Fucosylation of Linear Alcohols: A Study of Parameters Influencing the Stereochemistry of Glycosylation

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L-Fucose is a constituent of many glycoconjugates and often has a key role in the epitope involved in biological functions. The chemical synthesis of such compounds is necessary to generate sufficient material to explore the molecular details of their bioactivity. In this context, the development of practical and stereoselective α-fucosylation reactions is essential. Here are described several procedures for fucosylation of linear alcohols **9**–**16** with L-fucose (**1**) and a series of 2-*O*-benzyl-protected fucopyranosyl donors **3**–**8**, together with parameters influencing the stereochemistry of glycosylation, such as protecting groups, catalysts, and dielectric constants of solvents. Although high α-selectivities have often been reported for fucosylation reactions with glycosyl acceptors, complete α-selectivity was never observed here, using linear spacer alcohols **9**–**16**. Generally, the best α-selectivities were obtained in fucosylations of the alcohols under in situ anomerization conditions using tetrabutylammonium bromide (75–90% α-anomer), whereas promotion by NIS/TfOH(cat.) proceeded with poor stereoselectivity in treatment of the ethyl thiofucosides **3**–**5**. No directing effects from the 4-*O* protecting groups were noted. For the 2-*O*-benzyl-protected 1-*O*-thioethyl fucopyranosyl donors **3**–**5**, electronic effects of the fucosyl donor could not explain the observed stereoselectivity. The difference between the observed selectivities for α-fucosylations of glycosyl acceptors, in comparison with the linear spacer alcohols used here, is probably due to steric effects of the more bulky glycosyl acceptors.

Introduction

In naturally occurring glycoconjugates, L-fucose usually occupies a non-reducing position.[1] Procedures to synthesize oligosaccharides containing α-L-fucose residues have been the subject of many studies, and various fucosyl donors have been used: among them thiofucosides,[2−5] fucosyl halides,[6−9] fucosyl trichloroacetimidates,[10] fucosyl phosphites,[11] and fucosyl methoxyacetates.[12] Direct fucosylation of a spacer aglycon with L-fucose can be accomplished using a Fischer-type glycosylation reaction. The development of practical and stereoselective α-fucosylations is an important area. However, a practical problem is that glycosylation of (protected) fucose moieties often results in anomeric mixtures that are difficult to separate.[13−15] In this paper, the stereoselectivity of fucosylation reactions with some linear alcohols has been investigated. Several parameters important for the stereochemical outcome of the glycosylation reactions were studied, including the type of activating group, the type and position of donor protecting groups, the dielectric constants of solvent systems used, and the influence of the catalyst/promoter.

Results and Discussion

Stereochemical outcomes (in terms of the anomeric ratios) of the condensation reactions of fucose donors **1**−**8** were investigated for eight alcohols: ethanol (**9**), 1-propanol (**10**), allyl alcohol (**11**), 1-butanol (**12**), 3-bromopropanol (**13**), 3-azidopropanol (**14**), 5-azidopentanol (**15**), and 1-decanol (**16**).

Most coupling reactions gave moderate or high yields (Tables 1−5). The α/β ratio of the products was determined by integration of typical proton signals (using either anomeric or methyl protons) in the corresponding ^{1}H NMR spectra, measured at 300 MHz.

Synthesis of Fucopyranosyl Donors

Firstly, direct glycosylation was performed using L-fucose (**1**). Additionally, the effect on the α/β ratio of various protecting groups at O-3 and O-4 of some 2-*O*-benzyl-protected fucopyranosyl donors was also studied, in order to investigate participating and activating/deactivating effects during coupling reactions. For this reason, couplings using the 2,3,4-tri-*O*-benzylfucopyranosyl donor, the most often used donor described in the literature, were not studied here. Ethyl 3,4-di-*O*-acetyl-2-*O*-benzyl-1-thio-β-L-fucopyranoside (**3**) [donor **3** was prepared from ethyl 2-*O*-benzyl-1-thio-β-L-fucopyranoside[2] by acetylation (→ **3**, 92%)], ethyl 3-*O*-acetyl-2,4-di-*O*-benzyl-1-thio-β-L-fucopyranoside[14] (**4**), ethyl 2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside[2] (**5**), 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl bromide[16] (**6**), 3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-fucopyranosyl bromide[17] (**7**), and 2-*O*-benzyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl bromide (**8**) (glycosyl bromides **6**−**8** were obtained by treatment of the corresponding

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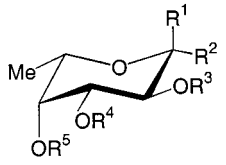
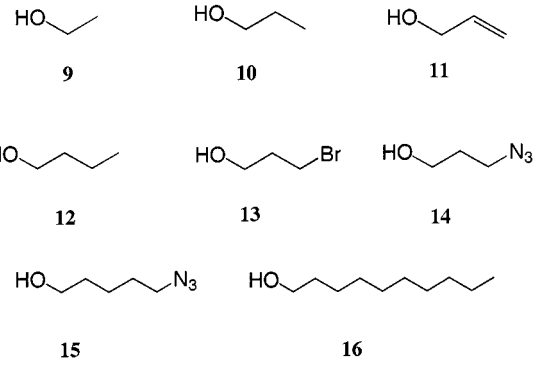
thioethyl analogues **3**−**5** with bromine) were selected as donors for treatment with aglycons **9**−**16** (Scheme 1).



	R^1	R^2	R^3	R^4	R^5
1	H, OH		H	H	H
2	H, OMe		H	H	H
3	H	SEt	Bn	Ac	Ac
4	H	SEt	Bn	Ac	Bn
5	H	SEt	Bn	$C(CH_3)_2$	
6	Br	H	Bn	Ac	Ac
7	Br	H	Bn	Ac	Bn
8	Br	H	Bn	$C(CH_3)_2$	



Scheme 1

Although α-selectivity has sometimes been reported in the literature with protected fucosyl donors possessing an anchimeric assistant 2-*O*-acetyl protecting group with glycosyl acceptors[18,19] or aliphatic alcohols,[20] we never succeeded in obtaining α-L-linked products using these approaches (results not shown).

Modified Fischer Glycosylation

Fischer fucosylations of **9**−**11**, **13**, **14**, and **16** with **1** were performed using the alcohol both as solvent and as reagent for the reaction. Either HCl or an ion-exchange resin [Dowex-50 (H^+)] were used as catalyst. Fucosylation of **14** with **2**[21,22] was performed using *p*-toluenesulfonic acid in *N*,*N*-dimethylformamide at 50°C. Most reactions proceeded smoothly in good yields (Table 1); all products (**19**−**24**) were obtained as mixtures of anomers (Scheme 2). Isolation of one anomer was sometimes possible, as is described for the preparation of allyl α-L-fucopyranoside by crystallization[23] (cf. entry 3). As well as the thermodynamically more stable pyranosides[24] (**19**−**24**), fucofuranosides were always observed to be present in the reaction mixtures (NMR analysis; data not shown). Performing the reactions at lower temperatures afforded more furanoside products (results not shown). The formation of anomeric products is evident from the proposed mechanism for this type of reaction. It is thought that the Fischer glycosylation of L-fucose occurs via a bicyclic intermediate (**17**) (Pater et al.,[25] Scheme 2), followed by an S_N1 ring-opening of **17**, allowing the alcohol to attack on both sides at ring **18**.

According to the literature,[25,26] preparation of methyl α/β-L-fucopyranosides utilizing cation exchange resins (H^+) in boiling methanol gave an anomeric ratio α/β = 67:33 after 12 h. For the alcohols used in this study, Table 1 shows that comparable stereochemical product distributions were obtained (entries 1, 3, 6, 8, 11). Repetition of these experiments, but changing the catalyst for HCl (achieved by the addition of acetyl chloride[27]) showed rapid conversions of **1**. In most cases, when using HCl as catalyst, the formation of α-linked products was slightly favored in comparison with the ion exchange-catalyzed procedures. So it might be that the product distribution is influenced either by the nature of the catalyst, or by whether a *heterogeneous* (ion exchange resin) or *homogeneous* (HCl) reaction mixture is used. Furthermore, the Lewis acid-catalyzed ($FeCl_3$) reaction of **1** with **11** in a homogeneous reaction mixture also gave a higher α-selectivity (compare entries 3, 4, 5). Relatively higher levels of the thermodynamically more favored α-adducts in homogeneous systems might be explained by equilibrated mixtures being reached earlier.[1] Finally, the anomeric ratios in Table 1 show that no significant influence of the length of the aglycon could be observed.

Experiments with 2-*O*-Benzyl-Protected Fucopyranosyl Donors

A series of experiments was performed using fucosyl donors possessing a non-participating benzyl function at O-2, with varying protecting groups at O-3 and O-4. Donors **3** or **6** (Table 2) have an electron-withdrawing 4-O substituent, donors **4** or **7** (Table 3) an electron donating one, whereas donors **5** and **8** (Table 4) have an acetonide function at O-3,4, thus existing as a distorted $^1C_4$ chair. The ethyl 1-thio-β-L-fucopyranoside donors (**3**−**5**) were coupled with **11** and **13**−**16** using the strongly thiophilic promoter system *N*-iodosuccinimide and trifluoromethanesulfonic acid (NIS/TfOH cat.), at different temperatures and in different solvents. Alternatively, they were converted into their corresponding α-bromides (**6**−**8**) for condensations with **10**, **11**, **13**, **14**, and **16** in the presence of tetrabutylammonium bromide (TBAB), using in situ anomerization conditions to convert α-bromides into the more reactive β-bromides.[28] Also, some miscellaneous coupling methods were applied with a limited number of examples. As shown in Tables 2 and 3, neither α- nor β-L-fucosides were ever formed exclusively, and all isolated products **25**−**33** showing as a single spot on TLC were isolated as inseparable mixtures of anomers (Scheme 3).

