JOC The Journal of Organic Chemistry

Article

Gold(III)-Catalyzed Glycosylation using Phenylpropiolate Glycosides (PPGs): Phenylpropiolic Acid An Easily Separable and Reusable Leaving Group

Mukta Shaw, Rima Thakur, and Amit Kumar

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b02422 • Publication Date (Web): 20 Dec 2018

ACS Publications

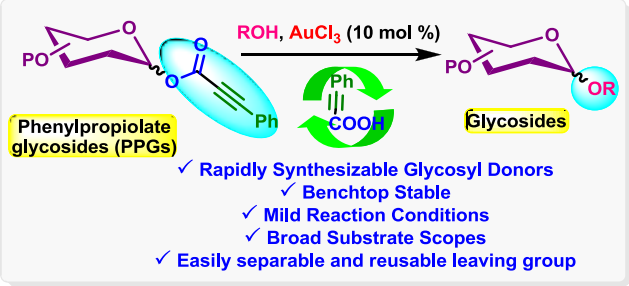
is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Gold(III)-Catalyzed Glycosylation using Phenylpropiolate Glycosides (PPGs): Phenylpropiolic Acid An Easily Separable and Reusable Leaving Group

Mukta Shaw,[†] Rima Thakur,*[,‡] and Amit Kumar*[,†]

[†]Department of Chemistry, Indian Institute of Technology Patna, Bihta 801106, Bihar, India, and

[‡]Department of Chemistry, National Institute of Technology Patna, Patna 800005, Bihar, India



ABSTRACT: An efficient and operationally simple gold(III)-catalyzed glycosylation protocol has been developed using newly synthesized benchtop stable phenylpropiolate glycosyl (PPG) donors. Gold(III)-catalyzed activation of PPGs proceeds well with various carbohydrate and non-carbohydrate based glycosyl acceptors and lead to their corresponding *O/N*-glycosides in good to excellent yields with regeneration of reusable and easily separable phenylpropiolic acid. Differentially protected PPGs reacted well under the optimized reaction conditions. In particular, good anomeric selectivity was observed with mannosyl and rhamnosyl PPG donors. A preliminary mechanistic study reveals that the presence of triple bond adjacent to the ester group is essential for the activation and PPG based donor shows higher reactivity than analogous acetate and benzoate donors.

INTRODUCTION

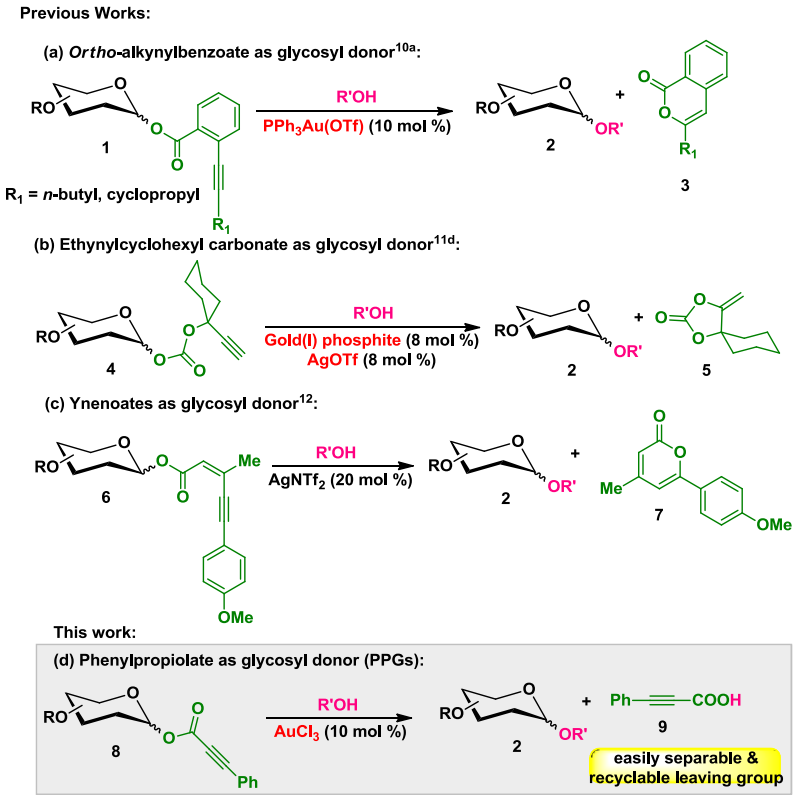
Carbohydrates are the most fundamental and abundant biomolecules present in the living system that play an important role in controlling the various biological processes, in particular at the cell surface for instance, cell-cell communication, cellular recognition, cell differentiation, *etc. via* the interaction of carbohydrate moiety with other biomolecules.[1] Besides their role in metabolism and as a structural source, carbohydrates are an indispensable source of new drugs and novel therapeutics.[2] Although nature extensively synthesizes oligosaccharides and glycoconjugates, it is their intrinsic heterogeneous nature which makes the quantitative isolation a formidably challenging task.[3] Therefore, chemical synthesis opens an alternate door for obtaining these precious complex compounds in the desired quantity.[4] Fully or partially protected saccharides bearing leaving group at the anomeric position - glycosyl donor – play a very important role in chemical glycosylation reactions. Some of the well-known glycosyl donors include glycosyl trichloroacetimidates,[5a,b] thioglycosides,[5c-e] glycals,[5f] glycosyl halides[5g,h] and others.[6] Nevertheless, these popular glycosyl donors frequently encounter drawbacks like low donor stability, require an equimolar amount of promoters, expensive and toxic metal catalysts, use of hazardous and foul-smelling reagents. In this regard, development of benchtop stable and efficient glycosyl donors bearing leaving group that may be rapidly introduced and can undergo effective glycosylation has been of significant interest to glycochemists.[7] Although acetate-based glycosyl donor was first introduced by Helferich *et al*. in 1933[8], this class of donor has not found extensive application owing to their high stability and requirement of the super-stoichiometric amount of promoter under harsh reaction conditions. To overcome these issues, in 1990 Kunz *et al.* has introduced bifunctional leaving group, for instance, glucosyl-4-pentenoates as glycosyl donor which could be easily activated under electrophilic conditions.[9] However, the

major breakthrough was achieved in 2008 by Yu group with the innovation of novel *ortho*-alkynylbenzoate as a bifunctional glycosyl donor to synthesize glycosides using gold(I) catalyst (Scheme 1a).[10] Afterward, Hotha and coworkers reported an elegant method for glycosylation using remote alkynyl carbonate glycoside as stable bifunctional glycosyl donor (Scheme 1b).[11] Very recently, Zhang *et al*. have disclosed glycosyl ynenoates as a very effective and stable bifunctional glycosyl donor, which could be activated under mild conditions using silver (I) salt as catalyst.[12] Unfortunately, the major disadvantages of these bifunctional ester based glycosyl donors are: (i) requirement of additional steps to get the desired coupling partners, (ii) the formation of lipophilic-byproducts (**3, 5** and **7,** Scheme 1) in a stoichiometric amount eventually increasing the challenge for purification of final products, and thus making it unsuitable for large-scale syntheses and industrial applications. In the view of these fundamental constraints, recently Jensen *et al*. have utilized the reusable glycosyl donor such as, *ortho*-methoxybenzoate for the glycosylation reactions, where the leaving group could be ideally recycled and reused after the reactions.[13]

Therefore, in the field of glycochemistry, it is a continuous demand to develop an efficient and versatile glycosyl donor, which can be directly prepared in *one-step* and may regenerate an easily separable and reusable leaving group. Guided by these facts, we anticipated that the bifunctional phenylpropiolate glycosides (PPG) **8** obtained *via* the coupling of lactols and commercially available phenylpropiolic acid could ideally serve as a stable and efficient glycosyl donor. The alkyne group present adjacent to the ester moiety in PPG could facilitate the site-control activation with soft Lewis acid, and that would result in a breaking of anomeric *C*-1-*O*-1 bond with the sole regeneration of phenylpropiolic acid and oxocarbenium ion. Further, the hydrophilic phenylpropiolic acid may be easily separated from the lipophilic product by simple

work-up procedure and eventually ease the purification process and could be potentially exploited for the large-scale synthesis.

Scheme 1. Bifunctional ester based glycosyl donors and their glycosidation

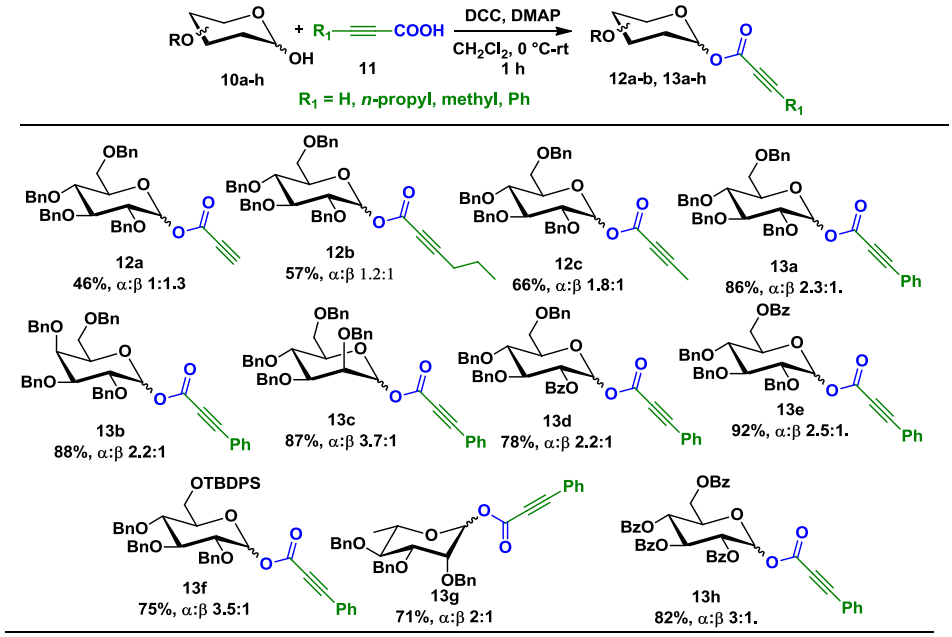


■ RESULTS AND DISCUSSION

With this understanding, a series of propiolate based glycosyl donors **12a-c** and **13a-h** were synthesized easily by coupling of various glycosyl hemiacetals (**10a-h**) and acids (*e.g.*, propiolic acid, 2-hexynoic acid, 2-butynoic acid, and phenylpropiolic acid) under Steglich esterification conditions (Scheme 2). The α:β ratios were estimated by ^{1}H NMR analysis of isolated products. All the synthesized PPG donors are stable at room temperature for months without any decomposition. Easy accessibility and high stability of phenylpropiolate glycosides and our own research interest in the development of a new synthetic route for glycoside bond formation,[14]

encouraged us to employ them for glycosylation reaction. Herein, we disclose our detailed studies with phenylpropiolate glycosides (PPGs) as an effective glycosyl donor.

Scheme 2. Synthesis of phenylpropiolate glycosyl (PPGs) donors

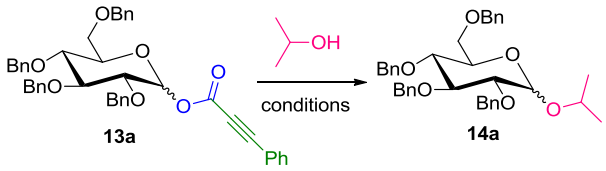


At the outset, a series of experiments were performed to optimize the reaction conditions using 2,3,4,6-tetra-*O*-benzyl-α/β-glucosyl phenylpropiolate **13a** as model glycosyl donor and isopropanol as model glycosyl acceptor with gold salt as the choice of catalyst, due to its high alkynophilicity and mild Lewis acid nature (table 1). Screening with different gold catalysts such as $Au(PPh_3)Cl$, $AuCl_3$, $AuBr_3$ at room temperature in dry CH_2Cl_2 failed to generate the corresponding glycosyl adduct, and a complex reaction mixture was observed on TLC plate under these conditions (entry 1-3). Interestingly, increasing the reaction temperature to 45 °C in the presence of 10 mol % of $AuCl_3$ afforded the desired glycoside **14a** in 92% isolated yield with expected selectivity (α:β 1:1.3) (entry 4). Addition of additive had no apparent impact on the reaction outcome (entry 5). A further decrease in the loading of the catalyst from 10 mol % to 5

mol % was futile, wherein the yield of the desired product decreased up to 68% (entry 6). Moreover, nature of the solvent plays a very critical role in the glycosylation reactions.[15] On identifying the suitable catalyst, the solvent was varied from CH_2Cl_2 to MeCN, DCE, and THF (entry 7-9) to improve the overall yield and selectivity of the product. However, we observed that none of these solvents gave better yield than CH_2Cl_2 (entry 4). A control experiment in the absence of gold salt yielded no product, and starting material remained intact (entry 10). Further, the glycosylation reaction was carried out in the inverse addition conditions; a solution of PPG donor was added to a previously stirred solution of acceptor and catalyst. However, there was no noteworthy effect on the yield and selectivity of produced glycoside (entry 11). Aware of the fact that hydrogen chloride (HCl), which is eventually generated *in situ* from the reaction of $AuCl_3$ and glycosyl acceptor, might be the real catalyst for the activation of PPG donor. Therefore, we conducted an additional experiment with 10 mol % of HCl in dioxane under similar reaction conditions (entry 12). Nevertheless, no desired product was observed even after 24 h (TLC analysis), and the PPG donor was completely intact (recovered through the column chromatography). From the above result, it appears that HCl did not have any role in this glycosylation reaction. Additionally, glycosylation reaction was further performed with 10 mol % of $HAuCl_4$. As expected, the desired product was obtained in 70% yield with moderate selectivity along with some hydrolyzed product (entry 13). Further, different metal salts were also investigated as a catalyst (entry 14-19), and among them, $Bi(OTf)_3$, $Sn(OTf)_2$, and $FeCl_3$ provided the corresponding glycoside **14a** in optimum yield, albeit under prolonged reaction time (12-24 h, entries 14, 16 and 19). Indeed, when the reaction was performed with Bronsted acid (TfOH, entry 20) glycosyl donor **13a** did not react at all even after stirring for 24 h. Furthermore, when the glycosylation reaction was performed with donors, **12a-c** under

established reaction conditions afforded the glycoside **14a** in somewhat lower yield (entry 21-23). After careful optimization of all reaction parameters, the donor **13a** and reaction conditions described in entry 4, Table 1, were selected as the standard conditions for further exploration. The merits of this developed glycosyl donors are: (i) direct synthesis of PPGs donor from the lactol under mild conditions, (ii) formation of hydrophilic phenylpropiolic acid as a reusable by-product, which can be easily separated from the reaction mixture, (iii) benchtop stable nature of glycosyl donor, and (iv) additive free glycosylation conditions.

Table1. Optimization of the reaction conditions[a]



entry	catalyst	temp (°C)	solvent	time (h)	yield[b]	α/β ratio[c]
1	$Au(PPh_3)Cl$	rt	CH_2Cl_2	24	n.d.[d]	-
2	$AuCl_3$	rt	CH_2Cl_2	24	n.d.[d]	-
3	$AuBr_3$	rt	CH_2Cl_2	24	n.d.[d]	-
4	**$AuCl_3$**	**45**	**CH_2Cl_2**	**1**	**92%**	**1:1.3**
5	$AuCl_3$[e]	45	CH_2Cl_2	1	88%	1:1
6	$AuCl_3$[f]	45	CH_2Cl_2	3	68%	1:1
7	$AuCl_3$	65	MeCN	2	54%	1:1.5
8	$AuCl_3$	45	DCE	2	30%	1:1
9	$AuCl_3$	45	THF	2	trace	-
10	-	45	CH_2Cl_2	24	n.r.[g]	-
11	$AuCl_3$	45	CH_2Cl_2	1	83%[h]	1.2:1
12	HCl[i]	45	CH_2Cl_2	24	n.r.[g]	-
13	$HAuCl_4$	45	CH_2Cl_2	16	70%	1.3:1
14	$Bi(OTf)_3$	45	CH_2Cl_2	12	62%	1.5:1
15	$Cu(OTf)_2$	45	CH_2Cl_2	24	n.r.[g]	-
16	$Sn(OTf)_2$	45	CH_2Cl_2	24	73%	1.7:1
17	AgOTf	45	CH_2Cl_2	24	n.r.[g]	-
18	$Yb(OTf)_3$	45	CH_2Cl_2	24	n.r.[g]	-
19	$FeCl_3$	45	CH_2Cl_2	24	58%	1:1.1
20	TfOH	45	CH_2Cl_2	24	n.r.[g]	-
21	$AuCl_3$[j]	45	CH_2Cl_2	1.5	70%	1.4:1

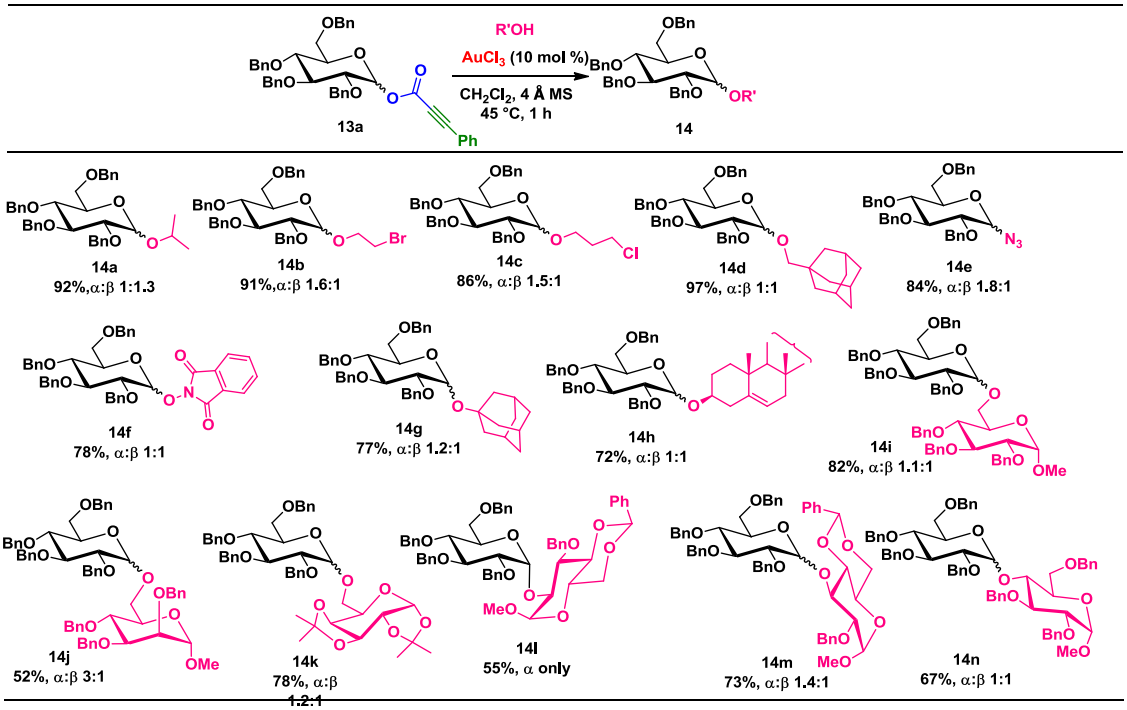
22	$AuCl_3$[k]	45	CH_2Cl_2	1	69%	1:1.3
23	$AuCl_3$[l]	45	CH_2Cl_2	1.5	78%	2:1

[a]Reaction conditions: **13a** (0.15 mmol), isopropanol (0.18 mmol), catalyst (10 mol %), 4 Å molecular sieves, solvent (3 mL) under nitrogen atmosphere. [b]Yield of the isolated product. [c]Anomeric ratio was determined by ^{1}H NMR spectroscopy. [d]n.d. - not determined. [e]10 mol % of AgOTf was used. [f]5 mol % of $AuCl_3$ was used. [g]n.r.- no reaction, starting material was intact. [h]Inverse addition condition. [i]HCl in dioxane was used. [j]**12a** was used as glycosyl donor. [k]**12b** was used as glycosyl donor. [l]**12c** was used as glycosyl donor.

