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Catalytic stereoselective alkene aziridination with sulfonimidamides

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Dedicated with respect and admiration to Professor Henri Kagan on the occasion of his 80th birthday

ABSTRACT

Diastereoselective copper-catalyzed alkene aziridination has been investigated using chiral nitrenes generated from sulfonimidamides in the presence of an iodine(III) oxidant. Starting from a stoichiometric amount of the substrates, the corresponding aziridines were isolated with excellent yields of up to 96%. Good levels of asymmetric induction were obtained in the case of electron-poor olefins, with an optimal de of 94% being reached starting from *tert*-butyl acrylate. Matching and mismatching effects were also observed upon the use of chiral copper catalysts for the aziridination of styrene.

1. Introduction

Aziridines, the smallest of saturated nitrogen heterocycles, offer unique opportunities for the preparation of nitrogen-containing compounds.[1] Most applications of aziridines in either natural product synthesis or medicinal chemistry derive from their ability to undergo ring-opening with a wide variety of nucleophiles as a consequence of their strained structure.[2] The latest developments in this field have culminated in the discovery of highly efficient chiral catalysts for the asymmetric ring-opening of *meso* aziridines.[3] Their use is not limited to the production of 1,2-difunctionalized scaffolds and new transformations based on these small-ring heterocycles have recently been uncovered. Thus, they can be engaged in ring-expansion reactions under various conditions to afford five- or six-membered rings,[1d,4] whereas their α-lithiated counterparts can be considered as carbenoid precursors useful, for example, in cyclopropanation.[5] Finally, not only are aziridines versatile synthetic intermediates, they are also found in the structures of various natural products the biological activity of which is generally the consequence of their nucleophilic ring-opening.[6]

The synthetic importance of aziridines has caused a surge of interest over the last two decades in developing efficient protocols for their preparation as reported by several recent reviews devoted to the field.[1,2,7] Classical 'cyclization methods' involve functional group transformations starting from epoxides, aminoalcohols, or azidoalcohols, while 'addition processes' include the addition of carbenes or ylides to imines, the aza-Darzens reaction and catalytic nitrene transfer to olefins.[8] The latter has recently received considerable attention with the emergence of new precursors and catalysts for the generation of highly reactive metallanitrenes. Thus, efficient catalytic olefin aziridinations have been reported starting from *N*-aminoheterocycles,[9] azides,[10] metal-nitrido complexes,[11] haloamines,[12] or *N*-sulfonyloxycarbamates.[13] In parallel, significant improvements have been achieved with the development of nitrene addition to alkenes mediated by hypervalent iodine reagents.[14] Under these conditions, inter- and intramolecular olefin aziridinations can be catalyzed by several transition metals such as copper[15] and rhodium,[16] but also ruthenium, manganese, iron, silver, gold, and rhenium.[17] Worthy of note has been the discovery of practical procedures for the in situ generation of iminoiodanes, which have allowed the formation of nitrenes from various synthetically useful precursors.[18] All these achievements have found applications in the total syntheses of natural products[19] and bioactive compounds[20] thereby highlighting the efficiency of catalytic olefin aziridination mediated by iodine(III) oxidants.

Several chiral ligands for copper[21] and rhodium[22] catalysts have been designed in order to induce enantioselective nitrene addition to alkenes. Very good to excellent enantiomeric excesses of greater than 99% have been reported for the catalytic intermolecular asymmetric aziridination of substituted styrenes, cinnamates, and chalcones. Yields were also generally very high provided that an excess (5 equiv) of substrate was used. Of course, the need to use an over-stoichiometric amount of substrate does not apply to analogous intramolecular processes that, in turn, allow extension of the scope of the reaction to aliphatic olefins.[21j,22a,b] Despite these noteworthy results, we felt that there was still room for improvement providing that the scope of the aforementioned one-pot procedure could be widened.[18] Whereas the in situ generation of iminoiodanes from carbamates and sulfamates had proved successful, we envisaged applying this protocol to the conception of a stereoselective alkene aziridination, which relies on the addition of a chiral metallanitrene formed by the combination of a copper salt with a

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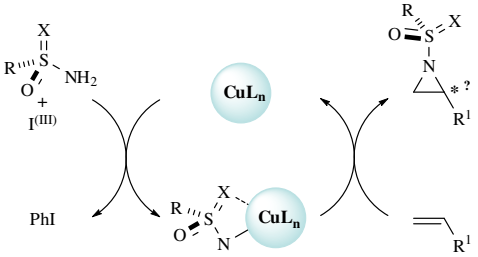
chiral nitrogen source (Scheme 1). Good levels of asymmetric induction were expected from the use of chiral sulfur agents based on theoretical calculations of Andersson and Norrby that have suggested a bidentate coordination of an *N*-(sulfonyl)nitrene to copper.[15g] Since in initial tests, sulfinamides did not survive the oxidizing conditions of the aziridination reaction, we were particularly attracted by the opportunities offered by the uncommon sulfonimidoyl moiety.

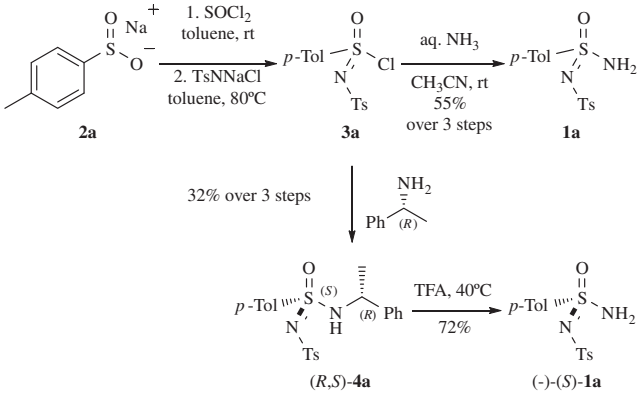


Scheme 1. Principle of the copper-catalyzed alkene aziridination with sulfonimidamides.

Sulfonimidamides were first described by Levchenko nearly 50 years ago but have received little attention until recently.[23–25] Initially used for the purpose of fundamental studies related to the stereochemistry of sulfur compounds,[24d] they then found applications in medicinal chemistry.[24g–i] Whereas recent studies have revisited their synthesis,[24f,25a,e] sulfonimidamides have also proven to be useful in coupling reactions,[25b,c] as organocatalysts,[25d] and in oxidative alkene addition for the formation of heterocycles.[25f] However, more significant contributions were made in the field of catalytic nitrene transfers[26] and the use of sulfonimidamides as nitrene precursors has resulted in the development of highly efficient diastereoselective processes such as catalytic aziridination,[27,28] sulfur imination,[29] and, particularly, rhodium-catalyzed C–H amination.[30] Herein we report a full account of our studies related to the stereoselective copper-catalyzed olefin aziridination with sulfonimidamides.[28a]

2. Results and discussion

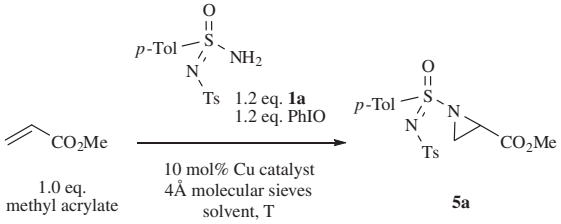
Sulfonimidamides are sulfur(VI) compounds analogous to sulfonamides in which one oxygen atom has been replaced by an imido moiety thereby offering the possibility of introducing various additional functions such as an alkyl group and an electron-withdrawing substituent. Free amido derivatives can be easily obtained by reaction between ammonia and sulfonimidoyl chlorides themselves prepared by either oxidation of sulfinamides with a chlorinating agent or imidation of sulfinyl chlorides with the sodium salt of haloamines.[23,24] Our initial experiments focused on the use of *N*-(alkyl)arenesulfonimidamides,[24b,24c] which did not prove satisfactory. Since the low yields of aziridination were obtained as a consequence of starting material degradation, we decided to turn our attention to sulfonimidamides substituted by a sulfonyl group on the imido function. Thus, we prepared *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide **1a** as described in the literature (Scheme 2).[24f] Starting from commercially available sodium *p*-toluenesulfinate **2a**, successive reactions with thionyl chloride and anhydrous chloramine-T afforded the sulfonimidoyl chloride **3a**. Whereas the addition of ammonia led to racemic **1a**, enantiomerically pure material was accessible via reaction of the racemic chloride **3a** with (*R*)-1-phenylethylamine and fractional recrystallization of the resulting sulfonimidamide **4a**. Cleavage of the crystalline (*R*,*S*)-**4a** with trifluoroacetic acid finally afforded (*S*)-**1a**, the (*R*)-enantiomer being also isolated with a good enantiomeric purity from (*S*)-1-phenylethylamine. The procedure was well adapted



Scheme 2. Synthesis of sulfonimidamide **1a**.

to prepare differently substituted sulfonimidamides (vide infra) from various sulfinyl chlorides[31] and by reaction with several chloramines. Moreover, X-ray crystallography studies allowed us to determine that the (−)-enantiomer corresponds to the (*S*)-configuration of the sulfonimidamide,[28b] an observation which is in agreement with previous literature data.[24f]

Sulfonimidamide **1a** was then tested as the nitrene precursor in the copper-catalyzed aziridination of olefins. Optimization of the reaction conditions was first undertaken using, as the test substrate, methyl acrylate which has previously been shown to be poorly reactive with sulfonamide-derived nitrenes (Scheme 3).[15b]



Scheme 3.

