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Synthesis of *cis*-*C*-Iodo-*N*-Tosyl-Aziridines using Diiodomethyllithium: Reaction Optimization, Product Scope and Stability, and a Protocol for Selection of Stationary Phase for Chromatography

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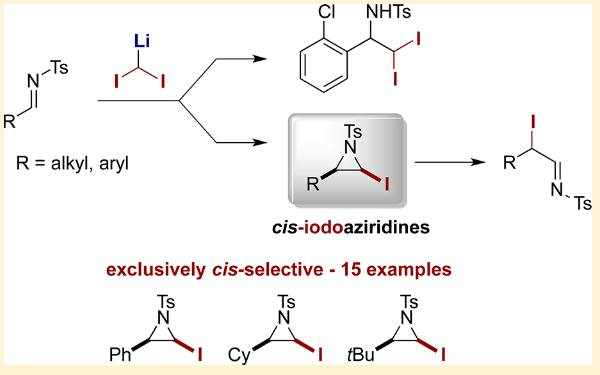
Supporting Information

ABSTRACT: The preparation of *C*-iodo-*N*-Ts-aziridines with excellent *cis*-diastereoselectivity has been achieved in high yields by the addition of diiodomethyllithium to *N*-tosylimines and *N*-tosylimine−HSO_2Tol adducts. This addition-cyclization protocol successfully provided a wide range of *cis*-iodoaziridines, including the first examples of alkyl-substituted iodoaziridines, with the reaction tolerating both aryl imines and alkyl imines. An *ortho*-chlorophenyl imine afforded a *β*-amino *gem*-diiodide under the optimized reaction conditions due to a postulated coordinated intermediate preventing cyclization. An effective protocol to assess the stability of the sensitive iodoaziridine functional group to chromatography was also developed. As a result of the judicious choice of stationary phase, the iodoaziridines could be purified by column chromatography; the use of deactivated basic alumina (activity IV) afforded high yield and purity. Rearrangements of electron-rich aryl-iodoaziridines have been promoted, selectively affording either novel *α*-iodo-*N*-Ts-imines or *α*-iodo-aldehydes in high yield.



■ INTRODUCTION

Aziridines, the smallest saturated aza-heterocycles, are important and common synthetic intermediates in organic chemistry.[1,2] The small bond angles and associated ring strain inherent in aziridines affords high reactivity toward ring-opening reactions with carbon and heteroatom nucleophiles, providing functionalized amines with stereocontrol.[3] Aziridines participate in a range of additional transformations that take advantage of the ring strain, including cycloaddition reactions and rearrangements, which have been employed particularly in the synthesis of other nitrogen heterocycles.[4,5] *C*-Halogen-substituted aziridines introduce additional structural complexity and a further range of reactivity.[6] Halo-aziridines bearing chlorine have been most widely investigated, especially *gem*-dihalogenated aziridines due to their ease of preparation by the addition of dichlorocarbene to imines,[7] and other suitable methods.[6,8,9] These have been used as important building blocks in the synthesis of heterocyclic compounds due to their high reactivity toward both ring-opening and ring expansion reactions.

The preparation and isolation of monohalogenated aziridines is less common and more challenging due to rearrangement chemistry dominating their reactivity.[6] Pioneering work in the formation of monochloroaziridines was reported by Deyrup and co-workers; a monochloroaziridine was generated by the reaction of dichloromethyllithium with *N*-benzylideneaniline at low temperatures, affording the *cis*-chloroaziridine (Figure 1A).[9a] Since this seminal investigation, *α*-chloroaziridines have been accessed via reductive halogenation from *gem*-dihalogented aziridines,[10] addition of acid chlorides across 2*H*-azirines,[11] nitrene addition to chloroalkenes,[12] and trapping of metalated aziridines with an electrophilic source of chlorine (Figure 1B).[13] Chlorinated aziridines have been shown to undergo nucleophilic displacement of chloride with a variety of nucleophiles including NaOMe, NaCN and $LiAlH_4$, leaving the aziridine intact.[9a]

The synthesis of bromoaziridines has only relatively recently been reported. Ziegler first disclosed a 4:1 *cis*/*trans* mixture of bromoaziridines, formed via a Barton decarboxylation-bromination sequence (Figure 1C).[14a] These bromoaziridine products were used to regenerate the radical from the C−Br bond to promote intramolecular cyclization, toward the synthesis of mitomycin-like antitumor agents.[14] More recently, Yudin adopted a nitrogen-transfer approach, generating nitrenes from *N*-aminophthalimide with $PhI(OAc)_2$ in the presence of bromoalkenes (Figure 1D).[15] Huang has formed bromoaziridines through a multiple electrophilic addition of $TsNBr_2$ to ene-ynoates.[16] Bromoaziridines have also been reported as intermediates, formed by the reaction of a

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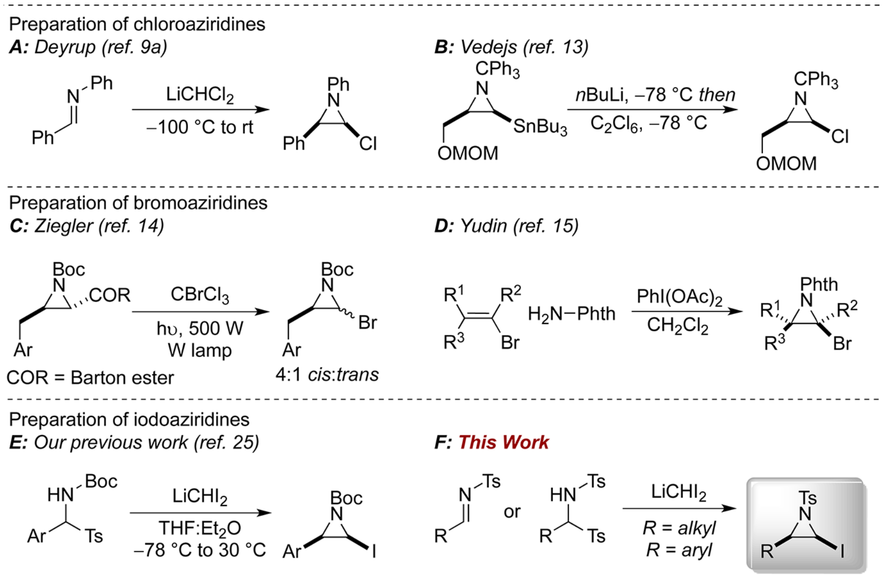


Figure 1. Preparation of mono-*C*-halogenated aziridines.

silyldibromomethyllithium with imines, from which bromide was displaced in situ (RMgX, $LiAlH_4$) leaving the aziridine intact.[17] Dibromoaziridines have been recently reported by Li through addition of bromoform to imines followed by cyclization.[18] Mono and difluoroaziridines have also been reported recently.[19]

There has been significant recent interest in the functionalization of intact aziridine rings as a divergent route to aziridine derivatives. To date this has largely been achieved through the formation of aziridine anions followed by reaction with electrophiles.[20] Deprotonation of unstabilized monosubstituted aziridines can occur regio- and stereoselectively: occurring *trans* to the substituent at the least hindered position for alkyl-aziridines, or at the benzylic position for aryl-aziridines.[21] Functional group exchange has also been demonstrated to be an effective method for generating aziridinyl anions, which react with electrophiles at the predefined position.[13,22] In addition, the palladium-catalyzed cross-coupling of intact aziridines has recently been achieved; separately Vedejs,[23] and ourselves[24] have reported the cross-coupling of aryl halides with aziridine metal species formed by Bu_3Sn−Li exchange and TolSO−Mg exchange respectively. In both examples, the cross-couplings proceeded via transmetalation to zinc and afforded retention of stereochemistry at the reacting center.

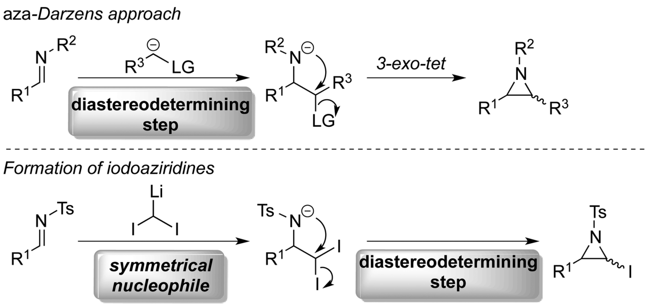
We are interested in methods for the functionalization of intact aziridines.[24] We envisaged that iodo-substituted aziridines would offer potential for functionalization of the intact ring via a variety of methods in a regio- and stereoselective fashion. We proposed that an efficient preparation of iodoaziridines would open possibilities for new complementary reactivity, with nucleophilic or electrophilic reagents, or via cross-coupling. We recently communicated the first examples of the iodoaziridine functional group bearing an *N*-Boc group through the reaction of diiodomethyllithium with *N*-Boc-imine−sulfinic acid adducts (Figure 1E).[25] This was successful with aromatic imine substrates, proceeding via a *gem*-diiodide intermediate in a highly diastereoselective manner, to afford aziridines bearing the aryl and iodo groups in a *cis*-relationship.

Here we disclose the full study into the preparation of a new class of alkyl and aromatic substituted iodoaziridines bearing an *N*-Ts group, isolated with excellent *cis*-diastereoselectivity, in high yields in one step from *N*-tosylimines and *N*-tosylimine−HSO_2Tol adducts (Figure 1F). We report in detail the development of the reaction to form *N*-Ts iodoaziridines, and their differing reactivity and stability to the *N*-Boc iodoaziridines. The present methodology extends the reaction scope, being successful for alkyl as well as aryl imine substrates, and we also report the diastereoselective reaction with a stereochemically pure *N*-sulfinyl imine. In addition, we report a protocol for determining the optimal stationary phase to use in chromatography for the purification of potentially unstable compounds, which resulted in increased yields for the iodoaziridines. The selective transformation of an iodoaziridine to novel α-iodo-*N*-Ts-imine and α-iodo-aldehyde functional groups is also reported.

■ RESULTS AND DISCUSSION

Reaction Optimization. We proposed iodoaziridines could be accessed by an addition-cyclization protocol involving the reaction of *N*-Ts-imines with diiodomethyllithium, analogous to the aza-Darzens reaction. The aza-Darzens reaction involves the addition of a carbon nucleophile bearing a leaving group to an imine to form a β-haloamine intermediate that undergoes cyclization to afford the aziridine (Scheme 1).[2c] Commonly the carbene equivalent reagent is stabilized by an electron-withdrawing group, often an ester (e.g., $R^3 = CO_2R$ in Scheme 1). In these cases, the diastereoselectivity in the aziridine product is determined in the initial addition, which is followed by a stereospecific cyclization. There are examples of unsubstituted, unstabilized MCH_2X reagents (R^3 = H) being used to afford terminal aziridines. Concellón has reported the enantioselective preparation of terminal aziridines using iodomethyllithium and enantioenriched imines.[26] Chloromethyllithium has been employed in a similar fashion.[27] Diiodomethylmetal reagents ($MCHI_2$) differ from both above scenarios, being unstabilized and substituted, and importantly as symmetrical nucleophiles, the initial addition step is not diastereodetermining. Consequently the cyclization step

Scheme 1. Comparison of the Stereochemical Outcome in the aza-Darzens Reaction



determines the diastereochemistry of the aziridine product through selecting one of two potential iodide leaving groups.

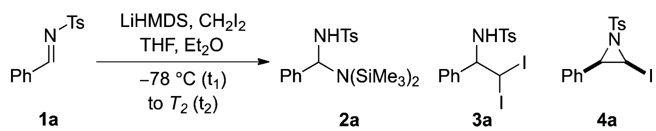
Since $MCHI_2$ reagents were first described by Seyferth and Lambert in 1973,[28] they have had relatively little use in synthesis, possibly due to the required low temperatures.[29] Charette recently described improved conditions for the formation of diiodomethane anions ($LiCHI_2$ and $NaCHI_2$) at −78 °C generating *gem*-diiodoalkanes by alkylation with primary alkyl iodides, and (*E*)-*β*-aryl vinyl iodides from benzyl bromides by alkylation/elimination.[30−32] Initial investigations were undertaken on the addition of $MCHI_2$ to phenyl *N*-Ts imine, chosen due to ready availability and stability. The tosyl group was expected to be an appropriate electron-withdrawing group to stabilize charge in the intermediate ($n_N-\sigma^*_{(S-O)}$),[33] and prevent elimination of iodide from the iodoaziridine products, while also providing a degree of steric bulk sufficient to engender diastereocontrol in the cyclization step.

In this study, $MCHI_2$ reagents were preformed by deprotonation of CH_2I_2 for 20 min at −78 °C, prior to addition of the imine, and the reaction quenched after 1 h at −78 °C to avoid any potential product decomposition on warming. The initial choice of solvent conditions (a mixture of THF:Et_2O) was selected due to the stabilizing effect on the carbenoid reagent.[28,30] Early studies varied the base used for deprotonation and workup procedures to ensure stability of the products.[34] The use of LiHMDS as base to afford $LiCHI_2$ was shown to be productive, affording a mixture of products, of which three components were identified: amino *gem*-diiodide **3a**, the desired iodoaziridine **4a**, as the *cis*-isomer, as well as aminal **2a** formed by the direct addition of LiHMDS to the imine (Table 1, entry 1). These products exhibited highly characteristic ^1H NMR signals: amino *gem*-diiodide **3a** characterized by signals at δ 5.34, 5.27, and 4.51 ppm (NH; CHI_2; CHPh); *cis*-iodoaziridine **4a**, characterized by doublets at δ 4.89 and 3.89 ppm (CHI; CHPh); aminal **2a** displayed doublets at δ 5.85 and 5.19 ppm (NH; CHPh). Both *gem*-diiodide **3a** and aziridine **4a** were observed at −78 °C, indicating cyclization was occurring at low temperature. It was notable that elimination to afford the vinyl iodide was not observed, even though this was the major side product in the *N*-Boc derivatives.[25] The ratio of products was determined by ^1H NMR of the crude reaction mixture in the presence of an internal standard.

We were concerned with minimizing the formation of the undesired aminal product **2a**, and aimed to optimize for the combined yield of diiodide **3a** and iodoaziridine **4a**. The formation of aminal **2a** suggested that deprotonation of CH_2I_2 was incomplete under these conditions, which was also implied by deuteration studies, leaving LiHMDS in solution. Increasing the equivalents of LiHMDS led to increased formation of **2a**. Indeed, in the absence of diiodomethane, treatment of imine **1a** with LiHMDS at −78 °C afforded aminal **2a** in almost quantitative yield.[35] The formation of aminal **2a** was irreversible under the reaction conditions,[36] and as a result varying the reaction time at −78 °C had no effect on the formation of **2a**. Increasing the deprotonation time to 40 min and 1 h caused a dramatic drop in the combined yield of **3a** and **4a**.

