PERKIN 1

Scope and limitations in sulfur ylide mediated catalytic asymmetric aziridination of imines: use of phenyldiazomethane, diazoesters and diazoacetamides †

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Imine aziridination using diazo-compounds and catalytic quantities of metal salts and sulfides has been investigated. A range of imines derived from benzaldehyde bearing electron-withdrawing groups (*N*-Ts, *N*-$SO_2CH_2CH_2SiMe_3$ (SES), *N*-$P(O)Ph_2$, *N*-CO_2Bn, *N*-CO_2Bu^t, *N*-$CO_2(CH_2)_2SiMe_3$, *N*-$CO_2C(CH_3)_2CCl_3$) were prepared and tested in the aziridination process using Me_2S and phenyldiazomethane. High yields were obtained with all imines but diastereoselectivity varied considerably (3 : 1–>10 : 1). A range of *N*-SES imines were tested with stoichiometric amounts of sulfides and high yields were obtained with both aromatic and aliphatic imines. These imines were subsequently tested with stoichiometric and sub-stoichiometric loadings of enantiomerically pure 1,3-oxathiane **3** with $Rh_2(OAc)_4$ and with $Cu(acac)_2$. Good yields and high enantioselectivities (89–95%) were observed with $Rh_2(OAc)_4$, although a small reduction in enantiomeric excess was observed with $Cu(acac)_2$ (85–95%) especially when sub-stoichiometric amounts of sulfide were employed. The same sulfide was also tested with a range of electron-withdrawing groups on the imine nitrogen and in all cases good yields and high enantioselectivities were maintained. Improved diastereoselectivity was observed with carbamate groups.

The aziridination process was extended to include diazoester and diazoacetamides with a range of *N*-Ts imines, and again good yields were obtained although diastereoselectivity varied according to the diazo-compound employed. Although the 1,3-oxathiane **3** could not be employed with these more stable diazo-compounds, (*R,R*)-2,5-dimethylthiolane **5** was found to be a suitable chiral catalyst and gave moderate enantio- and diastereoselectivities. Rationales for the origin of the diastereoselectivity and enantioselectivity are provided.

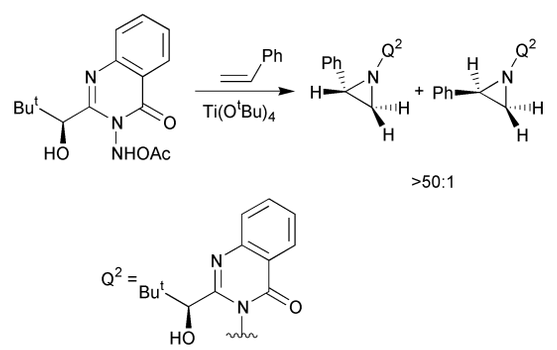
Introduction

In contrast to the well-developed methods for asymmetric epoxidation[1] there are few general methods for asymmetric aziridination.[2] There are a number of stoichiometric routes to non-racemic aziridines. Atkinson described the addition of enantiopure acetoxyaminoquinazolines[2d] to alkenes and depending on the exact structure of the reagent and the reaction conditions high diastereoselectivity was obtained with a range of mono and *trans* disubstituted alkenes (Scheme 1).

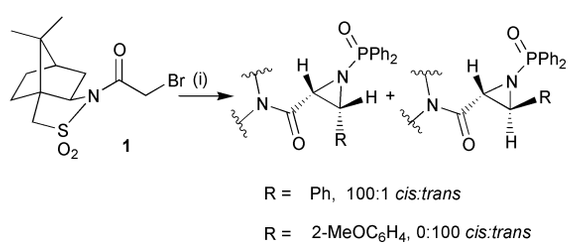
Sweeney and co-workers reported the Darzens-type addition of bromoacyl sultam **1** to imines and obtained the *cis*- or *trans*-aziridines (depending on the substitution of the imine) with a high level of diastereoselectivity relative to the auxilliary (Scheme 2).[3]

The addition of simple amines to α-bromo acrylates provides a complementary route to aziridines and using the Oppolzer sultam[4] or chiral imidazolidin-2-ones[5] as a chiral auxiliary, high levels of stereocontrol have been achieved. Davis and co-workers[6] have reported a Darzens-type reaction of ester enolates with enantiopure sulfinimines and obtained aziridines with high diastereoselectivity.

There are two direct routes to aziridines that lend themselves to asymmetric catalysis: the addition of nitrenoids to alkenes (route A) and the addition of carbenes/carbenoids to imines (route B), as shown in Fig. 1.



Scheme 1 Atkinson's aziridination.



Scheme 2 Darzens-type addition of a bromoacyl sultam. *Reagents and conditions*: (i) RCH=NP(O)Ph_2, LiHMDS, THF, −78 °C, 47–87% yield.

Evans,[7] Jacobsen[8] and more recently Scott[9] and their co-workers reported processes for asymmetric aziridination of alkenes using PhI=NTs as the nitrene precursor and a chiral copper catalyst (Scheme 3).[10,11] In the Evans' case, high enantioselectivity was limited to cinnamate esters, and in the Jacobsen

† Electronic supplementary information (ESI) available: further experimental details of imine synthesis and determination of enantiomeric excesses. See http://www.rsc.org/suppdata/p1/b1/b102578n/

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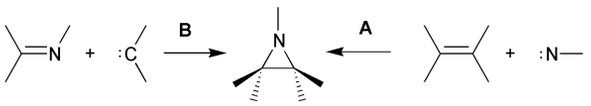
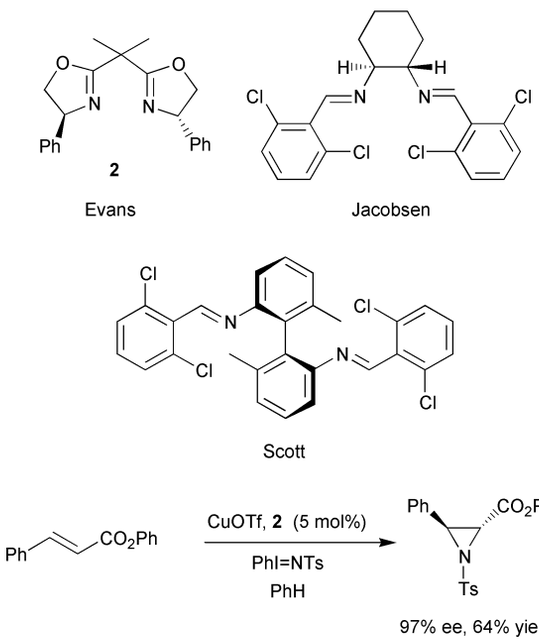


Fig. 1 Aziridination strategies.



Scheme 3 Copper catalysed asymmetric aziridination of alkenes.

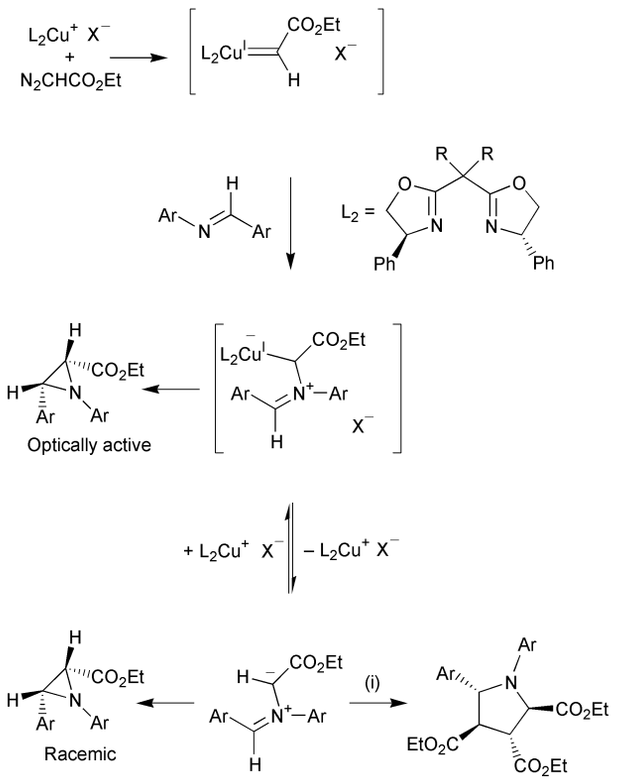
and Scott systems high enantioselectivity was achieved with chromene derivatives. Related studies using chiral rhodium catalysts have been less successful.[12]

Although PhI=NTs is usually employed, alternative reagents have been developed which have more readily cleavable groups on nitrogen than tosyl thereby enhancing the usefulness of this asymmetric process.[13]

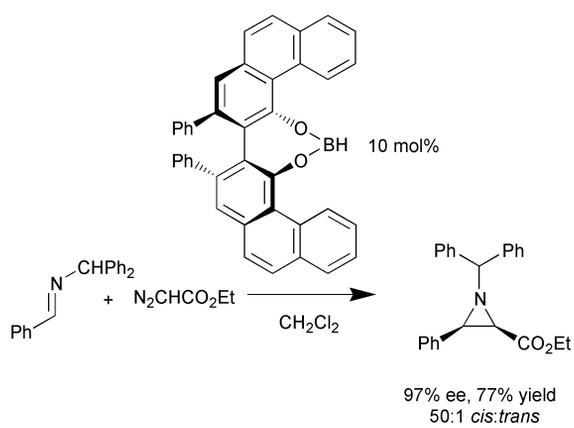
Compared to alkene aziridination, the asymmetric addition of metal carbenoids to imines has met with less success. Although many metals can catalyse the addition of diazo-compounds to imines the enantioselectivity observed is often poor.[14,15] In a series of elegant experiments Jacobsen and co-workers[14] (Scheme 4) showed that there were two pathways which led to the aziridine: one bearing the chiral metal species which yielded non-racemic aziridine and the second a planar azomethine ylide which gave racemic aziridine. This was proved by trapping the azomethine ylide with a dipolarophile. Evidently, the problem with the addition of metal carbenes to imines is that the C–N bond is formed before the C–C bond which leads to a planar azomethine ylide. If the C–C bond could be formed ahead of the C–N bond, then there would be no possibility of forming the achiral azomethine ylide.

