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Novel class of non-ionic monocatenary and bolaform alkylglycoside surfactants. Synthesis by microwave-assisted glycosylation and olefin cross-metathesis or by 'click-chemistry': physicochemical studies

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ABSTRACT

We develop herein the synthesis of a new class of monocatenary and bolaform surfactants from D-glucose, D-galactose and lactose. Two main pathways have been investigated: microwave-assisted glycosylation followed by olefin cross-metathesis, and the one-step click-chemistry methodology. Tensioactive properties of these new compounds have been studied in order to characterize the physicochemical behaviour of these new carbohydrate-based compounds in water.

1. Introduction

In the last two decades, academic institutions and industry have focused on renewable surfactants to reduce their impact on the environment. The development of surfactants from carbohydrates and vegetal oils is the result of this concept based on the exclusive use of natural substances.[1] Sugar-based surfactants are gaining increasing attention due to their advantages over other surfactants with regard to notable dermatological properties,[2] good compatibility with some standard products[3] and their favourable environmental profile.[4] In addition, their low toxicity, good biocompatibility and fast biodegradation make this class of molecules very attractive, not only for personal care products but also for a large range of technical applications[5]; this is particularly true for non-ionic sugar-based surfactants. Some compounds have already been described in the literature[6] such as monocatenary and bolaform structures.

Monocatenary compounds are defined as a hydrophobic tail bound to a polar head group (Fig. 1a). They are generally used as cleaning and washing agents,[7] and also as emulsifiers[8] in food and cosmetics. Bolaform surfactants, which are composed of sugar units at both ends of a hydrophobic chain (Fig. 1b), have the ability to form supramolecular arrangements such as ultrathin monolayers[9] or gels[10] and, for these reasons, have a potential use in pharmacy and chemistry[11] as components of drug delivery systems.

Figure 1. Structures of (a) monocatenary and (b) bolaform surfactants.

In this paper, we consider two different pathways to build carbohydrate-based monocatenary and bolaform surfactants. The first approach consists in microwave-assisted O-glycosylation followed by cross-metathesis. The second one uses the Huisgen's 1,3-dipolar cycloaddition named 'click-chemistry', to link together azide and alkyne patterns and generates original surfactants related to the previous O-glycosylated structures.

2. Results and discussion

2.1. Synthesis of monocatenary and bolaform surfactants

A new family of alkylglycosides was synthesized herein by O-glycosylation using a solvent-free method. Taking as starting point a previous work achieved in our laboratory[12], this *O*-linkage is

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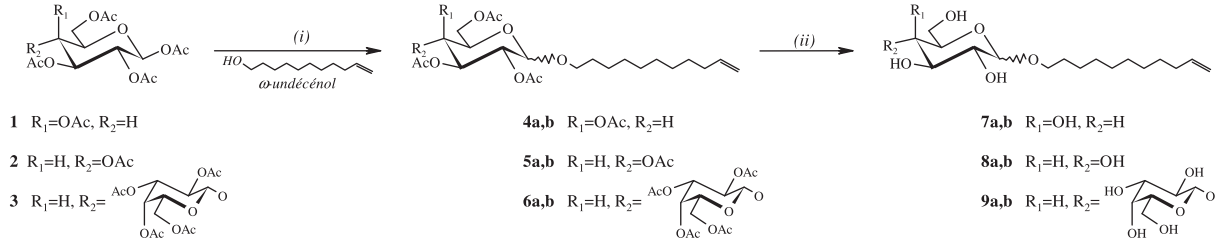
achieved by microwave activation. The following step consists in the dimerization of these alkylglycosides to build bolaforms by cross-metathesis using ruthenium benzylidene catalyst developed by Grubbs et al.[13]

*2.1.1. Microwave-assisted synthesis of monocatenary surfactants (**7**, **8** and **9**).* First of all, a series of six alkylglycosides (α and β anomers) were made up by grafting an aliphatic chain onto a polar head (compounds **7a**, **7b**, **8a**, **8b** and **9a**, **9b**). O-glycosylation of an ω-unsaturated fatty alcohol (ω-undecenol) was performed on carbohydrate peracetylated moieties derived from D-glucose, D-galactose or lactose, and followed by deprotection of hydroxyl groups of sugar units, to provide monocatenary surfactants (Scheme 1).

Structures of alkylglycosides **4**, **5** and **6** were clearly established by ^{1}H NMR. Three signals, respectively, ddt (5.81 ppm), dq (4.99 ppm) and dq (4.93 ppm), were assigned to the terminal aliphatic insaturation. The α anomer presented a doublet at 4.97 ppm with a coupling constant near 3 Hz, whereas compound β was characterized by a doublet at 4.45 ppm, with a $^3J_{1,2}$ of about 8 Hz. Mass spectroscopy (CIMS) gives expected values with *m*/*z* 501 for glucosides and galactosides (**4** and **5**) and *m*/*z* 789 for lactosidic compound **6**.

After deprotection by sodium methoxide, final monocatenary surfactants **7a**,**b**, **8a**,**b** and **9a**,**b** were isolated with 91% to quantitative yields. These final alkylglycosides were characterized by NMR, IR and mass spectroscopy.



Scheme 1. General procedure for synthesis of monocatenary compounds. (i) $ZnCl_2$, ω-undecenol, M.W. activation; (ii) MeONa in CH_2Cl_2/MeOH 1:1, rt. 'a' and 'b' refer to α and β anomers, respectively.

Several O-glycosylation methods have already been described in the literature.[14] Traditionally, such linkage could be prepared by Koenigs–Knorr method, starting from glycosyl bromides in the presence of promoters such as silver salts ($AgOTf$[15], $AgClO_4$[16]), mercury salts like $Hg(CN)_2$[17] or $HgBr_2$, or some Lewis acids like $FeCl_3$[18], $Sn(OTf)_2$[19] to avoid the use of heavy metal salts. Another effective method, widely employed, is Lewis acid-catalysed glycosylation using protected sugars like peracetylated sugars or other sugar donors such as anomeric halides,[20] 1-thio-sugars[21] or 1-*O*-trichloroacetimidates.[22] Typical acid catalysts employed as common glycosylation promoters are thus $SnCl_4$,[23] $BF_3{\cdot}Et_2O$[24] or $ZnCl_2$.[25] Glycosylations can also occur with other H^+ sources like acidic resin or with TsOH starting from unprotected sugars,[26] or enzymatically.[27] Among them we chose a microwave-assisted approach starting from protected sugars, initially reported by Loupy et al.[28] under solvent-free conditions.

Thus, peracetylated sugars **1**–**3** were mixed with zinc chloride and an excess of unsaturated alcohol without any solvent. Then, the mixtures were irradiated for 1–2 min in a microwave oven between 60 and 100 W. Table 1 presents the yield-optimized conditions used for the synthesis of monocatenary surfactants. Each one of the α and β anomers were separated and recovered by silica gel column chromatography.

*2.1.2. Synthesis of single-chain bolaform surfactants (**16**, **17** and **18**).* Olefin metathesis reaction represents an efficient synthetic tool for the construction of bolaform architecture. According to previous work on ω-alkenyl-*O*-glycopyranosides[12,29] homodimerization in the presence of first generation Grubbs' catalyst, we turned our attention on the development of a new class of bolaform surfactants, proceeding in the homodimerization of our previous α and β peracetylated, anomerically pure alkylglycosides **4**, **5** and **6** (Scheme 2).

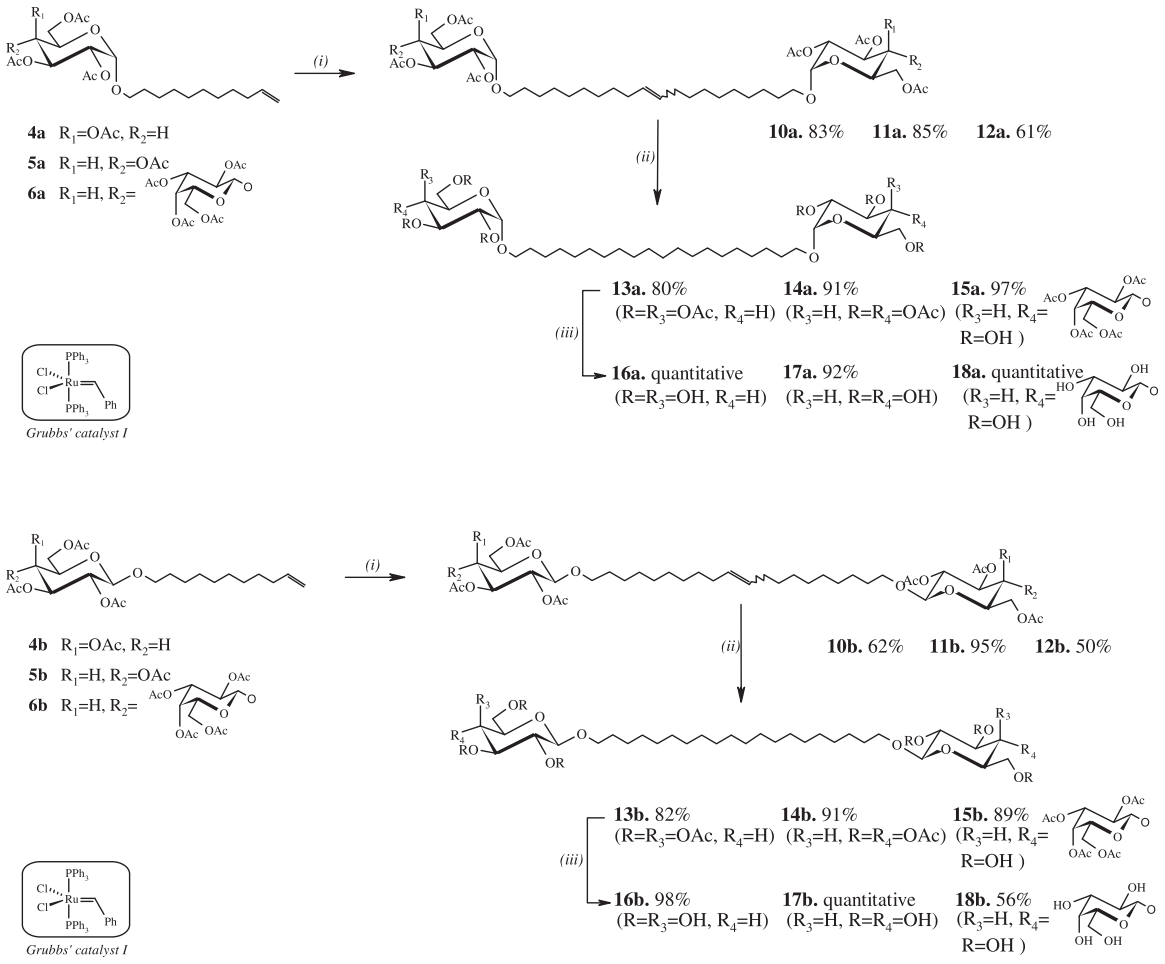
Homodimerization of ethylenic monocatenary molecules was independently achieved for α and β anomers with [Ru]' catalyst proportions close to 10 mol %, under argon flow, to afford homodimers α–α and β–β. Dimeric compounds (**10a**,**b**, **11a**,**b** and **12a**,**b**) were isolated by column chromatography with 50–95% yields as a mixture of *Z* and *E* stereoisomers. ^{1}H NMR spectra showed the disappearance of ethylenic protons at 4.93 and 4.99 ppm, respectively, for $=CH_2$ and HC=, with the appearance of new signals at 5.34 (te, *J* 4.5 Hz) and 5.38 ppm (te, *J* 3.6 Hz) respectively, for *cis* and *trans* internal ethylenic protons (HC=). It was also confirmed by ^{13}C NMR with the removal of signals at 139 and 115 ppm (respectively, HC= and $=CH_2$) whereas internal ethylenic carbon signal appears at 130 ppm. Because these stereoisomers could not be separated by chromatography, an additional step of catalytic

Table 1
Experimental conditions for carbohydrate-based monocatenary surfactant synthesis

	$ZnCl_2$ (eq)	ω-ROH (eq)	M.W. activation	Yields		α/β
1	2.2	2.5	2 min 60 W	64%	(**4a**: 26%–**4b**: 38%)	0.69
2	2.5	2.9	1 min 100 W then 2 min 60 W	85%	(**5a**: 31%–**5b**: 54%)	0.58
3	2.2	5	2 min 90 W	58%	(**6a**: 20%–**6b**: 38%)	0.53

Yields varied from 58 to 85%, with a marked preference to β anomers (α/β ratios ranging from 0.53 to 0.69). It should be noted that in the case of galactosides, the reacetylation of the remaining alcohol was necessary because it hampered the purification of α and β compounds, appearing with the same R_f as the galactosides. For that, DMAP and an excess of acetic anhydride were added to the crude and the mixture subjected to microwave activation (2 min—60 W).

reduction of the internal double bond was considered in order to avoid *E*/*Z* mixtures. Reactions were achieved with rhodium on alumina as catalyst and led to good yields varying from 80 to 97%. Lastly, removal of acetyl groups with sodium methoxide was realized in almost quantitative yields. NMR and MS analyses were consistent with the structures of expected bolaforms **16a**,**b**, **17a**,**b** and **18a**,**b**.

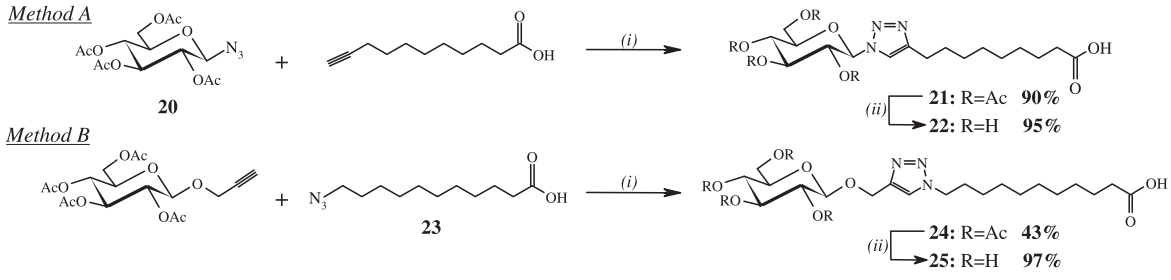


Scheme 2. Typical procedure for α and β bolaform surfactants synthesis. Reagents and conditions: (i) Grubbs' catalyst I (7.8–17.6 mol %), CH_2Cl_2, 40 °C; (ii) Rh/Al_2O_3, H_2; (iii) MeONa/MeOH.

2.2. Synthesis of monocatenary and bolaform surfactants by click-chemistry (22, 25 and 28)

In the field of organic chemistry, the recent discovery of copper (I) as catalyst in the Huisgen [3+2] cycloaddition seems to be interesting for the development of an efficient method for designing monocatenary and bolaform carbohydrate-based surfactants. The growing interest for this system comes from the near-perfect reliability of copper (I)-catalyzed 1,3-dipolar cycloaddition between regioisomer. Therefore such chemistry seemed to be convenient for binding building blocks readily and regioselectively.[32]

We describe herein a new series of monocatenary surfactants **22** and **25** by analogy to the previous *O*-glycosylated compounds. These compounds could also have bolaform behaviour in their sodium carboxylate form. To achieve our goal, we decided to connect a peracetylated glucose core (bearing azide or alkyne function on anomeric position) with an 11 carbon aliphatic acid (Scheme 3).



Scheme 3. 'Click-chemistry' strategy leading to new monocatenary sugar-based surfactants **22** and **25**. (i) $Cu(OAc)_2$, sodium ascorbate, $^tBuOH/H_2O$ 1:1; (ii) NH_3/MeOH.

a terminal alkyne and an organic azide. Generally high yielded, the 'click-chemistry' ligation or CuAAC (for Cu-catalyzed azide–alkyne cycloaddition) initially reported by Sharpless et al.[30] and Meldal et al.[31] gives exclusively the 1,4-disubstituted 1,2,3-triazole

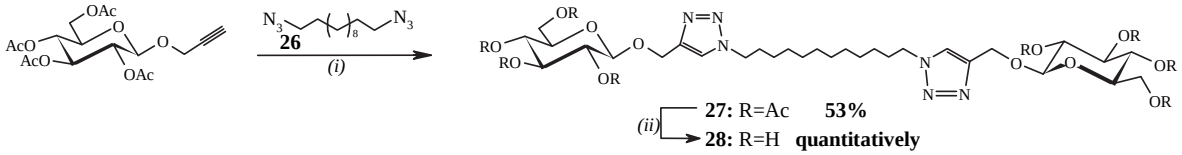
Before carrying out grafting by 'click-chemistry', we must prepare each azido intermediate (acetylenic ones being commercially available). Thus, starting from glucose pentaacetate, bromo derivative **19** was prepared by standard bromation with bromohydric

acid in acetic acid at 4 °C for 23 h. After purification, α-bromoglucose was isolated with 82% yield. Then, β-azidoglucose **20** was obtained with 74% yield after reacting with 2 equiv of NaN_3 in DMAc. In the same way, 11-azidoundecanoic acid **23** was isolated quasi-quantitatively by azidation of commercially available 11-bromoundecanoic acid by an excess of sodium azide.

Finally building blocks were attached together, using 'click-chemistry'. First cycloaddition (*Method A*) gave protected compound **21** in 90% yield starting from azido sugar **20** and 1.2 equiv of commercial undecynoic acid, in the presence of 1 equiv of copper (II) acetate and 2 equiv of sodium ascorbate for 23 h. Then, deprotection was carried out with excess ammonia (7 N) in methanol and gave final click-surfactant **22** in 95% yield. For each molecule (R=Ac or H), ^{1}H NMR spectra displayed a singlet at 7.51 ppm, corresponding to the triazole proton, along with glucidic protons from 5.85 to 4.00 ppm. The expected shielding of the saccharidic moiety was also observed for deprotected compound **22**.

