Supporting Information for

Insights into Interactions of Mycobacteria with the Host Innate Immune System from a Novel Array of Synthetic Mycobacterial Glycans

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Additional Experimental Methods

Materials

Fluorescein isothiocyanate, Alexa Fluor 555 *N*-hydroxysuccinimidyl ester, and streptavidin labelled with Alexa Fluor 488 or Alexa Fluor 555 were obtained from Life Technologies. DyLight 549 Anti-Streptavidin Antibody was purchased from Vector Laboratories and the Cy™3 IgG fraction monoclonal mouse anti-fluorescein from Jackson ImmunoResearch. All other reagents were purchased from Sigma.

Synthesis of Glycans

The synthesis of a subset of the glycans incorporated into the array has been reported previously: **21**,[1] **22**,[1] **44**,[2] and **56–59**.[3] The synthesis of the remaining glycans is described below.

Protein expression

The extracellular domains of DC-SIGN,[4] DC-SIGNR,[4] and the macrophage galactose receptor,[5] as well as a fragment representing the CRDs plus roughly half of the coiled-coil neck domain of langerin[6] and the isolated CRD of human dectin-2,[7] were expressed in the T7-driven systems described previously and were purified by affinity chromatography on immobilized carbohydrate columns. Versions of the CRDs from mincle[8] and BDCA-2[9] with C-terminal biotinylation target sequences were expressed in the presence of biotin ligase so that they were conjugated with biotin in the bacteria. The biotin-tagged CRDs were purified by affinity chromatography before complexing with fluorescently labeled streptavidin.

Fragments of the mannose receptor representing the extracellular domain and CRDs 1–8 were expressed in Chinese hamster ovary cells grown in serum-free medium and purified by affinity chromatography on mannose-Sepharose.[10-11]

Protein labeling

Proteins were labeled directly with fluorescein isothiocyanate in buffer containing 150 mM NaCl, 100 mM Bicine, pH 9.0, and 25 mM $CaCl_2$. Five aliquots of 10 μl of 1 mg/ml fluorescein isothiocyanate dissolved in dimethylsulfoxide were added to 1 ml of protein solution and allowed to react overnight at 4 ºC.

Direct labeling of proteins with Alexa Fluor 555 was performed on proteins dissolved in 150 mM NaCl, 100 mM Bicine, pH 9.0, and 25 mM $CaCl_2$, except for langerin, for which the $CaCl_2$

concentration was reduced to 5 mM. Alexa Fluor 555 *N*-hydroxysuccinimidyl ester, 100 µg dissolved in 10 µl of dimethylsulfoxide, was added and reacted for 1 h at room temperature.

Labelled proteins were re-purified by affinity chromatography on 1 ml affinity columns of mannose-Sepharose, except for the macrophage galactose receptor, for which 1 ml of galactose-Sepharose was used. Proteins were loaded in the reaction buffer, followed by washing of the column with 5 volumes of 150 mM NaCl, 25 mM Tris-Cl, pH 7.8, 25 mM $CaCl_2$. Columns were eluted with 6 x 0.5 ml of 150 mM NaCl, 25 mM Tris-Cl, pH 7.8, 2.5 mM EDTA and proteins were detected by SDS-polyacrylamide gel electrophoresis.

Complexes with Alexa Fluor 488- or 555-labeled streptavidin were formed by incubation of 100 µg of streptavidin with a 2- to 5-fold excess of biotin-tagged CRD in 150 mM NaCl, 25 mM Tris-Cl, pH 7.8, 25 mM $CaCl_2$ overnight at 4 ºC. For repurification, the complexes were applied to 1 ml affinity columns that do not bind the CRDs alone. For mincle, mannose-Sepharose was used in place of trehalose-Sepharose. For BDCA-2, mannose-Sepharose was used in place of the glycopeptide resin used for initial purification. In each case, after washing with 5 column volumes of 150 mM NaCl, 25 mM Tris-Cl, pH 7.8, 25 mM $CaCl_2$, the CRD-streptavidin complex was eluted with 150 mM NaCl, 25 mM Tris-Cl, pH 7.8, 2.5 mM EDTA.

Molecular modeling

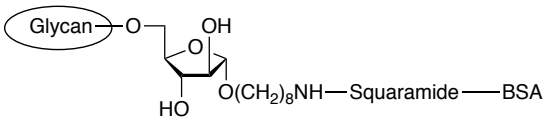
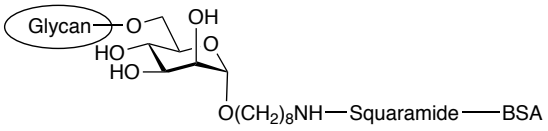
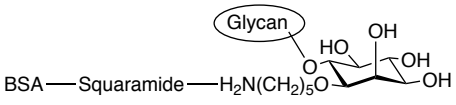
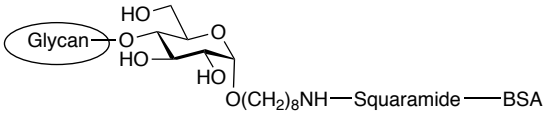
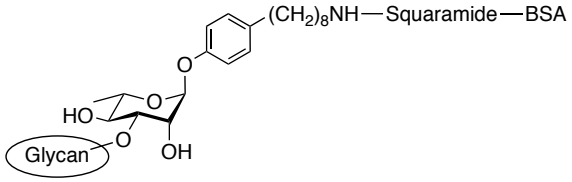
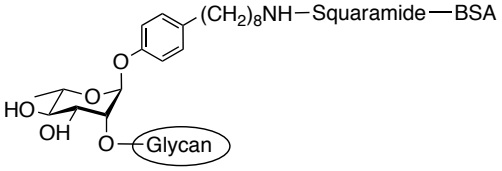
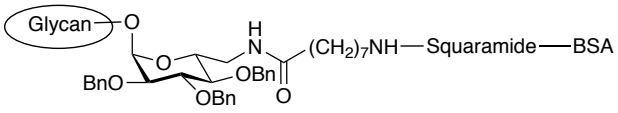
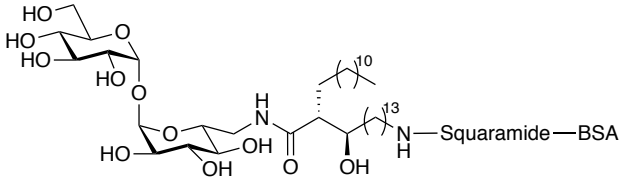
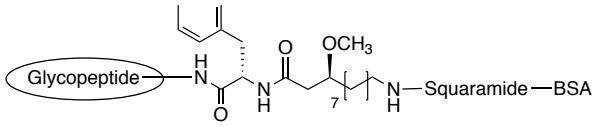
All modeling was undertaken using PyMOL. Conformations of glycans were not modified, but irrelevant regions were removed. Superpositions of individual monosaccharide residues were performed manually.

The crystal structure of trehalose monobutyrate bound to bovine mincle, Protein Data Bank entry 4ZRV, was used to model trehalose derivatives bound to mincle. The possible position of an additional glucose residue linked β1-4 to the glucose residue in the secondary binding site was modeled by superimposing the reducing monosaccharide of the Glcβ1-4Glc disaccharide, cellobiose, Cambridge Structural Database entry CELLOB, on the glucose residue in trehalose. For modeling the Glc1-4Glc disaccharides, the glucose residue from trehalose that occupies the secondary binding site in the mincle-trehalose monobutyrate structure was omitted and the reducing end of either the Glcα1-4Glcα1-4Glc trisaccharide or the Glcβ1-4Glc disaccharide was superimposed on the glucose residue in the primary binding site. The α-linked trisaccharide was abstracted from the structure of cycloamylose, Protein Data Bank entry 1C58 and the cellobiose disaccharide was as above. The same procedure was employed for Glc1-6Glc disaccharides, with

Glcα1-6Glc (isomaltose) and Glcβ1-6Glc (gentiobiose) from PubChem entry CID 439193 and Cambridge Structural Database entry GENTBS, respectively.

For modeling of rhamnose binding to a fucose-binding site, α-L-rhamnose, PubChem entry CID 25310 was superposed on a fucose residue in the primary binding site of langerin, which was obtained by removing all the other monosaccharide residues from the crystal structure of langerin with the blood group B trisaccharide, Protein Data Bank entry 3P5G. For modeling of rhamnose binding to a galactose-binding site, α-L-rhamnose was superposed on a galactose residue in the primary binding site of the scavenger receptor C-type lectin, which was obtained by removing all the other monosaccharide residues from the crystal structure of the scavenger receptor with the Lewis^x trisaccharide, Protein Data Bank entry 2OX9. Methyl α-D-arabinofuranoside was obtained from Cambridge Structural Database entry ARAFLTD1 and was overlayed on the D-mannopyranose residue in the primary binding site of langerin in complex with the Manα1-2Man disaccharide, Protein Data Bank entry 3P5F.

Table S1. Linkage Modes of Different Glycan Classes to BSA

Linker*	Class‡	Glycans with this linker
	LAM	**1**–**12**, **15**, **16**, **18**–**22**, **25**,ξ **44**, **45**, **49**
	LAM	**17**, **50**, **56**–**59**
	LAM	**23**
	GLU	**13**, **14**, **24**, **46**, **48**, **52**
	PGL	**26**–**29**, **33**–**37**, **40**–**43**, **51**, **53**
	PGL	**30**–**32**
	LOS	**38**, **54**, **55**
	TMM	**39**
	GPL	**47**, **60**, **61**

*In some glycans, the residue bearing the linker is further modified by additional glycosylation or methylation. See complete structures for complete details.

‡GPL = glycopeptidolipid; GLU = α-Glucan; LAM = Lipoarabinomannan; LOS = lipooligosaccharide; PGL = phenolic glycolipid; TMM = Trehalose Monomycolate

ξLinker chain length is $(CH_2)_5$ not $(CH_2)_8$

Table S2. Summary of Glycan Synthesis

Glycan	Class*	Section or Reference	Page	Glycan	Class*	Section or Reference	Page
1	LAM	Section 3	S9	**32**	PGL	Section 25	S166
2	LAM	Section 4	S16	**33**	PGL	Section 26	S169
3	LAM	Section 4	S16	**34**	PGL	Section 27	S175
4	LAM	Section 4	S16	**35**	PGL	Section 28	S178
5	LAM	Section 5	S27	**36**	PGL	Section 29	S179
6	LAM	Section 5	S27	**37**	PGL	Section 30	S184
7	LAM	Section 6	S40	**38**	LOS	Section 31	S185
8	LAM	Section 6	S40	**39**	TMM	Section 32	S189
9	LAM	Section 6	S40	**40**	PGL	Section 33	S196
10	LAM	Section 7	S54	**41**	PGL	Section 34	S201
11	LAM	Section 8	S63	**42**	PGL	Section 35	S205
12	LAM	Section 9	S73	**43**	PGL	Section 36	S209
13	GLU	Section 10	S82	**44**	LAM	Reference[2]	–
14	GLU	Section 11	S90	**45**	LAM	Section 37	S212
15	LAM	Section 12	S97	**46**	GLU	Section 38	S214
16	LAM	Section 13	S104	**47**	GPL	Section 39	S219
17	LAM	Section 14	S106	**48**	GLU	Section 40	S231
18	LAM	Section 15	S111	**49**	LAM	Section 41	S238
19	LAM‡	Section 16	S125	**50**	LAM	Section 42	S240
20	LAM	Section 17	S129	**51**	PGL	Section 43	S247
21	LAM‡	Reference[1]	–	**52**	GLU	Section 44	S251
22	LAM‡	Reference[1]	–	**53**	PGL	Section 45	S255
23	LAM	Section 18	S143	**54**	LOS	Reference[12]	–
24	GLU	Duplicate of **14**	–	**55**	LOS	Reference[12]	–
25	LAM	Reference[13]	–	**56**	LAM	Reference[3]	–
26	PGL	Section 19	S148	**57**	LAM	Reference[3]	–
27	PGL	Section 20	S156	**58**	LAM	Reference[3]	–
28	PGL	Section 21	S157	**59**	LAM	Reference[3]	–
29	PGL	Section 22	S158	**60**	GPL	Section 46	S257
30	PGL	Section 23	S160	**61**	GPL	Section 46	S257
31	PGL	Section 24	S164				

* GPL = glycopeptidolipid; GLU = α-Glucan; LAM = Lipoarabinomannan;
LOS = lipooligosaccharide; PGL = phenolic glycolipid; TMM = Trehalose Monomycolate
‡ Nominally fragments of arabinogalactan, but related to LAM.

1. Synthetic General Methods

All reagents were purchased from commercial sources without further purification, while reaction solvents were purified using a PURESOLV-400 system (Innovative Technology Inc., Newburyport, MA). All reactions were carried out in oven-dried glassware under a positive pressure of argon and monitored by TLC Silica Gel 60 F_{254} (0.25 mm, E. Merck) unless otherwise indicated. Plates were visualized under UV light and/or stained with a solution of *p*-anisaldehyde or 5% H_2SO_4 in ethanol. Column chromatography was performed using Silicycle UltraPure silica gel (SiliaFlash® P60, 40–63 μm, Cat# R12030 B). The ratio between silica gel and crude product ranged from 100:1 to 20:1 (w/w). Optical rotations were measured in a microcell (10 cm, 1 mL) at 22 ± 2 °C and are in units of degree·mL/(g·dm). Organic solutions were concentrated under vacuum at temperature below 50 °C on a rotary evaporator. ^{1}H NMR spectra were recorded at 400, 500, 600 or 700 MHz, and chemical shifts were referenced to $CDCl_3$ (7.26 ppm), CD_3OD (4.78 ppm) or D_2O (4.78 ppm). ^{1}H NMR data are reported as though they are first order and the peak assignments were made on the basis of 2D-NMR (^{1}H–^{1}H COSY and HMQC) experiments. ^{13}C NMR spectra were recorded at 100, 125, 150, or 175 MHz, and ^{13}C chemical shifts are referenced to $CDCl_3$ (77.23) or CD_3OD (48.90) or external acetone (31.07, D_2O). Electrospray mass spectra were recorded on samples suspended in mixtures of THF with CH_3OH and added NaCl. MALDI mass spectrometry was performed on a Voyager Elite time–of–flight spectrometer on samples suspended in 2, 5–dihydroxy benzoic acid or IAA using the delayed–extraction mode and positive–ion detection.

2. General Procedures

Depending on the glycan class, final compounds were stored either as the free amine, or the corresponding azide, trifluoroacetamide or squaramide derivative. For the trifluoroacetamide and azide derivatives, they were converted to the amine immediately before conjugation to the protein (via squaramide) using the general procedures outlined below. The procedure used to conjugate the amines to BSA via the squaramide linker is detailed in the main text of the manuscript.

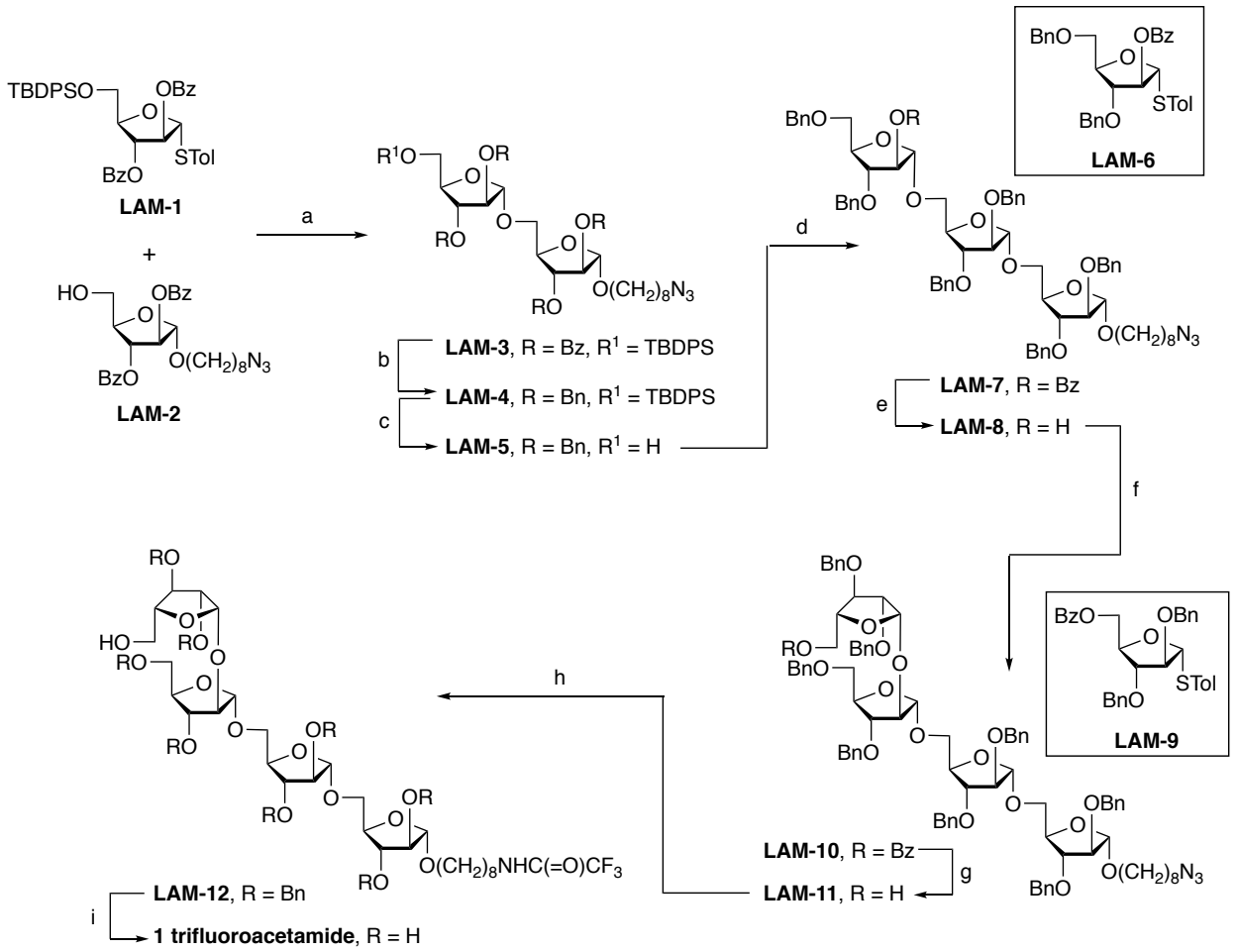
2.1 Conversion of trifluoroacetamide derivatives to amines

To a solution of the oligosaccharide trifluoroacetamide (10 mg) in CH_3OH (0.5 mL) was added 1M sodium methoxide solution (10.0 equiv.) and the mixture was stirred at rt for 16–24 h. The pH of the reaction mixture was then adjusted to just below 8.0 (as determined by wet pH paper) by careful addition of Amberlite IR 120 H^+ resin. After filtration of the solution, the filtrate was concentrated and the resulting residue was dried under vacuum to obtain the corresponding oligosaccharide amine, which was used in the squaramide coupling reactions.

2.2 Conversion of azide derivatives to amines

To a solution of the oligosaccharide azide (10 mg) in CH_3OH–H_2O (8–10 mL, 8:3) at rt was added 20% $Pd(OH)_2$–C or 10% Pd–C (10–12 mg), and the reaction mixture was stirred under H_2 (1 atm) for 4–16 h. The reaction mixture was diluted with CH_3OH (6 mL) and filtered through filter paper (medium porosity) to remove the catalyst. The filtrate was concentrated to give a syrup that was dissolved in distilled water (5 mL), filtered using a 13 mm Nylon 0.2 μm syringe filter unit and then lyophilized to give the corresponding amine, which was used in the squaramide coupling reactions.

3. Synthesis of 1



Scheme S1. Synthesis of **1 Trifluoroacetamide**. a) NIS, AgOTf, CH_2Cl_2, 86%; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, 93%; then BnBr, NaH, DMF, 90%; c) *n*-Bu_4NF, THF, 94%; d) **LAM-6**, NIS, AgOTf, CH_2Cl_2, 93%; e) $NaOCH_3$, CH_3OH, CH_2Cl_2, 94%; f) **LAM-9**, NIS, AgOTf, CH_2Cl_2, 87%; g) $NaOCH_3$, CH_3OH, CH_2Cl_2, 83%; h) H_2, Pd–C, pyridine; then trifluoroacetic anhydride, pyridine, 70%; i) H_2, Pd–C, THF, CH_3OH, 90%.

8-Azidooctyl 2,3-di-*O*-benzoyl-5-*O*-*t*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-3). Thioglycoside **LAM-1**[1] (5.2 g, 7.4 mmol) and **LAM-2**[1] (3.0 g, 6.2 mmol) were dried over P_2O_5 under vacuum for 6 h and then dissolved in CH_2Cl_2 (100 mL), and the resulting solution was cooled to 0 °C. Powdered 4 Å molecular sieves (4.5 g) were added, and the suspension was stirred for 30 min at 0 °C before *N*-iodosuccinimide (1.7 g, 7.4 mmol) and silver triflate (0.48 g, 1.8 mmol) were added. The reaction mixture was stirred for 20 min. at that temperature, neutralized with Et_3N, diluted with

CH_2Cl_2, and filtered through Celite. The filtrate was washed successively with a satd aq $Na_2S_2O_3$ soln (300 mL × 2) and water before being dried (Na_2SO_4), filtered and concentrated. The crude residue was purified by chromatography (10:1 hexanes–EtOAc) to afford **LAM-3** (5.7 g, 86%) as a syrup. R_f 0.44 (4:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.11–8.07 (m, 2 H), 8.03–7.99 (m, 2 H), 7.78–7.74 (m, 4 H), 7.60–7.52 (m, 2 H), 7.43–7.30 (m, 15 H), 7.29–7.20 (m, 5 H), 5.66 (dd, 1 H, *J* = 4.8, 1.1 Hz), 5.59 (d, 1 H, *J* = 1.1 Hz, H-1), 5.35 (s, 1 H, H-1), 5.09 (s, 1 H), 4.63 (d, 1 H, *J* = 11.8 Hz), 4.62 (d, 1 H, *J* = 11.8 Hz), 4.54 (d, 2 H, *J* = 11.8 Hz), 4.39–4.35 (m, 1 H), 4.30–4.25 (m, 1 H), 4.11–4.07 (m, 2 H), 4.04–3.95 (m, 3 H), 3.80–3.72 (m, 2 H), 3.43 (ddd, 1 H, *J* = 9.7, 6.6, 6.6 Hz), 3.25 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.66–1.57 (m, 4 H), 1.43–1.30 (m, 8 H), 1.08 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 165.5, 165.2, 137.9, 137.6, 135.7, 135.6, 133.3, 133.2, 133.1, 129.9, 129.6, 129.5, 129.3, 128.4, 128.3, 127.9, 127.8, 127.6, 106.0 (C-1), 105.8 (C-1), 88.5, 83.4, 83.3, 82.2, 79.8, 77.4, 72.1, 72.0, 67.6, 66.4, 63.5, 51.4, 29.5, 29.2, 29.1, 28.8, 26.8, 26.6, 26.0, 19.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{62}H_{67}N_3O_{13}SiNa$: 1112.4335. Found: 1112.4332.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-4). To a solution of **LAM-3** (32.0 g, 30 mmol) in CH_2Cl_2–CH_3OH (400 mL, 1:1) was added $NaOCH_3$ (0.8 g), and the resulting mixture was stirred for 12 h at rt. The reaction was neutralized by the addition of HOAc, concentrated, and the residue was purified by chromatography (2:1 hexanes–EtOAc) to give the corresponding debenzoylated compound (23.8 g, 93%). This compound was dissolved in DMF (200 mL) and the solution was cooled to 0 °C, followed by the addition NaH (2.43 g, 60.8 mmol) and BnBr (7.3 mL, 60.8 mmol) in succession. The reaction was warmed to rt and stirred over 16 h, followed by the dropwise addition of CH_3OH to quench the excess NaH. The mixture was diluted with CH_2Cl_2 and washed with a satd aq $NaHCO_3$ soln before being dried (Na_2SO_4), filtered and concentrated. The crude residue was purified by chromatography (10:1 hexanes–EtOAc) to afford **LAM-4** (25.7 g, 90%) as a syrup. R_f 0.27 (8:1 hexanes–EtOAc); $[\alpha]_D$ +37.6 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.72–7.65 (m, 4 H), 7.44–7.22 (m, 26 H), 5.18 (s, 1 H, H-1), 5.03 (s, 1 H, H-1), 4.62–4.44 (m, 8 H), 4.22–4.14 (m, 2 H), 4.12–4.06 (m, 3 H), 4.06–4.03 (m, 1 H), 3.91 (dd, 1 H, *J* = 11.5, 4.1 Hz), 3.84–3.78 (m, 2 H), 3.77–3.68 (m, 2 H), 3.42 (ddd, 1 H, *J* = 9.7, 6.7, 6.7 Hz), 3.25 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.63–1.55 (m, 4 H), 1.42–1.27 (m, 8 H), 1.09 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 138.1, 137.8, 137.7, 135.7,

135.6, 133.5, 133.4, 129.6, 129.5, 128.4, 128.3(4), 128.3, 128.2, 127.9, 127.8, 127.7(6), 127.7, 127.6(7), 127.6(4), 127.6, 106.4 (C-1), 106.1 (C-1), 88.7, 88.1, 83.3, 83.2, 82.4, 80.1, 72.3, 72.0, 71.9, 71.7, 67.6, 65.9, 63.7, 51.4, 29.5, 29.2, 29.1, 28.8, 26.8, 26.6, 26.0, 19.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{62}H_{75}N_3O_9SiNa$: 1056.5170. Found: 1056.5172.

8-Azidooctyl 2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-5). To a solution of **LAM-4** (24.8 g, 24 mmol) in THF (270 mL) was added a 1M *n*-Bu_4NF solution in THF (29 mL) and the reaction mixture was stirred for 16 h at rt, followed by concentration. The residue was purified by chromatography (4:1 hexanes–EtOAc) to provide **LAM-5** (17.9 g, 94%) as a colorless syrup. R_f 0.20 (4:1 hexanes–EtOAc); $[\alpha]_D$ +13.1 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.35–7.22 (m, 20 H), 5.18 (s, 1 H, H-1), 5.02 (d, 1 H, *J* = 1.2 Hz, H-1), 4.62–4.56 (m, 8 H), 4.20 (ddd, 1 H, *J* = 7.2, 4.0, 3.2 Hz), 4.15–4.08 (m, 3 H), 4.06 (dd, 1 H, *J* = 3.0, 1.2 Hz), 4.00 (dd, 1 H, *J* = 6.5, 3.0 Hz), 3.90 (dd, 1 H, *J* = 11.7, 4.0 Hz), 3.84 (dd, 1 H, *J* = 12.1, 2.8 Hz), 3.77–3.70 (m, 2 H), 3.66 (dd, 1 H, *J* = 12.1, 4.0 Hz), 3.42 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz), 3.26 (dd, 2 H, *J* = 6.9, 6.9 Hz), 1.90 (br s, 1 H), 1.64–1.58 (m, 4 H), 1.42–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.0, 137.8, 137.6, 137.4, 128.4(6), 128.4(2), 128.4, 128.3, 127.8, 127.7(7), 127.7, 127.6, 106.5 (C-1), 106.1 (C-1), 88.6, 87.7, 83.2, 82.8, 82.0, 80.1, 72.3, 72.2, 72.0, 71.9, 67.6, 65.9, 62.1, 51.4, 29.5, 29.2, 29.1, 28.8, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{46}H_{57}N_3O_9Na$: 818.3992. Found: 818.3992.

8-Azidooctyl 2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-7). Alcohol **LAM-5** (11.0 g, 13.8 mmol) was glycosylated with thioglycoside **LAM-6**[14] (8.2 g, 15.1 mmol) using in *N*-iodosuccinimide (3.9 g, 16.5 mmol) and silver triflate (0.43 g, 1.65 mmol) in CH_2Cl_2 (220 mL) containing powdered 4 Å molecular sieves (4.5 g) as described for the preparation of **LAM-3**. Purification of the product by chromatography (8:1 hexanes–EtOAc) yielded **LAM-7** (15.6 g, 93%) as an oil. R_f 0.36 (4:1 hexanes–EtOAc); $[\alpha]_D$ + 63.0 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.05–8.01 (m, 2 H), 7.62–7.58 (m, 1 H), 7.46–7.42 (m, 2 H), 7.38–7.23 (m, 30 H), 5.51 (s, 1 H), 5.30 (s, 1 H, H-1), 5.22 (s, 1 H, H-1), 5.07 (s, 1 H, H-1), 4.86 (d, 1 H, *J* = 12.0 Hz), 4.63–4.48 (m, 11 H), 4.36 (ddd, 1 H, *J* = 8.9, 5.0, 5.0 Hz), 4.27 (ddd, 1 H, *J* = 6.7, 4.2, 4.0 Hz), 4.21 (ddd, 1 H, *J* = 7.2, 5.0, 3.5 Hz), 4.16–4.04 (m, 5 H), 3.98 (dd, 1 H, *J* = 11.3, 4.2 Hz), 3.94 (dd, 1 H, *J* = 11.5, 4.2 Hz), 3.78–3.72 (m, 3 H), 3.68 (dd, 1 H, *J*

= 10.7, 3.5 Hz), 3.62 (dd, 1 H, *J* = 10.7, 5.0 Hz), 3.43 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz), 3.28 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.66–1.59 (m, 4 H), 1.44–1.34 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 138.2, 138.1, 138.0, 137.9, 137.8, 137.7, 133.3, 129.8, 129.6, 128.4(6), 128.4(2), 128.3(9), 128.3(8), 128.3(3), 127.91, 127.9, 127.8, 127.7(8), 127.7(7), 127.7(1), 127.6(8), 127.6(6), 127.5(9), 127.5(7), 106.4 (C-1), 106.1 (C-1), 106.1 (C-1), 88.7, 88.2, 83.6, 83.3, 83.2, 82.4, 81.6, 80.4, 80.2, 73.4, 72.3(7), 72.3(3), 72.2, 72.0, 71.8, 69.4, 67.6, 66.0, 65.9, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{72}H_{81}N_3O_{14}Na$: 1234.5616. Found: 1234.5619.

8-Azidooctyl 3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-8).

Trisaccharide **LAM-7** (27.4 g, 22.6 mmol) dissolved in CH_2Cl_2 (200 mL) and CH_3OH (200 mL) was treated with $NaOCH_3$ (0.6 g) at rt. After stirring for 12 h, the reaction mixture was neutralized by the addition of HOAc and then concentrated. The crude product was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-8** (23.6 g, 94%) as an oil. R_f 0.20 (3:1 hexanes–EtOAc); $[\alpha]_D$ +62.9 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.40–7.21 (m, 30 H), 5.18 (s, 1 H, H-1), 5.10 (s, 1 H, H-1), 5.03 (s, 1 H, H-1), 4.64–4.23 (m, 12 H), 4.22–4.00 (m, 8 H), 3.92–3.86 (m, 3 H), 3.75–3.69 (m, 3 H), 3.64 (dd, 1 H, *J* = 10.5, 2.7 Hz), 3.49 (dd, 1 H, *J* = 10.5, 2.1 Hz), 3.40 (ddd, 1 H, *J* = 9.7, 6.8, 6.8 Hz), 3.25 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.65 (br s, 1 H), 1.60–1.52 (m, 4 H), 1.38–1.23 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 138.2, 138.0, 137.9, 137.6(8), 137.6(2), 137.2, 128.5, 128.3(9), 128.3(7), 128.3(4), 128.2, 127.9(9), 127.9(8), 127.9(1), 127.8(3), 127.8(1), 127.8(0), 127.7(7), 127.7(5), 127.6(7), 127.6(2), 127.5, 109.2 (C-1), 106.3 (C-1), 106.0 (C-1), 88.6, 88.2, 84.8, 83.2, 83.0(6), 83.0(4), 80.6, 80.1, 78.0, 73.7, 72.3, 72.2, 71.9(9), 71.9(4), 71.9(1), 69.7, 67.6, 65.9, 65.8, 51.4, 29.5, 29.2, 29.1, 28.8, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{65}H_{77}N_3O_{13}Na$: 1130.5354. Found: 1130.5352.

8-Azidooctyl 5-*O*-benzoyl-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-10). Alcohol **LAM-8** (5.54 g, 5.0 mmol), and thioglycoside **LAM-9**[15] (2.97 g, 5.5 mmol) were dried under vacuum in the presence of P_2O_5 for 4 h and then dissolved in CH_2Cl_2 (500 mL) and powdered 4 Å molecular sieves (3 g) were added. The reaction mixture was cooled to –60 °C and then *N*-iodosuccinimide (1.42 g, 6.0

mmol) and silver triflate (140 mg, 0.55 mmol) were added. The reaction temperature was increased to –40 °C and the mixture was stirred until the color changed. After another 15 min, Et_3N was added until the pH of the solution was slightly basic (pH < 8) as determined by wet pH paper. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and filtered through Celite. The filtrate was washed with a satd aq soln of $Na_2S_2O_3$, water and brine. The organic layer was subsequently dried (Na_2SO_4), filtered, concentrated and the resulting crude residue was purified by chromatography (4:1 hexanes–EtOAc) to yield **LAM-10** (6.63 g, 87%) as an oil. R_f 0.38 (3:1 hexanes–EtOAc); $[\alpha]_D$ +33.0 (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.03–7.99 (m, 2 H), 7.56–7.52 (m, 1 H), 7.40–7.19 (m, 42 H), 5.22–5.19 (m, 3 H, H-1 × 3), 5.04 (s, 1 H, H-1), 4.75 (d, 1 H, J = 11.6 Hz), 4.68 (d, 1 H, J = 11.7 Hz), 4.64–4.34 (m, 17 H), 4.29–4.03 (m, 11 H), 3.93 (dd, 1 H, J = 11.7, 3.8 Hz), 3.89 (dd, 1 H, J = 11.5, 4.1 Hz), 3.77–3.68 (m, 3 H), 3.62–3.55 (m, 2 H), 3.40 (ddd, 1 H, J = 9.6, 6.5, 6.5 Hz), 3.27 (dd, 2 H, J = 7.0, 6.9 Hz), 1.66–1.57 (m, 4 H), 1.42–1.32 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.0, 138.1, 138.0, 137.9(6), 137.9(2), 137.7, 137.6(4), 137.6(0), 137.4, 132.9, 129.7, 129.6, 128.4, 128.3, 128.2(8), 128.2(2), 128.1, 127.9(5), 127.9(0), 127.8(7), 127.8(3), 127.7, 127.6(6), 127.6(1), 127.5, 127.4(8), 127.4(4), 127.3, 106.4 (C-1), 106.3 (C-1), 106.0 (C-1), 100.8 (C-1), 88.6, 88.1, 86.3, 84. 4, 83.7, 83.1, 83.0, 82.3, 81.7, 80.4, 80.0, 78.6, 73.2, 72.4, 72.3, 72.2(7), 72.2(3), 71.9, 71.7, 70.0, 67.5, 66.3, 65.8, 65.5, 51.3, 29.4, 29.1, 29.0, 28.7, 26.5, 25.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{91}H_{101}N_3O_{18}Na$: 1546.6978. Found: 1546.6975.

8-Azidooctyl 2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-11). Tetrasaccharide **LAM-10** (12.1 g, 7.9 mmol) in CH_2Cl_2 (250 mL) and CH_3OH (250 mL) was treated with 1M methanolic sodium methoxide until the pH of the solution was 9 (as determined with wet pH paper). The reaction mixture was stirred at rt for 3 h, neutralized with HOAc and concentrated. The crude product was purified by chromatography (4:1 hexanes–EtOAc) to yield **LAM-11** (9.3 g, 83%) as an oil. R_f 0.17 (4:1 hexanes–EtOAc); $[\alpha]_D$ +35.0 (c = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.38–7.23 (m, 40 H), 5.16 (s, 1 H, H-1), 5.13 (d, 1 H, J = 1.4 Hz, H-1), 5.12 (d, 1 H, J = 4.4 Hz, H-1), 5.04 (d, 1 H, J = 1.1 Hz, H-1), 4.74 (d, 1 H, J = 11.6 Hz), 4.65 (d, 1 H, J = 11.9 Hz), 4.62–4.46 (m, 14 H), 4.37–4.35 (m, 1 H), 4.26 (dd, 1 H, J = 7.0, 6.7 Hz), 4.23–4.16 (m, 3 H), 4.14–4.09 (m, 3 H), 4.08 (dd, 1 H, J =

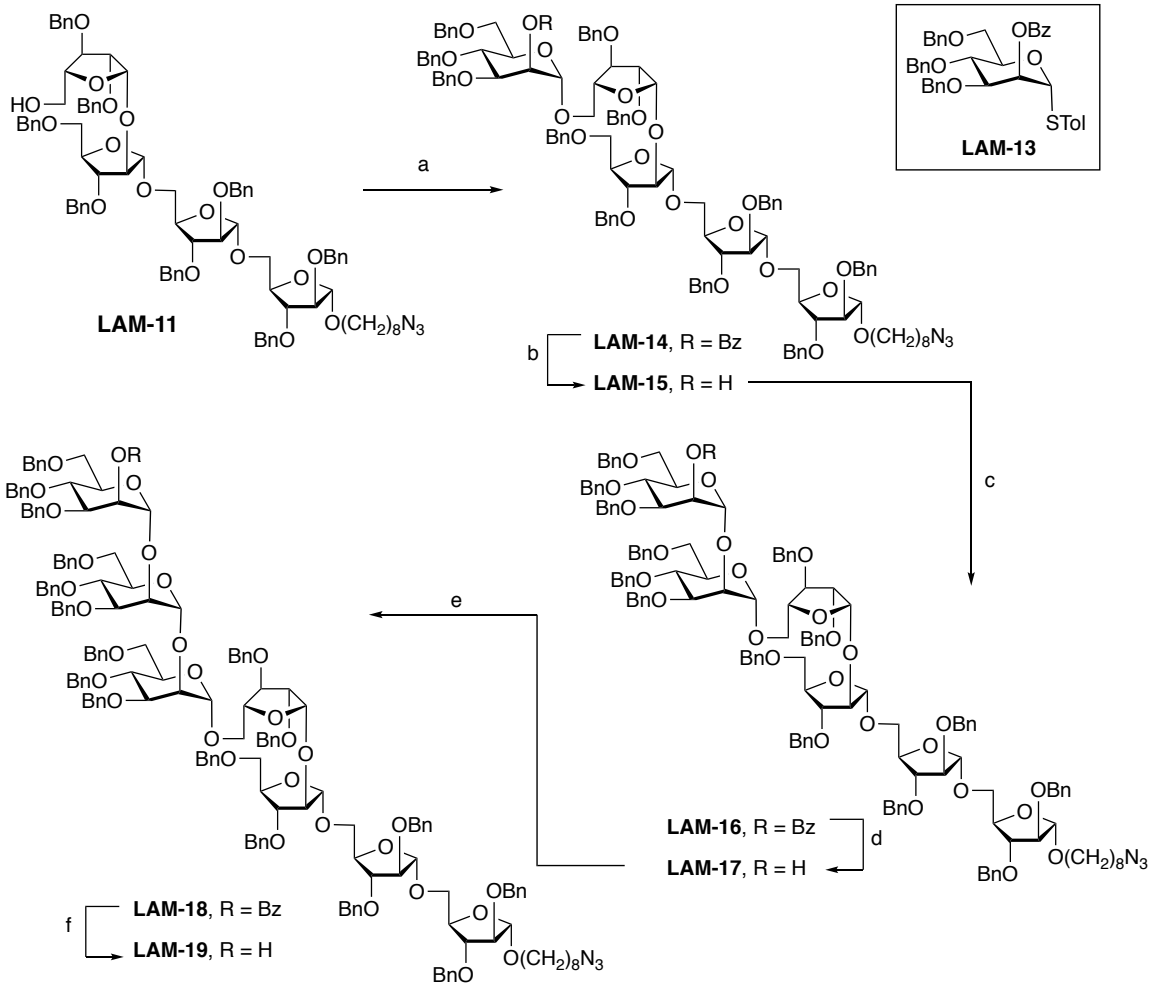
6.9, 3.5 Hz), 4.06–4.04 (m, 1 H), 4.03 (dd, 1 H, *J* = 6.9, 4.4 Hz), 4.00–3.97 (m, 1 H), 3.91 (dd, 1 H, *J* = 11.6, 3.9 Hz), 3.88 (dd, 1 H, *J* = 11.6, 4.1 Hz), 3.75–3.68 (m, 3 H), 3.64 (dd, 1 H, *J* = 9.0, 3.2 Hz), 3.61 (dd, 1 H, *J* = 10.6, 3.7 Hz), 3.58–3.53 (m, 2 H), 3.40 (ddd, 1 H, *J* = 9.7, 6.6, 6.6 Hz), 3.26 (dd, 2 H, *J* = 7.1, 6.9 Hz), 2.25 (br s, 1 H), 1.65–1.53 (m, 4 H), 1.38–1.25 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.1, 138.0(8), 138.0(7), 138.0(1), 137.9, 137.7, 137.6, 128.5, 128.4(2), 128.4(1), 128.3(9), 128.3(7), 128.3(3), 128.0, 127.9(7), 127.9(4), 127.8(7), 127.8(4), 127.7(6), 127.7(0), 127.6(7), 127.6(2), 106.4 (C-1), 106.3 (C-1), 106.1 (C-1), 100.1 (C-1), 88.7, 88.2, 86.0, 84.1, 83.4, 83.2(8), 83.2(4), 81.9, 81.1, 80.7, 80.5, 80.1, 73.4, 72.6, 72.4, 72.3, 72.1, 72.0, 71.9, 69.6, 67.6, 65.9, 63.4, 51.4, 29.5, 29.2, 29.1, 28.8, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{84}H_{97}N_3O_{17}Na$: 1442.6716. Found: 1442.6717.

8-Trifluoroacetamidooctyl 2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-12). A solution of **LAM-11** (241 mg, 0.170 mmol) in pyridine (3 mL) was treated with 10% Pd–C (17.8 mg) and H_2 (1 atm) for 3 h. The reaction mixture was filtered through Celite, diluted with pyridine (5 mL), cooled to 0 °C, and treated with trifluoroacetic anhydride (0.8 mL). The reaction mixture was stirred at rt for 13 h, the excess acylating agent quenched by the addition of a few drops of CH_3OH, and then the solution was diluted with CH_2Cl_2. The resulting solution was washed with a satd aq $NaHCO_3$ soln, water, and brine. The organic layer was then dried (Na_2SO_4), filtered and concentrated. The crude product was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-12** (178 mg, 70% over two steps) as an oil. R_f 0.29 (2:1 hexanes–EtOAc); $[\alpha]_D$ + 27.7 (*c* = 0.9, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.39–7.26 (m, 40 H), 6.49 (br s, 1 H), 5.18 (s, 1 H, H-1), 5.15 (d, 1 H, *J* = 1.3 Hz, H-1), 5.13 (d, 1 H, *J* = 4.4 Hz, H-1), 5.05 (d, 1 H, *J* = 0.8 Hz, H-1), 4.75 (d, 1 H, *J* = 11.8 Hz), 4.67 (d, 1 H, *J* = 11.9 Hz), 4.64–4.48 (m, 14 H), 4.38 (dd, 1 H, *J* = 3.4, 1.5 Hz), 4.28 (dd, 1 H, *J* = 7.0, 6.7 Hz), 4.25–4.18 (m, 3 H), 4.16–4.10 (m, 3 H), 4.09 (dd, 1 H, *J* = 6.9, 3.5 Hz), 4.07 (dd, 1 H, *J* = 3.5, 2.2 Hz), 4.05 (dd, 1 H, *J* = 6.3, 4.6 Hz), 4.02–3.99 (m, 1 H), 3.93 (dd, 1 H, *J* = 11.7, 3.9 Hz), 3.90 (dd, 1 H, *J* = 11.6, 4.3 Hz), 3.76–3.70 (m, 3 H), 3.66 (dd, 1 H, *J* = 12.2, 3.2 Hz), 3.63 (dd, 1 H, *J* = 10.8, 3.7 Hz), 3.59–3.55 (m, 2 H), 3.40 (ddd, 1 H, *J* = 9.7, 6.6, 6.6 Hz), 3.33 (ddd, 2 H, *J* = 6.9, 6.8, 6.8 Hz), 2.38 (br s, 1 H), 1.66–1.54 (m, 4 H), 1.41–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.2 (q, *J* = 36.2 Hz), 138.1, 138.0(8), 138.0(7), 138.0(5),

138.0(1), 137.9, 137.6(9), 137.6(4), 128.5, 128.4(4), 128.4(0), 128.3(9), 128.3(5), 128.0, 127.9(8), 127.8(8), 127.8(1), 127.7(9), 127.7(1), 127.6(9), 127.6(5), 115.9 (q, J = 287.5 Hz), 106.4 (C-1), 106.3 (C-1), 106.1 (C-1), 100.1 (C-1), 88.7, 88.3, 86.0, 84.1, 83.4, 83.3, 83.2, 81.9, 81.1, 80.7, 80.5, 80.2, 73.4, 72.6, 72.4, 72.3(7), 72.3(5), 72.1, 72.0, 71.9, 69.6, 67.6, 66.0, 63.5, 39.9, 29.5, 29.2, 29.1, 28.9, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{86}H_{98}NO_{18}F_3Na$: 1512.6628. Found: 1512.6624.

8-Trifluoroacetamidooctyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (1 Trifluoroacetamide). Tetrasaccharide **LAM-12** (146 mg, 0.098 mmol) in THF (0.6 mL) and CH_3OH (3 mL) was treated with 10% Pd–C (20 mg) and H_2 gas (1 atm) at rt for 16 h. The reaction mixture was filtered through Celite and concentrated. The crude product was purified by chromatography using Iatrobeads (3:1 CH_2Cl_2–CH_3OH) to yield **1 Trifluoroacetamide** (68 mg, 90%) as a white solid. R_f 0.30 (3:1 CH_2Cl_2–CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 5.06 (d, 1 H, J = 2.1 Hz, H-1), 5.02 (d, 1 H, J = 4.1 Hz, H-1), 4.94 (d, 1 H, J = 1.3 Hz, H-1), 4.84 (d, 1 H, J = 1.7 Hz, H-1), 4.13 (dd, 1 H, J = 4.8, 2.1 Hz), 4.08–3.92 (m, 8 H), 3.91–3.87 (m, 2 H), 3.86–3.76 (m, 4 H), 3.74–3.61 (m, 6 H), 3.41 (ddd, 1 H, J = 9.6, 6.6, 6.6 Hz), 3.26 (dd, 2 H, J = 7.2, 7.1 Hz), 1.61–1.52 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 158.9 (q, J = 36.5 Hz), 117.6 (q, J = 285.9 Hz), 109.6 (C-1), 109.5 (C-1), 107.5 (C-1), 102.4 (C-1), 89.2, 84.3, 84.0, 83.9, 83.6, 83.5, 83.2, 79.1, 78.9, 78.8, 76.4, 75.8, 68.9, 68.2(9), 68.2(1), 64.4, 62.4, 40.7, 30.6, 30.3, 30.2, 29.8, 27.7, 27.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{30}H_{50}NF_3O_{18}Na$: 792.2872. Found: 792.2872.

4. Synthesis of 2–4



Scheme S2. Synthesis of protected derivatives of Antigens **2–4**. a) **LAM-13**, NIS, AgOTf, CH_2Cl_2, 81%; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, 87%; c) **LAM-13**, NIS, AgOTf, CH_2Cl_2, 82%; d) $NaOCH_3$, CH_3OH, CH_2Cl_2, 95%; e) **LAM-13**, NIS, AgOTf, CH_2Cl_2, 83%; f) $NaOCH_3$, CH_3OH, CH_2Cl_2, 94%.

8-Azidooctyl 2-*O*-benzoyl-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-14). Alcohol **LAM-11** (4.00 g, 2.82 mmol) and thioglycoside **LAM-13**[16] (2.21 g, 3.28 mmol) were dissolved in CH_2Cl_2 (160 mL) and powdered 4 Å molecular sieves (1 g) were added. The solution was cooled to –10 °C and then *N*-iodosuccinimide (899 mg, 4.05 mmol) and silver triflate (256 mg, 1.00 mmol) were added. After stirring for 30 min at –10 °C, Et_3N was added

until the pH of the solution was neutral as determined by wet pH paper. The reaction was diluted with CH_2Cl_2, filtered through Celite and the filtrate was washed with a satd aq $Na_2S_2O_3$ soln, water, and brine. The organic layer was subsequently dried (Na_2SO_4), filtered and concentrated and the resulting crude residue was purified by chromatography (4:1 hexanes–EtOAc) to yield **LAM-14** (4.46 g, 81%) as an oil. R_f 0.39 (3:1 hexanes–EtOAc); $[\alpha]_D$ +16.0 (c = 1.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.09 (m, 2 H), 7.60–7.56 (m, 1 H), 7.40–7.20 (m, 56 H), 7.17–7.13 (m, 1 H), 5.63 (dd, 1 H, J = 3.0, 2.0 Hz), 5.15 (s, 2 H, 2 × H-1), 5.13 (d, 1 H, J = 4.3 Hz, H-1), 5.03 (d, 1 H, J = 1.1 Hz, H-1), 4.90 (d, 1 H, J = 2.0 Hz, H-1), 4.88 (d, 1 H, J = 10.9 Hz), 4.73–4.45 (m, 20 H), 4.39 (dd, 1 H, J = 2.9, 1.1 Hz), 4.38 (dd, 1 H, J = 11.3 Hz), 4.27–4.01 (m, 13 H), 3.94–3.83 (m, 5 H), 3.76–3.67 (m, 4 H), 3.65–3.57 (m, 3 H), 3.40 (ddd, 1 H, J = 9.6, 6.6, 6.6 Hz), 3.26 (dd, 2 H, J = 7.0, 7.0 Hz), 1.65–1.57 (m, 4 H), 1.43–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.5, 138.5, 138.2, 138.1, 138.0(8), 138.0(4), 138.0(3), 137.9, 137.7(5), 137.7(0), 130.1, 129.9(9), 129.9(4), 128.4(9), 128.4(2), 128.4(0), 128.3(7), 128.3(3), 128.2(6), 128.2(5), 128.0, 127.9(7), 127.9(6), 127.9(3), 127.9(1), 127.8, 127.7(6), 127.7(2), 127.5(8), 127.5(4), 127.4, 106.4 (C-1), 106.3 (C-1), 106.1 (C-1), 100.6 (C-1), 97.9 (C-1), 88.7, 88.3, 85.9, 84.2, 83.9, 83.8, 83.2(7), 83.2(2), 81.6, 80.5, 80.1, 79.3, 78.4, 75.2, 74.1, 73.4, 73.3, 72.4, 72.3(9), 72.3(6), 72.3(3), 72.2, 72.0(4), 72.0(2), 71.8, 71.5, 70.0, 69.8, 68.9, 68.8, 67.6, 65.9, 65.6, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{118}H_{129}N_3O_{23}Na$: 1978.8915. Found: 1978.8920.

8-Azidooctyl 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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-15). Pentasaccharide **LAM-14** (5.33 g, 2.72 mmol) was dissolved in CH_2Cl_2 (120 mL) and CH_3OH (120 mL) and then treated with 1M methanolic sodium methoxide (5 mL). After stirring for 8 h, the reaction mixture was neutralized with HOAc and concentrated. The crude product was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-15** (4.37 g, 87%) as an oil. R_f 0.12 (3:1 hexanes–EtOAc); $[\alpha]_D$ +30.3 (c = 0.7, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.18 (m, 55 H), 5.17 (s, 2 H, H-1 2 × H-1), 5.13 (d, 1 H, J = 4.4 Hz, H-1), 5.05 (s, 1 H, H-1 Ara), 4.92 (d, 1 H, J = 2.0 Hz, H-1), 4.84 (d, 1 H, J = 10.9 Hz), 4.72 (d, 1 H, J = 11.7 Hz), 4.68–4.45 (m, 20 H), 4.39 (m, 1 H), 4.28–4.02 (m, 12 H), 3.96–3.88 (m, 3 H), 3.86–3.69 (m, 7 H),

3.67–3.58 (m, 4 H), 3.41 (ddd, 1 H, J = 9.7, 6.6, 6.6 Hz), 3.27 (dd, 2 H, J = 7.0, 6.9 Hz), 2.48 (d, 1 H, J = 2.6 Hz), 1.66–1.59 (m, 4 H), 1.44–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.5, 138.3, 138.1(9), 138.1(6), 138.1(0), 138.0(8), 137.9, 137.7(7), 137.7(2), 137.7(1), 128.5(2), 128.5(0), 128.4(3), 128.4(1), 128.3(8), 128.3(4), 128.3(2), 128.0, 127.9(5), 127.8(9), 127.8(4), 127.7(9), 127.7(7), 127.7(5), 127.7(3), 127.6(9), 127.6(5), 127.5(9), 127.5(3), 106.4(8) (C-1), 106.4(2) (C-1), 106.1 (C-1), 100.6 (C-1), 99.3 (C-1), 88.7, 88.3, 86.2, 84.2, 83.9, 83.4, 83.2(9), 83.2(2), 81.5, 80.5, 80.2, 80.1, 79.2, 75.0, 74.1, 73.4, 73.3, 72.4(7), 72.4(2), 72.3(9), 72.3(5), 72.3(1), 72.0, 71.9, 71.8, 71.5, 69.9, 69.0, 68.8, 68.2, 67.6, 65.9, 65.6, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{111}H_{125}N_3O_{22}Na$: 1874.8652. Found: 1874.8653.

8-Azidooctyl 2-*O*-benzoyl-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)-2,3-di-*O*-benzyl- α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-16). To a solution of **LAM-15** (2.37 g, 1.28 mmol), **LAM-13**[16] (1.01 g, 1.53 mmol) in CH_2Cl_2 (100 mL) was added powdered 4 Å molecular sieves (0.9 g). The reaction mixture was cooled to –10 °C for 15 min and then *N*-iodosuccinimide (434 mg, 1.83 mmol) and silver triflate (118 mg, 0.46 mmol) were added. After stirring for 30 min, the reaction mixture turned dark red\brown and then Et_3N was added until the pH of the solution was neutral as determined by wet pH paper. The reaction was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with a satd aq $Na_2S_2O_3$ soln, water and brine. The organic layer was subsequently dried (Na_2SO_4), filtered and concentrated. The resulting crude residue was purified by chromatography (4:1 hexanes–EtOAc) to yield hexaccharide **LAM-16** (2.49 g, 82%) as an oil. R_f 0.37 (3:1 hexanes–EtOAc); $[\alpha]_D$ +17.2 (c = 0.4, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.09 (m, 2 H), 7.61–7.57 (m, 1 H), 7.42–7.12 (m, 72 H), 5.80 (dd, 1 H, J = 2.2, 2.0 Hz), 5.21 (d, 1 H, J = 2.0 Hz, H-1), 5.16–5.14 (m, 2 H, 2 × H-1), 5.12 (d, 1 H, J = 4.4 Hz, H-1), 5.04 (s, 1 H, H-1), 4.98 (d, 1 H, J = 1.6 Hz, H-1), 4.89 (d, 1 H, J = 10.9 Hz), 4.88 (d, 1 H, J = 11.0 Hz), 4.78 (d, 1 H, J = 11.2 Hz), 4.74–4.43 (m, 25 H), 4.38 (d, 1 H, J = 1.9 Hz), 4.25 (ddd, 1 H, J = 6.0, 6.0, 3.9 Hz), 4.20–4.17 (m, 2 H), 4.16–3.83 (m, 18 H), 3.82–3.55 (m, 10 H), 3.40 (ddd, 1 H, J = 9.6, 6.6, 6.6 Hz), 3.27 (dd, 2 H, J = 7.0, 7.0 Hz), 1.65–1.58 (m, 4 H), 1.43–1.33 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 138.6, 138.5(7), 138.5(2), 138.2(4),

138.2(1), 138.1(6), 138.1(3), 138.0(8), 138.0(7), 138.0, 137.7(5), 137.7(2), 137.6, 133.0, 130.1, 129.9, 128.4(9), 128.4(2), 128.4(0), 128.3(7), 128.3(4), 128.3(2), 128.2(9), 128.2(5), 128.2(2), 128.1, 128.0(5), 128.0(0), 127.9(8), 127.9(7), 127.9(4), 127.9(1), 127.8, 127.7(6), 127.7(3), 127.6(9), 127.6(6), 127.5(8), 127.5(4), 127.5(0), 127.4, 127.3(9), 127.3(2), 106.4 (C-1), 106.3 (C-1), 106.1 (C-1), 100.7 (C-1), 99.6 (C-1), 98.7 (C-1), 88.7, 88.3, 86.0, 84.3, 83.9(7), 83.9(4), 83.2(7), 83.2(0), 81.5, 80.5, 80.1, 79.9, 79.3, 78.2, 75.2, 75.1, 75.0, 74.4, 74.3, 73.3, 73.2, 72.4, 72.3(9), 72.3(4), 72.2(8), 72.2(2), 72.1, 72.0, 71.8, 71.6, 70.1, 69.5, 69.1, 67.6, 65.9, 65.5, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.1. LRMS (ESI) *m/z* calcd for (M+Na) $C_{145}H_{157}N_3O_{28}Na$: 2412.0885. Found: 2412.1.

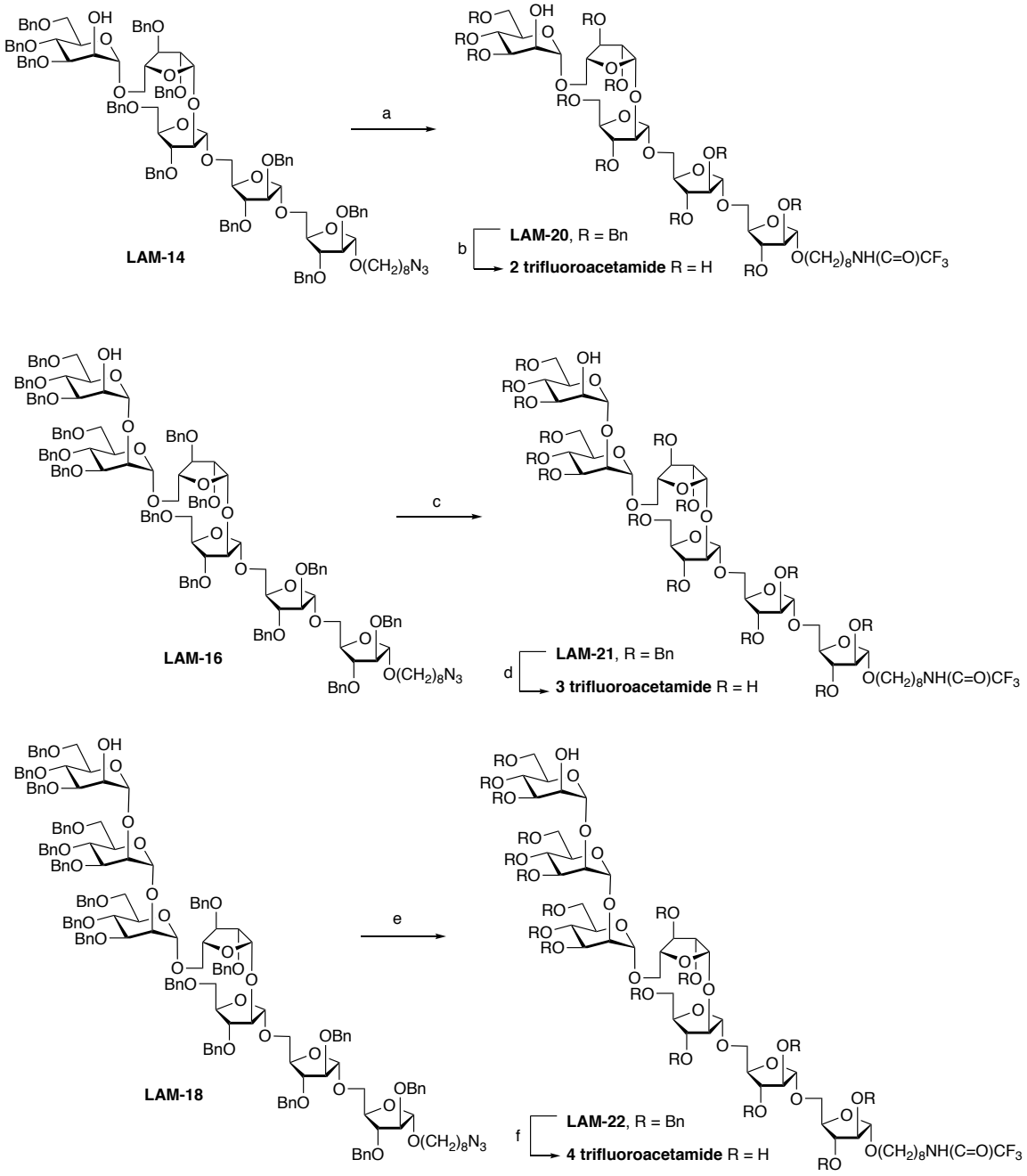
8-Azidooctyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl- α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-17). The hexasaccharide **LAM-16** (2.39 g, 1.0 mmol) in CH_2Cl_2 (30 mL) and CH_3OH (30 mL) was treated with 1M methanolic sodium methoxide (1.2 mL) at rt. After stirring for 16 h the reaction mixture was neutralized with HOAc and concentrated. The crude product was purified by chromatography (7:3 hexanes–EtOAc) to yield **LAM-17** (2.17 g, 95%) as an oil. R_f 0.47 (2:1 hexanes–EtOAc); $[\alpha]_D$ +28.3 (c = 0.8, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.38–7.14 (m, 70 H), 5.16 dd, 1 H, J = 0.9 Hz, H-1), 5.15 (s, 1 H, H-1), 5.14 (s, 1 H, H-1), 5.10 (d, 1 H, J = 2.0 Hz, H-1), 5.03 (s, 1 H, H-1), 4.99 (d, 1 H, J = 1.0 Hz, H-1), 4.84 (d, 1 H, J = 10.8 Hz), 4.83 (d, 1 H, J = 10.9 Hz), 4.71 (d, 1 H, J = 10.8 Hz), 4.67 (d, 1 H, J = 12.2 Hz), 4.64–4.42 (m, 24 H), 4.38 (d, 1 H, J = 1.7 Hz), 4.24 (ddd, 1 H, J = 5.8, 5.8, 3.7 Hz), 4.19–4.16 (m, 2 H), 4.15–4.05 (m, 8 H), 4.01–3.86 (m, 9 H), 3.84–3.77 (m, 3 H), 3.74–3.68 (m, 4 H), 3.66–3.55 (m, 5 H), 3.40 (ddd, 1 H, J = 9.7, 6.8, 6.8 Hz), 3.27 (dd, 2 H, J = 7.1, 6.9 Hz), 2.38 (d, 1 H, J = 2.4 Hz), 1.64–1.58 (m, 4 H), 1.41–1.33 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.6(7), 138.6(3), 138.4(9), 138.2(6), 138.2(1), 138.1(6), 138.0(8), 138.0(1), 137.7(5), 137.7(2), 137.6, 133.0, 130.1, 128.4(9), 128.4(7), 128.4(2), 128.4(1), 128.4(0), 128.3(7), 128.3(3), 128.3(0), 128.2, 127.9(8), 127.9(4), 127.9(2), 127.9(1), 127.8, 127.8(6), 127.8(3), 127.7(6), 127.7(3), 127.6(9), 127.6(5), 127.6(0), 127.5(7), 127.5(4), 127.5(2), 127.3(7), 127.3(4),106.4 (C-1), 106.3 (C-1), 106.1 (C-1), 101.1 (C-1), 100.7 (C-1), 98.7 (C-1), 88.7, 88.3, 86.0, 84.3, 83.9, 83.8, 83.2(7), 83.2, 81.5, 80.5, 80.2, 80.0, 79.9, 79.3, 75.1, 75.0, 74.8, 74.5, 74.3, 73.3, 73.2, 72.4, 72.3(8), 72.3(3), 72.3(1), 72.2, 72.1, 72.0, 71.8, 71.7, 70.1, 69.5, 69.1, 68.8, 68.5, 67.6, 65.9,

65.5, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.1. LRMS (ESI) *m/z* calcd for (M+Na) $C_{138}H_{153}N_3O_{27}Na$: 2308.0623. Found: 2308.1.

8-Azidooctyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-18). Alcohol **LAM-17** (1.01 g, 0.438 mmol) was glycosylated with thioglycoside **LAM-13**[16] (347 mg, 0.525 mmol) using *N*-iodosuccinimide (149 mg, 0.63 mmol) and silver triflate (48 mg, 0.19 mmol) in CH_2Cl_2 (50 mL) containing powdered 4 Å molecular sieves (0. 5 g) as described for the preparation of **LAM-16**. The product was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-18** (1.02 g, 83%) as an oil. R_f 0.22 (3:1 hexanes–EtOAc); $[\alpha]_D$ +19.2 (*c* = 0.4, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.12–8.10 (m, 2 H), 7.60–7.57 (m, 1 H), 7.42–7.12 (m, 86 H), 7.01–6.98 (m, 1 H), 5.77 (dd, 1 H, *J* = 2.2, 2.2 Hz), 5.25 (d, 1 H, *J* = 1.8 Hz, H-1), 5.12 (d, 1 H, *J* = 1.8 Hz, H-1), 5.12–5.10 (m, 2 H, 2 × H-1), 5.08 (d, 1 H, *J* = 4.4 Hz, H-1), 5.01 (d, 1 H, *J* = 1.0 Hz, H-1), 4.96 (d, 1 H, *J* = 1.7 Hz, H-1), 4.86 (d, 1 H, *J* = 10.9 Hz), 4.85 (d, 1 H, *J* = 11.0 Hz), 4.81 (d, 1 H, *J* = 10.9 Hz), 4.75 (d, 1 H, *J* = 11.2 Hz), 4.69–4.40 (m, 28 H), 4.36–4.31 (m, 3 H), 4.23–4.19 (m, 1 H), 4.16–4.08 (m, 6 H), 4.07–4.00 (m, 6 H), 3.97–3.51 (m, 24 H), 3.37 (ddd, 1 H, *J* = 9.7, 6.7, 6.7 Hz), 3.25 (dd, 2 H, *J* = 7.0, 6.9 Hz), 1.62–1.56 (m, 4 H), 1.40–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 138.7, 138.6(7), 138.6(4), 138.6(2), 138.5, 138.4, 138.2(9), 138.2(6), 138.2(1), 138.1(3), 138.0, 137.8, 137.7, 133.0, 130.2, 130.0, 128.5, 128.4(7), 128.4(4), 128.4(1), 128.3(8), 128.3(6), 128.3(5), 128.3(3), 128.2(7), 128.1(6), 128.1(0), 128.1, 128.0(0), 127.9(8), 127.9(4), 127.8(8), 127.8(0), 127.7(7), 127.7(3), 127.7(0), 127.6(3), 127.5(8), 127.5(6), 127.5(3), 127.5(0), 127.4(4), 127.4(2), 127.3(9), , 106.5 (C-1), 106.3 (C-1), 106.1 (C-1), 100.7 (C-1), 100.6 (C-1), 99.4 (C-1), 98.9 (C-1), 88.7, 88.3, 86.0, 84.3, 84.0, 83.9, 83.3, 83.2, 81.6, 80.6, 80.2, 79.9, 79.4, 78.2, 75.5, 75.2, 75.1(8), 75.1(3), 74.7(9), 74.7(2), 74.3, 73.4, 73.3(6), 73.3(2), 73.2, 72.5, 72.4, 72.3(7), 72.3(5), 72.2(9) (2), 72.2(0), 72.0, 71.9, 71.6, 70.2, 69.7, 69.2, 69.1(8), 69.1(5), 69.0, 67.6, 66.0, 65.5, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1. LRMS (ESI) *m/z* calcd for (M+Na) $C_{172}H_{185}N_3O_{33}Na$: 2845.2994. Found: 2845.3.

8-Azidooctyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-19). The heptasaccharide **LAM-18** (308 mg, 0.109 mmol) in CH_2Cl_2 (3 mL) and CH_3OH (1 mL) was treated with 1M methanolic sodium methoxide (0.2 mL) solution at rt. After stirring for 6 h, the reaction mixture was neutralized with HOAc and concentrated. The crude product was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-19** (278 mg, 94%) as an oil. R_f 0.50 (2:1 hexanes–EtOAc); $[\alpha]_D$ +30.7 (*c* 0.48, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.42–7.12 (m, 85 H), 5.30 (d, 1 H, *J* = 1.6 Hz, H-1), 5.21 (d, 1 H, *J* = 1.4 Hz, H-1), 5.18 (s, 1 H, H-1), 5.16 (s, 1 H, H-1), 5.13 (d, 1 H, *J* = 4.3 Hz, H-1), 5.06 (s, 1 H, H-1), 5.04 (d, 1 H, *J* = 1.4 Hz, H-1), 4.90–4.84 (m, 3 H), 4.74 (d, 1 H, *J* = 11.7 Hz), 4.70 (d, 1 H, *J* = 3.6 Hz), 4.68 (d, 1 H, *J* = 3.5 Hz), 4.66–4.44 (m, 27 H), 4.41–4.32 (m, 3 H), 4.30–4.25 (m, 1 H), 4.23–4.04 (m, 11 H), 4.03–3.56 (m, 25 H), 3.43 (ddd, 1 H, *J* = 9.7, 6.7, 6.7 Hz), 3.28 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.36 (br. s. 1 H), 1.65–1.58 (m, 4 H), 1.42–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.6(6), 138.6(3), 138.6(1), 138.4, 138.3, 138.2(8), 138.2(4), 138.1(9), 138.1(7), 138.1(1), 138.0, 137.7(8), 137.7(4), 128.5, 128.4(9), 128.4(5), 128.4(2), 128.4(0), 128.3(6), 128.3(4), 128.3(2), 128.2(8), 128.0, 127.9(7), 127.9(2), 127.9(1), 127.8(6), 127.8(2), 127.7(9), 127.7(6), 127.7(4), 127.6(9), 127.6(6), 127.6(0), 127.5(6), 127.5(5), 127.5(0), 127.4, 127.3, 106.5 (C-1), 106.3 (C-1), 106.1 (C-1), 100.9 (C-1), 100.7 (C-1), 98.8 (C-1), 88.7, 88.3, 86.0, 84.3, 84.0, 83.9, 83.2(9), 83.2(3), 81.6, 80.6, 80.2, 80.0, 79.8, 79.6, 79.4(3), 77.4, 77.1, 76.8, 75.1, 75.0(8), 75.0(0), 74.8(3), 74.8(1), 74.6, 74.2, 73.3(8), 73.3(6), 73.3(1), 73.2, 72.5, 72.4, 72.3(6), 72.3(3), 72.3, 72.1, 72.0, 71.9(8), 71.9(1), 71.7, 70.2, 69.7, 69.2, 69.1, 68.8, 68.6, 67.6, 66.0, 65.5, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{165}H_{181}N_3O_{32}Na$: 2739.2520. Found: 2739.2487.



Scheme S3. Synthesis of Antigens **2–4** trifluoroacetamide derivatives. a) H_2, Pd–C, pyridine; then trifluoroacetic anhydride, pyridine, 76%; b) H_2, Pd–C, EtOAc, CH_3OH, 91%; c) H_2, Pd–C, pyridine; then trifluoroacetic anhydride, pyridine, 72%; d) H_2, Pd–C, THF, CH_3OH, 89%; e) Ph_3P, H_2O, THF; then trifluoroacetic anhydride, pyridine, 70%; f) H_2, Pd–C, THF, CH_3OH, quantitative.

8-Trifluoroacetamidooctyl 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)-2,3-di-*O*-

benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-20). Pentasaccharide **LAM-14** (242 mg, 0.13 mmol) in pyridine (3.5 mL) was treated with 10% Pd–C (15 mg) and H_2 gas (1 atm), then more pyridine (3.5 mL) and trifluoroacetic anhydride (1.5 mL) as described for the synthesis of **LAM-12**. The crude product was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-20** (192 mg, 76% over two steps) as an oil. R_f 0.16 (2:1 hexanesEtOAc); $[\alpha]_D$ +31.0 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.20 (m, 55 H), 6.40 (br s, 1 H), 5.17 (s, 2 H, 2 × H-1), 5.14 (d, 1 H, J = 4.4 Hz, H-1), 5.05 (s, 1 H, H-1), 4.93 (s, 1 H, H-1), 4.85 (d, 1 H, J = 10.9 Hz), 4.73 (d, 1 H, J = 11.8 Hz), 4.69–4.45 (m, 20 H), 4.41–4.24 (m, 1 H), 4.22–4.17 (m, 2 H), 4.16–4.03 (m, 9 H), 3.96–3.70 (m, 10 H), 3.67–3.59 (m, 4 H), 3.42 (ddd, 1 H, J = 9.6, 6.7, 6.7 Hz), 3.34 (ddd, 2 H, J = 6.9, 6.8 Hz), 2.51 (br s, 1 H), 1.65–1.54 (m, 4 H), 1.42–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.1 (q, J = 36.6 Hz), 138.5, 138.3, 138.1(8), 138.1(4), 138.1(0), 138.0(7), 137.9, 137.7(5), 137.7(1), 128.5(2), 128.5(0), 128.4(4), 128.4(2), 128.3(9), 128.3(5), 128.3(3), 128.0, 127.9(9), 127.9(5), 127.9(0), 127.8, 127.7(9), 127.7(7), 127.7(5), 127.7(4), 127.7(0), 127.6(6), 127.6(0), 127.5, 115.9 (q, J = 287.3 Hz), 106.4(8) (C-1), 106.4(2) (C-1), 106.1 (C-1), 100.6 (C-1), 99.3 (C-1), 88.7, 88.3, 86.2, 84.2, 83.9, 83.3(9), 83.3(3), 83.2, 81.5, 80.5, 80.2, 80.1, 79.2, 75.0, 74.1, 73.4, 73.3, 72.4(7), 72.4(2), 72.4(0), 72.3(6), 72.3(2), 72.0, 71.9, 71.8, 71.5, 69.9, 69.0, 68.8, 68.2, 67.6, 66.0, 65.6, 40.0, 29.5, 29.2, 29.1, 28.9, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{113}H_{126}F_3NO_{23}Na$: 1944.8570. Found: 1944.8565.

8-Trifluoroacetamidooctyl α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (2 Trifluoroacetamide). Pentasaccharide **LAM-20** (170 mg, 0.088 mmol) in EtOAc (0.5 mL) and CH_3OH (4 mL) was treated with 10% Pd–C (34 mg) and H_2 gas (1 atm) at rt for 18 h. The reaction mixture was filtered through Celite and concentrated. The crude product was purified by chromatography using Iatrobeads (2:1 CH_2Cl_2–CH_3OH) to yield **2 Trifluoroacetamide** (75 mg, 91%) as a white solid; ^{1}H NMR (600 MHz, CD_3OD, δ_H) 5.08 (d, 1 H, J = 1.7 Hz, H-1), 5.02 (d, 1 H, J = 4.4 Hz, H-1), 4.94 (d, 1 H, J = 1.4 Hz, H-1), 4.85–4.83 (m, 2 H, 2 × H-1), 4.12 (dd, 1 H, J = 4.2, 1.7 Hz), 4.08–3.93 (m, 8 H), 3.92–3.79 (m, 8 H), 3.78–3.58 (m, 9 H), 3.41 (ddd, 1 H, J = 9.6, 6.5, 6.5 Hz), 3.26 (dd, 2 H, J = 7.2, 7.1 Hz), 1.62–1.52 (m, 4 H), 1.41–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 158.9 (q, J = 36.6 Hz), 117.6 (q, J = 285.9 Hz), 109.6 (C-1), 109.5

(C-1), 107.4 (C-1), 102.3 (C-1), 101.7 (C-1), 89.5, 84.4, 84.0, 83.6, 83.5, 83.2, 82.2, 79.1, 79.0, 78.4, 76.7, 76.0, 74.7, 72.5, 72.0, 69.6, 68.9, 68.7, 68.2, 68.1, 63.0, 62.4, 40.7, 30.6, 30.3, 30.2, 29.8, 27.7, 27.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{36}H_{60}NO_{23}F_3Na$: 954.3400. Found: 954.3409.

8-Trifluoroacetamidooctyl 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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-21). Hexasaccharide **LAM-16** (255 mg, 0.112 mmol) in pyridine (4 mL) was treated with 10% Pd–C (15 mg) and H_2 gas (1 atm) for 16 h at rt, then more pyridine (3 mL) and trifluoroacetic anhydride (1.5 mL) as described for the synthesis of **LAM-12**. The crude product was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-21** (189 mg, 72% over two steps) as an oil. R_f 0.29 (2:1 hexanes–EtOAc); $[\alpha]_D$ +30.9 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.37–7.13 (m, 70 H), 6.33 (br s, 1 H, NH), 5.15 (dd, 1 H, *J* = 1.3 Hz, H-1), 5.14 (s, 1 H, H-1), 5.13 (s, 1 H, H-1), 5.11 (d, 1 H, *J* = 4.3 Hz, H-1), 5.03 (s, 1 H, H-1), 4.99 (d, 1 H, *J* = 1.4 Hz, H-1), 4.84 (d, 1 H, *J* = 10.9 Hz), 4.83 (d, 1 H, *J* = 10.9 Hz), 4.71 (d, 1 H, *J* = 10.7 Hz,), 4.66 (d, 1 H, *J* = 12.2 Hz,), 4.64–4.41 (m, 24 H,), 4.37 (d, 1 H, *J* = 1.7 Hz), 4.24 (ddd, 1 H, *J* = 6.0, 6.0, 3.8 Hz), 4.19–4.15 (m, 2 H), 4.14–4.04 (m, 8 H), 4.01–3.86 (m, 9 H), 3.84–3.77 (m, 3 H), 3.74–3.67 (m, 4 H), 3.66–3.54 (m, 5 H), 3.40 (ddd, 1 H, *J* = 9.6, 6.7, 6.7 Hz), 3.34 (ddd, 2 H, *J* = 6.7, 6.7, 6.7 Hz, CH_2N), 2.38 (br s, 1 H), 1.63–1.54 (m, 4 H), 1.40–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.1 (q, *J* = 36.5 Hz), 138.6(8), 138.6(4), 138.5, 138.2(7), 138.2(1), 138.1, 138.0(9), 138.0(7), 138.0(1), 137.7(5)(, 137.7(0), 128.5, 128.4(8), 128.4(2), 128.4(1), 128.3(8), 128.3(5), 128.3(1), 128.2, 128.0, 127.9(5), 127.9(2), 127.8, 127.7(8), 127.7(4), 127.7(2), 127.6(7), 127.6(0), 127.5(6), 127.5(2), 127.3(9), 127.3(5), 115.9 (q, *J* = 287.3 Hz), 106.4 (C-1), 106.3 (C-1), 106.1 (C-1), 101.1 (C-1), 100.7 (C-1), 98.7 (C-1), 88.7, 88.3, 86.0, 84.3, 83.9, 83.8, 83.3, 83.2, 81.5, 80.5, 80.2, 80.0, 79.9, 79.3, 75.1, 75.0, 74.8, 74.5, 74.3, 73.3(4), 73.3(0), 72.4, 72.3(5), 72.3(2), 72.2, 72.1, 72.0, 71.9, 71.7, 70.1, 69.5, 69.1, 68.9, 68.5, 67.6, 66.0, 65.5, 40.0, 29.5, 29.2, 29.1, 28.9, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{140}H_{154}F_3NO_{28}Na$: 2377.0507. Found: 2377.0501.

8-Trifluoroacetamidooctyl 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-arabinofuranoside (3 Trifluoroacetamide).

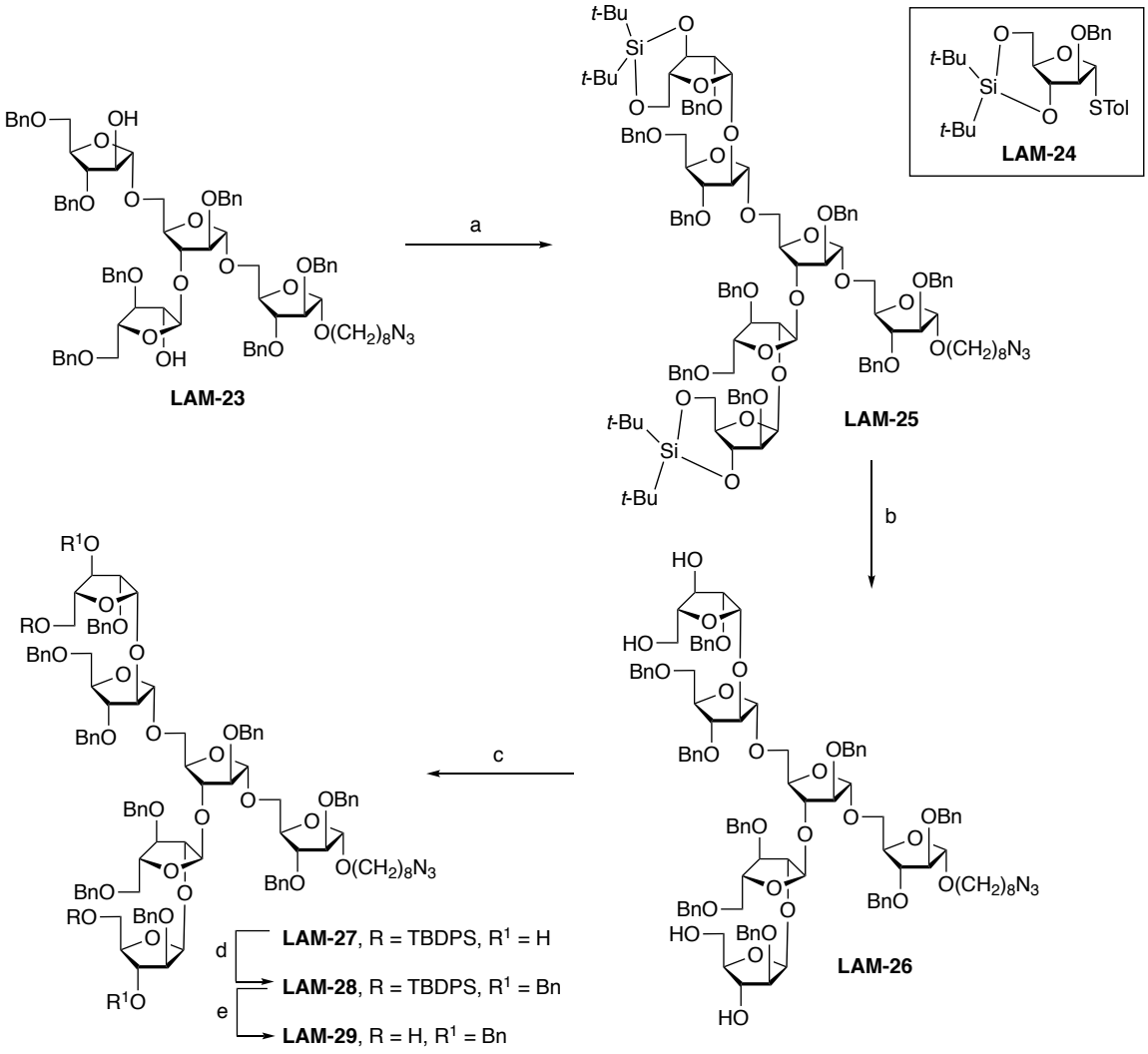
Hexasaccharide **LAM-21** (145 mg, 0.062 mmol) in THF (0.5 mL) and CH_3OH (3 mL) was treated with 10% Pd–C (29 mg) and H_2 gas (1 atm) at rt for 18 h. The reaction mixture was filtered through Celite and concentrated. The crude product was purified by chromatography using Iatrobeads (7:3 CH_2Cl_2–CH_3OH) to yield **3 Trifluoroacetamide** (60 mg, 89%) as a white solid. R_f 0.30 (7:3, CH_2Cl_2–CH_3OH); $[\alpha]_D$ +62.6 (*c* = 0.7, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 5.11 (d, 1 H, *J* =1.4 Hz, H-1), 5.08 (d, 1 H, *J* = 1.8 Hz, H-1), 5.02 (d, 1 H, *J* = 4.3 Hz, H-1), 4.98 (d, 1 H, *J* = 1.4 Hz, H-1), 4.94 (d, 1 H, *J* = 1.3 Hz, H-1), 4.84 (d, 1 H, *J* = 1.6 Hz, H-1), 4.12 (dd, 1 H, *J* = 4.3, 1.8 Hz), 4.08–4.03 (m, 2 H), 4.01–3.93 (m, 7 H), 3.92–3.77 (m, 11 H), 3.74–3.53 (m, 12 H), 3.41 (ddd, 1 H, *J* = 9.7, 6.6, 6.6 Hz), 3.26 (dd, 2 H, *J* = 7.3, 7.1 Hz), 1.61–1.52 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 158.9 (q, *J* = 36.6 Hz), 117.6 (q, *J* = 285.9 Hz), 109.6 (C-1), 109.5 (C-1), 107.3 (C-1), 104.1 (C-1), 102.3 (C-1), 100.1 (C-1), 89.2, 84.5, 83.9, 83.6, 83.5, 83.3, 82.2, 80.4, 79.1, 79.0, 78.5, 76.7, 76.3, 75.0, 74.7, 72.4, 72.0, 71.9, 70.2, 69.1, 68.9(3), 68.9(0), 68.1(9), 68.1(5), 63.2, 63.1, 62.4, 40.7, 30.6, 30.3, 30.2, 29.8, 27.7, 27.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{42}H_{70}NO_{28}F_3Na$: 1116.3928. Found: 1116.3921.

8-Trifluoroacetamidooctyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-22). Heptasaccharide **LAM-18** (225 mg, 0.083 mmol) in THF (6 mL) and water (3 drops) was treated with triphenylphosphine (28 mg, 0.099 mmol) for 2 days at rt and then concentrated. The concentrate was redissolved in pyridine (2 mL) and CH_2Cl_2 (2 mL) followed by the addition of trifluoroacetic anhydride (0.2 mL). The reaction mixture was stirred at rt for 18 h and worked up as described for the synthesis of **LAM-21**. The crude product was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-22** (162 mg, 70% over two steps) as an oil. R_f 0.21 (2:1 hexanes–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.36–7.09 (m, 85 H), 6.28 (br s, 1 H), 5.24 (d, 1 H, *J* = 1.8 Hz, H-1), 5.15 (d, 1 H, *J* = 1.5 Hz, H-1), 5.12 (s, 1 H, H-1), 5.10 (s, 1 H, H-1), 5.07

(d, 1 H, *J* = 4.4 Hz, H-1), 5.01 (s, 1 H, H-1), 4.97 (d, 1 H, *J* = 1.5 Hz, H-1), 4.84–4.79 (m, 3 H), 4.69–4.40 (m, 29 H), 4.34–4.33 (m, 1 H), 4.31 (d, 1 H, *J* = 11.7 Hz), 4.28 (d, 1 H, *J* = 12.2 Hz), 4.21 (ddd, 1 H, *J* = 6.0, 3.8, 3.8 Hz), 4.19–4.11 (m, 3 H), 4.10–3.99 (m, 7 H), 3.97–3.83 (m, 11 H), 3.82–3.47 (m, 14 H), 3.38 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz), 3.33 (ddd, 2 H, *J* = 6.8, 6.8, 6.8 Hz), 2.04 (br s, 1 H), 1.61–1.57 (m, 4 H), 1.38–1.28 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.4 (q, *J* = 36.6 Hz), 138.5(7), 138.5(4), 138.3, 138.2(2), 138.2(0), 138.1(7), 138.1(0), 138.0, 137.9, 137.7, 137.6, 129.7, 129.0, 128.4(5), 128.4(4), 128.4(0), 128.3(5), 128.3(1), 128.2(7), 128.2(3), 127.9(5), 127.9(1), 127.8(6), 127.8(5), 127.8(1), 127.7(7), 127.7(4), 127.7(0), 127.6(8), 127.6(3), 127.5(9), 127.5(6), 127.5(1), 127.4, 127.3(8), 127.3(3), 116.1 (q, *J* = 288.0 Hz), 106.4 (C-1), 106.2 (C-1), 106.1 (C-1), 100.9 (C-1), 100.7(5) (C-1), 100.7(0) (C-1), 98.8 (C-1), 88.6, 88.2, 86.0, 84.3, 83.9, 83.8, 83.2, 83.1, 81.5, 80.5, 80.1, 80.0, 79.7, 79.5, 79.3, 75.1, 75.0, 74.9, 74.7(6), 74.7(1), 74.5, 74.2, 73.3(3), 73.3(0), 73.2(5), 73.2(0), 72.4, 72.3(7), 72.3(2), 72.2(6), 72.0(9), 72.0(0), 71.9, 71.8, 71.6, 70.1, 69.6, 69.2, 69.0, 68.7, 68.5, 67.5, 65.9, 65.5, 39.9, 29.4, 29.1, 29.0, 28.9, 26.6, 26.0.

8-Trifluoroacetamidooctyl α-D-mannopyranosyl-(1→2)-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-arabinofuranoside (4 Trifluoroacetamide). Heptasaccharide **LAM-22** (79 mg, 0.028 mmol) in THF (0.5 mL) and CH_3OH (2 mL) was treated with 10% Pd–C (10 mg) and H_2 gas (1 atm) at rt for 24 h. The reaction mixture was filtered through Celite and concentrated. The crude product was purified by chromatography using Iatrobeads (3:2 CH_2Cl_2–CH_3OH) to yield **4 Trifluoroacetamide** (38 mg, quantitative) as a white solid. R_f 0.30 (7:3 CH_2Cl_2–CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 5.28 (s, 1 H, H-1), 5.11 (s, 1 H, H-1), 5.08 (d, 1 H, *J* = 1.4 Hz, H-1), 5.01 (d, 1 H, *J* = 4.3 Hz, H-1), 4.98 (s, 1 H, H-1), 4.94 (s, 1 H, H-1), 4.84 (d, 1 H, *J* = 1.4 Hz, H-1), 4.12 (dd, 1 H, *J* = 4.1, 1.4 Hz), 4.08–3.77 (m, 24 H), 3.74–3.50 (m, 16 H), 3.41 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz), 3.26 (dd, 2 H, *J* = 7.2, 7.1 Hz), 1.62–1.53 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 158.9 (C=O, q, *J* = 36.6 Hz), 117.6 (CF_3, q, *J* = 285.9 Hz), 109.6 (C-1), 109.5 (C-1), 107.3 (C-1), 104.0 (C-1), 102.4 (C-1), 102.3 (C-1), 100.1 (C-1), 89.2, 84.5, 84.0, 83.6, 83.5, 83.2, 82.2(9), 82.2(1), 80.5, 80.2, 79.1, 79.0, 78.5, 76.7, 76.3, 75.0, 74.9, 74.7, 72.4, 72.0, 71.9(8), 71.9(2), 70.2, 69.2, 69.1, 68.9, 68.8, 68.2, 68.1, 63.3, 63.2, 63.1, 62.4, 40.7, 30.6, 30.3, 30.2, 29.8, 27.7, 27.1.

5. Synthesis of 5 and 6



Scheme S4. Synthesis of protected core precursor to Antigens **5** and **6**. a) **LAM-24**, NIS, AgOTf, CH_2Cl_2, 72%; b) HF·pyridine, THF, pyridine, 82%; c) TBDPSCl, imidazole, pyridine, 86%; d) BnBr, NaH, THF, DMF, 87%; e) HF·pyridine, THF, pyridine, 85%

8-Azidooctyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-25). Diol **LAM-23**[2] (0.51 g, 0.38 mmol) and thioglycoside **LAM-24**[1] (0.52 g, 1.1 mmol) were dried under vacuum in the presence of P_2O_5 for 6 h. After drying, CH_2Cl_2 (30 mL) was added followed by powdered 4

Å molecular sieves (0.25 g) and the solution was stirred for 20 min. The reaction mixture was then cooled to –40 °C and *N*-iodosuccinimide (0.24 g, 1.1 mmol) and silver triflate (27 mg, 0.11 mmol) were added. After stirring for 20 min at –40 °C, Et_3N was added until the pH of the solution was slightly basic as determined by wet pH paper. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with a satd soln of $Na_2S_2O_3$, water and brine. The organic layer was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (85:15 hexanes–EtOAc) to yield **LAM-25** (0.56 g, 72%) as a thick syrup. R_f 0.46 (4:1 hexanes–EtOAc), $[\alpha]_D$ +5.9 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.20 (m, 45 H), 5.14 (d, 1 H, *J* = 1.0 Hz, H-1), 5.13 (d, 1 H, *J* = 1.1 Hz, H-1), 5.09 (d, 1 H, *J* = 1.2 Hz, H-1), 5.04–5.01 (m, 3 H), 4.98 (s, 1 H, H-1), 4.95 (d, 1 H, *J* = 5.1 Hz, H-1), 4.81 (d, 1 H, *J* = 12.3 Hz), 4.70–4.42 (m, 16 H), 4.35–4.27 (m, 5 H), 4.27–4.10 (m, 7 H), 4.06–4.00 (m, 4 H), 3.96 (dd, 1 H, *J* = 3.9, 11.9 Hz), 3.86–3.62 (m, 7 H), 3.60–3.50 (m, 6 H), 3.35 (ddd, 1 H, *J* = 6.5, 9.5, 13.2 Hz), 3.26 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.62–1.50 (m, 4 H), 1.40–1.23 (m, 8 H), 1.06 (s, 9 H), 1.03 (s, 9 H), 1.0 (1) (s, 9 H, $(CH_3)_3C$), 1.0 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.3, 138.1(4), 138.1, 138.0(1), 138.0, 137.9, 137.7(8), 137.7(5), 137.7, 128.4(0), 128.3(5), 128.3, 128.2(8), 128.2(5), 128.2, 127.9(9), 127.9(9), 127.9(6), 127.8(9), 127.8(5), 127.8(2), 127.8, 127.7(0), 127.6(7), 127.6(5), 127.6(2), 127.5(8), 127.5(5), 127.4(9), 127.4(7), 127.4, 106.8 (C-1), 106.1(4) (C-1), 106.1(0) (C-1), 105.7 (C-1), 99.8 (C-1), 99.7 (C-1), 88.7, 88.6, 86.9, 86.8, 83.2(2), 83.1(9), 83.1(6), 81.0, 80.9, 80.7, 80.6, 80.5, 80.2, 80.0, 79.2, 78.7, 78.4, 78.2, 74.4, 73.7, 73.6, 73.2(8), 72.3, 72.0, 71.9, 71.8, 71.7, 71.7, 69.8, 69.6, 68.5(2), 68.4(6), 67.6, 67.2, 65.9, 65.6, 51.5, 29.5, 29.3, 29.1, 28.8, 28.0, 27.6, 27.5(3), 27.5(2), 27.2(0), 27.1(8), 27.1, 26.7, 26.1, 22.6(2), 22.6(1), 20.0(5), 20.0(7). HRMS (ESI) *m/z* calcd for (M+Na) $C_{117}H_{151}N_3O_{25}Si_2Na$: 2077.0073. Found: 2077.0067.

8-Azidooctyl 2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-26). To a solution of the hexasaccharide **LAM-25** (0.5 g, 0.24 mmol) in THF–pyridine (13 mL, 12:1) at 0 °C was added 70% HF·pyridine (0.3 mL) dropwise. The solution was then stirred overnight while warming to rt. The reaction mixture was then poured into satd aq $NaHCO_3$ soln and extracted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated to a residue that was purified by chromatography (2:3

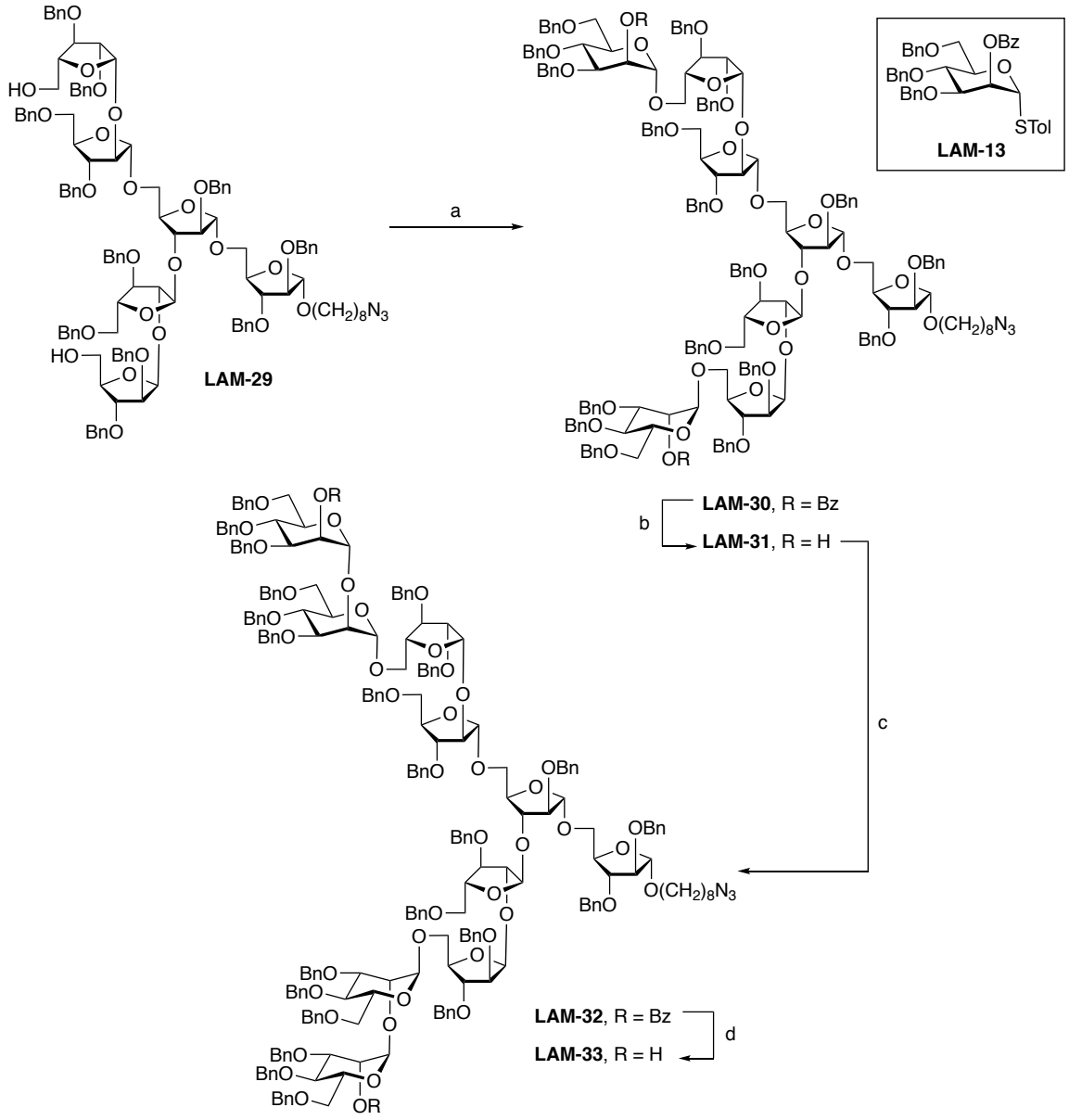
hexanes–EtOAc) to yield **LAM–26** (0.35 g, 82%) as a thick syrup. R_f 0.2 (1:1 hexanes–EtOAc); $[\alpha]_D$ +19.8 (*c* = 0.36, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.35–7.20 (m, 45 H), 5.15 (d, 1 H, *J* = 1.2 Hz, H-1), 5.12 (d, 1 H, *J* = 1.1 Hz, H-1), 5.09 (s, 1 H, H-1), 5.06 (d, 1 H, *J* = 4.4 Hz, H-1), 4.99 (d, 1 H, *J* = 4.4 Hz, H-1), 4.97 (s, 1 H, H-1), 4.62–4.40 (m, 18 H), 4.35–4.27 (m, 5 H), 4.22 (ddd, 1 H, *J* = 3.9, 4.4, 10.4 Hz), 4.19–4.04 (m, 6 H), 4.03–3.99 (m, 2 H), 3.96 (dd, 1 H, *J* = 3.9, 11.9 Hz), 3.85–3.70 (m, 6 H), 3.70–3.46 (m, 10 H), 3.32 (ddd, 1 H, *J* = 6.5, 9.5, 13.2 Hz), 3.26 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.30 (br. s, 4 H), 1.62–1.50 (m, 4 H), 1.40–1.23 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.0(4), 138.0(3), 138.0(1), 138.0, 137.9, 137.6(9), 137.6(8), 137.6, 128.6, 128.5, 128.4(4), 128.4, 128.3(1), 128.3(0), 128.0(2), 128.0, 127.9, 127.8(3), 127.7(7), 127.7(5), 127.6(9), 127.6(7), 127.6, 106.4 (C-1), 106.1(2) (C-1), 106.0(9) (C-1), 105.3 (C-1), 99.5 (2 × C-1), 88.6, 88.5, 86.0, 85.8, 84.3, 84.2, 83.3, 83.1, 83.0, 81.9(3), 81.9(1), 81.3, 80.8, 80.6, 80.1, 79.9, 73.3(7), 73.3(6), 73.3, 72.5(2), 72.5, 72.4, 72.1, 72.0, 71.8, 69.5, 69.4, 67.7, 66.0, 65.6, 62.8, 62.7, 51.5, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{101}H_{119}N_3O_{25}Na$: 1796.8030. Found: 1796.8024.

8-Azidooctyl 5-*O*-(*t*-butyldiphenylsilyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-(*t*-butyldiphenylsilyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-27). To a solution of **LAM-26** (0.5 mg, 0.28 mmol) in pyridine (8 mL) at 0 °C was added imidazole (0.1 g, 1.4 mmol) followed by t-butyldiphenylsilyl chloride (0.22 mL, 0.85 mmol). The solution was then stirred overnight with warming to rt before CH_3OH (1 mL) was added. After stirring for 30 min, the solution was poured into a satd aq $NaHCO_3$ soln and then extracted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated to a residue that was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-27** (0.55 g, 86%) as a thick syrup. R_f 0.23 (7:3 hexanes–EtOAc); $[\alpha]_D$ +13.4 (*c* = 0.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.64–7.57 (m, 8 H), 7.41–7.00 (m, 57 H), 5.11 (s, 1 H, H-1), 5.10 (s, 1 H, H-1), 5.09 (d, 1 H, *J* = 1.0 Hz, H-1), 5.04 (d, 1 H, *J* = 4.4 Hz, H-1), 4.96 (s, 1 H, H-1), 4.90 (d, 1 H, *J* = 4.4 Hz, H-1), 4.62–4.36 (m, 16 H), 4.36–4.26 (m, 4 H), 4.26–4.08 (m, 7 H), 4.05–3.99 (m, 3 H), 3.95 (dd, 1 H, *J* = 4.1, 12.0 Hz), 3.90–3.78 (m, 9 H), 3.78–3.61 (m, 5 H), 3.54–3.44 (m, 4 H), 3.33 (ddd, 1 H, *J* = 6.4, 9.4, 13.2 Hz), 3.25 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.15 (br. s, 2 H), 1.62–1.50 (m, 4 H), 1.40–1.23 (m, 8 H), 1.04 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.3, 138.0(3), 138.0(1),

137.9, 137.8, 137.7, 137.6, 135.5, 132.9(9), 132.9(5), 132.9, 129.9(1), 129.8(9), 129.8(6), 128.5, 128.4, 128.3(4), 128.3(3), 128.3, 128.1(3), 128.1(2), 128.1, 128.0(1), 128.0, 127.8(7), 127.8(6), 127.8(4), 127.8(3), 127.8, 127.7, 127.6(4), 127.6(0), 127.5(3), 127.5(1), 127.4(4), 127.4(2), 127.4, 127.3, 106.6 (C-1), 106.1 (C-1), 106.1 (C-1), 105.3 (C-1), 100.0 (C-1), 99.7 (C-1), 88.6(0), 88.6, 85.9, 85.6, 84.1(2), 84.0(5), 83.4, 83.3, 83.2, 81.6, 81.0(4), 81.0, 80.9, 80.6, 80.0(4), 80.0(1), 77.2, 73.2(2), 73.1(9), 72.3, 72.0(2), 72.0, 71.8, 70.0, 69.8, 67.6(2), 66.6, 66.5, 66.0, 65.4, 51.5, 29.5, 29.3, 29.1, 28.8, 26.9, 26.7, 26.1, 19.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{133}H_{155}N_3O_{25}Si_2Na$: 2273.0386. Found: 2273.0380.

8-Azidooctyl 5-*O*-(*t*-butyldiphenylsilyl)-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-(*t*-butyldiphenylsilyl)-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-28). To a solution of **LAM-27** (0.54 g, 0.24 mmol) in THF–DMF (10 mL, 4:1) at 0 °C under argon was added NaH (60% dispersion in mineral oil, 30 mg, 0.72 mmol). The mixture was stirred for 2–3 min before BnBr (0.14 mL, 1.2 mmol) was added dropwise. The solution was stirred for 6 h while warming to rt before CH_3OH (0.2 mL) was added. After stirring for 10 min, chilled water was added and the mixture extracted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (85:15 hexanes–EtOAc) to yield **LAM-28** (0.51 g, 87%) as a thick syrup. R_f 0.22 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.64–7.60 (m, 8 H), 7.40–7.00 (m, 67 H), 5.14–5.09 (m, 4 H, 4 × H-1), 4.98–4.96 (m, 2 H, 2 × H-1), 4.66–4.62 (m, 4 H), 4.62–4.24 (m, 20 H), 4.22–3.94 (m, 15 H), 3.89–3.64 (m, 10 H), 3.54–3.45 (m, 4 H), 3.34 (ddd, 1 H, J = 6.4, 9.4, 13.2 Hz), 3.26 (dd, 2 H, J = 7.0, 7.0 Hz), 1.62–1.50 (m, 4 H), 1.40–1.23 (m, 8 H), 1.05 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.3(6), 138.3, 138.1, 138.0, 137.8(2), 137.8, 137.7, 135.7, 135.5(8), 135.5(7), 135.5(5), 133.3, 133.2(4), 133.2, 129.7(9), 129.7(7), 129.7(4), 129.7, 128.4(4), 128.4(1), 128.3(4), 128.3(2), 128.2(9), 128.2(7), 128.2(0), 128.2, 128.1(1), 128.1(0), 128.0(1), 128.0, 127.9, 127.8(2), 127.8, 127.7, 127.7, 127.5(9), 127.5(8), 127.5(5), 127.5(2), 127.5, 127.4(2), 127.4(0), 127.4, 127.3, 106.5 (C-1), 106.2 (C-1), 106.1 (C-1), 105.2 (C-1), 100.6 (C-1), 100.3 (C-1), 88.6(3), 88.6, 85.8, 85.5, 84.7, 84.6, 84.3, 84.2, 84.1, 83.2, 82.0, 81.9, 81.4, 80.5, 80.1, 80.0, 73.1(9), 73.1(6), 72.3(4), 72.3(3), 72.3, 72.2, 72.1, 72.0(4), 72.0(2), 71.8, 70.2, 70.0, 67.6, 66.3, 66.2, 66.0, 65.4, 51.5, 29.5, 29.3, 29.1, 28.9, 26.9, 26.7, 26.1, 19.2.

8-Azidooctyl 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)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-29). Prepared from **LAM-28** (0.35 g, 0.14 mmol) and 70% HF·pyridine (0.3 mL) in THF–pyridine (7 mL, 5:2) as described for the synthesis of **LAM-26** to afford **LAM-29** (0.24 g, 85%) as a thick syrup. R_f 0.23 (7:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.34–7.18 (m, 55 H), 5.17 (d, 1 H, *J* = 1.2 Hz, H-1), 5.16 (d, 1 H, *J* = 1.1 Hz, H-1), 5.14–5.08 (m, 2 H, 2 × H-1), 5.05 (d, 1 H, *J* = 4.4 Hz, H-1), 4.98 (s, 1 H, H-1), 4.72 (d, 1 H, *J* = 11.7 Hz), 4.71 (d, 1 H, *J* = 11.7 Hz), 4.65–4.32 (m, 23 H), 4.28–3.92 (m, 16 H), 3.85 (dd, 1 H, *J* = 4.4, 11.7 Hz), 3.78 (dd, 1 H, *J* = 2.4, 11.7 Hz) 3.70–3.48 (m, 10 H), 3.35 (ddd, 1 H, *J* = 6.5, 9.5, 13.2 Hz), 3.24 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.34 (br. s, 2 H), 1.62–1.50 (m, 4 H), 1.40–1.23 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2, 138.1(2), 138.1, 138.0, 137.9, 137.7, 137.6(4), 137.6(2), 128.5, 128.4(4), 128.4(3), 128.4(0), 128.3(9), 128.3(8), 128.3(2), 128.3(1), 128.0, 127.9(3), 127.8(8), 127.8(5), 127.7(9), 127.7(7), 127.7(0), 127.6(8), 127.6(6), 127.6(3), 127.6(1), 106.4 (C-1), 106.2 (C-1), 106.1 (C-1), 105.2 (C-1), 99.9(9) (C-1), 99.9(6) (C-1), 88.6, 88.5, 86.2, 86.0, 84.1(2), 84.1(0), 83.3, 83.2, 83.1(5), 82.0, 81.9, 81.3, 80.8, 80.7(6), 80.7, 80.1, 79.9, 73.3(9), 73.3(7), 72.5(9), 72.5(5), 72.3(7), 72.3(5), 72.2, 72.0(9), 72.0(7), 71.8, 69.6, 69.5, 67.7, 65.9, 65.7, 63.9 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1. HRMS (ESI) ca1cd for (M+Na) $C_{l15}H_{131}N_3O_{25}Na$: 1976.8969. Found: 1976.8961.



Scheme S5. Synthesis of protected derivatives of Antigens **5** and **6**. a) **LAM-13**, NIS, AgOTf, CH_2Cl_2, 86%; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, 91%; c) **LAM-13**, NIS, AgOTf, CH_2Cl_2, 77%; d) $NaOCH_3$, CH_3OH, CH_2Cl_2, 79%;

8-Azidooctyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-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-2-*O*-benzoyl-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*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-30). Diol **LAM-29**

(0.85 g, 0.43 mmol) and thioglycoside **LAM-13**[16] (0.78 g, 1.18 mmol) were dried under vacuum in the presence of P_2O_5 for 6 h. After drying, CH_2Cl_2 (35 mL) was added followed by powdered 4 Å molecular sieves (0.4 g) and the solution was stirred for 20 min at rt. The mixture was then cooled to 0 °C and *N*-iodosuccinimide (0.28 g, 1.24 mmol) and silver triflate (30 mg, 0.11 mmol) were added. After stirring the mixture for 30 min at 0 °C, Et_3N was added until the pH of the solution was slightly basic as determined by wet pH paper. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with a satd aq soln of $Na_2S_2O_3$, water and brine, and then the organic layer was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-30** (1.13 g, 86%) as a thick syrup. R_f 0.32 (3:1 hexanes–EtOAc); $[\alpha]_D$ +4.2 (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.05 (m, 4 H), 7.60–7.50 (m, 2 H), 7.40–7.05 (m, 89 H), 5.62–5.58 (m, 2 H), 5.16–5.10 (m, 4 H), 5.00 (d, 1 H, J = 4.3 Hz, H-1), 4.97 (s, 1 H, H-1), 4.88–4.84 (m, 4 H), 4.72–4.26 (m, 36 H), 4.22–3.95 (m, 19 H), 3.85–3.74 (m, 8 H), 3.70–3.62 (m, 4 H), 3.62–3.52 (m, 6 H), 3.34 (ddd, 1 H, J = 6.5, 9.5, 13.2 Hz), 3.24 (dd, 2 H, J = 7.0, 7.0 Hz), 1.62–1.53 (m, 4 H), 1.40–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.5(8), 165.5(5), 138.6(2), 138.6(1), 138.6(0), 138.3, 138.2, 138.1(3), 138.0(8), 138.0(7), 138.0(5), 138.0(3), 138.0(2), 137.7(8), 137.7(6), 137.7(4), 137.6(8), 133.2, 133.1, 130.0(3), 129.9(9), 129.9(7), 128.4(9), 128.4(7), 128.4(4), 128.4(2), 128.3(7), 128.3(5), 128.3(1), 128.3, 128.1(2), 128.0(6), 128.0(1), 127.9(9), 127.9(5), 127.9(3), 127.9(0), 127.9, 127.8(2), 127.7(5), 127.7(4), 127.6(9), 127.6(0), 127.5(5), 127.5(1), 127.5, 106.6 (C-1), 106.1(8) (C-1), 106.1(5) (C-1), 105.3 (C-1), 100.8 (C-1), 100.5 (C-1), 98.0 (2 × C-1), 88.7, 88.6, 86.2, 86.0, 84.2, 84.0(7), 84.0(6), 84.0(4), 84.0(2), 83.3, 81.7, 81.3, 80.7, 80.2, 80.1, 79.5, 79.3, 78.5, 75.3(1), 75.3, 74.2, 73.5, 73.3(3), 73.3(1), 72.4, 72.3, 72.2, 72.0(8), 72.0(5), 71.9, 71.6(1), 71.5(7), 70.0, 69.9, 68.9(2), 68.8(6), 67.7, 66.0, 65.5, 51.5, 29.6, 29.3, 29.2, 28.9, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{183}H_{195}N_3O_{37}Na$: 3049.3367. Found: 3049.3362.

8-Azidooctyl 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)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-31). To a solution of **LAM-30** (0.6 g, 0.2 mmol) in CH_2Cl_2–CH_3OH (7:3, 30 mL) at rt was added 1M methanolic sodium methoxide solution until the pH

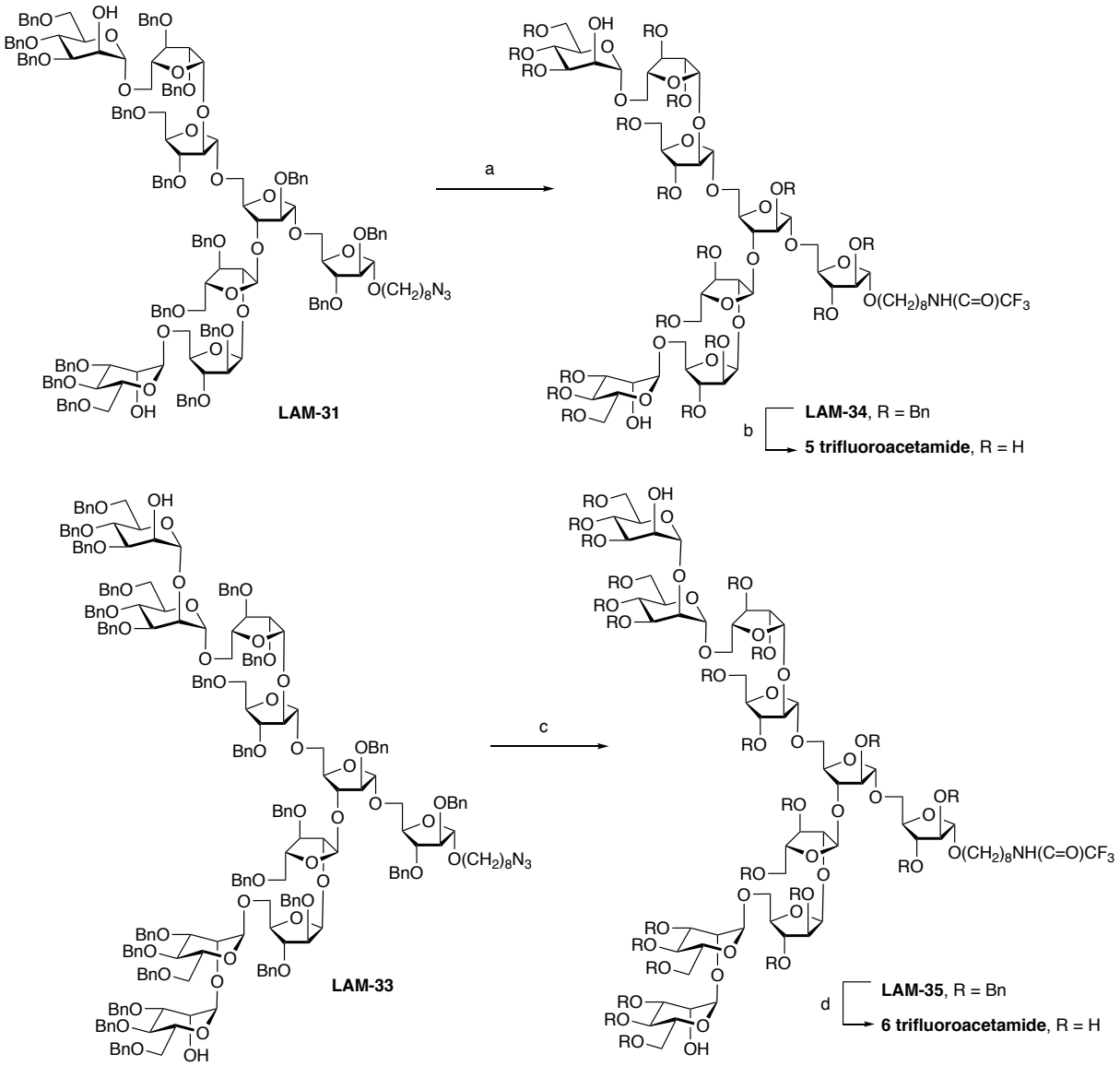
was 8–9 (as determined by wet pH paper) and the mixture was stirred overnight. The reaction mixture was then neutralized by the addition of Amberlite IR 120 H+ resin, filtered and concentrated to give a crude residue that was purified by chromatography (1:1 EtOAc–hexanes) to yield **LAM-31** (0.51 g, 91%) as a thick syrup. R_f 0.11 (7:3 hexanes–EtOAc); $[\alpha]_D$ +26.0 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.15 (m, 85 H), 5.18 (d, 2 H, *J* = 4.3 Hz, H-1), 5.14–5.11 (m, 2 H, 2 × H-1), 5.01 (d, 1 H, *J* = 4.4 Hz, H-1), 4.99 (s, 1 H, H-1), 4.91–4.88 (m, 2 H, 2 × H-1), 4.84 (d, 1 H, *J* = 1.1 Hz, H-1), 4.82 (d, 1 H, *J* = 1.0 Hz H-1), 4.72–4.42 (m, 31 H), 4.42–4.28 (m, 5 H), 4.24–3.53 (m, 39 H), 3.35 (ddd, 1 H, *J* = 6.5, 9.5, 13.2 Hz), 3.26 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.40 (br. s, 2 H), 1.63–1.53 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.6, 138.5, 138.3(3), 138.2(8), 138.2(2), 138.2, 138.1, 138.0, 137.9, 137.7(6), 137.7(5), 137.7(3), 137.7, 128.6, 128.5, 128.4(3), 128.4(0), 128.3(8), 128.3(5), 128.3(4), 128.3(1), 128.0, 127.9(0), 127.9, 127.8(3), 127.7(9), 127.7(7), 127.7(3), 127.7(1), 127.6(8), 127.6(6), 127.6(3), 127.5(9), 127.5(7), 127.5, 106.6 (C-1), 106.2 (C-1), 106.1 (C-1), 105.4 (C-1), 100.7 (C-1), 100.4 (C-1), 99.4 (C-1), 99.3 (C-1), 88.7, 88.6, 86.5, 86.2, 84.2, 84.1, 84.0, 83.9(5), 83.6, 83.5, 83.3, 81.7, 81.2, 80.6, 80.2, 80.1, 80.0, 79.3, 79.2, 75.0(7), 75.0(6), 74.2, 73.5, 73.3(1), 73.2(8), 72.4, 72.2(0), 72.2, 72.0, 71.8(8), 71.8(6), 71.5, 69.9, 69.7, 69.1(1), 69.0(6), 68.8, 68.2(2), 68.1(9), 67.6, 66.0, 65.4, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{169}H_{187}N_3O_{35}Na$: 2841.2843. Found: 2841.2837.

8-Azidooctyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-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-2-*O*-benzoyl-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*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-32). Prepared from diol **LAM-31** (0.28 g, 0.1 mmol), thioglycoside **LAM-13**[16] (0.3 g, 0.45 mmol), powdered 4 Å molecular sieves (0.2 g), *N*-iodosuccinimide (0.1 g, 0.45 mmol) and silver triflate (12 mg, 0.05 mmol) in CH_2Cl_2 (12 mL) as described for the synthesis of **LAM-30** to afford **LAM-32** (0.29 g, 77%) as a thick syrup. R_f 0.23 (3:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.16–8.06 (m, 4 H), 7.60–7.50 (m, 2 H), 7.40–7.04 (m, 119 H), 5.82 (br. s, 2 H), 5.23–5.10 (m, 6 H), 5.00–4.96 (m, 4 H), 4.90 (d, 2 H, *J* = 1.0 Hz, H-1), 4.88 (d, 2 H, *J* = 1.0 Hz, H-1), 4.80–4.28 (m, 46

H), 4.25-3.94 (m, 25 H), 3.94–3.74 (m, 12 H), 3.74–3.50 (m, 12 H), 3.36 (ddd, 1 H, J = 6.5, 9.5, 13.2 Hz), 3.26 (dd, 2 H, J = 7.0, 7.0 Hz), 1.63–1.54 (m, 4 H), 1.40–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 138.6(1), 138.6, 138.5(4), 138.5(1), 138.3, 138.2, 138.1(4), 138.1, 138.0, 137.8, 137.7(2), 137.6(9), 137.6(6), 133.9, 133.0, 130.4, 130.1, 130.0, 129.6, 128.4(8), 128.4(6), 128.4(4), 128.3(8), 128.3(6), 128.3(3), 128.3, 128.2, 128.1(4), 128.0(8), 128.0(6), 128.0(4), 128.0, 127.9(1), 127.8(8), 127.8(5), 127.8, 127.7(2), 127.7(1), 127.6(8), 127.6(5), 127.6, 127.5(0), 127.5, 127.4, 127.3, 106.6 (C-1), 106.2 (C-1), 106.1 (C-1), 105.3 (C-1), 100.8 (C-1), 100.4 (C-1), 99.7 (C-1), 99.6 (C-1), 98.7(2) (C-1), 98.7(0) (C-1), 88.6, 86.3, 86.0, 84.2(3), 84.2(0), 84.1, 84.0(4), 84.0, 83.3, 81.7, 81.3, 80.6, 80.2, 80.1(2), 80.1(1), 80.1, 80.0, 79.4, 79.3, 78.2, 75.2(4), 75.1(9), 75.1(7), 75.1(1), 75.0(6), 74.6, 74.4, 74.3, 73.4(2), 73.4, 73.3, 73.2, 72.4, 72.3(2), 72.3, 72.2(3), 72.2, 72.1, 71.9, 71.7, 70.0, 69.8, 69.5(2), 69.4(7), 69.4(5), 69.0(8), 69.0(5), 69.0, 67.6, 65.9, 65.4(1), 60.4(3), 51.5, 36.7, 29.5, 29.3, 29.1, 28.9, 28.6, 26.7, 26.1, 24.8, 23.4.

