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Highly β-Selective Glycosylation Reactions for the Synthesis of ω-Functionalized Alkyl β-Maltoside as a Co-crystallizing Detergent

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Abstract—Methods have been reported for the preparation of ω-functionalized alkyl maltoside and glycoside detergents via a simple and inexpensive synthetic route. The key step was stannic chloride-mediated glycosylation of long-chain alcohols or thiols with maltose octaacetate at 0 or –10°C, respectively, within a very short time (isolated yield 17–44%), which provided more than 98% β-selectivity.

Keywords: maltoside detergent, glycosylation, maltose octaacetate, β-selectivity, ω-functionalized glycoside

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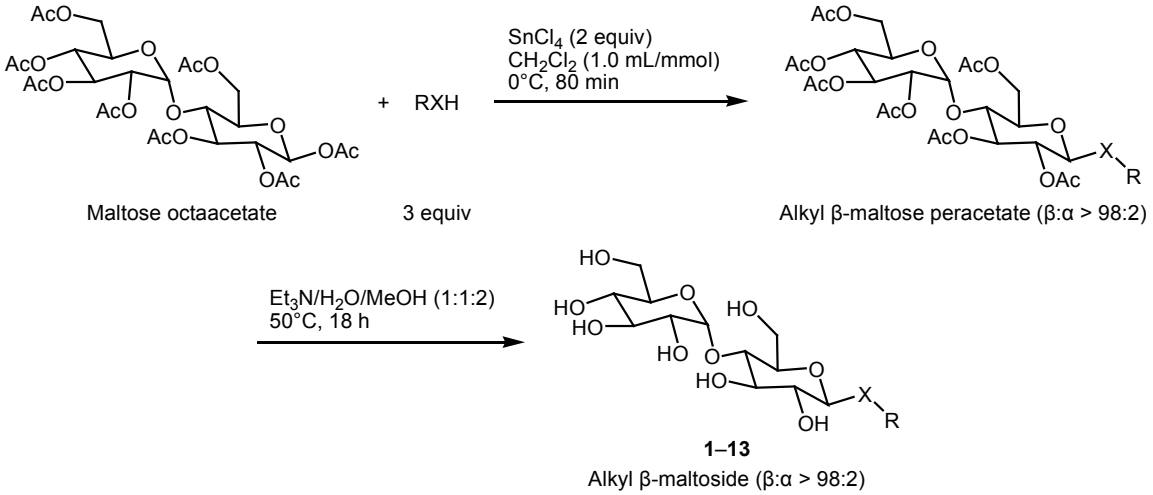
INTRODUCTION

Alkyl glycoside detergents are necessary for the crystallization of membrane proteins. The history of X-ray crystallography of cytochrome c oxidase clearly indicates that selectivity and purity of detergent are the most significant factors to achieve high structural resolution. Decyl maltoside detergent forms crystals with high resolution as revealed by X-ray crystallography [1–4]. High anomeric selectivity of the glycosylation reaction is very crucial for the synthesis of detergents.

Several β-selective glycosylation reactions have already been reported. Banoub and Bundle prepared a glycoside with high β-selectivity (61–68%) by reaction of maltose octaacetate with ethyl 9-hydroxynonanoate using stannic chloride at –10°C and at long reaction time [5]. Ferguson-Miller and co-workers [4] synthesized a glycoside of *n*-octanol by reaction with glucose pentaacetate through aceto-bromoglucose intermediate by using silver carbonate and iodine at room temperature. After preparation of octyl β-D-glucose peracetate, they synthesized octyl β-D-glucoside (detergent) with 60% isolated yield via solvolysis. However, the β/α-anomer ratio was not clearly mentioned in that report. The same research team also reported the synthesis of lauryl β-D-maltoside detergent with 25% yield via glycosylation using acetobromomaltose as intermediate and silver carbonate as catalyst [6]. Matsumoto and co-workers [7] synthesized decyl β-lactoside detergent with 78% yield through solvolysis of decyl β-lactose heptaacetate which was prepared by reaction with maltose octaacetate using boron trifluoride as Lewis acid with 25% yield. Hoheisel and Frauenrath [8] reported glycosylation of propargyl alcohol with pentaacetyl-β-D-glucose in 79% yield using boron trifluoride–ethyl ether complex at room temperature. An enzyme-based method for the synthesis of alkyl glycosides using C_1–C_{12} unbranched primary alcohols was described in [9]; however, it required a long reaction time. The synthesis of C_7–C_{16}-alkyl maltosides in the presence of tin(IV) chloride as a Lewis acid catalyst is also time dependent, and prolonged reaction time favored the formation of α-anomeric glycoside [10].

There are several types of detergents that have already been synthesized and used for crystallization of membrane proteins. Generally, the nature of the lipophilic chain of detergents plays an important role in the quality of protein crystals. However, detergents functionalized at the ω-position of the lipophilic chain, as well as those derived from long-chain thiols have not been synthesized as yet. Therefore, we focused on the synthesis of new ω-functionalized detergents to im-

Scheme 1.



1–**10**, **12**, X = O; **11**, **13**, X = S; **1**, R = CH_2=$CH(CH_2)_8$; **2**, R = $Cl(CH_2)_9$; **3**, R = $MeO(CH_2)_8$; **4**, R = $Me(CH_2)_8$; **5**, R = CH_2=$CH(CH_2)_9$; **6**, $Me(CH_2)_{10}$; **7**, R = $Me(CH_2)_{13}$; **8**, R = $Me_2CH(CH_2)_7$; **9**, R = $Me_2CH(CH_2)_8$; **10**, R = 8-cyclopropyloctyl; **11**, R = $Me(CH_2)_{11}$; **12**, **13**, R = $Me(CH_2)_6$.

prove the quality of crystals that could be obtained with their use.

Herein, we present the synthesis of ω-functionalized detergents from maltose octaacetate via glycosylation reaction using tin(IV) chloride as Lewis acid at 0°C with over 98% β-selectivity (68–88% yield). Stannic chloride is less expensive and easy to handle. We also prepared glucopyranoside detergent from pentaacetyl-β-D-glucose and achieved 78–80% yield using boron trifluoride–diethyl ether complex at room temperature with over 99% β-selectivity. To the best of our knowledge, this is the highest β-selectivity of maltoside detergent preparation through glycosylation reaction.