Increasing the excess of diiodomethane employed to 10 equiv did afford a significant increase in the formation of **3a** and

Table 1. Selected Optimization of the Reaction Protocol



entry[a]	LiHMDS (equiv)	CH_2I_2 (equiv)	concn [M][b]	time t_1[c] (min)	T_2 (°C)	time t_2 (min)	additive (equiv)	yields[d] (%) 2a	3a	4a
1	2.2	2.5	0.06	60				15	17	20
2	2.5	10	0.06	60				15	55	16
3	2.5	10	0.04	60				9	11	49
4	2.2	2.5	0.06	60			HMPA (1)	12	8	3
5	2.2	2.5	0.06	60			TMEDA (1)	19	1	48
6	2.2	2.5	0.06	60			DMPU (1)	8	55	19
7	2.2	2.5	0.04	60			DMPU (1)	12	14	54
8	2.0	2.3	0.15	60				8	8	31
9	3.0	3.4	0.15	60				5	15	55
10	4.0	4.5	0.15	60				7	19	63
11	3.0	3.4	0.16	30	0	15		14	0	64
12	3.0	3.4	0.16	–[e]	0	15		14	0	81

[a]Reaction conditions: imine **1a** (0.50 mmol), CH_2I_2, LiHMDS, THF/Et_2O. Deprotonation of CH_2I_2 over 20 min prior to addition of imine. [b]Concentration of base prior to addition of imine. [c]Time at −78 °C following complete addition of imine **1a**. Imine added over 5 min at −78 °C. [d]Yield of **2a**, **3a** or **4a** determined by ^1H NMR spectroscopy with reference to an internal standard (1,3,5-trimethoxybenzene). [e]Reaction warmed immediately following addition of imine.

4a (entry 2), though the formation of aminal **2a** remained at similar levels. Reaction concentration and ratio of THF:Et_2O were found to be important to the product distribution and these were thoroughly explored under these conditions, but with little overall increase in yield. Interestingly, reducing the concentration of the reaction, led to a notable increase in the proportion of the diiodide that underwent cyclization in the time frame of the reaction (compare entries 2 and 3). To reduce the excess diiodomethane employed, we examined the effect of Lewis basic additives (compare entries 1 and 4–7). The use of HMPA was detrimental, whereas TMEDA afforded an increase in the formation of **2a**, but promoted cyclization. The addition of 1 equiv DMPU afforded the highest combined yield of **3a** and **4a** (entry 6). We found that reducing the concentration under these conditions afforded an increase in cyclization product **4a** (entry 7). Despite extensive further investigation using DMPU as an additive, we were unable to make further improvements. Instead we examined the effect of increasing the equivalents of diiodomethane and base (up to 4 equiv LiHMDS) at a higher concentration, which gave rise to an increased combined yield of **3a** and **4a** (entries 8–10), presumably due to an increase in the amount of $LiCHI_2$ present in solution. Finally, it became apparent that the addition of diiodomethyllithium to the imine was rapid and the iodoaziridine product was decomposing under the reaction conditions. We continued with 3 equiv LiHMDS and it was identified that warming the reaction mixture to 0 °C was sufficient to promote rapid and complete cyclization, with minimum decomposition (entry 11). The precise mixture of THF:Et_2O was optimized, with a mixture of of 2.5:1 THF/Et_2O giving the maximum yield. Finally, reducing the time under the reaction conditions to a minimum, that is, warming the reaction as soon as addition of the imine was complete, afforded the highest yield of **4a**, with complete cyclization of any diiodide intermediate (entry 12). This provided our standard conditions for further study, affording an 81% ^1H NMR yield, which corresponded to a 76% isolated yield of iodoaziridine **4a**, exclusively as the *cis*-diastereoisomer.

Rationale of Diastereoselectivity. Throughout the optimization, only the *cis*-diastereoisomer of the iodoaziridine was observed, assigned on the basis of the magnitude of the coupling constant between CHAr and CHI protons (J = 6.1 Hz). These assignments are consistent with the coupling constants observed for *cis*-*N*-Boc iodoaziridines isolated by ourselves,[25] and for *cis*-*N*-Boc bromoaziridines by Ziegler and co-workers.[14] To rationalize the excellent *cis*-diastereoselectivity for the reaction, we invoke the steric properties of the bulky SO_2Tol group to discriminate between three possible conformations (Figure 2). The R and sulfonyl groups will align in an *anti* conformation to avoid the eclipsing interactions that make conformer **C-*trans*** unfavorable. Placing the *N*-group and iodide in an *antiperiplanar* fashion appropriate for cyclization therefore provides two possible conformations **A-*cis*** and **B-*trans***. In the transition state the pyramidalization of *N* will position the toluenesulfonyl group to one side of the ring, which clashes with other ring substituents.[37] We propose that an unfavorable interaction between the nondisplaced iodide and the toluenesulfonyl group is dominant. In the preferred conformation, **A-*cis***, the iodide is positioned away from the bulk of the tolyl-sulfonyl group leading to the *cis*-iodoaziridine.[38] In conformation **B-*trans***, the unfavorable interaction between the nondisplaced iodide and the large toluenesulfonyl group results in the conformation being disfavored.

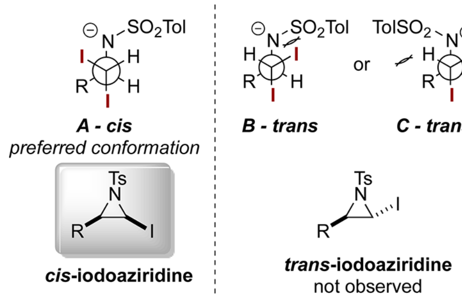
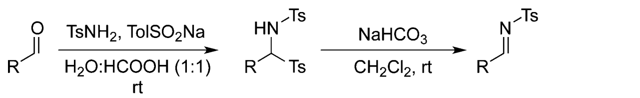


Figure 2. Rationale of diastereoselectivity in cyclization to afford *cis*-iodoaziridines.

Reaction Scope. To explore the scope of the iodoaziridination reaction a range of of *N*-Ts imines **1** and *N*-Ts imine–HSO_2Tol adducts **5** were prepared by literature procedures, with some minor modifications (Scheme 2 and Scheme 3).[39−41] Certain alkyl substrates with α-protons were retained as their imine–HSO_2Tol adducts, due to the increased stability to hydrolysis and enamine formation compared to the imines.

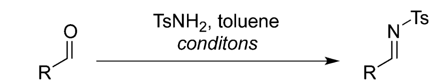
Scheme 2. Formation of Alkyl Imine–HSO_2Tol Adducts and Imines from Corresponding Aldehydes by Chemla's Two-step Procedure



Yield of imine–HO_2STol **5**
R = *c*Hex, 60%, **5i**
R = *i*Pr, 52%, **5j**
R = Et_2CH, 73%, **5k**
R = Et(Me)CH, 60%, **5l**
R = *n*Pr, 90%, **5o**
R = *n*Hex, 64%, **5p**

Yield of imine **1** (over 2 steps)
R = Ph, 79%, **1a**
R = (4-*t*Bu)C_6H_4, 55%, **1c**
R = (2-Me)C_6H_4, 60%, **1d**
R = (4-Cl)C_6H_4, 24%, **1g**
R = (2-Cl)C_6H_4, 70%, **1h**
R = *c*Hex, 80%, **1i**
R = (3-cyclohexene), 63%, **1m**

Scheme 3. Imine Formation by Direct Condensation

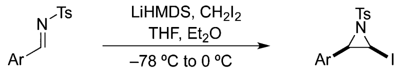


R = (4-Me)C_6H_4: 32% (Dean-Stark) **1b**
R = 1-napthyl: 22% (Dean-Stark) **1e**
R = (4-F)C_6H_4: 31% ($BF_3 \cdot Et_2O$, 8 mol %, reflux) **1f**
R = *t*Bu: 38% ($BF_3 \cdot Et_2O$, 8 mol %, reflux) **1n**

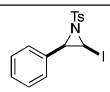
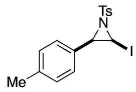
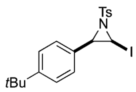
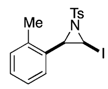
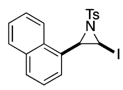
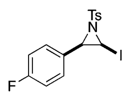
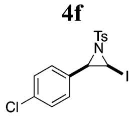
With a series of imines in hand we examined the scope of the iodoaziridination reaction under our optimized set of reaction conditions. Initially we examined the addition of diiodomethyllithium to aromatic imines under the reaction conditions optimized for **4a**, forming the iodoaziridines in high yields with exclusive *cis*-diastereoselectivity (Table 2).

Electron-donating groups were tolerated under the reaction conditions, as shown by the 4-Me and 4-*t*Bu-phenyl examples (Table 2, entries 2 and 3). It is notable that while phenyl iodoaziridine was stable to chromatography on silica, these more electron-rich examples were not; purification on deactivated basic alumina (activity IV) afforded the yields stated. The remainder of the scope was purified by chromatography using basic alumina (activity IV, see below for further discussion). *ortho*-Substituted aromatic substrates were warmed to rt as they required an increased temperature to

Table 2. Scope of Iodoaziridines with Aromatic Imines



1a-g 4a-g

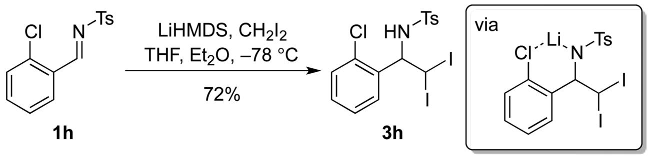
entry	Ar	method[a,b]	iodoaziridine	yield (%)	dr[c]
1	Ph	**A**	 **4a**	76	>95:5
2	(4-Me)C_6H_4	**A**	 **4b**	48	>95:5
3	(4-*t*Bu) C_6H_4	**A**	 **4c**	58	>95:5
4	(2-Me)C_6H_4	**B**	 **4d**	68	>95:5
5	1-napthyl	**B**	 **4e**	78	>95:5
6	(4-F)C_6H_4	**A**	 **4f**	47	>95:5
7	(4-Cl)C_6H_4	**A**	 **4g**	57	>95:5

[a]Method A: imine (0.50 mmol), *n*BuLi (1.50 mmol), HMDS (1.50 mmol), CH_2I_2 (1.70 mmol), THF:Et_2O (0.16 M at deprotonation), −78 to 0 °C. [b]Method B: identical to Method A but reaction warmed to rt for 20 min after addition of imine. [c]Where >95:5 stated, only the *cis*-diastereoisomer could be observed by ^{1}H NMR.

induce full cyclization from the intermediate *β*-amino *gem*-diiodides (entries 4 and 5, denoted Method B). For 2-tolyl imine **1d**, a 9:5 ratio of iodoaziridine (**4d**)/amino *gem*-diiodide (**3d**) was observed under the standard conditions. Warming to rt by removing the reaction flask from the dry ice bath ensured complete cyclization (>19:1) to yield the corresponding *cis*-iodoaziridine in high yield. This was similarly successful with the 1-napthyl substituent affording an excellent yield of iodoaziridine **4e** (entry 5). 4-Fluoro- and 4-chloro-substituted aromatics were also well tolerated under the reaction conditions (entries 6 and 7).

ortho-Chlorophenyl imine **1h** was subjected to the *ortho*-substituted reaction conditions (Method B) but no cyclization was observed, and attempts to promote cyclization by additional warming of the reaction mixture led to decomposition. The lack of cyclization was attributed to stabilizing coordinating interactions of the lone pairs of chlorine in the postulated lithiated intermediate (Scheme 4), preventing the required orientation for cyclization being achieved. The corresponding amino *gem*-diiodide **3h** could be isolated in high yield by quenching the reaction at −78 °C. Subjecting isolated **3h** to cyclization conditions previously developed for *β*-*N*-Boc diiodides to their corresponding iodoaziridines

Scheme 4. Amino *gem*-Diiodide Formation with 2-Cl(C_6H_4) Substituted *N*-Ts Imine and Postulated Coordination Preventing Cyclization



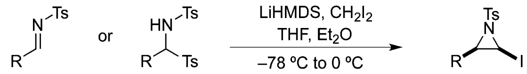
(Cs_2CO_3, DMF, rt),[25] only afforded degradation of the starting material.

In our previous work on *N*-Boc iodoaziridines, alkyl imines were unsuccessful.[25] Pleasingly with the *N*-Ts group, alkyl iodoaziridines could be successfully accessed, constituting a significant increase in reaction scope. Using the cyclohexyl imine **1i**, the reaction performed similarly to the aryl examples, that is, the diiodide formed rapidly and complete cyclization occurred to the iodoaziridine on warming the reaction mixture to 0 °C. The cyclohexyl substituted iodoaziridine **4i** was also obtained from the imine−HSO_2Tol adduct through the use of identical reaction conditions except for an additional equivalent of base and diiodomethane employed (Method C) to form the imine in situ. The two methods returned *cis*-iodoaziridine **4i** in comparable yields (68% from imine **1i** vs 57% from imine−HSO_2Tol adduct **5i**, Table 3 entries 1 and 2). Due to ease of synthesis and handling of the adducts, several of the alkyl imines were used in this form. A range of branched alkyl imine−HSO_2Tol adducts were examined under the modified reaction conditions (entries 3 to 5), each displaying complete *cis*-diastereoselectivity upon cyclization with good yields. Using the *α*-chiral imine generated from **5l** afforded excellent *cis*:*trans* selectivity in the cyclization step, but only minimal diastereoselectivity in the addition step (facial selectivity = 1.9:1). Alkene containing imine **1m** was also successful, but again without significant facial selectivity. The *t*Bu-substituted imine **1n** was submitted under the *ortho*-reaction conditions (Method B), due to concerns with the steric bulk of the *t*Bu group affecting the degree of cyclization. Remarkably, under these conditions, iodoaziridine **4n** was isolated in an excellent yield of 70%, and only the *cis*-iodoaziridine was observed, despite significant eclipsing interactions between the *t*Bu and iodide groups in the product.

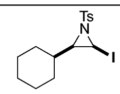
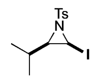
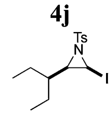
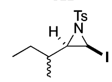
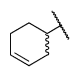
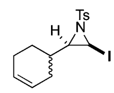
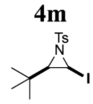
Primary alkyl imine−HO_2STol adducts did not perform well under the reaction conditions with *n*Pr and *n*Hex side chains returning only 6 and 4% yields of the corresponding *cis*-iodoaziridines respectively (Scheme 5). Here aminal formation was the major product from the reaction as the reduced steric demands of these primary alkyl substrates allows the irreversible addition of the bulky LiHMDS, which is prevented in the branched substrates. Attempts to increase the equivalents of diiodomethane, or of both diiodomethane and base, were unsuccessful and further optimization is required for this substrate class.

