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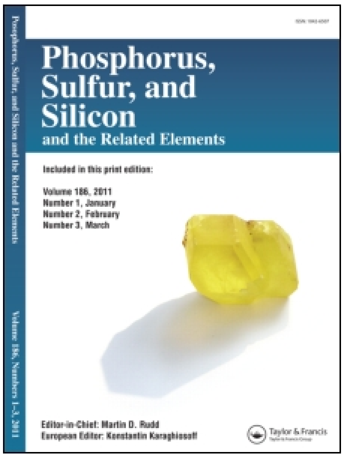

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Sucrose Analogs Containing Sulfur Functionalities

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Sucrose Analogs Containing Sulfur Functionalities

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Regioselective synthesis of sucrose monosulfides, with sulfur functionality placed either at the C-6 *(glucose part) or* C-6′ *(fructose) ends, is presented. The performed model dimerization of the mercaptane into the disulfide opens a convenient route to the open-chain sucrose dimers.*

Keywords Carbohydrates; sucrose disulfides; sucrose thiols

INTRODUCTION

Sucrose (β-D-fructofuranosyl α-D-glucopyranoside, **1**) is by far the most widely available low-weight carbohydrate. The overall production of this disaccharide in 2006 equals to 150 million tons; most of it is consumed on the food market. Nevertheless, a lot of work is performed to utilize this cheap raw material in other fields; the research on surfactants, emulsifiers, biodegrading polymers, or liquid crystals with the sucrose scaffold is intensively pursued.[1]

As a part of an ongoing program aimed at modification of sucrose with the preservation of the disaccharide skeleton, we have elaborated a convenient route to 2,3,3′,4,4′-penta-*O*-benzyl-sucrose (**2**), which allowed modification of this disaccharide at any of the terminal positions: *C*-1′, *C*-6, and *C*-6′ (Figure 1).[2]

Especially interesting, however, was another derivative, 1′,2,3,3′,4,4′-hexa-*O*-benzyl-sucrose (**3**),[3] which served as a useful precursor of macrocyclic receptors of type **4** with the sucrose scaffold. Different types of such macrocycles (X = O, N) were prepared (Figure 2).[4]

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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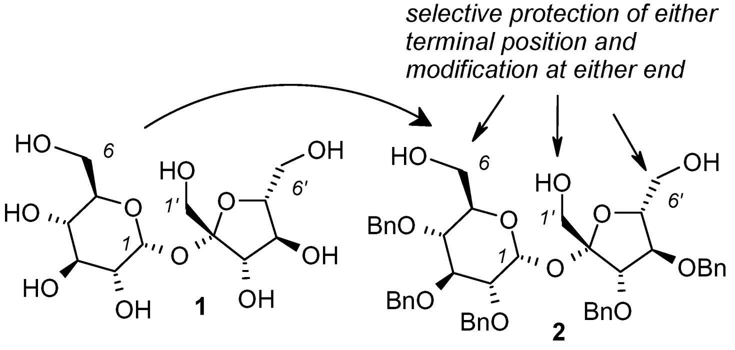


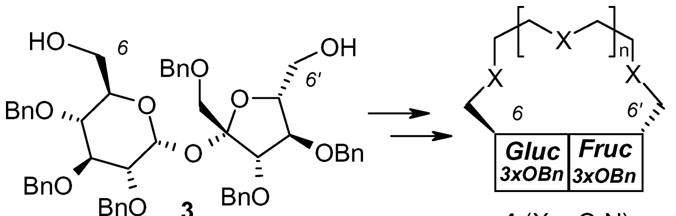
selective protection of either terminal position and modification at either end

FIGURE 1 Penta-O-benzylsucrose and its modifications at the terminal positions.

An interesting approach consists of the synthesis of sulfur derivatives of sucrose, which may serve as convenient precursors of macrocycles with higher symmetry built on the carbohydrate scaffold. Recently, dithiol **5** has been prepared from diol **3**[3]; we have found that this compound can be oxidized (I_2) to the disulfide **6**, which, after reduction ($LiAlH_4$), can be converted back into the initial dimercaptane **5**[3] (Figure 3).

RESULTS AND DISCUSSION

The process shown in Figure 3 allows us to obtain the "monomeric" sucrose macrocyles. (Formation of such disulfides from free sucrose was described in ref.[5]) In this article, we would like to propose another approach that may provide sucrose macrocycles with higher symmetry. This work is aimed, therefore, at the synthesis of the building blocks that should serve as starting materials in a macrocyclization process.



