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4,6-Di-O-Benzylidenyl group-directed preparation of 2-deoxy-2-azido-α-D-galactopyranosides promoted by 3-O-TBDPS

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ABSTRACT

In this study, we designed a method to prepare 2-deoxy-2-azido-α-D-galactopyranosidic bonds using 4,6-di-O-benzylidenyl-3-O-t-butyldiphenylsilyl protected 2-deoxy-2-azido-1-thio-D-galactopyranoside **5** as donors. The donor **5** gives a good to excellent α-selectivity in the glycosylation with secondary alcohols, which was found to be associated with the benzylidenyl on 4,6-di-O and TBDPS on 3-O of the donor **5**. Compared with results of the donor **6** and **7**, the 3-O-TBDPS could increase the activity of the thioglycoside, and the lone pairs on 4,6-di-O-benzylidenyl group enhanced the gg-cofnormation, which plays a role in improving the stereoselectivity. Finally, this method was demonstrated through the synthesis of a α-galactosamine -containing pentasaccharide **26**.

1. Introduction

Galactosamine is a key constituent in many important oligosaccharides and glycoconjugates existing in biologically active natural products and clinical agents, including anthracyclines, angucyclines, aureolic acid antibiotics, etc. Galactosamine exists in either α-or β-linked form [1].

The study demonstrated that the synthesis of β-form of galactosamine could be reliably achieved through the neighboring C-2-amide-group or carbamate-based protecting group. For the stereoselective preparation of α-form of galactosamine, on the contrary, the glycosyl donors with non-neighboring functionality on C-2, Such as 2-azido, have been extensively explored in order to maximize the anomeric effect, often with the aid of solvent effect or some cyclic protecting groups [2]. Recently, several research groups have reported alternative approaches to a galactosamine through these strategies. Among them, the corresponding 2-azido [3], 2,3-trans-oxazolidinone [4], 4,6-O-benzylidenyl [5], and 4,6-O-di-tert-butylsilylene [6] glycosamine derivatives are frequently used as essential building blocks.

In our previous study, we reported the preparation of 2-deoxy-α-D-galactopyranosidic bonds using 3,4-di-O-isopropylidene-6-O-t-butyldiphenylsilyl protected 2-deoxy-1-thio-D-galactopyranoside as a donor [7]. The approach gave an excellent α-selectivity in glycosylations, which was found to be associated with the isopropylidene on 3,4-di-O and TBDPS on 6-O of the donor. Based on these findings, we will study the role of other 2-deoxysugar counterparts in such reactions, particularly in the preparation of 2-amino-2-deoxy-α-D-galactopyranosides.

2. Results and discussion

To avoid the participating functionalities on C-2, 2-deoxy-2-azido-1-thio-galactosides are employed for the introduction of α-galactosamines. The azido moiety is a non-participating functionality and is stable under a wide variety of reaction conditions, also can readily be reduced to an amine with reagents such as phosphines and thiols, and by catalytic hydrogenation.

Following the design, this study begins with the synthesis with the preparation of the thioglycosides **3** and **5–7** as illustrated in Scheme 1. All of the thioglycosides have a nonparticipating azido moiety at C-2 site [8] and a cyclic prototective group at O-3,4 or O-4,6, respectively. The synthesis of these thioglycosides starting from the known thioglycoside **1**, which can be prepared from D-galactose following the Mong's method

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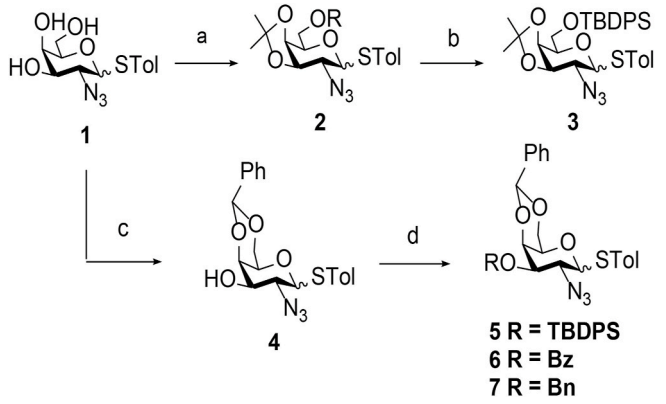
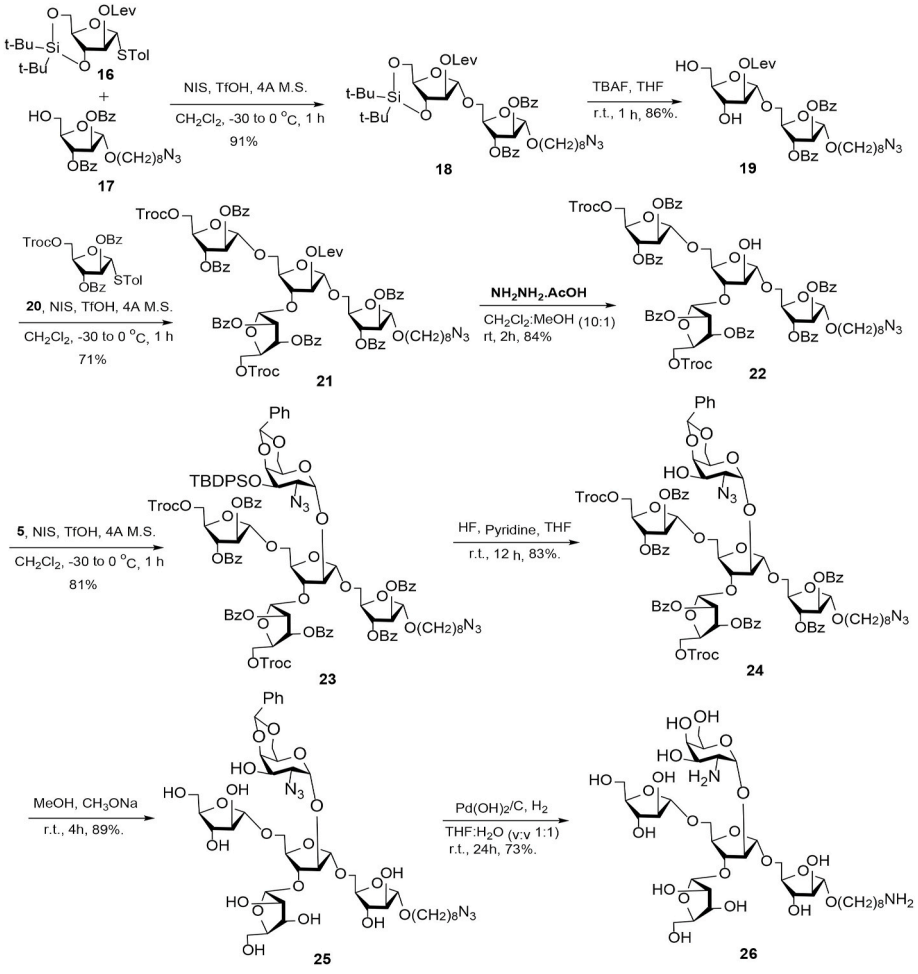


Scheme 1. Preparation of Compound **3**, **5**, **6** and **7**. Reagents and conditions: (a) $(CH_3)_2C(OMe)_2$, PPTs, acetone, r.t., 4 h, 71%; (b) TBDPS-Cl, Imidazole, DMF, 25 °C, 4 h, 79%; (c) $PhCH(OMe)_2$, PPTs, CH_3CN, r.t., 4 h; (d) for **5**: TBDPS-Cl, Imidazole, DMF, 25 °C, 4 h, 81%; for **6**: BzCl, Pyridine, 45 °C, 1 h, 95%; for **7**: BnBr, NaH, DMF, 0–25 °C, 2 h, 92%.

[9]. Acetalization of thioglycoside **1** via 2,2-dimethoxy propane yield 71% of **2,** following by the reaction with TBDPS-Cl to form O-6 silicon ether **3** with a yield of 79%. On the other hand, acetalization of thioglycoside **1** via benzaldehyde dimethanol will result in **4** with a yield of 74%. Treatment with TBDPS-Cl, thioglycoside **4** can be converted into its derivatives **5** in a yield of 81% Alkylation of thioglycoside **4** with benzyl bromide and sodium hydride gave **6** in 92% yield; Finally, reaction with benzoyl chloride in pyridine led to **7** in 95% yield (see Scheme 2).

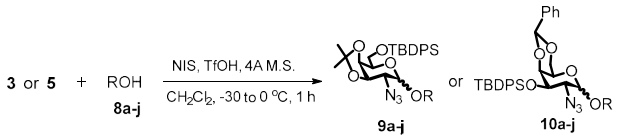
To investigate the α and β stereoselectivity of glycosylation reaction, we first applied thioglycoside **3** as the donor for synthesizing 2-amino-2-deoxy-α-D-galactopyranosides. The glycosylation was performed using the alcohol (**8a-j**, 1.0 equiv), thioglycoside **3** or **5** (1.2 equiv), NIS (1.5 equiv), and TfOH (0.1 equiv), at −30 to 0 °C in CH_2Cl_2. The product of the coupling between thioglycoside **3** and acceptor **8a** [10] show a mild α-selectivity (α:β, 3:1, entry 1, Table 1). The product stereochemistry was confirmed by $^3J_{H\text{-}1,H\text{-}2}$ in ^1H NMR in $CDCl_3$. For α-anomers, $^3J_{H\text{-}1,H\text{-}2}$ is 3–5 Hz, while for β-anomers $^3J_{H\text{-}1,H\text{-}2}$ is 9–10 Hz [11]. Besides, the chemical shift of the anomeric carbon in the α-anomer resonated at $<$ 100 ppm. In comparison, the chemical shift of the anomeric carbon in the β-anomer resonated at $>$ 100 ppm. The selectivity of the glycosylation was not superior to existed methods. Next, we carried out the glycosylation reaction of **3** with a more hindered secondary acceptor **8b.** The results are similar to the previous result (yield of 87%, α:β, 5:1, entry 2, Table 1).

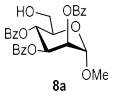
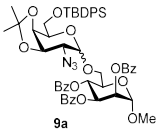
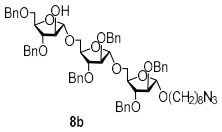
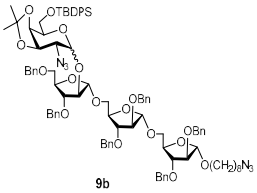
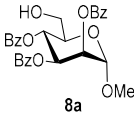
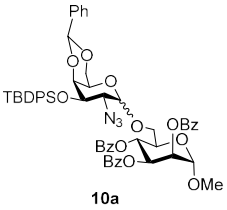
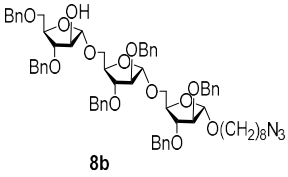
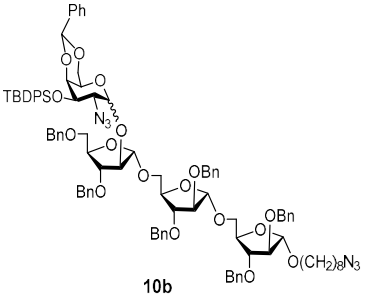
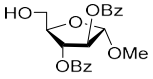
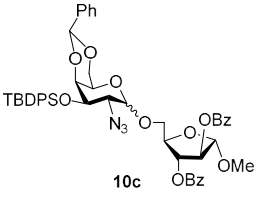
As a comparison, we set out to survey the glycosylation of another thioglycoside **5** with the acceptors **8a** and **8b**. The results showed that stereoselectivity of glycosylation reaction between the thioglycoside **5** with **8a** is slightly improved over the selectivity of thioglycoside **3** with **6a** (yield of 90%, α:β, 5:1, entry 3, Table 1). However, the α-selectivity was significantly improved between the thioglycoside **5** and **8b** [12] (α:β, 10:1, entry 4, Table 1). To further investigate the steric hindrance of the acceptor, we surveyed the glycosylation of **5** with a variety of alcohols **8c-j** [13]. All the glycosylations were run under NIS and TfOH at −30 °C and CH_2Cl_2 as the solvent. As summarized in Table 1, we can



Scheme 2. Synthesis of the pentasaccharide **26**.

