Accepted Manuscript

A catalytic Koenigs-Knorr glycosylation based on acceptor activation with $In(NTf_2)_3$

Changwei Li, Haijing Liang, Zhan-xin Zhang, Zhaoyan Wang, Lan Yu, Huanxiang Liu, Fengli An, Shaohua Wang, Lixia Ma, Weihua Xue

PII: S0040-4020(18)30639-2

DOI: 10.1016/j.tet.2018.05.080

Reference: TET 29587

To appear in: *Tetrahedron*

Received Date: 9 April 2018

Revised Date: 23 May 2018

Accepted Date: 28 May 2018

Please cite this article as: Li C, Liang H, Zhang Z-x, Wang Z, Yu L, Liu H, An F, Wang S, Ma L, Xue W, A catalytic Koenigs-Knorr glycosylation based on acceptor activation with $In(NTf_2)_3$, *Tetrahedron* (2018), doi: 10.1016/j.tet.2018.05.080.

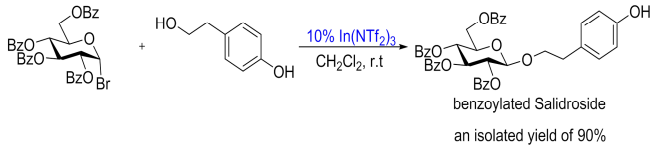
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

A catalytic Koenigs-Knorr glycosylation based on acceptor activation with $In(NTf_2)_3$

Leave this area blank for abstract info.

Changwei Li, Haijing Liang, Zhan-xin Zhang, Zhaoyan Wang, Lan Yu, Huanxiang Liu, Fengli An, Shaohua Wang, Lixia Ma, Weihua Xue*
School of Pharmacy, Lanzhou University



benzoylated Salidroside

an isolated yield of 90%

Tetrahedron
journal homepage: www.elsevier.com

A catalytic Koenigs-Knorr glycosylation based on acceptor activation with $In(NTf_2)_3$

Changwei Li, Haijing Liang, Zhan-xin Zhang, Zhaoyan Wang, Lan Yu, Huanxiang Liu, Fengli An, Shaohua Wang, Lixia Ma, Weihua Xue*

School of Pharmacy, Lanzhou University, Lanzhou, 730000, China

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Koenigs-Knorr Glycosylation
Acceptor activation
$In(NTf_2)_3$
catalytic
stereoselective

ABSTRACT

The development of efficient glycosylation methods is important for gaining better insight into biological processes of significance to medicinal chemistry. Herein, we describe an $In(NTf_2)_3$ - catalyzed Koenigs-Knorr glycosylation based on the activation of an alcoholic hydroxyl group. A catalytic amount of $In(NTf_2)_3$ enables effective glycosylation of diverse alcohols with peracylated aldosyl bromides as donors, leading to the stereoselective formation of a series of glycosides in satisfactory yields. The protocol is characterized by mild reaction conditions and good functional-group tolerance, while obviating any need for any additive. Moreover, the potential utility of this transformation is demonstrated by the convenient syntheses of key building blocks for biomolecules of medicinal relevance.

*Corresponding author. Tel: +86 0536 8915682; *E-mail address*: xuewh2018@sina.com

1. Introduction

Glycosides and polysaccharides are broadly prevalent in organisms. Their carbohydrate components are well known to be closely associated with many physiological processes relevant to human life.[1] Synthetic access to ample *O*-glycosidically linked carbohydrate units is often necessary to gain better insight in their involvement into biologically significant processes.[2] Chemical glycosylation is a common strategy for glycosidic-bond formation.

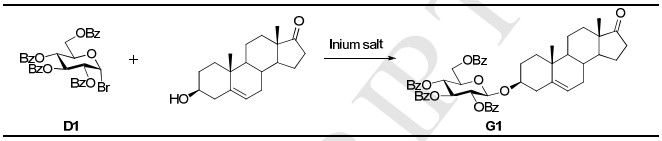
Currently the development of methods for accessing the glycosidic linkages has grown into a topic of intensive research interest in the field of glycochemistry. The generation of complex and diverse scaffolds from structurally simple glycosyl donors affords the advantages of operational simplicity and atom economy. The Koenigs-Knorr reaction[3] provides an attractive pathway to glycosides because aldosyl halides are a useful category of building blocks, a consequence of their low costs and ready accessibilities. Moreover, glycosyl bromides are prone to exist as single isomers, which make them relatively easily isolate and purify. Unfortunately, this named reaction relies on the use of stoichiometric halophilic reagents such as $Hg(CN)_2$,[4] $AgNO_3$,[5] AgOTf,[6] $AgClO_4$,[7] and Ag_2O,[8] as well as others.[9] Recently a remarkably modified version of the Koenigs-Knorr reaction was reported by Ye and co-workers,[10] who found that a wide range of alcohols could be converted into glycosides through an interactive process involving glycosyl chloride donors and a catalytic amount of thiourea. In spite of these encouraging results, large excess of additives in combination with the reflux conditions required to achieve the good yields is a major drawback of the method. Hence, the development of a novel catalyst that facilitates the easy formation of glycosides under mild condition is still important for continued advancements in this area.

We also paid significant attention to substantial advances made in the transition-metal-catalyzed syntheses of glycosides. In general, the use of a transition-metal catalyst provides a mild and orthogonal alternative approach to traditional glycosylation chemistry.[11-15] Recently, we reported the $InBr_3$-catalyzed syntheses of thioaldoses[16] through reactions of peracetylated aldoses with arylthiols, and subsequently discovered InI_3 to be an effective glucosidation catalyst with a glucosyl fluoride donor.[17] Taking into account on the above advances about glycochemistry, we wondered whether or not Koenigs-Knorr glycosylation would proceed under indium catalysis. Although several glycosylation protocols using indium halides as promoters have been reported,[18] they suffer from narrow substrate scope and relatively high promoter dosage. Herein we describe a new advance in the indium-catalyzed synthesis of glycoside.

2. Result and discussion

To test reaction conditions, perbenzoylated glucosyl bromide (**D1**) was initially exposed to with epiandrosterone (1.2 equiv) and catalytic $InBr_3$ (0.1 equiv) in CH_2Cl_2 at 23℃ under argon (**Table 1**). To our delight, our hypothesis was validated, with **G1** obtained in 43% isolated yield after 24 h (Entry 1, Table 1). However, the subsequent use of the reflux conditions did not help to further increase the yield (45%, Entry 2, Table 1), and the use of $InCl_3$ instead of $InBr_3$ resulted in a much lower yield (17%, Entry 3, Table 1).These results, together with our recent study on the indium-catalyzed (thio)glycosidations suggest that the activity of catalyst is significantly influenced by the counterions, consequently we further examine the effects of other commercially available indium salts. **G1** was formed in 51% isolated yield in the presence of catalytic $In(OTf)_3$ (0.1 equiv) (Entry 4, Table1), which increased to 62% when InI_3 was used as the catalyst (Entry 5, Table 1). We eventually discovered that the reaction was most efficient in the presence of $In(NTf_2)_3$ (0.01 mmol) in CH_2Cl_2 for 4h, which facilitated the isolation of **G1** in 96% yield (Entry 6, Table 1). We were able to decrease the catalyst loading to 0.05 equiv. with longer reaction times or under reflux with minimal effect on the yield (94-97%, Entries 7 and 8, Table 1). Hence, the conditions listed in Entry 6 were taken as optimal.

Table1. Optimizing the indium-catalyzed Koenigs-Knorr reaction[a]



Entry	Indium salt (equiv.)	T(℃)	Time(h)	Isolated yield[b](%)
1	$InBr_3$(0.1)	23	24	43
2	$InBr_3$(0.1)	40	24	45
3	$InCl_3$(0.1)	23	24	17
4	$In(OTf)_3$(0.1)	23	24	51
5	InI_3(0.1)	23	2	62
6	$In(NTf_2)_3$(0.1)	23	4	96
7	$In(NTf_2)_3$(0.05)	23	10	94
8	$In(NTf_2)_3$(0.05)	40	1	97

[a] Reaction conditions: **D1** (0.1 mmol), epiandrosterone (0.12 mmol), and 4Å molecular sieves, with stirring in CH_2Cl_2 (2 mL) under Ar. [b] Isolated yield based on **D1**.

Having established the optimal reaction conditions, we turned our attention to the scope of the reaction using known donors **D1-7** (**Figure 1**) and acceptors. We first investigated glycosylation with readily accessible aldosyl bromides **D1-5** including fully acylated glucosyl (**D1**, **D5)**, galactosyl(**D2**), mannosyl(**D3**), and rhamnosyl(**D4**) donors, which they were successively treated with a series of alcohols to construct glycosidic bonds.

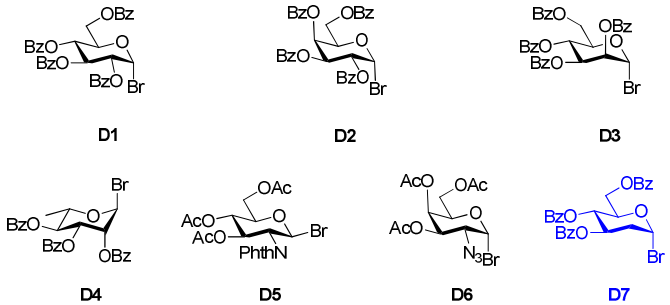


Figure 1. Glycosyl donors in $In(NTf_2)_3$-catalyzed glycosylation

As shown in **Figure 1**, primary, secondary, and tertiary alcohols were readily accommodated in this transformation to produce in corresponding glycosides **G2-18** in good yields and with 1, 2-*trans* stereocontrol. For instance, sterically bulky 1-adamantanol was effectively glucosidated, with the corresponding product **G2** obtained in a good yield (89%). Especially interestingly, an intermediate of significance to potential pharmaceutical molecules was examined to demonstrate the synthetic potential of this protocol. Tyrosol underwent the regioselective glucosidation to provide **G4** in a 90% yield; this glucoside, bearing a free phenolic hydroxyl group, is a direct precursor of salidroside, which is a significant bioactive component isolated from *Rhodiola sachalinensis*.[19] Consequently, the natural product, which was cumbersome to prepare previously using other methodologies,[20] are now economically obtained using our protocol and subsequent routine deprotection.