8-Azidooctyl 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)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-33). Prepared from **LAM-32** (0.29 g, 0.074 mmol) and 1M methanolic sodium methoxide solution in CH_2Cl_2–CH_3OH (7:3, 20 mL) as described for the synthesis of **LAM-31** to afford **LAM-33** (0.21 g, 79%) as a thick syrup. R_f 0.17 (7:3 hexanes–EtOAc); $[\alpha]_D$ +24.5 (c = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.10 (m, 115 H), 5.20–5.12 (m, 6 H, 6 × H-1), 5.03–4.98 (m, 4 H, 4 × H-1), 4.87 (d, 2 H, J = 4.9 Hz), 4.85 (d, 2 H, J = 4.9 Hz), 4.74–4.28 (m, 33 H), 4.25–3.51 (m, 36 H), 4.24–3.53 (m, 28 H), 3.37 (ddd, 1 H, J = 6.5, 9.5, 13.2 Hz), 3.27 (dd, 2 H, J = 7.0, 7.0 Hz), 2.40 (br. s, 2 H), 1.64–1.54 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.6(9), 138.6(5), 138.5(4), 138.5(2), 138.3(1), 138.2(9), 138.2(7), 138.2(5), 138.2, 138.1(2), 138.1(0), 138.0(8), 138.0(5), 138.0, 137.8, 137.7(4), 137.7(1), 137.6(7), 128.4(9), 128.4(6), 128.4(2), 128.4(1), 128.4, 128.3(4), 128.3(2), 128.1(9), 128.1(5), 128.1, 128.0(4), 128.0, 127.9(3), 127.9(0), 127.9, 127.8, 127.7(4), 127.6(9), 127.6(6), 127.6(3), 127.5(8), 127.5(4), 127.5(1), 127.4(0), 127.4, 106.6 (C-1), 106.2 (C-1), 106.1

(C-1), 105.3 (C-1), 101.1(9) (C-1), 101.1(8) (C-1), 100.8 (C-1), 100.4 (C-1), 98.8(0) (C-1), 98.7(8) (C-1), 88.6(7), 88.6(5), 86.3, 86.0, 84.3, 84.2, 84.1, 84.0, 83.3, 81.7, 81.2, 80.6, 80.2, 80.1, 80.0, 79.4, 79.3, 75.2, 75.1(4), 75.0(9), 74.9(1), 74.8(6), 74.6, 74.3, 73.4, 73.3, 73.2, 72.4, 72.3(0), 72.3, 72.2(1), 72.2, 72.1, 72.0(7), 71.9, 71.7, 70.0, 69.8, 69.6, 69.1, 68.9, 68.6, 67.6, 66.0, 65.4, 51.5, 29.5, 29.3, 29.2, 28.9, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{223}H_{243}N_3O_{45}Na$: 3705.6716. Found: 3705.6711.



Scheme S6. Synthesis of **5 Trifluoroacetamide** and **6 Trifluoroacetamide**. a) H_2, Pd–C, pyridine; then trifluoroacetic anhydride, pyridine, 73%; b) H_2, $Pd(OH)_2$–C, EtOAc, CH_3OH, THF, 84%; c) H_2, Pd–C, pyridine; then trifluoroacetic anhydride, pyridine, 73%; d) H_2, $Pd(OH)_2$–C, EtOAc, CH_3OH, THF, 83%.

8-Trifluoroacetamidooctyl 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)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-34). Prepared from **LAM-31** (0.25 g, 0.09 mmol), 20% $Pd(OH)_2$–C (50 mg), hydrogen (1 atm) and then trifluoroacetic anhydride (0.5 mL, 3.6 mmol) as described for the synthesis of **LAM-12** to afford **LAM-34** (0.19 g, 73%) as a thick syrup. R_f 0.31 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H); 7.38–7.17 (m, 85 H), 5.14 (s, 1 H, H-1), 5.13 (s, 1 H, H-1) 5.12–5.08 (m, 2 H, 2 × H-1), 4.97 (d, 1 H, J = 4.4 Hz, H-1), 4.95 (s, 1 H, H-1), 4.88–4.84 (m, 2 H), 4.81 (d, 1 H, J = 1.0 Hz, H-1), 4.79 (d, 1 H, J = 1.1 Hz, H-1), 4.68-4.38 (m, 33 H), 4.38–4.24 (m, 6 H), 4.20–3.92 (m, 18 H), 3.88 (dd, 1 H, J = 6.5, 6.5 Hz), 3.84–3.50 (m, 20 H), 3.35–3.28 (m, 3H) 1.60–1.48 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 157.3 (q, J = 36.1 Hz), 150.0, 144.2, 144.1(9), 139.2(4), 139.2(1), 138.8(3), 138.8(2), 138.8, 138.7(2), 138.7(1), 138.6(1), 138.6(0), 138.6, 138.3(3), 138.3(0), 138.2, 128.8(4), 128.8(0), 128.7(4), 128.7(3), 128.6, 128.5, 128.2(8), 128.2(5), 128.2(3), 128.2(1), 128.1(8), 128.1(6), 128.1(3), 128.1, 128.0(3), 127.9(9), 127.9(6), 127.9(2), 127.9(0), 122.8, 116.4 (q, J = 288.0 Hz), 107.0 (C-1), 106.6(2) (C-1), 106.5(7) (C-1), 105.8 (C-1), 101.0 (C-1), 100.8 (C-1), 99.8 (2 × C-1), 89.1, 88.9, 86.6, 86.4, 84.8, 84.7, 84.5(1), 84.4(8), 84.1(1), 84.0(9), 82.3, 81.8, 81.2, 80.7(4), 80.6(5), 79.9, 79.8, 75.3(4), 75.3(3), 74.5, 73.8, 73.6(8), 73.6(6), 72.8, 72.7(4), 72.7(1), 72.4, 72.3, 72.2(0), 72.1(9), 71.8(4), 71.8(3), 71.4, 71.2, 70.4, 70.3, 69.6, 69.4, 68.6(3), 68.6(1), 68.0, 66.7, 66.0, 40.4, 37.0, 30.1, 30.0, 29.7, 29.5, 29.3, 27.1, 26.5, 25.1, 23.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{171}H_{188}F_3N_1O_{36}Na$: 2911.2761. Found: 2911.2755.

8-Trifluoroacetamidooctyl α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (5 Trifluoroacetamide). Prepared from **LAM-34** (0.13 g, 0.045 mmol) and 20% $Pd(OH)_2$–C (63 mg) in EtOAc–CH_3OH–THF (10 mL, 3:5:2) as described for the synthesis of **1 Trifluoroacetamide** to afford **5 Trifluoroacetamide** (0.051 mg, 84%) as a foam. R_f 0.14 (6.5:3.5:0.5, CH_2Cl_2–CH_3OH–H_2O); $[\alpha]_D$ +56.0 (c = 0.1, H_2O); ^{1}H NMR (600 MHz, D_2O, δ_H) 5.25 (s, 1 H, H-1), 5.18 (s, 1 H, H-1), 5.14 (d, 2 H, J = 4.2 Hz, 2 × H-1), 5.10 (s, 1 H, H-1), 5.00

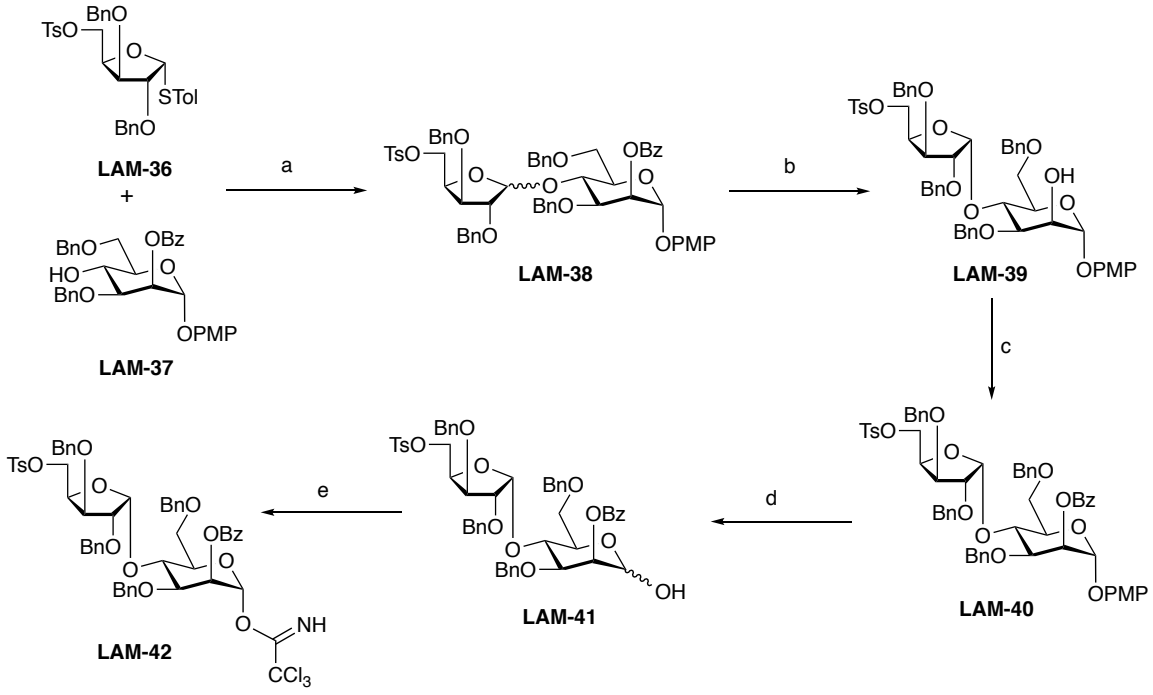
(d, 1 H, *J* = 2.0 Hz, H-1), 4.91 (s, 2 H, 2 × H-1), 4.32–4.27 (m, 2 H), 4.19–4.06 (m, 11 H), 4.06–3.96 (m, 7 H), 3.96–3.80 (m, 11 H), 3.80–3.60 (m, 12 H), 3.57 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 3.30 (dd, 2 H, *J* = 7.0, 7.0 Hz, CH_2N), 1.63–1.54 (m, 4 H), 1.40–1.28 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 159.8 (q, *J* = 37.1 Hz), 120.3, 116.8 (q, *J* = 285.9 Hz), 108.3 (C-1), 108.1 (C-1), 106.5 (C-1), 106.3 (C-1), 101.6 (C-1), 101.4 (C-1), 100.7 (2 × C-1), 88.4, 88.0, 84.1, 83.9, 83.3, 82.6, 82.4, 81.8, 80.6(8), 80.6(6), 80.6, 80.0, 77.2(1), 77.1(7), 77, 1, 76.9(3), 76.9(1), 76.0, 75.9(4), 75.8(5), 74.9, 73.8, 71.4, 70.9, 69.5, 68.9, 67.7, 67.6(1), 67.5(9), 67.3, 67.2, 61.8, 61.6, 61.5, 40.7, 29.5, 29.1(1), 29.0(5), 29.0, 28.6, 26.7, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{52}H_{86}N_1O_{36}F_3Na$: 1403.4666. Found: 701.7334 (M+2Na).

8-Trifluoroacetamidooctyl 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)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-35). Prepared from **LAM-33** (0.2 g, 0.054 mmol), 20% $Pd(OH)_2$–C (50 mg) in pyridine (8 mL), hydrogen (1 atm.) and then trifluoroacetic anhydride (0.5 mL, 3.6 mmol) as described for the synthesis of **LAM-12** to afford **LAM-35** (0.15 mg, 73%) as a thick syrup. R_f 0.30 (7:3 hexanes–EtOAc); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.35–7.08 (m, 115 H), 5.14–5.07 (m, 5 H, 5 × H-1), 4.98–4.94 (m, 3 H, 3 × H-1), 4.83 (d, 1 H, *J* = 1.2 Hz, H-1), 4.81 (d, 1 H, *J* = 1.1 Hz, H-1), 4.70–4.24 (m, 50 H), 4.20–3.48 (m, 53 H), 3.35–3.28 (m, 3H), 1.60–1.50 (m, 4 H), 1.40–1.25 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.1 (q, *J* = 36.6 Hz), 138.6(3), 138.6(0), 138.4(9), 138.4(8), 138.3, 138.2(4), 138.2(2), 138.1(1), 138.0(6), 138.0(5), 138.0(3), 138.0(0), 138.0, 137.7(2), 137.6(9), 137.6(6), 137.6, 130.9, 128.8, 128.4(4), 128.4(1), 128.3(8), 128.3(6), 128.3(1), 128.3(0), 128.3, 128.1, 128.0, 127.9(2), 127.9(0), 127.8(8), 127.8(6), 127.8(1), 127.8, 127.7, 127.6(4), 127.6(1), 127.5(4), 127.5, 127.4, 127.3, 116.0 (q, *J* = 288.0 Hz), 106.6 (C-1), 106.1 (2 × C-1), 105.3 (C-1), 101.1 (2 × C-1), 100.8 (C-1), 100.4 (C-1), 98.8 (C-1), 98.7 (C-1), 88.6(3) (2), 88.6(0), 86.3, 85.9, 84.3, 84.1(4), 84.1, 83.9, 83.3, 81.6, 81.2, 80.5, 80.2, 80.1, 80.0, 79.4, 79.2, 75.1(2), 75.1, 75.0, 74.9, 74.8, 74.5, 74.3, 73.4, 73.3, 73.2(4), 73.2(1), 72.3(3), 72.3, 72.2(4), 72.2, 72.1, 72.0, 71.8, 71.7, 70.0, 69.8, 69.5, 69.1, 68.8, 68.5, 68.2, 67.6, 66.0, 65.4, 40.0, 30.4, 29.7(2), 29.7, 29.5,

29.2, 29.1, 29.0, 28.9, 26.6, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{225}H_{244}F_3N_1O_{46}Na$: 3775.6634. Found: 3775.6628.

8-Trifluoroacetamidooctyl 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-arabinofuranoside (6 Trifluoroacetamide). Prepared from **LAM-35** (0.11 g, 0.03 mmol) and 20% $Pd(OH)_2$–C (40 mg) in EtOAc–CH_3OH–THF (12 mL, 3:5:2) as described for the synthesis of **1 Trifluoroacetamide** to afford **6 Trifluoroacetamide** (0.042 g, 83%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H) 5.25 (s, 1 H, H-1), 5.18 (s, 1 H, H-1), 5.16–5.12 (m, 4 H, 4 × H-1), 5.10 (s, 1 H, H-1), 5.03–4.97 (m, 3 H, 3 × H-1), 4.33–4.27 (m, 2 H), 4.20–3.98 (m, 20 H), 3.98–3.67 (m, 29 H), 3.65–3.54 (m, 5 H), 3.32 (dd, 2 H, *J* = 7.0, 7.0 Hz, CH_2N), 1.63–1.54 (m, 4 H), 1.40–1.28 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 159.6 (q, *J* = 36.6 Hz), 116.8 (q, *J* = 285.9 Hz), 108.3 (C-1), 108.1 (C-1), 106.5 (C-1), 106.3 (C-1), 103.2 (2 × C-1), 101.6 (C-1), 101.4 (C-1), 99.5 (C-1), 99.1 (C-1), 88.3, 87.9(4), 87.9, 84.1, 83.9, 83.28, 82.6, 82.5, 82.4, 81.8, 80.6(3), 80.6(2), 80.0, 79.7, 79.6, 77.2, 77.0, 76.9, 76.0, 75.9, 75.0(4), 75.0(1), 74.2, 73.9, 73.8, 71.2, 71.1, 70.9, 69.5, 69.2(3), 69.2, 67.9, 67.8, 67.3, 67.2(2), 67.1(8), 62.1, 61.9, 61.8, 61.6, 61.5, 40.7, 29.5, 29.1, 29.0, 28.5, 26.7, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{64}H_{106}F_3N_1O_{46}$: 1704.5836. Found: 1704.5830.

6. Synthesis of 7–9



Scheme S7. Synthesis of disaccharide needed for the synthesis of **7**–**9**. a) NIS, AgOTf, CH_2Cl_2, 87%, 3.5:1 α:β; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, 90%, c) BzCl, pyridine, 97%, d); CAN, CH_3CN, H_2O, 88%; e). Cl_3CCN, DBU, CH_2Cl_2.

***p*-Methoxyphenyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α/β-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranoside (LAM-38)**. Prepared from thioglycoside **LAM-36**[17] (3.1 g, 5.3 mmol), alcohol **LAM-37**[18] (1.86 g, 3.2 mmol), *N*-iodosuccinimide (1.2 g, 5.3 mmol), and silver triflate (84 mg, 0.33 mmol) in CH_2Cl_2 (100 mL) as described for the synthesis of **LAM-3**, to afford **LAM-38** (2.94 g, 87%, inseparable 3.5:1 α:β mixture) as a syrup. To facilitate the separation of the products, the benzoyl group was removed (next step).

***p*-Methoxyphenyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-mannopyranoside (LAM-39)**. Prepared from **LAM-38** (1.0 g, 0.96 mmol, 3.5:1 mixture) and 1 M methanolic sodium methoxide solution in CH_2Cl_2–CH_3OH (7:3, 30 mL) as described for the synthesis **LAM-31** to afford **LAM-39** (0.63 g, 90%, calculated based on percentage of α-glycoside in the starting diastereomeric mixture) as a thick syrup. R_f 0.24 (7:3 hexanes–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.72–7.65 (m, 2 H), 7.40–7.15 (m, 22 H),

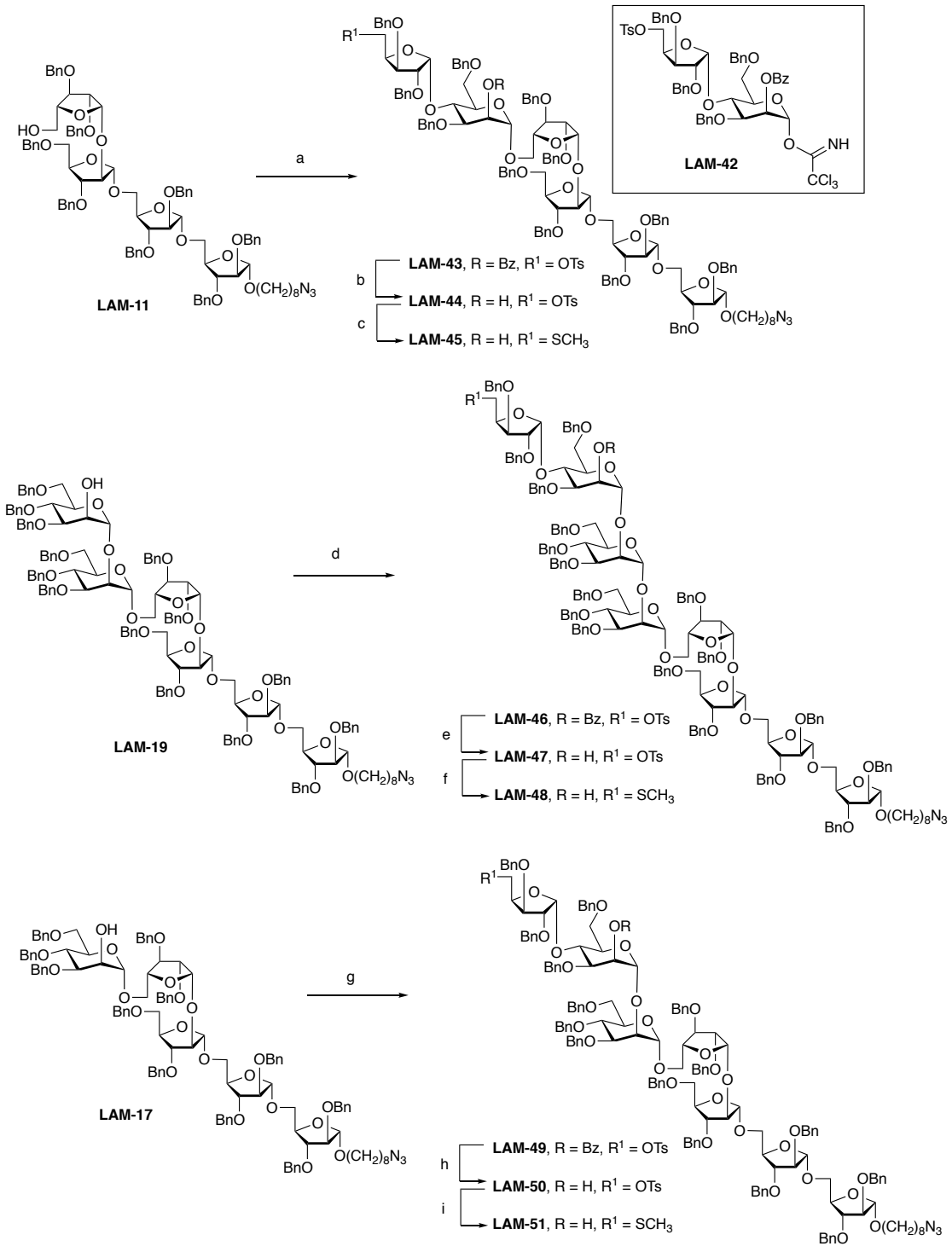
7.08–7.03 (m, 2 H), 6.84–6.80 (m, 2 H), 5.50 (d, 1 H, J = 1.8 Hz), 5.47 (d, 1 H, J = 4.4 Hz, H-1), 4.76 (d, 1 H, J = 11.5 Hz), 4.64 (d, 1 H, J = 11.8 Hz), 4.58–4.50 (m, 3 H), 4.45–4.40 (m, 3 H), 4.34 (d, 1 H, J = 11.9 Hz), 4.24 (br. s, 1 H), 4.20–4.02 (m, 5 H), 3.96 (dd, 1 H, J = 5.9, 10.6 Hz), 3.89 (dd, 1 H, J = 4.4, 6.5 Hz), 3.77 (s, 3 H), 3.69 (dd, 1 H, J = 1.7, 10.9 Hz), 3.64 (dd, 1 H, J = 5.6, 1.9 Hz), 2.39 (s, 3 H); HRMS (ESI) *m/z* calcd for (M+Na) $C_{53}H_{56}O_{13}SNa$: 955.3333. Found: 955.3337.

***p*-Methoxyphenyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranoside (LAM-40)**. A solution of **LAM-39** (0.5 g, 0.54 mmol) in dichloromethane-pyridine (10:1, 11 mL) was cooled to 0 °C and benzoyl chloride (0.1 mL, 0.8 mmol) was added to it dropwise. The reaction mass was then allowed to warm to r.t. and stirred for 16 h. Methanol (0.2 mL) was added and after stirring for 30 min, the reaction mixture was diluted with CH_2Cl_2 and poured into a satd aq $NaHCO_3$ soln. The organic layer was washed with water, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (4:1 hexanes–EtOAc) to afford **LAM-40** (0.54 g, 97%) as a foam. R_f 0.22 (4:1 hexanes–EtOAc); $[\alpha]_D$ +72.9 c = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08–8.03 (m, 2 H), 7.66–7.55 (m, 3 H), 7.40–7.06 (m, 26 H), 6.86–6.80 (m, 2 H), 5.81 (dd, 1 H, J = 2.5, 2.5 Hz), 5.58 (d, 1 H, J = 2.0 Hz), 5.48 (d, 1 H, J = 4.3 Hz, H-1), 4.92 (d, 1 H, J = 11.0 Hz), 4.63 (dd, 2 H, J = 11.7, 11.7 Hz), 4.56–4.49 (m, 2 H), 4.46–4.14 (m, 9 H), 3.92 (ddd, 1 H, J = 4.5, 7.0, 1.7 Hz), 3.82 (dd, 1 H, J = 4.5, 5.6 Hz), 3.80–3.76 (m, 5 H), 2.33 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.7, 155.3, 150.1, 144.6, 138.7, 137.7, 137.6, 137.4, 133.3, 132.9, 130.0, 129.6, 129.5, 128.5(2), 128.5, 128.4(4), 128.4, 128.3, 127.9(2), 127.8(9), 127.8(6), 127.8(3), 127.7(7), 127.7, 127.6, 127.3(3), 127.2(6), 118.3, 114.7, 101.0 (C-1), 97.0 (C-1), 82.3, 80.7, 78.2, 74.6, 73.2, 72.6, 72.0, 71.9, 71.3, 70.9, 69.3, 69.0, 67.9, 55.6, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{60}H_{60}O_{14}SNa$: 1059.3596. Found: 1059.3593.

5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranose (LAM–41). To a solution of **LAM-40** (0.56 g, 0.54 mmol) in CH_3CN–H_2O (30 mL 4:1) at 0 °C was added CAN (1.48 g, 2.7 mmol) and the solution was stirred for 40 min. The reaction mixture was diluted with EtOAc (75 mL) and brine (50 mL), and stirred well. The EtOAc layer was separated and the aqueous phase was extracted with EtOAc. The the combined organic layer was washed with water, aq $NaHCO_3$ soln and water, before being dried (Na_2SO_4), and concentrated to give a syrup that was purified by chromatography (3:2

hexanes–EtOAc) to afford **LAM-41** (0.44 g, 6:1 diastereomeric mixture, 88%) as a syrup. Data for major isomer: R_f 0.14 (7:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08–8.03 (m, 2 H), 7.69–7.65 (m, 2 H), 7.60–7.54 (m, 1 H), 7.45–7.06 (m, 24 H), 5.65 (dd, 1 H, *J* = 2.2, 2.2 Hz), 5.39 (d, 1 H, *J* = 4.3 Hz), 5.37 (s, 1 H), 4.86 (d, 1 H, *J* = 11.2 Hz), 4.72 (d, 1 H, *J* = 12.2 Hz), 4.59 (d, 2 H, *J* = 11.9 Hz), 4.55–4.50 (m, 2 H), 4.40–4.30 (m, 2 H), 4.40–4.15 (m, 3 H), 4.15–4.08 (m, 2 H), 4.03 (dd, 1 H, *J* = 9.5, 9.5 Hz), 3.98 (br. s, 1 H), 3.93–3.86 (m, 2 H), 3.78–3.62 (m, 2 H), 2.34 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.7, 144.6, 138.1, 137.8, 137.7, 137.3, 133.3, 132.9, 129.9, 129.7, 128.5, 128.4(4), 128.3(8), 128.3(6), 128.3, 128.1, 127.9(3), 127.8(6), 127.8(3), 127.8, 127.7, 127.6, 127.5, 127.2, 100.7 (C-1), 92.4 (C-1), 82.2, 80.6, 77.9, 74.4, 73.3, 72.6, 72.2, 72.0, 70.7, 70.4, 69.6, 69.0, 68.4, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{53}H_{54}O_{13}SNa$: 953.3177. Found: 953.3180.

5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (LAM–42). To a solution of **LAM-41** (0.3 g, 0.3 mmol) in CH_2Cl_2 (7 mL) at 0 °C was added trichloroacetonitrile (0.15 mL,1.5 mmol) followed by DBU (10 μL, 0.07 mmol). The reaction mixture was stirred at 0 °C for 30 min and then warmed to rt over 30 min. The solvent was then removed and a solution of dry hexane–toluene (8 mL, 2:3) was added. After stirring for 5 min, this solution was quickly filtered through a short column of silica gel and Na_2SO_4 (ca. 1:1). The resulting solution was then concentrated and dried under vacuum to yield the trichloroacetimidate derivative **LAM–42**, which was used without any further purification. Alternatively, the syrup obtained after the initial solvent evaporation following the reaction could be quickly filtered through silica gel (4:1 hexanes–EtOAc). The fractions containing the trichloroacetimidate derivative were concentrated, dried under vacuum for 1 h and used immediately for the glycosylation without any further purification.



Scheme S8. Synthesis of protected derivatives of **7**–**9**. a) **LAM-42**, TMSOTf, 76%, b) $NaOCH_3$, CH_3OH, CH_2Cl_2, 92%; c) $NaSCH_3$, CH_3CN, 72%; d) **LAM-42**, TMSOTf, 88%; e) $NaOCH_3$, CH_3OH, CH_2Cl_2, 90%; f) $NaSCH_3$, CH_3CN, 74%; g) **LAM-42**, TMSOTf, 79%; h) $NaOCH_3$, CH_3OH, CH_2Cl_2, 94%; i) $NaSCH_3$, CH_3CN, 70%.

8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-43). Trichloroacetimidate **LAM-42** (prepared from 0.42 g of hemiacetal **LAM-41** (Scheme S7), 0.6 mL of CCl_3CN and 10 μL of DBU) in CH_2Cl_2 (10 mL) was added to a solution of alcohol **LAM-11** (0.49 g, 0.35 mmol) in CH_2Cl_2 (10 mL) containing 4 Å molecular sieves (0.28 g; stirred already for about 20 min.) at –30 °C. A solution of TMSOTf (8 μL, 0.044 mmol) was added dropwise over a period of 5 min. The reaction mixture was warmed to –5 °C over 25 min, and the Et_3N (0.03 mL) was added. The solution was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was concentrated to a syrup that was purified by chromatography (4:1 hexanes–EtOAc) to afford **LAM-43** (0.61 g, 76%) as a syrup. R_f 0.35 (7:3 hexanes–EtOAc); $[\alpha]_D$ +34.2 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.05–8.02 (m, 2 H), 7.64–7.56 (m, 3 H), 7.40–7.05 (m, 60 H), 7.05–7.02 (m, 4 H), 5.60 (dd, 1 H, *J* = 2.2, 2.2 Hz), 5.38 (d, 1 H, *J* = 4.3 Hz, H-1), 5.16–5.10 (m, 3 H, 3 × H-1), 5.01 (d, 1 H, *J* = 1.0 Hz, H-1), 4.90 (d, 1 H, *J* = 2.1 Hz, H-1), 4.75–4.66 (m, 4 H), 4.63–4.42 (m, 18 H), 4.38–4.32 (m, 2 H), 4.26–3.82 (m, 23 H), 3.76–3.64 (m, 6 H), 3.64–3.54 (m, 3 H), 3.37 (ddd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.25 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.32 (s, 3 H), 1.63–1.55 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 144.5, 138.7, 138.2, 138.1(4), 138.1(2), 138.1, 138.0, 137.7(2), 137.6(9), 137.3, 133.2, 132.8, 129.9, 129.6(1), 129.6, 128.5(0), 128.5, 128.4(1), 128.4(0), 128.3(8), 128.3(5), 128.3(3), 128.3(0), 128.3, 128.0, 127.9(2), 127.8(7), 127.8(0), 127.8, 127.7(4), 127.7(2), 127.6(9), 127.6(8), 127.5(9), 127.5(6), 127.5(4), 127.5(2), 127.5, 127.4, 127.3, 127.1, 106.4(3) (C-1), 106.4 (C-1), 106.1 (C-1), 100.8 (C-1), 100.7 (C-1), 97.5 (C-1), 88.7, 88.3, 86.0, 84.1, 83.9, 83.2(1), 83.1(7), 82.1, 81.7, 80.6, 80.2, 79.1, 78.6, 74.4, 73.3, 73.2, 72.6, 72.3(9), 72.3(6), 72.3(3), 72.3, 72.2, 72.0, 71.9, 71.8, 71.7, 71.2, 70.6, 70.1, 69.7, 69.1, 69.0, 67.7, 67.6, 65.9, 65.5, 51.5, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{137}H_{149}N_3O_{29}SNa$: 2354.9895. Found: 2354.9889.

8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-44). To a solution of **LAM-43** (0.6 g, 0.26 mmol) in

CH_2Cl_2–CH_3OH (7:3, 30 mL) was added 1M methanolic sodium methoxide solution until the pH of the mixture was 8–9 (as determined wet pH paper). The reaction mixture was stirred for 12 h, neutralized by the addition of Amberlite IR 120 H+ resin, filtered and then concentrated to give a crude residue that was purified by chromatography (7:3 hexanes–EtOAc) to yield **LAM-44** (0.53 g, 92%) as a thick syrup. R_f 0.30 (7:3 hexanes–EtOAc); $[\alpha]_D$ +49.3 (*c* = 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.70–7.65 (m, 2 H), 7.35–7.10 (m, 60 H), 7.10–7.06 (m, 2 H), 5.39 (d, 1 H, *J* = 4.3 Hz, H-1), 5.13 (s, 1 H, H-1), 5.12 (s, 1 H, H-1), 5.10 (d, 1 H, *J* = 4.5 Hz, H-1), 5.01 (s, 1 H, H-1), 4.91 (s, 1 H, H-1), 4.71–4.34 (m, 24 H), 4.28–4.18 (m, 3 H), 4.18–3.98 (m, 13 H), 3.98–3.80 (m, 9 H), 3.73–3.51 (m, 8 H), 3.38 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.25 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.06 (s, 3 H), 1.63–1.55 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 144.6, 138.5, 138.2, 138.1(3), 138.1(2), 138.1, 137.7(2), 137.7, 137.4, 133.0, 129.7, 128.6, 128.5, 128.4(0), 128.3(8), 128.3(5), 128.3(1), 128.3, 127.9(9), 127.9(6), 127.9(4), 127.9, 127.7(9), 127.7(7), 127.7(2), 127.7, 127.6(1), 127.6, 127.4, 127.0, 106.5 (C-1), 106.4 (C-1), 106.1 (C-1), 100.7 (C-1), 100.6 (C-1), 99.0 (C-1), 88.7, 88.3, 86.4, 84.2, 83.9, 83.4, 83.3, 83.2, 82.3, 81.5, 80.7, 80.5, 80.3, 80.2, 79.1, 74.3, 73.3, 73.2, 72.7, 72.5, 72.4(0), 72.3(5), 72.3, 72.2, 72.0(1), 72.0, 71.9, 71.3, 70.7, 70.5, 69.9, 69.3, 68.9, 68.7, 67.6, 67.0, 66.0, 65.6, 51.5, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{130}H_{145}N_3O_{28}SNa$: 2250.9633. Found: 2250.9627.

8-Azidooctyl 5-deoxy-5-thiomethyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-45). To a solution of **LAM-44** (0.54 g, 0.24 mmol) in CH_3CN (9 mL) was added sodium thiomethoxide (0.07 g, 1.0 mmol). The reaction mixture was then heated at 80 °C for 2 h, cooled to rt and then filtered to remove undissolved solids and the filter cake was washed with CH_3CN. The filtrate was then concentrated to a crude residue that was purified by chromatography (72:28 hexanes–EtOAc) to yield **LAM-45** (0.36 g, 72%) as a thick syrup. R_f 0.27 (7:3 hexanes–EtOAc); $[\alpha]_D$ +43.5 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 7.40–7.15 (m, 60 H), 5.52 (d, 1 H, *J* = 4.2 Hz, H-1), 5.15–5.12 (m, 2 H, 2 × H-1), 5.10 (s, 1 H, H-1), 5.02 (s, 1 H, H-1), 4.91 (s, 1 H, H-1), 4.74–4.45 (m, 21 H), 4.35–4.30 (m, 4 H), 4.25–3.99 (m, 14 H), 3.95 (dd, 1 H, *J* = 4.4, 5.5 Hz), 3.93–3.82 (m, 6 H), 3.75–3.55 (m, 7 H), 3.40 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.25 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.71 (dd, 1 H, *J* = 5.4, 13.8

Hz), 2.55 (dd, 1 H, *J* = 7.2, 13.8 Hz), 2.39 (s, 1 H), 2.07 (s, 3 H), 1.63–1.55 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 139.2, 138.8, 138.7, 138.6(1), 138.5(9), 138.4, 138.3, 138.2, 128.9, 128.8, 128.7(4), 128.7(2), 128.6(9), 128.6(7), 128.6, 128.4(1), 128.4(0), 128.4, 128.2(3), 128.1(4), 128.1(1), 128.1, 128.0(3), 127.9(8), 127.9(5), 127.9(1), 127.8(5), 127.8(3), 127.8, 127.5, 106.9 (C-1), 106.8 (C-1), 106.5 (C-1), 101.2 (C-1), 101.0 (C-1), 99.4 (C-1), 88.9, 88.6(3), 86.5(5), 84.8, 84.4, 84.1, 83.9(4), 83.9(0), 83.3, 82.2, 82.0, 81.1, 81.0, 80.8, 79.7, 77.9, 73.6(4), 73.6(1), 72.8, 72.7(1), 72.6(7), 72.5, 72.4, 72.3(0), 72.2(5), 71.4, 71.3, 71.0, 70.5, 69.9, 69.2, 68.0, 67.5, 66.7, 66.3, 51.9, 34.9, 29.9, 29.7, 29.5, 29.2, 27.1, 26.5, 16.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{124}H_{141}N_3O_{25}SNa$: 2126.9467. Found: 2126.9462.

8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-46). Prepared from trichloroacetimidate **LAM-42** (prepared from 0.26 g (0.28 mmol) of hemiacetal **LAM-41** (Scheme S7), 0.6 mL of CCl_3CN and 10 μL of DBU) in CH_2Cl_2 (10 mL), alcohol **LAM-19** (0.5 g, 0.22 mmol) in CH_2Cl_2 (10 mL), 4 Å molecular sieves (0.46 g) and TMSOTf (10 μL, 0.06 mmol) at −30 °C as described for the synthesis of **LAM-43** to afford **LAM-46** (0.62 g, 88%) as a thick syrup. R_f 0.50 (7:3 hexanes–EtOAc); $[\alpha]_D$ +31.8 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08–8.02 (m, 2 H), 7.64–7.56 (m, 3 H), 7.40–7.00 (m, 94 H), 5.80 (dd, 1 H, *J* = 2.5, 2.5 Hz), 5.40 (d, 1 H, *J* = 4.3 Hz, H-1), 5.33 (s, 1 H, H-1), 5.16 (s, 1 H, H-1), 5.13 (s, 2 H, 2 × H-1), 5.10 (d, 1 H, *J* = 4.3 Hz, H-1), 5.04–5.00 (m, 2 H, 2 × H-1), 4.93–4.82 (m, 3 H), 4.72–4.62 (m, 3 H), 4.61–4.41 (m, 27 H), 4.40–4.22 (m, 6 H), 4.20–3.52 (m, 41 H), 3.40 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.26 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.32 (s, 3 H), 1.64–1.56 (m, 4 H), 1.42–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 144.5, 138.8, 138.6(4), 138.6(0), 138.6, 138.4, 138.3, 138.2(2), 138.2, 138.1, 138.0, 137.9, 137.7(7), 137.7(5), 137.7, 137.6, 133.1, 132.9, 130.0, 129.9, 129.6(0), 128.5(5), 128.5, 128.4(2), 128.3(9), 128.3(6), 128.3(3), 128.3(1), 128.3, 128.1, 128.0(1), 128.0, 127.9(3), 127.8(9), 127.8(6), 127.8(2), 127.8, 127.7(2), 127.6(9), 127.6(8), 127.6(6), 127.6(2), 127.6, 127.5(4), 127.5(1), 127.5, 127.4(4), 127.4(1), 127.4, 127.3, 106.5 (C-1), 106.3 (C-1), 106.1 (C-1), 100.9 (C-1), 100.8 (C-1), 100.7(6) (C-1), 99.3 (C-1), 98.9 (C-1),

88.7, 88.3, 86.1, 84.4, 84.0, 83.9, 83.3, 83.2(1), 82.2(3), 81.6, 80.7, 80.6, 80.2, 79.6, 79.5, 78.2, 75.6, 75.3, 75.1, 74.7(4), 74.7, 74.4, 73.3(4), 73.3, 73.2(0), 73.2, 72.6, 72.4, 72.3(2), 72.3, 72.0(2), 72.0, 71.9, 71.4, 70.6, 70.2, 69.8, 69.2(1), 69.2, 69.1(0), 69.1, 69.0(3), 68.0, 67.6, 66.0, 65.5, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1, 21.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{191}H_{205}N_3O_{39}SNa$: 3219.3769. Found: 3219.3763.

8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-47). Prepared from **LAM-46** (0.62 g, 0.19 mmol) and 1M methanolic sodium methoxide solution in CH_2Cl_2–CH_3OH (4:1, 30 mL) as described for the synthesis of **LAM-44** to afford **LAM-47** (0.54 g, 90%) as a thick syrup. R_f 0.26 (7:3 hexanes–EtOAc); $[\alpha]_D$ +44.5 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 7.72–7.64 (m, 2 H), 7.41–7.14 (m, 92 H), 5.48 (d, 1 H, *J* = 4.3 Hz, H-1), 5.30 (d, 1 H, *J* = 1.7 Hz, H-1), 5.18–5.10 (m, 5 H, 5 × H-1), 5.06 (s, 1 H, H-1), 4.88 (dd, 1 H, *J* = 11.1, 13.6 Hz), 4.76–4.30 (m, 36 H), 4.26–3.80 (m, 33 H), 3.80–3.54 (m, 11 H), 3.43 (ddd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.38 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.40 (s, 3 H), 1.63–1.54 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 145.3, 139.3(2), 139.2(8), 139.3, 139.2, 138.9(7), 138.9(5), 138.8, 138.6(9), 138.6(5), 138.6(3), 138.6, 138.4, 138.3(3), 138.2(8), 138.2(6), 133.3, 130.2, 128.9, 128.8(2), 128.8(0), 128.7(6), 128.7(3), 128.7(2), 128.7(1), 128.6(8), 128.6(4), 128.6(0), 128.6, 128.4(1), 128.4, 128.3(3), 128.2(8), 128.2(5), 128.2(3), 128.2(1), 128.1(9), 128.1(6), 128.1(2), 128.0(5), 127.9(9), 127.9(6), 127.9(5), 127.9(1), 127.9, 127.8(4), 127.8(3), 127.8, 127.6(7), 127.6(5), 106.9 (C-1), 106.7 (C-1), 106.6 (C-1), 101.3 (2 × C-1), 101.0(5) (C-1), 101.0(7) (C-1), 99.3 (C-1), 89.0, 88.7, 86.4, 85.0, 84.4, 84.3, 84.1, 83.9, 83.0, 82.0, 81.3, 81.2, 80.8, 80.6, 80.3, 80.0, 79.9, 75.7, 75.5, 75.3(9), 75.3(7), 75.1, 74.7, 73.7, 73.6(3), 73.6, 73.5, 73.1, 72.9, 72.7(7), 72.7(5), 72.7(0), 72.7, 72.4, 72.3(4), 72.3, 72.0, 71.6, 71.4, 71.1, 70.7, 70.3, 69.7, 69.5, 68.0, 67.8(0), 66.8, 66.3, 51.9, 30.0, 29.7, 29.5, 29.2, 27.1, 26.5, 21.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{184}H_{201}N_3O_{38}SNa$: 3115.3506. Found: 3115.3501.

8-Azidooctyl 5-deoxy-5-thiomethyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-48). Prepared from **LAM-47** (0.27 g, 0.09 mmol), and sodium thiomethoxide (0.03 g, 0.4 mmol) in CH_3CN (6 mL) as described for the synthesis of **LAM-45** to afford **LAM-48** (0.19 g, 74%) as a syrup. R_f 0.36 (7:3 hexanes–EtOAc); $[\alpha]_D$ +45.2 (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 7.40–7.10 (m, 90 H), 5.51 (d, 1 H, J = 4.3 Hz, H-1), 5.30 (d, 1 H, J = 1.5 Hz, H-1), 5.15–5.05 (m, 5 H, 5 × H-1), 5.05 (s, 1 H, H-1), 4.84 (dd, 2 H, J = 11.0, 11.0 Hz), 4.72–4.40 (m, 34 H), 4.36–4.28 (m, 3 H), 4.22–3.50 (m, 42 H), 3.39 (dd, 1 H, J = 6.6, 9.5, 13.2 Hz), 3.25 (dd, 1 H, J = 7.0, 7.0 Hz), 2.68 (dd, 1 H, J = 5.4, 13.8 Hz), 2.52 (dd, 1 H, J = 7.1, 13.8 Hz), 2.03 (s, 1 H), 2.06 (s, 3 H), 1.63–1.54 (m, 4 H), 1.41–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 139.3(4), 139.2(9), 139.2(7), 139.2, 139.1, 139.0, 138.8, 138.6(9), 138.6(6), 138.6(4), 138.6, 138.4(9), 138.4(7), 138.3(4), 138.2(8), 138.2(6), 128.9, 128.8(2), 128.7(9), 128.7(7), 128.7(1), 128.6(9), 128.6(4), 128.6(1), 128.6, 128.4(1), 128.4, 128.3(3), 128.2(9), 128.2(7), 128.2(1), 128.1(9), 128.1(7), 128.1(5), 128.1(2), 128.0(8), 128.0(5), 128.0(2), 128.0(0), 128.0, 127.9(4), 127.9, 127.8(2), 127.8(0), 127.7(7), 127.7, 127.6, 106.9 (C-1), 106.7 (C-1), 106.6 (C-1), 101.3(7) (C-1), 101.3(5) (C-1), 101.3 (C-1), 101.1 (C-1), 99.2 (C-1), 89.0, 88.7, 86.4, 85.0, 84.4, 84.3, 84.1, 83.9, 83.4, 82.3, 82.1, 81.2, 80.8, 80.7, 80.3, 80.0, 79.9, 77.8(3), 75.8, 75.5, 75.1, 73.7, 73.6, 73.5, 72.9, 72.7(7), 72.7(5), 72.7(0), 72.6(8), 72.6(6), 72.5, 72.3(4), 72.3, 72.0, 71.6(4), 71.6, 71.2, 70.7, 70.3, 69.9, 69.7, 68.0, 67.9, 66.8, 66.3, 51.9, 35.0, 30.0, 29.7, 29.5, 29.2, 27.1, 26.5, 16.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{178}H_{197}N_3O_{35}SNa$: 3014.3232. Found: 1507.1624 (M+2Na).

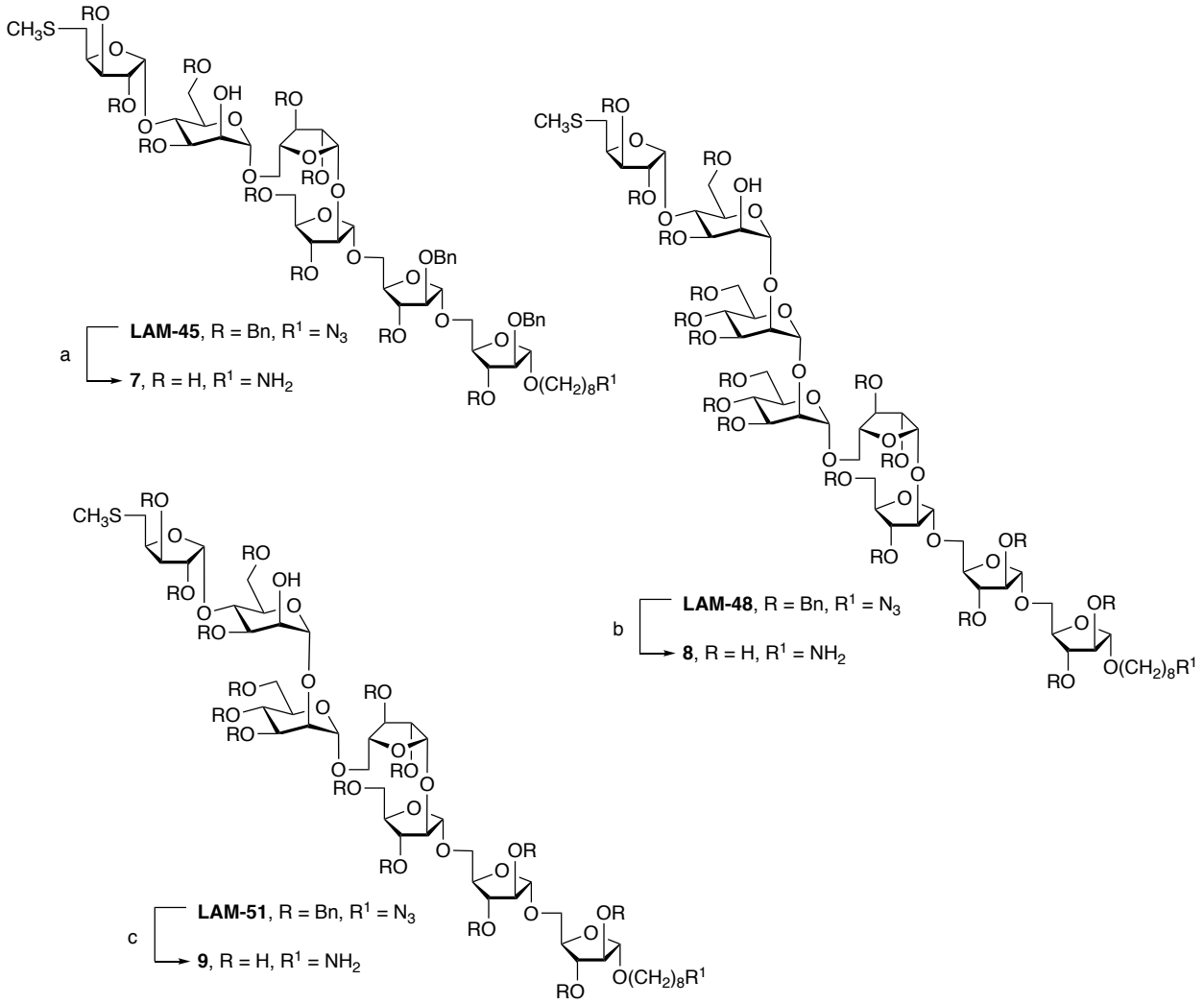
8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-49). Trichloroacetimidate **LAM-42** (prepared from 0.39 g of hemiacetal **LAM-41** (Scheme S7), 0.6 mL of CCl_3CN and 15 μL of DBU) in CH_2Cl_2 (10 mL), alcohol **LAM-17** (0.5 g, 0.27 mmol) in CH_2Cl_2 (10 mL), 4 Å molecular sieves (0.4 g) and TMSOTf (8 μL, 0.044 mmol) at –30 °C as described for the synthesis of **LAM-43** to afford **LAM-49** (0.59 g, 79%) as a thick syrup. R_f 0.39 (7:3 hexanes–EtOAc); $[\alpha]_D$ +39.0 (c = 0.3,

$CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.05–8.02 (m, 2 H), 7.64–7.56 (m, 3 H), 7.41–7.0 (m, 79 H), 5.82 (dd, 1 H, *J* = 2.3, 2.3 Hz), 5.36 (d, 1 H, *J* = 4.2 Hz, H-1), 5.23 (d, 1 H, *J* = 1.8 Hz, H-1), 5.16–5.10 (m, 3 H, 3 × H-1), 5.09 (s, 1 H, H-1), 5.03 (s, 1 H, H-1), 4.88 (dd, 2 H, *J* = 3.6, 11.2 Hz), 4.76–4.43 (m, 25 H), 4.40–4.30 (m, 2 H), 4.28–4.22 (m, 2 H), 4.20–4.03 (m, 15 H), 4.03–3.94 (m, 4 H), 3.94–3.54 (m, 18 H), 3.39 (ddd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.26 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.33 (s, 3 H), 1.64–1.56 (m, 4 H), 1.42–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 144.5, 138.7, 138.6, 138.2(4), 138.1(7), 138.1(5), 138.1(0), 138.1, 137.9, 137.8, 137.7(1), 137.7, 137.4, 133.2, 132.9, 129.9, 129.8, 129.6, 128.6, 128.5, 128.4(2), 128.3(9), 128.3(7), 128.3(3), 128.3(2), 128.2(9), 128.2, 128.0, 127.9(4)(Ar), 127.8(9), 127.8(5)(Ar), 127.8(3), 127.7(8), 127.7(6), 127.7(3), 127.7(0), 127.6(8), 127.6(4), 127.6, 127.5(4), 127.5(2), 127.5, 127.4(1), 127.4, 127.3(4), 127.3, 106.5 (C-1), 106.4 (C-1), 106.1 (C-1), 100.9 (C-1), 100.8 (C-1), 99.4 (C-1), 98.6 (C-1), 88.7, 88.3, 86.2, 84.5, 83.9, 83.7, 83.3, 83.2, 82.0, 81.6(0), 80.6(3), 80.6, 80.2, 80.0, 79.2, 78.2, 75.1, 74.7, 74.5, 74.3, 73.3(5), 73.3, 73.2, 72.7, 72.4(0), 72.3(8), 72.3(7), 72.3, 72.2(1), 72.1(6), 72.0, 71.9(3), 71.8(8), 71.8(5), 71.4, 70.7, 70.2, 69.6, 69.2, 69.1, 68.0, 67.6, 66.0, 65.6, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{164}H_{177}N_3O_{34}SNa$: 2787.1832. Found: 2787.1826.

8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-50). Prepared from **LAM-49** (0.35 g, 0.13 mmol) and 1M methanolic sodium methoxide solution in CH_2Cl_2–CH_3OH (7:3, 10 mL) as described for the synthesis of **LAM–44** to afford **LAM-50** (0.32 mg, 94%) as a thick syrup. R_f 0.24 (7:3 hexanes–EtOAc); $[\alpha]_D$ + 42.1 (*c* = 0.4, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, δ_H) 7.70–7.63 (m, 2 H), 7.35–7.10 (m, 77 H), 5.32 (d, 1 H, *J* = 4.3 Hz, H-1), 5.13 (d, 2 H, *J* = 1.5 Hz, H-1), 5.10 (d, 1 H, *J* = 0.8 Hz, H-1), 5.09 (s, 1 H, H-1), 5.07 (d, 1 H, *J* = 4.4 Hz, H-1), 5.06 (d, 1 H, *J* = 1.7 Hz, H-1), 4.99 (d, 1 H, *J* = 1.1 Hz, H-1), 4.81 (d, 1 H, *J* = 10.9 Hz), 4.70 (d, 1 H, *J* = 11.6 Hz), 4.66–4.30 (m, 28 H), 4.26–4.18 (m, 2 H), 4.16–3.98 (m, 13 H), 3.98–3.94 (m, 2 H), 3.94–3.74 (m, 12 H), 3.71–3.46 (m, 9 H), 3.38 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.24 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.38 (s, 3 H), 1.63–1.54 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 144.6, 138.6(9), 138.6(5), 138.6, 138.3, 138.2(2), 138.2, 138.1(2), 138.1(0), 137.8, 137.7(3), 137.7(1), 137.5, 133.1, 129.6(9), 128.6(8), 128.6(4), 128.6,

128.5, 128.4(0), 128.3(7), 128.3(3), 128.3(2), 128.3, 128.1, 127.9(8), 127.9(6), 127.9(4), 127.9, 127.8(3), 127.7(7), 127.7(6), 127.7(4), 127.7(0), 127.7, 127.5(9), 127.5(6), 127.5(2), 127.5, 127.2, 106.5 (C-1), 106.4(C-1), 106.1 (C-1), 100.8(8) (C-1), 100.8(6) (C-1), 100.6(0) (C-1), 98.7 (C-1), 88.7, 88.3, 86.2, 84.5, 83.9, 83.6, 83.3, 83.2(1), 82.2, 81.6, 80.7, 80.6, 80.2, 80.1, 79.1(3), 75.1, 74.7, 74.4, 74.2, 73.3(3), 73.3, 73.1, 72.8, 72.3(8), 72.3(6), 72.3(5), 72.3, 72.2(3), 72.2, 72.0, 71.9, 71.7, 70.9, 70.9, 70.3, 69.6, 69.3, 69.1, 69.0, 67.6, 67.5, 66.0, 65.6, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{157}H_{173}N_3O_{33}SNa$: 2683.1570. Found: 2683.1564.

8-Azidooctyl 5-deoxy-5-thiomethyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*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)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-51). Prepared from **LAM-50** (0.31 g, 0.12 mmol), and sodium thiomethoxide (0.04 g, 0.6 mmol) in CH_3CN (6 mL) as described for the synthesis of **LAM-45** to afford **LAM-51** (0.21 g, 70%) as a syrup. R_f 0.42 (7:3 hexanes–EtOAc, two runs); $[\alpha]_D$ + 54.3 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 7.40–7.15 (m, 75 H), 5.49 (d, 1 H, *J* = 4.3 Hz, H-1), 5.16 (d, 1 H, *J* = 1.0 Hz, H-1), 5.14–5.10 (m, 3 H, 3 × H-1), 5.09 (s, 1 H, H-1), 5.03 (s, 1 H, H-1), 4.86 (d, 1 H, *J* = 11.0 Hz), 4.74 (d, 1 H, *J* = 11.6 Hz), 4.70–4.40 (m, 28 H), 4.37–4.32 (m, 2 H), 4.24–3.54 (m, 35 H), 3.40 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.26 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.71 (dd, 1 H, *J* = 5.1, 13.8 Hz), 2.52 (dd, 1 H, *J* = 7.2, 13.8 Hz), 2.39 (s, 1 H), 2.06 (s, 3 H), 1.63–1.55 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 139.3, 139.2, 139.1, 138.8(2), 138.8, 138.7(0), 138.7, 138.6(2), 138.6, 138.4, 138.3, 138.2(4), 138.2(3), 128.9, 128.8(0), 128.8, 128.7(1), 128.6(9), 128.6(6), 128.6, 128.4(1), 128.3(7), 128.2(3), 128.2(1), 128.2, 128.1(3), 128.0(9), 128.0(6), 128.0(4), 127.9(9), 127.9(7), 127.9(2), 127.8(9), 127.8(7), 127.8(2), 127.8(1), 127.8, 127.6, 106.9 (C-1), 106.8 (C-1), 106.5 (C-1), 101.3 (C-1), 101.2 (C-1), 101.1 (C-1), 99.0 (C-1), 89.0, 88.6, 86.4, 85.0, 84.4, 84.1, 84.0, 83.9(0), 83.9, 82.2, 82.0, 81.1, 80.8(1), 80.8, 80.6, 79.6, 77.8, 75.3, 75.1, 74.7, 73.6(4), 73.6(0), 73.5, 72.9, 72.7(7), 72.7(5), 72.7(2), 72.7(0), 72.7, 72.4(8), 72.4(6), 72.3(1), 72.3, 71.6(0), 71.6, 71.3, 70.8, 69.9, 69.8, 69.6,68.0, 67.8, 66.7, 66.3, 51.9, 35.0, 30.0, 29.7, 29.5, 29.2, 27.1, 26.5, 16.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{151}H_{169}N_3O_{30}SNa$: 2559.1409. Found: 2559.1403.



Scheme S9. Synthesis of **7**–**9**. a) Na, NH_3 (l), THF; then CH_3OH, H_2O, 67%, b) Na, NH_3 (l), THF; then CH_3OH, H_2O, 59%; c) Na, NH_3 (l), THF; then CH_3OH, H_2O, 63%.

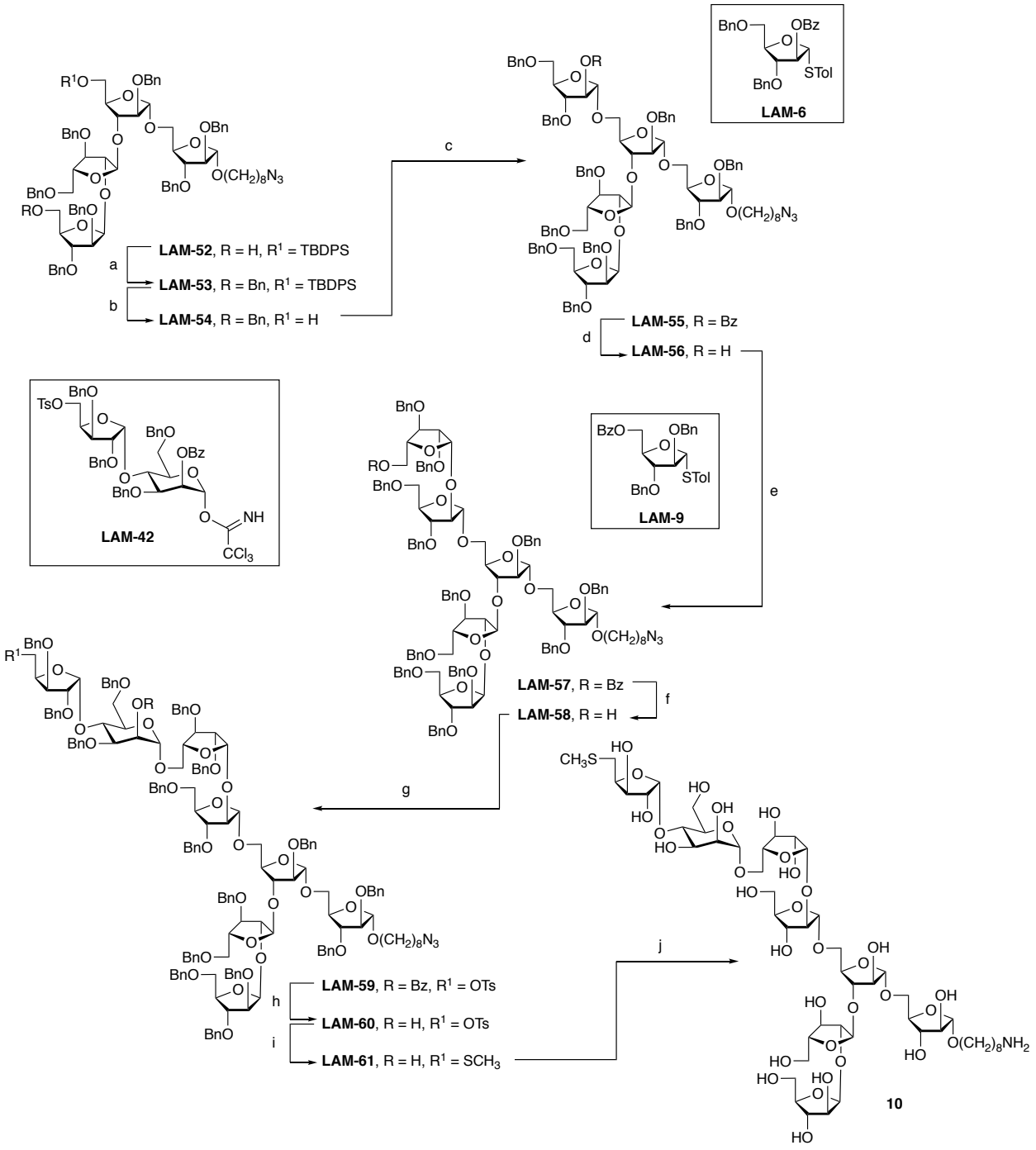
8-Aminooctyl 5-deoxy-5-thiomethyl-α-D-xylofuranosyl-(1→4)-α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (7). To a solution of liquid NH_3 (25 mL) at −78 °C was added sodium metal (0.1 g) until a deep blue solution was produced. A solution of **LAM-45** (83 mg, 0.04 mmol) in THF (2 mL) was then added over a period of 3–4 min, making sure that the deep blue color persisted and the reaction mixture was stirred at −78 °C for 45 min. Methanol was then added until the dark blue color disappeared and the solution appeared clear. The solution was then warmed to rt by blowing air gently over the solution, which also helped evaporate the NH_3. When the reaction mixture reached rt, a 1:1 solution of CH_3OH–H_2O (6 mL) was added

and the pH of the solution was brought to ~8 by the careful addition of Amberlite IR 120 H+ resin. The solution was filtered to remove the resin and the filtrate was concentrated. The residue was purified by C-18 chromatography (1:1 CH_3OH–H_2O) to give **7** (26 mg, 67%) as a thick syrup that was later lyophilized from water to give a fluffy solid. $[\alpha]_D$ + 73.3 (*c* = 0.1, CH_3OH); ^{1}H NMR (600 MHz, D_2O, δ_H) 5.41 (d, 1 H, *J* = 4.4 Hz, H-1), 5.17 (s, 1 H, H-1), 5.14 (d, 1 H, *J* = 4.2 Hz, H-1), 5.08 (s, 1 H, H-1), 5.01 (s, 1 H, H-1), 4.92 (s, 1 H, H-1), 4.40–4.35 (m, 1 H), 4.27–4.22 (m, 1 H), 4.22–3.95 (m, 14 H), 3.95–3.62 (m, 14 H), 3.57 (ddd, 2 H, *J* = 6.6, 10.0, 13.2 Hz), 2.89 (dd, 2 H, *J* = 7.5, 7.5 Hz), 2.79 (dd, 1 H, *J* = 4.9, 10.3 Hz), 2.68 (dd, 1 H, *J* = 8.4, 13.8 Hz), 2.17 (s, 3 H), 1.65–1.55 (m, 4 H), 1.40–1.25 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.4 (C-1), 108.2 (C-1), 106.6(2) (C-1), 103.4 (C-1), 101.5 (C-1), 100.8 (C-1), 88.0, 84.1, 83.2, 82.6, 82.6, 81.8(3), 81.7(9), 80.7(5), 80.7(2), 78.6(7), 77.7, 77.6, 77.5, 77.4(4), 77.4(0), 76.9, 76.5, 76.0, 75.0, 74.9, 73.8, 72.4, 71.5(3), 71.5, 71.1, 70.9, 69.5, 69.2, 67.8, 67.7, 61.9(2), 61.9, 61.7, 40.5, 33.9, 29.5, 29.0(4), 29.0, 27.7, 26.4, 26.0, 15.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{40}H_{72}N_1O_{25}SNa$: 998.4108. Found: 998.4110.

8-Aminooctyl 5-deoxy-5-thiomethyl-α-D-xylofuranosyl-(1→4)-α-D-mannopyranosyl-(1→2)-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-arabinofuranoside (8). Prepared from **LAM-48** (0.13 g, 0.044 mmol), liquid NH_3 (25 mL) and sodium metal (0.1 g) in THF (2 mL) as described for the preparation of **7** to give the **8** (34 mg, 59%) as a thick syrup that was later lyophilized from water to give a foam. $[\alpha]_D$ +69.8 (*c* = 0.1, CH_3OH); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.40 (d, 1 H, *J* = 4.4 Hz, H-1), 5.28 (d, 1 H, *J* = 1.2 Hz, H-1), 5.18 (d, 1 H, *J* = 1.7 Hz, H-1), 5.16–5.12 (m, 2 H, 2 × H-1), 5.08 (d, 1 H, *J* = 1.4 Hz, H-1), 5.05 (d, 1 H, *J* = 1.7 Hz, H-1), 5.01 (d, 1 H, *J* = 1.9 Hz, H-1), 4.42–4.36 (m, 1 H), 4.28–4.24 (m, 1 H), 4.24–3.50 (m, 41 H), 2.90 (dd, 2 H, *J* = 7.5, 7.5 Hz), 2.80 (dd, 1 H, *J* = 4.8, 13.8 Hz), 2.70 (dd, 1 H, *J* = 8.4, 13.8 Hz), 2.18 (s, 3 H), 1.65–1.55 (m, 4 H), 1.40–1.25 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.42 (C-1), 108.1 (C-1), 106.6 (C-1), 103.4 (C-1), 103.1 (C-1), 101.6 (C-1), 101.4 (C-1), 99.1 (C-1), 87.8, 84.1, 83.2, 82.6(2), 82.6, 81.8(1), 81.8, 80.6, 79.7, 79.3, 78.6, 77.6, 77.5, 77.4(0), 77.4, 77.0, 76.5, 76.0, 75.0, 75.0, 74.2, 73.8, 72.7, 71.3, 71.1(0), 71.0(8), 70.9, 69.5, 69.2, 68.0, 67.8, 67.7, 63.5, 62.0(4), 62.0(2), 62.0, 61.8, 61.6, 40.4, 33.9, 29.5, 29.0, 28.95, 27.6, 26.3, 26.0, 15.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{52}H_{92}N_1O_{35}SNa$: 1345.5057. Found: 672.7531 (M+H+2Na).

8-Aminooctyl 5-deoxy-5-thiomethyl-α-D-xylofuranosyl-(1→4)-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-arabinofuranoside (9). Prepared from **LAM-51** (82 mg, 0.032 mmol), liquid NH_3 (20 mL) and sodium metal (0.1 g) in THF (2 mL) as described for the synthesis of **7** to give **9** (23 mg, 63%) as a thick syrup that was later lyophilized from water to give a foam. $[\alpha]_D$ + 80.5 (*c* = 0.1, CH_3OH); ^{1}H NMR (600 MHz, D_2O, δ_H) 5.40 (d, 1 H, *J* = 4.5 Hz, H-1), 5.16–5.12 (m, 3 H, 3 × H-1), 5.08 (s, 1 H, H-1), 5.03 (s, 1 H, H-1), 5.01 (d, 1 H, *J* = 1.1 Hz, H-1), 4.40–4.36 (m, 1 H), 4.26 (dd, 1 H, *J* = 4.5, 4.5 Hz), 4.22–3.60 (m, 34 H), 3.57 (ddd, 2 H, *J* = 6.6, 10.0, 13.2 Hz), 2.90 (dd, 2 H, *J* = 7.5, 7.5 Hz), 2.79 (dd, 1 H, *J* = 4.8, 13.8 Hz), 2.68 (dd, 1 H, *J* = 8.4, 13.8 Hz), 2.17 (s, 3 H), 1.65–1.55 (m, 4 H), 1.40–1.25 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.4 (C-1), 108.1 (C-1), 106.5 (C-1), 103.3 (C-1), 103.2 (C-1), 101.4 (C-1), 99.2 (C-1), 87.8, 84.1, 83.2, 82.6(2), 82.5(9), 81.8(0), 81.7(8), 80.7, 79.5, 78.6(2), 77.6(3), 77.5, 77.4(1), 77.4, 77.0, 76.5, 76.0, 75.1, 75.0, 73.8(4), 72.8, 71.3, 71.1, 69.5, 69.3, 67.8, 67.7, 63.4, 62.2, 61.8, 61.6, 40.5, 33.9, 29.5, 29.0(2), 29.0, 27.6, 26.4, 26.0, 15.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{46}H_{82}N_1O_{30}SNa$: 1183.4529. Found: 591.7268 (M+H+2Na).

7. Synthesis of 10



Scheme S10. Synthesis of **10**. a) BnBr, NaH, THF, DMF, 97%, b) *n*-Bu_4NF, THF, 95%; c) **LAM-6**, NIS, AgOTf, 91%; d) $NaOCH_3$, CH_3OH, CH_2Cl_2, 94%; e) **LAM-9**, NIS, AgOTf, 83%; f) $NaOCH_3$, CH_3OH, CH_2Cl_2, 89%; g) **LAM-42**, TMSOTf, CH_2Cl_2, 68%; h) $NaOCH_3$, CH_3OH, CH_2Cl_2, 90%; i) $NaSCH_3$, CH_3CN, 70%; j) Na, NH_3 (l), THF; then CH_3OH, H_2O, 60%.

8-Azidooctyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-2-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-53). To a solution of **LAM-52**[19] (1.10 g, 0.70 mmol) in a mixture of DMF (5 mL) and THF (5 mL) at 0 °C was added NaH (0.056 g, 1.40 mmol, 60% dispersion in oil) and the solution was stirred for 10 min before benzyl bromide (0.1 mL, 0.84 mmol) was added dropwise. After stirring for 14 h at rt, a few drops of CH_3OH were added, the solution was diluted with CH_2Cl_2 (100 mL), and then washed with a satd aq $NaHCO_3$ soln and water. The organic layer was dried (Na_2SO_4), filtered, concentrated, and the resulting residue was purified by chromatography (6:1 hexanes–EtOAc) to provide **LAM-53** (1.13 g, 97%) as a colorless oil. R_f 0.23 (6:1 hexanes–EtOAc); $[\alpha]_D$ +22.2 (c = 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.76–7.72 (m, 4 H), 7.40–7.21 (m, 46 H), 5.20 (s, 1 H, H-1), 5.19 (s, 1 H, H-1), 5.08 (d, 1 H, J = 4.4 Hz, H-1), 5.02 (s, 1 H, H-1), 4.70 (d, 1 H, J = 11.8 Hz), 4.66–4.35 (m, 17 H), 4.24–4.20 (m, 1 H), 4.19–4.02 (m, 9 H), 3.94–3.89 (m, 3 H), 3.77–3.50 (m, 2 H), 3.60–3.47 (m, 4 H), 3.39 (ddd, 1 H, J = 9.6, 6.6, 6.6 Hz), 3.25 (dd, 2 H, J = 7.0, 6.9 Hz), 1.65–1.57 (m, 4 H), 1.42–1.30 (m, 8 H), 1.08 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2(8), 138.2(6), 138.2(2), 138.1, 138.0(8), 137.7(4), 137.9, 137.7, 137.6, 135.7, 135.6, 133.7, 133.6, 129.5(2), 129.5(0), 128.4, 128.3(5), 128.3(3), 128.3(0), 128.2(4), 128.0, 127.8(7), 127.8(4), 127.8(1), 127.7(8), 127.7(2), 127.6(7), 127.6(3), 127.5(8), 127.5(6), 127.5(1), 127.4, 106.1 (C-1 × 2), 105.4 (C-1), 100.2 (C-1), 88.6, 88.3, 86.0, 84.0, 83.9, 83.3, 83.1, 81.8, 81.4, 80.1, 80.0, 79.7, 73.3, 73.1, 72.3(8), 72.3(0), 72.1, 72.0, 71.8, 69.6, 67.6, 66.2, 63.3, 51.4, 29.5, 29.3, 29.1, 28.5, 26.8, 26.7, 26.1, 19.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{100}H_{115}N_3O_{17}SiNa$: 1680.7888. Found: 1680.7888.

8-Azidooctyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-54). Tetrasaccharide **LAM-53** (1.08 g, 0.65 mmol) in THF (10 mL) was treated with 1M *n*-Bu_4NF in THF solution (0.78 mL) and the reaction mixture was stirred at rt for 3 h. The mixture was concentrated and the resulting residue was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-54** (0.881 g, 95%) as an oil. R_f 0.21 (3:1 hexanes–EtOAc); $[\alpha]_D$ +25.4 (c = 0.4, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.38–7.24 (m, 40 H), 5.17 (d, 1 H, J = 1.6 Hz, H-1), 5.16 (s, 1 H, H-1), 5.06 (d, 1 H, J = 4.4 Hz, H-1), 5.04 (s, 1

H, H-1), 4.72 (d, 1 H, *J* = 11.9 Hz), 4.68–4.40 (m, 14 H), 4.41–4.38 (m, 2 H), 4.27–4.20 (m, 3 H), 4.18–4.03 (m, 8 H), 3.92–3.80 (m, 3 H), 3.78–3.72 (m, 2 H), 3.62–3.55 (m, 4 H), 3.41 (ddd, 1 H, *J* = 9.7, 6.6, 6.6 Hz), 3.28 (dd, 2 H, *J* = 7.0, 6.9 Hz), 2.21 (dd, 1 H, *J* = 7.7, 5.2 Hz), 1.66–1.60 (m, 4 H), 1.43–1.34 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2, 138.1, 138.0(7), 138.0(5), 137.7, 137.6, 128.5, 128.4(6), 128.4(3), 128.3(9), 128.3(2), 128.0, 127.9, 127.8(9), 127.8(0), 127.7(7), 127.7(5), 127.7(2), 127.6(9), 127.6(5), 127.6(2), 127.5, 106.1 (C-1), 106.0(3) (C-1), 106.0(1) (C-1), 100.1 (C-1), 88.6, 88.4, 85.7, 84.1, 83.9, 83.3, 82.9, 81.5, 81.2, 80.5, 80.1, 80.0, 73.3, 73.1, 72.4, 72.3, 72.2, 72.1(6), 72.1(0), 72.0, 69.9, 67.6, 66.1, 61.8, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{84}H_{97}N_3O_{17}Na$: 1442.6710. Found: 1442.6708.

8-Azidooctyl 2,3,4-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-di-*O*-benzyl-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-55). Alcohol **LAM-54** (875 mg, 0.616 mmol) and thioglycoside **LAM-6**[14] (400 mg, 0.739 mmol) were dried under vacuum in the presence of P_2O_5 for 2 h before being dissolved in CH_2Cl_2 (15 mL). The solution was cooled to 0 °C, powdered 4 Å molecular sieves (0.3 g) were added and the reaction mixture was stirred at 0 °C for 15 min before *N*-iodosuccinimide (210 mg, 0.887 mmol) and silver triflate (23 mg, 0.089 mmol) were added. After stirring for 20 min at 0 °C, Et_3N was added until the pH of the solution was neutral as determined by wet pH paper. The reaction was diluted with CH_2Cl_2, filtered through Celite and the filtrate was washed with a saturated a solution of $Na_2S_2O_3$, water and brine. The organic layer was subsequently dried (Na_2SO_4), filtered and concentrated, and the resulting crude residue was purified by chromatography (6:1 hexanes–EtOAc) to yield **LAM-55** (1.031 g, 91%) as an oil. R_f 0.41 (3:1 hexanes–EtOAc); $[\alpha]_D$ +30.9 (*c* = 0.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.02–7.98 (m, 2 H), 7.60–7.56 (m, 1 H), 7.43–7.39 (m, 2 H), 7.37–7.17 (m, 50 H), 5.51 (d, 1 H, *J* = 1.2 Hz), 5.33 (s, 1 H, H-1), 5.21–5.18 (m, 2 H, 2 × H-1), 5.02 (d, 1 H, *J* = 4.0 Hz, H-1), 5.01 (d, 1 H, *J* = 1.1 Hz, H-1), 4.83 (d, 1 H, *J* = 12.1 Hz), 4.70–4.33 (m, 22 H), 4.27–4.21 (m, 2 H), 4.21–3.98 (m, 10 H), 3.91 (dd, 1 H, *J* = 11.8, 4.3 Hz), 3.82 (dd, 1 H, *J* = 11.5, 2.4 Hz), 3.77–3.69 (m, 2 H), 3.65–3.52 (m, 6 H), 3.38 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz), 3.26 (dd, 2 H, *J* = 7.0, 6.9 Hz), 1.65–1.56 (m, 4 H), 1.42–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.2, 138.3,

138.2(8), 138.2(3), 138.1(4), 138.1(0), 138.0, 137.8(8), 137.8(1), 137.7, 133.1, 129.8, 129.7, 128.4(2), 128.4(0), 128.3(5), 128.3(1), 128.2(9), 128.2(6), 128.2(4), 128.0, 127.8(9), 127.8(1), 127.7(7), 127.7(2), 127.6(7), 127.6(3), 127.5(9), 127.5(6), 127.4, 106.2 (C-1), 106.1 (C-1), 106.0 (C-1), 105.5 (C-1), 100.0 (C-1), 88.7, 88.5, 85.6, 84.1, 83.5, 83.2, 83.1, 82.2, 81.7, 81.6, 80.5, 80.1, 80.0(6), 80.0(3), 73.3, 73.2, 73.1, 72.3(9), 72.3(0), 72.0(8), 72.0(4), 71.9, 69.8, 69.2, 67.6, 66.2, 65.8, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{110}H_{121}N_3O_{22}Na$: 1858.8334. Found: 1858.8330.

8-Azidooctyl 2,3,4-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-56). Pentasaccharide **LAM-55** (1.02 g, 0.56 mmol) was dissolved in CH_2Cl_2 (10 mL) and CH_3OH (5 mL) and then treated with 1M methanolic sodium methoxide (0.1 mL). After stirring for 12 h, the reaction mixture was neutralized with HOAc and concentrated. The crude product was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-56** (906 mg, 94%) as an oil. R_f 0.31 (7:3 hexanes–EtOAc); $[\alpha]_D$ +43.4 (*c* = 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38–7.22 (m, 50 H), 5.21 (d, 1 H, *J* = 1.4 Hz, H-1), 5.18 (s, 1 H, H-1), 5.12 (s, 1 H, H-1), 5.03 (d, 1 H, *J* = 1.1 Hz, H-1), 4.99 (d, 1 H, *J* = 4.4 Hz, H-1), 4.70 (d, 1 H, *J* = 11.9 Hz), 4.67–4.38 (m, 19 H), 4.36 (d, 1 H, *J* = 11.7 Hz)), 4.32 (m, 1 H), 4.28–4.18 (m, 4 H), 4.18–4.01 (m, 7 H), 3.99 (dd, 1 H, *J* = 6.5, 4.5 Hz), 3.91 (dd, 1 H, *J* = 11.7, 4.3 Hz), 3.86 (dd, 1 H, *J* = 4.3, 2.2 Hz), 3.78–3.72 (m, 3 H), 3.62–3.54 (m, 5 H), 3.40 (ddd, 1 H, *J* = 9.7, 6.7, 6.7 Hz), 3.38–3.34 (m, 2 H), 3.27 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.89 (br s, 1 H), 1.66–1.59 (m, 4 H), 1.43–1.33 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2(6), 138.1(9), 138.1(7), 138.0(8), 137.8, 137.6(9), 137.6(7), 137.5, 128.5, 128.5, 128.4(5), 128.4(4), 128.3(9), 128.3(7), 128.2(9), 128.0, 127.9, 127.8(6), 127.8(4), 127.8(0), 127.7(3), 127.7(0), 127.6(6), 127.6(3), 127.6(0), 127.5(7), 127.5(5), 109.0 (C-1), 106.1 (C-1), 106.0 (C-1), 105.5 (C-1), 100.1 (C-1), 88.6, 88.5, 85.7, 84.6, 84.3, 84.1, 83.2, 83.0, 82.4, 81.6, 80.5, 80.1, 80.0, 78.4, 73.6, 73.3, 73.1, 72.4, 72.3, 72.2, 72.1, 72.0, 71.9(8), 71.9(0), 70.0, 69.7, 67.0, 66.0, 65.7, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{103}H_{117}N_3O_{21}Na$: 1754.8071. Found: 1754.8069.

8-Azidooctyl 2,3,4-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzyl-5-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-

benzyl-α-D-arabinofuranoside (LAM-57). To a mixture of **LAM-56** (840 mg, 0.485 mmol), **LAM-9**[15] (378 mg, 0.699 mmol) and 4 Å molecular sieves (0.2 g) in CH_2Cl_2 (70 mL) was added *N*-iodosuccinimide (199 mg, 0.839 mmol) followed by silver triflate (25 mg, 0.11 mmol) at –60 °C. The reaction was slowly warmed up to –30 °C and kept stirring for 20 min at –30 °C. The reaction mixture turned dark red, Et_3N was added, and then diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with satd aq $Na_2S_2O_3$ soln, dried (Na_2SO_4), and concentrated to give a residue that was purified by chromatography (3:1 hexanes–EtOAc) to give **LAM-57** (863 mg, 83%) as a colorless syrup. R_f 0.34 (3:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.04–8.00 (m, 2 H), 7.56–7.51 (m, 1 H), 7.41–7.16 (m, 62 H), 5.23 (s, 1 H, H-1), 5.20–5.18 (m, 2 H, 2 × H-1), 5.16 (s, 1 H, H-1), 5.03 (d, 1 H, J = 4.4 Hz, H-1), 5.02 (s, 1 H, H-1), 4.77–4.32 (m, 33 H), 4.28–4.01 (m, 15 H), 3.90–3.81 (m, 2 H), 3.75–3.69 (m, 2 H), 3.62–3.54 (m, 6 H), 3.38 (ddd, 1 H, J = 9.6, 6.7, 6.7 Hz), 3.27 (dd, 2 H, J = 7.0, 7.0 Hz), 1.66–1.57 (m, 4 H), 1.43–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 138.3(3), 138.3(2), 138.2(8), 138.2(6), 138.2(1), 138.1(2), 138.1(0), 137.9(5), 137.7(9), 137.7(0), 137.6, 133.0, 129.8, 128.7, 128.5, 128.4(6), 128.4(5), 128.4(2), 128.3(9), 128.3(5), 128.3(3), 128.3(2), 128.2(7), 128.2(1), 128.0(9), 128.0(4), 127.9(8), 127.9(0), 127.8(6), 127.8(4), 127.8(1), 127.7(7), 127.7(3), 127.7(2), 127.6(7), 127.6(2), 127.5(7), 127.5(0), 127.4, 106.7 (C-1), 106.2 (C-1), 106.1 (C-1), 105.5 (C-1), 101.0 (C-1), 100.0 (C-1), 88.6, 86.6, 85.8, 84.4, 84.1, 83.8, 83.2, 83.1, 82.5, 81.6, 81.4, 80.7, 80.1, 80.0, 78.6, 73.3, 73.1, 72.4(7), 72.4(1), 72.3(9), 72.3(1), 72.2 (2), 72.1, 72.0, 71.8, 70.0, 69.8, 67.6, 66.5, 65.9, 65.4, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1.

8-Azidooctyl 2,3,4-tri-*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)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-58). Hexasaccharide **LAM-57** (851 mg, 0.40 mmol) was dissolved in CH_2Cl_2 (10 mL) and CH_3OH (5 mL) and then treated with 1M methanolic sodium methoxide (0.1 mL). After stirring for 6 h, the solution was neutralized with HOAc and concentrated. The crude product was purified by chromatography (4:1 hexanes–EtOAc) to yield **LAM-58** (718 mg, 89%) as an oil. R_f 0.23 (3:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.26 (m, 60 H), 5.21 (s, 1 H, H-1), 5.19 (d, 1 H, J = 1.4 Hz, H-1), 5.17 (d, 1 H, J = 4.8 Hz, H-1), 5.16 (s, 1 H, H-1), 5.06 (d, 1 H, J = 4.5 Hz, H-1), 5.02 (d, 1 H, J = 0.9 Hz, H-1), 4.78–4.37 (m, 27 H), 4.32–

4.24 (m, 3 H), 4.22–4.12 (m, 6 H), 4.11–3.97 (m, 7 H), 3.89 (dd, 1 H, *J* = 12.7, 4.3 Hz), 3.82 (dd, 1 H, *J* = 11.9, 2.3 Hz), 3.75–3.69 (m, 2 H), 3.67–3.53 (m, 8 H), 3.38 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz), 3.28 (dd, 2 H, *J* = 7.0, 6.9 Hz), 2.38 (dd, 1 H, *J* = 7.6, 5.2 Hz), 1.66–1.57 (m, 4 H), 1.44–1.33 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.3(1), 138.2(7), 138.2(4), 138.2(5), 138.1(3), 138.1(0), 137.7(9), 137.7(7), 137.7(1), 137.6, 128.5, 128.5, 128.4(7), 128.4(6), 128.4(3), 128.4(1), 128.4(0), 128.3(8), 128.3(6), 128.3(3), 128.2, 128.0(6), 128.0(4), 127.9(5), 127.9(1), 127.8(7), 127.8(2), 127.7(4), 127.7(1), 127.6(8), 127.6(3), 127.5(8), 127.5(3), 106.4 (C-1), 106.2 (C-1), 106.1 (C-1), 105.4 (C-1), 100.1 (C-1), 100.0 (C-1), 88.6, 86.0, 85.8, 84.1(5), 84.1(3), 84.0, 83.3, 83.1, 81.9, 81.7, 80.7, 80.6, 80.1, 80.0, 73.4, 73.1, 72.5, 72.3(9), 72.3(7), 72.3(3), 72.2, 72.1, 72.0, 71.8, 69.9, 69.6, 67.6, 66.0, 65.7, 63.5, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{122}H_{137}N_3O_{25}Na$: 2066.9439. Found: 2066.9435.

8-Azidooctyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-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*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-59). Trichloroacetimidate **LAM-42** (prepared from 0.34 g (0.37 mmol) of hemiacetal **LAM-41** (Scheme S7), 0.6 mL of CCl_3CN and 10 μL of DBU) in CH_2Cl_2 (10 mL), alcohol **LAM-58** (0.0.42 g, 0.21 mmol) in CH_2Cl_2 (10 mL), 4 Å molecular sieves (0.39 g) and TMSOTf (9 μL, 0.05 mmol) at −30 °C as described for the synthesis of **LAM-43** to afford **LAM-59** (0.41 g, 68%) as a thick syrup. R_f 0.37 (7:3 hexanes–EtOAc); $[\alpha]_D$ +25.8 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08–8.02 (m, 2 H), 7.65–7.56 (m, 3 H), 7.40–7.00 (m, 84 H), 5.61 (dd, 1 H, *J* = 2.6, 2.6 Hz), 5.40 (d, 1 H, *J* = 4.3 Hz, H-1), 5.18 (s, 1 H, H-1), 5.16 (s, 1 H, H-1), 5.13 (d, 1 H, *J* = 4.4 Hz, H-1), 5.12 (d, 1 H, *J* = 1.3 Hz, H-1), 5.00 (d, 1 H, *J* = 4.5 Hz, H-1), 4.99 (d, 1 H, *J* = 1.1 Hz, H-1), 4.89 (d, 1 H, *J* = 1.7 Hz, H-1), 4.76–4.30 (m, 35 H), 4.29–3.64 (m, 32 H), 3.64–3.50 (m, 7 H), 3.35 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.26 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.34 (s, 3 H), 1.64–1.56 (m, 4 H), 1.42–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 144.5, 138.7, 138.2(9), 138.2(8), 138.2(4), 138.2(2), 138.2, 138.0(8), 138.0(6), 137.7(4), 137.7(1), 137.7, 137.4, 133.2, 132.8, 130.0, 129.6, 128.5(1), 128.5, 128.4(2), 128.4(1), 128.4, 128.3(2), 128.2(9), 128.2(7), 128.2(5), 128.0(2), 128.0, 127.9(3), 127.9, 127.8(4), 127.8(2), 127.7(9), 127.7(5),

127.7(1), 127.7, 127.6(4), 127.6(2), 127.5(9), 127.5(5), 127.5(1), 127.5, 127.4(3), 127.4, 127.3(4), 127.2(9), 127.2(6), 127.2, 127.1, 106.6 (C-1), 106.2 (C-1), 106.1 (C-1), 105.3 (C-1), 100.8 (2 × C-1), 100.1 (C-1), 97.5 (C-1), 88.6, 86.2, 85.8, 84.4, 84.1, 84.0, 83.9, 83.3, 83.2(3), 83.2, 82.2, 81.6, 81.3, 80.7(2), 80.6(9), 80.6, 80.1(1), 80.1, 80.0, 79.1, 78.6, 74.4, 73.3, 73.2, 73.1, 72.6, 72.4, 72.3(4), 72.3(0), 72.3, 72.1(2), 72.1, 72.0, 71.8, 71.6, 71.1, 70.6, 70.0, 69.8, 69.7, 69.1, 69.0, 67.7, 67.6, 65.9, 65.4, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{175}H_{189}N_3O_{37}SNa$: 3002.2505. Found: 1501.1257 (M+2Na).

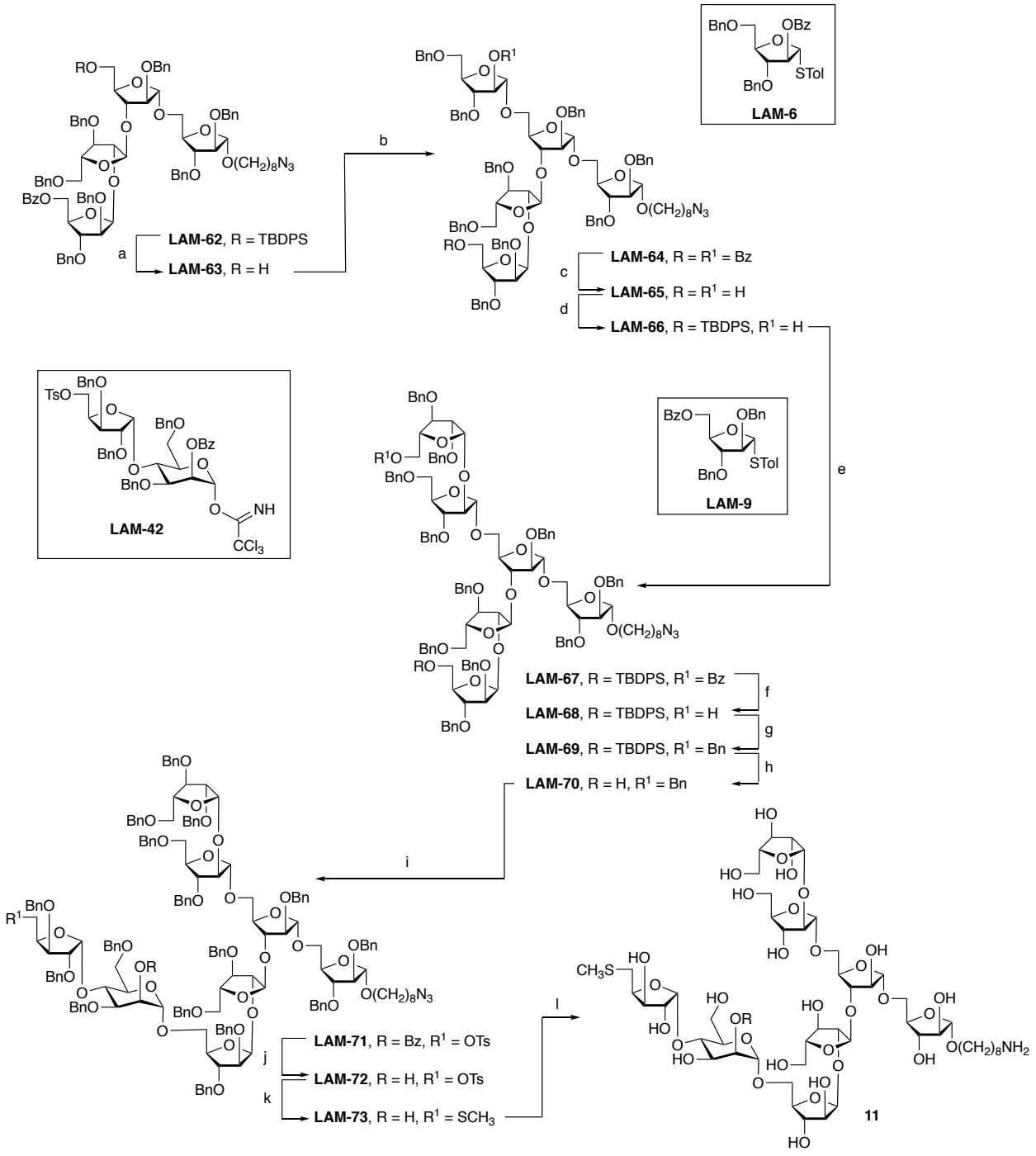
8-Azidooctyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→5)-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-60). Prepared from **LAM-59** (0.38 mg, 0.13 mmol) and 1M methanolic sodium methoxide solution in CH_2Cl_2–CH_3OH (4:1, 20 mL) as described for the synthesis of **LAM-44** to afford **LAM-60** (0.33 g, 90%) as a thick syrup. R_f 0.18 (7:3 hexanes–EtOAc); $[\alpha]_D$ + 37.2 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 7.73–7.64 (m, 2 H), 7.40–7.10 (m, 82 H), 5.46 (d, 1 H, *J* = 4.3 Hz, H-1), 5.17 (s, 1 H, H-1), 5.16–5.12 (m, 3 H, 3 × H-1), 5.06 (d, 1 H, *J* = 4.4 Hz, H-1), 5.01 (s, 1 H, H-1), 4.89 (s, 1 H, H-1), 4.76–4.24 (m, 37 H), 4.24–3.92 (m, 20 H), 3.90–3.78 (m, 6 H), 3.72–3.54 (m, 10 H), 3.37 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.26 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.41 (s, 3 H), 1.63–1.54 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 145.4, 139.1, 138.9, 138.8, 138.7, 138.6, 138.4, 138.3, 138.2(4), 138.2(3), 138.2(1), 133.3, 130.2, 129.0(1), 129.0, 128.9, 128.8(3), 128.8(2), 128.7(9), 128.7(5), 128.7(1), 128.7, 128.6, 128.5, 128.3(4), 128.3, 128.2(2), 128.1(9), 128.1(7), 128.1(3), 128.1(1), 128.1, 128.0(3), 127.9(9), 127.9(7), 127.9(1), 127.8(9), 127.8(7), 127.8(6), 127.5, 107.1 (C-1), 106.7 (C-1), 106.6 (C-1), 105.8 (C-1), 101.1 (2 × C-1), 100.6 (C-1), 99.5 (C-1), 89.1, 88.9, 86.8, 86.2, 84.8, 84.7, 84.5(1), 84.5, 84.1, 83.5, 83.0, 82.3, 81.8, 81.2, 81.0, 80.7, 80.6, 79.6, 74.8, 73.7, 73.6, 73.5, 73.1, 72.7(9), 72.7(6), 72.7(3), 72.6(9), 72.6(6), 72.6(3), 72.6, 72.4(1), 72.4, 72.3, 71.4, 71.2, 70.9, 70.4, 69.7, 69.5, 69.3, 68.0, 67.4, 66.7, 66.0, 51.9, 30.0, 29.7, 29.5, 29.2, 27.1, 26.5, 21.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{168}H_{185}N_3O_{36}SNa$: 2898.2243. Found: 1449.1123 (M+2Na).

8-Azidooctyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[5-deoxy-5-thiomethyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*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*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-61) Prepared from **LAM-60** (0.16 g, 0.06 mmol), and sodium thiomethoxide (0.02 g, 0.28 mmol) in CH_3CN (5 mL) as described for the synthesis of **LAM-45** to afford **LAM-61** (0.11 g, 70%) as a syrup. R_f 0.34 (7:3 hexanes–EtOAc); $[\alpha]_D$ +32.2 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 7.40–7.12 (m, 80 H), 5.52 (d, 1 H, *J* = 4.3 Hz, H-1), 5.15 (s, 1 H, H-1), 5.14–5.10 (m, 3 H, 3 × H-1), 5.04 (d, 1 H, *J* = 4.4 Hz, H-1), 4.99 (s, 1 H, H-1), 4.89 (d, 1 H, *J* = 1.1 Hz, H-1), 4.74–3.96 (m, 54 H), 3.96–3.92 (m, 2 H), 3.92–3.74 (m, 5 H), 3.74–3.52 (m, 12 H), 3.36 (dd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.25 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.70 (dd, 1 H, *J* = 5.1, 13.8 Hz), 2.53 (dd, 1 H, *J* = 7.2, 13.8 Hz), 2.39 (s, 1 H), 2.07 (s, 3 H), 1.62–1.52 (m, 4 H), 1.40–1.28 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 139.2, 138.9, 138.7(4), 138.7(0), 138.7, 138.4, 138.3, 138.2, 129.0(3), 129.0, 128.9, 128.7, 128.6, 128.4(3), 128.4, 128.2(9), 128.2(5), 128.2(0), 128.2, 128.0(1), 128.0, 127.9, 127.8, 127.5, 107.0 (C-1), 106.7 (C-1), 106.5 (C-1), 105.8 (C-1), 101.3 (C-1), 101.1 (C-1), 100.6 (C-1), 99.5 (C-1), 89.1, 88.9, 86.8, 86.1, 84.8, 84.7, 84.4(8), 84.4(5), 84.1(3), 84.1, 83.5, 83.4, 82.3, 82.2, 81.8, 81.2, 81.1, 80.7, 80.6, 79.6, 77.9, 73.7, 73.5, 72.9, 72.7(7), 72.7(5), 72.7(2), 72.7, 72.6(4), 72.6(1), 72.5(4), 72.5, 72.3(4), 72.3, 71.4(0), 71.4, 71.0, 70.4, 69.9, 69.3, 68.0, 67.5, 66.7, 66.0, 51.9, 34.9, 30.0, 29.7, 29.5, 29.2, 27.1, 26.5, 16.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{162}H_{181}N_3O_{33}SNa$: 2774.2082. Found: 1387.1044 (M+2Na).

8-Aminooctyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[5-deoxy-5-thiomethyl-α-D-xylofuranosyl-(1→4)-α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (10). Prepared from **LAM-61** (0.1 g, 0.037 mmol), liquid NH_3 (25 mL) and sodium metal (0.1 g) in THF (2 mL) as described for the synthesis of **7** to give **10** (28 mg, 60%) as a thick syrup that was later lyophilized from water to a foam. $[\alpha]_D$ +91.6 (*c* = 0.1, CH_3OH); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.42 (d, 1 H, *J* = 4.5 Hz, H-1), 5.24 (d, 1 H, *J* = 1.1 Hz, H-1), 5.18 (d, 1 H, *J* = 1.2 Hz, H-1), 5.15–5.12 (m, 2 H, 2 × H-1), 5.11 (s, 1 H, H-1), 5.01 (d, 1 H, *J* = 1.3 Hz, H-1), 4.92 (s, 1 H, H-1), 4.38 (ddd, 1 H, *J* = 4.9, 9.9, 13.3 Hz), 4.35–3.97 (m, 20 H), 3.97–3.65 (m, 19 H), 3.61–

3.52 (m, 2 H), 2.88 (dd, 2 H, J = 7.3, 7.3 Hz), 2.80 (dd, 1 H, J = 4.9, 13.8 Hz), 2.68 (dd, 1 H, J = 8.4, 13.8 Hz), 2.18 (s, 3 H), 1.65–1.55 (m, 4 H), 1.40–1.25 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.3 (C-1), 108.1 (C-1), 106.5 (C-1), 106.3(5) (C-1), 103.4 (C-1), 101.6 (C-1), 101.5 (C-1), 100.7 (C-1), 88.0(6), 88.0, 84.1, 83.7, 83.5, 82.9, 82.7, 82.4(1), 82.4(2), 81.9, 81.8, 80.7, 80.0, 78.6, 77.5(3), 77.5, 77.3, 77.2, 76.9, 76.5, 76.0, 75.6, 75.0(2), 75.0, 74.9(1), 74.9, 72.4, 71.5, 71.1(3), 71.1, 69.5, 69.2, 67.3, 67.2, 63.8(2), 63.8, 63.4, 61.9, 61.6, 61.5, 40.7, 33.9, 29.6, 29.5, 29.1(0), 29.1, 28.9, 26.5, 26.0, 15.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{50}H_{88}N_1O_{33}SNa$: 1262.4953. Found: 1262.4956.

8. Synthesis of 11



Scheme S11. Synthesis of **11**. a) HF·pyridine, pyridine, THF, 96%; b) **LAM-6**, NIS, AgOTf, CH_2Cl_2, 95%; c) $NaOCH_3$, CH_3OH, CH_2Cl_2, 99%; d) TBDPSCl, pyridine, CH_2Cl_2, 86%; e) **LAM-9**, NIS, AgOTf, CH_2Cl_2, 71%; f) $NaOCH_3$, CH_3OH, CH_2Cl_2, 93%; g) BnBr, NaH, DMF, 94%; h) *n*-Bu_4NF, THF, 99%; i) **LAM-42**, TMSOTf, CH_2Cl_2, 69%; j) $NaOCH_3$, CH_3OH, CH_2Cl_2, 88%; k) $NaSCH_3$, CH_3CN, 71%; l) Na, NH_3 (l), THF; then CH_3OH, H_2O, 55%.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-63). To a solution of **LAM-62**[19] (2.40 g, 1.43 mmol) in pyridine (6 mL) and THF (30 mL) was added 70% HF·pyridine (1.0 mL) at 0 °C and the mixture was stirred for 30 h while warming to rt. The reaction was concentrated, diluted with EtOAc and washed with a satd aq $NaHCO_3$ soln. The organic layer was dried (Na_2SO_4), filtered and concentrated and the resulting residue was purified by chromatography (7:3 hexanes–EtOAc) to afford **LAM-63** (1.98 g, 96%) as a colorless oil. R_f 0.28 (7:3 hexanes–EtOAc); $[\alpha]_D$ +30.8 (*c* = 1.1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.02–7.99 (m, 2 H), 7.55–7.51 (m, 1 H), 7.39–7.19 (m, 37 H), 5.17 (s, 1 H, H-1), 5.15 (d, 1 H, *J* = 1.5 Hz, H-1), 5.08 (d, 1 H, *J* = 4.4 Hz, H-1), 5.01 (s, 1 H, H-1), 4.74 (d, 1 H, *J* = 11.6 Hz), 4.67–4.42 (m, 14 H), 4.38–4.33 (m, 2 H), 4.30–4.17 (m, 5 H), 4.11–4.02 (m, 6 H), 3.90–3.69 (m, 5 H), 3.56 (dd, 1 H, *J* = 10.6, 4.1 Hz), 3.53 (dd, 1 H, *J* = 10.6, 5.9 Hz), 3.39 (ddd, 1 H, *J* = 9.5, 6.6, 6.6 Hz), 3.26 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.15 (br s, 1 H), 1.65–1.56 (m, 4 H), 1.42–1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 138.0, 137.8, 137.7, 137.6, 137.5, 133.1, 129.7(8), 127.7(5), 128.5, 128.4(4), 128.4(1), 128.3, 128.2, 128.0, 127.9, 127.8(8), 127.8(4), 127.7(7), 127.7(6), 127.7(2), 127.6(5), 127.6(0), 127.5, 106.1 (C-1), 106.0 (C-1), 105.9 (C-1), 100.8 (C-1), 88.6, 88.3, 86.6, 84.2, 83.9, 83.2, 82.3, 81.7, 81.3, 80.4, 79.9, 78.8, 73.3, 72.5(4), 72.5(1), 72.4, 72.3, 72.1, 71.9, 69.9, 67.6, 66.2, 66.0, 61.8, 51.4, 29.5, 29.2, 29.1, 28.8, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{84}H_{95}N_3O_{18}Na$: 1456.6502. Found: 1456.6504.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-di-*O*-benzyl-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-64). To a mixture of alcohol **LAM-63** (1.96 g, 1.37 mmol), **LAM-6**[14] (908 mg, 1.68 mmol) and 4 Å molecular sieves (0.6 g) in CH_2Cl_2 (40 mL) was added *N*-iodosuccinimide (477 mg, 2.01 mmol) followed by silver triflate (60 mg, 0.23 mmol) at 0 °C. The reaction mixture turned dark red after 15 min, Et_3N was added, and was then diluted with CH_2Cl_2 (60 mL) and filtered through Celite. The filtrate was washed with satd aq $Na_2S_2O_3$ soln, dried (Na_2SO_4) and concentrated to a residue that was purified by chromatography (3:1 hexanes–EtOAc) to give **LAM-64** (2.40 g, 95%) as a colorless syrup. R_f 0.39 (3:1 hexanes–EtOAc); $[\alpha]_D$ +42.0 (*c* = 0.8,

CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.03–7.98 (m, 4 H), 7.60–7.51 (m, 2 H), 7.43–7.15 (m, 49 H), 5.50 (d, 1 H, *J* = 1.3 Hz), 5.32 (s, 1 H, H-1), 5.20 (s, 1 H, H-1), 5.19 (d, 1 H, *J* = 1.8 Hz, H-1), 5.06 (d, 1 H, *J* = 4.4 Hz, H-1), 5.01 (d, 1 H, *J* = 1.2 Hz, H-1), 4.82 (d, 1 H, *J* = 12.2 Hz), 4.72 (d, 1 H, *J* = 11.6 Hz), 4.66–4.32 (m, 18 H), 4.30–4.17 (m, 5 H), 4.12–4.00 (m, 7 H), 3.91 (dd, 1 H, *J* = 11.8, 4.4 Hz), 3.82 (dd, 1 H, *J*= 11.4, 2.4 Hz), 3.77–3.69 (m, 2 H), 3.63 (dd, 1 H, *J* = 10.9, 3.6 Hz), 3.60–3.51 (m, 3 H), 3.37 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz), 3.26 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.64–1.56 (m, 4 H), 1.41–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 165.2, 138.3, 138.1, 138.0(8), 138.0(3), 137.8, 137.6(9), 137.6(6), 133.1, 133.0, 129.8, 129.7(6), 129.7(1), 128.4(9), 128.4(2), 128.3(9), 128.3(6), 128.3(5), 128.2(8), 128.2(6), 128.1, 128.0, 127.9(4), 127.9(1), 127.8(9), 127.8(3), 127.8(0), 127.7(7), 127.7(1), 127.6(7), 127.6(5), 127.5(8), 127.5(7), 127.4(8), 127.4(4), 127.4(3), 106.2 (C-1), 106.1 (C-1), 106.0 (C-1), 105.6 (C-1), 100.6 (C-1), 88.7, 88.4, 86.4, 84.3, 83.9, 83.5, 83.2, 82.5, 82.2, 81.8, 81.7, 80.4, 80.0(8), 80.0(3), 78.8, 73.3, 73.2, 72.4, 72.3(9), 72.3(3), 72.2, 72.0(8), 72.0(6), 71.8, 69.8, 69.2, 67.6, 66.4, 66.1, 65.7, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{110}H_{119}N_3O_{23}Na$: 1872.8122. Found: 1872.8126.

8-Azidooctyl 2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-65). Pentasaccharide **LAM-64** (2.31 g, 1.25 mmol) was dissolved in CH_2Cl_2 (30 mL) and CH_3OH (20 mL) and then treated with 1M methanolic sodium methoxide (2.5 mL). After stirring for 16 h, the reaction mixture was neutralized with HOAc and concentrated. The crude product was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-65** (2.02 g, 99%) as an oil. R_f 0.62 (3:2 hexanes–EtOAc); $[\alpha]_D$ +49.4 (*c* = 1.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.22 (m, 45 H), 5.20 (s, 1 H, H-1), 5.18 (d, 1 H, *J* = 1.0 Hz, H-1), 5.10 (s, 1 H, H-1), 5.03–5.01 (m, 2 H, 2 × H-1), 4.72 (d, 1 H, *J* = 11.7 Hz), 4.65–4.33 (m, 19 H), 4.32–4.29 (m, 1 H), 4.26–4.17 (m, 5 H), 4.15–4.12 (m, 1 H), 4.11–3.98 (m, 6 H), 3.90 (dd, 1 H, *J* = 11.7, 4.3 Hz), 3.85 (dd, 1 H, *J* = 5.2, 2.2 Hz), 3.77–3.70 (m, 3 H), 3.64 (dd, 1 H, *J* = 12.1, 3.1 Hz), 3.62–3.51 (m, 4 H), 3.41–3.36 (m, 2 H), 3.26 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.32 (br s, 1 H), 1.65–1.57 (m, 4 H), 1.42–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.1, 138.0, 137.9, 137.8, 137.7, 137.6, 137.5, 137.4, 128.5, 128.4(8), 128.4(5), 128.4(4), 128.4(0), 128.3, 128.0, 127.9, 127.7(9), 127.7(1), 127.5(8), 109.1

(C-1), 106.1 (C-1), 105.9 (C-1), 105.3 (C-1), 99.9 (C-1), 88.6, 88.4, 86.1, 84.5, 84.1, 83.4, 83.2, 82.4, 82.0, 81.2, 80.7, 80.4, 79.9, 78.5, 73.6, 73.4, 72.5, 72.3, 72.2, 72.1(4), 72.1(1), 71.9, 71.8, 69.7, 69.6, 67.6, 65.9, 65.8, 63.5, 51.4, 29.5, 29.2, 29.1, 28.8, 26.7, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{96}H_{111}N_3O_{21}Na$: 1664.7602. Found: 1664.7605.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-66). To a solution of **LAM-65** (1.93 g, 1.17 mmol) in pyridine (3 mL) and CH_2Cl_2 (15 mL) added t-butyldiphenylsilyl chloride (0.36 mL, 1.41 mmol) at 0 °C. The reaction mixture was stirred for 12 h while warming to rt. The solution was diluted with CH_2Cl_2 (60 mL) and then washed with satd aq $NaHCO_3$ soln, water and brine. The organic layer was subsequently dried (Na_2SO_4), filtered and concentrated and the resulting residue was purified by chromatography (2:1 hexanes–EtOAc) to yield **LAM-66** (1.91 g, 86%) as an oil. R_f 0.41 (2:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.67–7.62 (m, 4 H), 7.40–7.14 (m, 50 H), 7.07–7.04 (m, 2 H), 5.16 (d, 1 H, J = 1.6 Hz, H-1), 5.13 (s, 1 H, H-1), 5.06 (s, 1 H, H-1), 4.99 (s, 1 H, H-1), 4.94 (d, 1 H, J = 4.4 Hz, H-1), 4.63–4.26 (m, 20 H), 4.20–3.99 (m, 11 H), 3.96 (dd, 1 H, J = 6.1, 4.4 Hz, H-2β), 3.89–3.78 (m, 5 H), 3.74–3.67 (m, 3 H), 3.55–3.44 (m, 3 H), 3.36 (ddd, 1 H, J = 9.6, 6.7, 6.7 Hz), 3.32 (dd, 1 H, J = 10.5, 2.8 Hz), 3.25 (dd, 2 H, J = 7.1, 6.9 Hz), 1.64–1.55 (m, 4 H), 1.41–1.30 (m, 8 H), 1.04 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2, 138.1(8), 138.1(3), 138.0, 137.9, 137.8, 137.6(4), 137.6(2), 137.4, 135.5(7), 135.5(3), 133.2, 133.1, 129.8, 129.7, 128.4(7), 128.4(1), 128.4(0), 128.3(6), 128.3(5), 128.3(3), 128.1, 128.0, 127.8(8), 127.8(3), 127.8(0), 127.7(7), 127.7(0), 127.6(8, 127.6(3), 127.5(6), 127.5(2), 127.4, 108.9 (C-1), 106.0 (C-1), 105.9 (C-1), 105.3 (C-1), 100.3 (C-1), 88.6, 85.5, 85.4, 84.7, 84.6, 84.2, 84.1, 83.2, 82.3, 82.0, 81.8, 80.4, 79.9, 78.3, 73.5, 73.2, 72.3, 72.2(2), 72.2(0), 72.0(7), 72.0(4), 71.9, 71.8, 70.2, 69.7, 67.6, 66.1, 66.0, 65.7, 51.4, 29.5, 29.2, 29.1, 28.8, 26.8, 26.6, 26.0, 19.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{112}H_{129}N_3O_{21}Na$: 1902.8786. Found: 1902.8790.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzyl-5-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-67). To a mixture of

LAM-66 (1.78 g, 0.95 mmol), **LAM-9**[15] (614 mg, 1.14 mmol) and 4 Å molecular sieves (0.7 g) in CH_2Cl_2 (80 mL) at –60 °C was added *N*-iodosuccinimide (310 mg, 1.31 mmol) followed by silver triflate (50 mg, 0.20 mmol). The reaction was slowly warmed to –25 °C and kept stirring for 20 min at –25 °C. The reaction mixture turned dark red, Et_3N was added, and was then diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with satd aq $Na_2S_2O_3$ soln, dried (Na_2SO_4), and concentrated to give a residue that was purified by chromatography (3:1 hexanes–EtOAc) to give **LAM-67** (1.54 g, 71%) as a colorless oil. R_f 0.26 (3:1 hexanes–EtOAc); $[\alpha]_D$ +11.8 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.98–7.95 (m, 2 H), 7.64–7.60 (m, 4 H), 7.51–7.48 (m, 1 H), 7.38–7.11 (m, 61 H), 7.04–7.02 (m, 2 H), 5.15 (s, 1 H, H-1), 5.13 (d, 1 H, *J* = 4.5 Hz, H-1), 5.11 (s, 1 H, H-1), 5.08 (s, 1 H, H-1), 4.96–4.94 (m, 2 H, 2 × H-1), 4.70 (d, 1 H, *J* = 11.6 Hz), 4.65–4.24 (m, 27 H), 4.21–4.10 (m, 7 H), 4.09–3.95 (m, 8 H), 3.85 (dd, 1 H, *J* = 5.8, 2.4 Hz), 3.83–3.73 (m, 4 H), 3.67–3.62 (m, 2 H), 3.55–3.44 (m, 4 H), 3.31 (ddd, 1 H, *J* = 9.7, 6.7, 6.7 Hz), 3.24 (dd, 2 H, *J* = 7.0, 7.0 Hz), 1.62–1.52 (m, 4 H), 1.38–1.27 (m, 8 H), 1.02 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 138.3, 138.2(6), 138.2(4), 138.1, 138.0, 137.8, 137.7(9), 137.7(2), 137.7(2), 137.6, 137.5(9), 135.5(4), 135.5(1), 133.2,133.1, 132.9, 129.8, 129.7(5), 129.7(3), 128.4, 128.3(8), 128.3(6), 128.3(2), 128.2(9), 128.2(5), 128.1, 128.0(9), 128.0(2), 127.9(8), 127.9(1), 127.8(4), 127.8(0), 127.7(7), 127.7(5), 127.7(2), 127.6(6), 127.6(2), 127.5(6), 127.5(3), 127.5(1), 127.4, 127.3(8), 127.3(4), 106.6 (C-1), 106.1 (C-1), 106.0 (C-1), 105.2 (C-1), 100.9 (C-1), 100.3 (C-1), 88.5, 86.5, 85.5, 84.5, 84.3, 84.1, 83.7, 83.2, 82.5, 82.0, 81.8, 81.3, 80.5, 80.0, 79.9, 78.5, 73.2, 73.1, 72.4, 72.3(4), 72.3(1), 72.2(8), 72.2(1), 72.0(4), 72.0(0), 71.8, 69.9(7), 69.9(2), 67.5, 66.4, 66.1, 65.9, 65.3, 51.4, 29.4, 29.2, 29.1, 28.8, 26.8, 26.6, 26.0, 19.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{138}H_{153}N_3O_{26}SiNa$: 2319.0403. Found: 2319.0431.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-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)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-68). Hexasaccharide **LAM-67** (1.48 g, 0.64 mmol) was dissolved in CH_2Cl_2 (10 mL) and CH_3OH (5 mL) and then treated with 1M methanolic sodium methoxide (1.2 mL). After stirring at rt overnight, the reaction mixture was neutralized with HOAc and concentrated. The crude product was purified by chromatography

(3:1 hexanes–EtOAc) to yield **LAM-68** (1.31 g, 93%) as an oil. R_f 0.46 (3:1 hexanes–EtOAc); $[\alpha]_D$ +6.7 (c = 0.1, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.64–7.61 (m, 4 H), 7.38–7.12 (m, 59 H), 7.05–7.03 (m, 2 H), 5.13 (s, 1 H, H-1), 5.12–5.09 (m, 3 H, 3 × H-1), 4.98 (d, 1 H, J = 4.4 Hz, H-1), 4.96 (s, 2 H, H-1), 4.71 (d, 1 H, J = 11.8 Hz), 4.62–4.34 (m, 22 H), 4.31 (dd, 1 H, J = 7.3, 3.9 Hz), 4.26–4.21 (m, 3 H), 4.19–3.91 (m, 14 H), 3.85 (dd, 1 H, J = 5.8, 2.4 Hz), 3.83–3.76 (m, 3 H), 3.74 (dd, 1 H, J = 11.8, 2.2 Hz), 3.68–3.63 (m, 2 H), 3.60–3.45 (m, 6 H), 3.32 (ddd, 1 H, J = 9.7, 7.1, 7.1 Hz), 3.24 (dd, 2 H, J = 7.0, 6.9 Hz), 1.62–1.52 (m, 4 H), 1.38–1.28 (m, 8 H), 1.03 (s, 9 H, CH_3x3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.2(8), 138.2(2), 138.1, 138.0(7), 138.0(3), 138.0, 137.9, 137.7(7), 137.6(8), 137.6(3), 137.6(1), 135.5(4), 135.5(2), 133.2,133.1, 129.7(6), 129.7(4), 128.4(6), 128.4(0), 128.3(9), 128.3(7), 128.3(4), 128.3(2), 128.2(9), 128.2(6), 128.1, 128.0, 127.9, 127.8(8), 127.8(5), 127.8(1), 127.7(8), 127.7(5), 127.6(9), 127.6(5), 127.6(1), 127.5(7), 127.5(4), 127.5(1), 127.4, 127.3, 106.3 (C-1), 106.1 (C-1), 106.0 (C-1), 105.2 (C-1), 100.4 (C-1), 99.9 (C-1), 88.5, 85.9, 85.6, 84.5, 84.1, 84.0, 83.2, 83.1, 82.0, 81.9, 81.8, 80.6(6), 80.6(4), 80.5, 80.0, 79.9, 73.3, 73.1, 72.5, 72.3, 72.2, 72.0(6), 72.0(1), 71.8, 70.0, 69.4, 67.6, 66.1, 65.9, 65.6, 63.4, 51.4, 29.5, 29.2, 29.1, 28.8, 26.8, 26.6, 26.0, 19.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{131}H_{149}N_3O_{25}SiNa$: 2215.0141. Found: 2215.0158.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-69). To a solution of **LAM-68** (570 mg, 0.26 mmol) in DMF (2 mL) at 0 °C was added NaH (21 mg, 0.52 mmol, 60% dispersion in oil) and the solution was stirred for 2 min. Benzyl bromide (0.037 mL, 0.31 mmol) was added and the solution was stirred for 2 h at rt. The reaction mixture was quenched by adding a few drops of CH_3OH, diluted with CH_2Cl_2 (20 mL), and washed with a satd aq $NaHCO_3$ soln (20 mL) and water (20 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated, and the resulting residue was purified by chromatography (4:1 hexanes–EtOAc) to provide **LAM-69** (556 mg, 94%) as a colorless oil. R_f 0.25 (4:1 hexanes–EtOAc); $[\alpha]_D$ +9.3 (c = 1.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.65–7.61 (m, 1 H), 7.39–7.12 (m, 64 H), 7.06–7.03 (m, 2 H), 5.13 (s, 2 H, 2 × H-1), 5.11 (m, 2 H, 2 × H-1), 4.98 (d, 1 H, J = 4.4 Hz, H-1), 4.96 (s, 1 H, H-1), 4.67–4.25 (m, 27 H), 4.20–3.95 (m, 15 H), 3.86 (dd, 1 H, J = 5.7, 2.4 Hz), 3.84–3.73 (m, 4 H), 3.69–3.63

(m, 2 H), 3.59–3.46 (m, 6 H), 3.32 (ddd, 1 H, J = 9.6, 6.7, 6.7 Hz), 3.24 (dd, 2 H, J = 6.9, 6.9 Hz), 1.63–1.52 (m, 4 H), 1.40–1.28 (m, 8 H), 1.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.3(5), 138.3(3), 138.3(1), 138.2, 138.1, 138.0, 137.7(4), 137.8, 137.7, 137.6, 135.5(5), 135.5(2), 133.2, 133.1, 129.7(6), 129.7(4), 128.4, 128.3(9), 128.3(3), 128.2(9), 128.2(6), 128.2(1), 128.1, 127.9, 127.8(7), 127.7(8), 127.7(0), 127.6(6), 127.6(0), 127.5(7), 127.5(4), 127.5(2), 127.4, 127.3(9), 127.3(4), 106.6 (C-1), 106.1 (C-1), 106.0 (C-1), 105.2 (C-1), 100.3(4) (C-1), 100.3(1) (C-1), 88.6, 85.8, 85.5, 84.5, 84.1, 83.9, 83.2, 82.0, 81.8, 81.1, 80.5, 80.0(5), 80.0(2), 79.9, 73.2, 73.1, 73.0, 72.3, 72.2(8), 72.2(5), 72.2(2), 72.0(4), 72.0(2), 71.8, 69.9, 67.5, 66.1, 65.9, 65.4, 51.4, 29.5, 29.2, 29.1, 28.8, 26.8, 26.6, 26.0, 19.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{138}H_{155}N_3O_{25}SiNa$: 2305.0617. Found: 2305.0611.

