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ARTICLE TYPE

A Neighboring Group Participation Strategy: Direct and Highly Diastereoselective Synthesis of 2-Substituted and 2,2-Bisubstituted Perhydrofuro[2,3-*b*]pyran Derivatives

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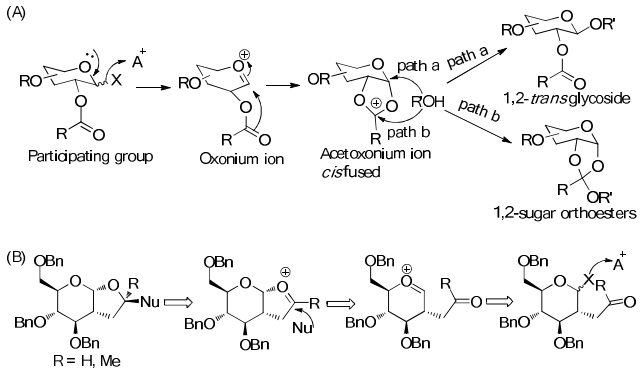
Treatment of methyl 2-*C*-formylmethyl-2-deoxy-β-D-glucopyranoside (5) or methyl 2-*C*-acetylmethyl-2-deoxy-β-D-glucopyranoside (1) with H_2SO_4-HOAc-Ac_2O gave 2-acetoxyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]hexahydrofuro[2,3-*b*]pyran (6) and acetyl 2-*C*-acetylmethyl-2-deoxy-α-D-glucopyranoside (7) respectively, which were further reacted with nucleophiles in the presence of TMSOTf and offered a series of 2-substituted and 2,2-disubstituted perhydrofuro[2,3-*b*] pyran derivatives in high yield with excellent diastereoselectivity.

Introduction

The perhydrofuro[2,3-*b*]pyran scaffolds constitute the core structural elements which are prevalent in a large number of naturally occurring biological active products.[1] Recent research also revealed that they would be used as potential HIV-1 protease inhibitor.[2] Among the myriad of elegant approaches to construct perhydrofuro[2,3-*b*]pyrans,[3] intramolecular cyclizations are particularly attractive with regard to stereoselectivity and chemoselectivity.[4] To this end, several different intramolecular cyclization strategies have been introduced to achieve the synthesis of substituted perhydrofuro[2,3-*b*]pyrans. Particularly, the use of 3-halogeno-2-allyloxy-perhydropyrans as substrates via radical cyclization to synthesize 3-substituted perhydrofuro[2,3-*b*]pyrans have been extensively studied and used to construct a number of complex natural or unnatural products.[5] Furthermore, in 2003, Yus and co-workers successfully synthesized 2,2-dialkyl-substituted perhydrofuro[2,3-*b*]pyrans via the oxidation-cyclization of methylidenic diols.[6] Very recently, Chandrasekaran and co-workers achieved the synthesis of 3-idio-perhydrofuro[2,3-*b*]pyrano-γ-butyrolactones and 3-idio-perhydrofuro[2,3-*b*]pyrans via NIS-mediated ring opening of 1,2-cyclopropanated sugar derivatives.[7] In most of these cases, much attention has been paid to the synthesis of 3-substituted perhydrofuro[2,3-*b*]pyrans. Installation of a heteroatom substituent or an active functional group at C(2) position of perhydrofuro[2,3-*b*]pyran, however, still represents a great challenge.

In the other hand, the use of neighboring group participation for regio- and stereo-chemical control is ubiquitous in organic chemistry.[8] Nowhere is this strategy more extensively exploited than in carbohydrate chemistry.[9] Neighboring group participation of a 2-*O*-carboxylate ester is the most reliable method for stereoselective constructing 1,2-*trans* glycosidic bond. Generally, in this strategy, a 2-*O*-carboxylate ester and an anomeric leaving group must be installed firstly (Scheme 1. A). Then, in the presence of a promoter, the leaving group is activated, followed by its departure with the help of the oxygen of the pyran-ring to form an oxonium ion. Then, the carbonyl group attacked to the oxonium ion formed a more stable acetoxonium ion. An alcohol can attack the anomeric center of the acetoxonium ion from only one face to provide 1,2-*trans* glycoside (Scheme 1. A, path a). An unavoidable by-product associated with this reaction is that the formation of 1,2-sugar orthoester derived from the attack of the alcohol to the acetoxonium ion (Scheme 1. A, path b).

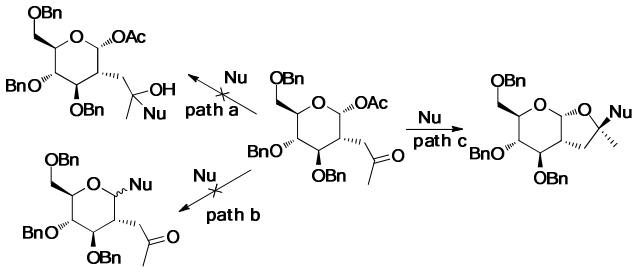


Scheme 1. (A) The neighboring group participation strategy in the synthesis of 1,2-*trans*-glycosides; (B) The construction of perhydrofuro[2,3-*b*]pyrans via neighboring group participation strategy.

