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*J. Org. Chem.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b02027 • Publication Date (Web): 06 Oct 2017



ACS Publications

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

# Nucleofuge Generating Glycosidations by the Remote Activation of Hydroxybenzotriazolyl Glycosides

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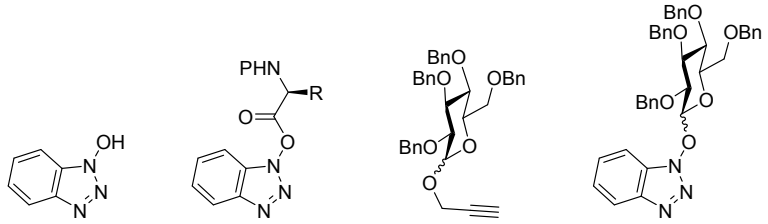
## Abstract

Hydroxybenzotriazole is routinely used in peptide chemistry for reducing racemization due to the increased reactivity. In this manuscript, very stable hydroxybenzotriazolyl glucosides were identified to undergo glycosidation. The reaction was hypothesized to go through the remote activation by the $Tf_2O$ at the N3-site of HOBt followed by the extrusion of the oxocarbenium ion that was attacked by the glycosyl acceptor. Further, equilibration of the zwitterionic benzotriazolyl species makes the leaving group non-competitive and generates the nucleofuge that has been reconverted to the glycosyl donor. The reaction is mild, high yielding, fast and suitable for donors containing both C2-ethers and C2-esters as well. The regenerative-donor glycosidation strategy is promising as it enables us to regenerate the glycosyl donor for further utilization. The utility of the methodology for the oligosaccharide synthesis was demonstrated by the successful synthesis of the branched pentamannan core of the HIV1-gp120 complex.

## Introduction

Burgeoning growth in all the allied fields of Glycosciences led to the identification of myriad roles played by glycoconjugates and oligosaccharides in many physiological and pathological processes.[1,2] A major impediment holding the exponential growth of the Glycosciences is the lack of pure, well characterized and homogenous oligosaccharides or glycoconjugates.[3] Isolating oligosaccharides from natural sources is a challenging task since they exist in tiny quantities as micro-heterogeneous forms.[3] Often, totally chemical[4] or chemoenzymatic[5] syntheses are the most popular strategies for obtaining sufficient quantity of oligosaccharides using a bottoms-up approach, wherein saccharide residues are sequentially condensed by a glycosidation reaction.[3] The glycosidation reaction involves two partners termed as glycosyl donor and glycosyl acceptor.[4] The glycosyl donor often contains a nucleofuge at the anomeric carbon which generates an oxocarbenium ion intermediate that will be attacked by the glycosyl acceptor upon the activation by a promoter. Several decades of research culminated into the development of numerous glycosyl donors' viz. glycosyl halides,[6-8] esters,[9] phosphates,[10] imidates,[11] carbonates,[12] thioglycosides,[13] selenyl glycosides,[14] glycals,[15] hemiacetals,[16,17] alkenyl[18] and alkynyl[19] glycosides.[4]

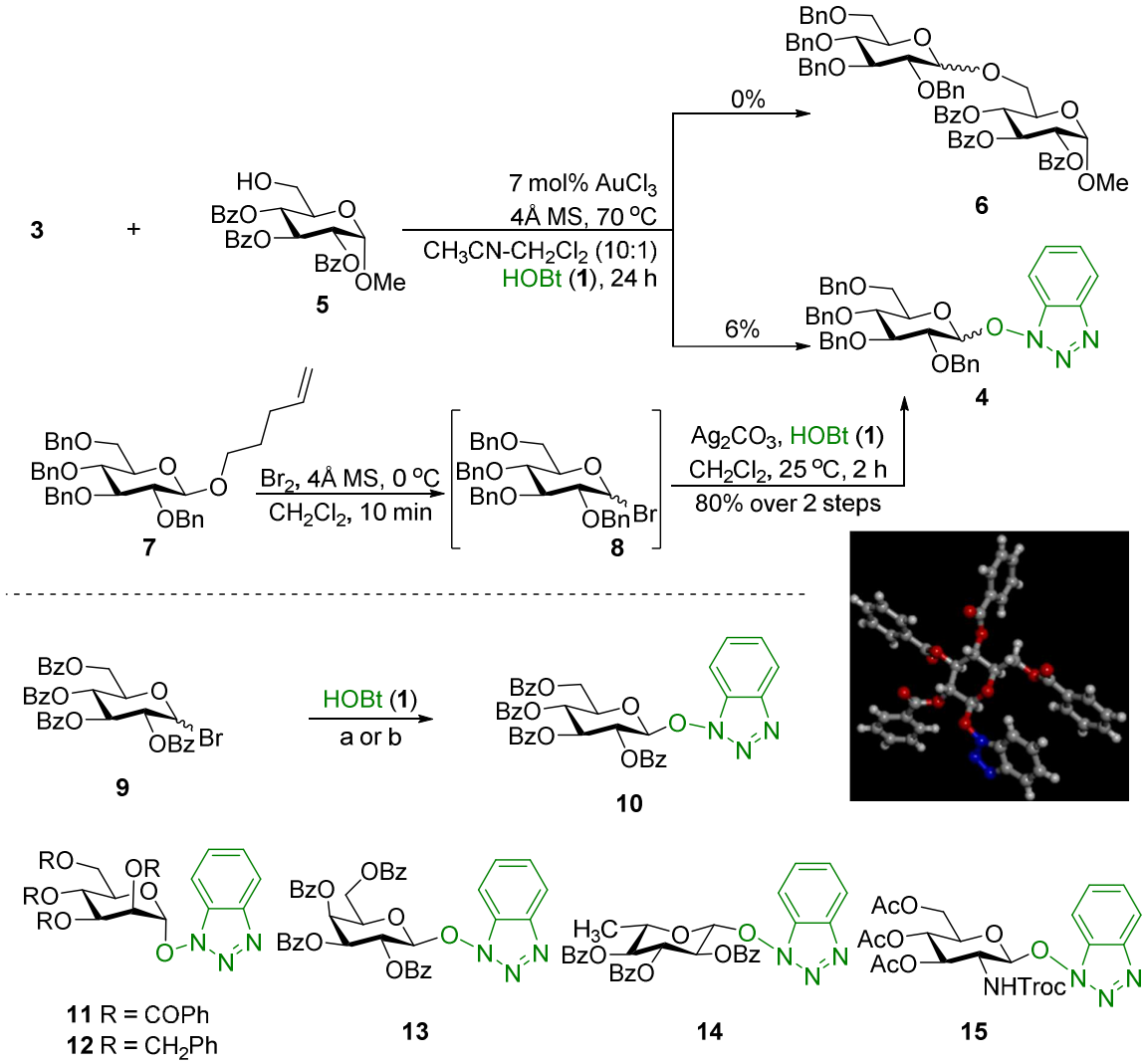



HOBt (**1**) Peptide-HOBt (**2**) Glucosyl Donor (**3**) Sugar-HOBt (**4**)

**Figure 1.** Structures of Hydroxybenzotriazole (HOBt) and Peptide-HOBt and Sugar-HOBt

Propargyl glycosides are observed to undergo glycosidation in the presence of catalytic amount of gold(III) halides in $CH_2Cl_2$ at 70 $^0$C.[19] They undergo glycosidation when *C*-2 position is protected as a benzyl ether only.[19] Enhanced reactivity by the addition of

hydroxybenzotriazole (HOBt) (**1**) is well documented in the peptide chemistry through the formation of activated ester **2** (Figure 1).[20] In this premise, addition of HOBt in the gold-catalysed glycosidation was hypothesized to further increase the overall turnover number (TON) of the gold-catalysed glycosidation (Scheme 1).



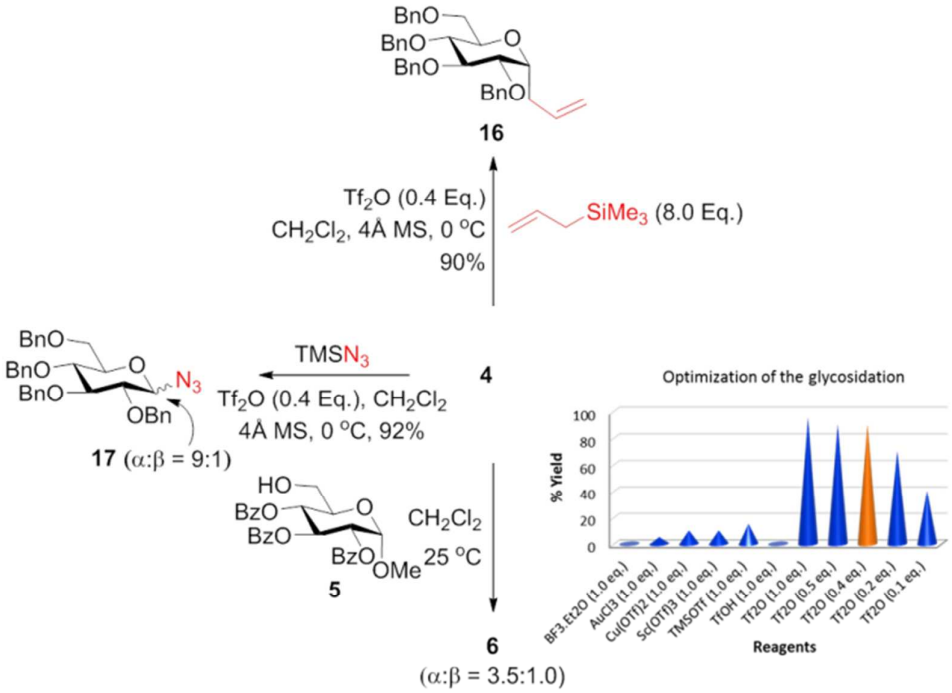

Scheme 1. Synthesis of HOBt glycosides.

**Results and Discussion**

Accordingly, donor **3** was treated with Sug-OH (**5**) and HOBt (**1**, 1.0 eq.) and catalytic amount of $AuCl_3$ in the presence of 4Å MS powder at 70 $^0$C for 24 h. To our surprise, the required disaccharide **6** was not noticed; instead HOBt glucoside **4** (6%) was observed

as the sole product that can be rationalized by the participation of the HOBt as the glycosyl acceptor. HOBt-glucoside **4** is easily accessible from pentenyl glucoside **7** *via* glucosyl bromide **8** in 80% over two steps (Scheme 1).[21]

Glucoside **4** is quite a stable compound; however, transformed partially (~10%) to the corresponding hemiacetal at 25 $^0$C over 6 months. Alternately, very stable per-*O*-benzoyl HOBt-glucoside (**10**) was conveniently synthesized from per-*O*-benzoyl bromoside (**9**) in high yield. Compound **10** was found to be very stable at 25 $^0$C for more than 6 months. In fact, we were able to grow single crystals in MeOH by slow evaporation method. The single crystal diffraction studies further confirmed the O-glycosidic linkage between the HOBt and the glycan moiety along with the overall structural integrity of the HOBt-glucoside **10**. Similar results were observed while synthesizing HOBt glycosides of Man*p*- (**11**, **12**), Galp- (**13**) and GlcNTroc- (**14**). Remarkable stability of these HOBt-glycosides intrigued us and encouraged us to investigate their further utility as glycosyl donors (Scheme 2).




Scheme 2. HOBt glycosides as glycosyl donors. MS = 4Å Molecular Sieves powder

Stability of the glucoside **4** and our interest in the development of stable glycosyl donors emboldened us to study its further utility for glycosylation. To begin the exploration, HOBt-glucoside **4** was treated with a model glucose-derived alcohol **5** in the presence of a molar equivalent of various Lewis and Brønsted acids (Scheme 2). Chemical glycosidation did not occur with $BF_3{\cdot}Et_2O$ at 25 $^0$C; however, Lewis acids which can produce Brønsted acids (HCl or TfOH) such as $AuCl_3$, $Cu(OTf)_2$, $Sc(OTf)_3$ and TMSOTf afforded the desired disaccharide **6** in 5-10% yield. No reaction was observed with 1 equivalent of TfOH presumably due to the neutralization of TfOH by the HOBt moiety. Diminished yields through the activation of the exocyclic C1-oxygen diverted our attention to the activation through the triazole moiety. Earlier independent investigations by Hanessian[23] and Woerpel[24] groups suggested that N3-nitrogen of the triazole moiety can be alkylated by MeOTf. Hence, Glcp-HOBt (**4**) was treated with MeOTf to observe no glycosidation. Nevertheless, addition of a molar equivalent of $Tf_2O$ afforded the required disaccharide **6** in 90% yield as α,β-mixture (3.5:1.0). Almost or similar yield of disaccharide **6** was observed with 0.5 or 0.4 equivalents of $Tf_2O$. Further decrease in $Tf_2O$ equivalents was noticed to diminish the overall performance (Scheme 2). Optimized reaction conditions were observed to be suitable for synthesizing even a *C*-glucoside **16** in the presence of $Tf_2O$ (0.4 eq.) and allyl trimethylsilane (8.0 eq.). Similarly, the protocol afforded the azido glucoside **17** (α:β = 9:1) in the presence of $TMSN_3$ and 0.4 equivalents of $Tf_2O$ at 0 $^0$C (Scheme 2).

