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Synthesis of Multivalent Glycoclusters from 1-Thio-β-D-galactose and Their Inhibitory Activity against the β-Galactosidase from *E. coli*

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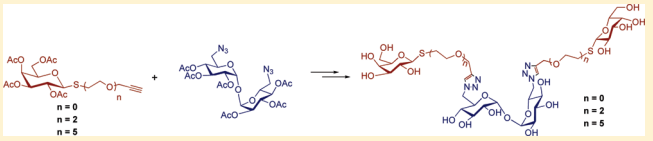
Supporting Information

ABSTRACT: The synthesis of multivalent glycoclusters, designed to be compatible with biological systems, is reported. A variety of 1-thio-β-D-galactosides linked to a terminal triple bond through oligoethyleneglycol chains of variable lengths has been synthesized. Also, azide-containing oligosaccharide scaffolds were prepared from trehalose, maltose, and maltotriose by direct azidation with $NaN_3/PPh_3/CBr_4$. Click reaction between the thiogalactoside residues and the azide scaffolds under microwave irradiation afforded a family of glycoclusters containing 1 to 4 residues of 1-thio-β-D-galactose. The yields went from moderate to excellent, depending on the valency of the desired product. Deacetylation with $Et_3N/MeOH/H_2O$ led to the final products. Complete characterization of the products was performed by NMR spectroscopy and HR-MS techniques. Their activities as inhibitors of β-galactosidase from *E. coli* were determined by using the Lineweaver−Burk method. The use of hydrophilic carbohydrate scaffolds for the synthesis of multivalent galactosides represents an interesting approach to improve their pharmacokinetics and bioavailability. In addition, the presence of the thioglycosidic bond will improve their stability in biological fluids.



INTRODUCTION

Carbohydrate−protein interactions are involved in cellular recognition processes that include viral and bacterial infections, inflammation, and tumor metastasis.[1] Recognition events, occurring in the active sites of glycosyltransferases and glycosyl hydrolases, account for the metabolism of carbohydrates. In some natural systems, the sometimes weak binding affinity of carbohydrates to their receptors is overcome by a multivalent display of sugar residues at the surface of cells, which leads to the so-called "glycoside clustering effect".

During the last years, multivalent ligands having β-galactoside or β-lactoside epitopes attached to a variety of scaffolds have been synthesized.[2] Most of them present *O*-linked saccharides and their preparation involves classic glycosylating methods. To connect the epitope to the scaffold, oligoethyleneglycol (EG) linkers are usually employed, due to their wide biomedical applications,[3] flexibility, and ability to prevent nonspecific adsorption to proteins.[4] The preparation of a variety of multivalent ligands differing in EG linker lengths can contribute to elucidate the mechanisms involved in the recognition processes.[5,6] The "cluster effect" has been extensively studied for several lectin systems,[7] but little is known about the influence of the multivalency on the activity of glycosidases. So far, we have shown that a trivalent iminosugar displayed a 6-fold affinity enhancement toward Jack bean α-mannosidase.[8] Also, a recent report on the multivalent effect of fullerene iminosugar balls on the inhibition of α-glucosidases suggests that alternative binding mechanisms are operative.[9] The interaction of lactose-functionalized gold glyconanoparticles with a lectin and with the β-galactosidase from *Escherichia coli* has been evaluated.[10] The proper selection of ligand densities and spacers led to an increased resistance of the lactose moiety of the nanoparticle to hydrolysis by the enzyme.

The β-galactosidase from *E. coli* is highly specific for β-galactopyranosyl nonreducing moieties, which may be linked to a variety of aglycons.[11] The enzyme is able to recognize *C*- and *S*-galactosyl residues that, in turn, may act as moderate to good inhibitors of its hydrolytic activity.[12] The interaction of this β-galactosidase with several substrates has been studied by X-ray[13] and NMR[12,14,15] experiments, and we have synthesized a family of thiodisaccharides that display an important inhibitory activity against the enzyme.[16,17] In contrast to natural *O*-linked sugars, the *S*-carbohydrate mimetics are usually resistant to metabolic processes[18,19] and are seen as potential precursors of promising carbohydrate-based therapeutics.[20] Particularly, the resistance of glycoclusters to enzyme hydrolysis is crucial to circumvent degradation when they are internalized in the cell. When designing glycoclusters to study biological processes, specificity, affinity, and stability against glycolytic enzymes are important factors to be considered. We assumed that the replacement of the interglycosidic oxygen atom by a sulfur atom

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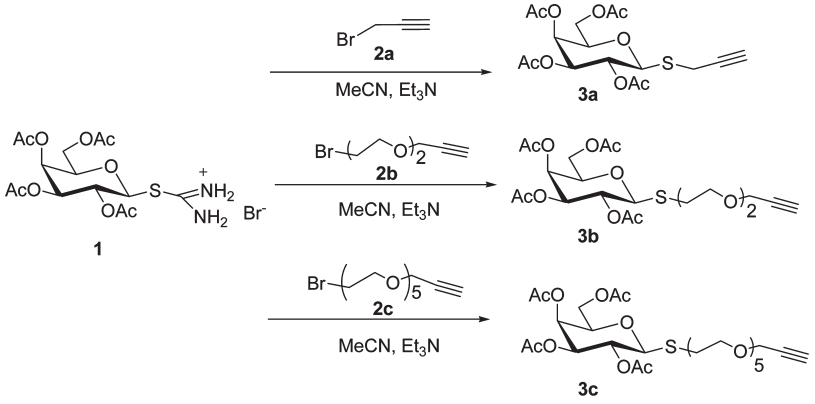
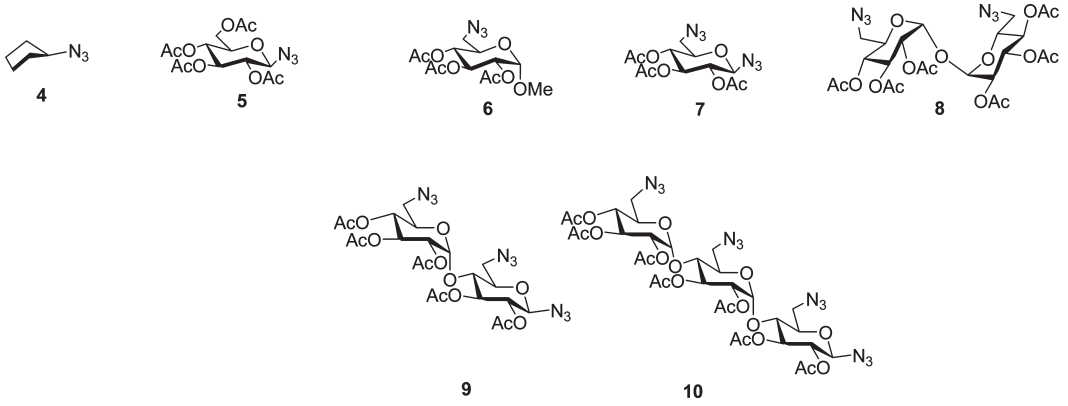
Scheme 1. Synthesis of Alkynyl-Armed *S*-Galactosides 3a−c



Scheme 2. Azide-Containing Oligosaccharide Scaffolds 4−10



in glycoclusters could increase the resistance to hydrolytic degradation by enzymes and can even cause inhibition of this activity. Therefore, we report here the synthesis of a family of glycoclusters based on carbohydrate scaffolds bearing one to four *S*-galactoside epitopes and EG spacers of different lengths. The copper-catalyzed azide−alkyne cycloaddition (CuAAC)[21] reaction was employed as the key step to connect the recognition elements to the scaffolds. The inhibition behavior against *E. coli* β-galactosidase was studied in order to determine the existence of cluster effects.

RESULTS AND DISCUSSION

The syntheses of the *S*-thiogalactosides (**3a**−**c**) having a terminal triple bond linked through spacers of different lengths were achieved by treatment of the thiouronium salt derived from galactose (**1**) with the appropriate bromides **2a**−**c** (Scheme 1). Linkers **2b** and **2c** were prepared by standard methods, starting from diethyleneglycol or pentaethyleneglycol and propargylbromide, followed by bromination. Thus, reaction of **1** with bromides **2a**, **2b**, or **2c**, in the presence of NEt_3,[22] led to thiogalactosides **3a**−**c**, respectively, in excellent isolated yields (71−100%). The spectra of compounds **3a**−**c** showed the characteristic signals of the H-1 protons in the region of 4.51−4.75 ppm, protected by the proximity of the sulfur atom, in accordance with those reported for other 1-thiogalactopyranosides.[17] Also, the diagnostic signals for the alkyne group in both the ^{1}H and ^{13}C NMR spectra were clearly observed (2.27−2.48 ppm for the alkyne proton, which appeared as a triplet, and signals at ∼80 and ∼74 ppm for the linked and terminal alkyne carbon atoms, respectively). The resonances of the nonequivalent protons of the methylene groups vicinal to the sulfur appeared well resolved in a clean region of the spectrum (2.85−3.58 ppm).

A variety of azide-containing scaffolds were prepared according to previously reported methods (Scheme 2). Thus, compound **4** was prepared by treatment of cyclopentanol with CBr_4/PPh_3/NaN_3. Reaction of glucose pentaacetate and azidotrimethylsilane in the presence of $SnCl_4$ afforded β-1-azidotetraacetilglucopyranose (**5**) in 94% yield.[23] Sugar scaffolds **6**−**10** were prepared by the direct azidation method reported by Kovensky, starting from the corresponding free sugar, sodium azide, PPh_3, and CBr_4 in anhydrous DMF, followed by acetylation.[24]

This methodology was also employed for the preparation of the 6,6′-diazido derivative **8** from trehalose, which was obtained in an excellent yield (80%), in comparison with previously reported methods using trehalose/PPh_3/CBr_4/LiN_3 (13%)[25] or by regioselective tosylation of C-6 and C-6′ followed by substitution with NaN_3 (14%).[26]

In the first instance, the coupling of thioglycoside **3a** with cyclopentylazide (**4**) was conducted as a model reaction, in order to verify if the conditions of the click reaction were compatible with the thioglycosides (Scheme 3). The reaction between **3a** and **4**, in the presence of copper sulfate and sodium ascorbate in DMF/H_2O, was completed at room temperature within 10−16 h.

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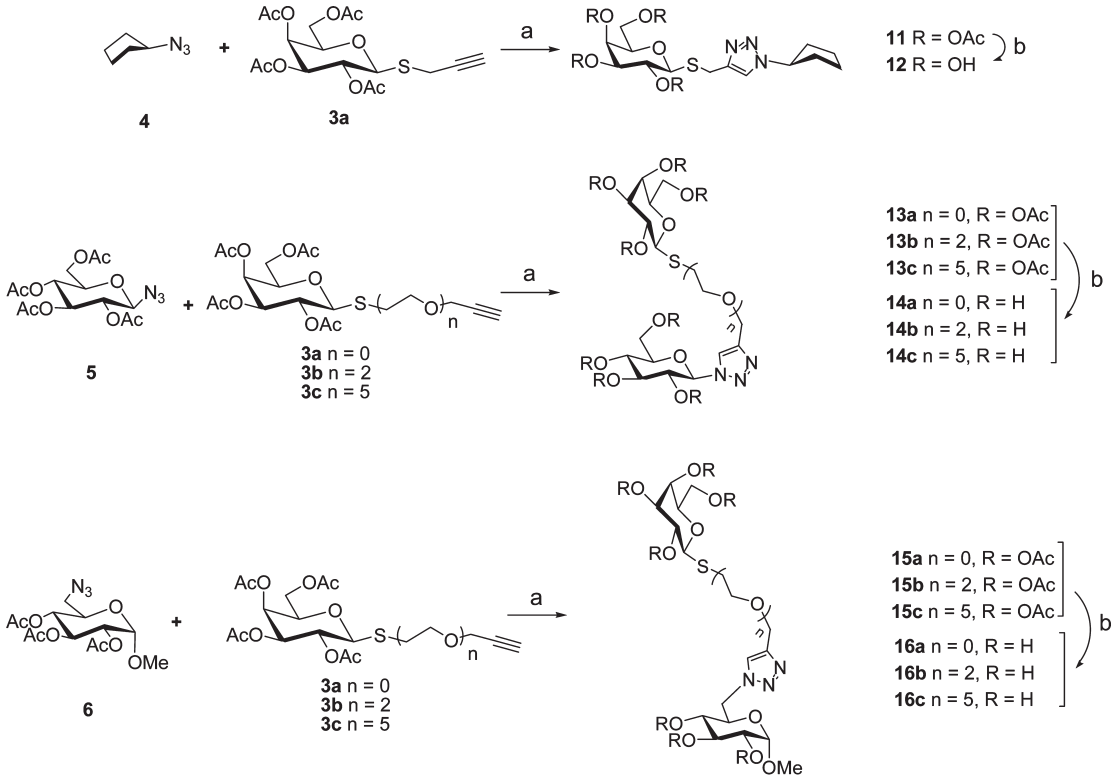
Scheme 3. Synthesis of Monovalent Thiogalactosides 11−16, Using the Click Reaction As the Key Step



(a) $CuSO_4$/sodium ascorbate/DMF/H_2O/microwave irradiation, 45 min.

(b) NEt_3/MeOH/H_2O (1:4:5), room temperature.

However, the reaction conducted under microwave irradiation required a much shorter reaction time (40−50 min), as reported for related systems.[27] These conditions proved to be very efficient in the case of the multivalent structures (polyazides) described below. In all cases, the consumption of the starting materials was followed by TLC and MS spectrometry. The latter technique was particularly useful to analyze reaction mixtures that involved polar partners, such as **3b** and **3c**, difficult to detect by TLC.

The click reaction between alkynes **3a**−**c** and the monoazides **5** or **6**, conducted under the conditions optimized for the coupling of **3a** and **4**, afforded the monovalent compounds **13a**−**c** and **15a**−**c** in 72−100% isolated yields. The ^{1}H NMR spectrum of these monovalent products showed the signals of both sugar residues, the glucose-scaffold and the thiogalactose, and a first order analysis was admitted. The assignments were further confirmed by 2D NMR techniques. In the description of the spectra, the signals corresponding to the thiogalactose moiety were labeled as "G". The thiogalactose anomeric protons (H-1G) of compounds **13a**−**c** and **15a**−**c** appeared at 4.33−4.63 ppm, whereas those of the Glc*p* moiety in **13a**−**c**, bonded to the nitrogen of triazole, appeared at a lower field (5.83−5.90 ppm). The aromatic proton of the triazole ring was identified as a singlet at δ 7.5−8.4. Accordingly, the ^{13}C NMR spectrum showed the characteristic signals at approximately 144 and 123 ppm respectively for C-4 and C-5 of the triazole ring. In all cases, the large $\Delta(\delta_{C\text{-}4} - \delta_{C\text{-}5})$ values observed for the different triazoles, ranging from 19 to 25 ppm, corroborated the 1,4-disubstituted pattern since much smaller values would be expected for 1,5-disubstituted regioisomers.[28] The methylene protons of the linker next to the sulfur appeared as two multiplets in the region 4.14−2.17 ppm, whereas the methylene protons of the ethyleneglycol moiety (CH_2O) showed a complex signal at ∼3.60 ppm. The resonances of H-6 and H-6′ in compounds **15a**−**c** were observed downfield, with respect to those of **13a**−**c**, due to the deshielding effect of the triazole ring at C-6. The collection of all these data served as a base for the spectroscopic analysis of the products of superior valency described below.

Two families of divalent cycloadducts **17a**−**c** and **19a**−**c** were prepared (Scheme 4), adjusting the reaction conditions to guarantee the reaction of the two azide groups, present in the scaffolds [a 2:1 molar ratio a alkyne (**3a**−**c**):diazide (**7** or **8**) was employed]. The reactions proceeded under microwave irradiation to afford the click products in high yields. Thus, the scaffold **7**, derived from glucose, led to adducts **17a**−**c** in 84−60% yield. The NMR spectra of these compounds were rather complex, in particular those of **17a**, due to the proximity of the signals of the two nonequivalent thiogalactose residues. Their structures were confirmed by comparison with the spectroscopic data of the monovalent compounds described above and with the assistance of 2D ^{1}H COSY and ^{1}H−^{13}C HSQC experiments.

For compound **17a**, the diagnostic resonance of H-1 (Glc residue) was observed as a doublet at 5.89 ppm, with a coupling constant of 8.9 Hz (β-configuration), and the resonances of the β-thiogalactoses anomeric protons, namely H-1G and H-1G′,

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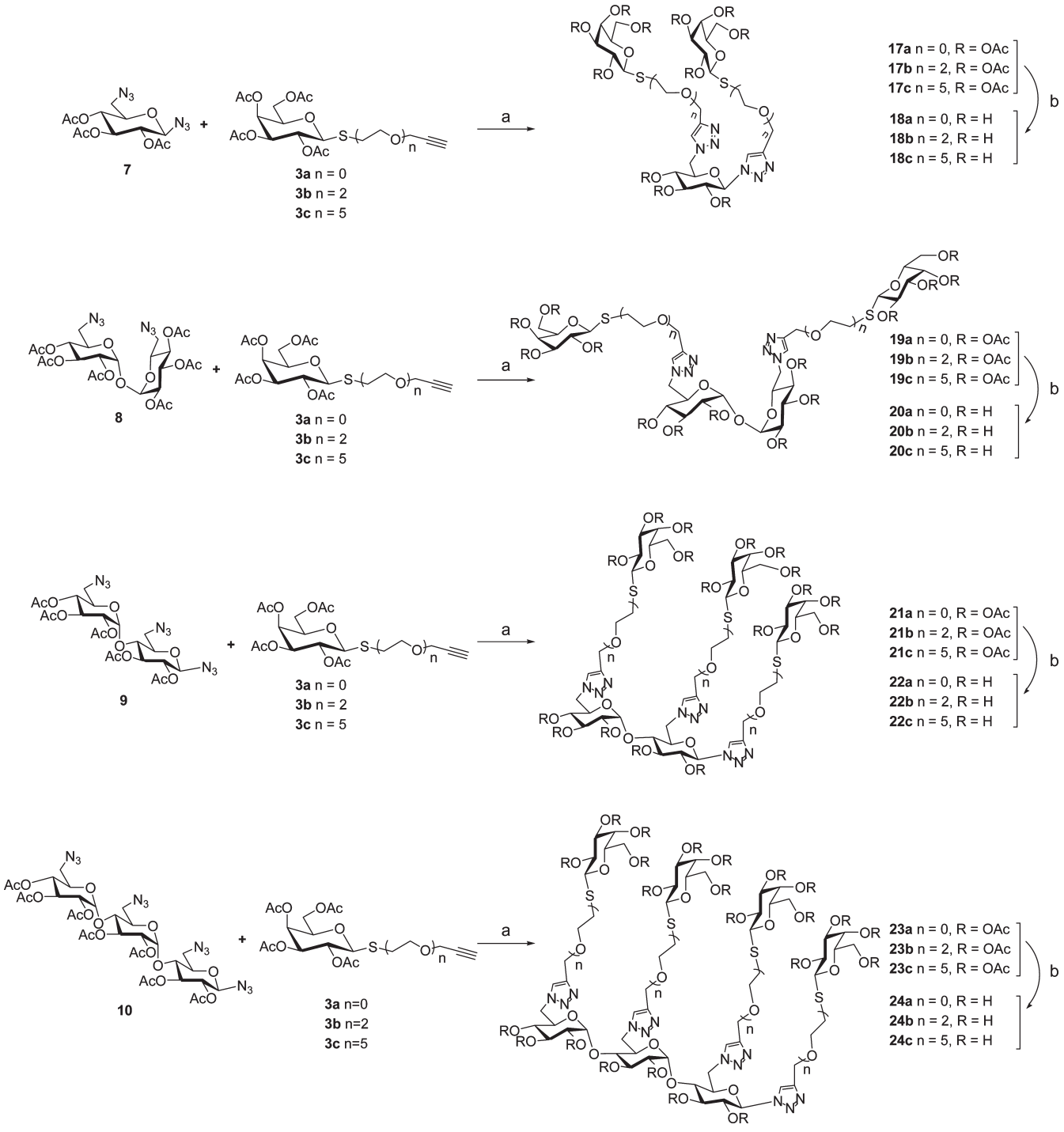
Scheme 4. Synthesis of Multivalent Thiogalactosides 17−24



appeared at 4.58 and 4.29 ppm ($J_{1,2} \approx 10.0$ Hz). As the length of the spacer increased in the sequence **17a** → **17b** → **17c**, the signals of both thiogalactose residues became more similar, and in fact, they appeared as identical in **17c**.

