JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.5b02083 • Publication Date (Web): 28 Oct 2015

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Development of an Orthogonal Protection Strategy for the Synthesis of Mycobacterial Arabinomannan Fragments

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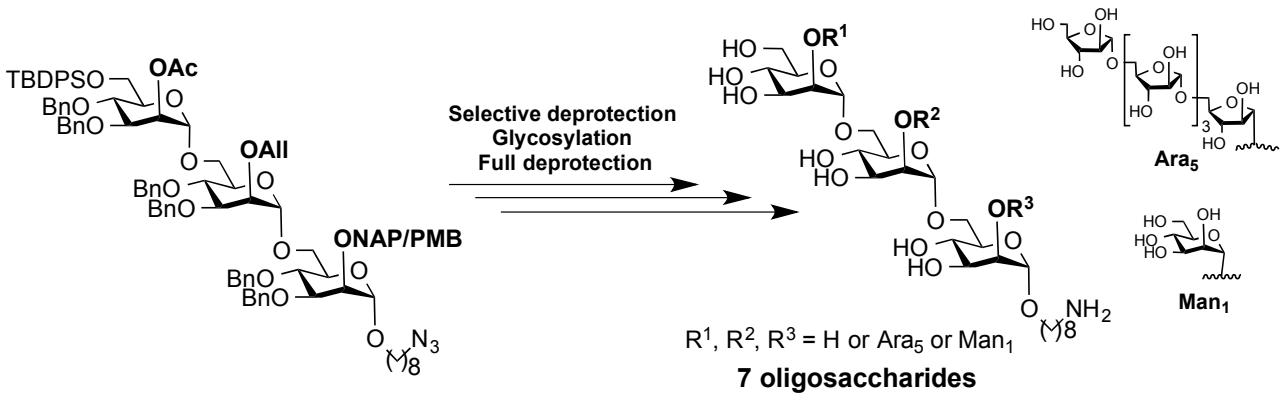
Abstract

Mycobacterium tuberculosis, the organism that causes tuberculosis (TB), has a carbohydrate-rich cell wall structure that possesses a number of immunogenic antigens. Circulating antibodies that recognize these glycans are present in patients infected by mycobacteria; detection of these antibodies could be the basis for new TB diagnostics. We describe here the synthesis of a panel of mycobacterial arabinomannan fragments for use in investigations directed at testing the feasibility of such a diagnostic method. In this study, we focused on structural motifs present in the core of the key immunogenic polysaccharide lipoarabinomannan (LAM). To access these compounds, we developed an efficient orthogonal protection strategy that allowed access to seven arabinomannan fragments of LAM (**1**–**7**). The targets included one tetrasaccharide, one pentasaccharide, three octasaccharides and two nonasaccharides. Starting from a differentially protected trimannopyranoside derivative (**8** or **9**) the targets were obtained using an approach that involved selective removal of the protecting group present at the O-2 position of a single mannopyranoside residue, followed by glycosylation with a pentaarabinofuranose thioglycoside and/or a mannopyranose trichloroacetimidate.

Graphical Abstract



Introduction

Tuberculosis (TB) continues to be one of the most important infectious diseases and leading causes of death worldwide. In 2013, 1.5 million people died from TB and another 9 million fell ill with the disease.[1] Access to reliable and cost-effective diagnostics for infections caused by *Mycobacterium tuberculosis* (the causative agent of TB) and other mycobacteria remain a challenge and is an area of significant research interest.[2] Like all mycobacteria, *M. tuberculosis* possesses a carbohydrate rich cell wall that protects the organism from the environment and influences the host immune response upon infection.[3] For example, previous work has shown that these glycans modulate cytokine induction[4] and also lead to a robust antibody response in the host.[3b,5] Thus, detecting the presence of antibodies that recognize various mycobacterial cell wall glycans could potentially be used in the diagnosis of TB.

A major mycobacterial cell wall glycan is lipoarabinomannan (LAM), a lipidated polysaccharide that plays a critical role in mycobacteria–host interactions.[6] The interaction of the host with this polysaccharide leads to significant titres of anti-LAM antibodies, underscoring the potential of LAM-based serology in TB diagnosis. Indeed, in a previous study, we demonstrated that detecting antibodies against a hexasaccharide fragment of LAM could discriminate between TB and non-TB patients.[7] The assay relied on the use of a synthetic derivative of this hexasaccharide, which was immobilized and used in ELISA. The sensitivity and specificity of this diagnostic were enhanced by inclusion of antibody responses against two protein antigens. We hypothesized that antibodies against other domains of LAM could also enhance the performance of the diagnostic and set out to prepare other fragments of this polysaccharide to test this possibility.

The structure of LAM, shown in a schematic form in Figure 1A, consists of a phosphatidyl-*myo*-inositol moiety, a core mannan, an arabinan domain and a terminal capping motif at the 'nonreducing' end of the molecule.[6,8] The core mannan consists of α-(1→6)-linked D-mannopyranose residues attached to the O-6 position of the inositol. Approximately half of these mannose residues are elaborated with branch consisting of a single α-(1→2)-D-mannopyranose motif. The mannan is further functionalized with an arabinan domain, containing mostly α-(1→5)-linked D-arabinofuranosyl chains with periodic α-(1→3)-linked branch points and terminal β-(1→2)-arabinofuranose residues. These β-linked arabinofuranose residues serve as the site to which a series of capping motifs (e.g., short mannopyranosyl oligosaccharides or inositol phosphate moieties) are attached.[8c,8d] A more detailed structure of the mannan core, and it attachment to the arabinan, is shown in Figure 1B.

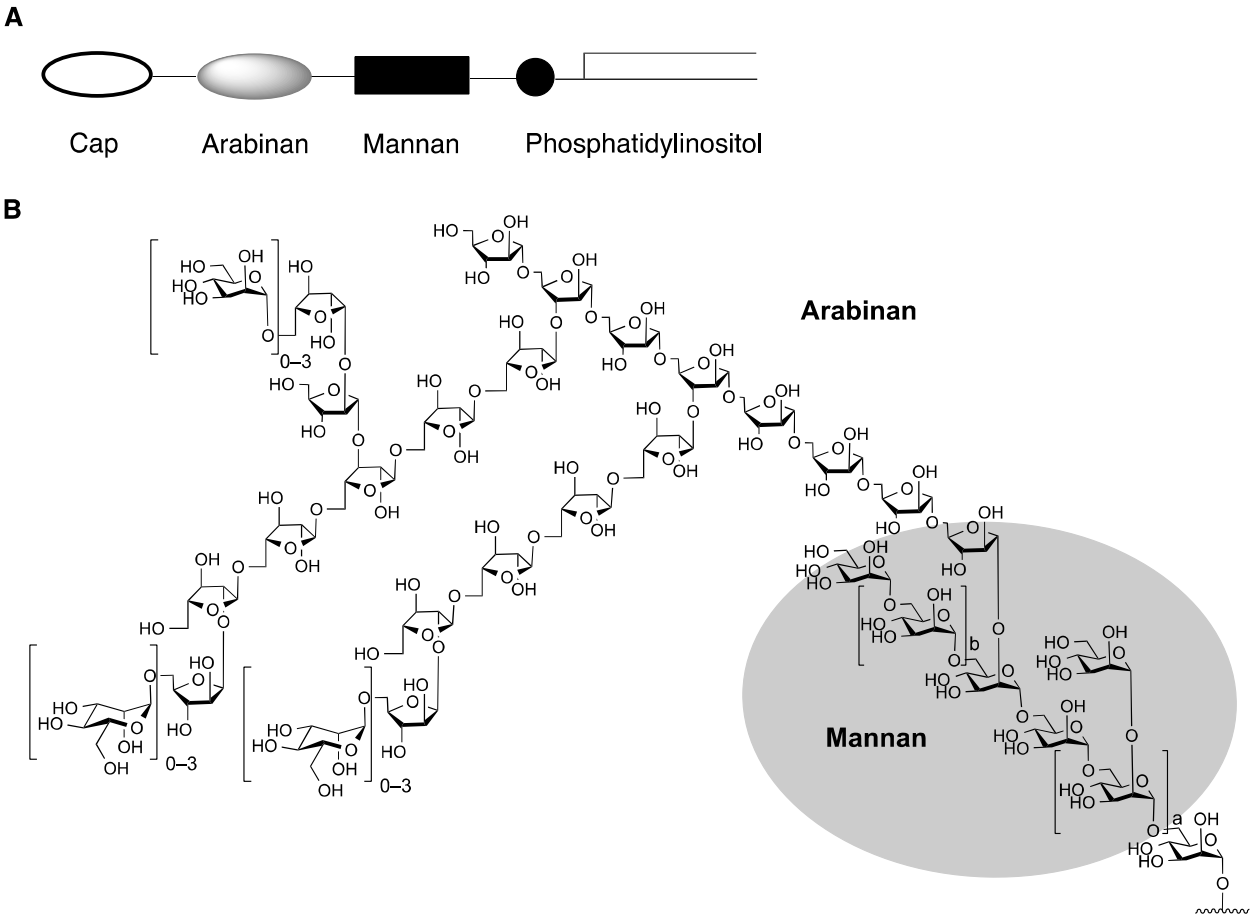
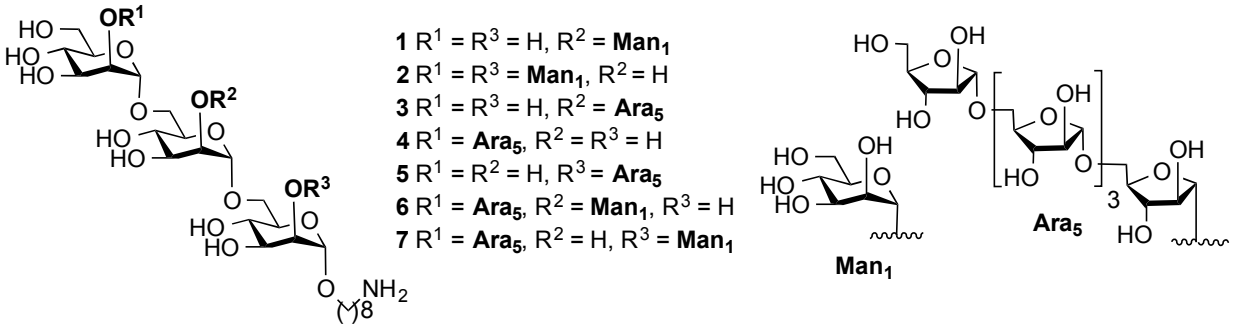


Figure 1. A. Schematic depiction of LAM. **B.** Composite structure of LAM highlighting the arabinomannan domain. The targets prepared in this study correspond to the region shaded in grey.

The hexasaccharide used in the aforementioned diagnostic[7] is a fragment found at the 'non-reducing' terminus of the arabinan domain. In choosing additional targets for synthesis we turned our attention to the mannan core in the hopes of generating structures that would target another subset of anti-LAM antibodies. Thus, we describe here the synthesis of seven oligosaccharides (**1**–**7**), which are anticipated fragments of the core arabinomannan domain of LAM (Figure 2). The oligosaccharides, ranging in size from a tetrasaccharide to a nonasaccharide, include those containing solely the mannan domain (**1** and **2**), as well as others containing both the mannan and arabinan domains (**3**–**7**). The targets were designed based on the

structural motifs suggested to be present in this region of LAM (Figure 1B). In particular, all of the compounds feature an α-(1→6)-mannopyranose backbone, with pendant α-mannopyranose residues and/or an α-(1→5)-linked pentaarabinofuranoside motif attached at O-2 of one of the α-(1→6)-mannopyranose residues. All oligosaccharides were synthetized with an aminooctyl linker to enable their conjugation to other species (e.g., proteins or solid supports for use in diagnostics). This work complements previous investigations from our group[9] and others[10] on the synthesis mycobacterial arabinomannan fragments.

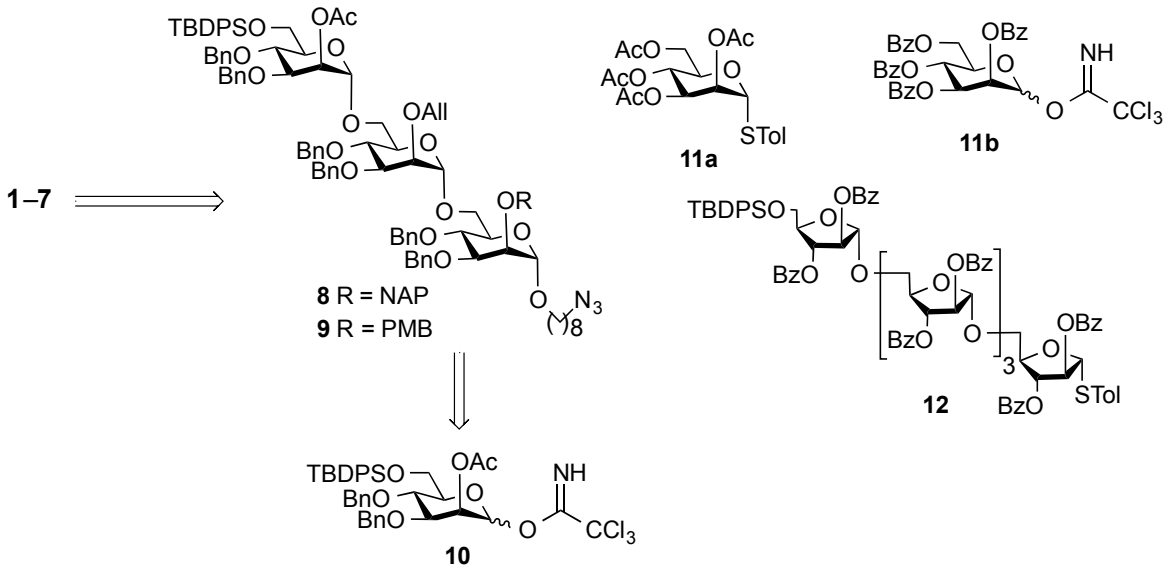
Figure 2. Oligosaccharide Targets **1**–**7**.



In developing a route to these compounds we envisioned an orthogonal protection strategy that would allow the preparation of the targets from a common trisaccharide (Scheme 1). One of the challenges was the need for three orthogonal protecting groups at the O-2 position of each residue in the trimannoside core (**8** or **9**). The selected protecting groups should be stable to acidic glycosylation conditions, provide α-selectivity to install the required (1→6) linkages and have a facile orthogonal deprotection procedure allowing the selective introduction of pentaarabinose (**Ara$_5$**) or mannose (**Man$_1$**) units as required for the different targets. Ultimately, we relied on a strategy in which the core structure was assembled through the use of glycosyl donor **10**, with the orthogonal protecting groups being added post-glycosylation. The side chain

appendages could be added through either the use of monosaccharide donors **11a** and **11b**, or pentasaccharide donor **12**.

Scheme 1. Retrosynthetic Analysis of **1–7**.



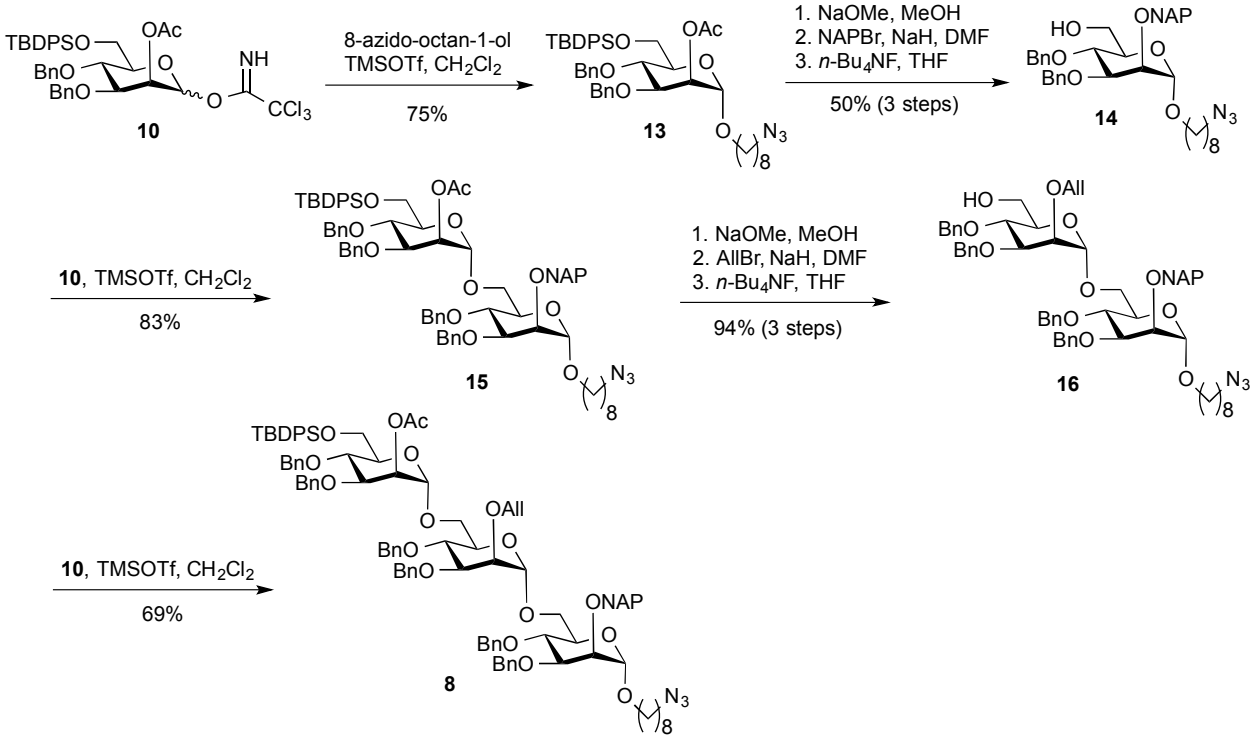
Results and Discussion

Implementation of the route outlined in Scheme 1 required access to four building blocks: trisaccharide **8**, monosaccharides **11a** and **11b**, and pentasaccharide **12**. Monosaccharides **11a** and **11b** were prepared as described previously.[11] The synthesis of **8** and **12** are described below. In the course of carrying out this work, it was necessary to redesign the trisaccharide building block and **9** was chosen as a target. The preparation of trisaccharide **9** is described later.

Synthesis of Trisaccharide 8. Trisaccharide **8** was synthesized starting from trichloroacetimidate **10** (Scheme 2).[12] Key features of **10** are the acetyl group on O-2, which secured the required α-selectivity in the glycoslyations, and the *tert*-butyldiphenylsilyl (TBDPS) group, which facilitated chain extension. The synthesis began with the glycosylation of 8-azido-octan-1-ol[13] with **10** activated by trimethylsilyl trifluoromethanesulfonate (TMSOTf) affording **13** in 75% yield. The acetate group was then removed by treatment with sodium methoxide. The

resulting hydroxyl group was protected as a naphtylmethyl (NAP) ether, and the TBDPS group was cleaved with tetra-*n*-butylammonium fluoride (*n*-Bu_4NF) in THF providing alcohol **14** in 50% yield over the three steps. Chain elongation was done by reaction between **14** and **10** using TMSOTf as the promoter to give disaccharide **15** in 83% yield. Disaccharide **16** was obtained in 94% yield following a similar sequence of deprotection/protection reactions as those described for the preparation of **14**, but introducing an allyl ether instead of a NAP ether. The final mannose residue was added using TMSOTf-promoted glycosylation of **16** with **10** affording the desired trisaccharide **8** in 69% yield. The α-stereochemistry of the glycosidic linkages in **8** was confirmed via coupled HSQC experiments to measure $^1J_{C\text{-}1,H\text{-}1}$ magnitudes. Values of 169, 171 and 172 Hz were obtained, consistent with the α-stereochemistry.[14]

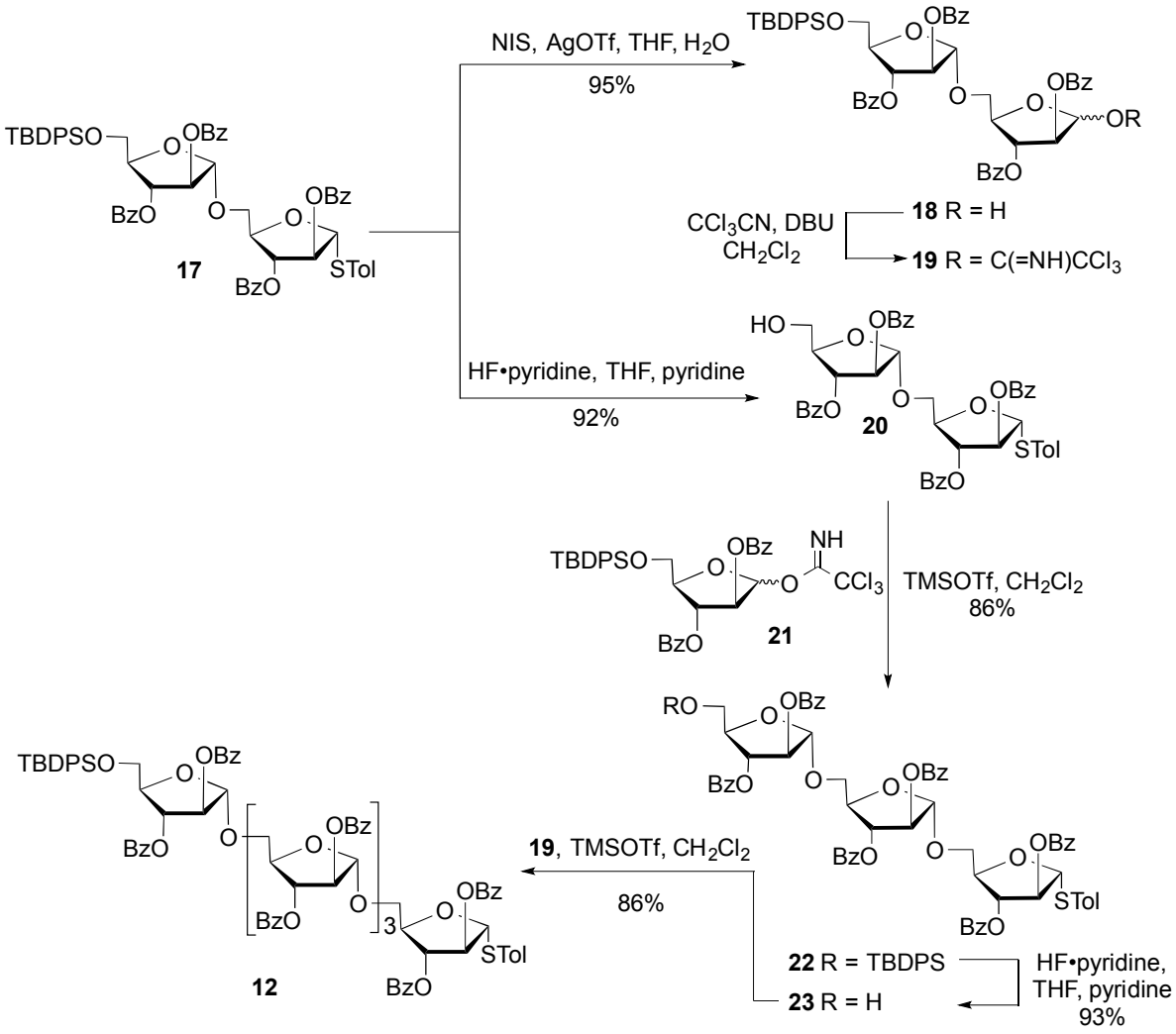
Scheme 2. Synthesis of Trisaccharide **8**.