Mechanistically, one can hypothesize that electron push from the endocyclic oxygen of the donor due to the remote activation of the N3-nitrogen of the triazole moiety can lead to the formation of the oxocarbenium ion **A** and a Zwitterionic species **B** along with $TfO^-$ (Figure 2). The $TfO^-$ can regenerate $Tf_2O$ and another intermediate **D**.[22] Acceptor ROH can attack on the oxocarbenium (R = $-CH_2Ph$) in a non-diastereoselective fashion to give

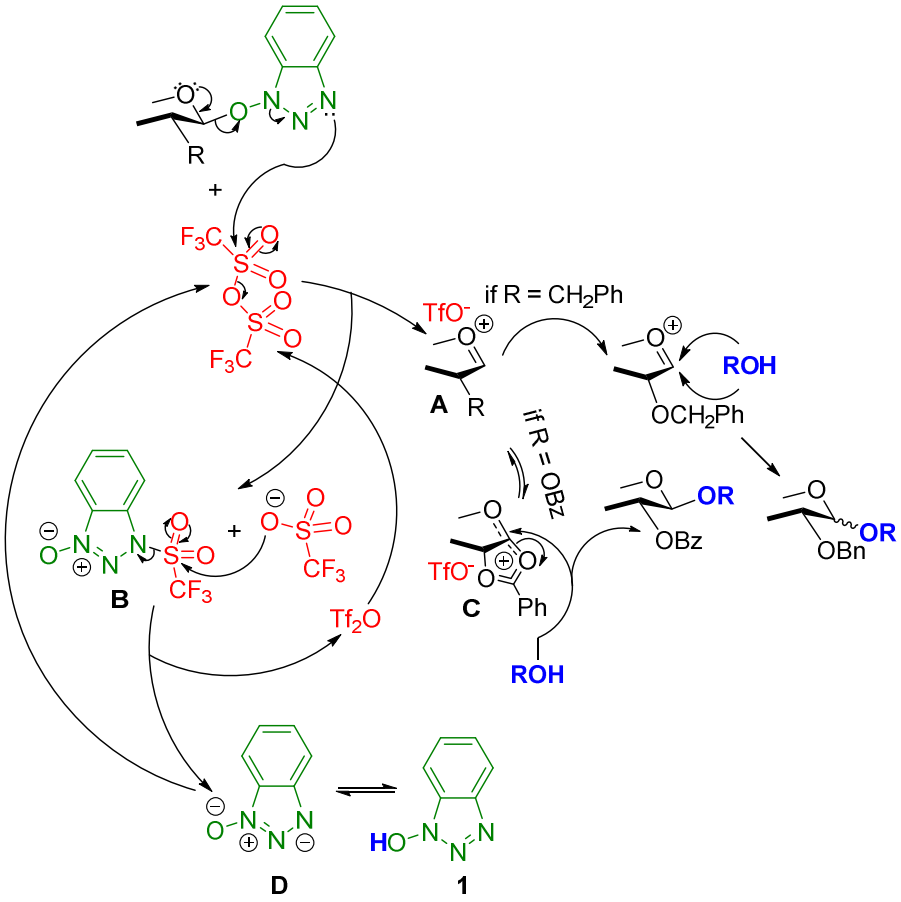



Figure 2. Plausible mechanism for the HOBt activation

α,β-mixture of glycosides or result in a 1,2-*trans* glycoside through trioxolenium ion **C** if the oxocarbenium ion **A** is stabilized with groups such as esters (-OBz). Hydrolysis of HOBt glycoside was noticed to afford the corresponding hemiacetal and trace amount of ROTf if the $Tf_2O$ was introduced prior to the addition of acceptor ROH. Equilibration[29] of species **D** to HOBt (**1**) is important because it makes the leaving group a non-competing nucleophile.[25-29] Minute variation in reaction time was observed with individual anomers of the donor **4** without any significance on the net stereochemical outcome of the disaccharide **6**. The regeneration of the nucleofuge was further investigated by UPLC-MS studies (Figure 3). The glycosylation reaction of **10**+**5** showed generation of the nucleofuge **1** along with the disaccharide **24**. Furthermore, thus generated HOBt (**1**) was treated with glucosyl bromide **9** to regenerate the glucosyl donor **10** (Figure 3).

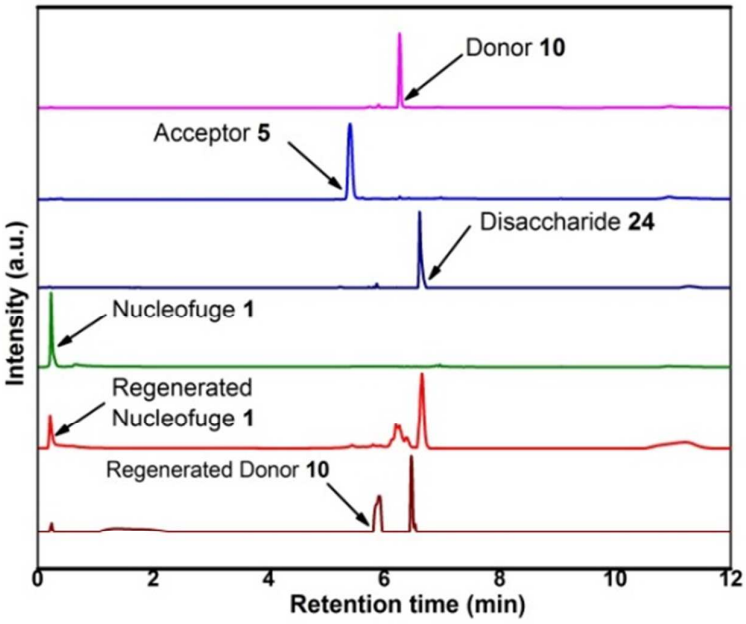
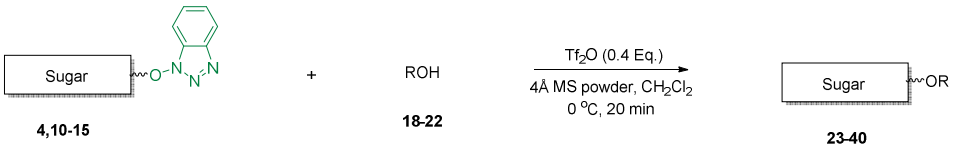
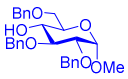
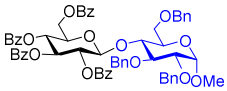
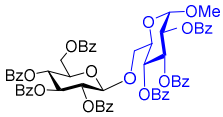
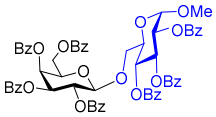
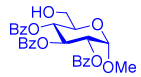
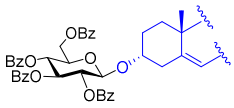
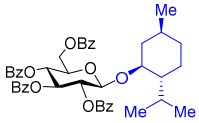
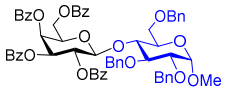
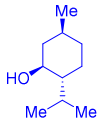
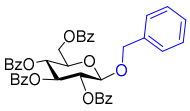
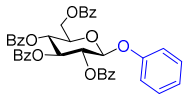
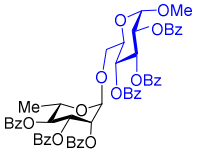
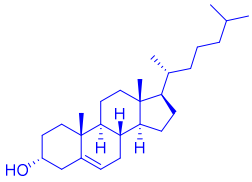
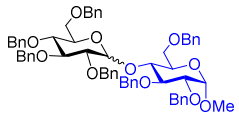
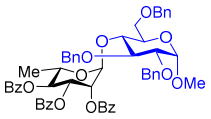
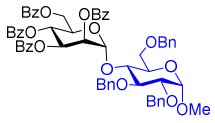
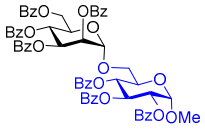
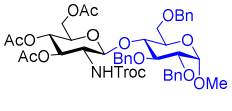
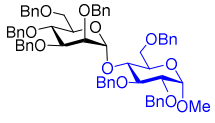
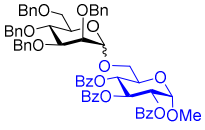
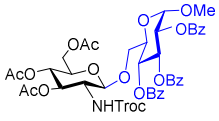



Figure 3. Regeneration of the nucleofuge (**1**) and the donor (**10**)

Donor-regenerative glycosidations is an emerging trend in the chemical glycosidation field. The concept has been investigated by Demchenko[30] using –OFox imidate donors, by Wan[31] through an interrupted Pummerer reaction using 2-(2-propylthiol)benzyl (PTB) glycosides and by Jensen[32] utilizing o-methoxybenzoates.

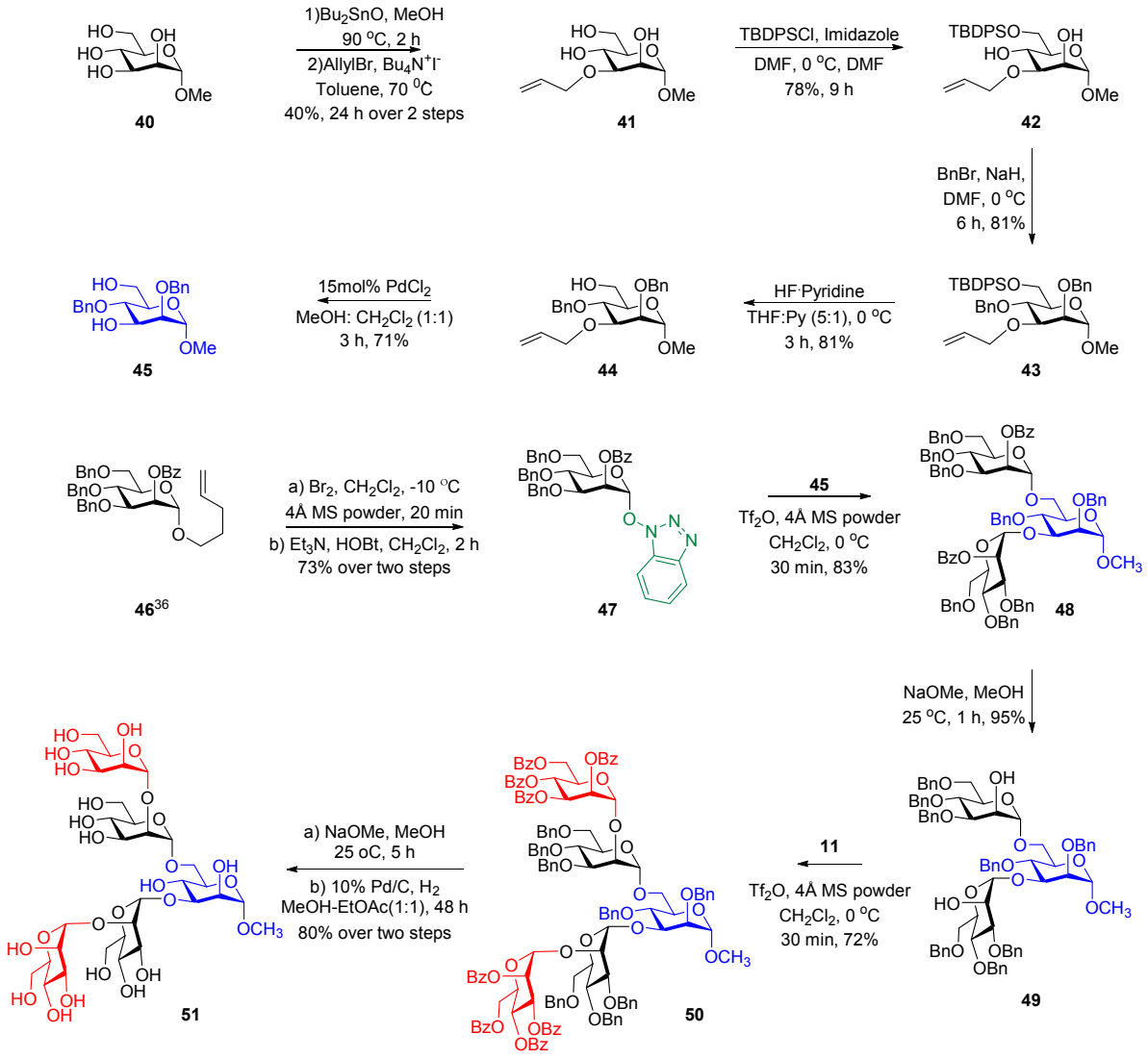
Further, a panel of diverse glycosyl donors (**4**, **10**-**15**) derived from various aldoses were explored for the glycoside synthesis using a set of glycosyl acceptors (**18**-**22**) to obtain glycosides and disaccharides (**24**-**39**) in very high yield (Scheme 3). Notably, routinely used protecting groups such as benzyl ethers, benzoates, acetates and Troc- were well tolerated under the reaction conditions. It has been identified that diastereomeric products were obtained whenever the *C*-2 position was occupied by a benzyl ether and only 1,2-*trans* diastereomer was noticed when the *C*-2 position has an ester (Scheme 3).[20]




| ROH | Glycosides and Disaccharides | | |
|---|---|---|---|
|  **18** |  **23** (93%) |  **24** (95%) |  **25** (95%) |
|  **5** |  **26** (90%) |  **27** (94%) |  **28** (91%) |
|  **19** |  **29** (93%) |  **30** (93%) |  **31** (94%) |
|  **20** |  **32** (94%; α:β = 2.2:1.0) |  **33** (94%) | |
|  **21** |  **34** (93%) |  **35** (91%) |  **36** (90%) |
|  **22** |  **37** (92%) |  **38** (95%; α:β = 2.2:1.0) |  **39** (90%) |

**Scheme 3.** HOBt glycosides as glycosyl donors for the synthesis of glycosides and saccharides

In continuation, the nuance of the just developed HOBt glycosyl donors is demonstrated by the successful synthesis of core pentamannan that is a constituent of the HIV1-GP120 complex.[33-35] Synthesis of pentamannan was envisioned from the monosaccharide building block containing two free hydroxyl groups so that one can realize a trisaccharide in a {2x1+1} fashion and almost similar strategy ({2x1+3}) can be applied to realize the pentamannan.