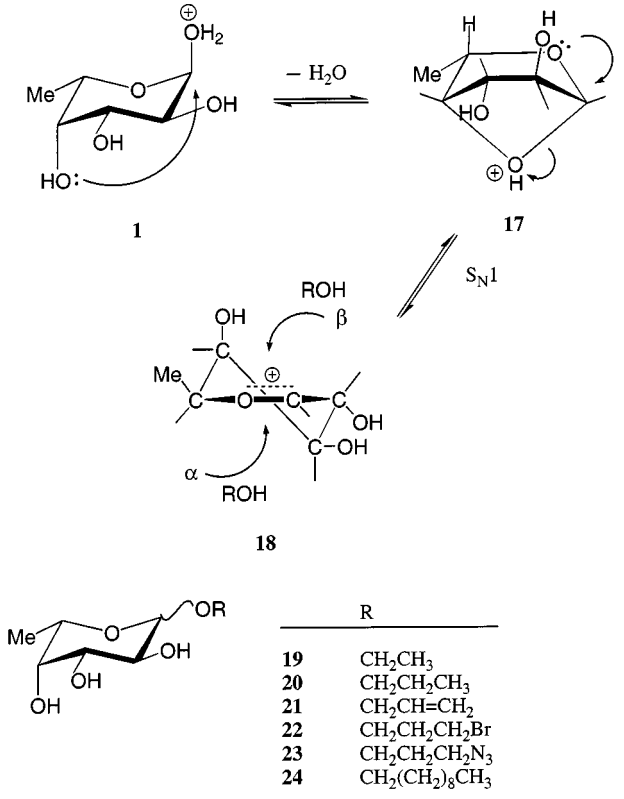
Iodonium-assisted Fucosylation With Donors 3 and 4

Treatment of **3** with **11**, **13**, and **16** was examined in the presence of NIS/TfOH at 0°C in dichloromethane (Table 2; entries 14, 18, and 21). Additionally, treatment of **3** with **11** was also studied, using either a mixture of dichlorome-

Table 1. Glycosylation of alcohols **9**−**11**, **13**, **14**, and **16** with donor **1** or **2**

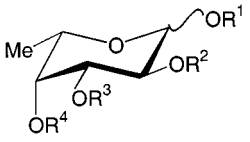
Entry	Donor	Alcohol	Method[a]	Product	Yield[b] [%]	Anomeric ratio (α/β)[c]
1	**1**	**9**	A	**19**	65	64:36
2	**1**	**10**	B	**20**	67	75:25
3	**1**	**11**	A	**21**	64	70:30
4	**1**	**11**	B	**21**	74	67:33
5	**1**	**11**	C	**21**	73	72:28
6	**1**	**13**	A	**22**	38	64:36
7	**1**	**13**	B	**22**	67	83:17
8	**1**	**14**	A	**23**	31	60:40
9	**1**	**14**	B	**23**	26	68:32
10	**2**	**14**	D	**23**	19	71:29
11	**1**	**16**	A	**24**	48	71:29
12	**1**	**16**	B	**24**	75	74:26

[a] A (*GP 1*): Dowex-50 (H^+), 75 °C, 12 h; B (*GP 2*): Acetyl chloride, 65 °C, 3 h; C: $FeCl_3$, 55 °C, 3 h; D: *p*TsOH.H_2O, DMF, 50 °C, 5 days. − [b] The yield is based on the isolation of only pyranosides. − [c] Anomeric ratios are only calculated for pyranoside products, and do not reflect the total anomeric composition of all formed products.



	R
19	CH_2CH_3
20	$CH_2CH_2CH_3$
21	$CH_2CH{=}CH_2$
22	$CH_2CH_2CH_2Br$
23	$CH_2CH_2CH_2N_3$
24	$CH_2(CH_2)_8CH_3$

Scheme 2



	R^1	R^2	R^3	R^4
25	$CH_2CH_2CH_3$	Bn	Ac	Ac
26	$CH_2CH{=}CH_2$	Bn	Ac	Ac
27	$CH_2CH_2CH_2Br$	Bn	Ac	Ac
28	$CH_2CH_2CH_2N_3$	Bn	Ac	Ac
29	$CH_2(CH_2)_8CH_3$	Bn	Ac	Ac
30	$CH_2CH{=}CH_2$	Bn	Ac	Bn
31	$CH_2CH_2CH_2Br$	Bn	Ac	Bn
32	$CH_2CH_2CH_2N_3$	Bn	Ac	Bn
33	$CH_2(CH_2)_8CH_3$	Bn	Ac	Bn

Scheme 3

thane/diethyl ether (entry 16), or dichloromethane/acetonitrile (entry 17). Coupling experiments with the more reactive donor **4** were performed in dichloromethane with **11**, **13**, **14**, and **16**, using identical reaction conditions (Table 3; entries 23, 26, 29, and 31). Treatment of **4** with **14** in dichloromethane was also studied at different temperatures (−30°C, 0°C, room temperature; entries 28−30), while couplings with **11** and **16** were also conducted in mixtures of dichloromethane/diethyl ether and dichloromethane/acetonitrile (Table 3; entries 24, 25, and 32).

Most fucosylations with **3** and **4** in dichloromethane proceeded in moderate or high yields, but with only marginal differences in stereoselectivity. In general, couplings with **3** and **4** in dichloromethane showed a slight α-selectivity, except for their reaction with **16**. No significant changes in the anomeric ratios were observed for reactions conducted in diethyl ether/dichloromethane (entries 14 versus 16 and 23 versus 24). However, reactions performed in dichloromethane showed an increased selectivity for the α-anomeric product at higher temperatures[29−31] (reaction of **4** with **14**; entries 28−30). The formation of β-fucosides was favored when **3** or **4** were coupled with some alcohols in a polar mixture of acetonitrile/dichloromethane (entries 17, 25, and 32).

According to the literature, high α-selectivities had sometimes been found in fucosylations of *glycosyl* acceptors, using the trichloroacetimidate method.[32] However, coupling of 3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl trichloroacetimidate[33] with **14** did not improve the α-selectivity (results not shown).

In order to find a possible explanation for the observed poor selectivity of iodonium-assisted fucosylations using either **3** or **4**, it should be noted first that the reported exclusive formation of 1,2-*cis* linkages with comparable donors (i.e., possessing a non-participating protecting group at O-2) relate to couplings with *glycosyl* acceptors.[2] Generally, the influence of protecting groups on fucosylations has been explained in terms of inductive effects,[9,11,34]

Table 2. Glycosylation of alcohols **10**, **11**, **13**, **14**, and **16** with donor **3** or **6**

Entry	Donor	Alcohol	Method[a]	Product	Yield [%]	Anomeric ratio (α/β)
13	**6**	**10**	A	**25**	87	77:23
14	**3**	**11**	B	**26**	90	62:38
15	**6**	**11**	A	**26**	85	87:13
16	**3**	**11**	C	**26**	62[b]	69:31
17	**3**	**11**	D	**26**	96	22:78
18	**3**	**13**	B	**27**	92	70:30
19	**6**	**13**	A	**27**	59	88:12
20	**6**	**14**	A	**28**	54	88:12
21	**3**	**16**	B	**29**	83	47:53
22	**6**	**16**	A	**29**	72	83:17

[a] A (*GP 5*): TBAB, DCM/DMF, room temp., 2 days; B (*GP 4 A*): NIS/TfOH, DCM, 0 °C, 1 h; C (*GP 4 B*): NIS/TfOH, Et_2O/DCM, 0 °C, 1 h; D (*GP 4 C*): NIS/TfOH, CH_3CN/DCM, 0 °C, 1 h. – [b] Total isolated material consisted of 62% fucosidation products (**26**) and 35% starting donor (**3**).

Table 3. Glycosylation of alcohols **11**, **13**, **14**, and **16** with donor **4** or **7**

Entry	Donor	Alcohol	Method[a]	Product	Yield [%]	Anomeric ratio (α/β)
23	**4**	**11**	A	**30**	93	61:39
24	**4**	**11**	B	**30**	92	56:44
25	**4**	**11**	C	**30**	80	36:64
26	**4**	**13**	A	**31**	95	60:40
27	**7**	**13**	D	**31**	71	77:23
28	**4**	**14**	E	**32**	27[b]	64:36
29	**4**	**14**	A	**32**	81[c]	72:28
30	**4**	**14**	F	**32**	96	83:17
31	**4**	**16**	A	**33**	93	44:56
32	**4**	**16**	C	**33**	88	27:73
33	**7**	**16**	D	**33**	76	73:27

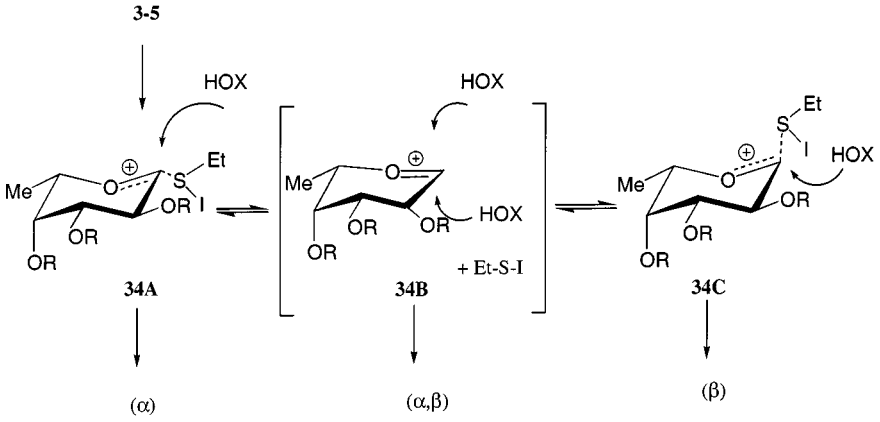
[a] A (*GP 4 A*): NIS/TfOH, DCM, 0 °C, 1 h; B (*GP 4 B*): NIS/TfOH, Et_2O/DCM, 0 °C, 1 h; C (*GP 4 C*): NIS/TfOH, CH_3CN/DCM, 0 °C, 1 h; D (*GP 5*): TBAB, DCM/DMF, room temp., 2 days; E (cf. *GP 4 A*): NIS/TfOH, DCM, −30°C, 1 h; F (cf. *GP 4 A*): NIS/TfOH, DCM, room temp., 1 h. – [b] The total isolated material consisted of 27% fucosidation products (**32**) and 34% starting donor (**4**). – [c] The total isolated material consisted of 81% fucosidation products (**32**) and 10% starting donor (**4**).