8-Azidooctyl 2,3-di-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-70). Hexasaccharide **LAM-69** (460 mg, 0.20 mmol) in THF (3 mL) was treated with 1M *n*-Bu_4NF in THF solution (0.24 mL) and the reaction mixture was stirred at rt for 6 h. The crude mixture was concentrated and purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-70** (408 mg, 99%) as an oil. R_f 0.21 (3:1 hexanes–EtOAc); $[\alpha]_D$ +11.7 (c = 0.6, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.37–7.19 (m, 60 H), 5.16–5.15 (m, 2 H, 2 × H-1), 5.12–5.10 (m, 2 H, 2 × H-1), 5.03 (d, 1 H, J = 4.5 Hz, H-1), 4.97 (s, 1 H, H-1), 4.72–4.37 (m, 24 H), 4.36–4.28 (m, 4 H), 4.23 (dd, 1 H, J = 6.9, 6.7 Hz), 4.19–4.11 (m, 4 H), 4.11–3.96 (m, 10 H), 3.85 (dd, 1 H, J = 11.7, 4.4 Hz), 3.78 (dd, 1 H, J = 12.0, 2.5 Hz), 3.70–3.64 (m, 2 H), 3.62–3.49 (m, 8 H), 3.34 (ddd, 1 H, J = 9.6, 6.6, 6.6 Hz), 3.25 (dd, 2 H, J = 7.0, 6.9 Hz), 2.22 (br s, 1 H), 1.62–1.53 (m, 4 H), 1.40–1.29 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.3, 138.2, 138.1(3), 138.1(1), 138.0, 137.9, 137.7(7), 137.7(0), 137.6, 128.4(7), 128.4(5), 128.4(2), 128.4(1), 128.3(6), 128.3(5), 128.3(0 128.2, 128.0, 127.9(9), 127.9(2), 127.8(9), 127.8(5), 127.7(7), 127.7(6), 127.7(2), 127.6(7), 127.6(3), 127.5(8), 127.5(2), 127.4, 106.6 (C-1), 106.1 (C-1), 106.0 (C-1), 105.1 (C-1), 100.3 (C-1), 99.9 (C-1), 88.6, 88.4, 86.1, 85.9, 84.1(3), 84.1(1), 83.9, 83.2(5), 83.2(0), 83.1, 81.9, 81.2, 80.8, 80.7, 80.1, 79.9, 73.3(6), 73.3(0), 73.0, 72.5, 72.3(6), 72.3(0), 72.2, 72.0(9), 72.0(6), 71.7, 70.0, 69.4, 67.6, 65.8,

65.4, 63.4, 51.4, 29.5, 29.2, 29.1, 28.8, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{122}H_{137}N_3O_{25}Na$: 2066.9439. Found: 2066.9433.

8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-benzoyl-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)-[2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-71). Prepared from the trichloroacetimidate **LAM-42** (prepared from 0.15 g (0.16 mmol) of hemiacetal **LAM-41** (Scheme S7), 0.6 mL of CCl_3CN and 10 μL of DBU) in CH_2Cl_2 (9 mL), alcohol **LAM-70** (0.25 g, 0.12 mmol) in CH_2Cl_2 (7 mL), 4 Å molecular sieves (0.29 g) and TMSOTf (5 μL, 0.03 mmol) at –30 °C as described for the synthesis of **LAM-43** to afford **LAM-71** (0.25 g, 69%) as a thick syrup. R_f 0.37 (7:3 hexanes–EtOAc); $[\alpha]_D$ +24.7 (*c* = 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 8.08–8.03 (m, 2 H), 7.68–7.58 (m, 3 H), 7.41–7.01 (m, 84 H), 5.63 (dd, 1 H, *J* = 2.2, 2.9 Hz), 5.42 (d, 1 H, *J* = 4.3 Hz, H-1), 5.18 (s, 1 H, H-1), 5.17–5.12 (m, 3 H, 3 × H-1), 5.08 (d, 1 H, *J* = 4.4 Hz, H-1), 5.01 (s, 1 H, H-1), 4.92 (d, 1 H, *J* = 1.8 Hz, H-1), 4.75–4.30 (m, 35 H), 4.30–3.78 (m, 30 H), 3.76–3.66 (m, 4 H), 3.65–3.52 (m, 4 H), 3.38 (ddd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.26 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.35 (s, 3 H), 1.64–1.54 (m, 4 H), 1.42–1.30 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 165.7, 145.3, 139.3, 138.9(0), 138.9, 138.8, 138.7(4), 138.7(2)(Ar), 138.6, 138.4, 138.2(9), 138.2(6), 138.2, 138.1, 133.7, 133.1(5), 130.2, 130.1, 128.9, 128.8(0), 128.7(7), 128.7(1), 128.7, 128.6, 128.4(4), 128.4(3), 128.4, 128.3(3), 128.3, 128.2(3), 128.2(1), 128.2, 128.0(9), 128.0(6), 128.0(3), 128.0(2), 128.0(0), 128.0, 127.9(1), 127.9, 127.8(3), 127.8, 127.5(2), 127.5, 107.0 (C-1), 106.6 (C-1), 106.5 (C-1), 105.8 (C-1), 101.2 (C-1), 100.9 (C-1), 100.8 (C-1), 97.9 (C-1), 89.1, 88.9, 86.2, 84.8(1), 84.8, 84.5(3), 84.5, 84.1, 83.5, 82.9, 82.3, 81.8, 81.1, 80.7(0), 80.7, 80.5, 79.8, 79.1, 74.8, 73.7, 73.6(3), 73.6, 73.4, 73.0, 72.8, 72.7(4), 72.7(1), 72.7, 72.6(1), 72.6, 72.5, 72.3(4), 72.3, 71.8, 71.0, 70.6, 70.3, 70.0, 69.6, 68.2, 68.0, 66.7, 65.9, 51.9(1), 29.9(4), 29.5, 29.2, 27.1, 26.5, 21.7; HRMS (ESI) *m/z* calcd for (M+Na) $C_{175}H_{189}N_3O_{37}SNa$: 2979.2618. Found: 2979.2612.

8-Azidooctyl 5-*O*-*p*-toluenesulfonyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*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)-[2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-

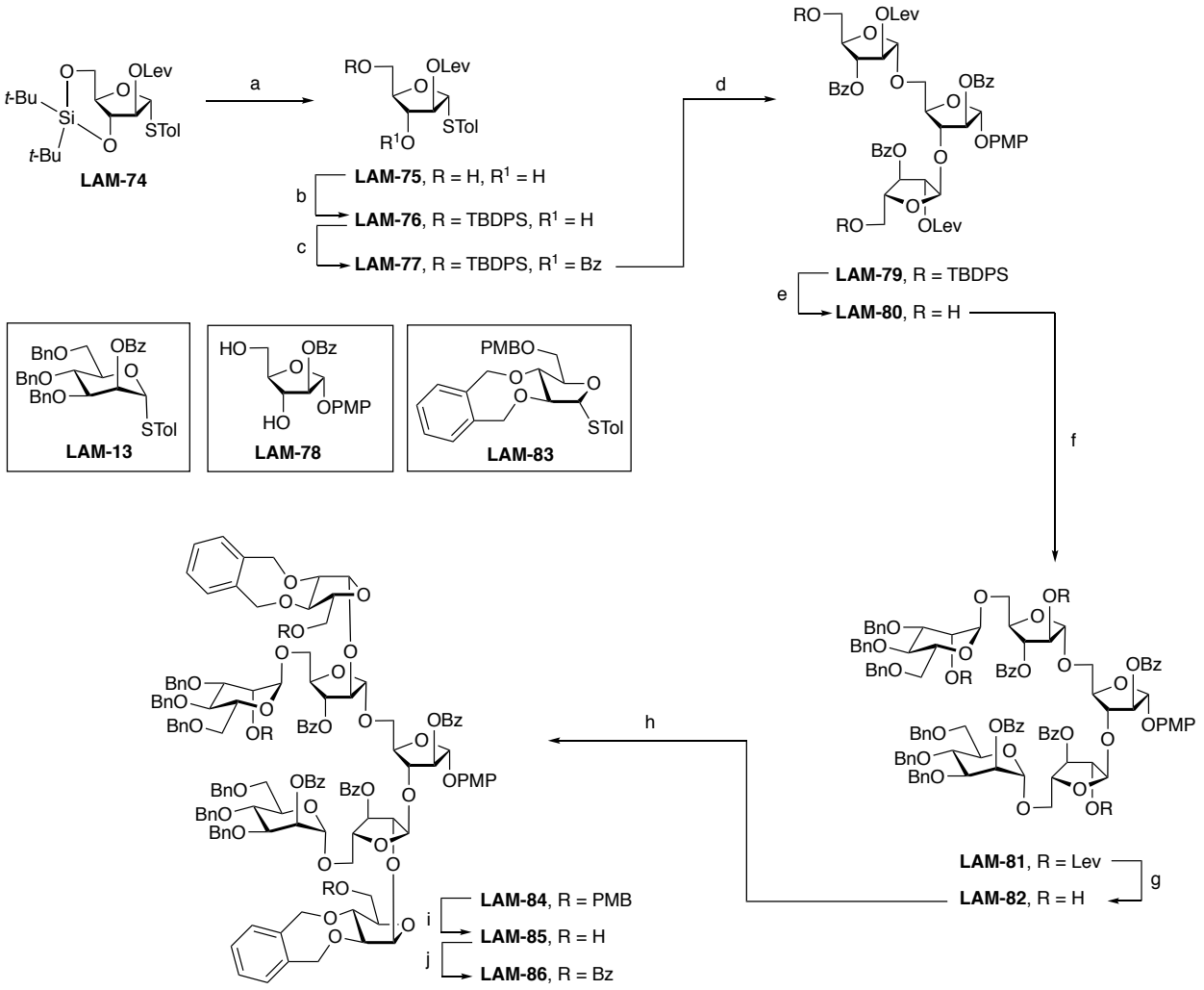
3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-72). Prepared from **LAM-71** (0.23 g, 0.08 mmol) and 1M methanolic sodium methoxide solution in CH_2Cl_2–CH_3OH (4:1, 10 mL) as described for the synthesis of **LAM-44** to afford **LAM-72** (0.19 g, 88%) as a thick syrup. R_f 0.18 (7:3 hexanes–EtOAc); $[\alpha]_D$ +36.8 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.73–7.64 (m, 2 H), 7.40–7.10 (m, 82 H), 5.40 (d, 1 H, *J* = 4.2 Hz, H-1), 5.18 (s, 1 H, H-1), 5.16 (s, 1 H, H-1), 5.14–5.10 (m, 2 H, 2 × H-1), 5.01 (d, 1 H, *J* = 4.3 Hz, H-1), 4.98 (s, 1 H, H-1), 4.90 (s, 1 H, H-1), 4.70–4.18 (m, 37 H), 4.18–3.75 (m, 27 H), 3.72–3.50 (m, 10 H), 3.34 (ddd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.25 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.40 (s, 3 H), 1.63–1.54 (m, 4 H), 1.42–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 144.6, 138.5, 138.4, 138.3(3), 138.3(0), 138.3, 138.2, 138.1(3), 138.1(0), 138.1, 137.8, 137.7(3), 137.7(1), 137.7, 137.5, 133.0, 129.7, 128.6, 128.5(3), 128.4(6), 128.4(5), 128.4(3), 128.4(2), 128.4(0), 128.4, 128.3, 128.2, 128.1, 128.0(1), 128.0(0), 128.0, 127.9(0), 127.8(5), 127.8(1), 127.8, 127.7(3), 127.7(2), 127.7(0), 127.7, 127.6(1), 127.5(9), 127.5(6), 127.5(4), 127.5(2), 127.5, 127.4, 127.0, 106.6 (C-1), 106.1 (2 × C-1), 105.4 (C-1), 100.7 (C-1), 100.4(4) (C-1), 100.4 (C-1), 98.9 (C-1), 88.7, 88.6, 86.2, 85.9, 84.1, 84.0(4), 84.0(0), 84.0, 83.9, 83.7, 83.3, 83.2, 82.3, 81.7, 81.2, 80.7, 80.6, 80.3, 80.1, 80.0, 79.9, 79.1, 74.3(2), 73.3(1), 73.3, 73.2, 73.1, 72.7, 72.4, 72.3(3), 72.3(1), 72.3, 72.1(4), 72.1(0), 72.0(6), 72.0, 71.8, 71.3, 70.7, 70.5, 70.0, 69.7, 69.3, 68.9, 68.8, 67.6, 67.0, 66.0, 65.5, 51.5, 29.5, 29.3, 29.1, 28.9, 26.7, 26.1, 21.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{168}H_{185}N_3O_{36}SNa$: 2875.2356. Found: 2875.2350.

8-Azidooctyl 5-deoxy-5-thiomethyl-2,3-di-*O*-benzyl-α-D-xylofuranosyl-(1→4)-3,6-di-*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)-[2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-73). Prepared from **LAM-72** (0.19 g, 0.067 mmol), and sodium thiomethoxide (0.02 g, 0.28 mmol) in CH_3CN (5 mL) as described for the synthesis of **LAM-45** to afford **LAM-73** (0.13 g, 71%) as a syrup. R_f 0.29 (7:3 hexanes–EtOAc); $[\alpha]_D$ +31.0 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2, δ_H) 7.40–7.12 (m, 80 H), 5.51 (d, 1 H, *J* = 4.3 Hz, H-1), 5.17 (s, 1 H, H-1), 5.14–5.10 (m, 3 H, 3 × H-1), 5.05 (d, 1 H, *J* = 4.3 Hz, H-1), 4.98 (s, 1 H, H-1), 4.88 (s, 1 H, H-1), 4.69–4.17 (m, 32 H), 4.17–3.75 (m, 20 H), 3.75–3.50 (m,

10 H), 3.74–3.52 (m, 10 H), 3.35 (ddd, 1 H, *J* = 6.6, 9.5, 13.2 Hz), 3.24 (dd, 1 H, *J* = 7.0, 7.0 Hz), 2.71 (dd, 1 H, *J* = 5.0, 13.8 Hz), 2.53 (dd, 1 H, *J* = 7.2, 13.8 Hz), 2.35 (s, 1 H), 2.06 (s, 3 H), 1.62–1.52 (m, 4 H), 1.40–1.28 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2, δ_C) 139.2, 138.9(2), 138.9, 138.8(4), 138.8(3), 138.8, 138.7, 138.6(3), 138.6, 138.4(2), 138.4, 138.3(1), 138.3, 138.2, 128.9, 128.8(0), 128.7(7), 128.7(6), 128.7(3), 128.7(1), 128.6(9), 128.6(8), 128.6(5), 128.6(3), 128.6, 128.4(2), 128.4(1), 128.3(3), 128.2(4), 128.2(0), 128.2, 128.1(3), 128.0(9), 128.0(7), 128.0(5), 128.0(2), 128.0, 127.9(0), 127.9, 127.8(4), 127.8(2), 127.8, 127.5, 107.0 (C-1), 106.6 (C-1), 106.5 (C-1), 105.9 (C-1), 101.3 (C-1), 100.9 (C-1), 100.8 (C-1), 99.4 (C-1), 89.1, 88.9, 86.4, 86.2, 84.8, 84.6, 84.5, 84.4, 84.3, 84.1, 83.6, 83.4, 82.3, 82.2, 81.8, 81.0(8), 81.0(6), 80.7(0), 80.7, 80.5, 79.7, 77.9, 73.6(5), 73.6, 73.4, 72.9, 72.8(4), 72.8, 72.7(1), 72.6(7), 72.6(1), 72.6, 72.5(4), 72.5, 72.4, 72.3, 71.4, 71.1, 70.6, 70.3, 69.9, 69.3, 68.0, 67.6, 66.7, 66.0, 51.9, 34.9, 29.9, 29.7, 29.5, 29.2, 27.1, 26.5, 16.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{162}H_{181}N_3O_{33}SNa$: 2751.2196. Found: 2751.2196.

8-Azidooctyl 5-deoxy-5-thiomethyl-α-D-xylofuranosyl-(1→4)-α-D-mannopyranosyl-(1→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (11). Prepared from **LAM-73** (0.13 g, 0.048 mmol), liquid NH_3 (25 mL) and sodium metal (0.1 mg) in THF (2 mL) as described for the synthesis of **7** to give **11** (33 mg, 55%) as a thick syrup which was later lyophilized to a foam. ^{1}H NMR (500 MHz, D_2O, δ_H) 5.42 (d, 1 H, *J* = 4.4 Hz, H-1), 5.24 (s, 1 H, H-1), 5.17 (s, 1 H, H-1), 5.14–5.12 (m, 2 H × H-1), 5.11 (s, 1 H, H-1), 5.01 (d, 1 H, *J* = 1.1 Hz, H-1), 4.92 (s, 1 H, H-1), 4.38 (ddd, 1 H, *J* = 4.9, 9.9, 13.3 Hz), 4.35–3.96 (m, 20 H), 3.96–3.64 (m, 19 H), 3.60-3.54 (m, 2 H), 2.97 (dd, 2 H, *J* = 7.3, 7.3 Hz), 2.79 (dd, 1 H, *J* = 4.9, 13.8 Hz), 2.68 (dd, 1 H, *J* = 8.4, 13.8 Hz), 2.18 (s, 3 H), 1.66–1.55 (m, 4 H), 1.40–1.25 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.3 (C-1), 108.1 (C-1), 106.6 (C-1), 106.3 (C-1), 103.4 (C-1), 101.7 (C-1), 101.5 (C-1), 100.7 (C-1), 88.4, 87.7, 83.9, 83.8, 83.3, 82.9, 82.6, 82.5, 81.9, 81.8, 80.7, 79.9, 78.7, 77.5, 77.2(3), 77.2, 76.9, 76.5, 75.8, 75.7, 75.1, 75.0(1), 75.0, 74.9(4), 74.9(2), 72.4, 71.5, 71.1, 69.5, 67.4, 67.2, 63.9, 63.4, 61.9, 61.5, 40.5, 33.8, 29.5, 29.1, 29.0, 27.7, 26.4, 26.0, 15.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{50}H_{88}N_1O_{33}SNa$: 1262.4953. Found: 1262.4960.

9. Synthesis of 12



Scheme S12. Synthesis of pentasaccharide **LAM-86**, a precursor to **12**. a) HF·pyridine, pyridine, THF, 95%; b) TBPDSCl, pyridine, CH_2Cl_2; c) BzCl, pyridine; 88% over two steps; d) **LAM-78**, NIS, AgOTf, CH_2Cl_2; e) HF·pyridine, pyridine, THF 89% over two steps; f) **LAM-13**, NIS, AgOTf, CH_2Cl_2, 80%; g) H_2NNH_2·HOAc CH_2Cl_2, CH_3OH, 96%; h) **LAM-83**, NIS, AgOTf, CH_2Cl_2, 71%; i) CF_3CO_2H, CH_2Cl_2, 62%; j) BzCl, pyridine, 95%.

***p*-Tolyl 2-*O*-levulinoyl-1-thio-α-D-arabinofuranoside (LAM-75)**. Prepared from compound **LAM-74**[1] (6.56 g, 13.2 mmol) and 70% HF·pyridine (6 mL) in THF–pyridine (150 mL, 4:1) as described for the synthesis of **LAM-26** to afford **LAM-75** (4.46 g, 95%) as a thick syrup. R_f 0.14 (2:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.43–7.39 (m, 2 H), 7.14–7.10 (m, 2 H), 5.48 (d, 1 H, J = 3.1 Hz, H-1), 4.94 (app t, 1 H, J = 3.4 Hz), 4.27–4.22 (m, 1 H, H-

4), 4.18–4.13 (m, 1 H), 3.90 (ddd, 1 H, J = 3.2, 4.8, 12.0 Hz), 3.77 (ddd, IH, J = 3.9, 7.9, 12.0 Hz), 3.43 (d, 1 H, J = 3.6 Hz), 2.85–2.70 (m, 2 H), 2.63–2.55 (m, 2 H), 2.33 (s, 3 H), 2.19 (s, 3 H), 2.13 (dd, 1 H, J = 4.9, 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.6, 173.5, 138.2, 132.8, 129.8, 129.7, 89.5 (C-1), 86.5, 82.8, 76.0, 61.3, 37.9, 29.8, 27.8, 21.1.

***p*-Tolyl 5-*O*-*t*-butyldiphenylsilyl-3-*O*-benzoyl-2-*O*-levulinoyl-1-thio-α-D-arabinofuranoside (LAM-77)**. Diol **LAM-75** (5.7 g, 16.1 mmol) was dissolved in CH_2Cl_2–pyridine (100 mL, 1:2), TBDPSCl (6 mL, 23.4 mmol) was added and the mixture was stirred at rt for 48 h to give **LAM-76**, which was not isolated. Instead, the solution was cooled to 0 °C and benzoyl chloride (2.5 mL, 21.5 mmol) was added dropwise and the resulting reaction mixture stirred at rt for 12 h before CH_3OH was added (2 mL). After stirring for 30 min, the reaction mixture was diluted with CH_2Cl_2 and poured into a satd aq $NaHCO_3$ soln. The organic layer was washed with water, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (3:1 hexanes–EtOAc) to afford **LAM-77** (9.86 g, 88% over two steps) as a thick syrup. R_f 0.36 (3:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.11–8.04 (m, 2 H), 7.72–7.64 (m, 4 H), 7.62–7.55 (m, 1 H), 7.52–7.30 (m, 10 H), 7.14–7.10 (m, 2 H), 5.57–5.54 (m, 2 H), 5.41 (app t, 1 H, J = 2.2 Hz), 4.53 (app q, 1 H, J = 4.3 Hz), 4.00 (dd, 1 H, J = 4.6, 11.2 Hz), 3.97 (ddd, 1 H, J = 3.9, 11.2 Hz), 2.80–2.45 (m, 4 H), 2.34 (s, 3 H), 2.15 (s, 3 H), 1.07 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.0, 171.6, 165.5, 137.8, 135.7, 133.4, 133.2, 133.1, 132.7, 130.0, 129.7, 129.3, 128.4, 127.7, 91.1, 83.1, 82.1, 77.6, 63.4, 37.8, 29.8, 27.8, 26.8, 21.2, 19.3.

***p*-Methoxyphenyl 3-*O*-benzoyl-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→5)-[3-*O*-benzoyl-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-80)**. Diol **LAM-78**[1] (4.78 g, 13.2 mmol) and thioglycoside **LAM-77** (25.0 g, 35.8 mmol) were dried under vacuum in the presence of P_2O_5 for 14 h. After drying, CH_2Cl_2 (600 mL) was added followed by powdered 4 Å molecular sieves (4.0 g) and the mixture was stirred for 30 min at rt. The solution was then cooled to 0 °C and *N*-iodosuccinimide (8.0 g, 35.6 mmol) and silver triflate (0.46 g, 1.8 mmol) were added. After stirring the mixture for 20 min at 0 °C, Et_3N was added until the pH of the solution was slightly basic as determined using wet pH paper. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with a satd aq soln of $Na_2S_2O_3$, water and brine. The organic layer dried (Na_2SO_4), filtered and concentrated to a residue that was dried under vacuum for 3 h. This compound (**LAM-79**), without any further purification, was dissolved in THF–pyridine (225 mL 7:2), cooled to 0 °C

and then 70% HF·pyridine (8 mL) was added dropwise. The reaction mixture was stirred at rt overnight and concentrated to ~50 mL. The solution was then diluted with CH_2Cl_2, poured into a satd aq $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic layer was washed with water, brine, dried (Na_2SO_4), filtered and concentrated to a residue that was purified by chromatography (1:4 hexanes–EtOAc) to afford **LAM-80** (12.15 g, 89% over two steps) as a thick syrup. R_f 0.1, (3:7 hexanes–EtOAc), $[\alpha]_D$ +52.5 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.03–7.98 (m, 4 H), 7.91–7.87 (m, 2 H), 7.56–7.44 (m, 3 H), 7.40–7.34 (m, 4 H), 7.32–7.26 (m, 2 H), 7.03–6.98 (m, 2 H), 6.80–6.76 (m, 2 H), 5.71 (s, 1 H), 5.57 (d, 1 H, *J* = 1.6 Hz), 5.36 (d, 1 H, *J* = 1.6 Hz), 5.33 (d, 1 H, *J* = 1.5 Hz), 5.29 (s, 1 H), 5.16 (dd, 1 H, *J* = 1.4, 4.8 Hz), 5.13 (dd, 1 H, *J* = 1.0, 4.8 Hz), 4.54 (dd, 1 H, *J* = 0.9, 5.8 Hz), 4.45–4.40 (m, 1 H), 4.29 (dd, 1 H, *J* = 3.8, 6.8 Hz), 4.24 (dd, 1 H, *J* = 4.8, 8.6 Hz), 3.98 (dd, 1 H, *J* = 4.0, 11.5 Hz), 3.95–3.76 (m, 6 H), 3.75 (s, 3 H), 2.82–2.55 (m, 10 H), 2.16 (s, 3 H), 2.15 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.4, 171.4, 166.0, 165.9, 165.5, 155.1, 150.2, 133.5, 133.4, 129.8(2), 129.8, 129.7, 129.1, 128.9, 128.5, 128.4, 118.4, 114.6, 105.3, 105.2, 105.1, 84.5, 83.7, 82.8, 82.1, 81.3, 81.1, 80.4, 77.8, 77.3, 65.1, 62.5, 55.7, 37.9, 29.7, 27.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{53}H_{56}O_{21}Na$: 1051.3206. Found: 1051.3200.

***p*-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→5)-[3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-81)**. Diol **LAM-80** (5.0 g, 4.86 mmol) was glycosylated with thioglycoside **LAM-13**[16] (8.9 g, 13.5 mmol), powdered 4 Å molecular sieves (3.0 g), *N*-iodosuccinimide (3.1 g, 13.8 mmol) and silver triflate (0.35 g, 1.36 mmol) in CH_2Cl_2 (280 mL) as described for the synthesis of **LAM-3** to afford **LAM-81** (16.34 g, 80%) as a thick syrup. R_f 0.21 (65:35 hexanes–EtOAc), $[\alpha]_D$ +45.8 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.08–8.02 (m, 6 H), 8.00–7.97 (m, 2 H), 7.94–7.88 (m, 2 H), 7.58–7.45 (m, 3 H), 7.45–7.42 (m, 2 H), 7.40–7.15 (m, 40H), 7.03–6.98 (m, 2 H), 6.78–6.75 (m, 2 H), 5.74 (s, 1 H), 5.71–5.69 (m, 2 H), 5.59 (d, 1 H, *J* = Hz), 5.48 (s, 1 H), 5.44 (dd, 1 H, *J* = 1.4, 4.8 Hz), 5.40 (d, 1 H, *J* = 1.5 Hz), 5.32 (d, 1 H, *J* = 4.7 Hz), 5.27 (d, 1 H, *J* = 1.2 Hz), 5.21 (s, 1 H), 5.09 (d, 1 H, *J* = 1.8 Hz), 5.05 (d, 1 H, *J* = 1.8 Hz), 4.83 (d, 1 H, *J* = 4.3 Hz), 4.81 (d, 1 H, *J* = 4.3 Hz), 4.76–4.70 (m, 4 H), 4.54–4.44 (m, 8 H), 4.36–4.31 (m, 2 H), 4.14–3.97 (m, 7 H), 3.96–3.82 (m, 6 H), 3.82–3.70 (m, 6 H), 2.67–2.54 (m, 8 H), 2.06 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 205.9,

171.8, 171.6, 165.4, 155.0, 150.3, 138.5, 138.1, 133.4, 133.3, 133.0, 129.9(4), 129.9, 129.8, 129.2, 129.1, 128.5, 128.4, 128.3, 128.2, 128.0, 127.5, 118.4, 114.5, 106.0, 105.3, 98.3(3), 98.3, 82.8, 82.6, 82.5, 82.2, 81.6, 81.4, 80.8, 78.5, 77.5, 77.4, 75.2, 74.2(1), 74.2, 73.4, 72.0(2), 72.0, 71.6, 69.0, 68.9, 68.8, 66.5, 66.4, 66.0, 55.6, 37.8, 37.7, 29.6, 27.8. HRMS (ESI) *m/z* calcd for (M+2Na) $C_{121}H_{120}O_{33}Na_2$: 1073.3748. Found: 1073.3750.

***p*-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-[3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-82)**. Prepared from **LAM-81** (16.3 g, 7.7 mmol) and hydrazine acetate (2.25 g, 24.4 mmol) in CH_2Cl_2–CH_3OH (380 mL, 6:1) as described for the synthesis of **LAM-116** to give **LAM-82** (14.2 g, 96%) as a foam. R_f 0.25 (65:35 hexanes–EtOAc), $[\alpha]_D$ +47.6 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.10–8.00 (m, 9 H), 7.96–7.92 (m, 2 H), 7.58–7.46 (m, 4 H), 7.38–7.16 (m, 40 H), 7.03–6.98 (m, 2 H), 6.81–6.76 (m, 2 H), 5.75 (s, 1 H), 5.67–5.64 (m, 2 H), 5.60 (d, 1 H, *J* = 1.5 Hz), 5.39 (s, 1 H), 5.18 (s, 1 H), 5.10 (dd, 1 H, *J* = 1.2, 4.1 Hz), 5.07 (d, 1 H, *J* = 1.9 Hz), 5.05 (d, 1 H, *J* = 1.9 Hz), 5.00 (dd, 1 H, *J* = 1.7, 4.7 Hz), 4.85 (d, 1 H, *J* = 2.4 Hz), 4.84 (d, 1 H, *J* = 2.4 Hz), 4.76 (d, 1 H, *J* = 2.4 Hz), 4.74 (d, 1 H, *J* = 2.4 Hz), 4.72 (d, 1 H, *J* = 3.5 Hz), 4.70 (d, 1 H, *J* = 3.4 Hz), 4.56–4.48 (m, 6 H), 4.46–4.40 (m, 2 H), 4.37–4.32 (m, 2 H), 4.26 (dd, 1 H, *J* = 1.8, 7.3 Hz), 4.14–4.04 (m, 6 H), 3.99 (dd, 1 H, *J* = 4.2, 11.7 Hz), 3.92–3.85 (m, 4 H), 3.84–3.66 (m, 8 H), 3.20 (dd, 2 H, *J* = 6.5, 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.6, 166.5, 165.6, 165.5, 155.1, 150.3, 138.5, 138.4, 138.0, 133.5, 133.2, 130.0, 129.8, 129.3, 129.1, 128.6, 128.5, 128.4, 128.3(4), 128.3, 128.1(3), 128.1, 127.6, 127.5, 118.5, 114.6, 108.5, 107.8, 105.3, 98.5, 98.4, 83.1, 82.9, 82.4, 81.6, 80.7, 80.4, 79.9, 79.4, 78.4, 75.3, 74.1, 74.0, 73.4, 72.2, 72.1, 71.8, 68.9, 68.8(3), 68.8, 67.0, 66.9, 66.1, 55.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{111}H_{108}O_{29}Na$: 1927.6868. Found: 1927.6892.

***p*-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-[5-*O*-*p*-methoxybenzyl-2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→5)-[3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-[(5-*O*-*p*-methoxybenzyl-2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2))]-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-84)**. Diol **LAM-82** (0.5 g, 0.26 mmol) and thioglycoside **LAM-83**[20] (0.39 g, 0.8 mmol) were dried under vacuum in the

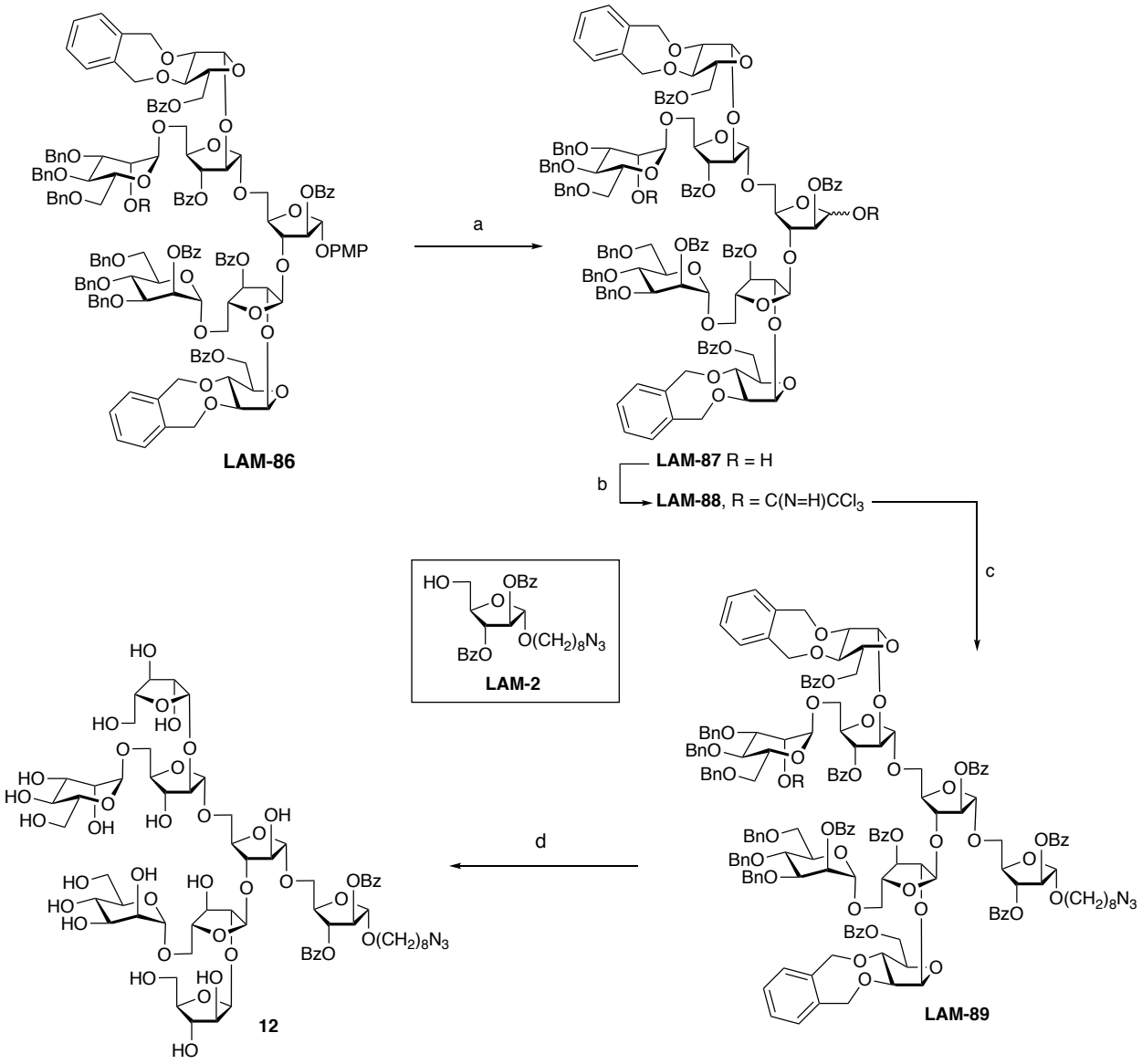
presence of P_2O_5 for 14 h. After drying, CH_2Cl_2 (40 mL) was added followed by powdered 4 Å molecular sieves (0.88 g) and the solution was stirred for 20 min at rt. The mixture was then cooled to –45 °C and *N*-iodosuccinimide (0.28 g, 1.24 mmol) and silver triflate (30 mg, 0.12 mmol) were added. The reaction mixture was stirred at –45 °C for 10 min, warmed to –35 °C over 1 h, and then Et_3N was added until the pH of the solution was slightly basic as determined using wet pH paper. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite and the filtrate was washed with a satd aq soln of $Na_2S_2O_3$, water and brine. The organic layer was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (65:35 hexanes–EtOAc) to yield **LAM-84** (0.49 g, 71%) as a thick syrup. R_f 0.17 (65:35 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.93 (m, 9 H), 7.56–7.40 (m, 5 H), 7.40–7.05 (m, 53 H), 7.00–6.96 (m, 2 H), 6.79–6.71 (m, 6 H), 5.72 (s, 1 H), 5.67–5.61 (m, 2 H), 5.61–5.56 (m, 2 H), 5.52–5.44 (m, 2 H), 5.26–5.20 (m, 2 H), 5.05 (d, 1 H, J = 4.9 Hz), 5.01 (d, 1 H, J = 1.8 Hz), 5.00 (d, 1 H, J = 1.7 Hz), 4.97 (d, 1 H, J = 12.6 Hz), 4.90 (d, 1H, J = 12.6 Hz), 4.86–4.60 (m, 11 H), 4.59–4.42 (m, 8 H), 4.40–4.19 (m, 8 H), 4.18–3.80 (m, 18 H), 3.77–3.66 (m, 15 H), 3.60–3.44 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.5, 165.4, 165.3, 159.0, 155.0, 150.3, 138.6, 138.2, 137.0, 135.7, 135.5, 133.4, 133.3, 133.2, 133.0, 131.5, 131.2, 131.1, 130.4, 130.0(2), 130.0, 129.9, 129.8, 129.5(3), 129.5, 129.3, 129.2, 129.0, 128.5(1), 128.5, 128.3, 128.2, 128.0, 127.9, 127.4, 118.3, 114.6, 113.6, 118.3, 114.6, 113.6, 106.8, 105.5, 105.3, 102.2, 98.4, 98.2, 84.3, 83.9, 83.0, 82.9, 82.8, 82.4, 82.3, 82.1, 82.0, 81.1, 80.7, 80.3, 78.5, 78.4, 77.9, 77.7, 75.1, 74.2, 74.1, 73.4, 72.6, 72.5, 72.3, 72.2, 71.9, 71.8, 71.5, 69.5, 69.4, 69.0, 68.9, 67.7, 67.6, 66.5, 55.6, 55.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{153}H_{152}O_{39}Na$: 2635.9803. Found: 2635.9778.

***p*-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-[2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→5)-[3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-[2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-85)**. To a solution of **LAM-84** (2.25 g, 0.86 mmol) in CH_2Cl_2 (225 mL) at 0 °C was added trifluoroacetic acid (4.5 mL, 2%) and the mixture was stirred at at 0 °C for 20 min. The solution was poured into a satd aq $NaHCO_3$ soln and extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (3:2 hexanes–EtOAc) to afford **LAM-85** (1.27 g,

62%) as a foam. R_f 0.19 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.06–8.00 (m, 6 H), 7.97–7.88 (m, 4 H), 7.55–7.40 (m, 4 H), 7.37–7.10 (m, 49 H), 6.98–6.92 (m, 2 H), 6.74–6.70 (m, 2 H), 5.71 (s, 1 H), 5.66–5.63 (m, 2 H), 5.53 (s, 1 H), 5.50 (dd, 2 H, J = 2.3, 4.5 Hz), 5.47 (s, 1 H), 5.38 (dd, 1 H, J = 2.3, 4.8 Hz), 5.25 (s, 1 H), 5.19 (d, 1 H, J = 5.1 Hz), 5.03–4.97 (m, 4 H), 4.92 (d, 1 H, J = 12.6 Hz), 4.82 (dd, 2 H, J = 3.9, 11.0 Hz), 4.78–4.61 (m, 10 H), 4.54–4.30 (m, 13 H), 4.14–4.05 (m, 5 H), 4.02 (dd, 1 H, J = 5.1, 6.6 Hz), 4.00–3.82 (m, 11 H), 3.82–3.64 (m, 11 H), 3.23 (q, 2 H, J = 5.9 Hz). HRMS (ESI) *m/z* calcd for (M+Na) $C_{137}H_{136}O_{37}Na$: 2395.8653. Found: 2395.8627.

***p*-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-[5-*O*-benzoyl-2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→5)-[3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-[5-*O*-benzoyl-2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-86)**. Diol **LAM-85** (3.0 g, 1.26 mmol) was dissolved in CH_2Cl_2–pyridine (110 mL, 10:1), cooled to 0 °C and benzoyl chloride (1.0 mL, 8.6 mmol) was added dropwise. The resulting mixture was stirred for 14 h while warming to rt and then CH_3OH (1 mL) was added and the solution was stirred for 30 min. The reaction mixture was then diluted with CH_2Cl_2 and poured into a satd aq $NaHCO_3$ soln. The organic layer was washed with water, dried (Na_2SO_4), filtered and concentrated to give a syrup that was purified by chromatography (3:2 hexanes–EtOAc) to afford **LAM-86** (3.1 g, 95%) as a foam. R_f 0.39 (3:2 hexanes–EtOAc), $[\alpha]_D$ +32.5 (c = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.12–8.00 (m, 4 H), 8.00–7.80 (m, 10 H), 7.60–7.12 (m, 59 H), 7.00–6.95 (m, 2 H), 6.75–6.70 (m, 2 H), 5.76 (s, 1 H), 5.65 (app t, 1 H, J = 2.6 Hz), 5.63 (app t, 1 H, J = 2.4 Hz), 5.60 (s, 1 H), 5.55 (dd, 1 H, J = 3.1, 4.9 Hz), 5.51 (s, 1 H), 5.46 (dd, 1 H, J = 2.9, 5.1 Hz), 5.31(d, 1 H, J = 4.9 Hz), 5.28 (s, 1 H), 5.11 (d, 1 H, J = 4.9 Hz), 5.04–4.98 (m, 3 H), 4.91 (d, 1 H, J = 12.5 Hz), 4.85–4.62 (m, 12 H), 4.59–4.56 (m, 1 H), 4.56–4.28 (m, 16 H), 4.27–4.22 (m, 2 H), 4.18–4.04 (m, 7 H), 3.98–3.84 (m, 8 H), 3.76–3.69 (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0, 165.9, 165.5, 165.4, 155.1, 150.3, 138.6, 138.2, 136.8, 135.7, 135.5, 133.5(4), 133.5, 133.2, 133.0, 132.8, 132.7, 131.6, 131.2, 131.1, 130.2, 130.0(4), 130.0, 129.8(1), 129.8, 129.4(4), 129.4, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.4(4), 127.4, 118.4, 114.6, 106.9, 105.7, 105.4, 102.7, 98.3, 98.2, 85.0, 84.4, 83.0, 82.9, 82.1, 82.0, 81.9, 81.3, 81.2, 80.9, 80.4, 78.4(3), 78.4, 78.0, 77.8, 76.6, 76.5, 75.1, 74.1,

73.4, 71.9, 71.8, 71.5, 69.6, 69.5, 69.0, 68.9(0), 68.9, 67.7, 67.6, 66.7, 66.4, 66.3, 55.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{151}H_{144}O_{39}Na$: 2603.9177. Found: 2603.9122.



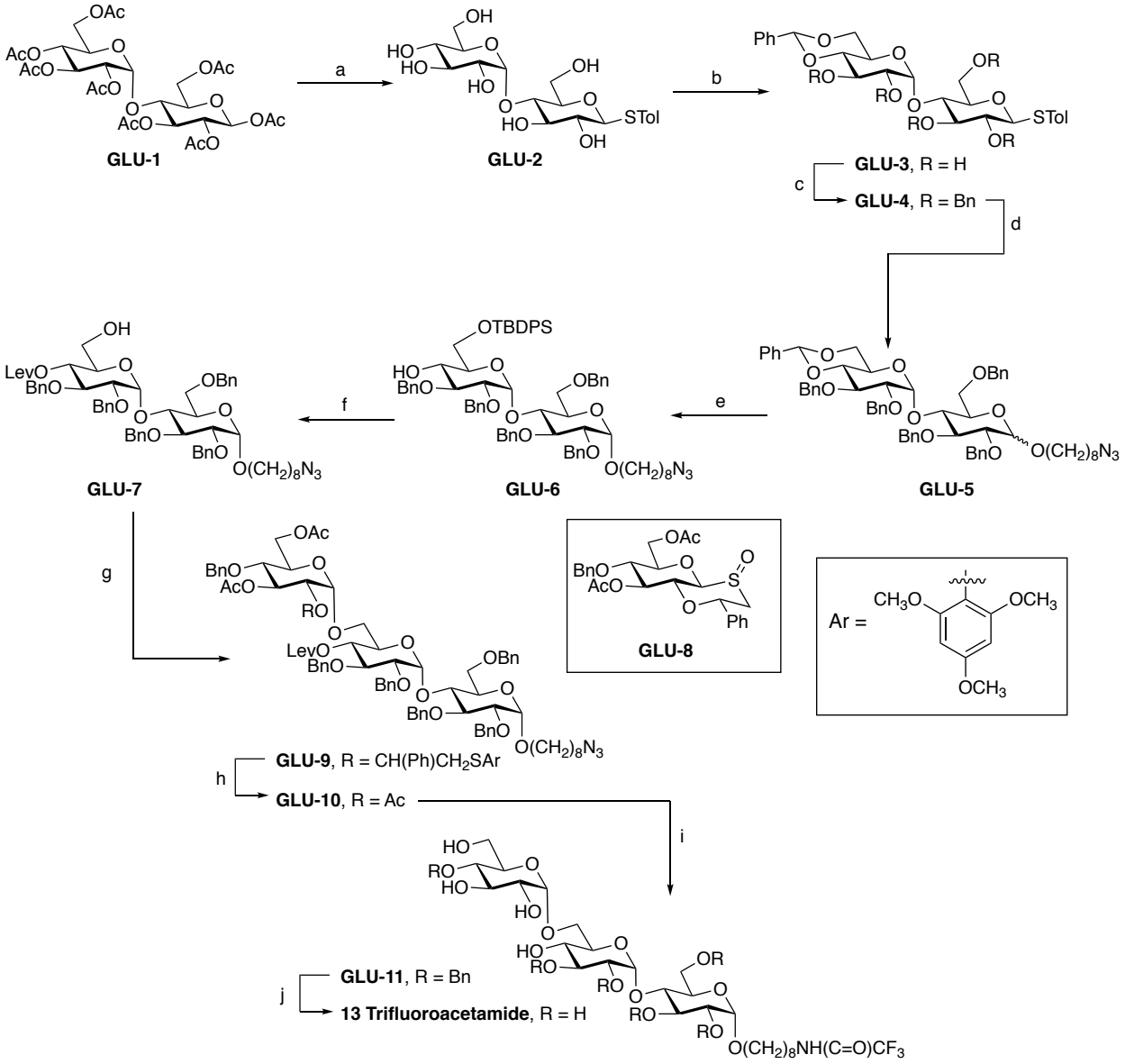
Scheme S13. Synthesis of **12**. a) CAN, H_2O, CH_3CN, 80%; b) Cl_3CCN, DBU, CH_2Cl_2; c) **LAM-2**, TMSOTf, CH_2Cl_2, 89% over two steps; d) Na, NH_3 (l), THF; then CH_3OH, H_2O, 65%.

8-Azidooctyl 3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-5-*O*-benzoyl-2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→5)-[3,4,6-tri-*O*-benzyl-2-*O*-benzoyl-α-D-mannopyranosyl-(1→5)-3-*O*-benzoyl-2-[5-*O*-benzoyl-2,3-*O*-xylylene-α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→3)]-2-*O*-

benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-89). To a solution of compound **LAM-86** (0.37 g, 0.14 mmol) in CH_3CN–H_2O (26 mL, 12:1) at 0 °C was added CAN (0.41 g, 0.75 mmol) and the mixture was stirred for 45 min before being diluted with EtOAc and brine and then stirred well. The EtOAc layer was separated, and the aqueous phase was extracted twice with EtOAc. The combined organic layers were washed with water, a satd aq $NaHCO_3$ soln and water again, before being dried (Na_2SO_4), filtered and concentrated to give a residue that was purified by chromatography (3:2 hexanes–EtOAc) to afford **LAM-87** (0.28 g, diastereomeric mixture, 80%) as a foam. HRMS (ESI) *m/z* calcd for (M+Na) $C_{144}H_{138}O_{38}Na$: 2497.8758. Found: 2497.8731. Trichloroacetimidate **LAM-88** was then prepared from hemiacetal **LAM-87** (0.28 g, 0.11 mmol) using DBU (10 μL) and trichloroacetonitrile (0.25 mL, 2.5 mmol) in CH_2Cl_2 (6 mL) as described for the synthesis of **LAM-42** (Scheme S7). The product was immediately used to glycosylate **LAM-2**[1] (0.09 g, 0.17 mmol) in CH_2Cl_2 (8 mL) using cat. TMSOTf (2 μL) as described for the synthesis of **LAM-43**, to afford **LAM-89** (0.29 g, 89% over two steps) as a syrup. R_f 0.45 (65:35 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.00 (m, 9 H), 8.00–7.85 (m, 10 H), 7.58–7.14 (m, 64 H), 5.65–5.62 (m, 2 H), 5.53–5.49 (m, 2 H), 5.48–5.42 (m, 4 H), 5.39 (s, 1 H), 5.29 (s, 1 H), 5.20 (d, 1 H, J = 4.9 Hz), 5.18 (s, 1 H), 5.17 (d, 1 H, J = 4.9 Hz), 5.00 (d, 1 H, J = 1.8 Hz), 4.99 (d, 1 H, J = 1.4 Hz), 4.96 (d, 1 H, J = 3.5 Hz), 4.94 (s, 1H), 4.85 (d, 1H, J = 2.9 Hz), 4.82 (d, 1H, J = 2.9 Hz), 4.80–4.64 (m, 10H), 4.56–4.33 (m, 18 H), 4.28 (dd, 2 H, J = 6.0, 6.0 Hz), 4.21–3.84 (m, 17 H), 3.76–3.68 (m, 5 H), 3.45 (ddd, 1 H, J = 6.2, 9.4, 12.5 Hz), 3.23 (dd, 2 H, J = 6.9, 6.9 Hz), 1.65–1.52 (m, 4 H), 1.41–1.22 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.9, 165.6, 165.5, 165.4(0), 165.3(9), 165.3(5), 165.3(3), 165.3, 138.6(7), 138.6(5), 138.6, 138.2, 136.9, 136.8, 135.8, 135.6, 133.5, 133.3, 133.0(4), 133.0, 132.9(4), 132.9, 132.8, 132.7, 131.6, 131.5, 131.2, 131.1, 130.0(7), 130.0(5), 130.0(3), 129.9(8), 129.9(6), 129.9, 129.8(1), 129.8, 129.7, 129.4(4), 129.4(0), 129.3(7), 129.3(5), 129.3, 129.2(1), 129.2, 128.5(9), 128.5(6), 128.5(1), 128.5, 128.4, 128.2(9), 128.2(7), 128.2(0), 128.2, 128.1, 128.0, 127.9, 127.5, 127.4(2), 127.4(1), 127.4, 127.3, 107.1, 106.1, 106.0, 105.5, 102.8, 102.6, 98.3, 98.2, 84.8, 84.7, 83.1, 82.3, 82.2(4), 82.2, 82.0, 81.9, 81.8, 81.6, 81.2, 80.7, 80.5, 78.4(2), 78.4, 78.0, 77.7, 77.6, 76.5, 76.4, 75.1(1), 75.1, 74.2, 74.1, 73.4, 73.3, 71.9, 71.8, 71.4(7), 71.4(5), 69.6, 69.0, 68.9(4), 68.9(1), 68.9, 67.8, 67.5, 67.4, 66.5, 66.4, 66.3, 66.2, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{171}H_{169}N_3O_{44}Na$: 2991.0971. Found: 2991.0842.

8-Aminooctyl α-D-mannopyranosyl-(1→5)-[α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→5)-[α-D-mannopyranosyl-(1→5)-[α-D-arabinofuranosyl-(1→2)]-α-D-arabinofuranosyl-(1→3)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (12). To a solution of **LAM-89** (0.09 g, 0.03 mmol) in CH_2Cl_2–CH_3OH (12 mL 9:3) at rt was added 1M sodium methoxide solution until the pH of the reaction mixture was 8–9 (as determined with wet pH paper). The reaction mixture was stirred for 24 h and then neutralized by the addition of Amberlyst–15 (H^+) cation exchange resin. The solution was filtered and the filtrate was concentrated to give syrup that was purified by chromatography (9:1 CH_2Cl_2–CH_3OH) to yield the expected de-benzoylated compound, which was dried under vacuum overnight; R_f 0.39 (9.5:0.5 CH_2Cl_2–CH_3OH). HRMS (ESI) *m/z* calcd for (M+Na) $C_{108}H_{133}N_3O_{35}Na$: 2054.8612. Found: 2054.8623. This material was used in the next step after drying overnight under vacuum. To a solution of liquid NH_3 (20 mL) at −78 °C was added sodium metal (0.04 g) until a deep blue solution was produced. A solution of de-benzoylated **LAM-89** in THF (2 mL) was then added over 3–4 min, making sure that the deep blue color persisted. The reaction mixture was stirred at −78 °C for 45 min and then CH_3OH was added until the dark blue color disappeared and the solution appeared clear. The solution was then warmed to rt by blowing air gently over the solution, which also facilitated removal of the NH_3. When the reaction mixture attained rt, and most of the NH_3 was evaporated, CH_3OH–H_2O (6 mL, 1:1) was added and the pH of the solution was brought to ~8 (as determined by wet pH paper) by the addition of Amberlite IR 120 H+ resin. The solution was filtered and the filtrate concentrated. The residue was re-dissolved in water and purified on a C-18 column (1:1 CH_3OH–H_2O) to give **12** (25 mg, 65%) as a thick syrup which was later lyophilized to a fluffy solid. ^{1}H NMR (500 MHz, D_2O, δ_H) 5.22 (s, 1 H), 5.16 (s, 1 H), 5.12 (d, 2 H, J = 4.5 Hz), 5.09 (s, 1 H), 4.99 (d, 1 H, J = 2.0 Hz), 4.91–4.88 (m, 2 H), 4.31–4.25 (m, 2 H), 4.20–4.09 (m, 9 H), 4.08–4.01 (m, 4 H), 4.01–3.96 (m, 3 H), 3.95–3.58 (m, 26 H), 3.58–3.50 (m, 1 H), 2.97 (dd, 2 H, J = 7.5, 7.5 Hz), 1.69–1.53 (m, 4 H), 1.40–1.20 (m, 8 H); HRMS (ESI) *m/z* calcd for (M+H) $C_{50}H_{88}NO_{35}Na$: 1262.5131. Found: 1262.5122.

10. Synthesis of 13



Scheme S14. Synthesis of **13 Trifluoroacetamide**. a) *p*-TolSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2; then $NaOCH_3$, CH_3OH, CH_2Cl_2, 95%; b) $PhCH(OCH_3)_2$, *p*-TsOH, DMF, 68%; c) BnBr, NaH, THF, DMF, 87%; d) 8-Azido-1-octanol NIS, TMSOTf, CH_2Cl_2, 80%; e) *p*-TsOH, CH_3OH, CH_2Cl_2; then TBDPSCl, CH_2Cl_2, pyridine, 53%; f) Levulinic acid, DMAP, DCC, CH_2Cl_2, 93%; then HF·pyridine, THF, pyridine, 96%; g) **GLU-8**, 1,3,5-trimethoxybenzene, Tf_2O, 2,6-di-*t*-butyl-4-methyl-pyridine, CH_2Cl_2, 95%; h) CF_3CO_2H, CH_2Cl_2; then Ac_2O, pyridine, DMAP 74%; i) $NaOCH_3$, CH_3OH, CH_2Cl_2; then $Pd(OH)_2$–C, pyridine; then trifluoroacetic anhydride, pyridine, 82%; j) H_2, Pd–C, EtOAc, THF, CH_3OH, 90%.

***p*-Tolyl α-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (GLU-2)**. To a solution of **GLU-1**[21] (15.0 g, 22.1 mmol) and *p*-thiocresol (3.29 g, 26.5 mmol) in CH_2Cl_2 (180 mL) at 0 °C was added $BF_3{\cdot}Et_2O$ (6.8 mL, 55.3 mmol) dropwise. The reaction mixture was warmed to rt and stirred for 12 h before being extracted with CH_2Cl_2 (150 mL × 2). The combined CH_2Cl_2 extracts were washed with water (200 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was dissolved in CH_2Cl_2–CH_3OH (5:1, 60 mL). To this solution was added 1M methanolic sodium methoxide until the pH was 8–9 (as determined by wet pH paper). Additional CH_3OH (100 mL in 3 portions) was added as the reaction progressed to aid solubility of the product. The reaction mixture was stirred for 24 h, neutralized by the addition of Amberlite IR 120 H+ resin, filtered and then concentrated to give a crude residue that was purified by chromatography (4:1 CH_2Cl_2–CH_3OH) to yield **GLU-2** (9.42 g, 95% over two steps) as a thick syrup. R_f 0.25 (4:1 CH_2Cl_2–CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 7.47−7.42 (m, 2 H), 7.14−7.09 (m, 2 H), 5.15 (d, 1 H, J = 3.9 Hz, H-1α), 4.52 (d, 1 H, J = 9.7 Hz, H-1β), 3.90−3.76 (m, 3 H), 3.69−3.56 (m, 4 H), 3.51 (dd, 1 H, J = 9.5, 9.5 Hz), 3.43 (dd, 1 H, J = 3.8, 9.7 Hz), 3.40−3.35 (m, 1 H), 3.28−3.20 (m, 2 H), 2.30 (s, 3 H); ^{13}C NMR (150 MHz, CD_3OD, δ_C) 138.8, 133.6, 131.0, 130.5, 102.8 (C-1), 89.6 (C-1), 80.8, 80.6, 79.4, 75.0, 74.7, 74.1, 73.3, 71.5, 62.7, 62.3, 21.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{19}H_{28}O_{10}SNa$: 471.1295. Found: 471.1291.

***p*-Tolyl 4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (GLU-3)**. To a solution of **GLU-2** (10.0 g, 22.3 mmol) in DMF (85 mL) was added α,α-dimethoxytoluene (8.4 mL, 55.7 mmol), *p*-$TsOH{\cdot}H_2O$ (0.46 g, 2.7 mmol) and the mixture was heated at 50 °C overnight under vacuum. When all the starting material was consumed (TLC), the reaction mixture was cooled to r.t. and then water (8.5 mL) and glacial HOAc (8.5 mL) were added and the solution was stirred for 30–40 min. Next, Et_3N (15 mL) was added and the mixture was concentrated to a thick syrup that was purified by chromatography (17:1 CH_2Cl_2–CH_3OH) to give **GLU-3** (8.13 g, 68%) as a thick syrup. R_f 0.37 (19:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +50.9 (c = 0.7, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD, δ_H) 7.50−7.44 (m, 4 H), 7.37−7.29 (m, 3 H), 7.14−7.09 (m, 2 H), 5.55 (s, 1 H), 5.18 (d, 1 H, J = 3.9 Hz, H-1α), 4.54 (d, 1 H, J = 9.7 Hz, H-1β), 4.22 (d, 1 H, J = 4.8, 10.1 Hz), 3.90−3.78 (m, 3 H), 3.76−3.68 (m, 2 H), 3.65 (dd, 1 H, J = 8.9, 8.9 Hz), 3.56 (dd, 1 H, J = 3.8, 9.3 Hz), 3.54−3.36 (m, 3 H), 3.24 (dd, 1 H, J = 9.0, 9.7

Hz), 2.30 (s, 3 H); ^{13}C NMR (100 MHz, CD_3OD, δ_C) 138.8, 138.5, 133.2, 130.8, 130.2, 129.6, 128.7, 127.2, 103.0 (C-1), 102.6, 89.2 (C-1), 82.1, 80.8, 80.1, 79.0, 74.4, 73.0, 71.8, 69.5, 64.7, 62.1, 20.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{26}H_{32}O_{10}SNa$: 559.1608. Found: 559.1608.

***p*-Tolyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (GLU-4)**. To a solution of **GLU-3** (5.4 g, 10.1 mmol) in THF–DMF (72 mL, 3:1) at 0 °C under argon was added NaH (60% dispersion in mineral oil, 2.42 g, 60.4 mmol) and the mixture was stirred for 2–3 min before BnBr (7.8 mL, 65.5 mmol) was added dropwise. The solution was warmed to rt and stirred for 6 h. The reaction mixture was then cooled to 0 °C and CH_3OH (6 mL) was added carefully. After stirring for 15 min, the reaction mixture was poured into chilled water (360 mL) and extracted with CH_2Cl_2 (200 mL × 2). The combined organic layer was washed with water (200 mL × 2) and brine (100 mL). The organic layer was then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (22:3 hexanes–EtOAc) to yield **GLU-4** (8.65 g, 87%) as a thick syrup. R_f 0.32 (85:15 hexanes–EtOAc); $[\alpha]_D$ +2.0 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.55−7.50 (m, 4 H), 7.44−7.23 (m, 21 H), 7.20−7.12 (m, 7 H), 7.09−7.04 (m, 2 H), 5.69 (d, 1 H, *J* = 3.9 Hz, H-1α), 5.55 (s, 1 H), 4.94−4.82 (m, 4 H), 4.77−4.68 (m, 3 H), 4.64−4.52 (m, 4 H), 4.19−4.12 (m, 2 H), 4.02 (dd, 1 H, *J* = 9.4, 9.4 Hz), 3.93−3.85 (m, 2 H), 3.85−3.80 (m, 2 H), 3.66−3.50 (m, 5 H), 2.47 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.7, 138.6, 138.5, 137.8(9), 137.8(5), 137.8, 137.6, 132.9, 129.7, 129.4, 128.9, 128.4(0), 128.4, 128.3(0), 128.2(9), 128.2(7), 128.2, 128.0, 127.9, 127.8, 127.6(2), 127.6, 127.4, 127.2, 126.4, 126.1, 101.2, 97.6 (C-1), 87.4 (C-1), 87.0, 82.4, 80.9, 78.8, 78.7, 78.5, 76.8, 75.3, 75.2, 74.2, 74.0, 73.4, 71.8, 69.0, 63.4, 21.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{61}H_{62}O_{10}SNa$: 1009.3956. Found: 1009.3967.

8-Azidooctyl 2,3-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-6). 8-Azido-1-octanol (1.36 g, 8.0 mmol) and **GLU-4** (4.2 g, 4.3 mmol) were dried under vacuum in the presence of P_2O_5 for 6 h. After drying, $CHCl_3$–Et_2O (1:1, 200 mL) was added, followed by powdered 4 Å molecular sieves (1.7 g) and the mixture was stirred for 30 min. The reaction mixture was cooled to 0 °C and then *N*-iodosuccinimide (1.7 g, 7.6 mmol) and TMSOTf (0.2 mL, 1.1 mmol) were added and the solution was stirred for 2 h before Et_3N was added until the pH of the solution was slightly basic as determined by wet pH paper. The mixture was diluted with CH_2Cl_2 (40 mL), filtered through Celite and the filtrate was washed with satd aq soln of $Na_2S_2O_3$ (50 mL), water (50 mL) and

brine (25 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (88:12 hexanes–EtOAc) to give **GLU-5** (3.5 g, 80% as an inseparable α:β (2.6:1) mixture); R_f 0.36 (85:15 hexanes–EtOAc, two runs); HRMS (ESI) *m/z* calcd for (M+Na) $C_{62}H_{71}N_3O_{11}Na$: 1056.4981. Found: 1056.4980. This compound (3.5 g, 3.38 mmol) was then dissolved in CH_2Cl_2–CH_3OH (5:3, 80 mL) and then *p*-TsOH·H_2O (0.96 g, 5.0 mmol) was added followed by two drops of water and the solution was stirred at rt for 24 h. The reaction mixture was then poured into water (250 mL) and extracted with CH_2Cl_2 (175 mL). The organic phase was washed with water (100 mL × 2), dried (Na_2SO_4), filtered and concentrated to a syrup that was dried under vacuum overnight to give the corresponding disaccharide diol as an inseparable α:β mixture; R_f 0.12 (7:3 hexanes–EtOAc); HRMS (ESI) *m/z* calcd for (M+Na) $C_{55}H_{67}N_3O_{11}Na$: 968.4668. Found: 968.4663. This compound was then dissolved in CH_2Cl_2–pyridine (2:1, 45 mL), TBDPSCl (5.0 mL, 19.5 mmol) was added and the mixture was stirred at rt for 24 h before CH_3OH (4 mL) was added. The reaction mixture was poured into a satd aq $NaHCO_3$ soln (40 mL) and extracted with CH_2Cl_2 (50 mL). The organic phase was washed with water (50 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (22:3 hexanes–EtOAc) to yield **GLU-6** (2.11 g (pure α-product), 53% over two steps) as a thick syrup. R_f 0.23 (85:15 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.65−7.61 (m, 4 H), 7.41−7.14 (m, 31 H), 5.67 (d, 1 H, *J* = 3.6 Hz, H-1α), 5.05 (d, 1 H, *J* = 11.6 Hz), 4.89 (d, 1 H, *J* = 11.3 Hz), 4.80 (d, 1 H, *J* = 11.5 Hz), 4.75 (d, 1 H, *J* = 3.6 Hz, H-1α), 4.70 (d, 1 H, *J* = 11.3 Hz), 4.66 (d, 1 H, *J* = 12.0 Hz), 4.57 (d, 1 H, *J* = 12.0 Hz), 4.55 (d, 1 H, *J* = 11.9 Hz), 4.51 (d, 1 H, *J* = 11.8 Hz), 4.48 (d, 1 H, *J* = 12.0 Hz), 4.41 (d, 1 H, *J* = 12.0 Hz), 4.08 (dd, 1 H, *J* = 9.2, 9.2 Hz), 3.98 (dd, 1 H, *J* = 9.8, 9.8 Hz), 3.92−3.86 (m, 1 H), 3.80−3.70 (m, 4 H), 3.68−3.60 (m, 4 H), 3.57 (dd, 1 H, *J* = 3.7, 9.5 Hz), 3.42−3.36 (m, 2 H), 3.23 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.33 (d, 1 H, *J* = 2.2 Hz), 1.70−1.57 (m, 4 H), 1.40−1.30 (m, 8 H), 1.02 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 139.1, 138.8, 138.2, 138.1, 137.9, 135.7, 135.6, 133.4, 133.1, 129.6, 128.5, 128.4, 128.3, 128.2(0), 128.2, 128.1, 127.9, 127.8, 127.6(9), 127.6(6), 127.6, 127.4(4), 127.4, 127.0, 126.7, 96.4 (C-1), 96.1 (C-1), 82.0, 81.1, 80.2, 79.3, 75.3, 74.1, 73.2, 72.9, 72.8, 72.5, 71.9, 71.0, 69.6, 69.3, 68.2, 63.8, 51.5, 29.4, 29.3, 29.1, 28.8, 26.9, 26.7, 26.0, 19.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{71}H_{85}N_3O_{11}SiNa$: 1206.5846. Found: 1206.5834.

8-Azidooctyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-7). To a solution of **GLU-6** (2.15 g, 1.81 mmol), levulinic

acid (0.28 mL, 2.73 mmol) and DMAP (0.11 g, 0.9 mmol) in CH_2Cl_2 (31 mL) was added DCC (0.56 g, 2.71 mmol) and the mixture was stirred at rt for 1 h. The reaction mixture was then filtered through Celite and the filter cake was washed with CH_2Cl_2. The filtrate was diluted with CH_2Cl_2 (20 mL), washed with satd aq $NaHCO_3$ soln (25 mL), water (25 mL) and brine (20 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated to a syrup that was purified by chromatography (4:1 hexanes–EtOAc) to afford the corresponding levulinate ester (2.16 g, 93%) as a thick syrup; R_f 0.29 (4:1 hexanes–EtOAc); HRMS (ESI) *m/z* calcd for (M+Na) $C_{76}H_{91}N_3O_{13}SiNa$: 1304.6213. Found: 1304.6221. To a solution of this compound (2.16 g, 1.68 mmol) in THF–pyridine (21:12, 33 mL) at 0 °C was added 70% HF·pyridine (1.0 mL) dropwise. The solution was warmed to rt and stirred overnight before being poured into a satd aq $NaHCO_3$ soln (30 mL), extracted with CH_2Cl_2 (40 mL) and the organic layer washed with brine (25 mL). The organic layer was then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (1:1 hexanes–EtOAc) to yield **GLU-7** (1.69 g, 96%) as a thick syrup. R_f 0.11 (65:35 hexanes–EtOAc); $[\alpha]_D$ +46.9 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.17 (m, 25 H), 5.73 (d, 1 H, *J* = 3.7 Hz), 5.10 (d, 1 H, *J* = 11.6 Hz), 4.92 (dd, a H, *J* = 9.9, 9.9 Hz), 4.87–4.81 (m, 2 H), 4.80 (d, 1 H, *J* = 3.5 Hz, H-1α), 4.74–4.51 (m, 6 H), 4.14 (dd, 1 H, *J* = 9.2, 9.2 Hz), 4.05 (dd, 1 H, *J* = 9.7, 9.7 Hz), 4.00–3.90 (m, 2 H), 3.85 (dd, 2 H, *J* = 3.9, 11.0 Hz), 3.74–3.60 (m, 3 H), 3.58–3.38 (m, 4 H), 3.30 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.82–2.73 (m, 1 H), 2.66–2.50 (m, 2 H), 2.43–2.30 (m, 2 H), 2.18 (s, 3 H), 1.80–1.60 (m, 4 H), 1.50–1.25 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 173.0, 139.0, 138.7, 138.2, 138.1, 137.7, 128.4(1), 128.4, 128.3(0), 128.3, 128.1, 127.8(8), 127.8(5), 127.7, 127.6(1), 127.6, 127.5, 127.1, 126.7, 96.6 (C-1), 96.5 (C-1), 81.8, 80.4, 79.0, 78.8, 75.2, 74.2, 73.5, 73.4, 73.1, 72.9, 71.0, 70.4, 69.7, 69.0, 68.3, 61.0, 51.5, 37.8, 29.7, 29.4, 29.3, 29.1, 28.9, 27.9, 27.0, 26.7, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{60}H_{73}N_3O_{13}Na$: 1066.5036. Found: 1066.5037.

8-Azidooctyl 2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-3,6-di-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-9). A mixture of sulfoxide donor **GLU-8**[22] (0.2 g, 0.41 mmol), 1,3,5-trimethoxybenzene (0.1 g, 0.6 mmol), 2,6-di-*t*-butyl-4-methyl pyridine (0.17 g, 0.82 mmol), and activated 4 Å molecular sieves (0.13 g) in CH_2Cl_2 (2.7 mL) was stirred for 1 h. After cooling to −10 °C, trifluoromethanesulfonic anhydride (0.075 mL, 0.44 mmol) was added. After 30 min, the reaction mixture was cooled to

−40 °C and a solution of **GLU-7** (0.34 g, 0.33 mmol) in CH_2Cl_2 (1.4 mL) was added slowly. The temperature of the reaction mixture was kept at −40 °C for 60 min and then warmed to rt. After stirring for 15 h at rt, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and the filtrate was concentrated to a residue that was purified by chromatography (3:2 hexanes–EtOAc) to yield **GLU-9** (0.52 g, 95%) as a foam. R_f 0.25 (3:2 hexanes–EtOAc); $[\alpha]_D$ +82.0 (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.80−7.20 (m, 37 H), 6.17 (s, 2 H), 5.66 (d, 1 H, J = 3.6 Hz, H-1α), 5.59 (dd, 1 H, J = 9.7, 9.7 Hz), 5.56 (d, 1 H, J = 3.5 Hz, H-1α), 5.04−4.78 (m, 5 H), 4.70−4.42 (m, 9 H), 4.35−4.25 (m, 3 H), 4.25−3.90 (m, 8 H), 3.90−3.82 (m, 10 H), 3.80−3.65 (m, 4 H), 3.55−3.42 (m, 4 H), 3.28 (dd, 2 H, J = 7.0, 7.0 Hz), 2.99 (dd, 1 H, J = 8.8, 14.1 Hz), 2.80 (dd, 1 H, J = 3.7, 14.1 Hz), 2.62−2.45 (m, 2 H), 2.45−2.36 (m, 2 H) 2.08 (s, 3 H), 2.06 (s, 3 H), 1.76−1.60 (m, 4 H), 1.50 (s, 3 H), 1.46−1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.1, 171.9, 170.6, 169.3, 161.8, 161.7, 142.2, 139.4, 139.0, 138.7(3), 138.7, 138.0, 137.7, 128.4, 128.3(4), 128.2(9), 128.2(5), 128.1(7), 128.1(6), 128.1, 128.0, 127.8, 127.7, 127.6(0), 127.6, 127.4(3), 127.4(1), 127.2, 127.0(0), 127.0, 126.4, 102.2, 97.3 (C-1), 96.5 (C-1), 96.3 (C-1), 91.0, 84.5, 81.6, 80.1, 79.5, 79.4, 78.8(4), 76.6, 75.1(3), 75.1(0), 73.8, 73.5, 73.0(9), 73.0(5), 72.9, 72.8, 71.3, 70.2, 69.9, 69.8, 68.0, 67.9, 67.6, 63.1, 56.0, 55.4, 51.5, 43.5, 37.9, 30.2, 29.6, 29.4(1), 29.4, 29.2, 28.9, 28.0, 26.8, 26.1, 20.9, 20.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{94}H_{111}N_3O_{23}SNa$: 1704.7221. Found: 1704.7197.

8-Azidooctyl 2,3,6-tri-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-10). To a solution of **GLU-9** (0.5 g, 0.3 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added trifluoroacetic acid (1.0 mL) and the mixture was stirred at that temperature for 20 min before being poured into a satd aq $NaHCO_3$ soln (25 mL) and extracted with CH_2Cl_2 (25 mL). The organic layer was washed with water (15 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was dried under vacuum for 3 h. The resulting product was then dissolved in CH_2Cl_2 (8 mL) and pyridine (2.5 mL), followed by the addition of DMAP (0.1 g, 0.82 mmol) and acetic anhydride (0.5 mL, 5.3 mmol). After stirring overnight, CH_3OH (1.0 mL) was added, and the solution was poured into a satd aq $NaHCO_3$ soln (20 mL) and extracted with CH_2Cl_2 (25 mL). The organic layer was washed with water (20 mL), dried (Na_2SO_4), filtered and concentrated to a residue that was purified by chromatography (62:38 hexanes–EtOAc) to yield **GLU-10** (0.31 g, 74% over two steps). R_f 0.16 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.35−7.15

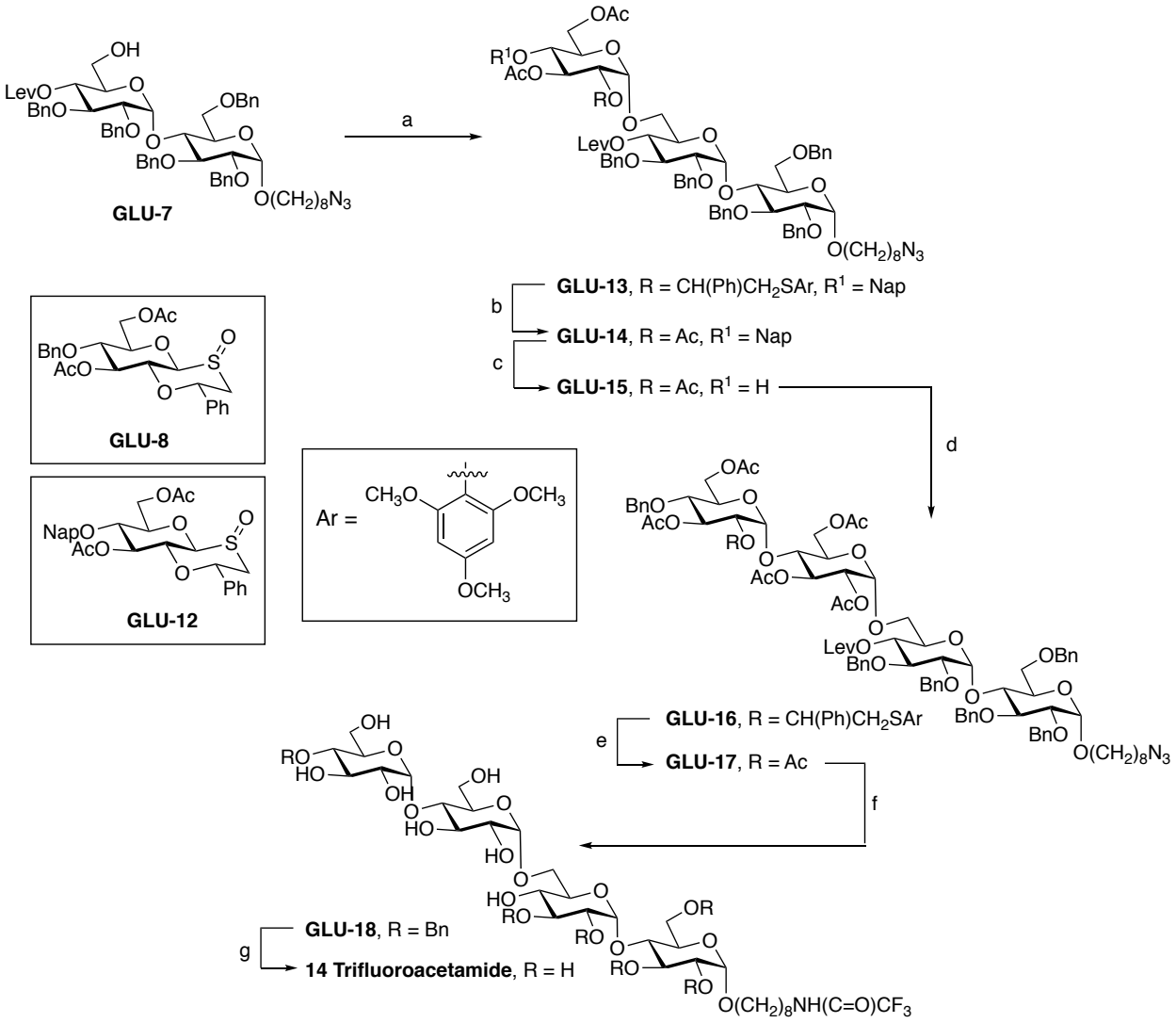
(m, 30 H), 5.66 (d, 1 H, J = 3.6 Hz, H-1α), 5.59 (dd, 1 H, J = 9.4, 10.1 Hz), 5.04 (d, 1 H, J = 11.6 Hz), 4.98 (d, 1 H, J = 3.7 Hz, H-1α), 4.94 (dd, 1 H, J = 9.3, 10.2 Hz), 4.86−4.78 (m, 4 H), 4.66 (d, 1 H, J = 12.0 Hz), 4.62−4.50 (m, 8 H), 4.32−4.24 (m, 2 H), 4.14−4.08 (m, 1 H), 4.06−3.88 (m, 6 H), 3.82−3.77 (m, 1 H), 3.73−3.62 (m, 3 H), 3.52 (dd, 1 H, J = 3.5, 7.8 Hz), 3.46−3.40 (m, 2 H), 3.35 (dd, 1 H, J = 2.1, 11.3 Hz), 3.27 (dd, 2 H, J = 7.0, 7.0 Hz), 2.76−2.68 (m, 1 H), 2.62−2.54 (m, 1 H), 2.54−2.44 (m, 1 H), 2.35−2.26 (m, 1 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 1.98 (s, 3 H), 1.93 (s, 3 H), 1.70−1.58 (m, 4 H), 1.44−1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.3, 171.4, 170.6, 170.5, 169.4, 139.1, 138.7, 138.4(1), 138.4, 137.8, 137.5, 128.5, 128.4, 128.3(4), 128.2(8), 128.2(6), 128.1, 128.0, 127.8(2), 127.8, 127.7, 127.6, 127.5, 127.4, 127.1, 126.8, 96.4 (C-1), 96.1 (C-1), 96.0 (C-1), 81.8, 80.2, 79.3, 78.9, 75.8, 75.1, 74.1, 74.0, 73.3, 73.2, 73.0(2), 73.0, 72.1, 71.2, 70.7, 69.7, 69.5, 69.3, 68.2, 68.1, 66.4, 62.6, 51.5, 37.8, 29.7, 29.3(8), 29.3(7), 29.2, 28.9, 27.9, 26.7, 26.1, 20.9(4), 20.9, 20.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{79}H_{95}N_3O_{21}Na$: 1444.6350. Found: 1444.6329.

8-Trifluoroacetamidooctyl 4-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-11). Compound **GLU-10** (0.31 g, 0.22 mmol) was dissolved in CH_2Cl_2–CH_3OH (7:1, 8 mL) and 1M methanolic sodium methoxide solution was added until the pH of the solution was 8–9 (as determined by wet pH paper). The reaction mixture was stirred for 5 h, neutralized by the addition of Amberlite IR 120 H+ resin, filtered and then concentrated to give a crude residue that was purified by chromatography (93:7 CH_2Cl_2–CH_3OH) to yield the expected trisaccharide tetraol (0.25 g, 96%) as a thick syrup; R_f 0.47 (9:1 CH_2Cl_2–CH_3OH). A portion of this compound (0.14 g, 0.12 mmol) was dissolved in pyridine (5 mL) and then 20% $Pd(OH)_2$–C (55 mg) was added and the mixture was stirred under H_2 (1 atm) for 6 h. The solution was filtered and the filter cake and washed with pyridine (2 mL). The combined filtrate was then cooled to 0 °C before trifluoroacetic anhydride (0.4 mL, 2.9 mmol) was added dropwise. After stirring overnight while warming to rt, the solution was diluted with CH_2Cl_2 (25 mL) and poured into a 1:1 solution of water and satd aq $NaHCO_3$ soln (25 mL). The organic layer was separated, washed with water (20 mL) containing 5–6 drops of aq ammonia for 10 min, and then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (1:3 hexanes–EtOAc) to give **GLU-11** (0.14 g, 82% over three steps) as a foam. R_f 0.26 (1:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.20 (m, 30 H), 6.40 (br. s, 1 H), 5.70 (d, 1 H, J = 3.7 Hz, H-1α), 5.10 (d, 1 H, J = 11.7

Hz), 4.96 (d, 1 H, J = 11.4 Hz), 4.89 (d, 1 H, J = 11.4 Hz), 4.83−4.76 (m, 2 H), 4.74−4.65 (m, 4 H), 4.62−4.52 (m, 5 H), 4.14 (dd, 1 H, J = 9.0, 9.0 Hz), 4.07 (dd, 1 H, J = 9.5, 9.5 Hz), 3.96−3.92 (m, 1 H), 3.88−3.62 (m, 11 H), 3.55 (dd, 1 H, J = 11.5 Hz), 3.48−3.34 (m, 7 H), 2.80 (br. s, 1 H), 2.71 (br. s, 1 H), 1.96−1.85 (m, 2 H), 1.75−1.55 (m, 4 H), 1.45−1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.1 (q, J = 36.6 Hz), 139.0, 138.6, 138.3, 138.2, 137.8, 128.6, 128.5, 128.4, 128.3, 128.0(9), 128.0(8), 127.9(1), 127.9, 127.8(3), 127.8, 127.6, 127.2, 126.7, 115.9 (q, J = 287.6 Hz), 98.4 (C-1), 96.4 (C-1), 96.1 (C-1), 81.9, 81.2, 80.5, 79.4, 77.2, 75.3(4), 75.3, 74.6, 74.0, 73.4, 73.0, 72.9, 72.8, 72.0(8), 72.0(7), 70.6, 70.2, 69.7, 69.1, 68.3, 67.2, 61.9, 40.0, 29.4, 29.3, 29.1, 29.0, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{70}H_{84}F_3NO_{17}Na$: 1290.5584. Found: 1290.5571.

8-Trifluoroacetamidooctyl α-D-glucopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranoside (13 Trifluoroacetamide). To a solution of **GLU-10** (0.135 g, 0.11 mmol) in EtOAc–THF–CH_3OH (15 mL 1:1:1) was added 20% $Pd(OH)_2$–C (80 mg) and the reaction mixture was stirred under H_2 (1 atm) for 24 h. The reaction mixture was filtered and the filtrate was concentrated to give a syrup that was re-dissolved in distilled water (8 mL) and extracted with CH_2Cl_2 (3 mL × 3). The aqueous phase was filtered using a 13 mm Nylon 0.2 μm syringe filter unit and the filtrate was then lyophilized to give **13 Trifluoroacetamide** (0.07 g, 90%) as a foam. R_f 0.43 (7:3 CH_2Cl_2–CH_3OH); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.37 (d, 1 H, J = 3.9 Hz, H-1α), 4.94 (d, 1 H, J = 3.5 Hz, H-1α), 4.89 (d, 1 H, J = 3.9 Hz, H-1α), 4.05−3.45 (m, 19 H), 3.42 (dd, 1 H, J = 9.5, 9.5 Hz), 3.30 (dd, 2 H, J = 7.0, 7.0 Hz), 1.66−1.50 (m, 4 H), 1.40−1.27 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 158.8 (q, J = 36.8 Hz), 116.0 (q, J = 285.5 Hz), 99.9 (C-1), 98.1 (C-1), 98.0 (C-1), 77.5, 73.6, 73.1(3), 73.1(0), 71.8, 71.7, 71.5, 71.4, 71.2, 70.3, 69.6, 69.4, 68.5, 65.9, 60.6, 60.5, 39.8, 28.6, 28.3, 28.2, 27.7, 25.8, 25.3.

11. Synthesis of 14



Scheme S15. Synthesis of **14 Trifluoroacetamide**. a) **GLU-12**, 1,3,5-trimethoxybenzene, Tf_2O, 2,6-di-*t*-butyl-4-methyl-pyridine, CH_2Cl_2, 72%; b) CF_3CO_2H, CH_2Cl_2; then Ac_2O, pyridine, 86%; c) DDQ, CH_2Cl_2, H_2O, 70%; d) **GLU-8**, 1,3,5-trimethoxybenzene, Tf_2O, 2,6-di-*t*-butyl-4-methyl-pyridine, CH_2Cl_2, 32%; e) CF_3CO_2H, CH_2Cl_2; then Ac_2O, pyridine, DMAP 63%; f) $NaOCH_3$, CH_3OH, CH_2Cl_2; then $Pd(OH)_2$–C, pyridine; then trifluoroacetic anhydride, pyridine, 87%; g) H_2, Pd–C, EtOAc, THF, CH_3OH, 95%.

8-Azidooctyl 2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-3,6-di-*O*-acetyl-4-*O*-naphthyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-13). A mixture of sulfoxide donor **GLU-12**[22] (0.75 g, 1.39 mmol), 1,3,5-trimethoxybenzene (0.35 g, 2.08 mmol),

2,6-di-*t*-butyl-4-methyl pyridine (0.57 g, 2.8 mmol), and activated 4 Å molecular sieves (0.45 g) in CH_2Cl_2 (9.3 mL) was stirred for 1 h. After cooling to −10 °C, trifluoromethanesulfonic anhydride (0.26 mL, 1.54 mmol) was added. After 30 min, the reaction mixture was cooled to −40 °C and a solution of **GLU-7** (1.16 g, 1.11 mmol) in CH_2Cl_2 (4.6 mL) was added slowly. The temperature of the reaction mixture was kept at −40 °C for 60 min and then warmed to rt. After stirring for 15 h at rt, the reaction mixture was diluted with CH_2Cl_2 (20 mL), filtered, and the filtrate was concentrated to a residue that was purified by chromatography (65:35 hexanes–EtOAc) to yield **GLU-13** (1.4 g, 72%) as a foam. R_f 0.25 (65:35 hexanes–EtOAc, two runs); $[\alpha]_D$ +70.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.80−7.67 (m, 3 H), 7.66−7.63 (m, 1 H), 7.47−7.41 (m, 2 H), 7.40−7.10 (m, 33 H), 6.16 (s, 2 H), 5.68−5.62 (m, 2 H), 5.55 (d, 1 H, *J* = 3.3 Hz, H-1α), 4.97 (d, 1 H, *J* = 11.4 Hz), 4.92−4.84 (m, 2 H), 4.83−4.76 (m, 2 H), 4.73−4.48 (m, 6 H), 4.46−4.25 (m, 5 H), 4.25−4.15 (m, 2 H), 4.15−3.39 (m, 5 H), 3.87 (s, 3 H), 3.84 (s, 6 H), 3.80−3.68 (m, 3 H), 3.61 (dd, 1 H, *J* = 3.7, 9.5 Hz), 3.54−3.48 (m, 3 H), 3.43 (ddd, 1 H, *J* = 7.2, 9.9, 14.1 Hz), 3.27 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.96 (dd, 1 H, *J* = 8.8, 14.1 Hz), 2.88 (dd, 1 H, *J* = 3.5, 14.1 Hz), 2.65−2.40 (m, 4 H), 2.05 (s, 3 H), 1.94 (s, 3 H), 1.82 (s, 3 H), 1.78−1.58 (m, 4 H), 1.43−1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.1, 171.9, 170.6, 169.4, 161.8, 161.7, 142.2, 139.4, 138.9, 138.7, 138.6, 137.9, 135.1, 133.2, 133.0, 128.3, 128.2(3), 128.2, 128.1, 128.0, 127.9, 127.8, 127.7(3), 127.7, 127.6, 127.5(3), 127.5, 127.4(2), 127.4, 127.2, 127.0, 126.8, 126.4, 126.1, 125.9(9), 125.9(6), 102.1, 97.3 (C-1), 96.5 (C-1), 96.2 (C-1), 91.0, 84.5, 81.6, 80.1, 79.5, 79.3, 78.8, 76.5, 75.1, 75.0, 73.8, 73.4, 73.1(2), 73.1, 72.8, 72.7, 71.3, 70.2, 69.9, 69.6, 67.9(3), 67.9, 67.6, 63.1, 56.0, 55.4, 51.5, 43.4, 37.8, 29.4, 29.6, 29.4, 29.3, 29.2, 28.9, 28.0, 26.7, 26.1, 20.7(2), 20.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{98}H_{113}N_3O_{23}SNa$: 1754.7378. Found: 1754.7350.

8-Azidooctyl 2,3,6-tri-*O*-acetyl-4-*O*-naphthyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-14). Prepared from compound **GLU-13** (1.4 g, 0.80 mmol) in CH_2Cl_2 (50 mL) and trifluoroacetic acid (2.5 mL) as described for the reaction of **GLU-9** to give the corresponding alcohol as a syrup. After drying under vacuum for 2 h, the compound was dissolved in pyridine (20 mL), acetic anhydride (6.0 mL, 63.0 mmol) was added and the mixture was heated at 50 °C overnight. The reaction mixture was cooled to rt, CH_3OH (5 mL) was added, and then the solution was poured into a satd aq $NaHCO_3$ soln (50.0 mL) and extracted with CH_2Cl_2 (50 mL).

The organic layer was washed with water (25 mL), 12% aq copper sulfate solution (until the pyridine was completely removed as determined by TLC), dried (Na_2SO_4), filtered, and concentrated to a syrup that was purified by chromatography (3:2 hexanes–EtOAc) to yield **GLU-14** (1.02 g, 86% over two steps). R_f 0.33 (3:2 hexanes–EtOAc); $[\alpha]_D$ +92.9 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.85−7.75 (m, 3 H), 7.74−7.72 (m, 1 H), 7.56−7.42 (m, 2 H), 7.40−7.18 (m, 26 H), 5.69 (d, 1 H, *J* = 3.7 Hz, H-1α), 5.66 (dd, 1 H, *J* = 9.4, 9.4 Hz), 5.08−4.92 (m, 3 H), 4.90−4.70 (m, 6 H), 4.65−4.50 (m, 8 H), 4.35−4.25 (m, 2 H), 4.13 (dd, 1 H, *J* = 9.2, 9.2 Hz), 4.08−4.00 (m, 2 H), 4.00−3.90 (m, 4 H), 3.80−3.68 (m, 2 H), 3.66 (dd, 1 H, *J* = 3.6, 9.4 Hz), 3.55 (dd, 1 H, *J* = 5.5, 11.2 Hz), 3.49−3.42 (m, 2 H), 3.38 (dd, 1 H, *J* = 2.0, 11.2 Hz), 3.29 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.80−2.70 (m, 1 H), 2.63−2.45 (m, 2 H), 2.36−2.26 (m, 1 H), 2.11 (s, 3 H), 1.98 (s, 3 H), 1.95 (s, 6 H), 1.74−1.60 (m, 4 H), 1.46−1.34 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.3, 171.5, 170.6, 170.5, 169.5, 139.1, 138.7, 138.4, 138.3, 137.8, 135.0, 133.2, 133.1, 128.3(4), 128.3(3), 128.3, 128.0, 127.8, 127.7(4), 127.7, 127.6, 127.5, 127.4, 127.1, 126.9, 126.8, 126.2, 126.1, 125.9, 96.4 (C-1), 96.1 (C-1), 96.0 (C-1), 81.8, 80.2, 79.3, 78.9, 75.7, 75.1, 74.1, 73.9, 73.3, 73.2, 73.0(0), 73.0, 72.2(1), 72.2(4), 70.7, 69.7, 69.6, 69.3, 68.2, 68.1, 66.4, 62.6, 51.5, 37.8, 29.7, 29.4, 29.1, 28.9, 27.9, 26.7, 26.1, 21.0, 20.7(0), 20.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{83}H_{97}N_3O_{21}Na$: 1494.6507. Found: 1494.6507.

8-Azidooctyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-15). To a solution of **GLU-14** (1.02 g, 0.69 mmol) in CH_2Cl_2–water (10:1, 88 mL) at rt was added DDQ (0.47 g, 2.0 mmol) and the solution was stirred for 1 h, at which point additional DDQ (0.24 g, 1.0 mmol) was added. After stirring for a total of 2 h, the mixture was diluted with CH_2Cl_2 (20 mL), washed with satd aq $NaHCO_3$ soln (50 mL) and brine (30 mL). The organic phase was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (52:48 hexane–EtOAc) to yield **GLU-15** (0.65 g, 70%) as a foam. R_f 0.28 (1:1 hexanes–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.40−7.25 (m, 18 H), 7.25−7.18 (m, 7 H), 5.67 (d, 1 H, *J* = 3.6 Hz, H-1α), 5.29 (dd, 1 H, *J* = 9.6, 9.6 Hz), 5.10−5.02 (m, 2 H), 4.93 (d, 1 H, *J* = 3.5 Hz, H-1α), 4.85 (dd, 2 H, *J* = 3.8, 7.5 Hz), 4.79 (dd, 1 H, *J* = 3.5, 10.0 Hz), 4.74−4.69 (m, 2 H), 4.64−4.56 (m, 6 H), 4.20−4.10 (m, 3 H), 3.99−3.94 (m, 2 H), 3.89−3.83 (m, 3 H), 3.77 (dd, 1 H, *J* = 3.6, 9.4 Hz), 3.72 (dd, 1 H, *J* = 2.1, 11.1 Hz), 3.70−3.64 (m, 2 H), 3.55−3.40 (m, 4 H), 3.32 (dd, 1 H, *J* = 1.5, 11.1 Hz), 3.28 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.80−2.72 (m, 1 H),

2.56−2.46 (m, 2 H), 2.27−2.20 (m, 1 H), 2.18 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 1.86 (s, 3 H), 1.72−1.58 (m, 4 H), 1.44−1.33 (m, 8 H); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 207.2, 171.5, 171.1, 171.0, 170.3, 138.6, 138.3(7), 138.3(5), 138.3, 137.7, 128.4(3), 128.4(0), 128.4, 128.3(1), 128.3, 128.1, 127.9(2), 127.9, 127.7, 127.5(4), 127.5, 127.4, 127.3, 96.4 (C-1), 95.8 (C-1), 95.5 (C-1), 82.2, 80.6, 79.4, 79.2, 75.2, 74.5, 73.3, 73.2(2), 73.2, 73.1, 71.5, 70.8, 70.2, 69.6, 69.5(2), 69.5, 69.3, 69.0, 68.3, 65.8, 62.7, 51.5, 37.6, 29.9, 29.4, 29.3, 29.1, 28.9, 27.8, 26.7, 26.1, 21.0, 20.9, 20.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{72}H_{89}N_3O_{21}Na$: 1354.5881. Found: 1354.5877.

8-Azidooctyl 2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-3,6-di-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-16). A mixture of sulfoxide donor **GLU-8**[22] (0.14 g, 0.29 mmol), 1,3,5-trimethoxybenzene (0.074 g, 0.44 mmol), 2,6-di-*t*-butyl-4-methyl pyridine (0.12 g, 0.59 mmol), and activated 4 Å molecular sieves (0.15 g) in CH_2Cl_2 (2 mL) was stirred for 1 h. After cooling to −10 °C, trifluoromethanesulfonic anhydride (0.055 mL, 0.32 mmol) was added. After 30 min, the reaction mixture was cooled to −40 °C and a solution of **GLU-15** (0.31 g, 0.24 mmol) in CH_2Cl_2 (1 mL) was added slowly. The temperature of the reaction mixture was kept at −40 °C for 60 min and then warmed to rt. After stirring for 15 h at rt, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and the filtrate was concentrated to a residue that was purified by chromatography (65:35 hexanes–EtOAc) to yield **GLU-16** (0.15 g, 32%) as a foam. R_f 0.39 (1:1 hexanes–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.36−7.12 (m, 35 H), 7.12−7.08 (m, 2 H), 6.20 (s, 2 H), 5.76 (d, 1 H, J = 3.2 Hz, H-1α), 5.68 (d, 1 H, J = 3.5 Hz, H-1α), 5.62 (dd, 1 H, J = 9.6, 9.6 Hz), 5.37 (dd, 1 H, J = 9.4, 9.4 Hz), 5.08−5.00 (m, 3 H), 4.86−4.79 (m, 3 H), 4.77 (d, 1 H, J = 3.6 Hz, H-1α), 4.71 (d, 1 H, J = 12.0 Hz), 4.63−4.50 (m, 8 H), 4.50−4.38 (m, 3 H), 4.21−3.95 (m, 6 H), 3.95−3.70 (m, 14 H), 3.70−3.63 (m, 2 H), 3.55−3.35 (m, 4 H), 3.28 (dd, 2 H, J = 7.0, 7.0 Hz), 3.02 (dd, 1 H, J = 3.7, 13.9 Hz), 2.92 (dd, 1 H, J = 8.3, 13.9 Hz), 2.74−2.66 (m, 1 H), 2.64−2.58 (m, 1 H), 2.49−2.42 (m, 1 H), 2.39−2.32 (m, 1 H), 2.14 (s, 3 H), 2.12 (s, 3 H), 2.04 (s, 3 H), 1.99 (s, 3 H), 1.94 (s, 3 H), 1.70−1.58 (m, 4 H), 1.44−1.34 (m, 8 H), 1.31 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.5, 171.2, 170.8, 170.5, 169.7, 169.4, 162.1, 161.6, 142.1, 139.0, 138.7, 138.3, 138.2, 137.8, 137.6, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.6(3), 127.6, 127.6, 127.5, 127.4, 127.2, 126.9, 126.6, 126.3, 101.1, 98.3 (C-1), 96.5 (C-1), 96.2 (C-1), 95.9 (C-1), 91.1(3), 91.1, 85.3, 81.9, 81.2, 80.2, 79.3, 79.0, 76.7, 76.5, 75.0, 73.6, 73.3, 73.0(9),

73.0(7), 72.9(1), 72.9, 71.4, 70.4, 70.3, 69.6, 69.5, 69.3, 69.0, 68.8(1), 68.8, 68.2, 65.7, 63.2, 63.1, 56.1, 56.0, 55.4, 51.5, 43.0, 37.9, 29.7, 29.3(9), 29.3(6), 29.1, 28.9, 27.9, 26.7, 26.1, 21.4, 20.9, 20.8(4), 20.8, 20.7, 20.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{106}H_{127}N_3O_{31}SNa$: 1992.8066. Found: 1992.8046.

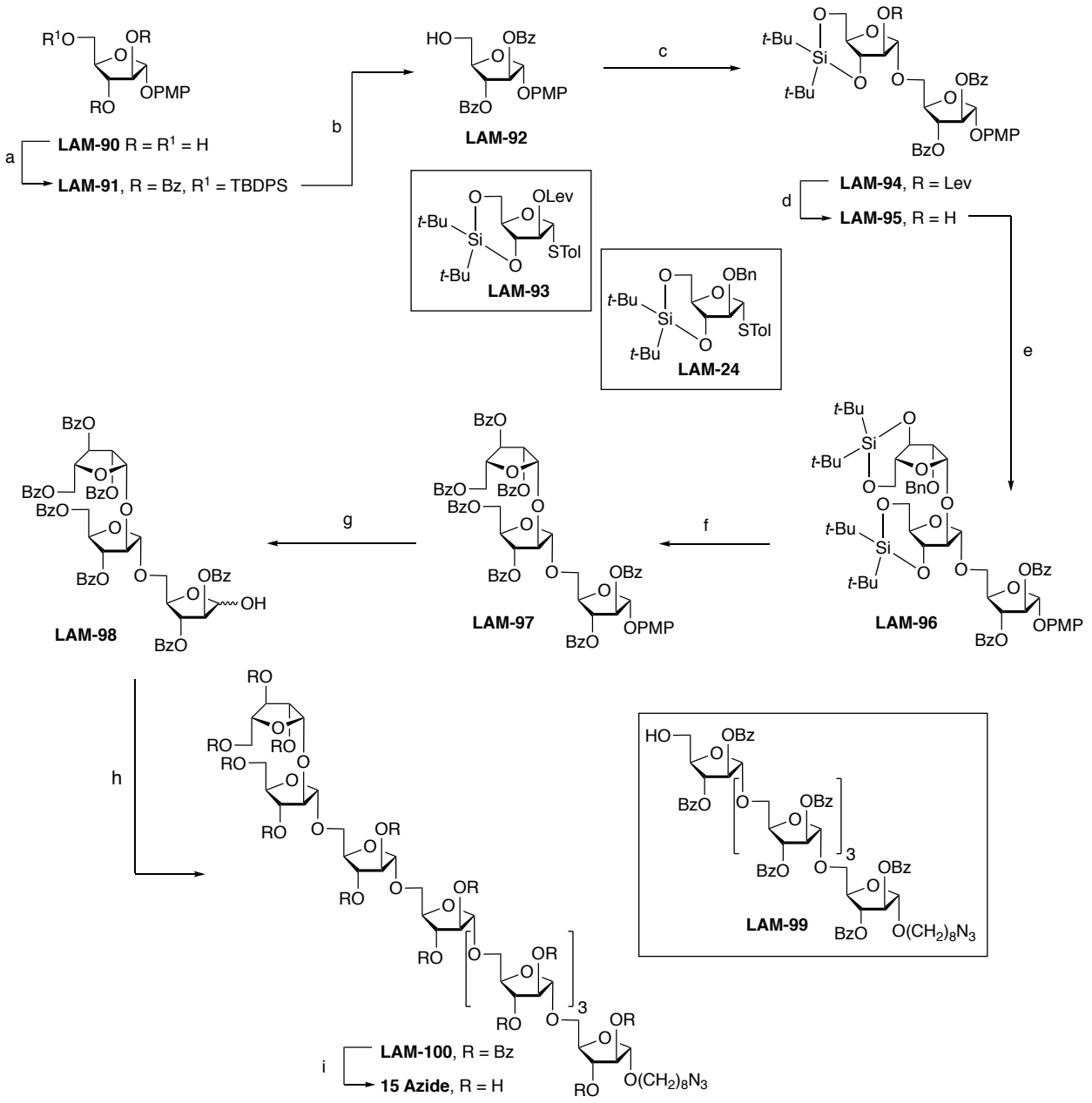
8-Azidooctyl 2,3,6-tri-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-17). Prepared from **GLU-16** (0.2 g, 0.10 mmol) in CH_2Cl_2 (10 mL) and trifluoroacetic acid (0.5 mL) as described for the reaction of compound **GLU-9** to give the corresponding alcohol as a syrup. After drying under vacuum for 2 h, the compound was dissolved in pyridine (7 mL), acetic anhydride (1.0 mL, 10.5 mmol) was added and the solution was heated at 50 °C overnight. The reaction mixture was cooled to rt, CH_3OH (1.0 mL) was added, and then the solution was poured into satd aq $NaHCO_3$ soln (20 mL) and extracted with CH_2Cl_2 (15 mL). The organic layer was washed with water (15 mL), 12% aq copper sulfate solution (until the pyridine was completely removed as determined by TLC), dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (55:45 hexane–EtOAc) to yield **GLU-17** (0.11 g, 63% over two steps). R_f 0.37 (1:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.15 (m, 30 H), 5.66 (d, 1 H, *J* = 3.5 Hz, H-1α), 5.54 (dd, 1 H, *J* = 8.6, 9.7 Hz), 5.46 (dd, 1 H, *J* = 10.3, 10.3 Hz), 5.36 (d, 1 H, *J* = 4.0 Hz, H-1α), 5.10−5.04 (m, 2 H), 5.01 (d, 1 H, *J* = 3.9 Hz, H-1α), 4.87−4.78 (m, 4 H), 4.75−4.69 (m, 2 H), 4.65−4.50 (m, 7 H), 4.44 (dd, 1 H, *J* = 2.2, 12.3 Hz), 4.33 (dd, 1 H, *J* = 2.0, 12.1 Hz), 4.28−4.18 (m, 2 H), 4.13 (dd, 1 H, *J* = 8.8, 8.8 Hz), 4.05 (d, 1 H, *J* = 9.0, 9.0 Hz), 4.0−3.62 (m, 12 H), 3.52−3.41 (m, 3 H), 3.36 (d, 1 H, *J* = 1.5, 11.7 Hz), 3.29 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.84−2.76 (m, 1 H), 2.71−2.62 (m, 1 H), 2.56−2.48 (m, 1 H), 2.43−2.36 (m, 1 H), 2.18 (s, 3 H), 2.14 (s, 3 H), 2.11 (s, 3 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 2.00 (s, 3 H), 1.88 (s, 3 H), 1.73−1.60 (m, 4 H), 1.46−1.34 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.6, 171.2, 171.1, 170.5(2), 170.5, 170.4, 169.5, 139.0, 138.7, 138.3, 137.8, 137.2, 128.6, 128.4(0), 128.4, 128.3(3), 128.3(0), 128.2(4), 128.2, 128.1(3), 128.1, 127.8(4), 127.8(2), 127.7, 127.6(4), 127.6(0), 127.4, 127.1, 126.8, 96.5 (C-1), 96.2 (C-1), 96.0 (C-1), 95.6 (C-1), 81.9, 80.3, 79.2, 78.9, 75.4, 75.0, 74.6, 74.1, 73.3, 73.1, 72.8, 72.7, 72.6, 71.5, 71.4, 70.5, 70.3, 69.7, 69.6, 69.5, 69.2, 68.3, 67.5, 65.8, 62.7, 62.2, 51.5, 37.9, 29.8, 29.3(8), 29.3(6), 29.1, 28.9, 28.0, 26.7, 26.1, 21.0, 20.8(7), 20.8(5), 20.7, 20.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{91}H_{111}N_3O_{29}Na$: 1732.7195. Found: 1732.7175.

8-Trifluoroacetamidooctyl 4-*O*-Benzyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (GLU-18). Compound **GLU-17** (0.11 g, 0.06 mmol) was dissolved in CH_2Cl_2–CH_3OH (3:1, 6 mL) and 1M methanolic sodium methoxide solution was added until the pH of the solution was 8–9 (as determined by wet pH paper). The reaction mixture was stirred at rt overnight, neutralized by the addition of Amberlite IR 120 H+ resin, filtered and then concentrated to give a crude residue that was purified by chromatography (92:8, CH_2Cl_2–CH_3OH) to yield the corresponding deacylated compound (0.085 g) as a thick syrup; R_f 0.45 (9:1 CH_2Cl_2–CH_3OH). The compound (0.14 g, 0.09 mmol) was dissolved in pyridine (4 mL), 20% $Pd(OH)_2$–C (44 mg) was added and the solution was stirred under H_2 (1 atm) for 3 h. The solution was filtered and the filter cake washed with pyridine (2 mL). The combined filtrate was then cooled to 0 °C and then trifluoroacetic anhydride (0.4 mL, 2.9 mmol) was added dropwise. After stirring at rt overnight, the reaction mixture was concentrated to a syrup that was redissolved in CH_2Cl_2–CH_3OH (2:1, 6 mL) and a few drops of aq ammonia solution was added and the solution was stirred for 10 min. The reaction mixture was concentrated to a syrup that was purified by chromatography (11:1 CH_2Cl_2–CH_3OH) to give **GLU-18** (0.08 g, 87% over three steps) as a foam. R_f 0.45, (9:1 CH_2Cl_2–CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$ + 3 drops of CD_3OD, δ_H) 7.40−7.10 (m, 30 H), 5.73 (d, 1 H, J = 3.5 Hz, H-1α), 5.12 (d, 1 H, J = 1.7 Hz), 5.04 (d, 1 H, J = 11.6 Hz), 4.90−4.82 (m, 2 H), 4.80−4.70 (m, 4 H), 4.68−4.48 (m, 7 H), 4.08 (dd, 1 H, J = 9.2, 9.2 Hz), 4.02 (dd, 1 H, J = 9.4, 9.4 Hz), 3.90−3.44 (m, 27 H), 3.43−3.20 (m, 7 H), 1.70−1.50 (m, 4 H), 1.40−1.20 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.4 (q, J = 36.8 Hz), 150.1, 145.9, 138.7, 138.4, 138.1, 138.0, 137.9, 137.7, 136.9, 128.4, 128.3(1), 128.3, 128.2, 128.1, 128.0, 127.9(3), 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 126.7(4), 126.7, 124.2, 121.7(4), 121.7, 114.9 (q, J = 287.4 Hz), 101.4 (C-1), 98.2 (C-1), 96.4 (C-1), 96.3 (C-1), 81.9, 81.5, 80.5, 80.0, 79.2, 77.7, 75.6, 74.7, 74.2, 74.0, 73.8, 73.3, 73.2, 72.9, 72.8, 72.4, 71.9, 71.8, 71.0, 70.7, 69.8, 69.5, 68.8, 68.3, 61.7, 60.7, 49.6, 49.4, 49.3, 49.1, 48.9, 48.8, 48.6, 39.9, 39.8, 29.3, 29.2, 29.1, 28.8, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{76}H_{94}F_3NO_{22}Na$: 1452.6112. Found: 1452.6106.

8-Trifluoroacetamidooctyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranoside (14 Trifluoroacetamide). Prepared from **GLU-17** (0.08 g, 0.06 mmol) and 20% $Pd(OH)_2$–C (65 mg) in EtOAc–CH_3OH–THF: (18 mL,

5:5:8) as described for the synthesis of **13 Trifluoroacetamide** to afford **14 Trifluoroacetamide** (0.047 g, 95%) as a foam. ^{1}H NMR (500 MHz, D_2O, δ_H) 5.36 (d, 1 H, J = 3.9 Hz, H-1α), 5.33 (d, 1 H, J = 4.0 Hz, H-1α), 4.92 (d, 1 H, J = 3.9 Hz, H-1α), 4.88 (d, 1 H, J = 3.9 Hz, H-1α), 4.02−3.35 (m, 25 H), 3.33−3.25 (m, 3 H), 1.75−1.50 (m, 4 H), 1.40−1.25 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, ^{13}C NMR (125 MHz, D_2O, δ_C) 163.0 (q, J = 35.3 Hz, 116.4 (q, J = 291.7 Hz 100.1 (C-1), 99.9 (C-1), 98.0 (C-1), 97.9 (C-1), 77.9, 77.2, 73.6, 73.5, 73.1, 72.9, 72.8, 71.8(3), 71.8, 71.4, 71.3, 71.1, 70.4, 69.5, 69.4, 68.5, 66.3, 62.5, 60.7, 60.5(3), 60.5, 48.9, 39.8, 28.6, 28.3, 28.2, 27.7, 25.8, 25.3, 22.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{34}H_{58}F_3NO_{22}Na$: 912.3295. Found: 912.3287.

12. Synthesis of 15



Scheme S16. Synthesis of **15 Azide**. a) TBDPSCl, pyridine; then BzCl, pyridine; b) HF·pyridine, pyridine, THF, 72% over three steps; c) **LAM-93**, NIS, AgOTf, CH_2Cl_2, 96%; d) H_2NNH_2, HOAc, CH_3OH, 93%; e) **LAM-24**, NIS, AgOTf, CH_2Cl_2, 71%; f) H_2, $Pd(OH)_2$–C EtOAc; then *n*-Bu_4NF, THF, HOAc; then BzCl, pyridine, 48%; g) CAN, THF, H_2O, 92%; h) Cl_3CCN, DBU, CH_2Cl_2, then **LAM-99**, TMSOTf, CH_2Cl_2, 92%; i) $NaOCH_3$, CH_3OH, CH_2Cl_2, quant.

***p*-Methoxyphenyl 2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-92)**. To a solution of **LAM-90**[1] (1.01 g, 3.9 mmol) in pyridine (10 mL) was added added *t*-butyldiphenylsilyl chloride (1.2 mL, 4.7 mmol). The reaction mixture was stirred at rt for 5 h at which point TLC indicated the full conversion of the substrate. The reaction was then cooled to 0 °C and benzoyl chloride (1.4 mL, 11.7 mmol) was added slowly. The reaction mixture was warmed to rt and stirred for 17 h before being diluted with CH_2Cl_2 and then washed with a satd aq $NaHCO_3$ soln. The organic layer was concentrated and purified by chromatography (8:1 hexanes–EtOAc) to give **LAM-91**, containing an inseparable impurity, which was carried forward to desilylation. To a solution of **LAM-91** in pyridine–THF (1:4, 30 mL) at 0 °C was added HF–pyridine (1.5 mL) dropwise. The reaction mixture was stirred for 16 h while warming to rt before being diluted with EtOAc, poured into a satd aq $NaHCO_3$ soln and extracted with EtOAc. The organic layer was washed with water, dried (Na_2SO_4), filtered and concentrated to give crude syrup that was purified by column chromatography (3:2, hexanes–EtOAc) to afford **LAM-92** (1.35 g, 72% over three steps) as a white foam. R_f 0.40 (7:3, hexanes–EtOAc); $[\alpha]_D$ +28.8 (c = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.15–8.06 (m, 4 H), 7.65–7.58 (m, 2 H), 7.52–7.45 (m, 4 H), 7.09–7.04 (m, 2 H), 6.89–6.83 (m, 2 H), 5.83 (s, 1 H, H-1), 5.80 (d, 1 H, J = 1.0 Hz), 5.57 (dd, 1 H, J = 4.0, 1.0 Hz), 4.50 (ddd, 1 H, J = 4.2, 4.0, 3.9 Hz), 4.08–4.01 (m, 2 H), 3.79 (s, 3 H), 2.35–2.30 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.1, 165.2, 155.2,149.9, 133.6(6), 133.6(2), 129.9, 129.81, 29.1, 128.9, 128.5(7), 128.5(4), 118.3, 114.6, 104.8 (C-1), 84.4, 81.9, 77.6, 62.1, 55.6. HRMS (ESI) calcd for (M+Na) $C_{26}H_{24}O_8Na$: 487.1363. Found: 487.1366.

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-94)**. Thioglycoside **LAM-93**[1] (1.54 g, 3.11 mmol) and alcohol **LAM-92** (1.22 g, 2.63 mmol) were dried over P_2O_5 under vacuum for 6 h and then dissolved in CH_2Cl_2 (40 mL) and the resulting solution was cooled to 0 °C. Powdered 4 Å molecular sieves (0.5 g) were added and the suspension was stirred for 30 min at 0 °C before *N*-iodosuccinimide (820 mg, 3.46 mmol) and silver triflate (80 mg, 0.31 mmol) were added. The reaction mixture was stirred for 15 min, neutralized with Et_3N, diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed successively with a satd aq $Na_2S_2O_3$ soln and water before being dried (Na_2SO_4), filtered and concentrated. The crude residue was purified by chromatography (3:1 hexanes–EtOAc) to afford **LAM-94** (2.10 g, 96%) as a white foam. R_f 0.35 (3:1 hexanes–EtOAc); $[\alpha]_D$ +39.8 (c = 0.4, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.13–8.09

(m, 4 H), 7.62–7.57 (m, 2 H), 7.51–7.46 (m, 4 H), 7.09–7.05 (m, 2 H), 6.87–6.83 (m, 2 H), 5.80 (s, 1 H, H-1), 5.74 (d, 1 H, J = 1.7 Hz), 5.62 (dd, 1 H, J = 4.9, 1.7 Hz), 5.17–5.15 (m, 1 H), 5.01 (d, 1 H, J = 2.1 Hz, H-1), 4.63 (ddd, 1 H, J = 4.9, 4.7, 4.4 Hz), 4.35–4.31 (m, 1 H), 4.10–4.03 (m, 3 H), 3.93–3.89 (m, 2 H), 3.78 (s, 3 H), 2.76–2.72 (m, 2 H), 2.64–2.59 (m, 2 H), 2.21 (s, 3 H), 1.04 (s, 9 H), 0.91 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.1, 171.7, 165.5, 165.3, 155.1, 150.3, 133.5, 133.3, 129.9(9), 129.9(3), 129.4, 129.1, 128.5, 128.4, 118.4, 114.6, 106.6 (C-1), 105.1 (C-1), 82.8, 82.2, 81.9, 80.3, 77.3, 73.5, 67.4(8), 67.4(0), 55.6, 37.9, 29.7, 27.8, 27.3, 26.9, 22.6, 20.0. HRMS (ESI) calcd for (M+Na) $C_{44}H_{54}O_{14}SiNa$: 857.3175. Found: 857.3167.

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-95)**. A solution of **LAM-94** (2.10 g, 2.45 mmol) and hydrazine monohydrate–HOAc (15 mL 1:2) in THF (25 mL) and CH_3OH (6 mL) was stirred for 1 h. The solvent was removed and the resulting oil was diluted with EtOAc (70 mL). The solution was washed with a satd aq $NaHCO_3$ soln (70 mL × 2) and brine (70 mL), dried (Na_2SO_4), filtered and concentrated. The crude residue was purified by cchromatography (4:1 hexanes–EtOAc) to afford **LAM-95** (1.72 g, 93%) as a white solid. R_f 0.32 (3:1 hexanes–EtOAc); $[\alpha]_D$ +35.8 (c = 0.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.14–8.07 (m, 4 H), 7.64–7.59 (m, 2 H), 7.52–7.46 (m, 4 H), 7.10–7.05 (m, 2 H), 6.88–6.84 (m, 2 H), 5.84 (s, 1 H, H-1), 5.72 (d, 1 H, J = 1.5 Hz), 5.68 (dd, 1 H, J = 4.8, 1.5 Hz), 5.02 (d, 1 H, J = 3.3 Hz, H-1), 4.58 (ddd, 1 H, J = 5.0, 4.8, 4.7 Hz), 4.31–4.28 (m, 1 H), 4.17–4.10 (m, 2 H), 4.00–3.96 (m, 2 H), 3.92–3.87 (m, 1 H), 3.84 (dd, 1 H, J = 11.3, 5.0 Hz), 3.78 (s, 3 H), 2.90 (d, 1 H, J = 4.0 Hz), 1.06 (s, 9 H), 0.95 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.6, 165.3, 155.2, 150.0, 133.6, 133.5, 129.9, 129.8, 129.2, 129.0, 128.5(7), 128.5(5), 118.3, 114.6, 108.8 (C-1), 104.9 (C-1), 82.3, 82.2, 81.5, 80.3, 81.1, 77.6, 73.8, 68.0, 67.4, 55.6, 27.4, 27.0, 22.6, 20.0. HRMS (ESI) calcd for (M+Na) $C_{39}H_{48}O_{12}SiNa$: 759.2807. Found: 759.2808.

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-96)**. To a mixture of **LAM-95** (1.81 g, 2.46 mmol), **LAM-24**[1] thioglycoside (1.49 g, 3.06 mmol), and 4 Å molecular sieves (1.0 g) in CH_2Cl_2 (120 mL) was added *N*-iodosuccinimide (860 g, 3.82 mmol) followed by silver triflate (80 mg, 0.31 mmol) at –40 °C. After stirring for 30 min, Et_3N was added. The mixture was then diluted with CH_2Cl_2 and

filtered through Celite. The filtrate was washed with a satd aq $NaHCO_3$ soln, a satd aq $Na_2S_2O_3$ soln, dried (Na_2SO_4), filtered and concentrated to give a crude residue that was purified by chromatography (8:1 hexanes–EtOAc) to afford **LAM-96** (1.90 g, 71%) as a white semi-solid. R_f 0.26 (8:1, hexanes–EtOAc); $[\alpha]_D$ –14.1 (c = 0.4, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.13–8.06 (m, 4 H), 7.63–7.57 (m, 2 H), 7.50–7.44 (m, 4 H), 7.39–7.36 (m, 2 H), 7.32–7.27 (m, 2 H), 7.24–7.20 (m, 1 H), 7.08–7.04 (m, 2 H), 6.85–6.81 (m, 2 H), 5.79 (s, 1 H, H-1), 5.72 (d, 1 H, J = 0.5 Hz), 5.64 (dd, 1 H, J = 4.9, 0.5 Hz), 5.08 (d, 1 H, J = 2.8 Hz, H-1), 5.02 (d, 1 H, J = 4.8 Hz, H-1), 4.76–4.74 (m, 2 H), 4.60 (ddd, 1 H, J = 4.9, 4.5, 4.5 Hz), 4.43 (dd, 1 H, J = 9.2, 9.1 Hz), 4.29 (dd, 1 H, J = 9.0, 5.0 Hz), 4.26 (dd, 1 H, J = 9.0, 4.8 Hz), 4.14 (dd, 1 H, J = 7.1, 2.8 Hz), 4.10–4.05 (m, 2 H), 4.02–3.93 (m, 2 H), 3.90–3.85 (m, 2 H), 3.81 (dd, 1 H, J = 9.2, 4.8 Hz), 3.78 (s, 3 H), 3.63 (ddd, 1 H, J = 9.1, 5.0, 4.8 Hz), 1.07 (s, 9 H), 1.04 (s, 9 H), 1.01 (s, 9 H), 0.94 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.5, 165.3, 155.2, 150.2, 137.8, 133.5, 133.4, 129.9 (Ar) (×4), 129.3, 129.1, 128.5, 128.4, 128.3, 128.0, 127.6, 118.2, 114.6, 107.4 (C-1'), 105.0, 99.7, 86.6, 82.3, 82.2, 80.6, 80.1, 78.1(6), 78.1(2), 74.1, 74.0, 71.8, 68.6, 67.5, 67.3, 55.6 (O*C*H$_3$), 27.5, 27.4, 27.1, 27.0, 22.6, 22.5, 20.1, 20.0. HRMS (ESI) calcd for (M+Na) $C_{59}H_{78}O_{16}Si_2Na$: 1121.4720. Found: 1121.4724.

***p*-Methoxyphenyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-97)**. To a solution of **LAM-96** (1.90 g, 1.73 mmol) in EtOAc (25 mL) was added 20% $Pd(OH)_2$–C (100 mg) and the reaction mixture was stirred under H_2 (1 atm) for 12 h. The catalyst was filtered off and the filtrate was concentrated to dryness and redissolved in THF (45 mL). 1M TBAF in THF solution (9 mL) and HOAc (1 mL) was added and the reaction mixture was stirred at rt for 30 h. The resulting mixture was filtered through a short column to remove salts and then benzoylated (20 mL pyridine and 4 mL benzoyl chloride) for 14 h. The reaction mixture was poured into a satd aq $NaHCO_3$ soln and extracted with CH_2Cl_2. The combined organic layer was washed a satd aq $NaHCO_3$ soln, dried (Na_2SO_4), filtered and concentrated to give a crude residue that was purified by chromatography (8:1 hexanes–EtOAc) to afford **LAM-97** (1.05 g, 48% over three steps) as a white semi-solid. R_f 0.31 (2:1 hexanes–EtOAc); $[\alpha]_D$ +0.1 (c = 1.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.93 (m, 12 H), 7.88–7.85 (m, 2 H), 7.61–7.55 (m, 2 H), 7.52–7.32 (m, 15 H), 7.28–7.20 (m, 4 H), 7.09–7.06 (m, 2 H), 6.86–6.82 (m, 2 H), 5.96 (dd, 1 H, J = 6.6, 5.2 Hz), 5.81 (s, 1 H, H-1), 5.77 (d, 1 H, J = 4.9 Hz, H-1), 5.72 (d, 1 H, J = 1.5 Hz),

5.70 (dd, 1 H, *J* = 5.1, 4.8 Hz), 5.44–5.39 (m, 2 H), 5.16 (s, 1 H), 4.80 (dd, 1 H, *J* = 11.7, 4.8 Hz), 4.70 (dd, 1 H, *J* = 11.7, 7.3 Hz), 4.60–4.55 (m, 3 H), 4.50 (ddd, 1 H, *J* = 7.3, 5.2, 4.8 Hz), 4.47 (dd, 1 H, *J* = 11.6, 4.4 Hz), 4.27 (dd, 1 H, *J* = 11.6, 6.4 Hz), 4.12 (dd, 1 H, *J* = 11.4, 4.5 Hz), 3.86 (dd, 1 H, *J* = 11.4, 3.3 Hz), 3.76 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0, 165.9(5), 165.9(3), 165.6(7), 165.6(1), 165.5, 165.3, 155.1, 150.1, 133.5–128.1, 118.2, 114.6, 105.9 (C-1), 104.9 (C-1), 100.4 (C-), 85.4, 82.4, 82.2, 80.3, 79.3, 78.3, 77.6, 77.1, 76.4, 66.0, 65.8, 64.3, 55.6. HRMS (ESI) calcd for (M+Na) $C_{71}H_{60}O_{21}Na$: 1271.3519. Found: 1271.3522.