Scheme 4. Synthesis of branched pentamannan core of HIV-1-GP120.

Our endeavour started with the well-known methyl α-D-mannopyranoside (**40**) which has converted into the aglycon **45** in five steps through compounds **41**-**44**. The glycosyl

donor **47** was easily obtained from *n*-pentenyl mannopyranoside **46**[36] in high yield following the aforementioned procedure through mannosyl bromide intermediate. The HOBt-mediated glycosidation between diol **45** and 2.2 equivalents of donor **47** was triumphantly achieved in the presence of $Tf_2O$ (0.4 eq.), 4Å MS powder, $CH_2Cl_2$, at 0 $^0$C for 20 min to afford the trisaccharide **48** in very high yield. Saponification followed by glycosidation with 2.2 equivalents of donor **11** afforded the pentamannan **50** which is part of the HIV-1 GP120 complex. Ester hydrolysis under Zemplén conditions (NaOMe/MeOH/25 $^0$C/0.5 h) followed by hydrogenolysis (Pd-C/$H_2$/MeOH/25 $^0$C/24 h) afforded the fully deprotected pentamannan **51** as a methyl glycoside (Scheme 4).[22]

**Conclusions**

In summary, hydroxybenzotriazolyl glycosides were identified as stable glycosyl donors that are well suited for the expedient synthesis of glycosides, azido-glycosides, *C*-glycosides and oligosaccharides under mild reaction conditions. Glycosidation with HOBt-glycosides hypothesized to occur by the remote activation of the N3-nitrogen of the benzotriazole in the presence of sub-stoichiometric amounts of $Tf_2O$. The glycosidation occurs with both armed as well as disarmed glycosyl donors. Regenerative-donor glycosidation approach is promising as it enables us to regenerate the glycosyl donor for further utilization. Utility of the HOBt-mediated glycosidation for the oligosaccharide synthesis was demonstrated by the successful convergent synthesis of branched pentamannan core of the HIV1-gp120 complex.

## Experimental Section

**General Methods:**

Unless otherwise noted, materials were obtained from Sigma-Aldrich and were used without further purification. Unless otherwise reported all reactions were performed under Nitrogen atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary

evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. MS powder means flame dried and freshly powdered 4Å molecular sieves. Analytical thin-layer chromatography was performed on pre-coated silica plates ($F_{254}$, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. Optical rotations were measured on a digital polarimeter. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded either on a 400 or a 500 MHz with $CDCl_3$ or $CD_3OD$ as the solvent and TMS as the internal standard. High resolution mass spectroscopy (HRMS) was performed using an ESI-TOF mass analyser. Low resolution mass spectroscopy (LRMS) was performed on UPLC-MS with TLC interface.

**(A) General Experimental Procedure for the Synthesis of Hydroxylbenzotriazolyl Glycosyl Donors: From Glycosyl Bromide with $Et_3N$ as base:** Glycosyl bromide (**9**) (500 mg, 758 µmol, 1 eq.) in dry $CH_2Cl_2$ (5 mL) was stirred under nitrogen atmosphere for 5 min. Solid HOBt **1** (113 mg, 834 µmol, 1.1 eq.) was added and followed by $Et_3N$ (53 µL, 3.79 mmol, 5 eq.). The resulting reaction mixture was stirred for 2 h at 25 $^oC$. At the end of the reaction as adjudged by TLC examination, the reaction mixture was concentrated in *vacuo.* The crude residue was purified by silica gel column chromatography to afford corresponding glycosyl donor **10** (510 mg, 92%) as white solid.

**From Glycosyl Bromide with $Ag_2CO_3$ as base:** Glycosyl bromide **9** (500mg, 758 µmol, 1 eq.) in dry $CH_2Cl_2$ (5 mL) was stirred under nitrogen atmosphere for 5 min. Solid HOBt (113 mg, 834 µmol, 1.1 eq.) followed by $Ag_2CO_3$ (209 mg, 758 µmol, 1 eq.) were added and refluxed for 2 h at 40 $^0C$. The reaction mixture was filtered through a pad of celite and the filtrate was concentrated in *vacuo.* The residue was purified by silica gel column chromatography to afford corresponding glycosyl donor **10** (421 mg, 79%).

**From Glycosyl Bromide with Phase Transfer Catalyst:** Solid HOBt **9** (113 mg, 834 µmol, 1.1 eq.) was dissolved in 2.5 mL of 1*N* solution of aqueous $NaHCO_3$. In another 25 mL round bottom flask, the glycosyl bromide **9** (500 mg, 758 µmol, 1 eq) was dissolved anhydrous $CH_2Cl_2$ (5 mL) was stirred under nitrogen for 5 min followed by addition of tetrabutylammonium hydrogensulphate (TBAHS) (276 mg, 1.14 mmol, 1.5 eq) as a phase transfer catalyst. 1*N* Solution of $NaHCO_3$ containing HOBt was added and resulting reaction mixture was stirred for 8 h. The reaction mixture was washed with 250 mL of water and organic phase was separated and was dried over Sodium sulphate and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography to afford glycosyl donor **10** (450 mg, 84%).

**(B) General Procedure for conversion of pent-4-enyl glycosides to glycosyl bromosides:** Pent-4-enyl glucoside (**7**) (1.0 g, 1.64 mmol, 1 eq.) in dry $CH_2Cl_2$ (10 mL) containing 4Å molecular sieves powder (0.5 g) was cooled to -10 $^0$C under nitrogen atmosphere. Molecular bromine (130 µL, 2.46 µmol, 1.5 eq.) in $CH_2Cl_2$ (1 mL) was added drop wise to the reaction mixture and stirred at -10 $^0$C for additional 10 minutes. The reaction mixture was concentrated under reduced pressure to afford 2,3,4,6-tetra-O-benzyl glycopyranosyl bromide as solid along with 4Å molecular sieves powder which was immediately used in next step without any additional purification using aforementioned procedure.

**(C) General Procedure for Glycosylation:** A solution of glycosyl donor **10** (50 mg, 70 µmol, 1 eq) and glycosyl acceptor **5** (39 mg, 77 µmol, 1.1 eq.) in dry $CH_2Cl_2$ (2.5 mL) in the presence of 4Å molecular sieves (25 mg) was stirred for 15 min at 0 $^o$C under $N_2$ atm. $Tf_2O$ (5 µL, 28 µmol, 0.4 eq) dissolved in 0.5 mL of $CH_2Cl_2$ was added at 0 $^o$C and stirred for 30 min. The reaction was quenched by the addition of $Et_3N$ (300 µL) and stirred for additional 15 min and filtered through a pad of celite, concentrated *in vacuo* and the

resulting residue was purified by silica gel column chromatography to afford discharide **23** (65 mg, 86%) as a white solid.

**(D) Synthesis of Compound 45:** To a solution of compound **40** (5.00 g, 25.75 mmol, 1 eq) in 250 mL of MeOH, $Bu_2SnO$ (6.41 g, 25.75 mmol, 1 eq) was added and refluxed for 2 h at 90 $^{O}$C. After two hours, methanol was completely evaporated under diminished pressure. The crude residue was redissolved in toluene (200 mL) and allyl bromide (17.80 mL, 206 mmol, 8 eq) and TBAI (4.7 g, 12.87 mmol, 0.5 eq) were added. The reaction mixture heated at 70 $^{o}$C for 24 h. Solvent was evaporated under diminished pressure and the resulting residue was separated by silica gel column chromatography using $CH_2Cl_2$ and methanol as mobile phase to afford **41** (2.5 g, 40 %) as a white solid.

Compound **41** (2.40 g, 10.25 mmol, 1eq) was dissolved in 25 mL dry DMF solvent and cooled to 0 $^{o}$C, imidazole (697 mg, 10.25 mmol, 1 eq) was added and stirred for 30 min at 0 $^{o}$C followed by addition of TBDPSCl (2.39 mL, 9.22 mmol, 0.9 eq) at 0 $^{o}$C and reaction mixture was stirred at 25 $^{o}$C for 12 h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine solution and ethyl acetate (3x50 ml). The organic layer was separated and dried over anhydrous $Na_2SO_4$. The organic solvent was evaporated under vacuum and the crude residue was purified by silica gel column chromatography to afford **42** (3.8 g, 78%) as a thick syrup.

Compound **42** (3.50 g, 7.41 mmol, 1 eq) dissolved in 35 mL of dry DMF was cooled to 0 $^{o}$C and sodium hydride (711 mg, 29.62 mmol, 4 eq) was added and stirred for 30 min at 0 $^{o}$C. Benzyl bromide (2.64 mL, 22.00 mmol, 3 eq) was added and stirred for 6 h at 25 $^{o}$C. The reaction mixture was diluted with water and washed ethyl acetate (3x40 mL) and combined organic layers were washed with brine solution. The organic layer was separated, dried ($Na_2SO_4$) and concentrated *in vacuo* to obtain a residue that was

purified by the silica gel column chromatography using ethyl acetate and n-hexane as mobile phase to afford **43** (4.1 g, 81%) as a thick syrup.

To a solution of silyl ether **43** (3.50 g, 5.36 mmol) in 40 mL of THF:Py (5:1) was added HF·Py (3 mL) at 0 $^0$C, allowed to warm to 25 $^0$C and stirred for 3 h. The reaction mixture was concentrated *in vacuo* to obtain a residue which was purified by silica gel column chromatography (ethyl acetate and n-hexane) to afford **44** ( 2.21 g, 81% yield).

Compound **44** (1.60 g, 3.86 mmol) was dissolved in 100 mL of dry methanol:$CH_2Cl_2$ (1:1) and $PdCl_2$ (102 mg, 579 µmol, 0.15 Eq.) dissolved in 5 mL methanol was added dropwise. The reaction mixture was stirred for additional 3 h at 25 $^o$C and quenched with $Et_3N$ and filtered through celite. The filtrate was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography to afford compound **45** (1.5 g, 71%) as a pale yellow syrup.

**(E) Synthesis of Compound 47:** Pent-4-enyl mannopyranoside (**46**) (1.20 g, 1.93 mmol, 1 eq.) in dry $CH_2Cl_2$ (12 mL) containing 4Å molecular sieves powder (0.6 g) was cooled to -10 $^0$C under nitrogen atmosphere. Molecular bromine (154 µL, 2.89 mmol, 1.5 eq.) in $CH_2Cl_2$ (1 mL) was added drop wise to the reaction mixture and stirred at -10 $^0$C for additional 10 minutes. The reaction mixture was concentrated under reduced pressure to afford mannopyranosyl bromide that was immediately redissolved in dry $CH_2Cl_2$ (10 mL) was stirred under nitrogen atmosphere for 5 min. Solid HOBt (**1**) (265 mg, 1.96 mmol, 1.1 eq.) was added and followed by $Et_3N$ (124 µL, 8.91 mmol, 5 eq.). The resulting reaction mixture was stirred for 2 h at 25 $^o$C. At the end of the reaction as adjudged by TLC examination, the reaction mixture was concentrated in *vacuo.* The crude residue was purified by silica gel column chromatography to afford corresponding glycosyl donor **47** (927 mg, 73%) as a thick syrup.

**(F) Synthesis of Compound 48:** A solution of glycosyl donor **47** (500 mg, 744 µmol, 1 eq) and glycosyl acceptor **45** (140 mg, 372 µmol, 0.5 eq.) in dry $CH_2Cl_2$ (10 mL) in the presence of 4Å molecular sieves (50mg) was stirred for 15 min at 0 $^oC$ under $N_2$ atm. $Tf_2O$ (50 µL, 297 µmol, 0.4 eq) dissolved in 0.5 mL of $CH_2Cl_2$ was added at 0 $^oC$ and stirred for 30 min. The reaction was quenched by the addition of $Et_3N$ (1 mL) and stirred for additional 15 min and filtered through a pad of celite, concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography to afford trisaccharide **48** (902 mg, 83%).

**(G) Synthesis of compound 49:** To a solution of trisaccharide **48** (850 mg, 587 µmol) methanol-$CH_2Cl_2$ (1:1) (8 mL) and freshly prepared NaOMe (12.69 mg, 234 µmol) was added and stirred for 1 h. The NaOMe was quenched with Amberlite IR-120 and filtered, the filtrate was concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography to afford trisaccharide **49** (670 mg, 95%).

**(H) Synthesis of compound 50:** A solution of glycosyl donor **11** (500 mg, 700 µmol, 1.0 eq) and glycosyl acceptor **49** (434 mg, 350 µmol, 0.5 eq.) in dry $CH_2Cl_2$ (10 mL) in the presence of 4Å molecular sieves (200 mg) was stirred for 15 min at 0 $^oC$ under $N_2$ atm. $Tf_2O$ (47 µL, 280 µmol, 0.4 eq) dissolved in 1 mL of $CH_2Cl_2$ was added at 0 $^oC$ and stirred for 30 min. The reaction was quenched by the addition of $Et_3N$ (1 mL) and stirred for additional 15 min and filtered through a pad of celite, concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography to afford pentasaccharide **50** (1.10 g, 72%).

