JOC The Journal of Organic Chemistry

Article

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Synthetic and Immunological Studies of Mycobacterial Lipoarabinomannan Oligosaccharides and Their Protein Conjugates

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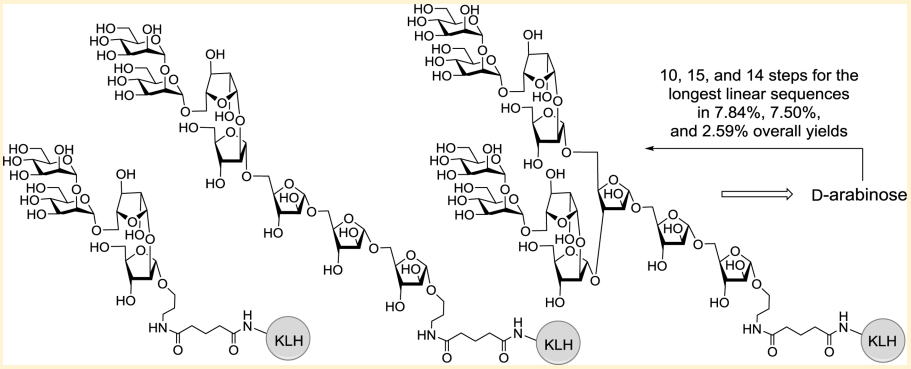
Supporting Information



ABSTRACT: Lipoarabinomannan (LAM) is one of the major constituents of the *Mycobacterium tuberculosis* cell wall and an attractive molecular scaffold for antituberculosis drug and vaccine development. In this paper, a convergent strategy was developed for the synthesis of LAM oligosaccharides with an α-1,2-linked dimannopyranose cap at the nonreducing end. The strategy was highlighted by efficient coupling of separately prepared nonreducing end and reducing end oligosaccharides. Glycosylations were mainly achieved with thioglycoside donors, which gave excellent yields and stereoselectivity even for reactions between complex oligosaccharides. The strategy was utilized to successfully synthesize tetra-, hepta-, and undecasaccharides of LAM from D-arabinose in 10, 15, and 14 longest linear steps and 7.84, 7.50, and 2.59% overall yields, respectively. The resultant oligosaccharides with a free amino group at their reducing end were effectively conjugated with carrier proteins, including bovine serum albumin and keyhole limpet hemocyanin (KLH), via a bifunctional linker. Preliminary immunological studies on the KLH conjugates revealed that they could elicit robust antibody responses in mice and that the antigen structure had some influence on their immunological property, thus verifying the potential of the oligosaccharides for vaccine development and other immunological studies.

INTRODUCTION

Tuberculosis (TB) is one of the most common infectious and lethal diseases worldwide.[1−3] Each year, more than 3 million people die of TB,[4] despite the fact that all governments over the world have made great efforts to prevent and treat the disease.[5] Antibiotic therapy is overall successful for TB treatment, but it usually takes many months and requires multiple antibiotic regimens.[3,6] Moreover, its efficacy has been severely affected by the rapid emergence of drug-resistant strains of *Mycobacterium tuberculosis*.[5−7] For TB protection, the 80 year old BCG is the only vaccine,[8] but its efficacy is questionable as its protection is highly variable (from 0 to 80%) in controlled trials in different countries.[8] Consequently, TB is an ever growing challenge, and novel strategies for the prevention and treatment of TB are in urgent demand.

M. tuberculosis possesses a unique and complex cell wall that is rich in polysaccharides and lipids.[1,9−11] Its two major structural components are arabinogalactan (AG) and lipoarabinomannan (LAM).[12,13] The structure of mycobacterial LAM has been well-established.[6,7] It has a mannan backbone composed of α-1,6- and α-1,2-linked mannopyranose residues, which is attached to a phosphatidylinositol moiety.[6,7] To the mannan backbone is linked an arabinan domain containing an α-1,5-linked D-arabinofuranosyl chain with two types of arabinan oligosaccharides attached to its nonreducing end, which are α-1,5- and β-1,2-linked tetraarabinofuranosides and α-1,5-, α-1,3-, and β-1,2-linked hexaarabinofuranosides.[7] The capping motif terminating the arabinan domain is an α-1,2-linked dimannopyranose at the arabinose 5-O-position.[6]

It has been well-documented that LAM plays an essential role in a number of important immunological events related to mycobacterial infection,[14,15] thus it is highly conserved in *M. tuberculosis*. For example, LAM was shown to promote the survival of the organism in host macrophages.[6] The oligosaccharides at the nonreducing end of LAM were also demonstrated to be a key player in mycobacterial infection.[16−20] When this portion was removed or replaced with

Received: July 21, 2015
Published: September 16, 2015

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

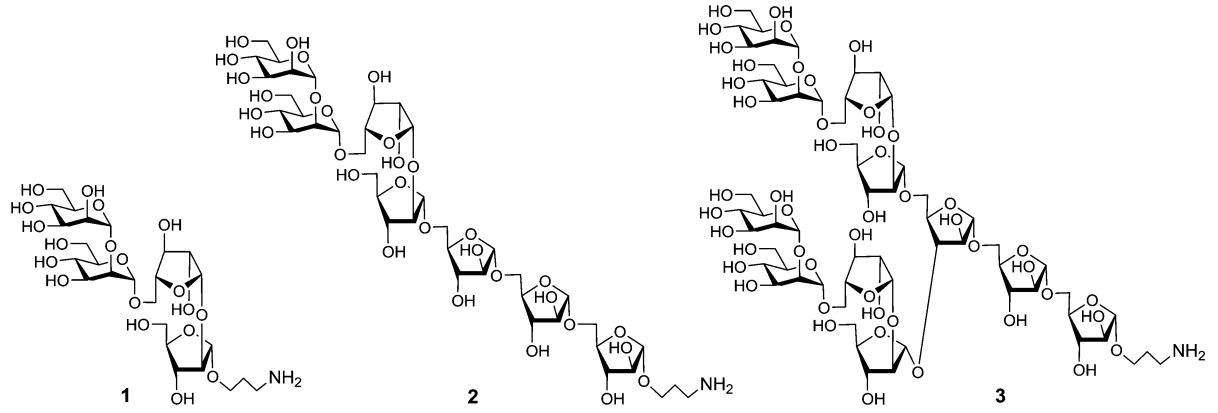
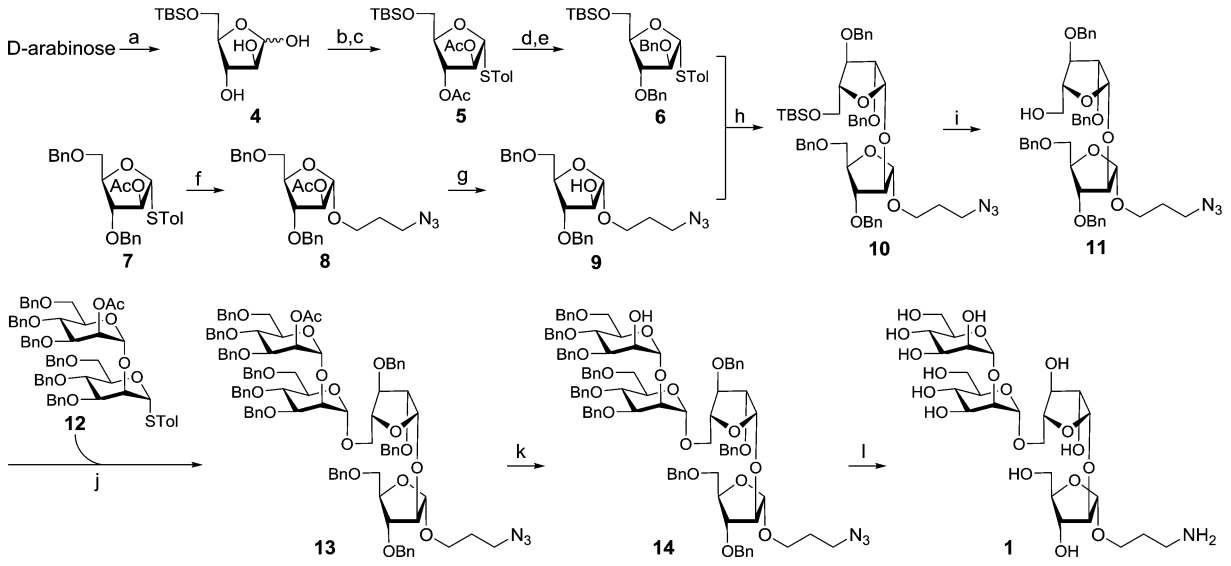


Figure 1. Structures of the synthesized LAM oligosaccharides.

Scheme 1. Synthesis of Tetrasaccharide 1[a]



[a]Reagents and conditions: (a) TBSCl, DMAP, pyridine, 72%; (b) Ac_2O, DMAP, pyridine, 90%; (c) thiocresol, $SnCl_4$, CH_2Cl_2, 0 °C to rt, 75%; (d) CH_3ONa, CH_3OH; (e) BnBr, NaH, DMF, 0 °C to rt, 74% for two steps; (f) 3-azidopropanol, NIS, AgOTf, CH_2Cl_2, −20 °C to rt, 87%; (g) CH_3ONa, CH_3OH, 91%; (h) NIS, AgOTf, CH_2Cl_2, −60 °C to rt, 51% of β-isomer (β/α 1.5/1); (i) TBAF, THF, 92%; (j) NIS, AgOTf, CH_2Cl_2, −20 °C to rt, 53% of α-isomer (α/β 1.8/1); (k) CH_3ONa, CH_3OH, 91%; (l) 10% Pd/C, AcOH/H_2O (v/v 10/1), rt, 36 h, 96%.

other oligosaccharides, many of the immunomodulatory activities of LAM were abolished.[9] Thus, oligosaccharides containing the nonreducing end portion of LAM can be useful tools for various immunological studies and for the development of carbohydrate-based TB vaccines.[8]

A series of studies on the synthesis of LAM oligosaccharides have been reported in the past several years,[21−43] and most of them were focused on the arabinan domain without the dimannose capping motif. Very few of the reports[41−43] had the oligosaccharides linked to proteins or other carrier molecules to perform the biological study. The present work is focused on synthesizing LAM oligosaccharides, such as **1**−**3** (Figure 1), containing the α-1,5-, α-1,3-, and β-1,2-linked arabinan domain with the nonreducing end 5-O-position capped with the α-1,2-linked dimannose motif. In **1**−**3**, an amino group is linked to the oligosaccharide reducing end to allow for their conjugation with carrier proteins, so as to obtain glycoconjugates that will be employed for various biological and immunological investigations.

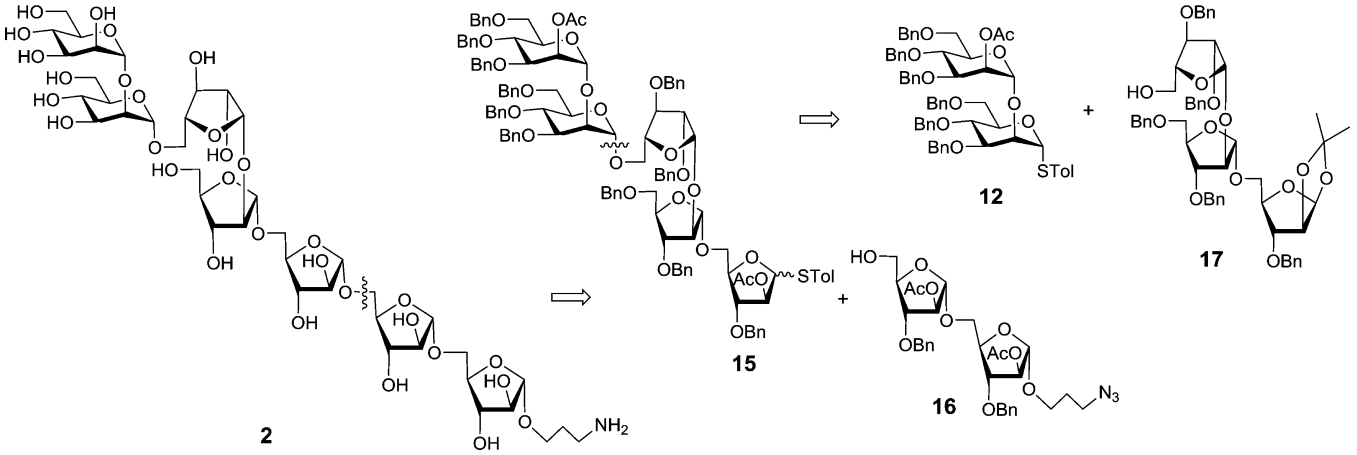
RESULTS AND DISCUSSION

Synthesis of Tetrasaccharide 1. Tetrasaccharide **1** is the universal cap at the nonreducing end of LAM. Its synthesis, as depicted in Scheme 1, started from D-arabinose that was converted into **6** through a series of well-established transformations, including regioselective 6-*O*-*tert*-butyldimethylsilylation with *tert*-butyldimethylsilyl chloride (→**4**), acetylation, thioglycosidation, and then replacing the acetyl groups with benzyl groups. For the thioglycosidation of acetylated **4**,[31] when $BF_3{\cdot}Et_2O$ was employed as the promoter, only a 30% yield of the desired product was obtained, and the major side reaction was desilylation. This problem was resolved by using $SnCl_4$ as the promoter, affording the thioglycosidation product in a 75% yield. In the meantime, the reducing end arabinose residue **9** was prepared by glycosylation of 3-azidopropanol with **7**[44] using NIS and AgOTf as the promoters, followed by deacetylation. This glycosylation reaction was stereoselective due to neighboring group participation.

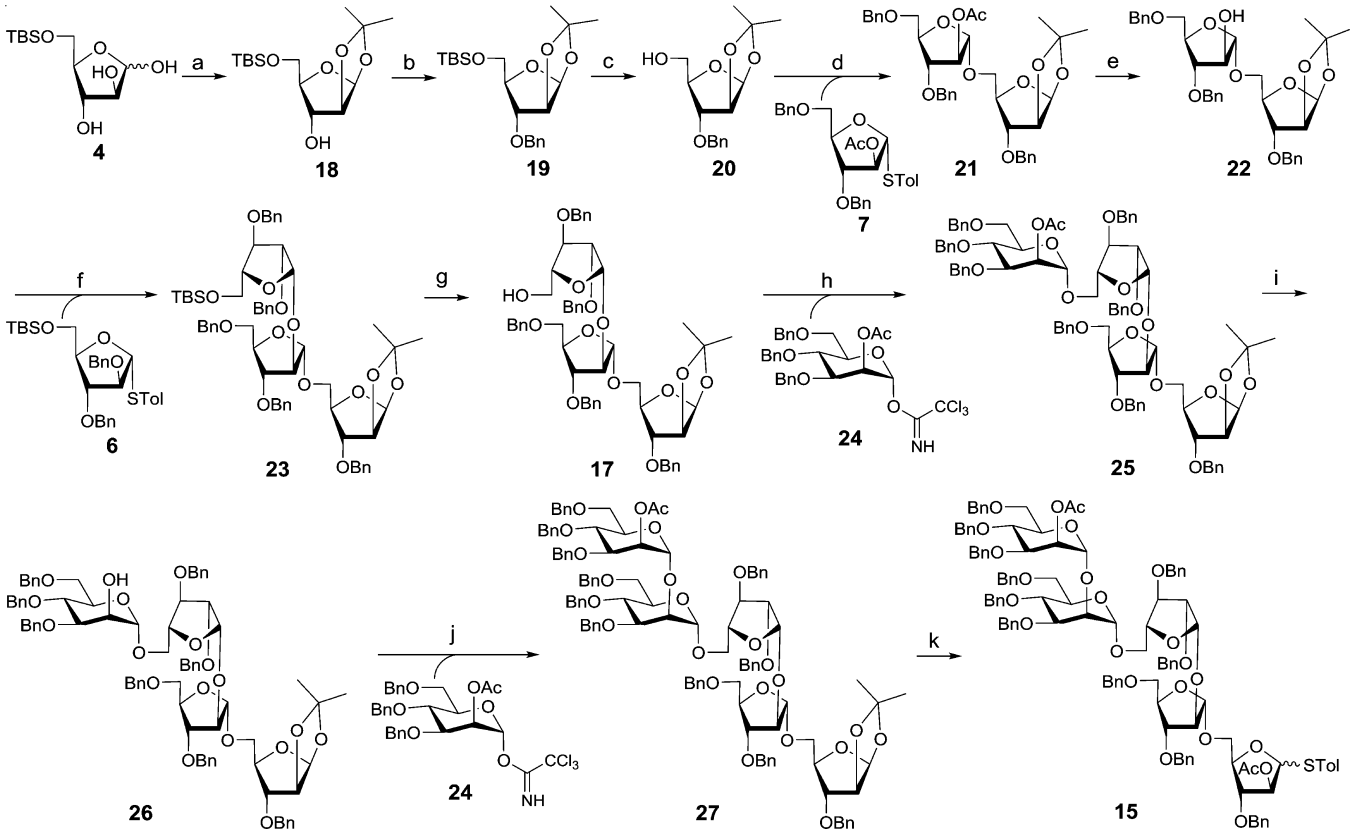
Once glycosyl donor **6** and acceptor **9** were obtained, their glycosylation reaction was carried out with the NIS−AgOTf

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

Scheme 2. Retrosynthesis of Heptasaccharide 2



Scheme 3. Synthesis of the Pentasaccharide Donor 15[a]



