Terminal Aziridines by Addition of Grignard Reagents or Organoceriums to an (α-Chloro)sulfinylimine

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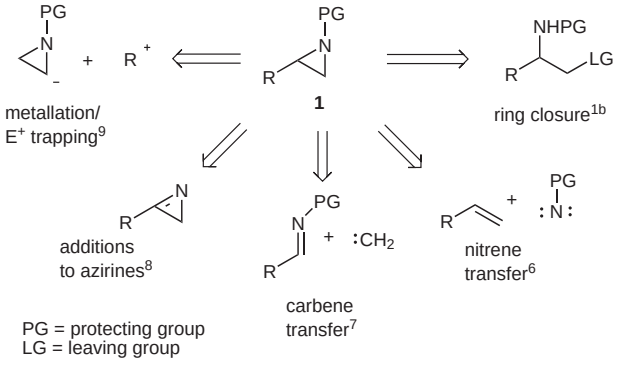
Abstract: Reaction of *N*-(2-chloroethylidene)-*tert*-butylsulfinamide with Grignard reagents or organoceriums gives terminal *N*-*tert*-butylsulfinyl aziridines in good yields and (mainly with organoceriums) good diastereomeric ratios. Oxidation of terminal *N*-*tert*-butylsulfinyl aziridines provides synthetically useful terminal *N*-Bus (Bus = *tert*-butylsulfonyl) aziridines.

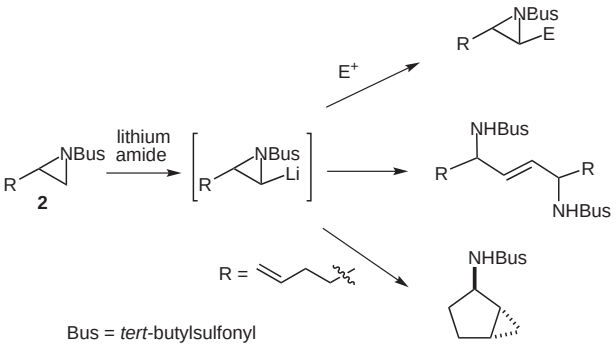
Key words: aziridines, chiral auxiliaries, imines, nucleophilic addition, organoceriums

Facilitating ways to introduce nitrogen-containing organic fragments into organic molecules is an important goal in synthetic chemistry. Aziridines, typically when bearing an electron-withdrawing/-activating group on nitrogen, are becoming increasingly important electrophiles.[1] Terminal aziridines **1** are probably the most useful aziridines of all, because of the ease, generality and predictable regioselectivity with which they undergo ring-opening reactions with nucleophiles.[2] Five strategically different ways that have been used to access terminal aziridines are outlined in Scheme 1.[1b,3] In the context of asymmetric synthesis, all of these strategies have been pursued with varying degrees of success, but it remains the case that there is currently no general and straightforward method to access highly enantioenriched 2-substituted (particularly 2-alkyl-substituted) aziridines in an efficient manner.[4,5]



Scheme 1 Synthetic approaches to terminal aziridines

We became aware of current limitations for the asymmetric synthesis of terminal aziridines during our recent development of several new transformations of terminal aziridines proceeding by α-lithiation, including trapping of electrophiles, dimerisation, and intramolecular cyclopropanation of terminal *N*-Bus (Bus = *tert*-butylsulfonyl) aziridines **2** (Scheme 2).[10] The Bus protecting group was originally introduced by Weinreb and co-workers as a base-stable (acid-labile) protecting group for nitrogen,[11] and we have found the Bus group uniquely suited for the range of chemistry shown in Scheme 2.



Scheme 2 Reactions of α-lithiated terminal *N*-Bus aziridines[10]

Where we used enantioenriched terminal *N*-Bus aziridines **2** in the chemistry in Scheme 2, the aziridines were typically prepared using *t*-$BuSO_2NH_2$ in a three-step regioselective epoxide ring-opening/aziridine ring-closure sequence, with the starting enantiopure terminal epoxides being accessed by Jacobsen's hydrolytic kinetic resolution protocol.[10d] With the aim of developing a more direct asymmetric synthesis of terminal *N*-Bus aziridines which avoided a resolution step, we were attracted to a report in 2006 by De Kimpe and co-workers concerning an asymmetric synthesis of 2,2,3-trisubstituted aziridines **4** by addition of Grignard reagents to nonenolisable α-chloroaldimines **3** (Scheme 3).[12,13] Successful adaptation of this latter chemistry to make terminal *N*-Bus aziridines **2** would require: (i) straightforward access to the *N*-*tert*-butylsulfinyl imine of α-chloroacetaldehyde **3** (R^1 = H), (ii) development of conditions for the efficient and highly diastereoselective addition of organometallics to this imine (which avoid enolisation and/or chloride displacement) followed by ring-closure (ideally in situ), and (iii) sulfinyl to sulfonyl oxidation while preserving the terminal aziridine. The present article describes the realisation of these goals.[14]

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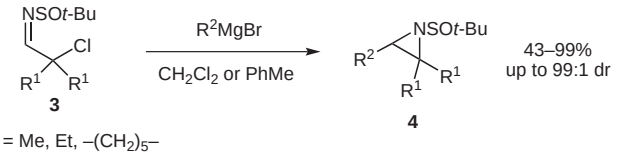
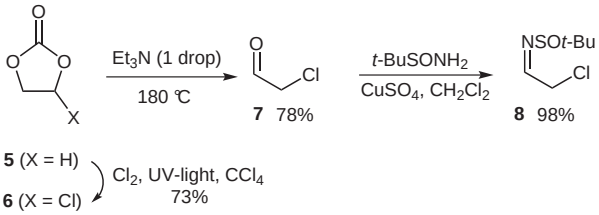


Scheme 3 Addition of Grignard reagents to α-chloroaldimines **3**[12]

De Kimpe and co-workers prepared their α-chloroaldimines **3** (R^1 = alkyl) by condensation of commercially available *t*-BuSONH$_2$ with the corresponding α-chloroaldehydes using Ti(OEt)$_4$ in THF at reflux, where the Lewis acid also acts as a trap for the generated water. As α-chloroacetaldehyde (**7**) is supplied in aqueous solution, which only gives the hemiacetal on extraction with organic solvents, we first attempted to prepare our desired imine **8** from commercially available chloroacetaldehyde dimethyl acetal and *t*-BuSONH$_2$; however, no reaction was seen in the presence of Ti(OEt)$_4$, whereas decomposition was observed using TiCl$_4$. Among the reported methods to access anhydrous α-chloroacetaldehyde (**7**),[15,16] in our hands only Et$_3$NHCl-catalysed loss of CO$_2$ from 4-chloro-1,3-dioxolan-2-one (**6**) proved viable (Scheme 4).[16] Dioxolanone **6** is commercially available (but now expensive); however, it can be conveniently prepared by chlorination of cheap 1,3-dioxolan-2-one (**5**) in CCl$_4$.[17] Although reaction of *t*-BuSONH$_2$ with anhydrous α-chloroacetaldehyde in the presence of Ti(OEt)$_4$ led to decomposition, milder conditions using anhydrous CuSO$_4$[18] did generate the desired imine **8**; the latter reaction is essentially quantitative and requires no further purification following filtration and solvent removal.



Scheme 4 Synthesis of imine **8**

Initial application of De Kimpe's conditions (CH$_2$Cl$_2$, –78 °C, 2 h)[12] using BuMgCl (1.1 equiv) as a representative Grignard reagent led to complete consumption of imine **8** and cleanly gave chloroamine **9** (80%); however, virtually no diastereoselectivity was observed (53:47, by GC of crude reaction mixture). Diastereoselectivity was not significantly improved by switching to THF as sol-

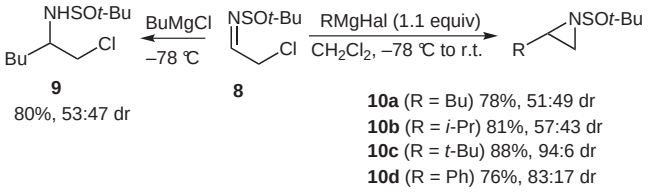
Biographical Sketches

David M. Hodgson obtained his first degree in Chemistry at Bath University. After a Ph.D. at Southampton University in the field of natural product synthesis (with P. J. Parsons) and a research position at Schering, he was appointed in 1990 to a lectureship at Reading University. In 1995 he moved to the Chemistry Department at Oxford University, where he is now a Professor of Chemistry. His research interests are broadly in the development and application of synthetic methods.

