One-pot Synthesis of *N*-*tert*-Butanesulfinyl Imines and Homoallylamine Derivatives from Epoxides

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The reaction of epoxides with *tert*-butanesulfinamide in the presence of a Lewis acid, such as erbium triflate or boron trifluoride etherate, in THF as solvent, under microwave or thermal activation, produces *N*-*tert*-butanesulfinyl imines in reasonable yields. Aromatic and *gem*-disubstituted and trisubstituted alkyl epoxides performed better than the monoalkylsubstituted ones. After imine formation, a subsequent indium-promoted allylation can be performed in the same reaction flask in a single synthetic operation leading to homoallylamine derivatives in general with high yields.

Introduction

The stereoselective addition of nucleophiles to imines is probably the most effective way of accessing molecules with a nitrogen atom bonded to a stereogenic center.[1] Many of these chiral aminated compounds are both natural or synthetic molecules that can display biological activity. In addition to the potential biological activity, they could also be envisioned as key synthetic intermediates in the way to prepare more complex molecular architectures. Among the stereoselective methodologies, the catalytic enantioselective addition[2] rely on the use of both chiral Lewis acids,[3] which bind to the electrophile activating it toward nucleophilic attack, or chiral Lewis bases.[4] Although the development of catalytic enantioselective addition reactions is an ideally very attractive field, it has some limitations. For instance, some of the reported catalytic methods make use of large excess of reagents to ensure the turnover of the catalyst, and sometimes when the activation mode do not significantly increase the reaction speed, the non-catalytic addition causes a lower enantioselection. That is the reason why in the synthesis of complex organic molecules, including natural products, the stereoselective nucleophilic additions to imines are more commonly performed with stoichiometric amounts of chiral reagents, namely chiral imines (substrate control), including chiral auxiliaries.[5] Over the past decade chiral imines derived from *tert*-butanesulfinamide have been extensively used as electrophiles in a wide range of synthetic applications. The ready availability of both enantiomers of *tert*-butanesulfinamide in large-scale processes, the easy

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deprotection of the amine under mild acidic conditions, and a practical procedure for recycling the chiral auxiliary have undoubtedly contributed to the widespread use of this approach.[6] The synthesis of these aldimines in an enantioselective fashion was performed for the first time by García-Ruano, I. Fernández and co-workers from a *tert*-butanesulfinate ester derived from diacetone-D-glucose, *tert*-butanesulfinamide (**1**) being involved as reaction intermediate although no isolated in this process.[7] Since the development by the group of Ellman of a protocol for the large-scale synthesis of sulfinamide **1**,[8] these imines could be prepared in a straightforward manner by direct condensation of *tert*-butanesulfinamide (**1**) with carbonyl compounds **2** in the presence of a Lewis acid and a water scavenger. Thus, Ellman and co-workers reported in 1997 the first synthesis of *N*-*tert*-butanesulfinyl aldimines **3** following this strategy.[9] An excess of magnesium sulfate in the presence of a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS), using dichloromethane as solvent at room temperature, promoted the effective condensation of aldehydes and sulfinamide **1**.[10] Aldimines **3** were also prepared more efficiently using copper sulfate in dichloromethane and titanium tetraethoxide in THF as condensation reagents.[10] However, these reaction conditions were not effective for the synthesis of ketimines **4** which were exclusively prepared under the influence of titanium tetraethoxide in refluxing THF.[10,11] More recently, new methods for the synthesis of *N*-*tert*-butanesulfinyl imines **3** through a condensation of aldehydes **2** and *tert*-butanesulfinamide (**1**) under the influence of acids or bases have been reported.[12] Interestingly, the condensation can be also performed using pyrrolidine as an organocatalyst in the absence of acids or bases, the process taking place through iminium activation in the presence of 4Å molecular sieves,[13] or under microwave irradiation.[14] In this last case, an environmentally friendly synthesis of both aldimines **3** and more challenging ketimines **4** was achieved under solvent-free conditions in short reaction times (Scheme 1).

<Insert Scheme 1>

With the aim of widening the number of methodologies to access to chiral *N*-*tert*-butanesulfinyl imines, we studied their synthesis starting from epoxides instead of from carbonyl compounds in a one-pot process. Epoxides are of interest because they are either commercially available or easily prepared in an enantiomerically pure form from carbonyl compounds[15] and olefins.[16] In order to perform this transformation, the isomerization of the epoxide to the corresponding carbonyl compound should occur first, followed by condensation with *N*-*tert*-butanesulfinamide. In principle, a Lewis acid should be involved in both steps, being the condensation greatly facilitated working in the presence of a water scavenger. In addition, an indium-promoted allylation[17] of the corresponding imine with an allylic bromide would yield homoallylamine derivatives in a single synthetic operation. Thus, the multi-step transformation of epoxides to imines, or to homoallylamines, in a one-pot process, avoiding the workup and isolation of intermediates, the so-called pot-economy,[18] would be of great interest considering environmental sustainability, because the amounts of waste, solvents, labour and time are considerably minimized (Scheme 2).

<Insert Scheme 2>

Results and Discussion

For being successful in the proposed multi-step one-pot strategy depicted on Scheme 2, all transformations should take place in high chemical yields. Thus, in order to find the best reaction conditions to carry out the regioselective isomerization of epoxides **5** to carbonyl compounds **2**, we took styrene oxide (**5a**) as the model substrate and erbium triflate as the Lewis acid promoter catalyst. It has been reported that erbium triflate is a very efficient catalyst for the regioselective rearrangement of epoxides to carbonyl compounds, performing well on a wide range of substrates.[19] Although many assays were undertaken, only the most significant ones are compiled in Table 1. Thus, the treatment of styrene oxide (**5a**) with 0.5 mol % of erbium triflate in dichloromethane at 23 ºC for 20 min led to the formation of phenylacetaldehyde (**2a**) in 40% yield, remaining in the reaction mixture a 35% of the starting epoxide **5a**, meanwhile, partial decomposition of aldehyde **2a** through probably aldol condensation (around 25%) was also observed (Table 1, entry 1). When the isomerization was performed using 1 mol % of the erbium salt, almost total conversion was observed, increasing both the yield of the aldehyde **2a** (64%) and the aldol condensation products (34%) (Table 1, entry 2). Isomerization in THF proceeded more slowly than in dichloromethane at 23 ºC, because after 20 min only 6% of aldehyde **2a** was formed (Table 1, entry 3). However, prolonged reaction times (8 h) at the same temperature led to phenylacetaldehyde (**2a**) in higher yield (84%), taking place the decomposition of the aldehyde in THF in a lesser extension compared to dichloromethane (Table 1, entry 4). In addition, reaction times can be shortened under microwave irradiation, and the amount of the desired aldehyde **2a** being tightly dependant on the temperature and the reaction time (Table 1, entries 5 and 6). Importantly, the isomerization in THF under thermal conditions at 50 ºC led after 45 min to the aldehyde **2a** in 78% yield (Table 1, entry 7), a rather similar result than (This result was rather similar to the one obtained when the process was performed under microwave irradiation) performing the process under microwave irradiation. Other Lewis and Brønsted acids led to poorer results under similar reaction conditions (Table 1, entries 8-11) except boron trifluoride etherate, which performed quite well to produce phenylacetaldehyde (**2a**) in 78% yield (Table 1, entry 12).

<Insert Table 1>

Isomerization of *gem*-dialkyl and trialkyl substituted expoxides takes place under the same reaction conditions as for aromatic epoxides. However, conversion of monalkyl substituted epoxides into the corresponding carbonyl compounds is more challenging. Thus, taking 1-octene oxide (**5j**) as a model compound and erbium triflate as the catalyst, we tried first to find the best reaction conditions for this transformation to proceed. The reaction did not take place in dichloromethane at 45 ºC for 45 min under microwave irradiation, the starting epoxide **5j** remaining unaltered (Table 2, entry 1). On the contrary, total conversion was observed working in THF at 50 ºC after 45 min, but expected octanal (**2j**) was formed in only 26% yield (Table 2, entry 2). Yields were improved by working at higher temperature in shorter reaction times (Table 2, entries 3-6). Isomerization also occurred effectively under thermal conditions (Table 2, entries 7-9). The highest yield was observed working in a high pressure tube at 150 ºC for 10 min (Table 2, entry 9). Unfortunately, other Lewis acids ($InCl_3$, $InBr_3$, $AlCl_3$, $BF_3{\cdot}OEt_2$) were not effective for carrying out this transformation.