Remarkably, this method was also applicable to 2-azidogalactosyl bromide (**D6**). **D6** and bulky acceptors were rapidly coupled to provide azide derivatives **G19** and **20** in high yields. In the case of a typical amino acid, the coupling of *N*-Fmoc threonine ester with **D6** delivered the glycosylation product **G21** (88%, α/β = 6:1), which often serves as a pivotal synthon in the syntheses of biologically important glycoproteins carrying *N*-acetylgalactosamine units α-*O*-glycosidically linked to threonine residues. Furthermore, 2-deoxyglycoside **G22** could be efficiently and α-selectively prepared when 2-deoxy sugar bromide (**D7**) was used as the donor. Our results also showed that the $In(NTf_2)_3$-promoted glycosylation reactions with glycosyl bromide donors tolerated a wide range of functional substituents, including azido(**G3**, **G19**), phenolic hydroxyl(**G4**), ketal(**G6**), halide(**G7**, **G8**), silyl(**G10**), ester(**G17**), and carbamate (**G14**, **G21**) groups; these coupling reactions proceeded smoothly within about 4 h.

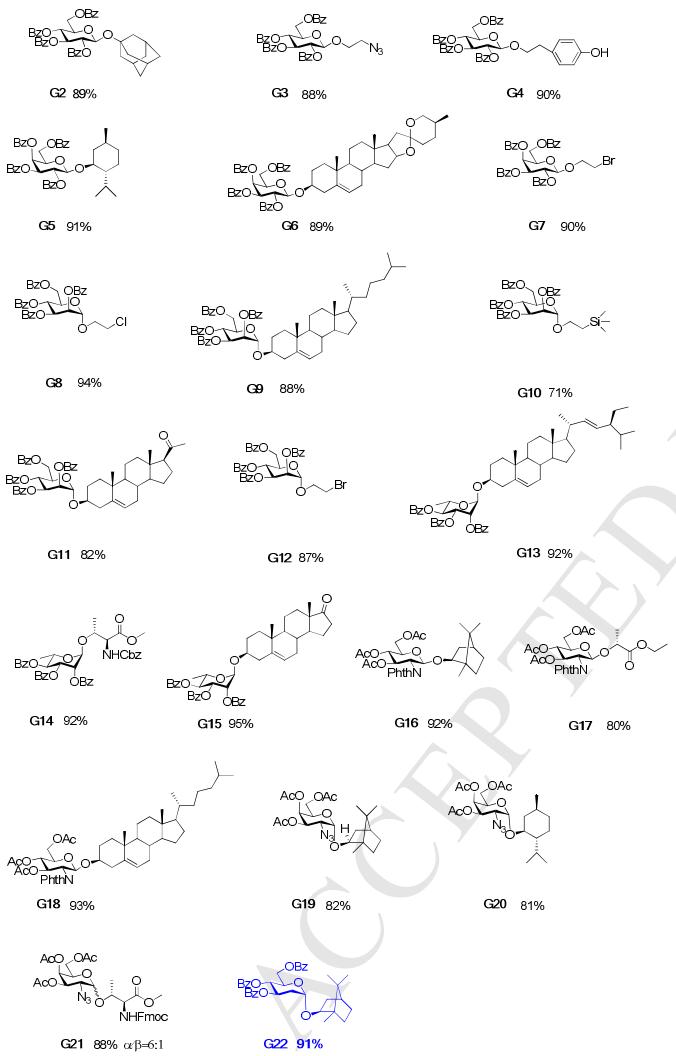
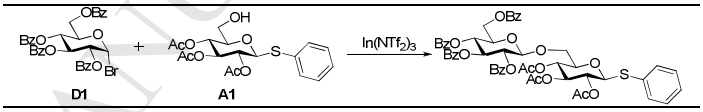


Figure 2. List of glycosides accessed by the $In(NTf_2)_3$-catalyzed glycosylation of common alcohols with donor **D1-6**. Reagents and conditions: donor (0.1 mmol), acceptor (0.12 mmol), $In(NTf_2)_3$(0.01 mmol), CH_2Cl_2 (2 mL) at room temperature under Ar. Isolated yields based on the donor molar equivalent and anomeric linkage as determined using the NMR spectra

Given the efficiencies of the indium-catalyzed glycosylations of ordinary nucleophiles we decided to investigate the extension of this methodology to the synthesis of disaccharides from alcohol containing carbohydrate motifs. Unexpectedly, glycosylation using compound **D1** as the donor and **A1** as the acceptor was sluggish and provided an unsatisfactory yield (46%) of the desired product **G23** even after 24 h. These results demonstrated the hydroxyl groups of sugar are less nucleophilic than those of the simple alcohols. Therefore, we were required to slightly modify the reaction conditions in order to efficiently glycosylating the alcohol moieties of sugars. In our attempts to improve the yields, $In(NTf_2)_3$ and **A1** dosages were screened. An increase in the dosage of A1 to only1.5 equiv led to a slightly higher yield (52%; Entry 1, Table 2) after stirring for 24h at room temperature. Notably, when the catalyst loading was increased to 0.15 equiv. and 1.5 equiv of **A1** was used, a good conversion of **D1** was observed (76%; Entry 2, Table 2); further increasing the amount of **A1** to 2.0 equiv led to a yield of 85% (Entry 3, Table 2), while subjecting the reaction to the reflux conditions resulted in no significant change in yield (Entry 4, Table 2).

Significantly, the yield dropped sharply when other solvents were used instead of CH_2Cl_2 (Entries 5-7, Table2). Using these modified conditions (Entry 3, Table 2), some other disaccharides **G 24-29** (**Figure 2**) were obtained in synthetically useful yields that ranged from 75 to 92%. Disaccharides **G23-28** were obtained with uniform 1, 2-*trans* stereoselectivity when donors **D1-5** were employed, whereas glycosyl donor **D6** afforded exclusively the disaccharide **G29** as an α- anomer.

Table2. Optimization for the $In(NTf_2)_3$-catalyzed Koenigs-Knorr reaction for disaccharide synthesis[a]



Entry	$In(NTf_2)_3$ (equiv)	**A1**(equiv)	Solvent	Isolated yields[b] (%)[b]
1	0.1	1.5	CH_2CH_2	52
2	0.15	1.5	CH_2CH_2	76
3	0.15	2.0	CH_2CH_2	85
4[c]	0.15	2.0	CH_2CH_2	87
5	0.15	2.0	toluene	61
6	0.15	2.0	THF	47
7	0.15	2.0	CH_3CN	40

[a] Reactions were run with **D1** (0.1 mmol), **A1** and 4Å MS in the stirred solvent (2 mL) under Ar for 24 h. [b] Isolated yields based on **D1**. [c]The reaction was carried out under reflux.

Donors **D1-5** bearing acyl groups at their C-2 position benefit from neighboring -group participation effect, and reacted to generate only the 1, 2-*trans* glycosides **G1-18, 23-28**. In contrast, **D6** benefits from the anomeric effect, resulting the α-selectivity during 2-azidogalactosylation. In addition, an acetyl group at C-6 of **D6** becomes involved in remote neighboring-group participation, which is also helpful for the formation of glycosides with the high α-anomeric selectivities; hence, **D6** exhibits the strong preference of the formation of products **G19-21, 29** in a 1, 2-*cis*-selective manner. As for 2-deoxysugar donor **D7**, the anomeric effect of 2-deoxyglycosides favors the formation of **G22** as a single α-isomer. All of the synthesized *O*-glycosides were structurally characterized by ^1H and ^{13}C NMR spectroscopies. Additionally, the α-anomeric configuration of mannosides was further confirmed by NOE-based NMR spectroscopy (see Supporting Information). NMR analyses confirmed that except **G21** other glycosylation products were formed as single anomers in these reactions. These favorable results are encouraging, as they demonstrate the feasibility of facilitating Koenigs-Knorr reaction with catalytic amounts of indium and bode well for future synthetic applications in carbohydrate chemistry.

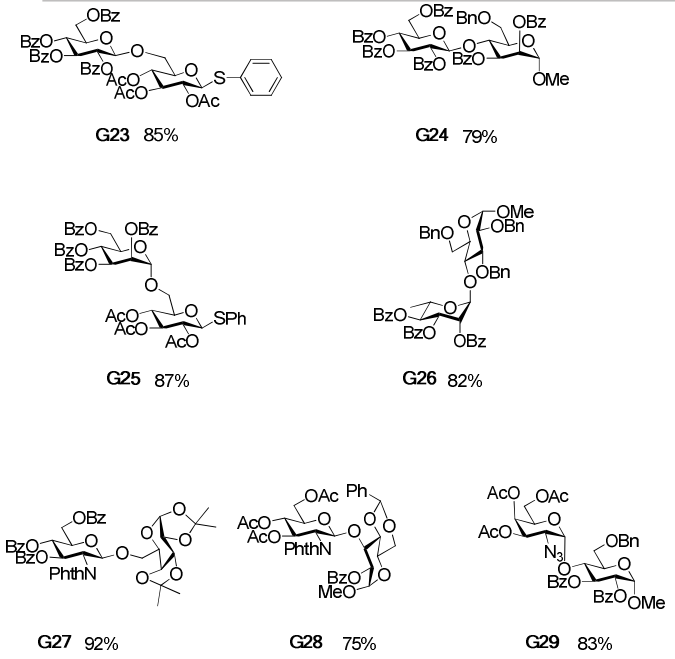


Figure 3. List of disaccharides accessed by the $In(NTf_2)_3$-catalyzed glycosylation of sugar alcohols with donor **D1-6**. Reagents and conditions: donor (0.1 mmol), acceptor (0.2 mmol), $In(NTf_2)_3$(0.015 mmol), CH_2Cl_2 (2 ml) at room temperature under Ar, isolated yields based on the donor molar equivalent and anomeric linkage as determined using the NMR spectra

