Lithiation-electrophilic trapping of *N*-sulfonyl-activated ethylene aziridines†

Jianhui Huang,[a] Stephen P. Moore,[a] Peter O'Brien,*[a] Adrian C. Whitwood‡[a] and John Gilday[b]

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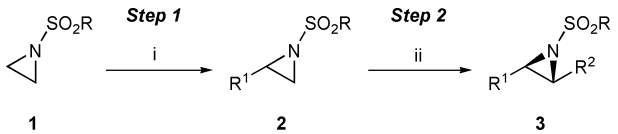
A detailed study on the lithiation-electrophilic trapping of *N*-sulfonyl ethylene aziridines is described. The optimum results required use of a *N*-2,4,6-tri-*iso*-propylbenzenesulfonyl activating group and lithiation using 3 equiv. of *s*-BuLi–PMDETA for 1 minute before addition of the electrophile. *In situ* trapping with Me_3SiCl was also successful. Electrophilic trapping with aldehydes provided a stereoselective route to *syn*-hydroxy aziridines. Alternatively, keto aziridines could be stereoselectively reduced to *syn*-hydroxy aziridines using $NaBH_4$–$CeCl_3$. The relative stereochemistry in two of the hydroxy aziridines was established unequivocally by X-ray crystallography.

Introduction

Deprotonation and subsequent electrophilic trapping is one of the fundamental strategies for the construction of organic molecules. Within the context of our ongoing studies into the chemistry of lithiated aziridines,[1–7] we envisaged a new strategy for the synthesis of *trans*-1,2-disubstituted aziridines **3** starting from *N*-sulfonyl-activated ethylene aziridines **1** (Scheme 1). In step 1, lithiation-trapping of ethylene aziridines **1** would be carried out to give monosubstituted aziridines **2**. Then, in step 2, lithiation-trapping at the terminal end of aziridines **2** should afford disubstituted aziridines **3**. In 2005, Hodgson *et al.* reported a detailed study on step 2 for the conversion of *N*-Bus activated aziridines **2** into **3** (Bus = *tert*-butylsulfonyl) where R^1 = alkyl and R^2 = $SiMe_3$, D, $SnBu_3$, $C(OH)R^3R^4$, $C(O)R^3$ and SO_2Ph.[8] However, at the outset of our studies, much less was known about the lithiation-trapping of ethylene aziridines **1** (step 1).



Scheme 1 *Reagents and conditions:* i, (a) Base; (b) R^{1+}. ii, (a) Base, R^{2+}.

To the best of our knowledge, there are three previous reports on the lithiation-trapping of ethylene aziridines. In 1994, Beak *et al.* described the lithiation (*s*-BuLi, TMEDA, Et_2O, –78 °C) and *in situ* Me_3SiCl-trapping of *N*-Boc aziridine **4** (80% yield of silylated aziridine).[9] Attempts at external trapping of *N*-Boc aziridine **4** were unsuccessful. Then, in 1997, Vedejs and Kendall reported the lithiation of aziridine borane **5** using *s*-BuLi in THF at –78 °C and subsequent trapping with a range of electrophiles (50–95% yields).[10] An asymmetric variant (*ca* 85 : 15 er) was subsequently optimised using *s*-BuLi–(–)-sparteine-mediated deprotonation.[11] Finally, in 2008, Hodgson *et al.* reported the successful lithiation-external trapping of *N*-*tert*-butylsulfinyl aziridine **6** (LTMP, TMEDA, THF, –98 °C; 52–81% yields) and *N*-Bus aziridine **7** (*s*-BuLi, TMEDA, THF, –105 °C; 51–96% yields).[12] These results demonstrate that the lithiation-trapping of *N*-sulfonyl, *N*-sulfinyl and *N*-Boc ethylene aziridines is not straightforward and either required use of *in situ* electrophilic trapping (with its associated limitations on compatible electrophiles) or temperatures of *ca.* –100 °C. As a result, our attention focused on developing useful lithiation conditions for *N*-sulfonyl ethylene aziridines (step 1).

In this paper, we report our studies on the lithiation-trapping of *N*-sulfonyl aziridines **7–9** (Fig. 1). In particular, we have developed a convenient protocol for the lithiation-trapping of a *N*-Tris-activated ethylene aziridine **9** (Tris = 2,4,6-tri-*iso*-propylbenzenesulfonyl), and show its synthetic potential with a stereoselective route to *syn*-hydroxy aziridines. Of note, our methodology requires neither an *in situ* electrophilic trap nor inconveniently low temperatures (*ca.* –100 °C).

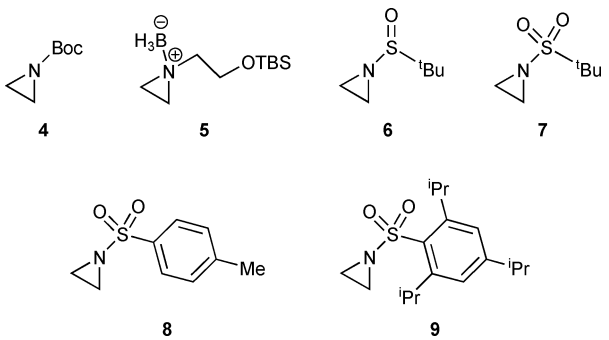


Fig. 1 Selection of *N*-activated ethylene aziridines.

Results and discussion

Initially, we decided to compare the lithiation-trapping of *N*-sulfonyl aziridines **7–9** equipped with *tert*-butylsulfonyl (Bus),

[a]*Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: paob1@york.ac.uk; Fax: +44 1904 432516; Tel: +44 1904 432535*
[b]*AstraZeneca, Process R & D, Avlon Works, Severn Road, Hallen, Bristol, UK BS10 7ZE*

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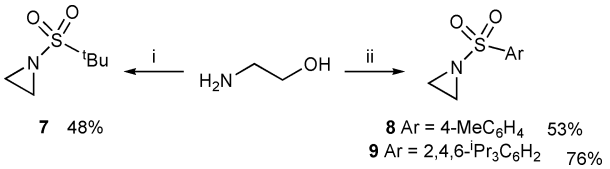
‡ Author to whom correspondence regarding the X-ray crystal structure should be addressed.

4-methylbenzenesulfonyl (Ts) and 2,4,6-tri-*iso*-propylbenzenesulfonyl (Tris) activating groups. *N*-Sulfonyl aziridines **7–9** were synthesised from ethanolamine as outlined in Scheme 2. Using a protocol for the preparation of a related *N*-Bus aziridine,[13] *N*- and *O*-sulfinylation of ethanolamine was accomplished using *t*-BuSOCl.[14] Then, *m*-CPBA oxidation was followed by base-mediated cyclisation to give *N*-Bus aziridine **7** (48% yield of 3 steps). A different procedure was used for the preparation of the arylsulfonyl aziridines **8** and **9**. *N*-Sulfonylation of ethanolamine was followed by a two-step procedure of *O*-mesylation and cyclisation.[15,16]



Scheme 2 *Reagents and conditions:* i, (a) 2.2 eq ^{t}BuSOCl, 5 : 1 MeCN–DMF, Et_3N, 0 °C → rt, 16 h; (b) 2.2 eq *m*-CPBA, CH_2Cl_2, rt, 16 h; (c) K_2CO_3, MeCN, reflux, 16 h. ii, (a) 1.0 eq $ArSO_2Cl$, CH_2Cl_2, Et_3N, 0 °C → rt, 16 h; (b) Py, MsCl, CH_2Cl_2, reflux, 6 h; (c) K_2CO_3, MeCN, reflux, 16 h.

To start with, aziridines **7–9** were compared in the lithiation-Me_3SiCl *in situ* trapping using *s*-BuLi and PMDETA (PMDETA = pentamethyldiethylenetriamine) (Table 1). *s*-BuLi and PMDETA (3 equiv. of each) were premixed in THF at −78 °C and then added to the aziridine and Me_3SiCl in THF at −78 °C. The reactions were quenched with $NH_4Cl_{(aq)}$ after 1 hour. Under these conditions, the highest yield of silylated aziridine was obtained using the *N*-Tris-activated aziridine **9** (66% yield of **12**, entry 3). Use of the *N*-Bus aziridine **7** gave 50% recovered starting material (entry 1). The *N*-Ts aziridine **8** suffered from competing *ortho*-lithiation of the arylsulfonyl group and a doubly silylated adduct **11** was generated in 22% yield (entry 2). *ortho*-Lithiation of arylsulfonyl groups is precedented by ourselves[15] and others.[17]

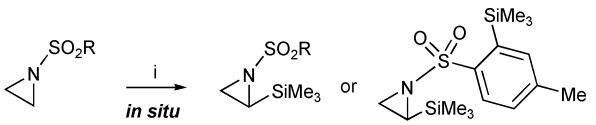
Next, we attempted to increase the yield for silylation of *N*-Tris aziridine **9**. Use of (−)-sparteine in place of PMDETA as the ligand gave a 12% yield of silyl aziridine **12** and 52% recovered starting material (entry 4), clearly showing that PMDETA is the preferred ligand. The enantiomeric ratio (er) of silyl aziridine **12** generated from the *s*-BuLi–(−)-sparteine reaction was not determined but lithiations using *s*-BuLi–(−)-sparteine in THF generally give low levels of enantioselectivity, as we have previously demonstrated in an aziridine lithiation process.[3]

After the 1 hour lithiation time at −78 °C, there was no improvement in silylation either by leaving the reaction for another 3 hours at −78 °C (63% yield of **12**, entry 5) or by allowing the reaction to warm to room temperature over 3 hours (58% yield of **12**, entry 6). Finally, the use of 3 equiv. of *s*-BuLi–PMDETA was optimal: lowering the amount of *s*-BuLi–PMDETA to 1.2 equiv. gave only a 28% yield of **12** and 59% starting material (entry 7). Overall, the best lithiation-silylation conditions involved using *N*-Tris aziridine **9** and 3 equiv. of each of *s*-BuLi, PMDETA and Me_3SiCl which gave a 66% yield of silyl aziridine **12** (entry 3). It is notable that, under these *in situ* trapping conditions, significant amounts of starting aziridines **7–9** were recovered from the reactions.

We then optimised conditions for the lithiation-silylation of *N*-Tris aziridine **9** under *external* trapping conditions, a more synthetically appealing protocol. The procedure adopted was as follows: *s*-BuLi and ligand (PMDETA, TMEDA or (−)-sparteine) were premixed in THF at −78 °C and then added to a solution of the aziridine in THF at −78 °C. After 1 minute, Me_3SiCl was added and the reactions were quenched with $NH_4Cl_{(aq)}$ after 1 hour. The results are summarised in Table 2.