Furthermore, it is well established that the 2-*C*-branched (acetylmethyl or acetonyl) sugars are the C2-carbon isosteres of the 2-*O*-acetyl-sugars or 2-*N*-acetamidosugars,[10] and the 2-*C*-branched sugars have been wildly used in the glycobiology.[10d-10f] Inspired by the neighboring group participation phenomenon and due to our continuing interest in the construction of 2-*C*-branched glycoside,[11] it was assumed that the perhydrofuro[2,3-*b*]pyran derivatives would be obtained from the nucleophilic capture of the bicyclic oxocarbenium ion, which could be generated through

the attack of the 2-carbonyl oxygen of the 2-formylmethyl/2-acetylmethyl to the anomeric center (Scheme 1. B). By this strategy, recently, we have reported a highly stereoselective synthesis of 2-*O/N* substituted perhydrofuro[2,3-*b*]pyran derivatives from *p*-tolyl 2-formylmethyl-2-deoxy-D-thioglucopyranoside.[11c] Mechanistic studies demonstrated that the formation of 2-*O/N* substituted perhydrofuro[2,3-*b*]pyran derivatives was partially through a S_N2-type reaction. Furthermore, we also successfully constructed the 2,2-disubstituted perhydrofuro[2,3-*b*]pyran (and furan) derivatives started from 1,2-cyclopropanated sugars via ring-opening-recyclization-addition in the presence of $BiCl_3$.[12] As a continuation of these works, herein, we describe the synthesis of 2-*C*-substituted and 2,2-disubstituted perhydrofuro[2,3-*b*]pyran derivatives by using 2-formylmethyl/2-acetylmethyl instead of 2-*O*-acetyl as a participating group, and the formation of 2,2-disubstituted perhydrofuro[2,3-*b*]pyran derivatives was a S_N1-type reaction.

The potential advantage of this approach over the previous methods was that the products could be further converted to other fused-ring derivatives conveniently due to the presence of allyl, carbonyl and cyano groups. Also, both the chemoselectivity and stereoselectivity are excellent, and there may be three different reaction pathways for nucleophiles (Scheme 2 path a) *vs.* anomeric oxocarbenium ion (Scheme 2 path b) *vs.* 6/5 fused bicyclic oxocarbenium ion (Scheme 2 path c), however, we only obtained the fused-cyclic products in high yield with only one diastereoisomer (when TMSCN was used as nucleophile, two diastereoisomers were obtained). Furthermore, it is well established that the neighboring group participation is not a predominant factor in the synthesis of *C*-glycosides,[13] interestingly, our research demonstrated that it is possible to use neighboring group participation to highly selectively construct fused-ring by slight changes the structure of substrate. Besides, these carbohydrate-based fused-cyclic compounds could be used to mimic the transition state geometry of glycosidases or glycosyltransferases,[14] thus they can be further tested as potential small-molecule inhibitors of glycosidases or glycosyltransferases.[15] Finally, this method furnished the products containing a chiral quaternary carbon center in stereoselective manner, which is perceived as a challenging problem in organic synthesis.[16] These features make it an exceeding efficient and practical method for synthesis of 2-substituted and 2,2-disubstituted perhydrofuro[2,3-*b*]pyran derivatives.



Scheme 2. The different reaction pathways between acetyl 2-*C*-acetylmethyl-α-D-glucopyranoside and nucleophiles

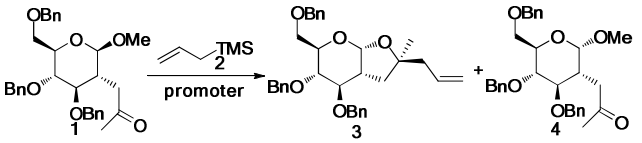
Results and Discussion

Initially, we selected the methyl 2-*C*-acetylmethyl-2-deoxy-β-D-glucopyranoside **1**[11h] and allyltrimethylsilane **2** as the model substrates to screen reaction conditions, the results were summarized in Table 1. As shown in Table 1, when 2.0 equiv. of TMSOTf and $BF_3{\cdot}OEt_2$ were used at -78 ºC-rt, we obtained the bicyclic compound **3** in 75% and 62% yield respectively (Table 1, entries 1 and 2). By the contrast, some other Lewis acids including $ZnCl_2$, $AlCl_3$, and $FeCl_3$ only gave the disappointment results (Table 1, entries 3-5). Interestingly, when we conducted the reaction in the presence of 2.0 equiv. of $BiCl_3$ in CH_2Cl_2 at -78 ºC-rt, we also obtained the 2,2-disubstituted perhydrofuro[2,3-*b*]pyran derivative in 54% yield (Table 1, entry 6).[12] Further optimization the reaction conditions showed the solvent have a great influence to this reaction. For example, we obtained the fused bicyclic product in 84% yield when the reaction was carried out in CH_3CN in the presence of 0.8 equiv. of TMSOTf (Table 1, entry 7), however, other solvents such as CH_2Cl_2,[17] $CHCl_3$, Et_2O, toluene, THF, DMF and acetone only isomerized methyl 2-*C*-acetylmethyl-2-deoxy-β-D-glucopyranoside (**1**) to the methyl 2-*C*-acetylmethyl-2-deoxy-α-D-glucopyranoside (**4**) (Table 1, entries 8-14). In all of cases, we could not avoid the presence of α-D-glucopyranoside **4** even when the reaction carried out at the -40 ºC-rt for two days.

In view of the methoxy group was not a good leaving group, which may lead to its isomerization.[18] Then, we further optimized the substrate by changing the methoxy group to acetoxyl group. Interestingly, when methyl 2-*C*-formylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-glucopyranoside (**5**) was treated with H_2SO_4-HOAc-Ac_2O,[19] we only obtained the fused-ring product **6**, while under the same reaction conditions, methyl 2-*C*-acetylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-glucopyranoside (**1**) was transformed to acetyl 2-*C*-acetylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-glucopyranoside (**7**) smoothly (Scheme 2).

