30 mg, 0.043 mmol). After being stirred for overnight, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 6:1) to give olefin **21** (2 mg, 10%) as a colorless syrup and recovered tosylate **17** (17 mg, 56%) and recovered **8** (44 mg, 77%).

4.1.16.9. Entry 9. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (89 mg, 0.165 mmol) in 15-crown-5 ether (97 μL, 0.488 mmol) was added NaH (7 mg, 0.165 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*p*-bromobenzenesulfonyl)-5a-carba-β-D-glucopyranose **18** (50 mg, 0.066 mmol). After being stirred for 26 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Toluene/EtOAc, 20:1) to give compound **22** (15 mg, 19%) as a colorless syrup and recovered **18** (17 mg, 34%) and recovered **8** (62 mg, 70%). Date for compound **22**: R_f = 0.31 (hexane/EtOAc, 3:1); [α] = +30.4° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75(m, 2H), 7.35–7.12(m, 40H), 6.65(m, 2H), 4.98(d, 1H, *J* = 10.9 Hz), 4.98(d, 1H, *J* = 11.1 Hz), 4.89(d, 1H, *J* = 11.6 Hz), 4.88(d, 1H,

J = 10.9 Hz), 4.86(d, 1H, J = 11.1 Hz), 4.83(d, 1H, J = 11.3 Hz), 4.80(d, 1H, J = 11.9 Hz), 4.76(d, 1H, J = 11.9 Hz), 4.71(d, 1H, J = 10.0 Hz), 4.70(s, 2H), 4.66(d, 1H, J = 10.0 Hz), 4.50(m, 1H, H-1′), 4.50(d, 1H, J = 11.6 Hz), 4.47(d, 1H, J = 11.3 Hz), 4.44(d, 1H, J = 13.0 Hz), 4.39(d, 1H, J = 13.0 Hz), 3.86–3.80(m, 2H, H-6a, H-6b), 3.64(dd, 1H, $J_{5',6'a}$ = 4.1 Hz, J_{gem} = 9.0 Hz, H-6′a), 3.62–3.54(m, 2H, H-2, H-3), 3.58(m, 1H, H-1), 3.52(m, 1H, H-4), 3.51(dd, 1H, $J_{3',4'}$ = 9.9 Hz, $J_{4',5'}$ = 10.3 Hz, H-4′), 3.51(dd, 1H, $J_{1',2'}$ = 10.0 Hz, $J_{2',3'}$ = 9.6 Hz, H-2′), 3.46(dd, 1H, H-3′), 3.42(dd, 1H, $J_{5',6'b}$ = 2.2 Hz, H-6′b), 2.26(ddd, 1H, $J_{1',5a'eq}$ = 4.7 Hz, $J_{5',5a'eq}$ = 3.4 Hz, J_{gem} = 12.8 Hz, H-5a′eq), 2.18(ddd, 1H, $J_{1,5aeq}$ = 3.5 Hz, $J_{5,5aeq}$ = 3.5 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.82(m, 1H, H-5), 1.81(ddd, $J_{1',5a'ax}$ = 12.3 Hz, $J_{5',5a'ax}$ = 12.3 Hz, H-5a′ax), 1.69(m, 1H, H-5′), 1.50(ddd, 1H, $J_{1,5aax}$ = 11.1 Hz, $J_{5,5aax}$ = 11.1 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.68, 138.71, 138.56, 138.48, 138.35, 138.18, 138.15, 138.06, 129.84, 128.64, 128.46, 128.41, 128.36, 128.33, 128.15, 128.13, 127.99, 127.87, 127.83, 127.81, 127.68, 127.67, 127.65, 127.62, 127.60, 127.57, 127.51, 127.39, 114.56, 86.28(C-3), 85.93(C-2), 85.85(C-3′), 83.16(C-2′), 81.84(C-1′), 79.95(C-1, C-4), 79.92(C-4′), 75.90, 75.86, 75.84, 75.39, 75.33, 75.28, 73.10, 72.55, 69.11(C-6′), 68.09(C-6), 38.68(C-5′), 38.15(C-5), 31.32(C-5a′), 30.21(C-5a); HRMS(ESI) m/z: calcd for $[M+Na]^+$ $C_{76}H_{78}O_{12}NaS$ 1237.5106, found 1237.5102.

4.1.16.10. Entry 10. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (40 mg, 0.075 mmol) in 15-crown-5 ether (44 μL, 0.22 mmol) was added NaH (3 mg, 0.075 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-(4-nitrobenzenesulfonyl)-5a-carba-β-D-glucopyranose **19** (22 mg, 0.030 mmol). After being stirred for 4 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Toluene/EtOAc, 20:1) to give compound **22** (7 mg, 19%) as a colorless syrup and recovered **8** (23 mg, 59%).

4.1.16.11. Entry 11. To a solution of 1,2,3,4-tetra-*O*-Benzyl-5a-carba-β-D-glucopyranose **8** (20 mg, 0.037 mmol) in 15-crown-5 ether (22 μL, 0.109 mmol) was added NaH (4 mg, 0.110 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (10 mg, 0.015 mmol). After being stirred for 5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **20** (5.8 mg, 37%) as a colorless syrup and olefin **21** (2.0 mg, 26%) as a colorless syrup and recovered **8** (17 mg, 88%).

4.1.16.12. Entry 12. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-ββ-D-glucopyranose **8** (20 mg, 0.037 mmol) in 15-crown-5 ether (22 μL, 0.11 mmol) was added NaH (1 mg, 0.037 mmol). After being stirred for 30 min under Ar, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (10 mg, 0.015 mmol). After being stirred at 50 °C for 23 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 6:1) to give **20** (4 mg, 24%) as a colorless syrup and olefin **21** (5 mg, 70%) as a colorless syrup and recovered **8** (17 mg, 84%).

4.1.16.13. Entry 13. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (80 mg, 0.149 mmol) in THF (44 μL) was added NaH (6 mg, 0.149 mmol) and 15-crown-5 ether (44 μL, 0.222 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (40 mg, 0.060 mmol). After being stirred for 6.5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **20** (29 mg, 47%) as a white amorphous solid and olefin **21** (10 mg, 33%) as a colorless syrup and recovered **8** (61 mg, 76%).

4.1.16.14. Entry 14. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (80 mg, 0.149 mmol) in MeCN (44 μL) was added NaH (6 mg, 0.149 mmol) and 15-crown-5 ether (44 μL, 0.222 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **21** (40 mg, 0.060 mmol). After being stirred for 10 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **20** (21 mg, 33%) as a white amorphous solid and olefin **21** (10 mg, 33%) as a colorless syrup and recovered **8** (68 mg, 85%).

4.1.16.15. Entry 15. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (60 mg, 0.112 mmol) in HMPA (33 μL) was added NaH (4 mg, 0.112 mmol) and 15-crown-5 ether (33 μL, 0.167 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (30 mg, 0.045 mmol). After being stirred for 5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **20** (13 mg, 28%) as a white amorphous solid and olefin **21** (8 mg, 37%) as colorless syrup and recovered **8** (57 mg, 95%).

4.1.16.16. Entry 16. To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (60 mg, 0.112 mmol) in 1,3-dimethyl-2-imidazolidinone (33 μL) was added NaH (4 mg, 0.112 mmol) and 15-crown-5 ether (33 μL, 0.167 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (30 mg, 0.045 mmol). After being stirred for 17 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **20** (21 mg, 46%) as a white amorphous solid and olefin **21** (7 mg, 28%) as a colorless syrup and recovered **8** (44 mg, 74%).

*4.1.17. 4,6-O-Benzylidene-2,3-O-isopropylidene-1-O-(p-methoxybenzyl)-5a-carba-β-D-glucopyranose (**23**)*

To a solution of 4,6-*O*-benzylidene-2,3-*O*-isopropylidene-5a-carba-β-D-glucopyranose **11** (2.89 g, 9.43 mmol) in DMF (25 mL) and NaH (1.13 g, 28.3 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 4-methoxybenzyl chloride (3.84 mL, 28.3 mmol). After being stirred for 1 h, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 5:1) to give compound **23** (3.63 g, 90%) as a white amorphous solid. R_f = 0.22 (hexane/EtOAc, 5:1); $[\alpha] = +4.2°$ (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.28(m, 7H), 6.90–6.86(m, 2H), 5.56(s, 1H, PhCH), 4.75(d, 1H, J = 11.5 Hz), 4.59(d, 1H, J = 11.5 Hz), 4.15(dd, 1H, $J_{5,6a}$ = 4.0 Hz,

J_{gem} = 10.9 Hz, H-6a), 3.80(s, 3H, OCH_3), 3.77(dd, 1H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 3.74(ddd, 1H, $J_{1,5aeq}$ = 4.3 Hz, $J_{1,2}$ = 9.1 Hz, $J_{1,5aax}$ = 10.2 Hz, H-1), 3.71(dd, 1H, $J_{5,6b}$ = 10.9 Hz, H-6b), 3.63(dd, 1H, $J_{2,3}$ = 9.4 Hz, H-3), 3.56(dd, 1H, H-2), 1.89(ddd, 1H, $J_{5,5aeq}$ = 4.3 Hz, J_{gem} = 14.3 Hz, H-5aeq), 1.88(m, 1H, H-5), 1.49(s, 3H, CH_3), 1.47(s, 3H, CH_3), 1.14(ddd, 1H, $J_{5,5aax}$ = 10.2 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.21. 137.61, 130.43, 129.36, 128.96, 128.13, 126.42, 113.79, 111.52, 101.65(PhCH), 82.48(C-2), 80.49(C-4), 78.10(C-3), 75.57(C-1), 71.36, 70.91, 55.26(OCH_3), 36.40(C-5), 30.20(C-5a), 26.88(CH_3), 26.87(CH_3); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{30}O_6Na$ 449.1935, found 449.1935.

4.1.18. 4,6-O-Benzylidene-1-O-(p-methoxybenzyl)-5a-carba-β-D-glucopyranose (24)

To a solution of 4,6-*O*-benzylidene-2,3-*O*-isopropylidene-1-*O*-(*p*-methoxybenzyl)-5a-carba-β-D-glucopyranose **23** (506 mg, 1.19 mmol) in MeOH (20 mL) was added AcOH (2 mL). After being stirred at 60 °C for 1.5 h, the solvent was concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 1:1) to give compound **24** (351 mg, 77%) as a white amorphous solid. R_f = 0.20 (hexane/EtOAc, 1:2); [α] = −38.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.23(m, 7H), 6.91–6.86(m, 2H), 5.52(s, 1H, PhCH), 4.62(d, 1H, *J* = 11.2 Hz), 4.53(d, 1H, *J* = 11.2 Hz), 4.16(dd, 1H, $J_{5,6a}$ = 4.5 Hz, J_{gem} = 11.0 Hz, H-6a), 3.80(s, 3H, OCH_3), 3.64(dd, 1H, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.61(dd, 1H, $J_{5,6b}$ = 11.0 Hz, H-6b), 3.55(dd, 1H, $J_{1,2}$ = 9.0 Hz, H-2), 3.44(dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 3.42(ddd, 1H, $J_{1,5aeq}$ = 4.3 Hz, $J_{1,5aax}$ = 11.1 Hz, H-1), 1.89(ddd, 1H, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 12.7 Hz, H-5aeq), 1.79(m, 1H, H-5), 1.05(ddd, 1H, $J_{5,5aax}$ = 11.3 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.38, 137.75, 130.11, 129.40, 129.08, 128.28, 126.24, 113.95, 101.81(PhCH), 82.26(C-4). 78.72(C-1), 76.91(C-2), 74.29(C-3), 71.65, 70.87(C-6), 55.27(OCH_3), 33.76(C-5), 27.75(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{26}O_6Na$ 409.1622, found 409.1622.

4.1.19. 2,3-Di-O-benzyl-4,6-O-benzylidene-1-O-(p-methoxybenzyl)-5a-carba-β-D-glucopyranose (25)

To a solution of 4,6-*O*-benzylidene-1-*O*-(*p*-methoxybenzyl)-5a-carba-β-D-glucopyranose **24** (400 mg, 1.04 mmol) in DMF (3 mL) and NaH (207 mg, 5.18 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added BnBr (615 μL, 5.18 mmol). After being stirred for overnight, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 5:1) to give compound **25** (543 mg, 93%) as a white amorphous solid. R_f = 0.20 (hexane/EtOAc, 1:2); [α] = −22.4° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.22(m, 17H), 6.87–6.83(m, 2H), 5.57(s, 1H, PhCH), 4.94(d, 1H, *J* = 11.0 Hz), 4.89(s, 2H), 4.78(d, 1H, *J* = 11.0 Hz), 4.62(d, 1H, *J* = 11.3 Hz), 4.59(d, 1H, *J* = 11.3 Hz), 4.18(dd, 1H, $J_{5,6a}$ = 4.5 Hz, J_{gem} = 11.0 Hz, H-6a), 3.80(s, 3H, OCH_3), 3.67(dd, 1H, $J_{2,3}$ = 8.9 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.62(dd, 1H, $J_{5,6b}$ = 10.9 Hz, H-6b), 3.61(dd, 1H, $J_{4,5}$ = 9.1 Hz, H-4), 3.56(ddd, 1H, $J_{1,2}$ = 8.9 Hz, $J_{1,5aeq}$ = 3.4 Hz, $J_{1,5aax}$ = 11.0 Hz, H-1), 3.54(dd, 1H, H-2), 1.86(ddd, 1H, $J_{5,5aeq}$ = 3.4 Hz, J_{gem} = 12.6 Hz, H-5aeq), 1.78(m, 1H, H-5), 1.07(ddd, 1H, $J_{5,5aax}$ = 11.0 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.22, 138.86, 138.77, 138.18, 130.57, 129.32, 128.71, 128.31, 128.28, 128.17, 128.16, 128.02, 127.55, 127.53, 125.93, 113.83, 101.03, 85.53(C-2), 83.50(C-4), 83.20(C-3), 79.72(C-1), 76.05, 75.61, 72.39, 71.02(C-6), 55.27(OCH_3), 33.83(C-5), 28.57(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{38}O_6Na$ 589.2561, found 589.2558.

4.1.20. 2,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-glucopyranose (26)

To a solution of *2,3-di-O-benzyl-4,6-O-benzylidene-1-O-(p-methoxybenzyl)-5a-carba-β-D-glucopyranose* **25** (645 mg, 1.14 mmol) in CH_2Cl_2–H_2O (18:1, 13.3 mL) was added DDQ (388 mg, 1.71 mmol). After being stirred for 1 h, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to give compound **26** (431 mg, 85%) as a white amorphous solid. R_f = 0.10 (hexane/EtOAc, 4:1); [α] = −63.9° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.25(m, 15H), 5.59(s, 1H, PhCH), 5.05(d, 1H, *J* = 11.3 Hz), 5.01(d, 1H, *J* = 10.9 Hz), 4.77(d, 1H, *J* = 10.9 Hz), 4.68(d, 1H, *J* = 11.3 Hz), 4.20(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 11.0 Hz, H-6a), 3.70(dd, 1H, $J_{2,3}$ = 8.9 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.66(dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.64(dd, 1H, $J_{5,6b}$ = 11.0 Hz, H-6b), 3.63(m, 1H, H-1), 3.35(dd, 1H, $J_{1,2}$ = 8.8 Hz, H-2), 2.40(d, 1H, $J_{1,OH}$ = 1.9 Hz, OH), 1.87(m, 1H, H-5), 1.79(ddd, 1H, $J_{5,5aeq}$ = 3.5 Hz, $J_{1,5aeq}$ = 4.7 Hz, J_{gem} = 12.7 Hz, H-5aeq), 1.09(ddd, 1H, $J_{1,5aax}$ = 11.6 Hz, $J_{5,5aax}$ = 11.6 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.53, 138.13, 138.13, 128.76, 128.65, 128.37, 128.21, 127.98, 127.97, 127.69, 125.92, 101.7(PhCH), 85.78(C-2), 84.15(C-4), 83.07(C-3), 75.62, 75.36, 71.19(C-1), 71.02(C-6), 34.16(C-5), 29.49(C-5a); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{28}H_{30}O_5Na$ 469.1985, found 469.1983.