Such a situation has been achieved in a highly effective chiral Lewis acid mediated aziridination of imines with ethyl diazoacetate using a biaryl boronate catalyst (Scheme 5). Excellent yields and selectivities were obtained with a range of imines.[16] Other chiral Lewis acids have been less successful in asymmetric aziridination.[17]

Another approach that allows C–C bond formation ahead of C–N formation (thus avoiding formation of the planar azomethine ylide) is the reaction of a sulfur ylide with an imine. Indeed sulfonium[18] and sulfoxonium ylides[19] have been reported to react with imines to give aziridines although it was found that sulfonium ylides were more efficient. Dai and co-workers have reported the use of chiral sulfur ylides derived from the camphor skeleton and whilst good diastereoselectivity has been obtained in some cases,[20] enantioselectivity was only moderate. The addition of achiral sulfonium and sulfoxonium



Scheme 4 Metal carbenoid additions to imines; intermediacy of azomethine ylides. *Reagents*: (i) $EtO_2CCH{=}CHCO_2Et$.



Scheme 5 Wulff's asymmetric aziridination.

ylides to enantiopure sulfinimines has also been described but only moderate diastereoselectivity was achieved.[21]

We previously reported a new catalytic process involving sulfur ylides for the conversion of carbonyl compounds into epoxides[22] and described the highly effective use of simple sulfide **3** for asymmetric epoxidation (Scheme 6).[23]

We therefore sought to exploit this new process for asymmetric aziridination[24] of imines and in this paper we describe our results in the development of this process in full.

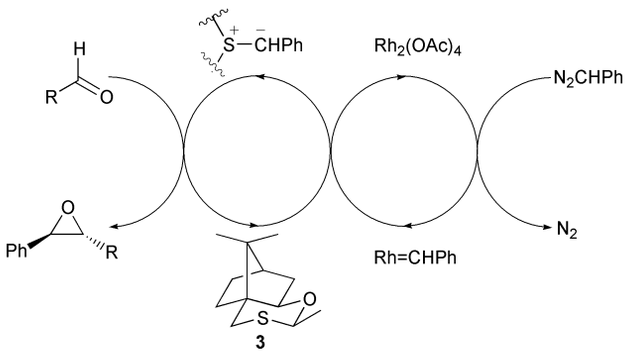
Results

We sought to develop an asymmetric aziridination process analogous to the epoxidation process using catalytic amounts of chiral sulfides (Scheme 7). In comparison to epoxidation of carbonyl compounds, aziridination of imines is more complex because an extra variable, namely the nature of the group on the nitrogen has to be considered. As the ultimate step in our proposed catalytic process is the reaction of a nucleophilic sulfur ylide with an imine, it was deemed necessary to incorporate an electron-withdrawing group on nitrogen to promote this process. In order to test which electron-withdrawing group

Table 1 Effect of different nitrogen protecting groups on diastereoselectivity with Me_2S[a]

Entry	R^1	*trans* : *cis*[b]	Yield (%)
1	Ts	3 : 1	82
2	SES	3 : 1	92
3	$P(O)Ph_2$	3 : 1	86
4	CO_2Me	>10 : 1	73
5	CO_2Bn	>10 : 1	56
6	$CO_2CH_2CH_2TMS$	>10 : 1	71
7	CO_2Bu^t	>10 : 1	85
8	$CO_2C(CH_3)_2CCl_3$	>10 : 1	74

[a] All reactions were performed in CH_2Cl_2 at RT with 1 mol% $Rh_2(OAc)_4$, 1 eq. of dimethyl sulfide, 1.5 eq. of phenyldiazomethane and 1 eq. of benzaldimine. [b] Determined by ^1H NMR of the crude reaction mixture.



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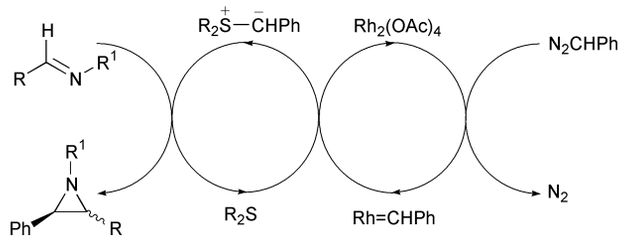
Scheme 6 Catalytic asymmetric process for epoxidation of aldehydes.



Scheme 7 Catalytic process for aziridination of imines.

would be the optimum, a range of imines bearing Ts,[25] SES ($SO_2CH_2CH_2SiMe_3$),[25] $P(O)Ph_2$,[26] CO_2Me,[27] CO_2Bn,[28] $CO_2(CH_2)_2SiMe_3$, CO_2Bu^t[28] and TcBoc ($CO_2C(CH_3)_2CCl_3$)[27] (see electronic supplementary information for details) derived from PhCHO were prepared. With a range of imines in hand we tested how they performed in aziridination reactions using reaction conditions that were broadly similar to those used in the epoxidation reactions (Scheme 7, Table 1).

We were delighted to find that good to high yields were obtained in all cases although the diastereoselectivity varied considerably. Whilst large electron-withdrawing groups on nitrogen only gave moderate *trans* selectivity (entries 1–3), the alkoxycarbonyl groups gave high *trans* selectivity (entries 4–8) (*vide infra*). These reactions were conducted with Me_2S. We were also interested to know how changes in the sulfide structure affected the efficiency and the diastereoselectivity of the process and so a range of simple sulfides were tested with *N*-SES and *N*-Moc (methoxycarbonyl) imines derived from PhCHO (Table 2). Whilst all the sulfides gave aziridines in high yield, we were greatly surprised at how minor variations in sulfide structure affected the diastereoselectivity in the reactions of alkoxycarbonyl imines but not of the sulfonyl imines (*vide infra*).

The process was applied to a range of *N*-SES imines (these are the easiest to prepare, the most stable and the SES group can be easily removed) derived from aromatic, unsaturated and aliphatic aldehydes with substoichiometric amounts

Table 2 Effect of sulfide structure on the diastereoselectivity[a]

Entry	Sulfide	R^1	*trans* : *cis*[b]	Yield (%)
1	Dimethyl sulfide	SES	3 : 1	92
2	1,4-Oxathiane	SES	4 : 1	89
3	Pentamethylene sulfide	SES	3 : 1	95
4	Tetrahydrothiophene	SES	3 : 1	84
5	Dimethyl sulfide	Moc	>10 : 1	73
6	1,4-Oxathiane	Moc	10 : 1	70
7	Pentamethylene sulfide	Moc	7 : 1	95
8	Tetrahydrothiophene	Moc	4 : 1	nd

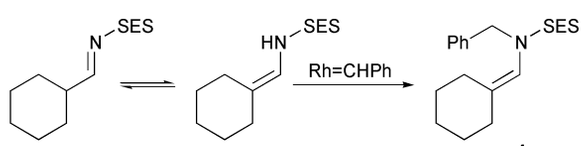
[a] All reactions were performed in CH_2Cl_2 at RT with 1 mol% $Rh_2(OAc)_4$, 1 eq. of sulfide, 1.5 eq. of phenyldiazomethane and 1 eq. of benzaldimine. [b] Determined by ^1H NMR of the crude reaction mixture.

Table 3 Exploring the range of *N*-SES imines in aziridination[a]

Entry	R	*trans* : *cis*[b]	Yield (%)
1	Ph	3 : 1	92
2	*p*-ClC_6H_4	3 : 1	88
3	*p*-MeC_6H_4	3 : 1	96
4	(*E*)-PhCH=CH	3 : 1	67
5	Bu^t	2 : 1	81
6	C_6H_{11}	1.2 : 1	68[c]
7	Bu^n	—	<5

[a] All reactions were performed in CH_2Cl_2 at RT with 1 mol% $Rh_2(OAc)_4$, 0.2 eq. of dimethyl sulfide, 1.5 eq. of phenyldiazomethane and 1 eq. of *N*-SES imine. [b] Determined by ^1H NMR of the crude reaction mixture. [c] 20% of **4** was also obtained.

of dimethyl sulfide (20 mol%) and again good yields were obtained with all of the non-enolisable imines tested, indicating that we had a process of broad generality (Table 3). The enolisable imine derived from cyclohexanecarbaldehyde was also an effective substrate (Table 3, entry 6), although lower yields of the corresponding aziridines were obtained together with by-product **4**. Evidently, in this case, following tautomerisation of the imine, insertion of the metal carbenoid into the NH bond competes with sulfur ylide formation (Scheme 8). Valeraldimine



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Scheme 8 Formation of by-product in aziridination.

only gave traces of the expected product possibly because of its instability to the reaction conditions or due to tautomerisation (Table 3, entry 7).

