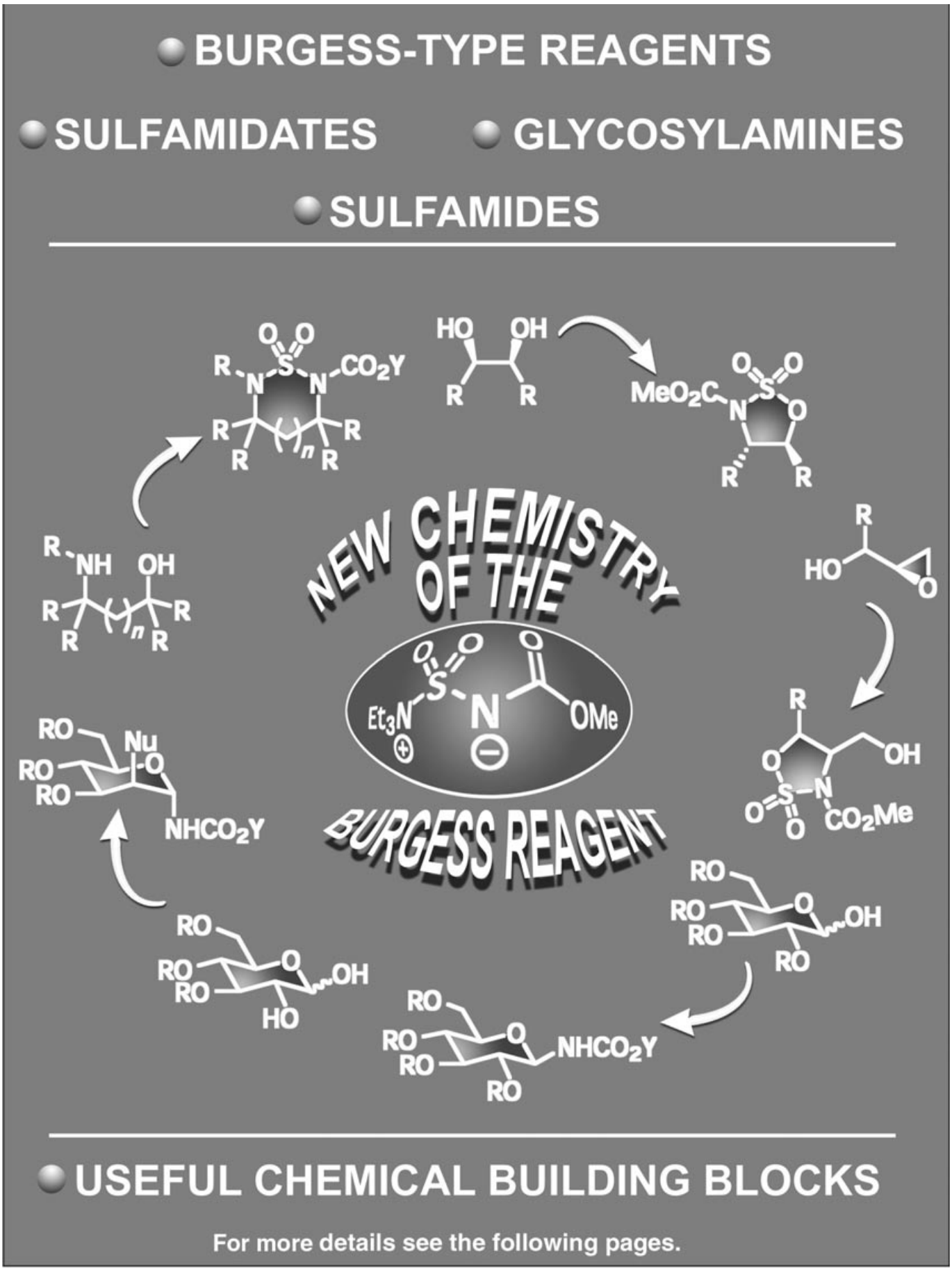

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New Uses for the Burgess Reagent in Chemical Synthesis: Methods for the Facile and Stereoselective Formation of Sulfamidates, Glycosylamines, and Sulfamides

K. C. Nicolaou,*[a, b] Scott A. Snyder,[a] Deborah A. Longbottom,[a] Annie Z. Nalbandian,[a] and Xianhai Huang[a]

Abstract: Although the Burgess reagent (methoxycarbonylsulfamoyltriethylammonium hydroxide, inner salt) has found significant use in chemical synthesis as a dehydrating agent, almost no work has been directed towards its potential in other synthetic applications. As this article will detail, we have found that the Burgess reagent is remarkably effective at accomplishing a number of non-dehydrative synthetic tasks when applied to appropriate substrates, such as the formation of sulfamidates from 1,2-diols or epoxyalcohols, α- and β-glycosylamines from carbohydrates, and cyclic sulfamides from 1,2-aminoalcohols. Beyond delineating the power of these new reaction manifolds, we also describe the construction of a group of alternative Burgess-type reagents that extends the scope of these new reactions even further.

Keywords: amines · Burgess reagent · diazo compounds · sulfamides · sulfur

Introduction

Ever since its introduction over three decades ago, the Burgess reagent (**1**, Scheme 1)[1] has proven to be a powerful tool in chemical synthesis as an agent for effecting a diverse set of dehydration reactions.[2] For example, it has been employed on numerous occasions to smoothly convert secondary and tertiary alcohols into their corresponding alkenes by means of *cis*-elimination pathways[3] as well as to dehydrate amides to their nitrile counterparts (Scheme 1a,b).[4] The Burgess reagent is also an excellent initiator of cyclodehydrations leading to heterocycles, such as the transformation of hydroxyamides into oxazolines[5] and the Robinson–Gabriel reaction converting ketoamides into oxazoles.[6] It was the latter of these processes that originally brought the Burgess reagent to our attention as we sought methods to complete the heteroaromatic core of the originally proposed structure of diazonamide A (**2**) by transforming advanced intermediate **3** into **4**.[7] While the Burgess reagent would ultimately fail to accomplish that rather difficult dehydration, our efforts in that context inspired us to ponder the following, more general, question: are there powers for this reagent beyond its capacity to remove water?

As a subsequent search of the literature revealed, there were only a few such reports in existence, all dedicated to the same process shown in Scheme 1c: the conversion of primary alcohols into their corresponding methyl urethane derivatives.[8] This finding, in turn, led us to wonder if related processes leading to the incorporation of nitrogen could be accomplished on other substrate types, such as 1,2-diols (a compound type that had seemingly never been subjected to its powers). Our subsequent efforts to answer that question began a line of investigation that ultimately revealed a wealth of newfound potential for the Burgess reagent, not as a dehydrative agent, but rather as a convenient source of multiple heteroatoms (S, O, and N). This article recounts those studies, work which has led to new methods for the stereoselective formation of diverse sulfamidates, α- and β-glycosylamines, and sulfamides.[9]

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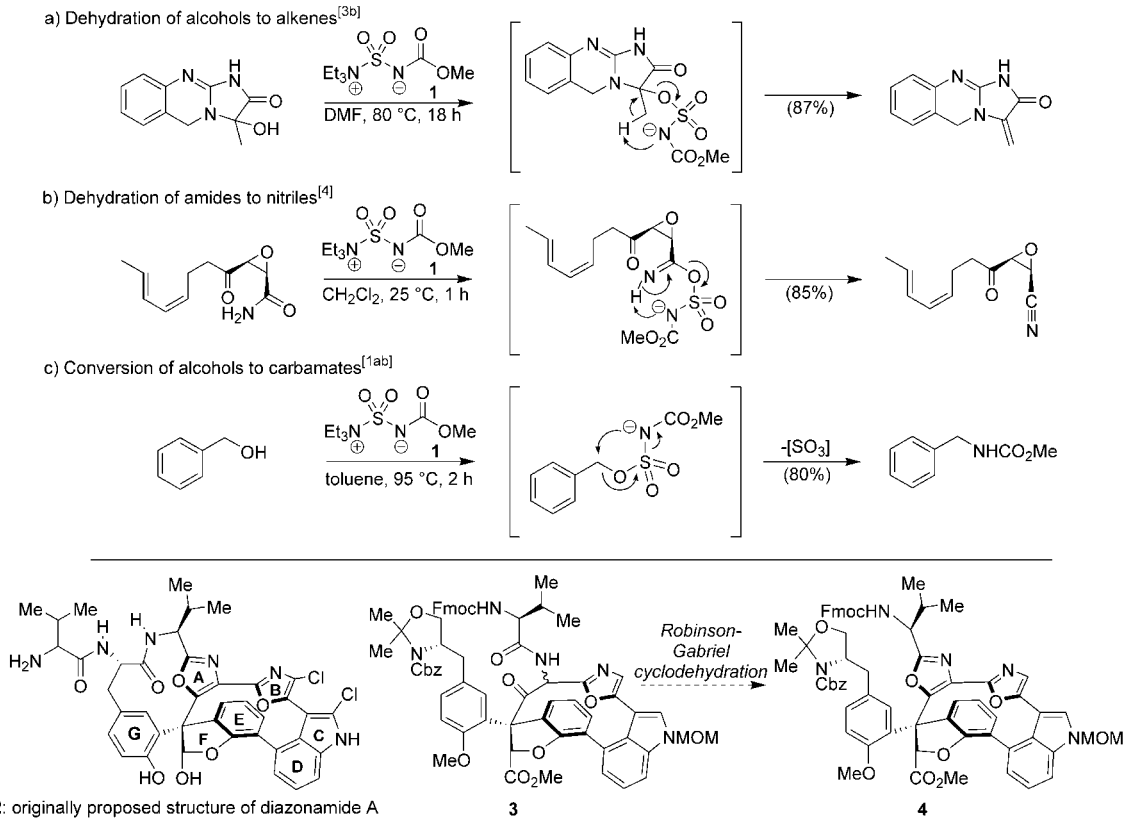
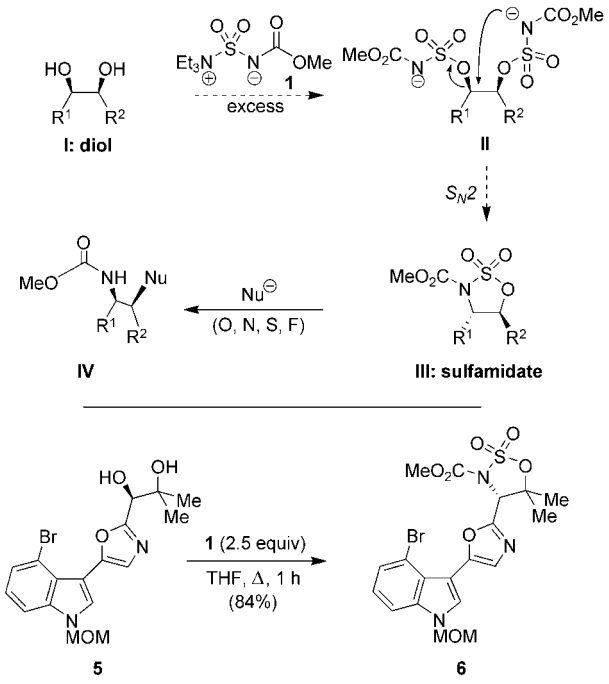


Scheme 1. Selected uses of the Burgess reagent (**1**) in chemical synthesis.

Results and Discussion

Sulfamidate synthesis from 1,2-diols using the Burgess reagent: Our expectation for what could happen to a 1,2-diol-containing substrate (**I**) following exposure to an excess amount of the Burgess reagent (at least two equivalents) is drawn in Scheme 2. Namely, if that starting material could be coaxed to form an intermediate of type **II** prior to either alcohol participating in a typical dehydrative pathway, then perhaps a sulfamidate (**III**) product could arise through the indicated S_N2 reaction. Assuming that this transformation would proceed through displacement of the more activated of the two potential leaving groups, then variation of the R^1 and R^2 substituents on enantiopure **I** could enable the stereo- and regioselective synthesis of sulfamidates (**III**) on a potentially large number of diverse structural types.



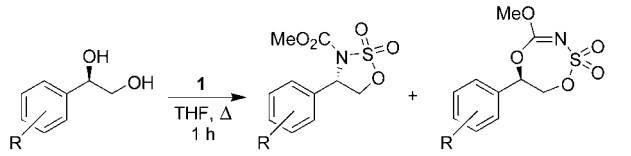
Scheme 2. Proposed conversion of 1,2-diols (**I**) to cyclic sulfamidates (**IV**) using Burgess reagent (**1**) and proof of principle (**5**→**6**).

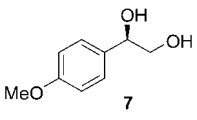
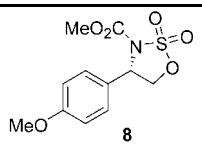
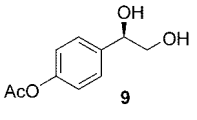
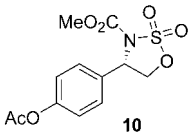
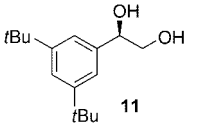
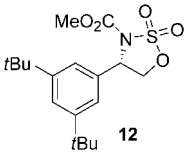
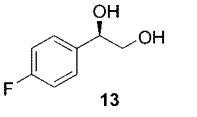
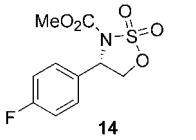
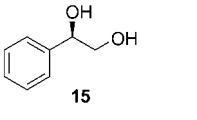
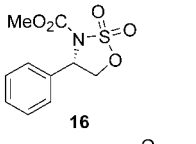
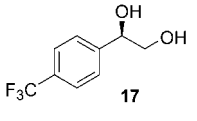
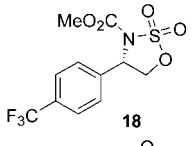
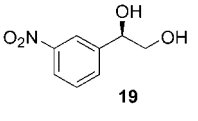
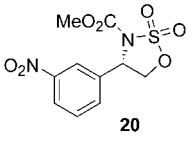
The proposed chemistry appealed to us not only because it would highlight a new use for the Burgess reagent if it worked, but also because its success would deliver an impor-

Abstract in Greek:

Παρόλο που το αντιδραστήριο Burgess (εσωτερικό άλας του μεθοξυκαρβονυλσυλφαμοΰλο-τριαιθυλαμμώνιου υδροξειδίου) έχει βρει σημαντική εφαρμογή στην οργανική σύνθεση ως αφυδατικό μέσο, η έρευνα δεν έχει στραφεί σχεδόν καθόλου προς δυνητικά διαφορετικές συνθετικές εφαρμογές. Όπως αυτό το άρθρο αναλύει, βρήκαμε ότι το αντιδραστήριο Burgess είναι αξιοσημείωτα αποτελεσματικό κατά την πραγματοποίηση ενός αριθμού μη αφυδατικών συνθετικών αντιδράσεων, όταν εφαρμόζεται στα κατάλληλα υποστρώματα, όπως ο σχηματισμός σουλφαμιδικών εστέρων από 1,2-διόλες ή εποξυαλκοόλες, α- και β-γλυκοζυλαμινών από υδατάνθρακες, και κυκλικών σουλφαμιδίων από 1,2-αμινοαλκοόλες. Πέρα από την παρουσίαση της δύναμης αυτών των νέων πολλαπλών αντιδράσεων, περιγράφουμε επίσης την δημιουργία μιας ομάδας εναλλακτικών αντιδραστηρίων τύπου Burgess που επεκτείνει το πεδίο αυτών των νέων αντιδράσεων ακόμα περεταίρω.

Table 1. Regioselective synthesis of sulfamidates from precursor 1,2-diols using Burgess reagent (**1**).



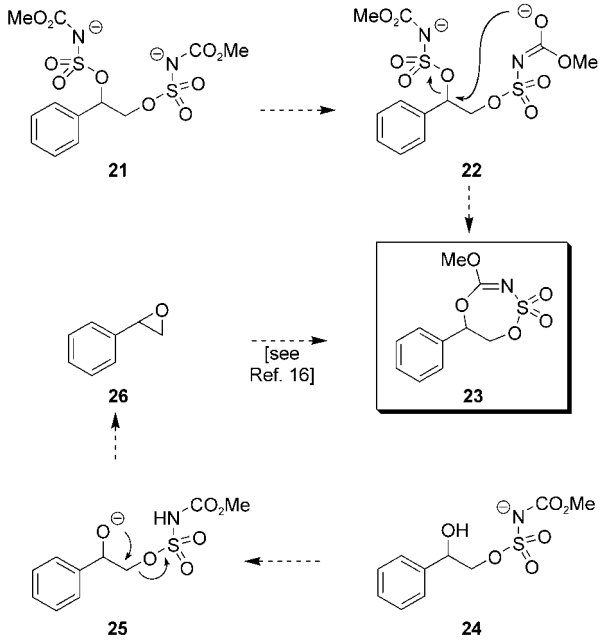
Entry	Starting material	Major product	Ratio of products[a]	Yield [%]
1	 **7**	 **8**	>98:2	91
2	 **9**	 **10**	95:5	88
3	 **11**	 **12**	95:5	87
4	 **13**	 **14**	95:5	79
5	 **15**	 **16**	93:7	92
6	 **17**	 **18**	85:15	83
7	 **19**	 **20**	55:45	86

[a] As determined by ^{1}H NMR analysis of the crude reaction products.

tant pharmacophore in far fewer steps than other methods could achieve.[10] Equally attractive, since sulfamidates are well precedented to undergo highly selective reactions with O-, S-, N-, and F-based nucleophiles to afford compounds of general structure **IV**,[11] we could subsequently use our synthesized materials to access a diverse array of products, including such valuable synthons as β-aminoalcohols.[12] To test the key element of this hypothesis, we heated a solution of diol **5** (synthesized from the precursor olefin by dihydroxylation under standard conditions) in THF at reflux for one hour in the presence of 2.5 equivalents of the Burgess reagent (**1**).[13] In line with our expectations, at the end of this time we obtained the desired sulfamidate product (**6**) in 84% yield as a single regioisomer based on NMR spectroscopic analysis.

With this important proof of principle achieved, we next sought to test the generality of this reaction process on a selection of styrene-derived diols possessing a broad range of aromatic substitution patterns to explore whether inductive effects would have any impact on the regioselectivity of the S_N2-based cyclization. Although we could have chosen any number of diols to probe the process further, we selected this particular class of compounds for two key reasons: 1) styrenes are the best substrates for Sharpless asymmetric dihydroxylation (AD)[14] in terms of both catalytic activity and enantioselectivity, and 2) styrene-type olefins display good, but highly variable, yields and regioselection in carbamate-based asymmetric aminohydroxylation (AA).[15]

As indicated by the results in Table 1, our Burgess-mediated sulfamidate synthesis proved quite effective with this group of substrates as long as the aromatic ring was electron-rich (entries 1–4) or electron-neutral (entry 5). However, when substituents with increasing electronegativity were appended onto the styrene core (entries 6 and 7), a second reactive pathway leading to substantial amounts of a seven-membered side-product was opened up. Scheme 3 provides two mechanisms that could account for the formation of these types of products (i.e., **23**), using styrene for the sake of their illustration. The first of these scenarios invokes the resonance form of **21** (i.e., **22**) as the source of an oxygen nucleophile that could displace the activated benzylic leaving group and lead to **23** directly. The second assumes only partial reaction of the Burgess reagent with substrate **24** to initiate entry into a different intramolecular displacement reaction leading to epoxide **26**, a compound already demonstrated to provide heterocycle **23** in its reaction with the Burgess reagent.[16] Although the results described thus far did not allow us to discern which, if either, of these two possible pathways was active, one experiment described below

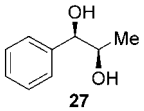
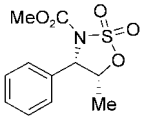
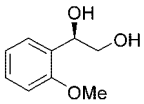
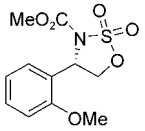
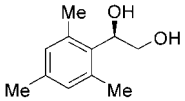
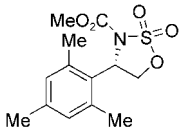
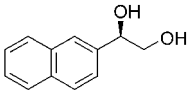
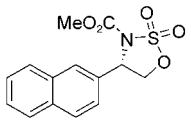
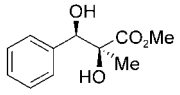
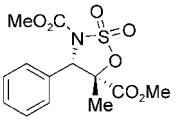
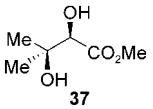
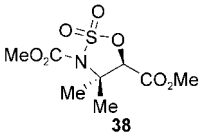
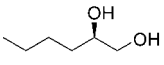
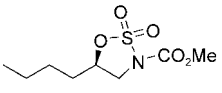
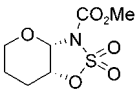


Scheme 3. Degenerate mechanistic proposals to account for the formation of the minor seven-membered ring product **23** in the reaction of 1,2-diols with excess Burgess reagent.

would provide such an insight. For now, however, we think it important to note that the desired sulfamidate products listed in Table 1 could be readily separated from their seven-membered ring counterparts by standard chromatography. In addition, the especially poor selectivity observed in the conversion of **19** to **20** (entry 7) could be improved to 75:25 by performing the reaction at 25 °C, albeit at the expense of yield (35 %).

Having explored electronic effects, we then sought to examine the role of steric encumbrance on the reaction process as well as its applicability to non-styrene derived diols by testing the substrates listed in Table 2. As one might expect, increasing steric bulk at the terminal position of the styrene core, simply through the addition of a single methyl group (entry 1), increased the selectivity of cyclic sulfamidate formation compared to that observed for the corresponding example in Table 1. This outcome suggests that the epoxide pathway mentioned above is the source of any seven-membered products, as the other mechanistic picture would not predict a different ratio based on this one simple change. Importantly, no decrease in yield or selectivity for the desired five-membered sulfamidate was observed when steric bulk was added onto the aromatic ring (entries 2 and 3). Equally significant, esters were well tolerated in the reaction. In entry 5, the near exclusive formation of sulfamidate **36** was achieved from **35** due to the reinforcing effects of α-position deactivation by the ester moiety and steric bulk imposed at that site by a methyl group, while competitive steric and electronic effects in entry 6 led to retarded S_N2 displacement at the preferred terminal site, leading to increased formation of the seven-membered side product and decreased reaction yield. Simple aliphatic examples (entries 7 and 8) proceeded with extremely high regioselectivity, presumably due to the well-established preference for nucleophilic displacement of primary or activated leaving groups over their secondary counterparts. Finally, to verify the potential of this reaction manifold for asymmetric synthesis, as all of the examples listed in Tables 1 and 2 were performed on racemic diol substrates, an X-ray crystal structure was obtained for sulfamidate **36**; this confirmed that inversion of stereochemistry had occurred at the benzylic position relative to the racemic *cis*-diol starting material (see Figure 1).

Table 2. Further examples of the regioselective synthesis of sulfamidates from precursor 1,2-diols using Burgess reagent (**1**).

Entry	Starting material	Major product	Ratio of products[a]	Yield [%]
1	 **27**	 **28**	> 98:2	72
2	 **29**	 **30**	> 98:2	92
3	 **31**	 **32**	> 98:2	94
4	 **33**	 **34**	85:15	82
5	 **35**	 **36**	> 98:2	81
6	 **37**	 **38**	71:29	41
7	 **39**	 **40**	> 98:2	76
8	 **41**	 **42**	> 98:2	71

[a] Determined by ^{1}H NMR analysis of the crude reaction products.

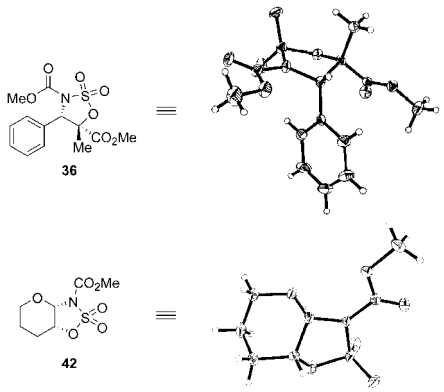
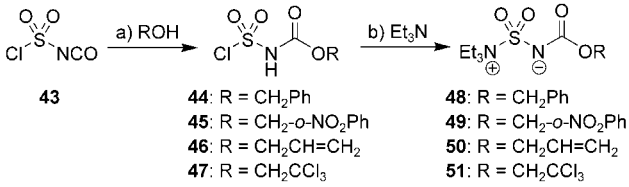


Figure 1. X-ray crystallographic structures for sulfamidates **36** and **42**.