Having optimal reaction conditions in hand, we then turned our attention to explore the scope of the phenylpropiolate glucosyl donor **13a** with various acceptors and results are tabulated in Scheme 3. Glycosylation of perbenzylated glucopyranosyl phenylpropiolate **13a** with halogen-containing primary alcohols such as 2-bromoethanol, 3-chloropropanol proceeded smoothly to give glycosides **14b** and **14c** in 91% and 86% yields respectively, with moderate α-selectivity. Reaction with bulky primary alcohol, for instance, 1-adamantanemethanol gave the corresponding glycoside **14d** in 97% yield. Off note, when the reaction was carried out with $TMSN_3$ under similar conditions, the glycosyl donor **13a** afforded the azidoglucoside **14e** in good yield (84%, α:β 1.8:1). Notably, on reaction with N-hydroxyphthalimide as acceptor also gave the corresponding glucoside **14f** in 78% yield. Similarly, other bulky acceptors such as 1-adamantanol, cholesterol reacted well to give **14g** and **14h** in reasonably good yields. Encouraged with these results, phenylpropiolate glucoside **13a** was further reacted with sugar-based acceptors containing 6-OH group and afforded the corresponding disaccharides **14i-k** in high yields with expected selectivity. Similarly, glycosylation with demanding acceptors having an unprotected hydroxyl group at 2-,3-,4-positions were also fruitful and gave the desired disaccharides **14l-n** in expected yields (up to 73%). However, to our surprise, in the case of 2-

hydroxy sugar acceptor**,** complete α-selectivity was observed, which might be contributed by the steric factor around the hydroxyl group.

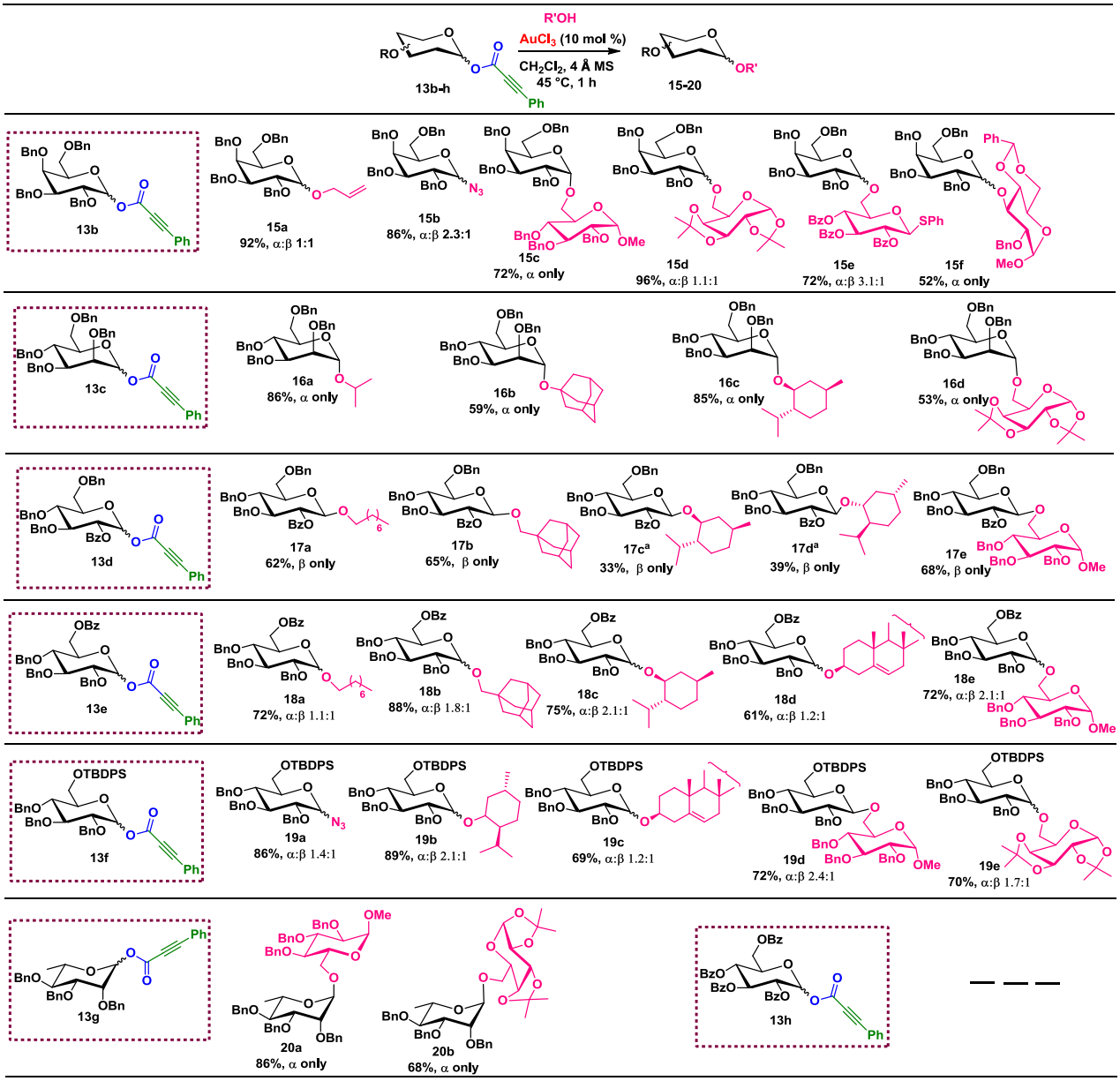
Scheme 3. $AuCl_3$ catalyzed glycosidation with glucosyl phenylpropiolate **13a** and various acceptors



Having success with perbenzylated glucopyranosyl phenylpropiolate **13a**, the scope of other glycosyl donors (**13b-h)** were also investigated with various acceptors (Scheme 4). Glycosylation of perbenzylated galactopyranosyl phenylpropiolate **13b** with a variety of glycosyl acceptors under the optimized reaction conditions gave their corresponding galactosides **15a-f** respectively in good to excellent yields. Indeed, we observed that galactosyl donor **13b** reacted much faster than the glucosyl donor **13a** under similar conditions. Noteworthy, nucleophile like allyl alcohol, which contains an additional alkene moiety, was also compatible under stabilized reaction conditions. Interestingly, when thioglucopyranoside containing free 6-OH group was

treated with donor **13b** under gold catalysis conditions, the corresponding glycoside **15e** was isolated in good yield (72%, α:β 3.1:1), and there was no evidence of thioglycoside activation, which was a primary concern.[16] This result demonstrates the orthogonality aspect of developed glycosyl donor. In addition, mannopyranosyl phenylpropiolate donor **13c** was also reacted smoothly with different acceptors such as isopropanol, adamantanol, (+)-menthol and acceptor containing 6-OH group under the optimized reaction conditions to afford the desired mannosides in good yields with excellent α-selectivity (**16a-d**).

Scheme 4. Substrate Scope



[a]Reaction time 2 h

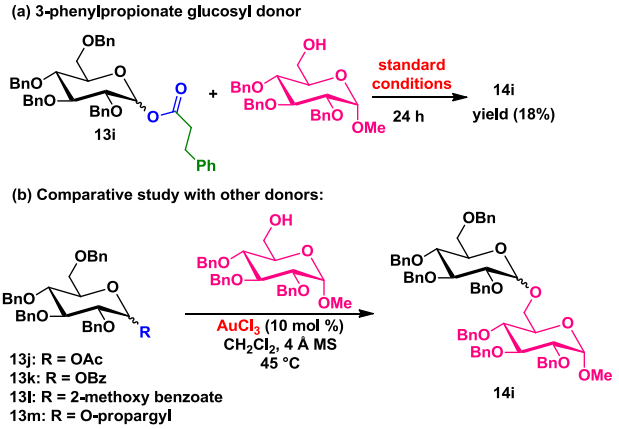
Furthermore, the glycosylation reaction was carried out with the donor containing the participating group such as 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13d** in the presence of several acceptors**.** The reaction with challenging acceptors, for instance, (+)-menthol, and (-)-menthol required longer reaction time to get the corresponding glucosides **17c** and **17d** in moderate yields along with some starting materials. Similarly, the glycosylation was further investigated with 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α/β-D-

glucopyranosylphenylpropiolate **13e** and 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α/β-D-glucopyranosyl phenylpropiolate **13f** containing bulky -*TBDPS* protecting group at 6-position**.** All the glycosylation reactions proceeded smoothly to provide the desired products (**18a-e** and **19a-e**) in good yields with marginal α-selectivity. Likewise, when the rhamnosyl donor **13g** was subjected to the established reaction conditions, the corresponding rhamnosides **20a**, and **20b** were obtained in good yields (up to 86%) with excellent α-selectivity. Unfortunately, the glycosylation reaction was unsuccessful with disarmed donor tetra-*O*-benzoylated phenylpropiolate glucoside **13h** and TLC analysis revealed that multiple uncharacterized products were formed along with some starting material.

In order to understand the mechanistic aspect of the glycosylation reactions of synthesized PPGs donor, several control experiments were further carried out. Based on the outcome, we believe that the alkyne moiety plays a critical role in this glycosylation reaction. Thus, a controlled experiment was set up with 3-phenylpropionate glucosyl donor **13i** and 6-OH acceptor under similar reaction conditions (Scheme 5a). However, only a small amount of desired glycoside **14i** (18% yield) was isolated and rest starting material was recovered through the column chromatography. This result illustrates the importance of the alkyne group adjacent to the ester moiety in the PPG donor. Furthermore, we become interested to compare the reactivity pattern of our developed PPGs donor with other established ester based glycosyl donors (**13j-m**), for instance, glycosyl-1-*O*-acetate **13j**, glycosyl-1-*O*-benzoate **13k,** glycosyl-*O*-o-methoxybenzoate **13l**, and propargyl glycoside **13m** (Scheme 5b)**.** For example, when glycosyl-1-*O*-acetate **13j** and glycosyl-1-*O*-benzoate **13k** donors were separately subjected under optimized reaction conditions, the desired disaccharide **14i** was isolated in lower yields (42% and 19% respectively) along with some uncharacterized products. Indeed, glycosyl-*O*-o-methoxybenzoate **13l**, and

propargyl glycoside **13m** gave only a trace amount of desired product under the reported conditions. Also, the competitive experiment was carried out with glycosyl phenylpropiolate **13a** and glycosyl-1-*O*-acetate **13j** under standard conditions**.** ^{1}H NMR of crude reaction mixture reveals the disappearance of an anomeric proton (H-1) of PPG **13a** is much faster compared to the anomeric proton (H-1) of glycosyl-1-*O*-acetate **13j** (for details, see supporting information, Figure S1). These results apparently support our hypothesis and demonstrate the clear advantages of PPGs donor over the other glycosyl donors.

Scheme 5. Control Experiments



entry	donor	time (h)	yield
1	**13j**	24	42%
2	**13k**	24	19%
3	**13l**	24	trace
4	**13m**	24	trace

Likewise, the reactivity pattern of PPG donor was further understood from the detailed NMR experiments. For example, glycosyl donor **13a** was treated under similar conditions in CD_2Cl_2 to acquire ^{1}H NMR and ^{13}C NMR spectra for crude reaction mixture (Figure 1). The results showed the disappearance of an anomeric H-1β proton (δ 5.77) of **13a** and downfield shift of C-1 (δ 91.6 and 95.1 ppm to 94.6 and 102.0 ppm, respectively). Further ^{13}C NMR spectra reveal the

regeneration of phenylpropiolic acid (peak at δ 154.9 ppm, which corresponds to the carbonyl carbon of phenylpropiolic acid). These chemical shift values clearly demonstrate the formation of *O*-glycoside and regeneration of phenylpropiolic acid in the glycosylation reaction.

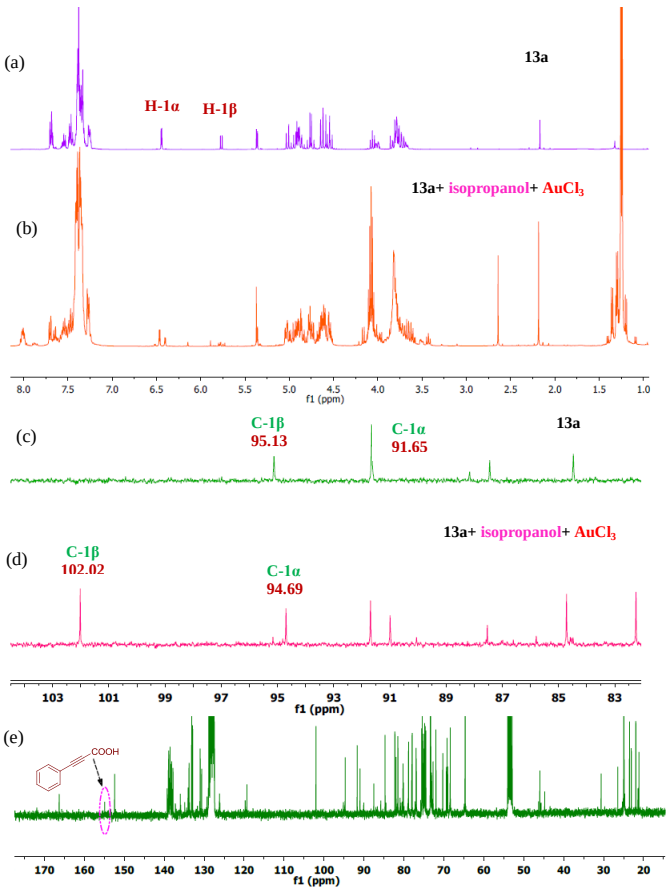
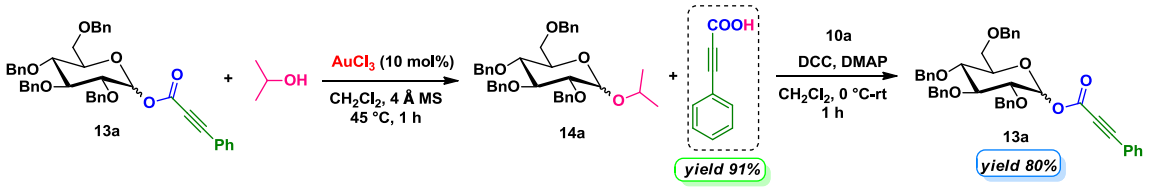


Figure 1. ^{1}H NMR spectra of (a) glycosyl donor **13a**, (b) reaction mixture of **13a**, isopropanol and 10 mol % of $AuCl_3$ at 45 °C after 30 min, and ^{13}C NMR spectra of (c) glycosyl donor **13a** (d) reaction mixture of **13a,** isopropanol and 10 mol % of $AuCl_3$ at 45 °C after 30 min in CD_2Cl_2. (e) Full ^{13}C NMR spectra of crude reaction mixture.

Aware of the fact that hydrophilic phenylpropiolic acid is regenerating during the glycosylation reaction, we became interested in demonstrating the reusability of phenylpropiolic acid. The reaction of glycosyl donor **13a** (200 mg, 0.3 mmol) was carried out with isopropanol under the

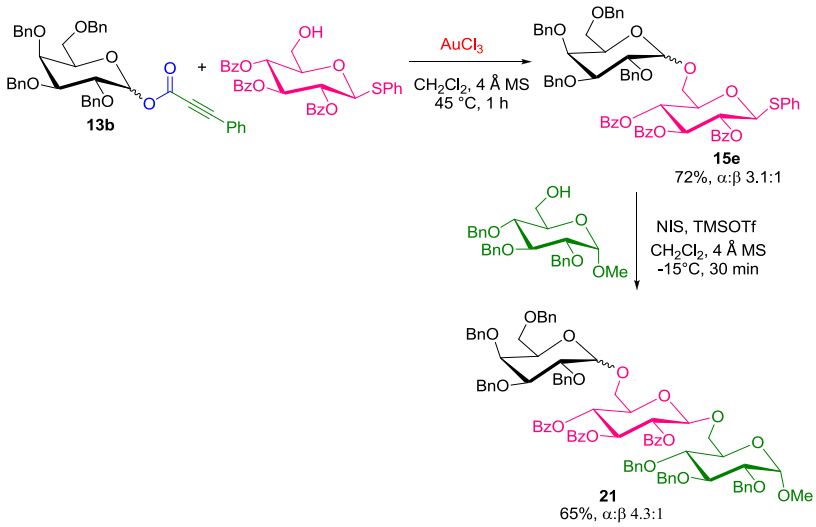
optimal reaction conditions **(**Scheme 6**)**. The reaction mixture was washed with a saturated aqueous solution of $NaHCO_3$, followed by acidification with 2 (M) HCl solutions to regenerate phenylpropiolic acid in 91% yield. Subsequently, the regenerated phenylpropiolic acid was coupled with glucosyl hemiacetal **10a** to produce the corresponding PPG donor **13a**.