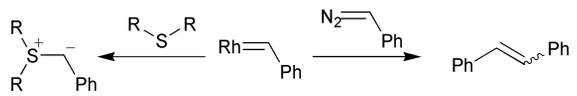
Our next goal was to explore asymmetric aziridination with chiral sulfides and for this purpose we tested oxathiane **3** which had worked so well in the related epoxidation process. The effect of solvent on efficiency, enantioselectivity and diastereoselectivity was briefly investigated with the *N*-Ts imine derived from benzaldehyde (Table 4). Substantial variation in yield and enantioselectivity was observed whilst diastereoselectivity was only marginally affected. Dichloromethane emerged as the optimum solvent on all counts (entry 1).

Having established CH_2Cl_2 as the optimum solvent, we screened a range of *N*-SES imines with both $Rh_2(OAc)_4$ and $Cu(acac)_2$ under stoichiometric and catalytic loadings of sulfide (Table 5). From this study a number of general observations were made.

(i) High enantioselectivity was observed with all the imines studied. The absolute configuration of all the aziridines is assumed to be (*R*,*R*) and this has been proved in the case of the aziridine derived from *N*-SES-benzaldimine.[24]

(ii) Using stoichiometric amounts of sulfide **3**, $Rh_2(OAc)_4$ and $Cu(acac)_2$ gave similar yields and enantioselectivities, except for the *N*-SES-cyclohexanecarbaldimine (*vide infra*).

(iii) Catalytic amounts of sulfide **3** often resulted in a reduction in yield compared to the use of stoichiometric amounts of sulfide **3** with concomitant formation of stilbenes. Stilbenes arise from the reaction of the metal carbenoid with phenyldiazomethane, a reaction which competes with the formation of the intermediate sulfur ylide (Scheme 9). Reduced sulfide



Scheme 9 Two competing modes of reaction for the rhodium carbenoid.

loading allows a greater chance for the alternative competing reaction to occur.

(iv) Although there was no variation in enantioselectivity on changing from stoichiometric to catalytic loading of sulfide with $Rh_2(OAc)_4$ there was a small reduction in enantioselectivity with $Cu(acac)_2$. This implies that in the case of $Cu(acac)_2$ there is a very small amount of direct addition of the copper carbenoid to the imine, which competes with ylide formation. With reduced sulfide loading there is a greater amount of direct addition of the copper carbenoid to the imine leading to a measurable reduction in enantiomeric excess. The direct addition of the copper carbenoid to the imine is well documented although its efficiency is strongly dependent on the nature of the group on the nitrogen: electron-rich imines give good yields whilst electron-deficient imines give poor yields.[15] Fortunately, we require electron-deficient imines to obtain efficient reactions with sulfur ylides and so direct addition of the copper carbenoid is minimised. In any case, using $Rh_2(OAc)_4$ the same enantioselectivities are obtained with stoichiometric and catalytic sulfide loading indicating the absence of direct addition of the rhodium carbenoid to the imine.

The *N*-SES-cyclohexanecarbaldimine gave poor results using catalytic amounts of sulfide with $Rh_2(OAc)_4$ or $Cu(acac)_2$, and the reason for these unexpected results is not known at present and is currently under investigation.

A number of chiral sulfides have been prepared in our group and so we screened some representative examples, based on tetrahydrothiophene (entry 2,[29] Table 6), thiane (entry 3,[30] Table 6) and 1,3- and 1,4-oxathiane (entries 1 and 4,[30] Table 6) to investigate their effect on yield, diastereoselectivity and enantioselectivity by analogy to the series of achiral sulfides we had used earlier (*cf.* Table 2). Although these sulfides gave good to excellent levels of enantioselectivity, there was no advantage in terms of diastereoselectivity and so 1,3-oxathiane **3** remains the optimum sulfide in this process.

Another method we have discovered for influencing the diastereoselectivity is through variation of the group on nitrogen. We therefore investigated the reactions of a range of imines with the 1,3-oxathiane **3** (Table 7). Pleasingly, high enantioselectivity was maintained with all of the imines studied without significant variation between them. Furthermore, the diastereoselectivity improved with alkoxycarbonyl groups compared to sulfonyl groups just as we had observed with dimethyl sulfide (*cf.* Table 1). Especially noteworthy is the high diastereoselectivity and enantioselectivity observed with Boc and TcBoc groups as further manipulation of these groups is easy and well documented (Table 7, entries 6 and 7).[31]

Table 4 Effect of solvent on asymmetric aziridination of *N*-Ts-benzaldimine using sulfide **3**[a]

Entry	Solvent	*trans* : *cis*[b]	Yield (%)	Ee (%)[c]
1	CH_2Cl_2	3 : 1	82	92
2	Toluene	3 : 1	41	61
3	DME	3 : 1	78	60
4	1,4-Dioxane	3 : 1	48	82
5	CH_3CN	2 : 1	41	56

[a] All reactions were performed at RT with 1 mol% $Rh_2(OAc)_4$, 0.2 eq. of chiral sulfide **3**, 1.5 eq. of phenyldiazomethane and 1 eq. of *N*-Ts benzaldimine. [b] Determined by ^1H NMR of the crude reaction mixture. [c] Ee of *trans* aziridine determined by HPLC using a Chiralcel OD column.

Origin of diastereoselectivity

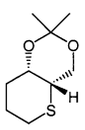
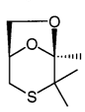
The reaction of the phenyl stabilised sulfur ylides with *N*-Ts imines has been found to be under kinetic control (*i.e.* formation of *syn*- and *anti*-betaines are irreversible).[32] Thus, the difference in energy between the transition states leading to the *syn*- and *anti*-betaines is responsible for the diastereo- and enantioselectivity. From calculations it has been suggested that sulfur ylides react with aldehydes in an "end-on" approach.[33] Assuming the same applies to reactions with *N*-Ts imines, this would give rise to transition states **A** and **B** (Fig. 2), which lead to *trans*- and *cis*-aziridines respectively. It is apparent that transition state **A** leading to the *trans*-aziridines (which is the major isomer observed) is less hindered than transition state **B**, which has all four groups *gauche* to one another.

Table 5 Asymmetric aziridination of *N*-SES imines with sulfide **3**[a]

Entry	R	Sulfide (eq.)	Metal salt	Yield (%) (*trans* : *cis*)[b]	Ee (%)[c]
1	Ph	1.0	$Rh_2(OAc)_4$	84 (5 : 1)	95
2	Ph	0.2	$Rh_2(OAc)_4$	47 (3 : 1)	95
3	Ph	1.0	$Cu(acac)_2$	83 (3 : 1)	95
4	Ph	0.2	$Cu(acac)_2$	62 (3 : 1)	90
5	*p*-MeC_6H_4	1.0	$Rh_2(OAc)_4$	88 (3 : 1)	95
6	*p*-MeC_6H_4	0.2	$Rh_2(OAc)_4$	91 (3 : 1)	93
7	*p*-MeC_6H_4	1.0	$Cu(acac)_2$	94 (3 : 1)	94
8	*p*-MeC_6H_4	0.2	$Cu(acac)_2$	50 (3 : 1)	88
9	*p*-ClC_6H_4	1.0	$Rh_2(OAc)_4$	70 (3 : 1)	89
10	*p*-ClC_6H_4	0.2	$Rh_2(OAc)_4$	58 (3 : 1)	88
11	*p*-ClC_6H_4	1.0	$Cu(acac)_2$	77 (3 : 1)	89
12	*p*-ClC_6H_4	0.2	$Cu(acac)_2$	44 (3 : 1)	85
13	(*E*)-PhCH=CH	1.0	$Rh_2(OAc)_4$	86 (5 : 1)	93
14	(*E*)-PhCH=CH	0.2	$Rh_2(OAc)_4$	62 (5 : 1)	93
15	(*E*)-PhCH=CH	1.0	$Cu(acac)_2$	50 (5 : 1)	93
16	(*E*)-PhCH=CH	0.2	$Cu(acac)_2$	25 (5 : 1)	85
17	C_6H_{11}	1.0	$Rh_2(OAc)_4$	72 (1 : 1)	89

[a] All reactions were performed in CH_2Cl_2 at RT with 1 mol% $Rh_2(OAc)_4$ or 5 mol% $Cu(acac)_2$, 1.5 eq. of phenyldiazomethane and 1 eq. of imine. [b] Determined by ^1H NMR of the crude reaction mixture. [c] Ee of *trans* aziridine determined by HPLC using a Chiralcel OD column. The absolute stereochemistry is *R*,*R* in all cases.

Table 6 Effect of sulfide structure on asymmetric aziridination[a]

Entry	Sulfide	*trans* : *cis*[b]	Yield (%)	Ee (%)[c]
1		3 : 1	47	95 (*R*,*R*)
2		3 : 1	34	95 (*R*,*R*)
3		3 : 1	36	79 (*S*,*S*)
4		3 : 1	24	77 (*R*,*R*)

[a] All reactions were performed in CH_2Cl_2 at RT with 1 mol% $Rh_2(OAc)_4$, 0.2 eq. of sulfide, 1.5 eq. of phenyldiazomethane and 1 eq. of *N*-Ts benzaldimine. [b] Determined by ^1H NMR of the crude reaction mixture. [c] Ee of *trans* aziridine determined by HPLC using a Chiralcel OD column.