RESULTS AND DISCUSSION

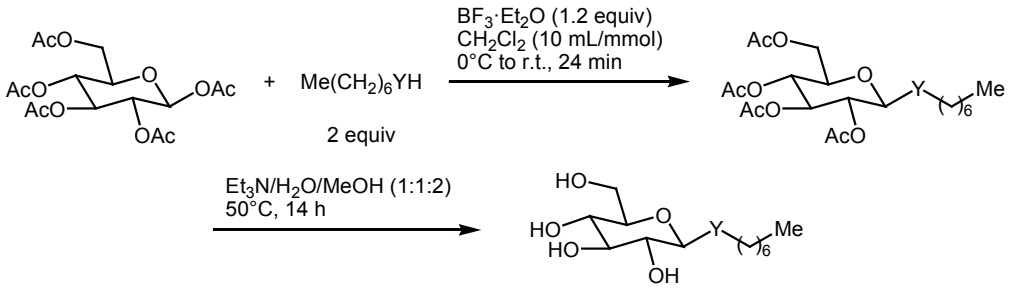
The glycosylation of 9-chlorononan-1-ol with maltose octaacetate was carried out at room temperature, but the fraction of the α-anomer was very high (β/α ratio 65/35; isolated yield 39%). We then performed this glycosylation at 0°C for about 1 h and achieved high β-selectivity (β/α >98%; isolated yield 18%). Prolongation of the reaction time in combination with higher temperature increased the fraction of α-glycosides due to β/α anomerization according to the mechanism described in [5, 11]. The other glycosylation reactions were performed under the optimized conditions (Scheme 1) using a very small amount of solvent (CH_2Cl_2) over a very short time maintaining the temperature at 0°C; the β-selectivity was higher than that reported in [12].

ω-Functionalized alcohols and thiols with different lipophilic chain lengths were involved in the glycosylation reaction. In case of thiols, the reaction occurred in a relatively short time due to high nucleophilicty of sulfur atom. The isolated yield varied from 17 to 44% (Table 1). In some cases, the isolated yield was relatively poor since it referred to the pure product after column chromatography, and isolation of the product by column chromatography was difficult due to overlapping with impurities. The overall β-selectivity was over 98% according to the ^{1}H NMR data. It was assumed that there was no effect of ω-functional groups on the selectivity.

After glycosylation, the corresponding alkyl β-maltosides were prepared by solvolysis (deacetylation). The solvolysis smoothly proceeded without loss of α/β ratio. The isolated yields were 68–88% (Scheme 1). The products were isolated by column chromatography on Dowex (OH) using methanol as eluent. The α/β ratio and chemical purity were determined, respectively, by ^{1}H NMR and HPLC (GL Sciences ODS-3 column, 4.6×250 mm, refractive index detector, eluent 30% H_2O in MeOH, flow rate 1.0 mL/min). The specific rotations were also in good agreement with β-selectivity [13, 14].

We also synthesized glucopyranoside detergents (Scheme 2). The glycosylation step was performed using tin(IV) chloride as catalyst. However, in the case of boron trifluoride–diethyl ether complex, the amount of impurities was lower, isolation of the products was relatively easier, and the β-selectivity was over 99%

Scheme 2.



(^{1}H NMR). The isolated yields were 27 (X = O) and 34% (X = S). Both isolation and analysis methods were the same as in the preparation of maltoside detergents. Thus, both maltoside and glucopyranoside detergents may be perfect detergents to enhance the quality of protein crystals.

Table 1 also contains the HPLC retention times of detergents **1**–**13**, which were used to estimate their polarity. The polarity increases as the retention time decreases. The polarity depends on the length of lipophilic chain and ω-functional group. Very high polarity was observed for C_8-detergent **3** with a methoxy group, and detergent **11** with a long lipophilic chain (C_{12}) and a sulfur atom was characterized by very low polarity. Compound **1** with a terminal C=C bond in the C_{10} chain is more polar than its saturated analog since C=C double bond is more polar than the single carbon–carbon bond. Cyclopropyl group behaves like a double bond (orbital structure), and C_{11} derivative **10** with a terminal cyclopropyl group is more polar than unbranched C_{11} derivative **6**. Higher polarity of the lipophilic chain of the glycoside detergent may favor crystallization of membrane proteins. Hence, maltoside detergent **3** with an ω-methoxy-substituted group could be efficient in co-crystallization system [15].

EXPERIMENTAL

Commercial tin(IV) chloride and Dowex (OH form) resin were used without any further treatment. Maltose octaacetate was prepared as described in [13, 16, 17]; dec-9-en-1-ol, nonan-1-ol, undec-10-en-1-ol, undecan-1-ol, tetradecan-1-ol, dodecane-1-thiol, heptan-1-ol, and heptane-1-thiol were commercial products; 8-methoxyoctan-1-ol, 9-chlorononan-1-ol, 8-methylnonan-1-ol, 8-cyclopropyloctan-1-ol, and 9-methyldecan-1-ol were prepared according to reported procedures.

Table 1. Yields of alkyl hepta-*O*-acetyl-β-maltosides and HPLC retention times of the corresponding alkyl β-maltosides

Alcohol	Number of carbon atoms	Yield of alkyl hepta-*O*-acetyl-β-maltoside,[a] %	Alkyl β-maltoside	Retention time,[b] min
Dec-9-en-1-ol	10	30	**1**	11.08
9-Chlorononan-1-ol	9	18	**2**	8.69
8-Metoxyoctan-1-ol	8	28	**3**	4.11
Nonan-1-ol	9	27	**4**	11.09
Undec-10-en-1-ol	11	19	**5**	18.28
Undecan-1-ol	11	37	**6**	31.17
Tetradecan-1-ol	14	44	**7**	
8-Methylnonan-1-ol	10	32	**8**	15.42
9-Methyldecan-1-ol	11	17	**9**	29.11
8-Cyclopropyloctan-1-ol	11	28	**10**	19.88
Dodecane-1-thiol	12	17[c]	**11**	64.19
Heptan-1-ol	7	22	**12**	5.90/6.22
Heptane-1-thiol	7	38[c]	**13**	6.96/7.46

[a] Isolated yield.
[b] HPLC; RI detector, ODS-3 column (GL Sciences), 30% H_2O in MeOH, flow rate 1.0 mL/min.
[c] Temperature –10°C, reaction time 55 min.

The ^{1}H NMR spectra were recorded on a a JEOL ECA-600 spectrometer operating at 600.17 MHz; the chemical shifts were measured relative to the residual proton signal of the solvent, and the coupling constants were measured with an accuracy of ±0.1 Hz. The optical rotations were measured with a Perkin Elmer 243B polarimeter. The high resolution mass spectra were run on Jeol JMS-AX505HF (electron impact) and Jeol JMS-T100LC (electronspray ionization) instruments. HPLC analyses were carried out using a Hitachi L-6200 intelligent pump, Shimadzu SPD-10A RI detector, and GL Sciences ODS-3 column.

General procedure for the synthesis of alkyl hepta-*O*-acetyl-β-maltosides. Tin(IV) chloride (2.0 equiv) was added very slowly to a solution of maltose octaacetate (1.0 mmol) in anhydrous methylene chloride (1.0 mL) at 0°C under a nitrogen atmosphere. After 15 min, the corresponding alcohol or thiol (3.0 equiv) was added slowly at 0°C (at –10°C in the case of thiol), and the mixture was stirred 0°C (or –10°C) for 80 min. The progress of the reaction was monitored by TLC on silica gel plates using ethyl acetate–hexane (1:1) as eluent. The mixture was diluted with cold (0°C) ethyl acetate, quenched with water, and extracted with ethyl acetate (3×50 mL). The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, and the residue was purified by column chromatography on Dowex (OH form) using ethyl acetate–hexane (15:100, 20:100, and 25:100) as eluent. The products were isolated as colorless viscous oils.

