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The use of *O*-trifluoroacetyl protection and profound influence of the nature of glycosyl acceptor in benzyl-free arabinofuranosylation

Polina I. Abronina[a], Ksenia G. Fedina[a,b], Nikita M. Podvalnyy[a], Alexander I. Zinin[a], Alexander O. Chizhov[a], Nikolay N. Kondakov[a], Vladimir I. Torgov[a], Leonid O. Kononov[a]*

[a]*N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Leninsky prosp., 47, 119991 Moscow, Russian Federation.*

[b]*Higher Chemical College of the Russian Academy of Sciences, Miusskaya pl. 9, 125047 Moscow, Russian Federation.*

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* Corresponding author. Tel: +7-495-9432946; fax: +7-499-1355328. E-mail: kononov@ioc.ac.ru, leonid.kononov@gmail.com.

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Abstract

The influence of *O*-trifluoroacetyl (TFA) groups at different positions of thioglycoside glycosyl donors on stereoselectivity of α-arabinofuranosylation leading to corresponding disaccharides was studied. It was shown that TFA group in thioglycoside glycosyl donors, when combined with 2-*O*-(triisopropylsilyl) (TIPS) non-participating group, may be regarded as an electron-withdrawing protecting group that may enhance 1,2-*cis*-selectivity in arabinofuranosylation, the results strongly depending on the nature of glycosyl acceptor. The reactivities of the glycosyl donors were compared with those of a similar thioglycoside with *O*-pentafluoropropionyl groups and the known phenyl 3,5-*O*-(di-*tert*-butylsilylene)-1-thio-α-D-arabinofuranosides with 2-*O*-TIPS and 2-*O*-benzyl groups. The "matching" in the donor–acceptor combination was found to be critical for achieving both high reactivity of glycosyl donor and β-stereoselectivity of arabinofuranosylation. The use of glycosyl donors with TFA and silyl

protection may be useful in the realization of the benzyl-free approach to oligoarabinofuranosides with azido group in aglycon – convenient building blocks for the preparation of neoglycoconjugates.

Keywords: arabinofuranose; benzyl-free approach; 1,2-*cis*-stereoselectivity; *O*-trifluoroacetyl group; electron-withdrawing protecting groups.

1. Introduction

There has been growing interest[1–12] in the synthesis of D-arabinofuranose oligosaccharides related to the mycobacterial cell wall components (arabinogalactan, lipoarabinomannan and arabinomannan from *Mycobacterium tuberculosis*), over recent years due to the necessity of creating means for diagnostics, prevention and treatment of human tuberculosis, which remains a major worldwide health problem and takes millions of lives annually.[13,14] Mycobacterial arabinan chains are composed of arabinofuranose residues forming (α1→3)-, (α1→5)- and (β1→2)-glycosidic linkages.[11]

The known direct and indirect methods for the synthesis of 1,2-*cis*-arabinofuranosides (β-glycosides) rely on the use of *O*-benzyl protecting groups[1–12,15–18] which are difficult to remove in the presence of azido group in aglycon, which may be useful for the preparation of neoglycoconjugates.[19] Recently we used a novel per-*O*-silyl protected thioglycoside glycosyl donor to create 1,2-*cis*-linkage and thus introduced[20] a *benzyl-free* approach, which may be useful in the preparation of oligoarabinofuranosides with azido group in aglycon. It is known that benzyl protecting groups are difficult to remove in the presence of azide. The use of catalytic hydrogenolysis for de-*O*-benzylation is not possible since the azido group is reduced faster than any substantial cleavage of *O*-benzyl groups occurs.

In continuation of this work we decided to study the influence of *O*-trifluoroacetyl (TFA) groups at different positions of thioglycoside glycosyl donors on stereoselectivity of arabinofuranosylation. Glycosyl donors with *O*-pentafluoropropionyl (PFP)[21–23] and *O*-benzyl

protecting groups were used for comparison. The choice of TFA groups was based on the following considerations.

Strongly electron-withdrawing *O*-protecting groups are known to modulate stereoselectivity of glycosylation.[24–28] Mostly *O*-alkane(arene)sulfonyl groups were used for this purpose.[24,28] Methanesulfonyl and benzenesulfonyl groups at O-2 of glycosyl donors are known to influence of stereoselectivity of β-mannosylation.[26] Crich and co-workers also reported that mannopyranosylation with donor bearing *O*-(trifluoromethyl)benzenesulfonyl group at the O-2 position was β-selective.[27] At the same time, the use of the latter group at O-2 position of arabinofuranosyl donor showed only moderate yield of the β-glycoside.[29] Remote electron-withdrawing groups at O-3, O-4 or O-6 of pyranosyl donors or at O-3 or O-5 of furanosyl donors (as in the case of β-ribofuranosylation), which would decrease the reactivity of glycosyl donors, also affect the outcome of glycosylation.[24,25]

In spite of numerous investigations of the influence of *O*-alkane(arene)sulfonyl groups on stereoselectivity of glycosylation, the application of *O*-acyl electron-withdrawing protecting groups for this purpose was scarce.[21–23,30] Electron-withdrawing substituents in *O*-acyl groups may considerably reduce basicity and nucleophilicity of their carbonyl moieties thus (1) making them less prone to stabilize oxocarbenium ion by neighboring or remote participation and (2) reducing their ability to act as hydrogen bond acceptors. The latter feature seems to be essential for the stereochemical outcome of glycosylation since the formation of hydrogen-bonded mixed supramers of glycosyl donor and glycosyl acceptor has recently been shown to be possible.[31,32]

O-Trifluoroacetyl (TFA) group has rarely been used as a protecting group for alcohols, because it is generally considered to be too labile.[33] Nevertheless, it is known that TFA and homologous PFP esters can be used in stereoselective synthesis of oligosaccharides.[21–23] However, there are few reports which describe remote participating effect of TFA-groups, evaluated in comparison with less electron-withdrawing acyl groups.[30] Here we report the results of the use of TFA-protected glycosyl donors in arabinofuranosylation of O-2 of arabinofuranose,

which allowed the preparation of Ara*f*-(β1→2)-Ara*f* disaccharide with functionalized aglycon with a azido group.

2. Results and discussion

Synthesis of a series of TFA-substituted arabinofuranosyl derivatives started from the known thioglycoside **1**[34] with 2-OH unprotected (Scheme 1). After introducing TIPS group (**1**→**2**) and *O*-debenzoylation (**2**→**3**), diol **3** was obtained in 95% yield. Treatment of diol **3** with trifluoroacetic anhydride in CH_2Cl_2 in the presence of catalytic amount of CF_3CO_2Na led to 3,5-bis(trifluoroacetate) **4** in 98% yield**.** This procedure (see Experimental for details) in which the excess of base (CF_3CO_2Na) is removed by filtration is more convenient than the standard reaction conditions[21] (trifluoroacetic anhydride in pyridine (Py)) since aqueous work-up is excluded. Our efforts to adapt the latter procedure for the synthesis of TFA derivatives was unsuccessful. *O*-Trifluoroacetylation with $(CF_3CO)_2O$ in the presence of soluble bases (Py or Et_3N) did not allow isolation of TFA-substituted arabinofuranosyl donors **4**, **7**, **11**, **13** in pure form apparently due to hydrolysis of *O*-trifluoroacetyl groups during aqueous extractions. Chromatography on silica gel was also unacceptable because of lability of *O*-trifluoroacetyl groups. High resolution electrospray mass spectrum of **4** showed the expected ion at *m/z* 613.1436 ($M+Na^+$). Besides, ^{19}F NMR spectrum of **4** showed two signals at δ_F −75.56 and −75.63 ppm of equal intensities corresponding to the two CF_3CO moieties.

Glycosyl donor **13** with 2-*O*-TFA group was synthesized by 2-*O*-trifluoroacetylation of the known alcohol **12**[20] with 3,5-di-*O*-*tert*-butyl silylene (DTBS) protecting group under the same conditions. ^{19}F NMR spectrum of **13** showed one signal of CF_3CO group at δ_F −74.57 ppm.

For the synthesis of monosubstituted derivatives **7** and **11** with TFA groups at remote positions differentiation of O-3 and O-5 positions in diol **3** was required. 5-Hydroxy group of **3** was selectively benzoylated with subsequent 3-*O*-trifluoroacetylation of the remaining free hydroxy group to give derivative **7** with TFA group at O-3. On the other hand, selective

tritylation of **3** with TrCl/Py (**3**→**8**), benzoylation (**8**→**9**), followed by detritylation by TFA–H_2O–CH_2Cl_2 (10:1:90) at 20 °C led to alcohol **10** in 53% yield over 3 steps. Its hydroxy group at C-5 was *O*-trifluoroacetylated as described above to give glycosyl donor **11** with TFA group at O-5 in 94% yield. ^{19}F NMR spectra of **7** and **11** showed one signal of CF_3CO group at δ_F −75.53 and δ_F −75.59 ppm, respectively. Glycosyl donor **5** with PFP groups at O-3 and O-5 was obtained by the treatment of diol **3** with $(CF_3CF_2CO)_2O$/Py, essentially as described.[21]

Having the series of TFA-substituted arabinofuranosyl glycosyl donors **4**, **7**, **11** and 3,5-bis-*O*-PFP-protected glycosyl donor **5** at hand, our attention was focused on synthesis of 2-*O*-unprotected glycosyl acceptors. Aiming at the realization of *benzyl-free* approach, we intended to use benzoyl and silyl groups for protection of non-reacting hydroxyl groups. Besides, we needed to prepare (β1→2)-linked disaccharide of arabinofuranose because it is known that terminal fragment of *M. tuberculosis* arabinans containing this disaccharide is essential for pathogenicity of *M. tuberculosis*. Hence, (β1→2)-linked disaccharide of arabinofuranose may be useful for biomedical purposes, in particular, for serodiagnosis of tuberculosis.[11,35,36]

Thus, previously synthesized bis-*O*-chloroacetate **14**[34] was converted into 4-(2-chloroethoxy)phenyl (CEP) glycoside **15** in 74% yield by reaction with 4-(2-chloroethoxy)phenol (CEP-OH)[37] in the presence of catalytic amount of TfOH (Scheme 2). After removal of *O*-chloroacetyl group by treatment with Py/H_2O, alcohol **16** with benzoyl groups and CEP aglycon was obtained. It should be noted that CEP group is a multipurpose aglycon with dual function which can easily be removed by oxidation (like 4-methoxyphenyl group) as well as functionalized after replacement of chlorine atom with azido group (like ω-chloroalkyl aglycons) to give 4-(2-azidoethoxy)phenyl group, which may be used in click chemistry. On the other hand, the azide may be directly converted into amine. These opportunities can further be used for the preparation of a wide range of neoglycoconjugates.[19]

Acetolysis of the known methyl glycoside **21**[38] led to glycosyl acetate **17** obtained as an anomeric mixture (Scheme 2). Reaction of **17** with CEP-OH in CH_2Cl_2 in the presence of a

catalytic amount of TfOH gave glycoside **18** with CEP aglycon as a single anomer in 86% yield. After debenzoylation (MeONa, MeOH) (**18**→**19**) and silylation ((*t*-Bu)$_2$Si(OTf)$_2$, Py) glycosyl acceptor **20** with free 2-OH and CEP aglycon was obtained. For investigation of influence of aglycon in glycosyl acceptor on the outcome of glycosylation, 2-*O*-unprotected methyl glycoside **23** was synthesized by analogous silylation of the known methyl arabinofuranoside **22**.[39]

It is well known that stereoselectivity of β-arabinofuranosylation is highly dependent upon the reaction temperature.[2,7,8] At low temperature the stereoselectivity of β-arabinofuranosylation is usually the best, while at higher temperatures all possible stereoisomeric glycosides may be produced in roughly equal amounts. In order to achieve a high β-stereoselectivity of arabinofuranosylation, herein glycosylations were performed at lowest possible temperature. Promoter (NIS, AgOTf) was added at low temperature (−78 °C) and then the temperature was allowed to rise slowly until appearance of persistent iodine color. This temperature (*T*) was taken as the temperature at which the activation of glycosyl donor occurs.

Glycosylation of 3,5-di-*O*-benzoyl protected CEP glycoside **16** with the arabinofuranosyl donors **4**, **7**, **11**, **13**, **24**,[20] **25**[7,29] (1.5 equiv) was performed under standard conditions (NIS, AgOTf, MS 4Å, CH_2Cl_2, −78 °C → *T* (for details see Experimental and Table 1) to afford anomeric mixtures of corresponding (1→2)-linked disaccharides (Scheme 3 and Table 1). After glycosylation, TFA groups were removed from the TFA-containing disaccharides obtained by treatment with NEt_3 in MeOH to give disaccharides **26**–**29**. Anomeric ratios of disaccharides **26**–**31** were determined from the ^{1}H NMR spectroscopic data for the disaccharide fractions obtained by gel-chromatography on Bio-Beads S×3 in toluene (Table 1). We found that TFA at O-2 position of thioglycoside **13** (entry 7, Table 1) resulted in 1,2-*trans*-stereoselectivity α:β = 3.3:1. This result probably indicates some neighboring participation of the TFA group, a possibility of which is usually considered unlikely.[30] When TFA groups were in remote O-3 or O-5 positions of glycosyl donors **7** and **11** with 2-*O*-TIPS non-participating group (entries 5 and 6, Table 1), equal

ratio of anomers was obtained (α:β ≈ 1:1). It is interesting to note that bis-TFA-protected thioglycoside **4** gave in reaction with glycosyl acceptor **16** moderate β-stereoselectivity (α:β = 1:2, entry 1, Table 1) which, surprisingly, was identical to that obtained in glycosylation of glycosyl acceptor **16** by the well-known 2-*O*-benzyl-protected glycosyl donor **25**[7,29] with 3,5-*O*-DTBS protection (α:β = 1:2, entry 10). In spite of moderate β-selectivity of glycosylation in the case of TFA-substituted arabinofuranosyl donors **4**, **7**, **11**, there is a direct dependence of the results of arabinofuranosylation on the positions of TFA groups in glycosyl donors.

Most commonly, stereochemical outcome of glycosylation is supposed to be linked to conformation of the saccharide residue.[40,41] For instance, glycosyl donors containing a cyclic 3,5-di-*O*-DTBS protecting group were successfully used to increase β-stereoselectivity in the preparation of arabinofuranosides.[7–9] The fused DTBS group makes the flexible furanose ring in a thioglycoside donor more rigid and, presumably, locks the oxacarbenium ion generated during glycosylation in a E_3 conformation that favors an attack of a nucleophile from β-face, hence β-selectivity. Thus, the use of per-silylated glycosyl donor **24**[20] with 3,5-di-*O*-DTBS protection improved the yield of β-anomer (α:β = 1:4.5, entry 8, Table 1). However, the situation is obviously more complex since the presence of 3,5-*O*-DTBS protection does not guarantee high β-stereoselectivity (α:β = 1:2, entry 10).

