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Rh-catalyzed alkene oxidation: a highly efficient and selective process for preparing *N*-alkoxysulfonyl aziridines

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Abstract—Unique alkoxysulfonyl aziridine heterocycles were prepared through selective intra- and intermolecular alkene oxidation reactions. These methods are general and perform efficiently at low Rh-catalyst loadings (1–2 mol %) with only a slight excess of an inexpensive commercial oxidant, $PhI(OAc)_2$. For intermolecular processes, trichloroethylsulfamate was identified as a novel and markedly effective N-atom source, allowing reactions to be conducted with limiting amounts of the olefin substrate. The aziridine products submit to facile, nucleophilic ring opening; these processes are regioselective and can be used to prepare polyfunctionalized amines, including α-aminoketones via the direct addition of Me_2SO.

1. Introduction

The versatility of aziridines as precursors to amine derivatives drives the development of preparative methods for this unique class of heterocycles.[1,2] Catalytic nitrogen atom transfer to alkenes is a particularly appealing strategy for the generation of aziridines because of the ready availability of olefinic starting materials and the direct nature of such a process. For this reason, intensive efforts by numerous labs have taken aim at the problem of alkene aziridination.[3] These studies have identified Cu-based catalysts as the most universal for promoting oxidation with hypervalent iodoimine-derived reagents of the general form $PhI{=}NSO_2Ar$. Nevertheless, the vast majority of reported protocols for effecting nitrene transfer employ multiple equivalents of the starting alkene, and thus the application of these processes has been largely relegated to simple, inexpensive substrates.[4] In our lab, alkoxysulfonamides (sulfamate esters) were found to be exceptional substrates for Rh-catalyzed C–H amination reactions (Fig. 1).[5] Related studies have further revealed the effectiveness of sulfamate esters for synthesizing aziridines

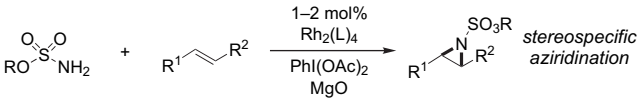

Figure 1. Rh-catalyzed oxidation affords *N*-alkoxysulfonyl aziridines.

in both intra- and intermolecular processes.[5b,6,7] Our methods thus make available a large and diverse set of alkoxysulfonyl-substituted aziridine products. In this report, we describe in detail the preparation and electrophilic reactivity of these novel compounds.

2. Results and discussion

2.1. Intra- and intermolecular aziridination

Interest in developing selective methods for alkene aziridination followed from our discovery that sulfamate esters were excellent substrates for Rh-catalyzed intramolecular C–H amination.[5a] Given the greater reactivity of π-bonds compared with σ-C–H centers toward chemical oxidants, we assumed that the Rh-mediated conditions would likely promote cyclization of homoallyl-derived sulfamates. Such expectations were indeed realized when homoallyl ester **1** was mixed with 2 mol % $Rh_2(oct)_4$, $PhI(OAc)_2$, and MgO to give the corresponding bicyclic aziridine **2** in 83% yield (Fig. 2). This unusual heterocycle is remarkably stable to chromatographic purification, and yet sufficiently reactive for ring opening under ambient conditions with common nucleophiles (vide infra). Following an empirical screen of different Rh complexes, the tetra-trifluoroacetamide adduct,

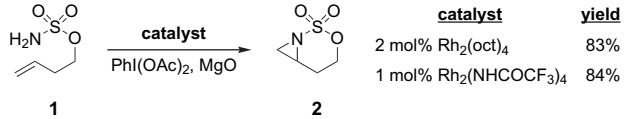

Figure 2. Intramolecular aziridination gives a novel bicyclic heterocycle.

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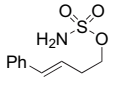
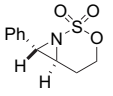
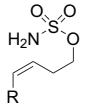
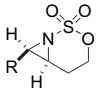
$Rh_2(NHCOCF_3)_4$, was found to be the catalyst of choice for effecting aziridine reactions across a varied spectrum of substituted starting materials.[8] In most cases, as little as 1 mol % of catalyst is needed to mediate the intramolecular aziridination event. Contemporaneous with these findings, others have delineated analogous processes for sulfamate-mediated aziridination using Cu- and Ru-based catalysts.[3g,9]

A number of differentially configured achiral and chiral unsaturated sulfamates have been prepared to map the scope of this aziridination process. Using standard conditions that employ 1–2 mol % $Rh_2(NHCOCF_3)_4$ and 1.1 equiv of commercial $PhI(OAc)_2$, substrates containing either *E*- or *Z*-alkenyl units are oxidized smoothly (Table 1). A notable feature of the Rh-catalyzed reaction follows from these collective data: *E*-olefins afford exclusively *trans* aziridines; conversely, *Z*-olefins give cis products. Stereospecificity is an invariant property of this Rh-mediated π-bond oxidation whether the reaction is performed in an intra- or intermolecular fashion. As seen in Table 1, cis-substituted vinylsilanes, α,β-unsaturated phosphonates, and conjugated enynes all engage in this process, giving single diastereomeric products (entry 2). These stable, heteroatom-substituted aziridines are rather unusual structural motifs, access to which is not readily apparent in the absence of this method.

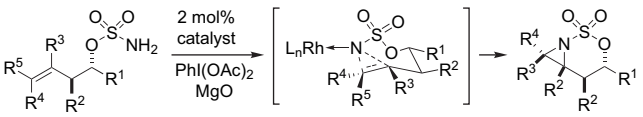
Table 1. Intramolecular reactions of achiral sulfamates

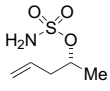
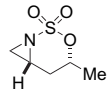
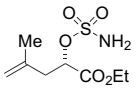
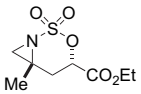
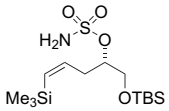
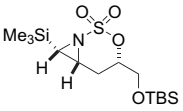
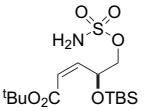
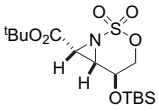
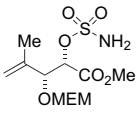
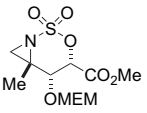
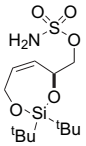
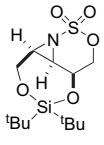
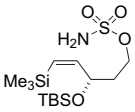
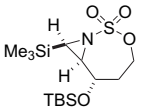
Entry[a]	Substrate	Product		% Yield
1				72
2			R = $SiPh_3$ = P(O)OEt_2 = –C≡C$SiiPr_3$	83 62 74

[a] All reactions conducted with 1–2 mol % $Rh_2(NHCOCF_3)_4$ in CH_2Cl_2 between 0 and 23 °C.

Our optimized conditions for intramolecular olefin aziridination can be employed with chiral sulfamate derivatives to give products with satisfactory levels of diastereocontrol. Several examples of such reactions are highlighted in Table 2. In these entries, product diastereoselectivities range from modest to high across a number of structurally dissimilar starting materials. While only moderate stereocontrol was noted for sulfamates prepared from secondary alcohols (entries 1 and 2, entry 3 being an exception), a sharp increase in diastereoselectivity was recorded for substrates containing a stereogenic element at the β-site (entries 4 and 5). These studies, along with previous work from our lab, have led us to propose a stereochemical model to account for the observed sense of induction.[5b] In brief, the recorded data are consistent with an aziridination event proceeding through a chair-like transition state that minimizes gauche and $A_{1,3}$-type interactions. It is interesting to note, however, that seven-membered ring oxathiazepane-fused aziridines (entry 7) can also be generated with useful levels of diastereocontrol. The scope of this latter finding has not been explored in full.[3f,10]

Table 2. Diastereoselective reactions of chiral sulfamates



Entry[a]	Substrate	Major product	Selectivity[b]	% Yield
1			4:1	84
2			4:1	92
3			15:1	69
4			20:1	87
5			20:1	82
6			20:1	61
7			10:1	66[c]

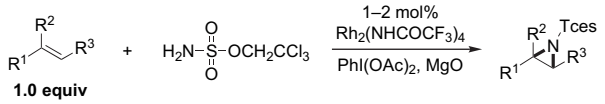
[a] Reactions conducted with 2 mol % $Rh_2(oct)_4$ in CH_2Cl_2 at 23 °C.
[b] Product diastereoselectivity determined by integration of the ^1H NMR of the unpurified reaction mixture.
[c] Reaction performed with 2 mol % $Rh_2(NHCOCF_3)_4$.