To gain direct insight into the progress of the reaction, we elected to perform control ^{1}H NMR experiments in $CDCl_3$. First, **D1** was dissolved in $CDCl_3$ at room temperature and treated with an equimolar amount of $In(NTf_2)_3$. No changes in the chemical shifts of signals of the mixture relative to those of **D1** alone were detected by NMR spectroscopy (see Figure 4 in the Supporting Information), and **D1** was almost quantitatively recovered by the chromatography. Schmidt et al. showed that $AuCl_3$ catalyst interacts with 2-propanol as an acceptor to give RO-$AuCl_3$-H adduct during glycosylation. [9d] In a similar manner, we also found $In(NTf_2)_3$ interacted with 2-propanol, as evidenced by NMR spectroscopy. Our spectrum (Figure 5 in the Supporting Information) fully corresponded with that of Schmidt. The presence of $In(NTf_2)_3$ in $CDCl_3$ caused the chemical shift of the OH group in isopropanol to the downfield. It is worth mentioning that in addition to Au, In and Pd are also able to interact with alcohols to initiate glycosylation. In the study reported by Galan the glycosylation reaction proceeded via an alkoxy-palladium intermediate that increased the proton acidity of the alcohol and the nucleophilicity of its oxygen.[21] Therefore, we reasonably surmise that a shift in the OH signal was ascribable to an adduct formed by the bonding of $In(NTf_2)_3$ to an alcoholic hydroxyl. The above results clearly corroborate the indium-mediated acceptor activation mechanism of our novel Koenigs-Knorr glycosylation system, which is different to the donor activation mechanism involved in thiourea-catalyzed Koenigs-Knorr reaction recently reported by Ye and co-workers. [8]

3. Conclusion

An efficient glycosylation protocol has been developed that employs indium-promoted Koenigs-Knorr reaction with $In(NTf_2)_3$ at low catalytic loadings. The reactions proceeded smoothly at room temperature to afford a variety of glycosides in the satisfactory yields and with the good stereocontrol. An additive is required, which is an important feature of this method. Finally, mechanistic investigations using NMR spectroscopy suggest that the reaction proceeds via the formation of an alkoxy-indium adduct that displays enhanced oxygen-centered nucleophilicity relative to a free alcohol. This represents an interesting example of a Koenigs-Knorr glycosylation process mediated by acceptor activation. Further investigations into the application of indium catalysts to glycosidation reactions are underway in our laboratory.

4. Experimental section

4.1 *General inforamation*

All operations were carried out in a nitrogen-filled glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Dichloromethane was dried over calcium hydride prior to use. $In(NTf_2)_3$ was purchased from Aldrich. All other reagents, obtained from commercial sources, were used without further purification. Flash column chromatography was carried out on Silica Gel 60 (230-400 mesh). The reactions were monitored by TLC. Spots were visualized by irradiation with a UV lamp at 280 nm or by spraying with 10% H_2SO_4 in ethanol and subsequently heating on a hot plate. NMR spectra were obtained on a Bruker AVANCE DMX 400 spectrometer operating at 400 MHz for ^{1}H-NMR and NOE spectra, 100 MHz for ^{13}C-NMR. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q=quatet, dd = doublet of doublets, m = multiplet. Coupling constants *J* were reported in hertz unit (Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. HRMS determinations were made with the use of JOEL MStation (JMS-700) Mass Spectrometer. Optical rotations were acquired on a JASCO DIP-370 digital polarimeter. Analytical and spectral data of all the known compounds are consistent with the reported values.

4.2 *Procedures for the $In(NTf_2)_3$-catalyzed glycosidation of the common alcohols*

To a solution of glycosyl bromide (0.1 mmol) in anhydrous CH_2Cl_2 (2 mL) containing $In(NTf_2)_3$ (9 mg, 0.01mmol) and 4 Å molecular sieves (5 mg), alcohol (0.12mmol) was added under Ar. The mixture was allowed to stir for 2 h at room temperature. The reaction mixture was evaporated under reduced pressure. The resultant residue was rapidly eluted through chromatograph on silica gel with toluene or hexane in EtOAc to yield the title compound.

4.2.1 *Pregnenolonyl 2, 3, 4, 6-tetra-O-Bz-β-D-glucopyranoside (G1)*

Yield 96% (83mg); White solid; mp 221-223 ℃ ; $[\alpha]_D^{23}$ +63.7(c=1.0, $CHCl_3$); R_f =0.30(Ethyl acetate/toluene, 1/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.91(d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.56-7.46 (m, 3H), 7.39 (ddd, *J* = 11.9, 7.9, 4.1 Hz, 6H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.90 (t, *J* = 9.6 Hz, 1H), 5.63 (t, *J* = 9.7 Hz, 1H), 5.52-5.45 (m, 1H), 4.94 (d, *J* = 7.9 Hz, 1H), 4.64-4.50 (m, 2H), 4.16 (s, 1H), 3.60 (dt, *J* = 11.2, 6.2 Hz, 1H), 2.48-2.31 (m, 2H), 2.05 (dt, *J* = 18.9, 9.0 Hz, 1H), 1.90 (s, 2H), 1.80-1.66 (m, 3H), 1.58 (d, *J* = 13.8 Hz, 2H), 1.48 (d, *J* = 12.1 Hz, 2H), 1.24-1.15 (m, 5H), 0.98 (s, 2H), 0.83 (s, 3H), 0.71 (s, 3H), 0.61 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 165.2, 165.0, 133.4, 133.2, 133.1, 133.0, 129.8, 129.7, 129.7, 129.6, 129.5, 129.0, 128.8, 128.8, 128.4, 128.3, 128.3, 128.2, 128.2, 125.3, 100.0, 79.9, 73.0, 72.1, 72.0, 70.1, 63.4, 51.4, 47.7, 44.6, 36.7, 35.8, 35.6, 34.9, 34.5, 31.5, 30.8,

29.2, 28.2, 21.7, 20.4, 13.8, 12.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{53}H_{55}O_{11}$ 867.3744; found: 867.3750.

4.2.2 Adamantyl 2, 3, 4, 6-tetra-O-Bz-β-D-glucopyranoside (G2)

Yield 89% (65 mg); White solid; mp 206-208 ℃ ; $[\alpha]_D^{23}$ +57.4(c=1.0, $CHCl_3$); R_f =0.18(Ethyl acetate/toluene, 1/60). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.94 (dd, *J* = 15.7, 7.6 Hz, 4H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.55-7.47 (m, 3H), 7.44-7.32 (m, 8H), 7.29 (d, *J* = 7.7 Hz, 1H), 5.93 (t, *J* = 9.6 Hz, 1H), 5.59-5.47 (m, 2H), 5.13 (d, *J* = 7.9 Hz, 1H), 4.59 (dd, *J* = 11.9, 3.0 Hz, 1H), 4.49 (dd, *J* = 11.9, 7.1 Hz, 1H), 4.18 (d, *J* = 7.0 Hz, 1H), 2.02 (s, 3H), 1.82 (d, *J* = 11.3 Hz, 3H), 1.66 (d, *J* = 11.5 Hz, 3H), 1.58-1.46 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 165.3, 164.9, 133.4, 133.1, 133.0, 129.8, 129.7, 129.7, 129.6, 129.5, 129.0, 128.9, 128.8, 128.4, 128.3, 128.3, 128.2, 128.2, 94.3, 75.8, 73.2, 72.1, 71.9, 70.3, 63.7, 42.3, 36.0, 30.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{44}H_{43}O_{10}$ 731.2856; found: 731.2859.

4.2.3 2'-Azidoethyl 2, 3, 4, 6-tetra-O- Bz -β-D-glucopyranoside (G3)

Yield 88% (59 mg); Colorless oil; $[\alpha]_D^{23}$ +10.2(c=1.0, $CHCl_3$); R_f =0.21(Ethyl acetate/hexane, 1/4).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.59 -7.46 (m, 3H), 7.44 -7.38 (m, 4H), 7.38-7.33 (m, 3H), 7.28 (d, *J* = 7.7 Hz, 2H), 5.92 (t, *J* = 9.6 Hz, 1H), 5.69 (t, *J* = 9.7 Hz, 1H), 5.56 (t, *J*=9.6, 1H), 4.94 (d, *J* = 7.8 Hz, 1H), 4.67 (dd, *J* = 12.1, 3.0 Hz, 1H), 4.51 (dd, *J*=12.1, 5.1Hz,1H), 4.18 (dt, *J* = 9.1, 4.0 Hz, 1H), 4.05 (dt, *J* = 10.4, 4.5 Hz, 1H), 3.75 (ddd, *J* = 11.2, 7.9, 3.7 Hz, 1H), 3.44 (ddd, *J* = 11.8, 7.8, 3.8 Hz, 1H), 3.30 (dt, *J* = 13.2, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.8, 165.1, 165.1, 133.4, 133.2, 133.2, 133.2, 129.8, 129.8, 129.7, 129.7, 129.5, 129.2, 128.7, 128.4, 128.3, 128.2, 101.2, 72.8, 72.4, 71.7, 69.6, 68.4, 63.0, 50.6.HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{36}H_{32}N_3O_{10}$ 666.2088; found: 666.2084.

