Carbohydrate Research 346 (2011) 1511–1518

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Gold catalyzed glycosidations for the synthesis of sugar acrylate/acrylamide hybrids and their utility

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ARTICLE INFO

Article history:
Available online 23 April 2011

Dedicated to Professor Andras Liptak on occasion of his 75th birthday

Keywords:
Glycopolymers
Carbohydrates
Glycosylation
Glycoacrylates
Glycoacrylamides
Gold

ABSTRACT

Propargyl glyco 1,2-orthoesters were exploited for the efficient synthesis of interesting glycomonomers such as glyco-acrylates and acrylamides using gold catalysts. It was observed that propargyl glyco 1,2-orthoesters with hydroxyethyl acrylates gives very good yield of the corresponding glyco-acrylates in a single step in the presence of catalytic amount of gold(III) catalyst; whereas, gold catalyzed glycosidation reaction on hydroxyethyl acrylamides was found to yield the corresponding acrylamidoyl 1,2-orthoester which was then converted to the corresponding glycol-acrylamide in the presence of catalytic amount of TMSOTf. Synthesized glyco-acrylate/acrylamide monomers are shown to undergo thiolate addition as well as free radical polymerization.

1. Introduction

Synthetic macromolecules with pendant saccharide residues are known as glycopolymers which are studied immensely for a variety of applications such as drug delivery agents, hydrogels, extracellular matrices for controlled cell culture, supports for chromatography, and sometimes as multivalent biological probes.[1] In addition, the multivalent display of pendant glycans is understood to be beneficial in mimicking natural cell surface oligosaccharides.[2] Nature uses glycolipids and glycoproteins effectively in cell signaling, cell–cell differentiation, and communication.[3] This happens as a result of very specific interactions that takes place between the glycans of the glycoproteins and their corresponding receptors at the cell surface.[4] Multivalent glycolipids and glycoproteins can, respectively, be defined as glycosides of long chain hydrocarbons and proteins. Isolation of naturally occurring glycopolymers from the nature is rather tedious as they exist in the microheterogenous forms and thus chemical synthesis of their mimics is the most convenient and effective route.[5] Synthesis of polymers with carbohydrate epitopes as pendants is an easy way to mimic glycolipids and glycoproteins. They also allow us to study the role of polyvalency that is known to be responsible for the high specificity of these glycan–receptor interactions.[6]

To investigate basic roles of carbohydrate moieties of glycoconjugates in these interactions, simple model polymers with excellent solubility in aqueous medium needs to be synthesized from polymerizable glycomonomers. However, for any useful glycopolymer, the simplicity in backbone structure is essential as it facilitates easy understanding of carbohydrate protein interactions. Further, general synthetic strategies should be designed in such a way that glycopolymers of various size, shapes, and grafting density can be synthesized easily.[7]

Existing methods for the synthesis of glycopolymers can be classified into two major classes. At the first instance, glycopolymers are advantageously synthesized by subjecting a sugar residue with a pendant polymerizable functional group to suitable polymerization conditions to obtain good glycosylation density (Fig. 1).[8] For example, glycopolymers can be synthesized by free radical polymerization of glycomonomers. The most commonly used glycomonomer for such polymerization reactions are acryloyl and acrylamido glycosides bearing ω-linker of various lengths. The resulting glycopolymers formed, such as polyacrylamide glycoside, is non-toxic and water soluble.[8b] Further the degree of incorporation of the oligosaccharide can be varied by copolymerization with another acrylamide monomer. Similarly, neoglycoproteins can be synthesized from glyco *N*-carboxyanhydrides which in turn can be obtained from amino acid glycoconjugates.[8c] However, multistep synthesis of the monomer, laborious work-up, and purification are the major limitations.

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doi:10.1016/j.carres.2011.04.018

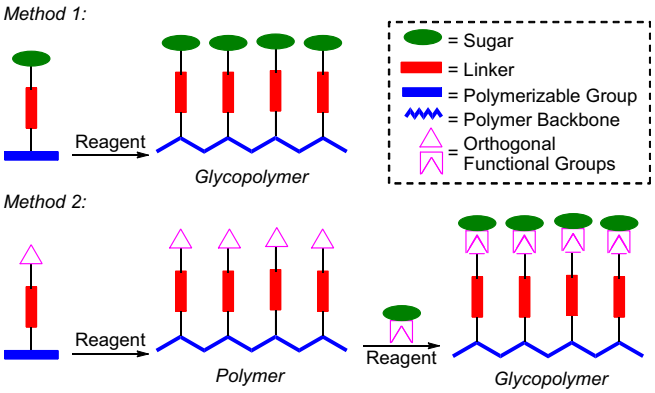


Figure 1. Strategies for glycopolymer synthesis.

Alternatively, glycopolymers can also be synthesized in a two step manner; first polymers are synthesized with a functional group that can then be used to stick a sugar monomer with an orthogonal functional group (Fig. 1). For example, Haddleton's group has successfully synthesized alkynated polymers and then attached sugar moieties through a CuAAC (or 'click') reaction.[9] Along with the inherent merits of the post-polymer synthesis grafting method, the ambiguous number of attached sugar residues which is often difficult to estimate and the distribution of glycosides along the polymeric backbone are the limitations. The key in both of these approaches is the easy access to sugar-monomer glycosides.[7] The existing methods for the preparation of sugar-monomers suffer from one or more of the drawbacks such as harsh reactions, high temperatures, tedious work-up, laborious purification procedures, and many a time the reaction conditions interfere with the functional groups present on the required aglycone.[7]

In this context, our recently identified methodology for 1,2-*trans* diastereoselective saccharides and glycosides from corresponding propargyl 1,2-orthoesters using $AuBr_3$ would be ideal as the glycosyl donor activation procedure tolerates a wide range of functional groups.[10] Some of the major advantages of glycosylation by means of propargyl 1,2-orthoesters are (i) the reaction is high yielding and stereoselective, (ii) the glycosyl donor is stable and can be easily accessed in two steps from the aldose and (iii) the glycosyl donor activation by $AuBr_3$ tolerates the presence of alkenes, ethers, esters, etc. Thus we envisioned that the $AuBr_3$ catalyzed glycosylation of versatile and polymerizable aglycones, such as hydroxyethyl acrylates/acrylamides and hydroxy-amino acids could be possible as the reagents used for glycosylation do not react with alkenes.[10]

