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Synthesis of β-D-arabinofuranosides: stereochemical differentiation between D- and L-enantiomers

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ABSTRACT

The glycosylation of 3,5-*O*-di-*tert*-butylsilylene-protected D-thioarabinofuranosides with a range of glycosyl acceptors using NIS/AgOTf as promoters proceeded in a stereoselective manner to give the corresponding β-D-arabinofuranosides in high yields.

Arabinosides are important constituents of proteoglycans, glycoproteins, and polysaccharides, and are widely distributed in living organisms, including plants.[1] Both D- and L-arabinofuranosides are found, with the D-form being the major component of mycobacterial cell walls and the L-form being an important component of plant cell walls. Although α-arabinofuranosides are more prevalent in both D- and L-series, β-arabinofuranosides occur often at the nonreducing end of the polysaccharides and may play pivotal roles in a number of biological events. For example, arabinogalactan, a major polysaccharide found in mycobacterial cell wall, contains β-D-arabinofuranosides at its nonreducing termini. Galactans in plant cell walls are also often modified by β-L-arabinofuranosides at their nonreducing termini and side chains. Therefore, the synthesis of β-arabinofuranosides,[2] particularly the development of effective β-arabinofuranosylating agents,[3] has received significant interest.

In contrast to α-arabinofuranosides, which are readily obtained through neighboring group participation, the stereoselective synthesis of β-arabinofuranosides is still a great challenge in carbohydrate chemistry. The use of arabinofuranosyl donors with a nonparticipating group at C-2 gives in general glycosides with poor anomeric selectivity, and α-anomers are often the major products due to both stereoelectronic and steric effects. Hence, several indirect approaches have been developed to synthesize β-arabinofuranosides. For example, the intramolecular aglycone delivery method, in which a glycosyl acceptor was first tethered to the C-2 hydroxyl group of an arabinofuranosyl donor followed by glycosylation,[4] has been used to introduce a β-D-arabinofuranoside moiety. Also, Lowary and co-workers[3c] successfully employed 2,3-anhydrofuranoyl donors as glycosylating agents to construct β-D-arabinofuranosidic linkages, in which the oxirane of the glycosylation products could be opened in a regioselective manner using lithium benzyl alkoxide in the presence of (−)-sparteine. The β-D-arabinofuranoside selectivity has also been improved by deactivation of the glycosyl donor and acceptor.[5]

Recently, Boons and co-workers[6] achieved the direct β-L-arabinofuranosylation of different glycosyl acceptors using a 3,5-*O*-di-*tert*-butylsilylene (DTBS)-protected L-thioarabinofuranoside as glycosyl donor on the basis of locking the donor in a conformation, in which nucleophilic attack from the β face was favored. This conformationally constrained donor gave excellent β-selectivity in a range of glycosylations with glycosyl acceptors having primary and secondary alcohols, and was successfully employed to synthesize an arabinogalactan fragment derived from the plant cell wall. Interestingly, soon after, Ito and co-workers[7] investigated the glycosylation property of an analogous DTBS-protected D-thioarabinofuranosides under the same activation conditions (NIS/AgOTf), and reported the predominant formation of β-glycosides but with a lower selectivity. Surprisingly, in their work an excellent β-selectivity was obtained in the activation of another conformationally less constrained donor, the 3,5-*O*-tetraisopropyldisiloxanylidene-protected thioglycoside. These results raised the question of whether our procedure is applicable to D-arabinofuranosides. A subsequent report by Crich et al. suggested that the DTBS-protected D-thioarabinofuranoside showed no significant β-selectivity on activation with BSP/Tf_2O or Ph_2SO/Tf_2O in the presence of different acceptors, while its enantiomer, that is, the corresponding

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L-thioglycoside, showed an excellent β-selectivity under NIS/AgOTf conditions.[8] However, they did not explore the reaction property of the D-thioglycoside under the action of NIS/AgOTf.[9]

Based on our previous results,[6] in order to investigate the glycosylating property of DTBS-protected D-thioglycosides, such as compound **4** (Scheme 1), particularly under NIS/AgOTf conditions, we decided to conduct some glycosylation reactions using compound **4** as the glycosyl donor, and wish to report here the observed stereochemical differentiation between D- and L-arabinofuranosylations.

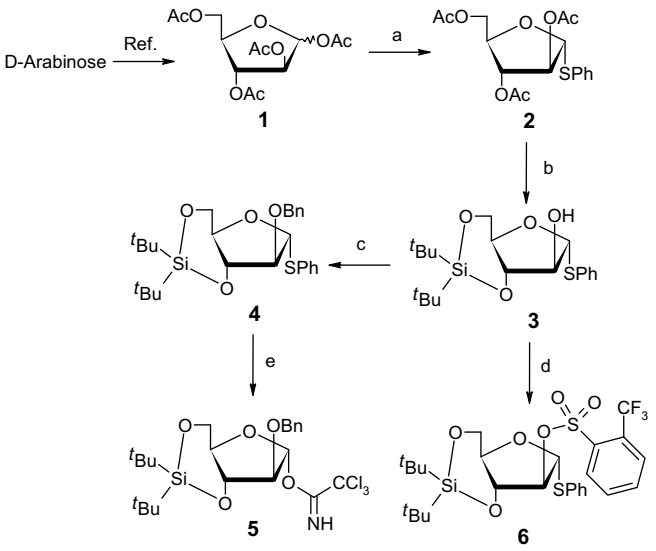
The excellent β-selectivity obtained in L-arabinofuranosylation reactions prompted us to investigate the applicability of the 3,5-di-*O*-*tert*-butylsilylene protecting group as a stereocontrolling element in D-arabinofuranosylations. In light of our previous work,[6] the fused silylene ring in thioglycoside **4** would result in an oxocarbenium ion being locked into a ^3E conformation, in which C-3 is displaced above the plane formed by C-4, O(*endo*), C-1 and C-2. Thus, nucleophilic attack from the α face of this structure would be disfavored due to unfavorable steric interaction with H-2, while β attack will encounter only staggered substituents, and thus be the favored mode of reaction. In the alternative E_3 conformation, the silylene ring would be distorted inducing considerable ring strain.

