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π–π Stacking versus Steric Effects in Stereoselectivity Control: Highly Diastereoselective Synthesis of *syn*-1,2-Diarylpropylamines

José L. García Ruano,*[a] José Alemán,[b] Inés Alonso,[a] Alejandro Parra,[a] Vanesa Marcos,[a] and José Aguirre[c]

Dedicated to Professor Dr. Joan Bosch on the occasion of his 60th birthday

Abstract: *N*-Arylarylideneamines react with sulfinylbenzyl carbanions derived from 2-(*p*-tolylsulfinyl)toluenes (*S*)-**1** and (*S*)-**2**, affording epimeric mixtures at C1 of 1,2-diarylethyl- and 1,2-diarylpropylamine derivatives. The sulfinyl group completely controls the configuration at C2 in the reactions of (*S*)-**2**. The configuration at C1 depends on the electron density of the ring adjacent to the iminic carbon atom which is modulated by π–π stacking interactions with the ring joined to the carbanionic centre. The stereoselectivity was controlled by modifying the acceptor character of the arylideneamine ring with appropriate substituents, the formation of the highly selective (*R*) configuration at C1 being made possible by electron-donating groups. *N*-(2,4,6-Trimethoxyphenyl)arylideneamines have been shown to be suitable starting materials for the preparation of (*R*)-1,2-diarylethyl- and (*1R*,*2S*)-1,2-diarylpropylamines (*syn* epimers) in a highly stereoselective manner.

Keywords: pi–pi stacking · amines · asymmetric synthesis · diastereoselectivity · arylimines · carbanions

Introduction

The 2-arylethylamine skeleton is present in a wide variety of natural products.[1] As a consequence, the search for new and efficient methods for preparing this structure with one or two chiral centres, in all their possible configurations, continues to be an interesting challenge in asymmetric synthesis. One of the most successful routes for synthesising chiral amines is the nucleophilic addition of organometallic reagents to C=N double bonds.[2] The use of benzylmetals as the nucleophile in these reactions is the most direct retrosynthetic route for preparing 2-arylethylamines (C–C disconnection), which is especially interesting with prochiral benzylmetals that allow the simultaneous creation of two chiral carbon atoms in the ethylenic fragment. *N*-Sulfinylimines are among the best iminic electrophiles because of their high conversion and stereoselective control as well as the ease with which the resulting *N*-sulfinylamines can be converted into free amines.[3] However, the stereoselectivity of their reactions with benzylmetals is not usually very satisfactory.[4] We have recently solved this problem by using 2-(*p*-tolylsulfinyl)benzyl carbanions as nucleophiles, which react with *N*-sulfinylaldimines[5] (Scheme 1) and -ketimines[6] as electrophiles with complete stereoselective control and very high yields. These reactions were also successfully used in the synthesis of 1,2-aminalcohols[6,7] and sulfides,[8] starting from the corresponding oxygenated and sulfurated carbanions.

The success of these reactions is a consequence of a double asymmetric induction process directed by the configuration of the two sulfinyl groups in the reagents. The sulfinyl group on the nucleophile controls the configuration of the benzylic position (1,4-asymmetric induction process) in all cases, whereas the configuration of the nitrogenated stereogenic centre depends on the relative configuration of the sulfur atom on the electrophile. When the configurations of

[a] Prof. Dr. J. L. García Ruano, Dr. I. Alonso, A. Parra, V. Marcos
Departamento de Química Orgánica (C-I)
Universidad Autónoma de Madrid
Cantoblanco, 28049-Madrid (Spain)
Fax: (+34) 91497466
E-mail: joseluis.garcia.ruano@uam.es

[b] Dr. J. Alemán
Current Address: Center for Catalysis, Department of Chemistry
University of Aarhus, 8000 Aarhus C (Denmark)

[c] Dr. J. Aguirre
Departamento de Ciencia Básicas, Universidad de Luján
Luján (Argentina)

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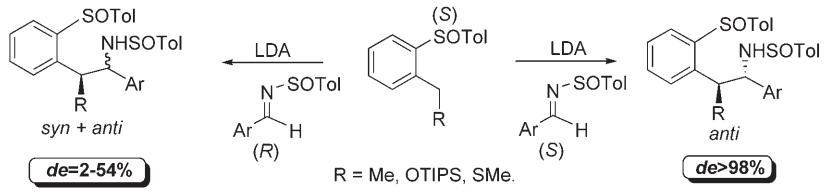
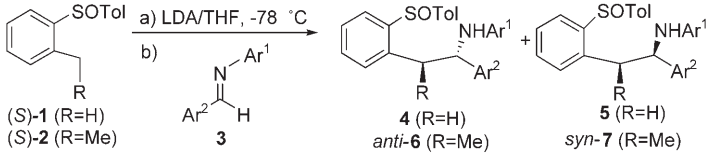


Scheme 1. Reactions of the 2-(*p*-tolylsulfinyl)benzyl carbanions with different *N*-sulfinylimines.

the two sulfinyl groups are identical (matched pair), stereoselective control is complete, thus providing one of the best methods for obtaining enantiopure 1,2-disubstituted 2-phenylethylamines with an *anti* stereochemistry (right-hand equation, Scheme 1).[5–8] However, the method was not appropriate for obtaining *syn* derivatives because the reactions of reagents with opposite configurations at their sulfinyl groups (mismatched pair) yielded mixtures of isomers (left-hand equation, Scheme 1). These results have been explained by a stereochemical model based exclusively on steric effects[5–8] (see below).

With the aim of searching for an alternative method to the synthesis of *syn* diastereoisomers we decided to investigate the reactions of the carbanions derived from (*S*)-**1** and (*S*)-**2** (Scheme 2) with other imine derivatives by using a



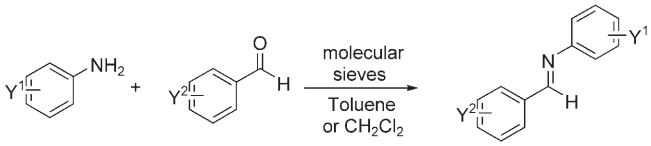
Scheme 2. Reactions of carbanions derived from (*S*)-**1** and (*S*)-**2** with imine derivatives **3** using a single asymmetric induction procedure.

single asymmetric induction procedure. We first investigated the behaviour of differently substituted *N*-arylarylideneamines **3** (Scheme 2) in order to explore the effect of the sulfinyl group on the nucleophile in controlling the configuration of the aminic carbon atom (1,5-asymmetric single induction process). This study revealed a strong relationship between the stereoselectivity of the reaction and the electron density on the rings next to the C=N moiety; therefore modulation of the electronic density on the rings allowed efficient control of the configuration at the iminic carbon atom. As this was not compatible with the previously reported stereochemical model, which was based only on steric grounds, a new model had to be postulated. Moreover, this dependence provided the basis for the design of a new protocol able to afford the enantiopure 1,2-disubstituted 2-phenylethylamine skeleton with *syn* stereochemistry. The results obtained in this study are reported herein.

Results and Discussion

Addition to imines: *N*-Phenylbenzylideneamine (**3a**) is the imine used as reference in this study. We have also studied the behaviour of different *N*-phenylarylideneamines **3b–p** (Table 1) and *N*-arylbenzylideneamines **3′b–p** (Table 1), with substituents on only one of the rings, and **3″a–h** with both rings substituted (Table 1). All these imines were synthesised by condensation of the anilines with the corresponding benzaldehydes in CH_2Cl_2 or toluene[9] in the presence of molecular sieves in good-to-excellent yields (see the Supporting Information).

Table 1. Synthesis of the aldimines used in this study.[a]



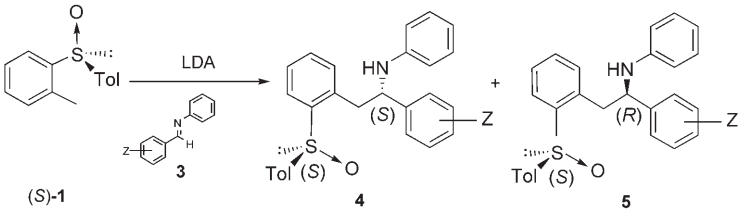
Imine Y^1=H	Y^2	Imine Y^2=H	Y^1	Imine Y^1=2,4,6-tri-MeO	Y^2
3a	H	–	–	**3″a**	H
3b	4-CN	**3′b**	4-CN	**3″b**	4-CN
3c	4-CF_3	–	–	**3″c**	4-CF_3
3d	3-Cl	**3′d**	3-Cl	**3″d**	3-Cl
3e	4-Cl	**3′e**	4-Cl	**3″e**	4-Cl
3f	3-MeO	**3′f**	3-MeO	**3″f**	3-MeO
3g	4-Me	**3′g**	4-Me	**3″g**	4-Me
3h	4-MeO	**3′h**	4-MeO	**3″h**	4-MeO
3i	2-MeO	**3′i**	2-MeO	–	–
3j	2-Br	–	–	–	–
–	–	**3′k**	4-NMe_2	–	–
3l	2,4-di-MeO	**3′l**	2,4-di-MeO	–	–
3m	3,4-di-MeO	**3′p**	3,4-di-MeO	–	–
3n	3,4,5-tri-MeO	–	–	–	–
3o	2,4,6-tri-MeO	–	–	–	–
3p	2-naphthyl	**3′m**	2,3,4-tri-MeO	–	–

[a] See the Supporting Information for details of the yields and experimental procedure.

The reaction of the γ-sulfinyl carbanion derived from (*S*)-**1** with *N*-phenylarylideneamines **3** provides a mixture of two diastereoisomers (**4** and **5**, Table 2) that differ in the configuration at the aminic carbon atom and which, in most cases, can be separated by chromatography (for configurational assignment see the Supporting Information).[10] *N*-Phenylbenzylideneamine **3a** affords a 40:60 mixture of **4a** and **5a** (entry 4, Table 2) with an (R,S_S) configuration for the major compound. Reactions with imines **3f–i**, **3l** and **3o**, bearing electron-donating groups on the arylidene moiety (entries 5–10, Table 2), provide mixtures with a larger proportion of the isomer **5**. The highest selectivity is observed for the 2,4,6-trimethoxy derivative **3o** (*de* = 84%, entry 10, Table 2).

In contrast, reactions with imines **3b–d** (entries 1–3, Table 2), supporting electron-withdrawing groups at the substituted ring, afford mixtures in which the (S,S_S)-**4** isomer is the major amine. The best stereoselectivity is observed for

Table 2. Reactions of (*S*)-**1** with *N*-phenylarylideneamines **3**.



Entry	Z	d.r.[a]	Product	Yield [%][b]
1	4-CN (**3b**)	85:15	**4b/5b**	84
2	4-CF_3 (**3c**)	65:35	**4c/5c**	82
3	3-Cl (**3d**)	66:34	**4d/5d**	79
4	H (**3a**)	40:60	**4a/5a**	80
5	3-MeO (**3f**)	37:63	**4f/5f**	65
6	4-Me (**3g**)	23:77	**4g/5g**	69
7	4-MeO (**3h**)	22:78	**4h/5h**	80
8	2-MeO (**3i**)	17:83	**4i/5i**	79
9	2,4-di-MeO (**3l**)	9:91	**4l/5l**	76
10	2,4,6-tri-MeO (**3o**)	8:92	**4j/5j**[c]	74 [d]

[a] Diastereomeric ratio, as measured by ^{1}H NMR spectroscopy. [b] Combined yield. [c] The yield of **4j** was too low for full charachterisation. [d] The yield for compound **5j** only.

the 4-nitrile derivative **3b** ($de = 70\%$, entry 1, Table 2). In all these cases, the observed *de* is clearly dependent on the electronic character of the substituent on the imine.

The plot of $\log\{[(S,S_S)\text{-}\mathbf{4}]/[(R,S_S)\text{-}\mathbf{5}]\}$ obtained for the monosubstituted arylideneamines **3a–f** and **3h** against Hammett's constants (σ)[11] for the Z substituents gives a straight line with a slope $\rho = 3.029$ and $R^2 = 0.94$ (Figure 1), which clearly indicates a linear relationship between the stereoselectivity of the reaction of (*S*)-**1** with **3**. A lower electron density on the ring joined to the carbon atom of the C=N group favours the formation of the (S,S_S) isomers. Other significant conclusions that can be drawn from Table 2 are the large influence of *ortho* substituents (an even larger effect than the *para* position, compare entries 7 and 8 of Table 2) and the additive nature of the effects of the substituents (compare entries 7 and 8 with 9 and 10 of Table 2).

We also studied the reactions of the sulfinyl carbanion derived from (*S*)-**2** with the *N*-phenylarylideneamines **3** (Table 3). The stereoselectivity of these reactions, in which the two stereogenic centres are simultaneously formed, must be controlled by the combined effects of the sulfinyl group and the steric interactions of the methyl group adjacent to the carbanionic centre. Therefore, some differences can be expected with respect to the results obtained from (*S*)-**1** (Table 2). Evidence was found in the reaction with **3a**, which affords a 91:9 mixture of ($1S,2S,S_S$)-**6a** (*anti*) and ($1R,2S,S_S$)-**7a** (*syn*) (entry 5, Table 3). Both compounds exhibit the same configuration at the benzylic carbon atom next to the sulfinyl group (C2), which completely controls the stereoselectivity at this position, as has been observed in the reactions of (*S*)-**2** with all the electrophiles studied so far.[5–8,12] Compounds *anti*-**6** and *syn*-**7** differ in the configuration of the aminic carbon atom

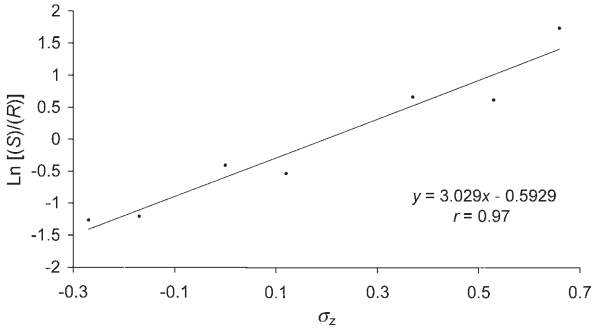
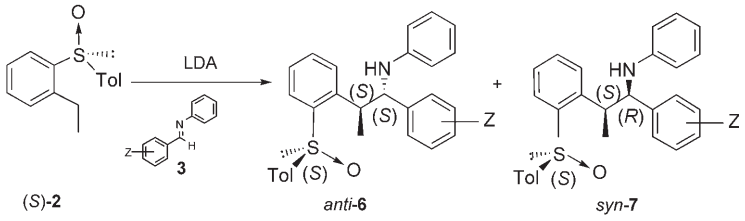


Figure 1. Hammett plot of $\log\{[(S,S_S)\text{-}\mathbf{4}]/[(R,S_S)\text{-}\mathbf{5}]\}$ against σ_Z for some of the reactions in Table 2.

