Tetrahedron 69 (2013) 7090–7097

Contents lists available at SciVerse ScienceDirect

Tetrahedron

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

The effect of electron withdrawing protecting groups at positions 4 and 6 on 1,2-*cis* galactosylation

Eva C. Lourenço, M. Rita Ventura *

Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Apartado 127, 2780-901 Oeiras, Portugal

ARTICLE INFO

Article history:
Received 17 April 2013
Received in revised form 5 June 2013
Accepted 11 June 2013
Available online 18 June 2013

Keywords:
α-Galactosides
α-Galactosylation
Thiogalactosides
4-Chloroacetyl ester

ABSTRACT

Ethyl 2,3,4-*O*-tribenzyl-6-*O*-chloroacetyl-1-D-thiogalactoside, phenyl 4,6-*O*-diacetyl-2,3-dibenzyl-1-D-thiogalactoside and phenyl 2,3-*O*-dibenzyl-4,6-*O*-dichloroacetyl-1-D-thiogalactoside were employed in the study of the stereoselectivity of the glycosylation reaction with several acceptors, ranging from unhindered linear primary alcohols to other sugars, using NIS/TfOH as activator. Higher α-selectivities were obtained in the glycosylation reactions with phenyl 2,3-*O*-dibenzyl-4,6-*O*-dichloroacetyl-1-D-thiogalactoside as the donor, showing that a stronger electron withdrawing 4-*O*-ester group had an influence in the anomeric selectivity favouring the formation of 1,2-*cis* galactosides.

1. Introduction

Recently, we reported that NIS/TfOH mediated glycosylations of ethyl 6-*O*-acetyl-2,3,4-*O*-tribenzyl-1-D-thioglucoside **1** afforded higher α-anomeric selectivities when compared with other 6-*O*-protecting groups. The choice of solvent was also found to be very important and ethyl ether was the solvent that afforded the higher α-selectivities.[1] We believe that the 6-*O*-acetyl group being electron withdrawing, reduced the reactivity at the anomeric position compared to e.g., the tetrabenzylated thioglycoside and favoured the formation of the α-glucosides (1,2-*cis* glucosylation).[1–3] It is well established that the overall reactivity of the donor affects the stereoselectivity of the glycosylation reaction, and the protecting groups of the donor have a strong influence in the anomeric outcome of the glycosylation reaction.[4–6] The corresponding glycosylation reactions of ethyl 6-*O*-acetyl-2,3,4-*O*-tribenzyl-1-D-thiogalactoside **7** in ethyl ether were generally less stereoselective than those with the corresponding glucoside donor, and changing the solvent or lowering the reaction temperature did not improve the results.[1] Thiogalactosides are more reactive than thioglucosides,[1,7–9] and it has been hypothesised that this increased reactivity results from the stabilisation of the oxacarbenium ion and the related species[5] by the axial substituents at C-4 of galactose. The solvation of the leaving group and/or the promoter may also play a role in the galactose/glucose reactivity difference, an axial substituent as in galactose, leads to better solvation, increasing the reactivity during the glycosylation reaction.[10]

We decided to explore the influence of C-6 and C-4 remote neighbouring groups on the reactivity of some thiogalactosides and hence attempt to improve the stereoselectivity of the glycosylation reaction.[11] The effect of having different electron withdrawing groups (acetate and chloroacetate) at C-6 and at both C-4 and C-6 was studied.

2. Results and discussion

Thiogalactoside **3**, having a chloroacetate group at position C-6, was obtained from donor **1**[1] in two steps as described in Scheme 1.

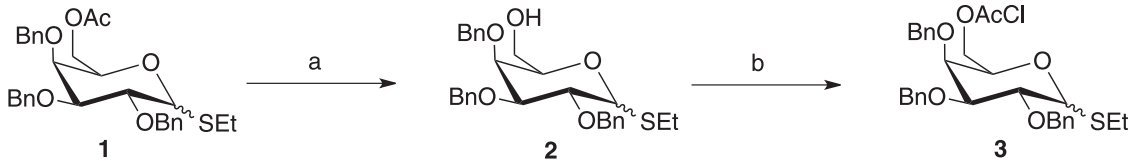
Donor **5**[12] with acetate groups at both C-4 and C-6 was prepared as previously described. Donor **6** with chloroacetate groups at C-4 and C-6,[13] was prepared from diol **4**[12,14,15] by esterification with chloroacetic anhydride (Scheme 2).

During a previous study with thiogalactoside **1**[1] the reactions were seen to be considerably more rapid in dichloromethane and changing the solvent did not improve the stereoselectivity. Thus for this study all of the glycosylation reactions were carried in this solvent.

The results of the glycosylation reactions of donors **3**, **5** and **6** with several acceptors using NIS/TfOH are described in Tables 1–3. For donor **3**, glycosylation with small secondary alcohols afforded anomeric selectivities very similar to those obtained with donor **1**.[1] With a less hindered acceptor (Table 1, entries 2, 4, 5, 8, 9, EPA—epiandrosterone), the stereoselectivity of the glycosylation reaction was lower and more β anomer was obtained. In the case of

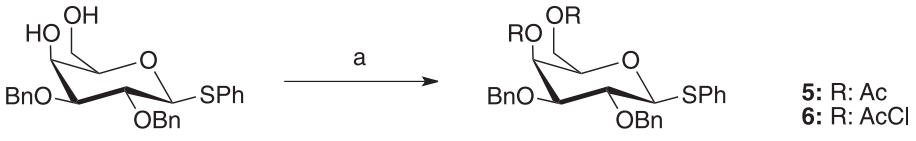
* Corresponding author. Tel.: +351 214469775; e-mail address: rventura@itqb.unl.pt (M.R. Ventura).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.06.038



a) NaOMe, MeOH, 0°C, h, 80%. b) Chloroacetic anhydride, pyr, DMAP, -10°C, 95%.

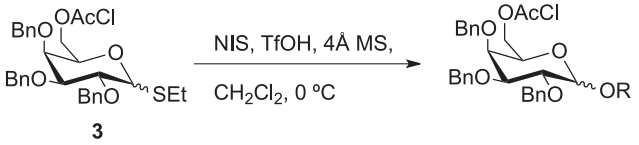
Scheme 1. Synthesis of donor **3**.

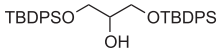
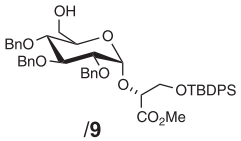
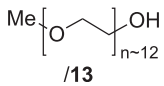


a) Chloroacetic anhydride , pyr, 0°C-rt, 68%.

Scheme 2. Synthesis of donors **5** and **6**.

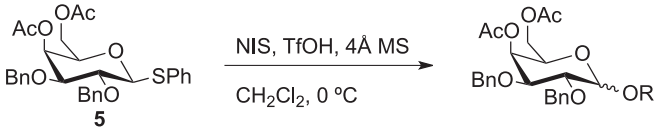
Table 1
Glycosylation reactions of thiogalactoside **3**

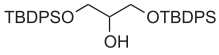
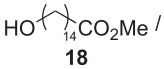
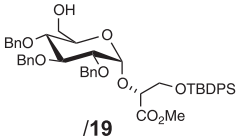
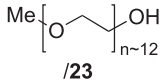


Entry	ROH/product	*t* (min)	Yield (%)	α/β
1	 /**7**	5	68	2:4:1
2	 /**8**	5	63	1:2.27
3	 /**9**	5	70	1.4:1
4	EPA/**10**	5	57	1:1.7
5	Adamantanol/**11**	5	82	1:1.3
6	Benzyl (*S*)-mandelate/**12**	5	70	1:0
7	 /**13**	30[a]	97	1:1
8	L-Menthol/**14**	5	85	1:1.5
9	Cyclohexanol/**15**	5	93	1:1.2
10	Boc-L-serine methyl ester/**16**	5	91	2:1

[a] Additional equivalents of TfOH were added during the reaction.

Table 2
Glycosylation reaction of thiogalactoside **5**



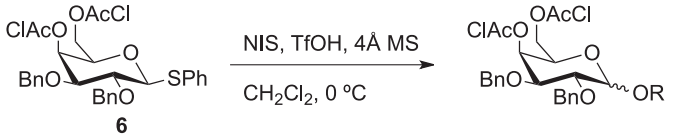
Entry	ROH/product	*t* (min)	Yield (%)	α/β
1	 /**17**	5	86	1:0
2	 /**18**	5	77	1.2:1
3	 /**19**	30	69	1:0
4	EPA/**20**	5	91	2.2:1
5	Adamantanol/**21**	5	98	6.5:1
6	Benzyl (*S*)-mandelate/**22**	5	68	1:0
7	 /**23**	40[a]	99	1.9:1
8	L-Menthol/**24**	5	85	2.7:1
9	Cyclohexanol/**25**	50[a]	78	1.12:1
10	Boc-L-serine methyl ester/**26**	5	69	2:1

[a] Additional equivalents of TfOH were added during the reaction.

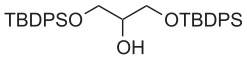
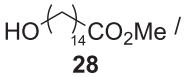
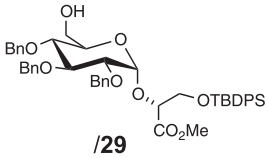
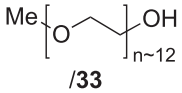
benzyl (*S*)-mandelate, only the α anomer was obtained (Table 1, entry 6).

Boons[16] and co-workers reported that iodonium-ion promoted glycosylations in 1,4-dioxane/toluene with a participating group at C-4 in galactosyl donors afforded high α-anomeric selectivities, and in his study the best results were obtained with electron-donating groups. In another study[11] using a galactosyl phosphite donor with 4- and 6-acyl groups, high α-anomeric selectivities were obtained in glycosylation reactions with sugar and hindered primary alcohol acceptors. Dibenzoyl ester groups at C-4 and C-6 on a galactosyl trichloroacetimidate donor and a 2-naphthylmethyl (NAP) group at C-2 and C-3 was less reactive, providing a higher α-selectivity with several sugar derived acceptors when compared with the same donor with benzylidene protection at C-4 and C-6.[17] We therefore studied the glycosylation reaction of thiogalactoside **5**, having a second acetate group at C-4 (Table 2). The stereoselectivity

Table 3
Glycosylation reaction of thiogalactoside **6**



6

Entry	ROH/product	*t* (min)	Yield (%)	α/β
1	 **/27**	5	69	1:0
2	 **28**	5	62	1.5:1
3	 **/29**	15	89	1:0
4	EPA/**30**	5	41	3.8:1
5	Adamantanol/**31**	5	89	6.2:1
6	Benzyl (*S*)-mandelate/**32**	5	79	1:0
7	 **/33**	60[a]	99	1.5:1
8	L-Menthol/**34**	5	94	3.43:1
9	Cyclohexanol/**35**	5	87	2.5:1
10	Boc-L-serine methyl ester/**36**	5	73	2:1

[a] Additional equivalents of TfOH were added during the reaction.

increased remarkably in all examples studied, and in some examples (Table 2, entries 1, 3, 6) only the α anomer was obtained.

Thiogalactosyl donor **6**, with chloroacetyl esters at C-4 and C-6 was also tested in the same glycosylation reactions (Table 3). Having stronger electron withdrawing esters, higher α-selectivity was expected. Indeed, this donor provided higher anomeric selectivities than donor **3** (Table 1) and donor **5** (Table 2) for acceptors EPA, L-menthol and cyclohexanol (Table 3, entries 4, 8, 9). The glycosylation reaction of each donor with *N*-Boc serine methyl ester always afforded the same anomeric ratio (α/β 2:1). Poor α/β selectivity has been attributed to the decreased nucleophilicity of *N*-acylated β-hydroxy amino acids, due to hydrogen bonding between the acceptor OH and NH groups.[18] Higher anomeric selectivities have been obtained with *N*-Fmoc serine allyl ester[11,19] which we did not test.

