# Stereoselective Synthesis of Polyhydroxyl Surfactants. Stereochemical Influence on Langmuir Monolayers 

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## Supporting Information

1. Preparation of $\mathbf{1 4}$ from ent- $\mathbf{6}$. ..... S2
1.1 Experimental data for compounds ent- 6 and ent-7. ..... S2
1.2 Experimental data for compounds $\mathbf{9}, \mathbf{1 4}, \mathbf{2 2}, 23$ and 24. ..... S3
2. Experimental data for compound $\mathbf{3 a}$, preparation of $\mathbf{4 a}$ and $\mathbf{4 b}$. ..... S5
3. Experimental data for compounds $\mathbf{3 0 a}, \mathbf{3 0 b}, 18 a$ and $\mathbf{1 8 b}$ ..... S9
4. Experimental data for compounds 31a, 31b, 32a, 32b, 2a and 2b. ..... S11
5. Analytical data for compounds ent-21a, ent-21b, ent-1a and ent-1b ..... S13
6. References ..... S15
7. NMR spectra for compounds:
1a, b, ent-1a, b, 2a, b, 4a, b, ent-6, 7, ent-7, 8-17, 20a, b, 21a, b, ent-21a, b, 22-24, 27, 30b, 31a, b, 32a, b.

General. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded in $\mathrm{CDCl}_{3}, \mathrm{CD}_{3} \mathrm{OD}$ or $\mathrm{C}_{6} \mathrm{D}_{6}$ using the residual peak of the corresponding solvent or added TMS ( $\delta 0.00$ ), as internal standard. Chemical shifts are reported in the $\delta$-scale with multiplicity (br=broad, $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=\mathrm{quartet}, \mathrm{m}=$ multiplet), integration and coupling constants $(\mathrm{Hz})$. Optical rotations, $[\alpha]_{\mathrm{D}} \quad$ measured at the sodium D line at ambient temperature. Only the strongest/structurally most important peaks $\left(\nu, \mathrm{cm}^{-1}\right)$ are listed in infrared spectra. Analytical thin layer chromatography plates were visualized with UV light and phosphomolybdic acid staining reagent ( $5 \mathrm{w} \%$ solution in EtOH ) or $p$-anisaldehyde (solution in EtOH ). Air-and moisture sensitive reactions were carried out in flamed-dried, septum-capped flasks under an atmospheric pressure of nitrogen. All liquid reagents were transferred via oven-dried syringes. THF was freshly distilled from sodium-benzophenone ketyl; dichloromethane from $\mathrm{CaH}_{2}$. Surface pressure-area isotherms were recorded on a computerized trough system of the single barrier movement type developed by KSV Instruments, Finland, mounted on an antivibrational table in a laminar flow cabinet. The trough was made of Teflon whereas the barrier was made of Delrin. Millipore filtered water was used as subphase in all experiments. Surface pressure was measured continuously with a Wilhelmy plate. The spreading solvent was $\mathrm{CHCl}_{3}$ with MeOH added up to $10 \%$ by volume. The concentration of the surfactants in the spreading solutions was 0.5 mM , and a volume of $100 \mu \mathrm{~L}$ was spread (using a micro syringe). Up to five minutes was allowed for the spreading solvent to evaporate before compression. The compression of the monolayer was carried out at ambient temperature, at a speed of $5.4 \AA^{2}$ molecule ${ }^{-1} \mathrm{~min}^{-1}$ to a molecular area of $100 \AA^{2}$ molecule ${ }^{-1}$ then at a speed of $0.5 \AA^{2}$ molecule ${ }^{-1} \mathrm{~min}^{-1}$. Enantiomerically pure surfactants $\mathbf{1}$, ent $\mathbf{- 1}$ and $\mathbf{2}$ were recrystallized from $\mathrm{H}_{2} \mathrm{O}: \mathrm{MeOH}$ prior to use. The racemate (rac-1) was prepared by mixing appropriate amounts of $\mathbf{1}$ and ent-1.

## 1. Preparation of 14 from ent-6.

### 1.1 Experimental data for compounds ent-6 and ent-7

## (E)-3-((4R,5R)-5-((4-Methoxybenzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-en-1-

 $\mathbf{o l}$ (ent-6) was prepared as previously reported, ${ }^{1}$ using AD-mix $\beta$ in place of $\mathrm{AD}-\mathrm{mix} \alpha$. This gave a yield of $84 \%$ and an $e e$ of $>99 \%$ according to HPLC using chiral column. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.28-$$7.24(\mathrm{~m}, 2 \mathrm{H}), 6.88(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 5.93(\mathrm{td}, J=15.5,5.1 \mathrm{~Hz}), 5.72(\mathrm{tdd}, J=15.5,7.6,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.52(\mathrm{~s}$, $2 \mathrm{H}), 4.24(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.17-4.14(\mathrm{~m}, 2 \mathrm{H}), 3.92-3.88(\mathrm{~m}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.60-3.52(\mathrm{~m}, 2 \mathrm{H}), 1.60$ (br s, 1H), $1.43(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 159.7,134.5,130.5,129.8,128.2,114.1,109.8$, 80.6, 79.0, 77.7, 73.7, 69.5, 63.1, 55.6, 27.5; IR (neat) 3432 (br) cm ${ }^{-1} ;[\alpha]_{\mathrm{D}}+14.4\left(c 1.00, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{17} \mathrm{H}_{24} \mathrm{O}_{5}(\mathrm{M}): 308.1624$, found: 308.1622.
(E)-3-((4R,5R)-5-((4-Methoxybenzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)allyl
methoxybenzoate (ent-7) was prepared from ent-6 as described for $7 .{ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 8.02 (d, $J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.28$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.94$ (d, $J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.89$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.01$ (td, $J=15.5,5.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.87(\mathrm{dd}, J=15.5,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.81(\mathrm{~d}, J=5.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.56(\mathrm{AB}-\mathrm{d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H})$, 4.54 (AB-d, $J=11.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.31(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.96-3.92(\mathrm{~m}, 1 \mathrm{H}), 3.89(\mathrm{~s}, 3 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.63-$ $3.57(\mathrm{~m}, 2 \mathrm{H}), 1.47(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 166.3,163.9,159.6,132.1,131.1,130.4,129.7$, $129.1,122.8,114.2,114.1,109.9,80.4,78.8,73.7,69.5,64.5,55.9,55.7,27.4,27.4$; IR (neat) 2986, 1713, $1607 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+15.7\left(c 1.04, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{25} \mathrm{H}_{31} \mathrm{O}_{7}(\mathrm{M}+\mathrm{H}): 443.2070$, found: 443.2077.

