JOC *The Journal of Organic Chemistry*

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Note

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Synthesis of Allylic Amines by Asymmetric Transfer Hydrogenation of α,β-Unsaturated *N*-(*tert*-Butylsulfinyl)imines

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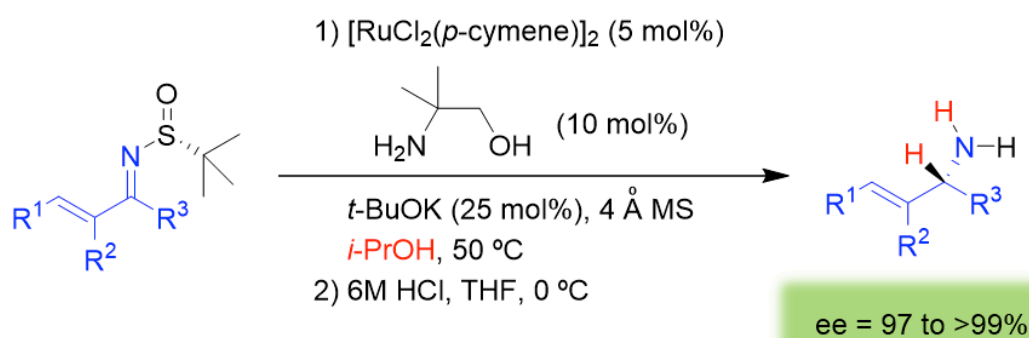
Abstract: Primary allylic amines with enantiomeric excesses from 97 to > 99% have been prepared by asymmetric transfer hydrogenation of α,β-unsaturated *N*-(*tert*-butylsulfinyl)ketimines followed

by removal of the sulfinyl group. The effect caused by different substituents at the C=C bond and at the iminic carbon atom on the chemoselectivity of the reduction has been studied. The desired enantiomer of the final allylic amine can be synthesized by choosing the sulfinyl group with the appropriate absolute configuration.

Keywords: allylic amine; asymmetric transfer hydrogenation; ATH; *N*-sulfinylimine; ruthenium catalyst; isopropyl alcohol.

The amine functionality has proved to be an important constituent of a variety of natural products and pharmacologically active compounds.[1] On the other hand, the C=C bond is very versatile due to the possibility of its derivatization by the functional group transformation strategy. The combination of both an amine and a C=C bond confers on the 2-propenamine substructure a high potential as a synthetic tool for the development of new therapeutic drugs and biologically active compounds. The allylic amine moiety is present in many natural products and compounds known to display biological and pharmacological activities. Some representative examples are cytosinine,[2] gabaculine,[3] lisuride[4] and vigabatrin.[5] Allylic amines are also building blocks for the synthesis of other polyfunctionalized nitrogenated compounds, such as α- or β-aminoacids,[6] alkaloids[7] and carbohydrates.[8] The importance of using enantiomerically enriched compounds in biological chemistry is well known and allylic amines are not an exception. Accordingly, considerable efforts have been made by chemists in order to try to develop efficient methods for their asymmetric synthesis. Among them, we can find: (a) partial hydrogenation of conjugated protected enamines,[9] (b) selective reduction of the C=N bond of α,β-unsaturated imines,[10,11] (c) addition of alkyl or aryl groups to α,β-unsaturated imines,[12] (d) alkenylation of aldimines,[12d,13] (e) nucleophilic substitution reactions in allylic systems,[14] (f) hydroamination of allenes,[15] (g) rearrangement processes.[16]
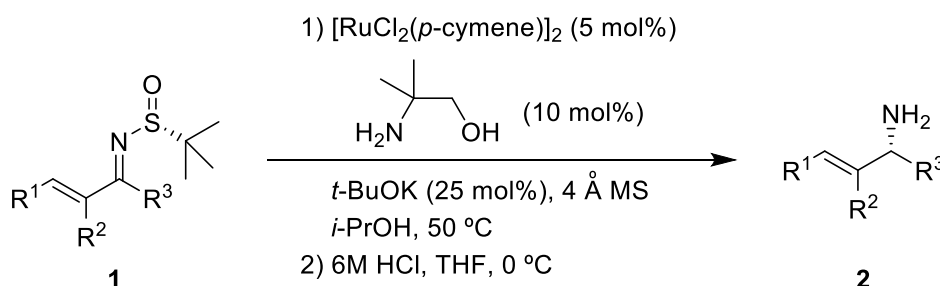
In the last years, our research group has applied a ruthenium-catalyzed asymmetric transfer hydrogenation (ATH) process to the preparation of highly enantiomerically enriched α-branched

primary amines by diastereoselective reduction of *N*-(*tert*-butylsulfinyl)ketimines in isopropyl alcohol followed by removal of the *tert*-butylsulfinyl chiral auxiliary.[17,18] Our experience in this field led us to think that the hydrogen transfer to α,β-unsaturated *N*-(*tert*-butylsulfinyl)ketimines could result in the selective reduction of the imine functionality, affording chiral sulfinamides bearing allylic substituents on the nitrogen atom, which are very interesting compounds, since they could have applications as potential ligands for asymmetric catalysis[19] and could be desulfinylated to give the corresponding deprotected allylic amines.[20] Very few examples of the selective reduction of the C=N bond of conjugated *N*-(*tert*-butylsulfinyl)ketimines can be found in the literature using aluminum or boron hydrides,[11] but high diastereoselectivities could only be obtained with specific substrates containing fluorine atoms in α position to the imine.[11b-d] Although the ATH methodology has proved to be very effective for the asymmetric reduction of several types of imines,[21] to the best of our knowledge, its application to the chemoselective reduction of conjugated sulfinylimines has not been reported. Due to the easy availability of enones[22] and the facility of conversion of ketones into the corresponding sulfinylimines,[23] we thought that the application of our ATH protocol to α,β-unsaturated *N*-(*tert*-butylsulfinyl)ketimines could lead to a straightforward procedure for the asymmetric synthesis of a variety of primary allylic amines. Herein we report the results of our studies on that matter.

We chose imine **1a** (Table 1) as a model substrate for the ATH process and we tested our two optimized conditions for the reduction of aromatic or aliphatic imines.[17b] Isopropyl alcohol was used as a hydrogen source, the catalyst was a ruthenium complex prepared in situ from [RuCl$_2$(*p*-cymene)]$_2$ and the achiral ligand 2-amino-2-methylpropan-1-ol and the reaction was performed at 50 °C. When we used 2.5 mol% of [RuCl$_2$(*p*-cymene)]$_2$ and 5 mol% of the aminoalcohol, the product of selective reduction of the C=N bond was the only one detected in the crude of the reaction, but there was some unreacted starting material left. We were delighted to see that changing to our optimized conditions for aliphatic imines, i.e., 5 mol% of [RuCl$_2$(*p*-cymene)]$_2$ and 10 mol% of the ligand, a complete conversion of the imine was achieved, leading to the expected sulfinamide in practically

pure form, which, after desulfinylation, gave the desired allylic amine **2a** in 80% yield and with an

ee > 99% (Table 1, entry 1).

