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Palladium(II) mediated aziridination of olefins with bromamine-T as the nitrogen source: scope and mechanism

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Abstract—The palladium(II)-promoted reaction of a variety of olefins and bromamine-T provided *N*-tosyl-2-substituted aziridines under mild conditions. Olefins bearing chiral appendages gave only a poor to modest diastereoselectivity. Appropriate deuterated olefins were selected to study the stereochemistry of the reaction. A Pd(IV) intermediate is proposed as the aziridinating species.

1. Introduction

Aziridines are versatile substances for the synthesis of biologically important substances such as amino acids, β-lactam antibiotics, and alkaloids.[1,2] Of late there has been an increased interest in the catalytic use of copper,[3–8] rhodium,[9,10] manganese,[11] and rhenium,[12] for the conversion of olefins to aziridines. Among these metals, copper in conjunction with tosylimino-phenyliodane[3–8,11,12] has been widely used as the nitrogen transfer reagent. Chloramine-T[13] or bromamine-T[14] extensively used to prepare epoxides,[15] α-hydroxyamines[16,17] and α- chloroamines[18] have also been amply used in aziridination reactions.[13,14,17,19] A combination of bromamine-T with porphyrin complexes of transition metals such as Mn, Fe, Ru, and Co was also shown to yield aziridines.[20,21] Polymers incorporating Mn and Fe were found to be efficient in aziridination reactions with bromamine-T.[22] In spite of the extensive use of palladium in organic synthesis,[23] intermolecular amination of simple olefins involving Pd^{+2} and primary or secondary amine was found to be inefficient.[24] The poor yield was attributed to strong coordination of the amines with palladium(II) catalyst.[25,26]

We had previously reported[27] a novel $PdCl_2$-assisted aziridination of olefins with bromamine-T as the nitrogen transfer reagent. Full details of this method, its probable reaction mechanism, its scope, and limitations are described herein. Also briefly summarized are our efforts to achieve enantio- and diastereoselection by employing appropriate substrates.

2. Results and discussion

A variety of acrylic acid derivatives and other simple allyl alcohols were subjected to the palladium(II) promoted aziridination with bromamine T as the nitrogen transfer reagent under two different experimental conditions. Method A consisted of addition of bromamine T (0.18 mmol) to a previously stirred solution of olefin (0.45 mmol) and bis-(acetonitrile)dichloropalladium (0.075 mmol) in acetonitrile (1/2 h). Method B involved addition in portions, of bromamine-T (0.06 mmol) to a previously stirred solution of olefin (0.15 mmol) and dichloropalladium (0.024 mmol) in acetonitrile (1/2 h), each addition being done only after a negative starch-iodide test for the oxidant was observed. Appropriate choice of the method led occasionally to a marked improvement in the yield. For example whilst method A gave 57% of aziridine for *N*,*N*-dimethylacrylamide, method B furnished the same product in 81% (Table 1, entry c). The catalytic efficiency of other palladium(II) compounds, such as $Pd(OAc)_2$, $Pd(CF_3COO)_2$, and $PdBr_2$, bearing different leaving groups on the metal was also examined. Palladium(II) chloride or bis(acetonitrile)dichloropalladium(II) was found to give best result. An examination of the Table 1 shows that a wide variety of olefins are aziridinated with varying degrees of efficiency. It can also be noted that the greater the deactivation of the double bond in acrylic acid derivatives the lower was the yield of aziridines ($CN<COR<CO_2R<CONMe_2$). A β substituent caused a dramatic fall in the yield (81% for entry c; 16% for entry d). Irrespective of the electronic nature of the

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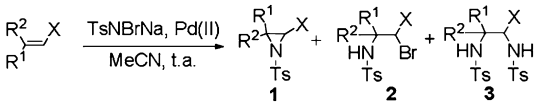
Table 1. Palladium(II) mediated aziridination of olefins with bromamine-T as the nitrogen source



Entry	R^1	R^2	X	**1**[a] (%)/Time of reaction (h)	**1**[b] %/Time of reaction (h)
a	H	H	COOMe	60/48	39/24
b	H	H	$COOC(Me)_3$	60/24	46/120
c	H	H	$CONMe_2$	57/24	81/24
d	Me	H	$CONMe_2$	16/192	—/192
e	H	H	COMe	25/24	23/24
f	H	H	SOPh	10/24	19/72
g	H	H	CN	22/48	13/24
h	H	H	CH_2CN	23/2	18/72
i	H	H	CH_2COOMe	25/2	13/24
j	H		$CO(CH_2)_3$	33/96	—/168
k	H		$CO(CH_2)_2$	—	—
l	H		$(CH_2)_4$	11/24	2/72
m[c]	H	H	CH_2OH	53/2	48/24
n	H	H	CH_2OEt	30/24	12/72
o	H	H	CH_2OCOMe	54/3	8/24
p	H	H	$(CH_3)_2COH$	21/17	—
q[c]	H	H	(±) CH(OH)Me	30/2	20/24
r[c]	H	H	$CHOHCH_2OH$	27/0.5	32/24
s[c]	H	CH_2OH	CH_2OH	12/4	6/72
t[c]	CH_2OH	H	CH_2OH	5/4	6/72
u	Ph	H	COPh	5/120	—

[a] Method A—olefin (2.5 equiv), TsNBrNa (1.0 equiv), and $Pd(MeCN)_2Cl_2$ (0.42 equiv).
[b] Method B—olefin (0.8 equiv), TsNBrNa (3×0.33 equiv), $PdCl_2$ (0.13 equiv).
[c] At the end of the reaction the solvent was removed and the compound purified by thin layer chromatography.

double bond, varying amounts of ring-opened products **2** and **3** were consistently obtained (Table 2).[28]

Allyl alcohol (entry m) provided only a moderate yield of aziridine (53%) possibly due to side reaction involving oxidation of the hydroxyl group.[29] *tert*-Alcohol (entry p) furnished a lower yield (21%) vis a vis the secondary alcohol (entry q) (30%) illustrating the deleterious effect of steric congestion around the OH group. Whilst protection of the OH group as its acetyl derivative (entry o) gave **1o** (54%), the ethyl ether (entry n) furnished the corresponding aziridine in 30% yield. It should be mentioned that only traces, if any, of aziridine was formed in the absence of Pd^{+2}. Simple olefins such as styrene and cyclohexene failed to produce any aziridine or products derived therefrom showing thereby

Table 2. Yields and reaction conditions for **2** and **3**

Entry	R^1	R^2	X	**2**[a] η%	**3**[a] η%
a	H	H	COOMe	6 (A)	
b	H	H	COOMe	3 (B)	8 (B)
c	H	H	$CONMe_2$	12 (B)	7 (B)
d	H	H	COMe	14 (A)	
e	H	H	COMe	5 (B)	16 (B)
f	H	H	SOPh	19 (B)	
g	H	H	CN	19 (A)	
m	H	H	CH_2OH		6 (B)
n	H	H	CH_2OEt	5.6 (B)	9 (B)

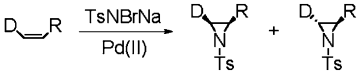
[a] RC (Reaction conditions): (A) Method A—olefin (2.5 equiv), TsNBrNa (1.0 equiv), $Pd(MeCN)_2Cl_2$ (0.42 equiv) and (B) Method B—olefin (0.8 equiv), TsNBrNa (3×0.33 equiv), $PdCl_2$ (0.13 equiv).

the necessity of the presence of a suitable functional group not too far removed from the double bond.

2.1. Stereochemistry and mechanism

Geometrically defined diols, (*Z*)-but-2-en-1,4-diol (entry s) and (*E*)-but-2-en-1,4-diol[30,31] (entry t) gave exclusively the corresponding aziridines *cis*-[3′-(hydroxymethyl)-1′-tosylaziridin-2′-yl]methanol (**1s**) and *trans*-[3′-(hydroxymethyl)-1′-tosylaziridin-2′-yl]methanol (**1t**). The ^1H NMR spectrum of the crude product did not reveal the presence of both isomers in the same reaction. However, the yields (12% and 5%, respectively) were poor, which prompted us to examine the reaction with *cis*-deutero propen-1-ol (**4a**)[30] (Table 3). Thus, **4a** gave aziridine ***5-cis*** exclusively. Such specificity, however, was not observed for *cis*-*N*,*N*-β-deutero-dimethylacrylamide (**4b**).[32] It gave rise to a 4:1 mixture of the *cis*- and the *trans*-aziridines. Interestingly, *cis*-β-deutero ethylacrylate (**4c**)[33–35] provided the *trans* isomer as the major product (cis/trans=1:2).

Table 3. Aziridination of β-deutero olefins



4	R	***5-cis***	***5-trans***
		Relative proportion	
a	CH_2OH	1	0
b	$CONMe_2$	4	1
c	COOEt	1	2

The *cis*- and *trans*-aziridines are clearly distinguished from each other from their respective ^1H NMR spectra. Thus, for the cis isomer hydrogen at C-2 and C-3 appears as doublets with coupling constants of 7.0 Hz. For the trans arrangement it is 4 Hz.

