INDIUM MEDIATED ALLYLATION OF N-tert-BUTANESULFINYL IMINES WITH 1,3-DIBROMOPROPENE: STEREOSELECTIVE SYNTHESIS OF AZIRIDINES

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Abstract – The reaction of N-tert-butanesulfinyl imines 1 with 1,3-dibromopropene (2), in the presence of indium metal, in saturated aqueous solution of sodium bromide, produced bromohomoallylamine derivatives 3 with total facial diastereoselectivity for the imine addition, and moderate yields. These compounds were easily transformed into the corresponding vinyl aziridines 5 upon deprotonation with KHMDS in THF, the intramolecular cyclization taking place in a stereospecific manner in moderate to high yields.

INTRODUCTION

Saturated three-membered heterocyclic compounds, such aziridines, have attracted increasing attention in recent years for different reasons. From a clinical point of view, several compounds, both natural and synthetic, that bear in their structure aziridine rings, display pharmacological activities. Some of these compounds are currently used to fight different types of cancer (bladder,1 lung,2 leukemia3), in the treatment of malaria4 and leishmaniasis,5 or as antimicrobials.6 In addition to the pharmacological interest, in recent years a large amount of aziridines have become important within the field of asymmetric synthesis, acting as metal ligands in a variety of stereoselective addition reactions of organozinc reagents to carbonyl compounds,7 in Henry-type reactions between nitro compounds and aldehydes,8 in aldol reactions9 and hydroxylation reactions of olefins,10 among others. These compounds have also been used as chiral auxiliaries in different processes.11 The chemistry of aziridines, including synthetic procedures for their preparation, has been extensively reviewed.12 Of special interest are those methodologies which
allow the formation of the aziridine ring in a stereoselective manner. There are three general strategies to reach the formation of the aziridine ring: (a) intramolecular nucleophilic substitution in amino compounds, (b) reaction between nitrenes or nitrenoids and olefins, and (c) reaction between carbenes or carbenoids with imines (Scheme 1).

Following the general strategy (a), different stereoselective syntheses of aziridines from chiral N-tert-butanesulfinyl α-chloroimines have been reported. In these transformations, a diastereoselective nucleophilic addition to the imine takes place first, followed by the intramolecular cyclization. Hydride (reduction of the imine),\textsuperscript{13} Grignard reagents,\textsuperscript{14} organocerium compounds\textsuperscript{14c,15} and allylic tellurium salts\textsuperscript{16} were used as nucleophiles (Scheme 2).
Aziridines were also prepared through a Corey-Chaykovsky reaction of chiral $N$-tert-butanesulfinyl aldimines and ketimines. Of special interest are vinyl aziridines, which were obtained when $S$-allyl tetrahydrothiophenium bromide was used as the precursor of the sulfonium ylide (Scheme 2).

It is worth mentioning that $N$-tert-butanesulfinyl imines have found high applicability in organic synthesis as electrophiles, because they are accessible in large-scale processes in an enantiopure form, and practical processes for recycling the tert-butanesulfinyl group have also been reported. With regards to this, we have extensively studied the stereoselective allylation and propargylation of $N$-tert-butanesulfinyl imines and the synthetic applications of the resulting homoallylamine derivatives. Continuing our interest in this topic, we herein report our approach to the indium-mediated addition of 1,3-dibromopropene to $N$-tert-butanesulfinyl aldimines, with the aim of synthesize $N$-tert-butanesulfinyl aziridines, upon intramolecular cyclization of the expected $\beta$-bromohomoallylamine derivatives (Scheme 2). To the best of our knowledge, there is only one report about the allylation of $N$-tert-butanesulfinyl aromatic aldimines with 1,3-dibromopropene, using zinc in THF at 50 ºC, to produce the corresponding trans-vinyl aziridines in moderate yields.

RESULTS AND DISCUSSION

The starting $N$-tert-butanesulfinyl aldimines 1 were easily prepared by condensation of the corresponding aldehyde and ($R$)-tert-butanesulfinamid in the presence of 2 equiv of Ti(OEt)$_4$ in THF at room temperature. No racemization occurred during the condensation process and the aldimines 1 exhibited exclusively $E$ configuration. In order to find the best reaction conditions to carry out the allylation of aldimines 1 with 1,3-dibromopropene (2, commercially available as an almost equimolecular mixture of cis and trans isomers), we took the imine derived from isovaleraldehyde 1a as the model substrate. Thus, the reaction of imine 1a with 4 equiv of 1,3-dibromopropene (2), in the presence of 4 equiv of indium, at room temperature for 12 hours, in a saturated aqueous solution of sodium bromide, led to a 59/41 mixture of the expected bromohomoallylamine derivative 3a and the allylated product 4a, taking place a total consumption of starting imine 1a (Table 1, entry 1). Almost total disappearance of starting imine 1a with formation of similar ratios of compounds 3a/4a was observed working with less equivalents of both, indium (2 equiv) and allylic bromide 2 (3 equiv), under the same reaction conditions (Table 1, entry 2). On the other hand, when the reaction was performed in a larger excess of 1,3-dibromopropene (2, 6 equivalents), the amount of the expected bromohomoallylamine derivative 3a in the reaction mixture was a little big higher (Table 1, entry 4). A similar result was also achieved when the allylindium intermediate was formed prior to the addition of the imine 1a (no Barbier reaction conditions) in the saturated aqueous solution of sodium bromide (Table 1, entry 3). Unfortunately, no reaction was observed working in THF and DMF at room temperature (Table 1, entries 5 and 7, respectively), and the conversion was very low.
when the reaction was carried out in THF at 60 ºC (Table 1, entry 6). The allylation did not proceed at all using zinc instead of indium in a saturated aqueous solution of sodium bromide, at room temperature (Table 1, entry 8), and the conversions were very low in DMF and THF working at the same temperature (Table 1, entries 9 and 10). Finally, the treatment of dibromo compound 2 with magnesium in THF for 2 hours at room temperature, followed by reaction of the resulting solution with imine 1a at temperatures ranging from 0 to 23 ºC did not produced any of the allylated product, probably because of decomposition of the organomagnesium compound initially formed (Table 1, entry 11). At this point it is worth mentioning that in all cases the anti diastereomer of compound 3a was predominant (anti/syn around 70:30).