Reaction of the diazide scaffold **8** derived from trehalose with thiogalactosides **3a**−**c** afforded the symmetric divalent ligands **19a**−**c** in good yields (∼70%). One major advantage of the use of scaffold **8**, in terms of the characterization of the products, was the simplicity of their NMR spectra, similar to those of thiodisaccharides,[16,17,19b,29] as a result of the symmetry. Comparison of ^{1}H and ^{13}C NMR spectra showed a conserved resonance pattern in the series **19a** → **19b** → **19c** not only for the "trehalose core", but also for the thiogalactose residue. Molecular weights, determined by MS, confirmed the dimeric structures.

To synthesize trivalent ligands, the maltose-derived triazide scaffold **9** was prepared. Cycloaddition reaction between **9** and thioglycosides **3a**−**c** led to compounds **21a**−**c** in good yields (54−67%). The trivalent glycoclusters **21b** and **21c** appeared to be quite polar, due to the EG-spacer, and mixtures of EtOAc/MeOH were required for their purification by column chromatography. The

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NMR spectra, although highly complex were clear enough to confirm their structures. In agreement with the formation of the three triazole rings were observed three aromatic protons signals at 7.81−8.20 ppm and three pairs of aromatic carbons at ∼145 and ∼125 ppm. The two anomeric protons of maltose appeared at ∼6.2 ($J_{1,2} \approx 9.0$ Hz) and 5.46 ppm ($J_{1',2'} = 3.6$ Hz), corresponding to the β- and α-glucose residues (H-1 and H-1′, respectively). These signals correlated with peaks at 84.3 and 96.6 ppm, respectively, in the ^{13}C NMR spectrum. The resonances for the anomeric carbons of the three thiogalactose residues were detected at 82.8, 82.7, and 82.4 ppm for **21a**, but appeared as a single peak (83.6 ppm) for **21b** and **21c**. Furthermore, MS confirmed the structures proposed.

Tetravalent ligands **23a**−**c** were synthesized (∼50% yield) from the tetraazide-scaffold **10**, derived from maltotriose, and thioglycosides **3a**−**c**. Diagnostic signals were observed in the ^1H NMR spectrum: four aromatic proton signals (8.2−7.7 ppm) and four pairs of aromatic carbon signals (∼145 and ∼125 ppm). The MS confirmed the structures.

All the glycocluster derivatives obtained were *O*-deacetylated by treatment with $Et_3N/MeOH/H_2O$ 1:4:5 (Schemes 3 and 4), and the reactions were followed by TLC. After desalting with an anion exchange resin and purification by reverse-phase chromatography, the deprotected products were recovered in good yields, and analyzed by NMR recorded for D_2O solutions. As the complexity of the spectra increased with the number of galactose residues attached to the platforms, complete and detailed assignment of the signals was not possible for all the products. Signals of anomeric protons and carbons, corresponding both to the sugar scaffold and the thiogalactose residues, were diagnostic and are shown as a table in the Supporting Information. MS and elemental analysis of the products confirmed the structures of the free glycoclusters.

EVALUATION OF THE INHIBITORY ACTIVITY

The resistance of the new products to enzymatic hydrolysis was evaluated by using the β-galactosidase from *E. coli*. The glycoclusters were dissolved in sodium phosphate buffer (pH 7.3) in concentrations identical with that of the *o*-nitrophenyl β-D-galactopyranoside substrate employed for the determination of the K_m. The solutions were incubated with the enzyme at 37 °C. To determine the stability of the glycoclusters toward the enzyme, aliquots of the solution were taken and examined by TLC and NMR. Even compound **20b**, which is a weak inhibitor of the enzyme as discussed later, was recovered practically intact after 24 h of incubation. Therefore, the glycoclusters seem to be slow substrates, or no substrates at all, of the enzyme and resistant to enzymatic hydrolysis.

The glycoclusters act as inhibitors of the β-galactosidase from *E. coli* as their presence in the incubation medium inhibited the hydrolysis of the *o*-nitrophenyl β-D-galactopyranoside employed as substrate of the enzyme. The kinetics of the inhibition was determined by the double reciprocal plot method, as exemplified in Figure 1 for compound **24a**.

All the glycoclusters are competitive inhibitors of the enzyme in the micromolar range (Table 1). The inhibition constants (K_i) are similar to those determined for other β-thiogalactosides previously reported.[30]

The length of the linker influences the inhibitory activity of the molecule. For the series **14a** → **14b** → **14c**, it seems that longer linkers contribute to an increase of the inhibition, probably by enhancing the flexibility and facilitating the accommodation of the thiogalactoside residue in the active site.

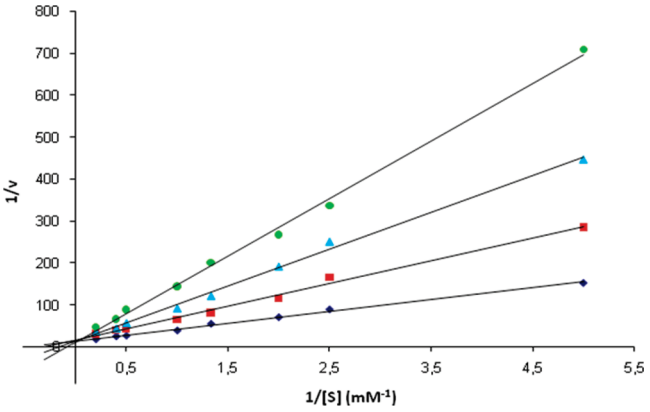

Figure 1. Lineweaver−Burk plot for inhibition of *E. coli* β-glactosidase by compound **24a** at different concentrations: (◆) 0.00, (■) 0.40, (▲) 0.80, and (●) 1.20 mM of inhibitor.

Table 1. K_i Values for the Inhibition of β-Galactosidase from *E. coli* by the β-*S*-Galactoside Glycoclusters, Determined by Using *o*-Nitrophenyl-β-D-galactopyranoside As Substrate, As Described in the Experimental Section[a]

		K_i value (mM)		
valency	compd	a	b	c
1	**12**	0.901 ± 0.009		
1	**14**	1.506 ± 0.009	1.192 ± 0.009	1.063 ± 0.009
1	**16**	0.283 ± 0.003	1.008 ± 0.007	1.102 ± 0.008
2	**18**	0.507 ± 0.007	0.713 ± 0.008	0.711 ± 0.006
2	**20**	0.419 ± 0.004	0.487 ± 0.005	0.490 ± 0.004
3	**22**	0.438 ± 0.006	0.386 ± 0.004	0.382 ± 0.004
4	**24**	0.254 ± 0.003	0.262 ± 0.003	0.255 ± 0.003

[a] The inhibition was competitive in all cases. (K_m = 1.378 ± 0.006 mM).

The comparison of K_i values for the monovalent derivatives shows the influence of the scaffold on the β-galactosidase inhibition as well. When the β-thiogalactose epitope is attached through a triazole ring to the C-6 of the scaffold (as in compound **16a**) an increment in the inhibition is observed, compared to the analogues that have thiogalactose attached to the triazole bonded to the anomeric position of the scaffold, as in **14a**. The increased inhibitory activity may be attributed to the higher flexibility of the ligand when linked to C-6, and to the presence of the vicinal heteroaromatic ring. In agreement with the higher inhibitory activity shown for compound **16a**, we have described that a β-thiogalactosyl residue attached to a flexible pentopyranose ring with an anomeric aromatic group results in a strong inhibition of *E. coli* β-galactosidase.[12,17] Thus, an increase of the linker length that separates the thiogalactose residue and the triazol, as in **16a** → **16b** → **16c**, results in a decrease of the inhibitory activity (K_i from 0.283 → 1.008 → 1.102). Therefore, when comparing the monovalent series **14a**−**c** and **16a**−**c**, the length of the linker has an opposite effect, which seems to depend on the relative position of the triazole on the scaffold.

As the scaffold for compounds **18a**−**c** is a 1,6-bistriazole-substituted monosaccharide, we can speculate that combined effects of the same kind as those operating in compounds **14a**−**c**

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and **16a**−**c** are involved. Thus, the K_i values for the series **18a** → **18b** → **18c** show that an increase in the distance between the thiosugar and the triazole ring at C-6 in the scaffold diminishes the inhibitory activity. This effect is opposite, and seems to be stronger, than the favorable effect imparted by longer linkers between the thiogalactose and the triazole bonded to C-1. The same tendency is observed for derivatives **20a** → **20b** → **20c**, which exhibited a somewhat higher activity, probably due to the role of the scaffold in the global shape of the glycocluster, that may affect the ability of the epitopes to reach the active site.

The K_i values listed in Table 1 show that moving from monovalent (**12**, **14a**−**c**, **16b**−**c**) to di- (**18a**−**c**, **20a**−**c**), tri- (**22a**−**c**), and tetravalent (**24a**−**c**) derivatives, increased inhibition is observed. However, this is probably due to a statistical effect, and no cluster or multivalency effect is observed for β-galactosidase inhibition. Cluster effects of multivalent azasugars on enzyme inhibition have been previously observed,[8] but only for some enzymes (for example, α-mannosidase), whereas for others no such effect was detected. Nevertheless, our present results show that the multivalent thiogalactosides are stronger inhibitors of galactosidase than the monomeric counterparts (with the exception of compound **16a**).

CONCLUSIONS

In conclusion, we report here an efficient and optimized synthetic strategy to obtain multivalent ligands bearing 1-thio-β-D-galactose residues, as promising molecules for in vivo studies. The reactions employed proved to be compatible with the thioglycosidic bonds. The acetylated precursors, as well as the free glycoclusters, were fully characterized by NMR spectroscopy and MS spectrometry. Moreover, as far as we know, this is the first report on the inhibitory behavior of multivalent thioglycoclusters.

These compounds are also interesting as putative inhibitors of galectin-mediated processes. Multivalent ligands having *O*-linked β-galactoside or β-lactoside residues attached to a variety of scaffolds have been synthesized and evaluated as inhibitors of lectins.[2] Also, some *S*-galactosides have shown inhibitory activity toward galectins.[31] Studies on the affinity of the glycoclusters reported here to lectins are in progress.

EXPERIMENTAL SECTION

General Methods. Analytical thin layer chromatography (TLC) was performed on Silica Gel 60 F254 aluminum supported plates (layer thickness 0.2 mm) with solvent systems given in the text. Visualization of the spots was effected by exposure to UV light and charring with a solution of 5% (v/v) sulfuric acid in EtOH, containing 0.5% *p*-anisaldehyde. Column chromatography was carried out with Silica Gel 60 (230−400 mesh). Optical rotations were measured at 20 °C in a 1 cm cell in the stated solvent; $[\alpha]_D$ values are given in 10^{-1} deg·cm^2·g^{-1} (concentration *c* given as g/100 mL). Microwave irradiation was carried out in a CEM Discover instrument, at 70 °C (power max 300 W). High-resolution mass spectra HRMS where obtained by Electrospray Ionization (ESI) and Q-TOF detection. For ^{1}H, ^{13}C nuclear magnetic resonance (NMR) spectra, chemical shifts are reported in parts per million relative to tetramethylsilane or a residual solvent peak ($CHCl_3$: ^{1}H, δ = 7.26; ^{13}C, δ = 77.2). Assignments of ^{1}H and ^{13}C were assisted by 2D ^{1}H−COSY and 2D ^{1}H−^{13}C CORR experiments.

General Procedure for the Synthesis of the Alkylbromides 2b and 2c. Diethylene glycol or pentaethylene glycol (4.71 mmol) and sodium hydride (170 mg, 7.08 mmol) were dissolved in anhydrous DMF (40 mL) and the mixture was stirred at 0 °C for 30 min. Then, propargyl bromide (0.60 mL, 7.08 mmol) was added dropwise and the resulting mixture was stirred for 6 h at rt. Methanol (5 mL) was added. The mixture was concentrated under reduced pressure and the residue was dissolved in EtOAc (20 mL). The organic layer was washed with saturated ammonium chloride (20 mL), the aqueous layer was extracted with EtOAc (2 × 20 mL), and the combined organic extracts were concentrated. The residue was purified by flash chromatography to give the corresponding alkynylalcohols (60−66% yield) as colorless oils, which were employed for the bromination step. Thus, the alkynylalcohols (0.634 mmol) and CBr_4 (232 mg, 0.697 mmol) were dissolved in CH_2Cl_2 (1 mL) and PPh_3 (183 mg, 0.697 mmol) was added slowly while the mixture was stirred at 0 °C. The resulting mixture was stirred at rt until TLC and MS indicated the disappearance of the starting materials (4 h). The mixture was concentrated under reduced pressure and the residue was subjected to flash chromatography with hexane/EtOAc (1:1) as eluent.

Compound 2b: yield 94%; R_f 0.49 (hexane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.22 (d, 2 H, $J_{1,3}$ = 2.4 Hz, H-3), 3.82 (t, 2 H, $J_{8,9}$ = 6.3 Hz, H-8), 3.71 (s, 4 H, H-5, H-6), 3.48 (t, 2 H, $J_{8,9}$ = 6.3 Hz, H-9), 2.44 (t, $J_{1,3}$ = 2.4 Hz, H-1); ^{13}C NMR (125 MHz, $CDCl_3$) δ 79.5 (C-2), 74.6 (C-1), 71.2 (C-8), 70.3, 69.0 (C-5, C-6), 58.5 (C-3), 30.2 (C-9). Anal. Calcd for $C_7H_{11}BrO_2$: C, 40.60; H, 5.35. Found: C, 40.52; H, 5.09. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_7H_{11}BrNaO_2$ 298.9835, found 298.9844.

Compound 2c: yield 82%; R_f 0.33 (hexane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (d, 2 H, $J_{1,3}$ = 2.4 Hz, H-3), 3.81 (t, 2 H, $J_{8,9}$ = 6.3 Hz, H-8), 3.69−3.64 (s, 16 H, H-5, H-6, H-8, H-9, H-11, H-12, H-14, H-15), 3.48 (t, 2 H, $J_{8,9}$ = 6.3 Hz, H-9), 2.43 (t, $J_{1,3}$ = 2.4 Hz, H-1); ^{13}C NMR (125 MHz, $CDCl_3$) δ 79.7 (C-2), 74.5 (C-1), 71.2 (C-17), 70.3, 69.0 (C-5, C-6, C-8, C-9, C-11, C-12, C-14, C-15), 58.4 (C-3), 30.4 (C-18). Anal. Calcd for $C_{13}H_{23}BrO_5$: C, 46.03; H, 6.83. Found: C, 46.33; H, 6.56. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{23}BrNaO_5$ 361.0627, found 361.0615.

General Procedure for the Synthesis of the Thiogalactosides 3a−c. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl isothiouronium bromide[16] (220 mg, 1.063 mmol) and the corresponding alkylbromide (**2a**, **2b**, or **2c**, 1.594 mmol) were dissolved in anhydrous acetonitrile (4 mL) and NEt_3 (371 μL, 2.658 mmol) was added dropwise. The resulting mixture was stirred at rt for 3 h, when TLC and MS indicated complete consumption of the starting material. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (cyclohexane/EtOAc 7:3).

Compound 3a: yield 100%; $[\alpha]^{20}_D$ −47.6 (*c* 0.7, $CHCl_3$); R_f 0.58 (hexane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (dd, 1 H, $J_{4,5}$ = 1.0 Hz, $J_{3,4}$ = 3.4 Hz, H-4), 5.27 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, H-2), 5.10 (dd, 1 H, $J_{3,4}$ = 3.2 Hz, $J_{2,3}$ = 10.0 Hz, H-3), 4.75 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.18 (dd, 1 H, $J_{5,6a}$ = 6.7 Hz, $J_{6a,6b}$ = 11.3 Hz, H-6a), 4.12 (dd, 1 H, $J_{5,6b}$ = 6.5 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6b), 3.97 (ddd, 1 H, $J_{4,5}$ = 1.1 Hz, $J_{5,6b}$ = 6.5 Hz, $J_{5,6a}$ = 6.7 Hz, H-5), 3.58, 3.31 (2 dd, 2 H, *J* = 2.6 Hz, J_{gem} = 16.5 Hz, CH_2S), 2.27 (t, 1 H, *J* = *J*′ = 2.6 Hz, C≡*CH*), 2.08, 2.07, 2.05, 2.04 (4 s, 12 H, 4 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 169.8, 169.7, 169.6 (−$COCH_3$), 82.5 (C-1), 78.7 (−*C*≡CH), 74.5 (C-5), 71.9, 71.8 (C-3, C≡*CH*), 67.2 (C-2), 67.0 (C-4), 61.3 (C-6), 20.7, 20.6 (×2), 20.5 (CH_3CO), 17.5 (SCH_2). Anal. Calcd for $C_{17}H_{22}O_9S$: C, 50.74; H, 5.51; S, 7.97. Found: C, 50.46; H, 5.77; S, 7.92. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{22}NaO_9S$ 425.0882, found 425.0884.