Scheme 6. Regeneration of phenylpropiolic acid



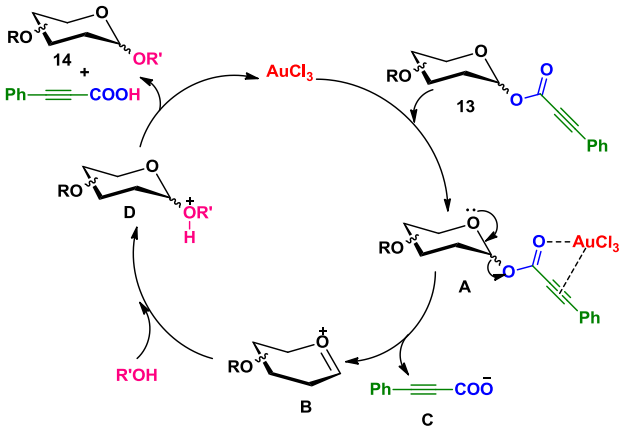
To demonstrate the application of the established donor in complex oligosaccharides synthesis, we next employed PPG donor for the synthesis of the trisaccharide **21** (Scheme 7). Treatment of 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl phenylpropiolate **13b** with 6-unprotected acceptor 2,3,4-tri-*O*-benzoyl-β-D-thioglucoside under the optimized reaction conditions afforded the disaccharide **15e** in 72% yield. Indeed, this result illustrates that PPG **13b** is orthogonal to the thioglycoside under our developed conditions. Further, compound **15e** was glycosylated with acceptor under previously established reaction condition to give trisaccharide **21** in 65% yield.[17]

Scheme 7. Application of PPG donor for the synthesis of a trisaccharide



Based on the aforementioned experimental results and literature precedents, a plausible reaction mechanism for Au(III) catalyzed activation of phenylpropiolate glycosyl (PPG) donor is given in Figure 2. At first, mild Lewis acid and alkynophilic $AuCl_3$ coordinates to both the carbonyl oxygen and alkyne bond of the glycosyl donor **13** to form a gold-alkyne complex **A**. Concomitantly, lone pair of electron from the endocyclic oxygen atom facilitates the expulsion of phenylpropiolate ion **C** from the complex **A** and generate the oxocarbenium ion **B**. Subsequently, species **B** react with glycosyl acceptor to give the corresponding glycoside **14** and release of proton further trapped by species **C** to regenerate the phenylpropiolic acid.

Figure 2. Anticipated mechanism for Au(III) catalyzed activation of phenylpropiolate glycosyl (PPG) donors



■ CONCLUSION

In conclusion, we have designed and developed phenylpropiolate glycosides (PPGs) as stable and effective glycosyl donor, which could be activated with gold(III) salt under mild conditions. Phenylpropiolate glycosyl (PPG) donors were reacted with a wide range of sugar and nonsugar acceptors to produce desired glycosides in good to excellent yields with expected selectivity. Some of the noteworthy features of the developed donors are a) formation of hydrophilic phenylpropiolic acid as reusable and easily separable leaving group, b) additive free catalytic system, c) direct synthesis of glycosyl donors, and d) long shelf life.

EXPERIMENTAL SECTION

General Methods.

All chemicals were purchased as reagent grade and used without further purification unless otherwise mentioned. Solvents were purified by standard procedures. All reactions were carried out under a nitrogen atmosphere with freshly distilled solvents unless otherwise mentioned.

Molecular sieves (4 Å) were flame dried before use. Reactions were monitored by analytical thin-layer chromatography 60 F_{254} silica gel, precoated on aluminum plates. TLC plates were visualized by spraying 10% H_2SO_4 in MeOH and heating until spots appeared or under UV light (254 nm). Column chromatography was performed using silica gel (100-200 mesh). Optical rotations were recorded on a digital polarimeter. IR spectra were recorded on an FT-IR spectrometer (UATR). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane or solvent residual signals (^{1}H NMR: solvent $CDCl_3$, δ = 7.26 ppm; CD_2Cl_2, δ = 5.30 ppm; $^{13}C\{^1H\}$ NMR: solvent $CDCl_3$, δ = 77.22 ppm; CD_2Cl_2, δ = 54.00 ppm). HRMS spectra were recorded on an ESI-mass spectrometer (Q-TOF, positive ion).

Experimental Procedures. General procedure for the synthesis glycosyl donors (A): An oven dried round bottom flask was charged with glycosyl hemiacetal (1.0 mmol) and acid coupling partner (propiolic acid or phenyl propiolic acid) (1.5 mmol) in dry CH_2Cl_2 (5 mL), and the mixture was stirred at 0 °C for 30 minutes. A solution containing the mixture of DCC (1.5 mmol) and DMAP (0.2 mmol) in dry CH_2Cl_2 (5 mL), was added to the reaction solution at 0 °C and the reaction mixture was bring to room temperature. The reaction mixture was stirred at room temperature until the completion of the reaction, monitored by TLC. After completion, the reaction mixture was diluted with CH_2Cl_2 and filtered through a pad of celite. The filtrate was concentrated in *vacuo* and purified by column chromatography (ethyl acetate-hexanes gradient elution) to afford the corresponding glycosyl donors.

*2,3,4,6-Tetra-O-benzyl-α/β-D-glucopyranosyl propiolate (**12a**).* The compound **12a** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose (540.6 mg, 0.6 mmol, 1.0 equiv) and propiolic acid (52 µL, 0.8 mmol, 1.5 equiv) following the general procedure **A** as

pale yellow liquid (151 mg, 46%, α/β 1:1.3). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v) , $[\alpha]_D^{28}$ = + 36.7 (c = 0.2, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3036, 2928, 2126, 1731, 1453, 1264, 1217; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.12 (m, 37.1H), 7.10 – 7.00 (m, 4.3H), 6.29 (d, J = 3.0 Hz, 0.8H), 5.57 (d, J = 7.8 Hz, 1.0H), 4.92 – 4.64 (m, 8.6H), 4.63 – 4.34 (m, 8.4H), 3.93 – 3.79 (m, 1.9H), 3.71 – 3.47 (m, 10.7H), 2.90 (s, 0.8H), 2.86 (s, 0.7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.1, 151.0, 138.6, 138.3, 138.0, 137.9, 137.8, 137.5, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 95.3, 92.0, 84.6, 81.5, 80.6, 78.7, 76.7, 76.2, 75.9, 75.8, 75.3, 75.2, 75.1, 74.3, 74.2, 73.6, 73.5, 73.3, 68.1, 67.9; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{36}O_7Na$ 615.2353; Found 615.2345.

*2,3,4,6-Tetra-O-benzyl-α/β-D-glucopyranosyl 2-hexynoate (**12b**).* The compound **12b** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose (1081.3 mg, 0.9 mmol, 1.0 equiv) and 2-hexynoic acid (157.0 µL, 1.4 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (328 mg, 57%, α/β 1.2:1). R_f: 0.39 (ethyl acetate/hexane 1:10 (v/v)), $[\alpha]_D^{28}$ = + 48.5 (c = 0.26, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3063, 3030, 2963, 2933, 2873, 2233, 2116, 1716, 1453, 1360, 1240, 1153; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 34.7H), 7.17 – 7.13 (m, 3.9H), 6.37 (d, J = 3.5 Hz, 1.0H), 5.66 (d, J = 8.0 Hz, 0.8H), 4.99 (d, J = 10.9 Hz, 1.1H), 4.94 – 4.60 (m, 11.2H), 4.57 – 4.44 (m, 4.1H), 4.05 – 3.90 (m, 2.3H), 3.80 – 3.56 (m, 10.8H), 2.37 – 2.29 (m, 4.7H), 1.68– 1.61 (m, 7.1H), 1.03 (t, J = 7.4 Hz, 7.3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.2, 152.0, 138.7, 138.4, 138.0, 137.9, 137.8, 137.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 95.0, 91.9, 91.3, 84.6, 81.6, 80.8, 78.8, 77.2, 76.9, 75.8, 75.7, 75.3, 75.1, 73.6, 73.5, 73.3, 73.0, 72.9, 68.2, 68.0, 21.0, 20.8, 20.7, 13.6, 13.5; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{42}O_7Na$ 657.2823; Found 657.2829.

*2,3,4,6-Tetra-O-benzyl-α/β-D-glucopyranosyl 2-butynoate (**12c**).* The compound **12c** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose (400.0 mg, 0.7 mmol, 1.0 equiv) and 2-butynoic acid (93.0 µL, 1.1 mmol, 1.5 equiv) following the general procedure **A** as colourless liquid (298 mg, 66%, α/β 1.8:1). R_f: 0.37 (ethyl acetate/hexane 1:10 (v/v)), $[\alpha]_D^{28}$ = + 38.4 (c = 0.20, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3064, 3030, 2925, 2868, 2243, 1719, 1496, 1452, 1358, 1246; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 26.4H), 7.16 – 7.13 (m, 2.9H), 6.35 (d, *J* = 3.4 Hz, 1.0H), 5.66 (d, *J* = 8.0 Hz, 0.5H), 4.98 (d, *J* = 10.9 Hz, 1.0H), 4.91 – 4.80 (m, 4.4H), 4.78 – 4.72 (m, 0.9H), 4.70 – 4.58 (m, 3.4H), 4.57 – 4.46 (m, 3.3H), 4.00 (t, *J* = 9.3 Hz, 1.1H), 3.93 (d, *J* = 10.0 Hz, 1.1H), 3.79 – 3.56 (m, 7.8H), 2.02 (s, 1.5H), 2.00 (s, 3.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.1, 152.0, 138.7, 138.4, 138.1, 138.0, 137.9, 137.8, 137.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 95.0, 91.3, 87.8, 87.3, 84.6, 81.6, 80.8, 78.7, 77.2, 76.8, 75.8, 75.7, 75.3, 75.1, 75.0, 73.6, 73.3, 73.1, 72.2, 72.0, 68.2, 68.0, 3.9; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{38}O_7Na$ 629.2510; Found 629.2496.

*2,3,4,6-Tetra-O-benzyl-α/β-D-glucopyranosyl phenylpropiolate (**13a**).* The compound **13a** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose (1081.3 mg, 2.0 mmol, 1.0 equiv) and phenylpropiolic acid (438.4 mg, 3.0 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (1150 mg, 86%, α/β 2.3:1). R_f : 0.37 (ethyl acetate/hexane 1:10 (v/v)), $[\alpha]_D^{28}$ = + 41.5 (c = 0.2, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3033, 2923, 2870, 2213, 1716, 1360, 1283; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2.9H), 7.53 (dd, *J* = 6.8, 4.9 Hz, 1.6H), 7.50 – 7.31 (m, 29.7H), 7.28 – 7.20 (m, 3.2H), 6.55 (d, *J* = 3.2 Hz, 1.0H), 5.85 (d, *J* = 7.8 Hz, 0.4H), 5.10 (d, *J* = 10.9 Hz, 1.0H), 5.05 – 4.86 (m, 4.6H), 4.84 – 4.67 (m, 3.4H), 4.66 – 4.55 (m, 2.7H), 4.20 – 4.07 (m, 2.0H), 3.96 – 3.81 (m, 4.9H), 3.80 – 3.70 (m,

1.9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.5, 152.3, 138.7, 138.4, 138.0, 137.9, 137.8, 137.5, 133.2, 131.0, 130.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 119.5, 119.3, 95.1, 91.6, 88.4, 87.9, 84.7, 81.6, 80.8, 80.3, 80.2, 78.8, 75.8, 75.4, 75.2, 75.1, 73.6, 73.4, 73.2, 68.1, 68.0; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{40}O_7Na$ 691.2672; Found 691.2686.

*2,3,4,6-Tetra-O-benzyl-α/β-D-galactopyranosyl phenylpropiolate (**13b**).* The compound **13b** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranose (540.65 mg, 1.0 mmol, 1.0 equiv) and phenylpropiolic acid (219.2 mg, 1.5 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (588 mg, 88%, α/β 2.2:1). R_f : 0.37 (ethyl acetate/hexane 1:10 (v/v), $[\alpha]_D^{28}$ = +48.13 (c = 0.3, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3036, 2923, 2873, 2216, 1713, 1456, 1356, 1280; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 6.7 Hz, 3.5H), 7.55 – 7.26 (m, 38.7H), 6.53 (d, J = 3.2 Hz, 1.0H), 5.77 (d, J = 7.5 Hz, 0.4H), 5.02 (d, J = 10.8 Hz, 1.6H), 4.93 – 4.73 (m, 6.5H), 4.72 – 4.42 (m, 6.1H), 4.32 – 4.02 (m, 6.1H), 3.94 – 3.56 (m, 4.8H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.7, 152.4, 138.7, 138.5, 138.2, 138.0, 137.8, 133.1, 130.8, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 119.6, 95.4, 92.6, 87.6, 82.3, 80.6, 78.7, 78.0, 75.5, 75.3, 75.0, 74.6, 73.6, 73.2, 73.0, 72.2, 68.3, 68.0; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{40}O_7Na$ 691.2672; Found 691.2674.

*2,3,4,6-Tetra-O-benzyl-α/β-D-mannopyranosyl phenylpropiolate (**13c**).* The compound **13c** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranose (1024 mg, 1.9 mmol, 1.0 equiv) and phenylpropiolic acid (415 mg, 2.8 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (1102.0 mg, 87%, α/β 3.7:1). R_f: 0.37 (ethyl acetate/hexane 1:10 (v/v)), $[\alpha]_D^{28}$ = -13.72 (c = 0.28, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3064, 3032, 2931, 2864, 2216, 1718, 1494, 1452, 1362, 1284; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 3.1H),

7.48 (t, *J* = 7.1 Hz, 2.4H), 7.45 – 7.25 (m, 27.5H), 7.22 – 7.14 (m, 3.0H), 6.33 (s, 1.0H), 5.73 (s, 0.3H), 4.96 – 4.86 (m, 1.9H), 4.83 – 4.72 (m, 2.2H), 4.70 – 4.54 (m, 7.3H), 4.14 (t, *J* = 9.6 Hz, 1.2H), 4.06 – 3.94 (m, 2.8H), 3.87 – 3.71 (m, 4.1H), 3.68 – 3.59 (m, 0.7H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.1, 152.0, 138.2, 137.7, 133.2, 133.1, 132.6, 131.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 119.3, 119.2, 94.1, 93.3, 81.9, 80.1, 79.2, 75.3, 75.1, 74.7, 74.2, 74.1, 73.5, 73.3, 73.1, 72.7, 72.3, 72.2, 69.0, 68.8; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{40}O_7Na$ 691.2672; Found 691.2674.

*2-O-Benzoyl-3,4,6-tri-O-benzyl-α/β-D-glucopyranosyl phenylpropiolate (**13d**).* The compound **13d** was obtained from the reaction between 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranose (554.6 mg, 1.0 mmol, 1.0 equiv) and phenylpropiolic acid (219.2 mg, 1.5 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (532 mg, 78%, α/β 2.2:1). R_f: 0.3 (ethyl acetate/hexane 1:10 (v/v), $[\alpha]_D^{28}$ = + 136.8 (c = 0.22, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3036, 2923, 2870, 2226, 1723, 1450, 1360, 1260; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.86 (m, 4.2H), 7.58 – 7.45 (m, 5.3H), 7.42 – 7.19 (m, 23.3H), 7.16 – 7.00 (m, 10.4H), 6.50 (d, *J* = 3.2 Hz, 1.0H), 5.85 (d, *J* = 8.1 Hz, 0.4H), 5.41 (t, *J* = 8.5 Hz, 0.4H), 5.35 – 5.29 (m, 0.7H), 5.22 (s, 0.7H), 4.89 – 4.68 (m, 4.4H), 4.63 – 4.42 (m, 5.8H), 4.20 (t, *J* = 7.9 Hz, 1.2H), 4.02 (d, *J* = 9.2 Hz, 1.1H), 3.90 – 3.61 (m, 5.8H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.5, 165.1, 152.3, 152.0, 138.0, 137.9, 137.8, 137.5, 133.7, 133.4, 133.3, 133.2, 131.0, 130.2, 130.0, 129.9, 129.8, 129.4, 129.3, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 119.3, 119.2, 93.0, 91.6, 88.2, 82.5, 79.9, 76.2, 75.7, 75.5, 75.2, 75.1, 73.6, 73.5, 72.3, 68.1, 67.9; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{38}O_8Na$ 705.2459; Found 705.2432.

*6-O-Benzoyl-2,3,4-tri-O-benzyl-α/β-D-glucopyranosyl phenylpropiolate (**13e**).* The compound **13e** was obtained from the reaction between 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α/β-D-

glucopyranose (538 mg, 0.97 mmol, 1.0 equiv) and phenylpropiolic acid (214 mg, 1.45 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (608 mg, 92%, α/β 2.5:1). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v), $[\alpha]_D^{28}$ = + 30.60 (c = 0.23, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3032, 2931, 2860, 2214, 1717, 1450, 1359, 1274; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4, 7.8 Hz, 2.9H), 7.64 (dd, J = 8.3, 1.3 Hz, 2.0H), 7.61 – 7.54 (m, 2.7H), 7.50 – 7.30 (m, 22.0H), 7.30 – 7.22 (m, 8.3H), 6.44 (d, J = 3.5 Hz, 1.0H), 5.80 (d, J = 7.9 Hz, 0.4H), 5.04 (d, J = 10.7 Hz, 1.0H), 4.98 – 4.69 (m, 6.5H), 4.66 – 4.47 (m, 4.8H), 4.22 – 4.10 (m, 2.2H), 3.86 – 3.71 (m, 4.2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 152.4, 152.1, 138.3, 138.1, 137.7, 137.5, 137.4, 133.2, 133.1, 130.9, 129.8, 129.7, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 119.4, 119.2, 95.0, 91.2, 88.1, 84.7, 81.6, 80.8, 80.3, 79.0, 76.0, 75.5, 75.3, 74.1, 73.5, 71.6, 63.0, 62.8; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{38}O_8Na$ 705.2459; Found 705.2445.