From Tables 2 and 3 it can be seen that an ester at C-4 is very important for the stereoselectivity of the glycosylation reaction with thiogalactosides, and a more electron withdrawing ester affords better results. Although the 4-*O*-chloroacetyl group could disarm the system slightly, the higher α-stereoselectivity can be attributed to a remote stereocontrolling and electronic effect of the C-4 ester in the galactoside donor.[20–22] Crich and co-workers studied possible neighbouring group participation in glycosylation reactions for esters in non-vicinal positions in several glycosyl donors[23] and ruled out neighbouring group participation from axial esters at C-4. Thus, the α-anomeric selectivity obtained with donors **5** and **6** could not be attributed to the direct participation of the ester at C-4, but to stereoelectronic and conformational influences.[23] These electron withdrawing groups will lower the stability of the intermediate carbocationic species. In this way covalent intermediates become more likely. Thus the increased α-selectivity could derive from the preferential formation of the β triflate, which is then substituted by the nucleophilic alcohol in an S_N2 manner to afford the α-galactoside. A coherent mechanism for this remote control has not yet been established.

During this study it was observed that the structure of the acceptor had a strong influence on the stereoselectivity of the glycosylation reaction. Most related studies[4,6,16,24,25] have used sugars as the acceptors in order to obtain di- and higher saccharides, and in these cases the α-galactosides were obtained with good to high selectivity. Indeed, when the acceptor was a sugar (Tables 2 and 3, entry 3), the corresponding α-galactoside was obtained exclusively. In general, more hindered small acceptors afforded higher anomeric selectivities (Table 3, entries 1, 3, 6). On the other hand lipophilic primary alcohols (Table 3, entries 2 and 7) did not afford good α selectivities. Lipids can aggregate easily, which changes their reactivity[26] and negatively influences the stereoselective outcome of the glycosylation reaction.

3. Conclusion

In conclusion, there is not yet a general method for stereoselective α-galactosylation. The influence of the solvent, temperature and the nature and position of the protecting groups in the donor have been a subject of study over many years, and the glycosylation methods optimised accordingly. However, when these methods are applied to different acceptors the α stereoselectivity is not predictable in many cases. This must be due to the stereoelectronic different natures of the reactive hydroxy groups on the acceptor and inter and intramolecular interactions during the glycosylation reaction. In fact it may be postulated that the reactivity of the acceptor influences the nature of the reactive glycosyl donor species that ultimately reacts.

4. Experimental section

4.1. General

^{1}H NMR spectra were obtained at 400 MHz in $CDCl_3$ with chemical shift values (δ) in parts per million downfield from tetramethylsilane, and ^{13}C NMR spectra were obtained at 100.61 MHz in $CDCl_3$. Assignments are supported by 2D correlation NMR studies. Medium pressure preparative column chromatography: Silica Gel Merck 60 H. Analytical TLC: Aluminium-backed Silica Gel Merck 60 F_{254}. Reagents and solvents were purified and dried according to Ref. [27]. All the reactions were carried out under an inert atmosphere (argon).

4.2. Ethyl 2,3,4-tri-*O*-benzyl-1-thio-α/β-D-galactopyranoside 2

A solution of NaOMe 1 N (1.28 μL, 1.28 mmol) in MeOH was added to a stirred solution of ethyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-thio-α/β-D-galactopyranoside (1.150 g, 2.14 mmol) in MeOH (4 mL) at 0 °C. After 1 h the reaction mixture was neutralised with satd aq NH_4Cl. The aqueous phase was extracted with EtOAc (3×10 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and the solvent was removed. The crude product was purified by flash column chromatography on silica gel (20:80, EtOAc/Hex) to afford the product **2** (0.856 g, 81%, α:β=2.6:1) as a white solid. α anomer: mp 84.0–85.1 °C. $[\alpha]_D^{20}$ +145.2 (*c* 1.03, CH_2Cl_2). FT-IR (KBr disk): 3422–3508 cm^{-1} (O–H). ^{1}H NMR ($CDCl_3$): δ 7.41–7.28 (m, 15H), 5.51 (d, 1H, *J*=3.5 Hz, H-1 (α)), 4.97 (d, 1H, *J*=7.3 Hz), 4.87 (d, 1H, *J*=7.5 Hz), 4.72 (q, 2H, *J*=7.3 Hz, *J*=9.3 Hz), 4.64 (d, 1H, *J*=7.3 Hz), 4.30 (dd, 1H, *J*=3.3 Hz, *J*=3.5 Hz), 4.13–4.10 (m, 1H), 3.88–3.87 (m, 1H), 3.73 (dd, 1H, *J*=3.3 Hz, *J*=4.0 Hz), 3.53 (dd, 1H, *J*=3.3 Hz,

J=3.8 Hz), 2.61–2.45 (m, 2H), 1.27 (t, 3H, J=4.5 Hz). ^{13}C NMR ($CDCl_3$): δ 138.6, 138.2, 138.1, 128.5–127.6, 83.4 (C-1), 79.5, 76.2, 75.2, 74.5, 73.7, 72.8, 70.5, 62.5, 23.5, 14.6. Anal. Calcd for $C_{29}H_{34}O_5S$: C, 70.42; H, 6.93; S, 6.48. Found: C, 69.93; H, 6.86; S, 6.18. β anomer: mp 100.3–101.4 °C. $[\alpha]_D^{20}$ +6.6 (c 0.89, CH_2Cl_2). FT-IR (KBr disk): 3420–3510 cm^{-1} (O–H). ^{1}H NMR ($CDCl_3$): δ 7.41–7.28 (m, 15H), 4.97 (d, 1H, J=7.3 Hz), 4.90 (d, 1H, J=6.3 Hz), 4.81 (d, 1H, J=6.3 Hz), 4.80–4.74 (m, 2H), 4.43 (d, 1H, J=6.3 Hz, H-1 (β)), 3.87–3.76 (m, 3H), 3.58 (dd, 1H, J=1.8 Hz, J=4.0 Hz), 3.47 (dd, 1H, J=3.3 Hz, J=3.8 Hz), 3.42–3.39 (m, 1H), 2.82–2.67 (m, 2H), 1.30 (t, 3H, J=4.5 Hz). ^{13}C NMR ($CDCl_3$): δ 138.3, 138.2, 138.19, 128.5–127.6, 85.4 (C-1), 84.1, 78.6, 78.5, 75.8, 74.1, 73.1, 73.0, 62.2, 24.9, 15.1. Anal. Calcd for $C_{29}H_{34}O_5S$: C, 70.42; H, 6.93; S, 6.48. Found: C, 70.17; H, 6.97; S, 6.32.

4.3. Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-chloroacetyl-1-thio-α/β-D-galactopyranoside 3

To a stirred solution of **2** (0.845 g, 1.70 mmol) in pyridine (5 mL) at 0 °C was added chloroacetic anhydride (0.320 g, 1.87 mmol). After complete conversion of the starting material water was added. The mixture was extracted with EtOAc, dried ($MgSO_4$) and concentrated to furnish a yellow viscous residue. Purification by column chromatography on silica gel (90:10 EtOAc/hexane) afforded the product **3** as a viscous colourless foam (0.878 g, 90%). α anomer: $[\alpha]_D^{20}$ +104.00 (c 1.60, CH_2Cl_2). FT-IR (film): 1745 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.40–7.28 (m, 15H), 5.47 (d, 1H, J=5.4 Hz, H-1), 4.96 (d, 1H, J=11.6 Hz), 4.87 (d, 1H, J=11.8 Hz), 4.76–4.67 (m, 3H), 4.62 (d, 1H, J=11.6 Hz), 4.32–4.25 (m, 3H), 4.15–4.06 (m, 1H), 3.96–3.88 (m, 2H), 3.85–3.83 (m, 1H), 3.79 (dd, 1H, J=9.7 Hz, J=2.8 Hz), 2.62–2.35 (m, 2H), 1.26 (t, 3H, J=7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 166.8, 138.5, 138.1, 138.0, 128.5–127.6, 83.2 (C-1), 79.2, 76.2, 74.4, 74.3, 73.8, 72.6, 68.5, 64.9, 40.6, 23.5, 14.7. β anomer: $[\alpha]_D^{20}$ +2.03 (c 1.02, CH_2Cl_2). FT-IR (film): 1747 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.40–7.28 (m, 15H), 4.99 (d, 1H, J=11.8 Hz), 4.89 (d, 1H, J=10.2 Hz), 4.83–4.75 (m, 3H), 4.65 (d, 1H, J=11.8 Hz), 4.42 (d, 1H, J=9.64 Hz, H-1), 4.31 (dd, 1H, J=11.1 Hz, J=6.8 Hz), 4.10 (dd, 1H, J=11.1 Hz, J=7.4 Hz), 3.96–3.81 (m, 4H), 3.59–3.55 (m, 2H), 2.81–2.65 (m, 2H), 1.30 (t, 3H, J=7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 166.8, 138.1, 128.5–127.6, 85.4 (C-1 (β)), 84.0, 78.3, 75.8, 75.5, 74.1, 73.3, 72.9, 64.8, 40.6, 24.9, 15.1. HRMS: calcd for $C_{31}H_{35}ClO_6SNa^+$ [M^++Na] 593.1740; found 593.1735.

4.4. Phenyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-1-thio-β-D-galactopyranoside 5

To a stirred solution of **4** (0.810 g, 1.78 mmol) in pyridine (5 mL) at 0 °C was added acetic anhydride (0.507 mL, 5.36 mmol) and a catalytic amount of DMAP. After complete conversion of the starting material water was added. The mixture was extracted with EtOAc, dried ($MgSO_4$) and concentrated to furnish a viscous residue. Purification by column chromatography on silica gel (70:30 EtOAc/hexane) afforded the product **5** as a viscous colourless foam (0.960 g, 100%). $[\alpha]_D^{20}$ +29.5 (c 0.50, CH_2Cl_2). FT-IR (film): 1741 cm^{-1} (C=O). HRMS: calcd for $C_{30}H_{32}O_7SNa^+$ [M^++Na]: 559.1766; found: 559.1761. The ^{1}H and ^{13}C NMR data were identical to those described in the literature.[28]

4.5. Phenyl 2,3-di-*O*-benzyl-4,6-di-*O*-chloroacetyl-1-thio-β-D-galactopyranoside 6

To a stirred solution of **4** (0.530 g, 1.17 mmol) in pyridine (3 mL) at 0 °C was added chloroacetic anhydride (0.440 g, 2.57 mmol). After complete conversion of the starting material water was added. The mixture was extracted with EtOAc, dried ($MgSO_4$) and concentrated to furnish a yellow viscous residue. Purification by column chromatography on silica gel on silica gel (80:20 EtOAc/hexane) afforded the product **5** as a viscous colourless foam (0.488 g, 69%). $[\alpha]_D^{20}$ +23.6 (c 0.59, CH_2Cl_2). FT-IR (film): 1747, 1762 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ 7.57–7.54 (m, 2H), 7.40–7.28 (m, 13H), 5.56 (d, 1H, J=2.9 Hz), 4.79–4.71 (m, 3H), 4.66 (d, 1H, J=9.3 Hz, H-1 (β)), 4.52 (d, 1H, J=10.9 Hz), 4.36–4.24 (m, 2H), 4.18–4.09 (m, 2H), 4.05 (s, 2H), 3.87 (t, 1H, J=6.5 Hz), 3.70–3.61 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 167.0, 166.9, 137.9, 137.0, 132.9, 132.5, 128.9, 128.5–127.9, 87.7 (C-1), 80.6, 76.5, 75.9, 73.9, 72.5, 68.7, 63.5, 40.7, 40.5. HRMS: calcd for $C_{30}H_{30}Cl_2O_7SNa^+$ [M^++Na]: 627.0987; found: 627.0982.