<Insert Table 2>

With the optimized reaction conditions of the isomerization step in hand, we studied next the one-pot two-step process for the synthesis of *N*-*tert*-butanesulfinyl imines **3** from epoxides **5**. Taking again styrene oxide (**5a**) as the model compound and erbium triflate as Lewis acid, we found that isomerization did not take place in appreciable extension when sulfinamide **1** was also present in the reaction medium. It seems that **1** inhibited the action of erbium triflate. For that reason, after isomerization of epoxide **5a** to aldehyde **2a**, *tert*-butanesulfinamide **1** was added to the reaction flask along with the corresponding reagents for the condensation step. Thus, performing first the isomerization in dichloromethane at room temperature for 20 min, followed by the successive addition of sulfinamide **1**, a catalytic amount of pyridinium *para*-toluenesulfonate (PPTS) and 2 equivalents of magnesium sulfate, and further reaction at the same temperature for 12 h, the expected *N*-*tert*-butanesulfinyl imine **3a** was obtained in 44% yield (Table 3, entry 1). When isomerization was carried out in 1,2-dichloroethane first, followed by condensation of the resulting aldehyde **2a** with sulfinamide **1**, in the presence of anhydrous magnesium sulfate under microwave irradiation at 60 ºC for 20 min, the imine **3a** was obtained in a lower yield (Table 3, entry 2). Switching to THF as solvent, and performing the isomerization at 23 ºC for 8 h, and the condensation at the same temperature for 48 h with magnesium sulphate, the imine **3a** was formed in only 24% yield (Table 3, entry 3). However, yields were considerably improved when the same combination of reagents in THF was submitted to microwave irradiation (Table 3, entries 4 and 5). Changing magnesium sulphate to titanium tetraethoxide as a condensation promoter, led to the expected imine **3a** in a similar yield (Table 3, entry 6). On the other hand, and performing the isomerization at 50 ºC for 45 min, and the condensation at room temperature with titanium tetraethoxide in THF for 12 h, the expected imine **3a** was formed in 46% yield (Table 3, entry 7), similar to the yields found in other processes performed in THF.

<Insert Table 3>

Although erbium triflate had been shown to be a little bit more efficient than boron trifluoride etherate in the isomerization of epoxide **5a**, we studied also the one-pot transformation of **5a** into aldimine **3a** involving this boron compound. Importantly, in this case the isomerization step was not affected by the presence of sulfinamide **1**, performing all the assays in THF with 5 mol % of boron trifluoride etherate with all the reagents in the reaction flask at the beginning of the experiment, that representing an advantage over the erbium triflate methodology. Thus, imine **3a** was formed in only 39% yield when 3Å MS were used as water scavenger at 50 ºC after 4 h (Table 4, entry 1). Longer reaction times (12 h) under the same reaction conditions led to a quite good 76% yield, considering this two-step process (Table 4, entry 2). Poorer yields were obtained when working at lower temperatures (23 ºC) or in the absence of MS (Table 4, entries 3 and 4). All these reactions were performed with an excess of starting epoxide **5a** (2:1 epoxide **5a**/sulfinamide **1**), because when almost stoichiometric amounts of the epoxide **5a** and the sulfinimide **1** were used, yields were considerably lower (Table 4, compare entries 2 and 5).

<Insert Table 4>

The substrate scope was then studied under the optimized reaction conditions. We found that for aromatic epoxides **5a**-**d**, method B led to higher yields than method A (Table 5, entries 1-8). Starting epoxides **5a** and **5b** were commercially available, meanwhile compound **5c** was prepared by epoxidation of *para*-acetoxystyrene with MCPBA, and 2-naphthalenecarbaldehyde was the precursor of 2-naphthyloxyrane (**5d**) upon epoxidation with chloroiodomethane/*n*-butyllithim.[20] We also observed that yields were slightly improved when the isomerization step with the erbium salt was performed under microwave irradiation (Table 5, entries 1, 5 and 11). Interestingly, methods A and B led to different *N*-*tert*-butanesulfinyl imines starting from epoxide **5c**, observing deacetilation when the condensation step was carried out in the presence of titanium tetraethoxide to give imine **3c'** (Table 5, entry 5). Dialkyl substituted epoxides **5e**-**g** performed well under both methods, leading commercially available highly volative isobutylene oxide **5e** to the highest yields (Table 5, entries 9 and 10). Epoxides **5f** and **5g** were prepared from 6-undecanone and (-)-menthone, respectively under the same reaction conditions as for **5d**.[20] Importantly, enantiomerically pure epoxide **5g** derived from (-)-menthone led to two diastereomeric aldimines **3g** and **3g'**, indicating that the isomerization step is not stereoselective, a planar tertiary carbocation being probably involved as reaction intermediate. In addition, the major diastereomer obtained when the isomerization is performed with the erbium salt (method A) seems to be the kinetic product **3g**, and the thermodinamically more stable **3g'** is the major component of the reaction mixture working in the presence of borono trifluoride (method B) (Table 5, entries 13 and 14). Surprisingly, commercially available trialkyl substituted (+)-limonene oxide **5h**, which is supllied as a mixture of *cis* and *trans* isomers, led to a mixture of *N*-*tert*-butanesulfinyl imines when applying modified method A (^{1}H-NMR of the reaction crude), but only the cyclohexenone derivative **3h** was isolated and characterized. The condensation step was carried out at 60 ºC instead of 23 ºC, because formation of *N*-*tert*-butanesulfinyl ketimines did not proceeded at room temperature in the presence of titanium tetraethoxide (Table 5, entry 15). However, ketimine **3h** was not obtained in any extension under the reaction conditions of method B, because condensation of *tert*-butanesulfinamide (**1**) with 3-isopropylene-6-methylcyclohexanone, the major product obtained after isomerization (>80%),[20] did not take place (Table 5, entry 16). The Lewis acid--pinene oxide **5i** to campholenic aldehyde[21] has been widely studied because these products are of interest in the -pinene oxide **5i** into the aldimine derived from campholenic aldehyde **3i** proceeded in a higher yield with method A (Table 5, entry 17), due probably to a less selective isomerization of the starting epoxide **5i** with boron trifluoride as Lewis acid (method B) (Table 5, entry 18). In both cases, and because of the formed stereogenic center of the cyclopentene ring, aldimine **3i** was obtained as a 3:1 mixture of diastereoisomers. Finally, the transformation of monoalkyl substituted epoxide **5j** into aldimine of octanal **3j** was only possible using modified method A (isomerization step was carried out under microwave irradiation a 80 ºC, 100 W, 7 mim), because boron trifluoride was not an effective reagent to promote the selective isomerization leading to the aldehyde intermediate (Table 5, entries 19 and 20).

<Insert Table 5>

We have been particularly interested in the indium-mediated allylation of *N-tert*-butanesulfinyl imines which produces homoallylamine derivatives in a highly diastereoselective fashion, and have also reported the aminoallylation of aldehydes with *tert*-butanesulfinamides and allylic bromides,[17b,c] we also decided to explore the one-pot transformation of starting epoxides into homoallylamine derivatives by adding allylic bromides to the reaction media in the presence of indium metal. In this study we compared also the isomerization step with erbium trifluoride under microwave irradiation (method A), with the boron trifluoride etherate under thermal conditions (method B). In addition, indium metal was in the reaction flask from the beginning in method B, meanwhile it was added after the isomerization step along with sulfinamide **1** and titanium tetraethoxide in method A, stirring all the components for 1 additional hour at room temperature in this last case. Finally, and after addition of the corresponding allylic bromide, the reaction mixture was heated at 60 ºC for 5 hours in both methodologies. We were please to find out that the expected homoallylamine derivatives **6** were obtained in reasonable yields (Table 6). Notably, sometimes the isolated yield of homoallylamine derivative **6** exceeded the yield of the corresponding imine precursor **3** (compare Table 5, entry 1 and Table 6, entry 1); the more efficient purification by column chromatography of compounds **6**, which are more robust than imines **3**, could be the only explanation for these experimental results. Regarding facial selectivity, the allylation step proceeded with high diastereoselectivity (>95:5 dr), taking place almost exclusively a *Si*-face attack of the allylic moiety to imines **3** with *R*-configuration at the sulfur atom. As a consequence of the previously commented lack of stereoselectivity -pinene oxide **5i** into campholenic aldehyde, compound **6i** was also obtained as 3:1 mixture of diastereoisomers, concerning the stereogenic center of the cyclopentene ring (Table 6, entry 11). As a proof of synthetic usefulness of these methodologies, *para*-acetoxystyrene **5c** was transformed into homoallylamine derivative **6c** (Table 6, entry 5), which could be an advanced intermediate in the synthesis of marine alkaloid aphanorphine (Figure 1).[22]

<Insert Table 6>

<Insert Figure 1>

Conclusions

In summary, one-pot reactions of commercially or easily available epoxides **5** and *tert*-butanesulfinamide **1** in the presence of Lewis acids were found to afford *N-tert*-butanesulfinyl imines **3** in reasonable yields. In addition, enantioenriched homoallylamine derivatives **6** could be also produced in high yields from the same precursors, when after imine formation, a subsequent indium-mediated allylation with allylic bromides is performed in the same reaction flask. The here described methodologies are a greener chemistry approach to the previous reported synthesis of both *N-tert*-butanesulfinyl imines **3**[6] and homoallylamines **6**,[6,17] by reducing the number of synthetic operations, representing examples of the so-called pot-economy.