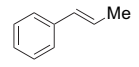
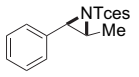
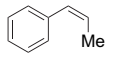
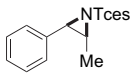
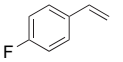
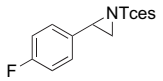
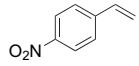
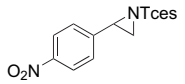
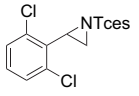
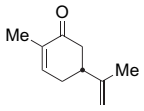
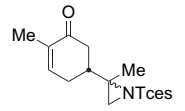
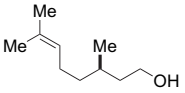
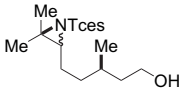
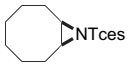
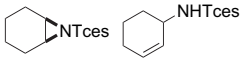
Our ability to oxidize alkenes in an intramolecular process with both high efficiency and chemoselectivity motivated the advancement of a related intermolecular protocol.[6] Identifying an N-functionalized starting material that itself would not undergo intramolecular C–H insertion was a prerequisite to the successful execution of this aim. In practice, use of the terminal oxidant $PhI(OAc)_2$ for aziridination offers a salient advantage by enabling the choice of any number of sulfonamide and/or carbamate derivatives as the N-atom source. This point is noteworthy, as previous aziridination methods that rely on $ArSO_2N{=}IPh$-type reagents are strictly limited to a small number of sulfonamide materials.[2,11] Accordingly, after screening a collection of aryl- and alkylsulfonamides, we identified 2,2,2-trichloroethylsulfamate ($TcesNH_2$) as the most effective reagent for Rh-catalyzed intermolecular amination reactions. The decision to utilize $TcesNH_2$ followed from a number of considerations, which included: (1) its ease and low cost of preparation from trichloroethanol;[12] (2) crystallinity and shelf-stability; and (3) the potential to

cleave the Tces-group from the product aziridine under mild reducing conditions (i.e., Zn). Later studies have shown that it is also the fastest nitrogen source to react under our conditions, a fact that may be responsible for its superior performance.[13]

Initial experiments using *trans*-β-methylstyrene as a test substrate in combination with $TcesNH_2$, $PhI(OAc)_2$, MgO, and 1 mol % $Rh_2(NHCOCF_3)_4$ afforded an 85% yield of the desired aziridine (Table 3, entry 1). Importantly, no product from competing allylic insertion, a problem encountered with other Rh(II) catalysts, was obtained. A second distinguishing characteristic of this process is its efficacy with only *a single equivalent of the olefinic substrate*. This feature is of paramount importance in the context of complex molecule synthesis, but is more the exception than the rule for previously reported catalytic aziridination methods. We have observed comparable results in reactions with a host of different aryl- and aliphatic alkenes applied as the limiting reagent. Of added note, the reactive nitrene-like oxidant can discriminate between electronically dissimilar olefins and, as would be expected for an electrophilic oxidant, the isopropylidene moiety in carvone is preferentially modified (entry 6). Although most styrenyl alkenes display exceptional performance under the Rh-catalyzed conditions, electron-deficient 2,6-dichlorostyrene (entry 5) presents a daunting test and in this case the product yield is reduced. By employing a larger number of equivalents of this alkene (i.e., 3 equiv), however, the aziridine can be generated in 77% yield (2 mol % catalyst). Finally, it should be noted that cyclopentene and cyclohexene (entry 9) are problematic substrates and fail to give even modest amounts of the corresponding aziridines. Allylic C–H insertion is also found to be competitive in these cases. Similar difficulties functionalizing both alkenes have been encountered using other transition metal-based aziridination methods.[3a,14] The inability to form either product in higher yield under our conditions is rather surprising, and lacks an obvious explanation at this time.

Table 3. A method for intermolecular olefin aziridination



Entry[a]	Substrate	Product	% Yield
1			85
2			85
3			91
4			71
5			40
6			85[b]
7			70[b]
8			82
9			15[c]

[a] Reactions conducted with 1 mol % $Rh_2(NHCOCF_3)_4$ in C_6H_5Cl from –10 to 23 °C.
[b] Product isolated as a 1:1 diastereomeric mixture.
[c] Isolated yield for each of the two products.

Knowledge of the scope of the Rh-mediated aziridination process coupled with a desire to showcase further its utility for synthesis gave us cause to explore reactions with glycal-based substrates.[15] Oxidation of such materials provides direct entry into value-added 2-amino sugars masked with a readily removable trichloroethoxysulfonyl (Tces) unit. By using Zn deprotection under non- or mildly acidic conditions, access to *N*-sulfated amino sugars, common structural units in heparins and in complex cell-surface carbohydrates, is also possible.[16] Much to our satisfaction, when 1 equiv of commercial tri-*O*-acetyl-D-glucal was subjected to oxidation (2 mol % catalyst), complete formation of the C2-aminated product occurred (Fig. 3). The product in this case is not the fused bicycle, but instead the 1,2-acetoxy-Tces-amine, presumed to result from in situ aziridine ring opening with AcOH. Although MgO is needed as a scavenger for AcOH, it is kinetically slow to remove the acid from solution; as such, the labile aziridine is displaced to give the anomeric acetate. We have observed similar patterns of reactivity with electron-rich aryl and strained aziridines, such as those derived from *p*-methoxystyrene and indene, respectively. Ring opening of the aziridine aside, the efficiency of this reaction to give the alkoxysulfonamide product using a limiting amount of triacetyl glucal is unprecedented, thus this method should find application in carbohydrate synthesis.

2.2. Nucleophilic ring openings of alkoxysulfonyl aziridines

In undertaking studies to advance our amination chemistry, we wished to examine systematically the electrophilic reactivity of these unusual alkoxysulfonylated strained heterocycles. Prior work by Dauban and Dodd, in accord with our own findings, indicated that the 6,3-bicyclic aziridines formed through intramolecular reactions ring open to favor the seven-membered oxathiazepane dioxide product

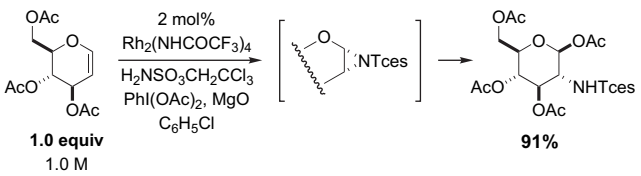


Figure 3. Glycal oxidation gives a sulfated 2-amino sugar in protected form.

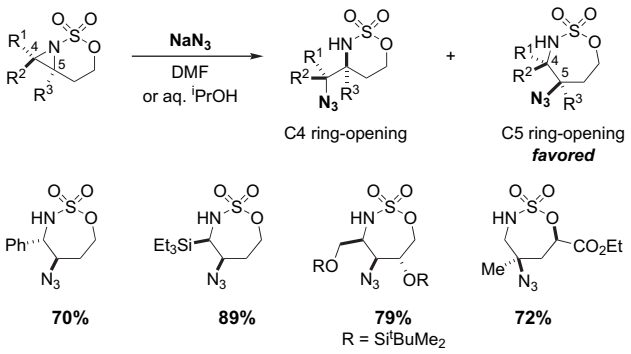


Figure 4. Regioselective nucleophilic opening favors seven-membered ring product.

(Fig. 4).[5b,9] We have found subsequently that substitution on the bicyclic framework does not adversely affect regioselectivity in these S_N2 processes. Regiocontrol in the ring opening of alkoxysulfonylaziridines was investigated using a small collection of differentially substituted starting materials and NaN_3 as the nucleophile. As a general rule, azide attack occurs with a strong preference to displace the C5–N bond giving the corresponding oxathiazepane. Substrates that displayed lower selectivity and afforded small amounts of the 6-membered oxathiazinane contained groups that strongly enhance electrophilicity at the C4 position (e.g., vinyl and alkynyl).

X-ray crystallography has provided some insight for understanding the high regioselectivity observed in these S_N2 reactions (Fig. 5).[17] Analysis of the ORTEP diagram of phenyl-substituted aziridine **3** shows only a very slight, albeit statistically discernible, variation between the C4–N (1.491 Å) and the C5–N bond lengths (1.497 Å). While this difference is biased in a way that is consistent with the observed regioselectivity for ring opening, it is so small that we presume other factors must be at play. An X-ray structure of the highly crystalline seven-membered azide product has led us to consider an alternative proposal. In comparing the starting material and product ORTEPs, it appears that minimal conformational reorganization occurs upon C5–N bond cleavage. Alternatively, nucleophilic attack at the C4 position would give the oxathiazinane product in a twist boat-like arrangement with the benzyl substituent aligned pseudo-axially. A large conformational change is then needed for the product to interconvert into its preferred chair-like structure. Presumably, such torsional strain energy is manifest in the transition state for C4 attack, thus disfavoring it as compared to azide addition at C5. A second possible

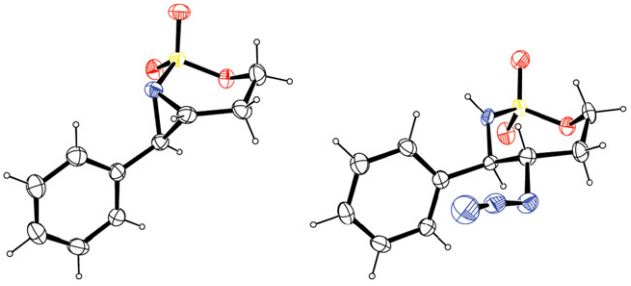


Figure 5. X-ray structures of bicyclic aziridine **3** and the azide-opened product.

explanation for the observed C5 regioselectivity follows from frontier molecular orbital theory. Density functional calculations (B3LYP/6-31G*) on the parent bicyclic aziridine **2** indicate that the coefficient of the LUMO orbital is substantially greater at C5 than at C4 (Fig. 6).[18] Similar observations are noted for the calculated structures of the LUMO+ orbital on **2** and for related alkyl-substituted aziridines of this type. Although the underlying factors biasing the shape of the LUMO and LUMO+ orbitals are unclear, such computational data are consistent with our experimental findings and the strong preference for these unusual heterocycles to ring open at the C5 center.

Regioselective ring opening of bicyclic aziridines such as **3** is observed with nucleophiles other than azide ion (Fig. 7). Oxygen- and sulfur-derived agents such as MeOH, H_2O, and PhSH are effective for the internal opening of alkoxysulfonyl aziridines to give oxathiazepane products, analogous to the results of Dauban and Dodd.[9] When H_2O and PhSH were employed, neither acid nor base was necessary for the reactions to proceed to completion, a fact that is demonstrative of the exceptional reactivity of these aziridinyl heterocycles.