**(I) Synthesis of compound 51:** To a solution of compound **50** (1.00 g, 417 µmol, 1eq) methanol-$CH_2Cl_2$ (1:1) (7 mL), a 1M solution of NaOMe in MeOH (1 mL) was added and stirred for 5 h. The NaOMe was quenched by Amberlite IR-120, filtered, and concentrated *in vacuo* and the residue was directly carried forward for hydrogenolysis

without further purification. The crude residue was redissolved in a 1:1 mixture of methanol and ethyl acetate (5 mL), 10% Pd/C (15 mg) was added and stirred vigorously for 48 h under $H_2$ atmosphere (balloon). The reaction mixture was filtered through a pad of Celite®, the filtrate was concentrated *in vacuo*. The residue was purified by BIO-RAD Bio-Gel P-4 Gel using distilled water as mobile phase. The compound **51** (320 mg, 80%) was obtained by lyophilization.

1*H*-benzo[*d*][1,2,3]triazol-1-yl-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (**4**): Eluent for purification: 15% ethyl acetate in *n*-hexane; white solid; yield 983 mg (80%); mp 124 $^oC$; $[\alpha]_D^{25}$ +30.5 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3034, 2912, 1454, 1362; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 3.47 (d, *J* = 3.7 Hz, 1H), 3.57 – 3.65 (m, 1H), 3.71 (dd, *J* = 11.0, 4.1 Hz, 1H), 3.77 – 3.88 (m, 2H), 3.93 (t, *J* = 8.3 Hz, 1H), 4.38 – 4.58 (m, 2H), 4.64 (d, *J* = 10.9 Hz, 1H), 4.89 (dd, *J* = 11.0, 2.5 Hz, 2H), 4.94 (d, *J* = 10.8 Hz, 1H), 5.02 (d, *J* = 10.9 Hz, 1H), 5.26 (d, *J* = 10.7 Hz, 1H), 5.40 (d, *J* = 7.9 Hz, 1H), 7.19 – 7.48 (m, 20H), 7.54 (d, *J* = 6.6 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 68.4, 73.6, 75.1, 75.3, 75.4, 75.9, 76.9, 80.2, 84.4, 109.3, 110.3, 119.9, 124.7, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.0, 128.0, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5,128.6, 128.6, 128.6, 129.1, 137.7, 137.9, 137.9, 138.3, 143.5; HRMS (ESI-MS): m/z calcd for $[C_{40}H_{39}N_3O_6Na^+]$: 680.2737; Found: 680.2737.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (**6**): Eluent for purification: 20% ethyl acetate in *n*-hexane; Pale yellow solid; yield 70 mg (90%); mp 55 $^oC$; $[\alpha]_D^{25}$ +52.2 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3031, 2929, 1730, 1600; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 3.44 (d, *J* = 22.8 Hz, 6H), 3.56 (ddd, *J* = 18.6, 10.3, 2.8 Hz, 4H), 3.61 – 3.94 (m, 10H), 4.01 (t, *J* = 9.3 Hz, 2H), 4.32 – 4.54 (m, 6H), 4.54 – 4.70 (m, 14H), 4.71 – 5.13 (m, 4H), 5.58 (s, 2H), 6.19 (s, 2H), 7.16 – 7.45 (m, 54H), 7.48 – 7.57 (m, 4H), 7.84 – 7.93 (m, 4H), 7.95 – 8.07 (m, 8H);$^{13}C$ NMR (100.67

MHz, $CDCl_3$): δ 55.6, 55.7, 66.7, 68.3, 68.6, 68.7, 68.9, 69.1, 69.7, 70.0, 70.3, 70.6, 70.7, 72.2, 72.3, 73.2, 73.5, 73.5, 74.9, 75.0, 75.1, 75.6, 75.8, 77.4, 77.7, 80.0, 81.8, 82.4, 84.6, 96.8, 96.9, 97.3, 104.1, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.8, 127.9, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.1, 128.1, 128.1, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 129.0, 129.1, 129.1, 129.2, 129.3, 129.3, 129.7, 129.7, 129.7, 129.8, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 133.1, 133.2, 133.4, 133.4, 133.4, 133.5, 138.0, 138.1, 138.2, 138.5, 138.5, 138.6, 138.7, 138.9, 165.3, 165.5, 165.8, 165.9, 165.9, 165.9; HRMS (ESI-MS): m/z calcd for $[C_{62}H_{60}O_{14}Na^+]$:1051.3881; Found: 1051.3877.

1*H*-benzo[*d*][1,2,3]triazol-1-yl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranoside (**10**): Eluent for purification: 20% ethyl acetate in *n*-hexane; crystalline white solid; yield 510 mg (92%); mp 213-216 $^oC$; $[\alpha]_D^{25}$ +8.1 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 1730, 1603, 1450; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 4.15 (ddd, *J* = 9.2, 6.0, 2.8 Hz, 1H), 4.45 (dd, *J* = 12.3, 6.1 Hz, 1H), 4.57 (dd, *J* = 12.3, 2.8 Hz, 1H), 5.75 – 5.87 (m, 2H), 5.97 (dd, *J* = 9.6, 8.1 Hz, 1H), 6.05 (t, *J* = 9.5 Hz, 1H), 7.21 – 7.36 (m, 8H), 7.37 – 7.57 (m, 6H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.73 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.83 – 7.94 (m, 5H), 8.06 (dd, *J* = 8.2, 1.1 Hz, 2H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$):δ 62.4, 68.9, 69.9, 72.4, 73.1, 106.4, 109.8, 119.7, 124.8, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.9, 129.0, 129.1, 129.1, 129.6, 129.6, 129.8, 129.8, 129.9, 129.9, 130.1, 130.1, 133.2, 133.5, 133.7, 133.7, 143.3, 165.1, 165.2, 165.6, 165.8; HRMS (ESI-MS): m/z calcd for $[C_{40}H_{31}N_3O_{10}Na^+]$: 736.1907; Found: 736.1921.

1*H*-benzo[*d*][1,2,3]triazol-1-yl 2,3,4,6-tetra-*O*-benzoyl α-D-mannopyranoside (**11**): Eluent for purification: 20% ethyl acetate in *n*-hexane; White solid; yield 433 mg (80%); mp 160

°C; $[\alpha]_D^{25}$ +37.7 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 1728, 1601, 1451; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 4.56 (dd, *J* = 12.6, 4.2 Hz, 1H), 4.78 (dd, *J* = 12.5, 2.3 Hz, 1H), 5.35 (ddd, *J* = 10.2, 3.9, 2.4 Hz, 1H), 6.01 (d, *J* = 1.7 Hz, 1H), 6.15 (dd, *J* = 10.1, 3.3 Hz, 1H), 6.23 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.33 (t, *J* = 10.2 Hz, 1H), 7.27 – 7.33 (m, 2H), 7.35 – 7.42 (m, 7H), 7.43 – 7.48 (m, 1H), 7.49 – 7.63 (m, 4H), 7.65 – 7.70 (m, 1H), 7.90 (dd, *J* = 8.3, 1.1 Hz, 2H), 8.00 – 8.07 (m, 7H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 62.2, 65.9, 68.3, 69.5, 71.5,103.2, 108.2, 120.6, 125.0, 127.2, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 128.8, 128.8, 129.6, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 133.1, 133.5, 133.7, 134.0, 143.5, 165.3, 165.4, 165.5, 166.0; HRMS (ESI-MS): m/z calcd for $[C_{40}H_{31}N_3O_{10}Na^+]$: 736.1907; Found: 736.1908.

1*H*-benzo[*d*][1,2,3]triazol-1-yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside (**12**): Eluent for purification: 15% ethyl acetate in *n*-hexane; white solid; yield 415 mg (80%); mp 108 °C; $[\alpha]_D^{25}$ -17.7 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3063, 3031, 2869, 1496, 1453, 1362; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 3.37 (ddd, *J* = 9.5, 5.1, 1.9 Hz, 1H), 3.56 – 3.66 (m, 2H), 3.73 (dd, *J* = 11.2, 5.1 Hz, 1H), 4.09 (t, *J* = 9.3 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 2.8 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.52 – 4.70 (m, 3H), 4.86 – 4.98 (m, 2H), 5.03 (d, *J* = 12.0 Hz, 1H), 5.41 (s, 1H), 7.14 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.18 – 7.40 (m, 18H), 7.43 – 7.58 (m, 2H), 7.67 – 7.83 (m, 1H), 7.94 (d, *J* = 8.3 Hz, 1H);$^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 69.0, 72.0, 73.4, 73.5, 73.9, 74.6, 75.1, 76.3, 81.4, 107.0, 110.5, 119.6, 124.7, 127.4, 127.5, 127.5, 127.5, 127.7, 127.7, 127.8, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 129.2, 137.7, 138.0, 138.1, 138.1, 143.4; HRMS (ESI-MS): m/z calcd for $[C_{40}H_{39}N_3O_6Na^+]$: 680.2737; Found:680.2738.

1*H*-benzo[*d*][1,2,3]triazol-1-yl 2,3,4,6-tetra-*O*-benzoyl β-D-galactopyranoside (**13**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 505 mg (90%); mp 211

°C; $[\alpha]_D^{25}$ +40.4 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 1727, 1451;$^1$H NMR (399.78 MHz, $CDCl_3$): δ 4.32 – 4.39 (m, 1H), 4.46 (dd, *J* = 11.6, 5.2 Hz, 1H), 4.58 (dd, *J* = 11.6, 7.5 Hz, 1H), 5.74 (dd, *J* = 10.3, 3.4 Hz, 1H), 5.82 (d, *J*= 8.4 Hz, 1H), 6.02 – 6.07 (m, 1H), 6.20 (dd, *J* = 10.3, 8.4 Hz, 1H), 7.21 – 7.31 (m, 5H), 7.33 – 7.55 (m, 8H), 7.61 – 7.73 (m, 4H), 7.81 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 1H), 8.04 – 8.16 (m, 4H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 62.0, 67.7, 67.8, 71.6, 72.7, 107.1, 109.9, 119.9, 124.9, 128.4, 128.4, 128.5, 128.5, 128.6, 128.7, 128.8, 128.8, 128.8, 128.9, 129.0, 129.0, 129.1, 129.7, 129.7, 129.7, 129.9, 129.9, 130.1, 130.1, 130.1, 130.1, 133.3, 133.7, 133.8, 134.0, 143.5, 165.5, 165.5, 165.5, 165.9; HRMS (ESI-MS): m/z calcd for $[C_{40}H_{31}N_3O_{10}Na^+]$: 736.1907; Found: 736.1915.

1*H*-benzo[*d*][1,2,3]triazol-1-yl 2,3,4-tri-*O*-benzoyl α-L-rhamnopyranoside (**14**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 405 mg (90%); mp 112 °C; $[\alpha]_D^{25}$ +17.1 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3067, 2983, 1729, 1353; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 1.49 (d, *J* = 6.2 Hz, 3H), 5.14 (dd, *J* = 9.9, 6.2 Hz, 1H), 5.88 – 5.99 (m, 2H), 6.12 (dd, *J* = 10.1, 3.6 Hz, 1H), 6.24 (dd, *J* = 3.6, 1.7 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.66 (m, 9H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.04 – 8.18 (m, 5H);$^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 17.4, 68.7, 69.5, 69.7, 70.9, 103.5, 108.3, 120.6, 124.9, 127.3, 128.4, 128.4, 128.6, 128.6, 128.6, 128.7, 128.8, 128.8, 128.8, 129.0, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 133.4, 133.6, 133.9, 143.5, 165.5, 165.5, 165.7; HRMS (ESI-MS): m/z calcd for $[C_{33}H_{27}N_3O_8Na^+]$: 616.1696; Found: 616.1694.

1*H*-benzo[d][1,2,3]triazol-1-yl 2-*deoxy*-2-(((2,2,2-trichloroethoxy)carbonyl)amino)-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (**15**): Eluent for purification: 35% ethyl acetate in *n*-hexane; white solid; yield 408 mg (90%); mp 186 °C; $[\alpha]_D^{25}$ +37.4 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3268, 3046, 1735, 1353;$^1$H NMR (399.78 MHz, $CDCl_3$): δ 1.88 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.81 (ddd, *J* = 10.0, 5.4, 2.3 Hz, 1H), 4.05 (dd, *J* = 12.3, 2.3 Hz, 1H),

4.12 – 4.21 (m, 1H), 4.26 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.86 (t, *J* = 18.6 Hz, 1H), 5.14 (t, *J* = 9.7 Hz, 1H), 5.48 – 5.57 (m, 1H), 5.68 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 9.1 Hz, 1H), 7.35 – 7.44 (m, 1H), 7.51 (ddd, *J* = 10.6, 5.7, 2.2 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H);$^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 20.6, 20.7, 20.7, 54.5, 61.7, 68.5, 71.5, 72.5, 74.7, 95.5, 106.3, 110.3, 119.9, 125.1, 128.6, 129.2, 143.4, 154.8, 169.6, 170.5, 170.7; HRMS (ESI-MS): m/z calcd for $[C_{21}H_{23}Cl_3N_4O_{10}Na^+]$: 619.0377; Found: 619.0371.