Under the standard external trapping conditions, 3 equiv. of *s*-BuLi–PMDETA was optimal and a 94% yield of silyl aziridine

Table 1 *In situ* lithiation-Me_3SiCl trapping of *N*-sulfonyl activated aziridines **7–9**



7 R = ^{t}Bu
8 R = 4-MeC_6H_4
9 R = 2,4,6-$^{i}Pr_3C_6H_2$

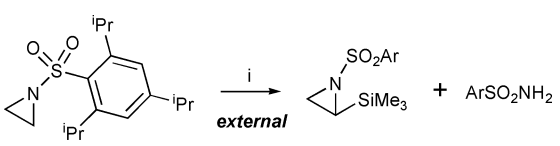
10 R = ^{t}Bu
12 R = 2,4,6-$^{i}Pr_3C_6H_2$

11

Entry[a]	SM[b]	R	Prod[c]	Yield (%)[d]	Yield of SM (%)[e]
1	**7**	*t*-Bu	**10**	36	50
2	**8**	4-MeC_6H_4	**11**	22	22
3	**9**	2,4,6-*i*-$Pr_3C_6H_2$	**12**	66	28
4[f]	**9**	2,4,6-*i*-$Pr_3C_6H_2$	**12**	12[g]	52
5[h]	**9**	2,4,6-*i*-$Pr_3C_6H_2$	**12**	63	30
6[i]	**9**	2,4,6-*i*-$Pr_3C_6H_2$	**12**	58	18
7[j]	**9**	2,4,6-*i*-$Pr_3C_6H_2$	**12**	28	59

[a] Reaction conditions: i, 3 eq *s*-BuLi–PMDETA, 3 eq Me_3SiCl, THF, −78 °C, 1 h (*in situ*). [b] SM = starting material. [c] Prod = product. [d] Yield of product after chromatography. [e] Yield of recovered starting material after chromatography. [f] Reaction carried out using (−)-sparteine in place of PMDETA. [g] Enantiomeric ratio (er) not determined. [h] Reaction left at −78 °C for 4 h. [i] Reaction allowed to warm to rt over 3 h. [j] Reaction carried out using 1.2 eq *s*-BuLi–PMDETA.

Table 2 *External* lithiation-Me_3SiCl trapping of *N*-sulfonyl activated aziridine **9**



9 **12** **13**

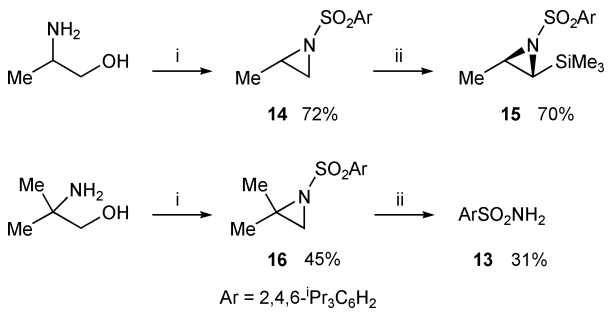
Ar = 2,4,6-$^{i}Pr_3C_6H_2$

Entry[a]	Equiv. of *s*-BuLi–ligand	Ligand	Yield of **12** (%)[b]	Yield of **13** (%)[b]	Yield of SM (%)[b,c]
1	3.0	PMDETA	94	0	0
2	2.5	PMDETA	46	0	40
3	1.2	PMDETA	0	0	—[d]
4[e]	3.0	PMDETA	0	78	0
5	3.0	TMEDA	34	62	0
6	2.5	TMEDA	22	54	0
7	1.5	TMEDA	0	0	—[d]
8[f]	3.0	(−)-Sparteine	0	0	—[d]

[a] Reaction conditions: i, (a) *s*-BuLi–ligand, THF, −78 °C, 1 min; (b) 3 eq Me_3SiCl, −78 °C, 1 h (*external*). [b] Yield of product after chromatography. [c] SM = starting material. [d] The ^{1}H NMR spectrum of the crude product showed only starting material. [e] Reaction left at −78 °C for 15 minutes after lithiation (instead of 1 minute). [f] Reaction carried out in Et_2O.

12 was obtained (entry 1). Reducing the amount of *s*-BuLi–PMDETA gave lower yields of silyl aziridine **12** and significant amounts of (presumably unreacted) starting material (entries 2–3). Notably, a very short lithiation time (1 minute) before addition of Me_3SiCl was necessary. When the lithiation time was extended to 15 minutes, 2,4,6-*i*-$Pr_3C_6H_2SO_2NH_2$ **13** was produced as the only isolable product (78% yield, entry 4). Clearly, the lithiated aziridine intermediate is not stable in the presence of excess *s*-BuLi: it likely undergoes carbenoid insertion into the organolithium reagent and loss of $TsNLi_2$ (reductive alkylation)[1] to give, after aqueous quench, a volatile alkene (not isolated) and 2,4,6-*i*-$Pr_3C_6H_2SO_2NH_2$ **13**. Using PMDETA as the ligand appears to suppress the reductive alkylation pathway compared to TMEDA: even using a 1 minute lithiation time with *s*-BuLi–TMEDA, 2,4,6-*i*-$Pr_3C_6H_2SO_2NH_2$ **13** was produced in 54–62% yield together with only 22–34% yield of silyl aziridine **12** (entries 5–6). We note in passing that Hodgson has reported 51–96% yields for electrophilic trapping using *N*-Bus aziridine **7** and lithiating with *s*-BuLi–TMEDA in THF at –98 °C for 5 minutes.[9] In contrast, reductive alkylation was the only reaction observed with *N*-Bus aziridine **7** and *s*-BuLi–PMDETA (1 minute lithiation time) at –78 °C: lithation of *N*-Bus aziridine **7** with 3.0 equiv. *s*-BuLi–PMDETA for 1 minute and external trapping with Me_3SiCl gave *t*-$BuSO_2NH_2$ (83% yield) as the only isolable product. Finally, an attempted asymmetric lithiation using *s*-BuLi–(–)-sparteine in Et_2O gave recovered starting aziridine **9** (entry 8).

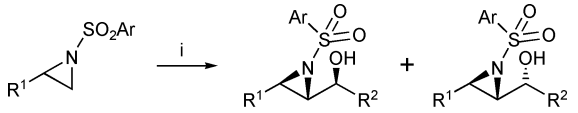
The optimised conditions for external silylation were also applied to terminal *N*-Tris-aziridine activated aziridines **14** and **16** (Scheme 3). Aziridines **14** (72% yield) and **16** (45% yield) were synthesised from 1-amino-2-propanol and 2-amino-2-methylpropan-1-ol respectively using the procedure previously used to synthesise aziridine **9**. External silylation of **14** gave a 70% yield of **15** and the *trans*-stereochemistry was assigned by X-ray crystal structures of two aldehyde-trapped products (*vide infra*) and by analogy with the LTMP-mediated process.[8] In contrast, attempted external silylation of aziridine **16** was unsuccessful and reductive alkylation occurred to give 2,4,6-*i*-$Pr_3C_6H_2SO_2NH_2$ **13** (31% yield) as the only isolable product.



Scheme 3 *Reagents and conditions:* i, (a) 1.0 eq $ArSO_2Cl$, CH_2Cl_2, Et_3N, 0 °C → rt, 16 h; (b) Py, MsCl, CH_2Cl_2, reflux, 6 h; (c) K_2CO_3, MeCN, reflux, 16 h. ii, (a) 3.0 eq *s*-BuLi–PMDETA, THF, –78 °C, 1 min; (b) 3 eq Me_3SiCl, –78 °C, 1 h.

With optimum conditions for the lithiation-silylation of *N*-Tris-aziridines **9** and **14** under external trapping established, we sought to apply the methodology to other electrophiles. We had some success using **9** and trapping with MeI but an inseparable 1 : 1 mixture of starting material and methylated aziridine were obtained. In contrast, we did not obtain any isolable adducts from lithiated **9** and the following electrophiles: *n*-BuBr, allyl bromide, Me_2SO_4, MeSSMe, Bu_3SnCl, $PhSO_2F$, Ph_2CO, Et_2CO, DMF and $PhCONMe_2$.

Table 3 *External* lithiation-aldehyde trapping of *N*-sulfonyl activated aziridines **9** and **14**



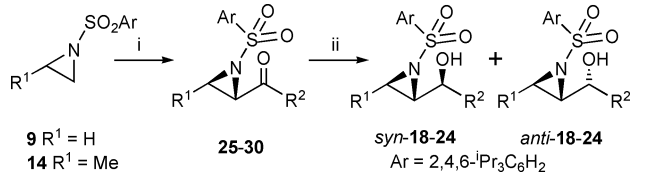
Entry[a]	SM[b]	R^1	R^2	Prod[c]	*syn* : *anti*[d]	Yield of *syn* (%)[e]	Yield of *anti* (%)[e]
1	**9**	H	*n*-Pr	**17**	60 : 40	29[f]	20
2	**9**	H	*i*-Pr	**18**	65 : 35	45	33
3	**9**	H	*t*-Bu	**19**	70 : 30	51	25
4	**9**	H	Ph	**20**	55 : 45	38	28
5	**14**	Me	*n*-Pr	**21**	n.d.[g]	21[h]	16
6	**14**	Me	*i*-Pr	**22**	60 : 40	46	23
7	**14**	Me	*t*-Bu	**23**	75 : 25	51	22
8	**14**	Me	Ph	**24**	n.d.[g]	25	43

[a] Reaction conditions: i, (a) *s*-BuLi/–PMDETA, THF, –78 °C, 1 min; (b) 3 eq R^2CHO, –78 °C, 1 h; (c) $NH_4Cl_{(aq)}$ (*external*). [b] SM = starting material. [c] Prod = product. [d] Ratio of *syn*- and *anti*-hydroxy aziridines determined from the ^1H NMR spectrum of the crude product. [e] Yield of product after chromatography. [f] 20% yield of SM **9** was recovered. [g] Not determined. [h] 25% yield of SM **14** was recovered.

However, trapping with different aldehydes gave satisfactory results for both *N*-Tris-aziridines **9** and **14** (Table 3). After lithiation at –78 °C in THF for 1 minute using 3 equiv. of *s*-BuLi–PMDETA, excess aldehyde was added followed by $NH_4Cl_{(aq)}$ after 1 hour at –78 °C. Where possible, the diastereoselectivity was determined from the ^1H NMR spectrum of the crude product and the diastereomeric adducts were then separated by chromatography. In general, additions of the lithiated aziridines to aldehydes proceeded with moderate but useful levels of *syn*-stereoselectivity. The best levels of *syn*-stereoselectivity were obtained with the most sterically hindered pivaldehyde (entries 3 and 7). The total yield of the diastereomeric adducts were generally good (65–78%; entries 2–4 and 6–8) except for butanal (37–49%; entries 1 and 5), presumably reflecting its ease of enolisation. For unequivocal proof of the assignment of stereochemistry in the hydroxy aziridines, we obtained X-ray crystal structures of *syn*-**24** and of the *p*-nitrobenzoate of *anti*-**22** (Fig. 2).