These results led us to conclude that the differing degree of selectivity observed for allylic alcohol on one hand and derivatives of acrylic acid on the other is likely to be due to different coordinating capacities of these functionalities for Pd. Thus, the OH group either by virtue of its strong coordination to or by bond formation with palladium gives exclusively the *cis* aziridines (**5**) (Table 3). The lack of stereospecificity observed in the aziridination of acrylic acid derivatives clearly indicates generation of an intermediate with certain ionic character in which a measure of rotation about the C_1–C_2 bond becomes possible. The degree of such rotation and hence the proportion of isomers formed would be dependent on the metal chelating property of the electron-withdrawing group. The greater coordinating property of a tertiary-amide compared with that of an ester group would explain our results.

To gain a better understanding of the nature of the aziridinating species involved, the reaction (Pd^{+2}, bromamine-T, acrylonitrile) was followed by ^1H NMR. As can be observed, δ values of olefinic hydrogens (Fig. 1a) remained unchanged on addition of the palladium catalyst (Fig. 1b). The ^1H NMR spectra, acquired immediately after the addition of bromamine-T (Fig. 1c), showed new sets of peaks adjacent to

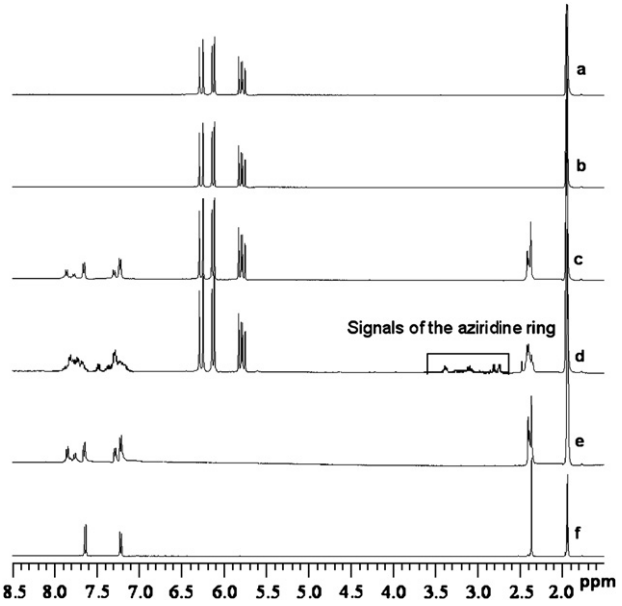
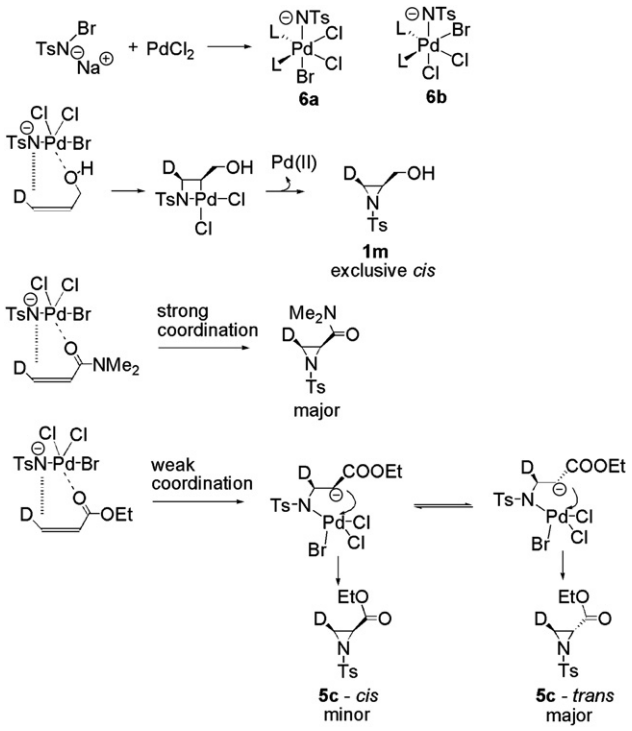


Figure 1. ^{1}H NMR (CD_3CN) recorded spectra for the aziridination reaction of acrylonitrile: (a) acrylonitrile, (b) acrylonitrile (0.8 equiv)+$PdCl_2$ (0.13 equiv), (c) acrylonitrile (0.8 equiv)+$PdCl_2$ (0.13 equiv)+bromamine-T (0.33 equiv) (after the addition), (d) acrilonitrile (0.8 equiv)+$PdCl_2$ (0.13 equiv)+bromamine-T (0.33 equiv) (1/2 h after the addition), (e) bromamine-T (1.0 equiv)+$PdCl_2$ (1.0 equiv), (f) bromamine-T.



Scheme 1. Proposed mechanism for the aziridination reaction.

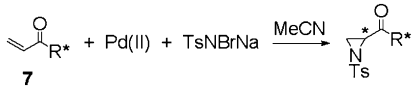
the signals of bromamine-T (Fig. 1f), which indicated the formation of at least two Pd containing species. The same signals were present on the ^{1}H NMR spectra when equimolar amounts of bromamine-T and $PdCl_2$ are mixed (Fig. 1f vs e). Signals due to aziridine became discernable only after a lapse of 1/2 h (Fig. 1d).

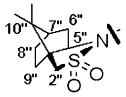
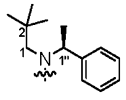
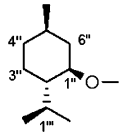
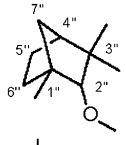
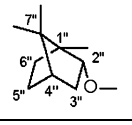
Based on these results, the following mechanism (Scheme 1) can be proposed. It is suggested that an oxidative addition of bromamine-T to $PdCl_2$ results in the formation of two organo Pd^{+4} complexes **6a** and **6b** in equilibrium[36] (several geometries for the intermediate Pd^{+4} can be written, **6a** and **6b** represent two of them). An exclusive *syn* addition to the olefinic bond of allyl alcohol (**4a**) occurs due to strong coordination of OH to Pd. The palladocycle thus formed subsequently collapses to aziridine, regenerating Pd^{+2} species. A similar situation largely obtains for acrylic amide **4b**. For acrylic ester (**4c**), however, the lack of such strong coordination would result in a stepwise addition generating a species with carbanionic character. A rotation about the C–C bond places the ester away from the bulky Pd reagent thus resulting in loss of stereospecificity.

The high selectivity observed in some substances led us to examine the possibility of inducing enantio-selection. Accordingly, the reactions with allyl alcohol were performed in the presence of (i) (*L*)-diethyl tartrate and (ii) (*R*)-1,1′-bi-2-naphtol as chiral complexing agents for $PdCl_2$. However in no instance could any ee be observed. Use of chiral phosphines such as DIOP and BINAP with $PdCl_2$ and (+)-di-μ-chloro-bis{2-[1-(dimethylamine)-ethyl]phenyl-C,N}dipalladium(II) also gave similar results.

Optical induction employing chiral auxiliaries is a useful method of achieving diastereoselection. Among many optically active acrylic acid derivatives, containing chiral appendages that were prepared and examined (Table 4), Oppolzer sultam gave the best result. Although the chemical

Table 4. Yields and de for the aziridination reaction of chiral olefins **7**



Entry	Chiral auxiliary R*	Aziridines	
		η% (RC)[a]	de (%)
a		**8a** and **8b** 61 (B)	27
b		**9a** and **9b** 31 (B)	22
c		**10a** and **10b** 42 (A)	3
d		**11a** and **11b** 50 (A)	12
e		**12a** and **12b** 41 (A)	0

[a] Reaction conditions: (A) Method A—olefin (2.5 equiv), TsNBrNa (1.0 equiv), $Pd(MeCN)_2Cl_2$ (0.42 equiv) and (B) Method B—olefin (0.8 equiv), TsNBrNa (3×0.33 equiv), $PdCl_2$ (0.13 equiv).

conversion of acryloyl-10, 2-sultamabornane (**7a)** (Table 4) into the corresponding aziridines **8a** and **8b** was reasonable (60%), the de as determined from ^{1}H NMR was disappointingly low (27%).[37]

Amide, *N*-[(1′*S*)-1′phenylethyl]-*N*-neopenthylpropenamide **(7b)** afforded a similar de (22%) but in diminished yield (31%). All optically active acrylic esters **7c–e** were found to be very unsatisfactory from the stand point of diastereoselection although modest yields of aziridines were obtained (Table 4). The relative proportion of diastereoisomers in each reaction was calculated from integration of ^{1}H NMR signals due to H_a and H_b hydrogens present in the aziridine mixture.

3. Conclusion

An experimentally simple and mild method involving Pd(II) induced aziridination of olefins and bromamine-T is detailed. Synthetically useful *N*-tosyl-2-substituted aziridines can be accessed by this procedure with moderate to good yields for olefins containing a variety of functional groups. The mechanism, probed by ^{1}H NMR spectroscopy using cis-β-deutero allyl alcohol, showed complete *syn* stereospecificity. Tertiary-amide and acrylic ester did not show similar selectivity. The degree of selectivity achieved is attributed to the ability of the functional group to coordinate with an electrophilic Pd(IV) proposed as an intermediate. Only Oppolzer sultam employed as the chiral auxiliary amongst many tested gave a modest diastereoselection.