3

4 (X = O,N)

FIGURE 2 Hexa-O-benzylsucrose and its conversion into the macrocyclic receptors.

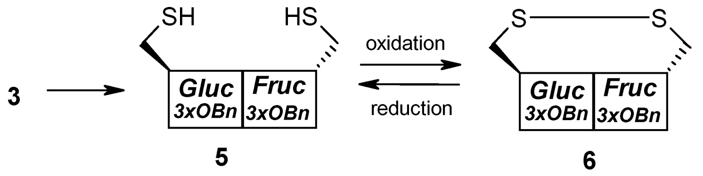
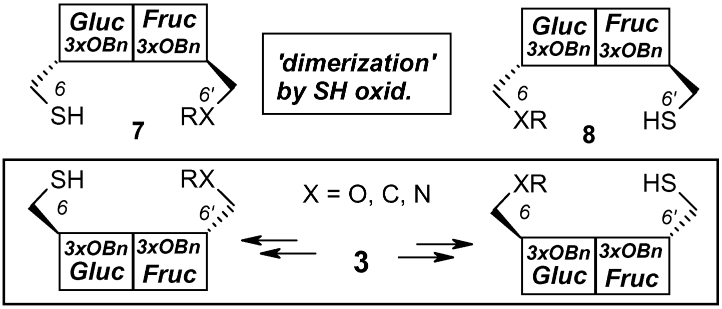


FIGURE 3 Synthesis of sucrose di-mercaptane and its cyclization.

The idea is outlined in Figure 4. Properly substituted sucrose monosulfides (e.g., **7** or **8**) can be oxidized to a disulfide in which the remaining primary positions are susceptible for the (eventual) coupling. After such coupling (which may be done on several routes), the C-2 symmetrical macrocyclic disulfides with the sucrose scaffold should be obtained. Another approach to the same macrocycles consists of coupling of the non-sulfated positions first, followed by oxidation of the dimercaptane.

Nevertheless, in both cases a convenient and simple route leading to sucrose mono-mercaptanes is required. In this communication, the synthesis of the monothiols of type **7** and **8** with the mercapto group placed at either terminal position (*C*-6 or *C*-6′) will be presented, as well as the approach of dimerization of these valuable synthons.

The first route started from 6′-O-(^{t}butyldiphenylsilyl)-hexa-*O*-benzylsucrose[6] **9**, which is readily available from the parent diol **3**. Standard transformations involving activation of the remaining primary 6-OH (at the glucose part) as mesylate **10**, followed by reaction with the SH$^-$ anion, provided the protected mercaptane **11** in good overall yield (Scheme 1). To prepare the alternative *C*-6′ mercaptane,

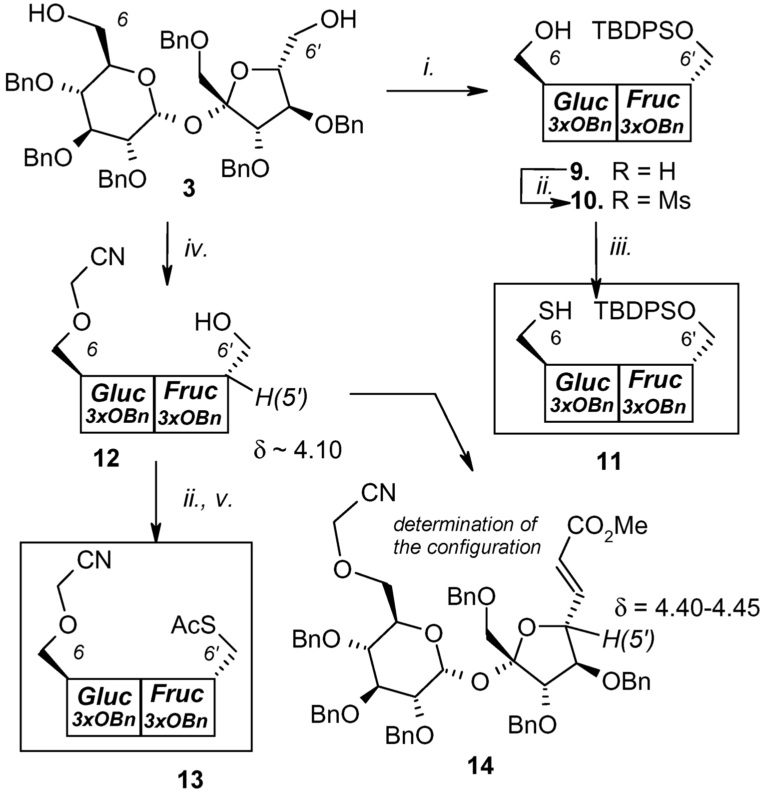


route to macrocycles: (a or b)

