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Synthesis and properties of new bolaform and macrocyclic galactose-based surfactants obtained by olefin metathesis

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Abstract—A series of galactose-based surfactants with various structures likely to display new interesting properties were synthesized. Four monocatenary surfactants were elaborated by microwave-assisted galactosylation of undecanol or 10-undecenol. These compounds were slightly soluble in water. Their tensioactive properties were determined at 45 °C. Olefin metathesis was used to synthesize the two single-chain bolaforms from undec-10-enyl galactopyranosides; two pseudomacrocyclic bolaforms were prepared by grafting two carbamates at O-4 and O-4′ sugar positions of the single-chain bolaforms. These four surfactants are insoluble in water and undergo monolayer compression. Cyclization of these bolaforms by olefin metathesis led to macrocyclic surfactant analogues of archaeobacterial membrane components.

Keywords: Surfactant; Bolaform; Metathesis; Microwave

1. Introduction

Because of their well-defined chemical composition, their natural origin and biodegradability, as well as their non-denaturing properties, sugar-based nonionic surfactants are interesting additives for use in cosmetic, pharmaceutic and food industries.[1] We now report on galactose-based surfactants with varied structures likely to display new interesting properties. This series of nine surfactants is composed of monocatenary molecules and five bolaforms of three different kinds: single chain, pseudomacrocyclic and macrocyclic (Fig. 1). Monocatenary surfactants could be used as emulsifiers in food and cosmetics. Bolaform surfactants, which are composed of two hydrophilic heads linked by one or several hydrophobic chains, are known to promote the formation of

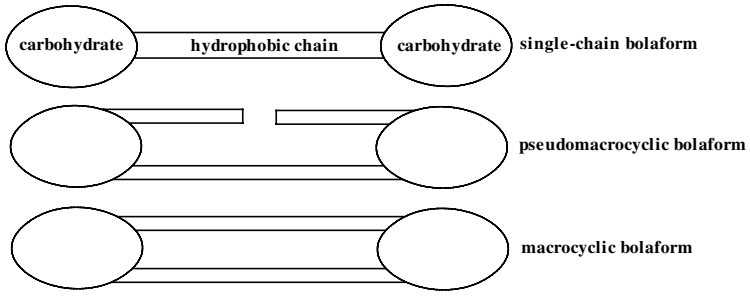

Figure 1. Bolaform surfactant.

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ultrathin monolayer membranes.[2] As a consequence, the bolaforms that we synthesized could be used as encapsulating agents. Moreover, an interesting property of many bolaforms is their ability to intercalate into lipidic membranes; depending on their structure, bolaforms can act either as membrane disturbing agents or as membrane stabilizers. Due to the high reactivity and remarkable functional group tolerance of the new Grubbs' ruthenium catalysts, olefin metathesis[3–5] has recently received a great deal of interest for the synthesis of complex molecules. In this paper, we used the homodimerization reaction[6–9] for the building of bolaform surfactants based on α- and β-galactosides. We also used ring closing metathesis to form the macrocyclic bolaform.

2. Results and discussion

In the present work, we synthesized a series of galactose-based surfactants composed of four monocatenary surfactants (**3a**,**b** and **8a**,**b**),[10–13] two single-chain bolaforms (**7a**,**b**), two pseudomacrocyclic bolaforms (**15a**,**b**) and one macrocyclic bolaform (**16**) (Fig. 2). All of these products are anomerically pure.

2.1. Syntheses

2.1.1. Synthesis of monocatenary surfactants 3a,b and 8a,b (Scheme 1). We first proceeded to galactosylation of saturated or ω-unsaturated fatty alcohols (compounds **2a**,**b** and **4a**,**b**). Among the numerous methods described in the literature,[14–16] we chose that of Limousin et al.[17] using microwave irradiation. This solvent-free reaction is carried out with a peracetylated carbohydrate **1** and undecanol or ω-undecenol in the presence of zinc chloride. The best yields (about 90%) were obtained with 2.5 equiv of alcohol and 2.1 equiv of zinc chloride. The mixtures were irradiated during 2 min at 90 W strength in the case of undecanol and 60 W in the case of ω-undecenol. Excess alcohol hampered the purification of the crude galactosides; so the remaining fatty alcohols were acetylated with acetic anhydride and *N*,*N*-

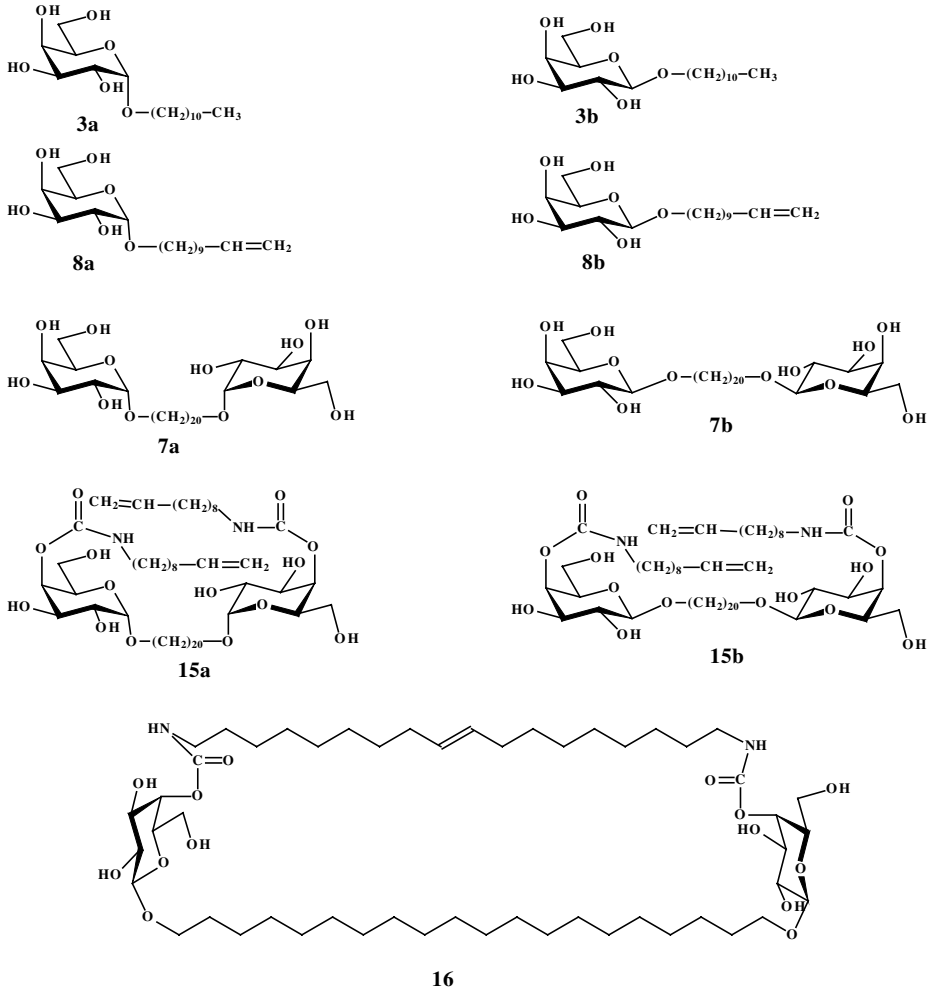
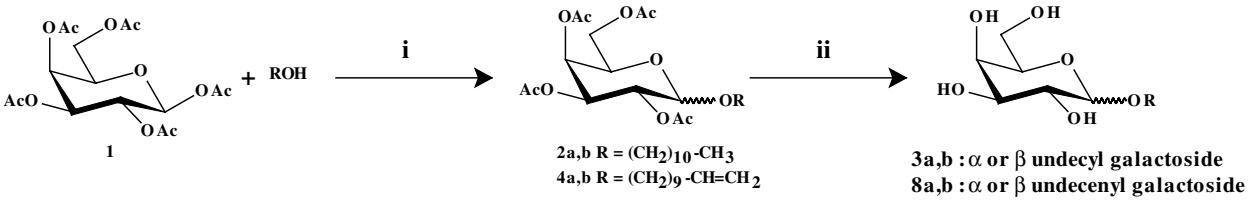


Figure 2. Galactose-based surfactants (a and b refer to α and β compounds, respectively).



Scheme 1. Preparation of monocatenary surfactants. Reagents and conditions: (i) $ZnCl_2$, microwave [**2a**: 60%, **2b**: 29% ($\alpha/\beta = 2.0$), **4a**: 46%, **4b**: 46% ($\alpha/\beta = 1.0$)]; (ii) MeONa, MeOH–CH_2Cl_2 1:1 (**3a**: 90%, **3b**: 65%, **8a**: 74%, **8b**: 79%).

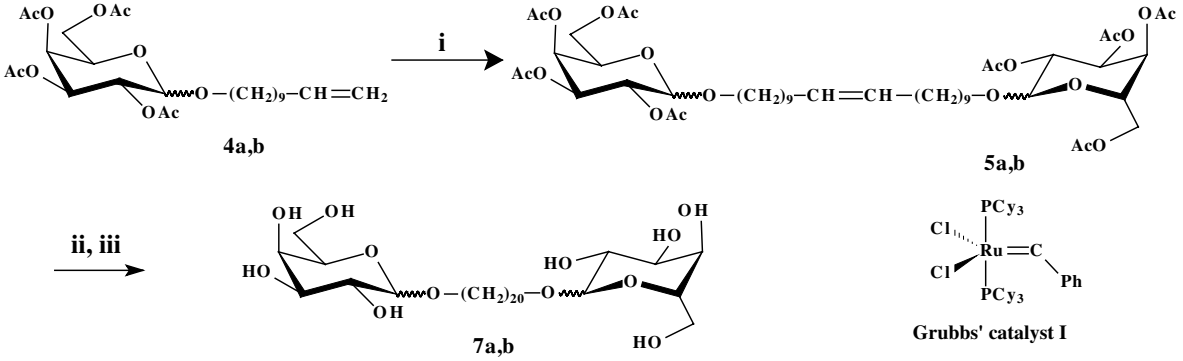
dimethyl-4-aminopyridine (DMAP). After separation on silica gel column, the two anomers were obtained with anomeric ratios α/β between 1:1 and 2:1 (^{1}H NMR).

Each of the four peracetylated galactosides (**2a**,**b** and **4a**,**b**) were deacetylated with sodium methoxide in methanol–dichloromethane. The yields varied from 65% to 90%.