2. Results and discussion

The most commonly studied glycopolymers have been the water soluble poly(vinylsachharides) which are typically glycopolymers with a pendant carbohydrate on a acrylate, acrylamide, polypeptide, or polystyrene backbone.[11] The first three glycopolymers mentioned above are typically synthesized by vinyl-type free-radical polymerization of well-defined saccharide-based monomers. The monomers are in turn prepared by coupling an unsaturated component to a carbohydrate derivative through an ether, ester, or amido linkage. A key challenge in this area has been the development of a general methodology that affords synthesis of such monomeric materials in high yields.[7]

Mannose-derived 1,2-orthoester (**1**)[10] prepared in three steps from D-mannose in an overall yield of 70% and commercially available hydroxyethyl acrylate (**2a**) were treated with 7 mol % of $AuBr_3$ in CH_2Cl_2/4 Å MS powder at room temperature for 10 h to obtain the acrylate mannopyranoside (**3a**) in 78% yield.[12] A similar reaction between orthoester **1** and hydroxyethyl methacrylate **2b** enabled the synthesis of corresponding methyl acrylate mannopyranoside **3b** in 76% (Scheme 1). In continuation of this, we also explored the utility of the current protocol to the other glycosyl 1,2-orthoesters, such as glucosyl (**4**), galactosyl (**6**) and lactosyl (**8**) 1,2-orthoesters (prepared, respectively, in 76%, 65%, and 63% yield from corresponding aldoses) to obtain corresponding glycosides **5a**, **5b**, **7a**, **7b**, **9a,** and **9b** from aglycones **2a** and **2b** in good yields (Scheme 1). Glycopolymers can be obtained from these acrylates easily by free radical polymerization and then exhaustive saponification of all benzoyl groups would be necessary in order to get the polyhydroxy glycopolymers. However, orthogonal deprotection of benzoates in the presence of acrylate esters poses a formidable task. Thus, hydroxylethyl acrylamides were considered to be superior as they would enable preparation of glycopolymers with acrylamide backbone and later facilitate easy saponification of benzoates to get water soluble polyacrylamides.

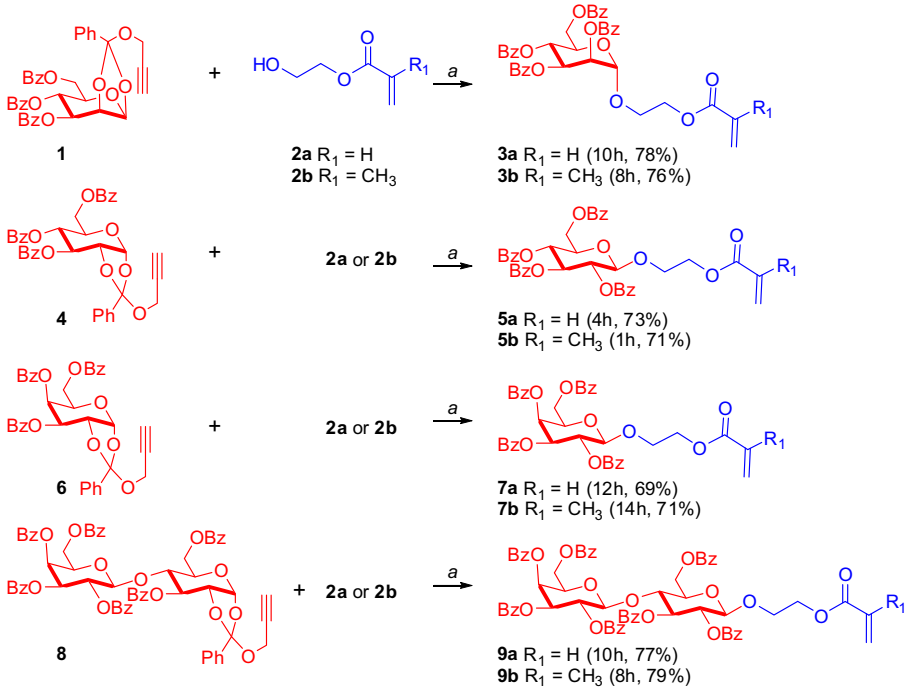
Accordingly, per-O-benzoylated mannose 1,2-orthoester (**1**) was allowed to react with commercially available hydroxyethyl acrylamide **10a** and hydroxyethyl methacrylamide **10b** in the presence of 7 mol % of $AuBr_3$. Surprisingly, a single product identified as per-O-benzoylated hydroxyethyl acrylamide 1,2-orthoester (**11a**) was isolated which was subsequently converted to the required mannose-hydroxy ethyl acrylamide conjugate **12a** by reacting with TMSOTf in CH_2Cl_2 at room temperature in 69% over two steps. A similar attempt with the hydroxyethyl methacrylamide also gave first the orthoester (**11b**) which could then be converted to the mannopyranoside **12b** with an overall yield of 68%. The general applicability of this methodology has been gauged with the other orthoesters **4**, **6,** and **8** to obtain corresponding acrylamides **13a**, **13b**, **14a**, **14b**, **15a,** and **15b** in very good yields (Scheme 2).[12] A single step conversion of orthoester **1** to **12a**, **12b** in the presence of TMSOTf was found to give only a small quantity of desired product (10%) and the major product was observed to be the propargyl 2,3,4,6-tetra-*O*-benzoyl α-D-mannopyanoside[10a] (70%) may be because of the strong Lewis and Bronsted acidity of TMSOTf. Hence preparation of the hybrids through gold catalyzed glycosidation is advantageous.

Glycosides of acrylate/acrylamide are excellent scaffolds for attaching cysteine or any mercaptan per se. BocCys(SH)OMe (**16**) was considered as a model substrate for the 'thiol-ene click' reaction.[13] For example, cysteine residue **16** smoothly reacted with acrylate (**3a**) or acrylamide (**12a**) in the presence of Et_3N in EtOH at room temperature to give Michael addition products **17a** and **17b**, respectively (Scheme 3).[14,12] Similarly, lactose derived acrylate **9a** gave the corresponding 'thio-click' product in 85% yield whereas galactose-methacrylate **7b** resulted in the isolation of thiolate addition product as a 1:1 diastereomeric mixture at the newly generated chiral center (Scheme 4).