*2,3,4-Tri-O-benzyl-6-O-(tert-butyldiphenylsilyl)-α/β-D-glucopyranosyl phenylpropiolate (**13f**).* The compound **13f** was obtained from the reaction between 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α/β-D-glucopyranose (554.6 mg, 1.0 mmol, 1.0 equiv) and phenylpropiolic acid (219 mg, 1.5 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (613 mg, 75%, α/β 3.5:1). R_f: 0.40 (ethyl acetate/hexane 1:10 (v/v), $[\alpha]_D^{28}$ = + 34.10 (c = 0.26, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3073, 3030, 2930, 2863, 2220, 1720, 1450, 1360, 1280; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.44 (m, 10.0H), 7.37 – 7.06 (m, 40.3H), 6.39 (d, J = 3.0 Hz, 1.0H), 5.63 (d, J = 7.7 Hz, 0.3H), 5.14 (d, J = 3.9 Hz, 0.4H), 4.94 – 4.72 (m, 4.8H), 4.70 – 4.55 (m, 3.9H), 4.02 – 3.94 (m, 1.1H), 3.92 – 3.77 (m, 5.4H), 3.74 – 3.58 (m, 2.5H), 3.38 (d, J = 9.3 Hz, 0.3H), 0.95 (s, 14.1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.6, 152.3, 138.6, 138.3, 138.2, 138.0, 137.7, 136.0, 135.9, 135.7, 133.6, 133.2, 133.0, 132.7, 130.8, 129.8, 129.7, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 119.5, 95.4, 91.7, 87.7, 84.7, 81.7, 81.2, 80.4,

80.3, 79.4, 76.5, 76.0, 75.5, 75.3, 74.3, 73.6, 62.2, 32.8, 30.8, 26.9, 19.4; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{52}H_{52}O_7SiNa$ 839.3375; Found 839.3351.

*2,3,4,-Tri-O-benzyl-α/β-L-rhamnopyranosyl phenylpropiolate (**13g**).* The compound **13g** was obtained from the reaction between 2,3,4-tri-*O*-benzyl-α/β-D-rhamnopyranose (330 mg, 0.8 mmol, 1.0 equiv) and phenylpropiolic acid (166 mg, 1.1 mmol, 1.5 equiv) following the general procedure **A** as pale yellow liquid (320 mg, 71%, α/β 2:1). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v)), $[\alpha]_D^{28}$ = + 41.5 (c = 0.2, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3064, 3029, 2980, 2932, 2867, 2216, 1718, 1491, 1452, 1365, 1281; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 3.6H), 7.53 – 7.44 (m, 3.1H), 7.43 – 7.27 (m, 25.8H), 6.22 (s, 1.0H), 5.68 (s, 0.5H), 5.00 – 4.92 (m, 2.5H), 4.77 (d, *J* = 3.0 Hz, 1.9H), 4.69 – 4.56 (m, 4.8H), 4.04 – 3.82 (m, 4.0H), 3.73 – 3.66 (m, 1.7H), 3.59 (dd, *J* = 9.3, 2.6 Hz, 0.5H), 3.56 – 3.47 (m, 0.7H), 1.40 (dd, *J* = 11.5, 6.1 Hz, 4.9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.1, 152.0, 138.3, 138.2, 138.1, 138.0, 137.7, 133.2, 133.1, 132.7, 131.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 119.3, 119.2, 94.0, 93.3, 88.2, 87.7, 82.1, 80.1, 79.8, 79.6, 79.2, 75.6, 75.5, 74.3, 73.5, 73.3, 73.1, 72.8, 72.3, 72.2, 70.9, 18.1, 17.9; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{34}O_6Na$ 585.2248; Found 585.2258.

*2,3,4,6-Tetra-O-benzoyl-α/β-D-glucopyranosyl phenylpropiolate (**13h**).* The compound **13h** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzoyl-α/β-D-glucopyranose (596.5 mg, 1.0 mmol, 1.0 equiv) and phenylpropiolic acid (220.0 mg, 1.5 mmol, 1.5 equiv) following the general procedure **A** as yellow solid (595 mg, 82%, α/β 3:1). R_f: 0.30 (ethyl acetate/hexane 1:4 (v/v) , $[\alpha]_D^{28}$ = + 15.6 (c = 0.25, CH_2Cl_2); IR (cm^{-1}, CH_2Cl_2): 3068, 2961, 2215, 1728, 1602, 1450, 1261; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 2.9H), 7.99 – 7.93 (m, 4.8H), 7.88 (d, *J* = 7.5 Hz, 2.7H), 7.71 (d, *J* = 7.2 Hz, 2.0H), 7.57 – 7.50 (m, 5.2H), 7.43 (dd, *J* = 10.2,

4.5 Hz, 7.0H), 7.40 – 7.30 (m, 9.3H), 6.75 (d, *J* = 3.7 Hz, 1.0H), 6.30 – 6.23 (m, 1.3H), 5.96 (t, *J* = 9.4 Hz, 0.4H), 5.86 – 5.73 (m, 1.8H), 5.62 (dd, *J* = 10.3, 3.7 Hz, 1.0H), 4.69 – 4.63 (m, 2.1H), 4.54 – 4.46 (m, 1.6H), 4.40 – 4.33 (m, 0.4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 165.6, 165.4, 165.1, 164.9, 151.8, 151.7, 133.6, 133.5, 133.4, 133.3, 133.2, 131.2, 131.1, 130.0, 129.9, 129.8, 129.6, 129.5, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 119.1, 92.8, 90.7, 89.4, 89.2, 79.7, 73.4, 72.8, 70.7, 70.6, 70.2, 68.9, 68.7, 62.7, 62.4; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{32}O_{11}Na$ 747.1837; Found 747.1842.

*2,3,4,6-Tetra-O-benzyl-α/β-D-glucopyranosyl-3-phenylpropionate (**13i**).* The compound **13i** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose (596.5 mg, 1.0 mmol, 1.0 equiv) and 3-phenylpropionic acid (220.0 mg, 1.5 mmol, 1.5 equiv) following the general procedure **A** as colourless liquid (595 mg, 82%, α/β 3:1). R_f: 0.32 (ethyl acetate/hexane 1:10 (v/v) , $[\alpha]_D^{28}$ = + 28.3 (c = 0.21, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.17 (m, 36.1H), 6.42 (d, *J* = 3.4 Hz, 1.0H), 5.69 (d, *J* = 8.1 Hz, 0.3H), 5.02 – 4.48 (m, 12.3H), 3.94 (t, *J* = 8.7 Hz, 1.1H), 3.85 – 3.70 (m, 5.9H), 3.63 (t, *J* = 8.7 Hz, 1.9H), 3.04 – 2.95 (m, 2.9H), 2.83 – 2.55 (m, 3.1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4, 171.3, 140.2, 138.7, 138.4, 138.1, 137.9, 137.8, 137.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 126.4, 126.3, 94.2, 90.1, 84.8, 81.6, 78.9, 75.7, 75.6, 75.3, 75.0, 73.6, 73.2, 72.9, 68.1, 35.8, 35.8, 30.8, 30.5; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{44}O_7Na$ 695.2979; Found 695.2985.

*2,3,4,6-Tetra-O-benzyl-1-O-acetyl-α/β-D-glucopyranose (**13j**).*[9e] The compound **13j** was synthesized using literature reported procedure and obtained as colourless liquid (288 mg, 90%, α/β 3.2:1). R_f: 0.42 (ethyl acetate/hexane 1:4 (v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 22.9H), 7.18 – 7.13 (m, 2.7H), 6.36 (d, *J* = 3.5 Hz, 1.0H), 5.61 (d, *J* = 8.1 Hz, 0.3H), 4.97 (d, *J* = 10.9 Hz, 1.0H), 4.89 – 4.75 (m, 3.7H), 4.73 – 4.59 (m, 3.5H), 4.50 (t, *J* = 10.6 Hz, 2.9H),

3.94 (d, *J* = 9.3 Hz, 1.1H), 3.87 (d, *J* = 9.9 Hz, 1.1H), 3.77 – 3.55 (m, 6.4H), 2.14 (s, 3.0H), 2.06 (s, 0.9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.4, 169.3, 138.7, 138.4, 138.1, 137.9, 137.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 94.1, 90.0, 84.8, 81.7, 81.1, 78.9, 75.7, 75.5, 75.3, 75.0, 73.6, 73.2, 72.9, 68.2, 21.1, 21.0.

*2,3,4,6-Tetra-O-benzyl-1-O-benzoyl-α/β-D-glucopyranose (**13k**).*[18] The compound **13k** was synthesized using literature reported procedure and obtained as colourless liquid (356 mg, 75%, α/β 1:8.1). R_f: 0.4 (ethyl acetate/hexane 1:7 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.06 (m, 3.7H), 7.64 – 7.58 (m, 1.7H), 7.51 – 7.44 (m, 3.9H), 7.35 – 7.26 (m, 16.0H), 7.21 (s, 4.2H), 7.16 (dd, *J* = 7.1, 2.4 Hz, 2.4H), 6.62 (d, *J* = 3.5 Hz, 0.1H), 5.90 (dd, *J* = 5.7, 2.0 Hz, 1.0H), 4.96 – 4.73 (m, 6.4H), 4.65 – 7.47 (m, 4.1H), 3.87 – 3.73 (m, 6.2H), 3.71 – 3.64 (m, 1.4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.9, 138.4, 138.1, 137.9, 137.8, 133.7, 133.6, 130.2, 130.1, 129.3, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 94.7, 84.9, 80.9, 75.7, 75.6, 75.1, 75.0, 73.5, 68.1.

*2,3,4,6-Tetra-O-benzyl-1-O-(o-methoxybenzoyl)-α/β-D-glucopyranose (**13l**).*[13d] The compound **13l** was obtained from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose (596.5 mg, 1.0 mmol, 1.0 equiv) and 2-methoxybenzoic acid (220.0 mg, 1.5 mmol, 1.5 equiv) following the general procedure **A** as colourless liquid (595 mg, 82%, α/β 3:1). R_f : 0.30 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (ddd, *J* = 5.9, 3.9, 1.4 Hz, 2.1H), 7.55 – 7.47 (m, 2.8H), 7.39 – 7.22 (m, 41.5H), 7.21 – 7.16 (m, 4.2H), 7.03 – 6.92 (m, 5.5H), 6.62 (d, *J* = 3.4 Hz, 1.0H), 5.89 (d, *J* = 7.6 Hz, 0.8H), 5.00 – 4.75 (m, 10.4H), 4.71 – 4.46 (m, 8.7H), 4.09 – 3.99 (m, 2.4H), 3.89 (d, *J* = 4.0 Hz, 8.9H), 3.84 – 3.73 (m, 8.9H), 3.71 – 3.64 (m, 2.5H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.4, 164.0, 159.9, 159.7, 138.7, 138.5, 138.3, 138.1, 138.0, 137.9, 137.8, 134.3, 134.1, 132.3, 132.2, 130.7, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8,

127.7, 127.6, 121.1, 120.2, 112.1, 111.0, 94.4, 90.3, 84.9, 81.8, 81.1, 79.0, 75.6, 75.2, 75.0, 74.9, 73.6, 73.5, 73.1, 72.9, 68.2, 55.8, 55.7.

*Propargyl 2,3,4,6-tetra-O-benzyl-α/β-glucopyranoside (**13m**).*[11a] The compound **13m** was synthesized using literature reported procedure and obtained as pale yellow solid (520 mg, 82%, α/β 3.2.1). R_f: 0.37 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.22 (m, 26.1H), 7.20 – 7.12 (m, 3.1H), 5.11 (d, J = 3.5 Hz, 1.0H), 5.04 – 4.92 (m, 2.1H), 4.89 – 4.43 (m, 11.8H), 4.29 (d, J = 1.5 Hz, 2.9H), 4.18 – 4.11 (m, 0.4H), 4.02 (t, J = 9.3 Hz, 1.1H), 3.83 – 3.60 (m, 7.2H), 3.51 (t, J = 8.1 Hz, 1.0H), 2.51 – 2.43 (m, 1.7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 138.4, 138.3, 138.1, 138.0, 137.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 101.5, 95.3, 84.6, 82.0, 81.9, 79.4, 79.1, 79.0, 77.7, 77.5, 75.8, 75.7, 75.1, 75.0, 74.9, 74.8, 73.5, 73.0, 70.8, 68.8, 68.4, 56.0, 54.4.

General procedure for glycosylation reaction (B). To a suspension of glycosyl donor (0.15 mmol), glycosyl acceptor (0.18 mmol, 1.2 equiv) and 4 Å MS (200 mg) in dry CH_2Cl_2 (3 mL) was added 10 mol % of $AuCl_3$ at room temperature. The reaction mixture was stirred at 45 °C until the completion of the reaction, monitored by TLC. After completion of the reaction, the mixture was diluted with CH_2Cl_2 and washed thrice with a cold saturated aqueous solution of $NaHCO_3$. The combined organic phase was washed with brine solution, dried over anhydrous Na_2SO_4, evaporated in *vacuo* and purified by column chromatography (using different fractions of ethyl acetate in hexane as eluting solvent) to afford the desired glycosides.

*Isopropyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranoside (**14a**).*[14a] The product **14a** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1.0 equiv) and isopropanol (14 µL, 0.18 mmol, 1.2 equiv) following the

general procedure **B** as colourless semisolid (80 mg, 92%, α/β 1:1.3). R_f : 0.39 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 31.3H), 7.20 – 7.12 (m, 3.4H), 5.03 – 4.86 (m, 3.4H), 4.85 – 4.52 (m, 9.7H), 4.51 – 4.44 (m, 2.4H), 4.08 – 3.97 (m, 1.7H), 3.93 – 3.83 (m, 1.4H), 3.74 (d, J = 12.2 Hz, 1.7H), 3.70 – 3.60 (m, 3.5H), 3.59 – 3.52 (m, 1.8H), 3.50 – 3.42 (m, 2.0H), 1.32 (d, J = 6.1 Hz, 3.0H), 1.24 (dd, J = 8.7, 6.3 Hz, 5.5H), 1.18 (d, J = 6.0 Hz, 2.2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 138.7, 138.6, 138.3, 138.2, 138.0, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 102.2, 94.8, 84.9, 82.4, 82.2, 80.0, 78.0, 77.9, 75.7, 75.2, 75.0, 74.8, 73.5, 73.2, 72.4, 70.1, 69.2, 69.1, 68.6, 23.8, 23.2, 22.3, 21.2.

Reisolation of phenylpropiolic acid and their utilization for the synthesis of glycosyl donor: To a suspension of **13a** (200 mg, 0.3 mmol), isopropanol (30 µL, 0.36 mmol) and 4 Å MS (400 mg) in dry CH_2Cl_2 (6 mL) was added 10 mol % of $AuCl_3$ at room temperature. The reaction mixture was stirred at 45 °C for 1h. After 1h, the reaction mixture was diluted with CH_2Cl_2 and washed with cold saturated aqueous solution of $NaHCO_3$. The aqueous phase was acidified with 1(M) cold solution of hydrochloric acid and extracted three times with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated in *vacuo* to get phenylpropiolic acid as white solid (40 mg, 91%).

The recovered phenylpropiolic acid was further coupled with 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose **10a** to obtain **13a** with 80% isolated yield.

*2-Bromoethyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranoside (**14b**).*[14a] The product **14b** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and 2-bromoethanol (13 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** as colourless liquid (88 mg, 91%, α/β 1.6:1). R_f: 0.39

(ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.12 (m, 24.5H), 7.09 – 7.00 (m, 2.9H), 4.97 – 4.81 (m, 1.8H), 4.78 – 4.67 (m, 4.6H), 4.64 (d, J = 11.0 Hz, 0.4H), 4.60 – 4.45 (m, 2.8H), 4.43 – 4.34 (m, 2.5H), 4.20 – 4.08 (m, 0.4H), 3.91 (t, J = 9.3 Hz, 1.0H), 3.85 – 3.68 (m, 3.3H), 3.67 – 3.35 (m, 9.1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.6, 138.5, 138.3, 138.2, 138.1, 137.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 103.8, 97.5, 84.6, 82.1, 82.0, 80.0, 77.7, 77.4, 75.8, 75.7, 75.1, 74.9, 73.5, 73.4, 70.7, 69.7, 68.9, 68.5, 68.3, 30.3, 30.0.

*3-Chloropropyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranoside (**14c**).*[14a] The product **14c** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and 3-chloropropanol (14 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** as colourless semi solid (80 mg, 86%, α/β 1.5:1). R_f : 0.39 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 31.8H), 7.06 (t, J = 7.2 Hz, 3.7H), 4.92 – 4.78 (m, 2.5H), 4.74 (dd, J = 10.4, 4.3 Hz, 3.1H), 4.69 (d, J = 3.4 Hz, 1.0H), 4.67– 4.62 (m, 1.9H), 4.60 – 4.50 (m, 2.7H), 4.49 – 4.35 (m, 3.7H), 4.31 (d, J = 7.7 Hz, 0.7H), 4.22 (t, J = 5.9 Hz, 0.2H), 3.99 – 3.92 (m, 0.7H), 3.91 – 3.84 (m, 1.2H), 3.75 (dd, J = 9.5, 5.8 Hz, 0.9H), 3.70 – 3.34 (m, 15.6H), 2.08 – 1.88 (m, 4.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.7, 138.4, 138.3, 138.2, 138.0, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 103.7, 97.3, 84.8, 82.3, 82.1, 80.2, 77.9, 77.8, 75.7, 75.2, 75.0, 74.9, 73.6, 73.3, 70.4, 68.9, 68.6, 66.4, 64.5, 41.8, 32.9, 32.4.

*1-Adamentanemethanol 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranoside (**14d**).*[14a] The product **14d** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and 1-adamentanemethanol (30 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as semi solid (100 mg, 97%, α/β 1:1). R_f:

0.4 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 1.3H), 7.30 – 7.15 (m, 36.7H), 7.13 – 7.04 (m, 4.4H), 4.98 – 4.82 (m, 3.1H), 4.78 – 4.59 (m, 7.3H), 4.57 – 4.36 (m, 7.1H), 4.26 (d, J = 7.7 Hz, 1.0H), 3.90 (t, J = 9.2 Hz, 1.0H), 3.66 (d, J = 6.7 Hz, 3.1H), 3.61 – 3.46 (m, 7.0H), 3.38 (t, J = 8.2 Hz, 2.1H), 3.19 (d, J = 9.1 Hz, 0.9H), 3.09 (s, 0.5H), 3.01 (d, J = 9.4 Hz, 1.0H), 2.79 (d, J = 9.1 Hz, 0.8H), 1.89 (s, 6.7H), 1.68 – 1.47 (m, 26.6H), 1.41 (s, 1.9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.1, 138.7, 138.5, 138.3, 138.2, 138.1, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 104.3, 97.3, 84.8, 82.3, 82.1, 80.8, 78.9, 78.1, 77.8, 75.7, 75.6, 75.2, 75.1, 75.0, 73.9, 73.5, 72.7, 70.0, 69.0, 68.6, 39.7, 39.1, 37.2, 34.0, 33.9.

