A Mild and Efficient Method for the Syntheses and Regioselective Ring-Opening of Aziridines

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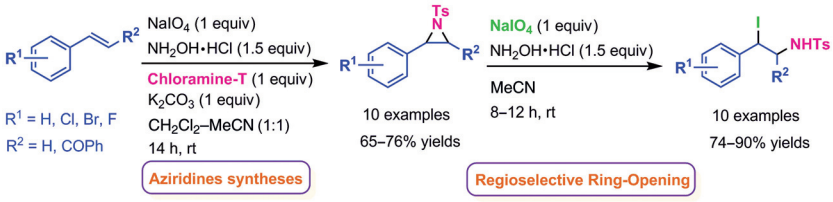

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Abstract We have developed a new synthetic method for the synthesis of aziridines using Chloramine-T as an effective reagent in the presence of $NH_2OH{\cdot}HCl$ and $NaIO_4$. We found that the same combination of $NH_2OH{\cdot}HCl$ and $NaIO_4$ is also very effective for nucleophilic ring opening of aziridines.

Key words aziridines, difunctionalization, aminoiodide, in situ generated iodine, room temperature

The synthetic utility of aziridines, which are strained-ring, nitrogen-containing heterocycles, lies in the fact that the ring can be opened up with a broad range of nucleophiles to produce 1,2-difunctional products.[1] This scaffold is incorporated in biologically active molecules such as the mitomycins, azinomycins, ficellomycin, the miraziridines, and the azicemicins (Figure 1).[2]

Chemistry based on ring opening of aziridines has been used for a wide range of synthetic applications[3] to produce vicinal diamines and aminols that are key motifs in medicinal chemistry.[4] Many biologically active compounds such as amino acids, β-lactam antibiotics and alkaloids can be derived from aziridines.[5] In addition, ring-opened 1,2-difunctional derivatives of aziridines provide excellent precursors for construction of β-aminosulfides, aminophosphonates, and other nitrogen-containing compounds[6] that are not easily accessible by other means.

Numerous protocols have been realized for the synthesis of aziridines and fused analogues.[7] These synthetic protocols mainly rely on transfer of a suitable nitrogen source to olefins, transfer of a suitable carbon source to imines and

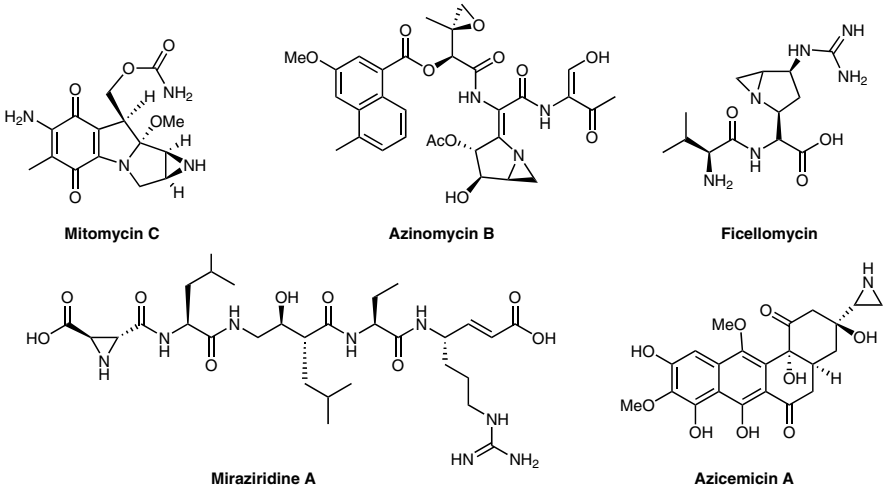


Figure 1 Some aziridine-containing biologically active molecules

intramolecular cyclization of amine derivatives.[8] Various catalytic[9] and non-catalytic[10] routes have been established for the direct aziridination of alkenes, some of which describe the use of halogenated compounds.[11] In particular, chloramine-T[12] and bromamine-T[13] have been used as the nitrogen source for the aziridination of alkenes.

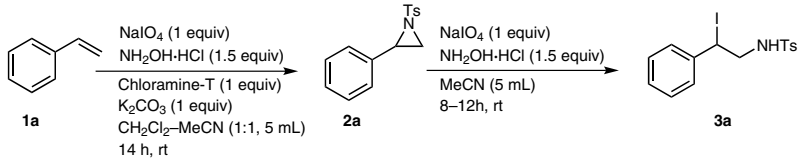
Similarly, there is a range of methods in the literature for ring opening of aziridines with various nucleophiles[14] in the presence Lewis acid[15] or Lewis base[16] catalysts and transition metals.[17]

Herein, we wish to report an interesting observation where the same reagent combination has been used for the construction as well as ring opening of the aziridine ring. In a continuation of our research for development of new methodologies in organic synthesis, we have observed a novel reagent combination for the selective oxidation of alcohols to carbonyl compounds.[18] We have successfully prepared β-iodo-β'-hydroxyethers, β-iodoethers, β-iodohydrins, and β-iodoacetoxy compounds[19a] and 1,2-diiodocarbonyl compounds[19b] using the same reagent combination in different reaction media. Inspired by these results, we planned to apply this combination to the synthesis as well as ring opening of aziridines.