A Method for the Assessment of Compound Stability to Stationary Phases for Chromatography. The isolation and purification of potentially unstable compounds is an essential skill of the synthetic chemist. Due to the acidic nature of silica gel, decomposition of compounds during silica chromatography can be a common occurrence. While there are several alternative materials that can be employed as stationary phases for chromatography,[42] there is not a method

Table 3. Scope of Iodoaziridines with Branched Alkyl Imines and Alkyl Imine–HO_2STol Adducts

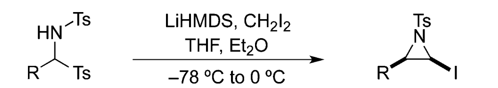


1i,m,n or **5i-l** → **4i-n**

entry	R	imine/ imine–HSO_2Tol adduct	method [a]	iodoaziridine	yield (%)	*dr* [b]
1	Cy	**1i**	**A**	 **4i**	68	>95:5
2		**5i**	**C**		57	>95:5
3	*i*Pr	**5j**	**C**	 **4j**	63	>95:5
4	CH(Et)Et	**5k**	**C**	 **4k**	63	>95:5
5	CH(Me)Et	**5l**	**C**	 **4l**	61	>95:5 [c,d]
6		**1m**	**A**	 **4m**	52	>95:5 [e,d]
7	*t*Bu	**1n**	**B**	 **4n**	70	>95:5

[a]Method A: imine (0.50 mmol), LiHMDS (1.50 mmol), CH_2I_2 (1.70 mmol), THF:Et_2O (0.16 M at deprotonation), −78 to 0 °C. Method B: identical to Method A but reaction warmed to rt for 20 min after addition of imine. Method C: imine–HO_2STol adduct (0.50 mmol), LiHMDS (2.00 mmol), CH_2I_2 (2.20 mmol), THF:Et_2O (0.16 M at deprotonation), −78 to 0 °C. [b]Where >95:5 stated, only the *cis*-diastereoisomer could be observed by ^{1}H NMR. [c]dr = 1.9:1. [d]Relative configurations not determined. [e]dr = 1.5:1.

Scheme 5. Iodoaziridine Synthesis with Primary Alkyl Imine–HO_2STol Adducts



R = *n*Pr **5o**
R = *n*Hex **5p**

R = *n*Pr, 6% **4o**
R = *n*Hex, 4% **4p**

to rapidly and quantitatively compare the performance of these alternatives with regard to the recovery of unstable compounds.

Whereas the majority of the *N*-Boc iodoaziridines were stable to silica,[25] it was quickly apparent in this study that the *N*-Ts derivatives behaved significantly differently and compounds **4b** and **4c** underwent major decomposition. While **4a** afforded a good recovery with respect to the yield determined by ^{1}H NMR, purification of iodoaziridine **4b** afforded <50% of the expected recovery. We therefore used compound **4b** to study the effect of different stationary phases on the recovery after purification. To achieve this, we developed a simple protocol for assessing the stability of potentially unstable compounds to chromatography, which enabled us to access the iodoaziridines in high yield.

A sample of **4b** was prepared as described above, and an internal standard added to obtain a yield by ^{1}H NMR prior to purification (Table 4, entry 1). To probe the stability of **4b** on a range of stationary phases, we subjected crude **4b** to conditions that model the experience of the compound during column chromatography, replicating both the solvent conditions and

Table 4. Comparison of the Effect of Different Stationary Phases on the Stability of 4b

entry	stationary phase	recovery of iodoaziridine **4b** (%)[a]	yield of α-iodo-aldehyde 7 (%)[a]
1	crude	59	0
2	–[b]	59	0
3	silica gel	25	32
4	silica gel + 1% Et_3N	26	30
5	neutral alumina	0	0
6	basic alumina (activity I)[c]	1	0
7	basic alumina (activity IV)[d]	53	0
8	florasil	41	15

[a]Yield determined by ^{1}H NMR spectroscopy with reference to an internal standard (1,3,5-trimethoxybenzene). [b]Sample of crude **4b** stirred in 5% EtOAc/hexane. [c]Basic alumina (activity I), oven-dried for 24 h prior to use. [d]Basic alumina (activity IV) prepared by addition of water (10% w/w) to basic alumina (activity I).

the length of time of a normal purification procedure. Samples of **4b** containing the standard were added to a slurry of the relevant stationary phase in EtOAc/hexane and stirred for 30 min.[35] The slurry was then filtered and the filtrate analyzed by ^{1}H NMR to assess the recovery of the iodoaziridine. On comparison of the yield determined by ^{1}H NMR, the levels of degradation could be quantified. A selection of stationary phases were compared as indicated in Table 4, in addition to a control experiment where no stationary phase was added.

The recovery of iodoaziridine **4b** was dramatically affected by changing the stationary phase (Table 4 and Figure 3). Exposure of **4b** to bench silica (entry 3) and base-doped silica (1% Et_3N, entry 4) caused major degradation of the iodoaziridine to iodo(phenyl)acetaldehyde **7** (vide infra). Neutral alumina and basic alumina (activity I) appeared to trap the aziridine, with poor yields being returned for iodoaziridine **4b** (entries 5 and 6). However, the stability of the iodoaziridine was greatly enhanced using deactivated basic alumina (activity IV vs activity I), with only a small drop in the recovery observed. Pleasingly, using column chromatography on basic alumina (activity IV) afforded an isolated yield of 48%, which closely resembled that observed in the crude mixture.

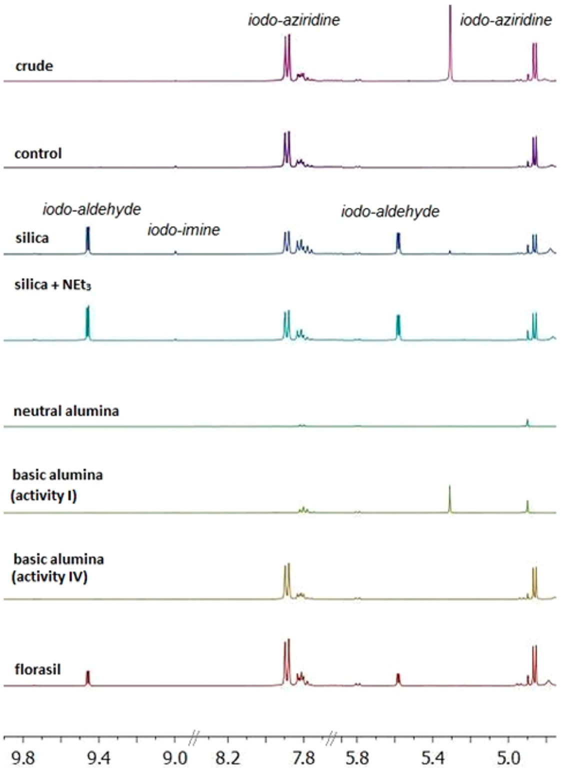


Figure 3. Selected sections of ^{1}H NMR indicating the stability of iodoaziridine **4b** to stationary phases.

By comparison, performing the analysis on phenyl analogue **4a** displayed essentially quantitative recovery on all potential stationary phases (Table 5), with the exception of neutral alumina and basic alumina (activity I), which trapped the product (entries 5 and 6). The minor products on bench silica and base-doped silica were assigned to be the corresponding α-iodo-aldehyde. This indicated that the method is appropriate, providing good recovery when the compound does not undergo degradation. As a consequence of these results, we used basic alumina (activity IV) for the remainder of the reaction scope above. We believe this protocol may be a useful approach to determine the optimal stationary phase for chromatography of other compounds unstable to silica. An additional advantage compared to directly performing chromotography on different stationary phases was that this protocol enables a more facile investigation into the identity of decomposition products, where these may be missed on collecting fractions.

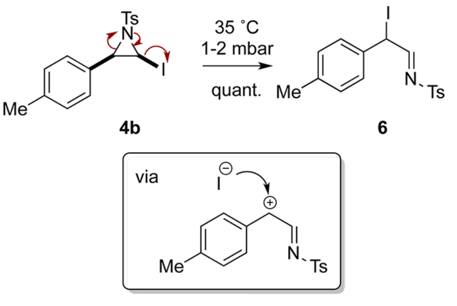
Table 5. Comparison of the Effect of Different Stationary Phases on the Stability of 4a

entry	stationary phase	yield of **4a** (%)[a]
1	crude	80
2	–[b]	80
3	silica gel	78
4	silica gel + Et_3N	77
5	neutral alumina	4
6	basic alumina (activity I)[c]	0
7	basic alumina (activity IV)[d]	79
8	florasil	79

[a]Yield determined by ^{1}H NMR spectroscopy with reference to an internal standard (1,3,5-trimethoxybenzene). [b]Sample of crude **4a** stirred in 5% EtOAc/hexane. [c]Basic alumina (activity I), oven-dried for 24 h prior to use. [d]Basic alumina (activity IV) prepared by addition of water (10% w/w) to basic alumina (activity I).

Stability of *N*-Ts-iodoaziridines: Rearrangement. During the isolation of more electron-rich iodoaziridines **4b** and **4c** it was observed that they were subject to rearrangement to form α-iodo imines (Scheme 6). This rearrangement could be achieved in quantitative conversion by submitting neat *cis*-iodoaziridine **4b** to mild heating under reduced pressure.[43]

Scheme 6. Rearrangement of *cis*-Iodoaziridine 4b to α-Iodo Imine 6

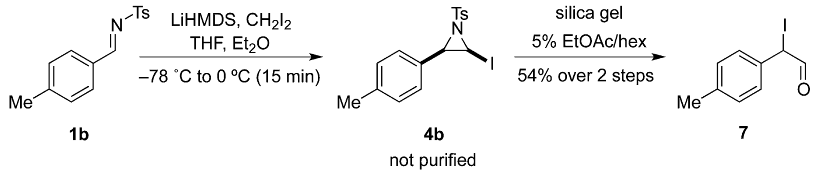


We propose this occurs by unimolecular opening of the iodoaziridine and elimination of iodide to afford a benzylic cation, which is trapped by iodide (Scheme 6). Similar rearrangements have been highlighted by Yudin converting α-bromoaziridines to α-bromohydrazones.[15] The rearrangement of more electron-rich aromatic *N*-Ts iodoaziridines (R = (4-*t*Bu)C_6H_4, **4c**) was also observed by ^{1}H NMR, but the resulting iodo-imine could not be isolated due to rapid decomposition.

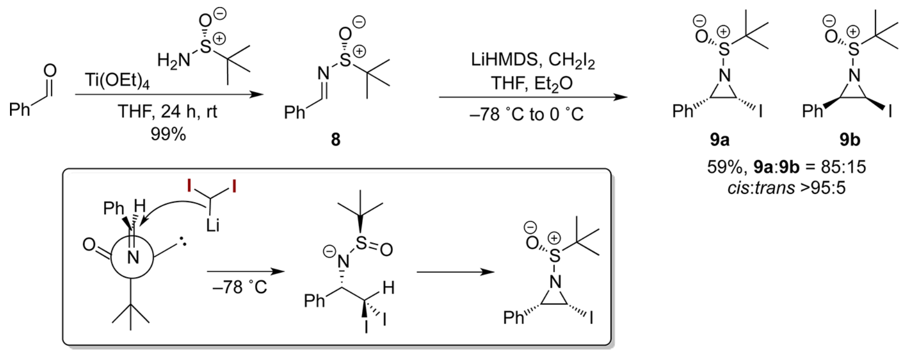
Following the observations made during the stability studies to silica above, we were keen to establish whether iodoaziridine **4b** could be converted directly to the iodo-aldehyde, which was observed on stirring crude **4b** with silica. Indeed, treating a crude sample of iodoaziridine **4b** with bench silica in a mixture of EtOAc/hexane and open to the air, afforded complete rearrangement/hydrolysis of the aziridine to iodoaldehyde **7** in 54% over the 2 steps following chromatography (Scheme 7).

Stereoselective Iodoaziridination with a Chiral *N-tert*-Butylsulfinyl Imine. We were keen to extend the current protocol of iodoaziridination to chiral *N*-protecting groups to provide facial selectivity in the initial addition to the imine. The use of Ellman's auxiliary has received significant attention in the stereoselective synthesis of aziridines via the aza-Darzens

Scheme 7. Preparation of Iodo-aldehyde 7



Scheme 8. Preparation of Chiral Sulfinyl Iodoaziridines 9a and 9b

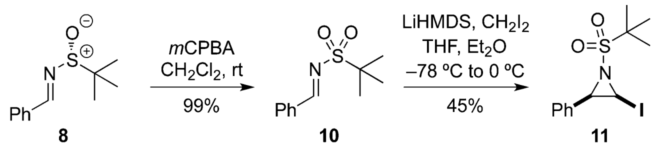


approach.[44,45] Attempts to use the comparable toluenesulfinyl group were unsuccessful, as this is known to undergo attack at sulfur with organometallic reagents.[46] Therefore, we investigated the *t*Bu sulfinyl group, which has been shown to offer stabilizing interactions in the functionalization of aziridinyl anions.[47] Phenyl *t*-butyl sulfinyl imine **9** was prepared by direct condensation using Ti(OEt)$_4$ (Scheme 8).[48]

Sulfinyl imine **8** was then subjected to the reaction conditions optimized for the *N*-Ts imines (Method A, Table 2). Pleasingly this successfully afforded the desired iodoaziridines **9a** and **9b** in a 59% yield with diastereoselectivity (dr = 85:15). Characteristic ^{1}H NMR signals for aziridine protons were observed for both products; doublets at δ 4.54 and 3.71 ppm for the major diastereoisomer and δ 4.83 and 3.30 ppm for the minor diastereoisomer, all with J = 6.0 Hz corresponding to the *cis*-isomer. Given the well-established models for stereocontrol for the 1,2-addition of organolithiums to aldimines the major and minor diastereoisomers could be predicted (Scheme 8, boxed).[44,49] In this model, the organolithium approaches from the least hindered face of the imine via the lone pair of the sulfinyl group, affording diastereoisomer **9a** as the major product. The dr obtained in the addition of diiodomethyllithium is comparable to that obtained for organolithium reagents attacking through an acyclic transition state, for example PhLi addition into *N*-*tert*-butylsulfinyl 4-chlorophenyl imine in THF at −78 °C, dr = 73:27.[49]

Due to the differing nature of the *N*-sulfinyl protecting group, stability tests were run to determine the best stationary phase for flash column chromatography in the manner described above. Here, the *N*-sulfinyl iodoaziridine was found show similar stability to **4a**, with the best recovery obtained with basic alumina (activity V, 15% w/w water added). Applying the optimized conditions to *t*Bu-sulfonyl imine **10** (Method A), prepared by oxidation of sulfinyl imine **8**,[50] afforded the corresponding *N*-Bus-iodoaziridine **11** in a moderate 45% yield (Scheme 9).