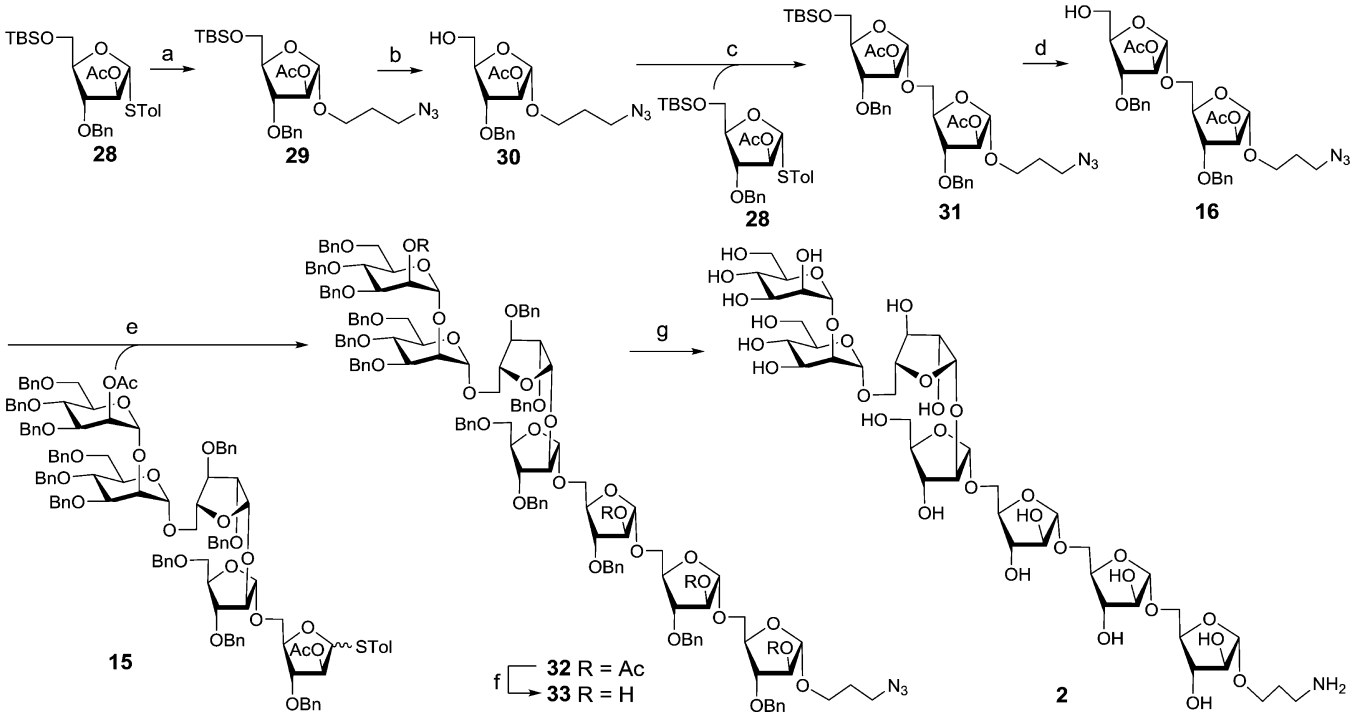
[a]Reagents and conditions: (a) 2,2-dimethoxypropane, *p*-toluenesulfonic acid, acetone, 84%; (b) BnBr, NaH, DMF, 0 °C to rt, 84%; (c) TBAF, THF, 93%; (d) NIS, AgOTf, CH_2Cl_2, −20 °C to rt, 89%; (e) CH_3ONa, CH_3OH, 90%; (f) NIS, AgOTf, CH_2Cl_2, −60 °C to rt, 57% of β-isomer (β/α 2/1); (g) TBAF, THF, 92%; (h) TMSOTf, CH_2Cl_2, −20 °C to rt, 91%; (i) CH_3ONa, CH_3OH, 93%; (j) TMSOTf, CH_2Cl_2, 0 °C to rt, 85%; (k) dioxane, 70% aq AcOH, 10% aq HCl, 50 °C; *n*-Bu_3P, *p*-tolyl disulfide, THF; Ac_2O, DMAP, pyridine, 80% for three steps.

activation system to afford a mixture of α- and β-linked disaccharides (1:1.5 ratio), which were readily separated by column chromatography to obtain the β-isomer **10** in a 51% isolated yield. The β-configuration of the newly formed glycosidic linkage was verified by ^{13}C NMR spectrometry.[28,45] According to literature, the anomeric carbon chemical shifts of α- and β-arabinofuranosides are in the ranges of 105−109 and 100−104 ppm, respectively.[28,45] The C-1 chemical shift of Ara-B in the ^{13}C NMR spectrum of **10** was 100.4 ppm, compared to 105.8 ppm for the C-1 chemical shift of Ara-A, indicating the β-glycosidic linkage for Ara-B. Removal of the TBS group using tetrabutylammonium fluoride (TBAF) afforded **11** in a 92% yield.

Fully protected tetrasaccharide **13** was assembled by glycosylation of **11** with **12**[46] under the promotion of NIS and AgOTf. Surprisingly, this reaction gave both anomers (α/β 1.8:1), despite the donor being a mannoside. Fortunately, the two isomers were readily separated by column chromatography, and the α-configuration of **13** (obtained in a 53% isolated yield) was confirmed according to the literature.[47,48] The $^1J_{CH}$

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

Scheme 4. Synthesis of Target Heptasaccharide 2[a]



[a]Reagents and conditions: (a) 3-azidopropanol, NIS, AgOTf, CH_2Cl_2, −20 °C to rt, 84%; (b) TBAF, HOAc, THF, 92%; (c) NIS, AgOTf, CH_2Cl_2, −20 °C to rt, 77%; (d) TBAF, HOAc, THF, 93%; (e) NIS, AgOTf, CH_2Cl_2, 0 °C to rt, 81%; (f) CH_3ONa, CH_3OH, THF, 86%; (g) 10% Pd/C, $HOAc/H_2O$ (v/v 10/1), rt, 48 h, 94%.

coupling constant of the anomeric carbon and hydrogen for α-mannopyranosides is above 170 Hz, and that for β-anomers is below 160 Hz.[47,48] The ^{1}H-coupled gHSQC spectrum of **13** revealed that the $^1J_{CH}$ coupling constant of the newly formed glycosidic linkage was 172.8 Hz. Finally, global deprotection of **13** was carried out in two steps, including deacetylation using CH_3ONa and concomitant azido group reduction and benzyl group removal by catalytic hydrogenation, to afford the desired tetrasaccharide **1**, which was purified by gel filtration chromatography. The final product, as well as the synthetic intermediates, was fully characterized with MS and NMR.

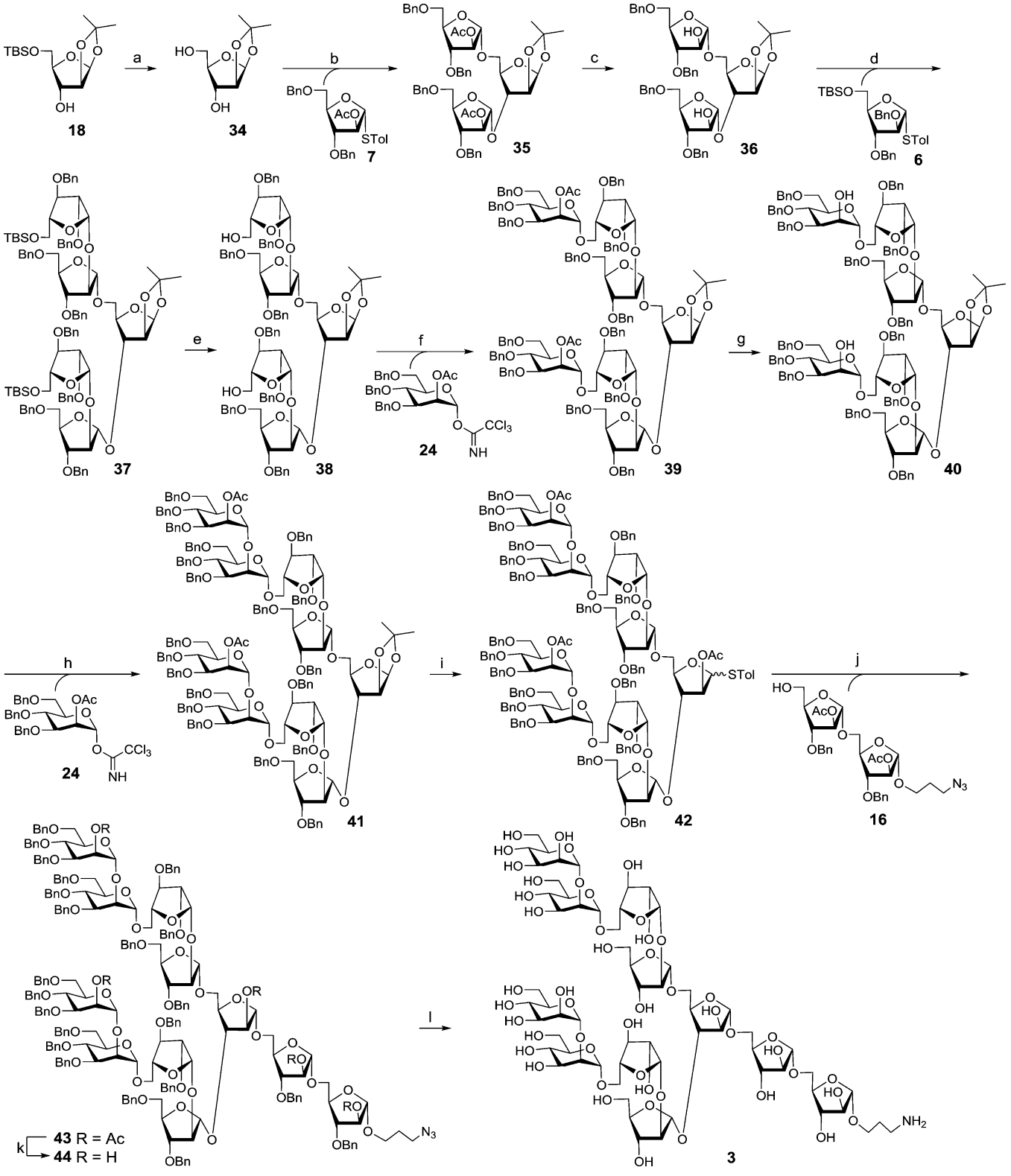
Synthesis of Heptasaccharide 2. In the synthesis of **2**, the most challenging task was probably the introduction of the β-arabinofuranosyl residue. Accordingly, our synthetic design, as outlined in Scheme 2, was to first assemble trisaccharide **17**[31] containing the difficult β-arabinofuranosyl linkage. Thereafter, the oligosaccharide chain could be sequentially elongated in both directions using disaccharides **12** and **16** to obtain the target molecule. Furthermore, we planned to use the acetyl group for the protection of 2-O-positions in all other glycosyl donors, such as **15** and the disaccharide building blocks of **12** and **16**, in order to take advantage of the neighboring group participation effect for stereoselective trans-glycosylation.

The synthesis of oligosaccharide donor **15** (Scheme 3) started with **4**, which was obtained by regioselective 5-O-silylation of D-arabinose as described above. Protection of its 1,2-O-positions with an isopropylidene group[31,49] upon reaction with 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-toluenesulfonic acid (→**18**) was followed by conventional 3-O-benzylation to give **19** smoothly in a good yield. After the TBS group in **19** was removed, the resulting **20**[31] was glycosylated with **7** under the promotion of NIS−AgOTf to afford disaccharide **21** in an 89% yield. This reaction was stereoselective, and the chemical shifts (106.2 and 105.6 ppm) of the anomeric carbon signals in the ^{13}C NMR spectrum of **21** verified the α-configuration of both glycosidic linkages. Next, **21** was deacetylated to give **22**,[31] which was glycosylated with **6** using NIS and AgOTf as the promoters. This reaction gave a mixture of α- and β-anomers (1:2), which could be easily separated by column chromatography, and the β-anomer **23** was obtained in a 57% yield. The stereochemistry of **23** was confirmed by its ^{13}C NMR spectrum, which showed that the chemical shifts of its anomeric carbons were 106.1, 105.5, and 100.5 ppm, respectively. Removal of the TBS group in **23** eventually afforded trisaccharide **17** as a glycosyl acceptor.

For subsequent carbohydrate chain elongation, initially, we intended to attach the dimannose moiety to **17** directly by means of glycosyl donor **12**. Similar to the results obtained above, the reaction afforded an α- and β-anomeric mixture. Unfortunately, the anomers were inseparable by column chromatography. To solve this problem, we switched to a stepwise glycosylation strategy as outlined in Scheme 3. Glycosylation of **17** with **24**[50] promoted by TMSOTf was smooth to give an excellent yield (91%) of the desired α-linked tetrasaccharide **25**. The reaction was α-selective probably due to neighboring group participation, and the stereochemistry of **25** was confirmed by NMR analysis as described above. Then, the acetyl group in **25** was removed, and the resulting alcohol **26** was glycosylated with **24** to obtain pentasaccharide **27** stereoselectively. Conversion of **27** into glycosyl donor **15** was achieved in three steps, including removal of the isopropylidene group in a mixture of dioxane, 70% aqueous AcOH, and 10% aqueous HCl (v/v/v 20:10:1),[31,51] thioglycosidation using P(*n*-Bu)$_3$-*p*-tolyl disulfide, and then acetylation using Ac_2O, pyridine, and DMAP. All of the three reactions were clean

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

Scheme 5. Synthesis of Undecasaccharide 3[a]



[a]Reagents and conditions: (a) TBAF, THF, 85%; (b) NIS, AgOTf, CH_2Cl_2, −20 °C to rt, 83%; (c) CH_3ONa, CH_3OH, 86%; (d) NIS, AgOTf, CH_2Cl_2, −60 °C to rt, 40% of β,β-isomer (β,β-isomer/other isomers 1:1.2); (e) TBAF, THF, 87%; (f) TMSOTf, CH_2Cl_2, 0 °C to rt, 74%; (g) CH_3ONa, CH_3OH, THF, 91%; (h) TMSOTf, CH_2Cl_2, 0 °C to rt, 81%; (i) dioxane, 70% aq AcOH, 10% aq HCl, 50 °C; *n*-Bu_3P, *p*-tolyl disulfide, THF; Ac_2O, DMAP, pyridine, 80% for three steps; (j) NIS, AgOTf, CH_2Cl_2, 0 °C to rt, 63%; (k) CH_3ONa, CH_3OH, THF, 81%; (l) 10% Pd/C, $HOAc/H_2O$ (v/v 10/1), rt, 72 h, 91%.

and effective, and **15** was isolated as a mixture of α- and β-anomers (1:1 ratio) in an 80% overall yield.

On the other hand, disaccharide **16** used for carbohydrate chain elongation from the reducing end was prepared from

DOI: 10.1021/acs.joc.5b01686
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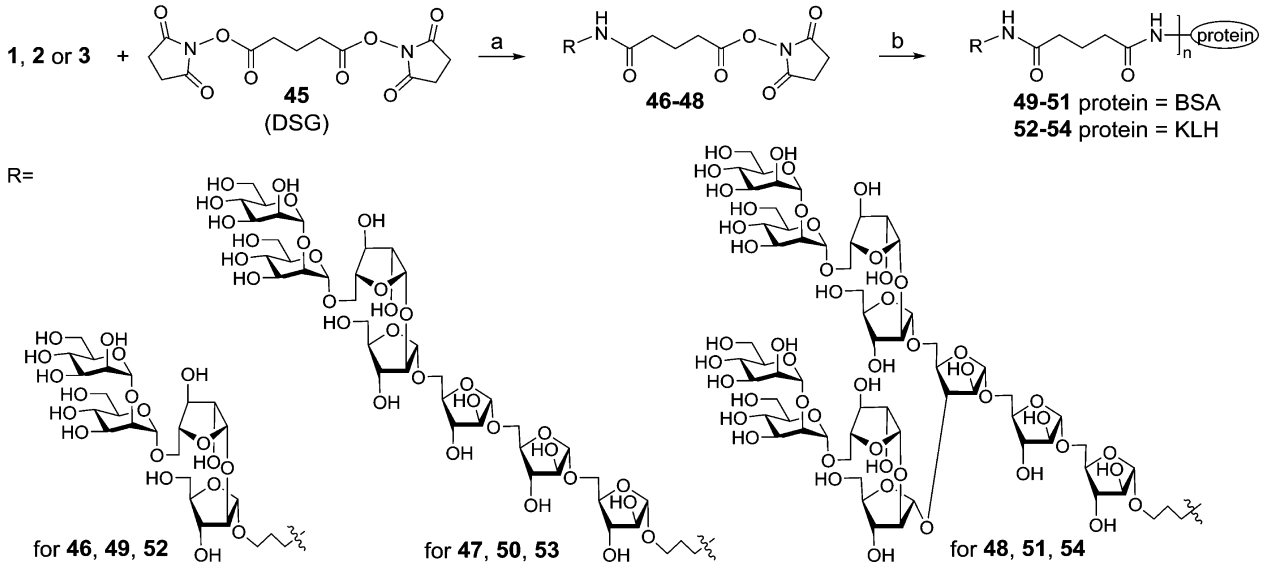
Scheme 6. Preparation of Protein Glycoconjugates of 1, 2, and 3[a]



[a]Reagents and conditions: (a) DMF, 0.1 M PBS (pH 8.0), rt, 4h; (b) BSA or KLH, 0.1 M PBS (pH 8.0), rt, 4 days.

28[44] (Scheme 4). Its glycosylation reaction with 3-azidopropanol in the presence of NIS and AgOTf gave the α-glycoside **29** in a good yield, which was desilylated with TBAF to afford **30**. For the desilylation reaction, the condition was critical because at high pH value deacetylation might occur.[40] Glycosylation of **30** with **28** was promoted by NIS and AgOTf to give **31** in a 77% yield. Again, desilylation of **31** was carried out under mildly acidic conditions to yield disaccharide **16** as a glycosyl acceptor. Subsequently, **15** was coupled with **16** under the promotion of NIS and AgOTf in dry dichloromethane, which was especially smooth and high-yielding to produce heptasaccharide **32** (81%) stereoselectively, despite the glycosyl donor **15** being large and complex. This observation enhanced our confidence about a highly convergent and effective synthetic design for more complex synthetic targets, such as undecasaccharide **3**. The stereochemistry of **32** was verified by the chemical shifts of its anomeric ^{13}C NMR signals at 106.3 (α-Ara), 106.1 (α-Ara), 106.0 (α-Ara), 105.9 (α-Ara), 100.6 (β-Ara), 99.5 (α-Man^{A}), and 98.5 (α-Man^{B}) ppm. Eventually, **32** was completely deprotected in two steps, including deacetylation using CH_3ONa to get **33** in an 86% yield and concomitant azido group reduction and benzyl ether deprotection by catalytic hydrogenation to produce the desired heptasaccharide **2** that was purified by gel filtration chromatography. The final product, as well as the synthetic intermediates, was fully characterized with MS and NMR.

Synthesis of Undecasaccharide 3. This synthesis (Scheme 5) was performed by a strategy somewhat similar to that employed to synthesize **2**. Our plan was to first prepare a trisaccharide **36** that contained the 3,5-O-branches and then conduct dual β-arabinofuranosylations to arrive at a branched pentasaccharide platform **37**, based on which the carbohydrate chain might be further elongated in both directions and in a convergent way. Moreover, except for glycosyl donor **6** that was used for β-arabinofuranosylation, the 2-O-position in all other glycosyl donors was protected with the acetyl group to facilitate stereoselective glycosylation reactions by taking advantage of its neighboring group participation ability. Therefore, in this synthetic design, there was only one glycosylation reaction that was not stereochemically controlled.