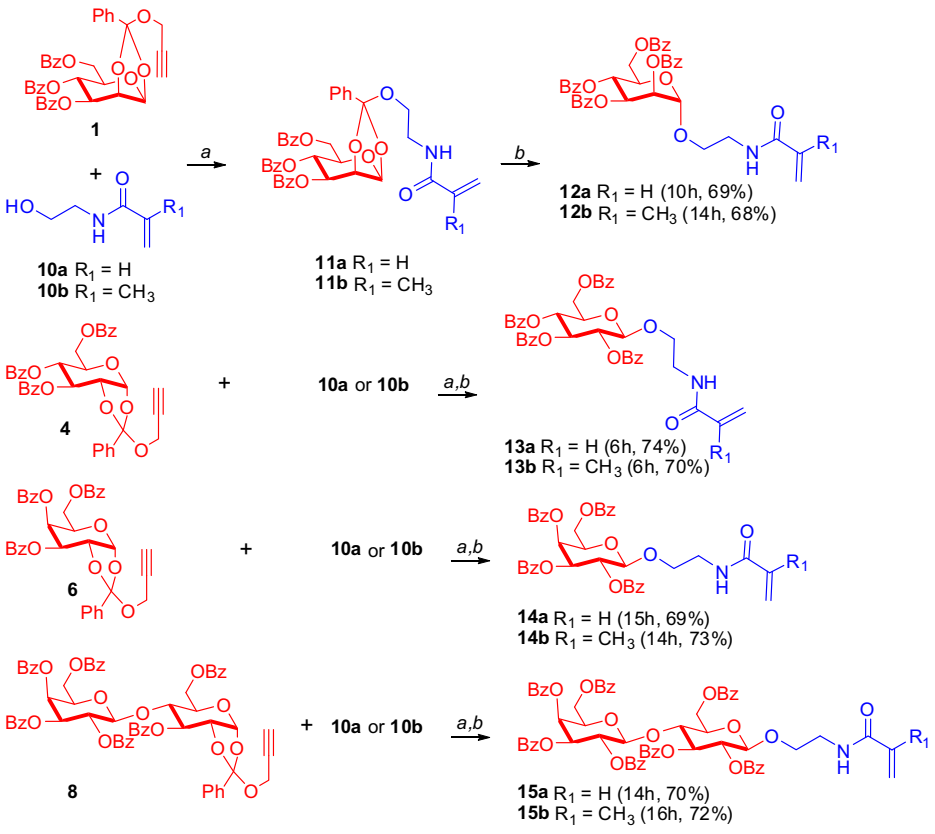
3. Synthesis of glycopolymers

Several methodologies have been developed for polymerization of carbohydrate based acrylamido monomers. These include both conventional free radical and stable free radical (SFRP) polymerization methods.[15] In an attempt to show that the monomers synthesized by our methodology can also be polymerized, we attempted the oligomerization of per-O-benzoylated glucose acrylamide monomer using AIBN as the initiator and 2-aminoethanethiol hydrochloride as the CTA in DMF.[16] The resulting polymer was characterized by both NMR and GPC analysis. The M_n was determined to be 5600 Da while the PDI was found to be 1.08.

Since, 2-aminoethanethiol hydrochloride was used as the CTA, the polymer chains had an amino end group which can be further

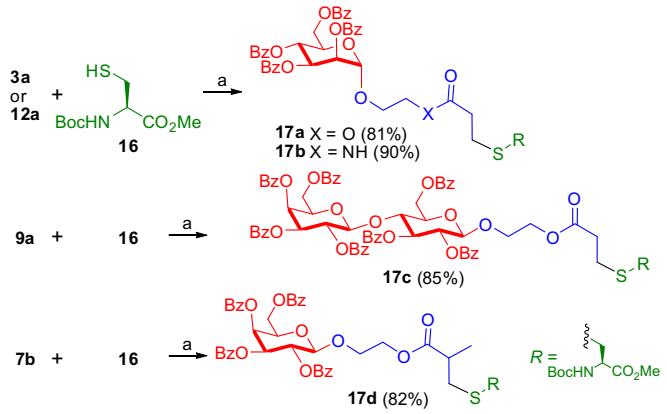


Scheme 1. Synthesis of sugar-acrylate monomers. Reagents: (a) $AuBr_3$, CH_2Cl_2, 4 Å MS, rt.



Scheme 2. Synthesis of sugar-acrylamide monomers. Reagents: (a) $AuBr_3$, CH_2Cl_2, 4 Å MS, rt; (b) TMSOTf, CH_2Cl_2, rt.

modified using amine reactive compounds. The per-*O*-benzoate groups of the resulting oligomer were removed under Zemplén conditions using sodium methoxide to afford the polymer containing free hydroxyl groups of the carbohydrate.[10] To be able to prove that the biofunctionality of the glucose moieties is still active and not lost during the polymerization process, the ligand-lectin binding ability of the glycopolymer was tested by specific binding using Concanavalin A lectins interaction with α-D-glucose moieties.[4] The



Scheme 3. Acrylate/acrylamide monomers for thiolate addition. Reagents: (a) Et_3N, EtOH, 8 h, rt.

rate of aggregation of the polymer with conA was monitored at 490 nm, where no absorbance of either the polymer or con-A is observed. This turbidity assay measures the changes in absorbance at a wavelength of 490 nm using UV–vis spectroscopy. The binding of the multivalent polymer to Con A forms a gel network with concomitant increase in size that causes significant scattering, thus leading to a turbid solution. The turbidity increases with conjugation time and plateaus after 3 min. Similar multivalent characteristics showed by the polyvalent glycopolymers were also observed earlier by Kiessling and co-workers.[17]

4. Conclusions

In conclusion, a new synthesis methodology was identified for the easy synthesis of sugar-acrylate/acrylamide from stable glycosyl 1,2-orthoesters taking the cue from gold catalyzed glycosylations. Thiolate Michael addition onto sugar-acrylate/acrylamide was also studied that would serve as an alternate synthesis for amino acid glycoconjugates as well as a strategy for the glycosylation of cysteine containing proteins. Furthermore, we showed that the sugar monomers prepared in this study are good for carrying out polymerization. We anticipate that this simple, easy, scalable, and stereoselective methodology for the sugar monomers would catalyze the easy preparation of glycopolymers.

5. Experimental section

5.1. General procedure for the synthesis of sugar-acrylate monomers

To a solution of glycosyl donor **1** (0.635 g, 1 mmol), glycosyl acceptor **2b** (0.143 g, 1.1 mmol) and 4 Å molecular sieves powder (100 mg) in anhydrous CH_2Cl_2 (10 mL) was added $AuBr_3$ (0.031 g, 0.07 mmol) under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the completion of the reaction is judged by TLC analysis. The reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate–petroleum ether as mobile phase.