Table 7 Effect of imine activating groups on aziridination with chiral sulfide **3**[a]

Entry	R^1	*trans* : *cis*[b]	Yield (%)	Ee (%)[c]
1	Ts	3 : 1	71	92
2	SES	3 : 1	84	95
3	CO_2Me	6 : 1	75	92
4	CO_2Bn	6 : 1	58	90
5	$CO_2CH_2CH_2TMS$	9 : 1	55	91
6	CO_2Bu^t	9 : 1	60	92
7	$CO_2C(CH_3)_2CCl_3$[d]	>10 : 1	58	92

[a] All reactions were performed in CH_2Cl_2 at RT with 1 mol% $Rh_2(OAc)_4$, 1 eq. of sulfide **3**, 1.5 eq. of phenyldiazomethane and 1 eq. of benzaldimine. [b] Determined by ^1H NMR of the crude reaction mixture. [c] Ee of *trans* aziridine determined by HPLC using a Chiralcel OD column.[d] The same results were obtained using 0.2 eq. of **3**.

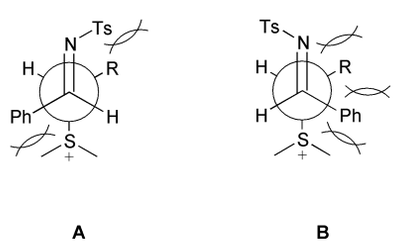


Fig. 2 End-on addition of sulfur ylide to imine.

Using this model one can understand the variation in diastereoselectivity with groups on nitrogen. Large bulky groups on nitrogen will increase the congestion in the transition state **A** leading to reduced *trans* selectivity. However, small groups on nitrogen (*e.g.* alkoxycarbonyl) will be accommodated in this transition state more easily leading to increased amounts of the *trans* isomer. These factors may account for the increased *trans* selectivity observed with alkoxycarbonyl groups compared to sulfonyl/phosphinyl groups but does not account for the variation in diastereoselectivity amongst the different alkoxycarbonyl groups. This aspect is difficult to explain. The variation in diastereoselectivity with sulfide structure is also not easy to explain.

Origin of enantioselectivity

We propose a similar model to account for the enantioselectivity of aziridination to that we proposed in the related epoxidation process[23] using the same sulfide catalyst (Fig. 3). In this model, ylide conformer **A** is favoured over conformer **B** due to 1,3-diaxial interactions and this conformer reacts with high face selectivity as a result of both steric (attack opposite the methyl group) and electronic (a combination of an anomeric effect and Cieplak effect) control.[23] It is believed that the minor enantiomer originates from the reaction of the minor conformation of the ylide **B**, which again reacts with the same high facial selectivity.

Table 8 Reaction of ethyl diazoacetate with *N*-Ts benzaldimine using tetrahydrothiophene[a]

Entry	R	*trans* : *cis*[b]	Yield (%)
1	*p*-$MeOC_6H_4$	2 : 3	62
2	Ph	1 : 3	83[c]
3	*p*-ClC_6H_4	1 : 5	41
4	*p*-$NO_2C_6H_4$	1 : 12	54
5	C_6H_{11}	1 : 11	76
6[d]	Ph	2 : 1	76

[a] All reactions were performed in THF at 60 °C with 1 mol% $Rh_2(OAc)_4$, 1 eq. of tetrahydrothiophene, 1.5 eq. of ethyldiazoacetate and 1 eq. of *N*-Ts benzaldimine. [b] Determined by ^1H NMR of the crude reaction mixture. [c] 57% yield obtained with 0.2 eq. of tetrahydrothiophene. [d] Using *N*,*N*-diethyldiazoacetamide.

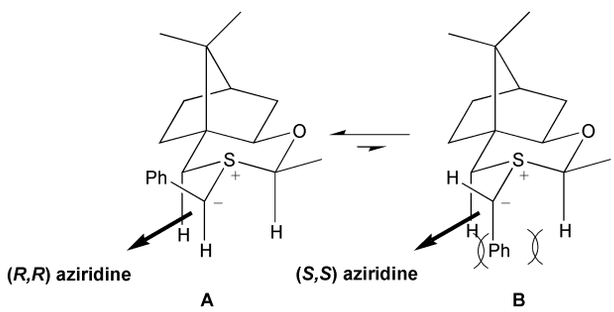


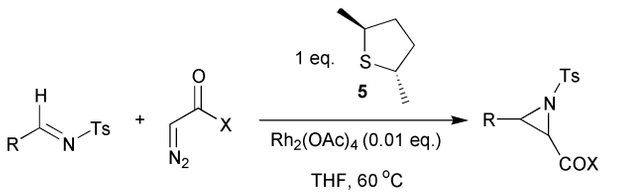
Fig. 3 Model for enantioselectivity.

Alternative diazo-compounds

The reactions of alternative diazo-compounds with *N*-Ts imines were also investigated and it was found that both diazoesters and diazoacetamides[34] could be used although higher temperatures were required to effect decomposition of these more stable diazo-compounds (Tables 8 and 9). Interestingly the reactions of diazoesters gave predominantly the *cis*-aziridines rather than the *trans* isomer observed with phenyldiazomethane and a range of imines. To understand this reverse diastereoselectivity with diazoesters several factors need to be considered. We have recently found that ester-stabilised ylides react reversibly with imines[35] and so the diastereoselectivity (and enantioselectivity) of the process is controlled in the ring closure step rather than the betaine-forming step. Thus *cis*-aziridines must be thermodynamically more stable than the corresponding *trans* isomers. Indeed, this has been verified experimentally as palladium catalysed isomerisation of unsaturated aziridines[36] and base catalysed isomerisation of aziridinyl ketones[37] give *cis*-aziridines predominantly. The thermodynamic preference for the *cis*-aziridine can be understood in terms of steric hindrance. The largest group on the three membered ring is the Ts group and this will prefer to be *anti* to the other substituents to minimise 1,2 steric interactions. Thus, the remaining two groups are *cis* to each other.

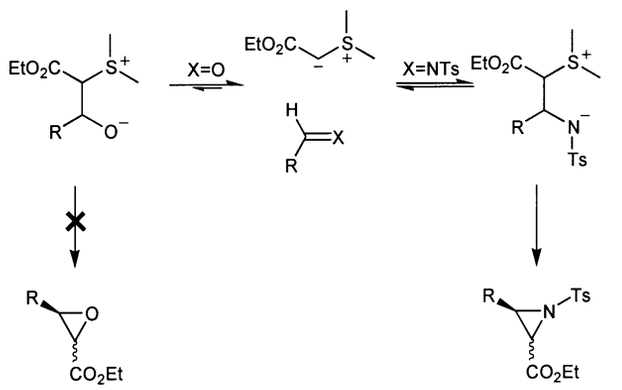
Interestingly, sulfur ylides stabilised by ester groups are too stable and do not react with aldehydes[38] but evidently are sufficiently reactive to react with activated imines. This difference in reactivity between the two electrophiles can be ascribed to the difference in position of the equilibria for betaine formation. As epoxides are not obtained there must be at least a

Table 9 Reaction of different diazo-compounds with *N*-Ts benzaldimine using chiral sulfide **5**



Entry	R [a]	X	*trans* : *cis* [b]	Yield (%)	Ee (%) [c]
1	*p*-$MeOC_6H_4$	OEt	2 : 3	53	45
2	Ph	OEt	1 : 3	80 [d]	58
3	*p*-ClC_6H_4	OEt	1 : 5	72	54
4	*p*-$NO_2C_6H_4$	OEt	1 : 12	83	56
5	C_6H_{11}	OEt	1 : 11	76	44
6	Ph	NEt_2	1 : 1	98	30

[a] All reactions were performed with 1 mol% $Rh_2(OAc)_4$, 1 eq. of chiral sulfide **5**, 1.5 eq. of diazo compound in THF at 60 °C. [b] Diastereomeric ratios were determined by ^{1}H NMR of the crude reaction mixture. [c] Ee of *cis* aziridine determined by HPLC using a Chiralcel OD column. [d] 0.2 eq. of chiral sulfide **5**.



Scheme 10 Stabilised ylide reacting with aldehyde/imine.

factor of 10^2 difference in the position of the equilibrium relative to imines (Scheme 10). The weaker π-bond strength of imines relative to aldehydes (average bond strengths: 296 *vs.* 372 kJ mol^{-1} respectively [39]) together with the lower pK_a of NH_2Ts relative to $HOPr^i$ (16.1 and 30.25 respectively in DMSO [40]) will both contribute to a greater equilibrium concentration of betaine in the case of the reaction with imines relative to aldehydes. Clearly the position of the equilibrium will also be affected by reaction conditions. Indeed, Dai and co-workers have reported that no reaction occurred between the same ester-stabilised sulfonium ylide and imine in the presence of metal salts.[41]

Unfortunately, oxathiane **3** was not compatible with the use of these more stable diazo compounds. However, 2,5-dimethyltetrahydrothiophene **5** [29] was a suitable catalyst and moderate enantioselectivity was obtained with a range of imines (Table 9).