### 1.2 Experimental data for compounds 9, 14, 22, 23 and 24

Scheme S1. Preparation of 14 from 9.


2,3-O-Isopropylidene-1-(4-methoxybenzyl)-D-iditol-6-(4-methoxybenzoate) (9) was prepared as describes for $\mathbf{8}$ and obtained in $82 \%$ yield and a diastereomeric ratio of 33:1 after flash chromatography
(EtOAc:pentane 0:1 $\rightarrow 1: 1$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.97(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.21(\mathrm{~d}, J=8,5 \mathrm{~Hz}, 2 \mathrm{H})$, $6.90(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.83(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.48(\mathrm{~s}, 2 \mathrm{H}), 4.41(\mathrm{~d}, J=5.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.30(\mathrm{td}, J=8.1,5.2$ $\mathrm{Hz}, 1 \mathrm{H}), 4.11-4.07(\mathrm{~m}, 1 \mathrm{H}), 4.00(\mathrm{dd}, J=8.1,2.7 \mathrm{~Hz}, 2 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.68(\mathrm{td}, J=9.0,2.7$ Hz, 1H), $3.64(\mathrm{dd}, J=10.2,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.55(\mathrm{dd}, J=10.2,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.97(\mathrm{~d}, J=3.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.70(\mathrm{~d}$, $J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.43(\mathrm{~s}, 3 \mathrm{H}), 1.41(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 166.3,163.6,159.3,131.8$, $129.7,129.4,122.2,113.9,113.7,109.9,80.8,75.8,73.3,71.3,69.8,69.1,65.3,55.4,55.2,27.1,26.8$; IR (neat): 3474 (br), $1607 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+8.1\left(c 1.02, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{25} \mathrm{H}_{33} \mathrm{O}_{9}(\mathrm{M}+\mathrm{H})$ : 477.2125, found: 477.2126.

2,3:4,5-Di- $O$-isopropylidene-1-(4-methoxybenxyl)-D-iditol-6-(4-methoxybenzoate) (22) was prepared from 9 as described for 10 and obtained in $53 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) $\delta 7.93$ (d, $J=8.9 \mathrm{~Hz}, 2 \mathrm{H}), 6.94(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.56(\mathrm{~d}, J=8.5 \mathrm{~Hz}), 6.38(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 2 \mathrm{H}), 4.46-4.41(\mathrm{~m}, 1 \mathrm{H})$, 4.37-4.33 (m, 1H), $4.31(\mathrm{dd}, J=11.8,3.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.22(\mathrm{dd}, J=11.8,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.09(\mathrm{~s}, 2 \mathrm{H}), 3.88-3.84$ (m, 2H), 3.39 (dd, $J=10.1,4.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.32$ (dd, $J=10.1 \mathrm{~Hz}, 5.3 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.09 (s, 3H), 2.93 (s, 3H), 1.27 (s, 3H), $1.25(\mathrm{~s}, 6 \mathrm{H}), 1.20(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) $\delta 166.2,164.1,160.1,132.4,130.9,129.7$, $123.2,114.4,114.3,110.3,110.0,78.0,77.5,76.8,76.2,73.6,70.7,64.6,55.1,55.0,27.84,27.83,27.22$, 27.19; IR (neat): 2987, 1713, $1607 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+15.8\left(c 1.17, \mathrm{CHCl}_{3}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{28} \mathrm{H}_{36} \mathrm{O}_{9}$ (M): 516.2359, found: 516.2360.

2,3:4,5-Di-O-isopropylidene-1-(4-methoxybenxyl)-D-iditol (23) was prepared from 22 as described for 11 and obtained in $90 \%$ yield. ${ }^{1} \mathrm{H}$ NMR: $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.31(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.93$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}) 4.58(\mathrm{AB}-\mathrm{d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.55(\mathrm{AB}-\mathrm{d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.32-4.28(\mathrm{~m}, 1 \mathrm{H}), 4.22-4.18$ (m, 1H), 4.02 (dd, $J=8.3,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.92(\mathrm{dd}, J=8.3,3.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H}), 3.84-3.81(\mathrm{~m}, 1 \mathrm{H}), 3.69-$ $60(\mathrm{~m}, 3 \mathrm{H}), 2.04(\mathrm{dd}, J=7.8,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.47(\mathrm{~s}, 9 \mathrm{H}), 1.46(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (125 MHz, $\left.\mathrm{CDCl}_{3}\right)$ : $\delta 159.7,130.3,129.8,114.2,110.1,109.9,77.8,77.7276 .6,76.5,73.6,70.7,62.0,55.7,27.63,27.60,27.2$, 27.1; IR (neat): 3438 (br), $1613 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+19.3$ (c $1.00, \mathrm{CHCl}_{3}$ ); HRMS (FAB+) calcd for $\mathrm{C}_{20} \mathrm{H}_{30} \mathrm{O}_{7}$ (M): 382.1992, found: 382.1990 .
was prepared form $\mathbf{2 3}$ as described for $\mathbf{1 2}$ and obtained in $99 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.80$ (d, $J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34$ (d, $J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.27$ (d, $J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 6.91$ (d, $J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.54$ (AB-d, $J=11.7 \mathrm{~Hz}, 1 \mathrm{H}) 4.52(\mathrm{AB}-\mathrm{d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.25-4.15(\mathrm{~m}, 3 \mathrm{H}), 4.10(\mathrm{dd}, J=10.8,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.92$ (dd, $J=8.1,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{dd}, J=8.1,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.83(\mathrm{~s}, 3 \mathrm{H}), 3.60(\mathrm{dd}, J=10.2,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.55(\mathrm{dd}$, $J=10.2,4.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.46(\mathrm{~s}, 3 \mathrm{H}), 1.42(\mathrm{~s}, 3 \mathrm{H}), 1.40(\mathrm{~s}, 3 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}), 1.35(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (125 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 159.2,144.9,132.6,129.8,129.4,128.0,113.8,110.1,109.7,77.1,76.2,75.9,74.5,73.1$, 69.9, 68.7, 55.2, 27.1, 26.8, 26.6, 26.5, 21.6; one signal is not visible; IR (neat): $1613,1368,1177 \mathrm{~cm}^{-1}$; $[\alpha]_{\mathrm{D}}+19.2\left(c 1.00, \mathrm{CHCl}_{3}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{27} \mathrm{H}_{36} \mathrm{O}_{9} \mathrm{~S}(\mathrm{M}): 536.2080$, found: 536.2084.

