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Click Multivalent Heterogeneous Neoglycoconjugates – Modular Synthesis and Evaluation of Their Binding Affinities

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Dedicated to Professor Hans Helmut Baer

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The efficient synthesis of structurally diverse, multivalent, heterogeneous neoglycoconjugates by means of a series of different click-based strategies is described. The methodology is highly efficient and versatile allowing for easy access to a series of mannose (α-Man)-containing glycoconjugates differing in their valency, nature of the scaffold, nature of the constitutive sugars and length of the linker. The influence of those structural parameters on the binding affinities of these glycomimics toward Concanavalin A (Con A) was evaluated.

Introduction

Carbohydrates are implicated in a number of important biological processes involving highly specific events in cell-cell recognition, cell-protein interactions, and the targeting of hormones, antibodies, and toxins.[1] In these processes, multivalent interactions[2] are especially prevalent,[3] where high-avidity interactions take place between multimeric, membrane-bound, carbohydrate-binding proteins (lectins) and their associated carbohydrate ligands, despite the low affinity provided by a typical monovalent interaction. A large variety of neoglycoconjugates[4] ranging from small molecules to macro- and supramolecular entities have been synthesized by chemists in attempts to understand, mimic, and perturb the natural, multivalent, lectin-carbohydrate interactions. By using these glycomimetics, it has been elucidated that factors[5] such as the rigidity, spacing, topology, and density of saccharides influence the avidity of multivalent carbohydrate-displaying structures for their respective lectins. The principal architecture of neoglycoconjugates usually comprise a core molecule of diverse type that serve as an oligovalent scaffold for the grafting sugar molecules of the same nature giving rise to chemically well-defined, homogeneous neoglycoconjugates such as glycoclusters, glycodendrimers,[6] glycocyclodextrins,[7,8] glycocalixarenes,[8] and glycopolymers.[9] However, in nature, a number of different sugar ligands may be essential for a biological recognition process. In spite of this, a limited number of synthetic, multivalent, heterogeneous neoglycoconjugates containing different sugar epitopes has been described to date.[10–18]

The reported hetero carbohydrate displays having a glycocluster,[10,11] glycodendrimer,[12–14] glycocyclodextrin,[15] or glycopolymer[16,17] architecture have been constructed by means of two different synthetic strategies for the incorporation of the different saccharide ligands: 1) by using an orthogonal protection of a polyfunctional core molecule for the successive attachment of the different sugar moieties[10,11,13] or 2) by controlling the relative proportions of the carbohydrate reagents in the reaction with a homogeneous, functionalized, reactive core.[12,14–17] In this last option, the heterogeneous functionalization can be performed following a sequential[12,14,15] or a simultaneous[16,17] conjugation pattern using pure carbohydrate reagents or mixtures of them, respectively, allowing in this way a modulation of the sugar density. The covalent attachment of sugar moieties to the selected scaffolds have been performed by means of amide,[10,11] thiourea,[10,12,14] thioether,[15] and triazole[13,16,17] linkage constructed by the reaction of sugar derivatives containing amino, acid, thiocyanate, thiol, and azide groups, respectively.

The biological studies performed with the heterogeneous, multivalent, carbohydrate displays have provided some insights into the biological processes in which they are involved. Thus, it has been demonstrated that the sugar density influences both the clustering rate and the stoichiometry of the neoglyconjugate-protein conjugates in assays performed with hetero glycopolymers.[16,17] In addition, the

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existence of strong synergistic effects (heterocluster effect)[15] on carbohydrate-protein recognition events have been evidenced by the comparison of the lectin-binding properties of highly dense, β-cyclodextrin-centered, homo and hetero glycoclusters with defined architecture. In a different approach, supramolecular chemistry principles have been used[18] for the generation and deconvolution of dynamic combinatorial libraries of di- and trivalent hetero glycoclusters.

In this context, the Cu^{I}-catalyzed azide–alkyne cycloaddition (CuAAC),[19] nowadays the best reaction under the "click chemistry" concept,[20] appears as an appealing synthetic tool for the construction of complex molecular architectures considering that its efficiency has been validated by numerous applications in almost all areas of chemistry (drug discovery,[21] bioconjugation,[22] polymer and material science,[23] supramolecular chemistry,[24] and other related areas[25]). In continuing our efforts in the implementation of the CuAAC methodology for the construction of multivalent structures[26,27] and materials[28] with a well-defined architecture, we report herein its applicability for the synthesis of heterogeneous neoglycoconjugates by using a modular strategy for the successive incorporation of clickable alkyne and azide sugar derivatives into suitable, complementary, functionalized scaffolds, thereby extending the results reported in the preceding contribution of this issue.[29]

Results and Discussion

Chemistry

We planned the synthesis of mannose (α-Man)-containing multivalent heterogeneous neoglycoconjugates differing in structural parameters such as the valency, length of the connecting linkers, nature of the scaffolds, and nature of the constitutive sugars. We pursued two goals: 1) to demonstrate the applicability of the click-chemistry methodology as a valuable synthetic tool for accessing complex neoglycoconjugates and 2) to evaluate the effect of the structural parameters of these glycomimics on the receptor binding affinity for Concanavalin A (Con A) from *Canavalia ensiformis*. We selected this tetrameric plant lectin as a suitable and widely used model lectin.

We chose the α-Man alkyne (**1**)[30] and azido (**6** and **7**)[31] derivatives as easily accessible, clickable, sugar derivatives to be used in a CuAAC synthetic strategy. We selected glucose (Glc) and glucosamine (GlcNAc), two rather ubiquitous sugars, as the second recognition motif to confer heterogeneity. We prepared the alkynyl (**2** and **3**)[32] and azido derivatives (**4** and **5**)[33] of those sugars following reported procedures. As denoted, we used all these clickable sugars as peracetylated derivatives to facilitate their solubility in the organic media required for the cycloaddition reactions (Figure 1). In general, we conducted the CuAAC reactions using the Cu catalyst $(EtO)_3P{\cdot}CuI$ (10 mol-%) in refluxing toluene or toluene/THF (1:1) as the optimal conditions considering our previous successful contributions.[26–28]

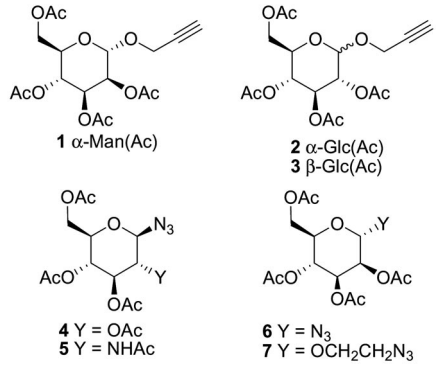
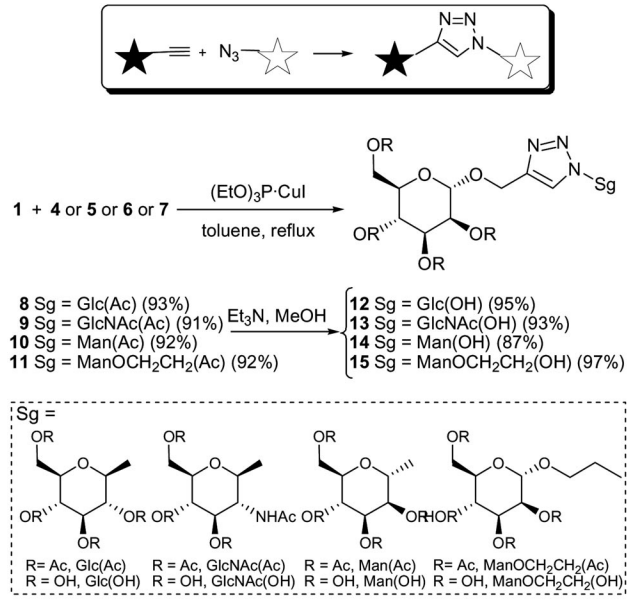


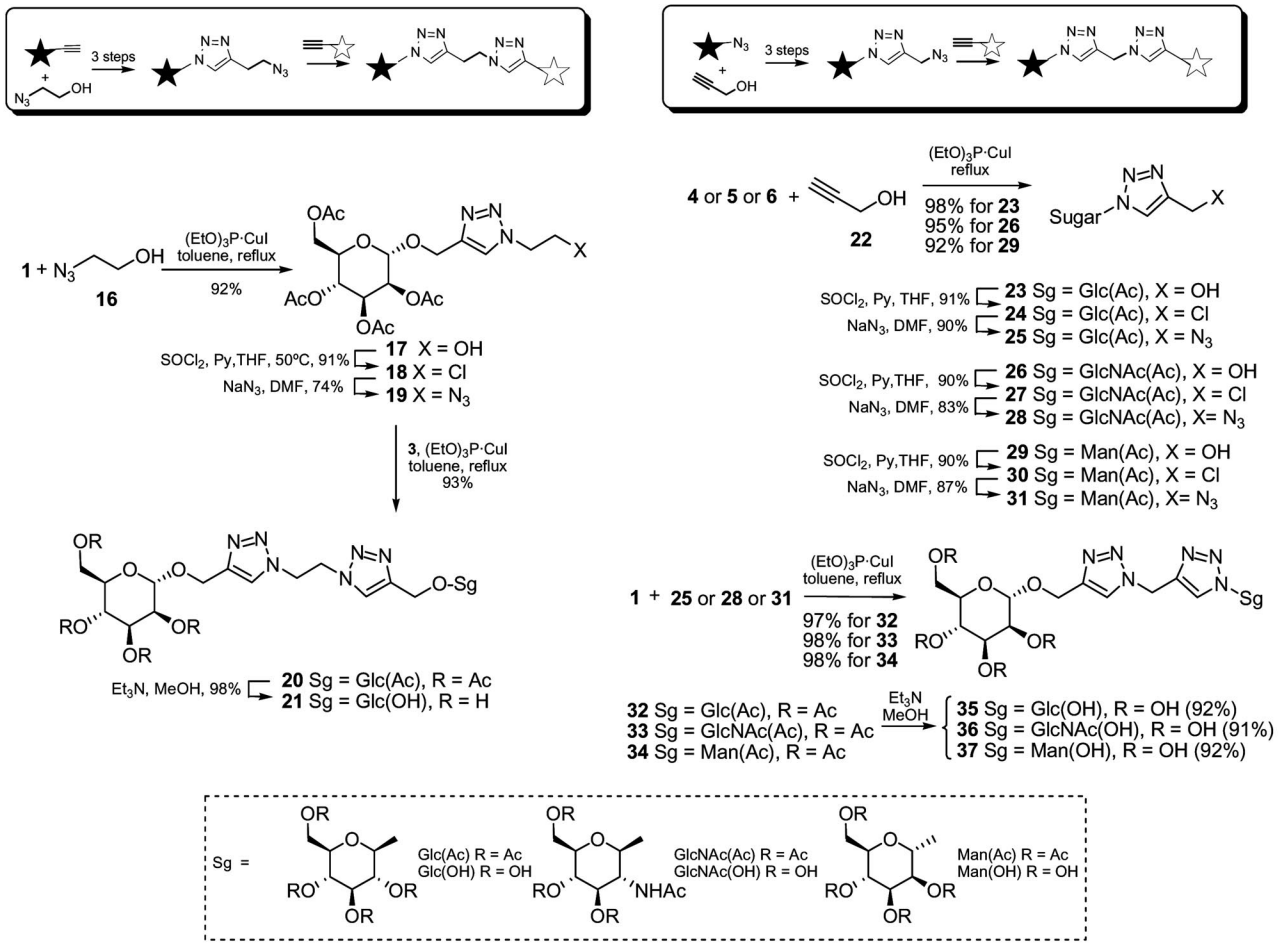
Figure 1. Clickable alkyne and azido sugar derivatives.

We initially prepared divalent neoglycoconjugates by means of two different strategies. In the first one (Scheme 1), the click reaction of **1** with the complementary functionalized Glc and GlcNAc azide derivatives **4** and **5** afforded the divalent **8** and **9** neoglycoconjugates, respectively, in which the 1,2,3-triazole ring acts as the bridging unit. We also prepared the α-Man-homogeneous divalent analogues **10** and **11** by the reaction of **1** with the α-Man-azido derivatives **6** and **7**, respectively, to be used as reference compounds in the binding assays.



Scheme 1. Click synthesis of divalent heterogeneous neoglycoconjugates **12**–**15**.

In a second strategy, we prepared divalent hetero neoglycoconjugates with carbohydrate motifs connected by a linker longer than that of the divalent systems **8** and **9** to evaluate the influence of the distance between the sugar moieties on the binding properties (Scheme 2). Thus, we first reacted the alkynyl α-Man derivative **1** and the azide Glc and GlcNAc derivatives **4** and **5** by CuAAC with 2-azidoethanol and propargyl alcohol, respectively. In this way, we obtained the corresponding glycosides containing a 1,2,3-triazole-based aglycon bearing a terminal hydroxy



Scheme 2. Modular click synthesis of divalent heterogeneous neoglycoconjugates.

group (**17**, **23**, and **26**) and transformed them into the azido sugars **19**, **25**, and **28** by a two-step procedure: we obtained their chloride derivatives (**18**, **24**, and **27**) and subsequently exposed them to nucleophilic substitution with sodium azide. A second CuAAC reaction of those azido compounds with the complementary functionalized alkynyl Glc derivative **3** (in the case of the α-Man-containing sugar **19**) and the alkynyl α-Man derivative **1** (in the case of the Glc- and GlcNAc-containing sugars **25** and **28**, respectively) led to the hetero divalent neoglycoconjugates **20**, **32**, and **34** possessing a bis(triazolylmethyl) linker. The α-Man homogeneous, divalent, neoglycoconjugate **34** was also synthesized to be used as a customized reference in the binding essays following an identical strategy starting from the azido α-Man derivative **6**.

We next undertook the synthesis of heterogeneous neoglycoconjugates with a valency higher that two. In order to develop a wide and flexible CuAAC-based strategy for the synthesis of such compounds, we considered polyhydroxylic molecules as suitable scaffolds to be used in the modular assembly of sugar derivatives differing in their nature. These scaffolds can be easily functionalized as azide and alkyne derivatives. The strategy is depicted in Figure 2 and shows an overall five-step sequence (orthogonal protection, functionalization, click ligation, functionalization, click ligation) that allows the controllable sequential introduction of the azide and/or the alkyne click functions onto those scaffolds and their successive ligation with complementary functionalized carbohydrate derivatives. In this Figure, the two variants of this strategy used in the present study are indicated: sequential introduction of azide groups in the two functionalization steps (strategy A), and introduction, first, of alkyne groups followed by the subsequent introduction of azide groups after the first epitope click grafting (strategy B).

We selected pentaerythritol,[26,34] methyl α-D-gluco- and galactopyranosides,[35] and α,α′-trehalose polyhydroxylated scaffolds. The advantages of carbohydrates over other synthetic scaffolds include their availability in a variety of diastereomeric forms and their inherent polyfunctionality. In addition, some of them are among the cheapest enantiopure organic compounds available.[10,36,37] On the other hand, the previous set of clickable alkynyl derivatives **1** and **3** and azides **4**–**7** was now expanded by including the 2-propynyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (**2**), the α-anomer of **3** (Figure 1).

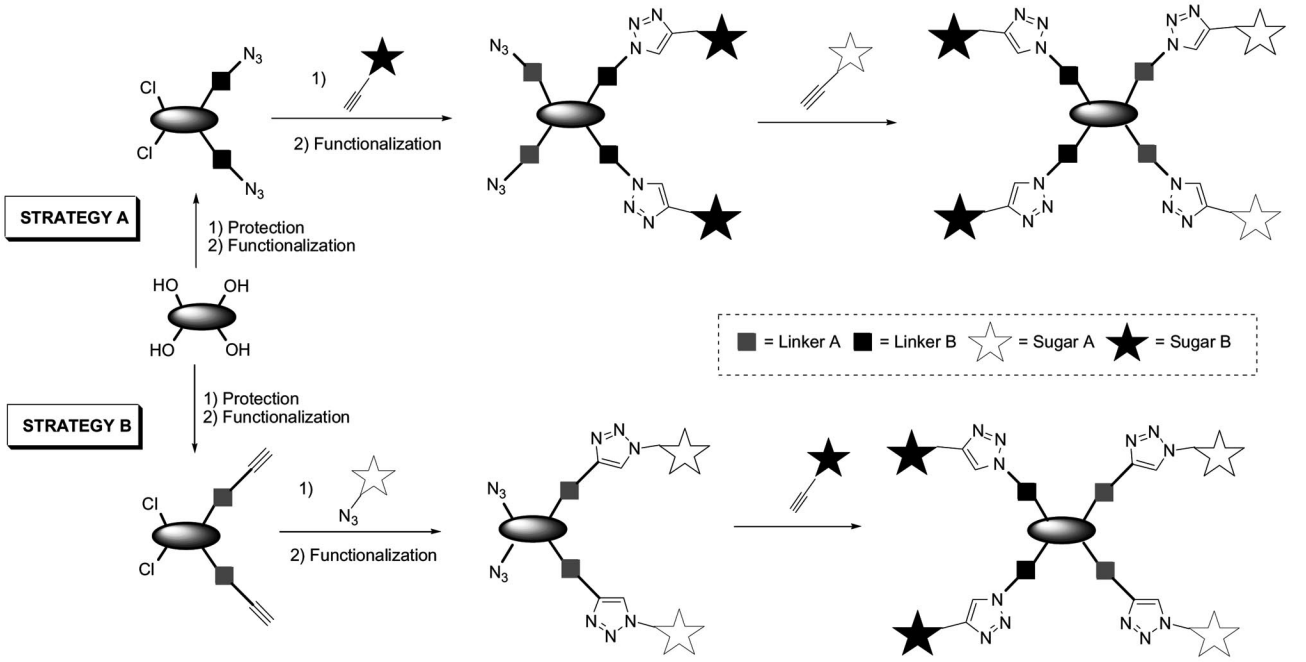


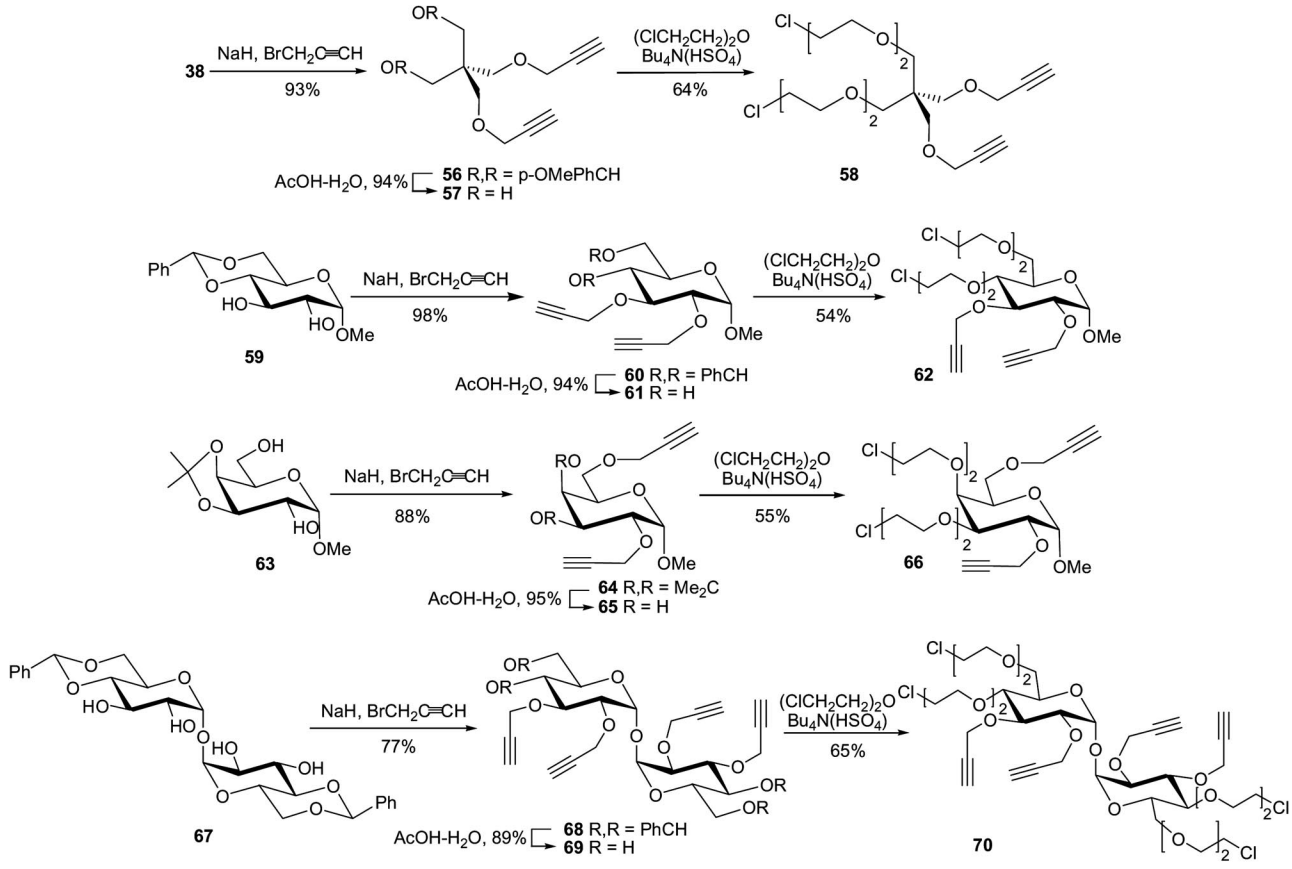
Figure 2. Modular assembly strategies for the synthesis of tetra- and octavalent heterogeneous neoglycoconjugates.