4.2.4 (4'-hydroxyphenyl)ethyl 2, 3, 4, 6-tetra-O-Bz-β-D-glucopyranoside (G4)

Yield 90% (64mg); Colorless oil; $[\alpha]_D^{23}$ +27.1(c=1.0, $CHCl_3$); R_f =0.33 (Ethyl acetate/hexane, 1/4).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.98-7.92 (m, 4H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.54 (dd, *J* = 13.1, 5.7 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.43-7.35 (m, 6H), 7.28 (dd, *J* = 14.2, 6.6 Hz, 3H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.15 (t, *J* = 9.8 Hz, 1H), 5.63 (t, *J* = 9.9 Hz, 1H), 5.32 (d, *J* = 3.5 Hz, 1H), 5.27 (dd, *J* = 10.1, 3.6 Hz, 1H), 4.49 (dd, *J* = 12.2, 2.5 Hz, 1H), 4.33 (dd, *J* = 12.2, 5.0 Hz, 1H), 3.99 (ddd, *J* = 9.6, 4.5, 2.7 Hz, 1H), 3.95-3.88 (m, 1H), 3.69 (dt, *J* = 9.4, 6.1 Hz, 1H), 2.86 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 165.8, 165.3, 154.2, 133.4, 133.4, 133.1, 130.7, 130.2, 129.9, 129.9, 129.7, 129.7, 129.6, 129.1, 129.0, 128.8, 128.4, 128.4, 128.3, 115.2, 95.5, 72.0, 70.5, 69.4, 68.9, 67.6, 62.9, 35.0.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{42}H_{37}O_{11}$ 717.2336; found: 717.2340.

4.2.5 (L)-Mentyl 2, 3, 4, 6-tetra-O-Bz-α-D-galactopyranoside (G5)

Yield 91% (67mg); Colorless oil; $[\alpha]_D^{23}$ +46.5(c=1.0, $CHCl_3$); R_f =0.47(Ethyl acetate/hexane, 1/5).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.58-7.46 (m, 5H), 7.40 (dt, *J* = 18.7, 7.7 Hz, 6H), 5.98 (d, *J* = 2.8 Hz, 1H), 5.74 (dd, *J* = 10.3, 8.0 Hz, 1H), 5.58 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.87 (d, *J* = 7.9 Hz, 1H), 4.62 (dd, *J* = 11.2, 6.7 Hz, 1H), 4.42 (dd, *J* = 11.3, 6.3 Hz, 1H), 4.29 (t, *J* = 6.5 Hz, 1H), 3.48 (td, *J* = 10.7, 4.2 Hz, 1H), 2.36 (s, 0H), 1.94 (d, *J* = 12.0 Hz, 1H), 1.59 (s, 3H), 1.24 (d, *J* = 13.9 Hz, 3H), 0.87 (d, *J* = 7.1 Hz, 3H), 0.74 (dd, *J* = 11.9, 6.7 Hz, 7H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.7, 165.6, 165.2, 133.5, 133.2, 133.1, 130.0, 129.8, 129.8, 129.7, 129.6, 129.5, 129.2, 128.9, 128.6, 128.4, 128.3, 99.9, 79.9, 72.1, 71.2, 70.0, 68.4, 62.3, 47.3, 41.2, 34.1, 31.4, 25.1, 23.0, 22.0, 20.9, 15.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{44}H_{47}O_{10}$ 735.3169; found: 735.3165.

4.2.6 Diosgenyl 2, 3, 4, 6-tetra-O-Bz-α-D-galactopyranoside (G6)

Yield 89% (87mg); Colorless oil; $[\alpha]_D^{23}$ +40.9(c=1.5, $CHCl_3$); R_f =0.36 (Ethyl acetate/toluene1/20).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.5 Hz, 2H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.56 (s, 2H), 7.52-7.47 (m, 3H), 7.40 (dt, *J* = 15.5, 7.6 Hz, 6H), 5.98 (d, *J* = 3.0 Hz, 1H), 5.77 (dd, *J* = 10.2, 8.0 Hz, 1H), 5.59 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.22 (s, 1H), 4.91 (d, *J* = 8.0 Hz, 1H), 4.68 (dd, *J* = 11.2, 6.8 Hz, 1H), 4.46-4.38 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 1H), 3.56 (s, 1H), 3.48 (d, *J* = 10.1 Hz, 1H), 3.37 (t, *J* = 10.9 Hz, 1H), 2.19 (s, 2H), 1.97 (s, 2H), 1.89-1.84 (m, 1H), 1.74 (dd, *J* = 14.8, 5.1 Hz, 4H), 1.66-1.59 (m, 4H), 1.46 (s, 3H), 1.26 (s, 3H),1.08 (s,1H), 0.97 (d, *J* = 6.9 Hz, 4H), 0.93 (s, 4H), 0.80- 0.76 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.6, 165.6, 165.2, 140.3, 133.5, 133.2, 133.1, 130.2, 130.1, 129.8, 129.6, 129.5, 129.5, 129.0, 128.8, 128.7, 128.6, 128.4, 128.4, 128.3, 128.3, 121.7, 109.3, 100.7, 80.8, 80.7, 71.9, 71.3, 67.0, 68.1, 66.8, 62.1, 56.5, 50.0, 41.6, 40.2, 39.7, 38.9, 37.1, 36.8, 32.0, 31.8, 31.4, 30.3, 29.6, 28.8, 20.8, 19.3, 17.1, 16.2, 14.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{60}H_{67}O_{12}$979.4633; found: 979.4635.

4.2.7Bromoethyl 2, 3, 4, 6-tetra-O-Bz-β-D-galactopyranoside (G7)

Yield 90% (63mg); Colorless oil; $[\alpha]_D^{23}$ -15.4(c=1.0, $CHCl_3$); R_f =0.48(Ethyl acetate/hexane, 1/3).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.47-7.41 (m, 4H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.27-7.22 (m, 2H), 6.00 (d, *J* = 3.4 Hz, 1H), 5.82 (dd, *J* = 10.4, 7.9 Hz, 1H), 5.62 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.92 (d, *J* = 7.9 Hz, 1H), 4.67 (dd, *J* = 11.3, 6.7 Hz, 1H), 4.44 (dd, *J* = 11.3, 6.4 Hz, 1H), 4.35 (t, *J* = 6.5 Hz, 1H), 4.23 (dt, *J* = 11.6, 5.9 Hz, 1H), 3.93 (dt, *J* = 11.2, 7.1 Hz, 1H), 3.49-3.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.5, 165.5, 165.3, 133.6, 133.3, 133.3, 133.2, 123.0, 129.8, 129.7, 129.3, 128.9, 128.7, 128.6, 128.5, 128.3, 128.3, 101.8, 71.6, 71.5, 69.9, 69.5, 68.0, 62.0, 29.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{36}H_{32}BrO_{10}$ 703.1179; found 703.1173.

4.2.8 Chloroethyl 2, 3, 4, 6-tetra-O-Bz-α-D-mannopyranoside (G8)

Yield 94% (67mg); Colorless oil; $[\alpha]_D^{23}$ +61.7(c=1.0, $CHCl_3$); R_f =0.34(Ethyl acetate/hexane, 1/4).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.62-7.55 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.45-7.34 (m, 8H), 7.28 (d, *J* = 7.7 Hz, 1H), 6.13 (t, *J* = 10.1 Hz, 1H), 5.93 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.75 (s, 1H), 5.16 (s, 1H), 4.71 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.57 (d, *J* = 10.1 Hz, 1H), 4.50 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.07 (dt, *J* = 11.6, 5.9 Hz, 1H), 3.94 (dt, *J* = 10.9, 5.3 Hz, 1H), 3.78 (t, *J* = 5.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.5, 165.4, 133.5, 133.4, 133.2, 133.0, 129.8, 129.7, 129.3, 129.1, 129.0, 128.6, 128.4,

128.3, 97.9, 70.4,70.0, 69.3, 68.8, 66.8, 62.8, 42.5. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{36}H_{32}ClO_{10}$ 659.1684; found: 659.1689.

4.2.9 Cholesteryl 2, 3, 4, 6-tetra-O-Bz-α-D-mannopyranoside (G9)

Yield 88% (85mg); Colorless oil; $[\alpha]_D^{23}$ -29.9(c=1.0, $CHCl_3$); R_f =0.56(Ethyl acetate/hexane, 1/6).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 7.5 Hz, 4H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.62-7.54 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (dt, *J* = 17.4, 8.2 Hz, 7H), 7.29-7.24 (m, 2H), 6.05 (t, *J* = 9.9 Hz, 1H), 5.95 (dd, *J* = 10.1, 3.1 Hz, 1H), 5.66 (s, 1H), 5.26 (s, 2H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.58-4.46 (m, 2H), 3.63 (s, 1H), 2.47 (d, *J* = 6.1 Hz, 2H), 2.06-1.80 (m, 6H), 1.60 (s, 3H), 1.49 (d, *J* = 10.6 Hz, 4H), 1.35 (d, *J* = 8.1 Hz, 3H), 1.26 (s, 2H), 1.13 (d, *J* = 6.3 Hz, 5H), 1.02 (d, *J* = 8.8 Hz, 5H), 0.93 (d, *J* = 6.4 Hz, 4H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.69 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.6, 165.5, 140.2, 133.4, 133.1, 133.0, 129.8, 129.8, 129.7, 129.4, 129.1, 129.0, 128.6, 128.4, 128.4, 128.3, 122.2, 96.0, 78.6, 71.2, 70.1, 68.9, 67.2, 63.3, 56.8, 56.2, 50.1, 42.3, 40.0, 39.8, 39.5, 36.9, 36.7, 36.2, 32.0, 31.9, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{61}H_{73}O_{10}$ 965.5204; found: 965.5213.

4.2.10 (2-Trimethylsilyl) ethyl 2, 3, 4, 6-tetra-O-Bz-α-D-mannopyranoside (G10)

Yield 71% (49mg); Colorless oil; $[\alpha]_D^{23}$ +14.5(c=1.5, $CHCl_3$); R_f =0.55(Ethyl acetate/hexane, 1/4).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 -8.05 (m, 4H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.62-7.54 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.47-7.30 (m, 8H), 7.26 (t, *J* = 7.7 Hz, 2H), 6.09 (t, *J* = 9.9 Hz, 1H), 5.94 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.67 (s, 1H), 5.13 (s, 1H), 4.69 (d, *J* = 10.1 Hz, 1H), 4.54-4.43 (m, 2H), 3.94 (td, *J* = 10.2, 6.2 Hz, 1H), 3.68 (td, *J* = 10.3, 6.2 Hz, 1H), 1.09 (tq, *J* = 13.8, 7.7 Hz, 2H), 0.07 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.5, 160.7, 133.4, 133.1, 133.0, 129.8, 129.8, 129.7, 129.4, 129.1, 129.0, 128.6, 128.4, 128.3, 97.1, 70.8, 70.1, 68.8, 67.1, 66.1, 63.1, 18.0, -1.4. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{39}H_{41}O_{10}Si$ 697.2469; found: 697.2476.