Scheme 9. Preparation of *N*-Bus Iodoaziridine under Optimized Conditions



■ CONCLUSION

We have developed an effective method to install iodide functionality onto a range of alkyl and aromatic substituted *N*-tosylaziridines. The addition of diiodomethyllithium to imines and imine−HO$_2$STol adducts at low temperature, followed by warming, afforded cyclization to the corresponding *cis*-*N*-Ts-iodoaziridines in a highly diastereoselective fashion and in good yields. The use of the *N*-Ts protecting group has enabled the formation of alkyl iodoaziridines for the first time. These novel alkyl and aromatic substituted iodoaziridines provide fascinating structures and potential synthetic intermediates for functionalization of the intact aziridine ring. The formation of these iodoaziridines was achieved in conjuction with our new protocol for assessing the best stationary phase for purification of this new class of compound. Rearrangement products of electron-rich aryl iodoaziridines were also discovered, and the formation of an enantioriched *N*-sulfinyl iodoaziridine was achieved for the first time.

■ EXPERIMENTAL SECTION

General Experimental Considerations. All nonaqueous reactions were run under an inert atmosphere (argon) with flame-dried glassware using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O, CH_2Cl_2). Flash column chromatography was performed using 230−400 mesh silica or 50−200 μm Brockmann basic alumina (activity IV or activity V) with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm), or aqueous potassium permanganate stain. Infrared spectra (ν_{max}, FTIR ATR) were recorded in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance spectra were recorded on 400 or 500 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ = 7.27 ppm). Data is reported

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as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz, integration]. ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($^{13}CDCl_3$: 77.0 ppm). ^{19}F NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million referenced to the standard monofluorobenzene: −113.5 ppm. J values are reported in Hertz. Assignments of $^1H/^{13}C$ spectra were made by the analysis of δ/J values, and COSY, HSQC, and HMBC experiments as appropriate. Melting points are uncorrected. **Reagents**: Commercial reagents were used as supplied or purified by standard techniques where necessary. **Compound Handling and Storage**: The *N*-Ts iodoaziridines displayed sensitivity to light and during all handling, exposure of iodoaziridines to light was minimized. However, the *N*-Ts iodoaziridines displayed a notable increase in stability to exposure to light in comparison to the *N*-Boc derivatives. Iodoaziridines were stored at −20 °C neat for short periods or as a solution in CH_2Cl_2 or $CHCl_3$ to prevent decomposition. For example, iodoaziridine **4i** was stored in a $CDCl_3$ solution for >4 months without displaying noticeable decomposition. **Deactivated basic alumina**: The activity of basic alumina was altered by the addition of water to commercial basic alumina (activity I) and evenly distributed (activity IV: 10% w/w water; activity V: 15% w/w).[51] **Imines**: Imines **1a,c−d,g,h−i** and imine−HSO_2Tol adducts **5i−l** and **5o−p** were synthesized according to the method of Chemla and co-workers. Imine **1m** was synthesized by a modification of the method of Chemla and co-workers.[39] Imines **1f** and **1n** by a modification of the method of Proctor,[41] and imines **1b**, **1e** by the method of Stalick.[40]

General Procedure 1: Imines 1a, 1c, 1d, 1g−1i. The relevant aldehyde (10.0 mmol, 1.0 equiv) was added to a solution of *p*-toluenesulfonamide (1.71 g, 10.0 mmol, 1.0 equiv) and sodium *p*-toluenesulfinate (1.96 g, 11.0 mmol, 1.1 equiv) in formic acid and water (1:1, 30 mL). The mixture was stirred at rt for 24 h to 7 days at rt, then filtered under reduced pressure and washed successively with water (50 mL) and hexane (50 mL). The resulting imine−HO_2STol adduct was dissolved in CH_2Cl_2 (100 mL) and saturated aqueous sodium bicarbonate solution (100 mL) was added. The resulting biphasic solution was vigorously stirred for 2 h at rt. The organic layer was separated, dried (Na_2SO_4) and the solvent was removed under reduced pressure to afford the imine, which was sufficiently pure or further purified where stated.

*N-[(E)-Phenylmethylidene]-4-methylbenzenesulfonamide (**1a**).* Prepared according to General Procedure 1 described above, starting from benzaldehyde (1.02 mL, 10.0 mmol). Purification by recrystallization (EtOAc/hexane) afforded imine **1a** as colorless crystals (2.06 g, 79%): mp = 106−108 °C (lit.[52] mp = 107 °C); ν_{max} (film)/cm^{-1} 3360, 3263, 3067, 2925, 2259, 1599, 1319, 1155, 1088, 907, 781, 756, 729, 688, 672; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H, CHN), 7.88−7.82 (m, 4H, 2 × SO_2Tol-H and 2 × Ph−H), 7.53 (t, J = 7.4 Hz, 1H, Ph−H), 7.40 (t, J = 7.6 Hz, 2H, 2 × Ph−H), 7.28 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 2.35 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9 (CHN), 144.4 (SO_2Tol-C quat.), 134.7 (SO_2TolC-CH_3 quat. and Ph−C), 131.9 (Ph−C quat.), 130.9 (2 × Ph−C), 129.5 (2 × SO_2Tol-C), 128.8 (2 × Ph−C), 127.7 (2 × SO_2Tol-C), 21.3 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[41]

*N-[(E)-4-Methylphenylmethylidene]-4-methylbenzenesulfonamide (**1b**).* 4-Tolualdehyde (2.83 mL, 24.0 mmol, 1.2 equiv) was added to a solution of *p*-toluenesulfonamide (3.42 g, 20.0 mmol, 1.0 equiv) in toluene (50 mL). The resulting mixture heated under Dean−Stark conditions for 48 h, after which the solvent was removed under reduced pressure. The crude imine was washed with hexane (50 mL), Et_2O (50 mL) and then washed with 1 M NaOH (50 mL) to afford imine **1b** as a brown solid (1.75 g, 32%): mp = 117−118 °C (lit.[53] mp = 118−119 °C); ν_{max} (film)/cm^{-1} 2922, 1590, 1558, 1447, 1413, 1364, 1315, 1155, 1086, 1018, 871, 791, 760, 667; ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H, CHN), 7.89 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.82 (d, J = 8.1 Hz, 2H, 2 × Tol-H), 7.36 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.30 (d, J = 8.1 Hz, 2H, 2 × Tol-H), 2.44 (s, 6H, SO_2Tol-CH_3 and Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9 (CHN), 146.3 (Tol-C quat.), 144.4 (SO_2Tol-C quat.), 135.2 (SO_2TolC-CH_3 quat.), 131.3 (2 × Tol-C), 129.8 (2 × SO_2Tol-C), 129.7 (2 × Tol-C and TolC-CH_3 quat.), 127.9 (2 × SO_2Tol-C), 21.9 (Tol-CH_3), 21.5 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[54]

*N-[(E)-4-tert-Butylphenylmethylidene]-4-methylbenzenesulfonamide (**1c**).* Prepared according to General Procedure 1 described above, starting from 4-*tert*-butylbenzaldehyde (1.67 mL, 10.0 mmol). Purification by recrystallization (EtOAc/hexane) afforded imine **1c** as a white solid (1.72 g, 55%): mp = 114−116 °C (lit.[55] mp = 116−117 °C); ν_{max} (film)/cm^{-1} 2967, 2366, 1741, 1598, 1327, 1159, 1090, 785; ^1H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H, CHN), 7.90−7.85 (m, 4H, 2 × SO_2Tol-H and 2 × *t*BuAr−H), 7.51 (d, J = 8.3 Hz, 2H, 2 × *t*BuAr−H), 7.34 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 2.44 (s, 3H, SO_2Tol-CH_3), 1.34 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0 (CHN), 159.3 (*t*Bu-CAr quat.), 144.4 (SO_2Tol-C quat.), 135.4 (SO_2TolC-CH_3 quat.), 131.3 (2 × *t*BuAr−C), 129.8 (*t*BuAr−C quat.), 129.7 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 126.2 (2 × *t*BuAr−C), 35.4 (*C*(CH_3)$_3$ quat.), 31.0 (C(CH_3)$_3$), 21.6 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[56]

*N-[(E)-2-Methylphenylmethylidene]-4-methylbenzenesulfonamide (**1d**).* Prepared according to General Procedure 1 described above, starting from 2-tolualdehyde (1.15 mL, 10.0 mmol). Purification by recrystallization (EtOAc/hexane) afforded imine **1d** as a white solid (1.65 g, 60%): mp = 93−95 °C (lit.[57] mp = 91−92 °C); ν_{max} (film)/cm^{-1} 1588, 1563, 1321, 1305, 1290, 1156, 1089, 818, 755, 673; ^1H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H, CHN), 8.02 (d, J = 8.4 Hz, 1H, Tol-H), 7.90 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.51−7.45 (m, 1H, Tol-H), 7.36 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.32−7.25 (m, 2H, 2 × Tol-H), 2.62 (s, 3H, Tol-CH_3), 2.45 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7 (CHN), 144.5 (SO_2Tol-C quat.), 142.3 (Tol-C quat.), 135.4 (SO_2TolC-CH_3 quat.), 134.6 (Tol-C), 131.6 (Tol-C), 130.7 (Tol-C), 130.4 (Tol-C quat.), 129.8 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 126.6 (Tol-C), 21.7 (SO_2Tol-CH_3), 19.7 (Tol-CH_3). Observed data was consistent with that reported in the literature.[57,58]

*N-[(E)-1-Napthalenylmethylidene]-4-methylbenzenesulfonamide (**1e**).* A mixture of *p*-toluenesulfonamide (7.47 g, 43.6 mmol, 1.0 equiv) and 1-naphthaldehyde (7.10 mL, 52.3 mmol, 1.2 equiv) in toluene (100 mL) was heated under Dean−Stark conditions for 3 days. The resulting mixture was filtered and the solvent was removed under reduced pressure. Purification by recrystallization (EtOAc/hexane) afforded imine **1e** as yellow crystals (2.98 g, 22%): mp = 142−144 °C (lit.[59] mp = 139−141 °C); ν_{max} (film)/cm^{-1} 3063, 2925, 2257, 1596, 1564, 1318, 1309, 1153, 1087, 804, 774, 729; ^1H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H, CHN), 9.01 (d, J = 8.6 Hz, 1H, Ar−H), 8.19−8.15 (m, 1H, Ar−H), 8.12 (d, J = 8.2 Hz, 1H, Ar−H), 7.99−7.91 (m, 3H, Ar−H and 2 × SO_2Tol-H), 7.72−7.66 (m, 1H, Ar−H), 7.64−7.56 (m, 2H, 2 × Ar−H), 7.37 (d, J = 7.9 Hz, 2H, 2 × SO_2Tol-H), 2.45 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (CHN), 144.5 (SO_2Tol-C quat.), 136.1 (Ar−C), 135.4 (SO_2TolC-CH_3 quat.), 135.2 (Ar−C), 133.8 (Ar−C quat.), 131.8 (Ar−C quat.), 129.8 (2 × SO_2Tol-C), 129.0 (Ar−C), 128.9 (Ar−C), 128.0 (2 × SO_2Tol-C), 127.6 (Ar−C quat.), 127.0 (Ar−C), 125.1 (Ar−C), 124.3 (Ar−C), 21.7 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[60]

*N-[(E)-4-Fluorophenylmethylidene]-4-methylbenzenesulfonamide (**1f**).* A mixture of *p*-toluenesulfonamide (1.71 g, 10.0 mmol, 1.0 equiv), toluene (20 mL), 4-fluorobenzaldehyde (1.07 mL, 10.0 mmol, 1.0 equiv) and boron trifluoride THF complex (89 μL, 0.80 mmol, 8 mol %) was heated under reflux for 12 h. After cooling to rt the reaction mixture was quenched with 1 M NaOH (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and the solvent was removed under reduced pressure. The crude imine was then recrystallized (EtOAc/hexane) to afford imine **1f** as a white solid (854 mg, 31%): mp = 110−111 °C (lit.[61] mp = 111 °C); ν_{max} (film)/cm^{-1} 1598, 1582, 1509, 1320, 1236, 1156, 1089, 814, 769, 670; ^1H NMR (400 MHz,

$CDCl_3$) δ 9.01 (s, 1H, CHN), 7.99−7.94 (m, 2H, 2 × FAr−H), 7.89 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.36 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.22−7.15 (m, 2H, 2 × FAr−H), 2.45 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 (CHN), 166.7 (d, *J* = 258.4 Hz, ArC-F quat.), 144.6 (SO_2Tol-C quat.), 134.9 (SO_2TolC-CH_3 quat.), 133.7 (d, *J* = 9.6 Hz, 2 × FAr−C), 129.8 (2 × SO_2Tol-C), 128.7 (d, *J* = 2.8 Hz, FAr−C quat.), 128.0 (2 × SO_2Tol-C), 116.5 (d, *J* = 22.3 Hz, 2 × FAr−C), 21.6 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[61]

*N-[(E)-4-Chlorophenylmethylidene]-4-methylbenzenesulfonamide (**1g**).* Prepared according to the General Procedure 1 described above, starting from 4-chlorobenzaldehyde (1.41 g, 10.0 mmol). Purification by recrystallization (EtOAc/hexane) afforded imine **1g** as colorless crystals (700 mg, 24%): mp = 173−174 °C (lit.[62] mp = 175−176 °C); ν_{max} (film)/cm^{-1} 3067, 2924, 1592, 1560, 1487, 1401, 1316, 1183, 1160, 1083, 1011, 869, 820, 786, 706, 692, 656; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H, CHN), 7.92−7.80 (m, 4H, 2 × ClAr−H and 2 × SO_2Tol-H), 7.47 (d, *J* = 8.5 Hz, 2H, 2 × ClAr−H), 7.36 (d, *J* = 8.1 Hz, 2H, 2 × SO_2Tol-H), 2.44 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6 (CHN), 144.8 (SO_2Tol-C quat.), 141.3 (C-ArCl quat.), 134.8 (SO_2TolC-CH_3 quat.), 132.3 (2 × ClAr−C), 130.7 (ClAr−C quat.), 129.8 (2 × SO_2Tol-C), 129.5 (2 × ClAr−C) 128.1 (2 × SO_2Tol-C), 21.6 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[62]