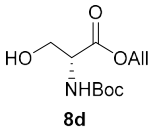
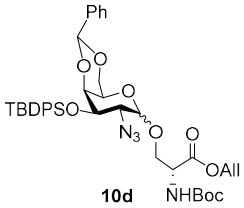
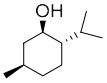
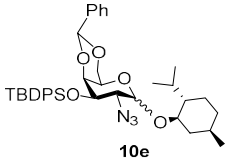
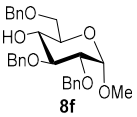
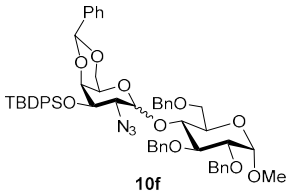
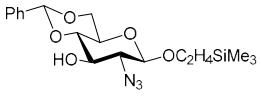
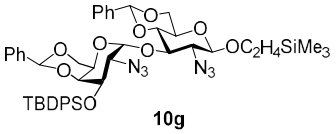
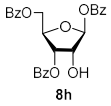
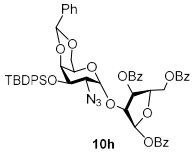
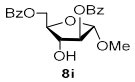
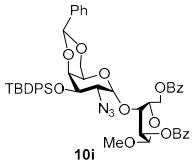
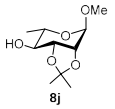
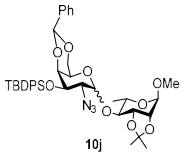
Table 1
Glycosylations of donors **3** or **5** with alcohol **8a-j**.



Entry	Donors	Accepors	Products	Yields[b] (α/β)[c]
1	3	 **8a**	 **9a**	93% (3:1)
2	3	 **8b**	 **9b**	87% (5:1)
3	5	 **8a**	 **10a**	90% (5:1)
4	5	 **8b**	 **10b**	81% (10:1)
5	5	 **8c**	 **10c**	91% (2:1)
6	5			87% (5:4)

(*continued on next page*)

Table 1 (*continued*)

Entry	Donors	Accepors	Products	Yields[b] (α/β)[c]
		 **8d**	 **10d**	
7	5	 **8e**	 **10e**	87% (15:1)
8	5	 **8f**	 **10f**	85% (13:1)
9	5	 **8g**	 **10g**	71% (α-only)
10	5	 **8h**	 **10h**	80% (α-only)
11	5	 **8i**	 **10i**	74% (α-only)
12	5	 **8j**	 **10j**	86% (7:1)

[a]All glycosylations were performed by employing the donor (1.2 equiv) and the acceptor (1.0 equiv) in the presence of NIS (1.5 equiv), catalytic TfOH (0.1 equiv), and 4 A molecular sieves (4A M.S.) in CH_2Cl_2, at −30 to 0 °C.

[b] The total yield of isomers.

[c] Determined on the basis of the 1H NM.

see that all acceptors surveyed demonstrated either mild α-selectivity (**10c-d**), highly α-selectivity (**10e-f**, **j**), or α-only (**10g-i**) glycoside products with 71–91% yields with the α-anomer as the dominant product.

Analysis of experimental results in Table 1, reactions with the primary alcohols **8a** and **8c-d** provided much lower α-selectivities than reactions with more hindered secondary alcohols **8b** and **8e-j** (entries 3, 5–6 vs entries 4, 7–12). Further illustrated that the steric hindrance from various acceptors would further enhance the α-selectivity behavior. Based on these results, we hypothesized that that benzylidenyl on 4,6-di-O and TBDPS on 3-O of the donor could control the nucleophile to attack the a-face of the donor. The X-ray diffraction analysis of the donor **5** (Fig. 1) also show that the β-face of the anomeric carbon of **5** is indeed of potential resistance.

The effect of 4,6-di-O-benzylidenyl group on the stereoselectivity of the glycosylation has been reported in literature [5]. To better understand the behavior of 3-O-TBDPS during the glycosylation reaction, the glycosylation of 3-*O*-Bz (**6**) or 3-*O*-Bn thioglycosides (**7**) (Table 2) were investigated.

Neither **6** nor **7** showed α-selectivity in the glycosylation with primary alcohol **8c**. In particular, there are more β-product than α-product in the reaction of compound **7**. Thioglycoside **6** could not react with the secondary hydroxyl **8h**. The reaction with **8i** could only be carried out at room temperature in a low yield and a mild α-selectivity (yield of 18%, α-only). The glycosylation between **7** and **8h** could not work at low temperature, but could be carried out at room temperature providing a complex product **13** in a yield of 76%. It was difficult to identify the ratio of isomers **13** due to some impurities which could not be separated. The α-selectivity of the reaction between **7** and **8i** was excellent at both low temperature and room temperature. With the increase of temperature, the yield of the reaction slightly increased, but the by-products increased at the same time.

Comparing the results of glycosylations of thioglycoside **5** in Table 1 with the results of glycosylations of thioglycosides **6–7** in Table 2, It displayed that 3-O-TBDPS could significantly improve the activity of the donor. This enabled thioglycoside **5** to react with various alcohols at a lower temperature, and the yield was significantly better than that of **6** or **7**. However, we also see that 3-O-TBDPS has a little effect on the stereoselectivity of the reaction. 3-O-TBDPS did not significantly affect the steric hindrance of the β-face of the anomeric carbon. The key to the stereoselectivity was 4,6-di-O-benzylidenyl group.

Finally, we targeted the preparation of a pentaccharide **26** [14]'

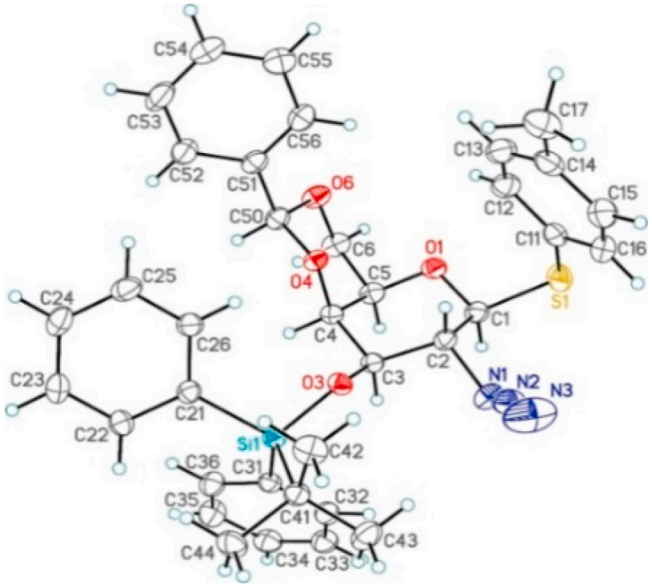
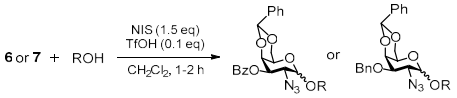
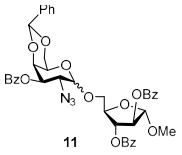
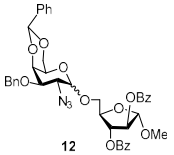
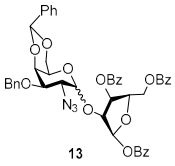
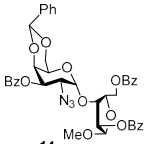
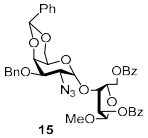
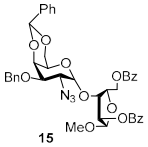


Fig. 1. X-ray of the donor **5**.

Table 2
Glycosylations of Donors **6** or **7** with Alcohol **8a, h-i**.



En.	donor	acceptor	product
1[a]	**6**	**8c**	 **11** (90%, α:β=1:1)
2[a]	**7**	**8c**	 **12** (86%, α:β=2:3)
3[a]	**6**	**8h**	No Reaction
4[a]	**7**	**8h**	 **13** (76%, a complex product)
5[a]	**6**	**8i**	No Reaction
6[b]	**6**	**8i**	 **14** (18%, α-only)
7[a]	**7**	**8i**	 **15** (48%, a-only)
8[b]	**7**	**8i**	 **15** (52%, a-only)

[a] All glycosylations were performed at −30 to 0 °C.
[b] All glycosylations were performed at 0–25 °C.

which contained 2-amino-2-deoxy-α-D-galactopyranosidic bonds by utilizing the developed approach. Treatment of **16** [13] and **17** [15] with NIS/TfOH yielded disaccharide **18** in 91% yield. Subsequent desilylation via TBAF in THF liberated the 3,5-OH of disaccharide **18**, thus affording **19** in 86% yield. Then, the coupling between **19** and thioglycoside **20** [16] at −30 °C for 1 h produced the tetrasaccharide **21** in 71% yield. Subsequent deacylation of levulinoyl protecting group via Hydrazine acetate liberated the 2-OH of the middle arabino-moiety of the tetrasaccharide **22**. Alcohol **22** underwent a facile NIS/TfOH promoted glycosylation with the thioglycoside **5**, to afford exclusively α-linked product **23**(H-1: δ 5.17, $J_{1,2} = 3.6$ Hz; C-1: δ 99.0, $J_{H1\text{-}C1}$ [17] = 172.5 > 165.0), in 81% yield (Scheme2). Deprotection of **23** involving desilylation via Pyridine hydrofluoride in pyridine generated the corresponding alcohol **24** in 83% yield. Then de-O-acetylation of Benzoyl ester and Troc afforded the polyol **25** in 89% yield. Finally, the reduction of azide and simultaneous hydrolysis of benzylidenyl group generated the target pentasaccharide **26** in 73% yield.

3. Conclusion

In summary, we reported a methodology for the synthesis of 2-azido-2-deoxy-α-galactopyranosides by using 4,6-di-*O*-benzylidenyl-3-*O*-*t*-butyldiphenylsilyl protected 2-deoxy-2-azido-1-thio-D-galactopyranoside **5** as donor. Although the method only showed excellent stereoselectivity in the glycosylation with secondary alcohols, not so good with primary alcohols. Finally, the approach was successfully applied to the synthesis of a protected pentasaccharide derivative **26**. The exact mechanism is advancing by means of computational chemistry.

4. Experiment procedures

Experimental Details. Dry CH_2Cl_2 was taken from a solvent purification system after successive passage through alumina columns. Dry CH_3OH was obtained via storage in a sealed bottle with activated 4 Å M S. overnight at rt. Unless otherwise stated, all reactions were carried out under an argon atmosphere and were monitored by TLC on silica gel 60 F_{254} (0.25 mm, Merck). Spots were visualized by UV light and/or by charring with 10% H_2SO_4 in EtOH. Column chromatography was performed on silica gel 60 (40–60 μm. ^{1}H NMR spectra were recorded at 500 and 600 MHz; and chemical shifts were referenced to $CHCl_3$ (7.26 ppm, $CDCl_3$). ^{13}C NMR spectra were recorded at 125 or 150 MHz, and chemical shifts were referenced to internal $CDCl_3$ (77.06 ppm, $CDCl_3$). Optical rotations were measured on a PerkinElmer 241 polarimeter at 22 ± 2 °C in units of (degree·mL)/(dm·g). Electrospray ionization spectra were recorded on an Aligent Technologies 6220 TOF spectrometer with samples dissolved in CH_2Cl_2, CH_3OH, or H_2O.

4.1. Toluene 3,4-di-O-isopropylidene-6-O-tert-butyldiphenylsilyl-1-thio-2-azido-2-deoxy-β-D-galactopyranoside (3)

To a solution of **1** (618 mg, 2.00 mmol) in dry acetone (20 mL) was added 2,2-Dimethoxypropane (0.37 ml, 3.00 mmol) and PTSA (38.2 mg, 0.20 mmol). The reaction mixture was stirred at rt for 4 h. The resulting mixture was added H_2O and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated. The residue **2,** imidazole (0.47 g, 6.9 mmol) and tert-Butyldiphenylchlorosilane (0.72 mL, 2.8 mmol) were dissolved in dry CH_2Cl_2 (7.2 mL). The reaction stirred under N_2 for 2 h, then quenched with MeOH. The resulting mixture was added H_2O and CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (10:1, Petroleum ether–EtOAc) to afford compound **3** as a white semisolid (836 mg, 71%). R_f 0.5 (6:1, petroleum ether–EtOAc); $[\alpha]_D$ 33.1 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71–7.68 (m, 4H), 7.46–7.36 (m, 8H), 7.09 (d, J = 8.0 Hz, 2H), 4.33 (d, J = 10.5 Hz, 1H), 4.24 (dd, J = 5.0, 2.0 Hz, 1H), 4.07 (dd, J = 7.5, 5.0 Hz, 1H), 3.97–3.91 (m, 2H)), 3.85 (td, J = 6.5, 2.5 Hz, 1H), 3.38 (dd, J = 10.5, 7.5 Hz, 1H), 2.31 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 135.6, 135.6, 133.4, 133.3, 129.8, 129.7, 128.0, 127.7, 127.7, 110.4, 86.1, 78.4, 77.2, 76.9, 72.5, 63.9, 62.8, 28.2, 26.8, 26.3, 21.2, 19.2; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{32}H_{39}N_3NaO_4SSi$: 612.2323. Found: 612.2324.