Alternatively, *Method B* proposes the anchorage of 11-azidoundecanoic acid **23** (1.2 equiv) and 2,3,4,6-tetra-*O*-acetylpropynyl-β-D-glucose, in the presence of 0.5 equiv $Cu(OAc)_2$ and 1 equiv of sodium ascorbate for 26 h. In these conditions, the reaction afforded the protected product **24** in 43% yield. Deacetylation was fulfilled as previously described with NH_3 in methanol and led to compound **25** in almost quantitative yield. NMR spectroscopy also showed the triazole singlet peak at 7.52 ppm along with carbon signals of triazole at 149 and 119 ppm (for C= and =CH), and the presence of two doublets (each integrating for 1H) assigned to H-a and H-b oxymethyl protons, at 4.93 and 4.83 ppm, respectively. As previously, deprotection was confirmed by the chemical shift shielding of the glucosidic moiety.

In the same way, di-triazolated bolaform **28** was elaborated as shown in Scheme 4. According to Rodinov et al.[33] we chose to use a diazido-alkyl chain as starting core. Indeed, polyazidated derivatives give better results compared to their polyacetylenic counterparts. They report that a diazide precursor leads mainly to the disubstituted compound. However, the use of a dipropargylated precursor as starting material generates the formation of a statistical mixture of mono- and di-triazoled compounds.



Scheme 4. Synthesis of di-triazolated bolaform **28** using double 'click-chemistry'. (i) $Cu(OAc)_2$, sodium ascorbate, ^{t}BuOH/H_2O 1:1; (ii) NH_3/MeOH.

First, 1,12-diazidododecane synthon **26** was quantitatively obtained by azidation of commercial 1,12-dibromododecane with an excess of NaN_3 in refluxing DMAc at 80 °C.

The triazole-linkage was then undertaken in the presence of acetylated propynyl-β-D-glucose (2.4 equiv), 0.5 equiv $Cu(OAc)_2$ and 1 equiv of sodium ascorbate, in *tert*-butanol/water 1:1 for 25 h. Compound **27**, bearing a peracetylated glucose unit at each end of the aliphatic chain, was isolated in 53% yield. Finally, deacetylation step with methanolic ammonia gave desired bolaform **28** quantitatively. The double linkage was confirmed by ^{1}H NMR spectroscopy with the presence of the triazole protons as a singlet at 7.50 ppm integrating for 2H. The same NMR spectrum clearly showed the presence of the two glucidic head groups as figures from 4.24 to 2.97 ppm integrating for 14H, along with oxymethyl protons H-a and H-b at 4.82 and 4.62 ppm, respectively. Deprotection by NH_3 in methanol was shown by the shielding of the carbohydrate pattern and also by IR spectroscopy with the appearance of a large hydroxyl band at 3347 cm^{-1}. Mass spectroscopy confirmed the final structures with an adduct peak $[M+Na]^+$ at 1047 for peracetylated bolaform **27** and 711 for deprotected homologue **28**.

3. Physicochemical properties

The most important property of surfactants deals with their self-organisation capacity in aqueous medium. It is mainly the relative equilibrium between lipophilic chain and hydrophilic head that leads to such properties and therefore their ability to build complex supramolecular structures like micelles, liposomes, lyotropic liquid crystalline phases, or microemulsions.[34]

The aim of this part is to examine physicochemical properties of the above monocatenary and bolaform non-ionic derivatives, in comparison with long-chain alkylglucosides and maltosides described in literature. Three different parameters were considered for the study of this novel series: critical micellar concentration (CMC), limit surface tension γ_{CMC}, and occupied area per surfactant molecule A_{min} at the air–water interface. To determine the structure–property relationships, the alkyl chain type was kept constant and the polar head group was changed systematically. This allowed us to investigate the influence of the head group size and chemical nature on the aggregation properties of these new compounds.

3.1. Tensioactive properties of monocatenary compounds (7, 8 and 9)

Micellization was studied by surface tension measurements. These measurements were carried out by the Wilhelmy method, and performed at 45 °C for an increased solubility. CMC and limit surface tension γ_{CMC} data were determined as usual at the break point of surface tension curves γ versus log C (see graph below). The interfacial area A_{min} was calculated as inversely proportional to the surface excess (Γ) given by the Gibbs isotherm:

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln C} = \frac{1}{N_a \cdot A_{min}}$$

where γ is the surface tension (mN m^{-1}), R the gas constant, T the absolute temperature (K), C the surfactant concentration, A_{min} the area occupied by a surfactant molecule at the air–water interface, and N_a the Avogadro's number.

The CMC and limit surface tension results obtained for each glycoside are listed in Figure 2.

3.1.1. Effect of the sugar unit and its anomeric centre. For β anomers, the behaviour of the glucosidic and galactosidic surfactants (with the OH-(4) residue oriented in equatorial or axial position, respectively) is quite similar (1.70 and 2.05 mM). It has to be noted that water solubility of **7b** is slightly lower, but however not significantly different. In contrast, the addition of a second glycosyl unit (compound **9b**) increases CMC, up to 2.85 mM. The larger size of the polar head justifies this value, consequence of a higher hydrophilicity.

On the other hand, the solution behaviour of α anomers is more complex, and particularly in the case of **8a** for which a cloud

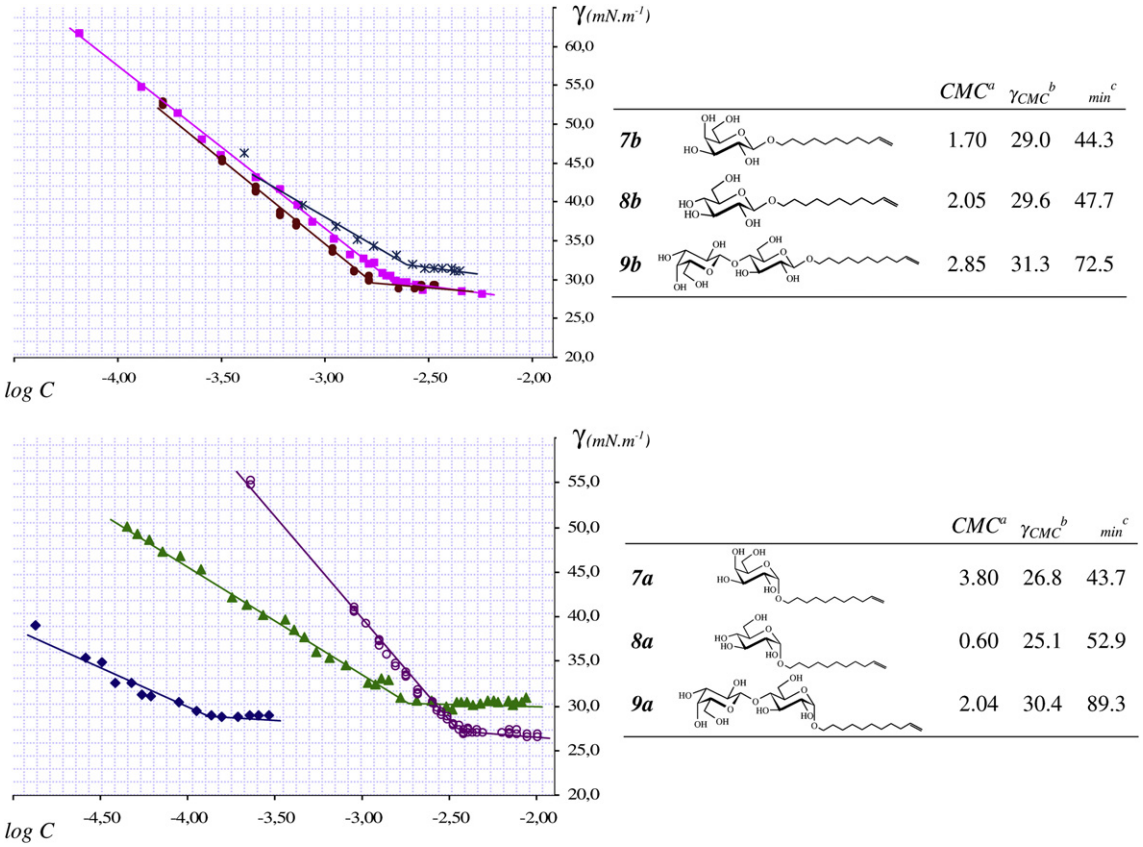


Figure 2. Surface tension curves of undecenyl glycosides (γ vs log *C*), performed at 45 °C. First graph represents β glycosides **7b** ●, **8b** ■, and **9b** ✳ and second graph shows α compounds **7a** ○, **8a** ◆, **9a** ▲. [a]CMC measurements in mM were done with a Dognon Abribat tensiometer (Prolabo). [b]Limit values of surface tension γ_{limit} determined at the CMC (mN m^{-1}). [c]Area occupied by a molecule of surfactant at the interface water/air (Å^2).

appears as soon as CMC is reached. That corresponds to the formation of a coacervat[35] for which one can observe the coexistence of two liquid phases: a lower phase, rich in surfactant and an upper phase, mainly constituted of water and a small amount of surfactant. Surprisingly, for these anomers, increase of the polar head group (**9a**) does not increase significantly the CMC value.

CMC of monocatenary surfactants **7–9** was shown not to depend on the hydrophilic part, since no drastic changes of CMC were observed for glucose, galactose or lactose head group. As the CMC appears to depend essentially on the nature of the hydrophobic part of the surfactant (chemical nature and length of the tail), it is interesting to compare these compounds to their saturated analogues.

3.1.2. Effect of insaturation. Since we have shown previously that CMC depends essentially on the hydrophobic tail, it is reasonable to expect that these new compounds afford a CMC close to that of saturated alkylglycosides already described in the literature. Commonly, CMC of non-ionic surfactants decreases by a factor 10 with the increase of the chain length by two CH_2.[36] In our case, we note that the introduction of a $CH_2{=}CH_2$ unit increases CMC. Thus, the C_{11} ethylenic compound has nearly the same CMC value as the saturated C_{10} compound. Introduction of an insaturation at the terminus of the C_{11} carbon chain increases the CMC by a factor 4 compared with the saturated counterpart, in the case of β glycosides (Table 2). This fact could be explained by the more hydrophilic behaviour of the ethylenic bond compared to the saturated one, and also by the rigid geometry of the terminal double bond that can disturb the tail organisation inside the micellae.

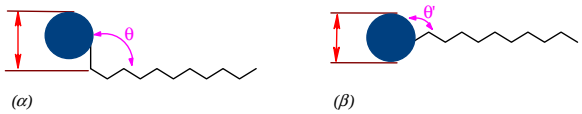
3.1.3. Influence of the sugar on the interfacial area. Molecular areas A_{min} at the air–water interface are small for all monosaccharidic compounds (less than 50 Å^2), which is a general trend for carbohydrate surfactants.[39] This can be attributed to intermolecular hydrogen bonding of surfactant head groups at the interface.[40] It is known that the area occupied by a molecule of surfactant at the liquid interface is directly related to the size of the polar head. Thus,

Table 2
Behaviour of unsaturated β-glucoside **8b** and β-lactoside **9b**, compared to the literature (López et al.[37] and Boyd et al.[38])

	CMC
β-C_8G_1	18.0
β-$C_{10}G_1$	1.80
β-$C_{11}G_1$	0.58
β-$C_{12}G_1$	0.18
8b	2.05
β-C_8G_2	19.1
β-$C_{10}G_2$	1.99
β-$C_{12}G_2$	0.13
9b	2.04

it has to be noticed that lactoside area is twice larger than that of the corresponding gluco and galactosides (Fig. 2).

One also can notice a different behaviour in relation to the nature of the osidic linkage. B compounds have, broadly speaking, a lower area than α anomers. This observation can be connected to the anomeric angle θ between the polar head and first CH_2 unit of the lipophilic chain, as shown in Scheme 5.



Scheme 5. Scheme illustrating α and β anomeric angles, which can influence the interfacial area A_{min}.

3.2. Tensioactive properties of click-surfactants (22, 25 and 28)

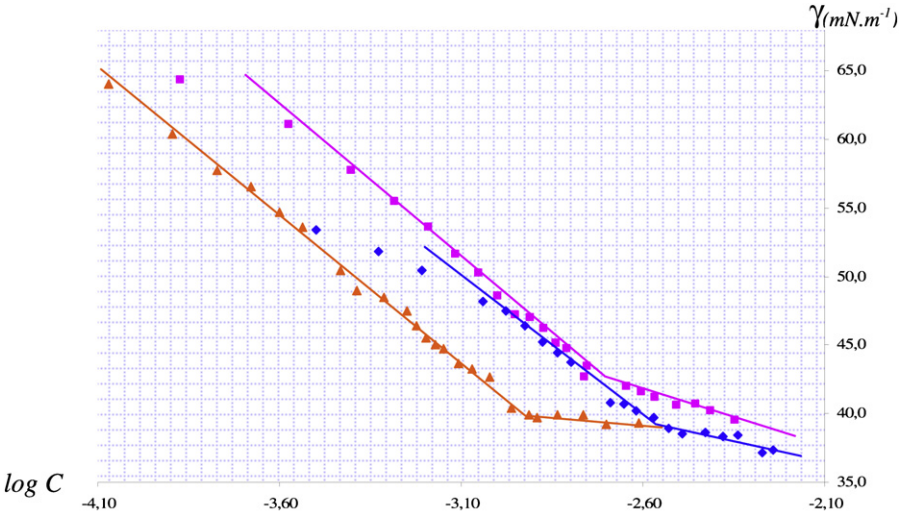
Tensioactive measurements of surfactants obtained via 'click-chemistry' linkage (also performed at 45 °C) are summarized in Figure 3.

In the case of compounds **22** and **25**, we studied the influence of pH on the tensioactive properties. At acidic pH, these surfactants are supposed to present a monocatenary behaviour. On the other hand, at basic pH, we can anticipate that these compounds have a bolaform behaviour, with carboxylate as a second polar group.

As expected, in acidic medium, the two monomers **22** and **25** have nearly the same CMC (2.19 and 1.90 mM), which are very similar to the previously studied ethylenic compounds with 11 carbons (Fig. 2). This means that the carboxylic acid function in acidic medium is only slightly hydrophilic. At basic pH values (10–11), these compounds were found to be very soluble in water and no CMC could be detected because the alkyl chain is too short.

Bolaforms **16**, **17** and **18** (from metathesis homocoupling) were not soluble in water, impairing the study of their tensioactive properties such as CMC. In contrast to homodimerized compounds, the introduction of two triazole moieties in the structure of click-bolaform **28** makes it hydrosoluble.

Bolaform **28** affords a CMC slightly lower than monocatenary surfactants **22** and **25** (1.19 vs 1.90 and 2.19 mM). This observation



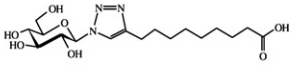
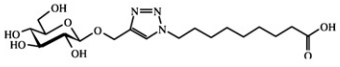
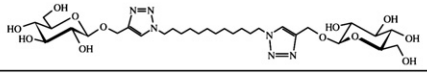
		CMC	γ_{CMC}	min
22		2.19	40.0	42.7
25		1.90	41.1	41.5
28		1.19	40.0	48.5

Figure 3. Surface tension curves γ versus log *C* (performed at 45 °C) of click-surfactants **22** ■, **25** ◆ (monocatenary) and **28** ▲ (bolaform).

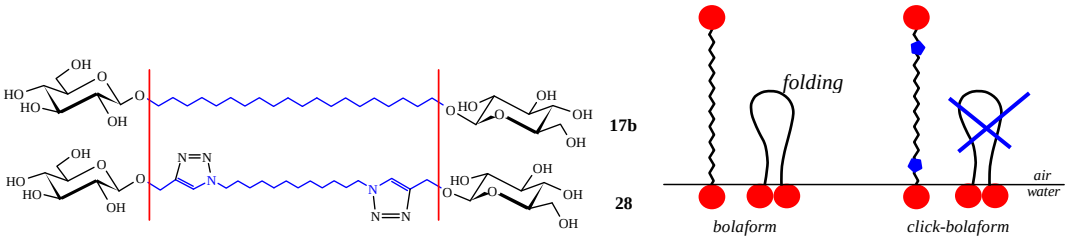


Figure 4. Comparison of the structure of bolaforms **17b** and **28**, obtained by cross-metathesis and click-chemistry, respectively.

means that bolaform has a propensity to micellize, which is related to the presence of two sugar units in the structure. We can also observe that the air–water interfacial area of **28** (48.5 Å^2) is close to those of monocatenary homologues **22** and **25** (42.7 and 41.5 Å^2). The advanced assumption considers the presence of the two triazole heterocycles, rigid and plane, which prevent the folding up of the molecule, unlike a traditional aliphatic chain (Fig. 4). A_{min} is thus directly related to the size of sugar constituting the polar head.

4. Conclusion

This paper presents an original method to complete the synthesis of carbohydrate-based monocatenary and bolaform surfactants. Two main synthetic routes have been studied, involving on the one hand a microwave-assisted glycosylation followed by an homodimerization via olefin cross-metathesis, and on the other hand an emergent way for grafting organic synthons together, the 'click-chemistry'. This second way, avoided some reactions and drastic purification steps.

A study of tensioactive properties showed that these new surfactants possess valuable surface properties compared to classical compounds. However, a more thorough study is needed to characterize more precisely these structures, with the help of electron microscopy or light scattering, and give information on the self-assembly of these surfactants and the shape of their micelles.

