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Glycosylated *N*-Sulfonylamidines: Highly Efficient Copper-Catalyzed Multicomponent Reaction with Sugar Alkynes, Sulfonyl Azides, and Amines†

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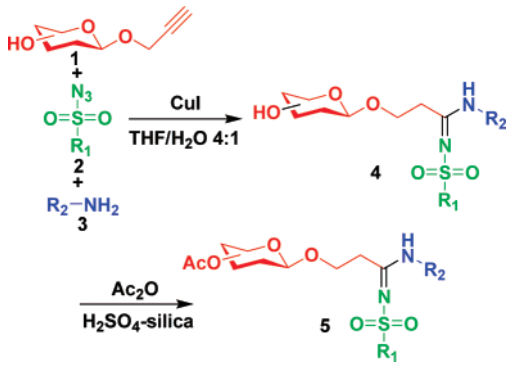

Copper-catalyzed multicomponent reactions with sugar alkynes, sulfonyl azides, and amines to furnish glycosylated *N*-sulfonylamidines are reported. The reaction is established to be general in terms of different combinations of sugar alkyne, sulfonyl azide, and amines.

Multicomponent reaction (MCR) is a powerful tool for generating highly functionalized molecules with complexity and diversity using a straightforward single-pot reaction. Therefore, MCR is growing in popularity for its application in combinatorial chemistry and drug discovery.[1] With respect to their profound application as important pharmacophores, synthetic intermediates, and efficient coordinating ligands, amidines are useful targets for drug discovery and development.[2] Moreover, they are abundant in various medicinally active natural products.[3] However, the chemical synthesis of amidine is not an easy task. Generally, they are prepared from synthetic intermediates such as aldoximes,[4] thioamides,[5] or isonitriles,[6] relying on simple functional group transformations. The MCR approach for the synthesis of amidines is still rare in the literature. Recently, Chang et al. reported an efficient copper-catalyzed MCR route to the *N*-sulfonylamidines.[7] During the regular practice of screening novel heterocycles as drug candidates against various diseases, we observed that several active molecules become toxic or incapable of delivering the exact function due to lack of specificity or insolubility. As sugars are well-known for their site-specific character and the presence of a large number of free hydroxyl groups renders solubility in aqueous media, we envisioned that coupling of sugars with active heterocycles may lead to satisfactory results.[8] Therefore, taking the cue from Chang's work and other copper-catalyzed MCR approaches, here we report a highly efficient route for the synthesis of glycosylated *N*-sulfonylamidines using sugar alkynes, sulfonyl azides, and amines. To judge the generality of our approach, a series of different sugar alkynes, sulfonyl azides, and amines are used in various combinations.

The copper-catalyzed Huisgen[9] cycloaddition reaction or so-called "click chemistry" has already earned a great deal of interest for preparation of functionalized molecules of medicinal interest.[10] Interestingly, replacement of the azide counterpart of the same reaction with sulfonyl azides leads to a different reaction mode. Exploiting this phenomenon, several methods have been developed to create functionally diverse classes of compounds using the MCR approach.[11] Similarly, when propargyl glucoside (**1a**) was reacted with *p*-toluenesulfonyl azide (**2a**) and benzylamine (**3a**) in the presence of CuI under Chang's condition, the corresponding glucosyl *N*-toluenesulfonylamidine (**4aaa**) was formed in 89% yield (Scheme 1). For easy interpretation, a portion of the product was acetylated using acetic anhydride in pyridine, and the resulting per-*O*-acetylated product was characterized by NMR and mass spectrometry. The

