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One-Pot Reactions

One-Pot Synthesis of *N-tert*-Butylsulfinylimines and Homoallylamine Derivatives from Epoxides

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Abstract: The reaction of epoxides with *tert*-butanesulfinamide in the presence of a Lewis acid, such as erbium triflate or boron trifluoride–diethyl ether, in THF as solvent, under microwave or thermal activation, produces *N-tert*-butylsulfinylimines in reasonable yields. Aromatic and *gem*-disubstituted and trisubstituted alkyl epoxides performed better than mono-alkyl-substituted compounds. After imine formation, a subsequent indium-promoted allylation can be carried out in the same reaction flask in a single synthetic operation leading to homoallylamine derivatives with generally 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 centre.[1] Many of these chiral aminated compounds are natural or synthetic molecules that may show biological activity. Such molecules could also be envisioned as key synthetic intermediates in the preparation of more complex molecular architectures. Among the stereoselective methods for the synthesis of these compounds is catalytic enantioselective addition.[2] This approach relies on the use of either chiral Lewis acids,[3] which bind to the electrophile activating it towards nucleophilic attack, or chiral Lewis bases.[4] Although the development of methods for catalytic enantioselective addition is a very attractive field, it has some limitations. For instance, some of the reported catalytic methods use a large excess of reagents to ensure the turnover of the catalyst. Sometimes, when the catalytic activation does not significantly increase the reaction rate, competitive noncatalytic addition results in a lower enantioselectivity. This is the reason why, in the synthesis of complex organic molecules, including natural products, stereoselective nucleophilic additions to imines are more commonly carried out 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 for a wide range of synthetic applications. The ready availability of both enantiomers of *tert*-butanesulfinamide on a large scale, the easy 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 carried out for the first time by García-Ruano, I. Fernández and coworkers from a *tert*-butanesulfinate ester derived from diacetone D-glucose; *tert*-butanesulfinamide (**1**) was involved as a reaction intermediate, but it was not isolated in this process.[7] Since the development by Ellman's group 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 coworkers reported in 1997 the first synthesis of *N-tert*-butylsulfinyl aldimines **3** following this strategy.[9] The condensation of aldehydes and sulfinamide **1** took place in the presence of an excess of magnesium sulfate and a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS), using dichloromethane as solvent at room temperature.[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*-butylsulfinylimines **3** through the 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 carried out using pyrrolidine as an organocatalyst in the absence of acids or bases, with the process taking place through iminium activation in the presence of molecular sieves (MS, 4 Å),[13] or under microwave irradiation (MW).[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).

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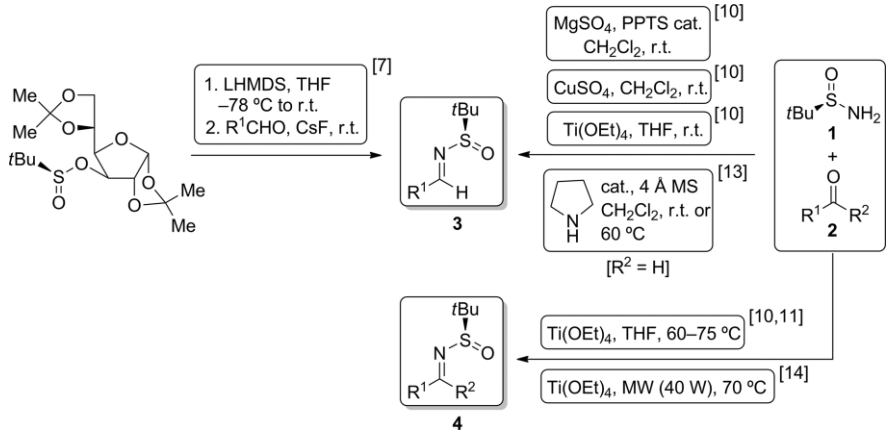
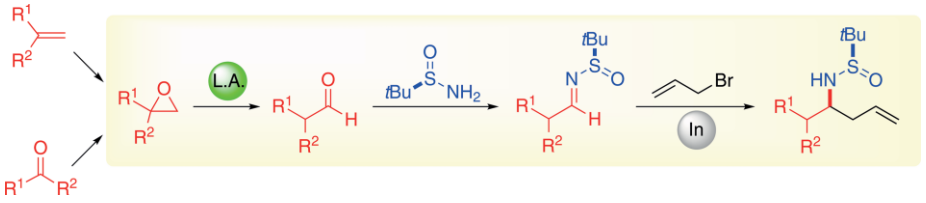


Scheme 1. Previously reported synthesis of *N-tert*-butylsulfinylimines; LiHMDS = lithium hexamethyldisilazide.



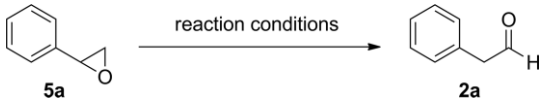
Scheme 2. Proposed one-pot transformation of epoxides into *N-tert*-butylsulfinylimines and homoallylamines.

With the aim of increasing the number of available methods to synthesize chiral *N-tert*-butylsulfinylimines, 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] or olefins.[16] In order to carry out this transformation, isomerization of the epoxide to the corresponding carbonyl compound should take place first, followed by condensation with *N-tert*-butanesulfinamide. In principle, a Lewis acid should be involved in both steps, and the condensation reaction is greatly facilitated by 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 multistep transformation of epoxides into imines, or into homoallylamines, in a one-pot process, avoiding the work-up and isolation of intermediates, the so-called pot economy,[18] would be of great interest. Such an approach would be more environmentally sustainable, because the amounts of waste, solvents, labour, and time would be considerably decreased (Scheme 2).

Results and Discussion

For the proposed multistep one-pot strategy shown in Scheme 2 to be successful, all the transformations should take place in high 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 a 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 with a wide range of substrates.[19] Many tests were carried out, but only the most significant results are compiled in Table 1. Thus, the treatment of styrene oxide (**5a**) with erbium triflate (0.5 mol-%) in dichloromethane at 23 °C for 20 min led to the formation of phenylacetaldehyde (**2a**) in 40 % yield, with 35 % of the starting epoxide (i.e., **5a**) remaining in the reaction mixture; partial decomposition (around 25 %) of aldehyde **2a**, probably through aldol condensation, was also observed (Table 1, entry 1). When the isomerization was carried out using 1 mol-% of the erbium salt, almost complete conversion was observed, and the yields of both aldehyde **2a** (64 %) and of the aldol condensation products (34 %) increased (Table 1, entry 2). In THF, the isomerization proceeded more slowly than in dichloromethane at 23 °C, and 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 %); the decomposition of the aldehyde took place to a lesser extent in THF than in dichloromethane (Table 1, entry 4). In addition, the reaction times could be shortened by using microwave irradiation, with the amount of the desired aldehyde (i.e., **2a**) being tightly dependent on the temperature and the reaction time (Table 1, entries 5 and 6). Importantly, the isomerization in THF under thermal conditions at 50 °C led, after 45 min, to aldehyde **2a** in 78 % yield (Table 1, entry 7). This result was rather similar to that obtained when the process was carried out under microwave irradiation. Other Lewis and Brønsted acids led to worse results under similar reaction conditions (Table 1, entries 8–12), except for boron trifluoride–diethyl

