One-Pot Stereoselective Synthesis of *anti* 3-Alkyl and 3-Aryl-*N*-*p*-tosyl-aziridine-2-ketones and 3-Aryl-*N*-*p*-tosyl-aziridine-2-carboxylates

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Dedicated to Professor Iwao Ojima on the occasion of his 60th birthday

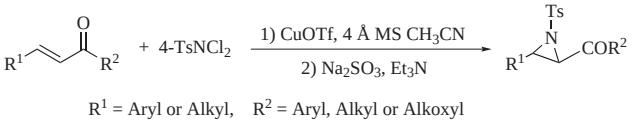
Abstract: An efficient and practical synthesis of *N*-*p*-tosyl-aziridine-2-ketones and carboxylates through the use of α,β-unsaturated esters and ketones has been reported. The synthesis was conducted via a one-pot procedure consisting of aminohalogenation and in situ intramolecular S_N2 substitution. Triethylamine was found to be an effective base for the in situ cyclization for most substrates. Interestingly, for several enone cases, a slightly modified procedure in which 1.0 equivalent of *p*-$TsNCl_2$ was slowly added into 2.0 equivalents of enone for aminohalogenation followed by quenching with aqueous Na_2SO_3 resulted in crude aziridines which were proven to be nearly pure by the crude ^1H NMR analysis. Moderate to good yields and excellent *anti* stereoselectivity were achieved for 21 examples.

Key words: aziridination, aminohalogenation, haloamines, cinnamates, enones

Aziridines are versatile building blocks in organic synthesis[1,2] because they can be readily converted into numerous biologically important compounds. For example, upon treatment with various nucleophiles, aziridines can undergo regio- and stereoselective ring-opening reactions to give unnatural amino acids, alkaloids, and amino sugars.[1,2]

Olefin-based aziridination reactions have served as major approaches to a variety of aziridine-2-ketones and carboxylates.[1,3–7] In these known processes, PhI=N-Ts, chloramine-T and TsNKI were commonly used as both nitrogen sources and oxidants in the presence of metal catalysts. Although much work on aziridination has been done so far, the large-scale and practical aziridination methods have not been very well documented in literature.[8]

Recently, we have reported the synthesis of *N*-protected aziridine carboxylates from cinnamate-based haloamines which were obtained from the aminohalogenation of cinnamate esters.[9,10] In this synthesis, haloamine products were obtained at first, and then were subjected to the reaction with K_2CO_3 in MeCN to give aziridine carboxylates. This work spurred our next efforts to further improve the experimental procedure. In this paper, we report the stereoselective synthesis of *anti* 3-alkyl and 3-aryl-*N*-*p*-tosyl-aziridine-2-ketones and carboxylates via a simple one-pot procedure (Scheme 1).



R^1 = Aryl or Alkyl, R^2 = Aryl, Alkyl or Alkoxyl

Scheme 1

The synthesis was performed by the formation of aminohalogenation products at first and then followed by in situ cyclization via intramolecular S_N2 reaction. Entry 1 of Table 1 was used as the model synthesis. Methyl cinnamate was subjected to aminochlorination reaction as previously described, in which the combination of MeCN (as solvent) and copper(I) triflate (as catalyst) was found to give the highest efficiency. The next work is to find effective in situ intramolecular S_N2 cyclization. Simply using common inorganic bases, such as NaOH, K_2CO_3, ammonia hydroxide, etc., together with reductive quenching reagent (aqueous sodium sulfite) resulted in partial cyclization with major haloamino products remained. We then turned our attention to the use of organic bases attempting to complete in situ intramolecular S_N2 cyclization.

Among several organic amines we employed, Et_3N was found to give complete cyclization within a period of 10 minutes. The results of a variety of cinnamate substrates are listed in Table 1. It was also found that at least 5 equivalents of Et_3N were necessary for the complete cyclization. Other organic amines, such as pyridine, DBU and DABCO, either failed to give any aziridine product or gave unknown products under the current conditions. Diisopropylamine did give aziridine products with diminished chemical yields.

As shown in Table 1, *N*-tosyl-aziridine-2-carboxylates were formed with excellent stereoselectivities. In fact, only *trans* isomers were observed in all cases as revealed by crude ^1H NMR analysis. As anticipated, the group on the ester side has no obvious effect on the cyclization (Table 1, entries 9 and 10). However, it was found that the aromatic substrates with electron-donating groups on their aromatic rings proceeded at faster rates than those with electron-withdrawing groups.