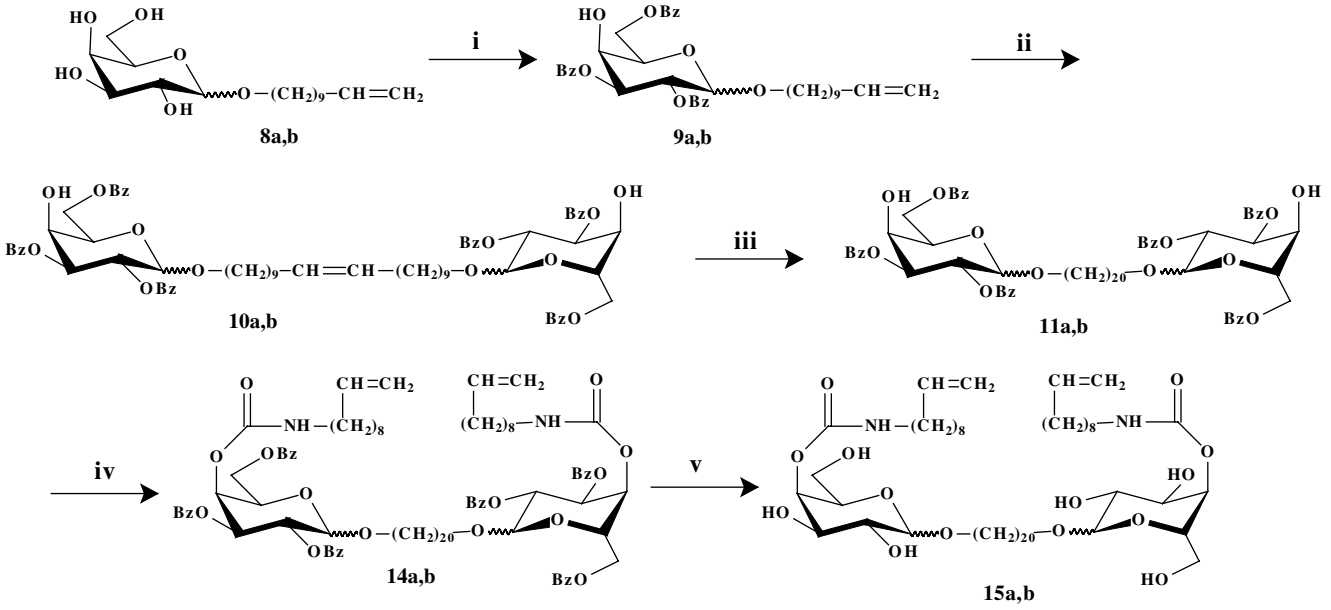
2.1.2. Synthesis of single-chain bolaform surfactants 7a,b. These compounds were obtained by homodimerization of **4a**,**b** followed by catalytic hydrogenation of the olefinic disaccharides (Scheme 2). We proceeded to homodimerization of α and β peracetylated ω-undecenyl-D-galactopyranosides **4a**,**b** by olefin metathesis in the presence of Grubbs' catalyst I. The reactions were conducted with catalyst proportions close to 10% (mol mol^{-1}). Dimeric compounds were obtained in 83% yield. The ^{1}H NMR spectra showed the disappearance of the external double bond signals at 4.95 and 5.81 ppm and the appearance of two new signals at 5.34 and 5.38 ppm for internal *Z* and *E* double bonds, respectively. The *E*/*Z* ratio was 1:3 for α-galactosides **5a** and of 1:6 for β-galactosides **5b**. Catalytic hydrogenation of the double bond was carried out with rhodium on alumina as catalyst. In these conditions, the saturated products **6a**,**b** were obtained with quasi-quantitative yields. NMR spectra showed the disappearance of the ethylenic protons. Deacetylations of these molecules were carried out with sodium methoxide in methanol–dichloromethane to give **7a**,**b** in almost quantitative yields.

2.1.3. Synthesis of pseudomacrocyclic bolaform surfactants 15a,b. In order to synthesize the pseudomacrocyclic compounds **15a** and **15b**, we proceeded to a selective benzoylation of the hydroxyl groups at C-2, C-3 and C-6[18] before dimerization. The reactions were carried out in pyridine at −30 °C and with 4.2 equiv of benzoyl chloride during 20 min (Scheme 3). α-Galactoside **9a** was obtained with 66% yield while the β-galactoside **9b** was obtained with only 35% yield. The lower reactivity of OH-4[18] generally observed in galactosides is thus more pronounced with the α than with the β anomer. NMR spectra showed the appearance of 15 aromatic protons accounting for the three benzoyl groups and the deshielding of the carbohydrate moiety. In order to check that the free hydroxyl is actually at C-4, we analyzed the differences between perbenzoylated and tribenzoylated products **9a**,**b**. The most important difference is observed for H-4. The homodimerization reaction was carried out as described above and the products **10a** and **10b** were obtained in 80% and 77% yield, respectively. In the same way, catalytic hydrogenation was achieved with rhodium on alumina and led to products **11a** and **11b** with yields of 86% and 88%, respectively.

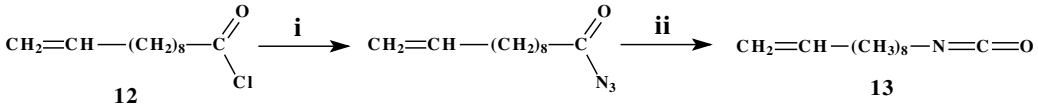
The method of Wathier et al.[19] was used for the preparation of ω-decenyl isocyanate **13**. The corresponding acyl azide was formed by reaction of sodium azide with ω-undecenyl chloride **12** at 10 °C (Scheme 4). Then, the medium was heated and a Curtius rearrangement took place to form compound **13** with 45% yield.



Scheme 2. Single-chain bolaforms preparation. Reagents and conditions: (i) Grubbs' catalyst I (10%), degassed CH_2Cl_2 (83%); (ii) Rh/Al_2O_3, H_2 (atm pressure), abs EtOH (100%); (iii) MeONa, 1:1 MeOH–CH_2Cl_2 (95%).



Scheme 3. Pseudomacrocyclic bolaforms preparation. Reagents and conditions: (i) BzCl (4.2 equiv), anhyd pyridine, ≈−30 °C (**9a** 66%, **9b** 35%); (ii) Grubbs' catalyst I (9%), degassed CH_2Cl_2 (≈80%); (iii) Rh/Al_2O_3, H_2, abs EtOH (≈87%); (iv) **13**, DABCO, anhyd toluene, 110 °C (≈75%); (v) MeONa, 10:1 MeOH–CH_2Cl_2 (≈36%).



Scheme 4. Isocyanate formation. Reagents and conditions: (i) NaN_3, 10:1 acetone–water, 10 °C; (ii) Δ (global yield = 45%).

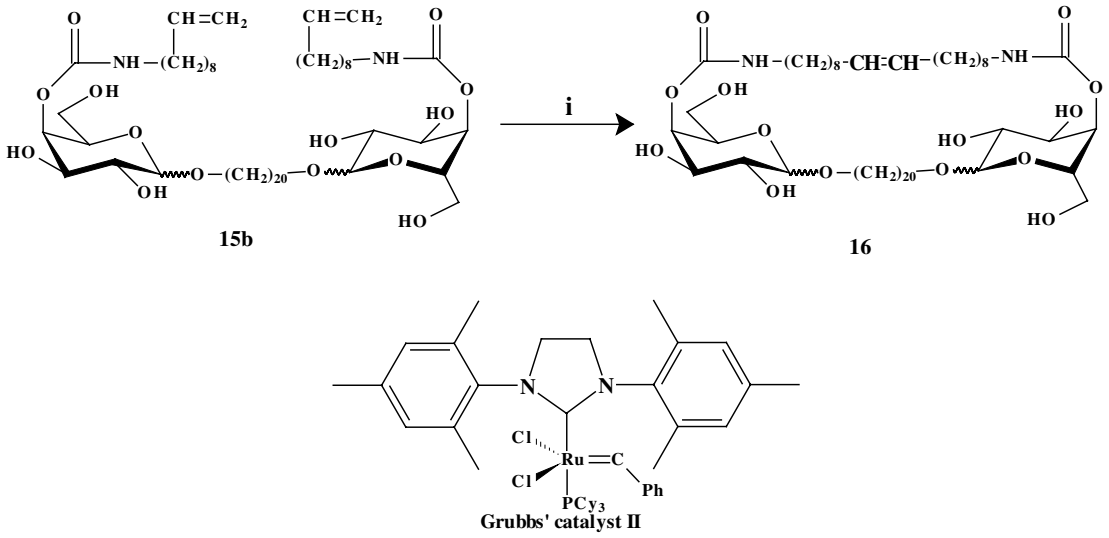
The next step consisted in the coupling reaction of isocyanate **13** and the selectively protected glycosides **11a** and **11b**, in order to obtain dicarbamates[19] **14a**,**b**. Generally, the reaction of an isocyanate and an alcohol requires the presence of a strong base. However, the presence of benzoyl groups restricted the number of usable bases. For this reason, we decided to use diazabicyclooctane (DABCO) since it does not split ester bonds. The reaction took place in refluxing toluene at pH 9 (Scheme 3). Compounds **14a** and **14b** were obtained with 79% and 70% yield, respectively. In each case, ^1H NMR spectra showed the appearance of a new terminal double bond.

Removal of benzoyl groups was carried out with sodium methoxide in 10:1 methanol–dichloromethane (Scheme 3). The moderate yields (31% and 44% for **15a** and **15b**, respectively) can be accounted for by the weak difference in reactivity between benzoyl and carbamate groups. The corresponding ^1H NMR spectra showed the expected shielding of the carbohydrate part.

2.1.4. Cyclization. In order to obtain macrocyclic bolaforms, we proceeded to ring closing metathesis (RCM) of compounds **15a** and **15b** (Scheme 5). In this reaction, the second generation Grubbs' catalyst was used because the first generation catalyst is sensitive to NH functions. The aim of this methodology was to favour RCM instead of acyclic diene metathesis (ADMet) polymerization. Attempts to perform RCM macrocyclization of **15a** at the water–toluene interphase, in the presence of dodecyl sulfate, were unsuccessful. Instead, we decided to cyclize the β anomer (**15b**) in 8:1 dichloromethane–methanol with 1.3 equiv of Grubbs' catalyst II during 69 h. NMR and HRMS analyses were consistent with the structure of the expected macrocycle **16**, which was finally obtained in 33% yield.