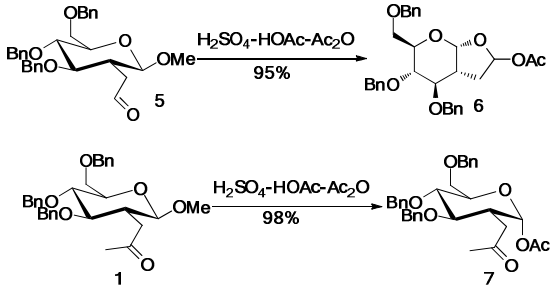
As desired, the fused-ring products were obtained in high yield as a single diastereoisomer except when TMSCN was used as

Table 1. Optimal of the reaction conditions.[a]



entry	promoter	solvent	T	product [b]
1[c]	TMSOTf	CH_2Cl_2	-78 ºC-rt (15 h)	**3** (75%)
2[c]	$BF_3{\cdot}OEt_2$	CH_2Cl_2	-78 ºC-rt (15 h)	**3** (62%)
3[c]	$ZnCl_2$	CH_2Cl_2	-78 ºC-rt (15 h)	NR
4[c]	$AlCl_3$	CH_2Cl_2	-78 ºC-rt (15 h)	trace
5[c]	$FeCl_3$	CH_2Cl_2	-78 ºC-rt (15 h)	decomposed
6[c]	$BiCl_3$	CH_2Cl_2	-78 ºC-rt (15 h)	**3**(54%)
7[d]	**TMSOTf**	**CH_3CN**	**-40 ºC-rt (2 h)**	**3 (84%)**
8	TMSOTf	CH_2Cl_2	-40 ºC-rt (18 h)	**4**
9	TMSOTf	$CHCl_3$	-40 ºC-rt (18 h)	**4**
10[d]	TMSOTf	Et_2O	-40 ºC-rt (18 h)	**4**
11[d]	TMSOTf	toluene	-40 ºC-rt (18 h)	**4**
12[d]	TMSOTf	THF	-40 ºC-rt (18 h)	**4**
13[d]	TMSOTf	DMF	-40 ºC-rt (18 h)	**4**
14[d]	TMSOTf	Acetone	-40 ºC-rt (18 h)	**4**

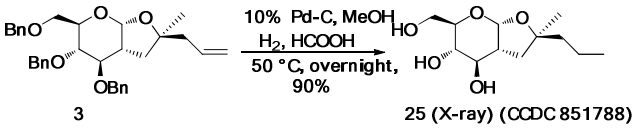
[a] All reactions were performed with methyl-glucoside **1** (0.1 mmol), allyltrimethylsilane **2** (0.2 mmol), 4 Å M.S. 100 mg. [b] Isolated yield. [c] 2.0 equiv of promoter were used. [d] 0.8 equiv of promoter were used.



Scheme 2. Synthesis of Acetate from Methyl 2-*C*-branched-Glycoside

nucleophile. Inspired by the initial success, under the optimal reaction conditions, acetyl 2-*C*-acetylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-glucopyranoside **(7)** was further treated with 0.8 equiv. of TMSOTf in the presence of nucleophiles. The nucleophiles included allyltrimethylsilane (**2**) and its analogue **9**, silyl enol ether derivates (**15**, **17**, **19**, and **21**) and TMSCN (**11**), the results were summarized in Table 2. Satisfactorily, the coupling reaction between **7** and the nucleophiles could proceed smoothly to furnish the 2,2-disubstituted perhydrofuro[2,3-*b*]pyrans in excellent yield with high stereoselectivity. However, when TMSCN was employed as a nucleophile, two isomers were obtained. The low selectivity of nucleophilic attack exhibited by trimethylsilyl cyanide can be explained by the high reactivity of the nucleophile, and smaller steric hindrance presented by this nucleophile may bring about the lower stereoselectivity as well.[20]

The stereochemistry of the products were firstly confirmed by the extensive NMR experiments (^{1}H-NMR, ^{13}C-NMR, and NOESY) of compounds **3**, **8**, **12**, **18**, **23** and **24** and further determined by X-ray crystallographic analysis of compound **25** (hydrogenation loss of benzyl product of **3**) (Scheme 3). [21]



Scheme 3. The hydrogenation loss of benzyl of products **3**

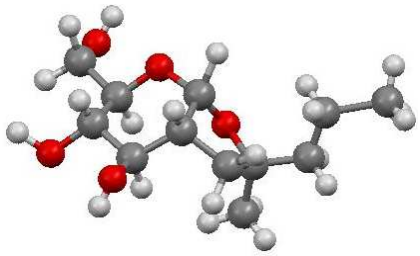


Figure 1. X-ray Crystal Structure of **25**

Based on the results of the experiments, a plausible mechanism is proposed for the formation of perhydrofuro[2,3-*b*]pyrans (Scheme 4). Starting from acetyl 2-*C*-acetylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-glucopyranoside **7**, TMSOTf coordinated to the carbonyl oxygen atom of OAc and enhanced its leaving ability, followed by its departure with the assistance of oxygen from pyranoid ring formed the 2-*C*-branched monocyclic pyran oxocarbenium ion. Subsequently, the carbonyl oxygen of the ketone served as an intramolecular nucleophile which attacked