Under the similar conditions, α,β-unsaturated ketones (enones) resulted in of *N*-tosyl-aziridine-2-ketones, but the yields were diminished because more side products were produced. α,β-Unsaturated ketones showed higher

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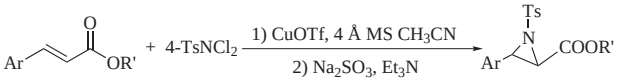
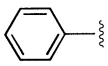
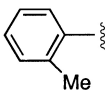
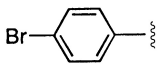
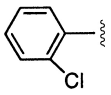
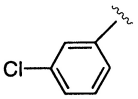
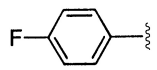
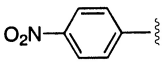
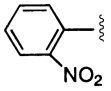
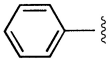
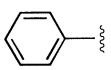
Table 1 Indirect Aziridination of Cinnamate Esters



	Ar	R′	Products	Yield[a] (%)
1		Me	**1-1**	66
2		Me	**1-2**	67
3		Me	**1-3**	64
4		Me	**1-4**	65
5		Me	**1-5**	64
6		Me	**1-6**	57
7		Me	**1-7**	81[b]
8		Me	**1-8**	78[b,c]
9		*i*-Pr	**1-9**	67
10		CH_2Ph	**1-10**	65

[a] Yields after purification via flash chromatography. Only *trans* isomers were observed.
[b] This reaction required 2.5 equiv of 4-$TsNCl_2$ for 2 d; otherwise, standard conditions.
[c] Even after 4 d there remained about 44% cinnamate ester unreacted.

reactivity toward *N,N*-dichloro-*p*-toluenesulfonamide (4-$TsNCl_2$) during aminohalogenation reaction than their ester counterparts. The aminohalogenation of enone substrates needed only 10 hours; but most alkylcinnamates took more than 20 hours for complete consumption of the starting materials. Furthermore, for aliphatic enones such as methyl vinyl ketone, the total reaction time for aminohalogenation and cyclization was only 2 hours.

Efforts to optimize the reaction conditions for aromatic enones were performed. The improvement was made by slowly adding the MeCN solution of $TsNCl_2$ into the reaction mixture at 0 ºC in the presence of CuOTf catalyst for aminohalogenation, and then followed by the reductive quenching and cyclization. The results are listed in Table 2.

As revealed in Table 2, for most cases only one isomer (*trans* isomer) was obtained. Interestingly, for entries 2, 5 and 8, 10% aqueous NH_4OH was proven to be better than Et_3N in controlling stereoselectivity. Essentially, only *trans* isomers were observed for entries 2 and 8 when aqueous ammonia hydroxide was used. Unfortunately, the aziridine product of methyl vinyl ketone cannot be purified by column chromatography, which resulted in the complete decomposition. Therefore, a modified procedure was developed in which the reaction was conducted at 0 °C with slow addition of 1.0 equivalent of 4-$TsNCl_2$ into 2 equivalents of methyl vinyl ketone. As revealed by ^1H NMR analysis, nearly pure products were obtained without further purification. Under the new condition, almost quantitative yields were achieved for cases described in entries 9, 10 and 11. The excess amount of unreacted enone starting materials can be recovered simply by distillation, which makes large scale reaction much easier to be performed. A noteworthy aspect of this modified procedure is shown by the fact that there was no base needed together with the quenching reagent. The quenching reagent, aqueous Na_2SO_3, is basic enough for exclusive aziridine formation.