5.2. General procedure for the synthesis of sugar-acrylamide monomers

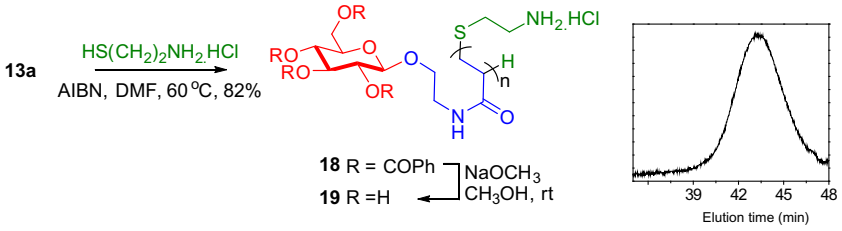
To a solution of glycosyl donor[10] **1** (0.635 gm, 1 mmol), glycosyl acceptor **10b** (0.142 g 1.1 mmol) and 4 Å molecular sieves powder (100 mg) in anhydrous CH_2Cl_2 (10 mL) was added $AuBr_3$ (0.031 g, 0.07 mmol) under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the completion of the reaction is judged by TLC analysis. The reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate–petroleum ether as mobile phase to obtain compound **11b**. Further, compound **11b** was dissolved in dry dichloromethane (10 mL) and trifluoromethanesulphonate (5 µL) was added and the reaction mixture was stirred for 5 min at room temperature and diluted with dichloromethane (10 mL) and water (10 mL). The organic layer was separated and concentrated in vacuo to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase.

5.3. Procedure for the thiolate addition

Acrylate monomer **3a** (0.200 g, 0.29 mmol) and cysteine derivative **16** (0.166 g, 0.72 mmol) were dissolved in ethanol (1 mL) and Et_3N (0.5 mL) under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the completion of the reaction is judged by TLC analysis. The reaction mixture was concentrated in vacuo to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate–petroleum ether as mobile phase to obtain thiolate addition product **17a** (0.21 g, 82%).

5.4. Procedure for the synthesis of glycopolymer 31

The per-O-benzoylated monomer (**13a**) (400 mg, 641.3 µmol), 2-aminoethanethiol hydrochloride (3.64 mg, 32.06 µmol) and AIBN (4% by weight of the monomer) were dissolved under N_2 in anhydrous DMF (0.4 mL) in a Schelnk tube with side arm, subjected to three freeze–pump–thaw cycles, cannulated into the polymerization flask, and magnetically stirred at 60 °C for 72 h. The reaction mixture was cooled, concentrated under diminished pressure, and poured into a large excess of Et_2O (100 mL/g of oligomer). The oligomer **30** was filtered and further purified through two dissolution (in tetrahydrofuran)/precipitation cycles (in Et_2O) until the disappearance of the residual monomers (**13a**) as monitored by TLC. The polymer was characterized by GPC in chloroform



Scheme 4. Free radical polymerization of gluco-acrylamide (inset: GPC of the resulting polymer).

and by NMR spectral analysis. A very narrow molecular weight distribution (MWD) was obtained from Gel Permeation Chromatography (M_w/M_n = 1.08). Yield: 72%. Subsequently, oligomer **30** was redissolved in 10 mL of anhydrous MeOH, freshly prepared sodium methoxide (1 mL) was added to the reaction mixture, and stirred for 4 h at room temperature. After 4 h the reaction mixture was quenched with Amberlite IR-120 resin, filtered, and concentrated in vacuo to obtain the glycopolymer **31**.

6. Compound characterization data

6.1. 2-(Acryloyloxy)ethyl 2,3,4,6-tetra-*O*-benzoyl α-D-mannopyranoside (3a)

$[\alpha]_D^{25}$ −52.5 (*c* 1.4, $CHCl_3$); IR ($CHCl_3$): 3057, 2976, 1726, 1603, 1264, 1215, 1109, 771 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 3.83–4.05 (m, 2H), 4.39–4.78 (m, 5H), 5.17 (d, 1H, *J* 1.8 Hz), 5.75 (dd, 1H, *J* 1.8, 3.3 Hz), 5.87 (dd, 1H, *J* 1.6, 10.4 Hz), 5.93 (dd, 1H, *J* 3.3, 10.3 Hz), 6.13 (t, 1H, *J* 10.3 Hz), 6.21 (dd, 1H, *J* 10.3, 17.3 Hz), 6.50 (dd, 1H, *J* 1.6, 17.3 Hz), 7.20–7.66 (m, 12H), 7.78–8.15 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 62.8, 63.1, 66.1, 66.8, 69.0, 69.9, 70.2, 97.6, 127.9, 128.3–129.8, 131.4, 133.1, 133.2, 133.4, 133.5, 165.3, 165.4, 165.4, 165.9, 166.1; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{39}H_{34}O_{12}+Na]^+$: 717.1948, found: 717.1938.

6.2. 2-(Methacryloyloxy)ethyl 2,3,4,6-tetra-*O*-benzoyl α-D-mannopyranoside (3b)

$[\alpha]_D^{25}$ −54.1 (*c* 1.3, $CHCl_3$); IR ($CHCl_3$): 3064, 2976, 1728, 1603, 1265, 1215, 1109, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.99 (dd, 3H, *J* 1.0, 1.5 Hz), 3.83–4.16 (m, 2H), 4.38–4.75 (m, 5H), 5.17 (d, 1H, *J* 1.8 Hz), 5.62 (quintet, 1H, *J* 1.5, 3.2 Hz), 5.73 (dd, 1H, *J* 1.8, 3.3 Hz), 5.93 (dd, 1H, *J* 3.3, 10.1 Hz), 6.07–6.23 (m, 2H), 7.21–7.68 (m, 12H), 7.76–8.15 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.3, 62.6, 63.1, 65.9, 66.7, 68.8, 69.8, 70.1, 97.4, 126.0, 128.1–129.8, 133.0, 133.1, 133.4, 133.4, 135.9, 165.2, 165.3, 165.3, 166.0, 167.0; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{40}H_{36}O_{12}+Na]^+$: 731.2104, found: 731.2135.

6.3. 2-(Acryloyloxy)ethyl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranoside (5a)

$[\alpha]_D^{25}$ +18.8 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$): 3064, 2974, 1732, 1602, 1248, 1215, 1105, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 3.81–3.93 (m, 1H), 4.04–4.35 (m, 4H), 4.49 (dd, 1H, *J* 5.1, 12.1 Hz), 4.65 (dd, 1H, *J* 3.3, 12.1 Hz), 4.92 (d, 1H, *J* 7.8 Hz), 5.50–5.98 (m, 5H), 6.20 (dd, 1H, *J* 1.7, 17.2 Hz), 7.21–7.63 (m, 12H), 7.78–8.09 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 63.0, 63.0, 67.5, 69.6, 71.6, 72.3, 72.7, 101.1, 127.7, 128.0–129.8, 130.9, 133.1, 133.2, 133.2, 133.4, 165.0, 165.1, 165.8, 165.8, 166.1; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{39}H_{34}O_{12}+Na]^+$: 717.1948, found: 717.1981.