4.2. Toluene 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-1-thio-2-azido-2-deoxy-β-D-galactopyranoside (5)

To a solution of **1** (627 mg, 2.00 mmol) in dry CH_3CN (10 mL) was added Benzaldehyde dimethyl acetal (0.44 mL, 2.90 mmol) and PTSA (31.3 mg, 0.164 mmol). The reaction mixture was stirred at rt for 4 h. The resulting mixture was added H_2O and extracted with CH_2Cl_2. The organic layer was washed with saturated aq $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated. The residue **4,** imidazole (0.47 g, 6.9 mmol) and tert-Butyldiphenylchlorosilane (0.72 mL, 2.8 mmol) were dissolved in dry CH_2Cl_2 (7.2 mL). The reaction stirred under N_2 for 2 h, then quenched with MeOH. The resulting mixture was added H_2O and CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (15:1, Petroleum ether–EtOAc) to afford compound **5** as a white semisolid (771 mg, 65%). R_f 0.3 (10:1, petroleum ether–EtOAc); $[\alpha]_D$ 40.4 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.70 (m, 4H), 7.60 (d, J = 8.0 Hz, 2H), 7.47–7.38 (m, 9H), 7.27 (t, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 5.11 (s, 1H), 4.30 (d, J = 9.5 Hz, 1H), 4.22 (dd, J = 7.5, 2.0 Hz, 1H), 3.79 (t, J = 9.5 Hz, 1H), 3.70 (dd, J = 12.0, 2.0 Hz, 1H), 3.64 (dd, J = 9.5, 3.0 Hz, 1H), 3.45 (d, J = 2.5 Hz, 1H), 3.10 (d, J = 1.0 Hz, 1H), 2.34 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 138.0, 135.9, 135.8, 134.3, 134.0, 132.4, 130.0, 129.8, 129.7, 129.0, 128.1, 127.9, 127.6, 126.8, 126.4, 100.6, 85.8, 77.2. 74.7, 74.5, 69.6, 69.2, 62.2, 26.7, 21.3, 19.3; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{36}H_{39}N_3NaO_4SSi$: 660.2328. Found: 660.2333.

4.3. Toluene 4,6-di-O-benzylidenyl-3-O-benzyl-1-thio-2-azido-2-deoxy-β-D-galactopyranoside (6)

To a solution of **4** (438 mg, 1.10 mmol) in pyridine (5.5 mL) was added benzoyl chloride (253 μL, 2.20 mmol). After being stirred for 1 h at 50 °C, the reaction was quenched with methanol, diluted with CH_2Cl_2, and then the mixture was washed with aq 1 N HCl, saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (7:1, petroleum ether–EtOAc) to afford compound 6 as a White solid (522 mg, 94.5%). R_f 0.35 (4:1, petroleum ether–EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (dd, J = 8.4, 1.2 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.43–7.34 (m, 7H), 7.08 (d, J = 8.4 Hz, 2H), 5.49 (s, 1H), 5.05 (dd, J = 10.8, 3.6 Hz, 1H), 4.55 (d, J = 9.6 Hz, 1H), 4.48 (d, J = 3.0 Hz, 1H) 4.42 (dd, J = 12.6, 1.2 Hz, 1H), 4.06 (dd, J = 12.6, 1.8 Hz, 1H), 4.00 (t, J = 10.2 Hz, 1H), 3.64 (d, J = 1.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, CDCl3): δ 165.97, 138.7, 137.6, 134.65, 133.55, 129.99, 129.16, 129.11, 128.48, 128.09, 126.43, 126.22, 100.8, 85.5, 77.25, 77.04, 76.8, 74.7, 72.8, 69.69, 69.24, 58.7, 29.7, 21.3; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{36}H_{39}N_3NaO_4SSi$: 660.2328. Found: 660.2333.

4.4. Toluene 4,6-di-O-benzylidenyl-3-O-benzyl-1-thio-2-azido-2-deoxy-β-D-galactopyranoside (7)

To a solution of **4** (484 mg, 1.21 mmol) in dry DMF (6 mL) was added benzyl bromide (288 μL, 2.42 mmol). After being stirred for 0.5 h at 0 °C, then sodium hydridethe (116 mg, 4.84 mmoL) was added, the reation mixture was gradually warmed to rt and was stirred for 1 h at the same

temperature,The mixture was diluted with CH_2Cl_2, and then the mixture was washed with aq 1 N HCl, saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (7:1, petroleum ether–EtOAc) to afford compound 6 as a White solid (543 mg, 91.6%). R_f 0.35 (4:1, petroleum ether–EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, J = 8.0, 1.5 Hz, 2H), 7.73 (dd, J = 8.0, 1.5 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.48–7.39 (m, 9H), 7.29 (d, J = 15 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 5.12 (s, 1H), 4.31 (d, J = 9.5 Hz, 1H), 4.23 (dd, J = 12.5, 2.0 Hz, 1H), 3.80 (t, J = 10 Hz, 1H), 3.71 (dd, J = 12.5, 2.0 Hz, 1H), 3.65 (dd, J = 10, 3.5 Hz, 1H), 3.47 (dd, J = 3.5, 1.0 Hz, 1H), 3.12 (d, J = 1.0 Hz, 1H), 2.36 (s, 3H) 1.55 (s, 1H) 1.04 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.3, 138.0, 135.9, 135.8, 134.3, 134.0, 132.4, 130.0, 129.8, 129.7, 128.9, 128.1, 127.9, 127.6, 126.8, 126.4, 100.6, 85.75, 77.3, 77.0, 76.8, 74.65, 69.6, 69.2, 26.7, 21.3, 19.3; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{36}H_{39}N_3NaO_4SSi$: 660.2328. Found: 660.2333.

4.5. General procedure for the glycosylation of **3** or **5**

A mixture of donor **3** or **5** (1.2 equiv), acceptor (1.0 equiv), and freshly activated 4 Å molecular sieves in dry CH_2Cl_2 (to a 0.1 N solvent) was cooled to −30 °C. The suspension was stirred for 15 min, then NIS (1.5 equiv), TfOH (0.1 equiv) was added. The reaction mixture was stirred for 1–2 h at the same temperature. The reaction mixture was gradually warmed to 0 °C and quenched with Et_3N. The mixture was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography to give the product. The ratio of the isomers was detected by NMR in all cases.

4.6. Methyl 3,4-di-O-isopropylidene-6-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**9a**)

Prepared from **3** (212 mg, 0.360 mmol) and **8a** (152 mg, 0.300 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 8:1) to afford compound **9a** as a light syrup (270 mg, yield of 92.7%, α:β = 3:1). R_f 0.3 (5:1, petroleum ether–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 7.0 Hz, 2H), 8.10 (d, J = 7.0 Hz, 0.7H), 7.96 (d, J = 7.0 Hz, 2H), 7.92 (d, J = 7.5 Hz, 0.7H), 7.82 (d, J = 7.0 Hz, 2.7H), 7.67–7.23 (m, 25H), 5.97 (t, J = 10.0 Hz, 1.4H), 5.88 (dd, J = 10.0, 3.0 Hz, 1.4H), 5.82 (t, J = 10.0 Hz, 0.7H), 5.68 (q, J = 1.5 Hz, 1H), 5.64 (q, J = 1.5 Hz, 0.4H), 4.99 (d, J = 1.5 Hz, 1.4H), 4.89 (d, J = 3.0 Hz, 1H), 4.47 (dd, J = 8.5, 5.0 Hz, 1H), 4.31–4.26 (m, 2.7H), 4.21 (dd, J = 5.0, 1.5 Hz, 0.4H), 4.16–3.74 (m, 7.4H), 3.67 (dd, J = 8.5, 3.5 Hz, 1H), 3.52 (s, 3H), 3.39 (dd, J = 8.5, 3.5 Hz, 1.4H), 1.50 (s, 1H), 1.50 (s, 2.5H), 1.36 (s, 2.5H), 1.50 (s, 1H), 1.01 (s, 3H), 0.98 (s, 7.5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 165.5, 165.4, 135.6, 135.5, 135.5, 133.5, 133.4, 133.1, 130.0, 129.8, 129.7, 129.3, 129.1, 129.0, 110.3, 109.6, 102.1, 98.7, 98.5, 97.9, 77.2. 73.9, 73.4, 72.8, 72.3, 70.6, 70.5, 70.2, 70.0, 69.9, 69.6, 68.4, 67.4, 67.0, 66.8, 65.7, 62.7, 62.4, 61.7, 55.5, 55.4, 28.4, 28.3, 26.7, 26.3, 26.2, 19.1, 14.2; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{55}H_{57}N_3NaO_{13}Si$: 994.3558. Found: 994.3552.

4.7. 8-Azidooctyl 3,4-di-O-isopropylidene-6-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 2)-3,5-di-O-benzyl-α-D-arabinofuanosyl-(1 → 5)-2,3-di-O-benzyl-α-D-arabinofuanosyl-(1 → 5)-2,3-di-O-benzyl-α-D-arabinofuanoside (**9b**)

Prepared from **3** (76 mg, 0.129 mmol) and **8b** (120 mg, 0.108 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 5:1) to afford compound **9b** as a light syrup (148 mg, yield of 87.1%, α:β = 5:1). For α: R_f 0.2 (5:1, petroleum ether–EtOAc); $[\alpha]_D$ 78.0 (c 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72–7.66 (m, 4H), 7.42–7.19 (m, 36H), 5.18 (s, 1H), 5.11 (d, J = 1.0 Hz, 1H), 4.98 (d, J = 1.0 Hz, 1 H), 4.79 (d, J = 3.5 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.55–4.43 (m, 10H), 4.41 (d, J = 12.0 Hz, 1H), 4.20–4.00 (m, 11H), 3.91–3.78 (m, 5H), 3.71–3.55 (m, 5H), 3.38–3.34 (m, 1H), 3.27 (dd, J = 8.5, 3.5 Hz, 1H), 3.25 (t, J = 7.0 Hz, 2H), 1.61–1.54 (m, 8H), 1.49 (s, 3H), 1.34 (s, 3H), 1.38–1.26 (m, 8H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 138.2, 138.1, 137.8, 137.7, 137.7, 135.7, 135.5, 133.3, 133.3, 129.7, 129.7, 128.4, 128.3, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 109.5, 106.4, 106.1, 105.8, 97.7, 88.7, 88.3, 87.3, 83.7, 83.2, 81.6, 80.2, 80.1, 77.2. 73.4, 73.2, 72.4, 72.3, 72.3, 72.0, 72.0, 71.8, 69.8, 68.6, 67.6, 65.9, 65.4, 62.4, 61.4, 51.5, 29.7, 29.5, 29.3, 29.1, 28.8, 28.4, 26.8, 26.7, 26.2, 26.1, 19.2; For β: R_f 0.18 (5:1, petroleum ether–EtOAc); $[\alpha]_D$ 80.0 (c 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71–7.64 (m, 4H), 7.43–7.20 (m, 32H), 7.13 (s, 4H), 5.22 (s, 1H), 5.17 (d, J = 1.5 Hz, 1H), 5.01 (d, J = 1.5 Hz, 1 H), 4.58–4.44 (m, 10H), 4.42–4.38 (m, 2H), 4.29 (d, J = 9.0 Hz, 1 H), 4.20–4.02 (m, 9H), 3.94–3.68 (m, 10H), 3.59–3.53 (m, 2H), 3.40–3.37 (m, 1H), 3.32 (t, J = 8.5 Hz, 1H), 3.25 (t, J = 7.0 Hz, 2H), 1.61–1.54 (m, 8H), 1.54 (s, 3H), 1.33 (s, 3H), 1.38–1.26 (m, 8H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 138.0, 138.0, 137.9, 137.7, 137.7, 135.6, 135.5, 133.2, 133.1, 129.8, 129.7, 128.4, 128.3, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 110.2, 106.8, 106.5, 106.1, 101.3, 88.7, 87.2, 83.8, 83.3, 83.0, 81.4, 80.2, 80.1, 77.2. 73.3, 73.1, 72.4, 72.3, 72.1, 72.0, 69.9, 67.6, 66.1, 65.4, 65.1, 62.1, 51.5, 29.5, 29.3, 29.1, 28.8, 28.4, 26.8, 26.8, 26.7, 26.2, 26.1, 19.2; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{90}H_{108}N_6NaO_{17}Si$: 1595.7438. Found: 1595.7443.