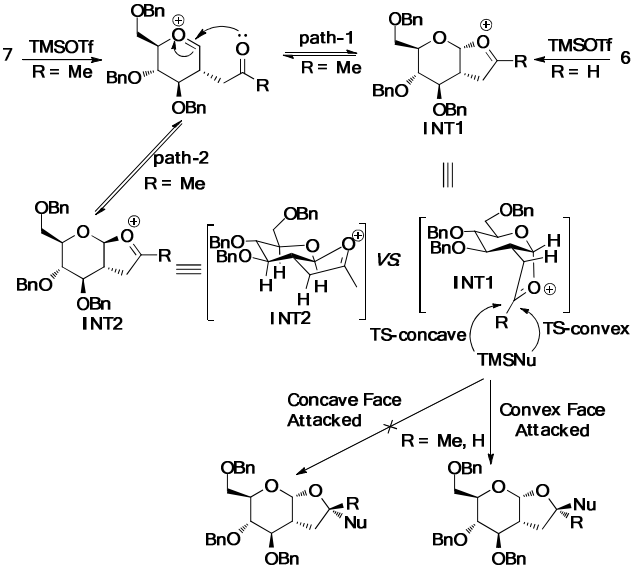
Table 2. The synthesis of 2-substituted and 2,2-disubstituted perhydrofuro[2,3-*b*]pyrans[a]

entry	donor	Nu	product	yield (%)[b]
1	**6**	TMS **2**	BnO, BnO, OBn **8**	75
2	**6**	TMS **9**	BnO, BnO, OBn **10**	85
3	**6**	TMSCN **(11)**	BnO, BnO, CN, OBn **12**	62
			BnO, BnO, CN, OBn **13**	24
4	**7**	TMS **2**	BnO, BnO, OBn **3**	89
5	**7**	TMS **9**	BnO, BnO, OBn **14**	81
6	**7**	OTMS **15**	BnO, BnO, OBn, O **16**	92
7	**7**	OTMS **17**	BnO, BnO, OBn, O **18**	95[c]
8	**7**	OTMS **19**	BnO, BnO, OBn, O **20**	86
9	**7**	OTMS **21**	BnO, BnO, OBn, O **22**	95
10	**7**	TMSCN **(11)**	BnO, BnO, CN, OBn **23**	58
			BnO, BnO, O, CN, OBn **24**	32

[a] All reactions were carried out using 2.0 equiv nucleophile, 0.8 equiv TMSOTf in CH_3CN at -40 ºC to r.t. with 100 mg of 4 Å M.S. unless otherwise noted. [b] Isolated yield. [c] A pair of inseparable diastereoisomers (1:1) were obtained due to prochiral centre of substituted cyclohexanone as determined by ^{1}H NMR.

the anomeric carbon from α (path-2) or β (path-1) face to form six-five fused-ring oxocarbenium ion intermediates **INT1** or **INT2** respectively.[22] The DFT calculations[23] on B3LYP/6-31+G** level showed that **INT1** is 8.7 kcal/mol more stable than **INT2.** Therefore, the major ring oxocarbenium ion is **INT1**. For the 2- acetoxyl-perhydrofuro[2,3-*b*]pyran **6**, in the presence of

TMSOTf, it can form the **INT1** directly. Thus, after the formation of **INT1**, theoretically, the nucleophiles can approach the **INT1** from either the **concave** or **convex** face to produce the *endo*- or *exo*-products respectively. However, the calculation demonstrated the concave face is more sterically hindered than the convex face,[22] thus, the major products of this reaction are *exo*-products, which is consistent well with the experimental observations.



Scheme 4. Plausible Mechanism for the synthesis of perhydrofuro[2,3-*b*]pyrans from 2-*C*-branched sugar

It is mentioned that in our previous report, we observed that the *p*-tolyl 2-*C*-formylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside can be used to synthesize 2-*O*/*N* substituted perhydrofuro[2,3-*b*]pyran partially through a S_N2-type reaction.[11c] However, in this study, when acetyl 2-*C*-acetylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside was employed as the starting material, the 2,2-di-substituted perhydrofuro[2,3-*b*]pyran can still be obtained in high yield with excellent diastereoselectivity, and this is a S_N1-type reaction, which means that the reaction proceeds in the different mechanisms by using various substrates.

Conclusions

In summary, a highly stereoselective synthesis of 2-substituted and 2,2-disubstituted perhydrofuro[2,3-*b*]pyran derivatives using 2-*C*-branched (formylmethyl or acetylmethyl)-2-deoxy-D-glucosides as starting material has been developed. The strategy takes full advantage of the classical neighboring group participation phenomenon using carbonyl (formylmethyl or acetylmethyl) as participation group to form the fused-ring products in good to excellent yield with excellent diastereoselectivity. Mechanistic studies demonstrated that the formation of 2,2-disubstituted perhydrofuro[2,3-*b*]pyrans from acetyl 2-*C*-acetylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside through a S_N1-type reaction to produce the pyran oxocarbenium ion, followed by intramolecular attacking by oxygen atom of ketone given *cis*-5/6-fused ring oxocarbenium ions intermediate preferentially, which was further trapped by the nucleophiles from the less sterically hindered convex face to afford the products.

Experimental Section

General Information: All reactions sensitive to air or moisture were carried out under nitrogen or argon atmosphere with anhydrous solvents. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Thin-layer chromatography was performed using silica gel GF254 precoated plates (0.20–0.25 mm thickness) with a fluorescent indicator. Visualization on TLC was achieved by UV light (254 nm) and a typical TLC indication solution (10% sulfuric acid/ethanol solution). Column chromatography was performed on silica gel 90, 200-300 and 300-400 mesh. Optical rotations were measured with a Perkin Elmer M341 Digital Polarimeter. ^{1}H and ^{13}C NMR (600 and 150 MHz, respectively) spectra were recorded on a Bruker Avance 600 spectrometer. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm; CD_3OD, δ 3.31 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm; CD_3OD, δ 49.0). ESI-HRMS spectra were recorded on BioTOFQ.

(3a*R*,4*R*,5*S*,6*R*,7*aR*)-2-acetoxyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-hexahydrofuro[2,3-*b*]pyran (6)

Methyl 2-*C*-formylmethyl-2-deoxy-3,4,6-tri-*O*-benzyl-glucopyran **5** (0.9 g, 1.8 mmol) was dissolved in 34 mL HOAc, and 20 mL Ac_2O was added. The mixture was cooled to 0 ºC, and 27 μL H_2SO_4 was added. The mixture was stirred at 0 ºC until all of **5** was disappeared (about 0.5 h). The reaction mixture was poured into ice water with the vigorous stirred, and extracted with CH_2Cl_2 (20 mL × 3). The combined organic phase was washed successively with saturation $NaHCO_3$, saturation NaCl, and dried with Na_2SO_4. The crude product was purified by flash column chromatography.

