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A dehydrative glycosylation protocol mediated by nonafluorobutanesulfonyl fluoride (NfF)

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ABSTRACT

A new dehydrative glycosylation protocol that proceeds through selective activation of glycosyl hemiacetals with nonafluorobutanesulfonyl fluoride (NfF) has been disclosed. Contrary to the major classical glycosylation reactions that proceed under acidic or neutral conditions, the present glycosylation reaction proceeds under mild basic conditions. In the absence of an external acceptor, self-condensation of the glycosyl hemiacetal occurs, providing the corresponding symmetrical 1,1′-disaccharides in high yields.

1. Introduction

The construction of glycosidic linkages represents a central issue in glycochemistry, and new glycosylation methods are continuously being developed [1a–e]. Of the various glycosylation strategies developed, the dehydrative glycosylation which allows for the direct use of glycosyl hemiacetals as glycosyl donors that react with alcoholic acceptors under mild activating conditions, is a very attractive alternative; and a number of dehydrative glycosylation conditions have been reported during the past few decades [2a–h,3a–c]. Among these dehydrative glycosylation conditions, selective transformation of the C1-hemiacetal into glycosyl triflate by a triflating reagent (usually Tf_2O) followed by glycosylation represents a straightforward approach [4a–c] [5a,b], [6a,b]. To realize such a glycosylation process, the first problem to address is how to selectively activate the C1-hemiacetal without affecting the alcoholic acceptor, since a triflating reagent (such as Tf_2O) could triflate both the hemiacetal and the acceptor. The second problem to address is how to avoid self-condensation of the C1-hemiacetal. To solve these problems, usually a co-promoter was used in combination with Tf_2O to modulate the activation process [7], such co-promoters include tetrabutylammonium bromide [4a], [1,2-benzenediolato(2)-*O*,*O*']oxotitanium [8], diphenyltin sulfide [9], diphenyl sulfoxide [10a,b], dibutyl sulfide [11], phthalic anhydride [12], triphenylphosphine oxide [13a,b], cyclic phosphonium anhydrides [14], and 2-aryl-1,3-dithiane 1-oxide [2a]. In the presence of these co-promoters, a much mild activating species was generated, thus to enable selective activation of the C1-hemiacetal. In 2014, a direct Tf_2O mediated dehydrative glycosylation was reported [15], and the key to success is the addition of a strained olefin into the reaction system to act as an acid scavenger.

It was noted that Tf_2O, a rather strong sulfonating agent, has been used in most of these dehydrative glycosylation protocols [16a–d]. We envisioned that a milder sulfonating agent could selectively react with the glycosyl C1-hemiacetal in the presence of a mild base without affecting the alcoholic acceptor, thus would enable a dehydrative glycosylation. Nonafluorobutanesulfonyl fluoride ($C_4F_9SO_2F$, NfF) [17], a readily available colorless liquid (boiling point at 64 °C), attracted our attention, because it could selectively react with the deprotonated phenolic hydroxyl group under mild heterogeneous basic conditions [18,19a–c]. Given the fact that the acidity of the glycosyl C1-hemiacetal (pKa ~12) is stronger than an ordinary alcoholic hydroxyl group (pKa ~16) [20],

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we expected that this reagent would be capable of selectively activating the depontoned glycosyl C1-hemiacetal (**B**) to generate a reactive glycosyl nonaflate intermediate (**C**), which could immediately react with the co-existed acceptor to afford the glycosylation product (Scheme 1). Herein, we report our preliminary attempts to develop a novel NfF mediated dehydrative glycosylation protocol.

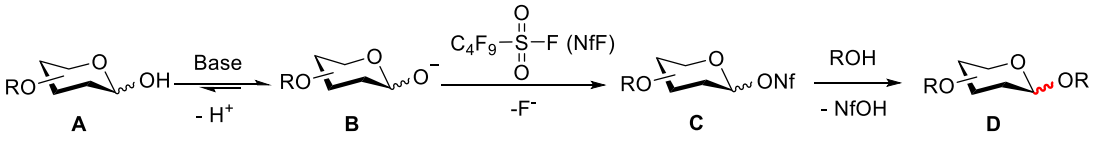
2. Results and discussion

The dehydrative glycosylation of alcoholic acceptor 2-methoxyethanol (**2a**) using 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **1a** as donor mediated by NfF was chosen as a model reaction. The reaction was carried out in chlorinated hydrocarbon solvents in the presence of an inorganic base and 3 Å molecular sieves at room temperature or 65 °C. After the reaction, the glycosylated product **3a** was isolated via flash column chromatography and the α/β ratio was determined by NMR analysis. The results were summarized in Table 1. In our initial attempt, the mole ratio of donor **1a**/acceptor **2a**/NfF was 1/2/5.3, K_2CO_3 (11.7 eq.) was chosen as the base, $ClCH_2CH_2Cl$ as the solvent, and no molecular sieves were added (entry 1). The reaction proceeded rather slowly at room temperature (less than 50% conversion after 3 days); at 65 °C, the reaction proceeded smoothly, after 25 h, the yield of **3a** reached 78% (α/β = 1.7/1), with a small amount of **1a** remained unreacted. We next switched the base to Cs_2CO_3 (5 eq.), under otherwise similar conditions, the reaction proceeded smoothly at room temperature; after 22 h, the yield of **3a** reached 82% (α/β = 1.7/1) (entry 2). Again, it was noted that a small amount of **1a** remained unreacted, neither extended reaction times nor additional equivalents of NfF or base improved the yield or conversion. Mechanistically, during this reaction 1 equiv. of acid ($C_4F_9SO_3H$) was generated, which could subsequently be neutralized by the base to generate 1 equiv. of water from the resultant H_2CO_3. As the reaction proceeded, the concentration of acceptor **2a** decreased while the concentration of water increased; the generated water could compete with acceptor **2a**, leading to incomplete conversion of the acceptor **2a**. To solve this problem, we added 3 Å molecular sieves to the reaction system to sequester the generated water. Gratifyingly, full conversion was achieved and the glycosylated product **3a** was isolated in 97% yield (α/β = 1.4/1) (entry 3). Reducing the ratio of donor **1a**/acceptor **2a**/NfF to 1/1.5/2 still led to the formation of product **3a** in a satisfying 87% yield (α/β = 1.7/1) (entry 4). Further reducing the ratio of donor **1a**/acceptor **2a**/NfF to 1/1.5/1.5, the yield of **3a** dropped to 83% (α/β = 2/1) (entry 5). When the reaction was conducted in the presence of excess donor (donor **1a**/acceptor **2**/NfF = 1.6/1/3.2), the yield of **3a** retained at a high level (87%, α/β = 1.2/1; entry 6). When the base was replaced with CaO, no glycosylated product was observed (entry 7). The performance of organic bases were also tested. In the presence of DIPEA, no glycosylation reaction occurred (entry 8); in the presence of DBU, the reaction proceeded rapidly, after 18 h, the glycosylation product **3a** was formed in 32% yield (α/β = 1/4; entry 9), with the major side product being identified to be the corresponding glucosyl fluoride. Taking into account the practicality and efficiency, the optimal reaction conditions were established as follows: the mole ratio of donor **1a**/acceptor **2a**/NfF/$CsCO_3$ was 1/1.5/2/2, the reaction was performed in CH_2Cl_2 at room temperature in the presence of 300 w/w% 3 Å molecular sieves.