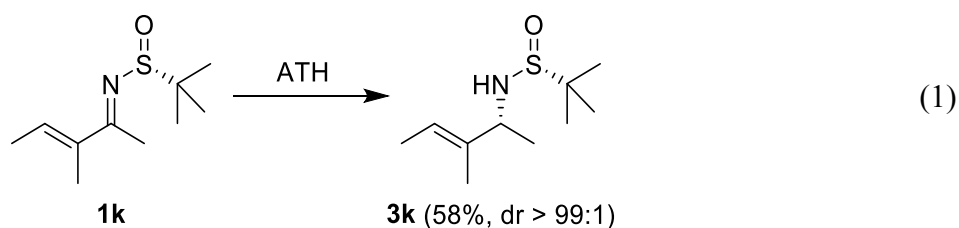**TABLE 1. Ruthenium-catalyzed asymmetric transfer hydrogenation of α,β-unsaturated imines 1.**[a]

Entry	Imine	R^1	R^2	R^3	Amine		
					No.	Yield[b] (%)	ee[c] (%)
1	**1a**	Ph	Me	Me	**2a**	80	>99
2	**1b**	4-MeC$_6$H$_4$	Me	Me	**2b**	75	>99
3	**1c**	4-MeOC$_6$H$_4$	Me	Me	**2c**	80	>99
4	**1d**	4-ClC$_6$H$_4$	Me	Me	**2d**	62	97
5	**1e**	4-NO$_2$C$_6$H$_4$	Me	Me	**2e**	55	>99
6	**1f**	2-naphthyl	Me	Me	**2f**	85	>99
7	**1g**	2-furyl	Me	Et	**2g**	95	>99
8	**1h**	2-thienyl	Me	Et	**2h**	74	97
9	**1i**	2-pyridyl	Me	Me	**2i**	60	>99
10	**1j**	3-pyridyl	Me	Me	**2j**	83	>99
11	**1l**	Ph	Et	Me	**2l**	68[d]	>99
12	**1m**	Ph	Ph	Me	**2m**	80	>99
13	**1n**	Ph	Me	Et	**2n**	78	>99
14	*ent*-**1n**	Ph	Me	Et	*ent*-**2n**	60	>99[e]

[a] The solution of imine **1** (0.9 mmol) in *i*-PrOH (7 mL) was added to a solution of the ruthenium catalyst [prepared by refluxing a mixture of [RuCl$_2$(*p*-cymene)]$_2$ (0.045 mmol), 2-amino-2-methylpropan-1-ol (0.09 mmol) and 4 Å molecular sieves (0.4 g) in *i*-PrOH (1.5 mL)] at 50 ºC. Then, *t*-BuOK (0.225 mmol, as a 0.1 M solution in *i*-PrOH) was added and the reaction was stirred at the same temperature for 2.5 h. [b] Yield of amine **2** isolated after acid-base extraction based on the starting imine **1**. [c] Determined for the corresponding benzamide by HPLC using a chiral column (see the Supporting Information for details). The (*R*)-enantiomer was the major product in all cases. [d] Estimated by ^{1}H NMR (see reference 29). [e] The (*S*)-enantiomer was the major product in this case.

Encouraged by this excellent result, we decided to study the substrate scope of our procedure. First, we tested different aromatic groups as R^1 substituents. When an alkyl (imine **1b**), an electron-releasing (imine **1c**) or an electron-withdrawing (imines **1d-e**) group was introduced at the *para* position of the benzene ring, the reduction of the imine functionality was also successful and only one enantiomer of the allylic amines could be detected by HPLC analysis, except for imine **1d**, which afforded the expected amine **2d** with a slightly lower ee of 97% (Table 1, entries 2-5). A 2-naphthyl substituent in R^1 led to the desired allylic amine **2f** in high yield and with > 99% ee (Table 1, entry 6). The same excellent enantioselectivities were obtained when our methodology was applied to imines **1g-j** bearing heteroaromatic substituents in R^1 (Table 1, entries 7-10), although for amine **2h**, bearing a 2-thienyl group, the ee very slightly decreased to 97%. It is worth noting that this is the first time that we have been able to reduce imines bearing pyridyl substituents using our ATH protocol. The obtained allylic amines **2i-j** could be especially interesting for further synthetic applications, since the pyridyl substructure is present in a variety of natural products and biologically active compounds.[24]

We also tested the ATH of imine **1k** (eq 1) in order to see if the diastereoselectivity was also high when an aliphatic substituent was introduced in R^1. The expected sulfinamide **3k** (eq 1) was obtained in practically pure form and only one diastereoisomer could be detected by ^{1}H NMR.[25] Unfortunately, after the desulfinylation step, a small amount of reaction crude was obtained as a complicated mixture. We also tried to prepare the racemic amine by reaction of (*E*)-3-methylpent-3-en-2-one with NH_3,[26] but again a mixture of products was obtained, which could not be separated. Our attempts to isolate the hydrochloride salt instead of the free amine were also unsuccessful. We assume that some side reactions could take place when the preparation of this amine is attempted, which complicate its isolation in pure form.

1k   **3k** (58%, dr > 99:1)   (1)

1o: R² = H, R³ = Me
1p: R² = Me, R³ = Ph

3o: R² = H, R³ = Me
3p: R² = Me, R³ = Ph

4o: R² = H, R³ = Me
4p: R² = Me, R³ = Ph

5o: R² = H, R³ = Me
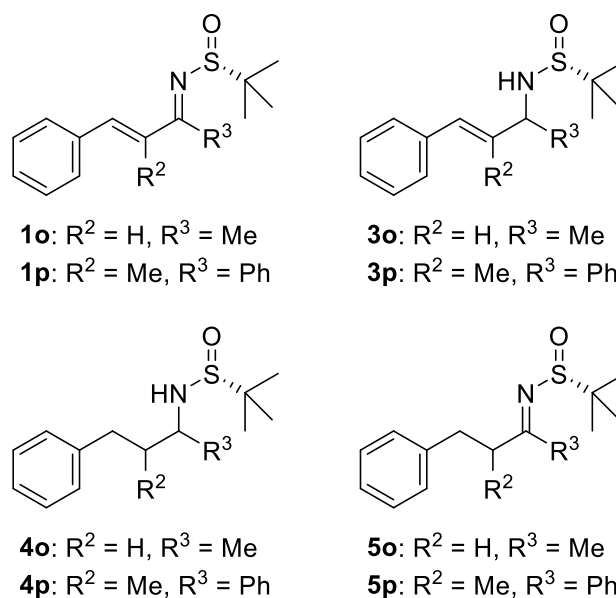5p: R² = Me, R³ = Ph

Figure 1. Structures of imines **1o** and **1p** and the products resulting from their ATH reactions.

