Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Efficient Syntheses of Bolaform Surfactants from L-Rhamnose and/or 3-(4-Hydroxyphenyl)Propionic Acid

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Keywords: surfactants, bolaform, rhamnose, 3-(4-hydroxyphenyl)propionic acid, solvent-free, enzymatic esterification, lipase, metathesis, antioxidant activity, elicitors.

Abstract

The efficient syntheses of new symmetric and asymmetric bolaamphiphiles derived from L-rhamnose and/or 3-(4-Hydroxyphenyl)propionic acid are described. The bolaamphiphiles are obtained with good to high yields through a two steps reaction sequence involving successively a glycosylation (or an esterification) and a metathesis. The glycosylations were performed without solvent because the alcohols could play this role. Concerning the esterifications, enzymatic catalysis led to the esters with high yields which increased with the carbon chain length. Finally, the metathesis steps were performed in the presence of Grubbs I catalyst without protecting steps in only dichloromethane without addition of methanol.

Introduction

The sugar-based biosurfactants are considered as environmental-friendly molecules due to their biocompatibility and biodegradability. Their use is then becoming wider during recent years because of the prompting of environmental and toxicity issues.[1]

The use of inexpensive raw materials such as agroindustrial wastes is an attractive strategy to reduce the production costs associated with biosurfactant production. At the same time, its contribute to the reduction of environmental impact generated by the discard of residues, and the treatment costs. Carbohydrate-rich substrates generate low rhamnolipid levels, whereas oils and lipid-rich wastes have shown excellent potential as alternative carbon sources.[2]

Rhamnolipids produced by the bacteria Pseudomonas aeruginosa are known as very efficient biosurfactant molecules. They are used for a wide range of industrial applications, especially in food, cosmetics and pharmaceutical formulations as well as in bioremediation of pollutants.[3-7] Rhamnolipids have also direct antifungal properties by inhibiting spore

germination and mycelium growth of *B. cinerea* and efficiently protect grapevine against the fungus.[8]

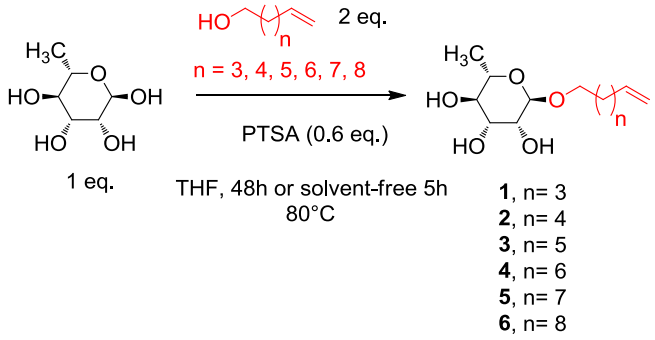
In this context since many years, our work was focused on sugar-based surfactants, D-xylosides,[9] D-xylosides-based bolaamphiphiles[9] and more recently L-rhamnosides[9] which could be considered as rhamnolipids. Recently, we compared the synthesis and the interfacial properties of a D-xyloside-based bolaamphiphile and a L-rhamnoside-based bolaamphiphile and revealed the importance of the hydrophilic head and also the eliciting behavior of the L-rhamnoside-based bolaamphiphile.[9]

In this paper, we will described the preparation of a wide range of L-rhamnosides or L-rhamnoside-based bolaamphiphiles and of fatty esters or fatty ester-based bolaamphiphiles derived from 3-(4-hydroxyphenyl)propionic acid which is known for its antioxidative activity.[10] Original asymmetric bolaamphiphiles coming from the association of some L-rhamnosides and fatty esters have also been synthetized. All glycosylations could be realized with solvent and the esterifications and metathesis are performed with good yields and selectivities using respectively enzymatic or catalytic pathways. Subsequently, the objective is to study the structure-property relationships between molecules obtained in order to better understand their assembly in solution for defined applications. This goal will not be the subject of our discussion in this document.

Results and discussion

Glycosylation of rhamnose

The glycosylation of the L-rhamnose with unsaturated alcohols following Fischer's method[11] led to the rhamnosides with very good stereoselectivity in favor to the monocatenar α as typically described for other glycosylations of L-rhamnose related in the literature.[12] The reactions were first realized in THF with PTSA in substoichiometric proportions and the yields after 48h of reaction were good (Scheme 1). Next, as the alcohols could play themselves the role of solvents, we decided to realize the reactions in the absence of THF and obtained slightly higher yields over 5 hours (Scheme 1), what represents a real advance according to the fifth principle of the green chemistry.



	Reaction yields[a] (%)	Reaction yields[b] (%)
1	70	75
2	75	80
3	80	85
4	85	90
5	90	95
6	95	97

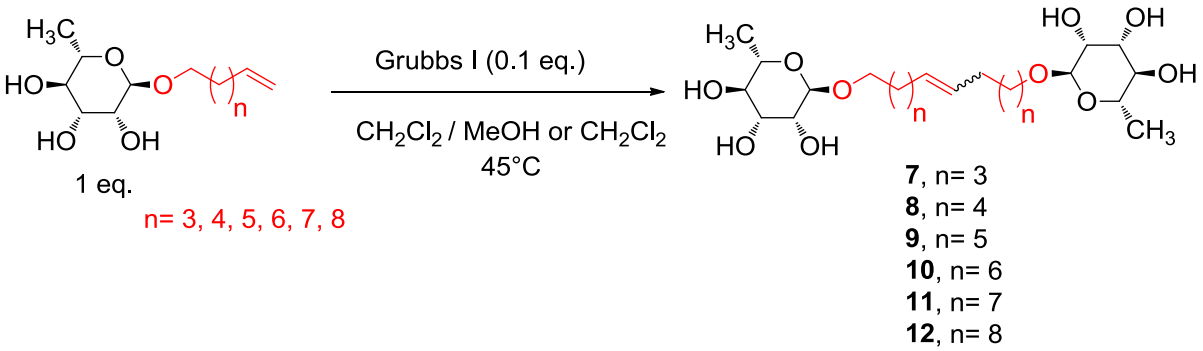
[a] With THF as solvent, 48h.

[b] Solvent free Reaction, 5h.

Scheme 1 - Glycolysation of rhamnosides

Metathesis of rhamnosides

In a second step, classical conditions of metathesis reaction[9b, c] in the presence of a catalytic quantity of Grubbs I catalyst gave the bolaamphiphiles **7-12** with yields between 50 to 75 % and a *Z/E* ratio around 20/80 (Scheme 2). Here again, compared to previous work,[9d] the yields were improved by modifying some reaction conditions (reaction time, purification and especially the solvent) without protecting/deprotecting steps. The use of dichloromethane alone led to slightly higher yields (Scheme 2). This may be due to the fact that the dichloromethane increases the solubility of all reactants and the catalyst's stability while enhancing its activity. That is why yields increase slightly and reaction times decrease (72h to 8h).



	Reaction yields[a] (%)	Reaction yields[b] (%)
7	50	55
8	55	60

9	60	65
10	65	70
11	70	75
12	75	80

[a] in CH_2Cl_2/MeOH, 72h [b] in CH_2Cl_2, 8h

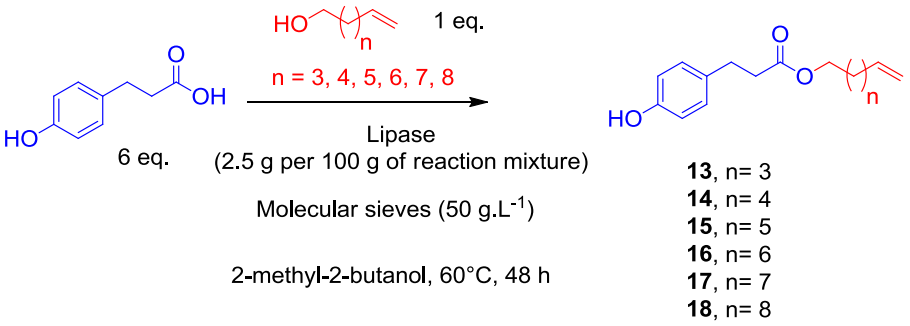
Scheme 2 - Metathesis of rhamnosides

As our goal was also to prepare mixed bolaamphiphilic compounds with two different terminal entities, we decided to use as hydrophilic moiety an acid showing furthermore antioxidant properties, the 3-(4-hydroxyphenyl)propionic acid.[13] The formation of monocatenar compounds obtained by chemo-enzymatic from phenolic compounds is a research topic that continued to interest the scientific world because the compounds obtained have original properties (antioxidant, anticarcinogenic, antimicrobial, anti-inflammatory) and can be used in various fields such as food, cosmetics, etc….[13] So, at first, we developed the synthesis of monocatenar surfactants from this acid through an enzymatic way.

Esterification of 3-(4-hydrophenyl)propionic acid

These monocatenar surfactants were prepared through an esterification reaction according a method described in the literature for the preparation of rhamnose-based esters, involving an enzymatic catalysis.[14] A lipase (lipase Novozym 435, lipase B from *Candida antarctica*, CALB)[15] was chosen and the reaction was realized in 2-methyl-2-butanol as solvent during 48h at 60°C, in the presence of 3Å molecular sieves (Scheme 3). The use of such a solvent is described in the literature for the esterification of aromatic acids with various alcohols (fatty, saturated or unsaturated ones).[16] Furthermore, the 2-methyl-2-butanol, which is commonly used in the food domain,[17] was chosen as solvent to favor the solubilization of both acid and alcohols.[18a-d] It also facilitates contact between the two substrates and improves both stability and activity of the enzyme.[18b] The discovery of the activity of enzymes in organic media is a determinant step in the development of biocatalyse.[18e-g] Furthermore, the 2-methyl-2-butanol, compared to more polar solvent as DMSO for example, is also able to prevent the water stripping.[19]

The esterification yields are good and increase with the length of the hydrocarbon chain (Scheme 3) what is probably due to the weak solubility of the esters with long chains in water.