The scope of this reaction was next investigated, and the results were given in Scheme 2. With respect to acceptor scope, apart from primary alcohol (**2a** and **2d**), secondary alcohol **2b** and tertiary alcohol **2c** could also be glycosylated in high yields under the optimized conditions. With respect to donor scope, armed pyranosyl donors including benzylated glucosyl donors **1a** and **1b**, benzylated rhamnosyl donor **1c**, and armed furanosyl donors, including diacetone-mannofuranosyl donor **1d** and benzylated arabinofuranosyl donor **1e** were suitable donors for the present glycosylation protocol. Under standard conditions, the glycosylation yields were typically high. It was noteworthy that the α-selectivity of the glucosylation applying benzylated glucosyl donors could be turned by switching the donor from 6-*O*-benzyl donor **1a** to 6-*O*-acetyl donor **1b** [22,23]. Thus, the glycosylation of perbenzylated glucosyl donor **1a** with acceptor **2a** and **2b** afforded glycosides **3a** and **3b** in 87% and 94% yield, respectively, with only moderate stereoselectivity (α/β = 1.7/1), whereas the glucosylation of 6-*O*-acetyl donor **1b** with acceptors **2a**-**2d** afforded the corresponding glycosides **3c-3f** in 88−99% yield with good α-selectivity (α/β > 4.5/1). Apart from glucosyl donor **1b**, diacetone-mannofuranosyl donor **1d** was also found to be an α-selective donor, with product **3h** being isolated in 88% yield with a high α-selectivity (α/β = 7.7/1). The other two tested benzylated donors, L-rhamnosyl donor **1c** and D-arabinofuranosyl donor **1e**, afforded the glycosylation products **3g** and **3i** in 93% and 85% yield with moderate α-selectivity (α/β = 2.7/1) and β-selectivity (α/β = 1/2.5), respectively.

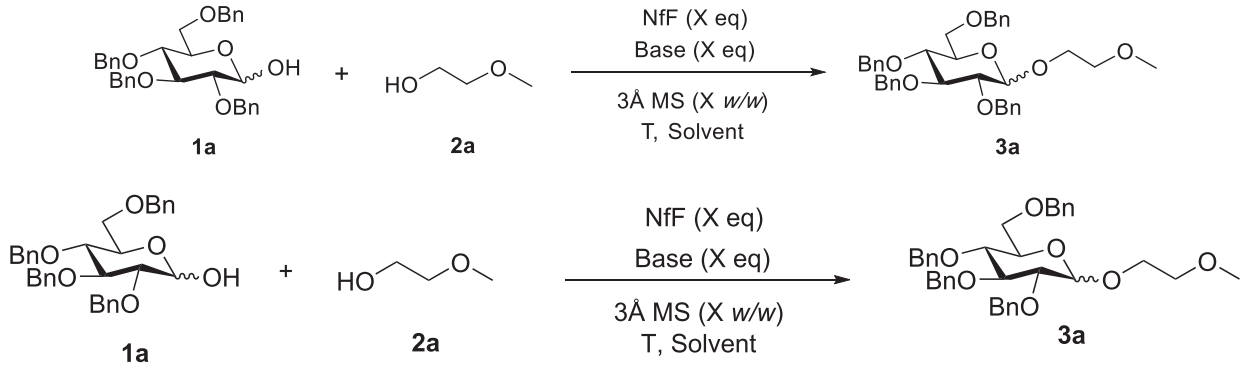
Inspired by the successful results with alcoholic acceptors, we next explored the present glycosylation with glycoside acceptors. Thus, the glycosylation between glycoside acceptor 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **4** (1.5 eq.) and glucosyl donor **1b** (1.0 eq.) was performed under the standard conditions. After the reaction, the products were isolated and characterized, and the results were shown in Scheme 3. The desired glycosylation product **5** was isolated in only 58% yield (α/β = 3.7/1). Interestingly, 1,2:3,4-di-*O*-isopropylidene-6-*O*-nonafluorobutanesulfonyl-α-D-galactopyranose **6** was isolated in 56% yield (based on **4**); another side product turned out to be glucosyl fluoride **7**, being isolated in 12% yield (α/β = 5/1). In addition, the unreacted donor **1b** was recovered in 28% yield. These results demonstrated that the hydroxyl group of a glycoside acceptor could be sulfonated under the present dehydrative conditions, thus competing with the glycosylation pathway to diminish the glycosylation yield [24].