2.2. Tensioactive properties

We first determined the water solubility of each surfactant. All bolaform molecules (single chain **7a** and **7b** and pseudomacrocycles **15a** and **15b**) are insoluble even in boiling water. However, all galactosides (**3a**, **3b**, **8a** and **8b**) are partially water soluble. Saturated products are less soluble than unsaturated ones (Fig. 3) and in each case, the solubilities of the β galactosides are higher than their α counterparts. These results are in accordance with the literature.[20] Krafft points were deduced from



Scheme 5. Macrocyclization by RCM. Reagents and conditions: (i) Grubbs' catalyst II (1.3 equiv), degassed 8:1 CH_2Cl_2–MeOH (33%).

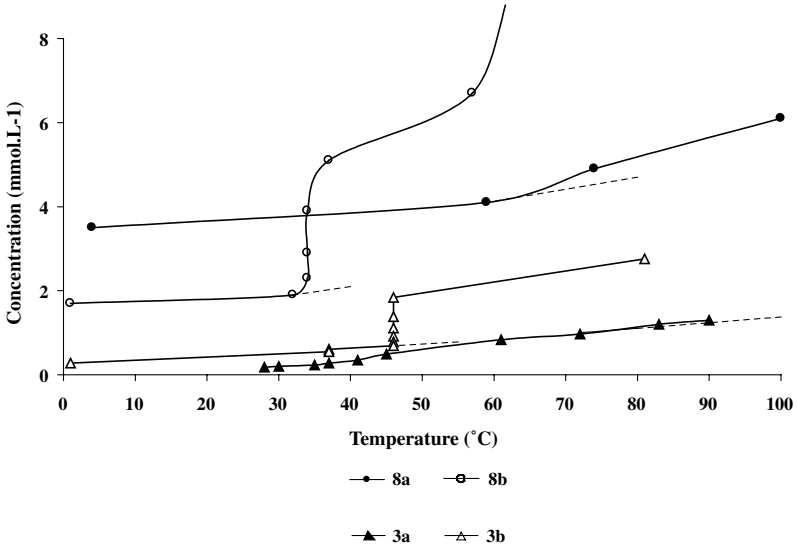


Figure 3. Water solubility of undecyl and undecylenyl galactosides.

the graphs concentration versus temperature. These values were higher for α anomers as compared to β anomers, as well as for saturated galactosides compared to unsaturated ones (Table 1).

Galactoside micellization was studied at 45 °C by surface tension measurements. According to this method, the critical micellar concentration (CMC) is equal to the ordinate of the angular point of the curve 'surface tension versus log *C*' (Fig. 4). These values that lie between 0.45 and 3.70 mmol L^{-1}, are in accordance with the literature (CMC = 1.6 mmol L^{-1} for decyl β-glucopyranoside).[21] CMC are much lower for saturated galactosides than for unsaturated ones (Table 2).

Table 1. Galactoside Krafft points

Galactoside	Krafft point (°C)
3a	76
3b	46
8a	64
8b	32

The surface excess [Γ (mol m^{-2})] is calculated from Gibbs' equation 1.

$$\Gamma = -\frac{10^{-3}}{2.3RT}\frac{d\gamma}{d\log C}, \quad (1)$$

in which γ (mN m^{-1}) is the surface tension, T, the temperature (K) and C, the concentration (mol L^{-1}).

The area per molecule [A (Å^2)] is calculated from Eq 2.

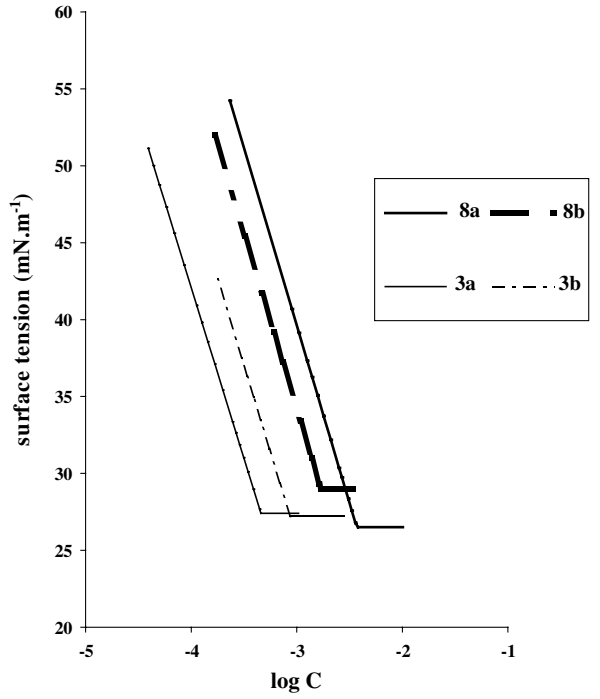


Figure 4. Surface tension of galactosides at 45 °C.

$$A = \frac{10^{20}}{N\Gamma}, \qquad (2)$$

where N is the Avogadro number. Surface excess and area per molecule are similar for the four galactosides; galactose configuration has no influence on these values. The minimal tensions are lower than 30 mN m^{-1}. These results are in accordance with the literature.[1,20]

Bolaforms and pseudomacrocyclic surfactants (**7a**, **7b**, **15a** and **15b**), which are insoluble in water, were studied for their monolayer properties on a home-made Langmuir trough (Fig. 5). The minimum area per molecule and the collapsed pressure were deduced from these data (Table 3). On the one hand α and β single-chain bolaforms display the same expanded film behaviour. Their minimum area per molecule is close to 150 Å^2. On the other hand, α and β pseudomacrocyclic bolaforms behave very differently: the β anomer is a condensed film ($A = 102$ Å^2) and the α anomer is a expanded film ($A = 175$ Å^2).

3. Experimental

3.1. General methods

All reagents used were commercially available and with high purity grade. The microwave reactor was a Synthewave® 402 (Prolabo). TLC were realized with Silica Gel 60F$_{254}$ (direct phase) or RP-18F$_{254}$ (reversed phase) (E. Merck). Direct phase chromatography column was conducted with Silica Gel MCL-CHROM 15–40 μm (E. Merck). Reversed phase medium pressure chromatography column was performed on a Jobin Yvon Miniprep LC apparatus with Li Chrosorb® RP-18 10 μm phase (E. Merck).

Table 2. Surface properties of galactosides

	CMC (mmol L^{-1})	Surface excess Γ (mol m^{-2})	Molecular area (Å^2)	Minimum surface tension (mN m^{-1})
8a	3.70	3.90×10^{-6}	43	26.8
8b	1.66	3.85×10^{-6}	43	29.0
3a	0.45	3.75×10^{-6}	45	27.4
3b	0.80	4.03×10^{-6}	42	27.2

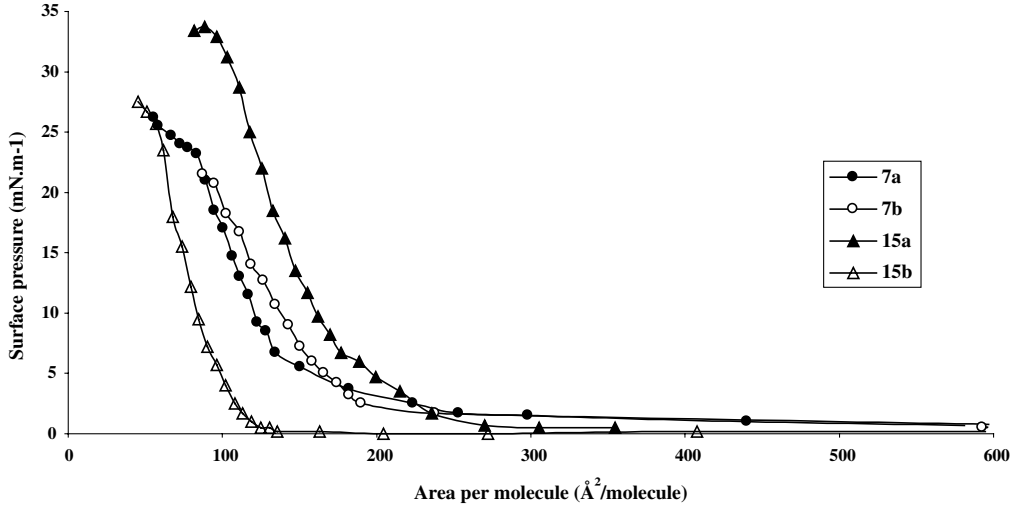


Figure 5. Compression isotherms of bolaforms and geminis.

Table 3. Data from compression isotherms for single chain and pseudomacrocyclic bolaforms

Compound	Collapsed pressure ($mN\,m^{-1}$)	Minimum area A_0 (Å^2)
7a	22	141
7b	20	158
15a	31	175
15b	26	102

Melting points were measured on a Leica VM HB system Köfler, NMR spectroscopy was performed with a Bruker DPX-400 MHz apparatus, IR spectrometry used a Perkin Elmer FT-IR Spectrometer SPECTRUM 1000, $[\alpha]_D^{20}$ were measured with a JASCO DIP-370 Digital Polarimeter, mass spectra using electrospray ionization were obtained at the Museum National d'Histoire Naturelle (ESA 8041 CNRS) with a Perkin Elmer Q TOF SCIEX apparatus, high resolution mass spectra with electrospray ionization were realized at the 'Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes', with a Varian MAT311 high resolution spectrometer, elemental analyses were performed at the SIARE (Université Pierre et Marie Curie, Paris V) or at the Service Central d'Analyse (CNRS, Vernaison).

All surfactants, except pseudomacrocyclic bolaforms, were purified on reverse phase medium pressure chromatography column before tensioactive properties determination. Solubilities were measured by using solutions with defined concentrations. Temperature was controlled with a Grant Y6 thermostat. Surface tensions were measured with a Dognon Abribat tensiometer (Prolabo). The Wilhelmy plate method was used (Pt plate $L = 1.955$ cm, $e = 0.010$ cm). Compression isotherms were performed in a home-made rectangular Teflon® trough (ca. 13.7×12.5 cm) with a movable Teflon® barrier. Each result is the average of three independent experiments.

