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Glycals in Organic Synthesis: A Systematic Strategy for the Preparation of Uncommon Piperidine 1,2-Dideoxy-L-azasugars and 2-Deoxy-1,5-anhydro-L-hexitols

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A systematic synthetic strategy has been developed for producing uncommon piperidine 1,2-dideoxy-L-azasugars. This method involves the formation of open intermediates such as **2**, **7**, and **10** easily by ring-opening of D-glycals with aqueous mercury(II) acetate/sodium borohydride. A concise sequence of regioselective amination and cyclization reactions then allowed us to prepare the cyclic compounds **5a** and **5b**, L enantiomers of naturally occurring fagomine congeners such as 3-*epi*-fagomine (**II**) and 3,4-di-*epi*-fagomine (**III**), from D-glucal and D-galactal, respectively. The unnatural 3,4-di-*epi*-6-deoxyfagomine **9** was obtained from L-rhamnal by the same reaction sequence. This straightforward chemistry has been shown to be useful for preparing glycosyl derivatives of 1,2-dideoxy-L-azasugars starting from glycosyl glycals such as D-lactal, D-cellobial, D-maltal, and D-melibial, thus avoiding the usually lengthy glycosylation procedures. The flexibility of our protocol has been demonstrated by the easy conversion of the above-described open intermediates into uncommon 2-deoxy-1,5-anhydro-L-hexitols, never previously described.

Introduction

Azasugars (or iminosugars) are carbohydrate analogues in which the ring oxygen has been replaced by a nitrogen atom and are found to be widespread in plants and microorganisms.[1] They have been shown to be potent inhibitors of many carbohydrate-processing enzymes,[2] such as glycosyltransferases,[3] metalloproteinases,[4] glycogen phosphorylases,[5] a sugar nucleotide mutase,[6] and nucleoside-processing enzymes.[7] Since these enzymes are involved in fundamental biological processes, azasugars are leads for the development of new therapeutic agents to treat a wide range of diseases, for example, diabetes,[8] viral infections,[9] and tumor metastasis.[10] The varied biological significance of azasugars has created huge interest in the synthesis of naturally occurring azasugars and their structural modification and has stimulated many groups to develop short and stereoselective synthetic routes. Many recent syntheses used readily available and inexpensive chiral-pool starting materials such as carbohydrates, amino acids, and tartaric acids.[11] In particular, the main structural features shared by azasugars and carbohydrates have made them ideal starting materials. In this context, many azasugars have been obtained from carbohydrates and the main challenge of this strategy is the differentiation of the hydroxy groups of an open carbohydrate-derived intermediate, the conversion of one of them into an amino group or precursor and then the intramolecular cyclization of the open intermediate, a crucial step determining the efficiency and viability of the syntheses.[11,12] The asymmetric synthesis of azasugars from achiral starting materials has been reported less frequently and usually involves lengthy procedures with low overall yields.[11,13]

Up to now, more than 100 polyhydroxylated alkaloids have been isolated from plants and microorganisms[11] and a large number of these compounds, particularly piperidinic 1-deoxy-azasugars, have already been described and their syntheses reported in a number of articles.[11]

Piperidine 1,2-dideoxy-azasugars represent a small but important niche in the fields of azasugar chemistry and azasugar bioactivity.[1b,7b,11] Thus, 1,2,5-trideoxy-1,5-imino-D-arabinitol (**I**) (fagomine in Figure 1) was first isolated in 1974 from buckwheat seeds[14] and recently was found to have a potent antihyperglycemic effect in streptozocin-induced diabetic mice and to potentiate markedly immunoreactive insulin release.[15] More recently, isomers of fagomine such as 3-*epi*-fagomine (**II**), 3,4-di-*epi*-fagomine (**III**), and their glucopyranosyl derivatives have been isolated from leaves and roots of *Xanthocercis zambesiaca*,[16] while 6-deoxy-fagomine (**IV**) has been found in the roots of *Lycium chinense* (Figure 1).[17] Concerning their biological activity, **II**, for instance, was found to be a more potent glycosidase inhibitor than **I**, particularly of mammalian α-glucosidase and β-galactosidase.[16]

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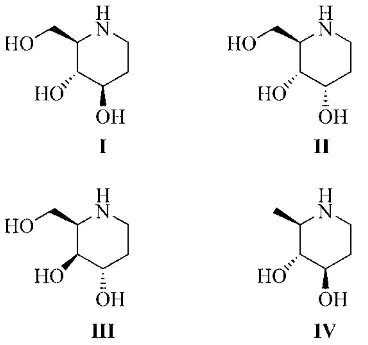


Figure 1. Compounds **I**–**IV**.

The asymmetric synthesis of fagomine (**I**) is repeatedly described in the literature.[18] For instance, recently Shipman and co-workers reported the asymmetric synthesis of **I** starting from an iminoglucal obtained from D-glucal.[12c,19] Thus far, the asymmetric synthesis of the fagomine isomers such as **II** and **III** has been reported just twice. Takahata and co-workers achieved the asymmetric synthesis of the four possible fagomine isomers by catalytic ring-closing metathesis (RCM). The synthesis involved the construction of a piperidine-type chiral building block by RCM starting from the D-serine-derived Garner's aldehyde, followed by hydroxylation.[20,21] Note that all the synthetic compounds possess the D configuration, as do the naturally occurring compounds. Only Shipman and co-workers were able to obtain an L-configured fagomine diastereomer as a byproduct.[12c] Interestingly, Clapés and co-workers were able to prepare fagomine and its isomers by stereoselective aldol addition catalyzed by dihydroxyacetone phosphate from linear chiral precursors, though as a D,L mixture.[22]

Owing to the high potential of azasugars in drug discovery, the synthesis of diastereoisomers or modified structures of naturally occurring azasugars remains a challenge.[23] In a recent paper, Asano and co-workers reported the asymmetric synthesis of enantiomers of naturally occurring 1-deoxy-D-azasugars and the systematic study of their glycosidase inhibitor activity.[24]

As part of our continuing exploitation of the reactivity and the usefulness of carbohydrate derivatives in organic synthesis,[25] we herein describe a new and expeditious strategy for the synthesis of uncommon piperidine 1,2-dideoxy-L-azasugars that allows access to these compounds in a few steps starting from readily available D-glycal derivatives. The versatility of this methodology was demonstrated by its application in disaccharide chemistry.

To the best of our knowledge, there is a lack of a general and flexible approach to the preparation of diastereoisomers of fagomine (**I**) and its congeners through a minimum number of steps.

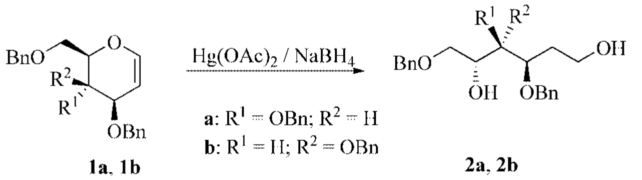
Furthermore, the synthetic strategy can be used in a rapid and profitable preparation of uncommon and never previously described 2-deoxy-1,5-anhydro-L-hexitols and their corresponding glycosyl derivatives. 2-Deoxy-1,5-anhydro-D-hexitols are often reported in the literature to have some interesting properties. For instance, Masumoto et al. prepared 2-deoxy-D-glucitol derivatives and then used them as chiral ligands in the catalytic enantioselective cyanosilylation of ketones.[26] More recently, the same authors[27] found that D-*arabino*- and D-*ribo*-configured 2,6-dideoxyhexitol derivatives showed strong activity as agonists for lysophosphatidic acids (LPA), a group of important extracellular signaling molecules that elicit a wide variety of biological responses, such as cell-growth stimulation, calcium mobilization, escape from apoptosis, tumor cell invasion, and smooth muscle contraction.[28]

The availability of simple and short reaction sequences for preparing uncommon 2-deoxy-1,5-anhydro-L-hexitols should represent a valuable goal from both synthetic and biological points of view.

Results and Discussion

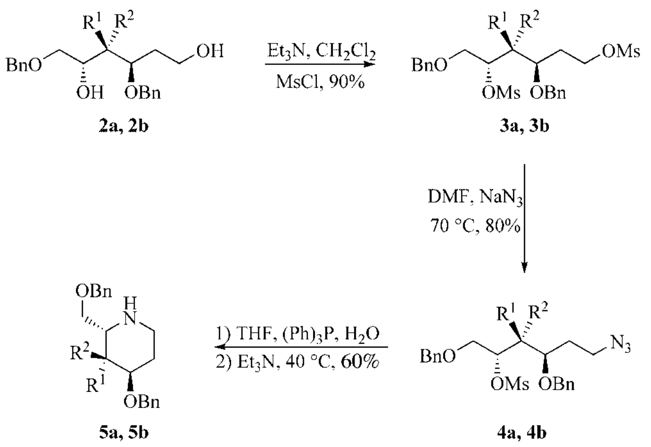
All the starting materials were prepared in one step from *O*-benzyl derivatives of glycals and glycosyl glycals according to our previously reported procedure[25,29] by treatment with aqueous mercury(II) acetate/sodium borohydride in one reaction flask and on a large scale.

To test the efficiency of our strategy, we prepared the enantiomerically pure (3*R*,4*R*,5*R*)-3,4,6-tris(benzyloxy)hexane-1,5-diol (**2a**) and the corresponding (3*R*,4*S*,5*R*) diastereoisomer **2b**, available from the corresponding D-glucal and D-galactal, respectively,[25,29] and characterized by the presence of a primary and secondary alcohol (Scheme 1). The intermediates **2a** and **2b** have a carbon skeleton with the required protected functionalities and the free hydroxy groups necessary for the introduction of the nitrogen atom in the right position to prepare the 1,5-iminosugar derivatives.



Scheme 1.

The free hydroxy groups of **2a** and **2b** were easily mesylated at room temperature in Et_3N/CH_2Cl_2 to obtain the corresponding dimesyl derivatives **3a** and **3b**, which have good leaving groups for the following domino process: first nucleophilic displacement, then the N-heterocyclization step. In fact, the reaction with sodium azide in DMF at 70 °C gave directly and regioselectively the corresponding 1-azido derivatives **4a** and **4b** in 80% yields. Reduction of the azido group with $(Ph)_3P/H_2O$ in THF followed by in situ treatment with Et_3N at 40 °C successfully afforded 3,4,6-tri-*O*-benzyl-2-deoxy-1,5-imino-L-hexitols **5a** and **5b** in 65% yield (Scheme 2). The L configuration of the stereogenic center located at the 5 position was achieved during the ring-closure process by chiral inversion of mesylates **4a** and **4b**, as is well-documented in heterocyclization reactions in carbohydrate chemistry.[23,31,32]

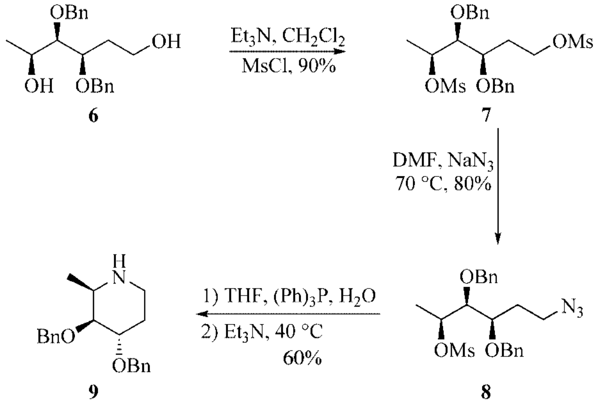


a: R^1 = OBn; R^2 = H
b: R^1 = H; R^2 = OBn

Scheme 2.