4.1.21. 2,3-Di-O-benzyl-4,6-O-Benzylidene-1-O-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose (27)

To a solution of 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranose **26** (300 mg, 0.672 mmol) in CH_2Cl_2 (8 mL) at −15 °C was added 2,6-di-*t*-butyl-4-methylpyridine (138 mg, 0.672 mmol) and Tf_2O (226 μL, 1.34 mmol). After being stirred for 15 min, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Toluene) to give compound **27** (311 mg, 80%) as a white amorphous solid. R_f = 0.12 (Toluene); [α] = −23.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.25(m, 15H), 5.58(s, 1H, PhCH), 4.96(d, 1H, *J* = 10.8 Hz), 4.88(d, 1H, *J* = 10.2 Hz), 4.88(ddd, 1H, $J_{1,5aeq}$ = 5.2 Hz, $J_{1,2}$ = 8.7 Hz, $J_{1,5aax}$ = 11.8 Hz, H-1), 4.80(d, 1H, *J* = 10.2 Hz), 4.74(d, 1H, *J* = 10.8 Hz), 4.24(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 11.0 Hz, H-6a), 3.73(dd, 1H, $J_{2,3}$ = 8.8 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.67(dd, 1H, $J_{5,6b}$ = 11.0 Hz, H-6b), 3.66(dd, 1H, H-2), 3.65(dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 2.08(ddd, 1H, $J_{5,5aeq}$ = 3.2 Hz, J_{gem} = 12.5 Hz, H-5aeq), 1.87(m, 1H, H-5), 1.48(ddd, 1H, $J_{5,5aax}$ = 11.8 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.06, 137.62, 137.33, 128.97, 128.40, 128.34, 128.27, 128.21, 128.18, 127.88, 127.84, 125.90, 101.28(PhCH), 87.07(C-1), 82.91(C-3), 82.70(C-4), 81.81(C-2), 76.14, 75.82, 70.36(C-6), 33.11(C-5), 29.01(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{29}H_{29}O_7NaSF_3$ 601.1478, found 601.1475.

4.1.22. 4,6-O-Benzylidene-1-O-(p-methoxybenzyl)-2,3-O-(o-xylylene)-5a-carba-β-D-glucopyranose (28)

To a solution of 4,6-*O*-benzylidene-1-*O*-(*p*-methoxybenzyl)-5a-carba-β-D-glucopyranose **24** (366 mg, 0.947 mmol) in DMF(60 mL) and NaH (189 mg, 4.73 mmol), and the mixture was stirred for 30 min under Ar. To the solution was added α,α′-dibromo-*o*-xylene (500 mg, 1.89 mmol). After being stirred for overnight, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Toluene → Toluene/EtOAc, 7:1) to give compound **28** (256 mg, 56%) as a white amorphous solid. R_f = 0.43 (Toluene/EtOAc, 7:1); [α] = +48.2° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50(m, 2H), 7.39–7.13(m, 9H), 6.92–6.89(m, 2H), 5.52(s, 1H, PhCH), 5.20(d, 1H, *J* = 14.2 Hz), 5.17(d, 1H, *J* = 13.8 Hz), 5.07(d, 1H, *J* = 14.2 Hz), 4.98(d, 1H, *J* = 13.8 Hz), 4.72(d, 1H, *J* = 11.4 Hz), 4.62(d, 1H, *J* = 11.4 Hz), 4.12(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 11.2 Hz, H-6a), 3.82(s, 3H, OCH_3), 3.62(dd, 1H, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 8.9 Hz, H-3), 3.53(dd, 1H, $J_{1,2}$ = 8.3 Hz, H-2), 3.53(dd, 1H, $J_{5,6b}$ = 11.6 Hz, H-6b), 3.49(ddd, 1H, $J_{1,5aeq}$ = 4.6 Hz, $J_{1,5aax}$ = 11.1 Hz, H-1), 3.46(dd,

1H, $J_{4,5}$ = 9.3 Hz, H-4), 1.78(ddd, 1H, $J_{5,5aeq}$ = 3.2 Hz, J_{gem} = 12.7 Hz, H-5aeq), 1.77(m, 1H, H-5), 1.03(ddd, 1H, $J_{5,5aax}$ = 11.1 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.21, 138.12, 137.18, 137.09, 130.83, 130.12, 129.42, 129.20, 129.02, 128.84, 128.20, 127.79, 127.70, 126.25, 113.83, 101.50(PhCH), 85.69(C-2), 82.30(C-3), 81.74(C-4), 78.62(C-1), 73.67, 73.24, 72.48, 70.95(C-6), 55.29(OCH_3), 33.77(C-5), 28.51(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{32}O_6Na$ 511.2091, found 511.2095.

4.1.23. 4,6-O-Benzylidene-2,3-O-(o-xylylene)-5a-carba-β-D-glucopyranose (29)

To a solution of 4,6-*O*-benzylidene-1-*O*-(*p*-methoxybenzyl)-2,3-*O*-(*o*-xylylene)-5a-carba-β-D-glucopyranose **28** (28 mg, 0.057 mmol) in CH_2Cl_2-H_2O (18:1, 570 μL) was added DDQ (14 mg, 0.063 mmol). After being stirred for 40 min, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to give compound **29** (20 mg, 97%) as a colorless syrup. R_f = 0.15 (Toluene/EtOAc, 5:1); [α] = +111.8° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52(m, 12H), 7.42–7.21(m, 6H), 7.09–7.07(m, 1H), 5.57(s, 1H, PhCH), 5.36(d, 1H, *J* = 12.6 Hz), 5.23(d, 1H, *J* = 15.2 Hz), 4.99(d, 1H, *J* = 15.2 Hz), 4.81(d, 1H, *J* = 12.6 Hz), 4.17(dd, 1H, $J_{5,6a}$ = 4.3 Hz, J_{gem} = 10.9 Hz, H-6a), 3.63(dd, 1H, $J_{5,6b}$ = 10.9 Hz, J_{gem} = 10.9 Hz, H-6b), 3.59(m, 1H, H-1), 3.59–3.52(m, 2H, H-3, H-4), 3.40(dd, 1H, $J_{1,2}$ = 8.8 Hz, $J_{2,3}$ = 8.8 Hz, H-2), 2.66(d, 1H, $J_{1,OH}$ = 1.7 Hz, OH), 1.78(ddd, 1H, $J_{1,5aeq}$ = 4.9 Hz, $J_{5,5aeq}$ = 3.0 Hz, J_{gem} = 13.2 Hz, H-5aeq), 1.13(ddd, 1H, $J_{1,5aax}$ = 11.5 Hz, $J_{5,5aax}$ = 11.5 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.15, 137.46, 136.39, 131.76, 128.83, 128.32, 128.21, 127.90, 127.55, 126.11, 101.42(PhCH), 84.97(C-2), 82.40(C-4), 82.34(C-3), 73.96, 72.83, 71.04(C-1), 70.92(C-6), 34.16(C-5), 29.28(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{24}O_5Na$ 391.1516, found 391.1519.

4.1.24. 4,6-O-Benzylidene-1-O-trifluoromethanesulfonyl-2,3-O-(o-xylylene)-5a-carba-β-D-glucopyranose (30)

To a solution of 4,6-*O*-benzylidene-2,3-*O*-(*o*-xylylene)-5a-carba-β-D-glucopyranose **29** (52 mg, 0.141 mmol) in CH_2Cl_2 (500 μL) and pyridine (500 μL) at −10 °C was added Tf_2O (36 μL, 0.212 mmol). After being stirred for 2 h, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 8:1) to give compound **30** (59 mg, 85%) as a white amorphous solid. R_f = 0.19 (Hexane/EtOAc, 8:1); [α] = +43.4° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.14(m, 9H), 5.53(s, 1H, PhCH), 5.13(d, 1H, *J* = 13.9 Hz), 5.12(d, 1H, *J* = 14.2 Hz), 5.04(d, 1H, *J* = 14.2 Hz), 5.03(d, 1H, *J* = 13.9 Hz), 4.81(brddd, 1H, $J_{1,2}$ = 9.1 Hz, $J_{1,5aeq}$ = 5.3 Hz, $J_{1,5aax}$ = 11.8 Hz, H-1), 4.20(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 11.1 Hz, H-6a), 3.70–3.64(m, 2H, H-2, H-3), 3.62(dd, 1H, $J_{5,6b}$ = 11.0 Hz), 3.51(brdd, 1H, $J_{3,4}$ = 9.9 Hz, $J_{4,5}$ = 9.9 Hz, H-4), 2.04(ddd, 1H, $J_{5,5aeq}$ = 3.2 Hz, J_{gem} = 12.5 Hz, H-5aeq), 1.85(m, 1H, H-5), 1.46(ddd, 1H, $J_{5,5aax}$ = 12.3 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.60, 136.52, 136.18, 129.97, 129.86, 129.07, 128.29, 128.12, 126.20, 101.68(PhCH), 86.87(C-1), 82.25(C-2), 81.50(C-3), 80.79(C-4), 73.57, 73.47, 70.31(C-6), 33.18(C-5), 28.92(C-5a); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{23}O_7NaF_3S$ 523.1009, found523.1007.

4.1.25. 4,6-Di-O-benzyl-1-O-(p-methoxybenzyl)-2,3-O-(o-xylylene)-5a-carba-β-D-glucopyranose (31)

To a solution of 4,6-*O*-benzylidene-1-*O*-(*p*-methoxybenzyl)-2,3-*O*-(*o*-xylylene)-5a-carba-β-D-glucopyranose **28** (339 mg, 0.694 mmol) was dissolved in AcOH (6 mL) and H_2O (4 mL) at 60 °C, and the mixture was stirred for 1 h. The solvent was concentrated *in vacuo*. To a solution of the residue was dissolved in DMF (3 mL) was added NaH (139 mg, 3.47 mmol), and the mixture was stirred for 30 min. After being cooled to 0 °C, to the solution was added BnBr (412 μL, 3.47 mmol). After being stirred for overnight, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 5:1) to give compound **31** (323 mg, 80%) as a colorless syrup. R_f = 0.28 (Hexane/EtOAc, 5:1); [α] = +69.8° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.22(m, 14H), 7.14–7.12(m, 2H), 6.91–6.87(m, 2H), 5.18(d, 1H, *J* = 13.8 Hz), 5.16(d, 1H, *J* = 14.3 Hz), 5.08(d, 1H, *J* = 14.3 Hz), 4.98(d, 1H, *J* = 13.8 Hz), 4.94(d, 1H, *J* = 11.0 Hz), 4.69(d, 1H, *J* = 11.4 Hz), 4.62(d, 1H, *J* = 11.4 Hz), 4.53(d, 1H, *J* = 11.0 Hz), 4.44(d, 1H, *J* = 12.2 Hz), 4.41(d, 1H, *J* = 12.2 Hz), 3.81(s, 3H. OCH_3), 3.54–3.51(m, 2H, H-6), 3.49(dd, 1H, $J_{2,3}$ = 8.6 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.43(dd, 1H, $J_{1,2}$ = 8.4 Hz, H-2), 3.38(m, 1H, H-1), 3.37(dd, 1H, $J_{4,5}$ = 10.5 Hz, H-4), 2.09(ddd, 1H, $J_{1,5aeq}$ = 3.7 Hz, $J_{5,5aeq}$ = 3.7 Hz, J_{gem} = 13.2 Hz, H-5aeq), 1.64(m, 1H, H-5), 1.40(ddd, 1H, $J_{1,5aax}$ = 11.3 Hz, $J_{5,5aax}$ = 11.3 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.09, 138.96, 138.43, 137.46, 137.19, 131.15, 129.67, 129.13, 129.10, 128.35, 128.31, 128.00, 127.67, 127.54, 127.51, 127.50, 113.77, 87.18(C-3), 86.57(C-2), 79.96(C-4), 78.46(C-1), 75.11, 74.09, 73.93, 73.10, 72.22, 70.24(C-6), 55.28(CH_3), 38.69(C-5), 30.69(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{37}H_{40}O_6Na$ 603.2717, found 603.2717.

4.1.26. 4,6-Di-O-benzyl-2,3-O-(o-xylylene)-5a-carba-β-D-glucopyranose (32)

To a solution of 4,6-di-*O*-benzyl-1-*O*-(*p*-methoxybenzyl)-2,3-*O*-(*o*-xylylene)-5a-carba-β-D-glucopyranose **31** (150 mg, 0.258 mmol) in CH_2Cl_2-H_2O (18:1, 2.52 mL) was added DDQ (64 mg, 0.284 mmol). After being stirred for 2 h, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to give compound **32** (107 mg, 91%) as a colorless syrup. R_f = 0.10 (Toluene/EtOAc, 3:1); [α] = +158.8° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.04(m, 14H), 5.29(d, 1H, *J* = 13.0 Hz), 5.21(d, 1H, *J* = 15.2 Hz), 5.01(d, 1H, *J* = 15.2 Hz), 4.93(d, 1H, *J* = 11.0 Hz), 4.83(d, 1H, *J* = 13.0 Hz), 4.59(d, 1H, *J* = 11.0 Hz), 4.44(s, 2H), 3.58(dd, 1H, $J_{5,6a}$ = 5.0 Hz, J_{gem} = 8.8 Hz, H-6a), 3.48(ddd, 1H, $J_{1,2}$ = 8.9 Hz, $J_{1,5aeq}$ = 4.6 Hz, $J_{1,5aax}$ = 11.8 Hz, H-1), 3.48(dd, 1H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 8.8 Hz, H-4), 3.47(dd, 1H, $J_{5,6b}$ = 2.9 Hz, H-6b), 3.41(dd, 1H, $J_{2,3}$ = 8.9 Hz, H-3), 3.29(dd, 1H, H-2), 2.62(br, 1H, 1-OH), 2.01(ddd, 1H, $J_{5,5aeq}$ = 3.4 Hz, J_{gem} = 12.9 Hz, H-5aeq), 1.67(m, 1H, H-5), 1.53(ddd, 1H, $J_{5,5aax}$ = 11.8 Hz, J_{gem} = 12.9 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.74, 138.39, 137.43, 136.60, 131.16, 128.41, 128.32, 128.10, 128.01, 127.74, 127.66, 127.51, 127.40, 87.04(C-3), 85.44(C-2), 80.51(C-4), 75.36, 74.26, 73.24, 73.06, 70.77(C-1), 69.84(C-6), 39.00(C-5), 31.60(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{29}H_{32}O_5Na$ 483.2142, found483.2142.