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(1) Tuch, A.; Wallé, S. In *Handbook of Combinatorial Chemistry*; Nicolaou, K. C., Hanko, R., Hartwig, W., Eds.; Wiley-VCH: Weinheim, Germany, 2002; Vol. 2, Chapter 23.
(2) (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Boyd, G. V. In *The Chemistry of Amidines and Imidates*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Vol. 2, Chapter 8.
(3) Greenhill, J. V.; Lue, P. *Prog. Med. Chem.* **1993**, *30*, 203.
(4) Takuwa, T.; Minowa, T.; Onishi, J. Y.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1717.
(5) Kumagai, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 478.
(6) Lange, U. E. W.; Schäfer, B.; Baucke, D.; Buschmann, E.; Mack, H. *Tetrahedron Lett.* **1999**, *40*, 7067.
(7) (a) Bae, I.; Han, H.; Chang, S. *J. Am. Chem. Soc.* **2005**, *127*, 2038−2039. (b) Yoo, E. J.; Bae, I, Cho, S. H.; Han, H.; Chang, S. *Org. Lett.* **2006**, *8*, 1347−1350.
(8) Roy, A. D.; Subramanian, A.; Mukhopadhyay, B.; Roy, R. *Tetrahedron Lett.* **2006**, *47*, 6857−6860.
(9) (a) Huisgen, R. *Pure Appl. Chem.* **1989**, *61*, 613−628. (b) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1.
(10) For Cu-catalyzed cycloaddition reactions see: (a) Dedola, S.; Nepogodiev, S. A.; Field, R. A. *Org. Biomol. Chem.* **2007**, *7*, 1006−1017. (b) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057−3064. (c) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599. (d) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021. (e) Kolb, H. C.; Sharpless, K. B. *Drug Discovery Today* **2003**, *8*, 1128−1137.
(11) For Cu-catalyzed MCRs with sulfonyl azides see: (a) Cassidy, M. P.; Raushel, J.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2006**, *45*, 3154−3157. (b) Whiting, M.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2006**, *45*, 3157−3161. (c) Cho, S. H.; Yoo, E. J.; Bae, I.; Chang, S. *J. Am. Chem. Soc.* **2005**, *127*, 16046−16047. (d) Xu, X.; Cheng, D.; Li, J.; Guo, H.; Yan, J. *Org. Lett.* **2007**, *9*, 1585−1587. (e) Cui, S-L.; Lin, X-F.; Wang, Y-G. *Org. Lett.* **2006**, *8*, 4517−4520. (f) Chang, S.; Lee, M.; Jung, D. Y.; Yoo, E. J.; Cho, S. H.; Han, S. K. *J. Am. Chem. Soc.* **2006**, *128*, 12366−12367. (g) Yoo, E. J.; Ahlquist, M.; Kim, S. H.; Bae, I, Fokin, V. V.; Sharpless, K. B.; Chang, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 1730−1733.

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SCHEME 1. Synthesis of Glycosylated *N*-Sulfonylamidines via CuI-Catalyzed MCR

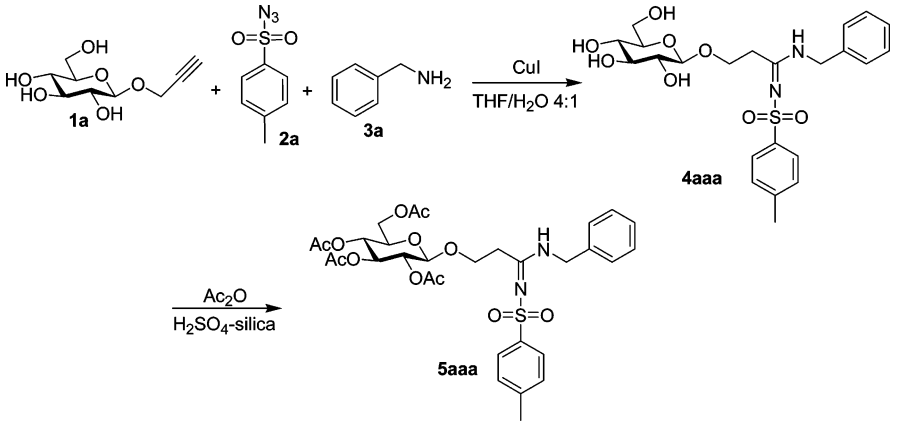
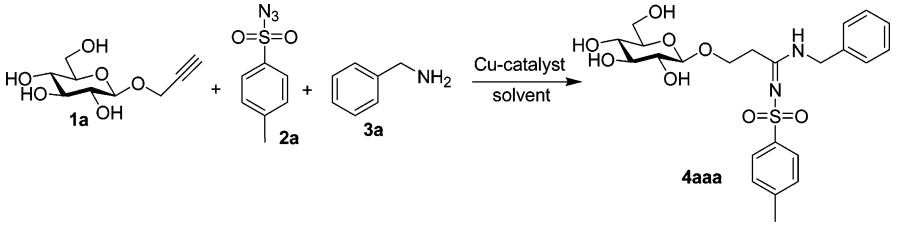