In order to provide an alternative synthetic route to *syn*-hydroxy aziridines and to aid in establishing the relative stereochemistry of all of the hydroxy aziridines, an oxidation–reduction approach was investigated. Thus, aziridines **9** and **14** were lithiated using *s*-BuLi–PMDETA in the usual manner and trapped with six aldehydes. Then, the crude mixture of hydroxy aziridines was oxidised with PCC to give keto aziridines **25–30** (44–61% yield over 2 steps, Table 4). Reduction of keto aziridines **25–30** using $NaBH_4$ in the presence of $CeCl_3 \cdot 7H_2O$ proceeded with ≥90 : 10 *syn*-stereoselectivity and allowed hydroxy aziridines *syn*-**18–20** and *syn*-**22–24** to be isolated in good to excellent yields (Table 4). Such *syn*-selectivity has been noted in our previous reductions of *N*-Ts keto aziridines[5] and other keto aziridine reductions;[18] it is

Table 4 Aldehyde trapping, oxidation and reduction route to *syn*-hydroxy aziridines



Entry[a]	SM[b]	R^1	R^2	Ketone	Yield (%)[c]	Prod[d]	*syn* : *anti*[e]	Yield of *syn* (%)[c]
1	**9**	H	*i*-Pr	**25**	56	**18**	90 : 10	64
2	**9**	H	*t*-Bu	**26**	61	**19**	>95 : 5	83
3	**9**	H	Ph	**27**	44	**20**	95 : 5	93
4	**14**	Me	*i*-Pr	**28**	52	**22**	90 : 10	77
5	**14**	Me	*t*-Bu	**29**	57	**23**	95 : 5	79
6	**14**	Me	Ph	**30**	58	**24**	90 : 10	88

[a] Reaction conditions: i, (a) *s*-BuLi–PMDETA, THF, −78 °C, 1 min; (b) 3 eq R^2CHO, −78 °C, 1 h; (c) $NH_4Cl_{(aq)}$; (d) PCC, CH_2Cl_2, rt, 2.5 h. ii, $NaBH_4$, $CeCl_3{\cdot}7H_2O$, MeOH, 0 °C, 2 h. [b] SM = starting material. [c] Yield of product after chromatography. [d] Prod = product. [e] Ratio of *syn*- and *anti*-hydroxy aziridines determined from the ^1H NMR spectrum of the crude product.

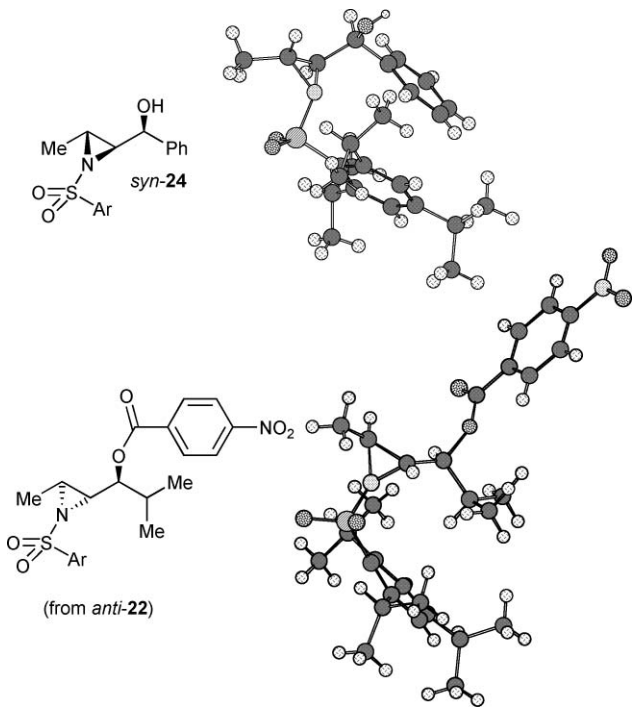
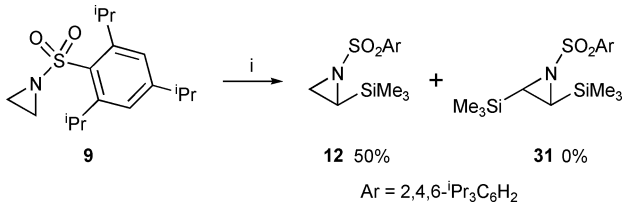


Fig. 2 X-Ray crystal structures of *syn*-**24** and of the *p*-nitrobenzoate of *anti*-**22**.

consistent with Felkin-Anh stereoselectivity. Assuming that reduction of the keto aziridines all show the same sense of induction, the X-ray structures of *syn*-**24** and of the *p*-nitrobenzoate of *anti*-**22** enabled us to assign the stereochemistry of hydroxy aziridines **18–20** and **22–24**. The stereochemistry of hydroxy aziridines **17** and **21** was assigned by analogy.

Finally, we wished to establish whether it was possible to carry out a one-pot double functionalisation of a *N*-sulfonyl ethylene aziridine **1** as a route to disubstituted aziridines **3**, as outlined in Scheme 1. To this end, *N*-Tris aziridine **9** was lithiated with *s*-BuLi–PMDETA for 1 minute and then Me_3SiCl was added. After 1 hour at −78 °C, a second lithiation-trapping using the same lithiation-Me_3SiCl trapping conditions was attempted. Unfortunately, there was no evidence for the formation of the hoped-for disilylated aziridine **31**. Instead, a 50% yield of mono-silyl aziridine **12** was obtained (Scheme 4).



Scheme 4 *Reagents and conditions:* i, (a) 3.0 eq *s*-BuLi–PMDETA, THF, −78 °C, 1 min; (b) 3 eq Me_3SiCl, −78 °C, 1 h; (c) 3.0 eq *s*-BuLi–PMDETA, THF, −78 °C, 1 min; (d) 3 eq Me_3SiCl, −78 °C, 1 h.

Conclusion

In summary, a convenient procedure for the lithiation-trapping of *N*-Tris activated ethylene aziridine **9** is described. The lithiation is accomplished using *s*-BuLi and PMDETA in THF at a convenient temperature (−78 °C) and trapping with a range of aldehydes provides a stereoselective route to *syn*-hydroxy aziridines. Our initial attempts at developing a route to disubstituted aziridines **3** *via* a one-pot approach proved unsuccessful. Nonetheless, with the appropriate choice of electrophiles, it seems likely that double functionalisation of a *N*-sulfonyl aziridine should be possible, perhaps even *via* a one-pot procedure.

Experimental

General

Water is distilled water. Et_2O and THF were freshly distilled from benzophenone ketyl; CH_2Cl_2 was freshly distilled from CaH_2. *s*-BuLi was titrated against *N*-benzylbenzamide before use. Petrol refers to the fraction of petroleum ether with a boiling point range of 40–60 °C. All reactions were carried out under O_2-free N_2 or Ar using oven-dried and/or flame dried glassware. PMDETA and diamines used in lithiation reactions were distilled before use. Flash column chromatography was carried out using silica gel 60 (0.035–0.070 mm particle size). Thin layer chromatography was carried out using F_{254} alumina-backed silica plates. Proton (400 MHz) and carbon (100.6 MHz) NMR spectra were recorded using an internal deuterium lock. All samples were recorded in $CDCl_3$. Chemical shifts are quoted in parts per million and referenced to $CHCl_3$ (7.27 for ^1H NMR and 77.0 for ^{13}C NMR spectroscopy). Carbon NMR spectra were recorded with broadband proton decoupling and were assigned using DEPT experiments. Infra-red spectra were recorded on an FT-IR spectrometer. Melting points were measured on a Gallenkamp melting point apparatus.

General procedure A: Lithiation-trapping of *N*-sulfonyl aziridines (external)

sec-BuLi (1.2–3.0 eq) was added dropwise to a stirred solution of PMDETA (pentamethyldiethylenetriamine), TMEDA or (−)-sparteine (1.2–3.0 eq) in THF or Et_2O (2 mL) at −78 °C under N_2. After stirring for 15 min at −78 °C, the solution was added

dropwise *via* canula to a stirred solution of aziridine (0.30 mmol) in THF or Et_2O (3 mL) at −78 °C under N_2. After stirring for 1 min at −78 °C, freshly distilled electrophile (0.90 mmol, 3.0 eq) was added and stirred at −78 °C for a further 1 h. Then, saturated $NH_4Cl_{(aq)}$ (10 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined Et_2O extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

General procedure B: Lithiation-trapping of *N*-sulfonyl aziridines and PCC oxidation

sec-BuLi (3.0 eq) was added dropwise to a stirred solution of PMDETA (3.0 eq) in THF at −78 °C under N_2. After stirring for 15 min at −78 °C, the solution was added dropwise *via* canula to a stirred solution of aziridine (0.60 mmol) in THF at −78 °C under N_2. After stirring for 1 min at −78 °C, freshly distilled aldehyde (1.8 mmol) was added and stirred at −78 °C for a further 1 h. Then, saturated $NH_4Cl_{(aq)}$ (20 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined Et_2O extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude hydroxy aziridines. A solution of the crude hydroxy aziridines (0.60 mmol) in CH_2Cl_2 (6 mL) was added dropwise *via* a cannula to a stirred solution of pyridinium chlorochromate (194 mg, 0.9 mmol) in CH_2Cl_2 (4 mL) at rt under N_2. The resulting mixture was stirred for 2.5 h and then diluted with Et_2O (20 mL). The solid was removed by filtration through Celite and the filtrate was evaporated to give the crude product.

General procedure C: Reduction of keto aziridines

$NaBH_4$ (1.2 eq) was added portionwise over 45 min to a stirred solution of keto aziridine (0.2 mmol) and $CeCl_3{\cdot}7H_2O$ (1.2 eq) in MeOH (1 mL) at 0 °C under N_2. The resulting solution was stirred at 0 °C for 2 h. After warming to rt, saturated $NH_4Cl_{(aq)}$ (2 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic extracts were washed with water (5 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

1-(2,4,6-Triisopropylphenylsulfonyl)aziridine 9

2,4,6-Tri-*iso*-propylbenzenesulfonyl chloride (6.05 g, 20.0 mmol) was added to a stirred solution of ethanolamine (1.22 g, 20.0 mmol) and Et_3N (5.6 mL, 40.0 mmol) in CH_2Cl_2 (30 mL) at 0 °C under N_2. The resulting solution was allowed to warm to rt and stirred at rt for 16 h. Then, the reaction mixture was washed with 5% $NaHCO_{3(aq)}$ (2 × 10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude sulfonamido alcohol. Then, pyridine (9.24 mL, 100.0 mmol) was added dropwise to a stirred solution of methanesulfonyl chloride (8.58 mL, 100.0 mmol) in CH_2Cl_2 (200 mL) at 0 °C under N_2. After stirring for 20 min, a solution of the crude sulfonamido alcohol in CH_2Cl_2 (5 mL) was added and the resulting solution was stirred for 20 min. Then, the solution was heated at reflux for 16 h. The solution was allowed to cool to rt and washed with brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude sulfonamido mesylate. A stirred mixture of the crude sulfonamido mesylate and K_2CO_3 (11.2 g, 80.0 mmol) in MeCN (200 mL) was heated at 45 °C under N_2 for 16 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 (20 mL). The mixture was washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave aziridine **9** (4.67 g, 76%) as a white solid, mp 94–96 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.6; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1317 (SO_2) and 1151 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.32 (2 H, sept, *J* 7.0, ArCH), 2.91 (1 H, sept, *J* 7.0, ArCH), 2.38 (4 H, br s, CH_2N), 1.27 (12 H, d, *J* 7.0, Me) and 1.26 (6 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.4 (*ipso*-Ar), 151.1 (*ipso*-Ar), 131.2 (*ipso*-Ar), 123.8 (Ar), 34.2 (ArCH), 29.7 (ArCH), 27.1 (CH_2N), 24.9 (Me) and 23.5 (Me); *m*/*z* (CI; NH_3) 310 [100%, $(M + H)^+$] and 267 (10) [Found $(M + H)^+$ 310.1840. $C_{17}H_{27}NO_2S$ requires *M* + H, 310.1841].