For the initial orthogonal protection of the scaffolds, we chose acetal derivatives in both of the strategies owing to their easy preparation and the effectiveness of the required ultimate hydrolytic deprotection. Thus, we prepared the pentaerythritol, Glc, and trehalose benzylidene derivatives **38**,[37] **59**,[38] and **67**,[38] respectively, and the isopropylidene Gal derivative **63**[39] following described methods in the literature. For the introduction of the azido function in those partially protected scaffolds, alkylation with bis(2-chloroethyl) ether was followed by nucleophilic substitution with sodium azide (see Schemes 3 and 4). In this way, we effectively introduced clickable, medium-sized linkers into the scaffolds, which are thereby prepared for the ultimate grafting of complementary sugar appendages. We prepared the alkynyl derivatives required in strategy B starting from the adequately protected hydroxyl scaffolds and by alkylation with propargyl bromide (see Scheme 4).

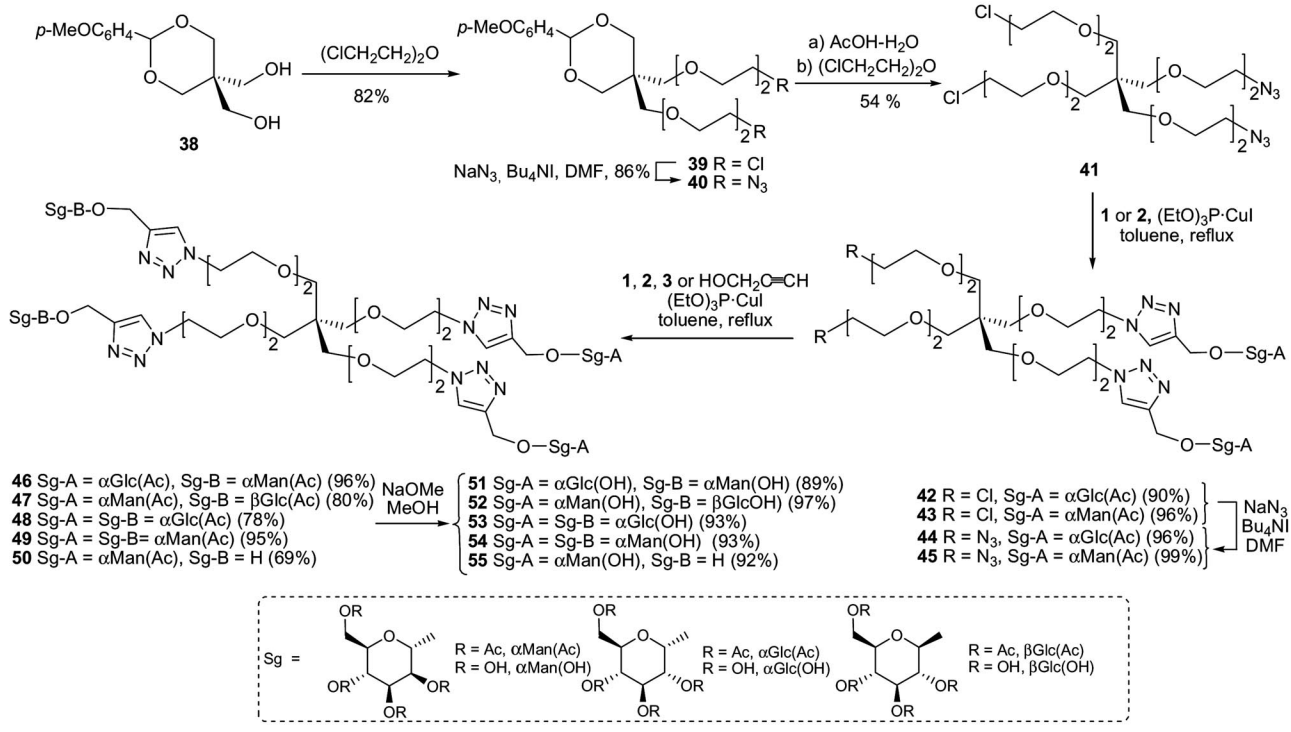
Using the above-indicated click reaction conditions, we prepared the pentaerythritol-centered hetero neoglycoconjugates **46** and **47** following strategy A. In this case, we performed the first functionalization process starting from **38**, which comprised *O*-alkylation with bis(2-chloroethyl) ether, nucleophilic substitution of the chlorine atom by the azide anion, hydrolysis of the acetal group, and, finally, a new alkylation reaction with bis(2-chloroethyl) ether giving access to the diazido-dichloro derivative **41**. From this compound the catalyzed cycloaddition reaction with the alkynyl sugar **2** and **1** led to the Glc- and α-Man-containing chloro derivatives **42** and **43**, respectively. The reaction of these compounds with sodium azide allowed for the introduction of new azide groups and the isolation of **44** and **45**, from which the CuAAC with the complementary alkynyl sugar **1** and **3**, respectively, gave the hetero neoglycoconjugates **46** and **47**. In order to have model compounds as references for the correct evaluation of the biological activity of such compounds, we also reacted **44** and **45** with **2** and **1**, respectively, to give the Glc- and α-Man-containing homo-neoglycoconjugates **48** and **49**, respectively Similarly, we treated **43** with propargyl alcohol to give **50** (see Scheme 3).

We applied strategy B for the construction of pentaerythritol-centered hetero neoglycoconjugates as well as for the synthesis of their sugar-centered counterparts. In these cases, the first functionalization step followed a similar pattern that in the strategy A with the only difference being that the first alkylation was performed with propargyl bromide starting from the protected derivatives **38**, **59**, **63**, and **67**. We thus isolated the corresponding polyalkynylchloro derivatives **58**, **62**, **66**, and **70** as indicated in Scheme 4. We then reacted these compounds with the azidoethyl α-Man derivative **7** giving the α-Man-containing chloro derivatives **71**, **77**, **81**, and **85**. The exchange of the chlorine atom for the azido group and a further cycloaddition with the alkynyl derivatives **2** or **3** yielded the hetero neoglycoconjugates **73**, **74**, **79**, **83**, **87**, and **88** (Scheme 5).

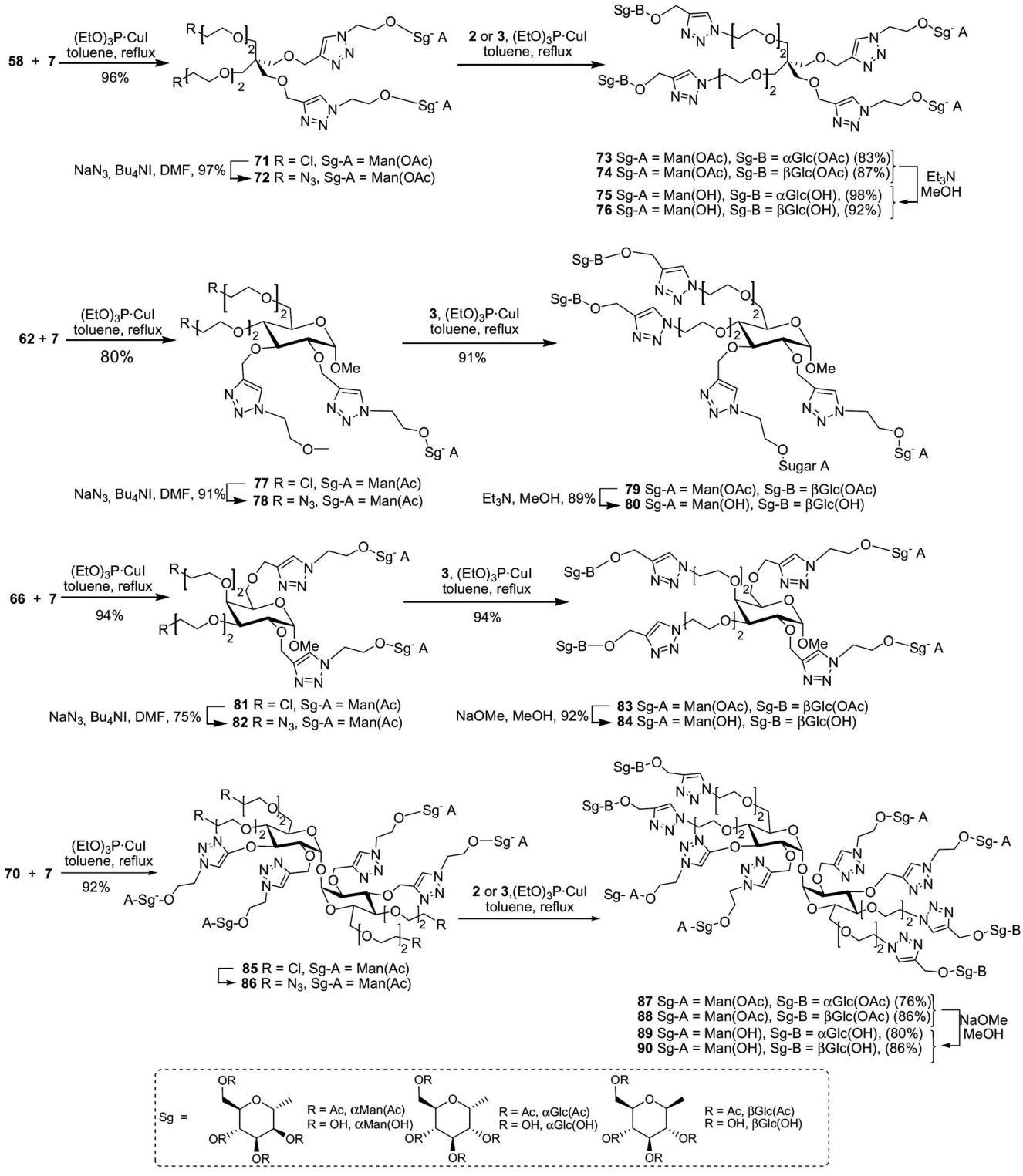
All the CuAAC reactions furnished the per-*O*-acetylated, multivalent, neoglycoconjugate derivatives in high yields. We performed de-*O*-protection of all these compounds using NaOMe or Et_3N in MeOH in order to obtain the corresponding hydroxylated compounds (**12**–**15**, **21**, **35**–**37**, **51**–**55**, **75**–**76**, **60**, **84**, and **89**–**90**) (see Schemes 1, 2, 3, 4, and 5) to be evaluated for their relative binding inhibitory properties against peroxidase-labeled Con A lectin. All the new compounds were adequately characterized by spectroscopic techniques.



Scheme 3. Synthesis of pentaerythritol-centered hetero neoglycoconjugates. Strategy A.



Scheme 4. Preparation of functionalizated scaffolds for the synthesis of hetero neoglycoconjugates. Strategy B.



Scheme 5. Synthesis of pentaerythritol- and carbohydrate-centered hetero neoglycoconjugates. Strategy B.

Lectin Affinity Evaluation

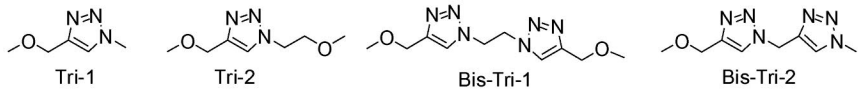
We evaluated the affinities of the new hetero neoglycoconjugates toward Con A by the ELISA-type protocol ELLA. This experiment measures the capacity of a soluble ligand to inhibit the lectin binding to a polymeric ligand coated onto a microtiter well. In the present case, we carried out competitive experiments using horseradish peroxidase-labeled Con A (HRP-Con A) as the lectin and yeast mannan as the microplate-fixed ligand. We also included methyl α-

Man and the homo-neoglycoconjugates **14**, **15**, **37**, **53**, and **54** in the tests as reference compounds. We considered up to six or seven different concentrations of each sample and determined the percentage of the inhibition of HRP-Con A-yeast mannan association spectrophotometrically. We determined the IC_{50} values, defined as the concentration of synthetic compound required to achieve 50% inhibition of this association, from the corresponding inhibition curves. We assumed IC_{50} values to be inversely proportional to the corresponding free energy of binding. The binding affinities of the references and the hetero neoglycoconjugates for Con A are summarized in Table 1 for the divalent compounds, and in Table 2 for the multivalent ones. The valency-corrected relative binding potencies are expressed per mol of α-Man residue and per mol of sugar moiety relative to the monovalent methyl α-Man.

As the new homo and hetero neoglycoconjugates display structural differences that are governed by the valency, scaffold architecture, sugar substitution, configurational (α or β) pattern, grafting pattern, and spacer length, we could evaluate the influence of such factors on carbohydrate-protein recognition. The whole set of compounds present three valency values (divalent, tetravalent, and octavalent compounds), three different sugar substitution patterns for the hetero neoglycoconjugates (α-Man/β-Glc, α-Man/β-GlcNAc, and α-Man/α-Glc) and two for the homo-neoglycoconjugate (α-Man/α-Man and α-Glc/α-Glc), two different 1,2,3-triazole-sugar grafting patterns (direct grafting to the anomeric position when **4**, **5**, and **6** are used and indirect grafting by means of an OCH_2 or OCH_2CH_2 tether when **1**–**3** and **7** are clicked), and six different spacer arms [Tri-1, Tri-2. Bis-Tri-1, and Bis-Tri-2 for the divalent compounds, and the OCH_2 and $(OCH_2CH_2)_2$ tether for the tetra- and octavalent derivatives] (see Table 2).

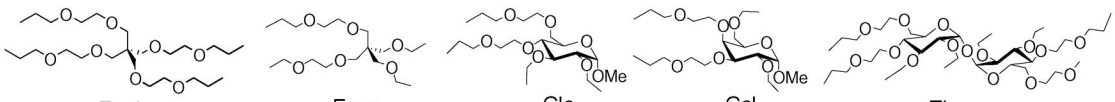
In the case of the divalent neoglycoconjugates, several conclusions can be extracted from the experimental data. Firstly, the binding affinities are a function of the distance between the sugar residues. This we observed in the hetero neoglycoconjugates **12**–**13** and **35**–**36** having the same substitution (α-Man/β-GlcNAc) and grafting pattern. In these

Table 1. Binding affinities toward Con A for the divalent hetero neoglycoconjugates.



Entry	Compound	Core	Sugar A	Sugar B	IC_{50} [mM]	Relative affinity	Relative potency per α-Man moiety	Relative potency per sugar moiety
1	Methyl α-D-Man				0.9	1		
2	**12**	Tri-1	α-Man	β-Glc	0.80	1.13	1.13	0.56
3	**13**	Tri-1	α-Man	β-GlcNAc	0.66	1.36	1.36	0.68
4	**14**	Tri-1	α-Man	α-Man	0.55	1.64	0.82	0.82
5	**15**	Tri-2	α-Man	α-Man	0.41	2.19	1.10	1.10
6	**21**	Bis-Tri-1	α-Man	β-Glc	0.52	1.73	1.73	0.86
7	**35**	Bis-Tri-2	α-Man	β-Glc	0.94	0.96	0.96	0.48
8	**36**	Bis-Tri-2	α-Man	β-GlcNAc	1.02	0.88	0.88	0.44
9	**37**	Bis-Tri-2	α-Man	α-Man	0.64	1.41	0.71	0.71

Table 2. Binding affinities toward Con A for the tetravalent and octavalent hetero neoglycoconjugates .



Entry	Compound	Core	Sugar A	Sugar B	IC_{50} [mM]	Relative affinity	Relative potency per α-Man moiety	Relative potency per sugar moiety
1	Methyl α-D-Man				0.90	1		
2	**51**	Ery-l	α-Man	α-Glc	0.21	4.28	2.14	1.07
3	**52**	Ery-l	α-Man	β-Glc	0.21	4.28	2.14	1.07
4	**53**	Ery-l	α-Glc	α-Glc	0.48	1.87	–	0.47
5	**54**	Ery-l	α-Man	α-Man	0.16	5.62	1.40	1.40
6	**55**	Ery-l	α-Man	OH	0.20	4.50	2.25	2.25
7	**75**	Ery-s	α-Man	α-Glc	0.23	3.91	1.95	0.98
8	**76**	Ery-s	α-Man	β-Glc	0.39	2.30	1.15	0.57
9	**80**	Glc	α-Man	β-Glc	0.40	2.25	1.12	0.56
10	**84**	Gal	α-Man	β-Glc	0.37	2.43	1.21	0.60
11	**89**	Thr	α-Man	α-Glc	0.087	10.34	2.58	1.29
12	**90**	Thr	α-Man	β-Glc	0.30	3	0.75	0.37

compounds, the relative binding affinities per mol of α-Man residue are higher for **12** and **13** (1.13 and 1.36), where the sugar residues are connected through the Tri-1 spacer arm, than they are for their counterparts **35** and **36** (0.96 and 0.88, valency-corrected affinity values, respectively) where the sugar residues are connected through the longer Bis-Tri-2 arm. We also observed this favorable effect for the homo divalent **14** and **37** (0.82 vs. 0.71). Secondly, the affinity values are also a function of the grafting pattern. Thus, we observed a higher relative potency per sugar moiety in both the homo and hetero neoglycoconjugates when the sugar was not directly connected through its anomeric position to the 1,2,3-triazole ring; compare **15** (Tri-2 spacer) and **21** (Bis-Tri-1 spacer) with their counterparts **12**–**14** (Tri-1 spacer) and **35**–**37** (Bis-Tri-2 spacer). We obtained these compounds when we used the azide glycosides **4**–**6** in click ligations, and these results point to a disfavored accessibility by the lectin receptors for the sugar residues owing to steric hindrance.

Concerning the tetravalent and octavalent neoglycoconjugates, we first observed that in compounds having the α-Man/β-Glc substitution pattern connected to the core by identical spacer arms (**76**, **80**, **84**, and **90**) there is neither an influence of the core, as **76**, **80**, and **84** have similar relative affinity values, nor an influence of the valency, as the observed increase in the relative affinity value for **90** is not indicative of a cluster effect. However, we did observe a cooperative effect, as expected, for those compounds wherein the anomeric configuration of the Glc moiety was inverted (α-Man/α-Glc substitution pattern); compare **75** and **89** (3.91 and 10.34 relative affinity values) with their counterparts **76** and **90** (2.30 and 3.0 relative affinity values). On the other hand, when we compared the ensemble of the pentaerythritol hetero derivatives (**51**, **52**, **55**, **75**, and **76**) in order to preclude the influence of the core, we observed that the main factor that contributes to the inhibitory properties of these compounds is the length of the spacer. Thus, **51**, **52**, and **55** with the $(OCH_2CH_2)_2$ spacer have higher affinity values than do their homologous **75** and **76** with the OCH_2 spacer irrespective of the nature of the second ligand. This fact points to the idea that only the α-Man residues are determinant in the carbohydrate-protein recognition because they have the adequate spatial arrangement to interact with the binding site of Con A. This is supported by the slight increase in the affinity value that we observed for the α-Man homo neoglycoconjugate **54** when compared with the rest of the pentaerythritol hetero derivatives bearing the same $(OCH_2CH_2)_2$ spacer (**51**, **52**, and **55**). Finally, we note that the homo neoglycoconjugates **53** and **54** showed the expected behavior, with a three-fold increase in the relative affinity of the α-Man derivative relative to that of its α-Glc counterpart.

Conclusions

In summary, the synthesis of a variety of multivalent neoglycoconjugates possessing two different sugars and differing in structural factors such as the valency, scaffold architecture, anomeric configuration (α or β) of these sugars, grafting pattern, and the length of the spacer that links the sugars to the core has been performed by means of a series of different modular click-based strategies. The flexibility and efficiency of click chemistry made the reported methodology a highly versatile and simple tool for accessing well-defined and custom-made, multivalent, heterogeneous neoglycoconjugates. All the heterogeneous neoglycoconjugates synthesized were α-Man-containing glycomimics, and assays to evaluate their binding properties toward the natural carbohydrate binding lectin Con A have allowed us to extract some conclusions about the influence of the above-mentioned structural factors on the inhibitory properties of these novel compounds. Remarkably, the substitution pattern and the distance between the sugar are the more important parameters influencing the binding capabilities of these compounds.