1-*deoxy*-1-allyl 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside (**16**): Eluent for purification: 10% ethyl acetate in *n*-hexane; pale yellow solid; yield 38 mg (90%); mp 59 $^{o}$C; $[\alpha]_D^{25}$ +55.8(*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3268, 3046, 2912, 1600, 1460, 1353; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 2.37 - 2.7(m, 2H), 3.57 – 3.84 (m, 6H), 4.14 (dt, J=1.2, 5.1, 1H), 4.42 – 4.51 (m, 2H), 4.59 – 4.54 (m, 2H), 4.66 – 4.73 (m, 1H), 4.81 (dd, *J*=10.7, 1.6, 2H), 4.94 (d, *J*=10.9, 1H), 5.10 (dt, *J*=10.2, 5.2, 2H), 5.82 (ddt, *J*=17.2, 10.2, 6.8, 1H), 7.12 (dd, *J*=6.9, 2.5, 2H), 7.21 – 7.4 (m, 18H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 68.2, 71.2, 73.2, 73.6, 73.6, 75.2, 76.6, 78.2, 80.2, 80.2, 82.5, 117.0, 127.7, 127.8, 127.9, 127.9, 127.9 (2C), 128.0 (2C), 128.5 (2C), 128.5 (2C), 128.5 (2C), 128.5 (4C), 128.6 (2C), 134.8, 138.1, 138.2, 138.3, 138.3; HRMS(ESI-MS): m/z calcd for $[C_{37}H_{40}O_5Na^+]$: 587.2773; Found: 587.2776.

1-*deoxy*-1-azido 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (**17**): Eluent for purification: 10% ethyl acetate in *n*-hexane; pale yellow solid; yield 40 mg (93%); mp 55 $^{o}$C; $[\alpha]_D^{25}$ +22.9 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3268, 3046, 2912, 2170, 1600, 1460, 1353; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.65 (ddd, *J* = 9.8, 6.4, 4.2 Hz, 6H), 3.79 – 3.69 (m, 2H), 3.87 (t, *J* = 9.3 Hz, 2H), 4.48 (dd, *J* = 11.4, 3.8 Hz, 4H), 4.53 – 4.62(m, 2H), 4.65 (dd, *J* = 15.1, 7.5 Hz, 2H), 4.79 (dd, *J* = 15.1, 8.3 Hz, 4H), 4.85 (dd,*J* = 12.4, 7.4 Hz, 4H), 4.93 (t, *J* = 11.3 Hz, 2H), 5.23 (d, *J* = 4.1 Hz, 2H), 7.08 – 7.21 (m, 4H), 7.22 -

7.44 (m, 36H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 68.2, 68.5, 72.6, 73.6, 73.7, 73.9, 75.2, 75.3, 75.9, 76.0, 77.1, 77.2, 77.4, 79.5, 81.8, 81.8, 81.9, 85.0, 88.2, 90.3, 127.8, 127.9, 127.9, 127.9 (3C), 128.1 (4C), 128.1 (5C), 128.2 (2C), 128.3, 128.6 (6C), 128.5 (6C), 128.6 (6C), 128.8 (4C), 137.7, 137.8, 137.8, 137.9, 138.0, 138.1, 138.4, 138.6; HRMS (ESI-MS): m/z calcd for [$C_{34}H_{35}O_5N_3Na^+$]: 588.2424; Found: 588.2439.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**23**): Eluent for purification: 20% ethyl acetate in *n*-hexane; fluffy solid; yield 69 mg (93%); mp 58 $^{o}$C; $[\alpha]_D^{25}$ - 25.2 (*c* 1.0, $CHCl_3$); IR(cm$^{-1}$, $CHCl_3$): 2925, 2856, 1725, 1600; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.27 (s, 3H), 3.38 – 3.55 (m, 3H), 3.73 (ddt, *J* = 11.0, 7.8, 3.6 Hz, 2H), 3.89 (t, *J* = 9.2 Hz, 1H), 3.98 (t, *J* = 9.4 Hz, 1H), 4.27 (dd, *J* = 12.1, 5.0 Hz, 1H), 4.35 (d, *J* = 12.1 Hz, 1H), 4.41 (dd, *J* = 12.1, 3.4 Hz, 1H), 4.50 – 4.62 (m, 2H), 4.70 – 4.85 (m, 4H), 5.09 (d, *J* = 11.2 Hz, 1H), 5.48 (dd, *J* = 9.4, 8.2 Hz, 1H), 5.52 – 5.70 (m, 2H), 7.16 – 7.28 (m, 10H), 7.29 – 7.41 (m, 9H), 7.41 – 7.54 (m, 8H), 7.77 – 7.81 (m, 2H), 7.88 (d, *J* = 7.5 Hz, 4H), 7.95 – 7.98 (m, 2H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 55.4, 63.2, 67.6, 69.5, 69.9, 71.9, 72.3, 73.2, 73.6, 73.7, 75.4, 77.3, 78.8, 80.0, 98.5, 100.5, 127.2, 127.5, 127.5, 127.8, 128.1, 128.1, 128.1, 128.1, 128.1, 128.1, 128.1, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.9, 128.9, 128.9, 129.1, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.8, 133.0, 133.2, 133.4, 133.4, 137.9, 138.4, 139.3, 164.9, 165.1, 165.8, 166.1; HRMS (ESI-MS): m/z calcd for [$C_{62}H_{58}O_{15}Na^+$]: 1065.3673; Found: 1065.3668.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranosyl) α-D-glucopyranoside (**24**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 68 mg (95%); mp 86 $^{o}$C; $[\alpha]_D^{25}$ +31.3 (*c* 1.0, $CHCl_3$); IR(cm$^{-1}$, $CHCl_3$): 1735, 1452, 1360; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.10 (s, 3H), 3.79 (dd, *J* = 11.3, 7.6 Hz, 1H), 4.07 – 4.18 (m, 2H), 4.19 – 4.27 (m, 1H), 4.45 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.61 (dd, *J* = 12.1,

3.1 Hz, 1H), 4.90 – 5.02 (m, 2H), 5.10 (dd, *J* = 10.2, 3.6 Hz, 1H), 5.32 (t, *J* = 9.9 Hz, 1H), 5.57 (dd, *J* = 9.7, 7.9 Hz, 1H), 5.66 (t, *J* = 9.7 Hz, 1H), 5.93 (t, *J* = 9.7 Hz, 1H), 6.08 (t, *J* = 9.8 Hz, 1H), 7.25 (td, *J* = 7.7, 4.2 Hz, 4H), 7.29 – 7.36 (m, 7H), 7.36 – 7.43 (m, 5H), 7.44 – 7.56 (m, 5H), 7.75 – 7.82 (m, 3H), 7.83 – 7.85 (m, 2H), 7.86 – 7.89 (m, 3H), 7.91 – 7.94 (m, 2H), 7.95 – 8.04 (m, 4H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 55.1, 63.1, 68.8, 69.0, 69.7, 69.8, 70.4, 72.0, 72.1, 72.4, 72.9, 96.5, 101.9, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.8, 128.9, 128.9, 129.1, 129.3, 129.4, 129.6, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 133.1, 133.2, 133.3, 133.3, 133.4, 133.5, 133.5, 165.3, 165.3, 165.5, 165.8, 165.8, 165.9, 166.2; HRMS (ESI-MS): m/z calcd for $[C_{62}H_{52}O_{18}Na^+]$:1107.3051; Found: 1107.3050.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranosyl) α-D-galactopyranoside (**25**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 68 mg (95%); mp 82 $^{o}$C; $[\alpha]_D^{25}$ +6.0 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3022, 1727; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.10 (s, 3H), 3.80 (dd, *J* = 11.3, 7.6 Hz, 1H), 4.18 (dd, *J* = 11.3, 1.6 Hz, 1H), 4.24 – 4.29 (m, 1H), 4.33 (s, 1H), 4.38 – 4.44 (m, 1H), 4.60 (dd, *J* = 11.2, 6.4 Hz, 1H), 4.90 – 4.98 (m, 2H), 5.06 (dd, *J* = 10.2, 3.6 Hz, 1H), 5.34 (t, *J* = 9.9 Hz, 1H), 5.64 (dd, *J* = 10.4, 3.5 Hz, 1H), 5.84 (dd, *J* = 10.4, 7.9 Hz, 1H), 6.00 (d, *J* = 3.3 Hz, 1H), 6.08 (t, *J* = 9.8 Hz, 1H), 7.20 – 7.30 (m, 4H), 7.32 – 7.60 (m, 17H), 7.75 – 7.82 (m, 4H), 7.91 (ddd, *J* = 18.1, 8.1, 1.0 Hz, 4H), 8.00 (ddd, *J* = 7.1, 3.4, 2.0 Hz, 4H), 8.04 – 8.08 (m, 2H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 55.2, 62.0, 68.2, 68.8, 69.3, 69.7, 69.9, 70.5, 71.5, 71.7, 96.6, 102.4, 128.3, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 128.9, 128.9, 129.1, 129.2, 129.3, 129.3, 129.5, 129.5, 129.7, 129.7, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 130.1, 130.1, 130.1, 133.2, 133.4, 133.4, 133.4, 133.4, 133.6, 133.7, 165.5, 165.6, 165.6,

165.7, 165.8, 165.8, 166.1;HRMS (ESI-MS): m/z calcd for [$C_{62}H_{52}O_{18}Na^+$] :1107.3051; Found:1107.3051.

Cholesteryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**26**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 61 mg (90%); mp 202 $^oC$; $[\alpha]_D^{25}$ -11.3(*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 2928, 2860, 1729; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 0.64 (s, 3H), 0.84 (d, *J* = 1.8 Hz, 3H), 0.86 (d, *J* = 1.7 Hz, 3H), 0.88 (s, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.95 – 1.24 (m, 9H), 1.27 – 1.71 (m, 14H), 1.86 – 1.95 (m, 2H), 1.95 – 2.03 (m, 1H), 2.04 – 2.22 (m, 2H), 3.52 (dt, *J* = 10.6, 5.4 Hz, 1H), 4.14 (ddd, *J* = 9.5, 5.9, 3.4 Hz, 1H), 4.51 (dd, *J* = 12.0, 5.9 Hz, 1H), 4.59 (dd, *J* = 12.0, 3.3 Hz, 1H), 4.93 (d, *J* = 7.9 Hz, 1H), 5.21 (d, *J* = 5.1 Hz, 1H), 5.49 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.62 (t, *J* = 9.7 Hz, 1H), 5.88 (t, *J* = 9.6 Hz, 1H), 7.20 – 7.42 (m, 9H), 7.43 – 7.57 (m, 3H), 7.77 – 7.85 (m, 2H), 7.89 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.91 – 7.97 (m, 2H), 7.95 – 8.06 (m, 2H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 12.0, 18.9, 19.4, 21.1, 22.7, 23.0, 23.9, 24.4, 28.2, 28.4, 29.7, 29.8, 31.9, 32.0, 35.9, 36.3, 36.8, 37.2, 39.0, 39.7, 39.9, 42.4, 50.2, 56.3, 56.9, 63.5, 70.2, 72.2, 72.2, 73.2, 80.6, 100.3, 122.1, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.9, 129.0, 129.6, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 133.2, 133.3, 133.3, 133.6, 140.5, 165.2, 165.4, 166.0, 166.2; HRMS (ESI-MS): m/z calcd for [$C_{61}H_{72}O_{10}Na^+$]: 987.5023; Found:987.5023.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**27**): Eluent for purification: 10% ethyl acetate in *n*-hexane; white solid; yield 48 mg (95%); mp 63 $^oC$; $[\alpha]_D^{25}$ - 19.7(*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 2953, 2951, 2866, 1729, 1601; $^1H$ NMR (399.78MHz, $CDCl_3$): δ 0.60 – 0.92 (m, 14H), 1.56 (d, *J* = 12.3 Hz, 2H), 1.94 (d, *J* = 12.2 Hz, 1H), 2.12 – 2.33 (m, 1H), 3.48 (d, *J* = 4.0 Hz, 1H), 4.04 – 4.22 (m, 1H), 4.49 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.57 – 4.74 (m, 1H), 4.93 (d, *J* = 8.0 Hz, 1H), 5.50 (dd, *J* = 9.8, 8.0 Hz, 1H), 5.65 (d, *J* = 9.7 Hz, 1H), 5.83 – 6.05 (m, 1H), 7.22 – 7.43 (m,

9H), 7.45 – 7.59 (m, 3H), 7.81 – 7.87 (m, 2H), 7.88 – 7.93 (m, 2H), 7.94 – 8.04 (m, 4H).$^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 15.7, 20.9, 22.1, 23.1, 25.2, 31.5, 34.2, 40.9, 47.4, 63.6, 70.3, 72.1, 72.2, 73.3, 79.2, 99.1, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 129.0, 129.0, 129.0, 129.0, 129.0, 129.6, 129.6,129.7, 129.7, 129.8, 129.9, 129.9, 133.2, 133.2, 133.3, 133.5, 165.2, 165.4, 166.0, 166.2; HRMS (ESI-MS): m/z calcd for $[C_{44}H_{46}O_{10}Na^+]$: 757.2989; Found: 757.2986.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl β-D-galactopyranosyl)-α-D-glucopyranoside (**28**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 67 mg (91%); mp 64 $^{o}$C; $[\alpha]_D^{25}$ - 23.9 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3030, 2925, 1724;$^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.30 (d, *J* = 1.1 Hz, 3H), 3.44 (d, *J* = 10.7 Hz, 1H), 3.46 – 3.58 (m, 2H), 3.70 (d, *J* = 9.9 Hz, 1H), 3.86 – 3.97 (m, 2H), 3.99 – 4.08 (m, 1H), 4.19 (ddd, *J* = 11.2, 7.6, 1.3 Hz, 1H), 4.32 (d, *J* = 12.2 Hz, 1H), 4.34 – 4.45 (m, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 4.59 – 4.68 (m, 1H), 4.71 – 4.83 (m, 3H), 4.91 (d, *J* = 11.1 Hz, 1H), 5.18 (d, *J* = 11.1 Hz, 1H), 5.23 – 5.37 (m, 1H), 5.70 (ddd, *J* = 9.9, 8.0, 1.4 Hz, 1H), 5.85 (d, *J* = 3.3 Hz, 1H), 7.14 – 7.32 (m, 10H), 7.33 – 7.58 (m, 17H), 7.72 – 7.79 (m, 2H), 7.80 – 7.88 (m, 2H), 7.90 – 7.98 (m, 2H), 7.97 – 8.06 (m, 2H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 55.5, 61.5, 67.7, 68.0, 69.6, 70.4, 71.1, 72.0, 73.7, 73.8, 75.4, 76.8, 78.8, 80.0, 98.7, 100.5, 127.3, 127.3, 127.3, 127.4, 127.9, 127.9, 128.2, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.7, 128.7, 128.9, 128.9, 128.9, 129.2, 129.3, 129.6, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 133.3, 133.3, 133.4, 133.5, 137.9, 138.5, 139.5, 165.0, 165.6, 165.6, 166.0; HRMS (ESI-MS): m/z calcd for $[C_{62}H_{58}O_{15}Na^+]$:1065.3673; Found: 1065.3670.