The major limitation of the present aziridine synthesis was found on the use of terminal disubstituted α,β-unsaturated ketones as the substrates. These substrates only gave diamination products predominantly under the current conditions.[11]

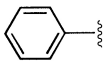
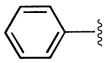
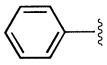
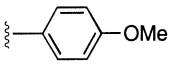
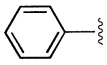
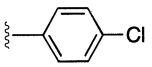
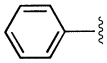
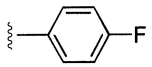
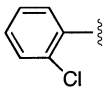
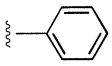
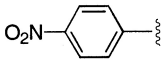
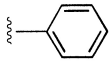
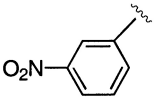
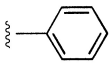
In summary, an efficient and practical one-pot protocol for the synthesis of *N*-tosyl-aziridine-2-ketones and carboxylates has been developed. The synthesis can be easily conducted via a one-pot procedure consisting of aminohalogenation and intramolecular S_N2 reactions. The modified procedure resulted in crude *N*-tosyl-aziridine-2-ketones, which were proven to be nearly pure by the crude ^1H NMR analysis.

All starting materials were commercially available and were used without further purification. Solvents were technical grade and carefully distilled before use. All IR spectra were obtained on samples deposited on NaCl plates. NMR spectra were recorded at 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR. $CDCl_3$ was used as solvent with TMS as the internal standard. Chemical shifts are reported downfield from TMS (0.00 ppm) for ^1H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR. The HRMS analysis was conducted by the mass spectroscopy laboratory of the Scripps Research Institute. Column chromatography was performed with silica gel Merck 60 (230–400 mesh).

Aziridination of Cinnamate Esters; General Procedure

Into a dry capped vial were added the cinnamate ester (1.0 mmol), copper(I) trifluoromethanesulfonate (CuOTf) benzene complex (50.3 mg, 0.10 mmol, 10 mol%), 4 Å molecular seives (500 mg) and newly distilled CH_3CN (2 mL). 4-$TsNCl_2$ (360 mg, 1.5 mmol) was dissolved in freshly distilled CH_3CN (4 mL), then the resulting solution was introduced into the reaction vial via syringe pump in a period of 30 min. The resulting solution was stirred at r.t. for 22 h under N_2 protection. The reaction was monitored by TLC. Upon completion the reaction was quenched with sat. aq Na_2SO_3 solution (5 mL) followed by Et_3N (5 mL), and stirred for 10 min to finish the cyclization. The phases were separated, and the aqueous phase was

Table 2 Aziridination Synthesis from α,β-Unsaturated Ketones

Entry	R^1	R^2	Product	Stereoselectivity[a] (*trans*/*cis*)	Yield (%)[b]
1		Me	**2-1**	> 20:1	55
2		Ph	**2-2**	0.6:1 (> 20:1)	66
3			**2-3**	> 20:1	65
4			**2-4**	> 20:1	53
5			**2-5**	1.4:1 (3:1)	71
6			**2-6**	> 20:1	54
7			**2-7**	> 20:1	63[c]
8			**2-8**	0.3:1 (> 20:1)	86[c]
9	Me	Et	**2-9**	1.6:1	54 (quant.)[e]
10	H	Et	**2-10**	N/A	66 (quant.)[e]
11	H	Me	**2-11**	N/A	-[d] (quant.)[e]

[a] Estimated by crude ^{1}H NMR determination. >20:1 means only *anti* isomers were observed. The ratios in parentheses are reactions quenched with 10% aq NH_3.
[b] Yields after purification via column chromatography.
[c] Required 2 equiv of 4-$TsNCl_2$ and 48 h to finish the reaction.
[d] Decomposed during purification by column chromatography.
[e] Yields in parentheses are obtained from modified method without further purification; 4-$TsNCl_2$ was used as the limiting reagent.

extracted with EtOAc (3 × 15 mL). The combined organic phase was washed with brine, and dried with anhyd Na_2SO_4. Purification by flash chromatography (EtOAc–hexane, 1:3) provided the pure product.

Aziridination of Enones; General Procedure

Into a dry capped vial were added the enone (1.0 mmol), copper(I) trifluoromethanesulfonate (CuOTf) benzene complex (50.3 mg, 0.10 mmol, 10 mol%), 4 Å molecular seives (500 mg) and newly distilled CH_3CN (2 mL). The reaction vial was put into 0 °C bath. 4-$TsNCl_2$ (360 mg, 1.5 mmol) was dissolved in newly distilled CH_3CN (4 mL), then the resulting solution was introduced into the reaction vial via slow addition over 30 min. The resulting solution was stirred at 0 °C for about 10 h under N_2 protection. The reaction was monitored by TLC. Later the reaction was quenched with sat aq Na_2SO_3 solution (5 mL) followed by Et_3N (5 mL) or 10% aq NH_4OH (5 mL). The phase was separated, and the aqueous phases were extracted with EtOAc (3 × 5 mL). The combined organic phase was washed with brine, and dried with anhyd Na_2SO_4. Purification by flash chromatography (EtOAc–hexane, 1:3) provided the pure product.