2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranose (LAM-98). Prepared from compound **LAM-97** (0.4 g, 0.3 mmol) in CH_3CN–H_2O (35 mL 4:1) and CAN (0.9 g, 1.6 mmol) as described for the synthesis of **LAM–41**, to afford **LAM-98** (0.34 g, 92%, 7:3 diastereomeric mixture) as a foam. R_f 0.18 (7:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.86 (m, 14 H), 7.65–7.33 (m, 17 H), 7.32–7.25 (m, 4 H), 6.00–5.94 (m, 1 H), 5.94–5.91 (m, 0.3 H), 5.81 (d, 0.3 H), 5.76 (d, 0.7 H, *J* = 4.8 Hz), 5.74–5.70 (m, 0.3 H), 5.60 (d, 0.7 H, *J* = 3.7 Hz), 5.56 (dd, 0.7 H, *J* = 1.6, 5.2 Hz), 5.53–5.46 (m, 2 H), 5.45–5.40 (m, 1 H), 5.33–5.32 (m, 0.7 H), 5.19 (s, 0.3 H), 5.16 (s, 0.7 H), 4.79–4.71 (m, 1 H), 4.69–4.45 (m, 6 H), 4.29–4.20 (m, 1.3 H), 4.09–4.03 (m, 1 H), 3.99 (d, 0.3 H, *J* = 7.4 Hz), 3.87–3.82 (m, 1 H), 3.36 (d, 0.7 H, *J* = 3.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.7, 166.5, 166.3, 166.2, 166.1, 166.0(3), 166.0(0), 165.9(6), 165.9(0), 165.8, 133.9(9), 133.9(4), 133.8(9), 133.8(3), 133.7, 133.5, 133.3, 133.2, 130.3, 130.2(3), 130.2(0), 130.1(4), 130.1(2), 130.0(8), 130.0(4), 129.9(7), 129.9(5), 129.8(6), 129.8(5), 129.7, 129.6(6), 129.6(3), 129.5(7), 129.5(4), 129.5(2), 129.5(0), 129.3, 129.2, 129.1, 128.9, 128.8(9), 128.8(7), 128.7(9), 128.7(0), 128.6(7), 128.6(4), 128.5(6), 128.5(4), 106.7 (C-1), 106.3 (C-1), 101.2 (C-1), 101.1 (C-1), 100.8 (C-1), 95.5 (C-1), 85.9, 85.7, 83.1, 81.9, 81.0, 80.8, 79.9, 79.7, 79.6, 78.7, 78.5, 78.4, 78.2, 78.0, 77.9, 76.8, 76.7(8), 75.7(4), 67.9, 67.1, 66.2, 66.0, 64.7, 64.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{64}H_{54}O_{20}Na$: 1165.3100. Found: 1165.3100.

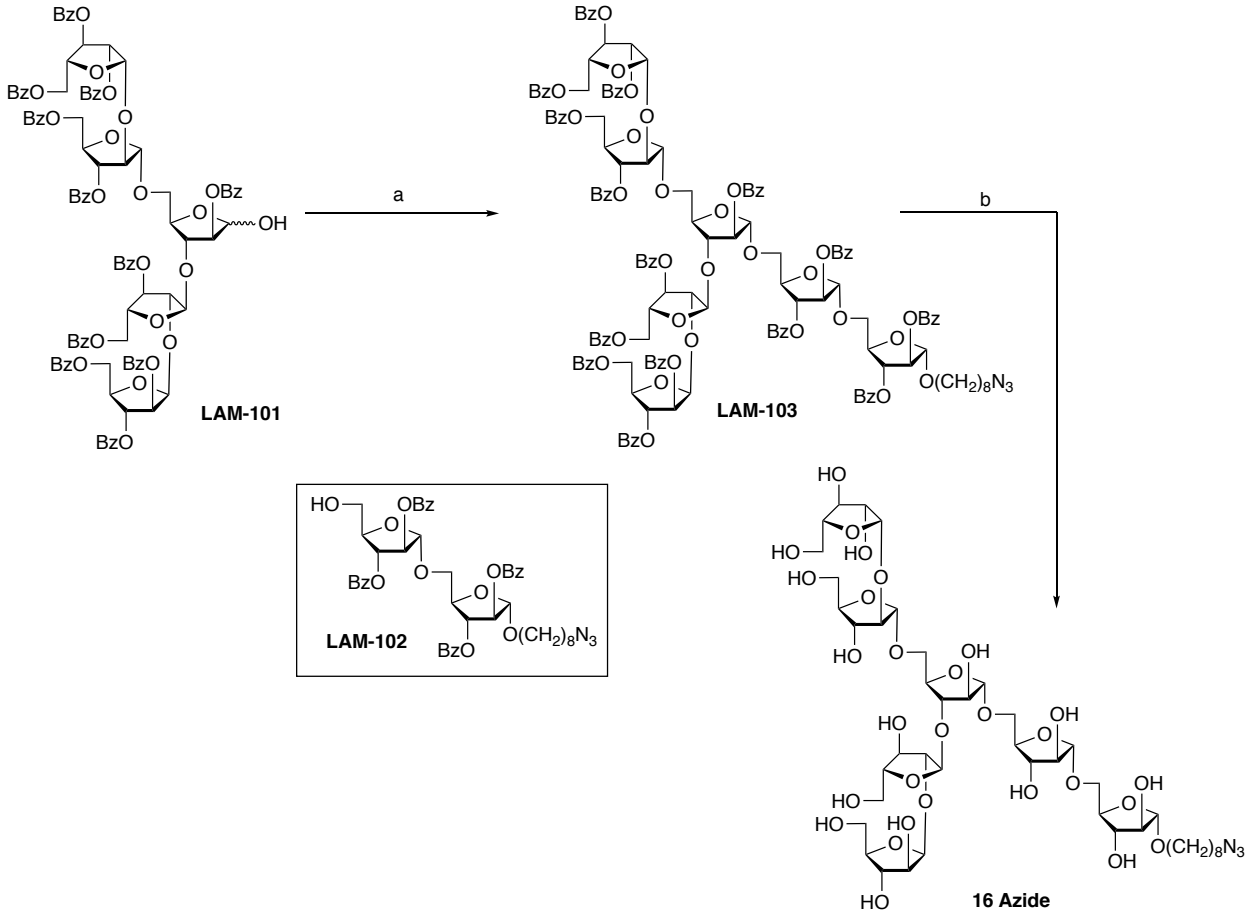
8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-100). The trichloroacetimidate derivative of the

hemiacetal **LAM-98** (0.22 g, 0.19 mmol) was prepared using DBU (10 μL) and trichloroacetonitrile (0.1 mL, 1 mmol) as described for the synthesis of **LAM-42** (Scheme S7). This was immediately subjected to coupling with alcohol **LAM-99**[1] (0.25 g, 0.13 mmol) as described for the synthesis of **LAM-43**, to afford **LAM-100** (0.4 g, 92% over two steps) as a foam. R_f 0.34 (3:2 hexanes–EtOAc); $[\alpha]_D$ –15.3 (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–7.99 (m, 18 H), 7.98–7.88 (m, 16 H), 7.88–7.82 (m, 2 H), 7.65–7.57 (m, 3 H), 7.56–7.21 (m, 46 H), 5.97 (dd, 1 H, J = 5.3, 6.7 Hz), 5.77 (d, 1 H, J = 4.8 Hz), 5.71–5.57 (m, 9 H), 5.55 (d, 1 H, J = 1.5 Hz), 5.52–5.47 (m, 2 H), 5.43–5.38 (m, 5 H), 5.37 (s, 1 H), 5.33–5.31 (m, 1 H), 5.23 (s, 1 H), 5.18–5.14 (m, 1 H), 4.75 (dd, 1 H, J = 4.8, 11.7 Hz), 4.71–4.41 (m, 11 H), 4.28–4.10 (m, 6 H), 4.10–4.02 (m, 1 H), 3.99–3.88 (m, 5 H), 3.85–3.70 (m, 2 H), 3.52 (ddd, 1 H, J = 6.2, 9.4, 12.5 Hz), 3.23 (dd, 2 H, J = 7.0, 7.0 Hz), 1.70–1.49 (m, 4 H), 1.45–1.21 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.3, 166.2(4), 166.2(0), 166.1, 166.0(4), 166.0(0), 165.9(7), 165.9(1), 165.9(0), 165.7, 165.6, 165.5, 134.0, 133.9, 133.8, 133.7, 133.6, 133.5, 133.4, 133.3(2), 133.3(0), 130.4, 130.3(1), 130.3(0), 130.1(7), 130.1(5), 130.1(1), 130.0(7), 130.0(0), 129.9(8), 129.9(1), 129.6(9), 129.6(3), 129.6(0), 129.5(7), 129.5(4), 129.4, 128.9(8), 128.9(1), 128.8, 128.7(9), 128.7(1), 128.6, 106.5 (C-1), 106.3 (C-1), 106.2(7) (C-1), 106.2(4) (C-1), 105.9 (C-1), 100.9 (C-1), 85.7, 82.4, 82.3, 82.2(8), 82.2(0), 82.1, 82.0, 80.9, 79.6, 78.7, 77.9, 77.8, 77.6(3), 77.6(1), 77.6(0), 76.9, 67.7, 66.4, 66.2, 64.7, 51.9, 29.9, 29.7, 29.5, 29.2, 27.1, 26.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{167}H_{149}N_3O_{50}Na$: 3018.9101. Found: 3018.9145.

8-Azidooctyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)- α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (15 Azide). Prepared from **LAM-100** (0.1 g, 0.033 mmol) and 1M sodium methoxide solution as described for the synthesis of **18 Azide**, to afford **15 Azide** (0.04 g, quantitative) as a fluffy solid. R_f 0.34 (6.5:3.5:0.5 CH_2Cl_2–CH_3OH–water); $[\alpha]_D$ +81.8 (c = 0.1, CH_3OH); ^{1}H NMR (600 MHz, D_2O, δ_H) 5.18 (d, 1 H, J = 2.0 Hz), 5.14 (d, 1 H, J = 4.6 Hz), 5.10–5.07 (m, 5 H), 5.01 (d, 1 H, J = 2.0 Hz), 4.24–4.19 (m, 6 H), 4.19–4.11 (m, 8 H), 4.11–4.03 (m, 4 H), 4.03–3.97 (m, 6 H), 3.94–3.65 (m, 20 H), 3.59 (ddd, 1 H, J = 6.5, 9.9, 13.0 Hz), 3.32 (dd, 2 H, J = 7.0, 7.0 Hz), 1.65–1.58 (m, 4 H), 1.40–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 108.4 (C-1), 108.1 (C-1), 106.6 (C-1), 101.5 (C-1), 87.6, 83.8, 83.2, 83.1, 82.9, 82.6, 81.7, 81.6(9), 77.6(7), 77.6(1), 77.6(0), 77.4, 77.1,

75.7, 75.0, 69.4, 67.8, 67.7, 63.8, 61.5, 52.1, 29.4, 29.1, 29.0, 28.8, 26.7, 25.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{48}H_{81}N_3O_{33}Na$: 1250.4644. Found: 1250.4642.

13. Synthesis of 16



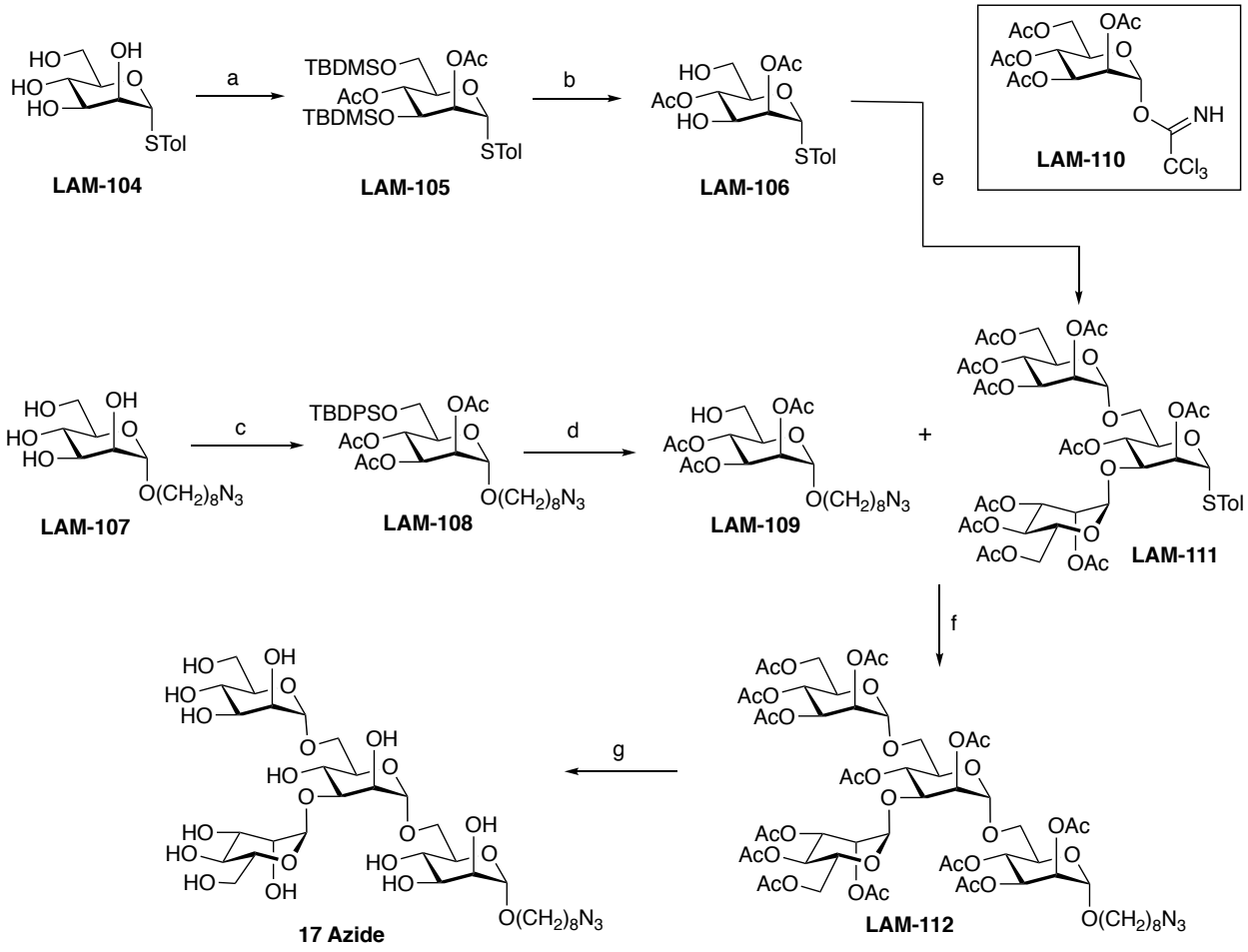
Scheme S17. Synthesis of **16 Azide**. a) Cl_3CCN, DBU, CH_2Cl_2, then **LAM-102**, TMSOTf, CH_2Cl_2, 69%; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, quant.

8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-103). The trichloroacetimidate derivative of the pentasaccharide hemiacetal **LAM-101**[1] (0.23 g, 0.13 mmol) was prepared using DBU (10 μL) and trichloroacetonitrile (0.1 mL, 1 mmol) as described for the synthesis of compound **LAM-42** (Scheme S7). This was immediately subjected to coupling with **LAM-102**[23] (0.075 g, 0.09 mmol) using TMSOTf (2 μL) as the activator as described for the synthesis of **LAM-43**, to afford **LAM-103** (0.16 g, 69% over two steps) as a glassy solid. R_f 0.27 (65:35 hexanes–EtOAc); $[\alpha]_D$ –29.9 (c = 0.30, $CHCl_3$); ^{1}H NMR (500 MHz,

$CDCl_3$, δ_H) 8.08–7.78 (m, 29 H), 7.60–7.10 (m, 46 H), 5.94 (dd, 1 H, *J* = 5.3, 6.6 Hz), 5.89 (dd, 1 H, *J* = 5.2, 6.3 Hz), 5.71 (dd, 2 H, *J* = 5.2, 5.2 Hz), 5.61 (d, 1 H, *J* = 4.3 Hz, H-1), 5.58 (d, 1 H, *J* = 1.2 Hz, H-1), 5.55 (d, 1 H, *J* = 4.7 Hz, H-1), 5.55 (dd, 1 H, *J* = 4.7, 6.4 Hz), 5.49 (s, 1 H, H-1), 5.43–5.35 (m, 6 H), 5.33–5.29 (m, 1 H), 5.20 (s, 1 H, H-1), 5.09 (s, 1 H, H-1), 4.78–4.70 (m, 2 H), 4.69–4.61 (m, 2 H), 4.58 (dd, 1 H, *J* = 4.5, 8.1 Hz), 4.56 (d, 1 H, *J* = 1.3 Hz), 4.52–4.27 (m, 10 H), 4.21 (dd, 1 H, *J* = 4.6, 11.2 Hz), 4.16–4.02 (m, 3 H), 3.99–3.88 (m, 3 H), 3.76–3.70 (m, 2 H), 3.48 (ddd, 1 H, *J* = 6.3, 9.5, 12.5 Hz), 3.21 (dd, 2 H, *J* = 6.9, 6.9 Hz), 1.65–1.52 (m, 4 H), 1.39–1.25 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.9(5), 165.9(3), 165.8, 165.7, 165.6(2), 165.6(4), 165.5, 165.4, 165.3(8), 165.3(3), 165.2, 133.5(2), 133.5(0), 133.4, 133.3(7), 133.3(3), 133.2, 133.1, 133.0, 132.8, 132.7, 129.9, 129.8, 129.7(6), 129.7(4), 129.7(0), 129.6(5), 129.6(0), 129.4, 129.3, 129.2, 129.13, 129.11, 129.07, 129.02, 128.97, 128.8, 128.76, 128.5, 128.4(7), 128.4(4), 128.4(0), 128.3, 128.2(8), 128.2(2), 128.1(7), 128.1(6), 128.1(2), 106.5 (C-1), 105.9 (C-1), 105.8 (C-1), 105.5 (C-1), 105.2 (C-1), 100.3 (C-1), 100.2 (C-1), 84.9, 84.8, 83.4, 82.0, 81.9, 81.8, 81.6, 80.7, 80.6(5), 80.6(2), 79.3, 79.1, 78.1, 78.0, 77.4(8), 77.4(0), 77.3, 77.0, 76.8, 76.5, 67.3, 66.2, 65.8, 65.7, 64.4, 64.2, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{148}H_{133}N_3O_{44}Na$: 2678.8154. Found: 2678.8129.

8-Azidooctyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (16 Azide). Prepared from compound **LAM-103** (0.09 g, 0.03 mmol) and 1M methanolic sodium methoxide solution as described for the synthesis of **18 Azide**, to afford **16 Azide** (0.037 g, quantitative) as a fluffy solid. $[\alpha]_D$ +53.6 (*c* = 0.2, CH_3OH); ^{1}H NMR (500 MHz D_2O, δ_H) 5.24 (d, 1 H, *J* = 1.8 Hz, H-1), 5.17 (d, 1 H, *J* = 1.7 Hz, H-1), 5.14 (d, 1 H, *J* = 4.6 Hz, H-1), 5.13 (d, 1 H, *J* = 4.6 Hz, H-1), 5.11 (s, 1 H, H-1), 5.07 (d, 1 H, *J* = 1.5 Hz, H-1), 5.01 (d, 1 H, *J* = 2.0 Hz, H-1), 4.32–4.27 (m, 2 H), 4.22–4.17 (m, 3 H), 4.17–3.96 (m, 14 H), 3.96–3.81 (m, 7 H), 3.81–3.75 (m, 5 H), 3.74–3.64 (m, 5 H), 3.60–3.53 (m, 1 H), 3.31 (dd, 2 H, *J* = 6.9, 6.9 Hz), 1.64–1.56 (m, 4 H), 1.40–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 108.4 (C-1), 108.3 (C-1), 108.1 (C-1), 106.5 (C-1), 106.4 (C-1), 101.6 (C-1), 101.5 (C-1), 87.9, 87.7, 83.8, 83.7, 83.4, 83.1, 82.1, 82.6, 82.5, 81.8, 80.0, 77.5, 77.4, 77.1, 75.7, 75.6, 75.0, 74.9, 69.4, 67.8, 67.3, 67.2, 63.8, 63.7, 61.5, 61.5, 52.1, 29.5, 29.1, 29.0, 28.8, 26.7, 25.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{43}H_{73}N_3O_{29}Na$: 1118.4221. Found: 1118.4220.

14. Synthesis of 17



Scheme S18. Synthesis of **17 Azide**. a) TBDMSCl, pyridine; then Ac_2O, pyridine, 91%; b) HF·pyridine, THF, pyridine, 81%; c) TBDPSCl, pyridine, then Ac_2O, pyridine, 96%; d) HF·pyridine, THF, pyridine, 95%; e) **LAM-110**, TMSOTf, CH_2Cl_2, 79% f) NIS, AgOTf, CH_2Cl_2, 86%; g) $NaOCH_3$, CH_3OH, 86%.

***p*-Tolyl 2,4-di-*O*-acetyl-3,6-di-*O*-*t*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (LAM-105):** To a solution of **LAM-104**[24] (3.0 g, 10.48 mmol) in pyridine (50 mL) was added TBDMSCl (3.47 g, 23.05 mmol). The reaction mixture was stirred at rt for 12 h and then acetic anhydride (1.90 mL, 23.05 mmol) was added and the solution was stirred for another 6 h. The mixture was diluted with CH_2Cl_2 (60 mL), washed with aq HCl (1M, 45 mL), satd aq soln of $NaHCO_3$, brine and then dried ($MgSO_4$) and filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (4:1 hexanes–EtOAc) to give **LAM-105** (5.70 g, 91%) as a foam. R_f 0.23 (4:1 hexanes–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.41 (d, 2 H, *J*

= 8.4 Hz), 7.10 (dd, 2 H, *J* = 0.5, 8.4 Hz), 5.34 (d, 1 H, *J* = 1.0 Hz, H-1), 5.31 (dd, 1 H, *J* = 1.5, 3.0 Hz), 5.15 (dd, 1 H, *J* = 10.0 Hz), 4.26 (ddd, 1 H, *J* = 3.0, 6.5, 9.5 Hz), 4.06 (dd, 1 H, *J* = 3.5, 9.0 Hz), 3.75 (dd, 1 H, *J* = 6.0, 11.0 Hz), 3.68 (dd, 1 H, *J* = 2.4, 11.0 Hz), 2.32 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 0.89 (s, 9 H), 0.84 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (150.86 MHz, $CDCl_3$, δ_c) 170.2, 169.6, 138.0, 132.5, 129.9, 129.8, 86.5 (C-1), 73.5, 72.9, 69.9, 69.2, 63.0, 25.9(4), 25.9(1), 25.4, 21.1(1), 21.1(0), 20.9, 18.4, 17.8, –4.8, –5.1, –5.3, –5.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{39}H_{54}O_7SSi_2Na$: 745.3128. Found: 745.3127.

***p*-Tolyl 2,4-di-*O*-acetyl-1-thio-α-D-mannopyranoside (LAM-106)**. To a solution of **LAM-105** (3.5 g, 5.85 mmol) in THF (25 mL) and pyridine (25 mL) at 0 °C was added dropwise 70% HF·pyridine (1.65 mL, 18.38 mmol) over 5 min. The mixture was stirred at rt for 12 h, diluted with EtOAc (70 mL) then a satd aq soln of $NaHCO_3$ was added. The organic layer was washed with brine, dried (Na_2SO_4) filtered and concentrated to give a residue that was purified by chromatography (1:2 hexanes–EtOAc) to give **LAM-106** (1.75 g, 81%) as colorless syrup. R_f 0.19 (1:2 hexanes–EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.38–7.35 (m, 2 H), 7.14–7.12 (m, 2 H), 5.48 (d, *J* = 1.2 Hz, 1 H, H-1), 5.37 (dd, *J* = 1.2, 3.6 Hz, 1 H), 5.14 (dd, *J* = 10.2 Hz, 1 H), 4.26 (ddd, *J* = 2.4, 4.2, 10.2 Hz, 1 H), 4.13 (ddd, *J* = 3.6, 7.8, 10.2 Hz, 1 H), 3.72–3.63 (m, 2 H), 2.58 (d, *J* = 7.8 Hz), 2.35 (d, *J* = 0.6 Hz), 2.33 (s, 3 H), 2.16 (s, 3 H), 2.15 (s, 3 H); ^{13}C NMR (150.86 MHz, $CDCl_3$, δ_c) 171.8, 170.5, 138.4, 132.6, 130.0, 129.0, 128.2, 86.1 (C-1), 73.8, 71.3, 69.8, 68.9, 61.3, 21.1, 20.9, 20.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{17}H_{22}O_7SNa$: 393.0983. Found: 393.0975.

8-Azidooctyl 2,3,4-tri-*O*-acetyl-6-*O*-*t*-butyldiphenylsilyl-α-D-mannopyranoside (LAM-108). To a solution of **LAM-107**[2] (1.05 g, 3.15 mmol) in pyridine (27 mL) was added *t*-butyldiphenylsilyl chloride (0.97 mL, 3.78 mmol). The reaction mixture was stirred at rt for 12 h and then acetic anhydride (1.07 mL, 11.34 mmol) was added and the solution was stirred for another 6 h. The mixture was diluted with EtOAc and washed with aq 1M HCl, a satd aq soln of $NaHCO_3$, brine dried ($MgSO_4$) and filtered. After concentration of the filtrate, the resulting residue was purified by chromatography (1:1 hexanes–EtOAc) to give **LAM-108** (2.11 g, 96% yield) as a foam. R_f 0.33 (1:1 hexanes–EtOAc); $[\alpha]_D$ +38.2 (*c* = 0.3, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.80–7.60 (m, 4 H), 7.50–7.30 (m, 6 H), 5.40–5.27 (m, 2 H), 5.21 (dd, 1 H *J* = 2.0, 2.8 Hz), 4.82 (d, 1 H, *J* = 1.6 Hz, H-1), 3.89–3.65 (m, 4 H), 3.43 (ddd, 1 H, *J* = 6.0, 6.6, 9.6 Hz), 3.24 (dd, 2 H, *J* = 6.8, 7.2 Hz), 2.12 (s, 3 H), 1.98 (s, 3 H), 1.88 (s, 3 H), 1.66–1.5 (m, 4 H),

1.46–1.24 (m, 8 H), 1.06 (s, 9 H); ^{13}C NMR (100.54 MHz, $CDCl_3$, δ_C) 169.8, 169.7, 169.2, 135.2, 132.5, 132.4, 129.5, 127.4, 96.7 (C-1), 71.0, 69.6, 69.1, 67.6, 66.1, 62.5, 51.0, 28.8, 28.6, 28.4, 26.3, 26.2, 25.6, 20.5, 20.4, 20.2, 18.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{36}H_{51}N_3O_9SiNa$: 720.3287. Found: 720.3274.

8-Azidooctyl 2,3,4-tri-*O*-acetyl-α-D-mannopyranoside (LAM-109). To a solution of **LAM-108** (1.05 g, 1.51 mmol) in THF (10 mL) and pyridine (10 mL) at 0 °C was added dropwise 70% HF·pyridine (0.32 mL, 3.27 mmol)) over 5 min. The mixture was stirred at rt for 12 h, diluted with EtOAc (25 mL) then a satd aq soln of $NaHCO_3$ was added carefully. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by chromatography (3:1 hexanes–EtOAc) to give **LAM-109** (0.66 g, 95%) as a colorless syrup. R_f 0.29 (3:1 hexanes–EtOAc); $[\alpha]_D$ +46.7 (*c* = 0.9, $CDCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 5.40 (dd, 1 H *J* = 3.6, 10.2 Hz), 5.25–5.21 (m, 2 H), 4.80 (d, 1 H, *J* = 1.8 Hz, H-1), 3.77 (ddd, 1 H, *J* = 2.4, 4.2, 9.6 Hz), 3.71–3.58 (m, 3 H), 3.43 (ddd, 1 H, *J* = 6.6, 6.6, 9.6 Hz), 3.26 (dd, 2 H, *J* = 6.6, 7.2 Hz), 2.35 (dd, 1 H, *J* = 6.0, 9.0 Hz), 2.15 (s, 3 H), 2.07 (s, 3 H), 2.00 (s, 3 H), 1.63–1.57 (m, 4 H), 1.39–1.32 (m, 8 H); ^{13}C NMR (150.9 MHz, $CDCl_3$, δ_C) 170.8, 170.1, 169.9, 97.6 (C-1), 70.5, 69.8, 68.9, 68.4, 66.6, 61.3, 51.4, 29.2(2), 29.1(7), 29.0, 28.8, 26.6, 26.0, 20.9, 20.7(4), 20.7(2). HRMS (ESI) *m/z* calcd for (M+Na) $C_{20}H_{33}N_3O_9Na$: 482.2109. Found: 482.2099.

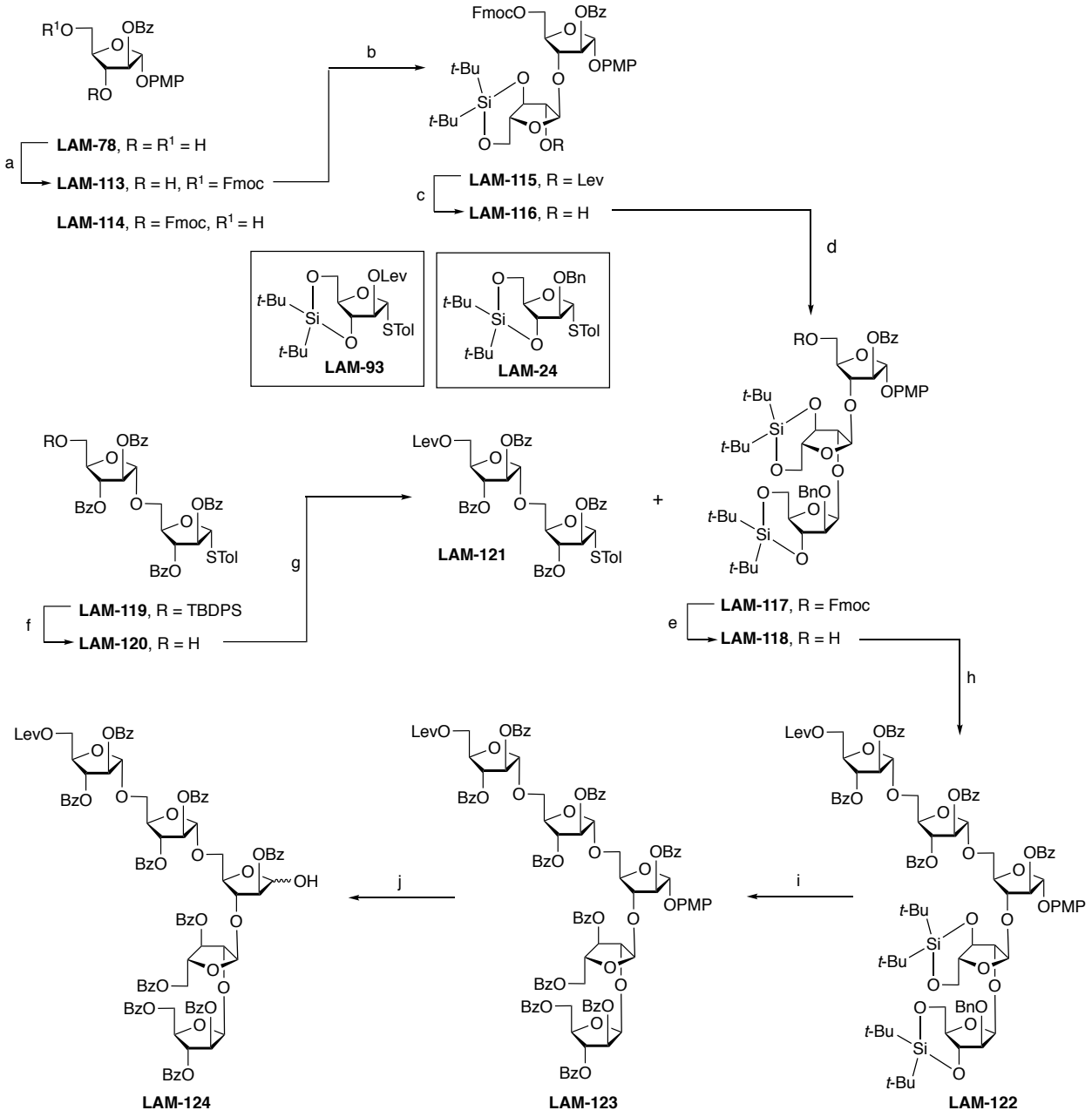
p-Tolyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-acetyl-1-thio-α-D-mannopyranoside (LAM-111). Trichloroacetimidate (**LAM-110**)[24] in CH_2Cl_2 (8 mL) was added to a solution of alcohol **LAM-106** (0.36 g, 0.97 mmol) in CH_2Cl_2 (12 mL) containing 4 Å molecular sieves (0.3 g) at –20 °C. A solution of TMSOTf (0.04 mL, 0.21 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise over a period of 5 min. The reaction mixture was then warmed to 15 °C over 45 min and then Et_3N was added. The solution was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated to syrup that was purified by chromatography (1:1 hexanes–EtOAc) to give **LAM-111** (1.75 g, 79%) as a foam. R_f 0.21 (4:1 hexanes–EtOAc); $[\alpha]_D$ +73.2 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.34–7.33 (m, 2 H), 7.16–7.13 (m, 2 H), 5.48 (dd, 2 H, *J* = 1.8, 3.6 Hz), 5.37 (d, 1 H, *J* = 1.2 Hz), 5.31–5.21 (m, 6 H), 5.03–5.02 (m, 2 H), 4.79 (s, 1 H), 4.39 (ddd, 1 H, *J* = 2.4, 6.0, 9.0 Hz), 4.27–4.23 (m, 2 H), 4.13 (dd, 1 H, *J* = 3.0, 9.6 Hz), 4.10–3.97 (m, 4 H), 3.80 (dd, 1 H, *J* = 5.39, 10.8 Hz), 3.52 (dd, 1 H, *J* = 3.0, 10.54 Hz), 2.31 (s, 3 H), 2.20 (s, 3 H), 2.16 (s, 3 H), 2.15 (s, 3

H), 2.14 (s, 3 H), 2.13 (s, 3 H), 2.08 (s, 3 H), 2.05 (s, 3 H), 2.05 (s, 3 H), 1.98 (s, 3 H), 1.98 (s, 3 H); ^{13}C NMR (150.86 MHz, $CDCl_3$, δ_c) 170.7, 170.6, 170.4, 170.0, 169.9, 169.8, 169.7, 169.5(3), 169.5(0), 138.4, 132.5, 130.0, 128.9, 98.9 (C-1), 97.8 (C-1), 86.3 (C-1), 77.0, 76.8, 75.0, 72.3, 70.2, 69.9, 69.9, 69.5, 69.3, 69.1, 69.0, 68.6, 68.4, 68.2, 67.1, 66.0, 62.6, 62.2, 21.1(2), 21.1(0), 20.8(4), 20.8(1), 20.7(2), 20.7(0), 20.7, 20.6(2), 20.5(9). HRMS (ESI) *m/z* calcd for (M+Na) $C_{45}H_{58}O_{25}SNa$: 1053.288. Found: 1053.2866.

8-Azidooctyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-α-D-mannopyranoside (LAM-112). To a solution of **LAM-111** (120.01 mg, 0.12 mmol) and **LAM-109** (68 mg, 0.15 mmol) in dry CH_2Cl_2 (2.5 ml) was added powdered 4Å MS (500 mg), and the mixture was stirred for 20 min at rt and then cooled to –20 °C. *N*-iodosuccinimide (35.3 mg, 0.16 mmol) and silver triflate (6.31 mg, 0.025 mmol) were added to the mixture. The reaction mixture then slowly warmed to 0 °C over 30 min and then neutralized by the addition of Et_3N. The solids were filtered and washed with CH_2Cl_2. The combined filtrate and washings were successively washed with a satd aq soln of $Na_2S_2O_3$ and water, dried (Na_2SO_4), filtered and concentrated. The product was purified by chromatography (3:1 hexanes–EtOAc) to give **LAM-112** (140.91 mg, 86%) as an oil. R_f 0.19 (3:1 hexanes–EtOAc) $[\alpha]_D$ +4.3 (*c* = 0.60, $CDCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 5.36–5.20 (m, 10 H), 5.06 (dd, 1 H, *J* = 1.8, 3.0 Hz), 5.01 (d, 1 H, *J* = 1.8 Hz, H-1), 4.90 (d, 1 H, *J* = 1.8 Hz, H-1), 4.83 (d, 1 H, *J* = 1.2 Hz, H-1), 4.76 (d, 1 H, *J* = 1.8 Hz, H-1), 4.31–4.25 (m, 2 H), 4.19 (dd, 1 H, *J* = 3.0, 9.6 Hz), 4.14–4.06 (m, 4 H), 3.98–3.92 (m, 1 H), 3.81–3.74 (m, 3 H), 3.68 (ddd, 1 H, *J* = 2.39, 4.19, 9.59 Hz), 3.60 (dd, 1 H, *J* = 2.4, 12.0 Hz), 3.51 (dd, 1 H, *J* = 3.0, 10.8 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 6.6, 9.6 Hz), 3.27 (dd, 2 H, *J* = 6.6, 7.2 Hz), 2.21 (s, 3 H), 2.16 (s, 3 H), 2.15 (s, 3 H), 2.15 (s, 3 H), 2.14 (s, 3 H), 2.12 (s, 3 H), 2.11 (s, 3 H), 2.05 (s, 6 H), 2.04 (s, 3 H), 2.00 (s, 3 H), 1.99 (s, 3 H), 1.98 (s, 3 H), 1.63–1.57 (m, 5 H), 1.39–1.32 (m, 9 H); ^{13}C NMR (150.9 MHz, $CDCl_3$, δ_C) 170.6, 170.5, 170.3, 170.1, 169.9(9), 169.9(7), 169.9(5), 169.9, 169.8, 169.7(2), 169.6(7), 169.6(2), 169.5(8), 99.1, 97.5, 97.4, 97.3, 75.0, 70.7, 69.9, 69.8, 69.5, 69.4(0), 69.3(9), 69.3, 69.0, 68.6(4), 68.5(7), 68.4, 68.3, 68.1, 66.7, 66.1, 66.0, 65.8, 65.7, 62.3, 62.1, 51.4, 29.6, 29.2(4), 29.2(1), 29.0, 28.8, 26.6, 26.0(0), 25.9(7), 20.9, 20.8(4), 20.7(6), 20.7(4), 20.7(2), 20.7(1), 20.6(8), 20.6(3), 20.5(7). HRMS (ESI) *m/z* calcd for (M+Na) $C_{58}H_{83}N_3O_{34}Na$: 1388.4750. Found: 1388.4714.

8-Azidooctyl α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→3)]-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (17 Azide). To a solution of **LAM-112** (140.92 mg, 0.103 mmol) in dry CH_3OH (11 mL), was added $NaOCH_3$ (60 mg, 1.10 mmol) dissolved in 2 mL CH_3OH. The reaction mixture was stirred at rt for 12 h, and then neutralized by the addition of Amberlite IR-120 H^+ resin. The solution was filtered, concentrated and the resulting residue was purified by chromatography (99:1 EtOAc–CH_3OH) to give **17 Azide** (72.6 mg, 86%) as a white solid. R_f 0.31 (99:1 EtOAc–CH_3OH); $[\alpha]_D$ +97.7 (*c* = 0.2, CH_3OH); ^1H NMR (500 MHz, D_2O, δ_H) 5.12 (d, 1 H, *J* = 1.2 Hz, H-1), 4.92 (d, 1 H, *J* = 1.2 Hz, H-1), 4.87 (d, 1 H, *J* = 1.5 Hz, H-1), 4.86 (d, 1 H, *J* = 1.2 Hz, H-1), 4.10 (dd, 1 H, *J* = 2.0, 2.0 Hz), 4.04 (dd, 1 H, *J* = 1.6, 3.3 Hz), 3.98–3.61 (m, 23 H), 3.54 (ddd, 1 H, *J* = 5.8, 9.9, 11.6 Hz), 3.29 (dd, 2 H, *J* = 6.9, 6.9 Hz), 1.65–1.53 (m, 4 H), 1.40–1.28 (m, 8 H); ^{13}C NMR (175 MHz, D_2O, δ_C) 103.2 (C-1), 100.6 (C-1), 100.3 (C-1), 100.0 (C-1), 79.5, 74.1, 73.5, 71.7(5), 71.7(1), 71.6, 71.4, 71.2, 70.9, 70.8, 70.4, 68.7, 67.5(9), 67.5(4), 67.5(0), 66.6, 66.5, 66.1, 61.8, 61.7, 52.0, 29.2, 29.0(9), 29.0(3), 28.7, 26.6, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{32}H_{57}N_3O_{21}Na$: 842.3377. Found 842.3380.

15. Synthesis of 18



Scheme S19. Synthesis of pentasaccharide **LAM-124**, a precursor to **18 Azide**. a) FmocCl, pyridine, CH_2Cl_2, pyridine, 82% (71% **LAM-113** and 11% **LAM-114**); b) **LAM-93**, NIS, AgOTf, CH_2Cl_2; c) H_2NNH_2·HOAc, CH_3OH, CH_2Cl_2 90% over two steps; d) **LAM-24**, NIS, AgOTf, CH_2Cl_2, 70%; e) Et_3N, CH_2Cl_2, 81%; f) HF·pyridine, THF, pyridine, 99%; g) Levulinic acid, DCC, DMAP, CH_2Cl_2, 94%; h) **LAM-121**, NIS, AgOTf, CH_2Cl_2, 91%; i) H_2, $Pd(OH)_2$–C, EtOAc, CH_2Cl_2; then HF·pyridine, THF, pyridine; then BzCl, pyridine, 72%; j) CAN, CH_3CN, H_2O, 91%.

***p*-Methoxyphenyl 5-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-113)** and ***p*-Methoxyphenyl 3-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-114)** To a solution of **LAM-78**[1] (1.8 g, 5.0 mmol) in CH_2Cl_2–pyridine (20:3, 46 mL) at 0 °C under argon was added FmocCl (1.6 g, 6.0 mmol, added in three portions over 90 min). The reaction mixture was maintained at 0–10 °C for 3 h and then warmed to rt and stirred overnight. The reaction mixture was then diluted, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (73:27 hexanes–EtOAc) to yield **LAM-113** (2.06 g, 71%) and **LAM-114** (0.32 g, 11%) as thick syrups. Data for **LAM-113**: R_f 0.5 (3:2 hexanes–EtOAc); $[\alpha]_D$ +68.9 (*c* = 0.30, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.14–8.03 (m, 3 H), 7.81–7.70 (m, 3 H), 7.64–7.54 (m, 3 H), 7.50–7.36 (m, 4 H), 7.32–7.23 (m, 3 H), 7.11–7.01 (m, 3 H), 6.91–6.77 (m, 3 H), 5.85 (s, 1 H), 5.39 (dd, 1 H, *J* = 1.2, 3.2 Hz), 4.62–4.49 (m, 3 H), 4.49–4.36 (m, 3 H), 4.31–4.20 (m, 3 H), 3.78 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.9, 155.3, 155.1, 150.2, 143.3, 141.3, 133.9, 129.9, 128.8, 128.6, 127.9, 127.2, 125.2, 120.0, 118.3, 114.7, 104.9 (C-1), 86.4, 81.7, 77.3, 77.0, 76.9, 76.8, 70.2, 66.5, 55.7, 46.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{34}H_{30}O_9Na$: 605.1782. Found: 605.1788. Data for **LAM-114**: R_f 0.40 (3:2 hexanes–EtOAc); $[\alpha]_D$ +51.2 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.03 (m, 3 H), 7.82–7.74 (m, 3 H), 7.67–7.57 (m, 3 H), 7.50–7.40 (m, 4 H), 7.37–7.30 (m, 3 H), 7.10–7.04 (m, 3 H), 6.90–6.82 (m, 3 H), 5.77 (s, 1 H), 5.71 (d, 1 H, *J* = 1.6 Hz), 5.34–5.27 (m, 1 H), 4.56–4.42 (m, 3 H), 4.31 (dd, 1 H, *J* = 7.3, 7.3 Hz), 4.0 (dd, 1 H, *J* = 3.3, 12.3 Hz), 3.92 (dd, 1 H, *J* = 3.7, 12.3 Hz), 3.79 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 155.4, 154.7, 149.9, 143.2, 143.0, 141.3(3), 141.3(2), 133.6(9), 129.9, 128.9, 128.6, 127.9, 127.3, 127.2, 125.2, 125.1, 120.1, 118.5, 114.7, 104.8 (C-1), 83.5, 81.9, 80.2, 77.3, 77.1, 76.8, 70.5, 61.9, 55.7, 46.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{34}H_{30}O_9Na$: 605.1782. Found: 605.1784;

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl-α-D-arabinofuranosyl-(1→3)-5-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-116)**. Alcohol **LAM-113** (0.45 g, 0.77 mmol) was glycosylated with **LAM-93**[1] (0.5 g, 1.0 mmol), powdered 4 Å molecular sieves (0.4 g), *N*-iodosuccinimide (0.25 g, 1.1 mmol) and silver triflate (15 mg, 0.06 mmol) in CH_2Cl_2 (20 mL) as described for the synthesis of **LAM-3** to afford the corresponding crude disaccharide (**LAM-115**) after work up, which was used directly in the next step. R_f 0.19

(4:1 hexanes–EtOAc). The crude disaccharide was then dissolved in a solution of CH_2Cl_2–CH_3OH (9:1, 25 mL) and hydrazine acetate (0.25 g, 2.7 mmol) was added. After stirring for 40 min at rt, the reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (4:1 hexanes–EtOAc) to yield **LAM-116** (0.66 g, 90% over two steps) as a thick syrup. R_f 0.39 (3:1 hexanes–EtOAc); $[\alpha]_D$ +61.1 (c = 0.40, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.13–8.04 (m, 2 H) 7.80–7.70 (m, 2 H), 7.62–7.50 (m, 3 H), 7.45–7.35 (m, 4 H), 7.35–7.20 (m, 2 H), 7.10–7.01 (m, 2 H), 6.90–6.81 (m, 2 H), 5.78 (s, H), 5.59 (d, 1 H, J = 1.8 Hz, H-1), 5.23 (d, 1 H, J = 3.2 Hz, H-1), 4.60–4.54 (m, 2 H), 4.48–4.28 (m, 6 H), 4.23 (dd, 1 H, J = 7.2, 7.2 Hz), 4.03–3.84 (m, 2 H), 3.92–3.84 (m, 1 H), 3.77 (s, 3 H), 1.06 (s, 9 H), 1.01 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.7, 155.3, 155.1, 150.2, 143.3, 141.3, 133.7, 129.9, 129.0, 128.5, 127.9, 127.2, 125.2, 125.1, 120.0, 118.5, 114.6, 108.4 (C-1), 105.2 (C-1), 83.1, 82.5, 81.5, 81.4, 81.3, 77.3, 77.0, 76.8, 74.0, 70.2, 67.4, 66.2, 55.7, 46.7, 27.5, 27.1, 22.7, 20.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{47}H_{54}O_{13}SiNa$: 877.3225. Found: 877.3225.

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-5-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-117)** and ***p*-Methoxyphenyl 3,5-*O*-(Di-*t*-butylsilanediyl)-2-*O*-benzyl-α-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-5-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-117α)**. Alcohol **LAM-116** (0.63 g, 0.7 mmol) and **LAM-24**[1] (0.46 g, 0.95 mmol) were dried under vacuum in the presence of P_2O_5 for 6 h. After drying, CH_2Cl_2 (24 mL) was added followed by powdered 4 Å molecular sieves (0.4 g) and the solution was stirred for 20 min at rt. The reaction mixture was then cooled to –40 °C and *N*-iodosuccinimide (0.21 g, 0.95 mmol) and silver triflate (24 mg, 0.09 mmol) were added. After stirring the reaction mixture for 20 min at –40 °C, Et_3N was added until the pH of the solution was slightly basic as determined by wet pH paper. The reaction was diluted with CH_2Cl_2 (20 mL) and filtered through Celite. The filtrate was washed with a satd aq soln of $Na_2S_2O_3$ (20 mL), water (20 mL) and brine (20 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (9:1 hexanes–EtOAc) to yield **LAM-117** (0.64 g, 80%, 1:7 α:β mixture) as a thick syrup. Data for **LAM-117**: R_f 0.37 (85:15

hexanes–EtOAc); $[\alpha]_D$ +1.9 (*c* = 0.30, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.05 (m, 2 H), 7.79–7.74 (m, 2 H), 7.62–7.50 (m, 3 H), 7.47–7.35 (m, 6 H), 7.33–7.19 (m, 6 H), 7.07–7.00 (m, 2 H), 6.86–6.80 (m, 2 H), 5.79 (s, 1 H), 5.54 (d, 1 H, *J* = 1.0 Hz), 5.36 (d, 1 H, *J* = 3.0 Hz), 5.20 (d, 1 H, *J* = 4.8 Hz), 4.87–4.80 (m, 2 H), 4.58–4.47 (m, 3 H), 4.47–4.34 (m, 3 H), 4.34–4.27 (m, 3 H), 4.26–4.19 (m, 2 H), 4.12 (dd, 1 H, *J* =7.7, 9.3 Hz), 4.03–3.90 (m, 4 H), 3.80–3.70 (m, 4 H), 1.09 (s, 9 H), 1.05 (s, 9 H), 1.01 (s, 9 H), 1.00 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.5, 155.2, 155.1, 150.1, 143.3, 141.3, 141.2, 137.9, 133.6, 129.9, 129.1, 128.5, 128.3, 127.9, 127.9, 127.6, 127.2, 125.2, 125.2, 120.1, 120.04, 118.3, 114.6, 106.9 (C-1), 105.0 (C-1), 99.6 (C-1), 85.9, 82.7, 81.8, 81.8, 80.7, 79.9, 78.0, 74.3, 74.2, 71.8, 70.2, 68.8, 67.4, 66.3, 55.7, 46.7, 27.6, 27.5, 27.4, 27.2, 27.1(5), 27.1(1), 22.6(3), 22.6(0), 20.1(5), 20.1(0); HRMS (ESI) *m/z* calcd for (M+Na) $C_{67}H_{84}O_{17}Si_2Na$: 1239.5139. Found: 1239.5138. **Data for LAM-117α**: R_f 0.47 (85:15 hexanes–EtOAc); $[\alpha]_D$ +51.4 (*c* = 0.40, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.06 (m, 2 H), 7.79–7.75 (m, 2 H), 7.63–7.51 (m, 3 H), 7.45–7.35 (m, 8 H), 7.33–7.25 (m, 3 H), 7.08–7.03 (m, 2 H), 6.87–6.81 (m, 2 H), 5.79 (s, 1 H), 5.63 (d, 1 H, *J* = 1.1 Hz), 5.41 (d, 1 H, *J* = 2.6 Hz), 5.28 (d, 1 H, *J* = 2.8 Hz), 4.79 (ABq, 2 H, *J* = 12.0 Hz), 4.60–4.51 (m, 2 H), 4.47–4.31 (m, 6 H), 4.23 (dd, 1 H, *J* = 7.4, 7.4 Hz), 4.17–4.04 (m, 5 H), 3.96–3.86 (m, 3 H), 3.78 (s, 3 H), 1.08 (s, 9 H), 1.06 (s, 9 H), 1.02 (s, 9 H), 1.01 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 155.1(2), 155.1(0), 150.2, 143.3, 141.3, 137.9, 133.6, 129.9, 129.2, 128.5, 128.4, 127.9(1), 127.9(0), 127.8, 127.7, 127.2, 125.2, 125.2, 120.0(6), 120.0(5), 118.3, 114.6, 107.5 (C-1), 106.2 (C-1), 105.3 (C-1), 87.9, 87.7, 82.0, 81.5, 81.4, 81.1(2), 81.1(0), 74.0, 73.3, 71.9, 70.2, 67.6, 67.5, 66.5, 55.7, 46.7, 27.5(2), 27.5(0), 27.2, 27.1, 22.7, 22.6, 20.1(3), 20.1(1).

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-118)**. To a solution of **LAM-117** (0.72 g, 0.59 mmol) in CH_2Cl_2 (20 mL) at rt was added Et_3N (0.49 mL, 3.5 mmol) and the solution was stirred overnight. The reaction mixture was then directly concentrated and the residue was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-118** (0.48 g, 81%) as a foam. R_f 0.30 (3:1 hexanes–EtOAc); $[\alpha]_D$ +6.3 (*c* = 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.04–7.98 (m, 2 H), 7.61–7.56 (m, 1 H), 7.46–7.39 (m, 4 H), 7.32–7.19 (m, 3 H), 7.04–6.99 (m, 2 H), 6.85–6.81 (m, 2 H), 5.73 (s, 1 H), 5.51 (s, 1 H), 5.32 (d, 1 H, *J* = 2.7 Hz), 5.19 (d, 1 H, *J* = 4.6 Hz), 4.82 (d, 1 H, *J* = 4.2 Hz), 4.49 (dd, 1 H, *J* = 9.2, 9.2 Hz), 4.40–4.36 (m, 1 H), 4.35–4.25 (m, 3 H), 4.20 (dd, 1 H, *J* = 2.6,

7.5 Hz), 4.11 (dd, 1 H, *J* = 8.1, 8.1 Hz), 4.02–3.87 (m, 6 H), 3.84–3.69 (m, 5 H), 1.08 (s, 9 H), 1.04 (s, 9 H), 1.01 (s, 9 H), 1.0 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 155.2, 150.1, 137.9, 133.6, 129.8, 129.1, 128.5, 128.3, 127.9, 127.6, 118.4, 114.6, 106.9 (C-1), 104.9 (C-1), 99.5 (C-1), 85.8, 83.9, 83.3, 81.7, 80.6, 79.8, 78.0, 74.3, 74.2, 71.7, 68.8, 67.4, 61.6, 55.7, 27.6, 27.4, 27.2, 27.1, 27.0(9), 22.6(2), 22.6(0), 20.1, 20.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{52}H_{74}O_{15}Si_2Na$: 1017.4458. Found: 1017.4463.

***p*-Tolyl 2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-thio-α-D-arabinofuranoside (LAM-120)**. Prepared from compound **LAM-119**[23] (1.45 g, 1.4 mmol) and HF·pyridine (1.0 mL) in THF–pyridine (35 mL, 2.5:1) as described for the synthesis of **LAM-26** to afford **LAM-120** (1.1 g, 99%) as a foam. R_f 0.15 (3:1 hexanes–EtOAc); $[\alpha]_D$ +38.3 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.0 (m, 6 H), 7.96–7.91 (m, 3 H), 7.63–7.56 (m, 3 H), 7.54–7.43 (m, 7 H), 7.42–7.36 (m, 3 H), 7.31–7.25 (m, 3 H), 7.12–7.07 (m, 3 H), 5.77–5.69 (m, 3 H), 5.64 (d, 1 H, *J* = 1.2 Hz), 5.45 (d, 1 H, *J* = 4.7 Hz), 5.4 (s, 1 H), 4.71 (dd, 1 H, *J* = 4.2, 7.6 Hz), 4.48 (dd, 1 H, *J* = 4.0, 8.3 Hz), 4.23 (dd, 1 H, *J* = 4.3, 11.3 Hz), 4.04–3.88 (m, 3 H), 2.34–2.21 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 165.6, 165.3, 165.1, 137.9, 133.6, 133.5, 133.3, 132.6, 129.9, 129.8(7), 129.8(3), 129.8(1), 129.1(4), 129.1(1), 128.9(8), 128.9(5), 128.5, 128.3, 105.8 (C-1), 91.5 (C-1), 83.7, 82.1, 81.9, 77.7, 77.5, 65.9, 62.3, 21.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{45}H_{40}O_{12}SNa$: 827.2132. Found: 827.2131.

***p*-Tolyl 5-*O*-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-1-thio-α-D-arabinofuranoside (LAM-121)**. To a solution of **LAM-120** (1.08 g, 1.3 mmol), levulinic acid (0.21 mL, 2.0 mmol), and DMAP (82 mg, 0.67 mmol) in CH_2Cl_2 (32 mL) was added DCC (0.42 g, 2.0 mmol) in one portion and the solution was stirred at rt for 1 h. The reaction mixture was filtered through Celite and the filter cake was washed with a minimum amount of CH_2Cl_2. The filtrate was washed with a satd aq $NaHCO_3$ soln and brine (20 mL) and then dried (Na_2SO_4), filtered, and concentrated to give a residue that was purified by chromatography (7:3, hexane–EtOAc) to afford **LAM-121** (1.14 g, 94%) as a white foam. R_f 0.21 (7:3, hexane–EtOAc); $[\alpha]_D$ +44.1 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.05 (m, 4 H), 8.02–7.99 (m, 3 H), 7.95–7.90 (m, 3 H), 7.63–7.57 (m, 3 H) 7.55–7.42 (m, 8 H), 7.42–7.36 (m, 3 H), 7.30–7.23 (m, 3 H), 7.12–7.06 (m, 3 H), 5.75–5.70 (m, 3 H), 5.60 (d, 1 H, *J* = 1.0 Hz) 5.43–5.39 (m, 3 H), 4.72 (dd, 1 H, *J* = 4.1, 7.6 Hz), 4.62– 4.53 (m, 3 H), 4.40 (dd, 1 H, *J* = 5.4, 11.8 Hz), 4.25 (dd, 1 H, *J* = 4.3, 11.3 Hz), 3.98 (dd, 1 H, *J* = 3.1, 11.3 Hz), 2.75–2.69 (m,

3 H), 2.63–2.56 (m, 3 H), 2.30 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.3, 172.4, 165.7, 165.5, 165.3, 165.1, 137.9, 133.6, 133.5(4), 133.5(1), 133.3, 132.6, 130.1, 129.9, 129.8(7), 129.8(3), 129.8(1), 129.1(3), 129.1(1), 128.9, 128.6, 128.5(4), 128.5(2), 128.3, 106.0 (C-1), 91.6 (C-1), 82.1, 81.9, 81.5, 81.2, 77.6, 77.5, 77.3, 77.1, 76.8, 66.0, 63.6, 37.9, 29.8 (6), 27.8(5), 21.12. HRMS (ESI) *m/z* calcd for (M+Na) $C_{50}H_{46}O_{14}SNa$: 925.2500. Found: 925.2498.

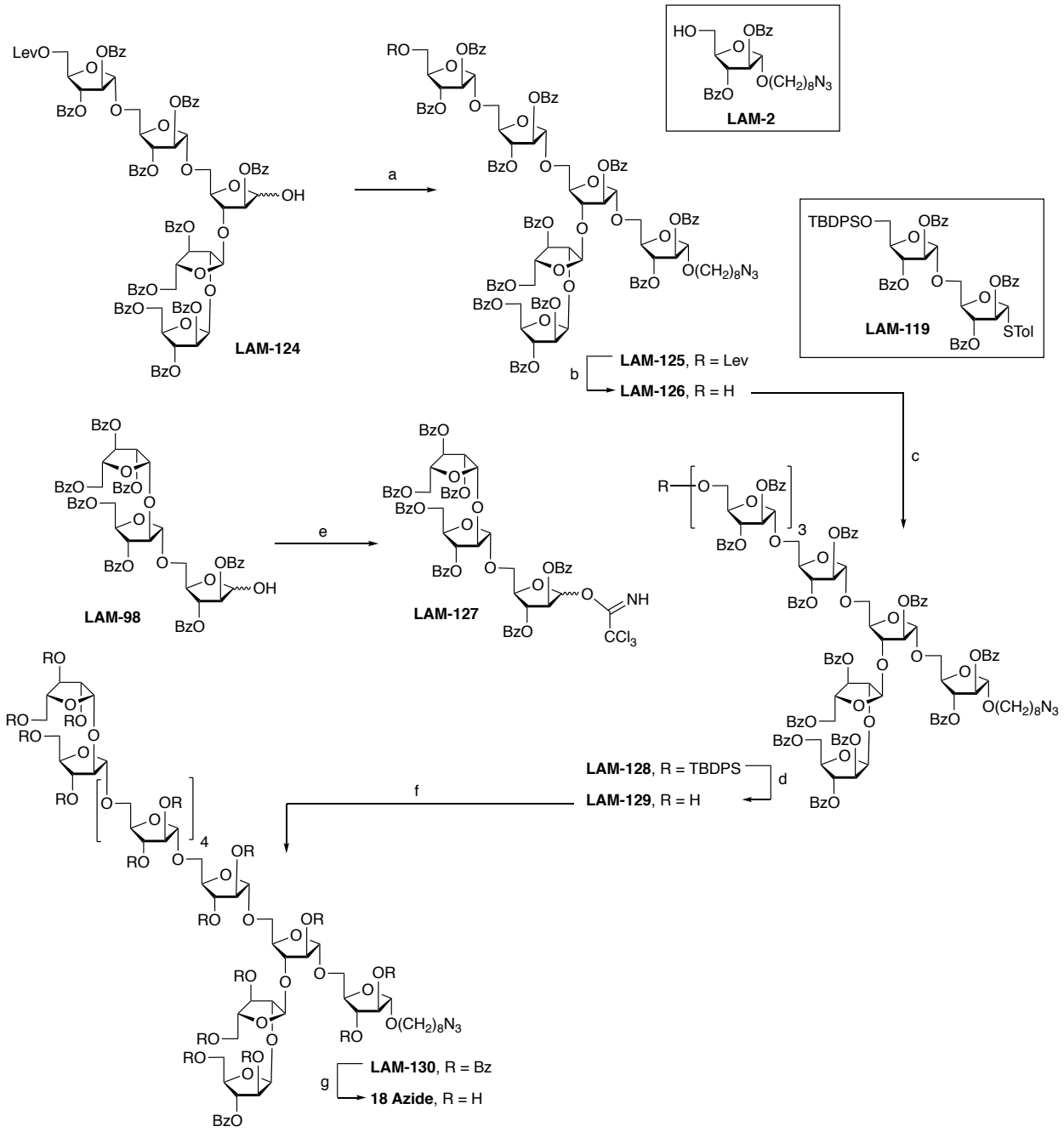
***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-122)**. Prepared from alcohol **LAM-118** (0.44 g, 0.44 mmol), thioglycoside **LAM-121** (0.52 g, 0.58 mmol), powdered 4 Å molecular sieves (0.35 g), *N*-iodosuccinimide (0.13 g, 0.58 mmol) and silver triflate (15 mg, 0.06 mmol) in CH_2Cl_2 (20 mL) as described for the synthesis of **LAM-3** to afford **LAM-122** (0.71 g, 91%) as a foam. R_f 0.26 (7:3 hexanes–EtOAc); $[\alpha]_D$ +6.3 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.11–8.05 (m, 3 H), 8.03–7.97 (m, 4 H), 7.94–7.88 (m, 4 H), 7.63-7.58 (m, 1 H), 7.54–7.34 (m, 13 H), 7.33-7.20 (m, 7 H), 7.02–6.96 (m, 3 H), 6.79-6.73 (m, 3 H), 5.74 (s, 1 H), 5.64–5.53 (m, 4 H) 5.43 (s, 1 H), 5.41 (d, 1 H, *J* = 4.4 Hz), 5.36 (s, 1 H), 5.30 (s, 3 H), 5.28 (d, 1 H, *J* = 3.1 Hz), 5.20 (d, 1 H, *J* = 4.7 Hz), 4.83 (ABq, 3 H, *J* = 12.5 Hz), 4.66–4.36 (m, 6 H), 4.30 (dd, 1 H, *J* = 5.1, 9.0 Hz), 4.25–4.14 (m, 3 H), 4.07–3.94 (m, 4 H), 3.94–3.69 (m, 7 H), 2.74–2.66 (m, 3 H), 2.63–2.55 (m, 3 H), 2.13 (s, 3 H), 1.08 (s, 9 H), 1.02 (s, 9 H), 1.01 (s, 9 H), 0.96 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 172.44, 165.6(2), 165.6(0), 165.4, 165.2, 165.1, 155.0, 150.2, 138.0, 133.6, 133.4, 133.3, 133.2(8), 129.9, 129.7(9), 129.7(3), 129.2, 129.0(7), 129.0(6), 128.9, 128.6, 128.5, 128.4(8), 128.3(7), 128.3(1), 128.2(9), 128.2(4), 127.9, 127.6, 118.2, 114.6, 106.5 (C-1), 106.1 (C-1), 106.0 (C-1), 105.1 (C-1), 99.4 (C-1), 85.6, 82.9, 82.6, 82.3, 81.5, 81.4, 81.3, 81.2, 80.6, 79.7, 78.00 77.6, 76.7, 74.3, 74.2, 71.7, 68.8, 67.4, 65.9, 65.3, 63.6, 55.6, 37.9, 29.8, 27.8, 27.6, 27.4, 27.2, 27.1, 22.6, 20.1, 20.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{95}H_{112}O_{29}Si_2Na$: 1795.6720. Found: 1795.6723.

***p*-Methoxyphenyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[5-O-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-123)**. To a solution of **LAM-122** (0.68 g, 0.38 mmol) in EtOAc–THF

(3:1, 12 mL) was added 20% $Pd(OH)_2$–C (70 mg) and the solution was stirred under H_2 (1 atm) for 14 h. The catalyst was then filtered and the filtrate concentrated to a syrup that was dried under vaccum for 2 h. The residue was then dissolved in THF–pyridine (15 mL, 2:1), cooled to 0 °C and 70% HF·pyridine (0.3 mL) was added. The reaction mixture was then warmed to rt and stirred for 20 h before being diluted with a solution of DMF–pyridine–EtOAc (25 mL, 15:5:5). Solid $NaHCO_3$ was added in portions with vigorous stirring until the solution became neutral (~ 2 h). The reaction mixture was then filtered and the solids were washed with DMF–pyridine–EtOAc (20 mL, 15:5:5). The combined organic phase was concentrated under vacuum to give a syrup that was quickly filtered through a short silica gel column (9:1 CH_2Cl_2–CH_3OH). The fractions containing the pentasaccharide were concentrated to give a syrup that was dried under vacuum for 2 h and then dissolved in pyridine (9 mL) and cooled to 0 °C. Benzoyl chloride (0.3 mL, 2.4 mmol) was added and the resulting mixture was stirred at rt for 12 h, before CH_3OH (0.4 mL) was added. The solution was stirred for another 20 min, diluted with CH_2Cl_2 and poured into a satd aq $NaHCO_3$ soln. The organic layer was washed with water, dried (Na_2SO_4), filtered and concentrated to give a syrup that was purified by chromatography (3:2 hexanes–EtOAc) to afford **LAM-123** (0.53 g, 72% over three steps) as a syrup. R_f 0.28 (3:2, hexanes–EtOAc); $[\alpha]_D$ +9.1 (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.02 (m, 4 H), 8.02–7.92 (m, 10 H), 7.92–7.85 (m, 6 H), 7.62–7.56 (m, 3 H), 7.54–7.33 (m, 16 H), 7.31–7.21 (m, 12 H), 6.99–6.94 (m, 3 H), 6.76–6.70 (m, 3 H), 5.95 (dd, 1 H, J = 5.2, 6.4 Hz), 5.81 (d, 1 H, J = 4.8 Hz), 5.72 (s, 1 H), 5.60 (d, 1 H, J = 4.8 Hz), 5.58–5.52 (m, 3 H), 5.49 (d, 1 H, J = 1.6 Hz, H-1), 5.45 (s, 1 H, H-1), 5.43 (dd, 1 H, J = 2.0, 4.4 Hz), 5.38 (d, 1 H, J = 4.3 Hz, H-1), 5.36 (s, 1 H, H-1), 5.29 (s, 1 H, H-1), 4.81 (dd, 1 H, J = 4.5, 11.7 Hz), 4.72 (dd, 1 H, J = 7.6, 11.7 Hz), 4.67 (d, 1 H, J = 1.9 Hz), 4.59–4.41 (m, 7 H), 4.38 (ddd, 3 H, J = 2.7, 4.9, 11.4 Hz), 4.16 (dd, 1 H, J = 6.6, 11.6 Hz), 4.09 (dd, 1 H, J = 4.0, 11.3 Hz), 4.02 (dd, 1 H, J = 4.5, 11.6 Hz), 3.88–3.80 (m, 3 H), 3.72 (s, 3 H), 2.75–2.66 (m, 3 H), 2.61–2.53 (m, 3 H), 2.12 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.3, 172.4, 166.0, 165.9, 165.8, 165.6, 165.5, 165.43(C=O), 165.1, 165.0, 155.0, 150.3, 133.6, 133.4, 133.3, 133.2(7), 133.2(4), 132.9, 132.8, 130.0, 129.9, 129.8(6), 129.7(8), 129.7(6), 129.7(3), 129.6(4), 129.6(2), 129.2, 129.1, 129.0(4), 129.0(2), 128.9, 128.8, 128.5(4), 128.5(0), 128.4(7), 128.4(4), 128.4(3), 128.3(7), 128.3(3), 128.2(8), 128.2(1), 128.2(0), 118.4, 114.5, 106.0 (C-1), 105.9 (C-1), 105.3 (C-1), 105.1 (C-1), 100.3 (C-1), 84.8, 83.1, 82.5, 82.3, 81.5, 81.4, 81.1, 80.9,

80.8, 79.5, 78.1, 77.6, 77.5, 76.9, 76.6, 65.8, 65.8, 65.6, 64.3, 63.61, 55.6, 37.8, 29.8, 27.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{107}H_{94}O_{34}Na$: 1945.5518. Found: 1945.5514.

2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[5-O-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranose (LAM-124). To a solution of **LAM-123** (0.25 g, 0.13 mmol) in CH_3CN–H_2O (18 mL, 8:1) at 0 °C was added CAN (0.36 g, 0.66 mmol) and the solution was stirred for 30 min. The reaction mixture was diluted with EtOAc and brine. The EtOAc layer was separated and the aqueous phase was extracted twice with EtOAc. The combined organic layer was washed with water, satd aq $NaHCO_3$ soln, dried (Na_2SO_4), and concentrated to give a residue that was purified by chromatography (1:1, hexanes–EtOAc) to afford **LAM-124** (0.22 g, 3:2 diastereomeric mixture, 91%) as a syrup. R_f 0.16 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.86 (m, 17 H), 7.63–7.21 (m, 27 H), 5.99–5.89 (m, 0.7 H), 5.82–5.77 (m, 0.6 H), 5.73–5.49 (m, 5 H), 5.47–5.22 (m, 6 H), 5.12 (dd, 0.3 H, J = 4.6, 6.2 Hz) 4.85–4.67 (m, 2.4 H), 4.66–4.35 (m, 10 H), 4.22–3.96 (m, 4.3 H), 3.95–3.79 (m, 3 H), 3.31 (s, 0.3 H), 2.74–2.66 (m, 3 H), 2.62–2.54 (m, 3 H), 2.12 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.3, 172.5, 165.9(7), 165.9(4), 165.8(6), 165.8(0), 165.7(7), 165.7(5), 165.7(3), 165.7(2), 165.6(9), 165.6(6), 165.6(3), 165.5(5), 165.5(0), 165.4(1), 165.4(0), 165.1(6), 165.1(4), 165.1(0), 133.6(4), 133.6(1), 133.5, 133.4, 133.3(6), 133.3(1), 133.2, 132.9(9), 132.9(4), 132.8(9), 132.8(7), 129.9, 129.8(8), 129.8(3), 129.7(8), 129.7(5), 129.7(0), 129.6(6), 129.6(4), 129.3, 129.1(9), 129.1(3), 129.1(2), 129.0(9), 129.0(4), 129.0(0), 128.9(5), 128.9(3), 128.8, 128.7(6), 128.7(0), 128.6, 128.5, 128.4(9), 128.4(7), 128.4(4), 128.4(0), 128.3(8), 128.3(2), 128.2(7), 128.2(3), 106.3 (C-1), 106.0 (C-1), 105.9 (C-1), 105.8 (C-1), 105.1 (C-1), 104.9 (C-1), 100.9 (C-1), 100.4 (C-1), 100.2 (C-1), 95.0 (C-1), 84.9, 84.7, 82.9, 82.1, 82.0, 81.9, 81.6, 81.5, 81.2, 81.1, 80.9(6), 80.9(0), 80.6, 79.5, 79.4(7), 79.4(0), 79.2, 78.1, 77.9(8), 77.9(0), 77.8, 77.7, 77.6(5), 77.6(0), 77.0, 76.8, 76.6, 66.7, 66.2, 66.0, 65.9, 65.7(2), 65.7(0), 64.3, 64.2, 63.6, 37.9, 29.8, 27.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{100}H_{88}O_{33}Na$: 1839.5100. Found: 1839.5091.



Scheme S20. Synthesis of **18 Azide**. a) Cl_3CCN, DBU, CH_2Cl_2; then **LAM-2**, TMSOTf, CH_2Cl_2, 91%; b) H_2NNH_2·HOAc, CH_3OH, CH_2Cl_2, 90%; c) **LAM-119**, NIS, AgOTf, CH_2Cl_2; d) HF·pyridine, THF, pyridine; 74% over two steps; e) Cl_3CCN, DBU, CH_2Cl_2; f) **LAM-127**, TMSOTf, CH_2Cl_2, 69% over two steps; g) $NaOCH_3$, CH_3OH, CH_2Cl_2, quant.

8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[5-*O*-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-

2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-125). To a solution of alcohol **LAM-124** (0.21 g, 0.11 mmol) and trichloroacetonitrile (0.1 mL, 1 mmol) in CH_2Cl_2 (4 mL) at 0 °C was added DBU (10 μL). The reaction mixture was stirred at 0 °C for 30 min and then was warmed to rt over 30 min. The solvent was evaporated and a solution of dry hexane–toluene (2:3, 10 mL) was added. After being stirred for 5 min, this solution was quickly filtered through a short column of silica gel and Na_2SO_4 (~1:1). The resulting solution was then concentrated to yield the trichloroacetimidate derivative, which was dried under vacuum for 1 h and used for glycosylation without any further purification. Alternatively, the syrup obtained after the initial solvent evaporation following the reaction could be quickly filtered through silica gel (3:2 hexanes–EtOAc containing about 0.1 % Et_3N). The fractions containing the trichloroacetimidate derivative were concentrated, dried under vacuum for 1 h and used immediately without any further purification. The trichloroacetimidate derivative in CH_2Cl_2 (4 mL) was added to a solution of alcohol **LAM-2**[1] (0.07 g, 0.13 mmol) in CH_2Cl_2 (4 mL) containing 4 Å molecular sieves (0.07 g; stirred already for about 30 min) at –30 °C. A solution of TMSOTf (2 μL, 0.01 mmol) in CH_2Cl_2 (0.06 mL) was added dropwise over 5 min. The reaction mixture was then warmed to –5 °C over 20 min and then Et_3N (0.05 mL) was added. The solution was diluted with CH_2Cl_2 and filtered and the filtrate was concentrated to a syrup that was purified by column chromatography (3:2 hexanes–EtOAc) to afford **LAM-125** (0.24 g, 91% over two steps) as a thick syrup: R_f 0.37 (3:2 hexanes–EtOAc); $[\alpha]_D$ +0.9 (c = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08–7.83 (m, 23 H), 7.62–7.20 (m, 37 H), 5.90 (dd, 1 H, J = 5.9, 5.9 Hz), 5.67 (d, 1 H, J = 4.8 Hz), 5.60 (d, 1 H, J = 4.7 Hz), 5.60–5.47 (m, 4 H), 5.43 (s, 1 H), 5.41 (s, 1 H), 5.40–5.32 (m, 5 H), 5.29 (s, 1 H), 5.19 (s, 1 H), 4.75 (dd, 1 H, J = 4.7, 11.7 Hz), 4.66 (dd, 1 H, J = 7.4, 11.6 Hz), 4.58 (d, 1 H, J = 1.1 Hz), 4.56–4.33 (m, 10 H), 4.18–4.05 (m, 3 H), 4.0 (dd, 1 H, J = 4.2, 11.7 Hz), 3.92 (dd, 1 H, J = 3.2, 11.4 Hz), 3.90–3.80 (m, 3 H), 3.74 (ddd, 1 H, J = 6.7, 9.5, 13.2 Hz), 3.47 (ddd, 1 H, J = 6.3, 9.5, 13.2 Hz), 3.20 (dd, 3 H, J = 7.0, 7.0 Hz), 2.72–2.67 (m, 3 H), 2.60–2.53 (m, 3 H), 2.11 (s, 3 H), 1.65–1.51 (m, 4 H), 1.40–1.22 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 172.4, 165.9, 165.7(3), 165.7(0), 165.6, 165.5(4), 165.5(0), 165.4, 165.3(9), 165.3(7), 165.0, 164.9, 133.6, 133.5 (4), 133.5(1), 133.3(4), 133.3(0), 133.2, 133.1(8), 133.1(2), 132.9, 132.8, 129.9, 129.8(5), 129.8(2), 129.7(9), 129.7(4), 129.7(0), 129.6(5), 129.6(2), 129.4, 129.2, 129.1, 129.0(9), 129.0(8), 128.9, 128.8, 128.6, 128.5, 128.4(9), 128.4(5),

128.4(0), 128.3, 128.1(9), 128.1(6), 105.9(5) (C-1), 105.9(2) (C-1), 105.8 (C-1), 105.5 (C-1), 105.4 (C-1), 100.3 (C-1), 84.9, 83.3, 82.2, 81.8, 81.7, 81.5, 81.4, 81.3(6), 81.3(2), 81.1, 80.6, 79.4, 78.2, 77.6, 77.4, 77.3, 76.9, 76.8, 76.7, 67.4, 66.1, 65.8, 65.7, 65.3, 64.2, 63.6, 51.4, 37.9, 29.8, 29.5, 29.3, 29.1, 28.8, 27.8, 26.6, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{127}H_{119}N_3O_{39}Na$: 2332.7312. Found: 2332.7304.

8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-126). Prepared from compound **LAM-125** (0.24 g, 0.1 mmol) and hydrazine acetate (0.1 g, 1 mmol) in CH_2Cl_2–CH_3OH (15 mL, 9:1) as described for the synthesis of compound **LAM-116** to give **LAM-126** (0.2 g, 90%) as a foam. R_f 0.22 (62:38 hexanes–EtOAc); $[\alpha]_D$ –4.0 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz $CDCl_3$, δ_H) 8.11–7.94 (m, 14 H), 7.94–7.85 (m, 10 H), 7.62–7.30 (m, 23 H), 7.30–7.20 (m, 13 H), 5.92 (dd, 1 H, *J* = 5.3, 6.3 Hz), 5.71 (d, 1 H, *J* = 4.8 Hz), 5.62 (d, 1 H, *J* = 4.7 Hz), 5.60 (d, 1 H, *J* = 1.3 Hz), 5.57–5.54 (m, 3 H), 5.51 (dd, 1 H, *J* = 4.8, 6.4 Hz), 5.48–5.29 (m, 9 H), 5.21 (s, 1 H), 4.77 (dd, 1 H, *J* = 4.6, 11.6 Hz), 4.68 (dd, 1 H, *J* = 7.4, 11.6 Hz), 4.61 (d, 1 H, *J* = 2.1 Hz), 4.55–4.35 (m, 9 H), 4.19 (dd, 1 H, *J* = 6.3, 11.6 Hz), 4.12 (dd, 1 H, *J* = 5.0, 11.4 Hz), 4.08–4.00 (m, 3 H), 3.99–3.82 (m, 5 H), 3.76 (ddd, 1 H, *J* = 6.7, 9.5, 13.2 Hz), 3.49 (ddd, 1 H, *J* = 6.3, 9.5, 13.2 Hz), 3.21 (dd, 3 H, *J* = 7.0, 7.0 Hz), 1.69–1.50 (m, 4 H), 1.42–1.22 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0, 165.9, 165.8, 165.7(4), 165.7(3), 165.5(7), 165.5(2), 165.4(6), 165.4(3), 165.3, 165.1, 133.5, 133.4, 133.3(8), 133.3(2), 133.2(5), 133.2(0), 133.1, 132.9, 132.8, 129.9, 129.8(6), 129.8(3), 129.8(0), 129.7(2), 129.7(1), 129.6, 129.4, 129.2, 129.1(8), 129.1(3), 129.0(7), 129.0, 128.9, 128.6, 128.5, 128.4(5), 128.4(0), 128.3, 128.2, 128.1, 105.9 (3 × C-1), 105.6 (C-1), 105.4 (C-1), 100.3 (C-1), 84.9, 83.6, 83.7, 82.2, 81.8(3), 81.8(1), 81.7, 81.5, 81.4, 81.3, 80.6, 79.4, 78.2, 77.7, 77.4, 77.3(6), 77.3(3), 77.1, 76.9, 76.8, 76.7, 67.4, 66.1, 65.9, 65.8, 65.3, 64.2, 62.3, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{122}H_{113}N_3O_{37}Na$: 2234.6945. Found: 2234.6949.

8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-

benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-129). Alcohol **LAM-126** (0.2 g, 0.09 mmol), was glycosylated with thioglycoside **LAM-119**[23] (0.14 g, 0.13 mmol), powdered 4 Å molecular sieves (0.1 g), *N*-iodosuccinimide (30 mg, 0.13 mmol) and silver triflate (5 mg, 0.02 mmol) in CH_2Cl_2 (9 mL) as described for the synthesis of compound **LAM-3**. After work up, the crude material was quickly filtered through a short silicagel column (3:2; hexane–EtOAc) and the fractions containing the octasaccharide were combined, concentrated and dried under vacuum for 2h. The vacuum-dried crude octasaccharide **LAM-128** was dissolved in THF–pyridine (5 mL, 4:1) and treated with 70% HF·pyridine (0.1 mL) as described for the synthesis of **LAM-26** to afford **LAM-129** (0.19 g, 74% over two steps) as a glassy solid. R_f 0.2 (3:2 hexanes–EtOAc); $[\alpha]_D$ +3.0 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.09–7.81 (m, 33 H), 7.61–7.17 (m, 48 H), 5.93–5.90 (m, 1 H), 5.70 (d, 1 H, *J* = 4.8 Hz), 5.66–5.60 (m, 6 H), 5.56 (s, 1 H), 5.54 (d, 1 H, *J* = 4.8 Hz), 5.51 (dd, 1 H, *J* = 4.9, 6.3 Hz), 5.45–5.32 (m, 9 H), 5.30 (s, 1 H), 5.21 (s, 1 H), 4.77 (dd, 1 H, *J* = 4.6, 11.7 Hz), 4.67 (dd, 1 H, *J* = 7.5, 11.6 Hz), 4.62–4.53 (m, 3 H), 4.53–4.35 (m, 8 H), 4.19–4.05 (m, 5 H), 4.04–3.71 (m, 10 H), 3.48 (ddd, 1 H, *J* = 6.3, 9.5, 13.2 Hz), 3.21 (dd, 3 H, *J* = 7.0, 7.0 Hz), 1.69–1.46 (m, 4 H), 1.42–1.21 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 165.9, 165.8, 165.7, 165.6, 165.5(9), 165.5(6), 165.4(9), 165.4(6), 165.4(2), 165.4(0), 165.1, 165.0(9), 165.0(5), 165.0(3), 133.5(3), 133.5(1), 133.4, 133.3, 133.2(9), 133.2(1), 133.1(9), 133.1(3), 133.1(0), 132.9, 132.8, 129.8(9), 129.8(6), 129.8(2), 129.7, 129.6(5), 129.6(3), 129.4, 129.1(8), 129.1(6), 129.1(4), 129.1, 129.0(4), 129.0, 128.9, 128.8(7), 128.6, 128.5, 128.4, 128.3, 128.2(4), 128.2(1), 128.1(7), 105.9(7) (C-1), 105.9(4) (C-1), 105.8(6) (3 × C-1), 105.6 (C-1), 105.4 (C-1), 100.3 (C-1), 84.9, 83.7, 83.3(0), 82.3(4), 82.1, 81.9, 81.8(3), 81.8(0), 81.7, 81.6, 81.5, 81.4(6), 81.4(1), 81.3, 80.6, 79.4, 78.2, 77.7, 77.4, 77.2, 76.9, 76.7, 67.4, 66.1, 65.8, 65.7(8), 65.6, 64.2, 62.3, 51.4, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{160}H_{145}N_3O_{49}Na$: 2914.8838. Found: 2914.8839.

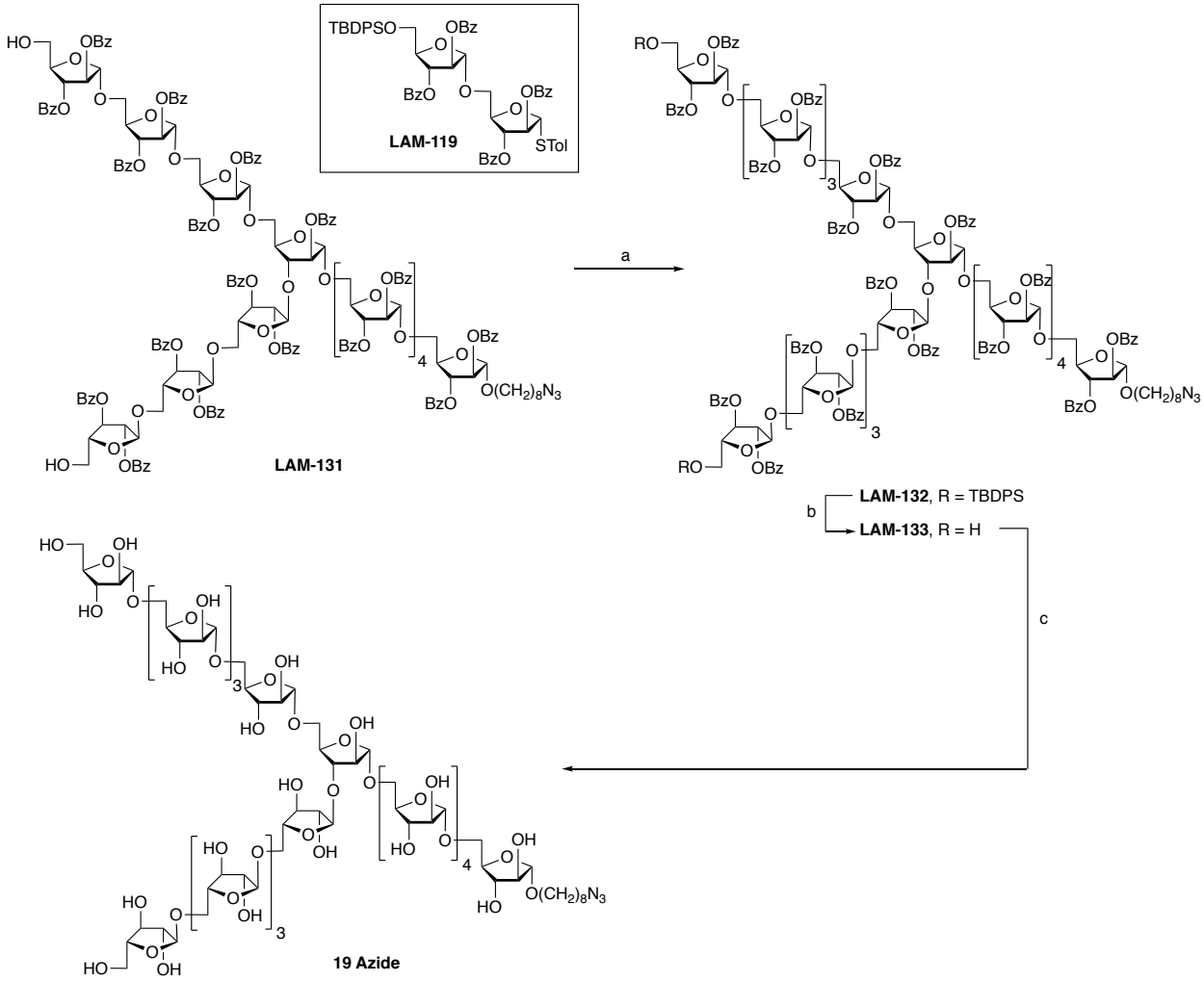
8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-

arabinofuranoside (LAM-130). Trichloroacetimidate **LAM-127** was prepared from hemiacetal **LAM-98** (0.1 g, 0.09 mmol) using DBU (10 μL) and trichloroacetonitrile (0.05 mL, 0.5 mmol) as described for the synthesis of **LAM-42** (Scheme S7). This intermediate was immediately subjected to coupling with alcohol **LAM-129** (0.175 g, 0.06 mmol) as described for the synthesis of **LAM-43**, to afford **LAM-130** (0.17 g, 69% over two steps) as a syrup. R_f 0.19 (3:2 hexanes–EtOAc); $[\alpha]_D$ –23.2 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.09–7.80 (m, 45 H), 7.61–7.15 (m, 70 H), 5.96 (dd, 1 H, *J* = 5.8, 5.8 Hz), 5.91 (dd, 1 H, *J* = 5.6, 5.6, Hz), 5.76 (d, 1 H, *J* = 4.7 Hz), 5.71–5.27 (m, 24 H), 5.20 (s, 1 H), 5.14 (s, 1 H), 4.80–4.74 (m, 3 H), 4.72–4.62 (m, 3 H), 4.61–4.34 (m, 15 H), 4.25 (dd, 1 H, *J* = 6.2, 11.6 Hz), 4.2–4.04 (m, 8 H), 4.01 (dd, 1 H, *J* = 3.8, 11.4 Hz), 3.96–3.70 (m, 9 H), 3.47 (ddd, 1 H, *J* = 6.2, 9.1, 13.2 Hz), 3.21 (dd, 3 H, *J* = 6.9, 6.9 Hz), 1.66–1.47 (m, 4 H), 1.43–1.19 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 166.0, 165.9(6), 165.9(3), 165.7(4), 165.7(1), 165.6(7), 165.5(7), 165.5(4), 165.5(1), 165.4(9), 165.4(7), 165.4(1), 165.4(0), 165.0(8), 165.0(5), 165.0(2), 133.6, 133.5(5), 133.5(2), 133.4(6), 133.4(2), 133.4(0), 133.3(9), 133.3(0), 133.2(4), 133.2(0), 133.1(7), 133.1(2), 133.0(8), 133.0(0), 132.8(7), 132.8(2), 132.8(0), 130.1(2), 130.1(0), 130.0(7), 130.0(4), 130.0(3), 130.0(1), 129.8(9), 129.8(5), 129.8(2), 129.7, 129.6(4), 129.6(2), 129.4 (4), 129.4(0), 129.1(3), 129.0(8), 129.0(5), 128.8(6), 128.8(1), 128.6, 128.5, 128.4(8), 128.4(7), 128.4(0), 128.3, 128.2, 128.1(9), 128.1(8), 128.1(7), 105.9(7) (3 × C-1), 105.8(7) (4 × C-1), 105.6 (C-1), 105.4 (C-1), 100.5 (C-1), 100.3 (C-1), 85.5, 84.9, 83.3, 82.3, 82.1, 81.8, 81.7, 81.5, 81.4(7), 81.4(4), 81.4(1), 81.3, 80.5, 80.4, 79.4, 79.3, 78.3, 78.2, 77.6, 77.4, 77.2, 76.9, 76.5, 67.4, 66.1, 65.9, 65.8, 65.7(7), 65.7(2), 65.7(1), 65.6, 64.3, 64.2, 51.4, 36.6, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1, 24.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{224}H_{197}N_3O_{68}Na$: 4039.1941. Found: 4039.1956.

8-Azidooctyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (18 Azide). To a solution of **LAM-130** (0.1 g, 0.025 mmol) in CH_2Cl_2–CH_3OH (8 mL, 3:1) at rt was added 1M methanolic sodium methoxide solution until the pH of the mixture was 8–9 as deteremined by wet pH paper. The reaction mixture was stirred for 48 h with occasional addition of CH_3OH (3 mL × 4) during the course of the reaction, and was neutralized by the addition of Amberlyst–15 (H^+) cation exchange resin. The solution was filtered to remove the resin and

concentrated to give syrup that was dissolved in distilled water (10 mL). The aqueous phase was repeatedly washed with EtOAc, CH_2Cl_2 and the separated aqueous phase was lyophilized to give **18 Azide** (0.041 g, quantitative) as a fluffy solid. $[\alpha]_D$ +85.7 (*c* = 0.2, CH_3OH); ^1H NMR (500 MHz, D_2O, δ_H) 5.23 (d, 1 H, *J* = 1.1 Hz, H-1), 5.16 (d, 1 H, *J* = 1.0 Hz, H-1), 5.14–5.04 (m, 8 H, 8 × H-1), 4.99 (d, 1 H, *J* = 1.6 Hz, H-1), 4.33–4.25 (m, 2 H), 4.25–4.17 (m, 7 H), 4.17–3.95 (m, 23 H), 3.95–3.62 (m, 25 H), 3.58 (dd, 1 H, *J* = 6.5, 9.9, 13.0 Hz), 3.31 (d, 3 H, *J* = 6.9, 6.9 Hz), 1.65–1.56 (m, 4 H), 1.43–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 108.4(0) (4 × C-1), 108.3 (2 × C-1), 108.0 (C-1), 106.6 (C-1), 106.3 (C-1), 101.6 (C-1), 101.5 (C-1), 87.9, 87.6, 83.8, 83.6, 83.4, 83.3, 83.2, 83.1, 82.9, 82.6, 82.4, 81.8, 81.7(3), 81.7(0), 79.9, 77.7, 77.6, 77.5, 77.2, 77.1(8), 77.1(2), 75.7, 75.5, 75.0, 74.9, 69.5, 67.8, 67.7, 67.6, 67.4, 67.2, 63.8, 63.7, 61.5, 61.4, 52.1, 29.5, 29.1, 29.0, 28.8, 26.8, 25.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{63}H_{105}N_3O_{45}Na$: 1646.5912. Found: 1646.5912.

16. Synthesis of 19



Scheme S21. Synthesis of **19 Azide**. a) **LAM-119**, NIS, AgOTf, CH_2Cl_2, 83%; b); HF·pyridine, THF, pyridine, 94%; c) $NaOCH_3$, CH_3OH, CH_2Cl_2, 98%.

8-Azidooctyl 2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-[2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-

di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM 132). Diol **LAM-131**[1] (0.1 g, 0.024 mmol) and thioglycoside **LAM-119** [23] (0.08 g, 0.076 mmol) were dried under vacuum in the presence of P_2O_5 for 14 h. After drying, CH_2Cl_2 (3 mL) was added, followed by powdered 4 Å molecular sieves (0.05 g) and the mixture was stirred for 20 min at rt. The reaction mixture was then cooled to 0 °C and *N*-iodosuccinimide (0.03 g, 0.13 mmol) and silver triflate (5 mg, 0.02 mmol) were added. After stirring for 20 min at 0 °C, Et_3N was added until the pH of the solution was slightly basic as determined with wet pH paper. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with a satd aq soln of $Na_2S_2O_3$, water, and brine. The organic layer was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (3:2 hexanes–EtOAc) to yield **LAM-132** (0.12 g, 83%) as a thick syrup. R_f 0.30 (3:2 hexane–EtOAc), $[\alpha]_D$ +14.4 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.80 (m, 61 H), 7.76–7.64 (m, 7 H), 7.60–7.10 (m, 107 H), 5.70–5.50 (m, 32 H), 5.46–5.22 (m, 1 5H), 4.66–4.36 (m, 17 H), 4.26–4.10 (m, 13 H), 4.06–3.74 (m, 20 H), 3.53 (ddd, 1 H, *J* = 6.1, 9.1, 12.3 Hz), 3.23 (dd, 2 H, *J* = 6.9, 6.9 Hz), 1.70–1.50 (m, 4 H), 1.50–1.20 (m, 8 H), 1.03 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.7, 165.6(1), 165.5(8), 165.5(5), 165.5, 165.3, 165.2, 165.1, 165.0(3), 165.0, 164.8, 135.7, 135.6, 133.4, 133.3, 133.2(2), 133.2, 133.1, 133.0, 130.0, 129.9, 129.8(3), 129.8, 129.7, 129.6, 129.4, 129.3(2), 129.3, 129.1, 129.0, 128.5, 128.4(3), 128.4, 128.2, 127.7, 106.0, 105.9(2), 105.9, 105.8, 105.6, 83.2, 82.7, 82.5, 82.1, 81.9, 81.8, 81.7, 81.6, 81.5, 77.2, 76.9, 67.4, 66.0, 65.8, 63.4, 51.4, 29.5(4), 29.5, 29.3, 29.1, 28.8, 26.8, 26.7, 26.1, 19.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{337}H_{305}N_1O_{96}Si_2Na$: 5979.8445 (loss of N_2), found 5979.8401 (loss of N_2).

8-Azidooctyl 2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-[2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-

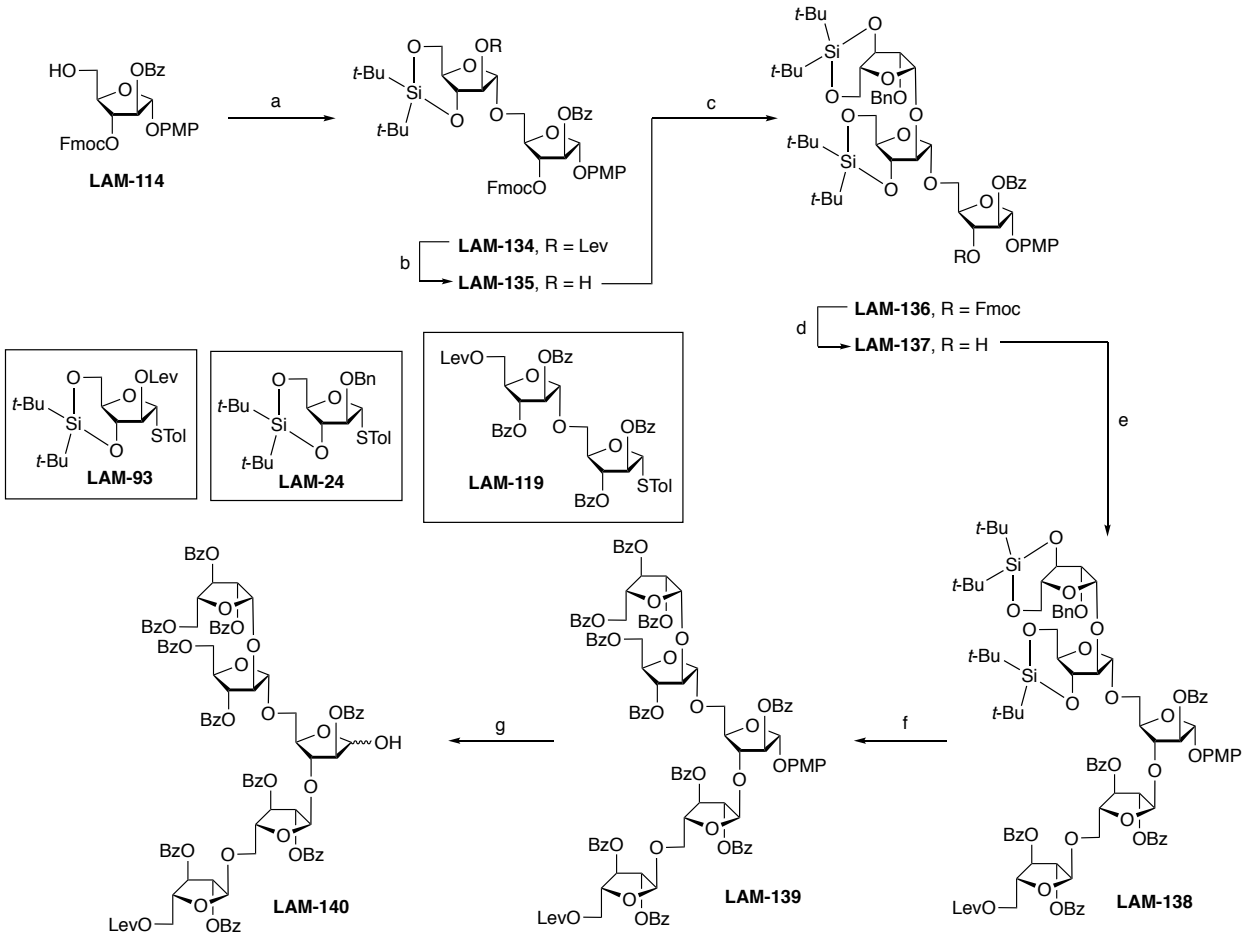
arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-133). To a solution of **LAM-132** (0.1 g, 0.02 mmol) in THF–pyridine (4 mL, 3:1) at 0 °C was added 70% HF·pyridine (0.1 mL) dropwise. The solution was then stirred overnight while warming to rt and then poured into a satd aq soln of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (1:1 hexanes–EtOAc) to yield **LAM-133** (0.09 g, 94%) as a thick syrup. R_f 0.17 (55:45 hexane–EtOAc), $[\alpha]_D$ +23.6 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.10–7.80 (m, 61 H), 7.60–7.14 (m, 94 H), 5.70–5.58 (m, 25 H), 5.58–5.50 (m, 6 H), 5.44–5.22 (m, 16 H), 4.66–4.36 (m, 18 H), 4.24–4.10 (m, 13 H), 4.06–3.73 (m, 21 H), 3.52 (ddd, 1 H, *J* = 6.1, 9.1, 12.3 Hz), 3.22 (dd, 2 H, *J* = 6.9, 6.9 Hz), 1.70–1.50 (m, 4 H), 1.40–1.20 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0, 165.7, 165.6(2), 165.6(0), 165.5(8), 165.5(5), 165.5(3), 165.5(2), 165.5, 165.4, 165.3, 165.2, 165.1(4), 165.1(2), 165.0(9), 165.0(8), 165.0(6), 165.0(2), 165.0, 133.5, 133.3(9), 133.3(6), 133.3(3), 133.3, 133.1(4), 133.1, 133.0, 130.0, 129.9, 129.8, 129.7, 129.4, 129.3, 129.2, 129.1(2), 129.1, 129.0(5), 128.9(9), 128.9(7), 128.5, 128.4(2), 128.4, 128.3(3), 128.3, 128.2, 105.9(0), 105.9, 105.7, 105.6, 83.7, 82.6, 82.2, 82.1, 82.0, 81.9, 81.8, 81.7, 81.6, 81.5, 77.7, 76.9, 76.8, 67.3, 66.1, 66.0(3), 66.0, 65.8, 65.7, 62.3, 51.4, 36.6, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1.

8-Azidooctyl α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-[α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→3)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (19 Azide). To a solution of **LAM-133** (0.08 g, 0.015 mmol) in CH_2Cl_2–CH_3OH (6 mL, 2:1) at rt was added 1M sodium methoxide solution until the pH of the mixture was 8-9 (as determined with wet pH paper). The reaction mixture was stirred for 48 h with occasional addition of CH_3OH to solubilize the product, and was then neutralized by the careful addition of Amberlyst 15 (H^+) cation exchange resin. The solution was filtered to remove the resin and concentrated to give syrup that was dissolved in distilled water. The aqueous phase was repeatedly washed with EtOAc and then CH_2Cl_2 and the aqueous phase was lyophilized to give **19 Azide** (0.033 g, 98%) as a fluffy solid. $[\alpha]_D$ 153.7 (*c* 0.25, H_2O); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.16 (d, 1 H, *J* = 1.4 Hz), 5.11 (s, 1 H), 5.10–5.06 (m, 13 H), 5.01 (d,

1H, *J* = 2.0 Hz), 4.32–4.27 (m, 3 H), 4.24–4.18 (m, 13 H), 4.18–4.10 (m, 17 H), 4.10–3.96 (m, 17 H), 3.96–3.68 (m, 33 H), 3.61–3.54 (m, 1 H), 3.32 (dd, 2 H, *J* = 6.9, 6.9 Hz), 1.65–1.57 (m, 4H), 1.42–1.32 (m, 8H); ^{13}C NMR (125 MHz, D_2O, δ_C) 108.4, 108.3, 108.1, 108.0, 84.8, 83.2, 83.1, 82.6, 82.0, 81.8, 81.7(3), 81.7, 79.9, 77.6, 77.4, 69.5, 67.7(8), 67.7, 67.5, 67.2, 62.1, 52.1, 29.4, 29.1, 29.0, 28.8, 26.7, 25.9; HRMS (ESI) *m/z* calcd for $(M+Na_2)^{2+}$ $C_{88}H_{145}N_3O_{65}Na_2$: 1164.8959. Found: 1164.8956.

.

17. Synthesis of 20



Scheme S22. Synthesis of pentasaccharide **LAM-140**, a precursor to **20 Azide**. a) **LAM-93**, NIS, AgOTf, CH_2Cl_2; b) H_2NNH_2·HOAc, CH_3OH, CH_2Cl_2 91% over two steps; c) **LAM-24**, NIS, AgOTf, CH_2Cl_2, 59%; d) Et_3N, CH_2Cl_2, 79%; e) **LAM-119**, NIS, AgOTf, CH_2Cl_2, 90%; f) H_2, $Pd(OH)_2$–C, EtOAc, CH_2Cl_2; then HF·pyridine, THF, pyridine; then BzCl, pyridine, 91%; g) CAN, CH_3CN, H_2O, 87%.

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl-α-D-arabinofuranosyl-(1→5)-3-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-135)**. Alcohol **LAM-114** (0.60 g, 1 mmol) was glycosylated with thioglycoside **LAM-93**[1] (0.66 g, 1.3 mmol), powdered 4 Å molecular sieves (0.45 g), *N*-iodosuccinimide (0.3 g, 1.3 mmol) and silver triflate (16 mg, 0.06 mmol) in CH_2Cl_2 (24 mL) as described for the synthesis of **LAM-3** to afford the corresponding crude disaccharide **LAM-134**, which, after work up, was used directly in the next step. The crude disaccharide was dissolved in a solution of CH_2Cl_2–CH_3OH (9:1, 26 mL), hydrazine acetate (0.3 g, 3.2 mmol) was added and the solution was stirred for 40 min at rt. The

reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (3:1 hexanes–EtOAc) to yield **LAM-135** (0.8 g, 91% over two steps) as a thick syrup. R_f 0.27 (3:1 hexanes–EtOAc); $[\alpha]_D$ +43.3 (c = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.09–8.04 (m, 3 H), 7.80–7.75 (m, 3 H), 7.68–7.58 (m, 3 H), 7.49–7.40 (m, 4 H), 7.37–7.31 (m, 3 H), 7.09–7.05 (m, 3 H), 6.89–6.83 (m, 3 H), 5.79 (s, 1 H, H-1), 5.66 (d, 1 H, J = 1.7 Hz, H-1), 5.35 (dd, 1 H, J = 1.6, 5.3 Hz), 5.00 (d, 1 H, J = 3.2 Hz), 4.58–4.48 (m, 3 H), 4.42 (dd, 1 H, J = 7.5, 10.4 Hz), 4.34–4.27 (m, 3 H), 4.14 (dd, 1 H, J = 3.4, 6.9 Hz), 4.07 (dd, 1 H, J = 4.3, 11.2 Hz), 4.00–3.94 (m, 3 H), 3.91–3.85 (m, 1 H), 3.83–3.76 (m, 4 H), 1.05 (s, 9 H), 0.93 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 155.3, 154.5, 150.1, 143.2, 143.1, 141.3, 141.3, 133.7, 129.9, 128.9, 128.6, 127.9, 127.3, 127.2, 125.2, 125.1, 120.1, 118.4, 114.6, 108.6 (C-1), 104.8 (C-1), 82.3, 81.6, 81.5, 81.3, 80.5, 73.9, 70.5, 67.5, 67.4, 55.7, 46.7, 27.4, 27.1, 22.6, 20.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{47}H_{54}O_{13}SiNa$: 877.3225. Found: 877.3224.

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)-3-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-136)** and ***p*-Methoxyphenyl 3,5-*O*-(Di-*t*-butylsilanediyl)-2-*O*-benzyl-α-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)-3-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-136α)**. Prepared from alcohol **LAM-135** (0.75 g, 0.87 mmol), thioglycoside **LAM-24**[1] (0.56 g, 1.1 mmol), powdered 4 Å molecular sieves (0.5 g), *N*-iodosuccinimide (0.28 g, 1.2 mmol) and silver triflate (44 mg, 0.17 mmol) in CH_2Cl_2 (30 mL) as described for the synthesis of **LAM-96** to afford **LAM 136** (0.83 g, 78%, α:β = 1:3) as a foam. **Data for LAM-136**: R_f 0.30 (85:15 hexanes–EtOAc). $[\alpha]_D$ +4.3 (c = 0.30, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.07–8.02 (m, 3 H), 7.80–7.76 (m, 3 H), 7.67–7.62 (m, 3 H), 7.60–7.55 (m, 1 H), 7.47–7.39 (m, 4 H), 7.38–7.21 (m, 7 H), 7.08–7.03 (m, 3 H), 6.86–6.81 (m, 3 H), 5.73 (s, 1 H, H-1), 5.66 (d, 1 H, J = 1.7 Hz, H-1), 5.33 (dd, 1 H, J = 1.6, 5.5 Hz), 5.06 (d, 1 H, J = 2.8 Hz), 5.00 (d, 1 H, J = 4.9 Hz, H-1), 4.78–4.66 (m, 3 H), 4.54 (dd, 1 H, J = 4.1, 9.3 Hz), 4.49 (dd, 1 H, J = 7.4, 10.4 Hz), 4.46–4.37 (m, 3 H), 4.30 (dd, 3 H, J = 5.6, 8.4 Hz), 4.24 (dd, 1 H, J = 5.1, 9.0 Hz), 4.13 (dd, 1 H, J = 2.8, 7.2 Hz), 4.08 (dd, 1 H, J = 7.4, 9.3 Hz), 4.04–3.92 (m, 3 H), 3.90–3.75 (m, 6 H), 3.64–3.56 (m, 1 H), 1.07 (s, 9 H), 1.03 (s, 9 H), 1.00 (s, 9 H), 0.92 (s, 9

H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 155.2, 154.5, 150.1, 143.2, 143.1, 141.3, 137.7, 133.6, 129.9, 129.0, 128.6, 128.4, 128.1, 127.9, 127.8, 127.3, 127.2, 125.2, 125.2, 120.1, 118.3, 114.6, 107.4 (C-1), 104.9 (C-1), 99.7 (C-1), 86.6, 82.4, 81.4, 80.6, 80.3, 80.2, 78.1, 74.1, 74.0, 71.8, 70.5, 68.7, 67.5, 66.9, 55.7, 46.7, 27.6, 27.4, 27.2, 27.1, 27.0(5), 27.0(1), 26.9, 22.6, 22.5, 20.2, 20.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{67}H_{84}O_{17}Si_2Na$: 1239.5139. Found: 1239.5135. **Data for 136α**: R_f 0.40 (85:15 hexanes–EtOAc). $[\alpha]_D$ +50.6 (*c* = 0.32, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–8.04 (m, 3 H), 7.81–7.74 (m, 3 H), 7.68–7.62 (m, 3 H), 7.60–7.55 (m, 1 H), 7.49–7.27 (m, 11 H), 7.10–7.05 (m, 3 H), 6.90–6.83 (m, 3 H), 5.75 (s, 1 H, H-1), 5.68 (d, 1 H, *J* = 1.3 Hz, H-1), 5.30–5.24 (m, 3 H), 5.04 (d, 1 H, *J* = 2.5 Hz, H-1), 4.77 (d, 1 H, *J* = 12.1 Hz), 4.69 (d, 1 H, *J* = 12.1 Hz), 4.58 (dd, 1 H, *J* = 4.7, 9.1 Hz), 4.50 (dd, 1 H, *J* = 7.5, 10.5 Hz), 4.41 (dd, 1 H, *J* = 7.5, 10.5 Hz), 4.36–4.28 (m, 3 H), 4.25 (dd, 1 H, *J* = 4.7, 8.7 Hz), 4.18 (dd, 1 H, *J* = 2.5, 6.9 Hz), 4.10–3.86 (m, 8 H), 3.84–3.76 (m, 4 H), 1.05 (s, 9 H), 1.04 (s, 9 H), 0.98 (s, 9 H), 0.91 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 155.2, 154.4, 150.2, 143.2, 143.1, 141.3, 137.9, 133.6, 129.9, 129.0, 128.6, 128.3, 127.9, 127.7, 127.6, 127.3, 127.2, 125.2(4), 125.2(1), 120.1, 118.5, 114.6, 107.2 (C-1), 106.7 (C-1), 104.9 (C-1), 87.7, 86.9, 81.9, 81.7, 81.6, 81.1, 80.4, 74.0, 73.4, 71.8, 70.4, 67.5, 67.4, 67.3, 55.7, 46.7, 27.6, 27.5, 27.4, 27.1, 27.0, 22.6, 20.1, 20.0.

***p*-Methoxyphenyl 3,5-*O*-(Di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→5)-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-137)**. Prepared from compound **LAM-136** (0.56 g, 0.46 mmol) and Et_3N (0.4 mL, 2.7 mmol) in CH_2Cl_2 (12 mL) as described for the synthesis of **LAM-118** to afford **LAM-137** (0.36 g, 79%) as a thick syrup. R_f 0.43 (3:1 hexanes–EtOAc); $[\alpha]_D$ +58.2 (*c* = 0.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.97 (m, 3 H), 7.62–7.56 (m, 1 H), 7.46–7.41 (m, 3 H), 7.41–7.37 (m, 3 H), 7.34–7.29 (m, 3 H), 7.28–7.23 (m, 1 H), 7.05–7.00 (m, 3 H), 6.84–6.79 (m, 3 H), 5.77 (s, 1 H, H-1), 5.33 (dd, 1 H, *J* = 1.2, 3.3 Hz), 5.05 (d, 1 H, *J* = 2.8 Hz, H-1), 4.98 (d, 1 H, *J* = 4.9 Hz, H-1), 4.77 (ABq, 3 H, *J* = 12.3 Hz), 4.44 (dd, 1 H, *J* = 9.2, 9.2 Hz), 4.38 (ddd, 1 H, *J* = 4.2, 6.8, 8.6 Hz), 4.33–4.27 (m, 1 H), 4.26–4.21 (m, 3 H), 4.10–4.03 (m, 3 H), 3.96–3.84 (m, 5 H), 3.79–3.72 (m, 4 H), 3.60 (ddd, 1 H, *J* = 5.1, 9.2, 10.6 Hz), 3.36 (d, 1 H, *J* = 4.3 Hz), 1.07 (s, 9 H), 1.02 (s, 9 H), 1.0 (s, 9 H), 0.94 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.90, 155.2, 150.3, 137.8, 133.7, 129.8, 128.9, 128.6, 128.4, 128.2, 127.8, 118.1, 114.6, 107.4 (C-1), 104.7 (C-1), 99.7 (C-1), 87.0, 86.4, 82.7, 80.4, 80.0, 78.1, 77.2, 74.2, 74.0,

71.8, 68.7, 67.5, 67.3, 55.6, 27.6, 27.4, 27.2, 27.1, 22.6 (4), 22.6, 20.1, 20.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{53}H_{74}O_{15}Si_2Na$: 1017.4458. Found: 1017.4456.

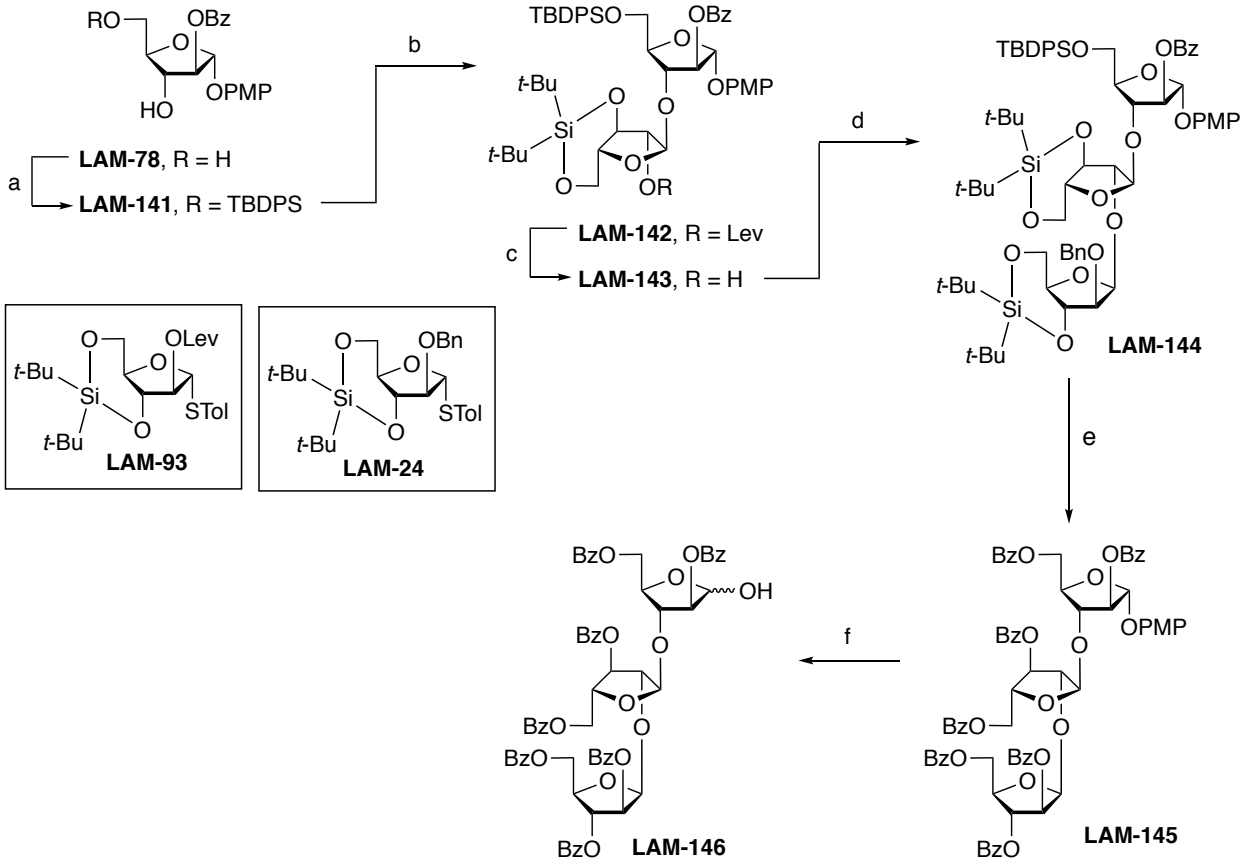
***p*-Methoxyphenyl 5-*O*-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[3,5-*O*-(Di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(Di-*t*-butylsilanediyl-α-D-arabinofuranosyl-(1→5))-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-138)**. Prepared from alcohol **LAM-137** (0.35 g, 0.35 mmol), thioglycoside **LAM-119**[23] (0.41 g, 4.5 mmol), powdered 4 Å molecular sieves (0.25 g), *N*-iodosuccinimide (0.1 g, 0.44 mmol) and silver triflate (12 mg, 0.05 mmol) in CH_2Cl_2 (12 mL) as described for the synthesis of **LAM-3** to afford **LAM-138** (0.56 g, 90%) as a foam. R_f 0.25 (7:3 hexanes–EtOAc); $[\alpha]_D$ +10.0 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.11–7.98 (m, 8 H), 7.92–7.87 (m, 3 H), 7.64–7.35 (m, 13 H), 7.35–7.19 (m, 7 H), 7.06–6.99 (m, 3 H), 6.81–6.73 (m, 3 H), 5.71 (s, 3 H), 5.67 (d, 1 H, *J* = 1.1 Hz, H-1), 5.64–5.59 (m, 3 H), 5.58 (d, 1 H, *J* = 0.9 Hz, H-1), 5.45–5.36 (m, 3 H), 5.02 (d, 1 H, *J* = 2.9 Hz, H-1), 4.97 (d, 1 H, *J* = 4.8 Hz, H-1), 4.67 (s, 3 H), 4.60 (dd, 1 H, *J* = 4.5, 8.9 Hz), 4.56–4.49 (m, 3 H), 4.49–4.36 (m, 4 H), 4.28–4.18 (m, 3 H Hz), 4.07 (dd, 1 H, *J* = 2.9, 7.4 Hz), 4.03–3.85 (m, 5 H), 3.84–3.68 (m, 6 H), 3.58 (ddd, 1 H, *J* = 5.0, 9.1, 10.5 Hz), 2.75–2.67 (m, 3 H), 2.64–2.53 (m, 3 H), 2.13 (s, 3 H), 1.06 (s, 9 H), 1.00 (s, 9 H), 0.99 (s, 9 H), 0.90 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 172.7, 165.6(1), 165.6(0), 165.5, 165.2, 165.0, 155.1, 150.3, 137.7, 133.5, 133.4(3), 133.4(1), 133.4(0), 133.3, 129.9, 129.8, 129.7(6), 129.7(2), 129.2, 129.1(5), 129.1(3), 128.9(5), 128.9(0), 128.4(8), 128.4(6), 128.3(4), 128.3(2), 128.1, 127.7, 118.3, 114.5, 107.3 (C-1), 106.0 (C-1), 105.4 (C-1), 105.3 (C-1), 99.6 (C-1), 86.2, 83.2, 82.9, 82.1, 81.5, 81.4, 81.2, 80.5, 80.4(8), 80.4(4), 80.0, 79.9, 78.1, 77.6, 74.2, 74.0, 71.7, 68.7, 67.5, 66.6, 65.9, 63.6, 55.6, 37.9, 29.8, 27.8, 27.5, 27.4, 27.2, 27.0, 22.6, 22.5(5), 20.1(4), 20.1(0), 19.98. HRMS (ESI) *m/z* calcd for (M+Na) $C_{95}H_{112}O_{29}Si_2Na$: 1795.6720. Found: 1795.6717.