Additionally, both racemic and enantiopure **33** were synthesized,[17] and comparison of the chiral HPLC traces of the resultant products (**34**) indicated that preexisting stereochemical information was communicated in the reaction with complete fidelity.[18]

With a much clearer sense of the scope possessed by our Burgess-mediated sulfamidate synthesis, we now desired to extend its overall utility one step further by constructing compounds bearing N-protection other than a methyl carbamate, a task which could be achieved simply by modification of **1**. To our surprise, however, such reagents represented novel chemical entities, as an extensive search of the litera-

ture indicated that no efforts had been expended to prepare any Burgess-type salts other than those originally described almost thirty years ago.[19] This result was unexpected, as **1** is known to be both thermal and moisture sensitive,[2a] features which might be modulated by differentiation of the carbamate portion. In any case, as shown in Scheme 4, we found



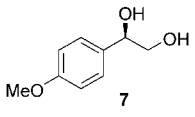
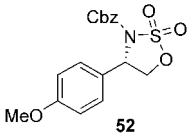
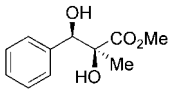
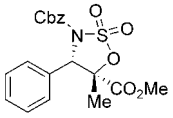
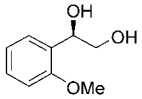
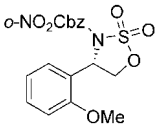
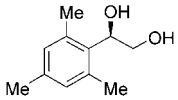
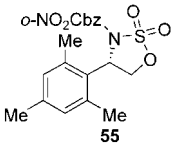
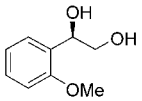
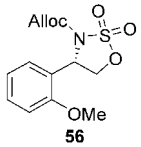
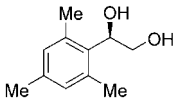
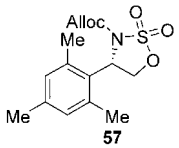
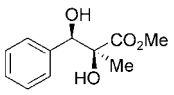
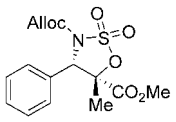
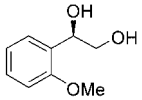
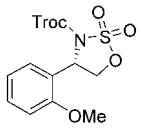
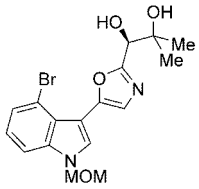
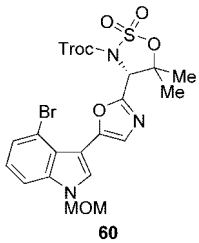
Scheme 4. Synthesis of the novel variants (**48**–**51**) of the original Burgess reagent: a) chlorosulfonyl isocyanate (1.0 equiv), ROH (1.05 equiv), CH_2Cl_2, 0 °C, 30 min, 89–95 %; b) Et_3N (2.5 equiv), C_6H_6, 25 °C, 1 h, 81–87 %.

it quite easy to prepare four different Burgess-type reagents (**48**–**51**), representing an orthogonal set of amine-protecting groups (based on deprotection by hydrogenation, photolysis, exposure to palladium-based catalysts, or treatment with Zn, respectively) by treating chlorosulfonylisocyanate (**43**) with the alcohol of interest and then exposing the resultant product to Et_3N.[20] Now the question was whether these reagents would perform with equal facility as **1** in sulfamidate synthesis. Pleasingly, the answer was yes as their exposure to several diol substrates resulted in the formation of the desired sulfamidate products (**52**–**60**, Table 3) in comparable efficiency and selectivity as observed previously with **1**.

Having synthesized such a diverse group of sulfamidates, we were now in a position to attempt their conversion into β-aminoalcohols. Accordingly, using a literature procedure[11k] that had been examined on only one sulfamidate substrate, we exposed a variety of these products (see Table 4) to a 1:1 mixture of aqueous HCl and 1,4-dioxane at 25 °C. In every case, a high yield of β-aminoalcohol product was observed irrespective of carbamate protecting group used. As such, the applicability of this method to a diverse set of 1,2-diol classes, combined with its facile use in a subsequent step to deliver β-aminoalcohol products, renders it an attractive alternative to protocols such as Sharpless AA should they fail to deliver a given product with acceptable levels of regio- and/or stereocontrol.

Glycosylamine synthesis using the Burgess reagent: In assessing additional directions in which we could take the Burgess reagent, new inspiration came when we thought more carefully about the conversion reported in entry 8 of Table 2 leading to the synthesis of **42** (whose *cis*-fused sulfamidate ring was verified by the X-ray crystal structure shown in Figure 1). Specifically, we wondered what would happen if this reaction were applied to a sugar template (**V**, see Scheme 5). Our experience suggested that the same type of sulfamidate product (**VII**) should arise through the departure of the most activated hydroxyl, either by the indicated S_N2 mechanism or by an oxonium alternative (not shown), with the C-2 group orchestrating the stereoselective delivery

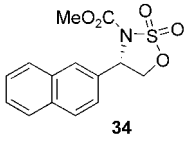
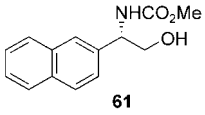
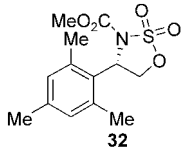
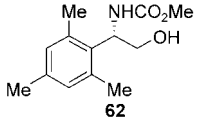
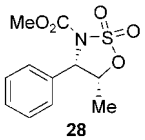
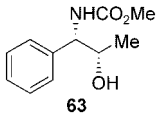
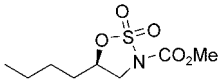
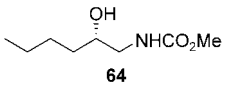
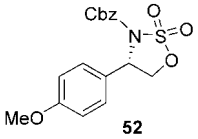
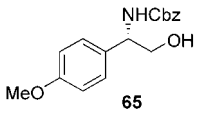
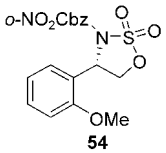
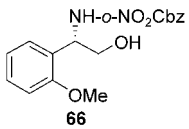
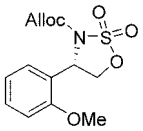
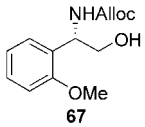
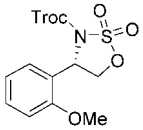
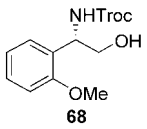
Table 3. Use of the new Burgess-type reagents **48**–**51** to prepare orthogonally protected sulfamidates (**52**–**60**).

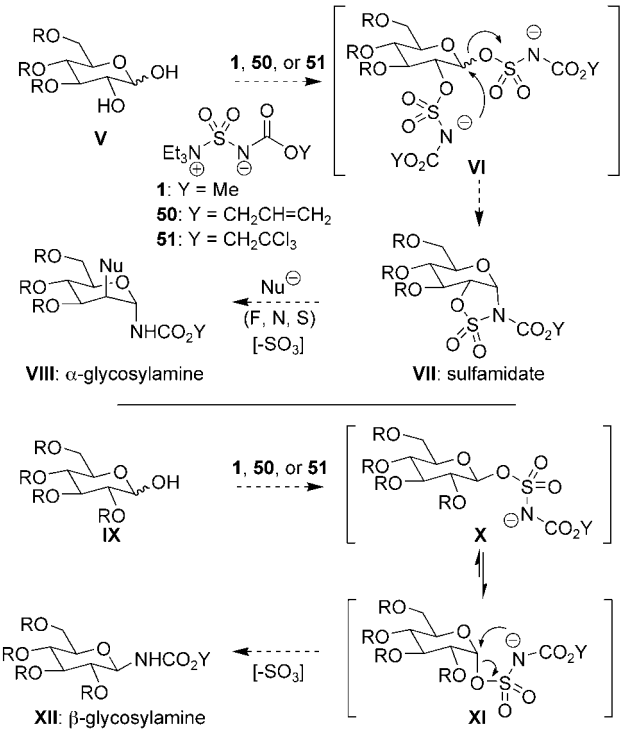
Entry	Starting material	Major product	Ratio of products[a]	Yield [%]
1	 **7**	 **52**	>98:2	90
2	 **35**	 **53**	95:5	81
3	 **29**	 **54**	>98:2	87
4	 **31**	 **55**	>98:2	82
5	 **29**	 **56**	>98:2	89
6	 **31**	 **57**	>98:2	87
7	 **35**	 **58**	>98:2	81
8	 **29**	 **59**	>98:2	78
9	 **5**	 **60**	>98:2	83

[a] As determined by ^{1}H NMR analysis of the crude reaction products. Cbz = CO_2CH_2Ph, *o*-NO_2Cbz = CO_2CH_2-*o*-NO_2Ph, Alloc = $CO_2CH_2CH=CH_2$, Troc = $CO_2CH_2CCl_3$.

of nitrogen. In this case, however, subsequent opening of this ring with a heteroatomic nucleophile would afford a 1,2-*trans*-difunctionalized glycosylamine product.[11] Thus, based on this model, a starting material derived from D-glucose would provide an α-glycosylamine product (**VIII**). Al-

Table 4. Deprotection of cyclic sulfamidates using aqueous HCl in 1,4-dioxane at ambient temperature to yield β-aminoalcohols (**61–68**).

Entry	Starting material	Product	Time [h]	Yield [%]
1	 **34**	 **61**	10	94
2	 **32**	 **62**	30	95
3	 **28**	 **63**	12	92
4	 **40**	 **64**	8	88
5	 **52**	 **65**	2	92
6	 **54**	 **66**	26	95
7	 **56**	 **67**	24	93
8	 **59**	 **68**	16	90



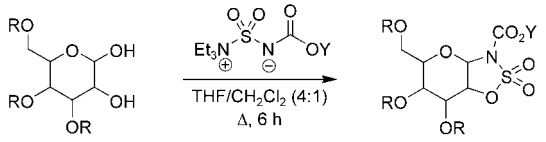
Scheme 5. Proposed synthesis of both α- and β-glycosylamines using Burgess-type reagents.

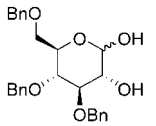
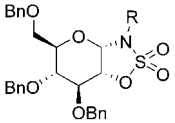
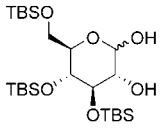
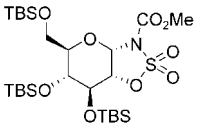
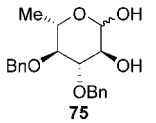
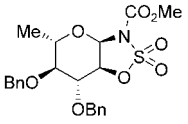
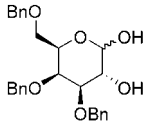
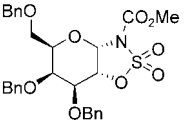
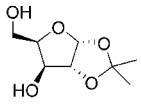
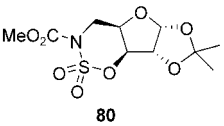
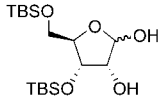
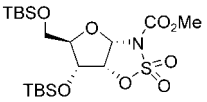
ternatively, if lactols bearing C-2 protection (**IX**) were exposed to the same general reaction conditions, it would be reasonable to expect that these materials would afford *N,O*-acetal products instead of sulfamidates, through the indicated mechanism, with stereocontrol in this "self-displacement" reaction arising from the established preference for anomeric triflates to exist as α-anomers (**XI**) over their β-disposed counterparts (**X**).[21] As such, D-glucose-based materials would afford only β-glycosylamine products (**XII**) in this reaction paradigm.[22]

While relatively simple ideas based on our previous success in reacting 1,2-diol substrates, their success would be of considerable value, since glycosylamines have proven to be exceedingly difficult to synthesize. Indeed, available methods based on the use of glycosyl azides, glycals,[23] Kochetkov aminations,[24] and α-hydroxy nitriles,[25] among others, typically lack substrate generality and often result in variable stereoselectivity, especially in complex contexts. In addition, none of these methods singularly provides a means to obtain both α- and β-anomers at will and in a controlled manner. As such, we immediately set out to test whether the Burgess reagent could rise to this task.

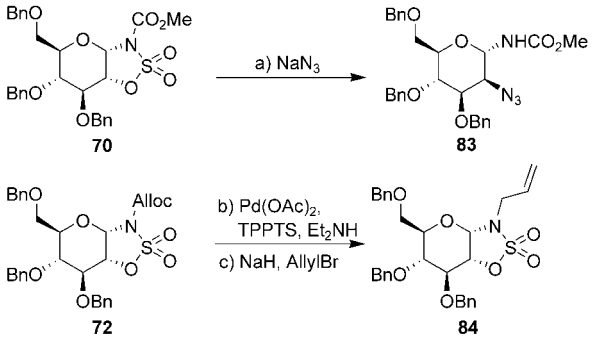
Gratifyingly, the Burgess reagent (**1**) and its relatives (**50** and **51**) did just that. As shown in Table 5, a variety of diols on diverse carbohydrate templates (D-glucose, D-galactose, L-rhamnose) were smoothly converted into their α-disposed sulfamidate counterparts (*cis*-fused rings) upon the action of 2.5 equivalents of **1**, **50**, or **51** in refluxing THF/CH_2Cl_2 (4:1) over the course of 6 h.[26] In every case, yields and α:β selectivity (determined by ^{1}H NMR spectroscopy; the minor isomer presumed to be the *trans*-fused β-anomer was not isolated but observed by NMR spectroscopy) were exceptionally high irrespective of which Burgess-type reagent was employed. As such, these findings can be taken as a sign that any carbamate-protecting group can be appended onto the sulfamidate products in Table 5, though we have only demonstrated that principle directly for D-glucose. Such flexibility is important, since we were able to subsequently open these products with nucleophiles to afford α-disposed glycosylamines such as **83**, or alternatively, convert them into functionalized sulfamidates like **84** simply by removing the carbamate protecting group and alkylating as shown in Scheme 6. Both of these manipulations should prove important in future applications relevant to the study of chemical biology, though compounds of type **84** offer several unique advantages as their sulfamidate ring provides untapped

Table 5. Synthesis of sulfamidates on carbohydrate templates.



Entry	Starting material	Product	Ratio α:β[a]	Yield [%]
1	 **69**	 **70**: R = CO_2Me **71**: R = Troc **72**: R = Alloc	8:1	88
2			15:1	75
3			15:1	83
4	 **73**	 **74**	10:1	79
5	 **75**	 **76**	10:1	82
6	 **77**	 **78**	>20:1	79
7	 **79**	 **80**	–	91
8	 **81**	 **82**	>20:1	74

[a] The minor isomer (β-anomer, *trans*-fused ring) was not isolated, but presumed to be that on the basis of ^{1}H NMR data (of the α/β mixture).



Scheme 6. Synthesis of functionalized α-glycosylamines from precursor sulfamidates: a) NaN_3 (5.0 equiv), DMF, 60 °C, 5 h, 83 %; b) $Pd(OAc)_2$ (0.1 equiv), TPPTS (0.2 equiv), Et_2NH (40 equiv), $MeCN/H_2O$ (1:1), 25 °C, 30 min; c) NaH (5.0 equiv), DMF, 25 °C, 5 min, then allyl bromide (4.0 equiv), 25 °C, 15 min, 73 % over two steps. TPPTS = 3,3′,3″-phosphidinynetris(benzenesulfonic acid) trisodium salt.

structural novelty and ensures that the disposition of the nitrogen atom cannot anomerize (as often occurs with unprotected α-glycosylamines simply upon standing in solution).

As indicated in Table 6, C-2 protected lactols reacted with Burgess-type reagents in a level of smoothness that matched their diol counterparts, affording a β-disposed, protected glycosylamine on every six-membered carbohydrate probed (entries 1–5), as verified by both X-ray crystallographic (see Figure 2)[27] and ^{1}H NMR analyses. Five-membered furanose

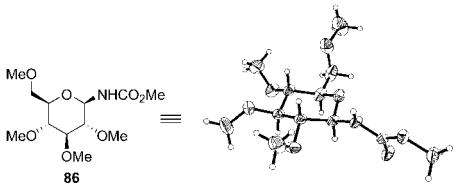


Figure 2. X-ray crystallographic structure of compound **86**.

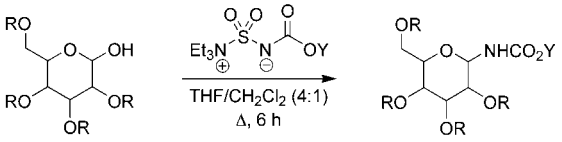
substrates performed equally well (entries 6–8), with anomeric stereochemistry in these products presumably controlled by the orientation of the C-2 substituent in a level commensurate to its bulk.[28] As discussed earlier, the reactions performed equally well irrespective of which Burgess-type reagent was employed in this manifold, though Alloc protection did provide one important benefit over the other carbamate alternatives: facile removal in near quantitative yield under conditions[29] that did not initiate any anomerization (see, for example, **89**→**102**) to afford free glycosylamines.

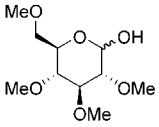
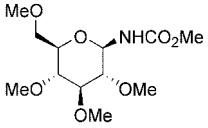
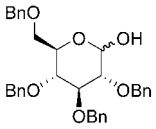
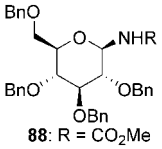
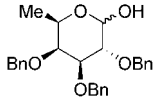
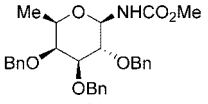
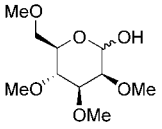
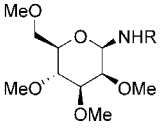
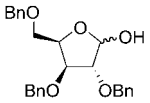
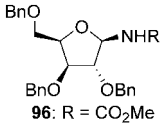
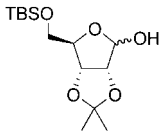
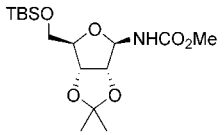
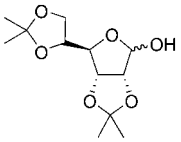
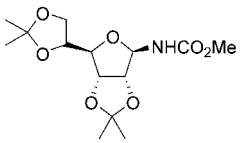
In closing this section, it is clear that the Burgess reagent (**1**) and its analogues (**50** and **51**) afford powerful and highly selective tools for the synthesis of both α- and β-glycosylamines on a wide variety of carbohydrate scaffolds. This new approach is not only exceedingly mild, operationally simple, and tolerant of numerous functional and protecting groups, but also appears to be applicable for large-scale syntheses (reactions up to 5 mmol have been performed with no drop in efficiency) and late-stage operations relevant to the synthesis of complex aminoglycosides and/or N-linked glycopeptides.[30]

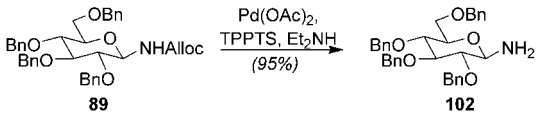
Hydroxysulfamidate synthesis using epoxyalcohols and the Burgess reagent: Having proven that 1,2-diol substrates could lead to sulfamidate products, we then wondered whether or not additional classes of molecules could be converted into similar materials. For example, would a hydroxylepoxide (**XIII**) derived from an allylic alcohol prove to be a willing participant in the pathway delineated in Scheme 7 leading to a hydroxysulfamidate product (**XV**)? As matters would transpire, the answer to that question was yes, though a great deal of reaction scouting was required before we identified conditions capable of reliably effecting that conversion.

Table 7 shows the final solution leading to five hydroxysulfamidate products: heating a hydroxyepoxide substrate with 1.3 equivalents of the Burgess reagent for 3 h in a 4:1 solvent mixture of THF/CH_2Cl_2, followed by column purification using the slightly basic material Florisil® instead of

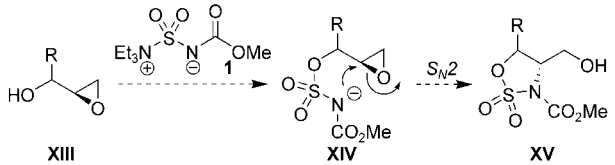
Table 6. Direct conversion of anomeric alcohols to β-glycosylamines.



Entry	Starting material	Product	Ratio β:α[a]	Yield [%]
1	 **85**	 **86**	>20:1	68
2	 **87**	 **88**: R = CO_2Me **89**: R = Alloc	>20:1	73
3			>20:1	78
4	 **90**	 **91**	>20:1	72
5	 **92**	 **93**: R = CO_2Me **94**: R = Alloc	>20:1	76
6			>20:1	73
7	 **95**	 **96**: R = CO_2Me **97**: R = Alloc	8:1	72
8			10:1	81
9	 **98**	 **99**	3:1	70
10	 **100**	 **101**	5:1	71



89 **102**



XIII **XIV** **XV**

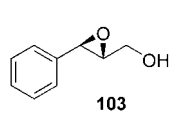
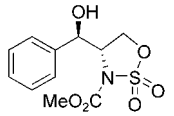
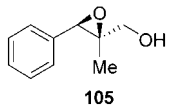
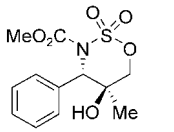
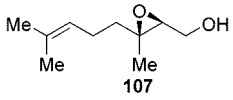
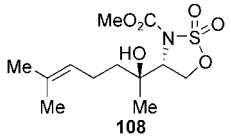
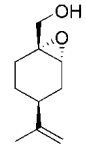
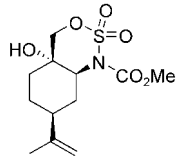
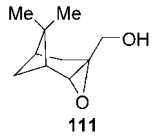
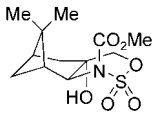
Scheme 7. Proposed conversion of epoxyalcohols into sulfamidates through the action of the Burgess reagent (**1**).

standard, acidic silica gel. Any deviation from this procedure led to a multiplicity of products.[31] We think it important to emphasize that, although we could reliably obtain the sulfamidate adducts shown in the yields indicated with this protocol, this particular reaction with the Burgess reagent is by far the most capricious of those that have been described to this point, and certainly the most experimentally challenging.[32]

Sulfamide synthesis using the Burgess reagent and 1,2-amino-alcohols: Within the realm of proven pharmacophores, the sulfamide functional group (thiadiazine-1,1-dioxide) stands out as one of the most important structural motifs found in high-affinity protein ligands and pharmaceutically useful agents. Indeed, a survey of the recent patent literature reveals several hundred proprietary documents illustrating that the incorporation of a sulfamide group within a suitable scaffold, often cyclic, leads to compounds with an impressive and diverse array of biological activities.[33] For instance, these agents have proven to be particularly effective as inhibitors of key enzymes, including HIV protease[34] and serine protease,[35] and have demonstrated utility as both agonists and antagonists of critical molecular receptors such as those used to regulate endogenous levels of seratonin[36] and histamine.[37] Beyond their evident significance in the treatment of disease, cyclic sulfamides have also been employed with considerable success as chiral ligands and auxiliaries,[38] and constitute an increasingly popular set of building blocks within the field of supramolecular chemistry.[39]

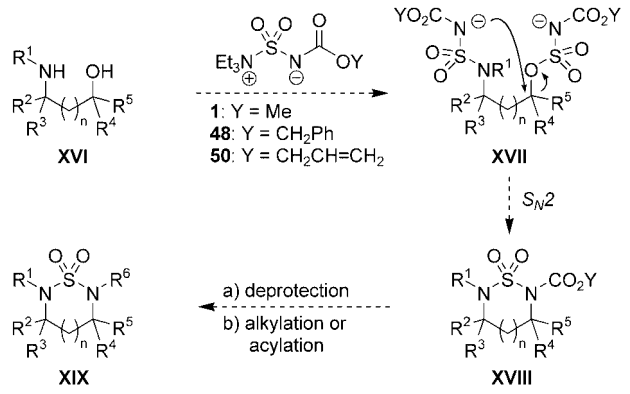
Despite the indisputable utility of these compounds, existing routes for their construction, particularly in a cyclic setting, are far from ideal. For example, typical procedures to fashion cyclosulfamides rely upon the reaction of a diamine with either SO_2Cl_2 or $H_2NSO_2NH_2$ at elevated temperatures,[40] conditions which often lead to a low yield of product due to the concomitant formation of polycondensation

Table 7. Synthesis of sulfamidates from epoxyalcohols.

Entry	Starting material	Product	Yield [%]
1	 **103**	 **104**	87
2	 **105**	 **106**	82
3	 **107**	 **108**	85
4	 **109**	 **110**	89
5	 **111**	 **112**	81

[a] All reactions were performed in THF/CH_2Cl_2 (4:1) at reflux with 1.3 equiv of **1**, followed by column chromatography using Florisil®.

side-products. Equally problematic is the scarcity of these starting materials in the repertoire of commercially available chemicals,[41] thereby resulting in only a limited collection of sulfamides. While these issues have led to the development of several alternative protocols for sulfamide synthesis,[42] these additional technologies have proven amenable only to specific substrate classes and have not yet alleviated the need for multistep protocols. Most significantly, none of these methods has enabled the efficient and selective synthesis of nonsymmetrical *N*,*N*′-disubstituted cyclosulfamides (see **XIX**, Scheme 8), perhaps the most versatile class of



Scheme 8. Proposed conversion of amino alcohols (**XVI**) to cyclic sulfamides (**XVIII**) using Burgess (**1**) and related reagents (**48** and **50**) and further elaboration leading to nonsymmetrically substituted, structurally diverse products (**XIX**).

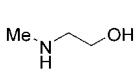
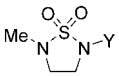
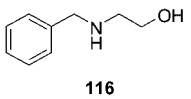
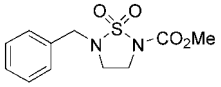
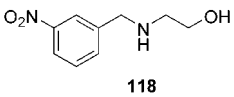
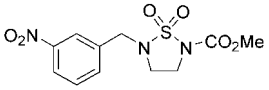
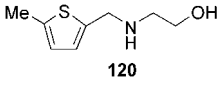
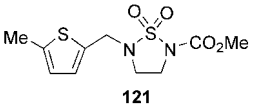
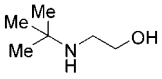
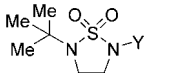
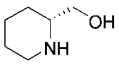
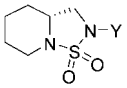
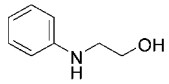
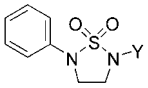
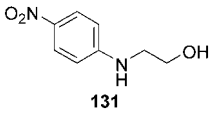
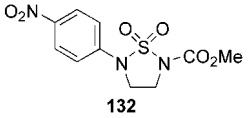
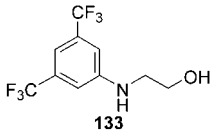
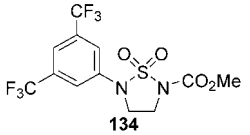
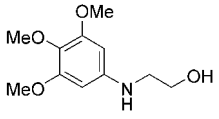
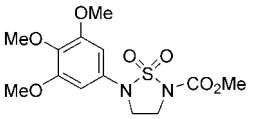
these compounds for generating pharmaceutically relevant molecular diversity.