When the glucosyl donor was used in excess, the formation of self-condensation product 1,1′-disaccharide was observed [25a,b]. Thus, the self-condensation of hemiacetal donors in the absence of acceptors under the present dehydrative glycosylation conditions was investigated. The results were summarized in Scheme 4. Starting from glucosyl donor **1a**, symmetrical 1,1′-disaccharide **8** was isolated in 85% yield (αα/αβ/ββ = 24/15/1), with glucosyl fluoride **9** being isolated in 15% yield (α/β = 1/5). When rhamnosyl donor **1c** was charged under similar conditions, 1,1′-dirhamnosides **10αα** and **10αβ** were isolated in 70% and 28% yields, respectively. When starting from 2-deoxy-D-glucosyl donor **11**, symmetrical 1,1′-disaccharide **12αα** and **12αβ** were isolated in 39% and 40% yields,



Scheme 1. Reaction design.

Table 1
Optimization of reaction conditions.



Entry	1a/2a/NfF	Base (eq.)	3 Å MS (w/w)	Solvent	T (°C)	Time	Yield of 3a	α/β[c]
1	1/2/5.3	K_2CO_3 (11.7)	0	$ClCH_2CH_2Cl$	65	25 h	78%[a]	1.7/1
2	1/2/4.4	Cs_2CO_3 (5.0)	0	$ClCH_2CH_2Cl$	RT	22 h	82%[a]	1.7/1
3	1/2/2.9	Cs_2CO_3 (3.6)	300%	CH_2Cl_2	RT	6 h	97%[a]	1.4/1
4	1/1.5/2	Cs_2CO_3 (2.0)	300%	CH_2Cl_2	RT	4 h	87%[a]	1.7/1
5	1/1.5/1.5	Cs_2CO_3 (1.5)	300%	CH_2Cl_2	RT	5 h	83%[a]	2/1
6	1.6/1/3.2	Cs_2CO_3 (4.0)	300%	CH_2Cl_2	RT	18 h	87%[a]	1.2/1
7	1/2/2.9	CaO (5.0)	300%	CH_2Cl_2	RT	5 h	NR	_
8	1/1.5/2	DIPEA (2.0)	300%	CH_2Cl_2	RT	18 h	NR	_
9	1/1.5/2	DBU (2.0)	300%	CH_2Cl_2	RT	18 h	32%[b]	1/4

[a] Isolated yield.
[b] NMR yield.
[c] The α/β ratio was determined by quantitative ^{13}C NMR analysis according to reference method (ref. 21).

respectively. Interestingly, an elimination-glycosylation product, i.e., unsymmetrical 1,1′-disaccharide **13αα**, was also isolated in 8% yield. The configurations of the two anomeric centers of product **13** were assigned by NOE experiments, and no other anomer of **13** was isolated from the reaction mixture. The formation of product **13** indicated the presence of a Ferrier-like reaction pathway in the present glycosylation system [26].

3. Conclusion

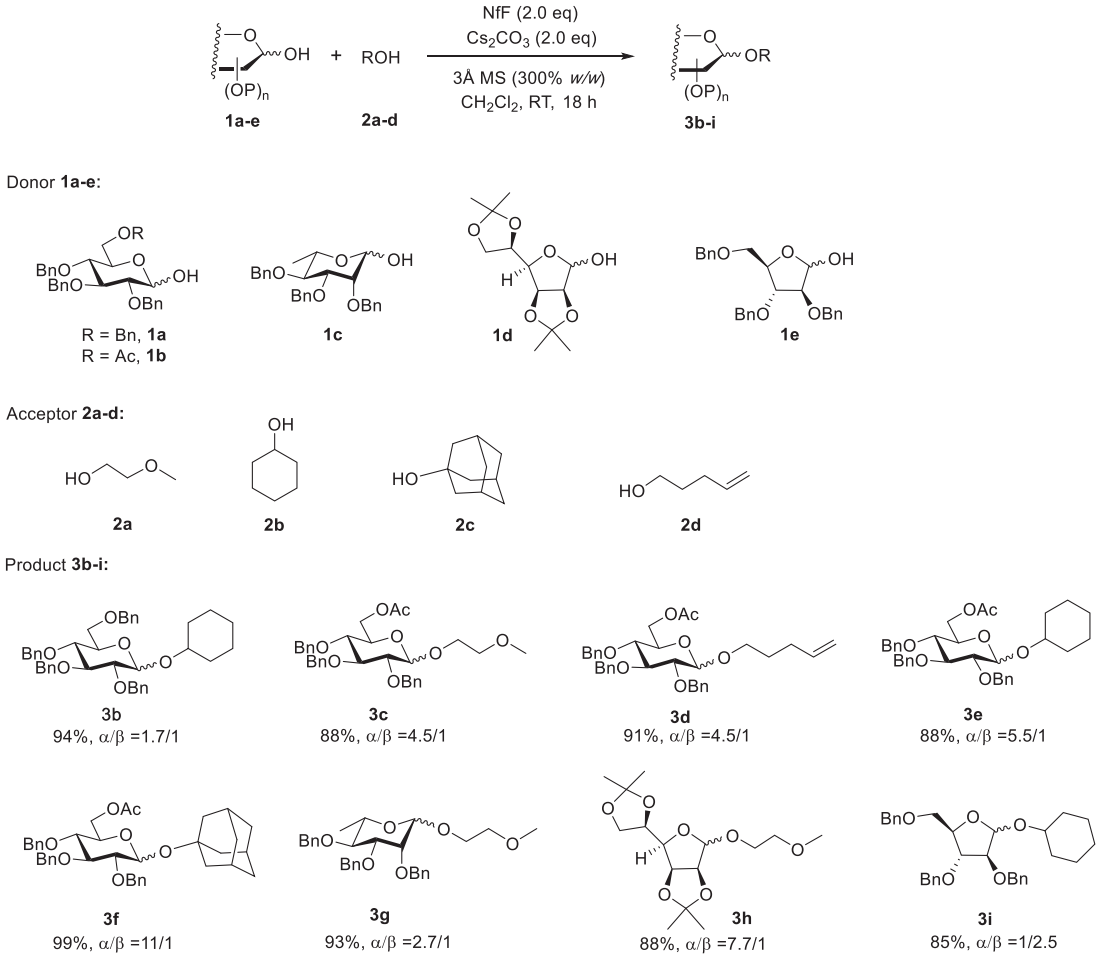
In summary, we have disclosed a new dehydrative glycosylation protocol mediated by nonafluorobutanesulfonyl fluoride (NfF). The reaction proceeds via selective activation of the deprotonated glycosyl hemiacetal with the mild nonaflating agent NfF to form reactive glycosyl nonaflate intermediates, which subsequently react with the co-existed alcoholic acceptor to deliver the glycosylation product. The reagents employed in this protocol are readily available and the protocol is operatically simple. A series of armed pyranosyl and furanosyl donors are shown to be suitable donors, and primary, secondary and tertiary alcoholic acceptors are suitable acceptors. In contrast to many other glycosylation protocols that proceed under acidic or neutral conditions, the present reaction proceed under mild basic conditions. Moreover, the present protocol also provides a convenient approach to the self-condensation of glycosyl hemiacetals to provide symmetrical 1,1′-disaccharides.