2-Methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridine 14

2,4,6-Tri-*iso*-propylbenzenesulfonyl chloride (1.21 g, 4.0 mmol) was added to a stirred solution of 1-amino-2-propanol (300 mg, 4.0 mmol) and Et_3N (1.12 mL, 8.0 mmol) in CH_2Cl_2 (6 mL) at 0 °C under N_2. The resulting solution was allowed to warm to rt and stirred at rt for 16 h. Then, the reaction mixture was washed with 5% $NaHCO_{3(aq)}$ (2 × 10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude sulfonamido alcohol. Then, pyridine (1.83 mL, 20.0 mmol) was added dropwise to a stirred solution of methanesulfonyl chloride (1.69 mL, 20.0 mmol) in CH_2Cl_2 (50 mL) at 0 °C under N_2. After stirring for 20 min, a solution of the crude sulfonamido alcohol in CH_2Cl_2 (5 mL) was added and the resulting solution was stirred for 20 min. Then, the solution was heated at reflux for 16 h. The solution was allowed to cool to rt and washed with brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude sulfonamido mesylate. A stirred mixture of the crude sulfonamido mesylate and K_2CO_3 (2.21 g, 16.0 mmol) in MeCN (50 mL) was heated at 45 °C under N_2 for 16 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 (20 mL). The mixture was washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave aziridine **14** (934 mg, 72%) as a white solid, mp 73–75 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.6; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1317 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.17 (2 H, s, Ar), 4.34 (2 H, sept, *J* 7.0, ArCH), 2.91 (1 H, sept, *J* 7.0, ArCH), 2.86–2.80 (1 H, m, CHN), 2.68 (1 H, d, *J* 7.0, CH_AH_BN), 2.01 (1 H, d, *J* 4.5, CH_AH_BN), 1.26 (18 H, d, *J* 7.0, Me) and 1.25 (3 H, d, *J* 5.5, Me); δ_C (100.6 MHz; $CDCl_3$) 153.2 (*ipso*-Ar), 150.9 (*ipso*-Ar), 131.6 (*ipso*-Ar), 123.7 (Ar), 35.3 (CHN), 34.4 (CH_2N), 34.1 (ArCH), 29.6 (ArCH), 24.8 (Me), 23.5 (Me) and 17.0 (Me); *m*/*z* (CI; NH_3) (CI, NH_3) 341 [20%, $(M + NH_4)^+$] and 324 (100) [Found $(M + H)^+$ 324.1991. $C_{18}H_{29}NO_2S$ requires *M* + H, 324.1997].

2,2-Dimethyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridine 16

2,4,6-Tri-*iso*-propylbenzenesulfonyl chloride (3.03 g, 10.0 mmol) was added to a stirred solution of 2-amino-2-methylpropan-1-ol (890 mg, 10.0 mmol) and Et_3N (2.8 mL, 20.0 mmol) in CH_2Cl_2 (15 mL) at 0 °C under N_2. The resulting solution was allowed to warm to rt and stirred at rt for 16 h. Then, the reaction mixture was washed with 5% $NaHCO_{3(aq)}$ (2 × 10 mL), dried

($MgSO_4$) and evaporated under reduced pressure to give the crude sulfonamido alcohol. Then, pyridine (4.58 mL, 50.0 mmol) was added dropwise to a stirred solution of methanesulfonyl chloride (4.23 mL, 50.0 mmol) in CH_2Cl_2 (200 mL) at 0 °C under N_2. After stirring for 20 min, a solution of the crude sulfonamido alcohol in CH_2Cl_2 (5 mL) was added and the resulting solution was stirred for 20 min. Then, the solution was heated at reflux for 16 h. The solution was allowed to cool to rt and washed with brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude sulfonamido mesylate. A stirred mixture of the crude sulfonamido mesylate and K_2CO_3 (5.55 g, 40.0 mmol) in MeCN (100 mL) was heated at 45 °C under N_2 for 16 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 (20 mL). The mixture was washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave aziridine **16** (152 mg, 45%) as a white solid, mp 66–67 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.6; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1315 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.16 (2 H, s, Ar), 4.38 (2 H, sept, *J* 7.0, ArCH), 2.91 (1 H, sept, *J* 7.0, ArCH), 2.46 (2 H, s, CH_2N), 1.56 (6 H, s, Me), 1.27 (12 H, d, *J* 7.0, Me) and 1.25 (6 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 152.7 (*ipso*-Ar), 150.3 (*ipso*-Ar), 134.3 (*ipso*-Ar), 123.6 (Ar), 47.8 ($NCMe_2$), 42.1 (CH_2N), 34.2 (ArCH), 29.6 (ArCH), 24.8 (Me), 23.6 (Me) and 23.0 (Me); *m*/*z* (CI; NH_3) (CI, NH_3) 338 [100%, $(M + H)^+$] [Found $(M + H)^+$ 338.2154. $C_{19}H_{31}NO_2S$ requires *M* + H, 338.2154].

1-(4-Methyl-2-(trimethylsilyl)phenylsulfonyl)-2-(trimethylsilyl)aziridine 11 (Table 1, entry 2)

sec-BuLi (1.28 mL of a 1.2 M solution in cyclohexane, 1.54 mmol) was added dropwise to a stirred solution of PMDETA (0.32 mL, 1.54 mmol) in THF (3 mL) at −78 °C under N_2. After stirring for 15 min at −78 °C, the solution was added dropwise *via* a canula to a stirred solution of aziridine **8** (100 mg, 0.51 mmol) and trimethylsilyl chloride (0.20 mL, 1.54 mmol) in THF (2 mL) at −78 °C under N_2. After stirring for 1 h at −78 °C, saturated $NH_4Cl_{(aq)}$ (10 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined Et_2O extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave disilyl aziridine **11** (39 mg, 22%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.6; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1322 (SO_2), 1249 ($SiMe_3$) and 1162 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.83 (1 H, d, *J* 8.0, Ar), 7.57 (1 H, s, Ar), 7.30–7.28 (1 H, m, Ar), 2.63–2.61 (1 H, m, SiCHN), 2.42 (3 H, s, Me), 1.99–1.98 (2 H, m, CH_2N), 0.44 (9 H, s, $SiMe_3$) and −0.09 (9 H, s, $SiMe_3$); δ_C (100.6 MHz; $CDCl_3$) 142.6 (*ipso*-Ar), 141.0 (*ipso*-Ar), 140.5 (*ipso*-Ar), 137.3 (Ar), 129.8 (Ar), 129.6 (Ar), 30.4 (CH_2N), 29.9 (CHSiN), 21.6 (Me), 1.1 ($SiMe_3$) and −3.7 ($SiMe_3$); *m*/*z* (CI; NH_3) 342 [20%, $(M + H)^+$] and 270 (100) [Found $(M + H)^+$ 342.1378. $C_{15}H_{27}NO_2Si_2S$ requires *M* + H, 342.1379] and starting aziridine **8** (22 mg, 22%).

1-(2,4,6-Triisopropylphenylsulfonyl)-2-(trimethylsilyl)aziridine 12 (Table 1, entry 3)

sec-BuLi (0.8 mL of a 1.2 M solution in cyclohexane, 0.96 mmol) was added dropwise to a stirred solution of PMDETA (0.2 mL, 0.96 mmol) in THF (3 mL) at −78 °C under N_2. After stirring for 15 min at −78 °C, the solution was added dropwise *via* a canula to a stirred solution of aziridine **9** (100 mg, 0.32 mmol) and trimethylsilyl chloride (0.12 mL, 0.96 mmol) in THF (2 mL) at −78 °C under N_2. After stirring for 1 h at −78 °C, saturated $NH_4Cl_{(aq)}$ (10 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined Et_2O extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave silyl aziridine **12** (81 mg, 66%) as a white solid, mp 48–50 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1317 (SO_2), 1252 ($SiMe_3$) and 1154 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.17 (2 H, s, Ar), 4.38 (2 H, sept, *J* 7.0, ArCH), 2.90 (1 H, sept, *J* 7.0, ArCH), 2.66 (1 H, dd, *J* 8.0 and 1.5, CHN), 2.03–1.98 (2 H, m, CH_2N), 1.27–1.24 (18 H, d, *J* 7.0, Me) and −0.07 (9 H, s, $SiMe_3$); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 151.0 (*ipso*-Ar), 131.5 (*ipso*-Ar), 123.7 (Ar), 34.2 (ArCH), 30.1 (CH_2N), 29.6 (ArCH), 29.0 (CHN), 25.0 (Me), 24.8 (Me), 23.6 (Me) and −3.7 ($SiMe_3$); *m*/*z* (CI; NH_3) 382 (100) [Found $(M + H)^+$ 382.2231. $C_{20}H_{35}NO_2SiS$ requires *M* + H, 382.2236] and starting aziridine **9** (28 mg, 28%).

1-(2,4,6-Triisopropylphenylsulfonyl)-2-(trimethylsilyl)aziridine 12 (Table 2, entry 1)

Using general procedure A, *sec*-BuLi (0.83 mL of a 1.15 M solution in cyclohexane, 0.96 mmol, 3.0 eq), PMDETA (0.2 mL, 0.96 mmol, 3.0 eq) in THF (2 mL), aziridine **9** (100 mg, 0.32 mmol) in THF (3 mL) and trimethylsilyl chloride (0.12 mL, 0.96 mmol) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave silyl aziridine **12** (116 mg, 94%).

2-Methyl-1-(2,4,6-triisopropylphenylsulfonyl)-3-(trimethylsilyl)aziridine 15

Using general procedure A, *sec*-BuLi (0.93 mL of a 1.0 M solution in cyclohexane, 0.93 mmol, 3.0 eq), PMDETA (0.19 mL, 0.93 mmol, 3.0 eq) in THF (2 mL), aziridine **14** (100 mg, 0.31 mmol) in THF (3 mL) and trimethylsilyl chloride (0.11 mL, 0.93 mmol) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave silyl aziridine **15** (85 mg, 70%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1317 (SO_2), 1254 ($SiMe_3$) and 1151 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.15 (2 H, s, Ar), 4.37 (2 H, sept, *J* 7.0, ArCH), 2.89 (1 H, sept, *J* 7.0, ArCH), 2.68 (1 H, app. pentet, *J* 6.0, MeCHN), 1.96 (1 H, d, *J* 6.0, SiCHN), 1.59 (3 H, d, *J* 6.0, Me), 1.27 (6 H, d, *J* 7.0, Me), 1.24 (12 H, d, *J* 7.0, Me) and −0.05 (9 H, s, $SiMe_3$); δ_C (100.6 MHz; $CDCl_3$) 152.8 (*ipso*-Ar), 150.5 (*ipso*-Ar), 133.7 (*ipso*-Ar), 123.5 (Ar), 42.3 (CHN), 39.8 (CHN), 34.2 (ArCH), 29.6 (ArCH), 24.9 (Me), 24.8 (Me), 23.6 (Me), 16.3 (Me) and −2.8 ($SiMe_3$); *m*/*z* (CI; NH_3) 396 [100%, $(M + H)^+$] and 129 (45) [Found $(M + H)^+$ 396.2396. $C_{21}H_{37}NO_2SiS$ requires *M* + H, 396.2393] and starting aziridine **14** (11 mg, 11%).