Compound **6** obtained as colorless syrup; yield: 95%. $[\alpha]_D^{20}$ +67.5 (*c* 0.29, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.12 (m, 15H), 6.84 (t, *J* = 4.5 Hz, 1H), 6.34 (d, *J* = 3.2 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 10.7 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 3.85 – 3.78 (m, 3H), 3.68 (d, *J* = 10.2 Hz, 2H), 2.30 – 2.23 (m, 1H), 2.21 – 2.16 (m, 1H), 2.12 (s, 3H), 1.97 – 1.93 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 138.1, 138.1, 137.9, 128.5, 128.4, 128.0, 127.9, 127.9, 127.8, 127.8, 92.5, 89.5, 80.2, 79.0, 75.4, 75.0, 73.7, 73.1, 68.3, 40.3, 30.3, 20.9, 20.8; ESI-HRMS: m/z calcd for $C_{31}H_{34}NaO_7$ $[M+Na]^+$: 541.2204; found: 541.2204.

Acetyl-2-*C*-acetonyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranoside (7)

Compound **7** was synthesized following the similar procedure with the compound **6**, and obtained as colorless syrup; yield: 98%. $[\alpha]_D^{20}$ +79.5 (*c* 0.28, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.15 (m, 15H), 6.20 (d, *J* = 2.8 Hz, 1H), 4.95 (d, *J* = 11.3 Hz, 1H), 4.79 (d, *J* = 10.7 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.59 (d, *J* = 10.7 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.86 – 3.85 (m, 1H), 3.84 – 3.81 (m, 1H), 3.80 (dd, *J* = 8.1, 2.9 Hz, 1H), 3.67 (dd, *J* = 11.0, 1.4 Hz, 1H), 3.64 (dd, *J* =

10.8, 8.4 Hz, 1H), 2.64 – 2.54 (m, 2H), 2.26 – 2.14 (m, 1H), 2.08 (s, 3H), 2.04 (d, J = 7.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 169.2, 138.2, 138.0, 137.9, 128.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 93.1, 79.9, 79.2, 75.0, 74.9, 73.6, 68.4, 41.2, 40.7, 29.8, 20.9； ESI-HRMS: m/z calcd for $C_{32}H_{36}NaO_7$ $[M+Na]^+$: 555.2359; found: 555.2349.

Generally procedures for synthesis of 2-*C*-branched perhydrofuro[2,3-*b*]pyrans

To a stirring solution of **6** or 7 (0.1 mmol) in anhydrous CH_3CN (1 mL) containing 100 mg 100 mg of 4 Å M.S. at -40 ºC and under N_2 atmosphere was added nucleophiles （0.2 mmol）. Then trimethylsilyl triflate (14.8 μL, 0.08mmol) was added dropwise. The reaction mixture was stir at -40 ºC for 1.5 h, then for 0.5 h at rt. The yellow mixture was diluted with CH_2Cl_2 (10 mL), and neutralized with saturated $NaHCO_3$ solution (10 mL). The organic layer was collected, and the aqueous layer was re-extracted with further CH_2Cl_2 (2 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated to give orange syrup. The crude material was slightly diluted with CH_2Cl_2 (0.2 mL) and purified by silica gel flash column chromatography (petroleum ether/ethyl acetate, 8:1).

(2*R*,3*aR*,4*R*,5*S*,6*R*,7*aR*)-2-allyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-hexahydrofuro[2,3-*b*]pyran (8)

Obtained as colorless syrup (39.2 mg, 78%); $[\alpha]_D^{20}$ + 70.6 (*c* 0.30, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 15H), 5.80 – 5.67 (m, 1H), 5.45 (d, J = 4.5 Hz, 1H), 5.12 – 5.01 (m, 2H), 4.88 (d, J = 11.5 Hz, 1H), 4.78 (d, J = 10.9 Hz, 1H), 4.68 (d, J = 11.6 Hz,, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 10.7 Hz, 1H), 4.55 (d, J = 12.1 Hz, 1H), 4.15 (dq, J = 12.0, 6.1 Hz, 1H), 3.82 (dd, J = 18.8, 7.9 Hz, 2H), 3.74 (t, J = 8.9 Hz, 1H), 3.70 (dd, J = 10.4, 1.4 Hz,1H), 3.54 (t, J = 8.6 Hz, 1H), 2.32 (dt, J = 12.8, 6.4 Hz, 2H), 2.21 (dt, J = 13.4, 6.5 Hz, 1H), 1.88 (dd, J = 12.5, 5.8 Hz, 1H), 1.71 – 1.64 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 138.3, 138.1, 133.9, 128.5, 128.4, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 117.5, 101.5, 80.7, 77.9, 76.6, 74.6, 74.4, 73.6, 72.2, 68.8, 44.3, 40.7, 33.8; ESI-HRMS: m/z calcd for $C_{32}H_{36}NaO_5$ $[M+Na]^+$:523.2460; found: 523.2455.