*2,3,4,6-Tetra-O-benzyl-D-glucopyranosyl azide (**14e**).*[9d] The product **14e** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and azidotrimethylsilane (24 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** as pale yellow liquid (71 mg, 84%, α/β 1.8:1). R_f: 0.39 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 32.0H), 7.09 – 7.03 (m, 3.5H), 5.15 (d, J = 4.1 Hz, 1.0H), 4.88 – 4.65 (m, 7.7H), 4.61 – 4.36 (m, 7.3H), 3.84 – 3.76 (m, 2.4H), 3.66 – 3.61 (m, 2.2H), 3.62 – 3.52 (m, 4.6H), 3.48 – 3.42 (m, 0.5H), 3.32 – 3.26 (m, 0.4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 138.0, 137.9, 137.7, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 90.2, 88.1, 84.9, 81.8, 79.5, 75.9, 75.8, 75.2, 75.1, 73.8, 73.6, 72.6, 68.4, 68.1.

*2,3,4,6-Tetra-O-benzyl-D-glucopyranosyl phthalamide (**14f**).* The product **14f** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and N-hydroxyphthalimide (29 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as colourless semisolid (80 mg, 78%, α/β 1:1). R_f : 0.32 (ethyl

acetate/hexane 1:10 (v/v), $[\alpha]_D^{28}$ = + 36.87 (c = 0.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.3, 3.0 Hz, 2.3H), 7.70 – 7.66 (m, 2.1H), 7.46 (d, *J* = 6.8 Hz, 1.9H), 7.33 – 7.00 (m, 48.9H), 5.54 (d, *J* = 3.7 Hz, 1.0H), 5.15 (d, *J* = 3.2 Hz, 1.0H), 5.04 – 4.84 (m, 3.3H), 4.83 – 4.63 (m, 7.2H), 4.60 (s, 2.1H), 4.55 – 4.27 (m, 8.3H), 4.11 – 4.01 (m, 2.2H), 4.00 – 3.96 (m, 1.3H), 3.86 – 3.79 (m, 1.4H), 3.75 – 3.40 (m, 8.4H), 3.31 (s, 1.2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.4, 138.9, 138.7, 138.4, 138.3, 138.2, 137.9, 137.6, 134.5, 129.0, 128.5, 128.3, 128.0, 127.7, 127.4, 123.6, 102.4, 94.4, 81.8, 81.4, 79.4, 78.6, 77.7, 75.9, 75.6, 75.2, 75.1, 73.5, 72.7, 72.3, 70.7, 68.2, 68.0; HRMS (ESI/Q-TOF) m/z: [M + Na] Calcd for $C_{42}H_{39}NO_8Na$ 708.2568; Found 708.2570.

*1-Adamentanol 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranoside (**14g**).*[14a] The product **14g** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and 1-adamentanol (28 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as semisolid (78 mg, 77%, α/β 1.2:1). R_f: 0.40 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 29.9H), 7.13 – 7.03 (m, 3.4H), 5.20 (d, *J* = 3.4 Hz, 1.0H), 4.92 (dd, *J* = 10.7, 7.9 Hz, 1.6H), 4.87 – 4.33 (m, 12.2H), 3.94 (t, *J* = 9.1 Hz, 2.1H), 3.72 – 3.64 (m, 1.5H), 3.60 – 3.32 (m, 6.0H), 2.06 (br s, 5.0H), 1.87 (d, *J* = 11.3 Hz, 1.9H), 1.76 (d, *J* = 10.2 Hz, 8.0H), 1.55 (br s, 11.6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.1, 138.7, 138.6, 138.4, 138.3, 138.2, 138.1, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 96.3, 89.9, 85.1, 82.4, 82.1, 80.1, 78.2, 75.8, 75.6, 75.1, 75.0, 74.6, 73.5, 73.4, 72.9, 69.7, 69.5, 68.8, 42.8, 42.5, 36.3, 30.7.

*Cholesteryl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranoside (**14h**).*[14a] The product **14h** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and cholesterol (70 mg, 0.18 mmol, 1.2

equiv) following the general procedure **B** as white solid (98 mg, 72%, α/β 1:1). R_f: 0.40 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 37.6H), 7.26 – 7.18 (m, 4.1H), 5.41 (s, 0.8H), 5.35 (s, 1.0H), 5.11 – 4.95 (m, 4.1H), 4.93 – 4.76 (m, 6.2H), 4.74 – 4.49 (m, 8.3H), 4.07 (t, J = 9.2 Hz, 1.1H), 3.95 (d, J = 8.8 Hz, 1.0H), 3.84 – 3.76 (m, 2.0H), 3.73 – 3.65 (m, 4.6H), 3.64 – 3.58 (m, 2.3H), 3.55 – 3.48 (m, 2.7H), 2.53 – 2.31 (m, 4.0H), 2.14 – 1.84 (m, 10.7H), 1.77 – 1.30 (m, 27.1H), 1.27 – 1.03 (m, 24.9H), 1.02 – 0.89 (m, 22.0H), 0.74 (d, J = 1.2 Hz, 6.4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.9, 140.6, 139.0, 138.7, 138.6, 138.4, 138.3, 138.2, 138.0, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 122.0, 121.8, 102.3, 94.7, 84.9, 82.4, 82.2, 80.0, 79.7, 78.1, 78.0, 76.6, 75.7, 75.2, 75.0, 74.8, 73.5, 73.4, 73.1, 70.1, 69.2, 68.7, 56.8, 56.2, 50.2, 42.4, 39.9, 39.8, 39.6, 39.2, 37.4, 37.2, 36.8, 36.2, 35.8, 32.0, 31.9, 30.0, 29.7, 28.3, 28.1, 27.6, 24.3, 23.9, 22.9, 22.6, 21.1, 19.5, 19.4, 18.8, 11.9.

*Methyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**14i**).*[19] The product **14i** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as white solid (122 mg, 82%, α/β 1.1:1). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 63.0H), 7.20 – 7.14 (m, 6.8H), 7.11 (dd, J = 7.0, 2.4 Hz, 2.1H), 4.99 – 4.88 (m, 7.2H), 4.84 – 4.51 (m, 22.7H), 4.50 – 4.33 (m, 4.3H), 4.17 (dd, J = 10.8, 1.8 Hz, 1.0H), 4.02 – 3.92 (m, 3.3H), 3.86 – 3.74 (m, 4.4H), 3.73 – 3.58 (m, 9.1H), 3.57 – 3.43 (m, 7.7H), 3.35 (s, 3.0H), 3.32 (s, 2.7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.8, 138.5, 138.4, 138.2, 138.1, 138.0, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 103.8, 98.1, 98.0, 97.3, 84.8, 82.1, 82.0, 81.7, 80.2, 80.0, 79.8, 78.0, 77.9, 77.8, 77.6, 75.7, 75.5, 75.1, 75.0, 74.9, 73.4, 72.4, 70.3, 69.9, 69.0, 68.6, 68.5, 66.1, 55.2, 55.1.

*Methyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (**14j**).*[19] The product **14j** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and methyl 2,3,4-tri-*O*-benzyl-*α*-D-mannopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as pale yellow liquid (77 mg, 52%, α/β 3:1). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.23 (m, 66.8H), 7.18 (d, J = 2.3 Hz, 3.7H), 5.16 – 4.93 (m, 4.8H), 4.91 – 4.43 (m, 28.2H), 4.04 (t, J = 9.3 Hz, 2.5H), 3.97 – 3.55 (m, 19.6H), 3.32 (s, 3.0H), 3.30 (s, 1.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.8, 138.6, 138.5, 138.3, 138.2, 138.1, 138.0, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 104.2, 99.0, 98.2, 96.6, 82.2, 81.7, 80.4, 80.1, 77.7, 75.5, 75.1, 75.0, 74.9, 74.8, 73.5, 73.4, 72.8, 72.6, 72.2, 71.7, 70.2, 70.1, 68.6, 66.0, 55.2, 54.7.

*2,3,4-Tri-O-benzyl-α/β-D-glucopyranosyl-(1→6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranose (**14k**).*[19] The product **14k** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and 1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (47 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as white semisolid (91 mg, 78%, α/β 1.2:1). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 5.7 Hz, 2.4H), 7.32 – 7.13 (m, 39.9H), 7.09 – 7.02 (m, 4.3H), 5.49 (d, J = 4.8 Hz, 1.0H), 5.44 (d, J = 4.8 Hz, 0.8H), 5.01 – 4.85 (m, 4.1H), 4.78 – 4.60 (m, 7.4H), 4.57 – 4.33 (m, 11.0H), 4.31 – 3.87 (m, 8.7H), 3.78 – 3.47 (m, 13.3H), 3.41 – 3.33 (m, 2.2H), 1.44 (d, J = 12.2 Hz, 6.3H), 1.37 (s, 5.6H), 1.23 (s, 12.4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 138.7, 138.4, 138.2, 138.0, 128.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 127.5, 109.4, 109.2, 108.6, 104.4, 97.1, 96.4, 96.3, 84.6, 82.0, 81.7, 79.8, 77.8,

77.6, 75.7, 75.0, 74.8, 74.4, 73.5, 72.4, 71.5, 70.9, 70.8, 70.7, 70.5, 70.3, 69.7, 68.8, 68.4, 67.4, 66.2, 65.7, 26.2, 26.1, 26.0, 25.1, 25.0, 24.7, 24.5.

*Methyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl-(1→2)-3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**14l**).*[19] The product **14l** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and methyl 3-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (67 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as colourless sticky liquid (74 mg, 55%, α only). R_f : 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 1.0H), 7.61 – 7.37 (m, 2.5H), 7.34 – 6.93 (m, 27.6H), 5.49 (s, 0.4H), 4.97 – 4.54 (m, 8.7H), 4.51 – 4.15 (m, 3.9H), 4.08 – 3.49 (m, 9.7H), 3.39 (s, 3.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.7, 138.5, 138.4, 138.1, 137.8, 134.5, 129.8, 129.0, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 126.0, 101.3, 97.2, 96.5, 94.1, 82.1, 80.5, 79.0, 76.1, 75.8, 75.7, 74.9, 74.4, 73.3, 72.9, 70.8, 70.7, 70.3, 68.2, 62.5, 55.0.

*Methyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**14m**).*[19] The product **14m** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and methyl 2-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (67 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as colourless sticky liquid (98 mg, 73%, α/β 1.4:1). R_f : 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 4.5 Hz, 2.4H), 7.34 – 7.02 (m, 41.5H), 5.49 (s, 0.7H), 5.39 (s, 1.0H), 5.02 – 4.83 (m, 2.2H), 4.78 – 4.63 (m, 3.9H), 4.62 – 4.21 (m, 12.3H), 4.03 (t, J = 9.3 Hz, 0.9H), 3.93 – 3.41 (m, 11.7H), 3.37 (s, 1.9H), 3.29 (d, J = 10.6 Hz, 2.8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.6, 138.4, 138.1, 138.0, 137.9, 137.4, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.1, 126.0,

104.4, 101.3, 100.6, 100.4, 84.7, 82.7, 81.9, 78.5, 78.2, 77.7, 76.1, 76.0, 75.7, 75.1, 75.0, 74.6, 74.4, 73.5, 73.4, 72.0, 71.8, 71.2, 69.2, 69.0, 65.4, 62.3, 62.2, 55.4.

*Methyl 2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (**14n**).*[19] The product **14n** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13a** (100 mg, 0.15 mmol, 1 equiv) and methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as colourless sticky liquid (90 mg, 67%, α/β 1:1). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.14 (m, 86.2H), 5.31 – 5.12 (m, 2.4H), 5.06 – 4.31 (m, 36.9H), 4.23 – 3.47 (m, 24.8H), 3.41 (d, J = 5.5 Hz, 5.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 138.9, 138.8, 138.7, 138.6, 138.4, 138.2, 138.1, 138.0, 137.9, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 127.1, 127.0, 126.8, 104.2, 100.7, 99.5, 96.7, 94.4, 84.7, 82.8, 82.1, 82.0, 81.8, 80.4, 79.7, 79.4, 77.7, 76.2, 76.1, 75.7, 75.6, 75.2, 75.1, 75.0, 74.5, 74.4, 73.5, 73.4, 73.2, 72.7, 72.1, 71.8, 71.2, 70.6, 69.6, 69.0, 68.2, 68.0, 65.5, 55.3, 55.2.

*Allyl 2,3,4,6-tetra-O-benzyl-α/β-D-galactopyranoside (**15a**).*[9d] The product **15a** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl phenylpropiolate **13b** (100 mg, 0.15 mmol, 1 equiv) and allyl alcohol (24 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as pale yellow liquid (80 mg, 92%, α/β 1:1). R_f: 0.38 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 30.7H), 6.03 – 5.90 (m, 1.5H), 5.40 – 5.27 (m, 1.6H), 5.26 – 5.17 (m, 1.6H), 4.98 (dd, J = 10.5, 3.7 Hz, 2.4H), 4.91 (d, J = 3.4 Hz, 1.0H), 4.89 – 4.58 (m, 7.2H), 4.53 – 4.40 (m, 5.0H), 4.22 – 3.97 (m, 5.8H), 3.94 – 3.85 (m, 1.6H), 3.66 – 3.48 (m, 4.8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.8, 138.7, 138.6, 138.1, 138.0, 134.3, 134.0, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7,

127.6, 127.5, 127.4, 118.0, 117.1, 103.0, 96.3, 82.3, 79.6, 79.2, 76.8, 76.5, 75.3, 74.8, 74.5, 73.6, 73.5, 73.4, 73.3, 73.1, 70.2, 69.4, 69.1, 68.9, 68.3.

*2,3,4,6-Tetra-O-benzyl-D-galactopyranosyl azide (**15b**).*[9d] The product **15b** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl phenylpropiolate **13b** (100 mg, 0.15 mmol, 1 equiv) and azidotrimethylsilane (24 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as pale yellow liquid (73 mg, 86%, α/β 2.3:1). R_f: 0.38 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 30.9H), 5.22 (d, J = 3.9 Hz, 1.0H), 4.90 – 4.57 (m, 7.7H), 4.54 – 4.29 (m, 5.5H), 4.07 – 3.89 (m, 4.0H), 3.76 – 3.64 (m, 1.7H), 3.59 – 3.40 (m, 3.8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 138.0, 137.8, 137.7, 128.5, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 90.6, 88.9, 82.5, 78.9, 78.8, 76.0, 75.6, 75.5, 74.9, 74.6, 74.0, 73.7, 73.5, 73.2, 72.9, 71.7, 68.5; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{35}N_3O_5Na$ 588.2469; Found 588.2466.

*Methyl 2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**15c**).*[19] The product **15c** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl phenylpropiolate **13b** (100 mg, 0.15 mmol, 1 equiv) and methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as white semisolid (117 mg, 79%, α only). R_f : 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 37.7H), 5.05 – 4.93 (m, 3.2H), 4.89 – 4.68 (m, 7.7H), 4.62 – 4.53 (m, 4.4H), 4.46 – 4.36 (m, 2.6H), 4.08 – 3.90 (m, 5.6H), 3.83 – 3.72 (m, 3.2H), 3.65 – 3.56 (m, 1.4H), 3.54 – 3.48 (m, 2.1H), 3.43 (dd, J = 9.7, 3.5 Hz, 1.1H), 3.31 (s, 3.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.8, 138.7, 138.5, 138.3, 138.1, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.5, 127.4, 98.0, 97.9, 82.1, 80.2, 78.3, 78.0, 76.6, 75.7, 75.1, 75.0, 74.8, 73.4, 72.8, 72.6, 70.3, 69.4, 69.0, 66.4, 55.1.

*2,3,4-Tri-O-benzyl-α/β-D-galactopyranosyl-(1→6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranose (**15d**).*[19] The product **15d** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl phenylpropiolate **13b** (100 mg, 0.15 mmol, 1 equiv) and 1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (47 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as colourless liquid (113 mg, 96%, α/β 1.1:1). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 6.1 Hz, 1.7H), 7.34 – 7.13 (m, 38.7H), 5.48 (d, J = 4.8 Hz, 0.7H), 5.43 (d, J = 4.9 Hz, 1.0H), 5.02 – 4.80 (m, 4.3H), 4.79 – 4.59 (m, 7.9H), 4.56 – 4.09 (m, 21.2H), 4.08 – 3.39 (m, 25.7H), 1.42 (d, J = 11.2 Hz, 5.8H), 1.35 (s, 5.5H), 1.21 (t, J = 12.2 Hz, 14.3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.1, 139.0, 138.8, 138.7, 138.1, 137.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 127.4, 109.3, 109.2, 108.6, 108.5, 104.7, 97.6, 96.4, 96.3, 81.9, 79.1, 79.0, 76.4, 74.9, 74.8, 74.6, 73.5, 73.4, 73.3, 73.1, 72.7, 71.5, 70.9, 70.8, 70.7, 70.6, 70.5, 69.7, 69.2, 68.7, 67.4, 66.3, 65.8, 26.2, 26.1, 26.0, 25.1, 25.0, 24.6, 24.5.

*Phenyl-O-(2,3,4,6-tetra-O-benzyl-α/β-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-1-thio-β-D-glucopyranoside (**15e**).*[20] The product **15e** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl phenylpropiolate **13b** (100 mg, 0.15 mmol, 1 equiv) and phenyl-2,3,4-tri-*O*-benzoyl-β-D-thioglucopyranoside (113 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as colourless semisolid (119 mg, 72%, α/β 3.1:1). R_f: 0.45 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.66 (m, 7.0H), 7.47 – 7.01 (m, 41.4H), 5.79 (t, J = 8.5 Hz, 1.0H), 5.37 (d, J = 8.8 Hz, 1.8H), 4.97 (d, J = 9.6 Hz, 1.0H), 4.83 (d, J = 11.2 Hz, 1.4H), 4.75 – 3.89 (m, 14.6H), 3.80 (s, 3.8H), 3.52 – 3.33 (m, 3.8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 165.4, 165.2, 165.1, 139.0, 138.7, 138.6, 138.2, 137.8, 133.5, 133.3, 133.2, 132.8, 132.1, 131.9, 129.9, 129.8, 129.2, 129.0, 128.9, 128.5, 128.4,

128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.3, 104.3, 97.8, 86.2, 85.7, 79.6, 79.0, 78.2, 75.2, 74.9, 74.4, 73.6, 73.5, 73.2, 70.6, 69.6, 69.0, 68.8, 68.6, 67.1.