Table 1. Optimization of the reaction of imine 1a and 1,3-dibromopropene (2)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal (equiv)</th>
<th>Solvent</th>
<th>2 (equiv)</th>
<th>T (ºC)</th>
<th>Conversion</th>
<th>3a/4a Ratio\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>In (4)</td>
<td>sat. NaBr-H\textsubscript{2}O</td>
<td>4</td>
<td>23</td>
<td>&gt;90</td>
<td>59/41</td>
</tr>
<tr>
<td>2</td>
<td>In (2)</td>
<td>sat. NaBr-H\textsubscript{2}O</td>
<td>3</td>
<td>23</td>
<td>&gt;90</td>
<td>52/48</td>
</tr>
<tr>
<td>3\textsuperscript{c}</td>
<td>In (1.5)</td>
<td>sat. NaBr-H\textsubscript{2}O</td>
<td>3</td>
<td>23</td>
<td>&gt;90</td>
<td>54/46</td>
</tr>
<tr>
<td>4</td>
<td>In (1.8)</td>
<td>sat. NaBr-H\textsubscript{2}O</td>
<td>6</td>
<td>23</td>
<td>&gt;90</td>
<td>60/40</td>
</tr>
<tr>
<td>5</td>
<td>In (1.5)</td>
<td>THF</td>
<td>3</td>
<td>23</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>In (1.5)</td>
<td>THF</td>
<td>3</td>
<td>60</td>
<td>15</td>
<td>60/40</td>
</tr>
<tr>
<td>7</td>
<td>In (1.5)</td>
<td>DMF</td>
<td>3</td>
<td>23</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Zn (1.8)</td>
<td>sat. NaBr-H\textsubscript{2}O</td>
<td>2</td>
<td>23</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Zn (1.8)</td>
<td>DMF</td>
<td>2</td>
<td>23</td>
<td>10</td>
<td>50/50</td>
</tr>
<tr>
<td>10</td>
<td>Zn (1.8)</td>
<td>THF</td>
<td>2</td>
<td>23</td>
<td>20</td>
<td>54/46</td>
</tr>
<tr>
<td>11\textsuperscript{c,d}</td>
<td>Mg (1.8)</td>
<td>THF</td>
<td>2</td>
<td>-78 to 23</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The reaction time was 12 h, except in the case of entry 1, which was 4 h. \textsuperscript{b} Reaction products ratio was determined by \textsuperscript{1}H-NMR analysis of the crude reaction mixtures. \textsuperscript{c} The organometallic compound was prepared prior to the addition of the imine 1a, under no Barbier reaction conditions. \textsuperscript{d} The reaction was set up at 0 ºC and the system was allowed to reach room temperature for 4 h.

We studied next the scope of the reaction of 1,3-dibromopropene (2) with different N-\textit{tert}-butanesulfinyl aldimines 1, by applying the optimized conditions (better reagent ratios and simplest manipulation) shown in Table 1, entry 2. We carried out first the allylation of aliphatic aldimines 1a-d (Table 2). In the
case of the imine derived from isovaredehyde 1a, product 3a was obtained in 37% yield (75:25 \textit{anti:} \textit{syn} ratio), and the dehalogenated product 4a in 26% yield, as a single diastereomer. The aldimine derived from nonanal 1b led to the formation of the bromoallylation product 3b in 34% yield and a slightly worse diastereomeric ratio (68:32 \textit{anti:} \textit{syn} ratio) than in 3a, while the byproduct 4b was isolated in 26% yield. On the other hand, compound 4c was the only isolated product in 16% yield, in the reaction of the imine 1c, derived from cyclohexanecarbaldehyde. Finally, the imine 1d, derived from phenylacetaldehyde, reacted with 1,3-dibromopropene (2) to give the bromoallylation product 3d in 33% isolated yield and a better diastereomeric ratio than in previous cases (78:22 \textit{anti:} \textit{syn} ratio), along with dehalogenated product 4d (22% yield).

Aromatic aldimines 1e-j displayed a different behavior compare to the aliphatic ones in these allylation reactions (Table 3). Thus, the reaction of the imine 1e, derived from benzaldehyde, at room temperature, led

<table>
<thead>
<tr>
<th>Table 2. Allylation of aliphatic aldimines 1a-d with 1,3-dibromopropene (2)\textsuperscript{a,b}</th>
</tr>
</thead>
</table>
| \begin{align*}
1a: & R = i-\text{Bu} \\
1b: & R = \text{Me(}CH_2\text{)}_3 \\
1c: & R = \text{Cy} \\
1d: & R = \text{PhCH}_2
\end{align*} |
| 1,3-dibromopropene (2) (3 equiv) |
| \begin{align*}
t-\text{Bu}
\text{HN} & \text{S}\cdots\text{O} \\
\text{R} & \text{Br}
\end{align*} |
| In (2 equiv) |
| sat. NaBr-H$_2$O, 23 °C, 12 h |
| \begin{align*}
t-\text{Bu}
\text{HN} & \text{S}\cdots\text{O} \\
\text{R} & \text{Br} \\
\text{3}
\end{align*} |
| + |
| \begin{align*}
t-\text{Bu}
\text{HN} & \text{S}\cdots\text{O} \\
\text{R} & \text{3}
\end{align*} |
<table>
<thead>
<tr>
<th>4</th>
</tr>
</thead>
</table>
| \begin{align*}
3a & (37\%, 75:25 \text{ dr}) \\
4a & (26\%, >95:5 \text{ dr}) \\
3b & (34\%, 68:32 \text{ dr}) \\
4b & (26\%, >95:5 \text{ dr}) \\
4c & (16\%, >95:5 \text{ dr}) \\
3d & (33\%, 78:22 \text{ dr}) \\
4d & (22\%, >95:5 \text{ dr})
\end{align*} |

\textsuperscript{a} Yields were determined for isolated compounds after column chromatography. \textsuperscript{b} Diastereomeric ratios for compounds 3 refer to \textit{anti:} \textit{syn} ratios.
to the formation of the product 4e in 16% yield, the expected bromoallylated product being not isolated. On the other hand, the imine derived from para-methylbenzaldehyde 1f did not react under these reaction conditions, due probably to the weak electrophilic character of this aromatic imine with an electron-donating substituent. The imine derived from para-fluorobenzaldehyde 1g reacted with 1,3-dibromopropene (2) to give the bromoallylated product 3g in 35% yield, and surprisingly, as a single anti diastereoisomer.

Table 3. Allylation of aromatic imines 1e–j with 1,3-dibromopropene (2)\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Imine</th>
<th>Product</th>
<th>Yield</th>
<th>Diastereomeric Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1e: R = Ph</td>
<td>4e</td>
<td>16%</td>
<td>&gt;95:5 dr</td>
</tr>
<tr>
<td>1f: R = 4-MeC\textsubscript{6}H\textsubscript{4}</td>
<td>3g</td>
<td>35%</td>
<td>&gt;95:5 dr</td>
</tr>
<tr>
<td>1g: R = 4-FC\textsubscript{6}H\textsubscript{4}</td>
<td>4g</td>
<td>34%</td>
<td>&gt;95:5 dr</td>
</tr>
<tr>
<td>1h: R = 4-ClC\textsubscript{6}H\textsubscript{4}</td>
<td>3i</td>
<td>25%</td>
<td>&gt;95:5 dr</td>
</tr>
<tr>
<td>1i: R = 4-CF\textsubscript{3}C\textsubscript{6}H\textsubscript{4}</td>
<td>4i</td>
<td>16%</td>
<td>&gt;95:5 dr</td>
</tr>
<tr>
<td>1j: R = 2-furyl</td>
<td>4j</td>
<td>10%</td>
<td>&gt;95:5 dr</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Yields were determined for isolated compounds after column chromatography. \textsuperscript{b} Diastereomeric ratios for compounds 3 refer to anti:syn ratios.
In addition, the dehalogenated product 4g was also isolated in 34% yield. The imine of para-chlorobenzaldehyde 1h led to compound 3h also with a high diastereoselectivity but a considerably lower yield of 20%. In the case of the imine 1i with a trifluoromethyl substituent (strong electron-withdrawing group) at para position, the bromoallylation product 3i was isolated in 25% yield in an almost diastereoselective manner, and the dehalogenated product 4i was also obtained in 16% yield. Finally, the imine derived from furfural 1j did not give rise to the bromoallylated product, the product 4j being exclusively isolated in 10% yield.