3.2. Syntheses

3.2.1. Undecyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (2a) and undecyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (2b). Galactose pentaacetate **1** (2.2 g, 5.8 mmol) and $ZnCl_2$ (1.7 g, 12 mmol) were crushed together and undecanol (3 mL, 14 mmol) was added. The medium was activated by microwave irradiation (2 min, 90 W). It was diluted in EtOAc (100 mL) and suction filtered. After evaporation of the solvent, DMAP (0.06 g, 1.7 mmol) and Ac_2O (3 mL, 203 mmol) were added and the medium was activated by microwave irradiation (1 min, 15 W then 14 min, 6 W), neutralized (solid $NaHCO_3$) and extracted with $CHCl_3$. The organic solution was washed with water, dried ($MgSO_4$) and purified by column chromatography (4:1 petroleum ether–EtOAc) to give in the order of elution **2a** (1.8 g) and **2b** (0.8 g) as yellow oils (89%); **2a**: $[\alpha]_D^{20}$ +86.0 (*c* 3.44, $CHCl_3$); R_f 0.33 (7:3 petroleum ether–EtOAc); IR (KBr): *v* 2920 (CH_3), 2849 (CH_2) and 1748 (ester); ^{1}H NMR ($CDCl_3$): δ 5.45 (dd, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ 1.0 Hz, H-4), 5.36 (m, 1H, H-1), 5.35 (m, 1H, H-2), 5.10 (m, 1H, H-3), 4.22 (te, 1H, $J_{5',6'}$ 6.8 Hz, H-5), 4.11 (m, 2H, H-6), 3.68 (dt, 1H, $J_{1'a,2'}$ 6.6, $J_{1'a,1'b}$ 9.8 Hz, H-1′a), 3.42 (dt, 1H, $J_{1'b,2'}$ 6.6, $J_{1'a,1'b}$ 9.8 Hz, H-1′b), 1.9–2.2 (s, 12H, acetyl), 1.59 (m, 2H, H-2′), 1.27 (m, 16H, H-3′–H-10′), 0.88 (t, 3H, $J_{10',11'}$ 6.6 Hz, H-11′); lit.[12] ($CDCl_3$): 5.49 (dd, *J* 9.4, 10.4 Hz, H-3), 5.46 (d, *J* 3.7 Hz, H-1), 5.06 (dd, *J* 3.6, 10.3 Hz, H-4), 4.86 (dd, *J* 3.9, 10.4 Hz, H-2), 4.20 (dd, *J* 2.4, 4.6, 12.2 Hz, H-6b), 4.13 (dd, *J* 2.4, 4.6, 12.2 Hz, H-6a), 4.02 (ddd, *J* 10.3, 4.8, 2.3 Hz, H-5), 3.67 (dt, *J* 9.6, 10.2, 6.9 Hz, H-1b′), 3.42 (dt, *J* 9.6, 10.2, 6.9 Hz, H-1a′), 2.02, 2.04, 2.06, 2.10 (4s, $OCOCH_3$), 1.60 (m, H-2′), 1.26 (m, H-3′–H-10′), 0.88 (t, *J* 6.4 Hz, H-11′); ESMS: *m*/*z* 525.19 $[M+K]^+$. Anal. Calcd for $C_{25}H_{42}O_{10}$: C, 59.74; H, 8.42. Found: C, 59.07; H, 8.77. **2b**: $[\alpha]_D^{20}$ +2.6 (*c* 0.80, $CHCl_3$); R_f 0.24 (7:3 petroleum ether–EtOAc); IR (KBr): *v* 2920 (CH_3), 2849 (CH_2) and 1753 (ester); ^{1}H NMR ($CDCl_3$): δ 5.39 (dd, 1H, $J_{3,4}$ 3.3, $J_{4,5}$ 0.8 Hz, H-4), 5.20 (dd, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.4 Hz, H-2), 5.02 (dd, 1H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 4.45 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.15 (m, 2H, H-6), 3.88 (m, 2H, H-5 and H-1′a), 3.47 (dt, 1H, $J_{1'b,2'}$ 6.8, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 1.9–2.2 (s, 12H, acetyl), 1.59 (m, 2H, H-2′), 1.26 (m, 16H, H-3′–H-10′), 0.88 (t, 3H, $J_{10',11'}$ 6.6 Hz, H-11′); lit.[12] ($CDCl_3$): δ 5.39 (dd, *J* 0.4, 3.4 Hz, H-4), 5.20 (dd, *J* 7.8, 10.5 Hz, H-2), 5.02 (dd, *J* 3.4, 10.5 Hz, H-3), 4.48 (d, *J* 7.8 Hz, H-1), 4.20 (dd, *J* 6.6, 11.3 Hz, H-6b), 4.12 (dd, *J* 6.6, 11.3 Hz, H-6a), 3.93 (ddd, *J* 1.0, 6.6, 6.6 Hz, H-5), 3.89 (dt, *J* 6.7, 10.3, 9.6 Hz, H-1b′), 3.48 (dt, *J* 6.7, 10.3, 9.6 Hz, H-1a′), 1.98, 2.05, 2.05, 2.15 (4s, $OCOCH_3$), 1.57 (m, H-2′), 1.27 (m, H-3′–H-10′), 0.88 (t, *J* 6.7 Hz, H-11′); ESMS: *m*/*z* 520.34 $[M+Na]^+$. Anal. Calcd for $C_{25}H_{42}O_{10}$: C, 59.74; H, 8.42. Found: C, 59.04; H, 8.70.

3.2.2. Undecyl α-D-galactopyranoside (3a). Compound **2a** (1.72 g, 3.4 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (50 mL). MeONa (13.5 mL) in MeOH (0.37 g, 6.8 mmol) was added. After 58 min neutralization with Amberlite IRN 77H$^+$ resin, filtration and evaporation yielded **3a** as a white solid (1.0 g, 3.1 mmol, 90%); mp 55 °C; $[\alpha]_D^{20}$ +114.0 (*c* 0.88, MeOH); R_f 0.55 (1:1 $CHCl_3$–EtOH); IR (KBr): *v* 3440 (alcohol), 2911 (CH_3) and 2849 (CH_2); ^{1}H NMR (CD_3OD): δ 4.80 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), 3.88 (m, 1H, H-3), 3.80 (m, 1H, H-5), 3.71 (m, 5H, H-2, H-4, H-6 and H-1′a), 3.43 (dt, 1H, $J_{1'b,2'}$ 6.5, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 1.63 (m, 2H, H-2′), 1.29 (m, 16H, H-3′–H-10′), 0.90 (t, 3H, $J_{10,11}$ 6.6 Hz, H-11′); ESMS: *m*/*z* 335.24 $[M+H]^+$. Anal.$^+$ Calcd for $C_{17}H_{34}O_6$: C, 61.05; H, 10.25. Found: C, 59.12; H, 10.16.

3.2.3. Undecyl β-D-galactopyranoside (3b). Deacetylation of **2b** (0.45 g, 0.9 mmol) as above afforded **3b** (0.2 g,

0.6 mmol, 65% yield) as a white solid; mp 72 °C; $[\alpha]_D^{20}$ −10.0 (*c* 1.02, MeOH); R_f 0.57 (5:5 $CHCl_3$–EtOH); IR (KBr): *v* 3354 (alcohol), 2920 (CH_3) and 2849 (CH_2); ^1H NMR (CD_3OD): δ 4.20 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 3.89 (dt, 1H, $J_{1'a,2'}$ 6.9, $J_{1'a,1'b}$ 9.5 Hz, H-1′a), 3.82 (d, 1H, $J_{4,5}$ 3.0 Hz, H-5), 3.73 (m, 2H, H-6), 3.53 (dt, 1H, $J_{1'b,2'}$ 6.7, $J_{1'a,1'b}$ 9.4 Hz, H-1′b), 3.47 (m, 3H, H-2, H-3 and H-4), 1.62 (quint, 2H, $J_{1',2',3'}$ 7.0 Hz, H-2′), 1.29 (m, 16H, H-3′–H-10′), 0.90 (t, 3H, $J_{10',11'}$ 6.6 Hz, H-11′); ESMS: *m/z* 335.23 $[M+H]^+$. Anal. Calcd for $C_{17}H_{34}O_6$: C, 61.05; H, 10.25. Found: C, 58.51; H, 10.08.

3.2.4. Undec-10-enyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (4a) and undec-10-enyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (4b). Galactose pentaacetate **1** (2.2 g, 5.8 mmol) and $ZnCl_2$ (1.6 g, 12 mmol) were crushed together and undecenol (2.9 mL, 14 mmol) was added. The medium was activated by microwave irradiation (2 min, 60 W). It was diluted into EtOAc (100 mL) and filtrated with suction. After evaporation of the solvent, DMAP (0.06 g, 1.7 mmol) and Ac_2O (3 mL, 203 mmol) were added and the medium was activated by microwave irradiation (1 min, 15 W then 14 min, 6 W), neutralized (solid $NaHCO_3$) and extracted with $CHCl_3$. The organic solution was washed with water, dried ($MgSO_4$) and purified by column chromatography (4:1 petroleum ether–EtOAc) to give **4a** (1.3 g) and **4b** (1.3 g) as yellow oils (89%); **4a**: $[\alpha]_D^{20}$ +64.3 (*c* 1.12, $CHCl_3$); R_f 0.31 (7:3 petroleum ether–EtOAc); IR (KBr): *v* 3018 (terminal olefin), 2920 (CH_3), 2849 (CH_2) and 1748 (ester); ^1H NMR ($CDCl_3$): δ 5.81 (m, 1H, H-10), 5.45 (de, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.35 (m, 1H, H-2), 5.11 (m, 1H, H-1), 5.09 (m, 1H, H-3), 4.95 (m, 2H, H-11′), 4.22 (te, 1H, $J_{5,6}$ 6.4 Hz, H-5), 4.10 (m, 2H, H-6), 3.68 (dt, 1H, $J_{1'a,2'}$ 6.6, $J_{1'a,1'b}$ 9.8 Hz, H-1′a), 3.41 (dt, 1H, $J_{1'b,2'}$ 6.6, $J_{1'a,1'b}$ 9.8 Hz, H-1′b), 1.9–2.2 (s, 12H, acetyl), 1.58 (m, 4H, H-2′ and H-9′), 1.27 (m, 12H, H-3′–H-8′); ESMS: *m/z* 501.24 $[M+H]^+$. Anal. Calcd for $C_{25}H_{40}O_{10}$: C, 59.99; H, 8.05. Found: C, 59.53; H, 8.28. **4b**: $[\alpha]_D^{20}$ −3.9 (*c* 1.03, $CHCl_3$); R_f 0.23 (7:3 petroleum ether–EtOAc); IR (KBr): *v* 3018 (terminal olefin), 2920 (CH_3), 2849 (CH_2) and 1753 (ester); ^1H NMR ($CDCl_3$): δ 5.81 (m, 1H, H-10), 5.38 (de, 1H, $J_{3,4}$ 3.3 Hz, H-4), 5.20 (dd, 1H, $J_{1,2}$ 7.9, $J_{2,3}$ 10.3 Hz, H-2), 5.01 (m, 1H, H-3), 4.97 (m, 2H, H-11′), 4.45 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.15 (m, 2H, H-6), 3.88 (m, 2H, H-5 and H-1′a), 3.47 (dt, 1H, $J_{1'b,2'}$ 6.9, $J_{1'a,1'b}$ 9.5 Hz, H-1′b), 1.9–2.2 (s, 12H, acetyl), 1.59 (m, 4H, H-2′ and H-9′), 1.28 (m, 12H, H-3′–H-8′); ESMS: *m/z* 501.24 $[M+H]^+$. Anal. Calcd for $C_{25}H_{40}O_{10}$: C, 59.99; H, 8.05. Found: C, 59.97; H, 8.12.