Compound 3b: yield 85%; $[\alpha]^{20}_D$ −6.9 (*c* 0.8, $CHCl_3$); R_f 0.46 (hexane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (dd, 1 H, $J_{4,5}$ = 0.9 Hz, $J_{3,4}$ = 3.4 Hz, H-4), 5.21 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, H-2), 5.05 (dd, 1 H, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.0 Hz, H-3), 4.65 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.21 (d, 2 H, *J* = 2.3 Hz, CH_2C≡CH), 4.16 (dd, 1 H, $J_{5,6a}$ = 6.6 Hz, $J_{5,6b}$ = 11.3, H-6a), 4.11 (dd, 1 H, $J_{5,6b}$ = 6.6 Hz, $J_{6a,6b}$ = 11.3, H-6b), 3.96 (ddd, 1 H, $J_{4,5}$ = 0.9 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 6.6 Hz, H-5), 3.77−3.64 (m, 6 H, CH_2O), 3.00 (ddd, 1 H, *J* = 6.9 Hz, *J* = 7.0, J_{gem} = 13.8 Hz, *CH*S), 2.79 (ddd, 1 H, *J* = 5.8 Hz, *J* = 7.0, J_{gem} = 13.8 Hz, *CH*S), 2.48 (t, *J* = 2.3 Hz,

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$CH_2C{\equiv}CH$), 2.16, 2.07, 2.05, 1.98 (4 s, 12 H, 4 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 170.2, 170.0, 169.6 ($-COCH_3$), 84.1 (C-1), 79.5 ($C{\equiv}CH$), 74.7 (C-5), 74.3 ($-C{\equiv}CH$), 71.8 (C-3), 71.4, 70.1, 69.0 (CH_2O), 67.4, 67.3 (C-4, C-2), 61.4 (C-6), 58.4 ($CH_2C{\equiv}CH$), 29.4 (CH_2S), 20.8, 20.7 (× 2), 20.6 (CH_3CO). Anal. Calcd for $C_{21}H_{30}O_{11}S$: C, 51.42; H, 6.16; S, 6.54. Found: C, 51.40; H, 6.12; S, 6.32. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{30}NaO_{11}S$ 513.1407, found 513.1401.

Compound 3c: yield 71%; $[\alpha]^{20}_D$ −12.9 (c 0.7, $CHCl_3$); R_f 0.33 (hexane/EtOAc 1:3); ^1H NMR (500 MHz, $CDCl_3$) δ 5.30 (br d, 1 H, $J_{4,5}$ < 1.0 Hz, $J_{3,4}$ = 3.3 Hz, H-4), 5.07 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, H-2), 4.92 (dd, 1 H, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.0 Hz, H-3), 4.51 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.07 (d, 2 H, J = 2.4 Hz, $CH_2C{\equiv}CH$), 4.02 (dd, 1 H, $J_{5,6a}$ = 6.5 Hz, $J_{6a,6b}$ = 11.6 Hz, H-6a), 4.00 (dd, 1 H, $J_{5,6b}$ = 6.7 Hz, $J_{6a,6b}$ = 11.6 Hz, H-6b), 3.86 (t, 1 H, $J_{5,6a}$ = 6.5 Hz, $J_{5,6b}$ = 6.7 Hz, H-5), 3.60−3.49 (m, 18 H, 9 CH_2O), 2.85, 2.67 (2 m, 2 H, J = 6.8 Hz, J_{gem} = 13.5 Hz, CH_2S), 2.39 (t, 1 H, J = 2.4 Hz, $-C{\equiv}CH$), 2.03, 1.94, 1.92, 1.85 (4 s, 12 H, 4 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 170.4, 170.2, 169.8 ($-COCH_3$), 84.28 (C-1), 80.1 ($-C{\equiv}CH$), 75.0 ($-C{\equiv}CH$), 74.7 (C-5), 72.1 (C-3), 72.1, 71.5, 70.9 (×4), 70.6 (×2), 69.4 (CH_2O), 67.7 (×2) (C-2, C-4), 61.8 (C-6), 58.6 ($CH_2C{\equiv}CH$), 29.7 (CH_2S), 21.0, 20.9 (×2), 20.8 (CH_3CO). Anal. Calcd for $C_{27}H_{42}O_{14}S$: C, 52.08; H, 6.80; S, 5.15. Found: C, 52.05; H, 6.86; S, 5.02. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{27}H_{42}NaO_{14}S$ 645.2193, found 645.2199.

General Procedures for the Synthesis of Azide-Containing Scaffolds 5−10

Procedure A: Compounds **6**−**10** were synthesized from the corresponding free sugar, sodium azide, PPh_3, and CBr_4 in anhydrous DMF as previously described.[21c,24] These products showed identical properties to those previously reported.[21c,24,26] Synthesis of **8** from trehalose was achieved in 80% yield, following the same methodology described to obtain the diazido derivative of maltose (**9**). Purification of **8** by column chromatography was performed with hexane/EtOAc (3:2 → 1:1).

Procedure B: Synthesis of 5: Glucose pentaacetate (150 mg, 0.384 mmol) and azidotrimethylsilane (56 μL, 0.423 mmol) were dissolved in anhydrous CH_2Cl_2 (4 mL) and $SnCl_4$ (45 μL, 0.384 mmol) was added dropwise.[23] The resulting mixture was stirred at rt until TLC indicated the disappearance of starting material (2 h). The mixture was extracted with $NaHCO_3$ (3 × 20 mL) and then washed with water (20 mL). The organic layer was dried (Na_2SO_4) and filtered, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography to give **5** (135 mg, 94% yield), mp 128.5, $[\alpha]^{20}_D$ −30.0 (c 0.5, $CHCl_3$) {lit.[32] mp 129 °C; $[\alpha]_D$ −33.0 (c 0.7, $CHCl_3$)}.[33]

General Procedure for the Click Reaction: Synthesis of Compounds 11, 13a−c, 15a−c, 19a−c, 21a−c, and 23a−c

The corresponding azido-saccharide **5**−**10** (1.00 mmol) and the selected alkynyl-thiogalactoside **3a**−**c** (1.00 mmol per mol of reacting azide) were dissolved in a dioxane/H_2O mixture (8:2 mL, 35 mL). Copper sulfate (0.25 mmol per mol of reacting azide) and sodium ascorbate (0.50 mmol per mol of azide reacting group) were added, and the mixture was stirred at rt until MS indicated the disappearance of starting materials and intermediates (10−16 h). Alternatively, the mixture was stirred under microwave irradiation during 40 min. The mixture was then poured into a 1:1 H_2O/NH_4Cl solution (60 mL) and extracted with EtOAc (4 × 30 mL). The organic layer was dried (Na_2SO_4) and filtered, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography, using the solvent systems indicated in each case.

Compound 11: solvent system hexane/EtOAc (2:1); yield 72%; $[\alpha]^{20}_D$ −43.1 (c 0.6, $CHCl_3$); R_f 0.35 (hexane/EtOAc 1:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1 H, H-triazole), 5.44 (dd, 1 H, $J_{4,5}$ = 1.0 Hz, $J_{3,4}$ = 3.4 Hz, H-4), 5.25 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, H-2), 5.05 (dd, 1 H, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.0 Hz, H-3), 4.91 (m, 1 H, J = 6.4 Hz, J = 7.5 Hz, CHN_{cyclo}), 4.63 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.12−4.08 (m, 3 H, H-6′a, H-6′b, CHS), 3.95 (ddd, 1 H, $J_{4,5}$ = 1.0 Hz, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.4 Hz, H-5), 3.93 (d, 1 H, J_{gem} = 14.3 Hz, CHS), 2.30−2.23, 2.10−2.00 1.92−1.88, 1.79−1.75 (4 m, 8 H, CH_{2cyclo}), 2.16, 2.05, 2.03, 1.98 (4 s, 12 H, 4 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 170.2, 170.0, 169.6 (-$COCH_3$), 144.4 (C-4 triazole), 120.4 (C-5 triazole), 83.4 (C-1), 74.4 (C-5), 71.7 (C-3), 67.2 (×2) (C-2, C-4), 61.8 ($C\text{-}1_{cyclo}$), 61.2 (C-6), 33.3 ($C\text{-}2_{cyclo}$), 24.5 (CH_2S), 24.0 ($C\text{-}3_{cyclo}$), 20.7, 20.6 (×2), 20.5 ($-COCH_3$). Anal. Calcd for $C_{22}H_{31}N_3O_9S$: C, 51.45; H, 6.08; N, 8.18; S, 6.24. Found: C, 51.12; H, 6.34; N, 7.98; S, 6.10. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{22}H_{31}N_3NaO_9S$ 536.1679, found 536.1697.

Compound 13a: solvent system hexane/EtOAc (1:1); yield 100%; mp 99−101 °C; $[\alpha]^{20}_D$ −49.7 (c 0.5, $CHCl_3$); R_f 0.28 (hexane/EtOAc 1:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1 H, H-triazole), 5.87 (m, 1 H, $J_{1,2}$ = 9.1 Hz, H-1), 5.47−5.44 (m, 3 H, H-2, H-3, H-4G), 5.34 (m, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 5.24 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.9 Hz, H-2G), 5.17 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G), 4.36 (dd, 1 H, $J_{5G,6aG}$ = 5.2 Hz, $J_{6aG,6bG}$ = 10.5 Hz, H-6aG), 4.33 (d, 1 H, $J_{1G,2G}$ = 9.9 Hz, H-1G), 4.33 (dd, 1 H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6a), 4.16 (dd, 1 H, $J_{5,6b}$ = 2.1 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6b), 4.14 (d, 1 H, J_{gem} = 14.2 Hz, CHS), 4.09 (ddd, 1 H, $J_{4G,5G}$ = 1.0 Hz, $J_{5G,6aG}$ = 5.1 Hz, $J_{5G,6bG}$ = 7.3 Hz, H-5G), 4.03 (dd, 1 H, $J_{5G,6bG}$ = 7.5 Hz, $J_{6aG,6bG}$ = 10.5 Hz, H-6bG), 4.02 (ddd, 1 H, $J_{5,6b}$ = 2.1 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{4,5}$ = 10.0 Hz, H-5), 3.85 (d, 1 H, J_{gem} = 14.2 Hz, CHS), 2.19, 2.15, 2.08, 2.07 (×2), 1.99, 1.97, 1.91 (8 s, 24 H, 8 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.4 (×2), 170.0, 169.8, 169.6, 169.4 (×2) ($-COCH_3$), 143.9 (C-4 triazole), 121.1 (C-5 triazole), 86.0 (C-1), 80.7 (C-1G), 75.2 (C-5), 73.6 (C-5G), 72.3* (C-2), 71.6 (C-3G), 70.5* (C-3), 67.7 (C-4), 67.5, 67.4 (C-2G, C-4G), 61.6, 61.4 (C-6, C-6G), 23.4 (CH_2S), 20.7, 20.6, 20.5, 20.4, 20.1 (CH_3CO). Anal. Calcd for $C_{31}H_{41}N_3O_{18}S$: C, 48.00; H, 5.33; N, 5.42; S, 4.13. Found: C, 47.91; H, 5.12; N, 5.12; S, 4.25. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{31}H_{41}N_3NaO_{18}S$ 798,2004, found 798,1980.

Compound 13b: solvent system hexane/EtOAc (1:1); yield 89%; $[\alpha]^{20}_D$ −19.7 (c 0.8, $CHCl_3$); R_f 0.34 (hexane/EtOAc 1:3); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1 H, H-triazole), 5.90 (d, 1 H, $J_{1,2}$ = 9.0 Hz, H-1), 5.46 (dd, 1 H, $J_{1,2}$ = 9.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.43 (dd, 1 H, $J_{4',5'}$ = 0.9 Hz, $J_{3',4'}$ = 3.3 Hz, H-4G), 5.43 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 5.25 (dd, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 5.21 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 10.0 Hz, H-2G), 5.05 (dd, 1 H, $J_{3G,4G}$ = 3.3 Hz, $J_{3G,4G}$ = 10.0 Hz, H-3G), 4.70 (sa, 2 H, CH_2Ar), 4.63 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.30 (dd, 1 H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.7 Hz, H-6a), 4.16 (m, 2 H, H-6a, H-6b), 4.11 (dd, 1 H, $J_{5G,6bG}$ = 7.5 Hz, $J_{6aG,6bG}$ = 11.3 Hz, H-6bG), 4.03 (ddd, 1 H, $J_{5,6b}$ = 1.9 Hz, $J_{5,6a}$ = 5.0 Hz, $J_{4,5}$ = 10.0 Hz, H-5), 3.97 (ddd, 1 H, $J_{4G,5G}$ = 0.9 Hz, $J_{5G,6aG}$ = 6.5 Hz, $J_{5G,6bG}$ = 7.5 Hz, H-5G), 3.74−3.63 (m, 6 H, 3 CH_2O), 2.99 (m, 1 H, J = 6.7 Hz, J = 7.1 Hz, J_{gem} = 13.5 Hz, CHS), 2.80 (m, 1 H, J = 6.1 Hz, J = 7.1 Hz, J_{gem} = 13.5 Hz, CHS), 2.15, 2.09, 2.07, 2.06, 2.05, 2.03, 1.99, 1.88 (8 s, 24 H, 8 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.3, 170.1, 169.9, 169.8, 169.5, 169.2, 168.8 ($-COCH_3$), 145.7 (C-4 triazole), 120.1 (C-5 triazole), 85.6 (C-1), 84.0 (C-1G), 75.0 (C-5), 74.3 (C-5G), 72.6 (C-3), 71.7 (C-3G), 71.1, 70.2, 70.1, 69.6 (C-2, 3 CH_2O), 67.6 (C-4), 67.2 (×2) (C-2G, C-4G), 64.3 (CH_2Ar), 61.5, 61.3 (C-6, C-6G), 29.4 (CH_2S), 20.7, 20.6 (×2), 20.5, 20.4 (×2), 20.1 (×2) (CH_3CO). Anal. Calcd for $C_{35}H_{49}N_3O_{20}S$: C, 48.66; H, 5.72; N, 4.86; S, 3.71. Found: C, 48.55; H, 5.74; N, 4.76; S, 4.02. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{35}H_{49}N_3NaO_{20}S$ 886.2528, found 886.2495.

Compound 13c: solvent system hexane/EtOAc (1:9); yield 72%; $[\alpha]^{20}_D$ −12.1 (c 1.1, $CHCl_3$); R_f 0.39 (EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1 H, H-triazole), 5.83 (d, 1 H, $J_{1,2}$ = 8.7 Hz, H-1), 5.41−5.32 (m, 3 H, H-2, H-3, H-4G), 5.17 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 5.12 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 10.0 Hz, H-2G), 4.98 (dd, 1 H, $J_{3G,4G}$ = 3.3 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G), 4.63 (s, 2 H, CH_2Ar), 4.53

(d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.23 (dd, 1 H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6a), 4.09 (dd, 1 H, $J_{5,6b}$ = 2.1 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6b), 4.08 (dd, 1 H, $J_{5G,6aG}$ = 6.5 Hz, $J_{6aG,6bG}$ = 11.2 Hz, H-6aG), 4.04 (dd, 1 H, $J_{5G,6bG}$ = 6.5 Hz, $J_{6aG,6bG}$ = 11.3 Hz, H-6bG), 3.96 (ddd, 1 H, $J_{5,6b}$ = 2.0 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{4,5}$ = 10.0 Hz, H-5), 3.89 (br dd, 1 H, $J_{4G,5G}$ < 1.0 Hz, $J_{5G,6aG}$ = 6.5 Hz, $J_{5G,6bG}$ = 6.7 Hz, H-5G), 3.65−3.54 (m, 18 H, 9 CH_2O), 2.90, 2.73 (2 m, 2 H, J = 6.8 Hz, J_{gem} = 13.4 Hz, CH_2S), 2.09, 2.02, 2.01, 2.00, 1.98, 1.96, 1.91, 1.80 (8 s, 24 H, 8 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 170.7, 170.6, 170.3, 170.2, 169.9, 169.7, 169.2 (−$COCH_3$), 146.3 (C-4 triazole), 121.4 (C-5 triazole), 86.0 (C-1), 84.5 (C-1G), 75.4 (C-5), 74.8 (C-5G), 73.1 (C-3), 72.2 (C-3G), 71.5 (C-2), 70.8 (×6), 70.7, 70.6, 70.1 (9 CH_2O), 68.1 (C-4), 67.8 (C-2G), 67.7 (C-4G), 64.8 (CH_2Ar), 62.0, 61.9 (C-6, C-6G), 29.9 (CH_2S), 21.1, 21.0 (×2), 20.9, 20.8, 20.5 (×3) (−$COCH_3$). Anal. Calcd for $C_{41}H_{61}N_3O_{23}S$: C, 49.44; H, 6.17; N, 4.22; S, 3.22. Found: C, 49.59; H, 6.09; N, 4.30; S, 3.46. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{41}H_{61}N_3NaO_{23}S$ 1018.3314, found 1018.3353.

Compound 15a: solvent system hexane/EtOAc (2:3); yield 75%; mp 88−90 °C; $[\alpha]^{20}_D$ +20.1 (c 0.4, $CHCl_3$); R_f 0.34 (hexane/EtOAc 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1 H, H-triazole), 5.48 (dd, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 10.2 Hz, H-3), 5.43 (dd, 1 H, $J_{4G,5G}$ = 1.0 Hz, $J_{3G,4G}$ = 3.4 Hz, H-4G), 5.26 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 10.0 Hz, H-2G), 5.04 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G), 4.92 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 4.81 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 4.76 (dd, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 10.1 Hz, H-4), 4.57 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.57 (dd, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{6a,6b}$ = 14.5 Hz, H-6a), 4.42 (dd, 1 H, $J_{5,6b}$ = 7.9 Hz, $J_{6a,6b}$ = 14.5 Hz, H-6b), 4.21 (ddd, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 7.9 Hz, $J_{4,5}$ = 10.1 Hz, H-5), 4.13 (m, 3 H, H-6aG, H-6bG, CHS), 3.96 (ddd, 1 H, $J_{4G,5G}$ = 1.0 Hz, $J_{5G,6aG}$ = $J_{5G,6bG}$ = 6.5 Hz, H-5G), 3.91 (d, 1 H, J_{gem} = 14.3 Hz, CHS), 3.18 (s, 3 H, −OCH_3), 2.16, 2.10, 2.06 (×2), 2.05, 2.01, 1.97 (7 s, 21 H, 7 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.2, 170.1, 169.9 (×2), 169.8, 169.6 (−$COCH_3$), 144.8 (C-4 triazole), 123.5 (C-5 triazole), 96.7 (C-1), 82.9 (C-1G), 74.4 (C-5G), 71.7 (C-3G), 70.7 (C-2), 69.7 (×2) (C-4, C-3), 67.6 (C-5), 67.3, 67.2 (C-2G, C-4G), 61.3 (C-6G), 55.5 (−OCH_3), 50.7 (C-6), 24.1 (CH_2S), 20.7 (×3), 20.6 (×3) (−$COCH_3$). Anal. Calcd for $C_{30}H_{41}N_3O_{17}S$: C, 48.19; H, 5.53; N, 5.62; S, 4.29. Found: C, 47.95; H, 5.68; N, 5.56; S, 4.07. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{30}H_{41}N_3NaO_{17}S$ 770.2054, found 770.2044.