The product oxathiazepanes are valuable precursors to polysubstituted amine derivatives. As with other cyclic sulfamates, the seven-membered heterocycles are susceptible to nucleophilic displacement of the C–O bond to give ring-opened products.[5a,19] Such reactions are possible using N–H or *N*-alkyl derived starting materials; however, the facility by which this S_N2 process occurs can be greatly improved if the N-center is first acylated (Fig. 8). This behavior is analogous to that observed for six-membered oxathiazinanes. Accordingly, *N*-Boc functionalization of **5** enables the subsequent addition of NaCN to give the diastereochemically-pure acyclic amine **7**. Thus, in four steps from a starting homoallylic alcohol, access to diverse product libraries of highly functionalized amines can be achieved.

Given the marked electrophilic reactivity of the intramolecular aziridine products, we expected that trichloroethoxysulfonyl aziridines synthesized through intermolecular olefin amination would display a similar propensity for ring

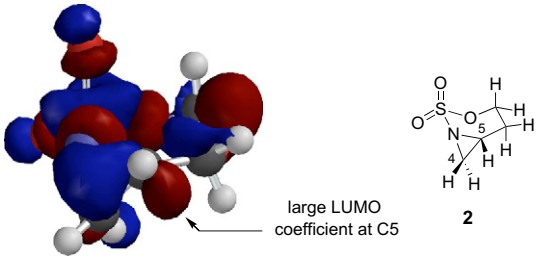


Figure 6. B3LYP/6-31G* calculated LUMO of unsubstituted bicyclic aziridine **2**.

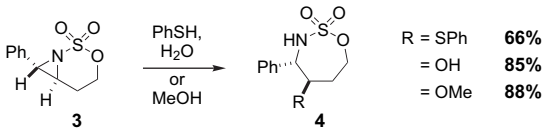


Figure 7. Ring opening occurs selectively with disparate nucleophiles.

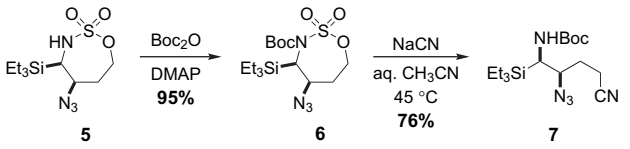
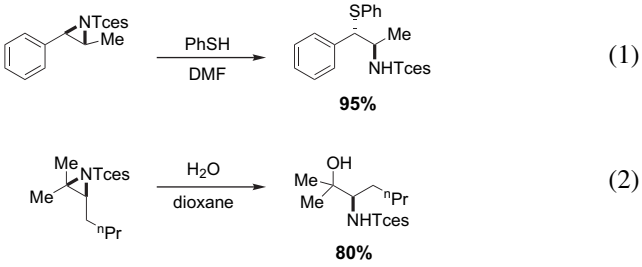


Figure 8. Activation and ring opening of seven-membered oxathiazepane.

opening. Nucleophiles such as PhSH, H_2O, NaN_3, and $BnNH_2$ do indeed react smoothly with these materials to give 1,2-difunctionalized amine products (Eqs. 1 and 2).[6] In the case of phenyl-substituted aziridines, a clear bias exists for opening at the benzylic position, and a single diastereomeric alkoxysulfonamide is formed. Similarly, trisubstituted aziridines are observed to open regioselectively and with absolute stereocontrol. As demonstrated previously, the trichloroethoxysulfonyl group may be removed from these products with a mild reducing agent such as Zn/Cu couple followed by acid treatment to cleave the sulfated amine. Consequently, this aziridination protocol should enjoy use in complex, multi-step synthesis due to the overall efficiency of the process (i.e., limiting amounts of alkene) and the ease by which the free amine can be liberated from the ring-opened product.



With the aim of employing an aziridination strategy in the context of a natural product synthesis, we required a direct method for converting *N*-alkoxysulfonyl aziridines to the corresponding α-aminoketones. Hiyama has shown that phenyl-substituted *N*-acylaziridines undergo oxidative ring opening in DMSO to give *N*-acyl-α-aminoketones, albeit at high temperatures (120 °C) and under long reaction times (Fig. 9).[20,21] In addition, application of this process typically leads to mixtures of regioisomeric products. Ring opening by the solvent followed by intramolecular deprotonation and elimination of Me_2S has been postulated as the mechanism for this transformation.

The ability of trichloroethoxysulfonyl aziridines to undergo facile displacement with common nucleophiles suggested that oxidative opening with DMSO would indeed be feasible (Fig. 10). Remarkably, the reaction of **8** in DMSO ensued with reasonable speed at 23 °C to give a single ketone product. As with other nucleophilic reactions of styrenyl-derived aziridines, DMSO addition is regioselective and furnishes

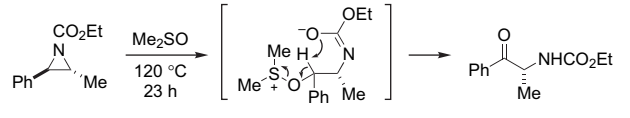
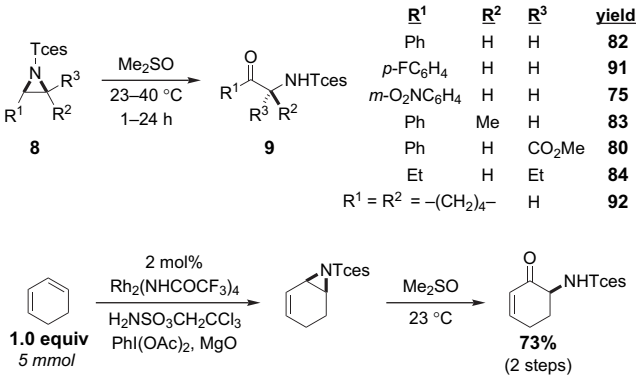


Figure 9. Hiyama's DMSO-promoted oxidative ring opening affords an α-aminoketone.[20]

the corresponding aryl ketones. Both aryl- and alkyl-substituted aziridines undergo smooth displacement by DMSO solvent at temperatures ranging from 23–40 °C. As no additional reagents are required to effect this reaction, the products may be easily obtained from a simple extractive work-up; yields in all cases exceed 75%. Taking advantage of this new protocol in combination with an effective aziridination method, we have found that 1,3-cyclohexadiene can be converted in a two-step sequence to a useful α-amino enone derivative. The intermediate vinylaziridine is generated quantitatively, but is unstable to both chromatography and crystallization. By simply stirring the unpurified aziridine in DMSO, the easily isolable, aminated product is obtained. Overall, the high performance of both reaction steps and low catalyst load (2 mol %) has enabled this transformation to be conducted with 5 mmol of cyclohexadiene, furnishing >1 g of crystalline aminoketone product.



R¹	R²	R³	yield
Ph	H	H	82
p-FC_6H_4	H	H	91
m-$O_2NC_6H_4$	H	H	75
Ph	Me	H	83
Ph	H	CO_2Me	80
Et	H	Et	84
$R^1 = R^2 = -(CH_2)_4-$		H	92

Figure 10. Tces-aziridines undergo facile ring opening with Me_2SO.

Selective oxidation of olefins to aziridines is a particularly appealing strategy for assembling functionally complex amines and amine derivatives. We have described a Rh-catalyzed process for effecting such chemistry in both intra- and intermolecular contexts. In the latter method, unparalleled efficiency with limiting amounts of the starting alkene is noted across a range of dissimilar substrates. When combined with the versatility of the alkoxysulfonylated azacycles for subsequent ring opening reactions, these processes should find great value in synthesis.

3. Experimental

3.1. General

All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (~15 Torr) by rotary evaporation. Dichloromethane, benzene, acetonitrile, *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were dried by passage under 12 psi of N_2 through two columns containing activated alumina. In addition, DMSO was also stored over 3 Å molecular sieves. *N*,*N*-Dimethyl acetamide (DMA) was dried over 4 Å molecular

sieves and used without further purification. All other solvents (^{i}PrOH and C_6H_5Cl) were used as received from commercial suppliers. Chlorosulfonyl isocyanate was obtained from Acros Chemicals, transferred via cannula to a Schlenk flask, and stored at –20 °C. Triethylamine was distilled from CaH_2 prior to use. Light magnesium oxide was flame dried under reduced pressure (~15 Torr). (Diacetoxy)iodobenzene was recrystallized from $CHCl_3$ and dried in vacuo (~1 Torr). Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (40–63 μm). Thin layer chromatography was performed on EM Science silica gel 60 F_{254} plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM) solution.

3.2. Instrumentation

Nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury-400 operating at 400 and 100 MHz or a Varian Inova-500 operating at 500 and 125 MHz for ^{1}H and ^{13}C, respectively, and are referenced internally according to residual solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; m, multiplet), integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Infrared spectra were recorded on a Thermo-Nicolet IR300 spectrometer using NaCl salt plates and are reported in terms of frequency of absorption. High-resolution mass spectra were obtained from the Mass Spectrometry Facility, University of California at San Francisco, supported by the NIH Division of Research and Resources, the High-Resolution Mass Spectrometry Facility, University of California at Riverside, and the Vincent Coates Foundation Mass Spectrometry Laboratory, Stanford University. Diffraction data were collected at the UC Berkeley CHEXRAY facility on Bruker-Siemens SMART and APEX diffractometers (λ=0.71073 Å, graphite monochromator). The structures were solved by direct methods (SIR-2002) and refined using Fourier techniques (SHELXL-97).