3.2.5. 1,20-Bis(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyloxy)eicos-10-ene (5a). Compound **4a** (0.20 g, 0.39 mmol) was dissolved in CH_2Cl_2 (2 mL) degassed under Argon. Grubbs' catalyst (0.04 g, 0.05 mmol) dissolved in the same solvent (10 mL) was added dropwise. After 5 h of reaction the medium was refluxed. Reaction lasted 21 h. After evaporation, the product was purified on a silica gel column (4:1 then 1:1 petroleum ether–EtOAc). A yellow oil was obtained containing a mixture of *Z* and *E* isomers (0.3 g, 0.32 mmol, 83%); R_f 0.44 (1:1 petroleum ether–EtOAc); IR (KBr): *v* 3018 (internal olefin), 2920 (CH_3), 2850 (CH_2), 1748 (ester), 962 (*E* olefin) and 755 (*Z* olefin); ^1H NMR ($CDCl_3$): δ 5.45 (dd, 2H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.1 Hz, H-4), 5.38 (m, 0.5H, H-10′, *E*), 5.36 (m, 2H, H-2), 5.34 (m, 1.5H, H-10′, *Z*), 5.12 (m, 2H, H-1), 5.10 (m, 2H, H-3), 4.22 (te, 2H, $J_{5,6}$ 6.2 Hz, H-5), 4.10 (m, 4H, H-6), 3.68 (dt, 2H, $J_{1'a,2'}$ 6.5, $J_{1'a,1'b}$ 9.8 Hz, H-1′a), 3.42 (dt, 2H, $J_{1'b,2'}$ 6.6, $J_{1'a,1'b}$ 9.8 Hz, H-1′b), 1.9–2.2 (s, 24H, acetyl), 1.58 (m, 8H, H-2′ and H-9′), 1.28 (m, 24H, H-3′–H-8′); ESMS: *m/z* 973.44 $[M+H]^+$. Anal. Calcd for $C_{48}H_{76}O_{20}$: C, 59.25; H, 7.87. Found: C, 59.09; H, 8.04.

3.2.6. 1,20-Bis(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)eicos-10-ene (5b). Compound **4b** (1.38 g, 2.76 mmol) was dissolved in 10 mL of CH_2Cl_2 degassed under Ar. Grubbs' catalyst (0.09 g, 0.11 mmol) was dissolved in the same solvent (15 mL) and added dropwise. After 23 h, a second portion of catalyst (0.13 g, 0.2 mmol) was added dropwise. Reaction lasted 71 h. After evaporation, the product was purified on a silica gel column (4:1 then 1:1 petroleum ether–EtOAc). A yellow oil was obtained containing a mixture of *Z* and *E* isomers (2.2 g, 2.29 mmol, 83%); R_f 0.38 (1:1 petroleum ether–EtOAc); IR (KBr): *v* 3018 (internal olefin), 2920 (CH_3), 2850 (CH_2), 1748 (ester), 962 (*E* olefin) and 755 (*Z* olefin); ^1H NMR ($CDCl_3$): δ 5.41 (m, 1.7H, H-10′, *E*), 5.37 (m, 0.3H, H-10′, *Z*), 5.34 (m, 2H, H-4), 5.20 (dd, 2H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.4 Hz, H-2), 5.01 (dd, 2H, $J_{2,3}$ 10.5, $J_{3,4}$ 3.4 Hz, H-3), 4.45 (d, 2H, $J_{1,2}$ 8.0 Hz, H-1), 4.16 (m, 4H, H-6), 3.89 (m, 2H, H-5), 3.88 (m, 2H, H-1′a), 3.47 (dt, 2H, $J_{1'b,2'}$ 6.9, $J_{1'a,1'b}$ 9.5 Hz, H-1′b), 1.9–2.2 (s, 24H, acetyl), 1.56 (m, 8H, H-2′ and H-9′), 1.26 (m, 24H, H-3′–H-8′); ESMS: *m/z* 973.44 $[M+H]^+$. Anal. Calcd for $C_{48}H_{76}O_{20}$: C, 59.25; H, 7.87. Found: C, 58.93; H, 8.08.

3.2.7. 1,20-Bis(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyloxy)eicosane (6a). Compound **5a** (0.53 g, 0.54 mmol) was dissolved in abs EtOH (50 mL). Rhodium on alumina was added and the reaction was carried out at room temperature under H_2 atmosphere during 5 h at 0.1 MPa. After filtration and evaporation, a yellow oil was obtained without further purification (0.53 g, 0.54 mmol, 100%); $[\alpha]_D^{20}$ +69.1 (*c* 0.30, $CHCl_3$); R_f 0.44 (1:1 petroleum ether–EtOAc); IR (KBr): *v* 2920 (CH_3), 2849 (CH_2) and 1748 (ester); ^1H NMR ($CDCl_3$): δ 5.45 (de, 2H, $J_{3,4}$ 2.4 Hz, H-4), 5.36 (m, 2H, H-2), 5.12 (m, 2H, H-1), 5.10 (m, 2H, H-3), 4.22 (te, 2H, $J_{5,6}$ 6.4 Hz, H-5), 4.10 (m, 4H, H-6), 3.67 (dt, 2H, $J_{1'a,2'}$ 6.6, $J_{1'a,1'b}$ 9.6 Hz, H-1′a), 3.42 (dt, 2H, $J_{1'b,2'}$ 6.6, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 1.9–2.2 (s, 24H, acetyl), 1.55 (m, 4H, H-2′), 1.26 (m,

32H, H-3′–H-10′); ESMS: m/z 997.59 $[M+K]^+$. Anal. Calcd for $C_{48}H_{78}O_{20}$: C, 59.12; H, 8.06. Found: C, 59.05; H, 8.23.

3.2.8. 1,20-Bis(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)eicosane (6b). Compound **5b** (0.06 g, 0.07 mmol) was transformed into **6b** using the same procedure as for **6a**. A yellow oil (0.06 g, 0.07 mmol, 95%) was obtained; $[\alpha]_D^{20}$ −10.6 (*c* 0.74, $CHCl_3$); R_f 0.38 (1:1 petroleum ether–EtOAc); IR (KBr): *v* 2923 (CH_3), 2846 (CH_2) and 1752 (ester); ^1H NMR ($CDCl_3$): δ 5.38 (de, 2H, $J_{3,4}$ 3.0 Hz, H-4), 5.20 (dd, 2H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.3 Hz, H-2), 5.01 (dd, 2H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.3 Hz, H-3), 4.45 (d, 2H, $J_{1,2}$ 8.0 Hz, H-1), 4.15 (m, 4H, H-6), 3.89 (m, 4H, H-5 and H-1′a), 3.47 (dt, 2H, $J_{1'b,2'}$ 6.8, $J_{1'a,1'b}$ 9.4 Hz, H-1′b), 1.9–2.2 (s, 24H, acetyl), 1.56 (m, 4H, H-2′), 1.25 (m, 32H, H-3′–H-10′); ESMS: m/z 997.51 $[M+K]^+$. Anal. Calcd for $C_{48}H_{78}O_{20}$: C, 59.12; H, 8.06. Found: C, 59.12; H, 8.03.

3.2.9. 1,20-Bis(α-D-galactopyranosyloxy)eicosane (7a). Deacetylation of **6a** (0.04 g, 0.04 mmol) as above afforded **7a** (0.03 g, 0.04 mmol, 98%) as a white solid; mp 106 °C; $[\alpha]_D^{20}$ +111.6 (*c* 0.32, MeOH); R_f 0.54 (1:1 $CHCl_3$–EtOH); IR (KBr): *v* 3376 (alcohol), 2920 (CH_3) and 2849 (CH_2); ^1H NMR (CD_3OD): δ 4.80 (d, 2H, $J_{1,2}$ 3.2 Hz, H-1), 3.88 (m, 2H, H-3), 3.80 (m, 2H, H-5), 3.72 (m, 10H, H-2, H-4, H-6 and H-1′a), 3.43 (dt, 2H, $J_{1'b,2'}$ 6.5, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 1.63 (m, 4H, H-2′), 1.29 (m, 32H, H-3′–H-10′); ESMS: m/z 639.41 $[M+H]^+$. Anal. Calcd for $C_{32}H_{62}O_{12}$: C, 60.16; H, 9.78. Found: C, 58.15; H, 9.62.

3.2.10. 1,20-Bis(β-D-galactopyranosyloxy)eicosane (7b). Deacetylation of **6b** (0.32 g, 0.32 mmol) as above afforded **7b** (0.19 g, 0.30 mmol, 95%) as a white solid; mp 110–117 °C; $[\alpha]_D^{20}$ −10.4 (*c* 0.85, pyridine); R_f 0.45 (1:1 $CHCl_3$–EtOH); IR (KBr): *v* 3336 (alcohol), 2911 (CH_3) and 2841 (CH_2); ^1H NMR (pyridine-d_5): δ 4.18 (d, 2H, $J_{1,2}$ 7.3 Hz, H-1), 3.87 (dt, 2H, $J_{1'a,2'}$ 7.0, $J_{1'a,1'b}$ 9.6 Hz, H-1′a), 3.81 (de, 2H, $J_{4,5}$ 2.6 Hz, H-5), 3.70 (m, 4H, H-6), 3.55 (m, 2H, H-1′b), 3.48 (m, 6H, H-2, H-3 and H-4), 1.60 (quint, 4H, $J_{1',2',3'}$ 7.0 Hz, H-2′), 1.26 (m, 32H, H-3′–H-10′); ESMS: m/z 639.41 $[M+H]^+$. Anal.$^+$ Calcd for $C_{32}H_{62}O_{12}$: C, 60.16; H, 9.78. Found: C, 57.89; H, 9.47.