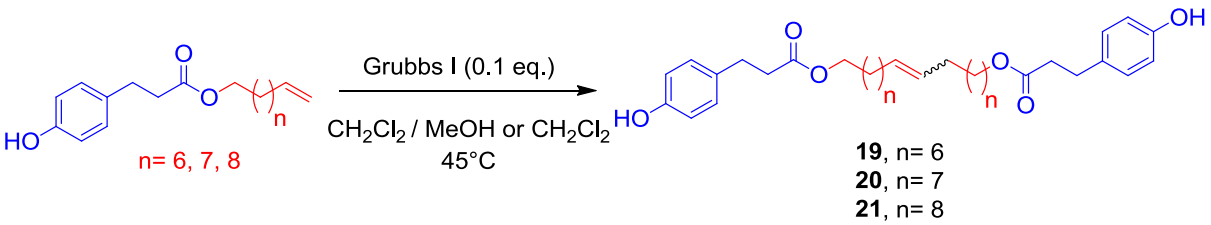


	Reaction yields (%)
13	70
14	75
15	80
16	85
17	90
18	95

Scheme 3 - Esterification of 3-(4-hydroxyphenyl)propionic acid

Metathesis of esters

Next, similar conditions of metathesis reaction as the further conditions employed for the metathesis of the rhamnosides, were chosen to produce the bolaamphiphiles **19-21** with good yields between 70 to 80 % (or 65 to 75% depending of the reaction solvent) and a *Z/E* ratio around 20/80 (Scheme 4). The reaction was performed with hydrophobic chains of 9 to 11 carbons in order to obtain some hydrophobic spacers presenting suitable lengths between the two hydrophilic heads. Here again, the use of dichloromethane alone led again to slightly higher yields (Scheme 4). The reasons are the same as those set out for the metathesis rhamnosides.



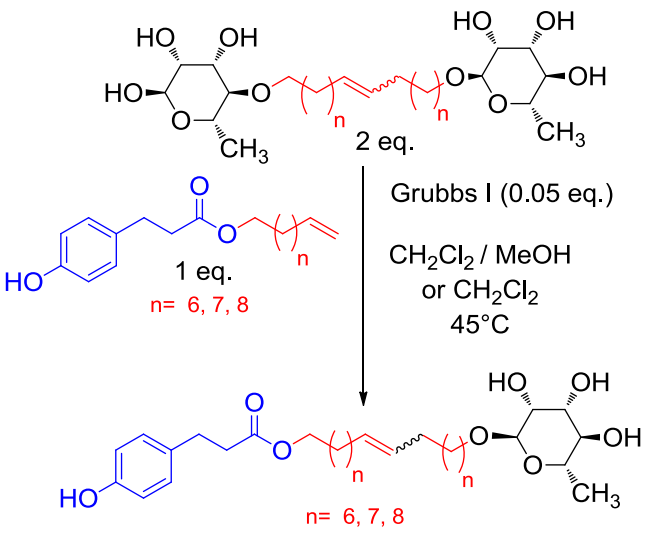
	Reaction yields[a] (%)	Reaction yields[b] (%)
19	65	70
20	70	75
21	75	80

[a] in CH_2Cl_2/MeOH, 72h [b] in CH_2Cl_2, 12h

Scheme 4 - Metathesis of esters

Cross Metathesis rhamnosides/esters

Finally, in order to obtain mixed bolaamphiphiles, different methods of cross metathesis[20] were tested according to pathways described in the literature by using various Ruthenium-based catalysts, various ratios rhamnosides/esters or reaction conditions (time, temperature). After testing a large panel of conditions (Grubbs I and Grubbs II 10 or 20% mol amounts, ratios rhamnosides/esters of 2/1, 1/2 or 1/3), mixed (or asymmetric) bolaamphiphiles were always obtained as minor compounds compared to symmetric ones. However, according to the work of Blechert,[21] we obtained three mixed bolaamphiphiles by reaction of symmetric bolaamphiphiles respectively from rhamnosides and esters presenting analog carbon chain lengths (Scheme 5). The cross metathesis reactions were realized in a mixture CH_2Cl_2/MeOH or in dichloromethane at 45°C respectively during 24h or 8h with 2 equivalents of rhamnoside-based bolaamphiphiles and 1 equivalent of esters. Three mixed (or asymmetric) bolaamphiphiles were obtained with yields up to 80%, depending on the nature of the solvent as seen previously, the reaction time (from 24h to 8h) and the yields being improved slightly with the use of dichloromethane.



	Reaction yields[a] (%)	Reaction yields[b] (%)
22 (n= 6)	65	70
23 (n= 7)	70	75
24 (n= 8)	75	80

[a] in CH_2Cl_2/MeOH, 24h

[b] in CH_2Cl_2, 8h

Scheme 5 - Cross-Metathesis reactions

These compounds present a bolaform structure with two different hydrophilic heads. One head could bring antioxidant properties as wide ranges of phenolic compounds in nature are

participating in the defense role and exhibit antioxidant and other biological properties;[13a] the other head could be able to confer the specific properties of rhamnolipids, known as very efficient biosurfactant molecules and used in a wide range of industrial applications including food, cosmetics, pharmaceutical formulations and bioremediation of pollutants.[8b]

Conclusion

In conclusion, we prepared a large panel of symmetric and asymmetric bolaamphiphiles derived from L-rhamnose and/or 3-(4-hydroxyphenyl)propionic by using reaction sequences involving solvent-free glycosylations or enzymatic esterifications and metathesis steps. No protection/deprotection steps of the biosourced starting materials are required and the yields are good and the purification of the products relatively easy. The determination of their respective interfacial, antioxidant and eliciting properties are currently underway.

Experimental section

All reagents were commercially available and used as received. Solvents were dried and distilled under argon before use (CH_2Cl_2 over $CaCl_2$ and THF over sodium/benzophenone) and stored over molecular sieves. ^1H and ^{13}C NMR spectra were recorded on an AC 250 Bruker in CD_3OD for ^1H and ^{13}C spectra. The infrared spectra were recorded with Spectrafile IR^{TM} Plus MIDAC. All electrospray ionization mass spectrometry experiments (MS and HRMS) were obtained on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode (EV = 30 V, 80°C, flow of injection: 5 µl/min). Chromatography was carried out on SDS Silica 60 (40-63 µm), Art 2050044 (flash-chromatography) or silica 60 F_{254} (TLC plates).

General Procedure for the preparation of the rhamnosides:

To a solution of L-rhamnose and unsaturated alcohol in THF (20 mL) or not (reaction without solvent during 5h) are added at 80°C, PTSA in three portions. After respectively 48 h or 5 h of reaction, the mixture is neutralized with addition of a 0.5 M MeONa solution (≈ 26 mL) and the purification of the major α anomer (ratio α/β: 95/5) is realized through flash chromatography (eluting mixture: CH_2Cl_2/MeOH 9:1).

Hex-5'-enyl-α-L-rhamnopyranoside 1

General Procedure for the preparation of the rhamnosides with L-rhamnose (4.006 g; 21.9 mmol; 1 eq) and 5-Hexen-1-ol (4.405 g; 43.9 mmol; 2 eq), 2.509 g of PTSA (13.19 mmol; 0.6 eq) in three portions (836 mg each h).

Compound **1** is obtained as a brown paste with a yield of 70 (48h) or 75 (5h) %. ν_{max} (ATR) /cm^{-1} 3374 (OH), 2926-2856 (C-H), 1641 (C=C), 1053-1123 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.28 (3H, d, J 7.5, **CH_3**), 1.52 (2H, overlap, -**CH_2**$CH_2CH=CH_2$), 1.60 (2H, overlap, -**CH_2**$CH_2CH_2CH=CH_2$), 2.10 (2H, m, CH_2**CH_2**$CH=CH_2$), 3.33-3.87 (6H, overlap, **CH**(CH_3)**CH**(OH)**CH**(OH)**CH**(OH)CH(O**CH_2**$(CH_2)_3CH=CH_2$), 4.68 (1H, broad, **CH**(OCH_2)-), 4.96 (3H, overlap, CH($OCH_2(CH_2)_3CH=$**CH_2**), -**OH**), 5.02 (1H, broad, $(CH_2)_3CH=$**CH_2**)), 5.82 (1H, m, $(CH_2)_3$**CH**$=CH_2$); δ_c (250.1 MHz; CD_3OD) 18.0 (**CH_3**), 26.6 (-**CH_2**$CH=CH_2$), 30.0, 34.5, (-CH_2**CH_2****CH_2**CH=), 68.3 (-**CH_2**CH_2CH_2CH), 69.6 (**CH**(CH_3)CH(OH), 72.3 (CH(CH_3)**CH**(OH), 73.4 (-**CH**(OH)CH(OH), 73.9 (-CH(OH)**CH**(OH)CH), 101.6 (**CH**(OCH_2), 115.1 $(CH_2)_3CH=$**CH_2**), 139.7 ($(CH_2)_3$**CH**$=CH_2$));HRMS, calcd For $C_{12}H_{22}O_5$ [M+Na$^+$]: 269.2926, found: 269.2925.

Hept-6'-enyl-α-L-rhamnopyranoside 2

General Procedure for the preparation of the rhamnosides with L-rhamnose (4.001 g; 21.9 mmol; 1 eq) and 6-Hepten-1-ol (5.015 g; 43.9 mmol; 2 eq), 2.506 g of PTSA (13.17 mmol; 0.6 eq) in three portions (835 mg each h).

Compound **2** is obtained as a brown paste with a yield of 75 (48h) or 80 (5h) %. ν_{max} (ATR) /cm^{-1} 3374 (OH), 2926-2856 (C-H), 1641 (C=C), 1053-1123 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.28 (3H, d, J 7.5, **CH_3**), 1.52 (2H, overlap, -**CH_2**$CH_2CH_2CH=CH_2$), 1.60 (2H, overlap, -**CH_2**$CH_2CH_2CH_2CH=CH_2$), 2.12 (2H, m, -CH_2**CH_2**$CH=CH_2$), 3.41-3.89 (6H, overlap, **CH**(CH_3)**CH**(OH)**CH**(OH)**CH**(OH)CH(O**CH_2**)-), 4.70 (1H, broad, -**CH**$(OCH_2(OC)$, 4.96 (3H, overlap, -CH($OCH_2(CH_2)_4CH=$**CH_2**), -**OH**), 5.07 (1H, broad, -$(CH_2)_4CH=$**CH_2**), 5.86 (1H, m, -$(CH_2)_4$**CH**$=CH_2$); δ_c (250.1 MHz; CD_3OD) 18.01 (**CH_3**), 26.7 (-**CH_2**$CH=CH_2$), 29.8, 30.4, 34,7 (-**CH_2****CH_2****CH_2**$CH_2CH=$), 68.4 (-**CH_2**$(CH_2)_4CH=$), 69.6 (**CH**(CH_3)CH(OH), 72.3 (CH(CH_3)**CH**(OH), 73.4 (**CH**(OH)CH(OH), 73.9 (CH(OH)**CH**(OH)CH), 101.6 (**CH**(OCH_2), 114.9 $(CH_2)_3CH=$**CH_2**), 139.8 ($(CH_2)_3$**CH**$=CH_2$)); HRMS, calcd For $C_{13}H_{24}O_5$ [M+Na$^+$]: 283.3194, found: 283.3193.