4.6. General glycosylation procedure

A suspension of thioglycoside donor (0.15 mmol), acceptor (0.15 mmol) and 4 Å MS in the solvent/mixture of solvents indicated in Tables 1–3 (1 mL) was stirred for 1 h at room temperature then cooled to the indicated temperature (Tables 1–3). *N*-Iodosuccinimide (0.19 mmol) and TfOH (0.9 μL) were added and when the reaction was complete (TLC), 10% $Na_2S_2O_3$ aqueous solution (2 mL) and satd aq $NaHCO_3$ (1 mL) were added and the mixture was extracted with CH_2Cl_2 (35 mL); the combined organic phases were dried ($MgSO_4$), filtered and the solvent was removed under vacuum. The crude product was purified by preparative TLC (3:7 EtOAc/hexane). The α/β ratio of the isolated product was measured by comparison of the integral of the α and β signals in ^{1}H NMR (400 MHz, $CDCl_3$) spectra. Yields and α/β ratio values are described in Tables 1–3.

4.6.1. Methyl (2R)-1,3-di-O-tert-butyldiphenylsilyl-2-O-(2,3,4-tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranosyl)-1,2,3-trihydroxypropane ***7***. FT-IR (film): 1746, 1763 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.66–7.57 (m), 7.40–7.11 (m), 5.11 (d, J=3.4 Hz, H-1 (α)), 4.96–4.79 (m), 4.73–4.56 (m), 4.45 (d, J=7.7 Hz, H-1 (β)), 4.08–3.72 (m), 3.69 (br s), 3.64 (d, J=15.0 Hz), 3.56 (d, J=15.0 Hz), 3.42 (dd, J=2.8 Hz, J=9.7 Hz), 3.34 (t, J=6.4 Hz), 1.03 (s), 1.02 (s), 1.00 (s), 0.98 (s). ^{13}C NMR ($CDCl_3$): δ 166.5, 138.8, 138.46, 138.41, 138.2, 138.1, 135.6–135.5, 133.7–133.0, 129.8–129.5, 128.6–127.5, 103.2 (C-1 (β)), 96.2 (C-1 (α)), 81.9, 80.7, 79.4, 78.7, 77.2, 76.4, 74.9, 74.3, 74.2, 73.7, 73.6, 72.9, 72.8, 71.4, 67.7, 64.6, 64.2, 63.9, 63.7, 63.2, 62.9, 40.5, 40.4, 26.9, 26.84, 26.82, 26.7, 19.3, 19.2, 19.1.

4.6.2. Methyl 15-O-(2,3,4-tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranosyl)decapentanoate ***8***. FT-IR (film): 1736 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.41–7.26 (m), 4.98–4.89 (m), 4.85–4.80 (m), 4.80 (d, J=3.2 Hz, H-1 (α)), 4.77–4.73 (m), 4.67–4.60 (m), 4.33 (d, J=7.6 Hz, H-1 (β)), 4.29 (dd, J=6.4 Hz, J=11.0 Hz, H-6 (β)), 4.22 (dd, J=7.1 Hz, J=11.1 Hz, H-6 (α)), 4.10 (dd, J=6.4 Hz, J=11.0 Hz, H′-6 (β)), 4.07–4.01 (m), 3.96–3.81 (m), 3.75 (d, J=2.1 Hz, H-4 (β)), 3.66 (s), 3.62–3.40 (m), 2.29 (t, J=7.5 Hz), 1.67–1.55 (m), 1.39–1.24 (m). ^{13}C NMR ($CDCl_3$): δ 174.5, 174.3, 166.82, 166.80, 138.7, 138.6, 138.5, 138.4, 138.1, 128.6–127.5, 103.9 (C-1 (β)), 97.4 (C-1 (α)), 82.1, 79.4, 78.9, 76.6, 75.2, 74.4, 74.3, 74.1, 73.6, 73.5, 73.3, 72.5, 71.5, 70.1, 68.4, 67.9, 65.1, 64.4, 51.4, 40.6, 34.1, 29.7–29.1, 26.2, 26.1, 24.9.

4.6.3. Methyl (2R)-3-O-tert-butyldiphenylsilyl-2-O-[2,3,4-tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranosyl-(1→6)-2,3,4-tri-O-benzyl-1-O-α-D-glucopyranosyl]-2,3-dihydroxypropanoate ***9***. FT-IR (film): 1751 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.70–7.66 (m), 7.43–7.08 (m), 5.23 (d, J=3.4 Hz, H-1′α Glucose), 5.15 (d, J=3.5 Hz, H-1′α Glucose), 4.99–4.89 (m), 4.93 (m, H-1α Galactose), 4.90–4.89 (m), 4.86–4.80 (m), 4.78–4.46 (m), 4.26–4.19 (m), 4.20 (d, J=7.8 Hz, H-1β Galactose), 4.15–3.42 (m), 3.72 (s), 3.57 (s), 1.02 (s), 1.01 (s). ^{13}C NMR ($CDCl_3$): δ 170.3, 170.2, 166.8, 166.7, 139.0–138.1, 135.7, 135.6, 133.1–132.9, 129.8, 129.7, 128.5–127.2, 104.0 (C-1β Galactose), 97.9 (C-1α Galactose), 94.5 (C-1′α Glucose), 94.4 (C-1′α

Glucose), 82.1, 81.7, 81.6, 79.6, 79.2, 79.0, 78.3, 77.6, 77.5, 76.5, 75.7, 75.6, 75.3, 74.7, 74.6, 74.5, 74.47, 74.43, 74.40, 74.2, 73.5, 73.4, 72.9, 72.5, 71.9, 71.8, 71.7, 70.8, 70.1, 68.3, 68.2, 66.2, 65.1, 64.8, 64.4, 52.0, 51.8, 40.6, 40.5, 26.7, 19.2.

4.6.4. 3-O-(2,3,4-Tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranosyl)-epiandrosterone ***10***. FT-IR (film): 1737 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.41–7.27 (m), 4.98–4.92 (m), 4.89 (d, *J*=3.7 Hz, H-1 (α)), 4.89–4.72 (m), 4.68–4.60 (m), 4.45 (d, *J*=7.7 Hz, H-1 (β)), 4.29 (dd, *J*=6.6 Hz, *J*=11.0 Hz, H-6 (β)), 4.23–4.18 (m, H-6 (α)), 4.11–4.00 (m), 3.96–3.95 (m), 3.92 (d, *J*=5.3 Hz, AcCl (α)), 3.88 (d, *J*=5.1 Hz, AcCl (β)), 3.86–3.80 (m), 3.74 (d, *J*=2.3 Hz, H-4 (β)), 3.65–3.57 (m), 3.53–3.47 (m), 2.43 (dd, *J*=8.7 Hz, *J*=19.1 Hz), 2.13–2.01 (m), 1.95–1.88 (m), 1.84–1.19 (m), 1.14–1.03 (m), 1.01–0.90 (m), 0.85 (s), 0.83 (s), 0.67 (ddd, *J*=3.4 Hz, *J*=11.4 Hz, *J*=11.4 Hz). ^{13}C NMR ($CDCl_3$): δ 165.8, 165.7, 137.7, 137.5, 137.1, 127.5–126.4, 101.2 (C-1 (β)), 94.5 (C-1 (α)), 81.2, 78.5, 78.0, 75.4, 75.3, 74.4, 73.0, 72.6, 72.2, 71.5, 70.4, 66.9, 64.3, 63.4, 53.4, 50.3, 46.7, 44.2, 39.5, 35.8, 34.8, 34.7, 34.0, 33.6, 30.5, 29.8, 28.4, 27.4, 26.3, 20.7, 19.4, 12.7, 11.3.

4.6.5. 1-O-Adamantanyl-2,3,4-tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranose ***11***. FT-IR (film): 1741, 1743 (C=O st) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.41–7.25 (m), 5.31 (d, *J*=3.4 Hz, H-1 (α)), 4.99–4.94 (m), 4.88 (d, *J*=11.6 Hz, Bn (α)), 4.82 (d, *J*=11.7 Hz, Bn (β)), 4.76–4.70 (m), 4.67–4.59 (m), 4.60 (d, *J*=7.6 Hz, H-1 (β)), 4.28 (dd, *J*=7.1 Hz, *J*=11.0 Hz, H-6 (β)), 4.28 (dd, *J*=7.1 Hz, *J*=10.5 Hz, H-6 (α)), 4.15 (t, *J*=5.3 Hz (α)), 4.07–3.95 (m), 3.92–3.87 (m), 3.81 (t, *J*=9.6, H-2 (β)), 3.72 (d, *J*=2.4 Hz, H-4 (β)), 3.53–3.49 (m), 2.12 (br s), 1.91–1.76 (m), 1.65–1.57 (m). ^{13}C NMR ($CDCl_3$): δ 165.8, 165.7, 137.8, 137.7, 137.5, 137.4, 137.3, 137.1, 127.7–127.2, 126.9–126.4, 95.5 (C-1 (β)), 89.5 (C-1 (α)), 81.5, 78.4, 78.0, 75.4, 74.2, 74.1, 73.5, 73.4, 73.3, 73.0, 72.6, 72.3, 72.0, 71.6, 70.3, 66.5, 64.2, 63.7, 41.6, 41.4, 39.6, 39.5, 35.2, 35.2, 29.7, 29.6.

4.6.6. Benzyl (2S)-2-O-(2,3,4-tri-O-benzyl-6-O-chloroacetyl-α-D-galactopyranosyl)-2-phenylacetate ***12***. $[\alpha]_D^{20}$ +72.9 (*c* 0.82, CH_2Cl_2). FT-IR (film): 1748 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.52–7.49 (m, 2H), 7.43–7.18 (m, 23H), 5.15 (s, 1H, C*H* mandelate), 5.12 (dd, 1H, *J*=6.5 Hz, *J*=16.5 Hz, CO_2Bn), 4.96 (d, *J*=11.6 Hz, Bn), 4.92 (d, *J*=11.6 Hz, Bn), 4.87 (d, *J*=3.6 Hz, H-1 (α)), 4.78 (d, *J*=11.6 Hz, Bn), 4.66 (d, *J*=11.7 Hz, Bn), 4.60 (d, *J*=11.6 Hz, Bn), 4.48 (d, *J*=11.7 Hz, Bn), 4.18–4.10 (m, 3H, H-3, H-5, H-6), 4.05–3.99 (m, 2H, H-2, H′-6), 3.91–3.82 (m, 3H, H-4, AcCl). ^{13}C NMR ($CDCl_3$): δ 169.9, 166.8, 138.6, 138.2, 138.1, 135.5, 135.4, 128.8–128.2, 127.9–127.5, 96.4 (C-1 (α)), 78.7 (C-3), 77.4 (*C*H mandelate), 76.2 (C-2), 74.4, 74.3 (C-4), 73.6, 73.1, 68.9 (C-5), 66.8 (CO_2CH_2Ph), 64.8 (C-6), 40.6 (CH_2Cl). HRMS: calcd for $C_{44}H_{43}ClO_9Na^+$ [M^++Na]: 773.2493; found: 773.2485.