Another possible explanation of the low anomeric selectivities in this series may be "matched/mismatched effect" in the donor–acceptor combination.[42,43] The importance of this effect in arabinofuranosylation has been demonstrated by comparison of stereoselectivities achieved with D- and L-configured glycosyl donors **25** and *ent*-**25**.[7,29] Taking into account this possibility, we conducted another series of arabinofuranosylation reactions using 3,5-*O*-DTBS-protected glycosyl acceptors **20** and **23** with CEP and methyl aglycons**,** respectively (Scheme 4). We found that β-selectivity of glycosylation of alcohol **20** with CEP aglycon (entries 2 and 3, Table 1) with bis-TFA-protected thioglycoside **4** is higher (α:β = 1:5.6 – 1:6.3) than that in the

case of per-*O*-silylated glycosyl donor **24** (entry 9, Table 1, α:β = 1:3). Analysis of results achieved in the reactions of glycosyl acceptor **23** bearing methyl aglycon (entries 3 and 4, Table 1) with glycosyl donors **4** and **5** showed that there is no remarkable difference in stereoselectivity of arabinofuranosylation in case of use of bis-TFA-protected thioglycoside **4** (entry 3, Table 1, α:β = 1:5.6) and bis-PFP-protected thioglycoside **5** (entry 4, Table 1, α:β = 1:5.5) as glycosyl donors. It is striking that the stereoselectivities obtained in reactions of **4** and **5** with glycosyl acceptor **23** matched that obtained in the reaction of glycosyl donor **4** with glycosyl acceptor **20** (entry 2, Table 1, α:β = 1:6.3). This means that the nature of aglycon in these reactions is not critical for achieving high stereoselectivity while the protecting group pattern of glycosyl acceptor is very important (see also a discussion below).

We may conclude that in the studied cases glycosyl donors with two electron-withdrawing acyl groups (TFA or PFP) at O-3 and O-5 and non-participating group 2-*O*-TIPS group strongly favor β-selective glycosylation. Although the influence of 2-*O*-TIPS protection on stereoselectivity seems to be very important, no unambiguous conclusions concerning the effects of 2-*O*-TIPS and *O*-TFA/PFP groups can be made at the moment. A study of influence of 2-*O*-TIPS group on stereoselectivity might be an interesting direction of future research.

The temperature *T* at which the glycosylation with 2-*O*-TIPS-protected glycosyl donors commences (characterized by appearance of iodine color) deserves a special discussion. Analysis of the data of Table 1 reavealed that the reactions of *O*-benzoylated glycosyl acceptor **16** with TFA-protected thioglycosides **4**, **7** and **11** (entries 1, 5, 6, Table 1) started at −22 °C irrespective of the number and position of *O*-TFA groups, while glycosylations of 3,5-*O*-DTBS-protected glycosyl acceptors **20** and **23** with bis-TFA-protected thioglycoside **4** (entries 2, 3, Table 1) started at −30 °C, *apparently* lower temperature favoring higher β-selectivities (up to α:β = 1:6.3) as one would expect basing on the known[2,7,8] precedents. This lower temperature of activation suggests higher reactivity of the *same* glycosyl donor **4**, which is clearly modulated by

the nature of protecting groups in the molecule of glycosyl *acceptor*. This observation may look trivial since lower reactivity was observed in reaction with aparently less nucleophilic glycosyl acceptor **16** with electron-withdrawing *O*-benzoyl groups. However this seemingly "bad" glycosyl acceptor **16** cleanly reacted with per-*O*-silylated glycosyl donor **24**, which was activated at even lower temperature (−39 °C, entry 8, Table 1), to give disaccharide **30** with lower but comparable stereoselectivity (α:β = 1:4.5). The same glycosyl donor **24** was activated at somewhat lower temperature (−42 °C, entry 9, Table 1) when reacted with "good" 3,5-*O*-DTBS-protected glycosyl acceptor **20**, but the stereoselectivity dropped even further (α:β = 1:3).

These data suggest that it is the "matching" in the donor–acceptor combination that is critical for achieving both high reactivity of glycosyl donor (low temperature *T* of activation) and β-stereoselectivity of arabinofuranosylation, and three types of donor–acceptor combination can be revealed. (1) When molecules of *both* glycosyl donor and glycosyl acceptor contain *O*-acyl groups (TFA, PFP, Bz) (entries 1, 5, 6, Table 1) the temperature T of activation is high and steroselectivity is low. (2) When only molecules of glycosyl acceptor *or* glycosyl donor contain *O*-acyl groups (entries 2, 3, 4, 8, Table 1) the temperature T of activation is lower and steroselectivity is high. (3) When molecules of *both* glycosyl donor and glycosyl acceptor do *not* contain any *O*-acyl groups (entries 9, 10, Table 1) the temperature T of activation is very low but steroselectivity is low too. The origin of this "matching" may be related to formation of differently arranged *hetero*-supramers[31] comprising molecules of both glycosyl donor and glycosyl acceptor. Indeed, acyl groups are the hydrogen-bond acceptor sites, and their presence and position in the molecules of glycosyl donors/acceptors would influence the structure of hydrogen-bonded supramers hence chemical properties.[31]

It is necessary to stress that all data shown in Table 1 correspond to disaccharide fractions obtained by gel-chromatography as anomeric mixtures since separation of anomers was impossible or very difficult at this stage (even with HPLC). Their anomeric composition was

determined by integration of the respective signals in the ^{1}H NMR spectra. In two cases (see below), in which the best (from the preparative point of view) glycosylation results were achieved, the disaccharide anomers were separated by preparative HPLC after change in protecting group pattern (the simultaneous presence of *O*-benzoyl and hydroxyl group(s) and the absence of silyl groups was found to facilitate separation). This allowed a new realization of the benzyl-free approach[20] to oligoarabinofuranosides with azido group in aglycon.

Thus, glycosylation of alcohol **16** with per-*O*-silyl-protected glycosyl donor **24** provided access to disaccharide **30** in 92% yield with good stereoselectivity (entry 8, Table 1, α:β = 1:4.5, corresponds to 75% yield of β-isomer). Similarly, glycosylation of alcohol **20** with bis-TFA-protected thioglycoside **4** gave disaccharide **32** in 84% yield and even better stereoselectivity (entry 2, Table 1, α:β = 1:6.3, corresponds to 73% yield of β-isomer). Disaccharide **30** was desilylated (TBAF) to give after HPLC purification partially protected disaccharide **36** in 59% yield as the single β-anomer (Scheme 5). The structure of the β-isomer of disaccharide **36** followed from NMR data, which revealed the presence of α-arabinofuranose residue (δ_C 106.4 (C-1^{I}); singlet at δ_H 5.89 (H-1^{I})) and β-arabinofuranose residue (δ_C 103.0 (C-1^{II}); doublet at δ_H 5.26 (H-1^{II}, J = 4.6 Hz)). Besides, the expected correlations in HMBC spectra: (C-2^{I}/H-1^{II} and C-1^{II}/H-2^{I}) were clearly observed, which proved the presence of (β1→2)-linkage.

Chlorine in the 2-chloroethyl moiety of **36** was substituted with azide (NaN_3, 18-crown-6, DMF) to give disaccharide **37** with azido group in aglycon in 78% yield. The presence of azido group in the aglycon followed from the position of the signal of terminal methylene group $CH_2CH_2N_3$ (δ_C 50.2) in the ^{13}C NMR spectrum of **37**. The positions of other characteristic signals in ^{1}H and ^{13}C NMR spectra of glycoside **37**, coupling constants and correlations in HSQC and HMBC spectra corresponded well to those observed for the β-isomer of glycoside **36** (see Experimental).

Triol **37** was debenzoylated (MeONa, MeOH) to give in 95% yield the target deprotected disaccharide **38** with 4-(2-azidoethoxy)phenyl aglycon, the structure of which was fully confirmed by 1D and 2D NMR spectra (see Experimental). In particular, HSQC spectrum showed the presence of correlations, which corresponded to α-arabinofuranose residue (δ_C 106.8 (C-1^I); doublet at δ_H 5.57 (H-1^I, J = 2.0 Hz)) and β-arabinofuranose residue (δ_C 102.8 (C-1^{II}); doublet at δ_H 5.03 (H-1^{II}, J=4.3 Hz)). Additional confirmation of the structure of disaccharide **38** was obtained from the presence of the following correlations in HMBC spectra: H-1^{II}/C-2^I and H-2^I/C-1^{II}.

Disaccharide **32** was benzoylated (BzCl, Py) and then desilylated (TBAF) to give after HPLC purification partially protected disaccharide **39** in 47% yield as the single β-anomer (Scheme 5). The structure of disaccharide **39** followed from NMR data, which revealed the presence of α-arabinofuranose residue (δ_C 104.7 (C-1^I); doublet at δ_H 5.56 (H-1^I, J = 2.1 Hz)) and β-arabinofuranose residue (δ_C 102.0 (C-1^{II}); doublet at δ_H 5.28 (H-1^{II}, J = 4.6 Hz)). Chlorine in the 2-chloroethyl moiety of **39** was substituted with azide (NaN_3, 18-crown-6, DMF) to give disaccharide **40** with azido group in aglycon. High resolution electrospray mass spectrum of **40** showed the expected ion at m/z 674.1953 $[M + Na]^+$. Azide **40** was debenzoylated (MeONa, MeOH) to give the target deprotected disaccharide **38** with 4-(2-azidoethoxy)phenyl aglycon in 90% yield (from **39** over two steps) identical to that obtained from **31** by a different route.

3. Conclusions

TFA and PFP groups in glycosyl donors are electron-withdrawing protecting groups which, when used in combination with 2-*O*-TIPS protecting group, may enhance 1,2-*cis*-selectivity in arabinofuranosylation. The reactivities of the corresponding glycosyl donors were compared with that of the known glycosyl donor with 2-*O*-benzyl and 3,5-*O*-DTBS groups. The "matching" in the donor–acceptor combination was found to be critical for achieving both high reactivity of

glycosyl donor (low temperature *T* of activation) and β-stereoselectivity of arabinofuranosylation. The use of glycosyl donors with TFA and silyl protection may be useful in the realization of the benzyl-free approach to oligoarabinofuranosides with azido group in aglycon – convenient building blocks for the preparation of neoglycoconjugates.

4. Experimental

4.1 General methods

All reactions sensitive to air and/or moisture were carried out under argon atmosphere. The reactions were performed with the use of commercial reagents (Aldrich, Fluka, Acros Organics) Anhydrous solvents were purified and dried (where appropriate) according to standard procedures. Sodium trifluoroacetate ($NaOCOCF_3$) was additionally dried by heating at 80 °C for 1 h before use. Powdered molecular sieves 4Å (Fluka) were activated before the reactions by heating at 220 °C in high vacuum (0.02 bar) for 6 h. Column chromatography was performed on silica gel 60 (40–63 μm, Merck). Thin-layer chromatography was carried out on plates with silica gel 60 on aluminum foil (Merck). Spots of compounds were visualized under UV light and by heating the plates (at *ca.* 150 °C) after immersion in a 1:10 (v/v) mixture of 85% aqueous H_3PO_4 and 95% EtOH. ^1H, ^{13}C and ^{19}F NMR spectra were recorded for solutions in Me_2CO-d_6, $CDCl_3$, or CD_3OD on a Bruker AC-200 instrument (200.13, 50.32, and 188.27 MHz for ^1H, ^{13}C and ^{19}F, respectively), a Bruker AM-300 instrument (300.13, 75.48, and 282.40 MHz for ^1H , ^{13}C and ^{19}F, respectively) or on a Bruker AVANCE 600 spectrometer (600.13 and 150.9 MHz for ^1H and ^{13}C, respectively). The ^1H NMR chemical shifts are referred to the residual signal of $CHCl_3$ (δ_H 7.27, CHD_2OD (δ_H 3.31), or CHD_2COCD_3 (δ_H 2.05), the ^{13}C NMR shifts – to the central line of $CDCl_3$ signal (δ_C 77.0), CD_3OD signal (δ_C 49.0) or $(CD_3)_2CO$ signal (δ_C 29.9). Assignments of the signals in the NMR spectra were performed using 2D-spectroscopy (COSY, HSQC, HMBC) and DEPT-135 experiments. High resolution mass spectra (electrospray ionization, HRESIMS)

were recorded in positive mode on a Bruker micrOTOF II mass spectrometer for 2×10^{-5} M solutions in MeCN or MeOH. Optical rotations were measured using a PU-07 automatic digital polarimeter (Russia). Analytical HPLC separations were performed on an Ultrasorb Si (5 μm) column (165×4.6 mm ID) at 1 mL/min flow rate. Preparative HPLC separations were performed on a Sialsorb 600 (7.5 μm) column (250 × 15 mm ID) with a 1:3:6 *i*-PrOH–$CHCl_3$–petroleum ether mixture as the eluent at 15 mL/min flow rate. A Knauer differential refractometer was used as the detector.

4.2. Phenyl 3,5-di-*O*-benzoyl-1-thio-2-*O*-triisopropylsilyl-α-D-arabinofuranoside (2)

To the solution of alcohol **1**[34] (417 mg, 0.93 mmol) in DMF (12 mL) collidine (370 μL, 2.78 mmol) and *i*-Pr_3SiOTf (400 μL, 1.48 mmol) were added. The reaction mixture was stirred for 1 h at 90 °C. The reaction mixture was diluted with $CHCl_3$ (50 mL), washed with H_2O (50 mL), 1 M $KHSO_4$ (50 mL), H_2O (50 mL) and satd aq $NaHCO_3$ (50 mL). The aqueous layer was extracted with $CHCl_3$ (10 mL). Combined organic extracts were filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~30 °C), dried *in vacuo*, and purified by silica gel column chromatography (light petroleum–EtOAc, 6 : 1) to give silyl ether **2** as a white foam (550 mg, 98%, R_f = 0.73, light petroleum–EtOAc, 6 : 1). $[\alpha]_D^{21}$ +105.8 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 629.2369 $[M + Na]^+$. Calcd for $C_{34}H_{42}O_6SSiNa$: 629.2364. ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.11 (br. s, 21 H, $CH(CH_3)_2$), 4.69–4.73 (m, 3 H, H-2, H-5a, H-5b), 4.76 (dd, J = 5.5, 2.7 Hz, 1 H, H-4), 5.43 (br. s, 1 H, H-3), 5.63 (s, 1 H, H-1), 7.26–7.36 (m, 3 H, Ph), 7.39–7.67 (m, 8 H, Ph), 8.06–8.21 (m, 4 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 11.9, 12.2 ($CH(CH_3)_2$), 17.7, 17.80, 17.81 ($CH(CH_3)_2$), 64.3 (C-5), 80.8 (C-3), 81.8 (C-4), 82.0 (C-2), 94.8 (C-1), 127.4, 128.3, 128.5, 129.0, 129.3, 129.7, 129.9, 130.0, 131.8, 133.0, 133.4, 134.6 (Ph), 165.5, 166.1 (CO).