Compound 15b: solvent system hexane/EtOAc (1:9); yield 79%; $[\alpha]^{20}_D$ +42.4 (c 0.4, $CHCl_3$); R_f 0.18 (hexane/EtOAc 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1 H, H-triazole), 5.41 (dd, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 10.1 Hz, H-3), 5.33 (dd, 1 H, $J_{4G,5G}$ = 0.9 Hz, $J_{3G,4G}$ = 3.4 Hz, H-4G), 5.13 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 10.0 Hz, H-2G), 4.96 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G), 4.83 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 4.78 (dd, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 10.1 Hz, H-4), 4.76 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 4.63 (m, 2 H, CH_2Ar), 4.55 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.52 (dd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 14.3 Hz, H-6a), 4.31 (dd, 1 H, $J_{5,6b}$ = 8.5 Hz, $J_{6a,6b}$ = 14.4 Hz, H-6b), 4.13 (ddd, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 8.7 Hz, $J_{4,5}$ = 10.1 Hz, H-5), 4.07 (dd, 1 H, $J_{5G,6aG}$ = 6.8 Hz, $J_{6aG,6bG}$ = 11.3 Hz, H-6aG), 4.02 (dd, 1 H, $J_{5G,6bG}$ = 6.6 Hz, $J_{6aG,6bG}$ = 11.3 Hz, H-6bG), 3.88 (ddd, 1 H, $J_{4G,5G}$ = 1.0 Hz, $J_{5G,6aG}$ = 6.8 Hz, $J_{5G,6bG}$ = 6.6 Hz, H-5G), 3.67−3.55 (m, 6 H, 3 CH_2O), 3.05 (s, 3 H, −OCH_3), 2.91 (m, 1 H, J = 7.0 Hz, J = 6.8 Hz, J_{gem} = 13.6 Hz, CHS), 2.72 (m, 1 H, J = 6.1 Hz, J = 6.9 Hz, J_{gem} = 13.5 Hz, CHS), 2.08, 2.03, 1.99 (×2), 1.98, 1.94, 1.91 (7 s, 21 H, 7 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 170.2, 170.1, 170.0, 169.8 (×2), 169.5, 169.6 (−$COCH_3$), 145.0 (C-4 triazole), 124.4 (C-5 triazole), 96.5 (C-1), 84.0 (C-1G), 74.3 (C-5G), 71.8 (C-3G), 71.2 (CH_2O), 70.7 (C-2), 70.2 (CH_2O), 70.0 (C-4), 69.7 (C-3), 69.6 (CH_2O), 67.7 (C-5), 67.3 (C-4G), 67.3 (C-2G), 64.4 (CH_2Ar), 61.4 (C-6G), 55.4 (−OCH_3), 50.7 (C-6), 29.4 (CH_2S), 20.8, 20.6 (×5), 20.5 (−$COCH_3$). Anal. Calcd for $C_{34}H_{49}N_3O_{19}S \cdot 0.5H_2O$: C, 48.34; H, 5.97; N, 4.97; S, 3.80. Found: C, 48.01; H, 5.74; N, 4.93; S, 3.64. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{34}H_{49}N_3NaO_{19}S$ 858.2573, found 858.2548; m/z $[M + H]^+$ calcd for $C_{34}H_{50}N_3O_{19}S$ 836.2754, found 836.2743.

Compound 15c: solvent system EtOAc/MeOH (98:2); yield 75%; $[\alpha]^{20}_D$ +45.8 (c 0.3, $CHCl_3$); R_f 0.2 (hexane/EtOAc 1:6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (sa, 1 H, H-triazole), 5.41 (dd, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{2,3}$ = 10.0 Hz, H-3), 5.35 (dd, 1 H, $J_{4G,5G}$ = 0.7 Hz, $J_{3G,4G}$ = 3.3 Hz, H-4G), 5.13 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 10.0 Hz, H-2G), 4.97 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G), 4.83 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 4.78 (dd, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 4.76 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 4.62 (m, 2 H, CH_2Ar), 4.52 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.51 (m, 1 H, $J_{5,6a}$ = 2.0 Hz, H-6a), 4.30 (dd, 1 H, $J_{5,6b}$ = 8.6 Hz, $J_{6a,6b}$ = 14.2 Hz, H-6b), 4.12 (ddd, 1 H, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 8.6 Hz, $J_{4,5}$ = 10.0 Hz, H-5), 4.07 (dd, 1 H, $J_{5G,6aG}$ = 6.7 Hz, $J_{6aG,6bG}$ = 11.5 Hz, H-6aG), 4.03 (dd, 1 H, $J_{5G,6bG}$ = 6.5 Hz, $J_{6aG,6bG}$ = 11.4 Hz, H-6bG), 3.87 (ddd, 1 H, $J_{4G,5G}$ = 0.7 Hz, $J_{5G,6aG}$ = 6.7 Hz, $J_{5G,6bG}$ = 6.5 Hz, H-5G), 3.65−3.55 (m, 18 H, 9 CH_2O), 3.05 (s, 3 H, −OCH_3), 2.89 (m, 1 H, J = 6.7 Hz, J = 6.9 Hz, J_{gem} = 13.5 Hz, CHS), 2.73 (m, 1 H, J = 6.1 Hz, J = 7.2 Hz, J_{gem} = 13.5 Hz, CHS), 2.08, 2.03, 1.99, 1.98, 1.97, 1.94, 1.91 (7 s, 21 H, 7 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$ + DMSO) δ 170.3, 170.2, 170.1, 170.0, 169.8 (×2), 169.5, 169.6 (−$COCH_3$), 144.5 (C-4 triazole), 124.2 (C-5 triazole), 96.3 (C-1), 83.8 (C-1G), 74.3 (C-5G), 71.5 (C-3G), 71.8, 71.1, 70.7, 70.6, 70.5, 70.4, 70.3, 70.2, 70.0, 69.7 (C-2, C-3, C-4, 9 × CH_2O), 67.7 (C-5), 67.3 (C-4G), 67.2 (C-2G), 64.5 (CH_2Ar), 61.4 (C-6G), 55.4 (−OCH_3), 50.8 (C-6), 29.4 (CH_2S), 20.8, 20.6 (×5), 20.5 (−$COCH_3$). Anal. Calcd for $C_{40}H_{61}N_3O_{22}S \cdot 0.5H_2O$: C, 49.17; H, 6.40; N, 4.30; S, 3.28. Found: C, 49.17; H, 6.32; N, 3.99; S, 3.11. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{40}H_{61}N_3NaO_{22}S$ 990.3360, found 990.3352; m/z $[M + H]^+$ calcd for $C_{40}H_{62}N_3O_{22}S$ 968.3540, found 868.3539.

Compound 17a: Solvent system, hexane/EtOAc (1:9); yield 60%; mp 125−127 °C; $[\alpha]^{20}_D$ −26.8 (c = 1.0, $CHCl_3$); R_f 0.17 (hexane/EtOAc 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82, 7.41 (2 s, 2 H, H-triazole), 5.89 (d, 1 H, $J_{1,2}$ = 8.9 Hz, H-1), 5.51−5.45 (m, 3 H, H-2, H-3, H-4G*), 5.44 (dd, 1 H, $J_{4G',5G'}$ = 0.9 Hz, $J_{3G',4G'}$ = 3.3 Hz, H-4G′*), 5.27−5.19 (m, 3 H, H-2G, H-2G′, H-4), 5.17 (dd, 1 H, $J_{3G',4G'}$ = 3.4 Hz, $J_{2G',3G'}$ = 9.9 Hz, H-3G′*), 5.07 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G*), 4.66 (dd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 14.8 Hz, H-6a), 4.58 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.51 (dd, 1 H, $J_{5,6b}$ = 7.0 Hz, $J_{6a,6b}$ = 14.8 Hz, H-6b), 4.42 (dd, 1 H, $J_{5G',6aG'}$ = 4.4 Hz, $J_{6aG',6bG'}$ = 11.0 Hz, H-6aG′), 4.29 (d, 1 H, $J_{1G',2G'}$ = 9.9 Hz, H-1G′), 4.26 (ddd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 7.0 Hz, $J_{4,5}$ = 9.8 Hz, H-5), 4.16 (d, 1 H, J_{gem} = 14.0 Hz, CHS), 4.10 (dd, 1 H, $J_{5G,6aG}$ = 6.5 Hz, $J_{6aG,6bG}$ = 11.2 Hz, H-6aG), 4.08−4.03 (m, 3 H, CHS, H-5G′, H-6bG′), 3.98 (dd, 1 H, $J_{5G',6bG'}$ = 7.4 Hz, $J_{6aG',6bG'}$ = 11.0 Hz, H-6bG′), 3.91 (ddd, 1 H, $J_{4G,5G}$ = 0.9 Hz, $J_{5G,6aG}$ ≈ $J_{5G,6bG}$ = 6.5 Hz, H-5G), 3.89 (d, 1 H, J_{gem} = 14.1 Hz, CHS*), 3.87 (d, 1 H, J_{gem} = 14.0 Hz, CHS′*), 2.20, 2.16, 2.15, 2.14, 2.06, 2.04, 2.01, 1.99, 1.98, 1.97, 1.90 (11 s, 33 H, 11 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 170.5, 170.3, 170.1, 170.0 (×2), 169.8, 169.7 (×2), 169.6, 169.4 (−$COCH_3$), 144.9, 143.7 (C-4 triazole), 123.4, 121.3 (C-5 triazole), 85.8 (C-1), 83.2 (C-1G), 80.4 (C-1G′), 75.3 (C-5), 74.5 (C-5G), 73.4 (C-5G′), 72.1 (C-3), 71.7, 71.6 (C-3G, C-3G′), 72.3 (C-2), 68.8 (C-4), 67.6, 67.4, 67.3 (×2) (C-2G, C-2G′, C-4G, C-4G′), 61.3, 61.1 (C-6G, C-6G′), 50.5 (C-6), 24.2, 23.2 (2 × CH_2S), 20.8 (×3), 20.7 (×3), 20.6 (×3), 20.2 (×2) (−CH_3CO). Anal. Calcd for $C_{46}H_{60}N_6O_{25}S_2$: C, 47.58; H, 5.21; N, 7.24; S, 5.52. Found: C, 47.94; H, 5.11; N, 7.15; S, 5.31. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{46}H_{60}N_6NaO_{25}S_2$ 1183.2947, found 1183.2968.

Compound 17b: solvent system hexane/EtOAc (1:9); yield 84%; $[\alpha]^{20}_D$ −4.6 (c 1.0, $CHCl_3$); R_f 0.32 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80, 7.56 (2 s, 2 H, H-triazole), 5.86 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 5.50 (t, 1 H, $J_{1,2}$ = 9.2 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 5.43 (t, 1 H, $J_{3,4}$ = 9.3 Hz, $J_{2,3}$ = 9.4 Hz, H-3), 5.43 (dd, 1 H, $J_{4G,5G}$ = 0.9 Hz, $J_{3G,4G}$ = 3.4 Hz, H-4G*), 5.39 (dd, 1 H, $J_{4G',5G'}$ = 1.0 Hz, $J_{3G',4G'}$ = 3.4 Hz, H-4G′*), 5.21 (t, 1 H, $J_{1G,2G}$ = 0.9 Hz, $J_{2G,3G}$ = 10.0 Hz, H-2G*), 5.18 (t, 1 H, $J_{1G',2G'}$ = $J_{2G',3G'}$ = 10.0 Hz, H-2G′*), 5.09 (dd, 1 H, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 10.1 Hz,

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H-4), 5.06 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ =10.0 Hz, H-3G*), 5.03 (dd, 1 H, $J_{3G',4G'}$ = 3.4 Hz, $J_{2G',3G'}$ =10.0 Hz, H-3G'*), 4.70 (s, 2 H, CH_2Ar), 4.67 (dd, 1 H, $J_{5,6a}$ = 2.6 Hz, $J_{6a,6b}$ =14.9 Hz, H-6a), 4.66 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.65 (s, 2 H, CH_2Ar), 4.64 (d, 1 H, $J_{1G',2G'}$ = 10.0 Hz, H-1G'), 4.49 (dd, 1 H, $J_{5,6b}$ = 7.6 Hz, $J_{6a,6b}$ = 14.9 Hz, H-6b), 4.29 (ddd, 1 H, $J_{5,6a}$ = 2.6 Hz, $J_{5,6b}$ = 7.6 Hz, $J_{4,5}$ = 10.2 Hz, H-5), 4.18−4.08 (m, 4 H, H-6aG, H-6bG, H-6aG', H-6bG'), 3.98 (ddd, 1 H, $J_{4G,5G}$ = 0.9 Hz, $J_{5G,6aG}$ = $J_{5G,6bG}$ = 6.6 Hz, H-5G), 3.96 (ddd, 1 H, $J_{4G',5G'}$ = 0.9 Hz, $J_{5G',6aG'}$ = $J_{5G',6bG'}$ = 6.6 Hz, H-5G'), 3.76−3.60 (m, 12 H, 6 CH_2O), 3.02−2.94 (m, 2 H, J = 6.9 Hz, J = 10.5 Hz, J_{gem} = 13.7 Hz, 2 × CHS), 2.84−2.74 (m, 2 H, J = 6.1 Hz, J = 7.1 Hz, J = 13.7 Hz, 2 × CHS), 2.16, 2.15, 2.13, 2.06, 2.05, 2.04 (×2), 2.03, 1.99, 1.98, 1.87 (11 s, 33 H, 11 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 170.4, 170.2 (×2), 170.0 (×2), 169.8, 169.6, 169.5, 168.7 (CH$_3$CO), 145.8, 145.2 (C-4 triazole), 124.0, 121.1 (C-5 triazole), 85.4 (C-1), 84.1, 84.0 (C-1G, C-1G'), 75.4 (C-5), 74.3 (×2) (C-5G, C-5G'), 72.4 (C-3), 71.8 (×2) (C-3G, C-3G'), 71.2 (×2), 70.2, 70.1, 70.0, 69.8 (6 CH$_2$O), 69.0 (C-4), 67.4, 67.3 (×2), 67.2 (C-2G, C-2G', C-4G, C-4G'), 64.4, 64.3 (2 CH_2Ar), 64.5, 61.4 (C-6G, C-6G'), 50.4 (C-6), 29.5 (×2) (CH$_2$S), 21.0, 20.8, 20.6 (×2), 20.4, 20.1 (CH$_3$CO). Anal. Calcd for $C_{54}H_{76}N_6O_{29}S_2$: C, 48.50; H, 5.73; N, 6.28; S, 4.80. Found: C, 48.24; H, 5.61; N, 6.54; S, 4.50. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{54}H_{76}N_6NaO_{29}S_2$ 1359.3990, found 1359.3973.

Compound 17c: solvent system hexane/EtOAc (6:94); yield 76%; $[\alpha]^{20}_D$ −0.4 (c 1.0, $CHCl_3$); $[\alpha]^{20}_D$ +5.1 (c 0.9, DMSO-d_6); R_f 0.11 (EtOAc/MeOH 1.9:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.36, 7.93 (2 s, 2 H, H-triazole), 6.30 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 5.66 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 5.55 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, H-3), 5.33 (m, 2 H, H-4G, H-4G'), 5.18 (dd, 2 H, $J_{3G,4G}$ = $J_{3G',4G'}$ = 3.4 Hz, $J_{2G,3G}$ = $J_{2G',3G'}$ = 9.7 Hz, H-3G, H-3G'), 5.11 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 4.99 (t, 2 H, $J_{1G,2G}$ = $J_{1G',2G'}$ = $J_{2G,3G}$ = $J_{2G',3G'}$ = 9.8 Hz, H-2G, H-2G'), 4.91 (d, 2 H, $J_{1G,2G}$ = $J_{1G',2G'}$ = 10.0 Hz, H-1G, H-1G'), 4.67 (m, 2 H, H-5, H-6a), 4.54 (m, 5 H, H-6b, 2 × CH_2Ar), 4.23 (m, 2 H, H-5, H-5G), 4.02 (m, 2 H, H-6aG, H-6aG', H-6bG, H-6bG'), 3.55−3.49 (m, 36 H, 18 CH_2O), 2.84, 2.74 (2 m, 4 H, J = 6.7 Hz, J_{gem} = 13.5, 2 CH_2S), 2.13 (×2), 2.06, 2.03 (×2), 2.01 (×2), 1.96, 1.93 (×2), 1.80 (11 s, 33 H, 11 CH_3CO); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.9 (×2), 170.8 (×2), 170.4, 170.3 (×2), 170.2, 170.1, 170.0, 169.4 (−COCH$_3$), 145.6, 144.9 (C-4 triazole), 125.7, 123.6 (C-5 triazole), 84.7 (C-1), 83.6 (×2) (C-1G, C-1G'), 74.5 (C-5), 74.3 (×2) (C-5G, C-5G'), 73.0 (C-3), 71.9 (×2) (C-3G, C-3G'), 71.1 (×2), 71.0, 70.6 (×4), 70.5 (×2), 70.4 (×2), 70.1, 69.9 (×2), 69.8 (×2), 69.7 (×2) (C-2, C-4, 18 CH$_2$O), 68.5 (×2) (C-4G, C-4G'), 68.1 (×2) (C-2G, C-2G'), 64.3, 64.2 (2 × CH_2Ar), 62.5 (×2) (C-6G, C-6G'), 50.8 (C-6), 30.1 (×2) (2 CH$_2$S), 21.4 (×2), 21.3 (×2), 21.2 (×2), 21.1 (×2), 21.0 (×2), 20.7 (−COCH$_3$). Anal. Calcd for $C_{66}H_{100}N_6O_{35}S_2$: C, 49.49; H, 6.29; N, 5.25; S, 4.00. Found: C, 49.70; H, 6.14; N, 4.95; S, 4.25. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{66}H_{100}N_6NaO_{35}S_2$ 1623.5569, found 1623.5592.