Dec-9-en-1-yl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (1.0 g, 1.47 mmol) and dec-9-en-1-ol (0.8 mL, 689 mg, 4.41 mmol) using 0.34 mL (766 mg, 2.94 mmol) of tin(IV) chloride. Yield 336 mg (30%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12–1.24 m (8H), 1.32–1.39 m (4H), 1.52 m (2H), 1.97 s (6H), 1.98 s (3H), 1.99 s (3H), 2.02 s (3H), 2.07 s (3H), 2.11 s (3H), 3.43 q (1H, *J* = 8.3 Hz), 3.64 m (1H), 3.81 m (1H), 3.93 d (1H, *J* = 9.6 Hz), 3.97 t (1H, *J* = 9.6 Hz), 4.01 d (1H, *J* = 12.0 Hz), 4.21 d.t (2H, *J* = 4.5, 12.0 Hz), 4.44 d.d (1H, *J* = 2.4, 12.0 Hz), 4.78 t (1H, *J* = 8.4 Hz), 4.83 d.d (1H, *J* = 4.2, 10.2 Hz), 4.90 d (1H, *J* = 9.6 Hz), 4.96 d (1H, *J* = 16.8 Hz), 5.02 t (1H, *J* = 9.6 Hz), 5.22 t (1H, *J* = 9.0 Hz), 5.33 t (1H, *J* = 10.2 Hz), 5.39 d (1H, *J* = 3.6 Hz), 5.77 m (1H).

9-Chlorononyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (5.0 g, 7.37 mmol) and 9-chlorononan-1-ol (3.95 g, 22.11 mmol) using 1.73 mL (3.84 g, 14.74 mmol) of tin(IV) chloride. Yield 1.06 g (18%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.14–1.18 m (8H), 1.30 m (2H), 1.44 m (2H), 1.65 m (2H), 1.90 s (6H), 1.91 s (3H), 1.92 s (3H), 1.93 s (3H), 1.99 s (3H), 2.04 s (3H), 3.37 q (1H, *J* = 15.9 Hz), 3.42 t (1H, *J* = 6.6 Hz), 3.58 d (1H, *J* = 9.6 Hz), 3.74 q (1H, *J* = 15.9 Hz), 3.87 d (1H, *J* = 10.2 Hz), 3.90 t (1H, *J* = 9.2 Hz), 3.94 d (1H, *J* = 12.0 Hz), 4.14 d.t (2H), 4.37 d.d (1H, *J* = 1.18, 12.6 Hz), 4.42 d (1H, *J* = 7.8 Hz), 4.71 t (1H, *J* = 8.4 Hz), 4.75 d.d (1H, *J* = 4.2, 10.2 Hz), 4.95 t (1H, *J* = 12.6 Hz), 5.15 t (1H, *J* = 9.6 Hz), 5.26 t (1H, *J* = 10.2 Hz), 5.31 d (1H, *J* = 3.6 Hz).

8-Methoxyoctyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (1.0 g, 1.47 mmol) and 8-methoxyoctan-1-ol (707 mg, 4.41 mmol) using 0.34 mL (766 mg, 2.94 mmol) of tin(IV) chloride. Yield 316 mg (28%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.10–1.15 m (8H), 1.33 m (2H), 1.42 m (2H), 1.85 s (3H), 1.86 s (3H), 1.87 s (3H), 1.88 s (3H), 1.90 s (3H), 1.96 s (3H), 2.00 s (3H), 3.18 s (3H), 3.22 t (2H, *J* = 6.9 Hz), 3.33 q (1H, *J* = 16.5 Hz), 3.70 q.d (1H, *J* = 9.0 Hz), 3.84 d (1H, *J* = 10.8 Hz), 3.87 t (1H, *J* = 9.3 Hz), 3.91 d (1H, *J* = 12.0 Hz), 4.12 m (2H), 4.33 d.d (1H, *J* = 1.8, 11.4 Hz), 4.39 d (1H, *J* = 7.8 Hz), 4.67 t (1H, *J* = 7.8 Hz), 4.72 d.d (1H, *J* = 4.2, 10.8 Hz), 4.91 t (1H, *J* = 9.6 Hz), 5.12 t (1H, *J* = 9.6 Hz), 5.22 t (1H, *J* = 10.8 Hz), 5.28 d (1H, *J* = 3.6 Hz).

Nonyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (1.0 g, 1.47 mmol) and nonan-1-ol (0.77 mL, 636 mg, 4.41 mmol) using 0.34 mL (766 mg, 2.94 mmol) of tin(IV) chloride. Yield 300 mg (27%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 t (3H, *J* = 6.3 Hz), 1.18–1.33 m (10H), 1.44–1.58 m (4H), 1.97 s (6H), 1.98 s (3H), 1.99 s (3H), 2.01 s (3H), 2.07 s (3H), 2.11 s (3H), 3.43 q (1H, *J* = 15.3 Hz), 3.64 q.d (1H, *J* = 9.6), 3.81 q (1H, *J* = 15.3 Hz), 3.92 d (1H, *J* = 9.6 Hz), 3.97 t (1H, *J* = 9.6 Hz), 4.01 d (1H, *J* = 12.6 Hz), 4.21d.t (2H, *J* = 3.6, 11.4 Hz), 4.43 d (1H, *J* = 11.4 Hz), 4.48 d (1H, *J* = 7.8 Hz), 4.78 t (1H, *J* = 7.8 Hz), 4.82 d.d (1H, *J* = 4.2, 10.5 Hz), 5.02 t (1H, *J* = 9.6 Hz), 5.22 t (1H, *J* = 9.6 Hz), 5.33 t (1H, *J* = 10.5 Hz), 5.38 d (1H, *J* = 3.6 Hz).