Aziridination of Aliphatic Enones; Modified Procedure

Into a dry vial were added the enone (2.0 mmol), 4 Å molecular sieves (500 mg), CuOTf benzene complex (50 mg, 0.1 mmol, 10 mol%) and freshly distilled MeCN (3.0 mL). A solution of 4-$TsNCl_2$ (240 mg, 1.0 mmol) in freshly distilled MeCN (6.0 mL) was then added slowly into the above mixture by syringe pump in 1 h under 0 ºC. The resulting solution was stirred at 0 ºC under Ar protection for 10 h, then quenched with sat. aq Na_2SO_3 solution (5 mL). The two phases were separated, and the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with brine, and dried with anhyd Na_2SO_4. Evaporation of the solvent afforded nearly pure products as revealed by crude purification.

Methyl 1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridine-2-carboxylate (1-1)

White solid; mp 44–45 °C.

IR: 1748, 1439, 1337, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76–7.80 (m, 2 H), 7.23–7.33 (m, 7 H), 4.44 (d, *J* = 4.0 Hz, 1 H), 3.86 (s, 3 H), 3.53 (d, *J* = 4.0 Hz, 1 H), 2.42 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.3, 144.4, 137.0, 132.5, 129.6, 128.9, 128.6, 127.5, 127.4, 127.3, 53.2, 47.7, 46.7, 21.6.

Methyl 3-(2-Methylphenyl)-1-[(4-methylphenyl)sulfonyl]aziridine-2-carboxylate (1-2)
White solid; mp 87–88 °C.

IR: 1753, 1599, 1450, 1341, 1167 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76–7.80 (m, 2 H), 7.02–7.32 (m, 6 H), 4.44 (d, *J* = 4.0 Hz, 1 H), 3.87 (s, 3 H), 3.55 (d, *J* = 4.0 Hz, 1 H), 2.44 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 144.5, 138.0, 136.6, 130.5, 130.1, 129.6, 128.8, 127.8, 126.5, 125.9, 53.2, 46.8, 45.3, 21.6, 19.1.

HRMS (MALDI–FTMS): *m*/*z* [M + H$^+$] calcd for $C_{18}H_{20}NO_4S$: 346.1107; found: 346.1104.

Methyl 3-(4-Bromophenyl)-1-[(4-methylphenyl)sulfonyl]aziridine-2-carboxylate (1-3)
White solid; mp 133–134 °C.

IR: 1745, 1602, 1446, 1337, 1167 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76–7.80 (m, 2 H), 7.42–7.46 (m, 2 H), 7.28–7.32 (m, 2 H), 7.10–7.15 (m, 2 H), 4.38 (d, *J* = 4.0 Hz, 1 H), 3.87 (s, 3 H), 3.49 (d, *J* = 4.0 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.0, 144.6, 136.8, 131.8, 131.6, 129.7, 129.0, 127.5, 123.1, 53.2, 46.9, 46.8, 21.6.

HRMS (MALDI–FTMS): *m*/*z* [M + H$^+$] calcd for $C_{17}H_{17}NO_4BrS$: 410.0056; found: 410.0054.

Methyl 3-(2-Chlorophenyl)-1-[(4-methylphenyl)sulfonyl]aziridine-2-carboxylate (1-4)
White solid; mp 105–106 °C.

IR: 1750, 1442, 1338, 1183 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.85 (m, 2 H), 7.30–7.38 (m, 3 H), 7.23–7.28 (m, 1 H), 7.14–7.19 (m, 1 H), 7.07–7.10 (m, 1 H), 4.67 (d, *J* = 4.0 Hz, 1 H), 3.89 (s, 3 H), 3.44 (d, *J* = 4.0 Hz, 1 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.0, 144.5, 136.7, 134.7, 131.0, 130.0, 129.7, 129.4, 128.0, 127.7, 126.9, 53.3, 46.3, 45.8, 21.7.

