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

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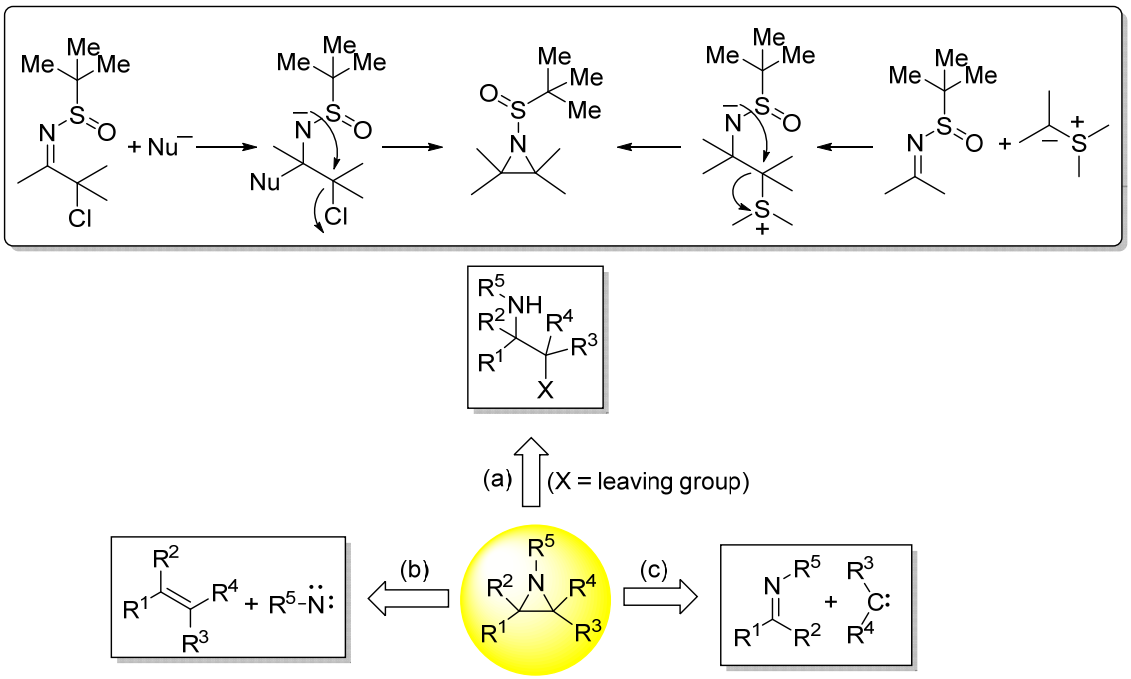
Abstract – The reaction of *N*-*tert*-butanesulfinyl imines **1** with 1,3-dibromopropene (**2**), in the presence of indium metal, in saturated aqueous solution of sodium bromide, produced bromohomoallylamine derivatives **3** as a variable *anti*:*syn* mixture of diastereoisomers, with total facial diastereoselectivity, and moderate yields. These compounds were easily transformed into the corresponding vinyl aziridines **5** upon deprotonation with KHMDS in THF, taking place the intramolecular cyclization 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, different 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] leukemia[3]), in the treatment of malaria[4] and leishmaniasis,[5] or as antimicrobials.[6] In addition to the pharmacological interest, in recent years different 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 reactions,[9] 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 with 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, follow by the intramolecular cyclization. Hydride (reduction of the imine),[13] Grignard reagents,[14] organocerium compounds[14c,15] and allylic tellurium salts[16] were used as nucleophiles in these processes (Scheme 1). Aziridines were also prepared through a Corey-Chaykovsky reaction of chiral *N*-*tert*-butanesulfinyl aldimines and ketimines.[17] Importantly, vinyl aziridines were obtained when *S*-allyl tetrahydrothiophenium bromide[18] was used as the precursor of the sulfonium ylide in these reactions (Scheme 1).



Scheme 1.

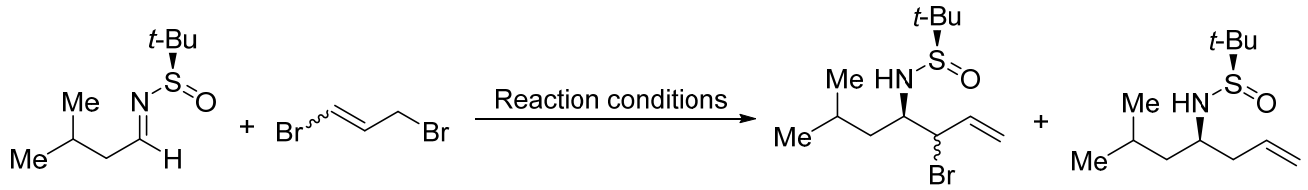
It is worth mentioning that *N*-*tert*-butanesulfinyl imines[19] have found high applicability in synthesis as electrophiles, because they are accessible in large-scale processes in an enantiopure form,[20] and practical processes for recycling the *tert*-butanesulfinyl group have also been reported.[21] With regards to this, we have extensively studied the stereoselective allylation and propargylation of *N*-*tert*-butanesulfinyl imines[22] and the application in synthesis of the resulting homoallyl amine derivatives.[23] 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 β-bromohomoallylamine derivatives. 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 in moderate yields the corresponding *trans*-vinyl aziridines.[24]