Compound 19a: solvent system hexane/EtOAc (2:3); yield 69%; mp 112−114 °C; $[\alpha]^{20}_D$ +5.8 (c 1.0, $CHCl_3$); R_f 0.17 (hexane/EtOAc 1:4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1 H, H-triazole), 5.39 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, H-3), 5.37 (br d, 1 H, $J_{4G,5G}$ < 1.0 Hz, $J_{3G,4G}$ = 3.3 Hz, H-4G), 5.18 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 10.0 Hz, H-2G), 4.98 (dd, 1 H, $J_{3G,4G}$ = 3.3 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G), 4.90 (dd, 1 H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4.86 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 4.77 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 4.51 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.43 (dd, 1 H, $J_{5,6a}$ = 0.8 Hz, $J_{6a,6b}$ = 14.0 Hz, H-6a), 4.27 (dd, 1 H, $J_{5,6b}$ = 8.3 Hz, $J_{6a,6b}$ = 13.8 Hz, H-6b), 4.19 (ddd, 1 H, $J_{5,6a}$ = 0.8 Hz, $J_{5,6b}$ = 8.6 Hz, $J_{4,5}$ = 9.9 Hz, H-5), 4.11−4.02 (m, 3 H, H-6aG, H-6bG, CHS), 3.89 (ddd, 1 H, $J_{4G,5G}$ < 1.0 Hz, $J_{5G,6aG}$ = $J_{5G,6bG}$ = 6.5 Hz, H-5G), 3.82 (d, 1 H, J_{gem} = 14.2 Hz, CHS), 2.10, 2.04, 1.99, 1.98, 1.97, 1.94, 1.91 (7 s, 21 H, 7 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 170.7, 170.4, 170.2, 170.1, 170.0, 169.9 (COCH$_3$), 145.5 (C-4 triazole), 123.8 (C-5 triazole), 92.3 (C-1), 83.3 (C-1G), 74.9 (C-5G), 72.2 (C-3G), 70.1 (C-4), 70.0 (C-3), 69.4 (C-2), 69.3 (C-5), 67.7 (×2) (C-2G, C-4G), 61.8 (C-6G), 51.0 (C-6), 24.5 (CH$_2$S), 21.2, 21.1, 21.0, 20.9, 20.8, 20.7, 20.5 (−COCH$_3$). Anal. Calcd for $C_{58}H_{76}N_6O_{33}S_2$: C, 48.06; H, 5.29; N, 5.80; S, 4.42. Found: C, 48,02; H, 5,17; N, 5.55; S, 4.58. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{58}H_{76}N_6NaO_{33}S_2$ 1471.3792, found 1471.3796.

Compound 19b: solvent system EtOAc/MeOH (99:2); yield 68%; $[\alpha]^{20}_D$ +32.9 (c 0.2, $CHCl_3$); R_f 0.42 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1 H, H-triazole), 5.42 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, H-3), 5.37 (br d, 1 H, $J_{4G,5G}$ < 1.0 Hz, $J_{3G,4G}$ = 2.7 Hz, H-4G), 5.17 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 10.0 Hz, H-2G), 4.98 (dd, 1 H, $J_{3G,4G}$ = 2.8 Hz, $J_{2G,3G}$ = 10.0 Hz, H-3G), 4.97 (dd, 1 H, $J_{1,2}$ = 3.3 Hz, $J_{2,3}$ = 10.3 Hz, H-2), 4.88 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 4.82 (d, 1 H, $J_{1,2}$ = 3.1 Hz, H-1), 4.66 (s, 2 H, CH_2Ar), 4.62 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.52 (dd, 1 H, $J_{5,6a}$ < 1.0 Hz, $J_{6a,6b}$ = 13.4 Hz, H-6a), 4.31 (dd, 1 H, $J_{5,6b}$ = 8.6 Hz, $J_{6a,6b}$ = 13.4 Hz, H-6b), 4.24 (ddd, 1 H, $J_{5,6a}$ < 1.0 Hz, $J_{5,6b}$ = 8.6 Hz, $J_{4,5}$ = 9.6 Hz, H-5), 4.12 (dd, 1 H, $J_{5G,6aG}$ = 6.7 Hz, $J_{6aG,6bG}$ = 11.2 Hz, H-6aG), 4.07 (dd, 1 H, $J_{5G,6bG}$ = 6.6 Hz, $J_{6aG,6bG}$ = 11.2 Hz, H-6bG), 3.94 (ddd, 1 H, $J_{4G,5G}$ < 1.0 Hz, $J_{5G,6aG}$ = $J_{5G,6bG}$ = 6.5 Hz, H-5G), 3.66 (m, 6 H, 3 CH_2O), 2.97, 2.77 (2 t, 2 H, J = 6.8 Hz, J_{gem} = 13.5 Hz, CH_2S), 2.13, 2.08, 2.04, 2.03, 2.02, 1.98, 1.96 (7 s, 21 H, 7 CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 170.6, 170.4, 170.2, 170.1, 170.0, 169.8 (−COCH$_3$), 145.8 (C-4 triazole), 124.4 (C-5 triazole), 92.1 (C-1), 84.4 (C-1G), 74.8 (C-5G), 72.2 (C-3G), 71.6, 70.5 (CH$_2$O), 70.2 (C-4), 70.1 (C-3), 70.0 (3 CH$_2$O), 69.4 (C-5), 69.1 (C-2), 67.8 (C-2G), 67.7 (C-4G), 64.8 (CH$_2$Ar), 61.9 (C-6G), 51.0 (C-6), 29.9 (CH$_2$S), 21.2, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6 (−COCH$_3$). Anal. Calcd for $C_{66}H_{92}N_6O_{37}S_2$: C, 48.76; H, 5.70; N, 5.17; S, 3.95. Found: C, 48.46; H, 5.61; N, 5.25; S, 4.09. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{66}H_{92}N_6NaO_{37}S_2$ 1647.4841, found 1647.4764.

Compound 19c: solvent system EtOAc/MeOH (95:5); yield 78%; $[\alpha]^{20}_D$ +38.1 (c 0.7, $CHCl_3$); R_f 0.49 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.98 (s, 1 H, H-triazole), 5.32 (br d, 1 H, $J_{4G,5G}$ < 1.0 Hz, $J_{3G,4G}$ = 3.2 Hz, H-4G), 5.28 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, H-3), 5.17 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ = 9.7 Hz, H-3G), 5.02 (dd, 1 H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 4.99 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, H-4), 4.97 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.6 Hz, H-2G), 4.91 (d, 1 H, $J_{1G,2G}$ = 10.0 Hz, H-1G), 4.83 (d, 1 H, $J_{1,2}$ = 3.2 Hz, H-1), 4.63 (dd, 1 H, $J_{5,6a}$ < 1.0 Hz, $J_{6a,6b}$ = 13.3 Hz, H-6a), 4.51 (m, 3 H, H-6b, CH_2Ar), 4.22 (m, 2 H, H-5, H-5G), 4.04 (m, 2 H, H-6aG, H-6bG), 3.52 (m, 18 H, 9 CH_2O), 2.84, 2.77 (2 m, 2 H, J' = 6.7, J_{gem} = 13.4 Hz, CH_2S), 2.13, 2.08, 2.03, 2.01, 2.00, 1.96, 1.93 (7s, 21 H, 7 CH_3CO); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.9, 170.8, 170.7, 170.6, 170.3, 170.2, 169.9 (COCH$_3$), 145.0 (C-4 triazole), 125.8 (C-5 triazole), 91.8 (C-1), 83.6 (C-1G), 74.3 (C-5G), 72.9 (C-3G), 71.1, 70.6, 70.5, 70.4, 70.1, 69.8 (C-3, C-4, 9 CH$_2$O), 69.4 (C-5), 69.0 (C-2), 68.5 (C-4G), 68.1 (C-2G), 64.2 (CH$_2$Ar), 62.5 (C-6G), 50.5 (C-6), 30.1 (CH$_2$S), 21.4, 21.3, 21.2, 21.1, 20.8, 20.7, 20.6 (−COCH$_3$). Anal. Calcd for $C_{78}H_{116}N_6O_{43}S_2$: C, 49.57; H, 6.19; N, 4.45; S, 3.39. Found: C, 49.79; H, 6.15; N, 4.33; S, 3.59. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{78}H_{116}N_6NaO_{43}S_2$ 1911.6414, found 1911.6376.

Compound 21a: solvent system cyclohexane/EtOAc (85:15); yield 54%; mp 120−122 °C; $[\alpha]^{20}_D$ −8.7 (c 0.7, $CHCl_3$); R_f 0.24 (hexane/EtOAc 1:6); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.11, 7.93, 7.81 (3s, 3 H, H-triazole), 6.26 (d, 1 H, $J_{1,2}$ = 9.1 Hz, H-1), 5.62 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.1 Hz, H-3), 5.46 (d, 1 H, $J_{1',2'}$ = 3.6 Hz, H-1'), 5.44 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 5.33 (m, 4 H, H-3', 3 × H-4G), 5.19 (m, 3 H, 3 × H-3G), 5.01 (m, 3 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.9 Hz, 3 × H-2G), 4.92 (dd, 1 H, $J_{1',2'}$ = 3.6 Hz, $J_{2',3'}$ = 10.4 Hz, H-2'), 4.87, 4.82, 4.66 (3d, 3 H, $J_{1G,2G}$ = 9.9 Hz, 3 × H-1G), 4.82 (t, 1 H, $J_{3',4'}$ = $J_{4',5'}$ = 9.4 Hz, H-4'), 4.73−4.62 (m, 2 H, H-6'a, H-6'b), 4.61−4.45 (m, 3 H, H-6a, H-5, H-5'), 4.33 (dd, 1 H, $J_{5,6b}$ = 6.9 Hz, $J_{6a,6b}$ = 13.8 Hz, H-6b), 4.23−4.15 (m, 3 H, 3 × H-5G), 4.11−3.86 (m, 13 H, H-4, 3 × CH_2S, 3 × H-6aG, 3 × H-6bG), 2.13, 2.04, 2.02, 2.01, 1.99, 1.98, 1.97, 1.96, 1.93, 1.92, 1.76 (11s, 51 H, 17 × CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.8, 170.7, 170.4, 170.3, 170.2, 170.1, 170.0, 169.8 (CH$_3$CO), 144.7,

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144.4, 144.0 (C-4 triazole), 125.4, 125.1, 122.9 (C-5 triazole), 96.6 (C-1′), 84.3 (C-1), 82.8, 82.7, 82.4 (C-1G), 75.1, 75.0 (C-4, C-5), 74.8 (C-3), 74.5, 74−4, 74−3 (C-5G), 71.9, 71.8, 71.7 (C-3G), 71.6 (C-2), 70.1 (C-2′), 69.8 (C-3′), 69.7 (C-4′), 69.4 (C-5′), 68.4, 68.3, 68.2, 68.1, 68.0 (C-2G, C-4G), 62.4, 62.2, 62.1 (C-6G), 50.9, 50.4 (C-6, C-6′), 24.5, 24.4, 24.1 (3 × CH_2S), 21.3, 21.2, 21.1 (CH_3CO). Anal. Calcd for $C_{73}H_{95}N_9O_{40}S_3$: C, 47.79; H, 5.22; N, 6.87; S, 5.24. Found: C, 47.58; H, 5.27; N, 6.69; S, 5.44. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{73}H_{95}N_9NaO_{40}S_3$ 1856.4736, found 1856.4706.

Compound 21b: solvent system EtOAc/MeOH (98:2); yield 67%; $[\alpha]^{20}_D$ +3.0 (c 0.3, $CHCl_3$); R_f 0.10 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.20, 8.07, 7.88 (3s, 1 H each, H-triazole), 6.22 (d, 1 H, $J_{1,2}$ = 9.1 Hz, H-1), 5.59 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 5.47 (d, 1 H, $J_{1',2'}$ = 3.4 Hz, H-1′), 5.45 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 5.33 (m, 4 H, H-3′, 3 × H-4G), 5.18 (m, 3 H, 3 × H-3G), 5.01−4.89 (m, 8 H, H-2′, H-4′, 3 × H-1G, 3 × H-2G), 4.72 (brd, 1 H, $J_{5',6'a}$ < 1 Hz, $J_{6'a,6'b}$ = 13.7 Hz, H-6′a), 4.62 (dd, 1 H, $J_{5',6'b}$ = 6.5 Hz, $J_{6'a,6'b}$ = 13.8 Hz, H-6′b), 4.56−4.41 (m, 9 H, 3 × CH_2-triazole, H-6a, H-5, H-5′), 4.25−4.15 (m, 4 H, H-6b, 3 × H-5G), 4.08−4.01 (m, 6 H, 3 × H-6aG, 3 × H-6bG), 3.92 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4), 3.62−3.50 (m, 18 H, 9 CH_2O), 2.83, 2.72 (2 m, 6 H, 3 × CH_2S), 2.13, 2.04, 2.03, 2.02, 2.00, 1.97, 1.93, 1.75 (8 s, 51 H, 17 × CH_3CO); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.9, 170.8, 170.7, 170.5, 170.4, 170.3, 170.2, 170.1, 169.5 (CH_3CO), 145.4, 144.9, 144.6 (C-4 triazole), 126.0, 125.9, 123.6 (C-5 triazole), 96.6 (C-1′), 84.2 (C-1), 83.6 (3 × C-1G), 75.2 (C-4), 74.9 (C-3, C-5), 74.3 (3 × C-5G), 71.9 (3 × C-3G), 71.5 (C-2), 71.0, 70.3 (CH_2O), 70.1, 69.9, 69.8, 69.7 (C-2′, C-3′, C-4′, C-5′), 68.5 (3 × C-4G), 68.2 (3 × C-2G), 64.3, 64.2, 64.1 (3 × CH_2-triazole), 62.5 (3 × C-6G), 50.7, 50.5 (C-6, C-6′), 30.1 (3 × CH_2S), 21.4, 21.2, 21.1 (CH_3CO). Anal. Calcd for $C_{85}H_{119}N_9O_{46}S_3$: C, 48.64; H, 5.71; N, 6.01; S, 4.58. Found: C, 48.39; H, 5.79; N, 6.05; S, 4.45. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{85}H_{119}N_9NaO_{46}S_3$ 2120.6309, found 2120.6365.

Compound 21c: solvent system EtOAc/MeOH (96:4); yield 67%; $[\alpha]^{20}_D$ +0.9 (c 0.9, $CHCl_3$); R_f 0.24 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19, 8.08, 7.88 (3s, 3 H, H-triazole), 6.22 (d, 1 H, $J_{1,2}$ = 8.8 Hz, H-1), 5.59 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 8.8 Hz, H-3), 5.47 (d, 1 H, $J_{1',2'}$ = 3.4 Hz, H-1′), 5.45 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 8.9 Hz, H-2), 5.32 (m, 4 H, H-3′, 3 × H-4G), 5.17 (m, 3 H, 3 × H-3G), 5.02−4.88 (m, 8 H, H-2′, H-4′, 3 × H-1G, 3 × H-2G), 4.62−4.40 (m, 11 H, 3 × CH_2Ar, H-6a, H-5, H-5′, H-6′a, H-6′b), 4.25−4.15 (m, 4 H, H-6b, 3 × H-5G), 4.08−4.01 (m, 6 H, 3 × H-6aG, 3 × H-6bG), 3.91 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4), 3.65−3.47 (m, 54 H, 27 CH_2O), 2.84, 2.72 (2 m, 3 H each, 3 × CH_2S), 2.12, 2.04, 2.03, 2.02, 2.00, 1.97, 1.93, 1.74 (8 s, 51 H, 17 × CH_3CO); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.9, 170.8, 170.7, 170.5, 170.4, 170.3, 170.2, 170.0, 169.6 (CH_3CO), 145.5 (C-4 triazole), 126.1, 123.7 (C-5 triazole), 96.6 (C-1′), 84.2 (C-1), 83.6 (3 × C-1G), 75.3 (C-4), 74.9 (C-3, C-5), 74−3 (3 × C-5G), 71.9 (3 × C-3G), 71.5 (C-2), 71.1, 70.6, 70.5, 70.4 (CH_2O), 70.1, 69.9, 69.8, 69.7 (C-2′, C-3′, C-4′, C-5′), 68.5 (3 × C-4G), 68.1 (3 × C-2G), 64.3, 64.2, 64.1 (3 × CH_2Ar), 62.5 (3 × C-6G), 50.7, 50.6 (C-6, C-6′), 30.1 (3 × CH_2S), 21.4, 21.2, 21.1 (CH_3CO). Anal. Calcd for $C_{103}H_{155}N_9O_{55}S_3$: C, 49.57; H, 6.26; N, 5.05; S, 3.85. Found: C, 49.42; H, 6.29; N, 5.02; S, 3.89. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{103}H_{155}N_9NaO_{55}S_3$ 2516.8668, found 2516.8620.

Compound 23a: solvent system cyclohexane/EtOAc (92:8); yield 39%; $[\alpha]^{20}_D$ +11.2 (c 0.7, $CHCl_3$); R_f 0.50 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.09, 8.00, 7.92, 7.77 (4s, 1 H each, H-triazole), 6.24 (d, 1 H, $J_{1,2}$ = 9.1 Hz, H-1), 5.65 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 5.41 (m, 3 H, H-2, H-1′, H-1″), 5.33 (m, 6 H, H-3′, H-3″, 4 × H-4G), 5.19 (m, 4 H, 4 × H-3G), 5.02 (m, 4 H, 4 × H-2G), 4.92−4.35 (m, 16 H, H-5, H-6a, H-6b, H-2′, H-5′, H-6′a, H-6′b, H-2″, H-4″, H-5″, H-6″a, H-6″b, 4 × H-1G), 4.23−4.15 (m, 4 H, 4 × H-5G), 4.11−3.86 (m, 17 H, H-4, 4 × CH_2S, 4 × H-6aG, 4 × H-6bG), 2.14, 2.13, 2.12, 2.04, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.77 (18s, 69 H, 23 × CH_3CO); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.4, 170.3, 170.2, 170.1, 170.0, 169.9, 169.8, 169.7, 169.5, 169.4 (CH_3CO), 144.2, 144.0, 143.5 (C-4 triazole), 125.8, 125.4, 125.1, 122.6 (C-5 triazole), 96.1, 95.9 (C-1′, C-1″), 84.0 (C-1), 82.5, 82.3 (×2), 81.9 (C-1G), 75.6, 74.7, 74.3, 74.0, 73.9, 73.7, 71.5, 71.0, 70.3, 69.5, 69.4, 68.7, 68.6, 68.0, 67.9, 67.8, 67.6, 67.6 (C-2 to C-5, C-2′ to C-5′, C-2″ to C-5″, C-2G to C-5G), 61.9, 61.7 (C-6G), 50.3, 50.2, 50.1 (C-6, C-6′, C-6″), 24.1, 24.0, 23.7 (4 × CH_2S), 21.3, 21.2, 21.0, 20.8 (CH_3CO). Anal. Calcd for $C_{100}H_{131}N_9O_{55}S_4$: C, 47.88; H, 5.22; N, 6.70; S, 5.11. Found: C, 47.69; H, 5.02; N, 6.99; S, 5.44. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{100}H_{132}N_{12}O_{55}S_4$ 2507.6694, found 2507.6690.

