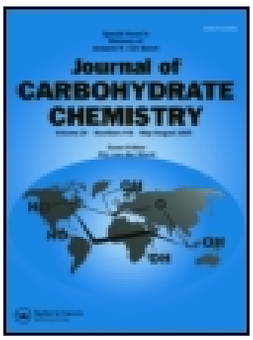

Journal of Carbohydrate Chemistry

ISSN: 0732-8303 (Print) 1532-2327 (Online) Journal homepage: http://www.tandfonline.com/loi/lcar20

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To cite this article: Guofang Yang, Xiaosheng Luo, Hong Guo, Qingbing Wang, Jiafen Zhou, Tianyun Huang, Jie Tang, Junjie Shan & Jianbo Zhang (2018): α-Selective synthesis of 2-deoxy-glycosides and disaccharides, Journal of Carbohydrate Chemistry, DOI: 10.1080/07328303.2018.1439498

To link to this article: https://doi.org/10.1080/07328303.2018.1439498

Published online: 19 Mar 2018.

JOURNAL OF CARBOHYDRATE CHEMISTRY
2018, VOL. 0, NO. 0, 1–25
https://doi.org/10.1080/07328303.2018.1439498

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α-Selective synthesis of 2-deoxy-glycosides and disaccharides

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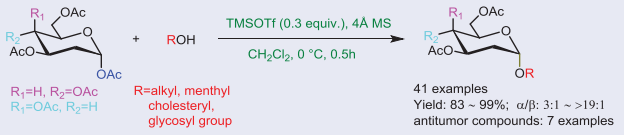
ABSTRACT

A metal-free catalytic method for the synthesis of 2-deoxy glycosides and disaccharides has been developed using stable 2-deoxy glucosyl and galactosyl acetate donors. They could react with a variety of acceptors in the presence of catalytic amount of TMSOTf at 0°C to form glycosides, glycoconjugates, and disaccharides with excellent α-selectivity (> 19:1) and yields (up to 99%) in a short time (0.5 h). With this expedient method, several new compounds against human K562 and SMMC7721 cell lines were obtained and tested with *in vitro* antitumor bioactivities.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 14 November 2017
Revised 6 February 2018
Accepted 7 February 2018

KEYWORDS
2-deoxy glycosides; 2-deoxy disaccharides; TMSOTf; α-selective glycosylation; antitumor activity

Introduction

2-Deoxyglycosides and 2-deoxysugar-containing oligosaccharides are common in naturally glycosylated products with a wide range of biological activities,[1] especially antitumor activities.[2–9] Owing to their important biological relevance, the synthesis of 2-deoxysugars and their derivatives has become an important field in carbohydrate chemistry and natural product synthesis.[10–11] However, the creation of 2-deoxy glycosidic linkages directly from 2-deoxy glycosyl donors is more challenging than other glycosidic bond formation due to the lack of stereo-directing anchimeric assistance from the C-2 position, which leads to a mixture of anomers at most situations.[12–16] Some remarkable progress has been made in the past few years in the synthesis of 2-deoxy glycosides by acid-catalyzed activation of glycals,[17–22] anomeric esters,[23] glycosyl halides,[24] thioglycosides,[25–26]

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lcar.

O-glycosides,[27] and 2,3-anhydrosugars.[28] However, unstable deoxy glycosyl donors, harsh reaction conditions, excess catalysts, high price, complicated operation, low efficiency and poor selectivity are usually encountered in the practice. Hence, there is still a need to explore general promoter systems for convenient and stereoselective synthesis of 2-deoxy glycosides.

In 2008, Ye et al.[29] reported the use of 3,4-*O*-carbonate protected thioglycosides to afford α-2-deoxy glycosides in good stereoselectivity by the preactivation protocol. In 2014, Mong et al.[30] applied it to activating 2-deoxythioglycosides for DMF modulated iterative one-pot glycosylation. Recently, Zeng et al.[31] reported the mild glycosylation conditions based on transition-metal catalyzed activation of ortho-alkynylbenzoate glycosides,[32–33] which was employed for the assembly of disaccharide in a 90% yield and in an α/β ratio of 8:1. Previously, α-2-deoxy aromatic glycosides was achieved when the glycosylation of 2-deoxyglycosyl acetates and phenols was carried out in the presence of catalytic amount of TMSOTf in our group.[34] In order to form a complete reaction system, this method has been applied to synthesize other kinds of α-2-deoxy alkyl glycosides and oligosaccharides with high yields and good α-selectivity.

Results and discussion

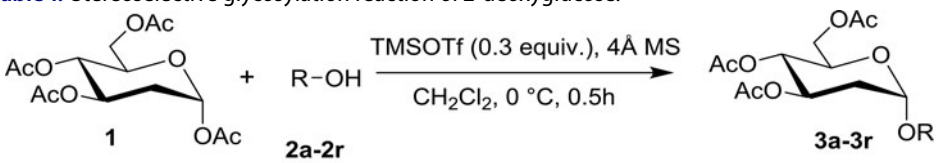
At the outset, the coupling of acetylated 2-deoxy sugar donor **1** and n-butyl alcohol **2d** furnished glycoside in a 90% yield and in an α/β ratio of 6:1 in the presence of TMSOTf. We next explored the use of other acceptors. As anticipated, the reactions between 2-deoxy glucosyl donor **1** and a series of acceptors including alcohols, amino acids, and sterols were carried out and the results are shown in Table 1.

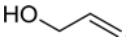
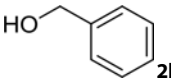
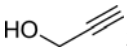
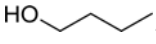
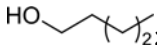
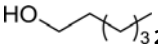
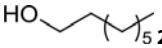
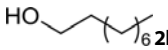
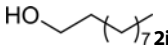
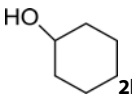
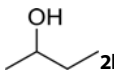
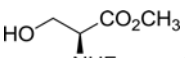
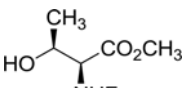
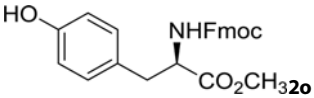
We found that primary alcohol acceptors (Table 1, entries 1–9) gave good to excellent yields (88%–98%) and high α-selectivity (α:β = 4:1 up to 10:1). The use of secondary alcohols as acceptors (Table 1, entries 10–12) led to a slight decrease in the yield, probably because of steric hindrance. In addition, when hindered and relatively complex acceptors, such as amino acids, were employed (Table 1, entries 13–15), they could also afforded 2-deoxyglycosides in excellent yields and high α-selectivity. Encouraged by these results, we further extended the scope of the 2-deoxyglycosylation reaction to sterols (Table 1, entries 16–18), and the reactions proceeded well to give yields of 88–93% and in this instance α/β ratios of 3:1–5:1 were observed. The results showed that good yields and stereoselectivity could be obtained when 2-deoxyglucosyl acetates as glycosyl donors were used.

Next, we sought to extend this glycosylation method to the generation of 2-deoxy galactosylglycosides. Excitingly, the system could also be applied to 2-deoxygalactosyl donor **4** and high yields and α:β stereoselectivity were obtained with these reaction as shown in Table 2.

From Table 2, we could conclude that not only primary alcohols (Table 2, entries 1–9) but also hindered secondary alcohols (Table 2, entries 10–12) could afford excellent results. All the reactions provided the corresponding 2-deoxy-α-alkyl-*O*-glycosides as the only detectable glycosylation products with high yields (84%–99%)

Table 1. Stereoselective glycosylation reaction of 2-deoxyglucose.



Entry	Acceptors	Products	Yield[c] (%)	α:β[d]
1[a]	 **2a**	**3a**	98	9:1
2[a]	 **2b**	**3b**	97	5.2:1
3[a]	 **2c**	**3c**	93	9:1
4	 **2d**	**3d**	90	6:1
5[b]	 **2e**	**3e**	96	9:1
6	 **2f**	**3f**	94	6:1
7	 **2g**	**3g**	95	5:1
8[b]	 **2h**	**3h**	96	10:1
9	 **2i**	**3i**	88	4:1
10	 **2j**	**3j**	90	8:1
11	 **2k**	**3k**	83	7:1
12	 **2l**	**3l**	90	9:1
13	 **2m**	**3m**	92	> 19:1
14	 **2n**	**3n**	84	> 19:1
15	 **2o**	**3o**	85	> 19:1

(*Continued on next page*)

Table 1. Continued

Entry	Acceptors	Products	Yield[c] (%)	α:β[d]
16	Cholesterol **2p**	**3p**	92	3:1
17	Diosgenin **2q**	**3q**	93	5:1
18	DHEA **2r**	**3r**	88	5:1

[a]ROH (2.0 equiv.); [b]TMSOTf (0.6 equiv.); [c]Isolated yield; [d]Determined by ^{1}H NMR.