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



5a **2a**

Entry	Reaction conditions Catalyst	Solvent	Temperature	Time	Products [%][b] **2a**	**5a**
1	$Er(OTf)_3$ (0.5 mol-%)	CH_2Cl_2	23 °C	20 min	40	35
2	$Er(OTf)_3$ (1 mol-%)	CH_2Cl_2	23 °C	20 min	64	2
3	$Er(OTf)_3$ (1 mol-%)	THF	23 °C	20 min	6	94
4	$Er(OTf)_3$ (1 mol-%)	THF	23 °C	8 h	84	8
5	$Er(OTf)_3$ (1 mol-%)	THF	MW (40 W), 35 °C	40 min	77	14
6	$Er(OTf)_3$ (1 mol-%)	THF	MW (40 W), 30 °C	45 min	83	10
7	$Er(OTf)_3$ (1 mol-%)	THF	50 °C	45 min	78	8
8	$InCl_3$ (5 mol-%)	THF	50 °C	45 min	10	90
9	TfOH (5 mol-%)	THF	50 °C	45 min	62	11
10	$InBr_3$ (5 mol-%)	THF	50 °C	45 min	18	82
11	$AlCl_3$ (5 mol-%)	THF	50 °C	45 min	26	59
12	$Ti(OEt)_4$ (5 mol-%)	THF	50 °C	45 min	<5	95
13	BF_3·OEt_2 (5 mol-%)	THF	50 °C	45 min	78	7

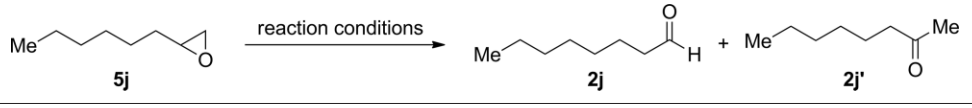
[a] All the reactions were carried out with **5a** (0.5 mmol) in the corresponding solvent (1.5 mL). [b] Yield was determined by GC. Where the combined yields (**2a** + **5a**) are lower than 100 %, other reaction products resulting mainly from aldol condensation of aldehyde **2a** were also formed.

ether, which performed quite well to produce phenylacetaldehyde (**2a**) in 78 % yield (Table 1, entry 13).

Isomerization of *gem*-dialkyl- and trialkyl-substituted epoxides 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 °C for 45 min under microwave irradiation, and starting epoxide **5j** remained unaltered (Table 2, entry 1). In contrast, complete conversion was observed after 45 min at 50 °C in THF, but the expected product, octanal (**2j**), was formed in only 26 % yield (Table 2, entry 2). The yields were improved by working at higher temperatures for 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 when the reaction was carried out in a high-pressure tube at 150 °C for 10 min (Table 2, entry 9). Unfortunately, other Lewis acids ($InCl_3$, $InBr_3$, $AlCl_3$, BF_3·OEt_2) were not effective for carrying out this transformation.

Having established optimized reaction conditions for the isomerization step, we went on to study the one-pot two-step process for the synthesis of *N*-*tert*-butylsulfinylimines **3** from epoxides **5**. Taking again styrene oxide (**5a**) as the model compound and erbium triflate as the Lewis acid, we found that isomerization did not take place to an appreciable extent when sulfinamide **1** was also present in the reaction medium. It seems that **1** inhibited the action of erbium triflate. For that reason, *tert*-butanesulfinamide **1** was added to the reaction flask after the isomerization of epoxide **5a** to aldehyde **2a**, along with the

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



5j **2j** **2j'**

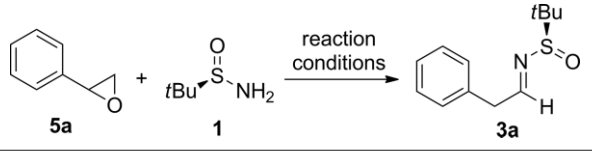
Entry	Reaction conditions $Er(OTf)_3$	Solvent	Temperature	Time	Products [%][b] **2j**	**2j′**	**5j**
1	1 mol-%	CH_2Cl_2	MW (40 W), 45 °C	45 min	–	–	97[c]
2	1 mol-%	THF	MW (40 W), 50 °C	45 min	26	2	–
3	1 mol-%	THF	MW (40 W), 60 °C	10 min	45	3	–
4	1 mol-%	THF	MW (90 W), 80 °C	5 min	34	2	40
5	1 mol-%	THF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

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

corresponding reagents for the condensation step. Thus, the isomerization was carried out first in dichloromethane at room temperature for 20 min. This was followed by the successive addition of sulfinamide **1**, a catalytic amount of pyridinium *para*-toluenesulfonate (PPTS), and magnesium sulfate (2 equiv.). After leaving the reaction mixture at the same temperature for a further 12 h, the expected *N*-*tert*-butylsulfinylimine (i.e., **3a**) was obtained in 44 % yield (Table 3, entry 1). When the isomerization was carried out in 1,2-dichloroethane first, followed by condensation of the resulting aldehyde (i.e., **2a**) with sulfinamide **1**, in the presence of anhydrous magnesium sulfate under microwave irradiation at 60 °C for 20 min, the imine (i.e., **3a**) was obtained in a lower yield (Table 3, entry 2). When THF was used as solvent instead, and the isomerization was carried out at 23 °C for 8 h, and the condensation at the same temperature for 48 h with magnesium sulfate, the imine (i.e., **3a**) was formed in only 24 % yield (Table 3, entry 3). However, the yields were considerably improved when the same combination of reagents in THF was submitted to microwave irradiation (Table 3, entries 4 and 5). When titanium tetraethoxide was used instead of magnesium sulfate as the condensation promoter, the expected imine (i.e., **3a**) was formed in a similar yield (Table 3, entry 6). On the other hand, when the isomerization was carried out at 50 °C for 45 min, and the condensation at room temperature with titanium tetraethoxide in THF for 12 h, the expected imine (i.e., **3a**) was formed in 46 % yield (Table 3, entry 7), similar to the yields of other processes carried out in THF.