Synthesis of Pentasaccharide 12. The synthesis of **12** was carried out starting with disaccharide thioglycoside **17** (Scheme 3), which was prepared as described previously.[15]

Cleavage of the silyl ether protecting group in **17** was achieved upon reaction with HF•pyridine to give glycosyl acceptor **20**[16] in 92% yield. Alternatively, the thiotoluyl group was hydrolyzed using NIS and AgOTf activation in aqueous THF to afford, in 95% yield, the corresponding lactol **18**, which subsequently was converted into trichloroacetimidate **19**.

Scheme 3. Synthesis of Pentasaccharide **12**.



Having accessed **19** and **20**, glycosylation of the latter with the trichloroacetimidate derivative **21**[15] afforded **22** in 86% yield. The TBDPS group was then deprotected using HF•pyridine to provide the trisaccharide acceptor **23** in 93% yield. The synthesis of the pentaarabinose building block **12** was then achieved, in 86% yield, through glycosylation of **23**

with **19** in the presence of TMSOTf in CH_2Cl_2. The α-anomeric configuration of the glycosidic linkages in **12** was confirmed from the ^{13}C NMR spectrum on the basis of the four signals clustered around 106.0 ppm and a fifth at 91.6 ppm, the latter corresponding to the anomeric carbon of the residue bearing the thiotoluyl group. [9,15,17] Furthermore, all five H-1 signals appear as singlets in ^1H NMR spectrum, consistent with previous literature for α-arabinofuranosides.[9,11]

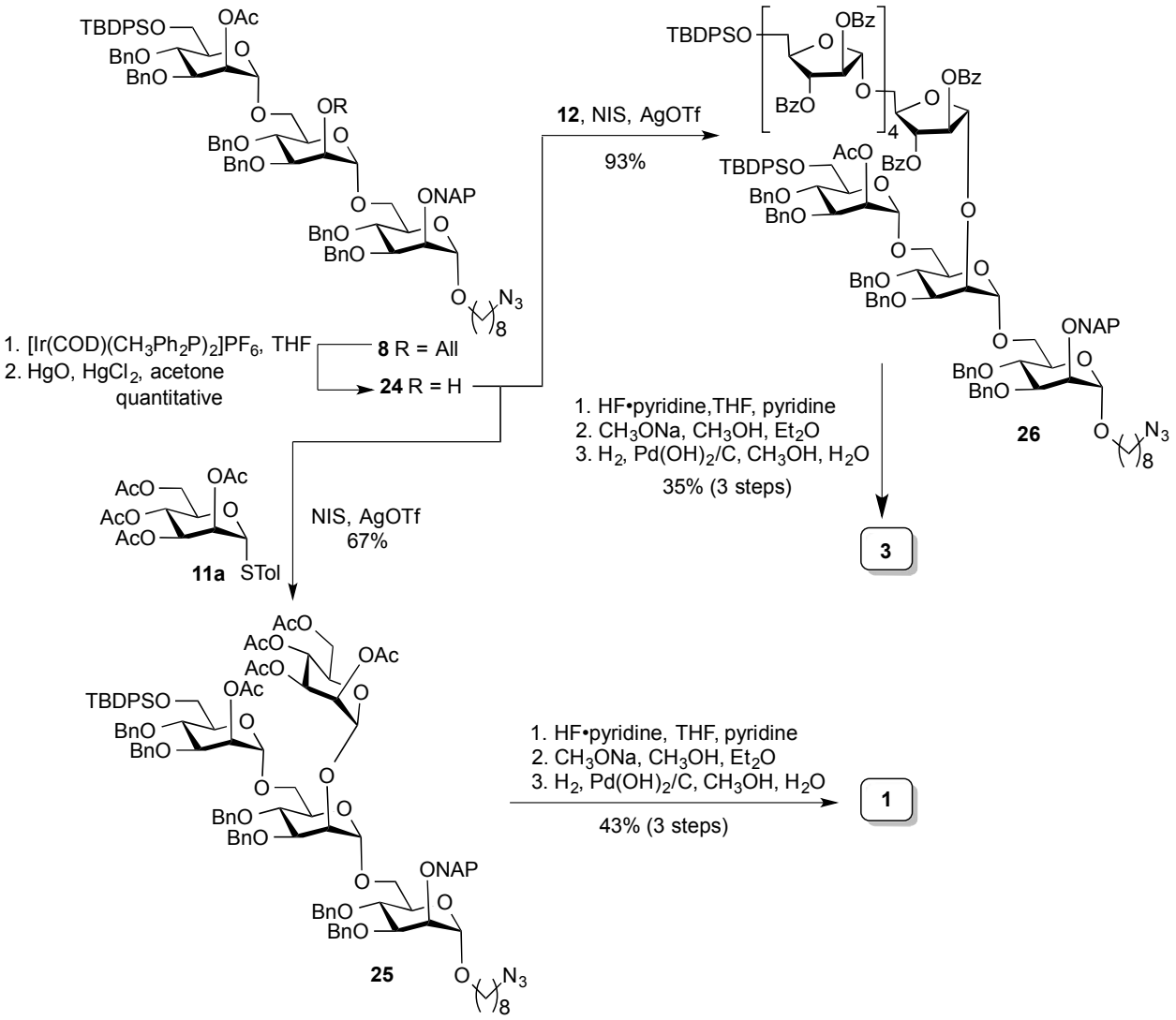
Synthesis of Oligosaccharides (1–7).

With trisaccharide **8**, monosaccharides **11a** and **11b**, and pentasaccharide **12** in hand, we next turned our attention to the synthesis of **1**–**7**. To accomplish this goal, selective deprotection of the acetate, allyl or napthylmethyl groups present at the O-2 positions of **8** is required. Although previous literature suggested that these selective deprotection steps would be straightforward, as outlined in the discussion below, we faced challenges that needed to be overcome.

Synthesis of Tetrasaccharide 1 and Octasaccharide 3. Initially, we focused on the synthesis of tetrasaccharide **1** and octasaccharide **3**, which required the selective cleavage of the allyl group in **8** (Scheme 4). Our first attempt to directly remove the allyl group in **8** using $PdCl_2$ under buffered conditions (AcOH, NaOAc)[18] led to decomposition of the starting material. On the other hand, attempted deprotection in the presence of catalytic amount of $Pd(PPh_3)_4$[19] did not proceed; only the starting material remained. Therefore, indirect approaches involving allyl group isomerization and then hydrolysis were explored. The use of Wilkinson catalyst[20] $RhCl(Ph_3P)_3$ gave a poor yield of the vinyl ether isomerization product (<20%). In contrast, the use of $[Ir(COD)(CH_3Ph_2P)_2]PF_6$[21] resulted in complete conversion of **8** into the corresponding vinyl

ether. Subsequent hydrolysis using HgO and $HgCl_2$[22] in wet acetone produced the desired alcohol **24** in quantitative yield.

Scheme 4. Synthesis of Tetrasaccharide **1** and Octasaccharide **3**.

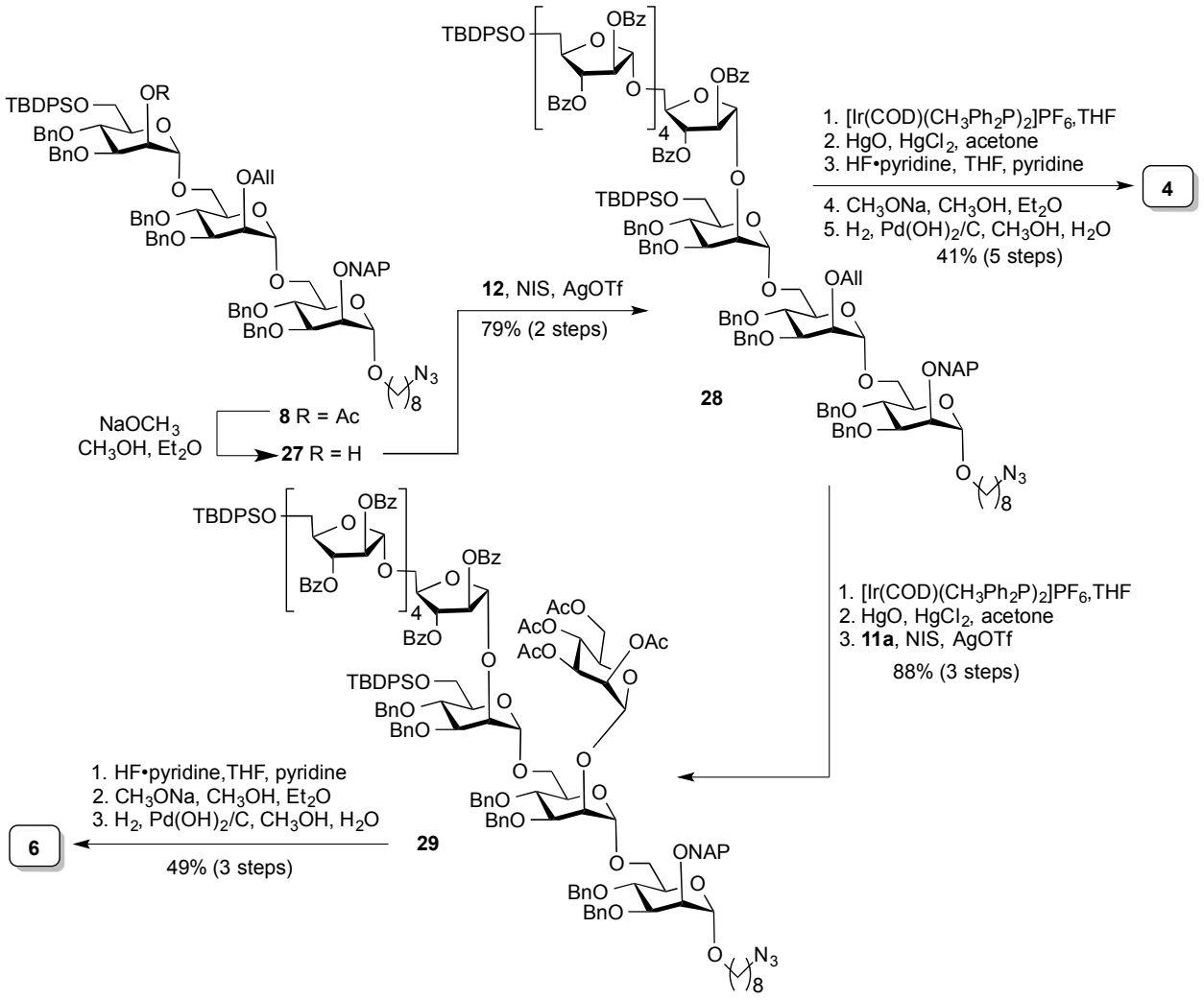


Trisaccharide **24** was further coupled with an excess of **11a**[11a] using NIS–AgOTf activation at 0 °C to afford tetrasaccharide **25** in 67% yield with complete α-selectivity ($^1J_{C\text{-}1,H\text{-}1}$= 171 Hz). In contrast, the glycosylation of **24** with pentasaccharide thioglycoside **12** under the same conditions did not proceed. However, complete conversion of the starting materials was observed when the reaction was carried out at room temperature leading to the formation of the

desired octasaccharide **26** in 93% yield. Tetrasaccharide **1** and octasaccharide **3** were obtained after removal of the protecting groups and conversion of the azide to an amine in a three-step protocol. The silyl ether was cleaved in the presence of HF•pyridine, and the esters were cleaved using sodium methoxide. Finally, the azide group was reduced and the benzyl protecting groups were removed by hydrogenolysis using $Pd(OH)_2/C$ in methanol and water to afford **1** and **3** in 43% and 35% yield, respectively, over three steps.

Synthesis of Octasaccharide 4 and Nonasaccharide 6. To synthesize **4** and **6** an approach similar to that used for the preparation of **1** and **3** was employed, but involving the selective deprotection of the acetate ester in trisaccharide **8** (Scheme 5). Thus, treatment of **8** with sodium methoxide in methanol and dichloromethane afforded **27**, which was used without further purification. Glycosylation of **27** with pentasaccharide thioglycoside **12** afforded the fully protected octasaccharide **28** in 79% yield with complete α-selectivity. Once **28** had been obtained, we could synthesize nonasaccharide **29** after selective deprotection of the allyl group using $[Ir(COD)(CH_3Ph_2P)_2]PF_6$ as described above, followed by glycosylation of the resulting alcohol with thioglycoside donor **11a** under NIS–AgOTf activation. Nonasaccharide **29** was obtained in 88% overall yield from **28**. Deprotection of the TBDPS ether, benzoate esters, benzyl ethers and azide reduction was carried out as described for **1** and **3** to provide octasaccharide **4** and nonasaccharide **6** in 41% and 49% yield, respectively.

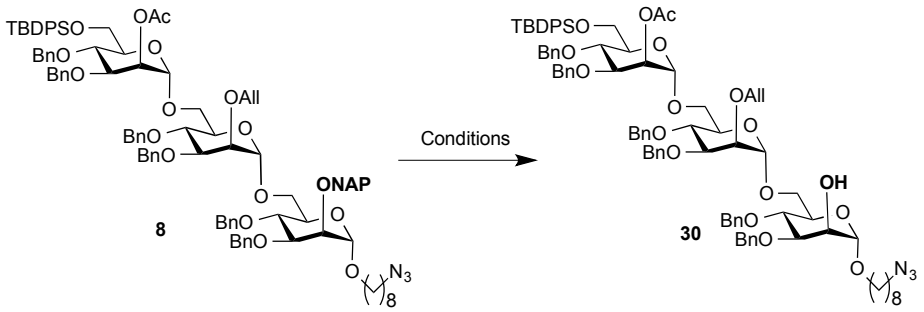
Scheme 5. Synthesis of Octasaccharide **4** and Nonasaccharide **6**.



Synthesis of Pentasaccharide 2 and Octasaccharide 5. To synthesize oligosaccharide targets **2** and **5**, the selective deprotection of the NAP ether in trisaccharide **8** was required. Our first attempts made use of oxidative procedures (Table 1, Entries 1–4). When **8** was treated with four equivalents of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)[23] in dichloromethane with methanol or water at room temperature, a mixture of several compounds was obtained, presumably due to the deprotection of the benzyl groups as well as cleavage of the NAP ether. Reducing the amount of DDQ to two equivalents and using lower reaction temperatures (0 °C) did not improve the selectivity. The use of a catalytic amount of DDQ[24] was also explored, but

the reaction did not proceed. Another oxidative agent, ceric ammonium nitrate (CAN),[25] was also investigated. Using two equivalents of the oxidant, a low (<10%) conversion into the desired product was observed. Increasing the amount of CAN to six equivalents led to a mixture of compounds. Given the failure of oxidative methods to affect the cleavage of the NAP ether, we turned to a recently reported method described by Liu and co-workers, which makes use of HF•pyridine in toluene (Table 1, Entry 5).[26] However, although this method has been shown to succeed with molecules containing silyl protecting groups, applying these conditions to **8** did not lead to the cleavage of the NAP ether. Instead, only the desilylation product was isolated. The difficulties encountered in the selective cleavage of the NAP ether in **8** mirror other (unpublished) results from our laboratory. We have often found it difficult to cleave selectively NAP ethers in the presence of large numbers of benzyl ethers (here six), without significant amounts of decomposition, which we assume is competitive debenzylation.

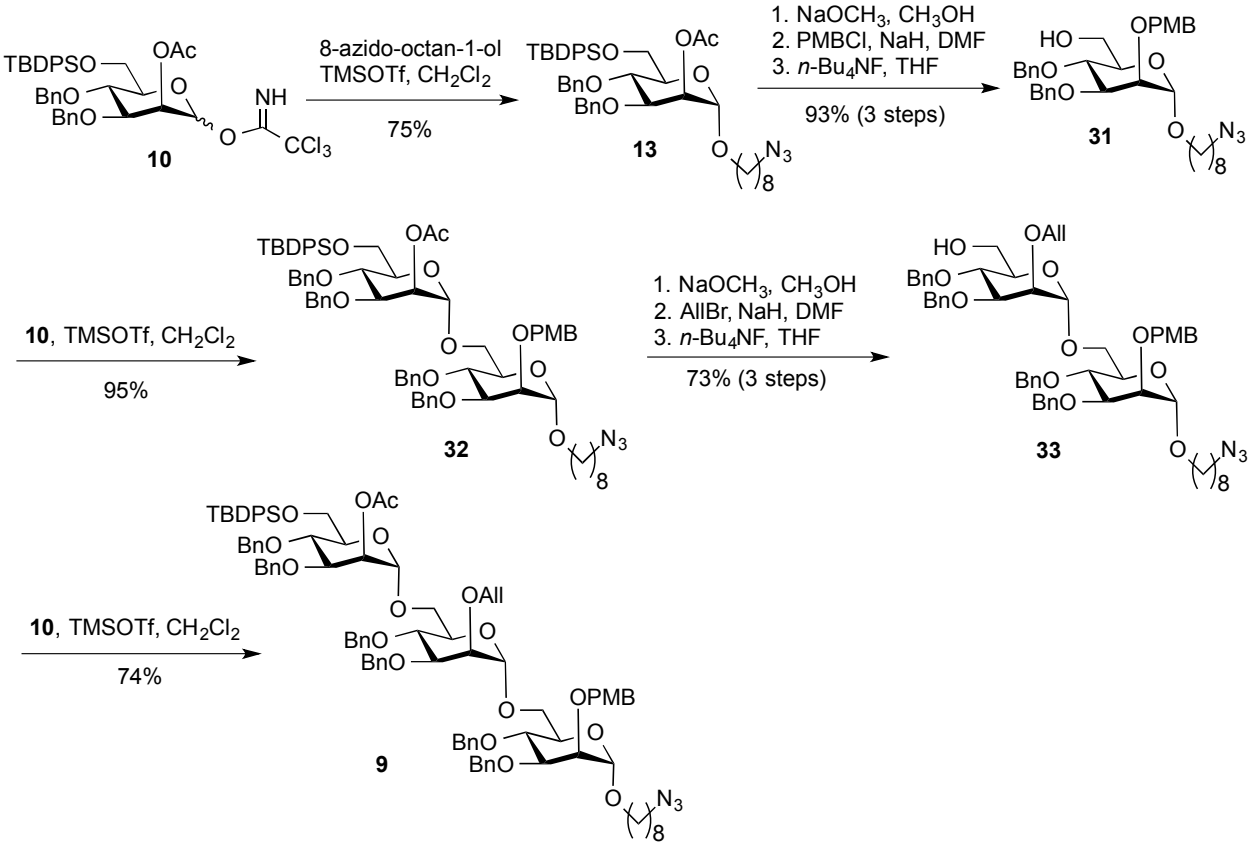
Table 1. Attempted cleavage of NAP ether in **8**.



Entry	Conditions	Result
1	DDQ (4 equiv.), CH_2Cl_2, CH_3OH or H_2O, rt.	Low yield + debenzylation
2	DDQ (2 equiv.), CH_2Cl_2/MeOH, 0 °C	Low conversion + debenzylation
3	DDQ (10%), $FeCl_3$, CH_2Cl_2/H_2O, rt.	No reaction
4	CAN (2 to 6 equiv.), CH_3CN/H_2O, rt.	Low conversion + debenzylation
5	HF•pyridine, toluene, rt.	Low conversion + desilylated product

Disappointed by these results, we altered the strategy and replaced the NAP ether with a *p*-methoxybenzyl (PMB) ether, which we anticipated could be removed selectively in the presence of acetate esters, allyl ethers, TBDPS ethers and benzyl ethers. Thus, we synthesized trisaccharide **9**, which differs from **8** by the substitution of the NAP ether with a PMB ether. As outlined in Scheme 6, compound **9** could be obtained in nine steps starting from the known trichloroacetimidate derivative **10** in 36% overall yield using the same route as that described above for trisaccharide **8**.

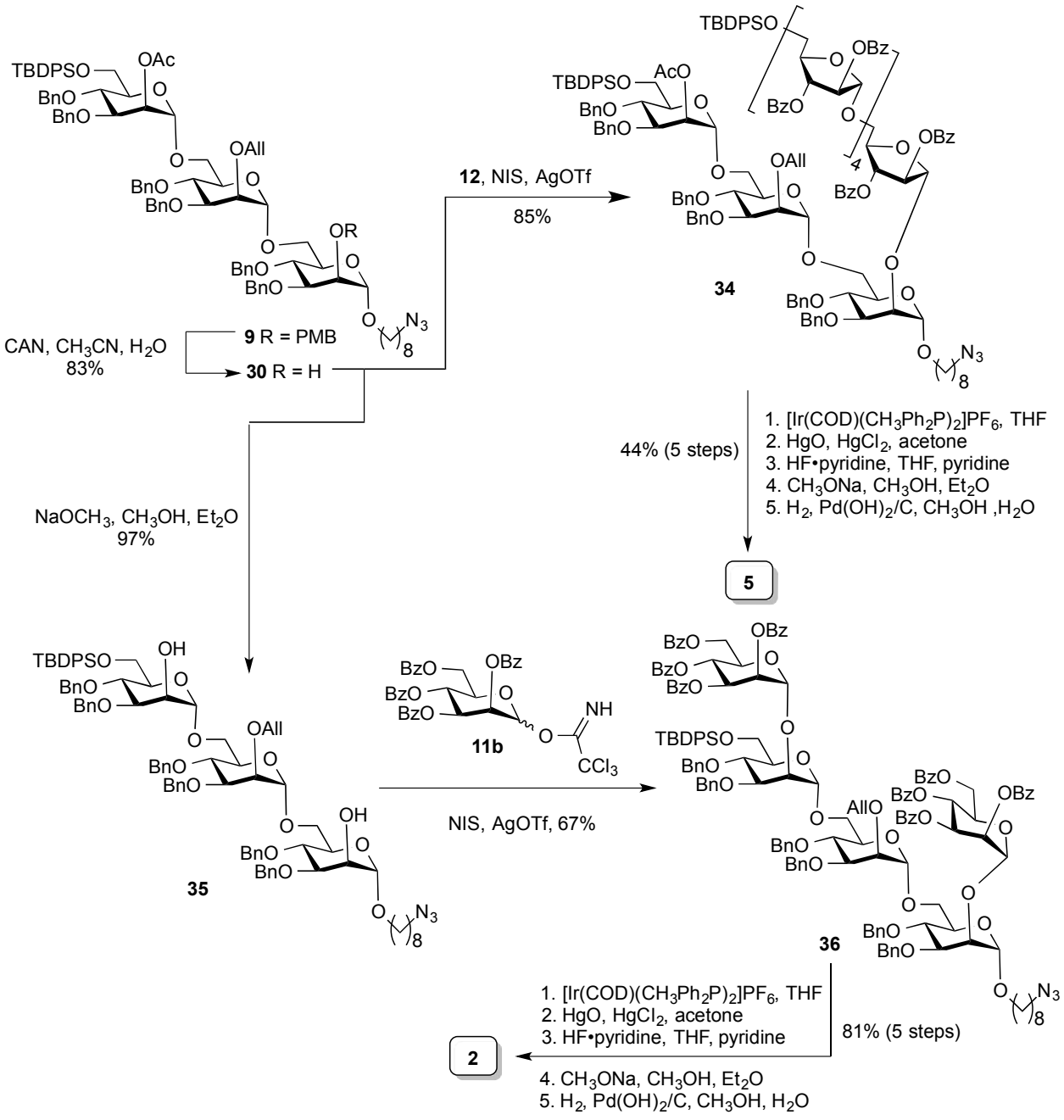
Scheme 6. Synthesis of Trisaccharide **9**.