Johannes Kloesges obtained his first degree in Chemistry at Oxford University (Oriel College), which included a final-year project on aminohydroxylation with Tim Donohoe. His graduate studies, in collaboration with GlaxoSmithKline, are concerned with aziridines.

Brian Evans obtained his first degree in Chemistry at the University of Liverpool. After a research position at Allen & Hanburys, and a Ph.D. at Liverpool on porphyrins (with K. M. Smith), he joined Glaxo-Allenburys Research in 1977 and stayed with Glaxo under the various name changes. His research activities have encompassed histamine H2 blockers (zantac), serotonin receptors (sumatriptan, ondansetron), adenosine receptors, β-stimulants (serevent), neurokinin receptors, combinatorial chemistry, and early-phase drug discovery.

vent, or by the use of additives such as dioxane (potentially driving the Schlenk equilibrium towards Bu_2Mg), LiCl (potential chelation of Li^+ to N and Cl), or $CeCl_3$, whereas using BuLi simply resulted in decomposition of imine **8**. Nevertheless, allowing a reaction under the original conditions to warm to room temperature did lead to ring-closure and isolation of terminal aziridine **10a** in 78% yield and unchanged diastereomeric ratio (51:49) (Scheme 5). In De Kimpe's study, imine **3** (R^1 = Me) was reduced with *i*-PrMgCl,[12] whereas in the present work less-hindered imine **8** efficiently gave aziridine **10b** [81%, only traces of the corresponding reduced imine, *N*-(2-chloroethyl)-*tert*-butylsulfinamide,[9] were detected], but the diastereoselectivity (57:43 dr) remained similar to that seen with BuMgCl. However, *t*-BuMgCl gave aziridine **10c** (88%) with significant diastereocontrol (94:6 dr) and PhMgBr gave aziridine **10d** (76%) with 83:17 dr.



Scheme 5 Addition of Grignard reagents to imine **8**

Repeating the reaction with *t*-BuMgCl, but using imine (R_S)-**8** [prepared as before, but using commercially available (R_S)-*t*-$BuSONH_2$][19] provided an opportunity to both study the viability of the desired subsequent sulfinyl to sulfonyl oxidation step, as well as establish the predominant sense of asymmetric induction [as the specific rotation of *N*-Bus aziridine (*R*)-**2c** is known].[10d] MCPBA has previously been reported to oxidise 2,3-disubstituted *N*-*tert*-butylsulfinyl aziridines to *N*-Bus aziridines,[20] and in the present case efficient oxidation of the sulfinyl aziridine from *t*-BuMgCl and imine (R_S)-**8** gave *N*-Bus aziridine (*R*)-**2c** (84%, Scheme 6), which illustrates asymmetric access to synthetically valuable terminal *N*-Bus aziridine functionality. The sense of asymmetric induction found using imine **8** with *t*-BuMgCl is opposite to that observed with non-functionalised *tert*-butylsulfinyl aldimines, but parallels that observed in De Kimpe's study (and in most other reports concerning *N*-sulfinyl imines containing α-coordinating groups).[12,13] With non-functionalised aldimines, the sense of asymmetric induction has been rationalised by invoking a chair-like transition state involving chelation of the incoming nucleophile to the sulfinyl oxygen of the *E*-imine, with the sterically demanding *t*-Bu group residing equatorial (**TS-A**, Figure 1). To explain the reversal with α-coordinating groups, it has been proposed that such groups either override sulfinyl oxygen chelation (**TS-B**),[21] or additionally chelate (**TS-C**),[22] the latter only being possible following to *E*- to *Z*-imine isomerisation under the reaction conditions.

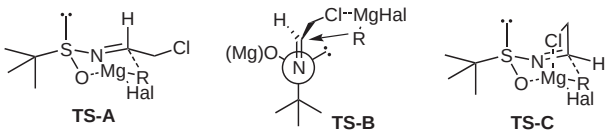
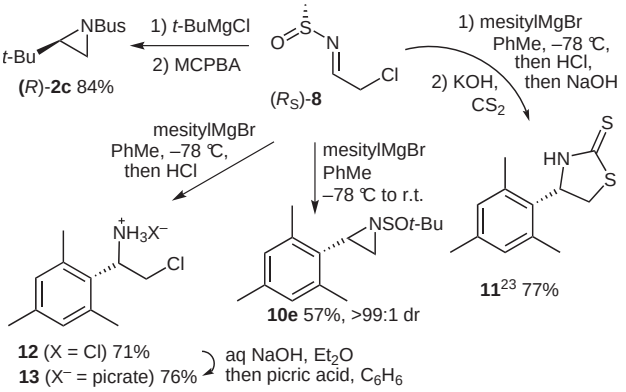


Figure 1 Possible transition states for addition of RMgHal to imine (R_S)-**8**



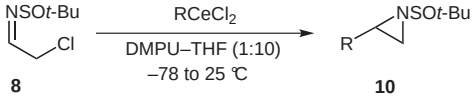
Scheme 6 Addition of Grignard reagents to imine (R_S)-**8**

During the course of our initial studies discussed above, Crimmins and Shamszad reported in a synthesis of thiazolidinethione **11** an isolated example of an addition to imine (R_S)-**8**, using mesitylmagnesium bromide (mesitylMgBr, 5 equiv) at –78 °C in toluene and which occurred with high/complete diastereoselectivity (Scheme 6).[23,24] While re-examination of the above three alkyl Grignard reagents (5 equiv) with imine **8** in toluene did not change the efficiency, or the magnitude (or sense) of stereoinduction found for aziridine formation in CH_2Cl_2, we were intrigued that Crimmins and Shamszad had noted the opposite sense of asymmetric induction with mesitylMgBr to that which we had determined with *t*-BuMgCl. We confirmed the remarkable complete reversal of asymmetric induction between these two hindered Grignard reagents by X-ray crystallographic analysis of picrate **13**.[25] Picrate **13** was derived from addition of mesitylMgBr to imine (R_S)-**8** with quenching at low temperature (the corresponding aziridine **10e** was formed in 57% yield and >99:1 dr if the reaction was allowed to warm to room temperature), followed by counter-anion exchange from the hydrochloride salt **12** (Scheme 6). Perhaps the more sterically demanding mesityl group prevents coordination to the α-chloro group, resulting in reaction proceeding by way of **TS-A** (Figure 1).[26]

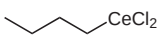
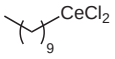
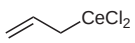
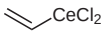
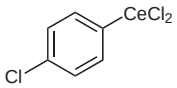
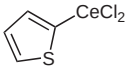
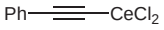
The addition of Grignard reagents to imine **8** furnished the desired aziridines **10** in good yields. However, aside from the significant diastereocontrol observed with the bulky *t*-Bu and mesityl Grignard reagents, there was an obvious shortfall in diastereoselectivity seen for the simple alkyl-substituted aziridines and for which efficient asymmetric access was a principal goal of the current study. Ellman and co-workers, in their seminal studies on additions of organometallics to simple *N*-*tert*-butylsulfinyl-substituted aldimines, noted in a single example (**8**, Me instead of Cl)

that $MeCeCl_2$ (THF, –78 °C) was inferior to MeMgBr (CH_2Cl_2, –48 °C) with respect to diastereoselectivity (78:22 compared with 97:3, respectively).[27] However, encouraged by Denmark and co-workers' earlier report on organocerium additions to SAMP-hydrazones,[28] we examined $BuCeCl_2$ (1.2 equiv) with imine **8** in THF or Et_2O at –78 °C and were pleased to observe significant rises in diastereoselectivity (93:7 and 87:13, respectively); allowing these reactions to warm to room temperature led to ring-closure and isolation of terminal aziridine **10a** in 82% and 77% yield, respectively, and unchanged diastereomeric ratios. The diastereoselectivity in THF could be further improved to >99:1 (GC analysis) by addition of HMPA or DMPU,[29] and warming to room temperature gave terminal aziridine **10a** in 83 and 86% yields, respectively and in unchanged diastereomeric ratio (Table 1, entry 1). Use of 10% DMPU in THF also improved the diastereomeric ratio as reported by Ellman and co-workers in the addition of $MeCeCl_2$ to imine **8** (Me instead of Cl) from 78:22 (89% yield)[27] to 96:4 (75% yield).