A speculative mechanism, which explains the formation of products 3 and 4, is depicted on Scheme 3. Thus, metallation of 1,3-dibromopropene (2) produces allylindium A, which reacts with the chiral imine 1 through a cyclic transition state, previously proposed in other allylations of this type, in which the indium atom is coordinated with the nitrogen of the imine, and oxygen of the sulfinyl group. The addition of the allylindium intermediate A, reacting at γ-position, takes place to the Si-face of the imine with Rs configuration, giving rise to the desired bromoallylated product 3, as a mixture of anti:syn diastereoisomers. Being in the presence of an excess of metal (2 equiv), after the first metallation, allylindium intermediate A could undergo a second metallation to generate the dianionic species B. Further reaction of B with imine 1 would produce allylindium intermediate C, which leads to the formation of 4 after hydrolysis. The formation of 4 could also be explained by reductive debromination of compound 3. Thus, in the presence of excess of indium, the bromoallylated product 3 could be reduced to generate the allylindium species C, followed by protonolysis to afford 4 (Scheme 3).

Scheme 3
The intramolecular cyclization of compounds 3 was carried out by deprotonation with a 1M solution of KHMDS in a 1:1 mixture of THF:toluene, at -78 °C to room temperature. Aliphatic substrates 3a,b,d were used as mixtures of anti:syn diastereomers to give trans and cis aziridines 5, which were easily isolated after chromatographic column purification. Aziridines 5a and 5d were obtained with moderate overall yields, close in both cases to 50% (Table 4, entries 1 and 3). The trans and cis aziridines 5 were isolated in practically the same ratio as the anti:syn ratio of their precursors 3 (the notation t and c as the second letter in the numbering of the aziridines refers to the trans and cis isomers, respectively). This shows that the cyclization reaction is stereospecific, and takes place over intermediates in which the nucleophile and the leaving group meet in an anti-periplanar arrangement. In the case of the anti isomers, the elimination leads to the formation of the trans aziridines. Likewise, the syn diastereomers lead to the cis aziridines. In the case of aziridine derived from nonanal 5b, lower yields were obtained (Table 4, entry 2). On the contrary, aromatic aziridines 5gt, 5ht and 5it (Table 4, entries 3-6) were isolated with higher yields, being excellent for the one derived from para-trifluoromethylbenzaldehyde (Table 4, entry 6).

The configuration of the aziridines 5 was determined by NOESY experiments. Bearing in mind that the cyclizations are stereospecific, once the configuration of the aziridines 5 is known, it is possible to assign the configuration of the diastereomers from which they are derived. Thus, aziridines with relative trans configuration 5t come from bromoallylated compounds 3 with relative anti configuration, and vice versa. Since trans aziridines are the major products in these cyclizations, this implies that compounds 3 with relative anti-configuration are the major component in the diastereomeric mixtures of the bromoallylation reactions. It is also conclusive to assign the relative configuration of the aziridines 5 the value of the coupling constants of the two heterocyclic protons in 1H-NMR spectra. The values of these constants for cis protons are between 5.5 and 8.0 Hz, and in the case of trans, between 2.5 and 3.5 Hz. Both the NOESY experiments and the values of the coupling constants were concordant and allowed without any doubt the assignment of the configurations of the aziridines 5, and consequently, those of the bromoallylated compounds 3.

In summary, a synthesis of N-tert-butanesulfinyl trans- and cis-vinyl aziridines 5 was carried out in two steps from both aliphatic, and aromatic N-tert-butanesulfinyl aldimines 1, and 1,3-dibromopropene (2). The bromoallylation of the imine is the key step of this synthetic strategy, the expecting products 3 being accessible in moderate yields from no sterically hindered aliphatic imines and aromatic imines bearing electron-withdrawing groups. The allylation reactions take place with total facial diastereoselectivity, concerning the addition to the imine, leading also mainly to diastereoisomers with anti relative configuration. The final intramolecular cyclization step proceeded in a stereospecific manner to give aziridines 5 in moderate to high yields.
EXPERIMENTAL

All chemicals were commercially available (Acros, Aldrich). TLC was performed on Merck silica gel 60 F254, using aluminum plates and visualized with phosphomolybdic acid (PMA) stain. Chromatographic purification was performed by flash chromatography using Merck silica gel 60 (0.040-0.063 mm) and different eluant. Low-resolution electron impact (EI) mass spectra were obtained at 70 eV on Agilent GC/MS-5973N apparatus equipped with a HP-5MS column (Agilent technologies, 30 m x 0.25 mm) and high resolution mass spectra (HRMS-ESI) were obtained on a Waters LCT Premier XE apparatus equipped with a time of flight (TOF) analyzer and the samples were ionized by ESI techniques and introduced through an ultra-high pressure liquid chromatography (UPLC) model Waters ACQUITY H CLASS. IR spectra were measured (film) with a Nicolet Impact 510 P-FT Spectrometer. RMN spectra were recorded with a Bruker AC-300, using CDCl3 as solvent, and TMS as internal standard. Optical rotations were measured on a Perkin Elmer 341 polarimeter.

Table 4. Synthesis of aziridines 5 from bromohomoallylamine derivatives 3a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bromohomoallylamine derivative 3</th>
<th>Aziridine 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Structure, No.</td>
<td>dr (anti:syn)</td>
</tr>
<tr>
<td>1</td>
<td><img src="image" alt="Structure 3a" /></td>
<td>75:25</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Structure 3b" /></td>
<td>68:32</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Structure 3d" /></td>
<td>78:22</td>
</tr>
</tbody>
</table>
Indium promoted reaction of imines 1 and 1,3-dibromopropene (2). General procedure.

To a suspension of the corresponding imine 1 (0.5 mmol) in a saturated aqueous solution of sodium bromide (0.5 mL) was added 1,3-dibromopropene (2, 0.299 g, 0.149 mL, 1.5 mmol), and indium (0.115 g, 1.0 mmol). The resulting mixture was stirred at 23 ºC for 12 h and after that, extracted with AcOEt (3 × 15 mL). The organic layer was washed with brine (2 × 10 mL), dried over anhydrous MgSO₄ and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/AcOEt) to yield compounds 3 and 4. Yields are given on Tables 2 and 3. Physical and spectroscopic data follow.

(RS₃S₄R)-3-Bromo-N-(tert-butanesulfinyl)-6-methylhept-1-en-4-amine (anti-3a). Pale yellow oil; Rₗ 0.55 (hexane/AcOEt 2:1); [α]₃ºD -21 (c 0.50, CH₂Cl₂); IR (film) ν 3203, 2968, 1640, 1450, 1376, 1057 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 0.87 (3H, d, J = 6.5 Hz, CH₃), 0.94 (3H, d, J = 6.7 Hz, CH₃), 1.26 [9H, s, (CH₃)₃], 1.58 (1H, ddd, J = 14.2, 10.0, 4.2 Hz, CH), 1.65-1.85 (1H, m, CH), 3.30 (1H, tt, J = 9.9, 3.2 Hz, CH), 3.76 (1H, d, J = 9.7 Hz, NH), 5.11 (1H, dd, J = 8.9, 2.8 Hz, CH), 5.16-5.26 (1H, m, CH), 5.39 (1H, dt, J = 16.8, 1.0 Hz, CH), 5.98 (1H, ddd, J = 16.8, 10.1, 8.9 Hz, CH); ¹³C RMN (75 MHz, CDCl₃) δ 21.4 (CH₃), 22.7 (CH₃), 23.5 (CH₃), 24.2 (CH), 40.1 (CH₂), 56.4 (C), 59.2 (CH), 64.9 (CH), 119.2 (CH₂), 135.2 (CH); LRMS (EI) m/z 174 (M⁺-135, 36%), 133 (32), 125 (9), 113 (100), 83 (25), 57 (60); HRMS calcd for C₁₂H₂₃BrNOS (M⁺) 309.0762, found 309.0755.