*N-[(E)-2-Chlorophenylmethylidene]-4-methylbenzenesulfonamide (**1h**).* Prepared according to General Procedure 1 described above, starting from 2-chlorobenzaldehyde (1.13 mL, 10.0 mmol) afforded imine **1h** as a white solid (2.05 g, 70%): mp = 130−131 °C (lit.[63] mp = 128−129 °C); ν_{max} (film)/cm^{-1} 3090, 1587, 1560, 1435, 1318, 1214, 1154, 1087, 1051, 863, 804, 786, 759, 707, 666; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H, CHN), 8.14 (dd, *J* = 7.9, 1.6 Hz, 1H, ClAr−H), 7.90 (d, *J* = 8.4 Hz, 2H, 2 × SO_2Tol-H), 7.54−7.50 (m, 1H, ClAr−H), 7.45 (dd, *J* = 8.1, 1.2 Hz, 1H, ClAr−H), 7.38−7.31 (m, 3H, ClAr−H and 2 × SO_2Tol-H), 2.44 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7 (CHN), 144.8 (SO_2Tol-C quat.), 138.8 (C-ArCl quat.), 135.6 (ClAr−C), 134.5 (SO_2TolC-CH_3 quat.), 130.4 (ClAr−C), 130.1 (ClAr−C.), 129.8 (2 × SO_2Tol-C), 129.6 (ClAr−C quat.) 128.2 (2 × SO_2Tol-C), 127.3 (ClAr−C), 21.6 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[63]

*N-[(E)-Cyclohexylmethylidene]-4-methylbenzenesulfonamide (**1i**).* Cyclohexanecarboxaldehyde (5.45 mL, 45.0 mmol, 1.5 equiv) was added to a stirred solution of *p*-toluenesulfonamide (5.14 g, 30.0 mmol, 1.0 equiv) and sodium *p*-toluenesulfinate (6.41 g, 36.0 mmol, 1.2 equiv) in formic acid and water (1:1, 90 mL) at 0 °C. The reaction was then warmed to rt and stirred for 24 h. The reaction mixture was then filtered under reduced pressure and washed successively with water (100 mL) and hexane (100 mL). The solid was then dissolved in CH_2Cl_2 (300 mL) and saturated aqueous sodium bicarbonate solution (300 mL) was added. The resulting biphasic solution was vigorously stirred for 2 h at rt, after which the organic layer was separated, dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude imine was then recrystallized (EtOAc) to afford imine **1i** as white crystals (6.39 g, 80%): mp = 109−110 °C (lit.[39] mp = 106 °C); ν_{max} (film)/cm^{-1} 3361, 3265, 2930, 2856, 1627, 1600, 1449, 1317, 1159, 1093, 901, 814, 676; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.4 Hz, 1H, CHN), 7.81 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.34 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 2.46−2.42 (m, 4H, Cy-H and SO_2Tol-CH_3), 1.92−1.63 (m, 5H, 5 × Cy-H), 1.40−1.18 (m, 5H, 5 × Cy-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0 (CHN), 144.5 (SO_2Tol-C quat.), 134.7 (SO_2TolC-CH_3 quat.), 129.7 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 43.6 (CH), 28.3 (2 × CH_2), 25.6 (CH_2), 25.0 (2 × CH_2), 21.6 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[39]

*N-[(E)-Cyclohex-3-en-1-ylmethylidene]-4-methylbenzenesulfonamide (**1m**).* 3-Cyclohexene-carboxaldehyde (1.76 mL, 15.0 mmol, 1.5 equiv) was added to a stirred solution of *p*-toluenesulfonamide (1.71 g, 10.0 mmol, 1.0 equiv) and sodium *p*-toluenesulfinate (2.14 g, 12.0 mmol, 1.2 equiv) in formic acid and water (1:1, 30 mL) at 0 °C. The reaction was then warmed to rt and stirred for 24 h. The reaction mixture was filtered under reduced pressure and the filter cake washed successively with water (50 mL) and hexane (50 mL). The solid was then dissolved in CH_2Cl_2 (50 mL) and washed rapidly with aqueous NaOH solution (1 M, 50 mL). The organic layer was separated, dried (Na_2SO_4), and the solvent was removed under reduced pressure affording imine **1m** as a white solid (1.65 g, 63%): mp = 118−119 °C; ν_{max} (film)/cm^{-1} 3028, 2922, 1625, 1597, 1437, 1320, 1291, 1156, 1090, 786, 739, 670; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.3 Hz, 1H, CHN), 7.82 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.35 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 5.73−5.65 (m, 2H, HC=CH), 2.76−2.68 (m, 1H, CH), 2.45 (s, 3H, SO_2Tol-CH_3), 2.27−2.07 (m, 4H, 2 × CH_2), 2.00−1.93 (m, 1H, CH), 1.66−1.55 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.6 (CHN), 144.6 (SO_2Tol-C quat.), 134.6 (SO_2TolC-CH_3 quat.), 129.7 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 127.0 (HC=CH), 124.4 (HC=CH), 40.0 (CH), 26.7 (CH_2), 24.5 (CH_2), 23.8 (CH_2), 21.6 (SO_2Tol-CH_3); HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{18}NO_2S^+$ [M + H]$^+$: 264.1053; found: 264.1050.

*N-[(E)-2,2-Dimethylpropylidene]-4-methylbenzenesulfonamide (**1n**).* A mixture of *p*-toluenesulfonamide (1.71 g, 10.0 mmol, 1.0 equiv), toluene (30 mL), pivaldehyde (1.14 mL, 10.5 mmol, 1.05 equiv) and boron trifluoride THF complex (89 μL, 0.80 mmol, 8 mol %) was refluxed for 16 h. After cooling to rt the reaction mixture was quenched with 1 M NaOH (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and the solvent was removed under reduced pressure. Excess sulfonamide was removed by precipitation (CH_2Cl_2/hexane) then filtration. The filtrate was concentrated under reduced pressure to afford the desired imine **1n** as a white solid (916 mg, 38%): mp = 90−94 °C (lit.[60] mp = 84−86 °C, lit.[63] mp = 102−103 °C); ν_{max} (film)/cm^{-1} 3359, 3261, 1741, 1530, 1389, 1305, 1157, 1098, 905, 816, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H, CHN), 7.66 (d, *J* = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.19 (d, *J* = 8.2 Hz, 2H, 2 × SO_2Tol-H), 2.26 (s, 3H, SO_2Tol-CH_3), 0.99 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.4 (C=N), 144.1 (SO_2Tol-C quat.), 134.3 (SO_2TolC-CH_3 quat.), 129.3 (2 × SO_2Tol-C), 127.5 (2 × SO_2Tol-C), 37.3 ($C(CH_3)_3$ quat.), 25.3 (3 × $C(CH_3)_3$), 21.1 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[63]

Synthesis of Aminal 2a. *N-{[Bis(trimethylsilyl)amino](phenyl)-methyl}-4-methylbenzene-1-sulfonamide (**2a**).* A solution of imine **1a** (130 mg, 0.50 mmol, 1.0 equiv) in THF (2.0 mL) was added dropwise over 5 min to a solution of LiHMDS (1.0 M solution in THF, 1.50 mL, 1.50 mmol, 3.0 equiv) in THF (5.2 mL) and Et_2O (2.7 mL) at −78 °C. The reaction mixture was then quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure affording aminal **2a** as a white solid (195 mg, 92%): mp = 110−112 °C; R_f 0.36 (15% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3305, 2959, 1331, 1252, 1160, 965, 909, 869, 829, 813, 734, 698, 664; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.35 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.31−7.20 (m, 5H, 5 × Ph−H), 5.88 (d, *J* = 7.7 Hz, 1H, NH), 5.17 (d, *J* = 7.7 Hz, 1H, CHN), 2.46 (s, 3H, SO_2Tol-CH_3), 0.15 (s, 18H, $Si(CH_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3 (SO_2Tol-C quat.), 143.0 (Ph−C quat.), 136.2 (SO_2TolC-CH_3 quat.), 129.6 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 127.4 (Ph−C), 127.0 (2 × Ph−C), 126.6 (2 × Ph−C), 69.7 (PhCN), 21.5 (SO_2Tol-CH_3), 3.1 ($Si(CH_3)_2$); HRMS (CI) *m/z* calculated for $C_{20}H_{36}N_3O_2SSi_2^+$ [M + NH_4]$^+$ 438.2061; found 438.2086.

Synthesis of Diiodide 3h. *N-[1-(2-Chlorophenyl)-2,2-diiodoethyl]-4-methylbenzenesulfonamide (**3h**).* Diiodomethane (137 μL, 1.70 mmol, 3.6 equiv) in THF (1.0 mL) was added dropwise to a solution of LiHMDS (1.0 M solution in THF, 1.50 mL, 1.50 mmol, 3.2 equiv) in THF (4.2 mL) and Et_2O (2.7 mL) at −78 °C in the dark. After 20 min at −78 °C, a solution of imine **1h** (137 mg, 0.47 mmol, 1.0 equiv) in THF (2.0 mL) was added dropwise to the reaction mixture. After a further 10 min at −78 °C, the reaction was quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layers were dried (Na_2SO_4), and the solvent was removed under reduced pressure. Purification by flash chromatography (50% Et_2O/hexane) afforded amino *gem*-diiodide **3h** as a white solid (191 mg, 72%): mp = 210−211 °C; R_f 0.20 (50% Et_2O/hexane); ν_{max} (film)/cm^{-1} 3237 (NH), 1473, 1437, 1335, 1281, 1160, 1081, 1035, 910, 837, 815, 752; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 7.37 (dd, J = 7.8, 1.5 Hz, 1H, ClAr−H), 7.30 (dd, J = 8.0, 1.4 Hz, 1H, ClAr−H), 7.26 (td, J = 8.0, 1.5 Hz, 1H, ClAr−H), 7.20 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 7.15 (td, J = 7.6, 1.4 Hz, 1H, ClAr−H), 5.40 (d, J = 8.1 Hz, 1H, NH), 5.37 (d, J = 3.2 Hz, 1H, CHI_2), 4.37 (dd, J = 8.1, 3.2 Hz, 1H, CHN), 2.37 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8 (SO_2Tol-C quat.), 136.3 (SO_2Tol*C*-CH_3 quat), 135.5 (ClAr−C quat.), 132.3 (ClAr−C quat.), 129.8 (ClAr−C), 129.6 (ClAr−C), 129.5 (2 × SO_2Tol-C), 129.3 (ClAr−C), 127.5 (2 × SO_2Tol-C), 126.7 (ClAr−C), 62.6 (CHN), 21.5 (SO_2Tol-CH_3), −22.1 (CHI_2); HRMS (ESI/TOF) m/z calculated for $C_{15}H_{15}ClI_2NO_2S^+$ [M + H]$^+$: 561.8596; found: 561.8592.

Synthesis of Imine−HSO_2Tol Adducts 5i−l, 5o−p. *General Procedure 2: Imine−HSO_2Tol Adducts.* The relevant aldehyde (15.0 mmol, 1.5 equiv) was added to a stirred solution of *p*-toluenesulfonamide (1.71 g, 10.0 mmol, 1.0 equiv) and sodium *p*-toluenesulfinate (2.14 g, 12.0 mmol, 1.2 equiv) in formic acid and water (1:1, 30 mL) at 0 °C. The reaction was then warmed to rt and stirred at this temperature. After 3 days at rt, the reaction mixture was filtered under reduced pressure, washed successively with water (50 mL) and hexane (50 mL) affording the corresponding imine−HO_2STol adduct.

*N-{2-Methyl-1-[(4-methylphenyl)sulfonyl]cyclohexyl}-4-tolylsulfonamide (**5i**).* Prepared according to the General Procedure 2 described above, starting from cyclohexanecarboxaldehyde (1.21 mL, 10.0 mmol) afforded imine−HO_2STol adduct **5i** as a white solid (2.52 g, 60%): mp = 99−102 °C (lit.[64] mp = 101−103 °C); ν_{max} (film)/cm^{-1} 3268, 2933, 2860, 1721, 1600, 1451, 1331, 1303, 1290, 1155, 1081, 906, 812, 731, 705, 661; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.45 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.23 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.17 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 5.17 (d, J = 10.7 Hz, 1H, NH), 4.47 (dd, J = 10.7, 2.9 Hz, 1H, *H*C-NH), 2.45 (s, 3H, SO_2Tol-CH_3), 2.42 (s, 3H, SO_2Tol-CH_3), 2.40−2.34 (m, 1H, Cy-H), 2.07−1.99 (m, 1H, Cy-H), 1.80−1.59 (m, 4H, 4 × Cy-H), 1.36−1.28 (m, 2H, 2 × Cy-H), 1.10−0.95 (m, 3H, 3 × Cy-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (SO_2Tol-C quat.), 143.5 (SO_2Tol-C quat.), 138.1 (SO_2Tol*C*-CH_3 quat.), 134.1 (SO_2Tol*C*-CH_3 quat.), 129.7 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 129.3 (2 × SO_2Tol-C), 126.6 (2 × SO_2Tol-C), 77.5 (CHN), 37.3 (CH), 31.0 (CH_2), 27.1 (CH_2), 26.2 (CH_2), 25.63 (CH_2), 25.61 (CH_2), 21.8 (SO_2Tol-CH_3), 21.6 (SO_2Tol-CH_3). Observed data was consistent with that reported in the literature.[64]

*N-{2-Methyl-1-[(4-methylphenyl)sulfonyl]propyl}-4-tolylsulfonamide (**5j**).* Prepared according to General Procedure 2 described above, starting from isobutyraldehyde (0.91 mL, 10.0 mmol) afforded imine−HO_2STol adduct **5j** as a white solid (2.00 g, 52%): mp = 86−88 °C; ν_{max} (film)/cm^{-1} 3283, 2968, 1598, 1442, 1332, 1290, 1160, 1132, 1082, 890, 813, 779, 702, 670; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H, 2 × SO_2Tol-H), 7.50 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.26 (d, J = 8.0 Hz, 2H, 2 × SO_2Tol-H), 7.18 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 5.38 (d, J = 10.6 Hz, 1H, NH), 4.52 (dd, J = 10.6, 2.7 Hz, 1H, *H*C-NH), 2.71 (dqq, J = 6.9, 2.7 Hz, 1H, CH), 2.45 (s, 3H, SO_2Tol-CH_3), 2.41 (s, 3H, SO_2Tol-CH_3), 1.05 (d, J = 6.9 Hz, 3H, CH_3), 0.87 (d, 3H, J = 6.9 Hz, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (SO_2Tol-C quat.), 143.4 (SO_2Tol-C quat.), 138.0 (SO_2Tol*C*-CH_3 quat.), 133.9 (SO_2Tol*C*-CH_3 quat.), 129.6 (2 × SO_2Tol-C), 129.4 (2 × SO_2Tol-C) 129.2 (2 × SO_2Tol-C), 126.6 (2 × SO_2Tol-C), 77.5 (HC-NH), 27.6 (CH), 21.7 (SO_2Tol-CH_3), 21.5 (SO_2Tol-CH_3), 20.8 (CH_3), 16.5 (CH_3). The above compound is previously reported without characterization data.[39]