Table 1 Aziridines **10** from α-Chloroimine **8** Using Organoceriums



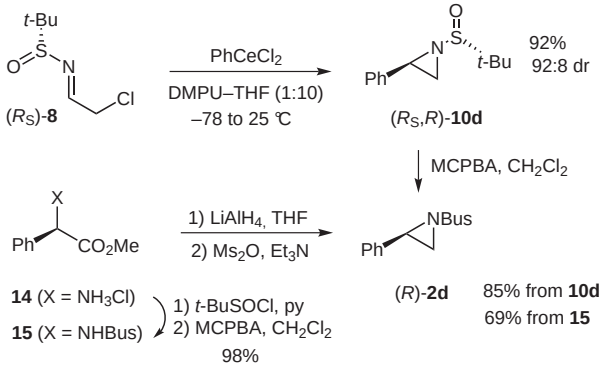
8 **10**

Entry	Organocerium reagent	Aziridine	Yield (%)	dr[a]
1		**10a**	86	>99:1
2	*t*-$BuCeCl_2$	**10c**	76	>99:1
3[b]		**10f**	78	97:3
4	$MeCeCl_2$	**10g**	81[c]	91:9
5		**10h**	83	99:1
6		**10i**	75[c]	86:14
7[d]	$PhCeCl_2$	**10d**	92	92:8
8		**10j**	84	85:15
9		**10k**	81	92:8
10		**10l**	82	85:15

[a] By GC of crude reaction mixture.
[b] Using (R_S)-**8**.
[c] Isolated as the corresponding *N*-Bus aziridine **2** following oxidation.
[d] Using HMPA instead of DMPU gave **10d** in 93% yield, 92:8 dr.

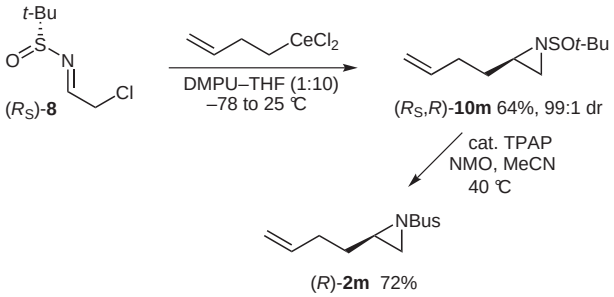
The scope of this reaction was then examined with a range of organocerium reagents (Table 1). The organocerium reagents were prepared from the corresponding organolithiums and $CeCl_3$. Alkyl- and allylcerium reagents added with essentially complete diastereocontrol, with the exception of $MeCeCl_2$ (entries 1–5). The reaction was less diastereoselective for alkenyl, aryl, heteroaryl, and alkynyl cerium reagents (entries 6–10). Entries 5, 6, 8, and 10 illustrate the ability to carry additional functionality into the aziridine **10**. Similarly to $BuCeCl_2$, the absence of 10% DMPU was shown to result in significantly lower diastereomeric ratios for methyl-, allyl- and phenylcerium additions [83% yield (63:37 dr), 91% yield (85:15 dr), and 90% (70:30 dr), respectively].

MCPBA oxidation of sulfinyl aziridine **10f**, formed from addition of $C_{10}H_{21}CeCl_2$ to imine (R_S)-**8** (Table 1, entry 3), gave known *N*-Bus aziridine (*R*)-**2** (R = $C_{10}H_{21}$)[10d] (87%, 96:4 er by chiral HPLC); this result indicates the sense of asymmetric induction for reaction of $C_{10}H_{21}CeCl_2$ with imine (R_S)-**8** is the same as that seen earlier for *t*-BuMgCl. The same predominant sense of asymmetric induction was also observed for phenylcerium and 4-chlorophenylcerium (Table 1, entry 8). For phenylcerium, the absolute sense of asymmetric induction was established using imine (R_S)-**8** by chemical correlation of sign of specific rotation following MCPBA oxidation to the corresponding *N*-Bus phenyl aziridine (*R*)-**2d**, with the latter being also derived from (*R*)-phenylglycine methyl ester hydrochloride (**14**) (Scheme 7). For 4-chlorophenylcerium, the relative stereochemistry of the major diastereomer of sulfinylaziridine **10j** was determined to be R_S*,*R** by X-ray crystallographic analysis.[30] As phenylcerium was observed to give the same predominant sense of asymmetric induction with imine **8** as was found earlier with PhMgBr (Scheme 5), then [now knowing both the absolute sense of asymmetric induction with phenylcerium and with mesitylMgBr (Scheme 6)] this establishes that PhMgBr gives the opposite sense of asymmetric induction to mesitylMgBr.



Scheme 7 Determination of sense of asymmetric induction with $PhCeCl_2$ and imine (R_S)-**8**

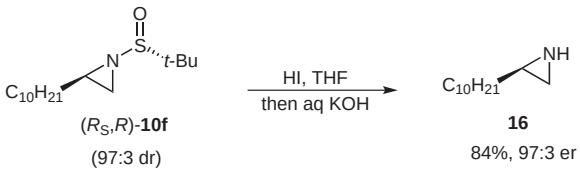
The above chemistry was exemplified in the preparation of highly enantioenriched unsaturated *N*-Bus terminal aziridine (*R*)-**2m** (Scheme 8). Aziridine **2m** has previously been shown to undergo the range of chemistry outlined in Scheme 2, with (*S*)-**2m** being obtained by the epoxide resolution strategy discussed earlier.[10d] Reaction of homoallylcerium with imine (R_S)-**8** gave sulfinylaziridine (R_S,*R*)-**10m** (64%, 99:1 dr). While oxidation of sulfinylaziridine (R_S,*R*)-**10m** using MCPBA was complicated by concomitant epoxidation, chemoselective oxidation at



Scheme 8 Synthesis of unsaturated *N*-Bus aziridine (*R*)-**2m**

sulfur was achieved using using catalytic TPAP/NMO in MeCN[31] to give unsaturated *N*-Bus aziridine (*R*)-**2m**, (72%). Similar conditions were found to be required for oxidation of vinyl aziridine **10i** (Table 1, entry 6).

Although deprotection of several *tert*-butylsulfinyl aziridines have been reported, typically using HCl in dioxane, in our hands these methods did not prove viable with terminal aziridines.[32–36] In particular, we sought deprotection conditions for alkyl-substituted terminal aziridines without degradation of enantiopurity.[37] With decylaziridine (*R*$_S$,*R*)-**10f** as a representative substrate, other methods previously reported for the deprotection of *t*-BuSO, Bus, and tosyl amines/aziridines were also examined, but without success;[11,38] our attempts either resulted in no reaction or decomposition of the starting aziridine. Finally, we considered the use of HI, anticipating it to be both capable of initiating deprotection by protonation on nitrogen[39] and S_N2 ring-opening by iodide of any putative transient aziridinium ion(s), thus leading to an intermediate α-iodo hydroiodide, which could be ring-closed to the desired NH aziridine on subsequent addition of base. In line with this analysis, reaction of decylaziridine (*R*$_S$,*R*)-**10f** with HI followed by addition of aqueous KOH gave deprotected aziridine **16** in good yield and without any loss of enantiointegrity (Scheme 9).



Scheme 9 Deprotection of aziridine **10f**

In conclusion, we have described the direct formation of terminal *N*-*tert*-butylsulfinyl aziridines **10** from addition of Grignard reagents or organoceriums to readily prepared *t*-BuSONH$_2$-derived *N*-(2-chloroethylidene)-*tert*-butylsulfinamide (**8**). The reactions proceed in good yields and (mainly with organoceriums) good diastereomeric ratios. Oxidation at sulfur of terminal *N*-*tert*-butylsulfinyl aziridines **10**, including selective oxidation in the presence of unsaturation, provides terminal *N*-Bus aziridines **2** of demonstrated[10] synthetic utility. By using one of the commercially available *t*-BuSONH$_2$ enantiomers we have also demonstrated that the chemistry provides an entry to terminal *N*-Bus aziridine functionality in high enantiomeric ratio, and that deprotection of a terminal *N*-*tert*-butylsulfinyl aziridine can be achieved (and without erosion of enantiopurity).