(RS₃R₄R)-3-Bromo-N-(tert-butanesulfinyl)-6-methylhept-1-en-4-amine (3a’). Mixture of anti:syn
diastereoisomers; yellow oil; \( R_f \) 0.55-0.48 (hexane/AcOEt 2:1); \([\alpha]^{20}_D\) -18 (c 0.75, CH\(_2\)Cl\(_2\)); IR (film) ν
3203, 2968, 1640, 1450, 1376, 1057, 962 cm\(^{-1}\); \(^1\)H RMN (300 MHz, CDCl\(_3\)) \( \delta \) 0.85-0.95 (12H, m, CH\(_3\)),
1.23 [9H, s, (CH\(_3\))\(_3\)], 1.26 [7.8H, s, (CH\(_3\))\(_3\)], 1.50-1.75 (1H, m, CH), 1.65-1.85 (2.3H, m, CH), 3.30 (0.7H,
m, CH), 3.49 (2H, m, CH, NH), 3.76 (1H, d, \( J = 9.7 \) Hz, NH), 4.82 (1H, d, \( J = 8.1 \) Hz, CH), 5.11 (0.7H,
dd, \( J = 8.9, 2.8 \) Hz, CH), 5.20 (0.7H, d, \( J = 10.2 \) Hz, CH), 5.26 (1H, dd, \( J = 10.1, 1.2 \) Hz, CH), 5.40 (1.7H,
m, CH), 6.00-6.50 (1.7H, m, CH); \(^{13}\)C RMN (75 MHz, CDCl\(_3\)) \( \delta \) 21.2 (CH\(_3\)), 21.4 (CH\(_3\)), 22.6 (CH\(_3\)),
22.7 (CH\(_3\)), 23.4 (CH\(_3\)), 23.5 (CH\(_3\)), 24.2 (CH), 24.5 (CH\(_3\)), 40.1 (CH\(_2\)), 41.2 (CH\(_2\)), 56.4 (C),
56.6 (C), 58.7 (CH), 59.2 (CH), 59.8 (CH), 64.9 (CH), 119.2 (CH\(_2\)), 120.4 (CH\(_2\)), 134.6 (CH), 135.2 (CH).

\((Rs,4R)-N-(tert-Butanesulfonyl)-6-methylhept-1-en-4-amine (4a)\). Colourless liquid; \(^1\)H RMN (300
MHz, CDCl\(_3\)) \( \delta \) 0.90 (3H, t, \( J = 6.6 \) Hz, CH\(_3\)), 0.94 (3H, d, \( J = 6.7 \) Hz, CH\(_3\)), 1.20 [9H, s, (CH\(_3\))\(_3\)], 1.38
(1H, m, CH), 1.74 (2H, dd, \( J = 9.6, 4.8 \) Hz, CH\(_2\)), 2.39 (2H, m, CH\(_2\)), 3.18 (1H, d, \( J = 7.4 \) Hz, NH), 3.37
(1H, m, CH), 5.17 (2H, m, CH\(_2\)), 5.79 (1H, ddd, \( J = 17.0, 12.1, 7.3 \) Hz, CH); \(^{13}\)C RMN (75 MHz, CDCl\(_3\))
\( \delta \) 22.0 (CH\(_3\)), 22.7 (CH\(_3\)), 23.0 (CH\(_3\)), 24.5 (CH), 41.1 (CH\(_2\)), 44.6 (CH\(_2\)), 53.7 (CH), 55.9 (C),
119.0 (CH\(_2\)), 134.1 (CH).

\((Rs,3S,4R)-3-Bromo-N-(tert-butanesulfonyl)dodec-1-en-4-amine (3b). Colourless liquid; \( R_f \) 0.65
(hexane/AcOEt 2:1); \([\alpha]^{30}_D\) -73 (c 0.56, CH\(_2\)Cl\(_2\)); IR (film) ν
2988, 2903, 1636, 1452, 1321, 1059, 857 cm\(^{-1}\); \(^1\)H RMN (300 MHz, CDCl\(_3\)) \( \delta \) 0.88 (3H, t, \( J = 6.7 \) Hz, CH\(_3\)),
1.26 [19H, s, (CH\(_2\))\(_2\), (CH\(_3\))\(_3\)], 1.58 (2H, ddd, \( J = 14.2, 10.0, 4.2 \) Hz, CH), 3.25 (1H, m, CH), 3.77 (1H, d,
\( J = 8.8 \) Hz, NH), 5.03 (1H, ddd, \( J = 9.0, 3.2 \) Hz, CH), 5.20 (1H, d, \( J = 10.2 \) Hz, CH), 5.38 (1H, d, \( J = 16.8 \) Hz, CH), 6.00 (1H,
ddd, \( J = 16.8, 10.1, 9.0 \) Hz, CH); \(^{13}\)C RMN (75 MHz, CDCl\(_3\)) \( \delta \) 14.1 (CH\(_3\)), 22.6 (CH\(_2\)), 22.7 (CH\(_3\)),
25.6 (CH\(_2\)), 29.2 (CH\(_2\)), 29.3 (CH\(_2\)), 29.4 (CH\(_2\)), 31.1 (CH\(_2\)), 31.8 (CH\(_2\)), 56.4 (C), 60.8 (CH),
63.6 (CH), 119.2 (CH\(_2\)), 135.3 (CH); LRMS (EI) \( m/z \) 311 (M\(^+\)-57, 4%), 309 (4), 213 (10), 211 (9), 189 (100), 105 (16),
96 (45), 82 (12), 67 (34), 57 (50); HRMS calc'd for C\(_16\)H\(_{32}\)BrNOS (M\(^+\)) 365.1388, found 365.1379.