Diazoacetamides were also successfully used in the aziridination process but only low selectivity with chiral sulfide **5** was observed (Table 9, entry 6). Alternative chiral sulfides are clearly required for the asymmetric aziridination process with these more stable diazo-compounds.

Conclusion

We have found that imines bearing electron-withdrawing groups on nitrogen are excellent substrates for aziridination using phenyldiazomethane and catalytic quantities of $Rh_2(OAc)_4$ and sulfides (*e.g.* Me_2S). This provides a versatile and general route to a range of aziridines bearing a variety of groups on nitrogen. As many of these groups are readily cleaved (SES, $POPh_2$, CO_2Bn, CO_2Bu^t, $CO_2(CH_2)_2SiMe_3$, $CO_2C(CH_3)_2CCl_3$) this process offers certain advantages over alkene aziridination where the Ts group is usually the group attached to nitrogen. Considerable variation in diastereoselectivity was observed in relation to the activating group on nitrogen, with alkoxycarbonyl groups providing higher diastereoselectivity than the much larger sulfonyl or phosphinyl groups. This improved diastereoselectivity has been rationalised by considering the steric interactions present in the transition state.

The chiral 1,3-oxathiane **3** was tested in the aziridination process and good yields and high enantioselectivities were achieved with a range of *N*-SES imines. $Rh_2(OAc)_4$ provided slightly higher enantioselectivities than $Cu(acac)_2$ especially when substoichiometric loadings of sulfide were employed. This was believed to be due to a small amount of direct addition of the copper carbenoid to the imine, a reaction that can begin to compete with ylide formation at low sulfide concentrations. The same sulfide was also employed with imines bearing a variety of activating groups. Good yields and high enantioselectivities were maintained and as with simple sulfides, improved diastereoselectivities were observed with alkoxycarbonyl groups.

Extension of the methodology to include the use of diazoesters and diazoacetamides with tetrahydrothiophene was also successful. *N*,*N*-Diethyldiazoacetamide gave predominantly *trans*-aziridines whilst ethyl diazoacetate gave *cis*-aziridines preferentially. The *cis* selectivity is due to the reversible addition of the ester-stabilised ylide to the imine, which leads to the thermodynamically more stable *cis*-aziridine. Although the 1,3-oxathiane **3** was not a suitable sulfide with these more stable diazo-compounds, *trans*-(*R*,*R*)-2,5-dimethylthiolane provided the corresponding compounds in good yield and with moderate enantioselectivity.

The process described herein provides a potentially useful method for the asymmetric aziridination of imines using phenyldiazomethane, although new chiral sulfides are required to extend this asymmetric process to include diazoesters and diazoacetamides. Nevertheless we have demonstrated that it is possible to use such diazo-compounds in this catalytic process, thus providing access to more functionalised aziridines.

Experimental

Flash chromatography was performed on silica gel (Merck Kiesegel 60 F_{254} 230–400 mesh) and TLC on aluminium backed silica plates (60 F_{254}). Melting points were determined on a Köfler hot stage. Infrared spectra were recorded on a Perkin-Elmer 157G Grating FT-IR spectrometer. Only selected absorbances (ν_{max}) are reported. ^{1}H NMR spectra were recorded at either 250 or 400 MHz, on Bruker AC-250 or Bruker AM-400 instruments, respectively. Chemical shifts (δ_H) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak, and *J* values are given in Hz. ^{13}C NMR spectra were recorded at either 63 or 101 MHz on Bruker AC-250 or Bruker AM-400 instruments, respectively. Chemical shifts (δ_C) are quoted in parts per million (ppm), referenced to the appropriate solvent peak. Low resolution mass spectra (*m*/*z*) were recorded on either VG Platform or VG Prospec spectrometers, with only molecular ions (M^+), and major peaks being reported with intensities quoted as percentages of the base peak. High-resolution mass spectra were recorded on a VG Prospec spectrometer. Microanalyses were performed using a Perkin Elmer 2400 CHN elemental analyzer.

General procedure for the preparation of aziridines using phenyldiazomethane

To a stirred solution of sulfide (1.0 or 0.2 eq., 0.5 or 0.1 mmol),

rhodium acetate (0.01 eq., 5 μmol) or copper acetoacetate (0.05 eq., 25 μmol) and imine (1.0 eq., 0.5 mmol) in solvent (0.5 mL), was added a solution of phenyldiazomethane (1.5 eq., 0.75 mmol) in solvent (0.5 mL) at room temperature *via* syringe pump over 3 hours. After a further hour, the solvent was removed *in vacuo* and the residue absorbed onto silica gel. Chromatography, eluting with petroleum ether–EtOAc gave the corresponding aziridine.

***N*-Tosyl-2,3-diphenylaziridine.**[7] White solid as a mixture of *cis* and *trans*. *trans*: R_f 0.30 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 2.38 (3H, s, ArCH_3), 4.24 (2H, s, 2 × CHPh), 7.00–7.10 (10H, m, Ar), 7.34 (2H, m, Ar), 7.98 (2H, m, Ar). *cis*: R_f 0.32 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 2.42 (3H, s, ArCH_3), 4.21 (2H, s, 2 × CH), 7.22 (2H, m, Ar), 7.30–7.44 (10H, m, Ar), 7.60 (2H, m, Ar).

***N*-(β-Trimethylsilylethylsulfonyl)-2,3-diphenylaziridine.** White solid as a mixture of *cis* and *trans* (Found: C, 63.63; H, 6.87; N, 3.91. $C_{19}H_{25}NO_2SSi$ requires C, 63.61; H, 6.96; 3.90%); ν_{max}(KBr)/cm^{-1} 1246 ($Si(CH_3)_3$), 1142 (SO_2N); *m/z* (EI) 359 (M^+, 20%), 344 (96, $M^+ - CH_3$), 196 (100, $M^+ - SES$), 73 ($Si(CH_3)_3$, 100). *trans*: R_f 0.35 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 0.01 (9H, s, Si(CH_3)$_3$), 0.93–1.20 (2H, m, CH_2Si), 2.95–3.10 (2H, m, SO_2CH_2), 4.26 (2H, s, 2 × CH), 7.35–7.60 (10H, m, Ar); δ_C(63 MHz; $CDCl_3$) −2.1, 9.8, 50.6, 51.6, 128.1, 128.6, 128.9, 133.4. *cis*: R_f 0.37 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 0.13 (9H, s, Si(CH_3)$_3$), 1.16–1.25 (2H, m, $CH_2Si(CH_3)_3$), 3.15–3.25 (2H, m, SO_2CH_2), 4.27 (2H, s, 2 × CH), 7.32–7.59 (10H, m, Ar).

***N*-(β-Trimethylsilylethylsulfonyl)-2-(*p*-chlorophenyl)-3-phenylaziridine.** White solid as a mixture of *cis* and *trans* (Found: C, 57.73; H, 6.16; N, 3.32. $C_{19}H_{24}ClNO_2SSi$ requires C, 57.94; H, 6.10; 3.56%); ν_{max}(KBr)/cm^{-1} 1250 ($Si(CH_3)_3$), 1143 (SO_2N); *m/z* (FAB) 394 (M^+, 21%), 228 (100, $M^+ - SES$) (Found: M^+, 394.1071. $C_{19}H_{25}ClO_2SSi$ requires 394.1064). *trans*: R_f 0.40 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 0.01 (9H, s, Si(CH_3)$_3$), 1.15–1.19 (2H, m, CH_2Si), 2.96–3.08 (2H, m, SO_2CH_2), 4.15 (1H, d, *J* 5, CHCH), 4.22 (1H, d, *J* 5, CHCH), 7.10–7.28 (2H, m, Ar), 7.35–7.54 (7H, m, Ar); δ_C(63 MHz; $CDCl_3$) −2.1, 9.7, 50.1, 50.3, 51.5, 127.9, 128.8, 129.0, 129.7, 133.2. *cis*: R_f 0.42 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 0.14 (9H, s, Si(CH_3)$_3$), 0.76–1.30 (2H, m, CH_2Si), 3.24–3.35 (2H, m, SO_2CH_2), 4.15–4.28 (2H, m, 2 × CH), 7.35–7.62 (9H, m, Ar).

***N*-(β-Trimethylsilylethylsulfonyl)-2-(*p*-methylphenyl)-3-phenylaziridine.** White solid as a mixture of *cis* and *trans* (Found: C, 64.17; H, 7.05; N, 3.66. $C_{20}H_{27}NO_2SSi$ requires C, 64.34; H, 7.24; 3.75%); ν_{max}(KBr)/cm^{-1} 1170 (SO_2N), 918 ($Si(CH_3)_3$). *trans*: *m/z* (FAB) 374 (M^+, 21%), 208 (100, $M^+ - SES$) (Found: M^+, 374.1617. $C_{20}H_{27}NO_2SSi$ requires 374.1610); δ_H(250 MHz; $CDCl_3$) 0.00 (9H, s, Si(CH_3)$_3$), 0.90–1.15 (2H, m, CH_2Si), 2.42 (3H, s, $ArCH_3$), 2.96–3.18 (2H, m, SO_2CH_2), 4.18 (1H, d, *J* 5, CHCH), 4.28 (1H, d, *J* 5, CHCH), 7.25 (2H, m, Ar), 7.31–7.58 (7H, m, Ar); δ_C(63 MHz; $CDCl_3$) −2.1, 9.7, 21.3, 49.9, 51.1, 51.4, 127.9, 128.3, 128.6, 128.7, 129.3. *cis*: *m/z* (FAB) 208 ($(M - SES)^+$, 100) (Found: M^+, 374.1617. $C_{20}H_{27}NO_2SSi$ requires 374.1610); δ_H(250 MHz; $CDCl_3$) 0.14 (9H, s, Si(CH_3)$_3$), 1.14–1.23 (2H, m, CH_2Si), 2.22 (3H, s, $ArCH_3$), 3.13–3.22 (2H, m, SO_2CH_2), 4.20 (1H, d, *J* 7, CHCH), 4.30 (1H, d, *J* 7, CHCH), 6.90–7.18 (9H, m, Ar); δ_C(63 MHz; $CDCl_3$) −2.0, 9.8, 21.1, 46.9, 47.1, 49.1, 127.7, 127.8, 128.1, 128.8, 129.0, 132.2, 137.6.