4-*O*-acyl participation,[17,35] or through-bond interactions.[2] Although fucosylation of *glycosyl* acceptors is controlled both by steric effects – i.e., the spatial orientation (axial or equatorial) of both the hydroxyl group to be glycosylated and the blocking groups around this hydroxyl group[36] – and by electronic effects, it might be expected that electronic effects exerted by protecting groups on the fucosyl donor would predominantly determine the stereochemical outcome of reactions with the reactive and flexible linear alcohols **11**, **13**, **14**, and **16**. However, as shown later, fucosyl donor electronic effects could not explain the observed stereoselectivity here.

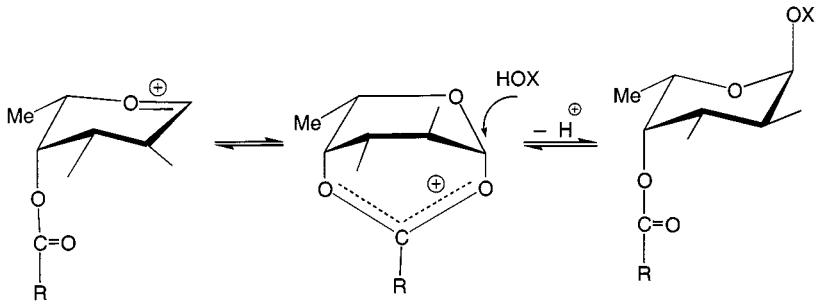
The mechanism of reactions promoted by NIS/TfOH (cat.) is shown in Scheme 4. The β- and α-iodosulfonium-oxocarbonium intermediates – **34A** and **34C**, respectively – will glycosylate by means of an S_N2-type bimolecular mechanism, whereas reaction of fucosyloxocarbonium ion **34B** will proceed by an S_N1-type mechanism, resulting in loss of steric control. In principle, it may be expected that reactions in solvents with a low dielectric constant (such as dichloromethane: $\varepsilon = 8.9$) should proceed with a high degree of α-selectivity by means of an S_N2 reaction of **34A**. Moreover, the tight β-ion pair **34A** will react more rapidly, since it is thermodynamically less stable than the corresponding tight α-ion pair (**34C**), and therefore energetically closer to its transition state.[28,37,38] Ethyl ether ($\varepsilon = 4.3$) can compete effectively with the alcohol, thanks to its high donicity,[34] thus providing time for anomerization of **34A**, whereas in acetonitrile (high dielectric constant: $\varepsilon = 38$) ion separation (→ **34B**), or anomerization into **34C** is favored.[37] Indeed, couplings conducted in dichloromethane/acetonitrile, of **3** with **11** (Table 2; entry 17) and of **4** with **11** and **16** (Table 3; entries 25 and 32, respectively), showed high selectivity for β-glycosides. However, besides anomerization of **34A** into **34C** being favored under these conditions, this high selectivity towards β-glycosides can also be explained by the occurrence of the "nitrile effect".[39,40]

The slight α-selectivity of couplings conducted in dichloromethane might indicate that the coupling reactions proceed predominantly via intermediates **34A** and **34B**. The increased selectivity at higher temperatures for α-fucosylation in dichloromethane (entries 28–30) can be explained by the higher reactivity of **34A** at higher temperatures.

As mentioned earlier, participation of the 4-*O*-acyl group is sometimes presumed to explain high α-stereoselectivities in glycosylation reactions, by means of an intermediate (1–4)-cyclic acyloxonium ion, as depicted in Scheme 5.[35] However, it is evident that 4-*O*-acyl participation is not an appropriate explanation in our study, since comparable stereochemical results were obtained for treatment of **3** and **4** in dichloromethane.



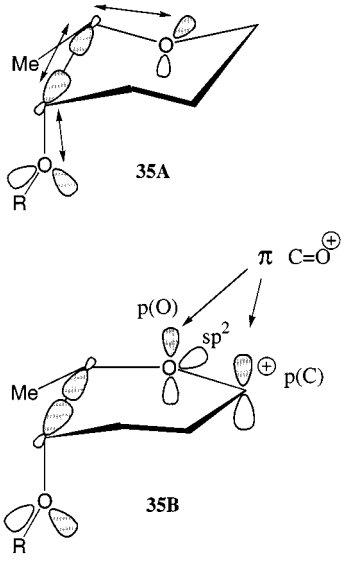
Scheme 4



Scheme 5

Furthermore, polar or resonance effects do not provide a suitable explanation for the fucosylations described here. In principle, inductive effects from the electron-withdrawing 4-*O*-acetyl group on **3** would destabilize the positive charge on **34B**, whereas **34B** would be stabilized by the presence of the electron-donating 4-*O*-benzyl group on the ring system of **4**. However, as shown, the α-selectivity is not lower in fucosidation reactions with **4** (cf. Table 2 and Table 3).

Alternatively, the occurrence of through-bond orbital interactions is sometimes used to explain why 4-*O equatorial* electron-withdrawing groups on glycopyranosyl donors suppress the formation of the intermediate oxocarbonium ion (cf. **34B**), and thus favor an S_N2 type of glycosylation reaction.[2,41] In through-bond models,[42–44] the lone pair of a particular atom lies *all-trans* to the σ-bond, or else a succession of such *trans* bridges is available to carry the interaction from one orbital to the other. According to the literature, the sometimes high, or exclusive, formation of 1,2-*cis* linked products in fucosylations of glycosyl acceptors with thioalkyl donors (cf. refs.[2,4]) can be explained by through-bond interactions, as the fucopyranosyl ring (**35A**, Scheme 6) comprises a system that is capable of relaying through-bond electronic interactions between the lone pairs (O-4 and the ring oxygen) and the σ-component (C-4–C-5) of **35A**. However, the results for the iodonium-assisted fucosylations of acceptors **11**, **13**, **14**, and **16** (Table 2 and 3) indicate that through-bond orbital interactions probably play only a minor role in favoring fucosylations via **34A**. Thus, steric influences both of the donor and of the acceptor might be predominantly responsible for the observed product composition. For example, the high degree of formation of 1,2-*cis* linked products involving **35B** can be explained by the fact that an attack of bulky *glycosyl* acceptors on the β-side of **35B** is sterically hindered by the O-3, O-4, and the methyl substituent on the donor. In contrast, the reactive and flexible linear alcohol acceptors have more conformational freedom, and thus might exert less steric hindrance by **35B**. This might explain the poor stereoselectivities resulting from treatment of **3** and **4** with the spacer alcohols **11**, **13**, **14**, and **16**.



Scheme 6

Usage of Donors 6 and 7 in TBAB-Catalyzed Fucosidations

From Table 2 and Table 3 it is clear that best α-selectivities were obtained with donors **6** and **7** under in situ anomerization conditions, using TBAB. No significant influence of the spacer length could be discerned. Reactions with **6** showed a slightly higher α-selectivity than coupling with **7**. It is tempting to suggest here a slight resonance effect of the 4-*O*-benzyl group on **7**, causing stabilization of the fucosyloxocarbonium ion (cf. **34B** or **35B**). Couplings via **34B** can thus compete with the S_N2 reaction between the in situ generated β-bromide analog of **7** (cf. β-bromide analog of **34C**) and the acceptor alcohol.

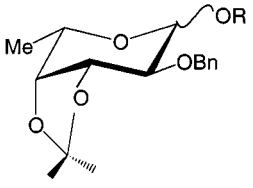
Fucosylations of Alcohols 11 and 13−16 with 5 and 8

Because of constraints imposed by the 3,4-acetonide function in **5** and **8**, the carbohydrate rings exist as distorted $^1C_4$ chairs.[45] In Table 4, it is indicated that for the NIS/TfOH-catalyzed reaction of **5** with the alcohols, giving products **36−40** (Scheme 7), almost equal amounts of α- and β-anomers were produced (entries 34, 35, 37, 39, 40), except for the coupling with **16**. It is reasonable to suggest that the conformational differences in the chair result in a better stabilization of the fucosyloxycarbonium ion (**34B** or **35B**). For TBAB-catalyzed couplings with **8**, α/β-ratios obtained were in the same range as those found for corresponding couplings using **6** and **7** (entries 36, 38, 41).

Table 4. Glycosylation of alcohols **11**, **13−16** with donor **5** or **8**

Entry	Donor	Alcohol	Method[a]	Product	Yield[b] [%]	Anomeric ratio (α/β)
34	**5**	**11**	A	**36**	77	51:49
35	**5**	**13**	A	**37**	63	51:49
36	**8**	**13**	B	**37**	57	87:13
37	**5**	**14**	A	**38**	68	46:54
38	**8**	**14**	B	**38**	48	89:11
39	**5**	**15**	A	**39**	74	48:52
40	**5**	**16**	A	**40**	56	31:69
41	**8**	**16**	B	**40**	74	88:12

[a] A (*GP 4 A*): NIS/TfOH, DCM, 0 °C, 1 h; B (*GP 5*): TBAB, DCM/DMF, room temp., 2 days.