a 1. oxidation to disulfide; 2. coupling of the remaing positions

b 1. coupling of the (X-R) positions; 2. oxidation to disulfide

FIGURE 4 A route to sulfur macrocycles with the sucrose scaffold.

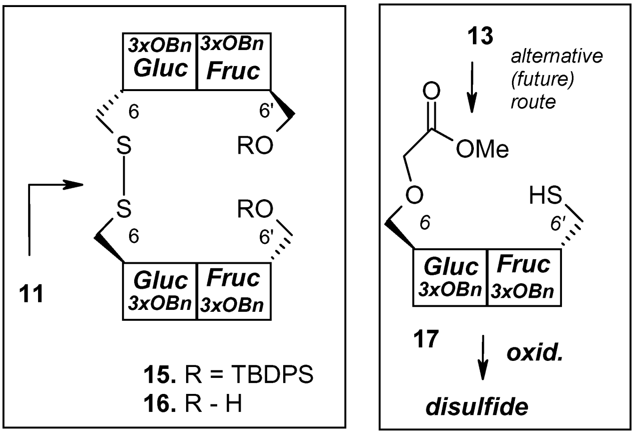


SCHEME 1 *i. ref.* 6; *ii.* MsCl, DMAP, CH_2Cl_2/NEt_3, 95%; *iii.* NaSHxnH_2O, DMF, 56%; *iv.* $ClCH_2CN$, toluene, 50% NaOH, 65%; *v.* AcSH, DBU, DMF, 60%

we took advantage of the different reactivity of both terminal hydroxyl groups in sucrose **3**. We have observed that the reactivity of the "glucose" hydroxyl group towards *C*-nucleophiles is much higher than the reactivity of the "fructose" (6′-OH) one. Reaction of the diol **3** with chloroacetonitrile under the PTC conditions[7] afforded the 6-*O*-protected derivative **12**. The position of the substitution was proven unambiguously by the chemical and spectral correlation. The Swern oxidation[8] of the free hydroxyl group in **12** followed by reaction with $Ph_3P{=}CHCO_2Me$ afforded the α,β-unsaturated ester **14**. The resonance of the H-5′ proton was shifted downfield by $\sim$ 0.3 ppm (from $\delta \sim 4.10$ ppm for **12** to $\delta = 4.40$–4.45 ppm for **14**), thus proving that unsaturation is located at the fructose part, hence the reaction of chloroacetonitrile occurred at the 6-OH (glucose) hydroxyl group.

Standard transformations of **12** (mesylation followed by reaction with thioacetate anion) provided derivative **13** in good yield (Scheme 1).

Application of the mono-thiols to the synthesis of dimeric sucrose derivatives is shown in Scheme 2. Oxidation of the mercaptane **11** with iodine led to the C_2-symmetrical disulfide **15** in good yield. Its structure was proven by the MS and NMR data (see the Experimental section). The silyl protecting groups were easily removed with the fluoride anion providing the diol **16** (Scheme 2).



SCHEME 2 *i*. benzene, 20% NaOH, I_2, 86%.

The alternative compound could be, eventually, prepared from the protected thiol **13** by its methanolysis (to **17**) followed by oxidation to disulfide with iodine. These results will be reported in due course.

