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A Route to Oligosaccharide-Appended Salicylaldehydes: Useful Building Blocks for the Synthesis of Metal−Salophen Complexes

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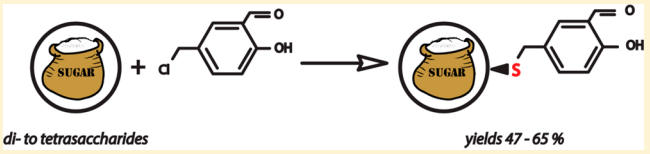
Supporting Information

ABSTRACT: A simple and general synthetic protocol to obtain oligosaccharide-appended salicylaldehydes, key intermediates for the synthesis of water-soluble metal−salophen complexes, is here reported. Six new aldehydes have been prepared and fully characterized as well as the corresponding zinc− and uranyl−salophen complexes. These new derivatives show very good solubility in water. Preliminary studies on the association of compound **19-U**, that is, the uranyl maltotetraose derivative, with hydrogen phosphate and fluoride provide very encouraging results and open up the possibility of using such compounds for the efficient recognition of anions in pure water.



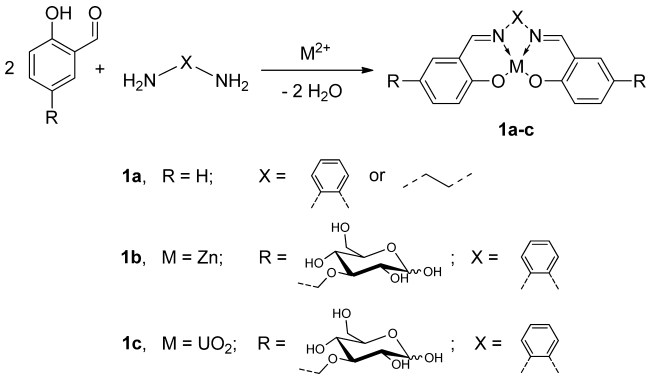
INTRODUCTION

Lately, the development of synthetic receptors that work in water has emerged as a central topic and a tricky challenge in supramolecular chemistry,[1] mostly nurtured by the potential practical applications.[2−4] The analytical detection of chemical species present at low concentrations in aqueous media represents a problem not only in environmental monitoring[5−7] but also in medical diagnostics.[8−13] The task is intrinsically difficult; however, recent acquisitions do suggest that solutions can be found through a supramolecular approach, which takes inspiration from the natural world.[14−17] Enzymes and antibodies achieve extremely high selectivity and affinity toward their substrates through the simultaneous establishment of multiple weak interactions, and many biochemical transformations, which take place in water, rely on these features.[18] In this context, the development of synthetic receptors or, in general, of building blocks that can selectively interact in water with a given substrate to yield highly responsive functional materials is a topic of increasing importance.

A common strategy is to suitably functionalize the backbone of artificial receptors whose binding properties toward selected substrates have been already successfully studied in lipophilic media, to allow their solubilization in water.[19]

In recent years, we have extensively reported that metal−sal(oph)en [salophen = *N*,*N*′-phenylenebis(salicylideneimine); salen = *N*,*N*′-ethylenebis(salicylideneimine)] type complexes, **1a**, behave as highly efficient receptors for anions and neutral species through Lewis acid−base interactions in organic solvents.[20] A great advantage of this class of compounds is that they are easily accessible through the reaction of the corresponding tetradentate Schiff base derived from the condensation of the diamine with 2 equiv of salicylaldehyde, and the corresponding metal salt (Chart 1). The large number of

Chart 1



synthetic routes to substituted salicylaldehydes and diamines gives access to a large variety of structures with subtle variations in the steric and electronic configuration. Thus, we decided to follow this route, introducing, as a first attempt, glucose moieties on the salicylaldehyde ring. The corresponding zinc and uranyl complexes, **1b** and **1c**, although poorly soluble, preserve their Lewis acidity even in water and behave as selective and efficient supramolecular receptors toward anions, such as fluoride, dihydrogen phosphate, nucleotides,[21] and aminoacids, providing also secondary stabilizing interactions ascribable to the presence of the appended sugar.[22]

To improve the water solubility of these derivatives and to obtain a library of potential artificial receptors able to work in aqueous media, we developed a simple and general protocol to

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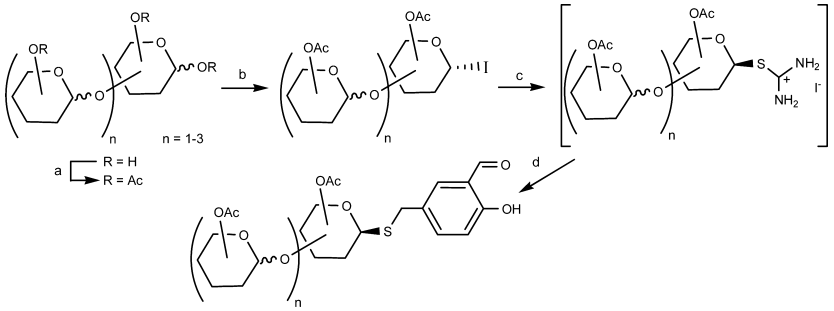
Scheme 1. (a) NaOAc, Ac_2O, 120 °C, 90 min; (b) I_2, Et_3SiH, CH_2Cl_2, reflux, 30 min; (c) thiourea, CH_3CN, 60 °C, 60 min; (d) 5-chloromethyl-salicylaldehyde, Et_3N, rt, 60 min



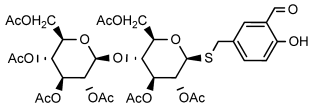
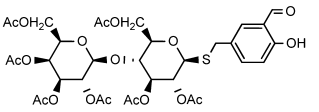
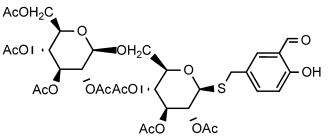
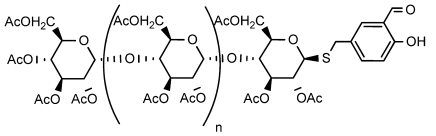
obtain a series of salicylaldehydes functionalized with a variety of oligosaccharides (up to a tetrasaccharide) via a stereospecific *S*-glycosidic junction, that is, applying the method previously described by Iadonisi and co-workers for the synthesis of thioglycosides from glycosyl acetates and alkyl halides.[23] As far as we know, this is the first time that this procedure is used on oligosaccharides higher than a disaccharide. The obtained aldehydes **8**−**13** were then reacted with *o*-phenylenediamine in the presence of zinc acetate and uranyl-acetate, respectively, to obtain the corresponding metal−salophen complexes **14**−**19** (Scheme 2). The complete NMR characterization of the aldehydes as well as that of the complexes is also reported.

RESULTS AND DISCUSSION

Synthesis. The obtainment of some carbohydrate-functionalized metal−salophen complexes has been recently reported using two different approaches. The first was proposed by MacLachlan and co-workers. It relies upon a Ag_2O-mediated glycosylation of 4,5-dinitrocatechol with per-*O*-acetyl-glucosyl or galactosyl bromide, followed by deacetylation, reduction of the nitro groups, and then complex formation by reacting the glycosyl phenylenediamines with salicylaldehyde in the presence of various metal ions.[24] To avoid the involvement of air- and light-sensitive intermediates, like the products obtained from the reduction step, we recently proposed a base-promoted conjugation of 5-chloromethyl-salicylaldehyde with a suitably protected glucose derivative, followed by global deprotection of the sugar-appended aldehyde and metal−template complex formation in the presence of *o*-phenylenediamine.[22] However, to the best of our knowledge, the synthesis of complexes that bear oligosaccharide moieties has not been reported to date. To achieve this goal, a general method for oligosaccharide−salicylaldehyde conjugation is necessary.

Alkyl and aryl-thioglycosides are very often prepared in synthetic carbohydrate chemistry as useful glycosyl donors for oligosaccharide and glycoconjugate synthesis.[25] Several protocols have been described for alkyl thioglycoside formation from per-*O*-acetyl sugars.[26] Among them, we focused our attention on a rather fast and efficient procedure recently developed by Iadonisi and co-workers, which generates the thioglycoside from an alkyl halide and an *S*-glycosyl isothiouronium intermediate obtained from the per-*O*-acetyl sugar through glycosyl iodide.[23] It is worth noting that this thioglycosylation procedure avoids the use of malodorous thiolic agents as well as harsh reagents, which could not be tolerated by the *O*-glycosidic bonds of the sugars. Thus, commercially available oligosaccharides (cellobiose, lactose, gentiobiose, maltose, maltotriose, and maltotetraose) were first per-*O*-acetylated under standard conditions, then treated with iodine and triethylsilane in CH_2Cl_2 under reflux to give glycosyl iodides, after a simple extractive workup. Subsequent reaction with thiourea in acetonitrile afforded *S*-glycosyl isothiouronium salts, which were *S*-alkylated (one-pot) with 5-chloromethyl-salicylaldehyde in the presence of triethylamine (Scheme 1).[27] Thioglycosides **2**−**7** were obtained with a high 1,2-*trans* stereoselectivity as pure β-anomers after silica-gel chromatography in acceptable yields (47−65% over four steps, Table 1), demonstrating that both α and β as well as 1→4 and

Table 1. Conversion of per-*O*-Acetyl Di-, Tri-, and Tetrasaccharides into the Corresponding Salicylaldehyde Thioglycoside Derivatives

entry	per-*O*-acetyl oligosaccharide	thioglycoside (% yield)
1	cellobiose	 **2** (64%)
2	lactose	 **3** (65%)
3	gentiobiose	 **4** (53%)
4	maltose (n=0)	 **5** (47%)
5	maltotriose (n=1)	**6** (56%)
6	maltotetraose (n=2)	**7** (47%)

1→6 glycosidic linkages were stable under reaction conditions. Noteworthy, although the thioglycosylation procedure developed by Iadonisi et al. has been already employed by other groups as well as by us,[28] we report now for the first time its use on oligosaccharides with more than two units.