Especially noteworthy are compounds **5a** and **5b**, which represent the benzylated derivatives of the enantiomers of the naturally occurring 3,4-di-*epi*-fagomine (**III**) and 3-*epi*-fagomine (**II**), respectively.

Interestingly, (3*R*,4*R*,5*S*)-3,4-bis(benzyloxy)hexane-1,5-diol (**6**), obtained from per-*O*-benzylated L-rhamnal,[25,29] was easily converted into the unknown 3,4-di-*O*-benzyl-2,6-dideoxy-1,5-imino-D-*xylo*-hexitol (**9**) in 60% yield via intermediates **7** and **8**, following the above procedure (Scheme 3).

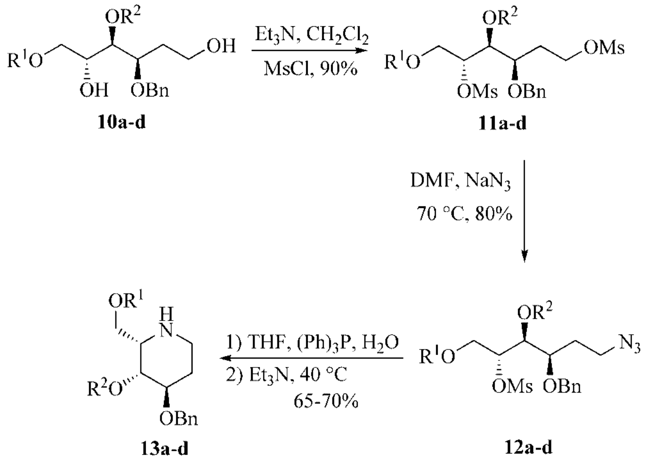


Scheme 3.

Prompted by these findings, we decided that it would be interesting to exploit the reactivity of glycosyl glycals in order to develop a short and efficient protocol for preparing glycosyl derivatives of 2-deoxy-1,5-imino-L-hexitols. The success of this strategy should render these compounds readily accessible, avoiding the usually lengthy glycosylation procedures. As is well known in oligosaccharide chemistry, regio- and stereospecific glycoside formation is the most important step,[31,33] and so has been investigated by using different protocols, mainly through a coupling reaction between sugar derivatives and glycosyl acceptors and by the use of a reaction promoter for the coupling reaction, generally a Lewis acid or enzymatic methods.[31,33] The yields vary from poor to good.[34,35]

The enantiomerically pure 3-(benzyloxy)hexane-1,4,5,6-tetraol derivatives **10a–d**, with a sugar moiety located either at C4 or C6, were easily prepared by the usual reaction with aqueous mercury(II) acetate/sodium borohydride in very high yields (about 90%), respectively, from per-*O*-benzylated D-lactal, D-cellobial, D-maltal, and D-melibial.[25,29]

The N-heterocyclized compounds **13a–d** were generated smoothly in 65–70% yields starting from **10a–d** through our three-step sequence: i) formation of 2,6-di-*O*-mesylates **11a–d** by reaction with methanesulfonyl chloride in triethylamine, ii) regioselective azidation by treatment with sodium azide in DMF to give **12a–d**, and iii) cyclization by reduction with $(Ph)_3P/H_2O$ and then triethylamine to provide **13a–d** (Scheme 4).

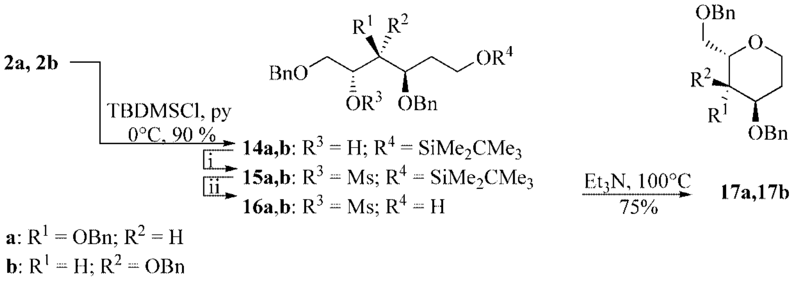


a: R^1 = Bn; R^2 = 2',3',4',6'-tetra-*O*-benzyl-β-D-galactopyranosyl
b: R^1 = Bn; R^2 = 2',3',4',6'-tetra-*O*-benzyl-β-D-glucopyranosyl
c: R^1 = Bn; R^2 = 2',3',4',6'-tetra-*O*-benzyl-α-D-glucopyranosyl
d: R^1 = 2',3',4',6'-tetra-*O*-benzyl-α-D-galactopyranosyl; R^2 = Bn

Scheme 4.

The outcome of the reaction clearly indicates that the presence of a sugar derivative adjacent to the secondary hydroxy group in **12a–d** does not influence the intramolecular ring closure between the amino group, first introduced at C1 as an azido group, and the mesylate leaving group at C5. In particular, steric hindrance due to the presence of a perbenzylated sugar unit close to the reaction center did not affect the reactivity. Note that **13a–d** represent the glycosyl derivatives of **5a**, an enantiomer of the naturally occurring 3,4-di-*epi*-fagomine (**III**).

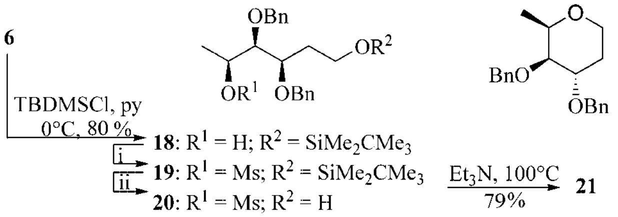
Our flexible strategy has allowed us to design a general synthesis for the preparation of the unknown 2-deoxy-1,5-anhydro-L-hexitols starting from the above-described chiral building blocks, for example, **2a** and **2b**. To achieve this goal, the primary hydroxy groups of **2a**,**b** were regioselectively protected by treatment with TBDMSCl/Py, giving **14a**,**b** in high yields (90%), which were further transformed into the corresponding mesylate derivatives **15a**,**b** by the us-



Scheme 5. Reagents and conditions: i) pyridine, Et_3N, $MeSO_2Cl$, room temp., 12 h, 90%; ii) THF, TBAF, room temp., 12 h, 74–80%.

ual procedure (90%). After removal of the silyl-protecting group of **15a**,**b** by reaction with TBAF in THF at room temp. (74–80%), Et_3N-promoted cyclization of **16a**,**b** successfully gave 3,4,6-tri-*O*-benzyl-2-deoxy-1,5-anhydro-L-hexitols **17a**,**b** in 75% yield (Scheme 5).

Analogously, the open-chain intermediate **6**, obtained from per-*O*-benzylated L-rhamnal, was easily converted into the unknown 3,4-di-*O*-benzyl-2,6-dideoxy-1,5-anhydro-D-*xylo*-hexitol (**21**) in a 45% overall yield via intermediates **18**, **19**, and **20**, following the above procedure (Scheme 6).



Scheme 6. Reagents and conditions: i) pyridine, Et_3N, $MeSO_2Cl$, room temp., 12 h, 90%; ii) THF, TBAF, room temp., 12 h, 80%.

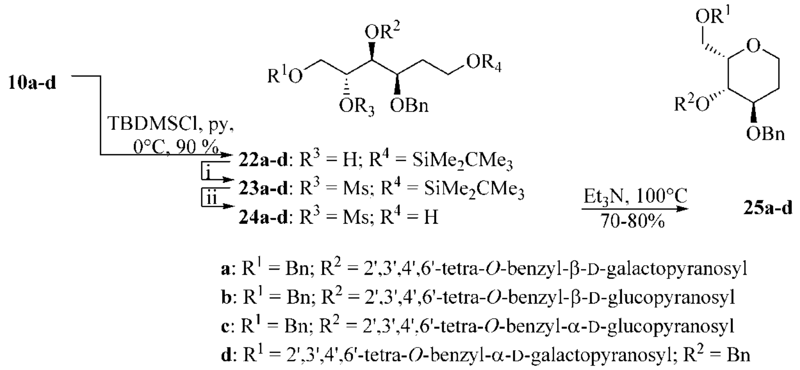
Clearly we considered it interesting to exploit the reactivity of the glycosyl glycals in order to develop a short protocol for the preparation of glycosyl derivatives of 2-deoxy-1,5-anhydro-L-hexitols, rendering these compounds easily accessible and avoiding the usually lengthy glycosylation procedures.[36]

O-Heterocyclized **25a–d** were generated smoothly starting from **10a–d** through our four-step protocol: i) regioselective formation of 6-silyl derivatives **22a–d** by reaction with TBDMSCl/Py (90%), ii) synthesis of the corresponding 2-mesyl derivatives **23a–d** by reaction with methanesulfonyl chloride in triethylamine (85–90%), iii) desilylation by treatment with TBAF to give **24a–d** (80%), and iv) Et_3N-promoted cyclization at 100 °C provided **25a–d** (70–80%) (Scheme 7). As previously described in the synthesis of **13a–d**, steric hindrance due to the presence of a perbenzylated sugar unit close to the reaction center did not affect the intramolecular ring closure.

Interestingly, compounds **25a–d** represent the glycosyl derivatives of the previously described *xylo*-configured 2-deoxy-1,5-anhydro-L-hexitol **17a**.

Conclusions

In conclusion, we have demonstrated that glycals and glycosyl glycals are the most attractive starting materials for the construction of uncommon piperidine 1,2-dideoxy-L-azasugars and 2-deoxy-1,5-anhydro-L-hexitols that should be biologically important. Note that our aim was to find simplified synthetic strategies and to be guided by readily available starting materials in conjunction with straightforward chemistry. This new strategy shows high flexibility, particularly in disaccharide chemistry, avoiding the extensive manipulations reported in classical glycosylation se-



Scheme 7. Reagents and conditions i) pyridine, Et_3N, $MeSO_2Cl$, room temp., 12 h, 85–90%; ii) THF, TBAF, room temp., 12 h, 80%.

quences. Application of this strategy to the synthesis of more complex heterosugars from trisaccharides is currently in progress.

Experimental Section

General: ^{1}H (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded with a Varian Gemini 200 spectrometer with $CDCl_3$ as the solvent and internal standard. IR spectra were recorded with an IR Equinox 55 Bruker spectrometer. HRMS spectra were recorded with a Micromass Q-TOF *micro* Mass Spectrometer (Waters). Optical rotations were measured with a DIP 370 Jasco digital polarimeter using the sodium D line. Yields are given for isolated products after column chromatography showed a single spot on TLC plates and no detectable impurities in the ^{1}H NMR spectrum. All reaction were performed under N_2 in flame-dried glassware. All solvents and commercially available reagents were used without purification unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC) carried out on Merck F-254 silica glass plates visualized with UV/light and heat-gun treatment with a 2 N H_2SO_4 solution. Column chromatography was performed with Merck silica gel 60 (230–400 mesh).