Moreover, the corresponding aziridine **5a** displays significant synthetic interest as a direct precursor of α- and β-amino acids.[15h] The results are summarized in Table 1. In agreement with the seminal paper of Evans et al.,[15b] the copper-catalyzed alkene aziridination proceeded best in polar solvents, acetonitrile being the solvent of choice (entry 3). Both reactivity and selectivity increased by decreasing the reaction temperature to −20 °C (entries 3–5). Optimal conversions were finally observed by concentrating the reaction medium (entry 6 vs 3) and using a copper(I) salt (entries 6

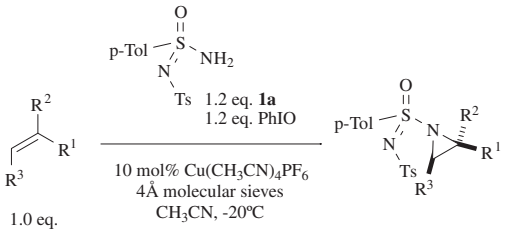
Table 1
Screening of the reaction parameters for the copper-catalyzed aziridination of methyl acrylate

Entry	Catalyst	Solvent	*T* (°C)	Yield[a] (%)	de[b] (%)
1	Cu(MeCN)$_4$PF$_6$	Toluene	−20	—	—
2	Cu(MeCN)$_4$PF$_6$	CH_2Cl_2	−20	17	30
3	Cu(MeCN)$_4$PF$_6$	MeCN	−20	67	50
4	Cu(MeCN)$_4$PF$_6$	MeCN	0	62	46
5	Cu(MeCN)$_4$PF$_6$	MeCN	20	57	40
6	Cu(MeCN)$_4$PF$_6$	MeCN	−20	81[c]	50
7	CuOTf	MeCN	−20	81[c]	45
8	Cu(OTf)$_2$	MeCN	−20	50[c]	43
9	Cu(acac)$_2$	MeCN	−20	22[c]	48

[a] Isolated yield after flash chromatography.
[b] Diastereoisomeric excess (de) was determined by NMR.
[c] The quantity of solvent introduced was reduced by 50%.

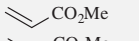
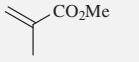
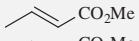
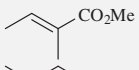
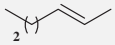
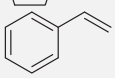
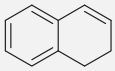
and 7 vs 8 and 9). Methyl acrylate proved to be an efficient nitrene acceptor under these conditions and an optimal yield of 81% was obtained starting from a stoichiometric amount of the olefin.[32,33] The diastereoisomeric excess of 50%, though modest, was encouraging since no stereoselective aziridination of methyl acrylate had been previously reported.

With the optimized experimental conditions in hand, we then decided to screen various alkenes (Scheme 4). The conditions appear particularly appropriate for the aziridination of α,β-unsaturated esters (Table 2). Thus, their application to methyl methacrylate and tiglate afforded nearly quantitative yields of aziridines **6a** and **8a** (96% and 92%, respectively, entries 2 and 4) whereas methyl crotonate proved to be less reactive affording the corresponding aziridine **7a** with a modest yield of 35% (entry 3). As with methyl acrylate, the diastereoselectivities remained moderate ranging from 38% to 50%. In the case of a terminal olefin with low reactivity such as 1-heptene, the good yield observed (60%, entry 5) once again demonstrated the higher efficiency of the nitrene species. This was also clearly indicated by the reaction with internal and cyclic alkenes (entries 6–9). Moreover, the exclusive isolation of *trans*- and *cis*-aziridines **10a** and **11a** from, respectively, *trans*- and *cis*-2-hexene supports a concerted stereospecific addition of the nitrene. However, the asymmetric induction in the case of these non-activated olefins was very low. Finally, the reaction with



Scheme 4.

Table 2
Copper-catalyzed alkene aziridination with sulfonimidamide **1a**

Entry	Substrate	Aziridine	Yield[a] (%)	de[b] (%)
1		**5a**	81	50
2		**6a**	96	41
3		**7a**	35	50
4		**8a**	92	38
5		**9a**	60	10
6		**10a**	40[c]	<10
7		**11a**	57[d]	<10
8		**12a**	62	—
9		**13a**	59	—
10		**14a**	63	20
11		**15a**	63	25

[a] Isolated yield after flash chromatography.
[b] Diastereoisomeric excess (de) was determined by NMR.
[c] *trans*-Aziridine.
[d] *cis*-Aziridine.

styrene and 1,2-dihydronaphthalene led to good conversions (isolated yields of 63%, entries 10 and 11) but low diastereoselectivities in the 20–25% range.[34]

These initial results convinced us of the superior performance of the sulfonimidamides as nitrene precursors. Screening of their substituted analogues was therefore envisaged in order to improve the yields and selectivities. The optimal conditions defined in Table 1 were thus applied to the catalytic aziridination of styrene and methyl acrylate, that is, two different classes of olefins, in the presence of various nitrene precursors. The results are summarized in Table 3.

The introduction of a *p*-nitro substituent onto one of the aromatic rings generally led to better diastereoselectivities in the case of methyl acrylate, however, this sometimes led to a decrease in the yield (entries 2, 4 and 6 vs entry 1). The best compromise was thus afforded by sulfonimidamide **1b** which led to aziridine-2-carboxylate **5b** in 70% yield and 75% de. Nevertheless, the nitro group appeared to be deleterious in the case of styrene since the corresponding aziridines **14b**, **14d**, and **14f** were isolated in 40–60% yields and with a very low diastereoselectivity. The use of the di-*p*-nitro sulfonimidamide **1e** induced the stereoselective aziridination of both methyl acrylate and styrene with des in the 60–70% range (entry 5). This good result, however, was counterbalanced by the observed modest yields of, respectively, 43% **5e** and 32% **14e** due to the low solubility of **1e**. In contrast, the presence of a *p*-methoxy, a *p*-chloro or a hydrogen substituent proved to be favorable to the reactivity in the case of styrene, the corresponding aziridines **14c**, **14g**, and **14h** being isolated in 86%, 83%, and 82% yield, respectively (entries 3, 7, and 8). This positive influence was less pronounced with methyl acrylate since products **5c**, **5g,** and **5h** were obtained in 50–66% yields and 35–65% des. Based on the coordination-assisted approach previously reported by Chang,[15p,q] we also prepared the pyridinylsulfonimidamide **1i** that, however, gave low yields of the expected derivatives **5i** and **14i** (entry 9). Finally, sulfonimidamides **1j** and **1k** allowed us to determine the influence of each aromatic ring with respect to the reactivity of these nitrene precursors. Replacement of the *p*-tolyl group on the imido function by a methyl demonstrated that the aromatic ring seems to play an important role because compounds **5k** and **14k** were isolated in moderate yields and selectivities (entry 11). By contrast, the other phenyl ring does not prove to be as important, with the ethylsulfonimidamide **1j** affording the corresponding products **5j** with a very good diastereoselectivity of 85% and **14j** in 75% yield (entry 10). Based on this screening, we ultimately decided to continue our studies using sulfonimidamide **1b**. Since the latter gives the best overall results with methyl acrylate, it paves the way for the development of a stereoselective synthesis of amino acids.[35] Moreover, it can be prepared on a multi-gram scale in either its racemic form or enantiomerically pure form.

The reactivity of several olefins was thus tested under slightly modified conditions, that is, using copper(I) triflate as the catalyst in the presence of 1.5 equiv of sulfonimidamide **1b** and iodosylbenzene (Scheme 5). As previously observed with sulfonimidamide **1a**, electron-poor alkenes such as acrylates and methyl methacrylate were highly reactive affording the corresponding aziridines **5b**, **16b**, and **6b** with yields ranging from 80% to 95% (Table 4, entries 1–3).[36] However, as an exception to this trend, acrylonitrile proved to react moderately (entry 4). The high efficiency of **1b** was also clearly demonstrated by the nearly quantitative yields obtained in the cases of 1-heptene and cyclic olefins (entries 5–7). Moreover, the use of sulfonimidamide **1b** resulted in very good levels of asymmetric induction, with *t*-butyl acrylate-derived aziridine **16b** being isolated with an excellent de of 94%.