RESULTS AND DISCUSSION

The starting *N*-*tert*-butanesulfinyl aldimines **1** were easily prepared by condensation of the corresponding aldehyde and (*R*)-*tert*-butanesulfinamide in the presence of 2 equiv of $Ti(OEt)_4$ in THF at room temperature.[25] 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 equivalents of 1,3-dibromopropene (**2**), in the presence of 4 equivalents 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 equivalents) and allylic bromide **2** (3 equivalents), 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 dibromomo compound **2** with magnesium in THF for 2 hours at room temperature, followed by reaction of 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**)[a]



1a **2** **3a** **4a**

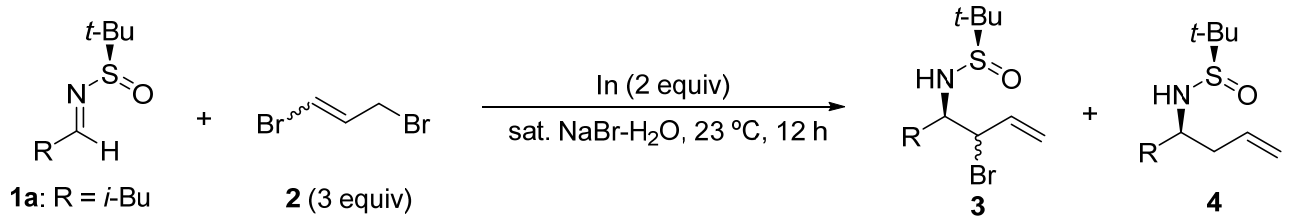
Entry	Metal (equiv)	Solvent	**2** (equiv)	T (ºC)	Conversion	**3a**/**4a** Ratio[b]
1	In (4)	sat. NaBr-H_2O	4	23	>90	59/41
2	In (2)	sat. NaBr-H_2O	3	23	>90	52/48
3[c]	In (1.5)	sat. NaBr-H_2O	3	23	>90	54/46
4	In (1.8)	sat. NaBr-H_2O	6	23	>90	60/40
5	In (1.5)	THF	3	23	0	-
6	In (1.5)	THF	3	60	15	60/40
7	In (1.5)	DMF	3	23	0	-
8	Zn (1.8)	sat. NaBr-H_2O	2	23	0	-
9	Zn (1.8)	DMF	2	23	10	50/50
10	Zn (1.8)	THF	2	23	20	54/46
11[c,d]	Mg (1.8)	THF	2	-78 to 23	0	-

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

We studied next the scope of the reaction of 1,3-dibromopropene (**2**) with different *N-tert*-butanesulfinyl aldimines **1**, by applying the optimized conditions shown in Table 1, entry 2.

We studied first the allylation of aliphatic aldimines **1a-d** (Table 2). In the case of the imine derived from isovareladehyde **1a**, product **3a** was obtained in 37% yield (75:25 *anti:syn* ratio), and the dehalogenated product **4a** in 26% yield, as a single diastereomeric. 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 *anti: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 phenylacetaldehyd, reacted with1,3-dibromopropene (**2**) to give the bromoalylation product **3d** in 33% isolated yield and a better diastereomeric ratio than in previous cases (78:22 *anti:syn* ratio), along with dehalogenated product **4d** (22% yield).

Table 2. Allylation of aliphatic aldimines **1a-g** with 1,3-dibromopropene (**2**)[a,b]

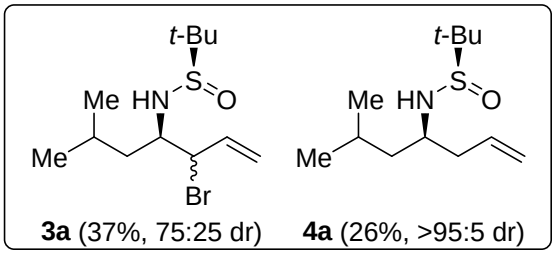


1a: R = *i*-Bu
1b: R = $CH_3(CH_2)_7$
1c: R = Cy
1d: R = $PhCH_2$

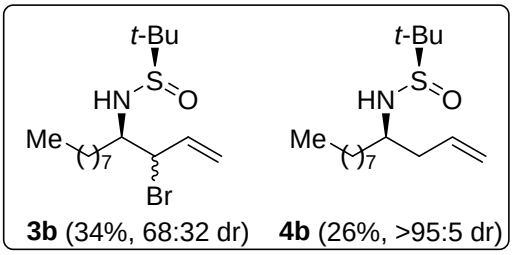
2 (3 equiv)

3

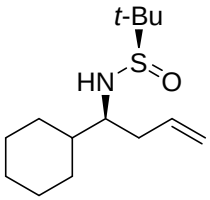
4



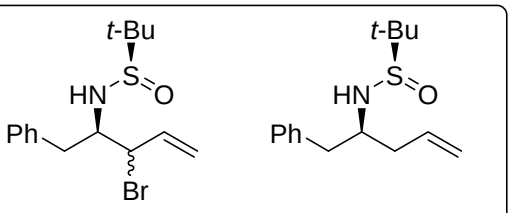
3a (37%, 75:25 dr) **4a** (26%, >95:5 dr)



3b (34%, 68:32 dr) **4b** (26%, >95:5 dr)



4c (16%, >95:5 dr)



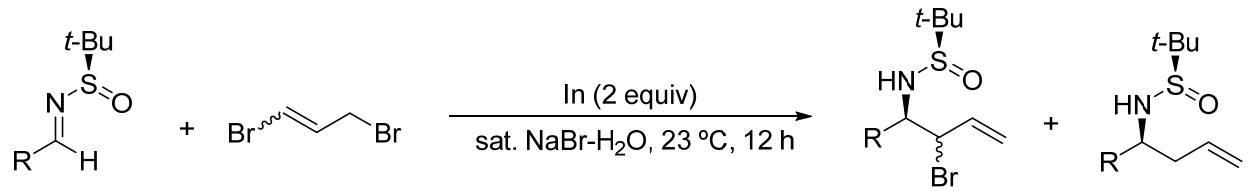
3e (33%, 78:22 dr) **4e** (22%, >95:5 dr)

[a] Yields were determined for isolated compounds after column chromatography. [b] Diastereomeric ratios for compounds **3** refer to *anti:syn* ratios.