***N*-(β-Trimethylsilylethylsulfonyl)-2-phenyl-3-[(*E*)-2-phenyleth-1-enyl]aziridine.** White solid as a mixture of *cis* and *trans* (Found: C, 65.26; H, 7.07; N, 3.85. $C_{21}H_{27}NO_2SSi$ requires C, 65.41; H, 7.05; N, 3.63%); ν_{max}(KBr)/cm^{-1} 1141 (SO_2N), 969 ($Si(CH_3)_3$); *m/z* (EI) 385 (M^+, 25%), 220 (100, $M^+ - SES$) (Found: M^+, 385.1524. $C_{21}H_{27}NO_2SSi$ requires 385.1532). *trans*: R_f 0.48 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 0.00 (9H, s, Si(CH_3)$_3$), 1.00–1.35 (2H, m, CH_2Si), 3.00–3.30 (2H, m, SO_2CH_2), 3.50 (1H, dd, *J* 10, 4, PhHC=CH-HCCHPh), 4.05 (1H, d, *J* 4, PhHC=CH-HCCHPh), 6.55 (1H, dd, *J* 14, 10, PhHC=CH-HCCHPh), 6.90 (1H, d, *J* 14, PhHC=CHCCHPh), 7.20–7.50 (10H, m, Ar); δ_C(63 MHz; $CDCl_3$) −2.1, 9.9, 48.9, 50.9, 54.5, 122.2, 126.3, 126.8, 128.3, 128.5, 128.6, 128.8, 137.7. *cis* R_f 0.49 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 0.10 (9H, s, Si(CH_3)$_3$), 1.00–1.35 (2H, m, CH_2Si), 3.10–3.25 (2H, m, SO_2CH_2), 3.50 (1H, m, PhHC=CH-HCCHPh), 4.05 (1H, d, *J* 7, PhHC=CH-HCCHPh), 6.55 (1H, dd, *J* 12, 10, PhHC=CH-HCCHPh), 6.90 (1H, d, *J* 12, PhHC=CHCCHPh), 7.20–7.50 (10H, m, Ar).

***N*-(β-Trimethylsilylethylsulfonyl-2-*tert*-butyl-3-phenylaziridine.** *trans* as a white solid: R_f 0.45 (90 : 10 petroleum ether–EtOAc); mp 110 °C; ν_{max}(KBr)/cm^{-1} 1313 (SO_2N), 1252 ($Si(CH_3)_3$), 1144 (SO_2N), 952 ($Si(CH_3)_3$); δ_H(250 MHz; $CDCl_3$) 0.00 (H, s, Si(CH_3)$_3$), 1.04 (9H, s, C(CH_3)$_3$), 1.04–1.15 (2H, m, CH_2Si), 2.75–2.88 (2H, m, SO_2CH_2), 3.46 (1H, d, *J* 4, CHCH), 3.75 (1H, d, *J* 4, CHCH), 7.30–7.36 (3H, m, Ar), 7.45–7.52 (2H, m, Ar); δ_C(62.9 MHz; $CDCl_3$) (one quaternary carbon signal not visible) −2.1, 9.6, 26.5, 48.3, 50.5, 53.3, 128.2, 129.0, 130.1; *m/z* (CI) 340 (MH^+, 44%), 324 (51, $M^+ - CH_3$), 174 (100, $M^+ - SES$), 73 ($Si(CH_3)_3$, 98) (Found: MH^+, 340.1759. $C_{17}H_{30}NO_2SiS$ requires *m/z*, 340.1767). *cis*: R_f 0.59 (90 : 10 petroleum ether–ethyl acetate); δ_H(250 MHz; $CDCl_3$) 0.00 (9H, s, Si(CH_3)$_3$), 0.72 (9H, s, C(CH_3)$_3$), 1.20–1.27 (2H, m, CH_2Si), 2.72 (1H, d, *J* 6, CHCH), 3.08–3.15 (2H, m, SO_2CH_2), 3.78 (1H, d, *J* 6, CHCH), 7.20–7.38 (5H, m, Ar); δ_C(63 MHz; $CDCl_3$) −2.0, 9.9, 27.7, 32.1, 46.0, 48.8, 53.4, 127.6, 128.0, 128.3, 128.7.

***N*-(β-Trimethylsilylethylsulfonyl)-2-cyclohexyl-3-phenylaziridine.** *trans* as a white solid: R_f 0.37 (15 : 1 petroleum ether–EtOAc); mp 110–112 °C (Found: C, 62.39; H, 8.78; N, 3.74. $C_{19}H_{31}NO_2SSi$ requires C, 62.42; H, 8.55; N, 3.83%); ν_{max}($CDCl_3$)/cm^{-1} 1320 (SO_2N), 1253 ($Si(CH_3)_3$), 1142 (SO_2N); δ_H(250 MHz; $CDCl_3$) 0.00 (9H, s, Si(CH_3)$_3$), 0.90–2.10 (12H, m), 2.38–2.50 (1H, m, CH_2CHCH_2), 2.72 (1H, dd, *J* 8, 4, PhCHCH), 3.05–3.14 (2H, m, SO_2CH_2), 3.70 (1H, d, *J* 4, PhCHCH), 7.28–7.45 (5H, m, Ar); δ_C(101 MHz; $CDCl_3$) −2.2, 10.0, 25.3, 25.6, 26.0, 31.5, 32.1, 37.8, 47.8, 51.1, 58.3, 126.4, 128.2, 128.6, 135.7; *m/z* (CI) 366 (MH^+, 80%), 350 (75, $M^+ - CH_3$), 200 (100) (Found: MH^+, 366.1927. $C_{19}H_{32}NO_2SSi$ requires 366.1923). *cis* as a colourless oil: R_f 0.31 (15 : 1 petroleum ether–EtOAc); ν_{max}($CDCl_3$)/cm^{-1} 2931, 1322 (SO_2N), 1253 ($Si(CH_3)_3$), 1142 (SO_2N); δ_H(250 MHz; $CDCl_3$) 0.00 (9H, s, Si(CH_3)$_3$), 0.85–1.60 (9H, m), 1.65–1.74 (1H, m), 1.75–1.92 (1H, m), 2.05–2.12 (1H, m), 2.18–2.28 (1H, m), 2.73 (1H, dd, *J* 8, 6, PhCHCH), 3.06–3.14 (2H, m, SO_2CH_2), 3.84 (1H, d, *J* 6, PhCHCH), 7.25–7.31 (5H, m, Ar); δ_C(101 MHz; $CDCl_3$), −2.1, 9.8, 25.1, 25.2, 26.0, 29.0, 31.2, 34.5, 45.9, 48.7, 50.2, 127.3, 128.3, 133.1; *m/z* (CI) 366 (MH^+, 80%), 350 (100, $M^+ - CH_3$) (Found: MH^+, 366.1926. $C_{19}H_{32}NO_2SSi$ requires 366.1923).

***N*-Benzyl-*N*-cyclohexylidenemethyl-2-trimethylsilylethanesulfonamide (4).** White solid: R_f 0.31 (15 : 1 petroleum ether–EtOAc); mp 110–112 °C; ν_{max}($CDCl_3$)/cm^{-1} 1333 (SO_2N), 1252 ($Si(CH_3)_3$), 1143 (SO_2N) (Found: C, 62.19; H, 8.68; N, 3.35. $C_{19}H_{31}NO_2SSi$ requires C, 62.42; H, 8.55; N, 3.83%); δ_H(250 MHz; $CDCl_3$) 0.00 (9H, s, Si(CH_3)$_3$), 1.01 (2H, m, SiCH_2), 1.06–1.43 (6H, m, $CH_2CH_2CH_2CH_2CH_2$), 1.94–2.04 (4H, m, CH_2CCH_2), 2.87 (2H, m, SO_2CH_2), 4.38 (2H, s, CH_2N), 5.40 (1H, br s, CHN), 7.23–7.31 (5H, m, Ar); δ_C(63 MHz; $CDCl_3$) −1.9, 9.9, 26.2, 26.6, 27.9, 28.7, 33.2, 46.9, 54.9, 117.2, 127.7,

128.3, 129.2, 136.5, 148.4 (Ar); *m/z* (EI) 365 (M^+, 29%), 200 (59), 91 ($C_7H_7^+$, 82), 73 ($Si(CH_3)_3$, 100) (Found: M^+, 365.1843. $C_{19}H_{31}NO_2SSi$ requires 365.1845).