6.4. 2-(Methacryloyloxy)ethyl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranoside (5b)

$[\alpha]_D^{25}$ +27.8 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$): 3069, 2976, 1730, 1603, 1265, 1215, 1106, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.74 (dd, 3H, *J* 1.0, 1.4 Hz), 3.85 (m, 1H), 4.04–4.36 (m, 4H), 4.49 (dd, 1H, *J* 4.5, 12.2 Hz), 4.65 (dd, 1H, *J* 3.2, 12.2 Hz), 4.92 (d, 1H, *J* 7.8 Hz), 5.33 (m, 1H), 5.50–5.98 (m, 4H), 7.22–7.60 (m, 12H), 7.78–8.10 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.0, 63.0, 63.2, 67.4, 69.6, 71.6, 72.3, 72.8, 101.0, 125.8, 128.1–130.0, 133.1, 133.2, 133.3, 133.4, 135.7, 165.0, 165.2, 165.8, 166.1, 167.1; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{40}H_{36}O_{12}+Na]^+$: 731.2104, found: 731.2171.

6.5. 2-(Acryloyloxy)ethyl 2,3,4,6-tetra-*O*-benzoyl β-D-galactopyranoside (7a)

$[\alpha]_D^{25}$ +76.0 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3072, 1726, 1603, 1267, 1111, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 3.89 (m, 1H), 4.13–4.51 (m, 4H), 4.71 (dd, 1H, *J* 5.5, 10.1 Hz), 4.94 (dd, 1H, *J* 0.7, 7.9 Hz), 5.58 (dd, 1H, *J* 1.7, 10.4 Hz), 5.65 (ddd, 1H, *J* 0.9, 3.5, 10.5 Hz), 5.80 (m, 2H), 6.03 (d, 1H, *J* 3.3 Hz), 6.19 (dd, 1H, *J* 1.7, 17.2 Hz), 6.44 (dd, 1H, *J* 1.7, 17.2 Hz), 7.12–7.68 (m, 12H), 7.73–8.15 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 61.9, 63.0, 67.5, 68.0, 69.5, 71.3, 71.5, 101.4, 127.6, 127.9–130.0, 130.8, 133.1, 133.2, 133.2, 133.5, 165.1, 165.4, 165.5, 165.7, 165.9; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{39}H_{34}O_{12}+Na]^+$: 717.1948, found: 717.1883.

6.6. 2-(Methacryloyloxy)ethyl 2,3,4,6-tetra-*O*-benzoyl β-D-galactopyranoside (7b)

$[\alpha]_D^{25}$ +78.5 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 3065, 2976, 1728, 1602, 1267, 1215, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.74 (s, 3H), 3.92 (qd, 1H, *J* 3.9, 6.8, 11.1 Hz), 4.11–4.49 (m, 5H), 4.69 (dd, 1H, *J* 4.7, 10.5 Hz), 4.03 (d, 1H, *J* 7.8 Hz), 5.33 (quintent, 1H, *J* 1.6, 3.1 Hz), 5.63 (dd, 1H, *J* 3.5, 10.5 Hz), 5.78–6.04 (m, 3H), 7.15–7.68 (m, 12H), 7.75–8.18 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.0, 61.9, 63.3, 67.4, 68.0, 69.5, 71.3, 71.6, 101.3, 125.7, 128.1–129.9, 133.1, 133.2, 133.2, 133.5, 135.6, 165.1, 165.5, 165.5, 166.0, 167.0; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{40}H_{36}O_{12}+Na]^+$: 731.2104, found: 731.2230.

6.7. 2-(Acryloyloxy)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (9a)

$[\alpha]_D^{25}$ +48.4 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3064, 2976, 1730, 1603, 1215, 1095, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 3.56–3.99 (m, 6H), 4.05–4.29 (m, 3H), 4.41 (dd, 1H, *J* 3.7, 12.3 Hz), 4.53 (dd, 1H, *J* 1.7, 12.3 Hz), 4.74 (ABq, 2H, *J* 7.9 Hz), 5.25–5.51 (m, 3H), 5.53–5.84 (m, 4H), 6.06 (dd, 1H, *J* 1.6, 17.0 Hz), 7.00–7.53 (m, 21H), 7.55–8.01 (m, 14H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 60.9, 62.2, 63.0, 67.4, 67.4, 69.8, 71.3, 71.5, 71.7, 72.7, 73.0, 75.8, 100.9, 101.0, 127.6, 128.0–129.9, 130.8, 133.1, 133.2, 133.3, 133.3, 133.3, 133.4, 133.5, 164.7, 165.0, 165.1, 165.3, 165.3, 165.5, 165.7, 165.8; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{66}H_{56}O_{20}+Na]^+$: 1191.3263, found: 1191.3123.

6.8. 2-(Methacryloyloxy)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (9b)

$[\alpha]_D^{25}$ +49.2 (*c* 1.3, $CHCl_3$); IR ($CHCl_3$): 3064, 2976, 1730, 1603, 1452, 1269, 1215, 1096, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.71 (s, 3H), 3.65–4.08 (m, 6H), 4.10–4.38 (m, 3H), 4.48 (dd, 1H, *J* 3.9, 12.4 Hz), 4.60 (dd, 1H, *J* 1.3, 12.4 Hz,), 4.82 (ABq, 2H, *J* 7.9 Hz), 5.28 (quintet, 1H, *J* 1.6, 3.2 Hz), 5.37 (dd, 1H, *J* 3.3, 10.3 Hz), 5.48 (dd, 1H, *J* 7.9, 9.9 Hz), 5.66–5.87 (m, 4H), 7.09–7.64 (m, 21H), 7.69–8.05 (m, 14H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.0, 61.0, 62.2, 63.2, 67.4, 67.5, 69.8, 71.4, 71.5, 71.7, 72.8, 73.0, 75.9, 100.9, 101.0, 125.7, 128.1–130.0, 133.2, 133.3, 133.4, 133.4, 133.4, 133.4, 133.5, 135.6, 164.8, 165.1, 165.2, 165.4, 165.4, 165.5, 165.8, 167.0; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{67}H_{58}O_{20}+Na]^+$: 1205.3419, found: 1205.3211.