4.2.11 Epiandrosteronyl 2, 3, 4, 6-tetra-O-Bz-α-D-mannopyranoside (G11)

Yield 82% (67mg); White solid; mp 105-107 ℃ ; $[\alpha]_D^{23}$ +35.4(c=1.0, $CHCl_3$); R_f =0.39(Ethyl acetate/hexane, 1/4).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 8.0 Hz, 4H), 7.98 (d, *J* = 7.3 Hz, 2H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.63-7.54 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (h, *J* = 8.4, 7.1 Hz, 7H), 7.30-7.24 (m, 2H), 6.06 (t, *J* = 10.0 Hz, 1H), 5.95 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.65 (s, 1H), 5.26 (s, 2H), 4.68 (d, *J* = 10.1 Hz, 1H), 4.52 (dd, *J* = 18.0, 11.6 Hz, 2H), 3.62 (s, 1H), 2.59-2.43 (m, 3H), 2.20 (d, *J* = 10.9 Hz, 1H), 2.13 (s, 2H), 2.07 (d, *J* = 9.8 Hz, 1H), 2.02-1.85 (m, 4H), 1.66 (dd, *J* = 21.7, 10.5 Hz, 4H), 1.52-1.43 (m, 3H), 1.26 (s, 3H), 1.04 (s, 5H), 0.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 166.2, 165.6, 165.5, 140.2, 133.4, 133.1, 133.0, 129.8, 129.8, 129.7, 129.4, 129.1, 129.0, 128.6, 128.4, 128.4, 128.3, 121.9, 96.1, 78.6, 71.2, 70.1, 69.0, 67.2, 63.7, 63.2, 56.9, 49.9, 44.0, 40.0, 38.8, 36.9, 36.7, 31.8, 31.5, 27.8, 24.5, 22.8, 21.0, 19.3, 13.2. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{55}H_{59}O_{11}$895.4057; found: 895.4069.

4.2.12 Bromoethyl 2, 3, 4, 6-tetra-O-Bz-α-D-galactopyranoside (G12)

Yield 87% (61mg); Colorless oil; $[\alpha]_D^{23}$ +42.4(c=1.0, $CHCl_3$); R_f =0.59(Ethyl acetate/hexane, 1/3).^{1}H NMR (400 MHz, $CDCl_3$) δ8.13-8.03 (m, 4H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.59 (q, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.47-7.33 (m, 8H), 7.28 (d, *J* = 7.7 Hz, 1H), 6.13 (t, *J* = 10.1 Hz, 1H), 5.94 (dd, *J* = 10.2, 3.2 Hz, 1H), 5.74 (s, 1H), 5.17 (s, 1H), 4.71 (dd, *J* = 12.1, 2.2 Hz, 1H), 4.59 (d, *J* = 10.1 Hz, 1H), 4.51 (dd, *J* = 12.1, 4.4 Hz, 1H), 4.13 (dt, *J* = 12.6, 6.3 Hz, 1H), 4.01 (dt, *J* = 11.3, 5.7 Hz, 1H), 3.61 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.4, 165.4, 133.5, 133.5, 133.2, 133.1, 130.1, 129.9, 129.8, 129.8, 129.7, 129.2, 129.0, 128.9, 128.8, 128.6, 128.6, 128.4, 128.4, 128.3, 97.8, 70.3, 69.9, 69.4, 68.6, 66.7, 62.8, 29.7. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{36}H_{32}BrO_{10}$703.1179; found : 703.1175.

4.2.13 Stigmasterol 2, 3, 4-tri-O-Bz-α-D-rhamnoside (G13)

Yield 92% (80mg); Colorless oil; $[\alpha]_D^{23}$ +70.4(c=1.0, $CHCl_3$); R_f =0.56(Ethyl acetate/hexane, 1/8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (q, *J* = 7.9 Hz, 4H), 7.39 (dt, *J* = 15.3, 7.6 Hz, 4H), 5.87 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.67 (t, *J* = 10.0 Hz, 1H), 5.63 (s, 1H), 5.38 (s, 1H), 5.20-5.13 (m, 2H), 5.02 (dd, *J* = 15.1, 8.6 Hz, 1H), 4.28 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.59 (s, 1H), 2.44 (d, *J* = 10.1 Hz, 1H), 2.35 (t, *J* = 12.0 Hz, 1H), 2.01 (d, *J* = 11.9 Hz, 5H), 1.91 (d, *J* = 13.3 Hz, 1H), 1.74 (d, *J* = 14.6 Hz, 3H), 1.57-1.49 (m, 6H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.26 (t, *J* = 11.3 Hz, 3H), 1.19 (s, 1H), 1.16 (d, *J* = 9.3 Hz, 2H), 1.12 (s, 1H), 1.07 (s, 3H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.2 Hz, 3H), 0.83 (s, 1H), 0.80 (d, *J* = 6.6 Hz, 6H), 0.72 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 165.5, 140.1, 138.3, 133.4, 133.2, 133.0, 129.9, 129.7, 129.7, 129.5, 129.3, 129.3, 129.2, 128.5, 128.4, 128.2, 122.1, 95.8, 78.0, 72.1, 71.5, 70.1, 66.7, 56.8, 55.9, 51.2, 50.2, 42.2, 40.5, 39.7, 38.5, 37.3, 36.7, 31.9, 31.9, 29.5, 28.9, 25.4, 24.3, 21.2, 21.1, 21.1, 19.4, 19.0, 17.7, 12.2, 12.0. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{56}H_{71}O_8$ 871.5149; found : 871.5153.

4.2.14 O-(2, 3, 4-tri-O-Bz-α-D-rhamosyl)- N-Cbz-L-threonine methyl ester(G14)

Yield 92% (67mg); Colorless oil; $[\alpha]_D^{23}$ +38.9(c=1.0, $CHCl_3$); R_f =0.31 (Ethyl acetate/hexane, 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (dt, *J* = 15.4, 7.5 Hz, 4H), 7.39 (dq, *J* = 12.7, 7.5 Hz, 8H), 7.32 (d, *J* = 7.0 Hz, 1H), 5.79 (d, *J* = 8.5 Hz, 1H), 5.66 (q, *J* = 10.5 Hz, 4H), 5.18 (s, 2H), 5.02 (s, 1H), 4.69 (d, *J* = 8.5 Hz, 1H), 4.28 (d, *J* = 7.2 Hz, 1H), 4.06-4.00 (m, 1H), 3.91-3.80 (m, 5H), 1.36 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 165.7, 165.5, 165.4, 155.9, 136.1, 133.5, 133.3, 133.1, 129.9, 129.6, 129.2, 129.2, 129.1, 128.6, 128.5, 128.4, 128.2, 128.2, 128.1, 128.1, 97.5, 71.5, 70.4, 69.7, 68.1, 67.2, 67.1, 54.2, 52.7, 17.6. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{40}H_{40}NO_{12}$ 726.2551; found: 726.2549.

4.2.15Epiandrosteronyl 2, 3, 4-tri-O-Bz-α-D-rhamnoside (G15)

Yield 95% (71mg); Colorless oil; $[\alpha]_D^{23}$ +59.1(c=1.0, $CHCl_3$); R_f =0.53(Ethyl acetate/hexane, 1/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (q, *J* = 8.2, 7.7 Hz, 3H), 7.40 (dt, *J* = 15.2, 7.5 Hz, 3H), 7.27-7.23 (m, 2H), 5.86 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.67 (t, *J* = 10.0 Hz, 1H), 5.59 (s, 1H), 5.18 (s, 1H), 4.26 (dd, *J* = 9.7, 6.3 Hz, 1H), 3.66 (s, 1H), 2.44 (dd, *J* = 19.2, 8.7 Hz, 1H), 2.07 (dt, *J* = 18.9, 9.0 Hz, 1H), 1.92 (s, 2H), 1.81 (d, *J* = 12.1 Hz, 2H), 1.77-1.75 (m, 1H), 1.68 (d, *J* = 9.6 Hz, 2H), 1.60 (dd, *J* = 10.6, 3.6 Hz, 1H), 1.54 (dd, *J* = 8.6, 3.2 Hz, 1H), 1.49 (dd, *J* = 9.4, 3.1 Hz, 1H), 1.44 (d, *J* = 12.8 Hz, 1H), 1.35 (d, *J* = 6.2 Hz, 4H), 1.29 (d, *J* = 5.4 Hz, 1H), 1.25 (d, *J* = 3.8 Hz, 1H), 1.14 (d, *J* = 12.4 Hz, 1H), 1.03 (td, *J* = 13.4, 4.1 Hz, 2H), 0.88 (d, *J* = 7.8 Hz, 6H), 0.75-0.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 165.5, 133.4, 133.2, 133.0, 129.8, 129.7, 129.6, 129.5, 129.3, 129.2, 128.5, 128.4, 128.2, 95.6,

77.15, 72.01, 71.6, 70.1, 66.6, 54.4, 51.4, 47.8, 44.8, 37.0, 35.8, 35.9, 35.0, 34.0, 31.5, 30.9, 29.2, 28.4, 21.7, 20.5, 17.7, 13.8, 12.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{46}H_{51}O_9$ 747.3533; found: 747.3528.