Synthesis of the glycosyl donor **4** was initiated from D-arabinose, which was first transformed into the known arabinose tetraacetate **1**[10], as shown in Scheme 1. Reaction of **1** with thiophenol in the presence of boron trifluoride etherate provided thioglycoside **2** in 78% yield. Subsequently, deacetylation of **2** with sodium methoxide followed by silylation with di-*tert*-butylsilane bis(trifluoromethanesulfonate) under the action of lutidine produced the 3-O-unprotected arabinofuranoside **3** in 81% yield. The 2-hydroxyl group of **3** was then benzylated in high yield to give the donor **4** by reaction with benzyl bromide in the presence of silver oxide. It is worth mentioning here that although compound **4** was expected to be mainly in a ^3E envelope conformation based on the previous computational work,[6] a recent X-ray study of the analogous *p*-tolyl thioglycoside indicated that the furanosyl ring may adopt an E_4 conformation.[11]

Having the glycosyl donor **4** in hand, attention was focused on the glycosylation of a range of different glycosyl acceptors (Fig. 1). Thus, coupling of the donor **4** with the galactosyl acceptor **7**[12] in the presence of NIS/AgOTf was first performed, but unexpectedly, the desired β-linked disaccharide **14** (Table 1, entry 1) was produced with a modest selectivity (β/α 5:1), compared with the previous exclusive β-selectivity obtained in the corresponding L-arabinofuranosylation reaction.[6] Fortunately, the α/β-isomers could be readily separated by flash column chromatography. We reasoned that there must be a 'mismatch' effect[13] in the donor–acceptor pair in the glycosidation reaction. For a specific glycosyl acceptor, L-thioarabinofuranoside donors, such as the enantiomer of compound **4**, could give a better β-selectivity than D-thioarabinofuranosides. As reported in the literature and in our previous work, the anomeric stereochemistry of the disaccharides was confirmed by the chemical shift of the anomeric carbon and the coupling constant $^3J_{H1-H2}$ value (the same hereinafter): β-isomer, δ(C-1) 97–104 ppm, $^3J_{H1-H2}$ = 4–6 Hz; α-isomer, δ(C-1) 104–111 ppm, $^3J_{H1-H2}$ = 1–3 Hz.

Donor **4** was also reacted with acceptors **8**[14] under the same activation conditions, giving rise to disaccharide **15** in 83% yield and very good β-selectivity (Table 1, entry 2). Similarly, mannosyl acceptor **9**[15] was also glycosylated with donor **4** in a β-selective manner to give compound **16** in 88% yield (Table 1, entry 3). To obtain more information on the glycosylation property of this donor, acceptors **10**[16] and **11**[17] having secondary hydroxyl groups were also coupled with **4**, and not unexpectedly, the corresponding disaccharides **17** and **18** were both generated in high yield and modest selectivity (Table 1, entries 4 and 5). The commercially available acceptor **12** was also glycosylated smoothly with donor **4**, leading to disaccharide **19** in high yield and β-selectivity (Table 1, entry 6). In addition, glycosylation of benzyl-protected acceptor **13**[14] with donor **4** gave also the corresponding disaccharide **20** in very good yield and modest β-selectivity (Table 1, entry 7).

In spite of the above modest selectivities, donor **4** could still glycosylate all the acceptors under the present conditions (NIS/AgOTf) in a selective manner in favor of the formation of β-glycosides. Moreover, all the glycosylation products were isolated in very high yields as indicated in Table 1, and more often, the pure β-anomers



Scheme 1. Synthesis of DTBS-protected D-arabinofuranosyl donors **4**–**6**. Reagents and conditions: (a) PhSH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 78%; (b) NaOMe, MeOH, then $^tBu_2Si(OTf)_2$, 2,6-lutidine, DMF–CH_2Cl_2, 81% (2 steps); (c) BnBr, Ag_2O, CH_2Cl_2, 83%; (d) *o*-trifluoromethylbenzenesulfonyl chloride, KI, Ag_2O, collidine, CH_2Cl_2, 70%; (e) NBS, acetone–H_2O, then Cl_3CCN, DBU, CH_2Cl_2, 45% (two steps).

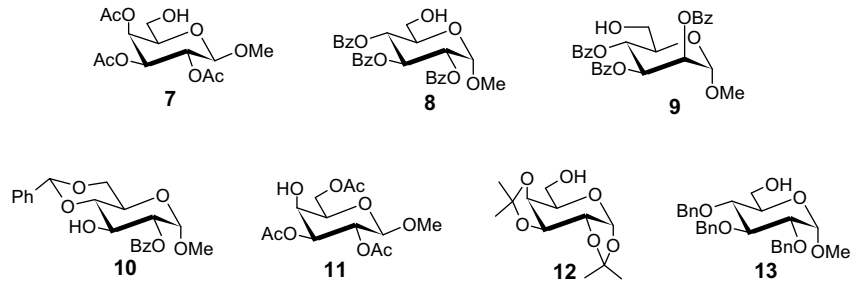
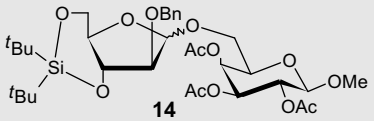
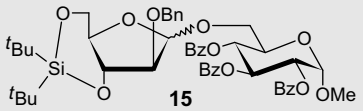
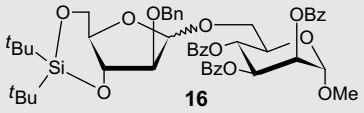
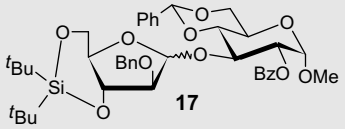
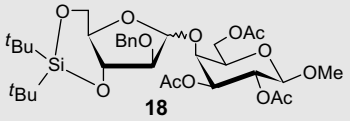
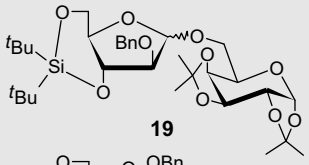
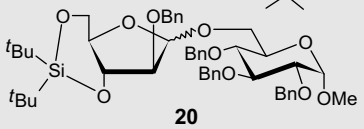
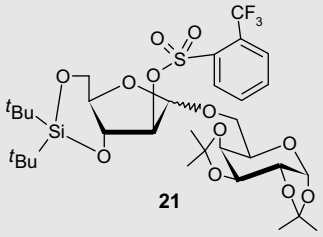


Figure 1. Selected glycosyl acceptors **7**–**13**.

Table 1
D-Arabinofuranosylation of DTBS-protected donors **4**–**6** with acceptors **7**–**11**

Entry	Donor	Acceptor	Product	Yield[a] (%)	β:α Ratio[b]
1	**4**	**7**	 **14**	90	5:1
2	**4**	**8**	 **15**	83	8:1
3	**4**	**9**	 **16**	88	3:1
4	**4**	**10**	 **17**	72	3:1
5	**4**	**11**	 **18**	88	4:1
6	**4**	**12**	 **19**	78	6:1
7	**4**	**13**	 **20**	75	2:1
8	**5**	**8**	**15**	84	4:1
9	**6**	**12**	 **21**	75	2:1

[a] Isolated yield.
[b] Determined by integration of proton signals in the ^{1}H NMR spectrum after chromatographic purification or by MS of the isolated pure isomers.

could be separated from the reaction mixture by flash column chromatography. From the fact that there are only very few convenient methods available in the literature for the synthesis of β-D-arabinofuranosides, donor **4** and its analogues can yet be regarded as an efficient β-D-arabinofuranosylating agent. This has been demonstrated very recently by Lowary and co-workers in the impressive synthesis of the arabinan domains of mycobacterial arabinogalactan and lipoarabinomannan, in which two β-D-arabinofuranosidic linkages were constructed at the same time by use of the corresponding *p*-tolyl thioglycoside of **4**.[18]

In this report, structural alteration of compound **4** with a view to enhancing further its glycosylation selectivity has also been made, but unfortunately, this turned out to be not very successful. For instance, glycosyl trichloroacetimidate **5** was prepared from thioglycoside **4** by a standard two-step procedure, as shown in Scheme 1, considering the fact that the leaving group of glycosyl donors is one of the most fundamental parameters responsible for the selectivity of glycosylation reactions. Glycosylation of **5** with acceptor **8** was then performed under the normal Schmidt glycosylation conditions;[19] however, the β-selectivity of this reaction even dropped slightly, compared with entry 2 in Table 1. Also, the 2-hydroxyl protecting group of donor **4** was altered from the present electron-donating benzyl group to the strong electron-withdrawing trifluorobenzenesulfonyl group with the hope of making α-glycosyl triflate the reaction intermediate, which could then undergo an S_N2 reaction to produce β-glycosides.[20] It should be noted that 2-sulfonyl protecting groups are generally thought as non-participating in glycosylation reactions, and have often been employed in the synthesis of 1,2-cis-glycosides.[21] Hence, compound **3** was then treated with commercially available *o*-trifluorobenzenesulfonyl chloride in the presence of KI–Ag_2O and collidine, as described previously,[20] to give sulfonate **6** in 70% yield.