3.3. General procedures

3.3.1. Alcohol sulfamoylation. Formic acid (0.70 mL, 18 mmol, 1.5 equiv) was added dropwise to neat $ClSO_2NCO$ (1.6 mL, 18 mmol, 1.5 equiv) at 0 °C with rapid stirring. Vigorous gas evolution was observed during the addition process and within 5 min the mixture solidified. To the solid mass was then added 9.2 mL of CH_3CN, and the resulting solution was stirred for 1 h at 0 °C and 8 h at 23 °C. The reaction was cooled to 0 °C and a solution of the alcohol (12.3 mmol) and pyridine (1.1 mL, 13.5 mmol, 1.1 equiv) in DMA was added dropwise via cannula. After stirring for 3 h at 23 °C, the solution was diluted with 25 mL of Et_2O and transferred to a separatory funnel with 25 mL of H_2O. The ethereal layer was collected washed successively with 1×25 mL of H_2O and 1×25 mL of saturated aqueous NaCl. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (conditions given below) afforded the desired sulfamate ester. Product yields range from 75–90%.

3.3.2. Intramolecular aziridination. To a solution of sulfamate (4.96 mmol) in 50 mL of CH_2Cl_2 were added sequentially MgO (460 mg, 11.4 mmol, 2.3 equiv) and 1–2 mol % $Rh_2(NHCOCF_3)_4$.[22] The mixture was cooled to 0 °C and a single portion of $PhI(OAc)_2$ (2.08 g, 6.45 mmol, 1.3 equiv) was added. The orange suspension was allowed to warm slowly to 23 °C over 2 h. After 6 h at 23 °C, during which time the colored mixture faded to a pale yellow, the reaction was filtered through a small pad of Celite. The flask and filter cake were washed thoroughly with CH_2Cl_2 and the combined filtrates were concentrated under reduced pressure. Purification by chromatography on silica gel (conditions given below) afforded the desired bicyclic aziridine product.

3.3.3. Intermolecular aziridination. To a solution of $Cl_3CCH_2OSO_2NH_2$ (251 mg, 1.1 mmol, 1.1 equiv) in 2.0 mL of C_6H_5Cl were added sequentially olefin (1.0 mmol, 1.0 equiv), MgO (93 mg, 2.3 mmol, 2.3 equiv), and $Rh_2(NHCOCF_3)_4$ (6 mg, 10 μmol, 0.01 equiv).[22] The resulting purple mixture was cooled to −10 °C (s-CO_2/ethylene glycol bath) and a single portion of $PhI(OAc)_2$ (420 mg, 1.3 mmol, 1.3 equiv) was added. Immediately following the addition of $PhI(OAc)_2$, the suspension turned orange. This mixture was allowed to warm slowly to 23 °C over 3 h. After 5 h at 23 °C, during which time the colored mixture faded to pale yellow, the reaction was diluted with 10 mL of CH_2Cl_2 and filtered through a small pad of Celite. The flask and filter cake were washed thoroughly with CH_2Cl_2 and the combined filtrates were concentrated under reduced pressure. The isolated material was purified by chromatography on silica gel (conditions given below) to afford the desired aziridine.

3.4. Characterization data for substrates and products

3.4.1. Compounds from Table 1.

3.4.1.1. Entry 1, *trans*-styrenyl sulfamate. Purified by chromatography on silica gel (3:2 hexanes/EtOAc); white solid: TLC R_f=0.45 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.30 (m, 4H), 7.28–7.24 (m, 1H), 6.53 (d, 1H, J=16.0 Hz), 6.19 (dt, 1H, J=16.0, 7.0 Hz), 5.02 (br s, 2H), 4.32 (t, 2H, J=6.5 Hz), 2.68 (qd, 2H, J=6.5, 2.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.8, 133.3, 128.6, 127.5, 126.1, 124.0, 70.4, 32.4 ppm; IR (thin film) ν 3415, 3315, 1536, 1362, 1181, 933 cm^{-1}; HRMS (ES^{+}) calcd for $C_{10}H_{13}NO_3S$ 227.0616 found 250.0516 (MNa^{+}).

3.4.1.2. Entry 1, *trans*-phenyl aziridine. Reaction performed with 1 mol % $Rh_2(NHCOCF_3)_4$. Purified by chromatography on silica gel (90:10:1 CH_2Cl_2/EtOAc/Et_3N); white solid (72%): TLC R_f=0.42 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.30 (m, 5H), 4.77 (ddd, 1H, J=12.5, 7.5, 6.0 Hz), 4.55 (ddd, 1H, J=12.5, 6.5, 6.5 Hz), 3.90 (d, 1H, J=4.0 Hz), 3.28 (ddd, 1H, J=6.5, 4.5, 2.5 Hz), 2.51 (dq, 1H, J=15.0, 6.0 Hz), 2.41 (dtd, 1H, J=17.0, 7.0, 2.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 134.1, 128.7 (2), 126.2, 68.9, 50.5, 47.6, 18.7 ppm; IR (thin film) ν 1366, 1186, 1051, 878, 783 cm^{-1}; HRMS (ES^{+}) calcd for $C_{10}H_{11}NO_3S$ 225.0460 found 248.0352 (MNa^{+}).

3.4.1.3. Entry 2, *cis*-triphenylsilyl sulfamate. Purified by chromatography on silica gel (3:1 hexanes/EtOAc); white solid: TLC R_f=0.32 (7:3 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61–7.57 (m, 6H), 7.45–7.36 (m, 9H), 6.69 (dt, 1H, J=14.4, 7.2 Hz), 6.21 (dt, 1H, J=14.0, 1.4 Hz), 4.52 (br s, 2H), 3.96 (t, 2H, J=6.6 Hz), 2.36 (qd, 2H, J=6.8, 1.2 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 135.7, 134.8, 129.6, 128.0, 127.9, 69.7, 33.3 ppm; IR (thin film) ν 3391, 3291, 3067, 1607, 1427, 1365, 1182, 1109, 928, 700 cm^{-1}; HRMS (ES^-) calcd for $C_{22}H_{23}NO_3SSi$ 409.1168 found 408.1102 (M^+-H).

3.4.1.4. Entry 2, *cis*-triphenylsilyl aziridine. Reaction performed with 2 mol % $Rh_2(NHCOCF_3)_4$. Purified by chromatography on silica gel (7:3 hexanes/EtOAc); white solid (83%): TLC R_f=0.13 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73–7.67 (m, 6H), 7.35–7.18 (m, 9H), 4.51 (td, 1H, J=11.6, 4.4 Hz), 3.72 (ddd, 1H, J=8.4, 6.8, 4.0 Hz), 3.64 (ddd, 1H, J=11.6, 7.0, 2.0 Hz), 2.88 (d, 1H, J=6.8 Hz), 2.39–2.28 (m, 1H), 2.13–2.05 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.2, 132.2, 130.1, 127.8, 69.4, 43.6, 37.0, 18.7 ppm; IR (thin film) ν 3070, 3050, 3014, 1428, 1370, 1182, 1110, 1049, 973, 895, 796 cm^{-1}; HRMS (ES^-) calcd for $C_{22}H_{21}NO_3SSi$ 407.1011 found 406.0938 (M^+-H).

3.4.1.5. Entry 2, *cis*-diethoxyphosphoryl sulfamate. Purified by chromatography on silica gel (98:2 Et_2O/MeOH); colorless oil: TLC R_f=0.34 (97:3 Et_2O/MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.60 (ddt, 1H, J_{HP}=52.2 Hz, J_{HH}=13.0, 3.8 Hz), 5.92 (br s, 2H), 5.76 (ddt, 1H, J_{HP}=18.0 Hz, J_{HH}=12.8, 1.2 Hz), 4.31 (t, 2H, J=6.2 Hz), 4.08 (dq, 4H, J_{HP}=7.2 Hz, J_{HH}=7.2 Hz), 3.04–2.97 (m, 2H), 1.32 (t, 6H, J=7.2 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0 (d, J_{CP}=3.8 Hz), 119.9 (d, J_{CP}=182.0 Hz), 68.8 (d, J_{CP}=3.0 Hz), 62.0 (d, J_{CP}=5.4 Hz), 30.1 (d, J_{CP}=8.4 Hz), 16.3 (d, J_{CP}=6.8 Hz) ppm; IR (thin film) ν 3337, 2985, 1629, 1574, 1367, 1226, 1178, 1021, 968, 775 cm^{-1}; HRMS (ES^+) calcd for $C_8H_{18}NO_6PS$ 287.0592 found 310.0478 (MNa^+).

3.4.1.6. Entry 2, *cis*-diethoxyphosphoryl aziridine. Reaction performed with 2 mol % $Rh_2(NHCOCF_3)_4$. Purified by chromatography on silica gel (24:1 Et_2O/MeOH); colorless oil (62%): TLC R_f=0.21 (24:1 Et_2O/MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.80 (ddd, 1H, J=11.6, 10.6, 4.6 Hz), 4.70 (ddd, 1H, J=11.6, 7.0, 3.2 Hz), 4.35–4.25 (m, 2H), 4.18 (dq, 2H, J=8.0, 7.2 Hz), 3.47 (dtd, 1H, J=8.0, 6.4, 4.0 Hz), 2.89–2.79 (m, 1H), 2.74 (t, 1H, J=5.8 Hz), 2.17 (dddd, 1H, J=14.8, 8.2, 4.6, 3.2 Hz), 1.39–1.33 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.6, 64.4 (d, J_{CP}=6.1 Hz), 62.4 (d, J_{CP}=6.8 Hz), 43.0, 38.8 (d, J_{CP}=184.3 Hz), 16.4 (d, J_{CP}=6.1 Hz), 16.3 (d, J_{CP}=6.0 Hz), 16.2 (d, J_{CP}=3.0 Hz) ppm; IR (thin film) ν 2986, 2915, 1376, 1256, 1187, 1053, 1025, 937, 804 cm^{-1}; HRMS (ES^-) calcd for $C_8H_{16}NO_6PS$ 285.0436 found 284.0349 (M^+-H).