5. Experimental

5.1. General methods and equipments

Microwave irradiation was performed in a monomode reactor (Synthewave® 402 from Prolabo) with focused waves. Analytical TLC was performed on Silica Gel 60 F_{254} precoated aluminium sheets (E. Merck), with detection by UV and also by 6 N H_2SO_4 spray followed by heating at 200 °C. Flash chromatography was performed with 15–40 μm MCL-CHROM Silica Gel columns (Merck). ^{1}H and ^{13}C NMR spectra of compounds in $CDCl_3$, CD_3OD or DMSO-d_6 were recorded using a DPX-400 Brüker spectrometer in with tetramethylsilane as internal standard. Optical rotation was measured with a Jasco (DIP-370 Digital) polarimeter in a 1 dm quartz cell at 22 °C. CMC measurements, expressed in mM, were measured with a Dognon Abribat Prolabo tensiometer, with a Wilhelmy platinum plate (ℓ: 1.955 cm *e* 0.01 cm). Limit values of surface tension (γ_{limit}) were determined at the CMC (mN m^{-1}), and area occupied by a molecule of surfactant at the air–water interface (Å^2), were calculated for concentrations just below the CMC.

5.2. General procedure for microwave-induced glycosylation under (4–6)

$ZnCl_2$ and corresponding commercially available peracetylated sugar (**1**–**3**) were crushed together and introduced in a microwave reactor under argon atmosphere. ω-Undecenol was then added and the medium was activated by microwave irradiation. After completion of the reaction, monitored by TLC, the resulting mixture was diluted with EtOAc and filtered over Celite. The organic solution was successively washed with $NaHCO_3$ and water, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and solvent removed. The residue was purified by chromatography over silica gel (7:3 petroleum ether/EtOAc) to give alkylglycoside compound as yellow oil.

*5.2.1. (2′,3′,4′,6′-tetra-O-acetyl)-1-undec-10-enyl-α-D-galactopyranoside (**4a**) and (2′,3′,4′,6′-tetra-O-acetyl)-1-undec-10-enyl-β-D-galactopyranoside (**4b**).* General procedure for glycosylation was used starting from **1** (2 g, 5.1 mmol), 2.2 equiv of $ZnCl_2$ and 2.5 equiv of ω-undecenol. The mixture was then irradiated for 2 min at 60 W. Work-up and isolation by column chromatography (petroleum ether/EtOAc 85:15→7:3) afforded **4a** (664 mg) and **4b** (956 mg) as yellow oils (64%). Compound **4a**: $[\alpha]_D^{20}$ +64.3 (*c* 1.1, $CHCl_3$); R_f 0.32 (7:3 EP/EtOAc); IR (KBr): ν 3018 (=C–H), 2920 (CH_2 ν_{asym}), 2849 (CH_2 ν_{sym}), 1748 (C=O), 1644 (C=C); ^{1}H NMR ($CDCl_3$): δ 5.81 (ddt, 1H, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.3 Hz, $J_{10,11trans}$ 17.0 Hz, H-10), 5.45 (de, 1H, $J_{4',3'}$ 3.3 Hz, H-4′ *gal*), 5.35 (dd, 1H, $J_{3',4'}$ 3.3 Hz, $J_{3',2'}$ 10.1 Hz, H-3′ *gal*), 5.11 (dd, 1H, $J_{2',1'}$ 3.6 Hz, $J_{2',3'}$ 11.0 Hz, H-2′ *gal*), 5.10 (d, 1H, $J_{1',2'}$ 3.6 Hz, H-1′α *gal*), 5.03 (dq, 1H, $J_{11trans,11cis}$ 1.8 Hz, $J_{11trans,10}$ 17.3 Hz, H-11 *trans*), 4.99 (dq, 1H, $J_{11cis,11trans}$ 1.1 Hz, $J_{11cis,10}$ 10.6 Hz, H-11 *cis*), 4.22 (m, 1H, H-5′ *gal*), 4.11 (dd, 1H, $J_{6'a,5'}$ 7.0 Hz, $J_{6'a,6'b}$ 13.4 Hz, H-6′a *gal*), 4.09 (dd, 1H, $J_{6'b,5'}$ 1.8 Hz, $J_{6'b,6'a}$ 13.6 Hz, H-6′b *gal*), 3.70 (dt, 1H, $J_{1a,2}$ 6.3 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.44 (dt, 1H, $J_{1b,2}$ 6.5 Hz, $J_{1b,1a}$ 9.8 Hz, H-1b), 2.14, 2.07, 2.05, 1.99 (s, 12H, acetyl), 1.70 (quint, 2H, $J_{2,1}$ 6.9 Hz, H-2), 1.56 (m, 2H, H-9), 1.27 (m, 12H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *galactose*: 96.2 (C-1′), 68.3 (C-2′), 68.2 (C-4′), 67.7 (C-3′), 66.2 (C-5′), 61.8 (C-6′), *alkyl chain*: 137.7 (CH=), 115.2 (=CH_2), 67.9 (C-1), 32.6 (C-9), 29.7, 29.6, 29.5, 29.3, 29.2 (C-3 to C-8), 26.1 (C-2), *protecting groups*: 170.4, 170.2, 170.0 (CO), 20.8, 20.7, 20.6 (CH_3); MS (CI): *m*/*z* 501 [M+H]$^+$. Compound **4b**: $[\alpha]_D^{20}$ −3.9 (*c* 1.0, $CHCl_3$); R_f 0.23 (7:3 EP/EtOAc); IR (KBr): ν 3018 (=C–H), 2920 (ν_{asym} CH_2), 2849 (ν_{sym} CH_2), 1753 (C=O), 1645 (C=C); ^{1}H NMR ($CDCl_3$): δ 5.81 (ddt, 1H,, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.3 Hz, $J_{10,11trans}$ 17.0 Hz, H-10), 5.39 (de, 1H, $J_{4',3'}$ 3.1 Hz, H-4′ *gal*), 5.20 (dd, 1H, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 10.4 Hz, H-2′ *gal*), 5.01 (dd, 1H, $J_{3',4'}$ 3.4 Hz, $J_{3',2'}$ 10.5 Hz, H-3′ *gal*), 4.97 (m, 2H, H-11), 4.45 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′β *gal*), 4.19 (dd, 1H, $J_{6'a,6'b}$ 6.5 Hz, $J_{6'a,5'}$ 11.2 Hz, H-6′a *gal*), 4.12 (dd, 1H, $J_{6'b,5'}$ 6.9 Hz, $J_{6'b,6'a}$ 11.2 Hz, H-6′b *gal*), 3.90 (dt, 1H, $J_{1a,2}$ 6.0 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.89 (m, 1H, H-5′ *gal*), 3.47 (dt, 1H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b), 2.17, 2.15, 2.06, 2.05 (s, 12H, acetyl), 1.59 (m, 4H, H-2 and H-9), 1.28 (m, 12H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *galactose*: 101.4 (C-1′), 71.0 (C-3′), 70.6 (C-5′), 69.0 (C-2′), 67.1 (C-4′), 61.3 (C-6′), *alkyl chain*: 69.4 (C-1), 137.8 (CH=), 115.1 (=CH_2), 32.6 (C-9), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2 (C-3 to C-8), 25.8 (C-2), *protecting groups*: 170.4, 170.3, 170.2, 169.4 (CO), 20.8, 20.7, 20.6 (CH_3); MS (CI): *m*/*z* 501 [M+H]$^+$.

*5.2.2. (2′,3′,4′,6′-tetra-O-acetyl)-1-undec-10-enyl-α-D-glucopyranoside (**5a**) and (2′,3′,4′,6′-tetra-O-acetyl)-1-undec-10-enyl-β-D-glucopyranoside (**5b**).* General procedure for glycosylation was used starting from **2** (1.1 g, 2.82 mmol), 2.5 equiv of $ZnCl_2$ and 2.9 equiv of ω-undecenol. The mixture was then irradiated successively for 1 min at 100 W, then 2 min 60 W. Work-up and isolation by column chromatography (petroleum ether/EtOAc 8:2→7:3) afforded **5a** (440 mg) and **5b** (760 mg) as yellow oils (85%). Compound **5a**: $[\alpha]_D^{20}$ +101.7 (*c* 1.7, $CHCl_3$); R_f 0.44 (7:3 EP/EtOAc); IR (KBr): ν 3074 (=C–H), 2928 (CH_2 ν_{asym}), 2856 (CH_2 ν_{sym}), 1757 (C=O), 1640 (C=C); ^{1}H NMR ($CDCl_3$): δ 5.81 (ddt, 1H, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.3 Hz, $J_{10,11trans}$ 17.0 Hz, H-10), 5.48 (t, 1H, $J_{3',2'}$ 9.8 Hz, H-3′ *glc*), 5.06 (d, 1H, $J_{1',2'}$ 3.8 Hz, H-1′ *glc*), 5.05 (te, 1H, $J_{4'-3'}$ 9.8 Hz, H-4′ *glc*), 4.99 (dq, 1H, $J_{11trans,11cis}$ 1.9 Hz, $J_{11trans,10}$ 17.1 Hz, H-11 *trans*), 4.93 (dq, 1H, $J_{11cis,11trans}$ 1.0 Hz, $J_{11cis,10}$ 10.2 Hz, H-11 *cis*), 4.85 (dd, 1H, $J_{2',1'}$ 3.7 Hz, $J_{2',3'}$ 10.2 Hz, H-2′ *glc*), 4.26 (dd, 1H, $J_{6'a,5'}$ 4.5 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6′a *glc*), 4.09 (dd, 1H, $J_{6'b,5'}$ 2.3 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′b *glc*), 4.01 (ddd, 1H, $J_{5',6'b}$ 2.4 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',4'}$ 10.2 Hz, H-5′ *glc*), 3.67 (dt, 1H, $J_{1a,2}$ 6.6 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.42 (dt, 1H, $J_{1b,2}$ 6.6 Hz, $J_{1b,1a}$ 9.8 Hz, H-1b), 2.09, 2.06, 2.03, 2.01 (s, 12H, acetyl), 1.65–1.56 (m, 4H, H-2 and H-9), 1.39–1.24 (m, 12H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *glucose*: 95.6 (C-1′), 71.0 (C-2′), 70.3 (C-3′), 68.7 (C-4′), 67.1 (C-5′), 62.0 (C-6′), *alkyl chain*: 139.2 (CH=), 114.1 (=CH_2), 68.8 (C-1), 33.8 (C-9), 29.5, 29.4, 29.32, 29.26, 29.1, 28.9 (C-3 to C-8), 26.0 (C-2), *protecting groups*: 170.7, 170.2, 170.1, 169.6 (CO), 20.73, 20.69, 20.65 (CH_3); MS (CI): *m*/*z* 501 [M+H]$^+$. Compound **5b**: $[\alpha]_D^{20}$ −14.8 (*c* 1.7, $CHCl_3$); R_f 0.36 (7:3 EP/EtOAc); IR (KBr): ν 3076 (=C–H), 2923 (ν_{asym}

CH_2), 2854 (ν_{sym} CH_2), 1757 (C=O), 1641 (C=C); ^{1}H NMR ($CDCl_3$): δ 5.81 (ddt, 1H, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.3 Hz, $J_{10,11trans}$ 17.0 Hz, H-10), 5.20 (t, 1H, $J_{3',2'}$ 9.5 Hz, H-3′ *glc*), 5.08 (t, 1H, $J_{4',3'}$ 9.6 Hz, H-4′ *glc*), 4.98 (dd, 1H, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 9.6 Hz, H-2′ *glc*), 4.98 (dq, 1H, $J_{11trans,11cis}$ 1.6 Hz, $J_{11trans,10}$ 17.2 Hz, H-11 *trans*), 4.93 (dq, 1H, $J_{11cis,11trans}$ 1.0 Hz, $J_{11cis,10}$ 9.1 Hz, H-11 *cis*), 4.49 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′ *glc*), 4.26 (dd, 1H, $J_{6'a,5'}$ 4.7 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6′a *glc*), 4.13 (dd, 1H, $J_{6'b,5'}$ 2.4 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′b *glc*), 3.86 (dt, 1H, $J_{1a,2}$ 6.3 Hz, $J_{1a,1b}$ 9.6 Hz, H-1a), 3.69 (ddd, 1H, $J_{5',6'b}$ 2.5 Hz, $J_{5',6'a}$ 4.7 Hz, $J_{5',4'}$ 9.9 Hz, H-5′ *glc*), 3.46 (dt, 1H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b), 2.08, 2.04, 2.02, 2.00 (s, 12H, acetyl), 1.59–1.53 (m, 4H, H-2 and H-9), 1.38–1.27 (m, 12H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *glucose*: 100.8 (C-1′), 72.9 (C-3′), 71.8 (C-5′), 71.4 (C-2′), 68.5 (C-4′), 62.0 (C-6′), *alkyl chain*: 139.2 (CH=), 114.1 (=CH_2), 70.2 (C-1), 33.8 (C-9), 29.5, 29.43, 29.39, 29.3, 29.1, 28.9 (C-3 to C-8), 25.8 (C-2), *protecting groups*: 170.7, 170.3, 169.4, 169.3 (CO), 20.75, 20.65, 20.61 (CH_3); MS (CI): *m*/*z* 501 $[M+H]^+$.

*5.2.3. (2′,3′,6′,2″,3″,4″,6″-hepta-O-acetyl)-1-undec-10-enyl-α-D-lactopyranoside (**6a**) and (2′,3′,6′,2″,3″,4″,6″-hepta-O-acetyl)-1-undec-10-enyl-β-D-lactopyranoside (**6b**).* General procedure for glycosylation was used starting from **3** (503 mg, 0.74 mmol), 2.2 equiv of $ZnCl_2$ and 5 equiv of ω-undecenol. The mixture was then irradiated for 2 min at 90 W. Work-up and isolation by column chromatography (petroleum ether/EtOAc 8:2→7:3) afforded **6a** (117 mg) and **6b** (221 mg) as yellow oils (58%). Compound **6a**: $[\alpha]_D^{20}$ +30.4 (*c* 0.5, $CHCl_3$); R_f 0.52 (7:3 EP/EtOAc); IR (KBr): ν 3075 (=C–H), 2926 (CH_2 ν_{asym}), 2855 (CH_2 ν_{sym}), 1748 (C=O), 1637 (C=C); ^{1}H NMR ($CDCl_3$): δ 5.81 (ddt, 1H, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.3 Hz, $J_{10,11trans}$ 16.9 Hz, H-10), 5.47 (t, 1H, $J_{3',2'}$ 9.6 Hz, H-3′ *glc*), 5.35 (de, 1H, $J_{4'',3''}$ 2.8 Hz, H-4″ *gal*), 5.12 (dd, 1H, $J_{2'',1''}$ 7.8 Hz, $J_{2'',3''}$ 10.4 Hz, H-2″ *gal*), 4.99 (dq, 1H, $J_{11trans,11cis}$ 1.6 Hz, $J_{11trans,10}$ 16.3 Hz, H-11 *trans*), 4.97 (d, 1H, $J_{1',2'}$ 3.4 Hz, H-1′ *glc*), 4.95 (dd, 1H, $J_{3'',4''}$ 3.3 Hz, $J_{3'',2''}$ 10.4 Hz, H-3″ *gal*), 4.92 (dq, 1H, $J_{11cis,11trans}$ 0.9 Hz, $J_{11cis,10}$ 10.8 Hz, H-11 *cis*), 4.77 (dd, 1H, $J_{2',1'}$ 3.8 Hz, $J_{2',3'}$ 10.2 Hz, H-2′ *glc*), 4.48 (d, 1H, $J_{1''-2''}$ 7.9 Hz, H-1″ *gal*), 4.44 (dd, 1H, $J_{6'a,5'}$ 2.0 Hz, $J_{6'a,6'b}$ 12.1 Hz, H-6′a *glc*), 4.15 (dd, 1H, $J_{6''a,5''}$ 6.4 Hz, $J_{6''a,6''b}$ 11.2 Hz, H-6″a *gal*), 4.08 (dd, 1H, $J_{6''b,5''}$ 7.5 Hz, $J_{6''b,6''a}$ 11.1 Hz, H-6″b *gal*), 4.06 (dd, 1H, $J_{6'b,5'}$ 3.6 Hz, $J_{6'b,6'a}$ 11.0 Hz, H-6′b *glc*), 3.91 (ddd, 1H, $J_{5',6'b}$ 1.5 Hz, $J_{5',6'a}$ 4.3 Hz, $J_{5',4'}$ 9.9 Hz, H-5′ *glc*), 3.87 (te, 1H, $J_{5''-6''}$ 6.8 Hz, H-5″ *gal*), 3.72 (t, 1H, $J_{4'-3'}$ 9.7 Hz, H-4′ *glc*), 3.65 (dt, 1H, $J_{1a,2}$ 6.6 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.39 (dt, 1H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.8 Hz, H-1b), 2.2–1.9 (s, 21H, acetyl), 1.61 (m, 4H, H-2 and H-9), 1.28 (m, 12H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *glucose*: 95.6 (C-1′), 76.7 (C-4′), 71.2 (C-2′), 70.1 (C-3′), 68.0 (C-5′), 62.0 (C-6′), *galactose*: 101.2 (C-1″), 71.1 (C-3″), 70.6 (C-5″), 69.2 (C-2″), 66.6 (C-4″), 60.8 (C-6″), *alkyl chain*: 139.2 (HC=), 114.1 (=CH_2), 68.7 (C-1), 33.8 (C-9), 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9 (C-3 to C-8), 26.0 (C-2), *protecting groups*: 170.44, 170.39, 170.3, 170.2, 170.1, 169.5, 169.1 (CO), 20.93, 20.87, 20.7, 20.6, 20.5 (CH_3); MS (CI): *m*/*z* 789.3 $[M+H]^+$. Compound **6b**: $[\alpha]_D^{20}$ −4.15 (*c* 0.56, $CHCl_3$); R_f 0.58 (7:3 EP/EtOAc); IR (KBr): ν 3081 (=C–H), 2929 (CH_2 ν_{asym}), 2855 (CH_2 ν_{sym}), 1751 (C=O), 1648 (C=C); ^{1}H NMR ($CDCl_3$): δ 5.80 (ddt, 1H, $J_{10,9}$ 6.6 Hz, $J_{10,11cis}$ 10.2 Hz, $J_{10,11trans}$ 16.9 Hz, H-10), 5.34 (de, 1H, $J_{4'',3''}$ 2.8 Hz, H-4″ *gal*), 5.19 (t, 1H, $J_{3',2'}$ 9.3 Hz, H-3′ *glc*), 5.11 (dd, 1H, $J_{2'',1''}$ 7.9 Hz, $J_{2'',3''}$ 10.4 Hz, H-2″ *gal*), 4.99 (dq, 1H, $J_{11trans,11cis}$ 1.7 Hz, $J_{11trans,10}$ 16.7 Hz, H-11 *trans*), 4.95 (dd, 1H, $J_{3'',4''}$ 3.0 Hz, $J_{3'',2''}$ 10.4 Hz, H-3″ *gal*), 4.93 (dq, 1H, $J_{11cis,11trans}$ 0.9 Hz, $J_{11cis,10}$ 10.8 Hz, H-11 *cis*), 4.88 (dd, 1H, $J_{2',1'}$ 8.8 Hz, $J_{2',3'}$ 9.5 Hz, H-2′ *glc*), 4.48 (d, 1H, $J_{1''-2''}$ 7.9 Hz, H-1″ *gal*), 4.48 (dd, 1H, $J_{6'a,5'}$ 1.7 Hz, $J_{6'a,6'b}$ 11.5 Hz, H-6′a *glc*), 4.45 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′ *glc*), 4.13 (dd, 1H, $J_{6''a,5''}$ 6.4 Hz, $J_{6''a,6''b}$ 11.2 Hz, H-6″a *gal*), 4.09 (dd, 1H, $J_{6'b,5'}$ 4.4 Hz, $J_{6'b,6'a}$ 11.8 Hz, H-6′b *glc*), 4.08 (m, 1H, H-6″b *gal*), 3.87 (te, 1H, $J_{5''-6''}$ 6.8 Hz, H-5″ *gal*), 3.82 (dt, 1H, $J_{1a,2}$ 6.4 Hz, $J_{1a,1b}$ 9.4 Hz, H-1a), 3.79 (t, 1H, $J_{4'-3'}$ 9.2 Hz, H-4′ *glc*), 3.59 (ddd, 1H, $J_{5',6'b}$ 1.8 Hz, $J_{5',6'a}$ 4.8 Hz, $J_{5',4'}$ 9.7 Hz, H-5′ *glc*), 3.44 (dt, 1H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b), 2.2–1.9 (s, 21H, acetyl), 1.60 (m, 4H, H-2 and H-9), 1.26 (m, 12H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *glucose*: 100.6 (C-1′), 76.7 (C-4′), 72.9 (C-3′), 72.6 (C-5′), 71.8 (C-2′), 62.1 (C-6′), *galactose*: 101.1 (C-1″), 71.0 (C-3″), 70.7 (C-5″), 69.1 (C-2″), 66.6 (C-4″), 60.8 (C-6″), *alkyl chain*: 139.2 (HC=), 114.1 (=CH_2), 70.2 (C-1), 33.8 (C-9), 29.5, 29.43, 29.41, 29.3, 29.1, 28.9 (C-3 to C-8), 25.8 (C-2), *protecting groups*: 170.4, 170.36, 170.2, 170.1, 169.8, 169.6, 169.1 (CO), 20.9, 20.8, 20.7, 20.6, 20.5 (CH_3); MS (CI): *m*/*z* 789.3 $[M+H]^+$.