Undec-10-en-1-yl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (1.0 g, 1.47 mmol) and undec-10-en-1-ol (0.88 mL, 4.41 mmol) using 0.34 mL (766 mg, 2.94 mmol) of tin(IV) chloride. Yield 215 mg (19%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18–1.19 m (10H), 1.28–1.32 m (4H), 1.48 m (2H), 1.93 s (6H), 1.94 s (3H),

1.96 s (3H), 1.97 s (3H), 2.03 s (3H), 2.07 s (3H), 3.39 q (1H, *J* = 15.6 Hz), 3.61 q.d (1H, *J* = 9.0 Hz), 3.77 q (1H, *J* = 15.6 Hz), 3.89 d (1H, *J* = 4.2 Hz), 3.94 t (1H, *J* = 9.3 Hz), 3.97 d (1H, *J* = 12.6 Hz), 4.18 d.t (2H, *J* = 3.6, 12.0 Hz), 4.40 d.d (1H, *J* = 1.8, 12.0 Hz), 4.45 d (1H, *J* = 8.4 Hz), 4.74 t (1H, *J* = 8.4 Hz), 4.79 d.d (1H, *J* = 4.2, 10.8 Hz), 4.85 d (1H, *J* = 10.8 Hz), 4.92 d (1H, *J* = 17.4 Hz), 4.98 t (1H, *J* = 9.9 Hz), 5.18 t (1H, *J* = 9.9 Hz), 5.29 t (1H, *J* = 9.9 Hz), 5.35 d (1H, *J* = 3.6 Hz), 5.73 m (1H).

Undecyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (1.0 g, 1.47 mmol) and undecan-1-ol (0.92 mL, 4.41 mmol) using 0.34 mL (766 mg, 2.94 mmol) of tin(IV) chloride. Yield 430 mg (37%). ^{1}H NMR ($CDCl_3$), δ, ppm: 0.86 t (3H, *J* = 6.9 Hz), 1.22–1.25 m (12H), 1.54 s (6H), 1.98 s (6H), 1.99 s (3H), 2.00 s (3H), 2.02 s (3H), 2.08 s (3H), 2.12 s (3H), 3.44 q (1H, *J* = 15.9 Hz), 3.65 q.d (1H, *J* = 9.6), 3.82 q (1H, *J* = 15.9 Hz), 3.93 d (1H, *J* = 10.2 Hz), 3.98 t (1H, *J* = 9.3 Hz), 4.01 d (1H, *J* = 13.2 Hz), 4.22 d.t (2H, *J* = 3.6, 12.0 Hz), 4.45 d.d (1H, *J* = 2.4, 12.0 Hz), 4.49 d (1H, *J* = 8.4 Hz), 4.79 t (1H, *J* = 8.4 Hz), 4.84 d (1H, *J* = 10.2 Hz), 5.03 t (1H, *J* = 9.9 Hz), 5.23 t (1H, *J* = 9.9 Hz), 5.34 t (1H, *J* = 9.9 Hz), 5.40 d (1H, *J* = 3.6 Hz).

Tetradecyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (1.0 g, 1.47 mmol) and tetradecan-1-ol (946 mg, 4.41 mmol) using 0.34 mL (766 mg, 2.94 mmol) of tin(IV) chloride. Yield 547 mg (44%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.71 t (3H, *J* = 6.6 Hz), 1.03–1.21 m (22H), 1.39 m (2H), 1.84 s (6H), 1.86 s (3H), 1.87 s (6H), 1.93 s (3H), 1.98 s (3H), 3.31 q (1H, *J* = 15.0 Hz), 3.53 q.d (1H, *J* = 9.0 Hz), 3.68 q (1H, *J* = 15.0 Hz), 3.82 d (1H, *J* = 12.6 Hz), 3.84 t (1H, *J* = 9.6 Hz), 3.88 d (1H, *J* = 12.6 Hz), 4.09 d.t (2H), 4.30 d (1H, *J* = 12.0 Hz), 4.37 d (1H, *J* = 7.8 Hz), 4.64 t (1H, *J* = 7.8 Hz), 4.69 d.d (1H, *J* = 4.2, 10.2 Hz), 4.89 t (1H, *J* = 10.2 Hz), 5.09 t (1H, *J* = 9.0 Hz), 5.20 t (1H, *J* = 9.9 Hz), 5.26 d (1H, *J* = 3.6 Hz).

8-Methylnonyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (875 mg, 1.29 mmol) and 8-methylnonan-1-ol (612 mg, 3.87 mmol) using 0.3 mL (672 mg, 2.58 mmol) of tin(IV) chloride. Yield 319 mg (32%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.79 d (6H, *J* = 6.6 Hz), 1.18–1.21 m (11H), 1.40 m (2H), 1.94 s (6H), 1.95 s (3H), 1.96 s (3H), 1.98 s (6H), 2.04 s (3H), 2.08 s (3H), 3.41 q (1H, *J* = 15.0 Hz), 3.62 q.d (1H, *J* = 9.0 Hz), 3.79 q (1H, *J* = 15.0 Hz), 3.90 d (1H, *J* = 9.6 Hz), 3.94 t (1H, *J* = 9.6 Hz), 3.98 d (1H, *J* = 12.6 Hz), 4.20 d.t (2H, *J* = 4.2, 11.4 Hz), 4.41 d (1H, *J* = 10.8 Hz), 4.46 d (1H, *J* = 8.4 Hz), 4.75 t (1H, *J* = 10.2 Hz), 4.80d.d (1H, *J* = 4.2, 10.2 Hz), 4.99 t (1H, *J* = 9.6 Hz), 5.19 t (1H, *J* = 9.6 Hz), 5.30 t (1H, *J* = 10.2 Hz), 5.36 d (1H, *J* = 3.6 Hz).

9-Methyldecyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (543 mg, 0.8 mmol) and 9-methyldecan-1-ol (414 mg, 2.4 mmol) using 0.19 mL (417 mg, 1.6 mmol) of tin(IV) chloride. Yield 105 mg (17%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.83 d (6H, *J* = 6.0 Hz), 1.12 m (2H), 1.19–1.32 m (9H), 1.45–1.54 m (4H), 1.98 s (6H), 1.99 s (3H), 2.00 s (3H), 2.02 s (3H), 2.08 s (3H), 2.12 s (3H), 3.40 q (1H, *J* = 16.2 Hz), 3.65 q (1H, *J* = 12.6 Hz), 3.82 q (1H, *J* = 16.2 Hz), 3.93 d (1H, *J* = 10.8 Hz), 3.98 t (1H, *J* = 9.0 Hz), 4.01 d (1H, *J* = 13.2 Hz), 4.22 d.t (2H, *J* = 4.2, 12.0 Hz), 4.44 d.d (1H, *J* = 2.4, 12.0 Hz), 4.49 d (1H, *J* = 7.8 Hz), 4.79 t (1H, *J* = 7.8 Hz), 4.83 d.d (1H, *J* = 3.6, 10.8 Hz), 5.03 t (1H, *J* = 9.6 Hz), 5.23 t (1H, *J* = 9.6 Hz), 5.34 t (1H, *J* = 10.2 Hz), 5.39 d (1H, *J* = 4.2 Hz).