*Methyl 2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**15f**).*[19] The product **15f** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl phenylpropiolate **13b** (100 mg, 0.15 mmol, 1 equiv) and methyl 2-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (67 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as colourless sticky liquid (71 mg, 52%, α only). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 25.3H), 7.23 – 7.15 (m, 10.4H), 7.10 (t, J = 7.6 Hz, 1.6H), 7.03 (d, J = 7.6 Hz, 4.0H), 5.61 (d, J = 3.3 Hz, 0.9H), 5.43 (s, 1.0H), 4.93 – 4.82 (m, 2.8H), 4.78 – 4.66 (m, 5.2H), 4.61 – 4.50 (m, 5.4H), 4.46 (d, J = 5.0 Hz, 1.0H), 4.42 – 4.28 (m, 5.9H), 4.21 (dd, J = 10.1, 4.6 Hz, 1.0H), 4.06 – 3.91 (m, 4.9H), 3.86 – 3.50 (m, 9.7H), 3.34 (s, 3.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 138.8, 138.4, 138.0, 137.1, 129.2, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.3, 101.8, 98.8, 96.7, 83.0, 78.3, 75.8, 75.3, 74.9, 74.7, 73.5, 73.3, 73.0, 72.9, 71.7, 69.2, 68.8, 68.5, 61.8, 55.2.

*Isopropyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**16a**).*[9d] The product 1**6a** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl phenylpropiolate **13c** (100 mg, 0.15 mmol, 1.0 equiv) and isopropanol (14 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** as colourless liquid (75 mg, 86%, α only). R_f: 0.38 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 18.0H), 7.19 (d, J = 7.5 Hz, 2.0H), 4.99 (s, 1.0H), 4.90 (d, J = 10.7 Hz, 1.0H), 4.83 – 4.65 (m, 5.0H), 4.55 (t, J = 11.4 Hz, 2.0H), 4.06 – 3.71 (m, 7.0H), 1.18 (d, J = 6.2 Hz, 3.0H), 1.08 (d, J = 6.0 Hz, 3.0H); ^{13}C{^{1}H} NMR (100

MHz, $CDCl_3$) δ 138.7, 138.5, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 95.9, 80.4, 75.4, 75.2, 73.4, 72.7, 72.2, 71.8, 69.4, 68.9, 23.3, 21.3.

*1-Adamentanol 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**16b**).*[21] The product **16b** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl phenylpropiolate **13c** (100 mg, 0.15 mmol, 1 equiv) and 1-adamentanol (28 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as yellow liquid (60 mg, 59%, α only). R_f: 0.39 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 18.0H), 7.19 (d, J = 7.4 Hz, 2.0H), 5.26 (s, 1.0H), 4.89 (d, J = 10.7 Hz, 1.0H), 4.81 – 4.47 (m, 7.0H), 3.98 (s, 3.0H), 3.86 – 3.78 (m, 1.0H), 3.72 (d, J = 10.6 Hz, 1.0H), 3.60 (s, 1.0H), 2.12 (d, J = 23.3 Hz, 3.0H), 1.72 (s, 6.0H), 1.63 – 1.52 (m, 6.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.8, 138.7, 138.6, 138.5, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 91.0, 80.3, 76.1, 75.4, 75.1, 74.4, 73.3, 72.5, 72.1, 71.4, 69.6, 42.3, 36.3, 30.6.

*(+)-Menthol 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**16c**).*[11a] The product 1**6c** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl phenylpropiolate **13c** (100 mg, 0.15 mmol, 1 equiv) and *(+)-menthol* (28 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as yellow liquid (87 mg, 85%, α only). R_f: 0.40 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.24 (m, 18.0H), 7.17 (dd, J = 6.9, 2.4 Hz, 2.0H), 5.01 (d, J = 1.3 Hz, 1.0H), 4.88 – 4.79 (m, 2.0H), 4.68 (d, J = 12.7 Hz, 4.0H), 4.52 (d, J = 11.3 Hz, 2.0H), 4.05 (t, J = 9.5 Hz, 1.0H), 3.94 – 3.75 (m, 3.0H), 3.73 – 3.65 (m, 2.0H), 3.43 (td, J = 10.5, 4.0 Hz, 1.0H), 2.22 – 2.09 (m, 1.0H), 2.01 – 1.94 (m, 1.0H), 1.83 (d, J = 11.9 Hz, 1.0H), 1.72 – 1.59 (m, 4.0H), 1.30 (dd, J = 10.8, 7.5 Hz, 2.0H), 1.24 – 1.07 (m, 1.0H), 1.04 – 0.79 (m, 11.0H), 0.73 (d, J = 6.9 Hz, 3.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.7, 138.5, 138.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 127.4, 94.6, 80.3, 75.8, 75.4, 75.2, 75.0,

73.5, 72.9, 72.5, 72.2, 71.6, 69.3, 50.2, 47.9, 45.1, 39.7, 34.6, 34.5, 31.3, 25.9, 25.2, 23.2, 22.8, 22.3, 22.2, 21.2, 21.0, 16.1, 15.4.

*(2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl)-(1→6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranose (**16d**).*[22] The product **16d** was isolated from the reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl phenylpropiolate **13c** (100 mg, 0.15 mmol, 1 equiv) and 1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (47 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as yellow liquid (62 mg, 53%, α only). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 18.0H), 7.17 (dd, J = 7.2, 2.1 Hz, 2.0H), 5.53 (d, J = 5.0 Hz, 1.0H), 5.03 (d, J = 1.6 Hz, 1.0H), 4.88 (d, J = 10.8 Hz, 1.0H), 4.77 – 4.49 (m, 10.0H), 4.35 – 4.31 (m, 1.0H), 4.17 (dd, J = 7.9, 1.7 Hz, 1.0H), 4.07 – 3.90 (m, 4.0H), 3.87 – 3.69 (m, 7.0H), 1.52 (s, 3.0H), 1.44 (s, 3.0H), 1.34 (s, 6.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.6, 138.5, 138.4, 128.3, 128.0, 127.8, 127.6, 127.5, 127.4, 109.4, 108.6, 97.3, 96.4, 75.1, 74.9, 74.7, 73.3, 72.4, 72.1, 71.0, 70.7, 70.6, 69.2, 65.4, 65.3, 26.1, 26.0, 24.9, 24.6.

*1-Octyl-2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**17a**).*[23] The product **17a** was isolated from the reaction between 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13d** (102 mg, 0.15 mmol, 1 equiv) and 1-octanol (24 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky colourless liquid (yield: 62 mg, 62%, β only). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.2 Hz, 2.0H), 7.56 (t, J = 7.1 Hz, 1.0H), 7.43 (t, J = 7.4 Hz, 2.0H), 7.38 – 7.27 (m, 8.0H), 7.23 – 7.09 (m, 7.0 H), 5.27 (t, J = 8.5 Hz, 1.0H), 4.86 – 4.54 (m, 7.0H), 4.50 (d, J = 7.8 Hz, 1.0H), 3.94 – 3.67 (m, 6.0H), 3.59 – 3.38 (m, 2.0H), 1.30 – 1.01 (m, 15.0H), 0.92 – 0.78 (m, 5.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 138.2, 138.0, 137.9, 133.0, 130.1, 129.7, 128.4, 128.3, 128.0, 127.8, 127.6, 101.2, 82.8, 78.1, 75.3, 75.1, 75.0, 73.9, 73.5, 69.9, 68.9, 31.7,

29.5, 29.3, 29.1, 25.8, 22.6, 14.1; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{42}H_{50}O_7Na$ 689.3449; Found 689.3442.

*1-Adamentanemethanol 2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**17b**).* The product **17b** was isolated from the reaction between 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13d** (102 mg, 0.15 mmol, 1 equiv) and 1-adamentanemethanol (30 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (69 mg, 65%, β only). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v), $[\alpha]_D^{28}$ = + 112.7 (c = 0.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2.0H), 7.56 (t, J = 7.2 Hz, 1.0H), 7.49 – 7.13 (m, 17.0H), 5.31 (t, J = 8.6 Hz, 1.0H), 4.87 – 4.52 (m, 7.0H), 4.42 (d, J = 7.8 Hz, 1.0H), 3.89 – 3.64 (m, 5.0H), 3.58 – 3.45 (m, 2.0H), 2.95 (d, J = 9.6 Hz, 1.0H), 1.75 (br s, 3.0H), 1.66 – 1.51 (m, 6.0H), 1.37 (br s, 10.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 138.2, 138.0, 137.9, 132.9, 130.2, 129.8, 128.4, 128.3, 128.1, 127.8, 127.6, 102.4, 82.7, 80.8, 78.1, 75.2, 75.1, 75.0, 74.0, 73.5, 68.9, 39.1, 36.9, 34.0, 28.0; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{45}H_{50}O_7Na$ 725.3449; Found 725.3423.

*(+)-Menthol-2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**17c**).* The product **17c** was isolated from the reaction between 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13d** (102 mg, 0.15 mmol, 1 equiv) and (+)-menthol (23 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (34 mg, 33%, β only). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 86.50 (c = 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.2 Hz, 2.0H), 7.48 (t, J = 6.9 Hz, 1.0H), 7.35 (t, J = 7.3 Hz, 2.0H), 7.30 – 7.11 (m, 11.0H), 7.05 (br s, 4.0H), 5.23 (t, J = 8.6 Hz, 1.0H), 4.80 – 4.43 (m, 8.0H), 3.80 – 3.45 (m, 6.0H), 3.18 (t, J = 8.2 Hz, 1.0H), 2.19 (d, J = 11.5 Hz, 1.0H), 1.80 (br s, 1.0H), 1.40 (d, J = 6.3 Hz, 1.0H), 0.79 (d, J = 6.3 Hz, 8.0H), 0.32 (dd, J = 22.7, 6.7 Hz, 6.0H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.1, 138.3, 138.0, 137.9, 132.9, 130.0, 129.8, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 102.7, 83.0, 82.6, 78.3, 75.1, 75.0, 74.1, 73.5, 69.1, 48.1, 43.2, 34.2, 31.9, 31.7, 24.6, 22.7, 22.3, 20.6; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{44}H_{52}O_7Na$ 715.3605; Found 715.3589.

*(-)-Menthol-2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**17d**).* The product **17d** was isolated from the reaction between 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13d** (102 mg, 0.15 mmol, 1 equiv) and (-)-menthol (23 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (40 mg, 39%, β only). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 138.20 (c = 0.33, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.3 Hz, 2.0H), 7.48 (t, J = 6.6 Hz, 1.0H), 7.35 (t, J = 7.3 Hz, 2.0H), 7.30 – 7.15 (m, 11.0H), 7.05 (s, 4.0H), 5.14 (t, J = 8.3 Hz, 1.0H), 4.76 (d, J = 10.8 Hz, 1.0H), 4.70 – 4.46 (m, 6.0H), 3.78 – 3.62 (m, 4.0H), 3.47 – 3.26 (m, 2.0H), 2.31 – 2.18 (m, 1.0H), 1.79 (d, J = 11.8 Hz, 1.0H), 1.09– 0.98 (m, 2.0H), 0.90 – 0.49 (m, 14.0 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.2, 138.3, 138.1, 138.0, 132.9, 130.3, 129.8, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 99.2, 82.9, 78.7, 78.2, 75.3, 75.0, 74.8, 74.0, 73.7, 69.2, 47.3, 41.0, 34.1, 31.3, 25.0, 23.0, 22.0, 21.0, 15.7; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{44}H_{52}O_7Na$ 715.3605; Found 715.3599.

*Methyl O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**17e**).*[19] The product **17e** was isolated from the reaction between 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13d** (102 mg, 0.15 mmol, 1 equiv) and methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as white solid (102 mg, 68%, β only). R_f: 0.45 (ethyl acetate/hexane 1:4 (v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.2 Hz, 2.0H), 7.39 (d, J =

6.9 Hz, 2.0H), 7.35 – 6.93 (m, 40.0H), 5.30 (t, *J* = 8.5 Hz, 1.0H), 4.86 – 4.36 (m, 16.0H), 4.23 (d, *J* = 10.9 Hz, 1.0H), 4.09 (d, *J* = 9.3 Hz, 1.0H), 3.96 (d, *J* = 6.8 Hz, 1.0H), 3.86 – 3.57 (m, 8.0H), 3.51 (br s, 1.0H), 3.43 – 3.25 (m, 3.0H), 3.15 (s, 3.0H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.0, 138.9, 138.2, 137.9, 137.8, 133.0, 129.9, 129.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 101.3, 97.9, 82.9, 81.9, 79.8, 78.1, 75.5, 75.1, 75.0, 74.6, 73.7, 73.5, 73.4, 69.5, 68.9, 68.1, 54.9.

*1-Octyl-6-O-benzoyl-2,3,4-tri-O-benzyl-α/β-D-glucopyranoside (**18a**).* The product **18a** was isolated from the reaction between 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13e** (102 mg, 0.15 mmol, 1 equiv) and 1-octanol (24 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky colourless liquid (72 mg, 72%, α/β 1.1:1). R_f : 0.35 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 31.2 (c = 0.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 4.1H), 7.56 (ddd, *J* = 7.5, 2.8, 1.4 Hz, 2.2H), 7.46 – 7.23 (m, 36.9H), 5.05 – 4.72 (m, 10.7H), 4.71 – 4.42 (m, 9.3H), 4.10 – 3.88 (m, 4.0H), 3.83 (d, *J* = 11.0 Hz, 0.2H), 3.78 – 3.38 (m, 10.5H), 1.70 – 1.57 (m, 7.5H), 1.43 – 1.29 (m, 7.8H), 0.92 – 0.83 (m, 8.0H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.3, 138.7, 138.4, 138.3, 137.8, 137.7, 133.0, 130.0, 129.9, 129.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 103.8, 96.7, 84.8, 82.3, 82.1, 80.3, 77.8, 75.9, 75.2, 74.9, 73.2, 73.0, 70.3, 68.8, 68.4, 63.6, 31.8, 29.7, 29.4, 29.3, 26.2, 26.1, 22.7, 14.1, 14.0; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{42}H_{50}O_7Na$ 689.3449; Found 689.3440.

*1-Adamentanemethanol-6-O-benzoyl-2,3,4-tri-O-benzyl-α/β-D-glucopyranoside (**18b**).* The product **18b** was isolated from the reaction between 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13e** (102 mg, 0.15 mmol, 1 equiv) and 1-adamentanemethanol (30 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as yellowish

liquid (93 mg, 88%, α/β 1.8:1). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 32.56 (c = 0.18, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.97 (m, 3.5H), 7.68 – 7.25 (m, 27.6H), 5.10 – 4.73 (m, 7.7H), 4.69 – 4.40 (m, 6.2H), 4.11 – 3.96 (m, 0.3H), 3.78 – 3.51 (m, 5.0H), 3.31 (d, *J* = 9.1 Hz, 0.9H), 3.10 (d, *J* = 9.5 Hz, 0.5H), 2.90 (d, *J* = 9.1 Hz, 1.0H), 2.00 (d, *J* = 13.7 Hz, 5.1H), 1.77 – 1.53 (m, 21.4H), 1.51 – 1.45 (m, 1.2H).; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 138.8, 138.5, 138.4, 137.8, 137.7, 133.1, 130.0, 129.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 104.3, 96.9, 84.8, 82.3, 82.1, 80.9, 80.8, 78.8, 77.9, 77.8, 75.8, 75.3, 75.1, 74.9, 73.0, 72.7, 68.7 63.7, 39.7, 39.6, 37.1, 33.9, 33.8, 28.2; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ Calcd for $C_{45}H_{50}O_7Na$ 725.3449; Found 725.3439.

*(+)-Menthol-6-O-benzoyl-2,3,4-tri-O-benzyl-α/β-D-glucopyranoside (**18c**).* The product **18c** was isolated from the reaction between 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13e** (123 mg, 0.15 mmol, 1 equiv) and (+)-menthol (28 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (78 mg, 75%, α/β 2.1:1). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 19.7 (c = 0.19, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 1.7H), 7.51 – 7.45 (m, 0.9H), 7.38 – 7.10 (m, 14.5H), 4.98 (s, 0.6H), 4.94 (d, *J* = 3.7 Hz, 1.0H), 4.90 – 4.66 (m, 3.0H), 4.64 – 4.52 (m, 1.8H), 4.44 (d, *J* = 2.6 Hz, 1.1H), 4.41 (d, *J* = 7.8 Hz, 0.3H), 4.32 (dd, *J* = 11.7, 6.4 Hz, 0.2H), 3.95 (dd, *J* = 16.8, 6.2 Hz, 1.4H), 3.67 – 3.47 (m, 2.0H), 3.44 – 3.34 (m, 0.9H), 3.28 (td, *J* = 10.6, 4.4 Hz, 0.2H), 2.27 – 2.14 (m, 1.1H), 1.90 (d, *J* = 11.9 Hz, 0.9H), 1.58 (d, *J* = 10.8 Hz, 1.7H), 1.36 (dd, *J* = 16.1, 7.5 Hz, 0.8H), 0.93 – 0.78 (m, 6.1H), 0.73 – 0.60 (m, 4.3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 166.2, 138.7, 138.4, 138.1, 137.8, 133.0, 130.0, 129.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 104.4, 93.2, 85.1, 82.7, 82.1, 81.5, 80.3, 78.3, 77.8, 75.9, 75.7, 75.4, 75.1, 73.7, 72.9, 69.3, 64.0, 63.5, 48.8, 47.4, 43.4, 39.8, 34.4, 34.2, 31.7, 31.5,

25.2, 24.7, 22.7, 22.4, 22.2, 21.3, 21.1, 15.9, 15.2; ~~;~~HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{44}H_{52}O_7Na$ 715.3605; Found 715.3585.