Methyl 3-(3-Chlorophenyl)-1-[(4-methylphenyl)sulfonyl]aziridine-2-carboxylate (1-5)
Colorless oil.

IR: 1748, 1600, 1453, 1344, 1180 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76–7.80 (m, 2 H), 7.14–7.32 (m, 6 H), 4.40 (d, *J* = 4.0 Hz, 1 H), 3.87 (s, 3 H), 3.48 (d, *J* = 4.0 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 144.6, 136.6, 134.7, 134.6, 129.9, 129.6, 129.0, 127.5, 127.3, 125.5, 53.2, 46.9, 46.5, 21.6.

Methyl 3-(4-Fluorophenyl)-1-[(4-methylphenyl)sulfonyl]aziridine-2-carboxylate (1-6)
White solid; mp 118–120 °C.

IR: 1749, 1602, 1514, 1444, 1337 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75–7.79 (m, 2 H), 7.27–7.32 (m, 2 H), 7.22–7.27 (m, 2 H), 6.97–7.02 (m, 2 H), 4.40 (d, *J* = 4.0 Hz, 1 H), 3.86 (s, 3 H), 3.53 (d, *J* = 4.0 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 164.0, 162.0, 144.5, 136.8, 129.6, 129.3, 129.2, 128.20, 128.18, 127.5, 115.7, 115.5, 53.2, 47.0, 46.6, 21.6.

Methyl 3-(4-Nitrophenyl)-1-[(4-methylphenyl)sulfonyl]aziridine-2-carboxylate (1-7)
White solid; mp 114–116 °C.

IR: 1746, 1523, 1444, 1346, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16–8.20 (m, 2 H), 7.80–7.84 (m, 2 H), 7.42–7.46 (m, 2 H), 7.31–7.35 (m, 2 H), 4.53 (d, *J* = 4.0 Hz, 1 H), 3.89 (s, 3 H), 3.49 (d, *J* = 4.0 Hz, 1 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.5, 148.2, 144.9, 140.1, 136.6, 129.7, 128.2, 127.5, 123.9, 53.4, 47.6, 45.9, 21.7.

HRMS (MALDI–FTMS): *m*/*z* [M + H$^+$] calcd for $C_{17}H_{17}N_2O_6S$: 377.0802; found: 377.0812.

Methyl 3-(2-Nitrophenyl)-1-[(4-methylphenyl)sulfonyl]aziridine-2-carboxylate (1-8)
White solid; mp 128–129 °C.

IR: 1752, 1529, 1441, 1345, 1163 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15–8.18 (m, 2 H), 7.86–7.90 (m, 2 H), 7.48–7.57 (m, 2 H), 7.30–7.38 (m, 2 H), 5.03 (d, *J* = 4.0 Hz, 1 H), 3.91 (s, 3 H), 3.36 (d, *J* = 4.0 Hz, 1 H), 2.47 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.5, 148.1, 144.8, 136.8, 134.1, 129.8, 129.7, 129.6, 129.4, 127.7, 125.1, 53.4, 47.1, 46.2, 21.7.

Isopropyl 1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridine-2-carboxylate (1-9)
Colorless oil.

IR: 1739, 1598, 1458, 1421, 1338, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.81 (m, 2 H), 7.24–7.32 (m, 7 H), 5.17(m, 1 H), 4.43 (d, *J* = 4.0 Hz, 1 H), 3.48 (d, *J* = 4.0 Hz, 1 H), 2.42 (s, 3 H), 1.33 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.2, 144.2, 137.3, 132.8, 129.5, 128.8, 128.6, 127.4, 127.3, 70.4, 47.7, 47.5, 21.63, 21.60, 21.57.

Benzyl 1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridine-2-carboxylate (1-10)
White solid; mp 98–99 °C.

IR: 1746, 1597, 1456, 1336, 1163 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75–7.79 (m, 2 H), 7.34–7.42 (m, 5 H), 7.28–7.32 (m, 3 H), 7.22–7.28 (m, 4 H), 5.28 (d, *J* = 5.5, 2 H), 4.46 (d, *J* = 4.0 Hz, 1 H), 3.57 (d, *J* = 4.0 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7, 144.3, 137.0, 134.8, 132.5, 129.6, 128.9, 128.64, 128.60, 128.59, 128.57, 127.5, 127.4, 68.2, 47.8, 46.9, 21.6.