8-Cyclopropyloctyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (2.12 g, 3.13 mmol) and 8-cyclopropyloctan-1-ol (1.60 g, 9.40 mmol) using 0.73 mL (1.63 g, 6.26 mmol) of tin(IV) chloride. Yield 686 mg (28%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.06 q (2H, *J* = 9.6 Hz). 0.33 q (2H, *J* = 12.6 Hz), 1.11–1.34 m (11H), 1.43 m (2H), 1.96 s (6H), 1.97 s (3H), 1.98 s (3H), 2.00 s (3H), 2.06 s (3H), 2.12 s (3H), 3.42 q (1H, *J* = 16.2 Hz), 3.63 q.d (1H, *J* = 9.6 Hz), 3.80 q (1H, *J* = 16.2 Hz), 3.93 d (1H, *J* = 10.2 Hz), 3.98 t (1H, *J* = 9.0 Hz), 4.01 d (1H, *J* = 12.6 Hz), 4.22 d.t (2H, *J* = 4.2, 12.0 Hz), 4.42 d.d (1H, *J* = 1.8, 12.0 Hz), 4.47 d (1H, *J* = 8.4 Hz), 4.77 t (1H, *J* = 8.4 Hz), 4.81 d.d (1H, *J* = 4.2, 10.2 Hz), 5.01 t (1H, *J* = 9.9 Hz), 5.21 t (1H, *J* = 9.9 Hz), 5.32 t (1H, *J* = 9.9 Hz), 5.37 d (1H, *J* = 4.2 Hz).

Dodecyl hepta-*O*-acetyl-1-thio-β-maltoside was synthesized from maltose octaacetate (500 mg, 0.74 mmol) and dodecane-1-thiol (0.53 mL, 449 mg, 2.22 mmol) using 0.17 mL (385 mg, 1.48 mmol) of tin(IV) chloride. Yield 103 mg (17%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.82 t (3H, *J* = 6.6 Hz), 1.19–1.37 m (18H), 1.52 m (2H), 1.95 s (6H), 1.96 s (3H), 1.97 m (3H), 1.99 m (3H), 2.01 m (3H), 2.05 m (3H), 2.08 s (3H), 2.54 m (2H), 3.63 q (1H), 3.92 m (1H), 3.99 t (1H, *J* = 10.2 Hz), 4.20 d.t (2H), 4.35 t (1H, *J* = 10.2 Hz), 4.40 d.d (1H, *J* = 1.8, 11.0 Hz), 4.47 d (1H, *J* = 9.6 Hz), 4.80 t (1H), 4.85 d.d (1H, *J* = 5.4, 9.6 Hz),

5.01 m (1H), 5.23 t (1H, *J* = 9.6 Hz), 5.34 t (1H, *J* = 11.0 Hz), 5.47 d (1H, *J* = 5.4 Hz).

Heptyl hepta-*O*-acetyl-β-maltoside was synthesized from maltose octaacetate (4.0 g, 5.89 mmol) and heptan-1-ol (2.5 mL, 2.05 g, 17.68 mmol) using 1.38 mL (3.07 g, 11.79 mmol) of tin(IV) chloride. Yield 959 mg (22%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.80 t (3H, *J* = 7.2 Hz), 1.15–1.31 m (8H), 1.47 m (2H), 1.93 s (6H), 1.94 s (3H), 1.95 s (3H), 1.97 s (3H), 2.03 s (3H), 2.07 s (3H), 3.40 q (1H, *J* = 16.2 Hz), 3.61 q.d (1H, *J* = 13.2 Hz), 3.77 q (1H, *J* = 16.2 Hz), 3.89 d (1H, *J* = 10.8 Hz), 3.93 t (1H, *J* = 9.6 Hz), 3.97 d (1H, *J* = 10.8 Hz), 4.17 d.t (2H, *J* = 4.8, 10.8 Hz), 4.39 d.d (1H, *J* = 2.4, 12.0 Hz), 4.45 d (1H, *J* = 8.4 Hz), 4.74 t (1H, *J* = 8.4 Hz), 4.78 d.d (1H, *J* = 4.2, 10.2 Hz), 4.98 t (1H, *J* = 9.9 Hz), 5.18 t (1H, *J* = 9.9 Hz), 5.29 t (1H, *J* = 9.9 Hz), 5.34 d (1H, *J* = 3.6 Hz).

Heptyl hepta-*O*-acetyl-1-thio-β-maltoside was synthesized from maltose octaacetate (1.0 g, 1.47 mmol) and heptan-1-thiol (0.7 mL, 583 mg, 4.41 mmol) using 0.34 mL (766 mg, 2.94 mmol) of tin(IV) chloride. Yield 423 mg (38%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, *J* = 6.9 Hz), 1.24–1.34 m (6H), 1.53–1.59 m (4H), 1.98 s (3H), 1.99 s (3H), 2.00 s (3H), 2.01 s (3H), 2.03 s (3H), 2.08 s (3H), 2.12 s (3H), 2.63 m (2H), 3.67 d (1H, *J* = 9.6 Hz), 3.93 d (1H, *J* = 9.6 Hz), 3.97 t (1H, *J* = 9.6 Hz), 4.02 d (1H, *J* = 11.4 Hz), 4.21 d.t (2H, *J* = 4.2, 12.6 Hz), 4.44 d.d (1H, *J* = 1.8, 12.6 Hz), 4.50 d (1H, *J* = 9.6 Hz), 4.83–4.85 m (2H), 5.03 t (1H, *J* = 9.9 Hz), 5.26 t (1H, *J* = 9.6 Hz), 5.34 t (1H, *J* = 9.9 Hz), 5.39 d (1H, *J* = 4.2 Hz).

General procedure for the synthesis of alkyl β-maltosides 1–13. Triethylamine (5.0 equiv) and distilled water were added at room temperature under a nitrogen atmosphere to a solution of alkyl hepta-*O*-acetyl-β-maltoside in methanol. The mixture was warmed to 50°C stirred for 18 h at that temperature (TLC, $CHCl_3$–MeOH, 1:2), and concentrated under reduced pressure. The residue was purified by column chromatography on Dowex (OH form) using methanol as eluent.

Dec-9-en-1-yl β-maltoside (1) was synthesized by reacting dec-2-en-1-yl hepta-*O*-acetyl-β-maltoside (335 mg, 0.43 mmol) with triethylamine (0.3 mL, 219 mg, 2.15 mmol) and distilled water (0.3 mL). Yield 185 mg (88%), white crystalline solid; $[\alpha]_D^{20}$ = +29.36° (*c* = 2.064, MeOH). IR spectrum, ν, cm^{-1}: 3420, 2089, 1636, 1558, 1540, 1507, 1473, 1456, 1026. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.21–1.36 m (12H), 2.00 q (2H, *J* = 13.8 Hz), 2.97m (1H), 3.05 m (1H), 3.20 m (2H), 3.28 t (2H, *J* = 9.9 Hz), 3.35–3.46 m (4H), 3.54 m (1H), 3.59 m (1H), 3.67 m (1H), 3.74 m (1H), 4.13 d (1H, *J* = 7.2 Hz), 4.46 t (1H, *J* = 5.7 Hz), 4.51 t (1H), 4.89–4.93 m (3H), 4.96–5.01 m (2H), 5.06 d (1H, *J* = 3.6 Hz), 5.45 s (1H), 5.48 s (1H), 5.78 m (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 25.48, 28.26, 28.47, 28.82, 28.85, 29.24, 33.15, 60.62, 60.77, 68.67, 69.90, 72.45, 72.98, 73.29, 73.42, 75.12, 76.44, 79.64, 100.77, 102.69, 114.63, 138.84. Mass spectrum (ESI): *m*/*z* 503.2413 [*M* + Na]$^+$. Calculated for $C_{22}H_{40}O_{11}Na$: 503.2468.