4. Experimental section

4.1. General experimental method

Solvents were purified by standard methods.[38] All commercial reagents were used as received unless otherwise mentioned. The chiral olefins, methylacrylate, bornyl acrylate, and fenchyl acrylate were kindly offer by Professor Manuela Pereira from our laboratory. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated were used, respectively. The spots were visualized using UV light and a $KMnO_4$ solution (1:0.02 mixture of 1% $KMnO_4$ and 7% K_2CO_3 solution/5% NaOH aqueous solution) followed by heating. Medium-performance liquid chromatography and flash column chromatography were performed using Merck, Kieselgel 60 with (0.063–0.200 mm) and (0.040–0.063 mm), respectively. Melting points were recorded on a Köfler apparatus, Reichert Thermovar model and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 683 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer at 400 and 100.62, respectively. ^{1}H shifts are reported relative to internal TMS. Carbon shifts are given relative to the ^{13}C signal of $CDCl_3$ (δ 77.0 ppm) or DMSO-d_6 (δ 39.5 ppm) as reference. High resolution mass spectra were recorded on a Finnigan FT/MS 2001-DT, FT-ICR spectrometer furnished with a 3.0 T superconductor magnet, at the Instituto Tecnológico Nuclear (ITN), Lisbon, Portugal. The spectra were obtained by laser desorption (LD) or electron impact (EI). The low resolution mass spectra recorded at INETI, Lisbon, Portugal, were obtained by GC–MS on a Finnigan GCQ plus with a TRACE 2000 series chromatograph using a DB-5 column, 0.32 mm DI, 0.25 μm df (initial temperature 50 °C held for 1 min, then 10 °C min^{-1} until 300 °C).

4.1.1. Preparation of *N*-halo-*N*-sodium sulfonamides.

4.1.1.1. Bromamine-T.[39] Bromine (0.8 ml, 15.57 mmol) was added to tosylamine (2.0 g, 11.69 mmol) in water (8 ml) protected from light and after 1/2 h the solution was set to 0 °C. A solution of NaOH 50% (3.0 ml, 37.5 mmol) was added dropwise. The precipitate was filtered and dried at reduced pressure over phosphorous pentoxide at 40 °C until constant weight. A light yellow solid (2.63 g) was obtained in 83% yield; mp 150–152 °C (lit.[40] 145–150 °C). IR (KBr) ν_{max}: 1244 (S═O), 1131 (S═O) cm^{-1}. ^{1}H NMR (DMSO) δ: 7.60 (2H, d, J=7.8 Hz, ArH_{2+6}), 7.25 (2H, d, J=7.7 Hz, ArH_{3+5}), 2.41 (3H, s, $ArCH_3$). ^{13}C NMR (DMSO) δ: 143.6 (ArC_1), 139.2 (ArC_4), 128.7 (ArC_{3+5}), 127.4 (ArC_{2+6}), 21.1 ($ArCH_3$).

4.1.2. Preparation of deutered olefins.

4.1.2.1. (*Z*)-[3-^{2}*H*]Prop-2-en-1-ol (4c), (*Z*)-[4-^{2}*H*]but-3-en-2-ol (4a), and (*S*)-(*Z*)-[4-^{2}*H*]but-3-en-2-ol (4b). These were prepared following the procedure of Bellamy.[31]

4.1.2.2. (*Z*)-[3-^{2}*H*]Ethyl propenoate (4e). Prepared as previously described[33] by heating ethyl 11,12-*cis*-12-deuterio-9,10-ethane-9,10-dihydroanthracene-11-carboxylate (6.32 g, 22.65 mmol) at 290–300 °C at atmospheric pressure. The volatile ester was slowly released and was collected in a cooled receiver affording pure (*Z*)-[3-^{2}*H*] ethyl propenoate (1.32 g) in 58% yield.

4.1.2.3. (*Z*)-[3-^{2}*H*] *N*,*N*-Dimethylacrylamide (4d). To a solution of *cis*-β-iodo-*N*,*N*-dimethylacrylamide[32] (1.0 equiv, 40 mg, 0.178 mmol) and $Pd(OAc)_2$ (0.1 equiv, 4 mg, 1.78×10^{-2} mmol) in deutero methanol at room temperature was added $NaBD_4$ (1.0 equiv, 6.7 mg, 0.178 mmol). The mixture after remaining at room temperature for 5 days was worked up in the usual manner. The title compound isolated by PTLC in 14% yield was found to consist of trans/cis isomers (a 1:19 mixture) as calculated by integration of appropriate signals in the ^{1}H NMR spectrum.

4.1.3. General methods for the preparation of aziridines.

Method A: Bis(acetonitrile)dichloropalladium(II) (0.42 equiv, 19.5 mg, 0.075 mmol) was added to the olefin (2.5 equiv, 0.45 mmol) in dry acetonitrile (2.5 ml) under nitrogen atmosphere. After 1/2 h of stirring at room temperature the bromamine-T (1.0 equiv, 50 mg, 0.18 mmol) was added and the reaction protected from light, allowed to proceed until a negative test (starch-iodide paper) for bromamine-T was observed. Upon following solvent evaporation the obtained residue was dissolved in dichloromethane, washed with aqueous sodium metabisulfite solution (15%) and water. The products were isolated by preparative TLC.

Method B: Palladium(II) chloride (0.13 equiv, 4.2 mg, 0.024 mmol) was added to the olefin (0.8 equiv, 0.15 mmol) in dry acetonitrile (2.0 ml) under nitrogen atmosphere. After 1/2 h of stirring at room temperature the bromamine-T was added (0.33 equiv, 16.3 mg, 0.06 mmol) and the reaction protected from light was allowed to proceed.

Two more bromamine-T additions (0.33 equiv each) were made and each addition was performed only after a negative test (starch-iodide paper) for bromamine-T was observed. Upon solvent evaporation the obtained residue was dissolved in dichloromethane, washed with aqueous sodium metabisulfite solution (15%) and water. The products were isolated by preparative TLC.

4.1.3.1. Methyl (1′-tosylaziridin-2′-yl)carboxylate (1a). Colorless oil obtained in 60% (method A) and 39% (method B) yields. Spectroscopic data were in agreement with those previously reported.[41]

4.1.3.2. *tert*-Butyl-(1′-tosylaziridin-2′-yl)carboxylate (1b). Colorless oil obtained in 60% (method A) and 46% (method B) yields. Spectroscopic data were in agreement with those previously reported.[41]

4.1.3.3. *N*,*N*-Dimethyl-(1′-tosylaziridin-2′-yl)carboxamide (1c). Colorless solid obtained in 57% (method A) and 81% (method B) yields; mp 61–63 °C (ethyl acetate/hexane). Spectroscopic data were in agreement with those previously reported.[42]

4.1.3.4. *trans*-*N*,*N*,3′-Trimethyl-1-(1′-tosylaziridin-2′-yl)carboxamide and *cis*-*N*,*N*,3′-trimethyl-1-(1′-tosylaziridin-2′-yl)carboxamide (1d). Colorless oil (16%), consisting of the trans (10%) and cis (6%) isomers (method A). IR (film) ν_{max}: 1658 (C═O), 1324 (S═O), 1159 (S═O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.86 (4H, d, J=8.4 Hz, ArH_{2+6}), 7.32 (4H, d, J=8.0 Hz, ArH_{3+5}), 3.50 (1H, d, J=7.2 Hz, $H_{2'\ cis}$), 3.45 (1H, d, J=4.0 Hz, $H_{2'\ trans}$), 3.24–3.21 (1H, m, $H_{3'\ trans}$), 3.13 (3H, s, $NCH_{3\ cis}$), 3.09 (3H, s, $NCH_{3'\ trans}$), 3.07–3.03 (1H, m, $H_{3'\ cis}$), 2.94 (3H, s, $NCH_{3\ trans}$), 2.92 (3H, s, $NCH_{3\ cis}$), 2.44 (3H, s, $ArCH_{3\ cis}$), 2.43 (3H, s, $ArCH_{3\ trans}$), 1.63 (3H, d, J=6.0 Hz, $CH_{3\ trans}$), 1.22 (3H, d, J=5.6 Hz, $CH_{3\ cis}$). ^{13}C NMR ($CDCl_3$) δ: 165.0 (CO), 144.4 (ArC_4), 136.9 (ArC_1), 129.6 (ArC_{3+5}), 127.6 (ArC_{2+6}), 44.4 ($C_{2'}$), 43.9 ($C_{3'}$), 37.1 (NCH_3), 35.7 (NCH_3), 21.6 ($ArCH_3$), 13.6 (CH_3). HRMSEI(+) calcd for *trans*-$C_{13}H_{19}N_2O_3S$ $[MH]^+$ 283.11109, found 283.11095.