5.3. General procedure for deacetylation under Zemplén conditions (7–9)

To a soln of peracetylated compound (**4–7**) in methanol, 0.5 M sodium methylate was added. The mixture was stirred at room temperature. After neutralization with Amberlite IRN-77H$^+$ resin, filtration and evaporation, deprotected compound was obtained as a white foam.

*5.3.1. Undec-10-enyl-α-D-galactopyranoside (**7a**).* Deacetylation of compound **4a** (262 mg, 0.52 mmol) as above with 4 equiv MeONa during 4 h afforded **7a** (171 mg, 98%) as a white foam; $[\alpha]_D^{20}$ +101.0 (*c* 1.1, MeOH); R_f 0.48 (1:1 $CHCl_3$/EtOH); IR (KBr): ν 3382 (OH), 3062 (=C–H), 2925 (ν_{asym} CH_2), 2854 (ν_{sym} CH_2), 1641 (C=C); ^{1}H NMR (CD_3OD): δ 5.80 (ddt, 1H, $J_{10,9}$ 6.8 Hz, $J_{10,11cis}$ 10.2 Hz, $J_{10,11trans}$ 17.1 Hz, H-10), 4.97 (dq, 1H, $J_{11trans,11cis}$ 1.8 Hz, $J_{11trans,10}$ 17.1 Hz, H-11 *trans*), 4.90 (dq, 1H, $J_{11cis,11trans}$ 1.0 Hz, $J_{11cis,10}$ 10.3 Hz, H-11 *cis*), 4.79 (d, 1H, $J_{1',2'}$ 3.2 Hz, H-1′α *gal*), 3.88 (de, 1H, $J_{3',4'}$ 1.8 Hz, H-3′ *gal*), 3.80 (dd, 1H, $J_{5',4'}$, 5.6 Hz, $J_{5',6'}$, 6.4 Hz, H-5′ *gal*), 3.75 (dd, 1H, $J_{6'a,5'}$ 3.3 Hz, $J_{6'a,6'b}$ 10.1 Hz, H-6′a *gal*), 3.74 (dd, 1H, $J_{2',1'}$ 3.1 Hz, $J_{2',3'}$ 4.3 Hz, H-2′ *gal*), 3.72 (dd, 1H, $J_{6'b,5'}$ 3.8 Hz, $J_{6'b,6'a}$ 6.1 Hz, H-6′b *gal*), 3.70 (dd, 1H, $J_{4',3'}$ 2.5 Hz, $J_{4',5'}$ 5.2 Hz, H-4′ *gal*), 3.69 (m, 1H, H-1a), 3.43 (dt, 1H, $J_{1b,2}$ 6.5 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b), 2.04 (quint, 2H, *J* 7.0 Hz, H-9), 1.63 (m, 2H, H-2), 1.31 (m, 12H, H-3 to H-8); ^{13}C NMR (CD_3OD): *galactose*: 100.5 (C-1′), 72.5 (C-5′), 71.7 (C-3′), 71.2 (C-2′), 70.4 (C-4′), 62.9 (C-6′), *alkyl chain*: 140.3 (CH=), 114.8 (=CH_2), 69.4 (C-1), 35.0 (C-9), 30.8, 30.75, 30.72, 30.4, 30.3 (C-3 to C-8), 27.5 (C-2); MS (CI): *m*/*z* 333 $[M+H]^+$.

*5.3.2. Undec-10-enyl-β-D-galactopyranoside (**7b**).* Deacetylation of compound **4b** (712 mg, 1.4 mmol) as above with 4 equiv MeONa during 2 h afforded **7b** (442 mg, 95%) as a white foam; $[\alpha]_D^{20}$ −16.6 (*c* 0.7, MeOH); R_f 0.46 (1:1 $CHCl_3$/EtOH); IR (KBr): ν 3565 (OH), 3062 (=C–H), 2925 (ν_{asym} CH_2), 2848 (ν_{sym} CH_2), 1652 (C=C); ^{1}H NMR (CD_3OD): δ 5.80 (ddt, 1H, $J_{10,9}$ 6.8 Hz, $J_{10,11cis}$ 10.2 Hz, $J_{10,11trans}$ 17.1 Hz, H-10), 4.97 (dq, 1H, $J_{11trans,11cis}$ 1.2 Hz, $J_{11trans,10}$ 17.1 Hz, H-11 *trans*), 4.90 (dq, 1H, $J_{11cis,11trans}$ 0.6 Hz, $J_{11cis,10}$ 10.3 Hz, H-11 *cis*), 4.19 (d, 1H, $J_{1',2'}$ 7.3 Hz, H-1′β *gal*), 3.88 (dt, 1H, $J_{1a,2}$ 7.1 Hz, $J_{1a,1b}$ 9.2 Hz, H-1a), 3.82 (dd, 1H, $J_{4',3'}$ 0.7 Hz, $J_{4',5'}$ 3.2 Hz, H-4′ *gal*), 3.75 (dd, 1H, $J_{6'a,5'}$ 6.8 Hz, $J_{6'a,6'b}$ 11.5 Hz, H-6′a *gal*), 3.71 (dd, 1H, $J_{6'b,5'}$ 5.6 Hz, $J_{6'b,6'a}$ 11.4 Hz, H-6′b *gal*), 3.54 (dt, 1H, $J_{1b,2}$ 6.9 Hz, $J_{1b,1a}$ 9.3 Hz, H-1b), 3.50 (dd, 1H, $J_{2',1'}$ 7.3 Hz, $J_{2',3'}$ 9.4 Hz, H-2′ *gal*), 3.45 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{3',2'}$ 9.7 Hz, H-3′ *gal*), 3.43 (m, 1H, H-5′ *gal*), 2.04 (quint, 2H, *J* 6.9 Hz, H-9), 1.62 (quint, 2H, *J* 6.9 Hz, H-2), 1.31 (m, 12H, H-3 to H-8); ^{13}C NMR (CD_3OD): *galactose*: 105.0 (C-1′), 76.6 (C-5′), 75.1 (C-3′), 72.6 (C-2′), 70.9 (C-4′), 62.5 (C-6′), *alkyl chain*: 140.2 (CH=), 114.7 (=CH_2), 70.3 (C-1), 34.9 (C-9), 30.9, 30.7, 30.62, 30.59, 30.2, 30.1 (C-3 to C-8), 27.1 (C-2); MS (CI): *m*/*z* 333 $[M+H]^+$.

*5.3.3. Undec-10-enyl-α-D-glucopyranoside (**8a**).* Deacetylation of compound **5a** (170 mg, 0.34 mmol) as above with 8 equiv MeONa during 3 h afforded **8a** (113 mg, quantitative yield) as a white foam; $[\alpha]_D^{20}$ +95.4 (*c* 1.1, MeOH); R_f 0.68 (7:3 $CHCl_3$/EtOH); IR (KBr): ν 3364 (OH), 3075 (=C–H), 2925 (ν_{asym} CH_2), 2854 (ν_{sym} CH_2), 1640 (C=C); ^{1}H NMR (CD_3OD): δ 5.80 (ddt, 1H, $J_{10,9}$ 6.8 Hz, $J_{10,11cis}$ 10.3 Hz, $J_{10,11trans}$ 17.1 Hz, H-10), 4.98 (dq, 1H, $J_{11trans,11cis}$ 1.7 Hz, $J_{11trans,10}$ 17.1 Hz, H-11 *trans*), 4.91 (dq, 1H, $J_{11cis,11trans}$ 1.0 Hz, $J_{11cis,10}$ 10.2 Hz, H-11 *cis*), 4.76 (d, 1H, $J_{1',2'}$ 3.7 Hz, H-1′α *glc*), 3.79 (dd, 1H, $J_{6'a,5'}$ 2.4 Hz, $J_{6'a,6'b}$ 11.8 Hz, H-6′a *glc*), 3.72 (dt, 1H, $J_{1a,2}$ 7.0 Hz, $J_{1a,1b}$

9.6 Hz, H-1a), 3.67 (dd, 1H, $J_{6'b,5'}$ 5.3 Hz, $J_{6'b,6'a}$ 12.0 Hz, H-6′b *glc*), 3.61 (t, 1H, $J_{3',4'}$ 7.9 Hz, H-3′ *glc*), 3.56 (ddd, 1H, $J_{5',6'a}$ 2.4 Hz, $J_{5',6'b}$ 5.4 Hz $J_{5',4'}$ 9.9 Hz, H-5′ *glc*), 3.44 (dt, 1H, $J_{1b,2}$ 6.4 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b), 3.37 (dd, 1H, $J_{2',1'}$ 3.7 Hz, $J_{2',3'}$ 9.7 Hz, H-2′ *glc*), 3.28 (dd, 1H, $J_{4',3'}$ 9.1 Hz, $J_{4',5'}$ 9.6 Hz, H-4′ *glc*), 2.04 (m, 2H, H-9), 1.61 (m, 2H, H-2), 1.31 (m, 12H, H-3 to H-8); ^{13}C NMR (CD_3OD): *glucose*: 100.1 (C-1′), 75.2 (C-3′), 73.6 (C-5′), 71.9 (C-4′), 68.8 (C-2′), 62.7 (C-6′), *alkyl chain*: 140.2 (CH═), 114.7 (═CH_2), 69.2 (C-1), 34.9 (C-9), 30.7, 30.66, 30.63, 30.3, 30.1 (C-3 to C-8), 27.4 (C-2); MS (CI): *m*/*z* 333 $[M+H]^+$.

*5.3.4. Undec-10-enyl-β-D-glucopyranoside (**8b**).* Deacetylation of compound **5b** (167 mg, 0.33 mmol) as above with 4 equiv MeONa during 2 h afforded **8b** (105 mg, 96%) as a white foam; $[\alpha]_D^{20}$ −18.3 (*c* 1.1, MeOH); R_f 0.67 (7:3 $CHCl_3$/EtOH); IR (KBr): *ν* 3365 (OH), 3076 (═C–H), 2923 (ν_{asym} CH_2), 2854 (ν_{sym} CH_2), 1639 (C═C); ^{1}H NMR (CD_3OD): *δ* 5.80 (ddt, 1H, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.2 Hz, $J_{10,11trans}$ 17.0 Hz, H-10), 4.97 (dq, 1H, $J_{11trans,11cis}$ 1.9 Hz, $J_{11trans,10}$ 17.1 Hz, H-11 *trans*), 4.90 (dq, 1H, $J_{11cis,11trans}$ 1.0 Hz, $J_{11cis,10}$ 10.2 Hz, H-11 *cis*), 4.24 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′β *glc*), 3.89 (dt, 1H, $J_{1a,2}$ 6.9 Hz, $J_{1a,1b}$ 9.5 Hz, H-1a), 3.85 (dd, 1H, $J_{6'a,5'}$ 2.0 Hz, $J_{6'a,6'b}$ 11.7 Hz, H-6′a *glc*), 3.66 (dd, 1H, $J_{6'b,5'}$ 5.3 Hz, $J_{6'b,6'a}$ 11.9 Hz, H-6′b *glc*), 3.53 (dt, 1H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.5 Hz, H-1b), 3.34 (t, 1H, $J_{3',4'}$ 8.4 Hz, H-3′ *glc*), 3.28 (t, 1H, $J_{4',3'}$ 7.2 Hz, H-4′ *glc*), 3.25 (m, 1H, H-5′ *glc*), 3.16 (dd, 1H, $J_{2',1'}$ 7.8 Hz, $J_{2',3'}$ 9.1 Hz, H-2′ *glc*), 2.04 (m, 2H, H-9), 1.60 (m, 2H, H-2), 1.30 (m, 12H, H-3 to H-8); ^{13}C NMR (CD_3OD): *glucose*: 104.4 (C-1′), 78.2 (C-3′), 77.9 (C-5′), 75.2 (C-2′), 71.7 (C-4′), 62.8 (C-6′), *alkyl chain*: 140.2 (CH═), 114.7 (═CH_2), 70.9 (C-1), 34.9 (C-9), 30.8, 30.7, 30.63, 30.59, 30.2, 30.1 (C-3 to C-8), 27.1 (C-2); MS (CI): *m*/*z* 333 $[M+H]^+$.

*5.3.5. Undec-10-enyl-α-D-lactopyranoside (**9a**).* Deacetylation of compound **6a** (33 mg, 0.04 mmol) as above with 12 equiv MeONa during 16 h afforded **9a** (26 mg, quantitative yield) as a white foam; $[\alpha]_D^{20}$ +83.4 (*c* 0.9, MeOH); R_f 0.47 (1:1 $CHCl_3$/EtOH); IR (KBr): *ν* 3381 (OH), 2917 (ν_{asym} CH_2), 2849 (ν_{sym} CH_2), 1644 (C═C); ^{1}H NMR (CD_3OD): *δ* 5.80 (ddt, 1H, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.2 Hz, $J_{10,11trans}$ 17.0 Hz, H-10), 4.97 (dq, 1H, $J_{11trans,11cis}$ 1.7 Hz, $J_{11trans,10}$ 17.1 Hz, H-11 *trans*), 4.91 (dq, 1H, $J_{11cis,11trans}$ 0.9 Hz, $J_{11cis,10}$ 10.2 Hz, H-11 *cis*), 4.75 (d, 1H, $J_{1',2'}$ 3.7 Hz, H-1′α *glc*), 4.35 (d, 1H, $J_{1'',2''}$ 7.6 Hz, H-1″ *gal*), 3.86 (dd, 1H, $J_{6'a,5'}$ 3.7 Hz, $J_{6'a,6'b}$ 12.1 Hz, H-6′a *glc*), 3.80 (m, 1H, H-6′b *glc*), 3.79 (m, 1H, H-4″ *gal*), 3.77 (m, 1H, H-3′ *glc*), 3.74 (dd, 1H, $J_{6''a,5''}$ 7.4 Hz, $J_{6''a,6''b}$ 11.0 Hz, H-6″a *gal*), 3.72 (m, 1H, H-6″b *gal*), 3.70 (m, 1H, H-1a), 3.68 (m, 1H, H-5′ *glc*), 3.58 (dd, 1H, $J_{5'',6''}$ 4.7 Hz, $J_{5'',4''}$ 7.5 Hz, H-5″ *gal*), 3.54 (dd, 1H, $J_{3',4'}$ 7.1 Hz, $J_{3',2'}$ 10.1 Hz, H-3′ *glc*), 3.53 (t, 1H, $J_{3'',2''}$ 3.6 Hz, H-3″ *gal*), 3.48 (dd, 1H, $J_{2'',1''}$ 6.6 Hz, $J_{2'',3''}$ 9.8 Hz, H-2″ *gal*), 3.45 (m,1H, H-1b), 3.44 (dd, 1H, $J_{2',1'}$ 3.6 Hz, $J_{2',3'}$ 9.7 Hz, H-2′ *glc*), 2.03 (quint, 2H, *J* 7.0 Hz, H-9), 1.62 (m, 2H, H-2), 1.31 (m, 12H, H-3 to H-8); MS (CI): *m*/*z* 495 $[M+H]^+$.