In addition, we have recently developed an efficient method for the regioselective ring-opening of aziridines by various nucleophiles under mild and solvent-free conditions by using a zwitterionic-type molten salt.[20] As a part of our ongoing studies on the chemistry of aziridines,[21] we became interested in using the same reagent combination for the synthesis and ring-opening of aziridines. Our method involves the reaction of olefins with a combination of hydroxylamine hydrochloride and sodium periodate in the presence of Chloramine-T/K_2CO_3 in dichloromethane–acetonitrile as solvent, wherein we observed that aziridine ring-opening took place regioselectively (Scheme 1).

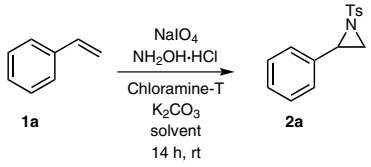
Initially, optimization of the reaction conditions was undertaken by varying the amount of $NaIO_4$ and $NH_2OH{\cdot}HCl$, Chloramine-T, K_2CO_3 and solvent as shown in Table 1 using styrene (**1a**) as the model substrate. All reactions were carried out on 1 mmol scale at room temperature. When we employed 1 equiv of $NaIO_4$, $NH_2OH{\cdot}HCl$, Chloramine-T, and K_2CO_3 in 5 mL of CH_2Cl_2 no desired product (**2a**) was observed after 14 h (Table 1, entry 1). Increasing the amount of all of reagents equally gave no reaction (entries 2–6). Use of a mixture of CH_2Cl_2 and acetonitrile (1:1 v/v) as solvent afforded **2a** in 52% yield in the presence of 1 equiv of all reagents (entry 7), indicating that the binary solvent system might play an important role in this conversion. By increasing the amount of $NH_2OH{\cdot}HCl$ from 1 to 1.5 equiv the yield of (**2a**) was increased to 76% (entry 8). Further increases in the amounts of all reagents in different ratios did not improve yields significantly (entries 9–11) but decreasing the amounts led to decreased yields (entries 12–14). In the absence of Chloramine-T or K_2CO_3 the reaction did not proceed (entries 15 and 16). We have also examined the role of solvent for this reaction and found that only a mixture of dichloromethane and acetonitrile was effective; the reaction did not proceed at all when only CH_2Cl_2 or acetonitrile was used (entries 4 and 17). No product, or only a negligible amount (20%) of product, was obtained when we used solvents such as toluene, dichloroethane or dimethyl sulfoxide (entries 18–22). Finally, we chose the optimized reaction conditions using 1 equiv of $NaIO_4$, 1.5 equiv of $NH_2OH{\cdot}HCl$, 1 equiv of Chloramine-T and 1 equiv of K_2CO_3 with respect to the 1 equiv of styrene (**1a**) in 5 mL of CH_2Cl_2 and acetonitrile (1:1 v/v) at room temperature for 14 h (entry 8).

With the optimized reaction conditions in hand, the substrate scope of this protocol was investigated; the results are presented in Table 2. At first, our attention was focused on the use of olefinic substrates with various substitutions. Styrenes possessing an electron-withdrawing halogen group on the aromatic ring showed good efficiency (**2a–e**), with the 4-chloro- and 2-chloro-substituted styrenes giving the corresponding **2b** and **2d** in 70% and 71% yields, respectively. Other halogen substituents equally afforded the desired products with satisfactory yields (**2c** and **2e**). In addition, different α,β-unsaturated carbonyl compounds were also examined and it was found that the method was effective for chalcone as well as substituted chalcones to produce the corresponding aziridines (**2f–j**). Chalcones with halogens on the aromatic ring gave the desired products efficiently (**2g**, **2h**, **2i** and **2j**) under the optimized reaction conditions. Known compounds were characterized by spectroscopic analysis and novel compounds by both spectroscopic analysis and elemental analysis. A single crystal X-ray analysis of **2f** was performed to confirm the structure (Figure 2).[22]



Scheme 1 Syntheses of aziridines followed by ring opening

Table 1 Optimization of the Reaction Conditions[a]



Entry	$NaIO_4$ (equiv)	$NH_2OH·HCl$ (equiv)	Chloramine-T (equiv)	K_2CO_3 (equiv)	Solvent (5 mL)	Yield (%)[b]
1	1	1	1	1	CH_2Cl_2	0
2	1	1	2	1	CH_2Cl_2	0
3	1	1	1	2	CH_2Cl_2	0
4	1	1.5	1	1	CH_2Cl_2	0
5	1	2	1	1	CH_2Cl_2	0
6	1.5	1	1	1	CH_2Cl_2	0
7	1	1	1	1	CH_2Cl_2–MeCN (1:1)	52
8	1	1.5	1	1	CH_2Cl_2–MeCN (1:1)	76
9	1.5	1.5	1	1	CH_2Cl_2–MeCN (1:1)	72
10	1	1.5	1	2	CH_2Cl_2–MeCN (1:1)	71
11	1	1.5	2	1	CH_2Cl_2–MeCN (1:1)	72
12	1	1.5	1	0.5	CH_2Cl_2–MeCN (1:1)	58
13	1	1.5	0.5	1	CH_2Cl_2–MeCN (1:1)	56
14	0.5	1.5	1	1	CH_2Cl_2–MeCN (1:1)	35
15	1	1.5	–	1	CH_2Cl_2–MeCN (1:1)	0
16	1	1.5	1	–	CH_2Cl_2–MeCN (1:1)	0
17	1	1.5	1	1	MeCN	0
18	1	1.5	1	1	toluene	0
19	1	1.5	1	1	1,2-dichloroethane (DCE)	0
20	1	1.5	1	1	DCE–MeCN (1:1)	20
21	1	1.5	1	1	DMSO	0
22	1	1.5	1	1	DMSO–MeCN (1:1)	0

[a] Reaction conditions: 1 mmol of styrene (**1a**) with various proportions of $NaIO_4$, $NH_2OH·HCl$, Chloramine-T and K_2CO_3 in solvent (5 mL).
[b] Isolated yield.