Oct-7'-enyl-α-L-rhamnopyranoside 3

General Procedure for the preparation of the rhamnosides with L-rhamnose (3.162 g; 17.3 mmol; 1 eq) and 7-Octen-1-ol (4.451 g; 34.7 mmol; 2 eq), 1.98 g of PTSA (10.4 mmol; 0.6 eq) in three portions (660 mg each h).

Compound **3** is obtained as a brown paste with a yield of 80 (48h) or 85 (5h) %. ν_{max} (ATR) /cm^{-1} 3374 (OH), 2926-2856 (C-H), 1641(C=C), 1053-1123 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.30 (3H, d, J 7.5, **CH_3**), 1.42 (6H, broad, -CH_2**CH_2****CH_2****CH_2**$CH_2CH=$), 1.63 (2H, m, -CH_2**CH_2**$(CH_2)_4CH=CH_2$), 2.11 (2H, m, -

CH$_2$CH$_2$(CH$_2$)$_4$), 3.40-3.91 (6H, overlap, **CH**(CH$_3$)**CH**(OH)**CH**(OH)**CH**(OH)CH(O**CH$_2$**(CH$_2$)$_5$)), 4.70 (1H, broad, **CH**(OCH$_2$)-), 4.96 (3H, overlap, CH(OCH$_2$(CH$_2$)$_5$CH=**CH$_2$**), **-OH**), 5.07 (1H, broad, (CH$_2$)$_5$CH=**CH$_2$**), 5.86 (1H, m, (CH$_2$)$_5$**CH**=CH$_2$)); δ_c (250.1 MHz; CD$_3$OD) 18.0 (**CH$_3$**), 27.1 (-**CH$_2$**CH=CH$_2$), 28.7, 29.9, 30.5, 34,8 (-**CH$_2$CH$_2$CH$_2$CH$_2$**CH$_2$-), 68.4 (-**CH$_2$**(CH$_2$)$_5$CH=CH$_2$), 69.6 (**CH**(CH$_3$)CH(OH)-), 72.3 (CH(CH$_3$)**CH**(OH)-), 73.4 (-**CH**(OH)CH(OH)-), 73.9 (-CH(OH)**CH**(OH)-), 101.6 (**CH**(OCH$_2$), 114.8 (-(CH$_2$)$_5$CH=**CH$_2$**)), 139.9 (-(CH$_2$)$_5$**CH**=CH$_2$)); HRMS, calcd For $C_{14}H_{26}O_5$ [M+Na$^+$]: 297.3462, found: 297.3461.

Non-8'-enyl-α-L-rhamnopyranoside 4

General Procedure for the preparation of the rhamnosides with L-rhamnose (4.0 g; 21.9 mmol; 1 eq) and 8-nonen-1-ol (6.246 g; 43.9 mmol; 2 eq), 2.506 g of PTSA (13.17 mmol; 0.6 eq) in three portions (835 mg each h).

Compound **4** is obtained as a brown paste with a yield of 85 (48h) or 90 (5h) %. ν_{max} (ATR) /cm^{-1} 3374 (OH), 2926-2856 (C-H), 1641 (C=C), 1053-1123 (C-O-C); δ_H (250.1 MHz; CD$_3$OD) 1.26 (3H, d, J 7.5, **CH$_3$**), 1.34 (8H, broad, **CH$_2$CH$_2$CH$_2$CH$_2$**CH$_2$CH=), 1.58 (2H, m, CH$_2$**CH$_2$**(CH$_2$)$_5$CH=), 2.04 (2H, m, (CH$_2$)$_5$**CH$_2$**CH=CH$_2$), 3.31-3.84 (6H, overlap, **CH**(CH$_3$)**CH**(OH)**CH**(OH)**CH**(OH)CH(O**CH$_2$**(CH$_2$)$_6$CH=CH$_2$), 4.65 (1H, broad, **CH**(OCH$_2$)-), 4.96 (3H, overlap, CH(OCH$_2$(CH$_2$)$_5$CH=**CH$_2$**), **-OH**), 5.01 (1H, broad, -(CH$_2$)$_5$CH=**CH$_2$**), 5.80 (1H, m, -(CH$_2$)$_5$**CH**=CH$_2$); δ_c (250.1 MHz; CD$_3$OD) 18.01 (**CH$_3$**), 27.3 (**CH$_2$**CH=CH$_2$), 28.7, 29.9, 30.03, 30.5, 34.8 -(**CH$_2$)$_5$**CH$_2$CH=), 68.5 -**CH$_2$**(CH$_2$)$_6$CH=CH$_2$), 69.6 (**CH**(CH$_3$)CH(OH)-), 72.3 (CH(CH$_3$)**CH**(OH)-), 73.4 (**CH**(OH)CH(OH)-), 73.9 (-CH(OH)**CH**(OH)CH-), 101.6 (**CH**(OCH$_2$), 114.7 (-(CH$_2$)$_7$CH=**CH$_2$**), 140.0 (-(CH$_2$)$_7$**CH**=CH$_2$); HRMS, calcd For $C_{15}H_{28}O_5$ [M+Na$^+$]: 311.373, found: 311.372.

Dec-9'-enyl-α-L-rhamnopyranoside 5

General Procedure for the preparation of the rhamnosides with L-rhamnose (4.007 g; 21.9 mmol; 1 eq) and 9-decen-1-ol (6.874 g; 43.9 mmol; 2 eq), 2.51 g of PTSA (13.19 mmol; 0.6 eq) in three portions (837 mg each h).

Compound **5** is obtained as a brown paste with a yield of 90 (48h) or 95 (5h) %. ν_{max} (ATR) /cm^{-1} 3374 (OH), 2926-2856 (C-H), 1641 (C=C), 1053-1123 (C-O-C); δ_H (250.1 MHz; CD$_3$OD) 1.23 (3H, d, J 7.5, **CH$_3$**), 1.32 (10H, broad, -(**CH$_2$)$_5$**CH$_2$CH=), 1.56 (2H, m, CH$_2$**CH$_2$**(CH$_2$)$_5$CH$_2$CH=CH$_2$), 2.03 (2H, m, -(CH$_2$)$_5$**CH$_2$**CH=CH$_2$), 3.33-3.87 (6H, overlap, **CH**(CH$_3$)**CH**(OH)**CH**(OH)**CH**(OH)CH(O**CH$_2$**(CH$_2$)$_7$), 4.63 (1H, broad, -**CH**(OCH$_2$)-, 4.91 (3H, overlap, CH=**CH**), 2 **OH**), 5.01 (1H, broad, CH=**CH$_2$**), 5.80 (1H, m, **CH**=CH$_2$); δ_c (250.1 MHz; CD$_3$OD) 18.1 (**CH$_3$**), 27.4 (-**CH$_2$**(CH$_2$)$_6$CH=CH$_2$), 30.1, 30.2, 30.5, 30.6, 30,7 -CH$_2$(**CH$_2$)$_5$**CH$_2$CH), 34.9 (CH$_2$)$_5$**CH$_2$**CH=), 68.5 (**CH$_2$**(CH$_2$)$_7$CH=), 69.7 (**CH**(CH$_3$)CH(OH), 72.4 (CH(CH$_3$)**CH**(OH)-), 72.5 (**CH**(OH)CH(OH)-), 73.9 (CH(OH)**CH**(OH)CH-), 101.6 (**CH**(OCH$_2$), 114.7 (-(CH$_2$)$_6$CH=**CH$_2$**), 140.0 (-(CH$_2$)$_6$**CH**=CH$_2$)); HRMS, calcd For $C_{16}H_{30}O_5$ [M+Na$^+$]: 325.3998, found: 325.3997.

Undec-10'-enyl-α-L-rhamnopyranoside 6

General Procedure for the preparation of the rhamnosides with L-rhamnose (4.004 g; 21.9 mmol; 1 eq) and 10-undecen-1-ol (7.485 g; 43.9 mmol; 2 eq), 2.508 g of PTSA (13.18 mmol; 0.6 eq) in three portions (836 mg each h).

Compound **6** is obtained as a brown paste with a yield of 95 (48h) or 97 (5h) %. ν_{max} (ATR) /cm^{-1} 3374 (OH), 2926-2856 (C-H), 1641 (C=C), 1053-1123 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.23 (3H, d, J 7.5, **CH_3**), 1.32 (12H, broad, (**CH_2)$_6$**CH_2CH=), 1.57 (2H, m, CH_2**CH_2**$(CH_2)_6CH_2CH$=), 2.03 (2H, m, $(CH_2)_6$**CH_2**$CH=CH_2$), 3.33-3.87 (6H, overlap, **CH**(CH_3)**CH**(OH)**CH**(OH)**CH**$(OH)CH(O$**CH_2**$(CH_2)_8$), 4.63 (1H, broad, **CH**(OCH_2)-), 4.92 (2H, overlap, -CH=**CH_2**), **-OH**), 5.01 (1H, broad, -CH=**CH_2**), 5.80 (1H, m, -**CH**$=CH_2$); δ_c (250.1 MHz; CD_3OD) 18.1 (**CH_3**), 27.4 (-**CH_2**$(CH_2)_7CH=CH_2$), 28.9, 30.1, 30.2, 30.5, 30.6, 30.7 (-CH_2(**CH_2)$_6$**CH_2CH), 34.9 (-$CH_2)_6$**CH_2**CH=), 68.5 (-**CH_2**$(CH_2)_8CH$=), 69.7 (**CH**$(CH_3)CH(OH)$-), 72.4 $(CH(CH_3)$**CH**$(OH)CH(OH)CH(OH)$-), 72.5 (-**CH**$(OH)CH(OH)$-), 73.9 (-$CH(OH)$**CH**$(OH)CH$-), 101.6 (**CH**(OCH_2), 114.7 (-$CH_2CH_2CH_2CH_2CH_2CH_2(CH_2)_3CH=$**$CH_2$**), 140.0 ($(CH_2)_9$**CH**$=CH_2$)); HRMS, calcd For $C_{17}H_{32}O_5$ [M+Na$^+$]: 339.4266, found: 339.4265.

General Procedure for the preparation of the rhamnoside-based bolaamphiphiles:

The rhamnoside is diluted in CH_2Cl_2 (35 mL) / MeOH (5mL) or CH_2Cl_2 (40 mL) in a Schlenk tube under argon and the Grubbs I catalyst is added in three portions over 3h. After 72 h or 8h of reaction at 45°C, the solvent is evaporated under reduced pressure and the residue is purified by flash chromatography (eluting mixture: CH_2Cl_2/MeOH 9:1).

1', 10'-bis-dec-5'-enyl-α-L-rhamnopyranoside 7

General Procedure for the preparation of the rhamnoside-based bolaamphiphiles with Compound **1** (2.36 g; 9.59 mmol; 1 eq) and Grubbs I catalyst (789.5 mg; 0.959 mmol; 0.1 eq) is added in three portions over 3h.