Unfortunately, the reaction of donor **6** with acceptor **12** did not bring any higher β-selectivity either (Table 1, entry 7).

In summary, the glycosylation property of the conformationally constrained D-arabinofuranosyl donor **4** has been investigated toward a range of different glycosyl acceptors as a continuation of our previous work.[6] The results indicated that β-D-arabinofuranosides could be synthesized from this donor in modest to high selectivities, though overall the selectivities were lower than those obtained in L-arabinofuranosylation reactions. In view of the challenge in synthesizing β-D-arabinofuranosides, compound **4** may yet be regarded as an efficient β-D-arabinofuranosylating agent. Structural modification of this compound has also been carried out in the hope of further enhancement of the glycosylation selectivity and this will continue to be our interest.

1. Experimental

1.1. General methods

Unless otherwise stated, all moisture-sensitive reactions were performed in oven-dried glassware under an argon atmosphere using dry solvents. These were evaporated under diminished pressure while maintaining the water bath temperature below 40 °C. All reactions were monitored by TLC using Silica Gel 60 F_{254} coated on aluminum sheet and the compounds were visualized by UV or by treatment with 8% H_2SO_4 in MeOH followed by heating. Flash chromatography was performed with the indicated solvent system using 40–60 μm silica gel. Optical rotations were measured at 20 °C with a Perkin–Elmer 343 polarimeter (1 dm cell). $CDCl_3$ and tetramethylsilane were used as solvent, and internal standard, respectively, for ^{1}H NMR (300 MHz and 400 MHz) spectra. ^{13}C NMR spectra were recorded at 75 MHz and 100 MHz by using $CDCl_3$ as solvent, and the signals were assigned with the aid of DEPT, HSQC. Yields refer to chromatographically pure compounds and are calculated based on reagents consumed.

1.2. Phenyl 2,3,5-tri-*O*-acetyl-1-thio-α-D-arabinofuranoside (2)

To a stirred soln of penta-*O*-acetyl-D-arabinofuranose (1.0 g, 3.10 mmol) in CH_2Cl_2 (10 mL) was added thiophenol (0.5 mL, 4.88 mmol). $BF_3{\cdot}OEt_2$ (0.23 mL, 1.83 mmol) was then added dropwise at 0 °C. After stirring at 0 °C for 3 h, the reaction was quenched by the addition of Et_3N (0.6 mL, 4.30 mmol), and the mixture was concentrated under diminished pressure. The residue was diluted with EtOAc, washed successively with water and brine, dried over $MgSO_4$, and then concentrated under diminished pressure. The residue was purified by flash chromatography (3:1→2:1 cyclohexane–EtOAc,) to afford the desired product **2** (822 mg, 72%) as a colorless syrup: $[\alpha]_D$ +155.8 (*c* 0.9 $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (m, 2H, PhH), 7.31 (m, 3H, PhH), 5.54 (d-like, *J* 2.1 Hz, 1H, H-1), 5.28 (t, *J* 2.1 Hz, 1H, H-2), 5.08 (dd, *J* 5.4, 2.1 Hz, 1H, H-3), 4.48 (q, *J* 5.4 Hz, 1H, H-4), 4.40 (dd, *J* 12.0, 3.9 Hz, 1H, H-5_a), 4.29 (dd, *J* 12.0, 5.4 Hz, 1H, H-5_b), 2.11, 2.09, 2.08 (3s, 9H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 170.0, 169.6 (3Me*C*O), 133.6, 132.2, 129.1, 127.9 (Ph), 90.9 (C-1), 81.6 (C-2), 80.2 (C-4), 77.3 (C-3), 62.9 (C-5), 20.8 (*C*H_3CO); ESIMS: *m/z* 391.1 $[M+Na]^+$; HRESIMS: calcd for $C_{17}H_{20}NaO_7S$ $[M+Na]^+$ 391.0827, found 391.0819.

1.3. Phenyl 3,5-*O*-(di-*tert*-butylsilanediyl)-1-thio-α-D-arabinofuranoside (3)

Compound **2** was deacetylated following a standard procedure, and the product was used without purification. To a soln of the crude phenyl 1-thio-α-D-arabinofuranoside (1.0 g, ~4.13 mmol) in a mixture of CH_2Cl_2 (35 mL) and DMF (7 mL) at 0 °C were added 2,6-lutidine (2.1 mL, 18 mmol) and di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (1.5 mL, 4.12 mmol). The resulting mixture was stirred for 2 h, after which it was concentrated under diminished pressure, diluted with EtOAc, and washed successively with water and brine. The organic layer was dried over $MgSO_4$ and concentrated under diminished pressure to give a residue that was purified by flash column chromatography (6:1 cyclohexane–EtOAc) to give **3** (1.15 g, 73%) as a white amorphous solid: $[\alpha]_D$ +182.8 (*c* 0.7 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H, PhH), 7.30 (m, 3H, PhH), 5.32 (d, *J* 5.7 Hz, 1H, H-1), 4.34 (q, *J* 3.6 Hz, 1H, H-5_a), 4.15 (t, *J* 6.6 Hz, 1H, H-2), 4.02 (dd-like, *J* 12.0, 7.2 Hz, 1H, H-3), 3.94 (m, 2H, H-4, H-5_b), 2.48 (br s, 1H, OH), 1.06 (s, 9H, ^{t}Bu), 0.99 (s, 9H, ^{t}Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.5, 131.7, 129.3, 127.8 (Ph), 91.4 (C-1), 81.3 (C-3), 81.2 (C-2), 74.0 (C-4), 67.6 (C-5), 27.7 (*Me*$_3$C), 27.3 (*Me*$_3$C), 22.9 (Me$_3$*C*), 20.4 (Me$_3$*C*); ESIMS: *m/z* 405.3 $[M+Na]^+$, 421.3 $[M+K]^+$; HRESIMS: calcd for $C_{19}H_{31}O_4SSi$ $[M+H]^+$ 383.1712, found 383.1725.