Next, we studied the influence on the stereoselectivity of substituent R^2. Keeping the R^1 = Ph and the R^3 = Me substituents of the model substrate **1a**, we varied the substituent R^2 to Et and Ph (imines **1l-m**). This variation did not cause any detriment of the enantioselectivity of the final product, since amines **2l-m** were isolated with excellent ee's (Table 1, entries 11 and 12). However, the importance of having a substituent in R^2 was pointed out when imine **1o** (Figure 1), in which R^2 = H, was tested as substrate. Its preparation from (*E*)-4-phenylbut-3-en-2-one gave a ca. 2:1 mixture of geometrical isomers of the C=N bond, which could not be separated by column chromatography. According to our previous experience,[27] the ATH of this mixture could lead to a lower ee of the final amine, but we attempted the reduction anyway. The ¹H NMR spectrum of the crude of the ATH reaction suggested the formation, as the major product, of sulfinamide **4o** (Figure 1), resulting from the reduction of both the C=N and the C=C bonds of **1o**, together with monoreduction products **3o** and **5o** (molar ratio **3o**:**4o**:**5o** ≈ 2:8:1, according to the integration of the ¹H NMR spectrum). Therefore, the substructure (*E*)-Ph-CH=CH- in the starting imine seems to favor the formation of the double reduction product in the ATH process.[28,29]

On the other hand, the change of the R^3 substituent of the model substrate **1a** to an Et group (imine **1n**) did not have any influence on either the yield or the stereoselectivity (compare entries 1 and 13 in Table 1), and the expected amine **2n** was isolated with an excellent optical purity. However, when the ATH of imine **1p** (Figure 1), with R^3 = Ph, was performed, a complex mixture of products was obtained, in which imine **5p**, derived from reduction of the C=C bond of substrate **1p**, seemed to predominate and we could also identify allylic sulfinamide **3p** in a small amount (molar ratio **3p**:**5p** ≈ 1:7, according to the ^{1}H NMR spectrum of the reaction crude). Therefore, a substrate with a phenyl group conjugated to the imine functionality is not suitable for reaching our goal of preparing enantiomerically enriched allylic amines.

Finally, we explored the possibility of preparing the enantiomeric allylic amines by changing the absolute configuration of the *tert*-butylsulfinyl chiral auxiliary. Imine *ent*-**1n**, with a sulfur atom with (*S*)-configuration, was prepared and submitted to our ATH protocol, which afforded the expected (*S*)-amine with > 99% ee. Therefore, both enantiomers of an allylic amine can be prepared using the same ruthenium catalyst by choosing the right conformation of the chiral auxiliary.

In our opinion, the transformation described herein represents a very efficient methodology for the preparation of allylic amines with very high optical purities from easily available enones. Our ATH process is more convenient than the few procedures of selective reduction of the C=N bond of conjugated *N*-(*tert*-butylsulfinyl)imines reported so far, which employ stoichiometric amounts of aluminum or boron reducing agents. Some advantages of our ATH protocol in comparison with the reported examples are: (a) it is much more versatile, since a broader variety of allylic amines can be prepared with excellent ee's; (b) our solvent and hydrogen source is isopropyl alcohol, which is environmentally friendly and appropriate for industrial scale applications;[30] (c) the ATH process is promoted by a catalytic amount of a ruthenium complex bearing a very cheap achiral ligand, which is very convenient from an economical point of view. The easy availability of α,β-unsaturated ketones, their straightforward transformation into both enantiomers of *N*-(*tert*-butylsulfinyl)imines and the very high diastereoselectivity of our ATH procedure can convert our proposal into a very useful tool for organic synthesis.

In conclusion, the results presented herein show that our ATH procedure can be effectively used to perform the chemo- and diastereoselective reduction of α,β-unsaturated *N*-(*tert*-butylsulfinyl)ketimines, which yields chiral sulfinamides bearing allylic substituents on the nitrogen atom that can be easily transformed into highly optically enriched allylic amines. The chemoselectivity has shown to depend on the nature of the substituents of the C=C bond and the iminic carbon atom. Allylic amines with excellent ee's are obtained when R^1 is an aromatic or heteroaromatic group, R^2 is an alkyl or aryl substituent and R^3 is an alkyl group. However, the ATH reaction preferentially gives the product of reduction of both the C=C and the C=N bonds when imines with an (*E*)-1,2-disubstituted alkene moiety are used as substrates. A phenyl group conjugated to the imine complicates the ATH reaction outcome, giving non synthetically useful mixtures of products. Primary allylic amines with the desired stereochemistry can be prepared by using the sulfinyl chiral auxiliary with the appropriate absolute configuration.

Experimental Section

General Information

All glassware was dried in an oven at 100 ºC and cooled to room temperature under argon before use. All reactions were carried out under an argon atmosphere. All starting materials needed for the synthesis of imines **1** and *ent*-**1n**, [RuCl$_2$(*p*-cymene)]$_2$ and 2-amino-2-methylpropan-1-ol were commercially available and were used as received. *tert*-BuOK was heated in a Kugel-Rohr distillation apparatus at 170-180 °C under vacuum for 4 h before use. Commercially available 4 Å molecular sieves were activated by heating in a Kugel-Rohr distillation apparatus at 120 ºC under vacuum for 5h before use. Commercially available anhydrous isopropyl alcohol was used as solvent in all the transfer hydrogenation reactions. Column chromatography was performed with silica gel 60 of 230-400 mesh. Thin layer chromatography (TLC) was performed on precoated silica gel plates; detection was done by UV_{254} light and staining with phosphomolybdic acid (solution of 1 g of phosphomolybdic acid in 24 mL of absolute ethanol); R_f values are given under these conditions. Melting points (mp) are uncorrected. Unless otherwise stated, NMR samples were prepared using

CDCl$_3$ as solvent. The internal references used for NMR spectra were tetramethylsilane (TMS) for ^{1}H NMR and CDCl$_3$ for ^{13}C NMR; chemical shifts are given in δ (ppm) and coupling constants (*J*) in Hz. ^{13}C NMR assignments were made on the basis of DEPT experiments. Infrared (FT-IR) spectra were obtained on a spectrophotometer equipped with an attenuated total reflectance (ATR) accessory. Mass spectra (EI) were obtained at 70 eV; fragment ions in *m/z* with relative intensities (%) in parenthesis are given. HRMS were measured with electron impact (EI) ionization at 70 eV and a double focusing mass analyzer (magnetic and electric fields). HPLC analyses were performed at 20 ºC.