Although erbium triflate was found to be a little bit more efficient than boron trifluoride–diethyl ether in the isomerization of epoxide **5a**, we also studied the one-pot transformation of **5a** into aldimine **3a** using this boron compound. Importantly, in this case, the isomerization step was not affected by the presence of sulfinamide **1**; all the reactions were carried out in THF with boron trifluoride–diethyl ether (5 mol-%) with all the reagents in the reaction flask at the beginning of the experiment. This represents an advantage over the erbium triflate approach. Thus, imine **3a** was formed in only 39 % yield after 4 h at 50 °C when molecular sieves (3 Å) were used as the water scavenger (Table 4, entry 1). Longer reaction times (12 h) under the same reaction conditions led to a quite good 76 % yield for the two-step process (Table 4, entry 2). Worse yields were obtained when working at lower temperatures (23 °C) or in the absence of molecular sieves (Table 4, entries 3 and 4). All these reactions were carried out with an excess of starting epoxide **5a** (2:1 epoxide **5a**/sulfinamide **1**), because when almost stoichiometric amounts of epoxide **5a** and sulfinimide **1** were used, the yields were considerably lower (Table 4, compare entries 2 and 5).

Table 4. Optimization of the boron trifluoride–diethyl ether catalysed one-pot transformation of epoxide **5a** into sulfinylimine **3a**.[a]

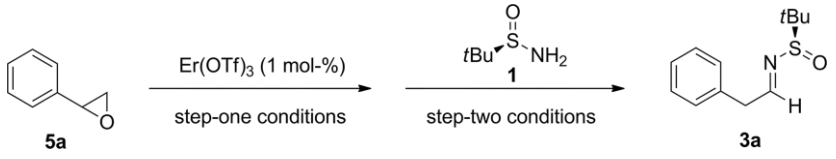


	Reaction conditions					
Entry	BF_3•OEt_2	Solvent	MS (3 Å)	Temperature	Time	Yield [%][b]
1	5 mol-%	THF	400 mg	50 °C	4 h	39
2	5 mol-%	THF	400 mg	50 °C	12 h	76
3	5 mol-%	THF	400 mg	23 °C	12 h	57
4	5 mol-%	THF	–	50 °C	12 h	47
5	5 mol-%	THF	400 mg	50 °C	12 h	53[c]

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

The substrate scope was then studied under the optimized reaction conditions. We found that for aromatic epoxides **5a**–**5d**, method B led to higher yields than method A (Table 5, entries 1–8). Starting epoxides **5a** and **5b** were commercially available. Compound **5c** was prepared by epoxidation of *para*-acetoxystyrene with MCPBA (*m*-chloroperbenzoic acid), and 2-naphthyloxirane (**5d**) was formed by epoxidation of 2-naphthalenecarbaldehyde with chloroiodomethane/*n*-butyllithium.[20] We also observed that the yields improved slightly when the isomerization step with the erbium salt was carried out under

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

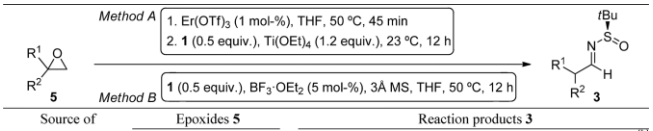


Entry	Conditions for step one	Conditions for step two	Yield [%][b]
1	CH_2Cl_2, 23 °C, 20 min	PPTS (5 mol-%), $MgSO_4$ (2 equiv.), 23 °C, 12 h	44
2	$(ClCH_2)_2$, 23 °C, 10 min	$MgSO_4$ (2 equiv.), MW (40 W), 60 °C, 20 min	28
3	THF, 23 °C, 8 h	$MgSO_4$ (2 equiv.), 23 °C, 48 h	24
4	THF, MW (40 W), 30 °C,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

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

microwave irradiation (Table 5, entries 1, 5, and 11). Interestingly, methods A and B led to different *N*-*tert*-butylsulfinylimines starting from epoxide **5c**; when the condensation step was carried out in the presence of titanium tetraethoxide, deacetylation was observed, and imine **3c′** was formed (Table 5, entry 5). Dialkyl-substituted epoxides **5e**–**5g** performed well under both sets of reaction conditions, with commercially available highly volatile isobutylene oxide (**5e**) giving 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 used 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, with a planar tertiary carbocation probably involved as a reaction intermediate. In addition, the major diastereomer obtained

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



Entry	Source of epoxide 5	Epoxides 5	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]

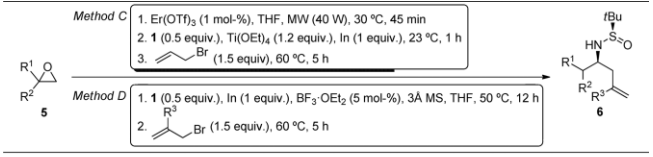
[a] All the reactions were carried out with **5** (1.0 mmol) and **1** (0.5 mmol), in THF (3.0 mL). [b] Yield was determined after purification by column chromatography, and is based on starting sulfinimide **1**. [c] Yield is given in parentheses when step one of method A was carried out under microwave irradiation at 30 °C (40 W). [d] The reaction was carried out with **5e** (1.5 mmol). [e] Diastereomeric ratio of aldimines **3g** + **3g′** is given in parentheses. [f] The condensation step was carried out at 60 °C; 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 carried out under microwave irradiation at 80 °C (100 W) for 7 min.

when the isomerization is carried out with the erbium salt (method A) seems to be the kinetic product **3g**, and the major component of the reaction mixture formed in the presence of boron trifluoride (method B) is the thermodynamically more stable **3g′** (Table 5, entries 13 and 14). Surprisingly, commercially available trialkyl-substituted (+)-limonene oxide (**5h**), which is supplied as a mixture of *cis* and *trans* isomers, led to a mixture of *N*-*tert*-butylsulfinylimines when modified method A was used (^{1}H NMR spectrum of the crude reaction mixture). However, only cyclohexenone derivative **3h** was isolated and characterized. The condensation step was carried out at 60 °C instead of 23 °C, because the formation of *N*-*tert*-butylsulfinylketimines did not proceed at room temperature in the presence of titanium tetraethoxide (Table 5, entry 15). However, ketimine **3h** was not obtained at all 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-catalysed isomerization of α-pinene oxide (**5i**) to campholenic aldehyde[21] has been widely studied because these compounds are of interest in the flavour and fragance industry. Thus, the one-pot transformation of α-pinene oxide (**5i**) into the aldimine derived from campholenic aldehyde **3i** proceeded in a higher yield with method A (Table 5, entry 17). This is probably because the isomerization of starting epoxide **5i** was less selective when boron trifluoride was used as Lewis acid (method B; Table 5, entry 18). In both cases, and because of the newly formed stereogenic centre 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 (the isomerization step was carried out under microwave irradiation at 80 °C, 100 W, 7 min), because boron trifluoride did not effectively promote the selective isomerization to the aldehyde intermediate (Table 5, entries 19 and 20).