4.1.3.5. 1-(1′-Tosylaziridin-2′-yl)ethanone (1e). Colorless solid obtained in 25% (method A) and 23% (method B) yields; mp 69–70 °C (ethyl ether/hexane). Spectroscopic data were in agreement with those previously reported.[42]

4.1.3.6. 2-(Phenylsulfinyl)-tosylaziridine (1f). Oil obtained in 10% (method A) and 19% (method B) yields. Spectroscopic data were in agreement with those previously reported.[27]

4.1.3.7. 1-Tosylaziridin-2-carbonitrile (1g). Oil obtained in 22% (method A) and 13% (method B) yields. Spectroscopic data were in agreement with those previously reported.[43]

4.1.3.8. 2-(1′-Tosylaziridin-2′-yl)acetonitrile (1h). Oil obtained in 23% (method A) and 18% (method B) yields. IR (film) ν_{max}: 1592 (CN), 1320 (S═O), 1159 (S═O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.83 (2H, d, J=8.0 Hz, ArH_{2+6}), 7.37 (2H, d, J=7.6 Hz, ArH_{3+5}), 3.01–3.00 (1H, m, $H_{2'}$), 2.74 (1H, d, J=6.8 Hz, $H_{3'\ cis}$), 2.68–2.66 (2H, m, H_2), 2.46 (3H, s, $ArCH_3$), 2.30 (1H, d, J=3.2 Hz, $H_{3'\ trans}$). ^{13}C NMR ($CDCl_3$) δ: 145.2 (ArC_4), 134.6 (ArC_1), 130.0 (ArC_{3+5}), 128.0 (ArC_{2+6}), 115.0 (CN), 33.7 ($C_{2'}$), 32.5 ($C_{3'}$), 21.7 ($ArCH_3$), 20.1 (C_2). MSLD(−) m/z: 236 $[M]^-$ (30.2), 196 $[M-CH_2CN]$ (21.4), 155 $[Ts]^-$ (100.0). HRMSLD(−) calcd for $C_{11}H_{12}N_2O_2S$ $[M]^-$ 236.06250, found 236.06254.

4.1.3.9. Methyl-2-(1′-tosylaziridin-2′-yl)acetate (1i). Colorless oil obtained in 25% (method A) and 13% (method B) yields. IR (film) ν_{max}: 1734 (C═O), 1320 (S═O), 1160 (S═O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.84 (2H, d, J=8.0 Hz, ArH_{2+6}), 7.35 (2H, d, J=8.0 Hz, ArH_{3+5}), 3.56 (3H, s, OCH_3), 3.12–3.06 (1H, m, $H_{2'}$), 2.72 (1H, d, J=6.8 Hz, $H_{3'\ cis}$), 2.50 (2H, dd, J=6.4 and 4.0 Hz, H_2), 2.16 (1H, d, J=4.4 Hz, $H_{3'\ trans}$), 2.45 (3H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 165.1 (CO), 140.1 (ArC_4), 133.8 (ArC_1), 129.5 (ArC_{3+5}), 128.1 (ArC_{2+6}), 51.9 (OCH_3), 38.5 (C_2), 35.8 ($C_{2'}$), 32.7 ($C_{3'}$), 21.6 ($ArCH_3$). MSEI(+) m/z: 269 $[M]^+$ (7.4), 155 $[Ts]^+$ (1.8), 114 $[M-Ts]^+$ (100.0). HRMSEI(+) calcd for $C_{12}H_{15}NO_4S$ $[M]^+$ 269.07163, found 269.07134.

4.1.3.10. *cis*-7-Tosyl-7-azabicyclo[4.1.0]heptan-2-one (1j). Colorless oil obtained in 33% yield (method A). Spectroscopic data were in agreement with those previously reported.[27]

4.1.3.11. *cis*-7-Tosyl-7-azabicyclo[4.1.0]heptane (1l). Colorless oil obtained in 11% (method A) and 2% (method B) yields. Spectroscopic data were in agreement with those previously reported.[5]

4.1.3.12. (1′-Tosylaziridin-2′-yl)methanol (1m). Colorless oil obtained in 53% (method A) and 48% (method B) yields. Spectroscopic data were in agreement with those previously reported.[44]

4.1.3.13. 2-(Ethoxymethyl)-1-tosylaziridine (1n). Colorless oil obtained in 30% (method A) and 12% (method B) yields. IR (film) ν_{max}: 1323 (S═O), 1161 (S═O), 1091 (C–O–C) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.84 (2H, d, J=8.0 Hz, ArH_{2+6}), 7.34 (2H, d, J=8.0 Hz, ArH_{3+5}), 3.53 (1H, dd, J=11.2 and 4.4 Hz, $H_{1'}$), 3.44–3.88 (3H, m, $H_{1'}$+$H_{1''}$), 3.00–2.95 (1H, m, H_2), 2.66 (1H, d, J=7.2 Hz, $H_{3\ cis}$), 2.45 (3H, s, $ArCH_3$), 2.20 (1H, d, J=4.4 Hz, $H_{3\ trans}$), 1.09 (3H, t, J=6.8 Hz, $H_{2''}$). ^{13}C NMR ($CDCl_3$) δ: 144.3 (ArC_4), 134.3 (ArC_1), 129.6 (ArC_{3+5}), 128.1 (ArC_{2+6}), 69.5 ($C_{1'}$), 66.6 ($C_{1''}$), 38.8 (C_2), 31.0 (C_3), 21.6 ($ArCH_3$), 15.0 ($C_{2''}$). GCMSEI(+) m/z: 210 $[M-OEt]^+$ (0.9), 155 $[Ts]^+$ (27.9), 91 $[C_7H_7]^+$ (85.8), 56 $[C_3H_6N]^+$ (100). HRMSEI(−) calcd for $C_{12}H_{17}NO_3$ $[M]^+$ 255.093463, found 255.09345.

4.1.3.14. (1′-Tosylaziridin-2′-yl)methyl acetate (1o). Colorless oil obtained in 54% (method A) and 8% (method B) yields. IR (film) ν_{max}: 1744 (C═O), 1324 (S═O), 1160 (S═O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.84 (2H, d, J=8.0 Hz, ArH_{2+6}), 7.36 (2H, d, J=8.4 Hz, ArH_{3+5}), 4.21 (1H, dd, J=12.0 and 4.0 Hz, H_1), 3.85 (1H, dd, J=12.0 and 7.2 Hz, H_1), 3.03–2.98 (1H, m, $H_{2'}$), 2.74 (1H, d, J=7.2 Hz, $H_{3'\ cis}$), 2.45 (3H, s, $ArCH_3$), 2.24 (1H, d, J=4.0 Hz, $H_{3'\ trans}$), 1.91 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.3 (CO), 144.7 (ArC_4), 134.6 (ArC_1), 129.6 (ArC_{3+5}), 128.1 (ArC_{2+6}),

65.2 (C_1), 37.3 ($C_{2'}$), 31.0 ($C_{3'}$), 21.6 ($ArCH_3$), 20.4 (CH_3). MSEI(+) *m/z*: 269 $[M]^+$ (1.6), 114 $[M-Ts]^+$ (100.0). HRMSEI(+) calcd for $C_{12}H_{15}NO_4S$ $[M]^+$ 269.07163, found 269.07134.

4.1.3.15. 2-(1′-Tosylaziridin-2′-yl)propan-2-ol (1p). Colorless oil obtained in 21% (method A) yield. Spectroscopic data were in agreement with those previously reported.[41]

4.1.3.16. (1*S*,2′*S*), (1*R*,2′*R*), (1*S*,2′*R*), and (1*R*,2′*S*)-1-(1′-Tosylaziridin-2′-yl)ethanol (1q). Colorless oil obtained in 30% (method A) and 20% (method B) yields. Spectroscopic data were in agreement with those previously reported.[45]

4.1.3.17. (1*S*,2′*S*), (1*R*,2′*R*), (1*S*,2′*R*), and (1*R*,2′*S*)-1-(1′-Tosylaziridin-2′-yl)ethane-1,2-diol (1r). Colorless oil obtained in 27% (method A) and 32% (method B) yields and 0% de. IR (film) ν_{max}: 3400 (O–H), 1321 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.83 (2H, d, J=8.4 Hz, ArH_{2+6a}), 7.82 (2H, d, J=8.0 Hz, ArH_{2+6b}), 7.29 (4H, d, J=7.6 Hz, $ArH_{3+5(a+b)}$), 3.76–3.54 (6H, m, $H_{1+2(a+b)}$), 3.00–2.91 (2H, m, $H_{2'(a+b)}$), 2.63 (1H, d, J=6.8 Hz, $H_{3'a\ cis}$), 2.56 (1H, d, J=7.2 Hz, $H_{3'b\ cis}$), 2.46 (6H, s, $ArCH_{3(a+b)}$), 2.38–2.36 (2H, m, $H_{3'(a+b)\ trans}$). ^{13}C NMR ($CDCl_3$) δ: 144.9 ($ArC_{4(a+b)}$), 134.5 ($ArC_{1(a+b)}$), 129.8 ($ArC_{3+5(a+b)}$), 128.1 (ArC_{2+6a}), 128.0 (ArC_{2+6b}), 69.3 (C_{2a}), 68.5 (C_{2b}), 64.8 (C_{1a}), 64.0 (C_{1b}), 40.2 ($C_{2'a}$), 39.8 ($C_{2'b}$), 31.5 ($C_{3'a}$), 29.5 ($C_{3'b}$), 21.6 ($ArCH_{3(a+b)}$). MSLD(−) *m/z*: 257 $[M]^-$ (9.3), 155 $[Ts]^-$ (100). HRMSLD(−) calcd for $C_{11}H_{15}NO_4S$ $[M]^-$ 257.072728, found 257.07272.