4.1.27. 4,6-Di-O-benzyl-2,3-O-(o-xylylene)-1-O-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose (33)

To a solution of 4,6-di-*O*-benzyl-2,3-*O*-(*o*-xylylene)-5a-carba-β-D-glucopyranose **32** (55 mg, 0.119 mmol) in CH_2Cl_2 (500 μL) and pyridine (500 μL) at −10 °C was added Tf_2O (30 μL, 0.179 mmol). After being stirred for 2 h, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 8:1) to give compound **33** (58 mg, 83%) as a white amorphous solid. R_f = 0.33 (hexane/EtOAc, 8:1); [α] = +67.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.12(m, 14H), 5.15(d, 1H, *J* = 13.7 Hz), 5.10(d, 1H, *J* = 14.5 Hz), 5.05(d, 1H, *J* = 14.5 Hz), 4.98(d, 1H, *J* = 13.7 Hz), 4.93(d, 1H, *J* = 11.0 Hz), 4.74(ddd, 1H, $J_{1,5aeq}$ = 5.2 Hz, $J_{1,2}$ = 8.8 Hz, $J_{1,5aax}$ = 12.2 Hz, H-1), 4.53(d, 1H, *J* = 11.0 Hz), 4.44(d,

1H, J = 12.0 Hz), 4.39(d, 1H, J = 12.0 Hz), 3.48(dd, 1H, $J_{5,6a}$ = 4.5 Hz, J_{gem} = 9.1 Hz, H-6a), 3.55(dd, 1H, $J_{2,3}$ = 8.8 Hz, H-2), 3.51(dd, 1H, $J_{3,4}$ = 8.8 Hz, H-3), 3.45(dd, 1H, $J_{4,5}$ = 9.0 Hz, H-4), 3.44(dd, 1H, $J_{5,6b}$ = 2.6 Hz, H-6b), 2.18(ddd, 1H, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 12.8 Hz, H-5aeq), 1.88(ddd, 1H, $J_{5,5aax}$ = 12.4 Hz, H-5aax), 1.69(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.54, 138.00, 136.56, 129.85, 129.17, 129.03, 128.42, 128.41, 128.22, 128.02, 127.81, 127.74, 127.66, 87.67(C-1), 85.84(C-3), 83.21(C-2), 78.55(C-4), 75.32, 74.08, 73.97, 73.20, 68.88(C-6), 38.22(C-5), 30.64(C-5a); HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{31}O_7NaF_3S$ 615.1635, found 615.1635.

4.1.28. 4,6-O-Benzylidene-2,3-O-isopropylidene-1-O-(2-naphthyl)-5a-carba-β-D-glucopyranose (34)

To a solution of 4,6-*O*-benzylidene-2,3-*O*-isopropylidene-5a-carba-β-D-glucopyranose **11** (1.50 g, 4.90 mmol) in DMF (12 mL) and NaH (392 mg, 9.8 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2-(bromomethyl) naphthalene (216 mg, 9.8 mmol). After being stirred for 1 h, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **34** (2.01 g, 92%) as a white amorphous solid. R_f = 0.28 (hexane/EtOAc, 5:1); [α] = +5.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.80(m, 4H), 7.50–7.27(m, 8H), 5.55(s, 1H, PhCH), 4.98(d, 1H, J = 12.3 Hz), 4.81(d, 1H, J = 12.3 Hz), 4.13(dd, 1H, $J_{5,6a}$ = 4.1 Hz, J_{gem} = 10.9 Hz, H-6a), 3.80(ddd, 1H, $J_{1,5aeq}$ = 4.3 Hz, $J_{1,2}$ = 8.9 Hz, $J_{1,5aax}$ = 10.2 Hz, H-1), 3.77(dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.3 Hz, H-4), 3.69(dd, 1H, $J_{5,6b}$ = 10.9 Hz, H-6b), 3.63(dd, 1H, $J_{2,3}$ = 9.0 Hz, H-3), 3.60(dd, 1H, H-2), 1.92(ddd, 1H, $J_{5,5aeq}$ = 4.3 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.86(m, 1H, H-5), 1.51(s, 3H, CH_3), 1.48(s, 3H, CH_3), 1.18(ddd, 1H, $J_{5,5aax}$ = 10.2 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.59, 135.84, 133.26, 132.94, 128.95, 128.11, 127.84, 127.66, 126.41, 126.39, 126.06, 125.83, 125.72, 111.57, 101.62(PhCH), 82.45(C-2), 80.44(C-4), 78.09(C-3), 75.93(C-1), 71.74, 70.86(C-6), 36.37(C-5), 30.18(C-5a), 26.89(CH_3); HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{30}O_5Na$ 469.1985, found469.1987.

4.1.29. 4,6-O-Benzylidene-1-O-(2-naphthyl)-5a-carba-β-D-glucopyranose (35)

To a solution of 4,6-*O*-benzylidene-2,3-*O*-isopropylidene-1-*O*-(2-naphthyl)-5a-carba-β-D-glucopyranose **34** (828 mg, 1.85 mmol) in MeOH (50 mL) was added AcOH (4 mL). After being stirred at 60 °C for 2 h, the solvent was concentrated *in vacuo*. The residue was purified by column chromatography (EtOAc) to give compound **35** (639 mg, 85%) as a white amorphous solid. R_f = 0.63 ($CHCl_3$/MeOH, 10:1); [α] = −28.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.79(m, 4H), 7.51–7.45(m, 5H), 7.38–7.33(m, 3H), 5.51(s, 1H, PhCH), 4.84(d, 1H, J = 11.8 Hz), 4.78(d, 1H, J = 11.8 Hz), 4.14(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 11.4 Hz, H-6a), 3.64(dd, 1H, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.59(dd, 1H, $J_{1,2}$ = 8.5 Hz, H-2), 3.59(dd, 1H, $J_{5,6b}$ = 10.6 Hz, H-6b), 3.48(ddd, 1H, $J_{5,5aeq}$ = 4.6 Hz, $J_{5,5aax}$ = 11.1 Hz, H-1), 3.43(dd, 1H, $J_{4,5}$ = 9.0 Hz, H-4), 2.98(br, 1H), 2.89(br, 1H), 1.92(ddd, 1H, $J_{5,5aeq}$ = 3.5, J_{gem} = 12.9 Hz, H-5aeq), 1.83(m, 1H, H-5), 1.09(ddd, 1H, $J_{5,5aax}$ = 11.1 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.74, 135.58, 133.24, 133.02, 129.09, 128.35, 128.28, 127.86, 127.71, 126.49, 126.24, 126.21, 126.01, 125.67, 101.80(PhCH), 82.22(C-4). 79.01(C-1), 77.00(C-2), 74.33(C-3), 72.13, 70.84(C-6), 33.72(C-5), 27.85(C-5a); HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{26}O_5Na$ 429.1672, found 429.1673.

4.1.30. 4-O-Benzyl-1-O-(2-naphthyl)-5a-carba-β-D-glucopyranose (36)

To a solution of 4,6-*O*-benzylidene-1-*O*-(2-naphthyl)-5a-carba-β-D-glucopyranose **35** (403 mg, 0.99 mmol) in THF (5.9 mL) was added THF·BH_3 (4.0 mL, 1.0 M in THF, 3.97 mmol) and $CoCl_2$ (515 mg, 3.97 mmol). After being stirred for 5 h, the solution was diluted with EtOAc, and was filtered through Celite. The filtrate was added aq $NaBH_4$ (30 mg, 0.794 mmol), and was filtered through Celite. The filtrate was washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc, 1:4) to give compound **36** (361 mg, 89%) as a white amorphous solid. R_f = 0.26 (hexane/EtOAc, 1:2); [α] = +12.7° (*c* 1.00, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.76(m, 4H), 7.49–7.25(m, 8H), 4.95(d, 1H, J = 11.3 Hz), 4.83(d, 1H, J = 11.7 Hz), 4.71(d, 1H, J = 11.3 Hz), 4.67(d, 1H, J = 11.7 Hz), 3.66–3.59(m, 2H, H-6), 3.58(dd, 1H, $J_{2,3}$ = 8.9 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.44(dd, 1H, $J_{1,2}$ = 9.0 Hz, H-2), 3.38(ddd, 1H, $J_{1,5aeq}$ = 4.0 Hz, $J_{1,5aax}$ = 11.0 Hz, H-1), 3.34(dd, 1H, $J_{4,5}$ = 10.4 Hz, H-4), 2.94(br, 1H, 2-OH), 2.81(br, 1H, 3-OH), 2.08(ddd, 1H, $J_{5,5aeq}$ = 4.0 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.94(br, 1H, 6-OH), 1.63(m, 1H, H-5), 1.26(ddd, 1H, $J_{5,5aax}$ = 11.0 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.26, 135.56, 133.24, 133.02, 128.60, 128.34, 128.29, 127.99, 127.86, 127.70, 126.52, 126.21, 126.01, 125.68, 81.37(C-4), 78.89(C-1), 77.47(C-3), 76.80(C-2), 74.48, 71.63, 64.53(C-6), 39.91(C-5), 29.12(C-5a); HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{28}O_5Na$ 431.1829, found431.1830.

4.1.31. 4-O-Benzyl-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-1-O-(2-naphthyl)-5a-carba-β-D-glucopyranose (37)

To a solution of 4-*O*-benzyl-1-*O*-(2-naphthyl)-5a-carba-β-D-glucopyranose **36** (302 mg, 0.739 mmol) in MeOH (7.4 mL) at 60 °C was added trimethyl orthoformate (808 μL, 7,39 mmol), 2,3-butanedione (257 μL, 2.96 mmol) and CSA (21 mg, 0.148 mmol). After being stirred for 4.5 h, the solution was neutralized with $NaHCO_3$, and the resin was filtered off. The filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 3:1) to give compound **37** (366 mg, 95%) as a white amorphous solid. R_f = 0.51 (hexane/EtOAc, 1:1); [α] = −48.1° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.79(m, 4H), 7.48(m, 8H), 5.07(d, 1H, J = 11.2 Hz), 4.99(d, 1H, J = 12.2 Hz), 4.84(d, 1H, J = 12.2 Hz), 4.66(d, 1H, J = 11.2 Hz), 3.77(dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.72(dd, 1H, $J_{1,2}$ = 9.3 Hz, H-2), 3.63(dd, 1H, $J_{5,6a}$ = 5.7 Hz, J_{gem} = 10.8 Hz, H-6a), 3.61(m, 1H, H-1), 3.58(dd, 1H, $J_{5,6b}$ = 4.2 Hz, H-6b), 3.51(dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.35(s, 3H, OCH_3), 3.32(s, 3H, OCH_3), 1.99(ddd, 1H, $J_{5,5aeq}$ = 4.0 Hz, $J_{1,5aeq}$ = 4.5 Hz, J_{gem} = 13.3 Hz, H-5aeq), 1.70(m, 1H, H-5), 1.40(s, 3H, CH_3), 1.38(s, 3H, CH_3), 1.31(ddd, 1H, $J_{1,5aax}$ = 11.2 Hz, $J_{5,5aax}$ = 11.2 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.29, 136.54, 133.27, 132.88, 128.54, 128.28, 127.96, 127.94, 127.82, 127.64, 125.97, 125.92, 125.68, 125,58, 99.23, 99.17, 79.69(C-4), 76.09(C-1), 75.09, 74.55(C-3), 74.02(C-2), 73.05, 65.14(C-6), 47.90(OCH_3), 47.85(OCH_3), 40.39(C-5), 31.01(C-5a), 17.85(CH_3), 17.84(CH_3); HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{38}O_7Na$ 545.2510, found 545.2508.

4.1.32. 4,6-Di-O-benzyl-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-1-O-(2-naphthyl)-5a-carba-β-D-glucopyranose (38)

To a solution of 4-*O*-benzyl-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-*O*-(2-naphthyl)-5a-carba-β-D-glucopyranose **37** (366 mg, 0.700 mmol) in DMF (2 mL) and NaH (70 mg, 1.75 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added BnBr (208 μL, 1.75 mmol). After being stirred for overnight, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **38** (411 mg, 96%) as a colorless syrup. R_f = 0.42 (hexane/EtOAc, 6:1); [α] = −51.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.79(m, 4H), 7.49–7.24(m, 13H), 5.00(d, 1H, J = 11.8 Hz), 4.97(d, 1H, J = 10.7 Hz), 4.84(d, 1H, J = 11.8 Hz), 4.52(d, 1H, J = 10.7 Hz), 4.45(d, 1H, J = 12.1 Hz), 4.41(d, 1H, J = 12.1 Hz), 3.77–3.71(m, 2H, H-2, H-3), 3.60(ddd, 1H, $J_{1,5aeq}$ = 4.6 Hz,

$J_{1,2}$ = 9.3 Hz, $J_{1,5aax}$ = 11.1 Hz, H-1), 3.56(m, 1H, H-4), 3.50(dd, 1H, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 8.8 Hz, H-6a), 3.49(dd, 1H, $J_{5,6b}$ = 2.6 Hz, H-6b), 3.35(s, 3H, OCH_3), 3.31(s, 3H, OCH_3), 2.15(ddd, 1H, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.71(m, 1H, H-5), 1.58(ddd, 1H, $J_{5,5aax}$ = 11.2 Hz, H-5aax), 1.39(s, 3H. CH_3), 1.38(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.85, 138.49, 136.74, 133.31, 132.88, 128.31, 128.30, 128.14, 127.92, 127.84, 127.64, 127.58, 127.46, 125.93, 125.89, 125.63, 99.20, 99.15, 77.45(C-4), 76.40(C-1), 75.27, 74.65(C-3), 74.16(C-2), 73.09, 73.04, 70.02(C-6), 47.90(OCH_3), 47.83(OCH_3), 39.32(C-5), 31.70(C-5a), 17.87(CH_3); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{38}H_{44}O_7Na$ 635.2979, found 635.2974.

4.1.33. 4,6-Di-O-benzyl-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-β-D-glucopyranose (39)

To a solution of 4,6-di-*O*-benzyl-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-*O*-(*p*-methoxybenzyl)-5a-carba-β-D-glucopyranose **38** (50 mg, 0.082 mmol) in CH_2Cl_2–H_2O (18:1, 1.9 mL) was added DDQ (28 mg, 0.122 mmol). After being stirred for 1 h, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to give compound **39** (31 mg, 81%) as a colorless syrup. R_f = 0.20 (hexane/EtOAc, 2:1); [α] = −48.4° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24(m, 10*H*), 4.96(d, 1H, *J* = 10.8 Hz), 4.52(d, 1H, *J* = 10.8 Hz), 4.46(d, 1H, *J* = 11.9 Hz), 4.41(d, 1H, *J* = 11.9 Hz), 3.70(ddd, 1H, $J_{1,5aeq}$ = 4.6 Hz, $J_{1,2}$ = 9.6 Hz, $J_{1,5aax}$ = 11.2 Hz, H-1), 3.67(dd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.61(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 8.9 Hz, H-6a), 3.60(dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 3.48(dd, 1H, $J_{5,6b}$ = 2.6 Hz, H-6b), 3.46(dd, 1H, H-2), 3.30(s, 3H, OCH_3), 3.29(s, 3H, OCH_3), 2.05(ddd, 1H, $J_{5,5aeq}$ = 4.4 Hz, J_{gem} = 13.0 Hz. H-5aeq), 1.74(m, 1H, H-5), 1.57(ddd, 1H, $J_{5,5aax}$ = 11.4 Hz, H-5aax), 1.36(s, 3H, CH_3), 1.34(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.82, 138.49, 128.29, 128.28, 128.09, 127.57, 127.45, 99.20, 77.49(C-4), 75.22, 74.11(C-3), 73.70(C-2), 73.03, 69.78(C-6), 68.94(C-1), 47.89(OCH_3), 47.86(OCH_3), 39.37(C-5), 32.27(C-5a), 17.84(CH_3), 17.66(CH_3); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{36}O_7Na$ 495.2353, found 495.2349.