Once compound **9** was available, the selective deprotection of the PMB ether was investigated. We found that the use of CAN[27] in acetonitrile and water cleanly provided the desired alcohol **30** in 83% yield (Scheme 7). Having successfully removed the PMB ether,

acceptor **30** was coupled with the pentasaccharide thioglycoside **12** under NIS and AgOTf activation. The expected octasaccharide, **34**, was isolated in 85% yield. Deprotection of the allyl group was achieved upon treatment with $[Ir(COD)(CH_3Ph_2P)_2]PF_6$ followed by hydrolysis of the resulting vinyl ether using HgO and $HgCl_2$. Subsequent deprotection of the silyl ether and ester groups and then hydrogenolysis provided the desired octasaccharide **5** in 44% yield over the five steps. Alternatively, methanolysis of the acetate ester in trisaccharide **30** (yielding diol **35**) followed by glycosylation with trichloroacetimidate derivative **11b** under TMSOTf activation, afforded pentasaccharide **36** in 67% yield. We note that the use of thioglycoside **11a** for this reaction led to a complex mixture of products. Compound **36** was deprotected using the same series of transformations as those described for the other oligosaccharides, giving pentasaccharide **2** in 81% yield over five steps.

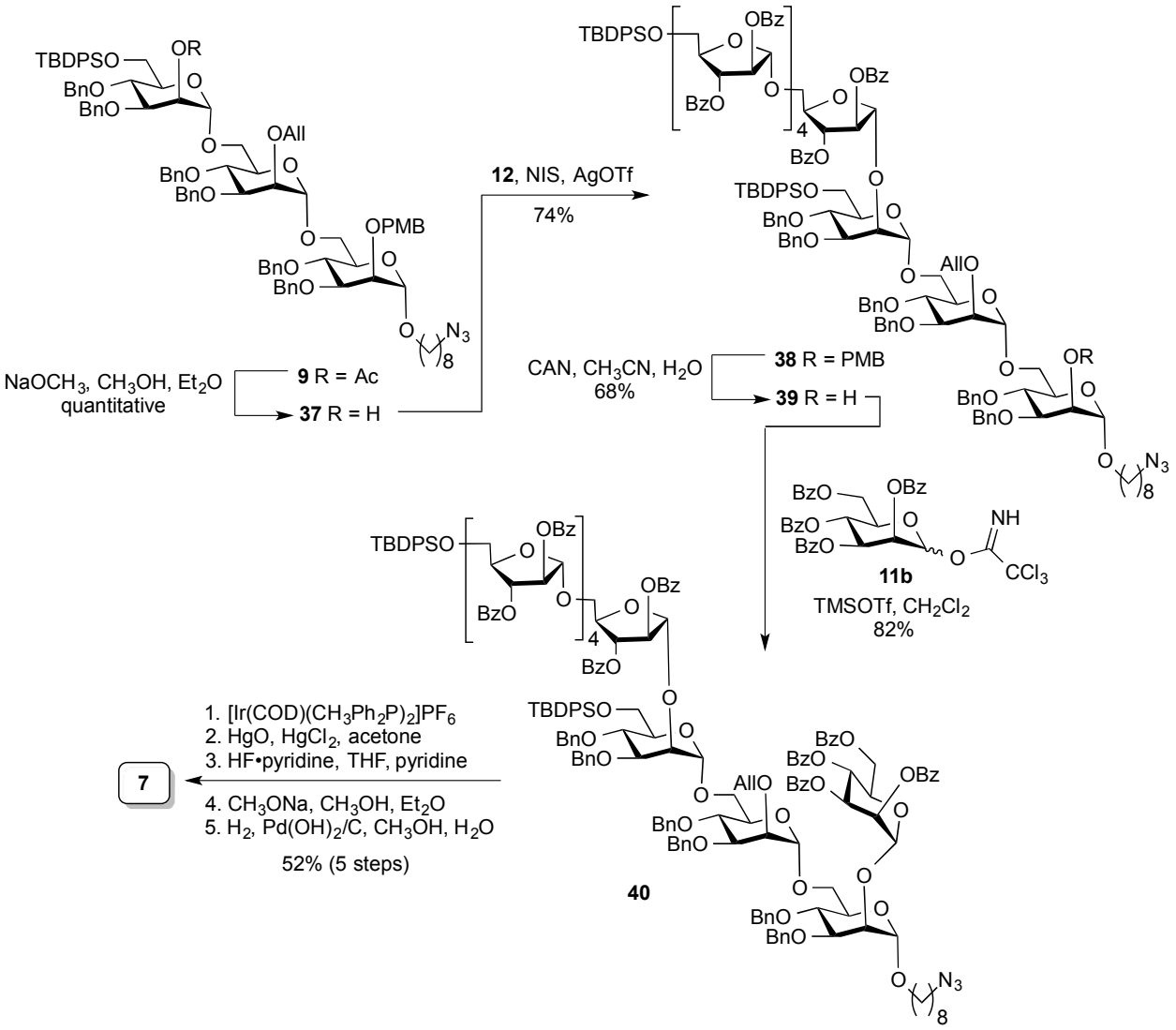
Scheme 7. Synthesis of Pentasaccharide **2** and Octasaccharide **5**.



Synthesis of Nonasaccharide 7. The final target, nonasaccharide **7**, was prepared as shown in Scheme 8, starting with trisaccharide **9**. Methanolysis of the acetate ester led quantitatively to **37**, which was subsequently coupled to thioglycoside **12** providing octasaccharide **38** in 74% yield. Subsequently, the PMB group in **38** was cleaved using CAN in

acetonitrile and water to give alcohol **39** in 68% yield. Glycosylation of **39** with trichloroacetimidate **11b** led to nonasaccharide **40** in 82% yield. Nonasaccharide **7** was obtained after deprotection of the protecting groups, as carried out for the other targets, in 52% yield over five steps.

Scheme 8. Synthesis of Nonasaccharide **7**.



Conclusion

In summary, we report here an efficient strategy to access seven complex oligosaccharide fragments of the arabinomannan domain of mycobacterial LAM. The route developed was a convergent one requiring as the key intermediate an orthogonally protected trisaccharide derivative (**8** or **9**), which could be selectively deprotected to liberate one of three hydroxyl groups. Initially, we chose the three orthogonal protecting groups to be an acetate ester, allyl ether and NAP ether (trisaccharide **8**). However, difficulties in the selective cleavage of the NAP ether led us to develop a different intermediate in which this group was replaced with a PMB ether (trisaccharide **9**). This underscores a problem we have frequently encountered in the synthesis of other complex glycans (to be reported elsewhere) where late stage cleavage of a NAP ether has been problematic and has forced the redesign of a route. Overall, we find the selective removal of a NAP ether in the presence of a large number of benzyl groups to be unpredictable, and its use in complex glycan synthesis should therefore be carefully considered. Subsequent glycosylation of the alcohol obtained from **8** or **9** with monosaccharide (**11a/11b**) and/or pentasaccharide (**12**) glycosyl donors gave compounds ranging in size from tetrasaccharide to nonasaccharides, which were then fully deprotected and isolated in good yields. All oligosaccharides were synthesized containing an amino group to facilitate their conjugation to proteins or to potential diagnostic devices. Downstream investigations using these compounds will be reported in the future.

Experimental Section

General Methods

All reagents were purchased from commercial sources and were used without further purification unless noted. Reaction solvents were purified by successive page through columns of alumina and copper under argon. Unless stated otherwise, all reactions were carried out at room temperature and under a positive pressure of argon and were monitored by TLC on Silica Gel G-25 F254 (0.25 mm). TLC spots were detected under UV light and/or by charring with a solution of *p*-anisaldehyde in ethanol, acetic acid and sulfuric acid. Column chromatography was performed on Silica Gel 60 (40–60 μm). Solvents were evaporated under reduced pressure on a rotary evaporator. Optical rotations were measured in a microcell (10 cm, 1 mL) at ambient temperature and are in units of degree·mL/(g·dm). ^{1}H NMR spectra were recorded at 400, 500, 600 or 700 MHz, and chemical shifts are referenced to residual $CHCl_3$ (7.26 ppm, $CDCl_3$), HOD (4.78 ppm, D_2O), or CHD_2OD (3.30 ppm, CD_3OD). ^{13}C NMR spectra were recorded at 126, 151 or 176 MHz, and chemical shifts are referenced to $CDCl_3$ (77.0 ppm) or CD_3OD (48.9 ppm, CD_3OD). Reported splitting patterns are abbreviated as s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, app = apparent. Assignments of NMR spectra were based on two-dimensional experiments (^{1}H–^{1}H COSY, HSQC, and HMBC). High resolution ESI-MS spectra (time-of-flight analyzer) were recorded on samples suspended in THF or CH_3OH and with added NaCl.

8-Aminooctyl α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (1). To a solution of tetrasaccharide **25** (77 mg, 0.039 mmol) in THF–pyridine (5:2, 700 μL) at 0 °C was added a solution of HF•pyridine 70% in pyridine (25 μL) dropwise. The reaction mixture was warmed to room temperature and

stirred for 2 days. After dilution with EtOAc (10 mL), the reaction mixture was poured into a satd aq solution of $NaHCO_3$ (15 mL) and extracted with EtOAc (2 × 10 mL). The organic layer was washed with H_2O (2 × 10 mL), dried (Na_2SO_4), filtered and concentrated under vacuum to give a syrup that was filtered through short silica gel column (4:1 hexane–EtOAc). The residue obtained after solvent evaporation was dissolved in Et_2O–CH_3OH (1:1, 2 mL), before adding a solution of $NaOCH_3$ in CH_3OH (1 mL, 0.1M). The reaction mixture was stirred overnight, neutralized by the addition of Amberlyst IR-120 (H^+) cation exchange resin, filtered and concentrated to give a syrup that was used without any further purification. This crude product was dissolved in H_2O–CH_3OH (1:1, 3 mL), then $Pd(OH)_2/C$ (10%) was added and the reaction mixture was stirred vigorously under hydrogen atmosphere (1 atm) overnight. The reaction mixture was diluted with H_2O–CH_3OH (1:1, 5 mL), filtered through Celite and finally purified by gel filtration chromatography (Sephadex, LH-20) using CH_3OH as the eluent. After solvent evaporation, the residue was dissolved in water and then lyophilized to give **1** (13.4 mg, 43% over 3 steps) as an amophorus fluffy white solid. $[\alpha]_D$ +2.4 (*c* = 0.10, H_2O); ^{1}H NMR (600 MHz, D_2O) δ_H = 5.09 (d, 1 H, *J* = 1.1 Hz, H-1), 4.98 (d, 1 H, *J* = 1.1 Hz, H-1), 4.89 (d, 1 H, *J* = 1.1 Hz, H-1), 4.81 (d, 1 H, *J* = 1.1 Hz, H-1), 4.04 (br s, 1 H), 3.97–3.87 (m, 3 H), 3.87–3.58 (m, 16 H), 3.53–3.47 (m, 5 H), 2.93 (d, 2 H, *J* = 7.1 Hz, CH_2N$_3$), 1.64–1.46 (m, 4 H, $OCH_2(CH_2)_6CH_2NH_2$), 1.38–1.16 (m, 8 H, $OCH_2(CH_2)_6CH_2NH_2$); ^{13}C NMR (126 MHz, D_2O) δ_C = 102.4 (C-1), 99.9 (C-1), 99.4 (C-1), 98.1 (C-1), 78.9, 73.3, 72.8, 71.1, 70.9, 70.7, 70.5, 70.4, 70.1, 70.1, 68.1, 68.1, 66.8, 66.7, 66.7, 66.7, 66.1, 65.3, 61.9, 61.1, 61.0, 39.7, 28.5 (2 C), 28.3, 28.1, 25.3, 25.0. HRMS (ESI) calcd for (M + H^+) $C_{32}H_{60}NO_{21}$: 794.3652. Found: 794.3653.

8-Aminoctyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-α-D-mannopyranoside (2). To a

solution of **37** (100 mg, 0.038 mmol) in THF (300 μL), degassed under vacuum and stirring under an Ar atmosphere, (1,5-cyclooctadiene)bis(methyldiphenylphosphane)iridium I hexafluorophosphate catalyst (3 mg, 0.0035 mmol) was added, followed by further degassing of the mixture under vacuum. The suspension was stirred for 15 min at 0 °C and the catalyst was then activated with hydrogen (2 minutes under hydrogen atmosphere). At this point, the solution became nearly colorless. The excess of hydrogen was removed by three cycles of vacuum/Ar. The reaction mixture was then stirred for 3 h at room temperature under argon atmosphere. The solvent was then evaporated and the residue was dissolved in acetone–water (10:1, 1.8 mL). Then, HgO (11.5 mg, 0.053 mmol) and $HgCl_2$ (12.5 mg, 0.046 mmol) were added. After 1 h, the solvent was evaporated and the residue was diluted with Et_2O (15 mL), washed with 10% KI solution (3 × 10 mL), a satd aq solution of $Na_2S_2O_3$ (2 × 10 mL) and water (3 × 10 mL). The aqueous layers were extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The crude residue was dissolved in CH_3CN–pyridine (5:1, 600 μL) at 0 °C and a solution of 70% HF•pyridine (20 μL) was then added dropwise. The reaction mixture was warmed to room temperature and stirred for 24 h. After dilution with EtOAc (10 mL), the reaction mixture was poured into a satd aq solution of $NaHCO_3$ (15 mL) and extracted with EtOAc (2× 10 mL). The organic layer was washed with H_2O (2×10 mL), dried (Na_2SO_4), filtered and concentrated under vacuum to give a syrup that was filtered through short silica gel column (4:1 hexane–EtOAc). The residue obtained after solvent evaporation was dissolved in Et_2O–CH_3OH (1:1, 2 mL), before adding a solution of $NaOCH_3$ in CH_3OH (1 mL, 0.1M). The reaction mixture was stirred overnight, neutralized by the addition of Amberlyst IR-120 (H^+) cation exchange resin, filtered and concentrated to give a syrup that was used without further purification. This crude material was dissolved in H_2O–EtOH (1:1, 3 mL), and $Pd(OH)_2/C$ (10%) was then added and the reaction mixture was stirred overnight under a hydrogen atmosphere (1

atm). The reaction mixture was diluted with H_2O–CH_3OH (1:1, 5 mL), filtered through Celite and finally purified by gel filtration chromatography (Sephadex, LH-20) using CH_3OH as the eluent. After solvent evaporation, the residue was dissolved in water and then lyophilized to give **2** (29 mg, 81% over 5 steps) as an amorphous fluffy white solid. $[\alpha]_D$ +25.5 (*c* = 0.11, H_2O); ^1H NMR (700 MHz, D_2O) δ_H = 5.13 (br s, 1 H, H-1), 5.07 (br s, 1 H, H-1), 5.03 (br s, 1 H, H-1), 5.01 (br s, 1 H, H-1), 4.89 (br s, 1 H, H-1), 4.07 (br s, 2 H), 4.02–3.52 (m, 30 H), 2.97 (t, 2 H, *J* = 7.3 Hz, C*H*$_2$NH$_2$), 1.72–1.57 (m, 4 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$NH$_2$), 1.40–1.23 (m, 8 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$NH$_2$); ^{13}C NMR (151 MHz, D_2O) δ_C = 102.4 (C-1), 102.3 (C-1), 99.6 (C-1), 98.3 (C-1), 98.1 (C-1), 79.0, 78.7, 73.3, 72.8, 72.1, 71.2, 71.1, 71.0, 70.5, 70.4, 70.3, 70.1, 70.0 (2 C), 68.2, 67.0, 66.9, 66.8, 66.7, 66.5, 65.9, 65.3, 62.5, 61.2, 61.1, 61.0, 39.6, 28.5, 28.2, 28.2, 28.1, 25.6, 25.3. HRMS (ESI) calcd for (M + H^+) $C_{38}H_{70}NO_{26}$: 956.4181. Found: 956.4175.

8-Aminooctyl α-D-mannopyranosyl-(1→6)-[(α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→2)]-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (3). The synthesis of **3** was achieved starting from the octasaccharide **26** (130 mg, 0.037 mmol) following the procedure described for the compound **1**. The product was purified by gel filtration chromatography (Sephadex, LH-20) using CH_3OH as the eluent. After solvent evaporation, the residue was dissolved in water and then lyophilized to give **3** (16.5 mg, 35% over 3 steps) as an amorphous fluffy white solid. $[\alpha]_D$ +27.7 (*c* = 0.06, CH_2Cl_2); ^1H NMR (600 MHz, CD_3OD) δ_H = 5.13 (br s, 1 H, H-1), 5.07–5.03 (m, 4 H, 4×H-1), 4.99 (br s, 1 H, H-1), 4.87 (br s, 1 H, H-1), 4.82 (br s, 1 H, H-1), 4.20–4.15 (m, 5 H), 4.12–4.02 (m, 6 H), 3.99–3.42 (m, 58 H), 1.77–1.62 (m, 6 H), 1.43–1.21 (m, 6 H); ^{13}C NMR (126 MHz, D_2O) δ_C = 110.4 (C-1), 108.5 (3 C, C-1), 108.4 (C-1), 100.8 (C-1), 100.5 (C-1), 99.8 (C-1), 84.9, 83.3 (3 C), 82.1, 81.9, 81.8 (3 C), 78.5,

77.7 (3 C), 77.5 (2 C), 73.7, 72.1, 71.9 (2 C), 71.8, 71.3, 71.1, 71.0, 69.1, 67.9 (3 C), 67.8 (2 C), 67.7, 67.6, 66.9, 66.7, 62.2 (2 C), 61.8, 40.5, 29.5, 28.2, 29.1, 27.7, 26.5, 26.3; HRMS (ESI) calcd for $(M + H^+)$ $C_{51}H_{90}NO_{36}$: 1292.5237. Found: 1292.5257.

8-Aminooctyl α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (4). The synthesis of **4** was achieved starting from the octasaccharide **28** (128 mg, 0.036 mmol) following the procedure described for the compound **2**. The product was purified by gel filtration chromatography (Sephadex, LH-20) using CH_3OH as the eluent. After solvent evaporation, the residue was dissolved in water and then lyophilized to give **4** (19 mg, 41% over 5 steps) as an amorphous fluffy white solid. $[\alpha]_D$ +48.3 (*c* = 0.10, H_2O); ^{1}H NMR (500 MHz, D_2O) δ_H = 5.17 (br s, 1 H, H-1), 5.07 (br s, 4 H, 4×H-1), 5.01 (br s, 1 H, H-1), 4.88 (br s, 1 H, H-1), 4.84 (br s, 1 H, H-1), 4.19 (br s, 5 H), 4.15–3.50 (m, 40 H), 2.96 (t, 2 H, *J* = 7.6 Hz, C*H*$_2$NH$_2$), 1.69–154 (m, 4 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$NH$_2$), 1.42–122 (m, 8 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$NH$_2$); ^{13}C NMR (126 MHz, D_2O) δ_C = 109.5 (C-1), 107.6 (2 C, C-1), 107.5 (C-1), 107.4 (C-1), 99.9 (C-1), 99.5 (C-1), 98.8 (C-1), 84.0, 82.4 (3 C), 82.3, 82.0, 81.2, 81.0, 80.9, 80.8 (2 C), 77.5, 76.8 (2 C), 76.7 (2 C), 76.6, 72.7, 71.1, 71.0, 70.9 (2 C), 70.4, 70.2, 70.0, 68.1, 66.9 (3 C), 66.7 (2 C), 66.6 (2 C), 65.8, 61.2, 60.8, 39.6, 28.5, 28.2 (2 C), 26.8, 25.5, 25.4; HRMS (ESI) calcd for $(M + H^+)$ $C_{51}H_{90}NO_{36}$: 1292.5237. Found: 1292.5227.

8-Aminooctyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-[α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→2)]-α-D-mannopyranoside (5). The synthesis of **5** was achieved starting from the octasaccharide **35** (130 mg, 0.038 mmol) following

the procedure described for the compound **2**. The product was purified by gel filtration chromatography (Sephadex, LH-20) using CH_3OH as the eluent. After solvent evaporation, the residue was dissolved in water and then lyophilized to give **5** (21.2 mg, 44% over 5 steps) as an amorphous fluffy white solid. $[\alpha]_D$ +21.8 (*c* = 0.20, H_2O); ^1H NMR (700 MHz, D_2O) δ_H = 5.12 (br s, 1 H, H-1), 5.04 (br s, 4 H, 4×H-1), 4.94 (br s, 1 H, H-1), 4.86 (br s, 1 H, H-1), 4.84 (br s, 1 H, H-1), 4.16 (br s, 5 H), 4.10–4.02 (m, 5 H), 3.98–3.59 (m, 34 H), 3.55–3.50 (m, 1 H, C*H*$_2$O), 2.94 (t, 2 H, *J* = 7.6 Hz, C*H*$_2$NH$_2$), 1.64–1.53 (m, 4 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$NH$_2$), 1.38–1.28 (br s, 8 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$NH$_2$); ^{13}C NMR (126 MHz, D_2O) δ_C = 110.4, 108.5 (3 C), 108.4, 100.5, 100.4, 100.0, 84.9, 83.3 (3 C), 83.0, 82.2, 81.9 (3 C), 81.8 (2 C), 78.7, 77.7 (2 C), 77.5, 73.7, 71.9, 71.8 (2 C), 71.6 (2 C), 71.0 (2 C), 70.9, 69.2, 67.9 (2 C), 67.8 (2 C), 67.7 (3 C), 67.6, 66.6, 66.4, 62.0, 40.5, 29.4, 29.1 (2 C), 27.8, 26.5, 26.3. HRMS (ESI) calcd for (M + H^+) $C_{51}H_{90}NO_{36}$: 1292.5237. Found: 1292.5256.

8-Aminooctyl α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (6). The synthesis of **6** was achieved starting from the nonasaccharide **29** (65 mg, 0.017 mmol) following the procedure described for the compound **1**. The product was purified by gel filtration chromatography (Sephadex, LH-20) using CH_3OH as the eluent. After solvent evaporation, the residue was dissolved in water and then lyophilized to give **6** (11.9 mg, 49% over 3 steps) as an amorphous fluffy white solid. $[\alpha]_D$ + 57.1 (*c* = 0.09, CH_2Cl_2); ^1H NMR (600 MHz, D_2O) δ_H = 5.15 (br s, 1 H, H-1), 5.10 (br s, 1 H, H-1), 5.08–5.04 (m, 4 H, 4×H-1), 5.00 (br s, 1 H, H-1), 4.98 (br s, 1 H, H-1), 4.82 (br s, 1 H, H-1), 4.21–4.15 (m, 5 H), 4.09 (br s, 3 H), 4.08–4.03 (m, 2 H), 4.00–3.95 (m, 6 H), 3.94–3.83 (m, 11 H), 3.81–3.58 (m, 21 H), 3.57–

3.41 (m, 3 H), 2.94 (t, 2 H, J = 7.4 Hz, CH_2NH$_2$), 1.71–1.55 (m, 4 H, OCH$_2$(CH_2)$_6$CH$_2$NH$_2$), 1.38–1.22 (m, 8 H, OCH$_2$(CH_2)$_6$CH$_2$NH$_2$); ^{13}C NMR (126 MHz, D$_2$O) δ_C = 109.5 (C-1), 107.5 (2×C-1), 107.4 (2×C-1), 102.3 (C-1), 99.9 (C-1), 98.8 (C-1), 98.2 (C-1), 84.0 (2 C), 82.4 (3 C), 82.0, 81.2, 80.9, 80.8 (2 C), 78.8, 77.5, 76.8 (2 C), 76.7 (2 C), 73.4, 73.3, 72.8, 71.2, 71.1, 71.0, 70.5 (2 C), 70.4, 70.1 (3 C), 68.1, 66.9, 66.8 (2 C), 66.7, 66.1, 65.8, 62.8, 62.5, 61.2 (2 C), 61.1, 60.8, 39.6, 28.5, 28.2 (2 C), 26.9, 25.6, 25.3. HRMS (ESI) calcd for (M + H$^+$) $C_{57}H_{100}NO_{41}$: 1454.5765. Found: 1454.5761.