Synthesis of *N*-(*tert*-butylsulfinyl)imines 1 and *ent*-1n. Imines **1** and *ent*-**1n** were prepared by condensation of the corresponding α,β-unsaturated ketones (5 mmol) with (*R*)-2-methylpropane-2-sulfinamide (for **1**) or (*S*)-2-methylpropane-2-sulfinamide (for *ent*-**1n**), following a procedure described by our research group.[23] (*E*)-3-methylpent-3-en-2-one (precursor of imine **1k**) was commercially available and was used as received. The other α,β-unsaturated ketones were synthesized as previously described.[31] The corresponding physical and spectroscopic data for compounds **1** and *ent*-**1n** follow.

(*R*)-2-Methyl-*N*-[(*E*)-3-methyl-4-phenylbut-3-en-2-ylidene]propane-2-sulfinamide (1a): 975 mg (74% yield); brownish oil; R_f 0.21 (hexane/ethyl acetate: 5/1); [α]$_D^{20}$ -52.0 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1611, 1569, 1068 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.29 (9H, s), 2.11 (3H, d, *J* = 1.1 Hz), 2.63 (3H, s), 7.25-7.43 (6H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.6, 18.9, 22.6, 57.2, 128.1, 128.5, 129.7, 136.1, 136.6, 139.0, 178.7; *m/z* (DIP) 263 (M[+], <1%), 207 (58), 158 (88), 143 (100); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_8$]$^+$ Calcd for C$_{11}$H$_{13}$NOS 207.0718; Found 207.0707.

(*R*)-2-Methyl-*N*-[(*E*)-3-methyl-4-(*p*-tolyl)but-3-en-2-ylidene]propane-2-sulfinamide (1b): 1.179 g (85% yield); brownish oil; R_f 0.40 (hexane/ethyl acetate: 3/1); [α]$_D^{25}$ -40.9 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1646, 1559, 1077 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.29 (9H, s), 2.11 (3H, d, *J* = 1.2 Hz),

2.38 (3H, s), 2.62 (3H, s), 7.21 (2H, d, J = 8.1 Hz), 7.26-7.30 (3H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.5, 18.8, 21.3, 22.4, 57.0, 129.1, 129.6, 133.7, 136.1, 138.12, 138.14, 178.7; *m/z* (DIP) 277 (M$^+$, 1%), 221 (59), 172 (98), 157 (100), 132 (31); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$SO]$^+$ Calcd for C$_{12}$H$_{14}$N 172.1126; Found 172.1123.

(R)-N-[(E)-4-(4-Methoxyphenyl)-3-methylbut-3-en-2-ylidene]-2-methylpropane-2-sulfinamide

(1c): 1.335 g (91% yield); yellow oil; R_f 0.56 (hexane/ethyl acetate: 1/1); [α]$_D^{20}$ -33.2 (*c* 1.1, CH$_2$Cl$_2$); IR (neat) 1604, 1562, 1251, 1066 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.29 (9H, s), 2.13 (3H, d, J = 1.1 Hz), 2.62 (3H, s), 3.84 (3H, s), 6.93 (2H, d, J = 8.7 Hz), 7.24 (1H, br s), 7.35 (2H, d, J = 8.7 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.6, 18.9, 22.5, 55.4, 57.0, 113.9, 129.1, 131.4, 136.0, 137.2, 159.6, 178.9; *m/z* (DIP) 293 (M$^+$, 1%), 237 (49), 188 (100), 173 (78), 148 (38); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_8$]$^+$ Calcd for C$_{12}$H$_{15}$NO$_2$S 237.0823; Found 237.0817.

(R)-N-[(E)-4-(4-Chlorophenyl)-3-methylbut-3-en-2-ylidene]-2-methylpropane-2-sulfinamide

(1d): 1.385 g (93% yield); yellow oil; R_f 0.24 (hexane/ethyl acetate: 3/1); [α]$_D^{23}$ -33.7 (*c* 1.5, CH$_2$Cl$_2$); IR (neat) 1629, 1572, 1067 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.30 (9H, s), 2.09 (3H, d, J = 1.2 Hz), 2.64 (3H, s), 7.23 (1H, br s), 7.31, 7.38 (2H each, 2 d, J = 8.5 Hz each); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.6, 18.9, 22.5, 57.2, 128.7, 130.9, 134.0, 134.6, 135.0, 139.5, 178.3; *m/z* (DIP) 299 (M$^+$ + 2, <1%), 297 (M$^+$, <1%), 243 (28), 241 (78), 194 (37), 192 (100), 180 (13), 179 (94), 178 (40), 177 (34); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$]$^+$ Calcd for C$_{11}$H$_{11}$ClNOS 240.0250; Found 240.0254.

(R)-2-Methyl-N-[(E)-3-methyl-4-(4-nitrophenyl)but-3-en-2-ylidene]propane-2-sulfinamide (1e): 694 mg (45% yield); orange oil; R_f 0.54 (hexane/ethyl acetate: 1/1); [α]$_D^{20}$ +7.1 (*c* 1.2, CH$_2$Cl$_2$); IR (neat) 1593, 1575, 1340, 1067 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.31 (9H, s), 2.11 (3H, d, J = 1.2 Hz), 2.66 (3H, s), 7.29 (1H, br s), 7.52, 8.26 (2H each, 2 d, J = 8.7 Hz each); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.8, 18.9, 22.6, 57.6, 123.7, 130.3, 133.0, 142.0, 143.3, 147.0, 177.6; *m/z* (DIP) 308 (M$^+$,

<1%), 252 (63), 203 (18), 189 (100), 188 (46); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_8$]$^+$ Calcd for C$_{11}$H$_{12}$N$_2$O$_3$S 252.0569; Found 252.0562.

(R)-2-Methyl-N-[(E)-3-methyl-4-(2-naphthyl)but-3-en-2-ylidene]propane-2-sulfinamide **(1f)**:

987 mg (63% yield); orange solid; mp 79-81 ºC; R_f 0.54 (hexane/ethyl acetate: 3/1); [α]$_D^{27}$ -13.3 (c 1.0, CH$_2$Cl$_2$); IR (neat) 1559, 1076 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.31 (9H, s), 2.19 (3H, d, J = 1.2 Hz), 2.68 (3H, s), 7.44 (1H, br s), 7.47-7.52 (3H, m), 7.84-7.86 (4H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.5, 18.7, 22.3, 57.0, 126.3, 126.4, 127.0, 127.5, 127.7, 128.0, 128.9, 132.6, 132.9, 133.9, 135.9, 139.0, 178.4; m/z (DIP) 313 (M$^+$, <1%), 257 (28), 208 (100), 194 (43), 193 (76); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$SO]$^+$ Calcd for C$_{15}$H$_{14}$N 208.1126; Found 208.1115.