*5.3.6. Undec-10-enyl-β-D-lactopyranoside (**9b**).* Deacetylation of compound **6b** (98 mg, 0.12 mmol) as above with 4 equiv MeONa during 4 h 30 min afforded **9b** (56 mg, 91%) as a white foam; R_f 0.39 (1:1 $CHCl_3$/EtOH); IR (KBr): *ν* 3415 (OH), 2919 (ν_{asym} CH_2), 2847 (ν_{sym} CH_2), 1637 (C═C); ^{1}H NMR (CD_3OD): *δ* 5.80 (ddt, 1H, $J_{10,9}$ 6.7 Hz, $J_{10,11cis}$ 10.2 Hz, $J_{10,11trans}$ 17.0 Hz, H-10), 4.97 (dq, 1H, $J_{11trans,11cis}$ 1.8 Hz, $J_{11trans,10}$ 17.1 Hz, H-11 *trans*), 4.90 (dq, 1H, $J_{11cis,11trans}$ 0.9 Hz, $J_{11cis,10}$ 10.2 Hz, H-11 *cis*), 4.35 (d, 1H, $J_{1',2'}$ 7.5 Hz, H-1′β *glc*), 4.27 (d, 1H, $J_{1'',2''}$ 7.8 Hz, H-1″ *gal*), 3.88 (dd, 1H, $J_{6'a,5'}$ 6.5 Hz, $J_{6'a,6'b}$ 12.5 Hz, H-6′a *glc*), 3.86 (m, 1H, H-1a), 3.84 (m, 1H, H-6′b *glc*), 3.81 (m, 1H, H-4″ *gal*), 3.77 (dd, 1H, $J_{6''a,5''}$ 7.6 Hz, $J_{6''a,6''b}$ 11.5 Hz, H-6″a *gal*), 3.69 (dd, 1H, $J_{6''b,5''}$ 4.6 Hz, $J_{6''b,6''a}$ 11.5 Hz, H-6″b *gal*), 3.59 (m, 1H, H-5″ *gal*), 3.57 (m, 1H, H-4′ *glc*), 3.54 (dd, 1H, $J_{2'',1''}$ 7.4 Hz, $J_{2'',3''}$ 9.8 Hz, H-2″ *gal*), 3.51 (t, 1H, $J_{3',4'}$ 8.8 Hz, H-3′ *glc*), 3.50 (m,1H, H-1b), 3.47 (dd, 1H, $J_{3'',2''}$ 3.1 Hz, $J_{3'',4''}$ 9.7 Hz, H-3″ *gal*), 3.38 (ddd, 1H, $J_{5',4'}$ 2.7 Hz, $J_{5',6'a}$ 3.9 Hz, $J_{5',6'b}$ 9.2 Hz, H-5′ *glc*), 3.23 (t, 1H, $J_{2',1'}$ 8.4 Hz, H-2′ *glc*), 2.03 (quint, 2H, *J* 7.0 Hz, H-9), 1.62 (m, 2H, H-2), 1.31 (m, 12H, H-3 to H-8); MS (CI): *m*/*z* 495 $[M+H]^+$.

5.4. General procedure for dimerization by cross-metathesis (10–13)

To a soln of peracetylated monocatenary compound in dry CH_2Cl_2 at 40 °C under refluxing conditions, Grubbs I catalyst, dissolved in the same solvent, was added dropwise. After completion of the reaction monitored by TLC (1:1 EP/EtOAc), the solvent was removed. The crude was purified over a silica gel column (EP/EtOAc gradient) and afforded dimeric compound as a yellow oil composed of a mixture of *Z* and *E* stereoisomers.

*5.4.1. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-α-D-galactopyranosyl]-eicos-10-ene (**10a**).* To a soln of compound **4a** (1.14 g, 2.28 mmol) in 10 mL dry CH_2Cl_2, metathesis procedure was done using 11.5 mol % of Grubbs I catalyst (215.5 mg, 0.26 mmol) in 7 mL dry CH_2Cl_2. After 20 h 30 min, compound **10a** was isolated after purification (4:1 → 1:1 EP/EtOAc) in 83% yield (923 mg); R_f 0.53 (1:1 EP/EtOAc); IR (KBr): *ν* 3022 (═C–H), 2925 (ν_{asym} CH_2), 2854 (ν_{sym} CH_2), 1752 (C═O), 1654 (C═C); ^{1}H NMR ($CDCl_3$): *δ* 5.45 (dd, 2H, $J_{4',3'}$ 1.1 Hz, $J_{4',5'}$ 3.4 Hz, H-4′ *gal*), 5.36 (m, 4H, H-2′ *gal* and H-10), 5.10 (dd, 2H, $J_{3',4'}$ 3.7 Hz, $J_{3',2'}$ 11.9 Hz, H-3′ *gal*), 5.09 (d, 2H, $J_{1',2'}$ 3.6 Hz, H-1′α *gal*), 4.22 (te, 2H, $J_{5',6'}$ 6.2 Hz, H-5′ *gal*), 4.10 (m, 4H, H-6′ *gal*), 3.68 (dt, 2H, $J_{1a,2}$ 6.5 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.42 (dt, 2H, $J_{1b,2}$ 6.6 Hz, $J_{1b,1a}$ 9.8 Hz, H-1b), 2.14, 2.07, 2.05, 1.99 (s, 24H, acetyl), 1.58 (m, 8H, H-2 and H-9), 1.28 (m, 24H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *galactose*: 96.1 (C-1′), 68.3 (C-3′), 68.2 (C-4′), 67.7 (C-2′), 66.2 (C-5′), 61.8 (C-6′), *alkyl chain*: 130.3 (CH═), 68.7 (C-1), 32.6 (C-9), 29.7, 29.6, 29.5, 29.3, 29.2 (C-3 to C-8), 26.1 (C-2), *protecting groups*: 170.4, 170.3, 170.1 (CO), 20.8, 20.70, 20.67 (CH_3); MS (CI): *m*/*z* 973 $[M+H]^+$.

*5.4.2. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-β-D-galactopyranosyl]-eicos-10-ene (**10b**).* To a soln of compound **4b** (1.87 g, 3.73 mmol) in 12 mL dry CH_2Cl_2, metathesis procedure was done using 12.6 mol % of Grubbs I catalyst (387.4 mg, 0.47 mmol) in 8 mL dry CH_2Cl_2. After 18 h, compound **10b** was isolated after purification (4:1 → 1:1 EP/EtOAc) in 62% yield (1.12 g); R_f 0.45 (1:1 EP/EtOAc); IR (KBr): *ν* 3018 (═C–H), 2920 (ν_{asym} CH_2), 2849 (ν_{sym} CH_2), 1748 (C═O), 1647 (C═C); ^{1}H NMR ($CDCl_3$): *δ* 5.39 (m, 2H, H-10), 5.34 (t, 2H, $J_{4',3'}$ 4.7 Hz, H-4′ *gal*), 5.20 (dd, 2H, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 10.4 Hz, H-2′ *gal*), 5.01 (dd, 2H, $J_{3',4'}$ 3.4 Hz, $J_{3',2'}$ 10.5 Hz, H-3′ *gal*), 4.45 (d, 2H, $J_{1',2'}$ 8.0 Hz, H-1′β *gal*), 4.19 (dd, 2H, $J_{6''a,5''}$ 6.4 Hz, $J_{6''a,6''b}$ 11.2 Hz, H-6′a *gal*), 4.13 (dd, 2H, $J_{6''b,5''}$ 7.0 Hz, $J_{6''b,6''a}$ 11.2 Hz, H-6′b *gal*), 3.89 (m, 2H, H-5′ *gal*), 3.88 (dt, 2H, $J_{1a,2}$ 6.4 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.47 (dt, 2H, $J_{1b,2}$ 6.9 Hz, $J_{1b,1a}$ 9.5 Hz, H-1b), 2.15, 2.05, 1.99 (s, 24H, acetyl), 1.57 (m, 8H, H-2 and H-9), 1.29 (m, 24H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *galactose*: 101.4 (C-1′), 71.0 (C-3′), 70.6 (C-5′), 69.0 (C-2′), 67.1 (C-4′), 61.3 (C-6′), *alkyl chain*: 130.3 (CH═), 70.3 (C-1), 32.6 (C-9), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2 (C-3 to C-8), 25.8 (C-2), *protecting groups*: 170.4, 170.3, 170.2, 169.4 (CO), 20.8, 20.7, 20.6 (CH_3). MS (CI): *m*/*z* 973 $[M+H]^+$.

*5.4.3. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-α-D-glucopyranosyl]-eicos-10-ene (**11a**).* To a soln of compound **5a** (307 mg, 0.61 mmol) in 12 mL dry CH_2Cl_2, metathesis procedure was done using 7.8 mol % of Grubbs I catalyst (39.7 mg, 0.048 mmol) in 5 mL dry CH_2Cl_2. After 15 h, compound **11a** was isolated after purification (7:3 → 3:2 → 1:1 EP/EtOAc) in 85% yield (253 mg); *E*/*Z* 3.39; R_f 0.55 (2:3 EP/EtOAc); IR (KBr): *ν* 3067 (═C–H), 2927 (ν_{asym} CH_2), 2855 (ν_{sym} CH_2), 1751 (C═O), 1650 (C═C); ^{1}H NMR ($CDCl_3$): *δ* 5.48 (t, 2H, $J_{3',2'}$ 9.8 Hz, H-3′ *glc*), 5.38 (te, 2H, $J_{10trans,9}$ 3.6 Hz, H-10 *trans*), 5.34 (te, 2H, $J_{10cis,9}$ 4.5 Hz, H-10 *cis*), 5.06 (t, 2H, $J_{1',2'}$ 3.8 Hz, H-1′α *glc*), 5.05 (t, 2H, $J_{4'-3'}$ 9.8 Hz, H-4′ *glc*), 4.85 (dd, 2H, $J_{2',1'}$ 3.7 Hz, $J_{2',3'}$ 10.2 Hz, H-2′ *glc*), 4.25 (dd, 2H, $J_{6'a,5'}$ 4.5 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6′a *glc*), 4.08 (dd, 2H, $J_{6'b,5'}$ 2.3 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′b *glc*), 4.01 (ddd,

2H, $J_{5',6'b}$ 2.3 Hz, $J_{5',6'a}$ 4.4 Hz, $J_{5',4'}$ 10.2 Hz, H-5′ *glc*), 3.67 (dt, 2H, $J_{1a,2}$ 6.5 Hz, $J_{1a,1b}$ 9.9 Hz, H-1a), 3.42 (dt, 2H, $J_{1b,2}$ 6.7 Hz, $J_{1b,1a}$ 9.8 Hz, H-1b), 2.09, 2.06, 2.03, 2.01 (s, 24H, acetyl), 1.96 (quint, 4H, $J_{9,10}$ 5.8 Hz, H-9), 1.59 (quint, 4H, $J_{2,1}$ 6.7 Hz, H-2), 1.28 (m, 24H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *glucose*: 95.6 (C-1′), 71.0 (C-2′), 70.3 (C-3′), 68.6 (C-4′), 67.1 (C-5′), 62.0 (C-6′), *alkyl chain*: 130.2 (CH═), 68.7 (C-1), 33.8 (C-9), 29.5, 29.4, 29.32, 29.26, 29.1, 28.9 (C-3 to C-8), 26.0 (C-2), *protecting groups*: 170.7, 170.2, 170.1, 169.6 (CO), 20.73, 20.69, 20.65 (CH_3); MS (CI): *m*/*z* 995.6. $[M+Na]^+$.

*5.4.4. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-β-D-glucopyranosyl]-eicos-10-ene (**11b**).* To a soln of compound **5b** (1.57 g, 3.1 mmol) in 12 mL dry CH_2Cl_2, metathesis procedure was done using 8.2 mol % of Grubbs I catalyst (211 mg, 0.26 mmol) in 5 mL dry CH_2Cl_2. After 15 h, compound **11b** was isolated after purification (7:3 → 3:2 → 1:1 EP/EtOAc) in 95% yield (1.45 g); *E*/*Z* 3.58; R_f 0.51 (2:3 EP/EtOAc); IR (KBr): ν 3062 (═C–H), 2926 (ν_{asym} CH_2), 2854 (ν_{sym} CH_2), 1756 (C═O), 1643 (C═C); ^{1}H NMR ($CDCl_3$): δ 5.37 (te, 2H, $J_{10trans,9}$ 3.6 Hz, H-10 *trans*), 5.34 (te, 2H, $J_{10cis,9}$ 4.7 Hz, H-10 *cis*), 5.20 (t, 2H, $J_{3',2'}$ 9.5 Hz, H-3′ *glc*), 5.08 (t, 2H, $J_{4',3'}$ 9.7 Hz, H-4′ *glc*), 4.98 (dd, 2H, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 9.6 Hz, H-2′ *glc*), 4.49 (d, 2H, $J_{1',2'}$ 8.0 Hz, H-1′β *glc*), 4.26 (dd, 2H, $J_{6'a,5'}$ 4.7 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6′a *glc*), 4.13 (dd, 2H, $J_{6'b,5'}$ 2.4 Hz, $J_{6'b,6'a}$ 12.2 Hz, H-6′b *glc*), 3.86 (dt, 2H, $J_{1a,2}$ 6.3 Hz, $J_{1a,1b}$ 9.6 Hz, H-1a), 3.68 (ddd, 2H, $J_{5',6'b}$ 2.6 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',4'}$ 10.0 Hz, H-5′ *glc*), 3.47 (dt, 2H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.5 Hz, H-1b), 2.08, 2.04, 2.02, 2.00 (s, 24H, acetyl), 1.95 (m, 4H, H-9), 1.57 (quint, 4H, $J_{2,1}$ 6.3 Hz, H-2), 1.25 (m, 24H, H-3 to H-8); ^{13}C NMR ($CDCl_3$): *glucose*: 100.8 (C-1′), 72.9 (C-3′), 71.8 (C-5′), 71.4 (C-2′), 68.5 (C-4′), 62.0 (C-6′), *alkyl chain*: 130.3 (CH═), 70.2 (C-1), 32.6 (C-9), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2 (C-3 to C-8), 25.8 (C-2), *protecting groups*: 170.7, 170.3, 169.4, 169.3 (CO), 20.75, 20.64 (CH_3); MS (CI): *m*/*z* 995.6. $[M+Na]^+$.

*5.4.5. 1,20-Bis [(2′,3′,6′,2″,3″,4″,6″-hepta-O-acetyl)-α-D-lactopyranosyl]-eicos-10-ene (**12a**).* To a soln of compound **6a** (164 mg, 0.21 mmol) in 5 mL dry CH_2Cl_2, metathesis procedure was done using 17.6 mol % of Grubbs I catalyst (30 mg, 0.036 mmol) in 5 mL dry CH_2Cl_2. After 27 h, compound **12a** was isolated after purification (3:2 → 1:1 → 0:1 EP/EtOAc) in 61% yield (98 mg); R_f 0.14 (1:1 EP/EtOAc); IR (KBr): ν 3019 (═C–H), 2927 (ν_{asym} CH_2), 2855 (ν_{sym} CH_2), 1752 (C═O), 1650 (C═C); ^{1}H NMR ($CDCl_3$): δ 5.47 (t, 2H, $J_{3',2'}$ 9.6 Hz, H-3′ *glc*), 5.38 (m, 2H, H-10), 5.34 (de, 2H, $J_{4'',3''}$ 3.0 Hz, H-4″ *gal*), 5.11 (dd, 2H, $J_{2'',1''}$ 7.9 Hz, $J_{2'',3''}$ 10.3 Hz, H-2″ *gal*), 4.96 (d, 2H, $J_{1',2'}$ 3.6 Hz, H-1′ *glc*), 4.95 (dd, 2H, $J_{3'',4''}$ 3.5 Hz, $J_{3'',2''}$ 10.4 Hz, H-3″ *gal*), 4.77 (dd, 2H, $J_{2',1'}$ 3.8 Hz, $J_{2',3'}$ 10.2 Hz, H-2′ *glc*), 4.48 (d, 2H, $J_{1''\text{-}2''}$ 7.9 Hz, H-1″ *gal*), 4.44 (dd, 2H, $J_{6'a,5'}$ 1.6 Hz, $J_{6'a,6'b}$ 11.9 Hz, H-6′a *glc*), 4.14 (dd, 2H, $J_{6''a,5''}$ 6.4 Hz, $J_{6''a,6''b}$ 11.1 Hz, H-6″a *gal*), 4.11 (m, 2H, H-6b *glc*), 4.08 (dd, 2H, $J_{6''b,5''}$ 7.6 Hz, $J_{6''b,6''a}$ 11.1 Hz, H-6″b *gal*), 3.92 (ddd, 2H, $J_{5',6'b}$ 2.2 Hz, $J_{5',6'a}$ 5.0 Hz, $J_{5',4'}$ 10.5 Hz, H-5′ *glc*), 3.87 (te, 2H, $J_{5''\text{-}6''}$ 6.9 Hz, H-5″ *gal*), 3.73 (t, 2H, $J_{4'\text{-}3'}$ 9.6 Hz, H-4′ *glc*), 3.64 (dt, 2H, $J_{1a,2}$ 6.7 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.38 (dt, 2H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.7 Hz, H-1b), 2.15, 2.12, 2.06, 2.05, 1.96 (s, 42H, acetyl), 1.59 (m, 8H, H-2 and H-9), 1.27 (m, 24H, H-3 to H-8).