Experimental Section

General: (R_S)-*tert*-Butanesulfinamide was a gift of Medalchemy (> 99% ee by chiral HPLC on a Chiracel AS column, 90:10 n-hexane/*i*-PrOH, 1.2 mL/min, λ=222 nm). TLC was performed on silica gel 60 F_{254}, using aluminum plates and visualized with phosphomolybdic acid (PMA) stain. Flash chromatography was carried out on handpacked columns of silica gel 60 (230- 400 mesh). Gas chromatographic analyses (GC) were carried out in a Agilent Technologies 6890N instrument equipped with a flame ionization detector and a 30.0 m capillary column (0.25 mm diam, 0.25 μm film thickness), using nitrogen (1.4 ml/min) as carrier gas, Tinjector = 275°C, Tcolumn = 60°C (3 min) and 60-270°C (15 °C/min). Melting points are uncorrected. Optical rotations were measured using a polarimeter with a thermally jacketted 5 cm cell at approximately 23 ºC and concentrations (*c*) are given in g/100 mL. Infrared analyses were performed with a spectrophotometer equipped with an ATR component; wavenumbers are given in cm^{-1}. Low-resolution mass spectra (EI) were obtained at 70 eV; and fragment ions in *m/z* with relative intensities (%) in parentheses. High-resolution mass spectra (HRMS) were also carried out in the electron impact mode (EI) at 70 eV and and on an 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. ^{1}H NMR spectra were recorded at 300 or 400 MHz for ^{1}H NMR and 75 or 100 MHz for ^{13}C NMR, using $CDCl_3$ as the solvent and TMS as internal standard (0.00 ppm). The data is being reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad signal, coupling constant(s) in Hz, integration. ^{13}C NMR spectra were recorded with ^{1}H-decoupling at 100 MHz and referenced to $CDCl_3$ at 77.16 ppm. DEPT-135 experiments were performed to assign CH, CH_2 and CH_3. All reactions requiring anhydrous conditions were performed in oven dried glassware under argon. Otherwise indicated, all commercially available chemicals were purchased from Acros or Sigma-Aldrich and used without purification.

General procedure for the synthesis of *N*-*tert*-butanesulfinyl imines 3 from epoxides 5 (Method A): A heterogeneous mixture of the corresponding epoxide **5** (1.0 mmol) and erbium triflate (0.0063 g, 0.01 mmol) in THF (3.0 mL) was stirred at 50 ºC for 45 min. Then, the reaction mixture was cooled down to 23 ºC, and *tert*-butanesulfinamide (**1**, 0.061 mg, 0.5 mmol) and titanium tetraethoxide (0.274 g, 0.251 mL, 1.2 mmol) were added. The resulting mixture was stirred for 12 additional h at the same temperature, and after that, quenched with brine (0.5 mL), and diluted with EtOAc (15 mL). The resulting suspension was filtered through a short path of Celite and concentrated Then, the reaction mixture was filtered through a short path of Celite and the solvent was evaporated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to yield pure compounds **3**. Yields for compounds **3** are given on Table 5. Physical and spectroscopic data follow.

(R_S)-*N*-(*tert*-Butanesulfinyl)-2-phenylethanimine (3a):[23] Colourless oil; $[\alpha]_D^{23}$ -194 (*c* 1.01, CH_2Cl_2); R_f 0.40 (hexane/EtOAc: 4/1); IR ν (film) 3028, 2957, 2869, 1619, 1582, 1496, 1454, 1363, 1180, 1079 cm^{-1}; δ_H 8.13 (t, *J* = 5.2 Hz, 1H), 7.37-7.19 (m, 5H), 3.89-3.75 (m, 2H), 1.18 (s, 9H); δ_C 167.54 (CH), 134.89 (C), 129.30, 128.94,

127.23 (CH), 56.98 (C), 42.74 (CH_2), 22.49 (CH_3); LRMS (EI) *m/z* 117 (M^+-C_4H_8, 100%), 116 (38), 90 (41), 89 (28), 63 (12), 51 (15).

(R_S)-*N*-(*tert*-Butanesulfinyl)-2-(4-chlorophenyl)ethanimine (3b): Colourless oil; $[\alpha]_D^{23}$ -92 (*c* 1.04, CH_2Cl_2); R_f 0.30 (hexane/EtOAc: 4/1); IR ν (film) 2962, 2864, 1707, 1619, 1491, 1412, 1362, 1175, 1089, 1014, 908, 823, 730 cm^{-1}; δ_H 8.10 (t, *J* = 5.1 Hz, 1H), 7.37-7.28 (m, 2H), 7.21-7.11 (m, 2H), 3.87-3.73 (m, 2H), 1.18 (s, 9H); δ_C 166.92 (CH), 133.34, 133.19 (C), 130.67, 129.07 (CH), 57.08 (C), 41.96 (CH_2), 22.48 (CH_3); LRMS (EI) *m/z* 257 (M^+, 1%), 201 (24), 154 (15), 138 (32), 126 (36), 71 (15), 69 (16), 57 (100), 55 (18), 43 (39), 41(25); HRMS (ESI): Calculated for $C_8H_8Cl^{35}NOS$ (M^+-C_4H_8) 201.0015, found 201.0011.

(R_S)-2-(4-Acetoxyphenyl)-*N*-(*tert*-butanesulfinyl)ethanimine (3c): Yellow oil; $[\alpha]_D^{23}$ -63 (*c* 1.04, CH_2Cl_2); R_f 0.60 (hexane/EtOAc: 1/1); IR ν (film) 2958, 2864, 1757, 1620, 1506, 1367, 1191, 1166, 1078, 1013, 910, 849, 729 cm^{-1}; δ_H 8.12 (t, *J* = 5.2 Hz, 1H), 7.26-7.21 (m, 2H), 7.10-7.03 (m, 2H), 3.90-3.75 (m, 2H), 2.30 (s, 3H), 1.19 (s, 9H); δ_C 169.51 (C), 167.16 (CH), 149.83, 132.44 (C), 130.28, 122.05 (CH), 56.99 (C), 41.99 (CH_2), 22.46, 21.19 (CH_3); LRMS (EI) *m/z* 225 (M^+-C_4H_8, 167), 183 (15), 135 (28), 133 (10), 121 (21), 120 (61), 107 (37), 94 (17), 77 (11), 57 (100), 43 (40), 41 (20); HRMS (ESI): Calculated for $C_{10}H_{11}NO_3S$ (M^+-C_4H_8) 225.0460, found 225.0453.

(R_S)-*N*-(*tert*-Butanesulfinyl)-2-(4-hydroxyphenyl)ethanimine (3c'): Yellow solid; mp 101-102 °C (hexane/CH_2Cl_2); $[\alpha]_D^{23}$ -22 (*c* 1.07, CH_2Cl_2); R_f 0.52 (hexane/EtOAc: 1/1); IR ν (KBr) 3180, 2957, 2918, 1762, 1620, 1594, 1517, 1459, 1365, 1267, 1193, 1052, 832 cm^{-1}; δ_H 8.09 (t, *J* = 5.3 Hz, 1H), 7.34 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.81-3.67 (m, 2H), 1.21 (s, 9H); δ_C 168.76 (CH), 155.70 (C), 130.32 (CH), 125.81 (C), 116.03 (CH), 57.37 (C), 41.97 (CH_2), 22.51 (CH_3); LRMS (EI) *m/z* 183 (M^+-C_4H_8, 70%), 169 (28), 135 (28), 121 (35), 120 (84), 108 (11), 107 (46), 94 (27), 77 (18), 57 (100), 41 (22); HRMS (ESI): Calculated for $C_8H_9NO_2S$ (M^+-C_4H_8) 183.0354, found 183.0350.

(R_S)-*N*-(*tert*-Butanesulfinyl)-2-(2-naphthyl)ethanimine (3d): Yellow oil; $[\alpha]_D^{23}$ -140 (*c* 1.02, CH_2Cl_2); R_f 0.33 (hexane/EtOAc: 4/1); IR ν (film) 3054, 2961, 2929, 1618, 1510, 1470, 1451, 1363, 1266, 1182, 1083, 857, 817, 734 cm^{-1}; δ_H 8.22 (t, *J* = 5.2 Hz, 1H), 7.86-7.77 (m, 3H), 7.69 (s, 1H), 7.54-7.44 (m, 2H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.07-3.92 (m, 2H), 1.20 (s, 9H); δ_C 167.43 (CH), 133.69, 132.54, 132.36 (C), 128.64, 127.97, 127.80, 127.68, 127.35, 126.41, 125.99 (CH), 57.04 (C), 42.83 (CH_2), 22.52 (CH_3); LRMS (EI) *m/z* 273 (M^+-C_4H_8, 1%), 218 (14), 217 (99), 169 (64), 168 (36), 167 (32), 166 (13), 155 (14), 154 (73), 142 (27), 141 (62), 140 (10), 139 (23), 128 (28), 115 (37), 57 (100), 41 (18); HRMS (ESI): Calculated for $C_{12}H_{11}NOS$ (M^+-C_4H_8) 217.0561, found 217.0551.

(R_S)-*N*-(*tert*-Butanesulfinyl)-2-methylpropanimine (3e):[23] Colourless oil; $[\alpha]_D^{23}$ -229 (*c* 1.01, CH_2Cl_2); R_f 0.49 (hexane/EtOAc: 4/1); IR ν (film) 2967, 2926, 2868, 1620, 1458, 1363, 1165, 1084 cm^{-1}; δ_H 7.99 (d, *J* = 4.4

Hz, 1H), 2.72 (m, 1H), 1.19 (s, 9H), 1.18 (d, *J* = 1.6 Hz, 3H), 1.16 (d, *J* = 1.5 Hz, 3H); δ_C 173.64 (CH), 56.53 (C), 34.93 (CH), 22.35, 18.96 (CH_3); LRMS (EI) *m/z* 175 (M^+-C_4H_8, 2%), 119 (20), 57 (100), 56 (52), 55 (11), 43 (12), 42 (16), 41 (82).