*Cholesteryl-6-O-benzoyl-2,3,4-tri-O-benzyl-α/β-D-glucopyranoside (**18d**).* The product **18d** was isolated from the reaction between 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13e** (123 mg, 0.15 mmol, 1 equiv) and cholesterol (70 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (67 mg, 61%, α/β 1.2:1). R_f: 0.35 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 33.71 (c = 0.24, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 3.5H), 7.52 – 7.44 (m, 2.1H), 7.38 – 7.14 (m, 33.8H), 5.25 (d, J = 5.1 Hz, 0.5H), 5.16 (d, J = 5.0 Hz, 1.0H), 5.00 – 4.89 (m, 2.2H), 4.87 (d, J = 3.2 Hz, 1.0H), 4.82 (s, 2.0H), 4.80 – 4.46 (m, 10.1H), 4.45 (d, J = 5.2 Hz, 0.8H), 4.40 – 4.32 (m, 2.7H), 4.08 – 3.94 (m, 3.8H), 3.73 – 3.35 (m, 9.1H), 2.43 – 2.19 (m, 8.2H), 1.99 – 1.71 (m, 12.6H), 1.63 – 1.13 (m, 46.7H), 1.12 – 0.75 (m, 46.8H), 0.61 (d, J = 3.4 Hz, 5.4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 166.2, 140.6, 138.7, 138.5, 138.1, 137.8, 137.7, 133.0, 129.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 121.8, 102.6, 94.4, 84.9, 82.3, 82.1, 80.4, 80.1, 78.0, 75.9, 75.3, 73.1, 68.9, 63.4, 56.8, 56.2, 50.1, 42.3, 39.9, 39.8, 39.5, 39.1, 37.1, 36.8, 36.7, 36.2, 35.8, 32.0, 31.9, 29.7, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{61}H_{78}O_7Na$ 945.5640; Found 945.5633.

*Methyl-6-O-benzoyl-2,3,4-tri-O-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**18e**).*[24] The product **18e** was isolated from the reaction between 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl phenylpropiolate **13e** (102 mg, 0.15 mmol, 1 equiv) and methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (93 mg, 72%, α/β 2.1:1). R_f: 0.4 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 3.0H), 7.59 –

7.53 (m, 1.7H), 7.45 – 7.21 (m, 49.0H), 7.19 – 7.15 (m, 1.1H), 5.03 – 4.89 (m, 7.0H), 4.87 – 4.76 (m, 4.5H), 4.74 – 4.55 (m, 10.3H), 4.54 – 4.45 (m, 2.4H), 4.42 – 4.37 (m, 1.7H), 4.14 (dd, *J* = 10.9, 1.6 Hz, 0.6H), 4.06 – 3.95 (m, 3.9H), 3.81 (td, *J* = 11.6, 5.0 Hz, 2.8H), 3.74 – 3.48 (m, 8.2H), 3.42 (dd, *J* = 9.6, 3.6 Hz, 1.1H), 3.36 (s, 3.0H), 3.30 (s, 1.4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 138.8, 138.5, 138.3, 138.2, 138.1, 138.0, 137.7, 133.1, 133.0, 130.0, 129.9, 129.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 104.0, 98.1, 97.9, 96.9, 84.8, 82.1, 82.0, 81.7, 80.2, 79.8, 77.9, 77.8, 77.6, 75.8, 75.0, 73.4, 73.1, 72.5, 70.4, 69.8, 68.9, 68.7, 66.0, 63.5, 55.2; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{62}H_{64}O_{12}Na$ 1023.4290; Found 1023.4288.

*2,3,4-tri-O-benzyl-6-O-(tert-butyldiphenylsilyl)-α/β-D-glucopyranosyl azide (**19a**).* The product **19a** was isolated from the reaction between 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α/β-D-glucopyranosyl phenylpropiolate **13f** (123 mg, 0.15 mmol, 1 equiv) and azidotrimethylsilane (24 µL, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as yellowish liquid (92 mg, 86%, α/β 1.4:1). R_f: 0.4 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 36.72 (c = 0.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.64 (m, 7.0H), 7.46 – 7.28 (m, 30.2H), 7.25 – 7.15 (m, 3.5H), 5.29 (d, *J* = 4.1 Hz, 1.0H), 4.97 – 4.62 (m, 10.4H), 4.00 – 3.81 (m, 6.2H), 3.76 – 3.63 (m, 2.8H), 3.47 – 3.39 (m, 1.0H), 1.10 – 1.05 (m, 13.2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 138.5, 138.3, 138.2, 137.9, 137.8, 137.7, 135.9, 135.8, 135.7, 135.4, 134.9, 133.5, 133.2, 129.7, 128.7, 128.5, 128.2, 128.1, 127.8, 127.7, 127.6, 89.9, 87.9, 84.9, 82.0, 81.8, 79.9, 76.0, 75.2, 73.9, 73.8, 62.5, 62.2, 26.9, 19.3; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{47}N_3O_5SiNa$ 736.3177; Found 736.3180.

*(+)-Menthol 2,3,4-tri-O-benzyl-6-O-(tertbutyldiphenylsilyl)-α/β-D-glucopyranoside (**19b**).* The product **19b** was isolated from the reaction between 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-

butyldiphenylsilyl)-α/β-D-glucopyranosyl phenylpropiolate **13f** (123 mg, 0.15 mmol, 1 equiv) and (+)-menthol (28 mg, 0.18 mmol, 1.2 equiv) following the general **B** and was obtained as sticky yellowish liquid (110 mg, 89%, α/β 2.1:1). R_f: 0.4 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 24.54 (c = 0.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.55 (m, 10.7H), 7.50 (d, *J* = 6.9 Hz, 1.7H), 7.40 – 7.09 (m, 71.1H), 7.00 (d, *J* = 3.1 Hz, 1.5H), 4.98 – 4.85 (m, 8.1H), 4.83 – 4.68 (m, 6.4H), 4.63 (d, *J* = 10.6 Hz, 5.0H), 4.50 – 4.39 (m, 11H), 3.89 (d, *J* = 9.9 Hz, 6.5H), 3.80 – 3.62 (m, 8.5H), 3.60 – 3.26 (m, 8.7H), 0.98 (d, *J* = 6.3 Hz, 28.5H), 0.88 (s, 9.7H), 0.84 – 0.69 (m, 19.9H), 0.62 (dd, *J* = 15.3, 6.7 Hz, 4.5H), 0.48 (d, *J* = 6.5 Hz, 6.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 138.7, 138.4, 138.1, 136.0, 135.7, 133.8, 133.4, 133.0, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.5, 104.6, 93.2, 85.2, 82.2, 80.6, 78.0, 75.9, 75.6, 75.4, 73.6, 71.8, 67.7, 62.6, 49.2, 47.4, 40.0, 34.4, 31.6, 26.9, 25.0, 24.7, 22.8, 22.5, 21.1, 19.4, 15.9, 15.2; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{52}H_{64}O_7SiNa$ 851.4314; Found 851.4311.

*Cholesteryl 2,3,4-tri-O-benzyl-6-O-(tert-butyldiphenylsilyl)-α/β-D-glucopyranoside (**19c**).* The product **19c** was isolated from the reaction between 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α/β-D-glucopyranosyl phenylpropiolate **13f** (123 mg, 0.15 mmol, 1 equiv) and cholesterol (70 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (110 mg, 69%, α/β 1.2:1). R_f: 0.4 (ethyl acetate/hexane 1:10 (v/v); $[\alpha]_D^{28}$ = + 39.72 (c = 0.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.49 (m, 7.6H), 7.39 – 6.94 (m, 42.0H), 5.27 (s, 1.4H), 5.15 (d, *J* = 1.5 Hz, 1.0H), 4.95 – 4.42 (m, 14.3H), 4.00 – 3.19 (m, 17.1H), 2.40 – 2.09 (m, 10.2H), 1.99 – 1.57 (m, 21.3H), 1.53 – 1.13 (m, 42.0H), 1.13 – 0.73 (m, 85.1H), 0.61 (d, *J* = 6.1 Hz, 8.1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.4, 140.6, 138.9, 138.7, 138.4, 138.2, 135.9, 135.7, 133.7, 133.4, 129.5, 128.1, 127.7, 127.6, 121.9, 121.4,

102.4, 93.9, 85.0, 82.7, 82.2, 80.4, 79.7, 78.2, 75.9, 75.2, 73.0, 71.6, 63.1, 56.8, 56.2, 50.2, 42.3, 39.8, 39.5, 37.1, 36.8, 36.2, 35.8, 31.9, 29.7, 28.3, 28.0, 27.3, 26.8, 24.3, 23.8, 22.9, 22.6, 21.1, 19.4, 19.3, 18.8, 11.9; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{70}H_{92}O_6SiNa$ 1079.6555; Found 1079.6530.

*Methyl 2,3,4-tri-O-benzyl-6-O-(tert-butyldiphenylsilyl)-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**19d**).*[25] The product **19d** was isolated from the reaction between 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α/β-D-glucopyranosyl phenylpropiolate **13f** (123 mg, 0.15 mmol, 1 equiv) and methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as sticky yellowish liquid (123 mg, 72%, α/β 2.4:1). R_f: 0.4 (ethyl acetate/hexane 1:5 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 0.7H), 7.64 – 7.55 (m, 5.5H), 7.34 – 7.10 (m, 57.3H), 7.08 – 7.03 (m, 3.3H), 4.96 – 4.78 (m, 7.8H), 4.76 – 4.69 (m, 4.2H), 4.66 – 4.39 (m, 10.7H), 4.25 (d, J = 7.7 Hz, 0.5H), 4.14 (dd, J = 10.9, 1.8 Hz, 0.5H), 3.96 – 3.87 (m, 2.9H), 3.82 (d, J = 2.7 Hz, 0.9H), 3.76 – 3.45 (m, 14.3H), 3.36 – 3.32 (m, 1.0H), 3.30 (s, 1.2H), 3.28 (s, 3.0H), 0.97 – 0.94 (m, 13.0H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.9, 138.8, 138.6, 138.4, 138.2, 135.9, 135.6, 133.7, 133.4, 129.6, 129.5, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 103.9, 98.3, 98.0, 97.0, 85.0, 82.3, 82.1, 81.8, 80.5, 80.2, 79.7, 77.8, 75.9, 75.7, 75.1, 75.0, 74.9, 74.8, 73.4, 72.4, 71.6, 70.5, 69.8, 68.1, 65.7, 63.0, 55.3, 55.1, 26.8, 19.3; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{71}H_{78}O_{11}SiNa$ 1157.5206; Found 1157.5205.

*2,3,4-tri-O-benzyl-6-O-(tert-butyldiphenylsilyl)-α/β-D-glucopyranosyl-(1→6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranose (**19e**).* The product **19e** was isolated from the reaction between 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α/β-D-glucopyranosyl phenylpropiolate **13f** (123 mg, 0.15 mmol, 1 equiv) and (1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (47

mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** and was obtained as yellowish liquid (98 mg, 70%, α/β 1.7:1). R_f: 0.4 (ethyl acetate/hexane 1:5 (v/v); $[\alpha]_D^{28}$ = + 38.61 (c = 0.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 9.6H), 7.37 – 7.17 (m, 49.2H), 7.11 (dd, *J* = 8.6, 5.1 Hz, 4.5H), 5.50 (d, *J* = 5.0 Hz, 0.5H), 5.43 (d, *J* = 5.0 Hz, 1.0H), 4.98 (t, *J* = 7.6 Hz, 1.5H), 4.94 – 4.78 (m, 5.2H), 4.77 – 4.57 (m, 8.8H), 4.53 – 4.50 (m, 1.6H), 4.41 (d, *J* = 7.7 Hz, 0.6H), 4.28 – 4.17 (m, 3.7H), 4.12 – 4.01 (m, 1.5H), 3.99 – 3.80 (m, 8.1H), 3.76 – 3.48 (m, 10.0H), 3.43 – 3.37 (m, 0.7H), 1.43 (s, 4.9H), 1.38 (s, 5.0H), 1.24 (d, *J* = 2.6 Hz, 10.6H), 0.98 (d, *J* = 4.9 Hz, 19.1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.7, 138.5, 138.4, 138.3, 135.9, 135.6, 133.7, 129.6, 129.5, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 127.5, 109.3, 109.2, 108.6, 104.1, 96.3, 84.7, 82.2, 82.1, 80.3, 75.8, 75.6, 75.1, 74.5, 72.2, 71.5, 71.3, 70.8, 70.7, 70.6, 67.2, 65.5, 65.4, 62.7, 26.9, 26.2, 26.1, 25.0, 24.9, 24.6, 24.4, 19.3; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ Calcd for $C_{55}H_{66}O_{11}SiNa$ 953.4267; Found 953.4290.

Methyl 2,3,4-tri-O-benzyl-α-L-rhamanopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside ***(20a)***.[19] The product **20a** was isolated from the reaction between 2,3,4-tri-*O*-benzyl-α/β-L-rhamnopyranosyl phenylpropiolate **13g** (84 mg, 0.15 mmol, 1 equiv) and methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (84 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as yellow liquid (114 mg, 86%, α only). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.20 (m, 35.0H), 5.06 – 4.96 (m, 2.0H), 4.83 (d, *J* = 12.0 Hz, 3.0H), 4.79 – 4.56 (m, 9.0H), 4.42 (d, *J* = 11.0 Hz, 1.0H), 4.00 (t, *J* = 9.2 Hz, 1.0H), 3.91 – 3.82 (m, 2.0H), 3.79 – 3.62 (m, 5.0H), 3.55 – 3.47 (m, 2.0H), 3.39 (t, *J* = 9.4 Hz, 1.0H), 3.31 (s, 3.0H), 1.35 (d, *J* = 6.1 Hz, 3.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 138.5, 138.3, 138.2, 138.1, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 98.2, 97.8, 82.0, 80.6, 80.0, 79.8, 77.9, 75.8, 75.5, 75.0, 73.3, 72.8, 72.4, 69.9, 68.1, 66.1, 55.0, 18.0.

*(2,3,4-Tri-O-benzyl-α-L-rhamanopyranosyl-(1→6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranose (**20b**).*[10i] The product **20b** was isolated from the reaction between 2,3,4-tri-*O*-benzyl-α/β-L-rhamanopyranosyl phenylpropiolate **13g** (84 mg, 0.15 mmol, 1 equiv) and 1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (47 mg, 0.18 mmol, 1.2 equiv) following the general procedure **B** as yellow liquid (69 mg, 68%, α only). R_f: 0.5 (ethyl acetate/hexane 1:4 (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 2.0H), 7.31 (t, J = 8.0 Hz, 13.0H), 5.52 (d, J = 4.9 Hz, 1.0H), 4.97 – 4.88 (m, 2.0H), 4.73 (s, 2.0H), 4.67 – 4.56 (m, 4.0H), 4.33 – 4.28 (m, 1.0H), 4.16 (d, J = 8.0 Hz, 1.0H), 3.93 – 3.88 (m, 1.0H), 3.87 – 3.70 (m, 4.0H), 3.66 – 3.52 (m, 2.0H), 1.51 (s, 3.0H), 1.43 (s, 3.0H), 1.32 (d, J = 7.0 Hz, 9.0H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 138.4, 128.3, 127.9, 127.6, 127.5, 127.4, 109.3, 108.6, 98.0, 96.3, 80.4, 80.0, 75.2, 74.8, 72.6, 72.0, 71.2, 70.6, 70.5, 68.1, 67.3, 66.0, 26.1, 26.0, 25.0, 24.4, 17.9.

*Methyl-2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-β-D-glucopyranosyl-(1→6)- 2,3,4-tri-O-benzyl-α-D-glucopyranoside (**21**).*[26] To a solution of disaccharide **15e (**40 mg, 0.04 mmol) in dry CH_2Cl_2 (1 mL) was added methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (17 mg, 0.04 mmol) and the mixture was stirred at room temperature for 5 minutes. Then this mixture was cooled at -15 °C and NIS (13 mg, 0.06 mmol) and TMSOTf (1 µL) was added subsequently. The mixture was stirred for 30 minutes and after completion of reaction, the mixture was evaporated in *vacuo* and purified by column chromatography to obtain the trisaccharide **21** as colourless liquid (36 mg, 65%, α/β 4.3:1) using 25% ethylacetate in hexane (Rf : 0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.70 (m, 14.1H), 7.49 – 7.06 (m, 96.6H), 6.97 – 6.85 (m, 2.8H), 6.14 – 6.04 (m, 0.8H), 5.75 (d, J = 9.3 Hz, 1.4H), 5.48 – 5.37 (m, 2.9H), 5.32 – 5.09 (m, 2.5H), 4.90 – 4.14 (m, 40.4H), 4.12 – 3.51 (m, 27.7H), 3.50 – 3.26 (m, 10.6H), 3.04 (s, 3.0H), 2.99 (s, 0.7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

δ 165.9, 165.8, 165.7, 165.6, 165.1, 164.9, 138.9, 138.8, 138.7, 138.6, 138.5, 138.3, 138.2, 138.1, 133.4, 133.3, 133.2, 133.0, 129.9, 129.8, 129.7, 129.3, 129.1, 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 100.8, 99.3, 98.2, 97.9, 90.0, 81.8, 79.8, 78.9, 78.7, 75.6, 75.5, 75.4, 75.1, 74.7, 74.6, 74.5, 73.7, 73.6, 73.5, 73.4, 73.3, 73.2, 73.1, 73.0, 72.2, 71.9, 70.5, 69.9, 69.8, 69.7, 69.6, 69.5, 69.4, 69.3, 69.1, 67.8, 67.5, 55.0, 54.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Copies of ^{1}H NMR, ^{13}C NMR, COSY and HSQC of starting materials and products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rima@nitp.ac.in

*E-mail: amitkt@iitp.ac.in

ORCID

Amit Kumar: 0000-0002-1683-7740

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.K. acknowledges DST-SERB, New Delhi, SB/FT/CS-069/2014 and IIT Patna for providing financial support. M.S. thanks IIT Patna for an institute research fellowship. The author is thankful to IIT Patna for NMR and SAIF-IIT Patna for HRMS instrumental facilities. The authors are also thankful to the reviewers for their constructive suggestions and for proposed

corrections to improve the manuscript. This work is dedicated to Prof. R. N. Mukherjee (Dept. of Chemistry, IIT Kanpur) on the occasion of his 65th birthday.

■ REFERENCES

(1) (a) Bertozzi, C. R.; Kiessling; L., L., Chemical Glycobiology. *Science* **2001,** *291*, 2357. (b) Rudd, P. M.; Elliott, T.; Cresswell, P.; Wilson, I. A.; Dwek, R. A., Glycosylation and the Immune System. *Science* **2001,** *291*, 2370. (c) Brandley, B. K.; Schnaar, R. L., Cell-Surface Carbohydrates in Cell Recognition and Response. *J. Leukoc. Biol.* **1986,** *40*, 97. (d) Crocker, P. R.; Feizi, T., Carbohydrate recognition systems: functional triads in cell-cell interactions. *Curr. Opin. Struct Biol.* **1996,** *6*, 679. (e) Carbohydrates in Chemistry and Biology; Ernst, B., Hart, G. W., Sinaÿ, P., Eds.; Wiley-VCH: Weinheim, 2000; Vols. 1-4. (f) Schmaltz, R. M.; Hanson, S. R.; Wong, C.-H., Enzymes in the Synthesis of Glycoconjugates. *Chem. Rev.* **2011,** *111*, 4259. (g) Varki, A., Biological roles of oligosaccharides: all of the theories are correct. *Glycobiology* **1993,** *3*, 97.