The combination of chiral copper complexes with sulfonimidamides was also investigated in order to induce matching and mismatching effects (Scheme 6). An initial screening of the ligands led

Table 3
Screening of sulfonimidamides **1** in the aziridination of methyl acrylate and styrene

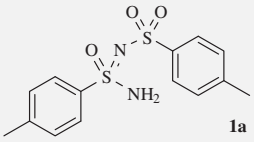
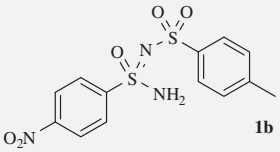
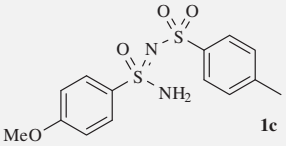
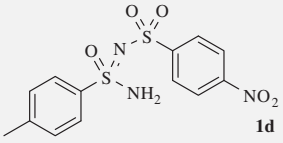
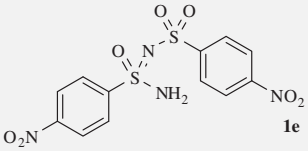
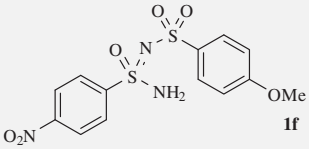
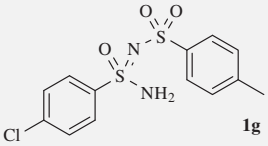
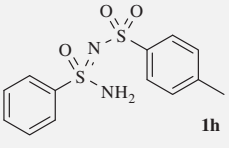
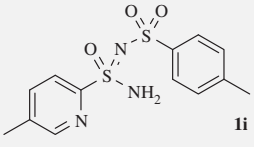
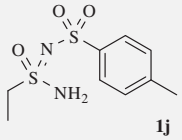
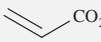
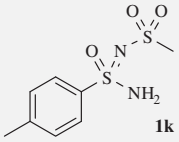
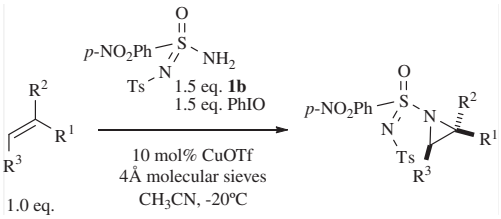
Entry	Sulfonimidamide	Yield[a] (%) de[b] (%)	 Yield[a] (%) de[b] (%)
1	 **1a**	**5a** 81 *50*	**14a** 63 *20*
2	 **1b**	**5b** 70 *75*	**14b** 40 *10*
3	 **1c**	**5c** 66 *35*	**14c** 86 *10*
4	 **1d**	**5d** 80 *55*	**14d** 60 *10*
5	 **1e**	**5e** 43 *70*	**14e** 32 *60*
6	 **1f**	**5f**[c] 45 *73*	**14f**[c] 50 *15*
7	 **1g**	**5g** 50 *65*	**14g** 83 *10*
8	 **1h**	**5h** 60 *55*	**14h** 82 *7*
9	 **1i**	**5i** <5 —	**14i** 21 —
10	 **1j**	**5j** 55 *85*	**14j** 75 *10*

Table 3 (*continued*)

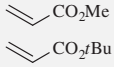
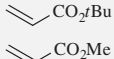
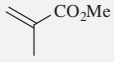
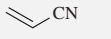
Entry	Sulfonimidamide	 Yield[a] (%) de[b] (%)	 Yield[a] (%) de[b] (%)
11	 **1k**	**5k** 54 *35*	**14k** 60 *5*

[a] Isolated yield after flash chromatography.
[b] Diastereoisomeric excess (de) was determined by NMR.
[c] Reactions were conducted in $MeNO_2$ since the sulfonimidamide **1f** is only very slightly soluble in MeCN.

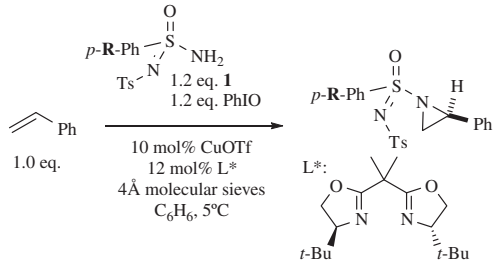


Scheme 5.

Table 4
Copper-catalyzed alkene aziridination with sulfonimidamide **1b**

Entry	Substrate	Aziridine	Yield[a] (%)	de[b] (%)
1		**5b**	88	80
2		**16b**	80 (65)[c]	94 (94)[c]
3		**6b**	95	36
4		**17b**	48	30
5		**9b**	92	<10
6		**12b**	93	—
7		**13b**	95	—

[a] Isolated yield after flash chromatography.
[b] Diastereoisomeric excess (de) was determined by NMR.
[c] Reaction performed on a 1 mmol scale.



Scheme 6.

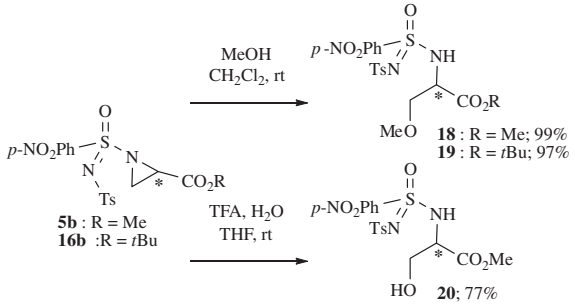
Table 5
Aziridination of styrene with a chiral copper catalyst

Entry	Sulfonimidamide	Aziridine	Yield[a] (%)	de[b] (%)
1	(*S*)-**1a**; R = Me	**14a**	91	61
2	(*R*)-**1a**; R = Me	**14a**	68	10
3	(*S*)-**1b**; R = NO_2	**14b**	39	54
4	(*S*)-**1g**; R = Cl	**14g**	70	65

[a] Isolated yield after flash chromatography.
[b] Diastereoisomeric excess (de) was determined by NMR.

us to find that the best selectivities could be obtained with C_2-symmetric bis(oxazolines)[37] and, particularly, *tert*-butyl-bis(oxazoline) which has been found optimal for various catalytic processes.[38] The application of classical conditions for the asymmetric copper-catalyzed aziridination[21] then allowed us to isolate the styrene-derived aziridine **14a** in 91% yield and 61% de by combining the (*S*,*S*)-*tert*-butylbis(oxazoline)-copper complex with sulfonimidamide (*S*)-**1a** (Table 5, entry 1). A mismatched pair for double induction was formed with (*R*)-**1a** thereby leading to a lower yield and a very weak asymmetric induction (entry 2). The matched pairing was confirmed with (*S*)-**1b** but the yield was lower due to the poor solubility of the *p*-nitrosulfonimidamide (entry 3). Finally, a slightly better de was observed with *p*-chlorosulfonimidamide (*S*)-**1g**, with the corresponding product **14g** being obtained with a yield of 70% and a de of 65% (entry 4). All our attempts to extend the double stereodifferentiation strategy to other alkenes were unsuccessful, with no reaction taking place starting with acrylates under these conditions.

Finally, *N*-(sulfinimidoyl)aziridines have been found to react with nucleophiles under mild conditions (Scheme 7). Reaction of aziridines **5b** and **16b** with methanol at room temperature quantitatively afforded the C-3 ring-opened products **18** and **19**,[39] whereas the direct introduction of a hydroxy group at the same position efficiently occurred using a mixture of trifluoroacetic acid, THF, and water leading to compound **20** in 77% yield. Since the sulfonimidoyl moiety can be cleaved under reductive conditions,[30] access to optically active β-substituted α-amino acids can be envisaged by application of this catalytic alkene aziridination.



Scheme 7. Nucleophilic ring-opening of acrylate-derived aziridines.

3. Conclusion

The reaction between the iodine(III) oxidant iodosylbenzene and a sulfonimidamide in the presence of a copper catalyst leads to the formation of a highly reactive chiral metallanitrene. The latter adds to various types of olefins used in stoichiometric amounts to afford the corresponding aziridines in very good yields of up to 96%. The catalytic aziridination can also take place with good diastereoselectivities, particularly in the case of α,β-unsaturated esters. Thus, the addition of the nitrene derived from *p*-nitrosulfonimidamide **1b** to *tert*-butyl acrylate takes place with an optimized de of 94%. This methodology can therefore be applied to the synthesis of substituted amino acids, since the resulting aziridines also undergo nucleophilic ring-opening under smooth conditions. Matching and mismatching effects have also been induced by combining the sulfonimidamide with a chiral copper catalyst thereby allowing us to improve the stereoselectivity of the aziridination, though only in the case of styrene. A particularly noteworthy feature of this transformation is that the addition of the electron-deficient nitrene species best occurs in the case of electron-poor olefins. Further studies are therefore currently underway in order to elucidate the mechanism as well as to understand the origin of the high reactivity of sulfonimidamide-derived nitrenes.

4. Experimental

Melting points were measured in capillary tubes on a Büchi B-540 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on Bruker spectrometers: Avance 300 MHz or 500 MHz. Carbon NMR (^{13}C) spectra were recorded at 125 or 75 MHz, using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence. NMR experiments were carried out in deutero-chloroform ($CDCl_3$), -methanol (CD_3OD), and -dimethylsulfoxide (DMSO). Chemical shifts (δ) are reported in parts per million (ppm) with reference to $CDCl_3$ (^{1}H: 7.26; ^{13}C: 77.00), CD_3OD (^{1}H: 3.31; ^{13}C: 49.00), and DMSO (^{1}H: 2.50; ^{13}C: 39.50). The following abbreviations are used for the proton spectra multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad. Coupling constants (*J*) are reported in hertz (Hz). Values in italics refer to the minor diastereomer, where applicable. Mass spectra were obtained either with a LCT (Micromass) instrument using electrospray ionization (ES), or from a Time of Flight analyzer (ESI-MS) for the high resolution mass spectra (HRMS). Elemental analyses were performed on a Perkin Elmer CHN 2400 analyzer with a detection by catharometry. Thin-layer chromatography was performed on Silica Gel 60 F254 on aluminum plates (Merck) and visualized under a UVP Mineralight UVLS-28 lamp (254 nm) and with ninhydrin and phosphomolybdic acid in ethanol. Flash chromatography was conducted on Merck Silica Gel 60 (40–63 μm) at medium pressure (300 mbar) or on CombiFlash (Serlabo Technologies). All reagents were obtained from commercial suppliers unless otherwise stated. Where necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under nitrogen. All solvents were freshly distilled when required.