Thioglycosides **2**−**7** were then de-*O*-acetylated by reaction with triethylamine in MeOH−CH_2Cl_2, affording water-soluble

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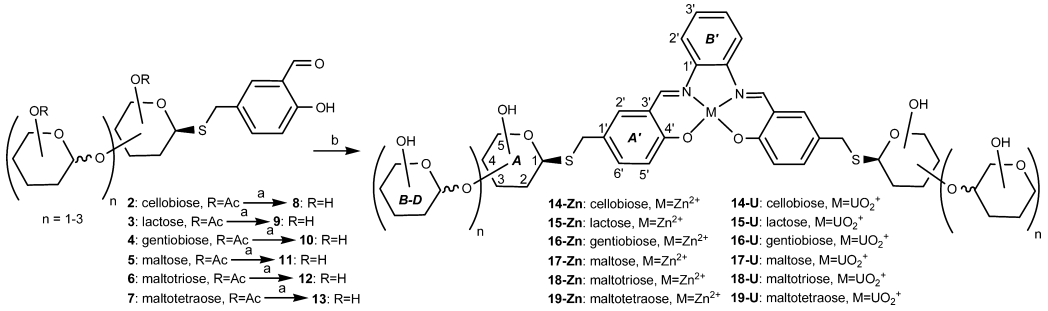
Scheme 2. (a) Et_3N, CH_2Cl_2, MeOH, rt, 5 h, 97−99% yield; (b) $Zn(CH_3COO)_2$ or $UO_2(CH_3COO)_2{\cdot}2H_2O$, *o*-phenylenediamine, MeOH, rt, 16 h, 60−70% yield



glycoconjugates **8**−**13** in quantitative yields (Scheme 2). The subsequent metal−template complex formation by condensation with *o*-phenylenediamine in the presence of the corresponding metal acetate afforded compounds **14**−**19** as yellow to orange precipitates, depending on the coordinated cation.

Characterization of Compounds. The solubility in water of the new metal derivatives, **14**−**19**, resulted to be satisfactory. The Zn^{2+} and UO^{2+} salophen complexes bearing disaccharide subunits are indeed soluble in water up to the 10^{-4} M concentration range, which is almost one order of magnitude higher than that of the glucose-functionalized compounds.[21,22] Even better is the solubility shown by complexes bearing tri- and tetrasaccharide moieties, which we estimated to be greater than a millimolar concentration.

Nevertheless, a detailed spectroscopic characterization of the synthesized complexes in water was prevented by the fact that their ^1H NMR spectra in D_2O feature very broad signals. Temperature dependence of spectra resolution was observed, consisting in a general sharpening of the signals on increasing the temperature. Unfortunately, the hydrolysis of the imine bonds, clearly detected by the appearance of new signals in the aldehydic region of the spectrum, becomes already significant below 323 K. We think that the low resolution at room temperature can be likely attributed to the occurrence of dynamic exchange phenomena on the NMR time scale comprising intermolecular hydrogen bonding interactions between the carbohydrate subunits and the metal center.

Well-resolved NMR spectra were instead obtained in DMSO-d_6. Complexes **14-Zn**−**19-Zn** and **14-U**−**19-U** were subjected to a detailed 2D-NMR (COSY, TOCSY, HSQC-DEPT and HMBC) analysis. The data are collected in the Experimental Section.

Preliminary Binding Measurements. To check the anion binding capabilities of these new water-soluble receptors, we undertook some preliminary measurements. We report here, as an example, the study performed on complex **19-U**, that is, the maltotetraose derivative. The association constant between this receptor and the hydrogen phosphate anion was determined by UV−vis spectroscopic titration experiments, by adding increasing amounts of a standard solution of sodium hydrogen phosphate to a solution of **19-U**, in bidistilled water. The titration data were analyzed using a 1:1 binding model and applying a nonlinear least-squares regression method (Figure 1). The receptor exhibited a quite strong interaction with the anion; the value of the binding constant is 3500 ± 70. M^{-1} Remarkably, this value is almost 8 times higher than that previously reported by us for the poorly water-soluble glucose derivative, **1c**,[21] and, as far as we know, is one of the highest ever reported for a neutral receptor in pure water. Furthermore, very preliminary titration

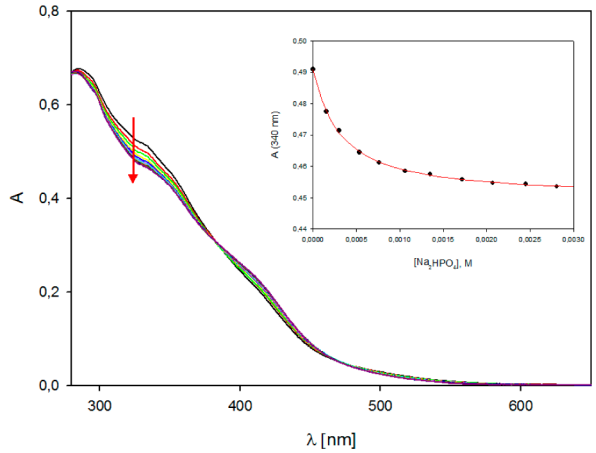


Figure 1. UV−vis absorption spectra of **19-U** upon addition of increasing amounts of disodium hydrogen phosphate. The inset shows the titration plot at 340 nm of a 4.07×10^{-5} M solution of compound **19-U** with hydrogen phosphate at 25 °C in bidistilled water. The points are experimental; the curve is calculated.

experiments performed with the same receptor and fluoride anion indicate a good interaction and an association constant in the order of 500 M^{-1}, which is quite noteworthy considering the extremely high hydration enthalpy of this anion. Complete binding studies on the affinities of all the derivatives are currently in progress and will be reported in due course.

CONCLUSIONS

Here, we have described a simple and general synthetic protocol to obtain oligosaccharide-appended salicylaldehydes, key intermediates for the synthesis of water-soluble metal−salophen complexes starting from commercially available materials. Remarkably, as far as we know, it is the first time that the thioglycosylation procedure here applied is successfully performed on tri- and tetrasaccharides. The particularly mild conditions used to achieve the *S*-glycosidic junction are perfectly tolerated by the sugar backbone as well as by the aldehyde moiety of the aglycon, and we do not foresee any intrinsic limitation in applying this procedure to differently substituted aryl halides or to higher oligosaccharides.

We have also reported the synthesis and the NMR characterization of the corresponding zinc− and uranyl−salophen complexes obtained by using the oligosaccharide-appended salicylaldehydes. The introduction of tri- and tetrasaccharide units on the skeleton of the complexes increases water solubility and allows the preparation of millimolar solutions in such a medium.

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Preliminary studies on the binding affinity of the newly synthesized complex **19-U** toward the hydrogen phosphate anion open up the possibilty of using such compounds for anion recognition in pure water. Moreover, given the well-established catalytic properties of uranyl−salophen complexes in organic solvents,[29] we will definitely investigate also the catalytic potentialities of the new derivatives in an aqueous environment.

EXPERIMENTAL SECTION

General Methods. Commercial grade reagents and solvents were used without further purification. ^{1}H and ^{13}C 1D-NMR spectra of the synthetic intermediates were recorded at 298 K on ^{1}H NMR, 200, 400, and 500 MHz, and ^{13}C NMR, 50, 100, and 125 MHz, instruments in $CDCl_3$ (internal standard, for ^{1}H: $CHCl_3$ at δ 7.26; for ^{13}C: $CDCl_3$ at δ 77.0) or in D_2O (acetone as internal standard, for ^{1}H: $(CH_3)_2CO$ at δ 2.22; for ^{13}C: $(CH_3)_2CO$ at δ 30.9). *J* values are given in hertz. 2D-NMR spectra of the complexes were recorded at 298 K on a DRX-600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) instrument equipped with a cryoprobe, in DMSO-d_6 (internal standard, for ^{1}H: CHD_2SOCD_3 at δ 2.49; for ^{13}C: CD_3SOCD_3 at δ 39.5). Double quantum-filtered phase-sensitive COSY and TOCSY experiments were performed using spectral widths of either 6000 in both dimensions, using data sets of 4096 × 512 points. Quadrature indirect dimensions were achieved through the States-TPPI method. Spectra were processed applying an unshifted Qsine function to both dimensions, and the data matrix was zero-filled by a factor of 2 before Fourier transformation. The TOCSY mixing time was set to 120 ms. HSQC experiments were measured in the ^{1}H-detected mode via single quantum coherence with proton decoupling in the ^{13}C domain, using data sets of 2048 × 512 points. HMBC spectra were measured using a data set of 2048 × 512 points; 64 scans were acquired for each t_1 value.

For the MALDI-MS spectra, compounds were dissolved in CH_3CN or in D_2O at a concentration of 0.1 mg/mL, and 1 μL of these solutions were mixed with 1 μL of a 20 mg/mL solution of 2,5-dihydroxybenzoic acid in 7:3 CH_3CN/H_2O. Analytical thin-layer chromatographies (TLCs) were performed on aluminum plates. The plates were treated with a 10% H_2SO_4 ethanolic solution and then heated to 130 °C. Column chromatographies were performed on silica (63−200 mesh).