Starting Materials: All the starting materials **2a**,**b**, **6**, and **10a**–**d** were prepared from their corresponding glycals or glycosyl glycals according to our previously described procedure.[25,29] Dimesyl derivatives **3a**,**b**, **7**, **11a**–**d** were prepared from the corresponding linear diols **2a**,**b**, **6**, and **10a**–**d** according to our previously described procedure.[25,29]

General Procedure for the Preparation of Compounds 4a,b, 8, and 12a–d: NaN_3 (30 equiv.) was added to a stirred solution of the appropriate dimesyl derivative in DMF (15 mL/mmol). The reaction mixture was heated at 70 °C for 12 h and after that time TLC (hexanes/EtOAc, 8:2) showed the disappearance of the starting material. The solution was then diluted with Et_2O (200 mL/mmol), washed in a separating funnel with H_2O (until neutrality) and then brine (100 mL/mmol), dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The residue was then purified by column chromatography.

Azide 4a: This compound was prepared from **3a** (100 mg, 0.17 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (73 mg, 0.13 mmol, 80 %). $[\alpha]_D$ = +16.7 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3010, 2960, 2910, 1620, 1510, 1460, 1350, 1060, 1020 cm^{-1}. ^{1}H NMR: δ = 7.48–7.30 (m, 15 H, Ph), 5.10–4.95 (m, 1 H, 2-H), 4.83–4.45 (m, 6 H, 3 CH_2Ph), 3.98–3.94 (m, 1 H, 3-H), 3.92–3.86 (m, 2 H, 1-H_A, 1-H_B), 3.74–3.62 (m, 1 H, 4-H), 3.38–3.15 (m, 2 H, 6-H_A, 6-H_B), 3.01 (s, 3 H, CH_3SO_2), 1.88–1.71 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 137.7, 137.3 (C_{quat}, Ph), 128.3, 128.1, 127.6 (Ph), 82.5, 79.8 (C-3, C-4), 75.9 (C-2), 74.1, 73.3, 72.9 (CH_2Ph), 68.9 (C-1), 47.7 (C-6), 38.3 (CH_3SO_2), 30.0 (C-5) ppm. HRMS: calcd. for $C_{28}H_{33}N_3O_6S$ 562.1982 [M + Na]$^+$; found 562.1970.

Azide 4b: This compound was prepared from **3b** (100 mg, 0.17 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 9:1), and obtained as a viscous oil (73 mg, 0.13 mmol, 80 %). $[\alpha]_D$ = +25.2 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2950, 2900, 1610, 1500, 1450, 1350, 1050, 1010 cm^{-1}. ^{1}H NMR: δ = 7.50–7.30 (m, 15 H, Ph), 4.93–4.88 (m, 1 H, 2-H), 4.90–4.48 (m, 6 H, 3 CH_2Ph), 4.08–4.02 (m, 1 H, 4-H), 3.88–3.75 (m, 3 H, 1-H_A, 1-H_B, 3-H), 3.48–3.38 (m, 2 H, 6-H_A, 6-H_B), 2.97 (s, 3 H, CH_3SO_2), 2.15–1.70 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 137.6, 137.5 (C_{quat}, Ph), 128.2, 127.7 (Ph), 81.3, 78.3 (C-3, C-4), 76.0 (C-2), 74.3, 73.4, 72.0 (CH_2Ph), 69.1 (C-1), 47.9 (C-6), 38.2 (CH_3SO_2), 29.6 (C-5) ppm. HRMS: calcd. for $C_{28}H_{33}N_3O_6S$ 562.1982 [M + Na]$^+$; found 562.1990.

Azide 8: This compound was prepared from **7** (100 mg, 0.21 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (74 mg, 0.17 mmol, 80 %). $[\alpha]_D$ = –2.8 (*c* = 1.2, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 2940, 2890, 1600, 1500, 1450, 136.0, 1050, 1015 cm^{-1}. ^{1}H NMR: δ = 7.42–7.25 (m, 10 H, Ph), 5.08–4.95 (m, 1 H, 2-H), 4.88–4.52 (m, 4 H, 2 CH_2Ph), 4.08–3.15 (m, 4 H, 6-H_A, 6-H_B, 3-H, 4-H), 2.94 (s, 3 H, CH_3SO_2), 2.08–1.84 (m, 2 H, 5-H_A, 5-H_B), 1.15 (d, $J_{1,2}$ = 6.5 Hz, 3 H, 1-H_A, 1-H_B, 1-H_C) ppm. ^{13}C NMR: δ = 138.0, 137.8 (C_{quat}, Ph), 128.2, 128.1, 127.9, 127.7 (Ph), 80.9, 79.0, 75.9 (C-2, C-3, C-4), 73.9, 73.4 (CH_2Ph), 47.9 (C-6), 38.4 (CH_3SO_2), 29.0 (C-5), 19.6 (C-1) ppm. HRMS: calcd. for $C_{21}H_{27}N_3O_5S$ 456.1564 [M + Na]$^+$; found 456.1550.

Azide 12a: This compound was prepared from **11a** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (80 mg, 0.08 mmol, 80 %). $[\alpha]_D$ = +2.8 (*c* = 1.2, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 1696, 1545, 1510, 1416, 1290, 1180, 1100, 1048 cm^{-1}. ^{1}H NMR: δ = 7.45–7.23 (m, 30 H, Ph), 5.09–4.12 (m, 14 H, 2-H, 1′-H, 6 CH_2Ph), 3.96–3.73 (m, 6 H, 3-H, 4-H, 2′-H, 3′-H, 6′-H_A, 6′-H_B), 3.68–3.48 (m, 4 H, 1-H_A, 1-H_B, 4′-H, 5′-H), 3.46–3.32 (m, 2 H, 6-H_A, 6-H_B), 2.92 (s, 3 H, CH_3SO_2), 2.10–1.63 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 138.6, 138.3, 137.8, 137.7, 137.6 (C_{quat}, Ph), 127.9, 127.8, 127.6, 127.5, 127.3 (Ph), 103.0 (C-1′), 82.4, 82.3, 79.2, 77.8, 75.8, 73.6, 73.3 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.0, 74.9, 74.5, 73.4, 72.8, 72.2, 68.9, 68.5 (C-1, C-6′, CH_2Ph), 48.0 (C-6), 38.4 (CH_3SO_2), 29.1 (C-5) ppm. HRMS: calcd. for $C_{55}H_{61}N_3O_{11}S$ 994.3919 [M + Na]$^+$; found 994.3907.

Azide 12b: This compound was prepared from **11b** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (78 mg, 0.08 mmol, 80 %). $[\alpha]_D$ = +10.0 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 1730, 1690, 1555, 1520, 1430, 1280, 1160, 1110, 1090 cm^{-1}. ^{1}H NMR: δ = 7.46–7.32 (m, 30 H, Ph), 5.13–4.52 (m, 14 H, 2-H, 1′-H, 6 CH_2Ph), 4.40–4.15 (m, 5 H, 3-H, 4-H, 2′-H, 3′-H, 4′-H), 3.96–3.65 (m, 5 H, 1-H_A, 1-H_B, 5′-H, 6′-H_A, 6′-H_B), 3.58–3.38 (m, 2 H, 6-H_A, 6-H_B), 2.96 (s, 3 H, CH_3SO_2), 2.15–1.82 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 138.4, 138.2, 137.8, 137.4 (C_{quat}, Ph), 128.2, 128.0, 127.6, 127.5 (Ph), 102.5 (C-1′), 84.6, 82.0, 77.7, 77.3, 75.8 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.5, 74.8, 74.7, 73.3, 73.2, 72.9, 72.1, 68.8 (C-1, C-6′, CH_2Ph), 47.8 (C-6), 38.4 (CH_3SO_2), 29.0 (C-5) ppm. HRMS: calcd. for $C_{55}H_{61}N_3O_{11}S$ 994.3919 [M + Na]$^+$; found 994.3931.

Azide 12c: This compound was prepared from **11c** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (76 mg, 0.08 mmol, 80 %). $[\alpha]_D$ = +45.6 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 1696, 1540, 1510, 1410, 1222, 1182, 1098, 1020 cm^{-1}. ^{1}H NMR: δ = 7.47–7.25 (m, 30 H, Ph), 5.15–4.40 (m, 14 H, 2-H, 1′-H, 6 CH_2Ph), 4.08–3.62 (m, 10 H, 3-H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 3.48–3.18 (m, 2 H, 1-H_A, 1-H_B), 3.02 (s, 3 H, CH_3SO_2), 2.10–1.55 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 138.6, 138.2, 138.0, 137.9, 137.3 (C_{quat}, Ph), 128.3, 127.9, 127.8, 127.7, 127.6, 127.4 (Ph), 96.7 (C-1′), 82.2, 79.5, 77.5, 76.7, 74.4, 71.1 (C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.3, 75.0, 73.3, 73.2, 72.3, 69.0, 68.1 (C-1, C-6′, CH_2Ph), 47.9 (C-6), 38.2 (CH_3SO_2), 29.6 (C-5) ppm. HRMS: calcd. for $C_{55}H_{61}N_3O_{11}S$ 994.3919 $[M + Na]^+$; found 994.3895.

Azide 12d: This compound was prepared from **11d** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (77 mg, 0.08 mmol, 80%). $[\alpha]_D$ = +74.1 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 1690, 1555, 1515, 1420, 1280, 1160, 1100, 1090 cm^{-1}. ^1H NMR: δ = 7.48–7.23 (m, 30 H, Ph), 5.03–4.38 (m, 14 H, 2-H, 1′-H, 6 CH_2Ph), 4.15–3.80 (m, 7 H, 3-H, 4-H, 2′-H, 3′-H, 4′-H, 6′-H_A, 6′-H_B), 3.72–3.48 (m, 3 H, 1-H_A, 1-H_B, 5′-H), 3.32–3.18 (m, 2 H, 6-H_A, 6-H_B), 2.94 (s, 3 H, CH_3SO_2), 1.86–1.68 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 138.5, 138.3, 138.1, 137.8, 137.5, 137.3 (C_{quat}, Ph), 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.3 (Ph), 97.4 (C-1′), 81.7, 80.0, 78.1, 76.1, 75.8, 74.5, 69.6 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.6, 74.1, 73.3, 73.2, 73.1, 72.7, 72.1, 68.7 (C-1, C-6′, CH_2Ph), 47.5 (C-6), 38.1 (CH_3SO_2), 29.8 (C-5) ppm. HRMS: calcd. for $C_{55}H_{61}N_3O_{11}S$ 994.3919 $[M + Na]^+$; found 994.3958.

General Procedure for the Preparation of Compounds 5a,b, 9, and 13a–d: PPh_3 (1.5 equiv.) was added at room temp. to a stirred solution of the appropriate 1-azido derivative (1 equiv.) in dry THF (20 mL/mmol). After 10 min, NEt_3 (1.2 mL/mmol) and H_2O (1 mL/mmol) were added and the reaction mixture was stirred at 40 °C for 12 h. After that time TLC (EtOAc/MeOH, 98:2) showed the disappearance of the starting material and the solvent was removed under reduced pressure. The residue was then purified by column chromatography.