1.4. Phenyl 2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-1-thio-α-D-arabinofuranoside (4)

BnBr (0.11 mL, 0.93 mmol) and Ag_2O (327 mg, 1.41 mmol) were added to a soln of **3** (183 mg, 0.48 mmol) in CH_2Cl_2 (5 mL), and the reaction was stirred vigorously at room temperature for 72 h, after which the mixture was filtered through a pad of silica gel. The filtrate was concentrated to give a residue, which was purified by flash chromatography (100:0→60:1 cyclohexane–EtOAc) to afford the title compound **4** (170 mg, 75%) as a pale yellow oil: $[\alpha]_D$ +126.8 (*c* 0.5 $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.19 (m, 10H, ArH), 5.43 (d, *J* 5.1 Hz, 1H, H-1), 4.78 (AB peak, *J* 12.0 Hz, 2H, PhC*H*$_2$), 4.32 (q-like, *J* 3.9 Hz, 1H, H-5_a), 4.14 (t-like, *J* 8.1 Hz, 1H, H-3), 3.96 (m, 3H, H-2, H-4, H-5_b), 1.07 (s, 9H, ^{t}Bu), 0.98 (s, 9H, ^{t}Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 134.7, 131.4, 129.1, 128.5, 128.1, 128.0, 127.9, 127.8, 127.5 (Ar), 90.1 (C-1), 87.1 (C-2 or C-4), 81.4 (C-3), 73.9 (C-2 or C-4), 72.4 (PhCH_2), 67.5 (C-5), 27.7 (*Me*$_3$C), 27.3 (*Me*$_3$C), 22.8 (Me$_3$*C*), 20.3 (Me$_3$*C*); ESIMS: *m/z* 495.3 $[M+Na]^+$; HRESIMS: calcd for $C_{26}H_{37}O_4SSi$ $[M+H]^+$ 473.2182, found 473.2186.

1.5. 2-*O*-Benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α-D-arabinofuranosyl trichloroacetimidate (5)

To a soln of **4** (160 mg, 0.34 mmol) in acetone (6.7 mL) and water (0.3 mL) was added NBS (120 mg, 0.67 mmol), and the mixture was stirred at room temperature for 1 h. The reaction was then quenched by the addition of solid $NaHCO_3$, and concentrated under diminished pressure. The residue was purified by flash chromatography (7:1 cyclohexane–EtOAc,) to afford the hemiacetal intermediate (78 mg, 60%) as an α/β mixture. A soln of the hemiacetal (50 mg, 0.13 mmol), CCl_3CN (72 μL, 0.72 mmol), and catalytic DBU in CH_2Cl_2 (5 mL) was stirred at room temperature for 30 min, after which the solvent was removed under diminished pressure, and the resulting residue was purified by flash column chromatography (8:1 cyclohexane–EtOAc + 1% Et_3N) to give the title compound **5** (51 mg, 75%) as a white foam: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (s, 1H, N*H*), 7.36–7.29 (m, 5H, PhH), 6.19 (d, *J* 2.7 Hz, 1H, H-1), 4.79 and 4.72 (AB peak, *J* 12.0 Hz, 2H, PhC*H*$_2$), 4.39 (dd, *J* 4.0 Hz, *J* 8.0 Hz, 1H, H-2), 4.28–4.10 (m, 2H, H-3, H-4), 4.10–3.95 (m, 2H, H-5), 1.08 (s, 9H, ^{t}Bu), 1.00 (s, 9H, ^{t}Bu). Imidate **5** was immediately used in the next step without further characterization.

1.6. Phenyl 3,5-*O*-(di-*tert*-butylsilanediyl)-2-*O*-(2-trifluoromethylbenzenesulfonyl)-1-thio-α-D-arabinofuranoside (6)

To a stirred soln of **3** (92 mg, 0.24 mmol) in CH_2Cl_2 (20 mL) were added *s*-collidine (62 μl, 0.47 mmol), KI (62 mg, 0.37 mmol), Ag_2O (88 mg, 0.38 mmol), and *o*-trifluoromethylbenzenesulfonyl chloride (36 μL, 0.23 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, allowed to warm up to room temperature and stirred for another 36 h, after which the mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite. The filtrate was washed successively with saturated aq $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under diminished pressure to give a residue, which was then purified by flash column chromatography (10:1 cyclohexane–EtOAc) to give **6** (99 mg, 70%) as a colorless oil: $[\alpha]_D$ +54.3 (*c* 2.1 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d-like, *J* 8.8 Hz, 1H, ArH), 7.86 (d-like, *J* 8.8, 1H, ArH), 7.67 (m, 2H, ArH), 7.42 (m, 2H, ArH), 7.23 (m, 3H, ArH), 5.38 (d, *J* = 4.8 Hz, 1H, H-1), 4.72 (dd, *J* 7.2, 4.8 Hz, 1H, H-2), 4.22 (q-like, *J* 3.6 Hz, 1H, H-5_a), 4.03 (dd, *J* 8.8, 7.2 Hz, 1H, H-3), 3.80 (m, 2H, H-5_b, H-4), 0.81 (s, 9H, ^{t}Bu), 0.77 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.0, 134.0, 133.1, 132.8, 132.7, 132.5, 129.3, 128.9 (q, J_{C-F} 6.1 Hz, 1C), 128.4 (Ar), 122.5 (q, J_{C-F} 273.0 Hz, 1C, *C*F_3), 88.8 (C-1), 88.4 (C-2), 79.2 (C-3), 73.4 (C-4), 67.1 (C-5), 27.3, 27.1 (2*Me*$_3$C), 22.7, 20.2 (2Me$_3$*C*); ESIMS: *m/z* 613.7 [M+Na]+; HRESIMS: calcd for $C_{26}H_{33}F_3O_6S_2Si$ $[M+Na]^+$ 613.1338, found 613.1352.

1.7. General procedure for the synthesis of disaccharides 14–21

A mixture of the thioglycoside **4** or **6** (0.18 mmol) and the corresponding sugar alcohol (0.12 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature in the presence of 4 Å molecular sieves (500 mg) for 20–30 min. After the mixture was cooled to −20 °C, NIS (61 mg, 0.27 mmol) followed by a soln of AgOTf (23 mg, 90 μmol) in toluene (0.2 mL) was added. The reaction mixture was warmed slowly to room temperature, and stirring was continued for 10–20 min. The reaction was quenched by the addition of Et_3N. The suspension was diluted with EtOAc and filtered through a pad of silica gel, and the filtrate was washed successively with saturated aq $Na_2S_2O_3$ and brine. The organic layer was dried over $MgSO_4$ and concentrated under diminished pressure to give a residue, which was purified by flash column chromatography (10:1 cyclohexane–EtOAc) to afford the corresponding disaccharide.