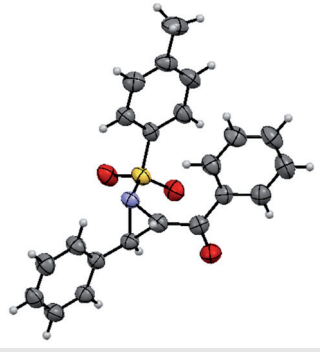
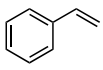
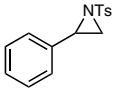
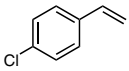
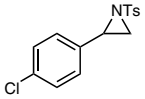
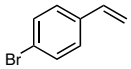
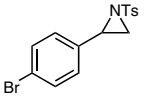
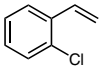
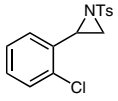
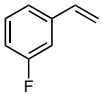
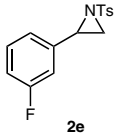
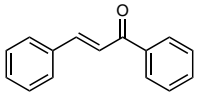
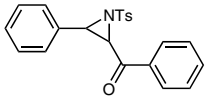
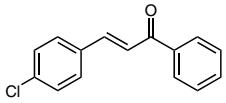
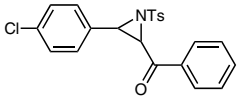
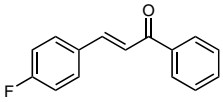
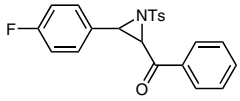
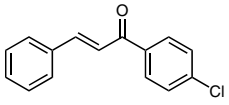
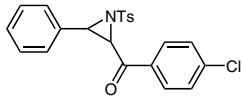
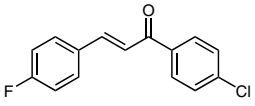
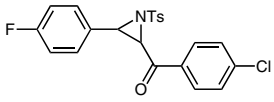


Figure 2 The single crystal X-ray diffraction structure of compound **2f**

We then turned our attention to the regioselective ring-opening of the synthesized aziridines **2**. We thus explored the possibility of applying the general tendency of aziridines towards ring opening using a $NaIO_4$ and $NH_2OH·HCl$ combination as an iodine source to obtain the iodinated ring opening products. Gratifyingly, the corresponding ring-opening products **3** were obtained regioselectively in good yields; the results are summarized in Table 3. All the synthesized aziridines gave the desired ring-opening products efficiently. For the ring-opening reaction we used only acetonitrile as solvent. We did not feel the need to spend much time on optimization of this ring opening step but found no need to use dichloromethane. We did not observe any by-products for any substrate, all of which reacted with high yield and regioselectivity under the protocol.

Table 2 Substrates Scope for the Synthesis of Aziridines[a]

Entry	Substrate **1**	Product **2**	Yield (%)[b]
1	 **1a**	 **2a**	76
2	 **1b**	 **2b**	70
3	 **1c**	 **2c**	72
4	 **1d**	 **2d**	71
5	 **1e**	 **2e**	74
6	 **1f**	 **2f**	72
7	 **1g**	 **2g**	69
8	 **1h**	 **2h**	66
9	 **1i**	 **2i**	68
10	 **1j**	 **2j**	65

[a] All reactions were performed on 1 mmol scale in the presence of $NaIO_4$ (1 mmol), Chloramine-T (1 mmol), K_2CO_3 (1 mmol) and $NH_2OH{\cdot}HCl$ (1.5 mmol) in 5 mL of CH_2Cl_2–MeCN (1:1 v/v) at room temperature for 14 h.
[b] Isolated yield.

Table 3 Regioselective Ring-Opening of the Synthesized Aziridines[a]