1-Amino-1-deoxy-2,3:4,5-di-O-isopropylidene-D-iditol-6-(4-methoxybenzoate)
(14) was prepared form $\mathbf{2 4}$ as described for $\mathbf{1 3}$ and obtained in $77 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.20(\mathrm{~d}$, $J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.47(\mathrm{AB}-\mathrm{d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.45(\mathrm{AB}-\mathrm{d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.20(\mathrm{td}$, $J=8.2,4.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.03-3.99(\mathrm{~m}, 1 \mathrm{H}), 3.80(\mathrm{dd}, J=8.2,3.1 \mathrm{~Hz}), 3.74(\mathrm{~s}, 1 \mathrm{H}), 3.72(\mathrm{dd}, J=8.3,3.1 \mathrm{~Hz}, 1 \mathrm{H})$, 3.54 (AB-dd, $J=10.3,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.51$ (AB-dd. $J=10.3,4.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.87$ (br d, $J=13.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.72 (dd, $J=13.2,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.98(\mathrm{br} \mathrm{s}, 2 \mathrm{H}), 1.37-1.36(\mathrm{~m}, 9 \mathrm{H}), 1.34(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 159.2,129.9,129.4,113.8,109.6,109.2,78.7,77.4,77.1,76.1,73.2,69.9,55.3,43.7,27.3,27.2,26.70$, 26.69; IR (neat): 2987, $1514 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+23.4$ (c 1.00, $\mathrm{CHCl}_{3}$ ); HRMS (FAB+) calcd for $\mathrm{C}_{20} \mathrm{H}_{32} \mathrm{NO}_{6}$ $(\mathrm{M}+\mathrm{H}): 382.2230$, found: 382.2227 .

## 2. Experimental data for compound $3 a$, preparation of $\mathbf{4 a}$ and $\mathbf{4 b}$.

Experimental procedure for the preparation of dimethyl 2-butyl malonate (3a). ${ }^{\mathbf{2}} \mathrm{NaH}$ ( 584 mg , $14.6 \mathrm{mmol}, 60 \mathrm{w} \%$ dispersion in oil) was washed twice with pentane, dried under vacuum and resuspended in THF/DMF (3:1, 40 mL ) at $0^{\circ} \mathrm{C}$. Dimethyl malonate ( $4.2 \mathrm{~mL}, 36.5 \mathrm{mmol}$ ) was added dropwise and the
clear solution was stirred for 15 min at rt , at which white crystals were formed. $n$-Butyl bromide ( 0.78 mL , 7.3 mmol ) was added and the mixture heated to reflux. After refluxing overnight the reaction mixture was allowed to cool, the THF was removed under vacuum and the residue poured into $\mathrm{H}_{2} \mathrm{O}(20 \mathrm{~mL})$ and extracted three times with pentane ( 15 mL ) and once with $\mathrm{Et}_{2} \mathrm{O}$ /pentane $(1: 1,20 \mathrm{~mL})$. The organic layers were combined, dried $\left(\mathrm{MgSO}_{4}\right)$ and the solvents were evaporated to give a yellow oil. Excess dimethyl malonate and dialkylated product was removed with repeated fractional distillation ( 2 torr, $45{ }^{\circ} \mathrm{C}$ ) to give $75 \%$ yield of $\mathbf{3 a}(1.0 \mathrm{~g}, 5.4 \mathrm{mmol}) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 3.74(\mathrm{~s}, 6 \mathrm{H}), 3.36(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H})$, $1.90(\mathrm{q}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.39-1.25(\mathrm{~m}, 4 \mathrm{H}), 0.90(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 170.1$, 52.5, 51.7, 29.5, 28.6, 22.3, 13.8.

Scheme S2. Preparation of 4a from 25.

(2R)-3-(4-Methoxybenzyloxy)-1,2-propanediol (26). ${ }^{\mathbf{3}}$ Allyl alcohol $\mathbf{2 5}^{4}$ ( $1.0 \mathrm{~g}, 5.6 \mathrm{mmol}$ ) was added to a suspension of $\mathrm{AD}-$ mix $\alpha(9.3 \mathrm{~g})$ and $\mathrm{K}_{2} \mathrm{OsO}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}(14.4 \mathrm{mg}, 0.039 \mathrm{mmol})$ in $t-\mathrm{BuOH}: \mathrm{H}_{2} \mathrm{O}$ (1:1, 20 mL ). The mixture was stirred at $0{ }^{\circ} \mathrm{C}$ for $45 \mathrm{~h} . \mathrm{Na}_{2} \mathrm{SO}_{3}(7.5 \mathrm{~g})$ was added and the reaction mixture stirred for two more hours at room temperature, then diluted with EtOAc ( 40 mL ) and $\mathrm{H}_{2} \mathrm{O}(20 \mathrm{~mL})$. The phases were separated and the water phase extracted with $\mathrm{EtOAc}(2 \times 30 \mathrm{~mL})$. After drying $\left(\mathrm{MgSO}_{4}\right)$ and evaporation of the solvent 1.1 g of a crude oil remained. Purification by flash chromatography on silica gel (EtOAc:MeOH 25:1) gave $68 \%$ of 26 as a white solid ( $797 \mathrm{mg}, 3.8 \mathrm{mmol}$ ). ee: $60 \%$ according to NMR using $\mathrm{Eu}(\mathrm{hfc})_{3}$ as chiral shift reagent; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.25(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 6.89$ (d, $J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.48(\mathrm{~s}, 2 \mathrm{H}), 3.90-3.84(\mathrm{~m}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.73-3.60(\mathrm{~m}, 2 \mathrm{H}), 3.57-3.49(\mathrm{~m}, 2 \mathrm{H}), 2.57$ $(\mathrm{d}, J=3.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.08(\mathrm{br} \mathrm{s}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 159.8,130.2,129.9,114.3,73.7,71.9$, 71.0, 64.5, 55.7.