4.8. Methyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**10a**)

Prepared from **5** (142 mg, 0.223 mmol) and **8a** (94 mg, 0.186 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 4:1 to 6:1) to afford compound **10a** as a light syrup (169 mg, yield of 89.5%, α:β = 3:1). For α: R_f 0.25 (3:1, petroleum ether–EtOAc); $[\alpha]_D$ 28.7 (c 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (dd, J = 7.5, 1.0 Hz, 2H), 7.91 (dd, J = 7.5, 1.0 Hz, 2H), 7.83 (dd, J = 7.5, 1.0 Hz, 2H), 7.78 (dd, J = 7.5, 1.0 Hz, 2H), 7.73 (dd, J = 7.5, 1.0 Hz, 2H), 7.60–7.34 (m, 17H), 7.28–7.23 (m, 3H), 5.85 (dd, J = 10.0, 3.5 Hz, 1H), 5.77 (t, J = 10.0 Hz, 1H), 5.64 (q, J = 1.5 Hz, 1H), 5.04 (d, J = 3.5 Hz, 1H), 5.01 (s, 1H), 4.87 (d, J = 1.5 Hz, 1H), 4.38 (dd, J = 10.0, 3.5 Hz, 1H), 4.28–4.23 (m, 1H), 3.98 (dd, J = 12.0, 1.5 Hz, 1H), 3.94 (dd, J = 10.5, 3.5 Hz, 1H), 3.88 (dd, J = 11.0, 7.0 Hz, 1H), 3.62 (dd, J = 11.0, 2.0 Hz, 1H), 3.56 (dd, J = 12.0, 1.5 Hz, 1H), 3.47 (d, J = 3.5 Hz, 1H), 3.36 (s, 1H), 3.32 (s, 3H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 165.4, 165.4, 137.8, 135.9, 135.9, 134.4, 133.5, 133.5, 133.1, 133.0, 129.9, 129.9, 129.8, 129.7, 129.3, 129.2, 129.0, 128.8, 128.6, 128.5, 128.3, 128.1, 127.8, 127.5, 126.1, 100.4, 98.7, 98.4, 77.2. 75.3, 70.6, 70.0, 69.6, 69.4, 69.0, 67.2, 66.8, 62.8, 61.0, 55.2, 26.9, 26.3, 19.4; For β: R_f 0.25 (3:1, petroleum ether–EtOAc); $[\alpha]_D$ −83.1 (c 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (dd, J = 7.5, 1.0 Hz, 2H), 7.94 (dd, J = 7.5, 1.0 Hz, 2H), 7.81 (dd, J = 7.5, 1.0 Hz, 2H), 7.77 (dd, J = 7.5, 1.0 Hz, 2H), 7.75 (dd, J = 7.5, 1.0 Hz, 2H), 7.61–7.22 (m, 20H), 5.89 (dd, J = 10.0, 3.5 Hz, 1H), 5.72 (t, J = 10.5 Hz, 1H), 5.65 (q, J = 1.5 Hz, 1H), 5.14 (s, 1H), 4.98 (d, J = 1.5 Hz, 1H), 4.38–4.34 (m, 1H), 4.25 (d, J = 8.0 Hz, 1H), 4.11–4.08 (m, 2H), 3.83–3.76 (m, 2H), 3.72 (dd, J = 12.0, 1.5 Hz, 1H), 3.57 (dd, J = 10.0, 3.5 Hz, 1H), 3.55 (s, 3H), 3.43 (d, J = 3.5 Hz, 1H), 3.02 (s, 1H), 1.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 165.6, 165.4, 137.8, 136.0, 135.8, 134.1, 133.4, 133.1, 132.6, 133.0, 129.9, 129.8, 129.7, 129.4, 129.2, 129.0, 128.8, 128.5, 128.2, 128.1, 127.8, 127.6, 126.1, 102.6, 100.6, 98.3, 77.2. 74.6, 72.7, 70.7, 70.0, 69.9, 69.2, 68.9, 67.6, 62.3, 64.4, 55.5, 26.9, 26.8, 19.4; HRMS–ESI–TOF calcd for $[M + NH_4]^+$ $C_{57}H_{61}N_4O_{13}Si$: 1037.3999. Found: 1037.3988.

*4.9. 8-Azidooctyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 2)-3,5-di-O-benzyl-α-D-arabinofuanosyl-(1 → 5)-2,3-di-O-benzyl-α-D-arabinofuanosyl-(1 → 5)-2,3-di-O-benzyl-α-D-arabinofuanoside (**10b**)*

Prepared from **5** (67 mg, 0.105 mmol) and **8b** (97 mg, 0.088 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 7:2) to afford compound **10b** as a light syrup (114 mg, yield of 80.6%, α:β = 10:1). R_f 0.35 (2:1, petroleum ether–EtOAc); $[\alpha]_D$ 69.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76–7.73 (m, 4H), 7.53–7.49 (m, 2H), 7.44–7.21 (m, 39H), 5.12 (s, 1H), 5.02 (s, 1H), 5.01 (s, 1H), 4.99 (s, 1H), 4.98 (d, *J* = 3.5 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.55–4.44 (m, 10H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.17–4.01 (m, 11H), 3.87–3.80 (m, 4H), 3.72–3.66 (m, 2H), 3.59–3.53 (m, 3H), 3.50 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.43 (d, *J* = 3.5 Hz, 1H), 3.38–3.33 (m, 1H), 3.32 (s, 1H), 3.25 (d, *J* = 7.0 Hz, 2H), 1.61–1.53 (m, 8H), 1.38–1.26 (m, 8H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 138.1, 137.8, 137.8, 137.7, 135.9, 135.8, 134.2, 132.8, 130.0, 129.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 126.2, 126.1, 106.3, 106.1, 106.1, 100.3, 98.8, 88.7, 88.2, 87.2, 83.6, 83.3, 83.2, 81.0, 80.4, 80.1, 77.2. 75.2, 73.3, 72.3, 72.3, 72.1, 72.0, 71.9, 69.7, 69.5, 69.0, 67.6, 66.0, 65.8, 63.3, 61.0, 51.5, 29.5, 29.3, 29.1, 28.8, 26.8, 26.8, 26.7, 26.1, 19.3; HRMS–ESI–TOF calcd for $[M + NH_4]^+$ $C_{94}H_{112}N_7O_{17}Si$: 1638.7884. Found: 1638.7878.

*4.10. Methyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**10c**)*

Prepared from **5** (95 mg, 0.149 mmol) and **8c** (46 mg, 0.124 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 8:1 to 4:1) to afford compound **10c** as a light syrup (101 mg, yield of 91.0%, α:β = 2:1). For α: R_f 0.3 (5:1, petroleum ether–EtOAc); $[\alpha]_D$ 94.1 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.2 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.74 (t, *J* = 6.6 Hz, 4H), 7.61–7.55 (m, 4H), 7.50–7.31 (m, 16H), 7.24 (t, *J* = 7.8 Hz, 2H), 5.48 (d, *J* = 1.8 Hz, 1H), 5.39 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.15 (d, *J* = 3.0 Hz, 1H), 5.06 (s, 2H), 4.38–4.35 (m, 1H), 4.35 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.07 (d, *J* = 12.6 Hz, 1H), 3.95 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.92–3.87 (m, 2H), 3.71 (d, *J* = 12.0 Hz, 1H), 3.54 (d, *J* = 1.8 Hz, 2H), 3.41 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.6, 137.8, 135.9, 135.9, 134.3, 133.5, 133.5, 132.9, 130.9, 129.9, 129.9, 129.7, 129.2, 129.2, 128.9, 128.5, 128.5, 128.1, 127.8, 127.5, 126.1, 106.7, 100.5, 99.1, 82.3, 80.6, 77.2, 77.0, 76.8, 75.5, 69.5, 69.2, 67.2, 65.6, 63.0, 61.0, 54.9, 30.6, 29.7, 26.8, 19.4, 19.2, 13.7, 1.0; For β: R_f 0.25 (5:1, petroleum ether–EtOAc); $[\alpha]_D$ 14.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (q, *J* = 7.8 Hz, 4H), 7.76 (d, *J* = 7.8 Hz, 4H), 7.59–7.53 (m, 4H), 7.46–7.36 (m, 12H), 7.30 (t, *J* = 7.8 Hz, 2H), 5.48 (d, *J* = 1.8 Hz, 1H), 5.47 (d, *J* = 6.0 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 2H), 4.48 (td, *J* = 6.6, 3.0 Hz, 1H), 4.36–4.32 (m, 2H), 4.17 (d, *J* = 12.0 Hz, 1H), 3.90–3.86 (m, 2H), 3.75 (d, *J* = 12.0 Hz, 1H), 3.61 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.47 (s, 3H), 3.44 (d, *J* = 3.6 Hz, 1H), 3.07 (s, 1H), 1.05 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 165.5, 137.8, 136.0, 135.9, 134.1, 133.4, 133.4, 132.7, 130.0, 129.9, 129.9, 129.8, 129.3, 129.3, 128.9, 128.5, 128.4, 128.1, 127.8, 127.6, 126.2, 106.8, 102.5, 100.7, 82.2, 81.2, 77.6, 77.3, 77.0, 76.8, 74.7, 72.8, 69.3, 68.9, 66.4, 64.0, 54.9, 31.9, 29.7, 29.4, 26.8, 22.7, 19.4, 14.1, 1.0; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{49}H_{51}N_3NaO_{11}Si$: 908.3191. Found: 908.3199.

*4.11. N-tert-Butyloxycarbonyl-3-O-(4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α-D-galactopyranosyl)-D-Threonine allyl ester (**10d**)*

Prepared from **5** (86 mg, 0.135 mmol) and **8d** (28 mg, 0.114 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 2:1) to afford compound **10d** as a light syrup (75 mg, yield of 86.6%, α:β = 5:4. For α: R_f 0.25 (3:1, petroleum ether–EtOAc); $[\alpha]_D$ 157.3 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (t, *J* = 6.6 Hz, 4H), 7.51–7.36 (m, 9H), 7.29 (t, *J* = 7.8 Hz, 2H), 5.92–5.85 (m, 1H), 5.34 (t, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 5.11 (s, 1H), 4.97 (d, *J* = 3.0 Hz, 1H), 4.65–4.58 (m, 2H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.13–4.09 (m, 2H), 4.06 (dd, *J* = 10.8, 3.0 Hz, 1H), 3.87–3.83 (m, 2H), 3.74 (dd, *J* = 12.6, 1.8 Hz, 1H), 3.54 (d, *J* = 3.0 Hz, 1H), 3.35 (s, 1H), 1.43 (s, 9H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.7, 155.3, 137.7, 135.95, 135.83, 134.1, 132.6, 131.5, 130.1, 129.9, 128.92, 128.18, 127.90, 127.56, 126.1, 118.8, 100.48, 100.22, 80.1, 77.24, 77.03, 76.8, 75.4, 69.71, 69.12, 69.05, 66.3, 63.3, 60.6, 54.2, 31.9, 29.72, 29.38, 26.8, 22.7, 19.3, 14.1. For β: R_f 0.15 (3:1, petroleum ether–EtOAc); $[\alpha]_D$ 80.1 (*c* 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77–7.74 (m, 5H), 7.54 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.47–7.45 (m, 1H), 7.43–7.38 (m, 7H), 7.30 (t, *J* = 7.8 Hz, 2H), 5.92–5.86 (m, 1H), 5.33 (dd, *J* = 17.4, 1.8Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 5.14 (s, 1H), 4.71 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.64 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.48 (d, *J* = 8.4 Hz, 1H), 4.33 (dd, *J* = 10.2, 3.0 Hz, 1H), 4.17 (d, *J* = 8.4 Hz, 1H), 4.14 (dd, *J* = 12.0, 1.2 Hz, 1H), 3.85–3.81 (m, 2H), 3.74 (dd, *J* = 12.6, 1.8 Hz, 1H), 3.56 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.43 (d, *J* = 3.0 Hz, 1H), 3.02 (d, *J* = 0.6 Hz, 1H), 1.45 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.8, 137.8, 135.98, 135.93, 135.87, 135.83, 134.0, 132.6, 131.6, 129.99,129.88, 128.91, 128.16, 127.82, 127.61, 126.2, 118.5, 102.3, 100.6, 79.9, 77.2, 77.0, 76.8, 74.5, 72.7, 69.5, 68.8, 66.32, 66.18, 64.0, 54.0, 28.3, 26.8, 19.4. HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{40}H_{50}N_4NaO_9Si$: 781.3245. Found: 781.3231.

*4.12. (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranoside (**10e**)*

Prepared from **5** (105 mg, 0.165 mmol) and **8e** (22 mg, 0.141 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 15:1) to afford compound **10e** as a light syrup (82 mg, yield of 86.9%, α:β = 15:1). R_f 0.6 (5:1, petroleum ether–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77–7.74 (m, 4H), 7.55 (d, *J* = 6.6 Hz, 2H), 7.47–7.37 (m, 8H), 7.76 (t, *J* = 7.8 Hz, 2H), 5.13 (s, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 4.09 (d, *J* = 12.0 Hz, 1H), 3.82 (q, *J* = 10.2 Hz, 1H), 3.73 (dd, *J* = 12.0, 1.2 Hz, 1H), 3.55 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.47–3.42 (m, 2H), 2.98 (s, 1H), 2.38–2.33 (m, 1H), 2.06 (d, *J* = 12.6 Hz, 1H), 1.64 (d, *J* = 10.8 Hz, 2H), 1.32–1.26 (m, 4H), 1.05 (s, 9H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.2, 136.0, 135.9, 134.3, 132.9, 129.9, 129.7, 128.9, 128.2, 127.8, 127.5, 126.4, 100.8, 99.3, 77.9, 77.2, 77.0, 74.8, 73.0, 69.1, 65.9, 64.2, 47.9, 40.3, 34.4, 31.6, 29.7, 26.8, 25.3, 23.4, 22.3, 20.9, 19.4, 16.0; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{39}H_{51}N_3NaO_5Si$: 692.3496. Found: 692.3488.