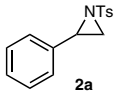
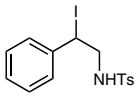
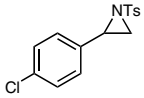
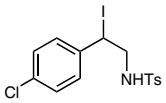
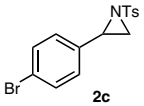
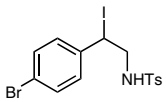
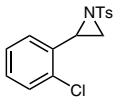
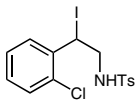
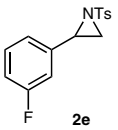
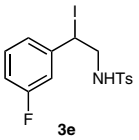
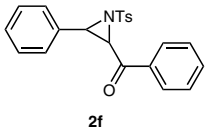
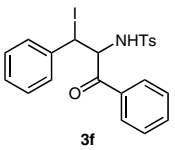
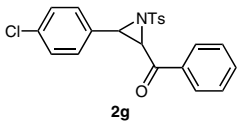
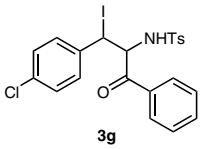
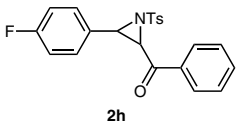
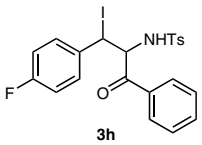
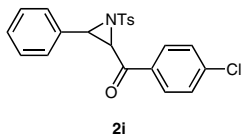
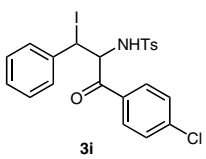
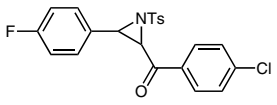
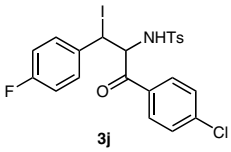
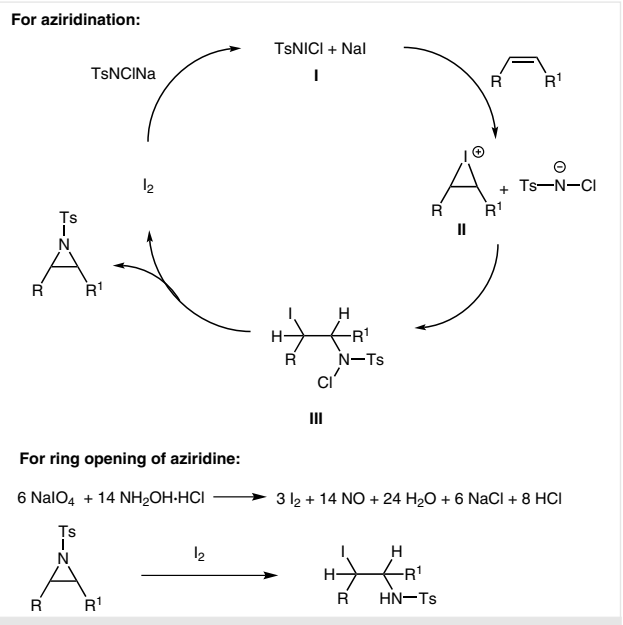
Entry	Aziridines **2**	Product **3**	Time (h)	Yield (%)[b]
1	 **2a**	 **3a**	9	90
2	 **2b**	 **3b**	9	82
3	 **2c**	 **3c**	9	85
4	 **2d**	 **3d**	9	78
5	 **2e**	 **3e**	9	80
6	 **2f**	 **3f**	12	83 (*syn*/*anti* 1:4)
7	 **2g**	 **3g**	12	82 (*syn*/*anti* 1:5)
8	 **2h**	 **3h**	12	74 (*syn*/*anti* 1:3)
9	 **2i**	 **3i**	12	77 (*syn*/*anti* 1:3)

Table 3 (continued)

Entry	Aziridines **2**	Product **3**	Time (h)	Yield (%)[b]
10	 **2j**	 **3j**	12	78 (*syn*/*anti* 1:3)

[a] All reactions were performed on 1 mmol scale in the presence of $NaIO_4$ (1 mmol) and $NH_2OH{\cdot}HCl$ (1.5 mmol) in 5 mL of MeCN at room temperature.
[b] Isolated yield.

Based on literature[7o,11d,23] and on our previous reports[18,19] we assume that the pathway for the aziridination is as depicted in Scheme 2. The iodine produced in situ acts as a source for the generation of I^+ ion. Initially, I^+ may react with the Chloramine-T to produce **I**, which can react with the alkene to afford the iodonium ion **II**. Then the reaction of the $TsNCl^-$ with iodonium ion **II** gives β-iodo-*N*-chloro-*N*-toluenesulfonamide **III**. Finally, cyclization of **III** in the presence of base forms the desired aziridine and species **I** is regenerated. In the second step, nucleophilic ring opening of the aziridine by iodine affords the ring opening product under the same reaction conditions.



Scheme 2 Proposed mechanistic pathway

In summary, we have developed a simple and general method for the synthesis of aziridines and their ring-opening products at room temperature by using a combination of $NH_2OH{\cdot}HCl$ and $NaIO_4$ as iodine source. The advantages of this present protocol are the use of in situ generated iodine, mild reaction conditions, and high yields. These features render this protocol facile and suitable to create a diversified library of aziridines and their ring-opening compounds.

Synthesis of 2; General Procedure

A mixture of alkene (1 mmol), $NaIO_4$ (1 mmol, 213 mg), and Chloramine-T (1 mmol, 228 mg) was dissolved in CH_2Cl_2 (2.5 mL) in a round-bottomed flask at r.t. and then $NH_2OH{\cdot}HCl$ (1.5 mmol, 104 mg) was added portion-wise over 5 min. The reaction mixture was stirred for 1 h at r.t. and then K_2CO_3 (1 mmol, 138 mg) and acetonitrile (2.5 mL) were added and the mixture stirred for further 12 h. After completion (TLC), the reaction mixture was diluted with a 1:1 mixture of water/EtOAc (10 mL) and washed with 10% (w/v) $Na_2S_2O_3$ (3 × 5 mL) followed by brine (1 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Evaporation of solvent furnished the crude product, which was subjected to column chromatography using EtOAc–petroleum ether (1:15) as eluent to obtain the analytically pure product.