Experimental Section

General: TLC was performed on Merck silica gel 60 F_{254} aluminum sheets. Reagents used for developing plates include ceric sulfate (1% w/v) and ammonium sulfate (2.5% w/v) in 10% (v/v) aqueous sulfuric acid, iodine, ethanolic sulfuric acid (10% v/v), and UV light when applicable. Flash column chromatography was performed on Silica Gel Merck (230–400 mesh, ASTM). Melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. Optical rotations were recorded with a Perkin–Elmer 141 polarimeter at room temp. IR spectra were recorded with a Satellite Mattson FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded at room temp. with a Bruker (300 or 400 MHz) spectrometer. Chemical shifts are given in ppm and referenced to internal $CDCl_3$. *J* values are given in Hz. Assignments were based on COSY, HMQC, NOESY, and DEPT experiments. FAB mass spectra were recorded with a Fissons VG Autospec-Q spectrometer, using *m*-nitrobenzyl alcohol or thioglycerol as the matrix. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed with a Bruker Daltonics (AUTOFLEX) spectrometer using DGB as the matrix. Compounds **1**–**7**, **38**, **59**, **63**, and **67** were obtained following the described methods in the literature.[30–33,37–39]

General Procedure for the Propargylation of Hydroxylated Derivatives: To a solution of the corresponding hydroxylated derivative (1 mmol) in dry DMF (5 mL) was added NaH (4 mmol). After the reaction mixture was stirred for 0.5 h under an argon atmosphere, propargyl bromide (6 mmol) was added, and the reaction was maintained at room temp. for 16 h. MeOH (5 mL) was then added, and the solvents were evaporated. The crude material was dissolved in toluene/diethyl ether (100 mL, 1:1) and washed with H_2O. The organic phase was dried, concentrated, and purified by column chromatography (diethyl ether/hexane, 1:1).

General Procedure for Acetal Hydrolysis: A solution of the corresponding acetal derivative (1 mmol) in AcOH/H_2O (7:3, 10 mL) was heated at 50 °C for 2 h. Evaporation of the solvent gave a crude material that was purified by column chromatography.

General Procedure for the Synthesis of Chloro Derivatives: A solution of the corresponding hydroxylated sugar derivative (1 mmol), $SOCl_2$ (0.12 mL, 1.7 mmol) and pyridine (0.15 mL, 1.8 mmol) in THF (15 mL) was keep at room temp. for 30 min. The reaction

mixture was evaporated and the resultant crude product was purified by column chromatography.

General Procedure for the Synthesis of (2-Chloroethoxy)ethyl Derivatives: A solution of the corresponding hydroxylated derivatives (1 mmol) and tetrabutylammonium hydrogensulfate (2 mmol) in bis(2-chloroethyl) ether (5 mL) was vigorously stirred at room temp. with 50% aq NaOH (5 mL) for 24 h. The reaction mixture was diluted in H_2O and CH_2Cl_2, the phases were separated, and the aqueous phase was washed with CH_2Cl_2. The organic extracts were combined, washed with H_2O, dried, and concentrated under vacuum. The resultant crude product was purified by column chromatography.

General Procedure for the Synthesis of the Azides: A solution of the corresponding (2-chloroethoxy)ethyl derivative (1 mmol), tetrabutylammonium iodide (0.01 mmol), and sodium azide (5 mmol) in dry DMF (7 mL) was heated at 75–80 °C for 20 h. After the mixture was cooled, the crude material was dissolved in toluene/diethyl ether (100 mL, 1:1) and washed with H_2O. The organic phase was dried, concentrated, and purified by column chromatography.

General Procedure for the CuAAC Reactions: The corresponding alkyne or azide (1 equiv.), was treated with the azido α-Man derivative **4**, **5**, **6**, or **7** or the propargyl glycoside **1**–**3** or propargyl alcohol (1.2 equiv.), respectively, using the copper catalyst $(EtO)_3P{\cdot}CuI$ (10 mol-%) in refluxing toluene or toluene/THF (1:1) for 20–30 min until TLC showed complete disappearance of the limiting reagent. The reaction mixture was concentrated, and the crude material was purified by short-column flash chromatography.

General Procedure for the De-*O*-Acetylation of Per-*O*-acetylated Multivalent Neoglycoconjugates. Method A: A solution of the corresponding per-*O*-acetylated neoglycoconjugate (0.1 mmol) in MeOH (8 mL) containing Et_3N (0.8 mL) was maintained at 50 °C for 2–3 h. The evaporation of the solvent was followed by purification of the crude material by short-column flash chromatography (MeOH) column.

Method B: To a solution of the corresponding per-*O*-acetylated neoglycoconjugate (0.1 mmol) in MeOH (15 mL) was added NaOMe (1 M, 0.1 mL). After 2 h, the solution was treated with Amberlite IR-120(H^+), filtered, and the solvent was evaporated. The resulting crude material was purified by short-column flash chromatography.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (8): Obtained from **1** (386 mg) and **4** (448 mg) following the general procedure for the cycloaddition reactions. Column chromatography (EtOAc/hexane, 5:2) gave **8** as a solid (706 mg, 93%); m.p. 93 °C. $[\alpha]_{436}^{20}$ = +23 (*c* = 1 in chloroform). IR (KBr) $\tilde{\nu}$ = 2952, 1747, 1368, 1324, 1037 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.86 (s, 1 H, H-5 triazole), 5.86 (m, 1 H, H-1 Glc), 5.46–5.38 (m, 2 H, H-2,3 Glc), 5.34–5.22 (m, 4 H, H-4 Glc, H-2,3,4 Man), 4.22 (br. s, 1 H, H-1 Man), 4.85 (d, *J* = 12.1 Hz, 1 H, CH_2O), 4.68 (d, *J* = 12.1 Hz, 1 H, CH_2O), 4.31 (dd, *J* = 12.6, 5.0 Hz, 1 H, H-6 Glc), 4.18–4.08 (m, 4 H, H-6′ Glc, H-5,6,6′ Man), 4.00 (ddd, *J* = 10.1, 4.9, 2.1 Hz, 1 H, H-5 Glc), 2.13, 2.11, 2.09, 2.06, 2.02, 1.97, 1.86 (7 s, 24 H, 8 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4, 169.7, 169.6, 169.5, 169.1, 168.7 (CO), 144.1 (C-4 triazole), 121.5 (C-5 triazole), 96.7 (C-1 Man), 85.5 (C-1 Glc), 74.9 (C-5 Glc), 72.4, 70.2 (C-2,3 Glc), 69.2, 68.9, 68.6, 67.6 (C-2,3,5 Man, C-4 Glc), 65.9 (C-4 Man), 62.2, 61.4 (C-6 Man, C-6 Glc), 60.6 (CH_2O), 20.6, 20.6, 20.5, 20.3, 19.9 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{31}H_{41}N_3O_{19}$ [M + Na]$^+$ 782.2232; found 782.2230.

1-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (9): Obtained from **1** (386 mg) and **5** (446 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc) gave **9** as a solid (690 mg, 91%); m.p. 80 °C. $[\alpha]_{436}^{20}$ = +14 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 2955, 1748, 1371, 1230, 1042 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.97 (s, 1 H, H-5 triazole), 6.82 (d, *J* = 9.1 Hz, 1 H, NH), 6.19 (d, *J* = 10 Hz, 1 H, H-1 GlcNAc), 5.59 (t, *J* = 9.9 Hz, 1 H, H-3 GlcNAc), 5.32–5.22 (m, 4 H, H-4 GlcNAc, H-2,3,4 Man), 4.95 (s, 1 H, H-1 Man), 4.85 (d, *J* = 12.3 Hz, 1 H, CH_2O), 4.73 (d, *J* = 12.3 Hz, 1 H, CH_2O), 4.54 (q, *J* = 9.9 Hz, 1 H, H-2 GlcNAc), 4.36–4.28 (m, 2 H, H-6 GlcNAc, H-6 Man), 4.19–4.09 (m, 4 H, H-5,6' GlcNAc, H-5,6' Man), 2.15, 2.13, 2.09, 2.07, 2.04, 1.98, 1.78 (7 s, 24 H, 8 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.6, 170.0, 169.9, 169.7, 169.3 (CO), 143.7 (C-4 triazole), 122.4 (C-5 triazole), 96.8 (C-1 Man), 85.7 (C-1 GlcNAc), 74.8, 72.1, 69.5, 69.0, 68.7, 68.2, (C-2,3,5 Man, C-3,4,5 GlcNAc), 65.9 (C-4 Man), 62.3, 61.7 (C-6 Man, C-6 GlcNAc), 60.7 (CH_2O), 53.6 (C-2 GlcNAc), 22.7 (*Me*CON), 20.8, 20.7, 20.6 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{31}H_{42}N_4O_{18}$ [M + Na]$^+$ 781.2392; found 781.2398.

1-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl)-4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-1*H*-1,2,3-triazole (10): Obtained from **1** (386 mg) and **6** (448 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/hexane, 3:1) gave **10** as a solid (698 mg, 92%); m.p. 60 °C. $[\alpha]_D^{20}$ = +54 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 2937, 1746, 1366, 1221, 1039 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.83 (s, 1 H, H-5 triazole), 6.06 [d, *J* = 2.8 Hz, 1 H, H-1 Man(N)], 5.97 [t, *J* = 3.3 Hz, 1 H, H-2 Man(N)], 5.92 [dd, *J* = 8.7, 3.7 Hz, 1 H, H-3 Man(N)], 5.39 [t, *J* = 8.7 Hz, 1 H, H-4 Man(N)], 5.33–5.30 [m, 2 H, H-3,4 Man(O)], 5.25 [br. s, 1 H, H-2 Man(O)], 4.97 [d, *J* = 1.2 Hz, 1 H, H-1 Man(O)], 4.90 (d, *J* = 12.4 Hz, 1 H, CH_2O), 4.73 (d, *J* = 12.3 Hz, 1 H, CH_2O), 4.42 [dd, *J* = 12.5, 5.3 Hz, 1 H, H-6 Man (N)], 4.31 [dd, *J* = 12.5, 5.3 Hz, 1 H, H-6' Man(N)], 4.16–4.07 [m, 3 H, H-5,6,6' Man(O)], 3.96 [ddd, *J* = 8.9, 5.3, 2.6 Hz, 1 H, H-5 Man(N)], 2.18, 2.16, 2.13, 2.10, 2.08, 2.06, 2.04, 1.99 (8 s, 24 H, 8 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 170.5, 169.9, 169.8, 169.7, 169.6, 169.2 (CO), 144.2 (C-4 triazole), 123.4 (C-5 triazole), 97.0 [C-1 Man(O)], 83.6 [C-1 Man(N)], 72.3 [C-5 Man(N)], 69.4, 69.0, 68.8, 68.7, [C-2,3,5 Man(O), C-3 Man(N)], 68.2 [C-2 Man(N)], 66.1 [C-4 Man(N), C-4 Man(O)], 62.3 [C-6 Man(O)], 61.5 [C-6 Man(N)], 60.7 (CH_2O), 20.8, 20.7, 20.6, 20.5 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{31}H_{41}N_3O_{19}$ [M + Na]$^+$ 782.2232; found 782.2238.

1-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (11): Obtained from **1** (386 mg) and **7** (500 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/hexane, 3:1) gave **11** as a syrup (802 mg, 92%): $[\alpha]_D^{20}$ = +37.5 (*c* = 1 in chloroform) IR (film): $\tilde{\nu}$ = 2750, 1436, 1369, 1234 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.79 (s, 1 H, H-5 triazole), 65.35–5.18 (m, 6 H), 5.00 (s, 1 H), 4.88 (dd, *J* = 12.2 Hz, 1 H), 4.61 (d, *J* = 12.3 Hz, 1 H), 4.82 (s, 1 H), 4.64 (t, *J* = 5.0 Hz, 2 H), 4.32 (dd, *J* = 12.5, 5.1 Hz, 1 H), 4.21 (dd, *J* = 12.3, 5.1 Hz,1 H), 4.16–4.10 (m, 3 H), 4.06 (dd, *J* = 12.4, 3.1 Hz, 1 H), 3.91 (dt, *J* = 10.7, 5.0 Hz, 1 H), 3.59 (m, 1 H), 2.15, 2.14, 2.21, 2.10, 2.05, 2.04, 2.00, 1.97 (8 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 170.3, 169.8, 169.6, 169.5, 169.4, 143.5, 124.3, 97.2, 96.9, 69.3, 69.0, 68.9, 68.6, 68.5, 66.0, 65.6, 62.2, 62.1, 60.7, 49.6, 20.7, 20.6, 20.5 ppm. HRMS (FAB+): calcd. for $C_{33}H_{45}N_3O_{20}$ [M + Na]$^+$ 826.2494; found 826.2491.

1-(β-D-Glucopyranosyl)-4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (12): Obtained from **8** (759 mg) following the general

procedure for the de-*O*-acetylation (method A). Column chromatography (EtOAc/MeOH, 1:1) gave **12** as a solid (402 mg, 95%); m.p. 156–158 °C. $[\alpha]_D^{20}$ = +39 (*c* = 1 in H_2O). IR (KBr): $\tilde{\nu}$ = 3386, 1641, 1560, 1455, 1408, 1235, 1126, 1047 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.25, (s, 1 H), 5.63 (d, *J* = 9.1 Hz, 1 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz, selected signals): δ = 145.3, 124.7, 100.8, 89.5, 81.0, 78.4, 74.8, 73.9, 72.4, 71.9, 70.8, 68.6, 62.9, 62.3, 60.7 ppm. HRMS (FAB+): calcd. for $C_{15}H_{25}N_3O_{19}$ $[M + Na]^+$ 446.1386; found 446.1386.

1-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (13): Obtained from **9** (758 mg) following the general procedure for the de-*O*-acetylation (method A). Column chromatography (EtOAc/MeOH, 1:1) gave **13** as a foamy solid (431 mg, 93%): $[\alpha]_D^{20}$ = +31 (*c* = 1 in MeOH). IR (KBr): $\tilde{\nu}$ = 3365, 1657, 1550, 1376, 1316, 1238, 1098 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.24 (s, 1 H), 5.82 (d, *J* = 9.7 Hz, 1 H), 1.79 (s, 3 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz, selected signals): δ = 173.6, 145.3, 124.2, 100.3, 88.0, 81.0, 75.7, 74.8, 72.4, 71.9, 71.2, 68.6, 62.9, 62.2, 60.4, 56.7, 25.3 ppm. HRMS (FAB+): calcd. for $C_{17}H_{28}N_4O_{11}$ $[M + Na]^+$ 487.16.52; found 487.1654.

1-(α-D-Mannopyranosyl)-4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (14): Obtained from **10** (759 mg) following the general procedure for the de-*O*-acetylation (method A). Column chromatography (EtOAc/MeOH, 1:1) gave **14** as a syrup (368 mg, 87%): $[\alpha]_D^{20}$ = +62 (*c* = 1 in H_2O). IR (film): $\tilde{\nu}$ = 3393, 1643, 1413, 1346, 1235, 1124, 1122 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.21 (s, 1 H), 6.04 (d, *J* = 2.7 Hz) ppm. ^{13}C NMR (CD_3OD, 75 MHz, selected signals): δ = 145.6, 125.3, 100.9, 88.3, 78.6, 74.9, 72.5, 72.4, 71.9, 70.0, 68.6, 68.6, 62.9, 62.5, 60.7 ppm. HRMS (FAB+): calcd. for $C_{15}H_{25}N_3O_{11}$ $[M + Na]^+$ 446.1386; found 446.1376.

1-(α-D-Mannopyranosyloxyethyl)-4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (15): Obtained from **11** (803 mg) following the general procedure for the de-*O*-acetylation (method A). Column chromatography (EtOAc/MeOH, 1:2) gave **15** as a foamy solid (453 mg, 97%): $[\alpha]_D^{20}$ = +63 (*c* = 1 in H_2O). IR (KBr): $\tilde{\nu}$ = 3400, 1641, 1133, 1056 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.06 (s, 1 H), 4.77 (s, 1 H), 4.72 (s, 1 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz, selected signals): δ = 143.9, 124.9, 100.4, 99.3, 73.7, 73.6, 71.2, 71.2, 70.7, 70.5, 67.3, 67.0, 65.5, 61.6, 61.5, 59.2, 49.9 ppm. HRMS (FAB+): calcd. for $C_{17}H_{29}N_3O_{12}$ $[M + Na]^+$ 490.1649; found490.1649.

1-(2-Hydroxyethyl)-4-(2,3,4,6-tetra-*O*-acetyl-*a*-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (17): Obtained from **1** (386 mg) and **16** (104 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc→EtOAc/MeOH, 10:1) gave **17** as a syrup (435 mg, 92%): $[\alpha]_D^{20}$ = +43 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 2940, 1746, 1369, 1226, 1047 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.79 (s, 1 H, H-5 triazole), 5.32, 5.29 (m, 2 H, H-3,4), 5.20 (s, 1 H, H-2), 5.96 (s, 1 H, H-1), 4.84 (d, *J* = 12.4 Hz, 1 H, OCH_2-triazole), 4.7 (d, *J* = 12.4 Hz, 1 H, OCH_2triazole), 4.51 (d, *J* = 4.9 Hz, 2 H, CH_2OH), 4.27 (dd, *J* = 12.3, 5.0 Hz, 1 H, H-6), 4.14–4.04 (m, 4 H, H-5,6', CH_2N), 3.66 (br. s, 1 H, OH), 2.15, 2.11, 2.04, 1.98 (4 s, 12 H, 4 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.2, 170.0, 169.7 (CO), 143.2 (C-4 triazole), 124.3 (C-5 triazole), 96.9 (C-1), 69.5, 69.1, 68.7 (C-2,3,5), 66.1 (C-4), 62.4 (C-6), 61.1, 61.0 (OCH_2-triazole, CH_2OH), 52.8 (CH_2N), 20.9, 20.8, 20.7 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{19}H_{27}N_3O_{11}$ $[M + Na]^+$ 496.1543; found 496.1539.

1-(2-Chloroethyl)-4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (18): Obtained from **17** (473 mg) following the general procedure for the synthesis of chloro derivatives. Column chromatography (EtOAc) gave **18** as a syrup (447 mg, 91%): $[\alpha]_D^{20}$ = +43 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 2927, 1746, 1226, 1047 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.75 (s, 1 H, H-5 triazole), 5.32–5.30 (m, 2 H, H-3,4), 5.25 (s, 1 H, H-2), 4.97 (s, 1 H, H-1), 4.87 (d, *J* = 12.4 Hz, 1 H, OCH_2-triazole), 4.74–4.70 (m, 3 H, CH_2Cl, OCH_2-triazole), 4.30 (dd, *J* = 12.2, 5.0 Hz, 1 H, H-6), 4.14–4.05 (m, 2 H, H-5,6'), 3.96 (t, *J* = 5.8 Hz, 2 H, CH_2N), 2.15, 2.12, 2.04, 1.99 (4 s, 12 H, 4 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.1, 169.9 (CO), 143.5 (C-4 triazole), 124.1 (C-5 triazole), 96.9 (C-1), 69.5, 69.0, 68.8 (C-2,3,5), 66.1 (C-4), 62.4 (C-6), 61.0 (CH_2O), 51.8 (CH_2N), 42.4 (CH_2Cl), 20.9, 20.8, 20.7 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{19}H_{26}ClN_3O_{10}$ $[M + Na]^+$ 514.1204; found 514.1207.

1-(2-Azidoethyl)-4-(2,3,4,6-tetra-*O*-acetyl-*a*-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazole (19): Obtained from **18** (491 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (EtOAc) gave **19** as a syrup (504 mg, 74%): $[\alpha]_D^{20}$ = +44 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 2103, 1747, 1361, 1226, 1045 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.71 (s, 1 H, H-5 triazole), 5.36–5.30 (m, 2 H, H-3,4), 5.25 (br. s, 1 H, H-2), 4.96 (br. s, 1 H, H-1), 4.87 (d, *J* = 12.4 Hz, 1 H, OCH_2-triazole), 4.72 (d, *J* = 12.4 Hz, 1 H, OCH_2-triazole), 4.53 (t, *J* = 5.6 Hz, 2 H, CH_2N), 4.30 (dd, *J* = 12.2, 5.1 Hz, 1 H, H-6), 4.15–4.07 (m, 2 H, H-5,6'), 3.85 (t, *J* = 5.6 Hz, 2 H, CH_2-triazole), 2.15, 2.12, 2.04, 1.99 (4 s, 12 H, 4 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.1, 170.0, 169.7 (CO), 143.9 (C-4 triazole), 123.9 (C-5 triazole), 96.9 (C-1), 69.5, 69.1, 68.8 (C-2,3,5), 67.2 (C-4), 62.4 (C-6), 61.0 (CH_2O), 50.7 (CH_2N), 49.5 (CH_2N_3), 20.9, 20.8, 20.7 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{19}H_{26}N_6O_{10}$ $[M + Na]^+$ 521.1608; found 521.1607.