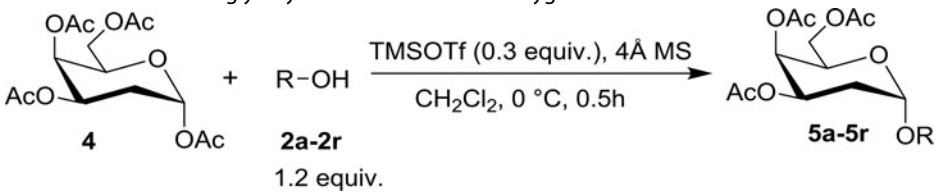
and α-stereoselectivity. Since some amino acid acceptors are sterically hindered and bulkier than typical primary alcohols and secondary alcohols, **5n** and **5o** (Table 2, entries 14 and 15) were afforded in slightly lower yields (87% and 84%), but they, as well as **5m** the glycosylation product of another amino acid, were formed with higher α-selectivity. Compared with Table 1, we can also find that between glucosyl donor and galactosyl donor, the stereoselectivity of the latter was generally better, which was probably resulted from yielding intermediate at the β-face due to the participation of the C4-acetoxyl group of galactosyl donor.[35–36]

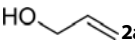
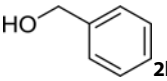
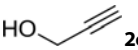
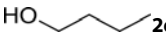
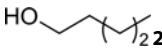
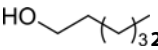
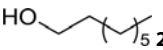
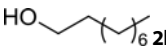
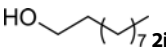
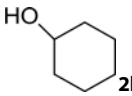
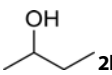
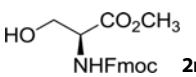
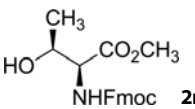
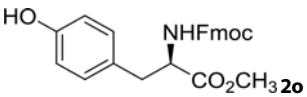
As we know, 2-deoxysugar-containing oligosaccharides are common in naturally glycosylated products,[1] such as landomycins,[37] olivomycins,[38] vancomycin,[39] and anthracyclines.[40] We would like to further explore the TMSOTf catalyzed reaction in the synthesis of 2-deoxysugar-containing disaccharides with different glycosyl acceptors. Delightfully, we also obtained high yields and remarkable α-stereoselectivity during the coupling reaction between 2-deoxyglycosyl acetate donors and glycosyl acceptors, as shown in Table 3, which were difficult to achieve under conventional conditions.[31]

Glycosyl acceptors with a primary alcohol, with either benzyl or benzoyl protecting groups, and with either trichloroethyl or thiophenyl linked to the anomeric position (Table 3, entries 1 and 5) gave excellent isolated yields (90–99%) and stereoselectivity (>19:1) of the desired product. This high stereoselectivity was maintained regardless of the position of the free hydroxyl group in the acceptors. Couplings to secondary hydroxyl groups at C-2, C-3, and C-4 (Table 3, entries 2–4) also proceeded extremely well with excellent isolated yields (87–99%) and stereoselectivity. It should be noted that the more challenging reactions of glucosyl donor gave lower α-selectivity than that of galactosyl donor. Nevertheless, the glycosylation could also furnish the expected disaccharide **7c** as the major product in excellent yield of 95% (Table 3, entry 3). These results highlighted that the TMSOTf catalyzed reaction is tolerant of most commonly used protecting groups, such as benzyl ethers and benzoyl esters. Furthermore, the reaction worked well across the board and the overall mild reaction condition makes this procedure general.

Cardiac glycosides show antitumor activities and their deoxy-sugar chains are vital for their antitumor effects.[41] In order to study the structure-activity relationship of cardiac glycosides toward tumors and get more potent antitumor agents, a series of 2-deoxy glycosides and disaccharides synthesized by this novel glycosylation method were evaluated *in vitro* against the human K562 and SMMC7721 cell lines by the standard MTT assay[42] for their antitumor activity. Interestingly, they

Table 2. Stereoselective glycosylation reaction of 2-deoxygalactose.



Entry	Acceptors	Products	Yield [c] (%)	α:β [d]
1[a]	 **2a**	**5a**	94	9:1
2[a]	 **2b**	**5b**	99	5:1
3[a]	 **2c**	**5c**	98	9:1
4	 **2d**	**5d**	90	6:1
5[b]	 **2e**	**5e**	97	9.5:1
6	 **2f**	**5f**	94	6:1
7	 **2g**	**5g**	95	5.3:1
8[b]	 **2h**	**5h**	99	11:1
9	 **2i**	**5i**	88	5:1
10	 **2j**	**5j**	90	9:1
11	 **2k**	**5k**	87	8.5:1
12	 **2l**	**5l**	89	10:1
13	 **2m**	**5m**	98	> 19:1
14	 **2n**	**5n**	87	> 19:1
15	 **2o**	**5o**	84	> 19:1

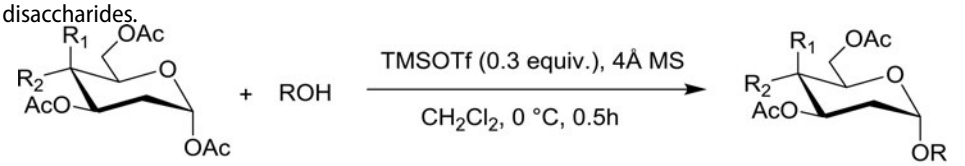
(*Continued on next page*)

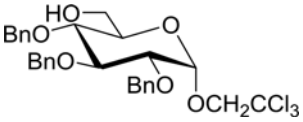
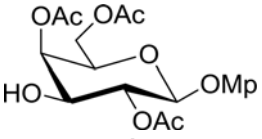
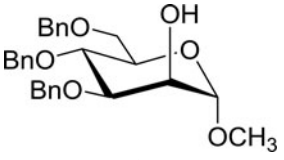
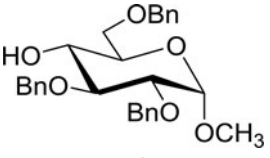
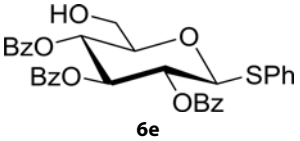
Table 2. Continued

Entry	Acceptors	Products	Yield [c] (%)	α:β [d]
16	Cholestsrerol **2p**	**5p**	93	3:1
17	Diosgenin **2q**	**5q**	93	5:1
18	DHEA **2r**	**5r**	90	6:1

[a]ROH (2.0 equiv.); [b]TMSOTf (0.6 equiv.); [c]Isolated yield; [d]Determined by ^{1}H NMR.

Table 3. α-Selective 2-deoxyglycosylation for the synthesis of 2-deoxysugar-containing disaccharides.



Entry	Acceptor	Product	Yield (%)[a]	α:β[b]
1	 **6a**	R_1 = H, R_2 = AcO **7a**	90	>19:1
		R_1 = AcO, R_2 = H **8a**	97	>19:1
2	 **6b**	R_1 = H, R_2 = AcO **7b**	89	>19:1
		R_1 = AcO, R_2 = H **8b**	99	>19:1
3	 **6c**	R_1 = H, R_2 = AcO**7c**	95	15:1
		R_1 = AcO, R_2 = H **8c**	98	>19:1
4	 **6d**	R_1 = H, R_2 = AcO **7d**	87	>19:1
		R_1 = AcO, R_2 = H **8d**	91	>19:1
5[c]	 **6e**	R_1 = H, R_2 = AcO **7e**	99	>19:1
		R_1 = AcO, R_2 = H **8e**	90	>19:1

[a]Isolated yield; [b]Ratio determined by ^{1}H NMR.; [c]The acceptor was used in 0.6 equiv.

Table 4. In vitro antitumor activity test of synthetic compounds against human K562 and SMMC7721 cell lines[a].

Entry	Compound	Sample concentration (μg/mL)	Inhibition rate (%)	
			K562	SMMC7721
1	DDP[b]	10	60.1	89.2
2	**3o**	100	11.3	17.3
3	**3p**	100	12.8	15.5
4	**7a**	100	12.8	21.8
5	**7c**	100	15.5	—
6	**8a**	100	13.9	—
7	**8b**	100	11.8	21.0
8	**8c**	100	14.3	30.5

[a]DMSO was used as solvent; [b]DDP: cis-Dichlorodiamminoplatinum-II.

were proven to possess good antitumor activity as shown in Table 4. Further research is still in progress.

In conclusion, we developed a metal-free catalytic α-selective glycosylation method for the synthesis of 2-deoxy glycosides using TMSOTf as the catalyst. Furthermore, the application of this method to disaccharide synthesis was also demonstrated. With this new method, several new 2-deoxy glycosides and disaccharides with moderate antitumor activity against human K562 and SMMC7721 cell lines were synthesized. As a number of natural products are glycosylated with deoxysugars, this novel glycosylation method should be useful for their preparation as well.

Experimental section

General procedures

All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Dichloromethane (CH_2Cl_2), pyridine, and toluene were distilled over calcium hydride (CaH_2). Methanol was distilled from magnesium. DMF was stirred with CaH_2 and distilled under reduced pressure. All reactions were carried out under nitrogen atmosphere with freshly distilled solvents, unless otherwise noted. Reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel GF_{254} precoated on glass plates (10–40 μm, Yantai, China). Spots were detected under UV (254 nm) and/or by staining with 10% (v/v) H_2SO_4 in ethanol. Solvents were evaporated under reduced pressure and below 40°C (bath temerature). Molecular sieves (4Å) used for reactions were crushed and activated *in vacuo* at 390°C for 8 h. Organic solutions of crude products were dried over anhydrous Na_2SO_4. Column chromatography was performed on silica gel (10–40 μm, Yantai, China). ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX 500 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in deuterated chloroform. Mass Spectra experiments were

performed on LTQ-XL (Thermo Scientific, USA) with an electrospray (ESI) ion source.

Allyl 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranoside (3a)

Glycosyl donor (30.0 mg, 0.09 mmol) and 4Å molecular sieves (30.0 mg) were weighed into a 25 mL round-bottom flask under N_2, followed by the addition of the acceptor (12.2 µL, 0.11 mmol, 1.2 equiv.) and TMSOTf (5.4 µL, 0.03 mmol, 0.3 equiv.) in anhydrous dichloromethane. The solution was then stirred under N_2 until the reaction was determined to be complete by TLC analysis of the crude material. The solution was then concentrated *in vacuum* and purified by column chromatography (hexane/EtOAc = 5:1) to afford **3a** as a colorless syrups (29 mg, 98% yield). ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.89–5.91 (1H, m), 5.34 (1H, ddd, J = 5.4, 9.5, 11.7 Hz), 5.28 (1H, dd, J = 1.5, 15.7 Hz), 5.21 (1H, dd, J = 1.2, 10.3 Hz), 4.99–5.03 (2H, m), 4.32 (1H, dd, *J* = 4.5, 12.2 Hz), 4.13 (1H, dd, *J* = 5.2, 7.7 Hz), 4.06 (1H, dd, *J* = 2.1, 12.2 Hz), 3.98–3.99 (2H, m), 2.27 (1H, dt, J = 5.2, 7.7 Hz), 2.10 (3H,s), 2.04 (3H, s), 2.01 (3H, s), 1.85 (1H, dt, *J* = 3.6, 11.7 Hz); ESI-MS: Calcd for $C_{15}H_{22}O_8Na$ $[M+Na]^+$: 353.12, found 353.11.