Table 3. Reactions of (*S*)-**2** with *N*-phenylarylideneamines **3**.



Entry	Z	d.r. (*anti*/*syn*)[a]	Product	Yield [%][b]
1	4-CN (**3b**)	≥98:≤2	**6b**	90
2	4-CF_3 (**3c**)	≥98:≤2	**6c**	69
3	3-Cl (**3d**)	97:3	**6d/7d**[d]	72
4	[c](**3p**)	94:6	**6p/7p**[d]	70
5	H (**3a**)	91:9	**6a/7a**	72
6	3-MeO (**3f**)	81:19	**6f/7f**	64
7	4-Me (**3g**)	78:22	**6g/7g**	80
8	2-Br (**3j**)	77:23	**6j/7j**	55
9	4-MeO (**3h**)	41:59	**6h/7h**	61
10	2-MeO (**3i**)	27:73	**6i/7i**[e]	61
11	3,4-di-MeO (**3m**)	33:67	**6m/7m**	76
12	2,4-di-MeO (**3l**)	≤2:≥98	**7l**	62
13	2,4,6-tri-MeO (**3o**)	33:66	**6o/7o**	54

[a] Diastereomeric ratio, as measured by ^{1}H NMR spectroscopy. [b] Combined yield. [c] (*E*)-*N*-(6-Naphthylmethylene)aniline was used. [d] The yields of **7d** and **7p** were too low for full characterisation. [e] The ORTEP structure of compound *syn*-**7i** can be found in the Supporting Information.

(C1), as it was observed in reactions of **3a** with (*S*)-**1**. However, the stereoselectivity of the reaction of **3a** with (*S*)-**2** (82% *de* in favour of the isomer with an *S* configuration at C1, entry 5 Table 3) is higher than that observed in the reaction with (*S*)-**1** (20% *de* with the major isomer exhibiting an *R* configuration at C1, entry 4 in Table 2), which must be attributed to the above-mentioned influence of the methyl group of the benzylic centre, which favours the formation of the *S* configuration at C1. This difference in behaviour occurs with all the imines studied, as shown in Table 3.

The influence of the electron density on the arylidene rings on the stereoselectivity is analogous to that observed in the reactions with (*S*)-**1**.[13] Electron-withdrawing groups favour the *S* configuration at C1, making the reactions almost completely stereoselective and yielding diastereoisomers *anti*-**6** (entries 1–4, Table 3). In contrast, electron-donating groups increase the proportion of epimers with the *R* configuration at C1, thus increasing the proportion of the *syn*-**7** isomers in the reaction mixtures (entries 6–13, Table 3). This isomer becomes the only product obtained from **3l** (entry 12, Table 3). As was observed in the reactions shown in Table 2, *ortho* groups have an even larger influence than *para* groups on the stereoselectivity of the reaction (compare entries 9 and 10, Table 3). The presence of two substituents on the aryl group has an additive effect on the diastereoselectivity of the reaction (see Table 3). Remarkably, the reaction with *N*-phenyl-2,4,6-trimethoxybenzylideneamine (**3o**) evolved with only moderate selectivity (33% *de*, entry 13 Table 3) despite the presence of the three favourably located methoxy groups. The steric interactions of the *ortho* substituents on the ring with the C=N group, which precludes their coplanarity, must be responsible for this anomalous behaviour.

Stereochemical model: The strong influence of electronic effects on the stereoselectivity of the reactions of Li-**1** and Li-**2** with the imines **3** clearly indicates that the stereochemical model assumed to explain the results obtained with *N*-sulfinylimines, which was based exclusively on steric considerations, is not valid for *N*-arylimines. On the other hand, this strong electronic influence suggests that some kind of interaction between the aromatic rings of the reagents controls the relative stability of the possible transition states and therefore the stereoselectivity of these reactions. By assuming a high electron density (strong electron-donating character) on the phenyl group joined to the carbanionic carbon atom and a low electron density (electron-accepting character) on the aryl group adjacent to the iminic carbon atom, a stabilising donor–acceptor interaction between the two rings can be considered whose magnitude should be dependent on the nature of the substituents. The stereochemical model so far proposed to explain the stereoselectivity of the reactions of (*S*)-**1** and (*S*)-**2** with *N*-sulfinylimines is based on the assumption that the nucleophile is the chelated species Li-**2** which adopts a half-chair conformation **A** (Figure 2). However, the rings in structure **A** cannot adopt the spatial arrangement necessary for π–π stacking because

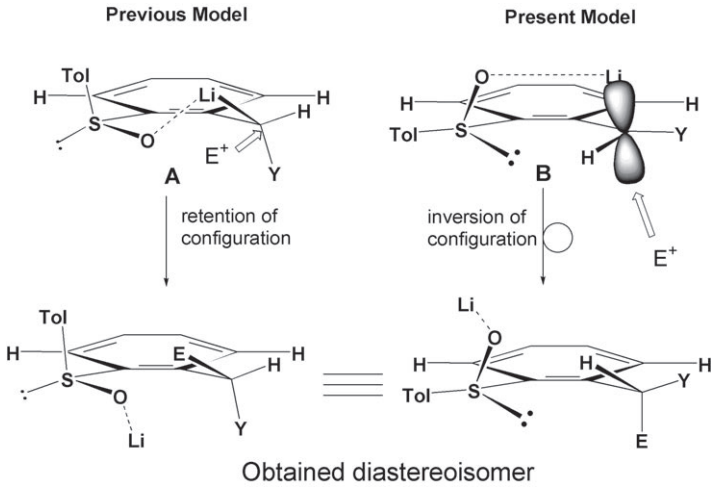


Figure 2. Comparison of the stereochemical models used to explain the reaction results.

the quasi-axial arrangement of the *p*-tolyl and methyl groups (so oriented to relieve their allylic strain with the *ortho*-protons) precludes the rings from reaching the proper distance. Thus, we have considered other possible structures of the chelated species Li-**1** and Li-**2**. By considering the fact that stabilisation of the benzylic carbanion requires coplanarity with the aromatic π system (which does not exist in species **A**), we believed the chelated species **B** (Figure 2) to be an alternative to **A** (also supported by DFT calculations). It adopts a quasi-boat type conformation with the hydrogen on the carbon atom and the lone-pair electron of the sulfur atom as the only substituents able to occupy the flagpoles of the boat and therefore be orientated inwards. This structure would allow π–π stacking interactions with the arylidene ring as the imine approaches the lower face of **B**.

The structures of these complexes have also been studied by DFT at the B3LYP[14] level of theory by using the Gaussian 03 program.[15] The standard 6-31G(d)[16] basis set was used for all the atoms. Harmonic frequencies were calculated at the same level of theory to characterise the stationary points and to determine the zero-point energies (ZPE). In the model structures the methyl group of the *p*-tolyl ring was eliminated and two molecules of dimethyl ether were included as a simplified model solvent. Among the possible conformations, with the methyl and sulfinyl groups in different orientations, only those with a boat-type arrangement could be optimised (Figure 3). Even in the case in which the methyl group at the benzylic position is directed towards the *ortho*-sulfinyl group (**B2**), only the boat-type conformation with the lone-pair electron conjugated to the aromatic π system was detected. This reveals the high contribution of this conjugation to the stability of the anion. The charge on the benzylic carbanion is stabilised by delocalisation through the aromatic ring, which is more effective in **B1** than in **B2** (the corresponding natural charges[17] being −0.59 and −0.60 a.u., respectively). Accordingly, a higher value of the Wiberg bond index between C1 and C2 is observed in **B1**

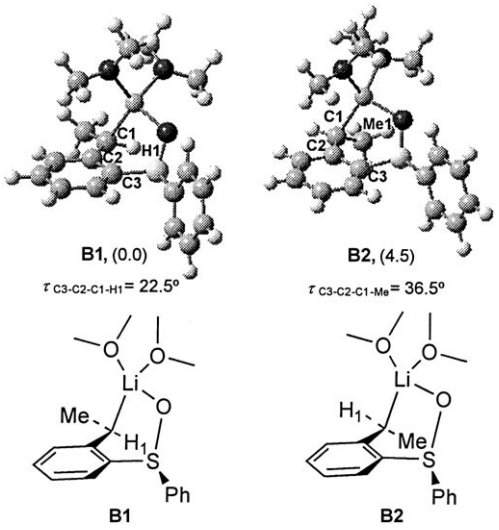


Figure 3. Spatial representation of intermediates **B**. Relative energies [kcal mol^{-1}] with ZPE correction included are given as well as the dihedral angles between selected atoms.

(1.43) than in **B2** (1.41). These effects are related to the coplanarity required between the aromatic ring and the benzylic carbon atom which is greater in the case of **B1** than in **B2** (see the dihedral angle in Figure 3) in which steric effects are more important. As a result **B2** is 4.5 kcal mol^{-1} less stable than **B1**.

The stereochemical results shown in Table 2 and Table 3 can be explained by assuming the formation of the **B** species (Figure 2). Because the metal blocks one of the faces of the carbanion, the electrophile must approach from the opposite side (inversion of the configuration), thus explaining the high stereoselective control observed at C2, which would depend only on the configuration at the sulfinyl sulfur atom regardless of the nature of the electrophile (this was explained with **A** as the model by assuming association of the electrophile with the lithium in a previous step of the intramolecular nucleophilic attack with retention of the configuration, as indicated in Figure 2). Concerning the configuration at C1, stabilising donor–acceptor interactions between the aromatic rings joined to the carbanionic and iminic carbon atoms would favour the approach $\mathbf{I_A}$ (Figure 4), which would evolve into compounds with the (*S*) configuration at C1 (*anti* isomer when R = Me, Figure 4). Although there are two possible approaches of the reagents exhibiting this interaction, the approach $\mathbf{I_B}$, yielding isomers with the (*R*) configuration at C1 (*syn* when R = Me), is destabilised by the repulsion of the lone-pair electrons of the sulfur and nitrogen atoms (Figure 4), which would be even stronger in the TS with a larger charge on the nitrogen atom.

The stability of the approaches not involving π–π stacking interactions will be governed by steric effects and therefore approach **II** must presumably be the most stable because of the *anti* relationship of the aryl groups, the most bulky groups (Figure 4). As in the previous case, $\mathbf{II_B}$ will be destabilised by the electronic repulsion of the lone-pair electrons on the sulfur and nitrogen atoms and therefore approach $\mathbf{II_A}$, which evolves into compounds with an *R* configuration at C1 (*syn* isomer when R = Me), must be favoured on steric grounds.

According to this description, the stereoselectivity of the reactions will be strongly related to the electron density on the arylidene ring as this will determine the magnitude of the donor–acceptor interactions with the aryl ring of the carbanion and therefore the relative stability of the $\mathbf{I_A}$ approach with respect to that of $\mathbf{II_A}$. Imines bearing electron-withdrawing groups, which increase the magnitude of the donor–acceptor interactions, will mainly evolve into compounds with an *S* configuration at C1 through $\mathbf{I_A}$, whereas imines bearing electron-donating groups, in which the donor–acceptor interactions are less significant, will provide a higher proportion of diastereoisomers with an *R* configuration at C1 through $\mathbf{II_A}$. According to this proposal, the result given in entry 13 of Table 3 is not unexpected on the basis of the lack of planarity of the imine, which would preclude π stacking of the rings.

Stereoselective synthesis of the (1*R*,S_S) and (1*R*,2*S*,S_S) amines (*syn* diastereoisomers): According to this mechanis-

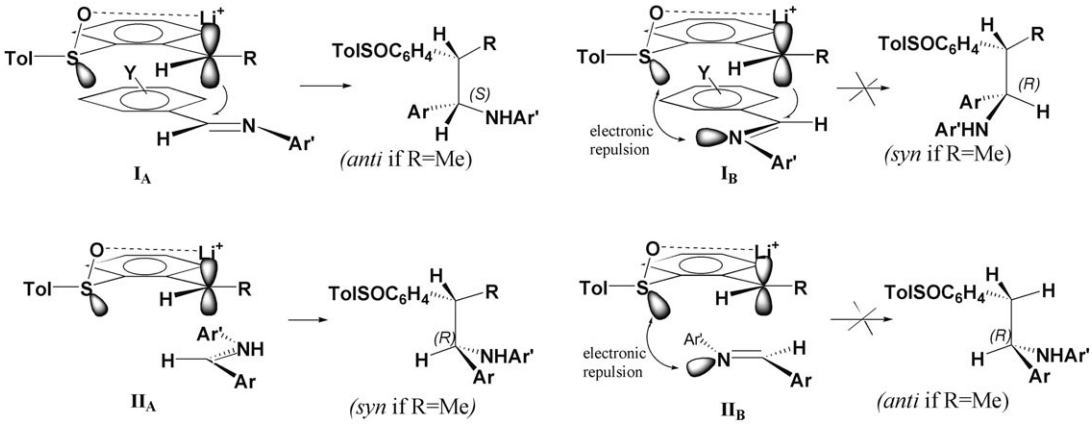
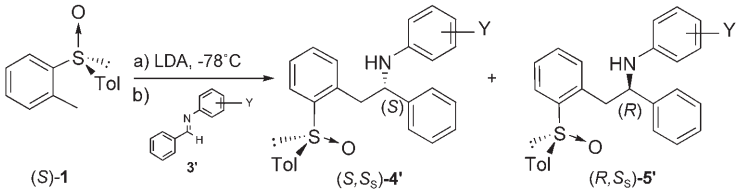


Figure 4. Rationalisation of the stereoselectivity observed for the reaction of 2-(*p*-tolylsulfinyl)benzyl carbanions with *N*-arylarylideneamines.

tic explanation, we can assume that any factor able to reduce the magnitude of the donor–acceptor interaction between the aromatic rings of the reagents would increase the proportion of isomers bearing the (*R*) configuration at C1 (the *syn* isomers in the reactions of **2**), resulting in the reaction evolving through $\mathbf{II_A}$ (Figure 4). In contrast, a larger proportion of isomers with the *S* configuration at C1 would be expected when the magnitude of the donor–acceptor interactions increases because of the preferred evolution through $\mathbf{I_A}$. In order to check this assumption we studied the reactions of (*S*)-**1** and (*S*)-**2** with the *N*-arylbenzylideneamines **3′b–l** (Table 4 and Table 5).