4.1. *N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidamide 1a

To an ice cooled suspension of anhydrous sodium *p*-toluenesulfinate **2a** (3.75 g, 21 mmol) in toluene (40 mL) under argon was slowly added thionyl chloride (7.5 mL). The reaction mixture was stirred at room temperature for 14 h before being evaporated under vacuum. The resulting yellow oil was dissolved in toluene (60 ml) and anhydrous chloramine-T (4.78 g, 21 mmol) (*Caution!* The trihydrate was dried in a drying pistol at 80 °C for 8 h. Explosion may occur at higher temperatures) was added at room temperature. The reaction mixture was stirred at 80 °C for 1.5 h. The sodium chloride precipitate was removed by filtration while the reaction mixture was still hot and the filtrate was evaporated. The crude *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl chloride **3a** was dissolved in acetonitrile (80 ml) and aqueous ammonia (80 ml) was added at 0 °C. After 30 min, the ice bath was removed and the reaction mixture was stirred overnight at room temperature. The organic layer was separated and washed successively with 10% HCl and water, dried with $MgSO_4$, and concentrated

under vacuum to afford a pasty yellow solid which was recrystallized from ethyl acetate. A white crystalline solid (2.4 g) was obtained while a second crop was obtained from the mother liquor (1.33 g) yielding a total of 3.73 g (11.6 mmol, 55%) of pure compound **1a**. Mp 152.0–152.5 °C (lit. 162–163 °C);[23a] IR (KBr, cm^{-1}) 3212, 1284, 1149, 1107, 1087, 810, 748, 660; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.42 (s, 3H), 5.60 (s, 2H), 7.25 (d, J = 7.5 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.79 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.6, 126.7, 127.2, 129.3, 129.8, 137.1, 140.0, 143.1, 145.0; mass spectrum (ES) m/z 347 $(M+Na)^+$; Anal. Calcd for $C_{14}H_{16}N_2O_3S_2$: C, 51.83; H, 4.97; N, 8.63; S, 19.77. Found: C, 51.58; H, 4.92; N, 8.55; S, 20.04.

4.2. (*S*)- and (*R*)-*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidamide (*S*)- and (*R*)-1a

The previously obtained crude *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl chloride **3a** was dissolved in dichloromethane (80 ml) and a mixture of (*R*)-(−)-α-methylbenzylamine (3.24 mL, 25.2 mmol) and sodium hydrogenocarbonate (2.1 g, 25.2 mmol) in water (50 ml) was added at 0 °C. After 30 min, the ice bath was removed and the reaction mixture was stirred overnight at room temperature. The organic layer was separated and washed successively with 10% HCl and water, dried with $MgSO_4$, and concentrated under vacuum to afford a pasty yellow solid. The latter was dissolved in ethyl ether (40 ml) and after cooling, filtration afforded 2.1 g of a white solid (de >95% as estimated by ^1H NMR). A second crop was obtained from the mother liquor (0.8 g) yielding a total of 2.9 g (6.77 mmol, 32%) of pure compound (*R*,*S*)-**4a**. Mp 156–156.5 °C; $[\alpha]_D^{20} = +118.8$ (c 0.44, $CHCl_3$); IR (cm^{-1}) 3232, 1594, 1301, 1152, 1106, 1070, 1017, 813, 755, 700, 657; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, J = 7.0 Hz, 3H), 2.41 (s, 3H), 2.43 (s, 3H), 4.52 (q, J = 7.0 Hz, 1H), 6.18 (d, J = 7.0 Hz, 1H), 7.26 (m, 9H), 7.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.6, 23.0, 54.0, 126.4, 126.9, 127.8, 127.9, 128.7, 129.3, 129.7, 136.2, 140.5, 141.8, 142.9, 144.7; mass spectrum (ES) m/z 451 $(M+Na)^+$; Anal. Calcd for $C_{22}H_{24}N_2O_3S_2$: C, 61.66; H, 5.64; N, 6.54; S, 14.96. Found: C, 61.26; H, 5.53; N, 6.57; S, 14.93.

The pure diastereoisomer (2.9 g, 6.77 mmol) was dissolved in trifluoroacetic acid (6 mL). After stirring for 40 h at 35 °C, the reaction mixture was evaporated under vacuum, leaving a crude green solid. The latter was purified by flash chromatography (heptane/ethyl acetate 1:1) and then crystallized from ethyl acetate to afford (−)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide (*S*)-**2a** (1.6 g, 72%). Mp 152.0–152.5 °C; $[\alpha]_D^{20} = -110$ (c 0.47, acetone); ee >99% (HPLC, Chiracel AD, 4.6 × 250, 10 μ).

Following the same procedure using (*S*)-(−)-α-methylbenzylamine, (*R*)-**1a** was isolated in 21% yield as a white solid. $[\alpha]_D^{20} = +110$ (c 0.47, acetone); ee >99% (HPLC, Chiracel AD, 4.6 × 250, 10 μ).

4.3. *N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidamide 1b

A well-stirred mixture of *p*-nitrothiophenol (10 g, 64.4 mmol) and acetic acid (3.7 mL, 64.4 mmol) was cooled to −40 °C. Sulfuryl chloride (10.9 mL, 135.2 mmol) was added dropwise (gas evolution was observed). Stirring was continued for 30 min at −40 °C, and the mixture was then allowed to return to room temperature over a period of 2 h. The mixture was then stirred at room temperature for 2 h, and then overnight at 30 °C (gas evolution ceased). The reaction mixture was then concentrated under vacuum to remove acetyl chloride, affording a yellow solid. This solid was dissolved in toluene (200 mL) and anhydrous chloramine-T (*Caution!* The trihydrate was dried in a drying pistol at 80 °C for 8 h. Explosion may occur at higher temperatures) (14.8 g, 65 mmol) was added at room temperature. The reaction mixture was stirred at 80 °C for 1.5 h. The sodium chloride precipitate was filtered while the reaction mixture was still hot and the filtrate was evaporated. The crude *N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl chloride was dissolved in acetonitrile (80 ml) and aqueous ammonia (80 ml) was added at 0 °C. After 30 min, the ice bath was removed and the reaction mixture was stirred overnight at room temperature. The organic layer was separated and washed successively with 10% HCl and water, dried with $MgSO_4$, and concentrated under vacuum to afford a yellow solid which was recrystallized from ethyl acetate. Pure compound **1b** was obtained as a white solid (4.6 g, 13.5 mmol, 21%). Mp 210–211 °C; IR (neat, cm^{-1}) 3306, 3207, 1598, 1522, 1351, 1272, 1142, 1108, 1098; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.30 (d, J = 7.5 Hz, 2H), 7.50 (br s, 2H), 7.68 (d, J = 7.9 Hz, 2H), 8.18 (d, J = 7.5 Hz, 2H), 8.41 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 125.0, 127.4, 129.4, 130.0, 142.0, 143.4, 148.8, 151.2; mass spectrum (ES) m/z 378 $(M+Na)^+$; HRMS m/z $(M+Na)^+$ calcd for $C_{13}H_{13}N_3NaO_5S_2$ 378.0194, found 378.0173.

4.4. (*S*)-*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidamide (*S*)-1b

The crude *N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl chloride was dissolved in dichloromethane (150 ml) and a mixture of (*R*)-(−)-α-methylbenzylamine (9.86 mL, 76.2 mmol) and sodium hydrogenocarbonate (6.4 g, 76.2 mmol) in water (110 ml) was added at 0 °C. After 30 min, the ice bath was removed and the reaction mixture was stirred overnight at room temperature. The organic layer was separated and washed successively with 10% HCl and water, dried with $MgSO_4$, and concentrated under vacuum to afford a pasty yellow solid. The latter was dissolved in a mixture of ethyl acetate (100 mL) and ethyl ether (200 mL). After refrigerating (in a few cases where no precipitate was formed, the two diastereoisomers were separated by flash chromatography on silica gel), filtration afforded 3.2 g of a white solid (de >90 % as estimated by ^1H NMR). A second crop was obtained from the mother liquor (2.1 g) yielding a total of 5.3 g (11.5 mmol, 18%) of pure compound. mp 148–149 °C; IR (neat, cm^{-1}) 3306, 1607, 1529, 1349, 1319, 1258, 1152, 1058, 1010, 950; ^1H NMR (300 MHz, $CDCl_3$) δ 1.62 (d, J = 6.9 Hz, 3H), 2.44 (s, 3H), 4.60 (q, J = 6.9 Hz, 1H), 7.01 (m, 5H), 7.14 (d, J = 6.7 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.94 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 23.5, 54.4, 123.5, 126.6, 126.8, 127.9, 128.4, 128.8, 129.4, 139.9, 140.1, 143.5, 144.9, 149.7; mass spectrum (ES) m/z 482 $(M+Na)^+$; HRMS m/z ((M+Na)+) calcd for $C_{21}H_{21}N_3NaO_5S_2$ 482.0820, found 482.0787.