(2*R*,3*aR*,4*R*,5*S*,6*R*,7*aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy) methyl]-2-(2-methylallyl)-hexahydrofuro[2,3-*b*]pyran (10)

Obtained as colorless syrup (43.7 mg, 85%); $[\alpha]_D^{20}$ + 74.6 (*c* 0.30, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 15H), 5.46 (d, J = 4.6 Hz, 1H), 4.88 (d, J = 11.6 Hz, 1H), 4.79 (d, J = 11.2 Hz, 2H), 4.69 (d, J = 11.2 Hz, 2H), 4.65 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 10.8 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 4.23 (dq, J = 12.6, 6.3 Hz, 1H), 3.82 (dd, J = 15.5, 6.4 Hz, 2H), 3.75 (t, J = 8.9 Hz, 1H), 3.70 (d, J = 8.8 Hz, 1H), 3.54 (t, J = 8.6 Hz, 1H), 2.33 (dd, J = 13.9, 6.5 Hz, 2H), 2.08 (dd, J = 14.0, 6.4 Hz, 1H), 1.88 (dd, J = 12.8, 5.9 Hz, 1H), 1.70 (s, 3H), 1.68 – 1.62 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.0, 138.5, 138.3, 138.1, 128.4, 128.4, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 112.6, 101.3, 80.6, 77.9, 75.8, 74.4, 74.4, 73.6, 72.2, 68.8, 44.8, 44.3, 34.4, 22.9; ESI-HRMS: m/z calcd for $C_{33}H_{38}NaO_5$ $[M+Na]^+$: 537.2617; found: 537.2621.

(2*R*,3*aR*,4*R*,5*S*,6*R*,7*aS*)-4,5-bis(benzyloxy)-6-[(benzyloxy) methyl]-2-cyano-hexahydrofuro[2,3-*b*]pyran (12)

Obtained as colorless syrup (30.1 mg, 62%); $[\alpha]_D^{20}$ +85.1 (*c* 0.12, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 15H), 5.46 (d, J = 4.3 Hz, 1H), 4.92 (d, J = 11.7 Hz, 1H), 4.77 (d, J = 11.0 Hz, 1H), 4.69 (d, J = 11.7 Hz, 1H), 4.65 (dd, J = 8.3, 2.8 Hz, 2H), 4.62 (d, J = 4.2 Hz, 1H), 44.54 (d, J = 12.1 Hz, 1H), 3.94 (d, J = 9.2 Hz, 1H), 3.83 (dd, J = 14.2, 5.9 Hz, 2H), 3.75 (d, J = 8.9 Hz, 1H), 3.72 (d, J = 10.4 Hz, 1H), 2.40-2.33 (m, 2H), 2.18 (d, J = 13.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 138.0, 137.9, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 119.0, 103.3, 79.9, 77.4, 75.0, 74.4, 73.6, 72.9, 68.4, 63.0, 42.8, 32.8; ESI-HRMS: m/z calcd for $C_{32}H_{31}NNaO_5$ $[M+Na]^+$:508.2100; found: 508.2094.

(2*S*,3*aR*,4*R*,5*S*,6*R*,7*aS*)-4,5-bis(benzyloxy)-6-[(benzyloxy) methyl]-2-cyano-hexahydrofuro[2,3-*b*]pyran (13)

Obtained as colorless syrup (11.6 mg, 24%); 1H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 13H), 7.20 (d, J = 7.3 Hz, 2H), 5.59 (d, J = 4.7 Hz, 1H), 4.81 (d, J = 11.9 Hz, 1H), 4.70 (d, J = 11.1 Hz, 1H), 4.64 – 4.61 (m, 3H), 4.58 – 4.53 (m, 2H), 3.80 (d, J = 9.1 Hz, 1H), 3.75 (dd, J = 13.9, 10.0 Hz, 2H), 3.69 – 3.67 (m, 1H), 3.44 (t, J = 7.3 Hz, 1H), 2.48 (s, 1H), 2.24 (dt, J = 22.0, 7.5 Hz, 2H).

(2*S*,3*aR*,4*R*,5*S*,6*R*,7*aR*)-2-allyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methylhexahydrofuro[2,3-*b*]pyran (3)

Obtained as colorless syrup (45.8 mg, 89%); $[\alpha]_D^{20}$ +46.2 (*c* 0.41, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 15H), 5.88 – 5.77 (m, 1H), 5.50 (d, J = 5.1 Hz, 1H), 5.12 (t, J = 12.2 Hz, 2H), 4.83 (d, J = 11.8 Hz, 1H), 4.75 (d, J = 11.1 Hz, 1H), 4.69 (d, J = 11.8 Hz, 1H), 4.68 (d, J = 12.2 Hz, 1H), 4.58 (t, J = 11.8 Hz, 2H), 3.95 (dt, J = 8.9, 3.0 Hz, 1H), 3.82 (dd, J = 10.7, 3.6 Hz, 1H), 3.79 (dd, J = 8.9, 6.9 Hz, 1H), 3.74 (dd, J = 10.6, 2.5 Hz, 1H), 3.70 (t, J = 6.9 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.30 – 2.21 (m, 2H), 2.01 (dd, J = 13.3, 8.4 Hz, 1H), 1.77 (dd, J = 13.3, 5.4 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2(2), 128.4(2), 128.0, 127.9(2), 127.8(2), 127.6, 118.2, 100.6, 80.9, 80.2, 77.4, 73.7, 73.5, 73.3, 71.9, 69.2, 47.0, 43.9, 38.0, 27.7; ESI-HRMS: m/z calcd for $C_{33}H_{38}NaO_5$ $[M+Na]^+$: 537.2617; found: 537.2611.