6.9. 3,4,6-Tri-*O*-benzoyl-1,2-*O*-[(2-acrylamidoethoxy) phenylmethylene]-β-D-mannopyrano-side (11a)

$[\alpha]_D^{25}$ −73.2 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$): 3439, 3393, 3323, 3065, 2955, 1724, 1664, 1524, 1450, 1269, 1076, 761 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 3.42–3.63 (m, 4H), 4.08 (ddd, 1H, *J* 3.3,

4.4, 7.7 Hz), 4.33 (dd, 1H, *J* 4.6, 12.2 Hz), 4.53 (dd, 1H, *J* 3.2, 12.2 Hz), 5.08 (dd, 1H, *J* 2.9, 3.2 Hz), 5.59 (d, 1H, *J* 1.8, 10.0 Hz), 5.63 (dd, 1H, *J* 3.6, 10.4 Hz), 5.81 (d, 1H, *J* 4.8 Hz), 5.85 (d, 1H, *J* 9.5 Hz), 5.97 (m, 1H), 6.08 (d, 1H, *J* 10.0 Hz), 6.24 (d, 1H, *J* 1.8, 16.9 Hz), 7.22–7.70 (m, 14H), 7.85–8.06 (m, 6H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 39.0, 62.8, 62.9, 66.2, 71.1, 71.8, 76.4, 97.8, 122.9, 126.2, 126.5, 128.1–129.7, 129.9, 130.5, 132.9, 133.4, 133.5, 136.3, 165.1, 165.4, 165.9, 165.9; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, found: 716.2220.

6.10. 3,4,6-Tri-*O*-benzoyl-1,2-*O*-[(2-methacrylamidoethoxy)phenylmethylene]-β-D-mannopyranoside (11b)

$[\alpha]_D^{25}$ −77.2 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3443, 3412, 3065, 2928, 1728, 1672, 1518, 1452, 1269, 1093, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.94 (s, 3H), 3.30 (m, 2H), 3.92–4.29 (m, 3H), 4.50 (dt, 2H, *J* 4.0, 11.9 Hz), 4.77 (dd, 1H, *J* 2.8, 12.2 Hz), 5.26 (t, 1H, *J* 1.4 Hz), 5.58 (d, 1H, *J* 2.4 Hz), 5.63 (dd, 1H, *J* 4.2, 9.9 Hz), 5.72 (br s, 1H), 6.11 (t, 1H, *J* 9.8 Hz), 6.35 (t, 1H, *J* 5.1 Hz), 7.22–7.65 (m, 14H), 7.89–8.15 (m, 6H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.6, 39.2, 62.2, 62.3, 66.1, 71.2, 71.8, 75.7, 95.7, 119.3, 123.5, 125.5, 128.2–130.0, 133.4, 133.5, 133.6, 137.8, 140.0, 165.1, 165.8, 166.0, 168.3; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{40}H_{37}NO_{11}+Na]^+$: 730.2264, found: 730.2245.

6.11. 2-Acrylamido ethyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (12a)

$[\alpha]_D^{25}$ −58.0 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$): 3393, 3308, 3064, 2932, 1732, 1628, 1452, 1267, 1109, 1070, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 3.55–3.89 (m, 3H), 3.97 (m, 1H), 4.40–4.56 (m, 2H), 4.70 (m, 1H), 5.12 (d, 1H, *J* 1.6 Hz), 5.69 (dd, 1H, *J* 2.4, 9.5 Hz), 5.74 (dd, 1H, *J* 1.8, 3.3 Hz), 5.91 (dd, 1H, *J* 3.3, 10.1 Hz), 6.12 (t, 1H, *J* 9.9 Hz), 6.28 (d, 1H, *J* 9.5 Hz), 6.34 (d, 1H, *J* 2.3 Hz), 6.45 (m, 1H), 7.20–7.65 (m, 12H), 7.70–8.14 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 39.2, 62.8, 66.8, 67.6, 69.0, 70.0, 70.2, 97.8, 126.9, 128.2–129.8, 130.6, 133.1, 133.3, 133.5, 133.5, 165.4, 165.4, 165.6, 165.7, 166.1; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, found:716.2220.

6.12. 2-Methacrylamido ethyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (12b)

$[\alpha]_D^{25}$ −53.5 (*c* 0.9, $CHCl_3$); IR ($CHCl_3$): 3480, 3439, 3086, 2930, 1730, 1662, 1452, 1267, 1109, 1068, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 2.0 (s, 3H), 3.58–3.80 (m, 3H), 4.10 (m, 1H), 4.44 (ddd, 1H, *J* 2.7, 4.3, 7.1 Hz), 4.52 (dd, 1H, *J* 4.6, 12.2 Hz), 4.71 (dd, 1H, *J* 2.5, 12.2 Hz), 5.15 (d, 1H, *J* 1.4 Hz), 5.41 (t, 1H, *J* 1.4 Hz), 5.74 (dd, 1H, *J* 1.7, 3.2 Hz), 5.81 (s, 1H), 5.93 (dd, 1H, *J* 3.3, 10.2 Hz), 6.12 (t, 1H, *J* 10.1 Hz), 6.41 (t, 1H, *J* 5.3 Hz), 7.25–7.68 (m, 12H), 7.83–8.12 (m, 8H); ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 18.7, 39.3, 62.8, 66.8, 67.4, 69.1, 69.9, 70.2, 97.7, 120.0, 128.3–129.9, 133.1, 133.3, 133.5, 133.6, 139.8, 165.4, 165.4, 165.6, 166.1, 168.5; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{40}H_{37}NO_{11}+Na]^+$: 730.2264, found: 730.2245.

6.13. 2-Acrylamido ethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (13a)

$[\alpha]_D^{25}$ +29.1 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$): 3391, 3310, 3064, 2957, 1732, 1669, 1452, 1269, 1177, 1109, 709 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 3.34–3.68 (m, 2H), 3.77 (ddd, 1H, *J* 3.2, 7.2, 10.3 Hz), 3.96 (m, 1H), 4.19 (ddd, 1H, *J* 2.9, 4.9, 7.9 Hz), 4.48 (dd, 1H, *J* 4.9, 12.2 Hz), 4.71 (dd, 1H, *J* 2.9, 12.2 Hz), 4.87 (d, 1H, *J* 8.0 Hz), 5.43 (dd, 1H, *J* 1.6, 10.2 Hz), 5.54 (dd, 1H, *J* 8.0, 9.8 Hz), 5.66–6.00 (m, 3H), 6.14 (dd, 1H, *J* 1.5, 16.9 Hz), 6.13 (s, 1H), 7.20–7.63 (m, 12H), 7.80–8.09 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 39.1, 62.7, 69.3, 69.3, 71.9, 72.4, 72.6. 101.4, 126.3, 128.2–129.8, 130.4, 133.3, 133.3, 133.5, 133.5, 165.1, 165.2, 165.4, 165.7, 166.1; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, found: 716.2194.