4.2.16 Borneolyl 3, 4, 6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (G16)

Yield 92% (53mg); Colorless oil; $[\alpha]_D^{23}$ +9.8(c=1.0, $CHCl_3$); R_f =0.63(Ethyl acetate/hexane, 1/2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H), 5.86 (dd, *J* = 10.8, 9.1 Hz, 1H), 5.29 (d, *J* = 8.4 Hz, 1H), 5.21-5.14 (m, 1H), 4.38-4.30 (m, 2H), 4.16 (dd, *J* = 12.1, 2.4 Hz, 1H), 3.95 (d, *J* = 8.7 Hz, 1H), 3.84 (d, *J* = 8.0 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 4H), 1.88 (s, 3H), 1.66 (d, *J* = 13.3 Hz, 1H), 1.45 (s, 2H), 1.04 (d, *J* = 12.3 Hz, 1H), 0.82 (s, 3H), 0.76 (d, *J* = 7.7 Hz, 6H), 0.59 (dd, *J* = 13.2, 2.9 Hz, 1H), 0.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.2, 169.5, 134.3, 131.4, 123.5, 96.9, 83.6, 71.7, 70.7, 69.4, 62.2, 54.9, 49.1, 47.7, 44.7, 35.8, 27.9, 26.3, 20.7, 20.6, 20.5, 19.6, 18.8, 13.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{38}NO_{10}$ 572.2496; found: 572.2502.

4.2.17 Ethyl O- (3, 4, 6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-L-lactate (G17)

Yield 80% (43mg); Colorless oil; $[\alpha]_D^{23}$ -19.3(c=1.0, $CHCl_3$); R_f =0.26(Ethyl acetate/hexane, 1/2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.90 (dd, *J* = 10.6, 9.2 Hz, 1H), 5.35 (d, *J* = 8.5 Hz, 1H), 5.17 (t, *J* = 9.6 Hz, 1H), 4.40-4.29 (m, 3H), 4.17 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.02-3.83 (m, 3H), 2.12 (s, 3H), 2.03 (s, 3H), 1.88 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 170.7, 170.1, 169.5, 134.1, 123.4, 97.2, 72.7, 71.7, 70.4, 69.0, 62.0, 60.9, 54.5, 20.7, 20.6, 20.5, 18.6, 13.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{30}NO_{12}$ 536.1768; found: 536.1772.

4.2.18 Cholesteryl 3, 4, 6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (G18)

Yield 93% (75mg); White solid; mp 85-87 ℃; $[\alpha]_D^{23}$ +125.5(c=1.0, $CHCl_3$); R_f =0.49(Ethyl acetate/hexane, 1/2).^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.2, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.83-5.74 (m, 1H), 5.48 (d, *J* = 8.5 Hz, 1H), 5.23 (s, 1H), 5.17 (t, *J* = 9.6 Hz, 1H), 4.30 (d, *J* = 10.7 Hz, 2H), 4.15 (d, *J* = 12.1 Hz, 1H), 3.87 (d, *J* = 12.2 Hz, 1H), 3.48 (s, 1H), 2.11 (s, 3H), 2.03 (s, 3H), 2.00-1.91 (m, 3H), 1.86 (s, 3H), 1.79 (d, *J* = 10.1 Hz, 2H), 1.54-1.40 (m, 6H), 1.32 (d, *J* = 8.0 Hz, 4H), 1.24 (d, *J* = 13.0 Hz, 2H), 1.09 (dd, *J* = 18.3, 8.8 Hz, 6H), 1.00 (dd, *J* = 19.5, 7.0 Hz, 5H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 7.4 Hz, 9H), 0.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.2, 169.5, 140.2, 134.2, 131.4, 123.6, 122.1, 96.8, 79.5, 71.7, 70.9, 69.2, 62.2, 56.7, 56.1, 54.9, 50.1, 42.3, 39.7, 39.5, 38.6, 37.1, 36.6, 36.2, 35.7, 31.9, 31.8, 29.3, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 20.8, 20.6, 20.4, 19.3, 18.7, 11.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{47}H_{66}NO_{10}$804.4687; found: 804.4690.

4.2.19 Borneolyl 3, 4, 6-tri-O-acetyl-2-deoxy-2-azido-α-D-galactopyranoside (G19)

Yield 82% (38mg); Colorless oil; $[\alpha]_D^{23}$ +88.1(c=1.0, $CHCl_3$); R_f =0.56(Ethyl acetate/hexane, 1/3). ^1H NMR (400 MHz, $CDCl_3$) δ 5.31 (d, *J* = 2.8 Hz, 1H), 4.73 (dd, *J* = 10.9, 3.3 Hz, 1H), 4.34 (d, *J* = 8.0 Hz, 1H), 4.19 (dd, *J* = 11.1, 6.4 Hz, 1H), 4.06 (dd, *J* = 17.8, 6.9 Hz, 2H), 3.80 (t, *J* = 6.7 Hz, 1H), 3.66 (dd, *J* = 10.8, 8.0 Hz, 1H), 2.16 (s, 3H), 2.04 (d, *J* = 6.8 Hz, 6H), 1.69 (d, *J* = 4.4 Hz, 3H), 1.27 (d, *J* = 9.5 Hz, 3H), 1.14 (dd, *J* = 13.2, 2.9 Hz, 1H), 0.90-0.85 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 169.8, 101.4, 85.0, 70.8, 70.5, 66.4, 61.3, 61.2, 49.1, 48.1, 44.8, 36.0, 28.1, 26.7, 20.7, 20.6, 19.8, 18.9, 13.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{34}N_3O_8$ 468.2346; found: 468.2350.

4.2.20 (L)-Mentyl 3, 4, 6-tri-O-acetyl-2-deoxy-2-azido-α-D-galactopyranoside (G20)

Yield 81% (40mg); Colorless oil; $[\alpha]_D^{23}$ +102.5(c=1.0, $CHCl_3$); R_f =0.55(Ethyl acetate/hexane, 1/3). ^1H NMR (400 MHz, $CDCl_3$) δ 5.31 (d, *J* = 2.9 Hz, 1H), 4.76 (dd, *J* = 10.9, 3.3 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 4.13 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.06 (dd, *J* = 11.2, 6.7 Hz, 1H), 3.82 (t, *J* = 6.6 Hz, 1H), 3.62 (dd, *J* = 10.7, 8.1 Hz, 1H), 3.47 (td, *J* = 10.7, 4.2 Hz, 1H), 2.32-2.26 (m, 1H), 2.16 (s, 3H), 2.04 (d, *J* = 9.9 Hz, 6H), 1.67 (d, *J* = 11.2 Hz, 2H), 1.33-1.24 (m, 2H), 1.11-1.02 (m, 2H), 0.93 (dd, *J* = 15.0, 6.8 Hz, 8H), 0.75 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 169.9, 100.0, 79.2, 71.2, 70.4, 66.5, 61.5, 60.8, 47.6, 40.2, 34.2, 31.5, 25.1, 23.0, 22.2, 20.9, 20.7, 20.6, 15.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{36}N_3O_8$ 470.2502; found: 470.2495.

4.2.21 O-(2-deoxy-2-azido- 3, 4, 6-tri-O-Ac-α-D-galactopyranosyl)- N-Fmoc-L-threonine methyl ester (G21-α)

Yield 75% (50mg); Colorless oil; $[\alpha]_D^{23}$ +11.2(c=1.0, $CHCl_3$); R_f =0.64(Ethyl acetate/hexane, 1/1).^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.67-7.62 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.34 (dd, *J* = 6.8, 3.5 Hz, 2H), 5.64 (d, *J* = 9.5 Hz, 1H), 5.46 (s, 1H), 5.29 (dd, *J* = 11.1, 3.1 Hz, 1H), 5.04 (d, *J* = 3.5 Hz, 1H), 4.46 (d, *J* = 10.1 Hz, 3H), 4.42-4.34 (m, 2H), 4.32-4.24 (m, 2H), 4.10 (d, *J* = 6.4 Hz, 2H), 3.81 (s, 2H), 3.69 (dd, *J* = 11.2, 3.6 Hz, 1H), 2.15 (s, 3H), 2.06 (d, *J* = 12.2 Hz, 6H), 1.35 (d, *J* = 6.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.3, 170.0, 169.8, 156.7, 143.8, 143.8, 141.3, 127.7, 127.1, 125.2, 120.0, 99.4, 68.2, 67.6, 67.5, 67.1, 61.8, 58.7, 57.8, 52.7, 47.1, 20.6, 20.6, 20.6, 18.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{37}N_4O_{12}$ 669.2408; found: 669.2413.

4.2.21O-(2-deoxy-2-azido- 3, 4, 6-tri-O-Ac-β-D-galactopyranosyl)- N-Fmoc-L-threonine methyl ester (G21-β)

Yield 13% (9mg); Colorless oil; $[\alpha]_D^{23}$ -31.4(c=1.0, $CHCl_3$); R_f =0.53(Ethyl acetate/hexane, 1/1).^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 5.60 (d, *J* = 9.4 Hz, 1H), 5.32-5.29 (m, 1H), 4.75 (dd, *J* = 10.9, 3.2 Hz, 1H), 4.53 (d, *J* = 6.3 Hz, 1H), 4.46 (d, *J* = 9.5 Hz, 1H), 4.41 (t, *J* = 6.6 Hz, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.09 (dd, *J* = 6.6, 2.6 Hz, 2H), 3.81 (t, *J* = 6.6 Hz, 1H), 3.77 (s, 2H), 3.66 (dd, *J* = 10.7, 8.1 Hz, 1H), 2.15 (s, 3H), 2.07-2.04 (m, 6H), 1.35 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.4, 170.0, 169.8, 156.6, 143.9, 143.7, 141.3, 141.3, 127.7, 127.1, 125.2, 125.1, 120.0, 100.3, 75.2, 70.6, 67.3, 66.1, 61.7, 60.9, 60.6, 58.4, 58.0; 52.6, 47.1, 20.7, 20.6, 20.6, 16.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{37}N_4O_{12}$ 669.2408; found: 669.2410.