	R
36	$CH_2CH{=}CH_2$
37	$CH_2CH_2CH_2Br$
38	$CH_2CH_2CH_2N_3$
39	$CH_2(CH_2)_3CH_2N_3$
40	$CH_2(CH_2)_8CH_3$

Scheme 7

Experimental Section

General: Solvents were purified by standard procedures; alcohols **9−13** and **16** were commercially available. − Thin layer chromatography (TLC): Kieselgel 60 F_{254} (Merck); compounds were developed by charring with ethanolic 10% H_2SO_4. − Column chromatography: Kieselgel 60 F_{254} (Merck). − Eluent systems: System A (dichloromethane/acetone, 9:1), System B (dichloromethane/acetone, 95:5), System C (dichloromethane/acetone, 97:3), System D (dichloromethane → dichloromethane/acetone, 95:5), System E (dichloromethane → dichloromethane/acetone, 97:3), System F (dichloromethane → dichloromethane/ethyl acetate, 95:5), System G (dichloromethane/methanol, 9:1), System H (dichloromethane/methanol, 95:5), System I (dichloromethane → dichloromethane/methanol, 9:1), System J (dichloromethane → dichloromethane/methanol, 95:5). − Optical rotations: Perkin−Elmer 241 polarimeter; 10 cm 1 mL cell at 20°C. − ^{1}H NMR: Bruker AC 300 (300 MHz) instrument; internal standard tetramethylsilane (δ 0) for solutions in $CDCl_3$. The α/β ratio of the glycosylation products was determined by integration of typical proton signals. − FABMS: JEOL JMS SX/SX 102A four-sector mass spectrometer; 10 kV accelerating voltage; JEOL MS-FAB 10 D FAB gun; 10 mA emission current; beam: 6 keV Xe atoms.

Ethyl 3,4-Di-*O*-acetyl-2-*O*-benzyl-1-thio-β-L-fucopyranoside (3): To a solution of ethyl 2-*O*-benzyl-1-thio-β-L-fucopyranoside[2] (170 mg, 0.57 mmol) in pyridine (2.6 mL) was added acetic anhydride (2.6 mL). After stirring for 16 h at room temperature, toluene (40 mL) was added and the solution was concentrated. The remaining oil was co-concentrated with toluene (2 × 25 mL), ethanol (2 × 25 mL), and dichloromethane (2 × 25 mL). Column chromatography (System E) of the residue yielded **3**, isolated as a colorless syrup (200 mg, 92%). − TLC (System A): R_f = 0.77. − $[\alpha]_D$ = −21° (*c* = 1, $CHCl_3$). − ^{1}H NMR: δ = 1.19 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.33 (t, 3 H, SCH_2CH_3), 1.93 and 2.15 (2 s, each 3 H, $COCH_3$), 2.74−2.82 (m, 2 H, SCH_2CH_3), 3.63 (t, $J_{1,2/2,3}$ = 9.7 Hz, 1 H, 2-H), 3.77 (m, $J_{4,5} < 1.0$ Hz, 1 H, 5-H), 4.52 (d, 1 H, 1-H), 4.60 and 4.87 (2 d, each 1 H, $C_6H_5CH_2$), 5.01 (dd, $J_{3,4}$ = 3.4 Hz, 1 H, 3-H), 5.25 (dd, 1 H, 4-H), 7.25−7.34 (m, 10 H, 2 $C_6H_5CH_2$). − $C_{19}H_{26}O_6S$ (382.4): MS (FAB$^+$) *m/z* = 405.1 [M + Na]$^+$.

Fischer Glycosylation with L-Fucose and Dowex-50 (H^+) Resin as Catalyst (GP 1): To L-fucose (**1**) was added the alcohol (**9**, **11**, **13**, **14**, and **16**; 10 equiv.) and Dowex-50 (H^+) resin. After stirring for 12 h at 75 °C, the mixture was filtered, and immediately purified by column chromatography to give the corresponding alkyl fucopyranoside. All products were obtained as a white glass unless otherwise stated.

Fischer Glycosylation of L-Fucose with Acetyl Chloride as Catalyst (GP 2): To L-fucose (**1**) was added the alcohol (**10**, **11**, **13**, **14**, and **16**; 10 equiv.), and, after cooling to 0 °C, acetyl chloride (2 equiv.) was added dropwise. The mixture was stirred for 3 h at 65 °C, then neutralized with solid $NaHCO_3$, and concentrated. Column chromatography of the residue yielded the corresponding alkyl fucopyranoside. All products were obtained as a white glass, unless otherwise stated.

Thioglycoside Activation with NIS/TfOH (cat.) (GP 4, A, B, C): The donors **3**, ethyl 3-*O*-acetyl-2,4-di-*O*-benzyl-1-thio-β-L-fucopyranoside[14] (**4**) and ethyl 2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside[2] (**5**) were dried for 12 h in the presence of 4 Å molecular sieves. After addition of the alcohol (**11**, **13**−**16**; 6 equiv.) to the donor, the mixture was stirred for 1 h under Ar in (A) dry dichloromethane; (B) dry dichloromethane/diethyl ether, 5:1; or (C) dry dichloromethane/acetonitrile, 5:1. Then, either at 0 °C or at room temperature, *N*-iodosuccinimide (NIS, 2.5 equiv.) and trifluoromethanesulfonic acid (TfOH) (0.3 equiv.) were added, and the mixture was stirred for 1 h at room temperature. Afterwards, the solution was neutralized with pyridine, filtered, diluted with ethyl acetate (80 mL), washed with aq. 5% $NaHSO_3$ (same vol., 3×), aq. 10% $NaHCO_3$ (same vol., 2×), and aq. 5% NaCl (half vol., 1×), dried ($MgSO_4$), filtered, and concentrated. Column chromatography of the residue gave the corresponding alkyl fucopyranoside. All products were isolated as colorless syrups, unless otherwise stated.

Fucopyranosyl Bromide Activation by Tetrabutylammonium Bromide (GP 5): A solution of donor **3**, **4**, or **5** in dry dichloromethane (0.4 mL) was cooled to 0 °C and treated for 20 min with bromine (2 equiv.). Then, cyclohexene was added dropwise until the orange color disappeared. A freshly prepared solution of the alcohol (**10**, **11**, **13**, **14**, and **16**; 6 equiv.), tetrabutylammonium bromide (Bu_4NBr, 1 equiv.) and 4 Å molecular sieves in dichloromethane/dimethylformamide (5:3), stirred for 1 h under Ar, was added to the freshly prepared fucopyranosyl bromide **6**, **7**, or **8**, and the mixture was stirred for 2 days at room temperature. Subsequently, the mixture was neutralized with pyridine, filtered over Celite, diluted with ethyl acetate (80 mL), washed with aq. 5% $NaHSO_3$ (same vol., 3 ×), aq. 10% $NaHCO_3$ (same vol., 2 ×), and aq. 5% NaCl (same vol., 1 ×), dried ($MgSO_4$), filtered, and concentrated. Column chromatography of the residue gave the corresponding alkyl fucopyranoside. All products were obtained as colorless syrups, unless otherwise stated.

Ethyl α/β-L-Fucopyranoside (19): *GP 2*, **1** (100 mg, 0.61 mmol), **9** (0.24 mL), acetyl chloride (0.11 mL). Purification (System I) gave **19** (76 mg, 65%); **19α** 64%, **19β** 36%. − TLC (System C): R_f = 0.24. − ^{1}H NMR ($CDCl_3$/CD_3OD, 1:1): **19α** δ = 1.19−1.32 (m, 6 H, 6,6,6-H and OCH_2CH_3), 3.53 and 3.76 (2 m, 2 H, OCH_2CH_3), 4.85 (d, $J_{1,2}$ < 1.0 Hz, 1 H, 1-H); **19β** δ = 1.19−1.32 (m, 6 H, 6,6,6-H and OCH_2CH_3), 4.21 (d, $J_{1,2}$ = 7.0 Hz, 1 H, 1-H). − $C_8H_{16}O_5$ (192.2): MS (FAB$^+$) *m*/*z* = 193.1 [M + H]$^+$.

Propyl α/β-L-Fucopyranoside (20): *GP 2*, **1** (100 mg, 0.61 mmol), **10** (0.46 mL), acetyl chloride (0.11 mL). Purification (System I) gave **20** (84 mg, 67%); **20α** 75%, **20β** 25%. − TLC (System C): R_f = 0.30. − ^{1}H NMR ($CDCl_3$/CD_3OD, 1:1): **20α** δ = 0.93 (t, 3 H, $OCH_2CH_2CH_3$), 1.24 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.62 (m, 2 H, $OCH_2CH_2CH_3$), 3.41 and 3.63 (2 m, 2 H, $OCH_2CH_2CH_3$), 4.82 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H); **20β** δ = 0.93 (t, 3 H, $OCH_2CH_2CH_3$), 1.31 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.64 (m, 2 H, $OCH_2CH_2CH_3$), 4.19 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H). − $C_9H_{18}O_5$ (206.2): MS (FAB$^+$) *m*/*z* = 207.1 [M + H]$^+$.

Allyl α/β-L-Fucopyranoside (21): *(i)*: *GP 1*, **1** (50 mg, 0.3 mmol), **11** (0.21 mL), Dowex-50 (H$^+$) resin (70 mg). Purification (System I) gave **21** (39 mg, 64%); **21α** 70%, **21β** 30%. − *(ii)*: *GP 2*, **1** (50 mg, 0.3 mmol), **11** (0.21 mL), acetyl chloride (56 μL). Purification (System I) gave **21** (45 mg, 74%); **21α** 67%, **21β** 33%. − *(iii)*: To **1** (110 mg, 0.67 mmol) was added **11** (0.46 mL). The solution was cooled to 0 °C, and $FeCl_3$ (160 mg, 0.95 mmol) was added slowly. The mixture was stirred for 3 h at 55 °C, when TLC indicated the reaction was complete. The solution was neutralized with triethylamine, then purified by column chromatography (System J) to furnish **21** (100 mg, 73%); **21α** 72%, **21β** 28%. − TLC (dichloromethane/methanol, 3:1): R_f = 0.80. − ^{1}H NMR ($CDCl_3$/CD_3OD, 1:1): **21α** δ = 1.26 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 4.87 (d, $J_{1,2}$ = 3.1 Hz, 1 H, 1-H), 5.20 and 5.32 (2 m, 2 H, $OCH_2CH{=}CH_2$), 5.87−6.00 (m, 1 H, $OCH_2CH{=}CH_2$); **21β** δ = 1.31 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6,6,6-H), 4.28 (d, $J_{1,2}$ = 6.9 Hz, 1 H, 1-H), 5.25 and 5.37 (2 m, 2 H, $OCH_2CH{=}CH_2$), 5.90−6.05 (m, 1 H, $OCH_2CH{=}CH_2$). − $C_9H_{16}O_5$ (204.2): MS (FAB$^+$) *m*/*z* = 205.1 [M + H]$^+$.