8-Aminooctyl α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-α-D-mannopyranoside (7). The synthesis of **7** was achieved starting from the nonasaccharide **41** (53 mg, 0.013 mmol) following the procedure described for the compound **2**. The product was purified by gel filtration chromatography (Sephadex, LH-20) using CH_3OH as the eluent. After solvent evaporation, the residue was dissolved in water and then lyophilized to give **7** (10 mg, 52% over 5 steps) as an amorphous fluffy white solid. $[\alpha]_D$ –5.4 (c = 0.10, CH_2Cl_2); ^{1}H NMR (700 MHz, D$_2$O) δ_H = 5.14 (br s, 1 H, H-1), 5.07–5.02 (m, 5 H, 5×H-1), 5.00–4.96 (m, 2 H, 2×H-1), 4.87 (br s, 1 H, H-1), 4.64 (s, 1 H), 4.20–4.14 (m, 4 H), 4.09 (br s, 3 H), 4.07–4.03 (m, 2 H), 3.98–3.88 (m, 11 H), 3.87–3.82 (m, 6 H), 3.81–3.58 (m, 22 H), 3.55–3.47 (m, 2 H), 2.93 (t, 2 H, J = 7.4 Hz, CH_2NH$_2$), 1.67–1.52 (m, 4 H, OCH$_2$(CH_2)$_6$CH$_2$NH$_2$), 1.38–1.26 (m, 8 H, OCH$_2$(CH_2)$_6$CH$_2$NH$_2$); ^{13}C NMR (176 MHz, D$_2$O) δ_C = 109.4 (C-1), 107.5 (2×C-1), 107.4 (2×C-1), 102.4 (C-1), 99.5 (C-1), 98.8 (C-1), 98.2 (C-1), 84.0 (2 C), 82.4 (2 C), 82.3, 82.0, 81.8, 81.1, 80.9 (2 C), 80.8 (2 C), 79.0, 77.5, 76.7 (2 C), 76.5 (2 C), 73.3, 72.7, 71.8, 71.1, 71.0, 70.5 (2 C), 70.3, 70.2, 70.0 (2 C), 68.5, 66.9 (2 C), 66.8 (2 C), 66.5, 65.9, 62.5, 61.2 (2 C), 61.1, 60.8,

39.6, 28.4, 28.2, 28.1, 26.9, 25.5, 25.3; HRMS (ESI) calcd for (M + H^+) $C_{57}H_{100}NO_{41}$: 1454.5765. Found: 1454.5766.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (8). A mixture of trichloroacetimidate **10** (1.036 g, 1.32 mmol), alcohol **16** (1.103 g, 1.064 mmol) and 4 Å molecular sieves (290 mg) in CH_2Cl_2 (12 mL) was stirred for 30 min at –20 °C under an argon atmosphere. Then, TMSOTf (20 μL, 0.106 mmol) was added dropwise over 5 min. The reaction mixture was warmed to 0 °C over 20 min and then the TMSOTf was quenched by the addition of Et_3N. The solution was concentrated under vacuum and the resulting syrup was purified by column chromatography (9:1 to 8.5:1.5 hexane−EtOAc) to afford **8** (1.22 g, 69%) as a syrup: R_f 0.59 (4:1 hexane–EtOAc); $[\alpha]_D$ +35.3 (*c* = 0.37, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.83–7.64 (m, 8 H, Ar), 7.57–7.08 (m, 39 H, Ar), 5.92 (dddd, 1 H, *J* = 5.0, 5.9, 10.4, 17.2 Hz, CH_2–C*H*=CH_2), 5.52 (dd, 1 H, *J* = 1.8, 3.4 Hz, H-2″), 5.30 (dd, 1 H, *J* = 1.4, 17.2 Hz, CH_2–CH=CH_2), 5.12 (dd, 1 H, *J* = 1.4, 10.4 Hz, CH_2–CH=CH_2), 5.08 (d, 1 H, *J* = 1.3 Hz, H-1′), 4.97–4.88 (m, 6 H, H-1″, CH_2NAP, 4× CH_2Ph), 4.87 (d, 1 H, *J* = 1.5 Hz, H-1), 4.72 (d, 1 H, *J* = 11.2 Hz, CH_2Ph), 4.67 (br s, 2 H, CH_2Ph), 4.64–4.57 (m, 2 H, CH_2Ph), 4.56–4.47 (m, 3 H, CH_2Ph), 4.43 (d, 1 H, *J* = 11.4 Hz, CH_2NAP), 4.18–4.05 (m, 3 H, 2×CH_2-CH=CH_2, H-3″), 4.05–3.81 (m, 9 H, H-4″, H-2′, H-2, H-3, H-3′, H-4, H-4′, H-6a″, H-6a), 3.80–3.49 (m, 8 H, H-5, H-5′, H-5″, H-6b″, H-6a′, H-6b, H-6b′, OCH_2), 3.34 (dt, 1H, *J* = 2×6.4, 9.6 Hz, OCH_2), 3.23 (t, 2 H, *J* = 6.9 Hz, CH_2N_3), 2.14 (s, 3 H, CH_3), 1.63–1.44 (m, 4 H, OCH_2(CH_2)$_6$$CH_2N_3$), 1.41–1.19 (m, 8 H, OCH_2(CH_2)$_6$$CH_2N_3$), 1.09 (m, 9 H, C(C$H_3$)$_3$); ^{13}C NMR (126 MHz, *CDCl*$_3$) δ_C = 170.2 (C═O), 138.9 (Ar), 138.8 (Ar), 138.6 (Ar), 138.5 (Ar), 138.2 (Ar), 138.0 (Ar), 136.0 (2 C, Ar), 135.8 (CH_2–*C*H=CH_2), 135.6 (2 C, Ar), 135.2 (Ar),

134.0 (Ar), 133.3 (Ar), 133.2 (Ar), 133.0 (Ar), 129.6 (Ar), 129.5 (Ar), 128.5 (3C, Ar), 128.4 (8 C, Ar), 128.2 (3 C, Ar), 128.1 (2 C, Ar), 128.0 (2 C, Ar), 127.8 (Ar), 127.7 (9 C, Ar), 127.6 (4 C, Ar), 127.5 (2 C, Ar), 127.3 (2 C, Ar), 127.2 (Ar), 126.7 (Ar), 126.2 (Ar), 126.0 (Ar), 125.9 (Ar), 116.9 (CH_2–CH=*C*H_2), 98.2 (C-1′), 98.1 (C-1″), 98.0 (C-1), 80.6 (C-3), 79.5 (C-3′), 77.9 (C-3″), 75.1 (2 C, *C*H_2NAP, *C*H_2Ph), 75.0 (C-4″), 74.8 (*C*H_2Ph), 74.7 (2 C, C-4, C-4′), 74.2, 73.9 (C-2, C-2′), 73.1 (*C*H_2Ph), 72.5 (C-5″), 72.3 (*C*H_2Ph), 71.5 (*C*H_2Ph), 71.4 (*C*H_2–CH=CH_2), 71.2 (C-5, C-5′), 68.6 (C-2″), 67.6 (*C*H_2O), 66.2, 66.1 (C-6, C-6′), 62.6 (C-6″), 51.4 (*C*H_2N_3), 29.4, 29.3, 29.1, 28.8 (4 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 26.8 (3 C, C(*C*$H_3$)$_3$), 26.7, 26.1 (2 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 21.1 (*C*$H_3$), 19.4 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + Na^+) $C_{100}H_{115}N_3O_{17}SiNa$: 1680.7888. Found: 1680.7880.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (9). The synthesis of **9** was achieved following the procedure described for the compound **8**, using disaccharide **34** (1.3 g, 1.28 mmol) and trichloroacetimidate **10** (1.205 g, 1.53 mmol) in the presence of TMSOTf (35 μL, 0.19 mmol) in Et_2O (16 mL). The crude residue was purified by column chromatography (9:1 → 8:2 hexane−EtOAc) to yield **9** (1.55 g, 74%) as a syrup. R_f 0.45 (4:1 hexane–EtOAc); $[\alpha]_D$ +33.5 (*c* = 0.46, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.76 (d, 2 H, *J* = 6.8 Hz, Ar), 7.68 (d, 2 H, *J* = 6.8 Hz, Ar), 7.46 –7.09 (m, 38 H, Ar), 6.83 (d, 2 H, *J* = 8.4 Hz, PhOCH_3), 5.95 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.53 (dd, 1 H, *J* = 1.7, 2.9 Hz, H-2″), 5.34 (dd, 1 H, *J* = 1.4, 17.1 Hz, CH_2–CH=C*H*$_2$), 5.16 (dd, 1 H, *J* = 1.4, 10.4 Hz, CH_2–CH=C*H*$_2$), 5.08 (d, 1 H, *J* = 1.2 Hz, H-1′), 4.95 (d, 1 H,*J* = 1.7 Hz, H-1″), 4.95 (d, 1 H, *J* = 10.8 Hz, C*H*$_2$Ph), 4.92 (d, 2 H, *J* = 11.2 Hz, C*H*$_2$Ph), 4.81 (d, 1 H, *J* = 1.4 Hz, H-1), 4.73 (d, 1 H, *J* = 11.4 Hz, C*H*$_2$Ph), 4.70 –4.63

(m, 5 H, CH_2Ph), 4.61 (d, 1 H, J = 11.0 Hz, CH_2Ph), 4.58–4.48 (m, 3 H, CH_2Ph), 4.44 (d, 1 H, J = 11.5 Hz, CH_2Ph), 4.17–4.13 (m, 2 H, CH_2–CH=CH_2), 4.11 (t, 1 H, J = 9.5 Hz, H-4″), 4.02 (dd, 1 H, J = 2.9, 9.5 Hz, H-3″), 3.99–3.83 (m, 7 H, H-4, H-4′, H-3, H-3′, H-6′a, H-2′, H-6″a), 3.81 (dd, 1 H, J = 2.2, 2.4 Hz, H-2), 3.79–3.65 (m, 8 H, H-6a, PhOCH_3, H6″b, H-6b, H-5, H-5′), 3.65–3.51 (m, 3 H, CH_2O, H-5″, H-6′b), 3.35 (dt, 1 H, J = 2×6.5, 9.5 Hz, OCH_2), 3.25 (t, 2 H, J = 6.9 Hz, CH_2N$_3$), 2.15 (s, 3 H, CH_3), 1.72–1.46 (m, 4 H, OCH$_2$(CH_2)$_6$CH$_2$N$_3$), 1.43–1.22 (m, 8 H, OCH$_2$(CH_2)$_6$CH$_2$N$_3$), 1.09 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR (126 MHz, *CDCl$_3$*) δ_C = 170.1 (C═O), 159.3 (Ar), 138.9 (Ar), 138.8 (Ar), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 138.0 (Ar), 136.0 (2C, Ar), 135.6 (2C, Ar), 135.3 (Ar), 134.1 (CH$_2$–*C*H=CH$_2$), 133.3 (Ar), 130.4 (Ar), 129.5 (4 C, Ar), 128.5 (2C, Ar), 128.4 (5 C, Ar), 128.3 (2 C, Ar), 128.2 (2 C, Ar), 128.1 (2 C, Ar), 128.0 (2 C, Ar), 127.7 (5 C, Ar), 127.6 (8 C, Ar), 127.5 (2 C, Ar), 127.3 (3 C, Ar), 127.2 (Ar), 116.9 (CH$_2$–CH=*C*H$_2$), 113.7 (2 C, Ar), 98.2 (2 C, C-1′, C-1″), 97.9 (C-1), 80.5 (C-3), 79.4 (C-3′), 77.9 (C-3″), 75.1 (2 C, *C*H$_2$Ph), 74.8 (*C*H$_2$Ph), 74.7, 74.6 (C-4, C-4′, C-2), 74.3 (C-2′), 74.0 (C-4″), 72.1 (*C*H$_2$Ph), 71.7 (2 C, *C*H$_2$Ph, C-5″), 71.5 (*C*H$_2$Ph), 71.4 (*C*H$_2$–CH=CH$_2$), 71.2 (2 C, C-5, C-5′), 68.7 (C-2″), 67.6 (*C*H$_2$O), 66.2, 66.1 (C-6, C-6′), 62.6 (C-6″), 55.2 (PhO*C*H$_3$), 51.5 (CH$_2$N$_3$), 29.4, 29.3, 29.1, 28.9 (4 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 26.8 (3 C, C(*C*H$_3$)$_3$), 26.7, 26.2 (2 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 21.2 (*C*H$_3$), 19.4 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + Na$^+$) C$_{97}$H$_{115}$N$_3$O$_{18}$SiNa: 1660.7837. Found: 1660.7840.

***p*-Tolyl 2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-thio-α-D-arabinofuranoside (12)**. To a solution of alcohol **18** (258 mg, 0.27 mmol) and trichloroacetonitrile (138 μL, 1.37 mmol) in CH_2Cl_2 (3.5 mL) at 0 °C was added DBU (4 μL, 0.027 mmol). The reaction mixture was stirred

for 1 h at 0 °C before the solvent was evaporated and the residue was filtered through short silica gel column (4:1 hexane–EtOAc, 1% Et_3N). The fractions containing the trichloroacetimidate derivative **19** were evaporated and the residue was used without any further purification. The trichloroacetimidate derivative **19** was diluted in CH_2Cl_2 (1 mL) and added to a solution of alcohol **23** (196 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) and 4 Å molecular sieves (86 mg) at –30 °C. After stirring for 30 min at –30 °C, TMSOTf (3 μL, 0.017 mmol) was added, and the reaction mixture was warmed to 0 °C over 30 min then neutralized by the addition of Et_3N. The solvent was evaporated and the residue was purified by flash chromatography (8.5:1.5 to 7.5:2.5, hexane–EtOAc) to yield **12** (304 mg, 86%) as a white foam. R_f 0.57 (3:2 hexane–EtOAc); $[\alpha]_D$ +41.3 (*c* = 0.09, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.13–7.85 (m, 19 H, Ar), 7.74–7.67 (m, 4 H, Ar), 7.63–7.19 (m, 39 H, Ar), 7.10 (d, 2 H, *J* = 7.9 Hz, Ar), 5.76–5.73 (m, 2 H, H-3, H-1), 5.72 (dd, 1 H, *J* = 1.5, 1.8 Hz, H-2), 5.67–5.62 (m, 7 H), 5.57 (br s, 1 H, H-2‴′), 5.40 (s, 2 H), 5.39 (s, 1 H), 5.38 (s, 1 H), 4.70 (app q,1 H, *J* = 4.0 Hz, H-4), 4.64–4.58 (m, 3 H, H-4′, h-4″, H-4‴), 4.50 (app q, 1 H, *J* = 4.1 Hz, H-4‴′), 4.24 (dd, 1 H, *J* = 4.2, 11.2 Hz, H-6a), 4.21–4.15 (m, 3 H), 4.00–3.89 (m, 6 H), 2.31 (s, 3 H, C*H*$_3$), 1.02 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 163.9 (3×C═O), 163.8 (2×C═O), 163.6 (C═O), 163.5 (2×C═O), 163.4 (2×C═O), 136.2 (Ar), 134.0 (5 C, Ar), 131.9 (Ar), 131.8 (Ar), 131.7 (2 C, Ar), 131.6 (4 C, Ar), 131.5 (Ar), 131.4 (2 C, Ar), 131.3 (Ar), 130.9 (2 C, Ar), 128.3 (4 C, Ar), 128.2 (10 C, Ar), 128.1 (8 C, Ar), 128.0 (3 C, Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (3 C, Ar), 127.4 (2 C, Ar), 127.3 (Ar), 126.9 (4 C, Ar), 126.8 (6 C, Ar), 126.7 (2 C, Ar), 126.6 (6 C, Ar), 126.5 (2 C, Ar), 126.0 (5 C, Ar), 106.0 (2 C, 2×C-1), 105.9 (2 C, 2×C-1), 91.6 (C-1), 83.2, 82.1 (4 C), 82.0 (2 C), 81.6 (2 C), 81.5, 77.4 (5 C), 65.9, 65.8 (2 C), 65.7, 63.4, 26.8 (3 C, C(*C*H$_3$)$_3$), 21.1 (*C*H$_3$), 19.3 (*C*(CH$_3$)$_3$); HRMS (ESI) calcd for (M + Na^+) $C_{118}H_{106}O_{30}SSiNa$: 2085.6151. Found: 2085.6160.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside (13). A mixture of trichloroacetimidate **10** (3.89 g, 4.95 mmol), azidooctanol (1.02 g, 5.96 mmol) and 4 Å molecular sieves (2.40 g) in CH_2Cl_2 (45 mL) was stirred for 30 min at – 30 °C under an argon atmosphere. Then, TMSOTf (135 μL, 0.74 mmol) was added dropwise over of 5 min. The reaction mixture was warmed to –5 °C over 30 min and then the TMSOTf was quenched by the addition of Et_3N. The solution was concentrated under vacuum and the resulting syrup was purified by column chromatography (95:5 hexane–EtOAc) to afford **13** (2.97 g, 75%) as a syrup: R_f 0.72 (4:1 hexane–EtOAc); $[\alpha]_D$ +14.7 (*c* = 2.76, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.77 (d, 2 H, *J* = 6.8 Hz, Ar), 7.73 (d, 2 H, *J* = 6.8 Hz, Ar), 7.49–7.24 (m, 14H, Ar), 7.20 (dd, 2H, *J* = 2.83, 6.7 Hz, Ar), 5.38 (t, 1H, *J* = 2.2 Hz, H-2), 4.93 (d, 1H, *J* = 10.7 Hz, C*H*$_2$Ar), 4.83 (d, 1H, *J* = 1.7 Hz, H-1), 4.75 (d, 1H, *J* = 11.2 Hz, C*H*$_2$Ar), 4.61 (d, 1H, *J* = 10.7 Hz, C*H*$_2$Ar), 4.59 (d, 1H, *J* = 11.2 Hz, C*H*$_2$Ar), 4.08–3.97 (m, 3H, H-3, H-4, H-6a), 3.92 (dd, 1H, *J* = 11.2, 1.6 Hz, H-6b), 3.77–3.69 (m, 1H, H-5), 3.66 (dt, 1H, *J* = 2×6.8, 9.6 Hz, OC*H*$_2$), 3.40 (dt, 1H, *J* = 2×6.4, 9.6 Hz, OC*H*$_2$), 3.25 (t, 2H, *J* = 6.7 Hz, C*H*$_2$N$_3$), 2.16 (s, 3H, OC*H*$_3$), 1.66–1.49 (m, 4H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.43–1.22 (m, 8H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.09 (s, 9H, C(C*H*$_3$)$_3$);^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 170.6 (C═O), 138.5 (Ar), 138.1 (Ar), 136.0 (2C, Ar), 135.6 (2 C, Ar), 133.9 (Ar), 133.3 (Ar), 129.6 (2 C, Ar), 128.4 (2 C, Ar), 128.3 (2 C, Ar), 128.1 (2 C, Ar), 127.9 (2 C, Ar), 127.7 (3 C, Ar), 127.6 (Ar), 127.5 (2 C, Ar), 97.5 (C-1), 78.5 (C-3), 75.4 (*C*H$_2$Ph), 74.3 (C-4), 72.7 (C-5), 71.8 (*C*H$_2$Ph), 69.2 (C-2), 67.6 (O*C*H$_2$), 63.0 (C-6), 51.5 (*C*H$_2$N$_3$), 29.4, 29.3, 29.1, 28.8 (4 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 26.8 (3 C, C(*C*H$_3$)$_3$), 26.7, 26.1, (2 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 21.1 (*C*H$_3$), 19.4 (*C*(CH$_3$)$_3$); HRMS (ESI) calcd for (M + Na^+) $C_{46}H_{59}N_3O_7SiNa$: 816.4014. Found: 816.3999.

8-Azidooctyl 3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (14). To a solution of **13** (3.32 g, 4.19 mmol) in CH_2Cl_2–CH_3OH (1:1, 9 mL) was added a solution of $NaOCH_3$ in CH_3OH (8 mL, 0.1M). The reaction mixture was stirred at room temperature for 1 h, neutralized by the addition of Amberlyst IR-120 (H^+) cation exchange resin, filtered and concentrated to give a syrup. The crude mixture was dissolved in DMF (20 mL) at 0 °C and sodium hydride (260 mg, 6.52 mmol) and 2-naphthylmethyl bromide (1.06 g, 4.79 mmol) were then added. The mixture was stirred for 3 h at room temperature, diluted with EtOAc and washed with water (4 × 20 mL). The organic layers were dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in THF at 0 °C and the *n*-Bu_4NF (1M in THF, 20.1 mL) was added. After stirring overnight at room temperature, the reaction mixture was concentrated to give a crude product that was purified by column chromatography (4:1 to 1:1 hexane–EtOAc) to afford **14** (1.36 g, 50% over 3 steps) as a syrup. R_f 0.42 (7:3 hexane–EtOAc); $[\alpha]_D$ +16.4 (*c* = 0.23, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.87–7.77 (m, 4 H, Ar), 7.57–7.46 (m, 3 H, Ar), 7.43–7.29 (m, 10 H, Ar), 4.98 (d, 1 H, *J* = 10.8 Hz, C*H*$_2$NAP), 4.97 (d, 1 H, *J* = 12.6 Hz, C*H*$_2$Ph), 4.88 (d, 1 H, *J* = 12.6 Hz, C*H*$_2$Ph), 4.84 (d, 1 H, *J* = 1.9 Hz, H-1), 4.71 (d, 1 H, *J* = 11.7 Hz, C*H*$_2$Ph), 4.69 (d, 1 H,*J* = 10.8 Hz, C*H*$_2$NAP), 4.68 (d, 1 H, *J* = 11.7 Hz, C*H*$_2$Ph), 4.03 (t, 1 H, *J* = 9.5 Hz, H-4), 3.96 (dd, 1 H, *J* = 2.9, 9.5 Hz, H-3), 3.88 (dd, 1 H, *J* = 3.1, 11.7 Hz, H-6a), 3.85 (dd, 1 H, *J* = 1.9, 2.9 Hz, H-2), 3.81 (dd, 1 H, *J* = 4.8, 11.8 Hz, H-6b), 3.67 (ddd, 1 H, *J* = 3.0, 4.6, 9.4 Hz, H-5), 3.62 (dt, 1 H, *J* = 2×6.8, 9.6 Hz, OC*H*$_2$), 3.33 (dt, 1 H, *J* = 2×6.5, 9.6 Hz, OC*H*$_2$), 3.26 (t, 2 H, *J* = 7.0 Hz, C*H*$_2$N$_3$), 1.74 (br s, 1 H, O*H*), 1.74 (m, 4 H, $OCH_2(CH_2)_6CH_2N_3$), 1.43–1.19 (m, 8 H, $OCH_2(CH_2)_6CH_2N_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 138.5 (Ar), 138.4 (Ar), 135.8 (Ar), 133.2 (Ar), 133.0 (Ar), 128.5 (2 C, Ar), 128.4 (2 C, Ar), 128.2 (Ar), 128.1 (2 C, Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (3 C, Ar), 126.7 (Ar), 126.1 (Ar), 125.9 (2 C, Ar), 98.3 (C-1), 80.4 (C-3), 75.3 (*C*H$_2$NAP), 75.1 (C-2), 74.9 (C-4), 73.0 (*C*H$_2$Ph),