Once again, we felt that the power of the Burgess reagent could be employed to solve these problems and smoothly deliver sulfamide products. As shown in Scheme 8, our expectation was that treatment of an aminoalcohol starting material (**XVI**, $R^1 = H$ or alkyl) with at least two equivalents of the Burgess reagent would lead to a monoprotected, nonsymmetrical, cyclic sulfamide (**XVIII**) in a single, stereocontrolled operation. Assuming that this reaction course could be successfully realized in preference to the typical rearrangement/dehydration pathways promoted by these reagents, subsequent deprotection of the carbamate in **XVIII**, followed by substitution with an appropriate electrophile, would then provide access to an assorted collection of sulfamides (**XIX**) with the potential to incorporate diversity at all possible sites.

To test this attractive hypothesis, we began our investigations of this new Burgess-mediated reaction by exploring a representative set of commercially available and easily synthesized secondary β-aminoalcohols. Most gratifyingly, exposure of all substrates listed in Table 8 to excess Burgess reagent (**1**) or its relatives (**48** and **50**) in refluxing THF for 8 h led to the formation of the desired cyclic sulfamide product in high yield, regardless of the nature of the group attached onto the amine. Of particular note, neither placing the amine in a hindered cyclic setting (entries 8 and 9) nor adding a bulky *tert*-butyl substituent (entries 6 and 7) retarded product formation. The latter of these substrates (**122**) is a particularly effective test for the power of this synthetic technology, as starting materials bearing this functionality have, in general, proven recalcitrant to sulfamide formation with other available methods.[36] Of equal importance, all aniline-derived systems (entries 12–14) proved readily amenable to the cyclization process regardless of the electron-withdrawing (entries 12 and 13) or donating (entry 14) properties of the appended aromatic ring, results indicative of the versatility of this intramolecular Burgess-mediated cyclization.[43]

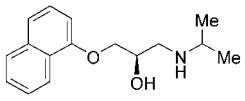
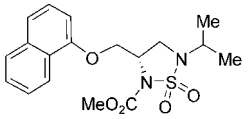
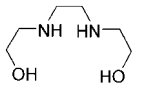
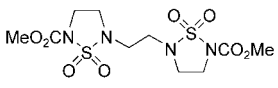
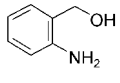
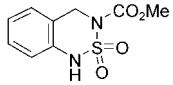
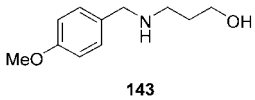
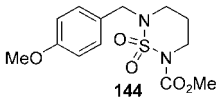
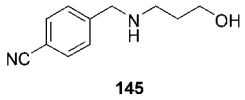
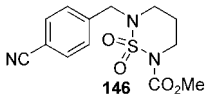
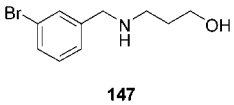
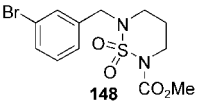
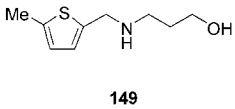
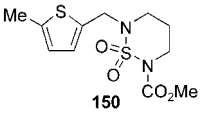
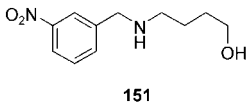
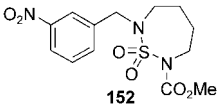
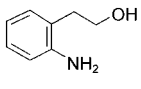
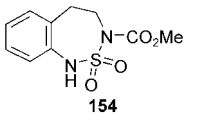
While certainly satisfied by these initial successes in which the two nitrogen atoms of the sulfamide product had been effectively differentiated, we next sought to more fully probe the limits of the Burgess-mediated sulfamide synthesis by exploring more challenging substrates. As shown in Table 9, employing a secondary alcohol (entry 1), even in a relatively hindered context, failed to engender any particular difficulties, although extension of the reaction time beyond the standard 8 h of heating was required to optimize yields. A double cyclization seeking to generate a bis-sulfamide (**140**, entry 2) was also smoothly effected, with reduced yield in this case solely due to difficulties encountered during isolation, because of this product's polar nature. Finally, following optimization of the reaction conditions, extension of the sulfamide cyclization to ring sizes beyond the five-membered ring products formed in the previous examples also proved attainable. Initial efforts focused on **141** (entry 3), wherein commencing the reaction at 0 °C and allowing it to warm to 25 °C overnight led to the desired product (**142**) in 45 % yield. All other conditions probed led to

Table 8. Synthesis of nonsymmetrical cyclic sulfamides from precursor aminoalcohols using Burgess-type reagents: initial explorations.

Entry	Starting material	Product	Yield [%]
1	 **113**	 **114**: Y = CO_2Me **115**: Y = Cbz	75
2			82
3	 **116**	 **117**	85
4	 **118**	 **119**	89
5	 **120**	 **121**	92
6	 **122**	 **123**: Y = CO_2Me **124**: Y = Alloc	81
7			75
8	 **125**	 **126**: Y = CO_2Me **127**: Y = Cbz	77
9			75
10	 **128**	 **129**: Y = CO_2Me **130**: Y = Alloc	92
11			82
12	 **131**	 **132**	75
13	 **133**	 **134**	82
14	 **135**	 **136**	69

[a] All reactions were performed in refluxing THF for 2 h.

Table 9. Synthesis of nonsymmetrical cyclic sulfamides from secondary aminoalcohols: advanced examples and exploration of ring size.

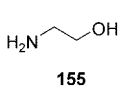
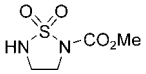
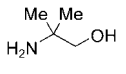
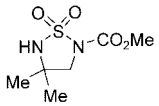
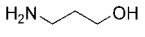
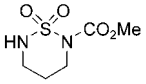
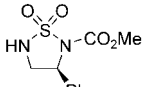
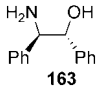
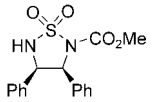
Entry	Starting material	Product	Yield [%]
1	 **137**	 **138**	89[a]
2	 **139**	 **140**	55[b]
3	 **141**	 **142**	45[c]
4	 **143**	 **144**	93[d]
5	 **145**	 **146**	87[d]
6	 **147**	 **148**	83[d]
7	 **149**	 **150**	89[d]
8	 **151**	 **152**	81[d]
9	 **153**	 **154**	90[d]

[a] THF, Δ, 21 h; [b] THF, Δ, 8 h; [c] 0 °C, 1 h, then 25 °C, 5 h; [d] THF, Δ, 2 h.

significant amounts of a major rearrangement side-product in which the alcohol had been converted to a urea derivative[8] (see Scheme 1c) instead of serving as a leaving group for the desired cyclization. Fortunately, when non-benzylic (i.e., less activated) alcohols were employed instead (entries 4–9), the propensity for this side-reaction was completely suppressed, leading to a series of six- and seven-membered ring analogues in excellent yield under standard reaction conditions (THF, reflux, 2 h). The smooth generation of compound **154** among these is of particular significance, because this bicyclic product is analogous to the benzodiazepine nucleus, a molecular scaffold that has been the subject of intensive biological investigations and the source of several clinically employed agents.[44]

Based on the successful formation of the latter sulfamide substrate in Table 9, we were hopeful that other primary aliphatic aminoalcohol substrates would perform in this Burgess-based protocol with equal proficiency as both sides of the resultant sulfamide product could then be substituted in turn, leading to greater structural diversity. Unfortunately, all three substrates examined within this class (entries 1–3, Table 10) gave rather disappointing yields of sulfamide products, leading in each case to the formation of side-products resulting from undesired rearrangements. In retrospect, the poor performance of these substrates in an intramolecular cyclization relative to their secondary amine counterparts is not so surprising, as in the absence of an additional alkyl or aryl substituent the nitrogen atom is far less nucleophilic, thereby leading to prolonged reaction times and greater op-

Table 10. Synthesis of nonsymmetrical cyclic sulfamides from primary aminoalcohols.

Entry	Starting material	Product	Yield [%]
1	 **155**	 **156**	62[a]
2	 **157**	 **158**	39[a]
3	 **159**	 **160**	42[a]
4	 **161**	 **162**	90[b]
5	 **163**	 **164**	76[b]

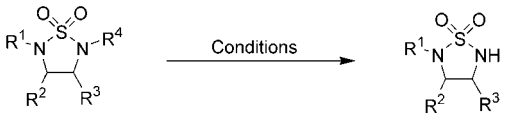
[a] THF, Δ, 8 h; [b] THF, 0 °C, 1 h, then 25 °C, 5 h.

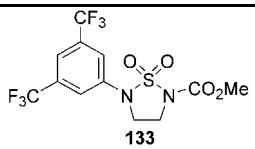
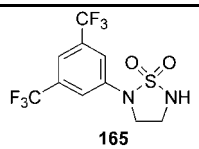
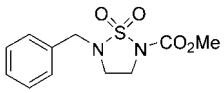
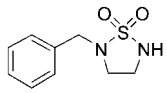
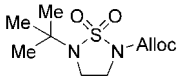
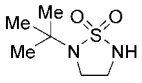
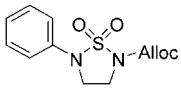
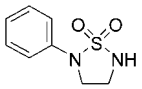
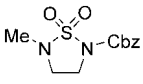
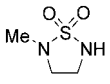
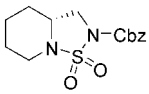
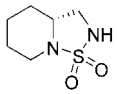
portunities for material to travel down alternative pathways. The modest yields observed in these examples, however, do not really reflect a limitation in strategy, as the successful debenzylation of **117** (entry 3, Table 8) through hydrogenation in the presence of Pearlman's catalyst [$Pd(OH)_2$/C] provided a route to the same product (**159**, entry 1, Table 10) in quantitative yield, thus alleviating the need to start with ethanolamine (**155**). As such, this approach provides a tactic to sequentially substitute both sides of any cyclic sulfamide product, if so desired. Finally, in contrast to the results in the rest of Table 10, when primary aliphatic amines were utilized in conjunction with a secondary benzylic alcohol (entries 4 and 5), product yields were excellent when the reaction was performed at low temperature. While these results were unanticipated based on the preceding discussion, they suggest that the activated nature of the leaving group (i.e., benzylic) is responsible for this altered, but useful, reactivity. The smooth formation of the last of these products (**164**) is especially interesting, for it is a desymmetrized, *meso*-sulfamide that could, in principle, be employed as a chiral ligand for applications in asymmetric synthesis.

With this collection of cyclic sulfamides in hand, we then verified that the subsequent removal of the carbamate group can be easily achieved (see Table 11) with conventional procedures and can be readily followed by substitution of appropriate electrophiles (see, for example, the conversion of **166** into **171**).[45] As such, the general and efficient synthesis of compounds represented by structure **XIX** (Scheme 8) has been realized.

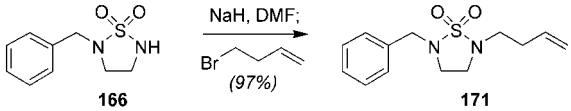
Finally, beyond the synthesis of cyclic sulfamides, we have also verified that the Burgess reagent (**1**) can smoothly effect the generation of nonsymmetrical, linear sulfamides from all classes of amines in excellent yield (Table 12).

Table 11. Deprotection of carbamate protecting groups from selected sulfamides.



Entry	Starting material	Product	Yield [%]
1	 **133**	 **165**	99[a]
2	 **117**	 **166**	99[a]
3	 **124**	 **167**	82[b]
4	 **130**	 **168**	98[b]
5	 **115**	 **169**	84[c]
6	 **127**	 **170**	87[c]

[a] NaOH, MeOH/H_2O (1:1), 25 °C, 2 h; [b] cat. $Pd(PPh_3)_4$, dimethyl malonate, THF, 25 °C, 3 h; [c] 10% Pd/C, H_2, EtOH/EtOAc (4:1), 25 °C, 2 h.



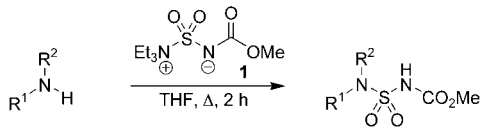
166 **171**

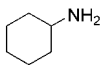
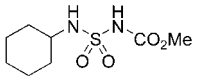
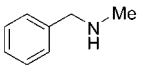
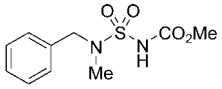
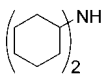
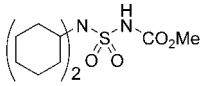
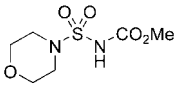
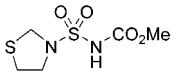
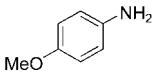
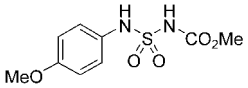
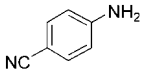
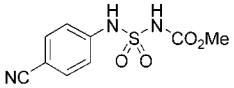
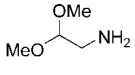
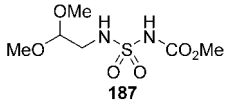
While this same conversion is more typically achieved by adding the amine to an appropriate chlorosulfonylisocyanate,[37,46] the present conditions provide a mild alternative, avoiding the direct use of these rather toxic and corrosive agents which often contain traces of HCl, making them incompatible with acid-sensitive functionality (such as that carried by amine **186**, entry 8).[47]

Conclusion

As these investigations have revealed, the Burgess reagent (**1**) and its relatives (**48**–**51**) are notably effective at accomplishing a number of non-dehydrative synthetic tasks when applied to appropriate substrates, such as the formation of sulfamidates from 1,2-diols or epoxyalcohols, α- and β-glycosylamines from carbohydrates, and cyclic sulfamides from 1,2-aminoalcohols. In each case, the synthetic approach is a marked improvement over those currently in the literature and should extend the potential of these synthons as tools

Table 12. Synthesis of linear sulfamides from primary and secondary amines.



Entry	Starting material	Product	Yield [%]
1	 **172**	 **173**	83
2	 **174**	 **175**	91
3	 **176**	 **177**	82
4	 **178**	 **179**	87
5	 **180**	 **181**	73
6	 **182**	 **183**	97
7	 **184**	 **185**	66
8	 **186**	 **187**	98[a]

[a] THF, −10→25 °C, 24 h.

for chemical biology, ligands for asymmetric synthesis, or starting materials for a variety of other applications. On a more global level, these discoveries validate the power of natural product total synthesis in leading to new chemistry, as we would not have been inspired to pursue these reactions in the absence of our attempts to use the Burgess reagent as part of our campaign to synthesize diazonamide A.[7]

Experimental Section

General procedures: All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, diethyl ether (Et_2O), and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker DRX-600, DRX-500, AMX-500 or AMX-400 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintuplet, sext = sextet, sep = septet, br = broad, app = apparent, AB = AB quartet. IR spectra were recorded on a Perkin–Elmer 1600 series FT-IR spectrometer. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on an API 100 Perkin–Elmer SCIEX single quadrupole mass spectrometer at 4000 V emitter voltage. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer using MALDI (matrix-assisted laser-desorption ionization).

General procedure for diol synthesis: The appropriate styrene (2.0 mmol, 1.0 equiv) was dissolved in acetone/H_2O (19:1, 20 mL) and OsO_4 (0.641 mL, 2.5 wt % in *t*BuOH, 0.05 mmol, 0.025 equiv) and quinuclidine (0.010 g, catalytic) were added sequentially at 25 °C. The resultant mixture was then stirred for 12 h at 25 °C. Upon completion, the reaction contents were quenched by the addition of saturated aqueous Na_2SO_3 (5 mL). After the resultant slurry had been stirred for an additional 30 minutes at 25 °C, the reaction mixture was poured into water (25 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were then washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow-brown residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

Data for 7: $R_f = 0.29$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3359, 1616, 1515, 1459, 1247, 1182, 1081, 1026, 893, 818, 548 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35$ (d, $J = 8.8$ Hz, 2H), 6.96 (d, $J =$ 8.5 Hz, 2H), 4.83 (dd, $J = 8.1$, 3.3 Hz, 1H), 3.88 (s, 3H), 3.78 (dd, $J = 11.4$, 3.3 Hz, 1H), 3.71 (dd, $J = 11.0$, 8.1 Hz, 1H), 2.61 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.3$, 132.6, 127.3, 113.9, 74.3, 68.0, 55.3; MS (ESI) calcd for $C_9H_{12}O_3Cl^-$ $[M+Cl^-]$ 203; found: 203.

Data for 9: $R_f = 0.11$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3447, 1739, 1636, 1508, 1373, 1236, 1202, 1081, 1019, 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.33$ (d, $J = 8.2$ Hz, 2H), 7.04 (d, $J = 8.2$ Hz, 2H), 4.71 (dd, $J = 7.6$, 2.6 Hz, 1H), 3.66 (d, $J = 11.2$ Hz, 1H), 3.56 (dd, $J = 10.8$, 8.2 Hz, 1H), 3.37 (s, 2H), 2.29 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 169.8$, 150.0, 138.2, 127.2, 121.5, 74.0, 67.8, 21.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{12}O_4Na^+$ $[M+Na]^+$: 219.0628; found: 219.0623.

Data for 11: $R_f = 0.60$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3418, 2961, 1636, 1467, 1360, 1247, 1194, 1085, 1027, 873, 713 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.39$ (s, 1H), 7.22 (s, 2H), 4.83 (dd, $J =$ 8.1, 3.7 Hz, 1H), 3.78 (dd, $J = 11.4$, 3.7 Hz, 1H), 3.72 (dd, $J = 11.4$, 8.5 Hz, 1H), 2.00 (brs, 2H), 1.34 ppm (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 151.1, 140.0, 122.2, 120.2, 75.4, 68.2, 34.9, 31.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{16}H_{26}O_2Na^+$ $[M+Na]^+$: 273.1825; found: 273.1831.

Data for 13: $R_f = 0.31$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3448, 1636, 1512, 1225, 1080, 656 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.34 (dd, $J = 8.1$, 5.5 Hz, 2H), 7.06 (t, $J = 8.4$ Hz, 2H), 4.82 (brs, 1H), 3.76 (brs, 1H), 3.64 (brs, 1H), 2.31 ppm (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.4$ (d, $J = 977$ Hz), 136.2, 127.7 (d, $J = 30.6$ Hz), 115.4 (d, $J = 83.9$ Hz), 74.0, 68.0 ppm; MS (GC/MS) calcd for $C_8H_9FO_2^+$ $[M]^+$: 156; found: 156.

Data for 15: $R_f = 0.35$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3448, 1636, 1490, 1454, 1194, 1071, 1025, 890, 760, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35$–7.28 (m, 5H), 4.79 (dd, $J = 8.5$, 3.3 Hz, 1H), 3.72 (dd, $J = 11.4$, 3.3 Hz, 1H), 3.63 (dd, $J = 11.7$, 8.4 Hz, 1H), 3.28 ppm (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 140.4$, 128.5, 127.9, 126.0, 74.7, 68.0 ppm; HRMS (MALDI-FTMS) calcd for $C_8H_{10}O_2Na^+$ $[M+Na]^+$: 161.0573; found: 161.0575.

Data for 17: $R_f = 0.23$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3391, 1620, 1323, 1174, 1117, 1059, 887, 830, 601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.63$ (d, $J = 8.2$ Hz, 2H), 7.50 (d, $J = 7.9$ Hz, 2H), 4.90 (dd, $J = 8.2$, 3.2 Hz, 1H), 3.81 (dd, $J = 11.4$, 3.5 Hz, 1H), 3.65 (dd, $J =$ 11.4, 8.2 Hz, 1H), 2.11 ppm (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 126.3, 125.5, 125.4, 74.0, 67.9 ppm; MS (GC/MS) calcd for $C_9H_9F_3O_2^+$ $[M]^+$: 206; found: 206.

Data for 19: $R_f = 0.14$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3391, 2932, 1528, 1352, 1195, 1072, 809, 736, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.28$ (s, 1H), 8.16 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.72 (d, $J = 7.9$ Hz, 1H), 7.55 (t, $J = 7.9$ Hz, 1H), 4.96 (dd, $J = 8.0$, 3.2 Hz, 1H), 3.86 (dd, $J = 11.2$, 3.2 Hz, 1H), 3.67 (dd, $J = 11.4$, 8.2 Hz, 1H), 2.40 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.7$, 132.2, 129.5, 122.9, 121.1, 73.5, 67.7 ppm; MS (GC/MS) calcd for $C_7H_6NO_3^+$ $[M-CH_2OH]^+$: 152; found: 152.

Data for 27: $R_f = 0.38$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3448, 1636, 1455, 1318, 1075, 594 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.39–7.36 (m, 4H), 7.30 (m, 1H), 4.69 (d, $J = 4.4$ Hz, 1H), 4.03 (dq, $J =$ 6.6, 4.4 Hz, 1H), 2.08 (br s, 2H), 1.10 ppm (d, $J = 6.3$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 140.3$, 128.4, 127.8, 126.6, 77.5, 71.3, 17.3 ppm; MS (GC/MS) calcd for $C_9H_{12}O_2^+$ $[M]^+$: 152; found: 152.

Data for 29: $R_f = 0.29$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3418, 1636, 1491, 1461, 1243, 1075, 1025, 756 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.37$ (d, $J = 7.4$ Hz, 1H), 7.26 (t, $J = 7.7$ Hz, 1H), 6.96 (t, $J =$ 7.4 Hz, 1H), 6.86 (d, $J = 7.9$ Hz, 1H), 5.05 (dd, $J = 7.9$, 3.1 Hz, 1H), 3.83 (s, 1H), 3.79 (m, 1H), 3.66 ppm (dd, $J = 11.0$, 8.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 156.4$, 128.8, 128.3, 127.2, 120.8, 110.3, 71.1, 66.5, 55.2 ppm; HRMS (MALDI-FTMS) calcd for $C_9H_{12}O_3Na^+$ $[M+Na]^+$: 191.0679; found: 191.0678.

Data for 31: $R_f = 0.28$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3444, 2953, 1636, 1440, 1081, 598 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 6.83 (s, 2H), 5.26 (dd, $J = 9.7$, 2.6 Hz, 1H), 3.97 (t, $J = 11.2$ Hz, 1H), 3.59 (d, $J = 9.1$ Hz, 1H), 2.52 (br s, 2H), 2.41 (s, 6H), 2.25 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.2$, 136.6, 132.4, 130.1, 72.6, 64.6, 20.8, 20.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{16}O_2Na^+$ $[M+Na]^+$: 203.1042; found: 203.1040.

Data for 33: $R_f = 0.29$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3190, 2931, 1089, 1049, 903, 863, 823, 742 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.85$ (m, 4H), 7.49 (m, 3H), 5.02 (dd, $J = 7.9$, 3.5 Hz, 1H), 3.87 (dd, $J = 11.4$, 3.5 Hz, 1H), 3.77 ppm (dd, $J = 11.3$, 8.3 Hz, 1H); ^{13}C NMR (125 MHz, 310 K, $CDCl_3$): $\delta = 138.0$, 133.3, 133.2, 128.4, 128.0, 127.7, 126.3, 126.1, 125.1, 124.0, 74.8, 68.0 ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{12}O_2Na^+$ $[M+Na]^+$: 211.0729; found: 211.0727.

Data for 35: $R_f = 0.46$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3441, 2953, 1735, 1632, 1453, 1370, 1254, 1119, 1046, 977, 906, 710 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.39$–7.32 (m, 5H), 4.83 (s, 1H), 3.83 (s, 3H), 1.17 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 176.3$, 138.6, 128.3, 128.1, 127.8, 78.0, 77.4, 53.1, 22.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{14}O_4Na^+$ $[M+Na]^+$: 233.0784; found: 233.0782.

Data for 37: $R_f = 0.22$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3420, 2981, 1736, 1639, 1443, 1381, 1277, 1215, 1163, 1095, 982, 756 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 3.94$ (s, 1H), 3.76 (s, 3H), 3.33 (br s, 2H), 1.24 (s, 3H), 1.16 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 173.4, 72.0, 52.3, 43.1, 25.6, 24.8 ppm; HRMS (MALDI-FTMS) calcd for $C_6H_{12}O_4Na^+$ $[M+Na]^+$: 171.0628; found: 171.0626.

Data for 39: $R_f = 0.18$ (silica gel, EtOAc/hexanes, 2:1); IR (film): $\nu_{max} =$ 3389, 2931, 2859, 1643, 1528, 1460, 1346, 1127, 1063 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.68$ (br m, 2H), 3.44 (br t, $J = 10.3$ Hz, 1H), 2.67 (s, 2H), 1.43–1.33 (br m, 6H), 0.91 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 72.3$, 66.7, 32.8, 27.7, 22.7, 14.0 ppm; MS (GC/MS) calcd for $C_5H_{11}O^+$ $[M-CH_2OH]^+$: 87; found: 87.