(*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-2-pentylheptan-1-imine (3f): Colourless oil; $[\alpha]_D^{23}$ -170 (*c* 1.07, CH_2Cl_2); R_f 0.69 (hexane/EtOAc: 4/1); IR ν (film) 2955, 2926, 2858, 1617, 1458, 1362, 1087, 780 cm^{-1}; δ_H 7.89 (d, *J* = 6.4 Hz, 1H), 2.57-2.43 (m, 1H), 1.67-1.43 (m, 4H), 1.36-1.23 (m, 12H), 1.21 (s, 9H), 0.93-0.81 (m, 6H); δ_C 173.63 (CH), 56.63 (C), 45.87 (CH), 32.28, 32.22, 32.03, 31.94, 27.03, 26.96, 22.63 (CH_2), 22.56, 14.15, 14.12 (CH_3); LRMS (EI) *m/z* 232 (M^+-C_4H_8, 3%), 231 (16), 149 (9) 97 (19), 71 (11), 70 (20), 69 (13), 61 (16), 57 (47), 55 (15), 45 (18), 43 (100), 41 (17); HRMS (ESI): Calculated for $C_{12}H_{25}NOS$ (M^+-C_4H_8) 231.1657, found 231.1658.

(*R*$_S$,1*S*,2*S*,5*R*)-*N*-(*tert*-Butanesulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g) + (*R*$_S$,1*R*,2*S*,5*R*)-*N*-(*tert*-Butanesulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g'): Mixture of diastereoisomers; colourless oil; R_f 0.64 (hexane/EtOAc: 4/1); IR ν (film) 2953, 2925, 2870, 1727, 1617, 1456, 1387, 1365, 1181, 1086, 732, 688 cm^{-1}; LRMS (EI) *m/z* 215 (M^+-C_4H_8, 20%), 167 (11), 152 (19), 151(13), 149(16), 137 (12), 97 (11), 95 (23), 83 (17), 81 (17), 77 (11), 71 (17), 70 (21), 69 (20), 61 (15), 57 (69), 55 (25), 45 (20), 44 (16), 43 (100), 42 (12), 41 (28); HRMS (ESI): Calculated for $C_{11}H_{21}NO_2S$ (M^+-C_4H_8) 215.1344, found 215.1347.

(*R*$_S$,1*S*,2*S*,5*R*)-*N*-(*tert*-Butanesulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g): δ_H 8.24 (d, *J* = 7.0 Hz, 1H), 3.06 (dd, *J* = 7.0, 3.8 Hz, 1H), 1.95-1.77 (m, 2H), 1.76-1.56 (m, 3H), 1.49-1.25 (m, 3H), 1.21 (s, 9H), 1.17-0.96 (m, 1H), 0.93-0.88 (m, 6H), 0.86 (d, *J* = 6.4 Hz, 3H); δ_C 172.52 (CH), 56.73 (C), 46.96, 43.17 (CH), 39.75, 35.50 (CH_2), 30.50, 27.70 (CH), 26.38 (CH_2), 22.76, 22.61, 21.48, 20.86 (CH_3).

(*R*$_S$,1*R*,2*S*,5*R*)-*N*-(*tert*-Butanesulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g'): δ_H 7.88 (d, *J* = 7.4 Hz, 1H), 2.53 (tdd, *J* = 11.4, 7.5, 3.7 Hz, 1H), 1.97-1.53 (m, 3H), 1.50-1.22 (m, 3H), 1.19 (s, 9H), 1.16-0.97 (m, 2H), 0.94-0.88 (m, 6H), 0.78 (d, *J* = 6.9 Hz, 3H); δ_C 173.19 (CH), 56.67 (C), 47.58, 45.39 (CH), 39.07, 34.72 (CH_2), 32.10, 29.28 (CH), 24.12 (CH_2), 22.54, 22.48, 21.28, 15.90 (CH_3).

(*R*$_S$,2*R*,5*R*)-*N*-(*tert*-Butanesulfinyl)-5-isopropenyl-2-methylcyclohexanimine (3h): Colourless oil; $[\alpha]_D^{23}$ -93 (*c* 0.91, CH_2Cl_2); R_f 0.56 (hexane/EtOAc: 4/1); IR ν (film) 2962, 2927, 2860, 1713, 1619, 1455, 1362, 1183, 1068, 888 cm^{-1}; δ_H 4.78-4.71 (m, 2H), 3.66-3.57 (m, 1H), 2.42-2.26 (m, 2H), 2.15-2.04 (m, 1H), 2.00-1.80 (m, 2H), 1.75 (s, 3H), 1.63-1.47 (m, 1H), 1.45-1.30 (m, 1H), 1.24 (s, 9H), 1.09 (d, *J* = 6.3 Hz, 3H); δ_C 189.77, 147.93 (C), 109.64 (CH_2), 56.46 (C), 47.29, 43.97 (CH), 39.54, 36.34, 31.10 (CH_2), 22.29, 20.87, 16.43 (CH_3); LRMS (EI) *m/z* 199 (M^+-C_4H_8, 39%), 151 (11), 149 (19), 136 (14), 123 (10), 111 (11), 109 (20), 107 (11), 97 (16), 95 (21), 93 (14), 85 (14), 83 (16), 82 (12), 81 (19), 71 (23), 70 (21), 69 (23), 67 (21), 61 (13), 57 (62), 55 (30), 45 (16), 44 (11), 43 (100), 42 (10), 41 (37); HRMS (ESI): Calculated for $C_{10}H_{17}NOS$ (M^+-C_4H_8) 199.1031, found 199.1029.

(R_S)-*N*-(*tert*-Butanesulfinyl)-2-(2,2,3-trimethylcyclopent-3-enyl)ethanimine (3i): Mixture of diastereoisomers (3:1); colourless oil; R_f 0.56 (hexane/EtOAc: 4/1); IR ν (film) 2955, 2867, 1620, 1458, 1362, 1186, 1088, 1014, 939, 797, 681 cm^{-1}; δ_H 8.16-8.03 (m, 1H), 5.26-5.21 (m, 1H), 2.72-2.60 (m, 1H), 2.57-2.43 (m, 1H), 2.40-2.27 (m, 1H), 2.25-2.08 (m, 1H), 1.97-1.84 (m, 1H), 1.64-1.61 (m, 3H), 1.21 (s, 9H), 1.02 (s, 3H), 0.84 (s, 3H); LRMS (EI) *m/z* 256 (M^++1, 8%), 200 (22), 199 (23), 149 (26), 135 (32), 133 (34), 121 (14), 109 (48), 108 (58), 107 (26), 95 (20), 93 (43), 91 (27), 81 (15), 79 (16), 71 (15), 70 (17), 67 (16), 57 (86), 55 (20), 45 (15), 43 (100), 41 (36); HRMS (ESI): Calculated for $C_{10}H_{16}NOS$ (M^+-C_4H_8) 198.0953, found 198.0951.

Major isomer: δ_C 170.01 (CH), 148.27 (C), 121.61 (CH), 56.65, 47.18 (C), 47.14 (CH), 37.43, 35.78 (CH_2), 25.83, 22.51, 20.07, 12.74 (CH_3).

Minor isomer: δ_C 169.84 (CH), 148.15 (C), 121.69 (CH), 56.75 (C), 47.18 (CH), 46.99, 37.34 (CH_2), 35.66, 25.83, 22.51, 20.12, 12.74 (CH_3).

General procedure for the synthesis of *N*-*tert*-butanesulfinyl imines 3 from epoxides 5 (modified Method A): A heterogeneous mixture of the corresponding epoxide **5** (1.0 mmol) and erbium triflate (0.0063 g, 0.01 mmol) in THF (3.0 mL) was irradiated for 45 min at 40 W power and 30 ºC (7 min at 100 W power and 80 ºC for epoxide **5j**). Then, the reaction mixture was cooled down to 23 ºC, and *tert*-butanesulfinamide (**1**, 0.061 mg, 0.5 mmol) and titanium tetraethoxide (0.274 g, 0.251 mL, 1.2 mmol) were added. The resulting mixture was stirred at the same temperature for 12 additional h, and after that quenched with brine (0.5 mL), and diluted with EtOAc (15 mL). The resulting suspension was filtered through a short path of Celite and concentrated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to yield pure compounds **3a**, **3c'**, **3f** and **3j**. Yields for these compounds **3** are given on Table 5. Physical and spectroscopic for compound **3j** follow; for the rest of compounds **3** the corresponding data were given above.

(R_S)-*N*-(*tert*-Butanesulfinyl)octan-1-imine (3j):[24] Colourless oil; $[\alpha]_D^{23}$ -207 (*c* 1.02, CH_2Cl_2); R_f 0.56 (hexane/EtOAc: 4/1); IR ν (film) 2952, 2925, 2857, 1621, 1458, 1363, 1186, 1086, 675 cm^{-1}; δ_H 8.07 (t, *J* = 4.8 Hz, 1H), 2.51 (td, *J* = 7.4, 4.8 Hz, 2H), 1.70-1.55 (m, 2H), 1.39-1.24 (m, 8H), 1.20 (s, 9H), 0.91-0.85 (m, 3H); δ_C 169.90 (CH), 56.57 (C), 36.21, 31.76, 29.28, 29.09, 25.60, 22.67 (CH_2), 22.42, 14.14 (CH_3); LRMS (EI) *m/z* 175 (M^+-C_4H_8, 19%), 149 (18), 129 (11), 127 (11), 115 (10), 111 (28), 109 (13), 105 (12), 99 (10), 97 (26), 95 (17), 91 (18), 87 (75), 85 (44), 83 (25), 81 (20), 73 (47), 71 (67), 70 (25), 69 (50), 67 (21), 57 (100), 56 (29), 55 (74), 45 (21), 44 (29), 43 (72), 41 (53).