2-[4-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-1-[4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-1*H*-1,2,3-triazol-1-yl]ethane (20): Obtained from **3** (463 mg) and **19** (498 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc) gave **20** as a syrup (822 mg, 93%): $[\alpha]_D^{20}$ = +5, $[\alpha]_{436}^{20}$ = +23 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 2103, 1750, 1370, 1226, 1043 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.45, 7.43 (2 s, 2 H, H-5 triazole), 5.31–5.28 (m, 2 H, H-3,4 Man), 5.21 (t, *J* = 9.4 Hz, 1 H, H-3 Glc), 5.20 (br. s, 1 H, H-2 Man), 5.09 (t, *J* = 9.6 Hz, 1 H, H-4 Glc), 4.98 (dd, *J* = 9.6, 8.0 Hz, 1 H, H-2 Glc), 4.95 (br. s, 4 H, 2 CH_2N), 4.94 (d, *J* = 1.7 Hz, 1 H, H-1 Man), 4.89 (d, *J* = 12.6 Hz, 1 H, CH_2O), 4.77 (d, *J* = 12.6 Hz, 1 H, OCH_2), 4.80 (d, *J* = 12.4 Hz, 1 H, CH_2O), 4.64 (d, *J* = 12.4 Hz, 1 H, CH_2O), 4.65 (d, *J* = 7.9 Hz, 1 H, H-1 Glc), 4.29 (dd, *J* = 12.3, 5.0 Hz, 1 H, H-6 Man), 4.26 (dd, *J* = 12.3, 4.4 Hz, 1 H, H-6 Glc), 4.19–4.09 (m, 2 H, H-6' Glc, H-6' Man), 4.06 (ddd, *J* = 9.7, 5.0, 2.4 Hz, 1 H, H-5 Man), 3.74 (ddd, *J* = 9.9, 4.5, 2.4 Hz, 1 H, H-5 Glc), 2.15, 2.12, 2.09, 2.05, 2.04, 2.03, 2.00, 1.98 (8 s, 24 H, 4 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 169.9, 169.7, 169.2 (CO), 144.4, 143.8 (C-4 triazole), 124.1 (C-5 triazole), 100.0 (C-1 Glc), 96.8 (C-1 Man), 72.7, 71.9, 71.1, 69.4, 69.0, 68.7, 68.3 (C-2,3,5 Glc, C-2,3,5 Man), 66.0 (C-4 Man), 62.8, 62.3 (C-6 Glc, C-6 Man), 61.7, 60.7 (2 CH_2O), 49.5, 49.4 (2 CH_2N), 20.8, 20.7, 20.6, 20.5 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{36}H_{48}N_6O_{20}$ $[M + Na]^+$ 907.2821; found 907.2833.

2-[4-(β-D-Glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-1-[4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]ethane (21): Obtained from **20** (884 mg) following the general procedure for the de-*O*-acetylation (method A). Column chromatography (EtOAc/MeOH, 1:1) gave **21** as a syrup (537 mg, 98%): $[\alpha]_D^{20}$ = +21 (*c* = 1 in H_2O). IR (KBr): $\tilde{\nu}$ = 3394, 1644, 1367, 1230, 1125, 1054 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz): δ = 7.87 (s, 1 H, H-5 triazole), 7.80

(s, 1 H, H-5 triazole), 4.92 (d, J = 12.7 Hz, 1 H), 4.78 (s, 1 H), 4.766 (d, J = 12.9 Hz, 1 H), 4.75 (d, J = 12.5 Hz, 1 H), 4.61 (d, J = 12.5 Hz, 1 H), 4.34 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 144.7, 144.2, 124.6, 124.5, 102.2, 99.3, 76.7, 73.7, 71.1, 70.6, 70.3, 67.3, 61.6, 61.5, 61.4, 59.2, 49.6 ppm. HRMS (FAB+): calcd. for $C_{20}H_{32}N_6O_{12}$ [M + Na]$^+$ 571.1976; found 571.1970.

4-(Hydroxymethyl)-1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-1,2,3-triazole (23): Obtained from **4** (373 mg) and **22** (67 mg) following the general procedure for the CuAAC reactions. Crystallization of the crude material (diethyl ether/hexane) gave **23** as a solid (420 mg, 98%); m.p. 156–158 °C. $[\alpha]_D^{20}$ = –18 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 3514, 1748, 1729, 1236, 1100, 1039 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79 (s, 1 H), 5.89 (m, 1 H), 5.48–5.39 (m, 2 H), 5.25 (m, 1 H), 4.82 (m, 2 H), 4.31 (dd, J = 12.6, 5.0 Hz, 1 H), 4.15 (dd, J = 12.6, 2.1 Hz, 1 H), 4.01 (ddd, J = 10.1, 5.0, 2.1 Hz, 1 H), 2.09, 2.07, 2.04, 1.89 (4 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 169.9, 169.4, 169.1, 149.2, 120.3, 85.8, 75.1, 72.7, 70.4, 67.8, 61.6, 56.4, 20.7, 20.6, 20.2 ppm. HRMS (FAB+): calcd. for $C_{17}H_{23}N_3O_{10}$ [M + Na]$^+$ 452.1281; found 452.1286.

4-(Chloromethyl)-1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-1,2,3-triazole (24): Obtained from **23** (429 mg) following the general procedure for the synthesis of chloro derivatives. Column chromatography of the crude material (EtOAc/hexane, 2:1) gave **24** as a solid (409 mg, 91%); m.p. 166–168 °C. $[\alpha]_D^{20}$ = –27 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1746, 1378, 1231, 1038 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.88 (s, 1 H), 5.92 (m, 1 H), 5.49–5.41 (m, 2 H), 5.27 (m, 1 H), 4.71 (s, 2 H), 4.32 (dd, J = 12.6, 5.0 Hz, 1 H), 4.16 (dd, J = 12.6, 1.9 Hz, 1 H), 4.05 (ddd, J = 10.1, 5.0, 1.9 Hz, 1 H), 2.09, 2.08, 2.04, 1.90 (4 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.8, 169.4, 168.9, 145.4, 121.2, 85.8, 75.2, 72.6, 70.3, 67.7, 61.5, 35.8, 20.6, 20.5, 20.1 ppm. HRMS (FAB+): calcd. for $C_{17}H_{22}ClN_3O_9$ [M + Na]$^+$ 470.0942; found 470.0947.

4-(Azidomethyl)-1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-1,2,3-triazole (25): Obtained from **24** (447 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (diethyl ether/hexane, 5:1) gave **25** as a solid (409 mg, 90%); m.p. 81–83 °C. $[\alpha]_D^{20}$ = –18.2 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 3124, 3079, 2924, 2853, 2101, 1748, 1458, 1373, 1223, 1040 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.83 (s, 1 H, H-5 triazole), 5.92 (m, 1 H, H-1), 5.49–5.41 (m, 2 H, H-2,3), 5.26 (m, 1 H, H-4), 4.51 (s, 2 H, CH_2N_3), 4.32 (dd, J = 12.7, 5.0 Hz, 1 H, H-6), 4.16 (dd, J = 12.6, 2.1 Hz, 1 H, H-6), 4.04 (ddd, J = 10.1, 5.0, 2.1 Hz, 1 H, H-5), 2.09, 2.08, 2.04, 1.90 (4 s, 12 H, 4 *Me*CO) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.9, 169.4, 169.0 (CO), 143.4 (C-4 triazole), 120.8 (C-5 triazole), 85.9 (C-1), 75.3 (C-5), 72.6, 70.3 (C-2,3), 67.7 (C-4), 61.6 (C-6), 45.5 (CH_2N_3), 20.7, 20.6, 20.1 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{17}H_{22}N_6O_9$ [M + Na]$^+$ 477.1346; found 477.1343.

1-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-4-(hydroxymethyl)-1*H*-1,2,3-triazole (26): Obtained from **5** (372 mg) and **22** (67 mg) following the general procedure for the CuAAC reactions. Crystallization of the crude material (diethyl ether) gave **26** as a solid (407 mg, 95%); m.p. 230–232 °C. $[\alpha]_D^{20}$ = –26 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 3480, 3344, 1743, 1718, 1664, 1530, 1238 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.93 (s, 1 H), 6.84 (d, J = 9.3 Hz, 1 H), 6.09 (d, J = 9.9 Hz, 1 H), 5.49 (t, J = 9.9 Hz, 1 H), 5.26 (t, J = 9.7 Hz, 1 H), 4.78 (br. s, 2 H), 4.61 (q, J = 9.8 Hz, 1 H), 4.29 (dd, J = 12.6, 4.6 Hz, 1 H), 4.15 (dd, J = 12.6, 2.0 Hz, 1 H), 4.07 (ddd, J = 10.0, 4.7, 2.0 Hz, 1 H), 3.37 (br. s, 1 H), 2.08, 2.07, 1.73 (3 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.0, 170.9, 170.6, 169.4, 148.1, 121.3, 85.9, 74.8, 72.5, 68.2, 61.8, 56.1, 53.5, 22.7, 20.7, 20.7, 20.6 ppm. HRMS (FAB+): calcd. for $C_{17}H_{24}N_4O_9$ [M + Na]$^+$ 451.1441; found 451.1437.

1-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-4-(chloromethyl)-1*H*-1,2,3-triazole (27): Obtained from **26** (428 mg) following the general procedure for the synthesis of chloro derivatives. Column chromatography of the crude material (EtOAc/MeOH, 20:1) gave **27** as a solid (448 mg, 90%); m.p. 210 °C (dec). $[\alpha]_D^{20}$ = –42 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 3343, 1742, 1663, 1524, 1233 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.91 (s, 1 H), 6.00 (d, J = 9.9 Hz, 1 H), 5.93 (d, J = 9.1 Hz, 1 H), 5.45 (t, J = 9.9 Hz, 1 H), 5.24 (t, J = 9.8 Hz, 1 H), 4.70 (s, 2 H), 4.56 (q, J = 9.9 Hz, 1 H), 4.30 (dd, J = 12.6, 4.8 Hz, 1 H), 4.15 (dd, J = 12.6, 1.8 Hz, 1 H), 4.01 (ddd, J = 9.9, 4.8, 2.0 Hz, 1 H), 2.09, 2.08, 1.78 (3 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.8, 148.7, 122.3, 85.9, 75.0, 72.2, 68.1, 61.8, 53.5, 35.8, 22.9, 20.7, 20.7 ppm. HRMS (FAB+): calcd. for $C_{17}H_{23}ClN_4O_8$ [M + Na]$^+$ 469.1102; found 469.1100.

1-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-4-(azidomethyl)-1*H*-1,2,3-triazole (28): Obtained from **27** (446 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (EtOAc/MeOH, 20:1) gave **28** as a solid (376 mg, 83%); m.p. >200 °C (dec). $[\alpha]_D^{20}$ = –27 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 2097, 1743, 1664, 1524, 1228 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.97 (s, 1 H), 6.64 (d, J = 9.3 Hz, 1 H), 6.11 (d, J = 10.0 Hz, 1 H), 5.52 (t, J = 10.0 Hz, 1 H), 5.25 (t, J = 9.7 Hz, 1 H), 4.63 (q, J = 10.0 Hz, 1 H), 4.54 (d, J = 14.4 Hz, 1 H), 4.48 (d, J = 14.4 Hz, 1 H), 4.31 (dd, J = 12.6, 4.8 Hz, 1 H), 4.16 (dd, J = 12.6, 2.9 Hz, 1 H), 4.07 (ddd, J = 10.0, 4.8, 2.1 Hz, 1 H), 2.08, 2.07, 1.78 (3 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.8, 169.1, 142.9, 122.1, 86.0, 75.1, 72.3, 68.1, 61.8, 53.4, 45.3, 22.8, 20.7, 20.6 ppm. HRMS (FAB+): calcd. for $C_{17}H_{23}N_7O_8$ [M + Na]$^+$ 476.1506; found 476.1508.

4-(Hydroxymethyl)-1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-1*H*-1,2,3-triazole (29): Obtained from **6** (373 mg) and **22** (62 mg) following the general procedure for the CuAAC reactions using DMF as solvent. Column chromatography (EtOAc) of the crude material gave **29** as a syrup (395 mg, 92%); m.p. 122–124 °C. $[\alpha]_D^{20}$ = 34 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 3540, 1750, 1374, 1239 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.76 (s, 1 H), 6.02 (d, J = 2.5 Hz, 1 H), 5.96 (t, J = 3.2 Hz, 1 H), 5.91 (dd, J = 8.6, 3.7 Hz, 1 H), 5.38 (t, J = 8.8 Hz, 1 H), 4.86 (s, 2 H), 4.38 (dd, J = 12.5, 5.4 Hz, 1 H), 4.06 (dd, J = 12.5, 2.6 Hz, 1 H), 3.92 (ddd, J = 9.0, 5.4, 2.6 Hz, 1 H), 2.2, 2.2, 2–07, 2.06 (4 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 169.6, 169.5, 148.5, 122.4, 83.6, 71.8, 68.8, 68.1, 67.5, 61.5, 55.9, 20.6, 20.5, 20.4 ppm. HRMS (FAB+): calcd. for $C_{17}H_{23}N_3O_{10}$ [M + Na]$^+$ 452.1281; found 452.1284.

4-(Chloromethyl)-1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-1*H*-1,2,3-triazole (30): Obtained from **29** (429 mg) following the general procedure for the synthesis of chloro derivatives. Column chromatography of the crude material (EtOAc/hexane, 2:1) gave **30** as a solid (402 mg, 90%); m.p. > 197 °C (dec). $[\alpha]_D^{20}$ = 41 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 3540, 1751, 1239, 1122, 1038 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80 (s, 1 H), 6.02 (d, J = 2.9 Hz, 1 H), 5.95 (t, J = 3.3 Hz, 1 H), 5.87 (dd, J = 8.7, 3.7 Hz, 1 H), 5.35 (t, J = 8.8 Hz, 1 H), 4.38 (dd, J = 12.5, 5.6 Hz, 1 H), 4.15 (d, J = 7.2 Hz, 1 H), 4.07 (d, J = 7.1 Hz, 1 H), 4.07 (dd, J = 12.5, 2.6 Hz, 1 H), 3.89 (ddd, J = 8.9, 5.0, 2.6 Hz, 1 H), 2.18, 2.09, 2.07, 2.06 (4 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.7, 148.4, 123.2, 83.6, 72.5, 68.7, 68.2, 66.2, 61.5, 35.8, 20.7, 20.6 ppm. HRMS (FAB+): calcd. for $C_{17}H_{22}ClN_3O_9$ [M + Na]$^+$ 470.0942; found 470.0948.

4-(Azidomethyl)-1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-1*H*-1,2,3-triazole (31): Obtained from **30** (447 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (diethyl ether/hexane, 5:1) of the crude material gave **31** (395 mg, 87%); m.p. 117–119 °C. $[\alpha]_D^{20}$ = 36 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 2098, 1745, 1041 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.82 (s, 1 H), 6.06 (d, *J* = 2.9 Hz, 1 H), 5.97 (t, *J* = 3.3 Hz, 1 H), 5.88 (dd, *J* = 8.7, 3.7 Hz, 1 H), 5.36 (t, *J* = 8.8 Hz, 1 H), 4.55 (s, 2 H), 4.39 (dd, *J* = 12.5, 5.6 Hz, 1 H), 4.07 (dd, *J* = 12.5, 2.5 Hz, 1 H), 3.89 (ddd, *J* = 8.9, 5.6, 2.6 Hz, 1 H), 2.09, 2.08, 2.08, 2.06 (4 s, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4, 169.6, 169.3, 143.4, 122.7, 83.5, 72.4, 68.7, 6.1, 66.1, 61.5, 45.5, 20.7, 20.6 ppm. HRMS (FAB+): calcd. for $C_{17}H_{22}N_6O_9$ $[M + Na]^+$ 477.1346; found 477.1351.

1-[(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-1,2,3-triazole-4-yl]-4-[(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]methane (32): Obtained from **1** (463 mg) and **25** (454 mg) following the general procedure for the CuAAC reactions. Column chromatography [diethyl ether/hexane (3:1)→EtOAc] gave **32** as a solid (815 mg, 97%); m.p. 90 °C. $[\alpha]_D^{20}$ = 11 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1746, 1224, 1039 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.83 (s, 1 H, H-5 triazole), 7.65 (s, 1 H, H-5 triazole), 5.78 (d, *J* = 8.8 Hz, 1 H, H-1 Glc), 5.64 (d, *J* = 15.4 Hz, 1 H, CH_2N), 5.57 (d, *J* = 15.4 Hz, 1 H, CH_2N), 5.38–5.26 (m, 2 H, H-2,3 Glc), 5.21–5.15 (m, 3 H, H-3 Glc, H-3,4 Man), 5.12 (br. s, 1 H, H-2 Man), 4.85 (d, *J* = 1.4 Hz, 1 H, H-1 Man), 4.73 (d, *J* = 12.3 Hz, 1 H, CH_2O), 4.57 (d, *J* = 12.4 Hz, 1 H, CH_2O), 4.25–3.90 (several m, 6 H, H-5,6,6' Glc, H-5,6,6' Man), 2.05, 2.02, 1.98, 1.97, 1.95, 1.93, 1.87, 1.78 (8 s, 24 H, 8 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.0, 169.9, 169.3, 169.0, 168.0 (CO), 143.9, 142.1 (C-4 triazole), 123.4, 122.0 (C-5 triazole), 96.9 (C-1 Man), 86.0 (C-1 Glc), 75.3 (C-5 Glc), 72.4, 70.6 (C-2,3 Glc), 69.5, 69.0, 68.7, 67.6 (C-2,3,5 Man, C-4 Glc), 66.1 (C-4 Man), 62.4, 61.5 (C-6 Man, C-6 Glc), 60.9 (CH_2O), 45.3 (CH_2N), 20.9, 20.8, 20.7, 20.5, 20.2 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{34}H_{44}N_6O_{19}$ $[M + Na]^+$ 863.2559; found 863.2563.

1-[(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-1*H*-1,2,3-triazole-4-yl]-[4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]methane (33): Obtained from **1** (463 mg) and **28** (453 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc→EtOAc/MeOH, 15:1) gave **33** as a solid (822 mg, 98%); m.p. > 215 °C (dec). $[\alpha]_D^{20}$ = +2.4 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1746, 1228, 1043 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.06 (s, 1 H, H-5 triazole), 7.84 (s, 1 H, H-5 triazole), 6.67 (d, *J* = 9.2 Hz, 1 H, NH), 6.04 (d, *J* = 9.9 Hz, 1 H, H-1 GlcNAc), 5.71 (d, *J* = 15.4 Hz, 1 H, CH_2N), 5.63 (d, *J* = 15.4 Hz, 1 H, CH_2N), 5.46 (t, *J* = 9.9 Hz, 1 H, H-3 GlcNAc), 5.26–5.18 (m, 4 H, H-4 GlcNAc, H-2,3,4 Man), 4.92 (d, *J* = 1.3 Hz, 1 H, H-1 Man), 4.79 (d, *J* = 12.3 Hz, 1 H, CH_2O), 4.64 (d, *J* = 12.3 Hz, 1 H, CH_2O), 4.52 (q, *J* = 9.8 Hz, 1 H, H-2 GlcNAc), 4.29–4.04 (m, 6 H, H-5,6,6' GlcNAc, H-5,6,6' Man), 2.15, 2.11, 2.07, 2.06, 2.05, 2.03, 1.98 (7 s, 21 H, 7 Ac), 1.73 (s, 3 H, AcN) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 170.1, 170.0, 169.7, 169.4 (CO), 143.9, 141.6 (C-4 triazole), 123.7, 122.8 (C-5 triazole), 97.0 (C-1 Man), 86.2 (C-1 GlcNAc), 75.05 (C-5 GlcNAc), 72.1, 70.6 (C-3 GlcNAc), 69.5, 69.2, 68.7, 68.1 (C-2,3,5 Man, C-4 GlcNAc), 66.1 (C-4 Man), 62.4, 61.5 (C-6 Man, C-6 GlcNAc), 61.0 (CH_2O), 53.7 (C-2 GlcNAc), 45.3 (CH_2N), 29.7 (*Me*CON), 20.9, 20.8, 20.7, 20.6, 20.2 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{34}H_{45}N_7O_{18}$ $[M + Na]^+$ 862.2719; found 862.2713.