3,4,6-Tri-*O*-benzyl-2-deoxy-1,5-imino-L-hexitol (5a): This compound was prepared from **4a** (100 mg, 0.18 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 3:7), and obtained as a viscous oil (46 mg, 0.11 mmol, 60%). $[\alpha]_D$ = –11.8 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2960, 2910, 1620, 1510, 1460, 1350, 1060, 1020 cm^{-1}. ^1H NMR: δ = 7.40–7.25 (m, 15 H, Ph), 4.63–4.42 (m, 6 H, 3 CH_2Ph), 3.78–3.30 (m, 5 H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 3.10–2.78 (m, 2 H, 1-H_A, 1-H_B), 2.10–2.00 (m, 1 H, NH), 2.03–1.65 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.5, 138.2 (C_{quat}, Ph), 128.4, 128.2, 127.5, 127.2 (Ph), 73.8, 73.2 (C-3, C-4), 72.4, 70.7, 70.6 (CH_2Ph, C-6), 54.2 (C-5), 40.3 (C-1), 26.5 (C-2) ppm. HRMS: calcd. for $C_{27}H_{31}NO_3$ 418.2377 $[M + H]^+$; found 418.2390.

3,4,6-Tri-*O*-benzyl-2-deoxy-1,5-imino-L-hexitol (5b): This compound was prepared from **4b** (100 mg, 0.18 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 3:7), and obtained as a viscous oil (45 mg, 0.11 mmol, 60%). $[\alpha]_D$ = –46.8 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2950, 2900, 1610, 1500, 1450, 1350, 1050, 1010 cm^{-1}. ^1H NMR: δ = 7.48–7.22 (m, 15 H, Ph), 4.75–4.35 (m, 6 H, 3 CH_2Ph), 4.02–3.60 (m, 5 H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 3.15–2.65 (m, 2 H, 1-H_A, 1-H_B), 2.40–2.25 (m, 1 H, NH), 1.60–1.20 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.8, 138.2 (C_{quat}, Ph), 128.4, 128.0, 127.6, 127.4, 127.1 (Ph), 78.2, 71.4 (C-3, C-4), 73.2, 71.0, 70.7 (CH_2Ph, C-6), 54.6 (C-5), 39.6 (C-1), 29.8 (C-2) ppm. HRMS: calcd. for $C_{27}H_{31}NO_3$ 418.2377 $[M + H]^+$; found 418.2364.

3,4-Di-*O*-benzyl-2,6-dideoxy-1,5-imino-D-*xylo*-hexitol (9): This compound was prepared from **8** (100 mg, 0.23 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 2:8), and obtained as a viscous oil (46 mg, 0.15 mmol, 65%). $[\alpha]_D$ = +108.3 (*c* = 1.2, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2940, 2890, 1600, 1500, 1450, 1360, 1050, 1015 cm^{-1}. ^1H NMR: δ = 7.40–7.23 (m, 10 H, Ph), 4.65–4.47 (m, 4 H, 2 CH_2Ph), 3.85–3-64 (m, 1 H, 3-H), 3.30–2.78 (m, 4 H, 1-H_A, 1-H_B, 4-H, 5-H), 2.42–2.18 (m, 1 H, NH), 1.94–1.58 (m, 2 H, 2-H_A, 2-H_B), 1.09 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6-H_A, 6-H_B, 6-H_C) ppm. ^{13}C NMR: δ = 138.0, 138.8 (C_{quat}, Ph), 128.2, 127.8, 127.6, 127.4, 127.3 (Ph), 76.7, 72.8 (C-3, C-4), 72.6, 70.7 (CH_2Ph), 49.9 (C-5), 40.5 (C-1), 26.0 (C-2), 17.7 (C-6) ppm. HRMS: calcd. for $C_{20}H_{25}NO_2$ 312.1958 $[M + H]^+$; found 312.1950.

Glycoside 13a: This compound was prepared from **12a** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 3:7), and obtained as a viscous oil (61 mg, 0.07 mmol, 70%). $[\alpha]_D$ = +15.5 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2970, 2930, 1650, 1500, 1450, 1350, 1050, 1010 cm^{-1}. ^1H NMR: δ = 7.42–7.19 (m, 30 H, Ph), 5.02–4.08 (m, 21 H, 3-H, 4-H, 5-H, 1′-H, 2′-H, 3′-H, 4′-H, 6′-H_A, 6′-H_B, 6 CH_2Ph), 3.98–3.25 (m, 3 H, 5′-H, 6-H_A, 6-H_B), 3.10–2.42 (m, 3 H, 1-H_A, 1-H_B, NH), 2.05–1.55 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.6, 138.3, 138.2, 138.1, 138.7 (C_{quat}, Ph), 128.0, 127.8, 127.6, 127.3, 127.1, 127.0 (Ph), 104.4 (C-1′), 82.6, 79.1, 74.3, 74.1, 73.4, 73.2 (C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.1, 74.4, 73.3, 72.8, 72.7, 70.6, 70.0, 68.7 (C-6, C-6′, CH_2Ph), 53.8 (C-5), 40.4 (C-1), 26.2 (C-2) ppm. HRMS: calcd. for $C_{54}H_{59}NO_8$ 850.4313 $[M + H]^+$; found 850.4349.

Glycoside 13b: This compound was prepared from **12b** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 3:7), and obtained as a viscous oil (62 mg, 0.07 mmol, 70%). $[\alpha]_D$ = –2.1 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2940, 2900, 1600, 1510, 1460, 1368, 1270, 1077 cm^{-1}. ^1H NMR: δ = 7.43–7.22 (m, 30 H, Ph), 5.08–4.30 (m, 14 H, 5′-H, 1′-H, 6 CH_2Ph), 4.03–3.32 (m, 10 H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 6′-H_A, 6′-H_B), 3.12–2.78 (m, 3 H, 1-H_A, 1-H_B, NH), 2.08–1.58 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.6, 138.3, 138.1, 138.0 (C_{quat}, Ph), 128.4, 128.1, 127.7, 127.5, 127.4, 127.3, 127.1 (Ph), 104.1 (C-1′), 84.9, 81.9, 77.7, 74.5, 74.4, 73.9 (C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.4, 74.7, 73.3, 73.2, 72.8, 70.6, 69.7, 68.8 (C-6, C-6′, CH_2Ph), 53.7 (C-5), 40.3 (C-1), 25.9 (C-2) ppm. HRMS: calcd. for $C_{54}H_{59}NO_8$ 850.4313 $[M + H]^+$; found 850.4331.

Glycoside 13c: This compound was prepared from **12c** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 2:8), and obtained as a viscous oil (57 mg, 0.07 mmol, 70%). $[\alpha]_D$ = +26.4 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 3000, 2900, 1610, 1500, 1450, 1350, 1050, 1010 cm^{-1}. ^1H NMR: δ = 7.47–7.24 (m, 30 H, Ph), 5.05–4.14 (m, 14 H, 5′-H, 1′-H, 6 CH_2Ph), 3.98–3.85 (m, 7 H, 3-H, 4-H, 2′-H, 3′-H, 4′-H, 6′-H_A, 6′-H_B), 3.65–3.25 (m, 3 H, 5-H, 6-H_A, 6-H_B), 3.10–2.45 (m, 3 H, 1-H_A, 1-H_B, NH), 2.08–1.58 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.7, 138.3, 138.0, 137.9, 137.8 (C_{quat}, Ph), 128.4, 128.2, 127.7, 127.5, 127.4, 127.3, 127.2 (Ph), 95.6 (C-1′), 81.7, 79.9, 72.0, 71.4, 71.1, 70.9 (C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.4, 74.8, 73.5, 73.4, 73.1, 70.7, 68.2 (C-6, C-6′, CH_2Ph), 53.9 (C-5), 40.1 (C-1), 25.6 (C-2) ppm. HRMS: calcd. for $C_{54}H_{59}NO_8$ 850.4313 $[M + H]^+$; found 850.4295.

Glycoside 13d: This compound was prepared from **12d** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 3:7), and obtained as a viscous oil (62 mg, 0.07 mmol, 70%). $[\alpha]_D$ = +26.3 (*c* = 1.3, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2950, 2900, 1610, 1500, 1450, 1350, 1050, 1010 cm^{-1}. ^1H NMR: δ = 7.48–7.20 (m, 30 H, Ph), 5.05–4.55 (m, 14 H, 5′-H, 1′-H, 6 CH_2Ph), 4.17–3.82 (m, 7 H, 3-H, 4-H, 2′-H, 3′-H, 4′-H, 6′-H_A, 6′-H_B), 3.73–3.28 (m, 3 H, 5-H, 6-H_A, 6-H_B), 2.98–2.42 (m, 3 H, 1-H_A, 1-H_B, NH), 2.03–1.63 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.6, 138.4, 138.1, 137.8, 137.2 (C_{quat}, Ph), 128.4, 128.1, 127.9, 127.5, 127.4, 127.2 (Ph), 98.3

(C-1′), 78.8, 77.1, 76.4, 74.8, 74.5, 70.5 (C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.2, 73.2, 72.8, 72.7, 72.3, 69.5, 69.2, 68.7 (C-6, C-6′, CH$_2$Ph), 54.3 (C-5), 39.9 (C-1), 26.1 (C-2) ppm. HRMS: calcd. for $C_{54}H_{59}NO_8$ 850.4313 [M + H]$^+$; found 850.4321.

General Procedure for the Preparation of Compounds 14a,b, 18, and 22a–d: TBDMSCl (2 equiv.) was added at 0 °C to a stirred solution of the appropriate linear diol (1 equiv.) in dry pyridine (9 mL/mmol). The reaction mixture was stirred at room temp. until TLC (hexanes/EtOAc, 9:1) showed the disappearance of the starting material (ca. 1 h) and then diluted with Et$_2$O (200 mL/mmol), washed in a separating funnel with 6 N HCl (26 mL/mmol), saturated aqueous NaHCO$_3$, H$_2$O (until neutrality), and brine (100 mL/mmol), dried with anhydrous Na$_2$SO$_4$, and the solvent removed under reduced pressure. The residue was then purified with column chromatography.

Silyl Ether 14a: This compound was prepared from **2a** (100 mg, 0.23 mmol) through the general procedure described above, purified by column chromatography (SiO$_2$; hexanes/EtOAc, 9:1), and obtained as a viscous oil (113 mg, 0.21 mmol, 90 %). $[\alpha]_D$ = +9.4 (*c* = 1.1, CHCl$_3$). IR (CHCl$_3$): $\tilde{\nu}$ = 3500, 2900, 1600, 1500, 1480, 1380, 1278, 1082 cm^{-1}. ^{1}H NMR: δ = 7.42–7.28 (m, 15 H, Ph), 4.75–4.53 (m, 6 H, 3 CH$_2$Ph), 4.12–3.98 (m, 2 H, 3-H, 4-H), 3.75–3.68 (m, 5 H, 1-H$_A$, 1-H$_B$, 2-H, 6-H$_A$, 6-H$_B$), 2.01–1.79 (m, 2 H, 5-H$_A$, 5-H$_B$), 0.94 [s, 9 H, C(CH$_3$)$_3$], 0.08 (s, 6 H, 2 CH$_3$) ppm. ^{13}C NMR: δ = 138.2, 138.1, 138.0 (C$_{quat}$, Ph), 128.2, 127.9, 127.7, 127.6, 127.5 (Ph), 77.4, 75.9, 70.8 (C-2, C-3, C-4), 73.3, 72.7, 71.2, 71.1 (C-1, CH$_2$Ph), 59.3 (C-6), 33.0 (C-5), 25.8 [SiC(*C*H$_3$)$_3$], 18.1 [Si*C*(CH$_3$)$_3$], –5.4 [Si(*C*H$_3$)$_2$] ppm. HRMS: calcd. for $C_{33}H_{46}O_5Si$ 573.3012 [M + Na]$^+$; found 573.3028.