Benzyl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranoside (**29**): Eluent for purification: 15% ethyl acetate in *n*-hexane; pale brown solid; yield 44 mg (93%); mp 55 $^{o}$C; $[\alpha]_D^{25}$ - 27.1 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 2957, 2927, 1726, 1601; $^1$H NMR (399.78MHz, $CDCl_3$): δ

4.40 – 4.52 (m, 2H), 4.62 – 4.74 (m, 2H), 4.86 (d, *J* = 11.9 Hz, 1H), 5.18 (d, *J* = 1.7 Hz, 1H), 5.76 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.96 (dd, *J* = 10.1, 3.4 Hz, 1H), 6.12 (t, *J* = 10.0 Hz, 1H), 7.21 – 7.30 (m, 2H), 7.32 – 7.46 (m, 12H), 7.46 – 7.53 (m, 1H), 7.53 – 7.65 (m, 2H), 7.83 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.91 – 7.97 (m, 2H), 8.04 (dd, *J* = 8.3, 1.1 Hz, 2H), 8.11 (dd, *J* = 8.2, 1.3 Hz, 2H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 63.0, 67.1, 69.2, 70.1, 70.3, 70.6, 97.1, 128.3, 128.3, 128.4, 128.4, 128.4, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 128.8, 128.8, 129.1, 129.2, 129.4, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 133.2, 133.3, 133.6, 133.6, 136.5, 165.5, 165.6, 165.6, 166.3; HRMS (ESI-MS): m/z calcd for [$C_{41}H_{34}O_{10}Na^+$]: 709.2050; Found: 709.2050.

Phenyl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranoside (**30**): Eluent for purification: 10% ethyl acetate in *n*-hexane; white solid; yield 44 mg (93%); mp 63 $^{o}$C; $[\alpha]_D^{25}$ +29.7(*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 1725, 1597; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 4.38 (ddd, *J* = 9.7, 6.7, 3.0 Hz, 1H), 4.57 (dd, *J* = 12.1, 6.7 Hz, 1H), 4.72 (dd, *J* = 12.1, 3.0 Hz, 1H), 5.44 (d, *J* = 7.8 Hz, 1H), 5.75 (t, *J* = 9.6 Hz, 1H), 5.86 (dd, *J*= 9.6, 7.8 Hz, 1H), 6.04 (t, *J* = 9.5 Hz, 1H), 7.00 – 7.11 (m, 3H), 7.16 – 7.24 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.43 (dt, *J* = 23.4, 7.7 Hz, 7H), 7.50 – 7.63 (m, 3H), 7.88 – 7.92 (m, 2H), 7.98 (ddd, *J* = 9.9, 8.3, 1.1 Hz, 4H), 8.07 (dd, *J* = 8.2, 1.2 Hz, 2H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 63.4, 69.8, 71.8, 72.7, 73.0, 99.8, 117.4, 117.4, 123.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.8, 128.9, 129.2, 129.6, 129.6, 129.7, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 133.3, 133.4, 133.5, 133.7, 157.1, 165.2, 165.4, 165.9, 166.2; HRMS (ESI-MS): m/z calcd for [$C_{40}H_{32}O_{10}Na^+$]: 695.1893; Found: 695.1889.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl α-L-rhamnopyranosyl)-α-D-glucopyranoside (**31**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 81 mg (95%); mp 62 $^{o}$C; $[\alpha]_D^{25}$ +108.2 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3067, 2948, 1728; $^1$H NMR (399.78MHz, $CDCl_3$): δ 1.28 (s, 3H), 3.59 (s, 3H), 3.84 (dd, *J* = 11.8, 7.1

Hz, 1H), 3.94 (dd, *J* = 11.8, 2.1 Hz, 1H), 4.11 – 4.20 (m, 1H), 4.38 (dd, *J* = 9.1, 6.4 Hz, 1H), 5.16 (d, *J* = 1.5 Hz, 1H), 5.27 – 5.32 (m, 2H), 5.52 (t, *J* = 9.9 Hz, 1H), 5.64 (t, *J* = 9.9 Hz, 1H), 5.72 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.79 (dd, *J* = 10.1, 3.4 Hz, 1H), 6.21 (t, *J* = 9.6 Hz, 1H), 7.22 – 7.32 (m, 4H), 7.39 (qd, *J* = 8.8, 7.5, 3.0 Hz, 8H), 7.46 – 7.54 (m, 5H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.79 – 7.82 (m, 2H), 7.86 – 7.90 (m, 2H), 7.94 – 8.02 (m, 6H), 8.07 – 8.11 (m, 2H);$^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 18.0, 56.3, 67.3, 67.4, 70.0, 70.2, 70.3, 70.9, 71.1, 72.3, 72.6, 97.3, 98.7, 128.7, 128.7, 128.7, 128.7, 128.9, 128.9, 128.9, 128.9, 128.9, 128.9, 129.0, 129.0, 129.3, 129.6, 129.7, 129.7, 129.8, 129.9, 130.1, 130.1, 130.2, 130.2, 130.2, 130.2, 130.4, 130.4, 130.4, 130.4, 130.4, 130.4, 133.5, 133.5, 133.8, 133.8, 133.9, 133.9, 165.9, 165.9, 165.9, 166.2, 166.3, 166.3; HRMS (ESI-MS): m/z calcd for [$C_{55}H_{48}O_{16}Na^+$]: 987.2840; Found: 987.2840.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl α,β-D-glucopyranosyl)-α-D-glucopyranoside (**32**): Eluent for purification: 20% ethyl acetate in *n*-hexane; Syrup; yield 71 mg (95%); $[\alpha]_D^{25}$ +39.9 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3030, 2921, 2804, 1732; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.40 (d, *J* = 5.2 Hz, 6H), 3.44 (s, 6H), 3.56 – 3.72 (m, 6H), 3.76 (d, *J* = 10.5 Hz, 2H), 3.89 (td, *J* = 12.4, 10.6, 6.5 Hz, 4H), 3.96 (d, *J* = 9.6 Hz, 2H), 4.11 (t, *J* = 9.1, 9.1 Hz, 2H), 4.31 (d, *J* = 12.3 Hz, 2H), 4.38 – 4.50 (m, 4H), 4.50 – 4.61 (m, 8H), 4.64 (d, *J* = 11.1 Hz, 4H), 4.73 (d, *J* = 12.2 Hz, 2H), 4.78 – 5.03 (m, 10H), 5.01 – 5.78 (m, 4H), 7.11 – 7.49 (m, 70H);$^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 55.2, 55.4, 67.9, 68.2, 69.1, 69.6, 70.1, 71.0, 72.3, 73.2, 73.3, 73.4, 73.5, 73.5, 73.7, 74.5, 74.9, 75.0, 75.0, 75.0, 75.2, 75.5, 75.6, 75.7, 76.7, 77.4, 77.7, 78.1, 78.9, 79.5, 80.3, 80.5, 82.1, 82.1, 82.9, 84.9, 96.7, 97.8, 98.5, 102.6, 126.8, 126.8, 126.8, 126.9, 126.9, 127.2, 127.2, 127.2, 127.3, 127.3, 127.3, 127.3, 127.3, 127.4, 127.4, 127.5, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 128.0, 128.1, 128.1, 128.1, 128.2, 128.3 (12C), 128.3, 128.3, 128.4, 128.4,

128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 137.9, 138.0, 138.1, 138.1, 138.2, 138.2, 138.4, 138.5, 138.6, 138.6, 138.7, 138.8, 139.0, 139.6; HRMS (ESI-MS): m/z calcd for [$C_{62}H_{66}O_{11}Na^+$]: 1009.4503; found: 1009.4501.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzoyl α-L-rhamnopyranosyl)-α-D-glucopyranoside (**33**): Eluent for purification: 20% ethyl acetate in *n*-hexane;white solid; yield 74 mg (94%); mp 58 $^oC$; $[\alpha]_D^{25}$ +41.3 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3067, 2948, 2961, 1728; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 0.89 (d, *J* = 6.0 Hz, 3H), 3.41 (s, 3H), 3.62 – 3.69 (m, 1H), 3.74 (d, *J* = 11.0 Hz, 1H), 3.87 (dd, *J* = 20.5, 10.1 Hz, 2H), 3.94 – 4.07 (m, 2H), 4.38 (td, *J* = 7.7, 6.9, 3.0 Hz, 1H), 4.57 (q, *J* = 11.9 Hz, 2H), 4.62 – 4.67 (m, 2H), 4.74 – 4.80 (m, 1H), 4.86 (d, *J* = 11.1 Hz, 1H), 5.15 – 5.28 (m, 2H), 5.56 – 5.58 (m, 1H), 5.62 (t, *J* = 10.0, 1.8 Hz, 1H), 5.79 (dt, *J* = 10.2, 2.5 Hz, 1H), 7.09 – 7.22 (m, 6H), 7.24 – 7.35 (m, 9H), 7.36 – 7.50 (m, 7H), 7.50 – 7.63 (m, 2H), 7.79 – 7.96 (m, 4H), 8.02 – 8.14 (m, 2H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 17.3, 55.4, 67.1, 68.4, 70.1, 70.2, 71.4, 71.8, 73.4, 73.5, 74.9, 75.6, 79.8, 80.4, 97.1, 98.1, 127.4 – 128.1 (8C), 128.3 – 128.7 (14C), 129.3 – 130.0 (8C), 133.3, 133.4, 133.6, 137.8, 138.0, 138.8, 165.8, 165.9, 165.9; HRMS(ESI-MS): m/z calcd for [$C_{55}H_{54}O_{13}Na$]$^+$: 945.3462; Found: 945.3459.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl α-D-mannopyranosyl)-α-D-glucopyranoside (**34**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 69 mg (93%); mp 64 $^oC$; $[\alpha]_D^{25}$ -23.8 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 2965, 1730; $^1H$ NMR (399.78 MHz, $CDCl_3$):δ 3.44 (d, *J* = 0.9 Hz, 3H), 3.54 – 3.61 (m, 1H), 3.78 (d, *J* = 10.4 Hz, 1H), 3.84 – 4.00 (m, 3H), 4.06 – 4.15 (m, 1H), 4.24 (dd, *J* = 12.1, 3.3 Hz, 1H), 4.36 (d, *J* = 10.0 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.54 – 4.68 (m, 4H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 5.07 (d, *J* = 11.0 Hz, 1H), 5.62 (s, 1H), 5.74 (dd, *J* = 2.9, 1.5 Hz, 1H), 5.83 – 5.92 (m, 1H), 6.04 (t, *J* = 10.1 Hz, 1H), 6.93 – 7.06 (m, 3H), 7.10 – 7.17 (m, 1H), 7.17 – 7.46 (m, 21H), 7.48 – 7.61 (m, 3H), 7.76 – 7.83 (m, 2H), 7.89 – 7.97 (m, 4H), 8.03 – 8.21 (m, 1H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 55.5, 62.8, 66.8,