General procedure for the synthesis of *N*-*tert*-butanesulfinyl imines 3 from epoxides 5 (Method B): A heterogeneous mixture of the corresponding epoxide **5** (1.0 mmol), *tert*-butanesulfinamide (**1**, 0.061 mg, 0.5 mmol), boron trifluoride etherate (0.0071 g, 11.8 µL, 0.05 mmol) and 3Å MS (400 mg) in THF (3.0 mL) was stirred at 50 ºC for 12 h. Then, the reaction mixture was cooled down to 23 ºC, diluted with EtOAc (15 mL) and the liquid filtered off. The liquid phase was hydrolyzed with water (10 mL), extracted with EtOAc (3×15 mL), dried with anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography

(hexane/EtOAc) to yield pure compounds **3**. Yields for these compounds are given on Table 5. Physical and spectroscopic were also given above.

General procedure for the synthesis of homoallylamine derivatives 6 from epoxides 5 (Method A): A heterogeneous mixture of the corresponding epoxide **5** (1.0 mmol) and erbium triflate (0.0063 g, 0.01 mmol) in THF (3.0 mL) was irradiated for 45 min at 40 W power and 30 ºC (7 min at 100 W power and 80 ºC for epoxide **5j**). Then, the reaction mixture was cooled down to 23 ºC, and *tert*-butanesulfinamide (**1**, 0.061 mg, 0.5 mmol), indium metal (0.115 g, 1.0 mmol), and titanium tetraethoxide (0.274 g, 0.251 mL, 1.2 mmol) were added. The resulting mixture was stirred at the same temperature for one additional h. Then allyl bromide (0.182 g, 0.130 mL, 1.5 mmol) was added and the reaction mixture heated for 5 h at 60 ºC. Then, the mixture was cooled down to room temperature, quenched with brine (0.1 mL), and diluted with EtOAc (15 mL). The resulting suspension was filtered through a short path of Celite and concentrated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to yield pure compounds **6**. Yields for these compounds are given on Table 6. Physical and spectroscopic follow.

(R_S,2*S*)-*N*-(*tert*-Butanesulfinyl)-1-phenylpent-4-en-2-amine (6a):[17b] Yellow wax; $[\alpha]_D^{23}$ -31 (*c* 1.07, CH_2Cl_2); R_f 0.40 (hexane/EtOAc: 1/1); IR ν (film) 3403, 3127, 2926, 1638, 1599, 1455, 1362, 1175, 1051, 907, 745, 698 cm^{-1}; δ_H 7.37-7.15 (m, 5H), 5.91-5.73 (m, 1H), 5.21 (s, 1H), 5.19-5.14 (m, 1H), 3.64-3.51 (m, 1H), 3.32 (d, *J* = 5.8 Hz, 1H), 2.87 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.75 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.48-2.25 (m, 2H), 1.11 (s, 9H); δ_C 138.27 (C), 134.24, 129.65, 128.41, 126.47 (CH), 119.20 (CH_2), 56.47 (CH), 55.91 (C), 41.64, 39.84 (CH_2), 22.58 (CH_3); LRMS (EI) *m/z* 209 (M^+-C_4H_8, 3%), 118 (100), 104 (27), 102 (11), 92 (8), 91 (41), 65 (8).

(R_S,2*S*)-*N*-(*tert*-Butanesulfinyl)-1-(4-chlorophenyl)pent-4-en-2-amine (6b): Yellow wax; $[\alpha]_D^{23}$ -25 (*c* 1.03, CH_2Cl_2); R_f 0.33 (hexane/EtOAc: 1/1); IR ν (film) 2924, 1638, 1492, 1408, 1362, 1175, 1091, 1052, 1015, 914, 834, 799, 731 cm^{-1}; δ_H 7.30-7.23 (m, 2H), 7.18-7.07 (m, 2H), 5.90-5.72 (m, 1H), 5.24-5.13 (m, 2H), 3.55 (m, 1H), 3.31 (d, *J* = 5.7 Hz, 1H), 2.84 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.74 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.48-2.24 (m, 2H), 1.12 (s, 9H); δ_C 136.82 (C), 134.01 (CH), 132.32 (C), 131.03, 128.55 (CH), 119.45 (CH_2), 56.27 (CH), 56.00 (C), 41.01, 39.81 (CH_2), 22.63 (CH_3); LRMS (EI) *m/z* 244 (M^+-C_4H_8, 3%), 243 (23), 202 (11), 201 (18), 127 (12), 125 (37), 118 (100), 57 (42), 41 (13); HRMS (ESI): Calculated for $C_{11}H_{14}Cl^{35}NOS$ (M^+-C_4H_8) 243.0485, found 243.0487.

(R_S,2*S*)-*N*-(*tert*-Butanesulfinyl)-1-(2-naphthyl)pent-4-en-2-amine (6d): Orange wax; $[\alpha]_D^{23}$ -28 (*c* 1.07, CH_2Cl_2); R_f 0.36 (hexane/EtOAc: 1/1); IR ν (film) 2925, 1737, 1638, 1598, 1510, 1363, 1239, 1046, 918, 815, 749 cm^{-1}; δ_H 7.88-7.74 (m, 3H), 7.64 (s, 1H), 7.50-7.42 (m, 2H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.92-5.76 (m, 1H), 5.22 (s, 1H), 5.20-5.15 (m, 1H), 3.76-3.61 (m, 1H), 3.39 (d, *J* = 5.3 Hz, 1H), 3.06 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.91 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.54-2.25 (m, 2H), 1.11 (s, 9H); δ_C 135.76 (C), 134.20 (CH), 133.46, 132.22 (C), 128.17, 127.96, 127.92, 127.63, 127.44, 126.06, 125.46 (CH), 119.20 (CH_2), 56.15 (CH), 55.84 (C), 41.79, 39.73

(CH_2), 22.56 (CH_3); LRMS (EI) *m/z* 260 (M^+-C_4H_8, 11%), 259 (61), 142 (27), 141 (100), 118 (54), 115 (23), 70 (47), 57 (28), 41 (10); HRMS (ESI): Calculated for $C_{15}H_{17}NOS$ (M^+-C_4H_8) 259.1031, found 259.1029.

(R_S,3*S*)-*N*-(*tert*-Butanesulfinyl)-2-methylhex-5-en-3-amine (6e):[25] Yellow oil; $[\alpha]_D^{23}$ -61 (*c* 1.09, CH_2Cl_2); R_f 0.47 (hexane/EtOAc: 1/1); IR ν (film) 3239, 2959, 2871, 1638, 1467, 1388, 1364, 1173, 1132, 1053, 1006, 907 cm^{-1}; δ_H 5.89-5.72 (m, 1H), 5.22-5.14 (m, 1H), 5.14 (s, 1H), 3.25-3.12 (m, 1H), 2.46-2.21 (m, 2H), 1.97-1.81 (m, 1H), 1.23 (s, 9H), 0.91 (d, *J* = 6.8 Hz, 6H); δ_C 134.84 (CH), 118.74 (CH_2), 60.03 (CH), 56.04 (C), 37.08 (CH_2), 31.08 (CH), 22.85, 18.48, 17.93 (CH_3); LRMS (EI) *m/z* 162 (M^+-C_4H_8, 2%), 161 (15), 120 (47), 119 (72), 118 (18), 62 (25), 59 (12), 57 (88), 56 (31), 55 (71), 43 (30), 42 (12), 41 (100).

(R_S,4*R*)-*N*-(*tert*-Butanesulfinyl)undec-1-en-4-amine (6j): Yellow wax; $[\alpha]_D^{23}$ -24 (*c* 1.05, CH_2Cl_2); R_f 0.52 (hexane/EtOAc: 1/1); IR ν (film) 2925, 2855, 1638, 1457, 1362, 1114, 1054, 993, 913, 723 cm^{-1}; δ_H 5.89-5.70 (m, 1H), 5.21-5.04 (m, 2H), 3.53-3.25 (m, 2H), 3.22 (d, *J* = 6.0 Hz, 1H), 2.49-2.20 (m, 2H), 1.44-1.21 (m, 12H), 1.21 (s, 9H), 0.94-0.82 (m, 3H); δ_C 134.37 (CH), 118.96 (CH_2), 55.90 (C), 54.97 (CH), 40.55, 35.07, 31.91, 29.57, 29.34, 25.58 (CH_2), 22.80 (CH_3), 22.75 (CH_3), 14.21 (CH_3); LRMS (EI) *m/z* 273 (M^+, 1%), 217 (17), 176 (68), 175 (58), 149 (35), 118 (26), 115 (61), 111 (26), 109 (18), 97 (39), 95 (26), 87 (17), 85 (31), 83 (33), 81 (27), 73 (60), 71 (69), 70 (35), 69 (62), 67 (19), 57 (80), 56 (23), 55 (88), 45 (22), 43 (100), 41 (56); HRMS (ESI): Calculated for $C_{11}H_{23}NOS$ (M^+-C_4H_8) 217.1500, found 217.1500.