Compound **7** is obtained as a brown wax with a yield of 50 % (72h) or 55 % (8h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3429 (OH), 2926-2855 (C-H), 1634 (C=C), 1057-1131 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.24 (6H, d, J 7.5, 2 **CH_3**), 1.42-1.54 (8H, overlap,-**$(CH_2)_2$**$CH_2CH=CHCH_2$**$(CH_2)_2$**CH_2-), 1.57 (4H, broad m, -**CH_2**$CH=CH$**CH_2**$(CH_2)_2$-), 3.34 (5H, overlap, $CH(CH_3)$**CH**$(OH)CH(OH)$-$CH(OH)CH(O$**CH_2**)-$(CH_2)_3CH=CH(CH_2)_3$**CH_2**), 3.78 (6H, overlap, **CH**$(CH_3)CH(OH)CH(OH)$-**CH**$(OH)CH(O$**CH_2**)-$(CH_2)_3CH=CH(CH_2)_3$**CH_2**), 3.84 (2H, broad, $CH(CH_3)CH(OH)$**CH**(OH)-), 4.65 (2H, broad, $CH(OH)$**CH**(OCH_2)-$(CH_2)_3CH$=), 5.41 (2H, m, -$(CH_2)_3$**CH**=**CH**$(CH_2)_3$); δ_c (250.1 MHz; CD_3OD) 18.02 (**CH_3**), 27.3 (-$(CH_2)_2$**CH_2**$CH_2CH=CHCH_2$**CH_2**$(CH_2)_2$), 30.0-33.3 (-CH_2**CH_2**CH_2**CH_2**$CH=CH$**CH_2CH_2**CH_2**CH_2), 68.4 (**CH_2**$CH_2CH_2CH_2CH=CHCH_2CH_2CH_2$**$CH_2$**), 69.6 (**CH**$(CH_3)CH(OH)CH$-), 71.8 $(CH(CH_3)$**CH**$(OH)CH(OH)$-), 72.3 (-$CH(OH)$**CH**(OH)), 73.9 $(CH(CH_3)CH(OH)CH(OH)$-**CH**$(OH)CH(OCH_2)$-), 101.5 (-$CH(OH)$**CH**(OCH_2)-), 130.8 (CH_2**CH**$(Z)=$**CH**$(Z)CH_2$), 131.3-131.5 (CH_2**CH**=**CH**CH_2); HRMS, calcd For $C_{22}H_{40}O_{10}$ [M+Na$^+$]: 487.5418, found: 487.5417.

1', 12'-bis-dodec-6'-enyl-α-L-rhamnopyranoside 8

General Procedure for the preparation of the rhamnoside-based bolaamphiphiles with compound **2** (1.7 g; 6.53 mmol; 1 eq) and Grubbs I catalyst (538.1 mg; 0.654 mmol; 0.1 eq). Compound **8** is obtained as a brown wax with a yield of 55 % (72h) or 60 % (8h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3429 (OH), 2926-2855 (C-H), 1634 (C=C), 1057-1131 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.26 (6H, d, J 7.5, 2 **CH_3**), 1.42-1.59 (12H, overlap, **$(CH_2)_3$**CH_2CH=$CHCH_2$**$(CH_2)_3$**CH_2), 2.03 (4H, broad m, $(CH_2)_3$**CH_2**CH=CH**CH_2**$(CH_2)_3$), 3.36 (5H, overlap, $CH(CH_3)$**CH**$(OH)CH(OH)$-$CH(OH)CH(O$**CH_2**$)$-$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**), 3.78 (6H, overlap, **CH**$(CH_3)CH(OH)CH(OH)$-**CH**$(OH)CH(O$**CH_2**$)$-$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**), 3.87 (2H, broad, $CH(CH_3)CH(OH)$**CH**(OH)-), 4.67 (2H, broad, $CH(OH)$**CH**(OCH_2)-$(CH_2)_4CH$=), 5.43 (2H, m, -$(CH_2)_3$**CH**=**CH**$(CH_2)_3$); δ_c (250.1 MHz; CD_3OD) 18.02 (**CH_3**), 27.3 (-$(CH_2)_2$**CH_2**CH_2CH=$CHCH_2$**CH_2**$(CH_2)_2$), 30.0-33.3 (-CH_2(**CH_2**$)_3CH_2CH$=$CHCH_2$(**CH_2**$)_3CH_2$), 68.4 (**$CH_2CH_2CH_2CH_2CH_2CH$**=$CH(CH_2)_4$**CH_2**), 69.6 (**CH**$(CH_3)CH(OH)$-), 71.8 $(CH(CH_3)$**CH**$(OH)CH(OH)$-), 72.3 (-$CH(OH)$**CH**(OH)), 73.9 (-**CH**$(OH)CH(OCH_2)$-), 101.5 (-$CH(OH)$**CH**(OCH_2)-), 130.8 (CH_2**CH**(Z)=**CH**$(Z)CH_2$), 131.3-131.5 (CH_2**CH**=**CH**CH_2); HRMS, calcd For $C_{24}H_{44}O_{10}$ [M+Na$^+$]: 515.5954, found: 515.5953.

1', 14'-bis-tetradec-7'-enyl-α-L-rhamnopyranoside 9

General Procedure for the preparation of the rhamnoside-based bolaamphiphiles with compound **3** (2.44 g; 8.9 mmol; 1 eq) and Grubbs I catalyst (732.8 mg; 0.89 mmol; 0.1 eq). Compound **9** is obtained as a brown wax with a yield of 60% (72h) or 65% (8h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3429 (OH), 2926-2855 (C-H), 1634 (C=C), 1057-1131 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.24 (6H, d, J 7.5, 2 **CH_3**), 1.27 (12H, broad, **$(CH_2)_3$**CH_2CH=$CHCH_2$**$(CH_2)_3$**CH_2), 1.57 (4H, broad m, -**CH_2**$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**CH_2), 1.98 (4H, broad m, (-**CH_2**CH=CH**CH_2**-), 3.36 (5H, overlap, **CH**$(OH)CH(OH)_2CH(O$**CH_2**$)$-$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**), 3.78 (6H, overlap, **CH**$(CH_3)CH(OH)CH(OH)$-**CH**$(OH)CH(O$**CH_2**$)$-$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**), 3.87 (2H, broad, $CH(OH)$**CH**(OH)-), 4.67 (2H, broad, -$CH(OH)$**CH**(OCH_2)-), 5.43 (2H, m, -**CH**=**CH**); δ_c (250.1 MHz; CD_3OD) 18.03 (**CH_3**), 27.3 (-$(CH_2)_2$**CH_2**$(CH_2)_3CH$=$CH(CH_2)_3$**CH_2**$(CH_2)_2$), 30.0-33.6 (**$(CH_2)_4$**CH_2CH=CH(**CH_2**$)_4CH_2$**CH_2**-), 68.4 (**CH_2**$(CH_2)_5CH$=$CHCH_2CH_2(CH_2)_4$**CH_2**), 69.6 (**CH**$(CH_3)CH(OH)$-), 71.8 $(CH(CH_3)$**CH**$(OH)CH(OH)$-), 72.3 (-$CH(OH)$**CH**(OH)), 73.9 (-**CH**$(OH)CH(OCH_2)$-), 101.5 (-$CH(OH)$**CH**(OCH_2)-), 130.8 (CH_2**CH**(Z)=**CH**$(Z)CH_2$), 131.3-131.5 (CH_2**CH**=**CH**CH_2); HRMS, calcd For $C_{26}H_{48}O_{10}$ [M+Na$^+$]: 543.649, found: 543.648.

1', 16'-bis-hexadec-8'-enyl-α-L-rhamnopyranoside 10

General Procedure for the preparation of the rhamnoside-based bolaamphiphiles with compound **4** (3.04 g; 10.5 mmol; 1 eq) and Grubbs I catalyst (868 mg; 1.05 mmol; 0.1 eq). Compound **10** is obtained as a brown wax with a yield of 65% (72h) or 70% (8h) as a mixture

Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3429 (OH), 2926-2855 (C-H), 1634 (C=C), 1057-1131 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.27 (6H, d, J 7.5, 2 **CH_3**), 1.34 (16H, broad, **$(CH_2)_4$**CH_2CH=$CHCH_2$**$(CH_2)_4$**CH_2), 1.59 (4H, broad m, (**CH_2**$(CH_2)_5CH$=$CH(CH_2)_5$**CH_2**CH_2), 2.0 (4H, broad m, (**CH_2CH=$CHCH_2$**), 3.36 (5H, overlap, **CH**$(OH)_3CH(O$**CH_2**)-$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**), 3.78 (6H, overlap, **CH**$(CH_3)CH(OH)_2$**CH**$(OH)CH(O$**CH_2**)-$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**), 3.87 (2H, broad, CH(OH)**CH**(OH)-), 4.67 (2H, broad, CH(OH)**CH**(OCH_2)-), 5.43 (2H, m, -**CH**=**CH**); δ_c (250.1 MHz; CD_3OD) 18.03 (**CH_3**), 27.3 (-$(CH_2)_2$**CH_2**$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**$(CH_2)_2$), 30.0-33.6 ((**$(CH_2)_5$**CH_2CH=$CH($**CH_2**$)_5$**CH_2**CH_2-), 68.4 (**CH_2**$(CH_2)_6CH$=$CH(CH_2)_6$**CH_2**), 69.6 (**CH**$(CH_3)CH(OH)$-), 71.8 ($CH(CH_3)$**CH**-), 72.3 (-CH(OH)**CH**(OH)), 73.9 (-**CH**$(OH)CH(OCH_2)$-), 101.5 (-CH(OH)**CH**(OCH_2)-), 130.8 (CH_2**CH**(Z)=**CH**(Z)CH_2), 131.3-131.5 (CH_2**CH**=**CH**CH_2); HRMS, calcd For $C_{28}H_{52}O_{10}$ [M+Na$^+$]: 571.7026, found: 571.7030.