72.4 (*C*H_2Ph), 72.1 (C-5), 67.7 (O*C*H_2), 62.5 (C-6), 51.5 (*C*H_2N_3), 29.4, 29.2, 29.0, 28.8, 26.7, 26.0 (6 C, $OCH_2(CH_2)_6CH_2N_3$). HRMS (ESI) calcd for ($M + Na^+$) $C_{39}H_{47}N_3O_6Na$: 676.3357. Found: 676.3351.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (15). A mixture of trichloroacetimidate **10** (118 mg, 0.15 mmol), alcohol **14** (83.3 mg, 0.13 mmol) and 4 Å molecular sieves (50 mg) in CH_2Cl_2 (2 mL) was stirred for 30 min at –20 °C under an argon atmosphere. Then, TMSOTf (135 μL, 0.74 mmol) was added dropwise over 5 min. The reaction mixture was warmed to 0 °C over 20 min and then the TMSOTf quenched by the addition of Et_3N. The solution was concentrated under vacuum and the resulting syrup was purified by column chromatography (95:5 hexane–EtOAc) to afford **15** (134.4 mg, 83%) as a syrup: R_f 0.64 (4:1 hexane–EtOAc); $[\alpha]_D$ +28.1 (*c* = 1.90, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.94–7.65 (m, 8 H, Ar), 7.56 (dd, 1 H, *J* = 1.2, 8.3 Hz, Ar), 7.50 7.17 (m, 28 H, Ar), 5.54 (dd, 1 H, *J* = 1.9, 3.1 Hz, H-2′), 5.00 (d, 1 H, *J* = 1.9 Hz, H-1′), 4.98–4.90 (m, 4 H, C*H*$_2$NAP, 3× C*H*$_2$Ph), 4.88 (d, 1 H, *J* = 1.6 Hz, H-1), 4.70–4.61 (m, 4 H, C*H*$_2$Ph), 4.53 (d, 1 H, *J* = 11.2 Hz, C*H*$_2$NAP), 4.48 (d, 1 H, *J* = 11.2 Hz, C*H*$_2$Ph), 4.13 (app t, 1 H, *J* = 9.6 Hz, H-4′), 4.04 (dd, 1 H, *J* = 3.1, 9.6 Hz, H-3′), 4.00–3.81 (m, 6 H, H-3, H-4, H-2, H-6′a, H-6′b, H-6a), 3.76–3.67 (m, 3 H, H-5′, H-5, H-6b), 3.62 (dt, 1H, *J* = 2×6.8, 9.5 Hz, OC*H*$_2$), 3.35 (dt, 1H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.23 (t, 2 H, *J* = 7.0 Hz, C*H*$_2N_3$), 2.16 (s, 3 H, CH_3), 1.62–1.46 (m, 4 H, $OCH_2(CH_2)_6CH_2N_3$), 1.40–1.23 (m, 8 H, $OCH_2(CH_2)_6CH_2N_3$), 1.10 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 170.2 (C═O), 138.8 (Ar), 138.6 (Ar), 138.4 (Ar), 138.0 (Ar), 136.0 (2 C, Ar), 135.9 (Ar), 135.6 (2 C, Ar), 134.0 (Ar), 133.3 (Ar), 133.2 (Ar), 133.0 (Ar), 129.5 (2 C, Ar), 128.4 (4 C, Ar), 128.3 (6 C, Ar), 128.2 (Ar), 127.9 (Ar), 127.7 (10 C, Ar), 127.6 (Ar), 127.5 (3 C, Ar), 127.4 (Ar), 126.6 (Ar), 126.1 (Ar), 126.0 (Ar), 125.8 (Ar), 98.0 (C-1), 97.6 (C-1′), 80.5 (C-3), 77.9 (C-3′), 75.2 (*C*H_2NAP),

75.0 (*C*H_2Ph), 74.8 (C-2), 74.7 (C-4), 74.0 (C-4′), 72.7 (*C*H_2Ph), 72.6 (C-5), 72.1 (*C*H_2Ph), 71.5 (*C*H_2Ph), 71.3 (C-5′), 68.8 (C-2′), 67.5 (O*C*H_2), 66.5 (C-6), 62.6 (C-6′), 51.4 (*C*H_2N_3), 29.4, 29.3, 29.1, 28.8 (4 C, $OCH_2(CH_2)_6CH_2N_3$), 26.8 (3 C, $C(CH_3)_3$), 26.6, 26.1 (2 C, $OCH_2(CH_2)_6CH_2N_3$), 21.1 (*C*H_3), 19.4 ($C(CH_3)_3$). HRMS (ESI) calcd for (M + Na^+) $C_{77}H_{89}N_3O_{12}SiNa$: 1298.6108. Found: 1298.6093.

8-Azidooctyl 2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (16). To a solution of **15** (1.44 g, 1.13 mmol) in CH_2Cl_2–CH_3OH (1:1, 6 mL) was added a solution of $NaOCH_3$ in CH_3OH (2.5 mL, 0.1M). The reaction mixture was stirred for 2 h, neutralized by the addition of Amberlyst IR-120 (H^+) cation exchange resin, filtered and concentrated to give a syrup. The crude mixture was dissolved in DMF (6.5 mL) at 0 °C and sodium hydride (57 mg, 1.41 mmol) and allyl bromide (200 μL, 4.79 mmol) were then added. The mixture was stirred for 3 h at room temperature, concentrated, diluted with EtOAc and washed with water (4 × 20 mL). The organic layers were dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in THF at 0 °C and the *n*-Bu_4NF (1M in THF, 9 mL) was then added. After stirring for 24 h at room temperature, the reaction mixture was concentrated to give a crude product that was purified by column chromatography (9:1 to 7:3 hexane–EtOAc) to afford **16** (1.103 g, 94% over 3 steps) as a syrup. R_f 0.24 (8:2 hexane–EtOAc); $[\alpha]_D$ +30.7 (*c* = 0.60, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.83–7.72 (m, 4 H, Ar), 7.54 (dd, 1 H, *J* = 1.3, 8.1 Hz, Ar), 7.50– 7.44 (m, 2 H, Ar), 7.41–7.18 (m, 20 H, Ar), 5.89 (dddd, 1 H, *J* = 5.0, 5.9, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.27 (dd, 1 H, *J* = 1.4, 17.2 Hz, CH_2–CH=C*H*$_2$), 5.15 (dd, 1 H, *J* = 1.4, 10.5 Hz, CH_2–CH=C*H*$_2$), 5.07 (d, 1 H, *J* = 1.3 Hz, H-1′), 4.97–4.86 (m, 4 H, C*H*$_2$NAP, 3× C*H*$_2$Ph), 4.86 (d, 1 H, *J* = 1.3 Hz, H-1), 4.68 (s, 2 H, C*H*$_2$Ph), 4.65–4.49 (m, 4 H, C*H*$_2$NAP, 3× C*H*$_2$Ph), 4.18–4.06 (m, 2 H, C*H*$_2$–CH=CH_2),

4.02–3.88 (m, 5 H, H-4, H-4′,H-3, H-3′,H-6′a), 3.86 (m, 2 H, H-2, H-2′), 3.81–3.64 (m, 5 H, H-6a, H-6′b, H-6b, H-5′, H-5), 3.60 (dt, 1H, $J = 2\times6.6$, 9.6 Hz, OCH_2), 3.34 (dt, 1H, $J = 2\times6.4$, 9.6 Hz, OCH_2), 3.24 (t, 2 H, J = 7.0 Hz, CH_2N_3), 1.94 (t, 1 H, J = 6.0 Hz, OH), 1.64–1.43 (m, 4 H, $OCH_2(CH_2)_6CH_2N_3$), 1.40–1.27 (m, 8 H, $OCH_2(CH_2)_6CH_2N_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 138.6 (Ar), 138.5 (Ar), 138.5 (Ar), 138.3 (Ar), 135.8 (Ar), 135.0 CH_2–*C*H=CH_2), 133.2 (Ar), 133.0 (Ar), 128.4 (6C, Ar), 128.3 (2 C, Ar), 128.2 (Ar), 127.9 (5 C, Ar), 127.8 (2 C, Ar), 127.7 (4 C, Ar), 127.6 (3 C, Ar), 126.7 (Ar), 126.2 (Ar), 126.0 (Ar), 125.9 (Ar), 117.1 (CH_2–CH=*C*H_2), 98.5 (C-1′), 97.9 (C-1), 80.5 (C-3′), 79.3 (C-3), 75.2 (*C*H_2NAP), 75.1(*C*H_2Ph), 75.0, 74.9 (C-2′, C-2), 74.8, 74.7 (C-4′, C-4), 73.1 (*C*H_2Ph), 72.3 (*C*H_2Ph), 72.2 (C-5′), 72.1 (*C*H_2–CH=CH_2), 71.7 (*C*H_2Ph), 71.6 (C-5), 67.6 (O*C*H_2), 66.1 (C-6′), 62.4 (C-6), 51.4 (*C*H_2N_3), 29.4, 29.3, 29.1, 28.8, 26.7, 26.1 (6 C, $OCH_2(CH_2)_6CH_2N_3$); HRMS (ESI) calcd for (M + Na^+) $C_{62}H_{73}N_3O_{11}Na$: 1058.5137. Found: 1058.5119.

2,3-di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranose (18). To a solution of thioglycoside **17** (4.63 g, 6.59 mmol) in THF–H_2O (40:1, 55.5 mL) at 0 °C was added NIS (2.72 g, 12.09 mmol) and AgOTf (673 mg, 2.62 mmol). The reaction mixture was stirred at 0 °C for 3.5 h and then neutralized by the addition of Et_3N. The solvent was evaporated and the residue was diluted with EtOAc (70 mL), washed with a satd aq solution of $Na_2S_2O_3$ (2 × 50 mL) and water (1 × 50 mL). The aqueous layers were extracted with EtOAc (2 × 30 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (4:1 → 7.5:2.5, hexane–EtOAc) to yield **18** (3.74 g, 95%, α/β: 4/1) as a white foam. R_f 0.56 (7:3 hexane–EtOAc); ^{1}H NMR (700 MHz, $CDCl_3$) δ_H = 8.14–7.94 (m, 9 H, Ar), 7.78–7.62 (m, 5 H, Ar), 7.65–7.25 (m, 23 H, Ar), 5.76–5.73 (m, 0.4 H, H-3, H-3′), 5.67–5.62 (m, 3 H, H-1, H-3, H-3′), 5.57 (d, 1 H, J =

0.9 Hz, H-2), 5.54 (d, 1 H, *J* = 0.9 Hz, H-2′), 5.52 (d, 0.2 H, *J* = 1.0 Hz, H-2), 5.50 (d, 0.2 H, *J* = 1.0 Hz, H-2′), 5.42 (br s, 0.2 H, H-1), 5.38 (br s, 1 H, H-1′), 5.33 (br s, 0.2 H, H-1′), 4.68 (app q, 1 H, *J* = 4.0 Hz, H-4), 4.60 (app q, 0.2 H, *J* = 4.7 Hz, H-4), 4.52 (app q, 1 H, *J* = 4.7 Hz, H-4′), 4.45 (app q, 0.2 H, *J* = 4.0 Hz, H-4′), 4.23 (dd, 0.2 H, *J* = 2.8, 11.2 Hz, H-6a), 4.19 (dd, 1 H, *J* = 5.0, 11.2 Hz, H-6a), 4.05–3.91 (m, 3.6 H, H-6′a; H-6b, H-6′b, H-6′a; H-6b, H-6′b), 3.03 (d, 1 H, *J* = 3.5 Hz, O*H*), 1.06 (s, 2 H, C(CH_3)$_3$), 1.04 (m, 9 H, C(CH_3)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 165.9 (2× C═O), 165.8 (C═O), 165.7 (C═O), 165.6 (C═O), 165.5 (2×C═O), 165.3 (C═O), 135.7 (2 C, Ar), 135.7 (Ar), 133.5 (3 C, Ar), 133.3 (4 C, Ar), 133.2 (4 C, Ar), 133.1 (Ar), 130.1 (Ar), 130.0 (3 C, Ar), 129.9 (4 C, Ar), 129.8 (2 C, Ar), 129.7 (2 C), 129.6, 129.3 (2 C, Ar), 129.2 (2 C, Ar), 129.1 (2 C, Ar), 129.0 (2 C, Ar), 128.5 (2 C, Ar), 128.4 (3 C, Ar), 128.3 (2 C, Ar), 128.1 (Ar), 127.7 (2 C, Ar), 106.6, 106.4, 106.0 (C-1′), 101.0 (C-1), 95.4, 84.6, 83.2 (C-4′), 83.0 (C-4′), 82.8 (C-4), 82.5, 82.4 (C-4), 82.2 (C-2, C-2′), 78.2 (C-3, C-3′), 77.6 (C-3, C-3′), 66.4 (C-6), 66.2 (C-6), 63.4 (C-6′), 63.3 (C-6′), 26.8 (6 C, 2×C(*C*H_3)$_3$), 19.3 (2×*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + Na^+) $C_{54}H_{52}O_{13}SiNa$: 959.3069. Found: 959.3073.

***p*-Tolyl 2,3-di-*O*-benzoyl-5-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-thio-α-D-arabinofuranoside (22)**. The synthesis of **22** was achieved following the procedure described for the compound **8**, using the disaccharide **20** (3.85 g, 4.79 mmol) and trichloroacetimidate **21** (4 g, 5.39 mmol) in the presence of TMSOTf (78 μL, 0.43 mmol) in CH_2Cl_2 (60 mL). The product was purified by column chromatography (9:1 → 7.5:2.5 hexane−EtOAc) to yield **22** (5.69 g, 86%) as a white foam. R_f 0.69 (7:3 hexane–EtOAc); $[\alpha]_D$ +29.8 (*c* = 1.20, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$) δ_H = 8.11–7.91 (m, 12 H, Ar), 7.71 (t, 4 H, *J* = 6.9 Hz, Ar), 7.62–7.23 (m, 26 H, Ar), 7.09 (d, 2 H, *J* = 7.9 Hz, Ar), 5.76–5.73 (m, 2 H, H-3, H-1), 5.72 (br s, 1 H, H-2), 5.67–5.62 (m, 3 H, H-3′, H-

2′, H-3″), 5.58 (app s, 1 H, H-2″), 5.39 (app s, 2 H, H-1′, H-1″), 4.70 (app q,1 H, J = 4.0 Hz, H-4), 4.63 (app q, 1 H, J = 4.2 Hz, H-4′), 4.51 (app q, 1 H, J = 4.1 Hz, H-4″), 4.25 (dd, 1 H, J = 4.2, 11.3 Hz, H-5a), 4.18 (dd, 1 H, J = 4.2, 11.3 Hz, H-5′a), 4.02–3.91 (m, 4 H, H-5b, H-5′b, H-5″a, H-5″b), 2.30 (s, 3 H, CH_3), 1.03 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 165.6 (C═O), 165.5 (2 C, 2×C═O), 165.3 (C═O), 165.2 (C═O), 165.2 (C═O), 137.9 (Ar), 135.7 (4 C, Ar), 133.5 (2 C, Ar), 133.3 (3 C, Ar), 133.2 (2 C, Ar), 133.0 (Ar), 132.6 (2 C, Ar), 130.0 (4 C, Ar), 129.9 (2 C, Ar), 129.8 (8 C, Ar), 129.6 (2 C, Ar), 129.3 (2 C, Ar), 129.2 (2 C, Ar), 129.1 (Ar), 129.0 (Ar), 128.5 (6 C, Ar), 128.4 (2 C, Ar), 128.3 (2 C, Ar), 128.2 (2 C, Ar), 127.7 (5 C, Ar), 106.0 (2 C, C-1′, C-1″), 91.6 (C-1), 83.2 (C-4″), 82.2 (2 C, C-2″, C-4′), 82.1 (C-2), 82.0 (C-4), 81.6 (C-2′), 77.5 (C-3), 77.4 (2 C, C-3′, C-3″), 65.8 (2 C, C-6, C-6′), 63.4 (C-6″), 26.7 (3 C, C(CH$_3$)$_3$), 21.2 (CH$_3$), 19.3 (C(CH$_3$)$_3$). HRMS (ESI) calcd for (M + Na^+) $C_{80}H_{74}O_{18}SSiNa$: 1405.4257. Found: 1405.4265.

***p*-Tolyl 2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-thio-α-D-arabinofuranoside (23)**. To a solution of trisaccharide **22** (1.27 g, 0.92 mmol) in THF–pyridine (4:1, 8 mL) at 0 °C was added a solution of 70% HF•pyridine (350 μL) dropwise. The reaction mixture was warmed to room temperature and stirred overnight. After dilution with EtOAc (20 mL), the reaction mixture was poured into a satd aq solution of $NaHCO_3$ (80 mL) and extracted with EtOAc (2 × 60 mL). The organic layer was washed with H_2O (2 × 50), dried (Na_2SO_4), filtered and concentrated under vacuum to give a syrup that was purified by column chromatography (9:1 → 7:3 hexane−EtOAc) to yield **23** (977.5 mg, 93%) as a white foam. R_f 0.24 (4:1 hexane–EtOAc); $[\alpha]_D$ +40.8 (c = 0.90, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$) δ_H = 8.14–8.03 (m, 7 H, Ar), 7.95 (dd, 4 H, J = 5.6, 6.9 Hz, Ar), 7.64–7.40 (m, 15 H, Ar), 7.29–7.16 (m, 6 H, Ar), 7.12 (d, 2 H, J = 7.9 Hz, Ar), 5.80–5.77 (m, 2

H, H-3, H-1), 5.76 (br s, 1 H, H-2), 5.70–5.66 (m, 3 H, H-3′, H-2′, H-2″), 5.47 (app d, 1 H, *J* = 4.6 Hz, H-3″), 5.46 (br s, 1 H, H-1′), 5.44 (br s, 1 H, H-1″), 4.73 (app q, 1 H, *J* = 4.0 Hz, H-4), 4.66 (app q,1 H, *J* = 4.2 Hz, H-4′), 4.52 (app q, 1 H, *J* = 4.1 Hz, H-4″), 4.28 (dd, 1 H, *J* = 4.1, 11.3 Hz, H-5a), 4.21 (dd, 1 H, *J* = 4.4, 11.3 Hz, H-5′a), 4.08–3.95 (m, 4 H, H-5b, H-5′b, H-5″a, H-5″b), 2.45 (dd, 1 H, *J* = 4.8, 8.0 Hz, O*H*), 2.32 (s, 3 H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 166.1 (C═O), 165.7 (C═O), 165.6 (C═O), 165.3 (C═O), 165.2 (C═O), 165.1 (C═O), 138.0 (Ar), 133.6 (2 C, Ar), 133.5 (2 C, Ar), 133.3 (2 C, Ar), 132.6 (2 C, Ar), 130.0 (2 C, Ar), 129.9 (10 C, Ar), 129.8 (2 C, Ar), 129.2 (2 C, Ar), 129.1 (2 C, Ar), 129.0 (Ar), 128.6 (8 C, Ar), 128.4 (4 C, Ar), 128.3 (Ar), 125.4 (Ar), 105.9 (2 C, C-1′, C-1″), 91.6 (C-1), 83.8 (C-4″), 82.1 (3 C, C-2, C-4, C-4′), 81.8, 81.7 (C-2′, C-2″), 77.8 (C-3″), 77.5 (C-3), 77.4 (C-3′), 66.2 (C-5′), 65.8 (C-5), 62.4 (C-5″), 21.2 (*C*H_3). HRMS (ESI) calcd for (M + Na^+) $C_{64}H_{56}O_{18}SNa$: 1167.3080. Found: 1167.3089.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (24). To a solution of **8** (96 mg, 0.058 mmol) in THF (300 μL), degassed under vacuum and stirring under an Ar atmosphere, (1,5-cyclooctadiene)bis(methyldiphenylphosphane)iridium I hexafluorophosphate catalyst (3 mg, 0.0035 mmol) was added, followed by further degassing of the mixture. The suspension was stirred for 15 min at 0 °C and the catalyst was then activated with hydrogen (2 minutes under hydrogen atmosphere. At this point, the solution became nearly colorless. The excess of hydrogen was removed by three cycles of vacuum/Ar. The reaction mixture was then stirred for 3 h at room temperature under Ar atmosphere. The solvent was then evaporated and the residue was dissolved in acetone–water (10:1, 4.4 mL). Then, HgO (17.5 mg, 0.081 mmol) and $HgCl_2$

(18.8 mg, 0.069 mmol) were added. After 1 h, the solvent was evaporated and the residue was diluted with Et_2O (15 mL), washed with 10% KI solution (3 × 10 mL), a satd aq solution of $Na_2S_2O_3$ (2 × 10 mL) and water (3 × 10 mL). The aqueous layers were extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (9:1 → 7:3, hexane–EtOAc) to yield **24** (93 mg, quant.) as a syrup. R_f 0.33 (4:1 hexane–EtOAc); $[\alpha]_D$ +26.0 (*c* = 0.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.83–7.62 (m, 8 H, Ar), 7.53 (d, 1 H *J* = 8.8 Hz, Ar), 7.47–7.08 (m, 38 H, Ar), 5.44 (dd, 1 H, *J* = 1.8, 3.4 Hz, H-2″), 5.06 (d, 1 H, *J* = 1.3 Hz, H-1′), 4.97 (d, 1 H, *J* = 1.3 Hz, H-1″), 4.95 (d, 1 H, *J* = 11.2 Hz, CH_2NAP), 4.93 (d, 1 H, *J* = 11.2 Hz, CH_2Ph), 4.91–4.88 (m, 2 H, C*H*$_2$Ph), 4.87 (d, 1 H, *J* = 1.5 Hz, H-1), 4.72 (d, 1 H,*J* = 11.2 Hz, C*H*$_2$Ph), 4.72 (d, 1 H, *J* = 11.4 Hz, C*H*$_2$Ph), 4.67 (s, 2 H, C*H*$_2$Ph), 4.62 (d, 1 H, *J* = 11.2 Hz, CH_2NAP), 4.57–4.50 (m, 3 H, C*H*$_2$Ph), 4.48–4.41 (m, 2 H, C*H*$_2$Ph), 4.16 (br s, 1 H, H-2′), 4.10 (t, 1 H, *J* = 9.6, H-4″), 4.03–3.81 (m, 7 H, H-4, H-3″, H-3, H-2, H-3′, H-6a, H-6a″), 3.81–3.65 (m, 6 H, H-4′, H-6b″, H-6a′, H-6b, H-5, H-5′), 3.64–3.53 (m, 3 H, H-5″, H6b′, OC*H*$_2$), 3.33 (dt, 1H, *J* = 2×6.4, 9.6 Hz, OC*H*$_2$), 3.22 (t, 2 H, *J* = 6.9 Hz, C*H*$_2$N$_3$), 2.40 (d, 1 H, *J* = 2.9 Hz, O*H*), 2.14 (s, 3 H, C*H*$_3$), 1.62–1.42 (m, 4 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.38–1.19 (m, 8 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.07 (m, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 170.4 (C═O), 138.8 (Ar), 138.6 (Ar), 138.5 (2 C, Ar), 138.0 (Ar), 137.8 (Ar), 136.0 (2 C, Ar), 135.6 (Ar), 135.0 (2 C, Ar), 134.0 (Ar), 133.3 (Ar), 133.2 (Ar), 133.0 (Ar), 129.5 (2 C, Ar), 128.5 (2C, Ar), 128.4 (6 C, Ar), 128.3 (4 C, Ar), 128.2 (3 C, Ar), 128.0 (2 C, Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (8 C, Ar), 127.6 (4 C, Ar), 127.5 (2 C, Ar), 127.4 (4 C, Ar), 126.5 (Ar), 126.1 (Ar), 125.9 (2 C, Ar), 98.8 (C-1′), 98.0 (C-1″), 97.7 (C-1), 80.5 (C-3), 79.7 (C-3′), 77.7 (C-3″), 75.2 (2 C, *C*H_2NAP, *C*H_2Ph), 75.0 (C-2″), 74.8 (*C*H_2Ph), 74.7 (C-4), 74.0 (C-4″), 73.8 (C-4′), 72.9 (*C*H_2Ph), 72.5 (C-5″), 72.2 (*C*H_2Ph), 71.7 (C-5), 71.6 (*C*H_2Ph), 71.2