Dual glycosylations of diol **34** with **7** were both α-selective to afford branched trisaccharide **35** in a very good yield (83%). The chemical shifts of its anomeric carbons were 106.0, 105.4, and 105.0 ppm, proving their α-configurations. The acetyl groups in **35** were then simultaneously removed with CH_3ONa to form **36**, which was ready for the carbohydrate chain elongation. Dual glycosylations of **36** with 3 equiv of **6** using NIS and AgOTf as promoters were effective but gave a mixture of all four potential isomers, that is, α,α-, α,β-, β,α-, and β,β-anomers, which were readily separated by column chromatography and then characterized according to their ^{1}H and ^{13}C NMR spectra. The ratio of the desired β,β-anomer **37** to all other isomers was 1:1.2, and **37** was obtained in a 40% isolated yield. The chemical shifts of the anomeric carbons around the newly formed glycosidic bond in **37** were 100.6 and 100.3 ppm, confirming their β-configurations. 5-O-Desilylation of **37** and subsequent α-mannosylations using glycosyl donor **24** followed the same protocols discussed in the synthesis of **2** to afford nonasaccharide **41** in an excellent yield (48%) over four steps. Both glycosylation reactions were α-selective because of the presence of an acetyl group at the 2-O-position of the donor. As described above, the conversion of **41** into glycosyl donor **42** was carried out in three steps, including removal of the isopropylidene group, thioglycosidation with P(n-Bu)$_3$ and p-tolyl disulfide, and acetylation, affording **42** as an α- and β-anomeric mixture (α/β 1:1, 80% overall yield). The coupling reaction between **42** and **16** under the promotion of NIS and AgOTf was smooth, stereoselective, and high-yielding (63%) to give fully protected undecasaccharide **43**. Its stereochemistry was verified by the chemical shifts of its anomeric ^{13}C NMR signals at 106.6 (α-Ara^{B}), 106.0 (α-Ara^{D1}), 105.9 (α-Ara^{D2}, α-Ara^{A}), 105.8 (α-Ara^{C}), 100.5 (β-Ara^{E2}), 100.1 (β-Ara^{E1}), 99.5 (α-Man^{B1}, α-Man^{B2}), 98.6 (α-Man^{A1}), and 98.5 (α-Man^{A2}) ppm. Then, **43** was globally deprotected in two steps, including deacetylation (→**44**) and concomitant azido group reduction and benzyl ether cleavage, as described above, to yield the desired undecasaccharide **3** that was purified by gel filtration chromatography. The final product, as well as the synthetic intermediates, was fully characterized with MS and NMR.

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

Conjugation of Oligosaccharides with Carrier Proteins. This was achieved through the free amino group linked to the oligosaccharide reducing end, which should be more reactive than the carbohydrate hydroxyl groups to enable a regioselective reaction outlined in Scheme 6. The linker was the bifunctional glutaryl group.[52] Treating **1**, **2**, and **3** with an excess of di(*N*-succinimidyl)glutarate (DSG, 15 equiv) in DMF for 4 h afforded armed oligosaccharides **46**, **47**, and **48** that contained an activated ester. The coupling reaction between **46**–**48** and carrier proteins, including bovine serum albumin (BSA) and keyhole limpet hemocyanin (KLH), was carried out in 0.1 M phosphate-buffered saline (PBS) buffer at pH 8.0. After 4 days of stirring at room temperature, the reaction mixtures were subjected to gel filtration column chromatography and then dialysis against distilled water. The dialysates were lyophilized to obtain glycoproteins **49**–**54** as white powders. The carbohydrate loadings of these conjugates were determined by the phenol–sulfuric acid method,[53,54] which was proven to be reliable;[55,56] the results of BSA conjugates **49** (10.0%), **50** (7.2%), and **51** (8.6%) were also verified with MALDI-TOF MS study, and the results of KLH conjugates **52** (7.2%), **53** (8.4%), and **54** (9.0%) were verified by SDS-PAGE analysis.

Preliminary Studies on the Immunological Properties of the Synthesized Conjugates 52–54. These evaluations were performed with female Balb/c mice. Conjugate **52**, **53**, or **54** (3 μg of carbohydrate antigen/mouse/injection) mixed with Titermax Gold adjuvant was subcutaneously (s.c.) injected to each group of six mice on days 1, 14, 21, 28, and 35, respectively. In the meantime, mice were also immunized with free oligosaccharides **1**–**3** by the same protocol. Blood samples were collected from the mice prior to and after immunization on days 0 and 36 to obtain antisera that were analyzed by enzyme-linked immunosorbent assays (ELISA) to determine their antigen-specific total (anti-kappa) antibody titers using BSA conjugates **49**–**51** as capture antigens. Here, antibody titers were defined as antiserum dilution numbers yielding an OD value of 0.1, and the ELISA results are shown in Figure 2.

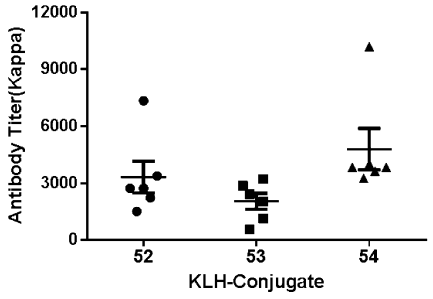


Figure 2. ELISA results of the day 36 antisera obtained with conjugates **52** (●), **53** (■), and **54** (▲). The titers of corresponding antigen-specific total (kappa) antibodies are displayed. Each graphic symbol represents the antibody titer of an individual mouse, and the black bar shows the average titer.

Clearly, all of the tested conjugates **52**–**54** elicited robust antigen-specific immune responses in mice, and the antibody titers induced by **52** and **54** were slightly higher than that induced by **53**. In contrast, antisera derived from mice immunized with free oligosaccharides **1**–**3** did not contain carbohydrate antigen-specific antibodies. Consequently, oligosaccharides **1**–**3** were proven to be immunogenic after conjugation with a carrier protein, such as KLH, and their structures were proven to have an impact on the immunological property. However, the elicited antibody titers were moderate overall; therefore, further optimization of the glycoconjugates is necessary for the development of functional vaccines.

CONCLUSION

A highly convergent strategy was developed for the synthesis of structurally well-defined lipoarabinomannan oligosaccharides, such as **1**–**3**, carrying the α-1,2-linked dimannopyranose cap at the nonreducing end and a free amino group at the reducing end to facilitate further regioselective modifications. The synthesis was highlighted by constructing the nonreducing end oligosaccharides first, which were further elaborated by coupling with reducing end oligosaccharides. Glycosylation reactions were achieved by using thioglycosides as glycosyl donors, which afforded excellent yields and stereoselectivity even for the coupling reactions between complex oligosaccharides. Eventually, tetrasaccharide **1**, heptasaccharide **2**, and undecasaccharide **3** were synthesized in 10, 15, and 14 steps from D-arabinose, counting the longest linear sequences, and in 7.84, 7.50, and 2.59% overall yields. It is worth mentioning that the dual glycosylation reactions of **38** and **40** and the glycosylation reactions using oligosaccharides **15** and **42** as donors were especially efficient and stereoselective. Consequently, we anticipated that the synthetic strategy might be used to prepare more complex lipoarabinomannan oligosaccharides.

Furthermore, the synthesized oligosaccharides **1**–**3** were successfully and effectively coupled with carrier proteins, such as BSA and KLH, via the DSG linker to result in glycoproteins **49**–**54** with desirable carbohydrate loadings. Preliminary immunological studies of the KLH conjugates **52**–**54** proved that oligosaccharides **1**–**3** were immunogenic upon conjugation with a carrier protein and that the carbohydrate antigen structures had some influence on their immunological property. Currently, studies to optimize LAM oligosaccharide-based glycoconjugate vaccines, for example, by coupling **1**–**3** with more immunogenic carrier proteins such as tetanus toxoid and diphtheria toxin mutant CRM_{197}, are underway, and the results will be communicated in due course.

EXPERIMENTAL SECTION

General Methods. Chemicals and materials were obtained from commercial sources and were used as received without additional purification unless otherwise noted. Molecular sieves (MS) AW-300 were flame-dried under high vacuum and cooled to room temperature under a nitrogen atmosphere before use. Optical rotations were determined at 26 °C with an automatic polarimeter. ^{1}H and ^{13}C NMR spectra were recorded with a 600 MHz spectrometer for solutions in $CDCl_3$ or D_2O. Chemical shifts (δ) are given in parts per million downfield from internal Me_4Si or with DHO signal as a reference when D_2O was used as the solvent. Positive-mode electrospray ionization (ESI) was used for high-resolution mass spectroscopy (HRMS). MALDI-TOF mass spectra were recorded with 2,5-dihydroxybenzoic acid (DHB) as the matrix. Thin layer chromatography (TLC) was performed on silica gel HF_{254} plates with detection by charring with 30% (v/v) H_2SO_4 in MeOH or by a UV detector. Silica gel column chromatography was conducted with mixtures of ethyl acetate and petroleum ether (bp 60–90 °C) or hexane as eluents. Solution concentrations were performed at <60 °C under diminished pressure.

*p-Tolyl 2,3-Di-O-acetyl-5-O-tert-butydimethylsilyl-1-thio-α-D-arabinofuranoside (**5**).* To a solution of D-arabinose (5.0 g, 33.3 mmol) in pyridine (100 mL) were added TBSCl (6.0 g, 39.81 mmol) and DMAP (50 mg) in an ice bath. The mixture was allowed to warm to rt

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060–10075

and stirred for 8 h before coevaporation with toluene (2 × 100 mL) to remove pyridine. The resulting crude product was purified by flash column chromatography (ethyl acetate) to give **4** (6.34 g, 72%) as colorless syrup. After **4** (5.0 g, 18.9 mmol) was dissolved in pyridine (50 mL) and acetic anhydride (20 mL), DMAP (100 mg) was added at 0 °C. The mixture was stirred at rt for 4 h, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography with petroleum ether and ethyl acetate (2:1) as the eluents to generate the peracetylated product (6.65 g, 90%, α/β 1.6:1) as colorless syrup, which (6.0 g, 15.4 mmol) was dissolved with *p*-thiocresol (2.29 g, 18.5 mmol) in anhydrous CH_2Cl_2 (50 mL). A catalytic amount of $SnCl_4$ (0.4 mL) was then added at 0 °C, and the mixture was stirred at rt for 30 min, at which time TLC (petroleum ether/ethyl acetate 4:1) indicated the completion of reaction. The mixture was neutralized with triethylamine and concentrated. The residue was subjected to flash column chromatography (petroleum ether/ethyl acetate 5:1) to yield **5** (5.24 g, 75%) as colorless syrup: $[\alpha]_D^{26}$ +131.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2 H, Ph), 7.10 (d, *J* = 7.8 Hz, 2 H, Ph), 5.44 (s, 1 H, H-1), 5.22 (s, 1 H, H-2), 5.18 (d, *J* = 4.8 Hz, 1 H, H-3), 4.29−4.28 (m, 1 H, H-4), 3.86−3.83 (m, 2 H, H-5a,b), 2.31 (s, 3 H, Ph−CH_3), 2.09 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 0.90 (s, 9 H, *t*Bu), 0.06 (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.8, 137.8, 132.6, 129.8, 129.7, 90.7 (C-1), 82.6, 81.7, 77.2, 62.5, 25.8, 21.1, 20.83, 20.79, 18.2, −5.4, −5.5; ESI-TOF HRMS *m*/*z* calcd for $C_{22}H_{38}NO_6SSi$ $[M + NH_4]^+$ 472.2184, found 472.2188.

*p-Tolyl 2,3-Di-O-benzyl-5-O-tert-butydimethylsilyl-1-thio-α-D-arabinofuranoside (**6**).* To a solution of **5** (5.0 g, 11 mmol) in MeOH (30 mL) was added NaOMe in MeOH (1 M) until the pH value reached 10. The solution was stirred at rt for 3 h, when TLC (petroleum ether/ethyl acetate 2:1) showed the disappearance of **5**. The mixture was neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The resulting crude product was dissolved in DMF (50 mL), and NaH (1.76 g, 60% in kerosene, 44 mmol) was slowly added at 0 °C. The mixture was stirred at rt for 30 min, and BnBr (5.64 g, 33 mmol) was added dropwise in 10 min at 0 °C. After the mixture was warmed to rt and stirred for 30 min, it was poured into cold water (100 mL) and extracted with ethyl acetate (200 mL). The organic layer was washed with brine (2 × 100 mL), dried over anhydrous Na_2SO_4, and then concentrated. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate 15:1) to yield **6** (4.50 g, 74% for two steps) as colorless syrup: $[\alpha]_D^{26}$ +93.1 (*c* 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2 H, Ph), 7.37−7.29 (m, 10 H, Ph), 7.11 (d, *J* = 7.8 Hz, 2 H, Ph), 5.49 (d, *J* = 1.8 Hz, 1 H, H-1), 4.63 (d, *J* = 12.0 Hz, 1 H, Bn), 4.57 (s, 2 H, Bn), 4.50 (d, *J* = 12.0 Hz, 1 H, Bn), 4.27−4.25 (m, 1 H, H-4), 4.12 (t, *J* = 3.0 Hz, 1 H, H-2), 4.04 (dd, *J* = 3.0, 5.4 Hz, 1 H, H-3), 3.81−3.75 (m, 2 H, H-5a,b), 2.33 (s, 3 H, Ph−CH_3), 0.89 (s, 9 H, *t*Bu), 0.05 (s, 6 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.9, 137.5, 137.2, 131.9, 131.1, 129.6, 128.4 (2C), 127.9, 127.8, 127.7 (2C), 90.4 (C-1), 88.4, 83.3, 82.1, 72.2, 72.1, 62.7, 25.9, 21.1, 18.3, −5.27, −5.33; ESI-TOF HRMS *m*/*z* calcd for $C_{32}H_{46}NO_4SSi$ $[M + NH_4]^+$ 568.2911, found 568.2915.

*3-Azidopropyl 2-O-Acetyl-3,5-di-O-benzyl-α-D-arabinofuranoside (**8**).* To a mixture of **7** (2.3 g, 4.81 mmol), 3-azide-1-propanol (583 mg, 5.77 mmol), and activated MS AW-300 (1.0 g) in anhydrous CH_2Cl_2 (15 mL) were added NIS (1.19 g, 5.29 mmol) and AgOTf (123 mg, 0.48 mmol) at −20 °C under a N_2 atmosphere. The mixture was stirred at −20 °C for 30 min and was then slowly warmed to rt, neutralized with triethylamine, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1) to give **8** (1.9 g, 87%) as colorless syrup: $[\alpha]_D^{26}$ +73.8 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33−7.25 (m, 10 H, Ph), 5.08 (s, 1 H, H-2), 5.00 (s, 1 H, H-1), 4.68 (d, *J* = 12.0 Hz, 1 H, Bn), 4.59−4.50 (m, 3 H, Bn), 4.23−4.21 (m, 1 H, H-4), 3.86 (d, *J* = 5.4 Hz, 1 H, H-3), 3.82−3.79 (m, 1 H, -OCH_2CH$_2$−), 3.62 (dd, *J* = 3.0, 10.8 Hz, 1 H, H-5a), 3.56 (dd, 1 H, *J* = 4.8, 10.8 Hz, 1H, H-5b), 3.52−3.48 (m, 1 H, -OCH_2CH$_2$−), 3.42−3.37 (m, 2 H, −CH_2N$_3$), 2.00 (s, 3 H, Ac), 1.89−1.82 (m, 2H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 137.9, 137.6, 128.4, 128.3, 127.8 (2C), 127.7 (2C), 106.0 (C-1), 83.1, 81.9, 81.6, 73.4, 72.2, 69.2, 63.9 (-OCH$_2$CH$_2$−), 48.3 (−CH$_2$N$_3$), 28.9 (−OCH$_2$CH$_2$−), 20.9; ESI-TOF HRMS *m*/*z* calcd for $C_{24}H_{33}N_4O_6$ $[M + NH_4]^+$ 473.2395, found 473.2390.

*3-Azidopropyl 3,5-Di-O-benzyl-α-D-arabinofuranoside (**9**).* To a solution of **8** (1.5 g, 3.30 mmol) in MeOH (10 mL) was added NaOMe in MeOH (1 M) until the pH value reached 10. It was stirred at rt for 3 h. After TLC (petroleum ether/ethyl acetate 8:1) showed the disappearance of **8**, the solution was neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The residue was purified by silica gel column chromatography with petroleum ether and ethyl acetate (5:1) as the eluents to give **9** (1.24 g, 91%) as colorless syrup: $[\alpha]_D^{26}$ +87.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.25 (m, 10 H, Ph), 5.00 (s, 1 H, H-1), 4.67−4.62 (m, 2 H, Bn), 4.51−4.48 (m, 2 H, Bn), 4.26 (t, *J* = 1.2 Hz, 1 H, H-4), 4.13 (s, 1 H, H-2), 3.87 (s, 1 H, H-3), 3.82−3.78 (m, 1 H, −OCH_2CH$_2$−), 3.68−3.66 (m, 1 H, H-5a), 3.52−3.49 (m, 2 H, H-5b, −OCH_2CH$_2$−), 3.38−3.36 (m, 2 H, −CH_2N$_3$), 1.87−1.83 (m, 2 H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.8, 136.9, 128.6, 128.4, 128.1, 127.9, 127.8, 127.7, 109.0 (C-1), 85.2, 83.7, 77.5, 73.8, 72.0, 69.7, 63.8 (−OCH$_2$CH$_2$−), 48.4 (−CH$_2$N$_3$), 29.1 (−OCH$_2$CH$_2$−); ESI-TOF HRMS *m*/*z* calcd for $C_{22}H_{31}N_4O_5$ $[M + NH_4]^+$ 431.2289, found 431.2292.

*3-Azidopropyl 2,3-Di-O-benzyl-5-O-tert-butydimethylsilyl-β-D-arabinofuranosyl-(**1→2**)-3,5-di-O-benzyl-α-D-arabinofuranoside (**10**).* To a mixture of **6** (2.3 g, 4.18 mmol), **9** (2.07 g, 5.01 mmol), and MS AW-300 (800 mg) in anhydrous CH_2Cl_2 (20 mL) were added NIS (1.13 g, 5.01 mmol) and AgOTf (108 mg, 0.42 mmol) at −60 °C under a N_2 atmosphere. After the mixture was stirred at −60 °C for 30 min, it was slowly warmed to rt, neutralized with triethylamine, filtered, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to give **10** (1.79 g, 51%) as colorless syrup: $[\alpha]_D^{26}$ −27.0 (*c* 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33−7.25 (m, 20 H, Ph), 5.06 (s, 1 H, H-1^{Ara-B}), 4.98 (s, 1 H, H-1^{Ara-A}), 4.69−4.47 (m, 8 H, Bn), 4.26 (d, *J* = 1.8 Hz, 1 H, H-2^{Ara-A}), 4.22−4.19 (m, 1 H, H-4^{Ara-A}), 4.09−4.07 (m, 2 H, H-2^{Ara-B}, H-3^{Ara-B}), 3.99−3.97 (m, 2 H, H-3^{Ara-A}, H-4^{Ara-B}), 3.81−3.77 (m, 1 H, −OCH_2CH$_2$−), 3.72 (dd, *J* = 6.0, 10.2 Hz, 1 H, H-5a^{Ara-B}), 3.67 (dd, *J* = 7.8, 10.2 Hz, 1 H, H-5a^{Ara-B}), 3.60 (dd, *J* = 4.2, 10.8 Hz, 1 H, H-5b^{Ara-B}), 3.57 (dd, *J* = 6.0, 10.8 Hz, 1 H, H-5b^{Ara-A}), 3.46−3.42 (m, 1 H, −OCH_2CH$_2$−), 3.39−3.33 (m, 2 H, −CH_2N$_3$), 1.86−1.82 (m, 2 H, −OCH$_2$CH_2−), 0.85 (s, 9 H, *t*Bu), 0.00 (s, 6 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 138.1, 137.9, 137.7, 128.4, 128.3 (3C), 127.9, 127.8, 127.7, 127.6 (4C), 105.8 (C-1^{Ara-A}), 100.4 (C-1^{Ara-B}), 86.0, 84.2, 84.1, 84.0, 82.2, 81.3, 73.3, 72.5, 72.3, 72.26, 70.1, 65.4, 63.9 (−OCH$_2$CH$_2$−), 48.4 (−CH$_2$N$_3$), 29.1 (−OCH$_2$CH$_2$−), 25.9, 18.3, −5.28, −5.33; ESI-TOF HRMS *m*/*z* calcd for $C_{47}H_{65}N_4O_9Si$ $[M + NH_4]^+$ 857.4515, found 857.4531.