4. Experimental section

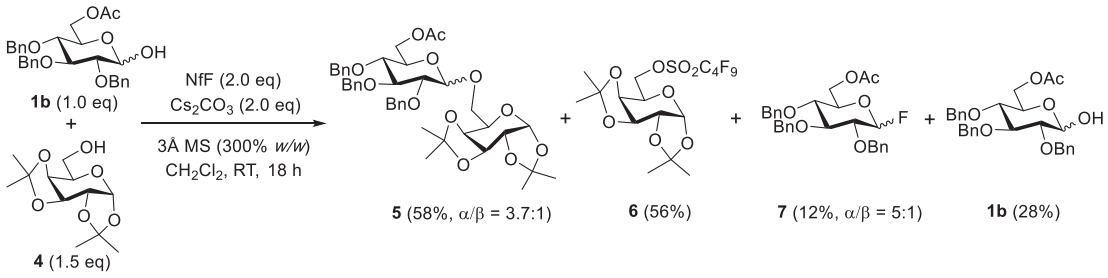
General. All reactions were performed using oven-dried glassware under an atmosphere of argon. Commercial reagents were used without further purification unless specialized. Crushed 3 Å molecular sieves were activated through flame-drying under high vacuum immediately prior to use. Extra dry dichloromethane (water ≤ 30 ppm) and extra dry 1,2-dichloroethane (water ≤ 50 ppm) were purchased from Innochem. Thin layer chromatography (TLC) was performed on TLC Silica Gel 60 F_{254} (Merck). The TLC plates were visualized with UV light and/or by staining with $EtOH/H_2SO_4$ (8%, v/v). Flash column chromatography was performed on Silica Gel 60 (40–64 μm, Fluka, Canada). NMR spectra were measured on Bruker AM 400, Agilent 500 or 600 MHz NMR spectrometer at 25 °C. ^1H and ^{13}C NMR signals were calibrated to the residual proton and carbon resonance of the solvent ($CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.16 ppm or CD_2Cl_2: δ_H = 5.32 ppm; δ_C = 53.86 ppm). High-resolution mass spectra were recorded with IonSpec 4.7 Tesla FTMS or APEXIII 7.0 Tesla FTMS. Optical rotations were measured on an Anton Paar MCP5500 polarimeter.

General procedure for the NfF mediated dehydrative glycosylation. A 25 mL glass Schlenk flask fitted with a resealable Teflon valve was equipped with a magnetic stir bar and charged with glycosyl donor (0.185 mmol, 1.0 eq), alcoholic acceptor (0.278 mmol, 1.5 eq), Cs_2CO_3 (0.370 mmol, 2.0 eq), and 3 Å molecular sieves (300 mg), then, under argon protection, dry CH_2Cl_2 (2.0 mL) was added, followed by NfF (0.370 mmol, 2.0 eq), the flask was sealed and stirred at room temperature (25–35 °C) until TLC indicated complete conversion. The mixture was filtered through a pad of celite, washed with CH_2Cl_2 (2 mL × 3) and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired glycosylation product.

2-Methoxyethyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranoside (**3a**). A reaction mixture of glycosyl donor **1a** (0.185 mmol, 100 mg) and acceptor **2a** (22 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 6 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg), and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 4/1. Yield of **3a**: 95 mg, 87%, α/β = 1.7/1. The spectral data of **3a** was identical with the literature data [27].



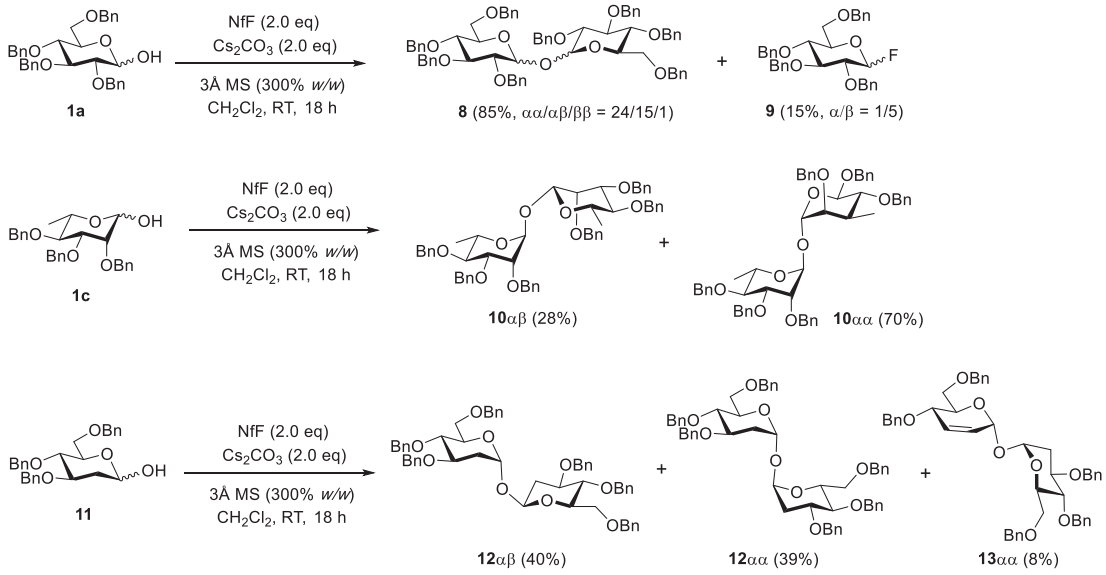
Scheme 2. Dehydrative glycosylation of alcohols mediated by NfF.