4.6.7. 1-ω-Methoxy-PEG$_{550}$yl-2,3,4-tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranoside ***13***. FT-IR (film): 1715, 1757 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.41–7.26 (m), 4.98–4.94 (m), 4.91–4.88 (m), 4.90 (d, *J*=3.5 Hz, H-1 (α)), 4.84–4.60 (m), 4.40 (d, *J*=7.6 Hz, H-1 (β)), 4.28 (dd, *J*=6.6 Hz, *J*=11.0 Hz), 4.21 (dd, *J*=7.0 Hz, *J*=11.0 Hz), 4.12–3.82 (m), 3.77–3.50 (m), 3.37 (s, OMe). ^{13}C NMR ($CDCl_3$): δ 166.88, 166.81, 138.7, 138.5, 138.3, 138.1, 138.0, 128.6–128.1, 127.9–127.5, 104.0 (C-1 (β)), 97.6 (C-1 (α)), 81.9, 79.2, 78.8, 76.4, 75.0, 74.4, 74.3, 73.6, 73.5, 73.2, 72.6, 71.9, 71.6, 70.5, 70.4, 70.3, 70.2, 68.9, 68.0, 66.9, 64.9, 64.4, 59.0 (OMe), 40.7 (AcCl), 40.6 (AcCl). HRMS: calcd for $C_{54}H_{81}ClO_{19}Na^+$ [M^++Na]: 1091.4953; found: 1091.4934.

4.6.8. O-1-L-Menthyl-2,3,4-tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranoside ***14***. FT-IR (film): 1762 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.40–7.27 (m), 5.01 (d, *J*=3.5 Hz, H-1 (α)), 4.97 (d, *J*=11.8 Hz, Bn (β)), 4.94 (d, *J*=10.8 Hz, Bn (α)), 4.88–4.64 (m), 4.61 (d, *J*=11.6 Hz, Bn (α)), 4.37 (d, *J*=7.7 Hz, H-1 (β)), 4.27–4.22 (m, H-6 (α), H-6 (β)), 4.10–4.01 (m), 3.98–3.91 (m), 3.87 (dd, *J*=14.8 Hz, *J*=18.4 Hz, AcCl), 3.77 (dd, *J*=7.8 Hz, *J*=11.0 Hz, H-2 (β)), 3.72 (d, *J*=2.3 Hz, H-4 (β)), 3.53–3.48 (m), 3.38 (td, *J*=4.2 Hz, *J*=10.6 Hz, C*H*–O menthol (β)), 3.32 (td, *J*=4.3 Hz, *J*=10.6 Hz, C*H*–O menthol (α)), 2.43–2.32 (m, C*H*$(CH_3)_2$ menthol), 2.12–2.09 (m, CHCH_2CH (β) menthol), 2.05–2.02 (m, CHCH_2CH (α) menthol), 1.67–1.56 (m, CH_2CH_2 menthol), 1.41–1.21 (m, C*H*CH_3, C*H*C$H(CH_3)_2$ menthol), 1.03–1.75 (m), 0.83 (d, *J*=7.1 Hz), 0.72 (d, *J*=6.8 Hz), 0.68 (d, *J*=6.9 Hz). ^{13}C NMR ($CDCl_3$): δ 166.9, 166.8, 138.7, 138.68, 138.61, 138.5, 138.25, 138.23, 128.6–128.2, 127.8–127.4, 101.9 (C-1 (β)), 99.3 (C-1 (α)), 82.5, 80.6, 79.3, 78.96, 78.92, 76.8, 75.2, 74.5, 74.4, 74.1, 73.7, 73.6, 73.1, 73.0, 71.5, 68.2, 65.4, 64.8, 48.8 (*C*HC$H(CH_3)_2$ (α) menthol), 47.9 (*C*HC$H(CH_3)_2$ (β) menthol), 42.9 (CHCH_2CH (α) menthol), 41.2 (CHCH_2CH (β) menthol), 40.63 (AcCl (α)), 40.62 (AcCl (β)), 34.4, 34.2, 31.7 (*C*HCH_3 menthol (α)), 31.5 (*C*HCH_3 menthol (β)), 24.8 (*C*H$(CH_3)_2$ menthol (β)), 24.5 (*C*H$(CH_3)_2$ menthol (α)), 23.0, 22.9, 22.4, 22.2, 21.1, 16.0, 15.5.

4.6.9. O-1-Cyclohexyl-2,3,4-tri-O-benzyl-6-O-chloroacetyl-α/β-D-galactopyranoside ***15***. FT-IR (film): 1759, 1744 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.41–7.21 (m), 4.98 (s, H-1 (α)), 4.98–4.73 (m), 4.68–4.60 (m), 4.44 (d, *J*=7.6 Hz, H-1 (β)), 4.32–4.27 (m, H-6 (β)), 4.23–4.19 (m, H-6 (β)), 4.09–4.01 (m), 3.96–3.80 (m), 3.73 (s, H-4 (β)), 3.70–3.62 (m), 3.52–3.50 (m), 1.95–1.89 (m), 1.82–1.73 (m), 1.54–1.12 (m). ^{13}C NMR ($CDCl_3$): δ 166.8, 166.7, 138.8, 138.7, 138.6, 138.4, 138.2, 138.1, 128.7–128.2, 127.9–127.5, 102.2 (C-1 (β)), 95.6 (C-1 (α)), 82.3 (C-3 (β)), 79.4 (C-2 (β)), 79.0 (C-3 (α)), 77.8, 76.5 (C-2 (α)), 75.8, 75.2, 74.4 (C-4 (α)), 74.1, 73.6, 73.1, 72.5 (C-4 (β)), 71.5 (C-5 (β)), 67.9 (C-5 (α)), 65.3 (C-6 (α)), 64.5 (C-6 (β)), 40.6 (AcCl), 33.6, 33.3, 31.9, 31.6, 25.6, 25.5, 24.5, 24.2, 24.0, 23.9.

4.6.10. 3-O-(2,3,4-Tri-O-Benzyl-6-O-chloroacetyl-α/β-D-galactopyranosyl)-N-Boc-L-ser-methyl ester ***16***. FT-IR (film) 1714, 1747 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.40–7.25 (m), 5.73 (d, *J*=8.6 Hz, N*H*Boc (α)), 5.46 (d, *J*=7.8 Hz, N*H*Boc (β)), 4.96 (d, *J*=11.5 Hz, Bn), 4.87–4.83 (m), 4.80–4.72 (m), 4.76 (s, H-1 (α)), 4.65–4.59 (m), 4.45–4.43 (m, *CH* serine), 4.32 (d, *J*=7.6 Hz, H-1 (β)), 4.29–4.19 (m), 4.15–3.96 (m), 3.92–3.73 (m), 3.74 (s, CO_2Me (β)), 3.66 (s, CO_2Me (α)), 3.53–3.50 (m), 1.43 (s, *t*-Bu (α)), 1.42 (s, t-Bu (β)). ^{13}C NMR ($CDCl_3$): δ 170.8, 170.7, 167.0, 166.8, 155.5, 138.4, 138.37, 138.30, 138.1, 137.9, 128.6–128.2, 127.9–127.5, 104.3 (C-1 (β)), 99.7 (C-1 (α)), 81.9, 78.9, 78.5, 76.3, 75.4, 74.5, 74.3, 74.2, 73.5, 73.4, 72.5, 71.8, 71.1, 69.0, 65.0 (C-6 (α)), 64.3 (C-6 (β)), 54.2 (*C*H serine (α)), 53.9 (*C*H serine (β)), 52.6 (CO_2Me (β)), 52.4 (CO_2Me (α)), 40.7 (AcCl (α)), 40.6 (AcCl (β)), 28.3 (*t*-Bu).

4.6.11. (2R)-1,3-Di-O-tert-butyldiphenylsilyl-2-O-(4,6-di-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-1,2,3-trihydroxypropane ***17***. $[\alpha]_D^{20}$ +62.4 (*c* 2.63, CH_2Cl_2). FT-IR (film): 1744 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.67–7.61 (m, 8H), 7.41–7.11 (m, 22H), 5.43 (d, 1H, *J*=2.9 Hz), 5.10 (d, 1H, *J*=3.5 Hz, H-1 (α)), 4.68 (d, 1H, *J*=10.9 Hz), 4.67 (d, 1H, *J*=11.9 Hz), 4.55 (d, 1H, *J*=11.9 Hz), 4.49 (d, 1H, *J*=11.0 Hz), 4.23 (t, 1H, *J*=6.7 Hz), 3.99–3.75 (m, 8H), 3.72 (dd, 1H, *J*=3.6 Hz, *J*=10.0 Hz), 2.08 (s, 3H), 1.91 (s, 3H), 1.00 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 170.4, 170.3, 138.4, 138.1, 135.6, 135.4, 133.4, 133.3, 133.2, 133.1, 129.7, 128.3–127.5, 96.2 (C-1 (α)), 77.3, 75.7, 75.4, 73.0, 72.3, 67.8, 66.4, 64.0, 62.8, 62.1, 26.84, 26.82, 20.9, 20.6, 19.2, 19.1. HRMS: calcd for $C_{59}H_{70}O_{10}Si_2Na^+$ [M^++Na]: 1017.4405; found: 1017.4400.

4.6.12. Methyl 15-O-(4,6-di-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranosyl)decapentanoate ***18***. FT-IR (film): 1740 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.33–7.25 (m), 5.55 (d, *J*=3.1 Hz, H-4 (α)), 5.49 (d, *J*=2.3 Hz, H-4 (β)), 4.88 (d, *J*=10.8 Hz), 4.82 (d, *J*=11.2 Hz), 4.81 (d, *J*=3.5 Hz, H-1 (α)), 4.76–4.70 (m), 4.62 (d, *J*=12.0 Hz), 4.56 (d, *J*=11.1 Hz), 4.53 (d, *J*=11.4 Hz), 4.38 (d, *J*=6.9 Hz, H-1 (β)), 4.16–4.09 (m), 4.07–4.04 (m), 3.99–3.91 (m), 3.78–3.73 (m), 3.66 (s),

3.65–3.42 (m), 2.29 (t, *J*=7.5 Hz), 2.14 (s), 2.11 (s), 2.07 (s), 2.05 (s), 1.70–1.54 (m), 1.41–1.25 (m). ^{13}C NMR ($CDCl_3$): δ 174.3, 170.57, 170.53, 170.48, 170.40, 138.6, 138.5, 138.1, 137.7, 128.3–127.6, 103.8 (C-1 (β)), 97.6 (C-1 (α)), 79.0, 78.8, 76.0, 75.6, 75.3, 73.4, 72.3, 72.2, 70.6, 70.5, 68.6, 67.9, 66.6, 66.5, 62.6, 62.0, 51.4, 34.1, 29.7–29.1, 26.2, 26.1, 24.9, 20.93, 20.90, 20.7.