4.3. Phenyl 2-*O*-triisopropylsilyl-1-thio-α-D-arabinofuranoside (3)

To the solution of dibenzoate **2** (171 mg, 0.28 mmol) in MeOH (4 mL) 1 M MeONa in MeOH (0.9 mL) was added and the mixture was stirred at ~20 °C for 48 h. The reaction was neutralized with Dowex 50W×4 (H^+) ion-exchange resin. The resin was filtered off and washed with MeOH (15 mL). The filtrate was concentrated and the residue was dissolved in CH_2Cl_2 (30 mL) and washed with satd aq $NaHCO_3$ (30 mL). The aqueous layer was extracted with CH_2Cl_2 (5 mL). Combained organic extracts were filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~30 °C), dried *in vacuo*, and purified by silica gel column chromatography (light petroleum–EtOAc) to give diol **3** as a colorless oil (100 mg, 89%; R_f = 0.19, petroleum ether–EtOAc, 4:1). $[\alpha]_D^{20}$ +107.3 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 421.1841 $[M + Na]^+$. Calcd for $C_{20}H_{34}O_4SSiNa$: 421.1839. ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.08 (br. s, 21 H, $CH(CH_3)_2$)) 3.82–3.87 (m, 2 H, H-5a, H-5b), 4.13 (d, *J* = 3.8 Hz, 1 H, H-3), 4.28–4.33 (m, 1 H, H-4), 4.34 (s, 1 H, H-2), 5.46 (s, 1 H, H-1), 7.28-7.40 (m, 3 H, Ph), 7.52 (d, *J* = 6.1 Hz, 2 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 12.0 ($CH(CH_3)_2$), 17.8 ($CH(CH_3)_2$), 62.2 (C-5), 79.2 (C-3), 83.6 (C-4), 85.9 (C-2), 93.4 (C-1), 127.7, 129.0, 132.2, 133.6 (Ph), 162.3 (CO).

4.4. Phenyl 2-*O*-triisopropylsilyl-3,5-di-*O*-trifluoroacetyl-1-thio-α-D-arabinofuranoside (4)

To the solution of diol **3** (20 mg, 0.052 mmol) in anhydrous CH_2Cl_2 (1 mL), $(CF_3CO)_2O$ (1 mL) and then solid $NaOCOCF_3$ (7 mg, 0.052 mmol) were added at 0 °C (ice-water bath). After 3 h at 20 °C the reaction mixture was concentrated under reduced pressure (bath temperature ~30 °C), the residue was dissolved in CCl_4 (30 mL), filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~30 °C), dried *in vacuo* to give trifluoroacetate **4** as a colorless oil (30 mg, 98%, R_f = 0.80, light petroleum–EtOAc, 4:1). $[\alpha]_D^{23}$ +66.5 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 613.1436 $[M + Na]^+$. Calcd. for $C_{24}H_{32}F_6NaO_6SSi$: 613.1485. ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.05 (s, 18 H, $CH(CH_3)_2$), 1.08 (s, 3 H, 3x$CH(CH_3)_2$), 4.56–4.68 (m, 4 H, H-5a, H-5b, H-4, H-2), 5.13 (dd, *J* = 3.7, 1.8 Hz, 1 H, H-3), 5.48 (d, *J* = 1.7 Hz, 1 H, H-1),

7.30–7.40 (m, 3 H, Ph), 7.46–7.57 (m, 2 H, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 11.9 ($CH(CH_3)_2$), 17.7 ($CH(CH_3)_2$), 65.9 (C-5), 79.1 (C-4 or C-2), 81.3 (C-4 or C-2), 83.7 (C-3), 94.3 (C-1), 114.25 (q, J_{CF} = 285.5 Hz, CF_3), 114.39 (q, J_{CF} = 285.4 Hz, CF_3), 128.0, 129.2, 132.2, 133.3 (Ph), 156.88 (q, J_{CF} = 43.8 Hz, CF_3CO),157.04 (q, J_{CF} = 43.2 Hz, CF_3CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ_F −75.58, −75.64 (CF_3CO).

4.5. Phenyl 3,5-di-*O*-pentafluoropropionyl-2-*O*-triisopropylsilyl-1-thio-α-D-arabinofuranoside (5)

To the solution of diol **3** (170 mg, 0.43 mmol) in anhydrous CH_2Cl_2 (0.5 mL) Py (1 mL) and $(CF_3CF_2CO)_2O$ (0.5 mL) were added at 0 °C (ice-water bath). After 1 h at 0 °C the reaction mixture was diluted with $CHCl_3$ (100 mL), washed with H_2O (100 mL), 1 M $KHSO_4$ (100 mL), H_2O (100 mL) and satd aq $NaHCO_3$ (100 mL). Organic extract was filtered through a cotton wool plug and concentrated under reduced pressure (bath temperature ~30 °C) and dried *in vacuo*. The residue was purified by silica gel column chromatography (light petroleum–toluene, 1:1) to give pentafluoropropionyl derivative **5** as a colorless oil (195 mg, 66%; R_f = 0.78, light petroleum–EtOAc, 4:1). $[\alpha]_D^{23}$ +68.8 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 713.1414 $[M + Na]^+$. Calcd for $C_{26}H_{32}F_{10}O_6SSiNa$: 713.1421. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.08 (br. s, 21 H, $CH(CH_3)_2$), 4.55–4.62 (m, 2 H, H-2, H-4), 4.62–4.73 (m, 2 H, H-5a, H-5b), 5.16 (dd, *J* = 3.7, 1.6 Hz, 1 H, H-3), 5.50 (d, *J* = 1.5 Hz, 1 H, H-1), 7.30–7.39 (m, 3 H, Ph), 7.44–7.55 (m, 2 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 11.9 ($CH(CH_3)_2$), 17.7 ($CH(CH_3)_2$), 66.0 (C-5), 79.3, 81.4, 83.8 (C-2, C-3, C-4), 94.3 (C-1), 102.0, 102.6, 105.6, 106.1, 109.1, 109.6, 115.2, 115.6, 116.1(CF_2CF_3); 127.2, 127.6, 128.0, 129.1, 132.1, 133.3 (Ph); 157.5, 157.6, 157.9, 158.3, 158.3 (CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ_F −83.38, −83.67, −122.15, −122.29 (CF_2CF_3).

4.6. Phenyl 5-*O*-benzoyl-2-*O*-triisopropylsilyl-1-thio-α-D-arabinofuranoside (6)

To the solution of diol **3** (232 mg, 0.61 mmol) in anhydrous CH_2Cl_2 (5 mL) Py (50 μL, 1.2 mmol) and BzCl (70 μL, 0.61 mmol) were added sequentially at 0 °C (ice-water bath). After 1 h at 0 °C the reaction mixture was diluted with $CHCl_3$ (100 mL), washed with H_2O (100 mL), 1 M $KHSO_4$ (100 mL), H_2O (100 mL) and satd aq $NaHCO_3$ (100 mL). Organic extract was filtered through a cotton wool plug and concentrated under reduced pressure, dried *in vacuo* to give alcohol **6** as a colorless oil (235 mg, 80%; R_f = 0.36, light petroleum–EtOAc, 4:1). $[\alpha]_D^{19}$ +101.3 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 525.2071 $[M + Na]^+$. Calcd for $C_{27}H_{38}O_5SSiNa$: 525.2101. ^{1}H NMR (300 MHz, $CDCl_3$); δ_H 1.06 (br. s, 21 H, $CH(CH_3)_2$), 2.81 (br. s, 1 H, OH), 4.09 (br. s, 1 H, H-3), 4.36 (t, *J* = 2.1 Hz, H-2), 4.43–4.61 (m, 3 H, H-4, H-5a, H-5b), 5.46 (d, *J* = 1.7 Hz, 1 H, H-1), 7.22–7.34 (m, 3 H, Ph), 7.37–7.45 (m, 3 H, Ph), 7.46–7.60 (m, 3 H, Ph), 8.04 (d, *J* = 7.2 Hz, 2 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 11.9 ($CH(CH_3)_2$), 17.8 ($CH(CH_3)_2$), 64.2 (C-5), 79.9 (C-3), 82.8 (C-4), 83.7 (C-2), 93.3 (C-1), 127.5, 128.3, 128.9, 129.7, 132.0, 133.1, 133.8 (Ph).

4.7. Phenyl 5-*O*-benzoyl-3-*O*-trifluoroacetyl-2-*O*-triisopropylsilyl-1-thio-α-D-arabinofuranoside (7)

To the solution of alcohol **6** (166 mg, 0.34 mmol) in anhydrous CH_2Cl_2 (1 mL), $(CF_3CO)_2O$ (1 mL) and solid $NaOCOCF_3$ (23 mg, 0.17 mmol) were added at 0 °C (ice-water bath). After 1 h at 0 °C the reaction mixture was concentrated under reduced pressure (bath temperature ~30 °C), then dissolved in CCl_4 (30 mL), filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~30 °C), and dried *in vacuo* to give trifluoroacatate **7** as a colorless oil (185 mg, 94%, R_f = 0.66 (petroleum ether–EtOAc, 9:1). HRESIMS: found *m/z* 525.2103 $[M-CF_3CO+H+Na]^+$. Calcd for $C_{27}H_{38}O_5SSiNa$: 525.2107. $[\alpha]_D^{19}$ +82.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.14 (br. s, 21 H, $CH(CH_3)_2$), 4.56–4.74 (m, 4 H, H-2, H-4, H-5a, H-5b), 5.26–5.37 (m, 1 H, H-3), 5.53 (d, *J* = 2.2 Hz, 1 H, H-1), 7.24–7.38 (m, 3 H, Ph), 7.39–7.68 (m, 5

H, Ph), 8.08 (d, J = 7.3 Hz, 2 H, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 11.9 ($CH(CH_3)_2$), 17.7 ($CH(CH_3)_2$), 63.5 (C-5), 80.0, 81.6 (C-2, C-4), 84.1 (C-3), 94.1 (C-1), 114.29 (q, J_{CF} = 285.7 Hz, CF_3), 127.8, 128.4, 129.1, 129.7, 132.0, 133.2 (Ph), 156.76 (q, J_{CF} = 43.2 Hz, CF_3CO), 165.9 (CO). ^{19}F NMR (50.32 MHz, $CDCl_3$): δ_F −75.53 (CF_3CO).

4.8. Phenyl 3-*O*-benzoyl-2-*O*-triisopropylsilyl-1-thio-α-D-arabinofuranoside (10)

To the solution of diol **3** (63 mg, 0.16 mmol) in anhydrous Py (0.75 mL) TrCl (66.0 mg, 0.24 mmol) was added at 0 °C (ice-water bath). The reaction mixture was stirred at room temperature ~20 °C for 24 h. After this time diol **3** was consumed and TLC indicated the presence of triryl ether **8**. Then BzCl (170 μL, 1.47 mmol) was added to the solution at 0 °C (ice-water bath). The reaction mixture was stirred at room temperature ~20 °C for 1 h and then diluted with CH_2Cl_2 (40 mL), washed with water (40 mL), 1 M $KHSO_4$ (40 mL), water (40 mL), satd aq $NaHCO_3$ (40 mL). The aqueous layer was extracted with CH_2Cl_2 (7 mL). The combined organic extracts were filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~40 °C), and dried *in vacuo*. To the solution of the obtained benzoate **9** in CH_2Cl_2 (5 mL) 90% aq TFA (0.5 mL) was added. After 30 seconds the reaction mixture became yellow and reaction mixture was poured into satd aq $NaHCO_3$ (30 mL) with stirring. Organic phase was filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~40 °C), dried *in vacuo* and purified by silica gel column chromatography (light petroleum–EtOAc) to give alcohol **10** as a colorless oil (42 mg, 53% over three steps from **3** via **8** and **9**; R_f = 0.30, light petroleum–EtOAc, 9:1). $[\alpha]_D^{22}$ +101.1 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 525.2101 $[M + Na]^+$. Calcd for $C_{27}H_{38}O_5SSiNa$: 525.2101. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.14–1.19 (m, 21 H, $CH(CH_3)_2$), 3.97 (d, J = 3.8 Hz, 2 H, H-5a, H-5b), 4.51 (ddd ~q, J = 3.8 Hz, 1 H, H-4), 4.69 (d, J = 1.0 Hz, 1 H, H-2), 5.25–5.29 (m, 1 H, H-3), 5.58 (s, 1 H, H-1), 7.27–7.38 (m, 3 H, Ph), 7.48–7.65 (m, 5 H, Ph), 8.11–8.20 (m, 2 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 11.9

($CH(CH_3)_2$), 17.8 ($CH(CH_3)_2$), 62.4 (C-5), 80.6 (C-3), 81.6 (C-2), 84.6 (C-4), 94.8 (C-1), 127.5, 128.5, 129.0, 129.2, 129.7, 129.9, 131.8, 133.5, 134.6 (Ph), 165.9 (CO).

4.9. Phenyl 3-*O*-benzoyl-5-*O*-trifluoroacetyl-2-*O*-triisopropylsilyl-1-thio-α-D-arabinofuranoside (11)

To the solution of alcohol **10** (85 mg, 0.17 mmol) in anhydrous CH_2Cl_2 (0.5 mL) and anhydrous $(COCF_3)_2O$ (1 mL) and solid $NaOCOCF_3$ (12 mg, 0.17 mmol) were added at 0 °C (ice-water bath). After 1 h at 0 °C the reaction mixture was concentrated under reduced pressure (bath temperature ~30 °C), coevaporated with CCl_4 (30 mL), then dissolved in CCl_4 (20 mL), filtered through a Teflon filter (0.45 μm), concentrated under reduced pressure (bath temperature ~30 °C), and dried *in vacuo* to give trifluoroacetate **11** as a colorless oil (102 mg, 94%, R_f = 0.66 (petroleum ether–EtOAc, 9:1)). $[\alpha]_D^{20}$ +99.2 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 621.1921 [M + Na]$^+$. Calcd for $C_{29}H_{37}O_6SF_3SiNa$: 621.1930. ^{1}H NMR (300 MHz, $CDCl_3$)^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.05–1.12 (m, 21 H, $CH(CH_3)_2$), 4.64–4.77 (m, 4 H, H-2, H-4, H-5a, H-5b), 5.20 (dd, *J* = 2.8, 1.2 Hz, 1 H, H-3), 5.56 (s, 1 H, H-1), 7.29–7.39 (m, 3 H, Ph), 7.47–7.57 (m, 4 H, Ph), 7.60–7.67 (m, 1 H, Ph), 8.11–8.17 (m, 2 H, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 11.9 ($CH(CH_3)_2$), 17.8 ($CH(CH_3)_2$), 66.9 (C-5), 80.6 (C-3); 81.1, 81.7 (C-2, C-4), 95.0 (C-1), 114.49 (q, J_{CF} = 285.4 Hz, CF_3), 127.6, 128.6, 129.0, 129.1, 130.0, 131.89, 131.92, 131.96, 133.6, 134.2, 157.22 (q, J_{CF} = 42.8 Hz, CF_3CO), 165.7 (CO). ^{19}F NMR (75.5 MHz, $CDCl_3$): δ −75.59 (CF_3CO).