4.1.34. 4,6-Di-O-benzyl-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-1-O-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose (40)

To a solution of 4,6-di-*O*-benzyl-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-β-D-glucopyranose **39** (96 mg, 0.203 mmol) in CH_2Cl_2 (1.0 mL) and pyridine(1.0 mL) at −10 °C was added Tf_2O (51 μL, 0.304 mmol). After being stirred for 2.5 h, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 10:1) to give compound **40** (106 mg, 87%) as a colorless syrup. R_f = 0.36 (hexane/EtOAc, 10:1); [α] = −51.6° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23(m, 10H), 4.94(d, 1H, *J* = 10.9 Hz), 4.83(ddd, 1H, $J_{1,5aeq}$ = 5.2 Hz, $J_{1,2}$ = 9.5 Hz, $J_{1,5aax}$ = 11.6 Hz, H-1), 4.50(d, 1H, *J* = 10.9 Hz), 4.45(d, 1H, *J* = 10.9 Hz), 4.39(d, 1H, *J* = 10.9 Hz), 3.77(dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 3.70(dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 3.66(dd, 1H, $J_{5,6a}$ = 4.3 Hz, J_{gem} = 9.0 Hz, H-6a), 3.62(dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.42(dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 3.27(s, 6H, OCH_3), 2.22(ddd, 1H, $J_{5,5aeq}$ = 4.0 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.96(ddd, 1H, $J_{5,5aax}$ = 11.8 Hz, H-5aax), 1.73(m, 1H, H-5), 1.35(s, 3H, CH_3), 1.30(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.43, 138.07, 128.40, 128.38, 128.13, 127.76, 127.71, 127.61, 99.52, 99.50, 85.53(C-1), 76.68(C-4), 75.32, 73.72(C-3), 73.18, 70.13(C-2), 68.70(C-6), 47.92(OCH_3), 47.89(OCH_3), 38.92(C-5), 31.34(C-5a), 17.71(CH_3), 17.28(CH_3); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{28}H_{35}O_9NaF_3S$ 627.1846, found627.1850.

4.1.35. 4,6-O-Benzylidene-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-β-D-glucopyranose (41)

To a solution of 4-*O*-benzyl-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-β-D-glucopyranose **37** (508 mg, 0.972 mmol) in MeOH (30 mL) and AcOH (500 μL) was added 10% Pd/C (103 mg, 0.097 mmol). The resulting suspension was hydrogenated at 1 atm for overnight. The solution was filtered through of Celite, and the solvent was evaporated. The residue in DMF (4 mL) at 60 °C was added benzaldehyde dimethyl acetal (218 μL, 1.46 mmol) and CSA (22 mg, 0.097 mmol). After being stirred for 15 min, the solution was cooled to 0 °C and neutralized with Et_3N. The solution was concentrated *in vacuo*, and the residue was purified by flash column chromatography (hexane/EtOAc, 1:1) to give compound **41** (288 mg, 78%) as a white amorphous solid. R_f = 0.17 (hexane/EtOAc, 1:1); [α] = −171.9° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.30(m, 5H), 5.54(s, 1H, PhCH), 4.16(dd, 1H, $J_{5,6a}$ = 4.2 Hz, J_{gem} = 11.0 Hz, H-6a), 3.81(ddd, 1H, $J_{1,5aeq}$ = 4.7 Hz, $J_{1,2}$ = 9.5 Hz, $J_{1,5aax}$ = 11.0 Hz, H-1), 3.79(dd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 3.68(dd, 1H, $J_{5,6b}$ = 11.0 Hz, H-6b), 3.66(dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 3.55(dd, 1H, H-2), 3.29(s, 6H, OCH_3), 2.47(br, 1H), 1.88(m, 1H, H-5), 1.84(ddd, 1H, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 13.3 Hz, H-5aeq), 1.34(s, 6H, CH_3), 1.15(ddd, 1H, $J_{5,5aax}$ = 11.0 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.12, 128.69, 128.08, 126.06, 101.03(PhCH), 99.50, 99.28, 79.54(C-4), 74.19(C-2), 70.97(C-6), 69.89(C-3), 69.01(C-1), 48.01(OCH_3), 47.90(OCH_3), 34.99(C-5), 30.01(C-5a), 17.65(CH_3), 17.60(CH_3); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{28}O_7Na$ 403.1727, found 407.1727.

4.1.36. 4,6-O-Benzylidene-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-1-O-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose (42)

To a solution of 4,6-*O*-benzylidene-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-β-D-glucopyranose **41** (100 mg, 0.263 mmol) in CH_2Cl_2 (1.0 mL) and pyridine(1.0 mL) at −10 °C was added Tf_2O (66 μL, 0.394 mmol). After being stirred for 2 h, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 8:1) to give compound **42** (122 mg, 92%) as a white amorphous solid. R_f = 0.29 (hexane/EtOAc, 8:1); [α] = −124.2° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.33(m, 5H), 5.53(s, 1H), 4.91(ddd, 1H, $J_{1,2}$ = 10.7 Hz, $J_{1,5aeq}$ = 5.3 Hz, $J_{1,5aax}$ = 11.0 Hz, H-1), 4.19(dd, 1H, $J_{5,6a}$ = 4.3 Hz, J_{gem} = 11.0 Hz, H-6a), 3.87(m, 1H, H-2), 3.85(m, 1H, H-3), 3.69(dd, 1H, $J_{5,6b}$ = 10.9 Hz, H-6b), 3.66(dd, 1H, $J_{3,4}$ = 9.8 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 3.28(s, 3H, OCH_3), 3.26(s, 3H, OCH_3), 2.10(ddd, 1H, $J_{5,5aeq}$ = 3.4 Hz, J_{gem} = 12.8 Hz, H-5aeq), 1.90(m, 1H, H-5), 1.52(ddd, $J_{5,5aax}$ = 11.4 Hz, H-5aax), 1.33(s, 3H, CH_3), 1.32(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.67, 128.90, 128.16, 126.03, 101.17(PhCH), 99.89, 99.63, 84.51(C-1), 78.28(C-4), 70.56(C-2), 70.34(C-6), 69.90(C-3), 48.02(OCH_3), 47.94(OCH_3), 34.27(C-5), 29.64(C-5a), 17.52(CH_3), 17.24(CH_3); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{27}O_9NaF_3S$ 535.1220, found 535.1226.

4.1.37. 2,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-glucopyranosyl-(1→6)-1,2,3,4-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (43)

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (233 mg, 0.173 mmol) in THF (130 μL) was added 15-crown-5 ether (125 μL, 0.634 mmol) and NaH (17 mg, 0.432 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **27** (100 mg, 0.173 mmol). After being stirred for 19 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (Toluene/EtOAc, 40:1) to give compound **43** (91 mg, 55%) as a white amorphous solid and olefin **44** (14 mg, 19%) as a colorless syrup and recovered **8** (172 mg, 74%). Date for 2,3-di-*O*-benzyl-4,6-*O*-

benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranoside (**43**): R_f = 0.26 (Toluene/EtOAc, 20:1); [α] = +25.0° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.22(m, 35H), 5.56(s, 1H, PhCH), 4.97(d, 1H, *J* = 10.5 Hz), 4.95(d, 1H, *J* = 10.3 Hz), 4.95(d, 1H, *J* = 11.2 Hz), 4.92(d, 1H, *J* = 10.6 Hz), 4.84(d, 1H, *J* = 10.5 Hz), 4.82(d, 1H, *J* = 10.3 Hz), 4.82(d, 1H, *J* = 10.6 Hz), 4.75(d, 1H, *J* = 11.9 Hz), 4.68(d, 1H, *J* = 11.9 Hz), 4.67(d, 1H, *J* = 11.5 Hz), 4.62(d, 1H, *J* = 11.5 Hz), 4.55(d, 1H, *J* = 11.2 Hz), 4.08(dd, 1H, $J_{5',6'a}$ = 4.4 Hz, J_{gem} = 11.0 Hz, H-6′a), 3.98(dd, 1H, $J_{2',3'}$ = 9.4 Hz, $J_{3',4'}$ = 9.2 Hz, H-3′), 3.74(dd, 1H, $J_{5,6a}$ = 2.6 Hz, J_{gem} = 8.9 Hz, H-6a), 3.73(m, 1H, H-1′), 3.68(dd, 1H, $J_{5,6b}$ = 5.1 Hz, H-6b), 3.54(dd, 1H, $J_{5',6'b}$ = 11.2 Hz, H-6′b), 3.53(m, 1H, H-2), 3.53(m, 1H, H-3), 3.51(dd, 1H, $J_{3',4'}$ = 9.2 Hz, $J_{4',5'}$ = 9.2 Hz, H-4′), 3.50(m, 1H, H-1), 3.47(dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.38(dd, 1H, $J_{1',2'}$ = 2.8 Hz, $J_{2',3'}$ = 9.4 Hz, H-2′), 2.26(m, 1H, H-5′), 2.16(ddd, 1H, $J_{1,5aeq}$ = 3.7 Hz, $J_{5,5aeq}$ = 3.7 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.68(m, 1H, H-5), 1.60(ddd, 1H, $J_{1',5a'eq}$ = 3.5 Hz, $J_{5',5a'eq}$ = 3.5 Hz, J_{gem} = 13.9 Hz, H-5a′eq), 1.52(ddd, 1H, $J_{1,5aax}$ = 12.4 Hz, $J_{5,5aax}$ = 12.4 Hz, H-5aax), 0.92(ddd, 1H, $J_{1',5a'ax}$ = 1.8 Hz, $J_{5',5a'ax}$ = 12.2 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.04, 138.88, 138.79, 138.73, 138.34, 128.63, 128.40, 128.34, 128.31, 128.20, 128.17, 128.12, 128.05, 127.78, 127.64, 127.57, 127.56, 127.49, 127.47, 127.44, 127.43, 126.06, 101.23(PhCH), 86.39(C-3), 85.99(C-2), 84.25(C-4′), 82.90(C-2′), 80.68(C-4), 80.51(C-3′), 80.28(C-1), 75.80, 75.78, 75.60, 75.22(C-1′), 75.10, 72.93, 72.27, 71.29(C-6′), 70.66(C-6), 39.13(C-5), 32.60(C-5′), 30.43(C-5a), 27.53(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{63}H_{66}O_9Na$ 989.4599, found 989.4596.

Date for olefin **44**: R_f = 0.46(Toluene/EtOAc, 20:1); [αα] = +38.4° (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.24(m, 15H), 5.75(ddd, 1H, $J_{1,2}$ = 2.9, $J_{1,5}$ = 2.9, $J_{1,5a}$ = 9.9 Hz, H-1), 5.63(s, 1H, PhCH), 5.39(ddd, 1H, $J_{5,5a}$ = 1.7 Hz, $^4J_{2,5a}$ = 1.7 Hz, H-5a), 5.02(d, 1H, *J* = 11.4 Hz), 4.80(d, 1H, *J* = 11.4 Hz), 4.74(d, 1H, *J* = 11.6 Hz), 4.67(d, 1H, *J* = 11.6 Hz), 4.29 (dd, 1H, $J_{5,6a}$ = 4.6 Hz, J_{gem} = 11.0 Hz, H-6a), 4.29(m, 1H, H-2), 4.00(dd, 1H, $J_{2,3}$ = 7.0 Hz, $J_{3,4}$ = 10.1 Hz, H-3), 3.81(dd, 1H, $J_{4,5}$ = 9.9 Hz, H-4), 3.64(dd, 1H, $J_{5,6b}$ = 11.2 Hz, H-6b), 2.70(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.72, 138.41, 138.16, 128.93(C-5a), 128.76, 128.37, 128.30, 128.18, 128.13, 128.11, 127.82, 127.64, 127.56, 125.96, 125.06(C-1), 101.51(PhCH), 82.15(C-4), 81.94(C-3), 80.65(C-2), 74.68, 72.26, 70.00(C-6), 38.57(C-5); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{28}H_{28}O_4Na$ 451.1880, found 451.1880.

*4.1.38. 4,6-O-Benzylidene-2,3-O-(o-xylylene)-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (**47**)*

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (108 mg, 0.200 mmol) in THF (59 μL) was added 15-crown-5 ether (59 μL, 0.296 mmol) and NaH (8 mg, 0.200 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 4,6-*O*-benzylidene-1-*O*-trifluoromethanesulfonyl-2,3-*O*-(*o*-xylylene)-5a-carba-β-D-glucopyranose **30** (40 mg, 0.080 mmol). After being stirred for 17.5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 4:1) to give compound **47** (24 mg, 35%) as a colorless syrup and recovered **8** (77 mg, 72%). R_f = 0.27(Hexane/EtOAc, 3:1); [α] = +87.0° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.05(m, 29H), 5.55(s, 1H, PhCH), 5.18(d, 1H, *J* = 13.3 Hz), 5.12(d, 1H, *J* = 14.6 Hz), 5.04(d, 1H, *J* = 14.6 Hz), 4.93(d, 1H, *J* = 10.6 Hz), 4.91(d, 1H, *J* = 10.8 Hz), 4.88(d, 1H, *J* = 10.9 Hz), 4.82(d, 1H, *J* = 13.3 Hz), 4.81(d, 1H, *J* = 10.6 Hz), 4.79(d, 1H, *J* = 10.8 Hz), 4.58(d, 1H, *J* = 11.7 Hz), 4.52(d, 1H, *J* = 11.7 Hz), 4.50(d, 1H, *J* = 10.9 Hz), 4.08(dd, 1H, $J_{5',6'a}$ = 4.4 Hz, J_{gem} = 10.9 Hz, H-6′a), 3.91(dd, 1H, $J_{2',3'}$ = 9.2 Hz, $J_{3',4'}$ = 9.2 Hz, H-3′), 3.78(dd, 1H, $J_{5,6a}$ = 2.5 Hz, J_{gem} = 9.0 Hz, H-6a), 3.76(m, 1H, H-1′), 3.64(dd, 1H, $J_{5,6b}$ = 5.0 Hz, H-6b), 3.53(dd, 1H, $J_{5',6'b}$ = 11.0 Hz, H-6′b), 3.49–3.41(m, 2H, H-2, H-3), 3.46(dd, 1H, $J_{1',2'}$ = 2.7 Hz, $J_{2',3'}$ = 9.2 Hz, H-2′), 3.44–3.34(m, 1H, H-4), 3.43(dd, 1H, $J_{4',5'}$ = 10.2 Hz, H-4′), 3.39(ddd, 1H, $J_{1,2}$ = 9.1 Hz, $J_{1,5aeq}$ = 3.9 Hz, $J_{1,5aax}$ = 11.4 Hz, H-1), 2.22(m, 1H, H-5′), 1.90(ddd, 1H, $J_{5,5aeq}$ = 3.9 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.56(ddd, 1H, $J_{1',5a'eq}$ = 2.5 Hz, $J_{5',5a'eq}$ = 3.5 Hz, J_{gem} = 13.5 Hz, H-5a′eq), 1.55(m, 1H, H-5), 1.30(ddd, 1H, $J_{5,5aax}$ = 11.4 Ha, H-5aax), 1.00(ddd, 1H, $J_{1',5a'ax}$ = 1.8 Hz, $J_{5',5a'ax}$ = 13.4 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.88, 138.80, 138.78, 138.27, 137.35, 136.99, 130.53, 128.74, 128.56, 128.36, 128.31, 128.27, 128.14, 128.04, 127.81, 127.77, 127.63, 127.56, 127.54, 127.47, 127.43, 127.39, 126.31, 101.61(PhCH), 86.29(C-3), 85.88(C-2), 83.14(C-2′), 82.91(C-4′), 80.59(C-4), 80.58(C-3′), 80.21(C-1), 76.30(C-1′), 75.73, 75.05, 73.98, 72.60, 71.98, 71.30(C-6′), 70.85(C-6), 39.07(C-5), 32.51(C-5′), 29.98(C-5a), 28.05(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{57}H_{60}O_9Na$ 911.4130, found 911.4130.