3.2.11. Undec-10-enyl α-D-galactopyranoside (8a). Deacetylation of **4a** (0.29 g, 0.59 mmol) as above afforded **8a** (0.14 g, 0.44 mmol, 74%) as a white paste; $[\alpha]_D^{20}$ +101.0 (*c* 1.10, MeOH); R_f 0.60 (1:1 $CHCl_3$–EtOH); IR (KBr): *v* 3336 (alcohol), 3062 (terminal olefin) and 2858 (CH_2); ^1H NMR (CD_3OD): δ 5.80 (m, 1H, H-10′), 4.95 (m, 2H, H-11′), 4.79 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 3.88 (m, 1H, H-3), 3.80 (m, 1H, H-5), 3.72 (m, 5H, H-2, H-4, H-6 and H-1′a), 3.43 (dt, 1H, $J_{1'b,2'}$ 6.4, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 2.04 (q, 2H, $J_{8',9',10'}$ 7.2 Hz, H-9′), 1.62 (m, 2H, H-2′), 1.31 (m, 12H, H-3′–H-8′); ESMS: m/z 333.22 $[M+H]^+$. Anal.$^+$ Calcd for $C_{17}H_{32}O_6$: C, 61.42; H, 9.70. Found: C, 59.87; H, 9.92.

3.2.12. Undec-10-enyl β-D-galactopyranoside (8b). Deacetylation of **4b** (0.63 g, 1.3 mmol) as above afforded **8b** (0,3 g, 1.0 mmol, 79%) as a white paste; $[\alpha]_D^{20}$ −16.6 (*c* 0.75, MeOH); R_f 0.55 (1:1 $CHCl_3$–EtOH); IR (KBr): *v* 3566 (alcohol), 3062 (terminal olefin) and 2850 (CH_2); ^1H NMR (CD_3OD): δ 5.80 (m, 1H, H-10′), 4.94 (m, 2H, H-11′), 4.20 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.83 (dt, 1H, $J_{1'a,2'}$ 7.2, $J_{1'a,1'b}$ 9.4 Hz, H-1′a), 3.82 (dd, 1H, $J_{5,6}$ 0.8, $J_{4,5}$ 3.0 Hz, H-5), 3.73 (m, 2H, H-6), 3.53 (dt, 1H, $J_{1'b,2'}$ 6.4, $J_{1'a,1'b}$ 9.4 Hz, H-1′b), 3.48 (m, 3H, H-2, H-3 and H-4), 2.04 (quint, 2H, $J_{8',9',10'}$ 7.2 Hz, H-9′), 1.62 (quint, 2H, $J_{1',2',3'}$ 6.8 Hz, H-2′), 1.31 (m, 12H, H-3′–H-8′); lit.[10] (CD_3OD): δ 5.83 (m, 1H, H-10′), 4.99 (br d, 1H, *J* 17.0 Hz, H-11′a), 4.93 (br d, 1H, *J* 17.0 Hz, H-11′b), 4.24 (d, 1H, *J* 7.2 Hz, H-1), 3.90 (m, 3H, H-1′a,1′b,5), 3.77 (d, 1H,*J* 6.2 Hz, H-4), 3.63–3.45 (m, 4H, H-6a,6b,2,3), 2.04 (m, 2H, H-9′a,b), 1.63 (m, 2H, H-2′a,b), 1.43–1.30 (br s, 12H, alkyl protons); ESMS: m/z 333.21 $[M+H]^+$. Anal.$^+$ Calcd for $C_{17}H_{32}O_6$: C, 61.42; H, 9.70. Found: C, 59.59; H, 9.75.

3.2.13. Undec-10-enyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside (9a). Compound **8a** (0.16 g, 0.48 mmol) was dissolved in anhyd pyridine (3.1 mL) at −30 °C under Ar. BzCl (0.23 mL, 0.28 g, 2.0 mmol) was added dropwise (20 min) and the flask was immediately opened. Pyridine was evaporated ($T < 40$ °C). The crude product was dissolved in $CHCl_3$ (30 mL) and washed with 0.1 M HCl (15 mL), 5% $NaHCO_3$ (15 mL) and water (15 mL). The organic phase was dried on $MgSO_4$, filtered and evaporated. After chromatography on a silica gel column ($CHCl_3$), a yellow paste was obtained (0.20 g, 0.32 mmol, 66%); $[\alpha]_D^{20}$ +93.7 (*c* 1.41, $CHCl_3$); R_f 0.65 (95:5 $CHCl_3$–EtOH); IR (KBr): *v* 3487 (alcohol), 3062 (aromatics), 3018 (terminal olefin), 2849 (CH_2) and 1717 (ester); ^1H NMR ($CDCl_3$): δ 7.2–8.1 (m, 15H, benzoyl), 5.80 (m, 1H, H-10′), 5.76 (dd, 1H, $J_{2,3}$ 10.6, $J_{3,4}$ 2.7 Hz, H-3), 5.66 (dd, 1H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.6 Hz, H-2), 5.30 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.96 (m, 2H, H-11′), 4.67 (dd, 1H, $J_{5,6a}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.54 (dd, 1H, $J_{5,6b}$ 6.7, $J_{6a,6b}$ 11.3 Hz, H-6b), 4.39 (m, 2H, H-4 and H-5), 3.75 (dt, 1H, $J_{1'a,2'}$ 6.4, $J_{1'a,1'b}$ 9.8 Hz, H-1′a), 3.45 (dt, 1H, $J_{1'b,2'}$ 6.6, $J_{1'a,1'b}$ 9.8 Hz, H-1′b), 2.01 (q, 2H, $J_{8',9',10'}$ 7.5 Hz, H-9′), 1.57 (m, 2H, H-2′), 1.18 (m, 12H, H-3′–H-8′); ESMS: m/z 667.20 $[M+Na]^+$. Anal. Calcd for $C_{38}H_{44}O_9$: C, 70.79; H, 6.88. Found: C, 70.30; H, 7.10.

3.2.14. Undec-10-enyl 2,3,6-tri-*O*-benzoyl-β-D-galactopyranoside (9b). Compound **8b** (1.27 g, 3.8 mmol) was dissolved in 24.5 mL of anhyd pyridine at −31 °C under Ar. BzCl (1.86 mL, 2.25 g, 16 mmol) was added dropwise (20 min) and the flask was immediately opened. Pyridine was evaporated ($T < 40$ °C). The crude product was

dissolved in $CHCl_3$ (100 mL) and washed with 0.1 M HCl (60 mL), 5% $NaHCO_3$ (60 mL) and water (60 mL). The organic phase was dried on $MgSO_4$, filtered and evaporated. After chromatography on a silica gel column (9:1 $CHCl_3$–petroleum ether) a yellow paste was obtained (0.86 g, 1.33 mmol, 35%); $[\alpha]_D^{20}$ +33.4 (*c* 0.99, CH_2Cl_2); R_f 0.47 (49:1 $CHCl_3$–EtOH); IR (KBr): *v* 3487 (alcohol), 3062 (aromatics), 3018 (terminal olefin), 2849 (CH_2) and 1717 (ester); ^1H NMR ($CDCl_3$): δ 7.3–8.1 (m, 15H, benzoyl), 5.80 (m, 1H, H-10′), 5.75 (dd, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.2 Hz, H-2), 5.35 (dd, 1H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.2 Hz, H-3), 4.96 (m, 2H, H-11′), 4.71 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.69 (dd, 1H, $J_{5,6a}$ 6.6, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.61 (dd, 1H, $J_{5,6b}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-6b), 4.35 (dd, 1H, $J_{3,4}$ 3.2, $J_{4,5}$ 5.2 Hz, H-4), 4.07 (te, 1H, $J_{4,5,6}$ 6.5 Hz, H-5), 3.91 (dt, 1H, $J_{1'a,2'}$ 6.2, $J_{1'a,1'b}$ 9.7 Hz, H-1′a), 3.52 (dt, 1H, $J_{1'b,2'}$ 6.6, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 2.01 (q, 2H, $J_{8',9',10'}$ 6.9 Hz, H-9′), 1.51 (m, 2H, H-2′), 1.17 (m, 12H, H-3′–H-8′); ESMS: *m*/*z* 645.30. Anal. Calcd for $C_{38}H_{44}O_9$: C, 70.79; H, 6.88. Found: C, 70.62; H, 7.01.

3.2.15. 1,20-Bis(2,3,6-tri-*O*-benzoyl-α-D-galactopyranosyloxy)eicos-10-ene (10a). Compound **9a** (0.25 g, 0.39 mmol) was dissolved in 1.8 mL CH_2Cl_2 degassed under Ar. Grubbs' catalyst (0.03 g, 0.04 mmol) was dissolved in the same solvent (10 mL) and added dropwise. Reaction lasted 21 h. After evaporation the product was purified on a silica gel column (49:1 $CHCl_3$–EtOH). A yellow paste was obtained (0.39 g, 0.31 mmol, yield = 80%); R_f 0.21 (49:1 $CHCl_3$–EtOH); IR (KBr): *v* 3487 (alcohol), 3062 (aromatics), 3018 (internal olefin), 2849 (CH_2), 1721 (ester), 971 (*E* olefin) and 711 (*Z* olefin); ^1H NMR ($CDCl_3$): δ 7.3–8.1 (m, 30H, benzoyl), 5.75 (dd, 2H, $J_{2,3}$ 10.6, $J_{3,4}$ 3.0 Hz, H-3), 5.67 (dd, 2H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.6 Hz, H-2), 5.37 (m, 2H, H-10′), 5.30 (d, 2H, $J_{1,2}$ 3.6, H-1), 4.67 (dd, 2H, $J_{5,6a}$ 5.8, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.54 (dd, 2H, $J_{5,6b}$ 6.7, $J_{6a,6b}$ 11.3, H-6b), 4.39 (m, 4H, H-4 and H-5), 3.75 (dt, 2H, $J_{1'a,2'}$ 6.4, $J_{1'a,1'b}$ 9.8 Hz, H-1′a), 3.44 (dt, 2H, $J_{1'b,2'}$ 6.5, $J_{1'a,1'b}$ 9.7 Hz, H-1′b), 1.93 (m, 4H, H-9′), 1.55 (m, 4H, H-2′), 1.18 (m, 24H, H-3′–H-8′); ESMS: *m*/*z* 1283.43 $[M+Na]^+$. Anal. Calcd for $C_{74}H_{84}O_{18}$: C, 70.46; H, 6.71. Found: C, 70.15; H, 6.82.