***p*-Methoxyphenyl 5-O-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D--arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranoside (LAM-139)**. Prepared from compound **LAM-138** (0.55 g, 0.3 mmol), 20% $Pd(OH)_2$–C (60 mg) in EtOAc–THF (12 mL, 3:1), then 70% HF·pyridine (0.3 mL) in THF–pyridine (10:5), 15 mL and then BzCl (0.25 mL) in pyridine (6 mL) as described for the synthesis of **LAM-123** to afford **LAM-139** (0.54 mg, 91% over three steps) as a foam. R_f 0.31

(3:2 hexanes–EtOAc); $[\alpha]_D$ –9.9 (*c* = 0.30, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.06–8.00 (m, 6 H), 8.00–7.95 (m, 4 H), 7.93–7.85 (m, 8 H), 7.85–7.81 (m, 3 H), 7.62–7.52 (m, 3 H), 7.51–7.34 (m, 13 H), 7.34–7.28 (m, 7 H), 7.28–7.15 (m, 7 H), 7.08–7.03 (m, 3 H), 6.82–6.76 (m, 3 H), 5.93 (dd, 1 H, *J* = 5.4, 6.4 Hz), 5.78 (s, 1 H), 5.71 (dd, 3 H, *J* = 4.6, 9.9 Hz), 5.65 (d, 1 H, *J* = 0.8 Hz), 5.61 (d, 1 H, *J* = 1.5 Hz), 5.56–5.51 (m, 3 H), 5.38–5.32 (m, 4 H), 5.30 (d, 1 H, *J* = 2.5 Hz), 5.13 (s, 1 H), 4.75 (dd, 1 H, *J* = 4.8, 11.7 Hz), 4.66 (dd, 1 H, *J* = 7.3, 11.6 Hz), 4.60–4.57 (m, 1 H), 4.56–4.52 (m, 3 H), 4.50–4.39 (m, 8 H), 4.35 (dd, 1 H, *J* = 5.3, 11.9 Hz), 4.21 (dd, 1 H, *J* = 6.3, 11.5 Hz), 4.17 (dd, 1 H, *J* = 3.6, 11.2 Hz), 3.97 (dd, 1 H, *J* = 3.9, 11.8 Hz), 3.85–3.79 (m, 3 H), 3.75 (s, 3 H), 2.70–2.65 (m, 3 H), 2.58–2.53 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 172.4, 166.0, 165.9, 165.8, 165.6(5), 165.5(8), 165.5(5), 165.4, 165.2, 165.0, 155.1, 150.3, 133.6, 133.5, 133.4(7), 133.4(1), 133.3(4), 133.3(0), 133.1, 132.9, 132.8, 129.9, 129.8, 129.7(5), 129.7(1), 129.7(0), 129.2, 129.1(4), 129.1(0), 129.0, 128.9(8), 128.9(7), 128.8(7), 128.7, 128.5(1), 128.5(0), 128.4, 128.3, 128.2, 128.1(7), 118.4, 114.6, 106.1 (C-1), 106.0 (C-1), 105.4 (C-1), 105.2 (C-1), 100.3 (C-1), 85.1, 83.1, 82.9, 82.4, 81.5, 81.4, 81.1, 80.6, 80.2, 79.2, 78.2, 77.6, 76.9, 76.4, 65.9, 65.8, 65.6, 64.3, 63.6, 55.7, 37.9, 29.8, 27.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{107}H_{94}O_{34}Na$: 1945.5518. Found: 1945.5512.

5-*O*-Levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranose (LAM-140). Prepared from compound **LAM-139** (0.25 g, 0.13 mmol) in CH_3CN–H_2O (18 mL, 8:1) and CAN (0.36 g, 0.66 mmol) as described for the synthesis of **LAM–41** to afford **LAM-140** (0.21 g, 3:2 diasteromeric ratio, 87%) as a foam. R_f 0.21 (3:2 hexanes–EtOAc); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.84 (m, 19 H), 7.63–7.16 (m, 31 H), 5.98–5.91 (m, 3 H), 5.80–5.69 (m, 2.3 H), 5.61–5.48 (m, 3.4 H), 5.43–5.23 (m, 5 H), 5.16 (s, 0.4 H), 5.11 (s, 0.6 H), 4.86–4.72 (m, 1.4 H), 4.71–4.32 (m, 9 H), 4.28–4.04 (m, 3.4 H), 3.98–3.55 (m, 4.6 H), 2.73–2.65 (m, 3 H), 2.61–2.52 (m, 3 H), 2.11 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.4, 206.3, 172.4(2), 166.5, 166.2, 165.9, 165.7, 165.6, 165.5, 165.4, 165.2, 165.0, 133.7, 133.6, 133.4, 133.3, 133.2, 133.1, 132.9, 132.8(7), 130.5, 130.4, 130.3, 129.9, 129.8, 129.7, 129.4, 129.3, 129.1, 129.0, 128.9(7), 128.8(9), 128.8, 128.7, 128.5, 128.3, 128.2, 127.9, 127.8, 127.8, 106.6 (C-1), 106.1 (C-1), 105.9 (C-1), 105.8 (C-1), 105.2 (C-1), 101.2 (C-1), 100.6 (C-1), 100.3 (C-1), 94.7 (C-1), 85.5, 85.1, 82.7, 82.5, 82.3, 81.9, 81.8, 81.4, 81.1(4), 81.0(6), 80.6, 80.4, 80.2, 79.3, 79.2, 79.0, 78.3, 78.1, 77.9,

77.7, 77.6(3), 76.6(1), 76.4(6), 76.4(1), 66.7, 65.9, 65.8, 65.7, 64.3, 63.7, 37.9, 29.7(9), 27.8(2). HRMS (ESI) *m/z* calcd for (M+Na) $C_{100}H_{88}O_{33}Na$: 1839.5100. Found: 1839.5093.



Scheme S23. Synthesis of trisaccharide **LAM-146**, a precursor to **20 Azide**. a) TBDPSCl, pyridine, 93%; b) **LAM-93**, NIS, AgOTf, CH_2Cl_2, 90%; c) H_2NNH_2, HOAc, CH_3OH, CH_2Cl_2, 91%; d) **LAM-24**, NIS, AgOTf, CH_2Cl_2, 76%; e) $_2$, $Pd(OH)_2$–C, EtOAc; then *n*-Bu_4NF, THF, HOAc; then BzCl, pyridine, 47%; f) CAN, CH_3CN, H_2O, 86%.

***p*-Methoxyphenyl 2-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranoside (LAM-141)**. **LAM-78**[1] (2.0 g, 5.55 mmol) was dissolved in pyridine (35 mL) and TBDPSCl (2.13 mL, 8.3 mmol) was added to it dropwise at 0 °C. The reaction mixture was allowed to warm to rt and stirred at 40 °C for 30 h before CH_3OH (2 mL) was added. The reaction mixture was poured into a satd aq $NaHCO_3$ soln and extracted with CH_2Cl_2. The organic phase was washed with water, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by

chromatography (6:1 hexanes–EtOAc) to yield **LAM-141** (3.09 g, 93%) as a semi solid. R_f 0.5 (7:3 hexanes–EtOAc).

***p*-Methoxyphenyl 3,5-*O*-(di-*t*-butylsilanediyl)-2-*O*-levulinoyl-α-D-arabinofuranosyl-(1→3)-2-*O*-benzoyl-5-*O*-*t*-butyldiphenylsilyl-α-D-arabinofuranoside (LAM-142)**. Prepared from thioglycoside **LAM-93**[1] (690 mg, 1.40 mmol), alcohol **LAM-141** (760 mg, 1.27 mmol), 4 Å molecular sieves (0.3 g), *N*-iodosuccinimide (400 g, 1.68 mmol) and silver triflate (40 mg, 0.29 mmol) in CH_2Cl_2 (20 mL) as described for the synthesis of **LAM-3**, to afford **LAM-142** (1.11 g, 90%) as a white foam. R_f 0.29 (4:1 hexanes–EtOAc); $[\alpha]_D$ +64.1 (c = 0.9, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.02–7.99 (m, 2 H), 7.71–7.67 (m, 4 H), 7.59–7.56 (m, 1 H), 7.44–7.30 (m, 8 H), 7.09–7.05 (m, 2 H), 6.86–6.83 (m, 2 H), 5.74 (s, 1 H, H-1), 5.57 (d, 1 H, J = 1.8 Hz), 5.33 (d, 1 H, J = 2.4 Hz, H-1), 5.24 (dd, 1 H, J = 7.0, 2.4 Hz), 4.58 (dd, 1 H, J = 5.6, 1.8 Hz), 4.44 (ddd, 1 H, J = 5.6, 4.2, 4.2 Hz), 4.25 (dd, 1 H, J = 8.8, 4.5 Hz), 4.15 (dd, 1 H, J = 9.3, 7.0 Hz), 4.01–3.89 (m, 4 H), 3.78 (s, 3 H), 2.83–2.79 (m, 2 H), 2.73–2.68 (m, 2 H), 2.16 (s, 3 H), 1.07 (s, 9 H), 1.03 (s, 9 H), 1.00 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.3, 171.9, 165.4, 154.9, 150.5, 135.6, 135.5, 133.3, 133.2(9), 133.2(7), 129.8, 129.7, 129.6, 129.3, 128.4, 127.6(8), 127.6(2), 118.3, 114.4, 105.7 (C-1), 105.2 (C-1), 83.6, 82.9, 82.5, 81.0, 79.9, 73.7, 67.4, 62.5, 55.6, 38.1, 36.6, 29.7, 28.0, 27.4, 27.0, 26.7, 20.0, 19.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{53}H_{68}O_{13}Si_2Na$: 991.4090. Found: 991.4090.

***p*-Methoxyphenyl 3,5-*O*-(Di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-2-*O*-benzoyl-5-*O*-*t*-butyldiphenylsilyl-α-D-arabinofuranoside (LAM-143)**. Prepared from **LAM-142** (1.08 g, 1.11 mmol), hydrazine monohydrate–HOAc (7 mL, 1:2), THF (12 mL), and CH_3OH (3 mL) at rt for 1 h as described for the synthesis of **LAM-95** to give **LAM-143** (880 mg, 91%) as a white foam. R_f 0.53 (4:1, hexanes–EtOAc); $[\alpha]_D$ +78.2 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.02–7.99 (m, 2 H), 7.71–7.66 (m, 4 H), 7.60–7.56 (m, 1 H), 7.44–7.31 (m, 8 H), 7.08–7.03 (m, 2 H), 6.86–6.82 (m, 2 H), 5.74 (s, 1 H, H-1), 5.59 (d, 1 H, J = 2.0 Hz), 5.20 (d, 1 H, J = 3.4 Hz, H-1), 4.53 (dd, 1 H, J = 5.8, 2.0 Hz), 4.40 (ddd, 1 H, J = 5.8, 3.9, 3.8 Hz), 4.28 (ddd, 1 H, J = 7.6, 4.0, 3.4 Hz), 4.22–4.18 (m, 1 H), 4.02–3.98 (m, 1 H), 3.95–3.89 (m, 4 H), 3.78 (s, 3 H), 2.86 (d, 1 H, J = 4.0 Hz), 1.08 (s, 9 H), 1.03 (s, 9 H), 1.01 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.7, 155.1, 150.4, 135.6, 135.5, 133.5, 133.3, 129.9, 129.6(9), 129.6(4), 129.1, 128.4, 127.6(6), 127.6(2), 118.3, 114.4, 108.1 (C-1), 105.3 (C-1), 83.8, 83.6, 82.0, 81.6,

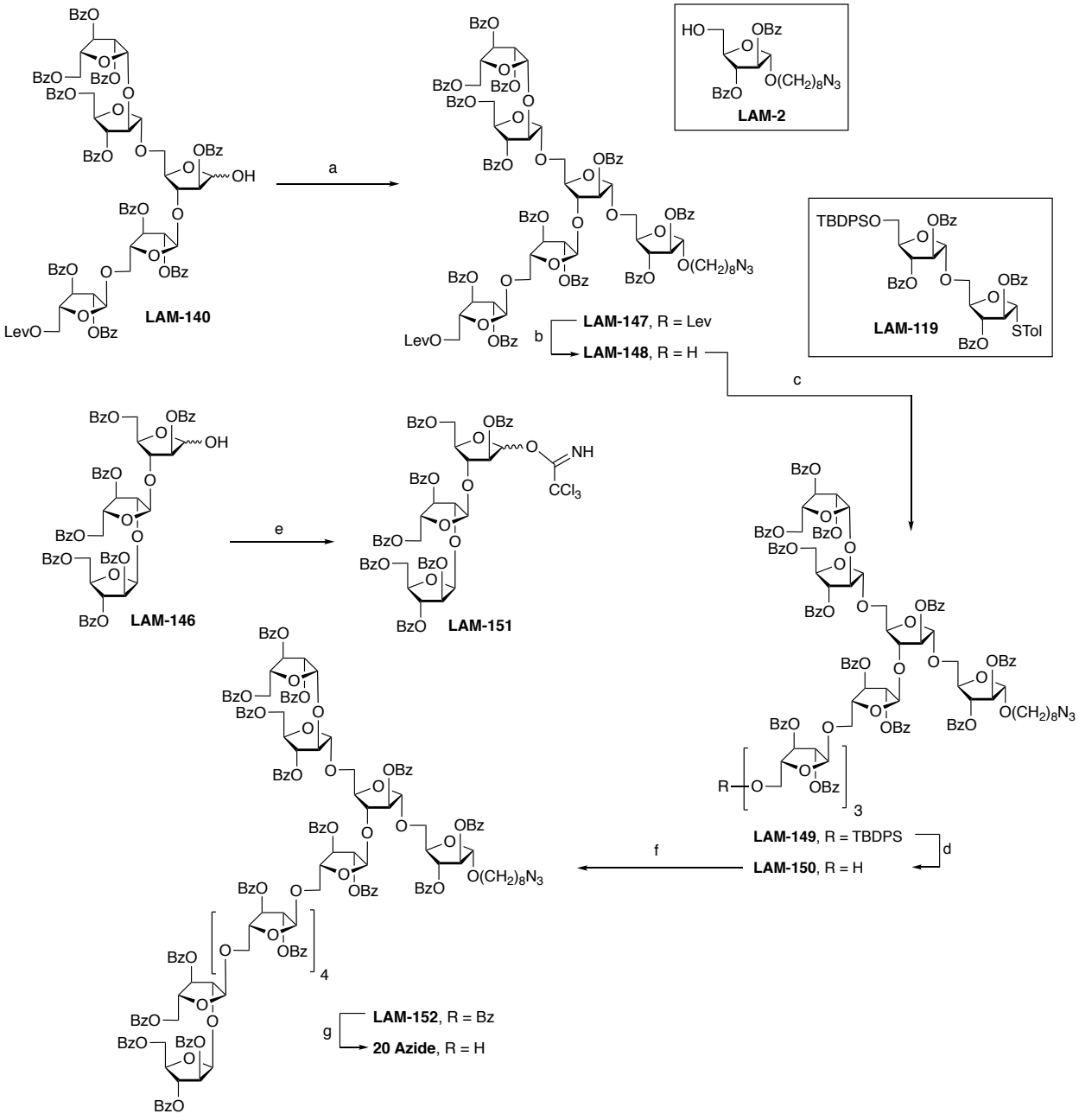
81.2, 73.9, 67.5, 62.3, 55.6, 27.4, 27.1, 26.7, 22.5, 20.1, 19.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{48}H_{62}O_{11}Si_2Na$: 893.3722. Found: 893.3733.

***p*-Methoxyphenyl 3,5-*O*-(Di-*t*-butylsilanediyl)-2-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-(di-*t*-butylsilanediyl)-α-D-arabinofuranosyl-(1→3)-2-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranoside (LAM-144)**. Prepared from thioglycoside **LAM-24**[1] (536 mg, 1.10 mmol), alcohol **LAM-143** (800 mg, 0.92 mmol), 4 Å molecular sieves (0.2 g), *N*-iodosuccinimide (315 g, 1.33 mmol) and silver triflate (30 mg, 0.22 mmol) in CH_2Cl_2 (40 mL) as described for the synthesis of **LAM-96**, to afford **LAM-144** (860 g, 76%) as a white foam. R_f 0.39 (8:1 hexanes–EtOAc); $[\alpha]_D$ +13.3 (*c* = 1.6, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.98–7.95 (m, 2 H), 7.70–7.67 (m, 4 H), 7.59–7.55 (m, 1 H), 7.45–7.27 (m, 12 H), 7.24–7.20 (m, 1 H), 7.03–7.00 (m, 2 H), 6.84–6.80 (m, 2 H), 5.72 (s, 1 H, H-1), 5.53 (d, 1 H, *J* = 0.5 Hz), 5.38 (d, 1 H, *J* = 3.0 Hz, H-1), 5.23 (d, 1 H, *J* = 4.7 Hz, H-1), 4.87 (d, 1 H, *J* = 12.5 Hz), 4.81 (d, 1 H, *J* = 12.5 Hz), 4.55 (dd, 1 H, *J* = 5.1, 0.5 Hz), 4.52 (dd, 1 H, *J* = 9.2, 9.1 Hz), 4.44–4.40 (m, 1 H), 4.31 (dd, 1 H, *J* = 9.1, 5.2 Hz), 4.23 (dd, 1 H, *J* = 7.6, 3.0 Hz), 4.20–4.17 (m, 1 H), 4.12 (dd, 1 H, *J* = 7.9, 7.6 Hz), 4.02–3.96 (m, 2 H), 3.93–3.85 (m, 4 H), 3.78 (s, 3 H), 3.76 (m, 1 H), 1.09 (s, 9 H), 1.06 (s, 9 H), 1.02 (s, 18 H), 0.99 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.3, 155.0, 150.3, 138.0, 135.6, 135.5, 133.3(9), 133.3(0), 133.2, 129.8, 129.6(9), 129.6(3), 129.2, 128.4, 128.2, 127.8, 127.6(6), 127.6(1), 127.5, 118.3, 114.5, 106.3 (C-1), 105.2 (C-1), 99.4 (C-1), 85.7, 84.3, 82.8, 81.0, 80.5, 79.8, 78.0, 74.3, 74.1, 71.6, 68.8, 67.5, 62.6, 55.6, 27.5, 27.4, 27.2, 27.1, 26.6, 22.6(2), 22.6(0), 20.1, 20.0, 19.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{68}H_{92}O_{15}Si_3Na$: 1255.5636. Found: 1255.5634.

***p*-Methoxyphenyl 2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-145)**. Prepared from **LAM-144** (710 mg, 0.58 mmol), 10% $Pd(OH)_2$–C (30 mg) in EtOAc (30 mL), then 1M TBAF in THF solution (1 mL), HOAc (0.3 mL) in THF (20 mL), and then pyridine (4 mL) and benzoyl chloride (1 mL) as described for the synthesis of **LAM-139**, to afford **LAM-145** (343 mg, 47% over three steps) as a white foam. R_f 0.28 (2:1 hexanes–EtOAc); $[\alpha]_D$ +4.3 (*c* = 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.13–7.91 (m, 14 H), 7.63–7.56 (m, 2 H), 7.52–7.20 (m, 19 H), 7.04–7.00 (m, 2 H), 6.83–6.79 (m, 2 H), 5.97 (dd, 1 H, *J* = 6.6, 5.2 Hz), 5.88 (d, 1 H, *J* = 4.7 Hz, H-1), 5.76 (s, 1 H, H-1), 5.59 (dd, 1 H, *J* = 6.6, 4.7 Hz), 5.47 (s, 1 H, H-1), 5.46–5.43 (m, 2 H), 4.82 (dd, 1 H, *J* = 11.8, 4.4 Hz), 4.76–4.67 (m, 3 H), 4.59–4.52 (m, 3 H),

4.49–4.42 (m, 3 H), 4.18 (dd, 1 H, J = 11.3, 6.6 Hz), 3.78 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0(8), 166.0(0), 165.9, 165.8, 165.7, 165.4, 165.3, 155.2, 150.1, 133.6–128.2, 118.5, 114.5, 105.5 (C-1), 105.1 (C-1), 100.4 (C-1), 85.0, 83.2, 81.8, 81.5, 81.0, 79.5, 78.0, 77.5, 76.4, 65.6, 64.3, 63.0, 55.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{71}H_{60}O_{21}Na$: 1271.3519. Found: 1271.3508.

2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-D-arabinofuranose (LAM-146). Prepared from compound **LAM-145** (0.27 g, 0.22 mmol) in CH_3CN–H_2O (20 mL, 4:1) and CAN (0.59 g, 1.1 mmol) as described for the synthesis of **LAM-41**, to afford **LAM-146** (0.21 g, 7:3 diastereomeric mixture, 86%) as a foam. R_f 0.18 (7:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.14–7.88 (m, 14 H), 7.66–7.21 (m, 21 H), 5.97–5.90 (m, 1 H), 5.82 (d, 0.7 H, J = 4.8 Hz) 5.75 (d, 0.3 H, J = 4.7 Hz) 5.68 (dd, 0.3 H, J = 4.4, 5.5 Hz), 5.60–5.54 (m, 1.4 H), 5.48–5.42 (m, 1.7 H), 5.40–5.38 (m, 0.6 H), 5.32–5.31 (m, 0.3 H), 5.20 (d, 0.7 H, J = 1.1), 5.14 (dd, 0.3 H, J = 4.3, 6.0 Hz), 4.79–4.72 (m, 1 H), 4.71–4.58 (m, 4 H), 4.57–4.39 (m, 5 H), 4.26 (ddd, 0.3 H, J = 4.0, 6.1, 6.1 Hz), 4.20–4.10 (m, 1.3 H), 3.39 (d, 0.3 H, J = 5.8 Hz), 3.23 (d, 0.7 H, J = 4.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.4, 166.3(4), 166.3(2), 166.2(5), 166.2(2), 166.1(8), 166.1(6), 166.1(4), 165.9, 165.8, 133.9, 133.8(9), 133.8(7), 133.8(2), 133.7, 133.5, 133.4, 133.3(2), 133.3(0), 130.3, 130.2, 130.1(7), 130.1(6), 130.1(5), 130.0(9), 130.0(7), 130.0, 129.9(6), 129.9(0), 129.7(1), 129.7(0), 129.6, 129.5(3), 129.5(1), 129.3, 129.0, 128.9(4), 128.9(1), 128.9(0), 128.8(8), 128.8(4), 128.7(8), 128.7(3), 128.7(0), 128.6(8), 128.6(6), 105.7 (C-1), 105.6 (C-1), 101.4 (C-1), 100.9 (C-1), 100.7 (C-1), 95.6 (C-1), 85.5, 85.1, 83.2, 82.0, 81.6, 81.5, 81.4, 79.8, 79.1, 79.0, 78.9, 78.4(1), 78.4(0), 78.1, 77.9, 76.8, 76.8, 66.1, 66.0, 65.5, 64.7, 64.6, 63.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{64}H_{54}O_{20}Na$: 1165.3100. Found: 1165.3099.



Scheme S24. Synthesis of **20 Azide**. a) CCl_3CN, DBU, CH_2Cl_2; then TMSOTf, CH_2Cl_2, 87%; b) H_2NNH_2·HOAc, CH_3OH, CH_2Cl_2, 95% c) **LAM-2**, NIS, AgOTf, CH_2Cl_2; d) HF·pyridine, THF, pyridine; 72% over two steps; e) CCl_3CN, DBU, CH_2Cl_2; f) **LAM-151**, TMSOTf, CH_2Cl_2, 68% over two steps; g) $NaOCH_3$, CH_3OH, CH_2Cl_2, quant.

8-Azidooctyl 5-*O*-levulinoyl-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-147). The trichloroacetimidate derivative of pentasaccharide **LAM-140** (0.2 g, 0.1 mmol) was prepared using DBU (10 μL) and trichloroacetonitrile (0.1 mL, 1 mmol) as described for the synthesis of **LAM-42** (Scheme S7). This was immediately subjected to coupling with alcohol **LAM-2**[1] (0.067 g, 0.13 mmol) as described for the synthesis of **LAM-43**, to afford **LAM-147** (0.22 g, 87% over two steps) as a syrup. R_f 0.36 (3:2 hexanes–EtOAc); $[\alpha]_D$ –8.4 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.80 (m, 23 H), 7.60–7.16 (m, 37 H), 5.95 (dd, 1 H, *J* = 5.9, 5.9 Hz), 5.73 (d, 1 H, *J* = 4.8 Hz), 5.60 (d, 1 H, *J* = 4.8 Hz), 5.58 (d, 1 H, *J* = 4.6 Hz), 5.53–5.45 (m, 5 H), 5.43–5.36 (m, 3 H), 5.36–5.30 (m, 3 H), 5.26 (s, 1 H), 5.21 (s, 1 H), 5.12 (s, 1 H), 4.74 (dd, 1 H, *J* = 4.9, 11.8 Hz), 4.63 (dd, 1 H, *J* = 7.1, 11.4 Hz), 4.60–4.36 (m, 10 H), 4.31 (dd, 1 H, *J* = 5.1, 11.8 Hz), 4.24–4.10 (m, 3 H), 4.0–3.90 (m, 3 H), 3.85–3.72 (m, 3 H), 3.50 (ddd, 1 H, *J* = 6.2, 9.5, 12.5 Hz), 3.20 (dd, 3 H, *J* = 6.9, 6.9 Hz), 2.70–2.63 (m, 3 H), 2.59–2.51 (m, 3 H), 2.09 (s, 3 H), 1.70–1.52 (m, 4 H), 1.45–1.20 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 172.4, 165.9(9), 165.9(2), 165.8, 165.6, 165.5(8), 165.5(5), 165.5(3), 165.5, 165.4, 165.3, 164.9, 164.8, 133.6, 133.5, 133.4(5), 133.4(1), 133.3, 133.2(9), 133.2(3), 133.2(0), 133.1, 132.9, 132.9, 129.9, 129.8, 129.7(5), 129.7(4), 129.6(9), 129.6(5), 129.4, 129.1(7), 129.1(5), 129.0(6), 129.0(1), 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 106.4 (C-1), 105.9(6) (C-1), 105.9 (C-1), 105.5 (C-1), 105.2 (C-1), 100.3 (C-1), 85.1, 82.9, 82.6, 81.9, 81.8, 81.7, 81.6, 81.4, 80.9, 80.8, 80.3, 79.2(3), 78.1(9), 77.5(8), 77.5(6), 77.3(4), 77.3(0), 77.2, 77.1, 76.8, 76.5, 67.4, 66.1, 65.8, 65.7, 64.3, 63.5, 51.4, 37.9, 29.8, 29.5, 29.3, 29.1, 28.8, 27.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{127}H_{119}N_3O_{39}Na$: 2332.7312. Found: 2332.7306.

8-Azidooctyl 2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-148). Prepared from **LAM-147** (0.22 g, 0.1 mmol) and hydrazine acetate (0.2 g, 2.1 mmol) in CH_2Cl_2–CH_3OH (15 mL, 9:1) as described for the synthesis of **LAM-116** to give **LAM-148** (0.2 g, 95%) as a foam. R_f 0.24 (62:38 hexanes–

EtOAc); $[\alpha]_D$ –21.3 (*c* = 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.10–7.80 (m, 24 H), 7.62–7.14 (m, 36 H), 5.97 (dd, 1 H, *J* = 5.3, 5.3 Hz), 5.76 (d, 1 H, *J* = 4.8 Hz) 5.60 (d, 3 H, *J* = 4.9 Hz) 5.52–5.46 (m, 5 H) 5.43 (dd, 1 H, *J* = 4.8, 5.6 Hz), 5.38 (s, 1 H), 5.36 (d, 3 H, *J* = 4.6 Hz), 5.24 (s, 1 H), 5.22 (s, 1 H), 5.15 (s, 1 H), 4.76 (dd, 1 H, *J* = 4.9, 11.7 Hz), 4.70 (dd, 1 H, *J* = 7.2, 11.7 Hz), 4.58–4.34 (m, 9 H), 4.25–4.15 (m, 3 H), 4.10–4.04 (m, 1 H), 4.04–3.74 (m, 7 H), 3.50 (ddd, 1 H, *J* = 6.2, 9.5, 12.5 Hz), 3.20 (dd, 3 H, *J* = 6.9, 6.9 Hz), 2.46 (br.s, H), 1.68–1.50 (m, 4 H), 1.42–1.25 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 165.9(5), 165.9(3), 165.6(6), 165.6(1), 165.5(3), 165.5(1), 165.4, 165.3, 165.0, 164.9, 133.6, 133.5, 133.4(2), 133.4(1), 133.3, 133.2(4), 133.2(1), 133.1, 132.9, 132.8, 129.8(9), 129.8(4), 129.8(1), 129.7(5), 129.7(1), 129.6(9), 129.6(7), 129.4, 129.2, 129.1(4), 129.1(2), 129.1(0), 129.0, 128.9(9), 128.9(6), 128.8, 128.5(2), 128.5(0), 128.4(8), 128.4(5), 128.4(3), 128.3(8), 128.3(2), 128.3(0), 128.2, 128.1(9), 128.1(8), 106.1(1) (C-1), 105.9 (C-1), 105.8 (C-1), 105.5 (C-1), 105.3 (C-1), 100.3 (C-1), 85.1, 83.6, 82.9, 82.6, 81.9, 81.8, 81.7, 81.6, 80.8, 80.3, 79.2, 78.3, 77.6, 77.4, 77.3, 77.1(4), 77.1(0), 76.8, 76.5, 67.4, 66.1, 65.8, 65.7, 65.6, 64.3, 62.2, 51.42 29.5, 29.3, 29.1, 28.8, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{122}H_{113}N_3O_{37}Na$: 2234.6945. Found: 2234.6946.

8-Azidooctyl 2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-150). Prepared from alcohol **LAM-148** (0.18 g, 0.08 mmol), thioglycoside **LAM-119**[23] (0.13 g, 0.12 mmol), powdered 4 Å molecular sieves (0.1 g), *N*-iodosuccinimide (28 mg, 0.12 mmol) and silver triflate (4 mg, 0.02 mmol) in CH_2Cl_2 (9 mL) as described for the synthesis of **LAM-3**. After work up, the crude material was quickly filtered through a short silicagel column (3:2; hexane–EtOAc) and the fractions containing the octasaccharide were combined, concentrated and dried under vacuum for 2h. The vacuum-dried crude octasaccharide **LAM-149** was dissolved in THF–pyridine (5 mL, 4:1) and treated with 70% HF·pyridine (0.1 mL) as described for the synthesis of **LAM-26** to afford **LAM-150** (0.17 g, 72% over two steps) as a semisolid. R_f 0.2 (3:2 hexanes–EtOAc). $[\alpha]_D$ –9.0 (*c* = 0.20, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.14–7.67 (m, 30 H), 7.61–7.07 (m, 50 H), 5.98–5.95 (m, 1 H), 5.75 (dd, 1 H, *J* = 4.8 Hz), 5.65–5.58 (m, 7 H), 5.57 (s, 1 H), 5.54 (d, 3 H, *J* = 4.3 Hz), 5.50–5.48 (m, 3 H), 5.43–5.34 (m, 7 H), 5.24 (s, 3 H), 5.14 (s, 1 H), 4.76 (dd, 1 H, *J* = 4.9, 11.6 Hz), 4.66

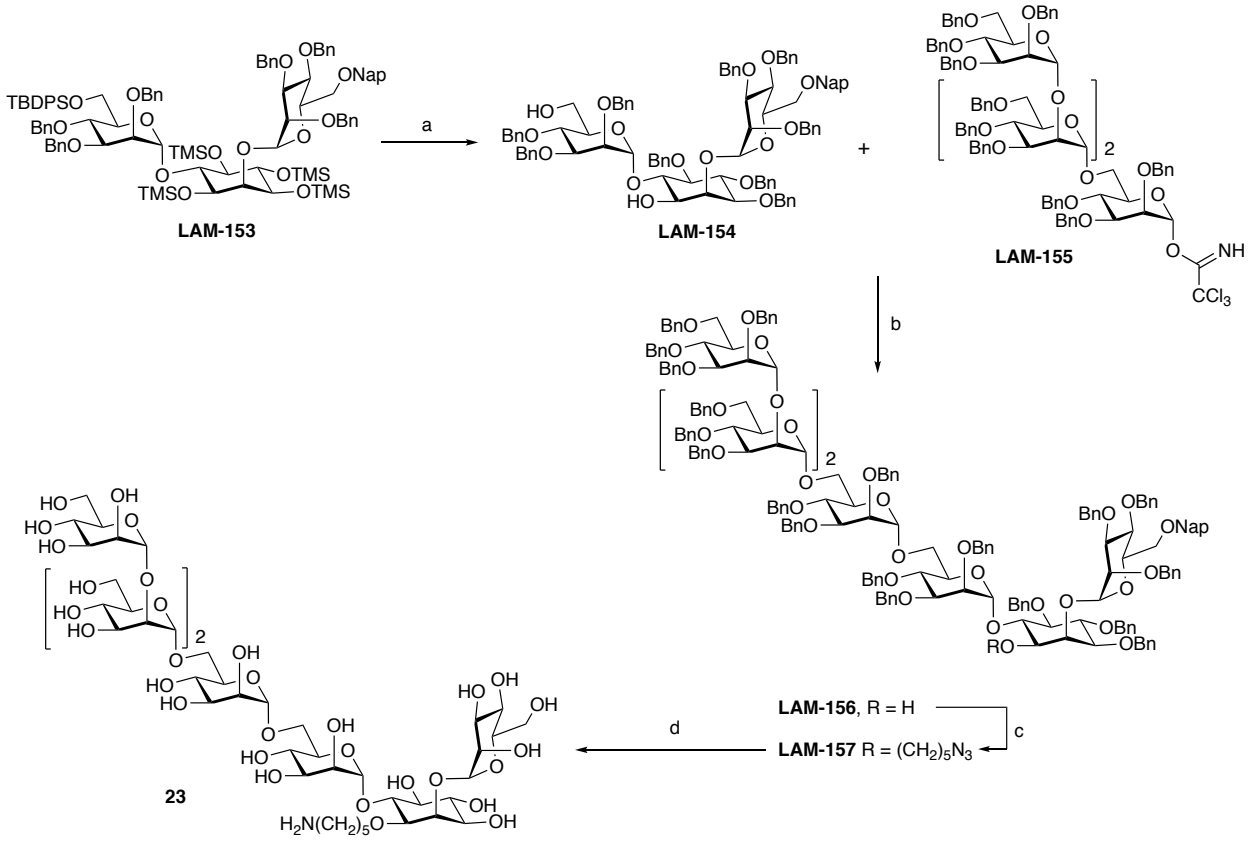
(dd, 1 H, J = 7.2, 11.6 Hz), 4.60–4.37 (m, 11 H), 4.23–4.04 (m, 5 H), 4.03–3.88 (m, 5 H), 3.86–3.72 (m, 4 H), 3.51 (ddd, 1 H, J = 6.3, 6.3, 9.5 Hz), 3.22 (dd, 3 H, J = 7.0, 7.0 Hz), 1.68–1.47 (m, 4 H), 1.38–1.20 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0(4), 166.0(0), 165.9, 165.8, 165.6(4), 165.6(1), 165.6(0), 165.5(4), 165.5(2), 165.4, 165.3, 165.1, 164.9(8), 164.9(0), 133.6, 133.5, 133.4(6), 133.4(2), 133.3(8), 133.3(2), 133.2(7), 133.2(5), 133.2(4), 133.2(3), 133.2(2), 133.1(9), 133.1(3), 133.1(0), 132.8(7), 132.8(5), 129.8(9), 129.8(8), 129.8(6), 129.8(3), 129.8(0), 129.8, 129.7(5), 129.7(3), 129.7(2), 129.6(9), 129.6(8), 129.6(6), 129.4, 129.1(8), 129.1(7), 129.1(4), 129.0(7), 129.0(3), 129.0(1), 128.9(8), 128.9(7), 128.7, 128.5, 128.4(9), 128.4(4), 128.4(1), 128.4(0), 128.2(9), 128.2(7), 128.2(5), 128.2(2), 128.2(1), 128.2(0), 128.1, 106.5 (C-1), 105.9 (C-1), 105.8(5) (C-1), 105.8(4) (C-1), 105.8 (C-1), 105.5 (C-1), 105.2 (C-1), 100.3 (C-1), 85.1, 83.6, 82.9, 82.7, 81.9(6), 81.9(3), 81.9(0), 81.7, 81.6, 81.6, 81.5, 80.8, 80.2, 79.1, 78.2, 77.7, 77.6, 77.4, 76.9, 76.5, 67.4, 66.1, 65.8, 64.3, 62.3, 51.4, 36.6, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1, 24.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{160}H_{145}N_3O_{49}Na$: 2914.8838. Found: 2914.8834.

8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-2,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-[2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-152) Trichloroacetimidate **LAM-151** was prepared from hemiacetal **LAM-146** (0.09 g, 0.08 mmol) using DBU (10 μL) and trichloroacetonitrile (0.05 mL, 0.5 mmol) as described for the synthesis of **LAM-42** (Scheme S7). This was immediately subjected to coupling with alcohol **LAM-150** (0.15 g, 0.05 mmol) as described for the synthesis of **LAM-43**, to afford **LAM-152** (0.14 g, 68%) as a syrup. R_f 0.19 (3:2 hexanes–EtOAc); $[\alpha]_D$ –27.6 (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.11–7.77 (m, 46 H), 7.61–7.15 (m, 69 H), 5.96 (dd, 3 H, J = 5.3, 11.6 Hz), 5.75 (dd, 3 H, J = 4.8, 8.6 Hz), 5.67–5.55 (m, 10 H), 5.53 (d, 3 H, J = 4.8 Hz), 5.50–5.43 (m, 3 H), 5.43–5.32 (m, 8 H), 5.23 (s, 3 H), 5.14 (s, 3 H), 4.82–4.61 (m, 5 H), 4.60–4.36 (m, 16 H), 4.28–4.03 (m, 8 H), 4.00–3.86 (m, 5 H), 3.85–3.73 (m, 5 H), 3.51 (ddd, 1 H, J = 7.0, 7.0 Hz), 1.68–1.48 (m, 4 H), 1.43–1.21 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 166.0, 165.9(7), 165.9(3), 165.9(2), 165.8(3), 165.6(7), 165.6(4), 165.6(0), 165.5(7), 165.5(6), 165.5(4), 165.5(1), 165.4, 165.3, 165.0(8), 165.0(5), 164.9(9), 164.9(0), 133.5(6), 133.5(1), 133.4(6), 133.4(2),

133.3(8), 133.3(1), 133.2(6), 133.2(2), 133.1(8), 133.1(3), 133.0(9), 133.0(5), 133.0(1), 132.9, 132.8(8), 132.8(5), 132.8(3), 129.9, 129.8(5), 129.8(1), 129.7(4), 129.7(0), 129.4, 129.1(7), 129.1(5), 129.1(4), 129.0(8), 129.0(4), 129.0, 128.8, 128.7, 128.4(9), 128.4(7), 128.4(1), 128.4(0), 128.2(9), 128.2(3), 128.2(0), 128.1, 106.5 (C-1), 105.9(8) (C-1), 105.9(5) (C-1), 105.9(0) (C-1), 105.8 (2 × C-1), 105.7 (C-1), 105.6 (C-1), 105.2 (C-1), 100.5 (C-1), 100.3 (C-1), 85.5, 85.1, 82.9, 82.7, 82.1, 81.9, 81.8(8), 81.8(4), 81.7(7), 81.7(4), 81.5(9), 81.5(4), 81.5(0), 80.8, 80.4, 80.2, 79.3, 79.1, 78.3, 78.2, 77.6, 77.5, 77.4, 77.2, 77.1, 76.9, 76.5, 76.4(6), 67.4(2), 66.1, 65.9(5), 65.9(1), 65.8(8), 65.8(3), 65.7(0), 65.6, 65.4, 64.3, 51.4, 36.6, 29.5, 29.3, 29.1, 28.8, 26.7, 26.1, 24.7; Low res MS (ESI) calcd for (M+Na) $C_{224}H_{197}N_3O_{68}Na$: 4041. Found: 4041.

8-Azidooctyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (20 Azide). Prepared from **LAM-152** (0.1 g, 0.025 mmol) and 1M sodium methoxide solution as described for the synthesis of **18 Azide**, to afford **20 Azide** (0.041 g, quantitative) as a fluffy solid. $[\alpha]_D$ +79.5 (*c* = 0.2, CH_3OH); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.17 (d, 1 H, *J* = 1.6 Hz, H-1), 5.15 (d, 1 H, *J* = 1.3 Hz, H-1), 5.14 (d, 1 H, *J* = 0.9 Hz, H-1), 5.12 (d, 1 H, *J* = 0.9 Hz, H-1), 5.10–5.07 (m, 6 H, 6 × H-1), 4.99 (d, 1 H, *J* = 2.0 Hz, H-1), 4.32–4.26 (m, 3 H), 4.23–4.16 (m, 6 H), 4.16–3.98 (m, 23 H), 3.98–3.64 (m, 26 H), 3.57 (ddd, 1 H, *J* = 6.5, 9.9, 13.0 Hz), 3.31 (dd, 3 H, *J* = 6.9, 6.9 Hz), 1.65–1.57 (m, 4 H), 1.40–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 108.3(9) (2 × C-1), 108.3(7) (2 × C-1), 108.3(0) (C-1), 108.1 (C-1), 108.0 (C-1), 106.6 (C-1), 106.5 (C-1), 101.5 (2 × C-1), 87.7, 87.6, 83.7, 83.3, 83.2, 83.1, 82.9, 82.5, 82.4, 82.0, 81.8, 81.7(2), 81.7(1), 81.7(0), 80.0, 77.6, 77.5, 77.2, 77.1(6), 77.1(2), 75.7, 75.6, 75.0(4), 75.0(2), 69.5, 67.7, 67.7, 67.5, 67.3(4), 67.3(0), 63.8, 61.4(9), 61.4(5), 52.1, 29.5, 29.1, 29.0, 28.8, 26.7, 25.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{63}H_{105}N_3O_{45}Na$: 1646.5912. Found: 1646.5916.

18. Synthesis of 23



Scheme S25. Synthesis of **23**. a) PhCHO, Et_3SiH, TMSOTf, CH_2Cl_2; then *n*-Bu_4NF, THF, 68%; b) TMSOTf, CH_2Cl_2, 70%; c) 5-azidopentyl iodide, NaH, DMF, 95%; d) H_2, $Pd(OH)_2$–C, phosphate buffer, CH_3OH, THF, 88%.

5-azidopentyl iodide. Synthesized as described previously.[25] ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 3.27 (t, 2 H, *J* = 6.9 Hz), 3.17 (t, 2 H, *J* = 6.9), 1.86–1.81 (m, 2 H), 1.63–1.58 (m, 2 H), 1.5–1.45 (m, 2 H); ^{13}C NMR (600 MHz, $CDCl_3$, δ_C) 35.1, 32.9, 27.8, 27.7, 6.3.

[2,3,4-Tri-*O*-benzyl-6-*O*-(2-naphthylmethyl)-α-D-mannopyranosyl]-(1→2)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol (LAM-154). Compound **LAM-153**[26] (110 mg, 0.06 mmol) and 3 Å molecular sieves (200 mg) in CH_2Cl_2 (5 mL) was stirred at rt for 1 h. The mixture was cooled –40 °C and benzaldehyde (39 μL, 0.39 mmol) was added. After stirring for 5 min, triethylsilane (67 μL, 0.42 mmol) and TMSOTf (4 μL, 18 mmol) were added and the resulting solution was stirred for 48 h. At that point, *n*-Bu_4NF (1M in THF, 0.3 mL) was added and the solution was warmed to rt and then stirred for 12 h. The

solution was filtered through Celite, the filtrate was diluted with CH_2Cl_2, washed with water, brine, dried ($MgSO_4$) and concentrated to give a residue that was purified by chromatography (2.5:1 hexanes–EtOAc) to yield **LAM-154** (64 mg, 68%). $[\alpha]_D$ +38.9 (*c* = 3.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) δ 7.76–7.67 (m, 4 H), 7.45–7.10 (m, 46 H), 7.01 (d, 2 H, *J* = 7.1 Hz), 5.44 (d, 1 H, *J* = 1.4 Hz, H-1), 5.27 (d, 1 H, *J* = 2.6 Hz, H-1), 4.86 (d, 1 H, *J* = 10.7 Hz), 4.83–4.51 (m, 17 H), 4.47 (d, 1 H, *J* = 12.2 Hz,), 4.41 (d, 1 H, *J* = 10.6 Hz), 4.24 (app t, 1 H, *J* = 2.4 Hz), 4.11–4.05 (m, 2 H), 3.93–3.75 (m, 8 H), 3.57 (dd, 1 H, *J* = 3.6, 10.6 Hz), 3.50–3.47 (m, 2 H), 3.45 (dd, 1 H, *J* = 4.1, 11.8 Hz), 3.45 (dd, 1 H, *J* = 4.1, 11.8 Hz), 3.40 (dd, 1 H, *J* = 1.3, 10.6 Hz), 3.28 (d, 1 H, *J* = 2.4, 9.8 Hz), 3.20 (app t, 1 H, *J* = 9.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 138.5(0), 138.4(6), 138.3(8), 138.37, 138.3, 138.2, 138.0(4), 138.0(3), 137.9, 135.7, 133.2, 132.9, 128.4(3), 128.3(7), 128.3(4), 128.3(2), 128.2(8), 128.2, 128.1, 128.0(1), 127.9(6), 127.9(3), 127.8(7), 127.8, 127.6(9), 127.6(5), 127.5(9), 127.5(5), 127.5, 127.4(2), 127.3(5), 127.2, 126.7, 126.1, 125.9, 125.7, 99.0 (C-1), 98.1 (C-1), 81.1, 80.9, 79.2, 78.8, 78.5, 75.7, 75.6, 75.4, 74.9, 74.8, 74.6, 74.5, 74.3, 73.5, 73.4, 72.5(4), 72.4(9), 72.1, 72.0, 71.9, 71.8, 71.7, 68.8, 61.9. HRMS (ESI) *m/z* calcd for (M+Na) calcd for $C_{92}H_{94}O_{16}Na$: 1477.6440. Found: 1477.6443. A small amount of **[2,3,4-tri-*O*-benzyl-6-*O*-(2-naphthylmethyl)-α-D-mannopyranosyl]-(1→2)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-4,5-di-*O*-benzyl-D-*myo*-inositol** (8.8 mg, 10%) was also isolated. $[\alpha]_D$ +53.9 (*c* = 2.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.78–7.69 (m, 4 H), 7.46–7.12 (m, 41 H), 7.04 (d, 2 H, *J* = 7.3 Hz), 5.42 (s, 1 H, H-1), 4.99 (d, 1 H, *J* = 3.7 Hz, H-1), 4.90 (d, 1 H, *J* = 11.1 Hz), 4.85 (d, 1 H, *J* = 10.8 Hz), 4.77–4.51 (m, 15 H), 4.49 (d, 1 H, *J* = 12.2 Hz), 4.44 (d, 1 H, *J* = 10.8 Hz), 4.30 (app t, 1 H, *J* = 2.2 Hz), 4.15–4.12 (m, 1 H), 4.08 (app t, 1 H, *J* = 9.5 Hz), 3.98–3.95 (m, 1 H), 3.88 (dd, 1 H, *J* = 2.7, 6.2 Hz), 3.83–3.76 (m, 4 H), 3.72–3.69 (m, 2 H), 3.60 (t, 1 H, *J* = 9.2 Hz), 3.57 (dd, 1 H, *J* = 3.9, 10.8 Hz), 3.90 (app t, 1 H, *J* = 9.2 Hz), 3.41–3.38 (m, 2 H), 3.34 (app t, 1 H, *J* = 9.2 Hz), 3.27 (dd, 1 H, *J* = 2.2, 9.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 138.6, 138.4(4), 138.4(1), 138.1(2), 138.0(3), 137.9(6), 137.8(8), 137.6(3), 135.6(9), 133.1(6), 132.9(1), 128.4(9), 128.4(5), 128.3(8), 128.3(7), 128.2(8), 128.2(6), 128.1(0), 128.0(9), 127.9(6), 127.9(2), 127.8(8), 127.8(5), 127.6(3), 127.5(9), 127.4, 127.3, 127.1, 126.7, 126.1, 125.9, 125.7, 99.9 (C-1), 98.6 (C-1), 83.1, 80.3, 79.0, 78.2, 76.6, 75.4, 75.3, 75.0, 74.6, 74.2, 73.8, 73.7, 73.5, 73.2, 73.1, 72.6, 72.5, 72.4, 72.1, 71.9, 71.7(3), 71.6(3), 68.8, 62.6. HRMS (ESI) *m/z* calcd for (M+Na) calcd for $C_{85}H_{88}O_{16}Na$: 1387.5970. Found: 1387.5983.

3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[2,3,4-Tri-*O*-benzyl-6-*O*-(2-naphthylmethyl)-α-D-mannopyranosyl-(1→2)]-3,4,5-tri-*O*-benzyl-D-*myo*-inositol (LAM-156). A mixture of **LAM-154** (140 mg, 0.095 mmol) and 3Å molecular sieves in Et_2O (10 mL) was stirred at rt for 1 h before being cooled to –40 °C. TMSOTf (3 μL, 0.02 mmol) was then added and then trichloroacetimidate **LAM-155**[26] (419 mg, 0.21 mmol) in Et_2O (2 mL) was added via syringe pump over 30 min. The solution was stirred at –40 °C for 2 h, Et_3N (10 μL) was added and then the mixture was filtered through Celite. The filtrate was diluted with EtOAc and washed successively with a satd aq soln of $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$) and concentrated to a residue that was purified by chromatography (1:2.5 EtOAc–hexanes) to provide **LAM-156** (221 mg, 70%). $[\alpha]_D$ +37.9 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.76–7.75 (m, 1 H), 7.69–7.61 (m, 3 H), 7.44–7.41 (m, 2 H), 7.33–6.99 (m, 111 H), 5.45 (d, 1 H, *J* = 1.1 Hz, H-1), 5.19 (d, 1 H, *J* = 1.4 Hz, H-1), 5.18 (d, 1 H, *J* = 2.1 Hz, H-1), 5.17 (d, 1 H, *J* = 1.5 Hz, H-1), 4.93 (d, 1 H, *J* = 1.4 Hz, H-1), 4.88–4.77 (m, 10 H), 4.70–4.26 (m, 37 H), 4.15 (app t, 1 H, *J* = 2.0 Hz), 4.10 (app t, 1 H, *J* = 1.9 Hz), 4.07–4.04 (m, 2 H), 3.93–3.73 (m, 20 H), 3.67–3.62 (m, 2 H), 3.59–3.56 (m, 1 H), 3.52–3.47 (m, 5 H), 3.22–3.29 (m, 2 H), 3.28 (dd, 1 H, *J* = 9.8, 2.4 Hz), 3.18 (app t, 1 H, *J* = 9.3 Hz); ^{13}C NMR (600 MHz, $CDCl_3$, δ_C) 138.8, 138.7(2), 138.7(0), 138.6(9), 138.6(0), 138.5(5), 138.4(4), 138.4(2), 138.3(7), 138.3(4), 138.3(1), 138.2, 138.1, 138.0, 137.9, 135.8, 133.2, 132.9, 128.4(4), 128.3(9), 128.3(7), 128.2(8), 128.2(5), 128.2(1), 128.1(9), 128.1(5), 128.1(2), 128.0(8), 127.9(7), 127.9(5), 127.8(7), 127.8(5), 127.8, 127.7(3), 127.7(1), 127.6(4), 127.6(1), 127.5(9), 127.5(4), 127.5(0), 127.4(3), 127.4(0), 127.3(6), 127.2(9), 127.2(8), 127.2, 127.1, 126.5, 126.0, 125.9, 125.6, 100.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 175.6 Hz, C-1), 99.2(4) ($^1J_{C\text{-}1,H\text{-}1}$, *J* = 171.1 Hz, 2 × C-1), 99.2(2) ($^1J_{C\text{-}1,H\text{-}1}$ = 171.1 Hz, C-1), 98.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 172.2 Hz, C-1), 98.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 170.0 Hz, C-1), 81.2, 80.4, 79.9, 79.8, 78.8(9), 78.8(5), 78.7, 75.5, 75.3, 74.9(3), 74.8(8), 74.8, 74.6(9), 74.6(5), 74.5, 74.3, 73.9, 73.4, 73.3, 73.23, 73.15, 72.7, 72.5(1), 72.4(6), 72.3, 72.1, 72.0(3), 72.0(1), 71.9(3), 71.9(0), 71.8(8), 71.8, 71.7, 71.5(1), 71.4(8), 71.2, 71.1, 69.2, 69.0, 68.9, 68.8, 66.7, 66.1.

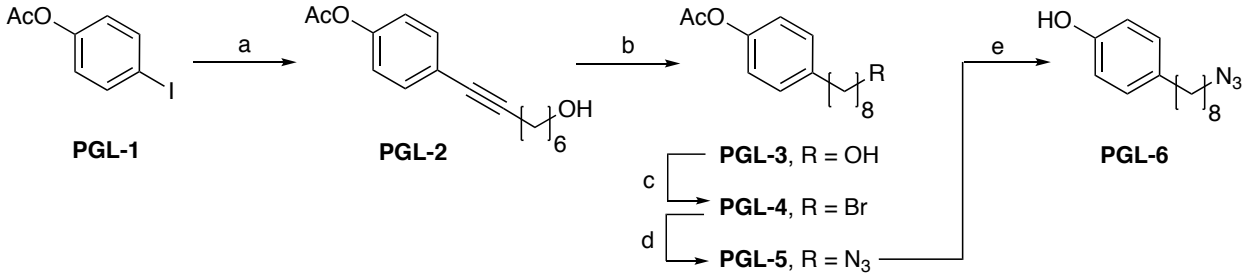
3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[2,3,4-Tri-*O*-

benzyl-6-*O*-(2-naphthylmethyl)-α-D-mannopyranosyl-(1→2)]-1-(5'-azidopentyl)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol (LAM-157). To a solution of **LAM-156** (100 mg, 0.3 mmol) and 5-azidopentyl iodide (37 mg, 0.16 mmol) in DMF (1 mL), was added sodium hydride (60% oil suspension, 11 mg, 0.26 mmol) at 0 °C. The solution was stirred for 20 h as it warmed to rt, diluted with EtOAc and water was added. The aqueous layer was extracted with twice with EtOAc and the combined organic layer was washed with water and then brine. After drying ($MgSO_4$), the organic layer was concentrated and the resulting residue was purified by chromatography (1:3 EtOAc–Hexanes) to give **LAM-157** (98 mg, 95%). $[\alpha]_D$ +28.2 (*c* = 5.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.89–7.66 (m, 4 H), 7.46–6.96 (m, 114 H), 5.47 (d, 1 H, *J* = 1.3 Hz, H-1), 5.23 (d, 1 H, *J* = 1.3 Hz, H-1), 5.21 (d, 1 H, *J* = 1.8 Hz, H-1), 5.20 (d, 1 H, *J* = 1.4 Hz, H-1), 5.01 (d, 1 H, *J* = 10.7 Hz), 4.94 (d, 1 H, *J* = 11.8 Hz), 4.90 (d, 1 H, *J* = 10.6 Hz), 4.86–4.26 (m, 44 H), 4.23 (d, 1 H, *J* = 11.9 Hz), 4.17–3.80 (m, 24 H), 3.68–3.62 (m, 3 H), 3.57–3.49 (m, 4 H), 3.41–3.25 (m, 9 H), 3.12–3.02 (m, 4 H), 1.65–1.57 (m, 2 H), 1.48–1.35 (m, 4 H); ^{13}C NMR (600 MHz, $CDCl_3$, δ_C) 139.0, 138.9, 138.8, 138.7(2), 138.6(6), 138.6(2), 138.5(9), 138.5(6), 138.5(2), 138.4(6), 138.4(3), 138.4(0), 138.3(2), 138.3(0), 138.2, 138.1, 138.0, 137.9, 137.8, 135.8, 133.2, 132.9, 128.4(9), 128.4(6), 128.3(4), 128.3(1), 128.2(9), 128.2(6), 128.2(4), 128.1(9), 128.1(4), 128.1(2), 128.1(0), 128.0(6), 128.0(4), 128.0(0), 127.9(2), 127.8(6), 127.8(3), 127.8(0), 127.7(7), 127.7(4), 127.6(8), 127.6(4), 127.5(8), 127.5(5), 127.5, 127.4(3), 127.3(8), 127.2(7), 127.2(5), 127.2, 127.1, 126.8, 126.7, 126.5, 125.9, 125.7, 100.3 (C-1), 99.2 (C-1), 99.1 (C-1), 98.9 (C-1), 98.7 (C-1), 98.3 (C-1), 82.7, 81.4, 80.7, 79.9(2), 79.8(9), 79.8(6), 79.1, 78.9, 78.8, 76.6, 76.1, 75.8, 75.7, 75.5, 74.9, 74.8, 74.8, 74.6(2), 74.6(0), 74.5, 74.4, 74.3, 74.2, 73.5, 73.4, 73.3(2), 73.2(6), 73.2, 72.8, 72.7, 72.5, 72.40, 72.36, 72.3, 72.21, 72.17, 72.1, 72.0, 71.9, 71.8(4), 71.8(1), 71.2, 71.1, 71.0, 70.8, 70.5, 70.1, 69.1, 68.9, 68.8, 68.7, 65.9, 65.7, 62.6, 51.0, 29.7, 28.6, 23.0. HRMS (ESI) *m/z* calcd for (M+2Na) calcd for $C_{212}H_{219}N_3O_{36}Na_2$: 1715.2675. Found: 1715.2708.

α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-1-(5'-aminopentyl)-D-*myo*-inositol (23). A solution of **LAM-157** (201 mg, 0.06 mmol) in a mixture of phosphate buffer–CH_3OH–THF (1:6:4, 20 mL) was degassed with argon and then 20% $Pd(OH)_2$ (1.0 g) was added. The mixture was further purged with H_2 gas and stirred under H_2 (1 atm) for 12 h. At that point, the mixture was filtered through Celite and the filtrate was

concentrated to a residue that was purified on a Sephadex column (water). The fractions containing the desired compound were pooled and lyophilized to give **23** (64 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 5.30 (s, 1 H, H-1), 5.21 (s, 1 H, H-1), 5.13 (s, 2 H, 2 × H-1), 5.06 (s, 2 H, 2 × H-1), 4.32–3.37 (m, 46 H), 3.08–3.00 (m, 1 H), 1.47–1.42 (m, 2 H), 1.34–1.16 (m, 2 H), 1.00–0.96 (m, 2 H). HRMS (ESI) *m/z* calcd for (M+H) calcd for $C_{47}H_{84}NO_{36}$: 1238.4773. Found: 1238.4801.

19. Synthesis of 26



Scheme S26. Synthesis of linker for PGL targets. a) 7-octyl-1-ol, $PdCl_2(PPh_3)_2$, Et_3N, CH_3CN, 91%; b) H_2, $Pd(OH)_2$–C, CH_3OH; c) CBr_4, PPh_3, Et_2O, 67% over two steps; d) NaN_3, DMF, 81%; e) $NaOCH_3$, CH_3OH, CH_2Cl_2, quant.

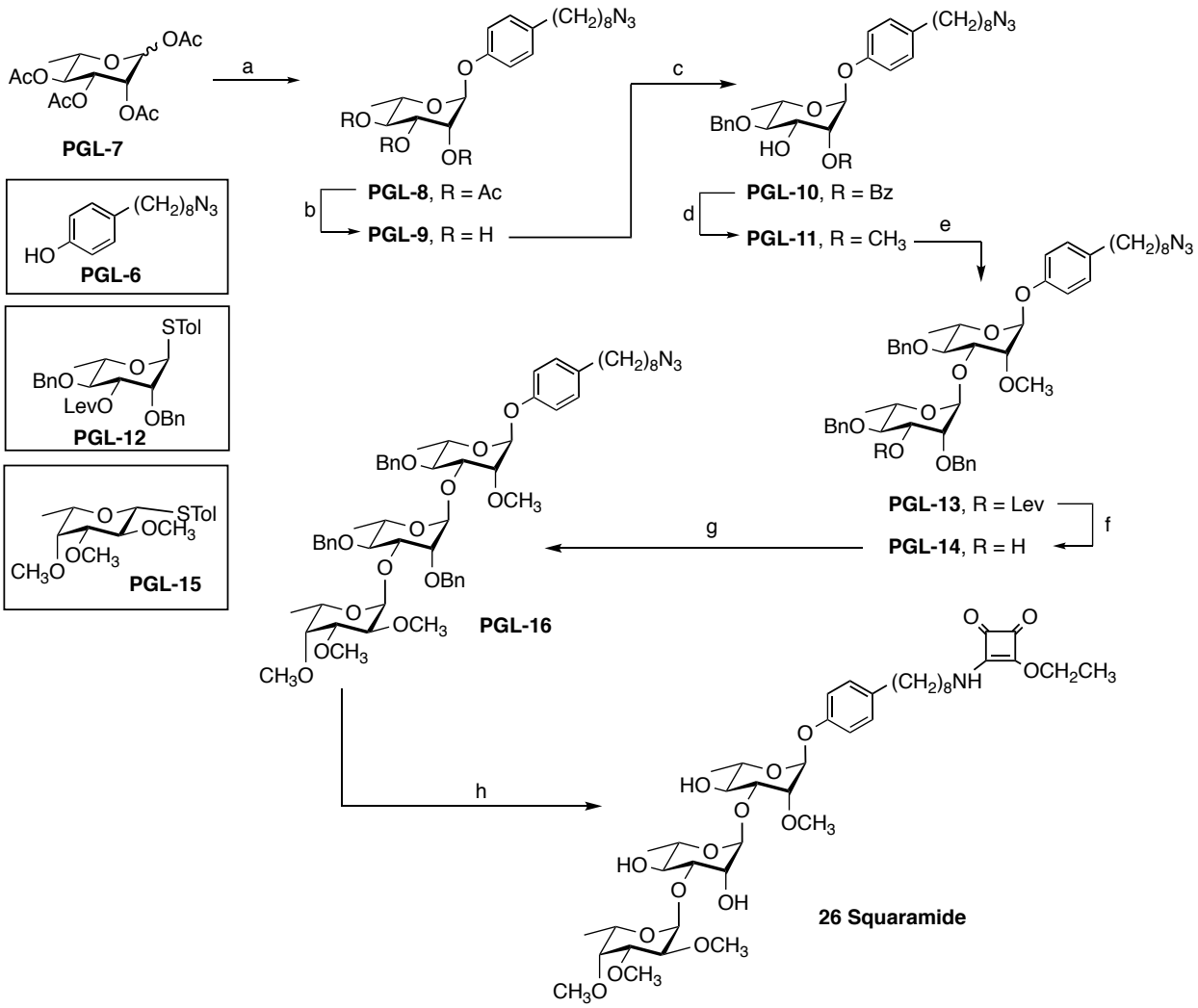
***p*-(8-Hydroxy-1-octynyl)phenyl acetate (PGL-2)**. To a solution of 7-octyn-1-ol [27] (431 mg, 3.42 mmol), 4-iodophenyl acetate[28], (**PGL-1**, 746 mg, 2.85 mmol) and $PdCl_2(PPh_3)_2$ (260 mg, 0.37 mmol) in 2:1 Et_3N–CH_3CN (6 mL) at rt was added CuI (81 mg, 0.43 mmol). The reaction mixture was stirred at rt for 4 h, concentrated and the residue was then co-evaporated twice with toluene. The resulting residue was purified by chromatography (3:7 EtOAc–hexane) to give **PGL-2** (674 mg, 91%) as a yellow oil. R_f 0.27 (2:3 EtOAc–hexane); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.43–7.30 (m, 2 H), 7.05–6.94 (m, 2 H), 3.66 (app t, 2 H, J = 6.4 Hz), 2.40 (app t, 2 H, J = 7.1 Hz), 2.28 (s, 3 H), 1.67–1.56 (m, 4 H), 1.49 (ddd, 2 H, J = 14.0, 9.3, 6.9 Hz), 1.45–1.37 (m, 2 H), 1.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.4, 150.1, 132.8, 122.0, 121.7, 90.5, 80.1, 63.2, 32.9, 28.9, 28.8, 25.5, 21.3, 19.5. HRMS (EI) *m/z* calcd for (M+Na) $C_{16}H_{20}O_3Na$: 283.1305. Found: 283.1299.

***p*-(8-Bromo-1-octynyl)phenyl acetate (PGL-4)**. To a solution of **PGL-2** (327 mg, 1.24 mmol) in CH_3OH (15 mL) at rt was added $Pd(OH)_2$–C (49 mg) and the solution was stirred under H_2 (1 atm) at rt for 2 d. The reaction mixture was filtered and concentrated to give **PGL-3** as a light yellow solid. To the solution of the resulting residue (384 mg, 1.45 mmol) and CBr_4 (1.06 g, 3.19 mmol) in Et_2O (12 mL) at rt was added PPh_3 (1.68 g, 6.39 mmol). The reaction mixture was stirred at rt for 40 min and concentrated and the resulting residue was purified by chromatography (3:97 EtOAc–hexane) to yield **PGL-4** (331 mg, 67%, two steps) as a colorless oil. R_f 0.47 (5:95 EtOAc–hexane); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.19–7.12 (m, 2 H), 7.01–6.94 (m, 2 H), 3.40 (app t, 2 H, J = 6.9 Hz), 2.62–2.55 (m, 2 H), 2.29 (s, 3 H), 1.89–1.80 (m, 2

H), 1.65–1.56 (m, 2 H), 1.42 (dt, 2 H, J = 14.7, 7.5 Hz), 1.36–1.27 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.9, 148.8, 140.5, 129.5, 121.4, 35.5, 34.2, 33.0, 31.6, 29.5, 29.3, 28.9, 28.4, 21.4. HRMS (EI) *m/z* calcd for (M+Na) $C_{16}H_{23}O_2BrNa$: 349.0774. Found: 349.0771.

***p*-(8-Azido-1-octynyl)phenyl acetate (PGL-5)**. A suspension of **PGL-4** (318 mg, 0.97 mmol) and NaN_3 (126 mg, 1.94 mmol) in DMF (5 mL) was stirred at 90 °C for 1 d and then cooled and concentrated. The resulting residue was purified by chromatography (3:97 EtOAc–hexane) to yield **PGL-5** (227 mg, 81%) as a colorless oil. R_f 0.41 (5:95 EtOAc–hexane); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.22–7.14 (m, 2 H), 7.02–6.93 (m, 2 H), 3.25 (app t, 2 H, J = 7.0 Hz), 2.64–2.54 (m, 2 H), 2.29 (s, 3 H), 1.64–1.55 (m, 4 H), 1.40–1.28 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.9, 148.8, 140.6, 129.5, 121.4, 51.7, 35.5, 31.6, 29.5, 29.3, 29.3, 29.0, 26.9, 21.4. HRMS (EI) *m/z* calcd for (M+Na) $C_{16}H_{23}O_2N_3Na$: 312.1682. Found: 312.1681.

4-(8-Azidooctyl)phenol (PGL-6). To a solution of **PGL-5** (200 mg, 691 μmol) in 1:1 CH_2Cl_2–CH_3OH (4 mL) was added sodium methoxide (26 mg, 481 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated to yield **PGL-6** (171 mg, quant) as a colorless oil. R_f 0.24 (1:9 EtOAc–hexane); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.04 (d, 2 H, J = 8.4 Hz), 6.75 (d, 2 H, J = 8.5 Hz), 4.65 (s, 1H), 3.25 (app t, 2 H, J = 7.0 Hz), 2.59–2.44 (m, 2 H), 1.59 (dt, 4 H, J = 14.1, 6.9 Hz), 1.41–1.23; ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 153.6, 135.3, 129.6, 115.3, 51.7, 35.2, 31.9, 29.5, 29.3, 29.0, 26.9. HRMS (EI) *m/z* calcd for (M+Na) $C_{14}H_{21}ON_3Na$: 270.1577. Found: 270.1573.



Scheme S27. Synthesis of **26 Squaramide**. a) **PGL-6**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 66%; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, 98%; c) $PhC(OCH_3)_3$, camphorsulfonic acid, CH_2Cl_2; then BnBr, NaH, DMF; then HOAc, H_2O, 77%; d) CH_3I, NaH, DMF; then $NaOCH_3$, CH_3OH, CH_2Cl_2, 55%; e) **PGL-12**, NIS, AgOTf, CH_2Cl_2, 92%; f) $NaOCH_3$, CH_3OH, CH_2Cl_2, 99%; g) **PGL-15**, NIS, AgOTf, CH_2Cl_2, 63%; h) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 69%.

4-(8-Azidooctyl)phenyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranoside (PGL-8). To a solution of **PGL-7** (1.54 g, 4.63 mmol) and **PGL-6** (1.29 g, 5.21 mmol) in CH_2Cl_2 (31 mL) at 0 °C was added neat $BF_3{\cdot}OEt_2$ (0.91 mL, 7.4 mmol). The reaction mixture was stirred at 0 °C for 10 h, at rt for 28 h and the concentrated before being co-evapaorated twice with toluene. The resulting residue was purified by chromatography (10:90 → 12:88 hexane–EtOAc) to yield **PGL-8** (1.58 g, 66%) as a colorless oil. R_f 0.61 (3:7 EtOAc–hexane); $[\alpha]_D$ –91.4 (*c* = 0.7,

$CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, δ_H) 7.10–7.08 (m, 2 H), 6.99–6.97 (m, 2 H), 5.51 (dd, 1 H, *J* = 10.1, 3.3 Hz), 5.42–5.40 (m, 2 H), 5.14 (app t, 1 H, *J* = 10.0 Hz), 4.01 (dd, 1 H, *J* = 9.8, 6.3 Hz), 3.25 (app t, 2 H, *J* = 7.0 Hz), 2.57–2.52 (m, 2 H), 2.18 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 1.61–1.55 (m, 4 H), 1.37–1.32 (m, 8 H), 1.20 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 170.3, 170.24, 170.23, 154.2, 137.4, 129.6, 116.5, 96.1 ($^1J_{C\text{-}1,H\text{-}1}$ = 175 Hz, C-1), 71.3, 70.0, 69.2, 67.2, 51.7, 35.3, 31.8, 29.5, 29.33, 29.29, 29.1, 26.9, 21.1, 21.0, 20.98, 17.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{26}H_{37}N_3O_8Na$: 542.2473. Found: 542.2465.

4-(8-Azidooctyl)phenyl α-L-rhamnopyranoside (PGL-9). To a solution of **PGL-8** (1.58 g, 3.04 mmol) in 1:1 CH_2Cl_2–CH_3OH (20 mL) at rt was added sodium methoxide (50 mg, 0.92 mmol). The reaction mixture was stirred at rt overnight, neutralizied with Amberlite IR-120 H^+ resin, filtered and concentrated to yield **PGL-9** (1.18 g, 98%) as a colorless wax. The crude product was used for next step without further purification. R_f 0.24 (95:5 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –80.4 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.09 (d, 2 H, *J* = 8.5 Hz), 6.97 (d, 2 H, *J* = 8.6 Hz), 5.47 (s, 1 H, H-1), 4.14 (s, 1H), 3.99 (ddd, 1 H, *J* = 9.4, 6.1, 3.6 Hz), 3.81 (tt, 1 H, *J* = 12.4, 6.2 Hz), 3.54 (app td, 1 H, *J* = 9.5, 3.5 Hz), 3.25 (app t, 2 H, *J* = 7.0 Hz), 2.61 (d, 1 H, *J* = 5.7 Hz), 2.56–2.53 (m, 2 H), 2.44 (d, 1 H, *J* = 3.9 Hz), 2.27 (s, 1H), 1.62–1.58 (m, 4 H), 1.39–1.30 (m, 8 H), 1.29 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.4, 137.0, 129.5, 116.5, 98.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 73.4, 71.9, 71.2, 68.9, 51.7, 35.3, 31.8, 29.6, 29.4, 29.3, 29.0, 26.9, 17.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{20}H_{31}N_3O_5Na$: 416.2156. Found: 416.2150.

4-(8-Azidooctyl)phenyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (PGL-10). To a solution of **PGL-9** (184 mg, 468 μmol) and trimethyl orthobenzoate (0.24 mL, 1.40 mmol) in CH_2Cl_2 (4 mL) at rt was added CSA (22 mg, 94 μmol). The reaction mixture was stirred at rt for 4 h, Et_3N (100 μL), was added and the mixture was concentrated and then co-evaporated twice with toluene to give a colorless oil. To the solution of the resulting oil and BnBr (72 μL, 608 μmol) in DMF (5 mL) at 0 °C was added NaH (60% dispersion in oil, 24 mg, 608 μmol). The reaction mixture was stirred overnight at rt and concentrated. The solution of the resulting oil in aqueous 80% AcOH (8 mL) was stirred at rt for 4 h concentrated and then and co-evaporated twice with toluene. The resulting residue was purified by chromatography (2:98 EtOAc–toluene) to yield **PGL-10** (211 mg, 77%, three steps) as a colorless oil. R_f 0.38 (5:95 EtOAc–hexane); $[\alpha]_D$ –43.6 (*c* = 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.11–8.04 (m, 2

H), 7.63–7.60 (m, 1H), 7.51–7.48 (m, 2 H), 7.42–7.33 (m, 4 H), 7.33–7.30 (m, 1H), 7.11–7.06 (m, 2 H), 7.00–6.93 (m, 2 H), 5.55 (d, 1 H, J = 1.7 Hz, H-1), 5.53 (dd, 1 H, J = 3.4, 1.8 Hz), 4.88 (d, 1 H, J = 11.2 Hz), 4.79 (d, 1 H, J = 11.1 Hz), 4.44 (dd, 1 H, J = 9.4, 3.4 Hz), 3.97 (app dq, 1 H, J = 9.6, 6.2 Hz), 3.55 (app t, 1 H, J = 9.4 Hz), 3.25 (app t, 2 H, J = 7.0 Hz), 2.59–2.50 (m, 2 H), 2.19 (s, 1H), 1.64–1.53 (m, 4 H), 1.40–1.28 (m, 11H); ^{13}C NMR (126 MHz, $CDCl_3$, δ_C) 166.4, 154.4, 138.3, 137.1, 133.7, 130.1, 129.8, 129.5, 128.8, 128.7, 128.3, 128.2, 116.5, 96.1 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 81.9, 75.4, 73.3, 70.6, 68.5, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{34}H_{41}N_3O_6Na$: 610.2888. Found: 610.2876.

4-(8-Azidooctyl)phenyl 4-*O*-benzyl-2-*O*-methyl-L-rhamnopyranoside (PGL-11). To a solution **PGL-10** (498 mg, 847 μmol) and CH_3I (211 μL, 3.39 mmol) in DMF (5 mL) at 0 °C was added NaH (60% dispersion in oil, 47 mg, 1.18 mmol). The reaction mixture was stirred overnight at rt and concentrated. To the solution of the resulting oil in 1:1 CH_2Cl_2–CH_3OH (10 mL) was added sodium methoxide (37 mg, 1.3 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (1:99 acetone–toluene) to yield **PGL-11** (234 mg, 55%, two steps) as a colorless oil. R_f 0.41 (1:9 acetone–toluene); $[\alpha]_D$ –68.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.32 (m, 4 H), 7.31–7.26 (m, 1H), 7.11–7.06 (m, 2 H), 6.99–6.94 (m, 2 H), 5.52 (d, 1 H, J = 1.5 Hz, H-1), 4.92 (d, 1 H, J = 11.1 Hz), 4.70 (d, 1 H, J = 11.1 Hz), 4.15 (app td, 1 H, J = 9.1, 3.8 Hz), 3.80 (app dq, 1 H, J = 12.5, 6.3 Hz), 3.67 (dd, 1 H, J = 3.8, 1.7 Hz), 3.55 (s, 1H), 3.34 (app t, 1 H, J = 9.4 Hz), 3.25 (app t, 2 H, J = 7.0 Hz), 2.59–2.51 (m, 1H), 2.43 (d, 1 H, J = 9.0 Hz), 1.64–1.53 (m, 4 H), 1.40–1.30 (m, 8 H), 1.29 (d, 3 H, J = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.7, 138.6, 136.9, 129.5, 128.6, 128.2, 128.0, 116.4, 94.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 82.3, 80.8, 75.3, 71.7, 68.1, 59.3, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{28}H_{39}N_3O_5Na$: 520.2782. Found: 520.2781.

4-(8-Azidooctyl)phenyl 2,4-di-*O*-benzyl-3-*O*-levulinoyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (PGL-13). A solution of **PGL-11** (53 mg, 107 μmol), **PGL-12**[29] (61 mg, 112 μmol), and crushed 4Å molecular sieves (50 mg) in CH_2Cl_2 (3.5 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (29 mg, 128 μmol) and silver triflate (5.5 mg, 21 μmol). The reaction mixture was stirred at –20 °C for another 30 min, then Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and

the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (25:75 EtOAc–toluene) to yield **PGL-13** (90 mg, 92%) as a colorless oil. R_f 0.34 (3:7 EtOAc–hexane); $[\alpha]_D$ –33.4 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.21 (m, 15 H), 7.09-7.06 (m, 2 H), 6.97–6.95 (m, 2 H), 5.46 (d, 1 H, *J* = 1.8 Hz, H-1), 5.32 (dd, 1 H, *J* = 9.5, 3.2 Hz), 5.11 (d, 1 H, *J* = 1.9 Hz), 4.81 (d, 1 H, *J* = 11.4 Hz), 4.74 (d, 1 H, *J* = 11.4 Hz), 4.65 (dd, 2 H, *J* = 11.4, 5.5 Hz), 4.42 (d, 1 H, *J* = 12.0 Hz), 4.35 (d, 1 H, *J* = 12.1 Hz), 4.20 (dd, 1 H, *J* = 9.6, 3.2 Hz), 4.01 (app dq, 1 H, *J* = 9.6, 6.3 Hz), 3.89 (dd, 1 H, *J* = 3.2, 2.0 Hz), 3.79 (app dq, 1 H, *J* = 9.3, 6.2 Hz), 3.72 (dd, 1 H, *J* = 3.1, 1.9 Hz), 3.67 (app t, 1 H, *J* = 9.5 Hz), 3.59–3.50 (m, 1H), 3.24 (app t, 1 H, *J* = 7.0 Hz), 2.71–2.38 (m, 6 H), 2.12 (s, 3 H), 1.61–1.54 (m, 4 H), 1.36 (d, 1 H, *J* = 6.3 Hz), 1.31 (br s, 8 H), 1.25 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.4, 172.2, 154.7, 138.8, 138.6, 138.3, 136.8, 129.5, 128.6, 128.6, 128.5, 128.0, 127.9, 127.87, 127.8, 127.7, 127.6, 116.4, 100.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 95.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 80.5, 80.3, 79.6, 79.2, 77.0, 75.3, 75.1, 74.2, 73.2, 69.0, 68.7, 59.3, 51.7, 38.0, 35.3, 31.8, 30.0, 29.6, 29.4, 29.3, 29.1, 28.3, 26.9, 18.5, 18.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{53}H_{67}N_3O_{11}Na$: 944.4668. Found: 944.4657.

4-(8-Azidooctyl)phenyl 2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (PGL-14). To a solution of **PGL-13** (195 mg, 211 μmol) in 1:1 CH_2Cl_2–CH_3OH (8 mL) was added sodium methoxide (65 mg, 1.2 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (25:75 EtOAc–hexane) to yield **PGL-14** (172 mg, 99%) as a colorless oil. R_f 0.66 (1:9 acetone–toluene); $[\alpha]_D$ –59.0 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.27 (m, 12 H), 7.26–7.21 (m, 1H), 7.20–7.16 (m, 2 H), 7.12–7.07 (m, 2 H), 7.00–6.96 (m, 2 H), 5.47 (d, 1 H, *J* = 1.8 Hz, H-1), 5.21 (d, 1 H, *J* = 1.2 Hz, H-1), 4.90 (d, 1 H, *J* = 11.3 Hz), 4.79 (d, 1 H, *J* = 11.7 Hz), 4.68 (dd, 2 H, *J* = 13.9, 11.4 Hz), 4.41 (d, 1 H, *J* = 11.7 Hz), 4.25 (dd, 1 H, *J* = 9.7, 3.2 Hz), 4.18 (d, 1 H, *J* = 11.7 Hz), 4.01 (dd, 1 H, *J* = 9.0, 3.5 Hz), 3.90 (app dq, 1 H, *J* = 9.4, 6.0 Hz), 3.82 (app dq, 1 H, *J* = 9.7, 6.1 Hz), 3.73 (dd, 1 H, *J* = 3.7, 1.5 Hz), 3.69 (dd, 1 H, *J* = 3.2, 1.9 Hz), 3.55 (app t, 1 H, *J* = 9.6 Hz), 3.52 (s, 3 H), 3.34 (app t, 1 H, *J* = 9.3 Hz), 3.24 (app t, 2 H, *J* = 7.0 Hz), 2.56–2.51 (m, 2 H), 1.62–1.53 (m, 4 H), 1.36 (d, 3 H, *J* = 6.3 Hz), 1.31 (s, 8 H), 1.25 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.7, 138.8, 138.7, 137.9, 136.9, 129.5, 128.7, 128.6, 128.2, 128.1, 127.9, 127.8, 127.2, 116.39, 99.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 95.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1),

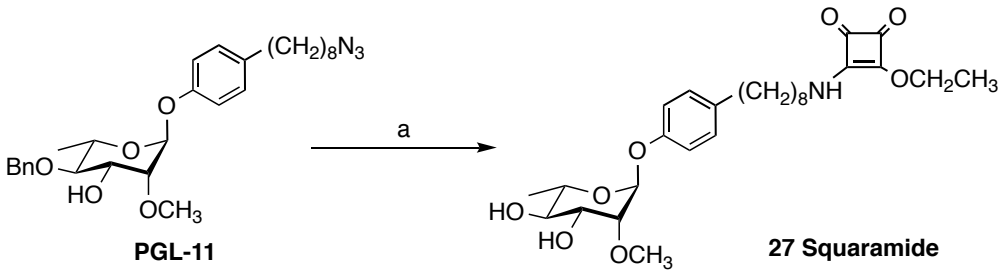
82.4, 80.7, 80.6, 79.5, 78.7, 75.3, 75.2, 72.8, 71.8, 69.1, 68.1, 59.3, 51.7, 35.30, 31.8, 29.6, 29.4, 29.3, 29.1, 26.9, 18.4, 18.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{48}H_{61}N_3O_9Na$: 846.4300. Found: 846.4286.

4-(8-Azidooctyl)phenyl 2,3,4-tri-*O*-methyl-α-L-fucopyranoside-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (PGL-16). A solution of **PGL-14** (66 mg, 80 μmol), **PGL-15**[29] (26 mg, 84 μmol), and crushed 4Å molecular sieves (85 mg) in CH_2Cl_2 (4 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (22 mg, 96 μmol) and silver triflate (4.1 mg, 16 μmol). The reaction mixture was stirred at –20 °C for another 20 min, and then Et_3N (50 μL) and a satd aq soln of $Na_2S_2O_3$ (200 μL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (5:95 acetone–toluene) to yield **PGL-16** (51 mg, 63%) as a colorless oil. R_f 0.31 (1:9 acetone–toluene); $[\alpha]_D$ –98.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.36 (m, 2 H), 7.33–7.25 (m, 13 H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.98 (d, 2 H, *J* = 8.6 Hz), 5.49 (d, 1 H, *J* = 1.6 Hz, H-1), 5.23 (d, 1 H, *J* = 1.4 Hz, H-1), 5.21 (s, 1 H, H-1), 5.19 (d, 1 H, *J* = 11.4 Hz), 4.86 (d, 1 H, *J* = 11.6 Hz), 4.67 (d, 1 H, *J* = 11.6 Hz), 4.61 (d, 1 H, *J* = 11.4 Hz), 4.56 (d, 1 H, *J* = 12.3 Hz), 4.27–4.21 (m, 2 H), 4.09 (dd, 1 H, *J* = 9.4, 3.1 Hz), 3.96 (app dq, 1 H, *J* = 9.5, 6.2 Hz), 3.85–3.78 (m, 2 H), 3.75 (dd, 1 H, *J* = 3.0, 2.0 Hz), 3.69 (q, 1 H, *J* = 6.8 Hz), 3.62 (app t, 1 H, *J* = 9.4 Hz), 3.58–3.55 (m, 3 H) 3.53 (s, 1H), 3.53 (s, 1H), 3.50 (s, 3 H), 3.32 (s, 3 H), 3.25 (app t, 2 H, *J* = 7.0 Hz), 3.20 (s, 1H), 2.58–2.51 (m, 2 H), 1.64–1.54 (m, 4 H), 1.40–1.28 (m, 11H), 1.24 (d, 3 H, *J* = 6.2 Hz), 0.98 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.8, 139.4, 138.7, 138.7, 136.8, 129.5, 128.6, 128.4, 128.4, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 116.4, 99.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 99.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 80.6, 80.3, 80.0, 79.8, 79.4, 79.2, 78.1, 75.1, 74.9, 71.6, 69.0, 66.6, 61.9, 59.3, 59.1, 58.2, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.1, 26.9, 18.4, 18.2, 16.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{57}H_{77}N_3O_{13}Na$: 1034.5349. Found: 1034.5331.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,3,4-tri-*O*-methyl-α-L-fucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranoside (26 Squaramide) A suspension of **PGL-16**[29] (50 mg, 48 μmol) and 20% $Pd(OH)_2$–C (50 mg) in 1:1 CH_2Cl_2–CH_3OH (10 mL) was stirred overnight under H_2 (1 atm) at rt. Another portion of 20% $Pd(OH)_2$–C (50 mg) was added and the mixture was stirred for another night at rt before being

filtered. After concentrating the filtrate, the resulting residue was dissolved in absolute ethanol (5 mL) and stirred at rt with diethyl squarate (67 μL, 455 μmol) and Et_3N (13 μL, 91 μmol) until the reaction was complete as monitored by TLC. The solution was then concentrated and the resulting residue was purified by column chromatography (5:95 CH_3OH–CH_2Cl_2) to yield **26 Squaramide** (30 mg, 69%) as a colorless oil. R_f 0.38 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –121.4 (*c* = 1.4, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 7.06–7.04 (m, 2 H), 6.97–6.90 (m, 2 H), 5.47 (d, 1 H, *J* = 1.6 Hz, H-1), 5.21 (d, 1 H, *J* = 3.8 Hz, H-1), 5.01 (d, 1 H, *J* = 1.6 Hz, H-1), 4.67 (p, 2 H, *J* = 7.2 Hz), 4.09 (q, 1 H, *J* = 6.7 Hz), 4.02 (dd, 1 H, *J* = 3.1, 1.8 Hz), 3.96 (dd, 1 H, *J* = 9.7, 3.2 Hz), 3.78 (app dq, 1 H, *J* = 9.7, 6.3 Hz), 3.74 (dd, 1 H, *J* = 9.6, 3.2 Hz), 3.68–3.64 (m, 2 H), 3.61 (m, 1H), 3.58–3.50 (m, 7 H), 3.49 (m, 7 H), 3.46 (s, 3 H), 3.35 (app t, 1H), 2.50 (app t, 2 H), 1.54 (d, 4 H), 1.39 (app t, 3 H, *J* = 7.1 Hz), 1.31–1.25 (m, 11H), 1.17 (app t, 3 H, *J* = 6.3 Hz), 1.14 (app t, 3 H, *J* = 6.3 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.5, 177.4, 174.7, 155.7, 137.8, 130.3, 117.5, 103.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 100.1 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 96.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 81.5, 81.3, 80.6, 80.4, 79.5, 79.2, 73.3, 73.0, 72.0, 70.8, 70.6, 70.4, 67.9, 61.9, 59.3, 58.8, 58.1, 45.4, 36.0, 32.7, 31.8, 31.4, 30.3, 30.0, 27.2, 18.1, 17.9, 16.6, 16.08. HRMS (ESI) *m/z* calcd for (M+Na) $C_{42}H_{65}NO_{16}Na$: 862.4196. Found: 862.4181.

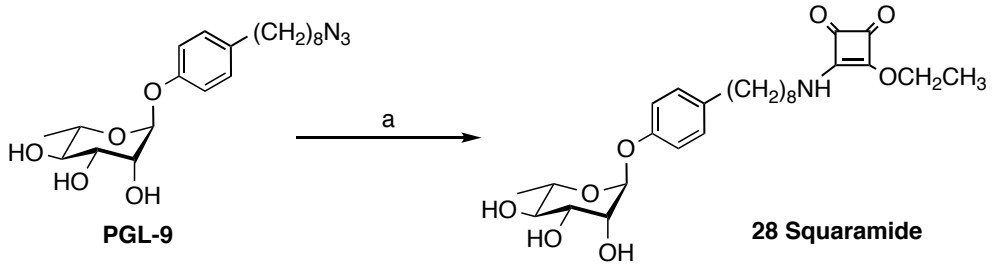
20. Synthesis of 27



Scheme S28. Synthesis of **27 Squaramide**. a) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 68%.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2-*O*-methyl-α-L-rhamnopyranoside (27 Squaramide). Treatment of **PGL-11** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **27 Squaramide** (68%, chromatography 4:96 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.64 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –48.7 (*c* = 1.3, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 7.04 (d, 2 H, *J* = 8.4 Hz), 6.92 (d, 2 H, *J* = 8.5 Hz), 5.46 (s, 1 H, H-1), 4.66 (p, 2 H, *J* = 7.2 Hz), 3.83 (dd, 1 H, *J* = 9.6, 3.4 Hz), 3.63–3.50 (m, 3 H), 3.46 (s, 3 H), 3.34 (dd, 2 H, *J* = 12.2, 6.9 Hz), 2.50 (app t, 2 H, *J* = 7.5 Hz), 1.54 (d, 4 H, *J* = 6.1 Hz), 1.39 (app t, 3 H, *J* = 7.0 Hz), 1.23–127 (m, 8 H), 1.16 (app t, 3 H, *J* = 5.9 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.5, 177.3, 174.7, 155.8, 137.7, 130.2, 117.4, 96.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 82.0, 74.1, 72.1, 70.5, 70.4, 59.4, 45.4, 35.9, 32.7, 31.4, 30.3, 30.04, 30.0, 27.2, 18.0, 16.1 (*C*H_3CH_2). HRMS (ESI) *m/z* calcd for (M+Na) $C_{27}H_{39}NO_8Na$: 528.2568. Found: 528.2563.

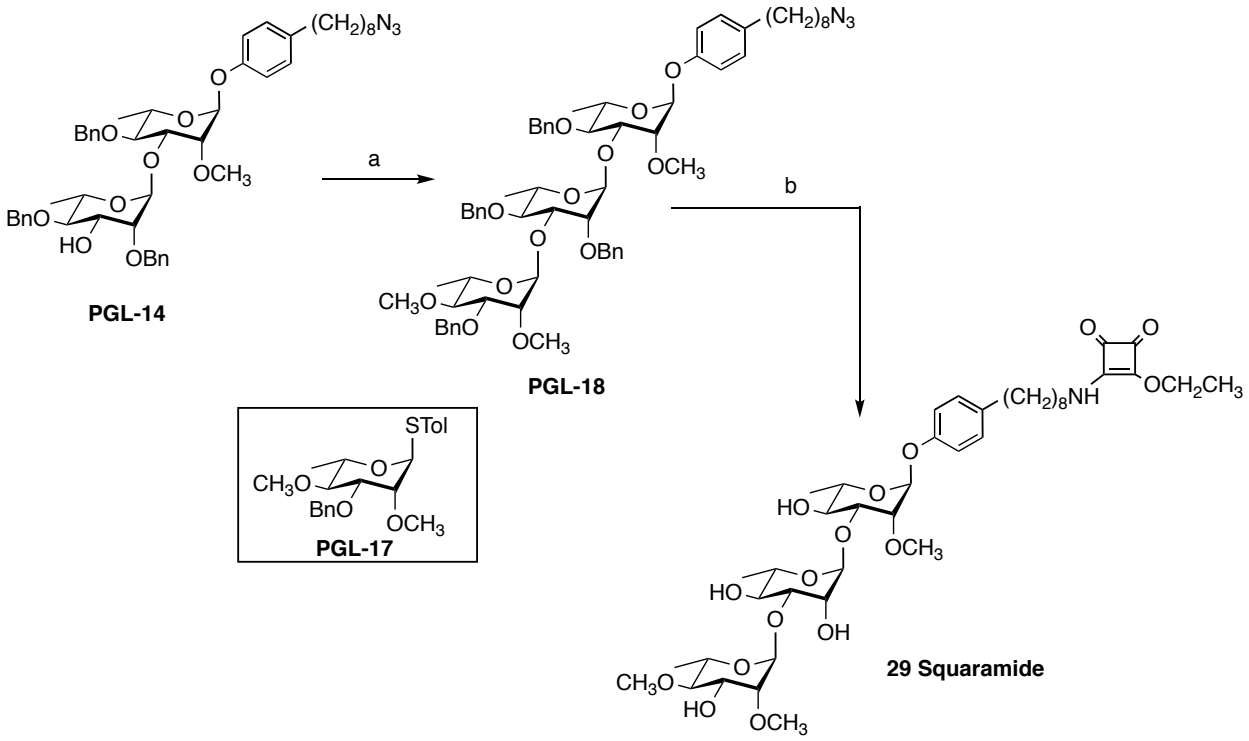
21. Synthesis of 28



Scheme S29. Synthesis of **28 Squaramide**. a) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 63%.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl α-L-rhamnopyranoside (28 Squaramide). Treatment of **PGL-9** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **28 Squaramide** (63%, chromatography 5:95 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.36 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –65.9 (*c* = 1.1, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 7.03 (d, 2 H, *J* = 8.6 Hz), 6.90 (d, 2 H, *J* = 8.6 Hz), 5.31 (d, 1 H, *J* = 1.5 Hz, H-1), 4.66 (p, 2 H, *J* = 7.3 Hz), 3.93 (dd, 1 H, *J* = 3.3, 1.8 Hz), 3.78 (dd, 1 H, *J* = 9.5, 3.4 Hz), 3.61 (app dq, 1 H, *J* = 9.6, 6.2 Hz), 3.52 (app t, 1 H, *J* = 7.1 Hz), 3.39 (app t, 1 H, *J* = 9.5 Hz), 3.35 (app t, 1 H, *J* = 7.0 Hz), 2.49 (app t, 2 H, *J* = 7.6 Hz), 1.54 (d, 4 H, *J* = 6.3 Hz), 1.38 (app t, 3 H, *J* = 7.1 Hz), 1.28 (s, 8 H), 1.17 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.5, 177.4, 174.7, 155.9, 137.6, 130.2, 117.4, 100.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 73.8, 72.2, 72.1, 70.6, 70.4, 45.4, 36.0, 32.7, 31.4, 30.3, 30.1, 30.0, 27.2, 17.9, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{26}H_{37}NO_8Na$: 514.2411. Found: 514.2408.

22. Synthesis of 29



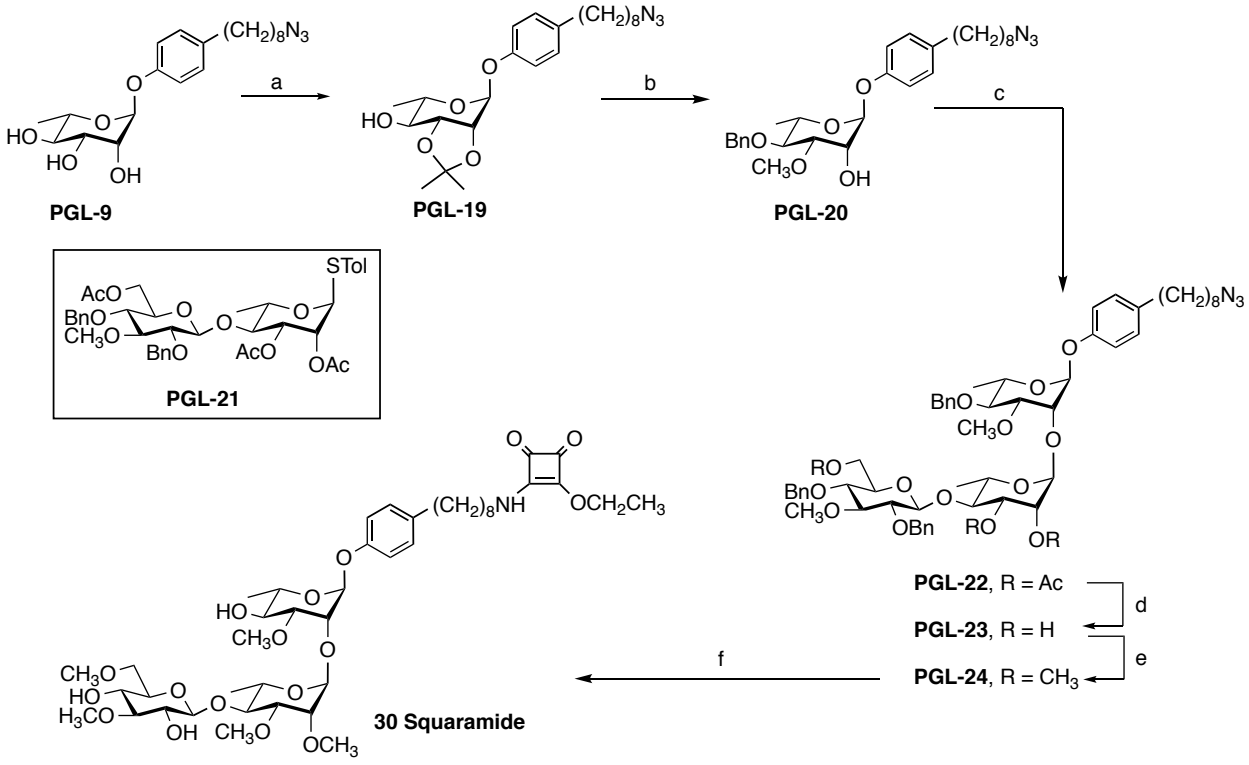
Scheme S30. Synthesis of **29 Squaramide**. a) **PGL-17**, NIS, AgOTf, CH_2Cl_2, 64%; b) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 62%.

4-(8-Azidooctyl)phenyl 3-*O*-benzyl-2,4-di-*O*-methyl-α-L-fucopyranoside-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (PGL-18). A solution of **PGL-14** (51 mg, 62 μmol), **PGL-17**[16] (25 mg, 65 μmol), and crushed 4Å molecular sieves (90 mg) in CH_2Cl_2 (4 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (17 mg, 74 μmol) and silver triflate (3.2 mg, 12 μmol). The reaction mixture was stirred at –20 °C for another 20 min, Et_3N (50 μL) was added, and then the solution was extracted with satd aq soln of $Na_2S_2O_3$ (200 μL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (1:9 EtOAc–hexane) to yield **PGL-18** (43 mg, 64%) as a colorless oil. R_f 0.21 (25:75 EtOAc–hexane); $[\alpha]_D$ –85.5 (*c* = 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.21 (m, 26 H), 7.11–7.07 (m, 2 H), 7.00–6.95 (m, 2 H), 5.48 (d, 1 H, *J* = 1.7 Hz, H-1), 5.23 (d, 1 H, *J* = 3.7 Hz, H-1), 5.22 (d, 1 H, *J* = 1.5 Hz, H-1), 5.20 (d, 1 H, *J* = 11.5 Hz), 4.84 (d, 1 H, *J* = 11.6 Hz), 4.79 (d, 1 H, *J* = 12.1 Hz), 4.69 (d, 1 H, *J* = 12.1 Hz), 4.66 (d, 1 H, *J* = 11.6 Hz), 4.61 (d, 1 H, *J* = 11.3 Hz), 4.52 (d, 1 H, *J* = 12.3

Hz), 4.28–4.22 (m, 2 H), 4.11 (dd, 1 H, *J* = 9.5, 3.1 Hz), 3.95 (app dq, 1 H, *J* = 9.7, 6.2 Hz), 3.85–3.78 (m, 3 H), 3.75 (dd, 1 H, *J* = 3.1, 2.0 Hz), 3.73–3.67 (m, 1H), 3.65 (dd, 1 H, *J* = 6.6, 3.6 Hz), 3.62 (dd, 1 H, *J* = 11.8, 3.4 Hz), 3.58–3.54 (m, 4 H), 3.53 (s, 3 H), 3.36 (s, 3 H), 3.25 (app t, 1 H, *J* = 7.0 Hz), 3.15 (d, 1 H, *J* = 2.1 Hz), 2.58–2.51 (m, 2 H), 1.63–1.54 (m, 4 H), 1.40–1.29 (m, 11H), 1.24 (d, 3 H, *J* = 6.2 Hz), 0.95 (d, 3 H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 139.4, 139.1, 138.7, 136.8, 129.5, 128.6, 128.6, 128.42, 128.40, 127.8, 127.7, 127.6, 127.55, 127.52, 127.4, 127.3, 116.4, 100.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 99.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 80.8, 80.6, 80.3, 80.0, 79.8, 79.7, 79.1, 78.7, 78.6, 75.2, 74.9, 72.8, 71.7, 69.0, 68.9, 66.7, 62.0, 59.6, 59.1, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.4, 18.2, 16.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{63}H_{81}N_3O_{13}Na$: 1110.5662. Found: 1110.5652.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,4-di-*O*-methyl-α-L-fucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranoside (29 Squaramide). Treatment of **PGL-18** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **29 Squaramide** (62%, chromatography 5:95 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.46 (12:88 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –119.8 (*c* = 1.0, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 7.07–7.03 (m, 2 H), 6.96–6.91 (m, 2 H), 5.47 (d, 1 H, *J* = 1.5 Hz, H-1), 5.23 (d, 1 H, *J* = 3.8 Hz, H-1), 5.00 (d, 1 H, *J* = 1.4 Hz, H-1), 4.67 (p, 2 H, *J* = 7.2 Hz), 4.13 (q, 1 H, *J* = 6.5 Hz), 4.03 (dd, 1 H, *J* = 2.9, 1.9 Hz), 3.99–3.92 (m, 2 H), 3.78 (app dq, 1 H, *J* = 9.6, 6.2 Hz), 3.74 (dd, 1 H, *J* = 9.6, 3.2 Hz), 3.67 (dd, 1 H, *J* = 3.0, 2.0 Hz), 3.61 (app dq, 1 H, *J* = 10.3, 6.1 Hz), 3.58–3.50 (m, 5 H), 3.51–3.43 (m, 7 H), 3.41 (dd, 1 H, *J* = 10.3, 3.7 Hz), 3.35 (app t, 1 H, *J* = 7.0 Hz), 3.30 (d, 1 H, *J* = 3.3 Hz), 2.50 (app t, 2 H, *J* = 7.5 Hz), 1.54 (d, 4 H, *J* = 5.5 Hz), 1.39 (app t, 3 H, *J* = 7.1 Hz), 1.31–1.25 (m, 11H), 1.17 (dd, 6 H, *J* = 7.9, 6.5 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.5, 177.4, 174.7, 155.7, 137.8, 130.3, 117.5, 103.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 99.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 96.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 84.4, 81.5, 80.6, 80.2, 79.2, 73.3, 73.0, 72.0, 71.0, 70.8, 70.6, 70.4, 67.8, 62.5, 59.3, 58.6, 45.4, 36.0, 32.7, 31.8, 31.4, 30.3, 30.0, 27.2, 18.1, 17.9, 16.6, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{41}H_{63}NO_{16}Na$: 848.4039. Found: 848.4024.

23. Synthesis of 30



Scheme S31. Synthesis of **30 Squaramide**. a) $(CH_3)_2C(OCH_3)_2$, *p*-TsOH·H_2O, acetone, 95%; b) NaH, BnBr, DMF; then *p*-TsOH·H_2O, CH_2Cl_2, CH_3OH; then *n*-Bu_2SnO, toluene; then CH_3I, *n*-Bu_4NI 71%; c) **PGL-21**, NIS, AgOTf, CH_2Cl_2, 83%; d) $NaOCH_3$, CH_2Cl_2, CH_3OH; e) CH_3I, NaH, DMF, 86% over two steps; f) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 60%

4-(8-Azidooctyl)phenyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (PGL-19). To a solution of **PGL-9** (1.18 g, 2.99 mmol) and 2,2-dimethoxypropane (1.10 mL, 8.97 mmol) in acetone (50 mL) at rt was added *p*-TsOH·H_2O (0.17 g, 0.90 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Et_3N (1 mL), concentrated and then the residue was co-evaporated with toluene. The resulting residue was purified by chromatography (75:25 hexane–EtOAc) to yield **PGL-19** (1.23 g, 95%) as a colorless oil. R_f 0.60 (6:4 hexane–EtOAc); $[\alpha]_D$ –55.2 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.12–7.07 (m, 2 H), 6.99–6.94 (m, 2 H), 5.67 (s, 1 H, H-1), 4.35 (d, 1 H, *J* = 5.7 Hz), 4.23 (dd, 1 H, *J* = 7.2, 5.8 Hz), 3.81 (app dq, 1 H, *J* = 9.7, 6.2 Hz), 3.47 (ddd, 1 H, *J* = 11.3, 7.8, 3.4 Hz), 3.25 (app t, 2 H, *J* = 7.0 Hz), 2.58–2.52 (m, 2 H), 2.19 (d, 1 H, *J* = 3.7 Hz), 1.64–1.54 (m, 7 H), 1.40 (s, 3 H), 1.39–1.28 (m, 8 H), 1.25 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.5, 136.9, 129.5, 116.5,

110.0, 95.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 78.6, 76.1, 74.9, 66.8, 51.7, 35.3, 31.7, 29.5, 29.3, 29.28, 29.0, 28.3, 26.9, 26.5 (*C*H_3), 17.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{23}H_{35}N_3O_5Na$: 456.2469. Found: 456.2460.

4-(8-Azidooctyl)phenyl 4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside (PGL-20). To a solution **PGL-19** (697 mg, 1.61 mmol) and BnBr (288 μL, 4.62 mmol) in DMF (5 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 90 mg, 2.25 mmol). The reaction mixture was stirred overnight at rt and concentrated. The resulting residue was purified by chromatography (2:98 EtOAc–hexane) to give a colorless oil. A solution of the resulting oil and *p*-TsOH·H_2O (66 mg, 346 μmol) in 1:1 CH_3OH–CH_2Cl_2 (24 mL) was stirred overnight at rt, before Et_3N (200 μL) was added and the mixture concentrated. The resulting oil was purified by chromatography (25:75 EtOAc–hexane) to give a colorless oil. A solution of the resulting oil (515 mg, 1.06 mmol) and *n*-Bu_2SnO (291 mg, 1.17 mmol) in toluene (30 mL) was heated refluxed with a Dean–Stark apparatus overnight, cooled, concentrated and dried on a vacuum pump for 1 h. The solution of this residue, *n*-Bu_4NI (472 mg, 1.28 mmol) and CH_3I (6.6 mL, 106 mmol) in toluene (10 mL) in a Schlenk tube was heated at 110 °C for 1 d, cooled and concentrated. The resulting residue was purified by chromatography (1:99 acetone–toluene) to give **PGL-20** (379 mg, 71%, 4 steps) as a colorless oil. R_f 0.34 (2:8 EtOAc–hexane); $[\alpha]_D$ –104.1 (*c* = 1.1, $CHCl_3$); IR ν 2096 (azide) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.38–7.27 (m, 5 H), 7.11–7.06 (m, 2 H), 6.98–6.93 (m, 2 H), 5.52 (d, 1 H, *J* = 1.7 Hz, H-1), 4.87 (d, 1 H, *J* = 11.0 Hz), 4.65 (d, 1 H, *J* = 11.0 Hz), 4.23 (dt, 1 H, *J* = 3.6, 1.9 Hz), 3.83 (app dq, 1 H, *J* = 9.6, 6.2 Hz), 3.76 (dd, 1H *J* = 9.1, 3.4 Hz), 3.56 (s, 3 H), 3.43 (app t, 1 H, *J* = 9.4 Hz), 3.25 (app t, 2 H, *J* = 7.0 Hz), 2.56–2.53 (m, 3 H, CH_2Ar), 1.63–1.53 (m, 4 H), 1.40–1.29 (m, 8 H), 1.26 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$, δ_C) 154.5, 138.7, 136.8, 129.5, 128.6, 128.2, 127.9, 116.4, 97.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 81.7, 80.1, 75.5, 68.1, 68.1, 57.8, 51.7, 35.3, 31.8, 29.6, 29.4, 29.3, 29.1, 26.9, 18.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{28}H_{39}N_3O_5Na$: 520.2782. Found: 520.2783.

4-(8-Azidooctyl)phenyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-methyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside (PGL-22). A solution of **PGL-20** (63 mg, 127 μmol), **PGL-21**[30] (83 mg, 110 μmol) and crushed 4Å molecular sieves (100 mg) in CH_2Cl_2 (3 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (30 mg, 132 μmol) and silver triflate (5.7 mg, 22 μmol). The reaction mixture was stirred at –20 °C for another 30 min, Et_3N

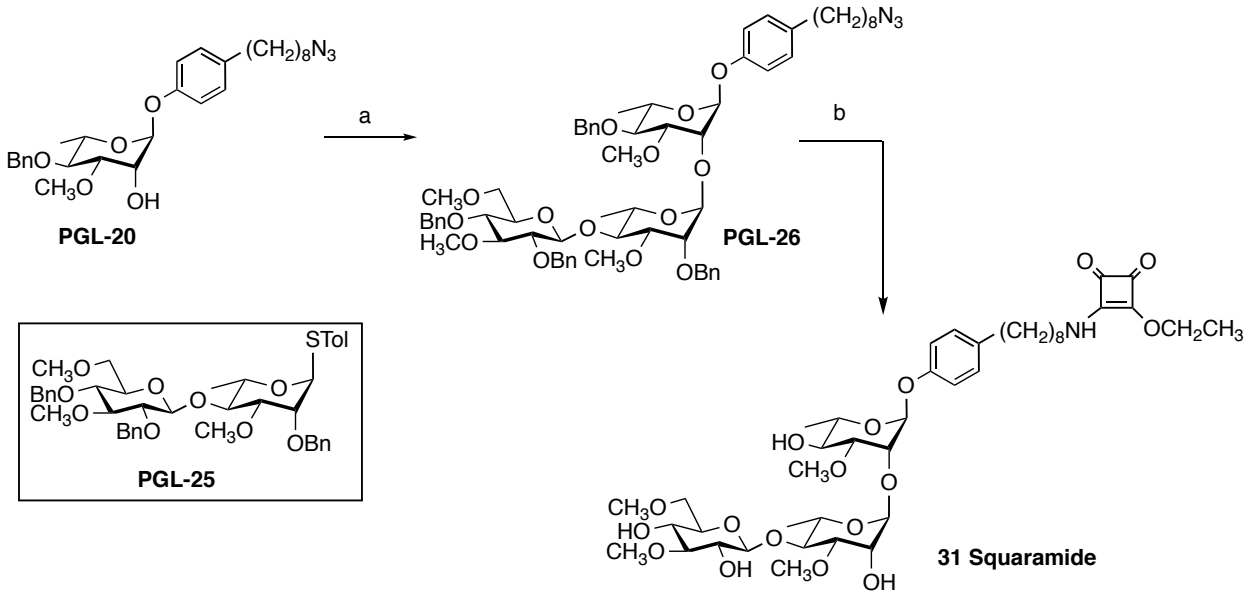
(50 μL) and a satd aq soln of $Na_2S_2O_3$ (200 μL) were added, and then the solution was dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (3:97 acetone–toluene) to yield **PGL-22** (102 mg, 83%) as a colorless oil. R_f 0.22 (3:7 EtOAc–hexane); $[\alpha]_D$ –46.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.27 (m, 15 H), 7.11–7.06 (m, 2 H), 6.98–6.92 (m, 2 H), 5.48–5.44 (m, 2 H), 5.35 (dd, 1 H, *J* = 9.8, 3.4 Hz), 5.05 (d, 1 H, *J* = 1.6 Hz, H-1), 4.91 (d, 1 H, *J* = 11.0 Hz), 4.85 (d, 1 H, *J* = 11.0 Hz), 4.77 (d, 1 H, *J* = 11.4 Hz), 4.66 (d, 1 H, *J* = 11.0 Hz), 4.60 (dd, 2 H, *J* = 13.9, 11.3 Hz), 4.50 (d, 1 H, *J* = 7.6 Hz, H-1), 4.37 (dd, 1 H, *J* = 11.7, 2.3 Hz), 4.22–4.18 (m, 1H), 4.16 (dd, 1 H, *J* = 11.8, 5.3 Hz), 3.90 (app dq, 1 H, *J* = 12.5, 6.1 Hz), 3.84–3.75 (m, 1H), 3.66 (app t, 1 H, *J* = 9.7 Hz), 3.62 (s, 3 H), 3.56 (app t, 1 H, *J* = 9.4 Hz), 3.51 (s, 3 H), 3.48 (ddd, 1 H, *J* = 9.6, 5.3, 2.3 Hz), 3.37 (app t, 1 H, *J* = 9.2 Hz), 3.30 (app t, 1 H, *J* = 8.8 Hz), 3.27–3.21 (m, 3 H), 2.57–2.51 (m, 2 H), 2.16 (s, 3 H), 2.03 (s, 3 H), 1.88 (s, 3 H), 1.64–1.54 (m, 4 H), 1.39–1.30 (m, 8 H), 1.28 (d, 3 H, *J* = 4.6 Hz), 1.27 (d, 3 H, *J* = 4.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.8, 170.1, 170.0, 154.5, 138.9, 138.6, 138.1, 136.9, 129.5, 128.7, 128.6, 128.5, 128.4, 128.35, 128.3, 128.2, 127.8, 127.79, 116.4, 103.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 163 Hz, C-1), 99.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 175 Hz, C-1), 97.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 87.2, 82.1, 81.7, 80.4, 77.8, 76.9, 75.6, 75.2, 75.0, 74.5, 72.6, 71.7, 70.4, 69.0, 68.1, 63.3, 61.5, 58.4, 51.7, 35.3, 31.8, 29.6, 29.4, 29.3, 29.1, 26.9, 21.3, 21.0, 21.97, 18.2, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{61}H_{79}N_3O_{17}Na$: 1148.5302. Found: 1148.5288.

4-(8-Azidooctyl)phenyl 2,4-di-*O*-benzyl-3,6-di-*O*-methyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside (PGL-24). To a solution of **PGL-22** (95 mg, 84 μmol) in 1:1 CH_2Cl_2–CH_3OH (4 mL) was added sodium methoxide (11.4 mg, 211 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated to give a colorless oil (triol **PGL-23**). To the solution of the resulting oil and CH_3I (24 μL, 389 μmol) in DMF (2 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 14 mg, 340 μmol). The reaction mixture was stirred at rt for 4 h, neutralized by the addition of AcOH and concentrated. The resulting residue was purified by chromatography (4:6 EtOAc–hexane) to yield **PGL-24** (73 mg, 86%, two steps) as a colorless oil. R_f 0.26 (3:7 EtOAc–hexane); $[\alpha]_D$ –57.4 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41 (d, 2 H, *J* = 7.1 Hz), 7.39–7.31 (m, 16 H), 7.31–7.24 (m, 3 H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.95 (d, 2 H, *J* = 8.6 Hz), 5.47 (d, 1 H, *J* = 1.7 Hz, H-1), 5.17 (d, 1 H, *J* = 1.6 Hz, H-1), 4.95–4.87 (m, 2 H), 4.82 (d, 1 H, *J*

= 10.9 Hz), 4.75–4.73 (m, 2 H), 4.64 (dd, 2 H, *J* = 12.9, 11.1 Hz), 4.25–4.21 (m, 1H), 3.86–3.78 (m, 2 H), 3.77–3.68 (m, 3 H), 3.67–3.61 (m, 4 H), 3.59–3.52 (m, 5 H), 3.51 (s, 3 H), 3.50–3.42 (m, 2 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 3.31 (ddd, 2 H *J* = 5.2, 4.6, 2.6 Hz), 3.27–3.22 (m, 3 H), 2.58–2.51 (m, 2 H), 1.58 (app td, 4 H, *J* = 14.7, 7.5 Hz), 1.36–1.25 (m, 14 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.5, 139.3, 138.7, 138.7, 136.9, 129.5, 128.6, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.6, 116.4, 103.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 166 Hz, C-1), 98.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 97.59 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 86.9, 82.9, 81.9, 81.2, 80.4, 78.0, 75.3, 75.0, 74.7, 74.6, 73.9, 71.4, 68.7, 68.2, 61.5, 59.8, 59.2, 58.3, 57.5, 51.7, 35.3, 31.8, 29.6, 29.4, 29.3, 29.1, 26.9, 18.4, 18.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{58}H_{79}N_3O_{14}Na$: 1064.5454. Found: 1064.5439.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 3,6-di-*O*-methyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-methyl-α-L-rhamnopyranoside (30 Squaramide). Treatment of **PGL-24** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **30 Squaramide** (60%, chromatography 5:95 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.40 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –54.9 (*c* = 0.8, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 7.08–7.03 (m, 2 H), 6.92–6.87 (m, 2 H), 5.45 (d, 1 H, *J* = 1.7 Hz, H-1), 5.44 (s, 1 H, N*H*), 5.05 (d, 1 H, *J* = 1.8 Hz, H-1), 4.67 (p, 4 H), 4.50 (d, 1 H, *J* = 7.8 Hz, H-1), 4.18 (dd, 1 H, *J* = 2.9, 2.2 Hz), 3.75–3.68 (m, 2 H), 3.66–3.59 (m, 2 H), 3.59–3.49 (m, 11H), 3.46–3.40 (m, 7 H), 3.38–3.29 (m, 5 H), 3.29–3.27 (m, 1H), 3.16 (dd, 1 H, *J* = 9.2, 7.8 Hz), 3.03 (dd, 1 H, *J* = 9.1, 8.5 Hz), 2.51 (app t, 2 H, *J* = 7.6 Hz), 1.55 (dd, 4 H, *J* = 13.0, 6.9 Hz), 1.39 (app td, 3 H, *J* = 7.0, 2.6 Hz), 1.29 (s, 8 H), 1.19 (d, 3 H, *J* = 6.2 Hz), 1.18 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (151 MHz, CD_3OD, δ_C) 189.8, 184.6, 177.4, 174.7, 155.8, 138.0, 130.3, 117.3, 104.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 163 Hz, C-1), 100.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 98.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 87.5, 82.0, 81.9, 79.1, 77.6, 76.7, 75.9, 75.4, 73.2, 72.9, 71.1, 70.6, 70.55, 69.1, 60.8, 59.7, 59.0, 58.4, 57.4, 45.4, 35.9, 32.7, 31.8, 31.4, 30.3, 30.0, 27.2, 18.2, 18.1, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{43}H_{67}NO_{17}Na$: 892.4301. Found: 892.4290.

24. Synthesis of 31



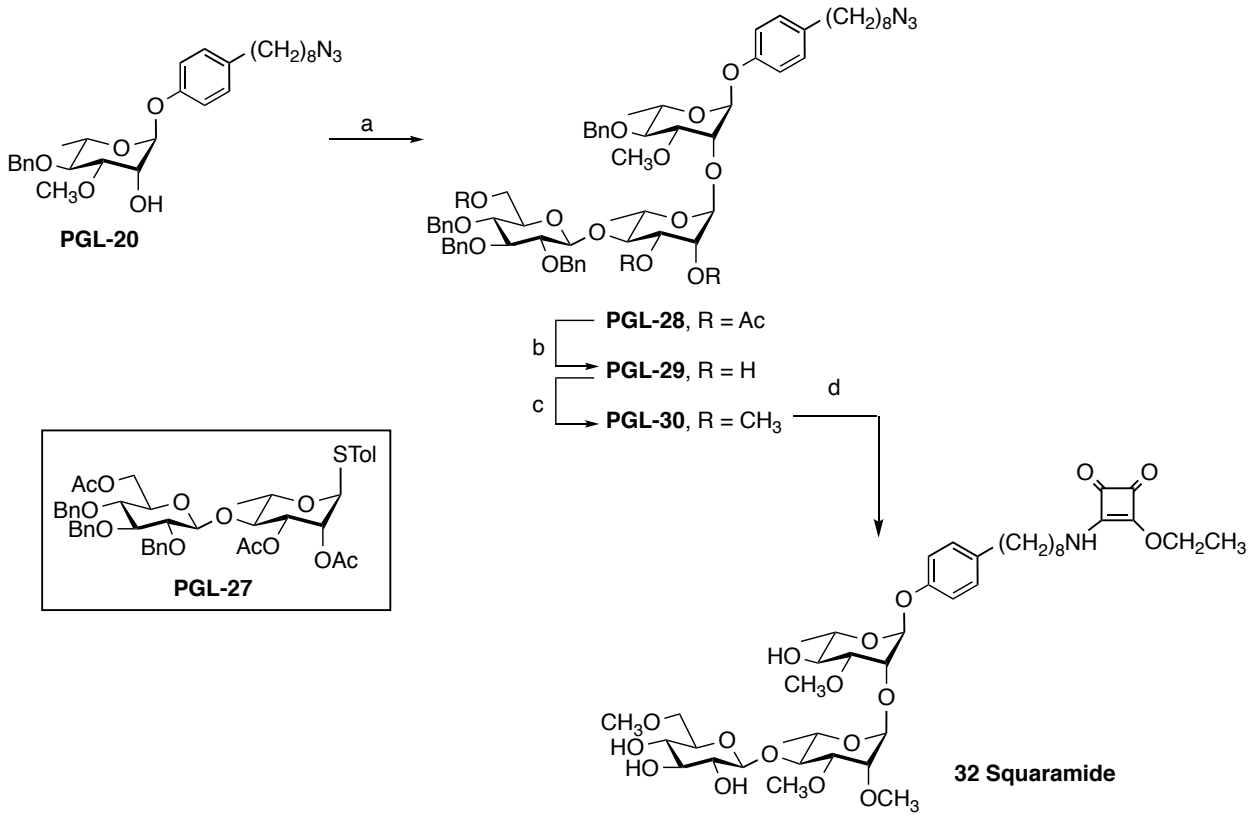
Scheme S32. Synthesis of **31 Squaramide**. a) **PGL-25**, NIS, AgOTf, CH_2Cl_2, 60%; b) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 57%.