1-[(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-1,2,3-triazole-4-yl]-[4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]methane (34): Obtained from **1** (463 mg) and **31** (454 mg) following the general procedure for the CuAAC reactions. Column chromatography [EtOAc/hexane (3:1)→EtOAc] gave **34** as syrup (823 mg, 98%): $[\alpha]_D^{20}$ = 46 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1748, 1225, 1045 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.93 (s, 1 H), 7.83 (s, 1 H), 6.07 (d, *J* = 2.6 Hz, 1 H), 5.95 (t, *J* = 3.1 Hz, 1 H), 5.88 (dd, *J* = 8.9, 3.7 Hz, 1 H), 5.72 (s, 2 H), 5.37 (t, *J* = 8.9 Hz, 1 H), 5.32–5.29 (m, 2 H), 5.22 (br. s, 1 H), 4.97 (d, *J* = 0.7 Hz, 1 H), 4.83 (d, *J* = 12.3 Hz, 1 H), 4.68 (d, *J* = 12.3 Hz, 1 H), 4.38 (dd, *J* = 12.5, 5.4 Hz, 1 H), 4.27 (dd, *J* = 12.6, 5.4 Hz, 1 H), 4.09–4.03 (m, 3 H), 3.89 (ddd, *J* = 8.9, 5.3, 2.5 Hz, 1 H), 2.17, 2.14, 2.11, 2.08, 2.07, 2.05, 2.04, 1.97 (8 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 170.4, 169.9, 169.7, 169.6, 169.5, 169.3, 142.2, 123.7, 123.5, 96.9, 83.7, 72.3, 69.3, 69.0, 68.7, 68.6, 67.9, 65.9, 65.8, 62.8, 62.3, 60.8, 45.0, 20.7, 20.6, 20.5 ppm. HRMS (FAB+): calcd. for $C_{34}H_{44}N_6O_{19}$ $[M + Na]^+$ 863.2559; found 863.2560.

1-[(β-D-Glucopyranosyl)-1*H*-1,2,3-triazole-4-yl]-[4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]methane (35): Obtained from **32** (840 mg) following the general procedure for the de-*O*-acetylation (method A). Column chromatography (EtOAc/MeOH, 1:1) gave **35** as a foamy solid (464 mg, 92%): $[\alpha]_D^{20}$ = +33 (*c* = 1 in H_2O). IR (KBr): $\tilde{\nu}$ = 3366, 1642, 1580, 1458, 1410, 1233, 1128, 1051 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.40 (s, 1 H, H-5 triazole), 8.16 (s, 1 H, H-5 triazole), 5.70 (s, 2 H), 5.54 (d, *J* = 9.2 Hz, 1 H), 5.45, 5.39, 5.21 (3 br. s, 3 H), 4.72 (br. s, 1 H), 4.66 (d, *J* = 12.1 Hz, 1 H), 4.55 (d, *J* = 12.1 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 143.8, 141.5, 124.2, 123.4, 99.0, 87.5, 80.0, 79.2, 76.8, 74.2, 72.0, 70.9, 70.1, 69.5, 67.0, 61.3, 60.7, 59.0, 49.4 ppm. HRMS (FAB+): calcd. for $C_{18}H_{28}N_6O_{11}$ $[M + Na]^+$ 527.1713; found 527.1709.

1-[(2-Acetamido-2-deoxy-α-D-mannopyranosyl)-1*H*-1,2,3-triazole-4-yl]-[4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]methane (36): Obtained from **33** (839 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (EtOAc/MeOH, 1:1) gave **36** as a syrup (496 mg, 91%): $[\alpha]_D^{20}$ = +8 (*c* = 1 in H_2O). $[\alpha]_{436}^{20}$ = +23 (*c* = 1, H_2O). IR (film): $\tilde{\nu}$ = 3455, 3327, 1658, 1539, 1134 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.26 (s, 1 H, H-5 triazole), 8.01 (s, 1 H, H-5 triazole), 7.86 (d, *J* = 9.0 Hz, 1 H), 5.67 (d, *J* = 10.1 Hz, 1 H), 5.64 (s, 2 H), 5.25 (m, 2 H), 4.69 (s, 1 H), 4.62 (d, *J* = 12.1 Hz, 1 H), 4.46 (d, *J* = 12.1 Hz, 1 H), 4.71–4.45 (several m, 5 H), 4.01 (q, *J* = 9.4 Hz, 1 H), 3.70–3.23 (several m, 11 H) ppm. ^{13}C NMR ([D$_6$]-DMSO, 75 MHz): δ = 170.2, 144.1, 141.5, 124.4, 123.5, 99.3, 86.5, 80.2, 74.2, 73.8, 70.9, 70.3, 70.0, 67.1, 61.4, 60.8, 59.3, 54.9, 44.7, 22.8 ppm. HRMS (FAB+): calcd. for $C_{20}H_{31}N_7O_{11}$ $[M + Na]^+$ 568.1979; found 568.1979.

1-[(β-D-Glucopyranosyl)-1*H*-1,2,3-triazole-4-yl]-[4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]methane (37): Obtained from **34** (840 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (EtOAc/MeOH, 1:1) gave **37** as a foamy solid (464 mg, 92%): $[\alpha]_D^{20}$ = +54 (*c* = 1 in H_2O). IR (KBr): $\tilde{\nu}$ = 3378, 1566, 1417, 1126, 1051 cm^{-1}. ^1H NMR ([D$_6$]DMSO + D_2O, 300 MHz): δ = 8.31 (s, 1 H, H-5 triazole), 8.12 (s, 1 H, H-5 triazole), 5.89 (d, *J* = 4.5 Hz, 1 H), 5.69 (s, 2 H), 4.80 (br. s, 1 H), 4.69 (s, 1 H), 4.63 (d, *J* = 12.2 Hz, 1 H), 4.48 (d, *J* = 12.2 Hz, 1 H), 4.35 (dd, *J* = 4.1, 3.2 Hz, 1 H), 3.81 (dd, *J* = 6.5, 3.1 Hz, 1 H), 3.70–3.30 (several m, 10 H) ppm. ^{13}C NMR ([D$_6$]-DMSO, 75 MHz): δ = 14e.8, 141.5, 124.1, 122.9, 99.0, 85.7, 78.5, 74.1, 71.1, 70.9, 70.1, 68.0, 67.7, 67.0, 61.2, 60.6, 59.0, 44.4 ppm. HRMS (FAB+): calcd. for $C_{18}H_{28}N_6O_{11}$ $[M + Na]^+$ 527.1713; found 527.1713.

5,5-Bis(7-chloro-2,5-dioxaheptyl)-2-(4-methoxyphenyl)-1,3-dioxane (39): Obtained from **38** (254 mg) following the general procedure for the synthesis of (2-chloroethoxy)ethyl derivatives. Column chromatography (diethyl ether/hexane, 2:1) gave **39** as a syrup (382 mg, 82%). IR (film): $\tilde{\nu}$ = 1614,1517,1250, 1097, 1033, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 8.7 Hz, 2 H), 5.38 (s, 1 H), 4.09 (d, J = 11.5 Hz, 2 H), 3.87 (d, J = 11.4 Hz, 2 H), 3.82–3.53 (several m, 16 H), 3.80 (s, 4 H), 3.68 (s, 3 H, OMe) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 160.0, 131.0, 127.4, 113.7, 101.7, 71.4, 71.3, 71.3, 71.2, 71.0, 70.5, 70.5, 70.0, 69.7, 55.3, 42.9, 38.9 ppm. HRMS (FAB+): calcd. for $C_{21}H_{32}Cl_2O_7$ $[M + Na]^+$ 489.1423; found 489.1427.

5,5-Bis(7-azido-2,5-dioxaheptyl)-2-(4-methoxyphenyl)-1,3-dioxane (40): Obtained from **39** (466 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (diethyl ether/hexane, 2:1) gave **40** as a syrup (413 mg, 86%). IR (film): $\tilde{\nu}$ = 2867, 2109, 1615, 1518, 1303, 1249, 1095, 1032, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 8.7 Hz, 2 H), 5.38 (s, 1 H), 4.09 (d, J = 11.8 Hz, 2 H), 3.88 (d, J = 11.7 Hz, 2 H), 3.80 (s, 4 H), 3.70–3.35 (several m, 16 H), 3.67 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 161.1, 131.0, 127.4, 113.7, 101.7, 71.4, 71.3, 71.1, 70.6, 70.6, 70.2, 70.1, 70.0, 69.8, 55.4, 50.9, 39.0 ppm. HRMS (FAB+): calcd. for $C_{21}H_{32}N_6O_7$ $[M + Na]^+$ 503.2230; found 503.2230.

1,15-Dichloro-8,8-bis(7-chloro-2,5-dioxahept-1-yl)-3,6,10,13-tetraoxapentadecane (41): Obtained from **40** (480 mg) following the general procedure for the acetal hydrolysis. The obtained crude material was directly transformed without purification following the general procedure for the synthesis of the (2-chloroethoxy)ethyl derivatives. Column chromatography (diethyl ether/hexane, 1:1) gave **41** as a syrup (310 mg, 54% overall yield from **40**). IR (film): $\tilde{\nu}$ = 2871, 2109, 1300, 1109 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.76 (t, J = 6.0 Hz, 4 H), 3.70–3.54 (m, 24 H), 3.46 (s, 8 H), 3.37 (t, J = 5.0 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 71.3, 71.1, 70.5, 70.5, 70.1, 70.0, 50.8, 45.6, 42.9 ppm. HRMS (FAB+): calcd. for $C_{21}H_{40}Cl_2N_6O_8$ $[M + Na]^+$ 597.218; found 597.218.

1,15-Dichloro-8,8-bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-3,6,10,13-tetraoxapentadecane (42): Obtained from **41** (287 mg) and **2** (463 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 20:1) gave **42** isolated as a syrup (606 mg, 90%): $[\alpha]_D^{20}$ = +60 (c = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1749, 1367, 1226, 1102, 1040 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.73 (s, 2 H), 5.47 (t, J = 9.9 Hz, 2 H), 5.21 (d, J = 3.7 Hz, 2 H), 5.08 (t, J = 9.8 Hz, 2 H), 4.89 (dd, J = 10.2, 3.7 Hz, 2 H), 4.84 (d, J = 12.3 Hz, 2 H), 4.67 (d, J = 12.3 Hz, 2 H), 4.55 (t, J = 5.1 Hz, 4 H), 4.27 (dd, J = 12.3, 4.2 Hz, 2 H), 4.14–4.05 (m, 4 H), 3.90 (t, J = 5.1 Hz, 4 H), 3.75 (t, J = 5.8 Hz, 4 H), 3.65–3.53 (m, 1 H), 3.42 (s, 8 H), 3.37 (t, J = 5.0 Hz, 4 H), 2.10, 2.03, 2.02, 2.00 (4 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.1, 143.5, 124.1, 95.2, 71.3, 71.1, 71.0, 70.7, 70.5, 70.5, 70.1, 70.0, 69.6, 69.5, 68.5, 67.5, 61.8, 61.4, 50.5, 45.6, 43.0, 20.8, 20.7, 20.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{55}H_{84}N_6O_{28}$ $[M + Na]^+$ 1369.460; found 1369.550.

1,15-Dichloro-8,8-bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-3,6,10,13-tetraoxapentadecane (43): Obtained from **41** (287 mg) and **1** (463 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 20:1) gave **43** isolated as a syrup (646 mg, 96%): $[\alpha]_D^{20}$ = +35 (c = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1750, 1370, 1227, 1134, 1089, 1049 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.77 (s, 2 H), 5.35–5.25 (m, 4 H), 5.23 (br. s, 2 H), 4.97 (s, 2 H), 4.84 (d, J = 12.2 Hz, 2 H), 4.69 (d, J = 12.2 Hz, 2 H), 4.55 (t, J = 5.1 Hz, 4 H), 4.31 (dd, J = 12.3, 5.1 Hz, 2 H), 4.14–4.07 (m, 4 H), 3.90 (t, J = 5.1 Hz, 4 H), 3.75 (t, J = 5.7 Hz, 4 H), 3.65–3.53 (m, 20 H), 3.43 (s, 8 H), 2.15, 2.12, 2.04, 1.98 (4 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.0, 169.9, 169.7, 143.3, 124.2, 96.8, 71.3, 71.1, 71.0, 70.5, 70.0, 69.9, 69.5, 69.4, 69.1, 68.7, 66.1, 62.4, 60.9, 45.5, 43.0, 20.9, 20.8, 20.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{55}H_{84}N_6O_{28}$ $[M + Na]^+$ 1369.460; found 1369.576.

1,15-Diazido-8,8-bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-3,6,10,13-tetraoxapentadecane (44): Obtained from **42** (449 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (EtOAc/MeOH, 20:1) gave **44** as a syrup (435 mg, 96%): $[\alpha]_D^{20}$ = +61 (c = 1 in chloroform). IR (film): $\tilde{\nu}$ = 2109, 1751, 1369, 1227, 1103, 1041 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.72 (s, 2 H), 5.47 (t, J = 9.8 Hz, 2 H), 5.21 (d, J = 3.7 Hz, 2 H), 5.08 (t, J = 9.7 Hz, 2 H), 4.88 (dd, J = 10.3, 3.8 Hz, 2 H), 4.83 (d, J = 12.5 Hz, 2 H), 4.69 (d, J = 12.3 Hz, 2 H), 4.54 (t, J = 5.1 Hz, 4 H), 4.27 (dd, J = 12.3, 4.1 Hz, 2 H), 4.15–4.05 (m, 4 H), 3.90 (t, J = 5.1 Hz, 4 H), 3.67 (t, J = 5.0 Hz, 4 H), 3.63–3.52 (m, 1 H), 3.42 (s, 8 H), 3.37 (t, J = 5.0 Hz, 4 H), 2.10, 2.03, 2.02, 2.00 (4 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.0, 169.6, 143.7, 124.0, 95.2, 71.3, 71.1, 71.0, 70.7, 70.6, 70.5, 70.1, 70.0, 69.6, 69.5, 67.6, 61.8, 61.4, 50.8, 50.5, 45.6, 20.8, 20.7, 20.7, 20.6 ppm. HRMS (MALDI-TOF): calcd. for $C_{55}H_{84}N_{12}O_{28}$ $[M + Na]^+$ 1383.541; found 1383.806.

1,15-Diazido-8,8-bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-3,6,10,13-tetraoxapentadecane (45): Obtained from **43** (449 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (EtOAc/MeOH, 20:1) gave **45** as a syrup (449 mg, 99%): $[\alpha]_D^{20}$ = +26 (c = 1 in chloroform). IR (film): $\tilde{\nu}$ = 2109, 1750, 1370, 1228, 1134, 1086, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.77 (s, 2 H), 5.32–5.24 (m, 4 H), 5.24 (br. s, 2 H), 4.98 (d, J = 1.2 Hz, 2 H), 4.84 (d, J = 12.2 Hz, 2 H), 4.69 (d, J = 12.2 Hz, 2 H), 4.55 (t, J = 5.1 Hz, 4 H), 4.31 (dd, J = 12.5, 5.2 Hz, 2 H), 4.14–4.10 (m, 4 H), 3.90 (t, J = 5.1 Hz, 4 H), 3.67 (t, J = 5.0 Hz, 4 H), 3.64–3.53 (m, 20 H), 3.44 (s, 8 H), 3.37 (t, J = 5.0 Hz, 4 H), 2.15, 2.12, 2.04, 1.98 (4 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.0, 169.8, 169.7, 143.2, 124.2, 96.8, 71.0, 71.0, 70.5, 70.4, 70.0, 69.9, 69.4, 69.4, 69.1, 68.7, 66.0, 62.3, 60.8, 50.7, 50.4, 45.5, 20.8, 20.8, 20.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{55}H_{84}N_{12}O_{28}$ $[M + Na]^+$ 1383.541; found 1383.82.

8,8-Bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-1,15-bis[4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (46): Obtained from **44** (340 mg) and **1** (232 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 20:1) gave **46** as a syrup (512 mg, 96%): $[\alpha]_D^{20}$ = +64 (c = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1748, 1371, 1235, 1135, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.77, 7.73 (2 s, 4 H), 5.47 (t, J = 9.8 Hz, 2 H), 5.35–5.25 (m, 4 H), 5.23 (s, 2 H), 5.21 (d, J = 3.9 Hz, 2 H), 5.08 (t, J = 9.8 Hz, 2 H), 4.98 (d, J = 0.7 Hz, 2 H), 4.88 (dd, J = 10.3, 3.7 Hz, 2 H), 4.83 (d, J = 12.0 Hz, 4 H), 4.68 (d, J = 12.1 Hz, 4 H), 4.54 (t, J = 5.0 Hz, 8 H), 4.31 (dd, J = 12.3, 5.0 Hz, 2 H), 4.27 (dd, J = 12.0, 4.2 Hz, 2 H), 4.18–4.07 (m, 8 H), 3.90 (t, J = 5.1 Hz, 8 H), 3.62–3.48 (m, 16 H), 3.37 (s, 8 H), 2.15, 2.12, 2.10, 2.04, 2.04, 2.02, 2.00, 1.98 (8 s, 48 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.4, 143.3, 124.1, 124.0, 96.8, 95.1, 70.9, 70.6, 70.3, 70.2, 70.0, 69.8, 69.4, 69.3, 69.0, 68.7, 68.4, 67.4, 66.0, 62.3, 61.7, 61.3, 60.8, 50.3,

45.4, 20.8, 20.7, 20. 20.6, 20.5 ppm. HRMS (MALDI-TOF): calcd. for $C_{89}H_{128}N_{12}O_{48}$ [M + Na]$^+$ 2155.784; found 2155.696.

8,8-Bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-1,15-bis[4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (47): Obtained from **45** (340 mg) and **3** (232 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 20:1) gave **47** as a syrup (426 mg, 80%): $[\alpha]_D^{20}$ = +3 (*c* = 1 in chloroform). $[\alpha]_{436}^{20}$ = +7.5 (*c* = 1, chloroform). IR (film): $\tilde{\nu}$ = 2877, 1751, 1433, 1370, 1228, 1048 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.76 (s, 2 H), 7.70 (s, 2 H), 5.32–5.29 (m, 4 H), 5.23 (br. s, 2 H), 5.20 (t, *J* = 9.3 Hz, 2 H), 5.09 (t, *J* = 9.6 Hz, 2 H), 4.93 (d, *J* = 12.5 Hz, 2 H), 4.84 (d, *J* = 12.2 Hz, 2 H), 4.81 (d, *J* = 12.5 Hz, 2 H), 4.71 (d, *J* = 8.0 Hz, 2 H), 4.68 (d, *J* = 12.2 Hz, 2 H), 4.56–4.50 (m, 8 H), 4.33–4.26 (m, 4 H), 4.17–4.07 (m, 6 H), 3.88 (m, 8 H), 3.58 (m, 8 H), 3.50 (m, 8 H), 3.36 (s, 8 H), 2.15, 2.12, 2.09, 2.04, 2.03, 1.99, 1.97 (8 s, 96 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.1, 170.1, 169.9, 169.8, 169.6, 169.6, 169.4, 169.3 (*C*OO), 143.8, 143.3, 124.1, 123.9, 99.9, 96.8, 72.8, 71.9, 71.2, 71.0, 70.4, 69.9, 69.4, 69.3, 69.1 (C-3), 68.7, 68.4, 66.1, 62.8, 62.4, 61.9, 60.1, 50.3, 45.4, 20.8, 20.7, 20.6, 20.6, 20.5 ppm.

8,8-Bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-1,15-bis[4-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (48): Obtained from **44** (340 mg) and **2** (232 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 20:1) gave **48** as a syrup (416 mg, 78%): $[\alpha]_D^{20}$ = +87 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1751, 1369, 1228, 1137, 1021 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.72 (s, 4 H), 5.46 (t, *J* = 9.8 Hz, 4 H), 5.21 (d, *J* = 3.7 Hz, 4 H), 5.08 (t, *J* = 9.8 Hz, 4 H), 4.88 (dd, *J* = 10.3, 3.7 Hz, 4 H), 4.83 (d, *J* = 11.8 Hz, 4 H), 4.68 (d, *J* = 11.8 Hz, 4 H), 4.54 (t, *J* = 5.0 Hz, 8 H), 4.26 (dd, *J* = 12.3, 4.0 Hz, 2 H), 4.13–4.05 (m, 8 H), 3.90 (t, *J* = 5.0 Hz, 8 H), 3.61–3.48 (m, 16 H), 3.36 (s, 8 H), 2.10, 2.02, 2.00 (3 s, 48 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.1, 169.6, 135.7, 95.2, 71.3, 71.1, 70.8, 70.5, 70.2, 70.0, 69.5, 68.6, 67.6, 61.9, 61.3, 50.7, 20.8, 20.7, 20.6 ppm. HRMS (MALDI-TOF): calcd. for $C_{89}H_{128}N_{12}O_{48}$ [M + Na]$^+$ 2155.784; found 2155.895.