4.10. 4-(2-Chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-chloroacetyl-α-D-arabinofuranoside (15)

Glycosyl chloroacetate **14** (1.6 g, 3.13 mmol) and CEP-OH[37] (1.08 g, 6.26 mmol) were dissolved under Ar in CH_2Cl_2 (19 mL) at 0 °C (ice-water bath). Neat TfOH (41 μL, 0.47 mmol) was added and the reaction mixture was stirred at ~20 °C for 1 h. The mixture was diluted with

CH_2Cl_2 (45 mL), washed with H_2O (45 mL), satd aq $NaHCO_3$ (45 mL) and 5% aq NaOH (40 mL). Aqueous layer was extracted with CH_2Cl_2 (2×10 mL). Combined organic extracts were filtered through a cotton wool plug, concentrated, dried *in vacuo*, and purified by silica gel column chromatography (toluene–EtOAc, 8:1) to give **15** as a colorless oil (1.37 g, 74%; R_f = 0.43, toluene–EtOAc, 8:1). $[\alpha]_D^{28}$ +44.7 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 611.0843 $[M + Na]^+$. Calcd for $C_{29}H_{26}O_9Cl_2Na$: 611.0846. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.79 (t, *J* = 5.9 Hz, 2 H, OCH_2CH_2Cl), 4.03 (d, *J* = 1.9 Hz, 2 H, $COCH_2Cl$), 4.20 (t, *J* = 5.9 Hz, 2 H, OCH_2CH_2Cl), 4.65–4.83 (m, 2 H, H-5a, H-5b), 4.70–4.73 (m, 1 H, H-4), 5.55 (d, *J* = 3.9 Hz, 1 H, H-3), 5.62 (s, 1 H, H-2), 5.74 (s, 1 H, H-1), 6.88 (d, *J* = 9.0 Hz, 2 H, OC_6H_4O), 7.05 (d, *J* = 9.0 Hz, 2 H, OC_6H_4O), 7.39–7.54 (m, 4 H, Ph), 7.54–7.68 (m, 2 H, Ph), 8.02–8.16 (m, 4 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 40.3 ($COCH_2Cl$), 41.9 (CH_2Cl), 63.2 (C-5), 68.7 (OCH_2), 77.3 (C-3), 81.6 (C-4), 82.9 (C-2), 104.4 (C-1), 115.8, 118.3 (OC_6H_4O), 128.4, 128.5, 129.7, 129.9, 133.2, 133.7 (Ph), 150.4, 153.9 (OC_6H_4O), 165.7, 166.0, 166.2 (CO).

4.11. 4-(2-Chloroethoxy)phenyl 3,5-di-*O*-benzoyl-α-D-arabinofuranoside (16)

Chloroacetate **15** (1.3 g, 2.21 mmol) was dissolved in Py (16 mL) and water (8 mL). The reaction mixture was stirred at 80 °C (bath temperature) for 1 h. The mixture was diluted with CH_2Cl_2 (45 mL), washed with 1 M $KHSO_4$ (45 mL), H_2O (45 mL) and a mixture of satd aq $NaHCO_3$ (45 mL) with satd NaCl (15 mL). Aqueous layer was extracted with CH_2Cl_2 (2×10 mL). Combined extracts were filtered through the cotton wool plug, concentrated, dried *in vacuo*, and purified by silica gel column chromatography (light petroleum–EtOAc) to give alcohol **16** as a white foam (766 mg, 68%; R_f = 0.32, light petroleum–EtOAc, 3:1). $[\alpha]_D^{20}$ +45.4 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 535.1127. Calcd for $C_{27}H_{25}O_8ClNa$: 535.1130. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.27 (br. s, 1 H, O*H*), 3.79 (t, *J* = 5.9 Hz, 2 H, CH_2Cl), 4.20 (t, *J* = 5.9 Hz, 2 H, OCH_2), 4.62 (br. s, 1 H, H-2), 4.60-4.73 (m, 2 H, H-5a, H-5b), 4.74–4.80 (m, 1 H, H-4), 5.16

(dd, J = 6.0, 2.6 Hz, 1 H, H-3), 5.71 (s, 1 H, H-1), 6.84–6.90 (m, 2 H, OC_6H_4O), 6.99–7.05 (m, 2 H, OC_6H_4O), 7.39–7.51 (m, 4 H, Ph), 7.53–7.66 (m, 2 H, Ph), 8.04–8.10 (m, 4 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 41.9 (CH_2Cl), 63.7 (C-5), 68.7 (OCH_2), 79.7 (C-4), 81.6 (C-2), 82.0 (C-3), 106.7 (C-1), 115.9, 118.1 (OC_6H_4O), 128.5, 128.6, 129.7, 129.9, 133.2, 133.8 (Ph), 150.8, 153.6 (OC_6H_4O), 166.2, 167.3 (CO).

4.12. 1-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-D-arabinofuranose (17)

To the stirring solution of tribenzoate **21**[38] (250 mg, 0.52 mmol) in CH_2Cl_2 (1 mL) $BF_3{\cdot}Et_2O$ (240 µL, 1.90 mmol) was added at 0 °C (ice-water bath) followed after 5 min by Ac_2O (800 µL, 8.49 mmol). The reaction mixture was stirred at 0 °C for 1.5 h and then diluted with CH_2Cl_2 (30 mL), washed with water (25 mL) and satd $NaHCO_3$ (25 mL). Organic extract was filtered through a cotton wool plug, diluted with toluene (2×20 mL) and concentrated (bath temperature 40–50 °C), dried *in vacuo*, and purified by silica gel column chromatography (light petroleum–EtOAc) to give glycosyl acetate **17** as a white foam (250 mg, 94%; R_f = 0.24, light petroleum –EtOAc, 3:1, α:β = 3.9:1). HRESIMS: found *m/z* 543.1051 $[M + K]^+$. Calcd for $C_{28}H_{24}O_9K$: 543.1052. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.95 (s, 3 H, CH_3CO-β), 2.20 (s, 3 H, CH_3CO-α), 4.60 (ddd~dt, J = 4.3 Hz, 5.8 Hz, 1 H, H-4β), 4.68–4.83 (m, 5 H, H-5aβ, H-5aα, H-5bα, H-5bβ, H-4α), 5.65 (d, J = 3.7 Hz, 1 H, H-3α), 5.67 (s, 1 H, H-2α), 5.82 (dd, J = 6.8, 4.7 Hz, 1 H, H-2β), 5.98–6.03 (m, 1 H, H-3β), 6.50 (s, 1 H, H-1α), 6.67 (d, J = 4.8 Hz, 1 H, H-1β), 7.28–7.68 (m, 9 H, Ph), 8.00–8.13 (m, 6 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.8 (CH_3CO-β), 21.0 (CH_3CO_3-α), 63.5 (C-5α), 64.7 (C-5β), 75.5 (C-3β), 76.0 (C-2β), 77.5 (C-2α), 79.9 (C-4β), 81.2 (C-3α), 83.1 (C-4α), 93.7 (C-1β), 99.4 (C-1α), 128.3, 128.3, 128.4, 128.5, 128.6, 128.6, 128.7, 128.9, 129.5, 129.7, 129.8, 129.8, 129.9, 129.9, 133.1, 133.1, 133.6, 133.7, 133.7 (Ph), 165.1, 165.5, 166.1, 169.1 (CO).

4.13. 4-(2-Chloroethoxy)phenyl 2,3,5- tri-*O*-benzoyl-α-D-arabinofuranoside (18)

To a stirred solution of glycosyl acetate **17** (842 mg, 1.67 mmol) in anhydrous CH_2Cl_2 (10 mL) CEP-OH[37] (576 mg, 3.34 mmol) was added. The mixture was cooled to 0 °C (ice-water bath), then TfOH (22 μL, 0.25 mmol) was added. The reaction mixture was stirred at 0 °C for 1 h, then diluted with CH_2Cl_2 (50 mL), washed with water (50 mL), satd aq $NaHCO_3$ (50 mL). Organic phase was concentrated and dried *in vacuo*. The residue was purified by silica gel column chromatography (light petroleum–EtOAc, 3:1) to give glycoside **18** as a white foam (846 mg, 86%). R_f = 0.17 (light petroleum– EtOAc, 85:15). $[\alpha]_D^{19}$ +21.7 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 639.1392 $[M+Na]^+$. Calcd. for $C_{34}H_{29}ClNaO_9$: 639.1392. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.80 (t, 2 H, *J* = 5.9 Hz, CH_2Cl), 4.20 (t, 2 H, *J* = 5.9 Hz, OCH_2CH_2Cl), 4.69–4.89 (m, 3 H, H-4, H-5a, H-5b), 5.72 (d, 1 H, *J* = 3.3 Hz, H-3), 5.81 (s, 1 H, H-2), 5.89 (s, 1 H, H-1), 6.86–6.95 (m, 2 H, OC_6H_4O), 7.11 (m, 2 H, OC_6H_4O), 7.22–7.69 (m, 10 H, Ph), 7.99–8.19 (m, 5 H, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 42.0 (CH_2Cl), 63.7 (C-5), 68.8 (OCH_2), 77.8 (C-3), 82.0, 82.3 (C-2, C-4), 105.1 (C-1), 116.0, 118.5 (OC_6H_4O), 128.4, 128.6, 129.6, 129.9, 130.0, 133.2, 133.7 (Ph), 150.7, 153.9 (OC_6H_4O), 165.5, 165.9, 166.3 (CO).

4.14. 4-(2-Chloroethoxy)phenyl α-D-arabinofuranoside (19)

Tribenzoate **18** (200 mg, 0.34 mmol) was dissolved in CH_2Cl_2 (2 mL) and 0.1 M MeONa in MeOH (2 mL) was added to the reaction mixture, which then was stirred at ~20 °C for 48 h. The reaction mixture was neutralized with ion-exchange resin Dowex 50W×4 (H^+). The resin was filtered off, washed with MeOH (10 mL) and the filtrate was concentrated. The residue was purified by silica gel column chromatography (toluene–acetone, 1:1) to give triol **19** as a white foam (89 mg, 86%; R_f = 0.33, EtOAc). $[\alpha]_D^{20}$ +57.2 (*c* 1.0, MeOH). HRESIMS: found *m/z* 327.0609 $[M+Na]^+$. Calcd. for $C_{13}H_{17}ClNaO_6$: 327.0606. ^{1}H NMR (300 MHz, acetone-d_6): δ_H 3.64–3.81 (m, 2 H, H-5a, H-5b), 3.88 (m, 2 H, CH_2Cl), 4.07 (d, *J* = 3.3 Hz, 1 H, H-4), 4.07–4.14 (m, 1 H, H-3), 4.22 (s, 1 H, H-2), 4.23–4.27 (m, 2 H, OCH_2), 5.44 (d, *J* = 1.7 Hz, 1 H, H-1), 6.86–6.93 (m, 2 H, OC_6H_4O), 6.96–7.04 (m, 2 H, OC_6H_4O). ^{13}C NMR (75 MHz, acetone-d_6): δ_C

43.6 (CH_2Cl), 62.7 (C-5), 69.7 (OCH_2), 78.5 (C-4), 83.3 (C-2), 86.7 (C-3), 108.7 (C-1), 116.5, 119.0 (OC_6H_4O), 152.6, 154.5 (OC_6H_4O).

4.15. 4-(2-Chloroethoxy)phenyl 3,5-*O*-(di-*tert*-butylsilylene)-α-D-arabinofuranoside (20)

Triol **19** (70 mg, 0.23 mmol) was dissolved in anhydrous Py (1 mL), the reaction mixture was cooled to 0 °C (ice-water bath) and $(t\text{-Bu})_2Si(OTf)_2$ (81 μL) was added. After 2 h at 0°C the reaction mixture was quenched by MeOH (0.1 mL), coevaporated with toluene (30×2 mL) and purified by silica gel column chromatography (light petroleum–AcOEt, 5:1) to give silyl ether **20** (80 mg, 78 %) as a white foam. $[\alpha]_D^{18}$ +73.24 (*c* 1.0, $CHCl_3$);HRESIMS found *m/z* 467.1641 $[M+Na]^+$. Calcd. for $C_{21}H_{33}ClNaO_6Si$: 467.1627. ^{1}H NMR (300 MHz, CD_3OD): δ_H 1.03 and 1.10 (2 s, 18 H, $C(CH_3)_3$), 3.79 (t, J = 5.6 Hz, 2 H, CH_2Cl), 3.88–4.01 (m, 1 H, H-5a), 4.14–4.26 (m, 4H, CH_2O, H-3, H-4), 4.28–4.40 (m, 1 H, H-5b), 4.40–4.51 (m, 1 H, H-2), 5.43 (s, 1 H, H-1), 6.87 (br. s, 2 H, OC_6H_4O), 6.91–7.05 (m, 2H, OC_6H_4O). ^{13}C NMR (75.5 MHz, CD_3OD): δ_C 20.1 and 22.7 ($C(CH_3)_3$), 27.1 and 27.4 ($C(CH_3)_3$), 41.9 (CH_2Cl), 67.4 (C-5), 68.8 (CH_2O), 74.2, 81.3, 81.7 (C-2, C-3, C-4), 106.5 (C-1); 115.9, 117.8 (OC_6H_4O); 151.5, 153.6 (OC_6H_4O).

4.16. Methyl 3,5-*O*-(di-*tert*-butylsilylene)-α-D-arabinofuranoside (23)

To the solution of triol **22**[39] (89 mg, 0.54 mmol) in anhydrous Py (0.9 mL) $(t\text{-Bu})_2Si(OTf)_2$ (193 μL, 0.60 mmol) and DMAP (3.3 mg, 0.03 mmol) were added at 0 °C (ice-water bath). The reaction mixture was stirred at 0 °C for 2 h and then was quenched with MeOH and coevaporated with toluene, dried *in vacuo*, and purified by silica gel column chromatography (toluene–EtOAc, 20:1) to give alcohol **23** as a colorless oil (102 mg, 62%; R_f = 0.21, toluene–EtOAc, 20:1). $[\alpha]_D^{22}$ +51.4 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 327.1601 $[M + Na]^+$. Calcd for $C_{14}H_{28}O_5SiNa$: 327.1598. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.00 and 1.07 (2 s, 18H, $C(CH_3)_3$), 3.42 (s, 3 H, OCH_3), 3.91–3.98 (m, 3 H, H-3, H-4, H-5a), 4.09–4.14 (m, 1 H, H-5b), 4.29-4.40 (m, 1 H, H-2),

4.81 (d, J = 3.3 Hz, 1 H, H-1). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.1 and 22.6 (C(CH_3)$_3$), 27.1 and 27.4 (C(CH_3)$_3$), 56.1 (OCH_3), 67.5 (C-5), 73.8 (C-4), 81.54 (C-2), 81.6 (C-3), 109.0 (C-1).