3.2.16. 1,20-Bis(2,3,6-tri-*O*-benzoyl-β-D-galactopyranosyloxy)eicos-10-ene (10b). Compound **9b** (0.25 g, 0.39 mmol) was dissolved in 1.8 mL of CH_2Cl_2 degassed under Ar. Grubbs' catalyst (0.03 g, 0.04 mmol) was dissolved in the same solvent (10 mL) and added dropwise. Reaction lasted 21 h. After evaporation, the product was purified on a silica gel column (49:1 $CHCl_3$–EtOH). A yellow paste was obtained (0.38 g, 0.30 mmol, 77%); R_f 0.33 (49:1 $CHCl_3$–EtOH); IR (KBr): *v* 3487 (alcohol), 3062 (aromatics), 3031 (internal olefin), 2849 (CH_2), 1722 (ester), 988 (*E* olefin) and 706 (*Z* olefin); ^1H NMR ($CDCl_3$): δ 7.3–8.1 (m, 30H, benzoyl), 5.75 (dd, 2H, $J_{1,2}$ 7.9, $J_{2,3}$ 10.3 Hz, H-2), 5.36 (m, 2H, H-10′), 5.35 (dd, 2H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.2 Hz, H-3), 4.72 (d, 2H, $J_{1,2}$ 7.9 Hz, H-1), 4.69 (dd, 2H, $J_{5,6a}$ 6.6, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.61 (dd, 2H, $J_{5,6b}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-6b), 4.35 (m, 2H, H-4), 4.07 (te, 2H, $J_{4,5,6}$ 6.5 Hz, H-5), 3.91 (dt, 2H, $J_{1'a,2'}$ 6.2, $J_{1'a,1'b}$ 9.7 Hz, H-1′a), 3.52 (dt, 2H, $J_{1'b,2'}$ 6.7, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 1.93 (m, 4H, H-9′), 1.51 (m, 4H, H-2′), 1.23 (m, 24H, H-3′–H-8′); ESMS: 1283.43 $[M+Na]^+$. Anal. Calcd for $C_{74}H_{84}O_{18}$: C, 70.46; H, 6.71. Found: C, 69.27; H, 7.06.

3.2.17. 1,20-Bis(2,3,6-tri-*O*-benzoyl-α-D-galactopyranosyloxy)eicosane (11a). Compound **10a** (0.15 g, 0.12 mmol) was transformed into **11a** using the same procedure as for **6a**. A yellow oil (0.13 g, 0.10 mmol, 86%) was obtained; $[\alpha]_D^{20}$ +122.7 (*c* 0.42, $CHCl_3$); R_f 0.21 (49:1 $CHCl_3$–EtOH); IR (KBr): *v* 3442 (alcohol), 3070 (aromatics), 2849 (CH_2) and 1717 (ester); ^1H NMR ($CDCl_3$): δ 7.3–8.1 (m, 30H, benzoyl), 5.76 (dd, 2H, $J_{2,3}$ 10.6, $J_{3,4}$ 3.0 Hz, H-3), 5.67 (dd, 2H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.6 Hz, H-2), 5.30 (d, 2H, $J_{1,2}$ 3.6, H-1), 4.67 (dd, 2H, $J_{5,6a}$ 5.8, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.54 (dd, 2H, $J_{5,6b}$ 6.8, $J_{6a,6b}$ 11.4 Hz, H-6b), 4.39 (m, 4H, H-4 and H-5), 3.76 (dt, 2H, $J_{1'a,2'}$ 6.4, $J_{1'a,1'b}$ 9.8 Hz, H-1′a), 3.45 (dt, 2H, $J_{1'b,2'}$ 6.6, $J_{1'a,1'b}$ 9.8 Hz, H-1′b), 1.56 (m, 4H, H-2′), 1.23 (m, 32H, H-3′–H-10′); ESMS: *m*/*z* 1285.58 $[M+Na]^+$. Anal. Calcd for $C_{74}H_{86}O_{18}$: C, 70.35; H, 6.86. Found: C, 69.91; H, 6.97.

3.2.18. 1,20-Bis(2,3,6-tri-*O*-benzoyl-β-D-galactopyranosyloxy)eicosane (11b). Compound **10b** (0.16 g, 0.13 mmol) was transformed into **11b** using the same procedure as for **6a**. A yellow oil (0.14 g, 0.11 mmol, 88%) was obtained; $[\alpha]_D^{20}$ −121.1 (*c* 1.43, $CHCl_3$); R_f 0.33 (49:1 $CHCl_3$–EtOH); IR (KBr): *v* 3452 (alcohol), 3068 (aromatics), 2836 (CH_2) and 1718 (ester); ^1H NMR ($CDCl_3$): δ 7.3–8.1 (m, 30H, benzoyl), 5.75 (dd, 2H, $J_{1,2}$ 7.9, $J_{2,3}$ 10.3 Hz, H-2), 5.35 (dd, 2H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.2 Hz, H-3), 4.71 (d, 2H, $J_{1,2}$ 7.9 Hz, H-1), 4.69 (dd, 2H, $J_{5,6a}$ 6.6, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.61 (dd, 2H, $J_{5,6b}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-6b), 4.35 (dd, 2H, $J_{3,4}$ 3.2, $J_{4,5}$ 5.3 Hz, H-4), 4.07 (te, 2H, $J_{4,5,6}$ 6.5 Hz, H-5), 3.91 (dt, 2H, $J_{1'a,2'}$ 6.2, $J_{1'a,1'b}$ 9.7 Hz, H-1′a), 3.52 (dt, 2H, $J_{1'b,2'}$ 6.7, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 1.51 (m, 4H, H-2′), 1.20 (m, 32H, H-3′–H-10′); ESMS: *m*/*z* 1285.45 $[M+Na]^+$. Anal. Calcd for $C_{74}H_{86}O_{18}$: C, 70.35; H, 6.86. Found: C, 68.83; H, 6.63.

3.2.19. Dec-9-enylisocyanate (13). 10-Undecenyl chloride (**12**; 2.5 mL, 2.36 g, 18 mmol) was dissolved in 100 mL of acetone. Sodium azide (3.1 g, 49 mmol) was dissolved in 10 mL cold water ($T < 10$ °C) and **12** was added dropwise. The reaction lasted 2 h at 10–15 °C. Then, 300 mL cold petroleum ether were added and the medium was stirred until NaCl was dissolved. The organic phase was dried on $MgSO_4$ and distilled under diminished pressure. A colourless liquid was obtained (1.47 g, 8.1 mmol, 45%); *d* 0.82; IR (KBr): *v* 3080 (terminal olefin), 2849

(CH_2) and 2265 (isocyanate); ^{1}H NMR ($CDCl_3$): δ 5.81 (m, 1H, H-9), 4.97 (m, 2H, H-10), 3.29 (t, 2H, $J_{1,2}$ 6.7 Hz, H-1), 2.04 (q, 2H, $J_{7,8,9}$ 7.4 Hz, H-8), 1.61 (quint, 2H, $J_{1,2,3}$ 7.0 Hz, H-2), 1.37 (m, 2H, H-7), 1.30 (m, 8H, H-3-H-6); ^{13}C NMR: δ 139.3 (C-9), 122.0 (quaternary carbon), 114.4 (C-10), 43.6 (C-8), 33.8 (C-1), 26–30 (C-2–C-7); CIMS: m/z 182 $[M+H]^+$.

3.2.20. 1,20-Bis[2,3,6-tri-*O*-benzoyl-4-*O*-(*N*-dec-9-enyl)-carbamoyl-α-D-galactopyranosyloxy]eicosane (14a). Compound **11a** (0.04 g, 0.03 mmol) was dissolved in anhyd toluene (2 mL) **13** (0.03 g, 0.14 mmol) and DABCO (0.01 g, 0.08 mmol dissolved in 0.05 mL anhyd toluene) were added. Reaction lasted 4 h at 110 °C. After evaporation, the crude product was dissolved in 20 mL $CHCl_3$ and washed with HCl 0.1 M (3×10 mL) and saturated $NaHCO_3$ (3×10 mL). The organic phase was dried on $MgSO_4$, filtered and evaporated. After purification on silica preparative TLC (99:1 chloroform–ethanol) a white paste was obtained (0.04 g, 0.11 mmol, 79%); $[\alpha]_D^{20}$ +128.8 (c 0.51, CH_2Cl_2); R_f 0.56 (49:1 $CHCl_3$–EtOH); IR (KBr): ν 3452 and 1726 (carbamate), 3062 (aromatics), 3031 (terminal olefin), 2849 (CH_2) and 1726 (ester); ^{1}H NMR ($CDCl_3$): δ 7.3–8.2 (m, 30H, benzoyl), 5.86 (dd, 2H, $J_{2,3}$ 10.7, $J_{3,4}$ 3.3 Hz, H-3), 5.78 (m, 2H, H-9″), 5.67 (m, 2H, H-4), 5.56 (dd, 2H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.7 Hz, H-2), 5.28 (d, 2H, $J_{1,2}$ 3.5 Hz, H-1), 4.96 (m, 4H, H-10″), 4.56 (m, 2H, H-6a), 4.53 (m, 2H, H-5), 4.37 (m, 2H, H-6b), 3.73 (m, 2H, H-1′a), 3.43 (m, 2H, H-1′b), 3.07 (m, 4H, H-1″), 2.02 (m, 4H, H-8″), 1.56 (m, 4H, H-2′), 1.34 (m, 4H, H-2″), 1.22 (m, 52H, H-3′–H-10′ and H-3″–H-7″); ^{13}C NMR: δ 165–166 (quaternary carbons from benzoyls), 155.2 (quaternary carbon from carbamate), 139.2 (C-9″), 128–134 (aromatic carbons from benzoyls), 114.2 (C-10″), 96.4 (C-11), 69.3 (C-2), 69.1 (C-4), 68.7 (C-1′), 68.4 (C-3), 67.0 (C-5), 62.9 (C-6), 41.2 (C-1″), 33.8 (C-8″), 26–30 (C-2′–C-10′ and C-2″–C-7″); ESMS: m/z 1647.87 $[M+Na]^+$. Anal. Calcd for $C_{96}H_{124}O_{20}N_2$: C, 70.91; H, 7.69; N, 1.72. Found: C, 70.72; H, 7.90; N, 1.75.