General procedure for the synthesis of homoallylamine derivatives 6 from epoxides 5 (Method B): A heterogeneous mixture of the corresponding epoxide **5** (1.0 mmol), *tert*-butanesulfinamide (**1**, 0.061 mg, 0.5 mmol), indium metal (0.115 g, 1.0 mmol), boron trifluoride etherate (0.0071 g, 11.8 μL, 0.05 mmol) and 3Å MS (400 mg) in THF (3.0 mL) was stirred at 50 ºC for 12 h. Then, the reaction mixture was cooled down to 23 ºC, and the corresponding allylic bromide (1.5 mmol). The resulting mixture was heated for 5 h at 60 ºC and after that it was cooled down, diluted with EtOAc (15 mL) and the liquid filtered off. The liquid phase was hydrolyzed with water (10 mL), extracted with EtOAc (3×15 mL), dried with anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to yield pure compounds **6**. Yields for these compounds are given on Table 6. Physical and spectroscopic for compounds **6c** and **6i** follow, and for the rest of compounds the corresponding data were also given above.

(R_S,2*S*)-*N*-(*tert*-Butanesulfinyl)-1-(4-acetoxyphenyl)pent-4-en-2-amine (6c): Yellow wax; $[\alpha]_D^{23}$ -48 (*c* 1.04, CH_2Cl_2); R_f 0.30 (hexane/EtOAc: 1/1); IR ν (film) 2925, 1761, 1507, 1442, 1366, 1214, 1192, 1166, 1049, 1016, 910, 852, 732 cm^{-1}; δ_H 7.24-7.17 (m, 2H), 7.04-6.98 (m, 2H), 4.90 (s, 1H), 4.82 (s, 1H), 3.72-3.56 (m, 1H), 3.41 (d, *J* = 3.5 Hz, 1H), 2.93 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.71 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.37-2.15 (m, 2H), 2.29 (s, 3H), 1.71 (s, 3H), 1.14 (s, 9H); δ_C 169.61, 149.32, 142.21, 135.79 (C), 130.66, 121.49 (CH), 114.55 (CH_2), 55.86 (C), 53.10 (CH), 43.87, 41.44 (CH_2), 22.62, 21.92, 21.21 (CH_3); LRMS (EI) *m/z* 282 (M^+-C_4H_8, 5%), 281

(13), 226 (14), 225 (100), 183 (24), 175 (26), 135 (20), 132 (48), 120 (43), 114 (19), 107 (67), 57 (41), 43 (15), 41 (13); HRMS (ESI): Calculated for $C_{10}H_{11}NO_3S$ [M^+-(C_4H_9+C_4H_7)] 225.0460, found 225.0451.

(R_S,2*S*)-*N*-(*tert*-Butanesulfinyl)-1-(2,2,3-trimethylcyclopent-3-enyl)pent-4-en-2-amine (6i): Mixture of diastereoisomers (3:1); yellow wax; R_f 0.52 (hexane/EtOAc: 1/1); IR ν (film) 2954, 2925, 1638, 1442, 1362, 1053, 911, 838, 796, 732 cm^{-1}; δ_H 5.91-5.72 (m, 1H), 5.27-5.10 (m, 3H), 3.41-3.25 (m, 1H), 3.19 (d, J = 8.2 Hz, 1H), 2.57-2.40 (m, 2H), 2.37-2.21 (m, 2H), 2.03-1.89 (m, 1H), 1.89-1.74 (m, 1H), 1.63-1.58 (m, 3H), 1.51-1.40 (m, 1H), 1.21,1.20 (2s, 1:3 ratio, 9H), 0.98, 0.95 (2s, 1:3 ratio, 3H), 0.76, 0.75 (2s, 1:3 ratio, 3H).

Major isomer: δ_C 148.76 (C), 134.15, 121.68 (CH), 119.09 (CH_2), 56.18 (C), 55.03 (CH), 46.81 (C), 46.30 (CH), 42.25, 36.20, 35.53 (CH_2), 25.68, 22.85, 19.84, 12.71 (CH_3); LRMS (EI) *m/z* 242 (M^+-C_4H_8, 16%), 241 (100), 192 (35), 150 (61), 147 (32), 136 (17), 133 (21), 122 (37), 121(63), 120 (43), 119 (26), 118 (53), 115 (39), 109 (69), 108 (48), 107 (44), 105 (19), 103 (32), 102 (41), 95 (37), 94 (40), 93 (50), 91 (48), 81 (21), 79 (34), 77 (34), 70 (67), 69 (20), 68 (15), 67 (30), 55 (22); HRMS (ESI): Calculated for $C_{13}H_{23}NOS$ (M^+-C_4H_8) 251.1500, found 241.1513.

Minor isomer: δ_C 148.60 (C), 134.04, 121.78 (CH), 119.36 (CH_2), 55.74 (C), 53.57 (CH), 47.10 (C), 46.54 (CH), 39.55, 35.93, 35.49 (CH_2), 25.89, 22.78, 19.78, 12.71 (CH_3); LRMS (EI) *m/z* 242 (M^+-C_4H_8, 15%), 241 (100), 192 (20), 150 (46), 147 (26), 136 (14), 133 (16), 122 (27), 121 (52), 120 (37), 119 (22), 118 (41), 115 (23), 109 (54), 108 (38), 107 (32), 105 (14), 103 (25), 102 (24), 95 (29), 94 (29), 93 (39), 91 (41), 81 (16), 79 (25), 77 (26), 70 (56), 69 (17), 68 (15), 67 (24), 55 (16); HRMS (ESI): Calculated for $C_{13}H_{23}NOS$ (M^+-C_4H_8) 241.1500, found 241.1505.

Supporting Information (see footnote on the first page of this article): Procedures and characterization data for epoxides **5c**, **5d**, **5f** and **5g**, and copies of ^1H, ^{13}C NMR and DEPT spectra for all the reported compounds.

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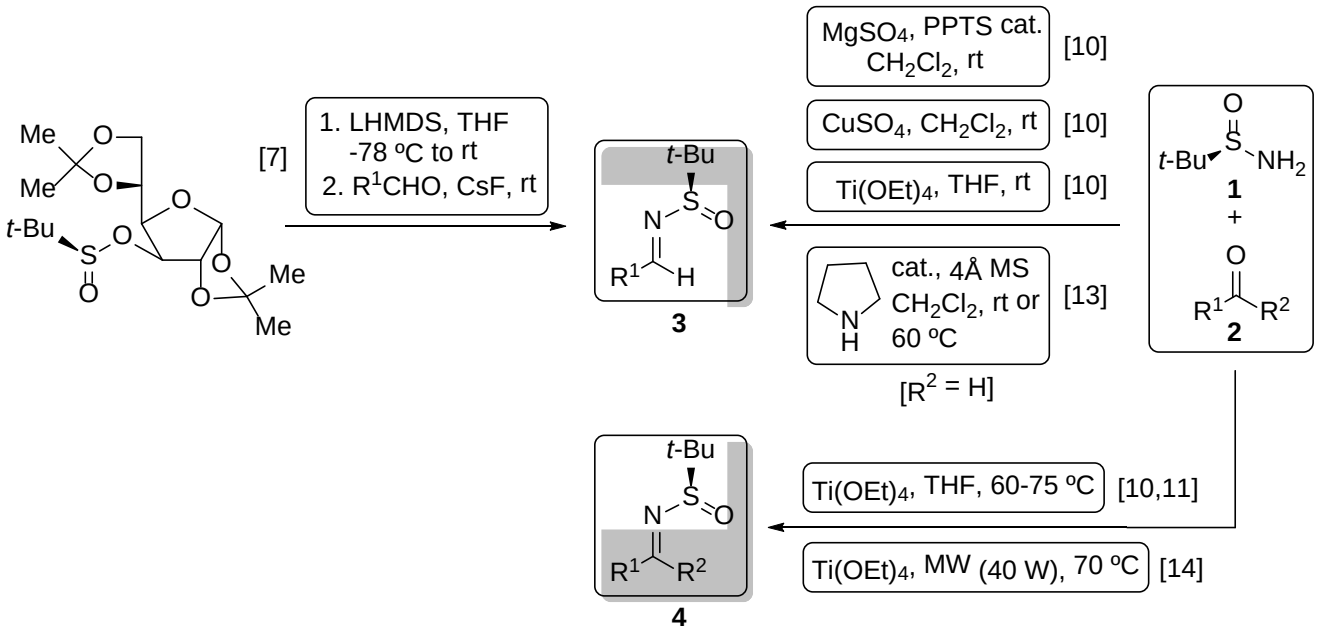
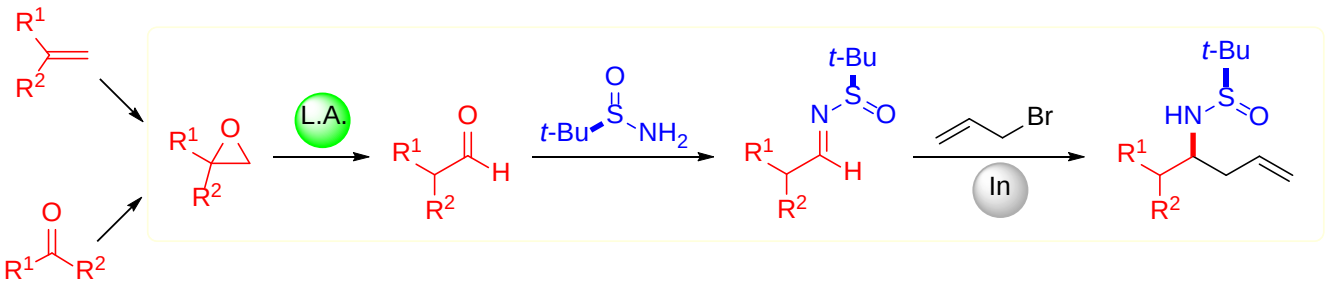
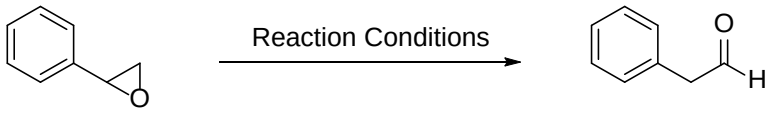