*3-Azidopropyl 2,3-Di-O-benzyl-β-D-arabinofuranosyl-(**1→2**)-3,5-di-O-benzyl-α-D-arabinofuranoside (**11**).* A solution of **10** (1.0 g, 1.19 mmol) in THF (10 mL) and TBAF (1.0 M in THF, 1.4 mL, 1.4 mmol) was stirred at rt for 2 h. After TLC (petroleum ether/ethyl acetate 4:1) indicated the disappearance of **10**, the reaction was concentrated, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afford **11** (800 mg, 92%) as colorless syrup: $[\alpha]_D^{26}$ −13.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.26 (m, 20 H, Ph), 5.05 (d, *J* = 4.8 Hz, 1 H, H-1^{Ara-B}), 4.98 (d, *J* = 1.2 Hz, 1 H, H-1^{Ara-A}), 4.73 (d, *J* = 12.0 Hz, 1 H, Bn), 4.65−4.48 (m, 7 H, Bn), 4.30−4.26 (m, 2 H, H-3^{Ara-B}, H-2^{Ara-A}), 4.19−4.17 (m, 1 H, H-4^{Ara-A}), 4.13−4.09 (m, 2 H, H-2^{Ara-B}, H-3^{Ara-A}), 4.02−3.99 (m, 1 H, H-4^{Ara-B}), 3.81−3.78 (m, 1 H, −OCH_2CH$_2$−), 3.65−3.60 (m, 2 H, H-5a^{Ara-A}, H-5a^{Ara-B}), 3.57−3.53 (m, 2 H, H-5b^{Ara-A}, H-5b^{Ara-B}), 3.48−3.44 (m, 1 H, −OCH_2CH$_2$−), 3.41−3.34 (m, 2 H, −CH_2N$_3$), 2.31 (t, *J* = 5.4 Hz, 1 H, −O*H*), 1.87−1.82 (m, 2 H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 137.9, 137.8, 137.5, 128.5, 128.4 (3C), 128.0 (2C), 127.9, 127.8 (2C), 127.7, 105.9 (C-1^{Ara-A}), 100.2 (C-1^{Ara-B}), 86.4, 84.1, 83.1, 82.0, 80.9, 80.5, 73.4, 72.7, 72.6, 72.2, 69.5, 64.2, 63.3 (−OCH$_2$CH$_2$−), 48.4 (−CH$_2$N$_3$), 29.1 (−OCH$_2$CH$_2$−); ESI-TOF HRMS *m*/*z* calcd for $C_{41}H_{51}N_4O_9$ $[M + NH_4]^+$ 743.3651, found 743.3666.

*3-Azidopropyl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→2**)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→5**)-2,3-di-O-*

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranoside (13). To a mixture of **11** (141 mg, 0.19 mmol), **12** (200 mg, 0.19 mmol), and MS AW-300 (200 mg) in anhydrous CH_2Cl_2 (5 mL) were added NIS (53 mg, 0.23 mmol) and AgOTf (10 mg, 38 μmol) at −20 °C under a N_2 atmosphere. After the mixture was stirred at −20 °C for 30 min, it was slowly warmed to rt and neutralized with triethylamine. The solution was diluted with CH_2Cl_2 (20 mL), filtered through a pad of Celite, and concentrated. The residue was purified by flash column chromatography (hexane/ethyl acetate 4:1) to afford **13** (168 mg, 53%) as colorless syrup: $[\alpha]_D^{26}$ +1.3 (*c* 1.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.12 (m, 50 H, Ph), 5.55 (dd, *J* = 1.8, 3.6 Hz, 1 H, H-2^{Man-B}), 5.08 (d, *J* = 1.8 Hz, 1 H, H-1^{Man-B}), 5.05 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-B}), 4.96 (s, 1 H, H-1^{Ara-A}), 4.92 (d, *J* = 1.8 Hz, 1 H, H-1^{Man-A}), 4.85−4.83 (m, 2 H, Bn), 4.68−4.51 (m, 13 H, Bn), 4.46−4.38 (m, 4 H, Bn), 4.35 (d, *J* = 10.8 Hz, 1 H, Bn), 4.28 (dd, *J* = 1.8, 3.6 Hz, 1 H, H-2^{Ara-A}), 4.20−4.17 (m, 1 H, H-4^{Ara-A}), 4.10−4.02 (m, 4 H, H-2,3,4^{Ara-B}, H-2^{Man-A}), 3.98−3.91 (m, 4 H, H-3,4^{Ara-A}, H-4,5^{Man-A}, H-3^{Man-B}), 3.89−3.87 (m, 2 H, H-3^{Man-A}, H-4^{Man-B}), 3.81−3.73 (m, 5 H, H-5a^{Ara-B}, H-6a,b^{Man-A}, H-5^{Man-B}, −OCH_2CH$_2$−), 3.64−3.52 (m, 5 H, H-5a,b^{Ara-A}, H-5b^{Ara-B}, H-6a,b^{Man-B}), 3.45−3.41 (m, 1 H, −OCH_2CH$_2$−), 3.36−3.29 (m, 2 H, −CH_2N$_3$), 2.11 (s, 3 H, Ac), 1.82−1.77 (m, 2 H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.1, 138.5 (2C), 138.3, 138.2, 138.1, 138.0, 137.9, 137.8, 137.6, 128.5, 128.4 (3C), 128.3 (4C), 128.2 (2C), 128.0 (2C), 127.8 (3C), 127.7 (2C), 127.6 (3C), 127.5, 127.4 (2C), 127.3, 127.2, 105.6 (C-1^{Ara-A}), 100.1 (C-1^{Ara-B}), 99.6 (C-1^{Man-B}), 98.5 (C-1^{Man-A}), 85.8, 84.0, 83.9, 83.4, 81.2, 79.8, 79.3, 78.2, 75.2, 75.1, 74.6, 74.3, 74.2, 73.29, 73.28, 72.5, 72.4, 72.3, 72.2, 72.0, 71.91, 71.90, 70.0, 69.5, 69.0, 68.7, 68.6, 64.0 (−OCH$_2$CH$_2$−), 48.3 (−CH$_2$N$_3$), 29.0 (−OCH$_2$CH$_2$−), 21.1; ESI-TOF HRMS *m*/*z* calcd for $C_{97}H_{109}N_4O_{20}$ [M + NH_4]$^+$ 1649.7630, found 1649.7637.

3-Azidopropyl 3,4,6-Tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranoside (14). To a solution of **13** (70 mg, 43 μmol) in MeOH (1 mL) was added NaOMe in MeOH (1 M) until the pH value reached 10. The solution was stirred at rt for 3 h before TLC (hexane/ethyl acetate 4:1) indicated the disappearance of **13**. The solution was neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The residue was purified by flash column chromatography (toluene/ethyl acetate 2:1) to afford **14** (62 mg, 91%) as colorless syrup: $[\alpha]_D^{26}$ +12.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.14 (m, 50 H, Ph), 5.13 (d, *J* = 1.8 Hz, 1 H, H-1^{Man-B}), 5.04 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-B}), 4.97 (d, *J* = 1.8 Hz, 1 H, H-1^{Man-A}), 4.95 (s, 1 H, H-1^{Ara-A}), 4.83−4.79 (m, 2 H, Bn), 4.68−4.38 (m, 18 H, Bn), 4.28 (dd, *J* = 1.8, 3.6 Hz, 1 H, H-2^{Ara-A}), 4.19−4.17 (m, 1 H, H-4^{Ara-A}), 4.12−4.11 (m, 1 H, H-2^{Man-B}), 4.09−4.06 (m, 1 H, H-4^{Ara-B}), 4.05−4.02 (m, 3 H, H-2,3^{Ara-B}, H-2^{Man-A}), 3.95−3.91 (m, 3 H, H-3^{Ara-A}, H-4^{Man-A}, H-4^{Man-B}), 3.90−3.87 (m, 1 H, H-3^{Man-A}), 3.85−3.83 (m, 2 H, H-4^{Man-A}, H-3^{Man-B}), 3.80−3.76 (m, 4 H, H-5a^{Ara-B}, H-6a^{Man-A}, H-5^{Man-B}, −OCH_2CH$_2$−), 3.70−3.67 (m, 1 H, H-6a^{Man-B}), 3.63−3.62 (m, 2 H, H-6b^{Man-A}, H-6b^{Man-B}), 3.60−3.58 (m, 1 H, H-5a^{Ara-A}), 3.56−3.53 (m, 2 H, H-5b^{Ara-A}, H-5b^{Ara-B}), 3.44−3.40 (m, 1 H, −OCH_2CH$_2$−), 3.36−3.27 (m, 2 H, −CH_2N$_3$), 2.38 (d, *J* = 2.4 Hz, 1 H, −O*H*), 1.81−1.77 (m, 2 H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 138.5, 138.4, 138.2 (2C), 138.1, 138.0, 137.9, 137.8, 137.6, 128.5, 128.4 (4C), 128.3 (3C), 128.2, 127.9 (3C), 127.8 (4C), 127.7 (3C), 127.6 (3C), 127.5 (2C), 127.3 (2C), 105.6 (C-1^{Ara-A}), 101.1 (C-1^{Man-B}), 100.0 (C-1^{Ara-B}), 98.6 (C-1^{Man-A}), 85.7, 84.0, 83.9, 83.3, 81.1, 80.0, 79.9, 79.3, 75.1, 75.0, 74.8, 74.5, 74.3, 73.29, 73.28, 73.2, 72.5, 72.4, 72.3, 72.27, 72.2, 72.1, 71.6, 70.0, 69.5, 69.0, 68.8, 68.5, 64.0 (−OCH$_2$CH$_2$−), 48.3 (−CH$_2$N$_3$), 29.0 (−OCH$_2$CH$_2$−); ESI-TOF HRMS *m*/*z* calcd for $C_{95}H_{107}N_4O_{19}$ [M + NH_4]$^+$ 1607.7524, found 1607.7535.

3-Aminopropyl α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranoside (1). To a solution of **14** (30 mg, 19 μmol) in acetic acid (2 mL) and H_2O (0.2 mL) was added 10% Pd/C (15 mg). The mixture was stirred under a H_2 atmosphere at rt for 36 h. The mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by gel filtration chromatography to give **1** (13 mg, 96%) as a white solid: $[\alpha]_D^{26}$ +54.7 (*c* 0.2, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 4.98 (s, 1 H, H-1^{Man-A}), 4.95 (d, *J* = 4.2 Hz, 2 H, H-1^{Ara-A}, H-1^{Ara-B}), 4.84 (s, 1 H, H-1^{Man-B}), 4.02−3.96 (m, 2 H), 3.95−3.92 (m, 2 H), 3.89−3.87 (m, 2 H), 3.86−3.83 (m, 2 H), 3.76 (dd, *J* = 3.6, 9.6 Hz, 1 H), 3.73 (t, *J* = 2.4 Hz, 1 H), 3.71−3.63 (m, 5 H), 3.62−3.58 (m, 2 H), 3.55−3.51 (m, 4 H), 3.49−3.41 (m, 3 H), 2.95 (t, *J* = 6.6 Hz, 2 H, −CH_2NH$_2$), 1.83−1.78 (m, 2 H, −CH_2NH$_2$), 1.73 (s, 3 H, Ac); ^{13}C NMR (150 MHz, D_2O) δ 105.3 (C-1^{Ara-A}), 102.2 (C-1^{Man-B}), 100.2 (C-1^{Ara-B}), 98.1 (C-1^{Man-A}), 86.5, 83.4, 79.6, 78.6, 75.8, 74.8, 73.8, 73.1, 72.8, 70.2, 70.0, 69.8, 68.1, 66.8, 66.7, 65.4, 61.0, 60.8, 60.7, 37.7, 26.5, 23.1; ESI-TOF HRMS *m*/*z* calcd for $C_{25}H_{46}NO_{19}$ [M + H]$^+$ 664.2659, found 664.2662.

5-O-tert-Butydimethylsilyl-1,2-O-isopropylidene-β-D-arabinofuranose (18). After a solution of **4** (6.2 g, 23 mmol), 2,2-dimethoxypropane (10 mL), and *p*-toluenesulfonic acid (100 mg) in acetone (20 mL) was stirred at rt for 30 min, it was neutralized with triethylamine and then concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1) to give **18** (6.0 g, 84%) as colorless syrup: $[\alpha]_D^{26}$ −6.1 (*c* 2.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (d, *J* = 4.2 Hz, 1 H, H-1), 4.56 (d, *J* = 3.6 Hz, 1 H, H-2), 4.33 (t, *J* = 3.0 Hz, 1 H, H-3), 3.96−3.94 (m, 1 H, H-4), 3.80−3.75 (m, 2 H, H-5a,b), 1.87 (t, *J* = 4.2 Hz, 1 H, −O*H*), 1.51 (s, 3 H, Me), 1.32 (s, 3 H, Me), 0.89 (s, 9 H, *t*Bu), 0.07 (s, 6 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 112.6, 105.5 (C-1), 87.3, 87.1, 76.5, 63.1, 27.0, 26.2, 25.9, 18.3, −5.3, −5.4; ESI-TOF HRMS *m*/*z* calcd for $C_{14}H_{32}NO_5Si$ [M + NH_4]$^+$ 322.2044, found 322.2047.

3-O-Benzyl-5-O-tert-butydimethylsilyl-1,2-O-isopropylidene-β-D-arabinofuranose (19). To a stirred solution of **18** (2.30 g, 7.57 mmol) in dried DMF (15 mL) was slowly added NaH (605 mg, 60% in kerosene, 15.13 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, and BnBr (1.35 mL, 11.36 mmol) was added dropwise. The mixture was stirred at rt for another 30 min, and then poured into ice water and extracted with ethyl acetate (150 mL). The organic layer was washed with brine (2 × 100 mL), dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **19** (2.50 g, 84%) as colorless syrup: $[\alpha]_D^{26}$ +1.8 (*c* 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.25 (m, 5 H, Ph), 5.89 (d, *J* = 4.2 Hz, 1 H, H-1), 4.65 (d, *J* = 4.2 Hz, 1 H, H-2), 4.57 (s, 2 H, Bn), 4.13 (dt, *J* = 1.8, 6.6 Hz, 1 H, H-4), 4.08 (d, *J* = 1.2 Hz, 1 H, H-3), 3.75 (d, *J* = 6.0 Hz, 2 H, H-5a,b), 1.52 (s, 3 H, C(CH_3)$_2$), 1.32 (s, 3 H, C(CH_3)$_2$), 0.88 (s, 9 H, *t*Bu), 0.05 (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.4, 128.5, 127.8, 127.7, 112.4, 105.7 (C-1), 85.3, 85.2, 82.6, 71.5, 62.8, 27.1, 26.2, 25.9, 18.3, −5.4; ESI-TOF HRMS *m*/*z* calcd for $C_{21}H_{38}NO_5Si$ [M + NH_4]$^+$ 412.2514, found 412.2508.

2-O-Acetyl-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-1,2-O-isopropylidene-β-D-arabinofuranose (21). To a solution of **19** (2.30 g, 5.84 mmol) in THF (15 mL) was added a solution of TBAF in THF (1 M, 7 mL, 7 mmol). The solution was stirred at rt for 2 h and then concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 2:1) to give **20** (1.51 g, 93%) as a white solid. To a mixture of **20** (100 mg, 0.357 mmol), **7** (205 mg, 0.429 mmol), and MS AW-300 (200 mg) in anhydrous CH_2Cl_2 (4 mL) were added NIS (97 mg, 0.429 mmol) and AgOTf (11 mg, 43 μmol) at −20 °C under a N_2 atmosphere. The mixture was stirred at −20 °C for 30 min and then slowly warmed to rt. After TLC (petroleum ether/ethyl acetate 3:1) indicated the completion of reaction, the mixture was neutralized with triethylamine, diluted with CH_2Cl_2 (20 mL), and filtered. The filtrate was concentrated, and the residue was purified by column chromatography (petroleum ether/ethyl acetate 3:1) to give **21** (202 mg, 89%) as colorless syrup: $[\alpha]_D^{26}$ +56.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.25 (m, 15 H, Ph), 5.87 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-A}), 5.11 (s, 1 H, H-2^{Ara-B}), 5.06 (s, 1 H, H-1^{Ara-B}), 4.71 (d, *J* = 12.0 Hz, 1 H, Bn), 4.63 (d, *J* = 4.2 Hz, 1 H, H-2^{Ara-A}), 4.55−4.46 (m, 5 H, Bn), 4.25−4.21 (m, 2 H, H-4^{Ara-A}, H-4^{Ara-B}), 4.10 (d, *J* = 3.0 Hz, 1 H, H-3^{Ara-A}), 3.89 (dd, *J* = 4.8, 10.2 Hz, 1 H, H-5a^{Ara-A}), 3.86 (d, *J* = 5.4 Hz, 1 H, H-3^{Ara-B}), 3.63 (dd, *J* = 4.8, 10.2 Hz, 1 H, H-5b^{Ara-A}), 3.60 (dd, *J* = 3.6, 10.8 Hz, 1 H, H-5a^{Ara-B}), 3.53 (dd, *J* = 4.8, 10.8 Hz, 1 H, H-

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

5b^{Ara-B}), 2.00 (s, 3 H, Ac), 1.50 (s, 3 H, C(CH_3)$_2$), 1.31 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 138.0, 137.7, 137.4, 128.4, 128.3, 127.9, 127.8 (2C), 127.73, 127.7, 127.6, 112.8, 106.2 (C-1^{Ara-B}), 105.6 (C-1^{Ara-A}), 85.3, 83.2, 83.0, 82.8, 82.1, 81.4, 73.4, 72.1, 71.7, 69.1, 66.6, 27.1, 26.3, 20.9; ESI-TOF HRMS m/z calcd for $C_{36}H_{46}NO_{10}$ [M + NH_4]$^+$ 652.3116, found 652.3124.