TABLE 1. Optimization of Copper-Catalyzed Multicomponent Reaction of Acetylated Propargyl Glucoside, *p*-Toluenesulfonyl Azide, and Salisaldehyde[a]



entry	solvent	catalyst	time	yield[b] (%)
1	CH_3CN-H_2O (4:1)	CuI	2 h	10
2	DMF	CuI	2 h	trace
3	$THF-H_2O$ (4:1)	CuI	45 min	89
4	$THF-H_2O$ (4:1)	CuCl	2 h	78
5	$THF-H_2O$ (4:1)	CuBr	2 h	trace
6	$THF-H_2O$ (4:1)	$CuSO_4 \cdot 5H_2O$	2 h	NI[c]

[a] Sugar alkyne (1 mmol), sulfonyl azide (1.2 mmol), amine (1.2 mmol), and Cu catalyst (0.1 mmol) in 10 mL of solvent at room temperature. [b] Isolated yield based on the alkyne. [c] NI = product not isolated.

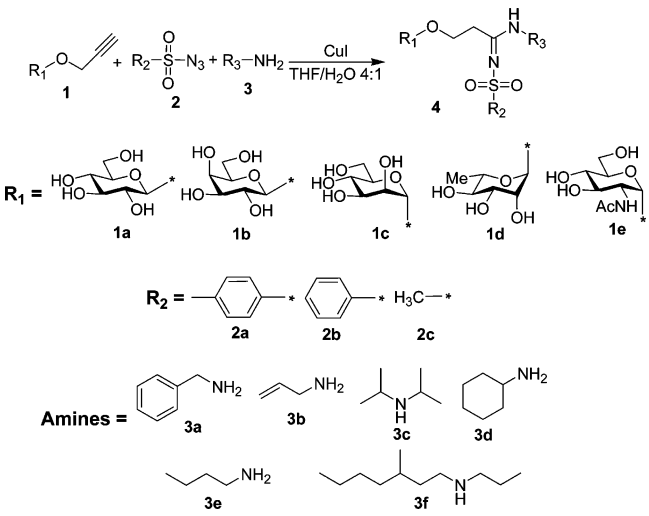
result differs considerably from that of Huisgen cycloaddition, which can be attributed to the dissimilar reactivity between sulfonyl azides and simple alkyl/aryl azides toward the copper acetylides formed in the first step of the reaction. Using 10% CuI, the reaction was complete in 45 min. Lowering the loading of CuI up to 2% also effectively furnished the target molecule in a longer time (12 h). However, for practical reasons, 10% CuI was used for all the reactions performed thereafter.

To optimize the reaction conditions, different solvent systems and copper salts were tested. Aqueous solvents were found to be necessary for the required solubility of unprotected sugar alkynes. With the precedence in carbohydrate chemistry, we started with the CH_3CN-H_2O system, but that was not successful. Only 10% conversion was obtained after 2 h at room temperature. Solvents such as DMF, which can provide the solubility parameter, were unsuccessful too. When the reaction was carried out in a 4:1 $THF-H_2O$ mixture, the reaction was complete in 45 min and the desired product was isolated in 89% yield. All these reactions were performed using CuI as the copper catalyst. Next, different copper salts were tested in a 4:1 $THF-H_2O$ mixture. When CuCl was used as the catalyst, the yield of the desired product was comparable with that from CuI-catalyzed reaction. However, CuBr or $CuSO_4 \cdot 5H_2O$ failed to catalyze the reaction. Considering the economic aspect and availability, CuI was the best choice for our investigation. The reaction optimization experiments are illustrated in Table 1.