General procdure for tosylation of 29 and 31 employing dibutyl tin oxide as catalyst. (2S)-3-(4-Methoxybenzyloxy)-2-hydroxypropyl 4-methylbenzenesulfonat (27). Diol 26 ( $420 \mathrm{mg}, 2.0$ $\mathrm{mmol})$ was stirred together with $\mathrm{Bu}_{2} \mathrm{SnO}(9.9 \mathrm{mg}, 0.04 \mathrm{mmol})$, $p-\mathrm{TsCl}(379 \mathrm{mg}, 1.42 \mathrm{mmol})$ and $\mathrm{Et}_{3} \mathrm{~N}$ ( $279 \mu \mathrm{~L}, 1.42 \mathrm{mmol}$ ) in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ for 4 h . The solvent was evaporated and the residue was suspended in EtOAc:pentane (1:1). The precipitate $\left(\mathrm{Et}_{3} \mathrm{NHCl}\right)$ was filtered off, the filtrate was taken care of and the solvent was evaporated. Purification by flash chromatography on silica gel (EtOAc:pentane 1:1) furnished $27 \mathrm{in} 88 \%$ yield as a colorless oil ( $640 \mathrm{mg}, 1.76 \mathrm{mmol}$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.79$ (d, J=8.3 Hz, $2 \mathrm{H}), 7.34$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.19(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.87(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 4.43$ (s, 2H), 4.13-3.96 (m, 3 H ), $3.81(\mathrm{~s}, 3 \mathrm{H}), 3.52-3.44(\mathrm{~m}, 2 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 159.8,145.5,133.0$, $130.4,130.0,129.9,128.4,114.3,73.6,71.0,70.1,68.8,55.7,22.1$; IR (neat): $3478,1357,1175 \mathrm{~cm}^{-1}$; HRMS (FAB+) calcd for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{O}_{6} \mathrm{~S}(\mathrm{M}): 366.1137$, found: 366.1143.
(2R)-1-(Methylamine)-3-(4-methoxybenzyloxy)-propan-2-ol (4a). Tosylate 27 (480 mg, 1.31 mmol ), methylamine ( $5 \mathrm{~mL}, 40 \mathrm{w} \%$ in water) and THF ( 10 mL ) were heated in a sealed tube at $75^{\circ} \mathrm{C}$ for 3h. The reaction mixture was allowed to cool to room temperature, and then THF was evaporated under reduced pressure. The residue was redissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ and extracted with $\mathrm{NaOH}(2 \mathrm{M}, 2 \mathrm{~mL})$. The water phase was extracted twice with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and the organic phases dried $\left(\mathrm{MgSO}_{4}\right)$. Evaporation of the solvent gave $\mathbf{4 a}$ in $97 \%$ yield ( $285 \mathrm{mg}, 1.27 \mathrm{mmol}$ ). The product was used without further purification. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.25(\mathrm{~d}, J=8.5,2 \mathrm{H}), 6.88(\mathrm{~d}, J=8.5,2 \mathrm{H}), 4.48(\mathrm{~s}, 2 \mathrm{H})$, 3.92-3.85 (m, 1H), 3.80 (s, 3H), 3.48 (AB-dd, $J=9.7,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.43(\mathrm{AB}-\mathrm{d}, J=9.7,6.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.69-$ $2.60(\mathrm{~m}, 2 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}), 2.26(\mathrm{br} \mathrm{s}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 159.7,130.6,129.8,114.2$, 73.5, 73.1, 69.0, 55.7, 54.7, 36.7; IR (neat): 3313 (br), $2840 \mathrm{~cm}^{-1}$; HRMS (FAB+) calcd for $\mathrm{C}_{12} \mathrm{H}_{20} \mathrm{NO}_{3}$ $(\mathrm{M}+\mathrm{H}): 226.1443$, found: 226.1447.

Scheme S3. Preparation of 4b from (S)-(-)-glycidol.

(2S)-3-Benzyloxy-1,2-propanol (28). ${ }^{5} \mathrm{NaH}(6.1 \mathrm{~g}, 152 \mathrm{mmol}$, $60 \mathrm{w} \%$ dispersion in oil) was washed twice with pentane and dried under vacuum. THF ( 100 mL ) was added and the suspension cooled in an ice/water bath. Benzyl alcohol ( $15.7 \mathrm{~mL}, 152 \mathrm{mmol}$ ) dissolved in THF $(50 \mathrm{~mL})$ was added dropwise at 0 ${ }^{\circ} \mathrm{C}$. The reaction mixture was stirred for 30 min and the $(\mathrm{S})-(-)$-glycidol $(4.5 \mathrm{~g}, 61 \mathrm{mmol})$ dissolved in THF $(50 \mathrm{~mL})$ was added carefully. The reaction mixture was stirred over night and the reaction was quenched with $\mathrm{NaHCO}_{3}$ (sat., 100 mL ). The phases were separated and the organic layer washed with brine and dried over $\mathrm{MgSO}_{4}$. Evaporation gave 20 g of a yellow oil that was purified by flash chromatography on silica gel (EtOAc:pentane 5:1) to give pure diol 28 in $65 \%$ yield ( $7.2 \mathrm{~g}, 40 \mathrm{mmol}$ ). ${ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.36-7.26 (m, 5H), $4.53(\mathrm{~s}, 3 \mathrm{H}), 3.89-3.84(\mathrm{~m}, 1 \mathrm{H}), 3.65(\mathrm{AB}-\mathrm{dd}, J=11.5,3.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.57$ (AB-dd, $J=11.5,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.53(\mathrm{AB}-\mathrm{dd}, J=9.6,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.51(\mathrm{AB}-\mathrm{dd}, J=9.6,6.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 138.1,128.9,128.3,128.2,74.0,72.2,71.2,64.4$.
(2R)-3-Benzyloxy-2-hydroxypropyl 4-methylbenzenesulfonat (29) ${ }^{6}$ was prepared from 28 as described for 27 and obtained in $91 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.79(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.36-$ $7.20(\mathrm{~m}, 7 \mathrm{H}), 4.49(\mathrm{~s}, 2 \mathrm{H}), 4.14-3.96(\mathrm{~m}, 3 \mathrm{H}), 3.54-3.47(\mathrm{~m}, 2 \mathrm{H}), 2.48(\mathrm{~d}, J=5.6,1 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 145.5,137.9,133.1,130.4,130.2,128.9,128.2,128.1,73.9,71.0,70.5,68.8$, 22.1.
(S)-1-Amino-3-(benzyloxy)propan-2-ol (4b). Tosylate 29 ( $3.0 \mathrm{~g}, 8.9 \mathrm{mmol}$ ) was dissolved in THF $(12 \mathrm{~mL})$ and ammonium hydroxide ( $30 \%$ in $\mathrm{H}_{2} \mathrm{O}, 23 \mathrm{~mL}$ ) was added. The reaction mixture was stirred in a sealed vessel for 24 h at $80{ }^{\circ} \mathrm{C}$. After cooling the THF was evaporated and the residue extracted with
$\mathrm{NaOH}(20 \mathrm{~mL}, 2 \mathrm{M})$ and $\mathrm{Et}_{2} \mathrm{O}(60 \mathrm{~mL})$. The water phase was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 * 60 \mathrm{~mL})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ $(1 * 60 \mathrm{~mL})$. After drying $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$ and evaporation of the solvent pure amino alcohol (4b) remained in $92 \%$ yield ( $1.5 \mathrm{~g}, 8.2 \mathrm{mmol}$ ). The product was used without further purification. $\mathrm{mp}: 58-63{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.37-7.26(\mathrm{~m}, 5 \mathrm{H}), 4.55(\mathrm{~s}, 2 \mathrm{H}), 3.78-3.73(\mathrm{~m}, 1 \mathrm{H}), 3.52-3.42(\mathrm{~m}, 2 \mathrm{H}), 2.83-2.67(\mathrm{~m}$, 2H), 2.10 (br s, 3H); ${ }^{13} \mathrm{C}^{\mathrm{N}} \mathrm{NR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) $\delta 138.5,128.9,128.21,128.19,73.9,73.0,71.5,44.8$; one signal is not visible; IR (neat): 3363 (br), 1332, $1101 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}-5.1\left(c 1.00, \mathrm{CH}_{3} \mathrm{Cl}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{10} \mathrm{H}_{16} \mathrm{NO}_{2}(\mathrm{M}+\mathrm{H})$ : 182.1181 , found: 182.1181 .