3.4.2. Compounds from Table 2.

3.4.2.1. Entry 1, pentenyl sulfamate. Purified by chromatography on silica gel (3:1 hexanes/EtOAc); colorless oil: TLC R_f=0.30 (7:3 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.79 (ddt, 1H, J=16.4, 10.8, 7.2 Hz), 5.18–5.15 (m, 1H), 5.13 (t, 1H, J=1.2 Hz), 4.98 (br s, 2H), 4.73 (sext, 1H, J=6.2 Hz), 2.48 (dddt, 1H, J=14.4, 7.2, 6.0, 1.2 Hz), 2.41 (dddt, 1H, J=14.4, 7.2, 6.0, 1.2 Hz), 1.41 (d, 3H, J=6.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.5, 118.9, 80.3, 40.7, 20.1 ppm; IR (thin film) ν 3378, 3289, 3082, 2982, 2938, 1644, 1558, 1359, 1181, 918 cm^{-1}; HRMS (ES^+) calcd for $C_5H_{11}NO_3S$ 165.0460 found 183.0800 (MNH_4^+).

3.4.2.2. Entry 1, bicyclic aziridine. Reaction performed with 2 mol % $Rh_2(oct)_4$ at 23 °C. Purified by chromatography on silica gel (1:1 hexanes/EtOAc); white solid (84%, 4:1 ds). *Major diastereomer*: TLC R_f=0.28 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.07 (dqd, 1H, J=11.0, 6.5, 4.5 Hz), 3.19 (dddd, 1H, J=5.0, 3.2 Hz), 2.57 (dd, 1H, J=5.4, 0.6 Hz), 2.43–2.40 (m, 1H), 2.30 (ddd, 1H, J=14.4, 8.2, 4.6 Hz), 1.93 (ddd, 1H, J=14.4, 10.8, 3.2 Hz), 1.42 (d, 3H, J=6.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 79.6, 40.8, 35.8, 26.3, 21.3 ppm; IR (thin film) ν 2988, 2931, 1366, 1187, 971, 863, 798 cm^{-1}; HRMS (ES^+) calcd for $C_5H_9NO_3S$ 163.0303 found 181.0653 (MNH_4^+). *Minor diastereomer*: TLC R_f=0.21 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.59 (dqd, 1H, J=11.4, 6.2, 4.3 Hz), 3.13 (dddd, 1H, J=5.2, 1.5 Hz), 2.86 (dd, 1H, J=5.0, 1.8 Hz), 2.61 (ddd, 1H, J=5.4, 2.0, 0.6 Hz), 2.43 (ddd, 1H, J=15.4, 11.4, 4.0 Hz), 2.29 (ddd, 1H, J=15.4, 4.2, 1.6 Hz), 1.46 (d, 3H, J=6.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.2, 40.9, 32.8, 26.1, 21.4 ppm; IR (thin film) ν 2923, 2851, 1361, 1184, 1023, 870, 800 cm^{-1}.

3.4.2.3. Entry 2, ethylpentenoate sulfamate. Purified by chromatography on silica gel (97:3 CH_2Cl_2/EtOAc); colorless oil: TLC R_f=0.22 (97:3 CH_2Cl_2/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.49 (br s, 2H), 5.01 (t, 1H, J=6.5 Hz), 4.87 (s, 1H), 4.81 (s, 1H), 4.22 (q, 2H, J=7.1 Hz), 2.57 (d, 2H, J=6.7 Hz), 1.76 (s, 3H), 1.27 (t, 3H, J=7.1 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 138.9, 115.0, 77.5, 62.2, 40.0, 22.1, 14.0 ppm; IR (thin film) ν 3374, 3280, 3082, 2984, 1741, 1654, 1560, 1376, 1186, 1054, 929, 781 cm^{-1}; HRMS (EI) calcd for $C_8H_{15}NO_5S$ 237.0671 found 237.0676 (M^+).

3.4.2.4. Entry 2, bicyclic aziridine. Reaction performed with 2 mol % $Rh_2(oct)_4$ at 23 °C. Purified by chromatography on silica gel (7:3 hexanes/EtOAc); white solid (92%, 4:1). *Major diastereomer*: TLC R_f=0.46 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.14 (t, 1H, J=7.4 Hz), 4.26 (q, 2H, J=7.1 Hz), 2.76 (s, 1H), 2.48 (dd, 1H, J=15.0, 7.0 Hz), 2.41 (dd, 1H, J=15.1, 8.0 Hz), 2.38 (s, 1H), 1.47 (s, 3H), 1.29 (t, 3H, J=7.1 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 76.0, 62.7, 48.2, 41.3, 25.9, 25.2, 14.0 ppm; IR (thin film) ν 2985, 1755, 1446, 1379, 1302, 1191, 1085, 1026, 946, 892, 830 cm^{-1}; HRMS (EI) calcd for $C_8H_{13}NO_5S$ 235.0514 found 235.0546 (M^+). *Minor diastereomer*: TLC R_f=0.29 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.84 (dd, 1H, J=10.8, 6.4 Hz), 4.28 (q, 2H, J=7.1 Hz), 2.95 (d, 1H, J=2.1 Hz), 2.65–2.48 (m, 3H), 1.46 (s, 3H), 1.29 (t, 3H, J=7.2 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 74.2, 62.6, 47.6, 39.2, 26.2, 24.4, 14.0 ppm; IR (thin film) ν 2985, 1758, 1371, 1306, 1185, 1076, 1029, 890, 784 cm^{-1}; HRMS (EI) calcd for $C_8H_{13}NO_5S$ 235.0514 found 235.0518 (M^+).

3.4.2.5. Entry 3, pentenylsilane sulfamate. Purified by chromatography on silica gel (13% EtOAc/hexanes); white solid: TLC R_f=0.40 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.31 (dt, 1H, J=14.5, 7.0 Hz), 5.74 (d, 1H, J=14.0 Hz), 4.97 (br s, 2H), 4.69 (ddd, 1H, J=12.8, 6.3, 4.5 Hz), 3.85–3.80 (m, 2H), 2.61–2.50 (m, 2H), 0.93 (s, 9H), 0.16 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.2, 133.8, 84.3, 65.2, 34.9, 25.8, 18.3, 0.1, −5.4, −5.5 ppm; IR (thin film) ν 3368, 3290, 2955, 2931, 2858, 1609, 1363, 1251, 1186, 1128, 933, 837, 779 cm^{-1}; HRMS (ES$^-$) calcd for $C_{14}H_{33}NO_4SSi_2$ 367.1669 found 366.1591 (M^+−H).

3.4.2.6. Entry 3, bicyclic aziridine. Reaction performed with 2 mol % $Rh_2(oct)_4$ at 23 °C. Reaction performed with 2 mol % $Rh_2(oct)_4$. Purified by chromatography on silica gel (13% EtOAc/hexanes); white solid (69%, 15:1 ds): TLC R_f=0.33 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.88 (ddt, 1H, J=9.8, 5.4, 4.4 Hz), 3.79 (dd, 1H, J=11.4, 4.2 Hz), 3.75 (dd, 1H, J=11.6, 4.0 Hz), 3.46 (q, 1H, J=6.8 Hz), 2.18–2.10 (m, 2H), 1.95 (d, 1H, J=7.2 Hz), 0.89 (s, 9H), 0.27 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 82.2, 64.1, 43.7, 40.3, 25.8, 21.6, 18.3, −0.8, −5.4, −5.5 ppm; IR (thin film) ν 2950, 2929, 2858, 1360, 1256, 1174, 972, 843, 776 cm^{-1}.

3.4.2.7. Entry 4, *tert*-butyl ester sulfamate. Purified by chromatography on silica gel (5:14:1 hexanes/CH_2Cl_2/Et_2O); colorless oil: TLC R_f=0.25 (5:14:1 hexanes/CH_2Cl_2/Et_2O); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.06 (dd, 1H, J=11.6, 3.6 Hz), 5.80 (dd, 1H, J=11.6, 1.6 Hz), 5.56 (dddd, 1H, J=7.6, 6.0, 3.6, 1.6 Hz), 5.03 (br s, 2H), 4.28 (dd, 1H, J=11.0, 3.6 Hz), 4.19 (dd, 1H, J=10.8, 6.0 Hz), 1.48 (s, 9H), 0.89 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.2, 146.3, 123.0, 81.5, 73.8, 67.7, 28.0, 25.7, 18.1, −4.8, −4.9 ppm; IR (thin film) ν 3369, 3284, 2955, 2931, 2858, 1710, 1369, 1254, 1186, 1113, 1001, 836 cm^{-1}; HRMS (ES$^+$) calcd for $C_{15}H_{31}NO_6SSi$ 381.1641 found 404.1539 (MNa^+).

3.4.2.8. Entry 4, bicyclic aziridine. Reaction performed with 2 mol % $Rh_2(oct)_4$ at 23 °C. Purified by chromatography on silica gel (7% EtOAc/hexanes); white solid (87%, 20:1 ds): TLC R_f=0.20 (19:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.82–4.77 (m, 1H), 4.58 (dd, 1H, J=11.4, 9.0 Hz), 4.41 (dd, 1H, J=11.4, 6.6 Hz), 3.25–3.21 (m, 2H), 1.51 (s, 9H), 0.89 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.0, 84.4, 73.6, 56.1, 50.9, 42.2, 27.7, 25.5, 17.9, −4.9, −5.0 ppm; IR (thin film) ν 2955, 2859, 1737, 1385, 1257, 1192, 1111, 995, 842, 788 cm^{-1}; HRMS (ES$^+$) calcd for $C_{15}H_{29}NO_6SSi$ 379.1485 found 402.1363 (MNa^+).