Synthesis of 3; General Procedure

To a mixture of aziridine **2** (1 mmol), $NaIO_4$ (1 mmol, 213 mg), and acetonitrile (5 mL) in a round-bottomed flask at r.t., was added $NH_2OH{\cdot}HCl$ (1.5 mmol, 104 mg) portion-wise over 5 min. The reaction mixture was then stirred at r.t. until completion (TLC). The reaction mixture was diluted with a 1:1 mixture of water/EtOAc (10 mL) and washed with 10% (w/v) $Na_2S_2O_3$ (3 × 5 mL) followed by brine (1 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Evaporation of solvent furnished the crude product, which was subjected to column chromatography using EtOAc–petroleum ether (1:15) as eluent to obtain the analytically pure product.

2-Phenyl-1-tosylaziridine (2a)[7l]

Yellowish-white solid (208 mg, yield 76%); mp 86–88 °C.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (d, *J* = 8.4 Hz, 2 H), 7.25–7.11 (m, 7 H), 3.70–3.67 (m, 1 H), 2.89 (d, *J* = 7.2 Hz, 1 H), 2.33 (s, 3 H), 2.30 (d, *J* = 4.4 Hz, 1 H).

2-(4-Chlorophenyl)-1-tosylaziridine (2b)[7l]

White solid (215 mg, yield 70%); mp 108–110 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 6.8 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 8.8 Hz, 2 H), 3.74–3.71 (m, 1 H), 2.96 (d, *J* = 7.2 Hz, 1 H), 2.42 (s, 3 H), 2.33 (d, *J* = 4.4 Hz, 1 H).

2-(4-Bromophenyl)-1-tosylaziridine (2c)[71]

White solid (254 mg, yield 72%); mp 123–125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.75 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 3.63–3.60 (m, 1 H), 2.87 (d, *J* = 7.2 Hz, 1 H), 2.32 (s, 3 H), 2.24 (d, *J* = 4.4 Hz, 1 H).

2-(2-Chlorophenyl)-1-tosylaziridine (2d)

Gummy mass (219 mg, yield 71%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.90 (d, *J* = 8.0 Hz, 2 H), 7.35–7.16 (m, 6 H), 4.06–4.03 (m, 1 H), 3.02 (d, *J* = 7.2 Hz, 1 H), 2.42 (s, 3 H), 2.29 (d, *J* = 4.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.8, 134.5, 133.7, 133.0, 129.8, 129.3, 129.1, 128.0, 127.4, 127.0, 38.8, 35.5, 21.6. Anal. Calcd for $C_{15}H_{14}ClNO_2S$: C, 58.53; H, 4.58; N, 4.55%. Found: C, 58.56; H, 4.62; N, 4.59%.

2-(3-Fluorophenyl)-1-tosylaziridine (2e)

Yellowish-white solid (216 mg, yield 74%); mp 82–84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (d, *J* = 8.4 Hz, 2 H), 7.27–7.15 (m, 3 H), 6.96–6.81 (m, 3 H), 3.69–3.66 (m, 1 H), 2.90 (d, *J* = 7.2 Hz, 1 H), 2.36 (s, 3 H), 2.27 (d, *J* = 4.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.0 (d, $^1J_{C-F}$ = 245 Hz), 145.0, 137.9, 137.8, 134.9, 130.3 (d, $^4J_{C-F}$ = 8 Hz), 129.9, 128.1, 122.6 (d, $^3J_{C-F}$ = 3 Hz), 115.5, 115.3, 113.5 (d, $^2J_{C-F}$ = 22 Hz), 40.4, 36.3, 21.8. Anal. Calcd for $C_{15}H_{14}FNO_2S$: C, 61.84; H, 4.84; N, 4.81%. Found: C, 61.80; H, 4.89; N, 4.87%.

Phenyl(3-phenyl-1-tosylaziridin-2-yl)methanone (2f)[11d]

White solid (272 mg, yield 72%); mp 139–141 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.06–8.04 (m, 2 H), 7.72 (d, *J* = 8.4 Hz, 2 H), 7.64–7.60 (m, 1 H), 7.50–7.46 (m, 2 H), 7.34 (s, 5 H), 7.26–7.21 (m, 2 H), 4.52 (d, *J* = 4.0 Hz, 1 H), 4.29 (d, *J* = 4.0 Hz, 1 H), 2.39 (s, 3 H).

(3-(4-Chlorophenyl)-1-tosylaziridin-2-yl)(phenyl)methanone (2g)[11d]

White solid (284 mg, yield 69%); mp 148–150 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.03 (d, *J* = 8.0 Hz, 2 H), 7.70 (d, *J* = 7.6 Hz, 2 H), 7.64–7.60 (m, 1 H), 7.50–7.46 (m, 3 H), 7.30–7.22 (m, 5 H), 4.48 (d, *J* = 4.0 Hz, 1 H), 4.24 (d, *J* = 4.0 Hz, 1 H), 2.40 (s, 3 H).