4.1.3.18. *cis*-[3′-(Hydroxymethyl)-1′-tosylaziridin-2′-yl]methanol (1s). Colorless oil obtained in 6% (method A) and 12% (method B) yields. IR (film) ν_{max}: 3399 (O–H), 1303 (S=O), 1156 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.86 (2H, d, J=8.0 Hz, ArH_{2+6}), 7.35 (2H, d, J=8.0 Hz, ArH_{3+5}), 4.02–3.99 (2H, m, H_1), 3.81–3.20 (2H, m, H_1), 3.22–3.20 (2H, m, $H_{2'+3'}$), 2.45 (3H, s, $ArCH_3$), 2.31 (2H, br s, exchange with D_2O, OH). ^{13}C NMR ($CDCl_3$) δ: 145.4 (ArC_4), 137.5 (ArC_1), 130.1 (ArC_{3+5}), 128.7 (ArC_{2+6}), 61.15 (C_1), 48.4 ($C_{2'+3'}$), 22.3 ($ArCH_3$). MSEI(+) *m/z*: 258 $[MH]^+$ (100.0), 155 $[Ts]^+$ (19.9). HRMSEI(+) calcd for $C_{11}H_{16}NSO_4$ $[MH]^+$ 258.07955, found 258.07940.

4.1.3.19. *trans*-[3′-(Hydroxymethyl)-1′-tosylaziridin-2′-yl]methanol (1t). Colorless oil obtained in 5% (method A) and 6% (method B) yields. IR (film) ν_{max}: 3324 (O–H), 3224 (O–H), 1325 (S=O), 1161 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.81 (2H, d, J=7.6 Hz, ArH_{2+6}), 7.37 (2H, d, J=7.6 Hz, ArH_{3+5}), 3.77–3.75 (2H, m, H_1), 3.61–3.59 (2H, m, H_1), 3.09–3.04 (2H, m, $H_{2'+3'}$), 2.78 (2H, br s, exchange with D_2O, OH), 2.46 (3H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 145.4 (ArC_4), 134.7 (ArC_1), 130.1 (ArC_{3+5}), 128.2 (ArC_{2+6}), 59.2 (C_1), 44.1 ($C_{2'+3'}$), 21.8 ($ArCH_3$). MSEI(+) *m/z*: 258 $[MH]^+$ (100.0), 155 $[Ts]^+$ (39.2). HRMSEI(+) calcd for $C_{11}H_{16}NSO_4$ $[MH]^+$ 258.07955, found 258.07931.

4.1.3.20. *trans*-2-Benzoyl-3-phenyl-1-tosylaziridine (1u). Colorless oil obtained in 5% yield as a mixture of cis (1%) and trans (4%) isomers (method A). Spectroscopic data were in agreement with those previously reported.[46]

4.1.3.21. (2′*R*) and (2′*S*)-{(7″*R*,1″*S*,5″*R*)-10″,10″-Dimethyl-3″-thia-tricyclo[5.2.1.0^{1,5}]decane-4″-yl}-(1′-tosylaziridin-2′-yl)carbonyls (8a and 8b). Oil obtained in 61% yield (method B) and 27% de. IR (film) ν_{max}: 1702 (C=O), 1333 (S=O), 1164 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.88 [4H, d, J=8.0 Hz, $ArH_{2+6(a+b)}$], 7.34 [2H, d, J=8.0 Hz, ArH_{3+5a}], 7.32 [2H, d, J=8.0 Hz, ArH_{3+5b}], 3.93–3.82 [4H, m, $H_{5''(a+b)}$+$H_{2'(a+b)}$], 3.55–3.43 [4H, m, $H_{2''(a+b)}$], 2.88 [1H, d, J=7.2 Hz, $H_{3'a\ cis}$], 2.82 [1H, d, J=6.8 Hz, $H_{3'b\ cis}$], 2.66 [2H, d, J=4.0 Hz, $H_{3'(a+b)\ trans}$], 2.43 [6H, s, $ArCH_{3(a+b)}$], 2.09–1.96 [4H, m, $H_{9''(a+b)}$], 1.96–1.76 [6H, m, $H_{6''(a+b)}$+$H_{8''(a+b)}$+$H_{7''(a+b)}$], 1.43–1.27 (4H, m, $H_{6''(a+b)}$+$H_{8''(a+b)}$], 0.97 (6H, s, CH_{3a}), 0.96 (6H, s, CH_{3b}). ^{13}C NMR ($CDCl_3$) δ: 164.3 (CO_{a+b}), 145.0 [$ArC_{4(a+b)}$], 135.3 [$ArC_{1(a+b)}$], 129.7 [$ArC_{3+5(a+b)}$], 128.7 [ArC_{2+6a}], 128.5 [ArC_{2+6b}], 65.2 ($C_{5''a}$), 65.1 ($C_{5''b}$), 54.9 [$C_{2''(a+b)}$], 49.1 [$C_{1''/10''(a+b)}$], 47.8 [$C_{1''/10''(a+b)}$], 44.4 [$C_{7''(a+b)}$], 38.0 [$C_{9''(a+b)}$], 36.3 [$C_{2'(a+b)}$], 32.7 [$C_{8''/9''(a+b)}$], 32.4 ($C_{3'a}$), 31.8 ($C_{3'b}$), 26.3 [$C_{8''/6''(a+b)}$], 21.5 [$ArCH_{3(a+b)}$], 20.8 (CH_{3a}), 20.6 (CH_{3b}). MSEI(+) *m/z*: 439 $[MH]^+$ (31.6), 283 $[M-Ts]^+$ (87.1), 224 $[M-NCH_2SO_2C_9H_{14}]^+$ (30.7), 214 $[NCH_2SO_2C_9H_{14}]^+$ (100.0), 155 $[Ts]^+$ (28.1). HRMSEI(+) calcd for $C_{20}H_{27}N_2O_5S_2$ $[MH]^+$ 439.13559, found 439.13544.

4.1.3.22. (2′*R*) and (2′*S*)-*N*-[(1″*S*)-1″-Phenylethyl]-*N*-neopenthyl-(1′-tosylaziridin-2′-yl)carboxamides (9a and 9b). Oil obtained in 20% yield (method B) and 16% de, *a* is the major diastereomer). IR (film) ν_{max}: 1660 (C=O), 1328 (S=O), 1162 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.86 [2H, d, J=8.0 Hz, ArH_{2+6b}], 7.71 [2H, d, J=8.0 Hz, ArH_{2+6a}], 7.40–7.27 [14H, m, $ArH_{(a+b)}$], 5.27–5.22 (1H, m, $H_{1''a}$), 4.66–4.61 (1H, m, $H_{1''b}$), 3.66–3.60 (2H, m, $H_{2'b}$+$1H_{1b}$), 3.45 (1H, dd, J=6.8 and 3.3 Hz, $H_{2'a}$), 3.26–3.18 (3H, m, $2H_{1a}$+H_{1b}), 2.64–2.56 [4H, m, $H_{3'(a+b)}$], 2.45 (3H, s, $ArCH_{3b}$), 2.43 (3H, s, $ArCH_{3a}$), 1.76 (3H, d, J=7.2 Hz, $C^{1''}CH_{3b}$), 1.68 (3H, d, J=7.2 Hz, $C^{1''}CH_{3a}$), 1.09 [6H, s, $(CH_3)_{3(a+b)}$], 0.81 [12H, s, $C(CH_3)_{3(a+b)}$]. ^{13}C NMR ($CDCl_3$) δ: 167.0 (CO_{a+b}), 141.0 [$ArC_{4(a+b)}$], 135.3 [$ArC_{1(a+b)}$], 129.7 [$ArC_{(a+b)}$], 129.0 [ArC], 128.2 [$ArC_{2+6(a+b)}$], 127.7 [$ArC_{(a+b)}$], 128.5 [$ArC_{(a+b)}$], 60.5 ($C_{1''b}$), 79.3 (C_{1b}), 57.3 ($C_{1''a}$), 56.6 (C_{1a}), 37.3 ($C_{2'a}$), 36.2 ($C_{2'b}$), 33.2 [$C_{2(a+b)}$], 32.4 [$C_{3'(a+b)}$], 28.8 [$C(CH_3)_{3a}$], 29.2 [$C(CH_3)_{3b}$], 22.3 [$ArCH_{3(a+b)}$], 20.4 [$C^{1''}CH_{3a}$], 18.1[$C^{1''}CH_{3b}$]. HRMSEI(+) calcd for $C_{23}H_{31}N_2O_3S$ $[MH]^+$ 415.20499, found 415.20504.