4.6.13. Methyl (2R)-3-O-tert-butyldiphenylsilyl-2-O-[4,6-di-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl-(1→6)-2,3,4-tri-O-benzyl-1-O-α-D-glucopyranosyl]-2,3-dihydroxypropanoate ***19***. $[\alpha]_D^{20}$ +11 2.06 (*c* 0.88, CH_2Cl_2). FT-IR (film): 1744 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.70–7.67 (m, 4H), 7.39–7.17 (m, 31H), 5.46 (d, 1H, *J*=3.0 Hz), 5.14 (d, 1H, *J*=3.5 Hz, H-1′ (α) Glucose), 4.98 (d, 1H, *J*=10.8 Hz), 4.97 (d, 1H, *J*=1.8 Hz, H-1 (α) Galactose), 4.87 (d, 1H, *J*=11.5 Hz), 4.83 (d, 1H, *J*=11.6 Hz), 4.74 (d, 1H, *J*=10.7 Hz), 4.70 (d, 1H, *J*=11.3 Hz), 4.69 (d, 1H, *J*=12.1 Hz), 4.60 (d, 1H, *J*=12.1 Hz), 4.59 (d, 1H, *J*=11.6 Hz), 4.53 (d, 1H, *J*=11.5 Hz), 4.52 (d, 1H, *J*=11.3 Hz), 4.48 (dd, 1H, *J*=4.0 Hz, *J*=5.9 Hz), 4.09–3.86 (m, 8H), 3.77–3.60 (m, 4H), 3.75 (s, 3H), 3.48 (dd, 1H, *J*=3.6 Hz, *J*=9.5 Hz), 2.09 (s, 3H), 1.94 (s, 3H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 170.5, 170.4, 170.2, 138.9, 138.7, 138.6, 138.3, 138.0, 135.7, 135.6, 133.1, 132.8, 129.7, 128.3–127.3, 98.0 (C-1 (α) Galactose), 94.5 (C-1′ (α) Glucose), 81.7, 79.5, 75.7, 75.5, 75.3, 74.7, 74.5, 72.7, 72.0, 71.9, 70.8, 67.9, 66.7, 66.1, 64.7, 62.5, 52.0, 26.7, 20.9, 20.7, 19.2. HRMS: calcd for $C_{71}H_{80}O_{16}SiNa^+$ [M^++Na]: 1239.5113; found: 1239.5108.

4.6.14. 3-O-(4,6-Di-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranosyl)-epiandrosterone ***20***. FT-IR (film): 1741 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.36–7.27 (m), 5.55 (d, *J*=3.0 Hz, H-4 (α)), 5.47 (d, *J*=2.8 Hz, H-4 (β)), 4.97 (d, *J*=3.6 Hz, H-1 (α)), 4.88 (d, *J*=10.9 Hz, Bn (β)), 4.80 (d, *J*=12.0 Hz, Bn (α)), 4.75–4.71 (m), 4.62 (d, *J*=12.0 Hz, Bn (α)), 4.54 (t, *J*=11.3 Hz), 4.48 (d, *J*=7.2 Hz, H-1 (β)), 4.23 (t, *J*=6.4 Hz, H-5 (α)), 4.19–4.10 (m), 4.03 (dd, *J*=7.3 Hz, *J*=11.1 Hz, H-6 (α)), 3.95 (dd, *J*=3.3 Hz, *J*=10.0 Hz, H-3 (α)), 3.77–3.73 (m), 3.64–3.48 (m), 2.43 (dd, *J*=8.9 Hz, *J*=19.2 Hz), 2.13 (s), 2.10 (s), 2.06 (s), 2.05 (s), 2.11–2.01 (m), 1.95–1.43 (m), 1.40–1.20 (m), 1.15–1.07 (m), 1.01–0.91 (m), 0.68 (ddd, *J*=3.3 Hz, *J*=11.5 Hz, *J*=11.5 Hz). ^{13}C NMR ($CDCl_3$): δ 170.5, 170.4, 138.6, 138.5, 138.1, 137.8, 128.3–127.6, 102.3 (C-1 (β)), 96.2 (C-1 (α)), 79.7, 79.2, 78.9, 76.1, 75.5, 75.4, 73.3, 72.3, 72.2, 70.5, 67.9, 66.6, 66.5, 62.7, 62.0, 54.4, 51.4, 47.8, 45.2, 44.8, 36.9, 35.85, 35.8, 35.0, 34.7, 31.5, 30.9, 29.5, 28.5, 28.4, 27.5, 21.7, 20.9, 20.7, 20.5, 13.8, 12.3, 12.2.

4.6.15. 1-O-Adamantanyl-4,6-di-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranose ***21***. FT-IR (film): 1744, 1745 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.36–7.25 (m), 5.56 (d, *J*=2.9 Hz, H-4 (α)), 5.46 (d, *J*=2.4 Hz, H-4 (β)), 5.32 (d, *J*=3.8 Hz, H-1 (α)), 4.92 (d, *J*=10.9 Hz, Bn (β)), 4.77–4.70 (m), 4.68–4.60 (m), 4.56–4.50 (m), 4.35 (t, *J*=6.6 Hz, H-5 (α)), 4.18–4.03 (m), 3.99 (dd, *J*=3.4 Hz, *J*=10.0 Hz, H-3 (α)), 3.75 (dd, *J*=3.8 Hz, *J*=10.0 Hz, H-2 (α)), 3.61–4.53 (m), 2.15 (m), 2.13 (s), 2.10 (s), 2.04 (s), 1.93–1.78 (m), 1.69–1.59 (m). ^{13}C NMR ($CDCl_3$): δ 170.5, 170.4, 138.6, 138.2, 137.8, 128.9–127.5, 96.3 (C-1 (β)), 90.7 (C-1 (α)), 79.5, 78.8, 76.1, 75.6, 75.5, 75.4, 73.1, 72.3, 72.1, 70.4, 68.0, 66.7, 66.2, 62.6, 62.2, 42.6, 42.4, 36.2, 35.8, 31.1, 30.6, 20.98, 20.92, 20.7.

4.6.16. Benzyl (2S)-2-O-4,6-di-O-acetyl-2,3-di-O-benzyl-α-D-galacto pyranosyl-2-phenylacetate ***22***. $[\alpha]_D^{20}$ +101.8 (*c* 1.57, CH_2Cl_2). FT-IR (film): 1743 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.44–7.15 (m, 20H), 5.57 (d, 1H, *J*=3.0 Hz, H-4), 5.19–5.09 (m, 3H, C*H* mandelate, CO_2CH_2Ph), 4.88 (d, 1H, *J*=3.6 Hz, H-1 (α)), 4.75 (d, 1H, *J*=10.8 Hz, Bn), 4.69 (d, 1H, *J*=11.8 Hz, Bn), 4.58 (d, 1H, *J*=10.8 Hz, Bn), 4.45 (d, 1H, *J*=11.8 Hz, Bn), 4.37 (t, 1H, *J*=6.4 Hz, H-5), 4.13 (dd, 1H, *J*=3.2 Hz, *J*=10.0 Hz, H-3), 4.08 (dd, 1H, *J*=6.0 Hz, *J*=11.2 Hz, H-6), 3.96 (dd, 1H, *J*=6.9 Hz, *J*=11.1 Hz, H-6′), 3.77 (dd, 1H, *J*=3.6 Hz, *J*=9.9 Hz, H-2), 2.09 (s, 3H, Ac), 2.03 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$): δ 170.5, 170.3, 169.7, 138.3, 138.0, 135.39, 135.34, 128.8–128.0, 127.9–127.3, 96.7 (C-1 (α)), 77.8 (C*H* mandelate), 75.9 (C-3), 75.3 (C-2), 73.3, 72.2, 67.7 (C-4), 67.4 (C-5), 66.9 (CO_2CH_2Ph), 62.2 (C-6), 20.8 (Ac), 20.7 (Ac). HRMS: calcd for $C_{39}H_{40}O_{10}Na^+$ [M^++Na]: 691.2519; found: 691.2504.

4.6.17. 1-ω-Methoxy-PEG$_{550}$yl-4,6-di-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranoside ***23***. FT-IR (film): 1716, 1742 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.37–7.26 (m), 5.55 (d, *J*=2.6 Hz, H-4 (α)), 5.48 (d, *J*=2.4 Hz, H-4 (β)), 4.91 (d, *J*=3.6 Hz, H-1 (α)), 4.90 (d, *J*=10.8 Hz), 4.80 (d, *J*=12.0 Hz), 4.74 (d, *J*=11.1 Hz), 4.71 (d, *J*=12.3 Hz), 4.64 (d, *J*=12.0 Hz), 4.56 (d, *J*=11.0 Hz), 4.52 (d, *J*=11.4 Hz), 4.44 (d, *J*=7.2 Hz, H-1 (β)), 4.21–4.18 (m), 4.15–4.10 (m), 4.06–4.01 (m), 3.98 (dd, *J*=3.4 Hz, *J*=9.9 Hz, H-3 (α)), 3.81–3.53 (m), 3.37 (s, OMe), 2.13 (s, Ac), 2.11 (s, Ac), 2.07 (s, Ac), 2.06 (s, Ac). HRMS: calcd for $C_{49}H_{79}O_{20}$ [M^++H]: 987.5165; found: 987.5157.

4.6.18. O-1-L-Menthyl-4,6-di-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranoside ***24***. FT-IR (film): 1746 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.36–7.25 (m), 5.56 (d, *J*=2.6 Hz, H-4 (α)), 5.46 (s, H-4 (β)), 5.02 (d, *J*=3.5 Hz, H-1 (α)), 4.87 (d, *J*=10.7 Hz, Bn (β)), 4.80 (d, *J*=11.6 Hz, Bn (α)), 4.73 (d, *J*=11.0 Hz, Bn (α)), 4.68 (d, *J*=10.7 Hz, Bn (β)), 4.62 (d, *J*=11.6 Hz, Bn (α)), 4.56–4.50 (m), 4.42 (d, *J*=6.2 Hz, H-1 (β)), 4.29 (t, *J*=6.2 Hz, H-5 (α)), 4.14–4.04 (m, 2H-6 (α), 2H-6 (β)), 3.99 (dd, *J*=3.0 Hz, *J*=10.0 Hz, H-3 (α)), 3.77 (dd, *J*=3.5 Hz, *J*=10.0 Hz, H-2 (α)), 3.72 (t, *J*=6.6 Hz, H-5 (β)), 3.57–3.50 (m, H-2 (β), H-3 (β)), 3.41 (td, *J*=4.1 Hz, *J*=10.6 Hz, C*H*–O menthol (β)), 3.34 (td, *J*=4.2 Hz, *J*=10.6 Hz, C*H*–O menthol (α)), 2.44–2.31 (m, C*H*$(CH_3)_2$ menthol), 2.14–2.05 (m, CHCH_2CH menthol), 2.14 (s, Ac (β)), 2.11 (s, Ac (α)), 2.07 (s, Ac (α)), 2.05 (s, Ac (β)), 1.67–1.60 (m, CH_2CH_2 menthol), 1.42–1.25 (m, C*H*CH_3, C*H*C$H(CH_3)_2$ menthol), 1.08–0.80 (m), 0.75 (d, *J*=6.7 Hz), 0.68 (d, *J*=6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 170.6, 170.59, 170.58, 170.4, 138.66, 138.62, 138.1, 137.9, 128.3–128.0, 127.9–127.4, 101.7 (C-1 (β)), 99.5 (C-1 (α)), 81.2 (C*H*–O menthol (α)), 79.5 (C*H*–O menthol (β)), 79.3, 78.7, 76.1 (C-3 (α)), 76.0 (C-2 (α)), 75.3, 73.8, 72.3, 71.8, 70.4 (C-5 (β)), 68.0 (C-4 (α)), 66.8 (C-5 (α)), 66.7 (C-4 (β)), 63.0 (C-6 (α)), 62.3 (C-6 (β)), 48.7 (C*H*C$H(CH_3)_2$ (α) menthol), 47.9 (CHC$H(CH_3)_2$ (β) menthol), 42.9 (CHCH_2CH (α) menthol), 41.3 (CHCH_2CH (β) menthol), 34.3, 34.2, 31.7 (C*H*CH_3 menthol (α)), 31.5 (CHCH_3 menthol (β)), 25.0 (C*H*$(CH_3)_2$ menthol (β)), 24.4 (C*H*$(CH_3)_2$ menthol (α)), 23.0, 22.9, 22.4, 22.2, 21.0, 20.98 (Ac), 20.92 (Ac), 20.8 (Ac), 20.7 (Ac), 16.0, 15.5.