Once the reaction condition was optimized, we focused our attention to judge the generality of the strategy with different alkynes, amines, and sulfonyl azides. Thus, a series of propargyl glycosides (**1a**−**1d**) were synthesized[12] and subjected to MCR with *p*-toluenesulfonyl azide (**2a**) and benzylamine (**3a**). Further we tried benzenesulfonyl azide (**2b**) and methanesulfonyl azide (**2c**) with different sugar alkynes. Finally a series of six different amines (**3a**−**3f**) were investigated. To our satisfaction, all reactions led to the formation of the corresponding glycosylated *N*-sulfonylamidines in good to excellent yields. Reactions with propargyl glycosides of deoxy sugars afforded the target compound in 30 min, whereas normal pyranosides are converted completely within 1 h. For *N*-acetylglucosamine derivatives, 2 h was required for complete conversion. The time difference for complete reaction can be attributed to the respective reactivity difference among various sugars. Although the reaction center is away from the sugar moiety, still it imparts an imperative effect toward the reaction. Results of these reactions are summarized in Table 2. After chromatographic purification of the resulting compounds, each of them was per-*O*-acetylated with Ac_2O in the presence of H_2SO_4−silica,[13] and the resulting compounds were characterized by NMR spectros-

(12) Our recently developed method for the synthesis of propargyl glycosides was utilized where possible to make the required sugar alkynes; see: Roy, B.; Mukhopadhyay, B. *Tetrahedron Lett.* **2007**, *48*, 3783−3787.

TABLE 2. Synthesis of Glycosylated *N*-Sulfonylamidines via Copper-Catalyzed MCR with Sugar Alkynes



entry	1	2	3	4	time (min)	yield[a] (%)
1	**1a**	**2a**	**3a**	**4aaa**	45	89
2	**1b**	**2a**	**3a**	**4baa**	45	87
3	**1c**	**2a**	**3a**	**4caa**	45	90
4	**1d**	**2a**	**3a**	**4daa**	30	93
5	**1e**	**2a**	**3a**	**4eaa**	120	88
6	**1a**	**2b**	**3a**	**4aba**	40	83
7	**1a**	**2c**	**3a**	**4aca**	40	86
8	**1b**	**2b**	**3a**	**4bba**	45	82
9	**1b**	**2c**	**3a**	**4bca**	45	87
10	**1a**	**2a**	**3b**	**4aab**	45	88
11	**1a**	**2a**	**3c**	**4aac**	45	89
12	**1a**	**2a**	**3d**	**4aad**	45	86
13	**1a**	**2a**	**3e**	**4aae**	45	85
14	**1a**	**2a**	**3f**	**4aaf**	40	80
15	**1c**	**2b**	**3a**	**4cba**	40	87

[a] Isolated yields after chromatographic purification.

copy. It is worth noting that 4-nitrobenzenesulfonyl azide did not lead to the desired glycosylated amidine under this reaction condition. Even after it was stirred at 60 °C for 5 h, only traces of conversion were observed. This can be attributed to the electron-withdrawing effect of the nitro group at the *para* position.

In conclusion, we have developed an efficient synthetic route for the preparation of glycosylated *N*-sulfonylamidines through the Cu-catalyzed MCR approach. The method is simple and afforded the target compounds in high yield and purity. These highly functionalized molecules will be evaluated for their bioactivity in due course.

Experimental Section

General Considerations. All reagents and solvents were dried prior to use according to standard methods.[14] Commercial reagents were used without further purification unless otherwise stated. Analytical TLC was performed on silica gel 60-F_{254} with detection by fluorescence and/or by charring following immersion in a 10% ethanolic solution of sulfuric acid. Flash chromatography was performed with silica gel, 230−400 mesh. ^{1}H NMR and ^{13}C NMR spectra were recorded on a spectrometer at 300 and 75 MHz, respectively, using Me_4Si as an internal standard, as appropriate. NMR characterization data are represented using peak-multiplicity abbreviations as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants are given in hertz. Low-resolution MS and HRMS spectra were obtained using ESI ionization.