Scheme 1. Previously Reported Synthesis of *N-tert*-Butanesulfinyl Imines



Scheme 2. Proposed One-pot Transformation of Epoxides into *N-tert*-Butanesulfinyl Imines and Homoallylamines

Table 1. Optimization of the Lewis acid-catalyzed rearrangement of epoxide **5a** to carbonyl compound **2a**[a]

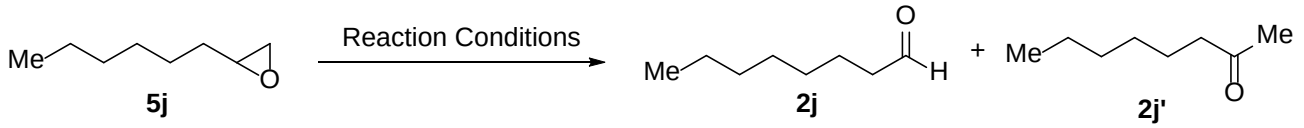


5a **2a**

	Reaction Conditions				Reaction Products (%)[b]	
Entry	Catalyst	Solvent	Temperature	Time	**2a**	**5a**
1	$Er(OTf)_3$ (0.5 mol %)	CH_2Cl_2	23 ºC	20 min	40	35
2	$Er(OTf)_3$ (1 mol %)	CH_2Cl_2	23 ºC	20 min	64	2
3	$Er(OTf)_3$ (1 mol %)	THF	23 ºC	20 min	6	94
4	$Er(OTf)_3$ (1 mol %)	THF	23 ºC	8 h	84	8
5	$Er(OTf)_3$ (1 mol %)	THF	MW (40 W), 35 ºC	40 min	77	14
6	$Er(OTf)_3$ (1 mol %)	THF	MW (40 W), 30 ºC	45 min	83	10
7	$Er(OTf)_3$ (1 mol %)	THF	50 ºC	45 min	78	8
8	$InCl_3$ (5 mol %)	THF	50 ºC	45 min	10	90
9	TfOH (5 mol %)	THF	50 ºC	45 min	62	11
10	$InBr_3$ (5 mol %)	THF	50 ºC	45 min	18	82
11	$AlCl_3$ (5 mol %)	THF	50 ºC	45 min	26	59
12	$BF_3{\cdot}OEt_2$ (5 mol %)	THF	50 ºC	45 min	78	7

[a] All the reactions were carried out with 0.5 mmol of **5a** in 1.5 mL of the corresponding solvent. [b] Yield was determined by GC. When combined yields (**2a**+**5a**) are lower than 100%, other reaction products resulting mainly from aldol condensation of the aldehyde **2a** are also formed.

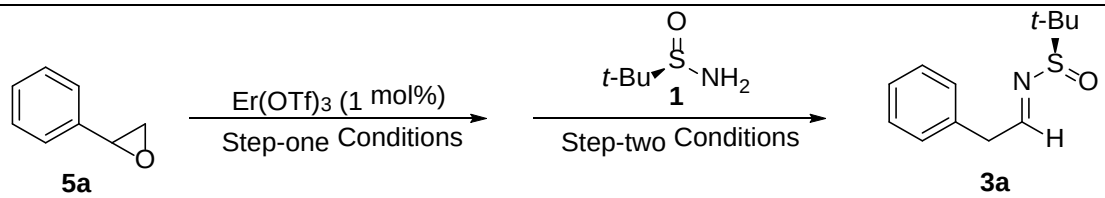
Table 2. Optimization of the Lewis acid-catalyzed rearrangement of epoxide **5j** to carbonyl compounds **2j**[a]



	Reaction Conditions				Reaction Products (%)[b]		
Entry	$Er(OTf)_3$	Solvent	Temperature	Time	**2j**	**2j'**	**5j**
1	1 mol %	CH_2Cl_2	MW (40 W), 45 ºC	45 min	--	--	97[c]
2	1 mol %	THF	MW (40 W), 50 ºC	45 min	26	2	--
3	1 mol %	THF	MW (40 W), 60 ºC	10 min	45	3	--
4	1 mol %	THF	MW (90 W), 80 ºC	5 min	34	2	40
5	1 mol %	THF	MW (100 W), 80 ºC	7 min	62	4	--
6	0.5 mol %	THF	MW (100 W), 80 ºC	7 min	55	4	8
7	1 mol %	THF	85 ºC	30 min	20	--	39
8	1 mol %	THF	120 ºC	30 min	38	2	--
9	1 mol %	THF	150 ºC	10 min	67	5	--

[a] All the reactions were carried out with 0.5 mmol of **5j** in 1.5 mL of the corresponding solvent. [b] Yield was determined by GC. When combined yields (**2j**+**2j'**+**5j**) are lower than 100%, other reaction products resulting mainly from aldol condensation of carbonyl compounds **2j** and **2j'** are also formed. [c] The reaction was performed in 3 mL of CH_2Cl_2.

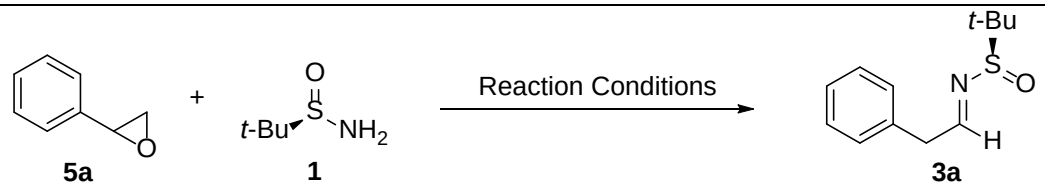
Table 3. Optimization of the erbium triflate-catalyzed one-pot, two-step transformation of epoxide **5a** into sulfinyl imine **3a**[a]



Entry	Step-one Conditions	Step-two Conditions	Yield (%)[b]
1	CH_2Cl_2, 23 ºC, 20 min	PPTS (5 mol%), $MgSO_4$ (2 equiv), 23 ºC, 12 h	44
2	$(ClCH_2)_2$, 23 ºC, 10 min	$MgSO_4$ (2 equiv), MW (40 W), 60 ºC, 20 min	28
3	THF, 23 ºC, 8 h	$MgSO_4$ (2 equiv), 23 ºC, 48 h	24
4	THF, MW (40 W), 30 ºC, 45 min	$MgSO_4$ (2 equiv), MW (40 W), 60 ºC, 20 min	45
5	THF, MW (40 W), 30 ºC, 45 min	$MgSO_4$ (2 equiv), MW (40 W), 60 ºC, 45 min	48
6	THF, MW (40 W), 30 ºC, 45 min	$Ti(OEt)_4$ (1 equiv), MW (60 W), 65 ºC, 20 min	49[c]
7	THF, 50 ºC, 45 min	$Ti(OEt)_4$ (1 equiv), 23 ºC, 12 h	46[c]

[a] All the reactions were carried out with 1.0 mmol of **5a** and 0.5 mmol of **1**, in 3.0 mL of the corresponding solvent. [b] Yield was determined after column chromatography purification and is based on the starting sulfinimide **1**. [c] The reaction was performed in 1.5 mL of THF.

Table 4. Optimization of the boron trifluoride etherate-catalyzed one-pot transformation of epoxide **5a** into sulfinyl imine **3a**[a]