4.2.22 Borneolyl 3, 4, 6-tri-O-Bz-2-deoxy-α-D-glucopyranoside (G22)

Yield 91% (39mg); Colorless oil; $[\alpha]_D^{23}$ +37.4(c=1.0, $CHCl_3$); R_f =0.55(Ethyl acetate/hexane, 1/5).^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.48 (dd, *J* = 7.4, 3.5 Hz, 2H), 7.41 (d, *J* = 7.8 Hz ,2H), 7.39-7.34 (m, 4H), 5.81-5.72 (m, 2H), 5.55 (t, *J* = 9.5 Hz, 1H), 5.08 (d, *J* = 2.9 Hz, 1H), 4.56 (t, *J* = 7.1 Hz, 1H), 4.48-4.41 (m, 1H), 3.89 (d, *J* = 8.7 Hz, 1H), 2.55 (dd, *J* = 12.6, 5.1 Hz, 1H), 2.25-2.15 (m, 1H), 2.14–2.06 (m, 1H), 2.01 (td, *J* = 12.5, 3.8 Hz, 1H), 1.77–1.69 (m, 1H), 1.59 (t, *J* = 4.3 Hz, 1H), 1.37-1.31 (m, 1H), 1.23 (td, *J* = 14.3, 13.4, 4.6 Hz, 2H), 0.86 (d, *J* = 7.9 Hz, 6H), 0.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.8, 165.6, 133.3, 133.0, 133.0, 129.8, 129.8, 129.7, 129.6, 129.6, 129.2, 128.4, 128.3, 128.3, 128.2, 98.6, 84.9,

70.5, 70.2, 68.5, 63.7, 49.5, 47.5, 45.0, 37.0, 35.7, 28.3, 26.7, 19.7, 18.7, 13.9. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{37}H_{41}O_8$ 613.2801; found: 613.2802.

4.3 Procedures for the In(NTf$_2$)$_3$-catalyzed synthesis of disaccharide

To a solution of glycosyl bromide (0.1 mmol) in anhydrous CH_2Cl_2 (2 mL) containing $In(NTf_2)_3$ (14 mg, 0.015mmol) and 4Å molecular sieves(5 mg), alcohol (0.12mmol) was added under Ar. The mixture was allowed to stir for 12h at room temperature. The suspension was filtered through a pad of Celite and concentrated in *vacuo*. The crude product was purified by flash column chromatography to yield the product.

4.3.1 Phenyl 6-O-(2, 3, 4, 6-tetra-O-Bz-β-D-glucopyranosyl)-(1→6)-2, 3, 4-tri-O-Ac-β-D-thioglucopyranoside (G23)

Yield 83% (67mg); White solid; mp 79-81℃; $[\alpha]_D^{23}$ +12.9(c=1.0, $CHCl_3$); R_f =0.13(Ethyl acetate/toluene, 1/10).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.97-7.87 (m, 4H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.59-7.47 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 5H), 7.36 (d, *J* = 4.2 Hz, 5H), 7.32-7.28 (m, 2H), 7.17 (d, *J* = 7.0 Hz, 1H), 5.84 (t, *J* = 9.6 Hz, 1H), 5.63 (t, *J* = 9.7 Hz, 1H), 5.53-5.44 (m, 1H), 5.13 (t, *J* = 9.3 Hz, 1H), 4.84 (ddd, *J* = 39.7, 20.6, 8.8 Hz, 3H), 4.67-4.58 (m, 2H), 4.46 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.06 (s, 1H), 3.79 (dd, *J* = 16.4, 9.4 Hz, 2H), 3.73-3.65 (m, 1H), 2.05 (s, 3H), 1.94 (d, *J* = 8.6 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.5, 169.2, 166.1, 165.7, 165.2, 165.1, 133.5, 133.2, 132.9, 131.6, 129.8, 129.8, 129.7, 129.5, 129.2, 129.0, 128.8, 128.8, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 100.8, 85.4, 77.9, 73.8, 72.9, 72.3, 71.7, 69.9, 69.6, 68.8, 68.0, 63.0, 20.7, 20.5, 20.5. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{52}H_{49}O_{17}S$ 977.2690; found: 977.2694.

4.3.2 Methyl 4-O-(2, 3, 4, 6-tetra-O-Bz-β-D-glucopyranosyl)-(1→4)-2, 3, 6-tri-O-Bz-α-D-mannopyranoside (G24)

Yield 79% (85mg); Colorless oil; $[\alpha]_D^{23}$ +58.1(c=1.0, $CHCl_3$); R_f =0.42 (Ethyl acetate/toluene, 1/10).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.93 (dd, *J* = 12.7, 7.2 Hz, 4H), 7.80 (d, *J* = 7.2 Hz, 4H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.54 (q, *J* = 7.4 Hz, 3H), 7.48-7.43 (m, 5H), 7.41-7.36 (m, 5H), 7.32 (dd, *J* = 8.2, 3.6 Hz, 4H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.16 (td, *J* = 7.8, 2.6 Hz, 4H), 5.76 (dd, *J* = 9.7, 3.4 Hz, 1H), 5.67 (t, *J* = 9.7 Hz, 1H), 5.56 (dd, *J* = 3.3, 1.9 Hz, 1H), 5.49-5.40 (m, 2H), 4.88-4.79 (m, 3H), 4.62 (t, *J* = 9.7 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.09 (d, *J* = 3.7 Hz, 2H), 3.87 (dd, *J* = 10.9, 2.5 Hz, 1H), 3.80 (d, *J* = 9.7 Hz, 1H), 3.72 (d, *J* = 9.9 Hz, 1H), 3.58 (d, *J* = 11.3 Hz, 1H), 3.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 165.4, 165.1, 164.9, 164.7, 138.4, 133.3, 133.3, 133.1, 133.0, 132.8, 129.8, 129.7, 129.7, 129.6, 129.6, 129.5, 129.3, 129.1, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0,127.7, 100.7, 98.5, 73.49, 73.2, 72.9, 72.0, 71.0, 70.7, 69.8, 69.6, 67.9, 63.0, 55.3. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{62}H_{55}O_{17}$ 1071.3439; found: 1070.3442.

4.3.3 Phenyl 6-O-(2, 3, 4, 6-tetra-O-Bz-α-D-mannopyranosyl)-(1→6)-2, 3, 4-tri-O-Ac-β-D-thioglucopyranoside (G25)

Yield 87% (85mg); Colorless oil; $[\alpha]_D^{23}$ -39.31(c=2.0, $CHCl_3$); R_f =0.38(Ethyl acetate/hexane, 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.62-7.54 (m, 4H), 7.44 (t, *J* = 7.0 Hz, 4H), 7.39 (td, *J* = 7.8, 3.0 Hz, 4H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.24 (dd, *J* = 11.6, 3.7 Hz, 4H), 6.11 (t, *J* = 10.1 Hz, 1H), 5.91 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.75 (s, 1H), 5.29 (t, *J* = 9.3 Hz, 1H), 5.10 (s, 1H), 5.03-4.94 (m, 2H), 4.82 (d, *J* = 10.2 Hz, 1H), 4.71-4.66 (m, 1H), 4.54 (d, *J* = 10.3 Hz, 1H), 4.45 (dd, *J* = 12.1, 4.4 Hz, 1H), 3.94 (dq, *J* = 16.8, 7.5 Hz, 2H), 3.67 (d, *J* = 10.2 Hz, 1H), 2.08 (d, *J* = 10.7 Hz, 6H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.5, 169.3, 166.0, 165.4, 165.3, 133.5, 133.3, 133.2, 133.0, 132.9, 131.6, 129.8, 129.8, 129.8, 129.7, 129.3, 129.2, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 97.4, 86.2, 76.41, 73.9, 70.1, 69.9, 69.0, 68.9, 67.1, 66.5, 62.6, 20.8, 20.6, 20.6. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{52}H_{49}O_{17}S$ 977.2690; found: 977.2687.

4.3.4 Methyl 4-O-(2, 3, 4-tri-O-Bz-α-D-rhamosyl)-(1→4)-2, 3, 6-tri-O-Bn-α-D-glucopyranoside (G26)

Yield 82% (76mg); White solid; mp 68-70℃; $[\alpha]_D^{23}$ +63.8(c=1.2, $CHCl_3$); R_f =0.55(Ethyl acetate/toluene, 1/10).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 2H), 7.87 (dd, *J* = 16.0, 7.3 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49-7.44 (m, 2H), 7.40 (q, *J* = 7.7, 7.1 Hz, 5H), 7.32 (s, 3H), 7.30-7.26 (m, 6H), 7.21-7.16 (m, 3H), 7.16-7.11 (m, 3H), 5.78 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.63-5.54 (m, 2H), 5.21 (d, *J* = 11.7 Hz, 2H), 4.85 (d, *J* = 11.1 Hz, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.66-4.60 (m, 2H), 4.59 -4.51 (m, 2H), 4.37 (dd, *J* = 9.9, 6.1 Hz, 1H), 3.99 (q, *J* = 8.9 Hz, 2H), 3.92-3.87 (m, 1H), 3.84 (d, *J* = 9.1 Hz, 1H), 3.73 (d, *J* = 10.9 Hz, 1H), 3.65 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.41 (s, 3H), 0.89 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.7, 138.7, 137.9, 137.7, 133.4, 133.2, 133.1, 129.7, 129.7, 129.6, 129.4, 129.2, 128.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.6, 127.4, 127.4, 127.3, 98.0, 97.0, 80.3, 79.7, 75.5, 74.8, 73.3, 73.3, 71.7, 71.3, 70.0, 70.0, 68.3, 67.0, 55.3, 17.1. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{55}H_{55}O_{13}$ 923.3643; found: 923.3639.