Silyl Ether 14b: This compound was prepared from **2b** (100 mg, 0.23 mmol) through the general procedure described above, purified by column chromatography (SiO$_2$; hexanes/EtOAc, 9:1), and obtained as a viscous oil (114 mg, 0.21 mmol, 90 %). $[\alpha]_D$ = –4.3 (*c* = 1.1, CHCl$_3$). IR (CHCl$_3$): $\tilde{\nu}$ = 3050, 3000, 2900, 1650, 1500, 1480, 1380, 1278, 1082 cm^{-1}. ^{1}H NMR: δ = 7.45–7.28 (m, 15 H, Ph), 4.78–4.55 (m, 6 H, 3 CH$_2$Ph), 4.12–3.97 (m, 2 H, 3-H, 4-H), 3.84–3.72 (m, 3 H, 2-H, 1-H$_A$, 1-H$_B$), 3.66–3.58 (m, 2 H, 6-H$_A$, 6-H$_B$), 1.98–1.82 (m, 2 H, 5-H$_A$, 5-H$_B$), 0.95 [s, 9 H, C(CH$_3$)$_3$], 0.10 (s, 6 H, 2 CH$_3$) ppm. ^{13}C NMR: δ = 138.2, 138.1, 138.0 (C$_{quat}$, Ph), 128.2, 127.9, 127.7, 127.5 (Ph), 79.4, 76.9, 70.1 (C-2, C-3, C-4), 73.5, 73.4, 72.9, 71.0 (C-1, CH$_2$Ph), 59.5 (C-6), 34.4 (C-5), 25.9 [SiC(*C*H$_3$)$_3$], 18.1 [Si*C*(CH$_3$)$_3$], –5.3 [Si(*C*H$_3$)$_2$] ppm. HRMS: calcd. for $C_{33}H_{46}O_5Si$ 573.3012 [M + Na]$^+$; found 573.3005.

Silyl Ether 18: This compound was prepared from **6** (100 mg, 0.30 mmol) through the general procedure described above, purified by column chromatography (SiO$_2$; hexanes/EtOAc, 9:1), and obtained as a viscous oil (108 mg, 0.24 mmol, 80 %). $[\alpha]_D$ = –15.3 (*c* = 1.1, CHCl$_3$). IR (CHCl$_3$): $\tilde{\nu}$ = 3050, 2960, 2900, 1600, 1550, 1450, 1380, 1200, 1082 cm^{-1}. ^{1}H NMR: δ = 7.42–7.27 (m, 10 H, Ph), 4.72–4.55 (m, 4 H, 2 CH$_2$Ph), 3.78–3.68 (m, 4 H, 2-H, 4-H, 6-H$_A$, 6-H$_B$), 3.42 (dd, $J_{3,2}$ = $J_{3,4}$ = 7.4 Hz, 1 H, 3-H), 2.02–1.73 (m, 2 H, 5-H$_A$, 5-H$_B$), 1.25 (d, $J_{1,2}$ = 6.8 Hz, 3 H, 1-H$_A$, 1-H$_B$, 1-H$_C$), 0.93 [s, 9 H, C(CH$_3$)$_3$], 0.08 (s, 6 H, 2 CH$_3$) ppm. ^{13}C NMR: δ = 138.5 (C$_{quat}$, Ph), 128.7, 128.4, 128.3, 128.1 (Ph), 81.1, 76.7, 67.9 (C-2, C-3, C-4), 73.5, 73.2 (CH$_2$Ph), 59.6 (C-6), 29.2 (C-5), 26.2 [SiC(*C*H$_3$)$_3$], 20.0 (C-1), 18.5 [Si*C*(CH$_3$)$_3$], –3.2 [Si(*C*H$_3$)$_2$] ppm. HRMS: calcd. for $C_{26}H_{40}O_4Si$ 467.2594 [M + Na]$^+$; found 467.2581.

Silyl Ether 22a: This compound was prepared from **10a** (100 mg, 0.11 mmol) through the general procedure described above, purified by column chromatography (SiO$_2$; hexanes/EtOAc, 9:1), and obtained as a viscous oil (103 mg, 0.10 mmol, 90 %). $[\alpha]_D$ = +13.3 (*c* = 1.1, CHCl$_3$). IR (CHCl$_3$): $\tilde{\nu}$ = 3050, 2980, 1600, 1500, 1400, 1380, 1200, 1082 cm^{-1}. ^{1}H NMR: δ = 7.42–7.27 (m, 30 H, Ph), 5.07–4.32 (m, 13 H, 1′-H, 6 CH$_2$Ph), 4.15–3.45 (m, 13 H, 1-H$_A$, 1-H$_B$, 2-H, 3-H, 4-H, 6-H$_A$, 6-H$_B$, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H$_A$, 6′-H$_B$), 2.14–1.77 (m, 2 H, 5-H$_A$, 5-H$_B$), 0.93 [s, 9 H, C(CH$_3$)$_3$], 0.08 (s, 6 H, 2 CH$_3$) ppm. ^{13}C NMR: δ = 138.8, 138.6, 138.4, 138.2, 137.8 (C$_{quat}$, Ph), 128.2, 128.1, 127.9, 127.7, 127.4 (Ph), 103.8 (C-1′), 82.4, 79.3, 77.1, 76.5, 73.8, 73.1, 71.1 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.1, 74.6, 73.4, 72.8, 72.5, 71.1, 70.9, 68.8 (C-1, C-6′, CH$_2$Ph), 59.8 (C-6), 32.8 (C-5), 25.9 [SiC(*C*H$_3$)$_3$], 18.1 [Si*C*(CH$_3$)$_3$], –5.3 [Si(*C*H$_3$)$_2$] ppm. HRMS: calcd. for $C_{60}H_{74}O_{10}Si$ 1005.4949 [M + Na]$^+$; found 1005.4985.

Silyl Ether 22b: This compound was prepared from **10b** (100 mg, 0.11 mmol) through the general procedure described above, purified by column chromatography (SiO$_2$; hexanes/EtOAc, 8:2), and obtained as a viscous oil (103 mg, 0.10 mmol, 90 %). $[\alpha]_D$ = +21.0 (*c* = 1.1, CHCl$_3$). IR (CHCl$_3$): $\tilde{\nu}$ = 3050, 2950, 1600, 1500, 1400, 1350, 1200, 1082 cm^{-1}. ^{1}H NMR: δ = 7.42–7.27 (m, 30 H, Ph), 5.04–4.39 (m, 13 H, 1′-H, 6 CH$_2$Ph), 4.20–3.39 (m, 13 H, 1-H$_A$, 1-H$_B$, 2-H, 3-H, 4-H, 6-H$_A$, 6-H$_B$, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H$_A$, 6′-H$_B$), 2.20 (s, 1 H, OH), 2.03–1.85 (m, 2 H, 5-H$_A$, 5-H$_B$), 0.95 [s, 9 H, C(CH$_3$)$_3$], 0.09 (s, 6 H, 2 CH$_3$) ppm. ^{13}C NMR: δ = 138.4, 138.1, 138.0 (C$_{quat}$, Ph), 128.1, 127.7, 127.6, 127.5, 127.3 (Ph), 102.0 (C-1′), 84.6, 82.1, 77.8, 77.0, 75.9, 74.6, 70.8 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.4, 74.7, 74.6, 73.2, 72.3, 71.2, 70.7, 69.1 (C-1, C-6′, CH$_2$Ph), 59.7 (C-6), 32.9 (C-5), 25.9 [SiC(*C*H$_3$)$_3$], 18.1 [Si*C*(CH$_3$)$_3$], –5.3 [Si(*C*H$_3$)$_2$] ppm. HRMS: calcd. for $C_{60}H_{74}O_{10}Si$ 1005.4949 [M + Na]$^+$; found 1005.4924.

Silyl Ether 22c: This compound was prepared from **10c** (100 mg, 0.11 mmol) through the general procedure described above, purified by column chromatography (SiO$_2$; hexanes/EtOAc, 8:2), and obtained as a viscous oil (103 mg, 0.10 mmol, 90 %). $[\alpha]_D$ = +57.7 (*c* = 1.1, CHCl$_3$). IR (CHCl$_3$): $\tilde{\nu}$ = 3050, 2950, 1650, 1500, 1450, 1350, 1200, 1082 cm^{-1}. ^{1}H NMR: δ = 7.40–7.26 (m, 30 H, Ph), 5.12 (d, $J_{1',2'}$ = 3.0 Hz, 1 H, 1′-H), 5.01–4.34 (m, 12 H, 6 CH$_2$Ph), 4.20–3.42 (m, 13 H, 1-H$_A$, 1-H$_B$, 2-H, 3-H, 4-H, 6-H$_A$, 6-H$_B$, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H$_A$, 6′-H$_B$), 2.23–1.76 (m, 2 H, 5-H$_A$, 5-H$_B$), 0.95 [s, 9 H, C(CH$_3$)$_3$], 0.05 (s, 6 H, 2 CH$_3$) ppm. ^{13}C NMR: δ = 138.6, 138.3, 138.2, 137.9, 137.7 (C$_{quat}$, Ph), 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.2 (Ph), 95.5 (C-1′), 79.9, 75.6, 75.5, 75.9, 75.6, 75.3, 71.3 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.7, 73.2, 73.1, 72.9, 72.4, 71.2, 70.7, 68.2 (C-1, C-6′, CH$_2$Ph), 59.4 (C-6), 32.4 (C-5), 25.9 [SiC(*C*H$_3$)$_3$], 18.1 [Si*C*(CH$_3$)$_3$], –5.5 [Si(*C*H$_3$)$_2$] ppm. HRMS: calcd. for $C_{60}H_{74}O_{10}Si$ 1005.4949 [M + Na]$^+$; found 1005.4906.