We have been particularly interested in the indium-mediated allylation of *N*-*tert*-butylsulfinylimines, which produces homoallylamine derivatives in a highly diastereoselective fashion, and we have also reported the aminoallylation of aldehydes with *tert*-butanesulfinamides and allylic bromides.[17b,17c] Thus, we also decided to explore the one-pot transformation of epoxide starting materials into homoallylamine derivatives by adding allylic bromides to the reaction media in the presence of indium metal. In this study we also compared the isomerization step with erbium trifluoride under microwave irradiation (method C), with the boron trifluoride–diethyl ether under thermal conditions (method D). In addition, indium metal was in the reaction flask from the beginning in method D, whereas it was added after the isomerization step along with sulfinamide **1** and titanium tetraethoxide in method C, with all the components stirred for a further 1 h at room temperature in this last case. Finally, after the addition of the appropriate allylic bromide, the reaction mixture was heated at 60 °C for 5 h in both methods. We were please to find that the expected homoallylamine derivatives (i.e., **6**) were obtained in reasonable yields (Table 6). Notably, sometimes the isolated yield of the

homoallylamine derivative (i.e., **6**) exceeded the yield of the corresponding imine precursor (i.e., **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**, can 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 with a *Si*-face attack of the allylic moiety onto imines **3** with an *R* configuration at the sulfur atom. As a consequence of the previously mentioned lack of stereoselectivity in the isomerization of α-pinene oxide (**5i**) into campholenic aldehyde, compound **6i** was also obtained as a 3:1 mixture of diastereoisomers, in terms of the stereogenic centre of the cyclopentene ring (Table 6, entry 11). As a proof of the synthetic utility of these methods, *para*-acetoxystyrene (**5c**) was transformed into homoallylamine derivative **6c** (Table 6, entry 5), which could be an advanced intermediate in the synthesis of the marine alkaloid aphanorphine (Figure 1).[22]

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



Entry	Allylic bromide	Epoxides **5**	Reaction products **6** Structure	Method	Yield (%)[b]
1	Br	**5a**	**6a**	C	71
2				D	72
3	Br	**5b**	**6b**	C	73
4				D	82
5	Me, Br	**5c**	**6c**	D	86
7	Br	**5d**	**6d**	C	57
8				D	85
9	Br	**5e**	**6e**	C	43
10				D	56
11	Br	**5i**	**6i**	D	69[c]
12	Br	**5j**	**6j**	C	69[d]

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

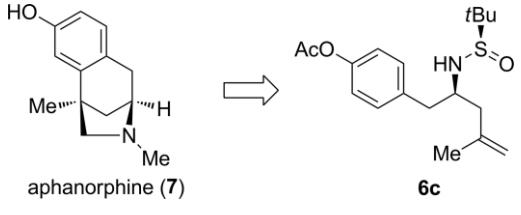


Figure 1. Homoallyl amine derivative **6c**, a precursor of the marine alkaloid aphanorphine (**7**).

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 give *N*-*tert*-butylsulfinylimines **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 was carried out in the same reaction flask. The methods described here represent a greener approach than previously reported syntheses of both *N*-*tert*-butylsulfinylimines **3**[6] and homoallylamines **6**.[6,17] The number of synthetic operations is decreased, and the reactions also represent examples of the so-called pot economy.

Experimental Section

General Remarks: (R_S)-*tert*-Butanesulfinamide was a gift from Medalchemy (>99 % *ee* by chiral HPLC on a Chiracel AS column; *n*-hexane/*i*PrOH, 90:10; 1.2 mL/min; λ = 222 nm). TLC was carried out on silica gel 60 F_{254} using aluminum plates, which were visualized with phosphomolybdic acid (PMA) stain. Flash chromatography was carried out on hand-packed columns of silica gel 60 (230–400 mesh). Gas-chromatographic analysis (GC) was carried out with an 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, $T_{injector}$ = 275 °C, T_{column} = 60 °C (3 min) and 60–270 °C (15 °C/min). Optical rotations were measured using a polarimeter with a thermally jacketed 5 cm cell at approximately 23 °C, and concentrations (*c*) are given in g/100 mL. Infrared spectroscopic analysis was carried out 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 are reported as *m/z* with relative intensities (%) in parentheses. High-resolution mass spectra (HRMS) were also measured in electron impact mode (EI) at 70 eV. Alternatively, high-resolution mass spectra were measured using an instrument equipped with a time-of-flight (TOF) analyser; samples were ionized by the ESI technique and introduced through an ultra-high-pressure liquid chromatograph (UPLC). 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 tetramethylsilane as internal standard (δ = 0.00 ppm). Data are 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 were referenced to $CDCl_3$ at δ = 77.16 ppm. DEPT-135 experiments were carried out to assign peaks as CH, CH_2, or CH_3. All reactions requiring anhydrous conditions were carried out in oven-dried glassware under argon. Unless otherwise indicated, all commercially available chemicals were purchased from Acros or Sigma–Aldrich, and were used without purification.

General Procedure for the Synthesis of *N*-*tert*-Butylsulfinylimines 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 °C for 45 min. Then, the reaction mixture was cooled down to 23 °C, 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 a further 12 h at the same temperature. After this time, the reaction was quenched with brine (0.5 mL), and the mix-

ture was diluted with EtOAc (15 mL). The resulting suspension was filtered through a short pad of Celite, and the solvent was evaporated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to give pure compounds **3**, yields for compounds **3** are given in Table 5. Physical and spectroscopic data follow.

(R_S)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 3028, 2957, 2869, 1619, 1582, 1496, 1454, 1363, 1180, 1079 cm^{-1}. ^1H NMR: δ = 8.13 (t, *J* = 5.2 Hz, 1 H), 7.37–7.19 (m, 5 H), 3.89–3.75 (m, 2 H), 1.18 (s, 9 H) ppm. ^{13}C NMR: δ = 167.54 (CH), 134.89 (C), 129.30, 128.94, 127.23 (CH), 56.98 (C), 42.74 (CH_2), 22.49 (CH_3) ppm. LRMS (EI): *m/z* (%) = 117 (100) $[M - C_4H_8]^+$, 116 (38), 90 (41), 89 (28), 63 (12), 51 (15).

(R_S)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2962, 2864, 1707, 1619, 1491, 1412, 1362, 1175, 1089, 1014, 908, 823, 730 cm^{-1}. ^1H NMR: δ = 8.10 (t, *J* = 5.1 Hz, 1 H), 7.37–7.28 (m, 2 H), 7.21–7.11 (m, 2 H), 3.87–3.73 (m, 2 H), 1.18 (s, 9 H) ppm. ^{13}C NMR: δ = 166.92 (CH), 133.34, 133.19 (C), 130.67, 129.07 (CH), 57.08 (C), 41.96 (CH_2), 22.48 (CH_3) ppm. LRMS (EI): *m/z* (%) = 257 (1) $[M]^+$, 201 (24), 154 (15), 138 (32), 126 (36), 71 (15), 69 (16), 57 (100), 55 (18), 43 (39), 41 (25). HRMS (ESI): calcd. for $C_8H_8Cl^{35}NOS$ $[M - C_4H_8]^+$ 201.0015; found 201.0011.