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

Table 3. Allylation of aromatic aldimines **1h-g** with 1,3-dibromopropene (**2**)[a,b]

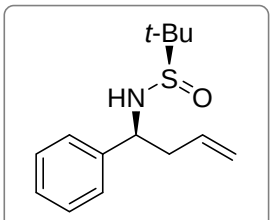


1e: R = Ph
1f: R = 4-MeC_6H_4
1g: R = 4-FC_6H_4
1h: R = 4-ClC_6H_4
1i: R = 4-$CF_3C_6H_4$
1j: R = 2-furyl

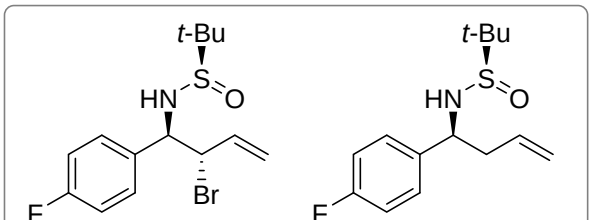
2 (3 equiv)

3

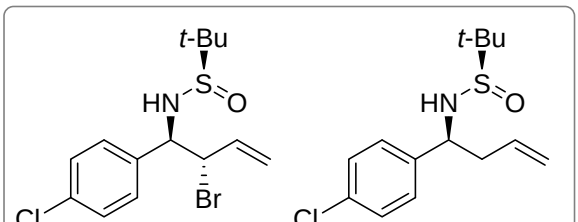
4



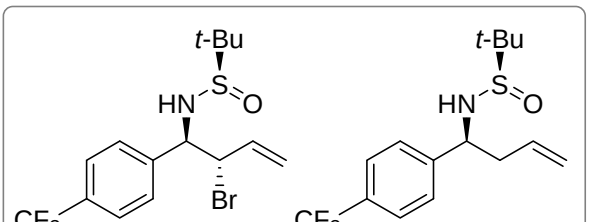
4e (16%, >95:5 dr)



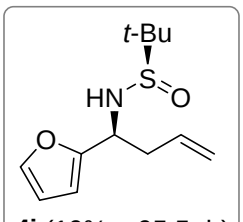
3g (35%, >95:5 dr) **4g** (34%, >95:5 dr)



3h (20%, >95:5 dr) **4h** (18%, >95:5 dr)



3i (25%, >95:5 dr) **4i** (16%, >95:5 dr)

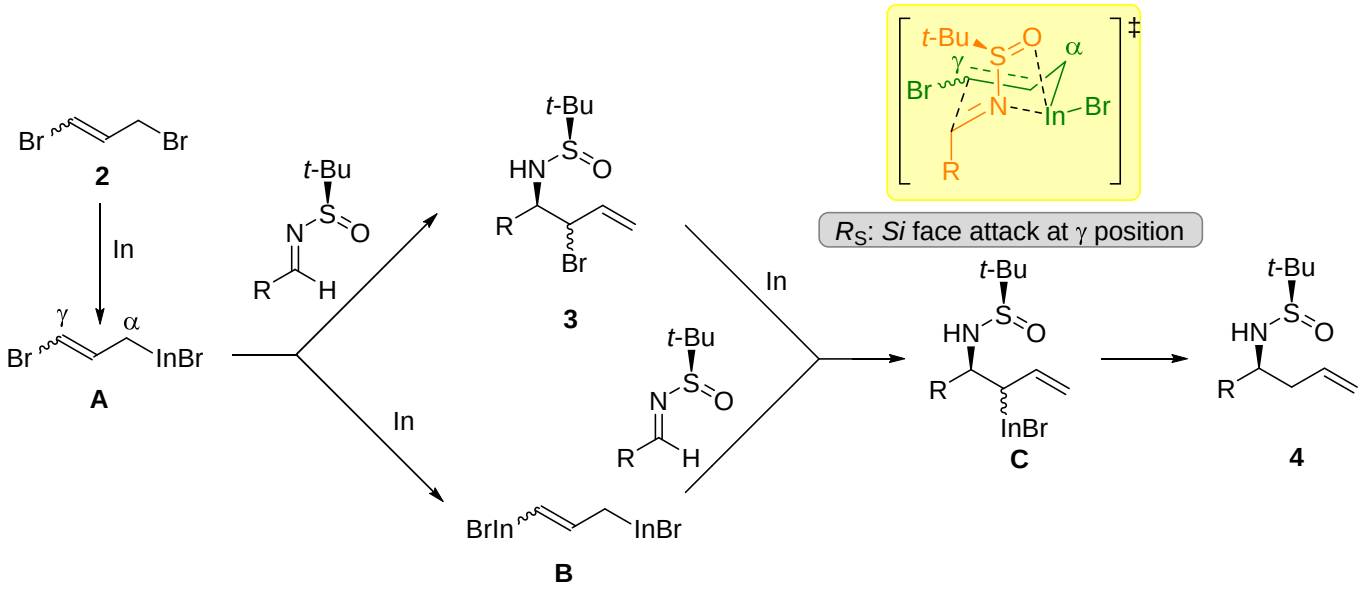


4j (10%, >95:5 dr)

[a] Yields were determined for isolated compounds after column chromatography. [b] Diastereomeric ratios for compounds **3** refer to *anti:syn* ratios.