1.7.1. Methyl 2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α/β-D-arabinofuranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-galactopyranoside (14)

β-Isomer: 42 mg (white amorphous solid): $[\alpha]_D$ −43.0 (*c* 1.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.19 (m, 5H, ArH), 5.33 (d, *J* 2.4 Hz, 1H, H-4), 5.09 (dd, *J* 10.4, 8.0 Hz, 1H, H-2), 4.93 (dd, *J* 10.4, 3.6 Hz, 1H, H-3), 4.86 (d, *J* 5.6 Hz, 1H, H-1′), 4.72 (AB, *J* 12.4 Hz, 2H, PhC*H*$_2$), 4.27 (d, *J* 8.0 Hz, 1H, H-1), 4.23 (t, *J* 10.4 Hz, H-3′), 4.18 (dd, *J* 8.8, 4.8 Hz, 1H, H-5′$_a$), 3.82 (m, 3H, H-2′, H-5′$_b$, H-5), 3.67 (dd, *J* 10.4, 5.2 Hz, 1H, H-6_a), 3.53 (m, 2H, H-4′, H-6_b), 3.37 (s, 3H, OMe), 2.03, 1.98, 1.90 (3s, 9H, Ac), 1.01, 0.91 (2s, 18H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 169.8 (3MeCO), 138.1, 128.6, 128.2, 128.0 (Ph), 102.2 (C-1), 100.9 (C-1′), 80.7 (C-2′), 78.6 (C-3′), 74.0 (C-4′), 72.5 (C-5), 71.9 (PhCH$_2$), 71.3 (C-3), 69.3 (C-2), 68.4 (C-5′), 67.9 (C-4), 67.0 (C-6), 57.2 (OCH$_3$), 27.8, 27.4 (2*Me*$_3$C), 22.8 (Me$_3$*C*), 21.0, 20.9, 20.8 (3*Me*CO), 20.3 (Me$_3$*C*); ESIMS: *m/z* 700.4 $[M+H_2O^+]$, 705.3 $[M+Na^+]$; HRESIMS: calcd for $C_{33}H_{50}NaO_{13}Si$ $[M + Na]^+$ 705.2918, found *m/z* 705.2903.

α-Isomer: 8 mg (white amorphous solid): $[\alpha]_D$ +10.6 (*c* 1.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.19 (m, 5H, ArH), 5.41 (d, *J* 3.2 Hz, 1H, H-4), 5.13 (dd, *J* 10.4, 8.0 Hz, 1H, H-2), 4.95 (dd, *J* 10.2, 3.6 Hz, 1H, H-3), 4.80 (d, *J* 3.2 Hz, 1H, H-1′), 4.67 and 4.53 (AB, *J* 12.0 Hz, 2H, PhC*H*$_2$), 4.31 (d, *J* 8.0 Hz, 1H, H-1), 4.29 (m, 1H, H-5′$_a$), 4.00 (t, *J* 8.0 Hz, 1H, H-4′), 3.84 (m, 3H, H-2′, H-3′, H-5′$_a$), 3.81 (t, *J* 6.8 Hz, 1H, H-5), 3.73 (dd, *J* 10.0, 6.4 Hz, 1H, H-6_a), 3.43 (s, 3H, OMe), 3.41 (overlapped with OMe, 1H, H-6_b), 2.04, 1.99, 1.92 (3s, 9H, Ac), 0.99, 0.93 (2s, 18H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.42, 170.36, 169.8 (3MeCO), 138.0, 128.6, 128.1, 128.0 (Ph), 107.8 (C-1′), 102.3 (C-1), 88.0 (C-2′), 81.6 (C-4′), 74.2 (C-3′), 72.3 (PhCH$_2$), 71.8 (C-5), 71.4 (C-3), 69.3 (C-2), 67.7 (C-5′), 67.6 (C-4), 66.4 (C-6), 57.2 (OCH$_3$), 27.7, 27.3 (2*Me*$_3$C), 22.8 (Me$_3$*C*), 21.1, 20.92, 20.85 (3*Me*CO), 20.3 (Me$_3$*C*); ESIMS: *m/z* 700.4 $[M+H_2O^+]$, 705.3 $[M+Na^+]$; HRESIMS: calcd for $C_{33}H_{50}NaO_{13}Si$ $[M + Na]^+$ 705.2918, found *m/z* 705.2904.

1.7.2. Methyl 2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α/β-D-arabinofuranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (15)

α/β-Mixture: 55 mg (white amorphous solid). Spectral data for the major β-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.26 (m, 20H, Ar), 6.12 (t, *J* 10.0 Hz, 1H, H-3), 5.47 (t, *J* 10.0 Hz, 1H, H-4), 5.20 (m, 2H, H-1, H-2), 5.09 (d, *J* 5.6 Hz, 1H, H-1′), 4.81 (AB, *J* 12.4 Hz, 2 H, PhC*H*$_2$), 4.35–4.22 (m, 3H, H-5, H-3′, H-5′$_a$), 3.96–3.85 (m, 3H, H-6_a, H-2′, H-5′$_b$), 3.71 (m, 1H, H-6_b), 3.61 (m, 1H, H-4′), 3.39 (s, 3H, OMe), 1.06 (s, 9H, ^{t}Bu), 0.98 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.02, 165.98, 165.5 (3PhCO), 138.3, 133.6, 133.5, 133.2, 130.2, 130.1, 130.0, 128.6, 128.48, 128.46, 128.1, 127.8 (Ar), 101.4 (C-1′), 96.9 (C-1), 81.1 (C-2′), 79.0 (C-3′), 73.6 (C-4′), 72.4 (PhCH$_2$), 71.9 (C-4), 70.8 (C-3), 69.8 (C-2), 69.5 (C-5′), 68.5 (C-5), 67.8 (C-6), 55.7 (OCH$_3$), 27.8, 27.4 (2*Me*$_3$C), 22.8, 20.3 (2Me$_3$*C*); ESIMS: *m/z* 886.6 $[M+H_2O]^+$, 891.5 $[M+Na]^+$; HRESIMS: calcd for $C_{48}H_{56}NaO_{13}Si$ $[M+Na]^+$ 891.3388, found *m/z* 891.3400.

1.7.3. Methyl 2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α/β-D-arabinofuranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (16)

α/β-Mixture: 28 mg (white amorphous solid). Spectral data for the major β-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* 7.2 Hz, 2H, Ar), 7.95 (d, *J* 7.2 Hz, 2H, Ar), 7.81 (d, *J* 7.2 Hz, 2 H, Ar), 7.60–7.23 (m, 14H, Ar), 5.84 (dd, *J* 10.0, 3.2 Hz, 1H, H-3), 5.76 (t, *J* 10.0 Hz, 1H, H-4), 5.63 (dd, *J* 3.2, 2.0 Hz, 1H, H-2), 5.12 (d, *J* 5.6 Hz, 1H, H-1′), 4.93 (d, *J* 1.2 Hz, H-1), 4.80 (AB, *J* 12.4 Hz, 2H, PhC*H*$_2$), 4.35–4.21 (m, 3 H, H-5, H-3′, H-5′$_a$), 3.94–3.77 (m, 4H, H-6, H-2′, H-5′$_b$), 3.61 (m, 1H, H-4′), 3.43 (s, 3H, OMe), 1.03 (s, 9H, ^{t}Bu), 0.97 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.83, 165.80, 165.7 (3PhCO), 138.2, 133.7, 133.6, 133.3, 130.2, 130.04, 129.95, 128.8, 128.7, 128.48, 128.46, 128.2 (Ar), 101.3 (C-1′), 98.5 (C-1), 81.0 (C-2′), 79.0 (C-3′), 73.8 (C-4′), 71.8 (PhCH$_2$), 70.73 (C-2), 70.67 (C-5), 70.3 (C-3), 68.6 (C-5′), 68.0 (C-6), 67.7 (C-4), 55.5 (OCH$_3$), 27.7, 27.4 (2*Me*$_3$C), 22.8, 20.3 (2Me$_3$*C*); ESIMS: *m/z* 891.5 $[M+Na]^+$; HRESIMS: calcd for $C_{48}H_{56}NaO_{13}Si$ $[M+Na]^+$ 891.3388, found *m/z* 891.3390.