*N-{1-[(4-Methylphenyl)sulfonyl]pentan-2-yl}-4-tolylsulfonamide (**5k**).* Prepared according to General Procedure 2 described above, starting from 2-ethylbutyraldehyde (1.85 mL, 15.0 mmol) afforded imine−HO_2STol adduct **5k** as a white solid (3.01 g, 73%): mp = 63−64 °C (lit.[64] mp = 56−57 °C); ν_{max} (film)/cm^{-1} 3265, 2965, 2876, 1598, 1450, 1332, 1154, 1129, 1084, 1083, 1067, 885, 810, 703, 676; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.52 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.28 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.20 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 5.23 (d, J = 10.6 Hz, 1H, NH), 4.68 (dd, J = 10.6, 2.0 Hz, 1H, *H*C-NH), 2.46 (s, 3H, SO_2Tol-CH_3), 2.42 (s, 3H, SO_2Tol-CH_3), 2.10−2.01 (m, 1H, CH), 1.89−1.79 (m, 1H, CH_2), 1.57−1.47 (m, 1H, CH_2), 1.15−1.03 (m, 1H, CH_2), 0.97−0.90 (m, 4H, CH_2 and CH_3), 0.87 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (SO_2Tol-C quat.), 143.5 (SO_2Tol-C quat.), 138.0 (SO_2Tol*C*-CH_3 quat.), 134.1 (SO_2Tol*C*-CH_3 quat.), 129.7 (2 × SO_2Tol-C), 129.4 (2 × SO_2Tol-C) 129.2 (2 × SO_2Tol-C), 126.5 (2 × SO_2Tol-C), 74.4 (HC-NH), 41.4 (CH), 22.7 (CH_2), 22.0 (CH_2), 21.7 (SO_2Tol-CH_3), 21.5 (SO_2Tol-CH_3), 11.9 (CH_3), 11.7 (CH_3). Observed data was consistent with that reported in the literature.[64]

*N-{1-[(4-Methylphenyl)sulfonyl]butan-2-yl}-4-tolylsulfonamide (**5l**).* Prepared according to General Procedure 2 described above, starting from 2-methylbutyraldehyde (1.61 mL, 15.0 mmol) afforded imine−HO_2STol adduct **5l** as a white solid (2.38 g, 60%): mp = 86−87 °C; ν_{max} (film)/cm^{-1} 3227, 2929, 1599, 1454, 1334, 1292, 1131, 1083, 813, 763, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 7.50 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.27 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 7.19 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 5.19 (d, J = 10.6 Hz, 1H, NH), 4.63 (dd, J = 10.6, 2.0 Hz, 1H, *H*C-NH), 2.46−2.42 (m, 1H, C*H*(CH_3)CH_2CH_3), 2.46 (s, 3H, SO_2Tol-CH_3), 2.42 (s, 3H, SO_2Tol-CH_3), 1.21−1.09 (m, 2H, CH(CH_3)C*H*$_2$$CH_3$), 1.05 (d, J = 6.8 Hz, 3H, CH(C*H*$_3$)CH_2CH_3) 0.87 (t, J = 7.3 Hz, 3H, CH(CH_3)CH_2C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (SO_2Tol-C quat.), 143.5 (SO_2Tol-C quat.), 138.0 (SO_2Tol*C*-CH_3 quat.), 134.0 (SO_2Tol*C*-CH_3 quat.), 129.7 (2 × SO_2Tol-C), 129.4 (2 × SO_2Tol-C) 129.2 (2 × SO_2Tol-C), 126.5 (2 × SO_2Tol-C), 75.8 (HC-NH), 33.9 (CH), 27.4 (CH_2), 21.8 (SO_2Tol-CH_3), 21.5 (SO_2Tol-CH_3), 14.1 ($CHCH_3$), 11.5 (CH_2CH_3). HRMS (ESI/TOF) m/z calculated for $C_{19}H_{24}NO_4S_2^+$ [M − H]$^+$: 394.1141; found: 394.1137.

*N-{1-[(4-Methylphenyl)sulfonyl]butyl}-4-tolylsulfonamide (**5o**).* Prepared according to General Procedure 2 described above, starting from butyraldehyde (1.34 mL, 15.0 mmol) afforded imine−HO_2STol adduct **5o** as a white solid (3.42 g, 90%): mp = 118−119 (lit.[64] mp = 119−120 °C); ν_{max} (film)/cm^{-1} 3214, 2932, 1597, 1460, 1441, 1334, 1291, 1210, 1166, 1127, 1078, 922, 815, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 7.54 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 7.28 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 7.21 (d, J = 8.1 Hz, 2H, 2 × SO_2Tol-H), 4.96 (d, J = 10.2 Hz, 1H, NH), 4.59 (dt, J = 10.2, 3.8 Hz, 1H, *H*C-NH), 2.45 (s, 3H, SO_2Tol-CH_3), 2.43 (s, 3H, SO_2Tol-CH_3), 2.17−2.08 (m, 1H, CH_2), 1.70−1.62 (m, 1H, CH_2), 1.45−1.38 (m, 1H, CH_2), 1.29−1.19 (m, 1H, CH_2), 0.87 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (SO_2Tol-C quat.), 143.6 (SO_2Tol-C quat.), 137.8 (SO_2Tol*C*-CH_3 quat.), 132.7 (SO_2Tol*C*-CH_3 quat.), 129.7 (2 × SO_2Tol-C), 129.6 (2 × SO_2Tol-C) 129.5 (2 × SO_2Tol-C), 126.7 (2 × SO_2Tol-C), 73.6 (HC-NH), 27.6 (CH_2), 21.7 (SO_2Tol-CH_3), 21.5 (SO_2Tol-CH_3), 18.4 (CH_2), 13.5 (CH_3). Observed data was consistent with that reported in the literature.[64]

*N-{1-[(4-Methylphenyl)sulfonyl]heptyl}-4-tolylsulfonamide (**5p**).* Prepared according to General Procedure 2 described above, starting from 1-heptanal (2.09 mL, 15.0 mmol) afforded imine−HO_2STol adduct **5p** as a white solid (2.67 g, 64%): mp = 76−77 °C; ν_{max} (film)/cm^{-1} 3261, 2925, 1597, 1451, 1334, 1301, 1161, 1129, 1081, 1038, 1010, 901, 813, 676; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.55 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.30 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.22 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 5.11 (d, J = 10.3 Hz, 1H, NH), 4.53 (dt, J = 10.3, 3.6 Hz, 1H, *H*C-NH), 2.45 (s, 3H, SO_2Tol-CH_3), 2.42 (s, 3H, SO_2Tol-CH_3), 2.19−2.01 (m, 1H, CH_2), 1.69−1.60 (m, 2H, 2 × CH_2), 1.22−1.07 (m, 7H, 7 × CH_2), 0.84 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3 (SO_2Tol-C quat.), 143.6 (SO_2Tol-C quat.), 137.9 (SO_2Tol*C*-CH_3 quat.), 132.6 (SO_2Tol*C*-CH_3 quat.), 129.7 (4 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 126.7 (2 × SO_2Tol-C), 73.8 (HC-NH), 31.3 (CH_2), 28.6 (CH_2), 28.0 (CH_2), 24.5 (CH_2), 22.3 (CH_2), 21.8 (SO_2Tol-CH_3), 21.5 (SO_2Tol-CH_3), 14.0 (CH_3). The above compound is previously reported without characterization data.[65]

Synthesis of *cis*-Iodoaziridines 4. *Method A.* *n*BuLi (1.50 mmol, 3.0 equiv) was added dropwise to a solution of hexamethyldisilazane (315 μL, 1.50 mmol, 3.0 equiv) in THF (5.7 mL) and Et_2O (2.7 mL) at −78 °C. After 30 min, diiodomethane (135 μL, 1.70 mmol, 3.4 equiv) in THF (1.0 mL) was added dropwise to the reaction mixture at −78 °C in the dark. After 20 min at −78 °C, a solution of the appropriate imine (0.50 mmol, 1.0 equiv) in THF (2.0 mL) was added dropwise to the reaction mixture over 5 min. The reaction was then immediately warmed to 0 °C in an ice bath and left at this temperature for 15 min. The reaction was then quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL), then the combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. Purification by flash chromatography on deactivated basic alumina (activity IV or activity V) afforded the *cis*-iodoaziridine.

Method B. For *ortho*-substituted aromatic imines and sterically hindered imines. Identical to Method A, except the reaction was warmed to rt for 20 min after addition of imine at −78 °C.

Method C. *n*BuLi (2.00 mmol, 4.0 equiv) was added dropwise to a solution of hexamethyldisilazane (420 μL, 2.00 mmol, 4.0 equiv) in THF (7.5 mL) and Et_2O (3.5 mL) at −78 °C. After 30 min, diiodomethane (177 μL, 2.20 mmol, 4.4 equiv) in THF (1.5 mL) was added dropwise to the reaction mixture at −78 °C in the dark. After 20 min at −78 °C, a solution of the appropriate imine−HO_2STol adduct (0.50 mmol, 1.0 equiv) in THF (2.0 mL) was added dropwise to the reaction mixture over 5 min. The reaction was then immediately warmed to 0 °C in an ice bath and left at this temperature for 15 min. The reaction was then quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layers were dried (Na_2SO_4), and the solvent was removed under reduced pressure. Purification by flash chromatography on deactivated basic alumina (activity IV or activity V) afforded the *cis*-iodoaziridine.

*cis-(±)-2-Iodo-3-phenyl-1-(4-tolylsulfonyl)aziridine (**4a**).* Prepared according to **Method A** described above, starting from imine **1a** (130 mg, 0.50 mmol). Purification by flash chromatography (10% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4a** as a yellow oil (152 mg, 76%): R_f 0.24 (15% Et_2O/hexane); ν_{max} (film)/cm^{-1} 3035, 2928, 1600, 1499, 1453, 1330, 1157, 1088, 902, 813, 763, 727, 696, 683, 666; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H, 2 × SO_2Tol-H), 7.42−7.33 (m, 5H, 3 × Ph−H and × SO_2Tol-H), 7.31−7.25 (m, 2H, 2 × Ph−H), 4.89 (d, *J* = 6.1 Hz, 1H, CHI), 3.89 (d, *J* = 6.1 Hz, 1H, CHPh), 2.47 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3 (SO_2C-Tol quat.), 134.1 (SO_2TolC-CH_3 quat.), 132.9 (PhC quat.), 129.9 (2 × SO_2Tol-C), 128.7 (Ph−C), 128.1 (2 × SO_2Tol-C), 127.8 (2 × Ph−C), 127.5 (2 × Ph−C), 44.9 (PhCN), 21.7 (SO_2Tol-CH_3), 16.4 (CHI); HRMS (ESI/TOF) *m/z* calculated for $C_{15}H_{15}INO_2S^+$ [M + H]$^+$ 399.9863; found 399.9856.

*cis-(±)-2-Iodo-3-(4-tolyl)-1-(4-tolylsulfonyl)aziridine (**4b**).* Prepared according to **Method A** described above, starting from imine **1b** (137 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4b** as a yellow oil (100 mg, 48%): R_f 0.16 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3022, 2923, 1616, 1598, 1517, 1329, 1292, 1242, 1158, 1089, 1037, 1019, 905, 842, 810, 766; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.38 (d, *J* = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.18−7.14 (m, 4H, 4 × Tol-H), 4.87 (d, *J* = 6.1 Hz, 1H, CHI), 3.84 (d, *J* = 6.1 Hz, 1H, CHAr), 2.46 (s, 3H, SO_2Tol-CH_3), 2.35 (s, 3H, Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (SO_2Tol-C quat.), 138.6 (TolC quat.), 134.2 (SO_2TolC-CH_3 quat.), 129.9 (2 × SO_2Tol-C), 129.8 (TolC quat.), 128.9 (2 × Tol-C), 127.8 (2 × SO_2Tol-C), 127.4 (2 × Tol-C), 44.9 (CHN), 21.7 (SO_2Tol-CH_3), 21.2 (Tol-CH_3), 16.8 (CHI); HRMS (ESI/TOF) *m/z* calculated for $C_{16}H_{17}INO_2S^+$ [M + H]$^+$: 414.0019; found: 414.0037.

*cis-(±)-2-Iodo-3-(4-tert-butylphenyl)-1-(4-tolylsulfonyl)aziridine (**4c**).* Prepared according to **Method A** described above, starting from imine **1c** (158 mg, 0.50 mmol). Purification by flash chromatography (hexane to 5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4c** as a yellow oil (131 mg, 58%): R_f 0.13 (15% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2966, 2908, 2871, 1602, 1333, 1242, 1159, 1089, 1020, 905, 839, 810, 753, 727, 671; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92−7.88 (m, 2H, 2 × SO_2Tol-H), 7.40−7.35 (m, 4H, 2 × SO_2Tol-H and 2 × *t*BuAr−H), 7.22−7.18 (m, 2H, 2 × *t*BuAr−H), 4.88 (d, *J* = 6.1 Hz, 1H, CHI), 3.85 (d, *J* = 6.1 Hz, 1H, CHAr), 2.47 (s, 3H, SO_2Tol-CH_3), 1.32 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8 (*t*Bu-CAr quat.), 145.2 (SO_2Tol-C quat.), 134.3 (SO_2TolC-CH_3 quat.), 129.9 (2 × SO_2Tol-C), 129.8 (*t*BuAr−C quat.), 127.9 (2 × SO_2Tol-C), 127.2 (2 × *t*BuAr−C), 125.1 (2 × *t*BuAr−C), 44.9 (CHN), 34.6 (C(CH_3)$_3$ quat.), 31.2 (C(CH_3)$_3$), 21.7 (SO_2Tol-CH_3), 16.6 (CHI); HRMS (ESI/TOF) *m/z* calculated for $C_{19}H_{23}INO_2S^+$ [M + H]$^+$ 456.0489; found 456.0490.