Reactions were performed in flame-dried glassware under an atmosphere of dry argon. MeCN and CH_2Cl_2 were degassed and dried over activated alumina under N_2. THF was distilled from sodium benzophenone ketyl in a continuous still under N_2. DMPU and HMPA were distilled from CaH_2 and stored over CaH_2 and 3 Å molecular sieves; all other reagents were used as received, unless indicated otherwise. Flash column chromatography was performed with silica gel (BDH, 0.040–0.063 mm or Machery-Nagel Kieselgel 60M). Petroleum ether (PE) refers to the fraction of petrol boiling in the range of 30–40 °C. Melting points were obtained in capillary tubes using a Griffin melting point apparatus and are uncorrected. Specific rotations $[\alpha]_D^T$ were measured with a cell of path length 10.0 cm at T °C and are given in 10^{-1} deg cm^{2}g^{-1} with concentrations *c* given in g/100 mL. Gas chromatographic analysis was performed using a Phenomenex Zebron ZB-5 high performance 5% polydimethylsiloxane column with He as carrier gas.

Further details about instrumentation, techniques and experimental details/characterisation data for aziridines not described below can be found in the supporting information of ref. 14.

4-Chloro-1,3-dioxolan-2-one (6)[17]

A solution of 1,3-dioxolan-2-one **5** (Huntsman Ultrapure® 200 g, 2.27 mol) in CCl_4 (300 mL) was irradiated with a sun-lamp (Osram Ultra-Vitalux®, 300 W) and Cl_2 gas was passed into the solution at a rate slow enough for the reaction mixture to remain colourless. After 5 h, ^{1}H NMR analysis indicated a mixture comprising 4-chloro-1,3-dioxolan-2-one (80%), 1,3-dioxolan-2-one (10%), and 4,5-dichloro-1,3-dioxolan-2-one (10%). The solvent was removed under reduced pressure and distillation of the residue (N_2-bleed inlet) gave the title compound [bp 96–98 °C/9 mbar (Lit.[17] bp 130–139 °C/39 Torr)] as a clear colourless liquid (203 g, 73%) in >95% purity by ^{1}H NMR spectrum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (dd, *J* = 5.7, 1.8 Hz, 1 H, CHCl), 4.84 (dd, *J* = 10.3, 5.7 Hz, 1 H, C*H*H′), 4.63–4.60 (m, 1 H, CH*H*′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4 (C=O), 85.3 (CHCl), 73.8 (CHH′).

MS (CI): *m*/*z* (%) = 140.0 (100, $[M + NH_4]^+$).

HRMS-CI: *m*/*z* $[M + NH_4]^+$ calcd for $C_3H_7ClNO_3$: 140.0114; found: 140.0116.

2-Chloroacetaldehyde (7)[16]

Et_3N (one drop) was added to 4-chloro-1,3-dioxolan-2-one (**6**; 7.35 g, 60 mmol) in a 25 mL round-bottomed flask equipped with a short path distillation kit. After heating the reaction to 180 °C (oil-bath temperature), distillation commenced and collection of the fraction boiling between 87–89 °C (Lit.[16b] bp 84–86 °C/760 Torr) furnished the title compound as a pale yellow-green liquid of acrid odour (3.67 g, 78%). The material thus obtained was analytically pure by ^{1}H NMR and ^{13}C NMR analyses and was used without further purification.

IR (neat): 2967, 2360, 2341, 1826, 1430, 1348, 1061, 1017, 763 cm^{-1}.

^{1}H NMR (250 MHz, C_6D_6): δ = 8.92 (br t, 1 H, CHO), 3.38 (br d, 2 H, CH_2Cl).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3 (CHO), 48.6 (CH_2Cl).

MS (FI): *m*/*z* (%) = 77.9 (100, $[M]^+$).

HRMS-FI: *m*/*z* $[M]^+$ calcd for C_2H_3Cl: 77.9872; found: 77.9874.

***N*-(2-Chloroethylidene)-2-methylpropane-2-sulfinamide (8)[23]**

To a solution of *t*-$BuSONH_2$ (3.64 g, 20 mmol) and anhyd $CuSO_4$ (9.58 g, 60 mmol) in CH_2Cl_2 (300 mL) was added dropwise anhyd 2-chloroacetaldehyde (**7**; 1.88 g, 24 mmol). After complete consumption of the *t*-$BuSONH_2$ (~8 h, TLC monitoring), the reaction mixture was filtered through a pad of Celite® and the filter cake washed with CH_2Cl_2 (4 × 20 mL). Evaporation of the solvent in vacuo afforded the title compound (3.57 g, 98%) as a pale yellow oil. The material thus obtained, pure by ^1H and ^{13}C NMR analyses, was used without further purification; R_f = 0.28 (PE–Et_2O, 2:1).

IR (neat): 2963, 1831, 1623, 1475, 1364, 1253, 1091, 720, 657, 582 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 8.02 (s, 1 H, CHN), 4.32 (d, *J* = 4.6 Hz, 2 H, CHCl), 1.21(s, 9 H, *t*-C_4H_9).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3 (CHN), 57.3 [*C*$(CH_3)_3$], 43.4 (CH_2Cl), 22.2 [C(*C*$H_3)_3$].

MS (CI): *m*/*z* (%) = 199.1 (100, $[M + NH_4]^+$), 182.3 (60, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + NH_4]^+$ calcd for $C_6H_{16}ClN_2OS$: 199.0672; found: 199.0676.

(R_S)-*N*-(2-Chloroethylidene)-2-methylpropane-2-sulfinamide [(R_S)-8]

Prepared as above, but using (R_S)-*t*-$BuSONH_2$ (Aldrich, 98% ee); $[\alpha]_D^{22}$ –351.1 (*c* 2.00, $CHCl_3$) {Lit.[23] $[\alpha]_D^{27}$ –295 (*c* 2.90, CH_2Cl_2)}.

***N*-(1-Chlorohexan-2-yl)-2-methylpropane-2-sulfinamide (9)**

BuMgCl (20 wt% in THF–toluene, 0.64 mL, 1.1 mmol) was added dropwise to a stirred solution of imine **8** (0.18 g, 1 mmol) in CH_2Cl_2 (5 mL) at –78 °C and the reaction mixture stirred for 2 h, then quenched with MeOH (5 mL) and warmed to r.t. Sat. aq NH_4Cl (10 mL) was added and, after extracting the aqueous layer with Et_2O (2 × 10 mL), the combined organic layers were washed with H_2O (2 × 15 mL) and brine (15 mL), dried (Na_2SO_4), and evaporated in vacuo. Purification of the residue by column chromatography (SiO_2, PE–EtOAc, 2:1) gave the title compound as a pale yellow oil (0.19 g, 80%, 53:47 dr by GC); R_f = 0.40 (PE–EtOAc, 2:1).

IR (neat): 3171, 2958, 2932, 2871, 1530, 1458, 1391, 1306, 1195, 1134, 1043, 931, 895 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.91–3.60 (m, 6 H, CH_2Cl and CH), 3.51–3.48 (m, 1 H, NH), 3.36 (d, *J* = 5.9 Hz, 1 H, NH), 1.81–1.26 (m, 12 H, $CH_2CH_2CH_2$), 1.23 [s, 9 H, $C(CH_3)_3$], 1.22 [s, 9 H, $C(CH_3)_3$], 0.92–0.88 (m, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.2 and 56.9 (CHN), 56.2 and 56.1 [*C*$(CH_3)_3$], 49.9 and 48.8 (CH_2Cl), 31.9 and 32.9 (CHN*C*$H_2CH_2CH_2$), 27.8 and 27.8 (CHNCH_2*C*H_2CH_2), 22.6 and 22.4 [C(*C*$H_3)_3$], 22.3 and 22.3 (CHNCH_2CH_2*C*H_2), 14.0 and 13.9 (CH_3).

MS (CI): *m*/*z* (%) = 240.1 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{23}ClNOS$: 240.1187; found: 240.1189.