1.7.4. Methyl 2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α/β-D-arabinofuranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (17)

β-Isomer: 37 mg (white foam): $[\alpha]_D$ −43.0 (*c* 1.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.0 Hz, 2H, ArH), 7.63 (t, *J* = 7.6 Hz, 1H, ArH), 7.50–7.38 (m, 7H, ArH), 7.14 (m, 3H, ArH), 7.01 (d, *J* 7.6 Hz, 2H, ArH), 5.53 (s, 1H, PhC*H*), 5.28 (d, *J* 4.8 Hz, 1H, H-1′), 5.23 (dd, *J* 9.6, 3.6 Hz, 1H, H-2), 5.08 (d, *J* 3.2 Hz, 1H, H-1), 4.59 and 4.39 (AB peak, *J* 12.6 Hz, 2H, PhC*H*$_2$), 4.49 (t, *J* 9.6 Hz, 1H, H-3), 4.32 (m, 2H, H-3′, H-5′$_a$), 3.95 (m, 2H, H-5, H-6_a), 3.77 (m, 3H, H-4, H-2′, H-5′$_b$), 3.56 (m, 2H, H-4′, H-6_b), 3.39 (s, 3H, OMe), 0.94 (s, 9H, ^{t}Bu), 0.92 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8 (PhCO), 137.7, 137.5, 133.6, 130.0, 129.7, 129.4, 128.9, 128.4, 128.3, 127.63, 127.57, 126.6 (Ar), 102.4 (PhCH), 99.8 (C-1′), 98.0

(C-1), 80.3 (C-2′), 79.7 (C-4), 77.9 (C-3′), 74.7 (C-2), 74.6 (C-4′), 72.6 (C-3), 71.4 (PhCH$_2$), 69.2 (C-5′), 68.2 (C-6), 63.0 (C-5), 55.5 (OCH$_3$), 27.6, 27.3 (2*Me*$_3$C), 22.6, 20.2 (2Me$_3$*C*); ESIMS: *m/z* 771.6 [M+Na]$^+$; HRESIMS: calcd for $C_{41}H_{53}O_{11}Si$ [M+H]$^+$ 749.3357, found *m/z* 749.3372.

α-*Isomer*: 13 mg (colorless syrup): $[\alpha]_D$ +72.0 (*c* 1.0 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* 7.6 Hz, 2H, ArH), 7.60 (t, *J* 7.6 Hz, 1H, ArH), 7.47 (m, 4H, ArH), 7.32–7.20 (m, 6H, ArH), 7.11 (m, 2H, ArH), 5.60 (s, 1H, PhC*H*), 5.35 (br s, *J* 1.6 Hz, 1H, H-1′), 5.17 (dd, *J* 9.6, 3.6 Hz, 1H, H-2), 4.99 (d, *J* 3.6 Hz, 1H, H-1), 4.54 (AB peak, *J* 11.6 Hz, 2H, PhC*H*$_2$), 4.41 (t, *J* 9.6 Hz, 1H, H-3), 4.33 (dd, *J* 10.0, 4.8 Hz, H-5′$_a$), 3.93 (m, 2H, H-3′, H-4′), 3.88 (dd-like, *J* 7.2, 1.6 Hz, H-2′), 3.84–3.75 (m, 3H, H-5′$_b$, H-4, H-6$_a$), 3.72 (t, *J* 10.0 Hz, 1H, H-6$_b$), 3.56 (td, *J* 10.0, 5.6 Hz, 1H, H-5), 3.40 (s, 3H, OMe), 0.96 (s, 9H, ^{t}Bu), 0.70 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0 (PhCO), 138.1, 137.2, 133.7, 130.1, 129.7, 129.2, 128.7, 128.5, 128.4, 127.8, 127.6, 126.2 (Ar), 107.8 (C-1′), 101.9 (PhCH), 98.4 (C-1), 88.5 (C-2′), 82.3 (C-4), 81.5 (C-3' or C-4′), 73.8 (C-3), 73.7 (C-5), 72.1 (PhCH$_2$), 71.8 (C-2), 69.2 (C-5′), 67.6 (C-6), 62.5 (C-4′ or C-3′), 55.7 (OCH$_3$), 27.6, 27.1 (2*Me*$_3$C), 22.7, 20.0 (2Me$_3$*C*); ESIMS: *m/z* 771.5 [M+Na]$^+$; HRESIMS: calcd for $C_{41}H_{53}O_{11}Si$ [M+H]$^+$ 749.3357, found *m/z* 749.3391.

1.7.5. Methyl 2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α/β-D-arabinofuranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-galactopyranoside (18)

β-*Isomer*: 74 mg (white foam): $[\alpha]_D$ −41.2 (*c* 1.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* 6.8 Hz, 2H, ArH), 7.34 (t, *J* 7.4 Hz, 2H, ArH), 7.28 (m, 1H, ArH), 5.40 (dd, *J* 10.4, 8.0 Hz, 1H, H-2), 5.11 (d, *J* 5.2 Hz, 1H, H-1′), 5.02 (dd, *J* 10.4, 2.8 Hz, 1H, H-3), 4.96 and 4.76 (AB peak, *J* 12.8 Hz, 2H, PhC*H*$_2$), 4.41 (d, *J* 7.6 Hz, 1H, H-1), 4.32 (t, *J* 10.2 Hz, 1H, H-3′), 4.22 (m, 3H, H-5′$_a$, H-6$_a$, H-6$_b$), 4.11 (d, *J* 2.4 Hz, 1H, H-4), 3.93 (m, 2H, H-5′$_a$, H-2′), 3.78 (t, *J* = 6.2 Hz, 1H, H-5), 3.58 (m, 1H, H-4′), 3.49 (s, 3H, OMe), 2.06, 2.05, 2.03 (3s, 9H, 3Ac), 1.07 (s, 9H, ^{t}Bu), 0.98 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.0, 169.3 (3MeCO), 138.2, 128.2, 127.6, 127.3 (Ar), 101.7 (C-1), 100.3 (C-1′), 80.5(C-2′), 78.0 (C-3′), 73.7 (C-4′), 73.5 (C-3), 71.84 (C-5), 71.80 (C-4), 71.2 (PhCH$_2$), 69.2 (C-2), 67.9 (C-5′), 63.3 (C-6), 56.4 (OCH$_3$), 27.5, 27.1 (2*Me*$_3$C), 22.6 (Me$_3$*C*), 20.81, 20.78, 20.76 (3*Me*CO), 20.0 (Me$_3$*C*); ESIMS: *m/z* 705.3 [M+Na]$^+$, 721.5 [M+K]$^+$; HRESIMS: calcd for $C_{33}H_{50}NaO_{13}Si$ [M+Na]$^+$ 705.2918, found *m/z* 705.2923.