*cis-(±)-2-Iodo-3-(2-tolyl)-1-(4-tolylsulfonyl)aziridine (**4d**).* Prepared according to **Method B** described above, starting from imine **1d** (137 mg, 0.50 mmol). Purification by flash chromatography (hexane to 5% EtOAc/hexane) on deactivated deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4d** as a yellow oil (141 mg, 68%): R_f 0.13 (5% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3030, 2923, 2860, 1597, 1492, 1460, 1331, 1240, 1158, 1089, 906, 754, 734, 713, 684, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.40 (d, *J* = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.31−7.24 (dt, *J* = 7.4, 1.6 Hz, 1H, Tol-H), 7.22−7.09 (m, 3H, 3 × Tol-H), 4.92 (d, *J* = 6.0 Hz, 1H, CHI), 3.89 (d, *J* = 6.0 Hz, 1H, CHAr), 2.47 (s, 3H, SO_2Tol-CH_3), 2.35 (s, 3H, Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3 (SO_2C-Tol quat.), 136.1 (Tol-C quat.), 134.2 (SO_2TolC-CH_3 quat.), 131.8 (Tol-C quat.), 130.0 (2 × SO_2Tol-C), 129.8 (Tol-C), 128.6 (Tol-C), 127.9 (2 × SO_2Tol-C), 127.4 (Tol-C), 125.7 (Tol-C), 44.5 (TolCN), 21.7 (SO_2Tol-CH_3), 19.0 (Tol-CH_3), 15.3 (CHI); HRMS (ESI/TOF) *m/z* calculated for $C_{16}H_{17}INO_2S^+$ [M + H]$^+$ 414.0019; found 414.0024.

*cis-(±)-2-Iodo-3-(1-napthyl)-1-(4-tolylsulfonyl)aziridine (**4e**).* Prepared according to **Method B** described above, starting from imine **1e** (155 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4e** as a yellow oil (176 mg, 78%): R_f 0.40 (15% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3287, 3054, 2926, 2259, 1922, 1722, 1600, 1511, 1330, 1157, 1088, 905, 801, 779, 758, 725, 682, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.95 (m, 3H, Ar−H and 2 × SO_2Tol-H), 7.95−7.90 (d, *J* = 8.1 Hz, 1H, Ar−H), 7.87 (d, *J* = 8.1 Hz, 1H, Ar−H), 7.63−7.53 (m, 2H, 2 × Ar−H), 7.45−7.35 (m, 4H, 2 × Ar−H and 2 × SO_2Tol-H), 5.07 (d, *J* = 6.0 Hz, 1H, CHI), 4.38 (d, *J* = 6.0 Hz, 1H, CHAr), 2.48 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4 (SO_2Tol-C quat.), 134.2 (SO_2TolC−CH_3 quat.), 133.1 (Ar−C quat.), 130.7 (Ar−C quat.), 130.0 (2 × SO_2Tol-C), 129.4 (Ar−C quat.), 129.0 (Ar−C), 128.8 (Ar−C), 128.0 (2 × SO_2Tol-C), 126.7 (Ar−C), 126.1 (Ar−C), 125.8 (Ar−C), 125.1 (Ar−C), 122.6 (Ar−C), 44.4 (ArCN), 21.7 (SO_2Tol-CH_3), 15.2 (CHI); HRMS (ESI/TOF) *m/z* calculated for $C_{19}H_{17}INO_2S^+$ [M + H]$^+$ 450.0019; found 450.0024.

*cis-(±)-2-Iodo-3-(4-fluorophenyl)-1-(4-tolylsulfonyl)aziridine (**4f**).* Prepared according to **Method A** described above, starting from imine **1f** (139 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4f** as a yellow oil (97 mg, 47%): R_f 0.24 (15% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3029, 2933, 2259, 1905, 1604, 1512, 1334, 1240, 1158, 1089, 904, 835, 814, 735, 706, 680, 666; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.40 (d, *J* = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.28−7.22 (m, 2H, 2 × FAr−H), 7.08−7.01 (m, 2H, 2 × FAr−H), 4.85 (d, *J* = 6.1 Hz, 1H, CHI), 3.85 (d, *J* = 6.1 Hz, 1H, CHAr), 2.48 (3 H, s, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 248 Hz, F-CAr quat.), 145.5 (SO_2Tol-C quat.), 134.1 (SO_2TolC-CH_3 quat.), 130.1 (2 × SO_2Tol-C), 129.4 (d, *J* = 8.5 Hz, 2 × FAr−C), 128.8 (d, *J* = 3.1 Hz, FAr−C quat.), 128.0 (2 × SO_2Tol-C), 115.4 (d, *J* = 22 Hz, 2 × FAr−C), 44.3 (ArCN), 21.8 (SO_2Tol-CH_3), 16.5 (CHI); ^{19}F NMR (377 MHz, $CDCl_3$) δ −112.3 (Ar−F); HRMS (ESI/TOF) *m/z* calculated for $C_{15}H_{14}FINO_2S^+$ [M + H]$^+$ 417.9768; found 417.9783.

cis-(±)-2-Iodo-3-(4-chlorophenyl)-1-(4-tolylsulfonyl)aziridine (4g). Prepared according to **Method A** described above, starting from imine **1g** (147 mg, 0.50 mmol). Purification by flash chromatography (10% EtOAc/hexane) afforded *cis*-iodoaziridine **4g** as a yellow oil (123 mg, 57%): R_f 0.13 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3022, 2923, 1596, 1493, 1332, 1305, 1241, 1158, 1088, 1036, 1014, 903, 844, 805, 735, 688, 668; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.38 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.32 (d, J = 8.5 Hz, 2H, 2 × ClAr−H), 7.20 (d, J = 8.5 Hz, 2H, 2 × ClAr−H), 4.85 (d, J = 6.1 Hz, 1H, CHI), 3.83 (d, J = 6.1 Hz, 1H, CHAr), 2.46 (s, 3H, SO_2Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5 (SO_2Tol-C quat.), 134.7 (ClAr−C quat.), 133.9 (SO_2Tol*C*-CH_3 quat.), 131.4 (ClAr−C quat.), 130.0 (2 × SO_2Tol-C), 128.8 (2 × ClAr−C), 128.4 (2 × ClAr−C), 127.8 (2 × SO_2Tol-C), 44.2 (CHN), 21.7 (SO_2Tol-CH_3), 16.1 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{15}H_{15}ClINO_2S^+$ [M + H]$^+$: 433.9473; found: 433.9467.

cis-(±)-2-Iodo-3-cyclohexyl-1-(4-tolylsulfonyl)aziridine (4i). Prepared according to **Method A** described above, starting from imine **1i** (133 mg, 0.50 mmol). Purification by flash chromatography (10% Et_2O/hexane) afforded *cis*-iodoaziridine **4i** as a colorless oil (137 mg, 68%): R_f 0.18 (10% Et_2O/hexane); ν_{max} (film)/cm^{-1} 2926, 2851, 1598, 1450, 1330, 1242, 1158, 1090, 968, 900, 883, 814, 732, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.37 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 4.53 (d, J = 6.0 Hz, 1H, CHI), 2.47 (s, 3H, SO_2Tol-CH_3), 2.26 (dd, J = 9.4, 6.0 Hz, 1H, CHCy), 1.84−1.71 (m, 2H, 2 × Cy-H), 1.70−1.62 (m, 2H, 2 × Cy-H), 1.60−1.53 (m, 1H, Cy-H), 1.33−0.99 (m, 6H, 6 × Cy-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (SO_2Tol-C quat.), 134.4 (2 × SO_2TolC−CH_3 quat.), 129.8 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 47.8 (Cy-CHN), 40.1 (Cy-CH), 30.3 (Cy-CH_2), 28.3 (Cy-CH_2), 25.9 (Cy-CH_2), 25.2 (Cy-CH_2), 25.1 (Cy-CH_2), 21.7 (SO_2Tol-CH_3), 13.5 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{15}H_{21}INO_2S^+$ [M + H]$^+$: 406.0332; found: 406.0328.

cis-(±)-2-Iodo-3-(propan-2-yl)-1-(4-tolylsulfonyl)aziridine (4j). Prepared according to **Method C** described above, starting from imine−HO_2STol adduct **5j** (191 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4j** as a yellow oil (114 mg, 63%): R_f 0.21 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2963, 2931, 2874, 1597, 1466, 1403, 1329, 1244, 1156, 1089, 1026, 954, 885, 831, 813, 734, 684, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.36 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 4.54 (d, J = 5.9 Hz, 1H, CHI), 2.46 (s, 3H, SO_2Tol-CH_3), 2.20 (dd, J = 9.7, 5.9 Hz, 1H, CHN), 1.92 (dqq, J = 9.7, 6.7, 6.7 Hz, 1H, C*H*(CH_3)$_2$), 0.99 (d, J = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$), 0.92 (d, J = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (SO_2Tol-C quat.), 134.3 (SO_2Tol*C*-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 49.3 (CHN), 31.5 (CH(CH_3)$_2$), 21.7 (SO_2Tol-CH_3), 20.0 (CH_3), 17.9 (CH_3), 13.8 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{12}H_{17}INO_2S^+$ [M + H]$^+$: 366.0019; found: 366.0034.

cis-(±)-2-Iodo-3-(pentan-3-yl)-1-(4-tolylsulfonyl)aziridine (4k). Prepared according to **Method C** described above, starting from imine−HO_2STol adduct **5k** (205 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4k** as a yellow oil (123 mg, 63%): R_f 0.31 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2963, 2930, 2877, 1597, 1458, 1330, 1244, 1157, 1089, 976, 887, 835, 813, 731, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.36 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 4.55 (d, J = 5.9 Hz, 1H, CHI), 2.46 (s, 3H, SO_2Tol-CH_3), 2.39 (dd, J = 9.6, 5.9 Hz, 1H, CHN), 1.53−1.20 (m, 5H, 2 × CH_2 and CH), 0.97 (t, J = 7.4 Hz, 3H, CH_3), 0.84 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (SO_2Tol-C quat.), 134.3 (SO_2Tol*C*-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 127.9 (2 × SO_2Tol-C), 47.1 (CHN), 42.1 (CH(CH_2CH_3)CH_2CH_3), 23.7 (CH(CH_2CH_3)CH_2CH_3), 22.3 (CH-(CH_2CH_3)CH_2CH_3), 21.7 (SO_2Tol-CH_3), 15.0 (CHI), 10.6 (CH-(CH_2CH_3)CH_2CH_3), 10.1 (CH(CH_2CH_3)CH_2CH_3); HRMS (ESI/TOF) m/z calculated for $C_{14}H_{21}INO_2S^+$ [M + H]$^+$: 394.0332; found: 394.0332.

cis-(±)-2-Iodo-3-(butan-2-yl)-1-(4-tolylsulfonyl)aziridine (4l). Prepared according to **Method C** described above, starting from imine−HO_2STol adduct **5l** (198 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded a mixture of *cis*-iodoaziridines **4l** (1.9:1 major:minor) as a yellow oil (115 mg, 61%): R_f 0.24 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2963, 2926, 1597, 1459, 1402, 1330, 1243, 1157, 1089, 1019, 940, 871. 813, 733, 686; **major** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.36 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 4.58 (d, J = 6.0 Hz, 1H, CHI), 2.46 (s, 3H, SO_2Tol-CH_3), 2.26 (d, J = 9.7, 6.0 Hz, 1H, CHN), 1.56−1.20 (m, 3H, CH and CH_2), 0.96 (t, J = 7.4 Hz, 3H, CH_2C*H*$_3$), 0.90 (d, J = 6.7 Hz, 3H, CHC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (SO_2Tol-C quat.), 134.3 (SO_2Tol*C*-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 48.7 (CHN), 37.4 (CH), 25.8 (CH_2), 21.7 (SO_2Tol-CH_3), 17.0 (CH_2CH_3), 14.6 (CHI), 11.1 ($CHCH_3$); **minor** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.36 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 4.50 (d, J = 6.0 Hz, 1H, CHI), 2.46 (s, 3H, SO_2Tol-CH_3), 2.29 (dd, J = 10.3, 6.0 Hz, 1H, CHN), 1.56−1.20 (m, 3H, CH and CH_2), 0.97 (d, J = 6.7 Hz, 3H, CH_2CH_3), 0.86 (t, J = 7.4 Hz, 3H, $CHCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (SO_2Tol-C quat.), 134.3 (SO_2Tol*C*-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 127.9 (2 × SO_2Tol-C), 48.1 (CHN), 37.0 (CH), 27.6 (CH_2), 21.7 (SO_2Tol-CH_3), 14.5 (CHI), 13.9 (CH_2CH_3), 10.7 ($CHCH_3$); HRMS (ESI/TOF) m/z calculated for $C_{13}H_{19}INO_2S^+$ [M + H]$^+$: 380.0176; found: 380.0186.

cis-(±)-2-Iodo-3-(cyclohex-3-en-1-yl)-1-(4-tolylsulfonyl)aziridine (4m). Prepared according to **Method A** described above, starting from imine **1m** (132 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded a mixture of *cis*-iodoaziridines (1.5:1 major:minor) **4m** as a yellow oil (105 mg, 52%): R_f 0.33 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3025, 2920, 1597, 1436, 1330, 1242, 1158, 1090, 1019, 957, 934, 893, 814, 732; **major** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.81 (m, 2H 2 × SO_2Tol-H), 7.39−7.36 (m, 2H, 2 × SO_2Tol-H), 5.73−5.56 (m, 2H, HC═CH), 4.57 (d, J = 6.0 Hz, 1H, CHI), 2.47 (s, 3H, SO_2Tol-CH_3), 2.38 (dd, J = 9.7, 6.0 Hz, 1H, CHN), 2.26−1.39 (m, 7H, 3 × CH_2 and CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (SO_2Tol-C quat.), 134.2 (SO_2Tol*C*-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 127.0 (HC═CH), 125.2 (HC═CH), 47.0 (CHN), 36.2 (CH), 28.6 (CH_2), 24.0 (CH_2), 23.6 (CH_2), 21.7 (SO_2Tol-CH_3), 13.2 (CHI); **minor** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.81 (m, 2H, 2 × SO_2Tol-H), 7.39−7.36 (m, 2H, 2 × SO_2Tol-H), 5.73−5.56 (m, 2H, HC═CH), 4.54 (d, J = 6.0 Hz, 1H, CHI), 2.47 (s, 3H, SO_2Tol-CH_3), 2.40 (dd, J = 9.7, 6.0 Hz, 1H, CHN), 2.26−1.39 (m, 7H, 3 × CH_2 and CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (SO_2Tol-C quat.), 134.2 (SO_2Tol*C*-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 127.4 (HC═CH), 124.2 (HC═CH), 46.9 (CHN), 36.1 (CH), 26.6 (CH_2), 25.7 (CH_2), 23.6 (CH_2), 21.7 (SO_2Tol-CH_3), 13.7 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{15}H_{19}INO_2S^+$ [M + H]$^+$: 404.0176; found: 404.0183.