4.17. Phenyl 3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-trifluoroacetyl-1-thio-α-D-arabinofuranoside (13)

To the solution of phenyl 3,5-*O*-(di-*tert*-butylsilylene)-1-thio-α-D-arabinofuranoside **38**[20] (56 mg, 0.15 mmol) in anhydrous CH_2Cl_2 (2 mL), $(CF_3CO)_2O$ (1 mL) and $NaOCOCF_3$ (10 mg, 0.07 mmol) were added to the stirring mixture at 0 °C (ice-water bath). After 1 h at 0 °C the reaction mixture was concentrated under reduced pressure (bath temperature ~30 °C), then dissolved in CCl_4 (30 mL), filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~30 °C), dried *in vacuo* to give **13** as a colorless oil (68 mg, 97%; R_f = 0.77, light petroleum–EtOAc, 10:1). HRESIMS: found *m/z* 501.3736 $[M + Na]^+$. Calcd for $C_{21}H_{29}O_5SF_3Si$: 501.1349. $[\alpha]_D^{19}$ +49.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.98–1.03, 1.03–1.08 (2 m, 18H, C(CH_3)$_3$), 3.89–4.15 (m, 2 H, H-5), 4.15–4.34 (m, 1 H, H-3), 4.33–4.50 (m, 1 H, H-4), 5.25–5.76 (m, 2 H, H-1, H-2), 7.23–7.45 (m, 2 H, Ph), 7.45–7.70 (m, 3 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.0 and 22.6 (C(CH_3)$_3$), 26.9 and 27.3 (C(CH_3)$_3$), 67.0 (C-5), 73.7 (C-4), 79.2 (C-3), 84.1 (C-2), 88.2 (C-1), 114.37 (q, J_{CF} = 285.6 Hz, CF_3), 126.6, 128.3, 129.1 (Ph), 156.56 (q, J_{CF} = 43.1 Hz, CF_3CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ_F −74.57 (CF_3CO).

4.18. General procedure for glycosylation of glycosyl acceptors. Preparation of compounds 26–35

A mixture of a thioglycosyde (**4**, **5**, **7**, **11**, **13**, **24**,[20] or **25**[7,29]) (0.042 mmol, 1.5 equiv.) and a glycosyl acceptor **16**, **20** or **23** (0.028 mmol, 1 equiv.) was dried *in vacuo* for 2 h, then anhydrous CH_2Cl_2 (1 mL) was added under argon. Freshly activated (220 °C, 6 h, *in vacuo*) powdered 4 Å molecular sieves (100 mg) were added under argon to the resulting solution and the reaction flask

was flushed with argon. The suspension was stirred under argon at ~22 °C for 1 h, then cooled to −78 °C (acetone–dry ice bath). Solid NIS (0.042 mmol, 1.5 equiv.) was added followed by AgOTf (0.003 mmol, 0.1 equiv, 1 mg). Then the temperature was allowed to rise slowly until appearance of persistent characteristic iodine color. This temperature, designated as *T* in Table 1, was kept for 30 min, and then the reaction mixture was allowed to warm to −10 °C during 30 min. The reaction was quenched by the addition of satd aq $NaHCO_3$ (50 μL). The reaction mixture was diluted with $CHCl_3$ (15 mL) and filtered through a Celite pad. The solids were thoroughly washed with $CHCl_3$ (50 mL) and the filtrate was successively washed with a mixture of satd aq $Na_2S_2O_3$ (50 mL) and satd. aq. $NaHCO_3$ (50 mL). The aqueous layer was back-extracted with $CHCl_3$ (2 × 5 mL). Combined organic extracts were filtered through a cotton wool plug, concentrated and dried in *vacuo*. In those cases when glycosyl donor contained TFA-groups the residue was additionally dissolved in MeOH (1.0 mL) and CH_2Cl_2 (1.0 mL) and then NEt_3 (40 μL) was added to the solution. The reaction mixture was stirred at ~20 °C for 40 min and then diluted with $CHCl_3$ (15 mL) and washed with satd aq $NaHCO_3$ (10 mL). The aqueous layer was back-extracted with $CHCl_3$ (2 × 5 mL). Combined organic extracts were filtered through a cotton wool plug, concentrated, dried in *vacuo*. The residue was applied onto a gel-chromatography column (50 × 2.5 cm) with Bio-Beads S×3 (200–400 mesh, Bio-Rad) using toluene as the eluent and a differential refractometer (Knauer) as the detector. The first eluted fraction contained disaccharides **26**–**35**, which was analyzed by NMR spectroscopy to give anomeric ratio values. The yields and α/β ratios are given in Table 1.

4.18.1. Data for 4-(2-chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[2-*O*-triisopropylsilyl-D-arabinofuranosyl]-α-D-arabinofuranoside (26) (entry 1, Table 1)

α/β = 1:2. R_f = 0.53, light petroleum–EtOAc, 4:1. HRESIMS: found *m/z* 823.283 [M + Na]$^+$. Calcd for $C_{41}H_{53}ClO_{12}SiNa$: 823.2887. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H = 0.96–1.06 (m, $CH(CH_3)_2$ (β and α), 3.66–3.72 (m, H-5^{II}α-a, H-5^{II}α-b), 3.72–3.76 (m, H-5^{II}β-a, H-5^{II}β-b, CH_2Cl),

3.76–3.79 (m, H-4^{II}β), 3.95 (br. s, H-3^{II}α), 4.13–4.16 (m, CH_2O, H-4^{II}α), 4.18 (s, H-2^{II}α), 4.19 (d, J = 4.5 Hz, H-2^{II}β), 4.26 (t, J = 7.63 Hz, H-3^{II}β), 4.47–4.55 (m, H-5^{I}α-a, H-5^{I}β-b, H-5^{I}β-a), 4.56 (br. s, H-2^{I}β), 4.59 (s, H-2^{I}α), 4.61 (d, J = 5.3 Hz, H-4^{I}α), 4.63–4.68 (m, H-4^{I}β, H-5^{I}α-b), 4.97 (d, J = 4.5 Hz, H-1^{II}β), 5.30 (s, H-1^{II}α), 5.32 (d, J = 3.8 Hz, H-3^{I}α), 5.56 (dd, J = 4.5, 2.4 Hz, H-3^{I}β), 5.65 (s, H-1^{I}β), 5.69 (s, H-1^{I}α), 6.81 (m, OC_6H_4O), 6.91 (d, J = 8.8 Hz, OC_6H_4O (β)), 6.97 (d, J = 9.1 Hz, OC_6H_4O (α)), 7.32–7.44, 7.46–7.52 (m, Ph), 7.55 (t, J = 7.0 Hz, Ph), 8.00 (t, J = 7.2 Hz, Ph), 8.03 (dd, J = 7.3, 4.4 Hz, Ph). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 11.8, 12.2 ($CH(CH_3)_2$, (β and α)), 17.7, 17.75, 17.83, 17.9 ($CH(CH_3)_2$ (β and α)), 41.9 (CH_2Cl), 62.7 (C-5^{II}α), 62.8 (C-5^{II}β), 63.8 (C-5^{I}α), 63.9 (C-5^{I}β), 68.8 (CH_2O), 74.5 (C-3^{II}β), 78.2 (C-3^{I}α, C-2^{II}β), 78.3 (C-3^{I}β), 78.6 (C-3^{II} α)), 80.4 (C-4^{I}β)), 80.9 (C-4^{I}α)), 81.7 (C-2^{II} α)), 82.2 (C-4^{II} β)), 84.9 (C-2^{I}α)), 85.9 (C-2^{I}β), 87.8 (C-4^{II} α), 102.0 (C-1^{II} β), 105.2 (C-1^{I}β), 105.7 (C-1^{I}α), 108.4 (C-1^{II} α), 115.88, 115.90 (OC_6H_4O (β and α)), 117.8 (OC_6H_4O (β)), 118.1 (OC_6H_4O (α)), 128.3, 128.4, 128.5, 129.15, 129.18, 129.7, 129.77, 129.79, 129.9, 130.0, 133.06, 133.14, 133.6, 133.7 (Ph (β and α)), 150.7 (OC_6H_4O (α)), 150.9 (OC_6H_4O (β)), 153.6 (OC_6H_4O (β)), 153.7 (OC_6H_4O (α)), 165.7, 166.2, 166.5 (CO).

4.18.2. Data for 4-(2-chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[5-*O*-benzoyl-2-*O*-triisopropylsilyl-D-arabinofuranosyl]-α-D-arabinofuranoside (27) (entry 5, Table 1)

α/β = 1.2:1. R_f = 0.25, light petroleum–EtOAc, 10:1. HRESIMS: found *m/z* 927.3077 [M + Na]$^+$, 922.3519 [M + NH_4]$^+$. Calcd for $C_{48}H_{57}ClO_{13}SiNa$: 927.3149. Calcd for $C_{48}H_{57}ClO_{13}SiNH_4$: 922.3595. Selected signals: ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.05 (br. s, 20 H, $CH(CH_3)_2$), 1.27 (s, $CH(CH_3)_2$), 3.75–3.87 (m, CH_2Cl), 3.96–4.06 (m), 4.09–4.25 (m), 4.11–4.24 (m, CH_2O), 4.26–4.34 (m), 4.38–4.73 (m, H-5^{I}α-a, H-5^{I}β-a, H-5^{I}α-b, H-5^{I}β-b, H-5^{II}α-a, H-5^{II}β-a, H-5^{II}α-b, H-5^{II}β-b), 5.14 (d, J = 3.5 Hz, 1 H, H-1^{II}β), 5.38 (s, 1 H, H-1^{II}α), 5.39–5.43 (m, 1 H, H-2^{I}α), 5.64 (dd, J = 4.6, 2.7 Hz, 1 H, H-3^{I}α), 5.73 (s, 1 H, H-1^{I}β), 5.82 (s, 1 H, H-1^{I}α), 6.72–

6.91 (m, 4 H, Ph), 6.93–7.06 (m, 4 H, OC_6H_4O), 7.14–7.26 (m, 4 H, OC_6H_4O), 7.32–7.66 (m, 20 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 11.8, 12.1 ($CH(CH_3)_2$), 17.7 $CH(CH_3)_2$), 41.9 (CH_2Cl), 62.8, 63.8, 64.1, 64.5 (C-5^{I}α, C-5^{I}β, C-5^{II}α, C-5^{II}β), 68.7 (CH_2O), 70.3, 76.4, 78.3, 78.6, 80.1, 80.4, 80.5, 81.0, 82.8, 84.2, 85.5, 86.4 (C-2α, C-2β, C-3α, C-3β, C-4α, C-4β), 102.2 (C-1^{II}β), 105.1 (C-1^{I}β), 106.1 (C-1^{I}α), 108.0 (C-1^{II}α), 115.8, 117.8, 118.0 (OC_6H_4O), 128.3, 128.5, 129.7, 129.8, 130.1, 133.1, 133.4, 133.5, 133.5, 133.6 (Ph), 153.6 (OC_6H_4O), 165.7, 166.0, 166.1, 166.1, 166.2 (CO).

4.18.3. Data for 4-(2-chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[3-*O*-benzoyl-2-*O*-triisopropylsilyl-D-arabinofuranosyl]-α-D-arabinofuranoside (28) (entry 6, Table 1)

α/β = 1:1. R_f = 0.25, light petroleum–EtOAc, 10:1. HRESIMS: found *m/z* 927.3067 [M + Na]$^+$, 922.3510 [M + NH_4]$^+$. Calcd for $C_{48}H_{57}ClO_{13}SiNa$: 927.3149. Calcd for $C_{48}H_{57}ClO_{13}SiNH_4$: 922.3595. Selected signals: ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.05 (br. s, 20 H, $CH(CH_3)_2$), 1.27 (s, $CH(CH_3)_2$), 3.23–4.02 (m, CH_2Cl), 4.02–4.12 (m), 4.12–4.27 (m), 4.27–4.41 (m, CH_2O), 4.43–4.91 (m), 5.01 (s), 5.14–5.27 (m), 5.36–5.54 (m), 5.84–5.67 (m, 1H), 6.94–6.68 (m, OC_6H_4O), 7.10–6.94 (m, OC_6H_4O), 7.33–7.10 (m, Ph), 7.71–7.33 (m, Ph), 8.25–7.92 (m, Ph), 8.42–8.29 (m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 11.8 ($CH(CH_3)_2$), 17.7 ($CH(CH_3)_2$), 41.9 (CH_2Cl) 62.8, 63.8, 64.1, 64.6 (C-5^{I}α, C-5^{I}β, C-5^{II}α, C-5^{II}β), 68.7 (CH_2O), 70.3, 76.4, 78.3, 78.6, 80.1, 80.6, 80.5, 81.0, 82.9, 84.2, 85.5, 86.4 (C-2α, C-2β, C-3α, C-3β, C-4α, C-4β), 102.2 (C-1^{II}β), 105.1 (C-1^{I}β), 106.2 (C-1^{I}α), 108.0 (C-1^{II}α), 115.9, 117.8, 118.0 (OC_6H_4O), 128.5, 128.4, 128.5, 129.2, 129.7, 129.8, 129.8, 129.9, 133.1, 133.4, 133.5 (Ph), 150.8, 150.9, 153.6 (OC_6H_4O), 165.7, 166.0, 166.1, 166.3 (CO).

4.18.4. Data for 4-(2-chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[3,5-*O*-(di-*tert*-butylsilylene)-D-arabinofuranosyl]-α-D-arabinofuranoside (29) (entry 7, Table 1)

α/β = 3.3:1. R_f = 0.26, light petroleum–EtOAc, 5:1. HRESIMS: found *m/z* 802.2964 $[M + NH_4]^+$, 807.2513 $[M + Na]^+$. Calcd for $C_{40}H_{49}ClO_{12}SiNH_4$: 802.3020. Calcd for $C_{40}H_{49}ClO_{12}Na$: 807.2574. Selected signals: ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.94–1.13 (m, $(CH_3)_3C$), 3.64–3.75 (m, H-4^{II}α), 3.75–3.83 (m, CH_2Cl), 3.85–4.14 (m, H-3^{II}α, H-5a^{II}), 4.14–4.26 (m, CH_2O, H-2^{II}α), 4.27–4.33 (m, 1 H, H-5^{II}-a), 4.52–4.75 (m, H-2^{I}α, H-4^{I}α, H-5^{I}-a, H-5^{I}-b), 4.76–4.85 (m, H-5^{II}-b), 5.25–5.32 (m, H-1^{II}α, H-1^{II}β), 5.43 (d, *J* = 3.5 Hz, H-3^{I}α), 5.77 (s, H-1^{I}β), 5.85 (s, H-1^{I}α), 6.82–6.92 (m, OC_6H_4O), 6.97–7.07 (m, OC_6H_4O), 7.38–7.52 (m, Ph), 7.52–7.65 (m, Ph), 8.01–8.13 (m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.1, 22.5 ($C(CH_3)_3$), 26.9, 27.4 ($C(CH_3)_3$), 41.9 (CH_2Cl), 63.7, 67.3 (C-5), 68.7 (CH_2O), 74.0 (C-4^{II}α), 78.3 (C-3^{I}α), 81.1 (C-3^{II}α), 81.5 (C-2^{II}α, C-4^{I}α), 85.8 (C-2^{I}α), 100.6 (C-1^{II}β), 105.0 (C-1^{I}β), 106.0 (C-1^{I}α), 108.1 (C-1^{II}α), 115.9, 117.9 (OC_6H_4O), 128.3, 128.5, 129.8, 133.3, 133.5 (Ph), 150.8, 153.5 (OC_6H_4O), 165.9, 166.4 (CO).