Aziridines 10 from Grignard Reagents; 2-Butyl-1-(*tert*-butylsulfinyl)aziridine (10a); Typical Procedure A

BuMgCl (20 wt% in THF–toluene, 0.64 mL, 1.1 mmol) was added dropwise to a stirred solution of imine **8** (0.18 g, 1 mmol) in CH_2Cl_2 (5 mL) at –78 °C and the reaction mixture was allowed to warm to r.t. overnight. Sat. aq NH_4Cl (10 mL) was added and after extracting the aqueous layer with Et_2O (2 × 10 mL), the combined organic layers were washed with H_2O (2 × 15 mL) and brine (15 mL), dried ($MgSO_4$), and evaporated in vacuo. Purification of the residue by column chromatography (SiO_2, PE–Et_2O, 4:1) gave aziridine **10a** as pale yellow oil (0.16 g, 78%, 51:49 dr by GC); R_f = 0.45 (PE–Et_2O, 4:1).

IR (neat): 2958, 2930, 2962, 1458, 1398, 1260, 1080, 923, 869, 628 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ (R_S*,*R**) = 2.56 (d, *J* = 6.7 Hz, 1 H, C*H*H′), 2.06–2.04 (m, 1 H, CHN), 1.63 (d, *J* = 4.1 Hz, 1 H, CH*H*′), 1.51–1.22 (m, 6 H, CH_2CH_2CH_2CH_2CH$_3$), 1.21 [s, 9 H, $C(CH_3)_3$], 0.90 (br t, 3 H, CH_3); δ (R_S*,*S**) = 2.64–2.61 (m, 1 H, CHN), 2.01 (d, *J* = 6.7 Hz, 1 H, C*H*H′), 1.81 (d, *J* = 3.9 Hz, 1 H, CH*H*′), 1.51–1.22 (m, 6 H, CH_2CH_2CH_2CH$_3$), 1.19 [s, 9 H, $C(CH_3)_3$], 0.90 (br t, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ (R_S*,*R**) = 56.9 [*C*$(CH_3)_3$], 33.5 (CHN), 31.5 (CH_2N), 28.8 (*C*$H_2CH_2CH_2CH_3$), 25.0 (CH_2*C*$H_2CH_2CH_3$), 22.7 [C(*C*$H_3)_3$], 22.4 (CH_2CH_2*C*H_2CH_3), 13.9 ($CH_2CH_2CH_2$*C*H_3); δ (R_S*,*S**) = 56.3 [*C*$(CH_3)_3$], 30.6 (CHN), 28.8 (*C*$H_2CH_2CH_2CH_3$), 28.0 (CH_2N), 25.0 (CH_2*C*$H_2CH_2CH_3$), 22.6 [C(*C*$H_3)_3$], 22.2 (CH_2CH_2*C*H_2CH_3), 13.9 ($CH_2CH_2CH_2$*C*H_3).

MS (ESI): *m*/*z* (%) = 203.9 (100, $[M + H]^+$).

HRMS-ESI: *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{21}NOS$ + Na: 226.1236; found: 226.1234.

1-(*tert*-Butylsulfinyl)-2-isopropylaziridine (10b)

Prepared according to Typical Procedure A, using *i*-PrMgCl (2.0 M in THF, 0.55 mL, 1.1 mmol); purification by column chromatography (SiO_2, PE–Et_2O, 5:1) gave aziridine **10b** as a pale yellow oil (0.153 g, 81%, 57:43 dr by GC); R_f = 0.45 (PE–Et_2O, 4:1).

IR (neat): 2960, 2935, 1455, 1383, 1265, 1263, 1084, 941, 872, 642 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.58–2.55 (m, 1 H, CHN), 2.54 (d, *J* = 6.7 Hz, 1 H, C*H*H′), 1.90 (d, *J* = 6.9 Hz, 1 H, CH*H*′), 1.90 (d, *J* = 4.3 Hz, 1 H, C*H*H′), 1.86–1.81 (m, 1 H, CHN), 1.67 (d, *J* = 4.1 Hz, 1 H, CH*H*′), 1.52–1.34 (m, 2 H, CH), 1.20 [s, 9 H, $C(CH_3)_3$], 1.19 [s, 9 H, $C(CH_3)_3$], 1.01–0.79 [m, 12 H, CH(C$H_3)_2$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.9 and 56.2 [*C*$(CH_3)_3$], 39.3 and 36.2 (CHN), 30.3 and 27.6 (CH), 25.1 and 24.0 (CH_2N), 22.7 and 22.5 [C(*C*$H_3)_3$], 20.2, 19.3, 18.9, and 17.1 (CH_3).

MS (CI): *m*/*z* (%) = 190.1 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_9H_{20}NOS$: 190.1266; found: 190.1258.

2-*tert*-Butyl-1-(*tert*-butylsulfinyl)aziridine (10c)

Prepared according to Typical Procedure A, using *t*-BuMgCl (2.0 M in Et_2O, 0.55 mL, 1.1 mmol); purification by column chromatography (SiO_2, PE–Et_2O, 4:1 with 3% Et_3N) gave aziridine **10c** as a pale yellow oil (0.17 g, 88%, 94:6 dr by GC); R_f = 0.3 (PE–Et_2O, 4:1).

IR (neat): 2963, 2935, 1451, 1388, 1265, 1087, 943, 859, 640 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ [major (R_S*,*R**)] = 2.46 (d, *J* = 6.8 Hz, 1 H, C*H*H′), 1.89 (dd, *J* = 6.8, 4.3 Hz, 1 H, CHN), 1.73 (d, *J* = 4.3 Hz, 1 H, CH*H*′), 1.19 [s, 9 H, SOC$(CH_3)_3$], 0.87 [s, 9 H, $C(CH_3)_3$]; δ [discernible data for minor (R_S*,*S**)] = 1.20 [s, 9 H, SOC$(CH_3)_3$], 0.91 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ (R_S*,*R**) = 57.0 [SO*C*$(CH_3)_3$], 41.9 [*C*$(CH_3)_3$], 30.0 (CHN), 26.1 (CH_2N), 22.6 [C(*C*$H_3)_3$], 22.0 [SOC(*C*$H_3)_3$]; δ (R_S*,*S**) = 56.0 [SO*C*$(CH_3)_3$], 42.3 [*C*$(CH_3)_3$], 29.4 (CHN), 25.2 (CH_2N), 22.5 [C(*C*$H_3)_3$], 21.9 [SOC(*C*$H_3)_3$].

MS (CI): *m*/*z* (%) = 204.2 (100, $[M + H]^+$).

HRMS-ESI: *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{22}NOS$: 204.1422; found: 204.1421.

(*R*)-2-*tert*-Butyl-1-(*tert*-butylsulfonyl)aziridine [(*R*)-2c][10d]

MCPBA (0.38 g, 2.2 mmol) was added to a solution of sulfinyl aziridine **10c** (prepared according to the Typical Procedure A from im-

ine (R_S)-**8**, 0.29 g, 1.0 mmol) in CH_2Cl_2 (10 mL). After 3 h, sat. aq $NaHSO_3$ (10 mL) was added and the reaction mixture stirred for 15 min; the layers were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with H_2O (10 mL), sat. aq $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by column chromatography (PE–Et_2O, 5:1) gave *N*-Bus aziridine (*R*)-**2c** (0.19 g, 84%) as a clear, colourless oil; $[\alpha]_D^{25}$ –81.0 (*c* 1.00, $CHCl_3$) {Lit.[10d] for pure (*R*): $[\alpha]_D^{25}$ –87.5 (*c* 1.00, $CHCl_3$)}; R_f = 0.3 (SiO_2, PE–Et_2O, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (dd, *J* = 7.1, 4.8 Hz, 1 H, CHN), 2.49 (dd, *J* = 7.0 Hz, 1 H, C*H*H′), 2.19 (d, *J* = 4.8 Hz, 1 H, CH*H*′), 1.50 [s, 9 H, $SO_2C(CH_3)_3$], 0.95 [9 H, s, $C(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.4 [$SO_2C(CH_3)_2$], 45.0 [$C(CH_3)_3$], 32.9 (CHN), 30.3 (CH_2N), 26.3 [$SO_2C(CH_3)_2$], 24.3 [$C(CH_3)_3$].

MS (CI): *m*/*z* (%) = 220.1 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{22}NO_2S$: 220.1371; found: 220.1370.