1-{1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}ethanone (2-1)
Colorless oil.

IR: 1724, 1597, 1332, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.73 (m, 2 H), 7.24–7.34 (m, 7 H), 4.27 (d, *J* = 4.5 Hz, 1 H), 3.73 (d, *J* = 4.5 Hz, 1 H), 2.42 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.4, 144.5, 136.5, 131.6, 129.6, 129.0, 128.5, 128.0, 127.5, 51.0, 48.7, 28.5, 21.6.

{1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}(phenyl)methanone (2-2)
White solid; mp 138–140 °C.

IR: 1692, 1597, 1449, 1331, 1225, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04–8.08 (m, 2 H), 7.70–7.74 (m, 2 H), 7.60–7.64 (m, 1 H), 7.46–7.51 (m, 2 H), 7.34 (s, 5 H), 7.20–

7.26 (m, 2 H), 4.52 (d, *J* = 4.0 Hz, 1 H), 4.29 (d, *J* = 4.0 Hz, 1 H), 2.40 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.3, 144.4, 136.6, 135.9, 134.1, 132.9, 129.5, 128.9, 128.8, 128.7, 128.6, 127.7, 127.5, 50.2, 47.5, 21.6.

(4-Methoxyphenyl){1-[(4-methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}methanone (2-3)
White solid; mp 108–110 °C.

IR: 1677, 1599, 1330, 1264, 1241, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03–8.07 (m, 2 H), 7.70–7.74 (m, 2 H), 7.33 (s, 5 H), 7.21–7.24 (m, 2 H), 6.93–6.97 (m, 2 H), 4.50 (d, *J* = 4.0 Hz, 1 H), 4.26 (d, *J* = 4.0 Hz, 1 H), 3.89 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.5, 164.3, 144.3, 136.7, 133.0, 131.4, 129.5, 129.1, 128.8, 128.6, 127.7, 127.5, 114.0, 55.6, 50.1, 47.4, 21.6.

(4-Chlorophenyl){1-[(4-methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}methanone (2-4)
White solid: mp 158–160 °C.

IR: 1693, 1596, 1448, 1333, 1224, 1163 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.98 (m, 2 H), 7.78–7.82 (m, 2 H), 7.34–7.39 (m, 4 H), 7.17 (s, 5 H), 4.33 (d, *J* = 2.0 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.2, 145.3, 140.4, 134.2, 134.0, 131.0, 129.9, 129.7, 129.0, 128.6, 128.4, 128.1, 127.2, 47.9, 46.4, 21.7.

(4-Fluorophenyl){1-[(4-methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}methanone (2-5)
Colorless oil.

IR: 1685, 1597, 1507, 1330, 1232, 1160 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08–8.13 (m, 2 H), 7.69–7.74 (m, 2 H), 7.30–7.36 (m, 5 H), 7.23–7.27 (m, 2 H), 7.14–7.19 (m, 2 H), 4.52 (d, *J* = 4.0 Hz, 1 H), 4.21 (d, *J* = 4.0 Hz, 1 H), 1.55 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.8, 144.5, 136.5, 132.9, 131.8, 131.7, 129.5, 128.7, 127.7, 127.4, 116.1, 115.9, 50.2, 47.3, 21.6.

{3-(2-Chlorophenyl)-1-[(4-methylphenyl)sulfonyl]aziridin-2-yl}(phenyl)methanone (2-6)
White solid; mp 159–161 °C.

IR: 1692, 1596, 1448, 1331, 1223, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96–8.00 (m, 2 H), 7.90–7.94 (m, 2 H), 7.52–7.57 (m, 1 H), 7.49–7.54 (m, 2 H), 7.35–7.39 (m, 2 H), 7.32–7.36 (m, 1 H), 7.17–7.21 (m, 1 H), 7.10–7.15 (m, 2 H), 4.61 (d, *J* = 8.0 Hz, 1 H), 4.57 (d, *J* = 7.5 Hz, 1 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.3, 145.3, 135.5, 134.2, 133.9, 133.4, 129.9, 129.7, 129.4, 129.0, 128.9, 128.6, 128.5, 128.1, 126.7, 47.1, 45.0, 21.7.