CONCLUSION

The convenient approach to sucrose-based monothiols from the readily available hexa-*O*-benzylsucrose is reported. Oxidation of the monosulfide to the disulfide is conveniently achieved with iodine in basic media. The proposed route opens an interesting way to the macrocyclic receptors with the sucrose scaffold. This may be achieved by coupling of the remaining positions (such as, e.g., both C-6′ positions in compound **16**, which can be performed by a variety of methods). Further study is in progress.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini 200 MHz or a Bruker AM 500 MHz spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Mass spectra (ESI) were recorded with a Mariner PE Biosystem apparatus. Most of the resonances were identified by the ^{1}H-^{1}H and ^{1}H-^{13}C NMR correlations. The aromatic signals occurring at the typical δ values (in ^{13}C and ^{1}H NMR) were omitted for simplicity. Optical rotations were measured with JASCO Polarimeter P-1020 (sodium lamp $\lambda = 589$ nm) for solutions in chloroform at room temperature for $c = 1$. Column chromatography was performed on silica gel (Merck, 70–230 or 230–400 mesh). All solutions were dried over anhydrous magnesium or sodium sulfate. The solvents were evaporated under diminished pressure.

6-O-Mesyl-6′-O-tert-butyldiphenylsilyl-1′,2,3,3′,4,4′-hexa-O-benzylsucrose (10)

6′-*O*-*tert*-butyldiphenylsilyl-1′,2,3,3′,4,4′-hexa-*O*-benzylsucrose (**9**, 0.343 g, 0.31 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL), to which triethylamine (2 mL) and DMAP (20 mg) were added. Mesyl chloride (0.3 mL) was added slowly; the reaction mixture was stirred at room temperature for 0.5 h and diluted with CH_2Cl_2 (25 mL). Water (25 mL) was added, the organic phase was separated and washed with water (20 mL), and the aqueous one extracted with CH_2Cl_2 (25 mL). Combined organic phases were dried, concentrated, and the product was isolated by column chromatography (hexane:ethyl acetate, 4:1) to give the title compound **10** (0.354 g, 0.295 mmol, 95%) as a colorless oil. $[\alpha]_D = +32.7$, MS (ESI) $m/z = 1221.2$ $[(C_{71}H_{78}O_{13}SSi)+Na^+]$; IR ($\nu$cm^{-1}): 3031, 2930, 2859, 1454, 1361, 1177, 1090, 1027, 1004, 737, 698, 504. ^{1}H NMR (500 MHz): $\delta = 5.90$ (d, $J_{1,2} = 3.7$ Hz, 1H, H-1), 4.87 (d, $J = 10.9$ Hz, 1H), 4.86 (d, $J = 10.9$ Hz, 1H), 4.70–4.63 (m, 4H), 4.62 (d, $J = 1.6$ Hz, 1H), 4.58–4.37 (m, 7H), 4.08 (ddd, $J = 2.5$, $J = 2.5$, $J = 10.3$ Hz, 1H, H-5 or H-5′), 4.02–3.95 (m, 2H), 3.92–3.81 (m, 4H), 3.69 (d, $J = 10.9$ Hz, 1H), 3.55 (d, $J = 10.9$ Hz, 1H), 3.47 (dd, $J = 8.9$, $J = 10.2$ Hz, 1H), 3.42 (dd, $J_{2,3} = 9.6$ Hz, 1H, H-2), 2.68 (s, 3H, OSO_2CH_3), 1.05 (s, 9H, C*Me*$_3$); ^{13}C NMR (125 MHz): $\delta = 137.9$, 137.8 (C$_{\text{quart}}$ benzyl), 135.7, 135.5 (phenyl-C from TBDPS), 133.2, 132.9 (C$_{\text{quart}}$ phenyl from TBDPS), 129.81, 129.77 (phenyl-C from TBDPS), 104.3 (C-2′), 88.8 (C-1), 84.0, 81.9, 81.0, 80.6, 79.9, 76.8 and 68.9 (C-2,3,3′,4,4, ′5,5′), 75.5, 74.8, 73.5, 72.7, 72.14, 72.06 and 68.3, 63.8 (*C*H$_2$Ph, C-1′,6,6′), 37.0 (OSO_2*C*H$_3$), 26.9 (C*Me*$_3$), 19.3 (*C*Me$_3$).