1-(1-(2,4,6-Triisopropylphenylsulfonyl)aziridin-2-yl)butan-1-ol *syn*-17 and *anti*-17

Using general procedure A, aziridine **9** (100 mg, 0.32 mmol) in THF (3 mL), *sec*-BuLi (0.80 mL of a 1.2 M solution in cyclohexane, 0.96 mmol, 3.0 eq) and PMDETA (0.2 mL, 0.96 mmol, 3.0 eq)

in THF (2 mL) and butyraldehyde (0.1 mL, 0.96 mmol) gave the crude product which contained a 60 : 40 mixture of alcohols *syn*-**17** and *anti*-**17** by ^{1}H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave starting aziridine **9** (20 mg, 20%), alcohol *syn*-**17** (36 mg, 29%) as a white solid, mp 50–52 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3551 (OH), 1318 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.32 (2 H, sept, *J* 7.0, ArCH), 3.53–3.47 (1 H, m, CHO), 2.94–2.86 (2 H, m, CHN and ArCH), 2.71 (1 H, d, *J* 7.0, CH_2N), 2.34 (1 H, d, *J* 4.5, CH_2N), 1.44–1.30 (4 H, m, CH_2), 1.27 (12 H, d, *J* 7.0, Me), 1.25 (6 H, d, *J* 7.0, Me) and 0.87 (3 H, t, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 151.0 (*ipso*-Ar), 131.5 (*ipso*-Ar), 123.9 (Ar), 69.3 (CHO), 43.4 (CHN), 37.6 (CH_2N), 34.2 (ArCH), 30.7 (CH_2), 29.8 (ArCH), 24.9 (Me), 23.5 (Me), 18.5 (CH_2) and 13.9 (Me); *m*/*z* (CI; NH_3) 382 (100) [Found $(M + H)^+$ 382.2413. $C_{21}H_{35}NO_3S$ requires *M* + H, 382.2416] and alcohol *anti*-**17** (25 mg, 20%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3507 (OH), 1317 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.31 (2 H, sept, *J* 7.0, ArCH), 3.78–3.77 (1 H, br s, CHO), 2.98–2.88 (2 H, m, CHN and ArCH), 2.62 (1 H, d, *J* 7.0, CH_2N), 2.33 (1 H, d, *J* 4.5, CH_2N), 1.44–1.30 (4 H, m, CH_2), 1.27 (12 H, d, *J* 7.0, Me), 1.25 (6 H, d, *J* 7.0, Me) and 0.87 (3 H, t, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.7 (*ipso*-Ar), 151.0 (*ipso*-Ar), 131.5 (*ipso*-Ar), 123.9 (Ar), 68.3 (CHO), 42.5 (CHN), 36.1 (CH_2N), 34.2 (ArCH), 29.9 (CH_2), 29.7 (ArCH), 24.9 (Me), 24.8 (Me), 23.5 (Me), 18.3 (CH_2) and 13.9 (Me); *m*/*z* (CI; NH_3) 382 (100) [Found $(M + H)^+$ 382.2414. $C_{21}H_{35}NO_3S$ requires *M* + H, 382.2416].

2-Methyl-1-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-18 and *anti*-18

Using general procedure A, aziridine **9** (100 mg, 0.32 mmol) in THF (3 mL), *sec*-BuLi (0.80 mL of a 1.2 M solution in cyclohexane, 0.96 mmol, 3.0 eq) and PMDETA (0.2 mL, 0.96 mmol, 3.0 eq) in THF (2 mL) and isobutyraldehyde (0.1 mL, 0.96 mmol) gave the crude product which contained a 65 : 35 mixture of alcohols *syn*-**18** and *anti*-**18** by ^{1}H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave starting aziridine **9** (7 mg, 7%), alcohol *syn*-**18** (55 mg, 45%) as a white solid, mp 56–57 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3542 (OH), 1317 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.32 (2 H, sept, *J* 7.0, ArCH), 3.11 (1 H, br td, *J* 7.0 and 6.0, CHO), 2.97 (1 H, td, *J* 7.0 and 4.5, CHN), 2.91 (1 H, sept, *J* 7.0, ArCH), 2.71 (1 H, d, *J* 7.0, CHN), 2.29 (1 H, d, *J* 4.5, CHN), 1.69 (1 H, octet, *J* 7.0, CH), 1.38 (1 H, d, *J* 6.0, OH), 1.27 (12 H, d, *J* 7.0, Me), 1.25 (6 H, d, *J* 7.0, Me), 0.97 (3 H, d, *J* 7.0, Me) and 0.94 (3 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.8 (*ipso*-Ar), 151.0 (*ipso*-Ar), 130.9 (*ipso*-Ar), 123.9 (Ar), 75.3 (CHO), 42.0 (CHN), 34.2 (ArCH), 32.9 (CH), 31.2 (CH_2N), 29.8 (ArCH), 24.8 (Me), 23.5 (Me), 18.3 (Me) and 18.1 (Me); *m*/*z* (CI; NH_3) 382 (100) [Found $(M + H)^+$ 382.2422. $C_{21}H_{35}NO_3S$ requires *M* + H, 382.2416] and alcohol *anti*-**18** (41 mg, 33%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3520 (OH), 1317 (SO_2) and 1154 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.30 (2 H, sept, *J* 7.0, ArCH), 3.59 (1 H, dd, *J* 5.5 and 3.0, CHO), 3.04 (1 H, ddd, *J* 7.0, 4.5 and 3.0, CHN), 2.91 (1 H, sept, *J* 7.0, ArCH), 2.62 (1 H, d, *J* 7.0, CH_2N), 2.36 (1 H, d, *J* 4.5, CH_2N), 1.73 (1 H, sept d, *J* 7.0 and 5.5, CH), 1.68 (1 H, br s, OH), 1.27 (6 H, d, *J* 7.0, 1.0, Me), 1.262 (6 H, d, *J* 7.0, Me), 1.259 (6 H, d, *J* 7.0, Me), 0.97 (3 H, d, *J* 7.0, Me) and 0.95 (3 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.7 (*ipso*-Ar), 151.0 (*ipso*-Ar), 131.0 (*ipso*-Ar), 123.9 (Ar), 72.3 (CHO), 40.9 (CHN), 34.2 (ArCH), 32.0 (CH), 29.8 (ArCH), 29.7 (CH_2N), 24.87 (Me), 24.79 (Me), 23.5 (Me), 18.3 (Me) and 17.6 (Me); *m*/*z* (CI; NH_3) 382 (100) [Found $(M + H)^+$ 382.2427. $C_{21}H_{35}NO_3S$ requires *M* + H, 382.2416].

2,2-Dimethyl-1-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-19 and *anti*-19

Using general procedure A, aziridine **9** (100 mg, 0.32 mmol) in THF (3 mL), *sec*-BuLi (0.80 mL of a 1.2 M solution in cyclohexane, 0.96 mmol, 3.0 eq) and PMDETA (0.2 mL, 0.96 mmol, 3.0 eq) in THF (2 mL) and trimethylacetaldehyde (0.11 mL, 0.96 mmol) gave the crude product which contained a 70 : 30 mixture of alcohols *syn*-**19** and *anti*-**19** by ^{1}H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave starting aziridine **9** (7 mg, 7%), alcohol *syn*-**19** (65 mg, 51%) as a white solid, mp 87–89 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3539 (OH), 1319 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.31 (2 H, sept, *J* 7.0, ArCH), 3.03–2.96 (2 H, m, CHO and CHN), 2.89 (1 H, sept, *J* 7.0, ArCH), 2.73 (1 H, d, *J* 7.0, CHN), 2.25 (1 H, d, *J* 4.5, CHN), 1.45 (1 H, d, *J* 4.5, OH), 1.28–1.24 (18 H, m, Me) and 0.95 (9 H, s, CMe_3); δ_C (100.6 MHz; $CDCl_3$) 153.8 (*ipso*-Ar), 151.1 (*ipso*-Ar), 130.9 (*ipso*-Ar), 124.0 (Ar), 78.4 (CHO), 41.0 (CHN), 34.6 (CMe_3), 34.2 (ArCH), 31.8 (CH_2N), 29.8 (ArCH), 25.6 (CMe_3), 24.86 (Me), 24.83 (Me) and 23.5 (Me); *m*/*z* (CI; NH_3) 396 (100) [Found $(M + H)^+$ 396.2570. $C_{22}H_{37}NO_3S$ requires *M* + H, 396.2572] and alcohol *anti*-**19** (32 mg, 25%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3542 (OH), 1318 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.30 (2 H, sept, *J* 7.0, ArCH), 3.55 (1 H, br s, CHO), 3.11 (1 H, ddd, *J* 7.0, 4.5 and 2.0, CHN), 2.91 (1 H, sept, *J* 7.0, ArCH), 2.63 (1 H, d, *J* 7.0, CHN), 2.40 (1 H, d, *J* 4.5, CHN), 1.68 (1 H, br s, OH), 1.28–1.25 (18 H, m, Me), and 0.96 (9 H, s, CMe_3); δ_C (100.6 MHz; $CDCl_3$) 153.7 (*ipso*-Ar), 151.0 (*ipso*-Ar), 131.0 (*ipso*-Ar), 123.9 (Ar), 74.3 (CHO), 39.7 (CHN), 34.6 (CMe_3), 34.2 (ArCH), 30.0 (CH_2N), 29.8 (ArCH), 25.8 (CMe_3), 24.89 (Me), 24.79 (Me) and 23.5 (Me); *m*/*z* (CI; NH_3) 396 (100) [Found $(M + H)^+$ 396.2559. $C_{22}H_{37}NO_3S$ requires *M* + H, 396.2572].

Phenyl-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)methanol *syn*-20 and *anti*-20

Using general procedure A, aziridine **9** (100 mg, 0.32 mmol) in THF (3 mL), *sec*-BuLi (0.80 mL of a 1.2 M solution in cyclohexane, 0.96 mmol, 3.0 eq) and PMDETA (0.2 mL, 0.96 mmol, 3.0 eq) in THF (2 mL) and benzaldehyde (0.1 mL, 0.96 mmol) gave the crude product which contained a 55 : 45 mixture of alcohols *syn*-**20** and *anti*-**20** by ^{1}H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave starting aziridine **9** (6 mg, 6%), alcohol *syn*-**20** (51 mg, 38%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3539 (OH), 1319 (SO_2) and 1153 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.26 (5 H, s, Ph), 7.19 (2 H, s, Ar), 4.50 (1 H, t, *J* 5.0, CHO), 4.29 (2 H, sept, *J* 7.0, ArCH), 3.13 (1 H, ddd, *J* 7.0, 5.0 and 4.5, CHN), 2.93 (1 H, sept, *J* 7.0, ArCH), 2.74 (1 H, d, *J* 7.0, CHN), 2.41 (1 H,

d, *J* 4.5, CHN), 2.04 (1 H, d, *J* 5.0, OH), 1.28 (12 H, d, *J* 7.0, Me) and 1.22 (6 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.8 (*ipso*-Ar), 151.2 (*ipso*-Ar), 139.9 (*ipso*-Ph), 130.8 (*ipso*-Ar), 128.6 (Ph), 128.2 (Ph), 126.0 (Ph), 124.0 (Ar), 72.9 (CHO), 44.6 (CHN), 34.2 (ArCH), 30.5 (CH_2N), 29.8 (ArCH), 24.89 (Me), 24.82 (Me), 23.56 (Me) and 23.54 (Me); *m*/*z* (CI; NH_3) 396 (100) [Found (M + H)$^+$ 416.2258. $C_{24}H_{33}NO_3S$ requires *M* + H, 416.2259] and alcohol *anti*-**20** (37 mg, 28%) as a white solid, mp 98–100 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3482 (OH), 1318 (SO_2) and 1152 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.30 (5 H, s, Ph), 7.19 (2 H, s, Ar), 4.90 (1 H, br s, CHO), 4.28 (2 H, sept, *J* 7.0, ArCH), 3.21 (1 H, ddd, *J* 7.0, 4.5 and 3.5, CHN), 2.94 (1 H, sept, *J* 7.0, ArCH), 2.63 (1 H, d, *J* 7.0, CHN), 2.46 (1 H, d, *J* 4.5, CHN), 2.14 (1 H, br s, OH), 1.27 (12 H, d, *J* 7.0, Me) and 1.25 (6 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.7 (*ipso*-Ar), 151.1 (*ipso*-Ar), 139.3 (*ipso*-Ar), 130.9 (*ipso*-Ar), 128.6 (Ph), 128.3 (Ph), 126.0 (Ph), 123.9 (Ar), 70.3 (CHO), 43.3 (CHN), 34.2 (ArCH), 30.3 (CH_2N), 29.8 (ArCH), 24.88 (Me), 24.84 (Me), and 23.6 (Me); *m*/*z* (CI; NH_3) 416 (100) [Found (M + H)$^+$ 416.2259. $C_{24}H_{33}NO_3S$ requires *M* + H, 416.2259].