1', 18'-bis-octadec-9'-enyl-α-L-rhamnopyranoside 11

General Procedure for the preparation of the rhamnoside-based bolaamphiphiles with compound **5** (4.21 g; 13.9 mmol; 1 eq) and Grubbs I catalyst (1.147 g; 1.39 mmol; 0.1 eq). Compound **11** is obtained as a brown wax with a yield of 70% (72h) or 75% (8h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3429 (OH), 2926-2855 (C-H), 1634 (C=C), 1057-1131 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.24 (6H, d, J 7.5, 2**CH_3**), 1.31 (20H, broad, **$(CH_2)_5$**CH_2CH=$CHCH_2$**$(CH_2)_5$**CH_2), 1.59 (4H, broad m, (**CH_2**$(CH_2)_6CH$=$CH(CH_2)_6$**CH_2**CH_2), 2.0 (4H, broad m, (**CH_2CH=$CHCH_2$**), 3.36 (5H, overlap, **CH**$(OH)_3CH(O$**CH_2**)-$(CH_2)_7CH$=$CH(CH_2)_7$**CH_2**), 3.78 (6H, overlap, **CH**$(CH_3)CH(OH)_2$-**CH**$(OH)CH(O$**CH_2**)-$(CH_2)_7CH$=$CH(CH_2)_7$**CH_2**), 3.87 (2H, broad, CH(OH)**CH**(OH)-), 4.67 (2H, broad, CH(OH)**CH**(OCH_2)-), 5.43 (2H, m, -**CH**=**CH**); δ_c (250.1 MHz; CD_3OD) 18.03 (**CH_3**), 27.3 (-$(CH_2)_2$**CH_2**$(CH_2)_5CH$=$CH(CH_2)_5$**CH_2**$(CH_2)_2$), 30.0-33.6 ((**$(CH_2)_5$**CH_2CH=$CH($**CH_2**$)_5$**CH_2**CH_2-), 68.4 (**CH_2**$(CH_2)_7CH$=$CH(CH_2)_3CH_2CH_2CH_2CH_2$**$CH_2$**), 69.6 (**CH**$(CH_3)CH$-), 71.8 ($CH(CH_3)$**CH**$(OH)CH(OH)$-), 72.3 (-CH(OH)**CH**(OH)), 73.9 (-**CH**$(OH)CH(OCH_2)$-), 101.5 (-CH(OH)**CH**(OCH_2)-), 130.8 (CH_2**CH**(Z)=**CH**(Z)CH_2), 131.3-131.5 (CH_2**CH**=**CH**CH_2); HRMS, calcd For $C_{30}H_{56}O_{10}$ [M+Na$^+$]: 599.7562, found: 599.7561.

1', 20'-bis-eicosa-10'-enyl-α-L-rhamnopyranoside 12

General Procedure for the preparation of the rhamnoside-based bolaamphiphiles with compound **6** (3.58 g; 11.3 mmol; 1 eq) and Grubbs I catalyst (932.3 mg; 1.13 mmol; 0.1 eq). Compound **12** is obtained as a brown wax with a yield of 75% (72h) or 80% (8h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3429 (OH), 2926-2855 (C-H), 1634 (C=C), 1057-1131 (C-O-C); δ_H (250.1 MHz; CD_3OD) 1.24 (6H, d, J 5.0 Hz, 2 **CH_3**), 1.31 (24H, broad, **$(CH_2)_6$**CH_2CH=$CHCH_2$**$(CH_2)_6$**CH_2), 1.59 (4H, broad m, (**CH_2**$(CH_2)_7CH$=$CH(CH_2)_7$**CH_2**CH_2), 2.0 (4H, broad m, (**CH_2CH=$CHCH_2$**), 3.36 (5H, overlap, **CH**$(OH)_3CH(O$**CH_2**)-$(CH_2)_8CH$=$CH(CH_2)_8$**CH_2**), 3.78 (6H, overlap, **CH**$(CH_3)CH(OH)_2$**CH**$(OH)CH(O$**CH_2**)-$(CH_2)_8CH$=$CH(CH_2)_8$**CH_2**), 3.87 (2H, broad, $CH(CH_3)CH(OH)$**CH**(OH)-), 4.67 (2H, broad, CH(OH)**CH**(OCH_2)-), 5.43 (2H, m, -**CH**=**CH**); δ_c (250.1 MHz; CD_3OD) 18.03 (**CH_3**), 27.3 (-$(CH_2)_2$**CH_2**$(CH_2)_6CH$=$CH(CH_2)_6$**CH_2**-), 30.0-33.6 ((**$(CH_2)_5$**CH_2CH=$CH($**CH_2**$)_6$**CH_2**CH_2-), 68.4

(**CH$_2$**(CH$_2$)$_8$CH=CH(CH$_2$)$_8$**CH$_2$**), 69.6 (**CH**(CH$_3$)CH(OH)-), 71.8 (CH(CH$_3$)**CH**(OH)-), 72.3 (-CH(OH)**CH**(OH)), 73.9 (-**CH**(OH)CH(OCH$_2$)-), 101.5 (-CH(OH)**CH**(OCH$_2$)-), 130.8 (CH$_2$**CH**(Z)=**CH**(Z)CH$_2$), 131.3-131.5 (CH$_2$**CH**=**CH**CH$_2$); HRMS, calcd For $C_{32}H_{60}O_{10}$ [M+Na$^+$]: 627.8098, found: 627.8100.

General Procedure for the preparation of the fatty esters derived from 3-(4-hydroxyphenyl)propionic acid:

In a 250 mL flask, 3-(4-hydroxyphenyl)propionic acid and 5-hexen-1-ol are dissolved in 60 mL of 2-methyl-2-butanol, under magnetic stirring. The whole is heated at 60°C for 30 minutes in presence of 3Å molecular sieves (50 g.L^{-1}). After adding appropriate amount of enzyme (2.5 g per 100 g of reaction mixture), the reaction mixture is left without stirring at room temperature for 48 hours. Once the reaction is completed, the reaction mixture is filtered through celite; the obtained solution is evaporated under reduced pressure and the residue formed is purified by chromatography on silica gel (eluting mixture: petroleum ether / ethyl acetate 6: 4).

Hex-5'-enyl-3-(4-hydroxyphenyl)propionic acid 13

General Procedure for the preparation of the fatty esters with 36.4 mmol of 3-(4-hydroxyphenyl)propionic acid (6.05 g; 6 eq) and 6.07 mmol of 5-hexen-1-ol (607.78 mg; 1 eq).

Compound **13** was obtained as a clear oil with a yield of 70%. ν_{max} (ATR) /cm^{-1} 3404 (OH), 2928-2857 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD$_3$OD) 1.27 (4H, broad, phenyl(OH)-(CH$_2$)$_2$COOCH$_2$**CH$_2$CH$_2$**CH$_2$CH=CH$_2$), 2.02 (2H, m, -(CH$_2$)$_3$**CH$_2$**CH=CH$_2$), 2.53 (2H, t, J 7.5, -CH$_2$**CH$_2$**COO-), 2.79 (2H, t, J 7.5, phenyl(OH)-**CH$_2$**CH$_2$COO-), 4.00 (2H, t, J 7.5, -COO**CH$_2$**CH$_2$CH$_2$-), 4.92 (2H, overlap, -CH=**CH$_2$**), 5.77 (1H, m, **-CH**=CH$_2$), 6.68 (2H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-)), 6.98 (2H, d, J 10, phenyl (**CH**=C (alkyl)-**CH**=); δ_c (250.1 MHz; CD$_3$OD) 26.9, 27.5 (-COOCH$_2$**CH$_2$CH$_2$**-), 33.4 (phenyl(OH)-**CH$_2$**CH$_2$COO-), 36.7, 37.4 (phenyl(OH)-CH$_2$**CH$_2$**COOCH$_2$CH$_2$CH$_2$**CH$_2$**CH=), 65.5 (-COO**CH$_2$**-), 114.6, 116.14, 130.19 (phenyl(**CH**=C(OH)-**CH**=CH-), -CH=**CH$_2$**), 139.9 (-**CH**=CH$_2$), 156.7 (phenyl(CH=**C**(OH)-CH=CH-)), 174.7 (-**CO**O-); HRMS, calcd For $C_{15}H_{20}O_3$ [M+Na$^+$]: 271.311, found: 271.310.

Hept-6'-enyl-3-(4-hydroxyphenyl)propionic acid 14

General Procedure for the preparation of the fatty esters with 36.4 mmol of 3-(4-hydroxyphenyl)propionic acid (6.05 g; 6 eq) and 6.07 mmol of 6-hepten-1-ol (692.91 mg; 1 eq).

Compound **14** was obtained as a clear oil with a yield of 75%. ν_{max} (ATR) /cm^{-1} 3404 (OH), 2928-2857 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD$_3$OD) 1.27 (4H, broad, phenyl(OH)-(CH$_2$)$_2$COOCH$_2$CH$_2$**CH$_2$CH$_2$**CH$_2$CH=CH$_2$), 1.53 (2H, m, -COOCH$_2$**CH$_2$**), 2.02 (2H, m, **-CH$_2$**CH=CH$_2$), 2.53

(2H, t, J 7.5, -CH_2**CH_2**COO-), 2.79 (2H, t, J 7.5, phenyl(OH)-**CH_2**CH_2COO-), 4.00 (2H, t, J 7.5, -COO**CH_2**CH_2CH_2-), 4.92 (2H, overlap, -CH=**CH_2**), 5.77 (1H, m, -**CH**=CH_2), 6.68 (2H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-)), 6.98 (2H, d, J 10, phenyl (**CH**=C (alkyl)-**CH**=); δ_c (250.1 MHz; CD_3OD) 26.9, 27.5 (-$COOCH_2$**CH_2****CH_2**-), 32.6, 33.4 (-**CH_2**$CH_2COO(CH_2)_3$**CH_2**-), 36.7, 37.4 (-CH_2**CH_2**$COO(CH_2)_4$**CH_2**CH=), 65.5 (-COO**CH_2**-), 114.6, 116.14, 130.19 (phenyl(**CH**=C(OH)-**CH**=CH-), -CH=**CH_2**), 139.9 (-**CH**=CH_2), 156.7 (phenyl(CH=**C**(OH)-CH=CH-)), 174.7 (-**CO**O-); HRMS, calcd For $C_{16}H_{22}O_3$ [M+Na^+]: 285.3378, found: 285.3377.

Oct-7'-enyl-3-(4-hydroxyphenyl)propionic acid 15

General Procedure for the preparation of the fatty esters with 36.4 mmol of 3-(4-hydroxyphenyl)propionic acid (6.05 g; 6 eq) and 6.07 mmol of 7-octen-1-ol (778.05 mg; 1 eq).