*5.4.6. 1,20-Bis[(2′,3′,6′,2″,3″,4″,6″-hepta-O-acetyl)-β-D-lactopyranosyl]-eicos-10-ene (**12b**).* To a soln of compound **6b** (316 mg, 0.4 mmol) in 10 mL dry CH_2Cl_2, metathesis procedure was done using 15.2 mol % of Grubbs I catalyst (5 mg, 0.061 mmol) in 5 mL dry CH_2Cl_2. After 21 h, compound **12b** was isolated after purification (3:2 → 1:1 EP/EtOAc) in 50% yield (156 mg); R_f 0.16 (1:1 EP/EtOAc); IR (KBr): ν 3023 (═C–H), 2926 (ν_{asym} CH_2), 2854 (ν_{sym} CH_2), 1754 (C═O), 1652 (C═C); ^{1}H NMR ($CDCl_3$): δ 5.37 (t, 2H, $J_{10,9}$ 3.5 Hz, H-10), 5.35 (de, 2H, $J_{4'',3''}$ 3.2 Hz, H-4″ *gal*), 5.19 (t, 2H, $J_{3',2'}$ 9.3 Hz, H-3′ *glc*), 5.11 (dd, 2H, $J_{2'',1''}$ 8.0 Hz, $J_{2'',3''}$ 10.4 Hz, H-2″ *gal*), 4.95 (dd, 2H, $J_{3'',4''}$ 3.4 Hz, $J_{3'',2''}$ 10.4 Hz, H-3″ *gal*), 4.88 (dd, 2H, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 9.4 Hz, H-2′ *glc*), 4.46 (m, 6H, H-1′ *glc*, H-1″ *gal* and H-6′a *glc*), 4.11 (m, 6H, H-6″ *gal* and H-6′b *glc*), 3.87 (m, 2H, H-1a), 3.80 (m, 4H, H-5″ *gal* and H-4′ *glc*), 3.59 (ddd, 2H, $J_{5',6'b}$ 1.7 Hz, $J_{5',6'a}$ 4.8 Hz, $J_{5',4'}$ 9.7 Hz, H-5′ *glc*), 3.44 (dt, 2H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.5 Hz, H-1b), 2.15, 2.12, 2.06, 2.04, 2.03, 1.96, (s, 42H, acetyl), 1.61 (m, 8H, H-2 and H-9), 1.29 (m, 24H, H-3 to H-8).

5.5. General procedure for hydrogenation of dimers (13–15)

To a soln of dimeric compound (**10**–**12**) in EtOH was added rhodium on alumina in catalytic amount. The reaction was carried out at room temperature under H_2 atmosphere during 4–5 h. After filtration, the solvent was removed to afford, without further purification, an yellow oil.

*5.5.1. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-α-D-galactopyranosyl]-eicosane (**13a**).* Compound **13a** was prepared from **10a** (923 mg, 0.94 mmol) in EtOH (20 mL) in 80% yield (88 mg); $[\alpha]_D^{20}$ 69.1 (*c* 0.3, $CHCl_3$), R_f 0.44 (EP/EtOAc 1:1); IR (KBr): ν 2920 (ν_{asym} CH_2); 2849 (ν_{sym} CH_2); 1748 (C═O); ^{1}H NMR ($CDCl_3$): δ 5.45 (de, 2H, *J* 2.4 Hz, H-4′ *gal*), 5.36 (m, 2H, H-2′ *gal*), 5.12 (m, 2H, H-1′ *gal*), 5.10 (m, 2H, H-3′ *gal*), 4.22 (t, 2H, $J_{5',6'}$ 6.4 Hz, H-5′ *gal*), 4.10 (m, 4H, H-6′ *gal*), 3.67 (dt, 2H, $J_{1a,2}$ 6.6 Hz, $J_{1a,1b}$ 9.6 Hz, H-1a), 3.42 (dt, 2H, $J_{1b,2}$ 6.6 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b),2.14, 2.07, 2.05, 1.99 (s, 24H, acetyl), 1.55 (m, 4H, H-2), 1.26 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 975. $[M+H]^+$.

*5.5.2. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-β-D-galactopyranosyl]-eicosane (**13b**).* Compound **13b** was prepared from **10b** (183 mg, 0.19 mmol) in EtOH (30 mL) in 82% yield (150 mg); $[\alpha]_D^{20}$ −10.6 (*c* 0.7, $CHCl_3$), R_f 0.38 (EP/EtOAc 1:1); IR (KBr): ν 2923 (ν_{asym} CH_2); 2846 (ν_{sym} CH_2); 1752 (C═O); ^{1}H NMR ($CDCl_3$): δ 5.38 (d, 2H, *J* 3.0 Hz, H-4′ *gal*), 5.20 (dd, 2H, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 10.3 Hz, H-2′ *gal*), 5.01 (dd, 2H, $J_{3',4'}$ 3.3 Hz, $J_{3',2'}$ 10.4 Hz, H-3′ *gal*), 4.45 (d, 2H, $J_{1',2'}$ 8.0 Hz, H-1′β *gal*), 4.15 (m, 4H, H-6′ *gal*), 3.89 (m, 4H, H-5′ *gal* and H-1a), 3.47 (dt, 2H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.4 Hz, H-1b),2.15, 2.05, 2.04, 1.99 (s, 24H, acetyl), 1.56 (m, 4H, H-2), 1.25 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 975. $[M+H]^+$.

*5.5.3. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-α-D-glucopyranosyl]-eicosane (**14a**).* Compound **14a** was prepared from **11a** (139 mg, 0.14 mmol) in EtOH (30 mL) in 91% yield (127 mg); $[\alpha]_D^{20}$ −34.8 (*c* 1.7, $CHCl_3$), R_f 0.61 (EP/EtOAc 1:1); IR (KBr): ν 2926 (ν_{asym} CH_2); 2854 (ν_{sym} CH_2); 1751 (C═O); ^{1}H NMR ($CDCl_3$): δ 5.48 (t, 2H, $J_{3',2'}$ 9.8 Hz, H-3′ *glc*), 5.06 (d, 2H, $J_{1',2'}$ 3.8 Hz, H-1α′ *glc*), 5.05 (t, 2H, $J_{4'\text{-}5'}$ 9.7 Hz, H-4′ *glc*), 4.85 (dd, 2H, $J_{2',1'}$ 3.7 Hz, $J_{2',3'}$ 10.2 Hz, H-2′ *glc*), 4.26 (dd, 2H, $J_{6'a,5'}$ 4.5 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6′a *glc*), 4.09 (dd, 2H, $J_{6'b,5'}$ 2.1 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′b *glc*), 4.01 (ddd, 2H, $J_{5',6'b}$ 2.2 Hz, $J_{5',6'a}$ 4.2 Hz, $J_{5',4'}$ 10.2 Hz, H-5′ *glc*), 3.67 (dt, 2H, $J_{1a,2}$ 6.6 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.42 (dt, 2H, $J_{1b,2}$ 6.7 Hz, $J_{1b,1a}$ 9.7 Hz, H-1b), 2.09, 2.06, 2.03, 2.01 (s, 24H, acetyl), 1.59 (m, 4H, H-2), 1.28 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 997.6. $[M+Na]^+$.

*5.5.4. 1,20-Bis[(2′,3′,4′,6′-tetra-O-acetyl)-β-D-glucopyranosyl]-eicosane (**14b**).* Compound **14b** was prepared from **11b** (149 mg, 0.15 mmol) in EtOH (25 mL) in 91% yield (136 mg); $[\alpha]_D^{20}$ −44.9 (*c* 1.4, $CHCl_3$), R_f 0.41 (EP/EtOAc 1:1); IR (KBr): ν 2925 (ν_{asym} CH_2); 2854 (ν_{sym} CH_2); 1756 (C═O); ^{1}H NMR ($CDCl_3$): δ 5.20 (t, 2H, $J_{3',2'}$ 9.5 Hz, H-3′ *glc*), 5.08 (t, 2H, $J_{4',5'}$ 9.7 Hz, H-4′ *glc*), 4.98 (dd, 2H, $J_{2',1'}$ 8.2 Hz, $J_{2',3'}$ 9.3 Hz, H-2′ *glc*), 4.48 (d, 2H, $J_{1',2'}$ 8.0 Hz, H-1β′ *glc*), 4.26 (dd, 2H, $J_{6'a,5'}$ 4.7 Hz, $J_{6'a,6'b}$ 12.2 Hz, H-6′a *glc*), 4.13 (dd, 2H, $J_{6'b,5'}$ 2.2 Hz, $J_{6'b,6'a}$ 12.2 Hz, H-6′b *glc*), 3.86 (dt, 2H, $J_{1a,2}$ 6.3 Hz, $J_{1a,1b}$ 9.5 Hz, H-1a), 3.68 (ddd, 2H, $J_{5',6'b}$ 2.4 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',4'}$ 9.9 Hz, H-5′ *glc*), 3.47 (dt, 2H, $J_{1b,2}$ 6.9 Hz, $J_{1b,1a}$ 9.4 Hz, H-1b), 2.08, 2.04, 2.02, 2.00 (s, 24H, acetyl), 1.55 (quint, 4H, *J* 5.9 Hz, H-2), 1.25 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 997.6. $[M+Na]^+$.

*5.5.5. 1,20-Bis[(2′,3′,6′,2″,3″,4″,6″-hepta-O-acetyl)-α-D-lactopyranosyl]-eicosane (**15a**).* Compound **15a** was prepared from **12a** (28 mg, 0.02 mmol) in EtOH (15 mL) in 97% yield (29 mg); $[\alpha]_D^{20}$

−16.0 (*c* 0.3, $CHCl_3$), R_f 0.37 (EP/EtOAc 1:1); IR (KBr): ν 2927 (ν_{asym} CH_2); 2855 (ν_{sym} CH_2); 1753 (C=O); ^{1}H NMR ($CDCl_3$): δ 5.47 (t, 2H, $J_{3',2'}$ 9.7 Hz, H-3′ *glc*), 5.35 (de, 2H, $J_{4'',3''}$ 3.0 Hz, H-4″ *gal*), 5.12 (dd, 2H, $J_{2'',1''}$ 7.9 Hz, $J_{2'',3''}$ 10.4 Hz, H-2″ *gal*), 4.95 (m, 4H, H-3″ *gal* and H-1′ *glc*), 4.77 (dd, 2H, $J_{2',1'}$ 3.8 Hz, $J_{2',3'}$ 10.2 Hz, H-2′ *glc*), 4.48 (d, 2H, $J_{1''\text{-}2''}$ 7.9 Hz, H-1″ *gal*), 4.44 (dd, 2H, $J_{6'a,5'}$ 2.1 Hz, $J_{6'a,6'b}$ 12.5 Hz, H-6′a *glc*), 4.12 (m, 6H, H-6″ *gal* and H-6b *glc*), 3.92 (ddd, 2H, $J_{5',6'b}$ 2.7 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',4'}$ 10.0 Hz, H-5′ *glc*), 3.87 (t, 2H, $J_{5''\text{-}6''}$ 6.6 Hz, H-5″ *gal*), 3.73 (t, 2H, $J_{4'\text{-}3'}$ 9.6 Hz, H-4′ *glc*), 3.65 (dt, 2H, $J_{1a,2}$ 6.6 Hz, $J_{1a,1b}$ 9.8 Hz, H-1a), 3.39 (dt, 2H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.8 Hz, H-1b), 2.17, 2.12, 2.06, 2.05, 1.97 (s, 42H, acetyl), 1.57 (m, 8H, H-2 and H-3), 1.25 (m, 28H, H-4 to H-10).

*5.5.6. 1,20-Bis[(2′,3′,6′,2″,3″,4″,6″-hepta-O-acetyl)-β-D-lactopyranosyl]-eicosane (**15b**).* Compound **15b** was prepared from **12b** (58 mg, 0.04 mmol) in EtOH (15 mL) in 89% yield (52 mg); R_f 0.47 (EP/EtOAc 1:1); IR (KBr): ν 2925 (ν_{asym} CH_2); 2854 (ν_{sym} CH_2); 1752 (C=O); ^{1}H NMR ($CDCl_3$): δ 5.34 (de, 2H, $J_{4'',3''}$ 2.9 Hz, H-4″ *gal*), 5.19 (t, 2H, $J_{3',2'}$ 9.2 Hz, H-3′ *glc*), 5.10 (dd, 2H, $J_{2'',1''}$ 7.9 Hz, $J_{2'',3''}$ 10.3 Hz, H-2″ *gal*), 4.96 (dd, 2H, $J_{3'',4''}$ 3.4 Hz, $J_{3'',2''}$ 10.4 Hz, H-3″ *gal*), 4.87 (dd, 2H, $J_{2',1'}$ 8.0 Hz, $J_{2',3'}$ 9.2 Hz, H-2′ *glc*), 4.47 (m, 6H, H-1′ *glc*, H-1″ *gal* and H-6′a *glc*), 4.11 (m, 6H, H-6″ *gal* and H-6′b *glc*), 3.86 (m, 2H, H-1a), 3.80 (m, 4H, H-5″ *gal* and H-4′ *glc*), 3.59 (ddd, 2H, $J_{5',6'b}$ 1.7 Hz, $J_{5',6'a}$ 4.8 Hz, $J_{5',4'}$ 9.5 Hz, H-5′ *glc*), 3.44 (dt, 2H, $J_{1b,2}$ 6.8 Hz, $J_{1b,1a}$ 9.5 Hz, H-1b), 2.15, 2.12, 2.06, 2.04, 2.03, 1.96, (s, 42H, acetyl), 1.54 (m, 8H, H-2 and H-3), 1.25 (m, 28H, H-4 to H-10).

5.6. Deacetylation of dimers under Zemplén conditions (16–18)

Deacetylation of dimers under Zemplén conditions (**16**–**18**), under the same conditions as previously described, with 0.5 M sodium methylate in methanol.

*5.6.1. 1,20-Bis-(α-D-galactopyranosyl)-eicosane (**16a**).* Deacetylation of compound **13a** (88 mg, 0.09 mmol) as above with 4.4 equiv MeONa during 16 h afforded **16a** in quantitative yield (58 mg) as a white foam; $[\alpha]_D^{20}$ −111.6 (*c* 0.3, MeOH); R_f 0.54 (1:1 $CHCl_3$/EtOH); IR (KBr): ν 3376 (OH), 2920 (ν_{asym} CH_2), 2849 (ν_{sym} CH_2); ^{1}H NMR (CD_3OD): δ 4.80 (d, 2H, $J_{1',2'}$ 3.2 Hz, H-1′α *gal*), 3.88 (m, 2H, H-3′ *gal*), 3.80 (m, 2H, H-5′ *gal*), 3.72 (m, 10H, H-2′ *gal*, H-4′ *gal*, H-6′ *gal*, H-1a), 3.43 (dt, 2H, $J_{1b,2}$ 6.5 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b), 1.63 (m, 4H, H-2), 1.29 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 639. $[M+H]^+$.

*5.6.2. 1,20-Bis-(β-D-galactopyranosyl)-eicosane (**16b**).* Deacetylation of compound **13b** (150 mg, 0.15 mmol) as above with 4.2 equiv MeONa during 12 h afforded **16b** (96 mg, 98%) as a white foam; $[\alpha]_D^{20}$ −10.4 (*c* 0.8, pyridine); R_f 0.45 (1:1 $CHCl_3$/EtOH); IR (KBr): ν 3336 (OH), 2911 (ν_{asym} CH_2), 2841 (ν_{sym} CH_2); ^{1}H NMR (CD_3OD): δ 4.18 (d, 2H, $J_{1',2'}$ 7.3 Hz, H-1′β *gal*), 3.87 (dt, 2H, $J_{1a,2}$ 7.0 Hz, $J_{1a,1b}$ 9.6 Hz, H-1a), 3.81 (de, 2H, *J* 2.6 Hz, H-5′ *gal*), 3.70 (m, 4H, H-6′ *gal*), 3.55 (m, 2H, H-1b), 3.48 (m, 6H, H-2′ *gal*, H-3′ *gal*, H-4′ *gal*), 1.60 (quint, 4H, *J* 7.0 Hz, H-2), 1.26 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 639. $[M+H]^+$.