9-Chlorononyl β-maltoside (2) was synthesized by reacting 9-chlorononyl hepta-*O*-acetyl-β-maltoside (1.06 g, 1.33 mmol) with triethylamine (0.9 mL, 673 mg, 6.65 mmol) and distilled water (0.9 mL). Yield 531 mg (79%), white crystalline solid; $[\alpha]_D^{20}$ = +19.71° (*c* = 0.718, MeOH). IR spectrum, ν, cm^{-1}: 3409, 2929, 2856, 2360, 2067, 1641, 1378, 1148, 1073, 1026. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.22–1.32 m (10H), 1.36 m (2H), 1.69 m (2H), 2.97 m (1H), 3.05 m (1H), 3.20 m (2H), 3.35–3.46 m (6H), 3.54 m (1H), 3.58–3.62 m (3H), 3.67 m (1H), 3.75 m (1H), 4.13 d (1H, *J* = 6.6 Hz), 4.45 t (1H, *J* = 6.6 Hz), 4.50 t (1H), 4.89 t (2H, *J* = 4.8 Hz), 4.99 d (1H, *J* = 3.0 Hz), 5.06 d (1H, *J* = 4.8 Hz), 5.44 s (1H), 5.48 s (1H). ^{13}C NMR spectrum (D_2O), δ_C, ppm: 26.35, 27.47, 29.45, 29.95, 30.00, 30.07, 33.22, 46.03, 61.22, 61.48, 69.91, 71.17, 72.52, 73.52, 73.69, 73.71, 75.37, 77.00, 78.19, 100.84, 103.15. Mass spectrum (ESI): *m*/*z* 525.2108 [*M* + Na]$^+$. Calculated for $C_{21}H_{39}O_{11}ClNa$: 525.2079.

8-Methoxyoctyl β-maltoside (3) was synthesized by reacting 8-methoxyoctyl hepta-*O*-acetyl-β-maltoside (316 mg, 0.41 mmol) with triethylamine (0.3 mL, 205 mg, 2.03 mmol) and distilled water (0.3 mL). Yield 147 mg (75%), white crystalline solid; $[\alpha]_D^{20}$ = +22.59° (*c* = 0.509, MeOH). IR spectrum, ν, cm^{-1}: 3419, 2067, 1636, 1540, 1456, 1027. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.22–1.32 m (10H), 1.47 m (2H), 2.97 t (1H), 3.05 m (1H), 3.19 s (3H), 3.27 t (2H, *J* = 6.3 Hz), 3.35–3.45 m (8H), 3.55 m (1H), 3.59 m (1H), 3.68 m (1H), 3.74 m (1H), 4.13 d (1H, *J* = 7.2 Hz), 4.46 t (1H), 4.51 t (1H), 4.90 t (2H), 4.99 d (1H, *J* = 4.2 Hz), 5.06 d (1H, *J* = 4.2 Hz), 5.45 s (1H), 5.48 s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 25.45, 25.63, 28.83, 28.86, 29.01, 29.23, 57.78, 60.61, 60.79, 68.68, 69.91, 71.91, 72.45, 72.96, 73.30, 73.44, 75.12, 76.43, 79.65, 100.78, 102.69. Mass spectrum (ESI): *m*/*z* 507.2486 [*M* + Na]$^+$. Calculated for $C_{21}H_{40}O_{12}Na$: 507.2417.

Nonyl β-maltoside (4) was synthesized by reacting nonyl hepta-*O*-acetyl-β-maltoside (300 mg, 0.39 mmol) with triethylamine (0.27 mL, 2.0 mmol) and distilled water (0.27 mL). Yield 125 mg (68%), white crystalline solid; $[\alpha]_D^{20}$ = +18.75° (*c* = 0.201, MeOH). IR spectrum, ν, cm^{-1}: 3420, 2067, 1636, 1541, 1507, 1456, 1028. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.85 t (3H, *J* = 6.6 Hz), 1.21–1.35 m (10H), 2.97 t (1H), 3.04 m (1H), 3.20 m (2H), 3.28 t (2H), 3.37–3.46 m (4H), 3.54 m (1H), 3.60 m (1H), 3.68 m (1H), 3.74 m (1H), 4.13 d (1H, *J* = 7.2 Hz), 4.46 t (1H, *J* = 7.2 Hz), 4.51 t (1H), 4.89 t (2H, *J* = 4.8 Hz), 4.99 d (1H, *J* = 3.0 Hz), 5.06 d (1H), 5.45 s (1H), 5.48 s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.95, 22.08, 25.51, 28.66, 28.92, 28.99, 29.26, 31.29, 60.57, 60.81, 68.68, 69.91, 72.45, 73.00, 73.30, 73.44, 75.12, 76.45, 79.64, 100.78, 102.69. Mass spectrum (ESI): *m*/*z* 491.2485 $[M + Na]^+$. Calculated for $C_{21}H_{40}O_{11}Na$: 491.2468.

Undec-10-en-1-yl β-maltoside (5) was synthesized by reacting undec-10-en-1-yl hepta-*O*-acetyl-β-maltoside (215 mg, 0.27 mmol) with triethylamine (0.20 mL, 138 mg, 1.37 mmol) and distilled water (0.20 mL). Yield 103 mg (76%), white crystalline solid; $[\alpha]_D^{20}$ = +23.47° (*c* = 1.255, MeOH). IR spectrum, ν, cm^{-1}: 3375, 3019, 2926, 2855, 2399, 1640, 1426, 1214, 1073, 1027, 756. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.21–1.38 m (14H), 1.99 q (2H, *J* = 8.4 Hz), 2.98 m (1H), 3.05 m (1H), 3.20 m (2H), 3.28 t (2H), 3.35–3.40 m (3H), 3.45 t (2H), 3.55 m (1H), 3.59 m (1H), 3.67 m (1H), 3.73 m (1H), 4.13 d (1H, *J* = 7.2 Hz), 4.46 t (1H, *J* = 6.0 Hz), 4.50 t (1H, *J* = 6.0 Hz), 4.88–4.93 m (3H), 4.97–4.99 m (2H), 5.06 d (1H, *J* = 4.8 Hz), 5.44 s (1H), 5.48 s (1H), 5.78 m (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 25.49, 28.26, 28.50, 28.82, 28.88, 28.98, 29.24, 33.16, 60.59, 60.79, 68.67, 69.86, 72.45, 72.98, 73.28, 73.44, 75.12, 76.44, 79.66, 100.79, 102.69, 114.63, 138.83. Mass spectrum (ESI): *m*/*z* 517.2592 $[M + Na]^+$. Calculated for $C_{23}H_{42}O_{11}Na$: 517.2625.