Compound **15** was obtained as a clear oil with a yield of 80%. ν_{max} (ATR) /cm^{-1} 3404 (OH), 2928-2857 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD_3OD) 1.27 (6H, broad, -**$CH_2CH_2CH_2CH_2CH_2$**$CH_2CH=CH_2$), 1.54 (2H, m, -$COOCH_2$**CH_2**-), 2.02 (2H, m, -$COO(CH_2)_5$**CH_2**$CH=CH_2$), 2.53 (2H, t, J 7.5, -CH_2**CH_2**COO-), 2.79 (2H, t, J 7.5, phenyl(OH)-**CH_2**CH_2COO-), 4.00 (2H, t, J 7.5, -COO**CH_2**CH_2CH_2-), 4.92 (2H, overlap, -CH=**CH_2**), 5.77 (1H, m, -**CH**=CH_2), 6.68 (2H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-)), 6.98 (2H, d, J 10, phenyl (**CH**=C (alkyl)-**CH**=); δ_c (250.1 MHz; CD_3OD) 26.9 (-$COOCH_2$**CH_2****CH_2**-), 29.6-33.4 (-**CH_2**$CH_2COOCH_2CH_2CH_2$**CH_2**CH_2-), 36.7, 37.4 (-CH_2**CH_2**$COO(CH_2)_5$**CH_2**-), 65.5 (-COO**CH_2**-), 114.6, 116.14, 130.19 (phenyl(**CH**=C(OH)-**CH**=CH-), -CH=**CH_2**), 139.9 (-**CH**=CH_2), 156.7 (phenyl(CH=**C**(OH)-CH=CH-)), 174.7 (-**CO**O-); HRMS, calcd For $C_{17}H_{24}O_3$ [M+Na^+]: 299.3646, found: 299.3650.

Non-8'-enyl-3-(4-hydroxyphenyl)propionic acid 16

General Procedure for the preparation of the fatty esters with 36.4 mmol of 3-(4-hydroxyphenyl)propionic acid (6.05 g; 6 eq) and 6.07 mmol of 7-octen-1-ol (863.12 mg; 1 eq).

Compound **16** was obtained as a clear oil with a yield of 85%. ν_{max} (ATR) /cm^{-1} 3404 (OH), 2928-2857 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD_3OD) 1.27 (8H, broad, -CH_2CH_2**$CH_2CH_2CH_2CH_2$**$CH_2CH=CH_2$), 1.54 (2H, m, -CH_2**CH_2**$(CH_2)_5CH=CH_2$), 2.02 (2H, m, -**CH_2**$CH=CH_2$), 2.53 (2H, t, J 7.5, -CH_2**CH_2**COO-), 2.79 (2H, t, J 7.5, phenyl(OH)-**CH_2**CH_2COO-), 4.00 (2H, t, J 7.5, -COO**CH_2**CH_2CH_2-), 4.92 (2H, overlap, -CH=**CH_2**), 5.78 (1H, m, -**CH**=CH_2), 6.68 (2H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-)), 6.98 (2H, d, J 10, phenyl (**CH**=C(alkyl)-**CH**=); δ_c (250.1 MHz; CD_3OD) 27.2 (-**CH_2**-$(CH_2)_4CH=CH_2$), 29.6-34.6 (-**CH_2**CH_2COOCH_2**CH_2**CH_2**CH_2CH_2**CH_2**-), 36.7, 37.4 (-CH_2**CH_2**$COO(CH_2)_6$**CH_2**-), 65.5 (-COO**CH_2**-), 114.6, 116.14, 130.19 (phenyl(**CH**=C(OH)-**CH**=CH-), -CH=**CH_2**), 139.9 (-**CH**=CH_2), 156.7 (phenyl(CH=**C**(OH)-)), 174.7 (-**CO**O-); HRMS, calcd For $C_{18}H_{26}O_3$ [M+Na^+]: 313.3914, found: 313.3913.

Dec-9'-enyl-3-(4-hydroxyphenyl)propionic acid 17

General Procedure for the preparation of the fatty esters with 39.17 mmol of 3-(4-hydroxyphenyl)propionic acid (6.51 g; 6 eq) and 6.53 mmol of 9-decen-1-ol (1.02 g; 1 eq). Compound **17** was obtained as a clear oil with a yield of 90%. ν_{max} (ATR) /cm^{-1} 3404 (OH), 2928-2857 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD_3OD) 1.27 (10H, broad, -$CH_2CH_2COOCH_2CH_2$**$CH_2CH_2CH_2CH_2CH_2$**$CH_2CH=CH_2$), 1.54 (2H, m, -$COOCH_2$**CH_2**$(CH_2)_6CH=CH_2$), 2.02 (2H, m, -$COO(CH_2)_7$**CH_2**$CH=CH_2$), 2.53 (2H, t, J 7.5, -CH_2**CH_2**COO-), 2.79 (2H, t, J 7.5, phenyl(OH)-**CH_2**CH_2COO-), 4.00 (2H, t, J 7.5, -COO**CH_2**CH_2CH_2-), 4.92 (2H, overlap, -$CH=$**CH_2**), 5.78 (1H, m, -**CH**$=CH_2$), 6.68 (2H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-)), 6.98 (2H, d, J 10, phenyl (**CH**=C (alkyl)-**CH**=); δ_c (250.1 MHz; CD_3OD) 26.9 (-$COO(CH_2)_2$**CH_2**-), 27.6-34.8 (-**CH_2**CH_2COOCH_2**CH_2**CH_2(**CH_2)$_4$**CH_2-), 36.7, 37.4 (-CH_2**CH_2**$COO(CH_2)_2CH_2CH_2CH_2CH_2$**$CH_2$**CH=), 65.5 (-$COO$**$CH_2$**-), 114.6, 116.14, 130.19 (phenyl(**CH**=C(OH)-**CH**=CH-), -CH=**CH_2**), 139.9 (-**CH**$=CH_2$), 156.7 (phenyl(CH=**C**(OH)-CH=CH-)), 174.7 (-**CO**O-); HRMS, calcd For $C_{19}H_{28}O_3$ [M+Na^+]: 327.4182, found: 327.4181.

Undec-10'-enyl-3-(4-hydroxyphenyl)propionic acid 18

General Procedure for the preparation of the fatty esters with 36.83 mmol of 3-(4-hydroxyphenyl)propionic acid (6.12 g; 6 eq) and 6.14 mmol of 10-undecen-1-ol (1.045 g; 1 eq).

Compound **18** was obtained as a clear oil with a yield of 90%. ν_{max} (ATR) /cm^{-1} 3404 (OH), 2928-2857 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD_3OD) 1.27 (12H, broad, -$CH_2CH_2COOCH_2CH_2$**$CH_2CH_2CH_2CH_2CH_2CH_2$**$CH_2CH=CH_2$), 1.54 (2H, m, -$COOCH_2$**CH_2**$(CH_2)_7CH=CH_2$), 2.02 (2H, m, -$COO(CH_2)_8$**CH_2**$CH=CH_2$), 2.53 (2H, t, J 7.5, -CH_2**CH_2**COO-), 2.79 (2H, t, J 7.5, phenyl(OH)-**CH_2**CH_2COO-), 4.00 (2H, t, J 7.5, -COO**CH_2**CH_2CH_2-), 4.92 (2H, overlap, -$CH=$**CH_2**), 5.78 (1H, m, -**CH**$=CH_2$), 6.68 (2H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-)), 6.98 (2H, d, J 10, phenyl (**CH**=C (alkyl)-**CH**=); δ_c (250.1 MHz; CD_3OD) 26.9 (-$COO(CH_2)_2$**CH_2**-), 27.3-34.8 (-**CH_2**CH_2COOCH_2**CH_2**CH_2(**CH_2)$_5$**CH_2-), 36.7, 37.4 (-CH_2**CH_2**$COO(CH_2)_8$**CH_2**CH=), 65.5 (-COO**CH_2**-), 114.6, 116.14, 130.19 (phenyl(**CH**=C(OH)-**CH**=CH-), -CH=**CH_2**), 139.9 (-**CH**$=CH_2$), 156.7 (phenyl(CH=**C**(OH)-CH=CH-)), 174.7 (-**CO**O-); HRMS, calcd For $C_{20}H_{30}O_3$ [M+Na^+]: 341.445, found: 327.444.

General Procedure for the preparation of the fatty ester-based bolaamphiphiles:

The fatty ester is diluted in CH_2Cl_2 (18 mL) / MeOH (2 mL) or CH_2Cl_2 (20 mL) in a Schlenk tube under argon and the Grubbs I catalyst is added in three portions over 3h. After 72h or 12h of reaction at 45°C, the solvent is evaporated under reduced pressure and the residue is purified by flash chromatography (eluting mixture: petroleum ether / ethyl acetate 6:4).

1', 16'-bis-hexadec-8'-enyl-3-(4-hydroxyphenyl)propionic acid 19

General Procedure for the preparation of the fatty ester-based bolaamphiphiles with compound **16** (0.8 g; 2.76 mmol; 1 eq) and Grubbs I catalyst (227 mg; 0.276 mmol; 0.1 eq). Compound **19** is obtained as liquid with a yield of 65% (72h) or 70% (12h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3424 (OH), 2940-2855 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD_3OD) 1.27 (16H, broad phenyl(OH)$(CH_2)_2COO(CH_2)_2$**$CH_2CH_2CH_2CH_2$**CH_2CH=$CHCH_2$**$CH_2CH_2CH_2CH_2$**-), 1.55 (4H, broad m, -$COOCH_2$**CH_2**$(CH_2)_5CH$=$CH(CH_2)_5$**CH_2**CH_2COO-), 2.00 (4H, broad m, -**CH_2**CH=CH**CH_2**-), 2.54 (4H, t, J 7.5, -CH_2**CH_2**COO-, -CH_2**CH_2**COO-), 2.80 (4H, t, J 7.5, -**CH_2**CH_2COO-, -$COOCH_2$**CH_2**-), 4.01 (4H, t, J 7.5, -COO**CH_2**$(CH_2)_6CH$=$CH(CH_2)_6$**CH_2**COO-), 5.38 (2H, broad m, -CH_2CH=$CHCH_2$-), 6.68 (4H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-), phenyl (**CH**=C(OH)-**CH**=CH-)), 6.99 (4H, d, J 10, phenyl (**CH**=C(alkyl)-**CH**=), phenyl (**CH**=C(alkyl)-**CH**=)); δ_C (250.1 MHz; CD_3OD) 26.9 (-**CH_2**$(CH_2)_4CH$=$CH(CH_2)_4$**CH_2**$(CH_2)_2COO$-), 28.1-30.3 (phenyl(OH)**CH_2**CH_2COOCH_2**CH_2**CH_2**$CH_2CH_2CH_2$**CH_2CH=$CHCH_2$**$CH_2CH_2CH_2$**CH_2-**CH_2**CH_2COO-), 30.5-31.2 (-**CH_2**$COO(CH_2)_6$**CH_2**CH=CH**CH_2**$(CH_2)_6COO$**CH_2**-), 65.6 (-COO**CH_2**$(CH_2)_6CH$=$CH(CH_2)_6$**CH_2**COO-), 116.14-130.11 (phenyl (**CH**=C(OH)**CH**=CH-), phenyl (**CH**=C(OH)**CH**=CH-)), 130.2-131.4 (phenyl (**CH**=C(alkyl)**CH**=), phenyl (**CH**=C(alkyl)-**CH**=), -**CH**=**CH**-), 132.7 (phenyl (CH=**C**(alkyl)CH=), phenyl (CH=**C**(alkyl)CH=)), 156.6 (phenyl (CH=**C**(OH)CH=CH-), phenyl (CH=**C**(OH)CH=CH-), 174.8 (-**CO**O); HRMS, calcd for $C_{34}H_{48}O_6$ [$M+Na^+$]: 575.7394, found: 575.7393.