Scheme 3. Dehydrative glycosylation of donor 1b and glycoside acceptor 4 mediated by NfF.

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranoside (**3b**). A reaction mixture of glycosyl donor **1a** (0.185 mmol, 100 mg) and acceptor **2b** (29 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 18 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg), and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 10/1. Yield of **3b**: 108 mg, 94%, α/β = 1.7/1. The spectral data of **3b** was identical with the literature data [28].

2-Methoxyethyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranoside (**3c**). A reaction mixture of glycosyl donor **1b** (0.18 mmol, 88 mg) and acceptor **2a** (22 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 18 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg) and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 3/1. Yield of **3c**: 86 mg, 88%, α/β = 4.5/1. **3c**: colorless syrup; $[\alpha]_D^{25} = 44.5$ (*c* 1.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.21 (m, 16H), 5.07–4.93 (m, 1.17H), 4.93–4.71 (m, 3.7H), 4.68 (d, *J* = 12.2 Hz, 0.92H), 4.56 (d, *J* = 10.9 Hz, 1.09H), 4.45 (d, *J* = 7.8 Hz, 0.26H), 4.38–4.16 (m, 2.7H), 4.04 (t, *J* = 9.3 Hz, 1.0H), 3.92 (d, *J* = 10.2 Hz, 0.8H), 3.80–3.44 (m, 6.73H), 3.37 (s, 3.58H), 2.08–1.96 (m, 3.72H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.79, 170.75, 138.76, 138.52, 138.23, 138.19, 137.93, 137.81, 137.58, 128.57, 128.52, 128.50, 128.47, 128.45, 128.40, 128.30, 128.21, 128.19, 128.16, 128.12, 128.08, 128.02, 128.00, 127.96, 127.94, 127.91, 127.87, 127.85, 127.73, 127.70, 103.95, 97.09, 84.65, 82.11, 81.97, 80.00, 77.33, 75.79, 75.08, 74.78, 73.04, 72.86, 71.77, 71.69, 70.19,



Scheme 4. Formation of 1,1′-disaccharides via self-condensation mediated by NfF.

69.23, 68.64, 67.07, 66.94, 63.20, 63.12, 59.03, 58.99, 58.97, 20.89; HRMS (ESI) calcd for $C_{32}H_{38}NaO_8$ $[M+Na]^+$ 573.2464, found 573.2459.

***n*-Pent-4-enyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranoside** (**3d**). A reaction mixture of glycosyl donor **1b** (0.185 mmol, 91 mg) and acceptor **2d** (29 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 18 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg) and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 6/1. Yield of **3d**: 95 mg, 91%, α/β = 4.5/1. The spectral data of **3d** was identical with the literature data [29].

Cyclohexyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranoside (**3e**). A reaction mixture of glycosyl donor **1b** (0.185 mmol, 91 mg) and acceptor **2b** (29 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 18 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg) and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 6/1. Yield of **3e**: 93 mg, 88%, α/β = 5.5/1. The spectral data of **3e** was identical with the literature data [30].

1-Adamantanyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranoside (**3f**). A reaction mixture of glycosyl donor **1b** (0.183 mmol, 90 mg) and acceptor **2c** (0.278 mmol, 42 mg, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 18 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg) and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 6/1. Yield of **3f**: 113 mg, 99%, α/β = 11/1. **3f**: white solid; $[\alpha]_D^{25} = 50.5$ (*c* 3.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.53–7.00 (m, 16.4H), 5.34 (d, *J* = 6.7 Hz, 0.09H), 5.34–5.12 (m, 1.53H), 5.01 (d, *J* = 10.7 Hz, 1.0H), 4.95–4.75 (m, 2.4H), 4.68 (s, 2.0H), 4.55 (d, *J* = 10.7 Hz, 1.12H), 4.32 (dd, *J* = 12.2, 4.9 Hz, 0.95H), 4.19 (d, *J* = 11.7 Hz, 1.15H), 4.14–3.99 (m, 1.78H), 3.81–3.31 (m, 2.48H), 2.26–2.06 (m, 5.6H), 2.00 (s, 3.4H), 1.92–1.76 (m, 6.3H), 1.75–1.52 (m, 12.3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 170.79, 170.75, 138.85, 138.17, 137.96, 128.53, 128.50, 128.47, 128.43, 128.41, 128.38, 128.23, 128.20, 128.16, 128.14, 128.12, 128.09, 127.93, 127.90, 127.87, 127.84, 127.63, 127.59, 96.27, 89.72, 85.07, 82.16, 81.99, 80.06, 77.84, 77.81, 76.33, 75.72, 75.59, 75.46, 75.32, 75.07, 74.95, 74.92, 74.90, 74.76, 72.85, 72.50, 68.21, 68.10, 63.55, 63.35, 62.74, 53.47, 45.34, 42.71, 42.43, 36.26, 36.10, 30.72, 30.66, 20.84; HRMS (ESI) calcd for $C_{39}H_{46}NaO_7$ $[M+Na]^+$ 649.3141, found 649.3136.