8,8-Bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-1,15-bis[4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (49): Obtained from **45** (340 mg) and **1** (232 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 20:1) gave **49** as a syrup (506 mg, 95%): $[\alpha]_D^{20}$ = +41 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1751, 1370, 1228, 1133, 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.77 (s, 4 H, H-4 triazole), 5.35–5.24 (m, 8 H, H-3,4 Man), 5.23 (s, 2 H, H-2 Man), 4.98 (s, 4 H, H-1), 4.84 (d, *J* = 12.2 Hz, 4 H, CH_2O-Man), 4.68 (d, *J* = 12.2 Hz, 4 H, CH_2O-Man), 4.55 (t, *J* = 5.1 Hz, 8 H, CH_2N), 4.31 (dd, *J* = 12.3, 5.1 Hz, 2 H, H-6), 4.15–4.06 (m, 8 H, H-5,6), 3.90 (t, *J* = 5.1 Hz, 8 H), 3.61–3.51 (m, 16 H), 3.38 (s, 8 H, CH_2C), 2.15, 2.12, 2.04, 1.98 (4 s, 48 H, 4 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 170.0, 169.9, 169.7 (COO), 143.2, 124.1 (triazole), 96.8 (C-1), 70.9, 70.4, 69.8, 69.3 (CH_2O), 69.4, 69.1, 68.7, 66.0 (C-2,3,4,5), 62.3 (C-6), 60.8 (CH_2O), 50.3 (CH_2N), 45.4 [(CH_2)*C*], 20.8, 20.7, 20.6, 20.6 ppm. HRMS (MALDI-TOF): calcd. for $C_{89}H_{128}N_{12}O_{48}$ [M + Na]$^+$ 2155.784; found 2155.048.

1,15-Bis[4-hydroxymethyl-1*H*-1,2,3-triazol-1-yl]-8,8-bis[7-{4-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-3,6,10,13-tetraoxapentadecane (50): Obtained from **45** (340 mg) and propargyl alcohol following the general procedure for the CuAAC reactions. Column chromatography (CH_2Cl_2/MeOH, 12:1) gave **50** as a syrup (254 mg, 69%): $[\alpha]_D^{20}$ = +36 (*c* = 1, in chloroform). IR (film): $\tilde{\nu}$ = 3463, 2876, 1750, 1370, 1228, 1134, 1087, 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.78 (br. s, 4 H), 5.4–5.2 (m, 6 H), 4.97 (s, 4 H), 4.83 (d, *J* = 12.2 Hz, 2 H), 4.76 (s, 2 H), 4.75 (br. s, 2 H), 4.67 (d, *J* = 12.2 Hz, 2 H), 4.50 (m, 8 H), 4.30 (dd, *J* = 12.3, 5.1 Hz, 2 H), 4.10 (m, 4 H), 3.86 (m, 8 H), 3.57–3.48 (m, 16 H), 3.33 (s, 8 H), 2.15, 2.12, 2.04, 1.97 (4 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.8, 170.1, 170.0, 169.7, 143.4, 124.2, 123.0, 96.9, 71.0, 70.9, 70.5, 70.5, 69.9, 69.5, 69.4, 69.2, 68.8, 66.1, 62.4, 60.9, 56.4, 50.4, 50.3, 45.5, 20.9, 20.8, 20.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{61}H_{92}O_{30}N_{12}$ [M + Na]$^+$ 1495.594; found 1495.582.

8,8-Bis[7-{4-(α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-1,15-bis[4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (51): Obtained from **46** (426 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (MeOH) gave **51** as a syrup (283 mg, 97%). $[\alpha]_D^{20}$ = +90 (*c* = 0.25 in water). IR (film): $\tilde{\nu}$ = 3408, 1053, 667 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz): δ = 8.06, 8.04 (2 s, 4 H), 4.92 (d, *J* = 3.6 Hz, 2 H), 4.82 (d, *J* = 12.4 Hz, 2 H), 4.79 (d, *J* = 12.4 Hz, 2 H), 4.66 (d, *J* = 12.4 Hz, 2 H), 4.64 (d, *J* = 12.4 Hz, 2 H), 4.57 (br. t, *J* = 4.5 Hz, 2 H), 3.89 (t, *J* = 5.1 Hz, 8 H), 3.85–3.45 (m), 3.42 (dd, *J* = 9.7, 3.7 Hz, 2 H), 3.35–3.30 (m) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 145.3, 145.2, 126.1, 100.8, 99.6, 75.0, 74.9, 74.0, 73.5, 72.5, 72.1, 72.0, 71.8, 68.6, 62.9, 62.7, 61.5, 60.8, 51.5, 44.0 ppm. HRMS (MALDI-TOF): calcd. for $C_{57}H_{96}N_{12}O_{32}$ [M + Na]$^+$ 1483.615; found 1483.787.

1,15-Bis[4-(β-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-8,8-bis[7-{4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-3,6,10,13-tetraoxapentadecane (52): Obtained from **47** (426 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (MeOH) gave **52** as a syrup (233 mg, 80%). $[\alpha]_D^{20}$ = +12 (*c* = 0.5 in H_2O). IR (film): $\tilde{\nu}$ = 3362, 1655, 1075 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz): δ = 8.00 (s, 4 H), 4.93 (d, *J* = 12.4 Hz, 2 H), 4.83 (d, *J* = 1.0 Hz, 2 H), 4.75 (d, *J* = 12.4 Hz, 2 H), 4.73 (d, *J* = 12.4 Hz, 2 H), 4.60 (d, *J* = 12.4 Hz, 2 H), 4.53 (t, *J* = 4.8 Hz, 4 H), 4.37 (d, *J* = 7.7 Hz, 2 H), 3.90–3.15 (several m, 76 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 145.4, 145.0, 126.1, 126.0,103.5, 100.7, 77.9, 77.9, 74.9, 74.9, 72.4, 72.0, 71.9, 71.5, 71.3, 70.5, 70.3, 68.5, 63.0, 62.8, 62.7, 60.7, 51.5, 46.6 ppm. HRMS (MALDI-TOF): calcd. for $C_{57}H_{96}N_{12}O_{32}$ [M + Na]$^+$ 1483.615; found 1483.761.

8,8-Bis[7-{4-(α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-1,15-bis[4-(α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (53): Obtained from **48** (426 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (MeOH) gave **53** as a syrup (259 mg, 89%): $[\alpha]_D^{20}$ = +37 (*c* = 0.25 in H_2O). IR (film): $\tilde{\nu}$ = 3407, 1655, 1460, 1230, 1044 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz): δ = 8.04 (s, 4 H), 4.91 (d, *J* = 3.7 Hz, 4 H), 4.81 (d, *J* = 12.4 Hz, 4 H), 4.66 (d, *J* = 12.4 Hz, 4 H), 4.56 (t, *J* = 5.0 Hz, 8 H), 3.89 (t, *J* = 5.1 Hz, 4 H), 3.79 (dd, *J* = 11.6, 2.0 Hz, 4 H), 3.70–3.45 (m), 3.40 (dd, *J* = 9.8, 3.7 Hz, 4 H), 3.37–3.25 (m) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 145.4, 126.0, 99.6, 75.0, 74.0, 73.5, 71.8, 72.1, 71.4, 70.7, 70.3, 62.7, 61.4, 51.5, 46.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{57}H_{96}N_{12}O_{32}$ [M + Na]$^+$ 1483.615; found 1483.766.

8,8-Bis[7-{4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-1,15-bis[4-(α-D-mannopyranosyloxymethyl)-

1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (54): Obtained from **49** (426 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (MeOH) gave **54** as a syrup (271 mg, 93%): $[\alpha]_D^{20}$ = +37 (*c* = 0.25 in H_2O). ^1H NMR (CD_3OD, 300 MHz): δ = 8.04 (s, 4 H), 4.87 (s, 4 H), 4.79 (d, *J* = 12.4 Hz, 4 H), 4.64 (d, *J* = 12.4 Hz, 4 H), 4.57 (t, *J* = 5.0 Hz, 8 H), 3.89 (t, *J* = 5.0 Hz, 8 H), 3.85 (dd, *J* = 12.0, 2.3 Hz, 4 H), 3.82–3.45 (several m, 36 H) 3.31 (s, 8 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 145.3, 126.1, 100.8, 74.9, 72.5, 72.0, 72.1, 71.4, 70.7, 70.3, 68.6, 62.9, 60.8, 51.5, 46.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{57}H_{96}O_{32}N_{12}$ $[M + Na]^+$ 1483.615; found 1483.636.

1,15-Bis[4-hydroxymethyl-1*H*-1,2,3-triazol-1-yl]-8,8-bis[7-{4-(α-D-mannopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl}-2,5-dioxahept-1-yl]-3,6,10,13-tetraoxapentadecane (55): Obtained from **50** (294 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (MeOH) gave **55** as a syrup (92%): $[\alpha]_D^{20}$ = +29 (*c* = 0. 5 in H_2O). ^1H NMR (CD_3OD, 300 MHz): δ = 8.00 (s, 2 H), 7.90 (s, 2 H), 4.81 (s, 2 H), 4.75 (d, *J* = 12.4 Hz, 2 H), 4.63 (s, 4 H), 4.60 (d, *J* = 12.4 Hz, 2 H), 4.53 (m, 8 H), 3.90–3.40 (m, 36 H), 3.27 (s, 8 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 148.9, 145.1, 125.9, 124.7, 100.8, 74.9, 72.5, 72.0, 71.4, 70.7, 70.4, 70.3, 68.6, 62.9, 60.7, 56.5, 51.5, 51.4, 46.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{45}H_{76}O_{22}N_{12}$ $[M + Na]^+$ 1159.509; found 1159.522.

2-(4-Methoxyphenyl)-5,5-bis(prop-2-ynyloxymethyl)-1,3-dioxane (56): Obtained from **38** (254 mg) following the general procedure for the propargylation. Column chromatography (diethyl ether/hexane, 1:1) gave **56** isolated as a syrup (307 mg, 93%). IR (KBr): $\tilde{\nu}$ = 3291, 2116, 1615, 1517, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.41 (d, *J* = 8.7 Hz, 2 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 5.38 (s, 1 H), 4.20 (d, *J* = 2.3 Hz, 2 H), 4.11 (d, *J* = 2.1 Hz, 2 H), 4.09 (d, *J* = 2.4 Hz, 2 H), 3.87 (d, *J* = 11.4 Hz, 2 H), 3.86 (s, 2 H), 3.79 (s, 3 H), 3.36 (s, 2 H), 2.43 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 160.2, 131.4, 127.4, 113.7, 101.8, 74.6, 74.3, 69.9, 69.9, 68.8, 58.8, 55.4, 38.6 ppm. HMRS (FAB+): calcd. for $C_{19}H_{22}O_5$ $[M + Na]^+$ 353.1365; found 353.1359.

2,2-Bis(prop-2-ynyloxymethyl)-1,3-propanediol (57): Obtained from **56** (330 mg) following the general procedure for the acetal hydrolysis. Column chromatography (EtOAc/hexane, 1:1) gave **57** as a syrup (199 mg, 94%). IR (KBr): $\tilde{\nu}$ = 3291, 2116, 1615, 1517, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.41 (d, *J* = 8.7 Hz, 2 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 5.38 (s, 1 H), 4.20 (d, *J* = 2.3 Hz, 2 H), 4.11 (d, *J* = 2.1 Hz, 2 H), 4.09 (d, *J* = 2.4 Hz, 2 H), 3.87 (d, *J* = 11.4 Hz, 2 H), 3.86 (s, 2 H), 3.79 (s, 3 H), 3.36 (s, 2 H), 2.43 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 79.5, 74.8, 70.9, 64.1, 58.8, 45.0 ppm. HMRS (FAB+): calcd. for $C_{11}H_{16}O_4$ $[M + Na]^+$ 235.0944; found 235.0944.

1,15-Dichloro-8,8-bis(prop-2-ynyloxymethyl)-3,6,10,13-tetraoxapentadecane (58): Obtained from **57** (212 mg) following the general procedure for the synthesis of the (2-chloroethoxy)ethyl derivatives. Column chromatography (EtOAc/hexane, 1:1) gave **58** as a syrup (271 mg, 64%). IR (film): $\tilde{\nu}$ = 3292, 2115, 1096 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.12 (d, *J* = 2.3 Hz, 4 H), 3.76 (t, *J* = 5.8 Hz, 4 H), 3.69–3.57 (m, 12 H), 3.52 (s, 4 H), 3.46 (s, 4 H), 2.41 (t, *J* = 2.3 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 80.2, 71.4, 71.1, 70.5, 69.9, 69.2, 58.7, 45.2, 42.9 ppm. HMRS (FAB+): calcd. for $C_{19}H_{30}O_6Cl_2$ $[M + Na]^+$ 447.131; found 447.131.

Methyl 4,6-*O*-Benzylidene-2,3-di-*O*-propargyl-α-D-glucopyranoside (60): Obtained from **59** (283 mg) following the general procedure for the propargylation. Column chromatography (diethyl ether/hexane, 1:1) gave **60** isolated as a syrup (351 mg, 98%): $[\alpha]_D^{20}$ = +33 (*c* = 1 in chloroform). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.47, 7.37 (2 m, 5 H), 5.54 (s, 1 H), 4.88 (d, *J* = 3.7 Hz, 1 H), 4.50–4.45 (m, 3 H), 4.39 (dd, *J* = 15.4, 2.3 Hz, 1 H), 4.29 (dd, *J* = 9.6, 4.2 Hz, 1 H), 3.99 (t, *J* = 9.2 Hz, 1 H), 3.83 (dt, *J* = 10.0, 4.4 Hz, 1 H), 3.74 (t, *J* = 9.8 Hz, 1 H), 3.70 (dd, *J* = 3.7, 9.2 Hz, 1 H), 3.60 (t, *J* = 9.2 Hz, 1 H), 3.44 (s, 3 H), 2.46 (t, *J* = 2.34 Hz, 1 H), 2.43 (t, *J* = 9.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 129.04, 128.28, 126.13, 101.42, 99.35, 82.07, 77.99, 69.09, 62.18, 60.08, 59.45, 55.34 ppm. HRMS (FAB+): calcd. for $C_{20}H_{22}O_6$ $[M + Na]^+$ 381.1314; found 381.1314.

Methyl 2,3-Di-*O*-propargyl-α-D-glucopyranoside (61): Obtained from **60** (358 mg) following the general procedure for the acetal hydrolysis. Column chromatography (EtOAc) gave **61** (254 mg, 94%) as a syrup: $[\alpha]_D^{20}$ = +90 (*c* = 1 in MeOH). ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.92 (d, *J* = 3.5 Hz, 1 H), 4.52 (dd, *J* = 15.8, 2.4 Hz, 1 H), 4.41 (dd, *J* = 15.8, 2.3 Hz, 1 H), 4.34 (m, 2 H), 3.84–3.54 (several m, 8 H), 3.44 (s, 3 H), 2.53 (t, *J* = 2.3 Hz, 1 H), 2.50 (t, *J* = 2.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 98.04, 80.79, 80.55, 79.69, 79.26, 75.17, 74.95, 70.97, 69.88, 62.11, 60.37, 58.45, 55.25 ppm. HRMS (FAB+): calcd. for $C_{13}H_{18}O_6$ $[M + Na]^+$ 293.1001; found 293.1000.

Methyl 4,6-Di-*O*-chloroethoxyethyl-2,3-di-*O*-propargyl-α-D-glucopyranoside (62): Obtained from **61** (270 mg) following the general procedure for the synthesis of the (2-chloroethoxy)ethyl derivatives. Column chromatography (EtOAc/hexane, 1:1) gave **62** as a syrup (260 mg, 54%): $[\alpha]_D^{20}$ = +54 (*c* = 1 in chloroform). ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.87 (d, *J* = 3.6 Hz, 1 H), 4.44 (d, *J* = 2.4 Hz, 2 H), 4.35 (d, *J* = 2.3 Hz, 1 H), 4.00 (ddd, *J* = 10.8, 5.0, 3.7 Hz, 1 H), 3.85–3.56 (m, 20 H), 3.42 (dd, *J* = 10.0, 9.0 Hz, 1 H), 3.38 (s, 3 H), 2.43 (t, *J* = 2.3 Hz, 1 H), 2.42 (t, *J* = 2.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 98.0, 81.3, 79.0, 77.9, 70.1, 79.9, 74.9, 74.0, 72.1, 71.3, 71.2, 70.9, 70.8, 70.5, 69.5, 60.3, 58.7, 55.0, 42.8 ppm. HRMS (FAB+): calcd. for $C_{21}H_{32}O_8$ $[M + Na]^+$ 505.1372; found 505.1377.

Methyl 3,4-Di-*O*-isopropylidene-2,6-di-*O*-propargyl-α-D-galactopyranoside (64): Obtained from **63** (234 mg) following the general procedure for the propargylation. Column chromatography (diethyl ether/hexane, 1:1) gave **64** isolated as a syrup (273 mg, 88%): $[\alpha]_D^{20}$ = +62 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 3265, 2117, 1242, 1221, 1101, 1073, 1042 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.87 (d, *J* = 3.5 Hz, 1 H), 4.42 (m, 4 H), 4.33–4.14, 3.87–3.75 (2 m, 6 H), 3.44 (s, 3 H), 2.47 (t, *J* = 2.4 Hz, 1 H), 2.45 (t, *J* = 2.3 Hz, 1 H), 1.56, 1.35 (2 s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 109.4, 98.3, 79.8, 79.6, 75.9, 75.9, 73.9, 66.5, 74.9, 74.7, 69.4, 58.7, 57.9, 55.5, 28.2, 26.4 ppm. HRMS (FAB+): calcd. for $C_{16}H_{22}O_6$ $[M + Na]^+$ 333.1314; found 333.1317.

Methyl 2,6-Di-*O*-propargyl-α-D-galactopyranoside (65): Obtained from **64** (310 mg) following the general procedure for the acetal hydrolysis Column chromatography (EtOAc) gave **65** as a syrup (257 mg, 95%): $[\alpha]_D^{20}$ = +101 (*c* = 1 in MeOH). IR (film): $\tilde{\nu}$ = 3450, 3261, 2216, 1143, 1093, 1044 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.02 (d, *J* = 3.3 Hz, 1 H, H-1), 4.41 (dd, *J* = 16.2, 2.4 Hz, 1 H, $OCH_2C{\equiv}CH$), 4.34 (dd, *J* = 16.2, 2.3 Hz, 1 H, $OCH_2C{\equiv}CH$), 4.23 (dd, *J* = 16.0, 2.4 Hz, 1 H, $OCH_2C{\equiv}CH$), 4.17 (dd, *J* = 16.0, 2.4 Hz, 1 H, $OCH_2C{\equiv}CH$), 4.10 (dd, *J* = 3.2, 1.0 Hz, 1 H, H-4), 4.02–3.96 (m, 2 H, H-3,5), 3.92 (dd, *J* = 9.8, 3.3 Hz, 1 H, H-2), 3.81 (dd, *J* = 10.0, 4.8 Hz, 1 H, H-6), 3.81 (dd, *J* = 10.0, 6.0 Hz, 1 H, H-6'), 3.46 (s, 3 H, OMe), 2.90–2.70 (br. s, 2 H, OH), 2.52 (t, *J* = 2.4 Hz, 1 H, C≡CH), 2.50 (t, *J* = 2.3 Hz, 1 H, C≡CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 97.8 (C-1), 79.9, 79.4 ($C{\equiv}CH$), 76.2 (C-2), 75.4, 75.1 ($C{\equiv}CH$), 69.9 (C-4), 69.6 (C-6), 69.3 (C-3), 68.3 (C-5), 58.9, 58.2 ($CH_2C{\equiv}CH$), 55.4 (MeO) ppm. HMRS (FAB+): calcd. for $C_{13}H_{18}O_6$ $[M + Na]^+$ 293.100; found 293.100.

Methyl 3,4-Di-*O*-chloroethoxyethyl-2,6-di-*O*-propargyl-α-D-galactopyranoside (66): Obtained from **65** (270 mg) following the general procedure for the synthesis of the (2-chloroethoxy)ethyl derivatives. Column chromatography (EtOAc/hexane, 1:1) gave **66** as a syrup (265 mg, 55%): $[\alpha]_D^{20}$ = +61 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 3288, 3255, 2215, 1352, 1096, 1049 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.90 (d, *J* = 3.7 Hz, 1 H, H-1), 4.41 (dd, *J* = 16.0, 2.4 Hz, 1 H), 4.35 (dd, *J* = 16.0, 2.3 Hz, 1 H), 4.25 (dd, *J* = 15.8, 2.4 Hz, 1 H), 4.28 (dd, *J* = 15.8, 2.3 Hz, 1 H), 4.12–3.60 (m, 22 H), 3.41 (s, 3 H), 2.47 (t, *J* = 2.3 Hz, 1 H), 2.43 (t, *J* = 2.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 98.8, 79.6, 76.1, 75.6, 74.7, 74.4, 72.5, 71.2, 71.2, 71.0, 70.8, 70.2, 69.1, 68.6, 59.0, 58.6, 55.3, 42.9, 42.9 ppm. HRMS (FAB+): calcd. for $C_{21}H_{32}O_8Cl_2$ [M + Na]$^+$ 505.1372; found 505.1369.