*4.1.39. 4,6-Di-O-benzyl-2,3-O-(o-xylylene)-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (**45**)*

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (90 mg, 0.168 mmol) in THF (49 μL) was added 15-crown-5 ether (49 μL, 0.248 mmol) and NaH (7 mg, 0.168 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 4,6-di-*O*-benzyl-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **33** (40 mg, 0.067 mmol). After being stirred for 14 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hexane/EtOAc, 6:1) to give compound **45** (21 mg, 32%) as a colorless syrup and olefin **46** (4.9 mg, 16%) as a colorless syrup and recovered **8** (66 mg, 74%). Date for 4,6-di-*O*-benzyl-2,3-*O*-(*o*-xylylene)-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranoside (**45**): R_f = 0.34(Hexane/EtOAc, 6:1); [α] = +82.7° (*c* 0.96, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.04(m, 34H), 5.12(d, 1H, *J* = 14.3 Hz), 5.12(d, 1H, *J* = 14.0 Hz), 5.05(d, 1H, *J* = 14.3 Hz), 4.96(d, 1H, *J* = 11.0 Hz), 4.91(d, 1H, *J* = 10.7 Hz), 4.89(d, 1H, *J* = 10.8 Hz), 4.86(d, 1H, *J* = 14.0 Hz), 4.84(d, 1H, *J* = 10.6 Hz), 4.79(d, 1H, *J* = 10.7 Hz), 4.78(d, 1H, *J* = 10.8 Hz), 4.58(d, 1H, *J* = 11.0 Hz), 4.55(d, 1H, *J* = 11.6 Hz), 4.49(d, 1H, *J* = 10.6 Hz), 4.48(d, 1H, *J* = 11.6 Hz), 4.39(s, 2H), 3.87(dd, 1H, $J_{2',3'}$ = 9.4 Hz, $J_{3',4'}$ = 9.0 Hz, H-3′), 3.74(m, 1H, H-1′), 3.73(dd, 1H, $J_{5,6a}$ = 2.3 Hz, J_{gem} = 9.0 Hz, H-6a), 3.65(dd, 1H, $J_{5',6'a}$ = 4.4 Hz, J_{gem} = 8.9 Hz, H-6′a), 3.61(dd, 1H, $J_{5,6b}$ = 5.0 Hz, H-6b), 3.44(dd, 1H, $J_{2,3}$ = 8.6 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.43(dd, 1H, $J_{4',5'}$ = 8.6 Hz, H-4′), 3.42(dd, 1H, $J_{1,2}$ = 8.3 Hz, H-2), 3.40(dd, 1H, $J_{1',2'}$ = 2.3 Hz, H-2′), 3.36(m, 1H, H-1), 3.36(dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.35(dd, 1H, $J_{5',6'b}$ = 2.1 Hz, H-6′b), 2.03(m, 1H, H-5′), 1.90(ddd, 1H, $J_{1,5aeq}$ = 3.8 Hz, $J_{5,5aeq}$ = 3.8 Hz, J_{gem} = 13.2 Hz, H-5aeq), 1.81(ddd, 1H, $J_{1',5a'eq}$ = 3.7 Hz, $J_{5',5a'eq}$ = 3.7 Hz, J_{gem} = 14.3 Hz, H-5a′eq), 1.53(m, 1H, H-5), 1.48(ddd, 1H, $J_{1',5a'ax}$ = 1.6 Hz, $J_{5',5a'ax}$ = 12.8 Hz, H-5a′ax), 1.28(ddd, 1H, $J_{1,5aax}$ = 11.4 Hz, $J_{5,5aax}$ = 11.4 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.13, 138.93, 138.87, 138.83, 138.80, 138.59, 137.50, 137.33, 130.09, 128.34, 128.31, 128.28, 128.25, 128.05, 127.98, 127.81, 127.72, 127.66, 127.58, 127.50, 127.47, 127.44, 127.43, 127.37, 127.35, 86.31(C-3), 85.91(C-2), 85.55(C-3′), 84.19(C-2′), 80.66(C-4), 80.62(C-4′), 80.27(C-1), 76.68(C-1′), 75.74, 75.24, 75.08, 74.66, 73.35, 72.98, 71.94, 70.39(C-6), 69.99(C-6′), 39.09(C-5), 37.19(C-5′), 30.03(C-5a), 29.91(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{64}H_{68}O_9Na$ 1003.4756, found 1003.4757.

Date for olefin **46**: R_f = 0.37(Hexane/EtOAc, 6:1); [α] = +235.2° (*c* 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.08(m, 14H), 5.64–5.59(m, 2H), 5.27(d, 1H, *J* = 12.8 Hz), 5.24(d, 1H, *J* = 14.7 Hz),

5.06(d, 1H, J = 14.7 Hz), 4.99(d, 1H, J = 11.0 Hz), 4.76(d, 1H, J = 12.8 Hz), 4.53(d, 1H, J = 11.0 Hz), 4.45(d, 1H, J = 12.3 Hz), 4.39(d, 1H, J = 12.3 Hz), 4.24(dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 7.2 Hz, H-2), 3.71(dd, 1H, $J_{3,4}$ = 10.5 Hz, H-3), 3.65(dd, $J_{4,5}$ = 9.6 Hz, H-4), 3.51–3.47(m, 2H, H-6), 2.40(m, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.75, 138.25, 137.24, 136.78, 132.05, 129.18(C-5a), 128.41, 128.38, 128.35, 128.23, 128.16, 127.75, 127.74, 127.67, 127.62, 127.25(C-1), 84.84(C-3), 79.76(C-2), 77.96(C-4), 75.41, 73.31, 73.08, 71.91, 69.17(C-6), 44.06(C-5); HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{30}O_4Na$ 465.2036, found 465.2031.

4.1.40. 4,6-Di-O-benzyl-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (48)

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (53 mg, 0.099 mmol) in THF (56 μL) was added 15-crown-5 ether (24 μL, 0.120 mmol) and NaH (2 mg, 0.099 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 4,6-di-*O*-benzyl-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **40** (16 mg, 0.026 mmol). After being stirred for 18.5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to give compound **48** (15 mg, 57%) as a colorless syrup and olefin **49** (2 mg, 9%) as a colorless syrup and recovered **8** (38 mg, 71%). Date for 4,6-di-*O*-benzyl-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranoside (**48**): R_f = 0.19 (Toluene/EtOAc, 20:1); [α] = −5.21° (c 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.22(m, 30H), 5.00(d, 1H, J = 11.0 Hz), 4.94(d, 1H, J = 10.8 Hz), 4.92(d, 1H, J = 10.8 Hz), 4.86(d, 1H, J = 11.4 Hz), 4.83(d, 1H, J = 10.8 Hz), 4.82(d, 1H, J = 10.8 Hz), 4.73(d, 1H, J = 11.6 Hz), 4.63(d, 1H, J = 11.6 Hz), 4.57(d, 1H, J = 11.4 Hz), 4.53(d, 1H, J = 11.0 Hz), 4.43(d, 1H, J = 11.9 Hz), 4.38(d, 1H, J = 11.9 Hz), 4.14(dd, 1H, $J_{2',3'}$ = 9.8 Hz, $J_{3',4'}$ = 9.7 Hz, H-3′), 3.90(d, 1H, J_{gem} = 8.7 Hz, H-6a), 3.76(dd, 1H, $J_{5,6b}$ = 3.0 Hz, H-6b), 3.70(dd, 1H, $J_{5',6'a}$ = 4.3 Hz, J_{gem} = 9.0 Hz, H-6′a), 3.62(m, 1H, H-1′), 3.58(dd, 1H, $J_{4',5'}$ = 10.3 Hz, H-4′), 3.56–3.46(m, 4H, H-1, H-2, H-3, H-4), 3.54(dd, 1H, $J_{1',2'}$ = 2.2 Hz, H-2′), 3.38(dd, 1H, $J_{5',6'b}$ = 2.4 Hz, H-6′b), 3.26(s, 6H), 2.18(m, 1H, H-5aeq), 2.10(m, 1H, H-5′), 1.80(ddd, 1H, $J_{1',5a'eq}$ = 3.8 Hz, $J_{5',5a'eq}$ = 3.8 Hz, J_{gem} = 14.1 Hz, H-5a′eq), 1.64–1.54(m, 2H, H-5aax, H-5a′ax), 1.61(m, 1H, H-5), 1.33(s, 3H), 1.30(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.22, 139.01, 138.97, 138.90, 138.71, 128.34, 128.30, 128.27, 128.24, 128.11, 128.07, 127.88, 127.73, 127.57, 127.52, 127.41, 127.40, 127.37, 127.32, 99.23, 98.86, 86.35(C-3), 86.11(C-2), 80.67(C-4), 80.54(C-1), 78.13(C-4′), 75.82, 75.70, 75.82, 75.70, 75.28, 75.26, 74.89(C-1′), 72.94, 72.31(C-2′, C-3′), 71.91, 70.41(C-6), 69.99(C-6′), 47.83, 47.59, 39.27(C-5), 37.78(C-5′), 31.14(C-5a′), 30.35(C-5a), 17.99, 17.83; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{62}H_{72}O_{11}Na$ 1015.4967, found 1015.4960.

Date for olefin **49**: R_f = 0.23 (Toluene/EtOAc, 20:1); [α] = +13.9° (c 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23(m, 10H), 5.61(m, 2H, H-1, H-5a), 5.00(d, 1H, J = 11.0 Hz), 4.50(d, 1H, J = 12.2 Hz), 4.46(d, 1H, J = 11.0 Hz), 4.39(d, 1H, J = 12.2 Hz), 4.39(m, 1H, H-2), 3.93(dd, 1H, $J_{2,3}$ = 9.1 Hz, $J_{3,4}$ = 10.4 Hz, H-3), 3.78(dd, 1H, $J_{4,5}$ = 8.6 Hz, H-4), 3.53–3.48(m, 2H, H-6), 3.30(s, 3H), 3.29(s. 3H), 2.52(m, 1H, H-5), 1.37(s, 3H, 1.34(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.97, 138.30, 128.88(C-5a), 128.34, 128.27, 128.10, 127.76, 127.61, 127.52, 126.52(C-1), 99.93, 99.67, 75.61(C-4), 74.98, 74.37(C-3), 73.04, 69.39(C-6), 68.27(C-2), 47.91, 47.76, 45.60(C-5), 17.99, 17.82; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{34}O_6Na$ 477.2248, found 477.2245.

4.1.41. 4,6-O-Benzylidene-2,3-O-(2,3-dimethoxybutane-2,3-diyl)-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (50)

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **8** (53 mg, 0.098 mmol) in THF (29 μL) was added 15-crown-5 ether (28 μL, 0.144 mmol) and NaH (4 mg, 0.098 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C to the solution was added 4,6-*O*-benzylidene-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **42** (20 mg, 0.039 mmol). After being stirred for 16.5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography (Toluene/EtOAc, 10:1) to give compound **50** (18 mg, 53%) as a colorless syrup and recovered **8** (38 mg, 71%). R_f = 0.20 (Toluene/EtOAc, 10:1); [α] = −19.3° (c 1.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.26(m, 25H), 5.53(s, 1H, PhCH), 4.97(d, 1H, J = 10.7 Hz), 4.95(d, 1H, J = 10.9 Hz), 4.90(d, 1H, J = 10.9 Hz), 4.85(d, 1H, J = 10.7 Hz), 4.84(d, 1H, J = 10.9 Hz), 4.75(d, 1H, J = 11.6 Hz), 4.66(d, 1H, J = 11.6 Hz), 4.58(d, 1H, J = 10.9 Hz), 4.19(dd, 1H, $J_{2',3'}$ = 9.8 Hz, $J_{3',4'}$ = 9.8 Hz, H-3′), 4.09(dd, 1H, $J_{5',6'a}$ = 4.2 Hz, J_{gem} = 10.9 Hz, H-6′a), 3.94(d, 1H, J_{gem} = 8.9 Hz, H-6a), 3.78(dd, 1H, $J_{5,6b}$ = 2.9 Hz, H-6b), 3.66(m, 1H, H-1′), 3.61–3.48(m, 5H, H-1, H-2, H-3, H-4, H-4′), 3.59(dd, 1H, $J_{1',2'}$ = 3.1 Hz, H-2′), 3.59(dd, 1H, $J_{5,6b}$ = 10.9 Hz, H-6′b), 3.24(s, 6H), 2.30(m, 1H, H-5′), 2.21(m, 1H, H-5aeq), 1.64(m, 1H, H-5), 1.63(m, 1H, H-5aax), 1.57(ddd, 1H, $J_{1',5a'eq}$ = 3.3 Hz, $J_{5',5a'eq}$ = 3.3 Hz, J_{gem} = 13.5 Hz, H-5a′eq), 1.30(s, 6H), 1.10(ddd, 1H, $J_{1',5a'ax}$ = 1.9 Hz, $J_{5',5a'ax}$ = 13.4 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.97, 138.93, 138.89, 138.38, 128.59, 128.36, 128.31, 128.28, 128.26, 128.10, 128.03, 127.81, 127.68, 127.57, 127.44, 127.38, 127.36, 126.23, 101.17, 99.43, 98.90, 86.39(C-3), 86.11(C-2), 80.62(C-4), 80.49(C-1), 80.47(C-4′), 75.83, 75.68, 75.23, 74.74(C-1′), 72.54(C-2′), 72.01, 71.40(C-6′), 70.72(C-6), 67.98(C-3′), 47.84, 47.78, 39.22(C-5), 33.52(C-5′), 30.36(C-5a), 29.24(C-5a′), 17.77, 17.75; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{55}H_{64}O_{11}Na$ 923.4341, found 923.4339.

4.1.42. 5a,5a′-Dicarba-β-D-isomaltose (1)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-*O*-benzyl-5a-carba-β-D-glucopyranoside **20** (63 mg, 0.059 mmol) in MeOH (5 mL) and AcOH (100 μL) was added Pd Black (2 mg, 0.019 mmol). The resulting suspension was hydrogenated at 1 atm for 2.5 h. The solution was filtered through of Celite, and the solvent was evaporated. The residue was chromatographed on a column of Amberlite 200CT ion-exchange resin (H^+ form) and IRA 96SB ion-exchange resin (OH^- form) to give compound **1** (18.9 mg, 95%) as a colorless syrup. R_f = 0.16 ($CHCl_3$/MeOH/H_2O, 10:5:1); [α] = +69.7° (c 0.50, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 3.84(ddd, 1H, $J_{1',2'}$ = 3.2 Hz, $J_{1',5a'eq}$ = 3.6 Hz, $J_{1',5a'ax}$ = 1.4 Hz, H-1′), 3.79(dd, 1H, $J_{5',6'a}$ = 3.6 Hz, J_{gem} = 11.2 Hz, H-6′a), 3.71(dd, 1H, $J_{5',6'b}$ = 5.9 Hz, H-6′b), 3.68–3.61(m, 2H, H-6), 3.65(dd, 1H, $J_{2',3'}$ = 9.6 Hz, $J_{3',4'}$ = 9.1 Hz, H-3′), 3.61(ddd, 1H, $J_{1,2}$ = 9.1 Hz, $J_{1,5aeq}$ = 4.3 Hz, $J_{1,5aax}$ = 11.9 Hz, H-1), 3.52(dd, 1H, H-2′), 3.39(dd, 1H, $J_{3,4}$ = 8.7 Hz, $J_{4,5}$ = 8.8 Hz, H-4), 3.33(dd, 1H, $J_{4',5'}$ = 11.2 Hz, H-4′), 3.33(dd, 1H, $J_{2,3}$ = 8.9 Hz, H-3), 3.28(dd, 1H, H-2), 2,18(ddd, 1H, $J_{5',5a'eq}$ = 3.6 Hz, J_{gem} = 14.6 Hz, H-5a′eq), 2.11(ddd, 1H, $J_{5,5aeq}$ = 4.2 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.91–1.79(m, 2H, H-5, H-5′), 1.35(ddd, 1H, $J_{5,5aax}$ = 12.0 Hz, J_{gem} = 13.0 Hz, H-5aax), 1.30(ddd, 1H, H-5a′ax); ^{13}C NMR (100 MHz, D_2O) δ 76.91(C-2), 76.80(C-1′), 76.76(C-3), 75.05(C-3′), 73.78(C-2′), 73.37(C-4), 73.10(C-4′), 71.05(C-1), 69.59(C-6′), 62.32(C-6), 38.39(C-5), 38.17(C-5′), 32.08(C-5a), 26.29(C-5a′); HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{26}O_9Na$ 361.1469, found 361.1471.