\((Rs,3R,4R)-3-Bromo-N-(tert-butanesulfonyl) dodec-1-en-4-amine (3b\(^*\)). Mixture of anti:syn
diastereoisomers; colourless oil; \( R_f \) 0.62 (hexane/AcOEt 2:1); \([\alpha]^{30}_D\) -63 (c 0.45, CH\(_2\)Cl\(_2\)); IR (film) ν
2989, 2903, 1636, 1450, 1420, 1321, 1059, 987 cm\(^{-1}\); \(^1\)H RMN (300 MHz, CDCl\(_3\)) \( \delta \) 0.88 (3H, t, \( J = 6.7 \) Hz, CH\(_3\)),
1.23 [8.1H, s, (CH\(_3\))\(_3\)], 1.26 [27H, s, (CH\(_2\))\(_9\), (CH\(_3\))\(_3\)], 1.58 (2H, ddd, \( J = 10.6, 6.0 \) Hz, CH\(_2\)), 3.24 (1H,
ddd, \( J = 8.6, 5.2, 2.4 \) Hz, CH), 3.28 (0.71H, dd, \( J = 8.9, 3.7 \) Hz, CH), 3.57 (0.68H, d, \( J = 9.1 \) Hz, NH),
3.76 (1H, d, \( J = 8.8 \) Hz, NH), 4.79 (0.7H, dd, \( J = 9.9, 3.6 \) Hz, CH), 5.03 (1H, dd, \( J = 9.0, 3.2 \) Hz, CH), 5.20
(1H, d, \( J = 10.2 \) Hz, CH), 5.25 (0.78H, dd, \( J = 10.1, 1.1 \) Hz, CH), 5.38 (1.7H, d, \( J = 16.8 \) Hz, CH),
5.93-6.20 (1.8H, m, CH); \(^{13}\)C RMN (75 MHz, CDCl\(_3\)) \( \delta \) 14.1 (CH\(_3\)), 22.6 (CH\(_2\)), 22.7 (CH\(_3\)), 22.9 (CH\(_3\)),
25.6 (CH\(_2\)), 29.2 (CH\(_2\)), 29.3 (CH\(_2\)), 29.4 (CH\(_2\)), 29.5 (CH\(_2\)), 29.6 (CH\(_2\)), 30.8 (CH\(_3\)), 31.1 (CH\(_2\)),
31.8 (CH\(_2\)), 32.0 (CH\(_2\)), 55.2 (C), 56.4 (C), 59.2 (CH), 60.8 (CH), 61.3 (CH), 63.6 (CH), 119.2 (CH\(_2\)),
120.5 (CH\(_2\)), 133.9 (CH), 135.3 (CH).
(R₄,4R)-N-(tert-Butanesulfinyl)dodec-1-en-4-amine (4b). Colorless liquid; ¹H RMN (300 MHz, CDCl₃) δ 0.88 (3H, t, J = 6.7 Hz, CH₃), 1.20 [9H, s, (CH₃)₃], 1.26 (12H, s, CH₂), 1.53 (2H, m, CH₂), 2.35 (2H, m, CH), 3.22 (1H, d, J = 6.2 Hz, NH), 3.30 (1H, m, CH), 5.15 (2H, dd, J = 13.7, 1.3 Hz, CH), 5.74-5.80 (1H, m, CH); ¹³C RMN (75 MHz, CDCl₃) δ 14.1 (CH₃), 22.6 (CH₂), 22.7 (CH₃), 25.7 (CH₂), 29.2 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 31.1 (CH₂), 31.8 (CH₂), 39.8 (CH₂), 56.3 (C), 60.1 (CH), 119.0 (CH₂), 135.1 (CH).

(R₃,2R,3S)-3-Bromo-N-(tert-butanesulfinyl)-1-phenylpent-4-en-2-amine (3d). Colourless oil; R₁ 0.38 (hexane/AcOEt 2:1); [α]²⁰D -100 (c 1.05, CH₂Cl₂); IR (film) ν 3020, 2925, 1642, 1452, 1312, 1201, 1049, 896 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.08 [9H, s, (CH₃)₃], 2.91 (2H, m, CH₂), 3.63 (1H, m, CH), 3.80 (1H, d, J = 8.3 Hz, NH), 4.98 (1H, dd, J = 9.0, 3.2 Hz, CH), 5.28 (1H, d, J = 10.2 Hz, CH), 5.42 (1H, d, J = 16.8 Hz, CH), 6.09 (1H, m, CH), 7.00-7.30 (5H, m, CH); ¹³C RMN (75 MHz, CDCl₃) δ 22.4 (CH₃), 37.7 (CH₂), 56.3 (C), 62.2 (CH), 62.3 (CH), 119.8 (CH₂), 126.6 (CH), 128.4 (CH), 129.5 (CH), 134.0 (CH), 134.7 (C); LRMS (EL) m/z 289 (M⁺-56, 7%), 287 (8), 240 (14), 238 (11), 198 (32), 196 (44), 182 (52), 180 (48), 145 (30), 117 (32), 91 (100); HRMS calcd for C₁₅H₂₂BrNOS (M⁺) 343.0605, found 343.0599.

(R₃,2R,3R)-3-Bromo-N-(tert-butanesulfinyl)-1-phenylpent-4-en-2-amine (3d'). Mixture of anti:syn diastereoisomers; colourless oil; R₁ 0.34 (hexane/AcOEt 2:1); [α]²⁰D -93 (c 0.68, CH₂Cl₂); IR (film) ν 3020, 2925, 1642, 1452, 1312, 1121, 1049 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.08 [15H, s, (CH₃)₃], 2.88-2.94 (1H, m, CH₂), 3.61-3.64 (1H, m, CH), 3.75-3.80 (1H, d, J = 8.4 Hz, NH), 4.74 (0.69 H, d, J = 9.6 Hz, CH), 4.98 (1H, dd, J = 9.0, 3.2 Hz, CH), 5.25-5.45 (3.6H, m, CH), 6.00-6.30 (1.7H, m, CH), 7.15-7.30 (11H, m, CH); ¹³C RMN (75 MHz, CDCl₃) δ 22.4 (CH₃), 37.7 (CH₂), 39.6 (CH₂), 56.3 (C), 56.5 (C), 62.2 (CH), 62.3 (CH), 62.7 (CH), 119.8 (CH₂), 120.3 (CH₂), 126.6 (CH), 126.7 (CH), 128.4 (CH), 128.6 (CH), 129.3 (CH), 129.5 (CH), 134.8 (CH), 134.9 (CH), 137.5 (C), 137.6 (C); LRMS (EL) m/z 211 (M⁺-132, 10%), 150 (100), 148 (97), 91 (70).

(R₃,2R)-N-(tert-Butanesulfinyl)-1-phenylpent-4-en-2-amine (4d). Colorless liquid; ¹H RMN (300 MHz, CDCl₃) δ 1.07 [9H, s, (CH₃)₃], 2.37-2.41 (2H, m, CH₂), 2.83 (2H, m, CH₂), 3.33 (1H, d, J = 5.7 Hz, NH), 3.55-3.59 (1H, m, CH), 5.17 (2H, m, CH), 5.80-5.84 (1H, m, CH), 7.15-7.30 (5H, m, CH); ¹³C RMN (75 MHz, CDCl₃) δ 22.4 (CH₃), 37.7 (CH₂), 56.3 (C), 62.2 (CH), 62.3 (CH), 119.8 (CH₂), 126.6 (CH), 128.4 (CH), 129.5 (CH), 134.0 (CH), 137.5 (C).

(R₃,1R)-N-(terc-Butanesulfinil)-1-fenilbut-3-en-1-amina (4e). Colourless liquid; ¹H RMN (300 MHz, CDCl₃) δ 1.20 [9H, s, (CH₃)₃], 2.35-2.60 (2H, m, CH₂), 3.69 (1H, br s, NH), 4.47 (1H, ddd, J = 7.9, 5.4, 2.2 Hz, CH), 5.20 (2H, dd, J = 7.7, 0.9 Hz, CH), 5.70-5.76 (1H, m, CH), 7.30-7.35 (5H, m, CH); ¹³C RMN (75 MHz, CDCl₃) 22.5 (CH₃), 43.3 (CH₂), 55.5 (CH), 57.1 (C), 119.1 (CH₂), 127.4 (CH), 127.6 (CH), 128.3 (CH), 134.1 (CH), 141.6 (C).