Silyl Ether 22d: This compound was prepared from **10d** (100 mg, 0.11 mmol) through the general procedure described above, purified by column chromatography (SiO$_2$; hexanes/EtOAc, 8:2), and obtained as a viscous oil (103 mg, 0.10 mmol, 90 %). $[\alpha]_D$ = +55.7 (*c* = 1.1, CHCl$_3$). IR (CHCl$_3$): $\tilde{\nu}$ = 3050, 2980, 1670, 1510, 1450, 1410, 1320, 1102 cm^{-1}. ^{1}H NMR: δ = 7.40–7.22 (m, 30 H, Ph), 5.06–4.40 (m, 13 H, 1′-H, 6 CH$_2$Ph), 4.20–3.53 (m, 13 H, 1-H$_A$, 1-H$_B$, 2-H, 3-H, 4-H, 6-H$_A$, 6-H$_B$, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H$_A$, 6′-H$_B$), 3.18–3.05 (m, 1 H, OH), 1.98–1.82 (m, 2 H, 5-H$_A$, 5-H$_B$), 0.97 [s, 9 H, C(CH$_3$)$_3$], 0.09 (s, 6 H, 2 CH$_3$) ppm. ^{13}C NMR: δ = 138.6, 138.4, 138.3, 138.2, 137.9 (C$_{quat}$, Ph), 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.3 (Ph), 98.6 (C-1′), 79.2, 78.9, 77.1, 76.0, 74.9, 70.4, 69.5 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.6, 73.5, 73.3, 72.8, 72.7, 70.4, 70.3, 68.8 (C-1, C-6′, CH$_2$Ph), 59.5 (C-6), 33.6 (C-5), 25.8 [SiC(*C*H$_3$)$_3$], 18.1 [Si*C*(CH$_3$)$_3$], –5.4 [Si(*C*H$_3$)$_2$] ppm. HRMS: calcd. for $C_{60}H_{74}O_{10}Si$ 1005.4949 [M + Na]$^+$; found 1005.4930.

General Procedure for the Preparation of Compounds 15a,b, 19, and 23a–d: CH_3SO_2Cl (1.2 equiv.) was added at 0 °C to a stirred solution of the appropriate alcohol (1 equiv.) in dry pyridine (11 mL/mmol) and NEt_3 (3 mL/mmol). The reaction mixture was stirred at room temp. overnight and after that time TLC (hexanes/Et_2O, 7:3) showed the disappearance of the starting material. The reaction mixture was then diluted with Et_2O (200 mL/mmol), washed in a separating funnel with H_2O (until neutrality) and then brine (20 mL/mmol), dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The residue was then purified by column chromatography.

Silyl Ether 15a: This compound was prepared from **14a** (100 mg, 0.18 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 8:2), and obtained as a viscous oil (102 mg, 0.16 mmol, 90%). $[\alpha]_D = +10.5$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 2970, 2950, 1600, 1500, 1480, 1300, 1278, 1082 cm^{-1}. ^1H NMR: δ = 7.44–7.28 (m, 15 H, Ph), 5.10–5.03 (m, 1 H, 2-H), 4.87–4.56 (m, 6 H, 3 CH_2Ph), 4.07–3.47 (m, 6 H, 1-H_A, 1-H_B, 3-H, 4-H, 6-H_A, 6-H_B), 3.01 (br. s, 3 H, CH_3SO_2), 1.93–1.73 (m, 2 H, 5-H_A, 5-H_B), 0.94 [s, 9 H, $C(CH_3)_3$], 0.08 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR: δ = 138.0, 137.5, 137.4 (C_{quat}, Ph), 128.2, 128.1, 127.8, 127.5, 127.4 (Ph), 83.1, 80.5, 75.7 (C-2, C-3, C-4), 74.1, 72.6, 71.7 (CH_2Ph), 68.1 (C-1), 58.0 (C-6), 38.2 (CH_3SO_2), 33.6 (C-5), 25.7 [$SiC(CH_3)_3$], 18.0 [$SiC(CH_3)_3$], –5.5 [$Si(CH_3)_2$] ppm. HRMS: calcd. for $C_{34}H_{48}O_7SSi$ 651.2788 $[M + Na]^+$; found 651.2771.

Silyl Ether 15b: This compound was prepared from **14b** (100 mg, 0.18 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 8:2), and obtained as a viscous oil (102 mg, 0.16 mmol, 90%). $[\alpha]_D = +14.3$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2970, 2950, 1600, 1550, 1480, 1300, 1278, 1082 cm^{-1}. ^1H NMR: δ = 7.40–7.30 (m, 15 H, Ph), 4.96–4.50 (m, 8 H, 2-H, 3-H, 3 CH_2Ph), 4.00–3.91 (m, 1 H, 4-H), 3.85–3.78 (m, 4 H, 1-H_A, 1-H_B, 6-H_A, 6-H_B), 2.92 (s, 3 H, CH_3SO_2), 2.12–1.68 (m, 2 H, 5-H_A, 5-H_B), 0.95 [s, 9 H, $C(CH_3)_3$], 0.09 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR: δ = 138.0, 137.5, 137.4 (C_{quat}, Ph), 128.2, 128.1, 127.9, 127.5 (Ph), 83.1, 80.5, 75.7 (C-2, C-3, C-4), 74.1, 73.2, 72.7 (CH_2Ph), 69.1 (C-1), 59.0 (C-6), 38.2 (CH_3SO_2), 33.6 (C-5), 24.7 [$SiC(CH_3)_3$], 18.0 [$SiC(CH_3)_3$], –5.5 [$Si(CH_3)_2$] ppm. HRMS: calcd. for $C_{34}H_{48}O_7SSi$ 651.2788 $[M + Na]^+$; found 651.2799.

Silyl Ether 19: This compound was prepared from **18** (100 mg, 0.22 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 8:2), and obtained as a viscous oil (105 mg, 0.20 mmol, 90%). $[\alpha]_D = -27.8$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2980, 2970, 1600, 1550, 1480, 1300, 1278, 1082 cm^{-1}. ^1H NMR: δ = 7.42–7.25 (m, 10 H, Ph), 5.02 (qd, $J_{2,1}$ = 7.0, $J_{2,3}$ = 1.9 Hz, 1 H, 2-H), 4.86–4.51 (m, 4 H, 2 CH_2Ph), 3.90–3.59 (m, 4 H, 3-H, 4-H, 6-H_A, 6-H_B), 2.92 (s, 3 H, CH_3SO_2), 1.96–1.61 (m, 2 H, 5-H_A, 5-H_B), 1.51 (d, $J_{1,2}$ = 7.0 Hz, 3 H, 1-H_A, 1-H_B, 1-H_C), 0.93 [s, 9 H, $C(CH_3)_3$], 0.09 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR: δ = 138.4, 138.2 (C_{quat}, Ph), 128.4, 127.8, 127.6, 127.2, 127.1 (Ph), 82.2, 79.8, 75.9 (C-2, C-3, C-4), 74.2, 73.3 (CH_2Ph), 59.2 (C-6), 38.6 (CH_3SO_2), 34.2 (C-5), 26.0 [$SiC(CH_3)_3$], 19.8 [$SiC(CH_3)_3$], 16.7 (C-1), –5.2 [$Si(CH_3)_2$] ppm. HRMS: calcd. for $C_{27}H_{42}O_6SSi$ 545.2369 $[M + Na]^+$; found 545.2345.

Silyl Ether 23a: This compound was prepared from **22a** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 8:2), and obtained as a viscous oil (97 mg, 0.09 mmol, 90%). $[\alpha]_D = +8.5$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 2970, 1600, 1500, 1400, 1300, 1250, 1082 cm^{-1}. ^1H NMR: δ = 7.45–7.27 (m, 30 H, Ph), 5.18–5.09 (m, 1 H, 2-H), 5.03–4.06 (m, 16 H, 1′-H, 1-H_A, 1-H_B, 3-H, 6 CH_2Ph), 4.02–3.48 (m, 9 H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.92 (s, 3 H, CH_3SO_2), 2.11–1.69 (m, 2 H, 5-H_A, 5-H_B), 0.94 [s, 9 H, $C(CH_3)_3$], 0.09 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR: δ = 138.6, 138.4, 138.3, 137.9, 137.6 (C_{quat}, Ph), 128.2, 128.0, 127.8, 127.7, 127.6, 127.4, 127.3 (Ph), 103.2 (C-1′), 83.4, 82.4, 79.4, 78.0, 75.7, 73.8, 73.2 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.9, 74.8, 74.6, 73.4, 72.8, 72.0 (CH_2Ph), 69.3, 68.3 (C-1, C-6′), 59.5 (C-6), 38.3 (CH_3SO_2), 33.1 (C-5), 25.9 [$SiC(CH_3)_3$], 18.1 [$SiC(CH_3)_3$], –5.3 [$Si(CH_3)_2$] ppm. HRMS: calcd. for $C_{61}H_{76}O_{12}SSi$ 1083.4724 $[M + Na]^+$; found 1083.4775.

Silyl Ether 23b: This compound was prepared from **22b** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (91 mg, 0.08 mmol, 85%). $[\alpha]_D = +22.0$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 2980, 2950, 1600, 1500, 1450, 1300, 1250, 1082 cm^{-1}. ^1H NMR: δ = 7.43–7.20 (m, 30 H, Ph), 5.00–5.05 (m, 1 H, 2-H), 5.01–4.12 (m, 15 H, 1′-H, 1-H_A, 1-H_B, 6 CH_2Ph), 4.08–3.39 (m, 10 H, 3-H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.93 (s, 3 H, CH_3SO_2), 2.14–1.79 (m, 2 H, 5-H_A, 5-H_B), 0.95 [s, 9 H, $C(CH_3)_3$], 0.09 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR: δ = 138.6, 138.4, 138.3, 138.1, 137.9, 137.6 (C_{quat}, Ph), 128.2, 127.9, 127.7, 127.5, 127.3, 127.2 (Ph), 102.2 (C-1′), 84.7, 83.0, 82.2, 77.8, 77.5, 77.6, 74.8 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.5, 74.7, 74.6, 73.4, 72.9, 72.0 (CH_2Ph), 69.1, 68.8 (C-1, C-6′), 59.5 (C-6), 38.4 (CH_3SO_2), 33.1 (C-5), 25.9 [$SiC(CH_3)_3$], 17.9 [$SiC(CH_3)_3$], –5.3 [$Si(CH_3)_2$] ppm. HRMS: calcd. for $C_{61}H_{76}O_{12}SSi$ 1083.4724 $[M + Na]^+$; found 1083.4695.

Silyl Ether 23c: This compound was prepared from **22c** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (97 mg, 0.09 mmol, 90%). $[\alpha]_D = +58.7$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 2970, 1600, 1500, 1450, 1300, 1250, 1082 cm^{-1}. ^1H NMR: δ = 7.45–7.29 (m, 30 H, Ph), 5.18–5.09 (m, 1 H, 2-H), 5.01 (d, $J_{1',2'}$ = 3.5 Hz, 1 H, 1′-H), 5.04–4.36 (m, 15 H, 1-H_A, 1-H_B, H-3, 6 CH_2Ph), 4.10–3.57 (m, 9 H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.98 (s, 3 H, CH_3SO_2), 2.08–1.85 (m, 1 H, 5-H_A), 1.84–1.62 (m, 1 H, 5-H_B), 0.93 [s, 9 H, $C(CH_3)_3$], 0.07 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR: δ = 138.6, 138.1, 137.9, 137.5, 137.4 (C_{quat}, Ph), 128.1, 127.8, 127.6, 127.5, 127.3, 127.2 (Ph), 95.9 (C-1′), 82.8, 81.7, 79.7, 77.6, 76.9, 74.5, 70.9 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.4, 75.1, 73.5, 73.2, 73.0, 72.4 (CH_2Ph), 69.3, 68.2 (C-1, C-6′), 59.8 (C-6), 38.3 (CH_3SO_2), 33.6 (C-5), 25.8 [$SiC(CH_3)_3$], 18.1 [$SiC(CH_3)_3$], –5.5 [$Si(CH_3)_2$] ppm. HRMS: calcd. for $C_{61}H_{76}O_{12}SSi$ 1083.4724 $[M + Na]^+$; found 1083.4750.