4.3.5 6-O- (3, 4, 6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)- (1→6)-1, 2: 3, 4-di-O-isopropylidene-α-D-galactopyranose (G27)

Yield92% (62mg); White solid; mp 220-222 ℃ ; $[\alpha]_D^{23}$ +113.2(c=1.0, $CHCl_3$); R_f =0.45(Ethyl acetate/hexane, 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.71 (dd, *J* = 5.3, 3.0 Hz, 2H), 5.84 (t, *J* = 9.9 Hz, 1H), 5.45 (d, *J* = 8.5 Hz, 1H), 5.16 (t, *J* = 9.6 Hz, 1H), 5.10 (d, *J* = 5.0 Hz, 1H), 4.40 (dd, *J* = 7.9, 2.1 Hz, 1H), 4.37-4.28 (m, 2H), 4.20-4.14 (m, 1H), 4.09 (dd, *J* = 4.9, 2.2 Hz, 1H), 3.99 (d, *J* = 8.0 Hz, 1H), 3.94 (d, *J* = 8.1 Hz, 1H), 3.89 (d, *J* = 10.1 Hz, 1H), 3.69 (d, *J* = 7.8 Hz, 2H), 2.11 (s, 3H), 2.03 (s, 3H), 1.86 (s, 3H), 1.39 (s, 3H), 1.23 (s, 3H), 1.03 (d, *J* = 3.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.1, 169.5, 133.7, 123.4, 109.3, 108.0, 99.3, 95.9, 71.6, 70.8, 70.7, 70.6, 70.1, 69.4, 69.0, 67.4, 62.0, 54.5, 25.8, 25.3, 24.6, 24.2, 20.8, 20.6, 20.5. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{32}H_{40}NO_{15}$ 678.2398; found: 678.2393.

4.3.6 Methyl 3-O- (3, 4, 6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)- (1→6)- 4, 6-benzylidene-2-O- Bz-α-D-glucopyranoside (G28)

Yield 75% (60mg); Colorless oil; $[\alpha]_D^{23}$ +22.1(c=1.0, $CHCl_3$); R_f =0.24(Ethyl acetate/hexane, 1/2). ^{1}H NMR (400 MHz, CDCl3) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49-7.41 (m, 5H), 7.36 (t, *J* = 7.8 Hz, 3H), 7.31 (d, *J* = 6.9 Hz, 3H), 5.73-5.67 (m, 1H), 5.62 (d, *J* = 8.4 Hz, 1H), 5.55 (s, 1H), 5.13-5.07 (m, 1H), 5.02 (dd, J = 9.8, 3.9 Hz, 1H), 4.90 (d, *J* = 3.9 Hz, 1H), 4.41 (t, *J* = 9.4 Hz, 1H), 4.30 (dd, *J* = 10.6, 8.5 Hz, 1H), 4.24 (dd, *J* = 9.4, 3.8 Hz, 1H), 4.11 (dd, *J* = 12.2, 3.6 Hz, 1H), 3.92 (dd, *J* = 12.3, 2.1 Hz, 1H), 3.87-3.81 (m, 1H), 3.77 (dd, *J* = 17.4, 8.4 Hz, 2H), 3.67 (d, *J* = 9.9 Hz, 1H), 3.29 (s, 3H), 1.94 (d, *J* = 11.2 Hz, 6H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 170.7, 170.0, 169.4, 165.6, 137.2, 133.9, 133.1, 130.8, 130.0, 129.1, 129.0, 128.3, 128.2, 126.0, 123.2, 101.3, 97.3, 96.9, 79.0, 75.8, 72.7, 71.4, 70.6, 68.9, 68.6, 62.2, 61.6, 55.3, 54.7, 20.6, 20.6, 20.3. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{41}H_{42}NO_{16}$ 804.2504; found: 804.2508.

4.3.7 Methyl 4-O-(2-deoxy-2-azido- 3, 4, 6-tri-O-Ac -β-D-galactopyranosyl)- (1→4)- 2, 3-di-O-Bz-6-O-Bn-α-D-glucopyranoside (G29)

Yield 83% (67mg); White solid; mp 75-77℃; $[\alpha]_D^{23}$ +50.2(c=1.0, $CHCl_3$); R_f =0.4(Ethyl acetate/hexane, 1/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 4H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.41-7.35 (m, 9H), 6.07 (t, *J* = 9.6 Hz, 1H), 5.32 (s, 1H), 5.25 (d, *J* = 3.5 Hz, 1H), 5.21-5.14 (m, 2H), 5.10 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.68 (d, *J* = 4.9 Hz, 2H), 4.20 (d, *J* = 9.5 Hz, 1H), 4.14 (dd, *J* = 12.4, 6.1 Hz, 1H), 4.06-3.98 (m, 1H), 3.92 (dt, *J* = 10.0, 4.1 Hz, 3H), 3.79 (d, *J* = 11.1 Hz,1H), 3.53 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.44 (s, 3H).2.07 (s, 3H), 1.99 (d, *J* = 13.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.8, 169.5, 166.0, 165.3, 138.0, 133.2, 132.9, 130.0, 129.9, 129.9, 129.6, 129.5, 129.1, 128.7, 128.5, 128.4, 128.3, 128.1, 127.8, 127.5, 98.8, 96.8, 75.7, 73.3, 72.3, 69.5, 68.7, 68.4, 67.2, 61.4, 57.4, 55.5, 20.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{40}H_{44}N_3O_{15}$ 806.2772; found: 806.2776.

Acknowledgments

The work was supported by the National Science Foundation of China (51501080, 21772071, 21675070, 21405067 and 31670350) and the Fundamental Research Funds for the Central Universities, Lanzhou University (lzujbky-2017-207, lzujbky-2017-k24, and lzujbky-2017-k25). We gratefully acknowledge the financial support from the Fundamental Research Funds for the Central Universities, Lanzhou University (lzujbky-2017-207, lzujbky-2017-k24, and lzujbky-2017-k25).

References

1. (a)Rudd P M, Elliott T, Cresswell P, Wilson I A, Dwek R A. *Science*, 2001; 291: 2370-2376; (b) Varki A. *Glycobiology* 1993; 3: 97-130; (c) Dwek R A. *Chem Rev*. 1996, 96: 683-720.
2. (a) Boltje TJ, Buskas T.and Boons G-J. *Nat Chem.* 2009; 1: 611-622; (b) Bertozzi C R.and Kiessling L L. *Science*, 2001; 291: 2357-2364; (c) Galoni´c D P and Gin D Y. *Nature*, 2007; 446: 1000-1007; (d) Seeberger P H and Werz D B. *Nature*, 2007; 446: 1046-1051.
3. Koenigs W, Knorr E. *Ber Dtsch Chem Ges.* 1901; 34: 957.
4. Gigg J, Gigg R, Payne S, Conant R. *J Chem Soc Perkin Trans.* 1, 1987; 1165-1170.
5. Tsui DSK, Gorin P A J. *Carbohydr Res.* 1985; 144: 137-147.
6. (a) Takahashi Y,Takahashi Y, Ogawa T. *Carbohydr Res.* 1987; 164: 277-296; (b) Ohnishi Y, Ando H, Kawai T, Nakahara Y, Ito Y. *Carbohydr Res.* 2000; 328: 263-276; (c) Ko Y-J, Shim S -B, Shin J-H. *Org Lett.* 2009; 11: 609-612.
7. Burkart M D, Zhang Z, Hung S -C, Wong C-H. *J Am Chem Soc.* 1997; 119: 11743-11746.
8. (a) Gouliaras C, Lee D, Chan L, Taylor M S. *J Am Chem Soc.* 2011; 133: 13926-13929; (b) Muramatsu W, Yoshimatsu H. *Adv Synth Catal.* 2013; 355: 2518-2524.
9. Kaeothip S, Pornsuriyasak P, Demchenko A V. *Tetrahedron Lett.* 2008; 49: 1542-1545.
10. Sun L, Wu X, Xiong DC, Ye XS. *Angew Chem Int Ed*. 2016; *55*: 8041-8045.
11. For selective references on Au-catalyzed glycosylation, see: (a) Li Y, Yang X., Liu Y, Zhu C, Yang Y, Yu B. *Chem Eur J.* 2010; 16: 1871-1882; (b) Zhu Y, Yu B. *Angew Chem Int Ed.* 2011; 50: 8329-8332; (c) Zhang Q, Sun J, Zhu Y, Zhang F, Yu B. *Angew Chem Int Ed.* 2011; 50: 4933-4936; (d) Peng P, Schmidt RR. *J Am Chem Soc*. 2015; 137: 12653-12659.
12. For glycosylation protocol using Cu as a catalyst, see: Wang HY, Simmons CJ, Blaszczyk SA, Balzer PG, Luo R, Duan X., Tang W. *Angew Chem Int Ed*. 2017; 56: 15698-15702.
13. For a reference on Pd-catalyzed glycosylation, see: Ji L, Xiang SH, Leng WL, Hoang Kle M, Liu XW. *Org. Lett.* 2015; 17: 1357-1360.
14. For a reference on Ni-catalyzed glycosylation, see: Mensah EA, Yu F, Nguyen HM. *J Am Chem Soc*. 2010; 132: 14288-14302.
15. For representative reviews on metal-catalyzed glycosylation, see (a) McKay MJ, Nguyen HM. *ACS Catal*. 2012; 2: 1563-1595; (b) Yu B. *Acc Chem Res.* 2018; 51: 507-516.
16. Ma T, Li C, Liang H, Zhang Z,Wang Z, Yu L, Xue W. *Synlett* 2017; 28: 2311-2314.
17. Ma T, Li C, Zhang Z, Wang Z, Yu L, Xue W. *Synlett* 2017; 28: 2633-2636.
18. (a)Mukherjee D, Yousuf SK, Taneja SC. *Tetrahedron lett*. 2008; 49: 4944-4948; (b) Mukherjee D, Ray PK, Chowdhury US. *Tetrahedron*, 2001; 57: 7701-7704; (c) Chandra S, Yadav RN, Paniagua A., Banik BK. *Tetrahedron lett.* 2016; 57: 1425-1429.
19. Saratikov A S. *Die Pharmazie*, 1968; 69: 394-398.
20. (a)Wang Q, Wei X., Liao K, Li H, Meng X, Li Z. *Tetrahedron lett.* 2016; 57: 2273; (b) Guo Y, Zhao Y, Zheng C, Meng Y, Yang Y. *Chem Pharm Bull*. 2010; 58: 1627-1629; (c) Shi T, Chen H, Jing, L, Liu X, Sun X. *Synthetic Comm*. 2011; 41: 2594-2600.
21. Sau A and Galan MC. *Org Lett*. 2017; 17: 2857-2860.

Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.