2-Methoxyethyl 2,3,4-tri-*O*-benzyl-α,β-L-rhamanopyranoside (**3g**). A reaction mixture of glycosyl donor **1c** (0.185 mmol, 81 mg) and acceptor **2a** (22 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 24 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg) and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 5/1. Yield of **3g**: 85 mg, 93%, α/β = 2.7/1. **3g**: yellow syrup; $[\alpha]_D^{25} = 18.8$ (*c* 3.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.52–7.43 (m, 1.2H), 7.43–7.20 (m, 19.2H), 5.03–4.97 (m, 0.62H), 4.95 (d, *J* = 10.6 Hz, 1.2H), 4.89 (d, *J* = 12.5 Hz, 0.54H), 4.84–4.81 (m, 0.83H), 4.81–4.71(m, 2.07), 4.68–4.65 (m, 0.76H), 4.65–4.61 (m, 2.33H), 4.51 (d, *J* = 11.9 Hz, 0.51H), 4.44 (d, *J* = 17.5 Hz, 0.85H), 4.32–4.26 (m, 0.4H), 4.07–4.01 (m, 0.46H), 3.96 (d, *J* = 3.0 Hz, 0.45H), 3.91 (d, *J* = 3.2 Hz, 0.47H), 3.90–3.86 (m, 1.32H), 3.78–3.67 (m, 1.89H), 3.68–3.52 (m, 4.1H), 3.52–3.48 (m, 1.54H), 3.46 (dd, *J* = 9.4, 3.0 Hz, 0.52H), 3.41 (s, 1.1H), 3.35 (s, 2.38H), 1.38 (d, *J* = 6.1 Hz, 1.29H), 1.34 (d, *J* = 6.1 Hz, 3.1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.85, 138.70, 138.63, 138.57, 138.44, 138.25, 128.52, 128.43, 128.39, 128.16, 128.12, 128.06, 127.94, 127.69, 127.64, 127.59, 127.53, 127.45, 101.57, 98.09, 82.08, 80.57, 80.22, 80.18, 75.50, 74.86, 74.00, 73.90, 72.85, 72.19, 71.97, 71.60, 71.35, 70.19, 68.69, 68.06, 66.96, 66.35, 59.11, 18.07; HRMS (ESI) calcd for $C_{30}H_{36}NaO_6$ $[M+Na]^+$ 515.2410, found 515.2404.

2-Methoxyethyl 2,3:5,6-di-*O*-isopropyliden-α,β-D-mannofuranoside (**3h**). A reaction mixture of glycosyl donor **1d** (0.185 mmol, 48 mg) and acceptor **2a** (22 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 23 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg) and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 3/1. Yield of **3h**: 59 mg, 88%, α/β = 7.7/1. **3h**: colorless syrup; $[\alpha]_D^{25} = 44.5$ (*c* 1.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 5.19 (s, 0.13H), 4.99 (s, 1.00H), 4.75 (s, 1.13H), 4.68–4.57 (m, 0.98), 4.53 (d, *J* = 5.8 Hz, 1H), 4.41–4.31 (m, 1.02H), 4.25 (s, 0.3H), 4.17–3.87 (m, 3.08H), 3.79–3.66 (m, 1.06H), 3.63–3.44 (m, 2.92H), 3.34 (s, 2.84H), 1.50–1.40 (m, 5.64H),

1.38–1.31 (m, 2.82H), 1.31–1.24 (m, 2.78H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.60, 109.26, 106.54, 101.61, 85.06, 81.02, 80.33, 79.55, 73.22, 73.06, 71.64, 70.21, 66.95, 66.41, 59.05, 26.95, 25.93, 25.25, 24.56; HRMS (ESI) calcd for $C_{15}H_{26}NaO_7$ $[M+Na]^+$ 341.1576, found 341.1571.

Cyclohexyl 2,3,4-tri-*O*-benzyl-α,β-D-arabinofuranoside (**3i**). A reaction mixture of glycosyl donor **1e** (0.185 mmol, 78 mg) and acceptor **2b** (29 μL, 0.278 mmol, 1.5 eq) in 2.0 mL dry CH_2Cl_2 was stirred for 18 h in the presence of Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), 3 Å molecular sieves (300 mg) and NfF (0.370 mmol, 68 μL, 2.0 eq) under the standard conditions. Eluent: petroleum ether/ethyl acetate = 15/1. Yield of **3i**: 79 mg, 85%, α/β = 1/2.5. **3i**: colorless syrup; $[\alpha]_D^{25}$ = −59.3 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.27 (m, 9.25H), 5.28 (s, 0.40H), 5.16 (d, *J* = 4.3 Hz, 1.0H), 4.74 (d, *J* = 11.9 Hz, 1.08H), 4.71–4.66 (m, 1.71H), 4.63 (d, *J* = 12.0 Hz, 1.17H), 4.60 (s, 2.88H), 4.58–4.51 (m, 1.58H), 4.28 (dt, *J* = 7.8, 3.8 Hz, 0.44H), 4.20–4.13 (m, 1.96H), 4.12–4.07 (m, 1.28H), 4.05–3.97 (m, 0.54H), 3.74–3.57 (m, 4.19), 2.00–1.85 (m, 2.92H), 1.84–1.72 (m, 3.19H), 1.63–1.55 (m, 1.57H), 1.50–1.13 (m, 7.94H); ^{13}C NMR (126 MHz, cdcl$_3$) δ 138.41, 138.26, 138.17, 138.12, 137.89, 137.78, 128.60, 128.49, 128.47, 128.45, 128.43, 128.38, 128.36, 128.16, 128.12, 127.98, 127.94, 127.88, 127.87, 127.82, 127.80, 127.77, 127.73, 127.69, 127.66, 127.60, 104.14, 98.81, 88.87, 84.07, 83.77, 83.64, 80.11, 80.04, 75.95, 74.96, 73.41, 73.38, 73.05, 72.34, 72.22, 72.13, 71.99, 69.84, 33.79, 33.73, 31.83, 31.72, 25.79, 25.68, 24.52, 24.33, 24.28, 24.14; HRMS (ESI) calcd for $C_{32}H_{38}NaO_5$ $[M+Na]^+$ 525.2617, found 525.2611.