3-Bromopropyl α/β-L-Fucopyranoside (22): *(i)*: *GP 1*, **1** (50 mg, 0.3 mmol), **13** (0.27 mL), Dowex-50 (H$^+$) resin (70 mg). Purification (System I) yielded **22** (33 mg, 38%); **22α** 64%, **22β** 36%. − *(ii)*: *GP 2*, **1** (100 mg, 0.61 mmol), **13** (0.54 mL), acetyl chloride (0.11 mL). Purification (System I) gave **22** (117 mg, 67%); **22α** 83%, **22β** 17%. − TLC (System C): R_f = 0.57. − ^{1}H NMR ($CDCl_3$/CD_3OD, 1:1): **22α** δ = 1.27 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6,6,6-H), 2.04−2.24 (m, 2 H, $OCH_2CH_2CH_2Br$), 4.86 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1-H); **22β** δ = 1.31 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6,6,6-H), 2.04−2.24 (m, 2 H, $OCH_2CH_2CH_2Br$), 4.22 (d, $J_{1,2}$ = 7.1 Hz, 1 H, 1-H). − $C_9H_{17}O_5Br$ (284.2): MS (FAB$^+$) *m*/*z* = 285.1 [M + H]$^+$.

3-Azidopropyl α/β-L-Fucopyranoside (23): *(i)*: *GP 1*, **1** (100 mg, 0.61 mmol), **14** (620 mg), Dowex-50 (H$^+$) resin (70 mg). Purification (System J) gave **23**, isolated as a colorless oil (47 mg, 31%); **23α** 60%, **23β** 40%. − *(ii)*: *GP 2*, **1** (100 mg, 0.61 mmol), **14** (620 mg), acetyl chloride (0.11 mL). Purification (System J) gave **23**, isolated as a colorless syrup (39 mg, 26%); **23α** 68%, **23β** 32%. − *(iii)*: To a solution of methyl α/β-L-fucopyranoside[21,22] (**2**) (140 mg, 0.79 mmol) in dry dimethylformamide (4 mL) were added **14** (800 mg) and *p*-toluenesulfonic acid (pH 3). The mixture was stirred for 5 days at 50 °C, filtered, and purified by column chromatography (System J), yielding **23**, isolated as a colorless oil (36 mg, 19%); **23α** 71%, **23β** 29%. − TLC (System C): R_f =0.29. − ^{1}H NMR ($CDCl_3$/CD_3OD, 1:1): **23α** δ = 1.27 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.87−1.95 (m, 2 H, $OCH_2CH_2CH_2N_3$), 3.39 (t, 2 H, $OCH_2CH_2CH_2N_3$), 4.85 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H); **23β** δ = 1.31 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6,6,6-H), 1.87−1.95 (m, 2 H, $OCH_2CH_2CH_2N_3$), 3.42 (t, 2 H, $OCH_2CH_2CH_2N_3$), 4.20 (d, $J_{1,2}$ = 7.4 Hz, 1 H, 1-H). − $C_9H_{17}O_5N_3$ (247.3): MS (FAB$^+$) *m*/*z* = 248.1 [M + H]$^+$.

Decyl α/β-L-Fucopyranoside (24): *(i)*: *GP 1*, **1** (100 mg, 0.61 mmol), **16** (1.16 mL), Dowex-50 (H$^+$) resin (70 mg). Purification (System J) yielded **24**, isolated as a colorless oil (89 mg, 48%); **24α** 71%, **24β** 29%. − *(ii)*: *GP 2*, **1** (50 mg, 0.3 mmol), **16** (0.59 mL), acetyl chloride (56 μL). Purification (System J) yielded **24**, isolated as a colorless oil (68 mg, 75%); **24α** 74%, **24β** 26%. − TLC (System C): R_f = 0.41. − ^{1}H NMR: **24α** δ = 0.88 [t, 3 H, $OCH_2(CH_2)_8CH_3$], 1.27 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6,6,6-H), 1.26−1.37 and 1.57−1.64 [2 m, 16 H, $OCH_2(CH_2)_8CH_3$], 3.44 and 3.67 [2 m, each 1 H, $OCH_2(CH_2)_8CH_3$], 4.84 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H); **24β** δ = 0.88 [t, 3 H, $OCH_2(CH_2)_8CH_3$], 1.31 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.26−1.37 and 1.57−1.64 [2 m, 16 H, $OCH_2(CH_2)_8CH_3$], 4.19 (d, $J_{1,2}$ = 7.4 Hz, 1 H, 1-H). − $C_{16}H_{32}O_5$ (304.4): MS (FAB$^+$) *m*/*z* = 305.2 [M + H]$^+$.

Propyl 3,4-Di-*O*-acetyl-2-*O*-benzyl-α/β-L-fucopyranoside (25): *GP 5*, **3** (22 mg, 58 μmol), bromine (5.9 μL). Then, residue (**6**), **10** (26 μL), Bu_4NBr (19 mg), molecular sieves (50 mg), solvent (0.4 mL). Purification (System B) gave **25** (19 mg, 87% overall); **25α** 77%, **25β** 23%. − TLC (System B): R_f = 0.76. − ^{1}H NMR: **25α** δ = 0.95 (t, 3 H, $OCH_2CH_2CH_3$), 1.11 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.59−1.68 (m, 2 H, $OCH_2CH_2CH_3$), 1.98 and 2.13 (2 s, each 3 H,

2 COCH_3), 3.37 and 3.59 (2 m, each 1 H, OCH_2CH$_2$CH$_3$), 3.83 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 10.1 Hz, 1 H, 2-H), 4.14 (m, $J_{4,5}$ = 1.3 Hz, 1 H, 5-H), 4.59 and 4.70 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.81 (d, 1 H, 1-H), 5.28 (dd, $J_{3,4}$ = 3.4 Hz, 1 H, 4-H), 5.33 (dd, 1 H, 3-H), 7.26−7.34 (m, 5 H, C$_6H_5$CH$_2$); **25β** δ = 0.97 (t, 3 H, OCH$_2$CH$_2$CH_3), 1.20 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6,6,6-H), 1.59−1.68 (m, 2 H, OCH$_2$CH_2CH$_3$), 1.95 and 2.13 (2 s, each 3 H, 2 COCH_3), 3.49 and 3.95 (2 m, each 1 H, OCH_2CH$_2$CH$_3$), 3.60 (dd, $J_{1,2}$ = 7.8, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 3.76 (m, $J_{4,5}$ = 1.1 Hz, 1 H, 5-H), 4.43 (d, 1 H, 1-H), 4.63 and 4.89 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.97 (dd, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 5.20 (dd, 1 H, 4-H), 7.26−7.34 (m, 5 H, C$_6H_5$CH$_2$). − C$_{20}$H$_{28}$O$_7$ (380.2): MS (FAB$^+$) *m/z* = 381.2 [M + H]$^+$, 403.2 [M + Na]$^+$.

Allyl 3,4-Di-*O*-acetyl-2-*O*-benzyl-α/β-L-fucopyranoside (26): *(i)*: *GP 4 A*, **3** (25 mg, 76 μmol), **11** (31 μL), molecular sieves (50 mg), solvent (1.2 mL), NIS (43 mg), TfOH (2 μL), T = 0 °C. Purification (System D) yielded **26** (26 mg, 90%); **26α** 62%, **26β** 38%. − *(ii)*: *GP 4 B*, **3** (28 mg, 85 μmol), **11** (35 μL), molecular sieves (50 mg), solvent (1.3 mL), NIS (48 mg), TfOH (2.2 μL), T = 0 °C. Purification (System D) furnished a mixture of starting donor and products (29 mg); **3** 35%, **26** 62% (**26α** 69%, **26β** 31%). − *(iii)*: *GP 4 C*, **3** (19 mg, 58 μmol), **11** (24 μL), molecular sieves (50 mg), solvent (0.9 mL), NIS (33 mg), TfOH (1.5 μL), T = 0 °C. Purification (System D) furnished **26** (21 mg, 96%); **26α** 22%, **26β** 78%.− *(iv)*: *GP 5*, **3** (24 mg, 73 μmol), bromine (7.4 μL). Then, residue (**6**), **11** (30 μL), Bu$_4$NBr (24 mg), molecular sieves (50 mg), solvent (0.5 mL). Purification (System D) gave **26** (23 mg, 85% overall); **26α** 87%, **26β** 13%. − TLC (System A): R_f = 0.81. − ^{1}H NMR: **26α** δ = 1.10 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.98 and 2.12 (2 s, each 3 H, 2 COCH_3), 3.84 (dd, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.60 and 4.67 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.88 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 5.21 and 5.33 (2 m, each 1 H, OCH$_2$CH=CH_2), 5.28 (dd, $J_{4,5}$ = 1.4 Hz, 1 H, 4-H), 5.35 (dd, $J_{3,4}$ = 3.4 Hz, 1 H, 3-H), 5.92 (m, 1 H, OCH$_2$CH=CH$_2$), 7.26−7.41 (m, 5 H, C$_6H_5$CH$_2$); **26β** δ = 1.20 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.94 and 2.12 (2 s, each 3 H, 2 COCH_3), 3.63 (dd, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.49 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H), 4.64 and 4.89 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.97 (dd, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 5.18 and 5.27 (2 m, each 1 H, OCH$_2$CH=CH_2), 5.32 (dd, $J_{4,5}$ = < 1 Hz, 1 H, 4-H), 5.93 (m, 1 H, OCH$_2$CH=CH$_2$), 7.26−7.41 (m, 5 H, C$_6H_5$CH$_2$). − C$_{20}$H$_{26}$O$_7$ (378.2): MS (FAB$^+$) *m/z* = 401.2 [M + Na]$^+$.