{3-(4-Nitrophenyl)-1-[(4-methylphenyl)sulfonyl]aziridin-2-yl}(phenyl)methanone (2-7)
White solid; mp 103–105 °C.

IR: 1692, 1598, 1522, 1449, 1346, 1223, 1162 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02–8.06 (m, 2 H), 7.95–7.99 (m, 2 H), 7.83–7.87 (m, 2 H), 7.54–7.59 (m, 1 H), 7.36–7.45 (m, 6 H), 4.51 (d, *J* = 7.5 Hz, 1 H), 4.41 (d, *J* = 7.5 Hz, 1 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 188.2, 147.9, 145.7, 138.4, 135.2, 134.3, 133.9, 130.1, 128.9, 128.4, 128.3, 128.1, 123.5, 47.9, 45.2, 21.7.

{3-(3-Nitrophenyl)-1-[(4-methylphenyl)sulfonyl]aziridin-2-yl}(phenyl)methanone (2-8)
White solid; mp 183–185 °C.

IR: 1684, 1596,1530, 1350, 1228, 1161 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17–8.21 (m, 1 H), 8.11–8.14 (m, 1 H), 8.03–8.08 (m, 2 H), 7.69–7.76 (m, 3 H), 7.63–7.67 (m, 1 H), 7.47–7.57 (m, 3 H), 7.24–7.28 (m, 2 H), 4.64 (d, *J* = 4.5 Hz, 1 H), 4.25 (d, *J* = 4.0 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.4, 148.4, 145.0, 135.9, 135.7, 135.6, 134.4, 133.8, 129.8, 129.7, 129.1, 128.9, 127.8, 123.8, 122.2, 50.6, 45.2, 21.6.

1-{3-Methyl-1-[(4-methylphenyl)sulfonyl]aziridin-2-yl}propan-1-one (2-9)
Colorless oil.

IR: 1711, 1597, 1326, 1161, 1090 cm^{-1}.

Trans-isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.86 (m, 2 H), 7.31–7.36 (m, 2 H), 3.36 (d, *J* = 4.5 Hz, 1 H), 3.00–3.05 (m, 1 H), 2.44 (s, 3 H), 2.37–2.47 (m, 1 H), 2.17–2.26 (m, 1 H), 1.76 (d, *J* = 6.0 Hz, 3 H), 0.90 (t, *J* = 7.0 Hz, 3 H).

Cis-isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.86 (m, 2 H), 7.33–7.38 (m, 2 H), 3.40 (d, *J* = 7.5 Hz, 1 H), 3.06–3.12 (m, 1 H), 2.46 (s, 3 H), 2.48–2.55 (m, 1 H), 2.23–2.31 (m, 1 H), 1.20 (d, *J* = 5.5 Hz, 3 H), 1.00 (t, *J* = 7.0 Hz, 3 H).

1-{1-[(4-Methylphenyl)sulfonyl]aziridin-2-yl}propan-1-one (2-10)
White solid; mp 62–64 °C.

IR: 1715, 1596, 1328, 1163, 1093 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.86 (m, 2 H), 7.35–7.39 (m, 2 H), 3.33 (dd, *J* = 4.0, 7.5 Hz, 1 H), 2.77 (d, *J* = 7.5 Hz, 1 H), 2.49 (d, *J* = 4.0 Hz, 1 H), 2.46 (s, 3 H), 2.34–2.52 (m, 2 H), 1.00 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 203.8, 145.3, 133.9, 129.9, 128.1, 41.1, 32.6, 32.1, 21.7, 7.0.

1-{1-[(4-Methylphenyl)sulfonyl]aziridin-2-yl}ethanone (2-11)
Colorless oil.

IR: 1713, 1597, 1329, 1163, 1093 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.87 (m, 2 H), 7.35–7.40 (m, 2 H), 3.29 (dd, *J* = 4.0, 7.5 Hz, 1 H), 2.81 (d, *J* = 7.5 Hz, 1 H), 2.50 (d, *J* = 4.0 Hz, 1 H), 2.47 (s, 3 H), 2.08 (S, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.7, 145.6, 134.1, 130.2, 128.9, 42.2, 32.1, 26.1, 21.9.

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