(R)-N-[(E)-1-(Furan-2-yl)-2-methylpent-1-en-3-ylidene]-2-methylpropane-2-sulfinamide **(1g)**:

869 mg (65% yield); brownish oil; R_f 0.46 (hexane/ethyl acetate: 3/1); [α]$_D^{20}$ -13.9 (c 1.0, CH$_2$Cl$_2$); IR (neat) 1624, 1554, 1067 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.23-1.29 (12H, m), 2.21 (3H, d, J = 1.0 Hz), 2.96-3.16 (2H, m), 6.53 (1H, dd, J = 3.5, 1.8 Hz), 6.63 (1H, d, J = 3.5 Hz), 7.06 (1H, br s), 7.54 (1H, d, J = 1.8 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.0, 14.8, 22.7, 24.8, 57.2, 112.4, 114.3, 122.9, 134.1, 143.8, 152.5, 182.8; m/z (DIP) 267 (M$^+$, 2%), 211 (46), 163 (100), 148 (20); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$]$^+$ Calcd for C$_{10}$H$_{12}$NO$_2$S 210.0589; Found 210.0590.

(R)-2-Methyl-N-[(E)-2-methyl-1-(thiophen-2-yl)pent-1-en-3-ylidene]propane-2-sulfinamide

(1h): 1.120 g (79% yield); yellow oil; R_f 0.55 (hexane/ethyl acetate: 5/1); [α]$_D^{23}$ -23.8 (c 1.0, CH$_2$Cl$_2$); IR (neat) 1618, 1559, 1067 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.26-1.31 (12H, m), 2.23 (3H, d, J = 1.0 Hz), 3.01-3.15 (2H, m), 7.12-7.14 (1H, m), 7.28 (1H, br s), 7.41-7.45 (1H, m), 7.49 (1H, d, J = 5.1 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.9, 14.9, 22.6, 24.8, 57.1, 127.4, 128.5, 129.0, 131.4, 134.0, 140.0, 182.8; m/z (DIP) 283 (M$^+$, 1%), 227 (100), 178 (76), 164 (27), 163 (27); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$SO]$^+$ Calcd for C$_{10}$H$_{12}$NS 178.0690; Found 178.0690.

(R)-2-Methyl-*N*-[(E)-3-methyl-4-(pyridin-2-yl)but-3-en-2-ylidene]propane-2-sulfinamide **(1i)**: 780 mg (59% yield); yellow oil; R_f 0.30 (ethyl acetate); $[\alpha]_D^{20}$ -29.6 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1634, 1582, 1081 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.30 (9H, s), 2.28 (3H, d, *J* = 1.0 Hz), 2.66 (3H, s), 7.19-7.24 (1H, m), 7.27 (1H, s), 7.40 (1H, d, *J* = 7.6 Hz), 7.73 (1H, td, *J* = 7.6, 1.9 Hz), 8.67-8.70 (1H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.5, 18.9, 22.5, 57.3, 122.3, 125.4, 134.3, 136.2, 141.8, 149.5, 155.6, 178.4; *m/z* (DIP) 264 (M$^+$, <1%), 208 (15), 159 (10), 146 (11), 145 (100), 144 (34); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$]$^+$ Calcd for C$_{10}$H$_{11}$N$_2$OS 207.0592; Found 207.0574.

(R)-2-Methyl-*N*-[(E)-3-methyl-4-(pyridin-3-yl)but-3-en-2-ylidene]propane-2-sulfinamide **(1j)**: 714 mg (54% yield); yellow oil; R_f 0.46 (hexane/ethyl acetate: 1/1); $[\alpha]_D^{27}$ -56.4 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1623, 1570, 1065 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.30 (9H, s), 2.10 (3H, d, *J* = 0.9 Hz), 2.65 (3H, s), 7.22 (1H, br s), 7.32-7.36 (1H, m), 7.67-7.71 (1H, m), 8.55 (1H, dd, *J* = 4.9, 1.5 Hz), 8.62-8.64 (1H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.7, 18.9, 22.6, 57.4, 123.3, 131.9, 132.5, 136.5, 141.1, 148.9, 150.6, 177.9; *m/z* (DIP) 264 (M$^+$, < 1%), 208 (22), 159 (100), 145 (15); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{14}$H$_{20}$N$_2$OS 264.1296; Found 264.1296.

(R)-2-Methyl-*N*-[(E)-3-methylpent-3-en-2-ylidene]propane-2-sulfinamide **(1k)**: 906 mg (90% yield); yellow oil; R_f 0.35 (hexane/ethyl acetate: 3/1); $[\alpha]_D^{27}$ -238.4 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1570, 1360, 1067 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.25 (9H, s), 1.84-1.89 (6H, m), 2.46 (3H, s), 6.42-6.53 (1H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 12.5, 15.0, 18.4, 22.3, 56.7, 133.8, 138.7, 178.4; *m/z* (DIP) 201 (M$^+$, 1%), 145 (91), 97 (100), 82 (19); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$SO]$^+$, Calcd for C$_6$H$_{10}$N 96.0813; Found 96.0818.

(R)-*N*-[(E)-3-ethyl-4-phenylbut-3-en-2-ylidene]-2-methylpropane-2-sulfinamide **(1l)**: 902 mg (65% yield); yellow oil; R_f 0.32 (hexane/ethyl acetate: 3/1); $[\alpha]_D^{25}$ -40.6 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1570, 1067 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.14 (3H, t, *J* = 7.4 Hz), 1.30 (9H, s), 2.60-2.65 (5H, m), 7.23 (1H, br s), 7.32-7.40 (5H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.2, 19.5, 20.7, 22.6,

57.0, 128.2, 128.6, 129.2, 135.9, 136.5, 145.0, 178.5; *m/z* (DIP) 277 (M$^+$, 2%), 221 (62), 172 (81), 158 (37), 157 (100), 130 (29); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$SO]$^+$ Calcd for C$_{12}$H$_{14}$N 172.1126; Found 172.1130.

(*R*)-*N*-[(*E*)-3,4-Diphenylbut-3-en-2-ylidene]-2-methylpropane-2-sulfinamide (1m): 976 mg (60% yield); yellow solid; mp 120-122 ºC; R_f 0.45 (hexane/ethyl acetate: 2/1); [α]$_D^{26}$ +50.9 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1621, 1600, 1070 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.09 (9H, s), 2.60 (3H, s), 6.98-7.17 (7H, m), 7.18-7.38 (4H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 19.9, 22.3, 57.4, 127.4, 128.2, 128.5, 128.6, 129.8, 130.6, 135.3, 135.5, 137.8, 142.9, 178.4; *m/z* (DIP) 325 (M$^+$, <1%), 269 (40), 220 (77), 206 (50), 205 (100), 178 (65); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$SO]$^+$ Calcd for C$_{16}$H$_{14}$N 220.1126; Found 220.1130.