General Procedure for Thioglycosylation. To a suspension of anhydrous sodium acetate (150 mg, 1.83 mmol) in acetic anhydride (3.3 mL, 34.9 mmol) heated at 120 °C was added the commercially available oligosaccharide (660 μmol). After a few minutes stirring at 120 °C, the suspension turned to a clear colorless solution. After 90 min, the solution was cooled to rt and then added to water (60 mL). After 2 h standing at 4 °C, the mixture was extracted with CH_2Cl_2 (60 mL). The organic layer was collected, dried over anhydrous sodium sulfate, filtered, and concentrated. The obtained per-*O*-acetylated oligosaccharide (660 μmol) was dissolved in anhydrous CH_2Cl_2 (3.2 mL) and treated with I_2 (226 mg, 890 μmol) and then Et_3SiH (142 μL, 890 μmol). The solution was stirred at reflux with a water-cooled condenser fitted with a drying tube (anhydrous $CaCl_2$). After 30 min, the solution was cooled to rt, diluted with CH_2Cl_2 (80 mL), and washed with a 1:1 v/v 1 M $NaHCO_3$/10% $Na_2S_2O_3$ mixture (80 mL). The organic layer was collected, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was dissolved in acetonitrile (3.2 mL) and treated with thiourea (55.2 mg, 725 μmol). After a few minutes, the mixture turned to a clear yellowish solution, and stirring was continued at 60 °C for 1 h. After cooling to rt, 5-chloromethyl-salicylaldehyde (191 mg, 1.12 mmol) was added, followed by triethylamine (367 μL, 2.64 mmol). The stirring was continued while a white precipitate was gradually formed. After 1 h, the mixture was concentrated, and the residue was subjected to column chromatography (hexane−ethyl acetate mixtures).

m-Formyl-p-hydroxy-benzyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranoside (**2**). 330 mg (64%) as a white powder; $[\alpha]_D^{22}$ −36 (*c* 0.5 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.95 (1H, bs, OH), 9.85 (1H, s, CHO), 7.48 (1H, d, J_{meta} 1.5, 2′-H), 7.44 (1H, dd, J_{ortho} 8.5, J_{meta} 1.5, 6′-H), 6.92 (1H, d, J_{ortho} 8.5, 5′-H),5.13 (1H, t, $J_{3,4} = J_{3,2}$ 9.5, 3_A-H), 5.12 (1H, t, $J_{3,4} = J_{3,2}$ 9.5, 3_B-H), 5.04 (1H, t, $J_{4,3} = J_{4,5}$ 9.5, 4_B-H), 4.97 (1H, t, $J_{2,3} = J_{2,1}$ 9.5, 2_A-H), 4.89 (1H, t, $J_{2,3} = J_{2,1}$ 9.5, 2_B-H), 4.51 (2H, m, 1_B-H^i, $6a_A$-H), 4.34 (1H, dd, J_{gem} 12.5, $J_{6a,5}$ 4.0, $6a_B$-H), 4.31 (1H, d, $J_{1,2}$ 9.5, 1_A-H), 4.06 (1H, dd, J_{gem} 12.0, $J_{6b,5}$ 5.0, $6b_A$-H), 4.02 (1H, dd, J_{gem} 12.5, $J_{6b,5}$ 1.5, $6b_B$-H), 3.87 (1H, d, J_{gem} 13.0, SC*H*HAr), 3.79 (1H, d, J_{gem} 13.0, SC*H*HAr), 3.75 (1H, t, $J_{4,3} = J_{4,5}$ 9.5, 4_A-H), 3.64 (1H, m, 5_B-H), 3.54 (1H, m, 5_A-H), 2.11 (3H, s, CH_3CO), 2.05 (3H, s, CH_3CO), 2.02 (3H, s, CH_3CO), 2.00 (3H, s, CH_3CO), 1.99 (3H, s, CH_3CO), 1.98 (3H, s, CH_3CO), 1.96 (3H, s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2 (CHO), 170.3−168.9 (*C*OCH$_3$), 160.8 (*C*-OH Ar), 137.6, 133.7, 128.3, 120.4, 117.9 (C-Ar), 100.6 (1_B-C), 81.8 (1_A-C), 77.2, 76.2, 73.2, 72.8, 71.9, 71.5, 69.9, 67.7, 61.9, 61.4 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 32.5 (SCH_2Ar), 20.7−20.4 (CH_3CO); TOF-MS (MALDI TOF positive) *m*/*z* 809.12 $[M + Na]^+$; Anal. Calcd for $C_{34}H_{42}O_{19}S$: C, 51.91; H, 5.38; S, 4.08. Found C, 51.80; H, 5.45; S, 4.00.

m-Formyl-p-hydroxy-benzyl-2,3,4,6-tetra-O-acetyl-β-D-galacto-pyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranoside (**3**). 336 mg (65%) as a white powder; $[\alpha]_D^{22}$ −39.4 (*c* 2.0 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.98 (1H, s, OH), 9.88 (1H, s, CHO), 7.50 (1H, d, J_{meta} 2.0, 2′-H), 7.47 (1H, dd, J_{ortho} 8.5, J_{meta} 2.0, 6′-H), 6.95 (1H, d, J_{ortho} 8.5, 5′-H),5.34 (1H, d, $J_{4,3}$ 3.0, 4_B-H), 5.17 (1H, t, $J_{3,4} = J_{3,2}$ 9.5, 3_A-H), 5.10 (1H, dd, $J_{2,1}$ 10.5, $J_{2,3}$ 8.0, 2_B-H), 4.99 (1H, t, $J_{2,1} = J_{2,3}$ 10.0, 2_A-H), 4.96 (1H, dd, $J_{3,2}$ 10.5, $J_{3,4}$ 3.5, 3_B-H), 4.51 (1H, dd, J_{gem} 12.5, $J_{6a,5}$ 2.0, $6a_A$-H), 4.48 (1H, d, $J_{1,2}$ 8.0, 1_B-H), 4.33 (1H, d, $J_{1,2}$ 10.5, 1_A-H), 4.09 (3H, m, $6a_B$-H, $6b_A$-H, $6b_B$-H), 3.88 (2H, m, 5_B-H,SC*H*HAr), 3.81 (1H, d, J_{gem} 12.5, SC*H*HAr), 3.78 (1H, t, $J_{4,3} = J_{4,5}$ 9.5, 4_A-H), 3.56 (1H, m, 5_A-H), 2.15 (3H, s, CH_3CO), 2.13 (3H, s, CH_3CO), 2.05 (3H, s, CH_3CO), 2.04 (6H, s, 2 CH_3CO), 2.03 (3H, s, CH_3CO), 1.96 (3H, s, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2 (CHO), 170.3−169.0 (*C*OCH$_3$), 160.9 (*C*-OH Ar), 137.7, 133.7, 128.3, 120.4, 118.0 (C-Ar), 101.0 (1_B-C), 81.8 (1_A-C), 76.8, 76.1, 73.6, 70.9, 70.7, 70.1, 69.1, 66.5, 62.1, 60.7 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 32.6 (SCH_2Ar), 20.8−20.5 (CH_3CO); TOF-MS (MALDI TOF positive) *m*/*z* 809.09 $[M + Na]^+$; Anal. Calcd for $C_{34}H_{42}O_{19}S$: C, 51.91; H, 5.38; S, 4.08. Found C, 51.74; H, 5.50; S, 3.98.

m-Formyl-p-hydroxy-benzyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-O-acetyl-1-thio-β-D-glucopyranoside (**4**). 274 mg (53%) as a white powder; $[\alpha]_D^{22}$ −29.3 (*c* 1.0 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (1H, s, OH), 9.90 (1H, s, CHO), 7.52 (1H, d, J_{meta} 2.0, 2′-H), 7.49 (1H, dd, J_{ortho} 8.5, J_{meta} 2.0, 6′-H), 6.98 (1H, d, J_{ortho} 8.5, 5′-H),5.21 (1H, t, $J_{3,4} = J_{3,2}$ 9.5, 3_B-H), 5.13 (1H, t, $J_{3,4} = J_{3,2}$ 9.5, 3_A-H), 5.09 (1H, t, $J_{4,3} = J_{4,5}$ 9.5, 4_B-H), 5.04 (2H, m, 2_A-H, 2_B-H), 4.89 (1H, t, $J_{4,3} = J_{4,5}$ 9.5, 4_A-H), 4.54 (1H, d, $J_{1,2}$ 7.5, 1_B-H), 4.30 (1H, dd, J_{gem} 12.0, $J_{6a,5}$ 4.5, $6a_B$-H), 4.22 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.14 (1H, dd, J_{gem} 12.0, $J_{6b,5}$ 2.0, $6b_B$-H), 3.95 (1H, d, J_{gem} 13.0, SC*H*HAr), 3.89 (1H, d, J_{gem} 8.5, $6a_A$-H), 3.78 (1H, d, J_{gem} 13.0, SC*H*HAr), 3.70 (1H, m, 5_B-H), 3.58 (2H, m, 5_A-H, $6b_A$-H), 2.11 (3H, s, CH_3CO), 2.03 (9H, s, 3 CH_3CO), 2.01 (3H, s, CH_3CO), 1.99 (3H, s, CH_3CO), 1.98 (3H, s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0 (CHO), 170.6−169.4 (*C*OCH$_3$), 160.9 (*C*-OH Ar), 137.9, 134.1, 128.1, 120.4, 118.2 (C-Ar), 100.7 (1_B-C), 81.2 (1_A-C), 73.6, 72.7, 72.0, 71.1, 71.0, 69.7, 68.9, 68.5, 68.3, 61.7 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 32.2 (SCH_2Ar), 20.8−20.5 (CH_3CO); TOF-MS (MALDI TOF positive) *m*/*z* 809.00 $[M + Na]^+$. Anal. Calcd for $C_{34}H_{42}O_{19}S$: C, 51.91; H, 5.38; S, 4.08. Found C, 51.81; H, 5.45; S, 3.99.

m-Formyl-p-hydroxy-benzyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranoside (**5**). 246 mg (47%) as a white powder; $[\alpha]_D^{22}$ +1.6 (*c* 1.0 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.01 (1H, s, OH), 9.91 (1H, s, CHO), 7.50 (2H, m, 2′-H, 6′-H), 6.98 (1H, d, J_{ortho} 8.5, 5′-H), 5.40 (1H, d, $J_{1,2}$ 4.0 Hz, 1_B-H), 5.35 (1H, t, $J_{3,4} = J_{3,2}$ 9.7, 3_B-H), 5.23 (1H, t, $J_{3,4} = J_{3,2}$ 9.0, 3_A-H), 5.05 (1H, t, $J_{4,5} = J_{4,3}$ 9.9 Hz, 4_B-H), 4.92 (1H, t, $J_{2,1} = J_{2,3}$ 9.7, 2_A-H), 4.85 (1H, dd, $J_{2,1}$ 10.5, $J_{2,3}$ 4.0, 2_B-H), 4.48 (1H, dd, J_{gem} 12.1, $J_{6a,5}$ 2.8, $6a_A$-H), 4.38 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.25 (2H, m, $6a_B$-H, $6b_A$-H), 4.07 (1H, dd, J_{gem} 12.4, $J_{6b,5}$ 2.2, $6b_B$-H), 4.00 (2H, m, 4_A-H, 5_B-H), 3.92 (1H, d, J_{gem} 13.1, SC*H*HAr), 3.80 (1H, d, J_{gem} 13.1, SC*H*HAr), 3.60 (1H, ddd, $J_{5,4}$ 9.7, $J_{5,6a}$ 4.4, $J_{5,6b}$ 3.1, 5_A-H), 2.16 (3H, s, CH_3CO), 2.11 (3H, s, CH_3CO), 2.04 (6H, s, 2 CH_3CO), 2.01 (3H, s, CH_3CO), 2.00 (6H, s, 2 CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3 (CHO), 170.5−169.4 (*C*OCH$_3$), 160.9 (*C*-OH Ar), 137.7, 133.7, 128.3, 120.5, 118.1 (C-Ar), 95.6 (1_B-C),

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81.4 (1_A-C), 76.2, 76.1, 72.8, 70.6, 69.9, 69.2, 68.5, 68.1, 63.0, 61.5 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 32.6 (SCH_2Ar), 20.8−20.4 (CH_3CO); TOF-MS (MALDI TOF positive) m/z 809.28 $[M + Na]^+$; Anal. Calcd for $C_{34}H_{42}O_{19}S$: C, 51.91; H, 5.38; S, 4.08. Found C, 51.77; H, 5.51; S, 4.00.