α-*Isomer*: 18 mg (white foam): $[\alpha]_D$ +27.2 (*c* 1.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.26 (m, 5H, Ar), 5.25 (dd, *J* 10.4, 8.0 Hz, 1H, H-2), 4.89 (d, *J* 2.8 Hz, 1H, H-1′), 4.71 and 4.67 (AB peak, *J* 11.6 Hz, 2H, PhC*H*$_2$), 4.69 (dd, *J* 10.0, 3.2 Hz, 1H, H-3), 4.44 (dd, *J* 10.2, 6.0 Hz, 1H, H-6$_a$), 4.34 (d, *J* 7.6 Hz, 1H, H-1), 4.26 (dd, *J* 10.4, 4.4 Hz, 1H, H-5′$_a$), 4.13–4.05 (m, 5H, H-4, H-2′, H-3′, H-4′, H-6$_b$), 3.91 (t, *J* 9.4 Hz, 1H, H-5′$_a$), 3.74 (t, *J* 7.2 Hz, 1H, H-5), 3.49 (s, 3H, OMe), 2.06, 2.02, 2.00 (3s, 9H, 3Ac), 1.05 (s, 9H, ^{t}Bu), 1.02 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.2, 169.4 (3MeCO), 137.7, 128.3, 127.9, 127.7 (Ar), 108.7 (C-1′), 102.0 (C-1), 87.5 (C-2′), 81.6 (C-3′), 74.0, 73.7 (C-4, C-4′), 72.2 (C-3), 72.1 (PhCH$_2$), 71.5 (C-5), 68.9 (C-2), 67.6 (C-5′), 61.2 (C-6), 56.8 (OCH$_3$), 27.4, 27.1 (2*Me*$_3$C), 22.6 (Me$_3$*C*), 20.9, 20.8, 20.7 (3Ac), 20.1 (Me$_3$*C*); ESIMS: *m/z* 705.6 [M+Na]$^+$; HRESIMS: calcd for $C_{33}H_{50}NaO_{13}Si$ [M+Na]$^+$ 705.2918, found *m/z* 705.2902.

1.7.6. 2-*O*-Benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α/β-D-arabinofuranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose (19)

β-*Isomer*: 80 mg (colorless syrup): $[\alpha]_D$ +186.6 (*c* 0.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.26 (m, 5H, PhH), 5.54 (d, *J* 4.8 Hz, 1H, H-1), 5.13 (d, *J* 5.2 Hz, 1H, H-1′), 4.81 (AB peak, *J* 12.8 Hz, 2H, PhC*H*$_2$), 4.57 (dd, *J* 8.0, 2.4 Hz, 1H, H-3), 4.36 (t, *J* 9.2 Hz, 1H, H-3′), 4.29 (m, 2 H, H-5′$_a$, H-2), 4.24 (dd, *J* 8.0, 2.0 Hz, H-4), 4.03 (m, 1H, H-5), 3.97–3.85 (m, 3H, H-5′$_a$, H-2′, H-6$_a$), 3.71 (dd, *J* 11.6, 6.8 Hz, H-6$_b$), 3.64 (m, 1H, H-4′), 1.47, 1.43, 1.32, 1.31 (4s, 12H, 4Me), 1.07 (s, 9H, ^{t}Bu), 0.98 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 128.4, 128.1, 127.7 (Ar), 109.4, 108.7 (2Me$_2$*C*), 100.6 (C-1′), 96.5 (C-1), 80.8 (C-2′), 78.7 (C-3'), 73.9 (C-4′), 71.7 (PhCH$_2$), 71.3 (C-4), 70.8 (C-2), 70.7 (C-3), 68.7 (C-5′), 67.9 (C-5), 67.0 (C-6), 27.8, 27.4 (2*Me*$_3$C), 26.3, 26.2, 25.2, 24.6 (4*Me*), 22.8, 20.3 (2Me$_3$*C*); ESIMS: *m/z* 645.6 [M+Na]$^+$; HRESIMS: calcd for $C_{32}H_{50}NaO_{10}Si$ [M+Na]$^+$ 645.3071, found *m/z* 645.3079.

α-*Isomer*: 14 mg (colorless syrup): $[\alpha]_D$ −102.3 (*c* 0.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.28 (m, 5H, PhH), 5.53 (d, *J* 5.2 Hz, 1H, H-1), 5.01 (d, *J* 3.2 Hz, 1H, H-1′), 4.73 (AB peak, *J* 12.0 Hz, 2H, PhC*H*$_2$), 4.62 (dd, *J* 8.0, 2.4 Hz, 1H, H-3), 4.32 (m, 2H, H-5′$_a$, H-2), 4.26 (dd, *J* 8.0, 2.0 Hz, H-4), 4.09 (dd, *J* 9.2, 7.2 Hz, 1H, H-3′), 4.01 (m, 2H, H-5, H-2′), 3.97–3.89 (m, 2H, H-4′, H-5′$_b$), 3.80 (dd, *J* 10.4, 6.4 Hz, 1H, H-6$_a$), 3.69 (dd, *J* 10.4, 7.2 Hz, H-6$_b$), 1.51, 1.44, 1.33, 1.26 (4s, 12H, 4Me), 1.06 (s, 9H, ^{t}Bu), 0.99 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 128.5, 128.0, 127.9 (Ar), 109.5, 108.8 (2Me$_2$*C*), 107.9 (C-1′), 96.6 (C-1), 87.9 (C-2′), 81.5 (C-3′), 74.1 (C-4′), 72.2 (PhCH$_2$), 71.1 (C-4), 70.9 (C-2 and C-3), 67.8 (C-5'), 67.5 (C-6), 66.3 (C-5), 27.7, 27.4 (2*Me*$_3$C), 26.3, 26.2, 25.2, 24.7 (4*Me*), 22.9, 20.4 (2Me$_3$*C*); ESI-MS: *m/z* 645.6 [M+Na]$^+$; HRESIMS: calcd for $C_{32}H_{50}NaO_{10}Si$ [M+Na]$^+$ 645.3071, found *m/z* 645.3079.

1.7.7. Methyl 2-*O*-benzyl-3,5-*O*-(di-*tert*-butylsilanediyl)-α/β-D-arabinofuranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (20)

β-*Isomer*: 49 mg (colorless syrup): $[\alpha]_D$ −14.5 (*c* 1.1 $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (m, 20H, ArH), 5.00 (d, *J* 5.4 Hz, 1H, H-1′), 4.97 (d, *J* 11.1 Hz, 1H, PhC*H*$_a$H$_b$), 4.87–4.62 (m, 7H, PhC*H*$_2$), 4.59 (d, *J* 3.0 Hz, 1H, H-1), 4.35 (t, *J* 9.0 Hz, 1H, H-3′), 4.27 (dd, *J* 9.3, 5.1 Hz, 1H, H-5′$_a$), 4.01–3.88 (m, 4H, H-2′, H-5′$_b$, H-3, H-6$_a$), 3.80–3.47 (m, 5H, H-5, H-4′, H-6$_b$, H-4, H-2), 3.32 (s, 3H, OMe), 1.05, 0.98 (2s, 18H, ^{t}Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1, 138.7, 138.4, 138.2, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.85, 127.80 (Ph), 101.2 (C-1'), 98.2 (C-1), 82.4 (C-2′), 81.0 (C-3), 80.2 (C-2), 79.2 (C-3'), 78.2 (C-4), 75.9, 75.1 (PhCH$_2$), 73.64 (C-4′), 73.57, 71.7 (PhCH$_2$), 70.5 (C-5), 68.5 (C-5′), 67.6 (C-6), 55.3 (OCH$_3$), 27.8, 27.4 (2*Me*$_3$C), 22.8, 20.3 (2Me$_3$*C*); ESIMS: *m/z* 844.9 [M+H$_2$O$^+$]; HRESIMS: calcd for $C_{48}H_{62}NaO_{10}Si$ [M+Na]$^+$ 849.4010, found *m/z* 849.4030.