Substituents modify the electron density on the aniline ring, but indirectly also modify the electron density on the phenyl ring joined to the iminic carbon atom and therefore its acceptor character. The results obtained, collected in Tables 4 and 5, indicate that the effects of the substituents are similar to those exerted when they are located on the benzylidene ring (Table 2 and Table 3), with electron-withdrawing groups favouring the formation of the (1*S*,S_S)-**4′** (Table 4) and *anti*-(1*S*,2*S*,S_S)-**6′** isomers (Table 5) and electron-donating groups favouring the (1*R*,S_S)-**5′** (Table 4) and *syn*-(1*R*,2*S*,S_S)-**7′** isomers (Table 5).

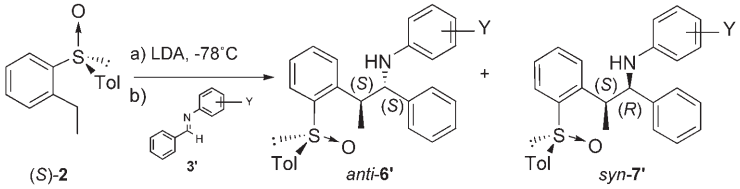
Table 4. Reactions of (*S*)-**1** with *N*-phenylarylideneamines **3′**.



Entry	Y	d.r.[a]	Product	Yield [%][b]
1	4-CN (**3′b**)	66:34	**4′b/5′b**	85
2	3-Cl (**3′d**)	62:38	**4′d/5′d**	78
3	H (**3a**)	40:60	**4a/5a**	81
4	3-MeO (**3′f**)	40:60	**4′f/5′f**	68
5	4-MeO (**3′h**)	27:73	**4′h/5′h**[c]	77
6	4-Me (**3′g**)	25:75	**4′g/5′g**	80
7	2-MeO (**3′i**)	22:78	**4′i/5′i**	57
8	4-NMe_2 (**3′k**)	21:79	**4′k/5′k**	71
9	2,3,4-tri-MeO (**3′m**)	16:84	**4′m/5′m**	73
10	2,4-di-MeO (**3′l**)	12:88	**4′l/5′l**	75

[a] Diastereomeric ratio, as measured by ^{1}H NMR spectroscopy. [b] Combined yield. [c] ORTEP structure of compound **5′i** can be found in the Supporting Information.

Table 5. Reactions of (*S*)-**2** with *N*-aryl-substituted imines.

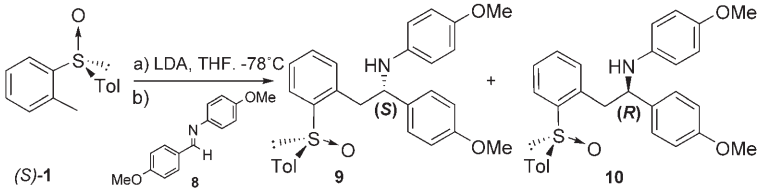


Entry	Y	d.r.[a]	Product	Yield [%][b]
1	4-CN (**3′b**)	96:4	**6′b/7′b**	88
2	3-Cl (**3′d**)	94:6	**6′c/7′c**	80
3	H (**3a**)	91:9	**6a/7a**	72
4	4-Cl (**3′e**)	85:15	**6′e/7′e**	58
5	3-MeO (**3′f**)	79:21	**6′f/7′f**[c]	61
6	4-Me (**3′g**)	66:33	**6′g/7′g**	81
7	4-MeO (**3′h**)	36:64	**6′h/7′h**[d]	78
8	3,4-di-MeO (**3′n**)	23:77	**6′n/7′n**	90
9	2,4-di-MeO (**3′l**)	11:89	**6′l/7′l**	76

[a] Diastereomeric ratio, as measured by ^{1}H NMR spectroscopy. [b] Combined yield. [c] The yield of **7′f** was too low for full charachterisation. [d] ORTEP structure of compound *anti*-**6′b** can be found in the Supporting Information.

Comparison of Tables 2 and 3 with Tables 4 and 5, respectively, reveals that the influence of the substituents is very similar regardless of the ring they occupy although, as expected, the magnitude of such influence is higher when they are directly joined to the ring involved in the donor–acceptor interaction.

We then investigated whether the effects of the substituents are additive in nature when they occupy different rings. We therefore studied the reaction of compound (*S*)-**1** with **8**, the latter bearing one methoxy group on each aryl ring of the imine. The reaction yields a 5:95 mixture of compounds **9** and **10** (Scheme 3). As we can see, the stereoselectivity is much better (90% *de*) than those of entry 5 in Table 4 (46% *de*) and entry 7 in Table 2 (56% *de*), thus confirming accumulative substituent effects even when the substituents occupy different rings.



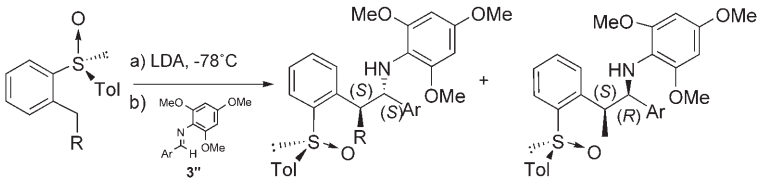
Scheme 3. Reaction of (*S*)-**1** with imine **8**.

On this basis we reasoned that the use of imines derived from strongly activated anilines would provide a good method for synthesising imines with an *R* configuration at the aminic carbon atom (*syn* derivatives starting from (*S*)-**2**). This would complement well the previously reported method of preparing epimers with an *S* configuration at C1 (*anti* derivatives starting from (*S*)-**2** using (*S*)-*N*-sulfinylimines as electrophiles).[5–8] It would be desirable for the aryl group joined to the nitrogen atom to be easily removed, thus allowing the synthesis of free amines. We believe that 2,4,6-trimethoxyaniline would be a good candidate because the *N*-aryl ring could be easily eliminated by an oxidative method.

After preparing the *N*-(2,4,6-trimethoxyphenyl)imines **3″** indicated in Table 1, which bear electron-withdrawing and -donating groups on the arylidene ring, their reactions with (*S*)-**1** and (*S*)-**2** were studied and the results are shown in Table 6. As can be seen, the isomers with an *R* configuration at C1 (**5″** and *syn*-**7″**) are the major products in all cases and they were isolated in good yields (Table 6). The reactions are completely stereoselective for the non-substituted imine **3″a** as well as for those containing electron-donating groups (**3″g** and **3″h**) and even weakly electron-withdrawing groups (**3″f**). As was expected, the stereoselectivity favours the formation of isomers with an (*R*) configuration at C1 (see Table 6).

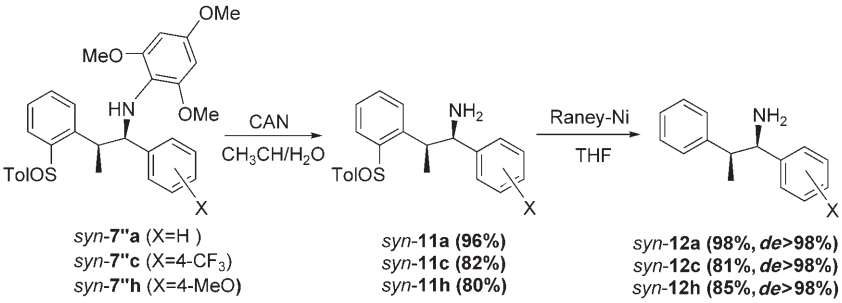
In order to be sure that these reactions were suitably efficient for the synthesis of enantiomerically pure *syn*-1,2-diarylpropylamines, thus providing a complementary procedure to that previously reported for the preparation of the *anti* isomers,[5] it was necessary to check that compounds *syn*-**7″** could be easily converted into the free amines *syn*-**11** by CAN oxidation of the aniline ring[18] and subsequent desulfinylation with Raney nickel to yield the amines *syn*-**12**.[5–7] With this in mind, we successfully attempted to transform the amines *syn*-**7″a**, *syn*-**7″c** and *syn*-**7″h** into *syn*-**12a**, *syn*-**12c** and *syn*-**12h**, respectively (Scheme 4). Both reactions proceed with very high yields and without appreciable epimerisation.[19]

Table 6. Reactions of (*S*)-**1** and (*S*)-**2** with *N*-(2,4,6-trimethoxyphenyl)arylideneamines **3″**.



Entry	Nu[a]	Ar	d.r.[b]	Products	Yield [%][c]
1	(*S*)-**1**	4-CN-C_6H_4 (**3″b**)	48:52	**4″b**/**5″b**	70[d]
2	(*S*)-**1**	3-MeO-C_6H_4 (**3″f**)	<2:>98	**5″f**	68
3	(*S*)-**1**	H-C_6H_4 (**3″a**)	<2:>98	**5″a**	74
4	(*S*)-**1**	4-Cl-C_6H_4 (**3″e**)	<2:>98	**5″e**	72
5	(*S*)-**1**	4-MeO-C_6H_4 (**3h**)	<2:>98	**5h**	76
6	(*S*)-**2**	4-CN-C_6H_4 (**3″b**)	36:64	**6″b**/**7″b**	72[d]
7	(*S*)-**2**	4-CF_3-C_6H_4 (**3″c**)	24:76	**6″c**/**7″c**	9:51
8	(*S*)-**2**	3-Cl-C_6H_4 (**3″d**)	17:83	**6″d**/**7″d**	6:47
9	(*S*)-**2**	3-MeO-C_6H_4 (**3″f**)	<2:>98	**7″f**	71
10	(*S*)-**2**	H-C_6H_4 (**3″a**)	<2:>98	**7″a**	61
11	(*S*)-**2**	4-Me-C_6H_4 (**3″g**)	<2:>98	**7″g**	72
12	(*S*)-**2**	4-MeO-C_6H_4 (**3″h**)	<2:>98	**7″h**	78

[a] Nucleophile. [b] Diastereomeric ratio, as measured by ^{1}H NMR spectroscopy. [c] Combined yield. [d] Chromatographic separation was not possible



Scheme 4. Free amines obtained by an oxidation/desulfinylation process.

Conclusion

In this work we have demonstrated that the reactions of the lithium carbanions derived from (*S*)-**1** and (*S*)-**2** with *N*-arylbenzylideneamines afford epimeric mixtures of *syn* and *anti* 1,2-disubstituted 1,2-diphenylethylamines, both exhibiting the same *S* configuration at C2 (completely controlled by the sulfinyl group) and differing in that at C1. The predominance of the *R* or *S* configuration at this carbon atom (*syn* or *anti* isomers from (*S*)-**2**) is strongly dependent on the electron density on the starting imine, with electron-donating groups favouring the *R* configuration (*syn* from (*S*)-**2**) and electron-withdrawing groups favouring the *S* configuration (*anti* from (*S*)-**2**). These results have been explained by assuming that substituents modulate the magnitude of the stabilising donor–acceptor interactions between the aromatic rings joined to the carbanionic centre and the iminic carbon atom, which exceed their steric repulsion. The reactions of the carbanions (*S*)-**1** and (*S*)-**2** with the aromatic aldimines derived from 2,4,6-trimethoxyaniline provide an excellent method for preparing (*R*)-1-aryl-2-phenylethylamines

and (1*R*,2*S*)-*syn*-1,2-diarylpropylamines in high enantiomeric excess.

Experimental Section

General methods: ^{1}H NMR spectra were acquired at either 200 or 300 MHz and ^{13}C NMR spectra were acquired at 75 MHz (unless otherwise indicated). Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ ($\delta = 7.26$ and 77.0 ppm). Mass spectra (MS) were recorded by using the FAB mode. Melting points were determined in open capillary tubes (GallenKamp Melting point apparatus). All reactions were carried out in anhydrous solvents and under argon. THF was distilled from sodium/benzophenone under argon. Toluene was dried with metallic sodium. Molecular sieves (4 Å) were activated by storing at 110 °C over four days. *i*Pr_2NH was distilled from KOH. Flash silica gel column chromatography was performed using Merck-60 silica gel (230–400 mesh). *n*BuLi (2.5 M solution in hexane) and compound **4a** (imine: PhCH=N–Ph) were purchased from Aldrich. Compounds **1** and **2** had been previously synthesised.[5–8] The procedure used to synthesise imines **3** is reported in the Supporting Information. The NMR spectra of some representative compounds of Tables 2–6 and Scheme 4 can be found in the Supporting Information as well as the ORTEP structures of compounds **5i**, *syn*-**7i** and *anti*-**6′b**.