69.3, 69.7, 69.7, 70.0, 70.6, 73.4, 73.6, 75.5, 76.3, 80.3, 81.5, 98.0, 99.0, 127.3, 127.6, 127.6, 127.7, 127.7, 127.7, 128.1, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 129.1, 129.2, 129.5, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 130.1, 133.1, 133.2, 133.4, 133.5, 138.0, 138.0, 138.3, 165.0, 165.4, 165.6, 166.2; HRMS (ESI-MS): m/z calcd for $[C_{62}H_{58}O_{15}Na^+]$: 1065.3673; Found: 1065.3672.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl α-D-mannopyranosyl)-α-D-glucopyranoside (**35**): Eluent for purification: 20% ethyl acetate in *n*-hexane; white solid; yield 65 mg (91%); mp 92 $^oC$; $[\alpha]_D^{25}$ +8.7(*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3022, 1727; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 3.62 (s, 3H), 3.78 (dd, *J* = 10.7, 1.9 Hz, 1H), 4.10 (dd, *J* = 10.8, 6.2 Hz, 1H), 4.30 – 4.46 (m, 2H), 4.54 (ddd, *J* = 10.0, 4.8, 2.2 Hz, 1H), 4.63 (dd, *J* = 12.1, 2.2 Hz, 1H), 5.16 (d, *J* = 1.5 Hz, 1H), 5.26 (dd, *J* = 10.2, 3.7 Hz, 1H), 5.33 (d, *J* = 3.7 Hz, 1H), 5.58 (t, *J* = 9.9 Hz, 1H), 5.77 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.99 (dd, *J* = 10.1, 3.3 Hz, 1H), 6.09 (t, *J* = 10.0 Hz, 1H), 6.21 (t, *J* = 9.8 Hz, 1H), 7.26 – 7.36 (m, 6H), 7.38 – 7.50 (m, 11H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.58 – 7.65 (m, 2H), 7.85 – 7.89 (m, 2H), 7.92 – 7.96 (m, 2H), 7.97 – 8.05 (m, 6H), 8.06 – 8.15 (m, 4H);$^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 55.8, 62.8, 66.6, 67.0, 68.4, 69.1, 69.5, 70.1, 70.5, 70.7, 72.2, 97.1, 97.6, 128.4, 128.4, 128.4,128.4, 128.4, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 128.7, 128.9, 129.2, 129.3, 129.3, 129.4, 129.4, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 130.0, 130.1, 130.1, 130.1, 130.1, 133.2, 133.2, 133.3, 133.5, 133.6, 133.6, 133.7, 165.5, 165.5, 165.5, 165.7, 165.9, 165.9, 166.2; HRMS (ESI-MS):m/z calcd for $[C_{62}H_{52}O_{18}Na^+]$: 1107.3051; Found: 1107.3049.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-*deoxy*-2-(((2,2,2-trichloroethoxy)carbonyl)amino)-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl) α-D-glucopyranoside (**36**): Eluent for purification: 25% ethyl acetate in *n*-hexane; white solid; yield 72 mg (90%); mp 78 $^oC$; $[\alpha]_D^{25}$ +41.3(*c* 1.0,

$CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3293, 3021, 2932, 1729, 1604; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 1.90 (s, 3H), 1.97 (s, 3H), 1.99 (s, 3H), 3.32 (s, 3H), 3.45 – 3.61 (m, 3H), 3.66 (dd, *J* = 10.8, 2.6 Hz, 2H), 3.75 – 3.92 (m, 4H), 4.10 (dd, *J* = 12.3, 4.2 Hz, 1H), 4.18 (d, *J* = 8.3 Hz, 1H), 4.31 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 3.3 Hz, 1H), 4.57 (s, 1H), 4.60 (s, 1H), 4.68 (s, 1H), 4.72 – 4.75 (m, 1H), 4.77 (d, *J* = 4.9 Hz, 1H), 4.83 (s, 1H), 4.86 (d, *J* = 6.3 Hz, 1H), 4.91 (d, *J* = 9.6 Hz, 1H), 4.97 (d, *J* = 11.5 Hz, 1H), 7.18 – 7.35 (m, 11H), 7.39 – 7.44 (m, 2H), 7.46 – 7.50 (m, 2H), 7.53 (d, *J* = 2.1 Hz, 1H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 20.8, 20.8, 20.8, 55.4, 56.3, 61.9, 67.3, 68.7, 69.2, 71.3, 72.5, 73.6, 73.8, 74.5, 75.3, 77.2, 78.7, 80.3, 95.7, 98.5, 100.8, 127.2, 127.2, 127.9, 128.2, 128.2, 128.3, 128.3, 128.5, 128.5, 128.6, 129.2, 129.2, 129.3, 129.6, 129.6, 137.5, 138.3, 139.7, 154.0, 169.6, 170.5, 170.8; HRMS (ESI-MS): m/z calcd for $[C_{43}H_{50}Cl_3NO_{15}Na]^+$: 948.2144; Found: 948.2139.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl α-D-mannopyranosyl)-α-D-glucopyranoside (**37**): Eluent for purification: 20% ethyl acetate in *n*-hexane; syrup; yield 71 mg (92%); $[\alpha]_D^{25}$ +18.5 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$):3030, 2921, 2864, 1732; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 3.40 (d, *J* = 5.2 Hz, 3H), 3.44 (s, 3H), 3.56 – 3.72 (m, 3H), 3.76 (d, *J* = 10.5 Hz, 1H), 3.89 (td, *J* = 12.4, 10.6, 6.5 Hz, 2H), 3.96 (d, *J* = 9.6 Hz,1H), 4.11 (t, *J* = 9.1, 9.1 Hz, 1H), 4.31 (d, *J* = 12.3 Hz, 1H), 4.38 – 4.50 (m, 2H), 4.50 – 4.61 (m, 4H), 4.64 (d, *J* = 11.1 Hz, 2H), 4.73 (d, *J* = 12.2 Hz, 1H), 4.78 – 5.03 (m, 5H), 5.01 – 5.78 (m, 2H), 7.11 – 7.49 (m, 35H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 55.3, 69.4, 69.8, 72.1, 72.3, 73.0, 73.2, 73.3, 74.9, 75.0, 75.0, 75.1, 76.3, 77.1, 77.8, 79.8, 80.0, 81.6, 97.7, 100.6, 126.8 (2C), 127.2 (2C), 127.5 (2C), 127.6 (2C), 127.7 (4C), 127.8 (2C), 128.7 (3C), 128.1 (2C), 128.2 (2C), 128.3 (8C), 128.4 (2C), 128.4 (2C), 128.5 (2C), 137.9, 138.4, 138.4, 138.6, 138.6, 138.7, 138.9; HRMS (ESI-MS): m/z calcd for $[C_{62}H_{66}O_{11}Na^+]$: 1009.4503; Found: 1009.4508.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl α,β-D-mannopyranosyl)-α-D-glucopyranoside (**38**): Eluent for purification: 20% ethyl acetate in *n*-hexane; amorphous solid; yield 74 mg (95%); mp 63 $^{o}$C; $[\alpha]_D^{25}$ +52.2 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 2944, 1733; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.44 (d, *J* = 22.8 Hz, 6H), 3.56 (ddd, *J* = 18.6, 10.3, 2.8 Hz, 4H), 3.61 – 3.94 (m, 11H), 4.01 (t, *J* = 9.3 Hz, 2H), 4.32 – 4.54 (m, 6H), 4.54 – 4.70 (m, 11H), 4.71 – 5.13 (m, 4H), 5.21 – 5.34 (m, 2H), 5.58 (s, 2H), 6.19 (s, 2H), 7.16 – 7.45 (m, 54H), 7.48 – 7.57 (m, 4H), 7.84 – 7.93 (m, 4H), 7.95 – 8.07 (m, 8H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 55.6, 55.7, 66.7, 68.3, 68.6, 68.7, 68.9, 69.1, 69.7, 70.0, 70.3, 70.6, 70.7, 72.2, 72.3, 73.2, 73.5, 73.5, 74.9, 75.0, 75.1, 75.6, 75.8, 77.4, 77.6, 77.7, 80.0, 81.8, 82.4, 84.6, 96.8, 96.9, 97.3, 104.1, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.8, 127.9, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.1, 128.1, 128.1, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 129.0, 129.1, 129.1, 129.2, 129.3, 129.7, 129.7, 129.7, 129.8, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 133.1, 133.2, 133.4, 133.4, 133.4, 133.5, 138.0, 138.1, 138.2, 138.5, 138.5, 138.6, 138.7, 138.9, 165.3, 165.5, 165.8, 165.9, 165.9, 165.9; HRMS (ESI-MS): m/z calcd for $[C_{62}H_{60}O_{14}Na^+]$: 1051.3881; Found: 1051.3880.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-*deoxy*-2-(((2,2,2-trichloroethoxy)carbonyl)amino)-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl) α-D-glucopyranoside (**39**): Eluent for purification: 25% ethyl acetate in *n*-hexane; amorphous solid; yield 80 mg (90%); mp 97 $^{o}$C; $[\alpha]_D^{25}$ +41.3 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3293, 3021, 2932, 1729, 1604; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 2.00 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 3.44 (s, 3H), 3.56 – 3.70 (m, 3H), 3.81 (dt, *J* = 10.8, 8.5 Hz, 1H), 4.03 – 4.27 (m, 4H), 4.54 (d, *J* = 8.5 Hz, 1H), 4.62 – 4.83 (m, 2H), 5.06 (t, *J* = 9.6 Hz, 1H), 5.15 – 5.31 (m, 3H), 5.55 (t, *J* = 9.7 Hz, 1H), 5.72 (d, *J* = 8.8

Hz, 1H), 6.13 (t, *J* = 9.8 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.36 (dt, *J* = 10.2, 7.5 Hz, 4H), 7.50 (dt, *J* = 13.8, 7.4 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.91 – 7.99 (m, 4H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 20.7, 20.8, 20.8, 55.8, 56.2, 62.0, 68.0, 68.5, 68.6, 69.3, 70.4, 71.9, 72.0, 72.6, 74.6, 95.7, 97.1, 101.5, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.7, 129.1, 129.2, 129.7, 129.7, 130.0, 130.0, 130.0, 130.0, 133.2, 133.5, 133.8, 154.5, 165.7, 165.8, 165.9, 169.5, 170.7, 170.8; HRMS (ESI-MS): m/z calcd for $[C_{43}H_{44}Cl_3NO_{18}Na]^+$: 990.1522; Found: 990.1525.

Methyl 3-*O*-allyl-α-D-mannopyranoside (**41**): Eluent for purification: 5% MeOH in $CHCl_3$; syrup; yield 2.4 g (40%); $[\alpha]_D^{25}$ +76.4 (*c* 1.0, MeOH); IR(cm$^{-1}$, MeOH): 3589(b), 3034, 2912; $^1$H NMR (399.78 MHz, $CD_3OD$): δ 3.40 (s, 3H), 3.47 – 3.57 (m, 2H), 3.67 – 3.78 (m, 2H), 3.85 (dd, *J* = 11.8, 2.4 Hz, 1H), 3.97 (dd, *J* = 3.3, 1.8 Hz, 1H), 4.09 – 4.31 (m, 2H), 4.68 (d, *J* = 1.9 Hz, 1H), 4.85 (s, 3H), 5.18 (dq, *J* = 10.4, 1.4 Hz, 1H), 5.34 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.90 – 6.20 (m, 1H); $^{13}$C NMR (100.67 MHz, $CD_3OD$): δ 55.2, 62.8, 67.4, 68.8, 71.7, 74.4, 80.0, 102.5, 117.3, 136.5; HRMS (ESI-MS): m/z calcd for $[C_{10}H_{18}O_6Na]^+$: 257.1001; Found: 257.1001

Methyl 3-*O*-allyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside (**42**): Eluent for purification: 40% ethyl acetate in *n*-hexane; syrup; yield 3.7 g (78%); $[\alpha]_D^{25}$ +31.7 (*c* 1.0, $CHCl_3$); IR(cm$^{-1}$, $CHCl_3$): 3570(b), 3034, 2912, 1632; $^1$H NMR (399.78MHz, $CDCl_3$): δ 1.07 (s, 9H), 2.58 – 2.68 (m, 1H), 2.99 (s, 1H), 3.33 (s, 3H), 3.61 (dd, *J* = 9.1, 3.4 Hz, 1H), 3.68 (dt, *J* = 9.8, 5.0 Hz, 1H), 3.84 – 4.02 (m, 4H), 4.16 (dd, *J* = 10.0, 6.4 Hz, 2H), 4.74 (s, 1H), 5.12 – 5.25 (m, 1H), 5.26 – 5.38 (m, 1H), 5.88 – 6.03 (m, 1H), 7.40 (t, *J* = 8.2 Hz, 6H), 7.67 – 7.76 (m, 4H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 19.3, 26.9, 26.9, 26.9, 54.8, 65.1, 67.7, 68.5, 70.9, 71.3, 79.1, 100.4, 117.9, 127.8 (8C), 129.8, 133.0, 133.1, 134.5, 135.7; HRMS (ESI-MS): m/z calcd for $[C_{26}H_{36}O_6SiNa]^+$: 495.2179; Found: 495.2185.

Methyl 2,4-Di-*O*-benzyl-3-*O*-allyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside (**43**): Eluent for purification: 10% ethyl acetate in *n*-hexane; syrup; yield 3.9 g (81%); $[\alpha]_D^{25}$ +12.4 (*c* 1.0, $CHCl_3$); IR ($cm^{-1}$, $CHCl_3$): 3034, 2912, 1640; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 1.06 (s, 9H), 3.30 (s, 3H), 3.65 (d, *J* = 14.2 Hz, 1H), 3.73 – 3.85 (m, 2H), 3.88 – 4.03 (m, 3H), 4.11 (d, *J* = 6.8 Hz, 2H), 4.55 (d, *J* = 10.8 Hz, 1H), 4.66 – 4.78 (m, 2H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 5.16 (d, *J* = 11.8 Hz, 1H), 5.31 (d, *J* = 19.0 Hz, 1H), 5.94 (d, *J* = 27.7 Hz, 1H), 7.11 – 7.29 (m, 4H), 7.31 – 7.44 (m, 10H), 7.73 (dd, *J* = 15.1, 7.3 Hz, 6H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 19.7, 27.0, 27.2, 27.2, 54.9, 63.8, 71.6, 73.1, 73.4, 75.2, 75.5, 75.6, 80.4, 99.2, 117.1, 127.9 (2C), 128.0 (2C), 128.0, 128.1 (2C), 128.1, 128.4 (4C), 128.7, 129.9 (2C), 130.1, 133.9, 134.3, 135.2, 135.5, 135.6, 136.1, 136.3, 139.0, 139.0; HRMS (ESI-MS): m/z calcd for $[C_{40}H_{48}O_6SiNa]^+$: 675.3118; Found: 675.3131.