***N*-Diphenylphosphinoyl-2,3-diphenylaziridine.** White solid as a mixture of *cis* and *trans*. ν_{max}(KBr)/cm^{-1} 1204 (P=O); *m/z* (FAB) 396 (MH^+, 100%) (Found: MH^+ 396.1514. $C_{26}H_{23}NOP$ requires 396.1517). *trans*: R_f 0.24 (95 : 5 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 4.10 (2H, d, *J* 15, 2 × PhC*H*), 7.23–7.54 (16H, m, Ar), 7.55–7.66 (2H, m, Ar), 7.81–7.95 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) 47.1, 47.2, 127.8, 128.0, 128.1, 128.2, 128.4, 128.6, 131.3, 131.5, 131.6, 131.8, 132.1; δ_P(250 MHz; $CDCl_3$) 28.1. *cis*: R_f 0.26 (95 : 5 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 4.23 (2H, d, *J* 16, 2 × C*H*Ph), 7.23–7.54 (20H, m, Ar); δ_P(250 MHz; $CDCl_3$) 34.0.

***N*-(Methoxycarbonyl)-2,3-diphenylaziridine.** Viscous colourless oil as a mixture of *cis* and *trans*. ν_{max}($CDCl_3$)/cm^{-1} 1700 (C=O); *m/z* (EI) 253 (M^+, 10%), 194 (($M - CO_2Me^+$), 100) (Found: M^+, 253.1105. $C_{16}H_{15}NO_2$ requires 253.1103). *trans*: R_f 0.29 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 3.50 (3H, s, OC*H*$_3$), 3.70 (2H, s, 2 × PhC*H*), 7.20–7.45 (10H, m, Ar); δ_C(63 MHz; $CDCl_3$) 48.4, 53.3, 126.4, 128.2, 128.6, 135.4, 160.9. *cis*: R_f 0.28 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 3.75 (3H, s, OC*H*$_3$), 3.92 (2H, s, C*H*), 7.00–7.20 (10H, m, Ar).

***N*-(Benzyloxycarbonyl)-2,3-diphenylaziridine.** White solid as a mixture of *cis* and *trans* (Found: C, 80.24; H, 5.77; N, 4.25. $C_{22}H_{19}NO_2$ requires C, 80.23; H, 5.96; N, 4.25%); ν_{max}($CDCl_3$)/cm^{-1} 1719 (C=O); *m/z* (EI) 329 (M^+, 10%), 194 (100, $M^+ - CO_2Bn$) (Found: M^+, 329.1414. $C_{22}H_{19}NO_2$ requires 329.1416). *trans*: R_f 0.31 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 3.75 (2H, s, 2 × PhC*H*), 4.95–5.15 (2H, AB system, C*H*$_2$), 6.90 (2H, m, Ar), 7.10–7.40 (13H, m, Ar); δ_C(63 MHz; $CDCl_3$) 48.4, 68.2, 126.6, 126.6, 128.2, 128.3, 128.4, 128.6, 129.2, 135.4, 162.0. *cis*: R_f 0.30 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz, $CDCl_3$) 3.90 (2H, s, 2 × PhC*H*), 5.20 (2H, s, C*H*$_2$), 7.00–7.40 (15H, m, Ar).

***N*-(β-Trimethylsilylethoxycarbonyl)-2,3-diphenylaziridine.** Viscous colourless oil as a mixture of *cis* and *trans*. ν_{max}($CDCl_3$)/cm^{-1} 1714 (C=O); *m/z* (EI) 340 (MH^+, 10%), 194 ($M^+ - CO_2CH_2CH_2SiMe_3$, 100) (Found: M^+, 339.1670. $C_{20}H_{25}NO_2Si$ requires 339.1655). *trans*: R_f 0.32 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz, $CDCl_3$) 0.00 (9H, s, $Si(CH_3)_3$), 0.65–0.95 (2H, m, C*H*$_2$Si), 3.75 (2H, s, 2 × PhC*H*), 4.00–4.25 (2H, m, C*H*$_2$O), 7.25–7.50 (10H, m, Ar); δ_C(63 MHz, $CDCl_3$) −1.6, 17.3, 48.2, 64.9, 126.7, 128.2, 128.6, 129.3, 161.0. *cis*: R_f 0.30 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 0.10 (9H, s, $Si(CH_3)_3$), 1.20–1.45 (2H, m, C*H*$_2$Si), 4.25 (2H, s, 2 × PhC*H*), 4.30–4.45 (2H, m, C*H*$_2$O), 7.15–7.25 (10H, m, Ar).

***N*-(*tert*-Butoxycarbonyl)-2,3-diphenylaziridine.** Colourless viscous oil as a mixture of *cis* and *trans*. ν_{max}($CDCl_3$)/cm^{-1} 1716 (C=O); *m/z* (CI^+) 296 (MH^+, 10%), 219 (100) (Found: M^+, 295.1561. $C_{19}H_{21}NO_2$ requires 295.1572). *trans*: R_f 0.33 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 1.20 (9H, s, $OC(CH_3)_3$), 3.75 (2H, s, 2 × PhC*H*), 7.20–7.30 (10H, m, Ar); δ_C(63 MHz; $CDCl_3$) 27.6, 47.6, 81.4, 127.0, 127.8, 128.5, 135.5, 156.4. *cis*: R_f 0.32 (90 : 10 petroleum ether–EtOAc); δ_H(250 MHz; $CDCl_3$) 1.45 (9H, s, $OC(CH_3)_3$), 3.80 (2H, s, 2 × PhC*H*), 7.00 (15H, m, Ar).

***N*-(2-Trichloromethylisopropoxycarbonyl)-2,3-diphenylaziridine.** Pale yellow viscous oil as a mixture of *cis* and *trans*. ν_{max}($CDCl_3$)/cm^{-1} 1712 (C=O); *m/z* (EI) 397 (M^+, 35%), 194 (100, M^+ − TcBoc) (Found: M^+, 397.0403. $C_{19}H_{18}NO_2Cl_3$ requires 397.0391). *trans*: R_f 0.31 (93 : 7 petroleum ether–EtOAc); δ_H(250 MHz, $CDCl_3$) 1.50 (3H, s, C*H*$_3$), 1.80 (3H, s, C*H*$_3$), 3.76 (2H, s, 2 × PhC*H*), 7.20–7.30 (10H, m, Ar); δ_C(63 MHz, $CDCl_3$) 20.7, 21.2, 48.2, 89.4, 105.6, 128.4, 128.6, 128.8, 135.2, 158.0. *cis*: R_f 0.29 (93 : 7 petroleum ether–EtOAc); δ_H(250 MHz, $CDCl_3$) 1.65 (6H, s, 2 × C*H*$_3$), 3.95 (2H, s, 2 × PhC*H*), 7.10–7.25 (10H, m, Ar).

General procedure for the preparation of aziridines using alternative diazo compounds

To a stirred solution of sulfide (1.0 or 0.2 eq., 0.5 or 0.1 mmol), rhodium acetate (0.01 eq., 5 μmol) and imine (1.0 eq., 0.5 mmol) in THF (0.5 mL), was added a solution of diazo compound (1.5 eq., 0.75 mmol) in THF (0.5 mL) *via* syringe pump over 3 hours at 60 °C. After a further hour, the solvent was removed *in vacuo* and the residue absorbed onto silica gel. Chromatography eluting with petroleum ether–EtOAc gave the corresponding aziridine.

***N*-Tosyl-2-ethoxycarbonyl-3-(4-methoxyphenyl)aziridine.** Viscous colourless oil as a mixture of *cis* and *trans*. R_f 0.30 (90 : 10 petroleum ether–EtOAc); ν_{max}($CDCl_3$)/cm^{-1} 1741 (C=O); *m/z* (EI) 376 (MH^+, 40%), 222 (100) (Found: MH^+, 376.1204. $C_{19}H_{22}NO_5S$ requires 376.1218). *trans*: δ_H(250 MHz; $CDCl_3$) 1.25 (3H, t, *J* 7, C*H*$_3$CH$_2$O), 2.30 (3H, s, C*H*$_3$Ar), 3.75–4.90 (7H, m, C*H*-C*H*, C*H*$_2$CH$_3$, C*H*$_3$O), 6.80 (2H, m, Ar), 7.15 (2H, m, Ar), 7.60 (2H, m, Ar), 7.90 (2H, m, Ar). *cis*: δ_H(250 MHz; $CDCl_3$) 0.95 (3H, t, *J* 7, C*H*$_3$CH$_2$O), 2.32 (3H, s, C*H*$_3$Ar), 3.55 (1H, d, *J* 7, C*H*-CH), 3.65 (3H, s, C*H*$_3$O), 3.75–3.95 (2H, m, C*H*$_2$CH$_3$), 3.98 (1H, d, *J* 7, CH-C*H*), 6.75 (2H, m, Ar), 7.10 (2H, m, Ar), 7.25 (2H, m, Ar), 7.85 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) (quaternary carbons not observed) 13.8, 21.7, 43.5, 45.0, 55.2, 61.5, 113.6, 128.1, 128.7, 129.8.