General procedure for the addition of sulfoxides 1 and 2 to imines (Tables 2–6): A solution of *n*BuLi (0.6 mmol, 2.3 M in hexane) was added to *i*Pr_2NH (0.9 mmol) in THF (3 mL) at 0 °C. After stirring for 15 min, the reaction was cooled to −78 °C. A solution of (*S*)-**1** or (*S*)-**2** (0.5 mmol) in THF (2 mL) was added. After stirring for 15 min, the corresponding *N*-arylimine **3** (0.5 mmol) in THF (1 mL) was added at −78 °C. When the reaction was completed (20–30 min), the reaction was hydrolysed (1 mL H_2O), extracted (3×10 mL Et_2O), washed (2×10 mL sat. NaCl), dried ($MgSO_4$) and the solvent removed under reduced pressure. Compounds were purified by flash silica gel column chromatography (the eluent is indicated in each case).

Products from the reactions of (*S*)-1 with *N*-phenylarylideneamines 3 (Table 2)

(1*S*)-*N*-Phenyl-1-(*p*-cyanophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4b): This compound was obtained as the major diastereoisomer by using imine **3b** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 74%; yellow solid; m.p. 98–100 °C. $[\alpha]_D^{20} = +34.5$ ($c = 0.7$ in MeOH). ^{1}H NMR (300 MHz): $\delta = 7.86$ (d, $J = 9.1$ Hz, 1H), 7.58 (d, $J = 8.3$ Hz, 2H), 7.49–7.38 (m, 6H), 7.27 (d, $J = 8.9$ Hz, 1H), 7.22 (d, $J = 8.2$ Hz, 2H), 7.00 (t, $J = 7.4$ Hz, 2H), 6.57 (t, $J = 7.3$ Hz, 1H), 6.32 (d, $J = 8.6$ Hz, 2H), 5.53 (brs, 1H), 4.48 (t, $J = 8.6$ Hz, 1H), 3.30 (dd, $J = 14.0$, 9.8 Hz, 1H), 2.86 (dd, $J = 14.0$, 4.7 Hz, 1H), 2.34 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.4$, 146.4, 142.6, 141.4, 141.0, 137.7, 132.4, 131.9, 131.7, 130.0, 128.8, 127.8, 127.6, 127.1, 125.1, 118.7, 117.0, 112.8, 110.8, 59.0, 39.4, 21.2 ppm. IR (NaCl): $\tilde{\nu} = 3315$, 2227, 1601, 1498 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{24}N_2OS$: C 77.03, H 5.54, S 7.35; found: C 77.35, H 5.44, S 7.38.

(1*R*)-*N*-Phenyl-1-(*p*-cyanophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5b): This compound was obtained as the minor diastereoisomer by using imine **3b** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 10%; yellow oil. $[\alpha]_D^{20} = -53.5$ ($c = 1.0$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta = 7.86$–7.01 (m, 14H), 6.69 (t, $J = 7.4$ Hz, 1H), 6.38 (d, $J = 8.7$ Hz, 2H), 5.07 (brs, 1H), 4.85 (dd, $J = 9.9$, 5.7 Hz, 1H), 3.40 (dd, $J = 14.1$, 9.9 Hz, 1H), 3.20 (dd, $J = 14.1$, 5.7 Hz, 1H), 2.32 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.4$, 143.5, 142.6, 141.7, 132.5, 132.2, 132.0, 131.5, 130.1, 130.0, 128.4, 127.7, 127.6, 126,8, 125.5, 124,9, 118.9, 111.1, 111.7, 53.4, 41.2, 21.4 ppm.

(1*S*)-*N*-Phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-1-(4-trifluoromethylphenyl)ethylamine (4c): This compound was obtained as the major diastereoisomer by using imine **3c** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 54%; yellow solid. $[\alpha]_D^{20} = -20.4$ ($c = 0.25$ in MeOH). ^{1}H NMR (300 MHz): $\delta = 7.60$–7.05 (m, 15H), 6.55 (t, $J = 7.4$ Hz, 1H), 6.30 (d, $J = 8.6$ Hz, 2H), 4.59 (dd, $J = 8.9$, 5.7 Hz, 1H), 3.32 (dd, $J = 14.4$, 8.9 Hz, 1H), 3.14 (dd, $J = 14.4$, 5.7 Hz, 1H), 2.29 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.0$, 147.4, 143.9, 141.8, 140.3, 137.0, 135.2, 131.6, 130.9, 130.1, 130.0, 129.5 (q, $J_{C,F} = 33.4$ Hz), 128.8, 128.2, 126.8, 125.9, 121.0 (q, $J_{C,F} = 350.7$ Hz), 120.3, 113.5, 58.7, 40.5, 21.4 ppm.

(1*R*)-*N*-Phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-1-(4-trifluoromethylphenyl)ethylamine (5c): This compound was obtained as the minor diastereoisomer by using imine **3c** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 28%; yellow solid; m.p. 74–76 °C. $[\alpha]_D^{20} = +8.0$ ($c = 0.5$ in MeOH). ^{1}H NMR (300 MHz): $\delta = 7.93$ (d, $J = 9.2$ Hz, 1H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 8.3$ Hz, 2H), 7.49–7.38 (m, 4H), 7.38–7.25 (m, 3H), 7.05 (t, $J = 7.4$ Hz, 2H), 6.62 (t, $J = 7.4$ Hz, 1H), 6.38 (d, $J = 8.7$ Hz, 2H), 5.50 (brs, 1H), 4.55 (dd, $J = 9.9$, 4.4 Hz, 1H), 3.35 (dd, $J = 14.0$, 10.0 Hz, 1H), 2.93 (dd, $J = 14.0$, 4.5 Hz, 1H), 2.39 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.9$, 146.7, 142.7, 141.4, 141.2, 137.9, 131.9, 131.6, 130.2, 129.3 (q, $J_{C,F} = 31.4$ Hz), 128.8, 127.7, 127.6, 126.6, 125.9, 125.6, 124.8, 120.0 (q, $J_{C,F} = 357.7$ Hz), 116.9, 112.9, 58.9, 39.7, 21.2 ppm. IR (NaCl): $\tilde{\nu} = 3318$, 1602, 1498, 1325, 1164 1123 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{25}NO_1S_1F_3$: C 70.13, H 5.04, N 2.92, S 6.69; found: C 69.94, H 5.14, N 2.94, S 6.55.

(1*S*)-*N*-Phenyl-1-(3-chlorophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4d): This compound was obtained as the major diastereoisomer by using imine **3d** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 52%; yellow oil. $[\alpha]_D^{20} = +73.9$ ($c = 1.3$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta = 7.79$ (d, $J = 9.2$ Hz, 1H), 7.40–7.05 (m, 11H), 6.92 (t, $J = 7.4$ Hz, 2H), 6.48 (t, $J = 7.3$ Hz, 1H), 6.23 (d, $J = 7.7$ Hz, 2H), 5.10 (brs, 1H), 4.32–4.28 (m, 1H), 3.16 (dd, $J = 14.1$, 9.7 Hz, 1H), 2.78 (dd, $J = 14.1$, 4.6 Hz, 1H), 2.26 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.8$, 146.0, 142.9, 141.5, 141.3, 137.9, 134.6, 131.9, 130.1, 130.0, 128.9, 127.7, 127.5, 127.4, 126.5, 125.6, 124.5, 117.0, 113.1, 59.0, 40.1, 21.4 ppm.

(1*R*)-*N*-Phenyl-1-(3-chlorophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5d): This compound was obtained as the minor diastereoisomer by using imine **3d** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 27%; colourless oil. $[\alpha]_D^{20} = -89.0$ ($c = 0.8$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta = 7.66$ (d, $J = 9.3$ Hz, 1H), 7.55–7.10 (m, 14H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.37 (d, $J = 8.7$ Hz, 2H), 4.60–4.50 (m, 1H), 3.36 (dd, $J = 10.6$, 8.5 Hz, 1H), 3.17 (dd, $J = 10.6$, 5.6 Hz, 1H), 2.36 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.7$, 145.5, 143.8, 141.7, 140.7, 140.5, 136.9, 134.6, 131.5, 130.8, 130.1, 130.0, 129.0, 128.1, 125.8, 125.5, 124.6, 124.3, 117.6, 113.4, 58.6, 40.6, 21.4 ppm.

(1*S*)-*N*-Phenyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4a): This compound was obtained as the minor diastereoisomer by using imine **3a** and (*S*)-**1** as the starting materials and was obtained mixed with 10% of starting material **1**. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 31%; colourless oil. ^{1}H NMR (200 MHz): $\delta = 7.90$ (d, $J = 9.1$ Hz, 1H), 7.40–7.23 (m, 14H), 6.50 (t, $J = 7.0$ Hz, 1H), 6.30 (d, $J = 7.8$ Hz, 2H), 5.01 (d, $J = 5.1$ Hz, 1H), 4.56–4.45 (m, 1H), 3.10 (dd, $J = 14.1$, 8.4 Hz, 1H), 2.80 (dd, $J = 14.1$, 5.6 Hz, 1H), 2.36 (s, 3H).

(1*R*)-*N*-Phenyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5a): This compound was obtained as major diastereoisomer by using imine **3a** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 49%; white solid; m.p. 192–194 °C. $[\alpha]_D^{20} = -100.0$ ($c = 0.5$ in $EtOH/CH_2Cl_2$, 1:1). ^{1}H NMR (200 MHz): $\delta = 7.70$ (d, $J = 9.3$ Hz, 1H), 7.40–7.23 (m, 14H), 6.61 (t, $J = 7.1$ Hz, 1H), 6.43 (d, $J = 7.7$, 1.1 Hz, 2H), 4.66–4.55 (m, 2H), 3.40 (dd, $J = 14.4$, 8.6 Hz, 1H), 3.21 (dd, $J = 14.4$, 5.6 Hz, 1H), 2.38 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 143.9$, 141.6, 137.2, 131.3, 130.0, 128.9 (2C), 128.7 (2C), 127.9 (2C), 127.3, 126.3 (2C), 125.8, 117.4, 113.5 (2C), 58.9, 40.7, 21.4 ppm. IR (NaCl): $\tilde{\nu} = 3330$, 3051, 1601, 1497, 1238 cm^{-1}.

(1*S*)-*N*-Phenyl-1-(3-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4f): This compound was obtained as the minor diastereoisomer by using imine **3f** and (*S*)-**1** as the starting materials and was obtained mixed with 10% of starting material (*S*)-**1**. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 24%; yellow oil. ^{1}H NMR (300 MHz): $\delta = 7.98$ (d, $J = 9.1$ Hz, 1H), 7.54–6.77 (m, 12H), 6.79 (d, $J = 8.1$ Hz, 1H), 6.56 (t, $J = 7.2$ Hz, 1H), 6.35 (d, $J = 7.7$ Hz, 2H), 4.99 (brs, 1H), 4.40 (dd, $J = 9.3$, 4.9 Hz, 1H), 3.78 (s, 3H), 3.25 (dd, $J = 14.1$, 9.4 Hz, 1H), 2.95 (dd, $J =$

14.1, 4.9 Hz, 1H), 2.37 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 159.9, 147.0, 145.4, 143.0, 141.7, 141.6, 137.9, 135.6, 131.7, 130.0, 130.8, 130.1, 129.7, 128.9, 127.6, 118.7, 116.8, 113.2, 112.4, 112.1, 59.3, 55.2, 40.6, 21.4, 18.6 ppm.

(1*R*)-*N*-Phenyl-1-(3-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5f): This compound was obtained as the major diastereoisomer by using imine **3f** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 41%; colourless oil. $[\alpha]_D^{20}=-117.0$ (c=1.0 in $CHCl_3$). ^{1}H NMR (300 MHz): δ=7.71 (d, J=9.2 Hz, 1H), 7.54–6.88 (m, 12H), 6.79 (dd, J=8.1, 2.3 Hz, 1H), 6.61 (t, J=7.2 Hz, 1H), 6.45 (d, J= 7.7 Hz, 2H), 4.58 (dd, J=8.4, 5.9 Hz, 1H), 4.53 (brs, 1H), 3.76 (s, 3H), 3.39 (dd, J=14.3, 8.4 Hz, 1H), 3.22 (dd, J=14.3, 5.8 Hz, 1H), 2.37 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.9, 147.0, 144.9, 143.9, 141.6, 140.8, 137.2, 131.4, 130.8, 130.0, 129.7, 128.9, 128.0, 126.3, 125.8, 118.7, 117.4, 113.5, 112.6, 112.1, 58.9, 55.2, 40.6, 21.4 ppm.

(1*S*)-*N*-Phenyl-1-(4-methylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4g): This compound was obtained as the minor diastereoisomer by using imine **3g** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 3:1; yield: 16%; yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.82 (d, J=9.4 Hz, 1H), 7.50–7.10 (m, 13H), 6.62 (t, J= 6.4 Hz, 2H), 6.28 (d, J=9.0 Hz, 1H), 4.59 (m, 1H), 3.0 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H) ppm.

(1*R*)-*N*-Phenyl-1-(4-methylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5g): This compound was obtained as the major diastereoisomer by using imine **3g** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 3:1; yield: 53%; yellow oil. $[\alpha]_D^{20}=-126.8$ (c=1.0 in CH_3Cl). ^{1}H NMR (300 MHz): δ=7.71 (d, J=9.3 Hz, 1H), 7.50–7.10 (m, 13H), 6.63 (t, J=7.3 Hz, 2H), 6.37 (d, J=8.5 Hz, 1H), 4.61 (dd, J=6.1, 6.7 Hz, 1H), 4.51 (brs, 1H), 3.39 (dd, J=14.4, 8.7 Hz, 1H), 3.26 (dd, J= 14.4, 5.8 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.1, 143.9, 141.6, 140.9, 139.9, 137.4, 136.8, 131.3, 130.7, 130.0, 129.4, 128.9, 128.8, 128.0, 126.3, 125.8, 117.3, 113.5, 58.7, 40.7, 21.4, 21.1 ppm.