Characterization Data of the Per-*O*-acetylated Glycosylated *N*-Sulfonylamidines. Data for 5aaa. Light yellow syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, 2H), 7.34−7.19 (m, 7H), 6.91 (br s, 1H), 5.14 (t, 1H, J = 9.3 Hz), 4.89 (t, 1H, J = 9.3 Hz), 4.84 (t, 1H, J = 9.3 Hz), 4.54 (d, 1H, J = 8.1 Hz), 4.41 (m, 2H), 4.07 (m, 4H), 3.69 (m, 1H), 3.22 (m, 1H), 3.06 (m, 1H), 2.40 (s, 3H), 2.01 (s, 3H), 2.00 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 169.6, 169.2, 169.0, 165.1, 141.7, 140.9, 136.7, 128.9(2), 128.6(2), 127.9-(2), 126.1(2), 100.7, 72.3, 71.9, 71.1, 68.1, 67.0, 61.5, 45.8, 34.3, 21.4, 20.5, 20.4(2). MS (ESI): m/z 685.2 $[M + Na]^+$. HRMS: m/z calcd for $C_{31}H_{38}O_{12}N_2SNa$ $(M + Na)^+$ 685.2043, found 685.2041.

Data for 5baa. Colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, 2H), 7.31−7.18 (m, 7H), 6.89 (br s, 1H), 5.31 (d, 1H, J = 3.3 Hz), 5.07 (dd, 1H, J = 7.8, 10.5 Hz), 4.97 (dd, 1H, J = 3.3, 10.5 Hz), 4.51 (d, 1H, J = 7.8 Hz), 4.41 (m, 2H), 4.14−3.92 (m, 5H), 3.25 (m, 1H), 3.06 (m, 1H), 2.39 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 169.7, 169.6, 169.5, 165.4, 141.7, 140.9, 136.8, 129.2(2), 129.0(2), 127.8(2), 127.4, 126.2(2), 101.3, 70.9, 70.4, 68.8, 66.9-(2), 61.0, 45.8, 34.2, 21.4, 20.6, 20.5, 20.4. MS (ESI): m/z 685.2 $[M + Na]^+$. HRMS: m/z calcd for $C_{31}H_{38}O_{12}N_2SNa$ $(M + Na)^+$ 685.2043, found 685.2042.

Data for 5caa. Light brown syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, 2H), 7.28 (m, 7H), 6.98 (br s, 1H), 5.21 (t, 1H, J = 9.6 Hz), 5.18 (m, 1H), 5.13 (br s, 1H), 4.79 (s, 1H), 4.46 (dd, 1H, J = 5.4, 14.4 Hz), 4.36 (dd, 1H, J = 5.4, 14.4 Hz), 4.25 (dd, 1H, J = 5.1, 12.3 Hz), 4.17 (m, 1H), 4.05 (dd, 1H, J = 2.1, 12.3 Hz), 3.90 (m, 1H), 3.79 (m, 1H), 3.14 (m, 2H), 2.42 (s, 3H), 2.15 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.7, 169.6, 169.2, 165.1, 141.8, 140.9, 136.7, 129.3(2), 129.0(2), 128.2(2), 127.6, 126.3(2), 97.1, 69.2(2), 68.9, 65.7, 64.8, 62.1, 46.1, 34.5, 21.5, 20.8, 20.6(2). MS (ESI): m/z 685.2 $[M + Na]^+$. HRMS: m/z calcd for $C_{31}H_{38}O_{12}N_2SNa$ $(M + Na)^+$ 685.2043, found 685.2040.

Data for 5daa. Light yellow syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, 2H), 7.25 (m, 7H), 5.11 (dd, 1H, J = 1.8, 3.6 Hz), 5.09 (m, 1H), 5.00 (t, 1H, J = 8.1 Hz), 4.69 (s, 1H), 4.47 (dd, 1H, J = 5.4, 14.4 Hz), 4.39 (m, 2H), 4.11 (m, 1H), 3.81−3.69 (m, 2H), 3.11 (m, 2H), 2.40 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.17 (d, 3H, J = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 169.8, 169.4, 165.3, 141.7, 140.9, 129.0(2), 128.6-(2), 128.0(2), 127.5, 126.2(2), 96.9, 70.6, 69.4, 69.3, 66.8, 64.4, 46.0, 34.3, 21.4, 20.8, 20.7, 20.6, 17.3. MS (ESI): m/z 627.2 $[M + Na]^+$. HRMS: m/z calcd for $C_{29}H_{36}O_{10}N_2SNa$ $(M + Na)^+$ 627.1988, found 627.1990.