6-Deoxy-6-thio-6′-O-tert-butyldiphenylsilyl-1′,2,3,3′,4,4′-hexa-O-benzylsucrose (11)

The mesylate **10** was dissolved in DMF (20 mL) to which NaSH × n H_2O (0.3 g) was added; the mixture was stirred at room temperature overnight and then partitioned between water (40 mL) and ether (40 mL). The water phase was extracted with ether (50 mL) and discarded. Combined organic phases were dried, concentrated, and the expected product was isolated from the more polar impurities by column chromatography (hexane:ethyl acetate, 12:1 to 6:1) as a colorless oil (0.214 g, 0.188 mmol, 56%). $[\alpha]_D = +37.1$; MS (ESI) $m/z = 1159.3$ $[(C_{70}H_{76}O_{10}SSi){+}Na^+]$; IR ($\nu$cm^{-1}): 3030, 2931, 2862, 1455, 1087, 1026, 737, 698, 504. ^{1}H NMR (500 MHz): $\delta = 5.85$ (d, $J_{1,2} = 3.6$ Hz, 1H, H-1), 4.87 (d, $J_{A,B} = 11.2$ 1H, Hz), 4.85 (d, $J_{A,B} = 10.7$ Hz, 1H), 4.69–4.43 (m, 12H), 4.38 (dd, $J = 7.6$, $J = 7.7$ Hz, 1H), 4.05 (ddd, $J = 3.6$, $J = 3.6$, $J = 9.8$ Hz, 1H, H-5 or H-5′), 4.02–3.95 (m, 2H), 3.90 (dd, $J = 9.6$, $J = 9.6$ Hz, 1H) 3.88–3.83 (m, 1H), 3.69 (d, $J_{A,B} = 11.0$ Hz, 1H, H-1′A), 3.61 (dd, $J = 9.4$, $J = 9.4$ Hz, 1H), 3.56 (d, 1H, H-1′B), 3.42 (dd, $J_{2,3} = 9.6$ Hz, 1H, H-2), 2.61–2.55 (m, 1H, H6A), 2.36–2.29 (m, 1H, H6B), 1.06 (s, 9H, C*Me*$_3$); ^{13}C NMR (125 MHz): $\delta = 138.9$, 138.7, 138.4, 138.2, 138.1, 138.0 (C_{quart} benzyl), 135.7, 135.5 (phenyl-C from TBDPS), 133.2, 133.0 (C_{quart} phenyl from TBDPS), 129.74, 129.69 (phenyl-C from TBDPS), 104.3 (C-2′), 89.0 (C-1), 83.9, 81.8, 81.2, 80.8, 80.3, 78.4, and 70.0 (C-2,3,3′,4,4,′,5,5′), 75.5, 74.7, 73.5, 73.2, 72.6, 72.2, 72.0 and 64.2 (CH_2Ph, C-1′,6′), 26.9 (C*Me*$_3$), 26.1 (C-6), 19.3 (*C*Me$_3$). Anal. Calcd for $C_{70}H_{76}O_{10}SSi$: C, 73.91, H, 6.73; S, 2.82. Found: C, 73.8; H, 6.7; S, 2.7%.

6-O-(Cyanomethyl)-1′,2,3,3′,4,4′-hexa-O-benzylsucrose (12)

1′,2,3,3′,4,4′-Hexa-*O*-benzylsucrose **3** (340 mg, 0.38 mmol) was dissolved in toluene (5 mL), to which 50% aqueous NaOH (5 mL) and tetrabutylammonium bromide (5 mg) were added. A solution of chloroacetonitrile (0.05 mL) in toluene (10 mL) was then added dropwise during 30 min, and the mixture was stirred vigorously for additional 2 h. Water (15 mL) was added, the layers were separated, and the aqueous one extracted with ethyl acetate (2 × 15 mL). Combined organic layers were washed with water (15 mL) and brine (15 mL), and dried. The solution was filtered and concentrated, and the product was isolated by column chromatography (hexane:ethyl acetate, 3:1) as a yellowish oil (230 mg, 0.25 mmol, 66%). HR MS (ESI) *m/z*: 944.3990; [calcd. for ($C_{56}H_{59}NO_{11}Na$ (M + Na^+): 944.3980]; ^{1}H NMR (500 MHz): $\delta = 5.51$ (d, $J_{1,2} = 3.4$ Hz, 1H, H-1). ^{13}C NMR (125 MHz): $\delta = 138.6$, 138.19, 138.15, 138.07, 138.0, 137.8 (C_{quart} benzyl), 115.8 (*C*N), 103.9 (C-2′), 90.9

(C-1); 83.7, 81.7, 81.2, 79.4, 79.3, 76.8, 70.8 (C-2,3,3′,4,4′,5,5′), 75.6, 75.1, 73.44, 73.37, 72.8, 72.6, 71.4, 69.7, 69.6 (O*C*H$_2$Ph, C-6,1′,6′).