Data for 41: $R_f = 0.24$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 3440, 2949, 1643, 1138, 1071, 1027, 658 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 1:1 mixture of anomers): $\delta = 5.50$ (d, $J = 4.8$ Hz, 1H), 4.95 (d, $J = 5.5$ Hz, 1H), 4.92 (s, 1H), 4.78 (dd, $J = 5.9$, 4.4 Hz, 1H), 3.95–3.87 (m, 3H), 3.67 (br s, 1H), 3.52–3.44 (m, 2H), 3.42–3.35 (m, 2H), 2.02 (m, 1H), 1.82 (m, 1H), 1.57 (m, 2H), 1.56 (m, 2H), 1.43 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 1:1 mixture of anomers): $\delta = 98.5$, 93.4, 70.2, 67.7, 65.1, 61.8, 29.3, 27.3, 24.1, 22.2 ppm; MS (GC/MS) calcd for $C_5H_{10}O_3^+$ $[M]^+$: 118; found: 118.

General procedure for the synthesis of CO_2Me-protected sulfamidates: The diol (0.5 mmol, 1.0 equiv) was dissolved in anhydrous THF (5 mL) and methoxycarbonylsulfamoyl-triethylammonium hydroxide (**1**, 0.293 g, 1.25 mmol, 2.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 2 h. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were then washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity. Note: although analysis by thin-layer chromatography (TLC) indicated reaction completion after a few minutes, some non-cyclized material (**II**, Scheme 2) remained at the baseline, and heating for additional time was required to effect complete conversion to product. The use of a preheated oil bath also ensured high yield, as the reaction proceeded slowly at ambient temperature and appeared to have other reaction pathways apart from the desired formation of **III**.

Data for 6: $R_f = 0.12$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2948, 1747, 1555, 1439, 1369, 1322, 1188, 1089, 898, 845, 822, 752, 607, 554 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.51$ (d, $J = 8.1$ Hz, 1H), 7.45 (s, 1H), 7.41 (d, $J = 7.7$ Hz, 1H), 7.32 (s, 1H), 7.16 (t, $J = 7.7$ Hz, 1H), 5.47 (s, 2H), 5.34 (s, 1H), 3.93 (br s, 3H), 3.31 (s, 3H), 1.91 (s, 3H), 1.46 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 163.4$, 150.4, 137.7, 131.1, 127.3, 126.2, 124.4, 114.1, 110.2, 104.1, 89.5, 78.2, 64.2, 56.5, 55.2, 51.3, 27.1, 24.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{19}H_{21}BrN_3O_7S^+$ $[M+H]^+$: 514.0278; found: 514.0280.

Data for 8: $R_f = 0.62$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2961, 1746, 1612, 1516, 1441, 1380, 1321, 1252, 1189, 1031, 921, 822 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.44$ (d, $J = 8.8$ Hz, 2H), 7.01 (d, $J =$ 6.6 Hz, 2H), 5.38 (dd, $J = 6.3$, 3.7 Hz, 1H), 4.98 (dd, $J = 9.2$, 6.6 Hz, 1H), 4.54 (dd, $J = 9.6$, 4.1 Hz, 1H), 3.91 (s, 3H), 3.89 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 160.3$, 150.1, 128.3, 127.8, 114.6, 72.4, 60.7, 55.3, 54.6 ppm; HRMS (MALDI-FTMS) for $C_{11}H_{13}NO_6SNa^+$ $[M+Na]^+$: calcd 310.0356; found: 310.0364.

Data for 10: $R_f = 0.30$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2949, 1742, 1634, 1373, 1320, 1192 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.46 (d, $J = 6.6$ Hz, 2H), 7.16 (d, $J = 7.2$ Hz, 2H), 5.36 (dd, $J = 6.6$, 3.3 Hz, 1H), 4.94 (dd, $J = 9.2$, 6.6 Hz, 1H), 4.49 (dd, $J = 9.5$, 3.7 Hz, 1H), 3.87 (s, 3H), 2.32 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 169.3$, 151.3, 143.1, 134.0, 127.6, 122.6, 72.2, 60.5, 54.8, 21.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{13}NO_7SNa^+$ $[M+Na]^+$: 388.0305; found: 338.0304.

Data for 12: $R_f = 0.79$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2950, 1750, 1636, 1441, 1383, 1320, 1191, 947, 821 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.45$ (s, 1H), 7.26 (s, 2H), 5.35 (dd, $J = 6.6$, 3.3 Hz, 1H), 4.94 (dd, $J = 9.2$, 6.3 Hz, 1H), 4.50 (dd, $J = 9.2$, 3.3 Hz, 1H), 3.87 (s, 3H), 1.33 ppm (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 151.9$, 150.2, 135.7, 123.4, 120.3, 72.7, 61.6, 54.6, 35.0, 31.4 ppm; MS (ESI) calcd for $C_{18}H_{28}NO_5S^+$ $[M+H]^+$: 370; found: 370.

Data for 14: $R_f = 0.56$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2953, 1750, 1654, 1608, 1512, 1442, 1381, 1321, 1231, 1190, 922, 815 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.43$ (dd, $J = 8.5$, 4.8 Hz, 2H), 7.12 (t, $J = 8.8$ Hz, 2H), 5.35 (dd, $J = 6.6$, 3.7 Hz, 1H), 4.94 (dd, $J = 9.2$, 6.6 Hz, 1H), 4.46 (dd, $J = 9.5$, 3.3 Hz, 1H), 3.86 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.1$, 162.1, 150.0, 128.2 (d, $J = 30.6$ Hz), 116.3 (d, $J = 87.8$ Hz), 72.2, 60.4, 54.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{10}FNO_5SNa^+$ $[M+Na]^+$: 298.0156; found: 298.0153.

Data for 16: $R_f = 0.56$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2955, 1744, 1654, 1636, 1442, 1380, 1321, 1191 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.44$–7.40 (m, 5H), 5.36 (dd, $J = 6.6$, 3.5 Hz, 1H), 4.95 (dd, $J = 9.2$, 6.6 Hz, 1H), 4.49 (dd, $J = 9.7$, 4.0 Hz, 1H), 3.86 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 150.1$, 136.4, 129.3, 129.2, 126.2, 72.3, 61.0, 54.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{11}NO_5SNa^+$ $[M+Na]^+$: 280.0250; found: 250.0253.

Data for 18: $R_f = 0.66$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2924, 1747, 1622, 1443, 1384, 1324, 1193, 1117, 1069, 1017, 1002, 923, 822, 771, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.78$ (d, $J = 8.1$ Hz, 2H), 7.65 (d, $J = 8.1$ Hz, 2H), 5.49 (dd, $J = 6.3$, 3.3 Hz, 1H), 5.06 (dd, $J = 9.6$, 6.6 Hz, 1H), 4.54 (dd, $J = 9.5$, 3.3 Hz, 1H), 3.96 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 150.0$, 140.4, 126.8, 126.5, 126.4, 71.9, 60.5,

55.0 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{10}F_3NO_5SNa^+$ $[M+Na]^+$: 348.0124; found: 348.0121.

Data for 20: $R_f = 0.36$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2994, 1732, 1643, 1538, 1324, 1192 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 8.36 (d, $J = 8.1$ Hz, 1H), 8.28 (d, $J = 7.4$ Hz, 1H), 7.87 (t, $J = 7.7$ Hz, 1H), 7.67 (t, $J = 7.7$ Hz, 1H), 5.48 (dd, $J = 6.6$, 2.9 Hz, 1H), 5.02 (dd, $J = 9.2$, 6.6 Hz, 1H), 4.48 (dd, $J = 9.3$, 6.3 Hz, 1H), 3.91 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 150.1, 132.2, 132.0, 130.7, 125.3, 124.4, 121.7, 78.4, 60.2, 55.0 ppm; MS (ESI) calcd for $C_{10}H_{10}N_2O_7SNa^+$ $[M+Na]^+$: 325; found: 325.

Data for 28: $R_f = 0.60$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2977, 1747, 1439, 1375, 1311, 1188, 1136, 1037, 964, 914, 870, 830, 755, 700, 611, 551 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.43$–7.39 (m, 5H), 4.93 (d, $J = 7.4$ Hz, 1H), 4.77 (quin, $J = 6.1$ Hz, 1H), 3.80 (s, 3H), 1.61 ppm (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 150.3, 135.5, 129.6, 126.8, 82.6, 68.4, 54.6, 17.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{13}NO_5SNa^+$ $[M+Na]^+$: 294.0407; found: 294.0402.

Data for 30: $R_f = 0.58$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2961, 1747, 1603, 1493, 1441, 1381, 1323, 1249, 1194, 1085, 1025, 1002, 921, 827, 777, 663 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.38$–7.34 (m, 2H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 7.9$ Hz, 1H), 5.74 (d, $J = 5.7$ Hz, 1H), 4.93 (dd, $J = 9.2$, 6.6 Hz, 1H), 4.44 (dd, $J = 9.2$, 2.2 Hz, 1H), 3.89 (s, 3H), 3.87 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 155.9, 150.3, 130.1, 125.9, 124.2, 121.1, 110.6, 72.5, 56.7, 55.5, 54.8 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{30}NO_6Na^+$ $[M+Na]^+$: 310.0356; found: 310.0369.

Data for 32: $R_f = 0.63$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2954, 1747, 1612, 1442, 1378, 1312, 1190, 1047, 962, 931, 819, 776, 734, 632 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 6.89$ (s, 2H), 5.87 (t, $J =$ 8.8 Hz, 1H), 4.74 (dd, $J = 9.6$, 8.1 Hz, 1H), 4.59 (t, $J = 7.5$ Hz, 1H), 3.84 (s, 3H), 2.45 (s, 6H), 2.27 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 150.6, 138.9, 136.8, 136.6, 126.3, 68.4, 57.3, 54.6, 20.8, 20.2 ppm; MS (ESI) calcd for $C_{14}H_{17}NO_5S^+$ $[M+H]^+$: 300; found: 300.

Data for 34: $R_f = 0.59$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2961, 1740, 1435, 1376, 1317, 1188, 1000, 923, 812, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.94$–7.85 (m, 4H), 7.56–7.52 (m, 3H), 5.53 (dd, $J = 6.6$, 3.7 Hz, 1H), 5.00 (dd, $J = 9.6$, 7.0 Hz, 1H), 4.56 (dd, $J = 9.6$, 4.0 Hz, 1H), 3.85 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 150.2, 133.6, 133.5, 133.1, 129.6, 128.2, 127.8, 126.9, 126.8, 126.1, 123.0, 72.1, 61.2, 54.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{14}H_{13}NO_5SNa^+$ $[M+Na]^+$: 330.0407; found: 330.0409.

Data for 36: $R_f = 0.40$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2966, 1746, 1441, 1376, 1311, 1194, 1135, 1059, 959, 918, 841, 765, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.43$ (m, 2H), 7.36 (m, 3H), 5.23 (s, 1H), 3.86 (s, 3H), 3.31 (s, 3H), 2.11 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 163.3, 150.0, 134.3, 129.8, 128.9, 127.8, 88.7, 69.7, 55.1, 53.1, 23.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{13}H_{15}NO_7SNa^+$ $[M+Na]^+$: 352.0461; found: 352.0474.

Data for 38: $R_f = 0.65$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2955, 1749, 1588, 1443, 1378, 1321, 1227, 1177, 1115, 1049, 976, 837, 643 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 5.32$ (s, 1H), 3.93 (s, 3H), 3.85 (s, 3H), 1.58 (s, 3H), 1.56 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 164.9, 158.6, 83.4, 59.2, 53.5, 25.3, 19.3 ppm; MS (ESI) calcd for $C_8H_{13}NO_7SNa^+$ $[M+Na]^+$: 290; found: 290.

Data for 40: $R_f = 0.60$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2948, 1747, 1444, 1375, 1328, 1194, 985, 851, 764 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 4.86$ (m, 1H), 4.12 (dd, $J = 10.1$, 4.8 Hz, 1H), 3.91 (s, 3H), 3.73 (t, $J = 9.7$ Hz, 1H), 1.95 (m, 1H), 1.78 (m, 1H), 1.47 (m, 1H), 1.40 (m, 3H), 0.94 ppm (t, $J = 5.0$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 150.7, 80.5, 54.8, 51.0, 32.3, 26.8, 22.3, 13.9 ppm; HRMS (MALDI-FTMS) calcd for $C_8H_{15}NO_5SNa^+$ $[M+Na]^+$: 260.0563; found: 260.0556.

Data for 42: $R_f = 0.15$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2962, 1749, 1443, 1380, 1327, 1295, 1182, 1123, 1071, 965, 899, 877, 831, 603, 560 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.50$ (d, $J = 2.6$ Hz, 1H), 4.83 (q, $J = 3.0$ Hz, 1H), 4.02 (m, 1H), 3.91 (s, 3H), 3.58 (ddd, $J = 13.2$, 10.3, 3.3 Hz, 1H), 2.36 (dt, $J = 13.2$, 2.2 Hz, 1H), 2.01–1.85 (m, 2H), 1.60 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 149.5, 81.9, 76.6, 63.4, 54.6, 23.8, 17.6 ppm; HRMS (MALDI-FTMS) calcd for $C_7H_{11}NO_6SNa^+$ $[M+Na]^+$: 260.0199; found: 260.0200.

General procedure for the synthesis of alternative Burgess reagents 48–51: A solution of the appropriate alcohol (105 mmol, 1.05 equiv) in CH_2Cl_2 (25 mL) was added over the course of 30 minutes to a solution of chlorosulfonylisocyanate (8.71 mL, 100 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL) at 0 °C. Once the addition was complete, the reaction contents were concentrated directly to give the desired sulfamoyl chloride intermediate (**44–47**) as a white solid. Pressing forward without any additional purification steps, a solution of the newly formed sulfamoyl chloride (20.0 mmol, 1.0 equiv) in benzene (40 mL) was added dropwise to a solution of Et_3N (6.27 mL, 45 mmol, 2.25 equiv) in benzene (25 mL) at 25 °C. After the addition was complete (~1 hour), the triethylammonium hydrochloride precipitate was removed by filtration, and the filtrate was concentrated to give **48–51** as clear oils which solidified upon standing.

Cbz-protected Burgess-type reagent 48: $R_f = 0.03$ (silica gel, EtOAc); IR (film): $\nu_{max} =$ 2985, 1688, 1455, 1376, 1330, 1255, 1097, 853, 786, 740, 700, 598, 548 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.41$–7.28 (m, 5H), 5.13 (s, 2H), 3.44 (q, $J = 7.4$ Hz, 6H), 1.39 ppm (t, $J = 7.4$ Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 157.5, 136.3, 128.4, 128.2, 128.0, 67.9, 50.4, 9.4 ppm; MS (ESI) calcd for $C_{14}H_{22}N_2O_4SNa^+$ $[M+Na]^+$: 337; found: 337.

***o*-NO_2-Cbz-protected Burgess-type reagent 49**: $R_f = 0.03$ (silica gel, EtOAc); IR (film): $\nu_{max} =$ 3516, 1697, 1527, 1485, 1341, 1246, 1100, 1060, 856, 730, 600, 548 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.99$ (d, $J =$ 8.0 Hz, 1H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J =$ 7.6 Hz, 1H), 5.42 (s, 2H), 3.38 (q, $J = 7.0$ Hz, 6H), 1.32 ppm (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 157.0, 133.8, 132.9, 129.0, 128.5, 128.3, 124.8, 64.5, 50.6, 9.3 ppm; MS (ESI) calcd for $C_{14}H_{22}N_3O_6S^+$ $[M+H]^+$: 360; found: 360.

Alloc-protected Burgess-type reagent 50: $R_f = 0.03$ (silica gel, EtOAc); IR (film): $\nu_{max} =$ 2995, 2948, 1693, 1457, 1332, 1161, 1098, 970, 859, 788, 714, 597, 548 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.91$ (m, 1H), 5.30 (d, $J = 16.2$ Hz, 1H), 5.18 (d, $J = 10.3$ Hz, 1H), 4.54 (s, 2H), 3.45 (q, $J =$ 7.4 Hz, 6H), 1.39 ppm (t, $J = 7.0$ Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 157.2, 132.5, 117.9, 66.6, 50.5, 9.3 ppm; MS (ESI) calcd for $C_{10}H_{21}N_2O_4S^+$ $[M+H]^+$: 265; found: 265.

Troc-protected Burgess-type reagent 51: $R_f = 0.03$ (silica gel, EtOAc); IR (film): $\nu_{max} =$ 2950, 1702, 1457, 1368, 1339, 1254, 1111, 1059, 857, 816, 716, 605, 548 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.75$ (s, 2H), 3.48 (q, $J =$ 7.4 Hz, 6H), 1.43 ppm (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 156.0, 95.4, 75.3, 50.7, 9.3 ppm; MS (ESI) calcd for $C_9H_{18}Cl_3N_2O_4S^+$ $[M+H]^+$: 355; found: 355.

General procedure for synthesizing sulfamidates with alternate protection: The diol (0.5 mmol, 1.0 equiv) was dissolved in anhydrous THF (5 mL) and the appropriate Burgess-type reagent (**48–51**, 1.25 mmol, 2.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 2 h. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were then washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

Data for 52: $R_f = 0.49$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2998, 1740, 1612, 1516, 1381, 1306, 1252, 1192, 1030, 974, 808, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.33$–7.30 (m, 5H), 7.25 (m, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.28 (dd, $J = 6.6$, 4.4 Hz, 1H), 5.21 (AB, $J = 12.3$ Hz, $\nu_{ab} = 59.2$ Hz, 2H), 4.87 (dd, $J = 9.2$, 6.5 Hz, 1H), 4.44 (dd, $J = 9.2$, 4.4 Hz, 1H), 3.81 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 161.2, 150.4, 135.2, 129.4, 129.3, 129.2, 128.8, 128.7, 115.5, 73.1, 70.2, 61.6, 56.2 ppm; HRMS (MALDI-FTMS) calcd for $C_{17}H_{17}NO_6SNa^+$ $[M+Na]^+$: 386.0669; found: 386.0666.

Data for 53: $R_f = 0.51$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2974, 1746, 1637, 1457, 1377, 1306, 1195, 1136, 1065, 847, 764, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.41$–7.23 (m, 10H), 5.23 (AB, $J =$ 12.2 Hz, $\nu_{ab} = 65.8$ Hz, 2H), 5.21 (s, 1H), 3.29 (s, 3H), 2.08 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 167.0, 150.1, 134.9, 130.5, 129.6, 129.5, 128.6, 128.4, 89.2, 70.5, 70.3, 53.7, 24.6 ppm; HRMS (MALDI-FTMS) calcd for $C_{19}H_{19}NO_7SNa^+$: $[M+Na]^+$ 428.0774; found: 428.0780.

Data for 54: $R_f = 0.36$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2967, 1746, 1603, 1529, 1493, 1464, 1383, 1345, 1317, 1250, 1194, 1025,

921, 815, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.15$ (d, $J = 8.1$ Hz, 1H), 7.81–7.62 (br m, 2H), 7.51 (t, $J = 8.4$ Hz, 1H), 7.38 (d, $J = 7.0$ Hz, 1H), 7.36 (t, $J = 8.1$ Hz, 1H), 7.01 (t, $J = 7.7$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 5.82–5.79 (m, 2H), 5.69 (br m, 1H), 4.99 (dd, $J = 9.2$, 6.3 Hz, 1H), 4.50 (dd, $J = 9.2$, 2.6 Hz, 1H), 3.87 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 155.9$, 149.0, 146.6, 134.3, 131.3, 130.2, 128.8, 128.2, 125.8, 125.1, 123.8, 121.1, 110.7, 72.6, 66.0, 56.6, 55.5 ppm; HRMS (MALDI-FTMS) calcd for $C_{17}H_{12}N_2O_8SNa^+$ $[M+Na]^+$: 431.0520; found: 431.0530.

Data for 55: $R_f = 0.50$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2969, 1740, 1612, 1528, 1381, 1301, 1193, 962, 814, 730, 633 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 8.15$ (d, $J = 7.9$ Hz, 1H), 7.64–7.57 (m, 2H), 7.50 (t, $J = 7.9$ Hz, 1H), 6.87 (s, 2H), 5.92 (t, $J = 8.8$ Hz, 1H), 5.68 (AB, $J = 12.8$ Hz, $\nu_{ab} = 15.3$ Hz, 2H), 4.77 (t, $J = 8.3$ Hz, 1H), 4.64 (t, $J =$ 9.2 Hz, 1H), 2.43 (s, 6H), 2.26 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 163.1$, 149.4, 146.5, 139.1, 134.3, 131.1, 128.8, 128.3, 128.0, 126.0, 125.1, 68.6, 66.0, 57.4, 20.8, 20.3 ppm; MS (ESI) calcd for $C_{19}H_{20}N_2O_7SNa^+$ $[M+Na]^+$: 443; found: 443.

Data for 56: $R_f = 0.43$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2945, 1745, 1603, 1494, 1464, 1380, 1314, 1249, 1193, 1025, 925, 826, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.37$ (t, $J = 7.7$ Hz, 1H), 7.34 (d, $J = 7.7$ Hz, 1H), 7.02 (t, $J = 7.3$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.89 (m, 1H), 5.76 (dd, $J = 6.3$, 2.2 Hz, 1H), 5.37 (br m, 1H), 5.27 (d, $J =$ 10.3 Hz, 1H), 4.94 (dd, $J = 9.2$, 6.2 Hz, 1H), 4.75 (ddd, $J = 25.3$, 13.2, 5.1 Hz, 2H), 4.45 (dd, $J = 9.2$, 2.2 Hz, 1H), 3.87 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 155.9$, 149.4, 130.5, 130.0, 125.8, 124.1, 121.0, 119.1, 110.6, 72.4, 68.1, 56.5, 55.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{13}H_{15}NO_6SNa^+$ $[M+Na]^+$: 336.0512; found: 336.0515.

Data for 57: $R_f = 0.56$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2953, 1740, 1649, 1381, 1305, 1192, 964, 819, 767, 632 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 6.89$ (s, 2H), 5.87 (dd, $J = 8.8$, 8.1 Hz, 1H), 5.82 (m, 1H), 5.31 (d, $J = 16.9$ Hz, 1H), 5.24 (dd, $J = 10.6$, 1.1 Hz, 1H), 4.75–4.71 (m, 2H), 4.66 (m, 1H), 4.58 (t, $J = 9.2$ Hz, 1H), 2.44 (s, 6H), 2.27 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 158.1$, 149.9, 138.9, 136.8, 130.4, 126.3, 119.2, 68.3, 68.0, 57.3, 20.8, 20.3 ppm; MS (ESI) calcd for $C_{15}H_{19}NO_5SNa^+$ $[M+Na]^+$: 348; found: 348.

Data for 58: $R_f = 0.48$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2954, 1749, 1455, 1373, 1306, 1189, 1131, 1060, 931, 849, 760, 696, 549 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.45$ (m, 2H), 7.36 (m, 2H), 5.86 (m, 1H), 5.34 (d, $J = 17.1$ Hz, 1H), 5.25 (d, $J = 10.6$ Hz, 1H), 5.24 (s, 1H), 4.73 (ABX, $J = 13.6$, 5.7 Hz, $\nu_{ab} = 39.5$ Hz, 2H), 3.32 (s, 3H), 2.11 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 166.4$, 149.4, 134.6, 130.6, 129.8, 128.9, 127.9, 119.5, 88.6, 69.9, 68.7, 53.0, 24.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{15}H_{17}NO_7SNa^+$ $[M+Na]^+$: 378.0618; found: 378.0612.

Data for 59: $R_f = 0.47$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 2966, 1754, 1603, 1494, 1464, 1384, 1316, 1250, 1196, 1149, 1025, 924, 830, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$ (d, $J = 7.3$ Hz, 1H), 7.36 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.02 (t, $J = 7.3$ Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 1H), 5.84 (dd, $J = 6.3$, 2.6 Hz, 1H), 4.98 (dd, $J = 9.2$, 6.3 Hz, 1H), 4.86–4.78 (m, 2H), 4.48 (dd, $J = 9.2$, 2.6 Hz, 1H), 3.87 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.0$, 148.3, 130.2, 126.0, 123.6, 121.1, 110.6, 75.7, 72.4, 56.6, 55.5, 43.3 ppm; MS (ESI) calcd for $C_{12}H_{13}Cl_3NO_6S^+$ $[M+H]^+$: 404; found: 404.

Data for 60: $R_f = 0.30$ (silica gel, EtOAc/hexanes, 1:2); IR (film): $\nu_{max} =$ 2938, 1750, 1376, 1315, 1270, 1198, 1137, 1098, 902, 830, 752, 607 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.52$ (d, $J = 9.7$ Hz, 1H), 7.44 (s, 1H), 7.42 (d, $J = 8.8$ Hz, 1H), 7.35 (s, 1H), 7.17 (t, $J = 9.7$ Hz, 1H), 5.48 (s, 2H), 5.39 (s, 2H), 4.97 (d, $J = 14.1$ Hz, 1H), 4.78 (br s, 1H), 3.30 (s, 3H), 1.95 (s, 3H), 1.50 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.3$, 148.6, 147.1, 137.7, 131.1, 127.3, 126.3, 126.1, 124.4, 114.1, 110.2, 104.1, 93.8, 89.7, 78.2, 76.2, 64.3, 56.5, 27.2, 24.5; HRMS (MALDI-FTMS) calcd for $C_{20}H_{20}BrCl_3N_3O_7SNa^+$ $[M+Na]^+$: 629.9265; found: 629.9263.