A speculative mechanism, which explains the formation of products **3** and **4**, is depicted on Scheme 2. 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 alyllations 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 system **A**, reacting at γ-position, takes place to the *Si*-face of the imine with R_S 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 equivalents), 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**, precursor after hydrolysis of the allylated product **4**. The formation of **4** could also be explained from compound **3**. Thus, in the presence of excess of indium, compound **3** could be reduced again by having a bromine in the allylic position and generating in this way intermediate **C**, precursor of the product **4** (Scheme 2).



Scheme 2.

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 cyclisation 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**, yields obtained were lower (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).

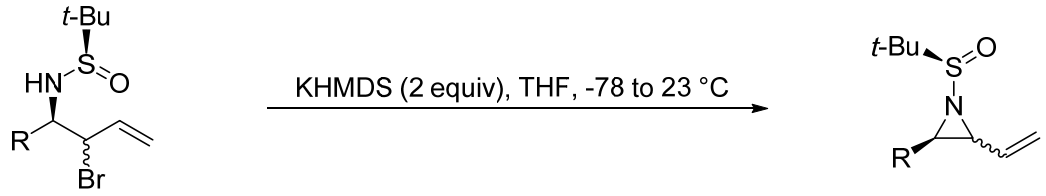
The configuration of the aziridines **5** was determined by NOESY experiments. Bearing in mind that the cyclizations are diastereoselective, once the configuration of the aziridines **5** is known, it is possible to assign the configuration of the diastereomers from which they are derived. Thus, aziridines 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 ^{1}H 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 allyltions reactions take place with total facial diastereoselectivity, concerding the addition to the imine, leading also preferently to diastereisomers with *anti* relative configuration. The final intramolecular cyclization step proceed in a stereospecific manner to give aziridines **5** in moderate to high yields.

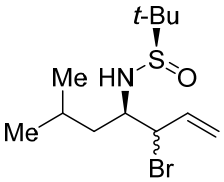
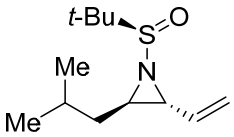
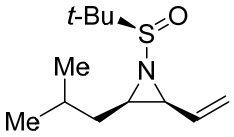
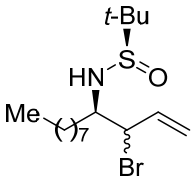
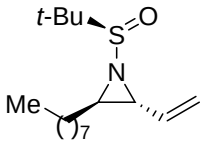
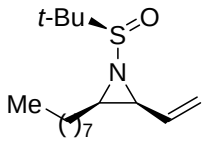
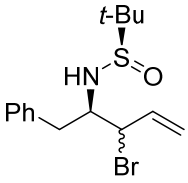
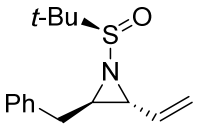
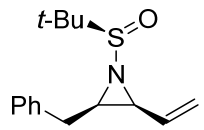
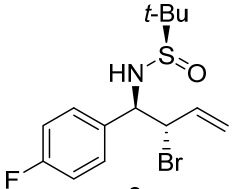
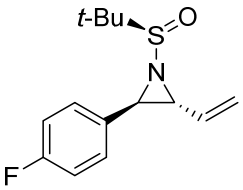
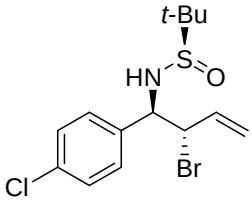
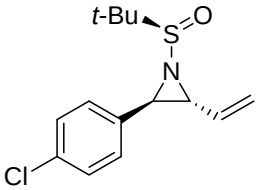
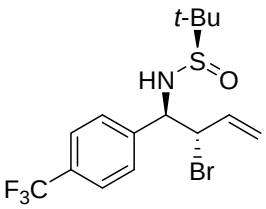
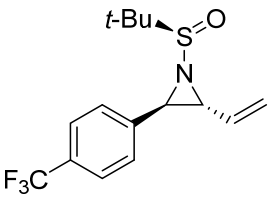
EXPERIMENTAL

All chemicals were commercially available (Acros, Aldrich). TLC was performed on Merck silica gel 60 F_{254}, 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 eluents. Low-resolution electron impact (EI) mass spectra were obtained at 70eV on Agilent GC/MS-5973N apparatus equipped with a HP-5MS column (Agilent technologies, 30 m × 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 chromatograph (UPLC) model Waters ACQUITY H CLASS. IR spectra were measured (film) with a Nicolet Impact 510 P-FT Spectrometer. NMR spectra were recorded with a Bruker AC-300 and a Bruker 500-AVANCE IIIHD, using $CDCl_3$ as solvent, and TMS as internal standard. Optical rotations were measured on a Perkin Elmer 341 polarimeter.