4-(8-Azidooctyl)phenyl 2,4-di-*O*-benzyl-3,6-di-*O*-methyl-β-D-glucopyranosyl-(1→4)-2-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside (PGL-26). A solution of **PGL-20** (33 mg, 66 μmol), **PGL-25**[30] (51 mg, 68 μmol) and crushed 4Å molecular sieves (85 mg) in CH_2Cl_2 (4 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (18 mg, 80 μmol) and silver triflate (3.4 mg, 13 μmol). The reaction mixture was stirred at –20 °C for another 30 min, Et_3N (50 μL) and a satd aq soln of $Na_2S_2O_3$ (200 μL) were added, and then the solution was dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (15:85 EtOAc–toluene) to yield **PGL-26** (43 mg, 60%) as a colorless oil. R_f 0.39 (25:75 EtOAc–hexane); $[\alpha]_D$ –47.5 (*c* = 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41 (dd, 4 H, *J* = 12.8, 7.5 Hz), 7.37–7.23 (m, 16 H), 7.08 (d, 2 H, *J* = 8.5 Hz), 6.94 (d, 2 H, *J* = 8.5 Hz), 5.45 (s, 1 H, H-1), 5.15 (s, 1 H, H-1), 4.92 (d, 1 H, *J* = 11.5 Hz), 4.85 (app t, 2 H, *J* = 11.2 Hz), 4.76–4.71 (m, 4 H), 4.64 (d, 1 H, *J* = 11.0 Hz), 4.60 (d, 1 H, *J* = 11.0 Hz), 4.19 (m, 1H), 3.88 (m, 1H), 3.84–3.71 (m, 4 H), 3.68–3.61 (m, 4 H), 3.58 (d, 1 H, *J* = 11.2 Hz), 3.56–3.49 (m, 2 H), 3.48 (s, 3 H), 3.40–3.33 (m, 6 H), 3.28–3.24 (m, 3 H), 3.21 (s, 3 H), 2.59–2.49 (m, 2 H), 1.59 (dt, 4 H, *J* =

14.3, 7.3 Hz), 1.43–1.28 (m, 11H), 1.24 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.5, 139.3, 138.8, 138.7, 138.4, 136.8, 129.5, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.5, 116.4, 103.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 166 Hz, C-1), 99.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 97.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 86.9, 82.8, 81.9, 81.4, 80.3, 78.0, 77.5, 75.3, 75.0, 74.7, 74.6, 73.6, 73.3, 72.6, 71.5, 68.7, 68.2, 61.4, 59.8, 58.1, 57.4, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.0, 26.9, 18.4, 18.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{64}H_{83}N_3O_{14}Na$: 1140.5767. Found: 1140.5750.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 3,6-di-*O*-methyl-β-D-glucopyranosyl-(1→4)-3-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-methyl-α-L-rhamnopyranoside (31 Squaramide). Treatment of **PGL-26** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **31 Squaramide** (57%, chromatography 8:92 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.19 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –48.9 (c = 0.8, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 7.07–7.04 (m, 2 H), 6.92–6.87 (m, 2 H), 5.46 (d, 1 H, J = 1.8 Hz, H-1), 4.93 (d, 1 H, J = 1.8 Hz, H-1), 4.66 (p, 2 H, J = 7.2 Hz), 4.52 (d, 1 H, J = 7.8 Hz, H-1), 4.18–4.14 (m, 1H), 4.09 (dd, 1 H, J = 3.1, 1.9 Hz), 3.74 (app dq, 1 H, J = 9.5, 6.3 Hz), 3.66–3.60 (m, 3 H), 3.58 (s, 3 H), 3.57–3.49 (m, 4 H), 3.48 (s, 3 H), 3.44 (d, 1 H, J = 9.5 Hz), 3.41 (s, 3 H), 3.37–3.32 (m, 4 H), 3.32–3.28 (m, 2 H), 3.16 (dd, 1 H, J = 9.2, 7.8 Hz), 3.03 (dd, 1 H, J = 9.2, 8.5 Hz), 2.50 (app t, 2 H, J = 7.6 Hz), 1.58–1.51 (m, 4 H), 1.39 (app td, 3 H, J = 7.1, 2.5 Hz), 1.29 (s, 8 H), 1.21 (d, 3 H, J = 6.2 Hz), 1.17 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.6, 177.4, 174.7, 155.8, 138.0, 130.3, 117.3, 104.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 164 Hz, C-1), 103.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 98.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 87.5, 82.1, 81.8, 79.0, 76.7, 75.6, 75.4, 73.1, 72.9, 71.1, 70.6, 70.55, 69.0, 67.7, 60.8, 59.7, 58.2, 56.8, 49.2, 36.0, 32.7, 31.8, 31.4, 30.3, 30.0, 27.2, 18.1, 18.06, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{36}H_{61}NO_{14}Na$: 754.3984. Found: 754.3982.

25. Synthesis of 32



Scheme S33. Synthesis of **32 Squaramide**. a) **PGL-27**, NIS, AgOTf, CH_2Cl_2, 59%; b) $NaOCH_3$, CH_2Cl_2, CH_3OH; e) CH_3I, NaH, DMF, 89% over two steps; f) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 71%.

4-(8-Azidooctyl)phenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside (PGL-28). A solution of **PGL-20** (63 mg, 127 μmol), **PGL-27**[30] (110 mg, 133 μmol) and crushed 4Å molecular sieves (100 mg) in CH_2Cl_2 (4 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (34 mg, 152 μmol) and silver triflate (6.5 mg, 25 μmol). The reaction mixture was stirred at –20 °C for another 30 min, Et_3N (50 μL) and a satd aq soln of $Na_2S_2O_3$ (200 μL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (3:97 acetone–toluene) to yield **PGL-28** (90 mg, 59%) as a colorless oil. R_f 0.39 (5:95 acetone–toluene); $[\alpha]_D$ –44.6 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.38–7.24 (m, 26 H), 7.10–7.07 (m, 2 H), 6.97–6.94 (m, 1H), 5.48 (dd, 1 H, *J* = 3.3, 1.8 Hz), 5.46 (d, 1 H, *J* = 1.9 Hz, H-1), 5.35 (dd, 1 H, *J* =

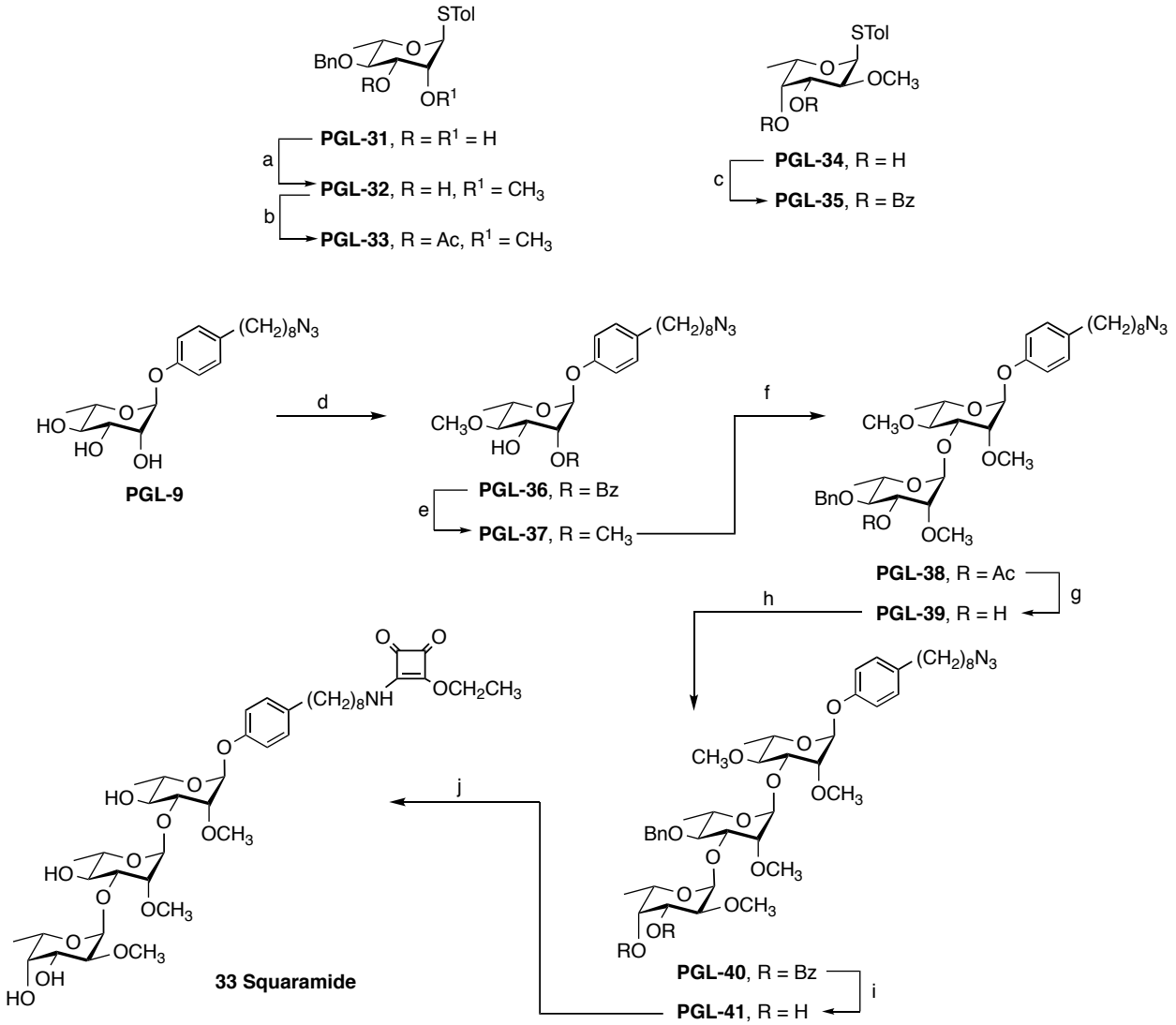
9.8, 3.4 Hz), 5.05 (d, 1 H, *J* = 1.7 Hz, H-1), 4.92 (dd, 2 H, *J* = 10.9, 8.7 Hz), 4.85 (d, 1 H, *J* = 11.0 Hz), 4.79 (dd, 2 H, *J* = 13.3, 11.2 Hz), 4.65 (dd, 2 H, *J* = 13.6, 11.3 Hz), 4.58 (d, 1 H, *J* = 11.1 Hz), 4.55 (d, 1 H, *J* = 7.8 Hz, H-1), 4.40 (dd, 1 H, *J* = 11.7, 1.9 Hz), 4.20–4.19 (m, 1H), 4.17 (dd, 1 H, *J* = 11.7, 4.7 Hz), 3.91 (app dq, 1 H, *J* = 12.5, 6.2 Hz), 3.83–3.76 (m, 2 H), 3.69 (app t, 1 H, *J* = 9.7 Hz), 3.61 (app t, 1 H, *J* = 8.7 Hz), 3.56 (app t, 1 H, *J* = 9.4 Hz), 3.52–3.46 (m, 5 H), 3.37 (dd, 1 H, *J* = 9.0, 7.9 Hz), 3.25 (app t, 2 H, *J* = 7.0 Hz), 2.56–2.53 (m, 2 H), 2.17 (s, 3 H), 2.03 (s, 3 H), 1.92 (s, 3 H), 1.62–1.56 (m, 4 H), 1.37–1.32 (m, 8 H), 1.29 (d, 3 H, *J* = 6.2 Hz), 1.27 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.8, 170.1, 170.0, 154.5, 138.9, 138.6, 138.5, 138.0, 136.9, 129.5, 128.7, 128.6, 128.5, 128.3, 128.2, 128.16, 127.9, 127.8, 127.78, 116.4, 103.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 164 Hz, C-1), 99.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 175 Hz, C-1), 97.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 85.1, 82.3, 81.6, 80.4, 77.9, 76.7, 75.9, 75.6, 75.3, 75.1, 74.5, 72.7, 71.8, 70.4, 69.0, 68.1, 63.2, 58.4, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.1, 26.9, 21.3, 21.0, 20.99, 18.2, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{67}H_{83}N_3O_{17}Na$: 1224.5615. Found: 1224.5603.

4-(8-Azidooctyl)phenyl 2,3,4-tri-*O*-benzyl-6-*O*-methyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside (PGL-30). To a solution of **PGL-28** (80 mg, 66 μmol) in 1:1 CH_2Cl_2–CH_3OH (4 mL) was added sodium methoxide (19 mg, 352 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated to give a colorless oil (triol **PGL-29**). To the solution of the resulting oil and CH_3I (20 μL, 317 μmol) in DMF (2 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 11 mg, 277 μmol). The reaction mixture was stirred at rt for 4 h, neutralized by the addition of AcOH and concentrated. The resulting residue was purified by chromatography (4:6 EtOAc–hexane) to yield **PGL-30** (66 mg, 89%, two steps) as a colorless oil. R_f 0.26 (4:6 EtOAc–hexane); $[\alpha]_D$ –59.4 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.33 (m, 6 H), 7.33–7.24 (m, 14 H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.95 (d, 2 H, *J* = 8.6 Hz), 5.47 (d, 1 H, *J* = 1.8 Hz, H-1), 5.18 (d, 1 H, *J* = 1.7 Hz, H-1), 4.98–4.87 (m, 3 H), 4.79 (ddd, 4 H, *J* = 29.4, 16.2, 10.1 Hz, H-1), 4.64 (app t, 2 H, *J* = 11.2 Hz), 4.25–4.21 (m, 1H), 3.85–3.79 (m, 2 H), 3.74 (dd, 2 H, *J* = 5.7, 2.3 Hz), 3.71 (dd, 1 H, *J* = 3.2, 1.9 Hz), 3.70–3.65 (m, 1H), 3.65–3.59 (m, 2 H), 3.59–3.54 (m, 5 H), 3.52 (s, 3 H), 3.45 (app t, 1 H, *J* = 9.4 Hz), 3.39–3.35 (m, 8 H), 3.25 (app t, 2 H, *J* = 7.0 Hz), 2.58–2.51 (m, 2 H), 1.59 (dt, 4 H, *J* = 14.3, 7.0 Hz), 1.41–1.29 (m, 11H), 1.27 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 139.2, 139.1, 138.7, 138.6, 136.9, 129.5, 128.6,

128.5, 128.4, 128.2, 128.17, 128.1, 128.0, 127.9, 127.6, 127.57, 116.4, 103.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 166 Hz, C-1), 98.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 97.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 85.1, 83.0, 81.9, 81.2, 80.4, 78.1, 76.9, 76.88, 75.8, 75.3, 75.2, 74.8, 74.77, 73.9, 71.4, 68.7, 68.2, 59.9, 59.2, 58.3, 57.4, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.1, 26.9, 18.4, 18.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{64}H_{83}N_3O_{14}Na$: 1140.5767. Found: 1140.5763.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 6-*O*-methyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-2-*O*-methyl-α-L-rhamnopyranoside (32 Squaramide). Treatment of **PGL-30** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **32 Squaramide** (71%, chromatography 1:9 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.18 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –49.7 (*c* = 1.0, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 7.08–7.03 (m, 2 H), 6.93–6.87 (m, 2 H), 5.46 (d, 1 H, *J* = 1.7 Hz, H-1), 5.06 (d, 1 H, *J* = 1.8 Hz, H-1), 4.67 (p, 2 H, *J* = 7.3 Hz), 4.50 (d, 1 H, *J* = 7.8 Hz, H-1), 4.21–4.16 (m, 1H), 3.75–3.69 (m, 2 H), 3.67–3.61 (m, 2 H), 3.60–3.52 (m, 5 H), 3.51 (s, 3 H), 3.46–3.41 (m, 7 H), 3.37–3.30 (m, 5 H), 3.30–3.28 (m, 1H), 3.24–3.20 (m, 1H), 3.11 (dd, 1 H, *J* = 9.1, 7.8 Hz), 2.51 (app t, 2 H, *J* = 7.6 Hz), 1.59–1.50 (m, 4 H), 1.39 (app td, 3 H, *J* = 7.0, 2.4 Hz), 1.29 (s, 8 H), 1.20 (d, 3 H, *J* = 6.2 Hz), 1.18 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (151 MHz, CD_3OD, δ_C) 189.8, 184.6, 177.4, 174.7, 155.8, 137.9, 130.3, 117.3, 104.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 163 Hz, C-1), 100.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 98.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 82.1, 81.9, 79.0, 77.8, 77.7, 76.8, 75.9, 75.5, 73.2, 73.0, 71.6, 70.6, 70.55, 69.1, 59.7, 59.0, 58.4, 57.4, 45.4, 35.9, 32.7, 31.8, 31.4, 30.3, 30.0, 27.2, 18.2, 18.1, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{42}H_{65}NO_{17}Na$: 878.4145. Found: 878.4127.

26. Synthesis of 33



Scheme S34. Synthesis of **33 Squaramide**. a) CH_3I, *n*-Bu_4NCl, 40% NaOH, CH_2Cl_2, 69% b) Ac_2O, pyridine, 83%; c) BzCl, pyridine, 53%; d) $PhC(OCH_3)_3$, camphorsulfonic acid, CH_2Cl_2; then CH_3I, NaH, DMF; then HOAc, H_2O, 93%; e) CH_3I, NaH, DMF; then $NaOCH_3$, CH_3OH, CH_2Cl_2, 59%; f) **PGL-33**, NIS, AgOTf, CH_2Cl_2; g) $NaOCH_3$, CH_3OH, CH_2Cl_2, 74% over two steps; h) **PGL-35**, NIS, AgOTf, CH_2Cl_2; i) $NaOCH_3$, CH_3OH, CH_2Cl_2, 81% over two steps; j) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 60%.

***p*-Tolyl 4-*O*-benzyl-2-*O*-methyl-1-thio-α-L-rhamnopyranoside (PGL-32)**. A solution of diol **PGL-31**[30] (335 mg, 929 μmol), CH_3I (67 μL, 1.1 μmo) and *n*-Bu_4NCl (310 mg, 1.12 μmol) in CH_2Cl_2 (12 mL) at rt was added aqueous 40% NaOH (250 μL). The reaction mixture

was stirred at rt for 3 d, concentrated and then co-evaporated twice with toluene. The resulting residue was purified by chromatography (4:96 acetone–toluene) to yield **PGL-32** (239 mg, 69%) as a colorless oil. R_f 0.40 (15:85 EtOAc–toluene); $[\alpha]_D$ –191.4 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.33 (m, 6 H), 7.29 (app t, 1 H, *J* = 7.8 Hz), 7.12 (d, 2 H, *J* = 8.2 Hz), 5.52 (s, 1 H, H-1), 4.92 (d, 1 H, *J* = 11.1 Hz), 4.69 (d, 1 H, *J* = 11.1 Hz), 4.18 (app dq, 1 H, *J* = 6.2, 9.4 Hz), 3.96 (app td, 1 H, *J* = 9.1, 3.7 Hz), 3.75 (dd, 1 H, *J* = 3.6, 1.3 Hz), 3.47 (s, 3 H), 3.35 (app t, 1 H, *J* = 9.3 Hz), 2.45 (d, 1 H, *J* = 9.0 Hz), 2.33 (s, 3 H), 1.33 (d, 1 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 137.8, 132.1, 130.9, 130.1, 128.7, 128.2, 128.0, 84.6 (C-1), 82.6, 82.4, 75.4, 72.3, 68.5, 58.3, 21.3, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{21}H_{26}O_4SNa$: 397.1444. Found: 397.1446.

***p*-Tolyl 3-*O*-acetyl-4-*O*-benzyl-2-*O*-methyl-1-thio-α-L-rhamnopyranoside (PGL-33)**. To a solution of **PGL-32** (212 mg, 5.66 μmol) in pyridine (5 mL) at 0 °C was added Ac_2O (212 μL, 2.26 mmol). The reaction mixture was stirred overnight at rt, concentrated and the residue was co-evaporated twice with toluene. The resulting residue was purified by chromatography (7:93 EtOAc–hexane) to yield **PGL-33** (195 mg, 83%) as a colorless oil. R_f 0.61 (2:8 EtOAc–hexane); $[\alpha]_D$ –132.6 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.27 (m, 7 H), 7.14–7.11 (m, 2 H), 5.45 (dd, 1 H, *J* = 1.9, 0.5 Hz, H-1), 5.21 (dd, 1 H, *J* = 9.4, 3.3 Hz), 4.74 (d, 1 H, *J* = 11.3 Hz), 4.66 (d, 1 H, *J* = 11.3 Hz), 4.25 (app dq, 1 H, *J* = 9.5, 6.3 Hz), 3.91 (dd, 1 H, *J* = 3.3, 1.9 Hz), 3.62 (app t, 1 H, *J* = 9.4 Hz), 3.42 (s, 3 H), 2.33 (s, 3 H), 2.07 (s, 3 H), 1.33 (dd, 3 H, *J* = 7.3, 3.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 138.4, 137.8, 132.1, 130.9, 130.0, 128.7, 128.0, 127.8, 85.1 (C-1), 80.2, 79.5, 75.3, 74.1, 69.1, 58.7, 21.3(4), 21.3(2), 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{23}H_{28}O_5SNa$: 439.1543. Found: 439.1550.

***p*-Tolyl 3,4-di-*O*-benzoyl-2-*O*-methyl-1-thio-α-L-fucopyranoside (PGL-35)**. To a solution of diol **PGL-34**[16] (1.06 g, 3.73 mmol) in pyridine (10 mL) at 0 °C was added BzCl (1.73 mL, 14.9 mmol). The reaction mixture was stirred overnight at rt, concentrated and the residue was and co-evaporated twice with toluene. The resulting residue was purified by chromatography (1:9 EtOAc–hexane) to yield **PGL-35** (1.11 g, 53%) as a colorless solid. R_f 0.55 (2:8 EtOAc–hexane); $[\alpha]_D$ –82.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.98–7.95 (m, 2 H), 7.85–7.83 (m, 2 H), 7.64–7.59 (m, 3 H), 7.51–7.43 (m, 3 H), 7.33–7.29 (m, 2 H), 7.21–7.19 (m, 2 H), 5.62 (dd, 1 H, *J* = 3.4, 0.8 Hz), 5.34 (dd, 1 H, *J* = 9.6, 3.3 Hz), 4.65 (d, 1 H, *J* = 9.6 Hz, H-1), 3.99 (qd, 1 H, *J* = 6.4, 0.9 Hz), 3.60 (app t, 1 H, *J* = 9.6 Hz), 3.49 (s, 3 H), 2.41 (s,

3 H, ArC*H*$_3$), 1.31 (d, 3 H, *J* = 6.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0, 165.7, 138.3, 133.8, 133.5, 133.3, 130.1, 129.9, 129.8, 129.8, 129.7, 129.0, 128.7, 128.5, 87.2 (C-1), 76.7, 75.8, 73.5, 71.8, 61.2, 21.5, 17.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{28}O_6SNa$: 515.1502. Found: 515.1499.

4-(8-Azidooctyl)phenyl 2-*O*-benzoyl-4-*O*-methyl-α-L-rhamnopyranoside (PGL-36). To a solution of **PGL-9** (841 mg, 2.14 mmol) and trimethyl orthobenzoate (1.47 mL, 8.55 mmol) in CH_2Cl_2 (23 mL) at rt was added CSA (99 mg, 0.43 mmol). The reaction mixture was stirred at rt for 4 h, Et_3N (0.5 mL) was added, concentrated and then the residue was co-evapaorated twice with toluene to give a colorless oil. To the solution of the resulting oil and CH_3I (266 μL, 4.27 mmol) in DMF (10 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 111 mg, 2.78 mmol). The reaction mixture was stirred overnight at rt and concentrated. The solution of the resulting oil in aqueous 80% AcOH (20 mL) was stirred at rt for 3 h, concentrated and the residue was co-evaporated twice with toluene. The resulting residue was purified by chromatography (1:9 EtOAc–hexane) to yield **PGL-36** (1.02 g, 93%, three steps) as a colorless oil. R_f 0.29 (15:85 EtOAc–hexane); $[\alpha]_D$ –53.8 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.09 (m, 2 H), 7.67–7.55 (m, 1H), 7.55–7.41 (m, 2 H), 7.14–7.04 (m, 2 H), 7.02–6.92 (m, 2 H), 5.62–5.48 (m, 2 H, H-1), 4.36 (dd, 1 H, *J* = 9.5, 2.9 Hz), 3.87 (app dq, 1 H, *J* = 9.5, 6.2 Hz), 3.63 (s, 3 H), 3.34–3.19 (m, 3 H), 2.64-2.44 (m, 2 H), 2.34 (br, 1H), 1.62–1.54 (m, 4 H), 1.39–1.28 (m, 11H); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 166.4, 154.5, 137.1, 133.7, 130.1, 129.8, 129.5, 128.7, 116.5, 96.2 (C-1), 83.9, 73.1, 70.3, 68.4, 61.2, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{28}H_{37}N_3O_6Na$: 534.2575. Found: 534.2575.

4-(8-Azidooctyl)phenyl 2,4-di-*O*-methyl-L-rhamnopyranoside (PGL-37). To a solution **PGL-36** (591 mg, 1.16 mmol) and CH_3I (288 μL, 4.62 mmol) in DMF (5 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 65 mg, 1.6 mmol). The reaction mixture was stirred overnight at rt and concentrated. To the solution of the resulting oil in 1:1 CH_2Cl_2–CH_3OH (12 mL) was added sodium methoxide (82 mg, 1.5 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (2:8 EtOAc–hexane) to yield **PGL-37** (290 mg, 59%, two steps) as a colorless oil. R_f 0.45 (4:6 EtOAc–hexane); $[\alpha]_D$ –57.9 (*c* = 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.11–7.06 (m, 2 H), 6.99–6.94 (m, 2 H), 5.50 (d, 1 H, *J* = 1.5 Hz, H-1), 4.03 (app td, 1 H, *J* = 9.1, 3.8 Hz), 3.70 (app dq, 1 H, *J* = 9.5, 6.3

Hz), 3.65 (dd, 1 H, J = 3.8, 1.7 Hz), 3.59 (s, 1H), 3.54 (s, 1H), 3.25 (app t, 2 H, J = 7.0 Hz), 3.05 (app t, 1 H, J = 9.4 Hz), 2.58–2.51 (m, 2 H), 2.44 (dd, 1 H, J = 8.8, 4.0 Hz), 1.62–1.53 (m, 4 H), 1.40–1.28 (m, 8 H), 1.27 (d, 3 H, J = 6.3 Hz); ^{13}C NMR (151 MHz, $CDCl_3$, δ_C) 154.7, 136.9, 129.5, 116.4, 94.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 83.9, 80.8, 71.4, 68.2, 61.1, 59.3, 51.8, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{22}H_{35}N_3O_5Na$: 444.2469. Found: 444.2468.

4-(8-Azidooctyl)phenyl 4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-39). A solution of **PGL-33** (270 mg, 648 μmol), **PGL-37** (260 mg, 617 μmol), and crushed 4Å molecular sieves (100 mg) in CH_2Cl_2 (8 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (166 mg, 740 μmol) and silver triflate (32 mg, 123 μmol). The reaction mixture was stirred at –20 °C for another 60 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and then the solution was dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (2:8 EtOAc–hexane) to give a colorless oil (disaccharide **PGL-38**). To the solution of the resulting oil in 1:1 CH_2Cl_2–CH_3OH (8 mL) was added sodium methoxide (15 mg, 278 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (3:7 EtOAc–hexane) to yield **PGL-39** (303 mg, 74%, two steps) as a colorless oil. R_f 0.23 (3:7 EtOAc–hexane); $[\alpha]_D$ –89.6 (c = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.27 (m, 5 H), 7.11–7.06 (m, 2 H), 6.99–6.94 (m, 2 H), 5.44 (d, 1 H, J = 1.7 Hz, H-1), 5.22 (d, 1 H, J = 1.2 Hz, H-1), 4.92 (d, 1 H, J = 11.2 Hz), 4.70 (d, 1 H, J = 11.2 Hz), 4.14 (dd, 1 H, J = 9.7, 3.2 Hz), 4.01 (app td, 1 H, J = 9.2, 3.8 Hz), 3.87 (app dq, 1 H, J = 9.4, 6.3 Hz), 3.70 (app dq, 1 H, J = 9.7, 6.3 Hz), 3.65 (dd, 1 H, J = 3.2, 1.9 Hz), 3.61 (dd, 1H. J = 3.7, 1.5 Hz), 3.55 (s, 3 H), 3.52 (s, 3 H), 3.51 (s, 3 H), 3.31 (app t, 1 H, J = 9.4 Hz), 3.27–3.22 (m, 3 H), 2.58–2.51 (m, 2 H), 2.40 (d, 1 H, J = 9.1 Hz), 1.63–1.54 (m, 4 H), 1.41–1.29 (m, 11H), 1.27 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.7, 138.7, 136.9, 129.5, 128.6, 128.2, 128.0, 116.4, 98.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 95.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 82.7, 82.3, 81.4, 80.5, 78.5, 75.3, 71.8, 69.0, 68.0, 61.2, 59.4, 58.9, 51.7, 35.3, 31.8, 29.5, 29.34, 29.29, 29.0, 26.9, 18.3, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{36}H_{53}N_3O_9Na$: 694.3674. Found: 694.3668.

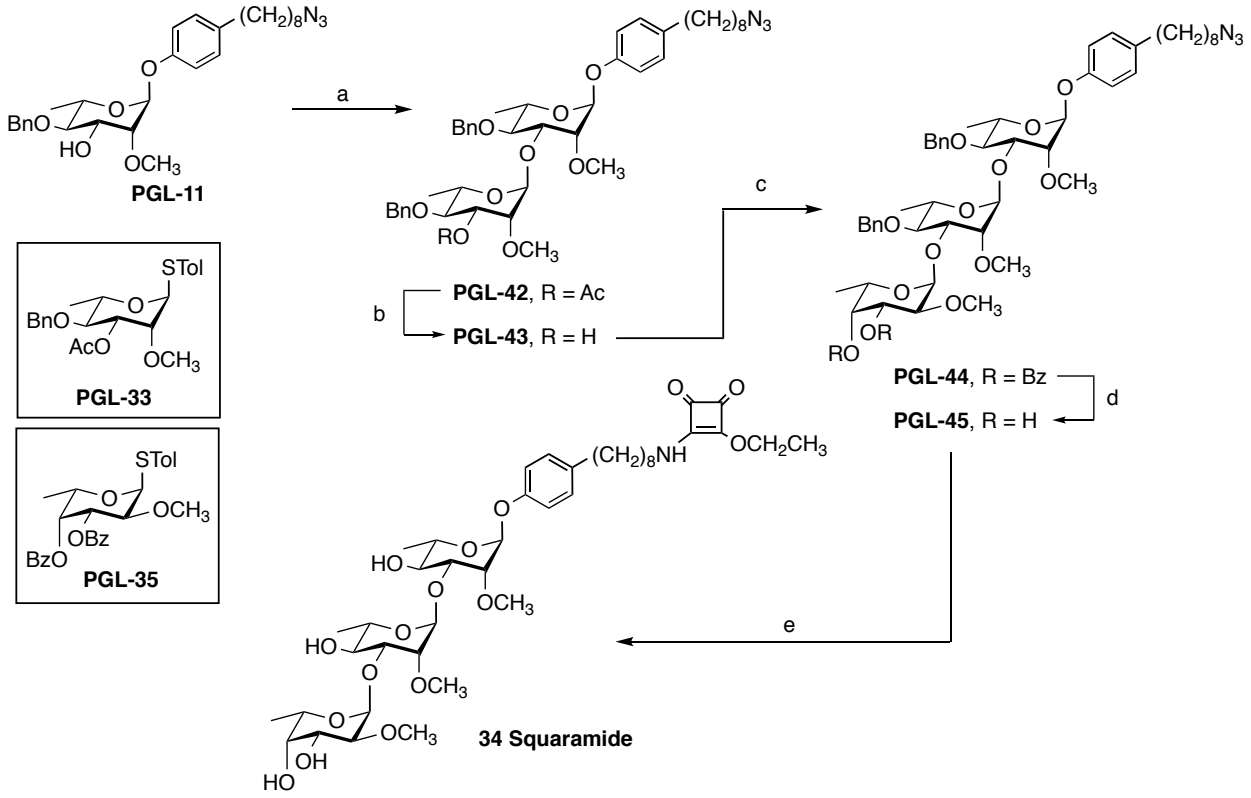
4-(8-Azidooctyl)phenyl 2-*O*-methyl-α-L-fucopyranoside-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-41). A

solution of **PGL-35** (440 mg, 773 μmol), **PGL-39** (433 mg, 645 μmol), and crushed 4Å molecular sieves (290 mg) in CH_2Cl_2 (17 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (174 mg, 773 μmol) and silver triflate (33 mg, 129 μmol). The reaction mixture was stirred at –20 °C for another 60 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and then the solution was dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (1:9 Et_2O–toluene) to give a colorless oil (trisaccharide **PGL-40**). To the solution of the resulting oil in 1:1 CH_2Cl_2–CH_3OH (8 mL) was added sodium methoxide (23 mg, 426 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (2:98 CH_3OH–CH_2Cl_2) to yield **PGL-41** (432 mg, 81%, two steps) as a colorless oil. R_f 0.50 (5:95 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –127.9 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.34 (dt, 4 H, *J* = 15.0, 7.4 Hz), 7.28–7.23 (m, 1H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.97 (d, 2 H, *J* = 8.6 Hz), 5.47 (d, 1 H, *J* = 1.6 Hz, H-1), 5.22 (d, 1 H, *J* = 3.6 Hz, H-1), 5.19 (d, 1 H, *J* = 1.4 Hz, H-1), 5.12 (d, 1 H, *J* = 11.5 Hz), 4.59 (d, 1 H, *J* = 11.5 Hz), 4.25 (q, 1 H, *J* = 6.7 Hz), 4.10 (d, 1 H, *J* = 3.1 Hz), 4.08 (d, 1 H, *J* = 3.1 Hz), 4.02 (dd, 1 H, *J* = 9.4, 3.2 Hz), 3.95 (app dq, 1 H, *J* = 9.5, 6.2 Hz), 3.87 (s, 1H), 3.77 (dd, 1 H, *J* = 2.9, 2.0 Hz), 3.72 (dd, 1 H, *J* = 3.1, 1.9 Hz), 3.71–3.65 (m, 1H), 3.56 (s, 3 H), 3.51 (s, 3 H), 3.50–3.45 (m, 5 H), 3.28 (s, 3 H), 3.27–3.20 (m, 3 H), 2.60 (d, 1 H, *J* = 2.0 Hz), 2.58–2.50 (m, 2 H), 2.38 (s, 1H), 1.63–1.54 (m, 4 H), 1.40–1.28 (m, 14 H), 1.27 (d, 1 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 139.3, 136.9, 129.5, 128.4, 127.6, 127.6, 116.4, 99.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 168 Hz, C-1), 98.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 95.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 168 Hz, C-1), 82.2, 80.9, 80.5, 80.2, 79.6, 78.4, 75.1, 71.6, 69.6, 69.0, 68.9, 66.1, 61.4, 59.1, 58.2, 57.9, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.0, 26.9, 18.5, 18.1, 16.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{43}H_{65}N_3O_{13}Na$: 854.4410. Found: 854.4397.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (33 Squaramide). Treatment of **PGL-41** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **33 Squaramide** (60%, chromatography 6:94 CH_3OH–CH_2Cl_2) as a light yellow foam. R_f 0.32 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –121.3 (*c* = 1.0, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 7.07–7.03 (m, 2 H), 6.95–6.90 (m, 2 H), 5.47 (d, 1 H, *J* = 1.5 Hz, H-1), 5.18 (d, 1 H, *J* = 3.8 Hz, H-1), 5.09 (d, 1 H, *J*

= 1.5 Hz, H-1), 4.67 (p, 2 H, *J* = 7.1 Hz), 4.07 (q, 1 H, *J* = 6.1 Hz), 4.01 (dd, 1 H, *J* = 9.6, 3.2 Hz), 3.84–3.77 (m, 3 H), 3.69 (dd, 1 H, *J* = 3.1, 2.0 Hz), 3.64 (dd, 1 H, *J* = 3.3, 0.7 Hz), 3.62–3.57 (m, 2 H), 3.55–3.49 (m, 4 H), 3.49–3.45 (m, 7 H), 3.45–3.41 (m, 4 H), 3.35 (app t, 1 H, *J* = 7.0 Hz), 3.18 (app t, 1 H, *J* = 9.5 Hz), 2.50 (app t, 2 H, *J* = 7.5 Hz), 1.54 (d, 4 H, *J* = 6.0 Hz), 1.39 (app t, 3 H, *J* = 7.1 Hz), 1.29 (s, 8 H), 1.25 (d, 3 H, *J* = 6.2 Hz), 1.19–1.16 (m, 6 H); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.5, 177.4, 174.7, 155.7, 137.9, 130.3, 117.5, 100.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 100.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 96.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 83.5, 82.0, 81.4, 80.9, 80.3, 79.7, 73.5, 73.0, 70.62, 70.6, 70.55, 69.9, 67.7, 61.5, 59.1, 58.8, 58.6, 45.4, 35.9, 32.7, 31.8, 31.4, 30.3, 30.0, 27.2, 18.2, 18.0, 16.7, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{42}H_{65}NO_{16}Na$: 862.4196. Found: 862.4191.

27. Synthesis of 34



Scheme S35. Synthesis of **34 Squaramide**. a) **PGL-33**, NIS, AgOTf, CH_2Cl_2; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, 57% over two steps; c) **PGL-35**, NIS, AgOTf, CH_2Cl_2; d) $NaOCH_3$, CH_3OH, CH_2Cl_2, 70% over two steps; e) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 66%.

4-(8-Azidooctyl)phenyl 4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (PGL-43). A solution of **PGL-33** (Scheme S34, 116 mg, 278 μmol), **PGL-11** (126 mg, 253 μmol), and crushed 4Å molecular sieves (100 mg) in CH_2Cl_2 (5 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (68 mg, 304 μmol) and silver triflate (13 mg, 51 μmol). The reaction mixture was stirred at –20 °C for another 45 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (3:97 EtOAc–hexane) to give a light yellow oil (disaccharide **PGL-42**). To the solution of the resulting oil in 1:1 CH_2Cl_2–CH_3OH (6 mL) was added sodium methoxide (16 mg, 296 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting

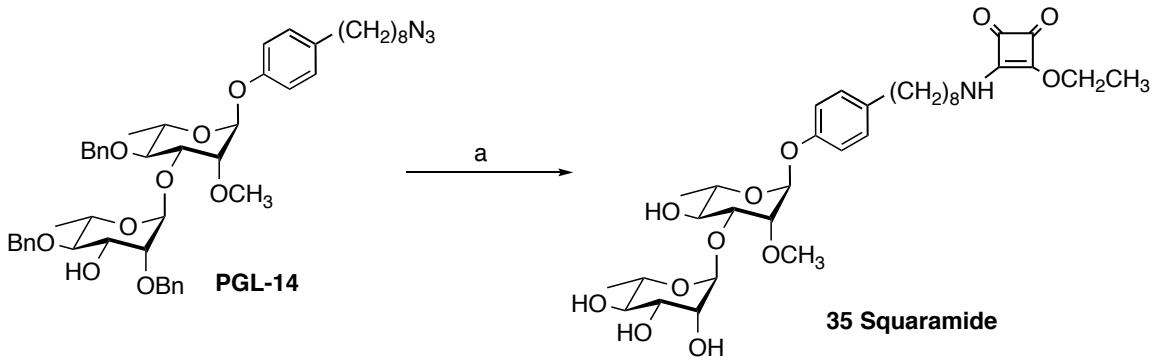
residue was purified by chromatography (2:8 EtOAc–hexane) to yield **PGL-43** (108 mg, 57%, two steps) as a colorless oil. R_f 0.40 (3:7 EtOAc–hexane); $[\alpha]_D$ –93.5 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.23 (m, 10 H), 7.09 (d, 2 H, *J* = 8.5 Hz), 6.98 (d, 2 H, *J* = 8.6 Hz), 5.48 (d, 1 H, *J* = 1.5 Hz, H-1), 5.16 (s, 1 H, H-1), 4.91 (d, 1 H, *J* = 11.2 Hz), 4.80 (d, 1 H, *J* = 11.4 Hz), 4.74–4.67 (m, 2 H), 4.25 (dd, 1 H, *J* = 9.7, 3.1 Hz), 4.00 (app td, 1 H, *J* = 9.2, 3.7 Hz), 3.88 (app dq, 1 H, *J* = 9.2, 6.1 Hz), 3.83 (ddd, 1 H, *J* = 12.4, 9.6, 6.0 Hz), 3.70 (dd, 1 H, *J* = 2.9, 2.0 Hz), 3.56 (app t, 1 H, *J* = 9.6 Hz), 3.52 (s, 3 H), 3.48 (dd, 1 H, *J* = 3.6, 1.3 Hz), 3.29 (app t, 1 H, *J* = 9.4 Hz), 3.25 (app t, 2 H, *J* = 7.0 Hz), 3.21 (s, 3 H), 2.59–2.52 (m, 2 H), 2.35 (d, 1 H, *J* = 9.1 Hz), 1.65–1.54 (m, 4 H), 1.40–1.29 (m, 11H), 1.27 (d, 1 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.7, 138.7, 138.6, 136.9, 129.5, 128.6, 128.2, 128.0, 127.9, 127.3, 116.4, 98.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 95.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 82.3, 81.2, 80.7, 80.6, 78.9, 75.3(1), 75.3(0), 71.8, 69.1, 68.0, 59.3, 58.8, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.3, 18.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{42}H_{57}N_3O_9Na$: 770.3987. Found: 770.3983.

4-(8-Azidooctyl)phenyl 2-*O*-methyl-α-L-fucopyranoside-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (PGL-45). A solution of **PGL-35** (Scheme S34, 70 mg, 124 μmol), **PGL-43** (84 mg, 112 μmol), and crushed 4Å molecular sieves (60 mg) in CH_2Cl_2 (5 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (30 mg, 135 μmol) and silver triflate (5.8 mg, 22 μmol). The reaction mixture was stirred at –20 °C for another 60 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (5:95 EtOAc–toluene) to give a colorless foam. To the solution of the resulting foam in 1:1 CH_2Cl_2–CH_3OH (4 mL) was added sodium methoxide (29 mg, 537 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (2:98 CH_3OH–CH_2Cl_2) to yield **PGL-45** (71 mg, 70%, two steps) as a colorless oil. R_f 0.62 (CH_3OH–CH_2Cl_2); $[\alpha]_D$ –119.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.25 (m, 10 H), 7.09 (d, 2 H, *J* = 8.5 Hz), 6.97 (d, 2 H, *J* = 8.5 Hz), 5.50 (d, 1 H, *J* = 1.2 Hz, H-1), 5.22 (d, 1 H, *J* = 3.4 Hz, H-1), 5.19 (d, 1 H, *J* = 1.0 Hz, H-1), 5.12 (d, 1 H, *J* = 11.5 Hz), 4.85 (d, 1 H, *J* = 11.2 Hz), 4.68 (d, 1 H, *J* = 11.2 Hz), 4.58 (d, 1 H, *J* = 11.5 Hz), 4.24–4.18 (m, 2 H), 4.07 (dd, 1 H, *J* = 10.0, 2.7 Hz), 4.03 (dd, 1 H, *J* = 9.3, 3.1 Hz), 3.96 (app dq, 1 H, *J* = 12.6, 6.2 Hz), 3.85–3.79 (m, 2 H), 3.76–3.75 (m, 2 H), 3.56–3.53 (m,

4 H), 3.50–3.45 (m, 2 H), 3.28–3.23 (m, 8 H), 2.59 (d, 1 H, J = 2.6 Hz), 2.56–2.53 (m, 2 H), 2.35 (s, 1H), 1.62–1.56 (m, 4 H), 1.37–1.31 (m, 11H), 1.28 (d, 3 H, J = 6.2 Hz), 1.23 (d, 3 H, J = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.7, 139.3, 138.5, 136.9, 129.5, 128.6, 128.4, 127.9, 127.7, 127.6, 127.5, 116.3, 98.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 98.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 168 Hz, C-1), 95.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 80.7, 80.6, 80.3, 80.2, 79.5, 78.3, 75.5, 75.1, 71.6, 69.6, 69.0, 68.7, 66.1, 58.9, 58.0, 57.7, 51.7, 35.3, 31.8, 29.5, 29.3, 29.29, 29.0, 26.9, 18.5, 18.3, 16.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{49}H_{69}N_3O_{13}Na$: 930.4723. Found: 930.4709.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranoside (34 Squaramide). Treatment of **PGL-45** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **34 Squaramide** (66%, chromatography 7:93 CH_3OH–CH_2Cl_2) as a light yellow foam. R_f 0.32 (1:9 CH_3OH – CH_2Cl_2; $[\alpha]_D$ –110.9 (c = 1.1, CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.09 (d, 2 H, J = 8.5 Hz), 6.99 (d, 2 H, J = 8.6 Hz), 5.87 (s, 1H), 5.51 (d, 1 H, J = 1.2 Hz, H-1), 5.22 (s, 1 H, H-1), 5.14 (d, 1 H, J = 3.6 Hz, H-1), 4.77 (m, 2 H), 4.23 (q, 1 H, J = 6.8 Hz), 4.05 (dd, 2 H), 3.89 (app dq, 1 H, J = 9.3, 6.1 Hz), 3.83 (s, 1H), 3.76 (m, 3 H), 3.73–3.66 (m, 2 H), 3.63 (app t, 1 H, J = 9.4 Hz), 3.57 (s, 1H), 3.56–3.51 (m, 4 H), 3.50 (s, 3 H), 3.47 (s, 3 H), 3.43–3.39 (m, 1H), 2.59 (d, 1 H, J = 4.3 Hz), 2.55 (app t, 2 H, J = 7.6 Hz), 2.36 (d, 2 H, J = 2.4 Hz), 1.61–1.54 (m, 4 H), 1.46 (app t, 3 H, J = 7.1 Hz), 1.32 (m, 17 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 189.6, 183.0, 177.6, 172.6, 154.8, 136.9, 129.5, 116.4, 100.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 168 Hz, C-1), 99.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 95.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 83.2, 80.4, 80.3, 80.2, 79.7, 72.2, 71.9, 71.7, 70.0, 69.9, 69.3, 69.2, 66.7, 59.5, 58.9, 58.8, 45.1, 35.3, 31.8, 30.8, 29.5, 29.3, 29.2, 26.5, 18.2, 18.0, 16.6, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{41}H_{63}NO_{16}Na$: 848.4039. Found: 848.4033.

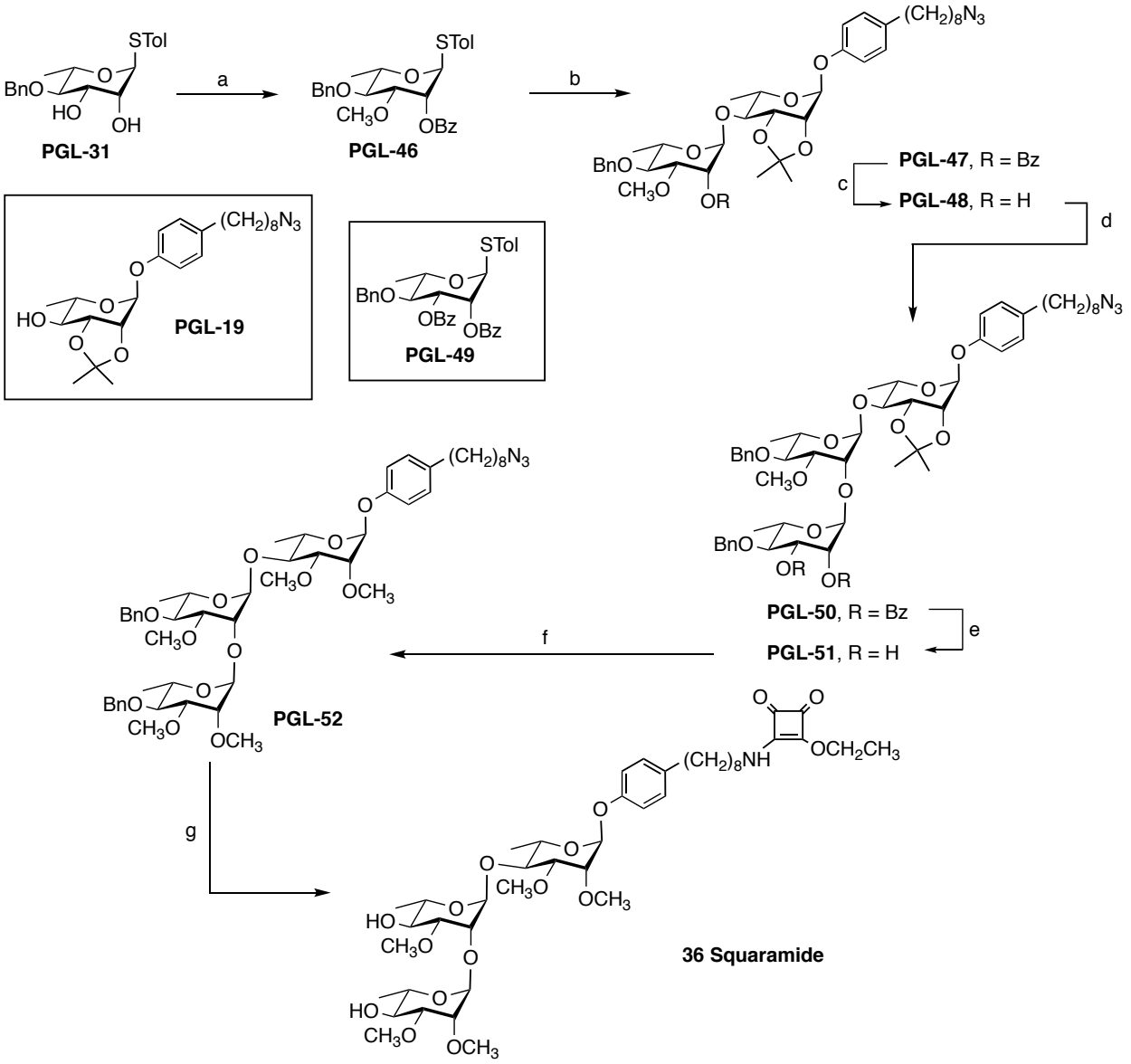
28. Synthesis of 35



Scheme S36. Synthesis of **35 Squaramide**. a) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 66%.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranoside (35 Squaramide). Treatment of **PGL-14** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **35 Squaramide** (66%, chromatography 1:9 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.29 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –80.3 (*c* = 0.7, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 7.04 (d, 2 H, *J* = 8.6 Hz), 6.93 (d, 2 H, *J* = 8.6 Hz), 5.46 (d, 1 H, *J* = 1.2 Hz, H-1), 5.01 (d, 1 H, *J* = 1.5 Hz, H-1), 4.71–4.63 (m, 2 H), 3.99–3.92 (m, 2 H), 3.74 (app dq, 1 H, *J* = 9.1, 6.3 Hz), 3.69–3.65 (m, 2 H), 3.61 (app dq, 1 H, *J* = 9.3, 6.2 Hz), 3.52 (app t, 1 H, *J* = 7.0 Hz), 3.49–3.42 (m, 4 H), 3.40–3.32 (m, 2 H), 2.50 (app t, 2 H, *J* = 7.6 Hz), 1.54 (d, 4 H, *J* = 4.8 Hz), 1.38 (app t, 3 H, *J* = 7.1 Hz), 1.32–1.21 (m, 11H), 1.15 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.5, 177.4, 174.7, 155.7, 137.8, 130.3, 117.5, 104.1 ($^1J_{C\text{-}1,H\text{-}1}$ = 173 Hz, C-1), 96.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 81.5, 79.3, 73.9, 73.4, 72.2, 72.1, 70.8, 70.6, 70.2, 59.3, 45.4, 36.0, 32.7, 31.4, 30.3, 30.03, 30.0, 27.2, 18.1, 17.9, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{33}H_{49}NO_{12}Na$: 674.3147. Found: 674.3137.

29. Synthesis of 36



Scheme S37. Synthesis of **36 Squaramide**. a) *n*-Bu_2SnO, toluene; then CH_3I, CsF, DMF; then BzCl, pyridine, 67%; b) **PGL-19**, NIS, AgOTf, CH_2Cl_2; c) $NaOCH_3$, CH_3OH, CH_2Cl_2, 67% over two steps; d) **PGL-49**, NIS, AgOTf, CH_2Cl_2; e) $NaOCH_3$, CH_3OH, CH_2Cl_2, 79% over two steps; f) *p*-TsOH·H_2O, CH_3OH, CH_2Cl_2; then CH_3I, NaH, DMF; 88%; g) $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 47%.

***p*-Tolyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-methyl-1-thio-α-L-rhamnopyranoside (PGL-46)**. A solution of diol **PGL-31**[30] (549 mg, 1.52 mmol) and *n*-Bu_2SnO (417 mg, 168 mmol) in toluene (35 mL) was heated at reflux with a Dean–Stark apparatus overnight, cooled,

concentrated and dried on a vacuum pump for 1 h. This residue was dissolved in DMF (12 mL) and CsF (254 mg, 1.68 mmol) and CH_3I (100 μL, 60 mmol) were added. The reaction mixture was stirred overnight at rt and concentrated. The resulting residue was purified by chromatography (6:94 acetone–toluene) to give a colorless oil. To the solution of the oil (570 mg, 1.52 mmol) in pyridine (10 mL) at 0 °C was added BzCl (235 μL, 2.28 mmol). The reaction mixture was stirred at rt for 4 h, concentrated and the residue was co-evaporated twice with toluene. The resulting residue was purified by chromatography (2:98 EtOAc–hexane) to yield **PGL-46** (487 mg, 67%, three steps) as a colorless oil. R_f 0.69 (2:8 EtOAc–hexane); $[\alpha]_D$ –127.5 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.07–8.03 (m, 2 H), 7.61–7.56 (m, 1H), 7.46 (app tt, 2 H, *J* = 6.7, 2.0 Hz), 7.41–7.34 (m, 6 H), 7.31 (dt, 1 H, *J* = 8.6, 2.1 Hz), 7.14–7.08 (m, 2 H), 5.80 (dd, 1 H, *J* = 3.2, 1.7 Hz), 5.47 (d, 1 H, *J* = 1.3 Hz, H-1), 4.94 (d, 1 H, *J* = 11.0 Hz), 4.68 (d, 1 H, *J* = 11.0 Hz), 4.30 (app dq, 1 H, *J* = 9.7, 6.4 Hz), 3.76 (dd, 1 H, *J* = 9.2, 3.2 Hz), 3.56 (app t, 1 H, *J* = 9.3 Hz), 3.49 (s, 3 H), 2.32 (s, 3 H), 1.38 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.9, 138.7, 138.1, 133.4, 132.6, 130.4, 130.1, 128.6, 128.6, 128.3, 127.9, 86.8 (C-1), 81.0, 80.5, 75.6, 70.9, 69.1, 57.7, 21.3, 18.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{28}H_{30}O_5SNa$: 501.1706. Found: 501.1698.

4-(8-Azidooctyl)phenyl 4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (PGL-48). A solution of **PGL-46** (148 mg, 310 μmol), **PGL-19** (Scheme S31, 112 mg, 258 μmol), and crushed 4Å molecular sieves (70 mg) in CH_2Cl_2 (7 mL) was stirred at 0 °C for 30 min. To this solution at –20 ºC was added *N*-iodosuccinimide (70 mg, 310 μmol) and silver triflate (13 mg, 52 μmol). The reaction mixture was stirred at –20 °C for another 60 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (5:95 EtOAc–toluene) to give a colorless oil (disaccharide **PGL-47**). To the solution of the resulting oil in 1:1 CH_2Cl_2–CH_3OH (12 mL) was added sodium methoxide (66 mg, 1.2 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (3:7 EtOAc–hexane) to yield **PGL-48** (118 mg, 67%, two steps) as a colorless oil. R_f 0.24 (2:8 EtOAc–hexane); $[\alpha]_D$ –89.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.31 (m, 4 H), 7.31–7.27 (m, 1H), 7.12–7.07 (m, 2 H), 6.98–6.94 (m, 2 H), 5.66 (s, 1 H, H-1), 5.43 (d, 1 H, *J* = 1.6 Hz, H-1), 4.84 (d, 1 H, *J* = 11.1 Hz), 4.62 (d, 1 H, *J* = 11.1 Hz), 4.34–

4.29 (m, 2 H), 4.09 (dt, 1 H, J = 3.3, 1.6 Hz), 3.80 (app dq, 1 H, J = 9.9, 6.3 Hz), 3.72 (app dq, 1 H, J = 9.2, 6.4 Hz), 3.59 (dd, 1 H, J = 9.9, 7.0 Hz), 3.51–3.45 (m, 4 H), 3.39 (app t, 1 H, J = 9.3 Hz), 3.25 (app t, 2 H, J = 7.0 Hz), 2.59–2.50 (m, 2 H), 2.40 (d, 1 H, J = 2.0 Hz), 1.63–1.54 (m, 7 H), 1.37–1.26 (m, 14 H), 1.21 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.5, 138.7, 136.9, 129.5, 128.6, 128.3, 127.9, 116.5, 110.0, 98.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 95.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 81.8, 79.9, 78.8, 77.5, 76.3, 75.5, 68.5, 68.0, 65.2, 57.6, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.0, 28.1, 26.9, 26.7, 18.3, 18.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{37}H_{53}N_3O_9Na$: 706.3674. Found: 706.3662.

4-(8-Azidooctyl)phenyl 4-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (PGL-51). A solution of **PGL-48** (46 mg, 67 μmol), **PGL-49**[31] (54 mg, 95 μmol), and crushed 4Å molecular sieves (50 mg) in CH_2Cl_2 (5 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (70 mg, 310 μmol) and silver triflate (13 mg, 52 μmol). The reaction mixture was stirred at –20 °C for another 45 min, Et_3N (50 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (3:97 acetone–toluene) to give a light yellow oil (trisaccharide **PGL-50**). To the solution of the resulting oil in 1:1 CH_2Cl_2–CH_3OH (3 mL) was added sodium methoxide (12 mg, 222 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (4:6 EtOAc–hexane) to yield **PGL-51** (47 mg, 79%, two steps) as a colorless foam. R_f 0.50 (6:4 EtOAc–hexane); $[\alpha]_D$ –76.7 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.26 (m, 10 H), 7.09 (d, 2 H, J = 8.6 Hz), 6.95 (d, 2 H, J = 8.6 Hz), 5.65 (s, 1 H, H-1), 5.34 (d, 1 H, J = 1.6 Hz, H-1), 5.06 (d, 1 H, J = 1.3 Hz, H-1), 4.84 (d, 1 H, J = 11.0 Hz), 4.80–4.71 (m, 2 H), 4.58 (d, 1 H, J = 11.0 Hz), 4.34–4.26 (m, 2 H), 4.13–4.06 (m, 2 H), 4.03–3.96 (m, 1H), 3.87 (app dq, 1 H, J = 10.1, 6.2 Hz), 3.77 (app dq, 1 H, J = 10.4, 6.2 Hz), 3.66 (app dq, 1 H, J = 9.5, 6.2 Hz), 3.53–3.47 (m, 2 H), 3.46 (s, 3 H), 3.37 (app td, 2 H, J = 9.3, 7.4 Hz), 3.25 (app t, 2 H, J = 7.0 Hz), 2.59–2.50 (m, 2 H), 2.38 (d, 1 H, J = 3.3 Hz), 2.29 (d, 1 H, J = 4.8 Hz), 1.63–1.55 (m, 7 H), 1.38 (d, 3 H, J = 6.3 Hz), 1.36–1.27 (m, 11H), 1.25 (d, 3 H, J = 6.2 Hz), 1.19 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.5, 138.8, 138.5, 136.9, 129.5, 128.9, 128.6, 128.2, 128.1, 127.9, 116.5, 109.9, 100.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 98.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 174 Hz, C-1), 95.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 81.9,

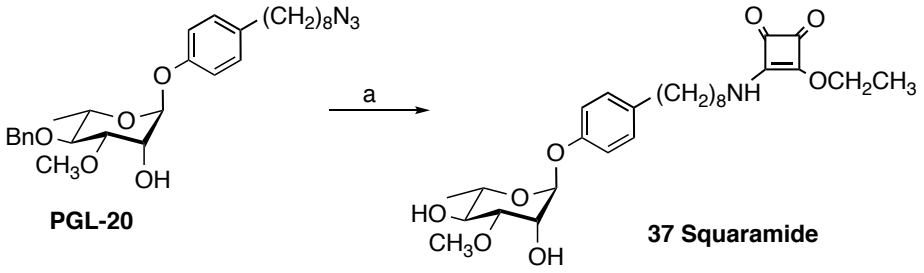
81.87, 80.4, 78.8, 78.5, 76.3, 75.5, 75.2, 74.0, 71.4, 71.39, 68.7, 68.0, 65.2, 58.1, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.0, 28.2, 26.9, 26.6, 18.2, 18.14, 18.12. HRMS (ESI) *m/z* calcd for (M+Na) $C_{50}H_{69}N_3O_{13}Na$: 942.4723. Found: 942.4715.

4-(8-Azidooctyl)phenyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranoside (PGL-52). To a solution of **PGL-51** (45 mg, 49 μmol) and *p*-TsOH·H_2O (8.7 mg, 46 μmol) in 1:1 CH_3OH–CH_2Cl_2 (3 mL) was stirred at rt for 4 d, then Et_3N (200 μL) was added and the mixture was concentrated. The resulting oil was purified by chromatography (8:2 EtOAc–hexane) to give a colorless oil. To the solution of the resulting oil and CH_3I (24 μL, 385 mmol) in dry DMF (2 mL) at 0 °C (ice bath) was added NaH (60% dispersion in mineral oil, 10.5 mg, 263 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of AcOH and concentrated. The resulting residue was purified by chromatography (3:7 EtOAc–hexane) to yield **PGL-52** (26 mg, 88%) as a colorless oil. R_f 0.28 (4:6 EtOAc–hexane); $[\alpha]_D$ –84.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.41–7.31 (m, 8 H), 7.28 (m, 2 H), 7.09 (d, 2 H, *J* = 8.4 Hz), 6.97 (d, 2 H, *J* = 8.4 Hz), 5.47 (s, 1 H, H-1), 5.18 (s, 1 H, H-1), 5.15 (s, 1 H, H-1), 4.91 (d, 1 H, *J* = 11.1 Hz), 4.84 (d, 1 H, *J* = 11.1 Hz), 4.68–4.56 (m, 2 H), 4.09 (s, 1H), 3.78 (m, 2 H), 3.70 (m, 5 H), 3.61 (dd, 1 H, *J* = 9.3, 3.1 Hz), 3.57–3.46 (m, 16 H), 3.42 (app t, 1 H, *J* = 9.4 Hz), 3.36 (app t, 1 H, *J* = 9.2 Hz), 3.25 (app t, 2 H, *J* = 6.9 Hz), 2.55 (app t, 2 H, *J* = 7.7 Hz), 1.58–1.61 (m, 4 H), 1.34 (m, 11H), 1.25 (d, 6 H, *J* = 4.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.8, 139.1, 138.8, 136.9, 129.5, 128.5, 128.49, 128.3, 127.9, 127.88, 127.7, 116.4, 100.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 175 Hz, C-1), 98.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 96.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 82.3, 82.1, 81.3, 80.8, 80.2, 78.2, 77.9, 76.5, 75.3, 75.2, 73.8, 68.7, 68.4, 68.2, 59.6, 59.2, 58.13, 58.1, 57.3, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.5, 18.2, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{51}H_{73}N_3O_{13}Na$: 958.5036. Found: 958.5024.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranoside (36 Squaramide). Treatment of **PGL-52** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **36 Squaramide** (47%, chromatography 5:95 CH_3OH–CH_2Cl_2) as a colorless foam. R_f 0.28 (5:95 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –67.9 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.09 (d, 2 H), 7.01–6.96 (m, 2 H), 6.02 (s, 1H), 5.49 (d, 1 H, *J* = 1.7 Hz, H-1), 5.25 (d, 1 H, *J* = 1.4 Hz, H-1), 5.14 (d, 1 H,

J = 1.1 Hz, H-1), 4.77 (m, 2 H), 4.16–4.13 (m, 1H), 3.79 (app t, 1 H, *J* = 2.0 Hz), 3.75–3.69 (m, 5 H), 3.67 (dd, 1 H, *J* = 2.9, 1.8 Hz), 3.57–3.54 (m, 5 H), 3.51 (s, 3 H), 3.49 (s, 3 H), 3.47 (d, 6 H, *J* = 1.3 Hz), 3.44–3.41 (m, 3 H), 3.36 (dd, 1 H, *J* = 9.5, 2.6 Hz), 2.61–2.50 (m, 2 H), 2.32 (s, 2 H), 1.62–1.56 (m, 4 H), 1.45 (app t, 3 H, *J* = 7.1 Hz), 1.34–1.25 (m, 17 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 189.4, 183.2, 177.5, 172.7, 154.7, 136.9, 129.6, 116.4, 101.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 176 Hz, C-1), 98.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 96.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 82.1, 80.9, 78.1, 76.4, 76.2, 71.94, 71.9, 71.4, 69.9, 69.3, 68.9, 68.1, 59.7, 59.2, 57.6, 57.3, 57.2, 45.1, 35.3, 31.8, 30.8, 29.5, 29.3, 29.2, 26.5, 18.6, 18.0, 17.8, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{43}H_{67}NO_{16}Na$: 876.4352. Found: 876.4340.

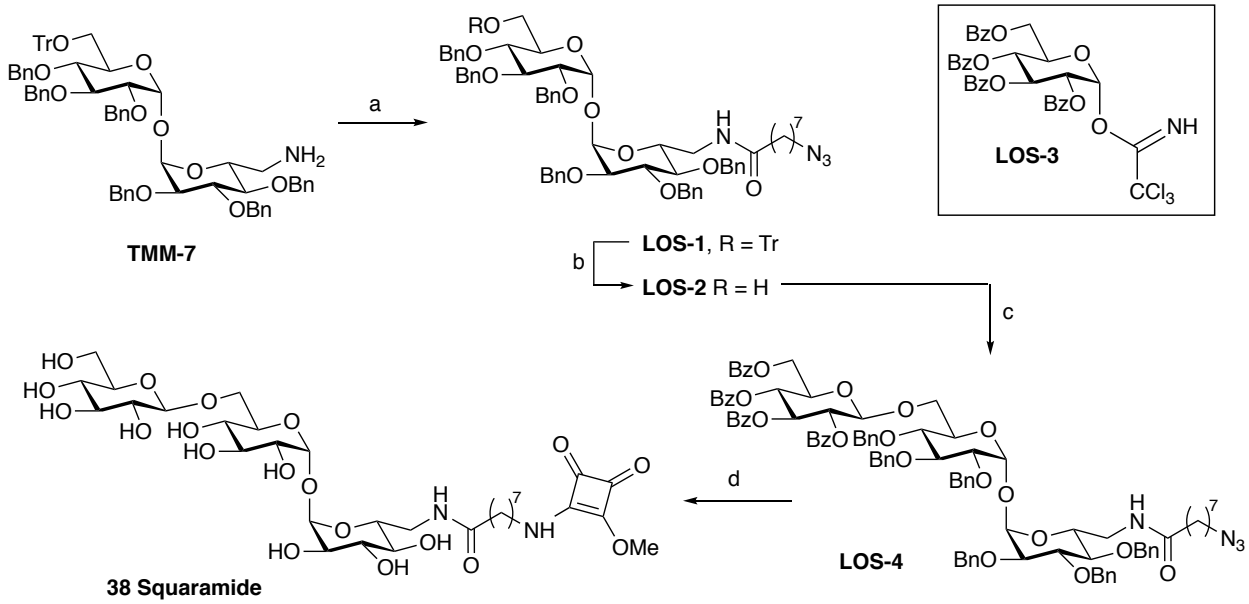
30. Synthesis of 37



Scheme S38. Synthesis of **37 Squaramide**. a) $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 61%.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 3-*O*-methyl-α-L-rhamnopyranoside (37 Squaramide). Treatment of **PGL-20** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **77 Squaramide** (61%, chromatography 3:96 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.50 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –61.9 (*c* = 1.7, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 7.04 (d, 2 H, *J* = 8.6 Hz), 6.91 (d, 2 H, *J* = 8.6 Hz), 5.35 (d, 1 H, *J* = 1.6 Hz, H-1), 4.66 (p, 2 H, *J* = 7.2 Hz), 4.14 (d, 1 H, *J* = 1.9 Hz), 3.62 (app dq, 1 H, *J* = 9.5, 6.5 Hz), 3.52 (app t, 1 H, *J* = 6.9 Hz), 3.49–3.42 (m, 5 H), 3.35 (app t, 1 H, *J* = 7.0 Hz), 1.54 (d, 4 H, *J* = 5.7 Hz), 1.38 (app t, 3 H, *J* = 7.1 Hz), 1.28 (s, 8 H), 1.17 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 189.8, 184.6, 177.4, 174.7, 155.8, 137.7, 130.2, 117.4, 99.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 81.9, 72.7, 70.6, 70.4, 68.0, 57.4, 45.4, 36.0, 32.7, 31.4, 30.3, 30.1, 30.0, 27.3, 18.0, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{27}H_{39}NO_8Na$: 544.2307. Found: 544.2315.

31. Synthesis of 38



Scheme S39. Synthesis of the **38 Squaramide**. a) 8-azidooctanoic acid, DIEA, TBTU, DMF, 87%; b) 60% aq HOAc, 82%; **LOS-3**, TMSOTf, CH_2Cl_2, 89%; d) $NaOCH_3$, CH_3OH; then H_2, $Pd(OH)_2$–C, H_2O, EtOH; then diethyl squarate, Na_2CO_3, H_2O, EtOH, 90% (three steps).

8-azidooctanoic acid. To a solution of 8-bromooctanoic acid (2.5 g, 11 mmol) in DMF (10 mL) was added NaN_3 (1.43 g, 22 mmol) at rt. After stirring at 80 °C for 6 h, the mixture was filtered through Celite and the filtrate was concentrated. The residue was purified by chromatography (2:1 hexanes–EtOAc) to give the product (1.87 g, 92%) as an oil: R_f 0.5 (2:1 hexanes–EtOAc); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 3.24 (t, J = 7.0 Hz, 2 H), 2.34 (t, J = 7.5 Hz, 2 H), 1.65–1.56 (m, 4 H), 1.39–1.31 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ_C) 179.7 (COOH), 51.4 (CH_2N_3), 34.0 (CH_2COOH), 28.9, 28.8, 26.5, 24.5. HRMS (ESI) *m/z* calcd for (M–H) $C_8H_{14}N_3O_2$: 184.1092. Found: 184.1091.

2,3,4-Tri-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-(8'-azidooctanamide)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (LOS-1). Aminosugar **TMM-7** (See **Scheme S41**, 0.448 g, 0.4 mmol) and 8-azidooctanoic acid (0.074 g, 0.4 mmol) were stirred with DIEA (0.1 mL, 0.6 mmol) and TBTU (0.192 g, 0.6 mmol) in DMF (20 mL) for 8 h. The mixture was diluted with EtOAc and the organic layer was washed with brine, dried (Na_2SO_4), filtered, concentrated and the residue was purified by chromatography (2:1 hexanes–EtOAc) to

give **LOS-1** (0.45 g, 87%) as a syrup. R_f 0.4 (2:1 hexanes–EtOAc); $[\alpha]_D$ –253.2 (*c* = 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.53–7.21 (m, 40 H), 7.10 (q, 4 H, *J* = 5.2, 4.3 Hz), 6.91–6.83 (m, 1 H), 5.44 (dd, 1 H, *J* = 7.9, 2.9 Hz), 5.36 (d, 1 H, *J* = 3.5 Hz, H-1), 5.34 (d, 1 H, *J* = 3.5 Hz, H-1), 5.03 (dd, 2 H, *J* = 18.2, 10.8 Hz), 4.96–4.87 (m, 4 H), 4.83–4.60 (m, 5 H), 4.35 (d, 1 H, *J* = 10.3 Hz), 4.23 (app t, 2 H, *J* = 10.6 Hz), 4.11 (app dt, 2 H, *J* = 11.5, 9.4 Hz), 3.94–3.87 (m, 2 H), 3.80 (dd, 1 H, *J* = 9.1, 4.1 Hz), 3.59 (dd, 1 H, *J* = 9.7, 3.5 Hz), 3.47–3.34 (m, 2 H), 3.26 (t, 2 H, *J* = 6.9 Hz), 3.16 (dd, 2 H, *J* = 17.3, 5.1 Hz), 2.08 (t, 2 H, *J* = 7.8 Hz), 1.64–1.59 (m, 4 H), 1.44–1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 172.8, 143.9, 138.7, 138.7, 138.3, 138.2, 138.0, 138.0, 128.9, 128.6, 128.5, 128.5, 128.5, 128.3, 128.2, 128.2, 128.0, 128.0, 127.8, 127.7, 127.7, 127.6, 127.4, 127.3, 127.1, 127.0, 94.5 (C-1), 93.8 (C-1), 86.3, 82.0, 81.6, 80.0, 79.9, 78.8, 78.1, 73.3, 72.8, 70.9, 69.6, 68.0, 61.9, 51.4, 39.4, 36.7, 29.2, 28.9, 28.8, 26.6, 25.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{81}H_{86}N_4O_{11}Na$: 1313.6185. Found: 1313.6172.

2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-(8'-azidooctanamide)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (LOS-2). A solution of **LOS-1** (0.463 g, 0.358 mmol) in 60% aq HOAc (20 mL) was heated at 60 °C overnight. The mixture was then cooled, concentrated and the residue was purified by chromatography (1:2 hexane–EtOAc) to give **LOS-2** (0.308 g, 82%) as a syrup: R_f 0.36 (1:2 hexanes–EtOAc); $[\alpha]_D$ –20.2 (*c* = 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.55–7.18 (m, 30 H), 5.41 (dd, 1 H, *J* = 8.0, 2.5 Hz), 5.14 (d, 1 H, *J* = 3.5 Hz, H-1), 5.12 (d, 1 H, *J* = 3.5 Hz, H-1), 5.01 (dd, 2 H, *J* = 15.9, 10.9 Hz), 4.94–4.85 (m, 4 H), 4.78–4.63 (m, 6 H), 4.15–4.04 (m, 4 H), 3.86 (ddd, 1 H, *J* = 14.0, 8.3, 3.8 Hz), 3.60 (d, 3 H, *J* = 9.8 Hz), 3.58–3.49 (m, 2 H), 3.33 (app t, 1 H, *J* = 9.4 Hz), 3.23 (t, 2 H, *J* = 6.9 Hz), 3.07 (app dt, 1 H, *J* = 14.1, 3.6 Hz), 2.05–1.99 (m, 2 H), 1.60–1.54 (m, 4 H), 1.37–1.26 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 172.8, 138.7, 138.6, 138.2, 138.1, 138.0, 128.5, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 94.1 (C-1), 93.7 (C-1), 81.5, 79.5, 78.8, 77.4, 75.7, 75.6, 75.3, 75.1, 73.2, 73.0, 71.4, 69.6, 61.6, 53.4, 51.4, 39.3, 36.7, 29.2, 28.8, 26.6, 25.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{62}H_{72}N_4O_{11}Na$: 1071.5090. Found: 1071.5081.

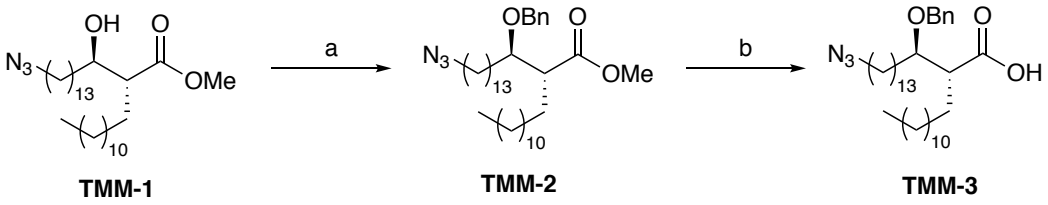
2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-Tri-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-(8'-azidooctanamide)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (LOS-4). To a mixture of **LOS-3**[32] (0.39 g, 0.53 mmol) and acceptor **LOS-2** (0.37 g, 0.352 mmol) in CH_2Cl_2 (10 mL) was added 4 Å molecular sieves (0.1

g) at rt. After stirring for 1 h and then cooling to –30 °C, TMSOTf (6.4 μL, 0.05 mmol) was added to the mixture and stirring was continued for an additional 1 h while warming to 0 °C at which point Et_3N (0.2 mL) was added. The solution was diluted with CH_2Cl_2 and filtered through Celite and the filtrate was then washed with brine. The organic layer was dried (Na_2SO_4), filtered, concentrated and the residue was purified by chromatography (2:1 hexane–EtOAc) to give **LOS-4** (0.509 g, 89%) as a white foam. R_f 0.28 (2:1 hexanes–EtOAc); $[\alpha]_D$ +44.1 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) δ 7.98 (dd, 2 H, *J* = 8.2, 1.5 Hz), 7.90 (ddd, 4 H, *J* = 8.3, 4.6, 1.5 Hz), 7.83 (dd, 2 H, *J* = 8.4, 1.3 Hz), 7.52–7.47 (m, 2 H), 7.43–7.19 (m, 38 H), 7.02 (dd, 2 H, *J* = 7.1, 2.3 Hz), 5.88 (app t, 1 H, *J* = 9.6 Hz), 5.70 (app t, 1 H, *J* = 9.7 Hz), 5.59 (dd, 1 H, *J* = 9.6, 7.7 Hz), 5.46 (dd, 1 H, *J* = 8.1, 3.1 Hz), 5.13 (d, 1 H, *J* = 3.5 Hz, H-1), 5.05 (d, 1 H, *J* = 3.5 Hz, H-1), 5.00 (d, 1 H, *J* = 10.8 Hz, H-1), 4.90–4.81 (m, 3 H), 4.75–4.53 (m, 10 H), 4.42 (d, 1 H, *J* = 11.1 Hz), 4.25 (d, 1 H, *J* = 11.1 Hz), 4.11–4.05 (m, 3 H), 4.05–4.01 (m, 1 H), 3.98–3.91 (m, 2 H), 3.84 (ddd, 1 H, *J* = 13.8, 8.1, 3.9 Hz), 3.53–3.41 (m, 4 H), 3.32–3.28 (m, 1 H), 3.22 (t, 2 H, *J* = 7.0 Hz), 3.08 (dt, 1 H, *J* = 13.9, 3.5 Hz), 2.05 (t, 3 H, *J* = 7.8 Hz), 1.60–1.54 (m, 4 H), 1.36–1.28 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) δ 172.7, 166.1, 165.8, 165.2, 164.9, 138.8, 138.6, 138.3, 138.1, 138.1, 138.0, 133.4, 133.3, 133.1, 133.1, 129.8, 129.8, 129.7, 129.7, 129.5, 129.1, 128.8, 128.8, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 101.2 (C-1), 93.9 (C-1), 93.4 (C-1), 81.5, 81.5, 79.6, 79.2, 78.8, 75.7, 75.3, 74.6, 73.0, 72.9, 72.8, 72.2, 71.8, 69.8, 69.7, 69.4, 67.8, 63.4, 60.4, 51.4, 39.3, 36.7, 29.2, 28.9, 28.8, 26.6, 25.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{96}H_{98}N_4O_{20}Na$: 1649.6667. Found: 1649.6649.

β-D-Glucopyranosyl-(1→6)-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-([8'-(1''-amino-2''-ethoxycyclobutene-3'',4''-dione)]-octanamide)-α-D-glucopyranoside (38 Squaramide derivative). Trisaccharide **LOS-4** (33 mg, 0.02 mmol) was dissolved in CH_2Cl_2 (3 mL) and CH_3OH (3 mL) and then $NaOCH_3$ (0.1 eq) was added. The mixture was stirred for 12 h before being neutralized by the addition of Amberlite IR-120 H^+ resin. The mixture was filtered and the filtrate was concentrated to a syrup. The resulting crude residue was purified by chromatography (20:1 CH_2Cl_2–MeOH) to give the deacetylated product (24 mg, 99%) as a syrup; R_f 0.5 (10:1 CH_2Cl_2–MeOH). The product was dissolved in H_2O−EtOH (1:1, 3 mL), $Pd(OH)_2$–C (10%) was then added, and the reaction mixture was stirred overnight under a H_2 (1 atm). The reaction mixture was diluted with H_2O−CH_3OH (1:1, 5 mL), filtered through Celite, concentrated and the

resulting residue and purified by gel filtration chromatography (Sephadex, LH-20) using 1:1 CH_2Cl_2−CH_3OH as the eluent to give the corresponding aminosugar (13 mg, 99%) as a syrup. To a solution of the aminosugar (13 mg, 0.02 mmol) in 1:1 EtOH−H_2O (2 mL) was added diethyl squarate (15 μL, 0.1 mmol), followed by slow addition of saturated aq Na_2CO_3 solution until the pH of the reaction mixture was 8. After stirring for 30 min, the solvent was evaporated and the residue was purified by gel filtration chromatography (Sephadex, LH-20) using 1:1 CH_2Cl_2−CH_3OH as the eluent to give **38 Squaramide** 14 mg, 92%) as a syrup: R_f 0.4 (5:2:1 EtOH–NH_4OH–H_2O); $[\alpha]_D$ + 8.8 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD, δ_H): 5.09 (d, 1 H, *J* = 3.5 Hz, H-1), 5.04 (d, 1 H, *J* = 3.5 Hz, H-1), 4.72 (dq, 2 H, *J* = 19.3, 7.0 Hz), 4.36 (d, 1 H, *J* = 7.8 Hz, H-1), 4.08 (dd, 1 H, *J* = 11.5, 2.0 Hz), 4.01 (ddd, 1 H, *J* = 10.0, 5.5, 1.9 Hz), 3.88–3.83 (m, 2 H), 3.79–3.73 (m, 3 H), 3.66 (dd, 1 H, *J* = 11.9, 5.4 Hz), 3.58 (t, 1 H, *J* = 7.0 Hz), 3.42–4.46 (m, 4 H), 3.41 (t, 1 H, *J* = 7.0 Hz), 3.39–3.35 (m, 1 H), 3.34–3.32 (m 3 H), 3.29–3.24 (m, 2 H), 3.21–3.17 (m, 1 H), 3.12 (app t, 1 H, *J* = 9.4 Hz), 2.22 (t, 2 H, *J* = 7.5 Hz), 1.65–1.57 (m, 4 H), 1.48–1.40 (m, 3 H), 1.37–1.34 (m, 6 H); ^{13}C NMR (126 MHz, CD_3OD, δ_C) 188.6, 188.5, 183.2, 183.0, 176.6, 176.1, 175.6, 175.5, 173.4, 173.3, 103.3 (C-1), 94.1 (2 × C-1), 76.6, 76.6, 73.7, 73.1, 72.6, 71.9, 71.8, 71.7, 70.7, 70.4, 70.1, 69.3, 69.3, 68.5, 61.3, 48.4, 48.2, 48.0, 44.1, 43.9, 39.9, 35.5, 30.5, 30.1, 28.7, 28.4, 25.9, 25.5, 14.8, 14.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{32}H_{52}N_2O_{19}Na$: 791.3056. Found: 791.3050.

32. Synthesis of 39



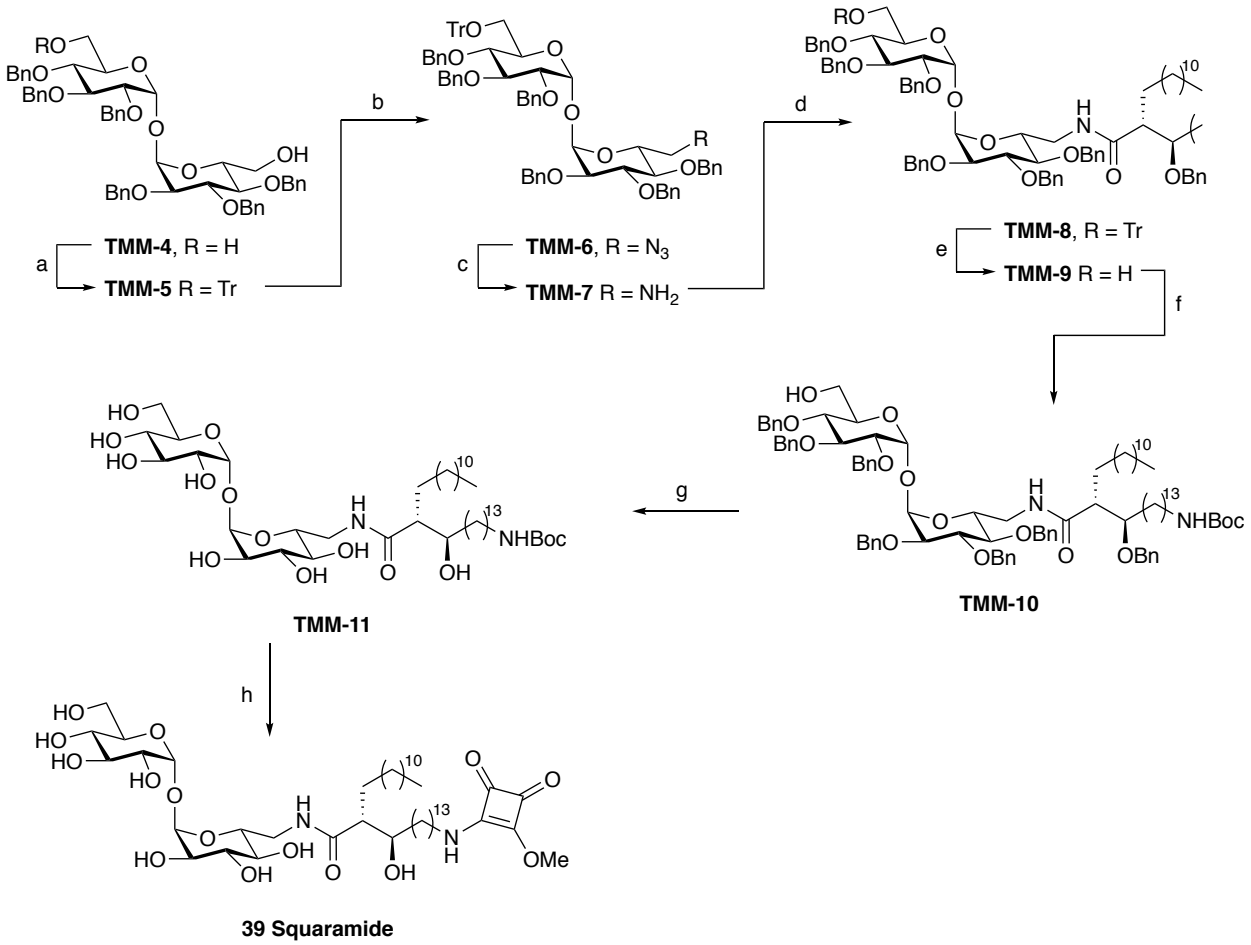
TMM-1 **TMM-2** **TMM-3**

Scheme S40. Synthesis of azide-functionalized mycolic acid derivative. a) $PhCH_2OC(=NH)CCl_3$, TfOH, CH_2Cl_2, cyclohexane 72%; b) NaOH, THF, CH_3OH, H_2O, 89%.

(2*R*,3*R*)-methyl-16-azido-3-(benzyloxy)-2-dodecylhexadecanoate (TMM-2). To a solution of **TMM-1**[33] (0.194 g, 0.39 mmol) in CH_2Cl_2 (6 mL) and cyclohexane (6 mL) was added 4 Å molecular sieves (0.05 g) at rt. After stirring for 10 min, benzyl 2,2,2-trichloroacetimidate (0.144 mL, 0.78 mmol) and triflic acid (3.4 μL, 0.039 mmol) were added at rt. After 24 h, CH_3OH was added and the reaction mixture was washed with brine, dried ($MgSO_4$), filtered and then concentrated to a residue that was purified by chromatography (10:1 hexanes–EtOAc) to give **TMM-2** (0.16 g, 72%) as a colorless oil. R_f 0.49 (10:1 hexanes–EtOAc); $[\alpha]_D$ +2.6 (*c* = 0.21, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H): 7.35–7.23 (m, 5 H, Ar), 4.52 (d, 1 H, *J* = 11.4 Hz), 4.47 (d, 1 H, *J* = 11.4 Hz), 3.66 (s, 3 H), 3.66–3.62 (m, 1 H), 3.25 (t, 2 H, *J* = 7.0 Hz), 2.66 (ddd, 1 H, *J* = 11.1, 7.8, 3.7 Hz), 1.64–1.46 (m, 6 H), 1.39–1.20 (m, 40 H), 0.91–0.85 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 175.3, 138.6, 128.3, 127.7, 127.5, 80.6, 72.1, 51.5, 51.4, 49.9, 31.9, 31.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 28.9, 27.9, 27.7, 26.9, 26.7, 24.6, 22.7, 14.1. HRMS (ESI) *m/z* calcd (M+Na) for $C_{36}H_{63}N_3O_3Na$: 608.4762. Found: 608.4760.

(2*R*,3*R*)-16-azido-3-(benzyloxy)-2-dodecylhexadecanoic acid (TMM-3). To a solution of **TMM-2** (60 mg, 0.102 mmol) in CH_3OH–THF–H_2O (1:1:1, 3 mL) was added 1M aq NaOH (1 mL). The reaction mixture was stirred at 70 °C for 2 days, and then cooled and acidified with 1M HCl solution to pH 4. The organic phase was separated, washed with brine, dried ($MgSO_4$), filtered and then concentrated to a residue that was purified by chromatography (5:1 hexanes–EtOAc) to give **TMM-3** (52 mg, 89%) as a colorless oil. R_f 0.51 (5:1 hexanes–EtOAc); $[\alpha]_D$ 0.00 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.35–7.26 (m, 5 H), 4.61 (d, 1 H, *J* = 11.4 Hz), 4.53 (d, 1 H, *J* = 11.4 Hz), 3.63 (app q, 1 H, *J* = 5.7 Hz), 3.25 (t, 2 H, *J* = 7.0 Hz), 2.65 (app dt, 1 H, *J* = 10.2, 5.1 Hz), 1.69–1.50 (m, 6 H), 1.40–1.22 (m, 40 H), 0.91–0.85 (m, 4 H); ^{13}C

NMR (125 MHz, $CDCl_3$, δ_C) 177.5, 137.8, 128.4, 127.9, 79.7, 72.4, 51.5, 49.7, 31.9, 31.5, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 29.2, 28.9, 28.5, 27.6, 26.7, 25.0, 22.7, 14.1. HRMS (ESI) *m/z* calcd for [M – H] $C_{35}H_{60}N_3O_3$: 570.4640. Found: 470.4650.



Scheme S41. Synthesis of TMM derivative **39 Squaramide**. a) TrCl, pyridine, 70%; b) TsCl, pyridine; then NaN_3, DMF, 89%; c) $(CH_3)_3P$, NaOH, H_2O, THF, 90%; d) **TMM-3**, TBTU, DIEA, DMF, 89%; e) TsOH, CH_2Cl_2, CH_3OH, 80%; f) $(CH_3)_3P$, NaOH, THF, H_2O; then Boc_2O, NaOH, THF, H_2O, 98%; g) H_2, $Pd(OH)_2$–C, H_2O, CH_3OH, 96%; h) 50% TFA in CH_2Cl_2; then diethyl squarate, Na_2CO_3, H_2O, CH_3OH, 99%.

2,3,4-Tri-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranosyl-(1↔1)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (TMM-5). To a solution of **TMM-4**[34] (1.1 g, 1.24 mmol) in pyridine (10 mL) was added trityl chloride (0.347 g, 1.24 mmol) at 0 °C. After stirring at rt for 4 h, CH_3OH (10 mL) was added and the resulting solution was concentrated. The residue was

dissolved in EtOAc and washed with brine. The organic phase was concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give **TMM-5** (0.96 g, 70%) as a syrup. R_f 0.5 (2:1 hexanes–EtOAc); $[\alpha]_D$ +74.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.52–7.16 (m, 39 H), 7.08–7.04 (m, 4 H), 6.86 (d, 2 H, *J* = 7.4 Hz), 5.38 (d, 1 H, *J* = 3.5 Hz, H-1), 5.33 (d, 1 H, *J* = 3.5 Hz, H-1), 5.01 (d, 2 H, *J* = 10.8 Hz), 4.94–4.87 (m, 3 H), 4.84 (d, 1 H, *J* = 11.9 Hz), 4.80 (d, 1 H, *J* = 11.9 Hz), 4.75–4.61 (m, 5 H), 4.33 (d, 1 H, *J* = 10.3 Hz), 4.22 (d, 1 H, *J* = 10.0 Hz), 4.14 (dt, 1 H, *J* = 10.6, 2.7 Hz), 4.10 (d, 1 H, *J* = 9.4 Hz), 4.06 (d, 1 H, *J* = 9.6 Hz), 3.88 (app t, 1 H, *J* = 9.6 Hz), 3.77 (dd, 1 H, *J* = 9.7, 3.6 Hz), 3.67–3.60 (m, 3 H), 3.58 (dd, 1 H, *J* = 9.6, 3.5 Hz), 3.40 (d, 1 H, *J* = 9.5 Hz), 3.15 (dd, 1 H, *J* = 10.3, 3.1 Hz), 1.54 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) δ 143.9, 138.9, 138.8, 138.4, 138.3, 138.1, 138.0, 128.9, 128.5, 128.5, 128.4, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0, 94.3 (C-1), 94.0 (C-1), 86.3, 82.0, 81.6, 80.0, 78.1, 77.4, 76.0, 75.6, 75.0, 73.1, 72.8, 71.3, 70.8, 61.9, 61.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{73}H_{72}O_{11}Na$: 1147.4967. Found: 1147.4963.

2,3,4-Tri-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-azido-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (TMM-6). To a solution of **TMM-5** (1.69 g, 1.5 mmol) in pyridine (30 mL) was added TsCl (1.43 g, 7.5 mmol) at 0 °C. The mixture was stirred at rt overnight and then concentrated. Without further purification, the crude product was dissolved in DMF (20 mL) and then NaN_3 (1.5 g, 23 mmol) was added and the mixture was heated with vigorous stirring at 100 °C for 2.5 h and then cooled. The mixture was diluted with EtOAc and washed with brine. The organic phase was dried ($MgSO_4$), filtered and then concentrated to a residue that was purified by chromatography (8:1, hexane–EtOAc) to give **TMM-6** (1.52 g, 89%) as a syrup. R_f 0.4 (8:1 hexanes–EtOAc); $[\alpha]_D$ +98.5 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.52–7.19 (m, 39 H), 7.06 (d, 4 H, *J* = 4.9 Hz), 6.86 (dd, 2 H, *J* = 8.0, 1.5 Hz), 5.41 (d, 1 H, *J* = 3.5 Hz, H-1), 5.35 (d, 1 H, *J* = 3.5 Hz, H-1), 5.02 (d, 1 H, *J* = 11.0 Hz), 5.01 (d, 1 H, *J* = 11.0 Hz), 4.94 (d, 1 H, *J* = 11.0 Hz), 4.89 (d, 1 H, *J* = 12.0 Hz), 4.86 (d, 1 H, *J* = 11.0 Hz), 4.83 (d, 1 H, *J* = 12.0 Hz), 4.73 (d, 1 H, *J* = 10.3 Hz), 4.68 (d, 1 H, *J* = 12.0 Hz), 4.65–4.60 (m, 2 H), 4.33 (d, 1 H, *J* = 10.3 Hz), 4.25 (dt, 1 H, *J* = 10.0, 3.3 Hz), 4.20 (dt, 1 H, *J* = 10.1, 2.5 Hz), 4.06 (td, 2 H, *J* = 9.3, 3.4 Hz), 3.94–3.88 (m, 1 H), 3.79 (dd, 1 H, *J* = 9.6, 3.7 Hz), 3.62 (dd, 1 H, *J* = 9.6, 3.6 Hz), 3.56 (dd, 1 H, *J* = 9.8, 9.1 Hz), 3.39 (dd, 1 H, *J* = 10.3, 1.9 Hz), 3.28–3.20 (m, 2 H), 3.14 (dd, 1 H, *J* = 10.3, 3.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 149.9,

143.9, 138.7, 138.7, 138.4, 138.2, 138.0, 137.9, 128.9, 128.5, 128.4, 128.2, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.3, 127.3, 127.0, 127.0, 94.7 (C-1), 94.1 (C-1), 86.3, 82.0, 81.5, 80.0, 78.3, 78.0, 75.9, 75.6, 75.2, 75.1, 73.2, 72.8, 70.9, 70.3, 61.8, 51.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{73}H_{71}N_3O_{10}Na$: 1172.5032. Found: 1172.5029.

2,3,4-Tri-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-amino-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (TMM-7). To a solution of **TMM-6** (1.15 g, 1 mmol) in THF (20 mL) was added trimethylphosphine (1.5 mL, 1.5 mmol, 1M in THF), followed by the addition of 1M aq NaOH (0.6 mL, 0.6 mmol) at rt. The mixture was heated at 50 °C for 2 h and then cooled. The solvent was evaporated and the residue was purified by chromatography (20:1, EtOAc–CH_3OH) to give **TMM-7** (0.32 g, 90%) as a syrup R_f 0.43 (20:1, EtOAc–CH_3OH); $[\alpha]_D$ +85.1 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.46–7.18 (m, 39 H), 7.04 (d, 4 H, *J* = 6.5 Hz), 6.86–6.81 (m, 2 H), 5.37 (d, 1 H, *J* = 3.5 Hz, H-1), 5.30 (d, 1 H, *J* = 3.5 Hz, H-1), 4.99 (dd, 2 H, *J* = 10.8, 7.8 Hz), 4.93–4.80 (m, 5 H), 4.72–4.58 (m, 4 H), 4.30 (d, 1 H, *J* = 10.3 Hz), 4.23–4.18 (m, 1 H), 4.07 (td, 3 H, *J* = 9.3, 5.1 Hz), 3.86 (app t, 1 H, *J* = 9.6 Hz), 3.76 (dd, 1 H, *J* = 9.7, 3.6 Hz), 3.55 (dd, 1 H, *J* = 9.6, 3.5 Hz), 3.47–3.41 (m, 1 H), 3.37 (dd, 1 H, *J* = 10.1, 1.4 Hz), 3.12 (dd, 1 H, *J* = 10.3, 3.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 143.9, 138.9, 138.8, 138.4, 138.3, 138.1, 138.0, 128.9, 128.5, 128.4, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.3, 127.2, 127.0, 126.9, 94.2 (C-1), 93.7 (C-1), 86.3, 82.0, 81.7, 80.2, 80.1, 78.4, 78.1, 75.9, 75.5, 75.0, 74.9, 73.2, 72.7, 70.8, 61.9, 61.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{73}H_{73}NO_{10}Na$: 1146.5127. Found: 1146.5125.

2,3,4-Tri-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-((2'*R*,3'*R*)-16'-azido-3'-(benzyloxy)-2'-dodecylhexadecanamide)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (TMM-8). Aminosugar **TMM-7** (63 mg, 0.056 mmol) and carboxylic acid **TMM-3** (32 mg, 0.056 mmol), were stirred with DIEA (15 μL, 0.6 mmol) and TBTU (27 mg, 0.084 mmol) in DMF (2 mL) for 18 h. The mixture was diluted with EtOAc and the organic layer was washed with brine, dried (Na_2SO_4), filtered, concentrated and the residue was purified by chromatography (2:1, hexane–EtOAc) to give **TMM-9** (81 mg, 89%) as a syrup. R_f 0.4 (2:1 hexanes–EtOAc); $[\alpha]_D$ +43.9 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.48–7.15 (m, 43 H), 7.03 (dq, 4 H, *J* = 11.4, 7.0, 4.9 Hz), 6.83 (d, 2 H, *J* = 6.8 Hz), 6.49 (d, 1 H, *J* = 7.7 Hz), 5.27 (d, 1 H, *J* = 3.5 Hz, H-1), 5.13 (d, 1 H, *J* = 3.5 Hz, H-1), 5.00–4.62 (m, 10 H), 4.56–4.47 (m, 3 H), 4.30 (d, 1 H, *J* = 10.4 Hz), 4.23–4.06 (m, 3 H), 4.01 (app q, 2 H, *J* = 9.6 Hz), 3.88 (app t, 1

H, *J* = 9.6 Hz), 3.72 (dd, 1 H, *J* = 9.6, 3.6 Hz), 3.59 (app q, 1 H, *J* = 5.8 Hz), 3.41–3.31 (m, 3 H), 3.29 (t, 2 H, *J* = 7.0 Hz), 3.11 (dd, 1 H, *J* = 10.3, 2.8 Hz), 3.05–2.98 (m, 1 H), 2.40–2.33 (m, 1 H), 1.79–1.20 (m, 46 H), 0.92 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 174.3, 143.9, 139.0, 138.7, 138.6, 138.2, 138.1, 138.0, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 127.4, 127.2, 127.0, 126.9, 94.6 (C-1), 93.9 (C-1), 86.2, 81.9, 81.3, 80.5, 80.1, 79.8, 78.5, 77.9, 76.0, 75.6, 75.5, 75.0, 73.0, 72.7, 70.8, 69.6, 61.8, 52.4, 51.5, 38.7, 32.6, 32.0, 30.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.2, 28.9, 27.8, 26.8, 25.4, 22.7, 14.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{108}H_{132}N_2O_{12}Na$: 1699.9734. Found: 1699.9725.

2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-((2'*R*,3'*R*)-16'-azido-3'-(benzyloxy)-2'-dodecylhexadecanamide)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (TMM-9). To a solution of **TMM-8** (81 mg, 0.048 mmol) in CH_2Cl_2–MeOH (1:1, 2 mL) was added *p*-TsOH·H_2O (28 mg, 0.144 mmol) at rt. After stirring for 20 h, the mixture was neutralized by adding Et_3N slowly at 0 °C. The solution was concentrated and the residue was purified by chromatography (3:1, hexane–EtOAc) to give **TMM-8** (55 mg, 80%) as a syrup. R_f 0.48 (2:1 hexanes–EtOAc); $[\alpha]_D$ +40.2 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.52–7.12 (m, 34 H), 6.48–6.38 (m, 1 H), 5.07 (d, 1 H, *J* = 3.5 Hz, H-1), 5.02–4.96 (m, 3 H, H-1), 4.93–4.85 (m, 3 H), 4.80 (d, 1 H, *J* = 10.0 Hz), 4.72–4.56 (m, 7 H), 4.49 (d, 1 H, *J* = 11.2 Hz), 4.13 (dt, 1 H, *J* = 10.0, 3.0 Hz), 4.11–4.01 (m, 4 H), 3.63–3.49 (m, 5 H), 3.40–3.32 (m, 2 H), 3.27 (t, 2 H, *J* = 7.0 Hz), 3.05–2.96 (m, 1 H), 2.37–2.29 (m, 1 H), 1.74–1.20 (m, 46 H), 0.90 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 138.9, 138.8, 138.6, 138.3, 138.2, 138.1, 137.9, 128.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 93.9 (C-1), 93.7 (C-1), 81.6, 81.4, 80.5, 79.6, 79.3, 78.6, 77.4, 75.6, 75.5, 75.0, 73.0, 71.2, 69.6, 61.6, 52.4, 51.5, 38.6, 32.5, 32.0, 30.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.2, 28.9, 27.7, 26.8, 25.4, 22.7, 14.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{89}H_{118}N_2O_{12}Na$: 1457.8638. Found: 1457.8633.

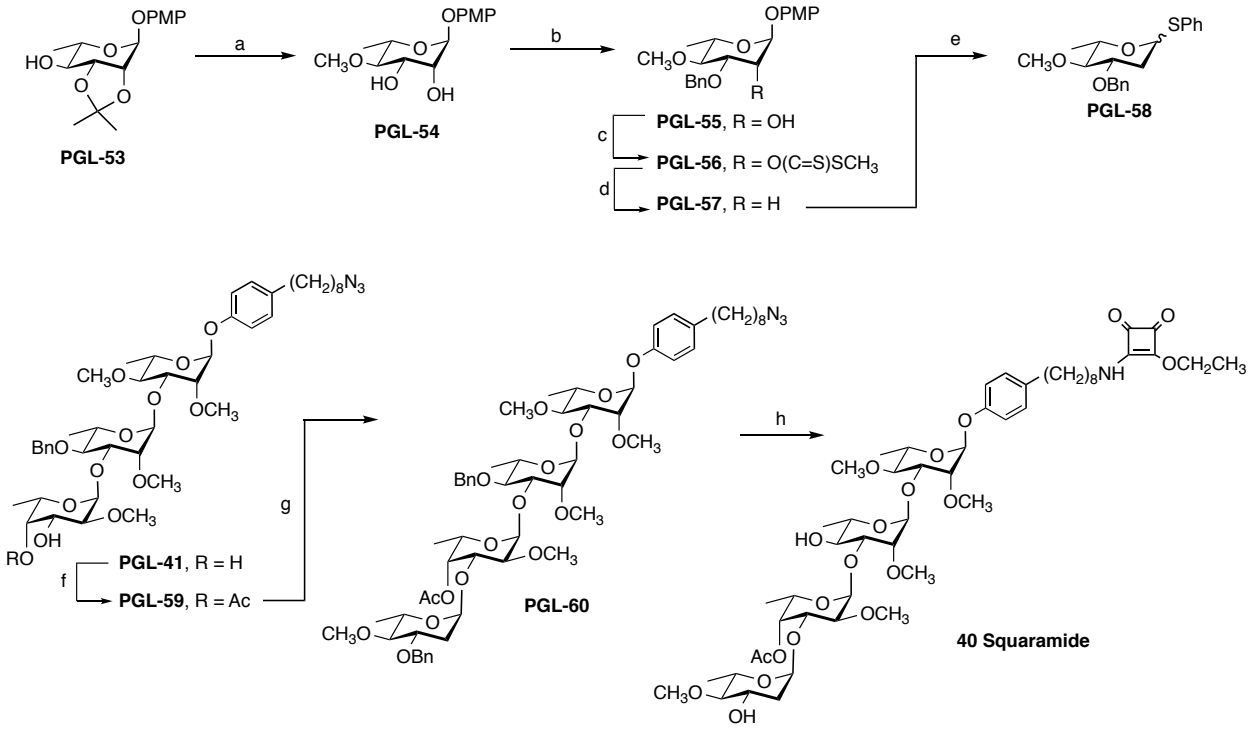
2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl-(1↔1)-6-deoxy-6-[(2*R*,3*R*)-3-(benzyloxy)-16-((*tert*-butoxycarbonyl)amino)-2-dodecylhexadecanamide]-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (TMM-10). To a solution of **TMM-9** (26 mg, 1 mmol) in THF (4 mL) was added trimethylphosphine (30 μL, 0.03 mmol, 1M in THF), followed by the addition of 1M aq NaOH solution (11 μL, 0.011 mmol) at rt. The mixture was heated at 50 °C for 2 h and then cooled. The solvent was evaporated and the residue was dissolved in a THF–H_2O solution (3:1, 1.6 mL), followed by the addition of di-*t*-butyl dicarbonate (5 mg, 0.022 mmol) and 1M aq

NaOH (56 μL, 0.056 mmol) at 0 °C. After stirring at rt for 16 h, the reaction mixture was diluted with CH_2Cl_2 and the organic layer was subsequently dried (Na_2SO_4), filtered, concentrated and the residue was purified by chromatography (2:1, hexane–EtOAc) to give **TMM-10** (26.7 mg, 98%) as a syrup. R_f 0.4 (2:1 hexanes–EtOAc); $[\alpha]_D$ +48.8 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.21 (m, 34 H), 6.45 (dd, 1 H, *J* = 8.5, 2.0 Hz), 5.07 (d, 1 H, *J* = 3.6 Hz, H-1), 5.01–4.96 (m, 3 H, H-1), 4.93–4.85 (m, 3 H), 4.80 (d, 1 H, *J* = 10.0 Hz), 4.73–4.56 (m, 7 H), 4.49 (d, 1 H, *J* = 11.2 Hz), 4.13 (dt, 1 H, *J* = 10.0, 3.0 Hz), 4.10–4.01 (m, 4 H), 3.60–3.50 (m, 5 H), 3.40–3.33 (m, 2 H), 3.13 (dd, 2 H, *J* = 6.6, 6.1 Hz), 3.01 (dt, 1 H, *J* = 14.0, 3.0 Hz), 2.33 (dt, 1 H, *J* = 9.6, 5.5 Hz), 1.75–1.20 (m, 46 H), 1.47 (s, 9 H), 0.91 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 174.3, 138.9, 138.8, 138.6, 138.3, 138.2, 138.1, 137.9, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 93.9 (C-1), 93.7 (C-1), 81.6, 81.4, 80.5, 79.6, 79.3, 78.6, 77.4, 75.6, 75.5, 75.0, 73.0, 71.2, 69.6, 61.6, 52.4, 40.7, 38.6, 32.5, 32.0, 30.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 28.5, 27.7, 26.9, 25.4, 22.7, 14.2. HRMS (ESI) *m/z* calcd for (M+H) $C_{94}H_{129}N_2O_{14}$: 1509.9438. Found: 1509.9450.

α-D-Glucopyranosyl-(1↔1)-6-deoxy-6-[(2*R*,3*R*)-3-(benzyloxy)-16-((*t*-butoxycarbonyl)amino)-2-dodecylhexadecanamide]-α-D-glucopyranoside (TMM-11). Compound **TMM-10** (38.7 mg, 0.026 mmol) was dissolved in H_2O−CH_3OH (1:1, 2 mL) and $Pd(OH)_2$–C (10%) was then added and the reaction mixture was stirred overnight under a H_2 (1 atm). The reaction mixture was diluted with H_2O−CH_3OH (1:1, 5 mL), filtered through Celite, and the filtrate was concentrated. The resulting residue was purified by chromatography (3:1 EtOAc−CH_3OH) to give **TMM-11** (22 mg, 96%) as a syrup. R_f 0.17 (3:1 EtOAc−CH_3OH); $[\alpha]_D$ +30.0 (*c* = 0.1, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 5.09 (d, 1 H, *J* = 3.5 Hz, H-1), 5.08 (d, 1 H, *J* = 3.5 Hz, H-1), 3.92 (ddd, 1 H, *J* = 9.7, 6.7, 2.8 Hz), 3.85–3.74 (m, 4 H), 3.67 (dd, 1 H, *J* = 11.8, 5.4 Hz), 3.63 (ddd, 1 H, *J* = 9.7, 5.0, 2.4 Hz), 3.57 (dd, 1 H, *J* =14.1, 2.8 Hz3.47 (dd, 1 H, *J* = 3.7, 1.6 Hz), 3.45 (dd, 1 H, *J* = 3.7, 1.7 Hz), 3.39–3.33 (m, 1 H), 3.31–3.29 (m, 1 H), 3.16–3.12 (m, 1 H), 3.00 (t, 2 H, *J* = 7.1 Hz), 2.26–2.21 (m, 1 H), 1.62–1.26 (m, 46 H), 1.42 (s, 9 H), 0.89 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 176.7, 157.1, 94.0 (2C, 2 × C-1), 78.3, 73.1, 72.7, 72.5, 72.1, 71.9, 71.9, 71.8, 70.6, 70.5, 61.3, 52.6, 40.0, 34.7, 31.7, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 27.4, 27.2, 26.5, 25.2, 22.3, 13.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{45}H_{86}N_2NaO_{14}$: 901.5901. Found: 901.5999.

α-D-Glucopyranosyl-(1↔1)-6-deoxy-6-[(2*R*,3*R*)-2-dodecyl-3-hydroxy-16-((2-methoxy-3,4-dioxocyclobut-1-en-1-yl)amino)hexadecanamide]-α-D-glucopyranoside (39 Squaramide). Disaccharide **TMM-11** was dissolved in 50% TFA in CH_2Cl_2 at rt. After 4 h, the reaction mixture was concentrated to a syrup. To a solution of the resulting amine (5 mg, 0.0064 mmol) in 1:1 MeOH−H_2O (1 mL) was added diethyl squarate (2.8 μL, 0.02 mmol), followed by slow addition of satd aq Na_2CO_3 soln until the pH of the mixture was 8. Then the solvent was evaporated and the residue was purified by C_{18} chromatography (4:1 CH_3OH–H_2O) to give **39 Squaramide** (5.6 mg, 99%) as a syrup (ester exchanged, OCH_2CH_3 was replaced by OCH_3 under the basic conditions). R_f 0.4 (4:1 CH_3OH–H_2O; $[\alpha]_D$ +26.2 (*c* = 0.1, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD, δ_H) 5.09 (d, 1 H, *J* = 3.5 Hz, H-1), 5.08 (d, 1 H, *J* = 3.8 Hz, H-1), 4.36 (d, 3 H, *J* = 14.1 Hz), 3.91 (ddd, 1 H, *J* = 9.7, 6.7, 2.8 Hz), 3.84–3.73 (m, 4 H), 3.66 (dd, 1 H, *J* =11.8, 5.4 Hz), 3.63 (ddd, 1 H, *J* = 8.3, 6.1, 3.2 Hz), 3.60–3.54 (m, 2 H), 3.47 (dd, 1 H, *J* = 3.7, 2.1 Hz3.45 (dd, 1 H, *J* = 3.7, 2.2 Hz), 3.41–3.33 (m, 2 H), 3.32–3.29 (m, 1 H), 3.14 (app t, 1 H, *J* = 9.6), 2.27–2.21 (m, 1 H), 1.66–1.26 (m, 46 H), 0.89 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 188.6, 188.5, 183.5, 183.3, 177.0, 176.7, 176.4, 173.1, 94.0 (2 × C-1), 73.1, 72.7, 72.5, 72.1, 71.9, 71.8, 71.8, 70.6, 70.5, 61.3, 59.7, 59.6, 52.6, 44.2, 43.9, 40.0, 34.7, 31.7, 30.6, 30.1, 29.4, 29.3, 29.2, 29.1, 28.8, 27.2, 26.0, 25.2, 22.3, 13.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{45}H_{80}N_2NaO_{15}$: 911.5451. Found: 911.5444.

33. Synthesis of 40



Scheme S42. Synthesis of **40 Squaramide**. a) CH_3I, NaH, DMF; then *p*-TsOH·H_2O, CH_3OH, 69%; b) *n*-Bu_2SnO, toluene; then BnBr, CsF, DMF, 85%; c) NaH, CS_2, THF; then CH_3I, 88%; d) *n*-Bu_3SnH, AIBN, benzene; e) PhSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 58% over two steps; f) $CH_3C(OCH_3)_3$, camphorsulfonic acid, CH_2Cl_2; then HOAc, H_2O, 98%; g) **PGL-58**, NIS, AgOTf, CH_2Cl_2, 69%; h) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 61%.

***p*-Methoxyphenyl 4-*O*-methyl-α-L-rhamnopyranoside (PGL-54)**. To a solution of **PGL-53**[16] (2.14 g, 6.89 mmol) and CH_3I (0.56 mL, 8.96 mmol) in dry DMF (18 mL) at 0 °C (ice bath) was added NaH (60% dispersion in mineral oil, 0.36 g, 8.96 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of AcOH and concentrated. The resulting residue was purified by chromatography (1:9 EtOAc–hexane) to yield a colorless oil. To the solution of oil in CH_3OH (40 mL) at rt was added *p*-TsOH·H_2O (126 mg, 0.66 mmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Et_3N and concentrated. The resulting residue was purified by chromatography (1:1 EtOAc–hexane) to yield **PGL-54** (1.29 g, 69%, two steps) as a colorless oil. R_f 0.41 (8:2 EtOAc–hexane); $[\alpha]_D$ –119.5 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.00–6.94 (m, 2 H), 6.85–6.78 (m, 2 H), 5.38 (d, 1 H, *J* = 1.2 Hz, H-1), 4.14 (s, 1H), 4.08–4.01 (m, 1H), 3.82–3.73 (m, 4 H), 3.58 (s, 3 H), 3.16 (app t, 1

H, J = 9.4 Hz), 2.65 (d, 1 H, J = 3.7 Hz), 2.62 (s, 1H), 1.29 (d, 3 H, J = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 155.1, 150.5, 117.8, 114.8, 98.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 83.5, 71.4, 71.2, 68.1, 61.1, 55.9, 18.2. HRMS (ESI) *m/z* calcd for (M+Na) $C_{14}H_{20}O_6Na$: 307.1152. Found: 307.1157.

***p*-Methoxyphenyl 3-*O*-benzyl-4-*O*-methyl-α-L-rhamnopyranoside (PGL-55)**. A solution of diol **PGL-54** (923 mg, 3.44 mmol) and *n*-Bu_2SnO (942 mg, 3.78 mmol) in toluene (40 mL) was heated at reflux with a Dean–Stark apparatus overnight, cooled, concentrated and the resulting residue dried on a vacuum pump for 1h. To a solution of this residue in DMF (15 mL) at rt was added CsF (575 mg, 3.78 mmol) and BnBr (0.45 mL, 3.8 mmol). The reaction mixture was stirred overnight at rt and concentrated. The resulting residue was purified by chromatography (2:8 EtOAc–hexane) to give **PGL-55** (1.10 g, 85%, two steps) as a colorless oil. R_f 0.34 (2:8 EtOAc–hexane); $[\alpha]_D$ –113.6 (c = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.44–7.30 (m, 5 H), 7.00–6.94 (m, 2 H), 6.84–6.80 (m, 2 H), 5.41 (d, 1 H, J = 1.8 Hz, H-1), 4.76 (ABq, 2 H, J = 11.5 Hz), 4.18 (dt, 1 H, J = 3.5, 1.8 Hz), 3.91 (dd, 1 H, J = 9.1, 3.4 Hz), 3.82–3.71 (m, 4 H), 3.59 (s, 3 H), 3.22 (app t, 1 H, J = 9.4 Hz), 2.57 (d, 1 H, J = 1.8 Hz), 1.40–1.20 (d, 3 H, J = 6.2); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 155.1, 150.5, 138.2, 128.8, 128.2, 128.0, 117.8, 114.8, 98.1 (C-1), 82.1, 79.8, 72.5, 68.9, 68.2, 61.3, 55.9, 18.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{21}H_{26}O_6Na$: 397.1622. Found: 397.1619.

***p*-Methoxyphenyl 3-*O*-benzyl-4-*O*-methyl-2-*O*-(thiomethoxycarbonyl)-α-L-rhamnopyranoside (PGL-56)**. To a solution of **PGL-55** (746 mg, 2.00 mmol) in THF (20 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 120 mg, 3.00 mmol) and imidazole (27 mg, 0.40 mmol). To this reaction mixture at rt was added CS_2 (1.2 mL, 20 mmol) and the solution was stirred for 1 h, before MeI (0.62 mL, 10 mmol) was added. The reaction mixture was stirred overnight at rt and concentrated. The resulting residue was purified by chromatography (5:95 EtOAc–hexane) to give **PGL-56** (817 mg, 88%) as a colorless oil. R_f 0.33 (1:9 EtOAc–hexane); $[\alpha]_D$ –35.8 (c = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38–7.26 (m, 5 H), 6.99–6.94 (m, 2 H), 6.84–6.79 (m, 2 H), 6.24 (dd, 1 H, J = 3.3, 2.0 Hz), 5.48 (d, 1 H, J = 1.8 Hz, H-1), 4.75 (d, 1 H, J = 11.5 Hz), 4.63 (d, 1 H, J = 11.5 Hz), 4.11 (dd, 1 H, J = 9.3, 3.4 Hz), 3.84 (app dq, 1 H, J = 9.6, 6.2 Hz), 3.77 (s, 3 H), 3.60 (s, 3 H), 3.27 (app t, 1 H, J = 9.4 Hz), 2.60 (s, 3 H), 1.32 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 216.2, 155.4, 150.3,

138.2, 128.6, 128.0, 127.9, 118.1, 114.8, 96.0 (C-1), 82.5, 77.8, 77.5, 72.2, 68.6, 61.5, 55.9, 19.3, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{23}H_{28}O_6S_2Na$: 487.1220. Found: 487.1220.

Phenyl 3-*O*-benzyl-4-*O*-methyl-2,6-dideoxy-1-thio-L-*arabino*-hexopyranoside (PGL-58). To a solution of **PGL-56** (785 mg, 1.69 mmol) in degassed benzene (20 mL) at 80 °C in a Schlenk tube was added dropwise a solution of *n*-Bu_3SnH (0.91 mL, 3.4 mmol) and AIBN (69 mg, 0.42 mmol) in benzene (10 mL) over 100 min using a syringe pump. The reaction mixture was stirred at 80 °C for 3 h, cooled and then concentrated. The resulting residue was purified by chromatography (1:99 EtOAc–toluene) to give a light yellow oil (2-deoxy glycoside **PGL-57**). To a solution of oil and thiophenol (166 μL, 162 mmol) in CH_2Cl_2 (17 mL) at 0 °C was added $BF_3{\cdot}OEt_2$ (183 μL, 1.48 mmol). The reaction mixture was stirred at 0 °C for 1 h, Et_3N (200 μL) was added, and then the solution was concentrated. The resulting residue was purified by chromatography (1:99 EtOAc–toluene) to give **PGL-58** (330 mg, 58%, two steps) as a colorless, oily mixture of 5:4 α:β isomers: $[\alpha]_D$ –106.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.49–7.33 (m, 10 H), 7.32–7.22 (m, 8 H), 5.56 (d, 1 H, *J* = 5.6 Hz, H-1α), 4.75–4.59 (m, 4.5 H), 4.13 (app dq, 1 H, *J* = 9.4, 6.2 Hz), 3.82 (ddd, 1 H, *J* = 11.6, 8.6, 4.9 Hz), 3.61 (s, 3 H), 3.60 (s, 2.4 H), 3.53 (ddd, 0.8 H, *J* = 11.2, 8.7, 5.2 Hz), 3.30 (app dq, 0.8 H, *J* = 9.4, 6.2 Hz), 2.89–2.83 (m, 1.8 H), 2.46–2.38 (m, 1.8 H), 2.05 (ddd, 1 H, *J* = 13.4, 11.6, 5.7 Hz), 1.74 (dt, 0.8 H, *J* = 19.9, 10.1 Hz), 1.36 (d, 2.4 H, *J* = 6.2 Hz), 1.30 (app t, 3 H, *J* = 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.7, 138.6, 135.5, 134.3, 131.5, 131.3, 129.1, 129.0, 128.6, 127.9, 127.86, 127.82, 127.5, 127.2, 86.7, 85.8, 84.0 (C-1α), 82.0 (C-1β), 80.4, 77.6, 75.9, 72.2, 71.9, 68.6, 61.3, 61.1, 37.4, 36.8, 18.5, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{20}H_{24}O_3SNa$: 367.1338. Found: 367.1336.