4.1.3.23. (2′*S*) and (2′*R*)-(1″*R*,2″*S*,5″*R*)-2″-Isopropyl-5″-methylcyclohexyl-(1′-tosylaziridin-2′-yl)carboxylates (10a and 10b). Oil obtained in 42% yield and 3% de (method A). IR (film) ν_{max}: 1742 (C=O), 1334 (S=O), 1164 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.85 [2H, d, J=8.4 Hz, ArH_{2+6a}], 7.84 [2H, d, J=8.0 Hz, ArH_{2+6b}], 7.34 [2H, d, J=8.0 Hz, $ArH_{3+5(a+b)}$], 4.69–4.62 [2H, m, $H_{1''(a+b)}$], 3.26–3.20 [2H, m, $H_{2'(a+b)}$], 2.81 (1H, d, J=7.2 Hz, $H_{3'a\ cis}$), 2.80 (1H, d, J=7.2 Hz, $H_{3'b\ cis}$), 2.60 (1H, d, J=4.4 Hz, $H_{3'a\ trans}$), 2.57 (1H, d, J=4.0 Hz, $H_{3'b\ trans}$), 2.45 [6H, s, $ArCH_{3(a+b)}$], 1.92–1.86 [2H, m, $H_{6''/4''(a+b)}$], 1.72–1.29 [12H, m, $H_{2''/1'''(a+b)}$+$H_{3''(a+b)}$+$H_{5''(a+b)}$+$2H_{6''/4''(a+b)}$], 1.05–0.92 [4H, m, $H_{6''/4''(a+b)}$+$H_{3''(a+b)}$], 0.88 (3H, d, J=6.4 Hz, $C^{5''}CH_{3a}$), 0.88 (3H, d, J=6.4 Hz, $C^{5''}H_{3b}$), 0.82 (3H, d, J=7.2 Hz, $C^{1'''}CH_{3a}$), 0.80 (3H, d, J=6.8 Hz, $C^{1'''}CH_{3b}$), 0.64 (3H, d, J=6.8 Hz, $C^{1'''}CH_{3a}$), 0.60 (3H, d, J=6.8 Hz, $C^{1'''}H_{3b}$). ^{13}C NMR ($CDCl_3$) δ: 168.3 (CO), 145.0 (ArC_4),

134.3 (ArC_1), 129.7 (ArC_{3+5}), 128.2 [ArC_{2+6a}], 128.1 [ArC_{2+6b}], 76.9 [$C_{1''(a+b)}$], 46.8 [$C_{1'''/2''(a+b)}$], 40.5 [$C_{6''/4''(a+b)}$], 38.6 ($C_{2'}$), 34.0 [$C_{6''/4''(a+b)}$], 31.6 ($C_{5''a}$), 31.5 ($C_{5''b}$), 33.3 ($C_{3'}$), 26.1 ($C_{1'''/2''a}$), 26.0 ($C_{1'''/2''b}$), 23.4 ($C_{3''a}$), 23.2 ($C^{5''}CH_{3b}$), 21.9 ($C^{5''}CH_{3a}$), 20.7 [$ArCH_{3(a+b)}$], 20.6 ($C^{1'''}CH_{3b}$), 20.5 ($C^{1'''}CH_{3a}$), 16.2 ($C^{1'''}CH_{3a}$), 16.1 ($C^{1'''}CH_{3b}$). HRMSEI(+) calcd for $C_{20}H_{30}NO_4S$ $[MH]^+$ 380.18900, found 380.18914.

4.1.3.24. (2′*R*) and (2′*S*)-(1″*S*,2″*R*)-1″,3″,3″-Trimethylbicyclo[2.2.1]hepta-2″-yl-(1′-tosylaziridin-2′-yl)carboxylates (11a and 11b). Oil obtained in 50% yield (method A); de 12% and 21% yield (method B); de 10% (**11b** is the predominant diastereomer). IR (film) ν_{max}: 1744 (C=O), 1333 (S=O), 1162 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.86–7.85 [2H, m, $ArH_{2+6(a+b)}$], 7.35 [4H, d, J=8.0 Hz, $ArH_{3+5(a+b)}$], 4.32 [2H, dd, J=7.6 and 1.6 Hz, $H_{2''(a+b)}$], 3.29–3.25 [2H, m, $H_{2'(a+b)}$], 2.86–2.83 [1H, m, $H_{3'(a+b)\ cis}$], 2.63 [1H, d, J=4.4 Hz, $H_{3'a\ trans}$], 2.60 [1H, d, J=4.0 Hz, $H_{3'b\ trans}$], 2.45 [6H, s, $ArCH_{3(a+b)}$], 1.69–1.41 [12H, m, $H_{4''(a+b)}+H_{6''/7''(a+b)}+H_{5''(a+b)}$], 1.24–1.06 [4H, m, $H_{6''/7''(a+b)}$], 1.03 [3H, s, $C^{3''}CH_{3b}$], 1.02 [3H, s, $C^{3''}CH_{3a}$], 0.91 (3H, s, $C^{1''}CH_{3a}$), 0.71 (3H, s, $C^{1''}CH_{3b}$), 0.64 (3H, s, $C^{3''}CH_{3b}$), 0.47 (3H, s, $C^{3''}CH_{3a}$). ^{13}C NMR ($CDCl_3$) δ: 167.0 (CO_{a+b}), 145.1 [$ArC_{4(a+b)}$], 134.3 [$ArC_{1(a+b)}$], 128.9 [$ArC_{3+5(a+b)}$], 127.5 [ArC_{2+6a}], 128.0 [ArC_{2+6b}], 87.3 ($C_{2''a}$), 86.8 ($C_{2''b}$), 48.2 [$C_{4''(a+b)}$], 41.2 [$C_{7''/6''(a+b)}$], 39.4 [$C_{3''(a+b)}$], 36.6 [$C_{2'(a+b)}$], 31.5 ($C_{3'b}$), 31.3 ($C_{3'a}$), 29.6 ($C^{3''}CH_{3b}$), 29.5 ($C^{3''}CH_{3a}$), 26.4 [$C_{6''/7''(a+b)}$], 25.5 [$C_{5''(a+b)}$], 21.6 [$ArCH_{3(a+b)}$], 19.8 ($C^{1''}CH_{3b}$), 19.4 ($C^{1''}CH_{3a}$), 19.2 ($C^{3''}CH_{3a}$), 19.1 ($C^{3''}CH_{3b}$). HRMSEI(+) calcd for $C_{20}H_{28}NO_4S$ $[MH]^+$ 378.173355, found 378.17317.

4.1.3.25. (2′*R*) and (2′*S*)-(1″*R*,2″*R*)-1″,7″,7″-Trimethylbicyclo[2.2.1]hepta-2″-yl-(1′-tosylaziridin-2′-yl)carboxylates (12a and 12b). Oil obtained in 41% yield and 0% de (method A). IR (film) ν_{max}: 1743 (C=O), 1334 (S=O), 1164 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.86 [4H, d, J=8.0 Hz, $ArH_{2+6(a+b)}$], 7.36 [4H, d, J=8.0 Hz, $ArH_{3+5(a+b)}$], 4.91–4.86 [2H, m, $H_{2''(a+b)}$], 3.31–3.28 [2H, m, $H_{2'(a+b)}$], 2.81 (1H, d, J=7.2 Hz, $H_{3'a\ cis}$), 2.80 (1H, d, J=7.2 Hz, $H_{3'b\ cis}$), 2.60 [2H, d, J=4.0 Hz, $H_{3'(a+b)\ trans}$], 2.45 [6H, s, $ArCH_{3(a+b)}$], 2.33–2.27 [2H, m, $H_{5''/3''(a+b)}$], 1.84–1.65 [6H, m, $H_{5''/3''(a+b)}+H_{4''(a+b)}+H_{6''(a+b)}$], 1.22–1.09 [4H, m, $H_{6''(a+b)}+H_{5''/3''(a+b)}$], 0.95–0.93 [2H, m, $H_{5''/3''(a+b)}$], 0.93 [12H, s, $C^{7''}CH_{3(a+b)}$], 0.77 [3H, s, $C^{1''}CH_{3a}$], 0.71 (3H, s, $C^{1''}CH_{3b}$). ^{13}C NMR ($CDCl_3$) δ: 166.9 (CO_{a+b}), 144.1 [$ArC_{4(a+b)}$], 135.2 [$ArC_{1(a+b)}$], 129.8 [$ArC_{3+5(a+b)}$], 128.1 [$ArC_{2+6(a+b)}$], 84.3 ($C_{2''a}$), 81.7 ($C_{2''b}$), 48.8 ($C_{7''a}$), 47.8 ($C_{7''b}$), 44.7 [$C_{4''(a+b)}$], 36.5 [$C_{5''/3''(a+b)}$], 36.3 [$C_{2'(a+b)}$], 31.6 ($C_{3'a+b}$), 27.9 ($C_{5''/3''a}$), 27.8 [$C_{5''/3''b}$], 26.9 [$C_{6''(a+b)}$], 21.6 [$ArCH_{3(a+b)}$], 19.6 ($C^{7''}CH_{3a}$), 18.7 ($C^{7''}CH_{3b}$), 13.3 ($C^{1''}CH_{3a}$), 13.2 ($C^{1''}CH_{3b}$). HRMSEI(−) calcd for $C_{20}H_{26}NO_4S$ $[M-H]^-$ 376.15880, found 376.15868.

4.1.3.26. *N*-β-Substituted ethyl-*p*-toluenesulfonamides (2 and 3).