Data for 5eaa. Colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, 2H), 7.22 (m, 7H), 6.91 (d, 1H, J = 9.3 Hz), 5.20 (t, 1H, J = 9.9 Hz), 5.04 (t, 1H, J = 9.9 Hz), 4.78 (d, 1H, J = 3.0 Hz), 4.43−4.26 (m, 3H), 4.17 (dd, 1H, J = 3.9, 12.6 Hz), 4.12 (m, 1H), 4.06 (dd, 1H, J = 2.1, 12.6 Hz), 3.83 (m, 1H), 3.67 (m, 1H), 3.18 (m, 2H), 2.41 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7(2), 170.6, 169.1, 165.5, 142.0, 140.9, 136.9, 129.1(2), 128.7(2), 128.0(2), 127.6, 126.2(2), 97.5, 71.4, 68.4, 67.8, 65.2, 61.9, 51.5, 45.8, 34.1, 29.7-(2), 22.7, 21.5, 20.7(2), 20.6, 14.2. MS (ESI): m/z 684.2 $[M + Na]^+$. HRMS: m/z calcd for $C_{31}H_{39}O_{11}N_3SNa$ $(M + Na)^+$ 684.2203, found 684.2201.

Data for 5aba. Light brown syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 2H), 7.49−7.21 (m, 8H), 6.93 (br s, 1H), 5.14 (t, 1H, J = 9.6 Hz), 4.89 (t, 1H, J = 9.6 Hz), 4.83 (dd, 1H, J = 8.1, 9.6 Hz), 4.53 (d, 1H, J = 8.1 Hz), 4.41 (m, 2H), 4.11−4.01 (m, 4H), 3.68 (m, 1H), 3.23 (m, 1H), 3.08 (m, 1H), 2.00 (s, 3H), 1.98 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 169.6, 169.3,

(13) Mukhopadhyay, B. *Tetrahedron Lett.* **2006**, *47*, 4337−4341.

(14) Perrin, D. D.; Amarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: London, 1996.

169.1, 165.3, 143.7, 136.7, 131.4, 128.7(2), 128.4(2), 128.0(2), 127.7, 126.1(2), 101.0, 72.4, 72.0, 71.2, 68.1, 67.0, 61.6, 46.0, 34.5, 20.5(2), 20.4(2). MS (ESI): *m/z* 671.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{30}H_{36}O_{12}N_2SNa$ $(M + Na)^+$ 671.1887, found 671.1884.

Data for 5aca. White foam. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37−7.26 (m, 5H), 6.82 (br s, 1H), 5.11 (t, 1H, $J = 9.3$ Hz), 4.86 (t, 1H, $J = 9.3$ Hz), 4.81 (dd, 1H, $J = 8.4$, 9.2 Hz), 4.51 (d, 1H, $J = 8.4$ Hz), 4.41 (m, 2H), 4.04 (m, 4H), 3.66 (m, 1H), 3.14 (m, 1H), 3.02 (m, 1H), 2.91 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 169.6, 169.2, 169.0, 165.1, 136.7, 129.0(2), 127.9(2), 127.7, 101.0, 72.3, 72.0, 71.2, 68.1, 67.0, 61.6, 45.7, 43.2, 34.4, 20.5(2), 20.4(2). MS (ESI): *m/z* 609.1 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{25}H_{34}O_{12}N_2$-SNa $(M + Na)^+$ 609.1730, found 609.1728.

Data for 5bba. Light yellow syrup. ^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, 2H), 7.49−7.22 (m, 8H), 6.92 (br s, 1H), 5.31 (d, 1H, $J = 3.0$ Hz), 5.09 (dd, 1H, $J = 7.8$, 10.2 Hz), 4.52 (d, 1H, $J = 7.8$ Hz), 4.49 (dd, 1H, $J = 5.4$, 15.6 Hz), 4.36 (dd, 1H, $J = 5.4$, 15.6 Hz), 4.13−3.90 (m, 5H), 3.28 (m, 1H), 3.08 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 169.7, 169.6, 169.5, 165.5, 143.7, 136.8, 131.4, 129.1(2), 128.6(2), 127.8(2), 127.5, 126.2(2), 101.4, 70.9, 70.4, 68.8, 66.9, 61.1, 45.9, 34.4, 20.7, 20.5, 20.4(2). MS (ESI): *m/z* 671.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{30}H_{36}O_{12}N_2SNa$ $(M + Na)^+$ 671.1887, found 671.1884.