*m-Formyl-p-hydroxy-benzyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranoside (**6**).* 395 mg (56%) as a white powder; $[\alpha]_D^{22}$ +53 (*c* 0.7 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.03 (1H, s, OH), 9.92 (1H, s, CHO), 7.53 (1H, d, J_{meta} 1.5, 2′-H), 7.49 (1H, dd, J_{ortho} 8.5, J_{meta} 1.5, 6′-H), 6.98 (1H, d, J_{ortho} 8.5, 5′-H), 5.38 (3H, m, 1_B-H, 3_B-H, 3_C-H),5.27 (1H, d, $J_{1,2}$ 4.0, 1_C-H), 5.23 (1H, t, $J_{3,4} = J_{3,2}$ 9.5, 3_A-H), 5.07 (1H, t, $J_{4,3} = J_{4,5}$ 10.0, 4_C-H), 4.90 (1H, t, $J_{2,3} = J_{2,1}$ 9.5, 2_A-H), 4.86 (1H, dd, $J_{2,3}$ 10.0, $J_{2,1}$ 4.0, 2_C-H), 4.72 (1H, dd, $J_{2,3}$ 10.0, $J_{2,1}$ 3.5, 2_B-H), 4.46 (2H, m, $6a_A$-H, $6a_B$-H), 4.34 (2H, m, 1_A-H, $6b_A$-H), 4.25 (1H, dd, J_{gem} 12.5, $J_{6a,5}$ 3.5, $6a_C$-H), 4.19 (1H, dd, J_{gem} 12.0, $J_{6b,5}$ 3.5, $6b_B$-H), 4.06 (1H, dd, J_{gem} 12.5, $J_{6b,5}$ 1.5, $6b_C$-H), 4.05−3.92 (m, 5H, 4_A-H, 4_B-H, 5_B-H, 5_C-H, SC*H*HAr), 3.80 (1H, d, J_{gem} 13.0, SC*H*HAr), 3.64 (1H, m, 5_A-H), 2.20 (3H, s, CH_3CO), 2.16 (3H, s, CH_3CO), 2.10 (3H, s, CH_3CO), 2.05 (6H, s, 2 CH_3CO), 2.04 (3H, s, CH_3CO), 2.00 (9H, s, 3 CH_3CO), 1.98 (3H, s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0 (CHO), 170.1−169.0 ($COCH_3$), 160.5 (*C*-OH Ar), 137.3, 133.5, 128.0, 120.1, 117.7 (C-Ar), 95.4, 95.2 (1_B-C, 1_C-C), 80.8 (1_A-C), 75.8, 73.5, 72.1, 71.2, 70.3, 70.0, 69.8, 68.9, 68.6, 68.1, 67.5, 62.8, 62.0, 61.0, 59.9 (2_A-C, 2_B-C, 2_C-C, 3_A-C, 3_B-C, 3_C-C, 4_A-C, 4_B-C, 4_C-C, 5_A-C, 5_B-C, 5_C-C, 6_A-C, 6_B-C, 6_C-C), 32.1 (SCH_2Ar), 20.6−20.1 (CH_3CO); TOF-MS (MALDI TOF positive) m/z 1096.99 $[M + Na]^+$; Anal. Calcd for $C_{46}H_{58}O_{27}S$: C, 51.39; H, 5.44; S, 2.98. Found C, 51.51; H, 5.55; S, 3.06.

*m-Formyl-p-hydroxy-benzyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranoside (**7**).* 424 mg (47%) as a white powder; $[\alpha]_D^{22}$ +82.1 (*c* 5.0 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (1H, s, OH), 9.93 (1H, s, CHO), 7.53 (1H, bs, 2′-H), 7.49 (1H, d, J_{ortho} 8.5, 6′-H), 6.98 (1H, d, J_{ortho} 8.5, 5′-H), 5.42−5.33 (4H, m, 1_B-H, 3_B-H, 3_C-H, 3_D-H), 5.28 (2H, m, 1_C-H, 1_D-H), 5.23 (1H, t, $J_{3,4} = J_{3,2}$ 9.6, 3_A-H), 5.08 (1H, t, $J_{4,3} = J_{4,5}$ 10.0, 4_D-H), 4.90 (1H, t, $J_{2,3} = J_{2,1}$ 9.6, 2_A-H), 4.87 (1H, dd, $J_{2,3}$ 10.0, $J_{2,1}$ 4.0, 2_D-H), 4.73 (2H, m, 2_B-H, 2_C-H), 4.49−4.40 (4H, m, $6a_A$-H, $6a_B$-H, $6a_C$-H, $6b_A$-H), 4.35 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.27−4.15 (3H, m, $6a_D$-H, $6b_B$-H, $6b_C$-H), 4.07−3.86 (8H, m, 4_A-H, 4_B-H, 4_C-H, 5_B-H, 5_C-H, 5_D-H, $6b_D$-H, SC*H*HAr), 3.79 (1H, d, J_{gem} 13.1, SC*H*HAr), 3.65 (1H, m, 5_A-H), 2.21 (3H, s, CH_3CO), 2.19 (3H, s, CH_3CO), 2.15 (3H, s, CH_3CO), 2.10 (3H, s, CH_3CO), 2.06 (3H, s, CH_3CO), 2.04 (6H, s, 2 CH_3CO), 2.03 (3H, s, CH_3CO), 2.01 (3H, s, CH_3CO), 2.00 (3H, s, CH_3CO), 1.99 (6H, s, CH_3CO), 1.98 (3H, s, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4 (CHO), 170.5−169.4 ($COCH_3$), 160.9 (*C*-OH Ar), 137.7, 133.7, 128.2, 120.4, 118.1 (C-Ar), 95.8, 95.6, 95.5 (1_B-C, 1_C-C, 1_D-C), 81.1 (1_A-C), 76.1, 75.9, 73.8, 73.5, 72.3, 71.6, 71.3, 70.6, 70.4, 70.3, 70.0, 69.2, 68.9, 68.4, 67.8, 63.2, 62.5, 62.1, 61.3, 60.3 (2_A-C, 2_B-C, 2_C-C, 2_D-C, 3_A-C, 3_B-C, 3_C-C, 3_D-C, 4_A-C, 4_B-C, 4_C-C, 4_D-C, 5_A-C, 5_B-C, 5_C-C, 5_D-C, 6_A-C, 6_B-C, 6_C-C, 6_D-C), 32.5 (SCH_2Ar), 20.8−20.4 (CH_3CO); TOF-MS (MALDI TOF positive) m/z 1385.11 $[M + Na]^+$; Anal. Calcd for $C_{56}H_{72}O_{34}S$: C, 50.91; H, 5.49; S, 2.43. Found C, 50.80; H, 5.57; S, 2.38.

General Procedure for Transesterification. Thioglycoside (100 μmol) was dissolved in 4:1 v/v MeOH/CH_2Cl_2 (7.5 mL), cooled to 0 °C, and treated with freshly prepared 0.15 M methanolic NaOMe (1.3 mL). The yellow solution was then stirred at rt. The deprotection of trisaccharide **6** required, after ∼4 h, further addition of 5.0 mL of MeOH to dissolve the partially deprotected species, and complete deacetylation. Analogously, deprotection of tetrasaccharide **7** required addition of MeOH (two 5.0 mL aliquots) after 1 and 4 h, respectively. After 5 h, the solutions were treated with Amberlyst 15 (H^+ form) until colorless, then filtered and concentrated to dryness. The residue was dissolved in a small amount of water and freeze-dried.

*m-Formyl-p-hydroxy-benzyl-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (**8**).* 48 mg (98%) as a white powder; $[\alpha]_D^{22}$ −50 (*c* 0.5 in H_2O); ^{1}H NMR (500 MHz, D_2O: δ 9.91 (1H, s, CHO), 7.72 (1H, d, J_{meta} 2.0, 2′-H), 7.63 (1H, dd, J_{ortho} 9.0, J_{meta} 2.0, 6′-H), 7.00 (1H, d, J_{ortho} 9.0, 5′-H), 4.48 (1H, d, $J_{1,2}$ 8.0, 1_B-H), 4.31 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.03−3.27 (14H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.7 (CHO), 159.5 (*C*-OH Ar), 138.7, 134.1, 130.6, 121.4, 118.1 (C-Ar), 103.1 (1_B-C), 84.6 (1_A-C), 79.2, 76.6, 76.3, 76.2, 73.8, 72.6, 70.1, 70.0, 61.2, 60.8 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 33.4 (SCH_2Ar); TOF-MS (MALDI TOF positive) m/z 515.21 $[M + Na]^+$; Anal. Calcd for $C_{20}H_{28}O_{12}S$: C, 48.77; H, 5.73; S, 6.51. Found C, 48.54; H, 5.83; S, 6.40.