(3-(4-Fluorophenyl)-1-tosylaziridin-2-yl)(phenyl)methanone (2h)

Gray solid (261 mg, yield 66%); mp 105–107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.05–8.02 (m, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.64–7.60 (m, 1 H), 7.50–7.46 (m, 2 H), 7.35–7.31 (m, 2 H), 7.26–7.22 (m, 2 H), 7.04–7.00 (m, 2 H), 4.49 (d, *J* = 4.0 Hz, 1 H), 4.28 (d, *J* = 4.4 Hz, 1 H), 2.40 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.3, 163.1 (d, $^1J_{C-F}$ = 246 Hz), 144.6, 136.6, 136.0, 134.3, 129.7, 129.6 (d, $^4J_{C-F}$ = 8 Hz), 129.0 (d, $^3J_{C-F}$ = 9 Hz), 128.8, 128.7, 127.8, 115.8 (d, $^2J_{C-F}$ = 21 Hz), 50.1, 46.9, 21.7. Anal. Calcd for $C_{22}H_{18}FNO_3S$: C, 66.82; H, 4.59; N, 3.54%. Found: C, 66.86; H, 4.65; N, 3.49%.

(4-Chlorophenyl)(3-phenyl-1-tosylaziridin-2-yl)methanone (2i)

White solid (280 mg, yield 68%); mp 144–146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.99 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.35–7.33 (m, 4 H), 7.26–7.23 (m, 2 H), 7.17 (s, 1 H), 4.53 (d, *J* = 4.4 Hz, 1 H), 4.18 (d, *J* = 4.0 Hz, 1 H), 2.41 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 189.6, 144.9, 141.1, 136.7, 134.7, 133.2, 130.7, 129.9, 129.5, 129.3, 129.0, 128.0, 127.7, 50.6, 47.5, 21.9. Anal. Calcd for $C_{22}H_{18}ClNO_3S$: C, 64.15; H, 4.40; N, 3.40%. Found: C, 64.19; H, 4.43; N, 3.35%.

(4-Chlorophenyl)(3-(4-fluorophenyl)-1-tosylaziridin-2-yl)methanone (2j)

Yellowish-white solid (279 mg, yield 65%); mp 143–145 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.99–7.97 (m, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.46–7.44 (m, 2 H), 7.32–7.28 (m, 2 H), 7.26–7.23 (m, 2 H), 7.04–7.00 (m, 2 H), 4.49 (d, *J* = 4.0 Hz, 1 H), 4.17 (d, *J* = 4.4 Hz, 1 H), 2.41 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 189.2, 163.1 (d, $^1J_{C-F}$ = 247 Hz), 144.8, 140.9, 136.4, 134.4, 130.5, 129.7, 129.5 (d, $^4J_{C-F}$ = 8 Hz), 129.3, 128.7 (d, $^3J_{C-F}$ = 3 Hz), 127.8, 115.8 (d, $^2J_{C-F}$ = 22 Hz), 50.2, 46.6, 21.7. Anal. Calcd for $C_{22}H_{17}ClFNO_3S$: C, 61.47; H, 3.99; N, 3.26%. Found: C, 61.54; H, 4.04; N, 3.21%.

***N*-(2-Iodo-2-phenylethyl)-4-methylbenzenesulfonamide (3a)**

Yellowish-white solid (360 mg, yield 90%); mp 79–81 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64 (d, *J* = 8.4 Hz, 2 H), 7.30–7.17 (m, 7 H), 4.98 (bs, 1 H), 4.80–4.77 (m, 1 H), 3.42–3.29 (m, 2 H), 2.35 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.9, 137.9, 137.0, 130.0, 129.2, 129.0, 127.3, 127.1, 61.7, 50.4, 21.6. Anal. Calcd for $C_{15}H_{16}INO_2S$: C, 44.90; H, 4.02; N, 3.49%. Found C, 44.86; H, 4.03; N, 3.38%.

***N*-(2-(4-Chlorophenyl)-2-iodoethyl)-4-methylbenzenesulfonamide (3b)**

Gray solid (357 mg, yield 82%); mp 100–102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65–7.62 (m, 2 H), 7.25–7.14 (m, 6 H), 4.87 (bs, 1 H), 4.81–4.78 (m, 1 H), 3.37–3.32 (m, 2 H), 2.37 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.1, 137.0, 136.5, 135.1, 130.0, 129.2, 128.8, 127.1, 60.9, 50.4, 21.7. Anal. Calcd for $C_{15}H_{15}ClINO_2S$: C, 41.35; H, 3.47; N, 3.21%. Found C, 41.28; H, 3.40; N, 3.25%.

***N*-(2-(4-Bromophenyl)-2-iodoethyl)-4-methylbenzenesulfonamide (3c)**

White solid (408 mg, yield 85%); mp 109–111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (d, *J* = 7.6 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 2 H), 7.25 (d, *J* = 7.6 Hz, 2 H), 7.11 (d, *J* = 7.6 Hz, 2 H), 5.29–5.26 (m, 1 H), 4.83–4.80 (m, 1 H), 3.39–3.35 (m, 2 H), 2.39 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.1, 137.2, 137.0, 132.2, 130.1, 129.2, 127.2, 123.2, 60.9, 50.4, 21.8. Anal. Calcd for $C_{15}H_{15}BrINO_2S$: C, 37.52; H, 3.15; N, 2.92%. Found: C, 37.48; H, 3.09; N, 2.87%.