Benzyl 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranoside (3b)

Compound **3b** was obtained as colorless syrups (33.2 mg, 97% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2b** (18.7 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.29–7.37 (5H, m), 5.36 (1H, ddd, J = 2.5, 5.0, 11.5 Hz), 4.99- 5.04 (2H, m), 4.66 (1H, d, J = 12.0 Hz), 4.50 (1H, d, J = 12.0 Hz), 4.29 (1H, dd, *J* = 4.5, 12.5 Hz), 3.97–4.01 (2H, m), 2.28 (1H, dd, *J* = 5.4, 12.8 Hz), 2.09 (3H, s), 2.03 (3H, s), 2.00 (3H, s), 1.84 (1H, dt, *J* = 3.5, 12.8 Hz); ESI-MS: Calcd for $C_{19}H_{24}O_8Na$ $[M+Na]^+$: 403.14, found 403.12.

Propargyl 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranoside (3c)

Compound **3c** was obtained as colorless syrups (29.9 mg, 93% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2c** (5.2 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.32 (1H, ddd, J = 5.5, 9.5, 11.5 Hz), 5.16 (1H, d, J = 2.7 Hz), 5.03 (1H, t, J = 10.0 Hz), 4.37 (1H, d, J = 1.9 Hz), 4.31 (1H, dd, J = 4.2, 12.2 Hz), 4.22 (2H, d, *J* = 2.0 Hz), 4.06 (1H, dd, *J* = 2.0, 12.0 Hz), 4.01 (1H, ddd, *J* = 2.0, 4.0, 10.0 Hz), 2.44 (1H, dd, J = 10.3, 12.8 Hz), 2.28 (1H, dd, J = 5.2, 13.1 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.02 (1H, dd, *J* = 12.5, 5.5 Hz), 1.86 (1H, dt, J = 3.5, 12.8 Hz); ESI-MS: Calcd for $C_{15}H_{20}O_8Na$ $[M+Na]^+$: 351.11, found 351.08.

n-Butyl 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranoside (3d)

Compound **3d** was obtained as colorless syrups (28.0 mg, 90% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2d** (9.8 μL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, ddd, J = 5.0, 9.5, 11.6 Hz), 4.99 (1H, t, J = 9.8 Hz), 4.94 (1H, d, *J* = 3.0 Hz), 4.30 (1H, dd, J = 4.7, 12.2 Hz), 4.06 (1H, dd, J = 2.1, 12.2 Hz), 3.97 (1H, ddd, J = 2.1, 4.5, 6.8 Hz), 3.63 (1H, dt, *J* = 3.0, 6.7 Hz), 3.39 (1H, dt, *J* = 3.3, 6.4 Hz), 2.22 (1H, dd, J = 5.0, 12.2 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.02 (3H, s), 1.82 (1H, dt, *J* = 2.8, 12.2 Hz), 1.55–1.59 (2H, m), 1.37–1.39 (2H, m), 0.93 (3H, t, J = 7.4 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.7, 170.1, 169.9, 96.8, 69.4, 69.1, 67.7, 67.5, 62.4, 35.0, 31.4, 20.9, 20.7, 19.3, 13.8. ESI-MS: Calcd for $C_{16}H_{26}O_8Na$ $[M+Na]^+$: 369.15, found 369.14.

n-Pentyl 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranoside (3e)

Compound **3e** was obtained as colorless syrups (31.0 mg, 96% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2e** (11.9 μL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) 5.33 (1H, ddd, *J* = 4.3, 5.3, 11.3 Hz), 4.99 (1H, t, *J* = 9.8 Hz), 4.93 (1H, d, *J* = 2.8 Hz), 4.31 (1H, dd, J = 4.6, 12.2 Hz), 4.04 (1H, d, J = 12.2 Hz), 3.95 (1H, ddd, *J* = 2.0, 2.3, 10.0 Hz), 3.59–3.64(1H, m), 3.35- 3.40 (1H, m), 2.22 (1H, dd, *J* = 5.3, 12.8 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.01 (3H, s), 1.82 (1H, dt, *J* = 3.5, 12.6 Hz), 1.58 (2H, t, J = 6.4 Hz), 1.25–1.34 (4H, m), 0.91 (3H, t, J = 6.4 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.6, 170.1, 169.8, 96.8, 69.4, 69.1, 67.8, 67.6, 62.3, 35.0, 29.6, 29.2, 29.0, 28.2, 20.9, 20.6, 13.9. ESI-MS: Calcd for $C_{17}H_{32}O_8N$ $[M+NH_4]^+$: 378.2, found 377.9.

n-Hexyl 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranoside (3f)

Compound **3f** was obtained as colorless syrups (34.0 mg, 94% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2f** (13.9 μL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, ddd, *J* = 5.0, 9.5, 12.0 Hz), 4.99 (1H, t, *J* = 9.5 Hz), 4.93 (1H, d, *J* = 3.5 Hz), 4.29 (1H, dd, J = 4.5, 12.0 Hz), 4.05 (1H, dd, J = 2.0, 12.5 Hz), 3.96 (1H, ddd, *J* = 2.0, 4.0, 10.0 Hz), 3.61 (1H, dt, *J* = 2.5, 6.5 Hz), 3.37 (1H, dt, *J* = 2.5, 6.5 Hz), 2.22 (1H, dd, *J* = 5.0, 12.0 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.01 (3H, s), 1.81 (1H, dt, *J* = 3.5, 12.0 Hz), 1.56–1.59 (2H, m), 1.28–1.35 (6H, m), 0.89 (3H, t, J = 7.0 Hz); ESI-MS: Calcd for $C_{18}H_{30}O_8Na$ $[M+Na]^+$: 397.18, found 397.16.

n-Octyl 2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranoside (3g)

Compound **3g** was obtained as colorless syrups (34.4 mg, 95% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2g** (20.9 μL, 0.11 mmol, 1.2 equiv.) under

the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, ddd, J = 5.5, 9.5, 11.6 Hz), 4.99 (1H, t, J = 9.8 Hz), 4.94 (1H, d, J = 3.0 Hz), 4.30 (1H, dd, J = 4.5, 12.5 Hz), 4.06 (1H, dd, J = 2.0, 12.0 Hz), 3.97 (1H, ddd, J = 2.0, 5.0, 10.5 Hz), 3.62 (1H, dt, J = 7.30, 10.0 Hz), 3.39 (1H, dt, J = 6.0, 9.5 Hz), 2.22 (1H, dd, J = 5.5, 11.6 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.10 (3H, s), 1.82 (1H, dty J = 3.5, 11.6 Hz), 1.57–1.59 (2H, m), 1.26–1.35 (10H, m), 0.89 (3H, t, J = 7.0 Hz); ESI-MS: Calcd for $C_{20}H_{34}O_8Na$ $[M+Na]^+$: 425.21, found 425.19.

n-Nonyl 2-deoxy-3,4,6-tri-O-acetyl- α -D-glucopyranoside (3h)

Compound **3h** was obtained as colorless syrups (72.0 mg, 96% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **2h** (38.2 µL, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, ddd, J = 3.4, 5.4, 11.4 Hz), 4.99 (1H, t, J = 9.8 Hz), 4.93 (1H, d, J = 3.0 Hz), 4.29 (1H, dd, J = 4.6, 12.2 Hz), 4.04 (1H, dd, J = 1.6, 12.2 Hz), 3.96(1H, ddd, J = 2.1, 2.3, 10.1 Hz), 3.59–3.64 (1H, m), 3.35–3.39 (1H, m), 2.23 (1H, dd, J = 5.4, 12.8 Hz), 2.09(3H, s), 2.04 (3H, s), 2.01 (3H, s), 1.82 (1H, dt, J = 3.6, 12.1 Hz), 1.58 (2H, t, J = 6.8 Hz), 1.25–1.33 (12H, m), 0.88(3H, t, J = 0.88 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.6, 170.1, 169.8, 96.8, 69.4, 69.1, 67.8, 67.6, 62.4, 35.0, 31.8, 29.6, 29.4, 29.3, 29.2, 26.1, 22.6, 20.9, 20.7, 14.0. ESI-MS: Calcd for $C_{21}H_{40}O_8N$ $[M+NH_4]^+$: 434.3, found 433.9.

n-Decyl 2-deoxy-3,4,6-tri-O-acetyl- α -D-glucopyranoside (3i)

Compound **3i** was obtained as colorless syrups (34.0 mg, 88% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2i** (20.9 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, ddd, J = 5.5, 9.5, 12.5 Hz), 4.99 (1H, t, J = 9.7 Hz), 4.94 (1H, d, J = 3.0 Hz), 4.30 (1H, dd, J = 4.5, 12.5 Hz), 4.05 (1H, dd, J = 2.0, 12.0 Hz), 3.95 (1H, ddd, J = 2.0, 4.5, 10.5 Hz), 3.61 (1H, dt, J = 7.0, 13.0 Hz), 3.37 (1H, dt, J = 6.5, 9.5 Hz), 2.22 (1H, dd, J = 5.5, 12.5 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.00 (3H, s), 1.82 (1H, dt, J = 4.0, 12.5 Hz), 1.55–1.61 (2H, m), 1.27–1.30 (14H, m), 0.93 (3H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.7, 170.2, 169.9, 96.8, 69.4, 69.2, 67.8, 67.7, 62.4, 35.0, 31.8, 29.5, 29.5, 29.3, 29.3, 29.2, 26.1, 22.6, 20.9, 20.7, 14.0. ESI-MS: Calcd for $C_{22}H_{38}O_8Na$ $[M+Na]^+$: 453.25, found 453.21.

i-Propyl 2-deoxy-3,4,6-tri-O-acetyl- α -D-glucopyranoside (3j)

Compound **3j** was obtained as colorless syrups (27.0 mg, 90% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2j** (8.4 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, ddd, J = 5.5, 9.5, 12.5 Hz), 5.05 (1H, d, J = 3.0 Hz), 4.97 (1H, t,

J = 10.0 Hz), 4.27 (1H, dd, J = 5.0, 12.0 Hz), 4.01–4.06 (2H, m), 3.84–3.87 (1H, m), 2.16 (1H, dd, J = 5.5, 12.0 Hz), 2.08 (3H, s), 2.03 (3H, s), 2.00 (3H, s), 1.83 (1H, dt, J = 3.5, 12.0 Hz), 1.20 (3H, d, J = 6.0 Hz), 1.03 (3H, d, J = 6.0 Hz). ESI-MS: Calcd for $C_{15}H_{24}O_8Na$ $[M+Na]^+$: 355.14, found 355.08.