(2) (a) Gruner, S. A. W.; Locardi, E.; Lohof, E.; Kessler, H., Carbohydrate-Based Mimetics in Drug Design: Sugar Amino Acids and Carbohydrate Scaffolds. *Chem. Rev.* **2002,** *102*, 491. (b) Ernst, B.; Magnani, J. L., From carbohydrate leads to glycomimetic drugs. *Nat. Rev. Drug Discov.* **2009,** *8*, 661. (c) Fernández-Tejada, A.; Cañada, F. J.; Jiménez-Barbero, J., Recent Developments in Synthetic Carbohydrate-Based Diagnostics, Vaccines, and Therapeutics. *Chem. Eur. J.* **2015,** *21*, 10616. (d) Oppenheimer, S. B.; Alvarez, M.; Nnoli, J., Carbohydrate-based experimental therapeutics for cancer, HIV/AIDS and other diseases. *Acta Histochem.* **2008,** *110*, 6.

(3) Ueno, K.; Lim, D. J., Heterogeneity of glycoconjugates in the secretory cells of the chinchilla middle ear and eustachian tubal epithelia: a lectin-gold cytochemical study. *J. Histochem. Cytochem.* **1991,** *39*, 71.

(4) (a) Galonić, D. P.; Gin, D. Y., Chemical glycosylation in the synthesis of glycoconjugate antitumour vaccines. *Nature* **2007,** *446*, 1000. (b) Boltje, T. J.; Buskas, T.; Boons, G.-J., Opportunities and challenges in synthetic oligosaccharide and glycoconjugate research. *Nat. Chem.* **2009,** *1*, 611. (c) Schumann, B.; Hahm, H. S.; Parameswarappa, S. G.; Reppe, K.; Wahlbrink, A.; Govindan, S.; Kaplonek, P.; Pirofski, L.-a.; Witzenrath, M.; Anish, C.; Pereira, C. L.; Seeberger, P. H., A semisynthetic Streptococcus pneumoniae serotype 8 glycoconjugate vaccine. *Sci. Transl. Med.* **2017,** *9*. (d) Seeberger, P. H.; Werz, D. B., Synthesis and medical applications of oligosaccharides. *Nature* **2007,** *446*, 1046. (e) Peng, P.; Schmidt, R. R., Acid-Base Catalysis in Glycosidations: A Nature Derived Alternative to the Generally Employed Methodology. *Acc. Chem. Res.* **2017,** *50*, 1171.

(5) (a) Schmidt, R. R.; Michel, J., Facile Synthesis of α- and β-O-Glycosyl Imidates; Preparation of Glycosides and Disaccharides. *Angew. Chem., Int. Ed.* **1980,** *19*, 731. (b) Schmidt, R. R., New Methods for the Synthesis of Glycosides and Oligosaccharides—Are There Alternatives to the Koenigs-Knorr Method?. *Angew. Chem., Int. Ed.* **1986,** *25*, 212. (c) Fügedi, P.; Garegg, P. J.; Lönn, H.; Norberg, T., Thioglycosides as glycosylating agents in oligosaccharide synthesis. *Glycoconjugate J.* **1987**, *4*, 97. (d) Crich, D.; Smith, M., 1-Benzenesulfinyl Piperidine/Trifluoromethanesulfonic Anhydride: A Potent Combination of Shelf-Stable Reagents for the Low-Temperature Conversion of Thioglycosides to Glycosyl Triflates and for the Formation of Diverse Glycosidic Linkages. *J. Am. Chem. Soc.* **2001,** *123*, 9015. (e) Demchenko, A. V.; Pornsuriyasak, P.;

Meo, C. D.; Malysheva, N. N., Potent, Versatile, and Stable: Thiazolyl Thioglycosides as Glycosyl Donors. *Angew. Chem., Int. Ed.* **2004,** *43*, 3069. (f) Danishefsky, S. J.; Bilodeau, M. T., Glycals in Organic Synthesis: The Evolution of Comprehensive Strategies for the Assembly of Oligosaccharides and Glycoconjugates of Biological Consequence. *Angew. Chem., Int. Ed.* **1996,** *35*, 1380. (g) Koenigs, W.; Knorr, E., Ueber einige Derivate des Traubenzuckers und der Galactose. *Ber. Dtsch. Chem. Ges.* **1901,** *34*, 957. (h) Shimizu, M.; Togo, H.; Yokoyama, M., Chemistry of Glycosyl Fluorides. *Synthesis* **1998,** *1998*, 799.

(6) (a) Witczak, Z. J.; Czernecki, S., Synthetic applications of selenium-containing sugars. *Adv. Carbohydr. Chem. Biochem.* **1998**, *53*, 143. (b) Mootoo, D. R.; Date, V.; Fraser-Reid, B., *n*-Pentenyl Glycosides Permit the Chemospecific Liberation of the Anomeric Center. *J. Am. Chem. Soc.* **1988**, *110*, 2662. (c) Campbell, A. S.; Fraser-Reid, B., First Synthesis of a Fully Phosphorylated GPI Membrane Anchor: Rat Brain Thy-l. *J. Am. Chem. Soc.* **1995,** *117*, 10387. (d) Plante, O. J.; Andrade, R. B.; Seeberger, P. H., Synthesis and Use of Glycosyl Phosphates as Glycosyl Donors. *Org. Lett.* **1999,** *1*, 211.

(7) (a) Hu, Y.; Yu, K.; Shi, L.-L.; Liu, L.; Sui, J.-J.; Liu, D.-Y.; Xiong, B.; Sun, J.-S., o-(p-Methoxyphenylethynyl)phenyl Glycosides: Versatile New Glycosylation Donors for the Highly Efficient Construction of Glycosidic Linkages. *J. Am. Chem. Soc.* **2017,** *139*, 12736. (b) Tanaka, M.; Nakagawa, A.; Nishi, N.; Iijima, K.; Sawa, R.; Takahashi, D.; Toshima, K., Boronic-Acid-Catalyzed Regioselective and 1,2-*cis*-Stereoselective Glycosylation of Unprotected Sugar Acceptors via S_Ni-Type Mechanism. *J. Am.Chem. Soc.* **2018,** *140*, 3644. (c) Nigudkar, S. S.; Demchenko, A. V., Stereocontrolled 1,2-cis glycosylation as the driving force of progress in synthetic carbohydrate chemistry.

Chem. Sci. **2015,** *6*, 2687. (d) Guisot, N. E. S.; Ella Obame, I.; Ireddy, P.; Nourry, A.; Saluzzo, C.; Dujardin, G.; Dubreuil, D.; Pipelier, M.; Guillarme, S., Reaction of Glyconitriles with Organometallic Reagents: Access to Acyl β-C-Glycosides. *J. Org. Chem.* **2016,** *81*, 2364. (e) Wang, H.-Y.; Simmons, C. J.; Blaszczyk, S. A.; Balzer, P. G.; Luo, R.; Duan, X.; Tang, W., Isoquinoline-1-Carboxylate as a Traceless Leaving Group for Chelation-Assisted Glycosylation under Mild and Neutral Reaction Conditions. *Angew. Chem., Int. Ed.* **2017**, *56*, 15698.

(8) Helferich, B.; Schmitz-Hillebrecht, E. Eine Neue Methode Zur Synthese von Glykosiden Der Phenole. *Ber. Dtsch. Chem. Ges. B* **1933**, *66*, 378.

(9) (a) Baek, J. Y.; Choi, T. J.; Jeon, H. B.; Kim, K. S., A Highly Reactive and Stereoselective β-Mannopyranosylation System: Mannosyl 4-Pentenoate/PhSeOTf. *Angew. Chem., Int. Ed.* **2006,** *45*, 7436. (b) Choi, T. J.; Baek, J. Y.; Jeon, H. B.; Kim, K. S., A new efficient glycosylation method employing glycosyl pentenoates and PhSeOTf. *Tetrahedron Lett.* **2006,** *47*, 9191. (c) Zhang, Y.; Wang, P.; Song, N.; Li, M., Bromodimethylsulfonium bromide/silver triflate-promoted glycosylations using glycosyl allenoates as donors. *Carbohydr. Res.* **2013,** *381*, 101. (d) Koppolu, S. R.; Niddana, R.; Balamurugan, R., Gold-catalysed glycosylation reaction using an easily accessible leaving group. *Org. Biomol. Chem.* **2015,** *13*, 5094. (e) Mallick, A.; Mallikharjunarao, Y.; Rajasekaran, P.; Roy, R.; Vankar, Y. D., Au^{III}-Halide/Phenylacetylene-Cata-lysed Glycosylations Using 1-*O*-Acetyl-furanoses and Pyranose 1,2-Ortho-esters as Glycosyl Donors. *Eur. J. Org. Chem.* **2016,** *2016*, 579. (f) Rashmi, R.; Parasuraman, R.; Asadulla, M.; D., Vankar. Y., Gold(III) Chloride and Phenylacetylene: A Catalyst System for the Ferrier Rearrangement, and O-Glycosylation

of 1-O-Acetyl Sugars as Glycosyl Donors. *Eur. J. Org. Chem.* **2014,** *2014*, 5564. (g) Kunz, H.; Wernig, P.; Schultz, M., A New Activating Principle in Glycoside Synthesis Based on Electrophile-Induced Lactonization of Glucosyl 4-Pentenoates. *Synlett* **1990,** *1990*, 631.

(10) (a) Li, Y.; Yang, Y.; Yu, B., An efficient glycosylation protocol with glycosyl *ortho*-alkynylbenzoates as donors under the catalysis of $Ph_3PAuOTf$. *Tetrahedron Lett.* **2008,** *49*, 3604. (b) Zhang, Q.; Sun, J.; Zhu, Y.; Zhang, F.; Yu, B., An Efficient Approach to the Synthesis of Nucleosides: Gold(I)-Catalyzed N-Glycosylation of Pyrimidines and Purines with Glycosyl *ortho*-Alkynyl Benzoates. *Angew. Chem., Int. Ed.* **2011,** *50*, 4933. (c) Xiao, G.; Yu, B., Total Synthesis of Starfish Saponin Goniopectenoside B. *Chem. Eur. J.* **2013,** *19*, 7708. (d) Tang, Y.; Li, J.; Zhu, Y.; Li, Y.; Yu, B., Mechanistic Insights into the Gold(I)-Catalyzed Activation of Glycosyl *ortho*-Alkynylbenzoates for Glycosidation. *J. Am. Chem. Soc.* **2013,** *135*, 18396. (e) Nie, S.; Li, W.; Yu, B., Total Synthesis of Nucleoside Antibiotic A201A. *J. Am. Chem. Soc.* **2014,** *136*, 4157. (f) Li, J.; Yu, B., A Modular Approach to the Total Synthesis of Tunicamycins. *Angew. Chem., Int. Ed.* **2015,** *54*, 6618. (g) Zhu, D.; Yu, B., Total Synthesis of Linckosides A and B, the Representative Starfish Polyhydroxysteroid Glycosides with Neuritogenic Activities. *J. Am. Chem. Soc.* **2015,** *137*, 15098. Zhu, D.; Yu, B. *J. Am. Chem. Soc.* **2015**, *137*, 15098. (h) Yu, B., Gold(I)-Catalyzed Glycosylation with Glycosyl *o*-Alkynylbenzoates as Donors. *Acc. Chem. Res.* **2018**, *51*, 507. (i) Zhu, Y.; Shen, Z.; Li, W.; Yu, B., Stereoselective synthesis of β-rhamnopyranosides via gold(i)-catalyzed glycosylation with 2-alkynyl-4-nitro-benzoate donors. *Org. Biomol. Chem.* **2016,** *14*, 1536.

(11) (a) Hotha, S.; Kashyap, S., Propargyl Glycosides as Stable Glycosyl Donors: Anomeric Activation and Glycoside Syntheses. *J. Am. Chem. Soc.* **2006,** *128*, 9620. (b) Kayastha, A. K.; Hotha, S., Versatile gold catalyzed transglycosidation at ambient temperature. *Chem. Commun.* **2012,** *48*, 7161. (c) Thadke, S. A.; Mishra, B.; Islam, M.; Pasari, S.; Manmode, S.; Rao, B. V.; Neralkar, M.; Shinde, G. P.; Walke, G.; Hotha, S., [Au]/[Ag]-catalysed expedient synthesis of branched heneicosafuranosyl arabinogalactan motif of *Mycobacterium tuberculosis* cell wall. *Nat. Commun.* **2017,** *8*, 14019. (d) Mishra, B.; Neralkar, M.; Hotha, S., Stable Alkynyl Glycosyl Carbonates: Catalytic Anomeric Activation and Synthesis of a Tridecasaccharide Reminiscent of Mycobacterium tuberculosis Cell Wall Lipoarabinomannan. *Angew. Chem., Int. Ed.* **2016,** *55*, 7786. (e) Sureshkumar, G.; Hotha, S., $AuBr_3$ mediated glycosidations: synthesis of tetrasaccharide motif of the Leishmania donovani lipophosphoglycan. *Glycoconj. J.* **2012,** *29*, 221. (f) Thadke, S. A.; Mishra, B.; Hotha, S., Facile Synthesis of β- and α-Arabinofuranosides and Application to Cell Wall Motifs of M. tuberculosis. *Org. Lett.* **2013,** *15*, 2466. (g) Kayastha, A. K.; Hotha, S., Gold-catalyzed glycosidation for the synthesis of trisaccharides by applying the armed–disarmed strategy. *Beilstein J. Org. Chem.* **2013,** *9*, 2147.

(12) Dong, X.; Chen, L.; Zheng, Z.; Ma, X.; Luo, Z.; Zhang, L., Silver-catalyzed stereoselective formation of glycosides using glycosyl ynenoates as donors. *Chem. Commun.* **2018,** *54*, 8626.

(13) Kristensen, S. K.; Salamone, S.; Rasmussen, M. R.; Marqvorsen, M. H. S.; Jensen, H. H., Glycosyl ortho-Methoxybenzoates: Catalytically Activated Glycosyl Donors with an Easily Removable and Recyclable Leaving Group. *Eur. J. Org. Chem.* **2016,** *2016*, 5365.

(14) (a) Shaw, M.; Kumar, Y.; Thakur, R.; Kumar, A., Electron-deficient pyridinium salts/thiourea cooperative catalyzed *O*-glycosylation via activation of *O*-glycosyl trichloroacetimidate donors. *Beilstein J. Org. Chem.* **2017**, *13*, 2385. (b) Shaw, M.; Kumar, A.; Thakur, R., Recent Developments in the Stereoselective Synthesis of *trans-β*- and 2-deoxy-*β*-Glycosides. *Trends Carbohydr. Res.* **2017**, *9*, 1.

(15) Satoh, H.; Hansen, H. S.; Manabe, S.; van Gunsteren, W. F.; Hünenberger, P. H., Theoretical Investigation of Solvent Effects on Glycosylation Reactions: Stereoselectivity Controlled by Preferential Conformations of the Intermediate Oxacarbenium-Counterion Complex. *J. Chem. Theory Comput.* **2010,** *6*, 1783.

(16) Vibhute, A. M.; Dhaka, A.; Athiyarath, V.; Sureshan, K. M., A versatile glycosylation strategy via Au(III) catalyzed activation of thioglycoside donors. *Chem. Sci.* **2016,** *7*, 4259.

(17) Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. Iodonium Ion Promoted Reactions at the Anomeric Centre. II An Efficient Thioglycoside Mediated Approach toward the Formation of 1,2-Trans Linked Glycosides and Glycosidic Esters. *Tetrahedron Lett.* **1990**, *31*, 1331.

(18) Feldman, K. S.; Lawlor, M. D.; Sahasrabudhe, K., Ellagitannin Chemistry. Evolution of a Three-Component Coupling Strategy for the Synthesis of the Dimeric Ellagitannin Coriariin A and a Dimeric Gallotannin Analogue. *J. Org. Chem.* **2000,** *65*, 8011.

(19) Sun, L.; Wu, X.; Xiong, D. C.; Ye, X. S., Stereoselective Koenigs–Knorr Glycosylation Catalyzed by Urea. *Angew. Chem., Int. Ed.,* **2016,** *55*, 8041.

(20) Medina, S.; Henderson, A. S.; Bower, J. F.; Galan, M. C., Stereoselective synthesis of glycosides using (salen)Co catalysts as promoters. *Chem. Commun.* **2015,** *51*, 8939.

(21) Heuckendorff, M.; Bendix, J.; Pedersen, C. M.; Bols, M., β-Selective Mannosylation with a 4,6-Silylene-Tethered Thiomannosyl Donor. *Org. Lett.* **2014,** *16*, 1116.

(22) Yang, J.; Cooper-Vanosdell, C.; Mensah, E. A.; Nguyen, H. M., Cationic Palladium(II)-Catalyzed Stereoselective Glycosylation with Glycosyl Trichloroacetimidates. *J. Org. Chem.* **2008,** *73*, 794.

(23) Ma, T.; Li, C.; Zhang, Z.-X.; Wang, Z.; Yu, L.; Xue, W., Indium(III) Iodide-Catalyzed Stereoselective Synthesis of β-Glucopyranosides by Using a Glucosyl Fluoride Donor with 2-*O*-Benzoyl-3,4,6-Tri-*O*-Benzyl Protection. *Synlett* **2017,** *28*, 2633.

(24) Tomono, S.; Kusumi, S.; Takahashi, D.; Toshima, K., Armed–disarmed effect of remote protecting groups on the glycosylation reaction of 2,3-dideoxyglycosyl donors. *Tetrahedron Lett.* **2011,** *52*, 2399.

(25) Hu, J.-C.; Feng, A.-F. W.; Chang, B.-Y.; Lin, C.-H.; Mong, K.-K. T., A flexible 1,2-cis *α*-glycosylation strategy based on *in situ* adduct transformation. *Org. Biomol. Chem.* **2017,** *15*, 5345.

(26) Smoot, J. T.; Demchenko, A. V., How the Arming Participating Moieties can Broaden the Scope of Chemoselective Oligosaccharide Synthesis by Allowing the Inverse Armed−Disarmed Approach. *J. Org. Chem.* **2008,** *73*, 8838.