(R₅,1R,2S)-2-Bromo-N-(tert-butanesulfinyl)-1-(4-fluorophenyl)but-3-en-1-amine (3g). Pale yellow
oil; $R_t$ 0.25 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -49 (c 1.20, CH₂Cl₂); IR (film) ν 3050, 2963, 1650, 1599, 1490, 1369, 1080, cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.22 [9H, s, (CH₃)₃], 4.04 (1H, d, $J = 2.2$ Hz, NH), 4.59 (1H, dd, $J = 6.1$, 2.5 Hz, CH), 4.65 (1H, dd, $J = 9.6$, 6.1 Hz, CH), 5.22 (1H, dd, $J = 10.1$, 0.6 Hz, CH), 5.29 (1H, d, $J = 16.9$ Hz, CH), 5.93 (1H, dt, $J = 16.9$, 9.9 Hz, CH), 7.21 (2H, d, $J = 8.4$ Hz, CH), 7.49 (2H, d, $J = 8.5$ Hz, CH); ¹³C RMN (75 MHz, CDCl₃) δ 22.6 (CH), 56.2 (C), 58.5 (CH), 61.9 (CH), 120.4 (CH), 129.3 (CH), 131.1 (C), 133.7 (CH), 140.7 (C), 161.9 (d, $J = 246.1$ Hz, C).

(RS,1R)-N-(tert-Butanesulfinyl)-1-(4-fluorophenyl)but-3-en-1-amine (4g). Colourless liquid; $R_t$ 0.20 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -43 (c 0.52, CH₂Cl₂); IR (film) ν 3056, 2963, 1648, 1595, 1475, 1362, 1225, 1107 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.19 [9H, s, (CH₃)₃], 2.40-2.60 (2H, m, CH₂), 3.68 (1H, s, NH), 4.41-4.46 (1H, m, CH), 5.15-5.19 (2H, m, CH₂), 5.68-5.71 (1H, m, CH), 7.20 (2H, d, $J = 8.4$ Hz, CH), 7.47 (2H, d, $J = 8.4$ Hz, CH); ¹³C RMN (75 MHz, CDCl₃) δ 22.6 (CH₃), 43.2 (CH₂), 55.2 (C), 58.8 (CH), 115.5 (d, $J = 22.4$ Hz, CH), 119.6 (CH₂), 129.3 (CH), 131.6 (CH), 133.7 (CH), 140.7 (C), 161.9 (d, $J = 246.1$ Hz, C).

(RS,1R,2S)-2-Bromo-N-(tert-butanesulfinyl)-1-(4-chlorophenyl)but-3-en-1-amine (3h). Colourless oil; $R_t$ 0.20 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -49 (c 0.75, CH₂Cl₂); IR (film) ν 3046, 2958, 1650, 1452, 1327, 1245, 926 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.19 [9H, s, (CH₃)₃], 2.30-2.60 (2H, m, CH₂), 3.68 (1H, s, NH), 4.44 (1H, t, $J = 6.9$ Hz, CH), 5.16 (2H, dd, $J = 11.0$, 6.3 Hz, CH₂), 5.65-5.69 (1H, m, CH), 7.20-7.35 (4H, m, CH); ¹³C RMN (75 MHz, CDCl₃) δ 22.6 (CH₃), 43.3 (CH₂), 55.2 (CH), 55.7 (C), 120.4 (CH₂), 128.7 (CH), 129.1 (CH), 129.2 (CH), 131.1 (C), 134.3 (C).

(RS,1R,2S)-2-Bromo-N-(tert-butanesulfinyl)-1-(4-trifluoromethylphenyl)but-3-en-1-amine (3i). Yellow oil; $R_t$ 0.23 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -50 (c 0.75, CH₂Cl₂); IR (film) ν 3046, 2958, 1650, 1452, 1327, 1245, 926 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.23 [9H, s, (CH₃)₃], 4.09 (1H, br s, NH), 4.60-4.80 (2H, m, CHN, CHBr), 5.24 (1H, d, $J = 10.2$ Hz, CH), 5.31 (1H, d, $J = 16.9$ Hz, CH), 5.80-6.00 (1H, m, CH), 7.46 (2H, d, $J = 8.1$ Hz, CH), 7.62 (2H, d, $J = 8.2$ Hz, CH); ¹³C RMN (75 MHz, CDCl₃) δ 22.5 (CH₃), 56.2 (C), 58.4 (CH), 61.9 (CH), 120.4 (CH₂), 123.9 (q, $J = 270.0$ Hz, C), 125.2 (q, $J = 3.6$ Hz, CH), 129.3 (CH), 130.7 (q, $J = 32.6$ Hz, C), 134.6 (CH), 141.4 (C); LRMS (EI) m/z 207 (M⁺-190, 6%), 144 (57), 129 (100), 115 (35), 91 (43), 77 (17); HRMS calcd for C₁₁H₁₀BrF₃N (M⁺-C₄H₁₀OS) 291.9949, found 291.9954.
(RS,1R)-N-(tert-Butanesulfinyl)-1-(4-trifluorophenyl)but-3-en-1-amine (4i). Colourless oil; \(^1\)H RMN (300 MHz, CDCl\(_3\)) \(\delta\) 1.21 [9H, s, (CH\(_3\))\(_3\)], 2.40-2.60 (2H, m, CH\(_2\)), 3.74 (1H, br s, NH), 4.52-4.58 (1H, m, CH), 5.17-5.23 (2H, m, CH\(_2\)), 7.45 (2H, d, \(J = 8.1\) Hz, CH), 7.60 (2H, d, \(J = 8.1\) Hz, CH); \(^1\)C RMN (75 MHz, CDCl\(_3\)) \(\delta\) 22.5 (CH\(_3\)), 43.2 (CH\(_2\)), 55.8 (C), 56.6 (CH), 119.8 (CH\(_2\)), 124.0 (q, \(J = 270.0\) Hz, C), 125.4 (q, \(J = 3.4\) Hz, CH), 127.8 (CH), 129.9 (q, \(J = 32.4\) Hz, C), 133.4 (CH), 145.8 (C).

(RS,1R)-N-(tert-Butanesulfinyl)-1-(2-furyl)but-3-en-1-amine (4j). Colourless oil; \(^1\)H RMN (300 MHz, CDCl\(_3\)) \(\delta\) 1.19 [9H, s, (CH\(_3\))\(_3\)], 2.40-2.70 (2H, m, CH\(_2\)), 3.59 (1H, s, NH), 4.52-4.56 (1H, m, CH), 5.11-5.17 (2H, m, CH\(_2\)), 5.68-5.73 (1H, m, CH\(_2\)), 6.21-6.24 (1H, s, CH), 6.30-6.36 (1H, m, CH), 7.35-7.40 (1H, m, CH); \(^1\)C RMN (75 MHz, CDCl\(_3\)) \(\delta\) 22.5 (CH\(_3\)), 39.8 (CH\(_2\)), 52.3 (CH), 55.9 (C), 107.4 (CH), 110.1 (CH), 119.4 (CH\(_2\)), 133.4 (CH), 142.1 (CH), 154.1 (C).