Cyclohexyl 2-deoxy-3,4,6-tri-O-acetyl- α -D-glucopyranoside (3k)

Compound **3k** was obtained as colorless syrups (27.8 mg, 83% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2k** (11.5 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.35 (1H, ddd, J = 5.4, 9.5, 11.6 Hz), 5.11 (1H, d, J = 3.0 Hz), 4.98 (1H, t, J = 9.7 Hz), 4.28 (1H, dd, J = 5.2, 12.6 Hz), 4.05–4.08 (2H, m), 3.51–3.55 (1H, m), 2.18 (1H, dd, J = 4.5, 11.9 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.01 (3H, s), 1.84 (3H, td, J = 3.8, 11.8 Hz), 1.73–1.74 (2H, m), 1.21–1.29 (6H,m)

2-Butyl 2-deoxy-3,4,6-tri-O-acetyl- α -D-glucopyranoside (3l)

Compound **3l** was obtained as colorless syrups (28.0 mg, 90% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2k** (9.8 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ5.33 (1H, ddd, J = 5.5, 9.0, 14.5 Hz), 5.07 (1H, d, J = 3.0 Hz), 5.04 (1H, d, J = 3.0 Hz), 4.97 (2H, t, J = 9.5 Hz), 4.26–4.29 (2H, m), 4.08 (2H, d, J = 1.5 Hz), 4.06 (2H, d, J = 12.0 Hz), 3.61–3.65 (2H, m), 2.20 (2H, dd, J = 5.5, 12.0 Hz), 2.08 (3H, s), 2.04 (3H, s), 2.01 (3H, s), 1.85 (1H, dd, J = 3.0, 12.0 Hz), 1.42–1.64 (4H, m), 1.19 (3H, d, J = 6.5 Hz), 1.11 (3H, d, J = 6.0 Hz), 0.93 (3H, t, J = 7.5 Hz), 0.88 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 169.5, 160.5, 168.9, 168.7, 95.4, 92.8, 75.1, 72.4, 68.5, 68.4, 68.0, 68.0, 66.7, 66.6, 61.3, 61.3, 34.3, 34.2, 28.7, 27.7, 19.7, 19.5, 19.5, 19.4, 17.1, 9.1, 8.3. ESI-MS: Calcd for $C_{16}H_{26}O_8Na$ $[M+Na]^+$: .369.15, found 369.14.

O-(2-deoxy-3,4,6-tri-O-acetyl- α -D-glucopyranosyl)-N-Fmoc-L-serine methyl ester (3m)

Compound **3m** was obtained as a white solid (101.5 mg, 92% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **2m** (75.1 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.32–7.78 (8H, m), 5.82 (1H, d, J = 8.2 Hz), 5.27 (1H, ddd, J = 3.3, 5.0, 11.1 Hz), 4.98 (1H, d, J = 11.3 Hz), 4.93 (1H, s), 4.57 (1H, d, J = 7.8 Hz), 4.41 (2H, d, J = 4.9 Hz), 4.28 (2H, dd, J = 4.8, 11.4 Hz), 4.07 (1H, d, J = 12.8 Hz), 3.93 (2H, d, J = 13.0 Hz), 3.80 (3H, s), 2.23 (1H, dd, J = 5.4, 13.0 Hz), 2.07 (3H, s), 2.04 (3H, s), 2.02 (3H, s), 1.83 (1H, td, J = 3.5, 12.8 Hz). ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.5, 170.3, 170.1, 169.8, 155.8, 143.7, 141.2, 127.6, 127.0, 125.0, 119.9, 97.9, 69.1, 68.8, 68.6, 68.5,

67.2, 62.1, 54.2, 52.7, 47.0, 34.7, 29.6, 20.8, 20.6. ESI-MS: Calcd for $C_{31}H_{35}NO_{12}Na$ $[M+Na]^+$: 636.21, found 636.33.

O-(2-deoxy-3,4,6-tri-*O*-acetyl- α-D-glucopyranosyl)-*N*-Fmoc-*L*-threnine methyl ester (3n)

Compound **3n** was obtained as a white solid (95.0 mg, 84% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **2n** (78.1 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.33–7.79 (8H, m), 5.56 (1H, d, J = 9.5 Hz), 5.28–5.29 (1H, m), 4.95–4.99 (2H,m), 4.42–4.44 (3H, m), 4.35 (1H, d, J = 5.5 Hz), 4.28 (2H, dd, J = 5.5, 7.0 Hz), 4.04–4.08 (2H, m), 3.74 (3H, s), 2.13 (1H, dd, J = 4.5, 12.5 Hz), 2.08 (3H, s), 2.06 (3H, s), 2.03 (3H, s), 1.80 (1H, td, J = 2.5, 12.5 Hz), 1.30 (3H, d, J = 1.0 Hz). ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.9, 170.6, 170.2, 169.8, 156.6, 143.8, 143.7, 141.2, 127.6, 127.0, 125.1, 119.9, 98.4, 76.2, 69.4, 68.6, 68.4, 67.4, 62.3, 58.6, 52.5, 47.1, 35.1, 29.6, 20.9, 20.6, 18.2. ESI-MS: Calcd for $C_{32}H_{37}NO_{12}Na$ $[M+Na]^+$: 650.22, found 650.33.

O-(2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-*N*-Fmoc-*L*-threnine methyl ester (3o)

Compound **3o** was obtained as a white solid (105.1 mg, 85% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **2o** (112.6 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.30–7.38 (8H, m), 6.99 (4H, s), 5.62 (1H, s), 5.51 (1H, ddd, J = 3.9, 5.5, 11.1 Hz), 5.25 (1H, d, J = 8.0 Hz), 5.09 (1H, t, J = 9.9 Hz), 4.63 (1H, d, J = 7.5 Hz), 4.46 (1H, dd, J = 7.2, 10.5 Hz), 4.36 (1H, dd, J = 6.8, 10.5 Hz), 4.29 (1H, dd, J = 4.0, 12.2 Hz), 4.20 (1H, t, J = 6.5 Hz), 4.03(1H, d, J = 8.6 Hz), 3.96 (1H, d, J = 12.5 Hz), 3.73 (3 H, s), 3.06 (2H, dd, J = 5.5, 13.0 Hz), 2.45 (1 H, dd, J = 5.2, 13.0 Hz), 2.05 (3 H, s), 2.04 (3 H, s), 2.02 (3 H, s), 1.98 (1 H, dd, J = 3.2, 12.2 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 14.1, 20.6, 20.7, 20.9, 22.6, 29.3, 29.6, 31.9, 35.0, 37.3, 47.1, 52.3, 54.8, 61.9, 66.8, 68.5, 68.8, 69.0, 95.3, 116.4, 120.0, 124.9, 125.0, 127.0, 127.7, 129.6, 130.3, 141.3, 143.6, 143.7,155.3, 155.5, 169.8, 170.2, 170.6, 171.8. ESI-MS: Calcd for $C_{37}H_{39}NO_{12}Na$ $[M+Na]^+$: 712.24, found 712.33.

Cholesteryl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (3p)

Compound **3p** was obtained as a white solid (52.1 mg, 92% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **2p** (56.3 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 0.68 (3 H, s), 0.85 (3 H, d, J = 2.1 Hz), 0.87 (3 H, d, J = 2.1 Hz), 0.91 (4 H, d, J = 6.5 Hz), 1.00 (3 H, s), 1.03–1.17 (7 H, m), 1.25 (3 H, s), 1.32–1.37 (4 H, m), 1.43–1.58 (8 H, m), 1.80–1.86 (4 H, m), 2.00 (3 H, s), 2.05 (3 H, s), 2.08 (3 H, s), 2.18 (1 H, dd, J = 5.2, 12.5 Hz), 2.30–2.33 (2 H, m), 3.42–3.44 (1 H, m), 4.07 (2 H,

dd, J = 4.3 Hz), 4.28 (1 H, ddd, J = 2.1 Hz), 4.99 (1 H, t, J = 9.6 Hz), 5.11 (1 H, d, J = 2.7 Hz), 5.32–5.37 (2 H, m). ESI-MS: Calcd for $C_{39}H_{62}O_8Na$ $[M+H]^+$: 659.44, found 659.11.

Diosgenyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (3q)

Compound **3q** was obtained as a white solid (114.0 mg, 93% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **2q** (89.6 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80 (6 H, d, J = 3.6 Hz), 0.88–0.95 (2 H, m), 0.97 (3 H, d, J = 6.9 Hz), 1.03 (3 H, s), 1.11–1.21 (3 H, m), 1.26 (3 H, s), 1.44–1.51 (6 H, m), 1.63–1.69 (2 H, m), 1.73–1.80 (3 H, m), 1.84–1.89 (4 H, m), 2.02 (3 H, s), 2.05 (3 H, s), 2.09 (3 H, s), 2.19 (1 H, dd, J = 5.7, 12.5 Hz), 2.32–2.34 (2 H, m), 3.38 (1 H, t, J = 10.8 Hz), 3.43–3.49 (2 H, m), 4.07 (2 H, d, J = 10.6 Hz), 4.28 (1 H, dd, J = 5.2, 12.6 Hz), 4.41 (1 H, dd, J = 7.0, 7.8 Hz), 4.98 (1 H, t, J = 9.6 Hz), 5.12 (1 H, d, J = 2.9 Hz), 5.33–5.38 (1 H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 16.2, 17.1, 19.3, 20.7, 20.8, 20.9, 27.7, 28.7, 29.6, 30.2, 31.3, 31.4, 31.8, 32.0, 35.5, 36.8, 36.9, 39.7, 39.9, 40.2, 41.5, 50.0, 54.7, 56.4, 62.0, 62.5, 66.8, 67.8, 69.1, 69.6, 80.7, 95.0, 109.2, 121.5, 140.6, 169.9, 170.2, 170.7. ESI-MS: Calcd for $C_{39}H_{58}O_{10}Na$ $[M+Na]^+$: 709.39, found 709.29.