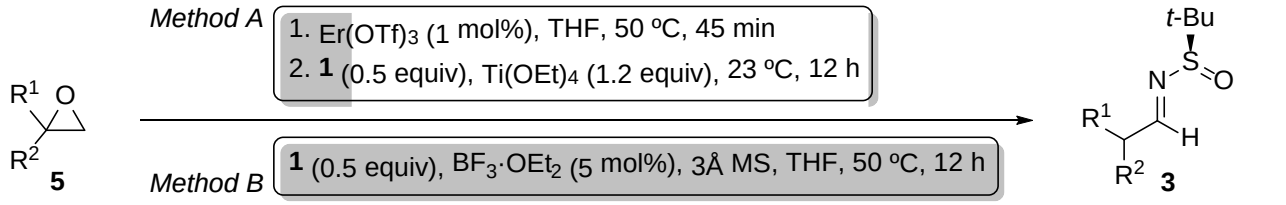


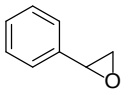
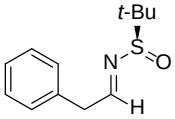
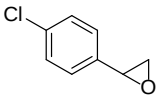
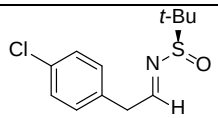
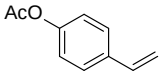
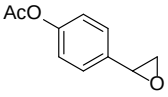
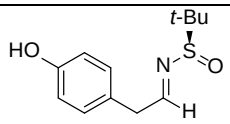
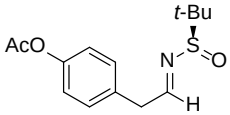
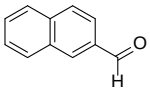
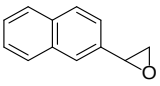
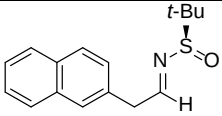
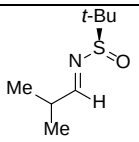
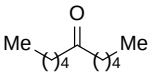
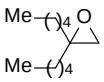
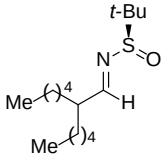
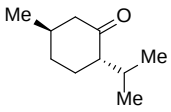
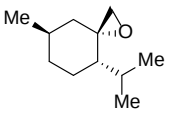
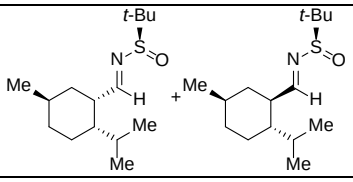
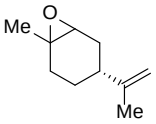
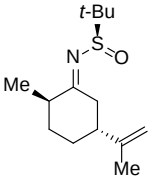
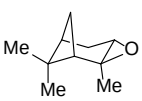
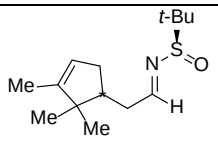
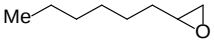
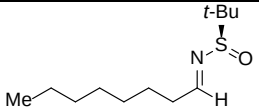
5a + **1** → **3a**

	Reaction Conditions					
Entry	$BF_3 \cdot OEt_2$	Solvent	MS (3Å)	Temperature	Time	Yield (%)[b]
1	5 mol %	THF	400 mg	50 ºC	4 h	39
2	5 mol %	THF	400 mg	50 ºC	12 h	76
3	5 mol %	THF	400 mg	23 ºC	12 h	57
4	5 mol %	THF	--	50 ºC	12 h	47
5	5 mol %	THF	400 mg	50 ºC	12 h	53[c]

[a] All the reactions were carried out with 1.0 mmol of **5a** and 0.5 mmol of **1**, in 3.0 mL of THF. [b] Yield was determined after column chromatography purification based on the starting sulfinimide **1**. [c] The reaction was performed with 0.6 mmol of **5a**.

Table 5. One-pot synthesis of *N-tert*-butanesulfinyl imines **3** from epoxides **5** and (*R*)-*tert*-butanesulfinadide **1**[a]

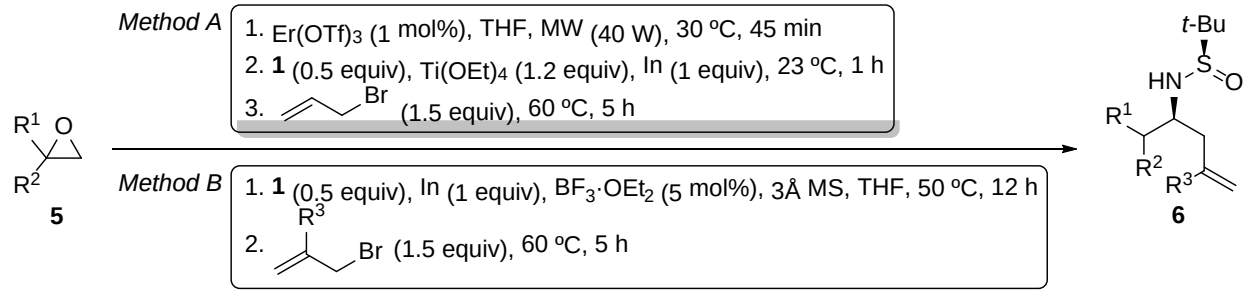


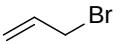
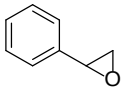
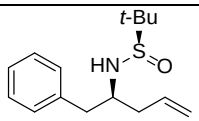
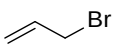
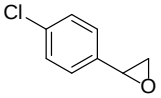
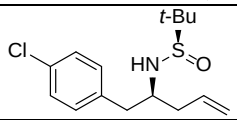
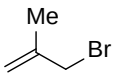
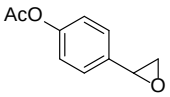
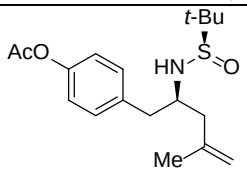
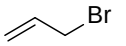
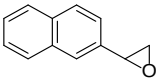
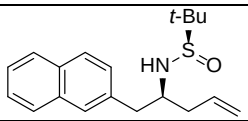
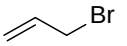
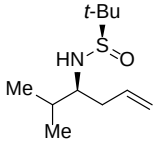
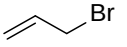
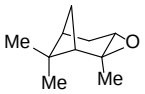
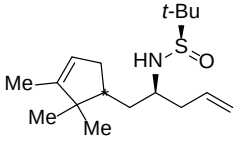
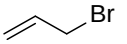
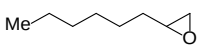
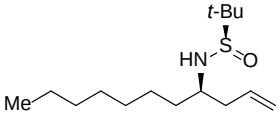
Entry	Source of epoxide **5**	Epoxides **5** No.	Epoxides **5**	Reaction Products **3** No.	Reaction Products **3** Structure	Method	Yield (%)[b]
1	Commercially available	**5a**		**3a**		A	46 (49)[c]
2						B	76
3	Commercially available	**5b**		**3b**		A	54
4						B	80
5		**5c**		**3c'**		A	62 (68)[c]
6				**3c**		B	84
7		**5d**		**3d**		A	51
8						B	72
9	Commercially available	**5e**		**3e**		A	91[d]
10						B	94[d]
11		**5f**		**3f**		A	75 (59)[c]
12						B	75
13		**5g**		**3g**+**3g'**		A	60 (10/6)[e]
14						B	48 (3/10)[e]
15	Commercially available	**5h**		**3h**		A	61 (24)[f]
16						B	--[g]
17	Commercially available	**5i**		**3i**		A	94[h]
18						B	58[h]
19	Commercially available	**5j**		**3j**		A	49[i]
20						B	--[g]

[a] All the reactions were carried out with 1.0 mmol of **5** and 0.5 mmol of **1**, in 3.0 mL of THF. [b] Yield was

determined after column chromatography purification and is based on the starting sulfinimide **1**. [c] Yield is given in parenthesis when step-one of method A was performed under microwave irradiation at 30 ºC (40 W). [d] The reaction was carried out with 1.5 mmol of **5e**. [e] Diastereomeric ratio of aldimines **3g**+**3g'** is given in parenthesis. [f] The condensation step was performed at 60 ºC and a mixture of three imines was obtained, but only compound **3h** was isolated as a single compound in 24% yield. [g] Imine formation was not observed. [h] Obtained as 3:1 mixture of diastereoisomers. [i] Step-one of method A was performed under microwave irradiation at 80 ºC (100 W) for 7 min.

Table 6. One-pot synthesis of homoallyl amine derivatives **6** from epoxides **5**, (*R*)-*tert*-butanesulfinadide **1** and allylic bromides[a]



Entry	Allylic bromide	Epoxides **5** No.	Epoxides **5**	Reaction Products **6** No.	Reaction Products **6** Structure	Method	Yield (%)[b]
1		**5a**		**6a**		A	71
2						B	72
3		**5b**		**6b**		A	73
4						B	82
5		**5c**		**6c**		B	86
7		**5d**		**6d**		A	57
8						B	85
9		**5e**		**6e**		A	43
10						B	56
11		**5i**		**6i**		B	69[c]
12		**5j**		**6j**		A	69[d]

[a] All the reactions were carried out with 1.0 mmol of **5** and 0.5 mmol of **1**, in 3.0 mL of THF. [b] Yield was determined after column chromatography purification based on the starting sulfinimide **1**. [c] Obtained as 3:1 mixture of diastereoisomers. [d] Step-one of method A was performed under microwave irradiation at 80 ºC (100 W) for 7 min.

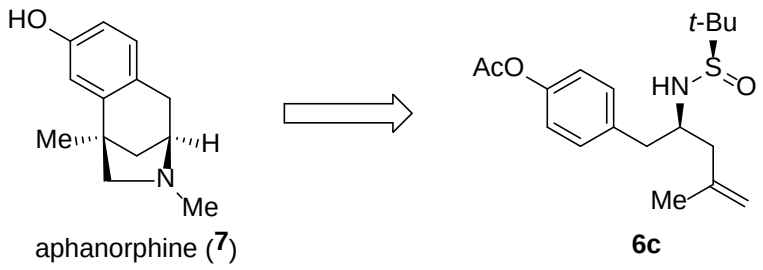


Figure 1. Homoallyl Amine Derivative **6c** as a Precursor of Marine Alkaloid Aphanorphine **7**

Table of Contents

Epoxides are precursors of *N*-*tert*-butanesulfinyl imines in a one-pot procedure through a successive Lewis acid-promoted epoxide isomerization to give first a carbonyl compound, and further condensation with *tert*-butanesulfinamide. Homoallylamine derivatives are also accessible in a single synthetic operation when the formation of the imine is carried out in the presence of indium metal, followed by addition of an allylic bromide.

Key Topic: Synthesis of *N*-*tert*-Butanesulfinyl Imines and Homoallylamine Derivatives from Epoxides