(*R*)-2-Methyl-*N*-[(*E*)-2-methyl-1-phenylpent-1-en-3-ylidene]propane-2-sulfinamide (1n): 999 mg (72% yield); yellow oil; R_f 0.70 (hexane/ethyl acetate: 1/1); [α]$_D^{20}$ -43.0 (*c* 1.0, CH$_2$Cl$_2$); IR (neat) 1616, 1567, 1070 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.25-1.32 (12H, m), 2.09 (3H, d, *J* = 1.0 Hz), 3.08-3.17 (2H, m), 7.29-7.42 (6H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.0, 14.9, 22.7, 25.0, 57.2, 128.1, 128.4, 129.7, 135.6, 136.7, 137.3, 183.5; *m/z* (DIP) 277 (M$^+$, 1%), 221 (53), 172 (62), 158 (29), 157 (100); HRMS (EI/Q-TOF) m/z: [M - C$_4$H$_9$]$^+$ Calcd for C$_{12}$H$_{14}$NOS 220.0796; Found 220.0799.

(*S*)-2-Methyl-*N*-[(*E*)-2-methyl-1-phenylpent-1-en-3-ylidene]propane-2-sulfinamide (*ent*-1n): 1.096 g (79% yield); [α]$_D^{20}$ +50.0 (*c* 1.0, CH$_2$Cl$_2$).

Asymmetric Transfer Hydrogenation of imines 1 and *ent*-1n. General procedure. A mixture of [RuCl$_2$(*p*-cymene)]$_2$ (28 mg, 0.045 mmol), 2-amino-2-methylpropan-1-ol (14 mg, 0.09 mmol), 4 Å molecular sieves (0.4 g) and anhydrous *i*-PrOH (1.5 mL) was heated up to 90 ºC (oil bath temperature) for 20 min. During this heating period, the initially orange reaction mixture turned into

a dark red color. The reaction was then cooled to 50 ºC and a solution of the imine **1** or *ent*-**1n** (0.9 mmol) in *i*-PrOH (7 mL) and *t*-BuOK (2.25 mL of a 0.1 M solution in *i*-PrOH, 0.225 mmol) were successively added. After completion of the reaction (2.5 h, monitored by TLC), the reaction mixture was passed through a small column of silica gel, the column was washed with ethyl acetate and the combined organic phases were evaporated. In general, the obtained sulfinamides were quite pure and could be directly submitted to the desulfinylation step. If necessary, the sulfinamide can be purified at this stage by column chromatography (silica gel, hexane/ethyl acetate). Physical and spectroscopic data for compound **3k** follow.

(*R*)-2-Methyl-*N*-[(*R,E*)-3-methylpent-3-en-2-yl]propane-2-sulfinamide (3k): 590 mg (58% yield); yellow solid; mp 78-80 ºC; R_f 0.22 (hexane/ethyl acetate: 1/1); $[\alpha]_D^{30}$ -122.7 (*c* 1.0, CH_2Cl_2); IR (neat) 1619, 1460, 1390, 1046; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (9H, s), 1.26 (3H, d, *J* = 6.5 Hz), 1.58-1.63 (6H, m), 3.11 (1H, d, *J* = 3.6 Hz), 3.81-3.92 (1H, m), 5.46-5.56 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4, 13.0, 19.4, 22.4, 55.1, 57.3, 120.9, 137.3; *m/z* (DIP) 203 (M^+, <1%), 147 (40), 83 (100), 57 (52); HRMS (EI/Q-TOF) m/z: $[M - C_4H_8]^+$, Calcd for $C_6H_{13}NOS$ 147.0718; Found 147.0715.

General procedure for the removal of the sulfinyl group. Isolation of amines 2 and *ent*-2n. The crude mixture of the transfer hydrogenation reaction was dissolved in THF (2 mL) and cooled to 0 ºC. A 6 M aqueous HCl solution (0.2 mL) was added and the mixture was stirred until the reaction was complete according to TLC (1-2 h). Then, H_2O (10 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The organic layers were discarded. The aqueous layer was basified with a 2 M aqueous NaOH solution until pH 12 and extracted with ethyl acetate (3 × 15 mL). The combined organic phases were dried ($MgSO_4$). After filtration and evaporation of the solvent, pure amines **2** and *ent*-**2n** were obtained. The corresponding physical and spectroscopic data follow.

(R,E)-3-Methyl-4-phenylbut-3-en-2-amine (2a):[32] 116 mg (80% yield); colorless oil; R_f 0.42 (CH$_2$Cl$_2$/MeOH: 9/1); $[\alpha]_D^{20}$ -6.8 (c 0.8, CH$_2$Cl$_2$, >99% ee); IR (neat) 3372, 1598, 1443, 1030 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.25 (3H, d, J = 6.6 Hz), 1.75 (2H, br s), 1.86 (3H, d, J = 1.3 Hz), 3.59 (1H, q, J = 6.6 Hz), 6.44 (1H, s), 7.16-7.35 (5H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.9, 22.4, 54.8, 123.5, 126.2, 128.1, 129.0, 138.2, 143.4; m/z 161 (M$^+$, 15%), 146 (97), 129 (100); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{11}$H$_{15}$N 161.1204; Found 161.1197.

(R,E)-3-Methyl-4-(p-tolyl)but-3-en-2-amine (2b): 118 mg (75% yield); yellow oil; R_f 0.45 (CH$_2$Cl$_2$/MeOH: 10/1); $[\alpha]_D^{27}$ +7.3 (c 1.0, CH$_2$Cl$_2$, >99% ee); IR (neat) 3457, 3317, 1512, 1372 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.26 (3H, d, J = 6.3 Hz), 1.85 (3H, d, J = 1.2 Hz), 2.09 (2H, br s), 2.33 (3H, s), 3.57-3.64 (1H, m), 6.40 (1H, s), 7.11-7.37 (4H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.9, 21.2, 22.2, 54.9, 123.7, 127.0, 128.9, 129.0, 135.2, 135.9; m/z 175 (M$^+$, <1%), 160 (65), 143 (100); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{12}$H$_{17}$N 175.1361; Found 175.1355.

(R,E)-4-(4-Methoxyphenyl)-3-methylbut-3-en-2-amine (2c): 138 mg (80% yield); brownish oil; R_f 0.46 (CH$_2$Cl$_2$/MeOH: 9/1); $[\alpha]_D^{20}$ -5.0 (c 1.0, CH$_2$Cl$_2$, >99% ee); IR (neat) 3362, 3292, 1509, 1246, 1176 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.22 (3H, d, J = 6.6 Hz), 1.49 (2H, br s), 1.84 (3H, s), 3.57 (1H, q, J = 6.6 Hz), 3.78 (3H, s), 6.37 (1H, br s), 6.86 (2H, d, J = 8.7 Hz), 7.19 (2H, d, J = 8.7 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.8, 22.3, 55.0, 113.5, 123.0, 130.1, 130.7, 141.6, 157.9; m/z 191 (M$^+$, 21%), 176 (100), 159 (84); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{12}$H$_{17}$NO 191.1310; Found 191.1303.