(1*S*)-*N*-Phenyl-1-(4-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4h): This compound was obtained as the minor diastereoisomer by using imine **3h** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 18%; colourless oil. $[\alpha]_D^{20}=+2.0$ (c=0.2 in MeOH). ^{1}H NMR (200 MHz): δ=7.81 (d, J=9.1 Hz, 1H), 7.41–7.14 (m, 10H), 6.91 (t, J=8.2 Hz, 1H), 6.75 (d, J=8.6 Hz, 2H), 6.46 (t, J=7.3 Hz, 1H), 6.24 (d, J=8.0 Hz, 2H), 4.70 (brs, 1H), 4.29 (dd, J=9.1, 5.0 Hz, 1H), 3.69 (s, 3H), 3.15 (dd, J=14.1, 9.3 Hz, 1H), 2.84 (dd, J=14.1, 5.0 Hz, 1H), 2.26 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=158.7, 147.1, 143.0, 141.6, 141.5, 137.9, 135.3, 131.5, 131.3, 130.0, 128.8, 127.5, 127.3, 126.8, 125.7, 116.7, 114.0, 113.2, 58.5, 55.2, 40.4, 21.3 ppm.

(1*R*)-*N*-Phenyl-1-(4-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5h): This compound was obtained as the major diastereoisomer by using imine **3h** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 62%; colourless oil. $[\alpha]_D^{20}=-172.2$ (c=0.5 in MeOH). ^{1}H NMR (300 MHz): δ=7.73 (d, J=9.2 Hz, 1H), 7.45–7.14 (m, 10H), 7.07 (t, J=8.5 Hz, 1H), 6.84 (d, J=8.5 Hz, 2H), 6.64 (t, J=7.3 Hz, 1H), 6.47 (d, J=7.7 Hz, 2H), 4.61 (dd, J=8.3, 5.9 Hz, 1H), 4.55 (brs, 1H), 3.82 (s, 3H), 3.40 (dd, J=14.2, 8.3 Hz, 1H), 3.22 (dd, J=14.2, 5.9 Hz, 1H), 2.38 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=158.7, 147.0, 143.7, 141.5, 140.7, 137.2, 134.8, 131.2, 130.7, 129.9, 128.9, 127.8, 127.4, 126.1, 125.7, 117.2, 113.9, 113.4, 58.2, 55.1, 40.7, 21.3 ppm. IR (NaCl): $\tilde{\nu}$=3330, 3052, 2931, 1601, 1510, 1246, 1031 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{27}NO_2S$: C 76.16, H 6.16, N 3.17, S 7.26; found: C 75.91, H 6.15, N 3.21, S 6.91.

(1*S*)-*N*-Phenyl-1-(2-methoxyphenyl)-{[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4i): This compound was obtained as the minor diastereoisomer by using imine **3i** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 13%; white solid; m.p. 79–81 °C. $[\alpha]_D^{20}=+27.6$ (c=0.25 in CH_2Cl_2/EtOH, 1:1). ^{1}H NMR (200 MHz): δ=7.81 (d, J= 7.8 Hz, 1H), 7.41–7.14 (m, 13H), 6.53 (d, J=10.9 Hz, 2H), 6.32 (d, J= 8.6 Hz, 1H), 5.15 (brs, 1H), 4.86 (dd, J=9.1, 4.6 Hz, 1H), 3.89 (s, 3H), 3.22 (dd, J=14.0, 9.1 Hz, 1H), 3.22 (dd, J=14.0, 4.6 Hz, 1H), 2.36 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=156.6, 147.2, 142.9, 141.6, 141.1, 131.6, 131.3, 130.8, 130.7, 129.9, 128.8, 127.2, 126.9, 126.0, 125.5, 124.4, 120.8, 116.4, 112.9, 110.3, 55.2, 54.2, 37.6, 21.2 ppm. MS (FAB$^+$): m/z (%): 442 (46) $[M+1]^+$, 39 (5), 212 (100), 154 (51), 137 (31), 136 (35). IR (NaCl): $\tilde{\nu}$=3320, 1601, 1490, 1237, 1028 cm^{-1}. HRMS: m/z calcd for $C_{28}H_{28}NO_2S$: 442.1840; found: 442.1836.

(1*R*)-*N*-Phenyl-1-(2-methoxyphenyl)-{[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5i): This compound was obtained as the major diastereoisomer by using imine **3i** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 66%; white solid; m.p. 76–78 °C. $[\alpha]_D^{20}=-208.8$ (c=0.7 in EtOH). ^{1}H NMR (300 MHz): δ=7.81 (d, J=9.1 Hz, 1H), 7.41–7.14 (m, 10H), 6.91 (t, J=8.2 Hz, 1H), 6.75 (d, J=8.6 Hz, 2H), 6.46 (t, J=7.3 Hz, 1H), 6.24 (d, J=8.0 Hz, 2H), 5.18 (t, J=6.8 Hz, 1H), 4.77 (brs, 1H), 4.29 (dd, J=9.1, 5.0 Hz, 1H), 3.89 (s, 3H), 3.43 (dd, J=14.1, 8.3 Hz, 1H), 2.84 (dd, J=14.1, 5.0 Hz, 1H), 2.26 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=156.7, 147.0, 143.8, 141.3, 137.7, 130.9, 130.5, 130.2, 129.8 (2C), 128.8, 128.0, 127.5, 127.1, 125.6, 125.3, 120.7, 116.9, 113.3, 110.3, 55.1, 53.8, 38.1, 21.2 ppm. IR (NaCl): $\tilde{\nu}$=3328, 1598, 1498, 1238 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{27}NO_2S$: C 76.16, H 6.16, N 3.17, S 7.26; found: C 76.57, H 6.14, N 3.10, S 7.01.

(1*S*)-*N*-Phenyl-1-(2,4-dimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (4l): This compound was obtained as the minor diastereoisomer by using imine **3l** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 7%; yellow solid; m.p. 82–84 °C. $[\alpha]_D^{20}=+31.3$ (c=0.3 in EtOH). ^{1}H NMR (300 MHz): δ=7.81 (dd, J=7.0, 1.9 Hz, 1H), 7.46–7.28 (m, 5H), 7.21 (d, J=9.8 Hz, 2H), 7.16 (d, J= 8.3 Hz, 2H), 7.02–6.96 (m, 2H), 6.53 (t, J=7.3 Hz, 1H), 6.45 (d, J= 2.3 Hz, 1H), 6.39 (dd, J=8.4, 2.3 Hz, 1H), 6.31 (dd, J=8.7, 1.1 Hz, 1H), 5.03 (brs, 1H), 4.75 (dd, J=9.0, 4.6 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 3.19 (dd, J=13.9, 9.0 Hz, 1H), 3.01 (dd, J=13.9, 4.7 Hz, 1H), 2.35 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.8, 157.7, 147.3, 142.9, 141.7, 141.2, 139.3, 131.6, 131.3, 129.9, 128.8, 127.7, 127.2, 126.8, 125.6, 123.1, 116.4, 113.0, 104.2, 98.6, 55.3, 55.3, 53.9, 37.9, 21.3 ppm. IR (NaCl): $\tilde{\nu}$= 3327, 1599, 1463, 1378, 1028 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NO_3S$: C 73.86, H 6.20, N 2.97, S 6.80; found: C 72.56, H 6.08, N 2.94, S 6.72.

(1*R*)-*N*-Phenyl-1-(2,4-dimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (5l): This compound was obtained as the major diastereoisomer by using imine **3l** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 69%; white solid; m.p. 76–78 °C. $[\alpha]_D^{20}=-163.4$ (c=0.6 in EtOH). ^{1}H NMR (300 MHz): δ=7.72 (d, J=9.2 Hz, 1H), 7.41 (d, J=10.2 Hz, 2H), 7.40–7.00 (m, 8H), 6.61 (t, J=7.3 Hz, 1H), 6.49 (dd, J=7.6, 1.1 Hz, 2H), 6.25 (d, J=2.3 Hz, 1H), 6.38 (dd, J= 8.3, 2.3 Hz, 1H), 4.95–4.90 (m, 1H), 4.65 (brs, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.32 (dd, J=14.2, 8.1 Hz, 1H), 3.23 (dd, J=14.2, 6.2 Hz, 1H), 2.36 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.9, 157.7, 147.1, 143.8, 141.4, 141.1, 137.8, 130.9, 130.6, 129.8, 128.9, 127.8, 127.6, 125.7, 125.4, 122.6, 117.0, 113.4, 104.1, 98.5, 55.2 (2C), 53.7, 38.4, 21.3 ppm. IR (NaCl): $\tilde{\nu}$=3327, 1598, 1462, 1426, 1028 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NO_3S$: C 73.86, H 6.20, N 2.97, S 6.80; found: C 73.76, H 6.12, N 2.99, S 6.82.

(1*R*)-*N*-Phenyl-1-(3,4,5-trimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfnyl]phenyl}ethylamine (5j): This compound was obtained as the major diastereoisomer by using imine **3j** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 74%; white solid; m.p. 140–142 °C. $[\alpha]_D^{20}=-102.6$ (c=0.5 in MeOH). ^{1}H NMR (300 MHz): δ=7.71 (d, J= 8.9 Hz, 1H), 7.50–7.30 (m, 4H), 7.23 (d, J=8.0 Hz, 2H), 7.15–7.00 (m, 3H), 6.66 (t, J=7.2 Hz, 1H), 6.56 (s, 2H), 6.48 (d, J=8.4, 2H), 4.68 (brs, 1H), 4.58 (dd, J=8.2, 6.1 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 6H), 3.43 (dd, J=14.2, 8.2 Hz, 1H), 3.22 (dd, J=14.2, 6.1 Hz, 1H), 2.37 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=153.2, 147.0, 143.7, 141.4, 140.5, 138.6, 137.1, 136.8, 131.2, 130.9, 128.8, 127.8, 125.5, 117.3, 113.4, 113.1, 103.1, 103.0, 60.6, 59.2, 55.9, 40.6, 21.2 ppm. IR (NaCl): $\tilde{\nu}$=3330, 1550, 1499, 1459, 1420, 1125 cm^{-1}. Elemental analysis calcd (%) for $C_{30}H_{31}NO_4S$: C 71.83, H 6.23, N 2.79, S 6.39; found: C 71.11, H 6.20, N 3.15, S 7.12.

Products from the reactions of (*S*)-2 with *N*-phenylarylideneamines 3 (Table 3)

(1*S*,2*S*)-*N*-Phenyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6a): This compound was obtained as the major diastereoisomer by using imine **3a** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/

AcOEt, 2:1; yield: 66%; brown solid; m.p. 165–167°C. $[\alpha]_D^{20}=+146.9$ ($c=1.0$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=7.96$ (d, $J=7.5$ Hz, 1H), 7.55–7.48 (m, 5H), 7.45–7.19 (m, 7H), 6.92 (t, $J=7.4$ Hz, 2H), 6.45 (t, $J=7.3$ Hz, 1H), 6.20 (d, $J=7.7$ Hz, 2H), 4.88 (d, $J=4.4$ Hz, 1H), 4.20 (dd, $J=10.2$, 4.8 Hz, 1H), 3.57 (dq, $J=10.1$, 6.8 Hz, 1H), 2.36 (s, 3H), 0.65 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=147.0$, 145.4, 142.6, 141.9, 141.8, 141.3, 132.5 (2C), 130.0, 128.6 (2C), 128.3, 127.8, 127.5 (2C), 127.1, 126.9, 125.5, 63.4, 40.2, 21.3, 19.3 ppm. IR (NaCl): $\tilde{\nu}=3310$, 3024, 1608, 1521, 1504 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{27}NOS$: C 79.02, H 6.39, N 3.29, S, 7.53; found: C 78.56, H 6.39, N 3.29, S 7.53.

(1*R*,2*S*)-*N*-Phenyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7a): This compound was obtained as the minor diastereoisomer by using imine **3a** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 6%; orange oil. ^1H NMR (300 MHz): $\delta=7.60$ (d, $J=7.6$ Hz, 1H), 7.55–7.48 (m, 3H), 7.45–7.19 (m, 7H), 7.02 (t, $J=7.5$ Hz, 2H), 6.60 (t, $J=7.3$ Hz, 1H), 6.40 (d, $J=7.8$ Hz, 2H), 4.83 (brs, 1H), 4.50 (d, $J=4.5$ Hz, 1H), 4.01 (dq, $J=6.8$, 6.0 Hz, 1H), 2.36 (s, 3H), 1.25 ppm (d, $J=6.8$ Hz, 3H).

(1*S*,2*S*)-*N*-Phenyl-1-(4-cyanophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6b): This compound was obtained as a unique diastereoisomer by using imine **3b** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 90%; white solid; m.p. 84–86°C (Et_2O). $[\alpha]_D^{20}=+138.8$ ($c=1.1$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=7.92$ (dd, $J=8.3$, 1.0 Hz, 1H), 7.64 (d, $J=8.3$ Hz, 2H), 7.58 (d, $J=8.3$ Hz, 2H), 7.55–7.48 (m, 2H), 7.46 (d, $J=8.2$ Hz, 2H), 7.45–7.35 (m, 2H), 7.29 (d, $J=8.2$ Hz, 2H), 6.97 (t, $J=7.4$ Hz, 2H), 6.52 (t, $J=7.3$ Hz, 1H), 6.28 (dd, $J=8.7$, 1.1 Hz, 2H), 5.64 (d, $J=7.1$ Hz, 1H), 4.28 (dd, $J=10.2$, 7.1 Hz, 1H), 3.68 (dq, $J=10.2$, 7.0, 1H), 2.38 (s, 3H), 0.55 ppm (d, $J=7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=148.9$, 146.4, 145.3, 141.5, 141.4, 140.9, 132.9, 132.2, 129.8, 129.0, 128.7, 128.2, 128.0, 126.9, 124.7, 118.7, 116.5, 112.5, 110.8, 63.5, 39.2, 21.1, 18.4 ppm. IR (NaCl): $\tilde{\nu}=3297$, 2298, 1557, 1518, 1496 cm^{-1}.