(*S*)-2-Chloro-1-mesitylethanaminium Chloride (12)

To a solution of imine (R_S)-**8** (0.55 g, 3 mmol) in toluene (15 mL) at –78 °C was added mesitylene magnesium bromide (1.0 M in Et_2O; 15 mL, 15 mmol); the reaction mixture stirred for 3 h, quenched with MeOH (5 mL) and warmed to r.t. After addition of aq HCl (6 M, 5 mL) and stirring for 3 h, the mixture was partitioned, washed with Et_2O (10 mL), and 15% aq NaOH added to the aqueous layer until pH 11. The aqueous layer was extracted with EtOAc (3 × 20 mL) and the combined organic layers dried (Na_2SO_4), concentrated in vacuo, dissolved in ice-cold dioxane (10 mL), treated with HCl gas until pH 1, stirred for 10 min, and concentrated in vacuo. Recrystallisation of the residue from boiling hexane–chloroform gave the title compound as an off-white, crystalline solid (0.49 g, 71%); mp 176–177 °C; $[\alpha]_D^{25}$ +13.7 (*c* 1.00, $CHCl_3$).

IR (KBr): 3374, 3209, 2973, 1657, 1559, 1475, 1442, 1392, 1161, 1033, 943, 767 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.06 (br s, 3 H, NH_3^+), 6.89 (s, 2 H_{arom}), 4.93 (dd, *J* = 6.3, 2.7 Hz, 1 H, CHN), 4.24 (dd, *J* = 11.9, 2.9 Hz, 1 H, C*H*H′), 3.82 (dd, *J* = 11.9, 5.7 Hz, 1 H, CH*H*′), 2.44 (s, 6 H, *o*-CH_3), 2.26 (s, 3 H, *p*-CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.2 (quat), 136.6 [br, *o*-*C*(CH_3)], 130.1 [br, *p*-*C*(CH_3)], 126.8 (CH), 53.2 (CHN), 43.2 (CH_2Cl), 21.4 (br, *o*-CH_3), 20.8 (*p*-CH_3).

(*S*)-2-Chloro-1-mesitylethanaminium 2,4,6-trinitrophenolate (13)

A solution of **12** (0.09 g, 0.4 mmol) in Et_2O (5 mL) was adjusted to pH 12 with 15% aq NaOH and vigorously stirred for 10 min. After partitioning, and extraction of the aqueous layer with EtOAc (2 × 10 mL), the combined organic layers were dried (Na_2SO_4), and concentrated in vacuo. The residual oil was dissolved in benzene (3 mL) and a dry sat. soln of picric acid in benzene [picric acid (1.5 g) was dissolved in benzene (25 mL) with gentle warming and the resulting, bright yellow solution dried ($MgSO_4$), filtered and used immediately] added dropwise, until no further precipitation occurred (pH 2). The precipitated yellow crystals were collected by filtration, washed with cold benzene and dried in vacuo. Recrystallisation from boiling benzene–hexane gave the title compound as an intensely yellow, crystalline solid (0.13 g, 76%). A single crystal suitable for X-ray crystallographic analysis[25] was grown by slow evaporation of a $CHCl_3$–MeOH solution; mp 189–190 °C; $[\alpha]_D^{25}$ +15.0 (*c* 1.00, MeOH).

IR (KBr): 2973, 1612, 1567, 1536, 1428, 1362, 1320, 1272, 1164, 1081, 914, 702, 648 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.70 (s, 2 H, picrate CH), 6.97 (s, 2 H, Mes CH), 5.67 (dd, *J* = 10.3, 4.4 Hz, 1 H, CHN), 4.46–4.41 (m, 1 H, C*H*H′), 4.04 (dd, *J* = 12.4, 4.4 Hz, 1 H, CH*H*′), 2.45 (s, 6 H, *o*-CH_3), 2.25 (s, 3 H, *p*-CH_3).

^{13}C NMR (126 MHz, acetone-d_6): δ = 162.3 (CO), 143.2 (*p*-CNO_2), 140.1 (*o*-CNO_2), 139.9 (br, quat), 137.6 [*o*-*C*(CH_3)], 131.8 [*p*-*C*(CH_3)], 129.1 (Mes CH), 126.1 (picrate CH), 63.3 (CHN), 43.9 (CH_2Cl), 20.4 (*o*-CH_3), 20.3 (*p*-CH_3).

(*S*)-1-[(*R*)-*tert*-Butylsulfinyl]-2-mesitylaziridine (10e)

To a solution of imine (R_S)-**8** (0.55 g, 3 mmol) in toluene (15 mL) at –78 °C was added mesitylene magnesium bromide (1.0 M in Et_2O, 15 mL, 15 mmol), and the reaction mixture slowly warmed to r.t. overnight. After quenching with MeOH (5 mL), then aq HCl (1 M, 5 mL), and partitioning, the aqueous layer was extracted with Et_2O (3 × 15 mL), and the combined organic layers washed with H_2O (2 × 20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (SiO_2, PE–Et_2O, 6:1) of the residue gave the title compound as a pale yellow oil (0.45 g, 57%); $[\alpha]_D^{25}$ +74.1 (*c* 1.00, $CHCl_3$); R_f = 0.6 (PE–Et_2O, 3:1).

IR (neat): 2960, 2923, 2733, 1612, 1573, 1475, 1456, 1376, 1260, 1189, 1084, 1030, 958, 851, 802, 739 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 6.67 (s, 2 H_{arom}), 3.84, (br s, 1 H, CHN), 2.36 (s, 6 H, *o*-CH_3), 2.02 (s, 3 H, *p*-CH_3), 2.00 (br d, 2 H, CH_2), 1.06 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (126 MHz, C_6D_6): δ = 138.2 (br, quat), 137.1 [br, *o*-*C*(CH_3)], 130.8 [br, *p*-*C*(CH_3)], 130.7 (CH), 56.4 [*C*(CH_3)], 29.2 (br, CHN), 22.6 (br, CH_2), 22.5 [$C(CH_3)_3$], 20.8 (*p*-CH_3), 20.3 (*o*-CH_3).

MS (CI): *m*/*z* (%) = 266.2 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{24}NOS$: 266.1579; found: 266.1577.

Anhydrous $CeCl_3$ Slurry for Organocerium Reagents

$CeCl_3 \cdot 7H_2O$ (Aldrich 99.999%, 0.45 g, 1.2 mmol) was placed in a Schlenk flask equipped with an ellipsoid stirrer bar fitted exactly to the inner diameter of the flask. After connection to high vacuum (<0.1 mbar), the flask was heated at 165 °C for 2 h (oil-bath temperature) with slight stirring; the anhyd $CeCl_3$ should be a snow-white, fine powder. The Schlenk flask was then disconnected from the vacuum, filled with argon whilst still hot and allowed to cool to r.t. After addition of anhyd THF (7 mL), the suspension was vigorously stirred for 2 h and employed in Typical Procedure B, described below.

Aziridines 10 from Organoceriums; 2-Butyl-1-(*tert*-butylsulfinyl)aziridine (10a); Typical Procedure B

n-BuLi (1.6 M in hexanes, 0.75 mL, 1.2 mmol) in THF (5 mL) was added dropwise to a stirred slurry of anhyd $CeCl_3$ (0.30 g, 1.2 mmol, prepared as described above) in THF (7 mL) at –78 °C under argon. After 45 min, DMPU (1.5 mL) was added, followed after 15 min by a solution of imine **8** (0.18 g, 1 mmol) in THF (3 mL) and the reaction mixture was then allowed to warm to r.t. overnight. Sat. aq NH_4Cl (10 mL) and Et_2O (5 mL) were added, the mixture filtered through a pad of Celite and the filter cake washed thoroughly with Et_2O (3 × 10 mL). The combined organic layers were washed with H_2O (2 × 15 mL) and brine (15 mL), dried ($MgSO_4$), and evaporated in vacuo. Purification by column chromatography (SiO_2, PE–Et_2O, 4:1) afforded the title compound as pale yellow oil (0.18 g, 86%, >99:1 dr by GC); R_f = 0.3 (PE–Et_2O, 4:1).