General procedure for synthesizing 1,2-aminoalcohols from sulfamidates: The desired substrate (0.05 mmol, 1.0 equiv) was dissolved in 4 M aqueous HCl/1,4-dioxane (1:1, 1 mL), and the resultant solution was stirred at 25 °C until complete conversion was observed by TLC (~10–12 h). Once finished, the reaction mixture was poured into EtOAc (10 mL), washed with 5% aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated to give the desired 1,2-aminoalcohol in high purity.

Data for 61: $R_f = 0.53$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 3204, 1694, 1537, 1438, 1265, 1053, 833, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.87$–7.84 (m, 3H), 7.79 (br s, 1H), 7.50 (m, 2H), 7.42 (br d, $J = 8.3$ Hz, 1H), 5.47 (br s, 1H), 5.25 (br s, 1H), 3.72 (s, 3H), 2.16 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.3$, 136.0, 133.2, 133.0, 128.7, 128.0, 127.7, 126.5, 126.3, 125.6, 124.2, 55.7, 52.5, 47.9 ppm; MS (GC/MS) calcd for $C_{14}H_{13}NO_2^+$ $[M-H_2O]^+$: 227; found: 227.

Data for 62: $R_f = 0.59$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 3418, 2966, 1698, 1534, 1452, 1376, 1254, 1192, 1058, 852, 776, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 6.85$ (s, 2H), 5.42 (br s, 1H), 5.24 (br s, 2H), 3.89 (t, $J = 9.9$ Hz, 1H), 3.73 (dd, $J = 11.4$, 6.6 Hz, 1H), 3.68 (s, 3H), 2.42 (s, 6H), 2.25 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.5$, 137.6, 136.0, 131.7, 130.5, 52.4, 46.2, 44.8, 20.9, 20.7 ppm; MS (GC/MS) calcd for $C_{12}H_{16}NO_2^+$ $[M-OMe]^+$: 206; found: 206.

Data for 63: $R_f = 0.68$ (silica gel, EtOAc/hexanes, 1:2); IR (film): $\nu_{max} =$ 3431, 2987, 1697, 1642, 1535, 1453, 1252, 1091, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.37$–7.31 (m, 5H), 5.54 (br s, 1H) 4.93 (br s, 1H), 4.46 (br s, 1H), 3.68 (s, 3H), 1.38 ppm (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.1$, 137.0, 128.3, 128.1, 127.9, 60.8, 59.6, 52.4, 21.6 ppm; GC-MS (ESI) calcd for $C_9H_9NO_2^+$ $[M-CH_3CH_2OH]^+$: 164; found: 164.

Data for 64: $R_f = 0.72$ (silica gel, EtOAc/hexanes, 1:2); IR (film): $\nu_{max} =$ 3349, 2958, 1698, 1643, 1535, 1463, 1259, 614 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.13$ (br s, 1H), 3.99 (t, $J = 4.1$ Hz, 1H), 3.69 (s, 3H), 3.64 (ddd, $J = 14.7$, 7.3, 3.3 Hz, 1H), 3.24 (ddd, $J = 14.0$, 8.1, 5.5 Hz, 1H), 1.74 (m, 1H), 1.68 (m, 1H), 1.53 (m, 1H), 1.44–1.30 (m, 3H), 0.91 ppm (t, $J =$ 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 157.0$, 63.2, 52.3, 47.5, 35.2, 28.4, 22.1, 13.9 ppm; GC-MS (ESI) calcd for $C_3H_6NO_2^+$ $[M-CH_3CH_2CH_2CH_2CHOH]^+$: 88; found: 88.

Data for 65: $R_f = 0.56$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 3332, 2956, 1693, 1611, 1513, 1462, 1294, 1248, 1179, 1036, 831, 740, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$–7.29 (m, 5H), 7.24 (d, $J =$ 8.4 Hz, 2H), 6.90 (d, $J = 8.4$ Hz, 1H), 5.35 (br s, 1H), 5.12 (AB, $J =$ 12.1 Hz, $\nu_{ab} = 16.9$ Hz, 2H), 5.03 (br s, 1H), 3.85 (m, 2H), 3.81 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.4$, 155.6, 136.1, 130.6, 128.5, 128.2, 128.1 (2C), 127.7, 114.1, 114.0, 67.1, 55.3, 55.1, 47.9 ppm; MS (GC/MS) calcd for $C_{17}H_{17}NO_3^+$ $[M-H_2O]^+$: 283; found: 283.

Data for 66: $R_f = 0.48$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 3417, 3342, 2955, 1712, 1609, 1523, 1463, 1344, 1244, 1050, 756, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.10$ (d, $J = 8.1$ Hz, 1H), 7.63 (m, 2H), 7.47 (t, $J = 7.0$ Hz, 1H), 7.32 (t, $J = 7.0$ Hz, 1H), 7.26 (d, $J = 8.7$ Hz, 1H), 6.98 (t, $J = 7.7$ Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 1H), 5.94 (d, $J = 9.2$ Hz, 1H), 5.54 (AB, $J = 15.0$ Hz, $\nu_{ab} = 31.2$ Hz, 2H), 5.22 (dt, $J = 9.2$, 6.3 Hz, 1H), 3.89 (s, 3H), 3.85 ppm (d, $J = 5.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.7$, 155.2, 133.7, 133.1, 129.5, 129.1, 128.8, 128.5, 125.8, 124.9, 120.8, 110.9, 63.5, 55.4, 54.2, 46.5 ppm; MS (GC/MS) calcd for $C_{16}H_{15}N_2O_5^+$ $[M-OMe]^+$: 315; found: 315.

Data for 67: $R_f = 0.56$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 3318, 1682, 1643, 1539, 1484, 1235, 1049, 932, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.30$ (dt, $J = 8.1$, 1.5 Hz, 1H), 7.25 (d, $J = 7.3$ Hz, 1H), 6.97 (t, $J = 7.7$ Hz, 1H), 6.91 (d, $J = 8.1$ Hz, 1H), 5.92 (m, 1H), 5.80 (d, $J = 8.8$ Hz, 1H), 5.32 (d, $J = 16.5$ Hz, 1H), 5.22 (m, 2H), 4.59 (m, 2H), 3.88 (s, 3H), 3.84 ppm (d, $J = 5.9$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.7$, 132.7, 129.4, 129.2, 126.1, 120.8, 118.0, 110.8, 65.8, 55.3, 54.0, 46.6 ppm; MS (GC/MS) calcd for $C_{12}H_9NO_3^+$ $[M-OMe]^+$: 220; found: 220.

Data for 68: $R_f = 0.68$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} =$ 3435, 1716, 1636, 1497, 1244, 1033, 721 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.38$ (t, $J = 7.4$ Hz, 1H), 7.27 (m, 1H), 6.98 (t, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 8.3$ Hz, 1H), 6.93 (d, $J = 8.3$ Hz, 1H), 6.00 (d, $J = 8.8$ Hz, 1H), 5.23 (dd, $J = 15.3$, 6.1 Hz, 1H), 4.75 (AB, $J = 11.9$ Hz, $\nu_{ab} = 39.1$ Hz, 2H), 3.91 (s, 3H), 3.86 ppm (dd, $J = 6.6$, 2.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 156.7$, 154.0, 129.6, 129.0, 125.5, 120.9, 110.9, 74.6, 55.4, 54.3, 46.3 ppm; MS (GC/MS) calcd for $C_{11}H_{11}Cl_3NO_3^+$ $[M-OMe]^+$: 310; found: 310.

3,4,6-Tri-*O*-benzyl-D-glucosyldiol (69): 4-Methylmorpholine *N*-oxide (0.351 g, 3.0 mmol, 3.0 equiv) and OsO_4 (0.641 mL, 2.5 wt% in *t*BuOH, 0.05 mmol, 0.05 equiv) were added sequentially at 25 °C to a solution of 3,4,6-tri-*O*-benzyl-D-glucal (0.417 g, 1.0 mmol, 1.0 equiv) in THF/*t*BuOH/H_2O (7:3:1, 5 mL), and the resulting orange solution was stirred for 12 h

at 25 °C. Upon completion, the reaction contents were then diluted with water (10 mL), treated with Na_2SO_3 (0.630 g, 5.0 mmol, 5.0 equiv), and allowed to stir for an additional 2 h at 25 °C. Once this operation was complete, the reaction mixture was poured into water (10 mL) and extracted with EtOAc (3×25 mL). The combined organic layers were then washed with water (2×15 mL), dried ($MgSO_4$), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, EtOAc/hexanes, 1:1) to give diol **69** (0.414 g, 92 %) as an amorphous white solid. R_f = 0.13 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3410, 2938, 1452, 1390, 1190, 1080, 886, 590 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 7.38–7.10 (m, 30H), 5.18 (d, J = 4.8 Hz, 1H), 4.81 (s, 2H), 4.75 (d, J = 13.9 Hz, 2H), 4.54–4.49 (m, 3H), 4.47 (appt, J = 5.5 Hz, 3H), 4.43 (d, J = 3.3 Hz, 1H), 4.01 (t, J = 6.4 Hz, 1H), 3.98 (d, J = 6.2 Hz, 1H), 3.74 (appt, J = 11.4 Hz, 1H), 3.63–3.58 (m, 3H), 3.51–3.46 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 138.5, 138.4, 138.0, 137.8, 137.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 96.7, 92.3, 84.3, 82.5, 77.6, 77.5, 75.5, 75.3, 74.8, 73.4, 72.7, 70.4, 68.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{27}H_{30}O_6Na^+$ $[M+Na]^+$: 473.1934; found: 473.1925.

3,4,6-Tri-*O*-TBS-D-glucosyldiol (73): 3,4,6-Tri-*O*-TBS-β-D-glucal (0.416 g, 1.0 mmol, 1.0 equiv) was dihydroxylated in a manner similar to the preparation of **71** to give diol **73** (0.391 g, 87 % yield) as a white amorphous solid. **73**: R_f = 0.32 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3446, 2931, 2858, 1472, 1255, 1095, 837 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.96 (d, J = 12.1 Hz, 1H), 4.03 (m, 3H), 4.00 (d, J = 9.2 Hz, 1H), 3.93 (appt, J = 7.7 Hz, 1H), 3.83 (dd, J = 9.6, 6.3 Hz, 1H), 3.80 (m, 1H), 3.71 (d, J = 11.0 Hz, 1H), 3.40 (dd, J = 11.0, 3.7 Hz, 1H), 0.88 (s, 9H), 0.87 (s, 9H), 0.86 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (apps, 6H), 0.03 (s, 3H), 0.02 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 87.7, 80.9, 71.5, 70.9, 68.2, 61.3, 25.8, 25.6 (2C), 18.1, 17.8, 14.1, −4.8, −5.0, −5.1, −5.2, −5.4 ppm (2C); HRMS (MALDI-FTMS) calcd for $C_{24}H_{54}O_6Si_3Na^+$ $[M+Na]^+$: 545.3120; found: 545.3110.

3,4-Di-*O*-benzyl-L-rhamnosyldiol (75): 4-*O*-Benzyl-L-rhamnal (0.220 g, 1.0 mmol, 1.0 equiv) was dissolved in DMF (5 mL) and treated with NaH (0.400 g, 60 % dispersion in mineral oil, 2.0 mmol, 2.0 equiv) at 25 °C. After stirring the resultant solution for 5 minutes at 25 °C, the reaction contents were cooled to 0 °C and benzyl bromide (0.238 mL, 2.0 mmol, 2.0 equiv) was added dropwise over the course of 10 minutes. The reaction mixture was then warmed to 25 °C over the course of 30 minutes. Upon completion, the reaction mixture was poured into 1 N aqueous HCl (10 mL) and extracted with Et_2O (3×25 mL). The combined organic layers were then washed with water (2×15 mL), dried ($MgSO_4$), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, Et_2O) to give the desired di-*O*-benzylated-L-rhamnal intermediate (0.292 g, 94 %) as an amorphous white solid. This compound was then dihydroxylated in a manner similar to the preparation of **71** to give diol **75** (0.314 g, 91 % yield) as a white amorphous solid. R_f = 0.40 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3388, 2870, 1645, 1453, 1363, 1091, 994, 734, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 7.40–7.32 (m, 20H), 5.34 (d, J = 3.0 Hz, 1H), 4.98 (d, J = 2.6 Hz, 1H), 4.95 (d, J = 2.6 Hz, 1H), 4.77 (brd, J = 8.4 Hz, 1H), 4.71–4.62 (m, 5H), 4.04 (m, 2H), 3.64 (ddd, J = 13.1, 8.5, 4.8 Hz, 1H), 3.40 (dd, J = 9.6, 6.3 Hz, 1H), 3.21 (brs, 1H), 3.15 (dt, J = 8.7, 3.7 Hz, 1H), 2.60 (brs), 2.43 (ddd, J = 12.5, 5.2, 2.2 Hz, 1H), 2.32 (ddd, J = 13.2, 5.2, 1.5 Hz, 1H), 1.74 (m, 1H), 1.43 (m, 1H), 1.35 (d, J = 6.3 Hz, 3H), 1.28 ppm (d, J = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 138.6, 138.5, 138.3, 138.2, 128.4 (3C), 128.3, 128.0 (2C), 127.7 (2C), 127.6 (2C), 93.8, 92.0, 84.3, 83.4, 78.9, 76.8, 75.2 (2C), 71.8 (2C), 71.5, 71.4, 67.4, 38.3, 37.7, 18.2 ppm (2C); MS (ESI) calcd for $C_{20}H_{22}O_4^+$ $[M-H_2O]^+$: 327; found: 327.

3,4,6-Tri-*O*-benzyl-D-galactosyldiol (77): 3,4,6-Tri-*O*-benzyl-β-D-galactal (0.417 g, 1.0 mmol, 1.0 equiv) was dihydroxylated in a manner similar to the preparation of **71** to give diol **77** (0.379 g, 91 % yield) as a white amorphous solid. R_f = 0.13 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3401, 2919, 2861, 1455, 1361, 1085, 738, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 15H), 5.31 (d, J = 3.5 Hz, 1H), 4.87 (dd, J = 11.8, 3.5 Hz, 1H), 4.70 (m, 2H), 4.61–4.39 (m, 4H), 4.14 (dd, J = 10.0, 3.8 Hz, 1H), 3.88 (m, 1H), 3.73 (dd, J = 10.0, 2.6 Hz, 1H), 3.61–3.50 (m, 3H), 3.41 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 138.0, 137.6, 128.5, 128.4, 128.2, 128.0 (2C), 127.8, 127.7, 92.6, 79.0, 74.5, 73.8, 73.4, 72.3, 69.6, 69.2, 68.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{27}H_{30}O_6Na^+$ $[M+Na]^+$: 473.1934; found: 473.1921.

3,5-Di-*O*-TBS-D-ribosyldiol (81): The requisite D-ribose glycal intermediate was prepared from thymidine following the procedure of Larsen and co-workers.[48] The resultant product was then dihydroxylated in a manner similar to the preparation of **71** to give diol **81** (0.378 g, 88 % yield) as a white amorphous solid. R_f = 0.35 (silica gel, EtOAc/hexanes, 1:2); IR (film): ν_{max} = 3425, 2930, 2858, 1471, 1391, 1255, 1095, 937, 779 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 5.24 (d, J = 6.8 Hz, 1H), 5.13 (d, J = 10.6 Hz, 1H), 4.24 (brd, J = 8.5 Hz, 1H), 4.18 (appt, J = 2.6 Hz, 1H), 4.09–4.06 (m, 2H), 3.91 (brd, J = 11.1 Hz, 1H), 3.86–3.81 (m, 2H), 3.77 (dd, J = 8.6, 2.6 Hz, 1H), 3.71 (d, J = 1.8 Hz, 1H), 3.63 (dd, J = 10.8, 2.0 Hz, 1H), 0.89 (s, 9H), 0.87 (s, 9H), 0.84 (s, 9H), 0.82 (s, 9H), 0.10 (s, 6H), 0.07–0.04 ppm (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 104.1, 97.6, 87.1, 84.8, 78.8, 78.5, 77.3, 69.9, 65.7, 63.5, 63.1, 25.7, 25.5, 17.7, 15.1, −4.7, −5.0, −5.1, −5.6, −5.7, −5.8 ppm; HRMS (MALDI-FTMS) calcd for $C_{17}H_{38}O_5Si_2Na^+$ $[M+Na]^+$: 401.2150; found: 401.2147.

General procedure for the synthesis of sulfamidates on carbohydrates: The appropriate carbohydrate diol (0.5 mmol, 1.0 equiv) was dissolved in THF/CH_2Cl_2 (4:1, 5 mL) and the desired Burgess-type reagent (**1**, **50**, or **51**, 1.25 mmol, 2.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 6 h. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were then washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

Data for 70: R_f = 0.68 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3037, 2866, 1753, 1444, 1385, 1312, 1196, 1094, 842, 741, 699, 665 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 13H), 7.21 (m, 2H), 6.02 (d, J = 4.8 Hz, 1H), 4.90 (t, J = 4.0 Hz, 1H), 4.60 (s, 2H), 4.47 (AB, J = 11.8 Hz, ν_{ab} = 88.6 Hz, 2H), 4.44 (AB, J = 11.9 Hz, ν_{ab} = 88.6 Hz, 2H), 4.09 (t, J = 3.5 Hz, 1H), 3.96 (dd, J = 11.4, 2.6 Hz, 1H), 3.94 (s, 3H), 3.92 (dd, J = 9.2, 3.5 Hz, 1H), 3.68 (dd, J = 11.0, 2.2 Hz, 1H), 3.61 ppm (dd, J = 10.9, 3.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.8, 137.8, 137.3, 136.6, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0 (2C), 127.8, 127.7, 81.6, 75.5, 73.3, 73.1, 72.9, 72.4, 68.9, 54.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{29}H_{31}NO_9SNa^+$ $[M+Na]^+$: 592.1612; found: 592.1608.

Data for 71: R_f = 0.67 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3363, 2923, 1763, 1453, 1390, 1294, 1199, 1092, 847, 738, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 15H), 6.09 (d, J = 5.2 Hz, 1H), 4.95 (d, J = 4.4 Hz, 1H), 4.90 (AB, J = 12.1 Hz, ν_{ab} = 48.4 Hz, 2H), 4.62 (s, 2H), 4.45 (AB, J = 11.7 Hz, ν_{ab} = 101.2 Hz, 2H), 4.43 (AB, J = 11.8 Hz, ν_{ab} = 44.8 Hz, 2H), 4.12 (t, J = 3.7 Hz, 1H), 3.99 (dt, J = 9.2, 2.6 Hz, 1H), 3.93 (dd, J = 9.2, 3.3 Hz, 1H), 3.68 (dd, J = 11.0, 2.2 Hz, 1H), 3.61 ppm (dd, J = 11.0, 3.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.1, 137.8, 137.3, 136.6, 128.7, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 93.6, 81.8, 76.0, 75.4, 73.4, 73.3, 72.9, 72.8, 72.5, 68.8 ppm; HRMS (MALDI-FTMS) calcd for $C_{30}H_{30}Cl_3NO_9SNa^+$ $[M+Na]^+$: 708.0599; found: 708.0611.

Data for 72: R_f = 0.68 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3398, 2865, 1746, 1453, 1376, 1300, 1284, 1197, 1088, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.29 (m, 13H), 7.20–7.18 (m 2H), 6.02 (d, J = 4.8 Hz, 1H), 5.93 (m, 1H), 5.42 (dd, J = 17.0, 1.1 Hz, 1H), 5.30 (m, 1H), 4.88 (dt, J = 8.1, 0.7 Hz, 1H), 4.79 (ABX, J = 16.1, 5.5 Hz, ν_{ab} = 21.6 Hz, 2H), 4.60 (s, 2H), 4.53 (AB, J = 12.1 Hz, ν_{ab} = 21.3 Hz, 2H), 4.38 (AB, J = 12.1 Hz, ν_{ab} = 22.4 Hz, 2H), 4.08 (t, J = 3.7 Hz, 1H), 3.95 (td, J = 7.4, 2.8 Hz, 1H), 3.89 (dd, J = 7.4, 3.7 Hz, 1H), 3.67 (dd, J = 9.3, 2.2 Hz, 1H), 3.59 ppm (dd, J = 9.1, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.1, 137.9, 137.4, 136.7, 31.4, 130.4, 128.7, 128.5, 128.4 (2C), 128.1 (2C), 127.9, 127.7, 119.6, 119.2, 81.6, 77.4, 75.6, 73.5, 73.4, 72.9, 72.8, 72.4, 69.0, 68.5, 66.8 ppm; HRMS (MALDI-FTMS) calcd for $C_{31}H_{33}NO_9SNa^+$ $[M+Na]^+$: 618.1768; found: 618.1773.

Data for 74: R_f = 0.75 (silica gel, EtOAc/hexanes, 1:2); IR (film): ν_{max} = 2932, 2858, 1757, 1636, 1442, 1389, 1314, 1256, 1196, 1114, 1008, 836, 778 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 5.86 (d, J = 4.4 Hz, 1H), 4.70 (t, J = 1.2 Hz, 1H), 4.11 (d, J = 3.1 Hz, 1H), 3.95 (s, 3H), 3.87 (d, J =

7.4 Hz, 1H), 3.81–3.73 (m, 3H), 0.89 ppm (s, 27H), 0.16–0.06 (m, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.2, 81.3, 75.7, 75.0, 70.8, 68.8, 62.4, 54.7, 25.8, 25.5 (2C), 18.2, 17.8, 17.7, −4.2, −4.5, −4.8, −4.9, −5.2, −5.5 ppm; HRMS (MALDI-FTMS) calcd for $C_{26}H_{55}NO_9SSi_3Na^+$ $[M+Na]^+$: 664.2797; found: 664.2790.

Data for 76: R_f = 0.60 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3248, 1752, 1636, 1494, 1444, 1381, 1314, 1196, 1146, 1077, 1001, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.29 (m, 8H), 7.27–7.25 (m, 2H), 5.88 (d, J = 5.3 Hz, 1H), 4.90 (ddd, J = 6.2, 3.5, 1.2 Hz, 1H), 4.57 (AB, J = 10.8 Hz, ν_{ab} = 11.8 Hz, 2H), 4.44 (AB, J = 12.0 Hz, ν_{ab} = 34.9 Hz, 2H), 4.02 (dd, J = 3.2, 2.0, Hz, 1H), 3.98 (m, 1H), 3.95 (s, 3H), 3.36 (ddd, J = 8.8, 1.8, 1.2 Hz, 1H), 1.28 ppm (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 137.3, 136.5, 128.8, 128.5 (2C), 128.1, 128.0 (3C), 81.5, 80.5, 75.2, 74.4, 72.6, 72.4, 67.9, 54.9, 19.3 ppm; HRMS (MALDI-FTMS) calcd for $C_{22}H_{25}NO_8SNa^+$ $[M+Na]^+$: 486.1193; found: 486.1202.

Data for 78: R_f = 0.66 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 2961, 1755, 1443, 1384, 1320, 1290, 1190, 1061, 991, 855, 732, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39–7.25 (m, 15H), 5.89 (d, J = 4.0 Hz, 1H), 5.02 (dd, J = 5.2, 3.5 Hz, 1H), 4.75 (AB, J = 11.0 Hz, ν_{ab} = 160.4 Hz, 2H), 4.73 (AB, J = 11.9 Hz, ν_{ab} = 68.8 Hz, 2H), 4.53 (AB, J = 11.9 Hz, ν_{ab} = 31.1 Hz, 2H), 4.20 (m, 1H), 4.15 (dd, J = 4.0, 1.7 Hz, 1H), 4.03 (dd, J = 5.3, 1.8 Hz, 1H), 3.92 (s, 3H), 3.71 (dd, J = 9.7, 7.4 Hz, 1H), 3.65 ppm (dd, J = 9.7, 6.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.5, 137.7, 137.4, 136.8, 128.6, 128.4, 128.2, 128.1, 128.0, 127.8 (2C), 127.6, 84.1, 80.3, 78.7, 75.4, 75.3, 73.7, 72.1, 66.9, 54.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{29}H_{31}NO_9SNa^+$ $[M+Na]^+$: 592.1612; found: 592.1633.

Data for 80: R_f = 0.33 (silica gel, EtOAc/hexanes, 1:2); IR (film): ν_{max} = 2978, 1746, 1437, 1412, 1294, 1249, 1187, 1073, 1023, 973, 861, 797, 609 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (d, J = 3.8 Hz, 1H), 5.13 (d, J = 2.4 Hz, 1H), 4.72 (dd, J = 15.0, 2.9 Hz, 1H), 4.71 (d, J = 3.5 Hz, 1H), 4.36 (q, J = 2.6 Hz, 1H), 4.09 (dd, J = 15.0, 2.6 Hz, 1H), 3.86 (s, 3H), 1.49 (s, 3H), 1.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 113.0, 104.9, 87.3, 82.5, 70.6, 54.9, 48.2, 26.5, 26.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{15}NO_8SNa^+$ $[M+Na]^+$: 332.0411; found: 332.0418.