4.1.43. 1,2,3-Tri-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-glucopyranose (51)

To a solution of 4,6-*O*-benzylidene-5a-carba-β-D-glucopyranose **10**

(520 mg, 1.95 mmol) in DMF (10 mL) and NaH (585 mg, 14.6 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added BnBr (1.7 mL, 14.6 mmol). After being stirred for overnight, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with Et_2O, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 7:1) to give compound **51** (977 mg, 94%) as a white amorphous solid. R_f = 0.48 (hexane/EtOAc, 4:1); [α] = −29.3° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.51–7.24(m, 20H), 5.58(s, 1H, PhCH), 4.95(d, 1H, J = 11.0 Hz), 4.90(s, 2H), 4.79(d, 1H, J = 11.0 Hz), 4.70(d, 1H, J = 11.5 Hz), 4.67(d, 1H, J = 11.5 Hz), 4.18(dd, 1H, $J_{5,6a}$ = 4.5 Hz, J_{gem} = 11.0 Hz, H-6a), 3.67(dd, 1H, $J_{2,3}$ = 8.9 Hz, $J_{3,4}$ = 9.1 Hz, H-3), 3.63(dd, 1H, $J_{5,6b}$ = 11.1 Hz, H-6b), 3.62(dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.58(ddd, 1H, $J_{1,2}$ = 8.9 Hz, $J_{1,5aeq}$ = 4.3 Hz, $J_{1,5aax}$ = 10.9 Hz, H-1), 3.56(dd, 1H, H-2), 1.89(ddd, 1H, $J_{5,5aeq}$ = 3.3 Hz, J_{gem} = 12.8 Hz, H-5aeq), 1.78(m, 1H, H-5), 1.10(ddd, 1H, $J_{5,5aax}$ = 10.9 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.80, 138.76, 138.47, 138.17, 128.72, 128.41, 128.32, 128.29, 128.18, 128.16, 128.05, 127.69, 127.66, 127.55, 125.93, 101.04(PhCH), 85.53(C-2), 83.51(C-4), 83.20(C-3), 80.04(C-1), 76.09, 75.62, 72.71, 71.01(C-6), 33.82(C-5), 28.55(C-5a); HRMS(ESI): $[M+Na]^+$ calcd for $C_{35}H_{36}O_5Na$ 559.2455, found 559.2458.

*4.1.44. 1,2,3,6-Tetra-O-benzyl-5a-carba-β-D-glucopyranose (**52**)*

To a solution of 1,2,3-tri-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranose **51** (1.127 g, 2.10 mmol) and trimethylamine borane (1.0 g, 14.7 mmol) in THF (42 mL) was added powdered MS4A (5.0 g), and the mixture was stirred for 1 h under Ar. To the solution was added $AlCl_3$ (1.9 g, 14.7 mmol), and the solution was stirred overnight. The solution was filtered through of Celite, and the solvent was evaporated. The residue was diluted with EtOAc, and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 4:1) to give compound **52** (953 mg, 84%) as a colorless syrup. R_f = 0.38 (hexane/EtOAc, 4:1); [α] = −14.6° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36–7.24(m, 20H), 4.97(d, 1H, J = 11.4 Hz), 4.96(d, 1H, J = 10.5 Hz), 4.82(d, 1H, J = 10.5 Hz), 4.74(d, 1H, J = 11.4 Hz), 4.69(d, 1H, J = 11.6 Hz), 4.64(d, 1H, J = 11.6 Hz), 4.51(s, 2H), 3.62(dd, 1H, $J_{5,6a}$ = 5.1 Hz, J_{gem} = 9.1 Hz, H-6a), 3.54(m, 1H, H-1), 3.53(dd, 1H, $J_{5,6b}$ = 5.7 Hz, H-6b), 3.50(dd, 1H, $J_{1,2}$ = 9.0 Hz, $J_{2,3}$ = 9.0 Hz, H-2), 3.36(dd, 1H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 3.34(dd, 1H, H-3), 2.14(ddd, 1H, $J_{1,5aeq}$ = 3.8 Hz, $J_{5,5aeq}$ = 3.8 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.71(m, 1H, H-5), 1.28(ddd, 1H, $J_{1,5aax}$ = 11.2 Hz, $J_{5,5aax}$ = 11.2 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.74, 138.57, 138.08, 128.53, 128.39, 128.36, 128.34, 128.02, 127.90, 127.75, 127.66, 127.65, 127.56, 85.78(C-3), 85.38(C-2), 80.28(C-1), 75.61, 75.57, 74.05(C-4), 73.38, 72.32, 72.06(C-6), 38.38(C-5), 30.14(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{38}O_5Na$ 561.2611, found 561.2611.

*4.1.45. 2,3,4,6-Tetra-O-benzyl-5a-carba-α-D-glucopyranosyl-(1 → 4)-1,2,3,6-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (**53**)*

To a solution of 1,2,3,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **52** (80 mg, 0.149 mmol) in THF (44 μL) was added NaH (6 mg, 0.149 mmol) and 15-crown-5 ether (44 μL, 0.222 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (40 mg, 0.060 mmol). After being stirred for overnight, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **53** (3 mg, 5%) as a colorless syrup and olefin **21** (24 mg, 80%) as a colorless syrup and recovered **52** (71 mg, 89%). R_f = 0.16 (Toluene/EtOAc, 20:1); [α] = +34.1° (*c* 0.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36–7.13(m, 40H), 5.00(d, 1H, J = 11.9 Hz), 4.91(d, 1H, J = 10.6 Hz), 4.87(d, 1H, J = 11.0 Hz), 4.84(d, 1H, J = 10.8 Hz), 4.75(d, 1H, J = 11.9 Hz), 4.70(d, 1H, J = 11.6 Hz), 4.69(d, 1H, J = 10.6 Hz), 4.65(d, 1H, J = 10.8 Hz), 4.64(d, 1H, J = 12.4 Hz), 4.64(d, 1H, J = 11.6 Hz), 4.61(m, 1H, H-1′), 4.57(d, 1H, J = 12.4 Hz), 4.48(d, 1H, J = 12.1 Hz), 4.47(d, 1H, J = 11.0 Hz), 4.38(d, 1H, J = 12.1 Hz), 4.30(d, 1H, J = 12.1 Hz), 4.25(d, 1H, J = 12.1 Hz), 3.94(dd, 1H, $J_{2',3'}$ = 9.5 Hz, $J_{3',4'}$ = 9.1 Hz, H-3′), 3.74(dd, 1H, $J_{5,6a}$ = 4.6 Hz, J_{gem} = 8.6 Hz, H-6a), 3.73(dd, 1H, $J_{3,4}$ = 8.1 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 3.61–3.51(m, 2H, H-2, H-3), 3.53(m, 1H, H-1), 3.51(dd, 1H, $J_{5',6'a}$ = 3.7 Hz, J_{gem} = 9.0 Hz, H-6′a), 3.45(dd, 1H, $J_{3',4'}$ = 9.1 Hz, $J_{4',5'}$ = 10.7 Hz, H-4′), 3.42(dd, 1H, $J_{5,6b}$ = 2.7 Hz, H-6b), 3.29(dd, 1H, $J_{1',2'}$ = 2.9 Hz, $J_{2',3'}$ = 9.5 Hz, H-2′), 3.14(dd, 1H, $J_{5',6'b}$ = 3.7 Hz, H-6′b), 2.15(ddd, 1H, $J_{1',5a'eq}$ = 3.5 Hz, $J_{5',5a'eq}$ = 3.5 Hz, J_{gem} = 14.8 Hz, H-5a′eq), 2.08(ddd, 1H, $J_{1,5aeq}$ = 3.2 Hz, $J_{5,5aeq}$ = 3.2 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.95(m, 1H, H-5′), 1.76(m, 1H, H-5), 1.58(ddd, 1H, $J_{1,5aax}$ = 11.3 Hz, $J_{5,5aax}$ = 11.3 Hz, H-5aax), 1.31(ddd, 1H, $J_{1',5a'ax}$ = 1.7 Hz, $J_{5',5a'ax}$ = 13.2 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.28, 139.23, 139.08, 138.74, 138.67, 138.60, 138.58, 138.54, 128.35, 128.27, 128.20, 128.18, 128.09, 127.82, 127.78, 128.66, 127.63, 127.56, 127.51, 127.48, 127.43, 127.31, 127.26, 127.24, 127.14, 126.98, 126.49, 86.70(C-3), 86.61(C-2), 83.84(C-3′), 82.79(C-2′), 80.98(C-4′), 80.25(C-1), 75.71, 75.28, 75.09, 74.00, 73.27(C-4), 72.96, 72.78(C-1′), 72.66, 72.60, 72.21, 70.35(C-6), 69.77(C-6′), 38.79(C-5), 36.73(C-5′), 30.50(C-5a), 27.13(C-5a′); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{70}H_{74}O_9Na$ 1081.5225, found 1081.5225.

*4.1.46. 2,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 4)-1,2,3,6-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (**54**)*

To a solution of 1,2,3,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **52** (85 mg, 0.158 mmol) in THF (47 μL) was added 15-crown-5 ether (46 μL, 0.233 mmol) and NaH (6 mg, 0.158 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **27** (36 mg, 0.063 mmol). After being stirred for 15 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography (Toluene/EtOAc, 10:1) to give compound **54** (12 mg, 20%) as a colorless syrup and olefin **44** (9 mg, 36%) as a colorless syrup and recovered **52** (68 mg, 80%). R_f = 0.13 (Toluene/EtOAc, 20:1); [α] = −11.4° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.52–7.13(m, 35H), 5.45(s, 1H, PhCH), 4.99(d, 1H, J = 11.7 Hz), 4.92(d, 1H, J = 10.6 Hz), 4.81(d, 1H, J = 11.0 Hz), 4.78(d, 1H, J = 11.7 Hz), 4.73(d, 1H, J = 12.1 Hz), 4.70(d, 1H, J = 11.7 Hz), 4.68(d, 1H, J = 10.6 Hz), 4.68(d, 1H, J = 11.0 Hz), 4.68(m, 1H, H-1′), 4.65(d, 1H, J = 11.7 Hz), 4.65(d, 1H, J = 12.1 Hz), 4.59(d, 1H, J = 11.0 Hz), 4.42(d, 1H, J = 12.1 Hz), 4.01(dd, 1H, $J_{2',3'}$ = 9.3 Hz, $J_{3',4'}$ = 9.6 Hz, H-3′), 3.99(dd, 1H, $J_{5',6'a}$ = 4.4 Hz, J_{gem} = 11.0 Hz, H-6′a), 3.81(dd, 1H, $J_{5,6a}$ = 4.4 Hz, J_{gem} = 11.0 Hz, H-6a), 3.75(dd, 1H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 9.1 Hz, H-4), 3.60(dd, 1H, $J_{2,3}$ = 8.7 Hz, H-3), 3.58–3.50(m, 2H, H-1, H-2), 3.50(dd, 1H, $J_{4',5'}$ = 10.1 Hz, H-4′), 3.48(dd, 1H, $J_{5',6'b}$ = 11.0 Hz, H-6′b), 3.41(dd, 1H, $J_{5,6b}$ = 2.3 Hz, H-6b), 3.31(dd, 1H, $J_{1',2'}$ = 2.9 Hz, H-2′), 2.19(m, 1H, H-5′), 2.06(ddd, 1H, $J_{1,5aeq}$ = 3.2 Hz, $J_{5,5aeq}$ = 3.2 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.98(ddd, 1H, $J_{1',5a'eq}$ = 3.3 Hz, $J_{5',5a'eq}$ = 3.3 Hz, J_{gem} = 14.4 Hz, H-5a′eq), 1.76(m, 1H, H-5), 1.64(ddd, 1H, $J_{1,5aax}$ = 11.3 Hz, $J_{5,5aax}$ = 11.3 Hz, H-5aax), 0.79(ddd, 1H, $J_{1',5a'ax}$ = 1.5 Hz, $J_{5',5a'ax}$ = 12.9 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.11, 138.67, 138.61, 138.58, 138.53, 128.57, 128.36, 128.27, 128.20, 128.17, 128.16, 128.09, 127.68, 127.64, 127.54, 127.49, 127.39, 127.36, 127.00, 126.47, 126.04, 101.12(PhCH), 86.61(C-2, C-3), 84.55(C-4′), 81.83(C-2′), 80.58(C-3′), 80.17(C-1), 75.72, 75.36, 73.90,

73.47(C-4), 73.25, 73.23(C-1′), 72.88, 72.24, 71.26(C-6′), 70.18(C-6), 38.72(C-5), 32.29(C-5′), 30.56(C-5a), 25.27(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{63}H_{66}O_9Na$ 989.4599, found 989.4599.

4.1.47. 5a,5a′-Dicarba-β-D-maltose (2)

To a solution of 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 4)-1,2,3,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranoside **54** (18 mg, 0.018 mmol) in MeOH (1.5 mL), THF (0.5 mL) and AcOH (0.3 mL) was added Pd Black (2 mg, 0.019 mmol). The resulting suspension was hydrogenated at 1 atm for overnight. The solution was filtered through of Celite, and the solvent was evaporated. The residue was chromatographed on a column of Amberlite 200CT ion-exchange resin (H^+ form) and IRA 96SB ion-exchange resin (OH^- form) to give compound **2** (4.8 mg, 80%) as a colorless syrup. R_f = 0.16 ($CHCl_3$/MeOH/H_2O, 10:5:1); [α] = +70.0° (*c* 0.15, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.17(ddd, 1H, $J_{1',2'}$ = 3.3 Hz, $J_{1',5a'eq}$ = 3.7 Hz, $J_{1',5a'ax}$ = 2.2 Hz, H-1′), 3.80(dd, 1H, $J_{5,6a}$ = 3.3 Hz, J_{gem} = 11.0 Hz, H-6a), 3.80(dd, 1H, $J_{5',6'a}$ = 3.3 Hz, J_{gem} = 11.1 Hz, H-6′a), 3.73(dd, 1H, $J_{5',6'b}$ = 2.8 Hz, H-6′b), 3.71(dd, 1H, $J_{5,6b}$ = 2.8 Hz, H-6b), 3.66(dd, 1H, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 9.2 Hz, H-3′), 3.61(ddd, 1H, $J_{1,2}$ = 9.1 Hz, $J_{1,5aeq}$ = 4.8 Hz, $J_{1,5aax}$ = 11.7 Hz, H-1), 3.56(dd, 1H, H-2′), 3.55(dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.41(dd, 1H, $J_{4,5}$ = 10.6 Hz, H-4), 3.34(dd, 1H, H-2), 3.32(dd, 1H, $J_{4',5'}$ = 9.3 Hz, H-4′), 2.08(ddd, 1H, $J_{5',5a'eq}$ = 3.7 Hz, J_{gem} = 14.2 Hz, H-5a′eq), 2.06(ddd, 1H, $J_{5,5aeq}$ = 3.7 Hz, H-5aeq), 1.91(m, 1H, H-5′), 1.72(m, 1H, H-5), 1.41(ddd, 1H, $J_{5',5a'ax}$ = 12.7 Hz, H-5a′ax), 1.37(ddd, 1H, $J_{5,5aax}$ = 11.9 Hz, H-5aax); ^{13}C NMR (100 MHz, D_2O) δ 82.03(C-4), 79.77(C-1′), 77.48(C-3), 76.76(C-2), 75.07(C-3′), 74.22(C-2′), 72.83(C-4′), 70.95(C-1), 62.19(C-6′), 61.72(C-6), 39.58(C-5), 38.66(C-5′), 31.63(C-5a), 28.70(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{26}O_9Na$ 361.1469, found 361.1470.