Determination of the Structure of 12; Synthesis of Olefin 14

To a cooled to −70°C solution of oxalyl chloride (0.04 mL) in dry dichloromethane (10 mL), a solution of DMSO (0.13 mL) in CH_2Cl_2 (0.5 mL) was added dropwise, followed by a solution of **12** (120 mg, 0.13 mmol) in dry CH_2Cl_2 (2 mL). The mixture was stirred at −70°C for 30 min, and then triethylamine (0.13 mL) was added. Stirring was continued for 1 h at −70°C, and the solution was allowed to warm to room temperature. Water (10 mL) was added, and the organic phase was separated, dried, and filtered. Phosphonium ylide ($Ph_3P{=}CHCO_2Me$, 126 mg, 0.35 mmol) was added, and the mixture was stirred at room temperature until completion (30 min; TLC monitoring in hexane:ethyl acetate, 3:1). Water (10 mL) was added; the layers were separated; the organic one was washed with water (10 mL) and brine (10 mL), dried, filtered, and concentrated; and the product was purified by column chromatography (hexane:ethyl acetate, 5:1) to afford compound **14** as colorless oil (85 mg, 0.087 mmol, 67% over 2 steps). ^{1}H NMR (500 MHz): $\delta = 7.03$ (dd, $J = 15.7$, $J = 6.7$ Hz, 1H, H_β), 6.07 (dd, $J = 1.1$ Hz, 1H, H_α), 5.48 (d, $J = 3.5$ Hz, 1H, H-1), 4.51–4.92 (m, 10H, OC*H*$_2$Ph), 4.40–4.45 (m, 2H, H-5′+ H-3′), 4.35–4.38 (m, 2H, OC*H*$_2$Ph), 4.08–4.14 (m, 3H, H-4′ + OC*H*$_2$CN), 4.02 (m, 2H, H-6), 3.96 (m, 1H, H-3), 3.73 (s, 3H, CO_2CH_3), 3.60–3.65 (m, 3H, H-1′ + H-5), 3.48–3.52 (m, 2H, H-2 + H-4). ^{13}C NMR (125MHz): $\delta = 166.4$ (*C*O$_2$CH$_3$), 145.5 (C_β), 138.7, 138.2, 138.1, 137.9, 137.70, 137.68 (C_{quart} benzyl groups), 122.4 (C_α), 116.0 (CN), 104.7 (C2′), 90.2 (C-1), 84.3 (C-4′), 83.2 (C-3′), 81.9 (C-3), 79.5 (C-2), 79.1 (C-5′), 77.2 (C-4), 70.9 (C-5), 75.6, 75.0, 73.41, 72.98, 72.96, 72.94 (O*C*H$_2$Ph), 70.5 (C-6), 69.8 (C-1′), 56.7 (O*C*H$_2$CN), 51.5 (CO$_2$*C*H$_3$).

6-O-(Cyanomethyl)-6′-deoxy-6′-thioacetyl-1′,2,3,3′,4,4′-hexa-O-benzylsucrose (13): Synthesis of the Thioacetic Salts

DBU salt: DBU (0.03 mL, 0.2 mmol) was dissolved in DMF (5 mL). Thioacetic acid (0.014 mL, 0.2 mmol) was added, and the mixture was stirred for 3 min and used in the S_N2 reaction.

Cesium salt: Cs_2CO_3 (65 mg, 0.2 mmol) was dissolved in methanol (10 mL). Thioacetic acid (0.028 mL, 0.4 mmol) was added to the mixture, and it was stirred for 3 min and then concentrated. The obtained yelow solid was dissolved in DMF (5 mL) and used in the S_N2 reaction.

Sucrose derivative **12** (210 mg, 0.22 mmol) was dissolved in dichloromethane (10 mL) containing Et_3N (2 mL) and DMAP (10 mg).