*4.1.3.26.1. Methyl 2-bromo-3-(tosylamino)propanoate (**2a**).* Oil obtained in 6% (method A) and 3% (method B) yields. IR (film) ν_{max}: 3289 (N–H), 1744 (C=O), 1331 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.75 (2H, d, J=8.1 Hz, ArH_{2+6}), 7.33 (2H, d, J=8.1 Hz, ArH_{3+5}), 5.11–5.08 (1H, m, exchange with D_2O, NH), 4.38 (1H, dd, J=6.7 and 4.4 Hz, H_2), 3.78 (3H, s, OCH_3), 3.53–3.35 (2H, m, H_3), 2.44 (3H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 168.6 (CO), 144.1 (ArC_4), 136.8 (ArC_1), 130.0 (ArC_{3+5}), 127.1 (ArC_{2+6}), 54.2 (C_2), 53.2 (OCH_3), 45.7 (C_3), 21.4 ($ArCH_3$). MS (EI) *m/z*: 338 $[M\ (^{81}Br)H]^+$ (5.9), 336 $[M\ (^{79}Br)H]^+$ (5.8), 256 $[M-Br]^+$ (100.0), $[M\ (^{81}Br)–Ts]^+$ 182 (39.1). HRMSEI(+) calcd for $C_{11}H_{15}N^{81}BrO_4S$ $[MH\ (^{81}Br)]^+$ 337.98792, found 337.98783, calcd for $C_{11}H_{15}N^{79}BrO_4S$ $[MH\ (^{79}Br)]^+$ 337.99052, found 335.98972.

*4.1.3.26.2. 2-Bromo-N,N-dimethyl-3-(tosylamino)propanamide (**2c**).* Oil obtained in 10% (method A) and 12% (method B) yields. IR (film) ν_{max}: 3231 (N–H), 1643 (C=O), 1330 (S=O), 1159 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.73 (2H, d, J=8.4 Hz, ArH_{2+6}), 7.31 (2H, d, J=8.0 Hz, ArH_{3+5}), 5.11–5.08 (1H, m, exchange with D_2O, NH), 4.53 (1H, dd, J=9.2 and 4.8 Hz, H_2), 3.57–2.83 (2H, m, H_3), 3.04 (3H, s, NCH_3), 2.97 (3H, s, NCH_3), 2.42 (3H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 167.3 (CO), 143.6 (ArC_4), 137.0 (ArC_1), 129.6 (ArC_{3+5}), 127.0 (ArC_{2+6}), 46.0 (C_3), 39.6 (C_2), 37.4 (NCH_3), 36.2 (NCH_3), 21.5 ($ArCH_3$). MS (EI) *m/z*: 351 $[M\ (^{81}Br)H]^+$ (10.0), 349 $[M\ (^{79}Br)H]^+$ (11.2), 269 $[M-Br]^+$ (100.0), 155 $[Ts]^+$ (40.6). HRMSEI(+) calcd for $C_{12}H_{18}N_2{}^{79}BrO_3S$ $[M\ (^{81}Br)H]^+$ 349.02160, found 349.02154.

*4.1.3.26.3. N-(2-Bromo-3-oxobutyl)tosylamine (**2e**).* Colorless solid obtained in 14% (method A) and 5% (method B) yields; mp 63–65 °C (ethyl acetate/*n*-hexane). IR (KBr) ν_{max}: 3232 (N–H), 1734 (C=O), 1332 (S=O), 1161 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.74 (2H, d, J=7.6 Hz, ArH_{2+6}), 7.33 (2H, d, J=7.6 Hz, ArH_{3+5}), 5.11–5.10 (1H, m, exchange with D_2O, NH), 4.45 (1H, dd, J=8.4 and 5.2 Hz, H_2), 3.49–3.31 (2H, m, H_1), 2.44 (3H, s, $ArCH_3$), 2.37 (3H, s, $COCH_3$). ^{13}C NMR ($CDCl_3$) δ: 201.6 (CO), 144.0 (ArC_4), 139.8 (ArC_1), 130.0 (ArC_{3+5}), 127.1 (ArC_{2+4}), 48.4 (C_2), 44.5 (C_1), 27.4 ($COCH_3$), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 321 $[M\ (^{81}Br)H]^+$ (2.4), 240 $[M-Br]^+$ (100.0). HRMSEI(+) calcd for $C_{11}H_{15}{}^{81}BrNO_3S$ $[M\ (^{81}Br)H]^+$ 321.99300, found 321.99342.

*4.1.3.26.4. N-[2-Bromo-2-(phenylsulfinyl)ethyl]tosylamine (**2f**).* Oil obtained in 7% (method A) and 19% (method B) yields. IR (film) ν_{max}: 3261 (N–H), 1330 (S=O), 1158 (S=O), 1045 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.78 (2H, d, J=8.2 Hz, ArH_{2+6}), 7.57–7.51 (5H, m, ArH), 7.36 (2H, d, J=8.0 Hz, ArH_{3+5}), 5.55 (1H, t, J=6.2 Hz, exchange with D_2O, NH), 4.80 (1H, dd, J=8.1 and 6.1 Hz, H_2), 3.74–3.49 (2H, m, H_1), 2.46 (3H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 144.1 (ArC_4), 135.1 (ArC_1), 132.1 (ArC), 130.0 (ArC_{3+5}), 125.5 (ArC), 123.4 (ArC), 65.7 (C_2), 45.6 (C_1), 29.72 ($ArCH_3$). MSEI(+) *m/z*: 404 $[M\ (^{81}Br)H]^+$ (1.8), 402 $[M\ (^{79}Br)H]^+$ (1.9), 322 $[M-Br]^+$ (3.8), 278 $[M\ (^{81}Br)-PhSO]^+$ (5.4), 276 $[M\ (^{79}Br)-PhSO]^+$ (5.3), 155 $[Ts]^+$ (100.0). HRMSEI(+) calcd for $C_{15}H_{17}{}^{81}BrNS_2O_3$ $[M\ (^{81}Br)H]^+$ 403.98072, found 403.98062; calcd for $C_{15}H_{17}{}^{79}BrNS_2O_3$ $[M\ (^{79}Br)H]^+$ 401.98332, found 401.98293.

*4.1.3.26.5. N-(2-Bromo-2-cyanoethyl)tosylamine (**2g**).* Colorless solid obtained in 19% (method A) and 5% (method B) yields; mp 110–113 °C (dichloromethane/*n*-hexane). IR (KBr) ν_{max}: 3306 (N–H), 2254 (CN), 1335 (S=O), 1154

(S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.77 (2H, d, J=8.2 Hz, ArH_{2+6}), 7.35 (2H, d, J=8.1 Hz, ArH_{3+5}), 5.43 (1H, t, J=6.6 Hz, exchange with D_2O, NH), 4.43 (1H, t, J=7.2 Hz, H_2), 3.59–3.44 (2H, m, H_1), 2.45 (3H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 144.5 (ArC_4), 137.0 (ArC_1), 132.8 (ArC_{3+5}), 127.2 (ArC_{2+6}), 115.4 (CN), 47.3 (C_1), 26.5 (C_2), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 304 [M (^{81}Br)H]$^+$(12.2), 302 [M (^{79}Br)]$^+$ (14.7), 184 [$TsNHNH_2$]$^+$ (100.0), 155 [Ts]$^+$ (12.2). HRMSEI(+) calcd for $C_{10}H_{10}N_2$ ^{81}BrS [M (^{81}Br)H]$^+$ 303.96986, found 303.97043, calcd for $C_{10}H_{11}N_2{}^{79}$BrS [M (^{79}Br)]$^+$ 301.97246, found 301.97134.

*4.1.3.26.6. N-[2-Bromo-1-(ethoxymethyl)ethyl]tosylamine (**2n**).* Oil obtained in 5.6% yield (method B). IR (film) ν_{max}: 3262 (N–H), 1331 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.8 (2H, d, J=8.0 Hz, ArH_{2+6}), 7.32 (2H, d, J=8.4 Hz, ArH_{3+5}), 5.03 (1H, d, J=7.6 Hz, exchange with D_2O, NH), 3.56–3.30 (7H, m, $H_{1'}$+H_1+H_2+$H_{1''}$), 2.44 (3H, s, $ArCH_3$), 1.20 (3H, t, J=7.2 Hz, $H_{2''}$). ^{13}C NMR ($CDCl_3$) δ: 143.8 (ArC_4), 137.4 (ArC_1), 129.8 (ArC_{3+5}), 127.1 (ArC_{2+6}), 70.5 ($C_{1'}$), 66.8 ($C_{1''}$), 53.2 (C_1), 33.1 (C_2), 21.5 ($ArCH_3$), 14.9 ($C_{2''}$). MSEI(+) *m/z*: 338 [M (^{81}Br)H]$^+$ (92.8), 336 [M (^{79}Br)H]$^+$ (87.6), 256 [M−Br]$^+$ (15.8), 155 [Ts]$^+$ (100.0). HRMSEI(+) calcd for $C_{12}H_{18}{}^{81}BrNSO_3$ [M (^{81}Br)H]$^+$ 338.02485, found 338.02185, calcd for $C_{12}H_{18}{}^{79}BrNSO_3$ [M (^{79}Br)H]$^+$ 336.02635, found 336.02661.