*4.13. Methyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (**10f**)*

Prepared from **5** (86 mg, 0.135 mmol) and **8f** (52 mg, 0.112 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 15:1 to 12:1) to afford compound **10f** as a light syrup (93 mg, yield of 84.9%, α:β = 13:1). For α: R_f 0.35 (8:1, petroleum ether–EtOAc); $[\alpha]_D$ 61.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80–7.75 (m, 4H), 7.49–7.16 (m, 26H), 5.77 (d, *J* = 4.0 Hz, 1H), 5.08 (d, *J* = 10.5 Hz, 1H), 4.97 (s, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 4.0 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 4.13–4.10 (m, 1H), 4.05 (t, *J* = 9.0 Hz, 1H), 3.83 (t, *J* = 10.0 Hz, 1H), 3.80 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.71 (d, *J* = 12.5, 1.0 Hz, 1H), 3.65 (ddd, *J* = 10.0, 4.0, 1.5 Hz, 1H), 3.55 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.43 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.39 (s, 3H), 3.34 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.24 (dd, *J*

= 12.0, 1.5 Hz, 1H), 3.11 (s, 1H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.6, 138.0, 137.9, 137.8, 136.0, 135.9, 134.2, 132.9, 130.0, 129.8, 128.8, 128.5, 128.4, 128.4, 128.1, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 127.0, 126.1, 100.4, 98.4, 97.9, 81.9, 80.5, 77.2, 75.6, 74.9, 73.3, 73.2, 72.4, 69.5, 69.4, 69.0, 69.0, 63.0, 60.6, 55.4, 26.8, 19.3; For β: R_f 0.2 (8:1, petroleum ether–EtOAc); $[\alpha]_D$ 8.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80–7.76 (m, 4H), 7.53–7.15 (m, 26H), 5.11 (t, *J* = 5.0 Hz, 2H), 4.82 (d, *J* = 12.5 Hz, 1H), 4.75 (d, *J* = 11.0 Hz, 1H), 4.64 (dd, *J* = 12.0, 5.0 Hz, 2H), 4.59 (d, *J* = 4.0 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 4.13 (d, *J* = 12.5 Hz, 1H), 4.05 (dd, *J* = 12.0, 1.5 Hz, 1H), 3.99 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.95–3.89 (m, 2H), 3.82–3.75 (m, 3H), 3.55–3.49 (m, 2H), 3.40 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.39 (s, 3H), 3.29 (d, *J* = 3.5 Hz, 1H), 2.50 (s, 1H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.2, 138.5, 138.1, 138.1, 136.0, 135.9, 134.1, 132.9, 130.0, 129.9, 128.8, 128.5, 128.4, 128.3, 128.1, 127.8, 127.8, 127.7, 127.6, 127.5, 127.2, 126.3, 101.5, 100.6, 98.3, 80.4, 79.3, 77.4, 77.2, 75.9, 74.5, 73.6, 73.2, 73.2, 69.7, 68.6, 66.1, 65.0, 55.4, 26.8, 19.4; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{57}H_{63}N_3NaO_{10}Si$: 1000.4180. Found: 1000.4179.

4.14. (2-Trimethylsilyl)-ethyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 3)-4,6-di-O-benzylidenyl-2-azido-2-deoxy-β-D-glucopyranoside (10g)

Prepared from **5** (84 mg, 0.132 mmol) and **8g** (43 mg, 0.109 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 12:1) to afford compound **10g** as a light syrup (70 mg, yield of 70.7%, α-only). R_f 0.3 (8:1, petroleum ether–EtOAc); $[\alpha]_D$ 77.7 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79–7.75 (m, 4H), 7.53–7.36 (m, 14H), 7.29 (t, *J* = 8.0 Hz, 2H), 5.61 (d, *J* = 3.5 Hz, 1H), 5.58 (s, 1H), 5.15 (s, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 4.35 (q, *J* = 5.0 Hz, 1H), 4.24 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.12 (dd, *J* = 12.5, 1.0 Hz, 1H), 3.83 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.80–3.61 (m, 7H), 3.39 (td, *J* = 10.0, 5.0 Hz, 1H), 3.25 (dd, *J* = 10.0, 8.0 Hz, 1H), 1.10 (s, 9H), 1.06–1.02 (m, 2H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 136.8, 136.0, 135.8, 134.3, 132.7, 130.1, 129.8, 128.8, 128.3, 128.1, 127.8, 127.5126.1, 125.9, 102.1, 101.4, 100.4, 98.8, 81.7, 77.2. 75.7, 74.2, 69.2, 68.9, 68.5, 68.3, 65.9, 65.2, 63.2, 60.1, 26.8, 19.3, 18.3, −1.4; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{47}H_{58}N_6NaO_9Si_2$: 929.3702. Found: 929.3696.

4.15. 4,6-Di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1 → 2)-1,3,4-tri-O-benzoyl-α-D-ribofuranose (10h)

Prepared from **5** (84 mg, 0.132 mmol) and **8h** (52 mg, 0.113 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 8:1) to afford compound **10h** as a light syrup (87 mg, yield of 79.8%, α-only). R_f 0.2 (8:1, petroleum ether–EtOAc); $[\alpha]_D$ 147.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.05 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.02 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.59–7.53 (m, 4H), 7.49 (d, *J* = 6.6 Hz, 2H), 7.47 (td, *J* = 8.4, 3.6 Hz, 4H), 7.39 (dd, *J* = 7.2, 3.6 Hz, 2H), 7.34–7.27 (m, 7H), 7.17 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 4.2 Hz, 1H), 5.60 (dd, *J* = 6.6, 1.8 Hz, 1H), 5.21 (d, *J* = 3.6 Hz, 1H), 4.86 (s, 1H), 4.80 (q, *J* = 5.4 Hz, 1H), 4.66 (q, *J* = 6.6 Hz, 1H), 4.60 (t, *J* = 3.0 Hz, 2H), 4.09 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.89 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.87 (dd, *J* = 12.6, 1.2 Hz, 1H), 3.50 (dd, *J* = 12.6, 1.2 Hz, 1H), 3.44 (s, 1H), 3.17 (d, *J* = 2.4 Hz, 1H), 0.9 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 165.98, 165.6, 137.6, 135.6, 135.5, 134.1, 133.6, 133.5, 133.3, 133.2, 130.1, 129.95, 129.82, 129.80, 129.75, 129.56, 129.24, 128.8, 128.7, 128.5, 128.3, 128.1, 127.6, 127.5, 126.1, 100.4, 98.5, 94.0, 82.5, 77.25, 77.0, 76.8, 74.8, 74.2, 71.4, 69.4, 68.9, 64.1, 63.5, 60.7, 26.8, 19.3; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{55}H_{53}N_3NaO_{12}Si$: 998.3296. Found: 998.3305.

4.16. Methyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-2,5-di-O-benzoyl-α-D-arabinofuranoside (10i)

Prepared from **5** (108 mg, 0.170 mmol) and **8i** (52 mg, 0.140 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 8:1) to afford compound **10i** as a light syrup (92 mg, yield of 74.4%, α-only). R_f 0.3 (6:1, petroleum ether–EtOAc); $[\alpha]_D$ 102.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (t, *J* = 8.4 Hz, 4H), 7.90 (d, *J* = 6.6 Hz, 2H), 7.76 (d, *J* = 6.6 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.53–7.35 (m, 14H), 7.30 (q, *J* = 15.6 Hz, 1H), 5.36 (d, *J* = 4.2 Hz, 2H), 5.09 (s, 1H), 5.01 (s, 1H), 4.55 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.44–4.42 (m, 1H), 4.27 (s, 2H), 4.25 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.96 (d, *J* = 12.6 Hz, 1H), 3.92 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.59 (d, *J* = 12.0 Hz, 1H), 3.49 (d, *J* = 3.0 Hz, 1H), 3.45 (s, 3H), 3.32 (s, 1H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2, 165.4, 137.7, 13.98.0, 135.89, 134.2, 133.5, 133.3, 132.8, 129.97, 129.86, 129.82, 129.64, 129.44, 129.14, 128.87, 128.51, 128.44, 128.12, 127.86, 127.57, 126.1, 106.9, 100.5, 98.6, 82.3, 81.5, 79.9, 77.3, 77.1, 76.8, 75.3, 69.3, 69.0, 63.5, 63.1, 60.3, 54.8, 26.8, 19.3; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{49}H_{51}N_3NaO_{11}Si$: 908.3191. Found 908.3188.

4.17. Methyl 4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1 → 4)-2:3-O-isopropylidene-α-L-rhamnopyranoside (10j)

Prepared from **5** (105 mg, 0.165 mmol) and **8j** (30 mg, 0.138 mmol) following the general Procedure. The residue was purified by column chromatography (Petroleum ether–EtOAc, 8:1) to afford compound **10j** as a light syrup (87 mg, yield of 86.4%, α:β = 7:1). For α: R_f 0.3 (6:1, petroleum ether–EtOAc); $[\alpha]_D$ 100.1 (*c* 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (t, *J* = 7.2 Hz, 4H), 7.49–7.46 (m, 3H), 7.42–7.35 (m, 7H), 7.27 (t, *J* = 7.8 Hz, 1H), 5.13 (d, *J* = 3.0 Hz, 1H), 5.01 (s, 1H), 4.83 (s, 1H), 4.28 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.05 (s, 1H), 4.04 (d, *J* = 6.6 Hz, 1H), 3.92–3.90 (m, 2H), 3.76 (s, 1H), 3.72 (d, *J* = 12.0 Hz, 1H), 3.69 (q, *J* = 10.2 Hz, 1H), 3.51 (d, *J* = 3.0 Hz, 1H), 3.37 (t, *J* = 4.8 Hz, 4H), 1.44 (s, 3H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.26 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.8, 135.9, 135.89, 134.3, 132.9, 130.0, 129.8, 128.8, 128.1, 127.8, 127.5, 126.1, 109.0, 100.4, 99.3, 97.7, 79.9, 77.2, 77.0, 76.9, 76.8, 76.1, 75.3, 69.6, 69.1, 65.0, 62.7, 61.3, 54.9, 31.9, 29.7, 28.1, 26.9, 26.4, 22.7, 19.3, 17.5, 14.1; For β: R_f 0.25 (6:1, petroleum ether–EtOAc); $[\alpha]_D$ 11.3 (*c* 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (qd, *J* = 7.8 1.2 Hz, 4H), 7.54 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.48–7.45 (m, 1H), 7.43–7.38 (m, 7H), 7.29 (t, *J* = 7.8 Hz, 2H), 5.10 (s, 1H), 4.85 (s, 1H), 4.68 (d, *J* = 8.4 Hz, 1H), 4.27 (t, *J* = 6.6 Hz, 1H), 4.11–4.09 (m, 2H), 3.80 (q, *J* = 10.2 Hz, 1H), 3.74 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.68 (q, *J* = 6.6 Hz, 2H), 3.64 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.38 (s, 1H), 3.37 (s, 3H), 3.01 (s, 1H), 1.44 (s, 3H), 1.32 (d, *J* = 5.4 Hz, 6H), 1.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.0, 136.1135.9, 134.2, 132.8, 129.89, 129.80, 128.9, 128.2, 127.8, 127.6, 126.2, 109.1, 100.7, 100.0, 99.8, 97.9, 78.1, 77.8, 77.2, 77.0, 76.8, 76.1, 74.6, 72.8, 69.0, 66.2, 64.5, 64.2, 54.8, 31.9, 29.7, 29.4, 27.8, 26.8, 26.4, 22.7, 19.4, 17.7, 14.1, 1.0; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{39}H_{49}N_3NaO_9Si$: 754.3136. Found: 754.3136.