6.14. 2-Methacrylamido ethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (13b)

$[\alpha]_D^{25}$ +29.1 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3391, 3310, 3064, 2957, 1728, 1603, 1451, 1215, 1113, 1026, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.74 (s, 3H), 3.32–3.68 (m, 2H), 3.77 (ddd, 1H, *J* 3.7, 7.5, 10.2 Hz), 3.96 (ddd, 1H, *J* 3.6, 5.6, 9.4 Hz), 4.19 (ddd, 1H, *J* 3.0, 5.1, 8.2 Hz), 4.49 (dd, 1H, *J* 5.2, 12.2 Hz), 4.66 (dd, 1H, *J* 2.9, 12.2 Hz), 4.89 (d, 1H, *J* 7.9 Hz), 5.10 (quintet, 1H, *J* 1.6, 2.9 Hz), 5.50 (s, 1H), 5.55 (dd, 1H, *J* 7.9, 9.7 Hz), 5.70 (t, 1H, *J* 9.7 Hz), 5.94 (t, 1H, *J* 9.7 Hz), 6.20 (t, 1H, *J* 5.3 Hz), 7.20–7.65 (m, 12H), 7.78–8.08 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.2, 39.1, 62.9, 69.0, 69.4, 71.9, 72.3, 72.6, 101.2, 119.5, 128.2–129.8, 133.2, 133.2, 133.4, 133.4, 139.5, 165.1, 165.1, 165.7, 166.0, 168.2; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{40}H_{37}NO_{11}+Na]^+$: 730.2264, found:730.2349.

6.15. 2-Acrylamido ethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (14a)

$[\alpha]_D^{25}$ +79.7 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3392, 3314, 3067, 2976, 1728, 1603, 1217, 1113, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 3.33–3.86 (m, 3H), 4.04 (ddd, 1H, *J* 3.7, 5.4, 8.9 Hz), 4.41 (m, 2H), 4.68 (dd, 1H, *J* 6.2, 10.6 Hz), 4.86 (d, 1H, *J* 7.7 Hz), 5.42 (dd, 1H, *J* 1.4, 10.6 Hz), 5.60–5.80 (m, 3H), 5.98–6.19 (m, 3H), 7.17–7.78 (m, 12H), 7.75–8.14 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 38.9, 62.0, 68.0, 69.1, 69.8, 71.2, 71.4. 101.6, 126.2, 128.2–130.0, 130.3, 133.3, 133.3, 133.5, 133.6, 165.4, 165.4, 165.4, 165.4, 166.0; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, found: 716.2123.

6.16. 2-Methacrylamido ethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (14b)

$[\alpha]_D^{25}$ +81.3 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3393, 3310, 3071, 2945, 1728, 1603, 1457, 1215, 1113, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.75 (s, 3H), 3.35–3.85 (m, 3H), 4.03 (ddd, 1H, *J* 3.7, 5.8, 9.4 Hz), 4.41 (m, 2H), 4.67 (dd, 1H, *J* 6.1, 10.5 Hz), 4.88 (d, 1H, *J* 7.9 Hz), 5.11 (quintet, 1H, *J* 1.4, 2.9 Hz), 5.51 (s, 1H), 5.66 (dd, 1H, *J* 3.3, 10.3 Hz), 5.82 (dd, 1H, *J* 7.7, 10.5 Hz), 6.02 (d, 1H, *J* 3.3 Hz), 6.25 (t, 1H, *J* 5.4 Hz), 7.18–7.69 (m, 12H), 7.78–8.15 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.2, 39.1, 62.0, 68.0, 68.8, 69.8, 71.4, 71.4, 101.4, 119.5, 128.2–129.9, 133.3, 133.3, 133.4, 133.6, 139.5, 165.3, 165.4, 165.4, 165.4, 168.4; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{40}H_{37}NO_{11}+Na]^+$: 730.2264, found:730.2194.

6.17. 2-(Acrylamido)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (15a)

$[\alpha]_D^{25}$ +46.2 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3390, 3315, 3066, 2976, 1730, 1603, 1452, 1269, 1215, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 3.25–4.06 (m, 8H), 4.27 (t, 1H, *J* 9.4 Hz), 4.49 (dd, 1H, *J* 3.8, 12.2 Hz), 4.66 (dd, 1H, *J* 1.3, 10.2 Hz), 4.78 (d, 1H, *J* 7.7 Hz), 4.93 (d, 1H, *J* 7.9 Hz), 5.33–5.51 (m, 3H), 5.64–5.90 (m, 4H), 6.03 (t, 1H, *J* 5.9 Hz), 6.09 (dd, 1H, *J* 1.7, 17.0 Hz), 7.10–7.69 (m, 21H), 7.70–8.08 (m, 14H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 38.9, 60.9, 62.0, 67.4, 69.2, 69.8, 71.3, 71.6. 71.7, 72.5, 73.1, 75.7, 100.9, 101.2, 126.1, 128.1–129.9, 130.3, 133.2, 133.2, 133.3, 133.4, 133.4, 133.4, 133.5, 164.7, 165.1, 165.2, 165.3, 165.3,

165.3, 165.5, 165.8; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{66}H_{57}NO_{19}+Na]^+$: 1190.3423, found: 1190.3345.

6.18. 2-(Methacrylamido)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (15b)

$[\alpha]_D^{25}$ +46.0 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$): 3456, 3310, 3086, 2883, 1734, 1603, 1452, 1269, 1095, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.69 (s. 3H), 3.24–3.96 (m, 8H), 4.25 (t, 1H, *J* 9.5 Hz), 4.48 (dd, 1H, *J* 4.2, 12.2 Hz), 4.61 (dd, 1H, *J* 1.6, 12.2 Hz), 4.70 (d, 1H, *J* 7.8 Hz), 4.88 (d, 1H, *J* 7.8 Hz), 5.03 (quintet, 1H, *J* 1.5, 2.3 Hz), 5.34–5.51 (m, 3H), 5.66–5.88 (m, 3H), 6.10 (t, 1H, *J* 5.3 Hz), 7.10–7.68 (m, 21H), 7.70–8.05 (m, 14H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 18.2, 39.1, 61.0, 62.2, 67.4, 69.0, 69.8, 71.3, 71.7, 71.8, 72.6, 73.1, 75.9, 100.9, 101.1, 119.4, 128.2–130.0, 133.2, 133.4, 133.4, 133.4, 133.4, 133.4, 133.5, 139.6, 164.7, 165.2, 165.2, 165.3, 165.4, 165.5, 165.8, 168.2; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{67}H_{59}NO_{19}+Na]^+$: 1204.3579, found:1204.3570.