Undecyl β-maltoside (6) was synthesized by reacting undecyl hepta-*O*-acetyl-β-maltoside (430 mg, 0.54 mmol) with triethylamine (0.37 mL, 273 mg, 2.7 mmol) and distilled water (0.37 mL). Yield 227 mg (84%), white crystalline solid; $[\alpha]_D^{20}$ = +20.13° (*c* = 0.755, MeOH). IR spectrum, ν, cm^{-1}: 3375, 2923, 2853, 2360, 1641, 1548, 1411, 1213, 1026, 748. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.84 t (3H, *J* = 6.6 Hz), 1.18–1.36 m (18H), 2.97 m (1H), 3.05 m (1H), 3.20 m (2H), 3.28 t (2H), 3.35–3.46 m (4H), 3.54 m (1H), 3.59 m (1H), 3.68 m (1H), 3.74 m (1H), 4.13 d (1H, *J* = 6.6 Hz), 4.46 t (1H, *J* = 6.6 Hz), 4.51 t (1H), 4.89 t (2H, *J* = 4.8 Hz), 4.99 d (1H, *J* = 4.2 Hz), 5.06 d (1H, *J* = 4.8 Hz), 5.45 s (1H), 5.48 s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.95, 22.08, 25.51, 28.70, 28.92, 29.01 (2C), 29.03, 29.26, 31.29, 60.62, 60.79, 68.68, 69.92, 72.40, 72.96, 73.30, 73.44, 75.13, 76.45, 79.65, 100.78, 102.70. Mass spectrum (ESI): *m*/*z* 519.2735 $[M + Na]^+$. Calculated for $C_{23}H_{44}O_{11}Na$: 519.2781.

Tetradecyl β-maltoside (7) was synthesized by reacting tetradecyl hepta-*O*-acetyl-β-maltoside (547 mg, 0.66 mmol) with triethylamine (0.46 mL, 3.3 mmol) and distilled water (0.46 mL). Yield 283 mg (80%), white crystalline solid; $[\alpha]_D^{20}$ = +26.44° (*c* = 0.191, MeOH). IR spectrum, ν, cm^{-1}: 3397, 2922, 2853, 2360, 1647, 1457, 1027, 794. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.84 t (3H, *J* = 6.6 Hz), 1.18–1.35 m (24H), 2.98 m (1H), 3.05 m (1H), 3.20 m (2H), 3.28 t (2H), 3.35–3.46 m (4H), 3.55 m (1H), 3.60 m (1H), 3.68 m (1H), 3.75 m (1H), 4.13 d (1H, *J* = 7.2 Hz), 4.46 t (1H, *J* = 7.2 Hz), 4.51 t (1H, *J* = 6.6 Hz), 4.89 t (2H, *J* = 6.6 Hz), 4.99 d (1H, *J* = 3.0 Hz), 5.06 d (1H, *J* = 5.4 Hz), 5.44 d (1H, *J* = 5.4 Hz), 5.47 d (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.96, 22.09, 25.53, 28.70, 28.93, 29.01, 29.03, 29.05 (4C), 29.27, 31.29, 60.63, 60.80, 68.72, 69.90, 72.45, 73.01, 73.32, 73.45, 75.15, 76.51, 79.70, 100.80, 102.70. Mass spectrum (ESI): *m*/*z* 561.3225 $[M + Na]^+$. Calculated for $C_{26}H_{50}O_{11}Na$: 561.3251.

8-Methylnonyl β-maltoside (8) was synthesized by reacting 8-methylnonyl hepta-*O*-acetyl-β-maltoside (319 mg, 0.41 mmol) with triethylamine (0.3 mL, 207 mg, 2.1 mmol) and distilled water (0.3 mL). Yield 153 mg (77%), white crystalline solid; $[\alpha]_D^{20}$ = +21.33° (*c* = 0.6, MeOH). IR spectrum, ν, cm^{-1}: 3375, 2924, 1653, 1541, 1458, 1031. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.84 d (6H, *J* = 7.2 Hz), 1.11–1.32 m (11H), 1.48 m (2H), 2.98 m (1H), 3.05 m (1H), 3.20–3.28 m (4H), 3.34–3.45 m (4H), 3.55 m (1H), 3.60 m (1H), 3.68 m (1H), 3.73 q (1H, *J* = 6.6 Hz), 4.13 d (1H, *J* = 8.4 Hz), 4.45 t (1H, *J* = 5.4 Hz), 4.49 t (1H), 4.87m (2H), 4.99 d (1H, *J* = 3.0 Hz), 5.04 d (1H), 5.43 s (1H), 5.47 s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 22.54 (2C), 25.53, 26.78, 27.41, 28.97, 29.27, 29.31, 38.50, 60.62, 60.79, 68.70, 69.92, 72.47, 73.02, 73.32, 73.46, 75.14, 76.47, 79.66, 100.80, 102.71. Mass spectrum (ESI): *m*/*z* 505.2595 $[M + Na]^+$. Calculated for $C_{22}H_{42}O_{11}Na$: 505.2625.

9-Methyldecyl β-maltoside (9) was synthesized by reacting 9-methyldecyl hepta-*O*-acetyl-β-maltoside (105 mg, 0.21 mmol) with triethylamine (0.15 mL,

107 mg, 1.06 mmol) and distilled water (0.15 mL). Yield 55 mg (83%), white crystalline solid; $[\alpha]_D^{20}$ = +17.47° (*c* = 0.518, MeOH). IR spectrum, ν, cm^{-1}: 3397, 2923, 1652, 1540, 1456, 1030. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.84 d (6H, *J* = 7.2 Hz), 1.13–1.36 m (13H), 1.47 m (2H), 2.97 m (1H), 3.04 m (1H), 3.20 m (2H), 3.28 t (2H), 3.36–3.44 m (4H), 3.55 m (1H), 3.59 m (1H), 3.68 m (1H), 3.74 m (1H), 4.13 d (1H, *J* = 7.8 Hz), 4.46 t (1H, *J* = 6.0 Hz), 4.49 t (1H), 4.88 m (2H), 4.99 d (1H, *J* = 3.6 Hz), 5.03 d (1H), 5.44 s (1H), 5.48 s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 22.53 (2C), 25.52, 26.79, 27.39, 28.92, 29.06, 29.26, 29.28, 38.49, 60.61, 60.81, 68.69, 69.93, 72.46, 73.01, 73.31, 73.45, 75.16, 76.47, 79.66, 100.78, 102.70. Mass spectrum (ESI): *m*/*z* 519.2735 $[M + Na]^+$. Calculated for $C_{23}H_{44}O_{11}Na$: 519.2781.