2,3-Di-O-benzyl-5-O-tert-butydimethylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-1,2-O-isopropylidene-β-D-arabinofuranose (23). To a solution of **21** (1.18 g, 1.86 mmol) in MeOH (10 mL) was added NaOMe in MeOH (1 M) until the pH value reached 10. The solution was stirred at rt for 3 h when TLC (petroleum ether/ethyl acetate 3:1) indicated the disappearance of **21**. The solution was neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **22** (995 mg, 90%) as colorless syrup. To a mixture of **22** (996 mg, 1.68 mmol), **6** (1.11 g, 2.02 mmol), and MS AW-300 (800 mg) in CH_2Cl_2 (10 mL) were added NIS (454 mg, 2.02 mmol) and AgOTf (51 mg, 0.20 mmol) at −60 °C under a N_2 atmosphere. The mixture was stirred at −60 °C for 30 min, and then slowly warmed to rt and neutralized with triethylamine. The mixture was diluted with CH_2Cl_2 (50 mL), filtered through a pad of Celite, and concentrated. Purification of the residue by column chromatography with petroleum ether/ethyl acetate (4:1) as the eluents gave **23** (976 mg, 57%) as colorless syrup: $[\alpha]_D^{26}$ −19.2 (*c* 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.24 (m, 25 H, Ph), 5.88 (d, *J* = 3.6 Hz, 1 H, H-1^{Ara-A}), 5.05 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-C}), 5.04 (s, 1 H, H-1^{Ara-B}), 4.69−4.58 (m, 5 H, H-2^{Ara-A}, Bn), 4.54−4.46 (m, 6 H, Bn), 4.29 (d, *J* = 1.8 Hz, 1 H, H-2^{Ara-B}), 4.22 (m, 2 H, H-4^{Ara-A}, H-4^{Ara-C}), 4.08−4.04 (m, 3 H, H-3^{Ara-A}, H-2^{Ara-B}, H-3^{Ara-C}), 4.00−3.95 (m, 2 H, H-3,4^{Ara-B}), 3.90 (dd, *J* = 4.8, 10.2 Hz, 1 H, H-5), 3.73−3.55 (m, 5 H, 5 × H-5), 1.51 (s, 3 H, C(CH_3)$_2$), 1.33 (s, 3 H, C(CH_3)$_2$), 0.85 (s, 9 H, *t*Bu), 0.00 (s, 6 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.1, 138.0, 137.7, 137.4, 128.4, 128.3 (3C), 127.9, 127.8 (3C), 127.7, 127.6 (2C), 127.5, 112.9, 106.1 (C-1^{Ara-B}), 105.5 (C-1^{Ara-A}), 100.5 (C-1^{Ara-C}), 86.0, 85.4, 84.3, 84.04, 84.03, 82.9, 82.8, 82.2, 81.5, 73.3, 72.5, 72.3, 72.2, 71.7, 70.0, 66.6, 65.4, 27.3, 26.5, 25.9, 18.3, −5.28, −5.32; ESI-TOF HRMS m/z calcd for $C_{59}H_{78}NO_{13}Si$ [M + NH_4]$^+$ 1036.5237, found 1036.5262.

2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-1,2-O-isopropylidene-β-D-arabinofuranose (25). To a solution of **23** (660 mg, 648 μmol) in THF (5 mL) was added a solution of TBAF in THF (1.0 M, 1.3 mL, 1.30 mmol) at rt, and the solution was stirred at rt for 3 h. After concentration, the residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **17** (540 mg, 92%) as colorless syrup. To a mixture of **17** (260 mg, 288 μmol), **24** (219 mg, 345 μmol), and MS AW-300 (300 mg) in dry CH_2Cl_2 (4 mL) was added TMSOTf (6 μL, 35 μmol) at −20 °C under a N_2 atmosphere. The mixture was stirred at −20 °C for 30 min and then slowly warmed to rt. The mixture was neutralized with triethylamine, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate 3:1) to give **25** (360 mg, 91%) as colorless syrup: $[\alpha]_D^{26}$ +4.4 (*c* 0.75, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.19 (m, 38 H, Ph), 7.12−7.10 (m, 2 H, Ph), 5.86 (d, *J* = 3.6 Hz, 1 H, H-1^{Ara-A}), 5.33 (s, 1 H, H-2^{Man}), 5.03 (d, *J* = 3.6 Hz, 1 H, H-1^{Ara-C}), 5.00 (s, 1 H, H-1^{Ara-B}), 4.80−4.78 (m, 2 H, H-1^{Man}, Bn), 4.66−4.42 (m, 14 H, Bn, H-2^{Ara-A}), 4.35−4.37 (d, *J* = 12.6 Hz, 1 H, Bn), 4.27 (d, *J* = 11.4 Hz, 2 H, H-2^{Ara-B}, Bn), 4.21−4.16 (m, 2 H, H-4^{Ara-A}, H-4^{Ara-C}), 4.05−4.01 (m, 4 H, H-3^{Ara-A}, H-4^{Ara-B}, H-2,3^{Ara-C}), 3.97 (dd, *J* = 3.0, 6.6 Hz, 1 H, H-3^{Ara-B}), 3.91−3.86 (m, 3 H, H-3,5^{Man}, H-5^{Ara}), 3.78−3.71 (m, 3 H, H-4^{Man}, H-5^{Ara}), 3.62−3.51 (m, 5 H, H-5^{Ara}, H-6a,b^{Man}), 2.11 (s, 3 H, Ac), 1.49 (s, 3 H, C(CH_3)$_2$), 1.31 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 138.4, 138.2, 138.1, 137.9, 137.8 (2C), 137.5, 137.4, 128.5, 128.4 (2C), 128.3 (2C), 128.2 (2C), 128.0, 127.9, 127.8 (3C), 127.7 (4C), 127.6 (2C), 127.5 (3C), 112.9, 106.0 (C-1^{Ara-B}), 105.5 (C-1^{Ara-A}), 100.5 (C-1^{Ara-C}), 97.8 (C-1^{Man}), 86.0, 85.3, 84.0, 83.7, 83.6, 82.83, 82.79, 81.3, 79.2, 78.3, 75.1, 74.0, 73.4, 73.3, 72.5, 72.33, 72.3, 71.72, 71.7, 69.8, 69.6, 68.5, 68.46, 66.7, 27.2, 26.4, 21.1; ESI-TOF HRMS m/z calcd for $C_{82}H_{94}NO_{19}$ [M + NH_4]$^+$ 1396.6415, found 1396.6450.

3,4,6-Tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-1,2-O-isopropylidene-β-D-arabinofuranose (26). To a solution of **25** (80 mg, 58 μmol) in MeOH (1 mL) was added NaOMe in MeOH (1M) until the pH value reached 10. The solution was stirred at rt for 3 h, and then neutralized with Amberlite IR 120 (H^+), filtered and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **26** (72 mg, 93%) as colorless syrup: $[\alpha]_D^{26}$ +4.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.20 (m, 38 H, Ph), 7.14−7.13 (m, 2 H, Ph), 5.86 (d, *J* = 3.6 Hz, 1 H, H-1^{Ara-A}), 5.03 (d, *J* = 4.8 Hz, 1 H, H-1^{Ara-C}), 5.02 (s, 1 H, H-1^{Ara-B}), 4.87 (s, 1 H, H-1^{Man}), 4.79 (d, *J* = 9.6 Hz, 1 H, Bn), 4.66−4.38 (m, 16 H, Bn, H-2^{Ara-A}), 4.28−4.27 (m, 1 H, H-2^{Ara-B}), 4.21−4.20 (m, 1 H, H-4^{Ara-A}), 4.19−4.16 (m, 1 H, H-4^{Ara-B}), 4.08−3.97 (m, 6 H), 3.89−3.85 (m, 2 H), 3.79−3.76 (m, 2 H), 3.73−3.68 (m, 2 H), 3.62−3.52 (m, 5 H), 2.49 (d, *J* = 2.4 Hz, 1 H, −O*H*), 1.49 (s, 3 H, C(CH_3)$_2$), 1.31 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 138.1, 138.0, 137.9 (2C), 137.8, 137.5, 137.4, 128.5, 128.4 (3C), 128.3 (4C), 128.0, 127.9, 127.8 (3C), 127.7 (4C), 127.6 (2C), 127.5, 112.9, 106.0 (C-1^{Ara-B}), 105.5 (C-1^{Ara-A}), 100.4 (C-1^{Ara-C}), 99.3 (C-1^{Man}), 86.2, 85.3, 84.0, 83.8, 83.2, 82.84, 82.81, 81.3, 80.1, 79.3, 75.0, 74.0, 73.4, 73.3, 72.5, 72.4, 72.3, 71.8, 71.7, 71.3, 69.6, 68.9, 68.6, 68.1, 66.7, 27.2, 26.4; ESI-TOF HRMS m/z calcd for $C_{80}H_{92}NO_{18}$ [M + NH_4]$^+$ 1354.6309, found 1354.6323.

2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1 → 5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-1,2-O-isopropylidene-β-D-arabinofuranose (27). To a mixture of **24** (323 mg, 509 μmol), **26** (340 mg, 254 μmol), and MS AW-300 (500 mg) in dry CH_2Cl_2 (5 mL) was added TMSOTf (9 μL, 51 μmol) at 0 °C under a N_2 atmosphere. The mixture was stirred at 0 °C for 30 min, and then slowly warmed to rt, neutralized with triethylamine. The mixture was diluted with CH_2Cl_2 (50 mL), filtered through a pad of Celite, and concentrated. Purification of the residue by column chromatography with petroleum ether/ethyl acetate (3:1) as the eluents gave **27** (391 mg, 85%) as colorless syrup: $[\alpha]_D^{26}$ +8.8 (*c* 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31−7.11 (m, 55 H, Ph), 5.86 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-A}), 5.52 (s, 1 H, H-2^{Man-B}), 5.05 (s, 1 H, H-1^{Man-B}), 5.03 (s, 1 H, H-1^{Ara-C}), 5.00 (s, 1 H, H-1^{Ara-B}), 4.90 (s, 1 H, H-1^{Man-A}), 4.81 (d, *J* = 10.8 Hz, 2 H, Bn), 4.66−4.32 (m, 21 H, Bn, H-2^{Ara-A}), 4.28 (d, *J* = 1.2 Hz, 1 H, H-2^{Ara-B}), 4.22−4.17 (m, 2 H, H-4^{Ara-A}, H-4^{Ara-C}), 4.06−4.04 (m, 2 H, H-3^{Ara-A}, H-4^{Ara-B}), 4.01−3.99 (m, 3 H, H-2, 3^{Ara-C}, H-2^{Man-A}), 3.94 (m, 2 H, H-3^{Ara-B}, H-3^{Man-B}), 3.91−3.82 (m, 5 H, H-3,4,5^{Man-A}, H-5^{Man-B}, H-5^{Ara-A}), 3.80−3.77 (dd, *J* = 6.6, 10.2 Hz, 1 H, H-5^{Ara}), 3.74−3.70 (m, 3 H, H-4^{Man-B}, H-5^{Ara}, H-6^{Man}), 3.62−3.50 (m, 6 H, 3 × H-5^{Ara}, 3 × H-6^{Man}), 2.09 (s, 3 H, Ac), 1.49 (s, 3 H, C(CH_3)$_2$), 1.31 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 138.5, 138.4, 138.2, 138.13, 138.06, 138.0, 137.9, 137.8, 137.5, 137.4, 128.5, 128.43, 128.4, 128.3 (4C), 128.2 (2C), 128.1, 128.0, 127.9, 127.8 (2C), 127.7 (2C), 127.6 (2C), 127.5 (3C), 127.4, 127.3, 127.1, 112.9, 106.0 (C-1^{Ara-B}), 105.5 (C-1^{Ara-A}), 100.5 (C-1^{Ara-C}), 99.5 (C-1^{Man-B}), 98.5 (C-1^{Man-A}), 86.0, 85.3, 84.0, 83.8, 83.7, 82.85, 82.8, 81.4, 79.8, 79.3, 78.2, 75.1, 75.09, 74.5, 74.3, 74.1, 73.3, 73.25, 73.24, 72.5, 72.3, 72.26, 72.2, 71.9, 71.88, 71.87, 71.7, 69.9, 69.4, 68.9, 68.6, 68.57, 66.7, 27.2, 26.4, 21.1; ESI-TOF HRMS m/z calcd for $C_{109}H_{122}NO_{24}$ [M + NH_4]$^+$ 1828.8351, found 1828.8388.

p-Tolyl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-2-O-acetyl-3-O-benzyl-1-thio-D-arabinofuranoside (15). A solution of **27** (240 mg, 133 μmol) in dioxane (4 mL), 70% AcOH (2 mL), and 10% HCl (0.2 mL) was heated to 50 °C for 8 h, when TLC (petroleum ether/ethyl acetate 3:1) showed the disappearance of **27**. The reaction mixture was cooled to rt and neutralized with saturated aqueous $NaHCO_3$. The mixture was diluted with ethyl acetate (50 mL), and the two phases were separated. The organic phase was washed with water (2 × 50 mL), dried over Na_2SO_4, and then concentrated. After the product was dissolved with *p*-tolyl disulfide (163 mg, 663 μmol) in dried THF (3 mL), *n*-Bu_3P (165 μL,

DOI: 10.1021/acs.joc.5b01686
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663 μmol) was added at 0 °C. The solution was stirred at rt for 6 h and concentrated. The residue was then dissolved in pyridine (3 mL) and Ac_2O (1 mL), and a catalytic amount of DMAP (15 mg) was added. The solution was stirred at rt for 2 h and concentrated. The residue was purified by column chromatography (4:1 petroleum ether/ethyl acetate) to give **15** (203 mg, 80%, α/β 1:1) as syrupy. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.11 (m, 57 H, Ph), 7.02 (d, *J* = 7.8 Hz, 2 H, Ph), 5.52 (s, 1 H, H-2^{Man-B}), 5.47 (d, *J* = 4.2 Hz, 0.5 H, H-2β^{Ara-A}), 5.43 (s, 0.5 H, H-2α^{Ara-A}), 5.41 (dd, *J* = 1.6, 4.2 Hz, 0.5 H, H-1β^{Ara-A}), 5.25 (s, 0.5 H, H-1α^{Ara-A}), 5.21 (d, *J* = 3.6 Hz, 0.5 H, H-1β^{Ara-C}), 5.14 (s, 0.5 H, H-1α^{Ara-C}), 5.05 (d, *J* = 5.4 Hz, 1.5 H, H-1^{Man-B}, H-1β^{Ara-B}), 5.01 (s, 0.5 H, H-1α^{Ara-B}), 4.88 (s, 1 H, H-1^{Man-A}), 4.81 (d, *J* = 10.8 Hz, 2 H, Bn), 4.68−4.32 (m, 20 H, Bn), 4.28 (d, *J* = 1.8 Hz, 1 H, H-2^{Ara-B}), 4.21−4.18 (m, 1 H), 4.13−4.10 (m, 1 H), 4.05−3.84 (m, 12 H), 3.80−3.68 (m, 5 H), 3.59−3.47 (m, 5 H), 2.26 (s, 1.5 H, Ac), 2.25 (s, 1.5 H, Ac), 2.10 (s, 1.5 H, Ph−CH_3), 2.08 (s, 3 H, Ac, Ph−CH_3), 1.95 (s, 1.5 H, Ac); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 170.0, 169.9, 138.5 (2C), 138.4 (2C), 138.2 (2C), 138.1 (2C), 138.0 (2C), 137.9 (2C), 137.8 (2C), 137.6 (4C), 137.5, 137.4, 132.4, 131.5, 130.7, 130.4, 129.8, 129.7, 128.4 (3C), 128.3 (5C), 128.2 (2C), 128.1, 128.0 (2C), 127.9 (2C), 127.8 (2C), 127.7 (6C), 127.6 (4C), 127.5 (2C), 127.4 (2C), 127.3 (2C), 127.1, 106.6, 106.3, 100.5, 100.4, 99.5, 98.5, 91.4, 89.1, 86.0, 85.7, 84.1, 84.0, 83.99, 83.9, 83.8, 83.4, 83.0, 82.9, 81.9, 81.5, 81.34, 81.31, 79.8, 79.3, 78.7, 78.1, 75.12, 75.11, 75.08, 74.5, 74.3, 74.1, 73.29, 73.28, 73.26, 73.23, 72.5, 72.4, 72.3, 72.28, 72.27, 72.25, 72.2, 71.94, 71.9, 71.8, 70.0, 69.9, 69.50, 69.4, 69.0, 68.7, 68.6, 66.3, 65.4, 21.1, 21.06, 21.02, 20.8, 20.7; MALDI-TOF MS *m*/*z* calcd for $C_{115}H_{122}O_{24}SNa$ $[M + Na]^+$ 1941.79, found 1941.47.

*3-Azidopropyl 2-O-Acetyl-3-O-benzyl-5-O-tert-butydimethylsilyl-α-D-arabinofuranoside (**29**).* To a mixture of **28** (500 mg, 0.996 mmol), 3-azido-1-propanol (121 mg, 1.20 mmol), and MS AW-300 (200 mg) in dry CH_2Cl_2 (6 mL) were added NIS (247 mg, 1.10 mmol) and AgOTf (26 mg, 0.10 mmol) at −20 °C under a N_2 atmosphere. The reaction mixture was stirred at −20 °C for 40 min, and then slowly warmed to rt and neutralized with triethylamine. The mixture was diluted with CH_2Cl_2 (30 mL), filtered through a pad of Celite, and concentrated. Purification of the residue by silica gel column chromatography with petroleum ether and ethyl acetate (10:1) as the eluents gave **29** (403 mg, 84%) as colorless syrup: $[\alpha]_D^{26}$ +66.4 (*c* 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.26 (m, 5 H, Ph), 5.10 (s, 1 H, H-2), 4.97 (s, 1 H, H-1), 4.69 (d, *J* = 12.0 Hz, 1 H, Bn), 4.55 (d, *J* = 12.0 Hz, 1 H, Bn), 4.11−4.09 (m, 1 H, H-4), 3.90 (d, *J* = 4.8 Hz, 1 H, H-3), 3.81−3.77 (m, 1 H, −OCH_2CH$_2$−), 3.75−3.70 (m, 2 H, H-5a,b), 3.52−3.49 (m, 1 H, −OCH_2CH$_2$−), 3.42−3.38 (m, 2 H, −CH_2N$_3$), 2.06 (s, 3 H, Ac), 1.88−1.83 (m, 2 H, −OCH$_2$CH_2−), 0.87 (s, 9 H, *t*Bu), 0.04 (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 137.8, 128.3, 127.8, 127.7, 106.0 (C-1), 83.6, 82.9, 81.8, 72.1, 63.7, 62.4, 48.3, 28.9, 25.8, 20.9, 18.3, −5.3, −5.4; ESI-TOF HRMS *m*/*z* calcd for $C_{23}H_{41}N_4O_6Si$ $[M + NH_4]^+$ 497.2790, found 497.2794.