Data for 5bca. White foam. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35−7.24 (m, 5H), 6.82 (br s, 1H), 5.29 (d, 1H, $J = 3.0$ Hz), 5.05 (dd, 1H, $J = 7.5$, 10.5 Hz), 4.97 (dd, 1H, $J = 3.0$, 10.5 Hz), 4.49 (d, 1H, $J = 7.5$ Hz), 4.47−4.35 (m, 4H), 4.11−3.89 (m, 5H), 3.19 (m, 1H), 3.03 (m, 1H), 2.04 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 169.7, 169.5-(2), 165.3, 136.8, 128.1(2), 127.7(2), 127.5, 101.3, 70.9, 70.6, 70.4, 66.9, 66.8, 61.1, 45.6, 43.5, 34.4, 20.6, 20.5, 20.4(2). MS (ESI): *m/z* 609.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{25}H_{34}O_{12}N_2SNa$ $(M + Na)^+$ 609.1730, found 609.1728.

Data for 5aab. Light brown syrup. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, 2H), 7.23 (d, 2H), 6.64 (br s, 1H), 5.81 (m, 1H), 5.22−5.10 (m, 3H), 5.00 (t, 1H, $J = 9.9$ Hz), 4.87 (t, 1H, $J = 9.9$ Hz), 4.56 (d, 1H, $J = 7.8$ Hz), 4.25 (dd, 1H, $J = 4.5$, 12.3 Hz), 4.07 (m, 3H), 3.84 (m, 2H), 3.72 (m, 1H), 3.20 (m, 1H), 3.09 (m, 1H), 2.39 (s, 3H), 2.04 (s, 3H), 2.01 (s, 6H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 169.6, 169.3, 169.1, 165.3, 141.7, 141.0, 132.4, 129.0(2), 126.3(2), 117.3, 100.8, 72.4, 71.9, 71.2, 68.1, 66.9, 61.5, 44.2, 34.2, 29.6, 21.4, 20.6(2), 20.4. MS (ESI): *m/z* 635.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{27}H_{36}O_{12}N_2SNa$ $(M + Na)^+$ 635.1887, found 635.1884.

Data for 5aac. White foam. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, 2H), 7.26 (d, 2H), 5.19 (t, 1H, $J = 9.3$ Hz), 5.07 (t, 1H, $J = 9.3$ Hz), 4.95 (dd, 1H, $J = 8.1$, 9.3 Hz), 4.31 (m, 2H), 4.21 (m, 2H), 4.15 (dd, 1H, $J = 1.8$, 12.6 Hz), 3.76 (m, 1H), 3.56 (m, 1H), 3.33 (m, 2H), 2.43 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.28 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 169.6, 169.1(2), 162.6, 141.6, 141.2, 128.9(2), 126.0(2), 100.9, 73.0, 71.8, 71.2, 68.1, 68.0, 61.6, 50.4, 48.0, 33.0, 29.6, 21.4, 20.6(2), 20.4(3), 19.9(2). MS (ESI): *m/z* 679.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{30}H_{44}O_{12}N_2SNa$ $(M + Na)^+$ 679.2513, found 679.2515.

Data for 5aad. Light yellow syrup. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, 2H), 7.23 (d, 2H), 6.33 (d, 1H, $J = 6.9$ Hz), 5.17 (t, 1H, $J = 9.6$ Hz), 5.01 (t, 1H, $J = 9.6$ Hz), 4.90 (dd, 1H, $J = 8.1$, 9.6 Hz), 4.54 (d, 1H, $J = 8.1$ Hz), 4.30 (dd, 1H, $J = 5.1$, 12.3 Hz), 4.10−4.20 (m, 3H), 3.73 (m, 1H), 3.10 (m, 2H), 2.41 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.71 (m, 1H), 1.35−1.17 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 169.4, 168.9(2), 164.1, 141.4, 141.2, 128.8(2), 126.0(2), 100.8, 72.4, 71.7, 71.1, 68.0, 67.1, 61.4, 34.1, 31.7, 31.3, 29.4, 25.2, 24.3(2), 21.2, 20.4(2), 20.2(2). MS (ESI): *m/z* 677.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{30}H_{42}O_{12}N_2SNa$ $(M + Na)^+$ 677.2356, found 677.2353.