Data for 82: R_f = 0.68 (silica gel, EtOAc/hexanes, 1:2); IR (film): ν_{max} = 2954, 2858, 1759, 1442, 1392, 1313, 1257, 1196, 1098, 1011, 838, 806, 781 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.12 (d, J = 4.4 Hz, 1H), 4.93 (d, J = 4.1 Hz, 1H), 4.61 (s, 1H), 4.12 (ddd, J = 8.5, 5.2, 1.9 Hz, 1H), 3.96 (s, 3H), 3.77 (dd, J = 10.7, 5.5 Hz, 1H), 3.71 (dd, J = 10.6, 8.8 Hz, 1H), 0.90 (s, 18H), 0.14 (d, J = 5.5 Hz, 6H), 0.07 ppm (d, J = 2.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.8, 88.8, 87.7, 86.2, 74.3, 61.7, 55.0, 25.8, 25.5, 18.3, 17.9, −4.9, −5.0, −5.5 ppm (2C); HRMS (MALDI-FTMS) calcd for $C_{19}H_{40}NO_8Si_2S^+$ $[M+H]^+$: 498.2008; found: 498.2015.

Azide-opened tri-benzylated glucose derivative 83: NaN_3 (0.033 g, 0.50 mmol, 5.0 equiv) was added in a single portion to a solution of glucose-derived sulfamidate **70** (0.057 g, 0.10 mmol, 1.0 equiv) in THF/CH_2Cl_2 (4:1, 1 mL) at 25 °C. The resulting clear solution was then warmed to 60 °C and stirred for 5 h. Upon completion, the reaction contents were diluted with Et_2O (5 mL), treated with 10% aqueous H_2SO_4 (1 mL), and allowed to stir for an additional 30 minutes at 25 °C. Once this operation was complete, the reaction mixture was poured into water (10 mL) and extracted with Et_2O (3 × 25 mL). The combined organic layers were then washed with water (2 × 15 mL), dried ($MgSO_4$), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, Et_2O/hexanes, 1:1) to give the azide-opened tri-benzylated glucose derivative **83** (0.049 g, 92%) as an amorphous white solid. R_f = 0.47 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3318, 2924, 2106, 1732, 1532, 1454, 1357, 1243, 1098, 1027, 738, 699 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26–7.15 (m, 15H), 5.42 (br s, 1H), 5.27 (br m, 1H), 4.65–4.47 (m, 5H), 3.82 (m, 2H), 3.74 (m, 2H), 3.68 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.7, 138.0, 137.6, 137.1, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 78.3, 73.8, 73.2, 72.8, 68.2, 60.0, 52.7, 53.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{34}H_{38}NO_5^+$ $[M+H]^+$: 555.2214; found: 555.2217.

Allylated sulfamidate 84: Et_2NH (0.354 mL, 6.71 mmol, 40 equiv) was added to a solution of sulfamidate **72** (0.100 g, 0.167 mmol, 1.0 equiv) in CH_3CN/H_2O (1:1, 3 mL) at 25 °C. After stirring this mixture for 5 minutes at 25 °C, $Pd(OAc)_2$ (0.002 g, 0.017 mmol, 0.1 equiv) and TPPTS (0.019 g, 0.033 mmol, 0.2 equiv) were added sequentially, providing a yellow solution which was stirred for an additional 30 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated to give the desired deprotected sulfamidate (0.075 g, 87% yield) as a white oil.[29] Pressing forward without any additional purification steps, this material (0.075 g, 0.146 mmol, 1.0 equiv) was dissolved in DMSO (2 mL) and treated with NaH (0.029 g, 60% dispersion in mineral oil, 0.730 mmol, 5.0 equiv) at 25 °C. After stirring the resultant reaction mixture for 10 minutes at 25 °C, allyl bromide (0.051 mL, 0.584 mmol, 4.0 equiv) was added in a single portion; the reaction mixture was then stirred for an additional 15 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then washed with water (2 × 15 mL), dried ($MgSO_4$), and concentrated. The resultant light yellow oil was purified by flash column chromatography (silica gel, EtOAc/hexanes, 1:3 → 1:1) to give the allylated sulfamidate **84** (0.067 g, 73% yield over two steps) as an amorphous white solid. R_f = 0.64 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 2890, 1452, 1352, 1193, 1114, 1052, 988, 741, 694, 606 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 15H), 5.87 (m, 1H), 5.35 (d, J = 17.1 Hz, 1H), 5.29 (s, 1H), 5.28 (d, J = 16.7 Hz, 1H), 4.95 (dd, J = 7.4, 5.3 Hz, 1H), 4.75 (AB, J = 11.0 Hz, ν_{ab} = 185.9 Hz, 2H), 4.73 (AB, J = 11.8 Hz, ν_{ab} = 76.7 Hz, 2H), 4.43 (AB, J = 11.8 Hz, ν_{ab} = 26.3 Hz, 2H), 4.12 (dd, J = 7.4, 2.6 Hz, 1H), 4.04 (t, J = 5.3 Hz, 1H), 4.00 (app s, 1H), 3.79 (dd, J = 14.5, 5.7 Hz, 1H), 3.73 (dd, J = 14.5, 7.9 Hz, 1H), 3.52 ppm (AB, J = 9.6 Hz, ν_{ab} = 16.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 137.8, 137.6, 137.4, 130.4, 128.5 (2C), 128.4, 128.2, 128.0 (2C), 127.9, 127.7 (2C), 121.1, 84.3, 82.2, 78.5, 74.9, 73.5 (2C), 72.8, 72.4, 67.7, 47.0 ppm; HRMS (MALDI-FTMS) calcd for $C_{30}H_{33}NO_7SNa^+$ $[M+Na]^+$: 574.1870; found: 574.1866.

2,3,4-Tri-*O*-benzyl-D-fucose (90): Concentrated H_2SO_4 (1 mL) was added to a solution of D-fucose (1.64 g, 10.0 mmol, 1.0 equiv) in MeOH (30 mL) at 25 °C, and the resultant mixture was stirred for 5 h. Upon completion, the reaction contents were neutralized by the addition of 3N aqueous NaOH (monitored using standard pH paper) and concentrated directly. The resulting white solid was then taken up in EtOAc (50 mL), filtered through a short silica gel, and concentrated to give 1-*O*-methyl-D-fucose (1.78 g, 100% yield) as a white solid. Pressing forward without any additional purification steps, this newly-formed material (1.78 g, 10.0 mmol, 1.0 equiv) was dissolved in DMF (10 mL) and treated with NaH (3.60 g, 60% dispersion in mineral oil, 90.0 mmol, 9.0 equiv) at 25 °C. After stirring the resultant solution for 5 minutes at 25 °C, the reaction contents were cooled to 0 °C and benzyl bromide (5.95 mL, 50.0 mmol, 5.0 equiv) added dropwise over the course of 10 minutes. The reaction mixture was then warmed to 25 °C over the course of 4 h. Upon completion, the reaction mixture was poured into 1N aqueous HCl (25 mL) and extracted with Et_2O (3 × 25 mL). The combined organic layers were then washed with water (2 × 15 mL), dried ($MgSO_4$), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, Et_2O/hexanes, 1:3 → 1:1) to give the desired tri-*O*-benzylated–fucose intermediate (3.7 g, 82%) as an amorphous white solid. Finally, a portion of this newly-formed product (0.452 g, 1.0 mmol, 1.0 equiv) was dissolved 6M aqueous HCl/concentrated HCl (1:1, 5 mL) at 25 °C. The resultant mixture was then warmed to 60 °C and stirred for 12 h. Upon completion, the reaction contents were concentrated directly. The resultant yellow oil was purified by flash column chromatography (silica gel, Et_2O/hexanes, 1:1) to give the desired D-fucose-derived starting material **90** (0.297 g, 68%) as an amorphous white solid. R_f = 0.54 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max} = 3416, 3031, 2867, 1453, 1364, 1208, 1098, 740, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 7.48–7.34 (m, 30H), 5.55 (s, 1H), 5.41 (dd, J = 9.5, 4.4 Hz, 1H), 4.83–4.49 (m, 11H), 4.35 (app t, J = 5.2 Hz, 1H), 4.30 (br d, J = 11.4 Hz, 1H), 4.25 (app t, J = 5.2 Hz, 1H), 4.13 (dd, J = 5.5, 4.8 Hz, 1H), 4.10 (dd, J = 2.2, 1.1 Hz, 1H), 4.05 (dd, J = 5.2, 2.2 Hz, 1H), 3.99 (dd, J = 4.8, 3.0 Hz, 1H), 3.78 (m, 1H), 3.63 (dd, J = 6.3, 3.0 Hz, 1H), 3.55 (br s, 1H), 3.48 (m, 1H), 1.38 (d, J = 4.6 Hz, 3H), 1.28 ppm (d, J = 4.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 1:1 mixture of anomers): δ = 138.5, 137.7, 137.5, 137.4 (2C), 137.3, 128.4 (2C), 128.3 (2C), 128.2, 128.0, 127.9 (2C), 127.8 (3C), 127.7, 127.5, 127.4, 126.9, 100.7, 96.0, 87.3, 85.2, 84.5, 84.4, 82.8, 82.2, 74.0, 73.9, 71.9 (2C), 71.8, 71.6, 71.2, 71.1, 65.1 ppm; MS (ESI) calcd for $C_{27}H_{30}O_9Cl^-$ $[M+Cl]^-$: 470; found: 470.

2,3,4,6-Tetra-*O*-methyl-D-mannose (92): D-Mannose (1.80 g, 10.0 mmol) was converted into **92** in a manner similar to the preparation of **90** by substituting methyl iodide for benzyl bromide, ultimately providing compound **92** (0.146 g, 62% yield) as a white amorphous solid. $R_f = 0.15$ (silica gel, EtOAc/hexanes, 1:2); IR (film): $\nu_{max} = 3402, 2932, 2828, 1644, 1453, 1193, 1109, 1030, 958, 792\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 5.25 (s, 1H), 4.62 (brs, 1H), 3.86 (td, $J = 7.3$, 1.8 Hz, 1H), 3.59–3.51 (m, 4H), 3.45 (s, 3H), 3.44 (s, 3H), 3.43 (s, 3H), 3.32 (s, 3H), 3.26 ppm (t, $J =$ 9.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 91.5$, 80.8, 74.5, 77.1, 72.7, 70.3, 60.6, 59.1, 58.8, 57.6 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{20}O_6Na^+$ $[M+Na]^+$: 259.1152; found: 259.1152.

2,3,5-Tri-*O*-benzyl-L-arabinofuranose (95): Lactol **95** was prepared from L-arabinose using the sequence established by Tejima and Fletcher.[49] $R_f = 0.51$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3418, 3030, 2866, 1495, 1454, 1365, 1264, 1208, 1099, 1028, 738, 698\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$, 1:1 mixture of anomers): $\delta = 7.36$–7.26 (m, 30H), 5.40 (s, 1H), 5.34 (d, $J = 3.7$ Hz, 1H), 4.66 (d, $J = 9.5$ Hz, 1H), 4.61–4.52 (m, 10H), 4.48–4.45 (m, 2H), 4.17 (t, $J = 4.0$ Hz, 1H), 4.09 (q, $J = 3.7$ Hz, 1H), 4.02 (t, $J = 4.0$ Hz, 1H), 3.98 (d, $J = 1.5$ Hz, 1H), 3.94 (m, 1H), 3.61–3.50 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 1:1 mixture of anomers): $\delta = 138.0$, 137.4, 137.3, 137.2 (2C), 128.6, 128.5 (4 C), 128.4 (2C), 128.3, 128.0 (2C), 127.9 (2C), 127.8 (2C), 127.7 (2C), 127.6, 101.1, 96.2, 86.3, 84.0, 82.6, 82.0, 81.8, 80.5, 76.8, 73.5, 73.3, 72.2, 72.0 (2C), 71.7, 70.4, 70.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{26}H_{28}O_5Na^+$ $[M+Na]^+$: 443.1829; found: 443.1809.

Furanose 98: The requisite lactol intermediate was prepared from D-ribose following the procedure of Kaskar and co-workers.[50] $R_f = 0.51$ (silica gel, EtOAc/hexanes, 1:2); IR (film): $\nu_{max} = 3416, 2934, 2858, 1469, 1381, 1257, 1211, 1075, 1004, 939, 838, 779\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.24$ (d, $J = 11.4$ Hz, 1H), 4.74 (d, $J = 11.7$ Hz, 1H), 4.66 (d, $J = 5.9$ Hz, 1H), 4.47 (d, $J = 5.9$ Hz, 1H), 4.31 (s, 1H), 3.75–3.72 (m, 2H), 1.45 (s, 3H), 1.29 (s, 3H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 111.9$, 103.3, 87.5, 86.8, 81.7, 64.7, 26.4, 25.7, 24.8, 18.1, −5.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{14}H_{28}O_5SiNa^+$ $[M+Na]^+$: 327.1598; found: 327.1592.

General procedure for the synthesis of β-disposed glycosylamines: The lactol starting material (0.5 mmol, 1.0 equiv) was dissolved in THF/CH_2Cl_2 (4:1, 5 mL) and the desired Burgess-type reagent (**1**, **50**, or **51**, 0.75 mmol, 1.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 6 h. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were then washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

CO_2Me-protected 2,3,4,6-tetra-*O*-methyl-β-D-glucosylamine (86): $R_f =$ 0.13 (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3329, 2937, 2836, 1712, 1544, 1450, 1278, 1158, 1099, 989, 945, 647\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.30$ (d, $J = 8.8$ Hz, 1H), 4.75 (t, $J = 8.4$ Hz, 1H), 3.68 (brs, 3H), 3.62 (s, 3H), 3.58–3.53 (m, 2H), 3.52 (s, 3H), 3.51 (s, 3H), 3.41 (s, 3H), 3.30 (m, 1H), 3.22 (d, $J = 6.7$ Hz, 2H), 2.91 ppm (brm, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.1$, 99.5, 87.2, 82.8, 81.6, 78.9, 75.8, 70.5, 60.8, 60.3, 59.1, 52.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{23}NO_7Na^+$ $[M+Na]^+$: 316.1367; found: 316.1363.

CO_2Me-protected 2,3,4,6-tetra-*O*-benzyl-β-D-glucosylamine (88): $R_f =$ 0.67 (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3326, 2869, 1733, 1535, 1496, 1454, 1362, 1252, 1101, 737, 698\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$–7.27 (m, 18H), 7.17 (m, 2H), 5.12 (brd, $J = 6.4$ Hz, 1H), 4.97 (m, 1H), 4.93 (AB, $J = 10.8$ Hz, $\nu_{ab} = 15.0$ Hz, 2H), 4.84 (dd, $J = 10.8$, 3.5 Hz, 1H), 4.74 (d, $J = 11.1$ Hz, 1H), 4.65 (d, $J = 12.0$ Hz, 1H), 4.56 (d, $J = 10.8$ Hz, 1H), 4.51 (d, $J = 11.1$ Hz, 1H), 3.76 (m, 4H), 3.72 (brs, 3H), 3.54 (brd, $J = 7.9$ Hz, 1H), 3.38 ppm (appt, $J = 6.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.1$, 138.3, 137.9, 137.7, 128.4, 128.3 (2C), 128.2, 127.9, 127.7, 127.6, 85.8, 81.7, 80.1, 77.4, 76.0, 75.6, 74.8, 74.6, 73.4, 68.0, 52.3 ppm; HRMS (MALDI-FTMS) calcd for $C_{36}H_{39}NO_7Na^+$ $[M+Na]^+$: 620.2610; found: 620.2614.

Alloc-protected 2,3,4,6-tetra-*O*-benzyl-β-D-glucosylamine (89): $R_f = 0.64$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3331, 3030, 2867, 1703, 1537, 1453, 1360, 1280, 1071, 735, 697\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.45$–7.32 (m, 18H), 7.19–7.17 (m, 2H), 5.93 (ddd, $J = 22.7$, 10.9, 5.7 Hz, 1H), 5.32 (d, $J = 17.1$ Hz, 1H), 5.23 (d, $J = 10.1$ Hz, 1H), 5.07 (d, $J = 10.1$ Hz, 1H), 4.92 (m, 1H), 4.91 (AB, $J = 11.0$ Hz, $\nu_{ab} = 18.8$ Hz, 2H), 4.82 (d, $J = 10.9$ Hz, 2H), 4.72 (d, $J = 11.0$ Hz, 1H), 4.64–4.60 (m, 3H), 4.53 (d, $J = 10.5$ Hz, 1H), 4.47 (d, $J = 12.3$ Hz, 1H), 3.73 (m, 4H), 3.52 (d, $J = 7.9$ Hz, 1H), 3.38 ppm (t, $J = 8.3$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 155.3$, 138.3, 138.0, 137.7, 132.4, 128.5, 128.4 (3C), 128.3 (3C), 128.2, 128.0, 127.8, 127.7, 127.6, 117.8, 85.9, 81.6, 80.1, 77.4, 76.1, 75.6, 74.9, 74.7, 73.5, 68.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{38}H_{41}NO_7Na^+$ $[M+Na]^+$: 646.2775; found: 646.2766.

CO_2Me-protected 2,3,4-tri-*O*-benzyl-β-D-fucosylamine (91): $R_f = 0.70$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3326, 2927, 1730, 1504, 1453, 1351, 1067, 736, 697\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.36$–7.31 (m, 15H), 5.81 (brd, $J = 6.4$ Hz, 1H), 5.76 (brs, 1H), 4.69 (AB, $J =$ 9.4 Hz, $\nu_{ab} = 21.4$ Hz, 2H), 4.67 (m, 1H), 4.57 (m, 3H), 4.24 (dd, $J = 4.7$, 2.6 Hz, 1H), 4.04 (d, $J = 1.5$ Hz, 1H), 3.98 (brs, 1H), 3.80 (m, 1H), 3.77 (brs, 3H), 1.20 ppm (d, $J = 4.9$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.8$, 138.6, 137.2, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8 (2C), 127.6, 127.4, 86.1, 85.3 (2C), 82.4, 74.1, 71.8, 71.4, 52.3, 15.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{29}H_{33}NO_6Na^+$ $[M+Na]^+$: 514.2200; found: 514.2191.

CO_2Me-protected 2,3,4,6-tetra-*O*-methyl-β-D-mannosylamine (93): $R_f =$ 0.27 (silica gel, EtOAc); IR (film): $\nu_{max} = 3205, 2928, 1722, 1445, 1257, 1100\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.59$ (brs, 1H), 5.44 (brs, 1H), 3.83 (m, 1H), 3.80 (s, 3H), 3.67–3.64 (m, 4H), 3.62 (m, 1H), 3.61 (s, 6H), 3.58 (s, 3H), 3.48 (m, 1H), 3.46 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.3$, 80.4, 77.1, 76.4, 73.3, 71.7, 68.4, 60.5, 59.7, 58.8, 58.4, 53.0 ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{23}NO_7Na^+$ $[M+Na]^+$: 316.1367; found: 316.1362.

Alloc-protected 2,3,4,6-tetra-*O*-methyl-β-D-mannosylamine (94): $R_f = 0.38$ (silica gel, EtOAc); IR (film): $\nu_{max} = 3332, 2934, 1726, 1529, 1450, 1305, 1237, 1100\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.90$ (ddd, $J = 23.1$, 10.7, 4.8 Hz, 1H), 5.52 (brs, 1H), 5.32 (d, $J = 17.2$ Hz, 1H), 5.22 (d, $J =$ 10.3 Hz, 1H), 4.60 (s, 2H), 3.63–3.48 (m, 15H), 3.45–3.42 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.5$, 132.7, 118.7, 80.4, 77.1, 76.4, 73.3, 71.6, 66.5, 59.7, 58.8, 58.3, 51.5 ppm; HRMS (MALDI-FTMS) calcd for $C_{14}H_{25}NO_7Na^+$ $[M+Na]^+$: 342.1523; found: 342.1522.

CO_2Me-protected 2,3,5-tri-*O*-benzyl-β-L-arabinofuranosylamine (96): $R_f = 0.63$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3317, 3030, 2865, 1732, 1498, 1454, 1363, 1238, 1058, 739, 698\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$–7.27 (m, 15H), 5.88 (brd, $J = 9.4$ Hz, 1H), 5.76 (brd, $J = 10.0$ Hz, 1H), 4.61–4.45 (m, 6H), 4.38 (appt, $J = 5.6$ Hz, 1H), 4.02 (s, 1H), 3.93 (s, 1H), 3.70 (brs, 3H), 3.64 (dd, $J = 9.4$, 5.9 Hz, 1H), 3.52 ppm (appt, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 155.8, 137.9, 137.1, 128.4 (2C), 128.3, 128.2, 127.9, 127.8, 127.7, 127.6 (2C), 85.5, 84.9, 82.7, 82.1, 73.2, 71.6, 71.4, 70.0, 52.2 ppm; HRMS (MALDI-FTMS) calcd for $C_{28}H_{31}NO_6Na^+$ $[M+Na]^+$: 500.2043; found: 500.2033.

Alloc-protected 2,3,5-tri-*O*-benzyl-β-L-arabinofuranosylamine (97): $R_f =$ 0.55 (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3322, 3030, 2866, 1730, 1503, 1454, 1366, 1232, 1094, 992, 738, 698\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.41$–7.32 (m, 15H), 6.01 (ddd, $J = 22.8$, 11.0, 5.9 Hz, 1H), 5.94 (d, $J = 9.9$ Hz, 1H), 5.84 (d, $J = 9.9$ Hz, 1H), 5.40 (d, $J =$ 16.9 Hz, 1H), 5.31 (dd, $J = 10.2$, 1.1 Hz, 1H), 4.69–4.58 (m, 7H), 4.53 (d, $J = 11.7$ Hz, 1H), 4.48 (ddd, $J = 9.8$, 7.3, 1.8 Hz, 1H), 4.08 (brs, 1H), 4.00 (brs, 1H), 3.70 (dd, $J = 9.5$, 5.5 Hz, 1H), 3.59 ppm (appt, $J = 7.7$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 155.5$, 138.5, 137.6, 133.0, 129.0, 128.9, 128.8 (2C), 128.3, 128.2, 128., 1280, 118.5, 86.1, 85.4, 83.2, 82.8, 73.8, 72.2, 71.9, 70.6, 66.3 ppm; HRMS (MALDI-FTMS) calcd for $C_{30}H_{33}NO_6Na^+$ $[M+Na]^+$: 526.2200; found: 526.2190.

CO_2Me-protected ribosylamine 99: $R_f = 0.67$ (silica gel, EtOAc/hexanes, 1:2); IR (film): $\nu_{max} = 3347, 2933, 1737, 1509, 1461, 1377, 1251, 1082, 931, 837, 779\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.27$ (brd, $J = 11.8$ Hz, 1H), 5.68 (brd, $J = 10.0$ Hz, 1H), 4.72 (d, $J = 5.9$ Hz, 1H), 4.50 (d, $J =$ 6.2 Hz, 1H), 4.29 (s, 1H), 3.77 (m, 1H), 3.71 (m, 3H), 3.66 (brs, 3H), 1.51 (s, 3H), 1.33 (s, 3H), 0.94 (s, 9H), 0.13 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.8$, 112.2, 89.0, 86.6, 86.0, 82.1, 79.4, 65.0, 51.8, 25.7, 24.8, 18.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{16}H_{31}NO_6SiNa^+$ $[M+Na]^+$: 84.1813; found: 384.1814.

CO_2Me-protected 101: $R_f = 0.41$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3304, 2988, 1702, 1541, 1377, 1296, 1248, 1209, 1067, 1039, 1018, 850\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.61$ (brs, 1H), 5.22 (brs, 1 h), 4.87 (brs, 2H), 4.36 (m, 1H), 4.08–3.98 (m, 3H), 3.67 (s, 3H), 3.67 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.32 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.1, 112.9, 109.1, 87.9, 85.2, 73.3, 66.6, 52.4, 26.9, 25.9, 25.0, 24.8$ ppm; HRMS (MALDI-FTMS) calcd for $C_{14}H_{23}NO_7Na^+$ $[M+Na]^+$: 340.1367; found: 340.1364.

2,3,4,6-Tetra-*O*-benzyl-β-D-glucosylamine (102): Et_2NH (0.179 mL, 3.40 mmol, 40 equiv) was added to a solution of intermediate **89** (0.053 g, 0.085 mmol, 1.0 equiv) in CH_3CN/H_2O (1:1, 2 mL) at 25 °C. After stirring this mixture for 5 minutes at 25 °C, $Pd(OAc)_2$ (0.002 g, 0.009 mmol, 0.1 equiv) and TPPTS (0.010 g, 0.017 mmol, 0.2 equiv) were added sequentially, providing a yellow solution which was stirred for an additional 30 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3×10 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated to give 2,3,4,6-tetra-*O*-benzyl-β-D-glucosylamine (0.043 g, 95% yield)[29] as an amorphous white solid. $R_f = 0.48$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3352, 3030, 2862, 1453, 1351, 1122, 1094, 1086, 1027, 750, 698\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.48–7.21$ (m, 20H), 5.08 (d, $J = 13.2$ Hz, 1H), 5.03 (d, $J = 13.1$ Hz, 1H), 4.94–4.86 (m, 3H), 4.65 (AB, $J = 14.3$ Hz, $\nu_{ab} = 37.4$ Hz, 2H), 4.58 (m, 1H), 4.20 (d, $J = 9.9$ Hz, 1H), 3.85–3.80 (m, 5H), 3.56 (dd, $J = 11.5$, 3.3 Hz, 1H), 3.30 (t, $J = 10.4$ Hz, 1H), 1.97 ppm (brs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 138.6, 138.3, 138.0, 137.9, 128.7, 128.4$ (2C), 128.3, 128.2, 127.9, 127.8 (2C), 127.7 (2C), 127.6, 86.2, 85.8, 83.4, 78.1, 75.7, 75.6, 75.0, 74.9, 73.5, 68.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{34}H_{38}NO_5^+$ $[M+H]^+$: 540.2744; found: 540.2750.[25]

General procedure for making epoxy alcohol starting materials: All epoxy alcohols were prepared following the method of Katsuki and Sharpless, and their spectral data matched that published.[51]

Perillyl epoxide 109: $R_f = 0.33$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 3347, 2933, 1632, 1509, 1461, 1371, 1224, 1042, 939, 837, 777\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.67$ (s, 1H), 4.64 (s, 1H), 3.58 (AB, $J = 12.0$ Hz, $\nu_{ab} = 43.7$ Hz, 2H), 3.32 (s, 1H), 2.36 (brs, 3H), 2.12 (AB, $J = 13.5$ Hz, $\nu_{ab} = 22.6$ Hz, 2H), 1.80 (m, 2H), 1.66 (s, 3H), 1.58 (appt, $J = 11.4$ Hz, 2H), 1.17 ppm (dd, $J = 11.4$, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.6, 109.1, 64.2, 60.0, 56.7, 36.7, 30.2, 24.6, 20.8$ ppm; MS (GC/MS) calcd for $C_{10}H_{16}O_2^+$ $[M]^+$: 168; found: 168.