(R,E)-4-(4-Chlorophenyl)-3-methylbut-3-en-2-amine (2d) : 109 mg (62% yield) ; yellow oil; R_f 0.38 (CH$_2$Cl$_2$/MeOH: 10/1); $[\alpha]_D^{24}$ +5.4 (c 2.0, CH$_2$Cl$_2$, 97% ee); IR (neat) 3358, 3274, 1490, 1166 cm^{-1} ; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.26 (3H, d, J = 6.6 Hz), 1.56 (2H, br s), 1.85 (3H, d, J = 1.3 Hz), 3.60 (1H, q, J = 6.6 Hz), 6.41 (1H, s), 7.19, 7.30 (2H each, 2 d, J = 8.5 Hz each); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.0, 22.4, 54.8, 122.4, 128.3, 130.3, 131.9, 136.7, 144.3; m/z 197 (M$^+$ + 2, 4%),

195 (M$^+$, 13%), 182 (34), 180 (100), 165 (29), 163 (74); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{11}$H$_{14}$ClN 195.0815; Found 195.0802.

(R,E)-3-Methyl-4-(4-nitrophenyl)but-3-en-2-amine (2e): 102 mg (55% yield); brownish oil; R_f 0.41 (CH$_2$Cl$_2$/MeOH: 9/1); [α]$_D^{20}$ -10.2 (*c* 1.1, CH$_2$Cl$_2$, >99% ee); IR (neat) 3365, 3281, 1509, 1337 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.28 (3H, d, *J* = 6.6 Hz), 1.41 (2H, br s), 1.91 (3H, s), 3.63 (1H, q, *J* = 6.6 Hz), 6.54 (1H, s), 7.40, 8.18 (2H each, 2 d, *J* = 8.8 Hz each); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.6, 22.4, 54.7, 121.8, 123.5, 129.6, 145.2, 145.9, 148.0 ; *m/z* 191 (M$^+$ - Me, 100%), 174 (12); HRMS (EI/Q-TOF) m/z: [M - Me]$^+$ Calcd for C$_{10}$H$_{11}$N$_2$O$_2$ 191.0821; Found 191.0817.

(R,E)-3-Methyl-4-(2-naphthyl)but-3-en-2-amine (2f): 162 mg (85% yield); yellow solid; mp 62-64 ºC; R_f 0.52 (CH$_2$Cl$_2$/MeOH: 20/1) ; [α]$_D^{27}$ -6.4 (*c* 2.7, CH$_2$Cl$_2$, >99% ee); IR (neat) 3163, 1599, 1451, 1372 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.29 (3H, d, *J* = 6.6 Hz), 1.83-2.04 (5H, m), 3.64 (1H, q, *J* = 6.6 Hz), 6.59 (1H, s), 7.37-7.46 (3H, m), 7.70-7.81 (4H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.1, 22.4, 54.9, 123.7, 125.6, 126.1, 127.5, 127.6, 127.7, 127.8, 127.9, 132.1, 133.5, 135.7, 143.9; *m/z* 211 (M$^+$, 40%), 196 (100), 179 (85); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{15}$H$_{17}$N 211.1361; Found 211.1349.

(R,E)-1-(Furan-2-yl)-2-methylpent-1-en-3-amine (2g) : 141 mg (95% yield); brownish oil; R_f 0.24 (CH$_2$Cl$_2$/MeOH: 10/1); [α]$_D^{22}$ -8.3 (*c* 1.0, CH$_2$Cl$_2$, >99% ee) ; IR (neat) 3360, 3247, 1577, 1490, 1018 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.87 (3H, t, *J* = 7.4 Hz), 1.47-1.56 (4H, m), 1.94 (3H, d, *J* = 1.2 Hz), 3.29 (1H, t, *J* = 6.8 Hz), 6.24-6.26 (2H, m), 6.39-6.41 (1H, m), 7.37 (1H, dd, *J* = 1.9, 0.7 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 10.9, 14.1, 28.5, 61.4, 108.3, 111.2, 114.3, 140.8, 141.0, 153.4; *m/z* 165 (M$^+$, 20%), 150 (12), 136 (100); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{10}$H$_{15}$NO 165.1154; Found 165.1142.

(R,E)-2-Methyl-1-(thiophen-2-yl)pent-1-en-3-amine (2h) : 121 mg (74% yield); brownish oil; R_f 0.26 (CH$_2$Cl$_2$/MeOH: 10/1); $[\alpha]_D^{21}$ +9.2 (*c* 1.0, CH$_2$Cl$_2$, 97% ee); IR (neat) 3361, 3253, 1589, 1491, 1250 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.88 (3H, t, *J* = 7.4 Hz), 1.48-1.69 (4H, m), 1.94 (3H, d, *J* = 1.2 Hz), 3.33 (1H, t, *J* = 6.9 Hz), 6.57 (1H, s), 6.90-7.04 (2H, m), 7.18-7.26 (1H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 10.9, 14.0, 28.4, 61.6, 118.7, 124.5, 126.6, 126.8, 140.1, 141.1; *m/z* 181 (M$^+$, 11%) 166 (16), 152 (100); HRMS (EI/Q-TOF) m/z: [M - C$_2$H$_5$]$^+$ Calcd for C$_8$H$_{10}$NS 152.0534; Found 152.0526.

(R,E)-3-Methyl-4-(pyridin-2-yl)but-3-en-2-amine (2i): 88 mg (60% yield); yellow oil; R_f 0.14 (CH$_2$Cl$_2$/MeOH: 10/1); $[\alpha]_D^{21}$ -3.8 (*c* 0.2, CH$_2$Cl$_2$, >99% ee); IR (neat) 3348, 3249, 1647, 1585, 1467, 1431 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.27 (3H, d, *J* = 6.7 Hz), 1.78 (2H, br s), 2.06 (3H, d, *J* = 2.0 Hz), 3.62 (1H, q, *J* = 6.9 Hz), 6.52 (1H, br s), 7.05-7.10 (1H, m), 7.21-7.24 (1H, m), 7.58-7.65 (1H, m), 8.57-8.59 (1H, m); ^{13}C NMR (100 MHz, CDCl$_3$) 14.3, 22.2, 54.9, 120.8, 123.1, 124.1, 135.9, 148.1, 149.1, 157.2; *m/z* 162 (M$^+$, <1%), 118 (100); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{10}$H$_{14}$N$_2$ 162.1157; Found 162.1138.