4.18.5. Data for 4-(2-chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-triisopropylsilyl-D-arabinofuranosyl]-α-D-arabinofuranoside (30) (entry 8, Table 1)

α/β = 1:4.5. R_f = 0.27, light petroleum–EtOAc, 20:1. HRESIMS: found *m/z* 958.4340 $[M + NH_4]^+$, 963.3906 $[M + Na]^+$. Calcd for $C_{49}H_{69}ClO_{12}Si_2NH_4$: 958.4354. Calcd for $C_{49}H_{69}ClO_{12}Si_2Na$: 963.3908. Selected signals: ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 0.98 (s, 9 H, $C(CH_3)_3$), 1.03–1.19 (m, 30 H, $C(CH_3)_3$, $CH(CH_3)_2$), 3.60–3.68 (m, 1 H, H-4^{II}β), 3.80 (t, *J* = 5.9 Hz, 2 H, CH_2Cl), 3.87–3.92 (m, 1 H, H-5^{II}β-a), 4.16 (dd, *J* = 9.2, 5.0 Hz, 1 H, H-5^{II}β-b), 4.19–4.23 (m, 3 H, CH_2O, H-3^{II}β), 4.24–4.30 (m, 2 H, H-2^{II}β), 4.57–4.61 (m, 3 H, H-2^{I}β, H-5^{I}β-a, H-5^{I}β-b), 4.71 (q, *J* = 5.2 Hz, 1 H, H-3^{I}β), 5.19 (d, *J* = 5.0 Hz, 1 H, H-1^{II}β), 5.21 (d, *J* = 3.0 Hz, 1 H, H-1^{II}α), 5.67 (dd, *J* = 4.5, 2.5 Hz, 1 H, H-4^{I}β), 5.79 (s, 1 H, H-1^{I}β), 5.85 (s, 1 H, H-1^{I}α), 6.85–6.90 (m, 2 H, OC_6H_4O), 7.02–7.06 (m, 2 H, OC_6H_4O), 7.35–7.66 (m, 6 H, Ph), 8.01–8.14 (m, 4 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 17.7 and 17.8 ($CH(CH_3)_2$), 20.0 and 22.6 ($C(CH_3)_3$), 27.1, 27.3, 27.4 ($C(CH_3)_3$), 41.9 (CH_2Cl), 64.4 (C-5^{I}), 68.2 (C-5^{II}), 68.8 (CH_2O), 73.8

(C-4^{II}), 77.9 (C-3^{II}), 78.4 (C-2^{II}), 78.8 (C-4^{I}), 81.1 (C-2^{I}), 87.2 (C-3^{I}), 102.0 (C-1^{II}β), 105.7 (C-1^{I}β), 106.0 (C-1^{II}α), 109.6 (C-1^{I}α), 115.9, 118.0 (OC_6H_4O), 128.3, 128.4, 129.5, 129.7, 129.8, 129.8 , 129.8, 133.0, 133.0, 133.3, 133.4 (Ph), 151.0, 153.6 (OC_6H_4O), 165.6, 166.1 (CO).

4.18.6. Data for 4-(2-chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-benzyl-D-arabinofuranosyl]-α-D-arabinofuranoside (31) (entry 10, Table 1)

α/β =1:2. R_f = 0.14, light petroleum–acetone, 10:1. HRESIMS: found *m/z* 897.3037 $[M + Na]^+$. Calcd for $C_{47}H_{55}ClO_{12}SiNa$: 897.3044. Selected signals: ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 1.00–1.10 (m, C(C*H*$_3$)$_3$), 5.20 (d, *J* = 4.9 Hz, H-1^{II}β), 5.34 (s, H-1^{I}β), 5.76 (s, H-1^{II}α), 5.83 (s, H-1^{I}α), 6.95–7.06 (m, OC_6H_4O), 7.14–7.66 (m, Ph), 8.08 (d, *J* = 7.6 Hz, Ph). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 27.1, 27.5 (C(CH$_3$)$_3$), 41.9 (CH_2Cl), 64.1, 64.2, 67.4, 68.1 (C-5^{II}α, C-5^{II}β, C-5^{I}α, C-5^{I}β), 68.8(CH_2O), 72.1, 72.2, 73.9, 74.1, 78.0, 78.3, 78.7, 81.1, 81.2, 81.2, 81.3, 86.3, 86.8, 87.6, 100.9 (C-1^{II}β), 105.4 (C-1^{II}α), 105.9 (C-1^{I}β), 107.4 (C-1^{I}α), 115.9, 117.9 (OC_6H_4O), 127.8, 128.0, 128.4, 128.5, 128.5, 129.8, 133.0, 133.1, 133.5 (Ph), 150.9, 153.6 (OC_6H_4O), 165.7, 166.2, 166.5 (CO).

4.18.7. Data for 4-(2-chloroethoxy)phenyl 3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-[2-*O*-triisopropylsilyl-D-arabinofuranosyl]-α-D-arabinofuranoside (32) (entry 2, Table 1)

α/β =1:6.3. R_f = 0.14, light petroleum–EtOAc, 3:2. HRESIMS: found *m/z* 755.3332 $[M + Na]^+$. Calcd for $C_{35}H_{61}ClO_{10}Si_2Na$: 755.3384. Selected signals: ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 0.92–1.13 (m, 39 H, C*H*(C*H*$_3$)$_2$), C(CH$_3$)$_3$)), 3.66 (dd, *J* = 13.0, 3.0 Hz, 1 H, H-5^{I}β-a), 3.87–3.92 (m, 4 H, CH_2Cl, H-5^{I}β-b, H-4^{II}β), 3.92–3.99 (m, 1 H, H-5^{II}β-a), 4.06–4.16 (m, 2 H, H-3^{I}β, H-4^{I}β), 4.19 (t, *J* = 5.9 Hz, 2 H, CH_2O), 4.24 (dd, *J* = 8.1, 4.4 Hz, 1 H, H-2^{II}β), 4.34 (dd, *J* = 9.2, 4.6 Hz, 1 H, H-5^{II}β-b), 4.50 (dd, *J* = 8.0, 3.9 Hz, 1 H, H-2^{I}β), 4.56 (t, *J* = 7.8 Hz, 1 H, H-3^{II}β), 5.04 (d, *J* = 4.5 Hz, 1 H, H-1^{II}β), 5.32 (s, H-1^{I}α), 5.40 (s, H-1^{II}α), 5.50 (d, *J* = 3.9 Hz, 1 H, H-1^{I}β), 6.82–6.87 (m, 2 H, OC_6H_4O), 6.95–6.99 (m, 2 H, OC_6H_4O). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 12.1 (*C*H(CH$_3$)$_2$), 17.8 (CH(*C*H$_3$)$_2$), 20.1 and 22.7 (C(*C*H$_3$)$_3$), 27.0 and 27.3 (*C*(CH$_3$)$_3$)), 41.9 (CH_2Cl), 61.3 (C-5^{I}β), 67.2 (C-5^{II}β), 68.8 (CH_2O), 73.4 (C-3^{I}β), 74.1 (C-3^{II}β), 78.4, 78.5 (C-2^{II}β, C-4), 84.6 (C-

4^{I}β), 85.5 (C-2^{I}β), 100.6 (C-1^{II}β), 105.1 (C-1^{I}β), 105.8 (C-1^{II}α), 108.2 (C-1^{I}α), 115.9, 117.3, 118.2 (OC_6H_4O), 151.5, 153.6 (OC_6H_4O).

4.18.8. Data for 4-(2-chloroetoxy)phenyl 3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-[3,5-*O*-(di-*tert*-butylsilylene)-D-arabinofuranosyl]-α-D-arabinofuranoside (33) (entry 9, Table 1)

α/β = 1:3. R_f =0.75, light petroleum–EtOAc 10:1. HRESIMS: found *m/z* 895.4433 $[M + Na]^+$. Calcd for $C_{43}H_{77}ClO_{10}Si_3Na$: 895.4405. Selected signals:^{1}H NMR (600 MHz, $CDCl_3$): δ_H 0.94–1.20 (m, $CH(CH_3)_2$, $C(CH_3)_3$), 3.69–3.76 (m), 3.77–3.85 (m), 3.78–3.83 (m, CH_2Cl), 3.85–4.02 (m), 4.05–4.18 (m), 4.19–4.22 (m, CH_2O), 4.23–4.41 (m), 5.12 (d, *J* = 4.1 Hz, H-1^{II}β), 5.15 (d, *J* = 3.0 Hz, H-1^{II}α), 5.48 (d, *J* = 2.9 Hz, H-1^{I}α), 5.57 (d, *J* = 3.0 Hz, 1 H, H-1β), 6.81–6.90 (m, OC_6H_4O), 6.91–7.02 (m, OC_6H_4O). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 12.0, 17.8 ($CH(CH_3)_2$), 22.6 and 22.7 ($C(CH_3)_3$), 27.0 and 27.3 ($C(CH_3)_3$), 41.9 (CH_2Cl), 67.4, 67.5 (C-5α, C-5β), 68.8 (CH_2O), 73.5, 73.7, 74.7, 76.4, 79.0, 79.2, 80.3, 88.1 (C-2α, C-2β, C-3α, C-3β, C-4α, C-4β), 101.2 (C-1^{II}β), 105.9 (C-1^{II}α), 106.6 (C-1^{I}α), 109.4 (C-1^{I}β), 115.7, 115.8, 117.7, 118.7 (OC_6H_4O), 151.5, 153.4 (OC_6H_4O).

4.18.9. Data for methyl 3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-[2-*O*-triisopropylsilyl-D-arabinofuranosyl]-α-D-arabinofuranoside (34) (entry 3, Table 1)

α/β =1:5.6. R_f = 0.27, light petroleum–EtOAc, 6:1. HRESIMS: found *m/z* 615.3356 $[M + Na]^+$. Calcd for $C_{28}H_{56}O_9Si_2Na$: 615.3356. Selected signals: ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 0.10–1.03 (m, $CH(CH_3)_2$), 1.50–1.13 (m, $C(CH_3)_3$, $C(CH_3)_3$), 3.35 (s, 3 H, CH_3), 3.63 (dd, *J* = 12.9, 2.9 Hz, 1 H, H-5^{I}β-a), 3.75–3.79 (m, 1 H, H-5^{I}β-b), 3.83–3.87 (m, 1 H, H-4^{I}β), 3.88–3.95 (m, 2 H, H-4^{II}β, H-5^{II}β-a), 4.03 (t, *J* = 8.7 Hz, 1 H, H-3^{II}β), 4.14–4.18 (m, 1 H, H-2^{II}β), 4.21–4.26 (m, 1 H, H-2^{I}β), 4.29–4.33 (m, 1 H, H-5^{II}β-b), 4.52 (t, *J* = 7.7 Hz, 1 H, H-3^{I}β), 4.79 (d, *J* = 3.0 Hz, H-1^{II}α), 4.83 (d, *J* = 3.9 Hz, 1 H, H-1^{II}β), 4.96 (d, *J* = 4.5 Hz, 1 H, H-1^{I}β), 5.26 (s, H-1^{I}α). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 12.2 ($CH(CH_3)_2$), 17.8 ($CH(CH_3)_2$), 22.6 ($C(CH_3)_3$), 27.3 and 27.3 ($C(CH_3)_3$)), 55.9 (CH_3), 61.4 (C-5^{I}β), 67.4 (C-5^{II}β), 73.4, 73.6 (C-3^{I}β, C-4^{II}β), 78.5, 78.7

(C-2^{I}β, C-3^{II}β), 81.8 (C-4^{I}β), 85.2 (C-2^{II}β), 100.5 (C-1^{I}β), 105.4 (C-1^{II}α), 107.7 (C-1^{II}β), 107.9 (C-1^{I}α).

4.18.10. Data for methyl 3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-[2-*O*-triisopropylsilyl-3,5-di-*O*-pentafluoropropionyl-D-arabinofuranosyl]-α-D-arabinofuranoside (35) (entry 4, Table 1)

α/β = 1:5.5. R_f = 0.77, toluene. HRESIMS: found *m/z* 1630.4665 $[M + Na]^+$. Calcd for $C_{81}H_{81}N_3O_{32}Na$: 1630.4695. Selected signals: ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 0.99 (br. s, $CH(CH_3)_2$), 1.02–1.18 (m, 18 H, $C(CH_3)_3$), 3.38 (br. s, 3 H, CH_3), 3.90–3.97 (m, 2 H, H-4^{II}β, H-5^{II}β-b), 4.07 (t, *J* = 8.5 Hz, 1 H, H-3^{II}β), 4.16–4.21 (m, 2 H, H-2^{II}, H-4^{I}), 4.32–4.36 (m, 1 H, H-5^{II}β-a), 4.59–4.64 (m, 2 H, H-2^{I}β, H-5^{I}β-b), 4.74 (d, *J* = 3.2 Hz, 1 H, H-1^{II}a), 4.77 (dd, *J* = 11.4, 6.2 Hz, 1 H, H-5^{I}β-a), 4.85 (d, *J* = 3.4 Hz, 1 H, H-1^{II}β), 5.14 (d, *J* = 4.2 Hz, 1 H, H-1^{I}β), 5.33 (s, 1 H, H-1^{I}a), 5.46 (dd, *J* = 6.6, 5.2 Hz, 1 H, H-3^{I}β). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 12.1 (*C*H$(CH_3)_2$), 17.6 and 17.7 (CH(*C*$H_3)_2$), 20.10 and 22.6 (*C*$(CH_3)_3$), 27.0, 27.3, 27.3, 29.7 (C(*C*$H_3)_3$), 55.8 (CH_3), 66.6, 67.44 (C-5^{I}α, C-5^{II}α), 67.39 (C-5^{II}β), 68.9 (C-5^{I}β), 73.4, 73.7, 77.6, 79.3 (C-2^{I}β), 79.6, 80.1, 80.9, 83.1, 83.3 (C-3^{I}β), 85.3 (C-4^{I}β), 100.9 (C-1^{II}β), 107.5 (C-1^{I}β, C-1^{II}α), 107.7 (C-1^{I}α).