4.18. Methyl 4,6-di-O-benzylidenyl-3-O-benzoyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (11)

A mixture of **6** (73 mg, 0.145 mmol), **8c** (44 mg, 0.120 mmol) and freshly activated 4 Å molecular sieves (117 mg) in dry CH_2Cl_2 (1.5 mL) was cooled to 0 °C. The suspension was stirred for 15 min, then NIS (49 mg, 0.217 mmol) and TfOH (1.3 μL, 015 mmol) were added. The reaction mixture was stirred for 5 min at the same temperature. The reaction mixture was gradually warmed to rt and was stirred for 1–2 h at the same temperature. The mixture was quenched with Et_3N and was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and

concentrated in vacuo. The crude material was quickly purified by column chromatography (4:1, petroleum ether–EtOAc) to afford compound **11** as a colorless syrup (80 mg, yield of 89.8%,α:β = 1:1). For α: R_f 0.45 (3:1, petroleum ether–EtOAc), ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09–8.06 (m, 6H), 7.61–7.58 (m, 2H), 7.48–7.45 (m, 7H), 7.41–7.38 (m, 2H), 7.35–7.33 (m, 3H), 5.57–5.55 (m, 1H), 5.54 (s, 1H), 5.53 (d, *J* = 1.8 Hz, 1H), 5.52–5.50 (m, 1H), 5.26 (d, *J* = 3.6 Hz, 1H), 5.15 (s, 1H), 4.66 (d, *J* = 3.6 Hz, 1H), 4.45–4.43 (m, 1H), 4.33 (dd, *J* = 6.6, 1.8 Hz, 1H) 4.20–4.17 (m, 1H), 4.16 (dd, *J* = 11.4, 5.4 Hz, 1H), 4.11–4.04 (m, 2H), 4.01–3.99 (m, 1H), 3.49 (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 165.8, 165.6, 137.6, 133.6, 133.48, 133.46, 129.97, 129.96, 129.94, 129.4, 129.11, 129.05, 129.95, 128.52, 128.49, 128.1, 126.0, 106.8, 100.6, 98.7, 82.3, 81.2, 77.5, 77.3, 77.1, 76.8, 73.5, 70.4, 69.2, 67.6, 62.8, 57.8, 55.0. For β: R_f 0.20 (3:1, petroleum ether–EtOAc), ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08–8.07 (m, 6H), 7.60–7.54 (m, 3H), 7.48–7.42 (m, 8H), 7.36–7.33 (m, 3H), 5.52 (s, 1H), 5.50–4.49 (m, 2H), 5.16 (s, 1H), 5.01 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 4.52–4.50 (m, 1H), 4.49 (d, *J* = 3.6 Hz, 1H), 4.44–4.44 (m, 1H), 4.37 (d, *J* = 1.2 Hz, 1H), 4.14 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.10–4.07 (m, 1H), 4.00–3.97 (m, 1H), 3.59 (s, 1H), 3.48 (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.0, 165.9, 165.5, 137.5, 133.54, 133.47, 133.46, 130.0, 129.9, 129.3, 129.2, 129.0, 128.51, 128.50, 128.47, 128.1, 126.2, 106.8, 102.5, 100.8, 82.3, 81.2, 77.6, 77.3, 77.0, 76.8, 72.82, 72.76, 69.4, 68.9, 66.5, 60.5, 54.9, 32.0, 31.5, 30.2, 29.7, 29.4, 22.7, 14.2; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{40}H_{37}N_3NaO_{12}$: 774.2275. Found: 774.2286.

4.19. Methyl 4,6-di-O-benzylidenyl-3-O-benzyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (12)

A mixture of **7** (98 mg, 0.200 mmol), **8c** (62 mg, 0.167 mmol) and freshly activated 4 Å molecular sieves (160 mg) in dry CH_2Cl_2 (2 mL) was cooled to −20 °C. The suspension was stirred for 15 min, then NIS (68 mg, 0.300 mmol) and TfOH (1.8 μL, 020 mmol) were added. The reaction mixture was stirred for 5 min at the same temperature. The reaction mixture was gradually warmed to 0 °C and was stirred for 1–2 h at the same temperature. The mixture was quenched with Et_3N and was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography (3:1, petroleum ether–EtOAc) to afford compound **12** as a colorless syrup (105 mg, yield of 85.5%, α:β = 2:3). For α: R_f 0.65 (2:1, petroleum ether–EtOAc), ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.08 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.62–7.59 (m, 1H), 7.55–7.52 (m, 1H), 7.51–7.43 (m, 6H), 7.37–7.28 (m, 8H), 5.50–5.49 (m, 2H), 5.44 (s, 1H), 5.16 (s, 1H), 5.14 (d, *J* = 3.6 Hz, 1H), 4.58 (dd, *J* = 21, 12 Hz, 2H), 4.43–4.40 (m, 1H), 4.26 (dd, *J* = 12, 1.2 Hz, 1H), 4.20 (d, *J* = 3.0 Hz, 1H), 4.06 (dd, *J* = 10.8, 5.4 Hz, 1H), 4.02–3.97 (m, 3H), 3.96 (dd, *J* = 12, 3.0 Hz, 1H), 3.84 (s, 1H), 3.47 (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 165.5, 138.0, 137.6, 133.62, 133.57, 129.94, 129.89, 129.2, 129.1, 129.0, 128.6, 128.5, 128.8, 128.2, 127.7, 127.6, 126.2, 106.8, 100.9, 98.7, 82.3, 81.1, 77.4, 77.2, 77.0, 76.8, 74.9, 73.0, 71.2, 69.4, 67.1, 63.0, 58.8, 54.9, 31.4, 30.2, 1.03. For β: R_f 0.35 (2:1, petroleum ether–EtOAc), ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07–8.06 (m, 4H), 7.59–7.52 (m, 4H), 7.46–7.29 (m, 12H), 5.51 (dd, *J* = 6, 1.8 Hz, 1H), 5.49 (d, *J* = 1.8 Hz, 1H), 5.47 (s, 1H), 5.45 (s, 1H), 4.75 (dd, *J* = 14.4, 12.6 Hz, 2H), 4.88 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.46 (d, *J* = 8.4 Hz, 1H), 4.39 (dd, *J* = 13.2, 3.0 Hz, 1H), 4.30 (dd, *J* = 12.6, 1.2 Hz, 1H), 4.07 (d, *J* = 3.0 Hz, 1H), 4.00 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.94–3.90 (m, 2H), 3.47 (s, 3H), 3.42 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.33 (s, 1H), ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 165.5, 137.7, 137.6, 133.4, 129.95, 129.88, 129.21, 129.17, 129.0, 128.5, 128.44, 128.43, 128.2, 127.9, 127.8, 126.4, 106.7, 102.5, 101.1, 82.4, 81.2, 77.8, 77.5, 77.2, 77.0, 76.8, 72.4, 71.6, 69.2, 69.1, 66.6, 61.9, 54.9; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{40}H_{39}N_3NaO_{11}$: 760.2482. Found: 760.2488.

4.20. 4,6-Di-O-benzylidenyl-3-O-benzyl-2-azido-2-deoxy-α,β-D-galactopyranosyl-(1 → 2)-1,3,4-tri-O-benzoyl-α-D-ribofuranose (13)

A mixture of **7** (120 mg, 0.245 mmol), **8h** (94 mg, 0.204 mmol) and freshly activated 4 Å molecular sieves (214 mg) in dry CH_2Cl_2 (2.5 mL) was cooled to −20 °C. The suspension was stirred for 15 min, then NIS (83 mg, 0.368 mmol) and TfOH (2.2 μL, 025 mmol) were added. The reaction mixture was stirred for 5 min at the same temperature. The reaction mixture was gradually warmed to 0 °C and was stirred for 2 h at the same temperature. The mixture was quenched with Et_3N and was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography (5:1, petroleum ether–EtOAc) to afford compound **13** as a colorless syrup (128 mg, yield of 76.2%, a complex product). R_f 0.40 (4:1, petroleum ether–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.15 (dd, *J* = 7.8, 1.2 Hz, 2H), 8.09–8.01 (m, 7H), 7.96 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.90 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.62–7.32 (m, 28H), 7.23–7.21 (m, 3H), 7.17–7.15 (m, 2H), 6.84 (d, *J* = 4.2 Hz, 1H), 5.82 (td, *J* = 8.4, 4.2 Hz, 1H), 5.78 (dd, *J* = 7.2, 2.4 Hz, 1H), 5.38 (s, 1H), 5.17 (d, *J* = 3.0 Hz, 1H), 4.93 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.74 (dd, *J* = 4.2, 3.0 Hz, 1H), 4.73 (d, *J* = 3.0 Hz, 1H), 4.63 (d, *J* = 3.6 Hz, 2H), 4.25 (s, 2H), 4.08 (dd, *J* = 12.6, 1.2 Hz, 2H), 3.95 (dd, *J* = 12.6, 1.8 Hz, 1H), 3.84 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.79 (s, 1H), 3.60 (dd, *J* = 10.8, 3.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 166.5, 166.2, 166.0, 165.62, 165.58, 165.47, 165.37, 165.26, 137.71, 137.48, 133.78, 133.66, 133.65, 133.58, 133.53, 133.45, 133.39, 133.36, 133.23, 130.1, 130.0, 129.84, 129.80, 129.79, 129.76, 129.75, 129.6, 129.39, 129.32, 129.19, 129.0, 128.9, 129.7, 128.6, 128.59, 128.56, 128.51, 128.50, 128.44, 128.41, 128.33, 128.29, 128.21, 127.8, 127.6, 126.2, 100.9, 100.5, 97.7, 95.8, 94.1, 81.7, 79.6, 79.3, 77.3, 77.0, 76.9, 76.2, 74.7, 73.1, 72.96, 72.4, 71.9, 71.8, 71.5, 69.1, 65.2, 64.18, 64.14, 63.8, 58.1, 31.96, 31.5, 30.2, 29.73, 29.69, 29.4, 26.9, 22.7, 14.2.

4.21. Methyl 4,6-di-O-benzylidenyl-3-O-benzoyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-2,5-di-O-benzoyl-α-D-arabinofuranoside (14)

A mixture of **6** (80 mg, 0.159 mmol), **8i** (49 mg, 0.133 mmol) and freshly activated 4 Å molecular sieves (129 mg) in dry CH_2Cl_2 (1.6 mL) was cooled to 0 °C. The suspension was stirred for 15 min, then NIS (53 mg, 0.238 mmol) and TfOH (1.4 μL, 016 mmol) were added. The reaction mixture was stirred for 5 min at the same temperature. The reaction mixture was gradually warmed to r.t. and was stirred for 2 h at the same temperature. The mixture was quenched with Et_3N and was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography (5:1, petroleum ether–EtOAc) to afford compound **14** as a colorless syrup (18 mg, yield of 18.2%, α-only). R_f 0.35 (3:1, petroleum ether–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 7.8, 1.2 Hz, 2H), 8.03 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.99 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.61–7.58 (m, 2H), 7.55–7.52 (m, 1H), 7.48–7.40 (m, 6H), 7.34–7.31 (m, 5H), 5.58–5.55 (m, 2H), 5.50 (s, 1 H), 5.38 (d, *J* = 0.6 Hz, 1H), 5.16 (s, 1 H), 4.65 (d, *J* = 3.6 Hz, 2H), 4.61 (d, *J* = 3.0 Hz, 1H), 4.51–4.49 (s, 1H), 4.38 (d, *J* = 6.0 Hz, 1H), 4.20–4.16 (m, 2H), 3.97 (dd, *J* = 12.6, 1.2 Hz, 1H), 3.87 (s, 1H), 3.47 (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.3, 166.1, 165.4, 137.4, 133.5, 133.3, 130.0, 129.8, 129.7, 129.4, 129.3, 129.1, 129.0, 128.52, 128.48, 128.1, 126.0, 106.9, 100.6, 98.1, 82.3, 81.8, 80.2, 77.2, 77.0, 76.8, 73.4, 69.9, 69.0, 63.3, 63.1, 57.1, 54.9, 31.5, 29.8. HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{40}H_{37}N_3NaO_{12}$: 774.2275. Found: 774.2277.

4.22. Methyl 4,6-di-O-benzylidenyl-3-O-benzyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1 → 3)-2,5-di-O-benzoyl-α-D-arabinofuranoside (15)

A mixture of **7** (88 mg, 0.180 mmol), **8i** (56 mg, 0.50 mmol) and freshly activated 4 Å molecular sieves (144 mg) in dry CH_2Cl_2 (1.8 mL) was cooled to −20 °C. The suspension was stirred for 15 min, then NIS

(61 mg, 0.270 mmol) and TfOH (1.6 μL, 0.018 mmol) were added. The reaction mixture was stirred for 5 min at the same temperature. The reaction mixture was gradually warmed to 0 °C and was stirred for 1–2 h at the same temperature. The mixture was quenched with Et_3N and was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography (3:1, petroleum ether–EtOAc) to afford compound **15** as a colorless syrup (53 mg, yield of 47.8%, α-only). R_f 0.35(2:1, petroleum ether–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (dd, J = 7.8, 1.2 Hz, 2H), 7.99 (dd, J = 8.4, 1.2 Hz, 2H), 7.60–7.57 (m, 1H), 7.55–7.53 (m, 1H), 7.49 (dd, J = 7.8, 1.8 Hz, 2H), 7.43–7.40 (m, 4H), 7.36–7.29 (m, 8H), 5.43 (s, 1H), 5.39 (d, J = 3.0 Hz, 2H), 5.13 (s, 1H), 4.78 (dd, J = 28.2, 11.4 Hz, 2H), 4.64 (dd, J = 12.0, 3.0 Hz, 1H), 4.59 (dd, J = 12.6, 4.8 Hz, 1H), 4.45–4.43 (m, 1H), 4.35 (d, J = 6.0 Hz, 1H), 4.21 (d, J = 3.0 Hz, 1H), 4.15 (dd, J = 12.6, 1.2 Hz, 1H), 4.04 (dd, J = 10.8, 3.6 Hz, 1H), 3.97 (dd, J = 10.8, 3.6 Hz, 1H), 3.92 (dd, J = 12.6, 1.2 Hz, 1H), 3.67 (s, 1H), 3.47 (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.3, 165.4, 137.9, 137.5, 133.5, 133.4, 129.8, 129.7, 129.4, 129.1, 129.0, 128.51, 128.47, 128.43, 128.2, 127.9, 127.7, 126.2, 107.0, 100.9, 99.3, 82.3, 81.8, 80.0, 77.2, 77.0, 74.4, 72.9, 71.3, 69.2, 63.5, 63.2, 58.2, 55.0, 31.5, 30.2; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{40}H_{39}N_3NaO_{11}$: 760.2482. Found: 760.2471.