1-(3-Methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)butan-1-ol *syn*-21 and *anti*-21

Using general procedure A, aziridine **14** (100 mg, 0.31 mmol) in THF (3 mL), *sec*-BuLi (0.78 mL of a 1.2 M solution in cyclohexane, 0.93 mmol, 3.0 eq) and PMDETA (0.19 mL, 0.93 mmol, 3.0 eq) in THF (2 mL) and butyraldehyde (0.1 mL, 0.93 mmol) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave the starting aziridine **14** (25 mg, 25%), alcohol *syn*-**21** (26 mg, 21%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3528 (OH), 1311 (SO_2), and 1149 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.17 (2 H, s, Ar), 4.28 (2 H, sept, *J* 7.0, ArCH), 3.73 (1 H, br s, CHO), 2.99 (1 H, qd, *J* 6.0 and 4.5, CHN), 2.90 (1 H, sept, *J* 7.0, ArCH), 2.74 (1 H, dd, *J* 7.0 and 4.5, CHN), 2.61 (1 H, br s, OH), 1.53–1.46 (4 H, m, CH_2), 1.43 (3 H, d, *J* 6.0, Me), 1.28 (6 H, d, *J* 7.0, Me), 1.25 (12 H, d, *J* 7.0, Me) and 0.91 (3 H, t, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 150.5 (*ipso*-Ar), 133.6 (*ipso*-Ar), 123.7 (Ar), 70.1 (CHO), 55.2 (CHN), 42.9 (CHN), 37.2 (CH_2), 34.2 (ArCH), 29.8 (ArCH), 24.8 (Me), 24.7 (Me), 23.6 (Me), 18.6 (CH_2), 15.4 (Me) and 14.1 (Me); *m*/*z* (CI; NH_3) 396 (100) [Found (M + H)$^+$ 396.2570. $C_{22}H_{37}NO_3S$ requires *M* + H, 396.2572] and alcohol *anti*-**21** (19 mg, 16%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3566 (OH), 1316 (SO_2), and 1152 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.17 (2 H, s, Ar), 4.33 (2 H, sept, *J* 7.0, ArCH), 3.66 (1 H, br s, CHO), 2.96–2.87 (3 H, m, ArCH and CHN), 1.83 (1 H, br s, OH), 1.65 (3 H, d, *J* 6.0, Me), 1.29–1.24 (22 H, m, CH_2 and Me) and 0.83 (3 H, t, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 150.5 (*ipso*-Ar), 133.7 (*ipso*-Ar), 123.7 (Ar), 68.5 (CHO), 51.6 (CHN), 42.6 (CHN), 36.4 (CH_2), 34.2 (ArCH), 29.7 (ArCH), 24.8 (Me), 24.7 (Me), 23.6 (Me), 18.3 (CH_2), 14.0 (Me) and 13.9 (Me); *m*/*z* (CI; NH_3) 396 (100) [Found (M + H)$^+$ 396.2560. $C_{22}H_{37}NO_3S$ requires *M* + H, 396.2572].

2-Methyl-1-(3-methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-22 and *anti*-22

Using general procedure A, aziridine **14** (500 mg, 1.55 mmol) in THF (8 mL), *sec*-BuLi (3.51 mL of a 1.32 M solution in cyclohexane, 4.64 mmol, 3.0 eq) and PMDETA (0.97 mL, 4.94 mmol, 3.0 eq) in THF (8 mL) and isobutyraldehyde (0.42 mL, 4.64 mmol) gave the crude product which contained a 60 : 40 mixture of alcohols *syn*-**22** and *anti*-**22** by ^{1}H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (7 : 1 then 2 : 1) as eluent gave alcohol *syn*-**22** (282 mg, 45%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3521 (OH), 1311 (SO_2) and 1148 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.17 (2 H, s, Ar), 4.29 (2 H, sept, *J* 7.0, ArCH), 3.35 (1 H, br td, *J* 8.0 and 3.0, CHO), 2.97 (1 H, qd, *J* 6.0 and 4.5, CHN), 2.90 (1 H, sept, *J* 7.0, ArCH), 2.78 (1 H, dd, *J* 8.0 and 4.5, CHN), 2.70 (1 H, br, s, OH), 1.77 (1 H, dsept, *J* 8.0 and 7.0, CH), 1.43 (3 H, d, *J* 6.0, Me), 1.28 (6 H, d, *J* 7.0, Me), 1.25 (12 H, d, *J* 7.0, Me), 1.01 (3 H, d, *J* 7.0, Me) and 0.95 (3 H, t, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 150.5 (*ipso*-Ar), 133.5 (*ipso*-Ar), 123.7 (Ar), 75.8 (CHO), 54.4 (CHN), 43.7 (CHN), 34.2 (ArCH), 32.7 (CH), 29.8 (ArCH), 24.8 (Me), 23.5 (Me), 18.7 (Me), 18.3 (Me) and 15.3 (Me); *m*/*z* (CI; NH_3) 396 (100) [Found (M + H)$^+$ 396.2565. $C_{22}H_{37}NO_3S$ requires *M* + H, 396.2572] and alcohol *anti*-**22** (143 mg, 23%) as a white solid, mp 68–69 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3509 (OH), 1315 (SO_2) and 1151 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.16 (2 H, s, Ar), 4.32 (2 H, sept, *J* 7.0, ArCH), 3.58 (1 H, br s, CHO), 3.02–2.97 (2 H, m, CHN), 2.90 (1 H, sept, *J* 7.0, ArCH), 1.84 (1 H, s, OH), 1.73 (1 H, octet, *J* 7.0, CH), 1.65 (3 H, d, *J* 6.0, Me), 1.27 (6 H, d, *J* 7.0, Me), 1.25 (12 H, dd, *J* 7.0 and 1.0, Me), 0.94 (3 H, d, *J* 7.0, Me) and 0.92 (3 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 150.4 (*ipso*-Ar), 133.8 (*ipso*-Ar), 123.8 (Ar), 71.8 (CHO), 50.3 (CHN), 41.9 (CHN), 34.2 (ArCH), 31.9 (CH), 29.7 (ArCH), 24.9 (Me), 24.7 (Me), 23.5 (Me), 18.4 (Me), 17.3 (Me) and 13.7 (Me); *m*/*z* (CI; NH_3) 396 (100) [Found (M + H)$^+$ 396.2574. $C_{22}H_{37}NO_3S$ requires *M* + H, 396.2572].

2,2-Dimethyl-1-(3-methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-23 and *anti*-23

Using general procedure A, aziridine **14** (100 mg, 0.31 mmol) in THF (3 mL), *sec*-BuLi (0.83 mL of a 1.2 M solution in cyclohexane, 0.93 mmol, 3.0 eq) and PMDETA (0.2 mL, 0.93 mmol, 3.0 eq) in THF (2 mL) and trimethylacetaldehyde (0.11 mL, 0.93 mmol) gave the crude product which contained a 75 : 25 mixture of alcohols *syn*-**23** and *anti*-**23** by ^{1}H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave alcohol *syn*-**23** (65 mg, 51%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3521 (OH), 1312 (SO_2) and 1149 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.17 (2 H, s, Ar), 4.30 (2 H, sept, *J* 7.0, ArCH), 3.21 (1 H, dd, *J* 9.0 and 2.0, CHO), 2.96–2.87 (2 H, m, CHN and ArCH), 2.85 (1 H, dd, *J* 9.0 and 4.5, CHN), 2.44 (1 H, br s, OH), 1.48 (3 H, d, *J* 6.0, Me), 1.29 (6 H, d, *J* 7.0, Me), 1.27 (12 H, d, *J* 7.0, Me) and 0.97 (9 H, s, CMe_3); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 150.6 (*ipso*-Ar), 133.5 (*ipso*-Ar), 123.8 (Ar), 76.7 (CHO), 52.9 (CHN), 44.8 (CHN), 34.6 (*C*Me$_3$), 34.2 (ArCH), 29.8 (ArCH), 25.8 (*CMe$_3$*), 24.8 (Me), 24.7 (Me), 23.54 (Me), 23.53 (Me) and 14.9 (Me); *m*/*z* (CI; NH_3) 410 (100) [Found (M + H)$^+$ 410.2719. $C_{23}H_{39}NO_3S$ requires *M* + H, 410.2729] and alcohol *anti*-**23** (28 mg, 22%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3534 (OH), 1316 (SO_2) and 1152 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.16 (2 H, s, Ar), 4.32 (2 H,

sept, *J* 7.0, ArCH), 3.45 (1 H, d, *J* 2.0, CHO), 3.10 (1 H, dd, *J* 4.5 and 2.0, CHN), 2.99 (1 H, qd, *J* 6.0 and 4.5, CHN), 2.90 (1 H, sept, *J* 7.0, ArCH), 1.69 (3 H, d, *J* 6.0, Me), 1.28 (6 H, d, *J* 7.0, Me), 1.26 (12 H, d, *J* 7.0, Me) and 0.94 (9 H, s, CMe_3); δ_C (100.6 MHz; $CDCl_3$) 153.3 (*ipso*-Ar), 150.4 (*ipso*-Ar), 133.9 (*ipso*-Ar), 123.8 (Ar), 74.2 (CHO), 49.0 (CHN), 42.0 (CHN), 34.5 (CMe_3), 34.2 (ArCH), 29.8 (ArCH), 25.8 (CMe_3), 25.0 (Me), 24.7 (Me), 23.6 (Me) and 13.3 (Me); *m*/*z* (CI; NH_3) 410 (100) [Found $(M + H)^+$ 410.2731. $C_{23}H_{39}NO_3S$ requires *M* + H, 410.2729].