Data for 5aae. Colorless syrup. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, 2H), 7.24 (d, 2H), 6.49 (br s, 1H), 5.16 (t, 1H, $J = 9.6$ Hz), 4.99 (t, 1H, $J = 9.6$ Hz), 4.89 (dd, 1H, $J = 8.1$, 9.6 Hz), 4.53 (d, 1H, $J = 8.1$ Hz), 4.29 (m, 2H), 4.12−3.97 (m, 3H), 3.73 (m, 1H), 3.28−3.06 (m, 5H), 2.40 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.52 (m, 2H), 1.30 (m, 2H), 0.86 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 169.6, 169.3, 169.1, 165.3, 141.6, 141.3, 129.0(2), 126.3(2), 101.0, 72.1, 71.7, 71.3, 68.2, 67.2, 61.6, 41.7, 34.3, 30.3, 29.7, 21.5, 20.6(2), 20.5, 20.0, 14.2. MS (ESI): *m/z* 651.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{28}H_{40}O_{12}N_2SNa$ $(M + Na)^+$ 651.2200, found 651.2196.

Data for 5aaf. White foam. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, 2H), 7.24 (d, 2H), 5.15 (t, 1H, $J = 9.3$ Hz), 4.98 (t, 1H, $J = 9.3$ Hz), 4.86 (dd, 1H, $J = 8.1$, 9.3 Hz), 4.53 (d, 1H, $J = 8.1$ Hz), 4.27 (dd, 1H, $J = 4.5$, 12.3 Hz), 4.10 (m, 3H), 3.69 (m, 1H), 3.23 (m, 3H), 2.82 (m, 1H), 2.63 (m, 2H), 2.52 (m, 3H), 2.42 (m, 1H), 2.40 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.79 (m, 2H), 1.43 (m, 4H), 1.24 (m, 1H), 0.89 (t, 9H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 169.7, 169.3, 169.1, 164.6, 141.5, 141.4, 129.0, 126.2, 101.0, 72.7, 71.9, 71.2, 68.2, 67.4, 61.7, 53.1(2), 52.7, 41.7, 35.2, 31.9, 29.7(3), 29.4, 27.8, 23.6, 22.7, 21.5, 20.6(2), 20.5(2), 14.2, 14.0(2). MS (ESI): *m/z* 749.3 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{35}H_{54}O_{12}N_2SNa$ $(M + Na)^+$ 749.3295, found 749.3297.

Data for 5cba. Light yellow syrup. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 2H), 7.49−7.21 (m, 9H), 5.24−5.10 (m, 3H), 4.77 (s, 1H), 4.45 (dd, 1H, $J = 5.4$, 14.7 Hz), 4.40 (dd, 1H, $J = 5.4$, 14.7 Hz), 4.24 (dd, 1H, $J = 5.1$, 12.3 Hz), 4.21 (m, 1H), 4.05 (dd, 1H, $J = 1.5$, 12.3 Hz), 3.92 (m, 1H), 3.74 (m, 1H), 3.21−3.09 (m, 2H), 2.13 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.8(2), 169.2, 165.2, 143.6, 136.6, 131.4, 129.1(2), 128.6(2), 128.1(2), 127.5, 126.2(2), 97.1, 69.2(2), 68.9, 65.6, 64.7, 62.1, 46.1, 34.5, 20.7(2), 20.6(2). MS (ESI): *m/z* 671.2 $[M + Na]^+$. HRMS: *m/z* calcd for $C_{30}H_{36}O_{12}N_2$-SNa $(M + Na)^+$ 671.1887, found 671.1883.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of per-*O*-acetylated glycosylated *N*-sulfonylamidines described in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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