4.19. 4-(2-Chloroethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[β-D-arabinofuranosyl]-α-D-arabinofuranoside (36)

Acetic acid (142 µL, 2.5 mmol) and a 1.0 M solution of Bu_4NF in THF (840 µL, 0.84 mmol) were added in that order to the solution of anomeric mixture (α/β = 1:4.5) of disaccharide **30** as a mixture of isomers (130 mg, 0.20 mmol) in anhydrous THF (2 mL) under argon (ice-water bath). The reaction mixture was stirred at ~20 °C for 24 h, then diluted with toluene (20 mL), concentrated (bath temperature 40–50 °C), dried *in vacuo*, and purified by silica gel column chromatography (light petroleum–acetone, 1:1) to give **36** as a colorless oil (89 mg, ~100% (mixture of isomers); R_f = 0.38, light petroleum–acetone, 1:1). This mixture was subjected to the

preparative HPLC (*i*-PrOH–$CHCl_3$–petroleum ether, 1:3:6) to give pure β-isomer of **36** (53 mg, 60% from **16** over two steps, t_R = 29.0 min (analytical HPLC in the same eluent)). $[\alpha]_D^{23}$ +33.8 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 667.1544 $[M + Na]^+$. Calcd for $C_{32}H_{33}O_{12}ClNa$: 667.1553. ^1H NMR (600 MHz, acetone-d_6): δ_H 3.66–3.72 (m, 2 H, H-5^{II}-a, H-5^{II}-b), 3.77–3.81 (m, 1 H, H-4^{II}), 3.87 (t, *J* = 5.4 Hz, 2 H, CH_2Cl), 4.05 (dd, *J* = 7.2, 4.6 Hz, 1 H, H-2^{II}), 4.14 (dd~t, *J* = 7.1 Hz, 1 H, H-3^{II}), 4.25 (t, *J* = 5.4 Hz, 2 H, OCH_2), 4.60–4.65 (m, 1 H, H-5^{I}-a), 4.68–4.71 (m, 1 H, H-5^{I}-b), 4.71–4.75 (m, 1 H, H-4^{I}), 4.77 (d, *J* = 1.7 Hz, 1 H, H-2^{I}), 5.26 (d, *J* = 4.6 Hz, 1 H, H-1^{II}), 5.70 (dd, *J* = 4.6, 1.7 Hz, 1 H, H-3^{I}), 5.89 (s, 1 H, H-1^{I}), 6.91–6.95 (m, 2 H, OC_6H_4O), 7.06–7.09 (m, 2 H, OC_6H_4O), 7.49 (m~t, *J* = 7.8 Hz, 2 H, Ph), 7.55 (m~t, *J* = 7.8 Hz, 2 H, Ph), 7.61 (m~t, *J* = 7.4 Hz, 1 H, Ph), 7.67 (m~t, *J* = 7.4 Hz, 1 H, Ph), 8.07 (m~d, *J* = 7.5 Hz, 2 H, Ph), 8.12 (m~d, *J* = 7.5 Hz, 2 H, Ph). ^{13}C NMR (151 MHz, acetone-d_6): δ_C 43.5 (CH_2Cl), 64.2 (C-5^{II}), 65.2 (C-5^{I}), 69.9 (OCH_2), 76.2 (C-3^{II}), 79.1 (C-2^{I}), 79.6 (C-3^{I}), 82.2 (C-4^{I}), 84.9 (C-4^{II}), 86.5 (C-2^{I}), 103.0 (C-1^{II}), 106.4 (C-1^{I}), 116.8, 119.4 (C_6H_4), 129.5, 129.6, 130.6, 130.7, 130.8, 131.1, 134.1, 134.5 (Ph), 152.0, 155.0 (OC_6H_4O), 166.8 (CO). HMBC data: C-2^{I}/H-1^{II} and C-1^{II}/H-2^{I}.

4.20. 4-(2-Azidoethoxy)phenyl 3,5-di-*O*-benzoyl-2-*O*-[β-D-arabinofuranosyl]-α-D-arabinofuranoside (37)

A mixture of CEP glycoside **36** (51 mg, 0.08 mmol), NaN_3 (16 mg, 0.24 mmol) and 18-crown-6 (10 mg, 0.04 mmol) in anhydrous DMF (0.8 mL) was stirred at 80 °C for 48 h. The reaction mixture was diluted with toluene (3 × 15 mL) and concentrated (bath temperature 40–50 °C) and dried *in vacuo*. The residue was dissolved in EtOAc (30 mL), washed with water (20 mL), aqueous layer was extracted with EtOAc (5 mL). Combined organic extracts were filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~35 °C) and purified by silica gel column chromatography (light petroleum–EtOAc) to give **37** as a white foam (40.6 mg, 78%; R_f = 0.23, light petroleum–EtOAc, 1:2). $[\alpha]_D^{24}$ +34.8 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 674.1949 $[M + Na]^+$. Calcd for $C_{32}H_{33}O_{12}N_3Na$: 674.1956749. ^1H NMR (600 MHz,

$CDCl_3$): δ_H 3.56 (t, J = 4.8 Hz, 2 H, CH_2N_3), 3.70–3.76 (m, 1 H, H-5^{II}-a), 3.82–3.88 (m, 2 H, H-4^{II}, H-5^{II}-b), 4.09 (t, J = 4.9 Hz, 2 H, OCH_2), 4.10–4.14 (m, 1 H, H-2^{II}), 4.30 (t, J = 7.6 Hz, 1 H, H-3^{II}), 4.59–4.63 (m, 2 H, H-5^{I}-a, H-5^{I}-b), 4.63–4.65 (m, 1 H, H-2^{I}), 4.74 (m, 1 H, H-4^{I}), 5.13 (d, J = 4.6 Hz, 1 H, H-1^{II}), 5.54 (d, J = 3.2 Hz, 1 H, H-3^{I}), 5.75 (s, 1 H, H-1^{I}), 6.84 (d, J = 8.9 Hz, 2 H, OC_6H_4O), 6.99 (d, J = 8.9 Hz, 2 H, OC_6H_4O), 7.38 (m~t, J = 7.7 Hz, 2 H, Ph), 7.46 (m~t, J = 7.7 Hz, 2 H, Ph), 7.52 (m~t, J = 7.4 Hz, 1 H, Ph), 7.61 (m~t, J = 7.4 Hz, 1 H, Ph), 8.01 (m~d, J = 7.6 Hz, 2 H, Ph), 8.08 (m~d, J = 7.6 Hz, 2 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 50.2 (CH_2N_3), 61.9 (C-5^{II}), 64.0 (C-5^{I}), 67.6 (O*C*H$_2$), 74.2 (C-3^{II}), 77.8 (C-2^{II}), 78.8 (C-3^{I}), 80.6 (C-4^{I}), 82.5 (C-4^{II}), 85.4 (C-2^{I}), 101.2 (C-1^{II}), 104.9 (C-1^{I}), 115.7, 117.9 (C_6H_4), 128.4, 128.5, 129.0, 129.5, 129.8, 129.9, 133.2, 133.7 (Ph), 150.5, 153.7 (OC_6H_4O), 166.4, 166.5 (CO). HMBC data: C-2^{I}/H-1^{II} and C-1^{II}/H-2^{II}.

4.21. 4-(2-Azidoethoxy)phenyl 2-*O*-(β-D-arabinofuranosyl)-α-D-arabinofuranoside (38)

4.21.1. Synthesis of 4-(2-Azidoethoxy)phenyl 2-*O*-(β-D-arabinofuranosyl)-α-D-arabinofuranoside (38)

A. To the solution of dibenzoate **37** (40 mg, 0.06 mmol) in MeOH (860 µL) 1 M MeONa in MeOH (195 µL) was added. After stirring at ~20 °C for 48 h the reaction was neutralized with CO_2, concentrated under reduced pressure (bath temperature ~35 °C), dissolved in water (15 mL) and washed with light petroleum (15 mL). The aqueous phase was stirred for 10 min with ion-exchange resin Dowex 50W×4 (PyH^+). The resin was filtered off, washed with H_2O (10 mL) and the filtrate was coevaporated with toluene (25 mL) and CCl_4 (25 mL), concentrated under reduced pressure (bath temperature ~45 °C), dried *in vacuo* to give **38** as a white solid (25 mg, 92%; R_f = 0.63, EtOAc–*i*-PrOH–AcOH, 7:13:1).

B. A mixture of CEP glycoside **39** (15 mg, 0.023 mmol), NaN_3 (4 mg, 0.07 mmol) and 18-crown-6 (3 mg, 0.01 mmol) in anhydrous DMF (0.5 mL) was stirred at 80 °C for 48 h. The reaction

mixture was diluted with toluene (3 × 15 mL) and concentrated (bath temperature 40–50 °C) and dried *in vacuo*. The residue was dissolved in EtOAc (30 mL), washed with water (20 mL), aqueous layer was extracted with EtOAc (5 mL). Combined organic extracts were filtered through a cotton wool plug, concentrated under reduced pressure (bath temperature ~35 °C) to give azide **40** (15 mg, quantitative yield; R_f = 0.23, light petroleum–EtOAc, 1:2). HRESIMS: found *m/z* 674.1953 [M + Na]. Calcd for $C_{32}H_{33}O_{12}N_3Na$: 674.1956; found *m/z* 674.2405 [M + NH_4]. Calcd for $C_{32}H_{33}O_{12}N_3$+NH_4: 690.1685; found *m/z* 1015.3915 [M + K]. Calcd for $C_{32}H_{33}O_{12}N_3K$: 690.1696. Azide **40** (15 mg, 0.023 mmol) without further purification was dissolved in MeOH (860 µL) and 1 M MeONa in MeOH (195 µL) was added. After stirring at ~20 °C for 48 h the reaction mixture was applied on a column with Sepadex LH-20 (packed in MeOH), the product was eluted with MeOH and then additionally purified on a Sep-Pak C18 cartridge (in water), which was eluted with water, then with gradient MeOH in water (0→100%) to give CEP glycoside **38** (9 mg, 90% from **39** over two steps) identical to the sample described above.

4.21.2. Data for 4-(2-azidoethoxy)phenyl 2-*O*-(β-D-arabinofuranosyl)-α-D-arabinofuranoside (38)

$[\alpha]_D^{25}$ +19.3 (*c* 1.0, MeOH). HRESIMS: found *m/z* 466.1426 $[M + Na]^+$. Calcd for $C_{18}H_{25}O_{10}N_3Na$: 446.1432. ^{1}H NMR (500 MHz, CD_3OD): δ_H 3.55 (t, *J* = 4.7 Hz, 2 H, CH_2N_3), 3.64–3.70 (m, 2 H, H-5^I-a, H-5^{II}-a), 3.74–3.83 (m, 2 H, H-5^I-b, H-5^{II}-b), 3.98–4.01 (m, 1 H, H-4^{II}), 4.02–4.06 (m, 2 H, H-4^I, H-2^{II}), 4.11 (t, *J* = 4.8 Hz, 2 H, OCH_2), 4.16 (dd, *J* = 7.8, 5.5 Hz, 1 H, H-3^I), 4.35 (dd, *J* = 5.5, 2.0 Hz, 1 H, H-2^I), 5.03 (d, *J* = 4.3 Hz, 1 H, H-1^{II}), 5.57 (d, *J* = 2.0 Hz, 1 H, H-1^I), 6.87 (d, *J* = 9.0 Hz, 2 H, OC_6H_4O), 7.01 (d, *J* = 9.0 Hz, 2 H, OC_6H_4O). ^{13}C NMR (125 MHz, CD_3OD): δ_C 51.6 (CH_2N_3), 62.4 (C-5^I), 64.5 (C-5^{II}), 69.1 (OCH_2), 75.8 (C-3^{II}), 76.1 (C-3^I), 78.9 (C-2^{II}), 84.6 (C-4^I, C-4^{II}), 89.9 (C-2^I), 102.8 (C-1^{II}), 106.8 (C-1^I), 116.6, 119.5 (OC_6H_4O), 152.8, 155.3 (OC_6H_4O). HMBC data: C-2^I/H-1^{II} and C-1^{II}/H-2^{II}.

4.22. 4-(2-Chloroethoxy)phenyl 2-*O*-[3,5-di-*O*-benzoyl-β-D-arabinofuranosyl]-α-D-arabinofuranoside (39)

To the solution of diol **32** (55 mg, 0.05mmol) in Py (1 mL) BzCl (30 μL, 0.25 mmol) was added at 0 °C (ice–water bath). After 1 h at 0 °C the reaction mixture was quenched by the addition of H_2O (0.2 mL), diluted with $CHCl_3$ (50 mL), washed with H_2O (50 mL), 1 M $KHSO_4$ (50 mL), H_2O (50 mL) and satd aq $NaHCO_3$ (50 mL). Organic extract was filtered through a cotton wool plug and concentrated under reduced pressure (bath temperature ~30 °C) and dried *in vacuo*. The residue was dissolved in THF (1 mL) then acetic acid (142 μL, 2.5 mmol) and a 1.0 M solution of Bu_4NF in THF (840 μL, 0.84 mmol) were added under argon (ice–water bath). The reaction mixture was stirred at ~20 °C for 24 h, then diluted with toluene (20 mL), concentrated (bath temperature 40–50 °C), dried *in vacuo* and purified by silica gel column chromatography (light petroleum– EtOAc, 5:1→3:1→1:1) to give **39** as a colorless oil (27 mg, ~84%; R_f = 0.68, light petroleum–acetone, 1:1). This mixture was subjected to the preparative HPLC (*i*-PrOH–$CHCl_3$–petroleum ether, 0.3:3:6) to give **39** as the sinle β-anomer (15 mg, 47% from **32** over two steps). $[\alpha]_D^{23}$ +9.8 (*c* 1.0, $CHCl_3$). HRESIMS: found *m/z* 667.1544 $[M + Na]^+$. Calcd for $C_{32}H_{33}O_{12}ClNa$: 667.1553. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 1.74 (br. s, 1 H, OH), 2.28 (br. s, 1 H, OH), 3.26 (br. s, 1 H, OH), 3.74 (dd, *J* = 12.3, 2.8 Hz, 1 H, H-5^I-a), 3.75–3.82 (m, 2 H, CH_2Cl), 3.89 (dd, *J* = 12.3, 2.67 Hz, 1 H, H-5^I-b), 4.15–4.23 (m, 3 H, CH_2O, H-4^I), 4.32–4.38 (m, 1 H, H-3^I), 4.43–4.46 (m, 1 H, H-4^{II}), 4.45–4.51 (m, 1 H, H-2^I), 4.55 (br. s, 1 H, H-2^{II}), 4.67 (dd, *J* = 11.9, 3.4 Hz, 1 H, H-5^{II}-a), 4.89 (dd, *J* = 11.9, 8.4 Hz, 1 H, H-5^{II}-b), 5.28 (d, *J* = 4.6 Hz, 1 H, H-1^{II}), 5.42 (t, *J* = 5.9 Hz, 1 H, H-3^{II}), 5.56 (d, *J* = 2.1 Hz, 1 H, H-1^I), 6.80–6.89 (m, 2 H, OC_6H_4O), 6.94–7.01 (m, 2 H, OC_6H_4O), 7.39–7.50 (m, 4 H, Ph), 7.53–7.65 (m, 2 H, Ph), 8.06 (t, *J* = 7.3 Hz, 4 H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 41.9 (CH_2Cl), 61.4 (C-5^I), 65.7 (C-5^{II}), 68.8 (CH_2O), 75.2 (C-3^I), 76.2 (C-2^{II}), 79.2 (C-3^{II}), 80.0 (C-4^{II}), 82.7 (C-4^I), 90.0 (C-2^I), 102.0

($C\text{-}1^{II}$), 104.7 ($C\text{-}1^{I}$), 115.9, 118.1 (OC_6H_4O), 128.5, 129.8, 133.5, 133.7 (Ph), 151.0,153.7 (OC_6H_4O), 166.5, 166.6 (CO).