Methyl 2,4-Di-*O*-benzyl-3-*O*-allyl-α-D-mannopyranoside (**44**): Eluent for purification: 25% ethyl acetate in *n*-hexane; syrup; yield 1.8 g (81%); $[\alpha]_D^{25}$ +40.6 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3034, 2912, 1640; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 1.25 (s,1H), 3.29 (s, 3H), 3.60 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.72 – 3.86 (m, 4H), 3.93 (d, *J* = 9.3 Hz, 1H), 4.10 (d, *J* = 5.4 Hz, 2H), 4.60 – 4.74 (m, 3H), 4.80 (d, *J* = 12.4 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 5.18 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.27 – 5.38 (m, 1H), 5.84 – 6.01 (m, 1H), 7.24 – 7.42 (m, 10H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 54.8, 62.5, 71.2, 72.1, 73.1, 74.7, 74.9, 75.3, 80.0, 99.5, 116.8, 127.8 (2C), 128.0 (2C), 128.2 (2C), 128.5 (2C), 128.5 (2C), 135.0, 138.4, 138.6; HRMS (ESI-MS): m/z calcd for $[C_{24}H_{30}O_6Na]^+$: 437.1940; Found: 437.1925.

Methyl 2,4-di-*O*-benzyl-α-D-mannopyranoside (**45**): Eluent for purification: 45% ethyl acetate in *n*-hexane; syrup; yield 1.1 g (71%); $[\alpha]_D^{25}$ +30.4 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3581(b),3034, 2912; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 2.56 (d, *J* = 8.6 Hz, 2H), 3.27 (s, 3H), 3.41 – 3.90 (m, 5H), 3.97 (s, 1H), 4.48 – 4.76 (m, 4H), 4.87 (d, *J* = 11.2 Hz,

1H), 7.31 (d, *J* = 6.9 Hz, 10H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 54.8, 62.1, 71.4, 71.7, 73.1, 74.8, 76.3, 78.4, 98.3, 127.7, 127.8 (2C), 127.9 (2C), 128.0, 128.4 (2C), 128.5 (2C), 137.7, 138.4.; HRMS (ESI-MS): m/z calcd for $[C_{21}H_{26}O_6Na]^+$: 397.1627; Found: 397.1620.

1*H*-benzo[*d*][1,2,3]triazol-1-yl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**47**): Eluent for purification: 20% ethyl acetate in *n*-hexane; syrup; yield 840 mg (73%); $[\alpha]_D^{25}$ +17.1 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3034, 2912, 1730; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.79 (dd, *J* = 11.1, 1.7 Hz, 1H), 3.96 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.21 – 4.36 (m, 2H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.63 (dd, *J* = 11.4, 7.0 Hz, 3H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.90 (dd, *J* = 21.1, 11.2 Hz, 2H), 5.82 – 5.91 (m, 1H), 6.01 – 6.14 (m, 1H), 7.21 – 7.46 (m, 19H), 7.59 (ddd, *J* = 10.1, 8.7, 4.7 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 1H), 8.05 – 8.10 (m, 2H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 67.5, 68.6, 72.3, 73.6, 73.7, 74.5, 75.4, 77.5, 104.9, 108.6, 120.5, 124.9, 127.6, 127.7, 127.7, 127.7, 127.9, 128.0, 128.1, 128.1, 128.2, 128.2, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.7, 128.7, 129.3, 130.2, 130.2, 133.7, 137.7, 138.2, 138.3, 143.6, 165.6; HRMS (ESI-MS): m/z calcd for $[C_{40}H_{37}N_3O_7Na^+]$: 694.2529; Found: 694.2529.

Methyl 2,4-di-*O*-benzyl-3,6-di-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**48**): Eluent for purification: 20% ethyl acetate in *n*-hexane; syrup; yield 950 mg (95%); $[\alpha]_D^{25}$ +5.5 (*c* 1.0, $CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3293, 3071, 2974, 1723; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 3.21 (s, 3H), 3.65 – 3.68 (m, 2H), 3.70 (d, *J* = 3.2 Hz, 1H), 3.75 (s, 1H), 3.83 (d, *J* = 4.6 Hz, 2H), 3.88 – 3.93 (m, 1H), 4.02 (d, *J* = 7.1 Hz, 2H), 4.09 (d, *J* = 8.5 Hz, 2H), 4.17 (dd, *J* = 9.4, 2.9 Hz, 2H), 4.46 (s, 1H), 4.49 (t, *J* = 3.2 Hz, 3H), 4.51 (s, 1H), 4.52 (s, 2H), 4.56 (s, 1H), 4.64 – 4.69 (m, 5H), 4.71 (d, *J* = 4.2 Hz, 1H), 4.73 (d, *J* = 1.9 Hz, 1H), 4.75 – 4.82 (m, 2H), 4.85 – 4.92 (m, 3H), 5.09 (d, *J* = 1.8 Hz, 1H), 5.33 (d, *J* = 1.6 Hz, 1H), 5.73 (t, *J* = 2.1 Hz, 1H), 5.74 – 5.77 (m, 1H), 7.17 (m, 8H),

7.20 (m, 7H), 7.26 (m, 15H), 7.30 (m, 2H), 7.32 – 7.37 (m, 10H), 7.54 (m, 3H), 8.05 (m, 5H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 54.9, 66.6, 68.8, 68.8, 69.1, 69.2, 69.5, 71.1, 71.2, 71.7, 71.7, 71.8, 72.5, 72.5, 73.5, 73.5, 73.6, 73.6, 74.3, 74.5, 75.2, 75.2, 75.3, 75.3, 78.3, 78.7, 98.3, 98.3, 99.8, 127.5, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 127.8, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.0, 128.1, 128.1, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 130.0, 130.1, 130.1, 130.1, 130.1, 130.1, 130.1, 130.1, 133.2, 133.2, 138.0, 138.0, 138.0, 138.3, 138.6, 138.6, 138.7, 138.8, 165.6, 165.7; HRMS (ESI-MS): m/z calcd for [$C_{89}H_{90}O_{18}Na^+$]:1469.6025; Found: 1469.6024.

Methyl 2,4-di-*O*-benzyl-3,6-di-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**49**): Eluent for purification: 35% ethyl acetate in *n*-hexane; syrup; yield 620 mg (95%); $[\alpha]_D^{25}$ +45.3 (*c* 1.0, $CHCl_3$); IR(cm$^{-1}$, $CHCl_3$): 3540(b), 3293, 3071, 2974, 1723; $^1$H NMR (399.78 MHz, $CDCl_3$): δ 1.83 (s, 1H), 2.44 (s, 1H), 3.17 – 3.28 (m, 3H), 3.54 – 4.04 (m, 16H), 4.08 – 4.18 (m, 2H), 4.43 – 4.72 (m, 15H), 4.84 (t, *J* = 10.7 Hz, 2H), 5.09 (s, 1H), 5.23 (s, 1H), 7.14 – 7.36 (m, 40H); $^{13}$C NMR (100.67 MHz, $CDCl_3$): δ 54.9, 66.2, 68.2, 68.8, 68.9, 69.5, 71.2, 71.5, 71.6, 72.0, 72.1, 72.4, 73.5, 73.6, 74.3, 74.5, 75.0, 75.0, 75.1, 75.2, 77.8, 79.1, 79.6, 80.2, 98.2, 99.8, 101.6, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 127.9, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.1, 128.1, 128.1, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 138.0, 138.0, 138.2, 138.3, 138.4, 138.4, 138.5, 138.6; HRMS (ESI-MS):m/z calcd for [$C_{75}H_{82}O_{18}Na^+$]:1261.5501; Found: 1261.5504.

Methyl 2,4-di-*O*-benzyl-3,6-di-*O*-(2-*O*-(2,3,4,6-tetra-*O*-benzoyl α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl α-D-mannopyranosyl)-α-D-mannopyranoside (**50**): Eluent for purification: 35% ethyl acetate in *n*-hexane; syrup; yield 1.2 g (71%); $[\alpha]_D^{25}$ - 1.5 (*c* 1.0,

$CHCl_3$); IR($cm^{-1}$, $CHCl_3$): 3293, 3071, 2974, 1723; $^1H$ NMR (399.78 MHz, $CDCl_3$): δ 3.24 (s, 3H), 3.56 – 3.73 (m, 5H), 3.73 – 3.87 (m, 3H), 3.91 (t, *J* = 9.6 Hz, 3H), 4.00 (t, *J* = 10.1 Hz, 5H), 4.13 (s, 2H), 4.28 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.37 – 4.45 (m, 3H), 4.51 (s, 2H), 4.55 (d, *J* = 4.9 Hz, 5H), 4.58 (d, *J* = 4.8 Hz, 2H), 4.61 (d, *J* = 5.5 Hz, 3H), 4.65 (d, *J* = 2.8 Hz, 2H), 4.66 – 4.75 (m, 2H), 4.79 (s, 1H), 4.92 (t, *J* = 10.6 Hz, 2H), 5.03 (s, 1H), 5.12 (s, 1H), 5.20 (s, 1H), 5.33 (s, 1H), 5.83 – 6.00 (m, 4H), 6.15 (dt, *J* = 25.4, 10.1 Hz, 2H), 6.89 – 7.04 (m, 5H), 7.10 (q, *J* = 7.5 Hz, 5H), 7.15 – 7.22 (m, 10H), 7.27 (ddd, *J* = 12.7, 6.3, 2.0 Hz, 25H), 7.34 – 7.48 (m, 15H), 7.52 – 7.63 (m, 4H), 7.81 – 7.90 (m, 8H), 8.04 (d, *J* = 8.0 Hz, 4H), 8.12 (d, *J* = 7.9 Hz, 4H); $^{13}C$ NMR (100.67 MHz, $CDCl_3$): δ 54.9, 62.7, 62.7, 66.4, 66.7, 66.9, 69.2, 69.3, 69.4, 69.6, 70.3, 70.3, 70.5, 70.6, 71.7, 71.8, 71.9, 72.2, 72.6, 72.7, 73.2, 73.4, 74.7, 74.8, 74.9, 74.9, 75.1, 75.4, 77.1, 77.4, 77.9, 78.7, 79.4, 79.7, 98.3, 99.5, 99.5, 99.8, 101.1, 127.1, 127.1, 127.1, 127.4, 127.4, 127.5, 127.5, 127.5, 127.5, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.7, 127.9, 127.9, 127.9, 128.0, 128.0, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 128.7, 128.7, 129.2, 129.2, 129.4, 129.5, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.1, 130.2, 133.0, 133.1, 133.1, 133.1, 133.4, 133.4, 133.4, 133.5, 138.2, 138.3, 138.3, 138.3, 138.5, 138.5, 138.7, 138.8, 165.2, 165.2, 165.4, 165.5, 165.5, 165.6, 166.2, 166.3; HRMS (ESI-MS): m/z calcd for $[C_{143}H_{134}O_{34}Na^+]$: 2418.8654; Found: 2418.8686.

Methyl 3,6-di-*O*-(2-*O*-α-D-mannopyranosyl)-α-D-mannopyranosyl-α-D-mannopyranoside (**51**): Purified by BIO-RAD Bio-Gel P-4 Gel using distilled water as eluent; syrup; yield 320 mg (80%); $[\alpha]_D^{25}$ +21.5 (*c* 1.0, $H_2O$); IR($cm^{-1}$, $H_2O$): 3590 (b), 3286, 3065, 2974; $^1H$ NMR (399.78 MHz, $D_2O$): δ 3.37 (s, 3H), 3.56 – 4.14 (m, 30H), 4.69 (s, 1H), 4.97 (d, *J* =

14.7 Hz, 1H), 4.99 (d, *J* = 14.7 Hz, 1H), 5.11 (s, 1H), 5.30 (s, 1H) [16 protons exchanged due to $D_2O$]; $^{13}C$ NMR (100.67 MHz, $D_2O$): δ 54.9, 60.9, 60.9, 61.1, 65.3, 65.6, 66.7, 66.8, 66.8, 66.9, 69.9, 69.5, 69.9, 70.1, 70.2, 70.3, 70.3, 70.8, 72.7, 73.2, 73.2, 73.2, 73.3, 78.4, 78.6, 78.8, 97.9, 100.8, 101.0, 102.3, 102.3; HRMS (ESI-MS): m/z calcd for $[C_{31}H_{54}O_{26}Na^+]$: 865.2801; Found: 865.2789.

**ACKNOWLEDGEMENTS**

MN and BM acknowledge the fellowship from CSIR-UGC-NET. SH thanks financial assistance from DST-SERB-New Delhi (SB-OC/CB-03/2014).

**SUPPORTING INFORMATION**

Copies of $^1H$, $^{13}C$ and DEPT NMR spectra, crystallographic data of compound **10**. This material is available free of charge via the Internet at http://pubs.acs.org

**Notes and references**

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**Nucleofuge Generating Glycosidation by the Remote Activation of Hydroxybenzotriazolyl Glycosides**

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