(R_S)-2-(4-Acetoxyphenyl)-*N*-(*tert*-butylsulfinyl)ethanimine (3c): Yellow oil. $[\alpha]_D^{23}$ = –63 (*c* = 1.04, CH_2Cl_2). R_f 0.60 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 2958, 2864, 1757, 1620, 1506, 1367, 1191, 1166, 1078, 1013, 910, 849, 729 cm^{-1}. ^1H NMR: δ = 8.12 (t, *J* = 5.2 Hz, 1 H), 7.26–7.21 (m, 2 H), 7.10–7.03 (m, 2 H), 3.90–3.75 (m, 2 H), 2.30 (s, 3 H), 1.19 (s, 9 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 225 (167) $[M - C_4H_8]^+$, 183 (15), 135 (28), 133 (10), 121 (21), 120 (61), 107 (37), 94 (17), 77 (11), 57 (100), 43 (40), 41 (20). HRMS (ESI): calcd. for $C_{10}H_{11}NO_3S$ $[M - C_4H_8]^+$ 225.0460; found 225.0453.

(R_S)-*N*-(*tert*-Butylsulfinyl)-2-(4-hydroxyphenyl)ethanimine (3c′): Yellow solid, m.p. 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 (KBr): $\tilde{\nu}$ = 3180, 2957, 2918, 1762, 1620, 1594, 1517, 1459, 1365, 1267, 1193, 1052, 832 cm^{-1}. ^1H NMR: δ = 8.09 (t, *J* = 5.3 Hz, 1 H), 7.34 (s, 1 H), 7.02 (d, *J* = 8.5 Hz, 2 H), 6.78 (d, *J* = 8.6 Hz, 2 H), 3.81–3.67 (m, 2 H), 1.21 (s, 9 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 183 (70) $[M - C_4H_8]^+$, 169 (28), 135 (28), 121 (35), 120 (84), 108 (11), 107 (46), 94 (27), 77 (18), 57 (100), 41 (22). HRMS (ESI): calcd. for $C_8H_9NO_2S$ $[M - C_4H_8]^+$ 183.0354; found 183.0350.

(R_S)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 3054, 2961, 2929, 1618, 1510, 1470, 1451, 1363, 1266, 1182, 1083, 857, 817, 734 cm^{-1}. ^1H NMR: δ = 8.22 (t, *J* = 5.2 Hz, 1 H), 7.86–7.77 (m, 3 H), 7.69 (s, 1 H), 7.54–7.44 (m, 2 H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1 H), 4.07–3.92 (m, 2 H), 1.20 (s, 9 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 273 (1) $[M - C_4H_8]^+$, 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): calcd. for $C_{12}H_{11}NOS$ $[M - C_4H_8]^+$ 217.0561; found 217.0551.

(R_S)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2967, 2926, 2868, 1620, 1458, 1363, 1165, 1084 cm^{-1}. ^1H NMR: δ = 7.99 (d, *J* = 4.4 Hz, 1 H), 2.72 (m, 1 H), 1.19 (s, 9 H), 1.18 (d, *J* = 1.6 Hz, 3 H), 1.16 (d, *J* = 1.5 Hz, 3 H) ppm. ^{13}C NMR: δ = 173.64 (CH), 56.53 (C), 34.93 (CH), 22.35, 18.96 (CH_3) ppm. LRMS (EI): *m/z* (%) = 175 (2) $[M - C_4H_8]^+$, 119 (20), 57 (100), 56 (52), 55 (11), 43 (12), 42 (16), 41 (82).

(R_S)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2955, 2926, 2858, 1617, 1458, 1362, 1087, 780 cm^{-1}. ^1H NMR: δ = 7.89 (d, *J* = 6.4 Hz, 1 H), 2.57–2.43 (m, 1 H), 1.67–1.43 (m, 4 H), 1.36–1.23 (m, 12 H), 1.21 (s, 9 H), 0.93–0.81 (m, 6 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 232 (3) $[M - C_4H_8]^+$, 231 (16), 149 (19), 97 (9), 71 (11), 70 (20), 69 (13), 61 (16), 57 (47), 55 (15), 45 (18), 43 (100), 41 (17). HRMS (ESI): calcd. 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*-Butylsulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g) and (R_S,1*R*,2*S*,5*R*)-*N*-(*tert*-Butylsulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g′): Mixture of diastereoisomers; colourless oil. R_f 0.64 (hexane/EtOAc, 4:1). IR (film): $\tilde{\nu}$ = 2953, 2925, 2870, 1727, 1617, 1456, 1387, 1365, 1181, 1086, 732, 688 cm^{-1}. LRMS (EI): *m/z* (%) = 215 (20) $[M - C_4H_8]^+$, 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): calcd. 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*-Butylsulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g): ^1H NMR: δ = 8.24 (d, *J* = 7.0 Hz, 1 H), 3.06 (dd, *J* = 7.0, 3.8 Hz, 1 H), 1.95–1.77 (m, 2 H), 1.76–1.56 (m, 3 H), 1.49–1.25 (m, 3 H), 1.21 (s, 9 H), 1.17–0.96 (m, 1 H), 0.93–0.88 (m, 6 H), 0.86 (d, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR: δ = 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) ppm.

(R_S,1*R*,2*S*,5*R*)-*N*-(*tert*-Butylsulfinyl)-(2-isopropyl-5-methylcyclohexyl)methanimine (3g′): ^1H NMR: δ = 7.88 (d, *J* = 7.4 Hz, 1 H), 2.53 (tdd, *J* = 11.4, 7.5, 3.7 Hz, 1 H), 1.97–1.53 (m, 3 H), 1.50–1.22 (m, 3 H), 1.19 (s, 9 H), 1.16–0.97 (m, 2 H), 0.94–0.88 (m, 6 H), 0.78 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR: δ = 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) ppm.

(R_S,2*R*,5*R*)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2962, 2927, 2860, 1713, 1619, 1455, 1362, 1183, 1068, 888 cm^{-1}. ^1H NMR: δ = 4.78–4.71 (m, 2 H), 3.66–3.57 (m, 1 H), 2.42–2.26 (m, 2 H), 2.15–2.04 (m, 1 H), 2.00–1.80 (m, 2 H), 1.75 (s, 3 H), 1.63–1.47 (m, 1 H), 1.45–1.30 (m, 1 H), 1.24 (s, 9 H), 1.09 (d, *J* = 6.3 Hz, 3 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 199 (39) $[M - C_4H_8]^+$, 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): calcd. for $C_{10}H_{17}NOS$ $[M - C_4H_8]^+$ 199.1031; found 199.1029.