3.4.2.9. Entry 5, bicyclic aziridine. Reaction performed with 2 mol % $Rh_2(oct)_4$ at 23 °C. Purified by chromatography on silica gel (11:9 hexanes/EtOAc); white solid (82%, 20:1 ds): TLC R_f=0.16 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.30 (d, 1H, J=2.7 Hz), 4.78 (d, 1H, J=7.3 Hz), 4.73 (d, 1H, J=7.3 Hz), 4.39 (d, 1H, J=2.8 Hz), 3.83 (s, 3H), 3.68–3.60 (m, 2H), 3.60–3.48 (m, 2H), 3.37 (s, 3H), 2.88 (s, 1H), 2.42 (s, 1H), 1.64 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.5, 95.0, 79.9, 71.3, 69.5, 68.0, 59.0, 54.6, 53.1, 38.6, 24.0 ppm; IR (thin film) ν 2933, 1773, 1387, 1196, 1024, 828, 690 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{19}NO_8S$ 325.0831 found 250.0389 (M^+−O(CH_2)OCH_3).

3.4.2.10. Entry 6, dioxasilylcycloheptene sulfamate. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid: TLC R_f=0.22 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.79–5.72 (m, 1H), 5.61 (ddt, 1H, J=12.0, 3.6, 1.8 Hz), 5.12–5.08 (m, 1H), 4.84 (br s, 2H), 4.71 (dq, 1H, J=17.2, 2.8 Hz), 4.51 (ddt, 1H, J=17.2, 4.0, 2.0 Hz), 4.24 (dd, 1H, J=10.2, 5.8 Hz), 4.21 (dd, 1H, J=9.8, 5.0 Hz), 1.04 (s, 9H), 1.03 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.1, 128.0, 73.9, 69.4, 64.2, 27.7, 21.3, 21.0 ppm; IR (thin film) ν 3370, 3291, 2935, 2859, 1560, 1473, 1364, 1185, 1116, 1000, 826 cm^{-1}; HRMS (ES$^-$) calcd for $C_{13}H_{27}NO_5SSi$ 337.1379 found 336.1301 (M^+−H).

3.4.2.11. Entry 6, bicyclic aziridine. Reaction performed with 2 mol % $Rh_2(oct)_4$ at 23 °C. Purified by chromatography on silica gel (15% EtOAc/hexanes); white solid (61%, 20:1 ds): TLC R_f=0.42 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.92–4.86 (m, 2H), 4.55 (dd, 1H, J=12.8, 1.6 Hz), 4.47 (dd, 1H, J=12.0, 10.8 Hz), 4.37 (dd, 1H, J=12.2, 6.2 Hz), 3.56 (t, 1H, J=6.4 Hz), 3.21 (dt, 1H, J=10.6, 6.2 Hz), 1.06 (s, 9H), 1.00 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 77.8, 63.2, 58.9, 48.3, 45.3, 27.2, 27.0, 21.4, 20.8 ppm; IR (thin film) ν 2930, 2858, 1472, 1371, 1257, 1182, 1063, 1010, 900, 787 cm^{-1}; HRMS (ES$^-$) calcd for $C_{13}H_{25}NO_5SSi$ 335.1223 found 358.1119 (M^+−H).

3.4.2.12. Entry 7, bicyclic aziridine. Reaction performed with 2 mol % $Rh_2(NHCOCF_3)_4$ at 23 °C. Purified by chromatography on silica gel (9:1 hexanes/Et_2O); white solid (66%, 10:1 ds): TLC R_f=0.48 (4:1 hexanes/Et_2O); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.44 (td, 1H, J=12.2, 1.8 Hz), 4.33 (ddd, 1H, J=12.2, 4.0, 3.0 Hz), 4.18 (ddd, 1H, J=10.2, 8.4, 2.4 Hz), 2.80 (dd, 1H, J=8.8, 3.2 Hz), 2.30 (d, 1H, J=7.2 Hz), 2.31–2.22 (m, 1H), 1.97 (dq, 1H, J=14.8, 2.2 Hz), 0.89 (s, 9H), 0.29 (s, 9H), 0.11 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 69.5, 69.2, 49.1, 43.9, 38.7, 25.6, 17.8, −0.7, −3.6, −3.9 ppm; IR (thin film) ν 2953, 2931, 2857, 1355, 1253, 1165, 1105, 954, 837 cm^{-1}; HRMS (ES$^-$) calcd for $C_{14}H_{31}NO_4SSi_2$ 365.1512 found 364.1432 (M^+−H).

3.4.3. Products from Table 3.

3.4.3.1. Entry 3, *p*-fluorophenyl aziridine. Purified by chromatography on silica gel (9:1 hexanes/EtOAc); white solid (91%): TLC R_f=0.52 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33–7.28 (m, 2H), 7.12–7.07 (m, 2H), 4.89 (d, 1H, J=11.0 Hz), 4.83 (d, 1H, J=11.0 Hz), 3.88 (dd, 1H, J=7.0, 4.5 Hz), 3.11 (d, 1H, J=7.5 Hz), 2.62 (d, 1H, J=4.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.2 (d, J_{CF}=248.8 Hz), 129.9 (d, J_{CF}=3.1 Hz), 128.6 (d, J_{CF}=8.0 Hz), 116.2 (d, J_{CF}=22.1 Hz), 93.0, 79.9, 42.4, 37.8 ppm; IR (thin film) ν 1515, 1382, 1182, 1011, 841, 784 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_9Cl_3FNO_3S$ 346.9353 found 346.9353 (MNa^+).

3.4.3.2. Entry 5, 2,6-dichlorophenyl aziridine. Purified by chromatography on silica gel (9:1 hexanes/EtOAc);

white solid (40%): TLC R_f=0.51 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38–7.35 (m, 2H), 7.28 (dd, 1H, J=7.0, 8.5 Hz), 4.94 (d, 1H, J=11.0 Hz), 4.90 (d, 1H, J=11.0 Hz), 4.02 (dd, 1H, J=7.5, 5.0 Hz), 3.26 (dd, 1H, J=7.5, 1.0 Hz), 2.84 (dd, 1H, J=5.0, 1.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.2, 130.4, 129.5, 128.8, 92.9, 79.7, 41.3, 36.7 ppm; IR (thin film) ν 1433, 1385, 1184, 1011, 781 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_8Cl_5NO_3S$ 396.8667 found 419.8576 (MNa^+).

3.4.3.3. Entry 6, carvone aziridine. Reaction performed with 2 mol % $Rh_2(NHCOCF_3)_4$. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (85%, 1:1 ds): TLC R_f=0.21 (3:1 hexanes/EtOAc). Higher R_f diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.75 (d, 1H, J=6.0 Hz), 4.78 (s, 2H), 2.72 (s, 1H), 2.58–2.49 (m, 1H), 2.49 (s, 1H), 2.42 (dt, 1H, J=18.5, 5.0 Hz), 2.36–2.27 (m, 2H), 2.11–2.03 (m, 1H), 1.78 (s, 3H), 1.62 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.9, 143.6, 135.7, 93.0, 79.4, 50.9, 42.5, 41.9, 40.1, 27.7, 15.6, 14.8 ppm; IR (thin film) ν 1672, 1366, 1179, 1012, 853, 781 cm^{-1}; HRMS (ES$^+$) calcd for $C_{12}H_{16}Cl_3NO_4S$ 374.9866 found 397.9758 (MNa^+).

3.4.3.4. Entry 7, citronellol aziridine. Purified by chromatography on silica gel (9:1 CH_2Cl_2/EtOAc); colorless oil (70%, 1:1 ds): TLC R_f=0.33 (9:1 CH_2Cl_2/EtOAc). Data reported for the mixture of diastereomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.77–4.70 (m, 4H), 3.72–3.60 (m, 4H), 2.84–2.82 (m, 2H), 1.62 (s, 6H), 1.66–1.24 (m, 14H), 1.32 (s, 6H), 0.90 (d, 3H, J=6.4 Hz), 0.89 (d, 3H, J=6.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 93.14, 93.13, 79.1, 60.64, 60.57, 55.02, 54.90, 51.9, 51.7, 39.45, 39.39, 34.1, 34.0, 29.1, 28.9, 25.2, 25.1, 21.0, 20.5, 20.4, 19.4 ppm; IR (thin film) ν 3315, 1364, 1177, 1016, 868, 777 cm^{-1}; HRMS (ES$^+$) calcd for $C_{12}H_{22}Cl_3NO_4S$ 381.0335 found 404.0248 (MNa^+).

3.4.3.5. Entry 9, cyclohexene aziridine. Purified by chromatography on silica gel (10:1 hexanes/EtOAc); white solid (15%): TLC R_f=0.61 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.80 (s, 2H), 3.14–3.09 (m, 2H), 2.02–1.84 (m, 4H), 1.51–1.39 (m, 2H), 1.35–1.24 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 93.1, 79.3, 42.0, 22.6, 19.2 ppm; IR (thin film) ν 2943, 1367, 1181, 1016, 784 cm^{-1}; HRMS (ES$^+$) calcd for $C_8H_{12}Cl_3NO_3S$ 306.9603 found 329.9506 (MNa^+).

3.4.3.6. Entry 9, cyclohexenyl amine. Purified by chromatography on silica gel (10:1 hexanes/EtOAc); white solid (15%): TLC R_f=0.54 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.93 (dtd, 1H, J=10.0, 3.6, 1.6 Hz), 5.72 (ddt, 1H, J=10.0, 4.4, 2.4 Hz), 4.70 (br d, 1H, J=8.0 Hz), 4.63 (s, 2H), 4.14–4.06 (m, 1H), 2.10–1.94 (m, 3H), 1.80–1.60 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.7, 126.0, 93.4, 78.1, 50.4, 29.7, 24.5, 19.1 ppm; IR (thin film) ν 3304, 2945, 1431, 1364, 1183, 855 cm^{-1}; HRMS (ES$^+$) calcd for $C_8H_{12}Cl_3NO_3S$ 306.9603 found 329.9503 (MNa^+).