Prasteryl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (3r)

Compound **3r** was obtained as a white solid (88.0 mg, 88% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **2r** (63.5 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3 H, s), 1.03 (3 H, s), 0.96–1.05 (2 H, m), 1.25–1.31 (3 H, m), 1.44–1.56 (3 H, m), 1.62–1.68 (3 H, m), 1.80–1.88 (4 H, m), 1.95 (1 H, td, J = 4.9, 13.3 Hz), 2.01 (3 H, s), 2.05 (3 H, s), 2.08 (3 H, s), 2.06–2.13 (2 H, m), 2.18 (1 H, dd, J = 4.9, 12.3 Hz), 2.33 (2 H, d, J = 7.5 Hz), 2.45 (1 H, dd, J = 8.7, 10.6 Hz), 3.43–3.45 (1 H, m), 4.06 (2 H, d, J = 10.6 Hz), 4.27 (1 H, dd, J = 5.3, 12.7 Hz), 4.98 (1H, t, J = 9.7 Hz), 5.11 (1 H, d, J = 2.5 Hz), 5.33–5.37 (2 H, m). ESI-MS: Calcd for $C_{31}H_{44}O_9Na$ $[M+Na]^+$: 583.29, found 583.21.

Allyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5a)

Compound **5a** was obtained as colorless syrups (30.0 mg, 94% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2a** (12.2 μL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.87–5.93 (1H, m), 5.27–5.33 (3H, m), 5.19 (1H, d, *J* = 10.0 Hz), 5.05 (1H, d, J = 2.5 Hz), 4.14 (2H, dd, 6.0, 13.0 Hz), 4.08 (2H, d, *J* = 6.5 Hz), 53.97 (1H, dd, *J* = 6.0, 12.5 Hz), 2.13 (3H, s), 2.07 (1H, dt, *J* = 4.0, 12.5 Hz), 2.06 (3H, s), 1.98 (3H, s), 1.88 (1H, dd, *J* = 5.0 12.5 Hz). ESI-MS: Calcd for $C_{15}H_{22}O_8Na$ $[M+Na]^+$: 353.12, found 353.11.

Benzyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5b)

Compound **5b** was obtained as colorless syrups (68.0 mg, 99% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **2b** (37.4 μL, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.29–7.40 (5H, m), 5.37 (1H, s), 5.34–5.36 (1H, m), 5.13 (1H, d, J = 3.2 Hz), 4.71 (1H, d, J = 11.8 Hz), 4.52 (1H, d, J = 11.8 Hz), 4.23 (1H, t, J = 6.6 Hz), 4.11–4.14 (2H, m), 2.16 (3H, s), 2.12 (1H, dd, J = 3.1, 12.1 Hz), 2.08 (3H, s), 2.0 (3H, s), 1.94 (1H, dd, J = 5.0, 12.5 Hz). ESI-MS: Calcd for $C_{19}H_{24}O_8Na$ $[M+Na]^+$: 403.14, found 403.12.

Propargyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D- galactopyranoside (5c)

Compound **5c** was obtained as colorless syrups (29.0 mg, 98% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2c** (12.2 μL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.34 (1H, s), 5.30 (1H, ddd, J = 3.0, 5.0, 8.0 Hz), 5.22 (1H, d, J = 3.0 Hz), 4.22 (2H, t, J = 2.5 Hz), 4.11–4.18 (1H, m), 4.09 (2H, dd, J = 3.0, 6.5 Hz), 2.45 (1H, t, J = 2.5 Hz), 2.14 (3H, s), 2.12 (1H, dd, J = 3.5, 12.5 Hz), 2.05 (3H, s), 1.98 (3H, s), 1.90 (1H, dd, J = 5.0, 12.5 Hz). ESI-MS: Calcd for $C_{15}H_{20}O_8Na$ $[M+Na]^+$: 351.11, found 351.08.

n-Butyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D- galactopyranoside (5d)

Compound **5d** was obtained as colorless syrups (28.0 mg, 90% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2d** (12.2 μL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, s), 5.29 (1H, ddd, J = 3.1, 4.7, 12.4 Hz), 5.00 (1H, d, J = 3.1 Hz), 4.14 (1H, dd, J = 6.6, 13.0 Hz), 4.07–4.10 (2H, m), 3.65 (1H, dt, J = 6.7, 13.4 Hz), 3.40 (1H, dt, J = 6.7, 13.4 Hz), 2.13 (3H, s), 2.09 (1H, dd, J = 3.5, 12.6 Hz), 2.04 (3H, s), 1.98 (3H, s), 1.86 (1H, dd, J = 4.9, 12.6 Hz), 1.55–1.59 (2H, m), 1.26–1.39 (2H, m), 0.93 (1H, t, J = 7.4 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.5, 170.3, 170.0, 97.4, 67.5, 66.7, 66.6, 66.3, 62.5, 31.5, 30.3, 20.8, 20.6, 19.3, 13.8. ESI-MS: Calcd for $C_{16}H_{26}O_8Na$ $[M+Na]^+$: 369.15, found 369.14.

n-Pentyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D- galactopyranoside (5e)

Compound **5e** was obtained as colorless syrups (31.5 mg, 97% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2e** (12.2 μL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, s), 5.30(1H, dd, J = 2.9, 12.3 Hz), 5.00 (1H, s), 4.14 (1H, dd, J = 5.8, 6.2 Hz), 4.08–4.09 (2H, m), 3.61–3.65 (1H, m), 3.37–3.41 (1H, m), 2.13 (3H, s), 2.08 (1H, dt, J = 3.4, 12.5 Hz), 2.05 (3H, s), 1.98 (3H, s), 1.85 (1H, dd, J = 4.9, 12.6 Hz), 1.58 (2H, t, J = 6.0 Hz), 1.25–1.33 (4H, m), 0.91 (3H, t, J = 6.3 Hz); ^{13}C

NMR (125 MHz; $CDCl_3$) δ 170.4, 170.2, 169.9, 97.3, 67.8, 66.7, 66.5, 66.2, 62.5, 30.2, 29.6, 29.0, 28.3, 22.3, 20.8, 20.6, 13.9. ESI-MS: Calcd for $C_{17}H_{32}O_8N$ $[M+NH_4]^+$: 378.2, found 377.9.

n-Hexyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5f)

Compound **5f** was obtained as colorless syrups (31.5 mg, 94% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2f** (12.2 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.35 (1H, s), 5.32 (1H, ddd, J = 3.1, 4.7, 12.4 Hz), 5.01 (1H, d, J = 3.1 Hz), 4.15 (1H, t, J = 6.7 Hz), 4.07–4.10 (2H, m), 3.65 (1H, dt, *J* = 6.7, 13.4 Hz), 3.40 (1H, dt, *J* = 3.0, 6.5 Hz), 2.14 (3H, s), 2.07 (1H, dd, *J* = 3.6, 12.6 Hz), 2.06 (3H, s), 1.99 (3H, s), 1.86 (1H, dd, *J* = 6.8, 12.4 Hz), 1.57–1.60 (2H, m), 1.26–1.36 (6H, m), 0.86 (3H, t, J = 7.1 Hz). ESI-MS: Calcd for $C_{18}H_{30}O_8Na$ $[M+Na]^+$: 397.18, found 397.13.

n-Octyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5g)

Compound **5g** was obtained as colorless syrups (34.5 mg, 95% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2g** (17.2 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.31 (1H, S), 5.27 (1H, ddd, J = 3.1, 4.8, 12.3 Hz), 4.97 (1H, d, J = 3.1 Hz), 4.12 (1H, dd, J = 5.6, 6.5 Hz), 4.03–4.08 (2H, m), 3.61 (1H, dt, *J* = 6.8, 9.5 Hz), 3.37 (1H, dt, *J* = 6.8, 9.5 Hz), 2.11 (3H, s), 2.09 (1H, dd, *J* = 3.6, 12.5 Hz), 2.03 (3H, s), 1.97 (3H, s), 1.84 (1H, dd, *J* = 4.9, 12.3 Hz), 1.23–1.33 (12H, m), 0.86 (3H, t, J = 7.1 Hz). ESI-MS: Calcd for $C_{20}H_{34}O_8Na$ $[M+Na]^+$: 425.21, found 425.20.

n-Nonyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5h)

Compound **5h** was obtained as colorless syrups (29 mg, 99% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2h** (19.1 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, s), 5.30 (1H, ddd, J = 3.0, 4.8, 12.4 Hz), 4.99 (1H, d, J = 2.9 Hz), 4.13 (1H, dd, J = 6.2, 6.7 Hz), 4.08–4.10 (2H, m), 3.60–3.65 (1H, m), 3.36–3.41 (1H, m), 2.13 (3H, s), 2.08 (1H, dt, *J* = 3.6, 12.6 Hz), 2.05 (3H, s), 1.98 (3H, s), 1.85 (1H, dd, *J* = 4.9, 12.7 Hz), 1.57 (2H, t, J = 6.7 Hz), 1.25–1.30 (12H, m), 0.88 (3H, t, J = 6.6 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.4, 170.3, 170.0, 97.3, 67.8, 66.7, 66.5, 66.2, 62.5, 31.8, 30.2, 29.6, 29.4, 29.3, 29.2, 26.1, 22.6, 20.8, 20.6, 14.0. ESI-MS: Calcd for $C_{21}H_{40}O_8N$ $[M+NH_4]^+$: 434.3, found 433.9.

n-Decyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5i)

Compound **5i** was obtained as colorless syrups (34 mg, 88% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2i** (12.2 µL, 0.11 mmol, 1.2 equiv.)