(R_S)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2955, 2867, 1620, 1458, 1362, 1186, 1088, 1014, 939, 797, 681 cm^{-1}. ^1H NMR: δ = 8.16–8.03 (m, 1 H), 5.26–5.21 (m, 1 H), 2.72–2.60 (m, 1 H), 2.57–2.43 (m, 1 H), 2.40–2.27 (m, 1 H), 2.25–2.08 (m, 1 H), 1.97–1.84 (m, 1 H), 1.64–1.61 (m, 3 H), 1.21 (s, 9 H), 1.02 (s, 3 H), 0.84 (s, 3 H) ppm. LRMS (EI): *m/z*

(%) = 256 (8) [M + 1]$^+$, 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): calcd. for $C_{10}H_{16}NOS$ [M – C_4H_8]$^+$ 198.0953; found 198.0951.

Data for major isomer: ^{13}C NMR: δ = 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) ppm.

Data for minor isomer: ^{13}C NMR: δ = 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) ppm.

General Procedure for the Synthesis of *N*-*tert*-Butylsulfinylimines 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 °C (7 min at 100 W power and 80 °C for epoxide **5j**). Then, the reaction mixture was cooled down to 23 °C, 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 a further 12 h. After this time, the reaction was quenched with brine (0.5 mL), and the mixture was diluted with EtOAc (15 mL). The resulting suspension was filtered through a short pad of Celite, and the filtrate was concentrated (15 Torr). The resulting residue was purified by column chromatography (hexane/EtOAc) to give pure compounds **3a**, **3c′**, **3f**, and **3j**, yields for these compounds **3** are given in Table 5. Physical and spectroscopic for compound **3j** follow; for the other compounds **3**, the data are given above.

(R_S)-*N*-(*tert*-Butylsulfinyl)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 (film): $\tilde{\nu}$ = 2952, 2925, 2857, 1621, 1458, 1363, 1186, 1086, 675 cm^{-1}. ^{1}H NMR: δ = 8.07 (t, *J* = 4.8 Hz, 1 H), 2.51 (td, *J* = 7.4, 4.8 Hz, 2 H), 1.70–1.55 (m, 2 H), 1.39–1.24 (m, 8 H), 1.20 (s, 9 H), 0.91–0.85 (m, 3 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 175 (19) [M – C_4H_8]$^+$, 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*-Butylsulfinylimines 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–diethyl ether (0.0071 g, 11.8 µL, 0.05 mmol), and molecular sieves (3 Å; 400 mg) in THF (3.0 mL) was stirred at 50 °C for 12 h. Then, the reaction mixture was cooled down to 23 °C, diluted with EtOAc (15 mL), and filtered. The liquid phase was hydrolysed with water (10 mL), and extracted with EtOAc (3 × 15 mL). The organic phase was dried with anhydrous $MgSO_4$, and the solvent was evaporated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to give pure compounds **3**, yields for these compounds are given in Table 5. Physical and spectroscopic are given above.

General Procedure for the Synthesis of Homoallylamine Derivatives 6 from Epoxides 5 (Method C): 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 °C (7 min at 100 W power and 80 °C for epoxide **5j**). Then, the reaction mixture was cooled down to 23 °C, 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 a further 1 h. Then allyl bromide (0.182 g, 0.130 mL, 1.5 mmol) was added, and the reaction mixture was heated for 5 h at 60 °C. 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 pad of Celite and concentrated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to give pure compounds **6**, yields for these compounds are given in Table 6. Physical and spectroscopic follow.

(R_S,2*S*)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 3403, 3127, 2926, 1638, 1599, 1455, 1362, 1175, 1051, 907, 745, 698 cm^{-1}. ^{1}H NMR: δ = 7.37–7.15 (m, 5 H), 5.91–5.73 (m, 1 H), 5.21 (s, 1 H), 5.19–5.14 (m, 1 H), 3.64–3.51 (m, 1 H), 3.32 (d, *J* = 5.8 Hz, 1 H), 2.87 (dd, *J* = 13.7, 7.0 Hz, 1 H), 2.75 (dd, *J* = 13.7, 6.7 Hz, 1 H), 2.48–2.25 (m, 2 H), 1.11 (s, 9 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 209 (3) [M – C_4H_8]$^+$, 118 (100), 104 (27), 102 (11), 92 (8), 91 (41), 65 (8).

(R_S,2*S*)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2924, 1638, 1492, 1408, 1362, 1175, 1091, 1052, 1015, 914, 834, 799, 731 cm^{-1}. ^{1}H NMR: δ = 7.30–7.23 (m, 2 H), 7.18–7.07 (m, 2 H), 5.90–5.72 (m, 1 H), 5.24–5.13 (m, 2 H), 3.55 (m, 1 H), 3.31 (d, *J* = 5.7 Hz, 1 H), 2.84 (dd, *J* = 13.8, 7.1 Hz, 1 H), 2.74 (dd, *J* = 13.8, 6.5 Hz, 1 H), 2.48–2.24 (m, 2 H), 1.12 (s, 9 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 244 (3) [M – C_4H_8]$^+$, 243 (23), 202 (11), 201 (18), 127 (12), 125 (37), 118 (100), 57 (42), 41 (13). HRMS (ESI): calcd. for $C_{11}H_{14}Cl^{35}NOS$ [M – C_4H_8]$^+$ 243.0485; found 243.0487.

(R_S,2*S*)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2925, 1737, 1638, 1598, 1510, 1363, 1239, 1046, 918, 815, 749 cm^{-1}. ^{1}H NMR: δ = 7.88–7.74 (m, 3 H), 7.64 (s, 1 H), 7.50–7.42 (m, 2 H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1 H), 5.92–5.76 (m, 1 H), 5.22 (s, 1 H), 5.20–5.15 (m, 1 H), 3.76–3.61 (m, 1 H), 3.39 (d, *J* = 5.3 Hz, 1 H), 3.06 (dd, *J* = 13.7, 6.8 Hz, 1 H), 2.91 (dd, *J* = 13.7, 6.8 Hz, 1 H), 2.54–2.25 (m, 2 H), 1.11 (s, 9 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 260 (11) [M – C_4H_8]$^+$, 259 (61), 142 (27), 141 (100), 118 (54), 115 (23), 70 (47), 57 (28), 41 (10). HRMS (ESI): calcd. for $C_{15}H_{17}NOS$ [M – C_4H_8]$^+$ 259.1031; found 259.1029.