The pure diastereoisomer (5.3 g, 11.5 mmol) was dissolved in trifluoroacetic acid (11 mL). After stirring for 40 h at 35 °C, the reaction mixture was evaporated under vacuum, leaving a crude green solid. The latter was purified by flash chromatography (heptane/ethyl acetate 1:1) and then crystallized from ethyl acetate to afford (−)-*N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidamide (*S*)-**1b** (3.0 g, 71%). $[\alpha]_D^{20} = -140.7$ (c 0.54, acetone); ee >99% (HPLC, Chiracel OD, 4.6 × 250, 10 μ, hexane + 0.1%HCOOH/EtOH + 0.1%HCOOH: 90/10, 1 mL/min).

4.5. (*S*)-*N*-(*p*-Toluenesulfonyl)-*p*-chlorobenzenesulfonimidamide (*S*)-1g

Prepared from *p*-chlorothiophenol according to the procedure described for the synthesis of (*S*)-**1b**, the corresponding sulfonimidamide (*S*)-**1g** was obtained as a white solid in 98% ee (HPLC,

Chiracel OD, 4.6 × 250, 10 μ, hexane + 0.1%HCOOH/EtOH + 0.1%HCOOH: 90/10, 1 mL/min). Mp 196–197 °C; $[\alpha]_D^{20} = -132.8$ (*c* 1.00, acetone); IR (KBr, cm^{-1}) 3173, 1573, 1394, 1248, 1051, 808, 752, 696, 655; ^1H NMR (300 MHz, CD_3COCD_3) δ 2.40 (s, 3H), 7.24–7.31 (m, 4H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 127.3, 129.7, 129.9, 130.0, 140.0, 142.0, 142.3, 143.2; mass spectrum (ES) *m/z* 344 (M+); HRMS *m/z* $(M+Na)^+$ calcd for $C_{13}H_{13}ClN_2NaO_3S_2$ 366.9954, found 366.9940.

4.6. Typical aziridination procedure with $Cu(CH_3CN)_4PF_6$

In an oven-dried tube were introduced activated 4 Å molecular sieves (50 mg), $Cu(CH_3CN)_4PF_6$ (8 mg, 0.02 mmol), the sulfonimidamide (0.24 mmol), and PhI=O (54 mg, 0.24 mmol). The tube was cooled to −30 °C and, under argon, acetonitrile (0.7 mL) followed by the olefin (0.2 mmol) were added. The mixture was placed in a freezer (−25 °C) for 48 h. After dilution with dichloromethane (5 mL), the molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording the aziridines as a mixture of diastereomers.

4.7. Typical aziridination procedure with CuOTf

In an oven-dried tube were introduced activated 4 Å molecular sieves (50 mg), the sulfonimidamide (0.24 mmol), and PhI=O (54 mg, 0.24 mmol). The tube was purged with argon and placed in a Sigma–Aldrich AtmosBag which was filled with argon. Under argon, CuOTf (10 mg, 0.02 mmol) was added, the tube was tightly closed and removed from the AtmosBag. The tube was cooled to −30 °C and, under argon, acetonitrile (0.7 mL) followed by the olefin (0.2 mmol) were added. The mixture was placed in a freezer (−25 °C) for 48 h. After dilution with dichloromethane (5 mL), the molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording the aziridines as a mixture of diastereomers.

4.8. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-2-methoxycarbonylaziridine 5a

Prepared according to the general procedure with $Cu(CH_3CN)_4PF_6$ from methyl acrylate, the corresponding aziridine **5a** was obtained (heptane/ethyl acetate 7/3) as a pasty white solid in 81% yield and 50% de. R_f (silica, EtOAc/heptane: 1/1): 0.40; IR (neat, cm^{-1}) 2938, 2878, 1747, 1595, 1439, 1322, 1157, 1106, 1089, 909, 814, 758, 704, 660; ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.43 (s, 3H), *2.52* (*d, J = 4.3 Hz, 1H*), 2.67 (d, *J* = 4.3 Hz, 1H), *2.85* (*d, J = 7.3 Hz, 1H*), 3.02 (d, *J* = 7.3 Hz, 1H), 3.46 (dd, *J* = 7.6 and 4.3 Hz, 1H), *3.57* (*dd, J = 7.6 and 4.3 Hz, 1H*), 3.70 (s, 3H), *3.74* (*s, 3H*), 7.20 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.7, *32.4*, 34.1, 36.5, *37.9*, *52.9*, 53.0, 126.6, 128.1, *128.2*, 129.2, 130.0, *133.3*, 133.4, 140.1, *140.2*, *142.9*, 143.0, 146.2, 166.4; Mass spectrum (ES) *m/z* 409 $(M+H)^+$, 431 $(M+Na)^+$; Anal. Calcd for $C_{18}H_{20}N_2O_5S_2$: C, 52.92; H, 4.93; N, 6.86; S, 15.70. Found: C, 52.88; H, 5.06; N, 6.68; S, 15.55.

4.9. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-2-methoxycarbonyl-2-methylaziridine 6a

Prepared according to the general procedure with $Cu(CH_3CN)_4PF_6$ from methyl methacrylate, the corresponding aziridine **6a** was obtained (heptane/ethyl acetate 7/3) as a pasty white solid in 96% yield and 41% de. R_f (silica, EtOAc/heptane: 1/1): 0.50; IR (neat, cm^{-1}) 2939, 2868, 1749, 1595, 1438, 1325, 1157, 1100, 1089, 900, 811, 758, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 1.60 (s, 3H), *1.72* (*s, 3H*), 2.37 (s, 3H), 2.43 (s, 3H), *2.68* (*s, 1H*), *2.75* (*s, 1H*), 2.93 (s, 1H), 3.03 (s, 1H), 3.66 (s, 3H), *3.72* (*s, 3H*), 7.27 (m, 4H), 7.81 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 21.4, 21.6, 37.6, *39.2*, *48.2*, 48.9, 53.0, *53.1*, 126.6, 127.7, *128.1*, 128.9, *129.0*, 129.7, *129.8*, 135.5, *135.7*, 140.3, *142.5*, 142.6, *145.4*, 145.5, *167.6*, 167.7; Mass spectrum (ES) 423 $(M+H)^+$, 445 $(M+Na)^+$; Anal. Calcd for $C_{19}H_{22}N_2O_5S_2$: C, 54.01; H, 5.25; N, 6.63; S, 15.18. Found: C, 54.25; H, 5.34; N, 6.46; S, 14.99.

4.10. *trans*-*N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-2-methoxycarbonyl-3-methylaziridine 7a

Prepared according to the general procedure with $Cu(CH_3CN)_4PF_6$ from *trans*-methyl crotonate, the corresponding aziridine **7a** was obtained (heptane/ethyl acetate 75/25) as a pasty white solid in 35% yield and 50% de. R_f (silica, EtOAc/heptane: 1/1): 0.55; IR (neat, cm^{-1}) 3031, 2955, 2925, 1748, 1595, 1442, 1404, 1320, 1244, 1156, 1106, 1089, 1063, 1016, 971, 908, 877, 814, 736, 705, 678, 657; ^1H NMR (300 MHz, $CDCl_3$) δ *1.49* (*d, J = 6.4 Hz, 3H*), 1.63 (d, *J* = 6.4 Hz, 3H), *2.38* (*s, 3H*), 2.39 (s, 3H), 2.43 (s, 3H), *2.45* (*s, 3H*), *3.14* (*m, 1H*), 3.26 (m, 1H), *3.30* (*d, J = 4.6 Hz, 1H*), 3.64 (s, 3H), 3.68 (d, *J* = 4.6 Hz, 1H), *3.76* (*s, 3H*), 7.23 (m, 4H), 7.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *12.2*, 13.0, 21.4, 21.6, 42.8, *44.5*, *46.1*, 46.4, 52.5, *52.8*, 126.6, *127.7*, 128.0, *129.0*, 129.1, *129.7*, 129.8, 135.1, 140.3, 142.9, 145.4, 166.6; Mass spectrum (ES) *m/z* 445 $(M+Na)^+$; Anal. Calcd for $C_{19}H_{22}N_2O_5S_2$: C, 54.01; H, 5.25; N, 6.63; S, 15.18. Found: C, 54.18; H, 5.39; N, 6.49; S, 15.03.