under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.31 (1H, s), 5.27 (1H, ddd, J = 3.2, 4.7, 12.4 Hz), 4.97 (1H, d, J = 3.1 Hz), 4.11 (1H, dd, J = 6.6, 6.7 Hz), 4.06 (2H, m), 3.60 (1H, dt, J = 6.6, 13.2 Hz), 3.36 (1H, dt, J = 6.6, 13.2 Hz), 2.10 (3H, s), 2.05 (1H, dt, *J* = 2.4, 12.6 Hz), 2.10 (3H, s), 2.05 (1H, dd, J = 2.4, 12.6 Hz), 2.02 (3H, s), 1.96 (3H, s), 1.83 (1H, dd, *J* = 5.0, 12.6 Hz), 1.52–1.56 (2H, m), 1.24–1.30 (14H, m), 0.86 (3H, t, J = 6.7 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.4, 140.3, 170.0, 97.4, 67.9, 66.7, 66.5, 66.3, 62.5, 31.8, 60.2, 29.6, 29.5, 29.4, 29.3, 26.2, 22.6, 20.8, 20.6, 19.3, 14.0. ESI-MS: Calcd for $C_{22}H_{38}O_8Na$ $[M+Na]^+$: 453.25, found 453.21.

i-Propyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5j)

Compound **5j** was obtained as colorless syrups (27 mg, 90% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2j** (8.4 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.31 (1H, s), 5.29 (1H, ddd, J = 3.0, 4.8, 12.3 Hz), 5.11 (1H, d, J = 3.2 Hz), 4.20 (1H, t, J = 6.4, 6.7 Hz), 4.06 (2H, dd, J = 2.0, 6.0 Hz), 3.85–3.87 (1H, m), 2.12 (3H, s), 2.07 (1H, dt, J = 3.7, 12.4 Hz), 2.03 (3H, s), 1.96 (3H, s), 1.78 (1H, dd, *J* = 4.9, 12.4 Hz), 1.19 (3H, d, J = 6.1 Hz), 1.13 (3H, d, J = 6.1 Hz). ESI-MS: Calcd for $C_{15}H_{24}O_8Na$ $[M+Na]^+$: 355.14, found 355.11.

Cyclohexyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5k)

Compound **5k** was obtained as colorless syrups (29.1 mg, 87% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2k** (11.5 µL, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (1H, s), 5.31 (1H, ddd, J = 3.1, 4.7, 12.2 Hz), 5.17 (1H, d, J = 3.1 Hz), 4.24 (1H, t, J = 6.4 Hz), 4.06–4.11 (2H, m), 3.54–3.56 (1H, m), 2.14 (3H, s), 2.06 (1H, dd, J = 3.6, 6.5 Hz), 2.04 (3H, s), 2.00 (3H, s), 1.82 (1H, td, J = 2.9, 11.6 Hz), 1.55–1.59 (2H, m), 1.24–1.29 (6H, m). ESI-MS: Calcd for $C_{18}H_{28}O_8Na$ $[M+Na]^+$: 395.17, found 395.16.

2-Butyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5l)

Compound **5l** was obtained as colorless syrups (55 mg, 89% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **2l** (19.6 µL, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 5.33 (3H, app.s), 4.33 (1H, t, J = 6.5 Hz), 4.02–4.09 (2H, m), 2.13 (3H, s), 2.08 (1H, dd, J = 3.5, 12.2 Hz), 2.03 (3H, s), 1.98 (3H, s), 1.72 (1H, dd, J = 4.5, 12.2 Hz), 1.25 (9H, s). ESI-MS: Calcd for $C_{16}H_{26}O_8Na$ $[M+Na]^+$: 369.15, found 369.14.

O-(2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*N*-Fmoc-*L*-serine methyl ester (5m)

Compound **5m** was obtained as a white solid (108.1 mg, 98% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **2m** (75.1 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.32–7.78 (8H, m), 5.84 (1H, d, J = 8.5 Hz), 5.34 (1H, s), 5.23 (1H, d, J = 11.2 Hz), 4.99 (1H, s), 4.57 (1H, dd, J = 3.8, 4.3 Hz), 4.41 (2H, dd, J = 6.2, 7.1 Hz), 4.26 (1H, dd, J = 6.8, 7.1 Hz), 4.10 (1H, d, J = 6.2 Hz), 4.05 (2H, d, J = 6.4 Hz), 3.94 (2H, s), 3.79 (3H, s), 2.13 (3H, s), 2.08 (1H, dd, J = 2.8, 12.5 Hz), 2.00 (3H, s), 1.98 (3H, s), 1.85 (1H, dd, J = 4.5, 12.8 Hz). ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.4, 170.3, 170.1, 169.9, 155.8, 143.7, 141.1, 127.6, 127.0, 125.0, 119.9, 98.1, 68.3, 67.2, 67.1, 66.3, 65.8, 62.3, 54.2, 52.6, 46.9, 29.8, 29.5, 20.7, 20.6, 20.5. ESI-MS: Calcd for $C_{31}H_{35}NO_{12}Na$ $[M+Na]^+$: 636.21, found 636.33.

O-(2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*N*-Fmoc-*L*-threnine methyl ester (5n)

Compound **5n** was obtained as a white solid (98.0 mg, 87% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **2n** (100.3 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.32–7.78 (8H, m), 5.48 (1H, d, J = 9.5 Hz), 5.34 (1H, s), 5.24 (1H, d, J = 12.0 Hz), 5.01 (1H, d, J = 2.5 Hz), 4.41–4.44 (3H,m), 4.37 (1H, d, J = 6.0 Hz), 4.28 (1H, dd, J = 7.0, 7.0 Hz), 4.22 (2H, dd, J = 6.0, 6.5 Hz), 4.09 (2H, d, J = 6.0 Hz), 3.76 (3H, s), 2.13 (3H, s), 2.05 (3H, s), 2.02 (1H, td, J = 3.5, 12.0 Hz), 1.99 (3H, s), 1.76 (1H, dd, J = 4.0 12.0 Hz), 1.31 (3H, d, J = 5.9 Hz). ^{13}C NMR (125 MHz; $CDCl_3$) δ 171.0, 170.4, 170.2, 170.1, 156.6, 143.7, 143.6, 141.2, 127.6, 127.0, 125.0, 119.9, 99.0, 76.0, 67.3, 67.1, 66.4, 65.8, 62.4, 58.6, 52.4, 47.1, 30.2, 29.6, 20.7, 20.6, 18.2. ESI-MS: Calcd for $C_{32}H_{37}NO_{12}Na$ $[M+Na]^+$: 650.22, found 650.33.

O-(2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*N*-Fmoc-*L*-threnine methyl ester (5o)

Compound **5o** was obtained as a white solid (52.1 mg, 84% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2o** (56.3 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.30–7.38 (8H, m), 6.98 (4H, m), 5.67 (1H, s), 5.47 (1H, ddd, J = 3.7, 4.4, 8.0 Hz), 5.37 (1H, s), 5.22 (1H, d, J = 8.2 Hz), 4.64 (1H, d, J = 7.5 Hz), 4.45 (1H, dd, J = 7.5, 10.5 Hz), 4.36 (1H, dd, J = 6.8, 10.5 Hz), 4.35 (1H, dd, J = 7.5, 10.5 Hz), 4.18 (2 H, d, J = 6.4 Hz), 4.04 (2 H, d, J = 6.4 Hz), 3.74 (3H, s), 3.06 (2H, dd, J = 6.0, 14.0 Hz), 2.23 (1 H, td, J = 3.2, 12.4 Hz), 2.16 (3 H, s), 2.07 (1 H, dd, J = 4.6, 12.8 Hz), 2.03 (3 H, s), 1.91 (3 H, s); ^{13}C NMR (125 MHz; $CDCl_3$) δ 14.1, 20.5, 20.7, 20.8, 29.6, 30.2, 37.3, 47.1, 52.3, 54.8, 61.9, 65.9, 66.3, 66.8, 67.4, 95.9,

166.5, 120.0, 124.9, 125.0, 127.0, 127.7, 129.5, 130.3, 141.3, 143.7, 143.8, 155.5, 170.1, 170.2, 170.3, 171.8. ESI-MS: Calcd for $C_{37}H_{39}NO_{12}Na$ $[M+Na]^+$: 712.24, found 712.33.

Cholesteryl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5p)

Compound **5p** was obtained as a white solid (52.1 mg, 84% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **2p** (56.3 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 0.68 (3 H, s), 0.85 (3 H, d, J = 1.5 Hz), 0.88 (3 H, d, J = 2.5 Hz), 0.92 (4 H, d, J = 6.5 Hz), 1.01 (3 H, s), 1.08–1.15 (7 H, m), 1.26–1.34 (8 H, m), 1.48 -1.52 (7 H, m), 1.81–1.87 (4 H, m), 1.99 (3 H, s), 2.05 (3 H, s), 2.11 (1 H, dd, J = 3.6, 6.5 Hz), 2.14 (3 H, s), 2.32 (2 H, d, J = 7.5 Hz), 3.45–3.48 (1 H, m), 4.06–4.10 (2 H, m), 4.26 (1 H, t, J = 6.5 Hz), 5.18 (1 H, d, J = 2.5 Hz), 5.30–5.37 (3 H, m). ESI-MS: Calcd for $C_{39}H_{62}O_8Na$ $[M+H]^+$: 659.44, found 659.11.

Diosgenyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5q)

Compound **5q** was obtained as a white solid (115.0 mg, 93% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **2q** (89.6 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76 (6 H, d, J = 3.5 Hz), 0.94 (3 H, d, J = 6.9 Hz), 1.00 (3 H, s), 1.23–1.27 (4 H, m), 1.40–1.49 (5 H, m), 1.58–1.65 (7 H, m), 1.70–1.86 (7 H, m), 1.95 (3 H, s), 2.02 (3 H, s), 2.05 (1 H, dd, J = 3.5, 12.5 Hz), 2.10 (3 H, s), 2.28–2.30 (2 H, m), 3.35 (1 H, t, J = 10.9 Hz), 3.40–3.45 (2 H, m), 4.04–4.08 (2 H, m), 4.23 (1 H, t, J = 6.5 Hz), 4.37 (1 H, dd, J = 7.7, 16.0 Hz), 5.14 (1 H, d, J = 2.7 Hz), 5.27–5.33 (3 H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 16.2, 17.1, 19.3, 20.7, 20.7, 20.8, 20.9, 27.8, 28.7, 30.2, 31.3, 31.4, 31.8, 32.0, 36.8, 37.0, 39.9, 40.2, 41.5, 50.7, 56.4, 62.6, 66.3, 66.7, 66.8, 66.9, 80.7, 95.7, 109.2, 121.5, 140.7, 170.0, 170.3, 170.5. ESI-MS: Calcd for $C_{39}H_{58}O_{10}Na$ $[M+Na]^+$: 709.39, found 709.31.