4.23. 8-Azidooctyl 3,5-O-(di-tert-butylsilylene)-2-O-levulinoyl-α-D-arabinofuranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (18)

A mixture of thioglycoside **16** (1.151 g, 2.330 mmol) and acceptor **17** (990 mg, 1.937 mmol), and freshly activated 4 Å molecular sieves (2.150 g) in dry CH_2Cl_2 (23 mL) was cooled to −30 °C. The suspension was stirred for 15 min, then NIS (678 mg, 3.01 mmol), TfOH (10 μL, 0.113 mmol) was added. The reaction mixture was stirred for 1 h −30 °C. The reaction mixture was gradually warmed to 0 °C and quenched with Et_3N. The mixture was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography (Petroleum ether–EtOAc, 5:1) to give the product **18** (1.555 g, yield of 91.2%) as a yellow syrup. For α: R_f 0.25 (4:1, petroleum ether–EtOAc); $[\alpha]_D$ 11.8 (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09–8.06 (m, 4H), 7.60–7.50 (m, 2H), 7.48 (dd, J = 15.5, 8.0 Hz, 4H), 5.46 (s, 1H), 5.46 (d, J = 4.0 Hz, 1H), 5.21 (s, 1H), 5.16 (dd, J = 6.5, 2.0 Hz, 1H), 5.00 (d, J = 2.0 Hz, 1H), 4.46 (dd, J = 9.5, 4.5 Hz, 1H), 4.35–4.32 (m, 1H), 4.12–4.06 (m, 2H), 4.04 (dd, J = 11.0, 5.5 Hz, 1H), 3.93–3.90 (m, 1H), 3.89 (dd, J = 11.0, 4.0 Hz, 1H), 3.79 (dt, J = 9.5, 7.0 Hz, 1H), 3.54 (dt, J = 9.5, 6.0 Hz, 1H), 3.24 (t, J = 7.0 Hz, 2H), 3.20 (t, J = 6.5 Hz, 2H), 2.76–2.73 (m, 2H), 2.58–2.55 (m, 2H), 2.18 (s, 3H), 2.04 (dd, J = 7.5, 5.5 Hz, 2H), 1.67–1.54 (m, 4H), 1.42–1.26 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.2, 171.8, 165.6, 165.5, 133.4, 133.3, 129.9, 129.9, 129.5, 129.3, 128.5, 128.4, 106.6, 105.7, 82.9, 81.9, 81.4, 80.4, 77.6, 77.2, 73.6, 67.8, 67.5, 67.4, 51.5, 37.9, 29.8, 29.5, 29.3, 29.1, 28.8, 27.9, 27.4, 27.0, 26.7, 26.1, 22.6, 20.0; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{45}H_{63}N_3NaO_{13}Si$: 904.4028. Found: 904.4034.

4.24. 8-Azidooctyl 2-O-levulinoyl-α-D-arabinofuranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (19)

To a solution of **18** (1.350 g, 1.53 mmol) in THF (12 mL) was added TBAF (3.0 mL, 1.0 M in THF, mmol) at 0 °C under N_2. The reaction mixture was gradually warmed to rt and stirred 1h. The mixture was concentrated in vacuo and extracted with CH_2Cl_2 and H_2O. The organic layer was washed with 1 N aq NH_4Cl, H_2O and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (Petroleum ether–EtOAc, 1:3) to give the product **19** (981 mg, yield of 85.8%) as a yellow syrup. R_f 0.25 (1:3, petroleum ether–EtOAc); $[\alpha]_D$ 33.7 (*c* 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (dd, J = 8.0, 1.5 Hz, 4H), 7.61–7.57 (m, 2H), 7.48 (td, J = 8.0, 2.5 Hz, 4H), 5.49 (d, J = 3.5 Hz, 1H), 5.49 (s, 1H), 5.23 (s, 1H), 5.21 (s, 1H), 4.94 (d, J = 2.0 Hz, 1H), 4.39 (dd, J = 8.5, 5.0 Hz, 1H), 4.25–4.22 (m, 1H), 4.13 (dd, J = 11.0, 5.0 Hz, 1H), 4.02 (td, J = 6.0, 2.5 Hz, 1H), 3.90–3.86 (m, 2H), 3.78–3.71 (m, 2H), 3.53 (dt, J = 9.5, 6.5 Hz, 1H), 3.24 (t, J = 7.0 Hz, 2H), 2.76–2.73 (m, 2H), 2.64–2.60 (m, 2H), 2.14 (s, 3H), 1.67–1.54 (m, 4H), 1.43–1.28 (m, 8H), 1.03 (s, 9H), 0.91 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.3, 172.9, 165.9, 165.4, 133.5, 130.0, 129.9, 129.2, 129.2, 128.6, 128.5, 105.6, 105.0, 85.4, 84.7, 81.9, 81.6, 77.4, 77.2, 76.4, 67.6, 65.8, 62.2, 51.4, 37.9, 29.7, 29.5, 29.3, 29.1, 28.8, 27.8, 26.7, 26.1; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{37}H_{43}N_3NaO_{13}Si$: 764.3007. Found: 764.3003.

4.25. Toluene 5-O-(2,2,2-trichloroethoxy)-carbonyl-2,3-di-O-benzoyl-α-D-arabinofuranoside (20)

To a solution of 2,3-di-*O*-benzoyl-1-thio-α-D-arabinofuranoside [20] (1.53 g, 3.30 mmol) in dry CH_2Cl_2 (6.6 mL) was added pyridine (0.37 mL, 3.00 mmol) and Troc-Cl (0.55 mL, 3.96 mmol). The reaction mixture was stirred at 0 °C for 1 h. The resulting mixture was added H_2O and extracted with CH_2Cl_2. The organic layer was washed with 1 N HCl, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (6:1, petroleum ether–EtOAc) to afford compound **20** as a yellow syrup (1.99 g, 88%). R_f 0.4 (4:1, petroleum ether–EtOAc); $[\alpha]_D$ 79.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (dd, J = 8.5, 1.0 Hz, 2H), 8.09 (dd, J = 8.5, 1.0 Hz, 2H), 7.64–7.44 (m, 8H), 7.15 (d, J = 8.0 Hz, 2H), 5.73 (t, J = 1.5 Hz, 1H), 5.52 (dt, J = 4.5, 1.0 Hz, 1H), 4.80 (d, J = 12.0 Hz, 1H), 4.76 (d, J = 12.0 Hz, 1H), 4.76–4.70 (m, 2H), 4.70 (dd, J = 12.0, 5.0 Hz, 1H), 2.34 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 165.3, 153.9, 138.2, 133.7, 133.6, 132.9, 130.1, 130.0, 129.9, 129.9, 129.8, 129.6, 94.3, 92.0, 81.9, 81.1, 77.9, 77.2, 77.0, 76.4, 67.4, 21.2; HRMS–ESI–TOF calcd for $[M + NH_4]^+$ $C_{29}H_{29}Cl_3NO_8S$: 656.0679. Found: 656.0672.

4.26. 8-Azidooctyl 3,5-di-O-[5-O-(2,2,2-trichloroethoxy)-carbonyl-2,3-di-O-benzoyl-α-D-arabinofuranosyl]-2-O-levulinoyl-α-D-arabinofuranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (21)

A mixture of thioglycoside **20** (795 mg, 1.246 mmol) and acceptor **19** (438 mg, 0.591 mmol), and freshly activated 4 Å molecular sieves (1.240 g) in dry CH_2Cl_2 (13 mL) was cooled to −30 °C. The suspension was stirred for 15 min, then NIS (351 mg, 1.560 mmol), TfOH (6 μL, 0.068 mmol) was added. The reaction mixture was stirred for 1 h −30 °C. The reaction mixture was gradually warmed to 0 °C and quenched with Et_3N. The mixture was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography (Petroleum ether–EtOAc, 5:2) to give the product **21** (745 mg, yield of 71.3%) as a yellow syrup. For α: R_f 0.3 (2:1, petroleum ether–EtOAc); $[\alpha]_D$ 18.5 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05–7.96 (m, 12H), 7.60–7.26 (m, 18H), 5.58 (d, J = 1.0 Hz, 1H), 5.56 (dd, J = 5.0, 1.0 Hz, 1H), 5.43 (dd, J = 6.0, 1.0 Hz, 2H), 5.40 (s, 1H), 5.39 (d, J = 4.5 Hz, 1H), 5.37 (s, 1H), 5.30 (dd, J = 5.0, 1.0 Hz, 1H), 5.26 (d, J = 2.0 Hz, 1H), 5.19 (s, 2H), 4.79–4.71 (m, 3H), 4.67 (d, J = 1.5 Hz, 2H), 4.65–4.53 (m, 4H), 4.49–4.42 (m, 2H), 4.36–4.32 (m, 2H), 4.11 (dd, J = 11.0, 4.0 Hz, 1H), 3.99 (dd, J = 11.5, 4.0 Hz, 1H), 3.90 (dd, J = 12.0, 2.5 Hz, 1H), 3.84 (dd, J = 11.0, 3.0 Hz, 1H), 3.76 (dt, J = 9.5, 6.5 Hz, 1H), 3.51 (dt, J = 9.5, 6.5 Hz, 1H), 3.23 (t, J = 7.0 Hz, 2H), 2.65–2.62 (m, 2H), 2.50 (t, J = 6.5 Hz, 2H), 2.06 (s, 3H), 1.65–1.52 (m, 4H), 1.41–1.24 (m, 8H), 1.03 (s, 9H), 0.91 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.0, 171.8, 165.8, 165.7, 165.5, 165.5, 165.1, 164.8, 154.0, 153.8, 133.5, 133.4, 133.3, 130.1, 130.0, 129.9, 129.9, 129.8, 129.3, 129.1, 129.0, 128.8, 128.5, 128.4, 128.4, 105.7, 105.6, 105.5, 105.5, 94.3, 94.3, 82.7, 81.9, 81.3, 81.2, 81.2, 81.0, 77.7, 77.6, 77.2, 77.2, 76.9, 76.8, 67.8, 67.6, 67.4, 65.8, 65.3, 51.4, 37.8, 29.6, 29.5, 29.3, 29.1, 28.8, 28.2, 27.9, 26.8, 26.7, 26.1; HRMS–ESI–TOF calcd for $[M + NH_4]^+$ $C_{81}H_{85}Cl_6N_4O_{29}$: 1787.3431. Found: 1787.3417.

*4.27. 8-Azidooctyl 3,5-di-O-[5-O-(2,2,2-trichloroethoxy)-carbonyl-2,3-di-O-benzoyl-α-D-arabinofuranosyl]-α-D-arabinofuranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**22**)*

To a solution of **21** (670 mg, 0.379 mmol) in CH_2Cl_2 (4.0 mL) and MeOH (0.4 mL) was added NH_2NH_2.AcOH (45 mg, 0.492 mmol). The reaction mixture was stirred at rt for 2 h. The resulting mixture was added H_2O and extracted with CH_2Cl_2. The organic layer was washed with 0.5 N HCl, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (5:2, petroleum ether–EtOAc) to afford compound **22** as a yellow syrup (533 mg, 84.3%). R_f 0.3 (2:1, petroleum ether–EtOAc); $[\alpha]_D$ 19.9 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08–7.90 (m, 12H), 7.63–7.26 (m, 18H), 5.59 (dd, J = 5.0, 1.0 Hz, 1H), 5.54 (d, J = 1.0 Hz, 1H), 5.43 (d, J = 4.5 Hz, 1H), 5.41 (d, J = 1.0 Hz, 1H), 5.40 (s, 1H), 5.38 (d, J = 1.5 Hz, 1H), 5.34 (dd, J = 5.0, 1.0 Hz, 1H), 5.22 (s, 1H), 5.16 (s, 1H), 5.13 (d, J = 1.5 Hz, 1H), 4.79–4.71 (m, 5H), 4.66 (dd, J = 11.5, 5.0 Hz, 1H), 4.65 (dd, J = 11.5, 3.5 Hz, 1H), 4.57–4.48 (m, 3H), 4.38–4.31 (m, 4H), 4.11 (dd, J = 11.0, 4.5 Hz, 1H), 3.99 (dd, J = 11.5, 2.5 Hz, 1H), 3.86 (dd, J = 11.5, 1.5 Hz, 1H), 3.84 (dd, J = 11.0, 4.0 Hz, 1H), 3.77 (dt, J = 9.5, 6.5 Hz, 1H), 3.52 (dt, J = 9.5, 6.5 Hz, 1H), 3.23 (t, J = 7.0 Hz, 2H), 3.19 (d, J = 7.5 Hz, 1H), 1.67–1.53 (m, 4H), 1.41–1.25 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 165.7, 165.6, 165.5, 165.4, 165.3, 154.0, 153.9, 133.7, 133.5, 133.5, 133.4, 130.0, 129.8, 129.8, 129.3, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4, 108.1, 106.1, 105.8, 105.5, 94.3, 82.8, 82.0, 81.9, 81.6, 81.4, 81.1, 81.0, 80.9, 77.5, 76.9, 67.8, 67.5, 67.4, 66.5, 64.9, 51.4, 29.4, 29.3, 29.1, 28.8, 26.7, 26.1; HRMS–ESI–TOF calcd for $[M + NH_4]^+$ $C_{76}H_{79}Cl_6N_4O_{27}$: 1689.3063. Found: 1689.3070.