Table 4. Synthesis of aziridines **5** from bromohomoalilamine derivatives **3**[a]



3 **5**

	Bromohomoallyl amine derivative **3**		Aziridine **5**	
Entry	Structure, No.	dr (*anti*:*syn*)	Structure, No. (yield, dr)	
1	 **3a**	75:25	 **5at** (38%, >95:5 dr)	 **5ac** (13%, >95:5 dr)
2	 **3b**	68:32	 **5bt** (20%, >95:5 dr)	 **5bc** (13%, >95:5 dr)
3	 **3d**	78:22	 **5dt** (36%, >95:5 dr)	 **5dc** (11%, >95:5 dr)
4	 **3g**	>95:5	 **5gt** (51%, >95:5 dr)[b]	
5	 **3h**	>95:5	 **5ht** (55%, >95:5 dr)[b]	
6	 **3i**	>95:5	 **5it** (86%, >95:5 dr)[b]	

[a] Yields were determined for isolated compounds after column chromatography. [b] A mixture of compounds **3** and **4** were used as starting materials in this transformation.

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-dibromopropne (**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 EtOAc (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/EtOAc) to yield compounds **3** and **4**. Yields are given on Tables 2 and 3. Physical and spectroscopic data follow.

(*R*$_S$,3*S*,4*R*)-3-Bromo-*N*-(*tert*-butanesulfinyl)-6-methylhept-1-en-4-amine (*anti*-3a).- Pale yellow oil; R_f 0.55 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -21 (*c* 0.50, CH_2Cl_2); IR (film) ν 3203, 2968, 1640, 1450, 1376, 1057 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 0.87 (3H, d, *J* = 6.5 Hz, CH_3), 0.94 (3H, d, *J* = 6.7 Hz, CH_3), 1.26 [9H, s, $(CH_3)_3$], 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 22.7 (CH_3), 23.5 (CH_3), 24.2 (CH), 40.1 (CH_2), 56.4 (C), 59.2 (CH), 64.9 (CH), 119.2 (CH_2), 135.2 (CH); LRMS (EI) *m/z* 174 (M^+-135, 36%), 133 (32), 125 (9), 113 (100), 83 (25), 57 (60); HRMS calcd for $C_{12}H_{24}BrNOS$ (M^+) 309.0762, founf 309.0755.

(*R*$_S$,3*R,4*R*)-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); $[\alpha]^{30}_D$ -18 (*c* 0.75, CH_2Cl_2); IR (film) ν 3203, 2968, 1640, 1450, 1376, 1057, 962 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 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 (100 MHz, $CDCl_3$) δ 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).

(*R*$_S$,4*R*)-*N*-(*tert*-Butanesulfinyl)-6-methylhept-1-en-4-amine (4a)[45].- Colourless liquid; ^1H RMN (300 MHz, $CDCl_3$) δ 0.90 (6H, 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), 3.18 (1H, d, *J* = 7.4 Hz, NH), 3.37 (1H, m, CH), 5.17 (2H, m, CH), 5.79 (1H, ddd, *J* = 17.0, 12.1, 7.3 Hz, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 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).

(*R*$_S$,3*S*,4*R*)-3-Bromo-*N*-(*tert*-butanesulfinyl)dodec-1-en-4-amine (3b).- Colourless liquid; R_f 0.65 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ –73 (*c* 0.56, CH_2Cl_2); IR (film) ν 2988, 2903, 1636, 1452, 1321, 1059, 857

cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 0.88 (6H, t, *J* = 6.7 Hz, CH_3), 1.26 [19H, s, $(CH_2)_5$, $(CH_3)_3$], 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, dd, *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 (100 MHz, $CDCl_3$) δ 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 calcd for $C_{16}H_{32}BrNOS$ (M^+) 365.1388, founf 365.1379.

(*R*S,3*R,4*R*)-3-Bromo-*N*-(*tert*-butanesulfinyl)-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_2Cl_2); IR (film) ν 2989, 2903, 1636, 1450, 1420, 1321, 1059, 987 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 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, dd, *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 (100 MHz, $CDCl_3$) δ 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_2), 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).

(*R*S,4*R*)-*N*-(*tert*-Butanesulfinyl)dodec-1-en-4-amine (4b)[45].- Colourless liquid; ^1H RMN (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.7 Hz, CH_3), 1.20 [9H, s, $(CH_3)_3$], 1.26 (12H, s, CH_2), 1.53 (2H, m, CH_2), 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 22.7 (CH_3), 25.7 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.1 (CH_2), 31.8 (CH_2), 39.8 (CH_2), 56.3 (C), 60.1 (CH), 119.0 (CH_2), 135.1 (CH).

(*R*S,2*R*,3*S*)-3-Bromo-*N*-(*tert*-butanosulfinyl)-1-phenylpent-4-en-2-amine (3d).- Colourless oil; R_f 0.38 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -100 (*c* 1.05, CH_2Cl_2); IR (film) ν 3020, 2925, 1642, 1452, 1312, 1201, 1049, 896 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.08 [9H, s, $(CH_3)_3$], 2.91 (1H, m, CH_2), 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.4 (CH_3), 37.7 (CH_2), 56.3 (C), 62.2 (CH), 62.3 (CH), 119.8 (CH_2), 126.6 (CH), 128.4 (CH), 129.5 (CH), 134.0 (CH), 137.5 (C); LRMS (EI) *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 $C_{15}H_{22}BrNOS$ (M^+) 343.0605, found 343.0599.