IR (neat): 2958, 2930, 2962, 1458, 1398, 1260, 1080, 923, 869, 628 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.61 (d, *J* = 6.7 Hz, 1 H, CHN), 2.05–2.04 (m, 1 H, C*H*H′), 1.65 (d, *J* = 4.1 Hz, 1 H, CH*H*′), 1.41–

1.22 [m, 15 H, $C(CH_3)_3$ and $CH_2CH_2CH_2CH_3$], 0.92 (br t, 3 H, $CH_2CH_2CH_2CH_3$).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 57.0 [$C(CH_3)_3$], 33.6 (CHN), 31.6 (CH_2N), 28.8 ($CH_2CH_2CH_2CH_3$), 25.1 ($CH_2CH_2CH_2CH_3$), 22.8 [$C(CH_3)_3$], 22.3 ($CH_2CH_2CH_2CH_3$), 14.0 ($CH_2CH_2CH_2CH_3$).

MS (ESI): *m*/*z* (%) = 203.9 (100, $[M + H]^+$).

HRMS-ESI: *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{21}NOS$ + Na: 226.1236; found: 226.1234.

1-(*tert*-Butylsulfonyl)-2-methylaziridine (2; R = Me)

MeLi (1.6 M in Et_2O, 0.75 mL, 1.2 mmol) was used following Typical Procedure B. GC-MS analysis indicated the formation of 1-(*tert*-butylsulfinyl)-2-methylaziridine (**10g**) in 91:9 dr, which was immediately oxidised to **2** (R = Me) as follows. Crude sulfinyl aziridine **10g** was dissolved in CH_2Cl_2 (5 mL), cooled to 0 °C and MCPBA (0.46 g, 3 mmol) added. After warming to r.t., and stirring for 4 h, the reaction was quenched with sat. aq $NaHSO_3$ (10 mL), partitioned, and the aqueous layer extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (20 mL), H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (SiO_2, PE–Et_2O, 3:1) provided the title compound as a clear, colourless oil (0.14 g, 81%); R_f = 0.3 (PE–Et_2O, 3:1).

IR (neat): 2973, 1657, 1559, 1475, 1442, 1394, 1161, 1091, 1033, 943, 767 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.81 (m, 1 H, CHN), 2.64 (d, *J* = 7.0 Hz, 1 H, C*H*H′), 2.15 (d, *J* = 4.6 Hz, 1 H, CH*H*′), 1.48 [s, 9 H, $C(CH_3)_3$], 1.42 (m, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.7 [$C(CH_3)_3$], 39.6 (CHN), 33.7 (CH_2N), 24.2 [$C(CH_3)_3$], 21.8 (CH_3).

MS (CI): *m*/*z* (%) = 178.1.1 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_7H_{16}NO_2S$: 178.0902; found: 178.0898.

1-(*tert*-Butylsulfonyl)-2-vinylaziridine (2; R = vinyl)

Freshly distilled tributyl(vinyl)stannane (0.46 g, 1.5 mmol) in Et_2O (5 mL) was cooled to –78 °C in a Schlenk flask and *n*-BuLi (1.6 M in hexanes, 0.94 mL, 1.5 mmol) added dropwise. After stirring for 1 h, the temperature was elevated to r.t. and the mixture stirred for a further 2 h, the solvent concentrated in vacuo, and the residue containing vinyllithium dissolved in THF (4 mL) and used immediately following Typical Procedure B. GC-MS analysis indicated the formation of 1-(*tert*-butylsulfinyl)-2-vinylaziridine (**10i**) in 86:14 dr, which was immediately oxidised to aziridine **2** (R = vinyl) as follows. Crude sulfinyl aziridine **10i** was dissolved in anhyd MeCN (5 mL) and, after the addition of NMO (0.35 g, 3 mmol), crushed 4 Å molecular sieves (0.75 g) and TPAP (0.035 g, 10 mol%), heated to 40 °C overnight. The mixture was cooled to r.t. and concentrated onto silica gel. Column chromatography (SiO_2, PE–Et_2O, 5:1) provided the title compound as a clear, colourless oil (0.16 g, 75%); R_f = 0.3 (PE–Et_2O, 5:1).

IR (neat): 2374, 2256, 2140, 1307, 1130, 933, 842, 742, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.61–5.51 (m, 2 H, C=CHH′), 5.34–5.31 (m, 1 H, C*H*=CHH′), 3.17 (ddd, *J* = 7.1, 4.4, 2.6 Hz, 1 H, CHN), 2.77 (d, *J* = 7.1 Hz, 1 H, C*H*H′), 2.22 (d, *J* = 4.4 Hz, 1 H, CH*H*′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.6 (CH_2=*C*H), 120.4 (*C*H_2=CH), 59.3 [$C(CH_3)_3$], 41.5 (CHN), 32.5 (CH_2N), 24.1 [$C(CH_3)_3$].

MS (CI): *m*/*z* (%) = 190.1 (100, $[M + H]^+$).

HRMS-ESI: *m*/*z* $[M + H]^+$ calcd for $C_8H_{16}NO_2S$: 190.0902; found: 190.0899.

(*R*)-1-[(*R*)-*tert*-Butylsulfinyl]-2-phenylaziridine [(R_S,*R*)-10d]

PhLi (2.0 M in Bu_2O, 0.6 mL, 1.2 mmol) and imine (R_S)-**8** were reacted following Typical Procedure B. Purification by column chromatography (SiO_2, PE–Et_2O, 4:1) afforded the title compound as a colourless oil (0.21 g, 92%, 92:8 dr by GC), which solidified upon standing; mp 54–55 °C; $[\alpha]_D^{25}$ –313.1 (*c* 0.80, $CHCl_3$) {Lit.[40] $[\alpha]_D^{20}$ –320.0 (*c* 0.5, $CHCl_3$); Lit.[34] $[\alpha]_D$ –335.0 (*c* 0.6, $CHCl_3$)}; R_f = 0.32 (PE–Et_2O, 4:1).

IR (KBr): 2927, 1461, 1308, 1216, 1130, 865, 709 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ [major (R_S,*R*)] = 7.34–7.25 (m, 5 H_{arom}), 3.11–3.09 (m, 1 H, CHN), 2.98 (d, *J* = 6.8 Hz, 1 H, C*H*H′), 1.99 (d, *J* = 4.0, 1 H, CH*H*′), 1.28 [s, 9 H, $C(CH_3)_3$]; δ [discernible data for minor (R_S,*S*)] = 3.60–3.59 (m, 1 H, CHN), 2.44 (d, *J* = 6.8 Hz, 1 H, C*H*H′), 2.16 (d, *J* = 4.0 Hz, 1 H, CH*H*′), 1.16 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ [major (R_S,*R*)] = 137.7 (quat), 128.4 (quat), 127.7, 126.3 (arom), 57.4 [$C(CH_3)_3$], 34.8 (CHN), 28.7 (CH_2N), 22.8 [$C(CH_3)_3$]; δ [discernible data for minor (R_S,*S*)] = 56.9 [$C(CH_3)_3$], 31.9 (CHN), 31.4 (CH_2N).

MS (CI): *m*/*z* (%) = 224.1 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{18}NOS$: 224.1109; found: 224.1110.

(*R*)-1-(*tert*-Butylsulfonyl)-2-phenylaziridine (2d)

MCPBA (0.38 g, 2.2 mmol) was added to a solution of sulfinyl aziridine (R_S,*R*)-**10d** (0.24 g, 1.0 mmol) in CH_2Cl_2 (10 mL). After 3 h, sat. aq $NaHSO_3$ (10 mL) was added and the reaction mixture stirred for 15 min; the layers were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with H_2O (10 mL), sat. aq $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by column chromatography (PE–Et_2O, 10:1) gave *N*-Bus aziridine **2d** as a clear, colourless oil (0.20 g, 85%); $[\alpha]_D^{25}$ –165.0 (*c* 0.50, $CHCl_3$) {Lit.[41] (>98% ee, *R*) $[\alpha]_D^{25}$ –184.5 (*c* 1.0, $CHCl_3$)}.