4,6:4′,6′-Di-*O*-benzylidene-2,3,2′,3′-tetra-*O*-propargyl-α,α-trehalose (68): Obtained from **67** (518 mg) following the general procedure for the propargylation Column chromatography (diethyl ether/hexane, 1:1) gave **68** isolated as a syrup (516 mg, 77%): $[\alpha]_D^{20}$ = +60 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 3287, 2250, 2118, 1453, 1372, 1088, 989, 752 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.55–7.30 (m, 10 H), 5.56 (s, 2 H), 5.26 (d, *J* = 3.9 Hz, 2 H), 4.55 (dd, *J* = 15.3, 2.4 Hz, 2 H), 4.46 (dd, *J* = 16.0, 2.4 Hz, 2 H), 4.44 (dd, *J* = 14.88, 2.4 Hz, 2 H), 4.39 (dd, *J* = 15.8, 2.4 Hz, 2 H), 4.34 (dd, *J* = 9.7, 4.9 Hz, 2 H), 4.24 (dt, *J* = 9.8, 4.9 Hz, 2 H), 3.99 (t, *J* = 9.2 Hz, 2 H), 4.75–3.67 (m, 4 H), 3.63 (t, *J* = 9.5 Hz, 2 H), 2.48 (t, *J* = 2.4 Hz, 2 H), 2.46 (t, *J* = 2.4 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 137.4, 129.0, 128.3, 126.1, 101.3, 94.9, 82.0, 80.2, 80.0, 78.2, 78.1, 74.8, 74.3, 69.0, 62.6, 60.2, 59.4 ppm. HRMS (FAB+): calcd. for $C_{38}H_{38}O_{11}$ [M + Na]$^+$ 693.2312; found 693.2310.

2,3,2′,3′-Tetra-*O*-propargyl-α,α-trehalose (69): Obtained from **68** (670 mg) following the general procedure for the acetal hydrolysis Column chromatography (EtOAc) gave **69** as a syrup (440 mg, 89%): $[\alpha]_D^{20}$ = +125 (*c* = 1 in MeOH). IR (film): $\tilde{\nu}$ = 3451, 3284, 2930, 2116, 1093, 1057, 998 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.27 (d, *J* = 3.7 Hz, 2 H), 4.55 (dd, *J* = 15.8, 2.4 Hz, 2 H), 4.42 (dd, *J* = 15.9, 2.3 Hz, 2 H), 4.29 (d, *J* = 2.3 Hz, 2 H), 4.03 (dt, *J* = 9.4, 3.7 Hz, 2 H), 3.89 (dd, *J* = 11.9, 3.1 Hz, 2 H), 3.82 (dd, *J* = 11.9, 4.4 Hz, 2 H), 3.78 (t, *J* = 9.2 Hz, 2 H), 3.65–3.54 (m, 4 H), 2.08 (br. s, 4 H), 2.54 (t, *J* = 2.3 Hz, 2 H), 2.48 (t, *J* = 2.3 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 94.0, 80.7, 80.5, 79.7, 79.0, 75.2, 75.0, 71.6, 69.9, 62.3, 60.4, 58.4 ppm. HRMS (FAB+): calcd. for $C_{24}H_{30}O_{11}$ [M + Na]$^+$ 517.1686; found 517.1686.

4,6:4′,6′-Tetra-*O*-chloroethoxyethyl-2,3,2′,3′-tetra-*O*-propargyl-α,α-trehalose (70): Obtained from **69** (494 mg) following the general procedure for the synthesis of the (2-chloroethoxy)ethyl derivatives. Column chromatography (diethyl ether) gave **70** as a syrup (598 mg, 65%): $[\alpha]_D^{20}$ = +80 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 3291, 2872, 2117, 1454, 1356, 1092 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.18 (d, *J* = 3.6 Hz, 2 H), 4.47 (d, *J* = 2.1 Hz, 4 H), 4.26 (m, 4 H), 4.08–3.98 (m, 4 H), 3.85–3.50 (m, 40 H), 3.43 (t, *J* = 9.6 Hz, 2 H), 2.48 (t, *J* = 2.3 Hz, 2 H), 2.42 (t, *J* = 2.3 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 94.0, 81.1, 80.4, 79.8, 78.6, 77.9, 74.7, 74.0, 72.0, 71.3, 71.1, 70.8, 70.5, 70.4, 69.4, 60.4, 58.2, 42.8, 42.7 ppm. HRMS (MALDI-TOF): calcd. for $C_{40}H_{58}Cl_4O_{15}$ [M + Na]$^+$ 943.258; found 943.258.

1,15-Dichloro-8,8-bis[1-(2,3,4,6-tetra-*O*-α-D-mannopyranosyloxyethyl)-1*H*-1,2,3-triazol-1-yl-4-methyloxy]-3,6,10,13-tetraoxapentadecane (71): Obtained from **58** (212 mg) and **7** (500 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 15:1) gave **71** as a syrup (604 mg, 96%): $[\alpha]_D^{20}$ = +21 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1748, 1370, 1226, 1138, 1091, 1048, 980 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (s, 2 H), 5.25–5.20 (m, 6 H), 4.81 (s, 2 H), 4.61 (br. s, 8 H), 4.22 (dd, *J* = 12.0, 5.1 Hz, 2 H), 4.18–4.10 (m, 2 H), 4.04 (br. d, *J* = 12.1 Hz, 2 H), 3.94–3.87 (m, 2 H), 3.75 (t, *J* = 5.6 Hz, 4 H), 3.65–3.54 (m, 14 H), 3.51 (s, 4 H), 3.45 (s, 4 H), 2.14, 2.10, 2.05, 1.99 (s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 169.9, 169.8, 169.7, 145.6, 123.7, 97.5, 71.2, 71.0, 70.4, 69.7, 69.3, 69.9, 69.9, 69.2, 65.7, 66.3, 64.8, 62.2, 49.6, 45.4, 43.0, 20.9, 20.8, 20.8, 20.7 ppm. HMRS (MALDI-TOF): calcd. for $C_{51}H_{76}N_6O_{26}Cl_2$ [M + Na]$^+$ 1281.408; found 1281.393.

1,15-Diazido-8,8-bis[1-(2,3,4,6-tetra-*O*-α-D-mannopyranosyloxyethyl)-1*H*-1,2,3-triazol-1-yl-4-methyloxy]-3,6,10,13-tetraoxapentadecane (72): Obtained from **71** (419 mg) following the general procedure for the synthesis of azido derivatives. Column chromatography (EtOAc/MeOH, 15:1) gave **72** as a syrup (411 mg, 97%): $[\alpha]_D^{20}$ = +22 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 2110, 1748, 1370, 1226, 1138, 1091, 1048, 980 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.69 (s, 2 H, H-triazole), 5.25–5.20 (m, 6 H, H-2,3,4), 4.81 (s, 2 H, H-1), 4.60 (br. s, 8 H, OCH_2CH_2-triazole, CH_2-triazole), 4.22 (dd, *J* = 12.0, 5.1 Hz, 2 H, H-6), 4.18–4.11 (m, 2 H, 2 CH_2O-sugar), 4.04 (dd, *J* = 12.4, 2.3 Hz, 2 H, H-6'), 3.91 (m, 2 H, 2 CH_2O-sugar), 3.67 (t, *J* = 5.0 Hz, 4 H, $N_3CH_2CH_2O$), 3.63–3.54 (m, 10 H, 2 $N_3CH_2CH_2OCH_2CH_2$, H-5), 3.51 (s, 4 H, OCH_2C), 3.46 (s, 4 H, OCH_2C), 3.37 (t, *J* = 5.0 Hz, 4 H, N_3CH_2), 2.14, 2.10, 2.04, 1.99 (4 s, 24 H, 4 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 169.9, 169.8, 169.6 (CO), 145.7 (*C*=CH), 123.6 (C=*C*H), 97.6 (C-1), 71.0, 70.4, 70.0, 69.8, 69.5 ($CH_2OCH_2CH_2OCH_2CCH_2$), 69.2, 69.0, 68.9, 65.7 (C-2,3,4,5), 66.3 (CH_2O-sugar), 64.8 (CH_2C=), 62.2 (C-6), 50.8 (CH_2N_3), 49.5 (CH_2N), 45.5 (C_{quat}), 20.8, 20.7, 20.7, 20.7 (*Me*CO) ppm. HMRS (MALDI-TOF): calcd. for $C_{51}H_{76}N_{12}O_{26}$ [M + Na]$^+$ 1295.489; found 1295.452.

8,8-Bis[1-(2,3,4,6-tetra-*O*-α-D-mannopyranosyloxyethyl)-4-methyloxy-1*H*-1,2,3-triazole-1,4-diyl]-1,15-bis[4-(2,3,4,6-tetra-*O*-α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (73): Obtained from **2** (231 mg) and **72** (318 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 15:1) gave **73** as a syrup (424 mg, 83%): $[\alpha]_D^{20}$ = +57.5 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1751, 1228, 1339, 1089, 1047 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.71, 7.69 (2 s, 2 H, H-5 triazole), 5.47 (t, 2 H, H-3 Glc), 5.29–5.18 (m, 6 H, H-2,3,4 Man), 5.22 (d, *J* = 3.6 Hz, 2 H, H-1 Glc), 5.08 (t, *J* = 9.9 Hz, 2 H, H-4 Glc), 4.88 (dd, *J* = 10.3, 3.6 Hz, 2 H, H-2 Glc), 4.82 (d, *J* = 12 Hz, 2 H, Glc-OCH_2), 4.81 (br. s, 2 H, H-1 Man), 4.67 (d, *J* = 12 Hz, 2 H, Glc-OCH_2), 4.60 (t, *J* = 5.0 Hz, 4 H, CH_2N), 4.58 (br. s, 4 H, OCH_2-triazole), 4.53 (t, *J* = 5.0 Hz, 4 H, CH_2N), 4.27 (dd, *J* = 12.1, 4.1 Hz, 2 H, H-6 Glc), 4.22 (dd, *J* = 12.2, 5.0 Hz, 2 H, H-6 Man), 4.17–4.03 (m, 8 H, H-5,6 Glc, H-6 Man, OCH_2-Man), 3.92 (m, 2 H, OCH_2-Man), 3.88 (t, *J* = 4.9 Hz, 4 H, OCH_2CH_2N), 3.63 (m, 2 H, H-5 Man), 3.60–3.48 (m, 8 H, OCH_2CH_2O), 3.48, 3.40 [2 s, 8 H, $C(CH_2)_4$], 2.14, 2.10, 2.10, 2.04, 2.02, 2.02, 1.9 (8 s, 48 H, 16 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.6, 170.1, 170.0, 169.6 (CO), 145.4, 143.4 (C-4 triazole), 124.1, 123.8 (C-5 triazole), 97.6 (C-1 Man), 95.1 (C-1 Glc), 71.1 (OCH_2CH_2O), 70.7 (C-2 Glc), 70.5 (OCH_2CH_2O), 70.2 (C-3 Glc), 69.9 (CCH_2O), 69.5 (OCH_2CH_2N), 69.4 (CCH_2O), 69.2 (C-2 Man), 69.1, 69.0 (C-3,5 Man), 68.6 (C-4 Glc), 67.6 (C-5 Glc), 66.3 (OCH_2CH_2N), 65.8 (C-4 Man), 64.8 (OCH_2-triazole), 62.3 (C-6 Man), 61.8 (C-6 Glc), 61.4 (CH_2O-Man), 50.5, 49.7 (2 CH_2N), 45.5 [$C(CH_2)_4$], 20.9, 20.8, 20.7, 20.6 (8 *Me*CO) ppm. HMRS (MALDI-TOF): calcd. for $C_{85}H_{120}N_{12}O_{46}$ [M + Na]$^+$ 2067.731; found 2067.771.

8,8-Bis[1-(2,3,4,6-tetra-*O*-α-D-mannopyranosyloxyethyl)-4-methyloxy-1*H*-1,2,3-triazole-1,4-diyl]-1,15-bis[4-(2,3,4,6-tetra-*O*-β-D-gluco-

pyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-3,6,10,13-tetraoxapentadecane (74): Obtained from **3** (231 mg) and **72** (218 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 15:1) gave **74** as a syrup (445 mg, 87%): $[\alpha]_D^{20}$ = –4.2 (*c* = 1 in chloroform). $[\alpha]_{436}^{20}$ = –9.3 (*c* = 1, chloroform). IR (KBr): $\tilde{\nu}$ = 1752, 1229, 1089, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.71, 7.72 (2 s, 2 H), 5.28–5.17 (m, 8 H), 5.09 (t, *J* = 9.5 Hz, 2 H), 4.97 (br. t, *J* = 8.0 Hz, 2 H), 4.92 (d, *J* = 12.6 Hz, 2 H), 4.82 (br. s, 2 H), 4.79 (d, *J* = 12.6 Hz, 2 H), 4.71 (d, *J* = 7.9 Hz, 2 H), 4.64–4.50 (m, 12 H), 4.28 (dd, *J* = 12.4, 4.6 Hz, 2 H), 4.22 (dd, *J* = 12.5, 5.1 Hz, 2 H), 4.15 (dd, *J* = 10.3, 2.2 Hz, 2 H), 4.15–4.10 (m, 2 H), 4.05 (dd, *J* = 12.4, 2.3 Hz, 2 H), 3.95–3.88 (m, 2 H), 3.86 (t, *J* = 5.2 Hz, 4 H), 3.76 (ddd, *J* = 9.9, 4.4, 2.3 Hz, 2 H), 3.64 (m, 2 H), 3.58–3.47 (m, 8 H), 3.46, 3.39 (2 s, 8 H), 2.14, 2.09, 2.04, 2.03, 1.99, 1.98, 1.97 (7 s, 48 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 170.1, 169.9, 169.5, 145.3, 143.7, 124.1, 123.8, 99.7, 97.5, 72.8, 71.8, 71.2, 70.9, 70.3, 69.8, 69.4, 69.1, 68.9, 68.9, 68.3, 66.2, 65.7, 64.8, 62.7, 62.2, 61.8, 50.4, 49.6, 45.3, 20.8, 20.7, 20.6, 20.6 ppm. HMRS (MALDI-TOF): calcd. for $C_{85}H_{120}N_{12}O_{46}$ $[M + Na]^+$ 2067.731; found 2067.826.

1,15-Bis[4-(α-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-8,8-bis[1-(α-D-mannopyranosyloxyethyl)-4-methyloxy-1*H*-1,2,3-triazole-1,4-diyl]-3,6,10,13-tetraoxapentadecane (75): Obtained from **73** (409 mg) following the general procedure for the de-*O*-acetylation (method A). Column chromatography (MeOH) gave **75** as a syrup (273 mg, 98%): $[\alpha]_D^{20}$ = +3, $[\alpha]_{436}^{20}$ = +9 (*c* = 0.5 in MeOH). IR (KBr): $\tilde{\nu}$ = 3390, 2919, 1651, 1479, 1057 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.05, 7.99 (2 s, 4 H, H-5 triazole), 4.91 (d, *J* = 3.6 Hz, 2 H), 4.73 (s, 2 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 146.2, 145.3, 126.1, 125.8, 101.6, 99.6, 75.1, 74.9, 74.0, 73.5, 72.5, 72.1, 71.9, 71.8, 71.4, 70.7, 70.4, 70.1, 68.4, 66.8, 65.3, 62.8, 62.7, 61.4, 51.5, 51.3, 46.6 ppm. HMRS (MALDI-TOF): calcd. for $C_{53}H_{88}N_{12}O_{30}$ $[M + Na]^+$ 1395.560; found 1395.579.

1,15-Bis[4-(β-D-glucopyranosyloxymethyl)-1*H*-1,2,3-triazol-1-yl]-8,8-bis[1-(α-D-mannopyranosyloxyethyl)-4-methyloxy-1*H*-1,2,3-triazole-1,4-diyl]-3,6,10,13-tetraoxapentadecane (76): Obtained from **74** (409 mg) following the general procedure for the de-*O*-acetylation (method A). Column chromatography (MeOH) gave **76** as a syrup (257 mg, 92%): $[\alpha]_D^{20}$ = +64 (*c* = 1 in MeOH). IR (KBr): $\tilde{\nu}$ = 3365, 2908, 1654, 1458, 1046 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.02, 7.98 (2 s, 4 H), 4.40 (d, *J* = 7.7 Hz, 2 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 146.2, 145.5, 126.1, 125.8, 103.6, 101.6, 78.0, 75.0, 74.9, 72.5, 72.1, 71.9, 71.6, 71.4, 70.4, 70.0, 68.4, 66.8, 65.3, 63.0, 62.8, 51.5, 51.2 ppm. HMRS (MALDI-TOF): calcd. for $C_{53}H_{88}N_{12}O_{30}$ $[M + Na]^+$ 1395.56; found 1395.55.

Methyl 4,6-Di-*O*-(5-chloro-3-oxapentyl)-2,3-di-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-α-D-glucopyranoside (77): Obtained from **62** (241 mg) and **7** (500 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 15:1) gave **77** as a syrup (526 mg, 80%): $[\alpha]_D^{20}$ = +50 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1752, 1228, 1139, 1091, 1049 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.99, 7.92 (2 s, 2 H, H-5 triazole), 5.30–5.19 (m, 6 H, H-2,3,4), 4.98 (AB system, *J* = 11.4 Hz, $\Delta\mu$ = 13.0 Hz, 2 H, OCH_2-triazole), 4.84 (d, *J* = 12.2 Hz, 1 H, OCH_2-triazole), 4.83 (d, *J* = 3.8 Hz, 1 H, H-1 Glc), 4.80–4.79 (2 s, 2 H, H-1 Man), 4.81 (d, *J* = 11.9 Hz, 1 H, OCH_2-triazole), 4.67–4.50 (m, 4 H, CH_2N), 4.27–3.88 (m, 8 H, H-6,6′ Man, CH_2O-Man), 3.84 (t, *J* = 9.4 Hz, 1 H, H-3 Glc), 3.80–3.57 (m, 21 H, H-5,6,6' Glc, H-5 Man, $ClCH_2CH_2$-OCH_2CH_2O), 3.53 (dd, *J* = 9.6, 3.5 Hz, 1 H, H-2 Glc), 3.42 (t, *J* = 9.2 Hz, 1 H, H-4 Glc), 3.38 (s, 3 H, OMe), 2.12, 2.08, 2.03, 1.97 (4 s, 24 H, 4 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 169.8, 169.7, 169.6 (COO), 145.4, 144.9, 124.4, 124.3 (triazole), 97.6, 97.5 (C-1), 81.4, 79.5, 78.0, 72.1, 71.2, 71.1, 70.8, 70.7, 70.5, 70.0, 69.5, 69.1, 69.1, 68.9, 66.3, 66.2, 65.7, 64.2, 64.2, 55.0, 49.5, 43.0, 42.8, 20.7, 20.6, 20.6 (*Me*CO) ppm. HRMS (FAB+): calcd. for $C_{53}H_{78}ClO_{28}N_6$ $[M + Na]^+$ 1339.414; found 1339.336.

Methyl 4,6-di-*O*-(5-azido-3-oxapentyl)-2,3-di-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-α-D-glucopyranoside (78): Obtained from **77** (439 mg) following the general procedure for the synthesis of the azido reactions. Column chromatography (EtOAc/MeOH, 15:1) gave **78** as a syrup (403 mg, 91%): $[\alpha]_D^{20}$ = +57 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 2110, 1749, 1227, 1138, 1090, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.96, 7.89 (2 s, 2 H), 5.30–5.15 (m, 6 H), 5.02–4.78 (m, 7 H), 4.70–4.50 (m, 4 H), 4.23 (dd, *J* = 12.4, 5.0 Hz, 2 H), 4.20–3.30 (several m, 28 H), 3.86 (t, *J* = 9.4 Hz, 1 H), 3.55 (dd, *J* = 9.6, 3.5 Hz, 1 H), 3.39 (s, 3 H), 2.17, 2.10, 2.04, 1.98 (4 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 169.8, 169.7, 169.6, 145.4, 144.9, 124.4, 124.1, 97.6, 81.4, 79.5, 78.0, 72.0, 70.8, 70.7, 70.5, 70.0, 69.9, 69.8, 69.5, 69.1, 69.0, 68.8, 68.8, 66.3, 65.7, 64.3, 61.1, 54.9, 50.7, 49.5, 20.7, 20.6, 20.6, 20.5 ppm. HRMS (FAB+): calcd. for $C_{53}H_{71}O_{28}N_{12}$ $[M + Na]^+$ 1353.495; found 1353.454.