1',18'-bis-octadec-9'-enyl-3-(4-hydroxyphenyl)propionic acid 20

General Procedure for the preparation of the fatty ester-based bolaamphiphiles with compound **17** (0.71 g; 2.33 mmol; 1 eq) and Grubbs I catalyst (192.2 mg; 0.233 mmol; 0.1 eq). Compound **20** is obtained as liquid with a yield of 70% (72h) or 75% (12h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3424 (OH), 2940-2855 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD_3OD) 1.27 (20H, broad, phenyl(OH)$(CH_2)_2COO(CH_2)_2$**$CH_2CH_2CH_2CH_2CH_2$**CH_2CH=$CHCH_2$**$(CH_2)_5$**CH_2-), 1.54 (4H, broad m, -$COOCH_2$**CH_2**$(CH_2)_6CH$=$CH(CH_2)_6$**CH_2**CH_2COO-), 1.96 (4H, broad m, -**CH_2**CH=CH**CH_2**-), 2.53 (4H, t, J 7.5, -CH_2**CH_2**COO-, -CH_2**CH_2**COO-), 2.79 (4H, t, J 7.5, -**CH_2**CH_2COO-, -$COOCH_2$**CH_2**-), 4.00 (4H, t, J 7.5, -COO**CH_2**$(CH_2)_7CH$=$CH(CH_2)_7$**CH_2**COO-), 5.36 (2H, broad m, -CH_2**CH**=**CH**CH_2-), 6.68 (4H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-), phenyl (**CH**=C(OH)-**CH**=CH-)), 6.99 (4H, d, J 10, phenyl (**CH**=C(alkyl)-**CH**=), phenyl (**CH**=C(alkyl)-**CH**=)); δ_c (250.1 MHz; CD_3OD) 26.9 (-$COO(CH_2)_2$**CH_2**$(CH_2)_5CH$=$CH(CH_2)_5$**CH_2**$(CH_2)_2COO$-), 28.1-30.3 (-**CH_2**CH_2COOCH_2**CH_2**$CH_2($**$CH_2)_4$**CH_2CH=$CHCH_2($**$CH_2)_4$**CH_2-**CH_2**CH_2COOCH_2**CH_2**-), 30.5-37.3 (-CH_2**CH_2**$COOCH_2(CH_2)_6$**CH_2**CH=CH**CH_2**$(CH_2)_7COO$**CH_2**-), 65.6 (-COO**CH_2**$(CH_2)_7CH$=$CH(CH_2)_7$**CH_2**COO-), 116.14-130.11 (phenyl (**CH**=C(OH)**CH**=CH-), phenyl (**CH**=C(OH)**CH**=CH-)), 130.2-131.4 (phenyl (**CH**=C(alkyl)**CH**=), phenyl (**CH**=C(alkyl)-**CH**=), -**CH**=**CH**-), 132.7 (phenyl (CH=**C**(alkyl)CH=), phenyl (CH=**C**(alkyl)CH=)), 156.7 (phenyl (CH=**C**(OH)CH=CH-), phenyl (CH=**C**(OH)CH=CH-), 174.8 (-**CO**O); HRMS, calcd for $C_{36}H_{52}O_6$ [$M+Na^+$]: 603.793, found: 603.792.

1',20'-bis-eicosa-10'-enyl-3-(4-hydroxyphenyl)propionic acid 21

General Procedure for the preparation of the fatty ester-based bolaamphiphiles with compound **18** (0.98 g; 3.08 mmol; 1 eq) and Grubbs I catalyst (253.6 mg; 0.308 mmol; 0.1 eq). Compound **21** is obtained as liquid with a yield of 75% (72h) or 80% (12h) as a mixture Z/E of 20/80. ν_{max} (ATR) /cm^{-1} 3424 (OH), 2940-2855 (C-H), 1736 (COOR), 1642 (C=C); δ_H (250.1 MHz; CD_3OD) 1.27 (24H, broad, phenyl(OH)$(CH_2)_2COO(CH_2)_2$(**CH_2)$_3$$CH_2CH_2CH_2$$CH_2CH$=$CHCH_2$(**$CH_2$)$_6$$CH_2CH_2$-), 1.54 (4H, broad m, -$COOCH_2$**$CH_2$**$(CH_2)_7CH$=$CH(CH_2)_7$**$CH_2$**$CH_2COO$-), 1.97 (4H, broad m, -**CH_2**CH=CH**CH_2**-), 2.53 (4H, t, J 7.5, -CH_2**CH_2**COO-, -CH_2**CH_2**COO-), 2.79 (4H, t, J 7.5, -**CH_2**CH_2COO-, -$COOCH_2$**CH_2**-), 4.00 (4H, t, J 7.5, -COO**CH_2**$(CH_2)_8CH$=$CH(CH_2)_8$**CH_2**COO-), 5.36 (2H, broad m, -CH_2**CH**=**CH**CH_2-), 6.68 (4H, d, J 10, phenyl (**CH**=C(OH)-**CH**=CH-), phenyl (**CH**=C(OH)-**CH**=CH-)), 6.99 (4H, d, J 10, phenyl (**CH**=C(alkyl)-**CH**=), phenyl (**CH**=C(alkyl)-**CH**=)); δ_c (250.1 MHz; CD_3OD) 26.9 (-**CH_2**$(CH_2)_6CH$=$CH(CH_2)_6$**CH_2**-), 28.1-30.5 (-**$CH_2CH_2COOCH_2$****CH_2****$CH_2(CH_2)_3CH_2CH_2CH_2CH$**=$CHCH_2$(**$CH_2$)$_5$$CH_2$-**$CH_2CH_2COOCH_2$****$CH_2$**-), 30.5-37.4 (-$CH_2$**$CH_2$**$COOCH_2(CH_2)_7$**$CH_2$**$CH$=$CH$**$CH_2$**$(CH_2)_8COO$**$CH_2$**-), 65.6 (-$COO$**$CH_2$**$(CH_2)_8CH$=$CH(CH_2)_8$**$CH_2$**$COO$-), 116.14-130.11 (phenyl (**CH**=C(OH)**CH**=CH-), phenyl (**CH**=C(OH)**CH**=CH-)), 130.2-131.4 (phenyl (**CH**=C(alkyl)**CH**=), phenyl (**CH**=C(alkyl)-**CH**=), -**CH**=**CH**-), 132.7 (phenyl (CH=**C**(alkyl)CH=), phenyl (CH=**C**(alkyl)CH=)), 156.7 (phenyl (CH=**C**(OH)CH=CH-), phenyl (CH=**C**(OH)CH=CH-), 174.8 (-**CO**O); HRMS, calcd for $C_{38}H_{56}O_6$ [M+Na^+]: 631.8466, found: 631.8465.

General Procedure for the preparation of the asymmetric fatty ester- and rhamnoside-based bolaamphiphiles:

The rhamnoside-based bolaamphiphile and the fatty ester-based bolaamphiphile are diluted in CH_2Cl_2 (35 mL) / MeOH (5mL) or CH_2Cl_2 (40 mL) in a Schlenk tube under argon and the Grubbs I catalyst is added in one portion. After 24h or 8h of reaction at 45°C, the solvent mixture is evaporated under reduced pressure and the residue is purified by flash chromatography (eluting mixture: CH_2Cl_2/MeOH 9:1).

1',16'-bis-decanon-8'-enyl-3-(4-hydroxyphenyl)propionic acid-α-L-rhamnopyranoside 22

General Procedure for the preparation of the asymmetric fatty ester- and rhamnoside-based bolaamphiphiles with compound **10** (1.82 g; 3.32 mmol; 2 eq), compound **16** (481.56 mg; 1.66 mmol; 1 eq) and Grubbs I catalyst (68.30 mg; 0.083 mmol; 0.05 eq). Compound **22** is obtained as viscous brown product with a yield of 65% (24h) or 70% (8h). ν_{max} (ATR) /cm^{-1} 3421 (OH), 2924-2852 (C-H), 1736 (COOR), 1642 (C=C), 1131-1050; δ_H (250.1 MHz; CD_3OD) 1.27-1.31 (19H, broad, rhamnose(**CH_3**)$(CH_2)_2$(**CH_2)$_4$$CH_2CH$=$CHCH_2$(**$CH_2$)$_4$$CH_2CH_2COO(CH_2)_2$phenyl(OH)), 1.58 (4H, broad m, rhamnose(O)CH_2**CH_2**$(CH_2)_5CH$=$CH(CH_2)_5$**CH_2**CH_2COO-), 2.00 (4H, broad m, -**CH_2**CH=CH**CH_2**-), 2.56 (2H, t, J 7.5, -CH_2COO**CH_2**CH_2-), 2.82 (2H, t, J 7.5, -$COOCH_2$**CH_2**phenyl(OH)), 3.36-3.82 (6H, overlap,

rhamnose (**CH**(CH_3)**CH**(OH)**CH**(OH)-**CH**(OH)-), -O**CH_2**-), 4.04 ((2H, t, J 7.5, -**CH_2**$COOCH_2CH_2$phenyl(OH)), 4.68 (1H, broad, rhamnose(O)**CH_2**CH_2-), 5.43 (2H, broad m, -CH_2**CH**=**CH**CH_2-), 6.71 (2H, d, J 5, phenyl(**CH**=C(OH)-**CH**=)), 7.00 (2H, d, J 7.5, phenyl (**CH**=C(alkyl)-**CH**=)); δ_c (250.1 MHz; CD_3OD) 18.02 (-**CH_3**), 26.9-33.3 (rhamnose(O)CH_2(**CH_2)$_5$**CH_2CH=$CHCH_2$-(**CH_2)$_3$**CH_2**CH_2**CH_2COOCH_2**CH_2**-), 33.7 (-**CH_2**CH=CH**CH_2**-), 34.7 (-COO**CH_2**CH_2-), 65.5 (-CH_2COO-), 68.4 (rhamnose(O)**CH_2**CH_2), 69.6 (rhamnose (**CH**(CH_3)-)), 71.8 (rhamnose(CH(CH_3)**CH**(OH)-), 72.3 (rhamnose(CH(CH_3)CH(OH)**CH**(OH)-)), 73.9 (rhamnose(-**CH**(OH)CH-)), 101.5 (rhamnose (-CH(OH)**CH**(OCH_2)-)), 130.1 (-CH_2**CH**(Z)=**CH**(Z)CH_2-), 131.4 (phenyl(**CH**=C(Oh)-**CH**=)), 132.8 (phenyl(**CH**=C(alkyl)CH=)), 139.9 (phenyl(CH=**C**(alkyl)CH=)), 156.6 (phenyl(CH=**C**(OH)CH=)), 174.7 (-**CO**O); HRMS, calcd for $C_{31}H_{50}O_8$ [M+Na^+]: 573.721, found: 573.720.