***N*-Tosyl-2-ethoxycarbonyl-3-phenylaziridine.** Viscous oil as a mixture of *cis* and *trans*. R_f 0.30 (90 : 10 petroleum ether–EtOAc); ν_{max}($CDCl_3$)/cm^{-1} 1743 (C=O); *m/z* (EI) 345 (MH^+, 11%), 190 (100, M^+ − Ts), 117 (87) (Found: M^+, 345.1025. $C_{18}H_{19}NO_4S$ requires 345.1025). *trans*: δ_H(250 MHz; $CDCl_3$) 1.35 (3H, t, *J* 7, C*H*$_3$CH$_2$O), 2.35 (3H, s, C*H*$_3$Ar), 3.45 (1H, d, *J* 4, C*H*CH), 4.15–4.35 (2H, m, C*H*$_2$CH$_3$), 4.40 (1H, d, *J* 4, C*H*CH), 7.10–7.20 (7H, m, Ar), 7.90 (2H, m, Ar). *cis*: δ_H(250 MHz; $CDCl_3$) 0.85 (3H, t, *J* 7, C*H*$_3$CH$_2$O), 2.40 (3H, s, C*H*$_3$-Ar), 3.60 (1H, d, *J* 7, C*H*CH), 3.75–4.00 (2H, m, C*H*$_2$CH$_3$), 4.05 (1H, d, *J* 7, C*H*CH), 7.10–7.20 (5H, m, Ar), 7.25 (2H, m, Ar), 7.90 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) (one quaternary carbon and carbonyl not observed) 14.0, 21.6, 47.1, 47.7, 62.5, 127.4, 127.5, 128.6, 128.9, 129.6, 132.7, 137.2.

***N*-Tosyl-2-ethoxycarbonyl-3-(4-chlorophenyl)aziridine.** Viscous colourless oil as a mixture of *cis* and *trans*. R_f 0.30 (90 : 10 petroleum ether–EtOAc); ν_{max}($CDCl_3$)/cm^{-1} 1744 (C=O); *m/z* (EI) 380 (MH^+, 15%), 226 (100) (Found: MH^+, 380.0724. $C_{18}H_{19}NO_4SCl$ requires 380.0723). *trans*: δ_H(250 MHz; $CDCl_3$) 1.25 (3H, t, *J* 7, C*H*$_3$CH$_2$O), 2.35 (3H, s, C*H*$_3$Ar), 3.45 (1H, d, *J* 4, C*H*-CH), 4.00–4.30 (2H, m, C*H*$_2$CH$_3$) 4.35 (1H, d, *J* 4, CH-C*H*), 7.15–7.25 (6H, m, Ar), 7.70 (2H, m, Ar). *cis*: δ_H(250 MHz; $CDCl_3$) 0.95 (3H, t, *J* 7, C*H*$_3$CH$_2$O), 2.35 (3H, s, C*H*$_3$Ar), 3.55 (1H, d, *J* 7, C*H*-CH), 3.75–3.95 (2H, m, C*H*$_2$CH$_3$), 4.00 (1H, d, *J* 7, CH-C*H*), 7.15 (4H, m, Ar), 7.25 (2H, m, Ar), 7.85 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) (quaternary Ar carbons not observed) 13.8, 21.7, 43.4, 44.5, 61.7, 128.1, 128.4, 128.9, 129.9.

***N*-Tosyl-2-ethoxycarbonyl-3-(4-nitrophenyl)aziridine.** Viscous pale yellow oil as a mixture of *cis* and *trans*. R_f 0.30 (90 : 10 petroleum ether–EtOAc) (Found: C, 53.36; H, 4.80; N, 7.01. $C_{18}H_{18}N_2O_6S$ requires C, 53.38; H, 4.63; N, 7.18%); ν_{max}($CDCl_3$)/cm^{-1} 1741 (C=O); *m/z* (EI) 390 (M^+, 5%), 235 (($M - Ts$)$^+$, 100) (Found: M^+, 390.0900. $C_{18}H_{18}N_2O_6S$ requires 390.0886). *trans*: δ_H(250 MHz; $CDCl_3$) 1.25 (3H, t, *J* 7, C*H*$_3$CH$_2$O), 2.35 (3H, s, C*H*$_3$Ar), 3.45 (1H, d, *J* 4, C*H*-CH),

4.20–4.30 (2H, m, C*H*$_2$CH$_3$), 4.45 (1H, d, *J* 4, C*H*-CH), 7.25–7.50 (6H, m, Ar), 7.75 (2H, m, Ar). *cis*: δ_H(250 MHz; $CDCl_3$) 0.95 (3H, t, *J* 7, CH$_3$CH$_2$O), 2.40 (3H, s, CH$_3$Ar), 3.65 (1H, d, *J* 7, C*H*-CH), 3.75–3.95 (2H, m, C*H*$_2$CH$_3$), 4.00 (1H, d, *J* 7, CH-C*H*), 7.25 (2H, m, Ar), 7.45 (2H, m, Ar), 7.75 (2H, m, Ar), 8.05 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) (quaternary Ar carbons not observed) 13.8, 21.7, 43.4, 44.5, 61.9, 123.4, 128.1, 128.7, 129.9, 163.8.

***N*-Tosyl-2-ethoxycarbonyl-3-cyclohexylaziridine.** Viscous colourless oil as a mixture of *cis* and *trans*. R_f 0.29 (93 : 7 petroleum ether–EtOAc); $\nu_{max}(CDCl_3)/cm^{-1}$ 1746 (C=O); *m*/*z* (CI) 369 (MNH_4^+, 20%), 352 (MH^+, 100) (Found: MH^+, 352.1577. $C_{18}H_{26}NO_4S$ requires 352.1582). *trans*: δ_H(250 MHz; $CDCl_3$) 0.95–1.75 (14H, m, CH$_3$CH$_2$O, Cy), 2.45 (3H, s, CH$_3$Ar), 3.00 (1H, dd, *J* 9, 4, CH$_2$CHCH$_2$), 3.20 (1H, d, *J* 4, C*H*-CH), 3.75–3.95 (3H, m, C*H*$_2$CH$_3$, C*H*-CH), 7.23 (2H, m, Ar), 7.80 (2H, m, Ar). *cis*: δ_H(250 MHz; $CDCl_3$) 1.25 (3H, t, *J* 7, CH$_3$CH$_2$O), 0.95–1.75 (11H, m, Cy), 2.45 (3H, s, CH$_3$Ar), 2.75 (1H, dd, *J* 9, 7, CH$_2$CHCH$_2$), 3.40 (1H, d, *J* 7, C*H*-CH), 3.75–3.95 (2H, q, *J* 7, C*H*$_2$CH$_3$), 7.25 (2H, m, Ar), 7.90 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) (quaternary Ar carbons not observed) 14.1, 21.7, 25.9, 29.5, 31.0, 35.0, 41.0, 49.5, 62.0, 128.3, 129.7, 167.0.

***N*,*N*-Diethyl-1-tosyl-3-phenylaziridine-2-carboxamide.** A viscous colourless oil as a mixture of *cis* and *trans. trans*: $\nu_{max}(CDCl_3)/cm^{-1}$ 1655 (C=O); δ_H(250 MHz; $CDCl_3$) 1.20 (3H, t, *J* 7, CH$_2$CH$_3$), 1.26 (3H, t, *J* 7, CH$_2$CH$_3$), 2.40 (3H, s, CH$_3$Ar), 3.23 (1H, m, NC*H*H), 3.39 (1H, m, NC*H*H), 3.50 (H, d, *J* 4, CH-C*H*), 3.67 (1H, m, NC*H*H), 3.83 (1H, m, NC*H*H), 4.49 (H, d, *J* 4, CH-C*H*), 7.00–7.25 (7H, m, Ar), 7.95 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) 12.4, 21.6, 14.3, 40.6, 42.1, 47.1, 48.4, 127.1, 127.7, 128.5, 128.5, 129.5, 133.5, 136.6, 162.6 (one quaternary Ar carbon not observed); *m*/*z* (EI) 372 (M^+, 10%), 91 ($C_7H_7^+$, 100) (Found: MH^+, 372.1506. $C_{20}H_{24}N_2O_3S$ requires 372.1508). *cis*: $\nu_{max}(CDCl_3)/cm^{-1}$ 1655; δ_H(250 MHz; $CDCl_3$) 0.65 (3H, t, *J* 7, CH$_2$CH$_3$), 0.95 (3H, t, *J* 7, CH$_2$CH$_3$), 2.35 (3H, s, CH$_3$Ar), 2.85 (1H, m, NC*H*H), 3.00 (1H, m, NC*H*H), 3.27–3.40 (2H, m, NC*H*$_2$), 3.68 (H, d, *J* 8, CH-C*H*), 4.05 (H, d, *J* 8, CH-C*H*), 7.00–7.25 (5H, m, Ar), 7.25 (2H, m, Ar), 7.90 (2H, m, Ar); δ_C(63 MHz; $CDCl_3$) 12.2, 14.1, 21.8, 39.8, 41.1, 45.1, 46.0, 127.2, 127.9, 128.2, 128.5, 129.8, 131.8, 134.5, 144.8 (carbonyl carbon not observed); *m*/*z* (EI) 372 (M^+, 10%), 207 (100) (Found: MH^+, 372.1502. $C_{20}H_{24}N_2O_3S$ requires 372.1508).

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