***N*-(2-(2-Chlorophenyl)-2-iodoethyl)-4-methylbenzenesulfonamide (3d)**

Yellowish-white solid (340 mg, yield 78%); mp 84–86 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.68–7.66 (m, 2 H), 7.43–7.40 (m, 1 H), 7.28–7.18 (m, 5 H), 5.31–5.28 (m, 1 H), 4.94–4.90 (m, 1 H), 3.55–3.49 (m, 1 H), 3.33–3.26 (m, 1 H), 2.36 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.9, 137.1, 135.3, 132.9, 130.2, 130.00, 129.98, 128.8, 127.6, 127.2, 58.1, 49.3, 21.7. Anal. Calcd for $C_{15}H_{15}ClINO_2S$: C, 41.35; H, 3.47; N, 3.21%. Found: C, 41.41; H, 3.41; N, 3.26%.

***N*-(2-(3-Fluorophenyl)-2-iodoethyl)-4-methylbenzenesulfonamide (3e)**

Yellowish-white solid (336 mg, yield 80%); mp 74–76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73–7.71 (m, 2 H), 7.33–7.26 (m, 3 H), 7.08–6.98 (m, 3 H), 4.97 (bs, 1 H), 4.88–4.84 (m, 1 H), 3.46–3.39 (m, 2 H), 2.44 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.9 (d, $^1J_{C-F}$ = 245 Hz), 144.1, 140.4, 140.3, 137.0, 130.6 (d, $^4J_{C-F}$ = 9 Hz), 130.0, 127.1, 123.1 (d, $^3J_{C-F}$ = 3 Hz), 116.3, 116.1, 114.5 (d, $^2J_{C-F}$ = 24 Hz), 60.9, 50.4, 21.7. Anal. Calcd for $C_{15}H_{15}FINO_2S$: C, 42.97; H, 3.61; N, 3.34%. Found: C, 42.92; H, 3.54; N, 3.29%.

***N*-(3-Iodo-1-oxo-1,3-diphenylpropan-2-yl)-4-methylbenzenesulfonamide (3f)**

Mixture of diastereomers [*syn*(A)/*anti*(B) = 1:4]; yellowish-white solid (421 mg, yield 83%); mp 114–116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.67–7.63 (m, 2.5 H, 2A+2B), 7.51–7.47 (m, 1.2 H, 1A+1B), 7.45–7.42 (m, 2 H, 2B), 7.38–7.36 (m, 0.5 H, 2A), 7.34–7.30 (m, 2.4 H, 2A+2B), 7.20–7.17 (m, 2.4 H, 2A+2B), 7.16–7.13 (m, 3.7 H, 3A+3B), 7.00–6.94 (m, 2.5 H, 2A+2B), 5.81–5.79 (m, 0.2 H, 1A), 5.60–5.57 (m, 1 H, 1B), 5.35–5.31 (m, 1 H, 1B), 5.24–5.21 (m, 0.2 H, 1A), 5.10 (d, *J* = 4.0 Hz, 0.2 H, 1A), 5.05 (d, *J* = 6.4 Hz, 1 H, 1B), 2.20 (s, 0.7 H, 3A), 2.18 (s, 3 H, 3B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.2, 143.7, 136.8, 136.6, 136.1, 135.3, 134.3, 129.6, 129.1, 129.0, 128.8, 128.6, 128.0, 127.2, 62.7, 61.8, 21.5. Anal. Calcd for $C_{22}H_{20}INO_3S$: C, 52.29; H, 3.99; N, 2.77%. Found: C, 52.35; H, 4.06; N, 2.82%.

***N*-(3-(4-Chlorophenyl)-3-iodo-1-oxo-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3g)**

Mixture of diastereomers [*syn*(A)/*anti*(B)= 1:5]; gray solid (442 mg, yield 82%); mp 130–132 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81–7.77 (m, 2.4 H, 2A+2B), 7.62–7.59 (m, 1.2 H, 1A+1B), 7.51–7.42 (m, 4.8 H, 4A+4B), 7.30 (d, *J* = 8.4 Hz, 0.4 H, 2A), 7.20–7.13 (m, 4.5 H, 2A+4B), 7.09 (d, *J* = 8.0 Hz, 0.4 H, 2A), 7.04 (d, *J* = 8.0 Hz, 2 H, 2B), 5.91 (d, *J* = 9.2 Hz, 0.2 H, 1A), 5.69 (d, *J* = 9.6 Hz, 1 H, 1B), 5.39–5.34 (m, 1 H, 1B), 5.28–5.25 (m, 0.2 H, 1A), 5.16 (d, *J* = 3.2 Hz, 0.2 H, 1A), 5.04 (d, *J* = 7.2 Hz, 1 H, 1B), 2.32 (s, 0.6 H, 3A), 2.29 (s, 3 H, 3B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.7, 144.1, 136.9, 135.4, 135.3, 135.1, 134.6, 134.4, 129.8, 129.7, 129.4, 129.1, 128.9, 128.8, 127.3, 62.5, 61.3, 21.8. Anal. Calcd for $C_{22}H_{19}ClINO_3S$: C, 48.95; H, 3.55; N, 2.59%. Found: C, 48.98; H, 3.52; N, 2.65%.