*m-Formyl-p-hydroxy-benzyl-β-D-galactopyranosyl-(1→4)-1-thio-β-D-glucopyranoside, (**9**).* 48 mg (98%) as a white powder; $[\alpha]_D^{22}$ −54 (*c* 0.6 in H_2O); ^{1}H NMR (500 MHz, D_2O) δ 9.92 (1H, s, CHO), 7.71 (1H, d, J_{meta} 2.0, 2′-H), 7.62 (1H, dd, J_{ortho} 9.0, J_{meta} 2.0, 6′-H), 7.00 (1H, d, J_{ortho} 9.0, 5′-H), 4.42 (1H, d, $J_{1,2}$ 7.0, 1_B-H), 4.31 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.02 (1H, d, J_{gem}14.0, SC*H*HAr), 3.94−3.36 (13H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.1 (CHO), 159.7 (*C*-OH Ar), 138.9, 134.4, 130.8, 121.5, 118.2 (C-Ar), 103.5 (1_B-C), 84.6 (1_A-C), 79.3, 78.8, 76.4, 76.0, 73.2, 72.5, 71.6, 69.2, 61.7, 60.8 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 33.5 (SCH_2Ar); TOF-MS (MALDI TOF positive) m/z 515.08 $[M + Na]^+$; Anal. Calcd for $C_{20}H_{28}O_{12}S$: C, 48.77; H, 5.73; S, 6.51. Found C, 48.49; H, 5.81; S, 6.33.

*m-Formyl-p-hydroxy-benzyl-β-D-glucopyranosyl-(1→6)-1-thio-β-D-glucopyranoside, (**10**).* 48 mg (98%) as a white powder; $[\alpha]_D^{22}$ −62 (*c* 0.5 in H_2O); ^{1}H NMR (500 MHz, D_2O) δ 9.94 (1H, s, CHO), 7.75 (1H, d, J_{meta} 2.0, 2′-H), 7.64 (1H, dd, J_{ortho} 8.5, J_{meta} 2.0, 6′-H), 7.01 (1H, d, J_{ortho} 8.5, 5′-H), 4.45 (1H, d, $J_{1,2}$ 8.0, 1_B-H), 4.32 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.11−3.29 (14H, m); ^{13}C NMR (50 MHz, D_2O) δ 197.8 (CHO), 159.6 (*C*-OH Ar), 138.9, 134.1, 130.7, 121.4, 118.1 (C-Ar), 103.4 (1_B-C), 85.1 (1_A-C), 79.3, 77.8, 76.6, 76.4, 73.8, 72.6, 70.3, 69.9, 69.2, 61.4 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 33.5 (SCH_2Ar); TOF-MS (MALDI TOF positive) m/z 515.07 $[M + Na]^+$; Anal. Calcd for $C_{20}H_{28}O_{12}S$: C, 48.77; H, 5.73; S, 6.51. Found C, 48.48; H, 5.85; S, 6.35.

*m-Formyl-p-hydroxy-benzyl-α-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside, (**11**).* 49 mg (99%) as a white powder; $[\alpha]_D^{22}$ −1.7 (*c* 1.1 in H_2O); ^{1}H NMR (400 MHz, D_2O) δ 9.89 (1H, s, CHO), 7.67 (1H, bs, 2′-H), 7.59 (1H, d, J_{ortho} 8.6, 6′-H), 6.97 (1H, d, J_{ortho} 8.6, 5′-H),5.36 (1H, d, $J_{1,2}$ 3.7, 1_B-H), 4.31 (1H, d, $J_{1,2}$ 9.9, 1_A-H), 4.00 (1H, d, J_{gem} 13.5 Hz, SC*H*HAr), 3.91 (1H, d, J_{gem} 13.5 Hz, SC*H*HAr), 3.86−3.36 (12H, m); ^{13}C NMR (100 MHz, D_2O): δ 197.9 (CHO), 159.6 (*C*-OH Ar), 138.8, 134.2, 130.7, 121.5, 118.1 (C-Ar), 100.3 (1_B-C), 84.6 (1_A-C), 79.1, 78.3, 77.4, 73.5, 73.4, 72.7, 72.3, 70.0, 61.5, 61.2 (2_A-C, 2_B-C, 3_A-C, 3_B-C, 4_A-C, 4_B-C, 5_A-C, 5_B-C, 6_A-C, 6_B-C), 33.4 (SCH_2Ar); TOF-MS (MALDI TOF positive) m/z 515.29 $[M + Na]^+$; Anal. Calcd for $C_{20}H_{28}O_{12}S$: C, 48.77; H, 5.73; S, 6.51. Found C, 48.59; H, 5.79; S, 6.46.

*m-Formyl-p-hydroxy-benzyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside, (**12**).* 65 mg (99%) as a white powder; $[\alpha]_D^{22}$ −4.8 (*c* 0.4 in H_2O); ^{1}H NMR (500 MHz, D_2O) δ 9.92 (1H, s, CHO), 7.71 (1H, d, J_{meta} 2.0, 2′-H), 7.62 (1H, dd, J_{ortho} 8.5, J_{meta} 2.0, 6′-H), 6.99 (1H, d, J_{ortho} 8.5, 5′-H), 5.39 (1H, d, $J_{1,2}$ 3.5, 1_B-H), 5.36 (1H, d, $J_{1,2}$ 3.5 Hz, 1_C-H), 4.31 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.02 (1H, d, J_{gem} 13.5, SC*H*HAr), 3.94−3.35 (19H, m); ^{13}C NMR (100 MHz, D_2O) δ 198.0 (CHO), 159.7 (*C*-OH Ar), 138.9, 134.4, 130.8, 121.5, 118.1 (C-Ar), 100.4, 100.1 (1_B-C^I,1_C-C), 84.6 (1_A-C), 79.0, 78.3, 77.4, 77.3, 74.0, 73.5, 73.4, 72.6, 72.4, 72.1, 71.8, 70.0, 61.4, 61.1, 61.0 (2_A-C, 2_B-C, 2_C-C, 3_A-C, 3_B-C, 3_C-C, 4_A-C, 4_B-C, 4_C-C, 5_A-C, 5_B-C, 5_C-C, 6_A-C, 6_B-C, 6_C-C), 33.4 (SCH_2Ar); TOF-MS (MALDI TOF positive) m/z 677.00 $[M + Na]^+$; Anal. Calcd for $C_{26}H_{38}O_{17}S$: C, 47.70; H, 5.85; S, 4.90. Found C, 47.45; H, 5.99; S, 4.70.

*m-Formyl-p-hydroxy-benzyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside, (**13**).* 81 mg (99%) as a white powder; $[\alpha]_D^{22}$ +41 (*c* 0.4 in H_2O); ^{1}H NMR (500 MHz, D_2O) δ 9.93 (1H, s, CHO), 7.73 (1H, d, J_{meta} 2.0, 2′-H), 7.63 (1H, dd, J_{ortho} 8.5, J_{meta} 2.0, 6′-H), 7.00 (1H, d, J_{ortho} 8.5, 5′-H), 5.38 (3H, m, 1_B-H, 1_C-H, 1_D-H), 4.30 (1H, d, $J_{1,2}$ 10.0, 1_A-H), 4.03 (1H, d, J_{gem} 14.0, SC*H*HAr), 3.98−3.35 (25H, m); ^{13}C NMR (100 MHz, D_2O) δ 198.0 (CHO), 160.1 (*C*-OH Ar), 138.9, 134.2, 130.5, 121.6, 118.4 (C-Ar), 100.4, 100.3, 100.1 (1_B-C, 1_C-C, 1_D-C), 84.6 (1_A-C), 79.0, 78.3, 77.5, 77.3, 74.0, 73.9, 73.5, 73.4, 72.7, 72.6, 72.4, 72.2, 72.1, 71.9, 70.0, 61.4, 61.3, 61.1 (2_A-C, 2_B-C, 2_C-C, 2_D-C, 3_A-C, 3_B-C, 3_C-C, 3_D-C, 4_A-C, 4_B-C, 4_C-C, 4_D-C, 5_A-C, 5_B-C, 5_C-C, 5_D-C, 6_A-C, 6_B-C, 6_C-C, 6_D-C), 33.5 (SCH_2Ar); TOF-MS (MALDI TOF positive) m/z

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839.09 [M + Na]$^+$; Anal. Calcd for $C_{32}H_{48}O_{22}S$: C, 47.06; H, 5.92; S, 3.93. Found C, 46.89; H, 6.03; S, 3.79.

General Procedure for the Synthesis of the Complexes 14–19. The aldehyde, **8–13** (100 μmol), was added to a solution of zinc or uranyl acetate (60 μmol) in MeOH (4 mL), followed by the addition of *o*-phenylenediamine (50 μmol). The solution was kept overnight at room temperature, under constant stirring. The volume was reduced to about half, and the precipitate was collected, washed three times with cold diethyl ether, and dried under vacuum.

*Complex **14-Zn**.* Yellow powder, 35 mg, yield 62%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.94 (1H, s, CHN), 7.85 (1H, bs, $2_{B'}$-H), 7.36 (2H, m, $2_{A'}$-H, $3_{B'}$-H), 7.22 (1H, d, J_{ortho} 7.1, $6_{A'}$-H), 6.66 (1H, d, J_{ortho} 7.1, $5_{A'}$-H), 5.27 (1H, d, $J_{H,OH}$ 5.9, 2_A-OH), 5.23 (1H, d, $J_{H,OH}$ 4.8, 2_B-OH), 5.01 (1H, d, $J_{H,OH}$ 4.9, 3_B-OH), 4.99 (1H, d, $J_{H,OH}$ 5.4, 4_B-OH), 4.77 (1H, t, $J_{H,OH}$ 5.9, 6_A-OH), 4.72 (1H, bs, 3_A-OH), 4.59 (1H, t, $J_{H,OH}$ 5.2, 6_B-OH), 4.24 (1H, d, $J_{1,2}$ 7.8, 1_B-H), 4.13 (1H, d, $J_{1,2}$ 9.7, 1_A-H), 3.84 (2H, m, $6a_A$-H, SC*H*HPh), 3.69 (2H, m, $6a_B$-H, SC*H*HPh), 3.62 (1H, m, $6b_A$-H), 3.38 (1H, m, $6b_B$-H), 3.31 (1H, m, 4_A-H), 3.26–3.12 (5H, m, 2_A-H, 3_A-H, 3_B-H, 5_A-H, 5_B-H), 3.03 (1H, m, 4_B-H), 2.97 (1H, m, 2_B-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.3 ($4_{A'}$-C), 162.1 (CN), 139.1 ($1_{B'}$-C), 135.9 ($2_{A'}$-C), 135.3 ($6_{A'}$-C), 127.0 ($3_{B'}$-C), 122.9 ($5_{A'}$-C), 121.6 ($1_{A'}$-C), 118.5 ($3_{A'}$-C), 116.3 ($2_{B'}$-C), 102.9 (1_B-C), 82.8 (1_A-C), 80.4 (4_A-C), 78.9 (5_A-C), 76.6 (5_B-C), 76.3 (3_A-C), 76.2 (3_B-C), 73.0 (2_B-C), 72.6 (2_A-C), 69.8 (4_B-C), 60.7 (6_B-C), 60.4 (6_A-C), 31.7 (CH_2S); MS (ESI-TOF) *m*/*z* 1143.57 [M + Na]$^+$.