**Synthesis of aziridines 5 from bromohomoallylamine derivatives 3. General procedure.**

To a solution of bromohomoallylamine derivative 3 (0.1 mmol) in THF (1.0 mL) was added dropwise at -78 ºC a 1M solution of KHMDS in a 1:1 mixture of THF:tolune (0.200 mL, 0.2 mmol). The reaction mixture was allowed to reach room temperature, and after that, it was stirred at the same temperature for 3 h. Solvents were evaporated (15 Torr), and the resulting residue was hydrolyzed with brine (10 mL), extracted with AcOEt (3 × 15 mL). The organic layer was dried over anhydrous MgSO\(_4\) and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/AcOEt) to yield pure compounds 5. Yields are given on Table 4. Physical and spectroscopic data follow.

(RS,2R,3S)-N-(tert-Butanesulfinyl)-2-isobutyl-3-vinylaziridine (5ac). Colourless oil; \(R_f\) 0.90 (hexane/AcOEt 2:1); [\(\alpha\)]\(^{30}\)_D \(-97\) (c 0.86, CH\(_2\)Cl\(_2\)); IR (film) \(\nu\) 2960, 2930, 1636, 1457, 1382, 1080 cm\(^{-1}\); \(^1\)H RMN (300 MHz, CDCl\(_3\)) \(\delta\) 0.90-0.97 (6H, m, CH\(_3\)), 1.20 [9H, s, (CH\(_3\))\(_3\)], 1.50-1.60 (2H, m, CH\(_2\)), 1.70-1.80 (1H, m, CH), 2.35 (1H, dd, \(J = 13.2, 6.9\) Hz, CH), 3.17-3.22 (1H, m, CH), 5.31 (1H, dd, \(J = 10.3, 1.6\) Hz, CH), 5.40 (1H, dd, \(J = 17.2, 1.2\) CH), 5.69 (1H, ddd, \(J = 17.2, 10.3, 8.1\) Hz, CH); \(^1\)C RMN (100 MHz, CDCl\(_3\)) \(\delta\) 22.5 (CH\(_3\)), 22.6 (CH\(_2\)), 27.1 (CH\(_3\)), 39.8 (CH\(_2\)), 52.3 (CH), 55.9 (C), 107.4 (CH), 110.1 (CH), 119.4 (CH\(_2\)), 133.4 (CH), 142.1 (CH), 154.1 (C); LRMS (EI) \(m/z\) 173 (M\(^+\)-56, 17%), 124 (29), 110 (83), 95 (60), 57 (100); HRMS calcd for C\(_8\)H\(_{15}\)NOS (M\(^+\)-C\(_4\)H\(_8\)) 173.0874, found 173.0886.

(RS,2R,3R)-N-(tert-Butanesulfinyl)-2-isobutyl-3-vinylaziridine (5at). Colourless oil; \(R_f\) 0.82 (hexane/AcOEt 2:1); [\(\alpha\)]\(^{30}\)_D \(-80\) (c 1.15, CH\(_2\)Cl\(_2\)); IR (film) \(\nu\) 2960, 2930, 1636, 1475, 1386, 1262, 1092, 902 cm\(^{-1}\); \(^1\)H RMN (300 MHz, CDCl\(_3\)) \(\delta\) 0.90-0.97 (6H, m, CH\(_3\)), 1.26 [9H, s, (CH\(_3\))\(_3\)], 1.38-1.42 (1H, m, CH), 1.79-1.83 (2H, m, CH\(_2\)), 2.52-2.57 (1H, m, CH), 2.77 (1H, dd, \(J = 9.0, 3.9\) Hz, CH), 5.20-5.26 (1H, m, CH), 5.34-5.39 (1H, m, CH), 5.98 (1H, ddd, \(J = 17.2, 10.2, 9.0\) Hz, CH); \(^1\)C RMN (100 MHz, CDCl\(_3\)) \(\delta\) 22.5 (CH\(_3\)), 22.9 (CH\(_3\)), 27.1 (CH\(_3\)), 39.4 (CH\(_2\)), 43.2 (CH), 50.2 (CH), 56.9 (C), 119.0 (CH\(_2\)), 135.0 (CH); LRMS (EI) \(m/z\) 229 (M\(^+\), 2%), 173 (8), 124 (16), 110 (66), 67 (36), 57 (100); HRMS calcd for C\(_8\)H\(_{15}\)NOS (M\(^+\)-C\(_4\)H\(_8\)) 173.0874, found 173.0875.
(Rs,2R,3S)-N-(tert-Butanesulfinyl)-2-octyl-3-vinylaziridine (5bc). Colourless oil; Rf 0.90 (hexane/AcOEt 2:1); [α]30D -90 (c 0.50, CH2Cl2); IR (film) ν 2985, 2970, 2902, 1633, 1460, 1370, 1215, 1078, 901 cm⁻¹; 1H RMN (300 MHz, CDCl3) δ 0.88 (3H, t, J = 6.8 Hz, CH3), 1.21 [9H, s, (CH3)3], 1.18-1.30 [12H, m, (CH2)6], 1.47-1.52 (2H, m, CH2), 2.31 (1H, dd, J = 13.4, 6.5 Hz, CH), 3.20 (1H, dd, J = 7.9, 7.2 Hz, CH), 5.32 (1H, dd, J = 10.3, 1.3 Hz, CH), 5.40 (1H, dd, J = 17.2, 1.7, 0.6 Hz, CH), 5.61-5.80 (1H, m, CH); 13C RMN (100 MHz, CDCl3) δ 14.1 (CH3), 22.7 (CH2), 22.9 (CH3), 27.0 (CH2), 27.3 (CH2), 29.2 (CH2), 29.4 (CH2), 29.7 (CH2), 31.9 (CH2), 36.1 (CH), 39.5 (CH), 56.8 (C), 120.3 (CH2), 132.2 (CH); LRMS (EI) m/z 172 (M⁺-113, 2%), 113 (60), 109 (19), 96 (33), 82 (12), 67 (34), 57 (100); HRMS calcd for C18H31NOS (M⁺) 285.2126, found 285.2138.

(Rs,2R,3R)-N-(tert-Butanesulfinyl)-2-octyl-3-vinylaziridine (5bt). Colourless oil; Rf 0.83 (hexane/AcOEt 2:1); [α]30D -88 (c 0.40, CH2Cl2); IR (film) ν 2985, 2970, 1633, 1460, 1370, 1218, 1078, 920 cm⁻¹; 1H RMN (300 MHz, CDCl3) δ 0.88 (3H, t, J = 6.8 Hz, CH3), 1.22-1.30 [23H, m, (CH2)7, (CH3)3], 2.51-2.55 (1H, m, CH), 2.78 (1H, dd, J = 9.0, 3.9, CH), 5.22 (1H, dd, J = 10.2, 1.2 Hz, CH), 5.37 (1H, dd, J = 17.1, 1.0 Hz, CH), 5.90-6.04 (1H, m, CH); 13C RMN (100 MHz, CDCl3) δ 14.1 (CH3), 22.6 (CH2), 22.9 (CH3), 27.0 (CH2), 27.3 (CH2), 29.2 (CH2), 29.3 (CH2), 29.7 (CH2), 31.8 (CH2), 44.4 (CH), 49.6 (CH), 56.9 (C), 118.9 (CH2), 135.1 (CH); LRMS (EI) m/z 180 (M⁺-105, 4%), 172 (1), 160 (5), 126 (40), 113 (100), 105 (6); HRMS calcd for C12H23NOS (M⁺-C4H8) 229.1500, found 229.1508.