4.6.19. O-1-L-Cyclohexyl-4,6-di-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranoside ***25***. FT-IR (film): 1744 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.36–7.25 (m), 5.56 (d, *J*=2.8 Hz, H-4 (α)), 5.48 (d, *J*=2.3 Hz, H-4 (β)), 4.99 (d, *J*=3.6 Hz, H-1 (α)), 4.91 (d, *J*=10.8 Hz, Bn), 4.79 (d, *J*=12.0 Hz, Bn), 4.75–4.69 (m), 4.62 (d, *J*=12.0 Hz, Bn), 4.57–4.49 (m), 4.48 (d, *J*=7.2 Hz, H-1 (β)), 4.23 (t, *J*=6.2 Hz, H-5 (α)), 4.20–4.09 (m), 4.03 (dd, *J*=7.4 Hz, *J*=11.2 Hz), 3.97 (dd, *J*=3.3 Hz, *J*=10.0 Hz, H-3 (α)), 3.78–3.73 (m), 3.70–3.63 (m), 3.61–3.49 (m), 2.13 (s, Ac), 2.10 (s, Ac), 2.06 (s, Ac), 2.05 (s, Ac), 1.99–1.84 (m), 1.77–1.75 (m), 1.62–1.17 (m). ^{13}C NMR ($CDCl_3$): δ 170.58, 170.56, 170.4, 138.6, 138.1, 137.8, 128.3–127.5, 102.1 (C-1 (β)), 95.9 (C-1 (α)), 79.4, 78.8, 78.5 (C*H* cyclohexanol), 76.3 (C*H* cyclohexanol), 76.1 (H-3 (α)), 75.6 (H-2 (α)), 75.3, 73.2, 72.2, 70.5 (C-5 (β)), 68.0 (C-4 (α)), 66.6 (C-4 (β), C-5 (α)), 62.6, 62.0, 33.7, 33.3, 32.0, 31.6, 25.58, 25.55, 24.5, 24.2, 24.1, 24.0, 20.97 (Ac), 20.92 (Ac), 20.77 (Ac), 20.75 (Ac).

4.6.20. 3-O-(4,6-Di-O-acetyl-2,3-di-O-benzyl-α/β-D-galactopyranosyl)-N-Boc-L-ser-methyl ester ***26***. α anomer: $[\alpha]_D^{20}$ +99.0 (*c* 1.25, CH_2Cl_2). FT-IR (film): 1715, 1745 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.32–7.26 (m, 10H), 5.62 (d, 1H, *J*=8.2 Hz, N*H*Boc), 5.55 (s, 1H, H-4), 4.80 (s, 1H, H-1 (α)), 4.77 (d, 1H, *J*=12.0 Hz, Bn), 4.73 (d, 1H, *J*=11.1 Hz, Bn), 4.58 (d, 1H, *J*=11.9 Hz, Bn), 4.53 (d, 1H, *J*=11.0 Hz, Bn), 4.47–4.45 (m, 1H, C*H* serine), 4.17–4.02 (m, 4H, H-5, H-6, H′-6, CH_2

serine), 3.90–3.83 (m, 2H, H-3, C*H*$_2$ serine), 3.77–3.74 (m, 1H, H-2), 3.66 (s, 3H, CO_2Me), 2.10 (s, 3H, Ac), 2.04 (s, 3H, Ac), 1.45 (s, 3H, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 170.7, 170.5, 170.2, 155.4, 138.4, 137.9, 128.36, 128.34, 127.9, 127.7, 127.6, 99.2 (C-1 (α)), 75.6 (C-3), 75.4 (C-2), 73.4, 72.1, 70.2 (*C*H$_2$ serine), 67.5 (C-4), 67.3 (C-5), 62.3 (C-6), 54.1 (*C*H serine), 52.5 (CO_2Me), 28.3 (*t*-Bu), 20.8 (Ac), 20.7 (Ac).

β anomer: $[\alpha]_D^{20}$ +38.8 (*c* 0.57, CH_2Cl_2). FT-IR (film): 1715, 1744 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.39–7.28 (m, 10H), 5.48 (s, 2H, N*H*Boc, H-4), 4.80 (d, 1H, *J*=10.7 Hz, Bn), 4.75–4.69 (m, 2H, Bn), 4.50 (d, 1H, *J*=11.3 Hz, Bn), 4.49–4.46 (m, 1H, C*H* serine), 4.36 (d, 1H, *J*=7.1 Hz, H-1 (β)), 4.35–4.31 (m, 1H, C*H*$_2$ serine), 4.13 (d, 2H, *J*=6.5 Hz, H-6, H′-6), 3.83 (dd, 1H, *J*=3.4 Hz, *J*=10.4 Hz, C*H*$_2$ serine), 3.75 (s, 3H, CO_2Me), 3.75–3.72 (m, 1H, H-5), 3.58–3.52 (m, 2H, H-2, H-3), 2.14 (s, 3H, Ac), 2.08 (s, 3H, Ac), 1.42 (s, 3H, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 170.7, 170.5, 170.3, 155.4, 138.2, 137.5, 128.3, 128.1, 128.0, 127.8, 127.7, 104.1 (C-1 (β)), 79.0, 78.3, 75.4, 72.1, 70.8 (C-5), 70.3 (*C*H$_2$ serine), 66.3 (C-4), 61.9 (C-6), 54.0 (*C*H serine), 52.6 (CO_2Me), 28.3 (*t*-Bu), 20.8 (Ac), 20.7 (Ac).

4.6.21. (2R)-1,3-Di-O-tert-butyldiphenylsilyl-2-O-(4,6-di-O-chloroacetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-1,2,3-trihydroxypropane ***27***. $[\alpha]_D^{20}$ +66.9 (*c* 12.15, CH_2Cl_2). FT-IR (film): 1747, 1766 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.63–7.61 (m, 8H), 7.43–7.27 (m, 18H), 7.18–7.14 (m, 4H), 5.39 (d, 1H, *J*=2.9 Hz), 5.06 (d, 1H, *J*=3.5 Hz, H-1 (α)), 4.64 (d, 2H, *J*=11.4 Hz), 4.54 (d, 1H, *J*=11.9 Hz), 4.50 (d, 1H, *J*=10.9 Hz), 4.26 (t, 1H, *J*=6.6 Hz), 4.14–3.91 (m, 6H), 3.88–3.72 (m, 6H), 3.67 (dd, 1H, *J*=3.4 Hz, *J*=10.0 Hz), 1.01 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 167.0, 166.6, 138.1, 137.8, 135.6–135.5, 133.3, 133.2, 133.0, 129.83, 129.80, 128.3, 128.2, 128.0, 127.8–127.6, 96.2 (C-1 (α)), 77.6, 75.4, 75.1, 73.1, 72.6, 70.0, 65.8, 64.1, 63.2, 62.8, 40.7, 40.4, 26.9, 26.8, 19.3, 19.1. HRMS: calcd for $C_{59}H_{68}O_{10}Cl_2Si_2Na^+$ [M$^+$+Na]: 1085.3626; found: 1085.3620.

4.6.22. Methyl 15-O-(2,3-di-O-benzyl-4,6-di-O-chloroacetyl-α/β-D-galactopyranosyl)decapentanoate ***28***. FT-IR (film): 1736, 1764 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.35–7.27 (m), 5.57 (d, *J*=3.3 Hz, H-4 (α)), 5.51 (d, *J*=2.1 Hz, H-4 (β)), 4.87 (d, *J*=10.8 Hz), 4.807 (d, *J*=3.6 Hz, H-1 (α)), 4.80 (d, *J*=12.0 Hz), 4.73 (d, *J*=11.0 Hz), 4.72 (d, *J*=10.9 Hz), 4.70 (d, *J*=10.4 Hz), 4.61 (d, *J*=12.2 Hz), 4.58 (d, *J*=11.0 Hz), 4.54 (d, *J*=11.2 Hz), 4.39 (d, *J*=7.1 Hz, H-1 (β)), 4.34–4.19 (m), 4.15 (d, *J*=2.2 Hz, AcCl (β)), 4.10 (d, *J*=2.8 Hz, AcCl (α)), 4.08 (s, AcCl (β)), 4.06 (s, AcCl (α)), 4.00 (dd, *J*=3.4 Hz, *J*=10.0 Hz, H-3 (α)), 3.95–3.90 (m), 3.83 (t, *J*=7.0 Hz, H-5 (β)), 3.73 (dd, *J*=3.6 Hz, *J*=10.0 Hz, H-2 (α)), 3.66 (s), 3.63–3.43 (m), 2.29 (t, *J*=7.5 Hz), 1.67–1.57 (m), 1.42–1.24 (m). ^{13}C NMR ($CDCl_3$): δ 174.3, 167.1, 167.0, 166.9, 166.8, 138.3, 137.7, 137.4, 128.4–127.7, 103.7 (C-1 (β)), 97.6 (C-1 (α)), 78.6, 78.5, 75.7, 75.4, 75.3, 73.4, 72.7, 72.6, 70.6, 70.0, 68.7, 68.6, 66.0, 63.7, 63.1, 51.4, 40.8, 40.7, 40.6, 40.5, 34.1, 29.6–29.1, 26.2, 26.1, 24.9. HRMS: calcd for $C_{40}H_{56}Cl_2O_{10}Na^+$ [M$^+$+Na]: 789.3143; found: 789.3119.

4.6.23. Methyl (2R)-3-O-tert-butyldiphenylsilyl-2-O-[2,3-di-O-benzyl-4,6-di-O-chloroacetyl-α-D-galactopyranosyl-(1→6)-2,3,4-tri-O-benzyl-1-O-α-D-glucopyranosyl]-2,3-dihydroxypropanoate ***29***. $[\alpha]_D^{20}$ +98.5 (*c* 0.76, CH_2Cl_2). FT-IR (film): 1751 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.69–7.68 (m, 4H), 7.40–7.17 (m, 31H), 5.48 (d, 1H, *J*=2.9 Hz, H-4 Galactose), 5.15 (d, 1H, *J*=3.3 Hz, H-1′ (α) Glucose), 4.98 (d, 1H, *J*=10.6 Hz), 4.92 (d, 1H, *J*=3.2 Hz, H-1 (α) Galactose), 4.88 (d, 1H, *J*=11.6 Hz), 4.84 (d, 1H, *J*=11.5 Hz), 4.73 (d, 1H, *J*=10.6 Hz), 4.67 (d, 2H, *J*=11.8 Hz), 4.60 (d, 1H, *J*=11.4 Hz), 4.58 (d, 1H, *J*=12.0 Hz), 4.53 (d, 1H, *J*=11.2 Hz), 4.52 (d, 1H, *J*=11.6 Hz), 4.48–4.46 (m, 1H), 4.19–3.88 (m, 13H), 3.76 (s, 3H), 3.74–3.58 (m, 4H), 3.51 (dd, 1H, *J*=3.4 Hz, *J*=9.4 Hz), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 170.2, 167.0, 166.7, 138.8, 138.6, 138.4, 138.2, 137.7, 135.6, 135.5, 133.0, 132.8, 129.7, 128.3–127.3, 97.8 (C-1 (α), Galactose), 94.4 (C-1′ (α), Glucose), 81.7, 79.5, 77.4, 75.7, 75.3, 75.0, 74.7, 74.5, 72.8, 72.4, 71.9, 70.8, 70.1, 66.3, 66.2, 64.7, 63.7, 52.0, 40.7, 40.5, 26.7, 19.2. HRMS: calcd for $C_{71}H_{78}O_{16}Cl_2SiNa^+$ [M$^+$+Na]: 1307.4334; found: 1307.4328.