*Complex **14-U**.* Orange powder, 43 mg, yield 65%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.55 (1H, s, CHN), 7.77 (1H, bs, $2_{B'}$-H), 7.73 (1H, s, $2_{A'}$-H), 7.59 (1H, d, J_{ortho} 8.2, $6_{A'}$-H), 7.53 (1H, bs, $3_{B'}$-H), 6.94 (1H, d, J_{ortho} 8.2, $5_{A'}$-H), 5.28 (1H, d, $J_{H,OH}$ 5.8, 2_A-OH), 5.22 (1H, d, $J_{H,OH}$ 4.6, 2_B-OH), 5.02 (1H, d, $J_{H,OH}$ 4.7, 3_B-OH), 4.99 (1H, d, $J_{H,OH}$ 5.3, 4_B-OH), 4.77 (1H, t, $J_{H,OH}$ 5.7, 6_A-OH), 4.71 (1H, bs, 3_A-OH), 4.58 (1H, t, $J_{H,OH}$ 5.0, 6_B-OH), 4.24 (1H, d, $J_{1,2}$ 7.8, 1_B-H), 4.18 (1H, d, $J_{1,2}$ 9.7, 1_A-H), 3.95 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.86 (1H, m, $6a_A$-H), 3.82 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.67 (1H, m, $6a_B$-H), 3.61 (1H, m, $6b_A$-H), 3.38 (1H, m, $6b_B$-H), 3.32–3.24 (3H, m, 3_A-H, 4_A-H, 5_A-H), 3.18–3.12 (3H, m, 2_A-H, 3_B-H, 5_B-H), 3.02 (1H, m, 4_B-H), 2.97 (1H, m, 2_B-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8 ($4_{A'}$-C), 166.1 (CN), 146.5 ($1_{B'}$-C), 136.9 ($6_{A'}$-C), 135.5 ($2_{A'}$-C), 128.6 ($3_{B'}$-C), 125.7 ($1_{A'}$-C), 123.6 ($3_{A'}$-C), 120.4 ($5_{A'}$-C), 120.0 ($2_{B'}$-C), 102.9 (1_B-C), 82.6 (1_A-C), 80.4 (4_A-C), 78.9 (5_A-C), 76.5 (5_B-C), 76.2 (3_A-C, 3_B-C), 73.0 (2_B-C), 72.7 (2_A-C), 69.7 (4_B-C), 60.6 (6_B-C), 60.2 (6_A-C), 31.4 (CH_2S); MS (ESI-TOF) *m*/*z* 1348.12 [M + Na]$^+$.

*Complex **15-Zn**.* Yellow powder, 39 mg, yield 70%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.94 (1H, s, CHN), 7.86 (1H, bs, $2_{B'}$-H), 7.36 (2H, m, $2_{A'}$-H, $3_{B'}$-H), 7.22 (1H, d, J_{ortho} 8.5, $6_{A'}$-H), 6.66 (1H, d, J_{ortho} 8.5, $5_{A'}$-H), 5.27 (1H, d, $J_{H,OH}$ 5.9, 2_A-OH), 5.09 (1H, d, $J_{H,OH}$ 3.0, 2_B-OH), 4.78 (1H, d, $J_{H,OH}$ 3.6, 3_B-OH), 4.74 (2H, m, 3_A-OH, 6_A-OH), 4.64 (1H, t, $J_{H,OH}$ 4.9, 6_B-OH), 4.50 (1H, d, $J_{H,OH}$ 3.0, 4_B-OH), 4.19 (1H, d, $J_{1,2}$ 6.3, 1_B-H), 4.14 (1H, d, $J_{1,2}$ 9.7, 1_A-H), 3.85 (2H, m, $6a_A$-H, SC*H*HPh), 3.71 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.60 (2H, m, 4_B-H, $6b_A$-H), 3.51–3.45 (3H, m, 5_B-H, $6a_B$-H, $6b_B$-H), 3.31–3.22 (5H, m, 2_B-H, 3_A-H, 3_B-H, 4_A-H, 5_A-H), 3.12 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 5.9 Hz, 2_A-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.4 ($4_{A'}$-C), 162.2 (CN), 139.2 ($1_{B'}$-C), 135.9 ($2_{A'}$-C), 135.4 ($6_{A'}$-C), 127.1 ($3_{B'}$-C), 123.2 ($5_{A'}$-C), 121.6 ($1_{A'}$-C), 118.5 ($3_{A'}$-C), 116.4 ($2_{B'}$-C), 103.7 (1_B-C), 82.9 (1_A-C), 80.5 (4_A-C), 78.9 (5_A-C), 76.3 (3_A-C), 75.1 (5_B-C), 72.9 (3_B-C), 72.6 (2_A-C), 70.1 (2_B-C), 68.0 (4_B-C), 60.5 (6_A-C), 60.1 (6_B-C), 31.7 (CH_2S); MS (ESI-TOF) *m*/*z* 1143.51 [M + Na]$^+$.

*Complex **15-U**.* Orange powder, 46 mg, yield 69%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.56 (1H, s, CHN), 7.77 (1H, bs, $2_{B'}$-H), 7.74 (1H, s, $2_{A'}$-H), 7.59 (1H, d, J_{ortho} 8.3, $6_{A'}$-H), 7.54 (1H, bs, $3_{B'}$-H), 6.94 (1H, d, J_{ortho} 8.3, $5_{A'}$-H), 5.29 (1H, d, $J_{H,OH}$ 5.9, 2_A-OH), 5.09 (1H, bs, 2_B-OH), 4.78 (1H, bs, 3_B-OH), 4.74 (2H, m, 3_A-OH, 6_A-OH), 4.63 (1H, t, $J_{H,OH}$ 5.0, 6_B-OH), 4.50 (1H, d, $J_{H,OH}$ 4.5, 4_B-OH), 4.19 (2H, m, 1_A-H, 1_B-H), 3.95 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.87 (1H, m, $6a_A$-H), 3.82 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.59 (2H, m, 4_B-H, $6b_A$-H), 3.51–3.44 (3H, m, 5_B-H, $6a_B$-H, $6b_B$-H), 3.30–3.25 (5H, m, 2_B-H, 3_A-H, 3_B-H, 4_A-H, 5_A-H), 3.12 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 5.9 Hz, 2_A-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8 ($4_{A'}$-C), 166.3 (CN), 146.6 ($1_{B'}$-C), 137.2 ($6_{A'}$-C), 135.8 ($2_{A'}$-C), 128.6 ($3_{B'}$-C), 126.0 ($1_{A'}$-C), 123.6 ($3_{A'}$-C), 120.6 ($5_{A'}$-C), 120.3 ($2_{B'}$-C), 103.8 (1_B-C), 82.8 (1_A-C), 80.7 (4_A-C), 78.9 (5_A-C), 76.3 (3_A-C), 75.3 (5_B-C), 73.0 (2_A-C, 3_B-C), 70.3 (2_B-C), 68.1 (4_B-C), 60.5 (6_A-C), 60.2 (6_B-C), 31.6 (CH_2S); MS (ESI-TOF) *m*/*z* 1348.09 [M + Na]$^+$.

*Complex **16-Zn**.* Yellow powder, 34 mg, yield 61%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.94 (1H, s, CHN), 7.83 (1H, bs, $2_{B'}$-H), 7.44 (1H, s, $2_{A'}$-H), 7.38 (1H, bs, $3_{B'}$-H), 7.24 (1H, d, J_{ortho} 8.0, $6_{A'}$-H), 6.67 (1H, d, J_{ortho} 8.0, $5_{A'}$-H), 5.10 (1H, bs, 2_A-OH), 5.05 (1H, bs, 3_A-OH), 5.02 (2H, bs, 2_B-OH, 3_A-OH), 4.97 (1H, d, $J_{H,OH}$ 2.0, 3_B-OH), 4.94 (1H, d, $J_{H,OH}$ 2.0, 4_B-OH), 4.57 (1H, t, $J_{H,OH}$ 1.6 Hz, 6_B-OH), 4.38 (1H, d, $J_{1,2}$ 7.6, 1_B-H), 4.11 (1H, d, J_{gem} 10.9 Hz, $6a_A$-H), 4.00 (1H, d, $J_{1,2}$ 2.8 Hz, 1_A-H), 3.84 (1H, d, J_{gem} 12.7 Hz, SC*H*HPh), 3.72 (1H, m, $6a_B$-H), 3.67 (1H, d, J_{gem} 12.7 Hz, SC*H*HPh), 3.56 (1H, m, $6b_A$-H), 3.48 (1H, m, $6b_B$-H), 3.23 (1H, m, 5_A-H), 3.17 (1H, m, 3_B-H), 3.13–3.04 (6H, m, 2_A-H, 3_A-H, 4_A-H, 2_B-H, 4_B-H, 5_B-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.2 ($4_{A'}$-C), 162.2 (CN), 139.2 ($1_{B'}$-C), 136.4 ($2_{A'}$-C), 135.4 ($6_{A'}$-C), 127.0 ($3_{B'}$-C), 123.0 ($5_{A'}$-C), 121.4 ($1_{A'}$-C), 118.3 ($3_{A'}$-C), 115.9 ($2_{B'}$-C), 102.9 (1_B-C), 82.5 (1_A-C), 79.6 (5_A-C), 77.9 (3_A-C), 76.7 (5_B-C), 76.6 (3_B-C), 73.4 (2_B-C), 72.6 (2_A-C), 70.0 (4_A-C), 69.8 (4_B-C), 68.5 (6_A-C), 60.7 (6_B-C), 31.7 (CH_2S); MS (ESI-TOF) *m*/*z* 1143.49 [M + Na]$^+$.