(3-Methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)(phenyl)methanol *syn*-24 and *anti*-24

Using general procedure A, aziridine **14** (100 mg, 0.31 mmol) in THF (3 mL), *sec*-BuLi (0.78 mL of a 1.2 M solution in cyclohexane, 0.93 mmol, 3.0 eq), PMDETA (0.19 mL, 0.93 mmol, 3.0 eq) in THF (2 mL) and benzaldehyde (0.1 mL, 0.93 mmol) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave starting aziridine **14** (3 mg, 3%), alcohol *syn*-**24** (33 mg, 25%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3504 (OH), 1312 (SO_2) and 1150 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.31–7.29 (5 H, m, Ph), 7.19 (2 H, s, Ar), 4.85 (1 H, dd, *J* 8.0 and 3.0, CHO), 4.31 (2 H, sept, *J* 7.0, ArCH), 3.25 (1 H, br s, OH), 3.19 (1 H, qd, *J* 6.0 and 4.5, CHN), 2.98–2.89 (2 H, m, ArCH and CHN), 1.35 (3 H, d, *J* 6.0, Me), 1.29 (6 H, d, *J* 7.0, Me) and 1.27 (12 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.4 (*ipso*-Ar), 150.6 (*ipso*-Ar), 140.1 (*ipso*-Ph), 133.5 (*ipso*-Ar), 128.6 (Ph), 128.0 (Ph), 125.8 (Ph), 123.8 (Ar), 72.7 (CHO), 55.9 (CHN), 43.2 (CHN), 34.2 (ArCH), 29.8 (ArCH), 24.8 (Me), 23.6 (Me) and 15.5 (Me); *m*/*z* (CI; NH_3) 430 (100) [Found $(M + H)^+$ 430.2418. $C_{25}H_{35}NO_3S$ requires *M* + H, 430.2416] and alcohol *anti*-**24** (57 mg, 43%) as a white solid, mp 97–99 °C (from 10 : 1 petrol–Et_2O); R_F (1 : 1 petrol–Et_2O) 0.4; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3479 (OH), 1315 (SO_2) and 1151 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.25–7.21 (5 H, m, Ph), 7.20 (2 H, s, Ar), 4.78 (1 H, d, *J* 4.0, CHO), 4.35 (2 H, sept, *J* 7.0, ArCH), 3.22 (1 H, t, *J* 4.0, CHN), 3.13 (1 H, qd, *J* 6.0 and 4.0, CHN), 2.93 (1 H, sept, *J* 7.0, ArCH), 2.34 (1 H, br s, OH), 1.68 (3 H, d, *J* 6.0, Me), 1.32 (6 H, d, *J* 7.0, Me), 1.31 (6 H, d, *J* 7.0, Me) and 1.27 (6 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 153.2 (*ipso*-Ar), 150.4 (*ipso*-Ar), 139.8 (*ipso*-Ph), 133.8 (*ipso*-Ar), 128.5 (Ph), 128.1 (Ph), 125.9 (Ph), 123.7 (Ar), 71.1 (CHO), 52.2 (CHN), 42.5 (CHN), 34.2 (ArCH), 29.7 (ArCH), 24.9 (Me), 24.7 (Me), 23.59 (Me), 23.56 (Me) and 13.8 (Me); *m*/*z* (CI; NH_3) 430 (100) [Found $(M + H)^+$ 430.2410. $C_{25}H_{35}NO_3S$ requires *M* + H, 430.2416].

2-Methyl-1-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-one 25

Using general procedure B, aziridine **9** (200 mg, 0.64 mmol) in THF (6 mL), *sec*-BuLi (1.60 mL of a 1.2 M solution in cyclohexane, 1.92 mmol, 3.0 eq), PMDETA (0.4 mL, 1.92 mmol, 3.0 eq) in THF (4 mL) and isobutyraldehyde (0.2 mL, 1.92 mmol) followed by PCC (207 mg, 0.96 mmol) in CH_2Cl_2 (10 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave ketone **25** (135 mg, 56%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1721 (C=O), 1322 (SO_2) and 1164 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.19 (2 H, s, Ar), 4.31 (2 H, sept, *J* 7.0, ArCH), 3.44 (1 H, dd, *J* 7.0 and 4.0, CHN), 2.91 (1 H, sept, *J* 7.0, ArCH), 2.80 (1 H, d, *J* 7.0, CH_2N), 2.69 (1 H, sept, *J* 7.0, CH), 2.50 (1 H, d, *J* 4.0, CH_2N), 1.26 (6 H, d, *J* 7.0, Me), 1.24 (12 H, d, *J* 7.0, Me), 1.04 (3 H, d, *J* 7.0, Me) and 0.98 (3 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 206.5 (C=O), 154.1 (*ipso*-Ar), 151.4 (*ipso*-Ar), 130.5 (*ipso*-Ar), 123.9 (Ar), 39.0 (CHN), 38.8 (CH), 34.2 (ArCH), 32.0 (CH_2N), 29.8 (ArCH), 24.9 (Me), 24.8 (Me), 23.5 (Me), 17.7 (Me) and 17.3 (Me); *m*/*z* (CI; NH_3) 380 (100) [Found $(M + H)^+$ 380.2258. $C_{21}H_{33}NO_3S$ requires *M* + H, 380.2259].

2,2-Dimethyl-1-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-one 26

Using general procedure B, aziridine **9** (200 mg, 0.64 mmol) in THF (6 mL), *sec*-BuLi (1.60 mL of a 1.2 M solution in cyclohexane, 1.92 mmol), PMDETA (0.4 mL, 1.92 mmol) in THF (4 mL) and trimethylacetaldehyde (0.2 mL, 1.92 mmol) followed by PCC (207 mg, 0.96 mmol) in CH_2Cl_2 (10 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave ketone **26** (153 mg, 61%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1717 (C=O), 1323 (SO_2) and 1163 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.17 (2 H, s, Ar), 4.30 (2 H, sept, *J* 7.0, ArCH), 3.61 (1 H, dd, *J* 7.0 and 4.0, CHN), 2.88 (1 H, sept, *J* 7.0, ArCH), 2.80 (1 H, d, *J* 7.0, CH_2N), 2.58 (1 H, d, *J* 4.0, CH_2N), 1.26 (6 H, d, *J* 7.0, Me), 1.24 (6 H, d, *J* 7.0, Me), 1.23 (6 H, d, *J* 7.0, Me) and 1.07 (9 H, s, CMe_3); δ_C (100.6 MHz; $CDCl_3$) 206.5 (C=O), 154.0 (*ipso*-Ar), 151.3 (*ipso*-Ar), 130.7 (*ipso*-Ar), 123.9 (Ar), 44.3 (CMe_3), 35.6 (CHN), 34.3 (ArCH), 32.2 (CH_2N), 29.8 (ArCH), 25.5 (CMe_3), 24.9 (Me), 24.8 (Me) and 23.5 (Me); *m*/*z* (CI; NH_3) 394 (100) [Found $(M + H)^+$ 394.2416. $C_{22}H_{35}NO_3S$ requires *M* + H, 394.2416].

Phenyl-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)methanone 27

Using general procedure B, aziridine **9** (200 mg, 0.64 mmol) in THF (6 mL), *sec*-BuLi (1.60 mL of a 1.2 M solution in cyclohexane, 1.92 mmol), PMDETA (0.4 mL, 1.92 mmol) in THF (4 mL) and benzaldehyde (0.2 mL, 1.92 mmol) followed by PCC (207 mg, 0.96 mmol) in CH_2Cl_2 (10 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (8 : 1) as eluent gave ketone **27** (117 mg, 44%) as a white solid, mp 94–96 °C, R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1690 (C=O), 1322 (SO_2) and 1163 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.94 (2 H, dd, *J* 7.0 and 1.0, *o*-Ph), 7.58 (1 H, br t, *J* 7.0, *p*-Ph), 7.42 (2 H, t, *J* 7.0, *m*-Ph), 7.18 (2 H, s, Ar), 4.32 (2 H, sept, *J* 7.0, ArCH), 4.13 (1 H, dd, *J* 7.0 and 4.0, CHN), 2.95 (1 H, d, *J* 7.0, CH_2N), 2.89 (1 H, sept, *J* 7.0, ArCH), 2.80 (1 H, d, *J* 4.0, CH_2N), 1.25 (6 H, d, *J* 7.0, Me), 1.24 (6 H, d, *J* 7.0, Me) and 1.21 (6 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 191.7 (C=O), 154.0 (*ipso*-Ar), 151.4 (*ipso*-Ar), 135.7 (*ipso*-Ph), 133.9 (Ph), 130.7 (*ipso*-Ar), 128.75 (Ph), 128.68 (Ph), 124.0 (Ar), 37.9 (CHN), 34.2 (ArCH), 32.0 (CH_2N), 29.8 (ArCH), 24.78 (Me), 24.75 (Me), 23.52 (Me) and 23.50 (Me); *m*/*z* (CI; NH_3) 414 (100) [Found $(M + H)^+$ 414.2097. $C_{24}H_{31}NO_3S$ requires *M* + H, 414.2103].

2-Methyl-1-(3-methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-one 28

Using general procedure B, aziridine **14** (200 mg, 0.62 mmol) in THF (6 mL), *sec*-BuLi (1.56 mL of a 1.2 M solution in cyclohexane, 1.86 mmol), PMDETA (0.38 mL, 1.86 mmol) in

THF (4 mL) and isobutyraldehyde (0.2 mL, 1.86 mmol) followed by PCC (200 mg, 0.93 mmol) in CH_2Cl_2 (10 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (8 : 1) as eluent gave ketone **28** (127 mg, 52%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1711 (C=O), 1322 (SO_2) and 1164 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.15 (2 H, s, Ar), 4.32 (2 H, sept, *J* 7.0, ArCH), 3.47 (1 H, d, *J* 4.0, CHN), 3.01 (1 H, qd, *J* 6.0 and 4.0, CHN), 2.89 (1 H, sept, *J* 7.0, ArCH), 2.58 (1 H, sept, *J* 7.0, CH), 1.76 (3 H, d, *J* 6.0, Me), 1.25 (12 H, d, *J* 7.0, Me), 1.23 (6 H, d, *J* 7.0, Me), 0.93 (3 H, d, *J* 7.0, Me) and 0.81 (3 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 206.5 (C=O), 153.6 (*ipso*-Ar), 150.8 (*ipso*-Ar), 133.1 (*ipso*-Ar), 123.7 (Ar), 48.5 (CHN), 44.9 (CHN), 37.4 (CH), 34.2 (ArCH), 29.7 (ArCH), 24.9 (Me), 24.6 (Me), 23.51 (Me), 23.48 (Me), 17.9 (Me), 17.2 (Me) and 13.7 (Me); *m*/*z* (CI; NH_3) 394 (100) [Found $(M + H)^+$ 394.2409. $C_{22}H_{35}NO_3S$ requires *M* + H, 394.2416].