The reaction of donor 1b and acceptor 4 mediated by NfF (Scheme 3). A 25 mL glass Schlenk flask fitted with a resealable Teflon valve was equipped with a magnetic stir bar and charged with glycosyl donor **1b** (0.189 mmol, 93 mg), glycosyl acceptor **4** (0.28 mmol, 74 mg, 1.5 eq), Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), and 3 Å molecular sieves (300 mg), then, under argon protection, dry CH_2Cl_2 (2.0 mL) was added, followed by NfF (0.370 mmol, 68 μL, 2.0 eq). The flask was sealed and the mixture stirred at room temperature for 18 h. The mixture was filtered through a pad of celite, washed with CH_2Cl_2 (2 mL × 3) and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate 15/1 to 4/1 to 3/1) to give four components (**A**-**D**), successively.

Component **A** was identified to be nonaflated acceptor 1,2:3,4-di-*O*-isopropylidene-6-*O*-nonafluorobutanesulfonyl-α-D-galactopyranose **6** (87 mg, 56%) as a colorless syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (d, *J* = 4.9 Hz, 1H), 4.71–4.57 (m, 3H), 4.35 (dd, *J* = 5.1, 2.6 Hz, 1H), 4.27–4.21 (m, 1H), 4.11 (t, *J* = 6.2 Hz, 1H), 1.51 (s, 3H), 1.44 (s, 3H), 1.36–1.29 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 110.28, 109.27, 96.30, 75.29, 70.84, 70.57, 70.43, 66.32, 25.98, 25.96, 24.96, 24.46; ^{19}F NMR (471 MHz, $CDCl_3$) δ −80.81 (t, *J* = 9.7 Hz), −110.73 (t, *J* = 14.4 Hz), −121.32 to −121.52 (m), −125.94 to −126.06 (m); HRMS (ESI) calcd for $C_{16}H_{19}F_9NaO_8S$ $[M+Na]^+$ 565.0555, found 565.0549.

Component **B** was identified to be 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D- glucopyranosyl fluoride **7** (12 mg, α/β = 5/1, 12%) as a pale yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.23 (m, 12.9H), 5.52 (dd, *J* = 53.0, 2.7 Hz, 0.21H), 5.28 (dd, *J* = 52.7, 6.5 Hz, 1.0H), 4.99 (d, *J* = 10.8 Hz, 0.22H), 4.91 (d, *J* = 11.0 Hz, 0.81H), 4.89–4.83 (m, 1.66H), 4.78 (d, *J* = 11.0 Hz, 0.84H), 4.70 (d, *J* = 11.2 Hz, 0.95H), 4.58 (d, *J* = 10.9 Hz, 0.89H), 4.38 (dd, *J* = 12.0, 2.2 Hz, 0.87H), 4.28 (dd, *J* = 10.2, 3.2 Hz, 0.39H), 4.22 (dd, *J* = 12.1, 4.8 Hz, 0.91H), 4.01 (d, *J* = 9.2 Hz, 0.36H), 3.77–3.50 (m, 3.26H), 2.05 (s, 2.02H), 2.03 (s, 0.43H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.80, 138.20, 137.69, 137.62, 128.75, 128.68, 128.64, 128.61, 128.30, 128.25, 128.22, 128.19, 128.16, 128.13, 128.01, 127.98, 109.66 (d, *J* = 216.9 Hz), 83.56 (d, *J* = 10.5 Hz), 81.39 (d, *J* = 22.4 Hz), 76.53, 75.48, 75.12, 74.46 (d, *J* = 2.1 Hz), 73.16 (d, *J* = 5.1 Hz), 62.90, 20.95; Elemental analysis calcd (%) for $C_{29}H_{31}FO_6$: C 70.43, H 6.32; found: C 70.24, H 6.38.

Component **C** was identified to be 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D- glucopyranosyl-(1 → 6)-1,2:3,4-*O*-diisopropylidene-α-D-galactopyranose **5** (81 mg, α/β = 3.7/1, 58%) as a colorless syrup. The spectral data of **5** was identical with the literature data [31].

Component **D** was identified to be the unreacted donor **1b** (26 mg, 28%).

Self-condensation of donor 1a mediated by NfF. A 25 mL glass Schlenk flask fitted with a resealable Teflon valve was equipped with a magnetic stir bar and charged with glycosyl donor **1a** (0.189 mmol, 100 mg), Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), and 3 Å molecular sieves (300 mg), then, under argon protection, dry CH_2Cl_2 (2.0 mL) was added, followed by NfF (0.370 mmol, 68 μL, 2.0 eq). The flask was sealed and the mixture stirred at room temperature for 18 h. The mixture was filtered through a pad of celite, washed with CH_2Cl_2 (2 mL × 3) and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate 10/1 to 6/1) to give two components (**A** and **B**), successively.

Component **A** was identified to be 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosyl fluoride **9** (15 mg, 15%) as a colorless syrup. The spectral data of **9** was identical with the literature data [19c].

Component **B** was identified to be 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl-(1↔1)-2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **8** (84 mg, αα/αβ/ββ = 24/15/1, 85%) as a colorless syrup. The spectral data of **8** was identical with the literature data [25a].

Self-condensation of donor 1c mediated by NfF. A 25 mL glass Schlenk flask fitted with a resealable Teflon valve was equipped with a magnetic stir bar and charged with glycosyl donor **1c** (0.19 mmol, 82 mg), Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), and 3 Å molecular sieves (300 mg), then, under argon protection, dry CH_2Cl_2 (2.0 mL) was added, followed by NfF (0.370 mmol, 68 μL, 2.0 eq). The flask was sealed and the mixture stirred at room temperature for 24 h. The mixture was filtered through a pad of celite, washed with CH_2Cl_2 (2 mL × 3) and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate 6/1 to 5/1) to give two components (**A** and **B**), successively.

Component **A** was identified to be 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl-(1↔1)-2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside **10αα** (57 mg, 70%) as a colorless syrup. The spectral data of **10αα** was identical with the literature data [25b].