*3-Azidopropyl 2-O-Acetyl-3-O-benzyl-α-D-arabinofuranoside (**30**).* To a solution of **29** (330 mg, 0.69 mmol) and TBAF (0.83 mmol) in THF (5.8 mL) was added AcOH (79 μL, 1.38 mmol). The solution was stirred at rt for 6 h and then concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **30** (230 mg, 92%) as colorless syrup: $[\alpha]_D^{26}$ +116.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.27 (m, 5 H, Ph), 5.10 (d, *J* = 1.2 Hz, 1 H, H-2), 4.98 (s, 1 H, H-1), 4.73 (d, *J* = 12.0 Hz, 1 H, Bn), 4.54 (d, *J* = 11.4 Hz, 1 H, Bn), 4.16−4.14 (m, 1 H, H-4), 3.90 (d, *J* = 6.0 Hz, 1 H, H-3), 3.85−3.78 (m, 2 H, H-5, −OCH_2CH$_2$−), 3.63−3.60 (m, 1 H, H-5), 3.53−3.49 (m, 1 H, −OCH_2CH$_2$−), 3.44−3.37 (m, 2 H, −CH_2N$_3$), 2.07 (s, 3 H, Ac), 1.88−1.84 (m, 2 H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 137.6, 128.4, 127.9, 106.1 (C-1), 83.1, 82.6, 81.7, 72.4, 63.9, 61.8, 48.2, 28.9, 20.9; ESI-TOF HRMS *m*/*z* calcd for $C_{17}H_{27}N_4O_6$ $[M + NH_4]^+$ 383.1925, found 383.1934.

*3-Azidopropyl 2-O-Acetyl-3-O-benzyl-5-O-tert-butydimethylsilyl-α-D-arabinofuranosyl-(1→5)-2-O-acetyl-3-O-benzyl-α-D-arabinofuranoside (**31**).* To a mixture of **28** (536 mg, 1.07 mmol), **30** (390 mg, 1.07 mmol), and MS AW-300 (500 mg) in dry CH_2Cl_2 (5 mL) were added NIS (265 mg, 1.18 mmol) and AgOTf (28 mg, 0.11 mmol) at −20 °C under a N_2 atmosphere. The mixture was stirred at −20 °C for 30 min, and then slowly warmed to rt, neutralized with triethylamine, filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 5:1) to give **31** (616 mg, 77%) as colorless syrup: $[\alpha]_D^{26}$ +100.3 (*c* 2.5 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.25 (m, 10 H, Ph), 5.16 (s, 1 H, H-2^{Ara-B}), 5.07 (s, 2 H, H-1^{Ara-B}, H-2^{Ara-A}), 4.96 (s, 1 H, H-1^{Ara-A}), 4.69 (d, *J* = 12.0 Hz, 1 H, Bn), 4.64 (d, *J* = 12.0 Hz, 1 H, Bn), 4.53 (d, *J* = 12.0 Hz, 2 H, Bn), 4.22−4.20 (m, 1 H, H-4^{Ara-A}), 4.02−3.99 (m, 1 H, H-4^{Ara-B}), 3.96 (d, *J* = 5.4 Hz, 1 H, H-3^{Ara-A}), 3.87 (d, *J* = 4.8 Hz, 1 H, H-3^{Ara-B}), 3.83 (dd, *J* = 4.2, 11.4 Hz, 1 H, H-5a^{Ara-A}), 3.80−3.76 (m, 1 H, −OCH_2CH$_2$−), 3.68−3.63 (m, 3 H, H-5b^{Ara-A}, H-5a,b^{Ara-B}), 3.50−3.47 (m, 1 H, −OCH_2CH$_2$−), 3.40−3.36 (m, 2 H, −CH_2N$_3$), 2.05 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.86−1.82 (m, 2 H, −OCH$_2$CH_2−), 0.85 (s, 9 H, *t*Bu), 0.02 (s, 3 H, SiMe), 0.01 (s, 3 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 169.7, 137.9, 137.8, 128.3 (2C), 127.7 (3C), 106.0 (C-1^{Ara-B}), 105.9 (C-1^{Ara-A}), 83.8, 83.2, 83.1, 81.7, 81.64, 81.62, 72.3, 72.1, 65.4, 63.8 (−OCH$_2$CH$_2$−), 62.3, 48.3 (−CH$_2$N$_3$), 28.9 (−OCH$_2$CH$_2$−), 25.8, 20.9, 20.8, 18.3, −5.3, −5.4; ESI-TOF HRMS *m*/*z* calcd for $C_{37}H_{57}N_4O_{11}Si$ $[M + NH_4]^+$ 761.3788, found 761.3793.

*3-Azidopropyl 2-O-Acetyl-3-O-benzyl-α-D-arabinofuranosyl-(1→5)-2-O-acetyl-3-O-benzyl-α-D-arabinofuranoside (**16**).* To a solution of **31** (200 mg, 0.269 mmol) and TBAF (0.54 mmol) in dry THF (2.5 mL) was added AcOH (31 μL, 0.538 mmol). The mixture was stirred at rt for 6 h and then concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **16** (157 mg, 93%) as colorless syrup: $[\alpha]_D^{26}$ +132.7 (c 0.2 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.25 (m, 10 H, Ph), 5.16 (d, *J* = 0.6 Hz, 1 H, H-2^{Ara-B}), 5.09 (s, 1 H, H-1^{Ara-B}), 5.08 (d, *J* = 1.8 Hz, 1 H, H-2^{Ara-A}), 4.98 (s, 1 H, H-1^{Ara-A}), 4.75−4.68 (m, 2 H, Bn), 4.56−4.52 (m, 2 H, Bn), 4.23−4.21 (m, 1 H, H-4^{Ara-A}), 4.03−4.01 (m, 1 H, H-4^{Ara-B}), 3.97 (d, *J* = 6.0 Hz, 1 H, H-3^{Ara-A}), 3.86−3.77 (m, 4 H, H-3^{Ara-B}, H-5a^{Ara-A}, H-5a^{Ara-B}, −OCH_2CH$_2$−), 3.69−3.66 (m, 1 H, H-5b^{Ara-A}), 3.56−3.53 (m, 1 H, H-5b^{Ara-B}), 3.51−3.48 (m, 1 H, −OCH_2CH$_2$−), 3.41−3.38 (m, 2 H, −CH_2N$_3$), 2.06 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.86−1.84 (m, 2 H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 169.7, 137.8, 137.7, 128.4 (2C), 127.8 (2C), 127.7 (2C), 106.1 (C-1^{Ara-B}), 105.9 (C-1^{Ara-A}), 83.3, 83.1, 82.9, 81.6 (2C), 81.5, 72.3, 72.2, 65.6, 63.9 (−OCH$_2$CH$_2$−), 61.8, 48.3 (−CH$_2$N$_3$), 28.9 (−OCH$_2$CH$_2$−), 20.9, 20.8; ESI-TOF HRMS *m*/*z* calcd for $C_{31}H_{43}N_4O_{11}$ $[M + NH_4]^+$ 647.2923, found 647.2926.

*3-Azidopropyl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-2-O-acetyl-3-O-benzyl-α-D-arabinofuranosyl-(1→5)-2-O-acetyl-3-O-benzyl-α-D-arabinofuranosyl-(1→5)-2-O-acetyl-3-O-benzyl-α-D-arabinofuranoside (**32**).* To a mixture of **15** (150 mg, 78 μmol), **16** (60 mg, 94 μmol), and MS AW-300 (150 mg) in dry CH_2Cl_2 (2 mL) were added NIS (21 mg, 94 μmol) and AgOTf (4 mg, 16 μmol) at 0 °C under a N_2 atmosphere. The mixture was stirred at 0 °C for 40 min, and then slowly warmed to rt, neutralized with triethylamine, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate 2:1) to give **32** (154 mg, 81%) as colorless syrup: $[\alpha]_D^{26}$ +24.8 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.10 (m, 65 H, Ph), 5.51 (dd, *J* = 1.8, 3.6 Hz, 1 H, H-2^{Man-B}), 5.12 (d, *J* = 1.2 Hz, 1 H, H-2^{Ara}), 5.10 (d, *J* = 1.8 Hz, 1 H, H-2^{Ara}), 5.06 (s, 3 H, 2 × H-1^{Ara}, H-2^{Ara}), 5.05 (d, *J* = 1.2 Hz, 1 H, H-1^{Man-B}), 5.03 (s, 1 H, H-1^{Ara-E}), 5.02 (s, 1 H, H-1^{Ara-D}), 4.95 (s, 1 H, H-1^{Ara}), 4.88 (d, *J* = 1.8 Hz, 1 H, H-1^{Man-A}), 4.79 (d, *J* = 10.8 Hz, 2 H, Bn), 4.66−4.32 (m, 24 H, Bn,), 4.27 (dd, *J* = 0.6, 2.4 Hz, 1 H, H-2^{Ara-E}), 4.20−4.18 (m, 1 H), 4.10−4.06 (m, 2 H), 4.04−3.97 (m, 5 H), 3.95−3.69 (m, 17 H), 3.63−3.46 (m, 9 H), 3.40−3.35 (m, 2 H, −CH_2N$_3$), 2.08 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.95 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 1.86−1.81 (m, 2 H, −OCH$_2$CH_2−); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.8 (2C), 138.4, 138.3, 138.1 (2C), 138.0, 137.9, 137.8 (3C), 137.5 (2C), 128.4 (2C), 128.3 (6C), 128.2, 128.1, 128.0, 127.9 (2C), 127.8 (2C), 127.7 (3C), 127.6 (3C), 127.5 (3C), 127.4 (3C), 127.1, 106.3 (C-1), 106.1 (C-1), 105.95 (C-1), 105.9 (C-1), 100.6 (C-1^{Ara-E}), 99.5 (C-1^{Man-B}), 98.5 (C-1^{Man-A}), 86.1, 84.1, 83.9,

DOI: 10.1021/acs.joc.5b01686
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83.8, 83.3, 83.2, 83.0, 82.04, 82.0, 81.68, 81.65, 81.6, 81.5, 81.4, 79.8, 79.3, 78.1, 75.15, 75.1, 74.4, 74.3, 74.1, 73.3, 73.2, 72.38, 72.37, 72.3, 72.2, 72.18, 72.15, 71.9, 71.88, 71.86, 70.0, 69.3, 68.9, 68.6, 68.5, 65.49, 65.36, 65.35, 63.8, 48.3, 29.7, 28.9, 21.1, 20.9, 20.85, 20.81, 20.8; ESI-TOF HRMS m/z calcd for $C_{139}H_{161}N_5O_{35}$ $[M + 2NH_4]^{2+}$ 1230.0481, found 1230.0490.

3-Azidopropyl 3,4,6-Tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-α-D-arabinofuranosyl-(1→5)-3-O-benzyl-α-D-arabinofuranoside (33). To a solution of **32** (87 mg, 36 μmol) in MeOH (2 mL) and THF (2 mL) was added NaOMe in MeOH (1 M) until the pH value reached 10. After the mixture was stirred at rt for 3 h, it was neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The residue was purified by column chromatography (ethyl acetate-toluene 2:1) to give **33** (70 mg, 86%) as colorless syrup: $[\alpha]_D^{26}$ +48.3 (c 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.13 (m, 65 H, Ph), 5.12 (s, 1 H, H-1^{Ara-E}), 5.00 (s, 1 H, H-1^{Ara}), 4.95−4.92 (m, 4 H, H-1^{Man-A}, H-1^{Man-B}, H-1^{Ara-D}, H-1^{Ara}), 4.84 (s, 1 H, H-1^{Ara}), 4.80−4.77 (m, 2 H, Bn), 4.68 (d, J = 12.6 Hz, 1 H, Bn), 4.61 (d, J = 12.6 Hz, 1 H, Bn), 4.58−4.33 (m, 21 H, Bn), 4.27−4.24 (m, 2 H), 4.11−4.09 (m, 3 H), 4.03−4.00 (m, 3 H), 3.97−3.96 (m, 1 H), 3.94−3.71 (m, 15 H), 3.68−3.64 (m, 5 H), 3.60 (d, J = 10.2 Hz, 2 H), 3.54−3.49 (m, 4 H), 3.43−3.35 (m, 7 H), 3.24 (d, J = 10.2 Hz, 1 H), 3.17 (d, J = 9.6 Hz, 1 H), 3.03 (d, J = 9.6 Hz, 1 H), 2.37 (s, 1 H), 1.88−1.84 (m, 2 H, $-OCH_2CH_2-$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5 (2C), 138.4, 138.2, 138.0, 137.9, 137.8, 137.6, 137.3 (2C), 137.1, 129.0, 128.5, 128.4 (4C), 128.3 (2C), 128.2 (2C), 128.0 (2C), 127.9 (3C), 127.8 (3C), 127.7 (5C), 127.6 (3C), 127.5 (2C), 127.3 (2C), 109.3 (C-1), 108.5 (C-1), 108.1 (C-1), 105.0 (C-1^{Ara-D}), 101.8 (C-1^{Ara-E}), 99.9 (C-1^{Man-B}), 98.6 (C-1^{Man-A}), 85.0, 84.1, 83.9, 83.8, 83.7, 83.6, 83.5, 83.3, 83.2, 82.9, 80.0, 79.9, 79.34, 78.3, 77.4, 75.1, 75.06, 74.7, 74.5, 74.2, 73.29, 73.27, 72.4, 72.3, 72.2, 72.1, 72.0, 71.9, 71.6, 71.5, 71.4, 70.1, 69.2, 69.1, 68.8, 68.4, 66.1, 65.8, 65.4, 63.8, 48.4, 29.0; ESI-TOF HRMS m/z calcd for $C_{131}H_{153}N_5O_{31}$ $[M + 2NH_4]^{2+}$ 1146.0270, found 1146.0282.

3-Aminopropyl α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (2). To a solution of **33** (28 mg, 12 μmol) in AcOH (2 mL) and H_2O (0.2 mL) was added 10% Pd/C (13 mg). The mixture was stirred under a H_2 atmosphere at rt for 48 h. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified by gel filtration column chromatography to give **2** (13 mg, 94%) as a white solid: $[\alpha]_D^{26}$ +15.0 (c 0.1, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.00 (s, 1 H, H-1^{Ara-D}), 4.98 (s, 1 H, H-1^{Man-A}), 4.97 (d, J = 4.2 Hz, 1 H, H-1^{Ara-E}), 4.91 (s, 2 H), 4.85 (s, 1 H), 4.84 (s, 1 H, H-1^{Man-B}), 4.04−4.00 (m, 4 H), 3.98−3.88 (m, 8 H), 3.86−3.81 (m, 5 H), 3.78−3.58 (m, 16 H), 3.56−3.41 (m, 8 H), 2.96−2.94 (m, 2 H, $-CH_2NH_2$), 1.81−1.79 (m, 2 H, $-OCH_2CH_2-$), 1.73 (s, 3 H, Ac); ^{13}C NMR (150 MHz, D_2O) δ 107.44, 107.41, 107.2, 105.5 (C-1^{Ara-D}), 102.2 (C-1^{Man-B}), 100.4 (C-1^{Ara-E}), 98.1 (C-1^{Man-A}), 86.8, 83.1, 82.6, 82.3, 82.2, 80.8, 80.7, 80.5, 79.7, 78.6, 76.6, 76.59, 76.4, 75.9, 75.0, 74.0, 73.2, 72.8, 70.2, 70.1, 69.9, 68.2, 67.0, 66.8, 66.6, 65.7, 61.1, 60.8, 60.6, 37.8 ($-CH_2NH_2$), 26.4 ($-OCH_2CH_2-$), 23.2; ESI-TOF HRMS m/z calcd for $C_{40}H_{70}NO_{31}$ $[M + H]^+$ 1060.3926, found 1060.3933.

2-O-Acetyl-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[2-O-acetyl-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-1,2-O-isopropylidene-β-D-arabinofuranose (35). To a solution of **18** (340 mg, 1.12 mmol) in THF (3 mL) was added TBAF in THF (1.0 M, 1.68 mL, 1.68 mmol) at rt. The mixture was stirred for 2 h and then concentrated. Purification of the residue by column chromatography with ethyl acetate as the eluents gave **34** (180 mg, 85%) as a white foamy solid. After a mixture of **34** (128 mg, 0.67 mmol), **7** (805 mg, 1.68 mmol), and MS AW-300 (500 mg) in dry CH_2Cl_2 (8 mL) was cooled to −20 °C, NIS (379 mg, 1.68 mmol) and AgOTf (44 mg, 0.17 mmol) were added under a N_2 atmosphere. The mixture was stirred and slowly warmed to rt in 1 h, and then neutralized with triethylamine, diluted with CH_2Cl_2 (50 mL), filtered through a pad of Celite, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 4:1) to give **35** (501 mg, 83%) as colorless syrup: $[\alpha]_D^{26}$ +99.9 (c 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.22 (m, 20 H, Ph), 5.86 (d, J = 4.2 Hz, 1 H, H-1^{Ara-A}), 5.15 (s, 1 H, H-1^{Ara-B2}), 5.11 (s, 1 H, H-2^{Ara-B1}), 5.07 (s, 1 H, H-1^{Ara-B1}), 5.05 (s, 1 H, H-2^{Ara-B2}), 4.68 (d, J = 12.0 Hz, 1 H, Bn), 4.63 (d, J = 12.0 Hz, 1 H, Bn), 4.61 (d, J = 4.2 Hz, 1 H, H-2^{Ara-A}), 4.52−4.49 (m, 4 H, Bn), 4.43−4.40 (m, 2 H, Bn), 4.33 (d, J = 3.2 Hz, 1 H, H-3^{Ara-A}), 4.28−4.26 (m, 1 H, H-4^{Ara-B1}), 4.21−4.19 (m, 1 H, H-4^{Ara-B2}), 4.18−4.16 (m, 1 H, H-4^{Ara-A}), 3.94 (d, J = 5.4 Hz, 1 H, H-3^{Ara-B2}), 3.90 (dd, J = 5.4, 10.2 Hz, 1H, H-5a^{Ara-A}), 3.85 (d, J = 5.4 Hz, 1H, H-3^{Ara-B1}), 3.66 (dd, J = 5.4, 10.2 Hz, 1 H, H-5b^{Ara-A}), 3.61−3.56 (m, 2 H, H-5a^{Ara-B1}, H-5a^{Ara-B2}), 3.53−3.48 (m, 2 H, H-5b^{Ara-B1}, H-5b^{Ara-B2}), 1.98 (s, 3 H, Ac), 1.97 (s, 3 H, Ac), 1.49 (s, 3 H, C(CH_3)$_2$), 1.30 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 169.7, 138.1, 138.0, 137.9, 137.7, 128.3 (3C), 127.8 (2C), 127.7 (2C), 127.6 (3C), 113.1, 106.0 (C-1^{Ara-B1}), 105.4 (C-1^{Ara-A}), 105.0 (C-1^{Ara-B2}), 85.2, 83.1, 83.0, 82.8, 82.2, 82.0, 81.9, 81.4, 79.8, 73.35, 73.34, 72.1, 71.9, 68.9, 68.7, 66.3, 27.2, 26.6, 20.9, 20.8; ESI-TOF HRMS m/z calcd for $C_{50}H_{62}NO_{15}$ $[M + NH_4]^+$ 916.4114, found 916.4136.