## 3. Experimental data for compounds 30a, 30b, 18a and 18b.

Scheme S4. Preparation of 18a and 18b from dimethyl malonate.


## General procedure for the alkylation of dimethyl malonate. Dimethyl 2,2-Didodeylmalonate

 (30b) A solution of KHMDS in THF ( $15.1 \mathrm{~mL}, 22.7 \mathrm{mmol}$ ) was added dropwise to a solution of dimethyl malonate ( $3.0 \mathrm{~g}, 22.7 \mathrm{mmol}$ ) in THF $(150 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$. When the addition was complete the turbid mixture was stirred for 15 min . Dodecyl bromide ( $5.5 \mathrm{~mL}, 22.9 \mathrm{mmol}$ ) was added and the reaction mixture refluxed for 10 h . The temperature was lowered to $0^{\circ} \mathrm{C}$, a second equiv. of KHMDS was added ( $15.1 \mathrm{~mL}, 22.7$ mmol ). The mixture was left for 15 min . and dodecyl bromide ( $5.5 \mathrm{~mL}, 22.9 \mathrm{mmol}$ ) was added. The mixture was allowed to reflux for 10 h , then cooled and diluted with $\mathrm{Et}_{2} \mathrm{O}$. The organic phase was washed three times with $\mathrm{NaOH}(2 \mathrm{M})$ and two times with HCl , then with brine. After drying $\left(\mathrm{MgSO}_{4}\right)$ and evaporation of the solvent, 10.2 g of a crude oil remained. The major part of the remaining dodecyl bromide and mono-alkylated product was removed by distillation under reduced pressure ( 0.1 torr, $100-200{ }^{\circ} \mathrm{C}$ ) and the rest was purified by flash chromatography (rp C18 silica, MeCN ). This afforded $23 \%$ of pure $\mathbf{3 0 b}$ ( 2.5 $\mathrm{g}, 5.2 \mathrm{mmol}) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 3.70(\mathrm{~s}, 6 \mathrm{H}), 1.88-1.84(\mathrm{~m}, 4 \mathrm{H}), 1.32-1.25(\mathrm{~m}, 36 \mathrm{H}), 1.14-$$1.08(\mathrm{~m}, 4 \mathrm{H}), 0.88(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 172.5,57.7,52.2,32.4,31.9,29.80$, 29.66, 29.63, 29.62, 29.5, 29.3, 29.3, 24.0, 22.7, 14.1; IR (neat): $1738 \mathrm{~cm}^{-1}$; HRMS (FAB+) calcd for $\mathrm{C}_{29} \mathrm{H}_{57} \mathrm{O}_{4}(\mathrm{M}+\mathrm{H}): 469.4257$, found: 469.4251

Dimethyl 2,2-Dioctylmalonate (30a) ${ }^{7}$ was prepared from dimethyl malonate and octyl bromide as described for $\mathbf{3 0 b}$ and obtained in $51 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 3.67(\mathrm{~s}, 6 \mathrm{H}), 1.84-1.80(\mathrm{~m}$, $4 \mathrm{H}), 1.27-1.22(\mathrm{~m}, 20 \mathrm{H}), 1.12-1.05(\mathrm{~m}, 4 \mathrm{H}), 0.84(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.3$, 58.1, 52.6, 32.9, 32.3, 30.2, 29.7, 29.6, 24.4, 23.1, 14.5

General procedure for the hydrolysis of malonic ester (30) to acid (18). 2,2-Dioctylmalonic acid (18a). ${ }^{8}$ Carboxylic ester 30a ( $2.26 \mathrm{~g}, 6.3 \mathrm{mmol}$ ) was dissolved in EtOH ( 20 mL ) and an aq. solution of $\mathrm{KOH}(50 \mathrm{~mL}, 1.2 \mathrm{M}$ ) was added. The solution was refluxed for 100 h , and then cooled using an external ice bath, and the excess KOH was neutralized by the addition of strongly acidic ion exchange resin (Amberlyst 15). The product precipitated as a white solid that was dissolved by the addition of $\mathrm{Et}_{2} \mathrm{O}$, and the resin was filtered off. The solvent was evaporated to give the product as a white powder in $94 \%$ yield $(1.95 \mathrm{~g}, 5.9 \mathrm{mmol}) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 3.70(\mathrm{~s}, 6 \mathrm{H}), 1.88-1.84(\mathrm{~m}, 4 \mathrm{H}), 1.32-1.25(\mathrm{~m}, 36 \mathrm{H})$, 1.14-1.08 (m, 4H), $0.88(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.6,57.8,34.7,31.8,29.6$, 29.20, 29.17, 24.6, 22.6, 14.1.