(CH_2Ph), 70.8 (C-5′), 69.0 (C-2″), 67.9 (C-2′), 67.6 (CH_2O), 66.4 (C-6′), 65.9 (C-6), 62.6 (C-6″), 51.4 (CH_2N_3), 29.4, 29.3, 29.1, 28.8 (4 C, $OCH_2(CH_2)_6CH_2N_3$), 26.9 (3 C, $C(CH_3)_3$), 26.7, 26.1 (2 C, $OCH_2(CH_2)_6CH_2N_3$), 21.2 (CH_3), 19.4 ($C(CH_3)_3$). HRMS (ESI) calcd for ($M + Na^+$) $C_{97}H_{111}N_3O_{17}SiNa$: 1640.7575. Found: 1640.7556.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)]-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (25). A mixture of **11a** (34 mg, 0.075 mmol), alcohol **24** (30 mg, 0.019 mmol) and 4 Å molecular sieves (10 mg) in CH_2Cl_2 (400 μL) was stirred for 30 min at 0 °C under an argon atmosphere. Then, NIS (6 mg, 0.027 mmol) and AgOTf (2 mg, 0.0078 mmol) were added. The reaction mixture was stirred at 0 °C for 3 h then neutralized by the addition of Et_3N. The solvent was evaporated and the residue was diluted with CH_2Cl_2 (10 mL), washed with a satd aq solution of $Na_2S_2O_3$ (2 × 10 mL) and water (1 × 10 mL). The aqueous layers were extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The crude residue was purified by gel-filtration chromatography (Sephadex, LH-20) with 1:1, CH_2Cl_2–CH_3OH as the eluent, followed by column chromatography (4:1, hexane–acetone) to yield **25** (24 mg, 67%) as a syrup. R_f 0.43 (7:3 hexane–acetone); $[\alpha]_D$ +2.7 (c = 0.03, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.83–7.66 (m, 8 H, Ar), 7.54 (d, 1 H, J = 8.2 Hz, Ar), 7.49–7.11 (m, 38 H, Ar), 5.52 (dd, 1 H, J = 1.2, 3.1 Hz, H-2‴), 5.49 (dd, 1 H, J = 1.7, 3.1 Hz, H-2″), 5.41 (dd, 1 H, J = 3.1, 10.0 Hz, H-3‴), 5.33 (t, 1 H, J = 10.0 Hz, H-4‴), 5.03 (d, 1 H, J = 1.2 Hz, H-1′), 5.01 (d, 1 H, J = 1.2 Hz, H-1‴), 4.99–4.93 (m, 3 H, 2× CH_2Ph, H-1″), 4.93–4.85 (m, 4 H, 3×CH_2Ph, H-1), 4.76 (d, 1 H, J = 11.2 Hz, CH_2Ph), 4.65–4.48 (m, 8 H, CH_2Ph), 4.34 (dd, 1 H, J = 4.7, 12.2 Hz, H-6‴), 4.25–4.19 (m, 1 H, H-5‴), 4.18–4.09 (m, 3 H), 4.07–3.82 (m, 8 H), 3.81–3.47 (m, 8

H), 3.33 (dt, 1 H, $J = 2\times6.5$, 9.5 Hz, OCH_2), 3.23 (t, 2 H, $J = 6.9$ Hz, CH_2N$_3$), 2.14 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 1.85(s, 3 H, CH_3), 1.65–1.45 (m, 4 H, OCH$_2$(CH_2)$_6$CH$_2$N$_3$), 1.38–1.21 (m, 8 H, OCH$_2$(CH_2)$_6$CH$_2$N$_3$), 1.09 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 170.7 (C═O), 170.1 (C═O), 169.9 (C═O), 169.7 (C═O), 169.5 (C═O), 138.9 (Ar), 138.5 (3 C, Ar), 138.4 (Ar), 137.9 (Ar), 136.0 (2 C, Ar), 135.8 (Ar), 135.6 (2 C, Ar), 134.0 (Ar), 133.3 (Ar), 133.2 (Ar), 133.0 (Ar), 129.5 (Ar), 128.4 (3 C, Ar), 128.3 (3 C, Ar), 128.2 (4 C, Ar), 128.1 (2 C, Ar), 127.9 (Ar), 127.7 (2 C, Ar), 127.6 (6 C, Ar), 127.5 (7 C, Ar), 127.4 (Ar), 127.2 (Ar), 126.6 (Ar), 126.1 (Ar), 126.0 (Ar), 125.9 (Ar), 99.7 (C-1‴), 99.2 (C-1′), 98.0 (C-1″), 97.8 (C-1), 80.5, 79.4, 78.2, 76.4, 75.2 (*C*H$_2$Ph), 75.1 (*C*H$_2$Ph), 75.0 (*C*H$_2$Ph), 74.6 (2 C), 74.3, 74.0, 72.7 (*C*H$_2$Ph), 72.4, 72.2 (*C*H$_2$Ph), 71.8 (*C*H$_2$Ph), 71.6 (*C*H$_2$Ph), 71.5, 71.0, 69.6, 69.3, 69.0 (2 C), 67.6, 66.6, 66.0, 65.6, 62.5 (2 C),51.4 (CH$_2$N$_3$), 29.4, 29.3, 29.1, 28.8 (4 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 26.8 (3 C, C(*C*H$_3$)$_3$), 26.7, 26.1(2 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 21.1, 20.9, 20.8, 20.7, 20.5 ($5\times$*C*H$_3$), 19.4 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + Na$^+$) $C_{111}H_{129}N_3O_{26}SiNa$: 1970.8526. Found: 1970.8519.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-[(2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→2)]-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (26). The synthesis of **26** was achieved following the procedure described for the preparation of compound **25**, using alcohol **24** (60 mg, 0.037 mmol), thioglycoside **12** (115 mg, 0.056 mmol) and 4 Å molecular sieves (15 mg) in CH_2Cl_2 (550 μL) at room temperature in the presence of NIS (23 mg, 0.103 mmol) and AgOTf (3 mg, 0.012 mmol) for 30 min. The crude

residue was purified by column chromatography (9:1 → 7.5:2.5, hexane–acetone) to yield **26** (123 mg, 93%) as a syrup. R_f 0.53 (7:3 hexane–acetone); $[\alpha]_D$ +17.0 (*c* = 0.20, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.06–7.84 (m, 20 H, Ar), 7.81–7.67 (m, 11 H, Ar), 7.60–7.03 (m, 76 H, Ar), 5.80 (s, 2 H), 5.72–5.62 (m, 8 H), 5.58 (s, 1 H), 5.52 (br s., 1 H, H-2″), 5.43–5.35 (m, 4 H), 5.05 (d, 1 H, *J* = 1.3 Hz, H-1′), 5.00 (d, 1 H, *J* = 1.1 Hz, H-1″), 4.96–4.90 (m, 3 H, C*H*$_2$Ph), 4.87–4.82 (m, 3 H), 4.69–4.41 (m, 14 H), 4.39 (br s, 1 H), 4.23 - 4.15 (m, 4 H), 4.14 - 4.06 (m, 2 H, H-4″, H-3″), 4.04 - 3.81 (m, 13 H), 3.80 - 3.59 (m, 7 H), 3.56 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.28 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.20 (t, 2 H, *J* = 6.9 Hz, C*H*$_2$N$_3$), 2.76 (s, 3 H, C*H*$_3$), 1.59 - 1.40 (m, 4 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.38 - 1.18 (m, 8 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.08 (s, 9 H, C(C*H*$_3$)$_3$), 1.03 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 169.9(C═O), 165.6 (3 C, C═O), 165.5 (2 C, C═O), 165.2, 165.1 (3 C, C═O), 165.0 (C═O), 138.9 (Ar), 138.7 (Ar), 138.6 (Ar), 138.5 (Ar), 138.2 (Ar), 137.9 (Ar), 136.0 (2 C, Ar), 135.8 (Ar), 135.7 (3 C, Ar), 135.6 (6 C, Ar), 134.0 (Ar), 133.3 (2 C, Ar), 133.2 (Ar), 133.1 (3 C, Ar), 133.0 (Ar), 130.0 (3 C, Ar), 129.9 (3 C, Ar), 129.8 (15 C, Ar), 129.6 (3 C, Ar), 129.5 (Ar), 129.3 (Ar), 129.3 (3 C, Ar), 129.2 (2 C, Ar), 129.1 (3 C, Ar), 128.5 (4 C, Ar), 128.4 (4 C, Ar), 128.3 (10 C, Ar), 128.3 (15 C, Ar), 128.2 (3 C, Ar), 128.1 (Ar), 127.8 (5 C, Ar), 127.7 (9 C, Ar), 127.6 (6 C, Ar), 127.5 (6 C, Ar), 127.4 (2 C, Ar), 127.2 (Ar), 126.6 (Ar), 126.0 (2 C, Ar), 125.8 (Ar), 106.2, 106.0 (2 C), 105.8 (2 C), 99.8, 97.8 (2 C), 83.2, 82.1 (5 C), 82.0, 81.7, 81.6, 81.5 (2 C), 80.6, 79.8, 78.3, 76.3 (3 C), 75.2, 75.0, 74.8,74.6 (2 C), 74.4, 74.0 (2 C), 72.6, 72.4, 72.1, 71.7, 71.5, 71.2, 68.7, 67.5, 66.3, 65.9 (2 C), 65.8, 65.6, 65.5, 63.4 (2 C), 62.5, 51.4, 29.6, 29.3, 29.0, 28.8 (4 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 26.8 (6 C, 2×C(*C*H$_3$)$_3$), 26.7, 26.1 (2 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 20.9 (*C*H$_3$), 19.4 (*C*(CH$_3$)$_3$), 19.3 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + 2 Na^+) $C_{208}H_{209}N_3O_{47}Si_2Na_2$: 1801.1690. Found: 1801.1715.

8-Azidooctyl 2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (28). To a solution of **8** (105 mg, 0.063 mmol) in Et_2O–CH_3OH (1:1, 300 μL) was added a solution of $NaOCH_3$ in CH_3OH (100 μL, 0.1M). The reaction mixture was stirred for 3 h, neutralized by the addition of Amberlyst IR-120 (H^+) cation exchange resin, filtered and concentrated to give **27** as a syrup. The residue was dissolved in CH_2Cl_2 (2 mL), thioglycoside **12** (125 mg, 0.061 mmol) and 4 Å molecular sieves (19 mg) were added and the mixture was stirred for 30 min at 0 °C before NIS (19 mg, 0.084 mmol) and AgOTf (4 mg, 0.016 mmol) were added, under an argon atmosphere. The reaction mixture was stirred at 0 °C for 3 h and then neutralized by the addition of Et_3N. The solvent was evaporated and the residue was diluted with CH_2Cl_2 (10 mL), washed with a satd aq solution of $Na_2S_2O_3$ (2 × 10 mL) and water (1 × 10 mL). The aqueous layers were extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (9:1 → 7.5:2.5, hexane–acetone) to yield **28** (156 mg, 73%) as a syrup. R_f 0.54 (7:3 hexane–acetone); $[\alpha]_D$ +30.4 (*c* = 0.46, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.06–7.82 (m, 21 H, Ar), 7.80–7.62 (m, 12 H, Ar), 7.59–7.03 (m, 74 H, Ar), 5.86 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.73 (d, 1 H, *J* = 4.8 Hz), 5.71–5.61 (m, 10 H), 5.57 (d, 1 H, *J* = 1.2 Hz), 5.42–5.36 (m, 4 H, 4×H-1), 5.25 (dd, 1 H, *J* = 1.5, 17.2 Hz, CH_2–CH=CH_2), 5.07 (dd, 1 H, *J* = 1.5, 10.5 Hz, CH_2–CH=CH_2), 5.02 (d, 1 H, *J* = 1.2 Hz, H-1), 5.01 (d, 1 H, *J* = 1.4 Hz, H-1), 4.93–4.83 (m, 6 H, H-1, 5×CH_2Ph), 4.72 (d, 1 H, *J* = 11.6 Hz,

C*H*$_2$Ph), 4.67–4.43 (m, 12 H), 4.41 (d, 1 H, *J* = 11.2 Hz), 4.35 (br s, 1 H), 4.23–4.13 (m, 4 H), 4.13–4.04 (m, 3 H), 4.02–3.80 (m, 15 H), 3.73–3.55 (m, 7 H), 3.51–3.46 (m, 1 H), 3.30 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.20 (t, 2 H, *J* = 6.9 Hz, C*H*$_2$N$_3$), 1.58–1.44 (m, 4 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.37–1.20 (m, 8 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.02 (br s, 18 H, 2×C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 165.6 (4 C, C═O), 165.5 (C═O), 165.2 (C═O), 165.1 (2C, C═O), 165.0 (2 C, C═O), 138.9 (Ar), 138.8 (Ar), 138.5 (2 C, Ar), 138.3 (Ar), 138.2 (Ar), 135.9 (2 C, Ar), 135.8 (Ar), 135.7 (3 C, Ar), 135.6 (3 C, Ar), 135.2 (2 C, Ar), 134.1 (Ar), 133.5 (Ar), 133.4 (CH$_2$–*C*H=CH$_2$), 133.3 (2 C, Ar), 133.2 (Ar), 133.1 (5 C, Ar), 130.0 (3 C, Ar), 129.9 (6 C, Ar), 129.8 (12 C, Ar), 129.6 (3 C, Ar), 129.4 (2 C, Ar), 129.3 (2 C, Ar), 129.2 (2 C, Ar), 129.1 (3 C, Ar), 128.5 (4 C, Ar), 128.4 (6 C, Ar), 128.3 (12 C, Ar), 128.2 (10 C, Ar), 128.1 (4 C, Ar), 128.0 (2 C, Ar), 127.9 (2 C, Ar), 127.8 (Ar), 127.7 (11 C, Ar), 127.6 (6 C, Ar), 127.5 (4 C, Ar), 127.3 (Ar), 127.2 (3 C, Ar), 126.7 (Ar), 126.1 (Ar), 126.0 (Ar), 125.9 (Ar), 116.9 (CH$_2$–CH=*C*H$_2$), 106.3 (C-1), 106.0 (3×C-1), 105.9 (C-1), 99.6, 98.4, 97.9 (C-1, C-1′, C-1″), 83.2 (3 C), 82.2, 82.1 (3 C), 81.9, 81.5 (3C), 80.6, 79.9, 79.6, 75.1, 75.0, 74.9, 74.7, 74.6 (2 C), 74.4 (2 C), 74.2, 73.1, 73.0, 72.4, 72.3, 71.9, 71.7, 71.6, 71.4, 71.3, 67.5 (2 C), 66.1, 65.9 (2 C), 65.8 (2 C), 65.7 (2 C), 65.5, 63.4 (2 C), 63.1, 51.4 (*C*H$_2$N$_3$), 29.6, 29.3, 29.0, 28.8 (4 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 26.9 (6 C, 2×C(*C*H$_3$)$_3$), 26.7, 26.1 (2 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 19.4 (*C*(CH$_3$)$_3$), 19.2 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + 2 Na$^+$) $C_{209}H_{209}N_3O_{46}Si_2Na_2$: 1800.1746. Found: 1800.1785.

8-Azidooctyl 2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)]-3,4-di-*O*-

benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-(2-methylnaphthyl)-3,4-di-*O*-benzyl-α-D-mannopyranoside (29) The synthesis of **29** was achieved following the procedure described for the preparation of **24**, starting from the octasaccharide **28** (93 mg, 0.026 mmol) and using (1,5-cyclooctadiene)bis (methyldiphenylphosphane) iridium I hexafluorophosphate catalyst (3 mg, 0.0035 mmol) in THF (500 μL), then HgO (8 mg, 0.037 mmol) and $HgCl_2$ (9 mg, 0.033 mmol) in acetone–water (10:1, 1.8 mL). The crude residue, used without any further purification, was dissolved in CH_2Cl_2 (600 μL). Then, **11a** (36 mg, 0.079 mmol) and 4 Å molecular sieves (18 mg) were added and the mixture was stirred for 30 min at 0 °C. NIS (19 mg, 0.084 mmol) and AgOTf (4 mg, 0.016 mmol) were then added, under an argon atmosphere. The reaction mixture was stirred at 0 °C for 2 h then neutralized by the addition of Et_3N. The solvent was evaporated and the residue was diluted with CH_2Cl_2 (10 mL), washed with a satd aq solution of $Na_2S_2O_3$ (2 × 10 mL) and water (1 × 10 mL). The aqueous layers were extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by gel-filtration chromatography (Sephadex, LH-20) with 1:1, CH_2Cl_2–CH_3OH as the eluent, to yield **29** (88.5 mg, 88% over 2 steps). R_f 0.34 (4:1, hexane–EtOAc); $[\alpha]_D$ +1.3 (*c* = 0.03, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.05–7.81 (m, 20 H, Ar), 7.80–7.62 (m, 12 H, Ar), 7.58–7.01 (m, 75 H, Ar), 5.76 (d, 1 H, *J* = 4.9 Hz), 5.72 (d, 1 H, *J* = 1.2 Hz), 5.71–5.60 (m, 8 H), 5.56 (br s, 1 H), 5.46 (dd, 1 H, *J* = 1.6, 3.2 Hz), 5.43–5.35 (m, 5 H), 5.28 (t, 1 H, *J* = 10.1 Hz), 5.01 (s, 3 H), 4.95–4.83 (m, 6 H), 4.78 (d, 1 H, *J* = 11.7 Hz, C*H*$_2$Ph), 4.67–4.45 (m, 13 H), 4.37 (br s, 1 H), 4.28 (dd, 1 H, *J* = 4.7, 11.9 Hz), 4.22–4.08 (m, 8 H), 4.03–3.79 (m, 14 H), 3.74 (m, 3 H), 3.68 (dd, 1 H, *J* = 2.9, 9.7 Hz), 3.64–3.52 (m, 3 H), 3.45 (d, 1 H, *J* = 10.4 Hz), 3.30 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.20 (t, 2 H, *J* = 6.9 Hz, C*H*$_2$N$_3$), 2.02 (s, 6 H, 2×C*H*$_3$), 1.88 (s, 3 H, C*H*$_3$), 1.81 (s, 3 H, C*H*$_3$), 1.58–1.43 (m, 4 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.35–1.18 (m, 8 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.02 (s, 9 H, C(C*H*$_3$)$_3$), 1.01 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz,

$CDCl_3$) δ_C = 170.6 (C═O), 170.0 (C═O), 169.6 (C═O), 169.4 (C═O), 165.6 (4 C, C═O), 165.5 (C═O), 165.2 (C═O), 165.1 (2 C, C═O), 165.0 (C═O), 164.9 (C═O), 139.0 (Ar), 138.7 (Ar), 138.5 (2 C, Ar), 138.4 (Ar), 137.9 (Ar), 135.9 (2 C, Ar), 135.8 (Ar), 135.7 (3 C, Ar), 135.6 (3 C, Ar), 134.0 (Ar), 133.5 (Ar), 133.3 (2 C, Ar), 133.2 (Ar), 133.1 (3 C, Ar), 133.0 (2 C, Ar),130.0 (3 C, Ar), 129.9 (6 C, Ar), 129.8 (12 C, Ar), 129.7 (3 C, Ar), 129.4 (2 C, Ar), 129.3 (2 C, Ar), 129.2 (2 C, Ar), 129.1 (3 C, Ar), 128.5 (4 C, Ar), 128.4 (6 C, Ar), 128.3 (12 C, Ar), 128.2 (10 C, Ar), 128.1 (4 C, Ar), 128.0 (2 C, Ar), 127.9 (2 C, Ar), 127.8 (Ar), 127.7 (12 C, Ar), 127.6 (6 C, Ar), 127.5 (5 C, Ar), 127.2 (3 C, Ar), 127.1 (Ar), 126.6 (Ar), 126.1 (Ar), 125.9 (Ar), 125.9 (Ar), 106.5 (C-1), 106.0 (3×C-1), 105.9 (C-1), 99.6 (2×C-1), 99.2 (C-1), 97.9 (C-1), 83.2 (3 C), 82.2, 82.0 (3 C), 81.9, 81.6, 81.5 (3 C), 81.4, 80.6, 80.1, 79.4, 78.5, 76.0, 75.1, 75.0, 74.9, 74.5 (2 C), 74.4 (2 C), 74.3, 73.2, 72.8 (2 C), 72.3 (2 C), 71.8 (2 C), 71.6, 71.5, 71.1, 70.9, 69.5, 69.1 (2 C), 68.9, 67.6 (2 C), 67.2, 66.0, 65.9 (2 C), 65.8 (2 C), 65.7 (2 C), 63.5 (2 C), 63.1, 62.4 (2 C), 51.4 (CH_2N_3), 29.7, 29.4, 29.0, 28.8 (4 C, $OCH_2(CH_2)_6CH_2N_3$), 26.8 (6 C, 2×C$(CH_3)_3$), 26.6, 26.1 (2 C, $OCH_2(CH_2)_6CH_2N_3$), 20.8 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 20.5(CH_3), 19.3 ($C(CH_3)_3$), 19.2 ($C(CH_3)_3$); HRMS (ESI) calcd for (M + 2 Na^+) $C_{220}H_{225}N_3O_{55}Si_2Na_2$: 1945.2112. Found: 1945.2137.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-α-D-mannopyranoside (30). To a solution of **9** (48 mg, 0.029 mmol) in CH_3CN–H_2O (10:1, 440 μL) was added CAN (32 mg, 0.058 mmol). After 1 h stirring, the reaction mixture was concentrated under vacuum. The residue was diluted with EtOAc (15 mL) and washed with an aq solution of $NaHCO_3$ (2 × 10 mL) and water (1 × 10 mL). The aqueous layers were extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue

was purified by flash chromatography (4:1 → 7:3, hexane–EtOAc) to yield **30** (37 mg, 83%) as a syrup. R_f 0.71 (3:2 hexane–EtOAc); $[\alpha]_D$ +40.5 (*c* = 0.50, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.76 (d, 2 H, *J* = 6.8 Hz, Ar), 7.68 (d, 2 H, *J* = 6.8 Hz, Ar), 7.47–7.10 (m, 36 H, Ar), 5.95 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.51 (dd, 1 H, *J* = 1.7, 2.9 Hz, H-2″), 5.34 (dd, 1 H, *J* = 1.4, 17.2 Hz, CH_2–CH=C*H*$_2$), 5.16 (dd, 1 H, *J* = 1.4, 10.5 Hz, CH_2–CH=C*H*$_2$), 5.02 (d, 1 H, *J* = 1.3 Hz, H-1′), 4.96–4.89 (m, 3 H, H-1″, 2× C*H*$_2$Ph), 4.88–4.83 (m, 2 H, H-1, C*H*$_2$Ph), 4.76–4.68 (m, 4 H, C*H*$_2$Ph), 4.64 (d, 1 H, *J* = 11.8 Hz, C*H*$_2$Ph), 4.61 (d, 1 H, *J* = 10.9 Hz, C*H*$_2$Ph), 4.66–4.58 (m, 2 H, C*H*$_2$Ph), 4.46 (d, 1 H, *J* = 11.4 Hz, C*H*$_2$Ph), 4.21–4.16 (m, 2 H, C*H*$_2$–CH=CH_2), 4.11 (t, 1 H, *J* = 9.6 Hz, H-4″), 4.05 (br s, 1 H, H-2), 4.02 (dd, 1 H, *J* = 2.9, 9.6 Hz, H-3″), 3.94–3.85 (m, 5 H, H-4, H-3, H-3′, H-6a, H-6″a), 3.83 (br s, 1 H, H-2′), 3.78–3.54 (m, 9 H, H-4′, H6″b, H-6b, H-6′a, H-6′b, H-5, H-5′, H-5″, C*H*$_2$O), 3.40 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.25 (t, 2 H, *J* = 6.9 Hz, C*H*$_2$$N_3$), 2.46 (d, *J* = 2.4 Hz, 1 H), 2.15 (s, 3 H, C*H*$_3$), 1.64–1.48 (m, 4 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.41–1.25 (m, 8 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.08 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 170.3 (C═O), 138.9 (Ar), 138.7 (Ar), 138.4 (Ar), 138.3 (Ar), 138.0 (Ar), 137.9 (Ar), 136.0 (2C, Ar), 135.5 (2C, Ar), 135.2 (Ar), 134.0 (CH_2–*C*H=CH_2), 133.3 (Ar), 129.5 (2C, Ar), 128.6 (2C, Ar), 128.4 (7 C, Ar), 128.2 (2 C, Ar), 128.1 (2 C, Ar), 128.0 (Ar), 127.9 (4 C, Ar), 127.7 (5 C, Ar), 127.6 (5 C, Ar), 127.5 (2 C, Ar), 127.3 (3 C, Ar), 127.2 (Ar), 117.2 (CH_2–CH=*C*H_2), 99.0 (C-1), 98.2 (C-1′), 97.8 (C-1″), 80.5 (C-3), 79.7 (C-3′), 77.9 (C-3″),75.1 (2 C, *C*H_2Ph), 74.8 (*C*H_2Ph), 74.6, 74.4 (C-4, C-4′, C-2), 74.1 (C-2′), 74.0 (C-4″), 72.5 (C-5″), 72.0 (*C*H_2Ph), 71.8 (2 C, *C*H_2Ph), 71.5 (*C*H_2–CH=CH_2), 71.1, 70.9 (C-5, C-5′), 68.7 (C-2″), 68.4 (C-2), 67.6 (*C*H_2O), 66.2 (2 C, C-6, C-6′), 62.6 (C-6″), 51.4 (CH_2N_3), 29.4, 29.3, 29.1, 28.8 (4 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 26.8 (3 C, C(*C*$H_3$)$_3$), 26.7, 26.1 (2 C, OCH_2(*C*H_2)$_6$$CH_2N_3$),

21.1 (CH_3), 19.4 ($C(CH_3)_3$); HRMS (ESI) calcd for (M + Na^+) $C_{89}H_{107}N_3O_{17}SiNa$: 1540.7262. Found: 1540.7256.