3-Bromopropyl 3,4-Di-*O*-acetyl-2-*O*-benzyl-α/β-L-fucopyranoside (27): *(i)*: *GP 4 A*, **3** (48 mg, 0.14 mmol), **13** (76 μL), molecular sieves (150 mg), solvent (2.5 mL), NIS (83 mg), TfOH (3.8 μL), T = 0 °C. Purification (System D) furnished **27** (59 mg, 92%); **27α** 70%, **27β** 30%. − *(ii)*: *GP 5*, **3** (25 mg, 76 μmol), bromine (7.7 μL). Then, residue (**6**), **13** (40 μL), Bu$_4$NBr (25 mg), molecular sieves (50 mg), solvent (0.4 mL). Purification (System C) yielded **27** (21 mg, 59% overall); **27α** 88%, **27β** 12%. − TLC (System B): R_f = 0.71. − ^{1}H NMR: **27α** δ = 1.12 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.95−2.16 (m, 2 H, OCH$_2$CH_2CH$_2$Br), 1.99 and 2.13 (2 s, each 3 H, 2 COCH_3), 3.47−3.88 (m, 4 H, OCH_2CH$_2$CH_2Br), 3.82 (dd, 1 H, 2-H), 4.14 (m, 1 H, 5-H), 4.60 and 4.69 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.83 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 5.27 (dd, $J_{4,5}$ = 1.5 Hz, 1 H, 4-H), 5.29 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 3.4 Hz, 1 H, 3-H), 7.26−7.33 (m, 5 H, C$_6H_5$CH$_2$); **27β** δ = 1.20 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.94 and 2.13 (2 s, each 3 H, 2 COCH_3), 4.44 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H), 4.62 and 4.84 (2 d, each 1 H, C$_6$H$_5$CH_2), 5.20 (dd, 1 H, 4-H), 7.26−7.33 (m, 5 H, C$_6H_5$CH$_2$). − C$_{20}$H$_{27}$O$_7$Br (458.2): MS (FAB$^+$) *m/z* = 459.1 [M + H]$^+$, 481.2 [M + Na]$^+$.

3-Azidopropyl 3,4-Di-*O*-acetyl-2-*O*-benzyl-α/β-L-fucopyranoside (28): *GP 5*, **3** (28 mg, 73 μmol), bromine (7.5 μL). Then, residue (**6**), **14** (44 mg), Bu$_4$NBr (28 mg), molecular sieves (50 mg), solvent (0.4 mL). Purification (System B) yielded **28** (17 mg, 54% overall); **28α** 88%, **28β** 12%. − TLC (System B): R_f = 0.67. − ^{1}H NMR: **28α** δ = 1.11 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.03−1.43 (m, 2 H, OCH$_2$CH_2CH$_2$N$_3$), 1.98 and 2.13 (2 s, each 3 H, 2 COCH_3), 3.83 (dd, $J_{2,3}$ = 10.1 Hz, 1 H, 2-H), 4.10 (m, 1 H, 5-H), 4.59 and 4.69 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.80 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 5.28 (dd, $J_{4,5}$ = 1.2 Hz, 1 H, 4-H), 5.30 (dd, $J_{3,4}$ = 3.6 Hz, 1 H, 3-H), 7.25−7.34 (m, 5 H, C$_6H_5$CH$_2$); **28β** δ = 1.20 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.03−1.43 (m, 2 H, OCH$_2$CH_2CH$_2$N$_3$), 1.94 and 2.14 (2 s, each 3 H, 2 COCH_3), 3.60 (dd, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 3.65 and 4.02 (2 m, each 1 H, OCH_2CH$_2$CH$_2$N$_3$), 4.42 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.63 and 4.83 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.97 (dd, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 5.20 (dd, $J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 7.25−7.34 (m, 5 H, C$_6H_5$CH$_2$). − C$_{20}$H$_{27}$N$_3$O$_7$ (421.4): MS (FAB$^+$) *m/z* = 422.2 [M + H]$^+$, 444.2 [M + Na]$^+$.

Decyl 3,4-Di-*O*-acetyl-2-*O*-benzyl-α/β-L-fucopyranoside (29): *(i)*: *GP 4 A*, **3** (70 mg, 0.2 mmol), **16** (0.23 mL), molecular sieves (150 mg), solvent (3.5 mL), NIS (121 mg), TfOH (5.5 μL), T = 0 °C. Purification (System D) yielded **29** (79 mg, 83%); **29α** 47%, **29β** 53%. − *(ii)*: *GP 5*, **3** (22 mg, 67 μmol), bromine (6.8 μL). Then, residue (**6**), **16** (75 μL), Bu$_4$NBr (22 mg), molecular sieves (50 mg), solvent (0.4 mL). Purification (System D) gave **29** (23 mg, 72% overall); **29α** 83%, **29β** 17%. − TLC (System A): R_f = 0.76. − ^{1}H NMR: **29α** δ = 0.88 [t, 3 H, OCH$_2$(CH$_2$)$_8$CH_3], 1.10 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.23−1.64 [m, 16 H, OCH$_2$(CH_2)$_8$CH$_3$], 1.97 and 2.12 (2 s, each 3 H, 2 COCH_3), 3.40 and 3.63 [2 m, each 1 H, OCH_2(CH$_2$)$_8$CH$_3$], 3.82 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.12 (m, $J_{4,5}$ = 1.3 Hz, 1 H, 5-H), 4.59 and 4.69 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.81 (d, 1 H, 1-H), 5.28 (dd, $J_{3,4}$ = 3.4 Hz, 1 H, 4-H), 5.32 (dd, 1 H, 3-H), 7.26−7.33 (m, 5 H, C$_6H_5$CH$_2$); **29β** δ = 0.87 [t, 3 H, OCH$_2$(CH$_2$)$_8$CH_3], 1.20 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.23−1.64 [m, 16 H, OCH$_2$(CH_2)$_8$CH$_3$], 1.94 and 2.12 (2 s, each 3 H, 2 COCH_3), 3.53 and 3.84 [2 m, each 1 H, OCH_2(CH$_2$)$_8$CH$_3$], 4.43 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.63 and 4.88 (2 d, each 1 H, C$_6$H$_5$CH_2), 4.96 (dd, $J_{2,.3}$ = 10.1, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 7.26−7.33 (m, 5 H, C$_6H_5$CH$_2$). − C$_{27}$H$_{42}$O$_7$ (478.3): MS (FAB$^+$) *m/z* = 501.3 [M + Na]$^+$.

Allyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-α/β-L-fucopyranoside (30): *(i)*: *GP 4 A*, **4** (38 mg, 88 μmol), **11** (37 μL), molecular sieves (75 mg), solvent (1.5 mL), NIS (50 mg), TfOH (2.3 μL), T = 0 °C. Purification (System D) yielded **30** (35 mg, 93%); **30α** 61%, **30β** 39%. − *(ii)*: *GP 4 B*, **4** (24 mg, 56 μmol), **11** (24 μL), molecular sieves (50 mg), solvent (1 mL), NIS (32 mg), TfOH (1.5 μL), T = 0 °C. Purification (System D) yielded **30** (22 mg, 92%); **30α** 56%, **30β** 44%. − *(ii)*: *GP 4 C*, **4** (25 mg, 58 μmol), **11** (25 μL), molecular sieves (50 mg), solvent (1 mL), NIS (33 mg), TfOH (1.6 μL), T = 0 °C. Purification (System D) yielded **30** (19 mg, 80%); **30α** 36%, **30β** 64%.− TLC (System B): R_f = 0.82. − ^{1}H NMR: **30α** δ = 1.15 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.98 (s, 3 H, COCH_3), 3.79 (dd, $J_{3,4}$ = 3.1, $J_{4,5}$ = 1.2 Hz, 1 H, 4-H), 4.02 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.59 and 4.65, 4.62 and 4.68 (4 d, each 1 H, 2 C$_6$H$_5$CH_2), 4.87 (d, 1 H, 1-H), 5.27 (dd, 1 H, 3-H), 5.85−5.98 (m, 1 H, OCH$_2$CH=CH$_2$), 7.25−7.34 (m, 10 H, 2 C$_6H_5$CH$_2$); **30β** δ = 1.23 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.92 (s, 3 H, COCH_3), 3.60 (m, 1 H, 5-H), 3.64 (dd, $J_{3,4}$ = 3.2, $J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 3.78 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 4.44 (d, 1 H, 1-H), 4.55 and 4.90, 4.62 and 4.68 (4 d, each 1 H, 2 C$_6$H$_5$CH_2), 4.87 (d, 1 H, 3-H), 5.85−5.98 (m, 1 H, OCH$_2$CH=CH$_2$), 7.25−7.34 (m, 10 H, 2 C$_6H_5$CH$_2$). − C$_{25}$H$_{30}$O$_6$ (426.3): MS (FAB$^+$) *m/z* = 449.1 [M + Na]$^+$.