(1*S*,2*S*)-*N*-Phenyl-1-(4-trifluoromethylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]-phenyl}propylamine (6c): This compound was obtained as a unique diastereoisomer by using imine **3c** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 69%; colourless oil. ^1H NMR (300 MHz): $\delta=$ 7.96 (d, $J=7.4$ Hz, 1H), 7.65–7.35 (m, 10H), 7.32 (d, $J=8.0$ Hz, 2H), 7.01–6.95 (m, 1H), 6.52 (t, $J=7.4$ Hz, 1H), 6.29 (d, $J=8.7$ Hz, 2H), 5.46 (d, $J=7.8$ Hz, 1H), 4.30 (dd, $J=10.2$, 7.8 Hz, 1H), 3.69 (dq, $J=10.2$, 7.0 Hz, 1H), 2.40 (s, 3H), 0.60 ppm (d, $J=10.2$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=147.3$, 146.7, 145.5, 141.7, 141.6, 132.9, 129.9 (2C), 128.7 (2C), 128.0, 127.8, 126.9, 125.4, 125.3 (q, $J_{C,F}=25.1$ Hz), 125.0, 120.6 (q, $J_{C,F}=269.8$ Hz), 116.4, 112.5, 63.5, 39.6, 21.2, 18.7 ppm.

(1*S*,2*S*)-*N*-Phenyl-1-(3-chlorophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6d): This compound was obtained as the major diastereoisomer by using imine **3d** and (*S*)-**2** as the starting materials and the minor diastereoisomer could not be isolated. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 72%; yellow solid; m.p. 149–151°C. $[\alpha]_D^{20}=+136.0$ ($c=1.2$ in $CHCl_3$). ^1H NMR (200 MHz): $\delta=7.96$ (d, $J=9.4$ Hz, 1H), 7.56–7.18 (m, 12H), 7.00–6.90 (m, 2H), 6.51 (t, $J=7.3$ Hz, 1H), 6.19 (d, $J=9.4$ Hz, 1H), 5.03 (d, $J=6.7$ Hz, 1H), 4.15 (dd, $J=10.2$, 6.7 Hz, 1H), 3.54 (dq, $J=10.2$, 6.8 Hz, 1H), 2.38 (s, 3H), 0.62 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=146.7$, 145.2, 141.7, 141.3, 134.3, 132.7, 130.0, 129.6, 128.7 (2C), 128.1 (2C), 127.8, 127.5, 127.4, 126.9, 125.7, 125.3, 116.4, 112.6, 63.3, 39.9, 21.3, 19.1 ppm.

(1*S*,2*S*)-*N*-Phenyl-1-naphthyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6p): This compound was obtained as the major diastereoisomer by using imine **3p** and (*S*)-**2** as the starting materials and the minor diastereoisomer could not be isolated. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 70%; yellow solid; m.p. 99–101°C. $[\alpha]_D^{20}=+190.0$ ($c=0.7$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=8.03$ (dd, $J=7.6$, 1.4 Hz, 1H), 7.97–7.84 (m, 3H), 7.60–7.20 (m, 11H), 7.01 (t, $J=7.4$ Hz, 2H), 6.54 (t, $J=7.4$ Hz, 1H), 6.42 (d, $J=8.7$ Hz, 2H), 5.33 (d, $J=7.0$ Hz, 1H), 4.49 (dd, $J=10.2$, 7.0 Hz, 1H), 3.81 (dq, $J=10.2$, 7.0 Hz, 1H), 2.41 (s, 3H), 0.72 ppm (d, $J=7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=147.0$, 145.6, 141.7, 141.6, 141.1, 140.2, 133.1, 132.8, 132.6, 129.8, 128.5, 128.3, 128.1, 127.9, 127.7, 127.5, 126.8, 126.7, 125.8, 125.5, 125.2, 125.0, 116.1, 112.7, 63.8, 39.9, 21.1, 19.1 ppm. IR (NaCl): $\tilde{\nu}=3330$, 1598, 1499, 1031 cm^{-1}. Elemental analysis calcd (%) for $C_{32}H_{29}NOS$: C 80.80, H 6.15, N 2.94, S 6.74; found: C 79.82, H 6.15, N 2.94, S 6.74.

(1*S*,2*S*)-*N*-Phenyl-1-(3-methoxyphenyl)-2–{[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (6f): This compound was obtained as the major diastereoisomer by using imine **3f** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 52%; yellow oil. $[\alpha]_D^{20}=+119.3$ ($c=0.6$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=7.98$ (d, $J=7.6$ Hz, 1H), 7.64–6.90 (m, 12H), 6.49 (t, $J=7.3$ Hz, 2H), 6.25 (d, $J=7.8$ Hz, 2H), 4.87 (brs, 1H), 4.20 (d, $J=10.1$ Hz, 1H), 3.84 (s, 3H), 3.59 (dq, $J=13.9$, 6.8 Hz, 1H), 2.38 (s, 3H), 0.69 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.8$, 147.1, 145.5, 144.6, 142.0, 141.9, 141.4, 132.7, 130.1, 129.3, 128.7, 127.9, 127.0, 126.0, 125.6, 120.2, 116.3, 113.1, 112.8, 112.5, 63.8, 55.2, 40.3, 21.4, 19.4 ppm.

(1*R*,2*S*)-*N*-Phenyl-1-(3-methoxyphenyl)-2-{[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (7f): This compound was obtained as the minor diastereoisomer by using imine **3f** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 12%; colourless oil. $[\alpha]_D^{20}=-9.3$ ($c=0.4$ in $CHCl_3$). ^1H NMR (200 MHz): $\delta=7.55$ (d, $J=7.1$ Hz, 1H), 7.45–6.80 (m, 12H), 6.60 (t, $J=7.3$ Hz, 2H), 6.40 (d, $J=7.8$ Hz, 2H), 4.90 (brs, 1H), 4.50 (d, $J=9.1$ Hz, 1H), 4.01 (dq, $J=6.8$, 5.9 Hz, 1H), 2.38 (s, 3H), 1.30 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=159.5$, 147.5, 143.9, 143.2, 140.9, 131.5 (2C), 129.8, 129.1, 128.9 (2C), 128.2, 127.6, 125.5 (2C), 119.9, 117.3, 113.6, 113.1, 112.5, 62.9, 55.1, 40.3, 21.3, 17.9 ppm.

(1*S*,2*S*)-*N*-Phenyl-1-(4-methylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6g): This compound was obtained as the major diastereoisomer by using imine **3g** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 62%; white solid; m.p. 194–196°C. $[\alpha]_D^{20}=+128.3$ ($c=1.2$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=7.93$ (d, $J=7.7$ Hz, 1H), 7.53–7.10 (m, 11H), 6.87 (t, $J=7.4$ Hz, 2H), 6.40 (t, $J=7.2$ Hz, 1H), 6.16 (d, $J=8.7$ Hz, 2H), 4.74 (d, $J=6.8$ Hz, 1H), 4.13 (dd, $J=10.1$, 6.8 Hz, 1H), 3.50 (dq, $J=10.1$, 6.9 Hz, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 0.62 ppm (d, $J=6.9$ Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): $\delta=147.0$, 145.5, 141.9, 141.8, 141.3, 139.5, 136.6, 132.5 (2C), 129.9, 129.0, 128.6, 127.7, 127.6, 126.9, 125.5, 116.1, 112.7, 63.3, 40.3, 21.3, 21.0, 19.3 ppm. Elemental analysis calcd (%) for $C_{29}H_{29}NOS$: C 79.23, H 6.65, N 3.19, S 7.29; found: C 78.99, H 6.55, N 3.27, S 7.11.

(1*R*,2*S*)-*N*-Phenyl-1-(4-methylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (7g): This compound was obtained as the minor diastereoisomer by using imine **3g** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 18%; yellow solid; m.p. 105–107°C. $[\alpha]_D^{20}=-22.3$ ($c=1.3$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=7.56$ (dd, $J=7.7$, 1.4 Hz, 1H), 7.53–7.00 (m, 13H), 6.59 (tt, $J=7.5$, 1.0 Hz, 1H), 6.41 (dd, $J=6.7$, 1.0 Hz, 2H), 4.74 (brs, 1H), 4.48 (d, $J=6.1$ Hz, 1H), 4.00 (dq, $J=6.9$, 6.1 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 1.25 ppm (d, $J=6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=147.45$, 143.96, 143.04, 141.12, 140.92, 138.33, 136.50, 131.52, 129.7, 128.9, 127.98, 127.62 (2C), 127.3, 125.6 (2C), 117.24, 113.54, 62.6, 40.5, 21.33, 21.05, 18.04 ppm.

(1*S*,2*S*)-*N*-Phenyl-1-(2-bromophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6j): This compound was obtained as the major diastereoisomer by using imine **3j** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 42%; white solid; m.p. 190–192°C (Et_2O). $[\alpha]_D^{20}=+128.3$ ($c=1.2$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=7.92$ (d, $J=8.0$ Hz, 1H), 7.69 (dd, $J=7.9$, 1.2 Hz, 1H), 7.61–7.52 (m, 4H), 7.49 (d, $J=8.3$ Hz, 2H), 7.42 (td, $J=7.5$, 1.3 Hz, 1H), 7.35 (dd, $J=7.5$, 1.1 Hz, 1H), 7.30 (d, $J=8.3$ Hz, 2H), 6.99 (td, $J=7.4$, 1.1 Hz, 2H), 6.50 (t, $J=7.3$ Hz, 1H), 6.35 (dd, $J=8.6$, 1.0 Hz, 2H), 5.57 (d, $J=6.9$ Hz, 1H), 4.96 (dd, $J=10.1$, 7.3 Hz, 1H), 3.76 (dq, $J=10.1$, 7.1 Hz, 1H), 2.39 (s, 3H), 0.64 ppm (d, $J=7.1$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=146.8$, 146.2, 142.1, 141.7, 141.3, 140.8, 133.0, 132.1, 129.8, 128.8, 128.7, 128.5, 128.4, 128.3, 127.9, 126.8, 125.4, 124.9, 116.1, 112.6, 61.0, 40.8, 21.2, 17.5 ppm. IR (NaCl): $\tilde{\nu}=3337$, 1934, 1601, 1522 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{26}BrNOS$: C 66.66, H 5.19, N 2.78, S 6.36; found: C 66.31, H 5.24, N 2.89, S 6.25.

(1*R*,2*S*)-*N*-Phenyl-1-(2-bromophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (7j): This compound was obtained as the minor diastereoisomer by using imine **3j** and (*S*)-**2** as the starting materials. Chromatog-

raphy: *n*-hexane/AcOEt, 2:1; yield: 13%. ^{1}H NMR (300 MHz): δ = 7.60–7.05 (m, 14H), 6.66 (t, J = 6.3 Hz, 1H), 6.52 (d, J = 8.5 Hz, 2H), 5.11 (d, J = 5.8 Hz, 1H), 4.80 (brs, 1H), 4.14 (dq, J = 7.0, 5.8 Hz, 1H), 2.38 (s, 3H), 1.38 ppm (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.7, 143.8, 143.2, 141.0, 140.9, 140.5, 133.1 (2C), 131.7, 129.7, 129.1, 128.9 (2C), 128.6, 127.9, 127.8, 127.4, 125.6, 117.7, 113.6, 60.7, 39.7, 21.3, 18.8 ppm.

(1*S*,2*S*)-*N*-Phenyl-1-(4-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (6h): This compound was obtained as the minor diastereoisomer by using imine **3h** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 25%; yellow oil. $[\alpha]_D^{20}$ = +138.1 (c = 1.2 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 7.96 (d, J = 7.3 Hz, 1H), 7.65–7.20 (m, 10H), 6.93 (t, J = 8.5 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 6.47 (t, J = 7.3 Hz, 1H), 6.30 (d, J = 7.7 Hz, 2H), 4.80 (d, J = 6.1 Hz, 1H), 4.16 (dd, J = 10.5, 6.9 Hz, 1H), 3.80 (s, 3H), 3.54 (dq, J = 10.5, 6.9 Hz, 1H), 2.38 (s, 3H), 0.67 ppm (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 147.0, 145.5, 141.9, 141.8, 141.3, 134.6, 132.5 (2C), 130.0, 128.6, 128.4, 127.7, 126.9, 125.5, 116.1, 113.7, 112.8, 62.9, 55.1, 40.4, 21.3, 19.3 ppm. IR (NaCl): $\tilde{\nu}$ = 3324, 2930, 1605, 1504 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NO_2S$: C 76.45, H 6.42, N 3.07, S 7.02; found: C 76.55, H 6.41, N 3.30, S 7.20.

(1*R*,2*S*)-*N*-Phenyl-1-(4-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (7h): This compound was obtained as the major diastereoisomer by using imine **3h** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 36%; yellow oil. $[\alpha]_D^{20}$ = −10.8 (c = 0.5 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 7.59 (dd, J = 7.7, 1.6 Hz, 1H), 7.37 (td, J = 7.4, 1.5 Hz, 1H), 7.31 (td, J = 7.6, 1.5 Hz, 1H), 7.22–7.08 (m, 5H), 7.07–6.99 (m, 4H), 6.70 (d, J = 6.7 Hz, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.43 (dd, J = 8.0, 1.0 Hz, 2H), 4.86 (brs, 1H), 4.48 (d, J = 5.6 Hz, 1H), 3.98 (dq, J = 7.2, 5.6 Hz, 1H), 3.75 (s, 3H), 2.37 (s, 3H), 1.23 ppm (d, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 147.5, 143.9, 143.0, 141.1, 140.9, 133.2, 131.5, 129.7, 129.2, 128.9, 128.5, 128.1, 127.6, 125.5, 117.2, 113.6, 62.3, 55.1, 40.5, 21.3, 18.2 ppm. IR (NaCl): $\tilde{\nu}$ = 3321, 1602, 1510, 1247, 1027 cm^{-1}.