Prasteryl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D- galactopyranoside (5r)

Compound **5r** was obtained as a white solid (91.0 mg, 90% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **2r** (63.5 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (3 H, s), 1.03 (3 H, s), 0.96–1.04 (2 H, m), 1.25–1.31 (3 H, m), 1.45–1.54 (3 H, m), 1.63–1.68 (3 H, m), 1.81–1.88 (4 H, m), 1.95 (1 H, dd, J = 2.6, 6.8 Hz), 1.98 (3 H, s), 2.04 (3 H, s), 2.06–2.12 (2 H, m), 2.13 (3 H, s), 2.32–2.34 (2 H, m), 2.45 (1 H, dd, J = 8.8, 10.5 Hz), 3.44–3.46 (1 H, m), 4.07–4.11 (2 H, m), 4.25 (1 H, dd, J = 6.4, 6.7 Hz), 5.17 (1 H, d, J = 2.9 Hz), 5.29–5.33 (2 H, m), 5.39 (1 H, d, J = 4.9 Hz); ESI-MS: Calcd for $C_{31}H_{44}O_9Na$ $[M+Na]^+$: 583.29, found 583.24.

Trichloroethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (7a)

Compound **7a** was obtained as colorless syrups (69.0 mg, 90% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **6a** (63.8 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (dt, J = 1.05, 12.3 Hz, 1 H), 2.01 (s, 3 H), 2.02(s, 3 H), 2.03 (s, 3 H), 2.27 (dd, J = 5.4, 12.9 Hz, 1 H), 3.56 (t, J = 9.6 Hz, 1 H), 3.63 (dd, J = 6.0, 9.8 Hz, 2 H), 3.81 (dd, J = 4.6, 11.4 Hz, 1 H), 3.88–3.97 (m, 3 H), 4.09 (d, J = 11.5 Hz, 1 H), 4.14 (dd, J = 4.5, 12.3 Hz, 2 H), 4.18 (d, J = 11.5 Hz, 1 H), 4.63 (d, J = 11.3 Hz, 1 H), 4.71 (d, J = 11.9 Hz, 1 H), 4.80 (d, J = 11.0 Hz, 2 H), 4.96–5.05 (m, 5 H), 5.28 (ddd, J = 1.8, 5.4, 9.6 Hz, 1 H), 7.26–7.40 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 20.8, 29.6, 34.7, 62.1, 65.8, 67.9, 68.9, 69.1 70.9, 72.9, 74.9, 75.6, 77.3, 79.4, 80.1, 81.5, 96.2, 97.1, 97.4, 127.4, 127.5, 127.7, 127.8, 127.8, 127.9, 128.3, 128.3, 128.4, 138.1, 138.5, 169.7, 169.9, 170.5; ESI-MS: Calcd for $C_{41}H_{47}O_{13}Na$ $[M+Na]^+$: 875.2, found 874.5.

trichloroethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-α-D-glucopyranoside (8a)

Compound **8a** was obtained as colorless syrups (74.0 mg, 97% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **6a** (63.8 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90 (dd, J = 5.0, 12.7 Hz, 1 H), 1.97 (s, 3 H), 2.00 (s, 3 H), 2.05 (dt, J = 3.4, 12.6 Hz, 1 H), 2.13 (s, 3 H), 3.53–3.57 (m, 1 H), 3.61 (dd, J = 3.7, 9.7 Hz, 1 H), 3.65 (dd, J = 1.5, 10.3 Hz, 1 H), 3.81 (dt, J = 4.8, 11.5 Hz, 1 H), 3.91 (dd, J = 4.0, 10.5 Hz, 1 H), 3.98–4.03 (m, 3 H), 4.06–4.11 (m, 2 H), 4.18 (dd, J = 4.5, 11.5 Hz, 1 H), 4.63 (d, J = 11.2 Hz, 1 H), 4.82 (d, J = 13.5 Hz, 2 H), 4.98–5.03 (m, 3 H), 5.07 (d, J = 2.8 Hz, 1 H), 5.24 (ddd, J = 4.5, 7.9, 12.4 Hz, 1 H), 5.29 (d, J = 2.4 Hz, 1 H), 726–7.41 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 20.8, 29.6, 29.9, 61.5, 62.3, 65.8, 65.9, 66.4, 66.7, 70.8, 72.9, 72.9, 75.1, 75.7, 77.3, 79.3, 79.4, 79.9, 80.0, 81.3, 81.5, 96.1, 97.3, 97.6, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 137.9, 138.0, 138.4, 169.8, 170.2,170.3; ESI-MS: Calcd for $C_{41}H_{47}O_{13}Na$ $[M+Na]^+$: 875.2, found 875.5.

4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-α-D-galactopyranoside (7b)

Compound **7b** was obtained as colorless syrups (110.0 mg, 89% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **6b** (90.7 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78 (dt, J = 3.0, 11.2 Hz, 1 H), 1.97 (s, 3 H), 2.01 (s, 3 H), 2.03 (s, 3 H), 2.07 (s, 3 H), 2.10 (dd, J = 3.3, 11.2 Hz, 1 H), 2.14 (s, 3 H), 2.19 (s, 3

H), 3.76 (s, 3 H), 3.90–3.94 (m, 3 H),4.11–4.25 (m, 4 H), 4.81 (d, J = 8.0 Hz, 1 H), 4.97 (t, J = 9.7 Hz, 1 H), 5.10–5.12 (m, 1 H), 5.19 (d, J = 2.4 Hz, 1 H), 5.37–5.42 (m, 2 H), 6.79 (d, J = 9.0 Hz, 2 H), 6.94 (dd, J = 2.2, 9.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 20.6, 20.7, 20.8, 34.0, 55.5, 61.4, 62.1, 64.8, 68.3, 68.5, 69.0, 69.4, 70.7, 72.3, 93.6, 100.9, 114.4, 118.5, 151.0, 155.6, 168.7, 169.7, 169.8, 170.3, 170.5, 170.6; ESI-MS: Calcd for $C_{31}H_{44}O_{17}N$ $[M+NH_4]^+$: 702.3, found 702.2.

4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-α-D-galactopyranoside (8b)

Compound **8b** was obtained as colorless syrups (69.3 mg, 99% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **6b** (90.7 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (dd, J = 5.0, 13.0 Hz, 1 H), 1.96 (s, 3 H), 2.03 (s, 3 H), 2.07 (s, 3 H), 2.08 (dd, J = 7.0, 13.0 Hz, 1 H), 2.14 (s, 3 H), 2.16 (s, 3 H), 2.19 (s, 3 H), 3.77 (s, 3 H), 3.93–3.97 (m, 2 H), 4.04 (dd, J = 5.2, 9.8 Hz, 1 H), 4.11–4.20 (m, 3 H), 4.25 (dd, J = 6.9, 11.4 Hz, 1 H), 4.84 (d, J = 8.0 Hz, 1 H), 5.07 (ddd, J = 3.0, 4.7, 8.0 Hz, 1 H), 5.26 (d, J = 2.8 Hz, 1 H), 5.33 (s, 1 H), 5.39 (dd, J = 2.2, 8.0 Hz, 1 H), 5.44 (d, J = 2.8 Hz, 1 H), 6.80 (d, J = 9.0 Hz, 2 H), 6.96 (dd, J = 3.5, 9.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 20.6, 20.6, 20.7, 29.0, 29.6, 55.5, 61.5, 62.0, 64.9, 65.7, 66.1, 67.1, 69.3, 70.7, 72.0, 94.0, 100.9, 114.4, 118.5, 151.0, 155.6, 169.0, 169.8, 170.2, 170.3, 170.5; ESI-MS: Calcd for $C_{31}H_{44}O_{17}N$ $[M+NH_4]^+$: 702.3, found 702.1.

methyl 3,4,6-tri-*O*-benzyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-α-D-mannopyranoside (7c)

Compound **7c** was obtained as colorless syrups (126.1 mg, 95% yield) from the reaction between **1** (60.0 mg, 0.18 mmol) and **6c** (100.3 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (dt, J = 9.0, 3.0 Hz, 1 H), 2.00 (s, 3 H), 2.02 (s, 3 H), 2.09 (s, 3 H), 2.39 (dd, J = 5.0, 12.5 Hz, 1 H), 3.35 (s, 3 H), 3.72–3.76 (m, 3 H), 3.86–3.92 (m containing dd, J = 12.0, 3.0 Hz, 2 H), 3.95 (d, J = 2.0 Hz, 1 H), 4.06 (dd, J = 2.0, 12.5 Hz, 1 H), 4.18 (ddd, J = 2.0, 5.0, 10.0 Hz, 1 H), 4.27 (dd, J = 5.0, 12.0 Hz, 1 H), 4.51 (d, J = 11.0 Hz, 1 H), 4.60–4.71 (m, 4 H), 4.78 (d, J = 1.5 Hz, 1 H), 4.82 (d, J = 10.5 Hz, 1 H), 4.99 (t, J = 10.5 Hz, 1 H), 5.12 (d, J = 3.0 Hz, 1 H), 5.39 (ddd, J = 5.5, 2.0, 9.5 Hz, 1 H), 7.16–7.18 (m, 2 H), 7.25–7.39 (m, 13 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 20.7, 20.9, 29.6, 35.0, 54.6, 62.5, 68.0, 68.8, 69.1, 69.5, 71.5, 72.2, 73.1, 74.7, 75.0, 75.2, 79.7, 98.7, 99.6, 127.2, 127.3, 127.5, 127.6,127.7, 127.8, 128.2, 128,3, 128.3, 138.2, 138.3, 169.9, 170.6; ESI-MS: Calcd for $C_{40}H_{52}O_{13}N$ $[M+NH_4]^+$: 754.3, found 754.2.

methyl 3,4,6-tri-*O*-benzyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-α-D-mannopyranoside (8c)