Component **B** was identified to be 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl-(1↔1)-2,3,4-tri-*O*-benzyl-β-L-rhamnopyranoside **10αβ** (23 mg, 28%) as a colorless syrup. $[\alpha]_D^{25}$ = 12.3 (*c* 0.51, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.21 (m, 29H), 4.96 (d, *J* = 11.2 Hz, 1H), 4.93 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 1.8 Hz, 1H), 4.80 (d, *J* = 12.5 Hz, 1H), 4.77 (d, *J* = 12.5 Hz, 1H), 4.72 (d, *J* = 12.5 Hz, 1H), 4.70–4.61 (m, 4H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.57–4.49 (m, 2H), 4.41 (s, 1H), 4.10–4.04 (m, 1H), 3.92 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.78 (d, *J* = 2.9 Hz, 1H), 3.69 (dd, *J* = 3.1, 1.8 Hz, 1H), 3.63 (t, *J* = 9.5 Hz, 1H), 3.59 (t, *J* = 9.3 Hz, 1H), 3.42 (dd, *J* = 9.4, 2.9 Hz, 1H), 3.30 (dd, *J* = 9.2, 6.2 Hz, 1H), 1.33 (d, *J* = 6.1 Hz, 3H), 1.29 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, cdcl$_3$) δ 139.07, 138.76, 138.67, 138.57, 138.43, 138.35, 128.51, 128.49, 128.48, 128.43, 128.40, 128.27, 128.23, 128.03, 127.87, 127.84, 127.81, 127.76, 127.71, 127.66, 127.53, 100.31, 98.92, 82.52, 80.68, 80.07, 79.88, 75.55, 75.46, 75.12, 74.21, 74.01, 73.02, 72.83, 72.33, 71.94, 69.19, 60.53, 18.11, 17.78; HRMS (ESI) calcd for $C_{54}H_{58}NaO_9$ $[M+Na]^+$ 873.3979, found 873.3973.

Self-condensation of donor 11 mediated by NfF. A 25 mL glass Schlenk flask fitted with a resealable Teflon valve was equipped

with a magnetic stir bar and charged with glycosyl donor **11** (0.185 mmol, 80 mg), Cs_2CO_3 (0.370 mmol, 121 mg, 2.0 eq), and 3 Å molecular sieves (300 mg), then, under argon protection, dry CH_2Cl_2 (2.0 mL) was added, followed by NfF (0.370 mmol, 68 μL, 2.0 eq). The flask was sealed and the mixture stirred at room temperature for 24 h. The mixture was filtered through a pad of celite, washed with CH_2Cl_2 (2 mL × 3) and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate 6/1 to 4/1) to give three components (**A**-**C**), successively.

Component **A** was identified to be 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl-(1↔1)-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-arabinohexopyranoside **13αα** (5.4 mg, 8%) as a colorless syrup: $[\alpha]_D^{25}$ = 79.5 (*c* 0.24, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.36–7.21 (m, 24H), 6.11 (dt, *J* = 10.2, 1.4 Hz, 1H), 5.74 (ddd, *J* = 10.3, 2.9, 1.9 Hz, 1H), 5.35 (dd, *J* = 3.7, 1.4 Hz, 1H), 5.27–5.25 (m, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 2H), 4.62–4.54 (m, 4H), 4.54–4.44 (m, 3H), 4.10 (dq, *J* = 9.4, 1.7 Hz, 1H), 3.95 (ddd, *J* = 11.4, 8.8, 5.0 Hz, 1H), 3.90 (ddd, *J* = 9.4, 4.2, 2.7 Hz, 1H), 3.79–3.72 (m, 2H), 3.73–3.65 (m, 3H), 3.56 (t, *J* = 9.1 Hz, 1H), 2.28 (ddd, *J* = 13.0, 5.1, 1.5 Hz, 1H), 1.71 (ddd, *J* = 13.1, 11.4, 3.8 Hz, 1H); ^{13}C NMR (151 MHz, CD_2Cl_2) δ 139.39, 139.26, 138.94, 138.91, 138.66, 130.97, 128.72, 128.69, 128.64, 128.60, 128.29, 128.27, 128.15, 128.11, 128.04, 127.98, 127.90, 127.86, 127.79, 126.83, 93.81, 89.91, 78.67, 77.77, 75.22, 73.70, 73.62, 71.91, 71.88, 71.57, 70.78, 70.25, 69.73, 69.64, 35.51; HRMS (ESI) calcd for $C_{47}H_{50}NaO_8$ $[M+Na]^+$ 765.3403, found 765.3398.

Component **B** was identified to be 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-arabino- hexopyranosyl-(1↔1)-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-arabinohexopyranoside **12αα** (31 mg, 39%) as a colorless syrup. The spectral data of **12αα** was identical with the literature data [32].

Component **C** was identified to be 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-arabino- hexopyranosyl-(1↔1)-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-arabinohexopyranoside **12αβ** (32 mg, 40%) as a colorless syrup: $[\alpha]_D^{25}$ = 45.9 (*c* 0.73, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.17 (m, 30H), 5.23 (d, *J* = 3.4 Hz, 1H), 4.92 (d, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 5.9 Hz, 1H), 4.73–4.46 (m, 10H), 4.36 (d, *J* = 12.1 Hz, 1H), 4.12 (dd, *J* = 9.9, 2.6 Hz, 1H), 4.08–4.00 (m, 1H), 3.76–3.62 (m, 5H), 3.60–3.49 (m, 2H), 3.42 (dd, *J* = 7.7, 4.3 Hz, 1H), 2.36–2.25 (m, 2H), 1.85–1.62 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.01, 138.91, 138.58, 138.54, 138.44, 138.38, 128.55, 128.47, 128.46, 128.39, 128.35, 128.13, 127.97, 127.82, 127.81, 127.77, 127.74, 127.64, 127.62, 127.60, 127.51, 99.19, 98.08, 79.61, 78.26, 78.00, 77.59, 75.41, 75.07, 74.87, 73.45, 72.10, 71.62, 71.58, 69.38, 68.60, 37.06, 35.67; HRMS (ESI) calcd for $C_{54}H_{58}NaO_9$ $[M+Na]^+$ 873.3979, found 873.3973.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2020.131800.

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