(1*S*,2*S*)-*N*-Phenyl-1-(2-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (6i): This compound was obtained as the minor diastereoisomer by using imine **3i** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 13%; yellow solid; m.p. 167–168°C. $[\alpha]_D^{20}$ = +115.6 (c = 0.6 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 7.92 (dd, J = 7.7, 1.4 Hz, 1H), 7.65–7.20 (m, 9H), 7.00–6.85 (m, 4H), 6.47 (td, J = 6.2, 1.1 Hz, 1H), 6.23 (dd, J = 7.7, 1.1 Hz, 2H), 4.89 (brs, 1H), 4.72 (brs, 1H), 3.92 (s, 3H), 3.62 (brs, 1H), 2.40 (s, 3H), 0.73 ppm (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCL_3$): δ = 157.7, 147.2, 146.1, 142.1, 141.9, 141.2, 132.4, 130.7, 129.9, 129.5, 129.2, 128.6, 128.0, 127.7,127.4, 126.8, 125.7, 121.1, 116.0, 112.6, 110.1, 55.4, 40.2, 21.3, 18.5 ppm. IR (NaCl): $\tilde{\nu}$ = 3221, 1601, 1491, 1239, 1026 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NO_2S$: C 76.45, H 6.42, N 3.07, S 7.02; found: C 76.50, H 6.34, N 3.10, S 6.71.

(1*R*,2*S*)-*N*-Phenyl-1-(2-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-propylamine (7i): This compound was obtained as the major diastereoisomer by using imine **3i** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 48%; green solid; m.p. 200–202°C (Et_2O). $[\alpha]_D^{20}$ = −32.7 (c = 0.7 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 7.55 (d, J = 8.0 Hz, 1H), 7.43–7.37 (m, 2H), 7.26–7.03 (m, 9H), 6.75–6.56 (m, 5H), 5.04 (d, J = 7.5 Hz, 1H), 4.70 (brs, 1H), 4.30 (dq, J = 7.5, 7.1 Hz, 3H), 3.74 (s, 3H), 2.37 (s, 3H), 1.46 ppm (d, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 147.4, 144.9, 143.7, 141.2, 140.5, 131.3, 129.5 (2C), 128.9, 128.5, 127.9, 127.8, 127.6, 127.3, 125.5, 120.4, 117.1, 113.3, 110.4, 57.6, 55.0, 39.5, 21.2, 19.1 ppm. IR (NaCl): $\tilde{\nu}$ = 3221, 1601, 1491, 1239, 1026 cm^{-1}.

(1*S*,2*S*)-*N*-Phenyl-1-(3,4-dimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6m): This compound was obtained as the minor diastereoisomer by using imine **3m** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 25%; yellow solid; m.p. 93.5–95.5°C. $[\alpha]_D^{20}$ = +128.3 (c = 0.4 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 7.96 (d, J = 7.3 Hz, 1H), 7.53 (d, J = 7.8 Hz, 2H), 7.45–7.35 (m, 5H), 7.29 (d, J = 7.8 Hz, 1H), 6.99–6.94 (m, 3H), 6.85 (d, J = 8.7 Hz, 1H), 6.50 (t, J = 7.3 Hz, 1H), 6.28 (d, J = 7.6 Hz, 2H), 5.05 (d, J = 4.7 Hz, 1H), 4.16 (dd, J = 10.1, 4.7 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.59 (dq, J = 10.1, 6.9 Hz, 1H), 2.39 (s, 3H), 0.64 ppm (d, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1, 148.0, 147.1, 145.7, 141.9, 141.6, 141.1, 135.3, 132.7, 129.9, 128.6 (2C), 128.2, 127.9, 126.8, 125.2, 120.1, 116.1, 112.8, 110.6, 109.7, 63.4, 55.7, 40.2, 21.2, 19.0 ppm. IR (NaCl): $\tilde{\nu}$ = 3319, 1602, 1512, 1258, 1027 cm^{-1}. Elemental analysis calcd (%) for $C_{30}H_{31}NO_3S$: C 74.20, H 6.43, N 2.88, S 6.60; found: C 74.69, H 6.43, N 2.87, S 6.31.

(1*R*,2*S*)-*N*-Phenyl-1-(3,4-dimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7m): This compound was obtained as the major diastereoisomer by using imine **3m** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 51%; yellow solid; m.p. 92–94°C (Et_2O). $[\alpha]_D^{20}$ = −44.7 (c = 0.9 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 7.57 (dd, J = 7.7, 1.5 Hz, 1H), 7.41–7.04 (m, 8H), 6.75–6.60 (m, 6H), 6.51 (dd, J = 8.6, 0.9 Hz, 1H), 5.09 (brs, 1H), 4.49 (d, J = 6.1 Hz, 1H), 4.07 (dq, J = 7.1, 6.1 Hz, 1H), 3.85 (s, 3H), 3.65 (s, 3H), 2.38 (s, 3H), 1.23 ppm (d, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.3, 144.7, 136.9, 135.9, 134.6, 134.0, 133.7, 124.3, 122.9, 122.6, 121.9, 121.4, 120.9, 120.4, 118.9, 118.4, 109.2, 107.6, 107.5, 106.3, 60.0, 48.5, 47.9, 33.5, 14.2, 11.1 ppm. IR (NaCl): $\tilde{\nu}$ = 3324, 1609, 1505, 1208, 1038 cm^{-1}. Elemental analysis calcd (%) for $C_{30}H_{31}NO_3S$: C 74.20, H 6.43, N 2.88, S 6.60; found: C: 74.67, H 6.41, N 2.71, S 6.63.

(1*R*,2*S*)-*N*-Phenyl-1-(2,4-dimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7l): This compound was obtained as the major diastereoisomer by using imine **3l** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 62%; yellow solid; m.p. 88–90°C (Et_2O). $[\alpha]_D^{20}$ = −34.8 (c = 0.6 in EtOH). ^{1}H NMR (300 MHz): δ = 7.58 (d, J = 8.1 Hz, 1H), 7.47–7.40 (m, 2H), 7.30–7.05 (m, 6H), 6.96 (d, J = 8.4 Hz, 2H), 6.70–6.55 (m, 3H), 6.34 (d, J = 2.3 Hz, 1H), 6.26 (dd, J = 8.4, 2.3 Hz, 1H), 4.99 (brs, 1H), 4.70 (brs, 1H), 4.29 (dq, J = 7.1, 6.0 Hz, 1H), 3.78 (s, 3H), 2.76 (s, 3H), 2.40 (s, 3H), 1.47 ppm (d, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.6, 157.7, 147.5, 145.1, 143.6, 141.4, 140.5, 131.2, 129.5, 129.1, 128.9, 127.9, 127.6, 127.3 (2C), 125.5, 121.9, 117.0, 113.3, 104.0, 98.3, 55.2, 55.0, 39.7, 21.2, 19.2 ppm. IR (NaCl): $\tilde{\nu}$ = 3324, 1609, 1505, 1208, 1038 cm^{-1}. Elemental analysis calcd (%) for $C_{30}H_{31}NO_3S$: C 74.20, H 6.43, N 2.88, S 6.60; found: C 73.39, H 6.36, N 2.89, S 6.36.

(1*S*,2*S*)-*N*-Phenyl-1-(2,4,6-trimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]-phenyl}propylamine (6o): This compound was obtained as the minor diastereoisomer by using imine **3o** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 18%; yellow solid; m.p. 181–183°C. $[\alpha]_D^{20}$ = −54.0 (c = 0.5 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 7.77 (dd, J = 7.8, 1.4 Hz, 1H), 7.65–7.45 (m, 4H), 7.40–7.25 (m, 2H), 7.00–6.90 (m, 2H), 6.50 (t, J = 7.3 Hz, 1H), 6.3 (d, J = 8.7 Hz, 2H), 6.15–6.12 (m, 2H), 5.26 (dd, J = 10.9, 10.4 Hz, 1H), 4.49 (d, J = 10.9 Hz, 1H), 4.16 (dq, J = 10.4, 7.0 Hz, 1H), 3.95 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 2.44 (s, 3H), 0.96 ppm (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 159.3, 159.1, 148.1, 147.0, 142.6, 142.4, 141.0, 131.9, 129.7, 128.6, 127.0 126.6, 126.5, 126.3, 116.4, 113.1, 109.0, 91.5, 90.3, 56.0, 55.5, 55.2, 53.9, 37.8, 21.3, 19.8 ppm. IR (NaCl): $\tilde{\nu}$ = 3346, 1603, 1030 cm^{-1}. Elemental analysis calcd (%) for $C_{31}H_{33}NO_4S$: C 72.20, H 6.45, N 2.72, S 6.22; found: C 72.74, H 6.37, N 2.72, S 6.14.

(1*R*,2*S*)-*N*-Phenyl-1-(2,4,6-trimethoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]-phenyl}propylamine (7o): This compound was obtained as the major diastereoisomer by using imine **3o** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 36%; yellow oil. $[\alpha]_D^{20}$ = −25.8 (c = 0.8 in EtOH). ^{1}H NMR (300 MHz): δ = 7.97 (d, J = 7.9 Hz, 1H), 7.60–7.20 (m, 6H), 7.00–6.97 (m, 2H), 6.70 (t, J = 7.1 Hz, 1H), 6.20 (d, J = 8.7 Hz, 2H), 6.25–6.22 (m, 2H), 5.36 (m, 1H), 5.00 (m, 1H), 4.60 (dq, J = 7.0, 6.4 Hz, 1H), 3.90 (s, 3H), 3.74 (s, 6H), 2.42 (s, 3H), 1.65 ppm (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 147.1, 145.7, 141.8, 141.4, 141.1, 138.7, 136.7, 132.7, 129.8, 128.6, 128.4, 127.9, 126.8, 125.0, 116.0, 112.6, 104.1, 64.0, 60.7, 56.0, 40.1, 21.2, 18.9 ppm.

Products from the reactions of (*S*)-1 with *N*-phenylarylideneamines 3′ (Table 4)

(1*S*)-*N*-(4-Cyanophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4′b): This compound was obtained as the major diastereoisomer by using imine **3′b** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 74%; yellow solid; m.p. 88–90°C. $[\alpha]_D^{20}$ = +67.0 (c = 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz): δ = 7.80 (d, J = 11.0 Hz, 1H),

7.60–7.24 (m, 10H), 7.23 (d, $J=7.1$ Hz, 2H), 7.04 (d, $J=6.0$ Hz, 1H), 6.62 (d, $J=8.5$ Hz, 1H), 6.35 (d, $J=8.7$ Hz, 2H), 4.54–4.31 (m, 1H), 4.26 (brs, 1H), 3.50 (dd, $J=14.0$, 10.6 Hz, 1H), 2.74 (dd, $J=14.0$, 3.9 Hz, 1H), 2.32 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=150.6$, 142.5 141.9, 141.0 (2C), 140.6, 139.2 (2C), 133.6, 133.1, 132.6, 132.4, 129.9, 129.1, 127.3, 126.6, 124.7, 114.3, 112.5, 59.6, 39.5, 21.1 ppm. IR (NaCl): $\tilde{\nu}=3352$, 2213, 1607, 1527, 1339, 1173 cm^{-1}. MS (FAB$^+$): m/z (%): 437 (70) $[M+1]^+$, 415 (53), 319 (51), 230 (21). HRMS: m/z calcd for $C_{28}H_{25}OSN_2$: 437.1687; found: 437.1677.

(1*R*)-*N*-(4-Cyanophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenylethylamine (5′b): This compound was obtained as the minor diastereoisomer by using imine **3′b** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 11%; yellow solid; m.p. 178–180°C. $[\alpha]_D^{20}=-119.5$ ($c=0.4$ in MeOH). ^{1}H NMR (200 MHz): $\delta=7.60$–7.24 (m, 14H), 6.37 (d, $J=8.7$ Hz, 2H), 6.15 (d, $J=5.4$ Hz, 1H), 4.65–4.57 (m, 1H), 3.53 (dd, $J=14.2$, 9.3 Hz, 1H), 2.74 (dd, $J=14.2$, 5.0 Hz, 1H), 2.40 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=142.0$, 141.8, 137.9, 133.2 (2C), 131.7, 131.1 (2C), 130.2, 128.8 (2C), 127.9, 127.6 (2C), 126.9, 126.2, 125.8, 112.8, 58.9, 40.2, 21.4 ppm. IR (NaCl): $\tilde{\nu}=3307$, 2212, 1607, 1525, 1340, 1173 cm^{-1}.

(1*S*/1*R*)-*N*-(3-Chlorophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (4′d): This compound was obtained as the major diastereoisomer by using imine **3′d** and (*S*)-**1** as the starting materials. This compound was obtained with **5′d** as an inseparable mixture of diastereoisomers. Yield: 78%. Major diastereoisomer **4′d**: ^{1}H NMR (200 MHz): $\delta=$ 7.80 (d, $J=9.1$ Hz, 1H), 7.40–7.05 (m, 11H), 6.92–6.23 (m, 5H), 4.60–4.50 (m, 1H), 3.40 (dd, $J=14.0$, 9.4 Hz, 1H), 3.30 (dd, $J=14.0$, 4.5 Hz, 1H), 2.27 ppm (s, 3H). Minor diastereoisomer **5′d**: ^{1}H NMR (200 MHz): $\delta=$ 7.60 (d, $J=9.0$ Hz, 1H), 7.40–7.05 (m, 11H), 6.90–6.30 (m, 5H), 4.45–4.40 (m, 1H), 3.35 (dd, $J=14.3$, 9.6 Hz, 1H), 3.10 (dd, $J=14.3$, 5.5 Hz, 1H), 2.27 ppm (s, 3H).