1',18'-bis-octadec-9'-enyl-3-(4-hydroxyphenyl)propionic acid-α-L-rhamnopyranoside 23

General Procedure for the preparation of the asymmetric fatty ester- and rhamnoside-based bolaamphiphiles with compound **11** (2.84 g; 4.93 mmol; 2 eq), compound **17** (0.75 g; 2.46 mmol; 1 eq) and Grubbs I catalyst (101.2 mg; 0.123 mmol; 0.05 eq). Compound **23** is obtained as viscous brown product with a yield of 70% (24h) or 75% (8h). ν_{max} (ATR)/cm^{-1} 3421 (OH), 2924-2852 (CH), 1736 (COOR), 1641 (C=C), 131-1050 (C-O-C); δ_H (2250.1 MHz; CD_3OD) 1.27-1.31 (23H, overlap, rhamnose(O)(CH_2)CH_2(**CH_2)$_5$**CH_2CH=$CHCH_2$(**CH_2)$_5$**CH_2CH_2COO-(CH_2)$_2$phenyl(OH)), 1.58 (4H, broad m, rhamnose(O)CH_2**CH_2**(CH_2)$_6$CH=CH(CH_2)$_6$**CH_2**CH_2-), 2.00 (4H, broad m, -CH_2CH=$CHCH_2$-), 2.56 (2H, t, J 7.5, -CH_2COO**CH_2**CH_2-), 2.82 (2H, t, J 7.5, -CH_2COOCH_2**CH_2**phenyl(OH)), 3.36-3.82 (6H, overlap, rhamnose(**CH**(CH_3)**CH**(OH)**CH**-(OH)**CH**(OH)-, O**CH_2**-), 4.04 (2H, t, J 7.5, -**CH_2**$COOCH_2CH_2$phenyl(OH)), 4.68 (1H, broad, rhamnose(O)**CH_2**CH_2-), 5.43 (2H, broad m, -CH_2**CH**=**CH**CH_2-), 6.71 (2H, d, J 7.5, phenyl(**CH**=C(OH)**CH**=)), 7.00 (2H, d, J 7.5, phenyl(**CH**=C(alkyl)**CH**=)); δ_c (250.1 MHz; CD_3OD) 18.02 (-**CH_3**), 26.9-33.3 (rhamnose(O)CH_2(**CH_2)$_6$**CH_2CH=CH-H_2(**CH_2)$_4$**CH_2**CH_2**CH_2COOCH_2**CH_2**-), 33.7 (-CH_2CH=$CHCH_2$-), 34.7 (COO**CH_2**CH_2-), 65.5 (-**CH_2**COO-), 68.4 (rhamnose(O)**CH_2**CH_2-), 69.6 (rhamnose(**CH**(CH_3)-), 71.8 (rhamnose(CH(CH_3)**CH**(OH)-), 72.3 (rhamnose(CH(CH_3)CH(OH)**CH**-), 73.9 (rhamnose(-**CH**(OH)CH(OCH_2)-)), 101.5 ((rhamnose(-CH(OH)**CH**(OCH_2)-)), 130.1 (-CH_2**CH**(Z)=**CH**(Z)CH_2-), 130.7 (-CH_2**CH**=**CH**CH_2-), 131.4 (phenyl(**CH**=C(OH)**CH**=)), 132.8 (phenyl(**CH**=C(alkyl)**CH**=), 139.9 (phenyl(CH=**C**(al-kyl)CH=)), 156.6 (phenyl(CH=**C**(OH)CH=)), 174.7 (-**CO**O); HRMS, calcd for $C_{33}H_{54}O_8$ [M+Na^+]: 601.7746, found: 601.7750.

1',20'-bis-octadec-10'-enyl-3-(4-hydroxyphenyl)propionic acid-α-L-rhamnopyranoside 24

General Procedure for the preparation of the asymmetric fatty ester- and rhamnoside-based bolaamphiphiles with compound **12** (1.8 g; 2.98 mmol; 2 eq), compound **18** (473.8 mg; 1.49 mmol; 1 eq) and Grubbs I catalyst (673.1 mg; 0.0745 mmol; 0.05 eq). Compound **24** is obtained as viscous brown product with a yield of 75% (24h) or 80% (8h). ν_{max} (ATR)/cm^{-1} 3421

(OH), 2924-2852 (CH), 1736 (COOR), 1641 (C=C), 131-1050 (C-O-C); δ_H (2250.1 MHz; CD_3OD) 1.27-1.33 (27H, overlap, rhamnose(O)$(CH_2)_2$(**CH_2)$_6$**CH_2CH=$CHCH_2$(**CH_2)$_6$**CH_2CH_2-), 1.58 (4H, broad m, rhamnose(O)CH_2**CH_2**$(CH_2)_7CH$=$CH(CH_2)_7$**CH_2**CH_2-), 2.00 (4H, broad m, -**CH_2**CH=CH**CH_2**-), 2.56 (2H, t, J 7.5, -CH_2COO**CH_2**CH_2-), 2.82 (2H, t, J 7.5, -CH_2**CH_2**phenyl(OH)), 3.36-3.82 (6H, overlap, rhamnose(**CH**(CH_3)**CH**(OH)**CH**-(OH)**CH**(OH)-, O**CH_2**-), 4.04 (2H, t, J 7.5, -**CH_2**$COOCH_2CH_2$-), 4.68 (1H, broad, rhamnose(O)**CH_2**CH_2-), 5.43 (2H, broad m, -CH_2**CH**=**CH**CH_2-), 6.71 (2H, d, J 7.5, phenyl(**CH**=C(OH)**CH**=)), 7.00 (2H, d, J 7.5, phenyl(**CH**=C(alkyl)**CH**=)); δ_C (2250.1 MHz; CD_3OD) 18.02 (-**CH_3**), 26.9-33.3 (-CH_2(**CH_2)$_6$**CH2CH=CH-CH_2(**CH_2)$_4$**CH_2**CH_2**CH_2COOCH_2**CH_2**-), 33.7 (-**CH_2**CH=CH**CH_2**-), 34.7 (COO**CH_2**CH_2-), 65.5 (-**CH_2**COO-), 68.4 (rhamnose(O)**CH_2**CH_2-), 69.6 (rhamnose(**CH**(CH_3)-$CH(OH)_3$-), 71.8 (rhamnose($CH(CH_3)$**CH**$(OH)_3$-), 72.3 (rhamnose($CH(CH_3)CH$(OH)**CH**(OH)CH(OH)-), 73.9 (rhamnose(-**CH**(OH)$CH(OCH_2)$-)), 101.5 ((rhamnose(-CH(OH)**CH**(OCH_2)-)), 130.1 (-CH_2**CH**(Z)=**CH**(Z)CH_2-), 130.7 (-CH_2**CH**=**CH**CH_2-), 131.4 (phenyl(**CH**=C(OH)**CH**=)), 132.8 (phenyl(**CH**=C(alkyl)**CH**=), 139.9 (phenyl(CH=**C**(al-kyl)CH=)), 156.6 (phenyl(CH=**C**(OH)CH=)), 174.7 (-**CO**O); HRMS, calcd for $C_{35}H_{58}O_8$ [M+Na^+]: 629.8282, found: 629.8281.

Acknowledgments

This work was supported by the ElidéRham program (Excellence Framework). We are grateful to the Public Authorities of Champagne-Ardenne and FEDER for material funds and post doctoral fellowship to F.O.A.

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Efficient Syntheses of Bolaform Surfactants from L-Rhamnose and/or 3-(4-Hydroxyphenyl)Propionic Acid

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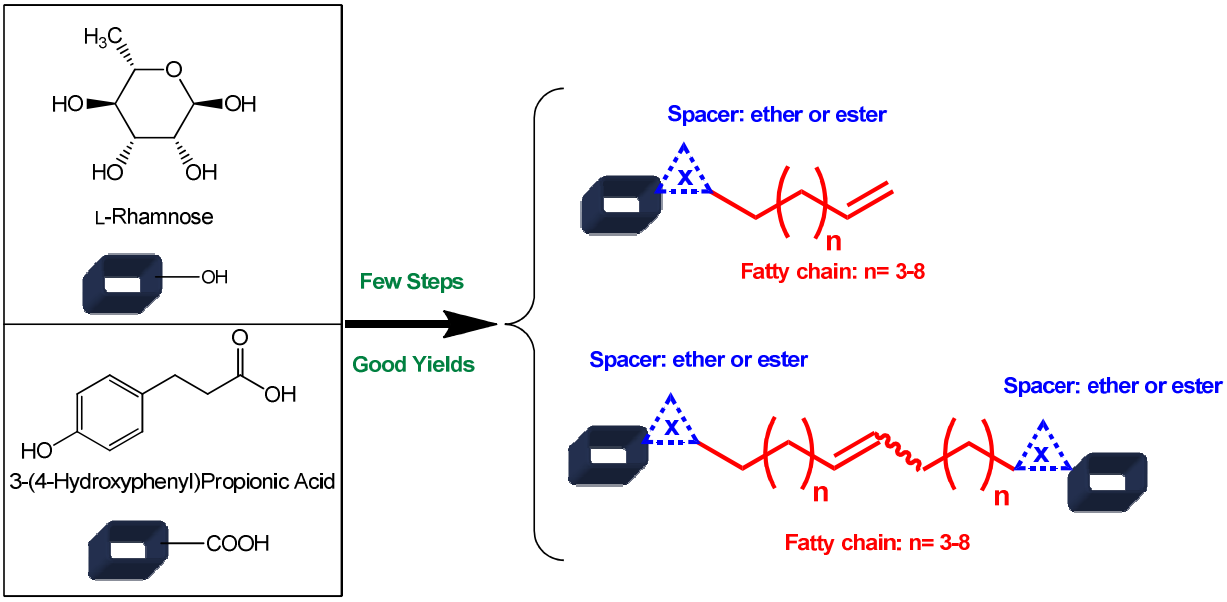

Efficient syntheses of symmetric and asymmetric bolaamphiphiles derived from L-rhamnose and/or 3-(4-Hydroxyphenyl)propionic acid.