4-(8-Azidooctyl)phenyl 4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranoside-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-59). To a solution of **PGL-41** (422 mg, 507 μmol) and trimethyl orthoacetate (387 μL, 3.04 mmol) in CH_2Cl_2 (10 mL) at rt was added CSA (27 mg, 117 μmol). The reaction mixture was stirred at rt for 4 h, Et_3N (300 μL) was added and the solution was concentrated. The residue was co-evaporated twice with toluene to give a colorless oil. A solution of the resulting oil in aqueous 80% AcOH (10 mL) was stirred at rt for 3 h, concentrated and the residue was and co-evaporated twice with toluene. The resulting residue was purified by chromatography (5:5 EtOAc–hexane) to yield **PGL-59** (434 mg, 98%, two steps) as a colorless oil. R_f 0.45 (7:3

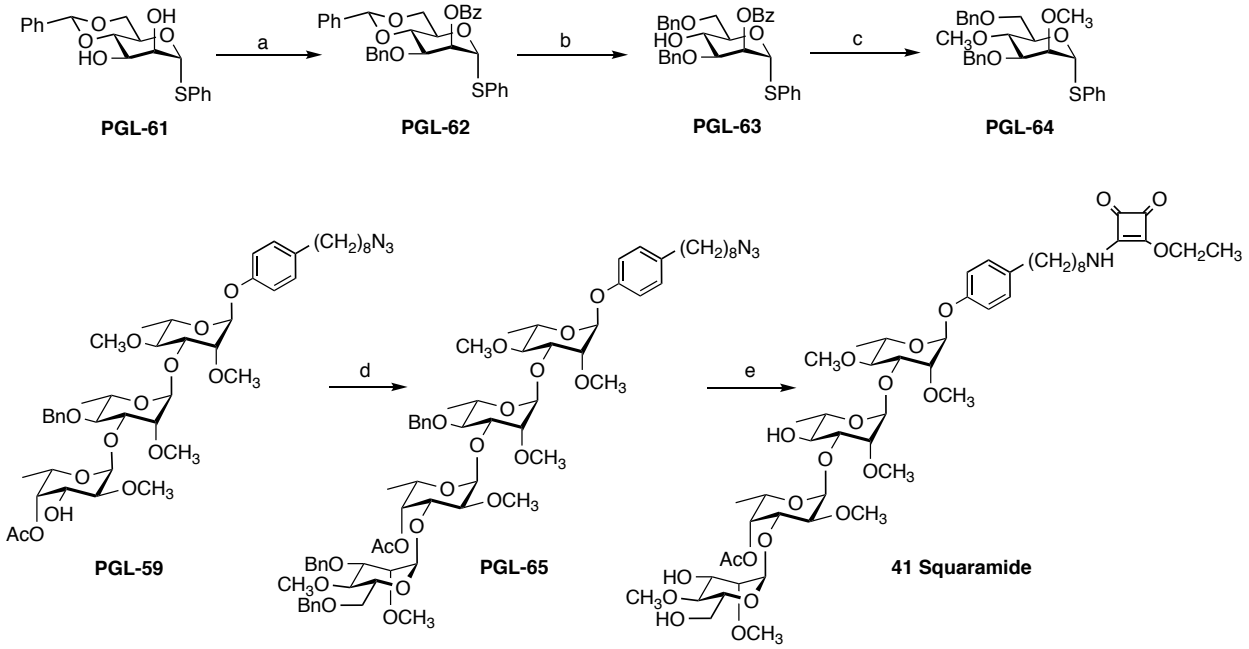
EtOAc–hexane); $[\alpha]_D$ –125.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.23 (m, 5 H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.96 (d, 2 H, *J* = 8.6 Hz), 5.46 (d, 1 H, *J* = 1.5 Hz, H-1), 5.29 (d, 1 H, *J* = 3.4 Hz), 5.24 (d, 1 H, *J* = 3.5 Hz, H-1), 5.19 (d, 1 H, *J* = 1.3 Hz, H-1), 5.13 (d, 1 H, *J* = 11.5 Hz), 4.59 (d, 1 H, *J* = 11.5 Hz), 4.35 (q, 1 H, *J* = 6.6 Hz), 4.25 (dt, 1 H, *J* = 10.2, 3.0 Hz), 4.09 (dd, 1 H, *J* = 9.6, 3.2 Hz), 4.02 (dd, 1 H, *J* = 9.4, 3.2 Hz), 3.95 (tt, 1 H, *J* = 12.5, 6.2 Hz), 3.74 (dd, 1 H, *J* = 2.9, 2.0 Hz), 3.72 (dd, 1 H, *J* = 3.1, 1.9 Hz), 3.71–3.65 (m, 1H), 3.55 (s, 3 H), 3.53–3.49 (m, 4 H), 3.49–3.44 (m, 4 H), 3.30 (s, 3 H), 3.28–3.19 (m, 3 H), 2.57–2.51 (m, 2 H), 2.28 (d, 1 H, *J* = 2.5 Hz), 2.18 (s, 3 H), 1.63–1.54 (m, 4 H), 1.39–1.28 (m, 11H), 1.27 (d, 3 H, *J* = 6.2 Hz), 1.15 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR (151 MHz, $CDCl_3$, δ_C) 171.4, 154.7, 139.2, 136.9, 129.5, 128.4, 127.6, 127.6, 116.4, 99.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 98.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 95.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 82.3, 81.7, 80.9, 80.5, 80.1, 79.5, 78.6, 75.2, 73.1, 69.0, 68.8, 68.2, 65.4, 61.4, 59.1, 58.3, 57.9, 51.7, 35.3, 31.8, 29.5, 29.34, 29.3, 29.0, 26.9, 21.0, 18.4, 18.1, 16.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{45}H_{67}N_3O_{14}Na$: 896.4515. Found: 896.4503.

***p*-(8-Azidooctylphenyl) 2,6-dideoxy-3-*O*-benzyl-4-*O*-Me-α-L-*arabino*-hexopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-60)**. A solution of **PGL-58** (94 mg, 273 μmol), **PGL-59** (183 mg, 209 μmol), and crushed 4Å molecular sieves (100 mg) in CH_2Cl_2 (12 mL) was stirred at 0 °C for 30 min. To this solution at –20 °C was added *N*-iodosuccinimide (61 mg, 271 μmol) and silver triflate (11 mg, 43 μmol). The reaction mixture was stirred at –20 °C for another 60 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (15:85 EtOAc–toluene) to yield **PGL-60** (160 mg, 69%) as a light yellow foam. R_f 0.32 (3:7 EtOAc–toluene); $[\alpha]_D$ –128.3 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.30 (m, 8 H), 7.29–7.24 (m, 2 H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.96 (d, 2 H, *J* = 8.6 Hz), 5.45 (d, 1 H, *J* = 1.6 Hz, H-1), 5.27 (d, 1 H, *J* = 2.5 Hz), 5.21–5.15 (m, 3 H), 5.04 (d, 1 H, *J* = 3.1 Hz, H-1), 4.64 (s, 2 H), 4.54 (d, 1 H, *J* = 11.0 Hz), 4.35 (q, 1 H, *J* = 6.8 Hz), 4.28 (dd, 1 H, *J* = 10.4, 3.3 Hz), 4.08 (dd, 1 H, *J* = 9.6, 3.2 Hz), 4.01 (dd, 1 H, *J* = 9.5, 3.1 Hz), 3.96–3.88 (m, 2 H), 3.82–3.73 (m, 2 H), 3.72–3.66 (m, 2 H), 3.55 (s, 3 H), 3.54 (s, 3 H), 3.52–3.48 (m, 4 H), 3.47 (s, 3 H), 3.45–3.42 (m, 1H), 3.32 (s, 3 H), 3.27–3.19 (m, 3 H), 2.80 (app t, 1 H, *J* = 9.2 Hz), 2.59–2.51 (m, 2 H), 2.15 (s, 3 H), 2.02 (dd, 1 H, *J* = 12.5, 5.1 Hz), 1.64 (dd, 1 H, *J* = 11.5, 9.4 Hz), 1.58 (m, 4 H), 1.39–1.29 (m, 11H), 1.26 (d, 3 H, *J* = 6.2 Hz), 1.14 (d,

3 H, J = 6.6 Hz), 1.11 (d, 3 H, J = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 154.8, 139.3, 139.1, 136.9, 129.5, 128.5, 128.4, 128.2, 127.8, 127.7, 127.6, 116.4, 100.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 98.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 93.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 86.7, 82.3, 82.2, 80.9, 80.5, 79.9, 79.5, 76.9, 75.4, 71.9, 70.4, 70.2, 69.0, 68.8, 67.4, 65.0, 61.4, 60.9, 59.3, 59.1, 57.7, 51.7, 35.6, 35.3, 31.8, 29.5, 29.4, 29.3, 29.0, 26.9, 21.1, 18.4, 18.3, 18.1, 16.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{59}H_{85}N_3O_{17}Na$: 1130.6000. Found: 1130.6000.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,6-dideoxy-4-*O*-Me-α-L-*arabino*-hexopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (40 Squaramide). Treatment of **PGL-60** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **40 Squaramide** (61%, chromatography 4:96 CH_3OH–CH_2Cl_2) as a light yellow powder. R_f 0.67 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –136.0 (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.08 (d, 2 H, J = 8.5 Hz), 6.97 (d, 2 H, J = 8.5 Hz), 5.90 (s, 1H), 5.46 (s, 1 H, H-1), 5.26 (d, 1 H, J = 2.6 Hz), 5.16 (s, 1 H, H-1), 5.08 (d, 1 H, J = 3.6 Hz, H-1), 5.04 (d, 1 H, J = 3.2 Hz, H-1), 4.80–4.72 (m, 2 H), 4.30–4.23 (m, 2 H), 4.12 (dd, 1 H, J = 9.6, 3.2 Hz), 3.95–3.78 (m, 4 H), 3.77–3.31 (m, 22 H), 3.23 (app t, 1 H, J = 9.5 Hz), 2.71 (app t, 1 H, J = 9.2 Hz), 2.54 (app t, 2 H, J = 7.6 Hz), 2.28 (s, 1H), 2.16 (s, 3 H), 1.94 (dd, 1 H, J = 13.0, 5.1 Hz), 1.72–1.67 (m, 1H), 1.65–1.58 (m, 4 H), 1.45 (dd, 3 H, J = 12.7, 5.6 Hz), 1.30 (m, 17 H), 1.12 (app t, 3 H, J = 7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.9, 154.7, 136.8, 129.5, 116.4, 101.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 168 Hz, C-1), 99.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 93.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 88.2, 83.7, 82.5, 80.8, 80.6, 79.0, 78.3, 71.9, 70.7, 69.9, 69.8, 69.2, 69.0, 68.9, 67.4, 65.6, 61.2, 61.0, 60.6, 59.2, 59.0, 45.1, 37.2, 35.3, 31.8, 29.5, 29.4, 29.3, 26.5, 21.0, 18.3, 18.1, 18.1, 16.6, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{51}H_{79}NO_{20}Na$: 1048.5088. Found: 1048.5070.

34. Synthesis of 41



Scheme S43. Synthesis of **41 Squaramide**. a) *n*-Bu_2SnO, toluene; then BnBr, CsF, DMF; then BzCl, pyridine 90%; b) Et_3SiH, CH_2Cl_2 CF_3CO_2H; 76%; c) $NaOCH_3$, CH_2Cl_2, CH_3OH; then CH_3I, NaH, DMF, quant; d) **PGL-64**, NIS, AgOTf, CH_2Cl_2, 45%; e) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 73%.

Phenyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (PGL-62). A solution of diol **PGL-61** [35] (3.83 g, 10.6 mmol) and *n*-Bu_2SnO (2.78 g, 11.1 mmol) in toluene (60 mL) was heated at refluxed with a Dean–Stark apparatus overnight, cooled, concentrated and the resulting residue dried on a vacuum pump for 1 h. To this residue in DMF (46 mL) was added CsF (1.69 g 11.1 mmol) and BnBr (1.39 mL, 11.7 mmol). The reaction mixture was stirred overnight at rt and concentrated. The resulting residue was purified by chromatography (3:7 EtOAc–hexane) to give a colorless oil. To a solution of the resulting oil (4.44 g, 9.85 mmol) in pyridine (50 mL) at 0 °C was added BzCl (1.54 mL, 13.3 mmol). The reaction mixture was stirred overnight at rt, concentrated and the residue was co-evaporated twice with toluene. The resulting residue was purified by chromatography (15:85 EtOAc–hexane) to yield **PGL-62** (5.29 g, 90%, three steps) as a colorless oil. R_f 0.61 (15:85 EtOAc–hexane); $[\alpha]_D$ +74.8 (*c* = 1.1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, δ_H) 8.13–8.08 (m, 2 H), 7.62–7.52 (m, 3 H), 7.50–7.15 (m, 15 H), 5.84 (dd, 1 H, *J* = 3.4, 1.5 Hz), 5.71 (s, 1H), 5.62 (d, 1 H, *J* =

1.4 Hz, H-1), 4.76 (ABq, 2 H, *J* = 12.2 Hz), 4.44 (app td, 1 H, *J* = 9.8, 4.9 Hz), 4.33–4.25 (m, 2 H), 4.14 (dd, 1 H, *J* = 9.9, 3.4 Hz), 3.93 (app t, 1 H, *J* = 10.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 138.0, 137.6, 133.6, 133.3, 132.4, 130.2, 129.9, 129.4, 129.3, 129.2, 128.7, 128.6, 128.4, 128.3, 127.9, 126.4, 101.9, 87.5 (C-1), 79.1, 74.5, 72.4, 72.2, 68.8, 65.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{33}H_{30}O_6SNa$: 577.1655. Found: 577.1649.

Phenyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside (PGL-63). To a stirred solution of **PGL-62** (544 mg, 981 μmol) and Et_3SiH (1.56 mL, 9.8 1 mmol) in dichloromethane (13 mL) at 0 °C (ice bath) was added dropwise neat trifluoroacetic acid (0.75 mL, 9.8 mmol). The reaction mixture was stirred at 0 °C for 5 min, concentrated and the residue was then co-evaporated with toluene. The resulting residue was purified by chromatography (15:85 EtOAc–hexane) to yield **PGL-63** (414 mg, 76%) as a colorless oil. R_f 0.45 (2:8 EtOAc–hexane); $[\alpha]_D$ +38.9 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.06–8.02 (m, 2 H), 7.58–7.50 (m, 3 H), 7.41–7.24 (m, 15 H), 5.84 (dd, 1 H, *J* = 3.0, 1.7 Hz), 5.65 (d, 1 H, *J* = 1.4 Hz, H-1), 4.82 (d, 1 H, *J* = 11.3 Hz), 4.68 (d, 1 H, *J* = 11.8 Hz), 4.56 (app t, 2 H, *J* = 11.6 Hz), 4.41 (ddd, 1 H, *J* = 9.5, 4.6, 3.0 Hz), 4.23 (app t, 1 H, *J* = 9.6 Hz), 3.92 (dd, 1 H, *J* = 10.8, 4.9 Hz), 3.88 (dd, 1 H, *J* = 6.0, 3.2 Hz), 3.86 (dd, 1 H, *J* = 7.3, 3.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 165.8, 138.4, 137.5, 133.7, 133.5, 132.3, 130.1, 129.8, 129.3, 128.8, 128.6, 128.5, 128.45, 128.3, 128.0, 127.8, 127.7, 86.73 (C-1), 78.20, 73.78, 72.61, 71.82, 70.20, 69.95, 67.76. HRMS (ESI) *m/z* calcd for (M+Na) $C_{33}H_{32}O_6SNa$: 579.1812. Found: 579.1810.

Phenyl 3,6-di-*O*-benzyl-2,4-di-*O*-methyl-1-thio-α-D-mannopyranoside (PGL-64). To a solution of **PGL-63** (170 mg, 298 μmol) in 1:1 CH_2Cl_2–CH_3OH (3 mL) at rt was added sodium methoxide (4.8 mg, 89 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR 120, filtered and concentrated to yield a colorless oil. To the solution of oil and CH_3I (24 μL, 387 μmol) in dry DMF (4 mL) at 0 °C (ice bath) was added NaH (60% dispersion in mineral oil, 15 mg, 387 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of AcOH and concentrated. The resulting residue was purified by chromatography (15:85 EtOAc–hexane) to yield **PGL-64** (143 mg, 100%, two steps) as a colorless oil. R_f 0.65 (25:75 EtOAc–hexane); $[\alpha]_D$ +118.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.52–7.47 (m, 2 H), 7.44–7.22 (m, 13 H), 5.61 (d, 1 H, *J* = 1.4 Hz, H-1), 4.73 (ABq, 2 H, *J* = 11.9 Hz), 4.65 (d, 1 H, *J* = 11.9 Hz), 4.50 (d, 1 H, *J* = 11.9 Hz), 4.22–4.15 (m, 1H), 3.79 (dd, 1 H, *J* = 10.9, 5.2 Hz), 3.75 (dd, 1 H, *J* = 7.0, 2.4 Hz), 3.73 (dd, 1 H, *J* = 8.7, 2.5 Hz), 3.71

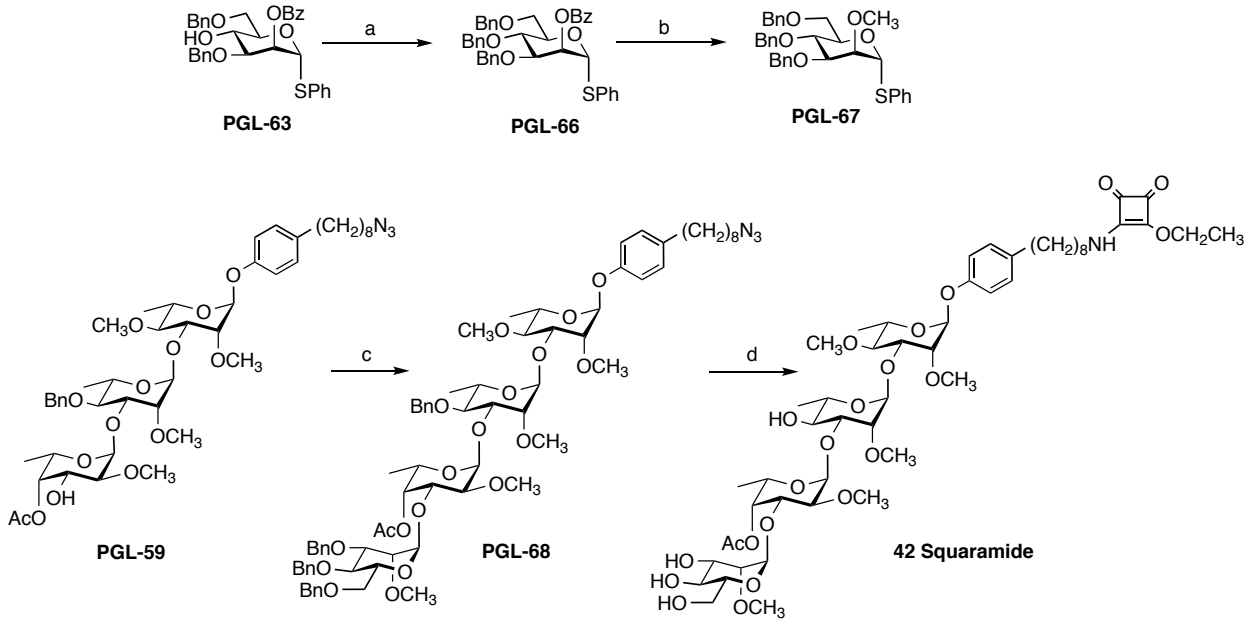
(dd, 1 H, *J* = 3.2, 1.7 Hz), 3.66 (app t, 1 H, *J* = 9.5 Hz), 3.53 (s, 3 H), 3.44 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.6, 138.4, 134.7, 131.6, 129.2, 128.7, 128.4, 128.2, 128.0, 127.9, 127.6, 127.5, 85.1 (C-1), 80.1, 79.7, 76.8, 73.5, 72.8, 72.6, 69.5, 61.1, 58.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{28}H_{32}O_5SNa$: 503.1863. Found: 503.1859.

4-(8-Azidooctyl)phenyl 3,6-di-*O*-benzyl-2,4-di-*O*-methyl-α-D-mannopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-65). A solution of **PGL-64** (51 mg, 106 μmol), **PGL-59** (77 mg, 88 μmol), and crushed 4Å molecular sieves (60 mg) in CH_2Cl_2 (6 mL) was stirred at 0 °C for 30 min. To this solution at –20 ºC was added *N*-iodosuccinimide (24 mg, 106 μmol) and silver triflate (4.5 mg, 18 μmol). The reaction mixture was stirred at –20 ºC for another 30 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and the solution was then dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (2:8 EtOAc–toluene) to yield **PGL-65** (49 mg, 45%) as a colorless oil. R_f 0.53 (1:1 EtOAc–toluene); $[\alpha]_D$ –68.6 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38 (m, 4 H), 7.35–7.22 (m, 11H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.97 (d, 2 H, *J* = 8.6 Hz), 5.46 (d, 1 H, *J* = 1.5 Hz, H-1), 5.23 (d, 1 H, *J* = 2.7 Hz), 5.16-5.18 (m, 2 H, H-1, H-1), 5.16 (d, 1 H, *J* = 1.4 Hz, H-1), 5.14 (d, 1 H, *J* = 11.3 Hz), 4.72 (m, 3 H), 4.54 (app t, 2 H, *J* = 11.9 Hz), 4.28 (q, 1 H, *J* = 6.5 Hz), 4.24 (dd, 1 H, *J* = 10.3, 3.5 Hz), 4.08 (dd, 1 H, *J* = 9.6, 3.2 Hz), 4.00 (dd, 1 H, *J* = 9.5, 3.1 Hz), 3.93 (app dq, 1 H, *J* = 12.6, 6.3 Hz), 3.82 (dd, 1 H, *J* = 4.6, 2.6 Hz), 3.77 (m, 1H), 3.73–3.66 (m, 4 H), 3.59 (m, 2 H), 3.53 (s, 3 H), 3.52–3.47 (m, 7 H), 3.47–3.43 (m, 2 H), 3.41 (s, 6 H), 3.25 (app t, 2 H, *J* = 7.0 Hz), 3.23–3.18 (m, 4 H), 2.59–2.51 (m, 2 H), 2.04 (s, 3 H), 1.64–1.55 (m, 4 H), 1.41–1.28 (m, 11H), 1.26 (d, 3 H, *J* = 6.2 Hz), 1.06 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 154.8, 139.4, 139.0, 138.9, 136.9, 129.51, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 127.46, 116.4, 99.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 175 Hz, C-1), 99.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 98.5 ($^1J_{C,H}$ = 171 Hz, C-1), 95.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 82.3, 81.9, 80.8, 80.5, 80.0, 79.5, 79.0, 78.8, 78.7, 76.7, 75.3, 73.7, 73.5, 73.4, 72.4, 72.2, 69.5, 68.9, 68.8, 65.6, 61.4, 60.8, 59.1, 58.9, 58.6, 57.9, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.0, 26.9, 20.9, 18.4, 18.1, 16.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{67}H_{93}N_3O_{19}Na$: 1266.6295. Found: 1266.6296.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,4-di-*O*-methyl-α-D-mannopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-

rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (41 Squaramide). Treatment of **PGL-65** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **41 Squaramide** (73%, chromatography 4:96 CH_3OH–CH_2Cl_2) as a light yellow foam. R_f 0.62 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –79.2 (*c* = 1.4, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 7.08 (d, 2 H, *J* = 8.3 Hz), 6.97 (d, 2 H, *J* = 8.3 Hz), 6.06 (s, 1H), 5.47 (s, 1 H, H-1), 5.23 (d, 1 H, *J* = 2.4 Hz), 5.18 (s, 1 H, H-1), 5.16 (s, 1 H, H-1), 5.11 (d, 1 H, *J* = 3.3 Hz, H-1), 4.77–4.76 (s, 2 H), 4.29 (dd, 1 H, *J* = 12.7, 6.2 Hz), 4.18 (dd, 1 H, *J* = 10.1, 3.2 Hz), 4.11 (dd, 1 H, *J* = 9.5, 2.8 Hz), 3.87 (m, 2 H), 3.79–3.72 (m, 3 H), 3.70 (m, 2 H), 3.67–3.60 (m, 4 H), 3.58–3.47 (m, 19 H), 3.42 (s, 2 H), 3.31 (app t, 1 H, *J* = 9.5 Hz), 3.22 (app t, 1 H, *J* = 9.5 Hz), 2.54 (app t, 2 H, *J* = 7.5 Hz), 2.42 (d, 1 H, *J* = 8.9 Hz), 2.15 (s, 3 H), 1.64–1.54 (m, 4 H), 1.45 (app t, 3 H, *J* = 6.8 Hz), 1.36 (d, 3 H, *J* = 6.1 Hz), 1.31 (s, 8 H), 1.26 (d, 3 H, *J* = 6.1 Hz), 1.09 (d, 3 H, *J* = 6.5 Hz); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 177.5, 170.8, 154.7, 136.9, 129.5, 116.4, 100.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 99.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 98.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 95.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 83.5, 82.5, 80.8, 80.7, 80.6, 79.8, 79.2, 78.0, 74.6, 73.3, 72.2, 71.8, 71.1, 69.8, 69.1, 69.0, 66.0, 62.5, 61.2, 60.7, 59.9, 59.2, 58.9, 58.8, 45.1, 35.3, 31.8, 29.5, 29.4, 29.3, 26.5, 21.0, 18.1, 18.1, 16.5, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{52}H_{81}NO_{22}Na$: 1094.5142. Found: 1094.5131.

35. Synthesis of 42



Scheme S44. Synthesis of **42 Squaramide**. a) BnBr, NaH, DMF, 95%; b) $NaOCH_3$, CH_2Cl_2, CH_3OH; then CH_3I, NaH, DMF, 82%; d) **PGL-67**, NIS, AgOTf, CH_2Cl_2, 53%; e) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 69%.

Phenyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (PGL-66). To a stirred solution of **PGL-63** (404 mg, 726 μmol) and BnBr (0.26 mL, 2.2 mmol) in dry DMF (8 mL) at 0 °C (ice bath) was added NaH (60% dispersion in mineral oil, 40 mg, 1.0 mmol). The reaction mixture was stirred at 0 °C for 2 h, neutralized by the addition of AcOH and concentrated. The resulting residue was purified by chromatography (7:93 EtOAc–hexane) to yield **PGL-66** (445 mg, 95%) as a colorless oil. R_f 0.64 (2:8 EtOAc–hexane); $[\alpha]_D$ +72.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.08–8.05 (m, 2 H), 7.58–7.53 (m, 1H), 7.53–7.48 (m, 2 H), 7.39–7.20 (m, 26 H), 5.87 (dd, 1 H, *J* = 3.0, 1.9 Hz), 5.65 (d, 1 H, *J* = 1.7 Hz, H-1), 4.91 (d, 1 H, *J* = 10.8 Hz), 4.82 (d, 1 H, *J* = 11.3 Hz), 4.71 (d, 1 H, *J* = 11.8 Hz), 4.62 (d, 1 H, *J* = 11.3 Hz), 4.58 (d, 1 H, *J* = 10.8 Hz), 4.51 (d, 1 H, *J* = 11.8 Hz), 4.40 (ddd, 1 H, *J* = 9.8, 4.1, 1.6 Hz), 4.17 (app t, 1 H, *J* = 9.6 Hz), 4.06 (dd, 1 H, *J* = 9.3, 3.0 Hz), 3.95 (dd, 1 H, *J* = 10.9, 4.1 Hz), 3.80 (dd, 1 H, *J* = 10.9, 1.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 165.8, 138.6, 138.51, 137.9, 133.9, 133.4, 132.1, 130.2, 130.0, 129.3, 128.63, 128.61, 128.6, 128.5, 128.4, 128.2,

128.0, 127.91, 127.9, 127.74, 127.70, 86.6 (C-1), 78.8, 75.6, 74.7, 73.6, 72.9, 71.9, 70.9, 69.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{40}H_{38}O_6SNa$: 669.2281. Found: 669.2278.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-methyl-1-thio-α-D-mannopyranoside (PGL-67). To a solution of **PGL-66** (175 mg, 271 μmol) in 1:1 CH_2Cl_2–CH_3OH (4 mL) at rt was added sodium methoxide (9 mg, 166 μmol). The reaction mixture was stirred at rt for 2 d, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated to yield a colorless oil. To asolution of oil (134 mg, 247 μmol) and CH_3I (20 μL, 321 μmol) in dry DMF (4 mL) at 0 °C (ice bath) was added NaH (60% dispersion in mineral oil, 13 mg, 321 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of AcOH and concentrated. The resulting residue was purified by chromatography (7:93 EtOAc–hexane) to yield **PGL-67** (112 mg, 82%, two steps) as a colorless oil. R_f 0.46 (2:8 EtOAc–hexane); $[\alpha]_D$ +167.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.51–7.47 (m, 2 H), 7.43–7.39 (m, 2 H), 7.38–7.20 (m, 16 H), 5.64 (d, 1 H, *J* = 1.4 Hz, H-1), 4.91 (d, 1 H, *J* = 10.8 Hz), 4.78–4.70 (m, 2 H), 4.63 (d, 1 H, *J* = 12.0 Hz), 4.52 (d, 1 H, *J* = 10.8 Hz), 4.47 (d, 1 H, *J* = 12.0 Hz), 4.28 (ddd, 1 H, *J* = 9.7, 5.1, 1.5 Hz), 3.97 (app t, 1 H, *J* = 9.6 Hz), 3.86 (dd, 1 H, *J* = 9.3, 3.1 Hz), 3.81 (dd, 1 H, *J* = 10.9, 5.1 Hz), 3.76–3.69 (m, 2 H), 3.46 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 138.6, 138.5, 138.3, 134.7, 131.6, 129.2, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 85.1 (C-1), 80.3, 79.7, 75.5, 75.2, 73.5, 72.8, 72.6, 69.3, 58.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{34}H_{36}O_5SNa$: 579.2176. Found: 579.2166.

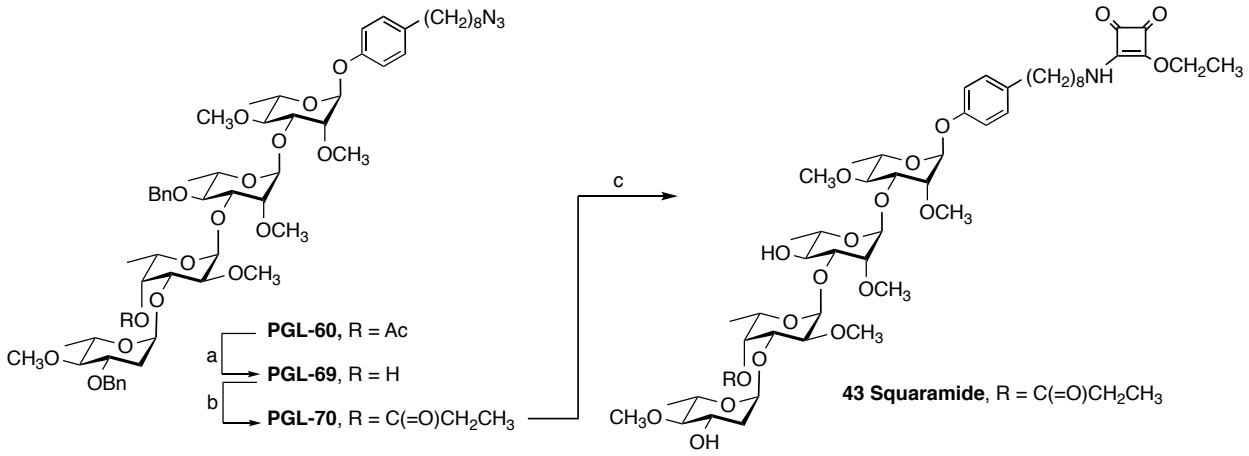
4-(8-Azidooctyl)phenyl 3,4,6-tri-*O*-benzyl-2-*O*-methyl-α-D-mannopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-68). A solution of **PGL-67** (43 mg, 77 μmol), **PGL-59** (56 mg, 64 μmol), and crushed 4Å molecular sieves (60 mg) in CH_2Cl_2 (5 mL) was stirred at 0 °C for 30 min. To this solution at –20 ºC was added *N*-iodosuccinimide (17 mg, 77 μmol) and silver triflate (3.3 mg, 13 μmol). The reaction mixture was stirred at –20 °C for another 30 min, Et_3N (100 μL) and a satd aq soln of $Na_2S_2O_3$ (0.5 mL) were added, and then solution was dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (2:8 EtOAc–toluene) to yield **PGL-68** (45 mg, 53%) as a colorless oil. R_f 0.50 (3:7 EtOAc–toluene); $[\alpha]_D$ –53.9 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38 (m, 6 H), 7.35–7.24 (m, 14 H), 7.12 (d, 2 H, *J* = 8.6 Hz), 7.00 (d, 2 H, *J* = 8.6 Hz), 5.49 (d, 1 H, *J* = 1.4 Hz, H-1), 5.29 (d, 1 H, *J* = 3.0 Hz), 5.20–5.22 (m, 3 H, H-1, H-1, H-1),

5.17 (d, 1 H, J = 11.2 Hz), 4.89 (d, 1 H, J = 11.3 Hz), 4.79–4.68 (m, 3 H), 4.62–4.49 (m, 3 H), 4.32 (d, 1 H, J = 6.8 Hz), 4.28 (dd, 1 H, J = 10.3, 3.4 Hz), 4.12 (dd, 1 H, J = 9.6, 3.2 Hz), 4.04 (dd, 1 H, J = 9.5, 3.1 Hz), 4.00–3.94 (m, 1H), 3.90 (m, 2 H), 3.80–3.69 (m, 6 H), 3.56 (s, 3 H), 3.55–3.48 (m, 6 H), 3.47 (s, 3 H), 3.46 (s, 3 H), 3.28 (app t, 2 H, J = 6.9 Hz), 3.26–3.20 (m, 4 H), 2.62–2.54 (m, 2 H), 2.08 (s, 3 H), 1.66–1.58 (m, 4 H), 1.42–1.32 (m, 11H), 1.30 (d, 3 H, J = 6.2 Hz), 1.10 (d, 3 H, J = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 154.8, 139.4, 139.1, 138.8, 136.9, 129.5, 128.5, 128.4, 128.4, 128.0, 128.0, 127.9, 127.8, 127.6, 127.54, 127.52, 127.5, 116.4, 99.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 99.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 98.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 95.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 82.3, 81.8, 80.8, 80.5, 80.0, 79.5, 79.4, 78.8, 78.7, 75.3, 75.0, 74.9, 74.0, 73.5, 73.4, 72.5, 72.3, 69.4, 69.0, 68.9, 65.7, 61.4, 59.1, 59.0, 58.7, 57.9, 51.7, 35.3, 31.8, 29.5, 29.4, 29.3, 29.0, 26.9, 20.9, 18.4, 18.1, 16.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{73}H_{97}N_3O_{19}Na$: 1342.6608. Found: 1342.6593.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2-*O*-methyl-α-D-mannopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (42 Squaramide). Treatment of **PGL-68** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **42 Squaramide** (69%, chromatography 5:95 CH_3OH–CH_2Cl_2) as a light yellow foam. R_f 0.42 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –74.0 (c = 1.1, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) δ 7.08 (m, 2 H), 6.99–6.94 (m, 2 H), 6.04 (s, 1H), 5.47 (d, 1 H, J = 1.6 Hz, H-1), 5.25 (dd, 1 H, J = 3.4, 0.8 Hz), 5.20 (d, 1 H, J = 1.0 Hz, H-1), 5.19 (d, 1 H, J = 1.0 Hz, H-1), 5.12 (d, 1 H, J = 3.7 Hz, H-1), 4.81–4.71 (m, 2 H), 4.30 (q, 1 H, J = 6.5 Hz), 4.21 (dd, 1 H, J = 10.1, 3.5 Hz), 4.12 (dd, 1 H, J = 9.6, 3.3 Hz), 3.92–3.84 (m, 2 H), 3.81 (m, 1H), 3.77 (dd, 1 H, J = 9.6, 3.3 Hz), 3.74–3.60 (m, 8 H), 3.58 (dd, 1 H, J = 10.1, 3.6 Hz), 3.54 (s, 3 H), 3.53 (s, 3 H), 3.52 (s, 3 H), 3.48 (dd, 1 H, J = 3.3, 1.5 Hz), 3.47 (s, 3 H), 3.46 (s, 3 H), 3.44–3.40 (m, 1H), 3.23 (app t, 1 H, J = 9.6 Hz), 2.78 (br s, 1H), 2.57 (br s, 1H), 2.55–2.51 (m, 2 H), 2.36 (s, 1H), 2.17 (s, 3 H), 1.75 (br s, 1H), 1.59 (m, 4 H), 1.45 (app t, 3 H, J = 7.1 Hz), 1.36 (d, 3 H, J = 6.2 Hz), 1.31 (s, 8 H), 1.27 (d, 3 H, J = 6.2 Hz), 1.11 (app t, 3 H, J = 6.2 Hz); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 189.4, 183.2, 177.5, 172.7, 171.0, 154.7, 136.9, 129.5, 116.4, 100.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 99.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 98.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 95.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 83.5, 82.5, 80.7, 80.6, 80.3, 79.8, 79.2, 74.3, 73.4, 72.7, 71.8, 71.5, 69.9, 69.3, 69.1, 69.0, 66.0, 62.9, 61.3, 59.8, 59.2, 58.9, 58.8, 45.1, 35.3, 31.8, 29.5, 29.4, 29.3, 26.5, 21.1, 18.1,

18.0, 16.4, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{51}H_{79}NO_{22}Na$: 1080.4986. Found: 1080.4973.

36. Synthesis of 43



Scheme S45. Synthesis of **43 Squaramide**. a) $NaOCH_3$, CH_2Cl_2, CH_3OH, 93%; b) Propionic anhydride, pyridine, 93%; c) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 65%.

***p*-(8-Azidooctylphenyl) 2,6-dideoxy-3-*O*-benzyl-4-*O*-Me-α-L-*arabino*-hexopyranosyl-(1→3)-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-69)**. To a solution of **PGL-60** (71 mg, 64 μmol) in 1:1 CH_2Cl_2–CH_3OH (6 mL) was added sodium methoxide (20 mg, 370 μmol). The reaction mixture was stirred overnight at rt, neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was purified by chromatography (1:1 EtOAc–hexane) to yield **PGL-69** (63 mg, 93%) as a colorless oil. R_f 0.38 (1:1 EtOAc–hexane); $[\alpha]_D$ –126.7 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.38–7.30 (m, 8 H), 7.29–7.24 (m, 2 H), 7.11–7.05 (m, 2 H), 6.98–6.94 (m, 2 H), 5.45 (d, 1 H, *J* = 1.8 Hz, H-1), 5.21–5.14 (m, 3 H, H-1, H-1), 5.06 (d, 1 H, *J* = 2.9 Hz, H-1), 4.68 (q, 2 H, *J* = 11.6 Hz), 4.55 (d,1 H, *J* = 11.1 Hz), 4.23 (dd, 1 H, *J* = 11.8, 5.1 Hz), 4.21 (dd, 1 H, *J* = 10.3, 3.2 Hz), 4.08 (dd, 1 H, *J* = 9.6, 3.2 Hz), 4.02 (dd, 1 H, *J* = 9.5, 3.2 Hz), 3.97 (app dq, 1 H, *J* = 9.5, 6.4 Hz), 3.93 (app dq, 1 H, *J* = 9.4, 6.2 Hz), 3.89–3.87 (m, 1H), 3.86–3.82 (ddd, 1 H, *J* = 11.3, 9.1, 5.3 Hz), 3.78 (dd, 1 H, *J* = 3.1, 1.9 Hz), 3.72–3.65 (m, 2 H), 3.57 (s, 3 H), 3.55 (s, 3 H), 3.51–3.48 (m, 7 H), 3.47 (dd, 1 H, *J* = 6.6, 3.7 Hz), 3.30 (s, 3 H), 3.27–3.20 (m, 3 H), 2.86–2.81 (m, 1H), 2.57–2.52 (m, 2 H), 2.24–2.17 (m, 2 H), 1.72 (ddd, 1 H, *J* = 13.1, 11.5, 3.7 Hz), 1.62–1.55 (m, 4 H), 1.38–1.29 (m, 14 H), 1.26 (d, 3 H, *J* = 6.2 Hz), 1.14 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.7, 139.3, 139.0, 136.9, 129.5, 128.6, 128.4, 128.1, 127.8, 127.8, 127.6, 116.4, 100.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1),

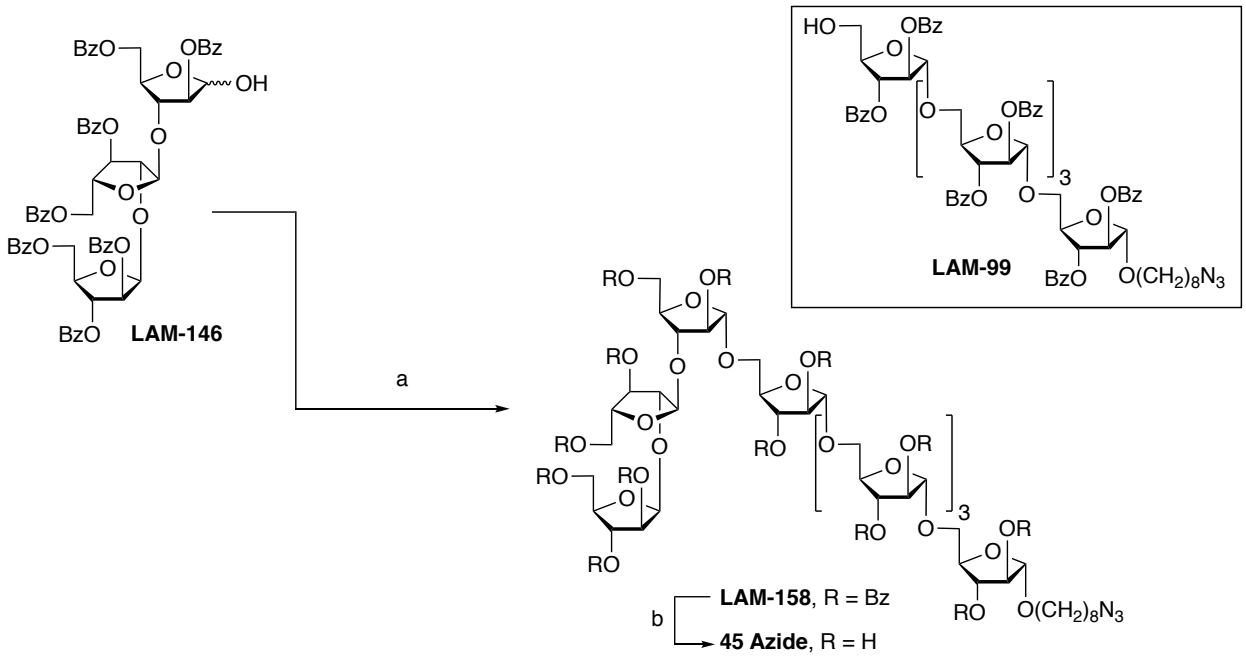
98.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 93.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 86.6, 82.3, 82.0, 80.9, 80.5, 80.0, 79.5, 76.9, 76.5, 75.3, 72.6, 72.3, 69.0, 68.9, 68.6, 67.6, 65.8, 61.4, 61.0, 59.2, 59.1, 57.8, 51.7, 36.1, 35.3, 31.8, 29.5, 29.4, 29.3, 29.1, 26.9, 18.4, 18.2, 18.1, 16.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{57}H_{83}N_3O_{16}Na$: 1088.5666. Found: 1088.5655.

***p*-(8-Azidooctylphenyl) 2,6-dideoxy-3-*O*-benzyl-4-*O*-Me-α-L-*arabino*-hexopyranosyl-(1→3)-4-*O*-propionyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (PGL-70)**. To a solution of **PGL-69** (39 mg, 37 μmol) in pyridine (4 mL) at rt was added dropwise propionic anhydride (1 mL, 7.8 mmol). The reaction mixture was stirred at rt for 5 d and concentrated and then the residue was co-evaporated with toluene. The resulting residue was purified by chromatography (3:7 EtOAc–toluene) to yield **PGL-70** (38 mg, 93%) as a light yellow oil. R_f 0.42 (3:7 EtOAc–toluene); $[\alpha]_D$ –121.1 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38–7.30 (m, 8 H), 7.28–7.24 (m, 2 H), 7.08 (d, 2 H, *J* = 8.6 Hz), 6.96 (d, 2 H, *J* = 8.6 Hz), 5.45 (d, 1 H, *J* = 1.3 Hz, H-1), 5.28 (d, 1 H, *J* = 2.7 Hz), 5.19–5.17 (m, 3 H), 5.04 (d, 1 H, *J* = 3.0 Hz), 4.62 (s, 2 H), 4.54 (d, 1 H, *J* = 11.0 Hz), 4.35 (q, 1 H, *J* = 7.0 Hz), 4.27 (dd, 1 H, *J* = 10.4, 3.3 Hz), 4.08 (dd, 1 H, *J* = 9.7, 3.2 Hz), 4.01 (dd, 1 H, *J* = 9.5, 3.0 Hz), 3.96–3.88 (m, 2 H), 3.79–3.72 (m, 2 H), 3.68 (m, 2 H), 3.55 (s, 3 H), 3.54 (s, 3 H), 3.51–3.48 (m, 4 H), 3.47 (s, 3 H), 3.42 (dd, 1 H, *J* = 10.4, 3.6 Hz), 3.32 (s, 3 H), 3.28–3.18 (m, 3 H), 2.80 (app t, 1 H, *J* = 9.2 Hz), 2.59–2.51 (m, 2 H), 2.44 (q, 2 H, *J* = 7.4 Hz), 2.00 (dd, 1 H, *J* = 12.9, 5.1 Hz), 1.67–1.54 (m, 5 H), 1.39–1.29 (m, 11H), 1.26 (d, 3 H, *J* = 6.2 Hz), 1.19 (app t, 3 H, *J* = 7.6 Hz), 1.14 (d, 3 H, *J* = 6.6 Hz), 1.11 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 174.5, 154.8, 139.3, 139.1, 136.9, 129.5, 128.5, 128.4, 128.2, 127.8, 127.7, 127.6, 116.4, 100.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 98.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 93.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 170 Hz, C-1), 86.7, 82.4, 82.2, 80.9, 80.5, 79.8, 79.5, 77.0, 76.8, 75.4, 71.9, 70.6, 69.9, 69.0, 68.8, 67.4, 65.1, 61.4, 60.9, 59.4, 59.2, 57.7, 51.7, 35.6, 35.3, 31.8, 29.5, 29.3, 29.29, 29.0, 27.8, 26.9, 18.4, 18.3, 18.1, 16.7, 9.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{60}H_{87}N_3O_{17}Na$: 1144.5928. Found: 1144.5920.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,6-dideoxy-4-*O*-Me-α-L-*arabino*-hexopyranosyl-(1→3)-4-*O*-propionyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (43 Squaramide). Treatment of **PGL-70** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **43 Squaramide** (65%, chromatography 3:97

CH_3OH–CH_2Cl_2) as a light yellow foam. R_f 0.59 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –111.1 (*c* = 0.7, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 7.10–7.07 (m, 2 H), 6.99–6.95 (m, 2 H), 5.88 (s, 1H), 5.46 (d, 1 H, *J* = 1.7 Hz, H-1), 5.28 (dd, 1 H, *J* = 3.3, 1.1 Hz), 5.16 (d, 1 H, *J* = 1.2 Hz, H-1), 5.08 (d, 1 H, *J* = 3.7 Hz, H-1), 5.05 (d, 1 H, *J* = 3.5 Hz, H-1), 4.82–4.71 (m, 2 H), 4.28 (qd, 1 H, *J* = 6.4, 0.8 Hz), 4.25 (dd, 1 H, *J* = 10.2, 3.3 Hz), 4.12 (dd, 1 H, *J* = 9.6, 3.3 Hz), 3.90–3.87 (m, 1H), 3.86–3.83 (m, 1H), 3.79 (app dq, 1 H, *J* = 9.4, 6.2 Hz), 3.76 (dd, 1 H, *J* = 9.6, 3.3 Hz), 3.71–3.67 (m, 2 H), 3.63–3.59 (m, 2 H), 3.56 (s, 3 H), 3.54 (s, 3 H), 3.52 (s, 3 H), 3.50 (s, 3 H), 3.49–3.46 (m, 4 H), 3.46–3.37 (m, 2 H), 3.23 (app t, 1 H, *J* = 9.6 Hz), 2.71 (app t, 1 H, *J* = 9.2 Hz), 2.58–2.52 (m, 2 H), 2.44 (qd, 2 H, *J* = 7.6, 2.6 Hz), 2.27 (d, 1 H, *J* = 2.8 Hz), 1.95–1.89 (m, 1H), 1.68 (ddd, 1 H, *J* = 13.2, 11.8, 3.8 Hz), 1.58 (dt, 4 H, *J* = 14.5, 7.2 Hz), 1.45 (app t, 3 H, *J* = 7.1 Hz), 1.35 (d, 3 H, *J* = 6.2 Hz), 1.31 (s, 8 H), 1.29 (d, 3 H, *J* = 6.3 Hz), 1.27 (d, 3 H, *J* = 6.2 Hz), 1.19 (app t, 3 H, *J* = 7.6 Hz), 1.13 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR (175 MHz,$CDCl_3$, δ_C) 189.3, 183.3, 177.5, 174.4, 172.7, 154.7, 136.8, 129.5, 116.4, 101.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 99.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 93.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 88.2, 83.7, 82.5, 80.8, 80.6, 78.9, 78.3, 71.9, 69.8, 69.5, 69.2, 69.0, 68.9, 67.4, 65.7, 61.2, 61.0, 60.6, 59.2, 59.1, 45.1, 37.2, 35.3, 31.8, 29.6, 29.4, 29.3, 27.7, 26.5, 18.3, 18.1, 18.06, 16.6, 16.1, 9.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{52}H_{81}NO_{20}Na$: 1062.5244. Found: 1062.5229.

37. Synthesis of 45



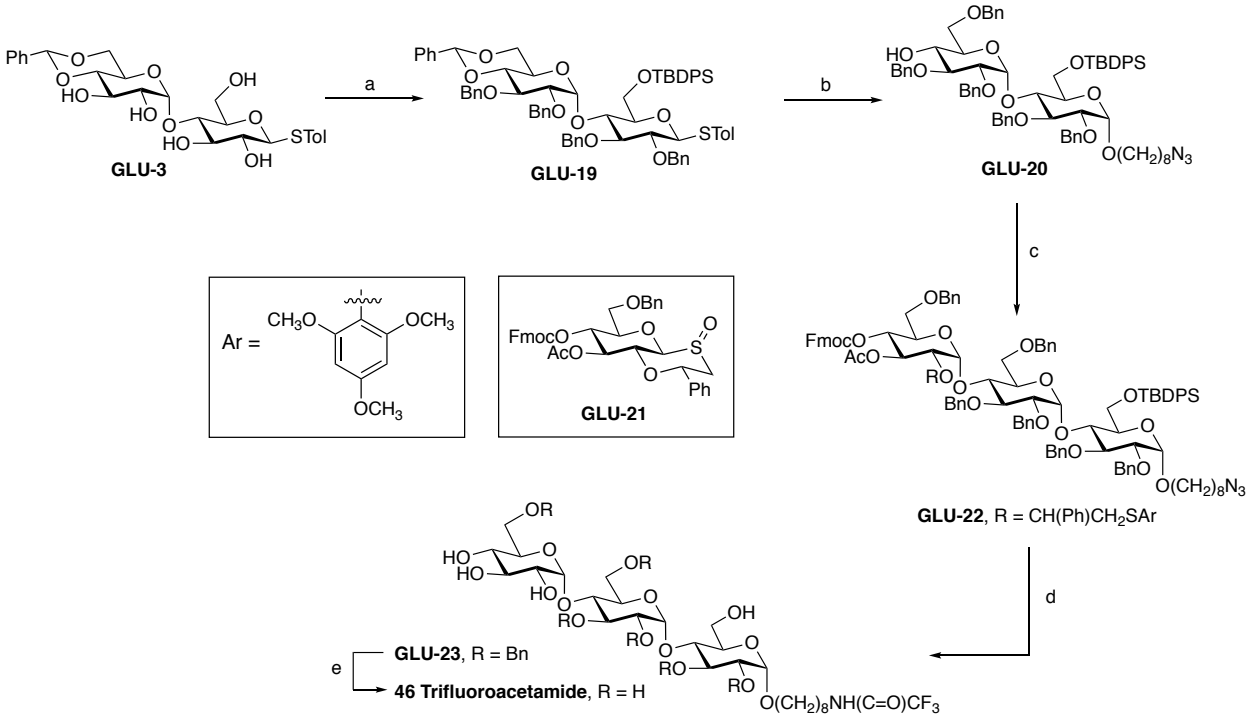
Scheme S46. Synthesis of **45 Azide**. a) CCl_3CN, DBU, CH_2Cl_2; then **LAM-99**, TMSOTf, CH_2Cl_2, quant; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, quant.

8-Azidooctyl 2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→3)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (LAM-158). The trichloroacetimidate derivative of hemiacetal **LAM-146** (0.21 g, 0.19 mmol) was prepared using DBU (10 μL) and trichloroacetonitrile (0.1 mL, 1 mmol) as described for the synthesis of **LAM-42** (Scheme S7). This was immediately subjected to coupling with alcohol **LAM-99**[1] (0.25 g, 0.13 mmol) as described for the synthesis of **LAM-43**, to afford **LAM-158** (0.4 g, quantitative) as a foam. R_f 0.34 (3:2 hexanes–EtOAc); $[\alpha]_D$ +6.8 (c = 0.34, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H), 8.10–7.80 (m, 34 H), 7.60–7.14 (m, 51 H), 5.91 (dd, 1 H, J = 5.4, 6.7 Hz), 5.70 (d, 1 H, J = 4.9 Hz), 5.70–5.60 (m, 7 H), 5.58–5.54 (m, 3 H), 5.49 (d, 1 H, J = 1.5 Hz), 5.43–5.36 (m, 6 H), 5.34–5.31 (m, 3 H), 5.22 (s, 1 H), 4.76–4.56 (m, 8 H), 4.54–4.40 (m, 6 H), 4.30 (dd, 1 H, J = 1.2, 6.0 Hz), 4.24–4.12 (m, 6 H), 4.08 (dd, 1 H, J = 4.6, 11.6 Hz), 4.00 (dd, 1 H, J = 3.4, 11.5 Hz), 3.96–3.87

(m, 4 H), 3.76 (ddd, 1 H, *J* = 6.7, 9.6, 13.5 Hz), 3.50 (ddd, 1 H, *J* = 6.2, 9.6, 12.5 Hz), 3.22 (dd, 3 H, *J* = 7.0, 7.0 Hz), 1.68–1.51 (m, 4 H), 1.42–1.25 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.3, 166.2, 166.1, 166.0, 165.9, 165.8(8), 165.8(3), 165.7, 165.5, 133.9, 133.8, 133.7, 133.5, 133.3, 133.2, 130.4, 130.2, 130.1, 130.0, 129.9, 129.8(7), 129.8(2), 129.6, 129.4, 128.9, 128.8, 128.7, 106.2 (6 × C-1), 105.9 (C-1), 100.9 (C-1), 85.6, 83.8, 82.4, 82.3, 82.1, 82.0, 81.3, 80.9, 79.6, 78.4, 77.7, 77.6, 76.9, 67.7, 66.4, 66.3, 66.2, 66.1, 64.7, 63.2, 54.3, 54.1, 53.8, 53.6, 53.4, 51.9, 29.9, 29.7, 29.5, 29.2, 27.0, 26.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{167}H_{149}N_3O_{50}Na$: 3018.9101. Found: 3018.9065.

8-Azidooctyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)- α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (45 Azide). Prepared from **LAM-158** (0.1 g, 0.033 mmol) and sodium methoxide solution (1 M solution) as described for the synthesis of **18 Azide**, to afford **45 Azide** (0.041 g, quantitative) as a fluffy solid. R_f 0.34 (6.5:3.5:0.5 CH_2Cl_2–CH_3OH–water); $[\alpha]_D$ +102.7 (*c* = 0.2, CH_3OH); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.24 (d, 1 H, *J* = 1.6 Hz, H-1), 5.14 (d, 1 H, *J* = 4.6 Hz, H-1), 5.10 (s, 1 H, H-1), 5.10–5.06 (m, 4 H, 4 × H-1), 5.01 (d, 1 H, *J* = 1.8 Hz, H-1), 4.28 (d, 1 H, *J* = 1.0 Hz), 4.24–4.08 (m, 13 H), 4.09–3.94 (m, 9 H), 3.95–3.64 (m, 18 H), 3.61–3.51 (m, 1 H), 3.32 (dd, 3 H, *J* = 6.8, 6.8 Hz), 1.71–1.52 (m, 4 H), 1.44–1.26 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 108.4 (4 × C-1), 108.3 (C-1), 108.1 (C-1), 106.2 (C-1), 101.6 (C-1), 87.9, 84.2, 83.7, 83.2, 83.1, 83.0, 82.9, 82.6, 81.7, 81.6, 79.9, 77.6(7), 77.6(1), 77.5, 77.4, 77.2, 77.1, 75.6, 74.9, 69.4, 67.8, 67.1, 63.8, 61.9, 61.5, 52.1, 29.4, 29.1, 29.0, 28.8, 26.7, 25.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{48}H_{81}N_3O_{33}Na$: 1250.4644. Found: 1250.4640.

38. Synthesis of 46



Scheme S47. Synthesis of **46 Trifluoroacetamide**. a) TBDPSCl, imidazole, pyridine; then BnBr, NaH, THF, DMF, 82%; b) 8-Azido-1-octanol, NIS, TMSOTf, CH_2Cl_2; then CF_3CO_2H, Et_3SiH, CH_2Cl_2, 45%; c) **GLU-21**, 1,3,5-trimethoxybenzene, Tf_2O, 2,6-di-*t*-butyl-4-methyl-pyridine, CH_2Cl_2, 21%; d) CF_3CO_2H, CH_2Cl_2; then $NaOCH_3$, CH_3OH, CH_2Cl_2; then *n*-Bu_4NF, THF; then H_2, $Pd(OH)_2$–C, pyridine; then trifluoroacetic anhydride, pyridine, 45%; e) H_2, $Pd(OH)_2$–C, EtOAc, THF, CH_3OH, quant.

***p*-Tolyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (GLU-19)**. To a solution of **GLU-3** (2.0 g, 3.7 mmol) in pyridine (22 mL) at 0 °C was added imidazole (27 mg, 0.4 mmol) followed by TBDPSCl (1.3 mL, 5.0 mmol). The solution was then stirred overnight while warming to rt before CH_3OH (0.1 mL) was added. The solution was stirred for 30 min and concentrated to a syrup that was purified by chromatography (97:3 CH_2Cl_2–CH_3OH) to yield the corresponding silyl ether (2.82 g, 97%) as a thick syrup; HRMS (ESI) *m/z* calcd for (M+Na) $C_{42}H_{50}O_{10}SSiNa$: 797.2786. Found: 797.2788. This compound (2.8 g, 3.6 mmol) was dissolved in THF–DMF (32 mL, 3:1) at 0 °C, NaH (60% dispersion in mineral oil, 0.72 g, 18.0 mmol) was added in portions and the solution was stirred for 2–3 min before BnBr (2.4 mL, 20.2 mmol) was added dropwise. The solution was stirred for 16 h while warming to rt. The solution was then

cooled to 0 °C, and then CH_3OH (3 mL) was added carefully. The mixture stirred for 10 min before being poured into chilled water (350 mL) and extracted with CH_2Cl_2 (100 mL × 2). The combined organic layer was washed with water (100 mL × 2) and brine (100 mL). The organic layer was then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (9:1 hexanes–EtOAc) to yield **GLU-19** (3.36 g, 82%) as a thick syrup. R_f 0.26 (9:1 hexane–EtOAc); $[\alpha]_D$ +7.2 (c = 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 7.80−7.71 (m, 4 H), 7.49−7.43 (m, 4 H), 7.41−7.19 (m, 29 H), 7.03−7.00 (m, 2 H), 5.58 (d, 1 H, J = 3.9 Hz, H-1α), 5.52 (s, 1 H), 4.94−4.82 (m, 4 H), 4.74−4.62 (m, 4 H), 4.54 (d, 1 H, J = 12.0 Hz), 4.12−3.99 (m, 4 H), 3.93 (dd, 1 H, J = 9.4, 9.4 Hz), 3.82−3.75 (m, 2 H), 3.60−3.48 (m, 5 H), 2.32 (s, 3 H), 1.09 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.8, 138.7, 138.1, 138.0, 137.5, 137.2, 135.9, 135.7, 133.7, 131.8, 130.8, 129.7, 129.6, 128.8, 128.4, 128.2(9), 128.2(8), 128.2, 128.1, 128.0, 127.8(0), 127.8, 127.7(0), 127.7, 127.5(8), 127.5(6), 127.2, 126.8, 126.1, 101.1, 98.3 (C-1), 88.2 (C-1), 86.4, 82.3, 81.1, 79.6, 78.9, 78.5, 75.3, 75.2, 75.0, 74.5, 73.6, 68.8, 63.8, 63.5, 27.1, 21.1, 19.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{70}H_{74}O_{10}SSiNa$: 1157.4664. Found: 1157.4673.

8-Azidooctyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (GLU-20). 8-Azido-1-octanol (1.0 g, 5.8 mmol) and thioglycoside **GLU-19** (4.4 g, 3.9 mmol) were dried under vacuum in the presence of P_2O_5 for 6 h. After drying, $CHCl_3$–Et_2O (1:1, 100 mL) was added followed by powdered 4 Å molecular sieves (1.15 g) and the mixture was stirred for 30 min. The reaction mixture was then cooled to 0 °C and *N*-iodosuccinimide (1.6 g, 7.1 mmol) and TMSOTf (0.07 mL, 0.39 mmol) were added. The solution was stirred for 1 h and then Et_3N was added until the pH of the solution was slightly basic (as determined by wet pH paper) before the mixture was diluted with CH_2Cl_2 (40 mL) and filtered through Celite. The filtrate was washed with a satd aq soln of $Na_2S_2O_3$ (50 mL), water (50 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (9:1 hexanes–EtOAc) to give **GLU-20** (3.98 g, 87%) as an inseparable α:β mixture; R_f 0.34 (85:15 hexanes–EtOAc). This compound (3.98 g, 3.37 mmol) was dried overnight under vacuum, dissolved in CH_2Cl_2 (60 mL), and then triethylsilane (6.45 mL, 40.4 mmol) was added. The solution was cooled to 0 °C and trifluoroacetic acid (2.57 mL, 33.7 mmol) was added dropwise. After stirring at 0 °C, for 2 h, CH_3OH (10 mL) was added followed by Et_3N (6 mL). After warming to rt, the mixture was concentrated to a syrup that was purified by chromatography (87:13 hexanes–EtOAc) to yield **GLU-20** (2.07 g, 45% over two

steps) as a thick syrup. R_f 0.15 (85:15 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.75−7.65 (m, 4 H), 7.42−7.16 (m, 31 H), 5.77 (d, 1 H, *J* = 3.7 Hz, H-1α), 5.10 (d, 1 H, *J* = 11.7 Hz), 4.92 (d, 1 H, *J* = 11.2 Hz), 4.83 (d, 1 H, *J* = 11.7 Hz), 4.77 (d, 1 H, *J* = 3.7 Hz, H-1α), 4.75−4.68 (m, 2 H), 4.62 (d, 1 H, *J* = 11.9 Hz), 4.58 (br. s, 2 H), 4.44 (d, 1 H, *J* = 12.1 Hz), 4.33 (d, 1 H, *J* = 12.1 Hz), 4.17−4.12 (m, 1 H), 4.02−3.88 (m, 4 H), 3.74−3.56 (m, 5 H), 3.49−3.34 (m, 4 H), 3.28 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.22 (d, 1 H, *J* = 1.8 Hz), 1.72−1.60 (m, 4 H), 1.43–1.30 (m, 8 H), 1.07 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 139.1, 138.9, 138.2, 138.0, 137.9, 135.9, 135.7, 134.0, 133.6, 129.6, 129.5, 128.5, 128.4, 128.3(2), 128.3(0), 128.3, 128.1, 127.8(4), 127.8, 127.7(0), 127.7, 127.6(1), 127.6, 127.1, 126.7, 96.8 (C-1), 95.8 (C-1), 81.9, 81.4, 80.7, 78.9, 75.3, 74.1, 73.5, 73.0(2), 73.0, 72.9, 71.1, 70.9, 70.7, 69.3, 67.8, 63.9, 51.5, 29.4, 29.3, 29.2, 28.9, 27.0, 26.7, 26.1, 19.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{71}H_{85}N_3O_{11}SiNa$: 1206.5846. Found: 1206.5847.

8-Azidooctyl 2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-3-*O*-acetyl-4-*O*-fluorenylmethoxycarbonyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (GLU-22). A mixture of sulfoxide donor **GLU-21**[22] (0.35 g, 0.53 mmol), 1,3,5-trimethoxybenzene (0.33 g, 1.96 mmol), 2,6-di-*t*-butyl-4-methyl pyridine (0.33 g, 1.6 mmol), and activated 4 Å molecular sieves (0.16 g) in CH_2Cl_2 (3.5 mL) was stirred for 1 h. After cooling to −10 °C, trifluoromethanesulfonic anhydride (0.1 mL, 0.59 mmol) was added. After 30 min, the reaction mixture was cooled to −40 °C and a solution of **GLU-20** (0.5 g, 0.42 mmol) in CH_2Cl_2 (1.8 mL) was added slowly. The temperature of the reaction mixture was kept at −40 °C for 60 min and then warmed to rt. After stirring for 15 h at rt, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and the filtrate was concentrated to a residue that was purified by chromatography (3:1 hexanes–EtOAc) to yield **GLU-22** (0.17 g, 21%) as a foam. R_f 0.18 (3:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.81−7.65 (m, 7 H), 7.61−7.58 (m, 2 H), 7.55−7.14 (m, 44 H), 7.00−6.94 (m, 2 H), 6.11 (d, 1 H, *J* = 3.3 Hz), 6.07 (s, 2 H), 5.62 (d, 1 H, *J* = 3.9 Hz), 5.55 (dd, 1 H, *J* = 9.7, 9.7 Hz), 5.07 (d, 1 H, *J* = 11.7 Hz), 5.00−4.76 (m, 5 H), 4.72 (d, 1 H, *J* = 11.9 Hz), 4.64 (d, 2 H, *J* = 12.8 Hz), 4.55 (d, 1 H, *J* = 11.9 Hz), 4.44−4.14 (m, 11 H), 4.12−4.02 (m, 2 H), 4.01−3.84 (m, 6 H), 3.82 (s, 3 H), 3.80−3.64 (m, 8 H), 3.58−3.52 (m, 2 H), 3.46 (ddd, 1 H, *J* = 7.1, 9.9, 13.9 Hz), 3.35 (dd, 1 H, *J* = 2.6, 10.8 Hz), 3.30−3.20 (m, 4 H), 2.92−2.82 (m, 2 H), 1.76−1.60 (m, 4 H), 1.46−1.30 (m, 8 H), 1.10 (s, 9 H); ^{13}C NMR (125 MHz,

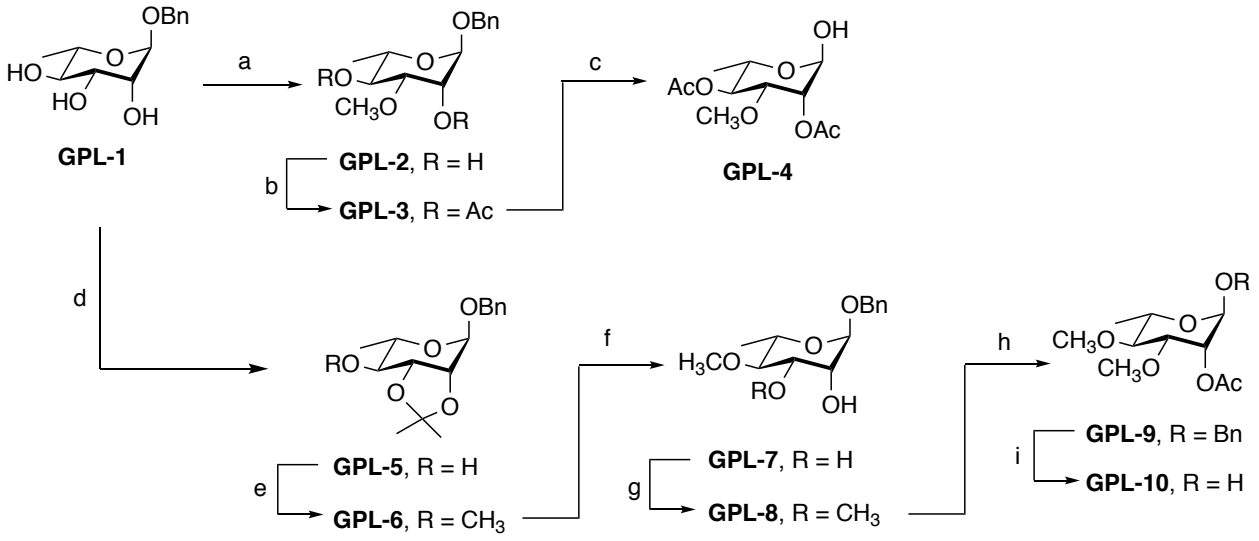
$CDCl_3$, δ_C) 170.0, 161.8, 161.6, 154.4, 143.5, 143.3, 142.0, 141.3, 141.2, 139.2, 139.1, 138.5, 138.3(8), 138.3(5), 138.1, 135.8, 135.7, 134.0, 133.5, 129.9, 129.7, 128.4(1), 128.4, 128.3(3), 128.3, 128.1(8), 128.1(5), 128.1(0), 128.1, 128.0(3), 128.0, 127.9, 127.7(8), 127.7(6), 127.7(5), 127.7, 127.6(3), 127.6, 127.5, 127.4, 127.3(2), 127.3, 127.2(4), 127.2, 127.0, 126.9, 126.3, 125.3, 125.2, 120.0, 101.6, 97.3 (C-1), 96.2 (C-1), 95.9 (C-1), 90.9, 84.0, 81.7, 80.5, 80.0, 78.9, 78.7, 75.1, 74.5, 73.8, 73.3, 73.2(1), 73.2, 73.0, 72.9, 72.4, 72.1, 71.2(1), 71.2, 70.1, 68.7, 68.3, 67.9, 67.7, 64.0, 55.9, 55.3, 51.5, 46.7, 42.9, 29.4, 29.3, 29.2, 28.9, 27.0, 26.9, 26.7, 26.1, 20.3, 19.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{118}H_{131}N_3O_{22}SSiNa$: 2024.8606. Found: 2024.8602.

8-Trifluoroacetamidooctyl 6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (GLU-23). To a solution of **GLU-22** (0.39 g, 0.2 mmol) in CH_2Cl_2 (15 mL) under argon at 0 °C was added trifluoroacetic acid (0.75 mL). The mixture was stirred at that temperature for 25 min before being poured into a satd aq $NaHCO_3$ soln (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic layer was washed with water (10 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was dried under vacuum for 2 h. This compound was dissolved in CH_2Cl_2–CH_3OH (6:1, 7 mL) and 1M methanolic sodium methoxide was added until the pH of the reaction mixture indicated 8–9 (as determined by wet pH paper). The reaction mixture was stirred for 16 h, neutralized by the addition of Amberlite IR 120 H+ resin, filtered and the filtrate concentrated to give a crude residue that was dried under vacuum for 2 h. This compound was then dissolved in THF (15 mL) and *n*-Bu_4NF (2.5 mL, 1M in THF) was added and the solution stirred at rt for 24 h. The reaction mixture was then concentrated to a syrup that was purified by chromatography (6:94 CH_3OH–CH_2Cl_2); R_f 0.38 (6:94 CH_3OH–CH_2Cl_2). To a solution of this compound (0.15 g, 0.088 mmol) in pyridine (5 mL) was added 20% $Pd(OH)_2$–C (25 mg) and the solution was stirred under H_2 (1 atm) for 16 h. The solution was filtered off and the filter cake washed with pyridine (5 mL). The combined filtrate was then cooled to 0 °C before trifluoroacetic anhydride (0.5 mL, 3.6 mmol) was added dropwise. After stirring at rt overnight, the solution was diluted with CH_2Cl_2 (30 mL) and poured into a 1:1 solution of water and satd aq $NaHCO_3$ soln (40 mL). The organic layer was washed with water (30 mL) containing about 5–6 drops of aq ammonia for 10 min and then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (1:3 hexanes–EtOAc) to give **GLU-23** (0.11 g, 45% over five steps) as a foam. R_f 0.28 (1:3 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40−7.10 (m, 30 H), 6.50 (br. s,

1 H), 5.57 (d, 1 H, J = 3.7 Hz), 5.14 (d, 1 H, J = 11.9 Hz), 5.10 (d, 1 H, J = 3.5 Hz), 5.00 (d, 1 H, J = 10.8 Hz), 4.80 (d, 1 H, J = 3.7 Hz), 4.77 (d, 1 H, J = 11.9 Hz), 4.72−4.44 (m, 9 H), 4.17 (dd, 1 H, J = 9.0, 9.0 Hz), 4.06 (dd, 1 H, J = 9.5, 9.5 Hz), 3.98−3.90 (m, 2 H), 3.90−3.42 (m, 15 H), 3.40−3.22 (m, 3 H), 2.94 (br. s, 1 H), 2.73 (br. s, 1 H), 2.60 (br. s, 1 H), 1.91 (br. s, 1 H), 1.75−1.55 (m, 4 H), 1.48−1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.2 (q, J = 36.6 Hz), 139.0, 138.0, 137.9, 137.7, 137.5, 137.4, 128.4(9), 128.4(6), 128.4, 128.3, 128.1, 128.0(0), 128.0, 127.8, 127.7(3), 127.7, 127.1, 126.4, 115.9 (q, J = 287.9 Hz), 100.3 (C-1), 96.6 (C-1), 96.5 (C-1), 81.7, 80.4, 80.2, 79.3, 75.2, 74.4, 74.0, 73.6, 73.5, 72.9(4), 72.9(1), 72.8, 72.3, 71.8, 71.5, 70.7, 70.2, 69.7, 68.7, 68.3, 61.4, 40.0, 29.4, 29.3, 29.0(8), 29.0, 26.7, 26.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{70}H_{84}F_3NO_{17}Na$: 1290.5584. Found: 1290.5560.

8-Trifluoroacetamidooctyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranoside (46 Trifluoroacetamide). To a solution of **GLU-23** (0.11 g, 0.087 mmol) in EtOAc–THF–CH_3OH (15 mL 1:1:1) at rt was added 20% $Pd(OH)_2$–C (60 mg) and the reaction mixture was stirred under H_2 (1 atm) for 24 h. The reaction mixture was filtered and the filtrate was concentrated to give a syrup that was re-dissolved in distilled water (8 mL) and extracted with CH_2Cl_2 (3 mL × 3). The aqueous phase was filtered using a 13 mm Nylon 0.2 μm syringe filter unit and the filtrate was lyophilized to give **46 Trifluoroacetamide** (0.063 g, quantitative) as a fluffy solid. R_f 0.21 (7:3 CH_2Cl_2–CH_3OH; ^{1}H NMR (500 MHz, D_2O, δ_H) 5.38−5.34 (m, 2 H, 2 × H-1α), 4.89 (d, 1 H, J = 3.9 Hz, H-1α), 3.98−3.90 (m, 2 H), 3.88−3.48 (m, 17 H), 3.40 (dd, 1 H, J = 9.7, 9.7 Hz), 3.30 (dd, 2 H, J = 7.0, 7.0 Hz), 1.66−1.52 (m, 4 H), 1.40−1.26 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 160.4 (q, J = 36.8 Hz), 116.0 (q, J = 285.8 Hz), 100.0 (C-1), 99.7 (C-1), 98.0 (C-1), 77.4, 77.1, 73.6, 73.4, 72.9, 72.8, 71.8, 71.6, 71.3, 71.2, 70.3, 69.3, 68.5, 67.9, 60.5(1), 60.5, 39.8, 28.6, 28.3, 28.2, 27.7, 25.8, 25.3, 25.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{28}H_{48}F_3NO_{17}Na$: 750.2767. Found: 750.2753.

39. Synthesis of 47



Scheme S48. Synthesis of monosaccharide building blocks required for the synthesis of **47**. a) *n*-Bu_2SnO, CH_3OH then CH_3I, DMF, 71%; b) Ac_2O, pyridine, 89%; c) H_2, $Pd(OH)_2$–C, CH_3OH, 86%; d) *p*-TsOH, $(CH_3)_2C(OCH_3)_2$, 86%; e) CH_3I, DMF, 81%; f) HOAc–H_2O (4:1), 87%; g) *n*-Bu_2SnO, CH_3OH then CH_3I, DMF, 77%; h) Ac_2O, pyridine, 93%; i) H_2, $Pd(OH)_2$–C, CH_3OH, 89%.

Benzyl 3-*O*-methyl-α-L-rhamnopyranoside (GPL-2). Rhamnopyranoside **GPL-1**[36] (1.96 g, 7.71 mmol) and *n*-Bu_2SnO (2.16 g, 8.48 mmol) were suspended in dry CH_3OH (15 mL) and heated at reflux until a clear solution was obtained and then an additional 2 h. The mixture was cooled, the solvent was evaporated and the residue was dried under vacuum overnight. The colorless foam was dissolved in dry DMF (12 mL), CH_3I (2.41 mL, 38.56 mmol) was added and the solution was stirred at 65 °C for 7 h. The solution was then cooled, filtered and the filtrate was concentrated to give a residue that was purified by chromatography (EtOAc) to give **GPL-2** (1.47 g, 71%) as a yellow oil R_f 0.53 (EtOAc) ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.30 (m, 5 H), 4.92 (d, 1 H, *J* = 1.6 Hz, H-1), 4.72 (d, 1 H, *J* = 11.8 Hz), 4.50 (d, 1 H, *J* = 11.8 Hz), 4.08-4.12 (m, 1 H), 3.75 (dq, 1 H, *J* = 9.4, 6.2 Hz), 3.54 (app dt, 1 H, *J* = 9.4, 2.6 Hz), 3.46–3.44 (m, 4 H), 2.41 (d, 1 H, *J* = 2.7 Hz), 2.40 (d, 1 H, *J* = 2.7 Hz), 1.33 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 137.3, 128.6, 128.2, 128.1, 98.7 (C-1), 81.4, 71.8, 69.3, 68.0, 67.1, 57.2, 17.8.

Benzyl 2,4-di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranoside (GPL-3) Compound **GPL-2** (320 mg, 1.19 mmol) was dissolved in pyridine (2 mL) and Ac_2O (2 mL) and stirred at rt overnight. The mixture was diluted with EtOAc and washed with 5% HCl, satd aq $NaHCO_3$ soln

and water and then dried (Na_2SO_4), filtered and concentrated to give **GPL-3 (**376 mg, 89%) as a colorless solid, R_f 0.42 (3:1 hexane–EtOAc) $[\alpha]_D$ –53.7 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.31 (m, 5 H), 5.36 (dd, 1 H, *J* = 3.4, 1.8 Hz), 4.99 (app t, 1 H, *J* = 9.8 Hz), 4.85 (d, 1 H, *J* = 1.8 Hz, H-1), 4.69 (d, 1 H, *J* = 11.8 Hz), 4.52 (d, 1 H, *J* = 11.8 Hz), 3.82 (dq, 1 H, *J* = 9.8, 6.2 Hz), 3.64 (dd, 1 H, *J* = 9.9, 3.5 Hz), 3.33 (s, 3 H), 2.13 (s, 3 H), 2.08 (s, 3 H), 1.20 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 170.2, 137.0, 128.7, 128.2, 128.2, 97.2 (C-1), 77.1, 72.7, 69.7, 68.2, 66.8, 57.8, 21.2, 21.1, 17.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{18}H_{24}O_7Na$: 375.1414. Found: 375.1410.

2,4-Di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranose (GPL-4). Benzyl glycoside **GPL-3** (745 mg, 2.11 mmol) was dissolved in CH_3OH (20 mL) and 20% $Pd(OH)_2$–C (370 mg) was added. The mixture was degassed and stirred under H_2 (1 atm) at rt overnight. The solution was filtered, the filtrate was concentrated and the resulting residue was purified by chromatography (1:1 hexanes–EtOAc) to give **GPL-4** (474 mg 86%) as a colorless syrup (9:1 α:β ratio). R_f 0.42 (1:1 hexanes–EtOAc). Data for α-isomer ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.33 (dd, 1 H, *J* = 3.3, 1.9 Hz), 5.16 (dd, 1 H, *J* = 3.9, 1.8 Hz), 4.97 (app t, 1 H, *J* = 9.8 Hz), 4.02 (dq, 1 H, *J* = 9.8, 6.3 Hz), 3.67 (dd, 1 H, *J* = 9.8, 3.3 Hz), 3.35 (s, 3 H), 2.14 (s, 3 H), 2.09 (s, 3 H), 1.19 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.7, 170.4, 92.5 (C-1), 76.6, 72.7, 68.6, 66.7, 57.8, 21.2, 21.1, 17.6.

Benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (GPL-5). Monosaccharide **GPL-1** (3.12 g, 12.27 mmol) and *p*-TsOH·H_2O (74 mg, 0.38 mmol) were dissolved in 2,2-dimethoxypropane (11.5 mL). After stirring at rt for 2.5 h, the solution was diluted with CH_2Cl_2 and poured into a 5% aq $NaHCO_3$ soln. The organic phase was washed with water, dried (Na_2SO_4), filtered and concentrated to yield **GPL-5** (3.11 g, 86%) as a colorless solid. R_f 0.57 (EtOAc–hexane 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.38–7.28 (m, 5 H), 5.05 (s, 1 H, H-1), 4.72 (d, 1 H, *J* = 11.8 Hz), 4.53 (d, 1 H, *J* = 11.8 Hz), 4.19 (dd, 1 H, *J* = 5.8, 0.6 Hz), 4.11 (dd, 1 H, *J* = 7.2, 5.8 Hz), 3.74 (dq, 1 H, *J* = 9.3, 6.3 Hz), 3.42 (ddd, 1 H, *J* = 9.2, 7.2, 4.5 Hz), 2.43 (d, 1 H, *J* = 4.5 Hz), 1.52 (s, 3 H), 1.35 (s, 3 H), 1.30 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 137.2, 128.7, 128.3, 128.1, 109.6, 96.4 (C-1), 78.5, 76.0, 74.7, 69.3, 66.2, 28.1, 26.3, 17.6.

Benzyl 2,3-*O*-isopropylidene-4-*O*-methyl-α-L-rhamnopyranoside (GPL-6). NaH (60% in oil, 159 mg, 3.93 mmol) was added at 0 °C to a solution of **GPL-5** (1.05 g, 3.57 mmol)

and CH_3I (446 μL, 7.15 mmol) in DMF (6 mL). The solution was stirred overnight while warming to rt before CH_3OH (2 mL) was added and the mixture was diluted with CH_2Cl_2. The solution was washed with water, dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (3:1 hexanes–EtOAc) to give **GPL-6** (895 mg, 81%) as a colorless syrup. R_f 0.57 (1:1 EtOAc–hexanes). $[\alpha]_D$ –61.3 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.37–7.28 (m, 5 H), 5.04 (s, 1 H, H-1), 4.70 (d, 1 H, *J* = 11.8 Hz), 4.50 (d, 1 H, *J* = 11.8 Hz), 4.18–4.14 (m, 2 H), 3.68 (dq, 1 H, *J* = 9.8, 6.3 Hz), 3.54 (s, 3 H), 2.96–3.04 (m, 1 H), 1.54 (s, 3 H), 1.35 (s, 3 H), 1.28 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 137.3, 128.6, 128.3, 128.1, 109.2, 96.3 (C-1), 83.8, 78.5, 76.2, 69.2, 65.0, 59.6, 28.2, 26.4, 17.8. HRMS (ESI) *m/z* calcd for (M+H) $C_{17}H_{24}O_5Na$: 331.1516. Found: 331.1514.

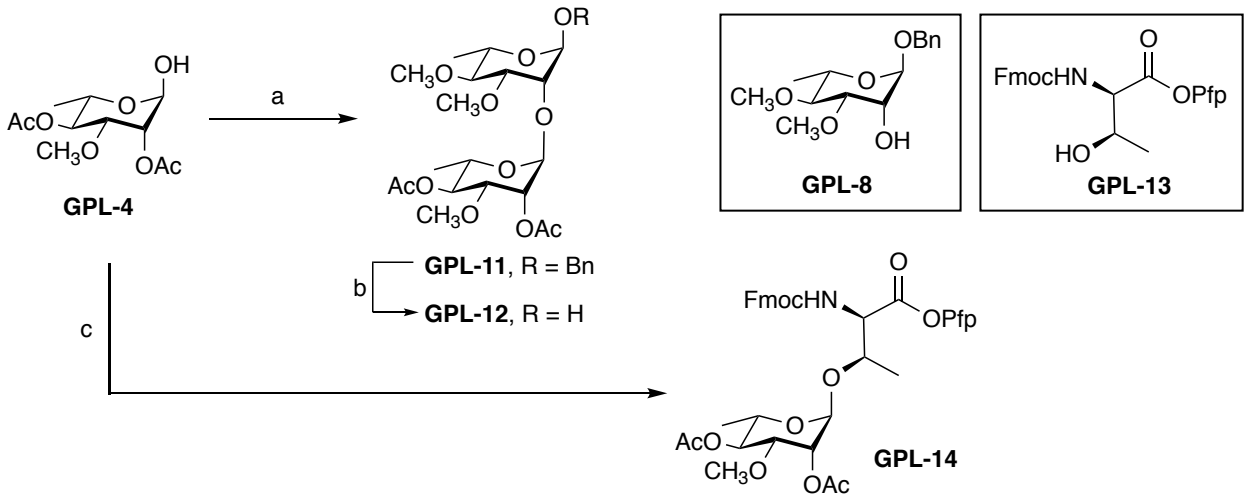
Benzyl 4-*O*-methyl-α-L-rhamnopyranoside (GPL-7). Monosaccharide **GPL-6** (875 mg, 3.26 mmol) was dissolved in HOAc–H_2O (4:1, 8 mL) stirred at 55 °C for 5 h, cooled to rt and then concentrated. The resulting oil was diluted with Et_2O and filtered through a pad of silica to give **GPL-7** (757 mg, 87%) as a colorless syrup. R_f 0.26 (EtOAc). $[\alpha]_D$ –83.1 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.37–7.27 (m, 5 H), 4.84 (d, 1 H, *J* = 1.6 Hz, H-1), 4.70 (d, 1 H, *J* = 11.9 Hz), 4.49 (d, 1 H, *J* = 11.9 Hz), 3.97 (dd, 1 H, *J* = 3.4, 1.6 Hz), 3.90 (dd, 1 H, *J* = 9.3, 3.4 Hz), 3.70 (dqd, 1 H, *J* = 9.5, 6.3, 0.5 Hz), 3.56 (s, 3 H), 3.10 (app t, 1 H, *J* = 9.4 Hz), 2.64–2.56 (m, 2 H), 1.33 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 137.4, 128.6, 128.0, 128.0, 98.7 (C-1), 83.5, 71.5, 71.3, 69.2, 67.6, 61.0, 18.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{14}H_{20}O_5Na$: 291.1203. Found: 291.1198.

Benzyl 3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-8). Monosaccharide **GPL-7** (735 mg, 2.74 mmol) and *n*-Bu_2SnO (766 mg, 3.01 mmol) were suspended in dry CH_3OH (15 mL) and heated at reflux until a clear solution resulted and then an additional 2 h. After cooling, the solvent was evaporated and the residue was dried under vacuum overnight. The colorless foam was dissolved in dry DMF (7 mL) and CH_3I (856 μL, 13.70 mmol) was added. The solution was heated at 65 °C for 7 h, cooled, filtered and then the filtrate was concentrated and the resulting residue purified by chromatography (2:1 EtOAc–hexanes) to give **GPL-8** (593 mg, 77%) as a light-yellow oil. R_f 0.64 (2:1 EtOAc–hexanes). $[\alpha]_D$ –94.0 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.37–7.27 (m, 5 H), 4.89 (d, 1 H, *J* = 1.6 Hz), 4.70 (d, 1 H, *J* = 11.8 Hz), 4.48 (d, 1 H, *J* = 11.8 Hz), 4.03–4.07 (m, 1 H), 3.68 (dq, 1 H, *J* = 9.6, 6.2 Hz), 3.54 (s, 3 H), 3.51–3.47 (m, 4 H), 3.09 (app t, 1 H, *J* = 9.4 Hz), 2.42 (d, 1 H, *J* = 2.2 Hz), 1.31 (d, 3 H, *J* = 6.3

Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 137.4, 128.6, 128.2, 128.0, 98.4 (C-1), 82.0, 81.4, 69.2, 68.1, 67.6, 61.0, 57.6, 17.9. HRMS (ESI) *m/z* calcd for (M+Na) $C_{15}H_{22}O_5Na$: 305.1359. Found: 305.1356.

Benzyl 2-*O*-acetyl-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-9). Monosaccharide **GLP-8** (600 mg, 2.13 mmol) was dissolved in pyridine (3 mL) and Ac_2O (3 mL) and the solution was stirred at rt overnight. The mixture was then diluted with CH_2Cl_2 and washed with a 5% HCl, satd aq $NaHCO_3$ soln and water. After drying (Na_2SO_4), the solution was filtered and the filtrate concentrated to give **GPL-9** (638 mg, 93%) as light-yellow syrup. R_f 0.70 (1:1 EtOAc–hexanes). $[\alpha]_D$ –68.7 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.28 (m, 5 H), 5.30 (dd, 1 H, *J* = 3.4, 1.8 Hz), 4.79 (d, 1 H, *J* = 1.8 Hz, H-1), 4.67 (d, 1 H, *J* = 11.8 Hz), 4.47 (d, 1 H, *J* = 11.8 Hz), 3.67 (dq, 1 H, *J* = 9.5, 6.2 Hz), 3.58 (dd, 1 H, *J* = 9.4, 3.5 Hz), 3.55 (s, 3 H), 3.07 (s, 3 H), 3.07 (app t, 1 H, *J* = 9.5 Hz), 2.12 (s, 3 H), 1.30 (d, 2 H, *J* = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 137.2, 128.6, 128.2, 128.1, 97.1 (C-1), 82.1, 79.7, 69.5, 68.8, 68.0, 61.1, 21.2, 18.0. HRMS (ESI)(M+Na): calcd for $C_{17}H_{24}NaO_6$ 347.1465. Found: 347.1461.

2-*O*-Acetyl-3,4-di-*O*-methyl-α-L-rhamnopyranose (GPL-10). Benzyl glycoside **GPL-9** (600 mg, 1.850 mmol) was dissolved in CH_3OH (20 mL) and 20% $Pd(OH)_2$–C (300 mg) was added. The mixture was degassed and stirred under H_2 (1 atm) overnight and then the reaction mixture was filtered and the filtrate was concentrated to give **GPL-10** (368 mg, 89%) as a colorless syrup (4:1 α:β-ratio). R_f 0.46 (1:1 hexanes–EtOAc). Data for α isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.27 (dd,1 H, *J* = 3.4, 1.9 Hz), 5.11 (d, 1 H, *J* = 1.9 Hz, H-1), 3.87 (dqd, 1 H, *J* = 9.5, 6.2, 0.5 Hz), 3.62 (dd, 1 H, *J* = 9.4, 3.6 Hz), 3.55 (s, 3 H), 3.42 (s, 3 H), 3.07 (app t, 1 H, *J* = 9.5 Hz), 2.13 (s, 3 H) 1.30 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.7, 92.4 (C-1), 82.1, 79.1, 69.2, 67.8, 61.0, 57.7, 21.2, 18.0.



Scheme S49. Synthesis of **GPL-12** and **GPL-14**, intermediates required for the synthesis of **47**. a) Cl_3CCN, DBU, CH_2Cl_2 then **GPL-8**, TMSOTf, CH_2Cl_2, 38%; b) H_2, $Pd(OH)_2$–C, CH_3OH, 89%; c) Cl_3CCN, DBU, CH_2Cl_2; then **GPL-13**, TMSOTf, CH_2Cl_2, 57%.

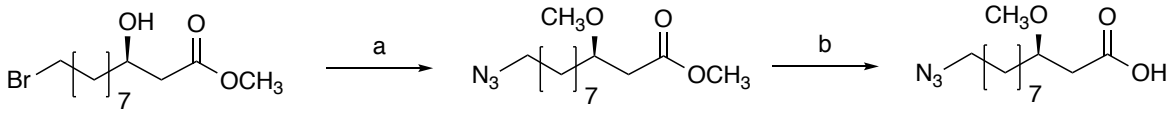
Benzyl 2,4-di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-11). Reducing sugar **GPL-4** (450 mg, 1.72 mmol) was dissolved in CH_2Cl_2 and trichloroacetonitrile (342 µL, 3.43 mmol) and DBU (54 µL, 0.34 mmol) were added. The solution was stirred at rt for 1 h and then concentrated. The resulting oil was purified by chromatography (EtOAc) to give the corresponding glycosyl trichloroacetimidate (693 mg (1.71 mmol) 99%) as a colorless syrup, which was used immediately in the glycosylation; R_f 0.60 (EtOAc). A solution of the trichloroacetimidate derived from **GPL-4** (669 mg, 1.65 mmol) and **GPL-8** (Scheme S48, 519 mg, 1.84 mmol) were dissolved in dry CH_2Cl_2 (4 mL) containing 4Å molecular sieves and cooled to –20 °C. A 0.5 M solution of TMSOTf in dry CH_2Cl_2 (1.32 mL, 0.66 mmol) was added dropwise. The mixture was stirred for 3 h while warming to rt before being filtered. The filtrate was diluted with CH_2Cl_2 and the resulting solution was washed with a satd aq $NaHCO_3$ soln and water. The organic phase was dried (Na_2SO_4), filtered, evaporated and the resulting residue was purified by chromatography (3:1 toluene–acetone) to give **GPL-11** as colorless syrup, as a 9:1 α:β mixture. To purify the compound, the mixture was deacetylated, and then reacetylated. Thus, impure **GPL-11** (536 mg, 1.02 mmol) was dissolved in CH_2Cl_2–CH_3OH (4:1, 5 mL) and sodium methoxide (12 mg, 0.22 mmol) was added. After stirring at rt for 4 h, the solution was neutralized by the addition of Amberlite IR 120 H^+. The resin was filtered and the filtrate was concentrated to give a residue that was purified by chromatography (3:1 toluene–

acetone) to give the product as a colorless syrup. Next, the deacetylated derivative of **GPL-11** (296 mg, 0.67 mmol) was dissolved in pyridine (2 mL) and Ac_2O (2 mL) and stirred at rt overnight. The solution was diluted with CH_2Cl_2 and washed with 5% HCl, a satd aq $NaHCO_3$ soln and water. The organic phase was dried (Na_2SO_4), filtered and concentrated to yield pure **GPL-11** (330 mg, 38%) as a colorless syrup. R_f 0.52 (3:1 toluene–acetone). $[\alpha]_D$ –71.5 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.32 (m, 5 H), 5.42 (dd, 1 H, *J* = 3.3, 1.9 Hz), 4.98 (d, 1 H, *J* = 1.7 Hz, H-1), 4.93 (app t, 1 H, *J* = 9.8 Hz), 4.79 (d, 1 H, *J* = 1.8 Hz), 4.69 (d, 1 H, *J* = 12.0 Hz), 4.47 (d, 1 H, *J* = 12.0 Hz), 4.01 (dd, 1 H, *J* = 3.0, 2.0 Hz), 3.72 (dq 1 H, *J* = 9.8, 6.2 Hz), 3.64 (dq, 1 H, *J* = 9.5, 6.3 Hz), 3.60–3.56 (m, 4 H), 3.53 (dd, 1 H, *J* = 9.3, 3.2 Hz), 3.44 (s, 3 H), 3.36 (s, 3 H), 3.11 (app t, 1 H, *J* = 9.4 Hz), 2.13 (s, 3 H), 2.07 (s, 3 H), 1.32 (d, 3 H, *J* = 6.2 Hz), 1.07 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.2, 170.1, 137.2, 128.6, 128.0, 99.2 (C-1), 97.9 (C-1), 82.3, 81.2, 76.9, 74.2, 72.6, 69.1, 68.3, 68.2, 67.0, 61.0, 58.1, 57.9, 21.3, 21.2, 18.1, 17.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{26}H_{38}O_{11}Na$: 549.2306. Found: 549.2293.

2,4-Di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-methyl-α-L-rhamnopyranose (GPL-12). Disaccharide **GPL-11** (142 mg, 0.27 mmol) was dissolved in CH_3OH (15 mL) and 20% $Pd(OH)_2$–carbon (40 mg) was added. The mixture was degassed and stirred under H_2 (1 atm) overnight. The reaction mixture was filtered and the filtrate was concentrated to give a residue that was purified by chromatography (2.5:1 EtOAc–hexanes) to give **GPL-12** (105 mg, 89%) as a colorless syrup (6:4 α:β ratio). R_f 0.38 (2.5:1 EtOAc–hexanes). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.42 (dd, 1 H, *J* = 3.3, 1.9 Hz), 5.16 (d, 1 H, *J* = 1.9 Hz), 5.02 (d, 1 H, *J* = 1.8 Hz), 4.95 (app t, 1 H, *J* = 9.8 Hz), 4.03 (app t, 1 H, *J* = 2.5 Hz), 3.86–3.79 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.7, 3.3 Hz), 3.55 (m, 4 H), 3.45 (s, 3 H), 3.36 (s, 3 H), 3.10 (app t, 1 H, *J* = 9.4 Hz), 2.13 (s, 3 H), 2.08 (s, 3 H), 1.30 (d, 3 H, *J* = 6.2 Hz), 1.17 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.4, 170.3, 99.2 (C-1), 93.7 (C-1), 82.3, 80.8, 76.9, 74.3, 72.7, 68.1(6), 68.1(5), 67.1, 60.9, 58.1, 57.9, 21.2, 21.1, 18.1, 17.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{19}H_{32}O_{11}Na$: 459.1837. Found: 459.1829.

2,4-Di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl (1→O) *N*-(9-Fluorenylmethoxy-carbonyl)-D-*allo*-threonine pentafluorophenyl ester (GPL-14). Reducing sugar **GPL-4** (552 mg, 2.10 mmol) was dissolved in CH_2Cl_2 and trichloroacetonitrile (420 μL, 4.21 mmol) and DBU (67 μL, 0.42 mmol) were added. The solution was stirred at rt for 1 h and then concentrated. The resulting oil was purified by chromatography (EtOAc) to give the

corresponding glycosyl trichloroacetimidate (854 mg, 99%) as a light yellow oil, which was used immediately in the glycosylation; R_f 0.60 (EtOAc). A solution of the trichloroacetimidate derived from **GPL-4** (604 mg, 1.83 mmol) and **GPL-13**[37] (906 mg, 1.79 mmol) in dry CH_2Cl_2 (4 mL) containing 4Å molecular sieves was cooled to –20 °C. A 0.5 M solution of TMSOTf in dry CH_2Cl_2 (298 μL, 0.15 mmol) was added dropwise. The mixture was stirred for 4 h while warming to rt before being filtered. The filtrate was diluted with CH_2Cl_2 and the resulting solution was washed with a satd aq $NaHCO_3$ soln. The organic phase was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (2:1 hexanes–EtOAc) to give **GPL-14** (765 mg, 57%) as a colorless syrup (9:1 α:β mixture). R_f 0.46 (2:1 hexanes–EtOAc). Data for α-isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.77 (d, 2 H, J = 7.4 Hz), 7.60 (d, 2 H, J = 7.6 Hz), 7.40 (app t, 2 H, J = 7.5 Hz), 7.33–7.29 (m, 2 H), 5.97 (d, 1 H, J = 8.4 Hz), 5.26 (br s, 1 H), 4.98 (app t, 1 H, J = 9.7 Hz), 4.88 (br s, 1 H, H-1), 4.78 (m, 1 H), 4.48 (d, 2 H, J = 6.8 Hz), 4.24 (t, 2 H, J = 6.9 Hz), 4.17–4.21 (m, 1 H), 3.89 (dq, 1 H, J = 9.8 6.2 Hz), 3.50–3.53 (m, 1 H), 3.32 (s, 3 H), 2.16 (s, 3 H), 2.07 (s, 3 H), 1.49 (d, 3 H, J = 6.4 Hz), 1.17 (d, 3 H, J = 6.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 170.3, 166.3, 155.9, 143.7, 142.1, 141.0, 140.1, 139.0, 137.1, 124.6, 141.5, 127.9, 127.2, 125.0, 120.2, 97.5 (C-1), 76.7, 76.4, 72.2, 68.7, 67.9, 67.6, 58.8, 57.7, 47.3, 21.1(4), 20.9(7), 17.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{36}H_{34}F_5NO_{11}Na$: 774.1944. Found: 774.1927.



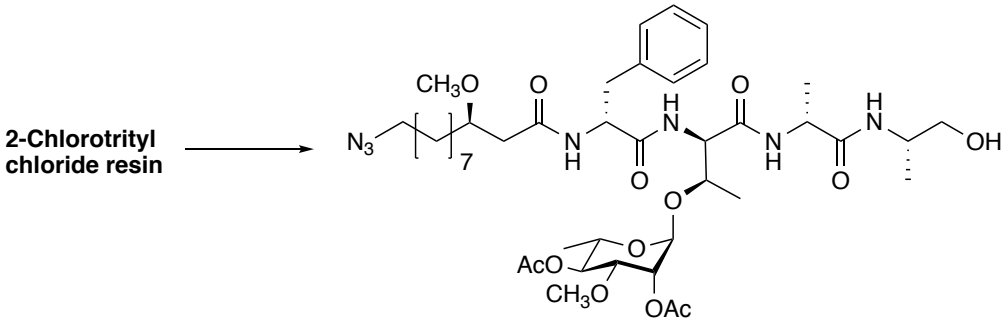
GPL-15 **GPL-16** **GPL-17**

Scheme S50. Synthesis of lipid building block. a) CH_3I, DMF, then NaN_3, DMF, 63%; b) $LiOH·H_2O$, CH_3OH–H_2O (4:1), 89%.

(*R*)-Methyl 11-azido-3-methoxyundecanoate (GPL-16). A solution of **GPL-15**[38] (1.66 g, 5.61 mmol) and CH_3I (699 μL, 11.23 mmol) in DMF (10 mL) was cooled to 0 °C and 60% NaH (237 mg, 6.17 mmol) was added. The solution was stirred overnight while warming to rt. To this solution was added CH_3OH (4 mL) and then CH_2Cl_2 before being washed with 5% HCl, water, dried (Na_2SO_4), filtered, and concentrated. The resulting residue was purified by chromatography (3:1 hexanes–EtOAc) to yield a mixture of (*R*)-methyl 11-bromo-3-

methoxyundecanoate and (*R*)-methyl 11-iodo-3-methoxyundecanoate in a 1:1 ratio as a colorless oil. R_f 0.59 (hexanes–EtOAc 3:1). The mixture of these two compounds (968 mg) was converted to the azide by stirring with NaN_3 (407 mg, 6.26 mmol) in DMF (15 mL) at 80 °C for 3 d. The mixture was cooled, diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), filtered and concentrated to yield **GPL-16** (962 mg, 63%) as a yellow oil. R_f 0.64 (3:1 hexanes–EtOAc) $[\alpha]_D$ –2.5 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 3.69 (s, 3 H), 3.62 (m, 1 H), 3.34 (s, 3 H), 3.25 (t, 2 H, *J* = 7.0 Hz), 2.54 (dd, 1 H, *J* = 15.1, 7.3 Hz), 2.41 (dd, 1 H, *J* = 15.1, 7.3 Hz), 1.63–1.55 (m, 2 H), 1.54–1.30 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 172.4, 77.9, 57.1, 51.7, 51.6, 39.4, 34.0, 29.7, 29.5, 29.2, 26.8, 25.2, 29.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{13}H_{25}N_3O_3Na$: 294.1788. Found: 294.1783.

(*R*)-11-azido-3-methoxyundecanoic acid (GPL-17). To a solution of **GPL-16** (435 mg, 1.60 mmol) in CH_3OH–H_2O (4:1, 5 mL) was added $LiOH{\cdot}H_2O$ (37 mg, 0.89 mmol). The solution was stirred at rt for 4 h and then the CH_3OH was evaporated before the remaining aqueous mixture was acidified with 5% aqueous HCl. The aqueous solution was extracted with CH_2Cl_2, and the combined organic extracts were dried (Na_2SO_4), filtered, and concentrated to yield **GPL-17** (367 mg, 89%) as a light-yellow oil. R_f 0.63 (9:1 CH_2Cl_2–CH_3OH). $[\alpha]_D$ –2.7 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 3.62–3.66 (m, 1 H), 3.39 (s, 3 H), 3.27 (t, 2 H, *J* = 6.9 Hz), 2.57 (dd, 1 H, *J* = 15.4, 7.0 Hz), 2.51 (dd, 1 H, *J* = 15.4, 7.0 Hz), 1.63–1.56 (m, 2 H), 1.54–1.31 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 176.6, 77.7, 57.1, 51.6, 39.2, 33.8, 29.7, 29.6, 29.2, 29.0, 26.9, 25.2. HRMS (ESI) *m/z* calcd for (M+Cl) $C_{12}H_{23}N_3O_3Cl$: 292.1433. Found: 292.1435.

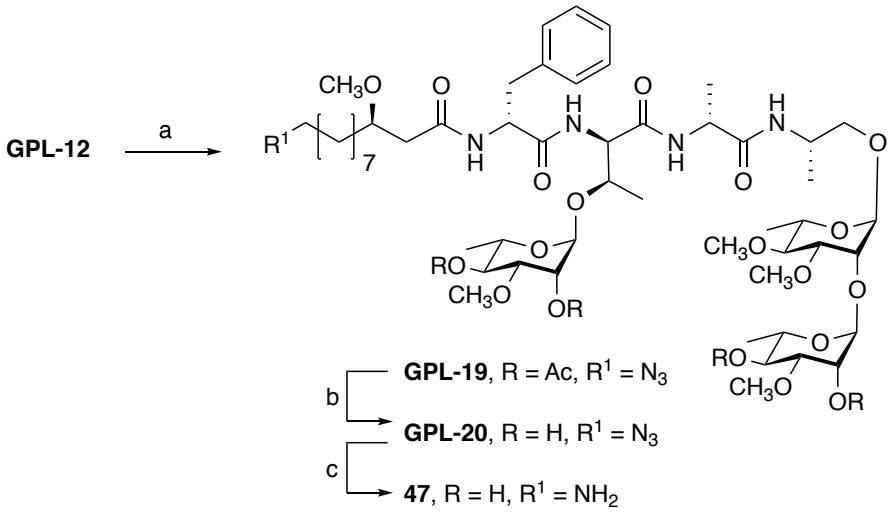


GPL-18

Scheme S51. Solid-phase synthesis of core glycopeptidolipid.

N^{α}-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(2,4-di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninol (GPL-18). 2-Chlorotrityl chloride resin (500 mg, loading 1.22 mmol/g) was incubated overnight with a solution of Fmoc-D-alaniol[39] (907 mg, 3.05 mmol) and DIPEA (1.33 mL, 7.63 mmol) in CH_2Cl_2–DMF (1:1, 4 mL) before CH_3OH was added and shaking of the resin was continued for 10 min. The resin was washed (3 × DMF, 3 × CH_2Cl_2) and then the loading (0.32 mmol/g) was determined via UV–Vis absorption of the Fmoc-cleavage product of a small sample. Fmoc-cleavage of the remaining was done by treatment of the resin with 20% piperidine in DMF (2 × 10 min) followed by washing the resin (3 × DMF, 3 × CH_2Cl_2). Subsequently, the resin was incubated for 4 h with L-alanine (949 mg, 3.05 mmol), HOBt·H_2O (413 mg, 3.05 mmol) and diisopropyl carbodiimide (DIC, 478 μL, 3.05 mmol) in DMF. The resin was washed (3 × DMF, 3 × CH_2Cl_2) and the Fmoc group was cleaved using 20% piperidine in DMF (2 × 10 min). After washing of the resin (3 × DMF, 3 × CH_2Cl_2), it was incubated with **GPL-14** (487 mg, 0.65 mmol) and HOBt·H_2O (88 mg, 0.65 mmol) in DMF (3 mL) for 4 h. The resin was washed (3 × DMF, 3 × CH_2Cl_2) and the Fmoc group was cleaved using 20% piperidine in DMF (2 × 10 min). The resin was washed (3 × DMF, 3 × CH_2Cl_2) and then shaken for 4 h in a solution of Fmoc-D-phenylalanine (314 mg, 0.82 mmol), HOBt·H_2O (127 mg, 0.82 mmol) and DIC (110 μL, 0.82 mmol) in DMF (4 mL). The Fmoc group was cleaved using 20% piperidine in DMF (2 × 10 min). The resin was washed the resin was washed (3 × DMF, 3 × CH_2Cl_2) and then shaken for 4 h in a solution of **GPL-17** (240 mg, 0.82 mmol), HOBt·H_2O (127 mg, 0.82 mmol) and DIC (110 μL, 0.82 mmol) in DMF (4 mL). The resin was washed (3 × DMF, 3 × CH_2Cl_2) and the product was cleaved from the resin using TFA–CH_2Cl_2–TIS–H_2O (47.5:47.5:2.5:2.5, 3 mL) for 2 h. The resin was filtered off and washed with AcOH (2 × 3 mL) and the combined filtrates were concentrated and purified by chromatography to give **GPL-18** (92 mg 65%) as a colorless powder. R_f 0.43 (9:1 CH_2Cl_2–CH_3OH). ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.38 (app t, 2 H, J = 7.3 Hz), 7.32 (d, 1 H, J = 7.3 Hz), 7.24 (d, 2 H, J = 7.0 Hz), 7.17 (d, 1 H, J = 8.6 Hz), 6.95 (d, 1 H, J = 3.7 Hz), 6.83 (d, 1 H, J = 5.5 Hz), 6.68 (d, 1 H, J = 8.0 Hz), 5.25 (dd, 1 H, J = 3.3, 2.1 Hz), 4.97 (app t, 1 H, J = 9.6 Hz), 4.90 (d, 1 H, J = 2.0 Hz), 4.56–4.60 (m, 1 H), 4.51–4.55 (m, 1 H), 4.42–4.46 (m, 1 H), 4.26–4.30 (m, 1 H), 4.05–4.09 (m, 1 H), 3.76 (dq, 1 H, J = 9.3, 6.3 Hz), 3.70 (dd, 1 H, J = 11.5, 3.1 Hz), 3.58–3.52 (m, 2 H), 3.45–3.49 (m, 1 H), 3.35 (s, 3 H), 3.29–3.24 (m, 3 H), 3.21 (s, 3 H), 2.94 (dd, 1 H, J = 14.1, 9.4 Hz), 2.48 (dd, 1 H, J = 15.3, 3.4 Hz), 2.30 (dd, 1

H, J = 15.3, 6.9 Hz), 2.15 (s, 3 H), 2.06 (s, 3 H), 1.63–1.57 (m, 2 H), 1.42–1.17 (m, 24 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 174.1, 173.0, 171.9, 170.6, 170.1, 168.1, 135.5, 129.3, 129.1, 127.8, 95.8 (C-1), 77.6, 76.8, 72.5, 71.6, 68.4, 67.8, 66.4, 59.1, 57.8, 56.8, 56.2, 51.6, 48.8, 48.1, 40.5, 37.2, 29.8, 29.6, 29.4, 29.2, 28.9, 26.8, 25.1, 21.2, 21.1, 17.7, 17.6, 16.7, 14.7. HRMS (ESI) *m/z* calcd for (M+H) $C_{42}H_{68}N_7O_{13}$: 878.4870. Found: 878.4861.



Scheme S52. Synthesis of **47**. a) CCl_3CN, DBU, CH_2Cl_2, then **GPL-18**, TMSOTf, CH_2Cl_2, 64%; b) $NaOCH_3$, CH_3OH, CH_2Cl_2, quant.; c) H_2, $Pd(OH)_2$–C, EtOAc, THF, CH_3OH, 82%.

***N*$^{\alpha}$-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(2,4-di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(2,4-di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-19)**. A solution of **GPL-12** (50 mg, 0.115 mmol), trichloroacetonitrile (22 μL, 0.230 mmol) and DBU (4.0 μL, 0.023 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 2 h and then concentrated. The resulting oil was purified by chromatography (2.5:1 EtOAc–hexanes) to give the corresponding glycosyl trichloroacetimidate (63 mg, 94%) as a colorless syrup, which was used immediately in the glycosylation; R_f 0.69 (2.5:1 EtOAc–hexanes). The trichloroacetimidate derived from **GPL-12** (8.1 mg, 0.014 mmol) and **GPL-18** (Scheme S51, 10 mg, 0.011 mmol) in CH_2Cl_2 (2 mL) containing 4Å molecular sieves was cooled to 0 °C. A 0.5 M solution of TMSOTf (1.2 μL, 0.0006 mmol) was added. The mixture was stirred for 3 h while warming to rt, neutralized with DIPEA (1 μL), concentrated and the resulting residue was purified by chromatography over (3:1

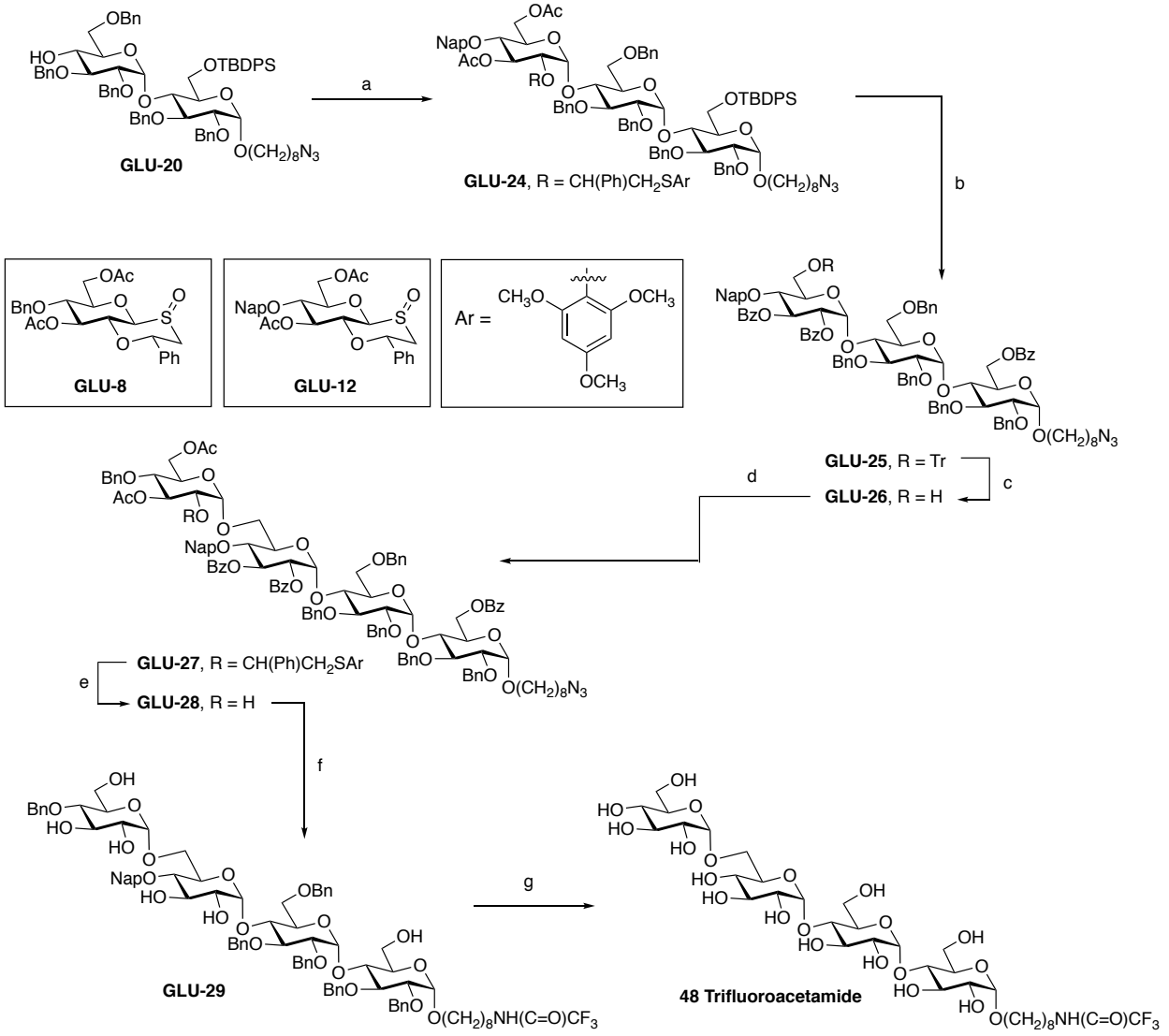
→ 2:1 toluene–acetone) to give **GPL-19** (9 mg, 64%) as a colorless powder after freeze drying (α:β 9:1). R_f 0.58 (9:1 CH_2Cl_2–CH_3OH). ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.36 (app t, 2 H, *J* = 7.4 Hz), 7.30 (d, 1 H, *J* = 7.4 Hz), 7.25 (d, 2 H, *J* = 7.3 Hz), 7.03 (d, 1 H, *J* = 7.5 Hz), 6.78 (d, 1 H, *J* = 4.7 Hz), 6.75 (d, 1 H, *J* = 6.5 Hz), 6.45 (d, 1 H, *J* = 8.0 Hz), 5.42 (dd, 1 H, *J* = 3.3, 1.9 Hz), 5.24 (dd, 1 H, *J* = 3.3, 2.0 Hz), 5.01 (d, 1 H, *J* = 1.6 Hz), 4.98–4.93 (m, 2 H), 4.87 (d, 1 H, *J* = 1.8 Hz), 4.73 (d, 1 H, *J* = 1.7 Hz), 4.49–4.53 (m, 1 H), 4.48–4.44 (m, 1 H), 4.38–4.42 (m, 1 H), 4.24–4.38 (m, 1 H), 4.12–4.17 (m, 1 H), 4.01 (app t, 1 H, *J* = 2.6 Hz), 3.81 (dq, 1 H, *J* = 9.9, 6.2 Hz), 3.74 (dd, 1 H, *J* = 9.6, 6.1 Hz), 3.61–3.43 (m, 13 H), 3.36 (s, 3 H), 3.33 (s, 3 H), 3.27–3.22 (m, 6 H) 3.09 (app t, 1 H, *J* = 9.3 Hz), 2.99 (dd, 1 H, *J* = 14.0, 9.0 Hz), 2.44 (dd, 1 H, *J* = 15.3, 3.4 Hz), 2.28 (dd, 1 H, *J* = 15.2, 7.1 Hz), 2.14 (s, 3 H), 2.13 (s, 3 H), 2.09 (s, 3 H), (s, 3 H), 1.62–1.56 (m, 2 H), 1.41–1.18 (m, 27 H), 1.14 (d, 3 H, *J* = 6.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.1, 172.3, 171.5, 170.6, 170.4, 170.3, 170.1, 168.3, 135.9, 129.21, 129.18, 127.7, 99.3, 99.1, 95.7, 82.3, 81.2, 77.7, 76.8(1), 76.7(6), 73.8, 72.7, 72.5, 71.7, 70.6, 68.4, 68.22, 68.22, 67.6, 67.2, 61.0, 57.9, 57.8, 58.6, 57.7, 56.3, 51.6, 49.5, 45.0, 40.5, 37.2, 32.3, 29.60, 29.50, 29.2, 26.8, 25.1, 29.0, 21.2(2), 21.1(6), 21.1(3), 21.1(2), 18.2, 17.9, 17.6(8), 17.6(6), 17.6(3), 14.7. HRMS (ESI) *m/z* calcd for (M+H) $C_{61}H_{98}N_7O_{23}$: 1296.6709. Found: 1296.6712.

***N*$^{\alpha}$-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(3-*O*-methyl-α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-20)**. To a solution of **GPL-19** (6.0 mg, 0.005 mmol) in CH_2Cl_2–CH_3OH (4:1, 5 mL) was added 1M sodium methoxide solution (0.016 mmol) and the mixture was stirred at rt for 20 h. The reaction mixture was carefully neutralized by adding Amberlite IR-120 H^+ resin and then filtered. The filtrate was concentrated to a residue that was purified by chromatography (10:1 CH_2Cl_2–CH_3OH) to obtain the **GPL-20** (5.0 mg, quant.) as an oil; ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.46 (d, 1 H, *J* = 7.7 Hz), 7.36–7.20 (m, 5 H), 6.90 (d, 1 H, *J* = 7.7 Hz), 6.36 (d, 1 H, *J* = 5.5 Hz), 5.16 (s, 1 H), 5.02 (d, 1 H, *J* = 1.6 Hz), 4.91 (d, 1 H, *J* = 1.8 Hz), 4.82–4.70 (m, 1 H), 4.43–4.36 (m, 1 H), 4.23–3.98 (m, 7 H), 3.94 (ddd, 1 H, *J* = 6.1, 9.6, 12.6 Hz), 3.78–3.70 (m, 2 H), 3.67–3.35 (m, 18 H), 3.32–3.22 (m, 4 H), 3.22–3.00 (m, 3 H), 2.60–2.50 (m, 1 H), 2.48–2.38 (m, 2 H), 2.35–2.28 (m, 1 H), 2.10 (s, 1 H), 1.68–1.58 (m, 4 H), 1.46–1.15 (m, 27 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 172.1, 171.7, 171.1, 169.5, 136.3, 129.2(4), 129.2, 129.1, 128.7(0), 128.7, 128.6, 127.0, 100.9, 100.6, 95.0, 82.3, 81.1, 80.9, 80.3, 77.9, 73.1, 73.0, 72.3, 71.7, 70.2, 68.7, 68.5, 68.1, 68.0, 66.7, 60.7,

58.1, 57.6, 57.2, 56.9, 56.7, 56.6, 53.9, 51.5, 50.2, 45.3, 40.5, 37.4, 32.8, 29.5, 29.4, 29.1, 28.8, 26.7, 25.2, 18.1, 17.9(8), 17.9(5), 17.8, 17.3, 14.3.

N^{α}-(*R*)-11-amino-3-methoxyundecanoyl-D-phenylalaninyl-(3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(3-*O*-methyl-α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (47). Compound **GPL-20** (5.0 mg) was dissolved in EtOAc (3 mL), THF (2 mL), CH_3OH (0.5 mL), H_2O (30 μL), and pyridine (40 μL) and then 20% $Pd(OH)_2$–C (6 mg) was added. The mixture was stirred under H_2 (1 atm) for 1 h. The catalyst was filtered off and then washed with THF. The combined filtrate was concentrated and dried under vacuum for 4 h to obtain the title compound **47** (4 mg, 82%). HRMS (ESI) *m/z* calcd for (M+Na) $C_{53}H_{91}N_5O_{19}Na$: 1124.6200. Found: 1124.6191.

40. Synthesis of 48



Scheme S53. Synthesis of **48 Trifluoroacetamide**. a) **GLU-12**, 1,3,5-trimethoxybenzene, Tf_2O, 2,6-di-*t*-butyl-4-methyl-pyridine, CH_2Cl_2, 59%; b) CF_3CO_2H, Et_3SiH, CH_2Cl_2; then $NaOCH_3$, CH_3OH, CH_2Cl_2; then TrCl, pyridine; then *n*-Bu_4NF, THF; then BzCl, pyridine, 59%; c) p-TsOH·H_2O, H_2O, CH_3OH, CH_2Cl_2, 86%; d) **GLU-8**, 1,3,5-trimethoxybenzene, Tf_2O, 2,6-di-*t*-butyl-4-methyl-pyridine, CH_2Cl_2, 72%; e) CF_3CO_2H, CH_2Cl_2 85%; f) $NaOCH_3$, CH_3OH, CH_2Cl_2; then H_2, $Pd(OH)_2$–C, pyridine; then trifluoroacetic anhydride, pyridine, 59%; g) H_2, $Pd(OH)_2$–C, EtOAc, THF, CH_3OH, 86%.