Compound **8c** was obtained as colorless syrups (130.1 mg, 98% yield) from the reaction between **4** (60.0 mg, 0.18 mmol) and **6c** (100.3 mg, 0.22 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 2.02–2.07 (m, 2 H), 2.06 (s, 3 H), 2.14 (s, 3 H), 3.37 (s, 3 H), 3.72–3.77 (m, 3 H), 3.86 (dd, J = 4.0, 9.3 Hz, 1 H), 3.92 (dd, J = 2.8, 9.3 Hz, 1 H), 4.00 (s, 1 H), 4.09 (dd, J = 2.7, 4.6 Hz, 2 H), 4.31 (t, J = 6.3 Hz, 1 H), 4.52 (d, J = 10.8 Hz, 1 H), 4.59 (d, J = 12.0 Hz, 1 H), 4.66 (d, J = 11.8 Hz, 1 H), 4.67 (d, J = 12.0 Hz, 1 H), 4.70 (d, J = 11.8 Hz, 1 H), 4.80 (d, J = 0.3 Hz, 1 H), 4.84 (d, J = 10.8 Hz, 1 H), 5.23 (d, J = 2.4 Hz, 1 H), 5.34 (s, 1 H), 5.30–5.33 (ddd, J = 2.4, 5.5, 9.0 Hz, 1 H), 7.12–7.19 (m, 2 H), 7.26–7.38 (m, 13 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 20.7, 20.8, 30.1, 54.7, 62.7, 66.0, 66.7, 67.0 69.1, 71.6, 72.2, 73.2, 74.6, 74.8, 75.0, 79.8, 99.1, 99.7, 127.3, 127.5, 127.5, 127.6, 127.8, 128.2, 128.3, 138.2, 138.3, 138.3, 169.8, 170.0, 170.4; ESI-MS: Calcd for $C_{40}H_{52}O_{13}N$ $[M+NH_4]^+$: 754.3, found 754.2.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (7d)

Compound **7d** was obtained as colorless syrups (57.7 mg, 87% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **6d** (51.1 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (dd, J = 3.7, 12.1 Hz, 1 H), 1.98 (s, 3 H), 2.02 (s, 6 H), 2.02–2.04 (m, 1 H), 3.41 (m, 3 H), 3.53 (dd, J = 3.4, 9.6 Hz, 1 H), 3.64–3.68 (m, 3 H), 3.76–3.78 (m, 2 H), 3.84 (d, J = 10.0 Hz, 1 H), 3.93 (t, J = 9.2 Hz, 1 H), 4.13 (dd, J = 4.0, 12.2 Hz, 1 H), 4.51 (d, J = 12.2 Hz, 1 H), 4.61–4.66 (m, 4 H), 4.72 (d, J = 12.0 Hz, 1 H), 4.90 (t, J = 9.7 Hz, 1 H), 5.03 (d, J = 11.3 Hz, 1 H), 5.21 (ddd, J = 1.9, 4.9, 11.3 Hz, 1 H), 5.41 (d, J = 3.0 Hz, 1 H), 7.27–7.33 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 20.6, 20.9, 22.6, 29.3, 29.6, 29.7, 31.8, 35.1, 55.2, 62.1,68.5, 68.7, 69.1, 69.2, 69.5, 73.1, 73.3, 75.3, 76.3, 80.0, 81.7, 97.7, 98.5, 127.4, 127.4, 127.4, 127.5, 127.9, 128.0, 128.3, 128.4, 128.4, 137.8, 138.0, 138.5, 169.9, 170.1, 170.5; ESI-MS: Calcd for $C_{40}H_{52}O_{13}N$ $[M+NH_4]^+$: 754.3, found 754.2.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-α-D-glucopyranoside (8d)

Compound **8d** was obtained as colorless syrups (60.3 mg, 91% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **6d** (51.1 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.72 (dd, J = 4.8, 12.3 Hz, 1 H), 1.91 (dt, J = 3.6, 12.3 Hz, 1 H), 1.96 (s, 3 H), 1.97 (s, 3 H), 2.09 (s, 3 H), 3.41 (s, 3 H), 3.52 (dd, J = 3.4, 9.7 Hz, 1 H), 3.64–3.68 (m, 3 H), 3.76–3.78 (m, 1 H), 3.88–3.94 (m, 3 H), 3.98 (t, J = 6.5 Hz, 1 H), 4.52 (d,

J = 12.2 Hz, 1 H), 4.62 (dd, J = 3.5, 11.6 Hz, 4 H), 4.72 (d, J = 12.0 Hz, 1 H), 5.04 (d, J = 11.2 Hz, 1 H), 5.16 (dd, J = 4.7, 11.1 Hz, 1 H), 5.20 (s, 1 H), 5.47 (d, J = 2.7 Hz, 1 H), 7.27–7.35 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 20.6, 20.8, 22.6, 29.3, 29.6, 29.7, 30.3, 31.8, 55.2, 62.2, 65.8, 66.4, 67.2, 69.1, 69.5, 73.0, 73.1, 75.3, 76.1, 80.6, 81.7, 97.6, 99.1, 127.4, 127.5, 127.6, 127.9, 128.1, 128.3, 128.4, 128.4, 137.8, 138.0, 138.4, 169.9, 170.2; ESI-MS: Calcd for $C_{40}H_{52}O_{13}N$ $[M+NH_4]^+$: 754.3, found 754.2.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (7e)

Compound **7e** was obtained as colorless syrups (76.3 mg, 99% yield) from the reaction between **1** (30.0 mg, 0.09 mmol) and **6e** (64.3 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.95 (4H, m), 7.82 (2H, m), 7.57–7.51 (4H, m), 7.46–7.33 (8H, m), 7.29 (2H, m), 5.92 (1H, t, J = 9.5 Hz), 5.54 (1H, t, J = 9.5 Hz), 5.53 (1H, t, J = 9.5 Hz), 5.37–5.32 (1H, m), 5.00 (1H, t, J = 10 Hz), 4.97 (1H, d, J = 3 Hz), 4.24 (1H, dd, J = 12.5, 4.5 Hz), 4.12–4.06 (2H, m), 3.97 (1H, dd, J = 12, 1.5 Hz), 3.93 (1H, dd, J = 11, 6 Hz), 3.67 (1H, dd, J = 11, 2 Hz), 2.24 (1H, dd, J = 12.5, 5.5 Hz), 2.07 (3H, s), 2.05 (3H, s), 1.98 (3H, s), 1.82 (1H, dt, J = 12.5, 4 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.69, 170.02, 169.89, 165.78, 165.16, 165.07, 133.55, 133.32, 133.22, 132.54, 132.27, 129.89, 129.85, 129.76, 129.18, 129.00, 128.79, 128.50, 128.40, 128.29, 128.15, 97.05, 86.53, 77.17, 74.21, 70.54, 69.56, 69.15, 69.05, 67.92, 66.66, 62.13, 34.71, 21.00, 20.74, 20.69. ESI-MS: Calcd for $C_{45}H_{44}O_{15}SNa$ $[M+Na]^+$: 879.23, found 879.17.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (8e)

Compound **8e** was obtained as colorless syrups (69.3 mg, 90% yield) from the reaction between **4** (30.0 mg, 0.09 mmol) and **6e** (64.3 mg, 0.11 mmol, 1.2 equiv.) under the same conditions described above for the synthesis of **3a.** ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.97 (4H, m), 7.81 (2H, m), 7.53 (4H, m), 7.40 (8H, m), 7.29 (2H, m), 5.92 (1H, t, J = 4.5 Hz), 5.59 (1H, t, J = 4.5 Hz), 5.51 (1H, t, J = 4.5 Hz), 5.25 (1H, s), 5.24–5.20 (1H, m), 5.11 (1H, d, J = 10 Hz), 5.04 (1H, d, J = 3 Hz), 4.101 (1H, t, J = 6 Hz), 4.07–4.03 (1H, m), 3.99 (2H, d, J = 6.5 Hz), 3.92 (1H, dd, J = 11, 5.5 Hz), 3.70 (1H, dd, J = 11, 2.5 Hz), 2.13 (3H, s), 2.06 (1H, dd, J = 8.5, 3.5 Hz), 2.02 (3H, s), 1.95 (3H, s), 1.82 (1H, dd, J = 12.5, 5.5 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 170.44, 170.28, 169.77, 165.80, 165.16, 165.06, 133.47, 133.32, 133.22, 132.46, 132.08, 129.89, 129.82, 129.76, 129.22, 129.10, 128.88, 128.80, 128.49, 128.40, 128.28, 97.57, 86.07, 77.18, 74.23, 70.60, 69.55, 66.84, 66.63, 66.51, 66.39, 66.07, 62.45, 29.83, 20.87, 20.70, 20.64. ESI-MS: Calcd for $C_{45}H_{44}O_{15}SNa$ $[M+Na]^+$: 879.23, found 879.17.

In vitro antitumor test

Human carcinoma cell line (SMMC-7721) was cultured in RPMI-1640 medium supplemented with 10% fetal bovine serum under an atmosphere of 5% carbon dioxide at 37°C. Cells were subcultured in the same medium under the same conditions after reaching 70–80% confluency and were maintained in the log phase for further experiments. The cell suspensions were dispensed (200 lL) in triplicate into 96-well culture plates at optimized concentrations of 1×10^4 cells/well in a complete medium. The tested samples at final concentrations of 10, 50 and 100 μg/ml in well. In control wells, only culture medium with vehicle was added. After an additional 72 h incubation period, the medium in each well was aspirated and replaced with 100 μL MTT working solution. The cells were incubated at 37°C for 4 h, and then the medium was aspirated and replaced with 100 μL DMSO to dissolve the formazan crystals that are formed. The culture plates were shaken for 5 min, and the absorbance of each well was read at 540 nm. The results were expressed as the inhibition ratio of tumor cell proliferation calculated as (A-B)/A × 100%. A and B are the average numbers of viable tumor cells of the control and the samples, respectively.

Acknowledgements

We thank the analytic center of East China Normal University for data measurement. The project was supported by Natural Science Foundation of Shanghai (11ZR1410400), "DAXIA" Foundation of East China Normal University (2011DX-084) and large instruments Open Foundation of East China Normal University (20151043&20162015).

Funding

Natural Science Foundation of Shanghai [11ZR1410400]; "DAXIA" Foundation of East China Normal University [2011DX-084]; large instruments Open Foundation of East China Normal University [20151043, 20162015].

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