Silyl Ether 23d: This compound was prepared from **22d** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (97 mg, 0.09 mmol, 90%). $[\alpha]_D = +42.2$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2980, 2950, 1600, 1500, 1400, 1300, 1250, 1082 cm^{-1}. ^1H NMR: δ = 7.45–7.29 (m, 30 H, Ph), 5.08–4.34 (m, 17 H, 1-H_A, 1-H_B, 2-H, 3-H, 1′-H, 6 CH_2Ph), 4.18–3.50 (m, 9 H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.82 (s, 3 H, CH_3SO_2), 2.05–1.81 (m, 2 H, 5-H_A, 5-H_B), 0.94 [s, 9 H, $C(CH_3)_3$], 0.08 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR: δ = 138.8, 138.5, 138.3, 138.1, 137.9 (C_{quat}, Ph), 128.2, 128.0, 127.8, 127.7, 127.4 (Ph), 97.6 (C-1′), 82.8, 80.7, 78.2, 76.2, 75.6, 74.6, 69.6 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.7, 74.2, 73.3, 72.7, 72.2 (CH_2Ph), 68.7 (C-6′), 66.1 (C-1), 59.4 (C-6), 38.1 (CH_3SO_2), 33.6 (C-5), 25.8 [$SiC(CH_3)_3$], 18.1 [$SiC(CH_3)_3$], –5.4 [$Si(CH_3)_2$] ppm. HRMS: calcd. for $C_{61}H_{76}O_{12}SSi$ 1083.4724 $[M + Na]^+$; found 1083.4766.

General Procedure for the Preparation of Compounds 16a,b, 20, and 24a–d: TBAF (1 equiv.) was added at room temp. to a stirred solution of the appropriate silyl ether (1 equiv.) in THF (12 mL/mmol). The reaction mixture was stirred at room temp. overnight and after that time TLC (hexanes/Et_2O, 1:1) showed the disappearance of the starting material. The reaction mixture was then diluted with Et_2O (200 mL/mmol), washed in a separating funnel with H_2O (until neutrality) and then brine (20 mL/mmol), dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The residue was then purified by column chromatography.

Mesyl Alcohol 16a: This compound was prepared from **15a** (100 mg, 0.16 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 1:1), and obtained as a viscous oil (66 mg, 0.13 mmol, 80%). $[\alpha]_D$ = +13.5 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3070, 2990, 1650, 1550, 1400, 1300, 1200, 1082 cm^{-1}. ^1H NMR: δ = 7.45–7.26 (m, 15 H, Ph), 5.10–5.03 (m, 1 H, 2-H), 4.86–4.43 (m, 6 H, 3 CH_2Ph), 4.05–3.61 (m, 6 H, 1-H_A, 1-H_B, 3-H, 4-H, 6-H_A, 6-H_B), 3.00 (s, 3 H, CH_3SO_2), 1.98–1.68 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 137.6, 137.4 (C_{quat}, Ph), 128.4, 128.3, 128.2, 128.1, 127.8, 127.7 (Ph), 82.8, 80.6, 77.0 (C-2, C-3, C-4), 74.4, 73.4, 72.9 (CH_2Ph), 69.0 (C-1), 59.6 (C-6), 38.2 (CH_3SO_2), 32.1 (C-5) ppm. HRMS: calcd. for $C_{28}H_{34}O_7S$ 537.1923 [M + Na]$^+$; found 537.1912.

Mesyl Alcohol 16b: This compound was prepared from **15b** (100 mg, 0.16 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 1:1), and obtained as a viscous oil (61 mg, 0.13 mmol, 74%). $[\alpha]_D$ = +17.3 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2990, 1650, 1550, 1400, 1300, 1278, 1082 cm^{-1}. ^1H NMR: δ = 7.42–7.28 (m, 15 H, Ph), 4.95–4.48 (m, 7 H, 2-H, 3 CH_2Ph), 4.04 (dd, $J_{3,4}$ = $J_{3,2}$ = 5.8 Hz, 1 H, 3-H), 3.95–3.85 (m, 1 H, 4-H), 3.77–3.68 (m, 4 H, 1-H_A, 1-H_B, 6-H_A, 6-H_B), 2.93 (s, 3 H, CH_3SO_2), 2.13 (br. s, 1 H, OH), 2.04–1.68 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 138.4, 138.2 (C_{quat}, Ph), 128.3, 128.0, 127.8, 127.6 (Ph), 81.6, 78.4, 77.2 (C-2, C-3, C-4), 74.4, 73.5, 72.0 (CH_2Ph), 69.4 (C-1), 59.5 (C-6), 38.3 (CH_3SO_2), 37.2 (C-5) ppm. HRMS: calcd. for $C_{28}H_{34}O_7S$ 537.1923 [M + Na]$^+$; found 537.1936.

Mesyl Alcohol 20: This compound was prepared from **19** (100 mg, 0.19 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 1:1), and obtained as a viscous oil (62 mg, 0.15 mmol, 80%). $[\alpha]_D$ = –19.0 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3040, 2990, 2970, 1650, 1570, 1400, 1300, 1278, 1082 cm^{-1}. ^1H NMR: δ = 7.44–7.26 (m, 10 H, Ph), 5.02 (qd, $J_{2,1}$ = 7.0, $J_{2,3}$ = 2.0 Hz, 1 H, 2-H), 4.86–4.48 (m, 4 H, 2 CH_2Ph), 3.90 (dd, $J_{3,4}$ = $J_{3,2}$ = 5.8 Hz, 1 H, 3-H), 3.82–3.68 (m, 3 H, 4-H, 6-H_A, 6-H_B), 2.94 (s, 3 H, CH_3SO_2), 2.28 (br. s, 1 H, OH), 1.97–1.58 (m, 2 H, 5-H_A, 5-H_B), 1.53 (d, $J_{1,2}$ = 7.0 Hz, 3 H, 1-H_A, 1-H_B, 1-H_C) ppm. ^{13}C NMR: δ = 138.7, 138.3 (C_{quat}, Ph), 128.3, 128.1, 127.9, 127.8, 127.7 (Ph), 81.7, 79.4, 77.5 (C-2, C-3, C-4), 74.2, 73.0 (CH_2Ph), 59.7 (C-6), 38.5 (CH_3SO_2), 33.3 (C-5), 16.7 (C-1) ppm. HRMS: calcd. for $C_{21}H_{28}O_6S$ 431.1504 [M + Na]$^+$; found 431.1510.

Mesyl Alcohol 24a: This compound was prepared from **23a** (100 mg, 0.09 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/Et_2O, 8:2), and obtained as a viscous oil (68 mg, 0.07 mmol, 80%). $[\alpha]_D$ = +12.0 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3020, 2950, 1650, 1500, 1400, 1300, 1270, 1082 cm^{-1}. ^1H NMR: δ = 7.49–7.20 (m, 30 H, Ph), 5.12–4.98 (m, 1 H, 2-H), 5.00–4.12 (m, 15 H, 1′-H, 6′-H_A, 6′-H_B, 6 CH_2Ph), 4.00–3.52 (m, 10 H, 1-H_A, 1-H_B, 3-H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H), 2.95 (s, 3 H, CH_3SO_2), 2.33 (br. s, 1 H, OH), 2.21–1.69 (m, 2 H, 5-H_A, 5-H_B) ppm. ^{13}C NMR: δ = 138.6, 138.4, 138.3, 138.1, 137.9, 137.6 (C_{quat}, Ph), 128.2, 127.9, 127.7, 127.5, 127.4 (Ph), 103.2 (C-1′), 82.5, 82.2, 79.2, 78.8, 77.1, 73.6, 73.2 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.9, 74.4, 72.7, 72.0, 71.9 (CH_2Ph), 69.1, 68.7 (C-1, C-6′), 60.1 (C-6), 38.3 (CH_3SO_2), 32.2 (C-5) ppm. HRMS: calcd. for $C_{55}H_{62}O_{12}S$ 969.3860 [M + Na]$^+$; found 969.3875.

Mesyl Alcohol 24b: This compound was prepared from **23b** (100 mg, 0.09 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (68 mg, 0.07 mmol, 80%). $[\alpha]_D$ = +16.5 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 2950, 1600, 1500, 1400, 1300, 1200, 1082 cm^{-1}. ^1H NMR: δ = 7.49–7.22 (m, 30 H, Ph), 5.08–4.98 (m, 1 H, 2-H), 5.05–4.17 (m, 15 H, 1′-H, 6′-H_A, 6′-H_B, 6 CH_2Ph), 4.03–3.45 (m, 10 H, 1-H_A, 1-H_B, 3-H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H), 2.95 (s, 3 H, CH_3SO_2), 2.54 (br. s, 1 H, OH), 2.15–1.69 (m, 2 H, 5-H_A 5-H_B) ppm. ^{13}C NMR: δ = 138.3, 138.2, 137.9, 137.8, 137.6, 137.5 (C_{quat}, Ph), 128.6, 128.1, 128.0, 127.9, 127.8 (Ph), 103.3 (C-1′), 85.0, 82.4, 79.1, 78.0, 77.0, 74.6, 72.1 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.9, 74.4, 73.2, 72.7, 72.0, 71.9 (CH_2Ph), 69.2, 69.0 (C-1, C-6′), 60.3 (C-6), 38.8 (CH_3SO_2), 32.6 (C-5) ppm. HRMS: calcd. for $C_{55}H_{62}O_{12}S$ 969.3860 [M + Na]$^+$; found 969.3845.

Mesyl Alcohol 24c: This compound was prepared from **23c** (100 mg, 0.09 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 7:3), and obtained as a viscous oil (68 mg, 0.07 mmol, 80%). $[\alpha]_D$ = +70.8 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3060, 2980, 1650, 1500, 1400, 1350, 1200, 1082 cm^{-1}. ^1H NMR: δ = 7.49–7.20 (m, 30 H, Ph), 5.18–5.08 (m, 1 H, 2-H), 5.02–4.40 (m, 15 H, 1′-H, 6′-H_A, 6′-H_B, 6 CH_2Ph), 4.08–3.53 (m, 10 H, 1-H_A, 1-H_B, 3-H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H), 2.99 (s, 3 H, CH_3SO_2), 2.30–1.62 (m, 3 H, 5-H_A, 5-H_B, OH) ppm. ^{13}C NMR: δ = 138.3, 138.2, 137.9, 137.8, 137.7 (C_{quat}, Ph), 128.2, 128.0, 127.9, 127.7, 127.5, 127.4 (Ph), 97.5 (C-1′), 82.2, 81.6, 79.4, 77.1, 75.5, 71.0 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 75.3, 75.0, 73.4, 73.3, 73.2, 72.1 (CH_2Ph), 69.1, 68.0 (C-1, C-6′), 59.8 (C-6), 38.2 (CH_3SO_2), 32.9 (C-5) ppm. HRMS: calcd. for $C_{55}H_{62}O_{12}S$ 969.3860 [M + Na]$^+$; found 969.3894.