Compound 23b: solvent system EtOAc/MeOH (97:3); yield 48%; $[\alpha]^{20}_D$ +6.1 (c 1.0, $CHCl_3$); R_f 0.53 (EtOAc/MeOH 1.95:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17, 8.11, 8.05, 7.83 (4 s, 4 H, H-triazole), 6.20 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 5.61 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 5.40 (m, 3 H, H-1′, H-1″, H-2), 5.32 (m, 6 H, H-3′, H-3″, 4 × H-4G), 5.17 (m, 4 H, 4 × H-3G), 5.01−4.89 (m, 9 H, H-2″, 4 × H-1G, 4 × H-2G), 4.86 (t, 1 H, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.7 Hz, H-4″), 4.77 (dd, 1 H, $J_{1',2'}$ = 3.4 Hz, $J_{2',3'}$ = 10.2 Hz, H-2′), 4.71 (brd, 1 H, $J_{5',6'a}$ < 1 Hz, $J_{6'a,6'b}$ = 13.7 Hz, H-6′a), 4.62 (dd, 1 H, $J_{5',6'b}$ = 6.2 Hz, $J_{6'a,6'b}$ = 14.2 Hz, H-6′b), 4.56−4.40 (m, 12 H, H-5, H-6a, H-5″, H-6″a, 4 × CH_2Ar), 4.35−4.20 (m, 6 H, H-5′, H-6″b, 4 × H-5G), 4.12−4.00 (m, 9 H, H-6b, 4 × H-6aG, 4 × H-6bG), 3.80 (m, 2 H, H-4, H-4′), 3.63−3.50 (m, 24 H, 12 CH_2O), 2.83, 2.74 (2 m, 8 H, 4 × CH_2S), 2.13, 2.04, 2.03, 2.02, 2.00, 1.98, 1.96, 1.93, 1.75 (9s, 69 H, 23 × CH_3CO); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.9, 170.8, 170.7, 170.5, 170.4, 170.3, 170.2, 170.1, 169.5 (CH_3CO), 145.3, 144.9, 144.5 (C-4 triazole), 126.3, 126.1, 123.7 (C-5 triazole), 96.5 (C-1′, C-1″), 84.2 (C-1), 83.6 (4 × C-1G), 76.0 (C-4), 75.2 (C-4′), 75.0 (C-3, C-5), 74.4 (4 × C-5G), 71.9 (4 × C-3G), 71.7, 71.4, 71.1, 71.0, 70.6, 70.3, 70.2, 70.0, 69.9, 69.8, 69.7, 69.6, 69.5, 69.4 (C-2, C-2′, C-3′, C-5′, C-2″ to C-5″, CH_2O), 68.5 (4 × C-4G), 68.1 (4 × C-2G), 64.3, 64.1 (4 × CH_2Ar), 62.5 (4 × C-6G), 50.7, 50.5, 50.4 (C-6, C-6′, C-6″), 30.1 (4 × CH_2S), 21.4, 21.3, 21.2, 21.1, 21.0, 20.7 (CH_3CO). Anal. Calcd for $C_{116}H_{162}N_{12}O_{63}S_4$: C, 48.70; H, 5.71; N, 5.88; S, 4.48. Found: C, 48.46; H, 5.89; N, 6.07; S, 4.65. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{116}H_{162}N_{12}NaO_{63}S_4$ 2881.8626, found 2881.8594.

Compound 23c: solvent system EtOAc/MeOH (88:12); yield 54%; $[\alpha]^{20}_D$ +5.4 (c 1.0, $CHCl_3$); R_f 0.48 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17, 8.11, 8.06, 7.83 (4s, 4 H, H-triazole), 6.20 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 5.61 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 5.41 (m, 3 H, H-1′, H-1″, H-2), 5.33 (m, 6 H, H-3′, H-3″, 4 × H-4G), 5.18 (dd, 4 H, $J_{3G,4G}$ = 3.6 Hz, $J_{2G,3G}$ = 9.8 Hz, 4 × H-3G), 4.99 (t, 4 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.9 Hz, 4 × H-2G), 4.93 (m, 5 H, $J_{1G,2G}$ = 10.0 Hz, H-2″, 4 × H-1G), 4.86 (t, 1 H, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.7 Hz, H-4″), 4.77 (dd, 1 H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 10.1 Hz, H-2′), 4.71 (brd, 1 H, $J_{5',6'a}$ < 1 Hz, $J_{6'a,6'b}$ = 13.7 Hz, H-6′a), 4.62 (dd, 1 H, $J_{5',6'b}$ = 6.2 Hz, $J_{6'a,6'b}$ = 14.2 Hz, H-6′b), 4.57−4.38 (m, 12 H, H-5, H-6a, H-5″, H-6″a, 4 × CH_2Ar), 4.35−4.20 (m, 6 H, H-5′, H-6″b, 4 × H-5G), 4.08−4.00 (m, 9 H, H-6b, 4 × H-6aG, 4 × H-6bG), 3.79 (m, 2 H, H-4, H-4′), 3.64−3.45 (m, 72 H, 36 CH_2O), 2.83, 2.74 (2 m, 8 H, 4 × CH_2S), 2.13, 2.04, 2.03, 2.02, 2.00, 1.98, 1.96, 1.93, 1.75 (9s, 69 H, 23 × CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0, 170.9, 170.8, 170.7, 170.5, 170.4, 170.3, 170.2, 170.0, 169.6 (CH_3CO), 145.4, 145.0, 144.6 (C-4 triazole), 126.3, 126.1, 126.0, 123.7 (C-5 triazole), 96.5 (C-1′, C-1″), 84.2 (C-1), 83.6 (3 × C-1G), 76.0 (C-4), 75.3 (C-4′), 75.0 (C-3, C-5), 74.3 (4 × C-5G), 71.9 (4 × C-3G), 71.7, 71.4, 71.1, 71.0, 70.6, 70.3, 70.2, 70.0, 69.9, 69.8, 69.7, 69.6, 69.5, 69.4 (C-2, C-2′, C-3′, C-5′, C-2″ to C-5″, CH_2O), 68.5 (4 × C-4G), 68.1 (4 × C-2G), 64.3, 64.2, 64.1 (4 × CH_2Ar), 62.6 (4 × C-6G), 50.7, 50.5, 50.4 (C-6, C-6′, C-6″), 30.1 (4 × CH_2S), 21.4, 21.3, 21.2, 21.1, 21.0; 20.7 (CH_3CO). Anal. Calcd for $C_{140}H_{210}N_{12}O_{75}S_4$: C, 49.61; H, 6.24; N, 4.96; S, 3.78. Found: C, 49.67; H, 6.54; N, 5.21; S, 3.87. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{140}H_{211}N_{12}O_{75}S_4$ 3388.1948, found 3388.1894.

General Procedure for the *O*-Deacetylation. Compounds **11**, **13a**−**c**, **15a**−**c**, **17a**−**c**, **19a**−**c**, **21a**−**c**, and **23a**−**c** (0.10 mmol) were suspended in a mixture of MeOH/Et_3N/H_2O 4:1:5 (10 mL) and stirred at room temperature. The solid was progressively dissolving and after 2 h TLC (EtOAc or EtOAc:MeOH 19: 1) showed complete consumption of the starting material. The solution was concentrated and the residue was dissolved in water (1 mL) and passed through a column filled with Dowex MR-3C mixed bed ion-exchange resin. The eluate was concentrated and further purified by filtration through an octadecyl C18 minicolumn. Evaporation of the solvent afforded the free product, which showed a single spot by TLC (*n*-BuOH/EtOH/H_2O 2.5:1:1) whose R_f is indicated in each case.

Compound 12: yield 87%; mp 50 °C; $[\alpha]^{20}_D$ −50.4 (*c* 0.6, H_2O); R_f 0.66; ^{1}H NMR (500 MHz, D_2O) δ 7.88 (s, 1 H, H-triazole), 4.86 (dd, 1 H, *J* = 6.5 Hz, *J* = 6.9 Hz, C*H*N), 4.28 (d, 1 H, $J_{1,2}$ = 9.6 Hz, H-1), 4.00 (d, 1 H, J_{gem} = 14.6 Hz, C*H*S), 3.86 (dd, 1 H, $J_{4,5}$ = 0.9 Hz, $J_{3,4}$ = 3.5 Hz, H-4), 3.88 (d, 1 H, J_{gem} = 14.6 Hz, C*H*S), 3.58 (m, 2 H, H-6a, H-6b), 3.53 (ddd, 1 H, $J_{4,5}$ = 0.8 Hz, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 6.9 Hz, H-5), 3.50 (m, 2 H, H-2, H-3), 2.15, 1.86, 1.72, 1.64 (4 m, 4 H, 2 CH_{2cyclo}); ^{13}C NMR (125 MHz, D_2O) δ 144.8 (C-4 triazole), 122.8 (C-5 triazole), 85.2 (C-1), 78.9 (C-5), 73.9, 69.4 (C-2, C-3), 68.7 (C-4), 62.4 (*C*HN), 60.9 (C-1), 32.8 (×2) (C-2_{cyclo}), 23.6 (×3) (C-3_{cyclo}, CH_2S). Anal. Calcd for $C_{14}H_{23}N_3O_5S\cdot0.5H_2O$: C, 47.44; H, 6.83; N, 11.86; S, 9.05. Found: C, 47.44; H, 6.76; N, 11.79; S, 8.86. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{23}N_3NaO_5S$ 368.1256, found 368.1251.

Compound 14a: yield 100%; mp 135−136 °C; $[\alpha]^{20}_D$ −22.8 (*c* 0.2, H_2O); R_f 0.36; ^{1}H NMR (500 MHz, D_2O) δ 8.10 (s, 1 H, H-triazole), 5.58 (d, 1 H, $J_{1,2}$ = 9.3 Hz, H-1), 4.26 (d, 1 H, $J_{1G,2G}$ = 9.6 Hz, H-1G), 4.00, 3.88 (2 d, 2 H each, J_{gem} = 14.8 Hz, CH_2S), 3.84 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 3.80 (dd, 1 H, $J_{4G,5G}$ = 0.8 Hz, $J_{3G,4G}$= 2.1 Hz, H-4G), 3.76 (dd, 1 H, $J_{5,6a}$ = 1.8 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 3.63 (dd, 1 H, $J_{5,6b}$ = 5.3 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6b), 3.59 (ddd, 1 H, $J_{5,6a}$ = 1.8 Hz, $J_{5,6b}$ = 5.3 Hz, $J_{4,5}$ = 9.4 Hz, H-5), 3.56 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3), 3.54 (dd, 1 H, $J_{5G,6aG}$ = 4.3 Hz, $J_{6aG,6bG}$ = 11.5 Hz, H-6aG), 3.50−3.45 (m, 4 H, H-3G, H-4, H-5G, H-6bG), 3.43 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.5 Hz, H-2G); ^{13}C NMR (125 MHz, D_2O) δ 145.6 (C-4 triazole), 123.5 (C-5 triazole), 87.4 (C-1), 85.2 (C-1G), 78.8 (×2) (C-5, C-5G), 75.9 (C-3), 73.8 (C-3G), 72.2 (C-2), 69.4 (C-2G), 68.9 (C-4), 68.7 (C-4G), 60.9 (C-6G), 60.4 (C-6), 23.6 (CH_2S). Anal. Calcd for $C_{15}H_{25}N_3O_{10}S\cdot H_2O$: C, 39.38; H, 5.95; N, 9.19; S, 7.00. Found: C, 39.50; H, 5.61; N, 8.96; S, 7.35. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{25}N_3NaO_{10}S$ 462.1158, found 462.1173.

Compound 14b: yield 95%; mp 90 °C; $[\alpha]^{20}_D$ −7.4 (*c* 0.6, H_2O); R_f 0.29; ^{1}H NMR (500 MHz, D_2O) δ 8.20 (s, 1 H, H-triazole), 5.68 (d, 1 H, $J_{1,2}$ = 9.3 Hz, H-1), 4.64 (s, 2 H, CH_2Ar), 4.42 (d, 1 H, $J_{1',2'}$ = 9.6 Hz, H-1G), 3.92 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 3.87 (br d, 1 H, $J_{3G,4G}$ = 3.2 Hz, $J_{4G,5G}$ < 1.0 Hz, H-4G), 3.83 (dd, 1 H, $J_{5,6a}$ = 1.5 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 3.72−3.61 (m, 10 H, 3 CH_2O, H-3, H-6aG, H-6bG), 3.61−3.57 (m, 2 H, H-5, H-5G), 3.54 (t, 1 H, $J_{3,4}$ ≈ $J_{4,5}$ = 9.5 Hz, H-4), 3.52 (dd, 1 H, $J_{2G,3G}$ = 9.6 Hz, $J_{3G,4G}$ = 3.2 Hz, H-3G), 3.54 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.6 Hz, H-2G), 2.90, 2.80 (2 m, 2 H, *J* = 6.4 Hz, J_{gem} = 14.0 Hz, CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.2 (C-4 triazole), 124.4 (C-5 triazole), 87.4 (C-1), 85.9 (C-1G), 78.9 (×2) (C-5, C-5G), 75.9 (C-3), 73.9 (C-3G), 72.2 (C-2), 70.2, 69.7, 69.3, 69.0, 68.9, 68.8 (C-2G, C-4, C-4G, 3 CH_2O), 63.0 (CH_2Ar), 61.0, 60.4 (C-6, C-6G), 29.1 (CH_2S). Anal. Calcd for $C_{19}H_{33}N_3O_{12}S\cdot0.5H_2O$: C, 42.53; H, 6.39; N, 7.83; S, 5.98. Found: C, 42.57; H, 6.01; N, 7.97; S, 5.95. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{33}N_3NaO_{12}S$ 550.1677, found 550.1658.

Compound 14c. yield 90%; $[\alpha]^{20}_D$ −8.7 (*c* 0.2, D_2O); R_f 0.25; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1 H, H-triazole), 5.73 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 4.70 (s, 2 H, CH_2Ar), 4.46 (d, 1 H, $J_{1G,2G}$ = 9.7 Hz, H-1G), 3.97 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.2 Hz, H-2), 3.93 (brd, 1 H, $J_{4G,5G}$ < 1 Hz, $J_{3G,4G}$ = 3.3 Hz, H-4G), 3.87 (dd, 1 H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 3.77−3.63 (m, 25 H, H-3, H-4, H-5, H-6b, H-5G, H-6aG, H-6bG, 9 CH_2O), 3.60 (dd, 1 H, $J_{3G,4G}$ = 3.3 Hz, $J_{2G,3G}$ = 9.4 Hz, H-3G), 5.12 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.6 Hz, H-2G), 2.94, 2.88 (2 m, 2 H, CH_2S); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7 (C-4 triazole), 124.8 (C-5 triazole), 87.9 (C-1), 86.4 (C-1G), 79.4, 79.3 (C-5, C-5G), 76.4 (C-3), 74.4 (C-3G), 72.7 (C-2), 70.6, 70.0 (×6), 69.8, 69.5 (9 CH_2O), 70.1 (C-2G), 69.4, 69.3 (C-4, C-4G), 63.5 (CH_2Ar), 61.5, 60,9 (C-6, C-6G), 29.6 (CH_2S). Anal. Calcd for $C_{25}H_{45}N_3O_{15}S$: C, 45.52; H, 6.88; N, 6.37; S, 4.86. Found: C, 45.42; H, 6.85; N, 6.51; S, 4.70. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{25}H_{45}N_3NaO_{15}S$ 682.2469, found 682.2479.

Compound 16a: yield 100%; mp 121 °C; $[\alpha]^{20}_D$ +4.1 (*c* 0.4, H_2O); R_f 0.33; ^{1}H NMR (500 MHz, D_2O) δ 7.89 (s, 1 H, H-triazole), 4.66 (dd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6a), 4.58 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 4.47 (dd, 1 H, $J_{5,6b}$ = 7.9 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6b), 4.21 (d, 1 H, $J_{1G,2G}$ = 9.7 Hz, H-1G), 3.97, 3.84 (2 d, 2 H, J_{gem} = 14.6 Hz, CH_2S), 3.81 (m, 1 H, H-4G), 3.80 (ddd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 7.9 Hz, $J_{4,5}$ = 10.0 Hz, H-5), 3.59 (dd, 1 H, $J_{5G,6aG}$ = 7.7 Hz, $J_{6aG,6bG}$ = 11.7 Hz, H-6aG), 3.55 (dd, 1 H, $J_{5G,6bG}$ = 4.5 Hz, $J_{6aG,6bG}$ = 11.7 Hz, H-6bG), 3.51 (dd, 1 H, $J_{3,4}$ = 9.2 Hz, $J_{2,3}$ = 9.8 Hz, H-3), 3.50 (ddd, 1 H, $J_{4G,5G}$ = 0.8 Hz, $J_{5G,6bG}$ = 4.5 Hz, $J_{5,6aG}$ = 7.7 Hz, H-5G), 3.43 (m, 2 H, H-2G, H-3G), 3.37 (dd, 1 H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 3.07 (dd, 1 H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 2.99 (s, 3 H, −OCH_3); ^{13}C NMR (125 MHz, D_2O) δ 145.0 (C-4 triazole), 125.3 (C-5 triazole), 99.1 (C-1), 84.9 (C-1G), 78.9 (C-5G), 73.9 (C-3G), 73.0 (C-3), 71.0 (C-2), 70.8 (C-4), 70.0 (C-5), 69.4 (C-2G), 68.7 (C-4G), 61.0 (C-6G), 54.8 (−O*C*H_3), 50.9 (C-6), 23.3 (CH_2S). Anal. Calcd for $C_{16}H_{27}N_3O_{10}S\cdot0.5H_2O$: C, 41.55; H, 6.10; N, 9.09; S, 6.93. Found: C, 41.14; H, 6.20; N, 8.81; S, 7.07. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{27}N_3NaO_{10}S$ 476.1315, found 476.1316.