*Complex **16-U**.* Orange powder, 40 mg, yield 60%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.56 (1H, s, CHN), 7.81 (1H, s, $2_{A'}$-H), 7.76 (1H, bs, $2_{B'}$-H), 7.63 (1H, d, J_{ortho} 8.6, $6_{A'}$-H), 7.54 (1H, bs, $3_{B'}$-H), 6.95 (1H, d, J_{ortho} 8.6, $5_{A'}$-H), 5.11 (1H, d, $J_{H,OH}$ 5.3, 2_A-OH), 5.08 (1H, d, $J_{H,OH}$ 4.8, 2_B-OH), 5.05 (1H, bs, 3_A-OH), 5.01 (1H, d, $J_{H,OH}$ 5.4, 4_A-OH), 4.98 (1H, d, $J_{H,OH}$ 4.4, 3_B-OH), 4.93 (1H, d, $J_{H,OH}$ 5.1, 4_B-OH), 4.55 (1H, t, $J_{H,OH}$ 5.9, 6_B-OH), 4.37 (1H, d, $J_{1,2}$ 7.7, 1_B-H), 4.10 (1H, d, J_{gem} 11.2, $6a_A$-H), 4.04 (1H, d, $J_{1,2}$ 8.3, 1_A-H), 3.93 (1H, d, J_{gem} 13.0, SC*H*HPh), 3.78 (1H, d, J_{gem} 13.0, SC*H*HPh), 3.70 (1H, m, $6a_B$-H), 3.56 (1H, m, $6b_A$-H), 3.45 (1H, m, $6b_B$-H), 3.28 (1H, m, 5_A-H), 3.16 (1H, m, 3_B-H), 3.12 (1H, m, 5_B-H), 3.07–3.02 (5H, m, 2_A-H, 2_B-H, 3_A-H, 4_A-H, 4_B-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.6 ($4_{A'}$-C), 166.4 (CN), 146.4 ($1_{B'}$-C), 137.1 ($6_{A'}$-C), 136.6 ($2_{A'}$-C), 128.5 ($3_{B'}$-C), 125.8 ($1_{A'}$-C), 123.5 ($3_{A'}$-C), 120.6 ($5_{A'}$-C), 120.0 ($2_{B'}$-C), 103.1 (1_B-C), 82.5 (1_A-C), 79.7 (5_A-C), 77.8 (3_A-C), 76.7 (3_B-C, 5_B-C), 73.4 (2_B-C), 72.8 (2_A-C), 70.2 (4_A-C), 69.8 (4_B-C), 68.6 (6_A-C), 60.8 (6_B-C), 31.4 (CH_2S); MS (ESI-TOF) *m*/*z* 1348.17 [M + Na]$^+$.

*Complex **17-Zn**.* Yellow powder, 36 mg, yield 64%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.95 (1H, s, CHN), 7.84 (1H, bs, $2_{B'}$-H), 7.37 (2H, bs, $2_{A'}$-H, $3_{B'}$-H), 7.22 (1H, d, J_{ortho} 8.5, $6_{A'}$-H), 6.66 (1H, d, J_{ortho} 8.0, $5_{A'}$-H), 5.56 (1H, bs, 3_A-OH), 5.42 (1H, d, $J_{H,OH}$ 6.0, 2_B-OH), 5.20 (1H, d, $J_{H,OH}$ 7.0, 2_A-OH), 5.02 (1H, d, $J_{1,2}$ 3.0, 1_B-H), 4.88 (2H, m, 3_B-OH, 4_B-OH), 4.70 (1H, t, $J_{H,OH}$ 5.5, 6_A-OH), 4.53 (1H, t, $J_{H,OH}$ 4.5, 6_B-OH), 4.12 (1H, d, $J_{1,2}$ 9.5, 1_A-H), 3.83 (2H, m, $6a_A$-H, SC*H*HPh), 3.71 (1H, d, J_{gem} 13.0, SC*H*HPh), 3.61 (2H, m, $6a_B$-H, $6b_A$-H), 3.45 (2H, m, 5_B-H, $6b_B$-H), 3.34 (3H, m, 3_A-H, 3_B-H, 4_A-H), 3.20 (2H, m, 2_B-H, 5_A-H), 3.11 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 7.0 Hz, 2_A-H), 3.05 (1H, m, 4_B-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.2 ($4_{A'}$-C), 162.1 (CN), 139.2 ($1_{B'}$-C), 135.7 ($2_{A'}$-C), 135.5 ($6_{A'}$-C), 127.1 ($3_{B'}$-C), 122.9 ($5_{A'}$-C), 121.5 ($1_{A'}$-C), 118.8 ($3_{A'}$-C), 116.0 ($2_{B'}$-C), 100.4 (1_B-C), 83.1 (1_A-C), 79.4 (4_A-C), 79.1 (5_A-C), 77.7 (3_A-C), 73.3 (5_B-C), 72.9 (3_B-C), 72.2 (2_A-C), 72.0 (2_B-C), 69.6 (4_B-C), 60.5 (6_A-C), 60.3 (6_B-C), 31.7 (CH_2S); MS (ESI-TOF) *m*/*z* 1143.54 [M + Na]$^+$.

*Complex **17-U**.* Orange powder, 42 mg, yield 63%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.57 (1H, s, CHN), 7.75 (2H, bs, $2_{A'}$-H, $2_{B'}$-H), 7.60 (1H, d, J_{ortho} 8.1, $6_{A'}$-H), 7.54 (1H, bs, $3_{B'}$-H), 6.94 (1H, d, J_{ortho} 8.1, $5_{A'}$-H), 5.55 (1H, d, $J_{H,OH}$ 3.1, 3_A-OH), 5.41 (1H, d, $J_{H,OH}$ 6.2, 2_B-OH), 5.23 (1H, d, $J_{H,OH}$ 6.2, 2_A-OH), 5.02 (1H, d, $J_{1,2}$ 3.8, 1_B-H), 4.90 (1H, d, $J_{H,OH}$ 5.6, 4_B-OH), 4.87 (1H, d, $J_{H,OH}$ 4.9, 3_B-OH), 4.71 (1H, t, $J_{H,OH}$ 5.8, 6_A-OH), 4.54 (1H, t, $J_{H,OH}$ 5.7, 6_B-OH), 4.16 (1H, d, $J_{1,2}$ 9.6, 1_A-H), 3.95 (1H, d, J_{gem} 13.2, SC*H*HPh), 3.82 (2H, m, $6a_A$-H, SC*H*HPh), 3.60 (2H, m, $6a_B$-H, $6b_A$-H), 3.48 (2H, m, 5_B-H, $6b_B$-H), 3.36–3.31 (3H, m, 3_A-H, 3_B-H, 4_A-H), 3.25 (1H, m, 5_A-H), 3.21 (1H, m, 2_B-H), 3.12 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 6.2 Hz, 2_A-H), 3.06 (1H, m, 4_B-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.2 ($4_{A'}$-C), 166.7 (CN), 146.5 ($1_{B'}$-C), 136.9 ($6_{A'}$-C), 135.5 ($2_{A'}$-C), 126.7 ($3_{B'}$-C), 126.2 ($1_{A'}$-C), 123.8 ($3_{A'}$-C), 120.6 ($5_{A'}$-C), 120.1 ($2_{B'}$-C), 100.6 (1_B-C), 82.9 (1_A-C), 79.5 (4_A-C), 79.1 (5_A-C), 77.8 (3_A-C), 73.4 (5_B-C), 73.2 (3_B-C), 72.6 (2_A-C), 72.2 (2_B-C), 69.7 (4_B-C), 60.6 (6_A-C), 60.5 (6_B-C), 31.5 (CH_2S); MS (ESI-TOF) *m*/*z* 1348.01 [M + Na]$^+$.

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Complex ***18-Zn***. Yellow powder, 48 mg, yield 66%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.94 (1H, s, CHN), 7.85 (1H, bs, $2_{B'}$-H), 7.36 (2H, bs, $2_{A'}$-H, $3_{B'}$-H), 7.23 (1H, d, J_{ortho} 8.7, $6_{A'}$-H), 6.66 (1H, d, J_{ortho} 8.7, $5_{A'}$-H), 5.59 (1H, bs, 3_A-OH), 5.54 (1H, d, $J_{H,OH}$ 6.1, 2_B-OH), 5.46 (2H, m, 2_C-OH, 3_B-OH), 5.23 (1H, d, $J_{H,OH}$ 5.6, 2_A-OH), 5.03 (1H, d, $J_{1,2}$ 3.5, 1_B-H), 4.98 (1H, d, $J_{1,2}$ 3.6, 1_C-H), 4.89 (2H, m, 3_C-OH, 4_C-OH), 4.73 (1H, t, $J_{H,OH}$ 5.9, 6_A-OH), 4.53 (2H, m, 6_B-OH, 6_C-OH), 4.14 (1H, d, $J_{1,2}$ 9.6, 1_A-H), 3.84 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.79 (1H, m, $6a_A$-H), 3.71 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.66−3.55 (6H, m, 3_B-H, 5_B-H, $6a_B$-H, $6a_C$-H, $6b_A$-H, $6b_B$-H), 3.46 (2H, m, 5_C-H, $6b_C$-H), 3.39−3.27 (5H, m, 2_B-H, 3_A-H, 3_C-H, 4_B-H, 5_A-H), 3.22 (2H, m, 2_C-H, 4_A-H), 3.11 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 5.6 Hz, 2_A-H), 3.05 (1H, m, 4_C-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.1 ($4_{A'}$-C), 162.1 (CN), 139.1 ($1_{B'}$-C), 136.0 ($2_{A'}$-C), 135.5 ($6_{A'}$-C), 127.1 ($3_{B'}$-C), 123.1 ($5_{A'}$-C), 121.6 ($1_{A'}$-C), 118.5 ($3_{A'}$-C), 116.3 ($2_{B'}$-C), 100.6 (1_B-C, 1_C-C), 83.1 (1_A-C), 79.8 (4_B-C), 79.2 (5_A-C), 79.0 (4_A-C), 77.7 (3_A-C), 73.1 (3_C-C, 5_C-C), 72.9 (3_B-C), 72.5 (2_A-C), 72.4 (2_C-C), 72.0 (2_B-C), 71.3 (5_B-C), 69.7 (4_C-C), 60.6 (6_A-C), 60.4 (6_C-C), 59.9 (6_B-C), 31.8 (CH_2S); MS (ESI-TOF) m/z 1467.84 $[M + Na]^+$.