8-Azidooctyl 3,4-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (31). The synthesis of **31** (2.86 g, 3.60 mmol) was achieved following the procedure described for the preparation of **14**, using $NaOCH_3$ in CH_3OH (7 mL, 0.1M), CH_2Cl_2–CH_3OH (1:1, 8 mL), sodium hydride (180 mg, 7.5 mmol), *p*-methoxybenzyl chloride (735 μL, 5.4 mmol), DMF (20 mL), *n*-Bu_4NF (1M in THF, 28 mL) and THF (9 mL). The product was purified by column chromatography (4:1 to 1:1 hexane–EtOAc) to afford **31** (1.62 g, 93% over 3 steps) as a syrup. R_f 0.23 (4:1 hexane–EtOAc); $[\alpha]_D$ +12.4 (*c* = 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.41–7.23 (m, 12 H, Ar), 6.85 (d, 2 H, *J* = 8.7 Hz, Ph–OCH_3), 4.94 (d, 1 H, *J* = 10.9 Hz, C*H*$_2$Ph), 4.76 (d, 1 H, *J* = 1.0 Hz, H-1), 4.72 (d, 1 H, *J* = 12.0 Hz, C*H*$_2$Ph), 4.68– 4.59 (m, 4 H, C*H*$_2$Ph), 3.95 (app t, 1 H, *J* = 9.2 Hz, H-4), 3.90 (dd, 1 H, *J* = 2.8, 9.2 Hz, H-3), 3.87–3.73 (m, 6 H, H-6a, PhOC*H*$_3$, H-6b, H-2), 3.68–3.56 (m, 2 H, H-5, OC*H*$_2$), 3.32 (dt, 1 H, *J* = 2×6.6, 9.5 Hz, OC*H*$_2$), 3.25 (t, 2 H, *J* = 6.9 Hz, OC*H*$_2$$N_3$), 2.01 (t, 1 H, *J* = 6.4 Hz, O*H*), 1.66–1.43 (m, 4 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.43–1.23 (m, 8 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 159.3 (Ar), 138.6 (Ar), 138.4 (Ar), 130.4 (Ar), 129.5 (2C, Ar), 128.5 (2 C, Ar),128.4 (2 C, Ar), 128.1 (2 C, Ar), 127.8 (Ar), 127.6 (2 C, Ar), 127.5 (Ar), 113.7 (2 C, Ar), 98.3 (C-1), 80.3 (C-3), 75.3 (*C*H_2Ph), 75.1 (C-4), 74.4 (C-2), 72.5(*C*H_2Ph), 72.2 (*C*H_2Ph), 72.0 (C-5), 67.6 (*C*H_2O), 62.5 (C-6), 55.3 (O*C*H_3), 51.5 (*C*$H_2$$N_3$), 29.4, 29.3, 29.1, 28.8, 26.7, 26.0 (6 C, OCH_2(*C*H_2)$_6$$CH_2N_3$); HRMS (ESI) calcd for (M + Na^+) $C_{36}H_{47}N_3O_7Na$: 656.3306. Found: 656.3303.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (32). The synthesis of **32** was achieved following the procedure described for the preparation of **15**, using alcohol **31**

(37.6 mg, 0.059 mmol) and trichloroacetimidate **10** (58 mg, 0.074 mmol) in the presence of TMSOTf (130 μL of a 0.07 M solution in Et_2O) in Et_2O (670 μL). The crude residue was purified by column chromatography (9:1 → 8.5:1.5 hexane−EtOAc) to yield **32** (70 mg, 95%) as a syrup. R_f 0.61 (8:2 hexane–EtOAc); $[\alpha]_D$ +23.0 (*c* = 0.57, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.79-7.73 (m, 2 H, Ar), 7.72–7.66 (m, 2 H, Ar), 7.46–7.13 (m, 28 H, Ar), 6.82 (d, 2 H, *J* = 8.5 Hz, $PhOCH_3$), 5.51 (dd, 1 H, *J* = 1.9, 2.8 Hz, H-2′), 4.96 (d, 1 H, *J* = 1.9 Hz, H-1′), 4.94 (d, 1 H, *J* = 11.5 Hz, C*H*$_2$Ph), 4.90 (d, 1 H, *J* = 11.2 Hz, C*H*$_2$Ph), 4.80 (d, 1 H, *J* = 1.0 Hz, H-1), 4.69 (d, 1 H, *J* = 11.5 Hz, C*H*$_2$Ph), 4.65–4.58 (m, 5 H, C*H*$_2$Ph), 4.52–4.45 (m, 2 H, C*H*$_2$Ph), 4.10 (t, 1 H, *J* = 9.4 Hz, H-4′), 4.01 (dd, 1 H, *J* = 2.7, 9.4 Hz, H-3′), 3.94 (dd, 1 H, *J* = 2.9, 11.1 Hz, H-6′a), 3.90–3.73 (m, 8 H, H-3, H-4, H-6a, H-6′b, H-2, PhOC*H*$_3$), 3.72–3.63 (m, 3 H, H-5, H-5′, H-6b), 3.63–3.57 (m, 1 H, OC*H*$_2$), 3.34 (dt, 1 H, *J* = 2×6.4, 9.5 Hz, OC*H*$_2$), 3.23 (t, 2 H, *J* = 6.9 Hz, OC*H*$_2$N$_3$), 2.15 (s, 3 H, C*H*$_3$), 1.63–1.45 (m, 4 H, $OCH_2(CH_2)_6CH_2N_3$), 1.41–1.23 (m, 8 H), 1.07 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 170.3 (C═O), 159.3 (Ar), 138.8 (Ar), 138.6 (Ar), 138.5 (Ar), 138.0 (Ar), 136.0 (Ar), 135.5 (3 C, Ar), 134.0 (Ar), 133.3 (Ar), 130.5 (Ar), 129.6 (2 C, Ar), 129.4 (3 C, Ar), 128.5 (2 C, Ar), 128.4 (2 C, Ar), 128.3 (4 C, Ar), 128.2 (2 C, Ar), 127.7 (4 C, Ar), 127.6 (4 C, Ar), 127.5 (3 C, Ar), 127.5 (Ar), 127.4 (Ar), 113.7 (2 C, Ar), 98.0 (C-1′), 97.6 (C-1), 80.4 (C-3), 77.9 (C-3′), 75.2 (*C*H_2Ph), 75.0 (*C*H_2Ph), 74.7 (C-4), 74.3 (C-4′),74.0 (C-2), 72.6 (C-5), 72.1 (*C*H_2Ph), 71.9 (*C*H_2Ph), 71.5 (*C*H_2Ph), 71.2 (C-5′), 68.7 (C-2′), 67.5 (*C*H_2O), 66.6 (C-6), 62.7 (C-6′), 55.3 (O*C*H_3), 51.5 (*C*H_2N_3), 29.4, 29.3, 29.1, 28.9 (4 C, $OCH_2(CH_2)_6CH_2N_3$), 26.9 (3 C, C(*C*H_3)$_3$), 26.7, 26.2 (2 C, $OCH_2(CH_2)_6CH_2N_3$), 21.1 (*C*H_3), 19.4 (*C*(CH$_3$)$_3$); HRMS (ESI) calcd for (M + Na^+) $C_{74}H_{89}N_3O_{13}SiNa$: 1278.6057. Found: 1278.6055.

8-Azidooctyl 2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (33). The synthesis of **33** (2.27 g, 1.8 mmol) was

achieved following the procedure described for the preparation of **16** using $NaOCH_3$ in CH_3OH (4 mL, 0.1M), CH_2Cl_2–CH_3OH (1:1, 6 mL), sodium hydride (92 mg, 3.8 mmol), allyl bromide (310 μL, 3.7 mmol), DMF (10 mL), *n*-Bu_4NF (1M in THF, 18 mL) and THF (6 mL). The product was purified by column chromatography (9:1 to 3:2 hexane–EtOAc) to afford **33** (1.33 g, 73% over 3 steps) as a syrup. R_f 0.32 (3:2 hexane–EtOAc); $[\alpha]_D$ +18.2 (*c* = 0.09, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 7.43–7.20 (m, 22 H, Ar), 6.85 (d, 2 H, *J* = 8.6 Hz, $PhOCH_3$), 5.93 (dddd, 1 H, *J* = 5.0, 5.6, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.31 (dd, 1 H, *J* = 1.2, 17.2 Hz, CH_2–CH=CH_2), 5.19 (dd, 1 H, *J* = 1.2, 10.6 Hz, CH_2–CH=CH_2), 5.07 (d, 1 H, *J* = 1.1 Hz, H-1′), 4.95 (d, 1 H, *J* = 11.2 Hz, CH_2Ph), 4.93 (d, 1 H, *J* = 11.2 Hz, CH_2Ph), 4.80 (d, 1 H, *J* = 1.1 Hz, H-1), 4.73–4.58 (m, 7 H, CH_2Ph), 4.52 (d, 1 H, *J* = 11.0 Hz, CH_2Ph), 4.20–4.10 (m, 2 H, CH_2–CH=CH_2), 3.97–3.86 (m, 6 H, H-4, H-4′, H-3, H-3′, H-6a, H-2′), 3.82–3.75 (m, 5 H, H-2, PhOCH_3, H-6′a), 3.74–3.65 (m, 4 H, H-6b, H-6′b, H-5, H-5′), 3.61 (dt, 1 H, *J* = 2×6.8, 9.5 Hz, OCH_2), 3.36 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OCH_2), 3.26 (t, 2 H, *J* = 7.0 Hz, CH_2N_3), 1.93 (br s, 1 H, O*H*), 1.66–1.49 (m, 4 H, $OCH_2(CH_2)_6CH_2N_3$), 1.41–1.26 (m, 8 H, $OCH_2(CH_2)_6CH_2N_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 159.3 (Ar), 138.6 (Ar), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 135.1 (CH_2–*C*H=CH_2), 130.4 (Ar), 129.5 (2 C, Ar), 128.4 (5 C, Ar), 128.3 (3 C, Ar), 127.9 (4 C, Ar), 127.8 (3 C, Ar), 127.6 (10 C, Ar), 117.1 (CH_2–CH=*C*H_2), 113.7 (2 C, Ar), 98.4 (C-1′), 97.8 (C-1), 80.4 (C-3), 79.3 (C-3′), 75.1 (2 C, *C*H_2Ph), 74.9 (C-2′), 74.8, 74.6 (C-4, C-4′), 74.5 (C-2), 72.5 (*C*H_2Ph), 72.2 (C-5), 72.1 (*C*H_2Ph), 71.7 (*C*H_2Ph), 71.6 (C-5′), 67.6 (*C*H_2O), 66.1 (C-6), 62.4 (C-6′), 55.2 (Ph*C*H_3), 51.4 (CH_2N_3), 29.4, 29.3, 29.1, 28.8, 26.7, 26.1 (6 C, $OCH_2(CH_2)_6CH_2N_3$). HRMS (ESI) calcd for (M + Na^+) $C_{59}H_{73}N_3O_{12}Na$: 1038.5086. Found: 1038.5093.

8-Azidooctyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[2,3-di-*O*-benzoyl-6-*O*-(*tert*-

butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→2)]-3,4-di-*O*-benzyl-α-D-mannopyranoside (34). The synthesis of **34** was achieved following the procedure described for the preparation of **25**, using alcohol **30** (86 mg, 0.057 mmol), thioglycoside **12** (140 mg, 0.068 mmol) and 4 Å molecular sieves (21 mg) in CH_2Cl_2 (800 μL) in the presence of NIS (22 mg, 0.098 mmol) and AgOTf (4 mg, 0.016 mmol). The product residue was purified by column chromatography (8.5:1.5 → 7.5:2.5, hexane–acetone) to yield **34** (166 mg, 85%) as a syrup. R_f 0.43 (7:3 hexane–acetone); $[\alpha]_D$ +27.2 (*c* = 0.15, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.06–7.85 (m, 20 H, Ar), 7.78–7.64 (m, 8 H, Ar), 7.60–7.06 (m, 73 H, Ar), 5.90 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.75–5.61 (m, 10 H), 5.58 (br s, 1 H), 5.54 (app t, 1 H, *J* = 2.1 Hz, H-2″), 5.44–5.36 (m, 4 H), 5.28 (dd, 1 H, *J* = 1.5, 17.2 Hz, CH_2–CH=CH_2), 5.10 (dd, 1 H, *J* = 1.5, 10.5 Hz, CH_2–CH=CH_2), 5.05 (d, 1 H, *J* = 1.2 Hz, H-1′), 4.97–4.82 (m, 5 H, H-1″, H-1, 3×CH_2Ph), 4.76–4.65 (m, 3H), 4.65–4.44 (m, 10 H), 4.42 (d, 1 H, *J* = 11.4 Hz, CH_2Ph), 4.24 (s, 1 H), 4.22–4.08 (m, 7 H), 4.05–3.59 (m, 20 H), 3.56 (d, 1 H, *J* = 9.4 Hz), 3.50 (d, *J* = 10.7 Hz, 1 H), 3.36 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OCH_2), 3.21 (t, 2 H, *J* = 7 Hz, CH_2N_3), 2.15 (s, 3 H, CH_3), 1.61–1.48 (m, 4 H, OCH_2(CH_2)$_6$$CH_2N_3$), 1.39–1.22 (m, 8 H, OCH_2(CH_2)$_6$$CH_2N_3$), 1.08 (s, 9 H, C(C$H_3$)$_3$), 1.03 (s, 9 H, C(C$H_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 170.1 (C═O), 165.6 (4 C, C═O), 165.5 (C═O), 165.2 (2 C, C═O), 165.1 (3 C, C═O), 138.9 (Ar), 138.8 (Ar), 138.4 (2 C, Ar), 138.2 (Ar), 138.0 (Ar), 136.0 (3 C, Ar), 135.7 (7 C, Ar), 135.6 (3 C, Ar), 135.2 (Ar), 134.0 (Ar), 133.5 (CH_2–*C*H=CH_2), 133.4 (2 C, Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (2 C, Ar), 133.0 (Ar), 130.0 (3 C, Ar), 129.9 (8 C, Ar), 129.8 (7 C, Ar), 129.6 (2 C, Ar), 129.5 (2 C, Ar), 129.3 (3 C, Ar), 129.2 (3 C, Ar), 129.1 (2 C, Ar), 128.5 (9 C, Ar), 128.4 (9 C, Ar), 128.3 (8 C, Ar), 128.2 (7

C, Ar), 128.1 (2 C, Ar), 127.8 (4 C, Ar), 127.7 (9 C, Ar), 127.6 (3 C, Ar), 127.5 (7 C, Ar), 127.3 (3 C, Ar), 127.2 (Ar), 116.9 (CH_2–CH=*C*H_2), 106.4, 106.0 (2 C), 105.9 (2 C), 99.4 (C-1), 98.3 (C-1″), 97.9 (C-1′), 83.2 (2 C), 82.1 (6 C), 82.0, 81.6 (2 C), 81.5 (3 C), 80.6, 80.2, 77.7 (2 C), 75.1 (2 C), 74.8, 74.7 (2 C), 74.2, 73.9, 72.5 (2 C), 72.1, 72.0, 71.7, 71.5, 71.4, 71.3, 68.6, 67.6 (*C*H_2O), 66.3, 66.1, 65.9, 65.8, 65.7, 63.4, 62.6, 60.4, 51.4 (*C*H_2N_3), 29.5, 29.4, 29.1, 28.8 (4 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 26.8 (6 C, 2×C(*C*$H_3$)$_3$), 26.7, 26.2 (2 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 21.1(*C*$H_3$), 19.4 (*C*(CH$_3$)$_3$), 19.3 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + 2 Na^+) $C_{200}H_{205}N_3O_{47}Si_2Na_2$: 1751.1533. Found: 1751.1559.

8-Azidooctyl 3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-α-D-mannopyranoside (35). To a solution of **30** (35 mg, 0.023 mmol) in Et_2O–CH_3OH (1:1, 400 μL) was added a solution of $NaOCH_3$ in CH_3OH (100 μL, 0.1M). The reaction mixture was stirred for 3 h, neutralized by the addition of Amberlyst IR-120 (H^+) cation exchange resin, filtered and concentrated to give a syrup that was purified by column chromatography (4:1 hexane–EtOAc) to afford **35** (33 mg, 97%) as a syrup. R_f 0.55 (3:2 hexane–EtOAc); $[\alpha]_D$ +40.9 (*c* = 0.16, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.76 (d, 2 H, *J* = 6.8 Hz, Ar), 7.69 (d, 2 H, *J* = 6.8 Hz, Ar), 7.45–7.12 (m, 36 H, Ar), 5.95 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.33 (dd, 1 H, *J* = 1.5, 17.2 Hz, CH_2–CH=C*H*$_2$), 5.16 (dd, 1 H, *J* = 1.5, 10.5 Hz, CH_2–CH=C*H*$_2$), 5.05 (d, 1 H, *J* = 1.2 Hz, H-1″), 4.99 (d, 1 H, *J* = 1.4 Hz, H-1′), 4.92–4.84 (m, 4 H, H-1, 3× C*H*$_2$Ph), 4.76–4.59 (m,7 H, C*H*$_2$Ph), 4.51 (d, 1 H, *J* = 11.1 Hz, C*H*$_2$Ph), 4.50 (d, 1 H, *J* = 11.2 Hz, C*H*$_2$Ph), 4.20–4.15 (m, 3 H, C*H*$_2$–CH=CH_2, H-2″), 4.06 (br s, 1 H, H-2), 3.99 (t, 1 H, *J* = 9.6 Hz, H-4″), 3.94–3.61 (m, 16 H, H-4, H-3, H-3′, H-3″, H-6a, H-6″a, H-2′, H-4′, H6″b, H-6b, H-6′a, H-6′b, H-5, H-5′, H-5″, C*H*$_2$O), 3.40 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.24 (t, 2 H, *J* = 6.9 Hz, C*H*$_2N_3$),

2.62 (d, *J* = 2.6 Hz, 1 H, O*H*), 2.54 (br s, 1 H, O*H*), 1.63–1.48 (m, 4 H, $OCH_2(CH_2)_6CH_2N_3$), 1.40–1.25 (m, 8 H, $OCH_2(CH_2)_6CH_2N_3$), 1.06 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 138.7 (Ar), 138.6 (Ar), 138.4 (Ar), 138.2 (Ar), 138.1 (Ar), 137.8 (Ar), 135.9 (2C, Ar), 135.6 (2C, Ar), 135.1 (Ar), 133.9 (CH_2–*C*H=CH_2), 133.4 (Ar), 129.5 (2C, Ar), 128.6 (2C, Ar), 128.5 (2 C, Ar), 128.4 (4 C, Ar), 128.3 (2 C, Ar), 128.2 (2 C, Ar), 128.0 (3 C, Ar), 127.9 (2 C, Ar), 127.8 (6 C, Ar), 127.7 (2 C, Ar), 127.6 (3 C, Ar), 127.5 (2 C, Ar), 127.4 (4 C, Ar), 127.3 (Ar), 117.2 (CH_2–CH=*C*H_2), 99.3 (C-1″), 98.8 (C-1), 97.9 (C-1′), 80.5, 80.0 (C-3, C-3′), 79.8 (C-3″), 75.2 (*C*H_2Ph), 75.1 (*C*H_2Ph), 74.8 (*C*H_2Ph), 74.7, 74.5 (C-4, C-4′), 74.2 (2 C, C-2′, C-4″), 72.4 (C-5″), 72.0 (*C*H_2Ph), 71.9 (2 C, *C*H_2Ph), 71.7 (*C*H_2–CH=CH_2), 70.9 (2 C, C-5, C-5′), 68.4 (C-2), 68.1 (C-2″), 67.7 (*C*H_2O), 66.1, 65.9 (2 C, C-6, C-6′), 63.0 (C-6″), 51.4 (CH_2N_3), 29.4, 29.3, 29.1, 28.8 (4 C, $OCH_2(CH_2)_6CH_2N_3$), 26.9 (3 C, $C(CH_3)_3$), 26.7, 26.2 (2 C, $OCH_2(CH_2)_6CH_2N_3$), 19.4 ($C(CH_3)_3$). HRMS (ESI) calcd for ($M + Na^+$) $C_{87}H_{105}N_3O_{16}SiNa$: 1498.7156. Found: 1498.7137.