4.11. *trans*-*N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-2,3-dimethyl-2-methoxycarbonylaziridine 8a

Prepared according to the general procedure with $Cu(CH_3CN)_4PF_6$ from *trans*-methyl tiglate, the corresponding aziridine **8a** was obtained (heptane/ethyl acetate 80/20) as a pasty white solid in 92% yield and 38% de. R_f (silica, EtOAc/heptane: 1/1): 0.60; IR (neat, cm^{-1}) 3023, 2955, 2910, 1748, 1595, 1442, 1404, 1320, 1244, 1156, 1106, 1089, 1063, 1016, 971 , 908, 877, 814, 736, 705, 678, 657; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, *J* = 5.8 Hz, 3H), *1.39* (*d, J = 5.8 Hz, 3H*), *1.40* (*s, 3H*), 1.48 (s, 3H), 2.37 (s, 3H), 2.44 (s, 3H), 3.*62* (*s, 3H*), 3.63 (s, 3H), 3.65 (q, *J* = 5.8 Hz, 1H), *3.90* (*q, J = 5.8 Hz, 1H*), 7.21 (m, 4H), 7.81 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.3, 15.4, *15.6*, 21.5, 21.7, 44.5, *45.8*, 52.9, *54.2*, 54.5, *126.7*, 126.9, *127.8*, 128.0, 128.9, *129.0*, 129.1, *129.4*, 129.7, 136.4, 140.4, 142.5, 145.1, *167.3*, 167.4; Mass spectrum (ES) *m/z* 459 $(M+Na)^+$; Anal. Calcd for $C_{20}H_{24}N_2O_5S_2$: C, 55.03; H, 5.54; N, 6.42; S, 14.69. Found: C, 55.36; H, 5.61; N, 6.33; S, 14.73.

4.12. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-2-pentylaziridine 9a

Prepared according to the general procedure with $Cu(CH_3CN)_4PF_6$ from heptene, the corresponding aziridine **9a** was obtained (heptane/ethyl acetate 70/30) as a pasty white solid in 60% yield and 10% de. R_f (silica, EtOAc/heptane: 1/1): 0.50; IR (neat, cm^{-1}) 2980, 2927, 2859, 1596, 1322, 1250, 1157, 1106, 1090, 1072, 975, 813, 757, 708, 664; ^1H NMR (300 MHz, $CDCl_3$) δ 0.8 (m, 3H), 1.00–1.5 (m, 8H), *2.09* (*d, J = 5.8 Hz, 1H*), 2.25 (d, *J* = 5.8 Hz, 1H), 2.36 (s, 3H), 2.43 (s, 3H), *2.74* (*d, J = 7.5 Hz, 1H*), *2.79* (*m, 1H*), 2.89 (d, *J* = 7.5 Hz, 1H), 2.94 (m, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.81 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 21.5, 21.7, 22.4, 26.1, 30.9, 31.2, 34.3, 43.0, 126.7, 128.1, 129.1, 129.8, 140.8, 142.0, *142.1*, 142.6, *143.1*, *144.5*, 145.4; Mass spectrum (ES)

m/z 443 $(M+Na)^+$; Anal. Calcd for $C_{21}H_{28}N_2O_3S_2$: C, 59.97; H, 6.71; N, 6.66; S, 15.25. Found: C, 60.01; H, 6.54; N, 6.54; S, 15.01.

4.13. *trans*-*N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-methyl-2-propylaziridine 10a

Prepared according to the general procedure with $Cu(CH_3CN)_4$-PF_6 from *trans*-hex-2-ene, the corresponding aziridine **10a** was obtained (heptane/ethyl acetate 80/20) as a pasty white solid in 40% yield. R_f (silica, EtOAc/heptane: 1/1): 0.50; IR (neat, cm^{-1}) 2953, 2902, 1591, 1354, 1317, 1253, 1123, 1088, 1070, 953, 830, 755, 712, 698; ^1H NMR (300 MHz, $CDCl_3$) δ *0.75* (*t, J = 7.4 Hz, 3H*), 0.85 (t, *J* = 7.4 Hz, 3H), 1.39 (d, *J* = 5.6 Hz, 3H), *1.43* (*d, J = 5.7 Hz, 3H*), 1.10–1.65 (m, 4H), 2.36 (s, 3H), 2.43 (s, 3H), 2.70–2.95 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, *13.6*, 14.2, *14.3*, 20.3, *20.4*, 21.6, 21.7, 31.5, *31.9*, 47.1, *47.5*, *49.6*, 51.4, 126.7, *126.8*, 127.6, 128.1, 129.0, *129.7*, 136.9, *137.1*, *140.7*, 140.9, 142.3, 144.8; Mass spectrum (ES) *m/z* 429 $(M+Na)^+$; Anal. Calcd for $C_{20}H_{26}N_2O_3S_2$: C, 59.08; H, 6.45; N, 6.89; S, 15.77. Found: C, 59.21; H, 6.67; N, 6.73; S, 15.59.

4.14. *cis*-*N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-methyl-2-propylaziridine 11a

Prepared according to the general procedure with $Cu(CH_3CN)_4$-PF_6 from *cis*-hex-2-ene, the corresponding aziridine **11a** was obtained (heptane/ethyl acetate 80/20) as a pasty white solid in 57% yield. R_f (silica, EtOAc/heptane: 1/1): 0.55; IR (neat, cm^{-1}) 2955, 2902, 1592, 1356, 1317, 1249, 1123, 1088, 1071, 954, 830, 757, 712, 698; ^1H NMR (300 MHz, $CDCl_3$) δ *0.79* (*t, J = 7.4 Hz, 3H*), 0.87 (t, *J* = 7.4 Hz, 3H), 1.16 (d, *J* = 5.8 Hz, 3H), *1.26* (*d, J = 5.9 Hz, 3H*), 1.10–1.55 (m, 4H), 2.36 (s, 3H), 2.43 (s, 3H), 2.85 (dt, *J* = 7.5 Hz and *J* = 5.8 Hz, 1H), *3.00* (*dt, J = 7.5 Hz and J = 5.8 Hz, 1H*), 3.01 (dq, *J* = 5.8 Hz and *J* = 7.5 Hz, 1H), *3.20* (*dq, J = 5.8 Hz and J = 7.5Hz, 1H*), 7.19 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.6, *13.6*, 13.8, 20.1, *20.2*, 21.6, 21.7 28.1, *41.2*, 43.2, 46.9, *47.4*, 126.7, 128.1, 129.1, 129.7, 135.0, 140.7, 142.5, 145.1; Mass spectrum (ES) *m/z* 429 $(M+Na)^+$; Anal. Calcd for $C_{20}H_{26}N_2O_3S_2$: C, 59.08; H, 6.45; N, 6.89; S, 15.77. Found: C, 59.13; H, 6.54; N, 6.78; S, 15.91.

4.15. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-7-azabicyclo[4.1.0]heptane 12a

Prepared according to the general procedure with $Cu(CH_3CN)_4$-PF_6 from cyclohexene, the corresponding aziridine **12a** was obtained (heptane/ethyl acetate 80/20) as a pasty white solid in 62% yield. R_f (silica, EtOAc/heptane: 1/1): 0.60; IR (neat, cm^{-1}) 2939, 2865, 1596, 1494, 1438, 1401, 1318, 1253, 1228, 1155, 1108, 1090, 1016, 962, 920, 847, 814, 794, 756, 718, 666; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (m, 2H), 1.37 (m, 2H), 1.70 (m, 2H), 1.84 (m, 2H), 2.37 (s, 3H), 2.42 (s, 3H), 3.06 (m, 1H), 3.26 (m, 1H), 7.18 (d, *J* = 9.5 Hz, 2H), 7.28 (d, *J* = 9.5 Hz, 2H), 7.77 (d, *J* = 9.5 Hz, 2H), 7.81 (d, *J* = 9.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 19.4, 21.6, 21.7, 22.5, 22.7, 41.2, 43.0, 126.8, 127.7, 129.2, 129.8, 135.3, 140.9, 142.5, 145.0; Mass spectrum (ES) *m/z* 459 $(M+Na+CH_3OH)^+$; Anal. Calcd for $C_{20}H_{24}N_2O_3S_2$: C, 59.38; H, 5.98; N, 6.92; S, 15.85. Found: C, 59.52; H, 5.96; N, 6.78; S, 15.71.

4.16. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-6-azabicyclo[3.1.0]hexane 13a

Prepared according to the general procedure with $Cu(CH_3CN)_4$-PF_6 from cyclopentene, the corresponding aziridine **13a** was obtained (heptane/ethyl acetate 70/30) as a pasty white solid in 59% yield. R_f (silica, EtOAc/heptane: 1/1): 0.50; IR (neat, cm^{-1}) 2937, 2865, 1587, 1494, 1398, 1318, 1226, 1155, 1133, 1108, 1093, 1014, 917, 853, 792, 755, 716; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (m, 4H), 1.86 (m, 1H), 1.98 (m, 1H), 2.37 (s, 3H), 2.42 (s, 3H), 3.45 (m, 1H), 3.63 (m, 1H), 7.20 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2H), 7.77 (d, *J* = 8 Hz, 2H), 7.81 (d, *J* = 8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 21.5, 21.7, 27.0, 27.1, 48.2, 49.9, 126.7, 127.7, 129.1, 129.8, 135.4, 140.8, 142.5, 145.0; Mass spectrum (ES) *m/z* 391 $(M+H)^+$, 413 $(M+Na)^+$; Anal. Calcd for $C_{19}H_{22}N_2O_3S_2$: C, 58.44; H, 5.68; N, 7.17; S, 16.42. Found: C, 58.67; H, 5.91; N, 6.94; S, 16.13.