(R_S,2*R*,3*R)-3-Bromo-*N*-(*tert*-butanesulfinyl)-1-phenylpent-4-en-2-amine (3d')**.- Mixture of *anti*:*syn* diastereoisomers; colourless oil; R_f 0.34 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -93 (*c* 0.68, CH_2Cl_2); IR (film) ν 3020, 2925, 1642, 1452, 1312, 1121, 1049 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.08 [15H, s, $(CH_3)_3$], 2.88-2.94 (1H, m, CH_2), 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.4 (CH_3), 37.7 (CH_2), 39.6 (CH_2), 56.3 (C), 56.5 (C), 62.2 (CH), 62.3 (CH), 62.7 (CH), 119.8 (CH_2), 120.3 (CH_2), 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 (EI) *m/z* 211 (M^+-132, 10%), 150 (100), 148 (97), 91 (70);

(R_S,2*R*)-*N*-(*tert*-Butanesulfinyl)-1-phenylpent-4-en-2-amine (4d)[45].- Colourless liquid; ^1H RMN (300 MHz, $CDCl_3$) δ 1.07 [9H, s, $(CH_3)_3$], 2.37-2.41 (2H, m, CH_2), 2.83 (2H, m, CH_2), 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.4 (CH_3), 37.7 (CH_2), 56.3 (C), 62.2 (CH), 62.3 (CH), 119.8 (CH_2), 126.6 (CH), 128.4 (CH), 129.5 (CH), 134.0 (CH), 137.5 (C).

(R_S,1*R*)-*N*-(*terc*-Butanosulfinil)-1-fenilbut-3-en-1-amina (4e)[45].- Colourless liquid; ^1H RMN (300 MHz, $CDCl_3$) δ 1.20 [9H, s, $(CH_3)_3$], 2.35-2.60 (2H, m, CH2), 3.69 1(H, 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); ^{13}C RMN (100 MHz, $CDCl_3$) 22.5 (CH_3), 43.3 (CH_2), 55.5 (CH), 57.1 (C), 119.1 (CH_2), 127.4 (CH), 127.6 (CH), 128.3 (CH), 134.1 (CH), 141.6 (C).

(R_S,1*R*,2*S*)-2-Bromo-*N*-(*tert*-butanesulfinyl)-1-(4-fluorophenyl)but-3-en-1-amine (3g).- Pale yellow oil; R_f 0.25 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -49 (*c* 1.20, CH_2Cl_2); IR (film) ν 3050, 2963, 1650, 1599, 1490, 1369, 1080, cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.22 [9H, s, $(CH_3)_3$], 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 56.1 (C), 58.6 (CH), 61.8 (CH), 120.2 (CH_2), 122.7 (C), 130.6 (CH), 131.5 (CH), 134.8 (CH), 136.3 (C); LRMS (EI) *m/z* 289 (M^+-57, 8%), 255 (60), 253 (50), 211 (62), 209 (62), 183 (20), 130 (100), 115 (28); HRMS calcd for $C_{14}H_{19}BrFNrOS$ (M^+) 347.0355, found 347.0356.

(R_S,1*R*)-*N*-(*tert*-Butanesulfinyl)-1-(4-fluorophenyl)but-3-en-1-amine (4g)[45].- Colourless liquid; ^1H RMN (300 MHz, $CDCl_3$) δ 1.19 [9H, s, $(CH_3)_3$], 2.40-2.60 (2H, m, CH_2), 3.68 (1H, s, NH), 4.41-4.46 (1H, m, CH), 5.15-5.19 (2H, m, CH_2), 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 43.2 (CH_2), 55.2 (C), 58.6 (CH), 120.2 (CH_2), 129.2 (CH), 129.4 (CH), 131.6 (CH), 132.1 (C), 140.7 (C).

(R_S,1*R*,2*S*)-2-Bromo-*N*-(*tert*-butanesulfinyl)-1-(4-chlorophenyl)but-3-en-1-amine (3h).- Colourless oil; R_f 0.20 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ –43 (*c* 0.52, CH_2Cl_2); IR (film) ν 3056, 2963, 1648, 1595, 1475, 1362, 1225, 1107 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.22 [9H, s, $(CH_3)_3$], 4.06 (1H, d, *J* = 1.9 Hz, NH), 4.58-4.68 (2H, m, CHN, CHBr), 5.23 (1H, d, *J* = 10.7 Hz, CH), 5.29 (1H, d, *J* = 16.9 Hz, CH), 7.26 (2H, m, CH), 7.34 (2H, m, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 55.6 (CH), 56.0 (C), 59.5 (CH), 120.1 (CH_2), 129.0 (CH), 129.4 (CH), 129.5 (CH), 131.9 (C), 135.3 (C); LRMS (EI) *m/z* 246 (M^+-119, 3%), 244 (5), 211 (30), 209 (11), 189 (7), 187 (19), 167 (36), 165 (100), 141 (22), 139 (7), 115 (15); HRMS calcd for $C_{10}H_{11}BrClNOS$ (M^+-C_4H_8) 306.9433, found 306.9422.