*4.28. 8-Azidooctyl 3,5-di-O-[5-O-(2,2,2-trichloroethoxy)carbonyl-2,3-di-O-benzoyl-α-D-arabinofuranosyl]-2-O-(4,6-di-O-benzylidenyl-3-O-tert-butyldiphenylsilyl-2-azido-2-deoxy-α-D-galactopyranosyl)-α-D-arabinofuranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**23**)*

A mixture of thioglycoside **5** (443 mg, 0.695 mmol) and acceptor **22** (775 mg, 0.464 mmol), and freshly activated 4 Å molecular sieves (1.150 g) in dry CH_2Cl_2 (13 mL) was cooled to −30 °C. The suspension was stirred for 15 min, then NIS (196 mg, 0.867 mmol), TfOH (3 μL, 0.035 mmol) was added. The reaction mixture was stirred for 1 h −30 °C. The reaction mixture was gradually warmed to 0 °C and quenched with Et_3N. The mixture was diluted with CH_2Cl_2 and added $Na_2S_2O_3$, filtered through celite and concentrated in vacuo. The crude material was quickly purified by column chromatography (Petroleum ether–EtOAc, 4:1) to give the product **23** (816 mg, yield of 80.5%) as a yellow syrup. For α: R_f 0.35 (5:2, petroleum ether–EtOAc); $[\alpha]_D$ 30.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06–7.91 (m, 12H), 7.71–7.67 (m, 4H), 7.58–7.30 (m, 27H), 7.25 (t, J = 8.0 Hz, 2H), 5.50 (s, 1H), 5.47–5.45 (m, 3H), 5.41 (t, J = 4.5 Hz, 2H), 5.37 (d, J = 1.0 Hz, 1H), 5.31 (s, 1H), 5.20 (s, 1H), 5.18 (d, J = 3.5 Hz, 1H), 5.05 (d, J = 1.5 Hz, 1H), 4.98 (s, 1H), 4.79–4.65 (m, 6H), 4.62 (td, J = 12.0, 5.0 Hz, 2H), 4.54–4.50 (m, 2H), 4.34–4.22 (m, 5H), 4.04 (dd, J = 10.5, 4.0 Hz, 2H), 3.91 (dd, J = 11.5, 5.0 Hz, 1H), 3.86 (dd, J = 7.5, 3.0 Hz, 1H), 3.84 (dd, J = 8.5, 3.0 Hz, 1H), 3.74 (dd, J = 8.5, 3.0 Hz, 1H), 3.72 (dd, J = 10.0, 6.5 Hz, 1H), 3.62 (d, J = 11.0 Hz, 2H), 3.49–3.43 (m, 3H), 3.22 (t, J = 7.0 Hz, 2H), 1.64–1.52 (m, 4H), 1.40–1.22 (m, 8H), 1.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.8, 165.7, 165.5, 165.4, 165.1, 165.1, 154.0, 153.9, 137.8, 135.8, 134.3, 133.5, 133.3, 132.8, 130.0, 129.9, 129.9, 129.8, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.5, 128.5, 128.4, 128.1, 127.8, 127.5, 126.1, 105.7 ($J_{H1\text{-}C1}$ = 179.1), 105.7 ($J_{H1\text{-}C1}$ = 179.5), 105.6 ($J_{H1\text{-}C1}$ = 175.6), 105.5 ($J_{H1\text{-}C1}$ = 174.7), 100.3, 99.0 ($J_{H1\text{-}C1}$ = 172.5), 94.4, 94.3, 88.1, 82.0, 81.9, 81.6, 81.4, 81.2, 81.1, 80.8, 79.2, 77.5, 77.4, 77.4, 77.2, 77.0, 76.9, 75.2, 69.7, 69.0, 67.8, 67.6, 67.4, 66.6, 66.0, 63.4, 61.1, 60.4, 51.4, 29.5, 29.3, 29.1, 28.8, 26.8, 26.7, 26.1, 21.1, 19.3, 14.2; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{105}H_{106}Cl_6N_6NaO_{31}Si$: 2207.4695. Found: 2207.4686.

*4.29. 8-Azidooctyl 3,5-di-O-[5-O-(2,2,2-trichloroethoxy)carbonyl-2,3-di-O-benzoyl-α-D-arabinofuranosyl]-2-O-(4,6-di-O-benzylidenyl-2-azido-2-deoxy-α-D-galactopyranosyl)-α-D-arabinofuranosyl-(1 → 5)-2,3-di-O-benzoyl-α-D-arabinofuranoside (**24**)*

To a solution of **23** (680 mg, 0.311 mmol) in THF (8.0 mL) and Pyridine (8.0 mL) was added HF.Pyridine (1.6 mL, 70% HF) at 0 °C under N_2(g). The reaction mixture was gradually warmed to rt and stirred 12h. The mixture was concentrated in vacuo and extracted with CH_2Cl_2. The organic layer was washed with 1 N aq HCl, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (Petroleum ether–EtOAc, 2:1) to give the product **24** (502 mg, yield of 82.9%) as a yellow syrup. R_f 0.25 (1:1, petroleum ether–EtOAc); $[\alpha]_D$ 44.1 (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08–7.94 (m, 12H), 7.62–7.34 (m, 23H), 5.57 (d, J = 1.0 Hz, 1H), 5.52 (s, 1H), 5.52 (dd, J = 6.0, 0.5 Hz, 1H), 5.50 (s, 1H), 5.49 (d, J = 1.5 Hz, 1H), 5.42 (d, J = 6.0 Hz, 2H), 5.41 (dd, J = 6.0, 1.0 Hz, 1H), 5.33 (s, 1H), 5.26 (s, 1H), 5.23 (d, J = 2.0 Hz, 1H), 5.18 (d, J = 3.5 Hz, 1H), 4.81–4.65 (m, 6H), 4.65 (dd, J = 11.5, 5.0 Hz, 2H), 4.60–4.56 (m, 2H), 4.52–4.50 (m, 1H), 4.43 (dd, J = 7.0, 3.5 Hz, 2H), 4.39 (dd, J = 4.0, 1.5 Hz, 1H), 4.38 (dd, J = 8.5, 5.0 Hz, 1H), 4.33–4.31 (m, 1H), 4.27 (dd, J = 12.0, 1.0 Hz, 1H), 4.09 (dd, J = 11.5, 5.0 Hz, 1H), 4.07 (dd, J = 10.5, 3.5 Hz, 1H), 4.03–4.00 (m, 1H), 4.00 (dd, J = 12.0, 4.0 Hz, 1H), 3.87–3.82 (m, 3H), 3.79 (dt, J = 9.5, 6.5 Hz, 1H), 3.56 (dd, J = 10.5, 3.5 Hz, 2H), 3.53 (dt, J = 9.5, 6.5 Hz, 1H), 2.40 (d, J = 10.5 Hz, 1H), 1.67–1.53 (m, 4H), 1.44–1.26 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 165.7, 165.6, 165.4, 165.3, 165.2, 154.0, 153.8, 137.4, 133.6, 133.4, 130.0, 129.9, 129.9, 129.8, 129.7, 129.3, 129.2, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 126.2, 106.1, 105.8, 105.6, 105.5, 101.2, 98.7, 94.3, 94.3, 88.4, 82.1, 81.6, 81.3, 81.1, 80.7, 79.5, 77.6, 77.5, 77.4, 77.2, 77.0, 76.9, 76.9, 75.3, 69.2, 67.8, 67.7, 67.5, 67.5, 66.8, 65.6, 63.4, 61.0, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1; HRMS–ESI–TOF calcd for $[M + NH_4]^+$ $C_{89}H_{88}Cl_6N_6NaO_{31}$: 1964.3969. Found: 1964.3962.

*4.30. 8-Azidooctyl 3,5-di-O-[α-D-arabinofuranosyl]-2-O-(4,6-di-O-benzylidenyl-2-azido-2-deoxy-α-D-galactopyranosyl)-α-D-arabinofuranosyl-(1 → 5)-α-D-arabinofuranoside (**25**)*

To a solution of **24** (470 mg, 0.242 mmol) in MeOH (12.0 mL) was added CH_3ONa (47 mg). The reaction mixture was stirred 12h, then concentrated in vacuo. The residue was purified by column chromatography (CH_2Cl_2–MeOH, 1:3) to give the product **25** (209 mg, yield of 88.8%) as a white syrup. R_f 0.2 (1:3, CH_2Cl_2–MeOH); $[\alpha]_D$ 160.8 (*c* 1.9, MeOH); ^{1}H NMR (500 MHz, CD_3OD): δ 7.56–7.53 (m, 2H), 7.39–7.34 (m, 3H), 5.64 (s, 1H), 5.24 (d, J = 3.5 Hz, 1H), 5.20 (d, J = 1.0 Hz, 1H), 5.11 (d, J = 1.5 Hz, 1H), 4.99 (d, J = 1.5 Hz, 1H), 4.32 (d, J = 3.0 Hz, 1H), 4.30 (dd, J = 2.5, 1.5 Hz, 1H), 4.26–4.20 (m, 3H), 4.16 (dd, J = 12.5, 1.5 Hz, 1H), 4.15 (dd, J = 10.5, 3.5 Hz, 1H), 4.05–3.94 (m, 8H), 3.87–3.83 (m, 4H), 3.80–3.69 (m, 6H), 3.68 (dd, J = 12.0, 5.0 Hz, 2H), 3.47 (dt, J = 9.5, 6.5 Hz, 1H), 3.29 (t, J = 7.0 Hz, 2H), 1.63–1.56 (m, 4H), 1.39–1.30 (m, 8H); ^{13}C NMR (125 MHz, CD_3OD): δ 139.7, 129.9, 129.1, 127.6, 109.5, 109.5, 109.1, 107.3, 102.3, 99.6, 87.5, 85.7, 85.6, 83.8, 83.6, 83.4, 83.4, 82.6, 82.3, 78.9, 78.8, 78.6, 77.6, 70.3, 69.0, 68.2, 67.7, 67.3, 65.2, 63.1, 63.0, 61.5, 52.5, 30.7, 30.4, 30.2, 29.9, 27.8, 27.2, 26.1; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{41}H_{62}N_6NaO_{21}$: 997.3860. Found: 997.3861.

*4.31. 8-Aminooctyl 3,5-di-O-[α-D-arabinofuranosyl]-2-O-(2-amino-2-deoxy-α-D-galactopyranosyl)-α-D-arabinofuranosyl-(1 → 5)-α-D-arabinofuranoside (**26**)*

To a stirred solution of **25** (35 mg, 0.036 mmol) in THF–H_2O (2.1 mL, v:v = 1:1) was added 20% $Pd(OH)_2$/C (8 mg). After stirring overnight under an H_2 atmosphere, the reaction mixture was filtered through Celite and the filtrate was concentrated to give the product **26** (22 mg,

yield of 73.4%) as a yellow syrup. R_f 0.15 (3:3:3:4 EtOAc–CH_3OH–AcOH–H_2O); $[\alpha]_D$ 105.5 (*c* 0.5, H_2O); ^1H NMR (700 MHz, D_2O): δ 5.37 (s, 1H), 5.18 (s, 1H), 5.12 (s, 2H), 5.03 (s, 1H), 4.37–4.34 (m, 1H), 4.32 (s, 1H), 4.27 (d, J = 3.5 Hz, 1H), 4.19–3.71 (m, 30H), 3.62 (dt, J = 7.0, 3.5 Hz, 1H), 3.38 (t, J = 2.1 Hz, 0.2H), 3.04–3.02 (m, 1H), 3.38 (t, J = 2.1 Hz, 0.2H), 3.01 (d, J = 7.7 Hz, 0.2H), 1.69–1.63 (m, 3H), 1.37–1.26 (m, 10H), 0.91 ((t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, D_2O): δ 108.3, 108.2, 107.7, 106.7, 97.0, 86.2, 85.1, 85.1, 82.5, 82.3, 82.2, 82.0, 81.8, 81.3, 77.6, 77.6, 77.2, 73.0, 69.6, 69.1, 68.1, 67.1, 67.0, 62.7, 62.2, 62.1, 62.0, 51.5, 49.8, 40.5, 29.5, 29.1, 29.0, 27.6, 26.4, 26.0, 24.2, 21.5, 14.2; HRMS–ESI–TOF calcd for $[M+Na]^+$ $C_{34}H_{62}N_2NaO_{21}$: 857.3740. Found 857.3737.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2021.108237.

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