4.17. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-2-phenylaziridine 14a

Prepared according to the general procedure with $Cu(CH_3CN)_4$-PF_6 from styrene, the corresponding aziridine **14a** was obtained (heptane/ethyl acetate 75/25) as a pasty white solid in 63% yield and 20% de. R_f (silica, EtOAc/heptane: 1/1): 0.45; IR (neat, cm^{-1}) 3035, 2965, 1596, 1319, 1155, 1106, 1089, 909, 813, 752, 700, 665; ^1H NMR (300 MHz, $CDCl_3$) δ *2.38* (*s, 3H*), 2.39 (s, 3H), 2.42 (s, 3H), *2.44* (*d, J = 4.8 Hz, 1H*), 2.58 (d, *J* = 4.8 Hz, 1H), *3.12* (*d, J = 7.6 Hz, 1H*), 3.24 (d, *J* = 7.6 Hz, 1H), 3.84 (dd, *J* = 7.6 and 4.8 Hz, 1H), *3.98* (*dd, J = 7.6 and 4.8 Hz, 1H*), 7.20 (m, 9H), 7.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 21.5, *36.0*, 37.6, *42.0*, 43.4, 126.4, 126.5, 126.6, 127.7, 128.5, 129.0, *129.1*, 129.8, 133.7, 134.1, *134.2*, 140.4, *142.5*, 142.6, 145.5; Mass spectrum (ES) *m/z* 426 $(M)^+$; Anal. Calcd for $C_{22}H_{22}N_2O_3S_2$: C, 61.95; H, 5.20; N, 6.57; S, 15.03. Found: C, 61.74; H, 5.21; N, 6.36; S, 15.01.

4.18. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1,2,3,4-tetrahydronaphthalen-1,2-imine 15a

Prepared according to the general procedure with $Cu(CH_3CN)_4$-PF_6 from 1,2-dihydronaphthalene, the corresponding aziridine **15a** was obtained (heptane/ethyl acetate 80/20) as a pasty white solid in 63% yield and 25% de. R_f (silica, EtOAc/Heptane: 1/1): 0.55; IR (neat, cm^{-1}) 2923, 1596, 1316, 1302, 1252, 1153, 1107, 1089, 944, 907, 875, 813, 751, 707, 667; ^1H NMR (300 MHz, $CDCl_3$) δ 1.68 (m, 2H), *2.33* (*m, 2H*), *2.38* (*s, 3H*), 2.39 (s,3H), 2.40 (s, 3H), *2.41* (*s, 3H*), 2.65 (m, 2H), *3.66* (*d, J = 7.2Hz, 1H*), 3.83 (d, *J* = 7.2 Hz, 1H), 3.89 (m, 1H), *4.10* (*m, 1H*), 7.20 (m, 8H), 7.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, *19.9*, 21.6, 21.7, 24.7, *42.9*, 43.4, 44.7, *44.9*, 126.3, 126.7, 127.6, *128.6*, 128.8, 129.2, *129.5*, 129.8, 133.1, 134.5, *135.2*, *136.6*, 136.8, *140.3*, 140.6, 142.6, *142.8*, *144.7*, 145.2; Mass spectrum (ES) *m/z* 507 $(M+Na+CH_3OH)^+$; Anal. Calcd for $C_{24}H_{24}N_2O_3S_2$: C, 63.69; H, 5.34; N, 6.19; S, 14.17. Found: C, 63.95; H, 5.61; N, 5.98; S, 13.83.

4.19. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-2-methoxycarbonylaziridine 5b

Prepared according to the general procedure with Cu(OTf) from methyl acrylate, the corresponding aziridine **5b** was obtained (heptane/ethyl acetate 7/3) as a white solid in 88% yield and 80% de (HPLC, Hypercarb column, 100 × 4.6 mm, 5 μ, MeCN + 0.1%TFA/H_2O: 80/20, 1 mL/min). R_f (silica, EtOAc/heptane: 1/1): 0.50; mp 43–44 °C; IR (neat, cm^{-1}) 3106, 2929, 1745, 1606, 1530, 1494, 1440, 1401, 1349, 1318, 1231, 1154, 1104, 1061; ^1H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), *2.69* (*d, J = 4.3 Hz, 1H*), 2.84 (d, *J* = 4.3 Hz, 1H), *2.98* (*d, J = 7.3 Hz, 1H*), 3.15 (d, *J* = 7.3 Hz, 1H), 3.56 (dd, *J* = 7.6 and 4.3 Hz, 1H), *3.69* (*dd, J = 7.6 and 4.3 Hz, 1H*), 3.74 (s, 3H), *3.78* (*s, 3H*), 7.26 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 2H), 8.39 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 34.7, 36.9, 53.3, 124.6, 126.8, 129.5, 129.7, 139.5, 142.7, 143.7, 151.2, 165.8; Mass spectrum (ES) *m/z* 462 $(M+Na)^+$ HRMS *m/z* $(M+Na)^+$ calcd for $C_{17}H_{17}N_3NaO_7S_2$ 462.0406, found: 462.0449.

4.20. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-2-*t*-butyloxycarbonylaziridine 16b

Prepared according to the general procedure with Cu(OTf) from *t*-butyl acrylate, the corresponding aziridine **16b** was obtained (heptane/ethyl acetate 7/3) as a white solid in 80% yield and 94% de (HPLC, Hypercarb column, 100 × 4.6 mm, 5 μ, MeCN + 0.1%TFA/H_2O: 80/20, 1 mL/min). R_f (silica, EtOAc/heptane: 1/1): 0.45; mp 133–134 °C; IR (neat, cm^{-1}) 3106, 2980, 1736, 1605, 1530, 1494, 1476, 1456, 1396, 1368, 1348, 1324, 1241, 1153, 1104, 1087, 1056, 1009; ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 9H), 2.41 (s, 3H), *2.66 (d, J = 4.6 Hz, 1H)*, 2.80 (d, *J* = 4.6 Hz, 1H), *2.96 (d, J = 7.3 Hz, 1H)*, 3.10 (d, *J* = 7.3 Hz, 1H), 3.43 (dd, *J* = 7.6 and 4.3 Hz, 1H), *3.58 (dd, J = 7.6 and 4.3 Hz, 1H)*, 7.27 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 8.20 (d, *J* = 8.0 Hz, 2H), 8.40 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 27.8, 34.5, 38.0, 84.0, 124.4, 126.7, 129.4, 129.6, 139.5, 143.1, 143.6, 151.1, 164.2; Mass spectrum (ES) *m/z* 504 $(M+Na)^+$; HRMS *m/z* $(M+Na)^+$ calcd for $C_{20}H_{23}N_3NaO_7S_2$ 504.0875, found 504.0859.

4.21. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-2-methoxycarbonyl-2-methylaziridine 6b

Prepared according to the general procedure with Cu(OTf) from methyl methacrylate, the corresponding aziridine **6b** was obtained (heptane/ethyl acetate 7/3) as a white solid in 95% yield and 36% de. R_f (silica, EtOAc/heptane: 1/1): 0.40; mp 44–45 °C; IR (neat, cm^{-1}) 3106, 2957, 1745, 1530, 1494, 1440, 1401, 1349, 1318, 1257, 1231, 1154, 1104, 1086, 1055, 1009; ^1H NMR (300 MHz, $CDCl_3$) δ 1.68 (s, 3H), *1.77 (s, 3H)*, 2.40 (s, 3H), *2.78 (s, 1H)*, *2.87 (s, 1H)*, 3.00 (s, 1H), 3.17 (s, 1H), 3.69 (s, 3H), *3.77 (s, 3H)*, 7.24 (m, 2H), 7.75 (m, 2H), 8.18 (m, 2H), 8.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ *15.1*, 15.6, 21.5, *38.3*, 40.4, *48.9*, 50.2, 53.3, *53.6*, *124.3*, 124.4, 126.7, 129.2, *129.3*, 129.7, 139.8, *143.3*, 143.4, *144.7*, 145.2, 150.7, 167.2, *167.4*; Mass spectrum (ES) *m/z* 476 $(M+Na)^+$ HRMS *m/z* $(M+Na)^+$ calcd for $C_{18}H_{19}N_3NaO_7S_2$ 476.0562, found 476.0565.

4.22. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-2-cyanoaziridine 17b

Prepared according to the general procedure with Cu(OTf) from acrylonitrile, the corresponding aziridine was obtained (heptane/ethyl acetate 7/3) as an oily solid in 48% yield and 33% de (HPLC, Hypercarb column, 100 × 4.6 mm, 5 μ, MeCN + 0.1%TFA/H_2O: 75/25, 1 mL/min). R_f (silica, EtOAc/heptane: 1/1): 0.50; ^1H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H), *2.85 (d, J = 3.6 Hz, 1H)*, 3.01 (d, *J* = 3.7 Hz, 1H), *3.18 (d, J = 7.1 Hz, 1H)*, 3.36 (d, *J* = 7.2 Hz, 1H), 3.68 (m, 1H), *3.78 (m, 1H)*, 7.34 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 8.27 (d, *J* = 8.0 Hz, 2H), 8.48 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 24.8, 26.7, 33.4, 35.3, 114.0, 124.8, 126.8, 129.6, 129.7, 139.0, 141.8, 144.2, 151.5; Mass spectrum (ES) *m/z* 429 $(M+Na)^+$ HRMS *m/z* $(M+Na)^+$ calcd for $C_{16}H_{14}N_4NaO_5S_2$ 429.0303, found 429.0329.