(R_S,3*S*)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 3239, 2959, 2871, 1638, 1467, 1388, 1364, 1173, 1132, 1053, 1006, 907 cm^{-1}. ^{1}H NMR: δ = 5.89–5.72 (m, 1 H), 5.22–5.14 (m, 1 H), 5.14 (s, 1 H), 3.25–3.12 (m, 1 H), 2.46–2.21 (m, 2 H), 1.97–1.81 (m, 1 H), 1.23 (s, 9 H), 0.91 (d, *J* = 6.8 Hz, 6 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): *m/z* (%) = 162 (2) [M – C_4H_8]$^+$, 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*-Butylsulfinyl)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 (film): $\tilde{\nu}$ = 2925, 2855, 1638, 1457, 1362, 1114, 1054, 993, 913, 723 cm^{-1}. ^{1}H NMR: δ = 5.89–5.70 (m, 1 H), 5.21–5.04 (m, 2 H), 3.53–

3.25 (m, 2 H), 3.22 (d, J = 6.0 Hz, 1 H), 2.49–2.20 (m, 2 H), 1.44–1.21 (m, 12 H), 1.21 (s, 9 H), 0.94–0.82 (m, 3 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): m/z (%) = 273 (1) [M – C_4H_8]$^+$, 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): calcd. 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 D): 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–diethyl ether (0.0071 g, 11.8 μL, 0.05 mmol) and molecular sieves (3 Å; 400 mg) in THF (3.0 mL) was stirred at 50 °C for 12 h. Then, the reaction mixture was cooled down to 23 °C, and the corresponding allylic bromide (1.5 mmol) was added. The resulting mixture was heated for 5 h at 60 °C, and after that it was cooled down, diluted with EtOAc (15 mL), and filtered. The liquid phase was hydrolysed with water (10 mL), and extracted with EtOAc (3 × 15 mL). The organic phase was dried with anhydrous $MgSO_4$, and the solvent was evaporated (15 Torr). The residue was purified by column chromatography (hexane/EtOAc) to give pure compounds **6**, yields for these compounds are given in Table 6. Physical and spectroscopic for compounds **6c** and **6i** follow, and for the other compounds the data are given above.

(R_S,2*S*)-*N*-(*tert*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2925, 1761, 1507, 1442, 1366, 1214, 1192, 1166, 1049, 1016, 910, 852, 732 cm^{-1}. ^{1}H NMR: δ = 7.24–7.17 (m, 2 H), 7.04–6.98 (m, 2 H), 4.90 (s, 1 H), 4.82 (s, 1 H), 3.72–3.56 (m, 1 H), 3.41 (d, J = 3.5 Hz, 1 H), 2.93 (dd, J = 13.7, 6.3 Hz, 1 H), 2.71 (dd, J = 13.8, 6.9 Hz, 1 H), 2.37–2.15 (m, 2 H), 2.29 (s, 3 H), 1.71 (s, 3 H), 1.14 (s, 9 H) ppm. ^{13}C NMR: δ = 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) ppm. LRMS (EI): m/z (%) = 282 (5) [M – C_4H_8]$^+$, 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): calcd. 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*-Butylsulfinyl)-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 (film): $\tilde{\nu}$ = 2954, 2925, 1638, 1442, 1362, 1053, 911, 838, 796, 732 cm^{-1}. ^{1}H NMR: δ = 5.91–5.72 (m, 1 H), 5.27–5.10 (m, 3 H), 3.41–3.25 (m, 1 H), 3.19 (d, J = 8.2 Hz, 1 H), 2.57–2.40 (m, 2 H), 2.37–2.21 (m, 2 H), 2.03–1.89 (m, 1 H), 1.89–1.74 (m, 1 H), 1.63–1.58 (m, 3 H), 1.51–1.40 (m, 1 H), 1.21, 1.20 (2 s, 1:3 ratio, 9 H), 0.98, 0.95 (2 s, 1:3 ratio, 3 H), 0.76, 0.75 (2 s, 1:3 ratio, 3 H) ppm.

Data for major isomer: ^{13}C NMR: δ = 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) ppm. LRMS (EI): m/z (%) = 242 (16) [M – C_4H_8]$^+$, 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): calcd. for $C_{13}H_{23}NOS$ [M – C_4H_8]$^+$ 251.1500; found 241.1513.

Data for minor isomer: ^{13}C NMR: δ = 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) ppm. LRMS (EI): m/z (%) = 242 (15) [M – C_4H_8]$^+$, 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): calcd. 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 ^{1}H and ^{13}C NMR and DEPT spectra for all the reported compounds.

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[1] For reviews, see: a) K. Yamada, K. Tomioka, *Chem. Rev.* **2008**, *108*, 2874–2886; b) S. Kobayashi, Y. Mori, J. S. Fossey, M. M. Salter, *Chem. Rev.* **2011**, *111*, 2626–2704.
[2] For reviews, see: a) S. Kobayashi, H. Ishitani, *Chem. Rev.* **1999**, *99*, 1069–1094; b) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763–2793; c) D. J. Ramón, M. Yus, *Angew. Chem. Int. Ed.* **2004**, *43*, 284–287; *Angew. Chem.* **2004**, *116*, 286–289; d) M. Yus, J. C. González-Gómez, F. Foubelo, *Chem. Rev.* **2011**, *111*, 7774–7854.
[3] a) S. Adachi, R. Moorthy, M. P. Sibi, in: *Copper-Catalyzed Asymmetric Synthesis* (Eds.: A. Alexakis, N. Krauser, S. Woodward), Wiley-VCH, Weinheim, Germany, **2014**, p. 283–324; b) Y. Takemoto, H. Miyabe, in: *Catalytic Asymmetric Synthesis*, 3rd ed. (Ed.: I. Ojima), John Wiley & Sons, Hoboken, **2010**, p. 227–267; c) C. Moberg, E. Wingstrand, *Synlett* **2010**, 355–367; d) M. Shibasaki, S. Matsunaga, N. Kumagai, in: *Acid Catalysis in Modern Organic Synthesis* (Eds.: H. Yamamoto, K. Ishihara), Wiley-VCH, Weinheim, Germany, **2008**, p. 635–720.
[4] a) M. Nakajima, in: *Comprehensive Chirality*, vol. 4 (Eds.: E. M. Carreira, H. Yamamoto), Elsevier E. V., Amsterdam, **2013**, p. 198–209; b) S. E. Denmark, S. Fujimori, in: *Modern Aldol Reactions* (Ed.: R. Mahrwald), Wiley-VCH, Weinheim, Germany, **2005**, p. 229–326.
[5] For reviews, see: a) A. K. Shaw, *J. Indian Chem. Soc.* **2013**, *90*, 1557–1568; b) K. Gademann, in: *Asymmetric Synthesis II* (Eds.: M. Christmann, S. Bräse), Wiley-VCH, Weinheim, Germany, **2012**, p. 317–322; c) M. Yus, J. C. González-Gómez, F. Foubelo, *Chem. Rev.* **2013**, *113*, 5595–5698; d) M. Hiersemann, T. Jaschinski, in: *Comprehensive Chirality*, vol. 2 (Eds.: E. M. Carreira, H. Yamamoto), Elsevier E. V., Amsterdam, **2012**, p. 625–647.
[6] For reviews, see: a) D. Morton, R. A. Stockman, *Tetrahedron* **2006**, *62*, 8869–8905; b) F. Ferreira, C. Botuha, F. Chemla, A. Pérez-Luna, *Chem. Soc. Rev.* **2009**, *38*, 1162–1186; c) M. T. Robak, M. A. Herbage, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 3600–3740; d) F. Foubelo, M. Yus, *Eur. J. Org. Chem.* **2014**, 485–491.
[7] J. L. García Ruano, I. Fernández, M. del Prado Catalina, A. Alcudia Cruz, *Tetrahedron: Asymmetry* **1996**, *7*, 3407–3414.
[8] a) D. J. Weix, J. A. Ellman, *Org. Lett.* **2003**, *5*, 1317–1320; b) D. J. Weix, J. A. Ellman, X. Wang, D. P. Curran, *Org. Synth.* **2005**, *82*, 157–165.
[9] G. Liu, D. A. Cogan, J. A. Ellman, *J. Am. Chem. Soc.* **1997**, *119*, 9913–9914.
[10] G. Liu, D. A. Cogan, T. D. Owens, T. P. Tang, J. A. Ellman, *J. Org. Chem.* **1999**, *64*, 1278–1284.
[11] D. A. Cogan, J. A. Ellman, *J. Am. Chem. Soc.* **1999**, *121*, 268–269.