2,2-Didodecylmalonic acid (18b) ${ }^{9}$ was prepared from 30b as described for $\mathbf{1 8 a}$ and obtained in $73 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.97-1.93(\mathrm{~m}, 4 \mathrm{H}), 1.32-1.06(\mathrm{~m}, 40 \mathrm{H}), 0.88(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 178.3,58.3,35.2,32.4,30.15,30.10,30.10,30.07,30.02,29.8,25.0,23.1$, 14.4.

## 4. Experimental data for compounds 31a, 31b, 32a, 32b, 2a and 2b.

Scheme S4. Preparation of surfactants 2a and $\mathbf{2 b}$.


## $N^{1}, N^{3}$-Bis-(1-deoxy-2,3:4,5-di- $O$-isopropylidene-D-iditol-6-(4-methoxybenzoate))-2,2-

dioctylmalonamide (31a) was prepared from 18a and 14 as described for 20a and obtained in 59\% yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.44(\mathrm{t}, J=5.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 6.90(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $4 \mathrm{H}), 4.54(\mathrm{AB}-\mathrm{d}, J=11.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.52(\mathrm{AB}-\mathrm{d}, J=11.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.31-4.27(\mathrm{~m}, 2 \mathrm{H}), 4.17-4.14(\mathrm{~m}, 2 \mathrm{H}), 3.88$ (dd, $J=8.3,3.2 \mathrm{~Hz}, 2 \mathrm{H}) ; 3,82(\mathrm{~s}, 6 \mathrm{H}), 3.69(\mathrm{dd}, J=8.3,3.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.61$ (dd, $J=10.3,5.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), $3.58-$ $3.52(\mathrm{~m}, 4 \mathrm{H}), 3.46(\mathrm{td}, J=14.2,5.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.84-1.81(\mathrm{~m}, 4 \mathrm{H}), 1.44-1.43(\mathrm{~m}, 18 \mathrm{H}), 1.40(\mathrm{~s}, 6 \mathrm{H}), 1.30-1.18$ $(\mathrm{m}, 24 \mathrm{H}), 0.89(\mathrm{t}, J=6.7 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.4,159.3,130.0,129.4,113.8,110.7$, $109.4,77.23,77.18,76.2,75.8,73.2,70.1,57.1,55.3,40.3,37.6,31.8,29.9,29.4,29.3,27.4,27.2,26.68$, 26.66, 25.0, 22.6, 14.1; IR (neat): $3370,1666,1514 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+14.9\left(c 0.70, \mathrm{CHCl}_{3}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{59} \mathrm{H}_{94} \mathrm{~N}_{2} \mathrm{O}_{14} \mathrm{Na}(\mathrm{M}+\mathrm{Na})$ : 1077.6603, found: 1077.6599.