(2*R*,3*aR*,4*R*,5*S*,6*R*,7*aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy) methyl]-2-methyl-2-(2-methylallyl)-hexahydrofuro[2,3-*b*]pyran (14)

Obtained as colorless syrup (42.8 mg, 81%); $[\alpha]_D^{20}$ +52.1 (*c* 0.17, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 19H), 5.44 (d, J = 5.1 Hz, 1H), 4.86 (s, 1H), 4.78 (d, J = 11.8 Hz, 1H), 4.70 (d, J = 11.4 Hz, 2H), 4.64 (d, J = 11.8 Hz, 1H), 4.64 (d, J = 12.1 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 4.52 (d, J = 12.6 Hz, 1H), 3.89 (dt, J = 8.9, 2.9 Hz, 1H), 3.79 – 3.73 (m, 2H), 3.70 (dd, J = 10.6, 2.5 Hz, 1H), 3.66 (t, J = 6.8 Hz, 1H), 2.42 (dd, J = 13.5, 6.4 Hz, 1H), 2.20 (d, J = 13.5 Hz, 1H), 2.13 (d, J = 13.4 Hz, 1H), 2.05 – 2.00 (m, 1H), 1.80 (s, 3H), 1.76 (dd, J = 13.2, 5.6 Hz, 1H), 1.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 138.5, 138.2, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 114.7, 100.5, 81.5, 80.1, 76.8, 73.7, 73.5, 73.3, 71.9, 69.2, 49.9,

43.8, 38.9, 27.8, 24.3; ESI-HRMS: m/z calcd for $C_{34}H_{40}NaO_5$ $[M+Na]^+$:551.2773; found: 551.2768.

(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-2-[(benzoyl)methyl]-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-hexahydro-furo[2,3-*b*]pyran (16)

Colorless syrup, 54.5 mg, yield: 92%, $[\alpha]_D^{20}$ +30.1 (*c* 0.25, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.27 (m, 13H), 7.20 (d, *J* = 6.5 Hz, 2H), 5.41 (d, *J* = 5.1 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 11.0 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 3.89 (dt, *J* = 8.5, 3.0 Hz, 1H), 3.78 – 3.70 (m, 2H), 3.68 (dd, *J* = 8.2, 4.8 Hz, 2H), 3.19 (d, *J* = 2.5 Hz, 2H), 2.47 – 2.41 (m, 1H), 2.34 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.02 (dd, *J* = 13.6, 5.8 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.6, 138.3, 138.2, 138.1, 137.5, 133.2, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 100.5, 80.8, 79.8, 77.1, 73.6, 73.5, 73.2, 72.0, 69.2, 49.7, 43.6, 38.4, 28.6. ESI-HRMS: m/z calcd for $C_{38}H_{40}NaO_6$ $[M+Na]^+$: 615.2717; found: 615.2717.

(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-(1-cyclohexanon-2-yl)-2-methylhexahydro-furo[2,3-*b*]pyran (18)

Colorless syrup, 54.2 mg, yield: 95%, $[\alpha]_D^{20}$ +75.9 (*c* 0.48, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 15H), 5.41 (dd, *J* = 7.4, 5.2 Hz, 1H), 4.81 (dd, *J* = 11.5, 3.5 Hz, 1H), 4.78 – 4.72 (m, 1H), 4.69 (t, *J* = 11.2 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.58 (dd, *J* = 14.3, 11.2 Hz, 1H), 4.54 (d, *J* = 12.2 Hz, 1H), 3.90 (dd, *J* = 12.5, 5.8 Hz, 1H), 3.79 (td, *J* = 10.3, 3.4 Hz, 1H), 3.74 – 3.66 (m, 3H), 2.53 (ddd, *J* = 57.9, 12.6, 4.7 Hz, 1H), 2.41 – 2.25 (m, 4H), 2.13 – 1.99 (m, 3H), 1.93 (s, 1H), 1.71 – 1.55 (m, 3H), 1.40 (s, 1H), 1.30 (s, 1H), 1.26 (dd, *J* = 8.4, 5.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.6, 211.5, 138.4, 138.4, 138.2, 138.2, 138.1, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 101.6, 100.5, 82.1, 81.4, 81.2, 80.7, 77.6, 74.2, 74.0, 73.9, 73.6, 72.1, 69.1, 69.0, 62.2, 60.6, 44.6, 44.0, 43.5, 43.4, 40.3, 36.1, 29.3, 29.2, 28.9, 28.3, 28.1, 25.4, 25.3, 23.6. ESI-HRMS: m/z calcd for $C_{36}H_{42}NaO_6$ $[M+Na]^+$: 593.2874; found: 593.2870.

(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-[(2,2-dimethyl-propionyl)methyl]-2-methylhexahydrofuro[2,3-*b*]pyran (20)

Colorless syrup, 49.2 mg, yield: 86%, $[\alpha]_D^{20}$ +68.7 (*c* 0.42, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 15H), 5.46 (d, *J* = 5.0 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.53 (d, *J* = 12.3 Hz, 1H), 3.90 (dd, *J* = 6.2, 2.7 Hz, 1H), 3.78 (dd, *J* = 10.6, 3.6 Hz, 1H), 3.76 – 3.72 (m, 1H), 3.72 – 3.66 (m, 2H), 2.84 (d, *J* = 17.4 Hz, 1H), 2.68 (d, *J* = 17.4 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.25 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.01 (dd, *J* = 13.8, 4.9 Hz, 1H), 1.36 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.2, 138.3, 138.2, 128.5, 128.4, 128.4, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 100.5, 80.3, 80.2, 77.4, 73.8, 73.5, 73.5, 72.1, 69.1, 47.8, 44.7, 43.9, 38.9, 27.9, 26.2. ESI-HRMS: m/z calcd for $C_{36}H_{44}NaO_6$ $[M+Na]^+$: 595.3030; found: 595.3049.