(Rs,2R,3S)-2-Benzyl-N-(tert-butanesulfinyl)-3-vinylaziridine (5dc). Pale yellow oil; Rf 0.79 (hexane/AcOEt 2:1); [α]30D -34 (c 0.63, CH2Cl2); IR (film) ν 3015, 2925, 1640, 1425, 1310, 949 cm⁻¹; 1H RMN (300 MHz, CDCl3) δ 1.22 [9H, s, (CH3)3], 2.58 (1H, dd, J = 13.2, 7.0 Hz, CH), 2.82-2.86 (1H, m, CH2), 3.30 (1H, dd, J = 7.3, 7.1 Hz, CH), 5.35-5.56 (2H, m, CH), 5.84 (1H, dd, J = 17.3, 10.3, 7.7 Hz, CH), 7.20-7.35 (5H, m, CH); 13C RMN (100 MHz, CDCl3) δ 22.8 (CH3), 33.7 (CH2), 36.1 (CH), 40.0 (CH), 56.8 (C), 120.8 (CH2), 126.5(CH), 128.5 (CH), 128.7 (CH), 131.8 (CH), 138.3 (C); LRMS (EI) m/z 207 (M⁺-56, 8%), 144 (58), 129 (100), 115 (34), 91 (38); HRMS calcd for C15H21NOS (M⁺) 263.1344, found 263.1354.

(Rs,2R,3R)-2-Benzyl-N-(tert-butanesulfinyl)-3-vinylaziridine (5dt). Yellow oil; Rf 0.72 (hexane/AcOEt 2:1); [α]30D -28 (c 0.60, CH2Cl2); IR (film) ν 3015, 2925, 1640, 1425, 1310, 1245, 1102 cm⁻¹; 1H RMN (300 MHz, CDCl3) δ 1.27 [9H, s, (CH3)3], 2.76-2.85 (1H, m, CH), 2.86-3.02 (1H, m, CH2), 3.11 (1H, dd, J = 14.5, 5.1 Hz, CH), 5.22 (1H, dd, J = 10.2, 1.3 Hz, CH), 5.38 (1H, dd, J = 17.3, 1.1 Hz, CH), 6.00 (1H, J = 17.1, 10.2, 9.0 Hz, CH), 7.06-7.46 (5H, m, CH); 13C RMN (100 MHz, CDCl3) δ 22.9 (CH3), 37.1 (CH2), 44.1 (CH), 50.0 (CH), 57.1 (C), 119.4 (CH2), 126.7 (CH), 128.5 (CH), 128.8 (CH), 134.6 (CH), 137.7 (C); LRMS (EI) m/z 207 (M⁺-56, 6%), 144 (57), 129 (100), 115 (35), 91 (43), 77 (17); HRMS calcd for C15H21NOS (M⁺) 263.1344, found 263.1350.

(Rs,2R,3R)-N-(tert-Butanesulfinyl)-2-(4-fluorophenyl)-3-vinylaziridine (5gt). White solid; mp
64–66 °C (hexane/CH₂Cl₂); Rf 0.65 (hexane/AcOEt 2:1); [α]₃⁰D -20 (c 0.83, CH₂Cl₂); IR (film) ν 3050, 2963, 1648, 1490, 1369, 1080, 967 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.28 [9H, s, (CH₃)₃], 3.12 (1H, dd, J = 9.4, 3.5 Hz, CH), 3.51 (1H, d, J = 3.5 Hz, CH), 5.36 (1H, dd, J = 10.2, 0.8 Hz, CH), 5.47 (1H, dd, J = 17.0, 0.7 Hz, CH), 6.22-6.27 (1H, m, CH), 7.16 (2H, d, J = 8.4 Hz, CH), 7.47 (2H, d, J = 8.5 Hz, CH); ¹³C RMN (100 MHz, CDCl₃) δ 23.0 (CH₃), 43.8 (CH), 54.2 (CH), 57.5 (C), 115.6 (q, J = 21.8 Hz, CH₂), 121.0 (CH₂), 128.0 (CH), 133.0 (CH), 135.8 (C), 163.1 (d, J = 245 Hz, C); LRMS (EI) m/z 210 (M⁺-57, 22%), 208 (22), 129 (100); HRMS calcd for C₁₀H₉FN (M⁺-C₄H₉OS) 162.0719, found 162.0724.

(RS₂R₂R₃)-N-(tert-Butanesulfinyl)-2-(4-chlorophenyl)-3-vinylaziridine (5ht). White solid; mp 67-69 °C (hexane/CH₂Cl₂); Rf 0.60 (hexane/AcOEt 2:1); [α]₃⁰D -19 (c 0.86, CH₂Cl₂); IR (film) ν 2963, 1645, 1595, 1475, 1220, 897 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.28 [9H, s, (CH₃)₃], 3.12 (1H, dd, J = 9.4, 3.5 Hz, CH), 3.52 (1H, d, J = 3.5 Hz, CH), 5.36 (1H, dd, J = 10.2, 1 Hz, CH), 5.47 (1H, dd, J = 16.3, 1 Hz, CH), 6.25 (1H, ddd, J = 17.0, 10.1, 9.5 Hz, CH), 7.21 (2H, d, J = 8.4 Hz, CH), 7.32 (2H, d, J = 8.5 Hz, CH); ¹³C RMN (100 MHz, CDCl₃) δ 23.0 (CH₃), 43.8 (CH), 54.2 (CH), 57.5 (C), 121.0 (CH₂), 127.6 (CH), 128.8 (CH), 133.0 (CH), 133.8 (C), 135.8 (C); LRMS (EI) m/z 227 (M⁺-56, 6%), 144 (57), 129 (100), 115 (35), 91 (43), 77 (17); HRMS calcd for C₁₄H₁₈ClNOS (M⁺) 283.0798, found 283.0789.

(RS₂R₂R₃)-N-(tert-Butanesulfinyl)-2-(4-trifluoromethylphenyl)-3-vinylaziridine (5it). Orange solid; mp 74-66 °C (hexane/CH₂Cl₂); Rf 0.61 (hexane/AcOEt 2:1); [α]₃⁰D -28 (c 0.75, CH₂Cl₂); IR (film) ν 2958, 1648, 1452, 1327, 1300, 1245 cm⁻¹; ¹H RMN (300 MHz, CDCl₃) δ 1.29 [9H, s, (CH₃)₃], 3.16 (1H, dd, J = 9.5, 3.5 Hz, CH), 3.61 (1H, d, J = 3.5 Hz, CH), 5.38 (1H, d, J = 10.6 Hz, CH), 5.48 (1H, d, J = 16.5 Hz, CH), 6.20-6.40 (1H, m, CH), 7.40 (2H, d, J = 8.1 Hz, CH), 7.61 (2H, d, J = 8.2 Hz, CH); ¹³C RMN (100 MHz, CDCl₃) δ 23.0 (CH₃), 43.6 (CH), 54.6 (CH), 57.6 (C), 121.2 (CH₂), 124.0 (q, J = 270.0 Hz, C), 125.6 (q, J = 3.5 Hz, CH), 126.6 (CH), 130.2 (q, J = 32.4 Hz, C), 132.9 (CH), 140.9 (C); LRMS (EI) m/z 260 (M⁺-57, 10%), 220 (15), 211 (35), 193 (28), 174 (100), 149 (60), 129 (36), 115 (20), 57 (90); HRMS calcd for C₁₅H₁₈F₃NOS (M⁺) 317.1061, found 317.1064.

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REFERENCES AND NOTES