(R_S,1*R*)-*N*-(*tert*-Butanesulfinyl)-1-(4-chlorophenyl)but-3-en-1-amine (4h)[45].- Colourless oil; ^1H RMN (300 MHz, $CDCl_3$) δ 1.19 [9H, s, $(CH_3)_3$], 2.30-2.60 (2H, m, CH_2), 3.68 (1H, s, NH), 4.44 (1H, t, *J* = 6.9 Hz, CH), 5.16 (2H, dd, *J* =11.0, 6.3 Hz, CH_2), 5.65-5.69 (1H, m, CH), 7.20-7.35 (4H, m, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 43.3 (CH_2), 55.2 (CH), 55.7 (C), 120.4 (CH_2), 128.7 (CH), 129.1 (CH), 129.2 (CH), 131.1 (C), 134.3 (C).

(R_S,1*R*,2*S*)-2-Bromo-*N*-(*tert*-butanesulfinyl)-1-(4-trifluoromethylphenyl)but-3-en-1-amine (3i).- Yellow oil; R_f 0.23 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -50 (*c* 0.75, CH_2Cl_2); IR (film) ν 3046, 2958, 1650, 1452, 1327, 1245, 926 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.23 [9H, s, $(CH_3)_3$], 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), 7.46 (2H, d, *J* = 8.1 Hz, CH), 7.62 (2H, d, *J* = 8.2 Hz, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 56.2 (C), 58.4 (CH), 61.9 (CH), 120.4 (CH_2), 125.2 (C), 129.3 (CH), 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 $C_{11}H_{10}BrF_3N$ (M^+-$C_4H_{10}OS$) 291.9949, found 291.9954.

(R_S,1*R*)-*N*-(*tert*-Butanesulfinyl)-1-(4-trifluorophenyl)but-3-en-1-amine (4i)[45].- Colourless oil; ^1H RMN (300 MHz, $CDCl_3$) δ 1.21 [9H, s, $(CH_3)_3$], 2.40-2.60 (2H, m, CH_2), 3.75 (1H, br s, NH), 4.52-4.58 (1H, m, CH), 5.27-5.32 (2H, m, CH_2), 5.67-5.72 (1H, m, CH), 7.46 (2H, d, *J* = 8.1 Hz, CH), 7.62 (2H, d, *J* = 8.1 Hz, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 56.2 (C), 58.4 (CH), 61.9 (CH), 120.4 (CH_2), 125.2 (C), 129.3 (CH), 134.6 (CH), 141.4 (C).

(R_S,1*R*)-*N*-(*tert*-Butanesulfinyl)-1-(2-furyl)but-3-en-1-amine (4j)[45].- Colourless oil; ^1H RMN (300 MHz, $CDCl_3$) δ 1.21 [9H, s, $(CH_3)_3$], 2.40-2.60 (2H, m, CH_2), 3.75 (1H, br s, NH), 4.52-4.58 (1H, m, CH), 5.27-5.32 (2H, m, CH_2), 5.67-5.72 (1H, m, CH), 7.46 (2H, d, *J* = 8.1 Hz, CH), 7.62 (2H, d, *J* = 8.1 Hz, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 56.2 (C), 58.4 (CH), 61.9 (CH), 120.4 (CH_2), 125.2 (C), 129.3 (CH), 134.6 (CH), 141.4 (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 EtOAc (3 × 15 mL). The organic layer was dried over anhydrous MgSO4 and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/EtOAc) to yield pure compounds **5**. Yields are given on Table 4. Physical and spectroscopic data follow.

(*R*$_S$,2*R*,3*S*)-*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_2Cl_2); IR (film) ν 2960, 2930, 1636, 1457, 1382, 1080 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 22.6 (CH_2), 22.8 (CH_3), 35.8 (CH), 36.2 (CH_2), 38.3 (CH), 56.7 (C), 120.2 (CH_2), 132.4 (CH); LRMS (EI) m/z 173 (M^+-56, 17%), 124 (29), 110 (83), 95 (60), 57 (100); HRMS calcd for $C_8H_{15}NOS$ (M^+-C_4H_8) 173.0874, found 173.0886.

(*R*$_S$,2*R*,3*R*)-*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_2Cl_2); IR (film) ν 2960, 2930, 1636, 1475, 1386, 1262, 1092, 902 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 0.92-0.97 (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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.3 (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 $C_8H_{15}NOS$ (M^+-C_4H_8) 173.0874, found 173.0875.

(*R*$_S$,2*R*,3*S*)-*N*-(*tert*-Butanesulfinyl)-2-octyl-3-vinylaziridine (5bc).- Colourless oil; R_f 0.90 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -90 (*c* 0.50, CH_2Cl_2); IR (film) ν 2985, 2970, 2902, 1633, 1460, 1370, 1215, 1078, 901 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz, CH_3), 1.21 [9H, s, $(CH_3)_3$], 1.18-1.30 [12H, m, $(CH_2)_6$], 1.47-1.52 (2H, m, CH_2), 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, ddd, *J* = 17.2, 1.7, 0.6 Hz, CH), 5.61-5.80 (1H, m, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 22.9 (CH_3), 27.0 (CH_2), 27.3 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 36.1 (CH), 39.5 (CH), 56.8 (C), 120.3 (CH_2), 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 $C_{16}H_{31}NOS$ (M^+) 285.2126, found 285.2138.