## $N^{1}, N^{3}$-Bis-(1-deoxy-2,3:4,5-di- $O$-isopropylidene-D-iditol-6-(4-methoxybenzoate))-2,2-

didodecylmalonamide (31b) was prepared from 18b and 14 as described for 20a and obtained in 57\% yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.44(\mathrm{t}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}), 6.90(\mathrm{~d}, J=8.5 \mathrm{~Hz}$, $4 \mathrm{H}), 4.54(\mathrm{AB}-\mathrm{d}, J=11.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.52(\mathrm{AB}-\mathrm{d}, J=11.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.31-4.27(\mathrm{~m}, 2 \mathrm{H}), 4.17-4.14(\mathrm{~m}, 2 \mathrm{H}), 3.88$ (dd, $J=8.3,3.2 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.82 (s, 6 H ), 3.69 (dd, $J=8.3,3.2 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.61 (dd, $J=10.3,5.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), $3.58-$ $3.52(\mathrm{~m}, 4 \mathrm{H}), 3.46 \mathrm{td}, J=14.2,5.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.84-1.81(\mathrm{~m}, 4 \mathrm{H}), 1.44-1.43(\mathrm{~m}, 18 \mathrm{H}), 1.40(\mathrm{~s}, 6 \mathrm{H}), 1.33-1.17$ $(\mathrm{m}, 40 \mathrm{H}), 0.90(\mathrm{t}, J=7.0 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.4,159.3,130.0,129.4,113.8$, 109.7,
$109.5,77.23,77.18,76.2,75.8,73.2,70.1,57.1,55.3,40.3,37.5,32.0,30.1,29.68,29.70,29.70,29.46$, $29.37,27.4,27.2,26.69,26.67,25.0,22.7,14.1$; one signal is not visible; IR (neat) $2926,1667,1514, \mathrm{~cm}^{-1}$; $[\alpha]_{\mathrm{D}}+12.9\left(c \quad 0.70, \mathrm{CHCl}_{3}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{67} \mathrm{H}_{110} \mathrm{~N}_{2} \mathrm{O}_{14} \mathrm{Na}(\mathrm{M}+\mathrm{Na}): 1089.7855$, found: 1089.7855.
$N^{1}, N^{3}$-Bis-(1-deoxy-2,3:4,5-di- $O$-isopropylidene-D-iditol)-2,2-dioctylmalonamide (32a) was prepared from 31a as described for 21a and obtained in $98 \%$ yield. ${ }^{1} \mathrm{H}$ NMR: ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.42$ (t, $J=5.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 4.21-4.17 (m, 4H), 4.02 (dd, $J=8.3,2.7 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.80 (dd, $J=11.8,4.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.77$3.72(\mathrm{~m}, 4 \mathrm{H}), 3.62-3.52(\mathrm{~m}, 4 \mathrm{H}), 2.59(\mathrm{br} \mathrm{s} 2 \mathrm{H}), 1.84-1.81(\mathrm{~m}, 4 \mathrm{H}), 1.46-1.44(\mathrm{~m}, 18 \mathrm{H}), 1.42(\mathrm{~s}, 6 \mathrm{H})$, 1.32-1.17 (m, 24H), $0.89(\mathrm{t}, J=7.0 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.7,109.6,109.4,77.2$, $76.9,76.3,75.9,62.3,57.4,40.0,37.1,31.8,29.9,29.31,29.23,27.31,27.25,26.6,26.5,24.9,22.6,14.1$; IR (neat): 2928, 1661, $1530 \mathrm{~cm}^{-1} ;[\alpha]_{D}-1.1\left(c 0.80, \mathrm{CHCl}_{3}\right)$; HRMS (FAB+) calcd for $\mathrm{C}_{43} \mathrm{H}_{78} \mathrm{~N}_{2} \mathrm{O}_{12} \mathrm{Na}$ $(\mathrm{M}+\mathrm{Na}): 837.5452$, found: 837.5453.
$N^{1}, N^{3}$-Bis-(1-deoxy-2,3:4,5-di- $O$-isopropylidene-D-iditol)-2,2-didodecylmalonamide (32b) was prepared from 31b as described for 21a and obtained in $93 \%$ yield. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.42(\mathrm{t}$, $J=5.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.21-4.17(\mathrm{~m}, 4 \mathrm{H}), 4.01(\mathrm{dd}, J=8.3,2.3 \mathrm{~Hz}, 2 \mathrm{H}), 3.80(\mathrm{dd}, J=11.9,4.7 \mathrm{~Hz}, 2 \mathrm{H}), 3.77-3.71$ $(\mathrm{m}, 4 \mathrm{H}), 3.62-3.52(\mathrm{~m}, 4 \mathrm{H}), 2.60(\mathrm{br} \mathrm{s}, 2 \mathrm{H}), 1.84-1.81(\mathrm{~m}, 4 \mathrm{H}), 1.45-1.44(\mathrm{~m}, 18 \mathrm{H}), 1.42(\mathrm{~s}, 6 \mathrm{H}), 1.33-$ $1.17(\mathrm{~m}, 40 \mathrm{H}), 0.90(\mathrm{t}, J=7.1 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 173.8,109.6,109.4,77.2,76.9$, $76.3,62.3,57.3,39.9,37.1,32.0,29.9,29.64,29.64,29.62,29.61,29.40,29.34,27.31,27.25,26.63,26.55$, 24.9, 22.7, 14.1; one signal is not visible; IR (neat): 2926, 1663, $1531 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}-1.0\left(c 1.00, \mathrm{CHCl}_{3}\right)$; HRMS (FAB+) calcd for $\mathrm{C}_{51} \mathrm{H}_{94} \mathrm{~N}_{2} \mathrm{O}_{12} \mathrm{Na}(\mathrm{M}+\mathrm{Na})$ : 949.6704, found: 949.6714.
$N^{1}, N^{3}$-Bis-(1-deoxy-D-iditol)-2,2-dioctylmalonamide (2a) was prepared from 32a as described for 1a and obtained as a white powder in $67 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ) $\delta 3.91-3.88(\mathrm{~m}, 2 \mathrm{H})$, $3.80-3.77(\mathrm{~m}, 4 \mathrm{H}), 3.71-3.64(\mathrm{~m}, 6 \mathrm{H}), 3.49(\mathrm{dd}, J=13.6,5.1 \mathrm{~Hz}, 2 \mathrm{H}), 3.39-3.35(\mathrm{~m}, 2 \mathrm{H}), 1.92-1.84(\mathrm{~m}$, $4 \mathrm{H}), 1.35-1.28(\mathrm{~m}, 4 \mathrm{H}), 1.21-1.17(\mathrm{~m}, 20 \mathrm{H}), 0.92(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{MeOH}$ )
$\delta 176.4,73.7,72.3,73.2,71.7,64.9,59.3,44.2,36.4,33.4,31.4,30.8,26.0,24.1,14.9$; one signal is not visible; IR (neat): 3350 (br), 1642, $1530 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+3.0(c 1.00, \mathrm{MeOH}) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{31} \mathrm{H}_{63} \mathrm{~N}_{2} \mathrm{O}_{12}(\mathrm{M}+\mathrm{H}): 655.4381$, found: 655.4381 .
$N^{1}, N^{3}$-Bis-(1-deoxy-D-iditol)-2,2-didodecylmalonamide (2b) was prepared form 32b as described for 1a and obtained as a white powder in $87 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}: \mathrm{CDCl}_{3} 1: 1,313 \mathrm{~K}$ ) $\delta 3.79-3.76(\mathrm{~m}, 2 \mathrm{H}), 3.71-3.66(\mathrm{~m}, 4 \mathrm{H}), 3.58(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 4 \mathrm{H}), 3.53(\mathrm{t}, J=3.8 \mathrm{~Hz}, 2 \mathrm{H}), 3.40(\mathrm{dd}, J=13.7$, $5.1 \mathrm{~Hz}, 2 \mathrm{H}), 3.29-3.24(\mathrm{~m}, 2 \mathrm{H}), 1.78-1.72(\mathrm{~m}, 4 \mathrm{H}), 1.94-1.17(\mathrm{~m}, 36 \mathrm{H}), 1.08-1.06(\mathrm{~m}, 4 \mathrm{H}), 0.78(\mathrm{t}, J=6.9$ $\mathrm{Hz}, 6 \mathrm{H}$ ) ${ }^{13} \mathrm{C}$ NMR (125 MHz, MeOH: $\mathrm{CDCl}_{3} 1: 1$ ) $\delta 174.7,72.4,72.3,72.0,70.5,63.7,58.1,43.0,34.5$, $32.1,30.2,29.9,29.8,29.8,29.6,29.5,24.6,22.8,13.9$; one signal is not visible; IR (neat): 3326 (br), 1644, $1529 \mathrm{~cm}^{-1}$; HRMS (FAB+) calcd for $\mathrm{C}_{39} \mathrm{H}_{79} \mathrm{~N}_{2} \mathrm{O}_{12}(\mathrm{M}+\mathrm{H}): 767.5633$, found: 767.5618.