***N*-(3-(4-Fluorophenyl)-3-iodo-1-oxo-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3h)**

Mixture of diastereomers [*syn*(A)/*anti*(B) = 1:3]; gummy mass (387 mg, yield 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79–7.74 (m, 2.7 H, 2A+2B), 7.60–7.57 (m, 1.3 H, 1A+1B), 7.55–7.53 (m, 0.6 H, 2A), 7.49–7.47 (m, 2.3 H, 1A+2B), 7.45–7.40 (m, 2.3 H, 1A+2B), 7.38–7.34 (m, 0.6 H, 2A), 7.23–7.19 (m, 2 H, 2B), 7.07 (d, *J* = 8.0 Hz, 0.6 H, 2A), 7.01 (d, *J* = 8.0 Hz, 2 H, 2B), 6.94–6.86 (m, 2.6 H, 2A+2B), 5.99–5.97 (m, 0.3 H, 1A), 5.83–5.81 (m, 1 H, 1B), 5.40–5.36 (m, 1 H, 1B), 5.29–5.26 (m, 0.3 H, 1A), 5.17 (d, *J* = 4.0 Hz, 0.3 H, 1A), 5.09 (d, *J* = 7.2 Hz, 1 H, 1B), 2.28 (s, 0.9 H, 3A), 2.26 (s, 3 H, 3B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.5, 163.0 (d, $^1J_{C-F}$ = 246 Hz), 143.8, 136.8, 135.3, 134.3, 132.5, 132.2, 129.9 (d, $^4J_{C-F}$ = 9 Hz), 129.6, 129.1, 128.9 (d, $^3J_{C-F}$ = 7 Hz), 127.1, 115.5 (d, $^2J_{C-F}$ = 21 Hz), 62.3, 61.2, 21.4. Anal. Calcd for $C_{22}H_{19}FINO_3S$: C, 50.49; H, 3.66; N, 2.68%. Found: 50.43; H, 3.69; N, 2.62%.

***N*-(1-(4-Chlorophenyl)-3-iodo-1-oxo-3-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3i)**

Mixture of diastereomers [*syn*(A)/*anti*(B) = 1:3]; gummy mass (416 mg, yield 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71–7.63 (m, 2.6 H, 2A+2B), 7.54 (d, *J* = 8.4 Hz, 0.6 H, 2A), 7.46 (d, *J* = 8.4 Hz, 2 H, 2B), 7.43–7.32 (m, 4 H, 3A+3B), 7.26–7.24 (m, 5.2 H, 4A+4B), 7.07 (d, *J* = 8.0 Hz, 0.6 H, 2A), 7.02 (d, *J* = 8.0 Hz, 2 H, 2B), 5.88 (d, *J* = 9.2 Hz, 0.3 H, 1A), 5.74 (d, *J* = 9.6 Hz, 1 H, 1B), 5.35–5.29 (m, 1 H, 1B), 5.27–5.23 (m, 0.3 H, 1A), 5.12 (d, *J* = 4.8 Hz, 0.3 H, 1A), 5.09 (d, *J* = 7.2 Hz, 1 H,1B), 2.29 (s,0.9 H, 3A), 2.28 (s, 3 H, 3B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.8, 144.0, 141.0, 136.9, 136.4, 133.5, 130.3, 129.8, 129.4, 129.3, 128.9, 128.2, 127.3, 62.8, 61.7, 21.7. Anal. Calcd. for $C_{22}H_{19}ClINO_3S$: C, 48.95; H, 3.55; N, 2.59%. Found: C, 48.98; H, 3.59; N, 2.63%.

***N*-(1-(4-Chlorophenyl)-3-(4-fluorophenyl)-3-iodo-1-oxopropan-2-yl)-4-methylbenzenesulfonamide (3j)**

Mixture of diastereomers [*syn*(A)/*anti*(B) = 1:3]; gummy mass (435 mg, yield 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.74 (d, *J* = 8.4 Hz, 2 H, 2B), 7.68 (d, *J* = 8.4 Hz, 0.6 H, 2A), 7.53 (d, *J* = 8.0 Hz, 0.6 H, 2A), 7.44–7.39 (m, 4.6 H, 2A+4B), 7.34–7.31 (m, 0.6 H, 2A), 7.26–7.20 (m, 2 H, 2B), 7.09 (d, *J* = 8.0 Hz, 0.6 H, 2A), 7.03 (d, *J* = 8.0 Hz, 2 H, 2B), 6.93–6.87 (m, 2.6 H, 2A+2B), 5.91 (d, *J* = 9.6 Hz, 0.3 H, 1A), 5.78 (d, *J* = 9.6 Hz, 1 H, 1B), 5.31–5.27 (m, 1 H, 1B), 5.24–5.20 (m, 0.3 H, 1A), 5.13 (d, *J* = 4.4 Hz,0.3 H,1A), 5.02 (d, *J* = 7.6 Hz, 1 H, 1B), 2.30 (s, 0.9 H, 3A), 2.29 (s, 3 H, 3B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.9, 163.0 (d, $^1J_{C-F}$ = 247 Hz), 143.9, 141.0, 136.7, 133.8, 132.7, 132.2 (d, $^4J_{C-F}$ = 3 Hz), 130.3, 129.9 (d, $^3J_{C-F}$ = 8 Hz), 129.6, 127.1, 115.6 (d, $^2J_{C-F}$ = 22 Hz), 62.2, 60.9, 21.5. Anal. Calcd for $C_{22}H_{18}ClFINO_3S$: C, 47.37; H, 3.25; N, 2.51%. Found: C, 47.41; H, 3.32; N, 2.55%.

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