6.19. Characterization data for compound 17a

$[\alpha]_D^{25}$ −56.9 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 3069, 2978, 1724, 1603, 1451, 1215, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.43 (s, 9H), 2.62–3.08 (m, 6H), 3.74 (s, 3H), 3.75–4.18 (m, 2H), 4.30–4.59 (m, 5H), 4.70 (m, 1H), 5.16 (d, 1H, *J* 1.6 Hz), 5.47 (d, 1H, *J* 7.8 Hz), 5.73 (dd, 1H, *J* 1.8, 3.3 Hz), 5.92 (dd, 1H, *J* 3.3, 10.1 Hz), 6.14 (t, 1H, *J* 10.1 Hz), 7.20–7.65 (m, 12H), 7.81–8.15 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 27.5, 28.2 (4C), 34.5, 34.5, 52.5, 53.3, 62.7, 63.7, 66.1, 66.8, 69.0, 69.8, 70.3, 97.7, 128.0–129.9, 133.1, 133.2, 133.4, 133.5, 155.3, 165.3, 165.4, 165.4, 166.1, 171.4, 171.5; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{48}H_{51}NO_{16}S+Na]^+$: 952.2826, found: 952.2731.

6.20. Characterization data for compound 17b

$[\alpha]_D^{25}$ −36.4 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$): 3420, 3371, 3065, 2978, 1732, 1662, 1452, 1267, 1167, 1097, 756, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400.13 MHz): δ 1.44 (s, 9H), 2.55 (t, 2H, *J* 7.1 Hz), 2.83 (t, 2H, *J* 6.9 Hz), 3.01 (ddd, 2H, *J* 5.2, 14.5, 18.5 Hz), 3.53 (m, 1H), 3.67–3.77 (m, 5H), 3.94 (dd, 1H, *J* 4.7, 8.8 Hz), 4.43–4.57 (m, 3H), 4.71 (dd, 1H, *J* 2.5, 11.8 Hz), 5.13 (s, 1H), 5.54 (d, 1H, *J* 7.8 Hz), 5.74 (s, 1H), 5.91 (dd, 1H, *J* 2.9, 10.0 Hz), 6.11 (t, 1H, *J* 10.0 Hz), 6.53 (br s, 1H), 7.23–7.65 (m, 12H), 7.80–8.11 (m, 8H); ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 28.2 (3C), 28.4, 34.7, 36.5, 39.1, 52.5, 53.4, 62.8, 66.8, 67.7, 69.0, 70.0, 72.2, 80.2, 97.8, 128.0–129.8, 133.1, 133.3, 133.5, 133.5, 155.2, 165.4, 165.4, 165.6, 166.1, 171.1, 171.5; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{48}H_{52}N_2O_{15}SN+Na]^+$: 951.2986, found: 951.2981.

6.21. Characterization data for compound 17c

$[\alpha]_D^{25}$ +42.8 (*c* 1.3, $CHCl_3$); IR ($CHCl_3$): 3433, 3373, 3070, 2980, 1728, 1603, 1452, 1269, 1176, 1071, 758, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.44 (s, 9H), 2.22 (t, 2H, *J* 7.0 Hz), 2.55 (t, 2H, *J* 7.4 Hz), 2.89 (d, 2H, *J* 5.2 Hz), 3.74 (s, 3H), 3.69 (m, 3H), 3.80–4.35 (m, 6H), 4.43–4.68 (m, 3H), 4.75 (d, 1H, *J* 7.8 Hz), 4.88 (d, 1H, *J* 7.8 Hz), 5.30–5.55 (m, 3H), 5.63–5.90 (m, 3H), 7.09–7.68 (m, 21H), 7.70–8.05 (m, 14H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 27.2, 28.2 (3C), 34.0, 34.5, 52.5, 53.1, 61.0, 62.2, 63.1, 67.4, 67.4, 69.8, 71.3, 71.4, 71.7, 72.7, 73.0, 75.9, 80.1, 100.9, 101.0, 128.1–130.0, 133.2, 133.2, 133.3, 133.4, 133.4, 133.4, 133.5, 155.1, 164.7, 165.0, 165.2, 165.3, 165.3, 165.5, 165.8, 171.3, 171.4; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{75}H_{73}NO_{24}S+Na]^+$: 1426.4141, found: 1426.3896.

6.22. Characterization data for compound 17d

$[\alpha]_D^{25}$ +61.3 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 3432, 3374, 3064, 2980, 1730, 1603, 1501, 1267, 1215, 1096, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.01 (d, 3H, *J* 6.3 Hz), 1.45 (s, 9H), 2.30–2.75 (m, 3H), 2.91 (d, 2H, *J* 5.2 Hz), 3.74 (s, 3H), 3.87 (m, 1H), 4.06–4.58 (m, 6H), 4.70 (dd, 1H, *J* 5.1, 9.8 Hz), 4.93 (dd, 1H, *J* 2.0, 7.8 Hz), 5.40 (d, 1H, *J* 7.7 Hz), 5.64 (dd, 1H, *J* 3.4, 10.4 Hz), 5.82 (dd, 1H, *J* 7.8, 10.4 Hz), 6.02 (d, 1H, *J* 3.3 Hz), 7.20–7.68 (m, 12H), 7.75–8.14 (m, 8H); ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 16.4, 16.5, 28.2 (6C), 34.9, 35.0, 35.6 (2C), 39.8 (2C), 52.4 (2C), 53.2 (2C), 61.9 (2C), 63.2 (2C), 67.4 (2C), 68.0 (2C), 69.5 (2C), 71.3 (2C), 71.5 (2C), 80.1 (2C), 101.2, 101.3, 128.1–133.0, 133.2 (6C), 133.5 (2C), 155.1 (2C), 165.1 (2C), 165.5 (4C), 166.0 (2C), 171.4 (2C), 174.4, 174.5; HRMS (MALDI-TOF): *m/z*: calcd for $[C_{49}H_{53}NO_{16}S+Na]^+$: 966.2983, found: 966.3002.

Acknowledgments

S.A.T. and M.K. thank the CSIR-New Delhi for the research fellowship. S.H. thanks the Director, NCL for the LC-MS facility. S.H. thanks the DST New Delhi for the SwarnaJayanti Fellowship and S.S.G. thanks the CSIR for research funds (NWP0051-C).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2011.04.018.

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