Myrtenol epoxide 111: $VO(acac)_2$ (0.100 g, catalytic) and *tert*-butyl hydroperoxide (0.70 mL, 2.0 mmol, 2.0 equiv) were added sequentially to a solution of (−)-myrtenol (0.152 g, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) at 25 °C. After stirring the resultant solution for 2 h at 25 °C, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and quenched by the addition of water (5 mL) and Na_2SO_3 (0.063 g, 0.5 mmol, 0.5 equiv). The reaction contents were then poured into water (25 mL) and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel, EtOAc/hexanes, 1:1) to provide myrtenol epoxide **111** (0.146 g, 87%) as a colorless oil. $R_f = 0.42$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max} = 2976, 2908, 1461, 1433, 1368, 1270, 1230, 1088, 1062, 1025, 865, 835, 770, 692\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.66$ (AB, $J = 12.6$ Hz, $\nu_{ab} = 69.5$ Hz, 2H), 3.37 (d, $J = 4.1$ Hz, 1H), 2.15 (brs, 1H), 2.04 (m, 1H), 2.01 (d, $J = 2.9$ Hz, 1H), 1.98 (t, $J = 5.6$ Hz, 1H), 1.93–1.87 (m, 1H), 1.75 (brm, 1H), 1.63 (d, $J = 9.7$ Hz, 1H), 1.25 (s, 3H), 0.89 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 63.9, 62.9, 53.3, 40.5, 40.1, 27.1, 26.4, 25.5, 20.0$ ppm; HRMS (MALDI-FTMS) calcd for $C_6H_{11}O_2^+$ $[M+H]^+$: 115.0754; found: 115.0758.

General procedure for the synthesis of sulfamidates from epoxy alcohols: The epoxy alcohol (1.0 mmol, 1.0 equiv) was dissolved in THF/CH_2Cl_2 (4:1, 5 ml) and the Burgess reagent (0.309 g, 1.3 mmol, 1.3 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 3 h. Upon completion, the reaction contents were concentrated directly, and the resultant residue was purified by flash column chromatography (Florisil®, EtOAc/MeOH, 1:0→98:2) to give the desired sulfamidate product in high purity.

Sulfamidate 104: $R_f = 0.35$ (silica gel, EtOAc/MeOH, 98:2); IR (film): $\nu_{max} = 3436, 3002, 1744, 1636, 1467, 1383, 1255, 1174, 953, 700, 597\ cm^{-1}$; ^1H NMR (400 MHz, CD_3CN): $\delta = 7.37–7.28$ (m, 5H), 4.70 (dd, $J = 11.8$, 2.5 Hz, 1H), 4.24 (dd, $J = 11.7$, 6.6 Hz, 1H), 3.90 (d, $J = 2.1$ Hz, 1H), 3.72 (s, 3H), 3.40 ppm (dt, $J = 6.4$, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 152.1, 136.9, 129.4, 126.7, 73.5, 59.1, 56.5, 54.2$ ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{14}NO_6S^+$ $[M+H]^+$: 288.0536; found: 288.0537.

Sulfamidate 106: $R_f = 0.32$ (silica gel, EtOAc/MeOH, 98:2); IR (film): $\nu_{max} = 3480, 2955, 1743, 1649, 1446, 1291, 1167, 1108, 1050, 987, 885, 796, 749, 702, 621\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.24–7.17$ (m, 5H), 4.22 (AB, $J = 17.2$ Hz, $\nu_{ab} = 68.6$ Hz, 2H), 4.15 (s, 1H), 3.55 (s, 3H), 1.03 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.3, 134.6, 128.0, 127.7, 126.5, 126.3, 72.3, 61.7, 61.0, 53.5, 13.1$ ppm; MS (ESI) calcd for $C_{12}H_{15}NO_6NaS^+$ $[M+Na]^+$: 323; found: 323.

Sulfamidate 108: $R_f = 0.28$ (silica gel, EtOAc/MeOH, 98:2); IR (film): $\nu_{max} = 3482, 2930, 1735, 1650, 1442, 1290, 1166, 1107, 985, 885\ cm^{-1}$; ^1H NMR (500 MHz, CD_3CN): $\delta = 5.09$ (m, 1H), 4.17 (dd, $J = 11.4$, 3.7 Hz, 1H), 3.88 (dd, $J = 11.8$, 7.0 Hz, 1H), 3.50 (s, 3H), 2.99 (dd, $J = 7.0$, 4.0 Hz, 1H), 2.05 (m, 2H), 1.65 (s, 3H), 1.58 (s, 3H), 1.55 (m, 1H), 1.40 (m, 1H), 1.24 ppm (s, 3H); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 161.8, 132.6, 124.4, 68.1, 61.2, 60.7, 52.5, 38.8, 25.6, 24.1, 17.5, 16.9$ ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{21}NO_6SNa^+$ $[M+Na]^+$: 330.0982; found: 330.0987.

Sulfamidate 110: $R_f = 0.31$ (silica gel, EtOAc/MeOH, 98:2); IR (film): $\nu_{max} = 3260, 2937, 1755, 1644, 1452, 1382, 1247, 1173, 959, 890, 776, 599\ cm^{-1}$; ^1H NMR (600 MHz, CD_3CN): $\delta = 4.72$ (t, $J = 1.3$ Hz, 1H), 4.68 (q, $J = 0.9$ Hz, 1H), 4.18 (AB, $J = 10.9$ Hz, $\nu_{ab} = 178.0$ Hz, 2H), 3.73 (s, 3H), 3.23 (brs, 1H), 2.12–2.08 (m, 1H), 2.05–1.95 (m, 2H), 1.78 (ddd, $J = 17.5$, 11.4, 6.1 Hz, 1H), 1.67 (s, 3H), 1.54 (m, 1H), 1.24–1.18 ppm (m, 2H); ^{13}C NMR (150 MHz, CD_3CN): $\delta = 151.9, 149.8, 109.6, 77.8, 58.1, 57.3, 54.2, 37.1, 30.6, 26.1, 20.9$ ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{19}NO_6SNa^+$ $[M+Na]^+$: 328.0825; found: 328.0826.

Sulfamidate 112: $R_f = 0.30$ (silica gel, EtOAc/MeOH, 98:2); IR (film): $\nu_{max} = 3482, 2924, 1644, 1445, 1389, 1296, 1166, 1109, 1052, 964, 883, 804, 736, 619\ cm^{-1}$; ^1H NMR (500 MHz, CD_3CN): $\delta = 4.05$ (AB, $J = 11.8$ Hz, $\nu_{ab} = 162.9$ Hz, 2H), 3.52 (s, 3H), 3.32 (m, 1H), 2.15 (t, $J = 5.9$ Hz, 1H), 2.06 (dt, $J = 7.2$, 5.8 Hz, 1H), 1.96 (m, 2H), 1.72 (m, 1H), 1.54 (d, $J = 9.6$ Hz, 1H), 1.29 (s, 3H), 0.92 ppm (s, 3H); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 162.3, 70.1, 62.2, 54.0, 52.9, 41.2, 40.9, 40.7, 27.7, 26.7, 26.0, 20.3$ ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{19}NO_6SNa^+$ $[M+H]^+$: 328.0825; found: 328.0820.

Synthesis of aminoalcohol starting materials (Procedure A): The appropriate aniline (5.0 mmol, 1.0 equiv) was dissolved in 2-bromoethanol (5 mL), and the resulting solution was heated at 70 °C until most of the starting material had been consumed (typically 2–8 h). Upon completion, the reaction contents were cooled to 25 °C, poured into water (5 mL), and extracted with EtOAc (3×10 mL). The combined organic layers were then washed with water (2×15 mL), dried ($MgSO_4$), and concentrated. The resultant oil was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired aminoalcohol product in high purity.

Data for 131: $R_f = 0.32$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3385, 2919, 1602, 1537, 1504, 1467, 1305, 1185, 1112, 1049, 833\ cm^{-1}$; ^1H NMR (500 MHz, CD_3CN): $\delta = 8.10$ (dd, $J = 7.0$, 1.9 Hz, 2H), 6.72 (dd, $J = 7.0$, 1.9 Hz, 2H), 3.77 (brt, $J = 5.2$ Hz, 2H), 3.39 ppm (t, $J = 5.5$ Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 154.8, 137.5, 126.5, 111.4, 60.2, 45.6$ ppm; HRMS (MALDI-FTMS) calcd for $C_8H_{11}N_2O_3^+$ $[M+H]^+$: 183.0764; found: 183.0765.

Data for 133: $R_f = 0.28$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3280, 2955, 1618, 1519, 1465, 1391, 1292, 1119, 964, 870, 700\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.16$ (s, 1H), 6.97 (s, 2H), 3.89 (t, $J = 5.0$ Hz, 2H), 3.87 (dd, $J = 5.6$, 4.1 Hz, 1H), 3.67 (dd, $J = 5.3$, 5.0 Hz, 1H), 3.35 ppm (brt, $J = 4.7$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.7$, 132.3 (d, $J = 133.4$ Hz), 112.1, 110.5, 60.8, 45.4 ppm; MS (ESI) calcd for $C_{10}H_{10}F_6NO^+$ $[M+H]^+$: 274; found: 274.

Data for 135: $R_f = 0.22$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3378, 2937, 1606, 1512, 1459, 1236, 1128, 1005, 601\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.89$ (s, 2H), 3.83 (t, $J = 5.3$ Hz, 2H), 3.81 (s, 6H), 3.76 (s, 3H), 3.27 ppm (t, $J = 5.3$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.9, 144.9, 92.6, 90.8, 61.3, 61.1, 55.9, 46.6$ ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{18}NO_4^+$ $[M+H]^+$: 228.1230; found: 228.1239.

Synthesis of aminoalcohol starting materials (Procedure B): $NaCNBH_3$ (0.200 g, 3.5 mmol, 1.0 equiv) was added to a solution of the desired alde-

hyde (3.5 mmol, 1.0 equiv) and amine (10.0 mmol, 2.85 equiv) in MeOH (25 mL) at 25 °C, and the resultant mixture was stirred for 12 h. Upon completion, the pH of the reaction media was acidified to a value of less than 2 using concentrated HCl; the contents were then concentrated directly. The resultant yellow residue was dissolved in water (10 mL) and extracted with Et_2O (15 mL) to remove any neutral impurities. The aqueous layer was then made alkaline (pH >10) using saturated aqueous K_2CO_3 and was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired aminoalcohol product in high purity.

Data for 118: R_f=0.01 (silica gel, EtOAc); IR (film): ν_{max}=3435, 2940, 1636, 1513, 1357, 694 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): δ=8.18 (s, 1H), 8.04 (d, J=7.9 Hz, 1H), 7.70 (d, J=7.5 Hz, 1H), 7.52 (t, J=7.9 Hz, 1H), 3.85 (s, 2H), 3.55 (t, J=5.3 Hz, 2H), 2.65 (t, J=5.2 Hz, 2H), 2.58 ppm (brs, 2H); ^{13}C NMR (150 MHz, CD_3CN): δ=149.2, 144.2, 135.3, 130.2, 123.4, 122.5, 61.5, 52.9, 51.6 ppm; HRMS (MALDI-FTMS) calcd for $C_9H_{13}N_2O_3^+$ $[M+H]^+$: 197.0921; found: 197.0921.

Data for 120: R_f=0.04 (silica gel, EtOAc); IR (film): ν_{max}=3439, 1636, 1452, 1041, 629, 542 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): δ=6.70 (d, J=3.1 Hz, 1H), 6.59 (d, J=2.2 Hz, 1H), 3.85 (s, 2H), 3.54 (t, J=5.3 Hz, 2H), 2.82 (brs, 2H), 2.66 (t, J=5.3 Hz, 2H), 2.41 ppm (s, 3H); ^{13}C NMR (150 MHz, CD_3CN): δ=142.8, 139.6, 125.8, 125.5, 61.3, 51.4, 48.6, 15.3 ppm; HRMS (MALDI-FTMS) calcd for $C_8H_{14}NOS^+$ $[M+H]^+$: 172.0791; found: 172.0791.

Data for 143: R_f=0.01 (silica gel, EtOAc); IR (film): ν_{max}=3418, 2953, 1636, 1514, 1467, 1303, 1249, 1180, 1030, 818, 602 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): δ=7.24 (d, J=8.3 Hz, 2H), 6.87 (d, J=8.8 Hz, 2H), 3.75 (s, 3H), 3.67 (brs, 2H), 3.59 (t, J=6.2 Hz, 2H), 2.69 (t, J=6.6 Hz, 2H), 1.65 ppm (quin, J=6.1 Hz, 2H); ^{13}C NMR (150 MHz, CD_3CN): δ=159.6, 132.7, 130.5, 114.5, 62.0, 55.8, 53.4, 47.9, 32.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{18}NO_2S^+$ $[M+H]^+$: 196.1332; found: 196.1330.

Data for 145: R_f=0.02 (silica gel, EtOAc); IR (film): ν_{max}=3434, 2970, 1636, 1471, 1409, 1309, 1061, 639 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): δ=7.65 (d, J=8.3 Hz, 2H), 7.47 (d, J=8.3 Hz, 2H), 3.79 (s, 2H), 3.58 (t, J=5.7 Hz, 2H), 2.77 (brs, 2H), 2.66 (t, J=6.6 Hz, 2H), 1.63 ppm (quin, J=6.1 Hz, 2H); ^{13}C NMR (150 MHz, CD_3CN): δ=147.5, 133.0, 129.6, 119.8, 111.0, 62.1, 53.7, 48.1, 32.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{15}N_2O^+$ $[M+H]^+$: 191.1179; found: 191.1178.

Data for 147: R_f=0.02 (silica gel, EtOAc); IR (film): ν_{max}=3429, 2940, 1641, 1566, 1471, 1067, 778, 667 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): δ=7.49 (s, 1H), 7.37 (d, J=7.8 Hz, 1H), 7.26 (d, J=7.4 Hz, 1H), 7.21 (t, J=7.9 Hz, 1H), 3.69 (s, 2H), 3.57 (t, J=6.2 Hz, 2H), 3.05 (brs, 2H), 2.65 (t, J=6.5 Hz, 2H), 1.63 ppm (quin, J=6.1 Hz, 2H); ^{13}C NMR (150 MHz, CD_3CN): δ=144.3, 131.8, 131.1, 130.6, 127.9, 122.8, 62.0, 53.5, 48.0, 32.8 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{15}BrNO^+$ $[M+H]^+$: 244.0331; found: 244.0333.

Data for 149: R_f=0.05 (silica gel, EtOAc); IR (film): ν_{max}=3447, 2940, 1636, 1469, 1060, 798, 602 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): δ=6.70 (d, J=3.1 Hz, 1H), 6.59 (d, J=2.2 Hz, 1H), 3.83 (s, 2H), 3.59 (t, J=6.1 Hz, 2H), 3.09 (brs, 2H), 2.70 (t, J=6.2 Hz, 2H), 2.41 (s, 3H), 2.13 ppm (quin, J=6.1 Hz, 2H); ^{13}C NMR (150 MHz, CD_3CN): δ=142.7, 139.5, 125.8, 125.6, 62.2, 48.9, 47.9, 32.7, 15.4 ppm; HRMS (MALDI-FTMS) calcd for $C_9H_{16}NOS^+$ $[M+H]^+$: 186.0947; found: 186.0946.

Data for 151: R_f=0.07 (silica gel, EtOAc/hexanes, 1:2); IR (film): ν_{max}=3376, 2934, 2861, 1650, 1528, 1476, 1349, 1062, 806, 733, 690 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ=8.13 (s, 1H), 8.06 (d, J=8.3 Hz, 1H), 7.66 (d, J=7.4 Hz, 1H), 7.47 (t, J=7.9 Hz, 1H), 3.86 (s, 2H), 3.56 (t, J=4.9 Hz, 2H), 3.28 (brs, 2H), 2.66 (t, J=5.7 Hz, 2H), 1.61 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=148.1, 141.4, 134.4, 129.4, 122.9, 122.1, 62.3, 52.8, 49.1, 31.5, 27.6 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{17}N_2O_3S^+$ $[M+H]^+$: 225.1234; found: 225.1239.

General procedure for the synthesis of sulfamides from precursor aminoalcohols: The aminoalcohol (0.5 mmol, 1.0 equiv) was dissolved in anhydrous THF (5 mL) and the appropriate Burgess-type reagent (1.25 mmol, 2.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 8 h. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were then washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

Data for 114: R_f=0.33 (silica gel, CH_2Cl_2); IR (film): ν_{max}=3447, 2877, 1730, 1458, 1328, 1245, 1217, 1159, 1133, 1081, 1018, 963, 936, 792, 764, 712, 644, 614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.84 (s, 3H), 3.82 (t, J=6.8 Hz, 2H), 3.33 (t, J=6.8 Hz, 2H), 2.75 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.9, 54.1, 46.0, 42.7, 33.1 ppm; HRMS (MALDI-FTMS) calcd for $C_5H_{10}N_2O_4SNa^+$ $[M+Na]^+$: 217.0253; found: 217.0250.

Data for 115: R_f=0.40 (silica gel, CH_2Cl_2); IR (film): ν_{max}=2966, 1731, 1458, 1390, 1323, 1166, 1079, 1018, 976, 942, 908, 842, 760, 700, 643 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.42–7.32 (m, 5H), 5.30 (s, 2H), 3.84 (t, J=6.4 Hz, 2H), 3.33 (t, J=6.8 Hz, 2H), 2.77 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.4, 134.7, 128.5, 128.4, 127.8, 68.8, 46.0, 42.7, 33.2 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{14}N_2O_4SNa^+$ $[M+Na]^+$: 293.0566; found: 293.0568.

Data for 117: R_f=0.67 (silica gel, EtOAc); IR (film): ν_{max}=2984, 1730, 1449, 1349, 1320, 1216, 1174, 1146, 1059, 1001, 972, 945, 919, 780, 732, 698, 641, 601, 542, 488 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.36 (m, 5H), 4.21 (s, 2H), 3.90 (s, 3H), 3.80 (t, J=6.8 Hz, 2H), 3.24 ppm (t, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.1, 133.8, 128.9, 128.8, 128.5, 54.3, 50.4, 43.0, 42.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{14}N_2O_4SNa^+$ $[M+Na]^+$: 293.0566; found: 293.0565.

Data for 119: R_f=0.20 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max}=2957, 1736, 1636, 1532, 1442, 1326, 1162, 729, 645, 545 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ=8.24 (s, 1H), 8.20 (d, J=8.3 Hz, 1H), 7.76 (d, J=7.5 Hz, 1H), 7.59 (t, J=7.9 Hz, 1H), 4.33 (s, 2H), 3.90 (s, 3H), 3.88 (t, J=6.2 Hz, 2H), 3.34 ppm (t, J=6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ=150.9, 148.4, 136.3, 134.6, 130.0, 123.5, 123.4, 54.4, 49.8, 43.7, 42.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{13}N_3O_6SNa^+$ $[M+Na]^+$: 338.0417; found: 338.0416.

Data for 121: R_f=0.43 (silica gel, EtOAc/hexanes, 1:1); IR (film): ν_{max}=2957, 1737, 1640, 1442, 1323, 1221, 1161, 1096, 1040, 792, 758, 645 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ=6.85 (d, J=3.5 Hz, 1H), 6.62 (m, 1H), 3.90 (s, 2H), 3.77 (t, J=6.5 Hz, 2H), 3.48 (s, 3H), 3.34 (t, J=6.5 Hz, 2H), 2.46 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ=151.1, 141.9, 133.3, 128.5, 124.9, 54.3, 45.7, 43.2, 42.7, 15.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{14}N_2O_4S_2Na^+$ $[M+Na]^+$: 313.0287; found: 313.0297.

Data for 123: R_f=0.34 (silica gel, CH_2Cl_2); IR (film): ν_{max}=2981, 1728, 1446, 1364, 1343, 1314, 1255, 1198, 1148, 1077, 1007, 954, 866, 806, 760, 675, 616, 501 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.86 (s, 3H), 3.77 (t, J=6.0 Hz, 2H), 3.40 (t, J=6.4 Hz, 2H), 1.41 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.0, 57.1, 54.1, 41.6, 39.7, 27.3 ppm; HRMS (MALDI-FTMS) calcd for $C_8H_{16}N_2O_4SNa^+$ $[M+Na]^+$: 259.0723; found: 259.0721.

Data for 124: R_f=0.30 (silica gel, CH_2Cl_2); IR (film): ν_{max}=2989, 2908, 1724, 1472, 1455, 1378, 1314, 1208, 1143, 1079, 1002, 938, 901, 862, 803, 761, 673, 615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=5.90 (m, 1H), 5.41 (dd, J=17.2, 1.6 Hz, 1H), 5.25 (dd, J=10.4, 1.6 Hz, 1H), 4.74 (dt, J=5.2, 1.6 Hz, 2H), 3.77 (t, J=6.0 Hz, 2H), 3.41 (t, J=6.4 Hz, 2H), 1.42 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.3, 130.9, 118.6, 67.4, 57.1, 41.5, 39.6, 27.3 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{18}N_2O_4SNa^+$ $[M+Na]^+$: 285.0879; found: 285.0879.

Data for 126: R_f=0.29 (silica gel, CH_2Cl_2); IR (film): ν_{max}=2957, 1734, 1444, 1320, 1273, 1224, 1183, 1159, 1006, 944, 896, 787, 761, 612 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.90 (dd, J=9.2, 6.0 Hz, 1H), 3.86 (s, 3H), 3.48 (m, 1H), 3.42 (dd, J=10.4, 9.2 Hz, 1H), 3.24 (m, 1H), 2.71 (dt, J=9.2, 2.8 Hz, 1H), 1.94 (m, 1H), 1.87 (m, 2H), 1.61 (m, 1H), 1.47–1.31 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.9, 54.1, 53.5, 49.3, 42.6, 28.5, 23.1, 22.0 ppm; HRMS (MALDI-FTMS) calcd for $C_8H_{14}N_2O_4SNa^+$ $[M+Na]^+$: 257.0566; found: 257.0558.

Data for 127: R_f=0.51 (silica gel, CH_2Cl_2); IR (film): ν_{max}=3423, 2931, 1731, 1390, 1320, 1167, 1002, 885, 615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.42–7.32 (m, 5H), 5.30 (s, 2H), 3.92 (dd, J=9.2, 5.6 Hz, 1H), 3.50 (dt, J=11.2, 3.4 Hz, 1H), 3.45 (appt, J=9.2 Hz, 1H), 3.22 (m, 1H), 2.74 (dt, J=12.4, 3.2 Hz, 1H), 1.91–1.82 (m, 2H), 1.64 (m, 2H), 1.40 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.5, 134.9, 128.6, 128.4, 127.8,

68.8, 53.6, 49.3, 42.7, 28.7, 23.3, 22.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{14}H_{18}N_2O_4SNa^+$ $[M+Na]^+$: 333.0879; found: 333.0875.

Data for 129: $R_f=0.30$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=2955$, 1743, 1602, 1590, 1496, 1149, 1372, 1326, 1273, 1214, 1167, 1143, 1079, 1061, 950, 756, 703, 650, 585 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.43$–7.34 (m, 4H), 7.27 (t, $J=7.2$ Hz, 1H), 4.00 (t, $J=6.4$ Hz, 2H), 3.91 (s, 3H), 3.83 ppm (t, $J=6.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=150.9$, 136.3, 129.6, 126.6, 121.7, 54.4, 43.5, 42.2 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{12}N_2O_4SNa^+$ $[M+Na]^+$: 279.0410; found: 279.0411.

Data for 130: $R_f=0.43$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=1720$, 1661, 1543, 1496, 1422, 1332, 1198, 1010, 920, 740, 602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.43$–7.40 (m, 2H), 7.39–7.35 (m, 2H), 7.28 (t, $J=6.6$ Hz, 1H), 5.96 (m, 1H), 5.47 (dd, $J=17.3$, 1.5 Hz, 1H), 5.30 (dt, $J=11.8$, 1.5 Hz, 1H), 4.81 (dt, $J=5.5$, 1.5 Hz, 2H), 4.04 (t, $J=6.6$ Hz, 2H), 3.87 ppm (t, $J=5.9$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=150.3$, 136.5, 130.8, 129.7, 126.8, 21.9, 119.1, 68.0, 43.6, 42.2 ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{14}N_2O_4SNa^+$ $[M+Na]^+$: 305.0566; found: 305.0566.