8-Azidooctyl 2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-3,6-di-*O*-acetyl-4-*O*-naphthyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (GLU-24). A

mixture of sulfoxide donor **GLU-12** [22] (0.53 g, 0.97 mmol), 1,3,5-trimethoxybenzene (0.25 g, 1.49 mmol), 2,6-di-*t*-butyl-4-methyl pyridine (0.4 g, 1.95 mmol), and activated 4 Å molecular sieves (0.3 g) in CH_2Cl_2 (6.5 mL) was stirred for 1 h. After cooling to −10 °C, trifluoromethanesulfonic anhydride (0.18 mL, 1.06 mmol) was added. After 30 min, the reaction mixture was cooled to −40 °C and a solution of **GLU-20** (0.92 g, 0.78 mmol), in CH_2Cl_2 (3.2 mL) was added slowly. The temperature of the reaction mixture was kept at −40 °C for 60 min and then warmed to rt. After stirring for 15 h at rt, the reaction mixture was diluted with CH_2Cl_2 (20 mL), filtered, and the filtrate was concentrated to a residue that was purified by chromatography (7:3 hexanes–EtOAc) to yield **GLU-24** (0.87 g, 59%) as a foam. R_f 0.10 (4:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.84−7.80 (m, 3 H), 7.67−7.76 (m, 5 H), 7.52−7.25 (m, 17 H), 7.25−7.12 (m, 17 H), 7.00−6.96 (m, 2 H), 6.07 (s, 2 H), 6.00 (d, 1 H, *J* = 3.3 Hz, H-1α), 5.61 (d, 1 H, *J* = 3.3 Hz, H-1α), 5.58 (dd, 1 H, *J* = 9.7, 9.7 Hz), 5.10 (d, 1 H, *J* = 11.9 Hz), 4.93 (d, 1 H, *J* = 11.4 Hz), 4.85 (d, 1 H, *J* = 12.1 Hz), 4.81−4.76 (m, 2 H), 4.70 (dd, 1 H, *J* = 11.9, 11.9 Hz), 4.66−4.56 (m, 4 H), 4.54 (d, 1 H, *J* = 11.9 Hz), 4.33, 4.35 (ABq, 2 H, *J* = 12.3 Hz), 4.27 (dd, 1 H, *J* = 4.8, 7.7 Hz), 4.20−4.10 (m, 2 H), 4.10−3.82 (m, 10 H), 3.80 (s, 3 H), 3.77−3.66 (m, 8 H), 3.65−3.51 (m, 3 H), 3.50−3.40 (m, 3 H), 3.30−3.20 (m, 3 H), 2.97 (dd, 1 H, *J* = 8.1, 13.5 Hz), 2.82 (dd, 1 H, *J* = 4.8, 13.7 Hz), 2.57 (br. s, 1 H), 1.85 (s, 3 H), 1.75−1.58 (m, 4 H), 1.47 (s, 3 H), 1.42−1.30 (m, 8 H), 1.06 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.4, 169.7, 161.8, 161.6, 141.8, 139.3, 139.2, 138.4, 138.3, 135.8, 135.6, 135.2, 133.9, 133.4, 133.2, 133.0, 129.9, 129.6, 128.4, 128.2(3), 128.2(1), 128.2, 128.1(3), 128.1, 128.0(2), 128.0, 127.9, 127.7(3), 127.7, 127.5, 127.4, 127.3, 127.1, 127.0, 126.9(3), 126.9, 126.8, 126.7, 126.6, 126.2, 126.0, 125.9, 101.9, 97.2 (C-1), 96.2 (C-1), 95.8 (C-1), 90.9, 83.9, 81.7, 80.5, 80.2, 79.2, 78.7, 76.4, 75.0, 74.4, 74.1, 73.5, 73.3, 73.2, 73.1, 73.0, 72.9, 71.3, 71.2, 68.6, 68.5, 67.7, 63.9, 62.8, 55.8, 55.3, 51.5, 42.7, 37.4, 30.0, 29.4, 29.3, 29.2, 28.9, 26.9, 26.7, 26.1, 20.7, 19.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{109}H_{125}N_3O_{21}SSiNa$: 1894.8188. Found: 1894.8162.

8-Azidooctyl 2,3-di-*O*-benzoyl-4-*O*-naphthyl-6-*O*-trityl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside (GLU-25). To a solution of **GLU-24** (0.85 g, 0.45 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added trifluoroacetic acid (2.0 mL) and the solution was stirred at 0 °C for 30 min. The reaction mixture was then poured into a satd aq $NaHCO_3$ soln (30 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was separated, washed with water (20 mL), dried (Na_2SO_4),

filtered and concentrated to a syrup that was dried under vacuum for 3 h. This compound was dissolved in CH_2Cl_2–CH_3OH (4:1, 10 mL) and 1M methanolic sodium methoxide solution was added until the pH of the reaction mixture was 8–9 (as determined by wet pH paper). The reaction mixture was stirred for 24 h, carefully neutralized by the addition of Amberlite IR 120 H+ resin, filtered and then concentrated to give a crude residue that was dried under vacuum overnight; R_f 0.04 (3:1 hexanes–EtOAc). This trisaccharide was dissolved in pyridine (10 mL) before TrCl (0.24 g, 0.86 mmol) was added and the mixture was stirred at 45 °C for 48 h. During this period, additional TrCl (0.24 g, 0.86 mmol) was added to push the reaction to completion. The reaction mixture was cooled to rt and then ice water (1.0 mL) was added and the solution was stirred for 15 min before being poured into water (20 mL) and extracted with CH_2Cl_2 (60 mL). The CH_2Cl_2 layer was washed with 12% aq copper sulphate solution (until all of the pyridine was removed as determined by TLC), water (25 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (hexanes–EtOAc, 3:1) to yield the corresponding trityl derivative, R_f 0.25 (3:1 hexane–EtOAc); HRMS (ESI) *m/z* calcd for (M+Na) $C_{107}H_{117}N_3O_{16}SiNa$: 1750.8095. Found: 1750.8068, which was dried under vacuum for 2 h. This compound was dissolved in THF (15 mL) and *n*-Bu_4NF (2.5 mL, 1M in THF) was added and the solution was stirred at rt for 36 h. The reaction mixture was then concentrated to a syrup that was purified by chromatography (1:1 hexane–EtOAc); R_f 0.2 (3:2 hexane–EtOAc) and dried under vacuum for 4 h. To a solution of this compound in pyridine (4 mL) was added benzoyl chloride (0.4 mL, 3.45 mmol) and the mixture was heated at 50 °C overnight. The reaction mixture was cooled to rt, CH_3OH (0.5 mL) was added and then the solution was poured into a satd aq $NaHCO_3$ soln (20 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was separated, washed with water (20 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (4:1 hexanes–EtOAc) to yield **GLU-25** (0.48 g, 59% over five steps) as a thick syrup, R_f 0.39 (3:1 hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12−8.08 (m, 2 H), 8.0−7.93 (m, 2 H), 7.87−7.81 (m, 2 H), 7.67−7.61 (m, 1 H), 7.60−7.02 (m, 54 H), 6.98−6.92 (m, 1 H), 6.05 (d, 1 H, *J* = 3.9 Hz), 5.97 (dd, 1 H, *J* = 10.0, 10.0 Hz), 5.64 (d, 1 H, *J* = 3.7 Hz, H-1α), 5.47 (dd, 1 H, *J* = 3.9, 10.2 Hz), 5.04 (d, 1 H, *J* = 11.5 Hz), 4.82−4.70 (m, 6 H), 4.62 (d, 1 H, *J* = 11.9 Hz), 4.60−4.42 (m, 6 H), 4.41 (d, 1 H, *J* = 11.2 Hz), 4.40−4.22 (m, 4 H), 4.21−4.05 (m, 3 H), 3.90−3.86 (m, 1 H), 3.75−3.50 (m, 6 H), 3.43 (ddd, 1 H, *J* = 7.3, 9.9, 14.1 Hz), 3.29 (dd, 2 H, *J* = 7.0, 7.0 Hz), 3.12 (dd, 1 H, *J* = 2.5, 10.6 Hz), 1.79−1.61 (m, 4 H),

1.45−1.32 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0, 165.9, 165.6, 144.0, 138.9, 138.4, 138.1(2), 138.1(0), 137.7, 135.2, 133.1, 133.0, 132.9, 132.8(2), 132.8, 130.2, 130.0, 129.8, 129.6, 129.2, 128.9, 128.6, 128.4, 128.3(3), 128.2(9), 128.2(5), 128.2, 128.1(4), 128.1, 127.9(2), 127.9, 127.8, 127.7, 127.6(0), 127.6, 127.2, 127.1, 127.0, 126.9, 126.8, 126.2, 125.8, 125.7, 96.9 (C-1), 96.3 (C-1), 95.6 (C-1), 86.4, 81.6, 81.2, 80.5, 79.5, 75.8, 74.5, 74.2(9), 74.2(7), 74.0, 73.2(3), 73.2, 73.0, 72.6, 72.4, 71.8, 71.1(7), 71.1(5), 68.7, 68.4(1), 68.4, 63.6, 61.7, 51.5, 29.4, 29.3, 29.1, 28.9, 26.7, 26.0.

8-Azidooctyl 2,3-di-*O*-benzoyl-4-*O*-naphthyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside (GLU-26). To a solution of **GLU-25** (0.47 g, 0.26 mmol) in CH_2Cl_2–CH_3OH (25:4, 29 mL) was added *p*-TsOH·H_2O (0.057 g, 0.30 mmol) followed by water (50 μL) and the mixture was stirred at rt for 24 h. The solution was poured into water (25 mL) and extracted with CH_2Cl_2 (25 mL). The organic layer was washed with water, a satd aq $NaHCO_3$ soln, water, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (7:3 hexane–EtOAc) to yield **GLU-26** (0.35 g, 86%) as a foam. R_f 0.19 (3:1 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.20−8.14 (m, 2 H), 8.00−7.92 (m, 2 H), 7.90−7.86 (m, 2 H), 7.77−7.70 (m, 2 H), 7.68−7.55 (m, 3 H), 7.50−7.40 (m, 6 H), 7.36−7.18 (m, 26 H), 7.15−7.06 (m, 4 H), 6.01 (dd, 1 H, J = 8.8, 10.6 Hz), 5.88 (d, 1 H, J = 4.0 Hz, H-1α), 5.67 (d, 1 H, J = 3.7 Hz), 5.28 (dd, 1 H, J = 4.0, 10.2 Hz), 5.07 (d, 1 H, J = 11.6 Hz), 4.83 (d, 1 H, J = 3.7 Hz, H-1α), 4.82−4.70 (m, 6 H), 4.64 (d, 1 H, J = 11.9 Hz), 4.58−4.44 (m, 5 H), 4.40 (d, 1 H, J = 12.1 Hz), 4.20−4.02 (m, 4 H), 3.98−3.80 (m, 4 H), 3.78−3.60 (m, 5 H), 3.53−3.42 (m, 3 H), 3.30 (dd, 1 H, J = 7.0, 7.0 Hz), 1.93−1.86 (m, 1 H), 1.80−1.60 (m, 4 H), 1.44−1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 165.8, 165.5, 138.9, 138.2, 138.1, 138.0, 137.6, 135.1, 133.2, 133.1(3), 133.1, 133.0, 132.9, 130.1, 130.0, 129.9, 129.7, 129.6, 129.1, 128.5, 128.3, 128.3(4), 128.3(1), 128.2(8), 128.2(7), 128.2(4), 128.2, 128.1, 128.0, 127.9, 127.7(0), 127.6(9), 127.6(7), 127.6(5), 127.5, 127.3, 127.2, 127.0, 126.7, 126.1, 125.9, 96.8 (C-1), 96.3 (C-1), 95.7 (C-1), 81.6, 81.4, 80.5, 79.5, 75.8, 74.8, 74.5, 74.4, 73.8, 73.7, 73.2, 73.1, 72.7, 72.5, 71.7, 71.3, 71.2, 68.4(4), 68.4(0), 68.3, 63.7, 61.4, 51.5, 29.4, 29.3, 29.1, 28.9, 26.7, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{93}H_{97}N_3O_{19}Na$: 1582.6608. Found: 1582.6584.

8-Azidooctyl 2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-3,6-di-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-*O*-naphthyl-α-D-

glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside (GLU-27). A mixture of sulfoxide donor **GLU-8**[22] (0.14 g, 0.28 mmol), 1,3,5-trimethoxybenzene (0.07 g, 0.42 mmol), 2,6-di-*t*-butyl-4-methyl pyridine (0.11 g, 0.54 mmol), and activated 4 Å molecular sieves (0.27 g) in CH_2Cl_2 (1.9 mL) was stirred for 1 h. After cooling to −10 °C, trifluoromethanesulfonic anhydride (0.052 mL, 0.31 mmol) was added. After 30 min, the reaction mixture was cooled to −40 °C and a solution of **GLU-26** (0.35 g, 0.22 mmol) in CH_2Cl_2 (1 mL) was added slowly. The temperature of the reaction mixture was kept at −40 °C for 60 min and then warmed to rt. After stirring for 15 h at rt, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and the filtrate was concentrated to a residue that was purified by chromatography (3:1 hexanes–EtOAc) to yield **GLU-27** (0.35 g, 72%) as a foam. R_f 0.37 (3:2 hexane–EtOAc); $[\alpha]_D$ +113.5 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.18−8.14 (m, 2 H), 7.92−7.88 (m, 2 H), 7.83−7.78 (m, 2 H), 7.75−7.72 (m, 1 H), 7.70−7.66 (m, 2 H), 7.61−7.54 (m, 2 H), 7.47−7.06 (m, 47 H), 6.97−6.94 (m, 1 H), 6.20 (s, 2 H), 6.06 (dd, 1 H, *J* = 9.9, 9.9 Hz), 6.00 (d, 1 H, *J* = 3.9 Hz), 5.83 (d, 1 H, *J* = 3.3 Hz), 5.72 (dd, 1 H, *J* = 9.5, 9.5 Hz), 5.63 (d, 1 H, *J* = 3.5 Hz), 5.42 (dd, 1 H, *J* = 3.9 Hz), 5.02 (d, 2 H, *J* = 11.6 Hz), 4.90 (d, 1 H, *J* = 11.6 Hz), 4.81 (d, 1 H, *J* = 11.6 Hz), 4.80−4.34 (m, 14 H), 4.30−4.19 (m, 2 H), 4.19−4.10 (m, 3 H), 4.10−4.01 (m, 2 H), 4.00−3.51 (m, 19 H), 3.50−3.42 (m, 2 H), 3.35−3.25 (m, 3 H), 3.00 (dd, 1 H, *J* = 9.0, 14.3 Hz), 2.35 (s, 3 H), 2.02 (s, 3 H), 1.77−1.60 (m, 4 H), 1.46−1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 169.9, 167.5, 166.0, 165.7, 165.5, 162.0, 161.5, 142.5, 140.0, 138.3, 138.2, 138.1, 137.8, 137.5, 135.9, 133.0, 132.9, 132.8, 132.6, 130.2, 129.9, 129.8, 129.6, 129.4, 128.5, 128.4(4), 128.4(2), 128.3, 128.2(3), 128.1(8), 128.1(5), 128.1(2), 128.1, 128.0, 127.9, 127.7, 127.5, 127.4(2), 127.4, 127.3, 127.1, 127.0, 126.8, 126.5, 126.0(9), 126.0(6), 125.6, 125.4, 116.2, 101.8, 98.2 (C-1), 96.9 (C-1), 96.3 (C-1), 95.9 (C-1), 91.0, 84.3, 81.7, 81.3, 80.6, 80.5, 79.5, 76.7, 76.4, 75.0, 74.4, 74.3, 74.1(2), 74.1, 73.8, 73.4, 73.2, 73.1(4), 73.1, 72.8, 72.0, 71.8, 71.3, 69.0, 68.4(1), 68.3(9), 68.3(6), 64.8, 63.7, 63.1, 55.9, 55.4, 51.5, 43.1, 37.4, 30.2, 29.4, 29.3, 29.1, 28.9, 26.7, 26.0, 20.8, 20.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{127}H_{135}N_3O_{29}SNa$: 2220.8794. Found: 2220.8807.

8-Azidooctyl 3,6-di-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-*O*-naphthyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside (GLU-28). To a solution of **GLU-27** (0.35 g, 0.16 mmol) in CH_2Cl_2 (10 mL) under argon at 0 °C was added trifluoroacetic acid

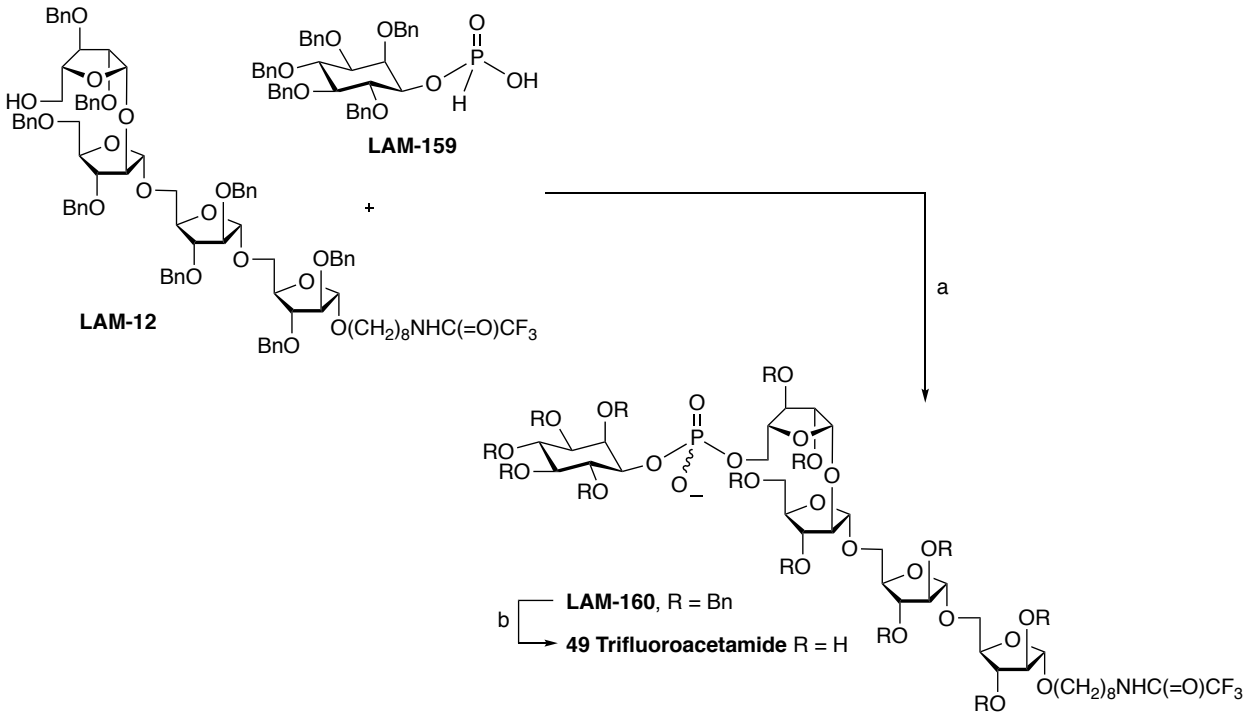
(0.6 mL) and the solution was stirred at that temperature for 50 min. The reaction mixture was then poured into a satd aq $NaHCO_3$ soln (25 mL) and extracted with CH_2Cl_2 (20 mL). The organic layer was washed with water (15 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (65:35 hexanes–EtOAc) to yield **GLU-28** (0.26 g, 85%) as a foam. R_f 0.37 (3:2 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.20−8.12 (m, 2 H), 8.0−7.92 (m, 4 H), 7.80−7.61 (m, 4 H), 7.60−7.53 (m, 1 H), 7.50−7.06 (m, 41 H), 6.05 (dd, 1 H, *J* = 10.0, 10.0 Hz), 5.89 (d, 1 H, *J* = 3.9 Hz), 5.69 (d, 1 H, *J* = 3.7 Hz), 5.47 (dd, 1 H, *J* = 9.7, 9.7 Hz), 5.30 (dd, 1 H, *J* = 3.9, 10.0 Hz), 5.06 (d, 1 H, *J* = 11.6 Hz), 4.88 (d, 1 H, *J* = 3.7 Hz), 4.90−4.40 (m, 15 H), 4.20−4.10 (m, 4 H), 4.10−3.96 (m, 4 H), 3.96−3.75 (m, 7 H), 3.75−3.50 (m, 6 H), 3.47 (ddd, 1 H, *J* = 7.1, 9.7, 14.1 Hz), 3.30 (dd, 2 H, *J* = 7.0, 7.0 Hz), 2.57 (d, 1 H, *J* = 11.0 Hz), 2.15 (s, 3 H), 2.02 (s, 3 H), 1.80−1.60 (m, 4 H), 1.50−1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.9, 170.6, 166.1, 165.7, 138.9, 138.3, 138.2, 138.1, 137.8, 137.5, 135.1, 133.1(6), 133.1, 132.9, 130.1, 130.0, 129.9, 129.7, 129.6, 129.2, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5(3), 127.5, 127.3, 127.2, 126.8, 126.6, 126.0, 125.8(4), 125.8, 99.2 (C-1), 96.7 (C-1), 96.3 (C-1), 95.6 (C-1), 81.7, 81.3, 80.5, 79.5, 76.3, 75.8, 75.5, 74.0, 74.7, 74.4(0), 74.4, 73.7, 73.6, 73.2, 73.1, 72.9, 72.8, 71.5(4), 71.5, 71.4, 70.5, 69.1, 68.8, 68.4, 68.3, 66.4, 63.9, 62.7, 56.3, 51.5, 29.4, 29.3, 29.2, 28.9, 26.7, 26.1, 21.3, 20.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{110}H_{117}N_3O_{26}Na$: 1918.7818. Found: 1918.7800.

8-Trifluoroacetamidooctyl 4-*O*-Benzyl-α-D-glucopyranosyl-(1→6)-4-*O*-naphthyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (GLU-29). Compound **GLU-28** (0.26 g, 0.13 mmol) was dissolved in CH_2Cl_2–CH_3OH (8:1, 9 mL) and 1M methanolic sodium methoxide solution was added until the pH of the reaction mixture was 8–9 (as determined by wet pH paper). The reaction mixture was stirred at rt overnight, carefully neutralized by the addition of Amberlite IR 120 H+ resin, filtered and then concentrated to give a crude residue that was purified by chromatography (93:7 CH_2Cl_2–CH_3OH) to yield the deacylated compound (0.2 g) as a thick syrup; R_f 0.05 (1:1 hexane–EtOAc). This compound (0.14 g, 0.09 mmol) was dissolved in pyridine (6 mL), 20% $Pd(OH)_2$–C (80 mg) was added the mixture was stirred under H_2 (1 atm) for 5 h. The catalyst was filtered off and the filter cake washed with pyridine (2 mL). The combined filtrate was then cooled to 0 °C. Trifluoroacetic anhydride (0.4 mL, 2.9 mmol) was then added dropwise and the solution was stirred at rt overnight before being diluted with CH_2Cl_2 (25 mL) and poured into a 1:1 solution of

water and satd aq $NaHCO_3$ soln (25 mL). The organic layer was washed with water (1 × 20 mL) containing 5–6 drops of aq ammonia for 10 min and was then dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (1:4 hexanes–EtOAc) to give **GLU-29** (0.086 g, 59% over three steps) as a foam. R_f 0.30 (1:4 hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.94−7.80 (m, 5 H), 7.52−7.48 (m, 4 H), 7.38−7.19 (m, 26 H), 7.15−7.10 (m, 2 H), 6.44 (br. s, 1 H), 5.87 (d, 1 H, *J* = 3.9 Hz), 5.17 (d, 1 H, *J* = 12.0 Hz), 5.13 (d, 1 H, *J* = 11.3 Hz), 5.06 (d, 1 H, *J* = 11.0 Hz), 4.90 (d, 1 H, *J* = 11.4 Hz), 4.88 (d, 1 H, *J* = 3.5 Hz), 4.82 (d, 1 H, *J* = 3.8 Hz), 4.78−4.67 (m, 4 H), 4.66−4.52 (m, 4 H), 4.52−4.44 (m, 2 H), 4.40 (d, 1 H, *J* = 11.7 Hz), 4.17 (dd, 1 H, *J* = 9.1, 9.1 Hz), 4.07 (dd, 1 H, *J* = 9.3, 9.3 Hz), 3.95−3.57 (m, 20 H), 3.54 (dd, 1 H, *J* = 3.7, 9.5 Hz), 3.47−3.40 (m, 3 H), 3.38−3.32 (m, 3 H), 3.25−3.18 (m, 2 H), 1.70−1.50 (m, 4 H), 1.42−1.30 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 157.1 (q, *J* = 36.9 Hz), 138.9, 138.3, 137.9(4), 137.9(0), 137.4, 137.2, 137.1, 135.6, 133.3, 133.1, 128.8, 128.6, 128.5(3), 128.5, 128.4, 128.3(4), 128.3, 128.2, 128.1,(4), 128.1(0), 128.0(3), 128.0, 127.9(3), 127.9, 127.8(0), 127.8, 127.6, 127.2, 126.9, 126.3(2), 126.3, 126.2, 126.1, 121.0, 115.8 (q, *J* = 287.7 Hz), 100.0 (C-1), 98.4 (C-1), 96.6 (C-1), 96.1 (C-1), 82.0, 80.5, 80.1, 79.6, 77.8, 77.2, 75.8, 75.7, 75.1, 75.0, 74.8, 74.6(9), 74.6(6), 73.9, 73.7, 73.5, 72.9, 72.7(1), 72.7, 71.5, 71.2, 71.0, 69.8, 68.6, 68.5(2), 68.5, 67.6, 61.8,61.2(8), 61.2(6), 40.0, 29.7, 29.4, 29.2, 29.0, 28.9, 26.6, 26.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{87}H_{102}F_3NO_{22}Na$: 1592.6738. Found: 1592.6730.

8-Trifluoroacetamidooctyl α-D-glucopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranoside (48 Trifluoroacetamide). Prepared from **GLU-29** (0.086 g, 0.05 mmol) and 20% $Pd(OH)_2$–C (60 mg) in EtOAc–CH_3OH–THF (18 mL, 1:1:1) as described for the synthesis of **46 Trifluoroacetamide** to afford **48 Trifluoroacetamide** (0.042 g, 86%) as a foam. R_f 0.1 (7:3 CH_2Cl_2–CH_3OH; ^{1}H NMR (500 MHz, D_2O, δ_H) 5.37−5.32 (m, 2 H, 2 × H-1α), 4.95 (d, 1 H, *J* = 3.7 Hz, H-1α), 4.89 (d, 1 H, *J* = 3.9 Hz, H-1α), 4.00−3.45 (m, 26 H), 3.41 (dd, 1 H, *J* = 9.5, 9.5 Hz), 3.30 (dd, 1 H, *J* = 7.0, 7.0 Hz), 1.70−1.52 (m, 4 H), 1.40−1.28 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 158.7 (q, *J* = 36.6 Hz), 116.0 (q, *J* = 285.5 Hz, 100.1 (C-1), 99.8 (C-1), 98.1 (C-1), 98.0 (C-1), 77.6, 77.5, 73.6, 73.3, 73.2, 73.1, 71.8(4), 71.8, 71.6, 71.5, 71.4, 71.3, 71.2, 70.3, 69.6, 69.4, 68.5, 66.0, 60.6, 60.5(1), 60.5, 39.8, 28.6, 28.4, 28.2, 27.7, 25.8, 25.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{34}H_{58}F_3NO_{22}Na$: 912.3295. Found: 912.3293.

41. Synthesis of 49



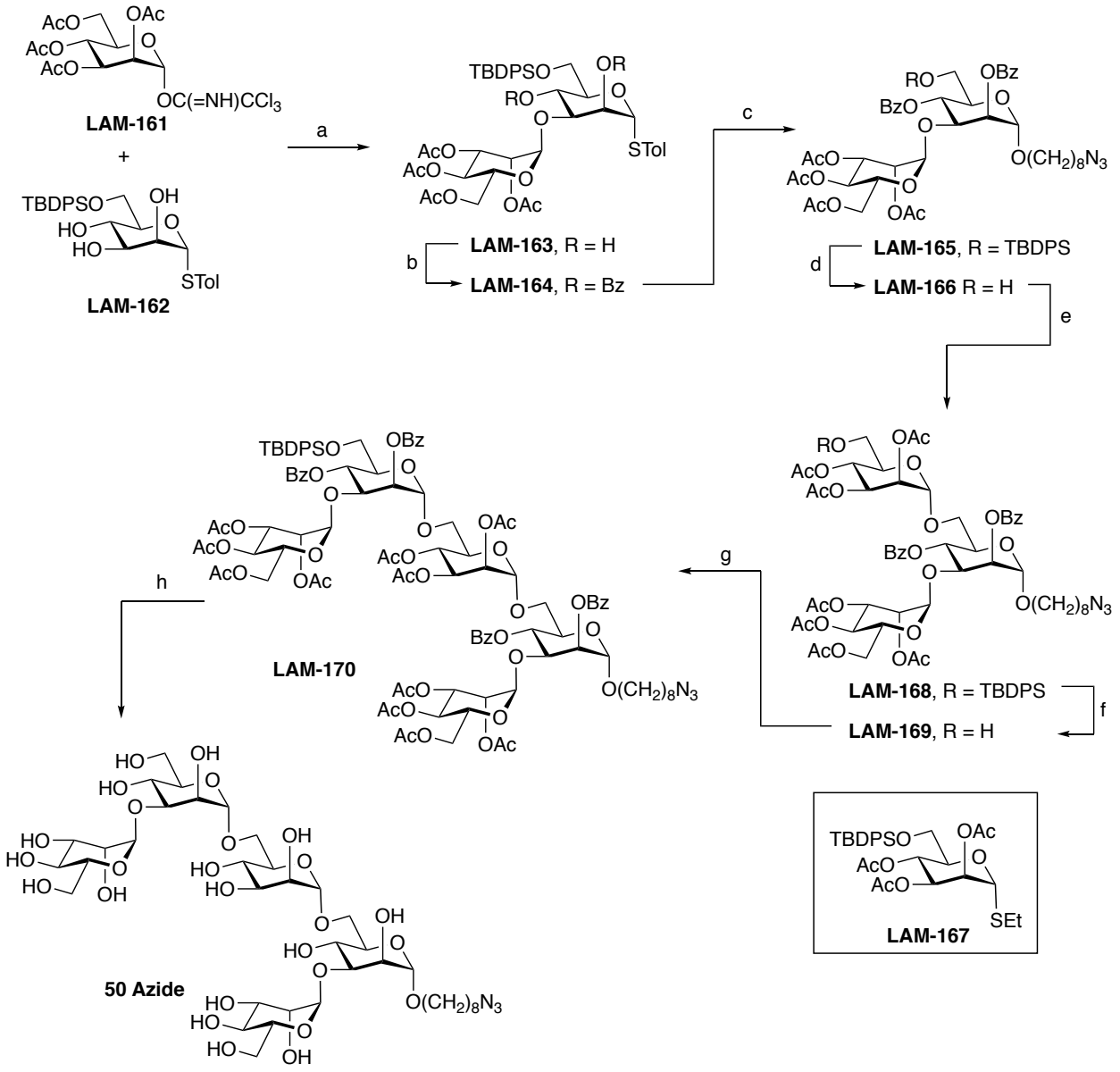
Scheme S54. Synthesis of **49 Trifluoroacetamide**. a) PivCl, pyridine, then I_2, pyridine, water, 69%; b) H_2, $Pd(OH)_2$-C, EtOH-CH_2Cl_2, 90%.

8-Trifluoroacetamidooctyl D-1,2,4,5,6-Penta-*O*-benzyl-*myo*-inositol-3-phosphate-(3→5)-2,3-di-*O*-benzyl-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (LAM-160) A mixture of **LAM-159**[40] (29.2 mg, 0.04 mmol), **LAM-12** (65.7 mg, 0.04 mmol) and powdered 4Å molecular sieves was dissolved in pyridine (2 mL) and stirred at rt for 0.5 h before pivaloyl chloride (26 μL, 0.22 mmol) was added. After stirring at rt for 2 h, a solution of I_2 (23mg, 0.09 mmol) in 95% aqueous pyridine (1 mL) was added and the reaction mixture was stirred for 0.5 h. The reaction mixture was then filtered through Celite, the filtrate was concentrated and the resulting residue was redissolved in CH_2Cl_2. After washing with a satd aq soln of $Na_2S_2O_3$, the organic layer was dried (Na_2SO_4), filtered and the filtrate was concentrated. The crude residue was purified by chromatography (50:1 CH_2Cl_2–CH_3OH) to afford **LAM-160** (64.5 mg, 69%) as colorless film. $[\alpha]_D$ = +17.1 (*c* 0.4, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 7.55–6.65 (m, 65 H), 5.24–3.38 (m, 60 H), 3.22 (t, *J* = 7.2 Hz, 2 H), 1.65–

1.41 (m, 4 H), 1.36–1.18 (m, 8 H); ^{13}C NMR (126 MHz, CD_3OD, δ_C) 138.9, 138.6, 138.4, 138.2, 137.9, 137.8, 137.8, 137.8, 137.5, 137.4, 128.8, 128.8, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.3, 127.2 (78 C), 106.4 (C-1), 106.1 (C-1), 106.0 (C-1), 101.1 (C-1), 88.4, 88.0, 86.0, 84.4, 84.3, 83.3, 83.3, 83.1, 83.0, 81.4, 81.4, 80.5, 80.2, 77.0, 76.9, 75.7, 75.6, 74.9, 73.1, 72.3, 72.2, 72.2, 72.0, 71.9, 71.8, 70.0, 67.6, 65.9, 65.3, 39.8, 29.3, 29.2, 29.0, 28.6, 26.6, 26.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 1.76. HRMS (ESI) *m/z* calcd for (M–H) $C_{127}H_{138}F_3NO_{26}P$: 2180.9202. Found: 2180.9231.

8-Trifluoroacetamidooctyl D-*myo*-inositol-3-phosphate-(3→5)-β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (49 Trifluoroacetamide). A solution of **LAM-160** (16 mg, 0.007 mmol), $Pd(OH)_2$–C in EtOH–CH_2Cl_2 (1.2 mL, 5:1) was stirred under H_2 (1 atm) for 48 h. The mixture was filtered through Celite and the filtrate was concentrated to afford **49 Trifluoroacetamide** (6.7 mg, 90%) as a colorless film. ^{1}H NMR (700 MHz, CD_3OD, δ_H) 5.06 (s, 1 H, H-1), 4.98 (d, *J* = 4.5 Hz, 1 H, H-1), 4.93 (d, *J* = 1.4 Hz, 1 H, H-1), 4.83 (d, *J* = 1.7 Hz, 1 H, H-1), 4.25–3.58 (m, 22 H), 3.42–3.37 (m, 2 H), 3.25 (t, *J* = 7.2 Hz, 2 H), 1.63–1.49 (m, 4 H), 1.44–1.19 (m, 8 H); ^{13}C NMR (176 MHz, CD_3OD, δ_C) 108.1 (C-1), 108.1 (C-1), 106.1 (C-1), 100.5 (C-1), 87.2, 83.5, 82.6, 82.2, 82.1, 81.8, 77.6, 77.4, 77.2, 77.1, 77.1, 75.6, 75.6, 74.8, 74.4, 72.6, 71.9, 71.8, 71.7, 71.4, 71.4, 67.5, 66.7, 61.0, 39.3, 29.2, 28.9, 28.8, 28.4, 26.3, 25.7 (octyl CH_2); ^{31}P NMR (162 MHz, $CDCl_3$) 0.49, 0.35 (diasteromers, 3:1 ratio). HRMS (ESI) *m/z* calcd for (M–H) $C_{36}H_{60}F_3NO_{26}P$: 1010.3099. Found: 1010.3111.

42. Synthesis of 50



Scheme S55. Synthesis of **50 Azide**. a) TBSOTf, CH_2Cl_2, 40%; b) BzCl, pyridine, 81%; c) $HO(CH_2)_8N_3$, NIS, AgOTf, CH_2Cl_2, 60%; d) HF–pyridine, THF, pyridine, 87%; e) **LAM-50-G**, NIS, NIS, AgOTf, CH_2Cl_2, 91%; f) HF–pyridine, THF, pyridine, 44%; g) **LAM-50-D**, NIS, NIS, AgOTf, CH_2Cl_2, 61%; h) *n*-Bu_4NF, CH_3CN, then $NaOCH_3$, CH_3OH, 70%.

***p*-Tolyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-6-*O*-*t*-butyldiphenylsilyl-1-thio-α-D-mannopyranoside (LAM-163)**. Monosaccharides **LAM-161**[24] (416 mg, 0.84 mmol) and **LAM-162**[26] (422 mg, 0.80 mmol) were stirred with 4Å molecular sieves in CH_2Cl_2 at –78

°C for 1 h and then TBSOTf (0.05 mL, 0.22 mmol) was added and the reaction was stirred while warming to rt over 2 h. The mixture was neutralized by addition of Et_3N, filtered through Celite and the filtrate was concentrated. The crude residue was purified by chromatography (2:1 hexanes–EtOAc) to afford **LAM-163** (254.8 mg, 40%) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.83–7.64 (m, 4 H), 7.54–7.19 (m, 8 H), 7.04 (d, 2 H, *J* = 7.9 Hz), 5.45–5.34 (m, 3 H), 5.27 (d, 1 H, *J* = 1.7 Hz, H-1), 5.26 (app t, 1 H, *J* = 9.8 Hz), 4.35–4.12 (m, 5 H), 4.11 (app dt, 1 H, *J* = 9.4, 2.8 Hz), 3.99–3.86 (m, 3 H), 2.88 (d, 1 H, *J* = 2.7 Hz), 2.51 (d, 1 H, *J* = 5.3 Hz), 2.31 (s, 3 H), 2.18 (s, 3 H), 2.15 (s, 3 H), 2.07 (s, 3 H), 2.02 (s, 3 H), 1.08 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ_C) 170.7, 170.0, 170.0, 169.8, 137.8, 135.7, 135.6, 133.0, 132.8, 132.1, 130.0, 129.9, 129.9, 127.8, 127.8, 99.1 ($^1J_{C\text{-}1,H\text{-}1}$ = 176.7 Hz, C-1,), 88.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 170.4 Hz C-1), 79.7, 72.3, 71.7, 69.4, 69.1, 68.7, 66.4, 64.6, 63.0, 26.9, 21.1, 20.9, 20.8, 20.7, 20.7, 19.2. HRMS (ESI) *m/z* calcd for (M+Na): $C_{43}H_{54}O_{14}SSiNa$: 877.2896. Found: 877.2891.

***p*-Tolyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-2,4-*di*-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-α-D-mannopyranoside (LAM-164)**. Disaccharide **LAM-163** (250 mg, 0.29 mmol) and BzCl (337 μL, 2.9 mmol) were dissolved in pyridine (3 mL) and the mixture was heated at 50 °C overnight before being cooled and concentrated. The resulting residue was purified by chromatography (2.5:1 hexanes–EtOAc) to afford **LAM-164** (251.3 mg, 81%) as a white foam: $[\alpha]_D$ +33.7 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.26–7.93 (m, 6 H), 7.77–7.00 (m, 18 H), 5.95 (app t, 1 H, *J* = 9.9 Hz), 5.77 (dd, 1 H, *J* = 3.2, 1.7 Hz), 5.71 (d, 1 H, *J* = 1.5 Hz, H-1), 5.17 (dd, 1 H, *J* = 9.6, 3.3 Hz), 5.12 (app t, 1 H, *J* = 9.7 Hz), 5.00 (d, 1 H, *J* = 1.9 Hz, H-1), 4.95 (dd, 1 H, *J* = 3.2, 1.9 Hz), 4.54 (ddd, 1 H, *J* = 10.2, 4.6, 2.2 Hz), 4.42 (dd, 1 H, *J* = 9.7, 3.2 Hz), 4.20 (dd, 1 H, *J* = 11.9, 6.0 Hz), 4.13 (ddd, 1 H, *J* = 9.2, 6.2, 1.9 Hz), 4.01 (dd, 1 H, *J* = 12.0, 1.9 Hz), 3.90 (dd, 1 H, *J* = 11.6, 4.5 Hz), 3.82 (dd, 1 H, *J* = 11.7, 2.2 Hz), 2.34 (s, 3 H), 2.19 (s, 3 H), 1.96 (s, 3 H), 1.89 (s, 3 H), 1.87 (s, 3 H), 1.01 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ_C) 170.8, 169.8, 169.2, 169.1, 165.9, 164.9, 138.1, 135.7, 135.5, 133.7, 133.6, 133.2, 133.1, 132.9, 132.2, 130.2, 130.1, 130.0, 129.9, 129.6, 129.5, 129.5, 129.3, 129.2, 128.6, 128.5, 128.4, 127.6, 127.5, 99.4 (C-1), 86.4 (C-1), 76.2, 73.5, 72.7, 69.4, 69.3, 68.5, 68.3, 66.1, 62.6, 62.5, 26.6, 21.2, 20.9, 20.7, 20.5, 20.5, 19.2. HRMS (ESI) *m/z* calcd for (M+Na): $C_{57}H_{62}O_{16}SSiNa$: 1085.3420. Found: 1085.3410.

8-Azidooctyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α-D-mannopyranoside (LAM-165). A mixture of thioglycoside **LAM-**

164 (115 mg, 0.11 mmol), 8-azidooctanol (185 mg, 1.10 mmol) and powdered 4Å molecular sieves were dissolved in CH_2Cl_2 (2.5 mL) and stirred at rt for 1 h. Then *N*-iodosuccinimide (15.0 mg, 0.06 mmol) and silver triflate (2.0 mg, 0.01 mmol) were added. After stirring at rt for 3 h, Et_3N (0.2 mL) was added and the reaction mixture was filtered through Celite. The filtrate was concentrated and the resulting crude residue was purified by chromatography (2.5:1 hexane–EtOAc) to afford **LAM-165** (71.8 mg, 60%) as a pale yellow syrup. $[\alpha]_D$ = –11.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.17 (dd, 2 H, *J* = 8.3, 1.2 Hz), 7.98 (dd, 2 H, *J* = 8.3, 1.2 Hz), 7.71–7.15 (m, 16 H), 5.80 (app t, 1 H, *J* = 10.0 Hz), 5.49 (dd, 1 H, *J* = 3.3, 1.8 Hz), 5.19–5.08 (m, 2 H′), 5.07 (d, 1 H, *J* = 1.6 Hz, H-1), 4.98 (d, 1 H, *J* = 1.7 Hz, H-1), 4.91 (dd, 1 H, *J* = 2.8, 2.0 Hz), 4.44 (dd, 1 H, *J* = 9.8, 3.3 Hz), 4.20 (dd, 1 H, *J* = 12.2, 5.4 Hz, 4.12–4.07 (m, 1 H), 4.02–3.94 (m, 2 H, H-5), 3.88 (dd, 1 H, *J* = 11.5, 5.3 Hz, H-6a), 3.81 (dd, 1 H, *J* = 11.5, 2.1 Hz), 3.78 (dt, 1 H, *J* = 9.7, 5.7 Hz), 3.51 (dt, 1 H, *J* = 9.8, 6.7 Hz), 3.28 (t, 2 H, *J* = 7.0 Hz), 2.12 (s, 3 H), 1.94 (s, 3 H), 1.89 (s, 3 H), 1.86 (s, 3 H), 1.70–1.58 (m, 4 H), 1.46–1.30 (m, 8 H), 1.04 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$, δ_C) 170.6, 169.7, 169.2, 169.0, 166.0, 165.0, 135.6, 135.6, 133.5, 133.2, 133.1, 133.1, 130.0, 129.9, 129.5, 129.4, 129.3, 128.6, 128.3, 127.5, 99.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 173.6 Hz, C-1), 97.1 ($^1J_{C\text{-}1,H\text{-}1}$ = 171.9 Hz, C-1), 76.3, 72.1, 71.6, 69.5, 69.2, 68.5, 68.4, 68.1, 66.0, 63.0, 62.2, 51.5, 29.4, 29.3, 29.1, 28.8, 26.7, 26.1, 20.7, 20.6, 20.5, 19.2. HRMS (ESI) *m/z* calcd for (M+Na): $C_{58}H_{71}N_3O_{17}SiNa$: 1132.4445. Found: 1132.4436.

8-Azidooctyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-D-mannopyranoside (LAM-166). Disaccharide **LAM-165** (30 mg, 0.03 mmol) was dissolved in THF–pyridine (4:1, 1.5 mL) and cooled to 0 °C before 70% HF·pyridine (50 μL) was added. The solution was stirred overnight while warming to rt and then another portion of 70% HF·pyridine (25 μL) was added. After stirring for another 24 h, the mixture was concentrated, the residue was dissolved in CH_2Cl_2 and washed with a satd aq $NaHCO_3$ soln. The organic layer was concentrated and the resulting residue was purified by chromatography (1.7:1 hexane–EtOAc) to afford **LAM-166** (120.4 mg, 87%) as white foam: $[\alpha]_D$ –26.4 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (498 MHz, $CDCl_3$, δ_H) 8.17–8.05 (m, 4 H), 7.68–7.43 (m, 6 H), 5.63 (app t, 1 H, *J* = 10.0 Hz), 5.49 (dd, 1 H, *J* = 3.3, 1.8 Hz), 5.19–5.11 (m, 2 H), 5.10 (d, 1 H, *J* = 1.7 Hz, H-1), 5.08 (d, 1 H, *J* = 1.5 Hz, H-1), 4.93 (dd, 1 H, *J* = 2.8, 2.0 Hz), 4.53 (dd, 1 H, *J* = 9.8, 3.4 Hz), 4.22 (dd, 1 H, *J* = 12.2, 5.5 Hz), 4.07 (ddd, 1 H, *J* = 9.3, 5.4, 1.8 Hz), 4.01 (dd, 1 H, *J* = 12.2, 2.2 Hz), 3.89 (app dt, 1 H, *J* = 10.2, 3.0 Hz), 3.81–3.69 (m, 3 H), 3.52 (dt, 1 H, *J* = 9.7, 6.6 Hz), 3.28 (t, 2 H, *J* = 6.9

Hz), 2.67 (t, 1 H, J = 7.0 Hz), 2.13 (s, 3 H), 1.93 (s, 3 H), 1.93 (s, 3 H), 1.85 (s, 3 H), 1.71–1.56 (m, 4 H), 1.46–1.31 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) δ 170.6, 169.7, 169.3, 169.1, 166.4, 166.0, 133.7, 133.6, 130.0, 130.0, 129.2, 128.8, 128.7, 128.5, 99.6 (C-1), 97.4 (C-1), 75.8, 72.0, 71.0, 69.4, 69.3, 69.0, 68.4, 68.3, 66.0, 62.2, 61.4, 51.4, 29.4, 29.3, 29.0, 28.8, 26.7, 26.0, 20.7, 20.6, 20.5, 20.5. HRMS (ESI) *m/z* calcd for (M+Na): $C_{42}H_{53}O_{17}Na$: 894.3267. Found: 894.3260.

8-Azidooctyl 2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-benzoyl-α-D-mannopyranoside (LAM-168). A mixture of **LAM-167**[3] (21 mg, 0.026 mmol), **LAM-166** (20 mg, 0.023 mmol) and powdered 4Å molecular sieves were dissolved in CH_2Cl_2 (1.5 mL) and stirred at rt for 1 h. Then *N*-iodosuccinimide (10.0 mg, 0.04 mmol) and silver trifluoromethanesulfonate (1.5 mg, 0.006 mmol) were added. After stirring at rt for 2 h, Et_3N (0.2 mL) was added and the reaction mixture was filtered through Celite. The filtrate was concentrated and the resulting crude residue was purified by chromatography (2:1 hexane–EtOAc) to afford **LAM-168** (33.2 mg, 91%) as a colorless oil: $[\alpha]_D$ –43.3 (c = 0.1, $CHCl_3$); ^{1}H NMR (498 MHz, $CDCl_3$, δ_H) δ 8.16 (dd, 2 H, J = 8.3, 1.2 Hz), 8.11 (dd, 2 H, J = 8.3, 1.2 Hz), 8.07 (dd, 2 H, J = 8.3, 1.2 Hz), 7.94 (dd, 2 H, J = 8.3, 1.2 Hz), 7.87 (dd, 2 H, J = 8.3, 1.2 Hz), 7.67–7.22 (m, 23 H), 7.12 (app t, 2 H, J = 7.6 Hz), 6.19 (app t, 1 H, J = 10.2 Hz), 5.84 (dd, 1 H, J = 10.2, 3.3 Hz), 5.71 (app t, 1 H, J = 10.0 Hz), 5.68 (dd, 1 H, J = 3.2, 1.6 Hz), 5.53 (dd, 1 H, J = 3.4, 1.7 Hz), 5.17–5.12 (m, 2 H), 5.11 (d, 1 H, J = 1.6 Hz, H-1), 5.08 (d, 1 H, J = 1.4 Hz, H-1), 5.05 (d, 1 H, J = 1.7 Hz, H-1), 4.93 (dd, 1 H, J = 2.9, 1.9 Hz), 4.52 (dd, 1 H, J = 9.7, 3.4 Hz), 4.29–4.17 (m, 3 H), 4.10 (ddd, 1 H, J = 9.5, 5.4, 2.2 Hz), 4.04 (dd, 1 H, J = 10.7, 7.0 Hz), 4.01 (dd, 1 H, J = 12.2, 2.1 Hz), 3.92 (dt, 1 H, J = 9.6, 6.8 Hz), 3.78 (dd, 1 H, J = 11.6, 3.7 Hz), 3.74 (dd, 1 H, J = 11.5, 2.0 Hz), 3.69 (dd, 1 H, J = 10.6, 1.9 Hz), 3.61 (dt, 1 H, J = 9.9, 6.6 Hz), 3.16 (t, 2 H, J = 7.0 Hz), 2.14 (s, 3 H), 1.94 (s, 3 H), 1.90 (s, 3 H), 1.86 (s, 3 H), 1.80–1.22 (m, 12 H), 1.01 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ_C) 170.6, 169.7, 169.2, 169.0, 166.2, 165.5, 165.4, 165.3, 165.2, 135.7, 135.5, 133.5, 133.4, 133.3, 133.1, 133.0, 132.9, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 129.2, 128.9, 128.7, 128.5, 128.4, 128.3, 127.6, 127.5, 99.6 (C-1), 97.3 (C-1), 97.3 (C-1), 76.1, 72.1, 71.3, 70.7, 70.6, 69.7, 69.4, 69.3, 68.9, 68.4, 68.4, 66.7, 66.4 , 66.1, 62.3, 62.3, 51.4, 29.4, 29.4, 29.2, 28.8, 26.7, 26.6), 26.1, 20.7, 20.6, 20.5, 20.5, 19.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{85}H_{93}N_3O_{25}SiNa$: 1606.5760. Found: 1606.5740.

8-Azidooctyl 2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-benzoyl-α-D-mannopyranoside (LAM-169). Trisaccharide **LAM-168** (32 mg, 0.02 mmol) was dissolved in THF–pyridine (4:1, 1 mL) and cooled to 0 °C before 70% HF·pyridine (50 μL) was added and the solution was stirred for 3 d while warming to rt. At this point, another portion of HF·pyridine (30 μL) was added and the reaction was stirred for 24 h before being concentrated. The mixture was dissolved in CH_2Cl_2, washed with a satd aq $NaHCO_3$ soln and the organic layer was concentrated and purified by chromatography (1.7:1 hexane–EtOAc) to afford **LAM-169** (12 mg, 44%) as a colorless foam: $[\alpha]_D$ –36.8 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) δ 8.25–8.18 (m, 2 H), 8.13–7.98 (m, 6 H), 7.85 (d, 2 H, *J* = 7.3 Hz), 7.67–7.27 (m, 15 H), 6.01 (dd, 1 H, *J* = 10.1, 3.3 Hz), 5.85 (app t, 1 H, *J* = 10.1 Hz), 5.77 (app t, 1 H, *J* = 10.0 Hz), 5.69 (dd, 1 H, *J* = 3.1, 1.6 Hz), 5.56 (dd, 1 H, *J* = 3.0, 1.6 Hz), 5.19–5.15 (m, 2 H), 5.14 (d, 1 H, *J* = 1.4 Hz, H-1), 5.11 (d, 1 H, *J* = 1.3 Hz, H-1), 5.07 (d, 1 H, *J* = 1.3 Hz, H-1), 4.95 (dd, 1 H, *J* = 2.9, 2.0 Hz), 4.53 (dd, 1 H, *J* = 9.7, 3.3 Hz), 4.29–4.20 (m, 2 H), 4.16–4.09 (m, 2 H), 4.06 (dd, 1 H, *J* = 9.2, 4.8 Hz), 4.03 (dd, 1 H, *J* = 11.9, 2.1 Hz), 3.92 (dt, 1 H, *J* = 9.6, 6.9 Hz), 3.82–3.68 (m, 2 H, H-6b), 3.67–3.58 (m, 2 H), 3.23 (t, 2 H, *J* = 7.0 Hz), 2.55 (br s, 1 H), 2.16 (s, 3 H), 1.96 (s, 3 H), 1.91 (s, 3 H), 1.88 (s, 3 H), 1.82–1.24 (m, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ_C) δ 170.6, 169.7, 169.2, 169.1, 166.5, 166.1, 165.4, 165.1, 133.6, 133.5, 133.1, 130.1, 129.9, 129.7, 129.3, 128.9, 128.8, 128.6, 128.5, 128.3, 99.6 (C-1), 97.5 (C-1), 97.4 (C-1), 76.0, 72.0, 71.0, 70.5, 69.6, 69.5, 69.4, 69.3, 68.8, 68.5, 68.4, 67.1, 66.9, 66.1, 62.3, 61.1, 51.4, 29.5, 29.4, 29.1, 28.8, 26.7, 26.1, 20.7, 20.6, 20.5, 20.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{69}H_{75}N_3O_{25}Na$: 1368.4582. Found: 1368.4564.

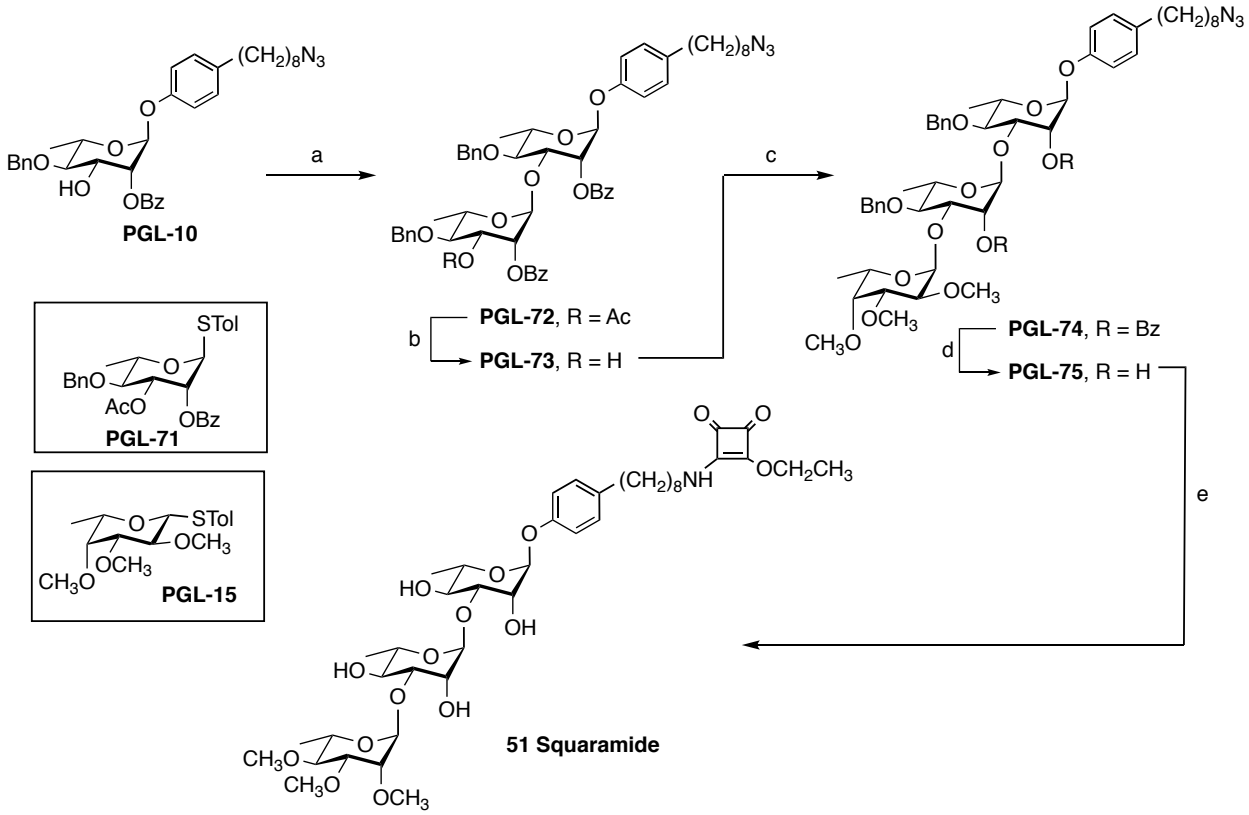
8-Azidooctyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-benzoyl-α-D-mannopyranoside (LAM-170). A mixture of **LAM-164** (25 mg, 0.026 mmol), **LAM-169** (21.4 mg, 0.016 mmol) and powdered 4Å molecular sieves were dissolved in CH_2Cl_2 (2.7 mL) and stirred at rt for 0.5 h. Then *N*-iodosuccinimide (9.8 mg, 0.04 mmol) and silver triflate (2.2 mg, 0.008 mmol) were added. After stirring at rt overnight, Et_3N (0.2 mL) was added and the reaction mixture was filtered through Celite. The filtrate was concentrated and the resulting residue was purified by chromatography (1:1 hexane–EtOAc) to afford **LAM-170** (25.8 mg, 61%) as a colorless film: $[\alpha]_D$ = –15.0 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) δ

8.27–7.82 (m, 14 H), 7.68–7.09 (m, 31 H), 6.10 (app t, 1 H, J = 10.2 Hz), 5.96 (app t, 1 H, J = 10.0 Hz), 5.89 (dd, 1 H, J = 10.2, 3.3 Hz), 5.82 (app t, 1 H, J = 10.0 Hz), 5.75 (dd, 1 H, J = 3.1, 1.4 Hz), 5.61–5.53 (m, 2 H), 5.22–5.13 (m, 4 H), 5.10–5.12 (m, 2 × H-1), 5.07 (d, 1 H, J = 1.7 Hz, H-1), 5.05 (d, 1 H, J = 1.5 Hz, H-1), 5.03–4.98 (m, 2 H), 4.95 (dd, 1 H, J = 2.9, 1.9 Hz), 4.55 (dd, 1 H, J = 9.8, 3.3 Hz), 4.49 (dd, 1 H, J = 9.8, 3.1 Hz), 4.32 (br d, 1 H, J = 10.4 Hz), 4.29–4.21 (m, 2 H), 4.15–4.10 (m, 1 H), 4.10–4.00 (m, 4 H), 3.96–3.88 (m, 2 H), 3.85 (dd, 1 H, J = 11.5, 3.4 Hz), 3.81–3.71 (m, 2 H), 3.66–3.56 (m, 2 H), 3.53 (dd, 1 H, J = 11.7, 3.7 Hz), 3.43 (dd, 1 H, J = 11.9, 1.4 Hz), 3.20 (t, 2 H, J = 7.0 Hz), 2.16 (s, 3 H), 2.02 (s, 3 H), 1.96 (s, 3 H), 1.94 (s, 3 H), 1.92 (s, 3 H), 1.91 (s, 3 H), 1.88 (s, 3 H), 1.87 (s, 3 H), 1.81–1.25 (m, 12 H), 0.95 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ_C) δ 177.0, 170.6, 170.5, 169.8, 169.7, 169.2, 169.1, 169.0, 166.2, 165.7, 165.4, 165.4, 165.2, 165.2, 164., 135.6, 135.5, 133.6, 133.5, 133.3, 133.0, 130.1, 130.0, 129.9, 129.8, 129.7, 129.7, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.6, 127.5, 127.4, 99.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 170.4 Hz, C-1), 99.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 172.3 Hz, C-1), 97.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 173.2 Hz, C-1), 97.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 173.0 Hz, C-1), 97.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 173.0 Hz, C-1), 77.3, 76.1, 72.1, 71.8, 71.3, 70.5, 70.5, 69.6, 69.5, 69.4, 69.4, 69.3, 69.1, 68.7, 68.7, 68.5, 68.4, 67.4, 66.9, 66.27, 66.08, 65.94, 65.5, 62.3, 62.0, 62.0, 51.4, 29.4, 29.4, 29.1, 28.8, 26.7, 26.6), 26.1, 20.7, 20.6, 20.6, 20.5, 19.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{119}H_{129}N_3O_{41}SiNa$: 2306.7763. Found: 2306.7737.

8-Azidooctyl α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→3)]-α-D-mannopyranoside (50 Azide). To a solution of **LAM-170** (13 mg, 0.005 mmol) in CH_3CN was added *n*-Bu_4NF (1M in THF, 30 μL). The resulting solution was stirred a rt for 3 h. Another portion of 1M *n*-Bu_4NF in THF (20 μL) was added and the reaction mixture was heated at 40 °C for 3 h until all starting material disappeared as determined by TLC. The solution was then concentrated and co-evaporated with toluene. The crude product was dissolved in CH_3OH and to this solution was added 3M methanolic sodium methoxide until the pH of the solution was 8-9. After stirring at rt for 72 h, the mixture was neutralized by the addition of Amberlite IR120 H^+ ion exchange resin, filtered and then concentrated. The crude product was dissolved in H_2O and washed with CH_2Cl_2. The aqueous layer was loaded onto a Sep-Pak C_{18} cartridge and the product was eluted with 50% CH_3OH in H_2O to afford **50 Azide** (6.5 mg, 70%) as a pale yellow foam. ^{1}H NMR (600 MHz, D_2O, δ_H) 5.09 (s, 1 H, H-1), 5.07 (s, 1 H, H-1), 4.86 (s, 1 H, H-1), 4.84 (s, 1 H, H-1), 4.79 (s, 1

H, H-1), 4.10–4.01 (m, 4 H), 3.97–3.59 (m, 28 H), 3.52 (dt, 1 H, J = 10.1, 5.9 Hz), 3.28 (t, 2 H, J = 7.0 Hz), 1.70–1.50 (m, 4 H), 1.45–1.23 (m, 8 H); ^{13}C NMR (126 MHz, D_2O, δ_C) 102.4 (C-1), 102.3 (C-1), 99.9(C-1), 99.4(C-1), 99.2 (C-1), 78.7, 78.3, 73.4, 72.9, 71.1, 70.9, 70.6, 70.4, 70.4, 70.1, 70.0, 69.8, 69.6, 68.1, 66.8, 66.7, 66.2, 65.9, 65.7, 65.4, 61.1, 60.9, 51.3, 28.5, 28.3, 28.2, 28.0, 25.9, 25.3. HRMS (ESI) *m/z* calcd for (M+Na) $C_{38}H_{67}N_3O_{26}Na$: 1004.3905. Found: 1004.3901.

43. Synthesis of 51



Scheme S56. Synthesis of **51 Squaramide**. a) **PGL-71**, NIS, AgOTf, CH_2Cl_2, 76%; b) HBF_4, CH_2Cl_2, CH_3OH, 86%; c) **PGL-15**, NIS, AgOTf, CH_2Cl_2, 42%; d) $NaOCH_3$, CH_3OH, CH_2Cl_2, 77%; e) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then diethyl squarate, CH_3CH_2OH, 61%.

***p*-(8-Azidooctylphenyl) 3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (PGL-72)**. A solution of **PGL-10** (0.160 g, 0.27 mmol) and **PGL-71**[41] (0.152 g, 0.30 mmol) in CH_2Cl_2 (3.5 mL) was stirred at rt for 1 h. The solution was then cooled to –20 °C and 30 min *N*-iodosuccinimide (0.092 g, 0.41 mmol) and silver triflate (0.012 g, 0.054 mmol) were added. The reaction mixture was stirred at –20 °C for 30 min, Et_3N was added and the solution was filtered and concentrated. The resulting residue was purified by chromatography (5:1 hexanes–EtOAc) to give **PGL-72** (0.20 g, 76%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.14 (d, 2 H, J = 7.0 Hz), 8.05 (d, 2 H, J = 7.0 Hz), 7.66–7.61 (m, 2 H), 7.55–7.48 (m, 4 H), 7.45 (d, 2 H, J = 8.0 Hz), 7.33 (app t, 2 H, J = 7.0 Hz), 7.32–7.24 (m, 8 H), 7.14 (dd, 2 H, J = 8.0, 2.5 Hz), 7.08 (d, 2 H, J = 10.0 Hz), 6.97 (d, 2 H, J = 11.5 Hz), 5.66 (s, 1 H), 5.61 (s, 1 H), 5.58 (s, 1 H), 5.42 (dd, 1 H, J = 10.0, 3.5 Hz), 5.25 (s, 1 H), 5.05 (d,

1 H, *J* = 11.0 Hz), 4.76 (d, 1 H, *J* = 9.5 Hz), 4.58 (q, 2 H, *J* = 11.5 Hz), 4.50 (dd, 1 H, *J* = 9.0, 3.5 Hz), 3.95–3.99 (m, 2 H), 3.75 (t, 1 H, *J* = 9.5 Hz), 3.59 (t, 1 H, *J* = 9.5 Hz), 3.27 (t, 2 H, *J* = 7.0 Hz), 2.55 (app t, 2 H, *J* = 7.5 Hz), 1.93 (s, 3 H), 1.36–1.27 (m, 12 H), 1.23 (d, 3 H, *J* = 6.0 Hz). HRMS (ESI) *m/z* calcd for (M+Na) $C_{56}H_{63}N_3O_{12}Na$: 992.4304. Found: 992.4287.

***p*-(8-Azidooctylphenyl) 2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (PGL-73)**. To a solution of **PGL-72** (0.739 g, 0.76 mmol) and fluoroboric acid (4.0 mL) in dry CH_3OH and CH_2Cl_2 (4:1, 20 mL) was stirred at rt for 21 h. A satd aq soln of $NaHCO_3$ was added carefully, followed by CH_2Cl_2. The layers were separated and the aqueous layer was extracted with additional CH_2Cl_2. The organic layers were combined, washed with satd aq soln of $NaHCO_3$, water and then dried (Na_2SO_4). The solution was filtered, concentrated and purified by chromatography (3:1 hexanes–EtOAc) to give **PGL-73** (0.605 g, 86%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12 (d, 2 H, *J* = 8.0 Hz), 8.03 (d, 2 H, *J* = 8.5 Hz), 7.67–7.60 (m, 2 H), 7.55–7.47 (m, 5 H), 7.41 (d, 2 H, *J* = 7.5 Hz), 7.24–7.34 (m, 7 H), 7.08 (d, 2 H, *J* = 8.5 Hz), 6.97 (d, 2 H, *J* = 8.7 Hz), 5.58 (s, 1 H), 5.56 (s, 1 H), 5.28 (s, 1 H), 4.96 (d, 1 H, *J* = 11.7 Hz), 4.74 (d, 1 H, *J* = 11.7 Hz), 4.69 (ABq, 2 H, *J* = 11.7 Hz), 4.51 (dd, 2 H, *J* = 8.5, 6.0 Hz), 4.29 (app t, 1H, *J* = 5.5 Hz), 3.90–3.99 (m, 2 H), 3.72 (app t, 1H, *J* = 9.5 Hz), 3.72 app t, 1 H, *J* = 10.7 Hz), 3.27 (app t, 2 H, *J* = 7.5 Hz), 2.55 (app t, 2 H, *J* = 7.5 Hz), 1.50–1.40 (m, 4 H), 1.26–1.36 (m, 15 H). HRMS (ESI) *m/z* calcd for (M+Na) $C_{54}H_{61}N_3O_{11}Na$: 950.4198. Found: 950.4190.

***p*-(8-Azidooctylphenyl) 2,3,4-tri-*O*-methyl-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (PGL-74)**. To a solution of compound **PGL-73** (0.148 g, 0.16 mmol) and **PGL-15**[29] (0.055 g, 0.18 mmol) was stirred in CH_2Cl_2 (2m L) at rt for 30 min. The solution was stirred at –30 °C for 10 min and then *N*-iodosuccinimide (0.054 g, 0.24 mmol) and silver triflate (0.007 g, 0.032 mmol) were added. After 15 min, Et_3N was added and the solution was filtered and concentrated. The resulting residue was purified by (3:1 hexanes–EtOAc) to give **PGL-74** (0.075 g, 42%) as an oil. δ_H) 8.13 (dd, 2 H, *J* = 8.5, 1.5 Hz), 8.08 (dd, 2 H, *J* = 8.0, 1.5 Hz), 7.63 (d, 2 H, *J* = 7.5 Hz), 7.50 (d, 4 H, *J* = 9.5 Hz), 7.46 (d, 2 H, *J* = 7.7 Hz), 7.37 (app t, 2 H, *J* = 8.7 Hz), 7.33–7.24 (m, 4 H), 7.19 (app d, 2 H, *J* = 6.5 Hz), 7.07 (d, 2 H, *J* = 9.7 Hz), 6.96 (d, 2 H, *J* = 9.5 Hz), 5.60 (app s, 1 H), 5.54 (app d, 2 H, *J* = 8.7 Hz), 5.29 (s, 1 H), 5.11 (d, 1 H, *J* = 3.5 Hz), 5.07 (dd, 2 H, *J* = 11.0, 7.5 Hz), 4.72 (d, 1 H, 11.7 Hz), 4.62 (d, 1 H, *J* = 11.5 Hz), 4.50 (dd, 1H, *J* = 9.5, 3.5

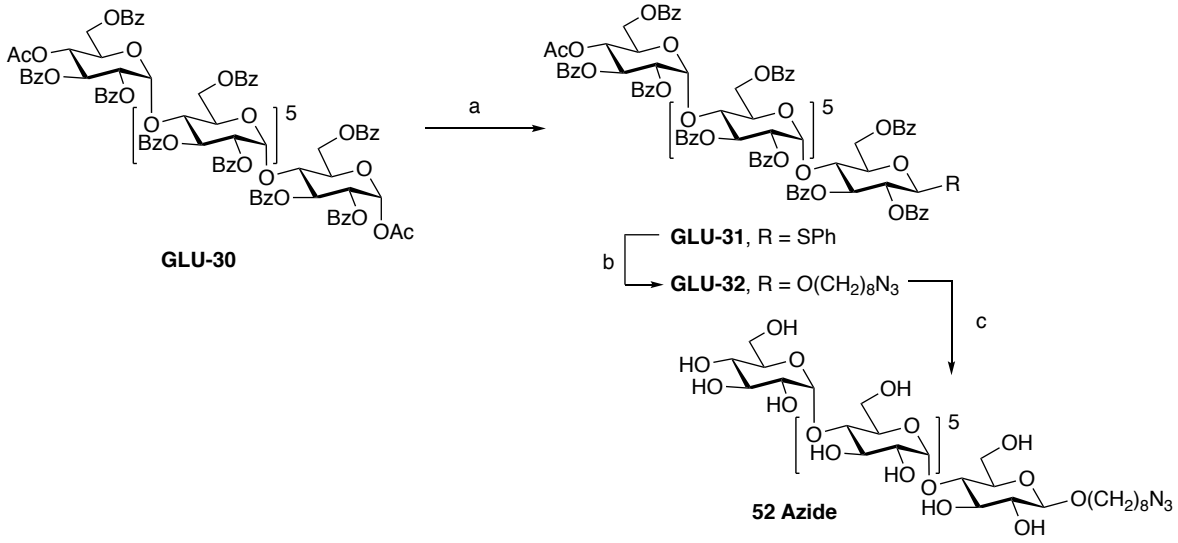
Hz), 4.18 (dd, 1 H, *J* = 9.0, 3.7 Hz), 3.85–3.97 (m, 2 H), 3.73 (app t, 1 H, *J* = 9.7 Hz), 3.57 (app t, 1H, *J* = 10.7 Hz), 3.51 (s, 3 H), 3.47 (app qd, 2 H, *J* = 10.5, 3.5 Hz), 3.40 (s, 3 H), 3.32 (s, 1 H), 3.28, (t, 2 H, *J* = 7.7 Hz), 3.22 (s, 3 H), 2.54 (t, 2 H, *J* = 7.5 Hz), 1.50–1.40 (m, 4 H), 1.36–1.27 (m, 12 H), 1.19 (d, 3 H, *J* = 6.7 Hz), 1.02 (d, 3 H, *J* = 6.5 Hz). HRMS (ESI) *m/z* calcd for (M+Na) $C_{63}H_{77}N_3O_{15}Na$: 1138.5247. Found: 1138.5234.

***p*-(8-Azidooctylphenyl) 2,3,4-tri-*O*-methyl-α-L-fucopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)- 4-*O*-benzyl-α-L-rhamnopyranoside (PGL-75)**. To a solution of **PGL-74** (0.060 g, 0.05 mmol) was stirred in CH_2Cl_2–CH_3OH (1:1, 1 mL) at rt before a solition of sodium methoxide was added until a pH of 8 was achieved. The mixture was concentrated and the residue was purified by chromatography (5:1 hexanes–EtOAc) to give **PGL-75** (0.04 g, 77%) as an oil. $[\alpha]_D$ –127.9 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.24 (m, 16 H), 7.07 (d, 2 H, *J* = 8.4 Hz), 6.95 (d, 2 H, *J* = 8.5 Hz), 5.44 (s, 1 H, H-1), 5.27 (d, 1 H, *J* = 3.1 Hz, H-1), 5.16 (s, 1 H, H-1), 5.10 (d, 1 H, *J* = 11.0 Hz), 4.79 (d, 1 H, *J* = 10.9 Hz), 4.62 (dd, 2 H, *J* = 10.9, 6.1 Hz), 4.24–4.14 (m, 2 H), 4.09–3.98 (m, 3 H), 3.92 (app dq, 1 H, *J* = 9.1, 6.3 Hz), 3.85 (app dq, 1 H, *J* = 12.6, 6.3 Hz), 3.66–3.60 (m, 2 H), 3.59 (s, 3 H), 3.55–3.49 (m, 5 H), 3.46 (s, 1H), 3.40 (s, 3 H), 3.25 (app t, 2 H, *J* = 6.9 Hz), 2.54 (app t, 2 H, *J* = 7.7 Hz), 2.31 (s, 1H), 2.27 (s, 1H), 1.58 (dd, 4 H, *J* = 14.4, 7.2 Hz), 1.37–1.27 (m, 11H), 1.25 (d, 3 H, *J* = 6.2 Hz), 1.16 (d, 3 H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.4, 138.7, 138.1, 136.8, 129.5, 128.7, 128.6, 128.1, 128.0, 127.9, 127.8, 116.4, 101.7 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 99.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 1171 Hz, C-1), 97.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 80.8, 80.3, 80.2, 80.0, 79.7, 79.2, 77.8, 75.7, 75.1, 71.7, 71.2, 68.8, 68.4, 67.3, 62.0, 59.7, 58.2, 51.7, 35.3, 31.8, 29.5, 29.3, 29.3, 29.0, 26.9, 18.2, 18.2, 16.8. HRMS (ESI) *m/z* calcd for (M+Na) $C_{49}H_{69}N_3O_{13}Na$: 930.4723. Found: 930.4711.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,3,4-tri-*O*-methyl-α-L-fucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (51 Squaramide) Treatment of **PGL-75** with H_2 and $Pd(OH)_2$ and then diethyl squarate and Et_3N as described for the synthesis of **26 Squaramide** gave **51 Squaramide** (61%, chromatography 4:96 CH_3OH–CH_2Cl_2) as a colorless oil. R_f 0.39 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –134.7 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.07 (d, 2 H, *J* = 8.6 Hz), 6.99–6.94 (m, 2 H), 6.25 (s, 1H), 5.44 (d, 1 H, *J* = 1.6 Hz, H-1), 5.19 (d, 1 H, *J* = 1.0 Hz, H-1), 5.14 (d, 1 H, *J* = 3.1 Hz, H-1), 4.77 (m, 2 H), 4.17 (d, 1 H, *J* = 1.5 Hz), 4.13 (s, 1H), 4.08 (q, 1 H, *J* = 6.6 Hz), 4.04 (dd, 1 H, *J* = 9.4, 3.2

Hz), 3.87 (app dq, 1 H, J = 9.4, 6.2 Hz), 3.82–3.79 (m, 1H), 3.77 (dd, 1 H, J = 9.4, 3.3 Hz), 3.70 (dd, 1 H, J = 9.6, 2.3 Hz), 3.68–3.63 (m, 4 H), 3.59 (s, 3 H), 3.58 (s, 3 H), 3.51 (s, 3 H), 3.47 (d, 1 H, J = 1.1 Hz), 3.40 (m, 1H), 2.60–2.47 (m, 5 H), 1.58 (d, 4 H, J = 5.8 Hz), 1.45 (app t, 3 H, J = 7.1 Hz), 1.34 (d, 3 H, J = 6.2 Hz), 1.30 (s, 8 H), 1.27 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 189.7, 182.8, 177.7, 172.6, 154.5, 136.8, 129.5, 116.5, 102.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 101.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 169 Hz, C-1), 98.1 ($^1J_{C\text{-}1,H\text{-}1}$ = 172 Hz, C-1), 83.1, 81.1, 79.4, 79.2, 79.0, 72.2, 71.7, 71.2, 71.0, 69.9, 69.2, 69.0, 67.7, 62.1, 60.4, 57.9, 45.1, 35.3, 31.7, 30.8, 29.5, 29.3, 29.2, 26.5, 17.9, 17.88, 16.9, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{41}H_{63}NO_{16}Na$: 848.4039. Found: 848.4027.

44. Synthesis of 52



Scheme S57. Synthesis of **52 Azide**. a) PhSTMS, ZnI, $ClCH_2CH_2Cl$, 95%, b) 8-Azido-octanol, NIS, AgOTf, TfOH, CH_2Cl_2; then CF_3CO_2H, CH_2Cl_2 48%; c) $NaOCH_3$, CH_3OH, CH_2Cl_2, 73%.

Phenyl 2,3,6-tri-*O*-benzoyl-4-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)- 2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (GLU-31). To a solution of **GLU-30**[42] (0.29 g, 0.085 mmol) in 1,2-dichloroethane (7 mL) was added 4 Å molecular sieves (0.23 g) and the solution was stirred at rt for 30 min. Zinc iodide (0.16 g, 0.5 mmol) was added followed by PhSTMS (0.1 mL, 0.53 mmol) and the mixture was stirred at rt overnight before being diluted with 1,2-dichloroethane (10 mL) and filtered through Celite. The filtrate was washed with a satd aq $NaHCO_3$ soln (15 mL), water (15 mL), dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (54:46 hexanes–EtOAc) to give **GLU-31** (0.275 g, 95%) as a foam. R_f 0.61 (1:1, hexane–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.30−8.20 (m, 8 H), 8.16−8.12 (m, 2 H), 8.10−8.02 (m, 4 H), 7.90−7.82 (m, 4 H), 7.78−7.06 (m, 92 H), 6.03−5.90 (m, 5 H), 5.86 (dd, 1 H, J = 9.4, 9.4 Hz), 5.77−5.70 (m, 2 H), 5.66−5.61 (m, 4 H), 5.59 (d, 1 H, J = 3.9 Hz), 5.44 (dd, 1 H, J = 9.7, 9.7 Hz), 5.26−5.20 (m, 2 H), 5.14−5.02 (m, 6 H), 5.0 (d, 1 H, J = 9.7 Hz), 4.91 (dd, 2 H, J = 12.1, 12.1 Hz), 4.84−4.70 (m, 3 H), 4.64−4.22 (m, 20 H), 4.21−4.16 (m, 1 H), 4.14−4.08

(m, 1 H), 1.90 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.3, 165.8(0), 165.8, 165.6, 165.5(0), 165.5, 165.4, 165.3, 165.1, 164.9, 164.6, 164.5, 133.5, 133.4, 133.3, 133.1, 133.0, 132.9, 132.8, 131.4, 130.2, 130.1, 130.0, 129.9(2), 129.9, 129.8, 129.7(2), 129.7, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 128.7(3), 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 96.9 (C-1), 96.8(3) (C-1), 96.7 (C-1), 96.6 (C-1), 96.4 (C-1), 85.4, 76.7, 76.2, 73.8, 73.4, 73.3, 73.2, 72.0, 71.9, 71.6, 70.9, 70.8, 70.7(1), 70.7, 70.6, 70.3, 70.2, 70.2 (4), 70.1, 69.9, 69.8, 69.0, 68.2, 63.0, 62.8, 62.4, 62.3, 62.2, 61.8, 20.5. HRMS (ESI) *m/z* calcd for (M+Na_2) $C_{197}H_{162}O_{57}S\ Na_2$:1758.4642. Found: 1758.4671.

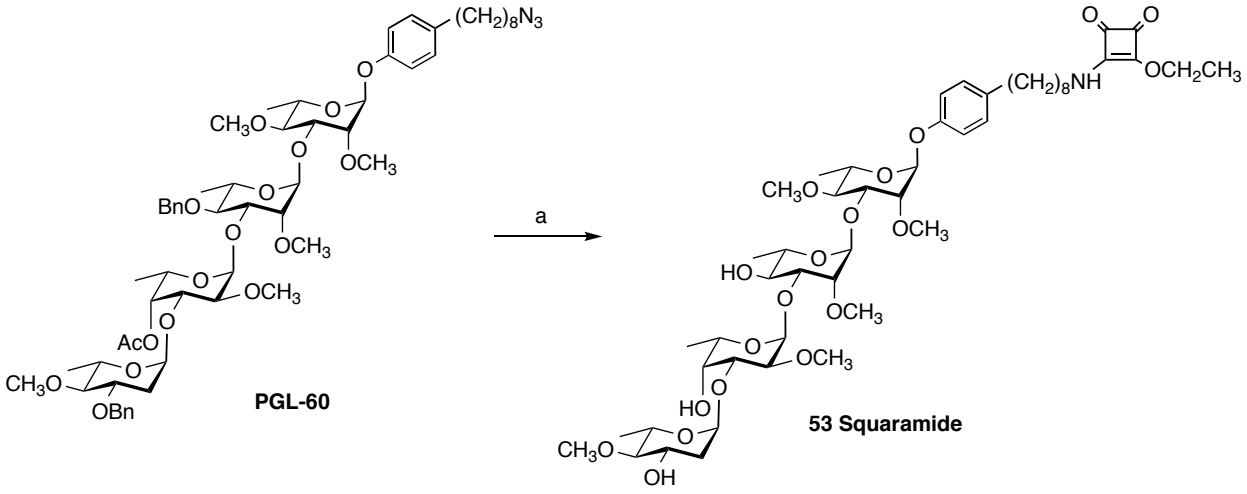
8-Azidooctyl 2,3,6-tri-*O*-benzoyl-4-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)- 2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranoside (GLU-32). 8-Azido-1-octanol (0.017 g, 0.1 mmol) and thioglycoside **GLU-31** (0.07 g, 0.02 mmol) were dried under vacuum in the presence of P_2O_5 for 6 h. After drying, 1,2-dichloroethane (3.5 mL) was added followed by powdered 4 Å molecular sieves (0.18 g) and the solution was stirred for 30 min. The reaction mixture was then cooled to 0 °C and *N*-iodosuccinimide (0.023 g × 4 times, 0.1 mmol) and silver triflate (10 mg × 4 times, 0.08 mmol) were added over 5 h. During this period, 5 μL of a solution of trifluoromethanesulfonic acid in CH_2Cl_2 (30 μL in 2 mL of CH_2Cl_2 stock solution) was also added five times. When the reaction was complete, Et_3N was added until the pH of the solution was slightly basic (as determined by wet pH paper) and then the mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. The filtrate was washed with a satd aq soln of $Na_2S_2O_3$ (15 mL), water (15 mL) and brine (15 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by chromatography (3:2 hexanes–EtOAc) to provide **GLU-32** and the corresponding orthoester in an approximately 3.4:1 glycoside–orthoester ratio; R_f 0.37 (3:2 hexane–EtOAc, three runs). This mixture was dissolved in CH_2Cl_2 (6 mL), cooled to 0 °C and trifluoroacetic acid (0.03 mL) was added and the solution was stirred at 0 °C for 3 h. The reaction mixture was poured into a satd aq $NaHCO_3$ soln (15 mL) and extracted with CH_2Cl_2 (15 mL). The organic layer was washed with water (15 mL), dried (Na_2SO_4), filtered and concentrated to a residue that was purified by chromatography (67:43 hexane–EtOAc) to yield **GLU-32** (0.034 g, 48% over two steps) as a foam. ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.30−8.18 (m, 8 H), 8.15−8.12 (m, 2 H),

8.08−8.01 (m, 4 H), 7.91−7.82 (m, 4 H), 7.76−7.72 (m, 2 H), 7.70−7.04 (m, 85 H), 6.02−5.86 (m, 8 H), 5.74−5.66 (m, 2 H), 5.65−5.58 (m, 5 H), 5.42 (dd, 1 H, *J* = 9.7, 9.7 Hz), 5.28 (dd, 1 H, *J* = 7.5, 9.2 Hz), 5.22 (dd, 1 H, *J* = 3.9, 10.5 Hz), 5.14−4.96 (m, 6 H), 4.90−4.84 (m, 2 H), 4.82−4.68 (m, 4 H), 4.64−4.34 (m, 13 H), 4.30−4.14 (m, 7 H), 4.09−4.04 (m, 1 H), 3.87 (ddd, 1 H, *J* = 6.2, 9.7, 12.3 Hz), 3.49 (ddd, 1 H, *J* = 6.4, 9.5, 13.4 Hz), 3.22 (dd, 1 H, *J* = 7.0, 7.0 Hz), 1.89 (s, 3 H), 1.56 −1.42 (m, 4 H), 1.27−1.03 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.3, 165.9, 165.8(3), 165.7(8), 165.7(6), 165.7(3), 165.7(0), 165.6, 165.5, 165.4(4), 165.4(2), 165.4(0), 165.3, 165.2, 165.0, 164.7, 164.6,(1), 164.6, 164.5(4), 164.5, 133.4, 133.3(3), 133.3(0), 133.3, 133.1, 133.0(0), 133.0, 132.9(3), 132.9, 132.8(6), 132.8, 132.0, 129.9(2), 129.9, 128.7(8), 128.7(6), 129.7(2), 129.7, 129.6(2), 129.6, 129.5(3), 129.5, 129.3, 129.1, 128.8, 128.7(3), 128.7(0), 128.7, 128.6, 128.4(1), 128.4, 128.3(4), 128.3, 128.2(3), 128.2, 128.1(4), 128.1, 128.0(9), 128.0, 127.9, 127.8, 100.6 (C-1), 96.8(8) (C-1), 96.8(5) (C-1), 96.8(2) (C-1), 96.8 (C-1), 96.6(8) (C-1), 96.6(5) (C-1), 96.3 (C-1), 75.1, 73.8, 73.6, 73.4, 73.3(1), 73.3, 73.2, 73.0, 72.4, 71.9(4), 71.8(8), 71.8, 71.6, 70.9(3), 70.9, 70.8(4), 70.8(1), 70.7(9), 70.7(5), 70.7, 70.6, 70.1(7), 70.1(5), 70.1(3), 70.1, 69.9(0), 69.9, 69.0, 68.2, 63.0, 62.8, 62.7, 62.4, 62.3, 62.2, 61.8, 51.4, 29.7, 29.3, 29.0, 28.9, 28.8(0), 28.8, 26.5, 25.7, 20.5. HRMS (ESI) *m/z* calcd for $(M+Na_2)^{2+}$ $C_{199}H_{173}N_3O_{58}Na_2$: 1789.0232. Found: 1789.0245.

8-Azidooctyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (52 Azide). To a solution of **GLU-32** (0.034 g, 0.01 mmol) in CH_2Cl_2–CH_3OH (7:3, 8 mL) was added 1M methanolic sodium methoxide until the pH of the reaction mixture was 8–9 (as determined by wet pH paper). Additional CH_3OH (12 mL in 2 portions) was added as the reaction progressed to aid solubility of the product as it formed. The reaction mixture was stirred for 24 h, neutralized by the addition of Amberlite IR 120 H+ resin, filtered and then concentrated to give a crude residue that was dried under vacuum for 3 h before purification by C-18 chromatography (1:1 water–CH_3OH) to yield **52 Azide** (9.1 mg, 73%) as a fluffy solid. ^{1}H NMR (500 MHz, D_2O, δ_H) 5.40−5.35 (m, 6 H, 6 × H-1 α), 4.45 (d, 1 H, *J* = 8.1 Hz, H-1β), 3.98−3.54 (m, 42 H), 3.40 (dd, 1 H, *J* = 9.4, 9.4 Hz), 3.34−3.24 (m, 3 H), 1.70−1.55 (m, 4 H), 1.40−1.29 (m, 8 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 102.1 (C-1), 99.8 (C-1), 99.6(9) (C-1), 99.6(5) (C-1), 99.5 (C-1), 77.0, 76.9(3), 76.9, 76.8, 76.3, 74.6, 73.3(8), 73.3(6), 73.1, 72.9, 72.8, 71.8, 71.6, 71.5, 71.3, 71.2, 70.7, 69.4, 60.8, 60.5(2), 60.5, 60.4, 51.3,

28.7, 28.3, 28.2, 28.0, 25.9, 25.0; HRMS (ESI) *m/z* calcd for $(M+Na)^+$ $C_{50}H_{87}N_3O_{36}Na$: 1328.4961. Found: 1328.4951.

45. Synthesis of 53

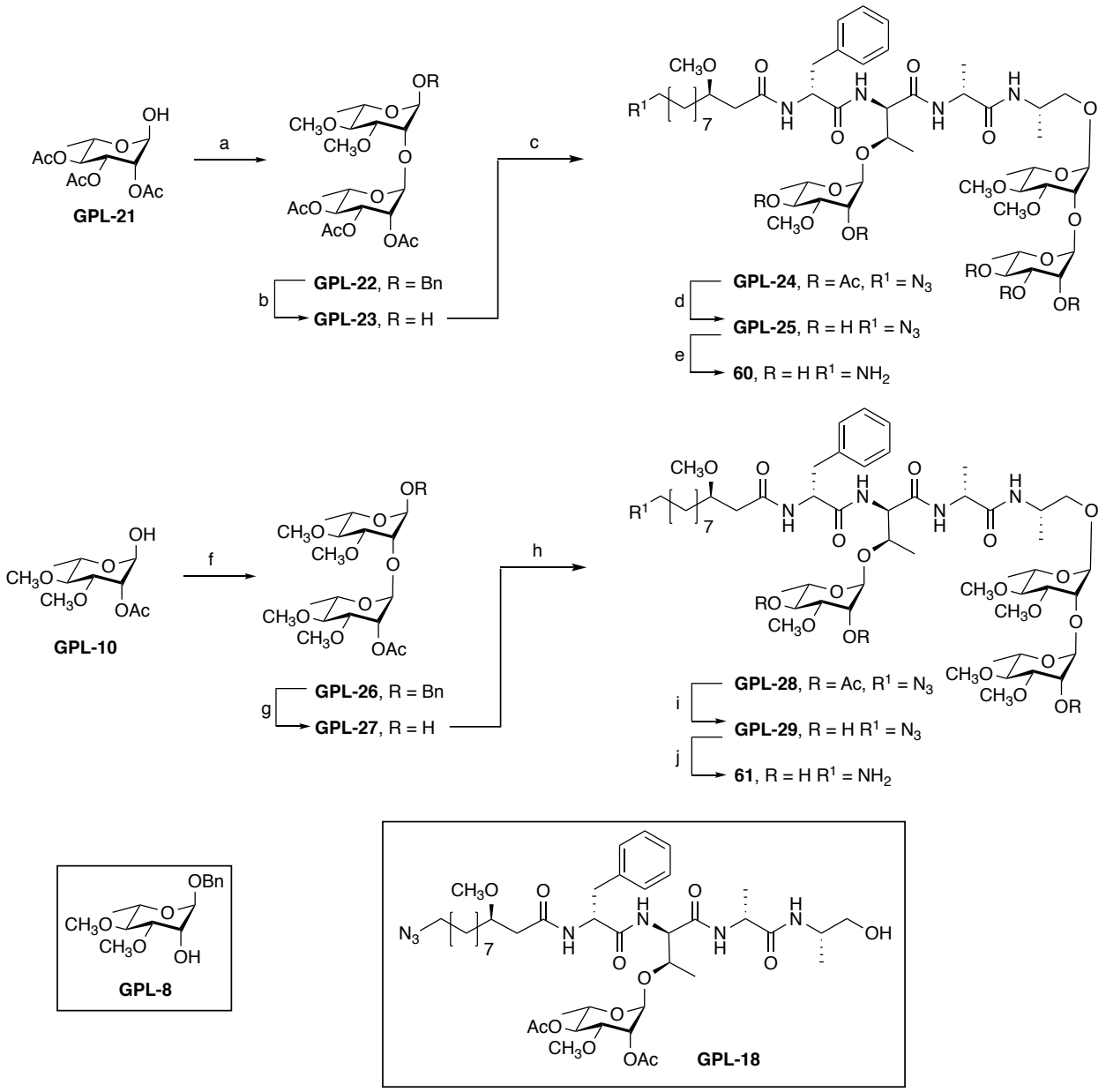


Scheme S58. Synthesis of **53 Squaramide**. a) H_2, $Pd(OH)_2$–C, CH_2Cl_2, CH_3OH; then NH_3, CH_3OH, Parr apparatus, heat; then diethyl squarate, CH_3CH_2OH, 40%.

4-[8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl]phenyl 2,6-dideoxy-4-*O*-Me-α-L-*arabino*-hexopyranosyl-(1→3)-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (53 Squaramide). A suspension of **PGL-60** (50 mg) and 20% $Pd(OH)_2$–C (50 mg) in 1:1 CH_2Cl_2–CH_3OH (10 mL) was stirred overnight under H_2 (1 atm) at rt. The reaction mixture was filtered and the filtrate was concentrated to give a colorless oil. A solution of the resulting oil in CH_3OH (15 mL) in a Parr apparatus at – 40 °C was bubbled with NH_3 gas for 30 min and sealed. The reaction mixture was stirred at 65 °C for 5 d and concentrated. To the resulting residue in absolute ethanol (4 mL) at rt was added diethyl squarate (67 μL, 455 μmol) and Et_3N (13 μL, 91 μmol). The reaction mixture was stirred at rt for 4 h and concentrated. The resulting residue was purified by chromatography (4:96 CH_3OH–CH_2Cl_2) to yield **53 Squaramide** (18 mg, 40%) as a yellow oil. R_f 0.55 (1:9 CH_3OH–CH_2Cl_2); $[\alpha]_D$ –130.0 (*c* = 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 7.08 (d, 2 H, *J* = 8.6 Hz), 6.97 (d, 2 H, *J* = 8.6 Hz), 5.46 (d, 1 H, *J* = 1.6 Hz, H-1), 5.17 (s, 1 H, H-1), 5.07–5.08 (m, 2 H, H-1, H-1), 4.77 (m, 2 H), 4.18 (m, 2 H), 4.12 (dd, 1 H, *J* = 9.6, 3.3 Hz), 4.01–3.94 (m, 1H), 3.89–3.85 (m, 2 H), 3.83 (m, 1H), 3.77–3.70 (m, 2 H), 3.70–3.66 (m, 2 H), 3.65–3.61 (m, 2 H), 3.60 – 3.42 (m, 17 H), 3.23 (app t, 1 H, *J* = 9.6 Hz), 2.74 (app t, 1 H, *J* = 9.2 Hz), 2.54 (app t, 2 H, *J* = 7.6 Hz), 2.34 (m, 2 H), 2.18–2.09 (m, 2 H), 1.78 (app td, 1 H, *J* = 13.1, 3.8 Hz), 1.58 (s,

4 H), 1.45 (app t, 3 H, J = 7.1 Hz), 1.35 (d, 3 H, J = 6.2 Hz), 1.33–1.25 (m, 17 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.7, 136.8, 129.5, 116.4, 101.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 99.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 95.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 93.0 ($^1J_{C\text{-}1,H\text{-}1}$ = 171 Hz, C-1), 88.1, 83.6, 82.5, 80.8, 80.6, 79.0, 77.8, 73.0, 71.9, 69.9, 69.2, 69.0, 68.8, 68.6, 67.6, 66.4, 61.2, 61.0, 60.3, 59.2, 59.0, 45.1, 37.6, 35.3, 31.8, 30.8, 29.5, 29.3, 29.3, 26.5, 18.3, 18.1, 18.06, 16.7, 16.1. HRMS (ESI) *m/z* calcd for (M+Na) $C_{49}H_{77}NO_{19}Na$: 1006.4982. Found: 1006.4973.

46. Synthesis of 60 and 61



Scheme S59. Synthesis of **60** and **61**. a) CCl_3CN, DBU, CH_2Cl_2; then **GPL-8**, TMSOTf, CH_2Cl_2, 77%; b) H_2, $Pd(OH)_2$–C, CH_3OH, 56%; c) CCl_3CN, DBU, CH_2Cl_2; then **GPL-18**, TMSOTf, CH_2Cl_2, 89%; d) $NaOCH_3$, CH_3OH, CH_2Cl_2, 80%.; e) H_2, $Pd(OH)_2$–C, EtOAc, THF, CH_3OH, quant.; f) CCl_3CN, DBU, CH_2Cl_2 then **GPL-8**, TMSOTf, CH_2Cl_2, 36%; g) H_2, $Pd(OH)_2$–C, CH_3OH, 38%; h) CCl_3CN, DBU, CH_2Cl_2 then **GPL-18**, TMSOTf, CH_2Cl_2, 50%; i) $NaOCH_3$, CH_3OH, CH_2Cl_2, 89%.; j) H_2, $Pd(OH)_2$–C, EtOAc, THF, CH_3OH, quant.

Benzyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-22). Reducing sugar **GPL-21**[43] (400 mg, 1.38 mmol) was dissolved in CH_2Cl_2 and trichloroacetonitrile (275 μL, 2.76 mmol) and DBU (43 μL, 0.28 mmol) were added. The solution was stirred at rt for 1 h and then concentrated. The resulting oil was purified by chromatography (1:1 hexanes–EtOAc) to give the corresponding glycosyl trichloroacetimidate (465 mg, 78%) as a colorless syrup, which was used immediately in the glycosylation; R_f 0.71 (1:1 hexanes–EtOAc). The trichloroacetimidate derived from **GPL-21** (380 mg, 0.87 mmol) and **GPL-8** (Scheme S48, 270 mg, 1.05 mmol) were dissolved in dry CH_2Cl_2 (6 mL) containing 4Å molecular sieves and the solution was cooled to –20 °C. To this mixture, a 1.1 M solution of TMSOTf in CH_2Cl_2 (287 μL, 0.26 mmol) was added dropwise and the mixture was stirred for 1 h while warming to rt. The solution was filtered and the filtrate was washed with CH_2Cl_2, a satd aq $NaHCO_3$ soln and water. The organic phase was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (1:1 hexanes–EtOAc) to give **GPL-22** (372 mg, 77%) as a colorless syrup. R_f 0.53 (1:1 hexanes–EtOAc); $[\alpha]_D$ –85.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.37–7.29 (m, 5 H), 5.38 (dd, 1 H, *J* = 3.4, 1.8 Hz), 5.29 (dd, 1 H, *J* = 10.1, 3.5 Hz), 5.02 (app t, *J* = 9.9 Hz), 4.95 (d, 1 H, *J* = 1.7 Hz, H-1), 4.79 (d, 1 H, *J* = 1.8 Hz), 4.69 (d, 1 H, *J* = 12.0 Hz), 4.47 (d, 1 H, *J* = 12.0 Hz), 4.00 (dd, 1 H, *J* = 3.0, 2.0 Hz), 3.85 (dq, 1 H, *J* = 9.8, 6.2 Hz), 3.63 (dq, 1 H, *J* = 9.4, 6.2 Hz), 3.55 (s, 3 H), 3.43 (s, 3 H), 3.50 (dd, 1 H, *J* = 9.3, 3.1 Hz), 3.15 (app t, 1 H, *J* = 9.4 Hz), 2.14 (s, 3 H), 2.03 (s, 3 H), 1.98 (s, 3 H), 1.31 (d, 3 H, *J* = 6.2 Hz), 1.09 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.2, 170.1(3), 170.0(6), 137.3, 128.6, 128.1, 128.0, 99.2 (C-1), 97.9 (C-1), 82.3, 81.3, 75.1, 71.3, 69.9, 69.2, 69.0, 68.5, 66.8, 61.1, 58.2, 21.1, 20.9(4), 20.8(8), 17.9, 17.4 (C-6). HRMS (ESI) *m/z* calcd for (M+Na) $C_{27}H_{38}NaO_{12}$: 577.2255. Found: 577.2242.

2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-methyl-α-L-rhamnopyranose (GPL-23). Disaccharide **GPL-22** (295 mg, 0.53 mmol) was dissolved in CH_3OH (15 mL) and 20% $Pd(OH)_2$–C (75 mg) was added. The mixture was degassed and stirred under H_2 (1 atm) overnight and then the solution was filtered and the filtrate was concentrated to a residue that was purified by chromatography (3:1 EtOAc–hexanes) to give **GPL-23** (137 mg, 56%) as a colorless syrup (4:1 α:β mixture). R_f 0.52 (3:1 EtOAc–hexanes). Data for α-isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.39 (dd, 1 H, *J* = 3.4, 1.8 Hz, H-1), 5.31 (dd, 1 H, *J* = 10.0, 3.5 Hz), 5.16 (d, 1 H, *J* = 1.8 Hz, H-1), 5.05 (app t, 1 H, *J* = 9.9 Hz), 5.00 (d, 1 H, *J* = 1.8 Hz, H-1),

4.02 (dd, 1 H, *J* = 2.8, 2.1 Hz), 3.94 (dq, 1 H, *J* = 9.8, 6.2 Hz), 3.79 (dq, 1 H, *J* = 9.4, 6.2 Hz, 1 H), 3.55 (s, 3 H), 3.44 (s, 3 H), 3.52 (dd, 1 H, *J* = 9.3, 3.0 Hz), 3.14 (app t, 1 H, *J* = 9.4 Hz), 2.15 (s, 3 H), 2.04 (s, 3 H), 1.98 (s, 3 H), 1.29 (d, 3 H, *J* = 6.2 Hz), 1.20 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.1(8), 170.1(5), 170.1, 99.1 (C-1), 93.7 (C-1), 82.3, 80.9, 75.1, 71.3, 69.9, 69.2, 68.4, 66.9, 61.1, 58.2, 21.1, 21.0, 20.9, 18.0, 17.6. HRMS (ESI) *m/z* calcd for (M+Na) $C_{20}H_{32}NaO_{12}$: 487.1786. Found: 487.1776.

***N*$^{\alpha}$-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(2,4-di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-24)**. A solution of **GPL-23** (50 mg, 0.108 mmol), trichloroacetonitrile (21 μL, 0.216 mmol) and DBU (4.0 μL, 0.023 mmol) in CH_2Cl_2 (3 mL) was stirred at rt for 1 h and then concentrated. The resulting oil was purified by chromatography (2.5:1 EtOAc–hexanes) to give the corresponding glycosyl trichloroacetimidate (65 mg, 98%) as a colorless syrup, which was used immediately in the glycosylation. R_f 0.74 (2.5:1 EtOAc–hexanes). The trichloroacetimidate derived from **GPL-23** (8.5 mg, 0.014 mmol) and **GPL-18** (Scheme S51, 10 mg, 0.011 mmol) in CH_2Cl_2 (1.5 mL) containing 4Å molecular sieves was cooled to 0 °C. A 0.5 solution of TMSOTf (1.2 μL, 0.0006 mmol) was added. The mixture was stirred for 3 h while warming to rt, neutralized with DIPEA (1 μL), concentrated and the resulting residue was purified by chromatography (CH_2Cl_2–CH_3OH 19:1) to give **GPL-24** (13 mg, 89%) as a colorless powder after freeze drying (α:β 3:1). R_f 0.60 (CH_2Cl_2–CH_3OH 9:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.37–7.23 (m, 5 H), 7.05 (d, 1 H, *J* = 7.6 Hz), 6.79 (d, 1 H, *J* = 5.7 Hz), 6.76 (d, 1 H, *J* = 11.4 Hz), 6.47 (d, 1 H, *J* = 8.0 Hz), 5.39 (dd, 1 H, *J* = 3.4, 1.9 Hz), 5.31 (dd, 1 H, *J* = 10.0, 3.5 Hz), 5.24 (dd, 1 H, *J* = 3.3, 2.0 Hz), 5.05 (app t, 1 H, *J* = 10.0 Hz), 4.99 (d, 1 H, *J* = 1.6 Hz), 4.95 (app t, 1 H, *J* = 9.7 Hz), 4.87 (d, 1 H, *J* = 1.6 Hz), 4.72 (d, 1 H, *J* = 1.6 Hz), 4.49–4.51 (m, 1 H), 4.44–4.47 (m, 1 H), 4.37–4.41 (m, 1 H), 4.23–4.27 (m, 1 H), 4.11–4.15 (m, 1 H), 4.00 (app t, 1 H, *J* = 2.4 Hz), 3.92 (dq, 1 H, *J* = 9.8, 6.2 Hz), 3.74 (dq, 1 H, *J* = 9.5, 6.4 Hz), 3.59–3.51 (m, 6 H), 3.50–3.42 (m, 6 H), 3.33 (s, 3 H), 3.27–3.20 (m, 6 H), 3.14 (app t, 1 H, *J* = 9.3 Hz), 2.98 (dd, 1 H, *J* = 14.3, 9.3 Hz), 2.44 (dd, 1 H, *J* = 15.3, 3.6 Hz), 2.28 (dd, 1 H, *J* = 15.2, 7.1 Hz), 2.15 (s, 3 H), 2.14 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 1.98 (s, 3 H), 1.62–1.55 (m, 2 H), 1.40–1.13 (m, 30 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 173.2, 172.3, 171.5, 170.6, 170.1(7), 170.1(5), 170.1(2), 170.1(0), 168.3, 135.9, 129.21, 129.17, 127.7, 99.1(4) (C-1), 99.0(7) (C-1), 95.7 (C-1), 82.3, 81.3, 77.7, 76.8, 74.7, 72.5, 71.7, 71.3, 70.5, 70.0,

69.2, 68.5, 68.4, 67.6, 67.0, 61.1, 58.0, 58.7, 57.7, 56.3(2), 56.3, 51.6, 49.4, 45.0, 40.5, 37.2, 32.3, 29.59, 29.50, 29.2, 26.8, 25.1, 21.2, 21.1(2), 21.1(1), 21.0, 20.9, 18.0, 17.9, 17.7, 17.6(4), 17.6(2), 14.7. HRMS (ESI) *m/z* calcd for (M+H) $C_{62}H_{98}N_7O_{24}$: 1324.6658. Found: 1324.6650.

N^{α}-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-25). To a solution of **GPL-24** (6.0 mg, 0.0045 mmol) in CH_2Cl_2–CH_3OH (4:0.5, 4.5 mL) was added 1M sodium methoxide solution (0.02 mmol) and the mixture was stirred at rt for 24 h. The solution was then carefully neutralized by adding Amberlite IR-120 H^+ resin and filtered. The filtrate was concentrated to a residue that was purified by chromatography (10:1 CH_2Cl_2–CH_3OH) to obtain **GPL-25** (4 mg, 80%) as an oil. R_f 0.05 (12:1 CH_2Cl_2–CH_3OH); ^{1}H NMR (500 MHz, CD_3OD + $CDCl_3$, δ_H) 7.32–7.20 (m, 5 H), 4.92 (d, 1 H, *J* = 1.6 Hz), 4.88 (d, 1 H, *J* = 1.6 Hz), 4.78 (d, 1 H, *J* = 1.6 Hz), 4.70–4.64 (m, 1 H), 4.46–4.40 (m, 1 H), 4.26–4.22 (m, 1 H), 4.12–3.98 (m, 3 H), 3.97–3.90 (m, 2 H), 3.70–3.64 (m, 2 H), 3.58–3.33 (m, 15 H), 3.29–3.23 (m, 7 H), 3.20–3.12 (m, 1 H), 3.08 (dd, 1 H, *J* = 9.5, 9.5 Hz), 2.94–2.87 (m, 1 H), 2.40 (dd, 1 H, *J* = 6.7, 14.4 Hz), 2.32–2.27 (m, 2 H), 1.62–1.54 (m, 4 H), 1.40–1.15 (m, 27 H); ^{13}C NMR (125 MHz, CD_3OD + $CDCl_3$, δ_C) 172.6(3), 172.6, 172.2, 169.6, 136.6, 129.0(1), 129.0, 128.3, 128.2, 126.7, 101.8 (C-1), 99.2 (C-1), 97.1 (C-1), 84.8, 82.2, 82.0, 80.9, 80.2, 80.0, 73.7, 73.0, 72.6, 71.9, 71.6, 70.9, 70.8, 70.6, 70.4, 70.2, 68.9(0), 68.9, 68.4, 97.8, 67.4, 67.2, 60.2, 60.1, 57.7, 57.4, 57.3, 57.1, 56.6, 56.4, 56.1, 54.6, 51.2, 49.6, 49.4, 45.0, 40.2, 37.1, 33.1, 31.7, 29.4, 29.3, 29.2, 29.1, 28.9, 28.6, 26.5, 24.8, 22.4, 17.8, 17.5, 17.3, 17.1(9), 17.1(5), 17.0, 16.7, 16.3, 14.3, 14.1, 13.4. HRMS (ESI) *m/z* calcd for (M+Na) $C_{52}H_{87}N_7NaO_{19}$: 1136.5949. Found: 1136.5940.

N^{α}-(*R*)-11-amino-3-methoxyundecanoyl-D-phenylalaninyl-(3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (60). To a solution of **GPL-25** (4.0 mg) in EtOAc (3 mL), THF (2 mL), CH_3OH (0.5 mL), H_2O (30 μL), and pyridine (40 μL) was added 20% $Pd(OH)_2$–C (8 mg). The mixture was stirred under H_2 (1 atm) for 1 h. The catalyst was filtered off and washed with THF. The combined filtrate was concentrated and dried under vacuum for 4 h to obtain **60** (4.0 mg, quant.) as an oil. HRMS (ESI) *m/z* calcd for (M+H) $C_{52}H_{89}N_5O_{19}$: 1088.6225. Found: 1088.6222.

Benzyl 2-*O*-acetyl-3,4,-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-26). Reducing sugar **GPL-10** (Scheme S48, 444 mg, 1.90 mmol) was dissolved in CH_2Cl_2 and trichloroacetonitrile (378 μL, 3.79 mmol) and DBU (60 μL, 0.38 mmol) were added. The solution was stirred at rt for 1 h and then concentrated. The resulting oil was purified by chromatography (EtOAc) to give the corresponding glycosyl trichloroacetimidate (695 mg, 97%) as a colorless syrup, which was used immediately in the glycosylation; R_f 0.78 (EtOAc). A solution of the trichloroacetimidate derived from **GPL-10** (Scheme S48, 622 mg, 1.64 mmol) and **GPL-8** (Scheme S48, 695 mg, 2.14 mmol) were dissolved in dry CH_2Cl_2 (4 mL) containing 4Å molecular sieves and cooled to –20 °C. A 0.5 M solution of TMSOTf in dry CH_2Cl_2 (368 μL, 0.18 mmol) was added dropwise. The mixture was stirred for 3 h while warming to rt before being filtered. The filtrate was diluted with CH_2Cl_2 (15 mL) and the resulting solution was washed with satd aq $NaHCO_3$ (30 mL) and water (30 mL). The organic phase was dried (Na_2SO_4), evaporated and the resulting residue was purified by chromatography (3:1 toluene–acetone) to give **GPL-26** as colorless syrup, as a 4:1 α:β mixture. To purify the compound, the mixture was deacetylated, and then reacetylatated. Thus, impure **GPL-26** (586 mg, 1.18 mmol) was dissolved in CH_2Cl_2–CH_3OH (4:1, 5 mL) and sodium methoxide (13 mg, 0.24 mmol) was added. After stirring at rt for 4 h, the solution was neutralized by the addition of Amberlite IR 120 H^+. The resin was filtered off and the filtrate was concentrated to give a residue that was purified by chromatography (3:1 toluene–acetone) to give the product as a colorless syrup; R_f 0.38 (3:1 toluene–acetone). Next the deacetylated derivative of **GPL-26** (273 mg, 0.60 mmol) was dissolved in pyridine (2 mL) and Ac_2O (2 mL) and stirred at rt overnight. The solution was diluted with CH_2Cl_2 (15 mL) and washed with 5% HCl (20 mL), sat aq $NaHCO_3$ (20 mL) and water (20 mL). The organic phase was dried (Na_2SO_4) and evaporated to yield pure **GPL-26** (296 mg, 36%) as a colorless oil. R_f = 0.46 (3:1 toluene–acetone); $[\alpha]_D$ –84.1 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.36–7.29 (m, 5 H), 5.36 (dd, 1 H, *J* = 3.4, 1.9 Hz), 4.94 (d, 1 H, *J* = 1.8 Hz), 4.79 (d, 1 H, *J* = 1.8 Hz), 4.67 (d, 1 H, *J* = 11.9 Hz), 4.44 (d, 1 H, *J* = 11.9 Hz), 3.99 (dd, 1 H, *J* = 3.1, 2.0 Hz), 3.63–3.58 (m, 2 H), 3.56–3.53 (m, 4 H), 3.53–3.50 (m, 4 H), 3.43 (s, 3 H), 3.42 (s, 3 H), 3.09 (app t, 1 H, *J* = 9.4 Hz), 3.02 (app t, 1 H, *J* = 9.5 Hz), 2.12 (s, 3 H), 1.28 (d, 3 H, *J* = 6.2 Hz), 1.20 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.3, 137.4, 128.6, 128.0(4), 127.9(8), 99.1 (C-1), 98.1 (C-1),

82.3, 82.0, 81.3, 79.4, 73.9, 69.1, 68.8, 68.2, 61.0(0), 60.9(6), 57.9, 57.8, 21.3, 18.05, 17.87. HRMS (ESI) *m/z* calcd for (M+Na) $C_{25}H_{38}NaO_{10}$: 521.2357. Found: 521.2345.

2-*O*-Acetyl-3,4,-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-methyl-α-L-rhamnopyranose (GPL-27). Disaccharide **GPL-26** (100 mg, 0.25 mmol) was dissolved in CH_3OH (15 mL) and 20% $Pd(OH)_2$–C (25 mg) was added. The mixture was degassed and stirred under H_2 (1 atm) overnight. The solution was filtered and the filtrate was concentrated to give a residue that was purified by chromatography (2.5:1 EtOAc–hexanes) to give **GPL-27** (38 mg, 38%) as a colorless syrup (6:4 α:β ratio). R_f 0.40 (2.5:1 EtOAc–hexanes). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.36 (dd, 1 H, *J* = 3.4, 1.9 Hz), 5.15 (d, 1 H, *J* = 1.9 Hz, H-1), 4.98 (d, 1 H, *J* = 1.8 Hz, H-1), 4.01 (dd, 1 H, *J* = 3.0, 2.1 Hz), 3.79 (dq, 1 H, *J* = 9.4, 6.1 Hz, 1 H), 3.68 (dq, 1 H, *J* = 9.5, 6.2 Hz, 1 H), 3.59–3.52 (m, 8 H), 3.44 (s, 3 H), 3.43 (s, 3 H), 3.09 (app t, 1 H, *J* = 9.6 Hz), 3.05 (app t, 1 H, *J* = 9.5 Hz), 2.13 (s, 3 H), 1.9 (d, 3 H, *J* = 6.2 Hz), 1.28 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.4, 99.0 (C-1), 93.7 (C-1), 82.3, 81.74, 80.8, 79.4, 73.9, 68.8, 68.1, 61.1, 61.0, 57.9, 57.8, 21.3, 18.1, 18.0. HRMS (ESI) *m/z* calcd for (M+Na) $C_{18}H_{32}NaO_{10}$: 431.1888. Found: 431.1876.

***N*$^{\alpha}$-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(2,4-di-*O*-acetyl-3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(2-*O*-acetyl-3,4-di-*O*-methyl-α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-28)**. A solution of **GPL-27** (24 mg, 0.059 mmol), trichloroacetonitrile (11 μL, 0.012 mmol) and DBU (2.0 μL, 0.012 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 2 h and then concentrated. The resulting oil was purified by chromatography (2.5:1 EtOAc–hexanes) to give the corresponding glycosyl trichloroacetimidate (29 mg, 90%) as a colorless syrup, which was used immediately in the glycosylation; R_f 0.57 (2.5:1 EtOAc–hexanes). The trichloroacetimidate derived from **GPL-27** (7.6 mg, 0.014 mmol) and **GPL-18** (Scheme S51, 10 mg, 0.011 mmol) in CH_2Cl_2 (1.5 mL) containing 4Å molecular sieves was cooled to 0 °C. A 0.5 M solution of TMSOTf (1.2 μL, 0.0006 mmol) was added. The mixture was stirred for 3 h while warming to rt, neutralized with DIPEA (1 μL), concentrated and the resulting residue was purified by chromatography (3:1 → 1:1 toluene–acetone) to give **GPL-28** (7 mg, 50%) as a colorless powder after freeze drying (α:β 4:1); R_f 0.58 (9:1 CH_2Cl_2–CH_3OH). ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.21 (m, 5 H), 7.04 (d, 1 H, *J* = 7.6 Hz), 6.78–6.75 (m, 2 H), 6.44 (d, 1 H, *J* = 8.3 Hz), 5.36 (dd, 1 H, *J* = 3.3, 1.9 Hz), 5.24 (dd, 1 H, *J* = 3.2, 2.0 Hz), 4.98–4.93 (m, 2 H), 4.87 (d, 1 H, *J* = 1.6 Hz), 4.72 (d, 1 H,

d, J = 1.8 Hz, 1 H), 4.51–4.45 (m, 2 H), 4.37–4.41 (m, 1 H), 4.21–4.27 (m, 1 H), 4.12–4.17 (m, 1 H), 3.98 (app t, 1 H, J = 2.4 Hz), 3.80–3.66 (m, 3 H), 3.59–3.50 (m, 9 H), 3.47–3.42 (m, 9 H), 3.33 (s, 3 H), 3.27–3.22 (m, 6 H), 3.11–3.05 (m, 2 H), 3.01 (dd, 1 H, J = 14.5, 5.6 Hz), 2.44 (dd, 1 H, J = 15.3, 3.4 Hz), 2.31 (dd, 1 H, J = 15.3, 7.1 Hz), 2.14 (s, 3 H), 2.13 (s, 3 H), 2.06 (s, 3 H), 1.62–1.56 (m, 2 H), 1.40–1.17 (m, 27 H), 1.14 (d, 3 H, J = 6.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 172.9, 172.1, 171.2, 170.5, 170.3, 170.0, 168.2, 135.8, 129.1, 127.5, 99.1 (C-1), 98.9 (C-1), 95.5 (C-1), 82.2, 81.9, 81.0, 79.3, 77.6, 76.7, 73.7, 72.4, 71.6, 70.5, 68.7, 68.3, 68.2, 68.1, 67.5, 60.9, 60.8, 58.5, 57.6(1), 57.5(5), 56.2, 56.1, 51.5, 49.3, 44.9, 40.4, 37.1, 32.2, 29.5, 29.4, 29.1, 26.7, 25.0, 28.8, 21.1, 21.0(3), 20.9(8), 18.0(1), 17.9(2), 17.8(5), 17.6, 17.5, 14.5. HRMS (ESI) *m/z* calcd for (M+Na) $C_{60}H_{97}N_7NaO_{22}$: 1290.6579. Found: 1290.6558.

N^{α}-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(3,4-di-*O*-methyl-α-L-rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (GPL-29). To a solution of **GPL-28** (6.0 mg, 0.005 mmol) in CH_2Cl_2–CH_3OH (4:1, 5 mL) was added 1 M sodium methoxide solution (0.02 mmol) and the solution was stirred at rt for 20 h. The mixture was then carefully neutralized by adding Amberlite IR-120 H^+ resin and filtered. The filtrate was concentrated to a residue that was purified by chromatography (14:1 CH_2Cl_2–CH_3OH) to obtain **GPL-29** (5 mg, 89%) as an oil. R_f 0.27 (14:1 CH_2Cl_2–CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$ + CD_3OD, δ_H) 7.30–7.20 (m, 5 H), 4.96 (d, 1 H, J = 1.8 Hz), 4.90 (d, 1 H, J = 1.6 Hz), 4.72 (d, 1 H, J = 1.8 Hz), 4.66–4.58 (m, 1 H), 4.40–4.34 (m, 2 H), 4.28–4.20 (m, 2 H), 4.10–3.90 (m, 7 H), 3.64 (m, 2 H), 3.60–3.40 (m, 20 H), 3.40–3.30 (m, 2 H), 3.27–3.21 (m, 4 H), 3.16–2.90 (m, 4 H), 2.36–2.24 (m, 2 H), 1.62–1.52 (m, 4 H), 1.40–1.10 (m, 27 H); ^{13}C NMR (125 MHz, $CDCl_3$ + CD_3OD, δ_C) 172.2, 172.0(4), 172.0, 171.6, 169.3, 136.3, 129.1, 128.5(2), 128.5, 126.9, 101.1, 99.9, 99.4, 99.3, 96.2, 84.7, 82.3, 82.0, 81.9, 81.8, 80.9, 80.2, 80.7, 80.6, 80.4(4), 80.4, 74.0, 71.8, 71.6, 70.8, 70.7(1), 70.7, 70.2, 68.6, 67.9, 67.6, 67.5, 67.3(4), 67.3, 60.8, 60.6(4), 60.6, 57.7(1), 57.7, 57.5, 57.4, 57.3, 57.2, 57.1, 56.9, 56.5, 54.5, 54.3, 51.4, 45.4, 45.3, 45.2, 45.1, 40.3(2), 40.3, 37.3, 32.9, 29.6, 29.4, 29.0, 28.8, 26.6, 25.0, 18.5, 17.9, 17.8, 17.7, 17.6, 17.5, 17.3(1), 17.3, 17.2, 17.0, 16.4, 14.7(2), 14.7. HRMS (ESI) *m/z* calcd for (M+Na) $C_{54}H_{91}N_7NaO_{19}$: 1164.6262. Found: 1164.6248.

N^{α}-(*R*)-11-azido-3-methoxyundecanoyl-D-phenylalaninyl-(3-*O*-methyl-α-L-rhamnopyranosyl)-D-*allo*-threoninyl-D-alaninyl-L-alaninolyl 2-*O*-(3,4-di-*O*-methyl-α-L-

rhamnopyranosyl)-3,4-di-*O*-methyl-α-L-rhamnopyranoside (61). To a solution of **GPL-29** (5.0 mg) in EtOAc (3 mL), THF (2 mL), CH_3OH (0.5 mL), H_2O (30 µL), and pyridine (40 µL) was added 20% $Pd(OH)_2$–C (9 mg). The mixture was stirred under H_2 (1 atm) for 2 h and then the catalyst was filtered off and washed with THF. The combined filtrate was concentrated and dried under vacuum for 4 h to yield **61** (5 mg, quant.) as an oil. HRMS (ESI) *m/z* calcd for (M+H) $C_{54}H_{94}N_5O_{19}$: 1116.6538. Found: 1116.6518.

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