8-Azidooctyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)]-3,4-di-*O*-benzyl-α-D-mannopyranoside (36). A mixture of trichloroacetimidate **11b** (250 mg, 0.34 mmol), alcohol **35** (83 mg, 0.056 mmol) and 4 Å molecular sieves (25 mg) in Et_2O (780 μL) was stirred for 30 min at –15 °C under an argon atmosphere. Then TMSOTf (325 μL of a 0.07M solution in Et_2O) was added dropwise over 5 min. The reaction mixture was stirred for 2 h at –15 °C and then the TMSOTf was quenched by the addition of Et_3N. The solution was concentrated under vacuum and the resulting syrup was purified by column chromatography (9:1 hexane–acetone) to afford **36** (99 mg, 67%) as a syrup: R_f 0.41 (7:3 hexane–acetone); $[\alpha]_D$ +1.3 (*c* = 0.08, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.16 (d, *J* = 7.5 Hz, 2 H, Ar), 8.12 (d, *J* = 7.5 Hz, 2

H, Ar), 8.09 (d, J = 7.5 Hz, 2 H, Ar), 8.02 (d, J = 7.5 Hz, 2 H, Ar), 7.95 (d, J = 7.5 Hz, 2 H, Ar), 7.87 (d, J = 7.5 Hz, 2 H, Ar), 7.84–7.76 (m, 4 H, Ar), 7.71 (app t, J = 6.4 Hz, 4 H, Ar), 7.65–7.51 (m, 4 H, Ar), 7.51–7.05 (m, 56 H, Ar), 6.17 (t, 1 H, J = 10.2 Hz), 6.10 (t, 1 H, J = 9.7 Hz), 6.01–5.93 (m, 4 H), 5.88 (dddd, 1 H, J = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.40 (br s, 1 H), 5.26 (br s, 2 H), 5.21 (dd, 1 H, J = 1.2, 17.2 Hz, CH_2–CH=C*H*$_2$), 5.11 (br s, 1 H), 5.06 (d, 1 H, J = 11.1 Hz, C*H*$_2$Ph), 4.97–4.86 (m, 4 H), 4.81 (d, 1 H, J = 11.6 Hz, C*H*$_2$Ph), 4.78–4.66 (m, 8 H), 4.59–4.52 (m, 3 H), 4.50 (d, 1 H, J = 11.9 Hz, C*H*$_2$Ph), 4.49 (d, 1 H, J = 11.7 Hz, C*H*$_2$Ph),4.39 (d, 1 H, J = 11.5 Hz, C*H*$_2$Ph), 4.30–4.21 (m, 4 H), 4.19 (br s, 1 H), 4.10 (br s, 1 H), 4.05–3.85 (m, 7 H), 3.83–3.54 (m, 7 H), 3.45 (d, 1 H, J = 11.2 Hz), 3.33 (dt, 1 H, J = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.23 (t, 2 H, J = 7.0 Hz, C*H*$_2$N$_3$), 1.66–1.49 (m, 4 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.40–1.24 (m, 8 H, OCH$_2$(C*H*$_2$)$_6$CH$_2$N$_3$), 1.12 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 166.1 (2 C, C═O), 165.6 (C═O), 165.5 (C═O), 165.2 (C═O), 165.1 (C═O), 164.9 (2 C, C═O), 139.1 (Ar), 138.8 (Ar), 138.5 (Ar), 138.4 (Ar), 138.3 (Ar), 137.9 (Ar), 135.9 (3 C, Ar), 135.6 (3 C, Ar), 135.3 (Ar), 134.0 (Ar), 133.5 (CH_2–*C*H=CH_2), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (2 C, Ar), 133.0 (2 C, Ar), 132.9 (Ar), 130.0 (Ar), 129.9 (6 C, Ar), 129.8 (5 C, Ar), 129.7 (3 C, Ar), 129.6 (Ar), 129.5 (2 C, Ar), 129.4 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.5 (8 C, Ar), 128.4 (3 C, Ar), 128.3 (6 C, Ar), 128.2 (10 C, Ar), 128.1 (2 C, Ar), 128.0 (2 C, Ar), 127.9 (4 C, Ar), 127.7 (3 C, Ar), 127.6 (4 C, Ar), 127.5 (4 C, Ar), 127.3 (2 C, Ar), 127.2 (3 C, Ar), 127.1 (Ar), 116.8 (CH_2–CH=*C*H$_2$), 100.5, 99.7, 99.3, 99.0, 98.5, 79.9, 78.7, 78.5, 75.2 (2 C), 75.1, 74.8 (2 C), 74.5, 74.2, 73.9, 72.7, 72.4, 71.8, 71.7, 71.3, 71.2, 70.7, 70.3, 70.1, 70.0, 69.4, 69.2, 67.7 (*C*H$_2$O), 67.1, 66.9, 66.2, 65.8, 63.0 (3 C), 51.4 (*C*H$_2$N$_3$), 29.5, 29.4, 29.1, 28.8 (4 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 27.0 (3 C, C(*C*H$_3$)$_3$), 26.7, 26.2 (2 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 19.3 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + Na$^+$) $C_{155}H_{157}N_3O_{34}SiNa$: 2655.0315. Found: 2655.0310.

8-Azidooctyl 3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (37). To a solution of **9** (120 mg, 0.073 mmol) in Et_2O–CH_3OH (1:1, 500 μL) was added a solution of $NaOCH_3$ in CH_3OH (120 μL, 0.1M). The reaction mixture was stirred for 3 h, neutralized by the addition of Amberlyst IR-120 (H^+) cation exchange resin, filtered and concentrated to give a syrup that was purified by column chromatography (4:1 hexane–EtOAc) to afford **37** (113 mg, 97%) as a syrup. R_f 0.45 (8:2 hexane–EtOAc); $[\alpha]_D$ +52.4 (*c* = 0.09, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.75 (d, 2 H, *J* = 6.8 Hz, Ar), 7.69 (d, 2 H, *J* = 6.8 Hz, Ar), 7.46 –7.09 (m, 38 H, Ar), 6.83 (d, 2 H, *J* = 8.4 Hz, $PhOCH_3$), 5.95 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.53 (dd, 1 H, *J* = 1.7, 2.9 Hz, H-2″), 5.34 (dd, 1 H, *J* = 1.4, 17.1 Hz, CH_2–CH=C*H*$_2$), 5.16 (dd, 1 H, *J* = 1.4, 10.4 Hz, CH_2–CH=C*H*$_2$), 5.07 (d, 1 H, *J* = 1.2 Hz, H-1′), 5.05 (d, 1 H, *J* = 1.7 Hz, H-1″), 4.94–4.87 (m, 3 H, C*H*$_2$Ph), 4.81 (d, 1 H, *J* = 1.1 Hz, H-1), 4.75–4.63 (m, 7 H, C*H*$_2$Ph), 4.61 (d, 1 H, *J* = 11.0 Hz, C*H*$_2$Ph), 4.56 (d, 1 H, *J* = 11.7 Hz, C*H*$_2$Ph), 4.48 (app t, 2 H, *J* = 10.6 Hz, C*H*$_2$Ph), 4.18 (br s, 1 H, H-2″), 4.15–4.10 (app d, 2 H, C*H*$_2$–CH=CH_2), 4.98 (t, 1 H, *J* = 9.5 Hz, H-4″),4.01–3.86 (m, 7 H, H-4, H-4′, H-3, H-3′, H-3″, H-6′a, H-2′), 3.85–3.73 (m, 7 H, H-6a, H-6″a, PhOC*H*$_3$, H6″b, H-2), 3.72–3.58 (m, 6 H, H-6b, H-5, H-5′, H-5″, H-6′b, C*H*$_2$O), 3.35 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.24 (t, 2 H, *J* = 6.9 Hz, C*H*$_2$$N_3$), 1.63–1.45 (m, 4 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.42–1.23 (m, 8 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.06 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 159.3 (Ar), 138.7 (Ar), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 138.0 (Ar), 135.9 (2C, Ar), 135.7 (2C, Ar), 135.3 (Ar), 133.9 (CH_2–*C*H=CH_2), 133.4 (Ar), 130.4 (Ar), 129.5 (4C, Ar), 128.5 (2C, Ar), 128.4 (4 C, Ar), 128.3 (2 C, Ar), 128.2 (4 C, Ar), 128.1 (2 C, Ar), 128.0 (2 C, Ar), 127.8 (Ar), 127.7 (5 C, Ar), 127.6 (8 C, Ar), 127.5 (1 C, Ar), 127.4 (3 C, Ar), 127.3 (Ar), 116.9 (CH_2–CH=*C*H_2), 113.8 (2 C, Ar), 99.8 (C-1″), 98.1 (C-1′,

98.0 (C-1), 80.5 (C-3), 79.8 (C-3″), 79.4 (C-3′), 75.1 (*C*H_2Ph), 75.0 (*C*H_2Ph), 74.9 (*C*H_2Ph), 74.8 (C-2′), 74.6 (C-2), 74.5, 74.3 (C-4, C-4′), 74.1 (C-4″),72.5 (*C*H_2Ph), 72.3 (C-5″), 72.1 (*C*H_2Ph), 71.8 (*C*H_2Ph), 71.7 (2 C, C-5, C-5′), 71.6 (*C*H_2Ph), 71.5 (*C*H_2–CH=CH_2), 68.1 (C-2″), 67.6 (*C*H_2O), 66.0 (2 C, C-6, C-6′), 62.9 (C-6″), 55.2 (PhO*C*H_3), 51.4 (CH_2N_3), 29.4, 29.3, 29.1, 28.8 (4 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 26.8 (3 C, C(*C*$H_3$)$_3$), 26.7, 26.1 (2 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 19.3 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + Na^+) $C_{95}H_{113}N_3O_{17}SiNa$: 1618.7731. Found: 1618.7719.

8-Azidooctyl 2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (38). The synthesis of **38** was achieved following the procedure described for the preparation of **25**, using alcohol **37** (100 mg, 0.071 mmol), thioglycoside **12** (147 mg, 0.071 mmol) and 4 Å molecular sieves (23 mg) in CH_2Cl_2 (2.4 mL) in the presence of NIS (19 mg, 0.084 mmol) and AgOTf (4 mg, 0.016 mmol). The crude residue was purified by column chromatography (9:1 → 4:1, hexane–acetone) to yield **38** (164 mg, 74%) as a syrup. R_f 0.74 (3:2 hexane–acetone); $[\alpha]_D$ +25.9 (*c* = 0.17, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.10–7.86 (m, 20 H, Ar), 7.79–7.65 (m, 8 H, Ar), 7.62–7.04 (m, 74 H, Ar), 6.83 (d, 1 H, *J* = 8.4 Hz, Ph-OMe), 5.93 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.77 (d, 1 H, *J* = 4.6 Hz), 5.75–5.65 (m, 9 H), 5.61 (br s, 1 H), 5.47–5.39 (m, 4 H, 4×H-1), 5.31 (dd, 1 H, *J* = 1.5, 17.2 Hz, CH_2–CH=CH_2), 5.13 (dd, 1 H, *J* = 1.5, 10.5 Hz, CH_2–CH=CH_2), 5.05 (br s, 2 H, 2×H-1), 4.98–4.88 (m, 3 H, CH_2Ph), 4.82 (br s, 1 H, H-1), 4.76 (d, 1 H, *J* = 11.7 Hz, CH_2Ph), 4.72–4.42 (m, 15 H), 4.38 (br s, 1 H), 4.27–4.10 (m, 7 H, CH_2–CH=CH_2), 4.05–3.57 (m,

25 H), 3.52 (app d, 1 H, J = 10.6 Hz, H-6), 3.34 (dt, 1 H, J = 2×6.5, 9.5 Hz, OCH_2), 3.24 (t, 2 H, J = 6.9 Hz, CH_2N$_3$), 1.67–1.46 (m, 4 H, OCH$_2$(CH_2)$_6$CH$_2$N$_3$), 1.41–1.22 (m, 8 H, OCH$_2$(CH_2)$_6$CH$_2$N$_3$),1.06 (br s, 18 H, 2×C(CH_3)$_3$); ^{13}C NMR (126 MHz, CDCl$_3$) δ_C = 165.7(C═O), 165.6 (3 C, C═O), 165.5 (C═O), 165.2 (C═O), 165.1 (2 C, C═O), 165.0 (2 C, C═O), 159.3 (Ar), 139.0 (Ar), 138.8 (Ar), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 138.2 (Ar), 136.0 (2 C, Ar), 135.7 (6 C, Ar), 135.6 (2 C, Ar), 135.2 (Ar), 134.1 (Ar), 133.6 (CH$_2$–*C*H=CH$_2$), 133.3 (2 C, Ar), 133.1 (4 C, Ar), 133.0 (Ar), 130.4 (Ar), 130.0 (3 C, Ar), 129.9 (10 C, Ar), 129.8 (7 C, Ar), 129.7 (2 C, Ar), 129.5 (3 C, Ar), 129.4 (Ar), 129.3 (Ar), 129.2 (2 C, Ar), 129.1 (2 C, Ar), 128.5 (5 C, Ar), 128.4 (13 C, Ar), 128.3 (11 C, Ar), 128.2 (4 C, Ar), 128.1 (5 C, Ar), 128.0 (2 C, Ar), 127.9 (2 C, Ar), 127.7 (10 C, Ar), 127.6 (8 C, Ar), 127.5 (2 C, Ar), 127.4 (Ar), 127.2 (2 C, Ar), 127.1 (Ar), 117.0 (CH$_2$–CH=*C*H$_2$), 113.7 (2 C, Ar), 106.3 (C-1), 106.0 (3×C-1), 105.9 (C-1), 99.6 (C-1), 98.4 (C-1), 97.9 (C-1), 83.2, 82.3, 82.1 (6 C), 81.9, 81.5 (3 C), 80.5, 79.9, 79.6, 77.2, 75.1, 75.0, 74.7, 74.6 (2 C), 74.5 (2 C), 74.3, 73.1, 72.5, 72.4, 72.1, 71.9, 71.7, 71.6, 71.4, 71.3, 67.5 (2 C), 66.1, 66.0, 65.9, 65.8 (2 C), 65.5, 63.4 (2 C), 63.1, 55.2 (PhO*C*H$_3$), 51.4 (*C*H$_2$N$_3$), 29.4, 29.3, 29.1, 28.8 (4 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 26.8(6 C, 2×C(*C*H$_3$)$_3$), 26.7, 26.2 (2 C, OCH$_2$(*C*H$_2$)$_6$CH$_2$N$_3$), 19.3 (2 C, 2×(*C*(CH$_3$)$_3$). HRMS (ESI) calcd for (M + 2 Na$^+$) C$_{206}$H$_{211}$N$_3$O$_{47}$Si$_2$Na$_2$: 1790.1768. Found: 1790.1774.

8-Azidooctyl 2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-α-D-mannopyranoside (39). The synthesis of **39** was achieved following the procedure

described for the synthesis of **30**, starting from the octasaccharide **38** (52 mg, 0.015 mmol) using CAN (16 mg, 0.029 mmol) in CH_3CN–H_2O (10:1, 1.1 mL). The crude residue was purified by column chromatography (99:1, CH_2Cl_2–acetone) to yield **39** (34 mg, 68%) as a syrup. R_f 0.53 (3:2 hexane–EtOAc); $[\alpha]_D$ +24.4 (*c* = 0.11, CH_2Cl_2); ^{1}H NMR (600 MHz, *CDCl3*) δ_H = 8.05–7.81 (m, 20 H, Ar), 7.74–7.61 (m, 8 H, Ar), 7.58–7.04 (m, 72 H, Ar), 5.90 (dddd, 1 H, *J* = 5.4, 6.2, 10.5, 17.2 Hz, CH_2–C*H*=CH_2), 5.73 (d, 1 H, *J* = 4.9 Hz), 5.70–5.60 (m, 9 H), 5.56 (br s, 1 H), 5.43–5.33 (m, 4 H, 4×H-1), 5.28 (dd, 1 H, *J* = 1.5, 17.2 Hz, CH_2–CH=C*H*$_2$), 5.12 (dd, 1 H, *J* = 1.5, 10.5 Hz, CH_2–CH=C*H*$_2$), 5.01 (d, 1 H, *J* = 1.2 Hz, H-1), 4.97 (d, 1 H, *J* = 1.5 Hz, H-1), 4.92–4.81 (m, 4 H, H-1, 3×C*H*$_2$Ph), 4.74–4.41 (m, 15 H), 4.34 (br s, 1 H), 4.22–4.06 (m, 8 H), 4.02 (br s, 1 H), 4.00–3.78 (m, 13 H), 3.76–3.57 (m, 6 H), 3.50 (app d, 1 H, *J* = 10.6 Hz, H-6), 3.35 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OC*H*$_2$), 3.21 (t, 2 H, *J* = 6.9 Hz, C*H*$_2$N$_3$), 2.37 (d, 1 H, *J* = 2.2 Hz, O*H*), 1.62–1.47 (m, 4 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$), 1.37–1.21 (m, 8 H, OCH_2(C*H*$_2$)$_6$$CH_2N_3$),1.01 (br s, 18 H, 2×C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, *CDCl3*) δ_C = 165.6 (4 C, C═O), 165.5 (C═O), 165.2 (C═O), 165.1 (2 C, C═O), 165.0 (2 C, C═O), 138.9 (Ar), 138.8 (Ar), 138.3 (3 C, Ar), 137.9 (Ar),136.0 (2 C, Ar), 135.7 (6 C, Ar), 135.6 (2 C, Ar), 135.2 (Ar), 134.1 (Ar), 133.5 (CH_2–*C*H=CH_2), 133.3 (4 C, Ar), 133.2 (2 C, Ar), 133.1 (4 C, Ar), 133.0 (Ar), 130.0 (3 C, Ar), 129.9 (5 C, Ar), 129.8 (10 C, Ar), 129.6 (2 C, Ar), 129.4 (2 C, Ar), 129.3 (2 C, Ar), 129.2 (2 C, Ar), 129.1 (3 C, Ar), 128.6 (2 C, Ar), 128.5 (5 C, Ar), 128.4 (9 C, Ar), 128.3 (7 C, Ar), 128.2 (8 C, Ar), 128.1 (4 C, Ar), 128.0 (Ar), 127.9 (6 C, Ar), 127.7 (9 C, Ar), 127.6 (5 C, Ar), 127.5 (2 C, Ar), 127.3 (Ar), 127.2 (2 C, Ar), 127.1 (Ar), 117.3 (CH_2–CH=*C*H$_2$), 106.4 (C-1), 106.0 (2×C-1), 105.9 (2×C-1), 99.5 (C-1), 99.0 (C-1), 98.4 (C-1), 83.2 (2 C), 82.2, 82.1 (4 C), 81.9, 81.5 (4 C), 80.5, 79.9, 79.8, 75.1, 75.0, 74.7, 74.6, 74.5, 74.4, 74.0, 73.1, 72.5, 71.9 (4 C), 71.8, 71.6, 71.4, 70.9, 68.3, 67.6, 66.1, 66.0, 65.9, 65.8, 65.7, 65.5, 63.4 (2 C), 63.1, 51.4 (*C*H$_2$N$_3$), 29.4, 29.3, 29.1, 28.8 (4 C, OCH_2(*C*H$_2$)$_6$$CH_2N_3$), 26.8 (6 C, 2×C(*C*H$_3$)$_3$), 26.7, 26.1 (2 C,

$OCH_2(CH_2)_6CH_2N_3$), 19.3 (2 C, 2×($C(CH_3)_3$). HRMS (ESI) calcd for (M + 2 Na^+) $C_{198}H_{203}N_3O_{46}Si_2Na_2$: 1730.1480. Found: 1730.1507.

8-Azidooctyl 2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)]-3,4-di-*O*-benzyl-α-D-mannopyranoside (40). The synthesis of **40** was achieved following the procedure described for the preparation of **36**, using alcohol **39** (26 mg, 0.0076 mmol), trichloroacetimidate **11b** (23 mg, 0.031 mmol) and 4 Å molecular sieves (6 mg) in CH_2Cl_2 (400 μL) in the presence TMSOTf (22 μL of a 0.07 M solution in CH_2Cl_2). The crude residue was purified by gel filtration chromatography (Sephadex, LH-20) with (1:1, CH_2Cl_2–CH_3OH) as the eluent, followed by column chromatography (99:1, CH_2Cl_2–acetone) to yield **40** (25 mg, 82%) as a syrup. R_f 0.73 (99:1, CH_2Cl_2–acetone); $[\alpha]_D$ +6.5 (*c* = 0.60, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.13–7.81 (m, 25 H, Ar), 7.75–7.52 (m, 12 H, Ar), 7.51–7.02 (m, 83 H, Ar), 6.08 (t, 1 H, *J* = 9.9 Hz, H-4‴), 5.97–5.87 (m, 3 H, H-2‴, H-3‴, CH_2–C*H*=CH_2), 5.74 (d, 1 H, *J* = 4.7 Hz), 5.71–5.59 (m, 9 H), 5.55 (br s, 1 H), 5.43–5.33 (m, 5 H, 4×H-1, H-1‴), 5.26 (dd, 1 H, *J* = 1.5, 17.2 Hz, CH_2–CH=CH_2), 5.07–5.03 (m, 2 H, H-1, CH_2–CH=CH_2), 5.01 (d, 1 H, *J* = 1.2 Hz, H-1), 4.97 (d, 1 H, *J* = 1.5 Hz, H-1), 4.93–4.83 (m, 4 H, H-1, 3×CH_2Ph), 4.78 (d, 1 H, *J* = 11.5 Hz, CH_2Ph), 4.74–4.42 (m, 15 H), 4.39 (d, 1 H, *J* = 11.5 Hz, CH_2Ph), 4.35 (br s, 1 H), 4.30–4.06 (m, 9 H), 4.03–3.79 (m, 13 H), 3.77–3.52 (m, 6 H), 3.46 (app d, 1 H, *J* = 10.9 Hz, H-6), 3.29 (dt, 1 H, *J* = 2×6.5, 9.5 Hz, OCH_2), 3.20 (t, 2 H, *J* = 6.9 Hz, CH_2N_3), 1.58–1.41 (m, 4 H, $OCH_2(CH_2)_6CH_2N_3$), 1.37–1.19 (m, 8 H, $OCH_2(CH_2)_6CH_2N_3$),1.01

(br s, 18 H, 2×C(C*H*$_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 166.1 (C═O), 165.7 (C═O), 165.6 (3 C, C═O), 165.5 (2 C, C═O), 165.3 (C═O), 165.2 (C═O), 165.1 (2 C, C═O), 165.0 (2 C, C═O), 164.9 (C═O), 139.0 (Ar), 138.8 (Ar), 138.4 (Ar), 138.3 (Ar), 138.2 (Ar), 137.9 (Ar), 135.9 (2 C, Ar), 135.7 (6 C, Ar), 135.6 (2 C, Ar), 135.3 (Ar), 134.1 (Ar), 133.6 (Ar), 133.5 (CH_2–*C*H=CH_2), 133.3 (4 C, Ar), 133.2 (2 C, Ar), 133.1 (4 C, Ar), 133.0 (Ar), 130.0 (4 C, Ar), 129.9 (9 C, Ar), 129.8 (15 C, Ar), 129.7 (2 C, Ar), 129.6 (3 C, Ar), 129.4 (4 C, Ar), 129.3 (2 C, Ar), 129.2 (2 C, Ar), 129.1 (4 C, Ar), 128.9 (Ar), 128.5 (8 C, Ar), 128.4 (6 C, Ar), 128.3 (11 C, Ar), 128.2 (11 C, Ar), 128.1 (3 C, Ar), 128.0 (4 C, Ar), 127.9 (2 C, Ar), 127.7 (10 C, Ar), 127.6 (4 C, Ar), 127.5 (4 C, Ar), 127.4 (Ar), 127.3 (Ar), 127.2 (Ar), 127.0 (2 C, Ar), 116.8 (CH_2–CH=*C*H_2), 106.3 (C-1), 106.0 (2×C-1), 105.9 (2×C-1), 99.6 (C-1), 99.3 (C-1), 99.0 (C-1), 98.5 (C-1), 83.2 (2 C), 82.2, 82.1 (5 C), 82.0, 81.5 (4 C), 80.1, 79.8, 75.1 (2 C), 75.0, 74.7 (2 C), 74.4 (2 C), 74.1, 73.0, 72.7, 72.3 (2 C), 71.6, 71.4 (3 C), 71.2, 70.1, 70.0, 69.4, 67.7, 67.0, 65.9 (2 C), 65.8 (2 C), 65.7, 65.5, 63.4 (2 C), 63.0 (2 C), 59.6 (2 C), 51.4 (*C*H_2N_3), 29.5, 29.4, 29.1, 28.8 (4 C, OCH_2(*C*H_2)$_6$$CH_2N_3$), 26.7, 26.2 (6 C, 2×C(*C*H_3)$_3$), 19.3 (2 C, 2×(*C*(CH_3)$_3$); HRMS (ESI) calcd for (M + 2 Na^+) $C_{232}H_{229}N_3O_{55}Si_2Na_2$: 2019.2269. Found: 2019.2287.

Supporting Information

NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgements

This work was supported by the Alberta Glycomics Centre, the Bill and Melinda Gates Foundation and the Canadian Institutes of Health Research

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