(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-2-[(acetyl)methyl]-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methylhexahydrofuro[2,3-*b*]pyran (22)

Colorless syrup, 47.8 mg, yield: 95%, $[\alpha]_D^{20}$ +43.1 (*c* 0.54, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 15H), 5.47 (d, *J* = 5.1 Hz, 1H), 4.77 (d, *J* = 11.8 Hz, 1H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.64 (t, *J* = 11.8 Hz, 2H), 4.54 (d, *J* = 11.0 Hz, 2H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.89 (dt, *J* = 8.6, 3.0 Hz, 1H), 3.77 (dd, *J* = 10.7, 3.8 Hz, 1H), 3.75 – 3.72 (m, 1H), 3.70 (dd, *J* = 10.7, 2.5 Hz, 1H), 3.66 (t, *J* = 6.7 Hz, 1H), 2.66 (d, *J* = 14.9 Hz, 1H), 2.56 (d, *J* = 14.9 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.17 (s, 3H), 2.14 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.90 (dd, *J* = 13.6, 5.6 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.4, 138.3, 138.1, 138.1, 128.5, 128.4, 128.4, 128.1, 127.9, 127.9, 127.9, 127.8, 127.6, 100.6, 79.9, 79.8, 77.1, 73.7, 73.5, 73.3, 72.0, 69.1, 54.8, 43.6, 38.8, 31.9, 28.0. ESI-HRMS: m/z calcd for $C_{33}H_{38}NaO_6$ $[M+Na]^+$: 553.2551; found:553.2561.

(2*R*,3*aR*,4*R*,5*S*,6*R*,7*aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-cyano-2-methylhexahydrofuro[2,3-*b*]pyran (23)

Colorless syrup, 25.3 mg, yield: 58%, $[\alpha]_D^{20}$ +49.5 (*c* 0.69, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 14H), 7.23 – 7.19 (m, 2H), 5.60 (d, *J* = 5.5 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.65 – 4.59 (m, 3H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 11.2 Hz, 1H), 3.84 – 3.80 (m, 1H), 3.76 – 3.70 (m, 2H), 3.68 (dd, *J* = 10.7, 2.6 Hz, 1H), 3.53 (t, *J* = 5.8 Hz, 1H), 2.68 – 2.60 (m, 1H), 2.41 (dd, *J* = 13.7, 8.1 Hz, 1H), 1.95 (dd, *J* = 13.7, 7.2 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 137.9, 137.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.7, 121.2, 101.6, 77.5, 76.4, 73.5, 73.4, 72.7, 72.7, 72.3, 69.0, 41.6, 39.8, 26.3; ESI-HRMS: m/z calcd for $C_{31}H_{33}NNaO_5$ $[M+Na]^+$: 522.2251; found: 522.2256.

(2*S*,3*aR*,4*R*,5*S*,6*R*,7*aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-cyano-2-methylhexahydrofuro[2,3-*b*]pyran (24)

Colorless syrup, 14 mg, yield: 32%, ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 13H), 7.22 (d, *J* = 6.7 Hz, 2H), 5.51 (d, *J* = 4.6 Hz, 1H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.78 (d, *J* = 11.1 Hz, 1H), 4.70 (d, *J* = 11.7 Hz, 1H), 4.64 (d, *J* = 12.9 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.27 – 4.25 (m, 1H), 3.97 – 3.94 (m, 2H), 3.82 (dd, *J* = 10.8, 3.2 Hz, 1H), 3.75 – 3.69 (m, 2H), 2.43 – 2.37 (m, 1H), 2.10 (dd, *J* = 6.8, 2.8 Hz, 1H), 2.04 (dd, *J* = 14.8, 8.0 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.0, 137.9, 128.7, 128.6, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 121.6, 102.6, 80.2, 77.6, 75.1, 74.4, 73.6, 72.9, 72.6, 68.4, 44.7, 40.8, 28.3. ESI-HRMS: m/z calcd for $C_{31}H_{33}NNaO_5$ $[M+Na]^+$: 522.2251; found: 522.2271.

Synthesis of (*2S*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-4,5-dihydroxy-6-(hydroxymethyl)-2-methyl-2-propanyl-hexahydrofuro[2,3-*b*]pyran (25)

To a solution of **3** (0.26 g, 0.51 mmol) in MeOH 10 mL was added 10% Pd-C 0.026 g and HCOOH 0.5 mL. The mixture was stirred at 50 °C under atmosphere of H_2 overnight. The mixture was cooled to room temperature, filter over diatomaceous earth, and concentrated in vacuo, purified by silica gel flash column

chromatography (ethyl acetate/ MeOH = 20:1) to afford compound **25** (0.11 g, 0.46 mmol, 90%) as a colourless solid; $[\alpha]_D^{20}$ +30.9 (*c* 0.14, $CHCl_3$); ^{1}H NMR (600 MHz, MeOH-d_4): δ 5.36 (d, *J* = 4.5 Hz, 1H), 3.78 (dd, *J* = 11.9, 2.6 Hz, 1H), 3.74 (dd, *J* = 11.9, 4.9 Hz, 1H), 3.64 (ddd, *J* = 9.4, 4.8, 2.6 Hz, 1H), 3.56 (t, *J* = 8.8 Hz, 1H), 3.35 (t, *J* = 9.1Hz, 1H), 2.10 – 2.05 (m, 1H), 2.02 (dd, *J* = 13.1, 7.6 Hz, 1H), 1.97 (dd, *J* = 13.2, 2.2 Hz, 1H), 1.49 (ddd, *J* = 16.3, 11.0, 4.8 Hz, 2H), 1.39 (ddd, *J* = 16.4, 12.2, 6.2 Hz, 2H), 1.35 (s, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, MeOH-d_4): δ 100.8, 80.5, 74.5, 74.0, 69.9, 61.3, 45.3, 45.2, 38.5, 26.5, 17.3, 13.5; ESI-HRMS: m/z calcd for $C_{12}H_{22}NaO_5[M+Na]^+$: 269.1359 found: 269.1362.

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Notes and references

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