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Supplementary data

Supplementary data section contains the copies of NMR spectra of prepared compounds. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.xxxxxx.

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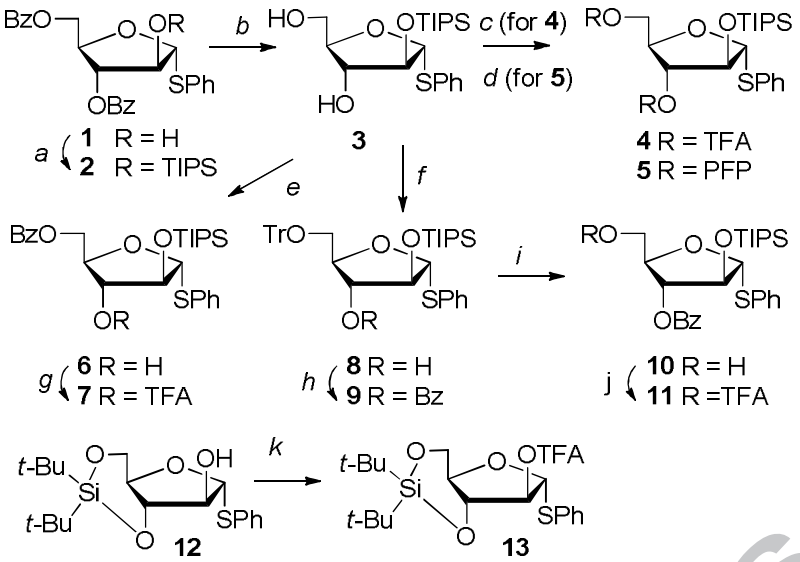
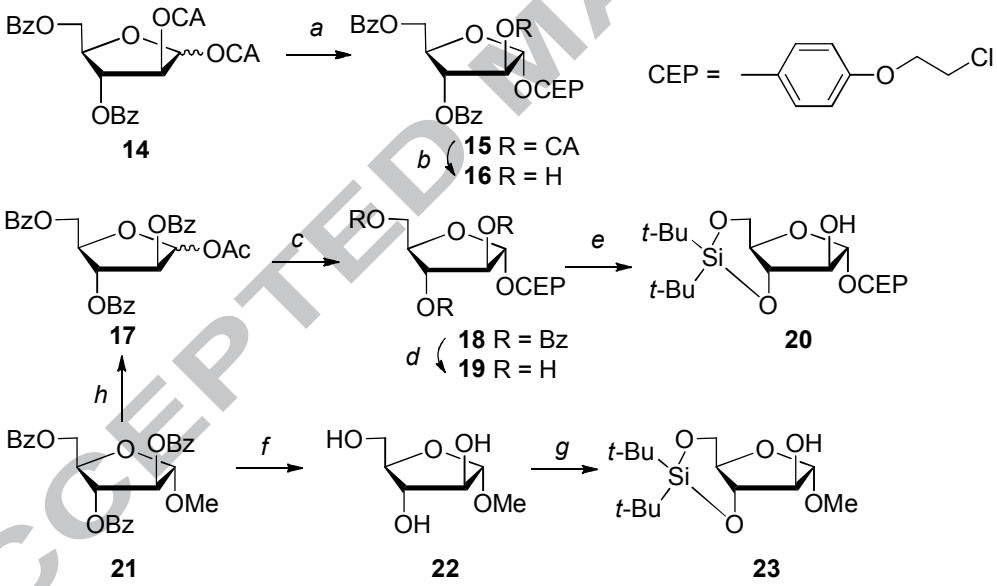
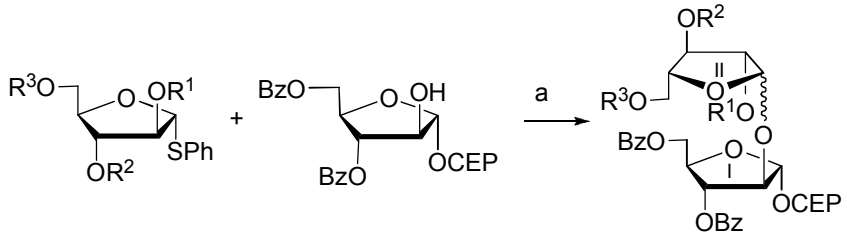


Scheme 1. Synthesis of TFA-protected glycosyl donors **4**, **7**, **11, 13** and PFP-protected glycosyl donor **5**. *Reagents and conditions*: *a*. TIPSOTf, *sym*-collidine, DMF, 90 °C (98%). *b*. MeONa, MeOH, 20 °C, 20 h (89%). *c*. $(CF_3CO)_2O$, CF_3CO_2Na (cat.), CH_2Cl_2 0 °C, 1.5 h (98%). *d.* $(CF_3CF_2CO)_2O$, Py, 0 °C, (66%). *e*. BzCl, Py, 0 °C (80%). *f.* TrCl, Py, 20 °C, 12 h. *g*. $(CF_3CO)_2O$, CF_3CO_2Na (cat.), CH_2Cl_2 0 °C, 1.5 h (94%). *h.* BzCl, Py, 20 °C. *i*. TFA–H_2O–CH_2Cl_2 (10:1:90), 20 °C (53% from **3** via **8** and **9** over 3 steps). *j.* $(CF_3CO)_2O$, CF_3CO_2Na (cat.), CH_2Cl_2 0→20 °C, 1.5 h (94%). *k.* $(CF_3CO)_2O$, CF_3CO_2Na (cat.), CH_2Cl_2 0 °C, 1.5 h (97%). TIPS = $(i\text{-Pr})_3Si$, PFP = $COCF_2CF_3$, TFA = $COCF_3$.



Scheme 2. Synthesis of glycosyl acceptors **16**, **20**, **23**. *Reagents and conditions*: *a*. CEP-OH, TfOH, CH_2Cl_2, 0 °C (74%). *b.* Py, H_2O, 80 °C, 1 h (68%). *c*. CEP-OH, TfOH, CH_2Cl_2, 0 °C, 1.5 h (86%). *d.* MeONa, MeOH, 20 °C, 20 h (86%). *e*. $(t\text{-Bu})_2Si(OTf)_2$, Py, 2 h, 20 °C (78%). *f.* MeONa, MeOH (see Ref. 39). *g*. $(t\text{-Bu})_2Si(OTf)_2$, Py, 2 h, 20 °C (62%). *h*. Ac_2O, $BF{\cdot}Et_2O$, CH_2Cl_2, 0 °C (94%).

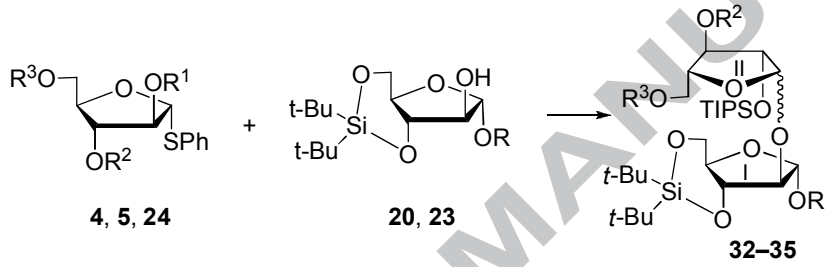


4, 7, 11, 13, 24, 25 **16** **26–31**

4 R^1 = TIPS, R^2 = R^3 = TFA
7 R^1 = TIPS, R^2 = TFA, R^3 = Bz
11 R^1 = TIPS, R^2 = Bz, R^3 = TFA
13 R^1 = TFA, R^2,R^3 = $(t\text{-Bu})_2$Si
24 R^1 = TIPS, R^2,R^3 = $(t\text{-Bu})_2$Si
25 R^1 = Bn, R^2,R^3 = $(t\text{-Bu})_2$Si

26 R^1 = H, R^2,R^3 = $(t\text{-Bu})_2$Si (from **13**+**16**)
27 R^1 = TIPS, R^2 = H, R^3 = Bz (from **7**+**16**)
28 R^1 = TIPS, R^2 = Bz, R^3 = H (from **11**+**16**)
29 R^1 = TIPS, R^2 = R^3 = H (from **4**+**16**)
30 R^1 = Bn, R^2,R^3 = $(t\text{-Bu})_2$Si (from **25**+**16**)
31 R^1 = TIPS, R^2,R^3 = $(t\text{-Bu})_2$Si (from **24**+**16**)

Scheme 3. Reactions of glycosyl acceptor **16** with glycosyl donors **4**, **7**, **11**, **13**, **24**, **25**. *Reagents and conditions*:1. AgOTf, NIS, MS 4Å, CH_2Cl_2, −78 °C → *T* °C, then 30 min at *T*, then → −10 °C over 30 min; 2. MeOH, NEt_3, CH_2Cl_2, 20 °C (for **26**–**29**). 3. Gel-chromatography on Bio-Beads S×3, toluene.



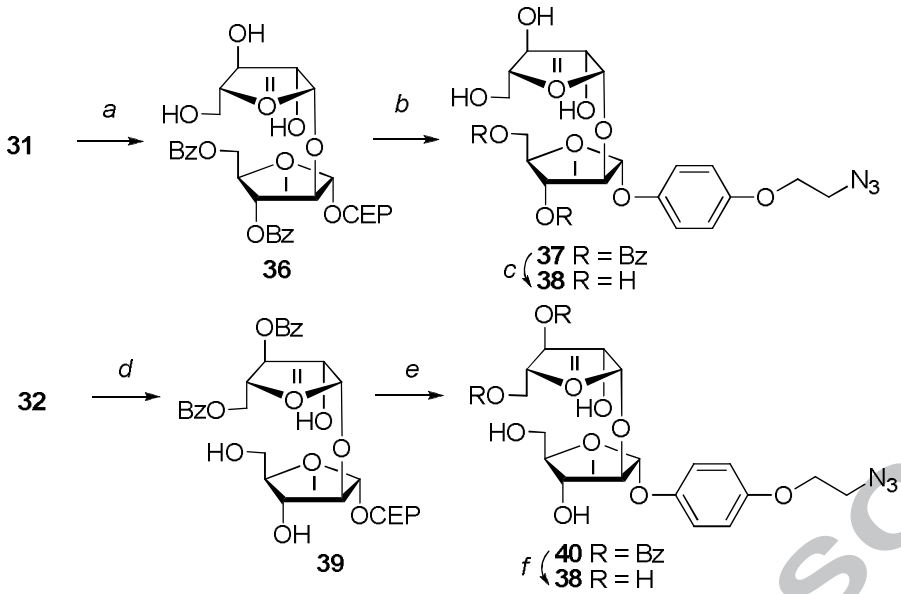
4, **5**, **24** **20**, **23** **32–35**

4 R^1 = TIPS, R^2 = R^3 = TFA
5 R^1 = TIPS, R^2 = R^3 = PFP
23 R^1 = TIPS, R^2,R^3 = $(t\text{-Bu})_2$Si

20 R = CEP
23 R = Me

32 R = CEP, R^2 = R^3 = H (from **4**+**20**)
33 R = CEP, R^2,R^3 = $(t\text{-Bu})_2$Si (from **24**+**20**)
34 R = CH_3, R^2 = R^3 = H (from **4**+**23**)
35 R = CH_3, R^1 = TIPS, R^2 = R^3 = PFP (from **5**+**23**)

Scheme 4. Reactions of glycosyl acceptors **20**, **23** with glycosyl donors **4, 5, 24**. *Reagents and conditions*:1. AgOTf, NIS, MS 4Å, CH_2Cl_2, −78 °C → *T* °C, then 30 min at *T*; 2. MeOH, NEt_3, CH_2Cl_2, 20 °C (for **32**, **34**). 3. Gel-chromatography on Bio-Beads S×3, toluene.



Scheme 5. Two routes to Ara*f*-(β1-2)-Ara*f* disaccharide **38** with a functionalized aglycon. *Reagents and conditions*: *a*. 1. TBAF, THF, AcOH, 12 h, 20 °C, 2. HPLC on silica gel, *i*-PrOH–$CHCl_3$–petroleum ether (1:3:6) (60% from **16** over 2 steps); *b*. NaN_3, DMF, 18-crown-6, 80 °C (78%); *c*. MeONa, MeOH, 20 °C, 20 h (92%); *d*. 1. BzCl, Py, 0 °C, 2. TBAF, THF, AcOH, 12 h, 20 °C, 3. HPLC on silica gel, *i*-PrOH–$CHCl_3$–petroleum ether (0.3:3:6) (47% from **32** over 2 steps); *e*. 1. NaN_3, DMF, 18-crown-6, 80 °C; *f*. MeONa, MeOH, 20 °C, 20 h (90% from **39** over 2 steps).

Table 1. Comparison of results of glycosylation (see Schemes 3 and 4).[a]

Entry	Glycosyl donor	Glycosyl-acceptor	Product	Anomeric ratio (α/β)[b]	*T*/°C[c]	Disaccharide yield (%)
1	**4**	**16**	**26**	1:2	−22	66
2	**4**	**20**	**32**	1:6.3	−30	84
3	**4**	**23**	**34**	1:5.6	−30	83
4	**5**	**23**	**35**	1:5.5	−30	87
5	**7**	**16**	**27**	1.2:1	−22	80
6	**11**	**16**	**28**	1:1	−22	85
7	**13**	**16**	**29**	3.3:1	−39	66
8	**24**[20]	**16**	**30**	1:4.5	−39	92
9	**24**[20]	**20**	**33**	1:3	−42	80
10	**25**[7,29]	**16**	**31**	1: 2	−51	94

[a] 1. AgOTf, NIS, MS 4Å, CH_2Cl_2, −78 °C → *T* °**C**, then 30 min at *T*; then →+10 °C over 30 min 2. MeOH, Et_3N, CH_2Cl_2, 20 °C, 40 min (only for TFA-containing disaccharides). 3. Gel-chromatography on Bio-Beads S×3, toluene. [b] ^{1}H NMR data. [c] The lowest temperature at which activation of glycosyl donor can be detected (visual detection of iodine color).

Highlights

- Influence of *O*-trifluoroacetyl protecting groups on stereoselectivity was studied.
- Outcome of glycosylation strongly depends on the nature of glycosyl acceptor.
- *O*-Benzyl groups are not required for construction of the 1,2-*cis*-linkage.
- Disaccharide of arabinofuranose with 4-(2-azidoethoxy)phenyl aglycon was prepared.

Graphical abstract