4.23. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-2-pentylaziridine 9b

Prepared according to the general procedure with Cu(OTf) from heptene, the corresponding aziridine **9b** was obtained (heptane/ethyl acetate 7/3) as an oily solid in 92% yield. R_f (silica, EtOAc/heptane: 1/1): 0.50; ^1H NMR (300 MHz, $CDCl_3$) δ 0.81 (m, 3H), 1.24 (m, 6H), 1.52 (m, 2H), *2.20 (d, J = 7.1 Hz, 1H)*, 2.37 (d, *J* = 7.1 Hz, 1H), 2.39 (s, 3H), *2.81 (d, J = 7.1 Hz, 1H)*, 2.96 (d, *J* = 7.1 Hz, 1H), *2.97 (m, 1H)*, 3.08 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 8.36 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, *13.9*, 21.5, 22.3, *22.4*, *26.1*, 26.2, 30.7, *30.8*, 30.9, *31.1*, *34.9*, 36.7, 42.6, *43.9*, 124.4, 126.7, 129.1, 129.4, 139.9, *140.0*, 143.2, 144.7, 150.8; Mass spectrum (ES) *m/z* 474 $(M+Na)^+$ HRMS *m/z* $(M+Na)^+$ calcd for $C_{20}H_{25}N_3NaO_5S_2$ 474.1133, found 474.1130.

4.24. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-7-azabicyclo[4.1.0]heptane 12b

Prepared according to the general procedure with Cu(OTf) from cyclohexene, the corresponding aziridine **12b** was obtained (heptane/ethyl acetate 7/3) as a white solid in 93% yield. R_f (silica, EtOAc/heptane: 1/1): 0.50; mp 143–144 °C; IR (neat, cm^{-1}) 3104, 2932, 1604, 1528, 1440, 1400, 1349, 1308, 1255, 1153, 1091, 1058, 954; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (m, 4H), 1.82 (m, 4H), 2.39 (s, 3H), 3.19 (m, 1H), 3.41 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 8.36 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 19.2, 21.5, 22.4, 22.5, 42.1, 44.0, 124.4, 126.7, 129.1, 129.4, 140.0, 143.1, 144.5, 150.6; Mass spectrum (ES) *m/z* 458 $(M+Na)^+$ HRMS *m/z* $(M+Na)^+$ calcd for $C_{19}H_{21}N_3NaO_5S_2$ 458.0820, found 458.0805.

4.25. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-7-azabicyclo[4.1.0]heptane 13b

Prepared according to the general procedure with Cu(OTf) from cyclohexene, the corresponding aziridine **13b** was obtained (heptane/ethyl acetate 7/3) as a white solid in 95% yield. R_f (silica, EtOAc/heptane: 1/1): 0.50; mp 148–149 °C; IR (neat, cm^{-1}) 3104, 2933, 1604, 1528, 1440, 1400, 1349, 1308, 1255, 1153, 1091, 1057, 955; ^1H NMR (300 MHz, $CDCl_3$) δ 1.37 (m, 1H), 1.66 (m, 3H), 1.88 (m, 1H), 2.02 (m, 1H), 2.38 (s, 3H), 3.55 (m, 1H), 3.75 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 2H), 8.34 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 21.5, 27.0, 27.1, 49.3, 51.0, 124.4, 126.7, 129.1, 129.4, 140.0, 143.1, 144.5, 150.6; Mass spectrum (ES) *m/z* 444 $(M+Na)^+$ HRMS *m/z* $(M+Na)^+$ calcd for $C_{18}H_{19}N_3NaO_5S_2$ 444.0664, found 444.0636.

4.26. *N*-[*N*-(*p*-Toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-2-phenylaziridine 14b

Prepared according to the general procedure with $Cu(CH_3CN)_4$-PF_6 from styrene, the corresponding aziridine **14b** was obtained (heptane/ethyl acetate 6/4) as a pasty white solid in 40% yield and 10% de. I.R. (neat, cm^{-1}) 2924, 2012, 1600, 1529, 1347, 1154, 1060, 853, 812, 743, 664; ^1H NMR (300 MHz, $CDCl_3$) δ *2.32 (s, 3H)*, 2.33 (s, 3H), *2.49 (dd, J = 0.8 and 4.9 Hz, 1H)*, 2.64 (dd, *J* = 0.8 and 4.9 Hz, 1H), *3.14 (dd, J = 0.8 and 7.3 Hz, 1H)*, 3.28 (dd, *J* = 0.8 and 7.3 Hz, 1H), 3.87 (dd, *J* = 4.9 and 7.3 Hz, 1H), *4.04 (dd, J = 4.9 and 7.3 Hz, 1H)*, 7.05–7.10 (m, 4H), 7.21–7.27 (m, 3H), 7.72 (dd, *J* = 8.3 and 10.0 Hz, 2H), 8.11 (d, *J* = 8.9 Hz, 2H), 8.21–8.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 38.4, *40.2*, 42.9, *44.5*, 124.4, 126.5, *126.6, 126.7*, 126.8, 128.8, 129.1, 129.3, 129.4, 133.0, 139.9, 143.3, 143.7, 148.4.

4.27. Methyl 3-methoxy-2-[*N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]amino-propionate 18

Aziridine **5b** (439 mg, 1 mmol) was dissolved in CH_2Cl_2 (2 mL) and MeOH (2 mL). The reaction mixture was stirred overnight at room temperature and then concentrated under reduced pressure. Trituration of the product with ethyl ether followed by evaporation of the solvent afforded **18** as a white solid in 99% yield (468 mg, 0.99 mmol). Mp 46–48 °C; R_f (silica, heptane/ethyl acetate: 1/1): 0.35; IR (neat, cm^{-1}) 3220, 3107, 2926, 1744, 1606, 1528, 1495, 14,36, 1402, 1348, 1304, 1290, 1263, 1152, 1105, 1063; ^1H NMR

(300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.38 (s, 3H), 3.61 (s, 3H), 3.70 (m, 1H), 3.87 (dd, J = 8.0 and 9.5 Hz, 1H), 4.27 (t, J = 3.3 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H), 8.33 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 53.0, 55.8, 59.5, 72.5, 124.1, 126.7, 128.9, 129.5, 140.0, 143.3, 144.8, 150.3, 168.7; MS (ES) m/z 494 (M+Na)+; HRMS m/z (M+Na)+ calcd for $C_{18}H_{21}N_3NaO_8S_2$ 494.0668, found 494.0681.

4.28. *tert*-Butyl 3-methoxy-2-[*N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]amino-propionate 19

Aziridine **16b** (120 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (1 mL) and MeOH (1 mL). The reaction mixture was stirred overnight at room temperature and then concentrated under reduced pressure. Trituration of the product with ethyl ether followed by evaporation of the solvent afforded **19** as a white solid in 97% yield (124 mg). Mp 49–51 °C; R_f (silica, heptane/ethyl acetate: 1/1): 0.43; IR (neat, cm^{-1}) 3214, 3100, 2925, 1733, 1604, 1529, 1456, 1347, 1317, 1304, 1259, 1152, 1107, 1064, 1011; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9H), 2.43 (s, 3H), 3.36 (s, 3H), 3.64–3.66 (m, 1H), 3.77–3.79 (m, 1H), 4.09–4.11 (m, 1H), 6.27 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 8.14 (d, J = 8.5 Hz, 2H), 8.32 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 27.7, 56.2, 59.4, 72.9, 83.5, 124.1, 126.8, 129.0, 129.4, 139.9, 143.4, 145.1, 150.4, 167.3; MS (ES) m/z 514 (M+H)+, 536 (M+Na)+; HRMS m/z (M+Na)$^+$ calcd for $C_{21}H_{27}N_3NaO_8S_2$ 536.1137, found 536.1125.

4.29. Methyl 3-hydroxy-2-[*N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]amino-propionate 20

Aziridine **5b** (439 mg, 1 mmol) was dissolved in THF (2 mL), water (2 mL), and TFA (2 mL). The reaction mixture was stirred overnight at room temperature and then diluted with water (5 mL) and ethyl ether (5 mL). After addition of $NaHCO_3$ until pH ~8, the organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were dried on magnesium sulfate and concentrated under reduced pressure. The resulting residue was then purified by flash chromatography (heptane/ethyl acetate: 3/7) to afford compound **20** as an oily solid in 77% yield (353 mg, 0.77 mmol). R_f (silica, heptane/ethyl acetate: 7/3): 0.15; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.48 (s, 3H), 3.72–3.89 (m, 2H), 4.19 (t, J = 3.5 Hz, 1H), 6.97 (br s, 1H), 7.31 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 8.03 (d, J = 8.6 Hz, 2H), 8.30 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 53.1, 58.5, 63.6, 125.2, 127.4, 129.9, 130.4, 141.2, 144.6, 145.9, 151.6, 170.1; MS (ES) m/z 480 (M+Na)$^+$; HRMS m/z (M+Na)$^+$ calcd for $C_{17}H_{19}N_3NaO_8S_2$ 480.0511, found 480.0515.

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