3.4.4. Experimental protocols from Figures 3, 4, 7, and 8.

3.4.4.1. β-1,3,4,6-Tetraacetyl-2-*N*-trichloroethoxysulfonyl glucosamine. Reaction performed with 2 mol % $Rh_2(NHCOCF_3)_4$ at 1.0 M substrate concentration. Purified by chromatography on silica gel (2:1 hexanes/EtOAc); white solid (91%): TLC R_f=0.43 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.19 (d, 1H, J=9.5 Hz), 5.71 (d, 1H, J=8.5 Hz), 5.21 (t, 1H, J=9.5 Hz), 5.07 (t, 1H, J=10.0 Hz), 4.62 (d, 1H, J=11.5 Hz), 4.58 (d, 1H, J=11.0 Hz), 4.26 (dd, 1H, J=12.5, 4.5 Hz), 4.09 (dd, 1H, J=12.5, 2.0 Hz), 3.88 (ddd, 1H, J=10.0, 4.5, 2.0 Hz), 3.76 (q, 1H, J=9.5 Hz), 2.19 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.7, 170.7, 169.7, 169.4, 93.2, 91.9, 78.5, 72.5, 72.4, 67.9, 61.4, 57.8, 21.0, 20.8, 20.7, 20.5 ppm; IR (thin film) ν 3262, 1755, 1369, 1218, 1079, 1043 cm^{-1}; HRMS (ES$^+$) calcd for $C_{16}H_{22}Cl_3NO_{12}S$ 556.9928 found 579.9823 (MNa^+).

3.4.4.2. *trans*-5-Azido-4-phenyl-[1,2,3]-oxathiazepane-2,2-dioxide. To a solution of 7-phenyl-3-oxa-2-thia-1-azabicyclo[4.1.0]heptane-2,2-dioxide (53 mg, 0.25 mmol) in 1.25 mL of DMF was added NaN_3 (20 mg, 0.31 mmol, 1.2 equiv). The solution was stirred for 35 min then transferred to a separatory funnel containing 10 mL of EtOAc and 10 mL of H_2O. The organic phase was collected and washed with an additional 1×10 mL of H_2O. The aqueous portions were combined and extracted with 1×10 mL of EtOAc. The collective organic extracts were washed with 1×10 mL of saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (2:1 hexanes/EtOAc) afforded the desired product as a white solid (47 mg, 70%): TLC R_f=0.57 (1:1 hexanes/EtOAc); ^{1}H NMR (CD_3CN, 500 MHz) δ 7.45–7.35 (m, 5H), 6.57 (br s, 1H), 4.46–4.34 (m, 2H), 4.24 (d, 1H, J=10.5 Hz), 3.99 (td, 1H, J=10.5, 4.5 Hz), 2.41 (dtd, 1H, J=15.5, 4.5, 1.0 Hz), 2.17–2.10 (m, 1H); ^{13}C NMR (CD_3CN, 125 MHz) δ 139.2, 129.8, 129.4, 128.3, 68.1, 64.5, 61.2, 35.3 ppm; IR (thin film) ν 3284, 2104, 1338, 1174, 758 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_{12}N_4O_3S$ 268.0630 found 291.0526 (MNa^+).

3.4.4.3. 4-Phenyl-5-(phenylthio)-[1,2,3]-oxathiazepane-2,2-dioxide. To a solution of aziridine **3** (53 mg, 0.25 mmol) in 2.5 mL of DMF was added neat PhSH (27 μL, 0.26 mmol, 1.05 equiv). The solution was stirred for 2 h then transferred to a separatory funnel with 10 mL of EtOAc and 10 mL of H_2O. The organic layer was collected and washed with 1×10 mL of H_2O. The aqueous layers were combined and extracted with 1×10 mL of EtOAc. The collective organic fractions were then washed with 1×10 mL of saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (3:1 hexanes/EtOAc) furnished the desired product as a white solid (55 mg, 66%): TLC R_f=0.70 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36–7.29 (m, 5H), 7.25–7.19 (m, 3H), 7.18–7.14 (m, 2H), 5.30 (br d, 1H, J=8.5 Hz), 4.47–4.34 (m, 3H), 3.71 (td, 1H, J=10.5, 4.0 Hz), 2.46 (dt, 1H, J=16.0, 4.0 Hz), 2.39–2.30 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.3, 133.5, 132.5, 129.1, 129.0, 128.7, 128.1, 127.2, 69.2, 61.4, 52.7, 36.2 ppm; IR (thin film) ν 3284, 1346, 1178, 944, 752 cm^{-1}; HRMS (ES$^+$) calcd for $C_{16}H_{17}NO_3S_2$ 335.0650 found 358.0547 (MNa^+).

3.4.4.4. 5-Hydroxy-4-phenyl-[1,2,3]-oxathiazepane-2,2-dioxide. To a solution of aziridine **3** (53 mg, 0.25 mmol)

in 1.67 mL of DMF was added 0.8 mL of H_2O. The solution was stirred for 60 h then all volatiles were removed in vacuo (~1 Torr). Purification of the solid residue by chromatography on silica gel (3:2 EtOAc/hexanes) afforded the desired product as a white solid (52 mg, 85%): TLC R_f=0.14 (1:1 hexanes/EtOAc); ^{1}H NMR (CH_3CN, 500 MHz) δ 7.44–7.33 (m, 5H), 6.40 (br d, 1H, J=10.4 Hz), 4.46–4.30 (m, 2H), 4.13 (t, 1H, J=10.4 Hz), 4.00 (dddd, 1H, J=9.6, 9.6, 5.2, 5.2 Hz), 3.01 (d, 1H, J=5.6 Hz), 2.32 (dtd, 1H, J=15.2, 4.4, 1.2 Hz), 2.14–2.02 (m, 1H) ppm; ^{13}C NMR (CD_3CN, 125 MHz) δ 140.0, 129.4, 128.7, 128.5, 72.8, 68.2, 62.8, 38.3 ppm; IR (thin film) ν 3456, 3279, 1341, 1177, 1051, 759 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_{13}NO_4S$ 243.0565 found 266.0471 (MNa^+).

3.4.4.5. 5-Methoxy-4-phenyl-[1,2,3]-oxathiazepane-2,2-dioxide. To a solution of aziridine **3** (53 mg, 0.25 mmol) in 2.5 mL of MeOH was added *p*-toluenesulfonic acid monohydrate (2 mg, 10 μmol, 0.04 equiv). The contents were stirred for 5 h, transferred to a separatory funnel with 10 mL of EtOAc, and washed with 2×10 mL of H_2O. The aqueous layers were combined and extracted with 1×10 mL of EtOAc. The collective organic fractions were washed with 1×10 mL of saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (3:1 hexanes/EtOAc) gave the desired product as a white solid (46 mg, 72%): TLC R_f=0.70 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45–7.40 (m, 2H), 7.39–7.34 (m, 1H), 7.33–7.28 (m, 2H), 4.72 (d, 1H, J=11.0 Hz), 4.55 (td, 1H, J=11.5, 2.5 Hz), 4.49 (ddd, 1H, J=11.5, 5.5, 1.5 Hz), 4.46 (d, 1H, J=3.0 Hz), 3.87 (tt, 1H, J=11.0, 3.0 Hz), 3.38 (s, 3H), 2.11–2.01 (m, 1H), 1.33–1.27 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.3, 128.8, 128.4, 126.4, 83.3, 71.7, 60.3, 57.7, 22.1 ppm; IR (thin film) ν 3255, 1410, 1359, 1190, 780 cm^{-1}; HRMS (ES$^+$) calcd for $C_{11}H_{15}NO_4S$ 257.0722 found 280.0622 (MNa^+).

3.4.4.6. *N*-(*tert*-Butoxycarbonyl)-2-azido-4-cyano-1-triethylsilylbutanamine. To a solution of *N*-Boc oxathiazepane (800 mg, 1.96 mmol) in 14 mL of CH_3CN was added an aqueous solution of NaCN (193 mg, 3.92 mmol, 2.0 equiv) in 6 mL of H_2O. The flask was sealed and the contents heated at 45 °C for 36 h. The reaction mixture was cooled to 23 °C and poured into a separatory funnel containing 50 mL of H_2O and 5 mL of aqueous 1 M HCl (*note*: appropriate caution must be taken when working up the reaction as HCN is generated). The aqueous layer was extracted with 4×25 mL of EtOAc. The combined organic extracts were washed with 1×30 mL of saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the solid residue by chromatography on silica gel (14:1 hexanes/EtOAc) gave the desired product as a white solid (530 mg, 76%). TLC R_f=0.32 (7:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.46 (br d, 1H, J=10.4 Hz), 3.60 (td, 1H, J=7.2, 1.7 Hz), 3.40 (dd, 1H, J=10.4, 2.0 Hz), 2.65 (dt, 1H, J=17.2, 7.4 Hz), 2.58 (dt, 1H, J=17.2, 6.6 Hz), 2.04–1.88 (m, 2H), 1.42 (s, 9H), 0.99 (t, 9H, J=7.8 Hz), 0.67 (q, 6H, J=7.8 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 118.7, 79.8, 62.8, 40.7, 28.2, 27.0, 14.2, 7.3, 2.4 ppm; IR (thin film) ν 2957, 2878, 2100, 1703, 1494, 1366, 1243, 1167, 1011 cm^{-1}; HRMS (ES$^+$) calcd for $C_{16}H_{31}N_5O_2Si$ 353.2247 found 376.2148 (MNa^+).