Mesyl chloride (0.2 mL) was added dropwise, and the mixture was stirred at room temperature for 4 h and partitioned between water (15 mL) and dichloromethane (10 mL). The layers were separated, and the aqueous one extracted with diethyl ether (2 × 10 mL). The combined organic layers were dried, filtered, and concentrated, and the product was isolated by column chromatography (hexane:ethyl acetate, 3:1) to give the corresponding mesylate as a yellowish oil (210 mg, 0.21 mmol, 95%). MS (ESI) *m/z*: 1022.2 [M($C_{57}H_{61}NO_{13}S$) + Na^+]; ^{1}H NMR (500 MHz): $\delta = 5.53$ (d, $J = 3.6$ Hz, 1H, H-1), 2.92 (s, 3H, mesyl group). ^{13}C NMR (125MHz): $\delta = 138.6$, 138.06, 138.03, 137.91, 137.62, 137.61 (C_{quart} benzyl), 115.9 (*C*N), 104.9 (C-2′), 90.4 (C-1), 83.5, 81.8, 81.5, 79.6, 78.0, 77.2, 70.5 (C2,3,3′,4,4′,5,5′), 75.6, 75.0, 73.4, 73.0, 72.9, 72.6, 70.7, 70.1, 69.8 (O*C*H_2Ph, C-6, C-1′, C-6′), 56.6 (O*C*H_2CN), 37.3 (OSO_2CH_3).

This mesylate (50 mg, 0.05 mmol) was dissolved in DMF (5 mL), to which a solution of DBU thioacetate (prepared according to procedure described above) was added, and the mixture was stirred at 80°C for 2 days. Then the mixture was cooled to room temperature, and partitioned between water (20 mL) and diethyl ether (20 mL). The layers were separated and the aqueous one extracted with diethyl ether (3 × 15 mL). The combined organic extracts were washed with water (15 mL) and brine (15 mL), dried over magnesium sulfate, filtered, and concentrated. The product was isolated by column chromatography (hexane:ethyl acetate, 4:1) to afford **13** as a yellow oil (30 mg, 0.031 mmole, 67%). Similar results were obtained with cesium thioacetate. MS (ESI) *m/z*: 980.6 [M($C_{58}H_{61}NO_{11}S$) + H^+]; ^{1}H NMR (500 MHz): 5.59 (d, $J = 3.6$ Hz, 1H, H-1), 1.99 (s, 3H, SAc). ^{13}C NMR (125 MHz): $\delta = 170.7$ (S*C*(O)CH_3); 138.8, 138.2, 138.1, 138.0, 137.9, 137.7 (C_{quart} benzyl), 115.9 (*C*N), 104.7 (C-2′), 90.0 (C-1), 83.7, 81.9, 81.8, 79.6, 78.2, 78.0, 70.3 (C-2,3,3′,4,4′,5,5′), 75.5, 75.0, 73.5, 73.0, 72.64, 72.55, 71.1, 70.0, 65.1 (O*C*H_2Ph, C-6, C-1′, C-6′), 56.6 (O*C*H_2CN), 20.8 (SC(O)*C*H_3).

Bis-(6-deoxy-6′-O-tert-butyldiphenylsilyl-1′,2,3,3′,4,4′-hexa-O-benzylsucros-6′-yl)-disulfide (15)

Monosulfide **11** (0.191 g, 0.168 mmol) was dissolved in benzene (10 mL), to which a solution of NaOH (0.152 g, 0.304 mmol) in water (0.5 mL) was added, followed by iodine (72 mg, 0.57 mmol). The mixture was stirred for 3.5 h at room temperature, and then 20% aqueous solution of NaOH was added until the color disappeared. Water (40 mL) and ethyl acetate (40 mL) were added, and the organic phase was separated, washed with 20% aqueous solution of NaOH (40 mL), dried, and concentrated. The product was isolated by column chromatography (hexane:ethyl acetate, 8:1 to 6:1) to afford **15** (0.165 g, 0.0727 mmol, 86%) as a colorless oil. $[\alpha]_D = +35.9$; MS (ESI) $m/z = 2295.9$ $[(C_{140}H_{150}O_{20}S_2Si_2)+Na^+]$. ^{1}H NMR (500 MHz): $\delta = 5.79$ (d, $J_{1,2} = 3.5$ Hz, 1H, H-1), 4.79 (d, $J = 11.3$ Hz, 1H), 4.77 (d, $J = 11.0$ Hz, 1H), 4.66–4.32 (m, 12 H), 4.13–4.08 (m, 1H), 4.04–3.87 (m, 3H), 3.82 (dd, $J = 9.2$, $J = 9.2$ Hz, 1H), 3.79 (d, $J = 11.1$ Hz, 1H, H-1′A), 3.54 (d, 1H, H-1′B), 3.41–3.33 [m, 2H, H and 3.35 (dd, $J_{2,3} = 9.7$ Hz, 1H, H-2)], 3.05 (dd, $J_{5,6A} = 3.1$, $J_{6A,6B} = 13.2$ Hz, 1H, H-6A), 2.77 (dd, $J_{5,6B} = 5.9$ Hz, 1H, H-6B), 1.28 (s, 9H, C*Me*$_3$); ^{13}C NMR (125 MHz): $\delta = 138.9$, 138.54, 138.45, 138.35, 138.2, 138.0 (C$_{\text{quart}}$ benzyl), 135.6, 135.5 (phenyl-C from TBDPS), 133.5, 133.2 (C$_{\text{quart}}$ phenyl from TBDPS), 129.7, 129.6 (phenyl-C from TBDPS), 104.7 (C-2′), 89.8 (C-1), 84.2, 82.8, 81.6, 81.5, 80.2, 79.8, and 69.7 (C-2,3,3′,4,4,′,5,5′), 75.5, 74.7, 73.4, 73.1, 72.6, 72.0, 71.0 and 65.2 (CH$_2$Ph, C-1′,6′), 42.8 (C-6), 27.0 (C*Me*$_3$), 19.3 (*C*Me$_3$). Anal. Calcd for $C_{140}H_{150}O_{20}S_2Si_2$: C, 73.98, H, 6.65; S, 2.82. Found: C, 74.0; H, 6.5; S, 2.7%.