3.2.21. 1,20-Bis[2,3,6-tri-*O*-benzoyl-4-*O*-(*N*-dec-9-enyl)-carbamoyl-β-D-galactopyranosyloxy]eicosane (14b). Compound **11b** (0.14 g, 0.11 mmol) was dissolved in anhyd toluene (7 mL). Compound **13** (0.10 g, 0.56 mmol) and DABCO (0.006 g, 0.05 mmol in 0.03 mL anhyd toluene) were added. Reaction lasted 23 h at 110 °C, TLC indicated the reaction was complete. After evaporation, the crude product was dissolved in 30 mL $CHCl_3$ and washed with HCl 0.1 M (3×15 mL) and saturated $NaHCO_3$ (3×15 mL). The organic phase was dried on $MgSO_4$, filtered and evaporated. After purification on silica preparative TLC [eluent CH_2Cl_2 (2×)] a white paste was obtained (0.13 g, 0.8 mmol, 70%); $[\alpha]_D^{20}$ +42.7 (c 1.22, $CHCl_3$); R_f 0.35 (99:1 $CHCl_3$–EtOH); IR (KBr): ν 3434, 1726 and 1638 (carbamate), 3071 (aromatics), 3037 (terminal olefin), 2849 (CH_2) and 1726 (ester); ^{1}H NMR ($CDCl_3$): δ 7.3–8.2 (m, 30H, benzoyl), 5.81 (m, 2H, H-9″), 5.69 (dd, 2H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.4 Hz, H-2), 5.63 (de, 2H, $J_{3,4}$ 3.0, H-4), 5.45 (dd, 2H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.3 Hz, H-3), 4.96 (m, 4H, H-10″), 4.72 (d, 2H, $J_{1,2}$ 7.9 Hz, H-1), 4.62 (m, 2H, H-6a), 4.32 (m, 2H, H-6b), 4.20 (m, 2H, H-5), 3.91 (m, 2H, H-1′a), 3.51 (m, 2H, H-1′b), 3.02 (m, 4H, H-1″), 2.02 (m, 4H, H-8″), 1.60 (m, 4H, H-2′), 1.36 (m, 4H, H-2″), 1.23 (m, 52H, H-3′–H-10′ and H-3″–H-7″); ^{13}C NMR: δ 165–167 (quaternary carbons from benzoyls), 155.1 (quaternary carbon from carbamate), 139.2 (C-9″), 128–131 (aromatic carbons from benzoyls), 114.2 (C-10″), 101.5 (C-1), 72.0 (C-3), 71.3 (C-5), 70.5 (C-1′), 69.9 (C-2), 68.0 (C-4), 62.1 (C-6), 41.2 (C-1″), 33.8 (C-8″), 25–30 (C-2′–C-10′ and C-2″–C-7″); ESMS: m/z 1647.87 $[M+Na]^+$. Anal. Calcd for $C_{96}H_{124}N_2O_{20}$: C, 70.91; H, 7.69; N, 1.72. Found: C, 71.12; H, 7.66; N, 1.74.

3.2.22. 1,20-Bis[4-*O*-(*N*-dec-9-enyl)carbamoyl-α-D-galactopyranosyloxy]eicosane (15a). Compound **14a** (0.16 g, 0.10 mmol) was dissolved in MeONa (10 mL) in MeOH (0.27 g, 5 mmol). CH_2Cl_2 (2 mL) was added. Reaction lasted 16 h, TLC indicated the reaction was complete. After neutralization with Amberlite IRN 77H$^+$ resin, filtration, evaporation and purification on silica gel column (9:1 then 85:15 $CHCl_3$–EtOH) a white solid was obtained (0.03 g, 0.03 mmol, 31%); mp 80 °C; $[\alpha]_D^{20}$ +43.4 (c 0.31, 4:1 $CHCl_3$–MeOH); R_f 0.39 (4:1 $CHCl_3$–EtOH); IR (KBr): ν 3434, 1726 and 1638 (carbamate), 3434 (alcohol), 3071 (aromatics), 3031 (terminal olefin), 2849 (CH_2) and 1726 (ester); ^{1}H NMR ($CDCl_3$): δ 5.81 (m, 2H, H-9″), 4.95 (m, 4H, H-10″), 4.89 (d, 2H, $J_{1,2}$ 2.6 Hz, H-1), 4.33 (dd, 2H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 11.3 Hz, H-6a), 4.15 (dd, 2H, $J_{5,6b}$ 7.2, $J_{6a,6b}$ 11.4 Hz, H-6b), 3.80–3.94 (m, 6H, H-2, H-3, H-4 and H-5), 3.67 (dt, 2H, $J_{1'a,2'}$ 7.0, $J_{1'a,1'b}$ 9.3 Hz, H-1′a), 3.45 (dt, 2H, $J_{1'b,2'}$ 6.5, $J_{1'a,1'b}$ 9.6 Hz, H-1′b), 3.14 (t, 4H, $J_{1'',2''}$ 7.0 Hz, H-1″), 2.03 (q, 4H, $J_{7'',8'',9''}$ 6.8 Hz, H-8″), 1.60 (m, 4H, H-2′), 1.48 (m, 4H, H-2″), 1.27 (m, 52H, H-3′–H-10′ and H-3″–H-7″); ^{13}C NMR: δ 156.6 (quaternary carbon), 139.1 (C-9″), 114.1 (C-10″), 98.5 (C-1), 68.3 69.0 (×2), 70.3 (C-2 C-3 C-4 C-5), 68.4 (C-1′), 63.5 (C-6), 40.9 (C-1″), 33.7 (C-8″), 22–31 (C-2′–C-10′ and C-2″–C-7″); ESMS: m/z 1002.75 $[M+H]^+$. Anal. Calcd for $C_{54}H_{100}N_2O_{14}$: C, 64.77; H, 10.07; N, 3.00. Found: C, 63.41; H, 10.01; N, 2.72.

3.2.23. 1,20-Bis[4-*O*-(*N*-dec-9-enyl)carbamoyl-β-D-galacto- pyranosyloxy]eicosane (15b). Compound **14b** (0.11 g, 0.07 mmol) was dissolved in 2 mL of MeONa in MeOH (0.005 g, 0.1 mmol). CH_2Cl_2 (1 mL) was added. Reaction lasted 16 h, TLC indicated the reaction was complete. After neutralization with Amberlite IRN 77H$^+$ resin, filtration, evaporation and purification on silica gel column (9:1 then 4:1 $CHCl_3$–EtOH) a white solid was obtained (0.03 g, 0.03 mmol, 44%); mp 90 °C;

$[\alpha]_D^{20}$ +23.8 (*c* 0.29, 1:1 $CHCl_3$–MeOH); R_f 0.37 (4:1 $CHCl_3$–EtOH); IR (KBr): *v* 3434, 1726 and 1642 (carbamate), 3434 (alcohol), 3080 (terminal olefin), 2849 (CH_2) and 1726 (ester); ^{1}H NMR ($CDCl_3$): δ 5.81 (m, 2H, H-9″), 4.95 (m, 4H, H-10″), 4.28 (m, 4H, H-6), 4.21 (d, 2H, $J_{1,2}$ 7.1 Hz, H-1), 3.88 (dt, 2H, $J_{1'a,2'}$ 7.0, $J_{1'a,1'b}$ 9.4 Hz, H-1′a), 3.84 (de, 2H, $J_{3,4}$ 2.4 Hz, H-4), 3.65 (m, 2H, H-5), 3.53 (m, 6H, H-2, H-3 and H-1′b), 3.13 (t, 4H, $J_{1'',2''}$ 7.1 Hz, H-1″), 2.04 (q, 4H, $J_{7'',8'',9''}$ 6.8 Hz, H-8″), 1.62 (quint, 4H, $J_{1',2',3'}$ 6.9 Hz, H-2′), 1.49 (quint, 4H, $J_{1'',2'',3''}$ 6.0 Hz, H-2″), 1.26 (m, 52H, H-3′–H-10′ and H-3″–H-7″); ^{13}C NMR: δ 156.9 (quaternary carbon), 139.3 (C-9″), 114.2 (C-10″), 103.3 (C-1), 71.5 and 73.4 (C-2 and C-3), 72.7 (C-5), 70.3 (C-1′), 68.4 (C-4), 63.0 (C-6), 41.1 (C-1″), 33.9 (C-8″), 28–30 (C-2′–C-10′ and C-2″–C-7″); ESHRMS: calcd for $C_{54}H_{100}N_2O_{14}Na^+$: 1023.7072. Found: 1023.7063. Anal. Calcd for $C_{54}H_{100}N_2O_{14}$: C, 64.77; H, 10.07; N, 3.00. Found: C, 63.73; H, 9.79; N, 2.77.

3.2.24. 1*S*,26*S*,27*R*,29*R*,52*R*,54*R*,55*R*,56*R*,57*R*,58*R*-4,23-Diaza-55,56,57,58-tetrahydroxy-27,54-dihydroxy-methyl-2,25,28,30,51,53-hexaoxa-3,24-dioxotricyclo-[50.2.2.2^{26,29}]-octapentacont-13-ene (16). Compound **15b** (26 mg, 0.026 mmol) was dissolved in 90 mL of degassed 8:1 CH_2Cl_2–MeOH. Second generation Grubbs' catalyst (16 mg, 0.021 mmol) was dissolved in 20 mL degassed CH_2Cl_2 and added dropwise. After 22 h, 8 mg (0.008 mmol) catalyst were added. After 51 h, 4 mg (0.005 mmol) catalyst were added. The reaction took place under argon at room temperature during 69 h. The solvent was evaporated and the product was purified on a silica gel chromatography column with 85:15, 3:1 and 1:1 $CHCl_3$–EtOH (0.008 g, 0.008 mmol, 33%); R_f 0.30 (4:1 $CHCl_3$–EtOH); ^{1}H NMR ($CDCl_3$): δ 5.32 (m, 2H, H-9″), 4.28 (m, 4H, H-6), 4.21 (d, 2H, $J_{1,2}$ 7.1 Hz, H-1), 3.88 (dt, 2H, $J_{1'a,2'}$ 7.0, $J_{1'a,1'b}$ 9.4 Hz, H-1′a), 3.84 (de, 2H, $J_{3,4}$ 2.4 Hz, H-4), 3.65 (m, 2H, H-5), 3.53 (m, 6H, H-2, H-3 and H-1′b), 3.13 (t, 4H, $J_{1'',2''}$ 7.1 Hz, H-1″), 2.04 (q, 4H, $J_{7'',8'',9''}$ 6.8 Hz, H-8″), 1.62 (quint, 4H, $J_{1',2',3'}$ 6.9 Hz, H-2′), 1.49 (quint, 4H, $J_{1'',2'',3''}$ 6.0 Hz, H-2″), 1.26 (m, 52H, H-3′–H-10′ and H-3″–H-7″); ESHRMS: calcd for $C_{52}H_{96}N_2O_{14}Na^+$: 995.5759. Found: 995.5748.

Note: $^+$Melting under diminished pressure did not improve the elemental analysis data for **3a**, **3b**, **7a**, **7b**, **8a**, **8b**, **15a**, **15b**, which then exceed the admitted deviation range from the theory.

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