4.6.24. 3-O-(2,3-Di-O-benzyl-4,6-di-O-chloroacetyl-α/β-D-galactopyranosyl)-epiandrosterone ***30***. FT-IR (film): 1737, 1764 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.35–7.27 (m), 5.58 (d, *J*=2.7 Hz, H-4 (α)), 5.50 (d, *J*=1.9 Hz, H-4 (β)), 4.97 (d, *J*=3.7 Hz, H-1 (α)), 4.88 (d, *J*=10.9 Hz, Bn (β)), 4.79 (d, *J*=12.0 Hz, Bn (α)), 4.74–4.69 (m), 4.54 (d, *J*=11.3 Hz), 4.50 (d, *J*=7.4 Hz, H-1 (β)), 4.34–4.30 (m), 4.25–4.20 (m), 4.15–4.04 (m), 3.99 (dd, *J*=10.0 Hz, *J*=3.4 Hz, H-3 (α)), 3.83 (t, *J*=7.0 Hz, H-5 (β)), 3.73 (dd, *J*=10.0 Hz, *J*=3.7 Hz, H-2 (α)), 3.57–3.48 (m), 2.44 (dd, *J*=19.2 Hz, *J*=8.5 Hz), 2.11–2.01 (m), 1.96–1.63 (m), 1.59–1.43 (m), 1.39–1.20 (m), 1.15.1.07 (m), 1.02–0.91 (m), 0.68 (ddd, *J*=0.63 Hz, *J*=11.4 Hz, *J*=11.4 Hz). ^{13}C NMR ($CDCl_3$): δ 167.2, 167.0, 166.9, 138.4, 138.3, 137.8, 128.4–127.7, 102.2 (C-1 (β)), 95.8 (C-1 (α)), 79.7, 78.8, 77.1, 75.7, 75.4, 75.2, 73.4, 72.6, 70.1, 70.0, 68.7, 66.0, 63.9, 63.2, 54.4, 51.4, 47.8, 45.2, 44.7, 40.8, 40.7, 40.5, 36.8, 35.8, 35.7, 35.0, 31.5, 30.8, 29.5, 28.4, 27.4, 21.7, 20.5, 14.2, 13.8, 12.9, 12.3. HRMS: calcd for $C_{43}H_{54}Cl_2O_9Na^+$ [M$^+$+Na]: 807.3043; found: 807.3018.

4.6.25. 1-O-Adamantanyl-2,3-di-O-benzyl-4,6-di-O-chloroacetyl-α/β-D-galactopyranoside ***31***. FT-IR (film): 1743, 1747, 1762, 1763 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.34–7.25 (m), 5.59 (d, *J*=2.4 Hz, H-4 (α)), 5.49 (d, *J*=2.2 Hz, H-4 (β)), 5.30 (d, *J*=3.7 Hz, H-1 (α)), 4.91 (d, *J*=10.9 Hz, Bn (β)), 4.75–4.66 (m), 4.63 (d, *J*=11.9 Hz, Bn (α)), 4.57 (d, *J*=10.6 Hz, Bn (α)), 4.53 (d, *J*=11.2 Hz, Bn (β)), 4.43 (t, *J*=6.5 Hz, H-5 (α)), 4.29 (dd, *J*=7.4 Hz, *J*=11.2 Hz, H-6 (β)), 4.24–4.16 (m), 4.14–4.08 (m), 4.05 (s), 4.02 (dd, *J*=3.4 Hz, *J*=10.0 Hz), 3.83 (t, *J*=6.5 Hz, H-5 (β)), 3.72 (dd, *J*=3.7 Hz, *J*=10.0 Hz, H-2 (α)), 3.60–3.53 (m), 2.15 (br s), 1.91–1.76 (m), 1.67–1.59 (m). ^{13}C NMR ($CDCl_3$): δ 167.2, 167.0, 166.9, 138.4, 138.3, 137.9, 137.4, 128.4–127.6, 96.3 (C-1 (β)), 90.6 (C-1 (α)), 79.0, 78.5, 75.8, 75.7, 75.4, 75.3, 74.9, 73.2, 72.7, 72.5, 70.2, 69.9, 68.9, 65.7, 63.9, 63.5, 42.6, 42.4, 40.8, 40.7, 40.6, 40.5, 36.2, 30.7, 30.6. HRMS: calcd for $C_{34}H_{40}Cl_2O_8Na^+$ [M$^+$+Na]: 669.1998; found: 669.1986.

4.6.26. Benzyl (2S)-2-O-(4,6-di-O-chloroacetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-2-phenylacetate ***32***. $[\alpha]_D^{20}$ +80.5 (*c* 2.10, CH_2Cl_2). FT-IR (film): 1747 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.49–7.13 (m, 20H), 5.58 (d, 1H, *J*=3.0 Hz, H-4), 5.18–5.11 (m, 3H, C*H* mandelate, CO_2CH_2Ph), 4.87 (d, 1H, *J*=3.6 Hz, H-1 (α)), 4.73 (d, 1H, *J*=10.8 Hz, Bn), 4.66 (d, 1H, *J*=11.8 Hz, Bn), 4.63 (d, 1H, *J*=10.8 Hz, Bn), 4.45–4.42 (m, 2H, H-5, Bn), 4.18–4.04 (m, 3H, H-3, H-6, H′-6), 4.08 (s, 2H, AcCl), 4.02 (s, 2H, AcCl), 3.73 (dd, 1H, *J*=3.6 Hz, *J*=10.0 Hz, H-2). ^{13}C NMR ($CDCl_3$): δ 169.7, 166.9, 166.8, 138.1, 137.7, 135.3, 135.1, 128.9–128.0, 127.9–127.4, 96.7 (C-1 (α)), 78.0 (CH mandelate), 75.5 (C-3), 75.1 (C-2), 73.3, 72.6, 69.9 (C-4), 67.0 (CO_2CH_2Ph), 66.9 (C-5), 63.4 (C-6), 40.7 (AcCl), 40.5 (AcCl). HRMS: calcd for $C_{39}H_{40}Cl_2O_{10}Na^+$ [M$^+$+Na]: 759.1740; found: 759.1726.

4.6.27. 1-ω-Methoxy-PEG$_{550}$yl-4,6-di-O-chloroacetyl-2,3-di-O-benzyl-α/β-D-galactopyranoside ***33***. FT-IR (film): 1716, 1760 (C=O st) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.46–7.25 (m), 5.58 (d, *J*=2.7 Hz, H-4 (α)), 5.50 (br s, H-4 (β)), 4.90 (d, *J*=10.5 Hz), 4.89 (d, *J*=3.6 Hz, H-1 (α)), 4.83–4.53 (m), 4.47 (d, *J*=6.7 Hz, H-1 (β)), 4.32–4.19 (m), 4.16–4.06 (m), 4.04–3.97 (m), 3.90–3.53 (m), 3.37 (s, OMe). ^{13}C NMR ($CDCl_3$): δ 167.1, 167.0, 166.9, 138.4, 138.2, 137.7, 137.3, 128.4–128.0, 127.9–127.6, 103.8 (C-1 (β)), 97.7 (C-1 (α)), 78.5, 78.4, 75.5 (C-3 (α)), 75.1, 73.4, 72.6, 72.5, 71.9, 71.8, 70.4, 70.3, 70.1, 70.0 (C-4 (α)), 69.3, 68.6 (C-4 (β)), 67.3, 66.0 (C-5 (α)), 63.5 (C-6 (α)), 63.1 (C-6 (β), 59.0 (OMe), 40.77 (AcCl), 40.75 (AcCl), 40.6 (AcCl), 40.5 (AcCl).

4.6.28. O-1-L-Menthyl-4,6-di-O-chloroacetyl-2,3-di-O-benzyl-α/β-D-galactopyranoside ***34***. α anomer: $[\alpha]_D^{20}$ +52.8 (*c* 2.48, CH_2Cl_2). FT-IR (film): 1748, 1765 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.32–7.26 (m, 10H), 5.58 (s, 1H, H-4), 5.00 (d, 1H, *J*=3.0 Hz, H-1 (α)), 4.77 (d, 1H,

J=11.6 Hz, Bn), 4.71 (d, 1H, J=10.9 Hz, Bn), 4.62 (d, 1H, J=11.6 Hz, Bn), 4.57 (d, 1H, J=10.9 Hz, Bn), 4.36 (t, 1H, J=6.4 Hz, H-5), 4.25–4.15 (m, 2H, H-6, H′-6), 4.11 (s, 2H, AcCl), 4.07 (s, 2H, AcCl), 4.02 (dd, 1H, J=2.0 Hz, J=10.0, H-3), 3.73 (dd, 1H, J=2.9 Hz, J=10.0 Hz, H-2), 3.34 (td, 1H, J=4.0 Hz, J=10.5 Hz, C*H*–O menthol), 2.41–2.35 (m, 1H, C*H*$(CH_3)_2$ menthol), 2.06–2.03 (m, 1H, CHC*H*$_2$CH menthol), 1.64–1.57 (m, 3H, C*H*$_2$C*H*$_2$ menthol), 1.43–1.35 (m, 1H, C*H*CH_3), 1.30–1.25 (m, 1H, C*H*CH$(CH_3)_2$ menthol), 1.07–0.77 (m, 2H, CHC*H*$_2$CH menthol, C*H*$_2$CH$_2$ menthol), 0.91 (d, 3H, J=6.5 Hz, CHC*H*$_3$ menthol), 0.83 (d, 3H, J=6.6 Hz, C*H*$(CH_3)_2$ menthol), 0.69 (d, 3H, J=6.7 Hz, C*H*$(CH_3)_2$ menthol). ^{13}C NMR ($CDCl_3$): δ 167.0, 166.9, 138.3, 137.7, 128.3, 128.2, 128.0, 127.7, 127.6, 127.5, 99.4 (C-1 (α)), 81.3 (*C*H–O menthol), 75.78, 75.75, 73.8, 72.2, 70.1 (C-4), 66.2 (C-5), 63.9 (C-6), 48.7 (*C*HCH$(CH_3)_2$ menthol), 42.8 (*C*H$_2$(CH)$_2$), 40.7 (AcCl), 40.5 (AcCl), 34.2 (*C*H$_2$CH$_2$ menthol), 31.7 (*C*H(CH_3) menthol), 24.5 (*C*H$(CH_3)_2$ menthol), 22.9 (CH_2*C*H$_2$ menthol), 22.4 (CH*C*H$_3$), 21.0 (CH$(CH_3)_2$), 16.0 (CH$(CH_3)_2$). HRMS: calcd for $C_{34}H_{44}Cl_2O_8Na^+$ [M^++Na]: 673.2311; found: 673.2294.