Bis-(6-deoxy-1′,2,3,3′,4,4′-hexa-O-benzylsucros-6′-yl)-disulfide (16)

Protected disulfide **15** (0.144 g, 0.0635 mmol) was dissolved in THF (10 mL), to which Bu$_4$NF × 3 H$_2$O (0.104 g, 0.33 mmol) was added. The mixture was boiled under reflux for 2.5 h, and after cooling to room temperature, was filtered through a short column with silica (hexane:ethyl acetate, 3:2 as eluent). Evaporation of the solvent left crude product **16** in almost quantitative yield (0.122 g; this product according to NMR was contaminated with small amounts of impurities). MS (ESI) m/z = 1818.6 $[(C_{108}H_{114}O_{20}S_2)+Na^+]$, IR ($\nu$cm^{-1}): 3475, 3031, 2916, 2868, 1454, 1362, 1088, 1070, 1026, 995, 737, 698. ^{1}H NMR (500 MHz): $\delta =$ 5.59 (d, $J_{1,2} = 3.5$ Hz, 1H, H-1), 4.88 (d, $J_{A,B} = 11.0$ Hz 1H), 4.84 (d, $J_{A,B} = 10.9$ Hz, 1H), 4.83 (d, $J_{A,B} = 11.0$ Hz, 1H), 4.68 (d, $J_{A,B} = 10.9$ Hz, 1H), 4.64–4.44 (m, 9 H), 4.39 (dd, $J = 8.0$, $J = 8.0$ Hz, 1H), 4.29 (d, $J_{A,B} = 12.0$ Hz, 1H), 4.22 (ddd, $J = 3.5$, $J = 3.5$, $J = 9.8$ Hz, 1H, H-5 or H-5 eluent:), 3.99–3.93 (m, 2H), 3.82 (dd, $J = 2.3$, $J = 12.7$ Hz, 1H), 3.67–3.60 (m, 1H), 3.59 (d, $J_{A,B} = 11.0$ Hz, 1H, H-1′A), 3.47 (d, 1H, H-1′B), 3.45 (dd, $J_{2,3} = 9.8$ Hz, 1H, H-2), 3.28 (dd, $J_{5,6A} = 3.5$, $J_{6A,6B} =$ 13.3 Hz, 1H, H-6A), 3.00 (dd, $J_{5,6B} = 3.6$ Hz, 1H, H-6B), ^{13}C NMR (125 MHz,): $\delta = 138.7$, 138.3, 138.24, 138.21, 138.1, 137.9 (C$_{\text{quart}}$ benzyl), 103.9 (C-2 eluent:), 90.5 (C-1), 83.6, 81.6, 81.1, 79.8, 79.7, 78.7, and 70.2 (C-2,3,3′,4,4,′,5,5′), 75.4, 75.0, 73.3, 73.1, 73.0, 72.7, 71.4 and 61.4 (CH$_2$Ph, C-1′,6′), 43.2 (C-6).

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