(R,E)-3-Methyl-4-(pyridin-3-yl)but-3-en-2-amine (2j): 121 mg (83% yield); brownish oil; R_f 0.58 (CH$_2$Cl$_2$/MeOH: 20/1); $[\alpha]_D^{25}$ -5.2 (*c* 1.0, CH$_2$Cl$_2$, >99% ee); IR (neat) 3423, 3269, 1568, 1026 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.26 (3H, d, *J* = 6.7 Hz), 1.64 (2H, br s), 1.87 (3H, s), 3.63 (1H, q, *J* = 6.7 Hz), 6.41 (1H, s), 7.22-7.27 (1H, m), 7.55-7.58 (1H, m), 8.41-8.51 (2H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.2, 22.4, 54.6, 119.9, 123.1, 133.9, 136.0, 146.1, 147.2, 150.2; *m/z* 162 (M$^+$, 11%), 147 (100), 118 (13); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{10}$H$_{14}$N$_2$ 162.1157; Found 162.1138.

(R,E)-3-Ethyl-4-phenylbut-3-en-2-amine (2l): 107 mg (68% yield); yellow oil; R_f 0.52 (CH$_2$Cl$_2$/MeOH: 10/1); $[\alpha]_D^{26}$ -14.2 (*c* 1.0, CH$_2$Cl$_2$, >99% ee); IR (neat) 3384, 3313, 1606, 1493, 1454 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.09 (3H, t, *J* = 7.5 Hz), 1.28 (3H, d, *J* = 6.6 Hz), 2.18-2.44 (2H, m), 3.64-3.67 (1H, m), 6.47 (1H, s), 7.19-7.34 (5H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ

14.1, 22.0, 23.3, 52.1, 123.1, 126.3, 128.2, 128.7, 138.3, 149.7; *m/z* 175 (M$^+$, <1%), 160 (15), 146 (23), 131 (100); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{12}$H$_{17}$N 175.1361; Found 175.1357.

(*R,E*)-3,4-Diphenylbut-3-en-2-amine (2m): 161 mg (80% yield); brownish oil; R_f 0.46 (CH$_2$Cl$_2$/MeOH: 10/1); [α]$_D^{30}$ -15.4 (*c* 1.2, CH$_2$Cl$_2$, >99% ee); IR (neat) 3371, 3299, 1441, 1077 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.20 (3H, d, *J* = 6.6 Hz), 1.65 (2H, br s), 3.88 (1H, qd, *J* = 6.6, 1.2 Hz), 6.57 (1H, d, *J* = 1.2 Hz), 6.80-6.97 (2H, m), 6.98-7.20 (5H, m), 7.26-7.37 (3H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 22.5, 54.4, 124.8, 126.5, 127.2, 127.9, 128.6, 129.1, 129.2, 136.9, 139.4, 148.1; *m/z* 224 (M$^+$ + 1, 18%), 223 (M$^+$, 100%), 208 (66), 178 (53), 146 (41); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{16}$H$_{17}$N 223.1361; Found 223.1358.

(*R,E*)-2-Methyl-1-phenylpent-1-en-3-amine (2n): 123 mg (78% yield); brownish oil; R_f 0.54 (CH$_2$Cl$_2$/MeOH: 9/1); [α]$_D^{20}$ -35.1 (*c* 1.0, CH$_2$Cl$_2$, >99% ee); IR (neat) 3328, 3259, 1444 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.91 (3H, t, *J* = 7.4 Hz), 1.49-1.61 (4H, m), 1.82 (3H, d, *J* = 1.4 Hz), 3.32 (1H, t, *J* = 6.9 Hz), 6.41 (1H, s), 7.17-7.21 (1H, m), 7.25-7.34 (4H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 11.0, 13.2, 28.5, 61.6, 125.5, 126.2, 128.1, 129.0, 138.1, 141.6; *m/z* 175 (M$^+$, 3%), 160 (16), 146 (100); HRMS (EI/Q-TOF) m/z: [M]$^+$ Calcd for C$_{12}$H$_{17}$N 175.1361; Found 175.1355.

(*S,E*)-2-Methyl-1-phenylpent-1-en-3-amine (*ent*-2n): 95 mg (60% yield); brownish oil; [α]$_D^{20}$ +42.7 (*c* 1.2, CH$_2$Cl$_2$, >99% ee).

Determination of the enantiomeric excesses of amines 2 and *ent*-2n. Amine **2** or *ent*-**2n** (0.4 mmol) was dissolved in CH$_2$Cl$_2$ (3 mL) and cooled to 0 ºC. A 2 M aqueous NaOH solution (5 mL) was added and the mixture was stirred for 5 minutes. Benzoyl chloride (93 μL, 0.8 mmol) was added dropwise, the cold bath was removed and the reaction mixture was stirred at room temperature for 3 h. Then, layers were separated, the organic phase was washed with a 2 M aqueous NaOH solution (3 × 5 mL) and the aqueous layers were discarded. The organic phase was washed with brine (2 × 5

mL) and then dried (MgSO$_4$). After filtration and evaporation of the solvent, the expected benzamides were obtained, which were analyzed by HPLC on a chiral column using a 254 nm UV detector and a mixture of hexane and isopropyl alcohol as eluent (see the Supporting Information for details about the conditions for the HPLC analysis and the retention times of the two enantiomers of all the benzamides). The major enantiomer was the one with lower retention time in all cases, except for amine *ent*-**2n**. The racemic amines were prepared by reductive alkylation of NH$_3$ with the corresponding α,β-unsaturated ketones, following a literature procedure,[26] and were benzoylated as described above. The (*R*) absolute configuration of the major enantiomer of amine **2a** was determined by comparison of the sign of the specific rotation of its benzamide with the data reported in the literature.[32] The major enantiomer of the benzamides derived from amines **2b-n** was, in all cases, the one having a lower retention time in HPLC, as it was the case for the benzamide of amine **2a**. Thus, we assume that, by analogy, the absolute configuration of amines **2b-n** is also (*R*).

Determination of the diastereomeric ratio of sulfinamide 3k. To estimate the diastereomeric purity of compound **3k**, a mixture of its diastereoisomers was prepared by a simple one-pot desulfinylation-resulfinylation procedure described in the literature.[25] Comparison of the ^{1}H NMR spectra of **3k** and the diastereomeric mixture showed that **3k** was a single diastereoisomer.

Acknowledgements

Supporting Information. HPLC retention times of benzamides derived from amines **2** and *ent*-**2n**; copies of ^{1}H NMR and ^{13}C NMR spectra for all imines **1**, all amines **2** and sulfinamide **3k**; a

copy of the ^{1}H NMR spectrum of the mixture of diastereoisomers of **3k**; HPLC traces for the determination of the enantiomeric excesses of amines **2** and *ent*-**2n**. This material is available free of charge via the Internet at http://pubs.acs.org.

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