Complex ***18-U***. Orange powder, 57 mg, yield 69%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.57 (1H, s, CHN), 7.75 (2H, bs, $2_{A'}$-H, $2_{B'}$-H), 7.59 (1H, d, J_{ortho} 8.6, $6_{A'}$-H), 7.55 (1H, bs, $3_{B'}$-H), 6.95 (1H, d, J_{ortho} 8.6, $5_{A'}$-H), 5.57 (1H, bs, 3_A-OH), 5.50 (1H, d, $J_{H,OH}$ 6.5, 2_B-OH), 5.48 (2H, m, 2_C-OH, 3_B-OH), 5.25 (1H, d, $J_{H,OH}$ 6.1, 2_A-OH), 5.05 (1H, d, $J_{1,2}$ 3.7, 1_B-H), 4.99 (1H, d, $J_{1,2}$ 3.1, 1_C-H), 4.92 (1H, d, $J_{H,OH}$ 5.6, 4_C-OH), 4.90 (1H, d, $J_{H,OH}$ 4.7, 3_C-OH), 4.76 (1H, t, $J_{H,OH}$ 5.8, 6_A-OH), 4.54 (2H, m, 6_B-OH, 6_C-OH), 4.18 (1H, d, $J_{1,2}$ 9.5, 1_A-H), 3.95 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.81 (2H, m, $6a_A$-H, SC*H*HPh), 3.66−3.56 (6H, m, 3_B-H, 5_B-H, $6a_B$-H, $6a_C$-H, $6b_A$-H, $6b_B$-H), 3.46 (2H, m, 5_C-H, $6b_C$-H), 3.39−3.28 (6H, m, 2_B-H, 3_A-H, 3_C-H, 4_A-H, 4_B-H, 5_A-H), 3.23 (1H, bs, 2_C-H), 3.12 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 6.1 Hz, 2_A-H), 3.06 (1H, m, 4_C-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8 ($4_{A'}$-C), 166.4 (CN), 146.7 ($1_{B'}$-C), 136.9 ($6_{A'}$-C), 135.5 ($2_{A'}$-C), 128.4 ($3_{B'}$-C), 126.0 ($1_{A'}$-C), 123.6 ($3_{A'}$-C), 120.3 ($5_{A'}$-C), 119.9 ($2_{B'}$-C), 100.6 (1_C-C), 100.2 (1_B-C), 82.8 (1_A-C), 79.6 (4_A-C), 79.4 (4_B-C), 79.1 (5_A-C), 77.6 (3_A-C), 73.2 (5_C-C), 73.1 (3_C-C), 72.9 (3_B-C), 72.4 (2_A-C), 72.3 (2_C-C), 71.7 (2_B-C), 71.5 (5_B-C), 69.7 (4_C-C), 60.8 (6_A-C), 60.5 (6_C-C), 60.1 (6_B-C), 31.6 (CH_2S); MS (ESI-TOF) m/z 1672.27 $[M + Na]^+$.

Complex ***19-Zn***. Yellow powder, 60 mg, yield 68%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.95 (1H, s, CHN), 7.84 (1H, bs, $2_{B'}$-H), 7.38 (2H, bs, $2_{A'}$-H, $3_{B'}$-H), 7.21 (1H, d, J_{ortho} 8.6, $6_{A'}$-H), 6.65 (1H, d, J_{ortho} 8.6, $5_{A'}$-H), 5.58 (2H, m, 2_B-OH, 3_A-OH), 5.54 (1H, d, $J_{H,OH}$ 6.2, 2_C-OH), 5.48 (3H, m, 2_D-OH, 3_B-OH, 3_C-OH), 5.24 (1H, d, $J_{H,OH}$ 6.0, 2_A-OH), 5.05 (1H, d, $J_{1,2}$ 3.4, 1_C-H), 5.00 (2H, m, 1_B-H, 1_D-H), 4.93 (2H, m, 3_D-OH, 4_D-OH), 4.73 (1H, t, $J_{H,OH}$ 5.6, 6_A-OH), 4.58 (1H, t, $J_{H,OH}$ 5.1, 6_C-OH), 4.53 (2H, m, 6_B-OH, 6_D-OH), 4.15 (1H, d, $J_{1,2}$ 9.6, 1_A-H), 3.84 (1H, d, J_{gem} 12.8, SC*H*HPh), 3.80 (1H, m, $6a_A$-H), 3.71 (1H, d, J_{gem} 12.8, SC*H*HPh), 3.67−3.56 (10H, m, 3_B-H, 3_C-H, 5_B-H, 5_C-H, $6a_B$-H, $6a_C$-H, $6a_D$-H, $6b_A$-H, $6b_B$-H, $6b_C$-H), 3.47 (2H, m, 5_D-H, $6b_D$-H), 3.39−3.22 (9H, m, 2_B-H, 2_C-H, 2_D-H, 3_A-H, 3_D-H, 4_A-H, 4_B-H, 4_C-H, 5_A-H), 3.12 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 6.0 Hz, 2_A-H), 3.06 (1H, q, $J_{4,5}$ = $J_{4,3}$ = $J_{H,OH}$ 5.8 Hz, 4_D-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.2 ($4_{A'}$-C), 162.1 (CN), 139.1 ($1_{B'}$-C), 136.0 ($2_{A'}$-C), 135.6 ($6_{A'}$-C), 127.2 ($3_{B'}$-C), 123.2 ($5_{A'}$-C), 121.5 ($1_{A'}$-C), 118.5 ($3_{A'}$-C), 116.3 ($2_{B'}$-C), 100.6 (1_B-C, 1_D-C), 100.3 (1_C-C), 83.2 (1_A-C), 79.5 (4_B-C, 4_C-C), 79.4 (5_A-C), 79.3 (4_A-C), 77.6 (3_A-C), 73.4 (5_D-C), 73.2 (3_D-C), 73.0 (3_B-C, 3_C-C), 72.4 (2_A-C), 72.3 (2_D-C), 71.9 (2_B-C, 2_C-C), 71.6 (5_B-C, 5_C-C), 69.8 (4_D-C), 60.9 (6_D-C), 60.8 (6_A-C), 60.1 (6_B-C, 6_C-C), 31.8 (CH_2S); MS (ESI-TOF) m/z 1792.11 $[M + Na]^+$.

Complex ***19-U***. Orange powder, 69 mg, yield 70%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.57 (1H, s, CHN), 7.75 (2H, bs, $2_{A'}$-H, $2_{B'}$-H), 7.59 (1H, d, J_{ortho} 8.5, $6_{A'}$-H), 7.57 (1H, bs, $3_{B'}$-H), 6.95 (1H, d, J_{ortho} 8.5, $5_{A'}$-H), 5.60 (1H, d, $J_{H,OH}$ 6.2, 2_B-OH), 5.55 (1H, d, $J_{H,OH}$ 3.0, 3_A-OH), 5.52−5.48 (4H, m, 2_C-OH, 2_D-OH, 3_B-OH, 3_C-OH), 5.26 (1H, d, $J_{H,OH}$ 6.2, 2_A-OH), 5.07 (1H, d, $J_{1,2}$ 3.4, 1_C-H), 5.01 (2H, m, 1_B-H, 1_D-H), 4.96 (1H, d, $J_{H,OH}$ 5.6, 4_D-OH), 4.94 (1H, d, $J_{H,OH}$ 4.9, 3_D-OH), 4.77 (1H, t, $J_{H,OH}$ 5.6, 6_A-OH), 4.58 (1H, t, $J_{H,OH}$ 4.5, 6_C-OH), 4.53 (2H, m, 6_B-OH, 6_D-OH), 4.17 (1H, d, $J_{1,2}$ 9.5, 1_A-H), 3.96 (1H, d, J_{gem} 12.9, SC*H*HPh), 3.82 (2H, m, $6a_A$-H, SC*H*HPh), 3.66−3.56 (10H, m, 3_B-H, 3_C-H, 5_B-H, 5_C-H, $6a_B$-H, $6a_C$-H, $6a_D$-H, $6b_A$-H, $6b_B$-H, $6b_C$-H), 3.48 (2H, m, 5_D-H, $6b_D$-H), 3.40 (2H, m, 3_A-H, 3_D-H), 3.36−3.24 (7H, m, 2_B-H, 2_C-H, 2_D-H, 4_A-H, 4_B-H, 4_C-H, 5_A-H), 3.13 (1H, q, $J_{2,3}$ = $J_{2,1}$ = $J_{H,OH}$ 6.2 Hz, 2_A-H), 3.08 (1H, q, $J_{4,5}$ = $J_{4,3}$ = $J_{H,OH}$ 5.6 Hz, 4_D-H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.3 ($4_{A'}$-C), 165.8 (CN), 146.3 ($1_{B'}$-C), 136.9 ($6_{A'}$-C), 135.5 ($2_{A'}$-C), 128.3 ($3_{B'}$-C), 125.5 ($1_{A'}$-C), 123.2 ($3_{A'}$-C), 120.3 ($5_{A'}$-C), 120.0 ($2_{B'}$-C), 100.4 (1_B-C, 1_D-C), 100.0 (1_C-C), 82.7 (1_A-C), 79.4 (4_B-C, 4_C-C), 79.1 (4_A-C), 79.0 (5_A-C), 77.5 (3_A-C), 73.1 (5_D-C), 73.0 (3_D-C), 72.7 (3_B-C, 3_C-C), 72.3 (2_A-C), 72.2 (2_D-C), 71.7 (2_B-C), 71.6 (2_C-C), 71.3 (5_B-C, 5_C-C), 69.6 (4_D-C), 60.7 (6_A-C), 60.3 (6_D-C), 59.9 (6_B-C, 6_C-C), 31.3 (CH_2S); MS (ESI-TOF) m/z 1996.75 $[M + Na]^+$.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **2**−**13** and ^{1}H and heteronuclear single quantum coherence (HSQC) 2D-NMR spectra for compounds **14**−**19** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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