4.1.48. 2,3,4,6-Tetra-O-benzyl-5a-carba-α-D-glucopyranosyl-(1 → 1)-2,3,4,6-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (55)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (80 mg, 0.149 mmol) in THF (44 μL) was added 15-crown-5 ether (44 μL, 0.222 mmol) and NaH (6 mg, 0.149 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (40 mg, 0.060 mmol). After being stirred for 7.5 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give compound **55** (23 mg, 37%) as a colorless syrup and olefin **21** (10 mg, 34%) as a colorless syrup and recovered **13** (62 mg, 77%). R_f = 0.28 (hexane/EtOAc, 6:1); [α] = +33.1° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.12(m, 40H), 5.18(d, 1H, *J* = 11.1 Hz), 4.90(d, 1H, *J* = 10.6 Hz), 4.87(d, 1H, *J* = 10.7 Hz), 4.86(d, 1H, *J* = 10.8 Hz), 4.79(d, 1H, *J* = 11.1 Hz), 4.78(d, 1H, *J* = 10.6 Hz), 4.73(d, 1H, *J* = 10.8 Hz), 4.66(d, 1H, *J* = 12.1 Hz), 4.62(d, 1H, *J* = 12.1 Hz), 4.54(d, 1H, *J* = 10.8 Hz), 4.50(d, 1H, *J* = 10.7 Hz), 4.49(d, 1H, *J* = 10.8 Hz), 4.44(s, 2H), 4.43(s, 2H), 4.06(m, 1H, $J_{1',5a'eq}$ = 3.6 Hz, $J_{1',5a'ax}$ = 1.3 Hz, H-1′), 3.98(dd, 1H, $J_{2',3'}$ = 9.6 Hz, $J_{3',4'}$ = 9.4 Hz, H-3′), 3.84(ddd, 1H, $J_{1',2'}$ = 8.7 Hz, $J_{1',5a'eq}$ = 4.2 Hz, J_{gem} = 11.6 Hz, H-1), 3.69(dd, 1H, $J_{5',6'a}$ = 4.4 Hz, J_{gem} = 8.8 Hz, H-6′a), 3.54(dd, 1H, $J_{5,6a}$ = 5.4 Hz, J_{gem} = 8.6 Hz, H-6a), 3.52(dd, 1H, $J_{2,3}$ = 8.5 Hz, H-3), 3.49(dd, 1H, $J_{5,6b}$ = 8.6 Hz, H-6b), 3.46(m, 1H, H-4′), 3.46(dd, 1H, $J_{5',6'b}$ = 5.5 Hz, H-6′b), 3.45(dd, 1H, H-2), 3.43(m, 1H, H-4), 3.34(dd, 1H, $J_{1',2'}$ = 2.6 Hz, H-2′), 2.18(m, 1H, H-5′), 2.08(ddd, 1H, $J_{5,5aeq}$ = 3.9 Hz, J_{gem} = 13.1 Hz, H-5aeq), 1.87(ddd, 1H, $J_{1',5a'eq}$ = 3.6 Hz, $J_{5',5a'eq}$ = 3.6 Hz, J_{gem} = 14.3 Hz, H-5a′eq), 1.64(m, 1H, H-5), 1.47(ddd, 1H, $J_{1',5a'eq}$ = 1.3 Hz, $J_{5',5a'eq}$ = 13.1 Hz, H-5a′ax), 1.36(ddd, 1H, $J_{1,5aax}$ = 11.6 Hz, $J_{5,5aax}$ = 11.9 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.37, 139.24, 139.01, 138.85, 138.80, 138.64, 138.62, 138.43, 128.34, 128.30, 128.26, 128.18, 128.16, 128.04, 127.96, 127.90, 127.89, 127.79, 127.56, 127.52, 127.48, 127.46, 127.39, 127.27, 127.18, 126.96, 86.29(C-3), 85.79(C-2), 84.00(C-3′), 83.76(C-2′), 81.06(C-4′), 80.73(C-4), 79.38(C-1), 75.82, 75.40, 75.26, 75.17, 73.10, 72.99, 72.74, 72.62(C-1′), 70.23(C-6), 70.16(C-6′), 38.86(C-5), 37.48(C-5′), 30.98(C-5a), 30.86(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{70}H_{74}O_9Na$ 1081.5225, found 1081.5225.

4.1.49. 2,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 1)-2,3,4,6-tetra-O-benzyl-5a-carba-β-D-glucopyranoside (56)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranose **13** (90 mg, 0.168 mmol) in THF (50 μL) was added 15-crown-5 ether (49 μL, 0.248 mmol) and NaH (7 mg, 0.168 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **27** (39 mg, 0.067 mmol). After being stirred for 20 h, MeOH was added, and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography (Toluene/EtOAc, 20:1) to give compound **56** (42 mg, 64%) as a white amorphous solid and olefin **44** (3 mg, 1%) as a colorless syrup and recovered **13** (57 mg, 64%). R_f = 0.35 (Toluene/EtOAc, 20:1); [α] = +11.1° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.13(m, 35H), 5.57(s, 1H, PhCH), 5.16(d, 1H, *J* = 10.8 Hz), 4.91(d, 1H, *J* = 10.7 Hz), 4.87(d, 1H, *J* = 11.0 Hz), 4.81(d, 1H, *J* = 10.8 Hz), 4.79(d, 1H, *J* = 10.7 Hz), 4.76(d, 1H, *J* = 12.1 Hz), 4.69(d, 1H, *J* = 11.0 Hz), 4.64(d, 1H, *J* = 12.1 Hz), 4.54(d, 1H, *J* = 11.0 Hz), 4.50(d, 1H, *J* = 11.0 Hz), 4.45(s, 2H), 4.18(dd, 1H, $J_{5',6'a}$ = 4.3 Hz, J_{gem} = 11.9 Hz, H-6′a), 4.08(m, 1H, H-1′), 4.04(dd, 1H, $J_{2',3'}$ = 9.4 Hz, $J_{3',4'}$ = 9.3 Hz, H-3′) , 3.88(ddd, 1H, $J_{1,2}$ = 8.4 Hz, $J_{1,5aeq}$ = 4.2 Hz, $J_{1,5aax}$ = 11.8 Hz, H-1), 3.58(dd, 1H, $J_{5,6b}$ = 11.0 Hz, H-6′b), 3.57–3.48(m, 2H, H-6), 3.52(dd, 1H, $J_{2,3}$ = 8.6 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.52(dd, 1H, H-4′), 3.48(dd, 1H, H-2), 3.44(dd, 1H, $J_{4,5}$ = 9.1 Hz, H-4′), 3.36(dd, 1H, $J_{1',2'}$ = 2.8 Hz, H-2′), 2.38(m, 1H, H-5′), 2.08(ddd, 1H, $J_{5,5aeq}$ = 4.0 Hz, J_{gem} = 13.0 Hz, H-5aeq), 1.66(m, 1H, H-5), 1.65(ddd, 1H, $J_{1',5a'eq}$ = 3.4 Hz, $J_{5',5a'eq}$ = 3.4 Hz, J_{gem} = 13.6 Hz, H-5a′eq), 1.52(ddd, 1H, $J_{5,5aax}$ = 12.0 Hz, H-5aax), 1.01(ddd, 1H, $J_{1',5a'ax}$ = 1.6 Hz, $J_{5',5a'ax}$ = 13.1 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.24, 139.11, 138.78, 138.57, 138.41, 138.35, 128.60, 128.34, 128.27, 128.17, 128.10, 128.08, 128.03, 127.96, 127.89, 127.58, 127.52, 127.41, 127.30, 127.27, 127.03, 125.99, 101.13(PhCH), 86.26(C-3), 85.65(C-2), 84.40(C-4′), 82.76(C-2′), 80.87(C-3), 80.67(C-4), 79.44(C-1), 75.83, 75.49, 75.30, 75.17, 73.20, 73.12, 72.86(C-1′), 71.36(C-6′), 70.21(C-6), 38.85(C-5), 32.74(C-5′), 30.90(C-5a), 28.98(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{63}H_{66}O_9Na$ 989.4599, found 989.4597.

4.1.50. 5a,5a′-Dicarba-α,β-D-trehalose (3)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-α-D-glucopyranosyl-(1 → 1)-2,3,4,6-tetra-*O*-benzyl-5a-carba-β-D-glucopyranoside **55** (19 mg, 0.018 mmol) in MeOH (1 mL), THF (100 μL) and AcOH (200 μL) was added Pd Black (2 mg, 0.020 mmol). The resulting suspension was hydrogenated at 1 atm for 5 h. The solution was filtered through of Celite, and the solvent was evaporated. The residue was chromatographed on a column of Amberlite 200CT ion-exchange resin (H^+ form) and IRA 96SB ion-exchange resin (OH^- form) to give compound **3** (6.1 mg, 100%) as a colorless syrup. R_f = 0.17 ($CHCl_3$/MeOH/H_2O, 10:5:1); [α] = +41.3° (*c* 0.30, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.10(ddd, 1H, $J_{1',2'}$ = 3.2 Hz, $J_{1',5a'eq}$ = 3.7 Hz, $J_{1',5a'ax}$ = 2.0 Hz, H-1′), 3.80(dd, 1H, $J_{5,6a}$ = 4.9 Hz, J_{gem} = 11.0 Hz, H-6a), 3.79(dd, 1H, $J_{5',6'a}$ = 4.9 Hz, J_{gem} = 11.0 Hz, H-6′a), 3.70(dd, 1H, $J_{5',6'b}$ = 10.8 Hz, H-6′b), 3.69 (dd, 1H, $J_{5,6b}$ = 10.9 Hz, H-6b), 3.65(dd, 1H, $J_{2',3'}$ = 9.7 Hz, $J_{3',4'}$ = 9.2 Hz, H-3′), 3.55 (ddd, 1H, $J_{1,2}$ = 9.2 Hz, $J_{1,5aeq}$ = 4.4 Hz, $J_{1,5aax}$ = 11.4 Hz, H-1), 3.51(dd, 1H, H-2′), 3.45(dd, 1H, $J_{2,3}$ = 9.1 Hz, H-2), 3.37(dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 3.33(dd, 1H, $J_{4.5}$ = 9.5 Hz, H-4), 3.32(dd, 1H, $J_{4',5'}$ = 10.7 Hz, H-4′), 2.12(ddd, 1H, $J_{5,5aeq}$ = 4.1 Hz, J_{gem} = 13.0 Hz, H-5aeq), 2,08(ddd, 1H,

$J_{5',5a'eq}$ = 3.7 Hz, J_{gem} = 14.8 Hz, H-5a′eq), 1.91(m, 1H, H-5′), 1.67(m, 1H, H-5), 1.44(ddd, 1H, $J_{5',5a'ax}$ = 12.9 Hz, H-5a′ax), 1.34(ddd, 1H, $J_{5,5aax}$ = 11.6 Hz, H-5aax); ^{13}C NMR (100 MHz, D_2O) δ 80.82(C-1), 78.98(C-1′), 76.73(C-3), 76.67(C-2), 75.15(C-3′), 74.32(C-2′), 72.90(C-4′), 72.41(C-4), 62.26(C-6′), 62.14(C-6), 40.01(C-5), 38.43(C-5′), 30.95(C-5a), 29.30(C-5a′); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{26}O_9Na$ 361.1469, found 361.1469.

4.1.51. 1-O-Acetyl-2,3-di-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-glucopyranose (57)

To a solution of 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranose **26** (230 mg, 0.515 mmol) in CH_2Cl_2 (7 mL) at −10 °C was added 2,6-di-*t*-butyl-4-methylpyridine (106 mg, 0.515 mmol) and Tf_2O (173 μL, 1.03 mmol). After being stirred for 10 min, the solution was diluted with CH_2Cl_2 and washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. To a solution of the residue in Toluene (7 mL) was added CsOAc (642 mg, 3.34 mmol) and 18-Crown-6 ether (272 mg, 1.03 mmol). After being stirred for 1 h, the solution was diluted with EtOAc. The solution washed with brine, and the organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc, 4:1) to give compound **57** (241 mg, 96%) as a white amorphous solid. R_f = 0.22 (hexane/EtOAc, 4:1); [α] = −5.3° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.24(m, 15H), 5.60(s, 1H), 5.49(ddd, 1H, $J_{1,2}$ = 3.2 Hz, $J_{1,5aeq}$ = 3.6 Hz, $J_{1,5aax}$ = 2.2 Hz, H-1), 4.92(d, 1H, *J* = 11.0 Hz), 4.82(d, 1H, *J* = 11.0 Hz), 4.74(d, 1H, *J* = 11.7 Hz), 4.62(d, 1H, *J* = 11.7 Hz), 4.17(dd, 1H, $J_{5,6a}$ = 4.3 Hz, J_{gem} = 10.9 Hz, H-6a), 3.94(dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.59(dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 3.59(dd, 1H, $J_{5,6b}$ = 10.9 Hz, H-6b), 3.48(dd, 1H, H-2), 2.26(m, 1H, H-5), 2.13(s, 3H), 1.73(ddd, 1H, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 14.5 Hz, H-5aeq), 1.15(ddd, 1H, $J_{5,5aax}$ = 13.1 Hz, H-5aax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.36, 138.91, 138.15, 138.01, 128.73, 128.35, 128.24, 128.18, 128.11, 127.98, 127.71, 127.52, 125.93, 101.18(PhCH), 83.73(C-4), 80.40(C-2), 80.37(C-3), 75.71, 72.51, 71.02(C-6), 68.08(C-1), 32.83(C-5), 27.20(C-5a), 21.24; HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{32}O_6Na$ 511.2091, found 511.2087.