2,2-Dimethyl-1-(3-methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-one 29

Using general procedure B, aziridine **14** (200 mg, 0.62 mmol) in THF (6 mL), *sec*-BuLi (1.56 mL of a 1.2 M solution in cyclohexane, 1.86 mmol), PMDETA (0.38 mL, 1.86 mmol) in THF (4 mL) and trimethylacetaldehyde (0.2 mL, 1.86 mmol) followed by PCC (200 mg, 0.93 mmol) in CH_2Cl_2 (10 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (8 : 1) as eluent gave ketone **29** (143 mg, 57%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1716 (C=O), 1320 (SO_2) and 1155 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.13 (2 H, s, Ar), 4.32 (2 H, sept, *J* 7.0, ArCH), 3.74 (1 H, d, *J* 4.0, CHN), 3.03 (1 H, qd, *J* 6.0, 4.0, CHN), 2.88 (1 H, sept, *J* 7.0, ArCH), 1.76 (3 H, d, *J* 6.0, Me), 1.26 (6 H, d, *J* 7.0, Me), 1.24 (6 H, d, *J* 7.0, Me), 1.23 (6 H, d, *J* 7.0, Me) and 1.08 (9 H, s, CMe_3); δ_C (100.6 MHz; $CDCl_3$) 206.9 (C=O), 153.4 (*ipso*-Ar), 150.8 (*ipso*-Ar), 133.2 (*ipso*-Ar), 123.7 (Ar), 45.7 (CHN), 45.0 (CHN), 44.0 (CMe_3), 34.2 (ArCH), 29.8 (ArCH), 25.5 (CMe_3), 24.8 (Me), 24.7 (Me), 23.55 (Me), 23.52 (Me) and 13.5 (Me); *m*/*z* (CI; NH_3) 408 (100) [Found $(M + H)^+$ 408.2564. $C_{23}H_{37}NO_3S$ requires *M* + H, 408.2572].

(3-Methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)(phenyl)methanone 30

Using general procedure B, aziridine **14** (200 mg, 0.62 mmol) in THF (6 mL), *sec*-BuLi (1.56 mL of a 1.2 M solution in cyclohexane, 1.86 mmol), PMDETA (0.38 mL, 1.86 mmol) in THF (4 mL) and benzaldehyde (0.2 mL, 1.86 mmol) followed by PCC (200 mg, 0.93 mmol) in CH_2Cl_2 (10 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (8 : 1) as eluent gave ketone **30** (230 mg, 58%) as a colourless oil, R_F (1 : 1 petrol–Et_2O) 0.8; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1690 (C=O), 1321 (SO_2) and 1163 (SO_2); δ_H (400 MHz, $CDCl_3$) 7.91 (2 H, dd, *J* 8.0 and 1.0, *o*-Ph), 7.57 (1 H, t, *J* 8.0 and 1.0, *p*-Ph), 7.41 (2 H, t, *J* 8.0, *m*-Ph), 7.12 (2 H, s, Ar), 4.34 (2 H, sept, *J* 7.0, ArCH), 4.19 (1 H, d, *J* 4.0, CHN), 3.28 (1 H, qd, *J* 6.0 and 4.0, CHN), 2.86 (1 H, sept, *J* 7.0, ArCH), 1.83 (3 H, d, *J* 6.0, Me), 1.24 (6 H, d, *J* 7.0, Me), 1.23 (6 H, d, *J* 7.0, Me) and 1.21 (6 H, d, *J* 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 192.2 (C=O), 153.4 (*ipso*-Ar), 150.7 (*ipso*-Ar), 135.8 (*ipso*-Ph), 133.8 (Ph), 133.2 (*ipso*-Ar), 128.7 (Ph), 128.5 (Ph), 123.7 (Ar), 46.8 (CHN), 45.5 (CHN), 34.2 (ArCH), 29.8 (ArCH), 24.8 (Me), 24.6 (Me), 23.5 (Me) and 13.9 (Me); *m*/*z* (CI; NH_3) 428 (100) [Found $(M + H)^+$ 428.2256. $C_{25}H_{33}NO_3S$ requires *M* + H, 428.2259].

2-Methyl-1-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-18 and *anti*-18

Using general procedure C, ketone **25** (75 mg, 0.2 mmol), $NaBH_4$ (9 mg, 0.24 mmol) and $CeCl_3.7H_2O$ (90 mg, 0.24 mmol) in MeOH (2 mL) gave the crude product which contained a 90 : 10 mixture of alcohols *syn*-**18** and *anti*-**18** by ^1H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave alcohol *syn*-**18** (48 mg, 64%) as a colourless oil and alcohol *anti*-**18** (5 mg, 7%) as a colourless oil.

2,2-Dimethyl-1-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-19 and *anti*-19

Using general procedure C, ketone **26** (75 mg, 0.19 mmol), $NaBH_4$ (9 mg, 0.23 mmol) and $CeCl_3.7H_2O$ (86 mg, 0.23 mmol) in MeOH (2 mL) gave the crude product which contained a >95 : 5 mixture of alcohols *syn*-**19** and *anti*-**19** by ^1H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave alcohol *syn*-**19** (62 mg, 83%) as a colourless oil.

Phenyl-(1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)methanol *syn*-20 and *anti*-20

Using general procedure C, ketone **27** (75 mg, 0.18 mmol), $NaBH_4$ (8.2 mg, 0.22 mmol) and $CeCl_3{\cdot}7H_2O$ (82 mg, 0.22 mmol) in MeOH (2 mL) gave the crude product which contained a 95 : 5 mixture of alcohols *syn*-**20** and *anti*-**20** by ^1H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave alcohol *syn*-**20** (70 mg, 93%) as a colourless oil and alcohol *anti*-**20** (3 mg, 4%) as a colourless oil.

2-Methyl-1-(3-methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-22 and *anti*-22

Using general procedure C, ketone **28** (75 mg, 0.19 mmol), $NaBH_4$ (9 mg, 0.23 mmol) and $CeCl_3{\cdot}7H_2O$ (86 mg, 0.23 mmol) in MeOH (2 mL) gave the crude product which contained a 90 : 10 mixture of alcohols *syn*-**22** and *anti*-**22** by ^1H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave alcohol *syn*-**22** (58 mg, 77%) as a colourless oil and alcohol *anti*-**22** (8 mg, 10%) as a colourless oil.

2,2-Dimethyl-1-(3-methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)propan-1-ol *syn*-23 and *anti*-23

Using general procedure C, ketone **29** (75 mg, 0.18 mmol), $NaBH_4$ (8.4 mg, 0.22 mmol) and $CeCl_3{\cdot}7H_2O$ (75 mg, 0.22 mmol) in MeOH (2 mL) gave the crude product which contained a 95 : 5 mixture of alcohols *syn*-**23** and *anti*-**23** by ^1H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave alcohol *syn*-**23** (59 mg, 79%) as a colourless oil.

(3-Methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)(phenyl)methanol *syn*-24 and *anti*-24

Using general procedure C, ketone **30** (50 mg, 0.12 mmol), $NaBH_4$ (5.3 mg, 0.14 mmol) and $CeCl_3{\cdot}7H_2O$ (52 mg, 0.14 mmol) in MeOH (1.5 mL) gave the crude product which contained a 90 : 10 mixture of alcohols *syn*-**24** and *anti*-**24** by ^{1}H NMR spectroscopy. Purification by flash chromatography on silica with petrol–Et_2O (10 : 1) as eluent gave alcohol *syn*-**24** (44 mg, 88%) as a colourless oil and alcohol *anti*-**24** (3 mg, 6%) as a colourless oil.

Crystal structure determination of (3-methyl-1-(2,4,6-triisopropylphenylsulfonyl)aziridin-2-yl)(phenyl)methanol *syn*-24

Crystal data. $C_{25}H_{35}NO_3S$, M = 429.60, monoclinic, a = 10.2117(11), b = 13.3903(14), c = 17.8587(19) Å, β = 104.642(2)°, U = 2362.7(4) Å^3, T = 110(2) K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 0.162 mm^{-1}, 18118 reflections measured, 4156 unique (R_{int} = 0.0334) which were used in all calculations. The final $R1$ was 0.0408 ($I > 2\sigma_I$) and w$R2$ was 0.1039 (all data). CCDC reference number 695489.

anti-4-Nitrobenzoic acid 2-methyl-1-[3-methyl-1-(2,4,6-triisopropylbenzenesulfonyl) aziridin-2-yl]propyl ester

A solution of 4-nitrobenzoyl chloride (101 mg, 0.54 mmol) in CH_2Cl_2 (2 mL) was added to a stirred solution of hydroxy aziridine *anti*-**22** (179 mg, 0.45 mmol) and Et_3N (0.19 mL, 1.35 mmol) in CH_2Cl_2 (3 mL) at 0 °C under N_2. The resulting pale yellow solution was allowed to warm to rt and stirred for 14 h. Water (5 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL) and the combined organics were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol–Et_2O (5 : 1) as eluent gave the *anti*-ester (29 mg, 12%) as a white crystalline solid, mp 110–111 °C; R_F (5 : 1 petrol–Et_2O) 0.3; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2966, 1726 (C=O), 1531, 1463, 1316 (SO_2), 1151 (SO_2), 1101, 969; δ_H (400 MHz, $CDCl_3$) 8.30 (2 H, d, J 9.0, *o*-$C_6H_4NO_2$), 8.14 (2 H, d, J 9.0, *m*-$C_6H_4NO_2$), 7.16 (2 H, s, Ar), 4.72 (1 H, dd, J 6.5 and 3.5, CHO), 4.33 (2 H, sept, J 6.5, ArCH), 3.06 (1 H, dd, J 6.0 and 3.5, CHN), 2.99 (1 H, qd, J 6.0 and 4.5, CHN), 2.91 (1 H, sept, J 7.0, ArCH), 1.76 (1 H, sept d, J 7.0 and 3.5, C*H*Me$_2$), 1.68 (3 H, d, J 6.0, Me), 1.27 (6 H, d, J 6.5, Me), 1.19 (6 H, d, J 6.5, Me), 1.26 (6 H, d, J 7.0, Me), 0.94 (3 H, d, J 7.0, Me), 0.87 (3 H, d, J 7.0, Me); δ_C (100.6 MHz; $CDCl_3$) 163.8 (C=O), 153.4 (*ipso*-Ar), 150.7 (*ipso*-Ar), 150.6 (*ipso*-Ar), 135.2 (*ipso*-Ar), 133.4 (*ipso*-Ar), 130.7 (*o*-$C_6H_4NO_2$), 123.6 (2 × CH, Ar), 78.3 (CHO), 46.2 (CHN), 44.7 (CHN), 34.2 (ArCH), 30.7 (ArCH), 29.7 (ArCH), 24.8 (Me), 24.7 (Me), 23.6 (Me), 18.7 (Me) 16.5 (Me), 13.6 (Me); m/z (ESI) 544 [(M + H),$^+$ 100], 438 (7) [Found (M + H)$^+$ 545.2680. $C_{29}H_{40}N_2O_6S$ requires M + H, 545.2685].

Crystal structure determination of *anti*-4-nitrobenzoic acid 2-methyl-1-[3-methyl-1-(2,4,6-triisopropylbenzenesulfonyl) aziridin-2-yl]propyl ester

Crystal data. $C_{29}H_{40}N_2O_6S$, M = 544.69, monoclinic, a = 9.7183(5), b = 19.6987(9), c = 15.3953(7) Å, β = 95.6970(10)°, U = 2932.7(2) Å^3, T = 110(2) K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 0.153 mm^{-1}, 29913 reflections measured, 7272 unique (R_{int} = 0.0320) which were used in all calculations. The final $R1$ was 0.0420 ($I > 2\sigma_I$) and w$R2$ was 0.1099 (all data). CCDC reference number 695490.

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