Methyl 2,3-Di-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-4,6-di-*O*-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-α-D-glucopyranoside (79): Obtained from **78** (266 mg) and **3** (185 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 10:1) gave **79** as a foamy solid (382 mg, 91%): $[\alpha]_D^{20}$ = +17 (*c* = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1754, 1372, 1231, 1139, 1089, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, selected signals): δ = 7.91, 7.89, 7.75, 7.67 (4 s, 2 H), 3.39 (s, 3 H), 2.14, 2.13, 2.10, 2.09, 20.4, 2.03, 2.02, 1.99, 1.97, 1.96, 1.95 (10 s, 48 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4, 170.4, 170.0, 169.8, 169.6, 169.4, 169.4, 145.0, 144.6, 143.6, 124.3, 124.0, 123.7, 99.6, 97.4, 81.2, 79.2, 77.8, 72.6, 71.7, 71.0, 70.6, 70.3, 69.2, 69.1, 69.0, 68.8, 68.7, 68.2, 66.1, 65.6, 62.6, 62.1, 61.7, 54.9, 50.1, 49.4, 20.6, 20.6, 20.5, 20.4 ppm. HRMS (FAB+): calcd. for $C_{87}H_{122}O_{48}N_{12}$ $[M + Na]^+$ 2125.737; found 2125.736.

Methyl 4,6-Di-*O*-[4-(β-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-2,3-Di-*O*-[1-(α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-α-D-glucopyranoside (80): Obtained from **79** (350 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (MeOH) gave **80** as a syrup (212 mg, 89%): $[\alpha]_D^{20}$ = –9 (*c* = 0.25 in H_2O). IR (KBr): $\tilde{\nu}$ = 3400, 2924, 1135, 1055 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.10, 8.06, 8.03, 8.01 (4 s, 4 H) ppm. ^{13}C NMR (CD_3OD, 75 MHz): δ = 146.4, 145.9, 145.6, 126.2, 126.1, 126.0, 103.8, 103.6, 101.6, 99.0, 82.5, 80.7, 79.1, 78.0, 75.0, 74.9, 73.0, 72.5, 72.4, 71.8, 71.7, 71.5, 71.4, 70.3, 70.2, 68.4, 67.0, 66.8, 66.7, 64.8, 63.2, 63.1, 62.8, 55.7, 51.5, 51.2, 49.9 ppm. HRMS (MALDI-TOF): calcd. for $C_{55}H_{90}O_{32}N_{12}$ $[M + Na]^+$ 1453.60; found 1453.60.

Methyl 3,4-Di-*O*-(5-chloro-3-oxapentanyl)-2,6-di-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-α-D-galactopyranoside (81): Obtained from **66** (241 mg) and **7** (500 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 15:1) gave **81** as a syrup (618 mg, 94%): $[\alpha]_D^{20}$ = +42 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1751, 1228, 1139, 1092, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.74 (s, 1 H), 7.69 (s, 1 H), 5.27–5.20 (m, 6 H), 4.96 (d, *J* = 12.1 Hz, 1 H), 4.83 (d, *J* = 12.1 Hz, 1 H), 4.82 (d, *J* =

3.7 Hz, 1 H), 4.80 (br. s, 2 H), 4.73 (d, J = 12.5 Hz, 1 H), 4.67 (d, J = 12.5 Hz, 1 H), 4.65–4.55 (m, 4 H), 4.27–3.55 (m, 28 H), 3.37 (s, 3 H), 2.14, 2.09, 2.05, 1.99 (4 s, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4, 169.7, 169.7, 169.4, 145.5, 145.0, 123.9, 123.7, 98.4, 97.5, 97.4, 79.4, 76.0, 72.3, 71.1, 71.0, 70.8, 70.2, 69.0, 68.9, 68.8, 68.7, 66.2, 66.1, 65.6, 64.6, 64.4, 62.1, 55.1, 49.6, 49.5, 43.1, 43.0, 20.7, 20.6, 20.5 ppm. HMRS (MALDI-TOF): calcd. for $C_{53}H_{78}N_6O_{28}Cl_2$ [M + Na]$^+$ 1318.115; found 1339.438.

Methyl 3,4-Di-*O*-(5-azido-3-oxapentyl)-2,6-di-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-α-D-galactopyranoside (82): Obtained from **81** (439 mg) following the general procedure for the synthesis of the azido derivatives. Column chromatography (EtOAc/MeOH, 15:1) gave **82** as a foamy solid (333 mg, 75%): $[\alpha]_D^{20}$ = +41.5 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 2211, 1749, 1228, 1139, 1092, 1048 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.71 (s, 1 H), 7.68 (s, 1 H), 5.28–5.19 (m, 6 H), 4.91 (d, J = 12.2 Hz, 1 H), 4.83 (d, J = 12.2 Hz, 1 H), 4.82 (d, J = 3.6 Hz, 1 H), 4.79 (br. s, 2 H), 4.73 (d, J = 12.2 Hz, 1 H), 4.67 (d, J = 12.2 Hz, 1 H), 4.64–4.52 (m, 4 H), 4.25–3.59 (m, 24 H), 3.41–3.35 (m, 4 H), 3.37 (s, 3 H), 2.14, 2.09, 2.05, 1.99 (4 s, J = 24 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.5, 169.9, 169.8, 169.6, 159.6, 145.6, 145.2, 123.9, 123.9, 98.6, 97.6, 97.5, 79.6, 76.2, 76.2, 72.5, 71.0, 70.9, 70.3, 69.0, 69.2, 69.1, 69.0, 69.0, 68.9, 68.8, 66.3, 66.2, 65.8, 65.8, 64.8, 64.6, 62.2, 55.3, 50.9, 50.8, 49.7, 49.6, 20.8, 20.7, 20.6 ppm. HMRS (MALDI-TOF): calcd. for $C_{53}H_{78}N_{12}O_{28}$ [M + Na]$^+$ 1331.495; found 1353.517.

Methyl 3,4-Di-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-2,6-di-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-1*H*-1,2,3-triazole-1,4-diyl]-α-D-galactopyranoside (83): Obtained from **82** (266 mg) and **3** (185 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 10:1) gave **83** as a foamy solid (395 mg, 94%): $[\alpha]_D^{20}$ = +9, $[\alpha]_{436}^{20}$ = +16 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 1755, 1231, 1138, 1092, 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.75, 7.68, 7.66, 7.63 (4 s, 4 H, H-5 triazole), 5.23 (t, J = 9.7 Hz, 2 H, H-4 Man), 5.20–5.14 (m, 6 H, H-2,3 Man, H-3 Glc), 5.07 (br. t, J = 9.6 Hz, 2 H, H-4 Glc), 4.96 (dd, J = 9.2, 8.0 Hz, 2 H, H-2 Glc), 4.88 (d, J = 12.5 Hz, 1 H, OCH_2-triazole), 4.87 (d, J = 12.5 Hz, 1 H, OCH_2-triazole), 4.86 (d, J = 12.1 Hz, 1 H, OCH_2-triazole), 4.78 (d, J = 3.5 Hz, 1 H, H-1 Gal), 4.77 (br. s, 2 H, H-1 Man), 4.76 (d, J = 12.1 Hz, 1 H, OCH_2-triazole), 4.75 (d, J = 12.5 Hz, 1 H, OCH_2-triazole), 4.74 (d, J = 12.5 Hz, 1 H, OCH_2-triazole), 4.69 (d, J = 8.0 Hz, 1 H, H-1 Glc), 4.68 (d, J = 8.0 Hz, 1 H, H-1 Glc), 4.65 (d, J = 12.4 Hz, 1 H, OCH_2-triazole), 4.58 (d, J = 12.4 Hz, 1 H, OCH_2-triazole), 4.60–4.45 (m, 8 H, 4 CH_2N), 4.27 (dd, J = 12.4, 4.5 Hz, 1 H, H-6 Glc), 4.26 (dd, J = 12.4, 4.5 Hz, 1 H, H-6 Glc), 4.23–4.00, 3.95–3.50 [2 m, 40 H, H-2,3,4, H-5,6,6' Gal, $(CH_2CH_2)_2O$, triazole-CH_2CH_2O, H-5 Glc, H-5 Man, H-6 Glc, 4 H-6 Man], 3.37 (s, 3 H, OMe), 2.13, 2.09, 2.04, 2.02, 1.99, 1.98, 1.96 (7 s, 48 H, 16 Ac) ppm. HRMS (MALDI-TOF): calcd. for $C_{87}H_{122}N_{12}O_{48}$ [M + Na]$^+$ 2125.737; found 2125.696.

Methyl 3,4-Di-*O*-[1-(β-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-2,6-di-*O*-[1-(α-D-mannopyranosyloxyethyl)-1*H*-1,2,3-triazole-1,4-diyl]-α-D-galactopyranoside (84): Obtained from **83** (350 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (MeOH) gave **84** as a syrup (219 mg, 92%): $[\alpha]_D^{20}$ = +10 (c = 0.25 in H_2O). IR (KBr): $\tilde{\nu}$ = 3395, 2924, 1135, 1090, 1055 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz, selected signals): δ = 8.08, 8.04, 8.01, 7.97 (4 s, 4 H), 3.34 (s, 3 H) ppm. ^{13}C NMR (CD_3OD, 100 MHz): δ = 146.1, 145.8, 145.5, 145.5, 126.2, 126.1, 126.0, 126.0, 103.7, 103.6, 101.6, 99.7, 80.4, 78.0, 78.0, 77.2, 76.9, 75.0, 74.9, 73.2, 72.4, 72.0, 71.9, 71.8, 71.8, 71.6, 71.0, 60.4, 70.2, 70.2, 70.1, 68.4, 68.3, 66.7, 65.1, 65.0, 63.1, 63.0, 62.8, 55.7, 51.5, 51.2, 49.6 ppm. MS (MALDI-TOF): calcd. for $C_{55}H_{90}N_{12}O_{32}$ [M + Na]$^+$ 1453.568; found 1453.67.

4,6:4′,6′-Tetra-*O*-(5-chloro-3-oxapentyl)-2,3,2′,3′-tetra-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-α,α′-trehalose (85): Obtained from **70** (230 mg) and **7** (500 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 15:1) gave **85** as a syrup (595 mg, 92%): $[\alpha]_D^{20}$ = +65 (c = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1751, 1372, 1228, 1139, 1091, 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, selected signals): δ = 8.09 (s, 2 H), 7.89 (s, 2 H), 2.14, 2.11, 2.10, 2.05, 2.04, 1.98 (6 s, 48 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 169.8, 169.7, 169.6, 145.3, 144.9, 124.5, 124.3, 97.6, 93.4, 80.6, 78.8, 77.8, 71.9, 71.1, 71.0, 70.7, 70.6, 70.3, 69.4, 69.0, 68.9, 68.8, 68.7, 68.7, 66.3, 66.2, 66.0, 65.6, 63.8, 62.2, 49.4, 49.3, 43.2, 42.8, 20.7, 20.6, 20.5 ppm. HRMS (MALDI-TOF): calcd. for $C_{104}H_{150}Cl_4O_{55}N_{12}$ [M + Na]$^+$ 2609.812; found 2609.880.

4,6:4′,6′-Tetra-*O*-(5-azido-3-oxapentyl)-2,3,2′,3′-tetra-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-α,α′-trehalose (86): Obtained from **85** (517 mg) following the general procedure for the synthesis of the azido reactions. Column chromatography (EtOAc/MeOH, 10:1) gave as a solid foamy **86** (418 mg, 80%): $[\alpha]_D^{20}$ = +68 (c = 1 in chloroform). IR (KBr): $\tilde{\nu}$ = 2113, 1751, 1227, 1139, 1090, 1048 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.09, 7.89 (2 s, 4 H, H-5 triazole), 5.30–5.18 (m, 14 H, H-1 trehalose, H-2,3,4 Man), 5.00, 4.95 (2 d, J = 11.3 Hz, 4 H, CH_2-triazole), 4.85, 4.82 (2 br. s, 4 H, H-1 Man), 4.83, 4.68 (2 d, 4 H, CH_2- triazole), 4.70–4.50 (m, 8 H, CH_2N triazole), 4.25 (m, 4 H, H-6 Man), 4.15 (m, 4 H, CH_2O-Man), 4.08 (bd, 4 H, H-6' Man), 4.08–3.90 (m, 6 H, CH_2 Man, H-5 trehalose), 3.85 (t, J = 9.3 Hz, 2 H, H-3 trehalose), 3.85–3.60 (m, 32 H, CH_2O spacer, H-6 trehalose, H-5 Man), 3.51 (dd, J = 9.6, 3.5 Hz, 2 H, H-2 trehalose), 3.47–3.30 (m, 10 H, CH_2N$_3$, H-4 trehalose), 2.13–1.97 (5 s, 48 H, CH_3CO) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 169.9, 169.8, 169.7 (CH_3CO), 145.6, 145.2 (C-4 triazole), 124.5, 124.2 (C-5 triazole), 97.8 (C-1 Man), 93.6 (C-1 trehalose), 81.0 (C-3 trehalose), 79.0 (C-2 trehalose), 78.1 (C-4 trehalose), 72.1, 71.0, 70.9, 70.8 (C-5 trehalose), 70.5, 69.9, 69.8 (CH_2 spacer), 69.5 (C-6 trehalose), 69.2, 69.0, 68.9 (C-2,3,5 Man), 66.5, 66.4 (CH_2 Man), 66.3 (CH_2 triazole), 65.9 (C-4 Man), 64.1 (CH_2 triazole), 62.3 (C-6 Man), 50.8, 50.7 [CH_2(N) triazole], 49.5, 49.4 (CH_2N_3), 20.9, 20.8, 20.8, 20.7 (CH_3COO) ppm. HRMS (MALDI-TOF): calcd. for $C_{104}H_{150}O_{55}N_{24}$ [M + Na]$^+$ 2637.973; found 2637.790.

2,3,2′,3′-Tetra-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-4,6:4′,6′-tetra-*O*-[4-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-α,α′-trehalose (87): Obtained from **2** (309 mg) and **86** (436 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 10:1) gave **87** as a foamy solid (527 mg, 76%): $[\alpha]_D^{20}$ = +88 (c = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1751, 1371, 1229, 1046 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, selected signals): δ = 8.10, 7.88, 7.79, 7.63 (4 s, 4 H, H-5 triazole), 5.46, 5.44 (2 t, J = 9.8 Hz, 2 H, H-3 Glc), 5.3–5.15 (m), 5.08 (t, J = 9.8 Hz, 2 H, H-4 Glc), 5.00–4.57 (m), 4.85 (s, 2 H, H-1 Man), 4.52 (t, J = 5.0 Hz, 2 H, CH_2), 4.30–3.35 (several m), 2.14, 2.13, 2.09, 2.04, 2.04, 2.02, 1.99, 1.98, 1.96 (several s, 96 H, 32 Ac) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 170.5, 170.0, 169.9, 169.5 (COO), 145.1, 144.7, 143.3 (C-4 triazole), 124.6, 124.1, 123.9 (C-5 triazole), 97.6, 97.5 (C-1 Man), 95.1 (C-1Glc),

93.2 (C-1 trehalose), 80.7, 78.8, 77.9, 71.8, 71.1, 70.7, 70.5, 70.3, 70.0, 69.3, 69.1, 68.9, 68.8, 68.4, 67.4, 66.2, 65.7, 63.8, 62.1, 61.6, 61.2, 61.1, 60.3, 50.1, 49.5, 49.4 (CH_2N), 20.7, 20.6, 20.6 (CH_3CO) ppm. HRMS (MALDI-TOF): calcd. for $C_{172}H_{238}N_{24}O_{95}$ [M + Na]$^+$ 4184.885; found 4184.896.

2,3,2′,3′-Tetra-*O*-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-4,6:4′,6′-tetra-*O*-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-α,α′-trehalose (88): Obtained from **3** (309 mg) and **86** (436 mg) following the general procedure for the CuAAC reactions. Column chromatography (EtOAc/MeOH, 10:1) gave **79** as a foamy solid (596 mg, 86%): $[\alpha]_D^{20}$ = +20 (*c* = 1 in chloroform). IR (film): $\tilde{\nu}$ = 1751, 1371, 1228, 1139, 1089, 1046 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, selected signals): δ = 8.09, 7.88, 7.75, 7.70 (4 s, 8 H), 2.14, 2.13, 2.10, 2.09, 2.08, 2.05, 2.04, 2.03, 1.99, 1.97, 1.96, 1.95 (several s, 96 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 170.1, 169.9, 169.6, 169.4, 169.3, 145.1, 144.7, 143.7, 143.7, 124.6, 124.2, 123.9, 99.8, 99.7, 97.5, 93.0, 80.5, 72.7, 71.8, 71.1, 70.7, 70.3, 69.2, 69.0, 68.9, 68.8, 68.3, 66.2, 65.7, 62.7, 62.1, 61.8, 50.2, 49.4, 20.7, 20.6, 20.5 ppm. HRMS (MALDI-TOF): calcd. for $C_{172}H_{238}N_{24}O_{95}$ [M + Na]$^+$ 4184.885; found 4184.896.

2,3,2′,3′-Tetra-*O*-[1-(α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-4,6:4′,6′-tetra-*O*-[4-(α-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-α,α′-trehalose (89): Obtained from **87** (520 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (acetonitrile/H_2O, 2:1) gave **89** as a syrup (303 mg, 86%): $[\alpha]_D^{20}$ = +76 (*c* = 0.25 in H_2O). IR (film): $\tilde{\nu}$ = 3406, 1104 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 300 MHz, selected signals): δ = 8.09, 8.06, 8.04, 8.01 (4 s, 8 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 145.2, 144.8, 144.4, 125.4, 125.3, 1235.2, 100.3, 98.6, 93.0, 81.2, 79.0, 77.9, 77.2, 74.3, 73.9, 73.2, 72.4, 71.4, 70.7, 70.1, 69.2, 67.3, 66.1, 65.6, 61.7, 61.5, 60.5, 60.4, 50.4, 50.2 ppm. HRMS (MALDI-TOF): calcd. for $C_{108}H_{174}N_{24}O_{63}$ [M + Na]$^+$ 2838.104; found 2837.929.

2,3,2′,3′-Tetra-*O*-[1-(α-D-mannopyranosyloxyethyl)-4-methyl-1*H*-1,2,3-triazole-1,4-diyl]-4,6:4′,6′-tetra-*O*-[4-(β-D-glucopyranosyloxymethyl)-1-(3-oxapentyl)-1*H*-1,2,3-triazole-1,4-diyl]-α,α′-trehalose (90): Obtained from **88** (520 mg) following the general procedure for the de-*O*-acetylation (method B). Column chromatography (acetonitrile/H_2O, 2:1) gave **90** as a syrup (281 mg, 80%): $[\alpha]_D^{20}$ = +8.7, $[\alpha]_{436}^{20}$ = +15.3 (*c* = 0.25 in H_2O). IR (film): $\tilde{\nu}$ = 3384, 1103 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 300 MHz, selected signals): δ = 8.10, 8.07, 8.06, 8.01 (4 s, 8 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 144.3, 143.9, 143.6, 124.5, 124.2, 124.0, 102.1, 99.8, 76.9, 76.7, 74.1, 74.0, 73.3, 70.8, 70.1, 70.0, 69.2, 68.6, 68.5, 66.8, 64.8, 63.2, 61.4, 61.1, 49.2 ppm. HRMS (MALDI-TOF): calcd. for $C_{108}H_{174}N_{24}O_{63}$ [M + Na]$^+$ 2838.104; found 2838.002.

Enzyme-Linked Lectin Assay (ELLA): ELLA assays were carried out as described previously.[33] Experiments were carried out with a Metertech Σ960 instrument. Microtitration plates were coated with *S. cerevisiae* mannan at 100 μL/well of a solution of 10 μg/mL in 10 mM phosphate buffer (PBS, pH 7.4) for 2 h at 37 °C. The wells were then washed twice with 10 mM phosphate buffer containing 1% (v/v) Tween 20 (PBST) and once with PBS. This washing procedure was repeated after each incubation period. Wells were then blocked with 300 μL/well of BSA/PBS (1% w/v) for 2 h at 37 °C. Each inhibitor was added in serial dilutions (60 μL/well) of the glycoconjugates or methyl α-D-Man in PBS (pH 6.8, containing 0.1 mM $Ca^{2+}$and 0.1 mM Mn^{2+}), and the peroxidase-labeled Con A (60 μL/well of a solution of 50 μg/mL in PBS, pH 6.8, containing 0.1 mM Ca^{2+} and 0.1 mM Mn^{2+}) was added. The mixtures of glycoclusters or methyl α-D-Man and the peroxidase-labeled lectin (100 μL/well) were added, and the plates were incubated for 2 h at 37 °C. After that, 50 μL/well of a solution of *o*-phenylenediamine dihydrochloride (20 mg/50 mL) in citrate–phosphate buffer (pH 5.0 with 0.4% H_2O_2) was added. The plates were incubated for 30 min at 37 °C. The reactions were stopped by addition of aqueous H_2SO_4 (50 μL/well, 1.25 M), and the absorbance measured at 492 nm.

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