*5.6.3. 1,20-Bis-(α-D-glucopyranosyl)-eicosane (**17a**).* Deacetylation of compound **14a** (163 mg, 0.2 mmol) as above with 32 equiv MeONa during 4.5 h afforded **17a** (87 mg, 92%) as a white foam; R_f 0.86 (9:1 MeOH/H_2O); IR (KBr): ν 3370 (OH), 2939 (ν_{asym} CH_2), 2858 (ν_{sym} CH_2); ^{1}H NMR (CD_3OD): δ 4.77 (d, 2H, $J_{1',2'}$ 3.7 Hz, H-1α′ *glc*), 3.79 (dd, 2H, $J_{6'a,5'}$ 2.4 Hz, $J_{6'a,6'b}$ 11.8 Hz, H-6′a *glc*), 3.72 (m, 4H, H-6′b *glc*, H-1a), 3.61 (t, 2H, $J_{3',2'}$ 7.9 Hz, H-3′ *glc*),3.56 (m, 2H, H-5′ *glc*), 3.44 (dt, 2H, $J_{1b,2}$ 6.4 Hz, $J_{1b,1a}$ 9.6 Hz, H-1b), 3.37 (dd, 2H, $J_{2',1'}$ 3.7 Hz, $J_{2',3'}$ 9.7 Hz, H-2′ *glc*), 3.28 (dd, 2H, $J_{4',3'}$ 9.1 Hz, $J_{4',5'}$ 9.6 Hz, H-4′ *glc*), 1.54 (m, 4H, H-2), 1.29 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 639 $[M+H]^+$.

*5.6.4. 1,20-Bis-(β-D-glucopyranosyl)-eicosane (**17b**).* Deacetylation of compound **14b** (43 mg, 0.044 mmol) as above with 24 equiv MeONa during 14 h afforded **17b** quantitatively (34 mg) as a white foam; $[\alpha]_D^{20}$ −24.7 (*c* 0.3, MeOH); R_f 0.78 (9:1 MeOH/H_2O); IR (KBr): ν 3339 (OH), 2923 (ν_{asym} CH_2), 2853 (ν_{sym} CH_2); ^{1}H NMR (CD_3OD): δ 4.08 (d, 2H, $J_{1',2'}$ 7.8 Hz, H-1β′ *glc*), 3.73 (dt, 2H, $J_{1a,2}$ 6.9 Hz, $J_{1a,1b}$ 9.7 Hz, H-1a), 3.64 (dd, 2H, $J_{6'a,5'}$ 1.8 Hz, $J_{6'a,6'b}$ 10.9 Hz, H-6′a *glc*), 3.41 (m, 4H, H-6′b *glc*, H-5′ *glc*), 3.39 (dt, 2H, $J_{1b,2}$ 6.9 Hz, $J_{1b,1a}$ 9.5 Hz, H-1b), 3.11 (te, 2H, $J_{3',2'}$ 8.6 Hz, H-3′ *glc*), 3.02 (m, 2H, H-4′ *glc*), 2.91 (t, 2H, *J* 8.3 Hz, H-2′ *glc*), 1.49 (quint, 4H, *J* 6.8 Hz, H-2), 1.25 (m, 32H, H-3 to H-10); ^{13}C NMR (CD_3OD): *glucose*: 102.8 (C-1′), 76.8 (C-3′), 76.7 (C-5′), 73.4 (C-2′), 70.1 (C-4′), 61.1 (C-6′), *alkyl chain*: 68.5 (C-1), 29.3, 29.1, 28.9 (C-3 to C-10), 25.5 (C-2); MS (CI): *m*/*z* 639 $[M+H]^+$.

*5.6.5. 1,20-Bis(α-D-lactopyranosyl)-eicosane (**18a**).* Compound **15a** (29 mg, 0.02 mmol) was dissolved in 3 mL CH_2Cl_2 and a soln of 7 N ammonia in methanol (2 mL) was added. After 3 days at room temperature, solvent was removed and compound **18a** was obtained quantitatively (18 mg) as a white foam; R_f 0.78 (1:1 $CHCl_3$/EtOH); IR (KBr): ν 3334 (OH), 2919 (ν_{asym} CH_2), 2852 (ν_{sym} CH_2); ^{1}H NMR (CD_3OD): δ 4.75 (d, 2H, $J_{1',2'}$ 3.7 Hz, H-1′ *glc*), 4.35 (d, 2H, $J_{1''\text{-}2''}$ 7.6 Hz, H-1″ *gal*), 3.86 (dd, 2H, $J_{6'a,5'}$ 3.7 Hz, $J_{6'a,6'b}$ 12.1 Hz, H-6′a *glc*), 3.80 (m, 2H, H-6b *glc*), 3.78 (m, 4H, H-3″ *gal* and H-3′ *glc*), 3.74 (dd, 2H, $J_{6''a,5''}$ 7.4 Hz, $J_{6''a,6''b}$ 11.0 Hz, H-6″a *gal*), 3.72 (m, 2H, H-6″b *gal*), 3.70 (m, 2H, H-1a), 3.68 (m, 2H, H-5′ *glc*), 3.58 (dd, 2H, $J_{5'',4''}$ 4.7 Hz, $J_{5'',6''}$ 7.5 Hz, H-5″ *gal*), 3.54 (dd, 2H, $J_{4',5'}$ 7.1 Hz, $J_{4',3'}$ 10.1 Hz, H-4′ *glc*), 3.53 (t, 2H, $J_{3'',2''}$ 3.6 Hz, H-3″ *gal*), 3.48 (dd, 2H, $J_{2'',1''}$ 6.6 Hz, $J_{2'',3''}$ 9.8 Hz, H-2″ *gal*), 3.48 (dd, 2H, $J_{2'',1''}$ 6.6 Hz, $J_{2'',3''}$ 9.8 Hz, H-2″ *gal*), 3.45 (m, 2H, H-1b), 3.44 (dd, 2H, $J_{2',1'}$ 3.6 Hz, $J_{2',3'}$ 9.7 Hz, H-2′ *glc*), 1.59 (m, 4H, H-2), 1.25 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 963 $[M+H]^+$.

*5.6.6. 1,20-Bis(β-D-lactopyranosyl)-eicosane (**18b**).* Deacetylation of compound **15b** (46 mg, 0.03 mmol) as above with 17 equiv MeONa during 20 h afforded **18b** (16 mg, 56%) as a white foam; R_f 0.62 (1:1 $CHCl_3$/EtOH); IR (KBr): ν 3382 (OH), 2923 (ν_{asym} CH_2), 2847 (ν_{sym} CH_2); ^{1}H NMR (CD_3OD): δ 4.34 (d, 2H, $J_{1',2'}$ 7.5 Hz, H-1′ *glc*), 4.28 (d, 2H, $J_{1'',2''}$ 7.8 Hz, H-1″ *gal*), 3.88 (dd, 2H, $J_{6'a,5'}$ 6.5 Hz, $J_{6'a,6'b}$ 12.5 Hz, H-6′a *glc*), 3.86 (m, 2H, H-1a), 3.82 (m, 4H, H-4″ *gal* and H-6′b *glc*), 3.77 (dd, 2H, $J_{6''a,5''}$ 7.6 Hz, $J_{6''a,6''b}$ 11.5 Hz, H-6″a *gal*), 3.69 (dd, 2H, $J_{6''b,5''}$ 4.6 Hz, $J_{6''b,6''a}$ 11.5 Hz, H-6″b *gal*), 3.59 (m, 2H, H-5″ *gal*), 3.57 (m, 2H, H-4′ *glc*), 3.54 (dd, 2H, $J_{2'',1''}$ 7.4 Hz, $J_{2'',3''}$ 9.8 Hz, H-2″ *gal*), 3.51 (t, 2H, *J* 8.8 Hz, H-3′ *glc*), 3.50 (m, 2H, H-1b), 3.47 (dd, 2H, $J_{3'',4''}$ 3.1 Hz, $J_{3'',2''}$ 9.7 Hz, H-3″ *gal*), 3.38 (ddd, 2H, $J_{5',6'b}$ 2.7 Hz, $J_{5',6'a}$ 3.9 Hz, $J_{5',4'}$ 9.2 Hz, H-5′ *glc*), 3.23 (t, 2H, *J* 8.4 Hz, H-2′ *glc*), 1.62 (m, 4H, H-2), 1.29 (m, 32H, H-3 to H-10); MS (CI): *m*/*z* 963 $[M+H]^+$.

5.7. 1-Bromo-(2,3,4,6-tetra-*O*-acetyl)-α-D-glucopyranose (19)

At 0 °C, to commercially available β-D-glucopyranoside pentaacetate (5.02 g, 12.8 mmol) were added 10 mL of bromohydric acid (33% in acetic acid), and the mixture was stirred for 4 h. The crude was dropped into a glass and organic layer was worked up with 25 mL CH_2Cl_2 and 50 mL of water. Then, this organic phase was neutralized with $NaHCO_3$ (2×10 mL), washed again with water (2×50 mL), and dried over $MgSO_4$. After filtration and solvent removal, the residue was recrystallized in Et_2O to afford compound **19** in 85% yield (4.48 g) as a white solid; $[\alpha]_D^{20}$ +196.0 (*c* 2.0, $CHCl_3$); mp 88 °C; R_f 0.57 (1:2 EP/AcOEt); ^{1}H NMR ($CDCl_3$): δ 6.61 (d, 1H, $J_{1',2'}$ 4.0 Hz, H-1′α *glc*), 5.56 (t, 1H, $J_{3',4'}$ 9.7 Hz, H-3′ *glc*), 5.16 (t, 1H, $J_{4',3'}$ 9.8 Hz, H-4′ *glc*), 4.84 (dd, 1H, $J_{2',1'}$ 4.0 Hz, $J_{2',3'}$ 9.9 Hz, H-2′ *glc*), 4.35 (dd, 1H, $J_{6'a,5'}$ 4.1 Hz, $J_{6'a,6'b}$ 12.1 Hz, H-6′a *glc*), 4.30 (ddd, 1H, $J_{5',6'b}$

1.7 Hz, $J_{5',6'a}$ 3.9 Hz, $J_{5',4'}$ 10.3 Hz, H-5′ *glc*), 4.13 (m, 1H, H-6′b *glc*), 2.11, 2.10, 2.05, 2.04 (s, 12H, acetyl).

5.8. 1-Azido-1-deoxy-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranose (20)

To a soln of **19** (4.25 g, 10,3 mmol) in DMAc (40 mL) were added 2 equiv sodium azide (1.35 g, 20.7 mmol) and the reaction was stirred at 60 °C. After 4 h stirring, DMAc was removed under vacuum and the mixture was extracted with $CHCl_3$ (2×100 mL), then neutralized with $NaHCO_3$, and washed with water. The organic layer was dried ($MgSO_4$), filtered and solvent removed. The residue was recrystallized in isopropyl ether to afford azido compound **20** as a yellow solid (2.85 g, 74%); $[\alpha]_D^{20}$ −19.0 (*c* 1.0, $CHCl_3$); mp 126 °C; IR (KBr): ν 2943 (ν_{asym} CH_2), 2120 (N_3), 1752 (C=O); ^{1}H NMR ($CDCl_3$): δ 5.22 (t, 1H, $J_{3',4'}$ 9.5 Hz, H-3′ *glc*), 5.11 (t, 1H, $J_{4',3'}$ 9.7 Hz, H-4′ *glc*), 4.96 (t, 1H, $J_{2',3'}$ 9.2 Hz, H-2′ *glc*), 4.65 (d, 1H, $J_{1',2'}$ 8.8 Hz, H-1′β *glc*), 4.28 (dd, 1H, $J_{6'a,5'}$ 4.8 Hz, $J_{6'a,6'b}$ 12.5 Hz, H-6′a *glc*), 4.17 (dd, 1H, $J_{6'b,5'}$ 2.3 Hz, $J_{6'b,6'a}$ 12.4 Hz, H-6′b *glc*), 3.80 (ddd, 1H, $J_{5',6'b}$ 2.3 Hz, $J_{5',6'a}$ 4.7 Hz, $J_{5',4'}$ 10.0 Hz, H-5′ *glc*), 2.11, 2.08, 2.03, 2.01 (s, 12H, acetyl); ^{13}C NMR ($CDCl_3$): *glucose*: 87.9 (C-1′), 74.0 (C-5′), 72.6 (C-3′), 70.6 (C-2′), 67.9 (C-4′), 61.7 (C-6′), *acetyl groups*: 170.6 (CO of C-6), 170.1 (CO of C-3), 169.3 (CO of C-4), 169.2 (CO of C-2), 20.7 (CH_3 of C-6), 20.5 (CH_3 of C-2, C-3 and C-4).

5.9. 11-Azidoundecanoic acid (23)

11-Bromoundecanoic acid (10.17 g, 38.4 mmol) and 3 equiv sodium azide (7.37 g, 0.11 mol) were dissolved in DMAc (60 mL) and heated at 80 °C. After 72 h, the solvent was removed and the crude was extracted with 150 mL $CHCl_3$. The organic layer was washed with 100 mL water acidified with 10 mL of 5% HCl, then by 100 mL water, dried with $MgSO_4$, filtered and concentrated. Compound **23** was obtained in 99% yield (8.63 g) as a brown oil, which crystallized in the fridge; IR (KBr): ν 2929 (ν_{asym} CH_2), 2856 (ν_{sym} CH_2), 2096 (N_3), 1709 (C=O); ^{1}H NMR ($CDCl_3$): δ 3.25 (t, 2H, $J_{11,10}$ 7.0 Hz, H-$11_{N3\text{-terminal}}$), 2.34 (te, 2H, $J_{2,3}$ 7.5 Hz, H-2 $_{COOH\text{-terminal}}$), 1.63 (quint, 2H, *J* 7.2 Hz, H-3), 1.60 (quint, 2H, *J* 7.2 Hz, H-10), 1.30 (m, 12H, H-4 to H-9); ^{13}C NMR ($CDCl_3$): 178.9 (*C*OOH), 51.5 (*C*H_2–N_3), 34.1 (*C*H_2–COOH), 29.4, 29.3, 29.2, 29.1, 29.0 (C-4 to C-8), 28.8 (C-10), 26.7 (C-9), 24.7 (C-3).

5.10. 1,12-Diazidododecane (26)

1,12-Dibromododecane (5.13 g, 15.6 mmol) and 6 equiv of sodium azide (6.10 g, 94 mmol) were dissolved in DMAc (30 mL) and heated at 80 °C. After 4 days, the solvent was removed. The crude was extracted with 150 mL $CHCl_3$ and the organic layer was washed with 150 mL water acidified with 10 mL of 1 M HCl, then again with water (3×150 mL), dried with $MgSO_4$, filtered and concentrated. Diazido compound **26** was obtained quantitatively (3.97 g) as a brown oil, which crystallized in the fridge; R_f 0.57 (98:2 EP/AcOEt); IR (KBr): ν 2929 (ν_{asym} CH_2), 2856 (ν_{sym} CH_2), 2096 (N_3); ^{1}H NMR ($CDCl_3$): δ 3.25 (t, 4H, *J* 7.0 Hz, H-1 and H-12), 1.59 (quint, 4H, *J* 7.1 Hz, H-2 and H-11), 1.32–1.28 (m, 16H, H-3 to H-10); ^{13}C NMR ($CDCl_3$): 51.5 (C-1 and C-12), 29.5 (C-2 and C-11), 29.4 (C-5 and C-8), 29.1 (C-6 and C-7), 28.8 (C-4 and C-9), 26.7 (C-3 and C-10).

5.11. 9-{1′-*N*1-(2″,3″,4″,6″-tetra-*O*-acetyl-β-D-glucopyranosyl)-[1′,2′,3′]-triazol-4′-yl}-undecan-1-oic acid (21)

Azidoglucose **20** (271 mg, 0.73 mmol) and 1.2 equiv of 10-undecynoic acid (159 mg, 0.87 mmol) were dissolved in 0.5 mL of *tert*-butanol, and stirred at room temperature. Then, 1 equiv copper II acetate (146 mg, 0.73 mmol) solubilized in 0.5 mL of *tert*-butanol and 2 equiv sodium ascorbate (293 mg, 1.48 mmol) solubilized in 1 mL of distilled water were added to the mixture. After 23 h of stirring, the crude was purified (without work-up) using preparative TLC (96:4 $CHCl_3$/EtOH) yielding **21** as a yellow oil (363 mg, 90%); $[\alpha]_D^{20}$ −5.6 (*c* 0.8, $CHCl_3$); R_f 0.34 (96:4 $CHCl_3$/EtOH); IR (KBr): ν 2932 (ν_{asym} CH_2), 2857 (ν_{sym} CH_2), 1755 (C=O *acetyl*), 1706 (C=O *carboxylic*); ^{1}H NMR ($CDCl_3$): δ 7.51 (s, 1H, H-*triazol*), 5.85 (d, 1H, $J_{1'',2''}$ 8.9 Hz, H-1″β *glc*), 5.42 (m, 2H, H-2″ *glc* and H-3″ *glc*), 5.24 (t, 1H, $J_{4'',3''}$ 9.6 Hz, H-4″ *glc*), 4.31 (dd, 1H, $J_{6''a,5''}$ 5.0 Hz, $J_{6''a,6''b}$ 12.6 Hz, H-6″a *glc*), 4.15 (dd, 1H, $J_{6''b,5''}$ 2.0 Hz, $J_{6''b,6''a}$ 12.5 Hz, H-6″b *glc*), 4.00 (ddd, 1H, $J_{5'',6''b}$ 2.0 Hz, $J_{5'',6''a}$ 5.0 Hz, $J_{5'',4''}$ 10.1 Hz, H-5″ *glc*), 2.71 (dd, 2H, *J* 6.7 Hz, *J* 8.3 Hz, H-2), 2.34 (t, 2H, *J* 7.5 Hz, H-9), 2.08, 2.07, 2.03, 1.86 (s, 12H, acetyl), 1.65 (m, 4H, H-3 and H-8), 1.33 (m, 8H, H-4 to H-7); ^{13}C NMR ($CDCl_3$): *triazol*: 149.2 (*C*=CH *triazol*), 118.8 (C=*C*H *triazol*), *glucose*: 85.7 (C-1″), 75.1 (C-5″), 72.8 (C-3″), 70.2 (C-2″), 67.8 (C-4″), 61.6 (C-6″), *carboxylic alkyl chain*: 178.7 (*C*OOH), 33.9 (C-2), 29.03, 28.96, 29.9 (C-4 to C-8), 25.5 (C-9), 24.7 (C-3), *acetyl groups*: 170.6 (CO of C-6), 169.9, 169.5, 169.0 (CO of C-2, C-3 and C-4), 20.7, 20.5, 20.1 (CH_3); MS (CI): *m*/*z* 594.3 $[M+K]^+$, 578.3 $[M+Na]^+$, 556.3 $[M+H]^+$.