3,5-Di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-1,2-O-isopropylidene-β-D-arabinofuranose (36). To a solution of **35** (450 mg, 0.50 mmol) in MeOH (5 mL) was added NaOMe in MeOH (1 M) until the pH value reached 10. The mixture was stirred at rt for 4 h, and then neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **36** (350 mg, 86%) as colorless syrup: $[\alpha]_D^{26}$ +95.6 (c 4.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.23 (m, 20 H, Ph), 5.83 (d, J = 4.2 Hz, 1 H, H-1^{Ara-A}), 5.14 (s, 1 H, H-1^{Ara-B2}), 5.03 (s, 1 H, H-2^{Ara-B1}), 4.64−4.53 (m, 5 H, Bn, H-2^{Ara-A}), 4.47−4.41 (m, 4 H, Bn), 4.35 (dd, J = 0.6, 3.6 Hz, 1 H), 4.29−4.28 (m, 1 H), 4.27−4.26 (m, 1 H), 4.15−4.12 (m, 2 H), 4.11 (s, 1 H), 3.90 (dd, J = 5.4, 11.4 Hz, 1 H), 3.86−3.82 (m, 2 H), 3.69 (dd, J = 5.4, 10.8 Hz, 1 H), 3.54−3.50 (m, 2 H), 3.42−3.38 (m, 2 H), 1.52 (s, 3 H, C(CH_3)$_2$), 1.32 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.9, 137.8, 137.1, 136.9, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8 (3C), 127.7 (2C), 127.6, 113.2, 109.2 (C-1^{Ara-B1}), 107.7 (C-1^{Ara-A}), 105.2 (C-1^{Ara-B2}), 85.5, 85.1, 84.9, 83.9, 83.1, 82.9, 79.4, 78.2, 77.4, 73.7, 73.6, 71.9, 71.8, 69.65, 69.6, 66.7, 27.3, 26.7; ESI-TOF HRMS m/z calcd for $C_{46}H_{58}NO_{13}$ $[M + NH_4]^+$ 832.3903, found 832.3919.

2,3-Di-O-benzyl-5-O-tert-butydimethylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-O-benzyl-5-O-tert-butydimethylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-1,2-O-isopropylidene-β-D-arabinofuranose (37). To a mixture of **6** (845 mg, 1.53 mmol), **36** (500 mg, 0.61 mmol), and MS AW-300 (800 mg) in dry CH_2Cl_2 (10 mL) that was cooled to −60 °C, were added NIS (412 mg, 1.83 mmol) and AgOTf (46 mg, 0.18 mmol) under a N_2 atmosphere. After the mixture was stirred at −60 °C for 40 min, it was warmed to rt, neutralized with triethylamine, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate 4:1) to give **37** (406 mg, 40%) as colorless syrup: $[\alpha]_D^{26}$ −12.4 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.21 (m, 40 H, Ph), 5.79 (d, J = 3.6 Hz, 1 H, H-1^{Ara-A}), 5.13 (s, 1 H, H-1^{Ara-B2}), 5.07 (d, J = 4.2 Hz, 1 H, H-1^{Ara-C1}), 5.04 (s, 1 H, H-1^{Ara-B1}), 4.99 (d, J = 3.6 Hz, 1 H, H-1^{Ara-C2}), 4.67−4.38 (m, 17 H, Bn, H-2^{Ara-A}), 4.31−4.30 (m, 2 H, H-3^{Ara-A}, H-2^{Ara-B1}), 4.27−4.24 (m, 2 H, H-2^{Ara-B2}, H-4^{Ara-C1}), 4.18−4.16 (m, 1 H, H-4^{Ara-C2}), 4.14−4.11 (m, 1 H, H-4^{Ara-A}), 4.06−3.99 (m, 6 H, H-3^{Ara-B1}, H-3^{Ara-B2}, H-2,3^{Ara-C1}, H-2,3^{Ara-C2}), 3.97−3.92 (m, 3 H, H-4^{Ara-B1}, H-4^{Ara-B2}, H-5a^{Ara-A}), 3.71−3.61 (m, 5 H, H-5b^{Ara-A}, H-5a,b^{Ara-B1}, H-5a,b^{Ara-B2}), 3.57−3.50 (m, 4 H, H-5a,b^{Ara-C1}, H-5a,b^{Ara-C2}), 1.50 (s, 3 H, C(CH_3)$_2$), 1.29 (s, 3 H, C(CH_3)$_2$), 0.84 (s, 9 H, tBu), 0.83 (s, 9 H, tBu), −0.01 (s, 6 H, SiMe), −0.02 (s, 6 H, SiMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.2 (2C), 138.1, 138.0, 137.7 (2C), 128.4 (2C), 128.3 (3C), 128.2 (2C), 127.9 (2C), 127.8, 127.6 (4C), 127.5 (3C), 127.4 (2C), 113.2, 106.0 (C-1^{Ara-B1}), 105.3 (C-1^{Ara-A}), 104.5 (C-1^{Ara-B2}), 100.6 (C-1^{Ara-C1}), 100.3 (C-1^{Ara-C2}), 86.3, 86.0, 85.5, 84.2 (2C), 84.1, 84.0 (2C), 83.0, 82.2, 82.1, 81.7, 81.1, 79.6, 73.23, 73.21, 72.5, 72.4, 72.3, 72.2, 72.19, 72.1, 69.8, 69.6, 66.3, 65.4,

DOI: 10.1021/acs.joc.5b01686
J. Org. Chem. 2015, 80, 10060−10075

65.3, 27.3, 26.7, 25.9, 18.28, 18.27, −5.29, −5.3, −5.33, −5.35; ESI-TOF HRMS m/z calcd for $C_{96}H_{126}NO_{21}Si_2$ $[M + NH_4]^+$ 1684.8355, found 1684.8349.

2,3-Di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-1,2-O-isopropylidene-β-D-arabinofuranose (38). To a solution of **37** (240 mg, 144 μmol) in THF (3 mL) was added TBAF in THF (1.0 M, 0.2 mL, 200 μmol). The solution was stirred at rt for 8 h and then concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 1:1) to give **38** (180 mg, 87%) as colorless syrup: $[\alpha]_D^{26}$ +10.7 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.22 (m, 40 H, Ph), 5.81 (d, *J* = 4.3 Hz, 1 H, H-1^{Ara-A}), 5.14 (s, 1 H, H-1^{Ara-B2}), 5.06 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-C1}), 5.03 (s, 1 H, H-1^{Ara-B1}), 4.98 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-C2}), 4.69 (d, *J* = 11.4 Hz, 2 H, Bn), 4.61−4.38 (m, 15 H, Bn, H-2^{Ara-A}), 4.30−4.29 (m, 2 H), 4.25−4.19 (m, 4 H), 4.17−4.12 (m, 4 H), 4.06−4.03 (m, 2 H), 3.98−3.91 (m, 3 H), 3.64−3.46 (m, 9 H), 1.50 (s, 3 H, C(CH_3)$_2$), 1.30 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0 (2C), 137.9 (2C), 137.8, 137.7, 137.51, 137.5, 128.5 (2C), 128.4 (3C), 128.3 (3C), 128.1, 127.9, 127.8 (2C), 127.7 (5C), 127.6, 113.1, 105.8 (C-1^{Ara-B1}), 105.4 (C-1^{Ara}), 104.7 (C-1^{Ara-B2}), 100.1 (C-1^{Ara-C1}), 100.07 (C-1^{Ara-C2}), 86.4, 86.3, 85.2, 84.1, 83.9, 83.2, 82.9, 82.0, 81.9, 81.5, 80.6, 80.56, 80.55, 79.7, 73.3, 72.7, 72.6, 72.57, 72.4, 72.2, 72.1, 69.2, 69.1, 66.7, 63.4, 63.3, 27.2, 26.6; ESI-TOF HRMS m/z calcd for $C_{84}H_{98}NO_{21}$ $[M + NH_4]^+$ 1456.6626, found 1456.6648.

2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-1,2-O-isopropylidene-β-D-arabinofuranose (39). After a mixture of **24** (175 mg, 275 μmol), **38** (180 mg, 125 μmol), and MS AW-300 (200 mg) in dry CH_2Cl_2 (5 mL) was cooled to 0 °C under a N_2 atmosphere, TMSOTf (5 μL, 28 μmol) was added. The mixture was allowed to slowly warm up to rt in 1 h, and then neutralized with triethylamine, filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 3:1) to give **39** (222 mg, 74%) as colorless syrup: $[\alpha]_D^{26}$ +10.9 (*c* 0.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.20 (m, 66 H, Ph), 7.12−7.11 (m, 4 H, Ph), 5.77 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-A}), 5.34−5.32 (m, 2 H, H-2^{Man-A1}, H-2^{Man-A2}), 5.09 (s, 1 H, H-1^{Ara-B2}), 5.07 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-C1}), 5.02 (s, 1 H, H-1^{Ara-B1}), 4.96 (d, *J* = 3.6 Hz, 1 H, H-1^{Ara-C2}), 4.79 (d, *J* = 10.8 Hz, 2H, Bn), 4.77 (d, *J* = 1.2 Hz, 1 H, H-1^{Man-A1}), 4.76 (d, *J* = 1.2 Hz, 1 H, H-1^{Man-A2}), 4.66−4.35 (m, 27 H, Bn, H-2^{Ara-A}), 4.32−4.27 (m, 4 H), 4.24−4.22 (m, 2 H), 4.15−4.12 (m, 1 H), 4.11−4.09 (m, 1 H), 4.05−3.99 (m, 8 H), 3.93−3.86 (m, 5 H), 3.77−3.71 (m, 6 H), 3.61−3.47 (m, 10 H), 2.12 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 1.49 (s, 3H, C(CH_3)$_2$), 1.28 (s, 3H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 170.2, 138.5, 138.4, 138.1 (3C), 138.0, 137.9 (2C), 137.8, 137.6, 137.5 (2C), 128.4 (3C), 128.3 (5C), 128.2, 128.0 (2C), 127.9 (3C), 127.8 (2C), 127.7 (4C), 127.6 (3C), 127.5 (4C), 113.2, 105.9 (C-1^{Ara-B1}), 105.2 (C-1^{Ara-A}), 104.4 (C-1^{Ara-B2}), 100.8 (C-1^{Ara-C1}), 100.2 (C-1^{Ara-C2}), 97.9 (C-1^{Man-A2}), 97.8 (C-1^{Man-A1}), 86.4, 85.8, 85.5, 83.9, 83.8 (2C), 83.7, 83.5, 83.0, 81.6, 81.0, 79.8, 79.3, 79.2, 78.3, 78.2, 75.16, 75.1, 74.0, 73.9, 73.4, 73.2, 72.5, 72.4, 72.37, 72.3, 72.2, 72.17, 71.73, 71.7, 71.66, 69.62, 69.6, 69.5, 68.5, 68.47, 68.45, 66.3, 27.3, 26.7, 21.1; ESI-TOF HRMS m/z calcd for $C_{142}H_{162}N_2O_{33}$ $[M + 2NH_4]^{2+}$ 1211.5525, found 1211.5533.

3,4,6-Tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-1,2-O-isopropylidene-β-D-arabinofuranose (40). To a solution of **39** (222 mg, 93 μmol) in MeOH (2 mL) and THF (1 mL) was added NaOMe in MeOH (1 M) until the pH value reached 10. The solution was stirred at rt for 5 h, and neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate1:1) to give **40** (194 mg, 91%) as colorless syrup: $[\alpha]_D^{26}$ +16.3 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.16 (m, 66 H, Ph), 7.14−7.13 (m, 4 H, Ph), 5.77 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-A}), 5.11 (s, 1 H, H-1^{Ara-B2}), 5.06 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-C1}), 5.04 (s, 1 H, H-1^{Ara-B1}), 4.96 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-C2}), 4.85 (d, *J* = 4.8 Hz, 2 H, H-1^{Man-A1}, H-1^{Man-A2}), 4.77 (d, *J* = 10.8 Hz, 2 H, Bn), 4.65−4.35 (m, 27 H, Bn, H-2^{Ara-A}), 4.29 (d, *J* = 3.0 Hz, 1 H, H-2^{Ara-B1}), 4.26 (d, *J* = 4.2 Hz, 1 H, H-3^{Ara-A}), 4.24−4.21 (m, 2 H), 4.14−4.10 (m, 2 H), 4.08−4.05 (m, 2 H), 4.03−3.97 (m, 8 H), 3.93−3.86 (m,4 H), 3.79−3.68 (m, 8 H), 3.61−3.47 (m, 10 H), 2.50 (t, *J* = 3.0 Hz, 2 H, −O*H*), 1.47 (s, 3 H, C(CH_3)$_2$), 1.26 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 138.3, 138.1 (3C), 138.0 (2C), 137.9 (3C), 137.8, 137.6 (2C), 128.5, 128.4 (4C), 128.3 (4C), 128.2 (2C), 128.0, 127.9, 127.8 (5C), 127.7 (3C), 127.6 (3C), 127.5 (4C), 113.2, 105.9 (C-1^{Ara-B1}), 105.3 (C-1^{Ara-A}), 104.5 (C-1^{Ara-B2}), 100.6 (C-1^{Ara-C1}), 100.2 (C-1^{Ara-C2}), 99.33 (C-1^{Man-A2}), 99.29 (C-1^{Man-A1}), 86.6, 86.1, 85.4, 83.9, 83.87, 83.8, 83.76, 83.3, 83.1, 83.0, 81.6, 81.0, 80.07, 80.06, 79.8, 79.3, 79.1, 75.1, 75.0, 74.0, 73.4, 73.2, 72.5, 72.45, 72.43, 72.4, 72.3, 72.2, 71.82, 71.8, 71.35, 71.33, 69.5, 69.3, 68.9, 68.88, 68.6, 68.12, 68.1, 66.3, 27.3, 26.7; ESI-TOF HRMS m/z calcd for $C_{138}H_{158}N_2O_{31}$ $[M + 2NH_4]^{2+}$ 1169.5419, found 1169.5450.

2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-1,2-O-isopropylidene-β-D-arabinofuranose (41). To a mixture of **40** (170 mg, 74 μmol), **24** (103 mg, 163 μmol), and MS AW-300 (200 mg) in dry CH_2Cl_2 (3 mL) was added TMSOTf (3 μL, 16.3 μmol) at 0 °C under a N_2 atmosphere. The mixture was allowed to slowly warm up to rt in 1 h, and then neutralized with triethylamine, filtered, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 2:1) to give **41** (194 mg, 81%) as colorless syrup: $[\alpha]_D^{26}$ +6.1 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28−7.09 (m, 100 H, Ph), 5.75 (d, *J* = 4.2 Hz, 1 H, H-1^{Ara-A}), 5.51 (s, 2 H, H-2^{Man-B1}, H-2^{Man-B2}), 5.06 (s, 1 H, H-1^{Ara-B2}), 5.05−5.04 (m, 3 H, H-1^{Ara-C1}, H-1^{Man-B1}, H-1^{Man-B2}), 5.00 (s, 1 H, H-1^{Ara-B1}), 4.94 (d, *J* = 3.0 Hz, 1 H, H-1^{Ara-C2}), 4.87 (s, 1 H, H-1^{Man-A1}), 4.86 (s, 1 H, H-1^{Man-A2}), 4.81−4.79 (m, 4 H, Bn), 4.65−4.29 (m, 37 H, Bn, H-2^{Ara-A}), 4.25−4.20 (m, 4 H), 4.13−4.10 (m, 1 H), 4.09−4.07 (m, 1 H), 4.05−3.81 (m, 21 H), 3.77−3.69 (m, 8 H), 3.59−3.44 (m, 11 H), 2.08 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 1.47 (s, 3 H, C(CH_3)$_2$), 1.26 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 138.5, 138.4 (3C), 138.2, 138.1 (3C), 138.0 (3C), 137.9 (2C), 137.8, 137.6, 137.5, 128.5, 128.4 (3C), 128.3 (4C), 128.2 (3C), 128.1, 128.0 (3C), 127.9, 127.8 (4C), 127.7 (4C), 127.6 (4C), 127.5 (4C), 127.4 (3C), 127.3, 127.2, 127.1, 113.2, 105.9 (C-1^{Ara-B1}), 105.2 (C-1^{Ara-A}), 104.3 (C-1^{Ara-B2}), 100.8 (C-1^{Ara-C1}), 100.1 (C-1^{Ara-C2}), 99.53 (C-1), 99.5 (C-1), 98.5 (C-1), 98.4 (C-1), 86.5, 85.7, 85.4, 84.0, 83.9, 83.89, 83.8, 83.7, 83.5, 82.9, 81.6, 81.0, 79.8, 79.2, 79.19, 78.17, 78.16, 75.14, 75.1, 75.0, 74.6, 74.3, 74.14, 74.1, 73.3, 73.25, 73.22, 73.2, 72.5, 72.44, 72.4, 72.3, 72.2, 72.19, 72.18, 72.14, 72.12, 72.0, 71.93, 71.92, 71.9, 69.7, 69.5, 69.4, 68.9, 68.7, 68.6, 66.3, 27.3, 26.7, 21.1; ESI-TOF HRMS m/z calcd for $C_{196}H_{218}N_2O_{43}$ $[M + 2NH_4]^{2+}$ 1643.7461, found 1643.7476.

p-Tolyl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→3)-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(1→5)-]-2-O-acetyl-1-thio-D-arabinofuranoside (42). A solution of **41** (100 mg, 31 μmol) in dioxane (2 mL), 70% AcOH (1 mL), and 10% HCl (0.1 mL) was heated at 50 °C for 8 h. After TLC (petroleum ether/ethyl acetate 2:1) indicated the complete disappearance of **41**, the reaction was cooled to rt and neutralized with saturated aqueous $NaHCO_3$. The mixture was diluted with ethyl acetate (50 mL), and the two phases were separated. The organic phase was washed with water (2 × 30 mL), dried over Na_2SO_4, and concentrated. The product was dissolved with *p*-tolyl disulfide (38 mg, 154 μmol) in dry THF (1 mL), and then to the solution was added *n*-Bu_3P (38 μL, 154 μmol) at 0 °C. The mixture was stirred at rt for 6 h and concentrated. The residue was dissolved in pyridine (2 mL) and Ac_2O (0.5 mL), and

DOI: 10.1021/acs.joc.5b01686
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then DMAP (5 mg) was added. The reaction was stirred at rt for 3 h and concentrated. The product was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give **42** (83 mg, 80%, α/β 1:1) as colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.06 (m, 100 H, Ph), 6.99−6.96 (m, 4 H, Ph), 5.51 (s, 2 H, H-2$^{Man\text{-}B1}$, H-2$^{Man\text{-}B2}$), 5.45 (s, 0.5 H), 5.38 (d, J = 4.2 Hz, 0.5 H), 5.35 (d, J = 4.2 Hz, 0.5 H), 5.31 (s, 0.5 H), 5.26−5.25 (m, 1.5 H), 5.23 (d, J = 4.8 Hz, 0.5 H), 5.18 (d, J = 4.2 Hz, 0.5 H), 5.14 (s, 0.5 H), 5.09 (d, J = 4.2 Hz, 0.5 H), 5.04−5.03 (m, 2.5 H), 4.87−4.85 (m, 2 H), 4.82−4.78 (m, 4 H), 4.66−4.29 (m, 36 H), 4.27−4.24 (m, 2 H), 4.21−4.19 (m, 1 H), 4.17−4.15 (m, 1 H), 4.12−3.82 (m, 23 H), 3.79−3.68 (m, 9 H), 3.58−3.44 (m, 10 H), 2.24 (s, 1.5 H), 2.20 (s, 1.5 H), 2.08 (s, 6 H), 2.07 (s, 1.5 H), 1.92 (s, 1.5 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 170.1, 170.0, 138.5 (2C), 138.4 (3C), 138.2 (3C), 138.1 (4C), 138.0, 137.9 (2C), 137.8, 137.7 (4C), 137.6, 137.4, 137.2, 132.6, 131.1, 130.8, 129.8, 129.7, 128.4 (5C), 128.3 (5C), 128.2 (3C), 128.1 (3C), 128.0 (5C), 127.9, 127.8 (5C), 127.7 (3C), 127.6 (4C), 127.5 (4C), 127.4 (4C), 127.3 (2C), 127.2, 127.1 (2C), 107.0, 106.7, 106.5, 105.3, 105.1, 100.3, 100.0, 99.6, 99.5, 98.5, 98.4, 91.1, 88.5, 85.6, 85.0, 84.3, 84.2, 84.19, 84.1, 84.02, 84.0, 83.95, 83.94, 83.8, 83.6, 83.5, 83.4, 83.3, 81.6, 81.5, 81.0, 80.9, 80.7, 80.1, 79.6, 79.83, 79.81, 79.4, 79.3, 79.26, 79.22, 79.2, 78.2, 78.18, 78.17, 78.15, 75.13, 75.1, 75.07, 74.6, 74.5, 74.29, 74.27, 74.14, 74.1, 73.4, 73.3, 73.25, 73.21, 73.2, 72.4, 72.23, 72.21, 72.18, 72.15, 72.13, 72.1, 72.0, 71.9, 71.88, 71.85, 71.2, 70.0, 69.7, 69.7, 69.5, 69.0, 68.9, 68.6, 68.5, 65.0, 64.8, 29.7, 21.1, 21.05, 21.01, 20.7, 20.6; MALDI-TOF MS m/z calcd for $C_{202}H_{214}O_{43}SNa$ $[M + Na]^+$ 3382.42, found 3382.95.