cis-(±)-2-Iodo-3-(tert-butyl)-1-(4-tolylsulfonyl)aziridine (4n). Prepared according to **Method B** described above, starting from imine **1n** (120 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4n** as a yellow oil (132 mg, 70%): R_f 0.17 (15% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2964, 2874, 1600, 1330, 1258, 1158, 1089, 953, 931, 852, 734, 677, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 7.36 (d, J = 8.2 Hz, 2H, 2 × SO_2Tol-H), 4.36 (d, J = 6.4 Hz, 1H, CHI), 2.45 (s, 3H, SO_2Tol-CH_3), 2.43 (d, J = 6.4, 1H, CHN) 0.98 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 (SO_2Tol-C quat.), 134.1 (SO_2Tol*C*-CH_3 quat.), 129.7 (2 × SO_2Tol-C), 128.0 (2 × SO_2Tol-C), 50.2 (HCC(CH_3)$_3$), 31.4 (*C*(CH_3)$_3$ quat.), 27.0 (C(*C*H$_3$)$_3$), 21.7 (SO_2Tol-CH_3), 6.6 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{13}H_{19}INO_2S^+$ [M + H]$^+$ 380.0176; found 380.0203.

cis-(±)-2-Iodo-3-propyl-1-(4-tolylsulfonyl)aziridine (4o). Prepared according to **Method C** described above, starting from imine−HO_2STol adduct **5o** (191 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4o** as a yellow oil (11 mg, 6%): R_f 0.23 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2960, 2931, 2873, 1598, 1331, 1245, 1160, 1090, 902, 717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.37 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 4.55 (d, J = 5.9 Hz, 1H, CHI), 2.58 (m, 1H, CHN), 2.47 (s, 3H, SO_2Tol-CH_3), 1.65−1.34 (m, 4H, CH_2CH_2), 0.95 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (SO_2Tol-C quat.), 134.5 (SO_2TolC-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 127.9 (2 × SO_2Tol-C), 43.7 (CHN), 33.5 (CH_2), 21.7 (SO_2Tol-CH_3), 19.7 (CH_2), 14.5 (CH_3), 13.7 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{12}H_{17}INO_2S^+$ [M + H]$^+$: 366.0019; found: 366.0031.

cis-(±)-2-Iodo-3-hexyl-1-(4-tolylsulfonyl)aziridine (4p). Prepared according to **Method C** described above, starting from imine−HO_2STol adduct **5p** (212 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **4p** as a yellow oil (9 mg, 4%): R_f 0.24 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2955, 2927, 2858, 1597, 1458, 1402, 1334, 1246, 1161, 1091, 717. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 7.37 (d, J = 8.3 Hz, 2H, 2 × SO_2Tol-H), 4.56 (d, J = 6.0 Hz, 1H, CHI), 2.54 (dt, J = 7.3, 6.0 Hz, 1H, CHN), 2.47 (s, 3H, SO_2Tol-CH_3), 1.65−1.46 (m, 2H, CH_2), 1.39−1.17 (m, 8H, 4 × CH_2), 0.88 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (SO_2Tol-C quat.), 134.5 (SO_2TolC-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 127.9 (2 × SO_2Tol-C), 43.9 (CHN), 31.6 (CH_2), 28.7 (CH_2), 26.2 (CH_2), 22.4 (CH_2), 21.7 (SO_2Tol-CH_3), 14.5 (CH_3), 14.0 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{15}H_{23}INO_2S^+$ [M + H]$^+$: 408.0489; found: 408.0509.

Synthesis of Rearrangement Products 6 and 7. *N-[(1E)-2-Iodo-2-(4-methylphenyl)ethylidene]-4-methylbenzenesulfonamide (6).* Neat *cis*-iodoaziridine **4b** (95 mg, 0.23 mmol) was stirred under reduced pressure (~2 mbar) for 5 h at 20 °C and 1 h at 35 °C, where *cis*-iodoaziridine **4b** rearranged to α-iodo-imine **6** (93 mg, 99%): R_f 0.15 (10% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3031, 2921, 1611, 1512, 1449, 1320, 1157, 1088, 910, 812, 786, 731, 675; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.3 Hz, 1H, CHN), 7.82 (d, J = 8.2 Hz, 2H, SO_2Tol-H), 7.39−7.35 (m, 4H, 2 × SO_2Tol-H and 2 × Tol-H), 7.16 (d, J = 7.9 Hz, 2H, 2 × Tol-H), 5.90 (d, J = 8.3 Hz, 1H, CHI), 2.45 (s, 3H, SO_2Tol-CH_3), 2.33 (s, 3H, Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4 (C═N), 145.1 (SO_2Tol-C quat.), 139.7 (Tol-C quat.), 133.9 (SO_2TolC-CH_3 quat.), 132.1 (Tol-C quat.), 130.1 (2 × Tol-C), 129.9 (2 × SO_2Tol-C), 128.3 (2 × Tol-C), 128.2 (2 × SO_2Tol-C), 28.5 (CHI), 21.7 (SO_2Tol-CH_3), 21.3 (Tol-CH_3); HRMS (ESI/TOF) m/z calculated for $C_{16}H_{15}INO_2S^-$ [M − H]$^-$: 411.9874; found: 411.9869.

Iodo(phenyl)acetaldehyde (7). Crude iodoaziridine **4b** was prepared by **Method A** starting from imine **1b** (0.50 mmol). The crude *cis*-iodoaziridine was dissolved in CH_2Cl_2 (5 mL) and then added to a stirred suspension of silica (150 g) in a mixture of hexane/EtOAc (300 mL). The resulting suspension was stirred in the dark for 3 h, filtered, washed with CH_2Cl_2 (100 mL) and the solvent was removed under reduced pressure. Purification by flash chromatography (5% EtOAc/hexane) afforded iodo-aldehyde **7** as a yellow oil (70 mg, 54% over 2 steps): R_f 0.16 (5% EtOAc/hexane); ν_{max} (film)/cm^{-1} 3024, 2956, 1715, 1608, 1511, 1449, 1383, 1275, 1181, 1045, 1004, 813, 772, 715, 672; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, J = 3.8 Hz, 1H, CHO), 7.38 (d, J = 8.0 Hz, 2H, 2 × Tol-H), 7.18 (d, J = 8.0 Hz, 2H, 2 × Tol-H), 5.58 (d, J = 3.8 Hz, 1H, CHI), 2.34 (s, 3H, Tol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6 (C═O), 139.4 (Tol-C quat.), 131.0 (Tol-C quat.), 129.9 (2 × Tol-C), 129.2 (2 × Tol-C), 35.4 (CHI), 21.3 (Tol-CH_3); HRMS (CI) m/z calculated for $C_9H_{13}INO^+$ [M + NH_4]$^+$: 278.0036; found: 278.0049.

Determination of Stationary Phase for Chromatography. Crude iodoaziridines **4a** and **4b** were prepared by **Method A** starting from imines **1a**/**b** (0.50 mmol). The crude *cis*-iodoaziridine was dissolved in CH_2Cl_2 (16 mL) and c.a. 30 mg of 1,3,5-trimethoxybenzene, as an internal standard, was added to the crude mixture. The mixture was then split into 2 mL portions and each portion was added to a slurry of a different stationary phase (30 g stationary phase/75 mL eluant) and stirred for 30 min to replicate a purification procedure. After 30 min, the slurry was filtered, eluting with CH_2Cl_2 (50 mL). The solvent was then removed under reduced pressure to afford the recovered sample, which was analyzed by ^{1}H NMR against the internal standard to determine the recovery of the iodoaziridine. A typical screening process involved the following stationary phases: (A) control (sample stirring in solvent system, 5% EtOAc/hex); (B) silica gel; (C) silica gel +1% NEt_3; (D) neutral alumina; (E) basic alumina (activity I); (F) basic alumina (activity IV); (G) florasil.

Synthesis of *N*-Bus Imine 10. *(R)-(+)-2-Methyl-N-(phenylmethylidene)propane-2-sulfinamide (8).* $Ti(OEt)_4$ (2.05 g, 9.0 mmol, 3.0 equiv), benzaldehyde (306 μL, 3.0 mmol, 1.0 equiv) and (*R*)-(+)-2-methyl-2-propanesulfinamide (364 mg, 3.0 mmol, 1.0 equiv) were sequentially added to THF (6 mL). The reaction was stirred at rt for 24 h, after which brine (6 mL) was added, while stirring vigorously. The resulting suspension was filtered through Celite and was washed with EtOAc (100 mL). The filtrate was transferred to a separating funnel, water was added (10 mL) and the aqueous layer was extracted with EtOAc (3 × 30 mL). The organic layers were washed with brine, dried (Na_2SO_4) and the solvent was removed under reduced pressure to afford sulfinylimine **8** as a colorless oil (625 mg, 99%), which was used without further purification: R_f 0.29 (25% EtOAc/hexane); $[\alpha]^{28}_D$ −103.0° (*c* 2.00, $CHCl_3$); ν_{max} (film)/cm^{-1} 3063, 2961, 2925, 2868, 1606, 1573, 1450, 1363, 1216, 1171, 1084, 1026, 855, 759, 729, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H, CHN), 7.89−7.84 (m, 2H, 2 × Ph−H), 7.56−7.45 (m, 3H, 3 × Ph−H), 1.28 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (C═N), 134.0 (Ph−C quat.), 132.4 (Ph−C), 129.4 (2 × Ph−C), 128.9 (2 × Ph−C), 57.8 ($C(CH_3)_3$ quat.), 22.6 ($C(CH_3)_3$). Observed data was consistent with that reported in the literature.[48]

2-Methyl-N-(phenylmethylidene)propane-2-sulfonamide (10). Prepared according to the procedure of Ruano,[50] *m*CPBA (227 mg, 1.31 mmol, 1.1 equiv) was added at rt in one portion to a solution of sulfinylimine **8** (254 mg, 1.19 mmol, 1.0 equiv) in CH_2Cl_2 (6 mL). After 5 min, the reaction was diluted with CH_2Cl_2 (12 mL) and then washed with saturated aqueous sodium bicarbonate solution (3 × 10 mL). The organic layer was dried (Na_2SO_4) and the solvent was removed under reduced pressure, affording sulfonylimine **10** as a colorless oil (268 mg, 99%), which was used without further purification: R_f 0.43 (30% EtOAc/hexane); ν_{max} (film)/cm^{-1} 2984, 1608, 1575, 1479, 1452, 1397, 1366, 1299, 1222, 1176, 1124, 1074, 1023, 862, 810, 786, 760, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H, CHN), 7.95 (d, J = 7.8 Hz, 2H, 2 × Ph−H), 7.63 (t, J = 7.6 Hz, 1H, Ph−H), 7.51 (t, J = 7.7 Hz, 2H, 2 × Ph−H), 1.48 (s, 9H, $C(CH_3)$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8 (C═N), 134.9 (Ph−C), 132.3 (Ph−C quat.), 131.0 (2 × Ph−C), 129.1 (2 × Ph−C), 58.2 ($C(CH_3)_3$ quat.), 23.9 ($C(CH_3)_3$). Observed data was consistent with that reported in the literature.[66]

(2R,3S)-2-Iodo-1-[(R)-2-methylpropane-2-sulfinyl]-3-phenylaziridine (major, 9a) and (2S,3R)-2-Iodo-1-[(R)-2-methylpropane-2-sulfinyl]-3-phenylaziridine (minor, 9b). Prepared according to **Method A** described above, starting from imine **8** (105 mg, 0.50 mmol). Purification by flash chromatography (5% EtOAc/hexane) on deactivated basic alumina (activity V) afforded a mixture of *cis*-iodoaziridines **9a** (major; 85:15) and **9b** (minor) as a yellow oil (103 mg, 59%): R_f = 0.36 (25% EtOAc/hexane); $[\alpha]^{18}_D$ −21.3° (*c* 0.66, $CHCl_3$); ν_{max} (film)/cm^{-1} 2960, 2867, 1605, 1495, 1475, 1454, 1363, 1312, 1238, 1170, 1080, 1026, 906, 847, 817, 791, 758, 699, 676; **major** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.33 (m, 5H, 5 × Ph−H), 4.54 (d, J = 6.0 Hz, 1H, CHI), 3.71 (d, J = 6.0 Hz, 1H, CHPh), 1.20 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8 (Ph−C quat.), 128.5 (Ph−C), 128.2 (2 × Ph−C), 128.1 (2 × Ph−C), 57.5 (CHPh), 35.4 ($C(CH_3)_3$), 22.6 ($C(CH_3)_3$), 17.8 (CHI); **minor** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.33 (m, 5H, 5 × Ph−H), 4.83 (d, J = 5.9 Hz, 1H, CHI), 3.30 (d, J = 5.9 Hz, 1H, CHPh), 1.41 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7 (Ph−C quat.), 128.4 (Ph−C), 128.0 (2 × Ph−C), 127.7 (2 × Ph−C), 58.6 (CHPh), 38.6 ($C(CH_3)_3$), 23.3 ($C(CH_3)_3$), 15.4 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{12}H_{17}INOS^+$ [M + H]$^+$ 350.0070; found 350.0078.

cis-(±)-2-Iodo-1-(2-methylpropane-2-sulfonyl)-3-phenylaziridine (11). Prepared according to **Method A** described above, starting from imine **10** (113 mg, 0.50 mmol). Purification by flash chromatography

(5% EtOAc/hexane) on deactivated basic alumina (activity IV) afforded *cis*-iodoaziridine **11** as a yellow oil (82 mg, 45%): R_f = 0.24 (15% Et_2O/hexane); ν_{max} (film)/cm^{-1} 2987, 1457, 1314, 1249, 1175, 1126, 905, 862, 765, 730, 699, 670; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46−7.35 (m, 5H, 5 × Ph−H), 4.90 (d, J = 6.0 Hz, 1H, CHI), 3.86 (d, J = 6.0 Hz, 1H, CHPh), 1.58 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.1 (Ph−C quat.), 128.9 (Ph−C), 128.3 (2 × Ph−C), 127.7 (2 × Ph−C), 60.1 ($C(CH_3)_3$ quat.), 43.3 (CHN), 24.0 ($C(CH_3)_3$), 19.0 (CHI); HRMS (ESI/TOF) m/z calculated for $C_{12}H_{17}INO_2S^+$ $[M + H]^+$ 366.0019; found 366.0021.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra for new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(36) Submission of isolated **2a** to the optimized reaction conditions returned only starting material, with none of *cis*-iodoaziridine **4a** observed.
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