Compound 16b: yield 89%; $[\alpha]^{20}_D$ +63.7 (*c* 0.2, H_2O); R_f 0.23; ^{1}H NMR (500 MHz, D_2O) δ 7.98 (s, 1 H, H-triazole), 4.70 (dd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6a), 4.59 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 4.55 (s, 2 H, CH_2-triazole), 4.49 (dd, 1 H, $J_{5,6b}$ = 8.0 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6b), 4.35 (d, 1 H, $J_{1G,2G}$ = 9.6 Hz, H-1G), 3.81 (m, 1 H, H-4G), 3.80 (ddd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 8.0 Hz, $J_{4,5}$ = 10.1 Hz, H-5), 3.62−3.52 (m, 10 H, 3 × CH_2O, H-3, H-5G, H-6aG, H-6bG), 3.47 (dd, 1 H, $J_{3G,4G}$ = 3.3 Hz, $J_{2G,3G}$ = 9.4 Hz, H-3G), 3.40 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.3 Hz, H-2G), 3.38 (dd, 1 H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.7 Hz, H-2), 3.09 (dd, 1 H, $J_{3,4}$ = 9.1 Hz, $J_{4,5}$ = 9.9 Hz, H-4), 2.98 (s, 3 H, −OCH_3), 2.83, 2.75 (2 m, 2 H, CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.1 (C-4 triazole), 126.3 (C-5 triazole), 99.2 (C-1), 85.9 (C-1G), 78.9 (C-5G), 73.9 (C-3G), 73.0 (C-3), 71.1 (C-2), 70.9 (C-4), 70.2, 69.3, 68.8 (3 × CH_2O), 69.9 (C-5), 69.7 (C-2G), 68.8 (C-4G), 63.0 (CH_2-triazole), 61.1 (C-6G), 54.8 (−O*C*H_3), 50.9 (C-6), 29.2 (CH_2S). Anal. Calcd for $C_{20}H_{35}N_3O_{12}S\cdot H_2O$: C, 42.93; H, 6.66; N, 7.51. Found: C, 42.60; H, 6.34; N, 7.70. HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{35}N_3NaO_{12}S$ 564.1834, found 564.1850; *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{36}N_3O_{12}S$ 542.2014, found 542.2023.

Compound 16c: yield 87%; $[\alpha]^{20}_D$ +70.7 (*c* 0.2, H_2O); R_f 0.16; ^{1}H NMR (500 MHz, D_2O) δ = 7.97 (s, 1 H, H-triazole), 4.70 (dd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6a), 4.59 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 4.55 (s, 2 H, CH_2-triazole), 4.49 (dd, 1 H, $J_{5,6b}$ = 8.1 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6b), 4.35 (d, 1 H, $J_{1G,2G}$ = 9.7 Hz, H-1G), 3.82 (dd, 1 H, $J_{4G,5G}$ = 0.6 Hz, $J_{3G,4G}$ = 3.4 Hz, H-4G), 3.80 (ddd, 1 H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 8.1 Hz, $J_{4,5}$ = 10.1 Hz, H-5), 3.64−3.51 (m, 22 H, 9 × CH_2O, H-3, H-5G, H-6aG, H-6bG), 3.49 (dd, 1 H, $J_{3G,4G}$ = 3.4 Hz, $J_{2G,3G}$ = 9.3 Hz, H-3G), 3.40 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.5 Hz, H-2G), 3.38 (dd, 1 H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 3.09 (dd, 1 H, $J_{3,4}$ = 9.1 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 2.98 (s, 3 H, −OCH_3), 2.84, 2.77 (2 m, 2 H, CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 143.9 (C-4 triazole), 126.2 (C-5 triazole), 99.2 (C-1), 86.0 (C-1G), 79.0 (C-5G), 73.9 (C-3G), 73.0 (C-3), 71.1 (C-2), 70.9 (C-4), 70.1, 69.9, 69.7, 69.6, 69.5, 69.4, 69.3, 69.2, 68.9, 68.8 (9 × CH_2O, C-5, C-2G, C-4G), 63.0 (CH_2-triazole), 61.1 (C-6G), 54.8 (−O*C*H_3), 50.9 (C-6), 29.2 (CH_2S). Anal. Calcd for $C_{26}H_{47}N_3O_{15}S\cdot H_2O$: C, 45.14; H, 7.14; N, 6.07. Found: C, 44.90; H, 6.98; N, 5.99. HRMS (ESI) *m*/*z* $[M + Na]^+$

calcd for $C_{26}H_{47}N_3NaO_{15}S$ 696.2620, found 696.2648; m/z $[M + H]^+$ calcd for $C_{26}H_{48}N_3O_{15}S$ 674.2801, found 674.2827.

Compound 18a: yield 91%; mp 142−144 °C; $[\alpha]^{20}_D$ −46.7 (c 0.4, H_2O); R_f 0.18; ^{1}H NMR (500 MHz, D_2O) δ 8.08, 7.80 (2 s, 2 H, H-triazole), 5.62 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 4.78 (dd, 1 H, $J_{5,6a}$ = 2.3 Hz, $J_{6a,6b}$ = 15.0 Hz, H-6a), 4.60 (dd, 1 H, $J_{5,6b}$ = 7.1 Hz, $J_{6a,6b}$ = 15.0 Hz, H-6b), 4.34, 4.12 (2 d, 2 H, $J_{1G,2G}$ = $J_{1G',2G'}$ = 9.6 Hz, H-1G, H-1G′), 4.06, 4.01, 3.95, 3.87 (4 d, 4 H, J_{gem} = 14.8 Hz, 2 × CH_2S), 4.01 (ddd, 1 H, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 7.0 Hz, $J_{4,5}$ = 9.7 Hz, H-5), 3.88, 3.82 (2 dd, 2 H, $J_{4G,5G}$ = $J_{4G',5G'}$ = 0.8 Hz, $J_{3G,4G}$ = $J_{3G',4G'}$ = 3.2 Hz, H-4G, H-4G′), 3.81 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 3.64 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3), 3.62−3.51 (m, 6 H, H-5G, H-5G′, H6aG, H-6aG′, H-6bG, H-6bG′), 3.49 (dd, 1 H, $J_{3G,4G}$ = 3.0 Hz, $J_{2G,3G}$ = 9.5 Hz, H-3G*), 3.48 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 3.42 (dd, 1 H, $J_{3G',4G'}$ = 3.3 Hz, $J_{2G',3G'}$ = 9.4 Hz, H-3G′*), 3.33−3.29 (m, 2 H, H-2G, H-2G′); ^{13}C NMR (125 MHz, D_2O) δ 145.6, 144.7 (C-4 triazole), 125.3, 123.2 (C-5 triazole), 87.3 (C-1), 85.3, 84.5 (C-1G, C-1G′), 79.0, 79.9 (C-5G, C-5G′), 76.6 (C-5), 75.7 (C-3), 73.8 (×2) (C-3G, C-3G′), 72.2 (C-2), 70.0 (C-4), 69.4, 69.3 (C-2G, C-2G′), 68.7 (×2) (C-4G, C-4G′), 61.0, 60.9 (C-6G, C-6G′), 50.7 (C-6), 23.6, 23.2 (2 × CH_2S). Anal. Calcd for $C_{24}H_{38}N_6O_{14}S_2$: C, 41.25; H, 5.48; N, 12.03; S, 9.18. Found: C, 40.93; H, 5.44; N, 11.93; S, 8.98. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{38}N_6NaO_{14}S_2$ 721.1785, found 721.1802.

Compound 18b: yield 93%; $[\alpha]^{20}_D$ −4.3 (c 0.6, D_2O); R_f 0.15; ^{1}H NMR (500 MHz, D_2O) δ 8.17, 7.92 (2 s, 2 H, H-triazole), 5.70 (d, 1 H, $J_{1,2}$ = 9.3 Hz, H-1), 4.85 (dd, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{6a,6b}$ = 14.8 Hz, H-6a), 4.70 (m, 1 H, $J_{5,6b}$ = 7.2 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6b), 4.68, 4.61 (2 s, 4 H, CH_2Ar), 4.46, 4.45 (2 d, 2 H, $J_{1G,2G}$ = $J_{1G',2G'}$ = 9.7 Hz, H-1G, H-1G′), 4.07 (m, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 7.2 Hz, $J_{4,5}$ = 9.8 Hz, H-5), 3.93 (m, 2 H, H-4G, H-4G′), 3.91 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 3.73−3.56 (m, 21 H, H-3, H-3G, H-3G′, H-5G, H-5G′, H-6aG, H-6aG′, H-6bG, H-6bG′, 6 CH_2O), 3.51 (t, 2 H, $J_{1G,2G}$ = $J_{1G',2G'}$ = $J_{2G,3G}$ = $J_{2G',3G'}$ = 9.5 Hz, H-2G, H-2G′), 3.36 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.93, 2.84 (m, 4 H, 2 CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.3, 143.8 (C-4 triazole, 126.3, 124.2 (C-5 triazole), 87.2 (C-1), 85.9 (×2) (C-1G, C-1G′), 78.9 (×2) (C-5G, C-5G′), 76.3 (C-5), 75.6 (C-3), 73.9 (×2) (C-3G, C-3G′), 72.1 (C-2), 70.1 (×2), 70.0, 69.7 (×2), 69.3 (×2), 69.0, 68.8 (×2), 68.7 (C-2G, C-2G′, C-4, C-4G, C-4G′, 6 CH_2O), 63.0, 62.9 (CH_2Ar), 61.1 (×2) (C-6G, C-6G′), 50.6 (C-6), 29.1 (×2) (CH_2S). Anal. Calcd for $C_{32}H_{54}N_6O_{18}S_2$: C, 43.93; H, 6.22; N, 9.61; S, 7.33. Found: C, 43.64; H, 6.27; N, 9.87; S, 6.94. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{32}H_{54}N_6NaO_{18}S_2$ 897.2834, found 897.2829.

Compound 18c: yield 92%; $[\alpha]^{20}_D$ −2.1 (c 1.0, D_2O); R_f 0.11; ^{1}H NMR (500 MHz, D_2O) δ 8.20, 7.94 (2 s, 1 H, H-triazole), 5.71 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 4.86 (dd, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{6a,6b}$ = 14.8 Hz, H-6a), 4.70 (m, 1 H, H-6b), 4.63 (2s, 4 H, 2 × CH_2Ar), 4.47 (d, 2 H, $J_{1G,2G}$ = $J_{1G',2G'}$ = 9.7 Hz, H-1G, H-1G′), 4.08 (m, 1 H, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 7.2 Hz, $J_{4,5}$ = 9.2 Hz, H-5), 3.95 (m, 2 H, H-4G, H-4G′), 3.92 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.3 Hz, H-2), 3.75−3.56 (m, 45 H, H-3, H-3G, H-3G′, H-5G, H-5G′, H-6aG, H-6aG′, H-6bG, H-6bG′, 18 CH_2O), 3.50 (t, 2 H, $J_{1G,2G}$ = $J_{1G',2G'}$ = $J_{2G,3G}$ = $J_{2G',3G'}$ = 9.5 Hz, H-2G, H-2G′), 3.38 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 2.95, 2.89 (2 m, 4 H, CH_2S); ^{13}C NMR (50.28 MHz, D_2O) δ 144.8, 144.4 (C-4 triazole), 126.7, 124.7 (C-5 triazole), 87.8 (C-1), 86.4 (×2) (C-1G, C-1G′), 79.4 (×2) (C-5G, C-5G′), 76.9 (C-5), 76.1 (C-3), 74.4 (×2) (C-3G, C-3G′), 72.6 (C-2), 70.7 (×3), 70.1 (×10), 69.9 (×2), 69.6 (×2), 69.3 (18 CH_2O), 70.6 (C-4), 70.2 (C-2G, C-2G′), 69.4 (C-4G, C-4G′), 63.5 (×2) (2 × CH_2Ar), 61.6 (×2) (C-6G, C-6G′), 50.2 (C-6), 29.6 (×2) (2 × CH_2S). Anal. Calcd for $C_{44}H_{78}N_6O_{24}S_2 \cdot H_2O$: C, 45.67; H, 6.97; N, 7.26; S, 5.54. Found: C, 45.47; H, 7.01; N, 7.41; S, 5.72; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{44}H_{78}N_6NaO_{24}S_2$ 1161.4407, found 1161.4358.

Compound 20a: yield 84%; $[\alpha]^{20}_D$ +10.9 (c 0.2, D_2O); R_f 0.23; ^{1}H NMR (500 MHz, D_2O) δ 7.95 (s, 1 H, H-triazole), 4.74 (dd, 1 H, $J_{5,6a}$ = 2.3 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6a), 4.56 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 4.52 (dd, 1 H, $J_{5,6b}$ = 8.2 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6b), 4.34 (d, 1 H, H-1G), 4.09 (d, 1 H, J_{gem} = 14.5 Hz, CHS), 4.03 (m, 1 H, $J_{5,6a}$ = 2.2 Hz, $J_{5,6b}$ = 8.0 Hz, $J_{4,5}$ = 10.2, H-5), 3.96 (m, 2 H, J_{gem} = 14.5 Hz, CHS, H-4G), 3.74 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 3.70 (dd, 1 H, $J_{5G,6aG}$ = 7.7 Hz, $J_{6aG,6bG}$ = 11.8 Hz, H-6aG), 3.67 (dd, 1 H, $J_{5G,6bG}$ = 4.5 Hz, $J_{6aG,6bG}$ = 11.8 Hz, H-6bG), 3.60 (br dd, 1 H, $J_{4G,5G}$ < 1.0 Hz, $J_{5G,6bG}$ = 4.5 Hz, $J_{5G,6aG}$ = 7.7 Hz, H-5G), 3.55 (m, 2 H, H-2G, H-3G), 3.48 (dd, 1 H, $J_{1,2}$ = 3.9 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 3.20 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4); ^{13}C NMR (125 MHz, D_2O) δ 145.4 (C-4 triazole), 125.6 (C-5 triazole), 93.7 (C-1), 85.4 (C-1G), 79.5 (C-5G), 74.3 (C-3G), 73.1 (C-3), 71.4 (C-4), 71.0 (C-2), 70.8 (C-5), 69.9 (C-2G), 69.2 (C-4G), 61.5 (C-6G), 51.3 (C-6), 23.7 (CH_2S). Anal. Calcd for $C_{30}H_{48}N_6O_{19}S_2$: C, 41.86; H, 5.62; N, 9.76; S, 7.45. Found: C, 41.97; H, 5.73; N, 8.91; S, 7.08. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{30}H_{48}N_6NaO_{19}S_2$ 883.2313, found 883.2336.

Compound 20b: yield 94%; $[\alpha]^{20}_D$ +41.8 (c 0.3, D_2O); R_f 0.17; ^{1}H NMR (500 MHz, D_2O) δ 8.02 (s, 1 H, H-triazole), 4.75 (dd, 1 H, $J_{5,6a}$ = 1.6 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6a), 4.65 (s, 2 H, CH_2Ar), 4.58 (d, 1 H, $J_{1,2}$ = 4.2 Hz, H-1), 4.56 (dd, 1 H, $J_{5,6b}$ = 7.9 Hz, $J_{6a,6b}$ = 14.6 Hz, H-6b), 4.46 (d, 1 H, $J_{1G,2G}$ = 9.5, H-1G), 4.03 (m, 1 H, $J_{5,6a}$ = 1.7 Hz, $J_{5,6b}$ = 7.9 Hz, $J_{4,5}$ = 9.6, H-5), 3.93 (d, 1 H, $J_{4G,5G}$ < 1 Hz, $J_{3G,4G}$ = 3.1 Hz, H-4G), 3.74 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, H-3), 3.72−3.66 (m, 3 H, H-5G, H-6aG, H-6bG), 3.66−3.62 (m, 6 H, 3 CH_2O), 3.58 (dd, 1 H, $J_{3G,4G}$ = 3.1 Hz, $J_{2G,3G}$ = 9.5 Hz, H-3G), 3.52 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.5 Hz, H-2G), 3.40 (dd, 1 H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 3.19 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.94, 2.86 (2 m, 2 H, J = 6.5 Hz, J_{gem} = 13.4 Hz, CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.3 (C-4 triazole), 126.5 (C-5 triazole), 93.8 (C-1), 86.4 (C-1G), 79.4 (C-5G), 74.4 (C-3G), 73.0 (C-3), 71.3 (C-4), 71.1 (C-2), 70.8 (C-5), 70.6, 69.8, 69.3 (CH_2O), 70.1 (C-2G), 69.3 (C-4G), 63.4 (CH_2Ar), 61.5 (C-6G), 51.3 (C-6), 29.6 (CH_2S). Anal. Calcd for $C_{38}H_{64}N_6O_{23}S_2 \cdot H_2O$: C, 43.26; H, 6.31; N, 7.97; S, 6.08. Found: C, 43.53; H, 6.40; N, 7.51; S, 5.70. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{38}H_{64}N_6NaO_{23}S_2$ 1059.3362, found 1059.3342.

Compound 20c. yield 90%; $[\alpha]^{20}_D$ +22.2 (c 0.7, D_2O); R_f 0.20 (double development); ^{1}H NMR (500 MHz, D_2O) δ 8.01 (s, 1 H, H-triazole), 4.76 (dd, 1 H, $J_{5,6a}$ = 1.4 Hz, $J_{6a,6b}$ = 14.4 Hz, H-6a), 4.65 (s, 2 H, CH_2Ar), 4.58 (d, 1 H, $J_{1,2}$ = 4.5 Hz, H-1), 4.55 (dd, 1 H, $J_{5,6b}$ = 7.8 Hz, $J_{6a,6b}$ = 14.5 Hz, H-6b), 4.45 (d, 2 H, $J_{1G,2G}$ = 9.7 Hz, H-1G), 4.04 (m, 1 H, $J_{5,6a}$ = 1.5 Hz, $J_{5,6b}$ = 8.1 Hz, $J_{4,5}$ = 9.5 Hz, H-5), 3.93 (d, 1 H, $J_{4G,5G}$ < 1 Hz, $J_{3G,4G}$ = 2.8 Hz, H-4G), 3.74 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 3.72−3.66 (m, 6 H, H-5G, H-6aG, H-6bG), 3.66−3.62 (m, 18 H, 9 CH_2O), 3.59 (dd, 1 H, $J_{3G,4G}$ = 2.9 Hz, $J_{2G,3G}$ = 9.4 Hz, H-3G), 3.52 (t, 1 H, $J_{1G,2G}$ = $J_{2G,3G}$ = 9.5 Hz, H-2G), 3.40 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 3.18 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 2.94, 2.87 (2 m, 2 H, CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.3 (C-4 triazole), 126.5 (C-5 triazole), 93.8 (C-1), 86.4 (C-1G), 79.4 (C-5G), 74.4 (C-3G), 73.0 (C-3), 71.4 (C-4), 71.2 (C-2), 70.8 (C-5), 70.6 (×2), 70.4 (×4), 70.2 (×2), 69.4 (CH_2O), 70.1 (C-2G), 69.3 (C-4G), 63.5 (CH_2Ar), 61.5 (C-6G), 51.3 (C-6), 29.6 (CH_2S). Anal. Calcd for $C_{50}H_{88}N_6O_{29}S_2 \cdot H_2O$: C, 45.52; H, 6.88; N, 6.37; S, 4.86. Found: C, 45.61; H, 7.07; N, 6.03; S, 4.74. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{50}H_{88}N_6NaO_{29}S_2$ 1323.4935, found 1323.4979.