4.1.52. 1,2,3-Tri-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-glucopyranose (58)

To a solution of 1-*O*-acetyl-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranose **57** (205 mg, 0.420 mmol) in MeOH (4 mL) was added NaOMe (45 mg, 0.839 mmol). After being stirred for 7 h, the solution was neutralized with Amberlite 200CT (H^+), and the resin was filtered off. The filtrate was concentrated *in vacuo*. To a solution of the residue in DMF (1.5 mL) and NaH (47 mg, 1.16 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added BnBr (138 μL, 0.256 mmol). After being stirred for 30 min, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc, 4:1) to give compound **58** (224 mg, 90%) as a white amorphous solid. R_f = 0.34 (hexane/EtOAc, 4:1); [α] = −8.8° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.24(m, 20H), 5.57(s, 1H), 4.94(d, 1H, *J* = 10.9 Hz), 4.84(d, 1H, *J* = 10.9 Hz), 4.75(d, 1H, *J* = 12.0 Hz), 4.74(d, 1H, *J* = 12.2 Hz), 4.67(d, 1H, *J* = 12.0 Hz), 4.65(d, 1H, *J* = 12.2 Hz), 4.13(dd, 1H, $J_{5,6a}$ = 4.5 Hz, J_{gem} = 11.0 Hz, H-6a), 4.11(dd, 1H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.90(ddd, m, 1H, H-1), 3.56(dd, 1H, $J_{5,6b}$ = 11.0 Hz, H-6b), 3.54(dd, 1H, $J_{4,5}$ = 10.2 Hz, H-4), 3.41(dd, 1H, $J_{1,2}$ = 3.0 Hz, H-2), 2.38(m, 1H, H-5), 1.71(ddd, 1H, $J_{1,5aeq}$ = 3.6 Hz, $J_{5,5aeq}$ = 3.6 Hz, J_{gem} = 14.0 Hz, H-5aeq), 0.91(ddd, 1H, $J_{1,5aax}$ = 1.9 Hz, $J_{5,5aax}$ = 13.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.12, 138.70, 138.64, 138.39, 128.62, 128.29, 128.20, 128.17, 128.13, 127.66, 127.65, 127.51, 127.49, 127.41, 125.99, 101.16(PhCH), 84.34(C-4), 82.64(C-2), 80.73(C-3), 75.67, 73.67(C-1), 72.94, 71.76, 71.34(C-6), 32.37(C-5), 26.92(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{36}O_5Na$ 559.2455 found 559.2452.

4.1.53. 1,2,3,4-Tetra-O-benzyl-5a-carba-α-D-glucopyranose (59)

To a solution of 1,2,3-tri-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranose **58** (176 mg, 0.328 mmol) in THF (0.9 mL) was added $THF{\cdot}BH_3$ (1.3 mL, 1.0 M in THF, 1.31 mmol) and $CoCl_2$ (170 mg, 1.31 mmol). After being stirred for 2 h, the solution was diluted with EtOAc, and was filtered through Celite. The filtrate was added aq $NaBH_4$ (9.9 mg, 0.262 mmol), and was filtered through Celite. The filtrate was washed saturated $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to give compound **59** (163 mg, 93%) as a white amorphous solid. R_f = 0.11 (hexane/EtOAc, 4:1); [α] = +52.6° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.26(m, 20H), 5.03(d, 1H, *J* = 10.8 Hz), 4.98(d, 1H, *J* = 11.1 Hz), 4.83(d, 1H, *J* = 10.8 Hz), 4.70(d, 1H, *J* = 12.1 Hz), 4.67(d, 1H, *J* = 11.1 Hz), 4.65(s, 2H), 4.64(d, 1H, *J* = 12.1 Hz), 4.08(dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.1 Hz, H-3), 3.88(ddd, m, 1H, H-1), 3.62(ddd, 1H, $J_{5,6a}$ = 3.6 Hz, $^2J_{6a,OH}$ = 7.4 Hz, J_{gem} = 10.8 Hz, H-6a), 3.53(ddd, 1H, $J_{5,6b}$ = 5.1 Hz, $^2J_{6b,OH}$ = 3.8 Hz, H-6b), 3.38(dd, 1H, $J_{1,2}$ = 2.9 Hz, H-2), 3.38(dd, 1H, $J_{4,5}$ = 10.8 Hz, H-4), 2.11(m, 1H, H-5), 1.85(ddd. 1H, $J_{1,5aeq}$ = 3.7 Hz, $J_{5,5aeq}$ = 3.7 Hz, J_{gem} = 14.5 Hz, H-5aeq), 1.66(dd, 1H, OH), 1.11(ddd, 1H, $J_{1,5aax}$ = 1.9 Hz, $J_{5,5aax}$ = 12.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.01, 138.74, 138.58, 138.41, 128.55, 128.33, 128.27, 127.98, 127.88, 127.70, 127.64, 127.53, 127.47, 127.45, 83.87(C-3), 83.60(C-2), 82.32(C-4), 75.64, 74.93, 72.86(C-1), 72.43, 71.30, 64.74(C-6), 38.23(C-5), 28.01(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{38}O_5Na$ 561.2611, found 561.2613.

4.1.54. 2,3,4,6-Tetra-O-benzyl-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-O-benzyl-5a-carba-α-D-glucopyranoside (60)

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-α-D-glucopyranose **59** (40 mg, 0.075 mmol) in THF (22 μL) was added 15-crown-5 ether (22 μL, 0.111 mmol) and NaH (3 mg, 0.075 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3,4,6-tetra-*O*-benzyl-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **14** (20 mg, 0.030 mmol). After being stirred for 19 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography (hexane/EtOAc, 6:1) to give compound **60** (3.8 mg, 12%) as a colorless syrup and olefin **21** (10.2 mg, 66%) as a colorless syrup and recovered **8** (35 mg, 87%). R_f = 0.17 (hexane/EtOAc, 6:1); [α] = +47.6° (*c* 0.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.21(m, 40H), 5.00(d, 1H, *J* = 10.7 Hz), 4.96(d, 1H, *J* = 11.1 Hz), 4.92(d, 1H, *J* = 10.8 Hz), 4.88(d, 1H, *J* = 11.0 Hz), 4.81(d, 1H, *J* = 10.7 Hz), 4.79(d, 1H, *J* = 10.8 Hz), 4.64(s, 6H), 4.56(d, 1H, *J* = 11.1 Hz), 4.51(d, 1H, *J* = 11.0 Hz), 4.36(s, 2H), 4.03(dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.86(dd, 1H, $J_{2',3'}$ = 9.6 Hz, $J_{3',4'}$ = 9.3 Hz, H-3′), 3.84(dd, 1H, $J_{5,6a}$ = 5.2 Hz, J_{gem} = 9.0 Hz, H-6a), 3.84(m, 1H, H-1), 3.71(m, 1H, H-1′), 3.62(dd, 1H, $J_{5',6'a}$ = 4.2 Hz, J_{gem} = 8.9 Hz, H-6′a), 3.58(dd, 1H, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.48(dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.46(dd, 1H, $J_{4',5'}$ = 9.2 Hz, H-4′), 3.39(dd, 1H, $J_{1,2}$ = 2.8 Hz, H-2), 3.36(dd, 1H, $J_{1',2'}$ = 2.7 Hz, H-2′), 3.30(dd, 1H, $J_{5',6'b}$ = 2.4 Hz, H-6′b), 2.14–1.98(m, 2H, H-5, H-5′), 1.89(ddd, 1H, $J_{1,5aeq}$ = 3.7 Hz, $J_{5,5aeq}$ = 3.7 Hz, J_{gem} = 14.6 Hz, H-5aeq), 1.83(ddd, 1H, $J_{1',5a'eq}$ = 3.7 Hz, $J_{5',5a'eq}$ = 3.7 Hz, J_{gem} = 14.4 Hz, H-5a′eq), 1.44(ddd, 1H, $J_{1,5aax}$ = 1.7 Hz, $J_{5,5aax}$ = 14.6 Hz, H-5aax), 1.39(ddd, 1H, $J_{1',5a'ax}$ = 1.4 Hz, $J_{5',5a'ax}$ = 12.8 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.14, 139.13, 138.99, 138.84, 138.75, 138.74, 138.33, 128.62, 128.36, 128.29, 128.22, 128.19, 128.15, 128.13, 128.00, 127.69, 127.66, 127.54, 127.49, 127.45, 127.40, 127.36, 126.01, 101.16, 84.30(C-4′), 84.04(C-3), 83.69(C-2), 83.03(C-2′), 80.80(C-4), 80.22(C-3′), 75.70,

75.42, 75.11, 74.85(C-1′), 73.03(C-1), 72.78, 72.44, 71.30(C-6′), 71.05, 70.41(C-6), 37.35(C-5), 32.68(C-5′), 28.30(C-5a), 27.69(C-5a′); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{70}H_{74}O_9Na$ 1081.5225, found 1081.5221.

4.1.55. 2,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-O-benzyl-5a-carba-α-D-glucopyranoside (61)

To a solution of 1,2,3,4-tetra-*O*-benzyl-5a-carba-α-D-glucopyranose **59** (93 mg, 0.173 mmol) in THF (52 μL) was added 15-crown-5 ether (50 μL, 0.256 mmol) and NaH (7 mg, 0.173 mmol), and the mixture was stirred for 30 min under Ar. After being cooled to 0 °C, to the solution was added 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-*O*-trifluoromethanesulfonyl-5a-carba-β-D-glucopyranose **27** (40 mg, 0.691 mmol). After being stirred for 14 h, MeOH was added and the solution was concentrated *in vacuo*. The residue was diluted with EtOAc, and washed brine. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography (hexane/EtOAc, 4:1) to give compound **61** (25 mg, 37%) as a colorless syrup and olefin **44** (10 mg, 34%) as a colorless syrup and recovered **59** (73 mg, 79%). R_f = 0.13 (hexane/EtOAc, 6:1); [α] = +38.1° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.20(m, 35H), 5.55(s, 1H, PhCH), 5.01(d, 1H, J = 10.8 Hz), 5.00(d, 1H, J = 11.3 Hz), 4.90(d, 1H, J = 11.0 Hz), 4.81(d, 1H, J = 10.8 Hz), 4.81(d, 1H, J = 11.0 Hz), 4.73(d, 1H, J = 11.8 Hz), 4.66(d, 1H, J = 11.8 Hz), 4.66(d, 1H, J = 12.2 Hz), 4.65(s, 2H), 4.62(d, 1H, J = 12.2 Hz), 4.57(d, 1H, J = 11.3 Hz), 4.04(dd, 1H, $J_{5',6'a}$ = 4.7 Hz, J_{gem} = 11.2 Hz, H-6′a), 4.04(dd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.92(dd, 1H, $J_{2',3'}$ = 9.3 Hz, $J_{3',4'}$ = 9.5 Hz, H-3′), 3.85(m, 1H, H-1), 3.84(dd, 1H, $J_{5,6a}$ = 3.6 Hz, J_{gem} = 8.9 Hz, H-6a), 3.71(m, 1H, H-1′), 3.62(dd, 1H, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.52(dd, 1H, $J_{5',6'b}$ = 11.3 Hz, H-6′b), 3.50(dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4′), 3.49(dd, 1H, $J_{4,5}$ = 10.8 Hz, H-4), 3.40(dd, 1H, $J_{1,2}$ = 2.8 Hz, H-2), 3.36(dd, 1H, $J_{1',2'}$ = 2.8 Hz, H-2′), 2.22(m, 1H, H-5′), 2.10(m, 1H, H-5), 1.89(ddd, 1H, $J_{1,5aeq}$ = 3.7 Hz, $J_{5,5aeq}$ = 3.7 Hz, J_{gem} = 14.7 Hz, H-5aeq), 1.57(ddd, 1H, $J_{1',5a'eq}$ = 3.4 Hz, $J_{5',5a'eq}$ = 3.4 Hz, J_{gem} = 13.4 Hz, H-5a′eq), 1.42(ddd, 1H, $J_{1,5aax}$ = 1.4 Hz, $J_{5,5aax}$ = 13.1 Hz, H-5aax), 0.90(ddd, 1H, $J_{1',5a'ax}$ = 1.2 Hz, $J_{5',5a'ax}$ = 13.3 Hz, H-5a′ax); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.18, 139.15, 139.11, 138.91, 138.88, 138.81, 138.79, 138.56, 128.32, 128.30, 128.28, 128.22, 128.03, 128.02, 127.94, 127.70, 127.66, 127.58, 127.57, 127.44, 127.37, 127.35, 84.04(C-3), 84.00(C-2′), 83.77(C-3′), 83.72(C-2), 80.98(C-4′), 80.84(C-4), 75.72, 75.59, 75.28, 75.17, 74.57(C-1′), 73.09(C-1), 72.93, 72.44, 72.28, 71.06, 70.02(C-6), 69.90(C-6′), 37.43(C-5, C-5′), 29.45(C-5a′), 28.38(C-5a); HRMS(ESI) *m/z*: $[M+Na]^+$ calcd for $C_{63}H_{66}O_9Na$ 989.4599, found 989.4600.

4.1.56. 5a,5a′-Dicarba-α-D-isomaltose (4)

To a solution of 2,3,4,6-tetra-*O*-benzyl-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,2,3,4-tetra-*O*-benzyl-5a-carba-α-D-glucopyranoside **60** (6 mg, 0.0056 mmol) in MeOH (1 mL) and AcOH (100 μL) was added Pd Black (2 mg, 0.018 mmol). The resulting suspension was hydrogenated at 1 atm for 19 h. The solution was filtered through of Celite, and the solvent was evaporated. The residue was chromatographed on a column of Amberlite 200CT ion–exchange resin (H^+ form) and IRA 96SB ion–exchange resin (OH^- form) to give compound **4** (2.1 mg, 100%) as a colorless syrup. R_f = 0.14 ($CHCl_3$/MeOH/H_2O, 10:5:1); [α] +69.3° (*c* 0.30, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.13(ddd, 1H, $J_{1,2}$ = 3.2 Hz, $J_{1,5aeq}$ = 3.6 Hz, $J_{1,5aax}$ = 2.1 Hz, H-1), 3.83(ddd, 1H, $J_{1',2'}$ = 3.2 Hz, $J_{1',5a'eq}$ = 3.6 Hz, $J_{1',5a'ax}$ = 1.5 Hz, H-1′), 3.79(dd, 1H, $J_{5',6'a}$ = 3.6 Hz, J_{gem} = 11.3 Hz, H-6′a), 3.71(dd, 1H, $J_{5',6'b}$ = 6.1 Hz, H-6′b), 3.69 (dd, 1H, $J_{5,6a}$ = 6.8 Hz, J_{gem} = 9.3 Hz, H-6a), 3.65(dd, 1H, $J_{2',3'}$ = 9.6 Hz, $J_{3',4'}$ = 9.2 Hz, H-3′), 3.64(dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 3.58(dd, 1H, $J_{5,6b}$ = 4.0 Hz, H-6b), 3.51(dd, 1H, H-2′), 3.50(dd, 1H, H-2), 3.38(dd, 1H, $J_{4,5}$ = 9.0 Hz, H-4), 3.33(dd, 1H, $J_{4',5'}$ = 10.6 Hz, H-4′), 2,18(ddd, 1H, $J_{5',5a'eq}$ = 3.6 Hz, J_{gem} = 14.7 Hz, H-5a′eq), 2.12–2.01(m, 1H, H-5), 2.01(ddd, 1H, $J_{5,5aeq}$ = 4.2 Hz, J_{gem} = 14.6 Hz, H-5aeq), 1.93–1.81(m, 1H, H-5′), 1.55(ddd, 1H, $J_{5,5aax}$ = 12.7 Hz, J_{gem} = 14.6 Hz, H-5aax), 1.30(ddd, 1H, $J_{5',5a'ax}$ = 13.2 Hz, H-5a′ax); ^{13}C NMR (100 MHz, D_2O) δ 76.70(C-1′), 75.06(C-3′), 74.45(C-3), 73.88(C-4), 73.85(C-2, C-2′), 73.10(C-4′), 69.67(C-6), 68.83(C-1), 62.33(C-6′), 38.15(C-5′), 36.43(C-5), 30.55(C-5a), 26.28(C-5a′); HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{26}O_9Na$ 361.1469, found 361.1466.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bmc.2018.12.027.

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