3.5. General protocol for oxidative ring opening of Tces-aziridines

Aziridine (0.25 mmol) was dissolved in DMSO and stirred until TLC analysis indicated the complete consumption of starting material (1–24 h). The solution was transferred to a separatory funnel with 10 mL of EtOAc and washed with 2×10 mL of H_2O. The aqueous layers were combined and extracted with 1×10 mL of EtOAc. The collective organic fractions were then washed with 1×10 mL of saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (as indicated below) furnished the desired ketone.

3.5.1. Characterization data for products from Figure 10.

3.5.1.1. (2-Oxo-2-phenylethyl)sulfamic acid 2,2,2-trichloroethyl ester. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (82%): TLC R_f=0.23 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (dd, 2H, J=6.4, 1.5 Hz), 7.67 (tt, 1H, J=7.2, 1.2 Hz), 7.55–7.50 (m, 2H), 6.05 (br t, 1H, J=4.4 Hz), 4.72 (d, 2H, J=4.4 Hz), 4.67 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.0, 134.8, 133.4, 129.2, 128.0, 93.2, 78.3, 49.2 ppm; IR (thin film) ν 3285, 1694, 1371, 1183, 857 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_{10}Cl_3NO_4S$ 344.9396 found 367.9292 (MNa^+).

3.5.1.2. [2-(4-Fluorophenyl)-2-oxo-ethyl]sulfamic acid 2,2,2-trichloroethyl ester. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (91%): TLC R_f=0.31 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02–7.96 (m, 2H), 7.24–7.18 (m, 2H), 5.99 (t, 1H, J=4.0 Hz), 4.69 (d, 2H, J=4.4 Hz), 4.67 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.5, 166.6 (d, J_{CF}=258.7 Hz), 130.8 (d, J_{CF}=10.0 Hz), 129.9 (d, J_{CF}=3.0 Hz), 116.5 (d, J_{CF}=22.1 Hz), 93.2, 78.4, 49.1 ppm; IR (thin film) ν 3270, 1687, 1597, 1408, 1236, 1181, 861 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_9Cl_3FNO_4S$ 362.9302 found 385.9196 (MNa^+).

3.5.1.3. [2-(3-Nitrophenyl)-2-oxo-ethyl]sulfamic acid 2,2,2-trichloroethyl ester. Reaction performed at 0.1 M in olefin substrate. Purified by chromatography on silica gel (2:1 hexanes/EtOAc); yellow solid (75%): TLC R_f=0.22 (2:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.78 (t, 1H, J=2.0 Hz), 8.53 (ddd, 1H, J=8.0, 2.0, 1.0 Hz), 8.28 (ddd, 1H, J=7.5, 2.5, 1.5 Hz), 7.78 (t, 1H, J=7.5 Hz), 5.90 (t, 1H, J=4.5 Hz), 4.78 (d, 2H, J=4.5 Hz), 4.70 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.4, 148.6, 134.6, 133.4, 130.6, 128.9, 122.9, 93.2, 78.5, 49.6 ppm; IR (thin film) ν 3303, 1705, 1534, 1353, 1183, 1086, 858 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_9Cl_3N_2O_6S$ 389.9247 found 412.9153 (MNa^+).

3.5.1.4. (1-Methyl-2-oxo-2-phenylethyl)sulfamic acid 2,2,2-trichloroethyl ester. Reaction performed at 40 °C. Purified by chromatography on silica gel (5:1 hexanes/EtOAc); white solid (83%): TLC R_f=0.24 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97–7.94 (m, 2H), 7.64 (tt, 1H, J=6.8, 1.2 Hz), 7.54–7.49 (m, 2H), 6.27 (br d, 1H, J=7.6 Hz), 5.20 (quint, 1H, J=7.2 Hz), 4.68 (d, 1H, J=10.8 Hz), 4.54 (d, 1H, J=10.8 Hz), 1.55 (d, 3H, J=7.2 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.5, 134.5, 132.9, 129.1, 128.8, 93.1, 78.1, 54.4, 20.5 ppm; IR (thin film) ν

3290, 1687, 1369, 1186, 973, 854 cm^{-1}; HRMS (ES^+) calcd for $C_{11}H_{12}Cl_3NO_4S$ 358.9553 found 381.9462 (MNa^+).

3.5.1.5. 3-Oxo-3-phenyl-2-(2,2,2-trichloroethoxysulfonylamino)propionic acid methyl ester. Purified by chromatography on silica gel (3:1 hexanes/EtOAc); white solid (80%): TLC R_f=0.49 (2:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.10–8.06 (m, 2H), 7.68 (tt, 1H, J=7.2, 1.2 Hz), 7.56–7.51 (m, 2H), 6.48 (d, 1H, J=8.8 Hz), 5.84 (d, 1H, J=8.4 Hz), 4.69 (d, 1H, J=10.8 Hz), 4.64 (d, 1H, J=10.8 Hz), 3.76 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.4, 166.1, 135.2, 133.0, 129.6, 129.1, 93.0, 78.4, 60.5, 53.8 ppm; IR (thin film) ν 3276, 1753, 1690, 1449, 1377, 1242, 1187, 858 cm^{-1}; HRMS (ES^+) calcd for $C_{12}H_{12}Cl_3NO_6S$ 402.9451 found 425.9340 (MNa^+).

3.5.1.6. (1-Ethyl-2-oxo-butyl)sulfamic acid 2,2,2-trichloroethyl ester. Purified by chromatography on silica gel (6:1 hexanes/EtOAc); colorless oil (84%): TLC R_f=0.17 (9:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.89 (d, 1H, J=7.5 Hz), 4.64 (d, 1H, J=10.5 Hz), 4.57 (d, 1H, J=10.5 Hz), 4.29 (ddd, 1H, J=6.0, 6.0, 4.5 Hz), 2.63 (dq, 1H, J=18.0, 7.5 Hz), 2.51 (dq, 1H, J=18.0, 7.5 Hz), 2.04 (dddd, 1H, J=15.0, 15.0, 7.5, 5.0 Hz), 1.74 (sept, 1H, 7.0 Hz), 1.13 (t, 3H, J=7.0 Hz), 0.96 (t, 3H, J=7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.9, 93.2, 78.0, 62.8, 32.8, 25.2, 8.7, 7.5 ppm; IR (thin film) ν 3285, 2978, 1721, 1373, 1188, 1008, 858 cm^{-1}; HRMS (ES^+) calcd for $C_8H_{14}Cl_3NO_4S$ 324.9709 found 347.9613 (MNa^+).

3.5.1.7. (2-Oxo-cyclohexyl)sulfamic acid 2,2,2-trichloroethyl ester. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (92%): TLC R_f=0.22 (4:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.98 (br d, 1H, J=4.5 Hz), 4.62 (d, 1H, J=11.0 Hz), 4.58 (d, 1H, J=11.0 Hz), 4.18–4.12 (m, 1H), 2.73–2.67 (m, 1H), 2.62 (ddddd, 1H, J=14.0, 2.5, 2.5, 2.5, 2.5 Hz), 2.40 (ddd, 1H, J=13.5, 6.5, 1.0 Hz), 2.20–2.13 (m, 1H), 1.98–1.92 (m, 1H), 1.82–1.72 (m, 1H), 1.71–1.54 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 205.3, 93.2, 78.2, 61.4, 40.7, 35.9, 27.4, 23.8 ppm; IR (thin film) ν 3302.86, 2918, 1720, 1374, 1184, 1020, 858 cm^{-1}; HRMS (ES^+) calcd for $C_8H_{12}Cl_3NO_4S$ 322.9553 found 345.9445 (MNa^+).

3.5.1.8. 5-(2,2,2-Trichloroethoxysulfonylamino)cyclohex-2-enone. To a solution of $Cl_3CCH_2OSO_2NH_2$ (1.25 g, 5.5 mmol, 1.1 equiv) in 10.0 mL of C_6H_5Cl were added sequentially 1,3-cyclohexadiene (5.0 mmol), MgO (460 mg, 11.5 mmol, 2.3 equiv), and $Rh_2(NHCOCF_3)_4$ (64 mg, 0.10 mmol, 0.02 equiv). The purple mixture was cooled to −10 °C (s-CO_2/ethylene glycol bath) and $PhI(OAc)_2$ (210 mg, 0.65 mmol, 1.3 equiv) was added in a single portion. After 40 min of stirring at −10 °C, the reaction was warmed to 23 °C. The reaction was stirred for 1 h then diluted with 30 mL of CH_2Cl_2 and filtered through a pad of Celite. The flask and filter cake were washed thoroughly with CH_2Cl_2 and the combined filtrates were concentrated under reduced pressure. The isolated material was dissolved in 25 mL of DMSO and the mixture was stirred for 12 h. The solution was transferred to a separatory funnel with 100 mL of EtOAc and washed with 2×100 mL of H_2O. The aqueous washes were combined and extracted with 1×100 mL of EtOAc. The collective organic fractions were washed with 1×50 mL of saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (3:1 hexanes/EtOAc) yielded the desired product as a white solid (1.29 g, 73%). TLC R_f=0.54 (1:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.10–7.05 (m, 1H), 6.14 (ddd, 1H, J=10.0, 3.0, 1.0 Hz), 6.08 (br d, 1H, J=3.0 Hz), 4.66 (d, 1H, J=11.0 Hz), 4.62 (d, 1H, J=10.5 Hz), 4.19 (ddd, 1H, J=14.0, 5.0, 3.5 Hz), 2.73–2.67 (m, 1H), 2.66–2.51 (m, 2H), 2.01–1.92 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 193.9, 152.4, 127.2, 93.2, 78.3, 58.7, 30.3, 25.6 ppm; IR (thin film) ν 3291, 1687, 1389, 1185, 1020, 859 cm^{-1}; HRMS (ES^+) calcd for $C_8H_{10}Cl_3NO_4S$ 320.9396 found 343.9288 (MNa^+).

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