Compound 22a: yield 89%; $[\alpha]^{20}_D$ +4.3 (c 0.5, D_2O); R_f 0.21 (double development); ^{1}H NMR (500 MHz, D_2O) δ 8.06, 7.98, 7.73 (3s, 3 H, H-triazole), 5.58 (d, 1 H, $J_{1,2}$ = 8.6 Hz, H-1), 5.36 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1′), 4.90 (br d, 1 H, $J_{5',6'a}$ < 1 Hz, $J_{6'a,6'b}$ = 14.1 Hz, H-6′a), 4.52 (dd, 1 H, $J_{5',6'b}$ = 8.7 Hz, $J_{6'a,6'b}$ = 13.9 Hz, H-6′b), 4.37, 4.30, 4.07 (3 d, 3 H, $J_{1G,2G}$ = 9.1 Hz, 3 × H-1G), 4.15−3.84 (m, 9 H, H-2, H-3, H-5, H-6a, H-6b, H-5′, 3 × H-4G), 3.79−3.40 (m, 25 H, H-4, H-2′, H-3′, H-4′, 3 × H-2G, 3 × H-3G, 3 × H-5G, 3 × H-6aG, 3 × H-6bG, 3 × CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 145.6, 144.8, 144.4 (C-4 triazole), 125.7, 125.5, 123.2 (C-5 triazole), 101.1 (C-1′), 87.0 (C-1), 85.3, 85.2, 84.3 (3 × C-1G), 79.9, 79.1, 79.0, 76.0, 75.7, 75.6, 75.0, 73.9, 72.5, 72.4, 72.8, 71.7, 71.1, 71.0, 69.6, 69.5, 69.4, 68.7 (C-2 to C-5, C-2′ to C-5′, 3 × C-2G to C-5G), 61.1, 61.0, 60.7 (3 × C-6G), 51.5 (C-6′), 50.2 (C-6), 23.6, 23.2, 23.0 (3 × CH_2S). Anal.

Calcd for $C_{39}H_{61}N_9O_{23}S_3$: C, 41.82; H, 5.49; N, 11.25; S, 8.59. Found: C, 41.74; H, 5.72; N, 11.05; S, 8.23. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{39}H_{62}N_9O_{23}S_3$ 1120.3121, found 1120.3118.

Compound 22b: yield 80%; $[\alpha]^{20}_D$ +5.7 (c 0.8, D_2O); R_f 0.19 (double development); ^{1}H NMR (500 MHz, D_2O) δ ^{1}H NMR (500 MHz, D_2O) δ 8.11, 8.07, 7.79 (3s, 3 H, H-triazole), 5.61 (d, 1 H, $J_{1,2}$ = 8.7 Hz, H-1), 5.38 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1′), 4.92 (br d, 1 H, $J_{5',6'a}$ < 1 Hz, $J_{6'a,6'b}$ = 13.8 Hz, H-6′a), 4.60, 4.32 (3 s, 6 H, 3 × CH_2Ar), 4.59 (dd, 1 H, $J_{5',6'b}$ = 8.7 Hz, $J_{6'a,\ 6'b}$ = 13.7 Hz, H-6′b), 4.46 (d, 3 H, $J_{1G,2G}$ = 9.7 Hz, 3 × H-1G), 4.15 (ddd, 1 H, $J_{5',6'a}$ = 1.6 Hz, $J_{5',6'b}$ = 8.3 Hz, $J_{4',5'}$ = 9.9 Hz, H-5′), 4.10−3.96 (m, 3 H, H-5, H-6a, H-6b), 3.94 (m, 5 H, H-2, H-3, 3 × H-4G), 3.78 (t, 1 H, $J_{2',3'} = J_{3',4'}$ = 9.5 Hz, H-3′), 3.74−3.49 (m, 35 H, H-4, H-2′, 3 × H-2G, 3 × H-3G, 3 × H-5G, 3 × H-6aG, 3 × H-6bG, 9 CH_2O), 3.37 (t, 1 H, $J_{3',4'} = J_{4',5'}$ = 9.2 Hz, H-4′), 2.93, 2.82 (2 m, 6 H, CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.8, 144.3, 144.2 (C-4 triazole), 126.9, 126.7, 124.7 (C-5 triazole), 101.4 (C-1′), 87.3 (C-1), 86.4 (C-1G), 80.2 (C-4), 79.4 (C-5G), 76.2 (C-3), 75.1 (C-5), 74.4 (C-3G), 72.9 (C-3′), 72.5 (C-5′), 72.1 (C-2′), 72.0 (C-2), 71.4 (C-4′), 70.6, 70.5, 70.4, 70.1, 69.8, 69.7, 69.5, 69.3, 69.1 (C-2G, C-4G, 9 CH_2O), 63.5, 63.4, 63.3 (3 × CH_2Ar), 61.5 (C-6G), 51.9 (C-6′), 50.4 (C-6), 29.6 (CH_2S). Anal. Calcd for $C_{51}H_{85}N_9O_{29}S_3$: C, 44.24; H, 6.19; N, 9.11; S, 6.95. Found: C, 44.05; H, 6.38; N, 9.35; S, 7.12. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{51}H_{86}N_9O_{29}S_3$ 1384.4694, found 1384.4670.

Compound 22c: yield 96%; $[\alpha]^{20}_D$ +10.7 (c 0.4, D_2O); R_f 0.12 (double development); ^{1}H NMR (500 MHz, D_2O) δ 8.10, 8.05, 7.78 (3s, 3 H, H-triazole), 5.60 (d, 1 H, $J_{1,2}$ = 8.8 Hz, H-1), 5.38 (d, 1 H, $J_{1',2'}$ = 3.4 Hz, H-1′), 4.91 (br d, 1 H, $J_{5,6'a}$ < 1 Hz, $J_{6'a,6'b}$ = 14.4 Hz, H-6′a), 4.60 (m, 5 H, H-6′b, 2 × CH_2Ar), 4.44 (d, 3 H, $J_{1G,2G}$ = 9.6 Hz, 3 × H-1G), 4.32 (m, 2 H, CH_2Ar), 4.15−4.00 (m, 4 H, H-5, H-6a, H-6b, H-5′), 3.94 (m, 5 H, H-2, H-3, 3 × H-4G), 3.73−3.49 (m, 72 H, H-4, H-2′, H-3′, 3 × H-2G, 3 × H-3G, 3 × H-5G, 3 × H-6aG, 3 × H-6bG, 27 CH_2O), 3.34 (t, 1 H, $J_{3',4'} = J_{4',5'}$ = 9.2 Hz, H-4′), 2.93, 2.85 (2 m, 6 H, 3 × CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.8, 144.3, 144.2 (C-4 triazole), 126.8, 126.6, 124.6 (C-5 triazole), 101.4 (C-1′), 87.4 (C-1), 86.4 (C-1G), 80.2 (C-4), 79.4 (C-5G), 76.3 (C-3), 75.2 (C-5), 74.4 (C-3G), 72.9 (C-3′), 72.4 (C-5′), 72.1 (C-2′), 72.0 (C-2), 71.4 (C-4′), 70.6, 70.1, 69.8, 69.7, 69.5, 69.3, 69.1 (C-2G, C-4G, CH_2O), 63.5, 63.4, 63.3 (3 × CH_2-triazole), 61.5 (C-6G), 51.9 (C-6′), 50.4 (C-6), 29.6 (3 × CH_2S). Anal. Calcd for $C_{69}H_{121}N_9O_{38}S_3$: C, 46.53; H, 6.85; N, 7.08; S, 5.40. Found: C, 46.76; H, 7.09; N, 7.34; S, 5.69. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{69}H_{122}N_9O_{38}S_3$ 1780.7044, found 1780.7053.

Compound 24a: yield 89%; $[\alpha]^{20}_D$ +7.6 (c 0.2, D_2O); R_f 0.12 (double development); ^{1}H NMR (500 MHz, D_2O) δ 8.06, 7.98, 7.91, 7.73 (4s, 4 H, H-triazole), 5.58 (d, 1 H, $J_{1,2}$ = 8.6 Hz, H-1), 5.31 (2d, 1 H each, $J_{1',2'} = J_{1'',2''}$ = 3.9 Hz, H-1′, H-1″), 4.90 (br d, 1 H, $J_{5'',6''a}$ < 1 Hz, $J_{6''a,6''b}$ = 14.1 Hz, H-6″a), 4.52 (dd, 1 H, $J_{5'',6'b}$ = 8.7 Hz, $J_{6''a,\ 6''b}$ = 13.9 Hz, H-6″b), 4.42, 4.37, 4.30, 4.07 (4 d, 4 H, $J_{1G,2G}$ = 9.1 Hz, 4 × H-1G), 4.19−3.33 (m, 48 H, H-2 to H-5, H-6a, H-6b, H-2′ to H-5′, H-6′a, H-6′b, H-2″ to H-5″, 4 × H-2G to H-5G, 4 × H-6aG, 4 × H-6bG, 4 × CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 146.1, 146.0, 145.1 (C-4 triazole), 126.3, 126.1, 123.6 (C-5 triazole), 101.2, 101.1 (C-1′, C-1″), 87.4 (C-1), 85.7, 85.6, 85.5, 84.8 (4 × C-1G), 81.3, 80.3, 79.5, 79.4, 79.3, 76.1, 75.3, 74.3, 72.9, 72.2, 71.5, 70.0, 69.9, 69.8, 69.7, 69.6, 69.4, 69.3, 69.2, 69.1 (C-2 to C-5, C-2′ to C-5′, C-2″ to C-5″, 4 × C-2G to C-5G), 61.7, 61.6, 61.5, 61.4 (4 × C-6G), 51.9, 51.3, 50.5 (C-6, C-6′, C-6″), 24.0, 23.6, 23.5, 23.4 (4 × CH_2S). Anal. Calcd for $C_{54}H_{84}N_{12}O_{32}S_4$: C, 42.07; H, 5.49; N, 10.90; S, 8.32. Found: C, 42.34; H, 5.66; N, 11.12; S, 8.01. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{54}H_{84}N_{12}NaO_{32}S_4$ 1563.4095, found 1563.4099.

Compound 24b: yield 81%; $[\alpha]^{20}_D$ +3.2 (c 0.3, D_2O); R_f 0.18 (triple development); ^{1}H NMR (500 MHz, D_2O) δ 8.09, 8.05, 7.96, 7.76 (4s, 4 H, H-triazole), 5.60 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1), 5.38, 5.33 (2d, 1 H each, $J_{1',2'} = J_{1'',2''}$ = 3.3 Hz, H-1′, H-1″), 4.93 (br d, 1 H, $J_{5'',6''a}$ < 1 Hz, $J_{6''a,6''b}$ = 14.1 Hz, H-6″a), 4.66, 4.64, 4.35, 4.29 (4 d, 8 H, 4 × CH_2Ar), 4.56 (dd, 1 H, $J_{5'',6''b}$ = 9.3 Hz, $J_{6''a,\ 6''b}$ = 14.3 Hz, H-6″b), 4.46 (m, 4 H, 4 × H-1G), 4.15−3.35 (m, 64 H, H-2 to H-5, H-6a, H-6b, H-2′to H-5′, H-6′a, H6′b, H-2″ to H-5″, 4 × H-2G to H-5G, 4 × H-6aG, 4 × H-6bG, 12 CH_2O), 2.90 (m, 8 H, 4 × CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.7, 144.4, 144.3, 144.2 (C-4 triazole), 126.4, 126.3, 124.3 (C-5 triazole), 101.0, 100.6 (C-1′, C-1′), 86.8 (C-1), 85.9 (4 × C-1G), 80.7, 80.3, 79.5, 76.3, 76.2, 75.2, 74.2, 73.0, 72.9, 72.8, 72.6, 71.9, 71.4, 71.3, 70.3, 69.9, 69.7, 69.6, 69.4, 69.3, 69.1, 68.8 (C-2 to C-5, C-2′ to C-5′, C-2″ to C-5″, 4 × C-2G to C-5G, CH_2O), 63.5, 63.4, 62.9 (4 × CH_2Ar), 61.1 (C-6G), 50.9, 50.8, 50.3 (C-6, C-6′, C-6″), 29.2 (CH_2S). Anal. Calcd for $C_{70}H_{116}N_{12}O_{40}S_4$: C, 44.39; H, 6.17; N, 8.87; S, 6.77. Found: C, 44.56; H, 6.29; N, 9.03; S, 6.86. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{70}H_{117}N_{12}O_{40}S_4$ 1893.6362, found 1893.6318.

Compound 24c: yield 94%; $[\alpha]^{20}_D$ +4.2 (c 0.3, D_2O); R_f 0.13 (triple development); ^{1}H NMR (500 MHz, D_2O) δ 8.10, 8.04, 7.95, 7.76 (4s, 4 H, H-triazole), 5.59 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1), 5.36, 5.30 (2 d, 2 H, $J_{1',2'} = J_{1'',2''}$ = 3.4 Hz, H-1′, H-1″), 4.93 (br d, 1 H, $J_{5'',6''a}$ < 1 Hz, $J_{6''a,6''b}$ = 14.1 Hz, H-6″a), 4.66, 4.64, 4.35, 4.29 (4 d, 8 H, 4 × CH_2Ar), 4.56 (dd, 1 H, $J_{5'',6''b}$ = 9.2 Hz, $J_{6''a,\ 6''b}$ = 14.4 Hz, H-6″b), 4.46 (d, 4 H, $J_{1G,2G}$ = 9.6 Hz, 4 × H-1G), 4.15−3.35 (m, 112 H, H-2 to H-5, H-6a, H-6b, H-2′to H-5′, H-6′a, H6′b, H-2″ to H-5″, 4 × H-2G to H-5G, 4 × H-6aG, 4 × H-6bG, 36 CH_2O), 2.90 (m, 8 H, 4 × CH_2S); ^{13}C NMR (125 MHz, D_2O) δ 144.7, 144.4, 144.3, 144.2 (C-4 triazole), 126.8, 126.7, 124.7 (C-5 triazole), 101.4, 101.0 (C-1′, C-1″), 87.3 (C-1), 86.4 (4 × C-1G), 81.0, 80.2, 79.4, 76.2, 76.1, 75.0, 74.4, 73.1, 73.0, 72.9, 72.8, 71.9, 71.8, 71.4, 71.3, 70.4, 70.3, 70.2, 69.9, 69.7, 69.6, 69.5, 69.4, 69.3, 69.2, 69.1, 68.8 (C-2 to C-5, C-2′ to C-5′, C-2″ to C-5″, 4 × C-2G to C-5G, CH_2O), 63.5, 63.4, 63.3, 63.2 (4 × CH_2-triazole), 61.5 (C-6G), 51.9, 51.2, 50.3 (C-6, C-6′, C-6″), 29.6 (CH_2S). Anal. Calcd for $C_{94}H_{164}N_{12}O_{52}S_4$: C, 46.60; H, 6.82; N, 6.94; S, 5.29. Found: C, 46.89; H, 7.11; N, 7.09; S, 5.45. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{94}H_{165}N_{12}O_{52}S_4$ 2421.9519, found 2421.9522.

Enzymatic Assays:

Stability of the Glycoclusters toward the β-Galactosidase

A solution of the glycoclusters (1 mM) in sodium phosphate buffer (100 mM, pH 7.3, $MgCl_2$ 1.2 mM, 2-mercaptoethanol 100 mM) was incubated with the β-galactosidase from *E. coli* (0.6 U/mL) at 37 °C. Aliquots of the solution were taken after 8, 16, and 24 h, evaporated, and examined by TLC and NMR.

Inhibition of β-Galactosidase. The inhibitory activity of compounds **12**, **14a**−**c**, **16a**−**c**, **18a**−**c**, **20a**−**c**, **22a**−**c**, and **24a**−**c** toward *E. coli* β-galactosidase (grade VIII, Sigma, EC 3.2.1.23, 117 U/mg) was determined under standard conditions.[16,17] The enzyme (0.3 U; 1U = 1 enzyme unit hydrolyses 1 μmol of *o*-nitrophenyl galactopyranoside per minute) was incubated with *o*-nitrophenyl-β-D-galactopyranoside (concentration range: 0.2 to 5.0 mM) in sodium phosphate buffer (100 mM, pH 7.3, $MgCl_2$ 1.2 mM, 2-mercaptoethanol 100 mM) in the absence or presence of the free glycoclusters (**12**, **14a**−**c**, **16a**−**c**, **18a**−**c**, **20a**−**c**, **22a**−**c**, and **24a**−**c**; concentration range: 0.6 to 4.0 mM); the final volume was 0.50 mL. After incubation for 10 min at 37 °C, the reaction was quenched by addition of sodium borate buffer 0.2 M (4.0 mL, pH 10.0). The release of *o*-nitrophenol was measured by visible absorption spectroscopy at 410 nm. The K_i and K_m values and the inhibition type were determined from Lineweaver−Burk plots. The errors were estimated by the linear regression standard method.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for compounds **2b**−**c**, **3a**−**c**, **11**, **12**, **13a**−**c**, **14a**−**c**, **15a**−**c**, **16a**−**c**, **17a**−**c**, **18a**−**c**, **19a**−**c**, **20a**−**c**, **21a**−**c**, **22a**−**c**, **23a**−**c**, and **24a**−**c** and COSY and HSQC for compounds **13b**, **14b**, **15b**, **16b**, **17a**, **18a**, **19a**, **20a**, **21b**, **22b**, **23c**, and **24c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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