3-Bromopropyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-α/β-L-fucopyranoside (31): *(i)*: *GP 4 A*, **4** (32 mg, 74 μmol), **13** (40 μL), molecular sieves

(75 mg), solvent (1.3 mL), NIS (42 mg), TfOH (1.9 μL), T = 0 °C. Purification (System E) yielded **31** (36 mg, 95%); **31α** 60%, **31β** 40%. − *(ii)*: *GP 5*, **4** (30 mg, 69 μmol), bromine (7 μL). Then, residue (**7**), **13** (37 μL), Bu_4NBr (23 mg), molecular sieves (50 mg), solvent (0.3 mL). Purification (System E) furnished **31** (25 mg, 71% overall); **31α** 77%, **31β** 23%. − TLC (System B): R_f = 0.79. − ^{1}H NMR: **31α** δ = 1.16 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.98 (s, 3 H, $COCH_3$), 2.06−2.26 (m, 2 H, $OCH_2CH_2CH_2Br$), 3.78 (dd, $J_{3,4}$ = 3.5, $J_{4,5}$ = 1.1 Hz, 1 H, 4-H), 4.01 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.59 and 4.65, 4.61 and 4.68 (4 d, each 1 H, 2 $C_6H_5CH_2$), 4.82 (d, 1 H, 1-H), 5.21 (dd, 1 H, 3-H), 7.25−7.35 (m, 10 H, 2 $C_6H_5CH_2$); **31β** δ = 1.22 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6,6,6-H), 1.91 (s, 3 H, $COCH_3$), 2.06−2.26 (m, 2 H, $OCH_2CH_2CH_2Br$), 3.50 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 3.60 (m, 1 H, 5-H), 3.66 (dd, $J_{3,4}$ = 3.2, $J_{4,5}$ = < 1.0 Hz, 1 H, 4-H), 4.39 (d, 1 H, 1-H), 4.56 and 4.66, 4.64 and 4.85 (4 d, each 1 H, 2 $C_6H_5CH_2$), 5.21 (dd, 1 H, 3-H), 7.25−7.35 (m, 10 H, 2 $C_6H_5CH_2$). − $C_{25}H_{31}O_6Br$ (506.3): MS (FAB$^+$) m/z = 507.0 [M + H]$^+$, 529.3 [M + Na]$^+$.

3-Azidopropyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-α/β-L-fucopyranoside (32): *(i)*: *GP 4 A*, **4** (23 mg, 53 μmol), **14** (32 mg), molecular sieves (50 mg), solvent (1 mL), NIS (30 mg), TfOH (1.4 μL), T = −30 °C. Purification (System D) yielded a mixture of starting donor and products (15 mg); **4** 34%, **32** 27% (**32α** 64%, **32β** 36%). − *(ii)*: *GP 4 A*, **4** (21 mg, 48 μmol), **14** (30 mg), molecular sieves (50 mg), solvent (0.9 mL), NIS (28 mg), TfOH (1.2 μL), T = 0 °C. Purification (System D) yielded a mixture of starting donor and products (20 mg); **4** 10%, **32** 81% (**32α** 72%, **32β** 28%). − *(iii)*: *GP 4 A*, **4** (27 mg, 62 μmol), **14** (38 mg), molecular sieves (50 mg), solvent (1.2 mL), NIS (35 mg), TfOH (1.6 μL), T = room temperature. Purification (System D) yielded **32** (28 mg, 96%); **32α** 83%, **32β** 17%. − TLC (System B): R_f = 0.62. − ^{1}H NMR: **32α** δ = 1.16 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.98 (s, 3 H, $COCH_3$), 1.84−1.92 (m, 2 H, $OCH_2CH_2CH_2N_3$), 3.42 (t, 2 H, $OCH_2CH_2CH_2N_3$), 3.79 (dd, $J_{3,4}$ = 3.1, $J_{4,5}$ = 1.2 Hz, 1 H, 4-H), 4.01 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.56 and 4.65, 4.61 and 4.68 (4 d, each 1 H, 2 $C_6H_5CH_2$), 4.79 (d, 1 H, 1-H), 5.21 (dd, 1 H, 3-H), 7.25−7.35 (m, 10 H, 2 $C_6H_5CH_2$); **32β** δ = 1.22 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.91 (s, 3 H, $COCH_3$), 1.84−1.92 (m, 2 H, $OCH_2CH_2CH_2N_3$), 3.40 (t, 2 H, $OCH_2CH_2CH_2N_3$), 3.42 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 3.66 (dd, $J_{3,4}$ = 3.2, $J_{4,5}$ = < 1.0 Hz, 1 H, 4-H), 4.37 (d, 1 H, 1-H), 4.56 and 4.65, 4.59 and 4.84 (4 d, each 1 H, 2 $C_6H_5CH_2$), 4.86 (dd, 1 H, 3-H), 7.25−7.35 (m, 10 H, 2 $C_6H_5CH_2$). − $C_{25}H_{31}O_6N_3$ (469.4): MS (FAB$^+$) m/z = 492.1 [M + Na]$^+$.

Decyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-α/β-L-fucopyranoside (33): *(i)*: *GP 4 A*, **4** (25 mg, 58 μmol), **16** (66 μL), molecular sieves (50 mg), solvent (1 mL), NIS (33 mg), TfOH (1.5 μL), T = 0 °C. Purification (System C) furnished **33** (28 mg, 93%); **33α** 44%, **33β** 56%. − *(ii)*: *GP 4 C*, **4** (25 mg, 58 μmol), **16** (66 μL), molecular sieves (50 mg), solvent (1 mL), NIS (33 mg), TfOH (1.5 μL), T = 0 °C. Purification (System C) gave **33** (27 mg, 88%); **33α** 27%, **33β** 73%.− *(iii)*: *GP 5*, **4** (30 mg, 70 μmol), bromine (7.1 μL). Then, residue (**7**), **16** (80 μL), Bu_4NBr (23 mg), molecular sieves (50 mg), solvent (0.3 mL). Purification (System C) furnished **33** (28 mg, 76% overall); **33α** 73%, **33β** 27%. − TLC (System B): R_f = 0.91. − ^{1}H NMR: **33α** δ = 0.88 [t, 3 H, $OCH_2(CH_2)_8CH_3$], 1.14 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.23−1.66 [m, 16 H, $OCH_2(CH_2)_8CH_3$], 1.97 (s, 3 H, $COCH_3$), 3.39 and 3.59 [2 m, each 1 H, $OCH_2(CH_2)_8CH_3$], 3.80 (dd, $J_{3,4}$ = 3.1, $J_{4,5}$ = < 1.0 Hz, 1 H, 4-H), 4.00 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.58 and 4.65, 4.61 and 4.69 (4 d, each 1 H, 2 $C_6H_5CH_2$), 4.80 (d, 1 H, 1-H), 5.23 (dd, 1 H, 3-H), 7.25−7.35 (m, 10 H, 2 $C_6H_5CH_2$); **33β** δ = 0.87 [t, 3 H, $OCH_2(CH_2)_8CH_3$], 1.22 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.23−1.66 [2 m, 16 H, $OCH_2(CH_2)_8CH_3$], 1.91 (s, 3 H, $COCH_3$), 3.48 and 3.94 [2 m, each 1 H, $OCH_2(CH_2)_8CH_3$], 3.59 (m, 1 H, 5-H), 3.65 (d, 1 H, 4-H), 3.74 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 4.37 (d, 1 H, 1-H), 4.56 and 4.89, 4.58 and 4.65 (4 d, each 1 H, 2 $C_6H_5CH_2$), 4.86 (dd, $J_{3,4}$ = 3.2 Hz, 1 H, 3-H), 7.25−7.35 (m, 10 H, 2 $C_6H_5CH_2$). − $C_{32}H_{46}O_6$ (526.3): MS (FAB$^+$) m/z = 549.2 [M + Na]$^+$.

Allyl 2-*O*-Benzyl-3,4-*O*-isopropylidene-α/β-L-fucopyranoside (36): *GP 4 A*, **5** (38 mg, 0.11 mmol), **11** (46 μL), molecular sieves (100 mg), solvent (2 mL), NIS (62 mg), TfOH (2.9 μL), T = 0 °C. Purification (System C; 0.1% TEA) gave **36** (28 mg, 77%); **36α** 51%, **36β** 49%. − TLC (System A): R_f = 0.82 (**36α**) and 0.87 (**36β**). − ^{1}H NMR: **36α** δ = 1.31 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 1.33 and 1.40 [2 s, 6 H, $C(CH_3)_2$], 3.52 (dd, $J_{2,3}$ = 7.9 Hz, 1 H, 2-H), 3.86 (m, 1 H, 5-H), 4.04 (dd, $J_{4,5}$ = 2.7 Hz, 1 H, 4-H), 4.34 (dd, $J_{3,4}$ = 5.4 Hz, 1 H, 3-H), 4.79 and 4.86 (2 d, each 1 H, $C_6H_5CH_2$), 4.79 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 5.19 and 5.32 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.86−6.02 (m, 1 H, $OCH_2CH{=}CH_2$), 7.34 (m, 5 H, $C_6H_5CH_2$); **36β** δ = 1.34 and 1.40 [2 s, 6 H, $C(CH_3)_2$], 1.39 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 3.40 (dd, $J_{2,3}$ = 7.1 Hz, 1 H, 2-H), 3.80 (m, 1 H, 5-H), 3.97 (dd, $J_{4,5}$ = 2.1 Hz, 1 H, 4-H), 4.12 (dd, $J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.32 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 4.70 and 4.79 (2 d, each 1 H, $C_6H_5CH_2$), 5.21 and 5.34 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.86−6.02 (m, 1 H, $OCH_2CH{=}CH_2$), 7.34 (m, 5 H, $C_6H_5CH_2$). − $C_{19}H_{26}O_5$ (334.2): MS (FAB$^+$) m/z = 357.1 [M + Na]$^+$.