*3-Azidopropyl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→2**)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→5**)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(**1→2**)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(**1→3**)-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→2**)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→5**)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(**1→2**)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(**1→5**)-]-2-O-acetyl-α-D-arabinofuranosyl-(**1→5**)-2-O-acetyl-3-O-benzyl-α-D-arabinofuranosyl-(**1→5**)-2-O-acetyl-3-O-benzyl-α-D-arabinofuranoside (**43**).* To a mixture of **42** (40 mg, 12 μmol), **16** (9 mg, 14 μmol), and MS AW-300 (50 mg) in dry CH_2Cl_2 (2 mL) were added NIS (3 mg, 14 μmol) and AgOTf (1 mg, 3.6 μmol) at 0 °C under a N_2 atmosphere. The mixture was stirred at 0 °C for 40 min, and then was allowed to warm up to rt and stirred for another 1 h, when TLC (petroleum ether/ethyl acetate 3:2) indicated the disappearance of **42**. The reaction was neutralized with triethylamine, filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 3:2) to give **43** (29 mg, 63%) as colorless syrup: $[\alpha]_D^{26}$ +34.1 (c 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.05 (m, 110 H, Ph), 5.51 (s, 2 H, H-2$^{Man\text{-}B1}$, H-2$^{Man\text{-}B2}$), 5.22 (s, 1 H, H-1$^{Ara\text{-}C}$), 5.21 (d, J = 4.2 Hz, 1 H, H-1$^{Ara\text{-}E1}$), 5.09 (s, 2 H, H-1$^{Ara\text{-}E2}$, H-2^{Ara}), 5.08 (s, 1 H, H-1$^{Ara\text{-}B}$), 5.05−5.03 (m, 5 H, H-1$^{Ara\text{-}D1}$, H-1$^{Ara\text{-}D2}$, H-1$^{Man\text{-}B1}$, H-1$^{Man\text{-}B2}$, H-2^{Ara}), 5.00 (s, 1 H, H-2^{Ara}), 4.93 (s, 1 H, H-1$^{Ara\text{-}A}$), 4.84 (s, 2 H, H-1$^{Man\text{-}A1}$, H-1$^{Man\text{-}A2}$), 4.80−4.78 (m, 4 H, Bn), 4.64−4.29 (m, 40 H, Bn), 4.22−4.19 (m, 1 H), 4.17−4.14 (m, 2 H), 4.12−4.09 (m, 1 H), 4.05−3.80 (m, 26 H), 3.78−4.73 (m, 4 H), 3.71−3.65 (m, 8 H), 3.58−3.44 (m, 14 H), 3.38−3.33 (m, 2 H), 2.07 (s, 6 H, Ac), 1.99 (s, 3 H, Ac), 1.95 (s, 3 H, Ac), 1.88 (s, 3 H, Ac), 1.83−1.79 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0 (2C), 169.7, 138.5 (2C), 138.4 (2C), 138.2, 138.1 (4C), 138.0 (2C), 137.9 (2C), 137.8, 137.7 (2C), 137.5, 128.4 (2C), 128.3 (4C), 128.2 (4C), 128.1 (2C), 128.0 (2C), 127.9 (2C), 127.8 (2C), 127.7 (5C), 127.6 (3C), 127.5 (2C), 127.4 (3C), 127.3 (2C), 127.1, 106.6 (C-1$^{Ara\text{-}B}$), 106.0 (C-1$^{Ara\text{-}D}$), 105.9 (2C, C-1$^{Ara\text{-}D}$, C-1$^{Ara\text{-}A}$), 105.8 (C-1$^{Ara\text{-}C}$), 100.5 (C-1$^{Ara\text{-}E2}$), 100.1 (C-1$^{Ara\text{-}E1}$), 99.5 (2C, C-1$^{Man\text{-}B1}$, C-1$^{Man\text{-}B2}$), 98.6 (C-1$^{Man\text{-}A1}$), 98.5 (C-1$^{Man\text{-}A2}$), 86.22, 86.2, 85.33, 85.32, 85.31, 84.2, 84.19, 84.05, 84.0, 83.9, 83.61, 83.6, 83.2, 83.04, 82.0, 81.7, 81.6, 81.5, 81.26, 81.25, 81.24, 81.2, 81.1, 79.8, 79.4, 79.3, 78.15, 78.13, 75.1, 75.08, 75.07, 75.05, 74.5, 74.27, 74.26, 74.2, 73.3, 73.2, 73.16, 72.3, 72.24, 72.21, 72.2, 72.16, 72.14, 72.1, 71.93, 71.92, 71.9, 71.8, 69.81, 69.8, 69.7, 69.4, 69.3, 68.94, 68.93, 68.9, 68.6, 68.58, 68.55, 65.5, 65.3, 64.6, 64.5, 63.8, 48.3, 28.8, 21.1, 20.9, 20.8, 20.7; ESI-TOF HRMS m/z calcd for $C_{226}H_{253}N_5O_{54}$ $[M + 2NH_4]^{2+}$ 1950.3597, found 1950.3522.

*3-Azidopropyl 3,4,6-Tri-O-benzyl-α-D-mannopyranosyl-(**1→2**)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→5**)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(**1→2**)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(**1→3**)-[3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→2**)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(**1→5**)-2,3-di-O-benzyl-β-D-arabinofuranosyl-(**1→2**)-3,5-di-O-benzyl-α-D-arabinofuranosyl-(**1→5**)-]-α-D-arabinofuranosyl-(**1→5**)-3-O-benzyl-α-D-arabinofuranosyl-(**1→5**)-3-O-benzyl-α-D-arabinofuranoside (**44**).* To a solution of **43** (50 mg, 13 μmol) in MeOH (1 mL) and THF (1 mL) was added NaOMe in MeOH until its pH value reached 10. The solution was stirred at rt for 2 h, neutralized with Amberlite IR 120 (H^+), filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 3:2) to afford **44** (38 mg, 81%) as colorless syrup: $[\alpha]_D^{26}$ +50.8 (c 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.07 (m, 110 H, Ph), 5.19 (d, J = 3.0 Hz, 1 H, H-1$^{Ara\text{-}E}$), 5.12 (s, 1 H, H-1$^{Man\text{-}B}$), 5.07 (s, 1 H, H-1$^{Man\text{-}B}$), 4.99 (s, 1 H, H-1$^{Ara\text{-}D}$), 4.98 (s, 1 H, H-1$^{Ara\text{-}D}$), 4.96 (d, J = 3.6 Hz, 1 H, H-1$^{Ara\text{-}E}$), 4.94 (s, 1 H, H-1^{Ara}), 4.93 (s, 1 H, H-1$^{Man\text{-}A}$), 4.91 (s, 1 H, H-1$^{Man\text{-}A}$), 4.89 (s, 1 H, H-1^{Ara}), 4.80−4.72 (m, 6 H, Bn, H-1^{Ara}), 4.65−4.29 (m, 39 H, Bn), 4.23−4.21 (m, 2 H), 4.17−4.14 (m, 2 H), 4.09 (s, 1 H), 4.06−4.04 (m, 3 H), 4.01−3.93 (m, 10 H), 3.89−3.39 (m, 39 H), 3.36 (t, J = 6.6 Hz, 2 H), 3.30 (d, J = 9.6 Hz, 1 H), 3.18 (s, 1 H), 3.17 (s, 1 H), 3.12 (d, J = 9.6 Hz, 1 H), 2.41 (d, J = 2.4 Hz, 1 H), 2.36 (d, J = 1.8 Hz, 1 H), 1.83 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5 (2C), 138.4 (2C), 138.2, 138.1 (2C), 138.0 (3C), 137.9 (2C), 137.6, 137.4, 137.3, 128.4 (5C), 128.3 (3C), 128.2 (2C), 127.9 (3C), 127.8 (4C), 127.7 (3C), 127.6 (3C), 127.5 (3C), 127.4, 127.3 (2C), 109.2 (C-1), 108.4 (C-1), 108.3 (C-1), 106.3 (C-1$^{Ara\text{-}D}$), 105.5 (C-1$^{Ara\text{-}D}$), 101.8 (C-1$^{Ara\text{-}E}$), 101.1 (C-1$^{Man\text{-}B}$), 101.0 (C-1$^{Man\text{-}B}$), 100.1 (C-1$^{Ara\text{-}E}$), 98.6 (2C, C-1$^{Man\text{-}A1}$, C-1$^{Man\text{-}A2}$), 87.4, 84.9, 84.8, 84.5, 84.4, 83.9, 83.8, 83.6, 83.5 (3C), 83.4, 83.2, 82.8, 81.7, 81.5, 80.0, 79.9, 79.87, 79.3, 79.1, 78.3, 77.9, 75.1, 75.07, 75.04, 75.0, 74.8, 74.7, 74.5, 74.4, 74.2, 73.3, 73.2, 73.17, 72.7, 72.3, 72.26, 72.24, 72.2, 72.17, 72.1, 72.05, 72.0, 71.96, 71.65, 71.6, 71.56, 71.5, 70.0, 69.8, 69.4, 69.2, 69.0, 68.97, 68.8, 68.7, 68.4, 66.0, 65.8, 65.6, 63.7, 48.4, 29.0; ESI-TOF HRMS m/z calcd for $C_{216}H_{243}N_5O_{49}$ $[M + 2NH_4]^{2+}$ 1845.3333, found 1845.3354.

*3-Aminopropyl α-D-Mannopyranosyl-(**1→2**)-α-D-mannopyranosyl-(**1→5**)-β-D-arabinofuranosyl-(**1→2**)-α-D-arabinofuranosyl-(**1→3**)-[α-D-mannopyranosyl-(**1→2**)-α-D-mannopyranosyl-(**1→5**)-β-D-arabinofuranosyl-(**1→2**)-α-D-arabinofuranosyl-(**1→5**)-]-α-D-arabinofuranosyl-(**1→5**)-α-D-arabinofuranosyl-(**1→5**)-α-D-arabinofuranoside (**3**).* To a solution of **44** (26 mg, 7 μmol) in AcOH (2 mL) and H_2O (0.2 mL) was added 10% Pd/C (10 mg), and the mixture was stirred under a H_2 atmosphere at rt for 72 h. It was then filtered and concentrated under reduced pressure. The crude product was purified by gel filtration column chromatography to give **3** (11 mg, 91%) as a white solid: $[\alpha]_D^{26}$ +78.0 (c 0.1, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.07 (s, 1 H, H-1$^{Ara\text{-}D}$), 5.00 (s, 1 H, H-1$^{Ara\text{-}D}$), 4.98−4.96 (m, 4 H, H-1$^{Ara\text{-}E1}$, H-1$^{Ara\text{-}E2}$, H-1$^{Man\text{-}A1}$, H-1$^{Man\text{-}A2}$), 4.94 (s, 1 H, H-1^{Ara}), 4.91 (s, 1 H, H-1^{Ara}), 4.86−4.84 (m, 3 H, H-1^{Ara}, H-1$^{Man\text{-}B1}$, H-1$^{Man\text{-}B2}$), 4.14−4.12 (m, 2 H), 4.02−3.84 (m, 22 H), 3.78−3.41 (m, 37 H), 2.97−2.94 (m, 2 H), 1.83−1.78 (m, 2 H), 1.73 (s, 3 H); ^{13}C NMR (150 MHz, D_2O) δ 107.4 (C-1^{Ara}), 107.3 (C-1^{Ara}), 107.2 (C-1^{Ara}), 105.4 (C-1$^{Ara\text{-}D}$), 105.3 (C-1$^{Ara\text{-}D}$), 102.2 (2C, C-1$^{Man\text{-}B1}$, C-1$^{Man\text{-}B2}$), 100.6 (C-1$^{Ara\text{-}E}$), 100.3 (C-1$^{Ara\text{-}E}$), 98.1 (2C, C-1$^{Man\text{-}A1}$, C-1$^{Man\text{-}A2}$), 87.2, 86.8, 83.0, 82.9, 82.6, 82.2, 82.1, 80.8, 80.7, 80.4, 79.6, 79.0, 78.6, 76.4, 76.36, 75.9, 74.9, 74.88, 73.9, 73.1, 72.8, 70.2, 70.0, 69.8, 68.1, 66.9, 66.8, 66.2, 66.1, 65.6, 61.0, 60.8, 60.5, 37.8, 26.4, 23.1; ESI-TOF HRMS m/z calcd for $C_{62}H_{106}NO_{49}$ $[M + H]^+$ 1648.5828, found 1648.5838.

*Preparation of Activated Esters **46**−**48**.* After a mixture of **1**, **2**, or **3** (3 mg) and DSG **45** (15 equiv) in DMF and PBS buffer (0.1 M, pH 8.0) (v/v 4:1, 0.5 mL) was gently stirred at rt for 4 h, the solvents were removed under reduced pressure. Products **46**−**48** were separated from excessive DSG through precipitation upon addition of 9 volumes of ethyl acetate to the reaction mixture, which was followed by further purification by washing with ethyl acetate 10 times and drying under high vacuum. The products were used directly for protein conjugation.

*Preparation of Glycoproteins **49**−**54**.* Each activated oligosaccharide **46**, **47**, or **48** and BSA or KLH in a mass ratio of 1:2 (oligosaccharide/protein) were dissolved in PBS buffer (0.1 M, 0.5

DOI: 10.1021/acs.joc.5b01686
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mL, pH 8.0), and the solution was gently stirred at rt for 4 days. It was then applied to a Biogel A0.5 column to remove unreacted oligosaccharides through gel filtration chromatography using 0.1 M PBS buffer (pH 8.0) as the eluent. Fractions containing glycoproteins, confirmed by the bicinchoninic acid assay for proteins and the phenol sulfuric acid assay for carbohydrates, were combined and dialyzed against distilled water (3 × 5 mL). The residual solution was finally lyophilized to give the desired glycoconjugate as white fluffy powder. The carbohydrate loadings of glycoconjugates **49**–**54** were analyzed by a previously reported protocol.[55,56]

Immunization of Mice. Each KLH conjugate **52**, **53**, or **54** (~1.5 mg) was dissolved in 0.3 mL of 10× PBS buffer and then diluted with water to form a 2× PBS solution (1.5 mL). It was then thoroughly mixed with 1.5 mL of Titermax Gold adjuvant to form an emulsion according to the protocol provided by the manufacturer. Each group of six female Balb/c mice was initially immunized (day 1) by s.c. injection of 0.1 mL of the emulsion described above; thus each dose contained about 3 μg of the carbohydrate antigen. Following the initial immunization, mice were boosted four times on days 14, 21, 28, and 35 by s.c. injection of the same glycoconjugate emulsion. Blood samples were collected through the tail veins of each mouse on day 0 prior to the initial immunization and on days 22, 29, and 36 after the boost immunizations. Finally, antisera were obtained from the clotted blood samples according standard protocols.

ELISA. ELISA plates were treated with a solution of each BSA conjugate **49**, **50**, or **51** (100 μL/well, 2 μg/mL) dissolved in coating buffer (0.1 M aqueous bicarbonate, pH 9.6) at 4 °C overnight and at 37 °C for 1 h, which was followed by washing with PBS buffer containing 0.05% Tween-20 (PBST) three times. Plates were then incubated with the blocking buffer (1% BSA in PBS) at rt for 1 h and washed with PBST three times. Each mouse serum with serial dilutions from 1:300 to 1:72900 in PBS (100 μL/well) was added to the coated plates, which were incubated at 37 °C for 2 h. After being washed with PBST, the plates were incubated at rt for 1 h with a 1:1000 diluted solution of alkaline phosphatase-linked goat anti-mouse kappa antibody. Again, the plates were washed with PBST three times and then developed with a *p*-nitrophenylphosphate solution (1.67 mg/mL in buffer, 100 μL) for 30 min at rt, which was followed by colorimetric readout using a microplate reader at 405 nm wavelength. The optical density (OD) values were plotted against serum dilution values, and a best-fit line was obtained. The equation of the line was employed to calculate the dilution value at which an OD value of 0.1 was achieved, and the antibody titer was calculated at the inverse of the dilution value.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01686.

One- and two-dimensional ^{1}H and ^{13}C NMR spectra of the synthesized compounds, results of the sugar loading analyses of glycoconjugates **49**–**54**, MALDI-TOF MS spectra of BSA conjugates **49**–**51**, and SDS-PAGE results of KLH and its conjugates **52**–**54** (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Major Scientific and Technological Special Project for "Significant New Drugs Development" (2012ZX09502001-005) and the National Basic Research (973) Program (2012CB822102) of China. We thank Mr. Zhicheng Gu for the NMR measurements.

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