β anomer: $[\alpha]_D^{20}$ −0.75 (c 0.53, CH_2Cl_2). FT-IR (film): 1763 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.36–7.27 (m, 10H), 5.49 (d, 1H, J=3.2 Hz, H-4), 4.87 (d, 1H, J=10.8 Hz, Bn), 4.71 (d, 1H, J=11.2 Hz, Bn), 4.67 (d, 1H, J=10.8 Hz, Bn), 4.54 (d, 1H, J=11.2 Hz, Bn), 4.44 (d, 1H, J=7.6 Hz, H-1 (β)), 4.28–4.12 (m, 4H, AcCl, H-6, H′6), 4.05 (s, 2H, AcCl), 3.80 (t, 1H, J=6.4 Hz, H-5), 3.57 (dd, 1H, J=3.4 Hz, J=9.6 Hz, H-3), 3.50 (dd, 1H, J=7.6 Hz, J=9.5 Hz, H-2), 3.42 (td, 1H, J=4.2 Hz, J=10.7 Hz, C*H*–O menthol), 2.34–2.26 (m, 1H, C*H*$(CH_3)_2$ menthol), 2.11–2.08 (m, 1H, CHC*H*$_2$CH menthol), 1.67–1.64 (m, 2H, C*H*$_2$C*H*$_2$ menthol), 1.39–1.24 (m, 2H, C*H*CH_3, C*H*CH$(CH_3)_2$ menthol), 1.02–0.80 (m, 9H), 0.74 (d, 3H, J=6.8 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 167.2, 166.9, 138.4, 137.5, 128.4, 128.2, 128.17, 128.14, 127.8, 127.6, 101.4 (C-1 (β)), 79.1 (*C*H–O menthol), 79.0 (C-3), 78.5 (C-2), 75.3, 72.7, 69.2 (C-5), 68.9 (C-4), 63.4 (C-6), 47.9 (*C*HCH$(CH_3)_2$ menthol), 41.1 (CHC*H*$_2$CH menthol), 40.8 (AcCl), 40.5 (AcCl), 34.3, 31.5 (*C*HCH$_3$ menthol), 25.1 (*C*H$(CH_3)_2$), 23.0, 22.1, 21.0, 15.6.

4.6.29. O-1-Cyclohexyl-4,6-di-O-chloroacetyl-2,3-di-O-benzyl-α/β-D-galactopyranoside ***35***. α anomer: $[\alpha]_D^{20}$ +94.0 (c 1.06, CH_2Cl_2). FT-IR (film): 1744, 1762 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.32–7.28 (m, 10H), 5.58 (d, 1H, J=2.9 Hz, H-4), 4.98 (d, 1H, J=3.6 Hz, H-1 (α)), 4.77 (d, 1H, J=11.9 Hz, Bn), 4.71 (d, 1H, J=10.7 Hz, Bn), 4.63–4.57 (m, 2H, Bn), 4.31 (t, 1H, J=6.4 Hz, H-5), 4.24–4.17 (m, 2H, H-6, H′-6), 4.14–4.06 (m, 4H, AcCl), 4.00 (dd, 1H, J=3.3 Hz, J=10.0 Hz, H-3), 3.73 (dd, 1H, J=3.3 Hz, J=10.0 Hz, H-2), 3.56–3.49 (m, 1H, C*H* cyclohexanol), 1.92–1.74 (m, 4H), 1.58–1.53 (2H, m), 1.47–1.14 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 167.0, 166.9, 138.3, 137.8, 128.3, 128.0, 127.8, 127.7, 95.8 (C-1 (α)), 76.4 (CH cyclohexanol), 75.7 (C-3), 75.3 (C-2), 73.3, 72.6, 70.1 (C-4), 66.0 (C-5), 63.8 (C-6), 40.7 (AcCl), 40.5 (AcCl), 33.3, 31.5, 25.5, 24.4, 24.1. HRMS: calcd for $C_{30}H_{36}Cl_2O_8Na^+$ [M^++Na]: 617.1685; found: 617.1675.

β anomer: $[\alpha]_D^{20}$ +22.7 (c 0.65, CH_2Cl_2). FT-IR (film): 1748, 1760 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 7.35–7.27 (m, 10H), 5.50 (d, 1H, J=1.8 Hz, H-4), 4.90 (d, 1H, J=10.8 Hz, Bn), 4.70 (t, 2H, J=11.4 Hz, Bn), 4.54 (d, 1H, J=11.2 Hz, Bn), 4.49 (d, 1H, J=7.4 Hz, H-1 (β)), 4.32 (dd, 1H, J=6.9 Hz, J=11.2 Hz, H-6), 4.23 (dd, 1H, J=6.5 Hz, J=11.2 Hz, H′-6), 4.15 (dd, 2H, J=15.1 Hz, J=18.1 Hz, AcCl), 4.07 (s, 2H, AcCl), 3.82 (t, 1H, J=6.7 Hz, H-5), 3.70–3.63 (m, 1H, C*H* cyclohexanol), 3.60–3.53 (m, 2H, H-2, H-3), 1.98–1.91 (m, 2H), 1.79–1.74 (m, 2H), 1.57–1.50 (m, 2H), 1.47–1.37 (m, 2H), 1.34–1.17 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 167.2, 166.9, 138.3, 137.4, 128.4, 128.3, 128.15, 128.11, 127.8, 127.7, 102.1 (C-1 (β)), 78.8, 78.6 (*C*H cyclohexanol), 78.5, 75.3, 72.6, 70.0 (C-5), 68.7 (C-4), 63.2 (C-6), 40.8 (AcCl), 40.5 (AcCl), 33.6, 31.9, 25.5, 24.0, 23.9.

4.6.30. 3-O-(4,6-Di-O-chloroacetyl-2,3-di-O-benzyl-α/β-D-galactopyranosyl)-N-Boc-L-ser-methyl ester ***36***. FT-IR (film): 1714, 1715, 1747 (C=O st) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37–7.27 (m), 5.58 (d, 2H, J=8.2 Hz, N*H*Boc, H-4 (α)), 5.49 (d, J=2.7 Hz, H-4 (β)), 5.44 (d, J=7.9 Hz, N*H*Boc (β)), 4.80 (d, J=10.7 Hz, Bn (β)), 4.79 (s, H-1 (α)), 4.77–67 (m), 4.59–4.51 (m), 4.48–4.45 (m, C*H* serine), 4.37 (d, J=7.6 Hz, H-1 (β)), 4.31–4.16 (m), 4.15–4.06 (m), 3.92 (dd, J=3.3 Hz, J=10.0 Hz, H-3 (α)), 3.86–3.80 (m), 3.78–3.71 (m, H-2 (α)), 3.76 (s, CO_2Me (β)), 3.67 (s, CO_2Me (α)), 3.59 (dd, J=3.0 Hz, J=9.6 Hz, H-3 (β)), 3.53 (dd, J=9.3 Hz, J=17.0 Hz, H-2 (β)), 1.45 (s, *t*-Bu (α)), 1.42 (s, *t*-Bu (β)). ^{13}C NMR ($CDCl_3$): δ 170.7, 167.0, 166.99, 166.94, 138.1, 137.5, 137.1, 128.4–127.7, 104.0 (C-1 (β)), 99.3 (C-1 (α)), 78.6 (β), 78.0 (β), 75.5 (β), 75.3 (C-3 (α)), 75.1 (C-2 (α)), 73.5 (α), 72.59 (β), 72.52 (α), 70.6 (*C*H$_2$ serine (α)), 70.4 (*C*H$_2$ serine (β)), 70.2 (C-5 (β)), 69.7 (C-4 (α)), 68.4 (C-4 (β)), 66.8 (C-5 (α)), 63.5 (C-6 (α)), 63.0 (C-6 (β)), 54.1 (*C*H serine (α)), 54.0 (*C*H serine (β)), 52.6 (CO_2Me (β)), 52.5 (CO_2Me (α)), 40.7 (AcCl (β)), 40.67 (AcCl (α)), 40.61 (AcCl (α)), 40.5 (AcCl (β)), 28.3 (*t*-Bu). HRMS: calcd for $C_{33}H_{41}Cl_2O_{12}NNa^+$ [M^++Na]: 736.1904; found: 736.1889.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia (FCT) through grant PEst-OE/EQB/LA0004/2011. E.L. acknowledges FCT for a PhD grant SFRH/47702/2008. We thank CERMAX for the use of the NMR spectrometers, which were purchased within the framework of the National Programme for Scientific Re-equipment, contract REDE/1517/RMN/2005, with funds from POCI 2010 (FEDER) and FCT. This work was motivated by collaboration with Professor Helena Santos.

References and notes

1. Lourenço, E. C.; Ventura, M. R.; Maycock, C. D. *Carbohydr. Res.* **2011**, *346*, 163–168.
2. Lourenço, E. C.; Ventura, M. R.; Maycock, C. D. *Carbohydr. Res.* **2009**, *344*, 2073–2078.
3. Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155–224.
4. Kim, J.-W.; Yang, H.; Khot, V.; Whitfield, D. M.; Boons, G.-J. *Eur. J. Org. Chem.* **2006**, 5007–5028.
5. Huang, M.; Garrett, G. E.; Birlirakis, N.; Bohé, L.; Pratt, D. A.; Crich, D. *Nat. Chem.* **2012**, *4*, 663–667.
6. Kumar, R.; Whitfield, D. M. *J. Org. Chem.* **2012**, *77*, 3724–3729.
7. Whitfield, D. M. *Adv. Carbohydr. Chem. Biochem.* **2009**, *62*, 83–159.
8. Bohé, L.; Crich, D. *C. R. Chim.* **2011**, *14*, 3–16.
9. Beaver, M. G.; Woerpel, K. A. *J. Org. Chem.* **2010**, *75*, 1107–1118.
10. Whitfield, D. *Carbohydr. Res.* **2012**, *356*, 180–190.
11. Cheng, Y.-P.; Chen, H.-T.; Lin, C.-C. *Tetrahedron Lett.* **2002**, *43*, 7721–7723.
12. Crich, D.; la Mora, M.; Vinod, A. U. *J. Org. Chem.* **2003**, *68*, 8142–8148.
13. Suzuki, K.; Ito, Y.; Kanie, O. *Carbohydr. Res.* **2012**, *359*, 81–91.
14. Sugimura, H.; Watanabe, K. *Synth. Commun.* **2001**, *31*, 2313–2321.
15. Compain-Batissou, M.; Mesrari, L.; Anker, D.; Doutheau, A. *Carbohydr. Res.* **1999**, *316*, 201–205.
16. Demchenko, A.; Rousson, E.; Boons, G.-J. *Tetrahedron Lett.* **1999**, *40*, 6523–6526.
17. Khaja, S. D.; Kumar, V.; Ahmad, M.; Xue, J.; Matta, K. L. *Tetrahedron Lett.* **2010**, *51*, 4411–4414.
18. Polt, R.; Szabò, L.; Treiberg, J.; Li, Y.; Hruby, V. J. *J. Am. Chem. Soc.* **1992**, *114*, 10249–10258.
19. Lin, C.-C.; Shimazaki, M.; Heck, M.-P.; Aoki, S.; Wang, R.; Kimura, T.; Ritzèn, H.; Takayama, S.; Wu, S.-H.; Weitz-Schmidt, G.; Wong, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6826–6840.
20. Baek, J. Y.; Lee, B.-Y.; Jo, M. G.; Kim, K. S. *J. Am. Chem. Soc.* **2009**, *131*, 17705–17713.
21. Ma, Y.; Lian, G.; Li, Y.; Yu, B. *Chem. Commun.* **2011**, 7515–7517.
22. Kalikanda, J.; Li, Z. *J. Org. Chem.* **2011**, *76*, 5207–5218.
23. Crich, D.; Hu, T.; Cai, F. *J. Org. Chem.* **2008**, *73*, 8942–8953.
24. Maity, S. K.; Basu, N.; Ghosh, R. *Carbohydr. Res.* **2012**, *354*, 40–98.
25. Durón, S. G.; Polat, T.; Wong, C.-H. *Org. Lett.* **2004**, *6*, 839–841.
26. Konokov, L. O.; Malysheva, N. M.; Orlova, A. V.; Zinin, A. I.; Laptinskaya, T. V.; Kononova, E. G.; Kolotyrkina, N. G. *Eur. J. Org. Chem.* **2012**, 1926–1934.
27. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, fifth ed.; Elsevier.
28. Li, Z.; Gildersleeve, J. G. *J. Am. Chem. Soc.* **2006**, *128*, 11612–11619.