Data for 132: $R_f=0.22$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=2986$, 1727, 1639, 1509, 1433, 1339, 1286, 1163, 1133, 1081, 834, 751, 722, 687, 622 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): $\delta=8.28$ (dt, $J=9.2$, 3.2 Hz, 2H), 7.47 (dt, $J=8.8$, 3.6 Hz, 2H), 4.05 (t, $J=6.2$ Hz, 2H), 3.98 (t, $J=6.4$ Hz, 2H), 3.88 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): $\delta=151.6$, 126.3, 119.2, 118.3 (2C), 55.1, 43.9, 43.0 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{11}N_3O_6SNa^+$ $[M+Na]^+$: 324.0261; found: 324.0257.

Data for 134: $R_f=0.40$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=2958$, 1733, 1619, 1472, 1437, 1390, 1325, 1273, 1173, 1120, 1073, 1006, 871, 806, 760, 698, 682, 612 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): $\delta=7.89$ (s, 1H), 7.86 (s, 2H), 4.04 (m, 2H), 3.98 (m, 2H), 3.88 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): $\delta=151.3$, 139.9, 133.1 (d, $J=132.0$ Hz), 120.9, 119.7, 54.9, 44.0, 43.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{10}F_6N_2O_4SNa^+$ $[M+Na]^+$: 415.0158; found: 415.0169.

Data for 136: $R_f=0.14$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=2942$, 2837, 1713, 1601, 1502, 1461, 1431, 1326, 1249, 1213, 1112, 1014, 864, 806, 763, 622 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): $\delta=6.64$ (s, 2H), 3.97 (t, $J=6.4$ Hz, 2H), 3.85 (s, 3H), 3.83 (m, 2H), 3.82 (s, 6H), 3.72 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): $\delta=155.5$, 152.6, 138.3, 134.3, 101.7, 61.5, 57.5, 55.5, 45.5, 44.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{13}H_{18}N_2O_7SNa^+$ $[M+Na]^+$: 369.0727; found: 369.0738.

Data for 138: $R_f=0.46$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=3472$, 2966, 1737, 1572, 1455, 1443, 1396, 1326, 1273, 1243, 1179, 1149, 1096, 1070, 955, 861, 791, 773, 621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.26$ (m, 1H), 7.83 (m, 1H), 7.54–7.47 (m, 3H), 7.37 (t, $J=7.6$ Hz, 1H), 6.89 (d, $J=7.6$ Hz, 1H), 4.67 (dt, $J=11.6$, 8.4 Hz, 1H), 4.44 (dd, $J=9.2$, 3.6 Hz, 1H), 4.35 (t, $J=9.2$ Hz, 1H), 3.94 (s, 3H), 3.88 (sep, $J=6.4$ Hz, 1H), 3.58 (m, 2H), 1.30 ppm (appt, $J=7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=153.6$, 151.1, 134.5, 127.6, 126.6, 125.8, 125.5, 121.7, 121.2, 104.9, 65.4, 52.7, 43.3, 41.0, 20.9, 19.8 ppm; HRMS (MALDI-FTMS) calcd for $C_{18}H_{22}N_2O_5SNa^+$ $[M+Na]^+$: 401.1142; found: 401.1129.

Data for 140: $R_f=0.40$ (silica gel, EtOAc); IR (film): $\nu_{max}=3420$, 1637, 1432, 1329, 1156, 1024, 984, 756, 702, 657 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta=2.90$ (t, $J=6.4$ Hz, 4H), 2.84 (s, 6H), 2.57 (t, $J=6.4$ Hz, 4H), 2.35 ppm (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta=150.6$, 54.0, 44.8, 44.0, 43.5 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{18}N_4O_8S_2Na^+$ $[M+Na]^+$: 409.0458; found: 409.0447.

Data for 142: $R_f=0.24$ (silica gel, MeOH/CH_2Cl_2, 3:97); IR (film): $\nu_{max}=3272$, 2919, 1731, 1496, 1455, 1355, 1326, 1237, 1161, 961, 861, 756, 591 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.45$ (d, $J=7.6$ Hz, 1H), 7.29 (dt, $J=8.4$, 1.6 Hz, 1H), 7.22 (dd, $J=8.0$, 1.6 Hz, 1H), 7.16 (t, $J=7.2$ Hz, 1H), 5.29 (brs, 1H), 4.72 (s, 2H), 3.71 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=151.9$, 135.1, 131.8, 129.5, 129.2, 125.9, 122.3, 63.2, 53.7 ppm; HRMS (MALDI-FTMS) calcd for $C_9H_{10}N_2O_4SNa^+$ $[M+Na]^+$: 265.0253; found: 265.0256.

Data for 144: $R_f=0.40$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max}=2957$, 1724, 1636, 1513, 1440, 1382, 1291, 1250, 1176, 1030, 775, 624 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta=7.23$ (d, $J=8.8$ Hz, 2H), 6.87 (d, $J=8.3$ Hz, 2H), 4.30 (s, 2H), 4.01 (t, $J=5.7$ Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.42 (t, $J=6.1$ Hz, 2H), 1.79 ppm (quin, $J=6.1$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=159.4$, 153.7, 129.8, 126.6, 114.0, 55.2, 54.2, 51.5, 47.4, 46.6, 19.2 ppm; HRMS (MALDI-FTMS) calcd for $C_{13}H_{18}N_2O_5SNa^+$ $[M+Na]^+$: 337.0829; found: 337.0828.

Data for 146: $R_f=0.24$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max}=2982$, 2231, 1732, 1636, 1435, 1359, 1297, 1253, 1170, 1032, 949, 864, 584 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta=7.65$ (d, $J=8.3$ Hz, 2H), 7.46 (d, $J=7.9$ Hz, 2H), 4.42 (s, 2H), 4.06 (t, $J=5.7$ Hz, 2H), 3.86 (s, 3H), 3.49 (t, $J=5.7$ Hz, 2H), 1.86 ppm (quin, $J=6.1$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.5$, 140.8, 132.5, 128.6, 118.3, 111.9, 54.4, 51.9, 48.2, 47.5, 19.5 ppm; HRMS (MALDI-FTMS) calcd for $C_{13}H_{15}N_3O_4SNa^+$ $[M+Na]^+$: 332.0675; found: 332.0681.

Data for 148: $R_f=0.44$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max}=2956$, 1729, 1571, 1437, 1383, 1307, 1273, 1176, 1023, 953, 843, 777, 609, 564 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta=7.46$ (s, 1H), 7.42 (d, $J=7.9$ Hz, 1H), 7.24 (d, $J=7.9$ Hz, 1H), 7.21 (t, $J=7.4$ Hz, 1H), 4.31 (s, 2H), 4.02 (t, $J=5.7$ Hz, 2H), 3.84 (s, 3H), 3.45 (t, $J=5.7$ Hz, 2H), 1.81 ppm (quin, $J=6.1$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.6$, 137.4, 131.2, 131.1, 130.3, 126.8, 122.7, 54.3, 51.5, 47.5, 47.4, 19.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{12}H_{16}BrN_2O_4S^+$ $[M+H]^+$: 363.0009; found: 363.0011.

Data for 150: $R_f=0.45$ (silica gel, EtOAc/hexanes, 1:1); IR (film): $\nu_{max}=2970$, 1726, 1636, 1439, 1383, 1298, 1265, 1176, 854, 775, 596 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta=6.78$ (s, 1H), 6.59 (s, 1H), 4.46 (s, 2H), 4.00 (t, $J=6.1$ Hz, 2H), 3.86 (s, 3H), 3.52 (t, $J=5.7$ Hz, 2H), 2.45 (s, 3H), 1.78 ppm (brm, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.8$, 141.4, 134.7, 127.8, 124.9, 54.4, 47.5, 47.3, 46.7, 19.6, 15.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{11}H_{16}N_2O_4S_2Na^+$ $[M+Na]^+$: 327.0444; found: 327.0443.

Data for 152: $R_f=0.42$ (silica gel, EtOAc/hexanes, 1:2); IR (film): $\nu_{max}=2953$, 1725, 1531, 1437, 1350, 1274, 1164, 925, 765, 602 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta=8.25$–8.19 (m, 2H), 7.78 (d, $J=9.2$ Hz, 1H), 7.59 (t, $J=8.3$ Hz, 1H), 7.69 (s, 2H), 3.90 (s, 3H), 3.85 (t, $J=4.8$ Hz, 2H), 3.35 (t, $J=5.2$ Hz, 2H), 1.97 (brm, 2H), 1.87 ppm (brm, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.6$, 148.2, 138.0, 133.7, 129.9, 123.0, 122.5, 54.2, 51.1, 46.3, 46.1, 28.0, 23.7 ppm; HRMS (MALDI-FTMS) calcd for $C_{13}H_{18}N_3O_6S^+$ $[M+H]^+$: 344.0911; found: 344.0909.

Data for 154: $R_f=0.63$ (silica gel, EtOAc); IR (film): $\nu_{max}=3251$, 2958, 1743, 1661, 1602, 1473, 1455, 1367, 1237, 1167, 1108, 1061, 985, 856, 756, 591 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.31$ (d, $J=8.0$ Hz, 1H), 7.20–7.16 (m, 2H), 7.03 (t, $J=7.6$ Hz, 1H), 5.28 (brs, 1H), 4.31 (t, $J=8.8$ Hz, 2H), 3.64 (s, 3H), 3.15 ppm (t, $J=8.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=151.7$, 140.6, 131.5, 127.6, 125.3, 123.8, 113.9, 53.5, 51.6, 27.9 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{12}N_2O_5SNa^+$ $[M+Na]^+$: 279.0410; found: 279.0412.

Data for 156: $R_f=0.25$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=3252$, 2962, 1730, 1443, 1408, 1337, 1208, 1167, 1097, 1021, 950, 921, 786, 757, 651, 633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=3.81$ (t, $J=6.4$ Hz, 2H), 3.76 (s, 3H), 3.49 (brs, 1H), 3.40 ppm (t, $J=6.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=151.5$, 54.0, 48.2, 39.1 ppm; HRMS (MALDI-FTMS) calcd for $C_4H_8N_2O_4SNa^+$ $[M+Na]^+$: 203.0097; found: 203.0097.

Data for 158: $R_f=0.49$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=3286$, 1732, 1470, 1454, 1347, 1252, 1154, 1057, 882, 771, 590 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta=5.63$ (brs, 1H), 3.89 (s, 3H), 3.62 (s, 2H), 1.40 ppm (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=152.5$, 69.6, 58.9, 53.9, 24.3 ppm; HRMS (MALDI-FTMS) calcd for $C_6H_{12}N_2O_4SNa^+$ $[M+Na]^+$: 231.0410; found: 231.0412.

Data for 160: $R_f=0.44$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=3270$, 1731, 1443, 1351, 1270, 1174, 1081, 1010, 774, 625, 568 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta=4.91$ (brt, $J=7.7$ Hz, 1H), 4.09 (t, $J=5.5$ Hz, 2H), 3.93 (s, 3H), 3.62 (dt, $J=7.4$, 5.9 Hz, 2H), 1.95 ppm (quin, $J=5.9$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=153.7$, 54.5, 47.3, 44.3, 24.7 ppm; HRMS (MALDI-FTMS) calcd for $C_5H_{10}N_2O_4SNa^+$ $[M+Na]^+$: 217.0253; found: 217.0254.

Data for 162: $R_f=0.52$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max}=3288$, 1732, 1472, 1352, 1250, 1160, 1065, 874, 764, 702, 587 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta=7.32$–7.25 (m, 5H), 6.10 (brt, $J=5.7$ Hz, 1H), 4.87 (dd, $J=8.8$, 3.1 Hz, 1H), 3.72 (s, 3H), 3.37 (m, 1H), 3.22 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=152.5$, 140.6, 128.9, 128.4, 126.1, 72.7, 53.9, 50.8 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{12}N_2O_4SNa^+$ $[M+Na]^+$: 279.0410; found: 279.0411.

Data for 164: $R_f = 0.55$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3540$, 3301, 1730, 1455, 1416, 1360, 1253, 1165, 1092, 1060, 969, 852, 772, 702, 606, 552 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): $\delta = 7.30–7.21$ (m, 10H), 6.46 (d, $J = 9.2$ Hz, 1H), 4.98 (d, $J = 6.1$ Hz, 1H), 4.54 (dd, $J = 9.2$, 6.1 Hz, 1H), 3.43 ppm (s, 3H); ^{13}C NMR (150 MHz, CD_3CN): $\delta = 152.4$, 142.1, 138.4, 129.3, 129.3, 128.8, 128.6, 128.5, 128.4, 127.7, 76.4, 64.6, 53.4 ppm; HRMS (MALDI-FTMS) calcd for $C_{16}H_{16}N_2O_4SNa^+$ $[M+Na]^+$: 355.0723; found: 355.0724.

General conditions for the removal of methyl carbamate protection from cyclic sulfamides: 10% aqueous NaOH (0.5 mL) was added to a solution of the CO_2Me-protected sulfamidate (0.2 mmol, 1.0 equiv) in MeOH/H_2O (2:1, 3 mL) at 25 °C. After stirring this mixture for 2 h at 25 °C, the reaction contents were poured into saturated aqueous NH_4Cl (5 mL), acidified with 1 M aqueous HCl (2 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated to give the desired deprotected sulfamidate in high purity.

Data for 165: $R_f = 0.14$ (silica gel, MeOH/CH_2Cl_2, 3:97); IR (film): $\nu_{max} =$ 3440, 3225, 1621, 1473, 1387, 1318, 1282, 1176, 1127, 1002, 788 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.61$ (s, 1H), 7.58 (s, 2H), 4.99 (t, $J =$ 7.9 Hz, 1H), 4.00 (t, $J = 6.5$ Hz, 2H), 3.77 ppm (q, $J = 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.4$, 132.9 (q, $J = 137.3$ Hz), 123.8, 122.0, 116.8, 48.8, 39.4 ppm; MS (ESI) calcd for $C_{10}H_7F_6N_2O_2S^+$ $[M-H]^+$: 333; found: 333.

Data for 166: $R_f = 0.12$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3244$, 2904, 1449, 1296, 1161, 1021, 897, 779, 715, 688, 616 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.37–7.30$ (m, 5H), 4.71 (br s, 1H), 4.17 (s, 2H), 3.46 (t, $J =$ 6.4 Hz, 2H), 3.27 ppm (t, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.1$, 128.7, 128.6, 128.1, 50.4, 48.1, 39.9 ppm; HRMS (MALDI-FTMS) calcd for $C_9H_{12}N_2O_2SNa^+$ $[M+Na]^+$: 235.0512; found: 235.0515.

General conditions for the removal of allyl carbamate protection from cyclic sulfamides: Et_2NH (0.828 mL, 8.0 mmol, 40 equiv) was added to a solution of the Alloc-protected sulfamidate (0.2 mmol, 1.0 equiv) in CH_3CN/H_2O (1:1, 3 mL) at 25 °C. After stirring this mixture for 5 minutes at 25 °C, $Pd(OAc)_2$ (0.002 g, 0.020 mmol, 0.1 equiv) and TPPTS (0.023 g, 0.040 mmol, 0.2 equiv) were added sequentially, providing a yellow solution which was stirred for an additional 30 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated to give the desired deprotected sulfamidate in high purity.[29]

Data for 167: $R_f = 0.11$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3258$, 3056, 2982, 1374, 1266, 1206, 1155, 1005, 739 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 4.27$ (br s, 1H), 3.51 (d, $J = 6.6$ Hz, 6H), 3.45 (d, $J = 6.6$ Hz, 2H), 1.42 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 63.2$, 45.2, 39.0, 27.2 ppm; HRMS (MALDI-FTMS) calcd for $C_6H_{14}N_2O_4SNa^+$ $[M+Na]^+$: 201.0668; found: 201.0665.

Data for 168: $R_f = 0.14$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3190$, 1596, 1417, 1298, 1232, 1154, 1118, 1031, 950, 747, 688, 615, 464 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.38–7.35$ (m, 2H), 7.23 (d, $J = 7.5$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H), 4.86 (br s, 1H), 3.88 (t, $J = 6.1$ Hz, 2H), 3.65 ppm (t, $J = 6.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 137.7$, 129.5, 124.1, 118.2, 48.7, 39.6 ppm; MS (ESI) calcd for $C_8H_{10}N_2O_2SNa^+$ $[M+Na]^+$: 221; found: 221.

General conditions for the removal of benzyl carbamate protection from cyclic sulfamides: Pd/C (0.002 g, 10 wt%, catalytic) was added to a solution of the Cbz-protected sulfamidate (0.2 mmol, 1.0 equiv) in EtOH/EtOAc (4:1, 3 mL) at 25 °C. The resultant suspension was then equipped with a balloon containing hydrogen gas (pressure of ~2 atm) and allowed to stir for 24 h at 25 °C. Upon completion, the reaction contents were filtered through Celite and concentrated to give the desired deprotected sulfamidate in high purity.

Data for 169: $R_f = 0.22$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3548$, 3254, 2925, 1454, 1389, 1295, 1201, 1154, 1014, 914, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.61$ (br s, 1H), 3.58 (t, $J = 5.2$ Hz, 2H), 3.47 (t, $J = 5.2$ Hz, 2H), 2.82 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.5$, 39.7, 32.7 ppm; HRMS (MALDI-FTMS) calcd for $C_3H_9N_2O_4S^+$ $[M+H]^+$: 137.0379; found: 137.0373.

Data for 170: $R_f = 0.10$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3559$, 3264, 2944, 2854, 1636, 1444, 1397, 1303, 1220, 1159, 1064, 1025, 1003, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.32$ (br s, 1H), 3.50 (m, 2H), 3.22–3.14 (m, 2H), 2.67 (dt, $J = 11.2$, 3.2 Hz, 1H), 1.90–1.80 (m, 3H), 1.59 (m, 1H), 1.42–1.26 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 57.6$, 47.6, 43.1, 29.6, 23.6, 22.5 ppm; HRMS (MALDI-FTMS) calcd for $C_6H_{12}N_2O_2SNa^+$ $[M+Na]^+$: 199.0512; found: 199.0515.

Alkylated sulfamide 171: Sulfamide **166** (0.053 g, 0.250 mmol, 1.0 equiv) was dissolved in DMSO (2 mL) and treated with NaH (0.050 g, 60% dispersion in mineral oil, 1.25 mmol, 5.0 equiv) at 25 °C. After stirring the resultant reaction mixture for 10 minutes at 25 °C, 4-bromo-1-butene (0.102 mL, 1.0 mmol, 4.0 equiv) and TBAI (0.01 g, catalytic) were added sequentially; the reaction mixture was then stirred for an additional 15 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then washed with water (2 × 15 mL), dried ($MgSO_4$), and concentrated. The resultant light yellow oil was purified by flash column chromatography (silica gel, EtOAc/hexanes, 1:3 → 1:1) to give alkylated sulfamidate **171** (0.059 g, 89% yield) as an amorphous white solid. $R_f = 0.18$ (silica gel, CH_2Cl_2/hexanes, 2:1); IR (film): $\nu_{max} = 3524$, 2925, 1635, 1448, 1301, 1166, 1143, 1113, 914, 779, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.37–7.30$ (m, 5H), 5.82 (m, 1H), 5.14 (dd, $J =$ 17.0, 2.0 Hz, 1H), 5.11 (dd, $J = 10.5$, 1.6 Hz, 1H), 4.19 (s, 2H), 3.29 (dd, $J = 6.0$, 1.2 Hz, 2H), 3.18–3.13 (m, 4H), 2.40 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 134.9$, 134.5, 128.7, 128.6, 128.1, 77.2, 51.3, 47.3, 45.6, 44.8, 32.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{13}H_{18}N_2O_2SNa^+$ $[M+Na]^+$: 289.0981; found: 289.0981.

General conditions for the synthesis of linear sulfamides: The diol (0.5 mmol, 1.0 equiv) was dissolved in anhydrous THF (5 mL) and the Burgess reagent (**1**, 0.75 mmol, 1.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 2 h. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were then washed with water (50 mL), dried ($MgSO_4$), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

Data for 173: $R_f = 0.25$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3276$, 3201, 2940, 1714, 1490, 1454, 1348, 1166, 1084, 1008, 850, 778, 608 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.83$ (s, 1H), 5.29 (d, $J = 7.0$ Hz, 1H), 3.81 (s, 3H), 3.30 (br dd, $J = 7.0$, 3.5 Hz, 1H), 1.94 (m, 2H), 1.74 (m, 2H), 1.58 (m, 1H), 1.36–1.27 (m, 4H), 1.18 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 152.0$, 53.6, 53.5, 33.2, 25.1, 24.5 ppm; HRMS (MALDI-FTMS) calcd for $C_8H_{16}N_2O_4SNa^+$ $[M+Na]^+$: 259.0723; found: 259.0728.

Data for 175: $R_f = 0.16$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3260$, 2924, 1750, 1460, 1419, 1355, 1231, 1155, 1131, 1002, 943, 855, 773, 732, 603, 579 cm^{-1}; ^1H NMR (300 MHz, CD_3CN): $\delta = 7.31–7.20$ (m, 5H), 5.24 (s, 1H), 4.43 (s, 2H), 3.74 (s, 3H), 2.80 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 152.0$, 135.6, 128.7, 128.1 128.0, 55.1, 53.5, 35.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{10}H_{14}N_2O_4SNa^+$ $[M+Na]^+$: 281.0566; found: 281.0567.

Data for 177: $R_f = 0.38$ (silica gel, CH_2Cl_2); IR (film): $\nu_{max} = 3448$, 3271, 2919, 1748, 1449, 1361, 1331, 1225, 1137, 1102, 1049, 1026, 979, 861, 585 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): $\delta = 7.49$ (br s, 1H), 3.75 (s, 3H), 3.43 (br m, 2H), 1.81–1.60 (m, 14H), 1.31–1.24 (m, 4H), 1.08 ppm (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 151.3$, 58.9, 53.1, 32.1, 26.3, 25.1 ppm; HRMS (MALDI-FTMS) calcd for $C_{14}H_{26}N_2O_4SNa^+$ $[M+Na]^+$: 341.1505; found: 341.1501.

Data for 179: $R_f = 0.47$ (silica gel, EtOAc); IR (film): $\nu_{max} = 3275$, 2907, 1748, 1461, 1361, 1261, 1167, 1114, 1079, 1015, 950, 862, 768, 721, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.41$ (br s, 1H), 3.73 (s, 3H), 3.70 (t, $J = 4.8$ Hz, 4H), 3.33 ppm (t, $J = 4.8$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.8$, 66.1, 53.4, 46.4 ppm; HRMS (MALDI-FTMS) calcd for $C_6H_{12}N_2O_5SNa^+$ $[M+Na]^+$: 247.0359; found: 247.0361.

Data for 181: $R_f = 0.63$ (silica gel, EtOAc); IR (film): $\nu_{max} = 3256$, 2957, 1742, 1466, 1420, 1355, 1308, 1238, 1155, 1062, 950, 856, 759, 591 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.19$ (br s, 1H), 4.51 (s, 2H), 3.79 (t, $J =$ 6.4 Hz, 2H), 3.75 (s, 3H), 3.03 ppm (t, $J = 6.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.6$, 53.6, 51.7, 50.6, 30.9 ppm; HRMS (MALDI-FTMS) calcd for $C_5H_{10}N_2O_4S_2Na^+$ $[M+Na]^+$: 248.9974; found: 248.9981.

Data for 183: $R_f = 0.20$ (silica gel, MeOH/CH_2Cl_2, 3:97); IR (film): $\nu_{max} =$ 3260, 2959, 1731, 1510, 1468, 1351, 1250, 1215, 1162, 1030, 962, 865, 826, 772, 587, 541 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53$ (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 8.8$ Hz, 2H), 5.84 (s, 1H), 5.70 (br s, 1H), 4.12 (s, 3H), 4.07 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 158.0$, 152.1, 128.3, 124.8, 114.5, 55.4, 53.5 ppm; HRMS (MALDI-FTMS) calcd for $C_9H_{12}N_2O_5SNa^+$ $[M+Na]^+$: 283.0359; found: 283.0359.

Data for 185: $R_f = 0.53$ (silica gel, EtOAc); IR (film): $\nu_{max} = 3465$, 3111, 2954, 2225, 1743, 1607, 1507, 1460, 1361, 1225, 1161, 955, 932, 879, 832, 767, 573 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.42$ (d, $J = 8.8$ Hz, 2H), 7.08 (d, $J = 8.8$ Hz, 2H), 4.71 (br s, 2H), 3.42 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): $\delta = 153.4$, 143.4, 134.6, 119.8, 119.0, 107.6, 53.6 ppm; MS (ESI) calcd for $C_9H_9N_3O_4SNa^+$ $[M+Na]^+$: 278; found: 278.

Data for 187: $R_f = 0.14$ (silica gel, EtOAc); IR (film): $\nu_{max} = 3248$, 2945, 2838, 1749, 1467, 1361, 1237, 1149, 1073, 983, 860, 776, 584 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (br s, 1H), 4.49 (t, $J = 5.2$ Hz, 1H), 3.76 (s, 3H), 3.40 (s, 6H), 3.39 (m, 2H), 3.01 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.7$, 103.7, 54.7, 53.4, 52.7, 37.2 ppm; HRMS (MALDI-FTMS) calcd for $C_7H_{16}N_2O_6SNa^+$ $[M+Na]^+$: 279.0621; found: 279.0622.

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