## 5. Analytical data for compounds ent-21a, ent-21b, ent-1a and ent-1b.

$N^{1}, N^{3}$-Bis-(1-deoxy-2,3:4,5-di- $O$-isopropylidene-D-galactitol)-2,2-dioctylmalonamide (ent-21a) was prepared from 18a and 17 as described for 20a and obtained as a clear oil in $45 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.59(\mathrm{dd}, J=6.6,4.3 \mathrm{~Hz}, 2 \mathrm{H}), 4.09-4.06(\mathrm{~m}, 4 \mathrm{H}), 3.87-3.73(\mathrm{~m}, 8 \mathrm{H}), 3.66(\mathrm{t}, J=7.8$ $\mathrm{Hz}, 2 \mathrm{H}), 3.51(\mathrm{td}, J=13.9,4.3 \mathrm{~Hz}, 2 \mathrm{H}), 2.30(\mathrm{dd}, J=8.6,4.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.87-1.80(\mathrm{~m}, 4 \mathrm{H}), 1.47(\mathrm{~s}, 6 \mathrm{H}), 1.45$ $(\mathrm{s}, 6 \mathrm{H}), 1.43(\mathrm{~s}, 6 \mathrm{H}), 1.39(\mathrm{~s}, 6 \mathrm{H}), 1.32-1.17(\mathrm{~m}, 24 \mathrm{H}), 0.89(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 173.2,110.1,109.8,80.9,79.7,79.2,78.6,62.5,57.1,40.8,37.5,31.8,29.9,29.4,29.3,27.1$, 27.0, 26.9, 26.8, 24.9, 22.6, 14.1; IR (neat): 3389 (br), 1666, $1530 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}+6.9\left(c 0.90, \mathrm{CHCl}_{3}\right) ;$ HRMS (FAB+) calcd for $\mathrm{C}_{43} \mathrm{H}_{79} \mathrm{~N}_{2} \mathrm{O}_{12} \mathrm{Na}(\mathrm{M}+\mathrm{H}): 815.5633$, found: 815.5641.

## $N^{1}, N^{3}$-Bis-(1-deoxy-2,3:4,5-di- $O$-isopropylidene-D-galactitol)-2,2-didocecylmalonamide (ent-

 21b) was prepared from $\mathbf{1 8 b}$ and 17 as described for 20 a and obtained as a clear oil in $45 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.55(\mathrm{dd}, J=6.52,4.32 \mathrm{~Hz}, 2 \mathrm{H}), 4.07-4.03(\mathrm{~m}, 4 \mathrm{H}), 3.85-3.69(\mathrm{~m}, 8 \mathrm{H}), 3.64(\mathrm{t}$, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.49(\mathrm{td}, J=13.9,4.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.36(\mathrm{dd}, J=7.86,4.30 \mathrm{~Hz}, 2 \mathrm{H}), 1.85-1.77(\mathrm{~m}, 4 \mathrm{H}), 1.44(\mathrm{~s}$,$6 \mathrm{H}), 1.43(\mathrm{~s}, 6 \mathrm{H}), 1.40(\mathrm{~s}, 6 \mathrm{H}), 1.37(\mathrm{~s}, 6 \mathrm{H}), 1.23-.118(\mathrm{~m}, 40 \mathrm{H}), 0.88(\mathrm{t}, J=13.7,6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 173.6,110.5,110.2,81.3,80.2,79.6,79.0,62.9,57.5,41.2,37.9,32.3,30.3,30.1$, $30.1,30.1,29.9,29.8,27.53,27.50,27.3,27.2,25.4,23.1,14.5$; one signal is not visible; IR (neat): 3374 (br), 1667, 1530, $\mathrm{cm}^{-1} ;[\alpha]_{\mathrm{D}}+6.0\left(c 1.09, \mathrm{CHCl}_{3}\right)$ HRMS (FAB+) calcd for $\mathrm{C}_{51} \mathrm{H}_{94} \mathrm{~N}_{2} \mathrm{O}_{12} \mathrm{Na}(\mathrm{M}+\mathrm{Na})$ : 949.6704, found: 949.6710.
$N^{1}, N^{3}$-Bis-(1-deoxy-D-galactitol)-2,2-dioctylmalonamide ent-1a was prepared from ent-21a as described for $\mathbf{1 a}$ and obtained as a white powder in $99 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ) $\delta 3.98$ (br t, $J=6.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.91 (br t, $J=5.7 \mathrm{~Hz}, 2 \mathrm{H}$ ), $3.66-3.63(\mathrm{~m}, 6 \mathrm{H}), 3.53$ (br d, $J=9.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.45 (dd, $J=13.5$, $5.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.86-1.82(\mathrm{~m}, 4 \mathrm{H}), 1.31-1.28(\mathrm{~m}, 20 \mathrm{H}), 1.20-1.02(\mathrm{~m}, 4 \mathrm{H}), 0.88(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (125 MHz, MeOD): $\delta 176.1,72.0,71.9,71.3,70.0,65.0,58.8,49.9,44.2,35.9,33.1,31.0,30.4,25.5,23.8$, 14.5; IR (neat): 3339 (br), 1627, $1439 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}-10.8$ (c 1.00, $\mathrm{CHCl}_{3}$ ); HRMS (FAB+) calcd for $\mathrm{C}_{31} \mathrm{H}_{63} \mathrm{~N}_{2} \mathrm{O}_{12}(\mathrm{M}+\mathrm{H}): 655.4381$, found: 655.4380 .
$N^{1}, N^{3}$-Bis-(1-deoxy-D-galactitol)-2,2-didodecylmalonamide ent-1b was prepared form ent-21b as described for $\mathbf{1 a}$ and obtained as a white powder in $99 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}: \mathrm{CDCl}_{3} 1: 1$, $313 \mathrm{~K})$ § 3.97-3.90(m, 4H), 3.70-3.62 (m, 6H), 3.52-3.47 (m, 4H), 1.87-1.82 (m, 4H), 1.32-1.12 (m, $40 \mathrm{H}), 0.88(\mathrm{t}, J=6.82 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{MeOD}: \mathrm{CDCl}_{3} 1: 1,313 \mathrm{~K}$ ): $\delta 174.6,71.2,70.9,70.8$, $69.1,64.3,58.1,49.3,43.2,34.0,32.1,30.2,29.89,29.85,29.85,29.6,29.5,24.5,22.8,13.9$; IR (neat): 3339 (br) 1627, $1439 \mathrm{~cm}^{-1}$; HRMS (FAB+) calcd for $\mathrm{C}_{39} \mathrm{H}_{79} \mathrm{~N}_{2} \mathrm{O}_{12}(\mathrm{M}+\mathrm{H})$ : 767.5633, found: 767.5635.

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7. NMR spectra for compounds $1 \mathbf{a}, \mathbf{b}$, ent $\mathbf{- 1} \mathbf{a}, \mathbf{b}, \mathbf{2 a}, \mathbf{b}, \mathbf{4 a}, \mathbf{b}$, ent-6, 7, ent-7, 8-17, 20a, b, 21a, b, ent-21a, b, 22-24, 27, 30b, 31a, b, 32a, b.



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