α-*Isomer*: 24 mg (colorless syrup): $[\alpha]_D$ −52.0 (*c* 1.2 $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (m, 20H, ArH), 5.03 (d, *J* 3.0 Hz, 1H, H-1'), 4.98 (d, *J* 10.8 Hz, 1H, PhC*H*$_a$H$_b$), 4.88–4.73 (m, 4H, PhC*H*$_2$), 4.67–4.60 (m, 4H, PhC*H*$_2$, H-1), 4.19 (m, 1H, H-5′$_a$), 4.08 (t-like, *J* 8.1 Hz, 1H, H-3′), 4.02–3.88 (m, 5H, H-2′, H-5′$_b$, H-3, H-4′, H-6$_a$), 3.75 (m, 1H, H-5), 3.65–3.55 (m, 2H, H-6$_b$, H-4), 3.53 (dd, *J* 9.6, 3.6 Hz, 1H, H-2), 3.36 (s, 3H, OMe), 1.05, 0.95 (2s, 18H, ^{t}Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 138.5, 138.4, 138.0, 128.70, 128.66, 128.58, 128.30, 128.26, 128.1, 128.00, 127.95, 127.87 (Ph), 107.5 (C-1'), 98.3 (C-1), 88.0 (C-2′), 82.3 (C-3), 81.8 (C-3′), 80.3 (C-2), 78.0 (C-4), 76.1, 75.3 (PhCH$_2$), 74.2 (C-4′), 73.6, 72.1 (PhCH$_2$), 70.2 (C-5), 67.7 (C-5′), 67.0 (C-6), 55.4 (OCH$_3$), 27.7, 27.3 (2*Me*$_3$C), 22.8, 20.3 (2Me$_3$*C*); ESIMS: *m/z* 844.9 [M+H$_2$O$^+$]; HRESIMS: calcd for $C_{48}H_{62}NaO_{10}Si$ [M + Na]$^+$ 849.4010, found *m/z* 849.4023.

1.7.8. 3,5-*O*-(Di-*tert*-butylsilanediyl)-2-*O*-(2-trifluoromethylbenzenesulfonyl)-α/β-D-arabinofuranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose (21)

β-*Isomer*: (38 mg, colorless syrup): $[\alpha]_D$ +187.7 (*c* 1.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* 7.2 Hz, 1H, Ar), 7.84 (d, *J* 7.2 Hz, 1H, Ar), 7.66 (m, 2H, Ar), 5.44 (d, *J* 4.8 Hz, 1H, H-1), 5.15 (d, *J* 5.2 Hz, 1H, H-1′), 4.63 (dd, *J* 9.2, 5.2 Hz, 1H, H-2′), 4.54 (dd, *J* 8.0, 2.0 Hz, 1H, H-3), 4.33 (t, *J* 9.2 Hz, 1H, H-3'), 4.24–4.18 (m, 3H, H-2, H-4, H-5′$_a$), 3.96 (t-like, *J* 6.0 Hz, 1H, H-5), 3.81 (m, 2H, H-5′$_b$, H-6$_a$), 3.60 (dd, *J*

10.8, 6.0 Hz, H-6_b), 3.54 (m, 1H, H-4′), 1.50, 1.36, 1.26, 1.19 (4s, 12H, 4Me), 0.89 (s, 9H, ^{t}Bu), 0.77 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 133.9, 132.3, 131.9 (Ar), 129.3 (q, J_{C-F} 33.7 Hz, 1C, Ar), 128.8 (q, J_{C-F} 5.9 Hz, 1C, Ar), 122.5 (q, J_{C-F} 273.0 Hz, 1C, Ar), 109.3, 109.0 ($2Me_2C$), 99.1 (C-1′), 96.5 (C-1), 82.1 (C-2'), 76.0 (C-3′), 73.2 (C-4′), 71.0 (C-4), 70.84 (C-2), 70.79 (C-3), 68.4 (C-5′), 67.2 (C-6), 66.7 (C-5), 27.4, 27.2 ($2Me_3C$), 26.3, 26.2, 25.2, 24.7 (4*Me*), 22.7, 20.2 ($2Me_3C$); ESIMS: *m/z* 763.9 $[M+Na]^+$; HRESIMS: calcd for $C_{32}H_{47}F_3NaO_{12}SSi$ $[M+Na]^+$ 763.2407, found 763.2414.

α-Isomer: 19 mg (colorless syrup): $[\alpha]_D$ +79.3 (*c* 1.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* 6.8 Hz, 1H, Ar), 7.85 (d, *J* 6.8 Hz, 1H, Ar), 7.68 (m, 2H, Ar), 5.46 (d, *J* 5.2 Hz, 1H, H-1), 5.10 (d, *J* 2.8 Hz, 1H, H-1'), 4.65 (dd, *J* 7.2, 2.4 Hz, 1H, H-2′), 4.55 (dd, *J* 8.0, 2.4 Hz, 1H, H-3), 4.27–4.21 (m, 3H, H-2, H-4, H-$5'_a$), 4.00 (t, *J* 8.4 Hz, 1H, H-3'), 3.95 (t-like, *J* 7.2 Hz, 1H, H-5), 3.81 (m, 2H, H-$5'_b$, H-4′), 3.75 (dd, *J* 10.4, 6.0 Hz, 1H, H-6_a), 3.57 (dd, *J* 10.8, 7.2 Hz, H-6_b), 1.49, 1.37, 1.30, 1.27 (4s, 12H, 4Me), 0.84 (s, 9H, ^{t}Bu), 0.77 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.8, 134.2, 133.0, 132.4 (Ar), 129.3 (q, J_{C-F} 33.7 Hz, 1C, Ar), 128.9 (q, J_{C-F} 6.1 Hz, 1C, Ar), 122.5 (q, J_{C-F} 273.0 Hz, 1C, Ar), 109.5, 108.9 ($2Me_2C$), 106.2 (C-1'), 96.5 (C-1), 89.4 (C-2′), 79.4 (C-3′), 73.3 (C-4′), 70.9 (C-4), 70.81 (C-2), 70.75 (C-3), 68.2 (C-6), 67.4 (C-5′), 66.6 (C-5), 27.3, 27.2 ($2Me_3C$), 26.3, 26.2, 25.2, 24.5 (4*Me*), 22.7, 20.2 ($2Me_3C$); ESI-MS: *m/z* 763.9 $[M+Na]^+$; HRESIMS: calcd for $C_{32}H_{47}F_3NaO_{12}SSi$ $[M+Na]^+$ 763.2407, found *m/z* 763.2414.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.09.006.

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