Mesyl Alcohol 24d: This compound was prepared from **23d** (100 mg, 0.09 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 7:3), and obtained as a viscous oil (68 mg, 0.07 mmol, 80%). $[\alpha]_D$ = +43.9 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3050, 2990, 2980, 1650, 1500, 1450, 1350, 1200, 1082 cm^{-1}. ^1H NMR: δ = 7.48–7.27 (m, 30 H, Ph), 5.11–4.40 (m, 16 H, 2-H, 1′-H, 6′-H_A, 6′-H_B, 6 CH_2Ph), 4.16–3.56 (m, 10 H, 1-H_A, 1-H_B, 3-H, 4-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H), 2.83 (s, 3 H, CH_3SO_2), 2.18–1.68 (m, 3 H, 5-H_A, 5-H_B, OH) ppm. ^{13}C NMR: δ = 138.5, 138.1, 138.2, 137.9, 137.5, 137.4 (C_{quat}, Ph), 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4 (Ph), 97.5 (C-1′), 81.6, 81.2, 78.3, 77.0, 76.2, 74.6, 69.7 (C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′), 74.7, 74.5, 73.6, 73.3, 72.9, 72.3 (CH_2Ph), 68.9, 65.7 (C-1, C-6′), 59.4 (C-6), 38.2 (CH_3SO_2), 33.4 (C-5) ppm. HRMS: calcd. for $C_{55}H_{62}O_{12}S$ 969.3860 [M + Na]$^+$; found 969.3835.

General Procedure for the Preparation of Compounds 17a,b, 21, and 25a–d: NEt_3 (2.5 mL/mmol) was added to a stirred solution of the appropriate mesyl alcohol (1 equiv.) in DMF (10 mL/mmol). The reaction mixture was stirred at 100 °C overnight and after that time TLC (hexanes/EtOAc, 7:3) showed the disappearance of the starting material. The reaction mixture was then diluted with Et_2O (200 mL/mmol), washed in a separating funnel with H_2O (until neutrality) and then brine (20 mL/mmol), dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The residue was then purified by column chromatography.

3,4,6-Tri-*O*-benzyl-2-deoxy-L-hexitol (17a): This compound was prepared from **16a** (100 mg, 0.19 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 85:15), and obtained as a viscous oil (60 mg, 0.14 mmol, 75%). $[\alpha]_D$ = –5.3 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 1650, 1500, 1450, 1360, 1278, 1082 cm^{-1}. ^1H NMR: δ = 7.45–7.25 (m, 15 H, Ph), 4.67–4.43 (m, 6 H, 3 CH_2Ph), 4.04–4.01 (m, 1 H, 3-H), 3.90–3.62 (m, 3 H, 1-H_A, 1-H_B, 4-H), 3.57–3.43 (m, 3 H, 5-H, 6-H_A, 6-H_B), 2.23–2.04 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.3, 138.1, 138.0 (C_{quat}, Ph), 128.1, 127.9, 127.6, 127.4, 127.3, 127.2 (Ph), 73.8, 73.2, 71.0 (C-3, C-4, C-5), 73.3, 72.5, 72.4 (CH_2Ph), 70.0 (C-6), 62.4 (C-1), 29.9 (C-2) ppm. HRMS: calcd. for $C_{27}H_{30}O_4$ 441.2042 $[M + Na]^+$; found 441.2049.

3,4,6-Tri-*O*-benzyl-2-deoxy-L-hexitol (17b): This compound was prepared from **16b** (100 mg, 0.19 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 85:15), and obtained as a viscous oil (60 mg, 0.14 mmol, 75%). $[\alpha]_D$ = –9.2 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 2980, 1650, 1550, 1480, 1360, 1278, 1082 cm^{-1}. ^1H NMR: δ = 7.45–7.20 (m, 15 H, Ph), 4.72–4.38 (m, 6 H, 3 CH_2Ph), 4.04–3.70 (m, 6 H, 1-H_A, 1-H_B, 3-H, 5-H, 6-H_A, 6-H_B), 3.57 (dd, $J_{4,3}$ = 9.5, $J_{4,5}$ = 3.1 Hz, 1 H, 4-H), 2.00–1.62 (m, 2 H, 2-H_A, 2-H_B) ppm. ^{13}C NMR: δ = 138.7, 138.2 (C_{quat}, Ph), 128.2, 127.8, 127.6, 127.5 (Ph), 75.9, 74.5, 70.8 (C-3, C-4, C-5), 73.5, 71.3, 71.0 (CH_2Ph), 69.8 (C-6), 62.2 (C-1), 29.6 (C-2) ppm. HRMS: calcd. for $C_{27}H_{30}O_4$ 441.2042 $[M + Na]^+$; found 441.2054.

3,4-Di-*O*-benzyl-2,6-dideoxy-D-hexitol (21): This compound was prepared from **20** (100 mg, 0.24 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 85:15), and obtained as a viscous oil (60 mg, 0.19 mmol, 79%). $[\alpha]_D$ = +12.7 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 1650, 1550, 1400, 1360, 1270, 1082 cm^{-1}. ^1H NMR: δ = 7.45–7.28 (m, 10 H, Ph), 4.68–4.43 (m, 4 H, 2 CH_2Ph), 3.87–3.71 (m, 4 H, 1-H_A, 1-H_B, 3-H, 4-H), 3.21–3.15 (m, 1 H, 5-H), 2.20–1.98 (m, 1 H, 2-H_A), 1.75–1.58 (m, 1 H, 2-H_B), 1.21 (d, $J_{5,6}$ = 6.5 Hz, 3 H, 6-H_A, 6-H_B, 6-H_C) ppm. ^{13}C NMR: δ = 138.7, 138.3 (C_{quat}, Ph), 128.4, 128.3, 128.2, 127.8, 127.7, 127.5 (Ph), 76.1, 71.8, 70.8 (C-3, C-4, C-5), 72.9, 70.9 (CH_2Ph), 62.5 (C-1), 26.0 (C-2), 17.1 (C-6) ppm. HRMS: calcd. for $C_{20}H_{24}O_3$ 335.1623 $[M + Na]^+$; found 335.1630.

Glycoside 25a: This compound was prepared from **24a** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (68 mg, 0.08 mmol, 80%). $[\alpha]_D$ = –85.0 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 2990, 1650, 1550, 1400, 1300, 1270, 1082 cm^{-1}. ^1H NMR: δ = 7.49–7.20 (m, 30 H, Ph), 5.14–4.24 (m, 13 H, 1′-H, 6 CH_2Ph), 4.15–3.46 (m, 13 H, 1-H_A, 1-H_B, 3-H, 4-H, 5-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.32–2.12 (m, 1 H, 2-H_A), 1.66 (d, $J_{2B,3}$ = 10.5 Hz, 1 H, 2-H_B) ppm. ^{13}C NMR: δ = 138.7, 138.5, 138.4, 138.3 (C_{quat}, Ph), 128.2, 128.1, 127.6, 127.4, 127.2 (Ph), 105.0 (C-1′), 82.3, 79.0, 74.1, 73.6, 73.5, 73.3 (C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 74.9, 74.5, 73.4, 73.0, 72.9, 70.6, 69.7, 68.8 (C-6, C-6′, CH_2Ph), 62.6 (C-1), 26.0 (C-2) ppm. HRMS: calcd. for $C_{54}H_{58}O_9$ 873.3978 $[M + Na]^+$; found 873.3997.

Glycoside 25b: This compound was prepared from **24b** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (67 mg, 0.08 mmol, 80%). $[\alpha]_D$ = +7.7 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 2970, 1650, 1550, 1400, 1300, 1200, 1082 cm^{-1}. ^1H NMR: δ = 7.49–7.25 (m, 30 H, Ph), 5.16–4.29 (m, 13 H, 1′-H, 6 CH_2Ph), 4.16–3.32 (m, 13 H, 1-H_A, 1-H_B, 3-H, 4-H, 5-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.32–2.10 (m, 1 H, 2-H_A), 1.71 (d, $J_{2B,3}$ = 10.5 Hz, 1 H, 2-H_B) ppm. ^{13}C NMR: δ = 138.7, 138.4, 138.2, 138.1, 138.0 (C_{quat}, Ph), 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2 (Ph), 104.5 (C-1′), 84.7, 81.9, 77.7, 74.2, 73.6, 73.5 (C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 75.5, 74.8, 73.4, 73.0, 70.8 (CH_2Ph), 69.5, 68.9 (C-6, C-6′), 62.7 (C-1), 26.1 (C-2) ppm. HRMS: calcd. for $C_{54}H_{58}O_9$ 873.3978 $[M + Na]^+$; found 873.3967.

Glycoside 25c: This compound was prepared from **24c** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (65 mg, 0.08 mmol, 80%). $[\alpha]_D$ = +32.0 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3000, 2995, 1600, 1550, 1400, 1300, 1250, 1082 cm^{-1}. ^1H NMR: δ = 7.47–7.25 (m, 30 H, Ph), 5.07–4.32 (m, 13 H, 1′-H, 6 CH_2Ph), 4.18–3.36 (m, 13 H, 1-H_A, 1-H_B, 3-H, 4-H, 5-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.25–2.09 (m, 1 H, 2-H_A), 1.58 (d, $J_{2B,3}$ = 10.2 Hz, 1 H, 2-H_B) ppm. ^{13}C NMR: δ = 138.4, 138.2, 138.1, 137.8, 137.6 (C_{quat}, Ph), 128.1, 127.9, 127.7, 127.6, 127.5, 127.3, 127.2 (Ph), 95.6 (C-1′), 81.7, 79.8, 77.5, 73.6, 72.2, 70.9, 70.7 (C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 75.4, 74.7, 73.4, 73.3, 73.2, 70.5, 70.3, 68.1 (C-6, C-6′, CH_2Ph), 62.3 (C-1), 25.5 (C-2) ppm. HRMS: calcd. for $C_{54}H_{58}O_9$ 873.3978 $[M + Na]^+$; found 873.3956.

Glycoside 25d: This compound was prepared from **24d** (100 mg, 0.10 mmol) through the general procedure described above, purified by column chromatography (SiO_2; hexanes/EtOAc, 8:2), and obtained as a viscous oil (68 mg, 0.08 mmol, 80%). $[\alpha]_D$ = +26.8 (c = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2995, 2990, 1600, 1550, 1400, 1300, 1250, 1082 cm^{-1}. ^1H NMR: δ = 7.52–7.28 (m, 30 H, Ph), 5.08–4.33 (m, 13 H, 1′-H, 6 CH_2Ph), 4.11–3.46 (m, 13 H, 1-H_A, 1-H_B, 3-H, 4-H, 5-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B), 2.18–2.09 (m, 1 H, 2-H_A), 1.72 (d, $J_{2B,3}$ = 10.4 Hz, 1 H, 2-H_B) ppm. ^{13}C NMR: δ = 138.9, 138.6, 138.3, 138.0, 137.6 (C_{quat}, Ph), 128.2, 128.1, 127.7, 127.5, 127.3, 127.1 (Ph), 98.0 (C-1′), 78.7, 76.3, 75.0, 74.1, 73.6, 71.0, 69.2 (C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 74.6, 73.3, 73.2, 72.5, 70.6, 68.7, 68.0 (C-6, C-6′, CH_2Ph), 62.2 (C-1), 26.0 (C-2) ppm. HRMS: calcd. for $C_{54}H_{58}O_9$ 873.3978 $[M + Na]^+$; found 873.3968.

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