[12] a) S. Higashibayashi, H. Tohmiya, T. Mori, K. Hashimoto, M. Nakata, *Synlett* **2004**, 457–460; b) Z. Huang, M. Zhang, Y. Wang, Y. Qin, *Synlett* **2005**, 1334–1336; c) Z.-Y. Jiang, W. H. Chan, A. W. M. Lee, *J. Org. Chem.* **2005**, *70*, 1081–1083; d) M. Ardej-Jakubisiak, R. Kawecki, A. Swietlinska, *Tetrahedron: Asymmetry* **2007**, *18*, 2507–2509; e) R. Fan, D. Pu, F. Wen, Y. Ye, X. Wang, *J. Org. Chem.* **2008**, *73*, 3623–3625; f) M. D. Visco, J. T. Reeves, M. A. Marsini, I. Volchkov, C. A. Busacca, A. E. Mattson, C. H. Senanayake, *Tetrahedron Lett.* **2016**, *57*, 1903–1905.
[13] S. Morales, F. G. Guijarro, J. L. García Ruano, M. B. Cid, *J. Am. Chem. Soc.* **2014**, *136*, 1082–1089.
[14] J. F. Collados, E. Toledano, D. Guijarro, M. Yus, *J. Org. Chem.* **2012**, *77*, 5744–5750.
[15] For reviews, see: a) V. K. Aggarwal, in: *Asymmetric Synthesis*, 2nd ed. (Eds.: M. Christmann, S. Bräse), Wiley-VCH, Weinheim, Germany **2008**, p. 56–61; b) V. K. Aggarwal, E. M. McGarrigle, M. A. Shaw, in: *Science of Synthesis*, vol. 2 (Eds.: J. G. De Vries, G. A. Molander, P. A. Evans), Thieme, Stuttgart, Germany, **2011**, p. 311–347.
[16] For reviews, see: a) K. Matsumoto, T. Katsuki, in: *Asymmetric Synthesis*, 2nd ed. (Eds.: M. Christmann, S. Bräse), Wiley-VCH, Weinheim, Germany, **2008**, p. 123–127; b) Z. Li, H. Yamamoto, *Acc. Chem. Res.* **2013**, *46*, 506–518; c) Q.-P. Shi, Z.-H. Shi, N.-G. Li, Y.-P. Tang, W. Li, H. Tang, W. Zhang, M.-Z. Shen, J.-A. Duan, *Curr. Org. Chem.* **2013**, *17*, 2936–2970; d) F. G. Gelalcha, *Adv. Synth. Catal.* **2014**, *356*, 261–299; e) Y. Zhu, Q. Wang, R. G. Cornwall, Y. Shi, *Chem. Rev.* **2014**, *114*, 8199–8256.
[17] a) F. Foubelo, M. Yus, *Tetrahedron: Asymmetry* **2004**, *15*, 3823–3825; b) J. C. González-Gómez, M. Medjahdi, F. Foubelo, M. Yus, *J. Org. Chem.* **2010**, *75*, 6308–6311; c) J. C. González-Gómez, F. Foubelo, M. Yus, *Org. Synth.* **2012**, *89*, 88–97; d) J. A. Sirvent, J. F. Foubelo, M. Yus, *Chem. Commun.* **2012**, *48*, 2543–2545.
[18] Y. Hayashi, *Chem. Sci.* **2016**, *7*, 866–880.
[19] A. Procopio, R. Dalpozzo, A. De Nino, M. Nardi, G. Sindona, A. Tagarelli, *Synlett* **2004**, 2633–2635.
[20] K. M. Sadhu, D. S. Matteson, *Tetrahedron Lett.* **1986**, *27*, 795–798.
[21] a) Y.-W. Suh, N.-K. Kim, W.-S. Ahn, H.-K. Rhee, *J. Mol. Catal. A* **2003**, *198*, 309–316; b) L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs, D. E. De Vos, *Chem. Eur. J.* **2006**, *12*, 7353–7363; c) S. M. Bruno, A. C. Gomes, M. Abrantes, A. A. Valente, M. Pillinger, I. S. Goçalves, *J. Organomet. Chem.* **2015**, *799–800*, 179–183.
[22] M. Medjahdi, J. C. González-Gómez, F. Foubelo, M. Yus, *Eur. J. Org. Chem.* **2011**, 2230–2234.
[23] M. S. Maji, R. Fröhlich, A. Studer, *Org. Lett.* **2008**, *9*, 1847–1850.
[24] F. Ferreira, M. Audouin, F. Chemla, *Chem. Eur. J.* **2005**, *11*, 5269–5278.
[25] M. Medjahdi, J. C. González-Gómez, F. Foubelo, M. Yus, *J. Org. Chem.* **2009**, *74*, 7859–7865.

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One-Pot Reactions

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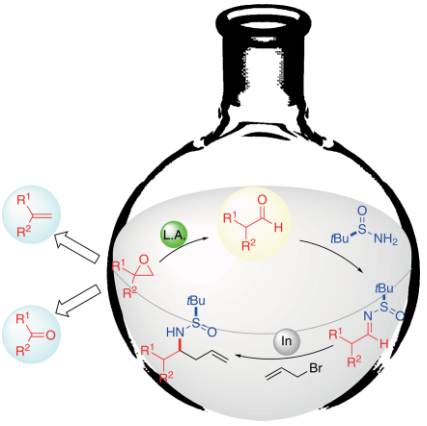
One-Pot Synthesis of *N-tert*-Butylsulfinylimines and Homoallylamine Derivatives from Epoxides



Epoxides are transformed into *N-tert*-butylsulfinylimines in a one-pot procedure involving a Lewis-acid-promoted isomerization to give a carbonyl compound, followed by condensation with *tert*-butanesulfinamide. Homoallylamine derivatives are also accessible in one pot when the formation of the imine is carried out in the presence of indium metal, followed by addition of an allylic bromide.

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