IR (KBr): 2956, 2933, 1466, 1308, 1216, 1130, 950, 865, 709 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.29 (m, 5 H_{arom}), 3.63 (dd, *J* = 7.1, 4.4 Hz, 1 H, CHN), 2.97 (d, *J* = 7.2 Hz, 1 H, C*H*H′), 2.36 (d, *J* = 4.4 Hz, 1 H, CH*H*′), 1.47 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.3 (quat), 128.7 (*p*-CH), 128.3 (CH), 126.3 (CH), 59.4 [$C(CH_3)_3$], 41.5 (CHN), 34.7 (CH_2N), 24.1 [$C(CH_3)_3$].

MS (CI): *m*/*z* (%) = 257.1 (100, $[M + NH_4]^+$), 240.1 (80, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{18}NO_2S$: 240.1058; found: 240.1057.

Methyl (*R*)-2-(1,1-Dimethylethylsulfonamido)-2-phenylacetate (15)

t-Butylsulfinyl chloride (1.41 mL, 10 mmol) was added to a solution of (*R*)-phenylglycine methyl ester hydrochloride (**14**; 2.02 g, 10 mmol) in anhyd pyridine (25 mL) and the mixture stirred overnight. After the addition of EtOAc (50 mL), and adjusting to pH 5 using aq 5 M HCl, the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with aq 2 m HCl (30 mL), sat. aq $CuSO_4$ (20 mL), H_2O (30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated in vacuo. To an ice-cold solution of the residue in CH_2Cl_2 (50 mL) was added MCPBA (3.45 g, 20 mmol) and mixture stirred for 6 h. After quenching with sat. aq $NaHSO_3$ (30 mL), the aqueous layer was extracted with Et_2O (3 × 15 mL) and the combined organic layers were washed with 15% aq NaOH (25 mL), H_2O (25 mL) and brine (25 mL), dried ($MgSO_4$), and concentrated in vacuo to yield the title compound as a white crystalline solid, which was used without further purification (2.80 g, 98%); mp 139–140 °C; $[\alpha]_D^{25}$ –102.6 (*c* 0.50, $CHCl_3$).

IR (KBr): 3410, 2980, 2913, 1709, 1466, 1308, 1216, 1130, 1051, 950, 893, 865, 709 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.35 (m, 5 H_{arom}), 5.28 (d, *J* = 8.8 Hz, 1 H, NH), 5.22 (d, *J* = 8.8 Hz, 1 H, CH), 3.75 (s, 3 H, CH_3), 1.30 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6 (CO_2CH_3), 136.6 (quat), 129.0 (*p*-CH), 128.7 (CH), 127.1 (CH), 60.0 [$C(CH_3)_3$], 53.1 (CO_2CH_3), 24.0 [$C(CH_3)_3$].

MS (CI): *m*/*z* (%) = 303.1 (100, $[M + NH_4]^+$), 286.1 (20, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + NH_4]^+$ calcd for $C_{13}H_{23}N_2O_4S$: 303.1379; found: 303.1386.

(*R*)-1-(*tert*)-Butylsulfonyl-2-phenylaziridine (2d)

To and ice-cold solution of ester **15** in THF (30 mL) was added $LiAlH_4$ (0.76 g, 20 mmol) in small portions, and the reaction mixture then stirred overnight while allowing to warm to r.t. After cooling to 0 °C, the reaction was quenched with H_2O (0.8 mL), 15% aq NaOH (0.8 mL) and H_2O (2.5 mL), the suspension filtered through a pad of Celite® and the filter cake washed with EtOAc (3 × 50 mL). The filtrate, combined with the washings was concentrated in vacuo. To an ice-cold solution of the residue in CH_2Cl_2 (50 mL) was added mesyl anhydride (1.74 g, 10 mmol), then Et_3N (1.51 g, 15 mmol) and the mixture stirred overnight. After quenching with sat. aq NH_4Cl (15 mL), the mixture was partitioned and the aqueous layer extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with aq NaOH (15%, 20 mL), H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by column chromatography furnished the title compound as a white solid (1.64 g, 69%); mp 54–56 °C; $[\alpha]_D^{25}$ –194.0 (*c* 0.50, $CHCl_3$). All other data as described for **2d** earlier.

(*R*)-2-(But-3-enyl)-1-[(*R*)-*tert*-butylsulfinyl]aziridine (10m)

4-Iodobut-1-ene[42] (passed through a plug of basic, activated alumina immediately before use; the liquid obtained must be colourless, 0.24 g, 1.3 mmol) was dissolved in pentane (3 mL) and Et_2O (2 mL) and cooled to –78 °C, then *t*-BuLi (1.5 M in pentane, 1.9 mL, 2.86 mmol) was added dropwise. After 15 min, the cold bath was replaced by an ice bath, the reaction mixture slowly warmed to r.t., stirred for 2 h, the reaction solvent removed in vacuo, and the residue redissolved in anhyd THF (4 mL). This solution of homoallyllithium[43] and imine (R_S)-**8** were reacted following Typical Procedure B. Purification of the residue by column chromatography (SiO_2, PE–EtOAc, 5:1) gave the title compound as a pale yellow oil (0.13 g, 64%, 99:1 dr by GC); $[\alpha]_D^{25}$ –265.7 (*c* 0.40, CCl_4); R_f = 0.3 (PE–EtOAc, 4:1).

IR (neat): 2926, 2855, 1640, 1461, 1310, 1131, 938, 867, 709 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 5.65 (ddt, *J* = 10.2, 6.8, 3.2 Hz, 1 H, C*H*=HH′), 4.98–4.92 (m, 1 H, CH=*H*H′), 3.91 (dd, *J* = 14.4, 7.3 Hz, 1 H, CH=CH*H*′), 2.64 (d, *J* = 6.6 Hz, 1 H, C*H*H′), 2.03–1.90 (m, 1 H, CHN), 1.41–1.12 (m, 5 H, CH_2CH_2 and CH*H*′), 1.09 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (126 MHz, C_6D_6): δ = 138.2 (*C*H=CHH′), 115.6 (CH=*C*HH′), 57.9 [*C*$(CH_3)_3$], 33.4 (CHN), 31.9 (CH_2CH_2CH=CHH′), 31.5 (CH_2CH_2CH=CHH′), 25.1 (CH_2N), 23.1 [C(*C*$H_3)_3$].

MS (CI): *m*/*z* (%) = 202.1 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{20}NOS$: 202.1266; found: 202.1264.

(*R*)-2-(But-3-enyl)-1-(*tert*-butylsulfonyl)aziridine (2m)

To a stirred solution of sulfinyl aziridine **10m** (0.13 g, 0.65 mmol) in anhyd MeCN (5 mL) was added NMO (0.23 g, 1.95 mmol), crushed 4 Å molecular sieves (0.5 g), and TPAP (0.022 g, 10 mol%), and the reaction mixture heated to 40 °C overnight. The mixture was cooled to r.t. and concentrated onto SiO_2. Column chromatography (PE–Et_2O, 5:1) provided the title compound as a clear, colourless oil (0.10 g, 72%); $[\alpha]_D^{25}$ –51.9 (*c* 1.0, $CHCl_3$) {Lit.[10d] pure *S*: $[\alpha]_D^{25}$ +66.9 (*c* 1.0, $CHCl_3$); R_f = 0.3 (PE–Et_2O, 5:1).

IR (neat): 2982, 2932, 1641, 1455, 1366, 1130, 914, 870, 712 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.83 (ddt, *J* = 10.4, 6.6, 3.6 Hz, 1 H, C*H*=CHH′), 5.10–5.00 (m, 2 H, CH=C*HH*′), 2.78–2.72 (m, 1 H, CHN), 2.59 (d, *J* = 7.1 Hz, 1 H, C*H*H′N), 2.23–2.19 (m, 2 H, CH_2CH_2CH=CHH′), 2.09 (d, *J* = 4.5 Hz, 1 H, CH*H*′N), 1.77–1.55 (m, 2 H, CH_2CH_2CH=CHH′), 1.49 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1 (*C*H=CHH′), 115.5 (CH=*C*HH′), 59.2 [*C*$(CH_3)_3$], 37.7 (CHN), 34.2 (CH_2N), 30.7 (CH_2CH_2CH=CHH′), 30.6 (CH_2CH_2CH=CHH′), 24.2 [C(*C*$H_3)_3$].

MS (CI): *m*/*z* (%) = 218.1 (100, $[M + H]^+$).

HRMS-CI: *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{20}NO_2S$: 218.1215; found: 218.1218.

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