(*R*$_S$,2*R*,3*R*)-*N*-(*tert*-Butanesulfinyl)-2-octyl-3-vinylaziridine (5bt).- Colourless oil; R_f 0.83

(hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -88 (*c* 0.40, CH_2Cl_2); IR (film) ν 2985, 2970, 1633, 1460, 1370, 1218, 1078, 920 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz, CH_3), 1.22-1.30 [21H, m, $(CH_2)_6$, $(CH_3)_3$], 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 (H, m, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 22.9 (CH_3), 27.0 (CH_2), 27.3 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 44.4 (CH), 49.6 (CH), 56.9 (C), 118.9 (CH_2), 135.1 (CH); LRMS (EI) *m/z* 180 (M^+-105, 4%), 172 (1), 160 (5), 126 (40), 113 (100), 105 (6); HRMS calcd for $C_{12}H_{23}NOS$ (M^+-C_4H_8) 229.1500, found 229.1508.

(*R*S,2*R*,3*S*)-2-Benzyl-*N*-(*tert*-butanesulfinyl)-3-vinylaziridine (5dc).- Pale yellow oil; R_f 0.79 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -34 (*c* 0.63, CH_2Cl_2); IR (film) ν 3015, 2925, 1640, 1425, 1310, 949 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.22 [9H, s, $(CH_3)_3$], 2.58 (1H, dd, *J* = 13.2, 7.0 Hz, CH), 2.82-2.86 (1H, m, CH_2), 3.30 (1H, dd, *J* = 7.3, 7.1 Hz, CH), 5.35-5.56 (2H, m, CH), 5.84 (1H, ddd, *J* = 17.3, 10.3, 7.7 Hz, CH), 7.20-7.35 (5H, m, CH); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.8 (CH_3), 33.7 (CH_2), 36.1 (CH), 40.0 (CH), 56.8 (C), 120.8 (CH_2), 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 $C_{15}H_{21}NOS$ (M^+) 263.1344, found 263.1354.

(*R*S,2*R*,3*R*)-2-Benzyl-*N*-(*tert*-butanesulfinyl)-3-vinylaziridine (5dt).- Yellow oil; R_f 0.72 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -28 (*c* 0.60 CH_2Cl_2); IR (film) ν 3015, 2925, 1640, 1425, 1310, 1245, 1102 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.27 [9H, s, $(CH_3)_3$], 2.76-2.85 (1H, m, CH), 2.86-3.02 (1H, m, CH_2), 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 22.9 (CH_3), 37.1 (CH_2), 44.1 (CH), 50.0 (CH), 57.1 (C), 119.4 (CH_2), 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 $C_{15}H_{21}NOS$ (M^+) 263.1344, found 263.1350.

(*R*S,2*R*,3*R*)-*N*-(*terct*-Butanesulfinyl)-2-(4-fluorophenyl)-3-vinylaziridine (5gt).- White solid; mp 64-66 ºC (hexane/CH_2Cl_2); R_f 0.65 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -20 (*c* 0.83 CH_2Cl_2); IR (film) ν 3050, 2963, 1648, 1490, 1369, 1080, 967 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.28 [9H, s, $(CH_3)_3$], 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 43.8 (CH), 54.2 (CH), 57.5 (C), 121.0 (CH_2), 121.9 (C), 128.0 (CH), 131.8 (CH), 133.0 (CH_2), 135.8 (C); LRMS (EI) *m/z* 210 (M^+-57, 22%), 208 (22), 129 (100); HRMS calcd for $C_{10}H_9FN$ (M^+-C_4H_9OS) 162.0719, found 162.0724.

(*R*S,2*R*,3*R*)-*N*-(*tert*-Butanesulfinyl)-2-(4-chlorophenyl)-3-vinylaziridine (5ht).- White solid; mp 67-69 ºC (hexane/CH_2Cl_2); R_f 0.60 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -19 (*c* 0.86, CH_2Cl_2); IR (film) ν 2963, 1645,

1595, 1475, 1220, 897 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.28 [9H, s, $(CH_3)_3$], 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 43.8 (CH), 54.2 (CH), 57.5 (C), 121.0 (CH_2), 127.6 (CH), 128.8 (CH), 133.0 (CH), 133.8 (C), 135.8 (C); LRMS (EI) *m/z* 207 (M^+-56, 6%), 144 (57), 129 (100), 115 (35), 91 (43), 77 (17); HRMS calcd for $C_{14}H_{18}ClNOS$ (M^+) 283.0798, found 283.0789.

(*R*S,2*R*,3*R*)-*N*-(*tert*-Butanesulfinyl)-2-(4-trifluoromethylphenyl)-3-vinylaziridine (5it).- Orange solid; mp 74-66 ºC (hexane/CH_2Cl_2); R_f 0.61 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ -28 (*c* 0.75, CH_2Cl_2); IR (film) ν 2958, 1648, 1452, 1327, 1300, 1245 cm^{-1}; ^1H RMN (300 MHz, $CDCl_3$) δ 1.29 [9H, s, $(CH_3)_3$], 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); ^{13}C RMN (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 43.6 (CH), 54.6 (CH), 57.6 (C), 121.2 (CH_2), 125.6 (CH), 125.7 (CH), 126.6 (CH), 132.9 (CH), 140.1 (C); LRMS (EI) *m/z* 207 (M^+ – 56, 6%), 144 (57), 129 (100), 115 (35), 91 (43), 77 (17); HRMS calcd for $C_{15}H_{18}F_3NOS$ (M^+) 317.1061, found 317.1064.

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Indium Mediate Allylation of *N-tert*-Butanesulfinyl Imines with 1,3-Dibromopropene: Stereoselective Synthesis of Aziridines

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