3-Bromopropyl 2-*O*-Benzyl-3,4-*O*-isopropylidene-α/β-L-fucopyranoside (37): *(i)*: *GP 4 A*, **5** (43 mg, 0.12 mmol), **13** (65 μL), molecular sieves (150 mg), solvent (2.2 mL), NIS (70 mg), TfOH (3.3 μL), T = 0 °C. Purification (System C; 0.1% TEA) gave **37** (30 mg, 63%); **37α** 51%, **37β** 49%. − *(ii)*: *GP 5*, **5** (56 mg, 0.16 mmol), bromine (16.2 μL). Then, residue (**8**), **13** (85 μL), Bu_4NBr (53 mg), molecular sieves (100 mg), solvent (0.7 mL). Purification (System C, 0.1% TEA) yielded **37** (36 mg, 57% overall); **37α** 87%, **37β** 13%. − TLC (System B): R_f = 0.75. − ^{1}H NMR: **37α** δ = 1.32 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 1.35 and 1.39 [2 s, each 3 H, $C(CH_3)_2$], 2.01−2.25 (m, 2 H, $OCH_2CH_2CH_2Br$), 3.51 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 7.9 Hz, 1 H, 2-H), 3.52 (t, 2 H, $OCH_2CH_2CH_2Br$), 3.48 and 3.85 (2 m, each 1 H, $OCH_2CH_2CH_2Br$), 4.04 (dd, $J_{3,4}$ = 5.4, $J_{4,5}$ = 2.6 Hz, 1 H, 4-H), 4.13 (m, 1 H, 5-H), 4.29 (dd, 1 H, 3-H), 4.68 and 4.79 (2 d, each 1 H, $C_6H_5CH_2$), 4.74 (d, 1 H, 1-H), 7.24−7.38 (m, 5 H, $C_6H_5CH_2$); **37β** δ = 1.35 and 1.43 [2 s, each 3 H, $C(CH_3)_2$], 1.39 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 2.01−2.25 (m, 2 H, $OCH_2CH_2CH_2Br$), 3.37 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 7.0 Hz, 1 H, H-2), 3.54 (t, 2 H, $OCH_2CH_2CH_2Br$), 3.68 and 4.00 (2 m, each 1 H, $OCH_2CH_2CH_2Br$), 3.83 (m, $J_{4,5}$ = 2.2 Hz, 1 H, 5-H), 3.98 (dd, $J_{3,4}$ = 5.5 Hz, 1 H, 4-H), 4.13 (dd, 1 H, 3-H), 4.28 (d, 1 H, 1-H), 4.78 and 4.82 (2 d, each 1 H, $C_6H_5CH_2$), 7.24−7.38 (m, 5 H, $C_6H_5CH_2$). − $C_{19}H_{27}O_5Br$ (414.2): MS (FAB$^+$) m/z = 415.0 [M + H]$^+$.

3-Azidopropyl 2-*O*-Benzyl-3,4-*O*-isopropylidene-α/β-L-fucopyranoside (38): *(i)*: *GP 4 A*, **5** (47 mg, 0.13 mmol), **14** (79 mg), molecular sieves (150 mg), solvent (2.5 mL), NIS (76 mg), TfOH (3.6 μL), T = 0 °C. Purification (System E, 0.1% TEA) yielded **38** (32 mg, 68%); **38α** 46%, **38β** 54%. − *(ii)*: *GP 5*, **5** (25 mg, 69 μmol), bromine (8.6 μL). Then, residue (**8**), **14** (42 mg), Bu_4NBr (28 mg), molecular sieves (75 mg), solvent (0.4 mL). Purification (System E, 0.1% TEA) gave **38** (12 mg, 48% overall); **38α** 89%, **38β** 11%. − TLC (System A): R_f = 0.67 (**38α**) and 0.68 (**38β**). − ^{1}H NMR: **38α** δ = 1.32 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 1.34 and 1.39 [2 s, each 3 H, $C(CH_3)_2$], 1.80−1.95 (m, 2 H, $OCH_2CH_2CH_2N_3$), 3.40 (t, 2 H, $OCH_2CH_2CH_2N_3$), 3.52 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 7.8 Hz, 1 H, 2-

H), 4.04 (dd, $J_{3,4}$ = 5.5, $J_{4,5}$ = 2.4 Hz, 1 H, 4-H), 4.09 (m, 1 H, 5-H), 4.30 (dd, 1 H, 3-H), 4.68 and 4.79 (2 d, each 1 H, $C_6H_5CH_2$), 4.72 (d, 1 H, 1-H), 7.26−7.35 (m, 5 H, $C_6H_5CH_2$); **38β** δ = 1.34 and 1.41 [2 s, each 3 H, $C(CH_3)_2$], 1.39 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.80−1.95 (m, 2 H, $OCH_2CH_2CH_2N_3$), 3.37 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 7.2 Hz, 1 H, 2-H), 3.98 (dd, $J_{3,4}$ = 5.5, $J_{4,5}$ = 2.2 Hz, 1 H, 4-H), 4.09 (dd, 1 H, 3-H), 4.26 (d, 1 H, 1-H), 4.80 (s, 2 H, $C_6H_5CH_2$), 7.26−7.35 (m, 5 H, $C_6H_5CH_2$). − $C_{19}H_{27}N_3O_5$ (377.4): MS (FAB^+) *m/z* = 378.2 $[M + H]^+$, 400.2 $[M + Na]^+$.

5-Azidopentyl 2-*O*-Benzyl-3,4-*O*-isopropylidene-α/β-L-fucopyranoside (39): *GP 4 A*, **5** (78 mg, 0.22 mmol), **15** (171 mg), molecular sieves (250 mg), solvent (4 mL), NIS (126 mg), TfOH (6 μL), *T* = 0 °C. Purification (toluene/ethyl acetate, 4:1; 0.1% TEA) yielded **39** (63 mg, 74%); **39α** 48%, **39β** 52%. − TLC (System B): R_f = 0.65. − ^1H NMR: **39α** δ = 1.10−1.73 [m, 6 H, $OCH_2(CH_2)_3CH_2N_3$], 1.31 (d, $J_{5,6}$ = 6.4 Hz, 3 H, 6,6,6-H), 1.35 and 1.41 [2 s, each 3 H, $C(CH_3)_2$], 3.25 [t, 2 H, $OCH_2(CH_2)_3CH_2N_3$], 3.39 and 3.65 [2 m, each 1 H, $OCH_2(CH_2)_3CH_2N_3$], 3.51 (dd, $J_{2,3}$ = 7.8 Hz, 1 H, 2-H), 4.04 (dd, $J_{4,5}$ = 2.5 Hz, 1 H, 4-H), 4.31 (dd, $J_{3,4}$ = 5.4 Hz, 1 H, 3-H), 4.69 and 4.80 (2 d, each 1 H, $C_6H_5CH_2$), 4.73 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 7.26−7.35 (m, 5 H, $C_6H_5CH_2$); **39β** δ = 1.24−1.70 [m, 6 H, $OCH_2(CH_2)_3CH_2N_3$], 1.34 and 1.38 [2 s, each 3 H, $C(CH_3)_2$], 1.39 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 3.24 [m, 2 H, $OCH_2(CH_2)_3CH_2N_3$], 3.48 and 3.93 [2 m, each 1 H, $OCH_2(CH_2)_3CH_2N_3$], 3.37 (dd, $J_{2,3}$ = 7.1 Hz, 1 H, 2-H), 3.98 (dd, $J_{4,5}$ = 2.1 Hz, 1 H, 4-H), 4.12 (dd, $J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.25 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 4.79 and 4.84 (2 d, each 1 H, $C_6H_5CH_2$), 7.26−7.35 (m, 5 H, $C_6H_5CH_2$). − $C_{21}H_{31}N_3O_5$ (405.4): MS (FAB^+) *m/z* = 406.1 $[M + H]^+$, 428.1 $[M + Na]^+$.

Decyl 2-*O*-Benzyl-3,4-*O*-isopropylidene-α/β-L-fucopyranoside (40): *(i)*: *GP 4 A*, **5** (43 mg, 0.12 mmol), **16** (0.14 mL), molecular sieves (150 mg), solvent (2.5 mL), NIS (70 mg), TfOH (3.3 μL), *T* = 0 °C. Purification (System C; 0.1% TEA) yielded **40** (28 mg, 56%); **40α** 31%, **40β** 69%. − *(ii)*: *GP 5*, **5** (27 mg, 75 μmol), bromine (9.3 μL). Then, residue (**8**), **16** (86 μL), Bu_4NBr (30 mg), molecular sieves (75 mg), solvent (0.3 mL). Purification (System C, 0.1% TEA) yielded **40** (23 mg, 74% overall); **40α** 88%, **40β** 12%. − TLC (System A): R_f = 0.84. − ^1H NMR: **40α** δ = 0.90 [t, 3 H, $OCH_2(CH_2)_8CH_3$], 1.31 (d, $J_{5,6}$ = 6.7 Hz, 3 H, 6,6,6-H), 1.33 and 1.36 [2 s, each 3 H, $C(CH_3)_2$], 1.27−1.59 [2 m, 16 H, $OCH_2(CH_2)_8CH_3$], 3.50 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 7.9 Hz, 1 H, 2-H), 3.37 and 3.62 [2 m, each 1 H, $OCH_2(CH_2)_8CH_3$], 4.03 (dd, $J_{3,4}$ = 5.5, $J_{4,5}$ = 2.6 Hz, 1 H, 4-H), 4.31 (dd, 1 H, 3-H), 4.69 and 4.79 (2 d, each 1 H, $C_6H_5CH_2$), 4.73 (d, 1 H, 1-H), 7.25−7.39 (m, 5 H, $C_6H_5CH_2$); **40β** δ = 0.90 [t, 3 H, $OCH_2(CH_2)_8CH_3$], 1.34 and 1.41 [2 s, each 3 H, $C(CH_3)_2$], 1.39 (d, $J_{5,6}$ = 6.6 Hz, 3 H, 6,6,6-H), 1.27−1.59 [2 m, 16 H, $OCH_2(CH_2)_8CH_3$], 3.36 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 7.1 Hz, 1 H, 2-H), 3.97 (dd, $J_{3,4}$ = 5.5, $J_{4,5}$ = 2.1 Hz, 1 H, 4-H), 3.80 (m, 1 H, 5-H), 4.10 (dd, 1 H, 3-H), 4.25 (d, 1 H, 1-H), 4.79 and 4.89 (2 d, each 1 H, $C_6H_5CH_2$), 7.25−7.39 (m, 5 H, $C_6H_5CH_2$). − $C_{26}H_{42}O_5$ (434.3): MS (FAB^+) *m/z* = 435.2 $[M + H]^+$.

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