*4.1.3.26.7. Methyl 2,3-bis(tosylamino)propanoate (**3a**).* Colorless solid obtained in 8% yield (method B); mp 135–136 °C (ethyl acetate/*n*-hexane). IR (KBr) ν_{max}: 3307 (N–H), 3279 (N–H), 1742 (C=O), 1345 (S=O), 1153 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.72–7.68 (4H, m, ArH_{2+6}), 7.33–7.29 (4H, m, ArH_{3+5}), 5.55 (1H, d, J= 7.0 Hz, exchange with D_2O, NH), 5.07 (1H, t, J=6.7 Hz, exchange with, NH), 3.93–3.89 (1H, m, H_2), 3.62 (3H, s, OCH_3), 3.36–3.30 (2H, m, H_3), 2.44 (3H, s, $ArCH_3$), 2.43 (3H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 169.4 (CO), 144.1 ($ArC_{4/4'}$), 143.7 ($ArC_{4/4'}$), 136.5 ($ArC_{1/1'}$), 135.8 ($ArC_{1/1'}$), 129.8 (ArC_{3+5}), 127.2 (ArC_{2+6}), 127.1 (ArC_{2+6}), 55.4 (C_2), 53.3 (OCH_3), 45.3 (C_3), 21.5 ($ArCH_3$). MSESI(+) *m/z*: 427 [MH]$^+$, 449 [MNa]$^+$, 425 [M−H]$^-$.

*4.1.3.26.8. N,N-Dimethyl-2,3-bis(tosylamino)propanamide (**3c**).* Colorless solid obtained in 9% (method A) and 7% (method B) yields; mp 148–150 °C (dichloromethane/*n*-hexane). IR (KBr) ν_{max}: 3259 (N–H), 3140 (N–H), 1640 (C=O), 1323 (S=O), 1158 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.71–7.65 (4H, m, ArH_{2+6}), 7.30–7.27 (4H, m, ArH_{3+5}), 6.18 (1H, d, J=9.6 Hz, exchange with D_2O, NH), 5.86 (1H, t, J=7.6 Hz, exchange with D_2O, NH), 4.37–4.21 (1H, m, H_2), 3.13–3.06 (1H, m, H_3), 2.92 (3H, s, NCH_3), 2.95–2.84 (1H, m, H_3), 2.72 (3H, s, NCH_3), 2.42 (6H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$) δ: 168.9 (CO), 143.9 ($ArC_{4/4'}$), 143.7 ($ArC_{4/4'}$), 136.9 ($ArC_{1/1'}$), 136.6 ($ArC_{1/1'}$), 129.8 (ArC_{3+5}), 129.7 (ArC_{3+5}), 127.3 (ArC_{2+6}), 127.2 (ArC_{2+6}), 52.4 (C_2), 44.7 (C_3), 37.1 (NCH_3), 35.8 (NCH_3), 21.34 ($ArCH_3$). MSEI(+) *m/z*: 440 [MH]$^+$ (44.9), 155 [Ts]$^+$ (8.2). HRMSEI(+) calcd for $C_{19}H_{25}N_3O_5S_2$ [MH]$^+$ 440.13084, found 440.13096.

*4.1.3.26.9. 3,4-Bis(tosylamino)butan-2-one (**3e**).* Colorless solid obtained in 16% yield (method B); mp 140–142 °C (ethyl acetate/*n*-hexane). IR (KBr) ν_{max}: 3269 (N–H), 1720 (C=O), 1329 (S=O), 1161 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.81–7.66 [4H, m, $ArH_{(2+6)+(2'+6')}$], 7.33–7.27 [4H, m, $ArH_{(3+5)+(3'+5')}$], 5.85 (1H, d, J=6.7 Hz, exchange with D_2O, NH), 5.01–5.84 (1H, m, exchange with D_2O, NH), 3.83–3.80 (1H, m, H_2), 3.38–3.32 (1H, m, H_1), 3.20–3.14 (1H, m, H_1), 2.44 (3H, s, $ArCH_3$), 2.43 (3H, s, $ArCH_3$), 2.22 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$) δ: 203.6 (*C*O), 144.3 ($ArC_{4/4'}$), 144.1 ($ArC_{4/4'}$), 136.1 ($ArC_{1/1'}$), 135.9 ($ArC_{1/1'}$), 130.0 ($ArC_{3+5/3'+5'}$), 130.0 ($ArC_{3+5/3'+5'}$), 127.3 ($ArC_{2+6/2'+6'}$), 127.1 ($ArC_{2+6/2'+6'}$), 61.2 (C_2), 44.1 (C_1), 26.7 (CH_3), 21.37 ($ArCH_3$), 21.36 ($ArCH_3$). MSEI(+) *m/z*: 411 [MH]$^+$ (37.9), 367 [M−CH_3CO]$^+$ (89.3), 227 [$TsNHCH_2CH$]$^+$ (100.0), 155 [Ts]$^+$ (28.1). HRMSEI(+) calcd for $C_{18}H_{23}N_2O_5S_2$ [MH]$^+$ 411.10429, found 411.10432.

*4.1.3.26.10. N-[(3-Hydroxy-2-tosylamino)propyl]tosylamine (**3m**).* Oil obtained in 6% yield (method B). IR (film) ν_{max}: 3520 (O–H), 3291 (N–H), 1319 (S=O), 1153 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.74 (2H, d, J=8.0 Hz, $ArH_{2+6/2'+6'}$), 7.67 (2H, d, J=8.4 Hz, $ArH_{2+6/2'+6'}$), 7.31–7.29 [4H, m, $ArH_{(3+5)+(3'+5')}$], 5.43 (1H, d, J=7.6 Hz, exchange with D_2O, NH), 5.23 (1H, t, J=6.4 Hz, exchange with D_2O, NH), 3.64 (1H, m, H_1), 3.52 (1H, m, H_1), 3.28 (1H, m, H_2), 3.06–3.04 (2H, m, H_3), 2.42 (6H, s, $ArCH_3$), 1.67 (1H, br s, exchange with D_2O, OH). ^{13}C NMR ($CDCl_3$) δ: 143.8 ($ArC_{4/4'}$), 136.9 ($ArC_{1/1'}$), 138.3 ($ArC_{1/1'}$), 129.9 ($ArC_{3+5/3'+5'}$), 127.1 ($ArC_{2+6/2'+6'}$), 127.0 ($ArC_{2+6/2'+6'}$), 61.8 (C_1), 53.9 (C_2), 43.9 (C_3), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 399 [MH]$^+$ (100.0), 381 [M−H_2O]$^+$ (20.7). HRMSEI(+) calcd for $C_{17}H_{23}N_2O_5S_2$ [MH]$^+$ 399.10429, found 399.10439.

*4.1.3.26.11. N-[(3-Ethoxy-2-tosylamino)propyl]tosylamine (**3n**).* Oil obtained in 9% yield (method B). IR (film) ν_{max}: 3292 (N–H), 1330 (S=O), 1159 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.73 (2H, d, J=8.0 Hz, $ArH_{2+6/2'+6'}$), 7.69 (2H, d, J=8.0 Hz, $ArH_{2+6/2'+6'}$), 7.30 [4H, d, J=8.4 Hz, $ArH_{(3+5)+(3'+5')}$], 5.14 (1H, d, J=6.8 Hz, exchange with D_2O, N^2H), 5.02 (1H, t, J=6.2 Hz, exchange with D_2O, N^1H), 3.41–3.21 (6H, m, $1H_1$+$2H_3$+$1H_2$+$2H_{1''}$), 3.03–2.96 (1H, m, H_1), 2.44 (6H, s, $ArCH_3$), 1.07 (3H, t, J=7.2 Hz, $H_{2''}$). ^{13}C NMR ($CDCl_3$) δ: 143.7 ($ArC_{4/4'}$), 143.6 ($ArC_{4/4'}$), 136.9 ($ArC_{1/1'}$), 136.5 ($ArC_{1/1'}$), 129.8 [$ArC_{(3+5)+(3'+5')}$], 127.2 ($ArC_{2+6/2'+6'}$), 127.1 ($ArC_{2+6/2'+6'}$), 60.8 (C_3), 66.8 ($C_{1''}$), 53.3 (C_2), 42.7 (C_1), 21.5 ($ArCH_3$), 14.9 ($C_{2''}$). MSEI(−): 426 [M]$^-$ (22.4), 424 [M−H]$^-$ (100.0), 155 [Ts]$^-$ (28.7). HRMSEI(−) calcd for $C_{19}H_{26}N_2O_5S_2$ [M]$^-$ 426.12831, found 426.12773.

4.2. NMR studies

4.2.1. Aziridination reaction of acrylonitrile. A mixture of acrylonitrile (0.8 equiv, 0.06 mmol, 4 μl) and palladium(II) chloride (0.13 equiv, 0.01 mmol, 1.6 mg) in CD_3CN (750 μL) was stirred (1/2 h) at room temperature. First portion of bromamine-T (0.33 equiv, 0.02 mmol, 6.3 mg) was added followed by two further additions (0.02 mmol each). Each addition was performed only after a negative test (starch-iodide paper) for bromamine-T was observed. ^1H NMR spectra were acquired for every 7 min over a period of 10 h.

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