5.12. 9-{1′-*N*1-(β-D-glucopyranosyl)-[1′,2′,3′]-triazol-4′-yl}-undecan-1-oic acid (22)

Compound **21** (188 mg, 0.34 mmol) was deacetylated as previously with 2 mL of a soln of methanolic ammonia (7 N), and stirred at room temperature for 5 days. After solvent removal, compound **22** was afforded in 95% yield as a white foam (125 mg); $[\alpha]_D^{20}$ −4.8 (*c* 1.2, MeOH); R_f 0.59 (3:2 $CHCl_3$/EtOH); IR (KBr): ν 3353 (OH), 2928 (ν_{asym} CH_2), 2856 (ν_{sym} CH_2), 1710 (C=O *carboxylic*); ^{1}H NMR (CD_3OD): δ 7.93 (s, 1H, H-*triazol*), 5.54 (d, 1H, $J_{1'',2''}$ 9.2 Hz, H-1″β *glc*), 3.87 (t, 1H, $J_{2'',1''}$ 8.8 Hz, H-2″ *glc*), 3.87 (dd, 1H, $J_{6''a,5''}$ 2.2 Hz, $J_{6''a,6''b}$ 12.4 Hz, H-6″a *glc*), 3.70 (dd, 1H, $J_{6''b,5''}$ 5.4 Hz, $J_{6''b,6''a}$ 12.2 Hz, H-6″b *glc*), 3.54 (t, 1H, $J_{3'',4''}$ 8.8 Hz, H-3″ *glc*), 3.56 (ddd, 1H, $J_{5'',6''b}$ 2.3 Hz, $J_{5'',6''a}$ 4.3 Hz, $J_{5'',4''}$ 10.3 Hz, H-5″ *glc*), 3.48 (t, 1H, $J_{4'',3''}$ 9.2 Hz, H-4″ *glc*), 2.71 (t, 2H, *J* 7.6 Hz, H-2), 2.27 (t, 2H, *J* 7.4 Hz, H-9), 1.68 (quint, 2H, *J* 7.1 Hz, H-3), 1.59 (quint, 2H, *J* 7.0 Hz, H-8), 1.34 (m, 8H, H-4 to H-7); ^{13}C NMR (CD_3OD): *triazol*: 149.3 (*C*=CH *triazol*), 122.5 (C=*C*H *triazol*), *glucose*: 89.6 (C-1″), 81.2 (C-5″), 78.6 (C-3″), 74.0 (C-2″), 70.9 (C-4″), 62.4 (C-6″), *carboxylic alkyl chain*: 177.7 (*C*OOH), 35.0 (C-9), 30.5 (C-3), 30.3, 30.2, 30.1 (C-4 to C-7), 26.3 (C-2), 26.1 (C-8); MS (CI): *m*/*z* 410.2 $[M+Na]^+$, 388.3 $[M+H]^+$.

5.13. 11-{4′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-[1′,2′,3′]-triazol-1′-yl}-undecan-1-oic acid (24)

Commercially available peracetylated propynyl-β-D-glucose (306 mg, 0.79 mmol), 1.2 equiv of compound **23** (216 mg, 0.95 mmol) and 0.5 equiv copper II acetate (79 mg, 0.4 mmol) were dissolved in 0.7 mL of *tert*-butanol, and stirred at room temperature. Then, 1 equiv sodium ascorbate (158 mg, 0.8 mmol) solubilized in 0.7 mL of distillated water was added to the mixture. After 26 h of stirring, the crude was solubilized with 5 mL $CHCl_3$ and washed with 5 mL of water acidified with 1 M HCl (1 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated. The residue was purified by preparative TLC (93:7 $CHCl_3$/MeOH) yielding **24** as a yellow oil (208 mg, 43%); $[\alpha]_D^{20}$ −11.9 (*c* 1.1, $CHCl_3$); R_f 0.49 (93:7 $CHCl_3$/MeOH); IR (KBr): ν 2931 (ν_{asym} CH_2), 2856 (ν_{sym} CH_2), 1756 (C=O*acetyl*), 1706 (C=O*carboxylic*); ^{1}H NMR ($CDCl_3$): δ ^{1}H NMR ($CDCl_3$): δ 7.52 (s, 1H, H-*triazol*), 5.20 (t, 1H, $J_{3'',4''}$ 9.5 Hz, H-3″ *glc*), 5.09 (t, 1H, $J_{4'',3''}$ 9.7 Hz, H-4″ *glc*), 5.01 (t, 1H, $J_{2'',3''}$ 8.7 Hz, H-2″ *glc*), 4.93 (d, 1H, $J_{\alpha,\beta}$ 12.3 Hz, H-a *oxymethyl*), 4.83 (d, 1H, $J_{\beta,\alpha}$ 12.1 Hz, H-b *oxymethyl*), 4.69 (d, 1H, $J_{1'',2''}$ 7.9 Hz, H-1″β *glc*), 4.35 (t, 2H, $J_{11,10}$ 7.2 Hz, H-11), 4.27 (dd, 1H, $J_{6''a,5''}$ 4.6 Hz, $J_{6''a,6''b}$ 12.3 Hz, H-6″a *glc*), 4.15 (dd, 1H, $J_{6''b,5''}$ 1.6 Hz, $J_{6''b,6''a}$ 12.2 Hz, H-6″b *glc*), 3.73 (ddd, 1H, $J_{5'',6''b}$ 2.1 Hz, $J_{5'',6''a}$ 4.4 Hz, $J_{5'',4''}$ 9.9 Hz, H-5″ *glc*), 2.34 (t,

2H, *J* 7.4 Hz, H-2), 2.11, 2.02, 1.99, 1.98 (s, 12H, acetyl), 1.89 (m, 2H, H-10), 1.64 (m, 2H, H-3), 1.40 (m, 12H, H-4 to H-9); ^{13}C NMR ($CDCl_3$): *triazol*: 144.1 (*C*=CH *triazol*), 122.6 (C=*C*H *triazol*), *glucose*: 99.9 (C-1″), 72.8 (C-3″), 71.9 (C-5″), 71.3 (C-2″), 68.3 (C-4″), 61.8 (C-6″), *carboxylic alkyl chain*: 178.1 (*C*OOH), 63.0 (*C*H$_2$ *oxymethyl*), 50.4 (C-11), 33.8 (C-2), 30.2 (C-10), 29.1, 29.0, 28.9, 28.8, 26.4 (C-4 to C-9), 24.7 (C-3), *acetyl groups*: 170.7, 170.2, 169.5, 169.4 (CO), 20.8, 20.65, 20.6 (CH_3); MS (CI): *m*/*z* 649.4 $[M+K]^+$, 636.4 $[M+Na]^+$, 614.3 $[M+H]^+$.

5.14. 11-{4′-(β-D-Glucopyranosyloxymethyl)-[1′,2′,3′]-triazol-1′-yl}-undecan-1-oic acid (25)

Deacetylation of compound **24** (203 mg, 0.33 mmol) in 2 mL of a methanolic soln of ammonia (7 N) for 5 days afforded **25** as a white foam in 97% yield (144 mg); $[\alpha]_D^{20}$ −23.4 (*c* 1.2, MeOH); R_f 0.49 (3:7 $CHCl_3$/EtOH); IR (KBr): ν 3340 (OH), 2922 (ν_{asym} CH_2), 2852 (ν_{sym} CH_2), 1717 (C=O*carboxylic*); ^{1}H NMR (DMSO-d_6): δ 8.10 (s, 1H, H-*triazol*), 4.83 (d, 1H, $J_{\alpha,\beta}$ 12.2 Hz, H-a *oxymethyl*), 4.63 (d, 1H, $J_{\beta,\alpha}$ 12.2 Hz, H-b *oxymethyl*), 4.32 (t, 2H, $J_{11,10}$ 7.1 Hz, H-11), 4.24 (d, 1H, $J_{1'',2''}$ 7.8 Hz, H-1″β *glc*), 3.71 (dd, 1H, $J_{6''a,5''}$ 1.6 Hz, $J_{6''a,6''b}$ 11.7 Hz, H-6″a *glc*), 3.46 (dd, 1H, $J_{6''b,5''}$ 6.1 Hz, $J_{6''b,6''a}$ 11.7 Hz, H-6″b *glc*), 3.14 (t, 1H, $J_{4'',3''}$ 8.8 Hz, H-4″ *glc*), 3.13 (m, 1H, H-5″ *glc*), 3.05 (t, 1H, $J_{3'',4''}$ 9.1 Hz, H-3″ *glc*), 2.98 (t, 1H, $J_{2'',1''}$ 8.3 Hz, H-2″ *glc*), 2.71 (t, 2H, *J* 7.3 Hz, H-2), 1.79 (quint, 2H, $J_{10,11}$ 7.1 Hz, H-10), 1.47 (quint, 2H, *J* 6.7 Hz, H-3), 1.24 (m, 12H, H-4 to H-9); ^{13}C NMR (DMSO-d_6): *triazol*: 145.7 (*C*=CH *triazol*), 125.3 (C=*C*H *triazol*), *glucose*: 103.7 (C-1″), 78.1 (C-3″), 75.08 (C-2″), 71.7 (C-5″), 70.1 (C-4″), 62.8 (C-6″), *carboxylic alkyl chain*: 178.3 (*C*OOH), 63.1 (*C*H$_2$ *oxymethyl*), 51.4 (C-11), 35.4 (C-2), 31.3 (C-10), 30.5–30.4–30.3–30.1–27.5 (C-4 to C-9), 26.3 (C-3); MS (CI): *m*/*z* 468.2 $[M+Na]^+$, 446.1 $[M+H]^+$.

5.15. 1,12-Bis-{4′-(2″,3″,4″,6″-tetra-*O*-acetyl-β-D-glucopyranosyloxymethyl)-1′H-[1′,2′,3′]-triazol-1′-yl}-dodecane (27)

Diazido compound **26** (93.5 mg, 0.37 mmol) and 2.4 equiv of commercially available peracetylated propynyl-β-D-glucose (342 mg, 0.88 mmol) were dissolved in 0.7 mL of *tert*-butanol and stirred at room temperature. Then, 0.5 equiv of copper II acetate (37.4 mg, 0.19 mmol) and sodium ascorbate (74.3 mg, 0.375 mmol) solubilized in 0.7 mL of distilled water, were added to the mixture. After 25 h of stirring, the crude was purified, without work-up, by preparative TLC (96:4 $CHCl_3$/EtOH) yielding **27** as a yellow foam (201 mg, 53%); $[\alpha]_D^{20}$ −18.3 (*c* 1.1, $CHCl_3$); R_f 0.53 (96:4 $CHCl_3$/EtOH); IR (KBr): ν 2930 (ν_{asym} CH_2), 2857 (ν_{sym} CH_2), 1756 (C=O*acetyl*); ^{1}H NMR ($CDCl_3$): δ ^{1}H NMR ($CDCl_3$): δ 7.50 (s, 2H, H-*triazol*), 5.20 (t, 2H, $J_{3'',4''}$ 9.4 Hz, H-3″ *glc*), 5.09 (t, 2H, $J_{4'',3''}$ 9.6 Hz, H-4″ *glc*), 5.01 (dd, 2H, $J_{2'',1''}$ 8.0 Hz, $J_{2'',3''}$ 9.4 Hz, H-2″ *glc*), 4.94 (d, 2H, $J_{\alpha,\beta}$ 12.6 Hz, H-a *oxymethyl*), 4.83 (d, 2H, $J_{\beta,\alpha}$ 12.5 Hz, H-b *oxymethyl*), 4.69 (d, 2H, $J_{1'',2''}$ 7.9 Hz, H-1″β *glc*), 4.33 (t, 4H, *J* 7.2 Hz, H-1 and H-12), 4.27 (dd, 2H, $J_{6''a,5''}$ 4.8 Hz, $J_{6''a,6''b}$ 12.3 Hz, H-6″a *glc*), 4.15 (dd, 2H, $J_{6''b,5''}$ 2.3 Hz, $J_{6''b,6''a}$ 12.3 Hz, H-6″b *glc*), 3.74 (ddd, 2H, $J_{5'',6''b}$ 2.3 Hz, $J_{5'',6''a}$ 4.7 Hz, $J_{5'',4''}$ 9.9 Hz, H-5″ *glc*), 2.09, 2.03, 1.99, 1.98 (s, 12H, acetyl), 1.89 (quint, 4H, *J* 6.5 Hz, H-2 and H-11), 1.32 (m, 8H, H-3, H-4, H-9 and H-10), 1.25 (m, 8H, H-5 to H-8); ^{13}C NMR ($CDCl_3$): *triazol*: 144.1 (*C*=CH *triazol*), 122.5 (C=*C*H *triazol*), *glucose*: 99.9 (C-1″), 72.8 (C-3″), 71.9 (C-5″), 71.3 (C-2″), 68.3 (C-4″), 61.8 (C-6″), *alkyl chain*: 63.1 (*C*H$_2$ *oxymethyl*), 50.4 (C-1 and C-12), 30.3 (C-2 and C-11), 29.4 (C-5 and C-8), 29.3 (C-6 and C-7), 29.0 (C-4 and C-9), 26.5 (C-3 and C-10), *acetyl groups*: 170.6 (CO of C-6), 170.2 (CO of C-3), 169.44 (CO of C-4), 169.36 (CO of C-2), 20.8 (CH_3 of C-6), 20.7 (CH_3 of C-2), 20.6 (CH_3 of C-3 and C-4); MS (CI): *m*/*z* 1063.5 $[M+K]^+$, 1047.5 $[M+Na]^+$, 1025.5 $[M+H]^+$.

5.16. 1,12-Bis-{4′-(β-D-glucopyranosyloxymethyl)-1′H-[1′,2′,3′]-triazol-1′-yl}-dodecane (28)

Deacetylation of compound **27** (63 mg, 0.0615 mmol) in 2 mL of a methanolic soln of ammonia (7 N) for 5 days afforded **28** as a white foam in quantitative yield (52 mg); $[\alpha]_D^{20}$ −25.0 (*c* 0.5, MeOH); R_f 0.31 (3:7 $CHCl_3$/EtOH); IR (KBr): ν 3347 (OH), 2923 (ν_{asym} CH_2), 2849 (ν_{sym} CH_2); ^{1}H NMR (DMSO-d_6): δ 8.10 (s, 2H, H-*triazol*), 5.00 (d, 2H, *J* 4.9 Hz, O*H-glc2*″), 4.92 (d, 2H, *J* 4,8 Hz, O*H-glc*3″), 4.90 (d, 2H, *J* 5.2 Hz, O*H-glc4*″), 4.82 (d, 2H, $J_{\alpha,\beta}$ 12.2 Hz, H-a *oxymethyl*), 4.62 (d, 2H, $J_{\beta,\alpha}$ 12.2 Hz, H-b *oxymethyl*), 4.55 (t, 2H, *J* 5.9 Hz, O*H-glc*6″),4.32 (t, 4H, *J* 7.1 Hz, H-1 and H-12), 4.24 (d, 2H, $J_{1'',2''}$ 7.8 Hz, H-1″β *glc*), 3,71 (ddd, 2H, $J_{5'',4''}$ 1.6 Hz, $J_{5'',6''a}$ 6.1 Hz, $J_{5'',6''b}$ 11.6 Hz, H-5″ *glc*), 3.45 (quint, 2H, *J* 5.9 Hz, H-6″a *glc*), 3.14 (m, 2H, H-6″b *glc*), 3.13 (dt, 2H, $J_{3'',OH}$ 5.2 Hz, $J_{3'',4''}$ 8.6 Hz, H-3″ *glc*), 3.04 (dt, 1H, $J_{4'',OH}$ 5.2 Hz, $J_{4'',3''}$ 9.0 Hz, H-3″ *glc*), 2.97 (dt, 2H, $J_{2'',OH}$ 5.0 Hz, $J_{2'',1''}$ 8.3 Hz, H-2″ *glc*), 1.79 (quint, 4H, *J* 7.2 Hz, H-2 and H-11), 1.24 (m, 16H, H-3 to H-10); ^{13}C NMR (DMSO-d_6): *triazol*: 143.7 (*C*=CH *triazol*), 124.0 (C=*C*H *triazol*), *glucose*: 102.1 (C-1″), 76.9 (C-3″), 76.7 (C-5″), 73.4 (C-2″), 70.1 (C-4″), 61.2 (C-6″), *alkyl chain*: 61.5 (*C*H$_2$ *oxymethyl*), 49.2 (C-1 and C-12), 29.7 (C-2 and C-11), 28.9 (C-5 and C-8), 28.8 (C-6 and C-7), 28.4 (C-4 and C-9), 25.8 (C-3 and C-10); MS (CI): *m*/*z* 727.4 $[M+K]^+$, 711.3 $[M+Na]^+$.

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