8-Cyclopropyloctyl maltoside (10) was synthesized by reacting 8-cyclopropyloctyl hepta-*O*-acetyl-β-maltoside (686 mg, 0.87 mmol) with triethylamine (0.6 mL, 440 mg, 4.35 mmol) and distilled water (0.6 mL). Yield 346 mg (81%), white crystalline solid; $[\alpha]_D^{20}$ = +23.71° (*c* = 0.464, MeOH). IR spectrum, ν, cm^{-1}: 3374, 2923, 2853, 1640, 1379, 1148, 1073, 1028. ^1H NMR spectrum (DMSO-d_6), δ, ppm: –0.038 q (2H), 0.35 q (2H), 1.24–1.35 m (12H), 1.61 m (2H), 1.94 m (1H), 2.97 m (1H), 3.05 m (1H), 3.20 m (2H), 3.28 t (2H, *J* = 9.3 Hz), 3.36–3.41 m (3H), 3.45 m (2H), 3.54 m (1H), 3.60 m (1H), 3.68 m (1H), 3.74 m (1H), 4.13 d (1H, *J* = 7.2 Hz), 4.46 t (1H, *J* = 5.4 Hz), 4.50 t (1H, *J* = 6.0 Hz), 4.89 t (2H, *J* = 6.0 Hz), 4.99 d (1H, *J* = 3.0 Hz), 5.05 d (1H, *J* = 5.4 Hz), 5.44 d (1H, *J* = 5.4 Hz), 5.47 d (1H, *J* = 3.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 4.28 (2C), 10.65, 25.46, 28.83, 28.88, 29.03, 29.13, 29.19, 34.01, 60.64, 60.77, 68.62, 69.86, 72.38, 72.96, 73.24, 73.40, 75.09, 76.40, 79.62, 100.75, 102.67. Mass spectrum (ESI): *m*/*z* 517.2590 $[M + Na]^+$. Calculated for $C_{23}H_{42}O_{11}Na$: 517.2625.

Dodecyl 1-thio-β-maltoside (11) was synthesized by reacting dodecyl hepta-*O*-acetyl-1-thio-β-maltoside (102 mg, 0.125 mmol) with triethylamine (0.1 mL, 63 mg, 0.625 mmol) and distilled water (0.1 mL). Yield 49 mg (74%), white crystalline solid; $[\alpha]_D^{20}$ = +60.39° (*c* = 0.255, MeOH). IR spectrum, ν, cm^{-1}: 3581, 2922, 1725, 1658, 1548, 1529, 1481, 1466, 1410, 1057. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.84 t (3H, *J* = 7.2 Hz), 1.18–1.32 m (18H), 1.48 m (2H), 2.60 m (2H), 3.02–3.07 m (2H), 3.22–3.29 m (4H), 3.49 m (2H), 3.53 m (1H), 3.60 m (1H), 3.66 m (1H), 3.76 m (1H), 4.26 d (1H, *J* = 9.6 Hz), 4.47 m (1H), 4.52 m (1H), 4.90 m (2H), 4.97 d (1H, *J* = 4.2 Hz), 5.00 d (1H, *J* = 4.2 Hz), 5.43 s (1H), 5.47 s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.96, 22.09, 28.37, 28.45, 28.63, 28.65, 28.70, 28.97, 29.02, 29.04, 29.30, 31.29, 60.78, 69.90, 71.05, 72.44, 72.64, 73.32, 73.76, 77.90, 79.53, 79.76, 85.01, 100.82. Mass spectrum (ESI): *m*/*z* 549.2698 $[M + Na]^+$. Calculated for $C_{24}H_{46}O_{10}NaS$: 549.2709.

Heptyl β-maltoside (12) was synthesized by reacting heptyl hepta-*O*-acetyl-β-maltoside (959 mg, 1.3 mmol) with triethylamine (0.9 mL, 6.5 mmol) and distilled water (0.9 mL). Yield 461 mg (80%), white crystalline solid; $[\alpha]_D^{20}$ = +28.05° (*c* = 0.164, MeOH). IR spectrum, ν, cm^{-1}: 3375, 2925, 2360, 1725, 1709, 1658, 1629, 1548, 1529, 1410, 1028. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.85 t (3H, *J* = 7.2 Hz), 1.18–1.35 m (10H), 2.98 m (1H), 3.05 m (1H), 3.18–3.29 m (4H), 3.38–3.45 m (4H), 3.55 m (1H), 3.59 m (1H), 3.67 m (1H), 3.74 q (1H, *J* = 6.0 Hz), 4.13 d (1H, *J* = 8.4 Hz), 4.46 t (1H, *J* = 5.4 Hz), 4.51 t (1H), 4.89 t (2H, *J* = 5.4 Hz), 4.99 d (1H, *J* = 3.0 Hz), 5.07 d (1H, *J* = 4.8 Hz), 5.45 s (1H), 5.48 d (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.95, 22.05, 25.46, 28.56, 29.25, 31.25, 60.59, 60.84, 68.67, 69.90, 72.41, 72.98, 73.28, 73.42, 75.17, 76.43, 79.67, 100.76, 102.69. Mass spectrum (ESI): *m*/*z* 463.2129 $[M + Na]^+$. Calculated for $C_{19}H_{36}O_{11}Na$: 463.2155.

Heptyl 1-thio-β-maltoside (13) was synthesized by reacting heptyl hepta-*O*-acetyl-1-thio-β-maltoside (423 mg, 0.563 mmol) with triethylamine (0.4 mL, 2.82 mmol) and distilled water (0.4 mL). Yield 216 mg (84%), white crystalline solid; $[\alpha]_D^{20}$ = +28.5° (*c* = 0.6, MeOH). IR spectrum, ν, cm^{-1}: 3366, 2924, 2360, 1725, 1658, 1457, 1027. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.85 t (3H, *J* = 7.2 Hz), 1.18–1.35 m (10H), 2.60 m (2H), 3.01–3.07 m (2H), 3.24 m (2H), 3.37–3.44 m (4H), 3.54 m (1H), 3.59 m (1H), 3.68 m (1H), 3.72 m (1H), 4.27 d (1H, *J* = 11.2 Hz), 4.46 t (1H, *J* = 5.4 Hz), 4.52 t (1H), 4.90 t (2H, *J* = 4.8 Hz), 5.00 d (1H, *J* = 4.8 Hz), 5.20 d (1H), 5.44 s (1H), 5.57 s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.96, 22.06, 28.29, 28.33, 28.88, 29.32, 31.20, 60.73, 60.85, 69.94, 72.50, 72.67, 73.33, 73.46, 77.88, 79.22, 79.51, 85.01, 100.76. Mass spectrum (ESI): *m*/*z* 479. $[M + Na]^+$. Calculated for $C_{19}H_{36}O_{10}NaS$: 479.1927.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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