(1*S*)-*N*-(3-Methoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (4′f): This compound was obtained as the minor diastereoisomer and mixed with sulfoxide **1** by using imine **3′f** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 27%. ^{1}H NMR (200 MHz): $\delta=7.70$ (d, $J=9.3$ Hz, 1H), 7.40–7.23 (m, 14H), 6.61 (t, $J=7.1$ Hz, 1H), 6.43 (d, $J=7.7$, 1.1 Hz, 2H), 4.66–4.55 (m, 2H), 3.62 (s, 3H), 3,40 (dd, $J=14.4$, 8.6 Hz, 1H), 3.21 (dd, $J=14.4$, 5.6 Hz, 1H), 2.38 ppm (s, 3H).

(1*R*)-*N*-(3-Methoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (5′f): This compound was obtained as a major by using imine **3′f** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 41%; white solid; m.p. 68–70°C. $[\alpha]_D^{20}=-116.0$ ($c=1.4$ in $CHCl_3$). ^{1}H NMR (200 MHz): $\delta=7.69$ (d, $J=9.1$ Hz, 1H), 7.45–7.13 (m, 12H), 6.94 (t, $J=7.9$ Hz, 1H), 6.19 (dd, $J=8.1$, 2.3 Hz, 1H), 6.07 (dd, $J=8.1$, 2.3 Hz, 1H), 5.98 (t, $J=2.3$ Hz, 1H), 4.60 (dd, $J=8.7$, 1.2 Hz, 1H), 3.65 (s, 3H), 3.38 (dd, $J=14.4$, 8.4 Hz, 1H), 3.18 (dd, $J=14.4$, 8.7 Hz, 1H), 2.36 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=151.6$, 142.9, 141.6, 140.7, 137.1, 131.3, 130.7, 129.9, 129.5, 128.6, 127.9, 127.4, 127.3, 126.2, 125.7, 125.6, 125.2, 106.5, 102.6, 99.4, 58.8, 54.8, 40.5, 21.3 ppm. IR (NaCl): $\tilde{\nu}=3330$, 3051, 1601, 1497, 1238 cm^{-1}.

(1*S*)-*N*-(4-Methoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (4′h): This compound was obtained as the minor diastereoisomer by using imine **3′h** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 21%; white solid; m.p. 88–90°C. $[\alpha]_D^{20}=-19.6$ ($c=0.5$ in MeOH). ^{1}H NMR (200 MHz): $\delta=7.92$ (d, $J=9.1$ Hz, 1H) 7.41–7.14 (m, 12H), 6.61 (d, $J=9.0$ Hz, 2H), 6.31 (d, $J=9.0$ Hz, 2H), 4.56 (brs, 1H), 4.45–4.30 (m, 1H), 3.64 (s, 3H), 3.25 (dd, $J=14.0$, 8.9 Hz, 1H), 3.02 (dd, $J=14.0$, 5.2 Hz, 1H), 2.35 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=151.5$, 143.4, 143.0, 141.4, 141.1, 131.3 (2C), 131.1, 130.0 (2C), 128.8, 127.5, 127.0, 126.3, 126.4, 125.7, 114.4, 114.2, 59.7, 55.6, 40.4, 21.2 ppm. IR (NaCl): $\tilde{\nu}=3330$, 1465, 1235, 1030 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{27}NO_2S$: C 76.16, H 6.16, N 3.17, S 7.26; found: C 75.89, H 6.09, N 3.15, S 7.12.

(1*R*)-*N*-(4-Methoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (5′h): This compound was obtained as the major diastereoisomer by using imine **3′h** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 56%; yellow solid; m.p. 94–96°C. $[\alpha]_D^{20}=-166.2$ ($c=0.55$ in MeOH). ^{1}H NMR (200 MHz): $\delta=7.78$ (d, $J=$ 9.3 Hz, 1H), 7.41–7.14 (m, 12H), 6.68 (d, $J=9.0$ Hz, 2H), 6.44 (d, $J=$ 9.0 Hz, 2H), 4.59 (dd, $J=8.5$, 6.1 Hz, 1H), 4.30 (brs, 1H), 3.70 (s, 3H), 3.40 (dd, $J=14.4$, 8.5 Hz, 1H), 3.22 (dd, $J=14.4$, 6.1 Hz, 1H), 2.39 ppm (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=151.9$, 143.8, 143.1, 141.5, 141.1, 140.9, 137.1, 131.2, 130.7, 130.0, 129.9, 128.6, 127.9, 127.2, 126.1, 125.6, 114.7, 114.5, 59.7, 55.6, 40.7, 21.0 ppm. IR (NaCl): $\tilde{\nu}=3330$, 1512, 1236, 1033 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{27}NO_2S$: C 76.16, H 6.16, N 3.17, S 7.26; found: C 75.82, H 6.11, N 3.21, S 7.14.

(1*R*/1*S*)-*N*-(4-Methylphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethylamine (5′g/4′g): These compounds were obtained as an inseparable mixture of diastereoisomers by using imine **3′g** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 80%. Major diastereoisomer (1*R*)-**5′g**: ^{1}H NMR (200 MHz): $\delta=7.90$ (d, $J=9.1$ Hz, 1H), 7.50–7.10 (m, 14H), 6.83 (d, $J=8.6$ Hz, 2H), 6.37 (d, $J=8.6$ Hz, 1H), 4.59 (dd, $J=8.5$, 5.9 Hz, 1H), 3.37 (dd, $J=14.4$, 8.5 Hz, 1H), 3.17 (dd, $J=14.4$, 5.9 Hz, 1H), 2.35 (s, 3H), 2.17 ppm (s, 3H). Minor diastereoisomer (1*S*)-**4′g**: ^{1}H NMR (200 MHz): $\delta=7.74$ (d, $J=9.0$ Hz, 1H), 7.50–7.10 (m, 14H), 6.81 (d, $J=8.5$ Hz, 2H), 6.25 (d, $J=8.5$ Hz, 1H), 4.42 (dd, $J=9.1$, 5.1 Hz, 1H), 3.21 (dd, $J=10.8$, 9.1 Hz, 1H), 3.03 (dd, $J=10.8$, 5.1 Hz, 1H), 2.35 (s, 3H), 2.13 ppm (s, 3H).

(1*R*/1*S*)-*N*-(2-Methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-1-phenylethylamine (4′i/5′i): These compounds were obtained as an inseparable mixture of diastereoisomers by using imine **3′i** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 57%. Major diastereoisomer (1*R*)-**5′i**: ^{1}H NMR (200 MHz): $\delta=7.74$ (d, $J=9.0$ Hz, 1H), 7.50–7.10 (m, 13H), 6.70–6.40 (m, 2H), 6.05 (d, $J=7.5$ Hz, 1H), 4.26–4.24 (m, 1H), 3.70 (s, 3H), 3.37 (dd, $J=14.3$, 7.9 Hz, 1H), 3.17 (dd, $J=14.3$, 5.9 Hz, 1H), 2.35 ppm (s, 3H). Minor diastereoisomer (1*S*)-**4′i**: ^{1}H NMR (200 MHz): $\delta=7.90$ (d, $J=9.1$ Hz, 1H), 7.50–7.10 (m, 13H), 6.70–6.40 (m, 2H), 6.12 (d, $J=7.7$ Hz, 1H), 4.45–4.40 (m, 1H), 3.72 (s, 3H), 3.40 (dd, $J=14.4$, 7.6 Hz, 1H), 3.22 (dd, $J=14.4$, 5.9 Hz, 1H), 2.35 ppm (s, 3H).

(1*R*/1*S*)-*N*-(*N*′,*N*′-Dimethylaminophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylphenylamine (5′k/4′k): These compounds were obtained as an inseparable mixture of diastereoisomers by using imine **3′k** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 71%. Major diastereoisomer (1*R*)-**5′k**: ^{1}H NMR (200 MHz): $\delta=7.79$ (d, $J=9.3$ Hz, 1H), 7.51–7.08 (m, 12H), 6.63 (d, $J=8.5$ Hz, 2H), 6.46 (d, $J=$ 8.5 Hz, 2H), 4.59 (dd, $J=8.5$, 6.1 Hz, 1H), 4.15 (brs, 1H), 3.70 (s, 3H), 3.40 (dd, $J=14.4$, 8.5 Hz, 1H), 3.22 (dd, $J=14.4$, 6.1 Hz, 1H), 2.74 (s, 6H), 2.39 ppm (s, 3H). ^{13}C NMR (50 MHz): $\delta=143.8$, 141.5, 141.4, 141.0, 137.0, 131.1, 130.9, 130.6, 129.9, 129.8, 127.8, 127.5, 127.0, 126.3, 126.0, 125.8, 125.4, 114.4, 59.6, 42.1, 40.7, 21.2 ppm. Minor diastereoisomer (1*S*)-**4′k**: ^{1}H NMR (200 MHz): $\delta=7.95$ (d, $J=9.1$ Hz, 1H), 7.41–7.14 (m, 12H), 6.59 (d, $J=8.5$ Hz, 2H), 6.33 (d, $J=8.5$ Hz, 2H), 4.61–4.58 (m, 1H), 4.41–4.39 (m, 1H), 3.24–3.18 (m, 1H), 3.03 (dd, $J=14.1$, 5.4 Hz, 1H), 2.74 (s, 6H), 2.36 ppm (s, 3H).

(1*R*/1*S*)-*N*-(2,3,4-Trimethoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]-phenyl}ethylamine (5′m/4′m): These compounds were obtained as an inseparable mixture of diastereoisomers by using imine **3′m** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 73%. Major diastereoisomer (1*R*)-**5′m**: ^{1}H NMR (300 MHz): $\delta=7.73$ (d, $J=9.3$ Hz, 1H), 7.50–7.10 (m, 14H), 5.72 (s, 2H), 4.62 (dd, $J=8.4$, 6.0 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 6H), 3.45 (dd, $J=13.9$, 8.4 Hz, 1H), 3.22 (dd, $J=13.9$, 6.0 Hz, 1H), 2.34 ppm (s, 3H). ^{13}C NMR (75 MHz): $\delta=$ 153.5, 143.8, 143.1, 141.5, 141.3, 140.6, 138.1, 137.1, 131.3, 130.8, 129.8, 128.7 (2C), 127.9, 127.9, 127.2, 126.3, 126.1, 125.4, 91.2, 60.8, 59.4, 55.5 (2C), 40.4, 21.3 ppm. Minor diastereoisomer (1*S*)-**4′m**: ^{1}H NMR (300 MHz): $\delta=7.90$ (d, $J=9.1$ Hz, 1H), 7.50–7.10 (m, 14H), 5.62 (s, 2H), 4.42 (dd, $J=8.3$, 6.0 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 6H), 3.33 (dd, $J=13.9$, 8.3 Hz, 1H), 2.98 (dd, $J=13.9$, 6.0 Hz, 1H), 2.34 ppm (s, 3H).

(1*R*/1*S*)-*N*-(2,4-Dimethoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5′l/4′l): These compounds were obtained as an inseparable mixture of diastereoisomers by using imine **3′l** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1. yield: 75%. Major diastereoisomer (1*R*)-**5′l**: ^{1}H NMR (300 MHz): $\delta=7.77$ (d, $J=9.2$ Hz, 1H), 7.50–7.10 (m, 12H), 6.60 (d, $J=8.6$ Hz, 1H), 6.15 (d, $J=2.5$ Hz,

1H), 5.98 (dd, $J=8.7$, 2.5 Hz, 1H), 4.61 (dd, $J=8.4$, 6.1 Hz, 1H), 4.40 (brs, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.43 (dd, $J=14.3$, 8.4 Hz, 1H), 3.23 (dd, $J=14.3$, 6.1 Hz, 1H), 2.38 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=149.6$, 143.8, 143.1, 141.8, 141.4, 141.3, 140.8, 137.0, 131.2, 130.7, 129.9, 127.9, 126.3, 126.0, 125.5, 112.9, 104.4, 99.5, 59.7, 56.5, 55.4, 40.6, 21.2 ppm. Minor diastereoisomer (1*R*)-**4′l**: ^{1}H NMR (300 MHz): $\delta=7.86$ (d, $J=9.2$ Hz, 1H), 7.55–7.10 (m, 11H), 6.58 (d, $J=8.7$ Hz, 1H), 6.05 (d, $J=2.6$ Hz, 1H), 5.86 (dd, $J=8.7$, 2.6 Hz, 2H), 4.45 (m, 2H), 3.73 (s, 3H), 3.70 (s, 3H), 3.34 (dd, $J=14.5$, 4.7 Hz, 1H), 3.01 (dd, $J=14.5$, 5.4 Hz, 1H), 2.36 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=143.9$, 143.8, 143.1, 141.8, 141.4, 141.3, 140.8, 137.0, 131.2, 130.7, 129.9, 127.9, 126.2, 126.0, 125.6, 112.9, 103.9, 99.1, 59.9, 59.7, 56.8, 40.3, 20.9 ppm.

Products from the reactions of (*S*)-2 with *N*-aryl-substituted imines (Table 5)

(1*S*,2*S*)-*N*-(4-Cyanophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′b): This compound was obtained as the major diastereoisomer by using imine **3′b** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 86%; yellow solid; m.p. 188–190°C. $[\alpha]_D^{20}=152.8$ ($c=0.8$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta=7.77$ (dd, $J=7.8$, 1.4 Hz, 1H), 7.65–7.45 (m, 4H), 7.40–7.25 (m, 2H), 7.00–6.90 (m, 2H), 6.50 (t, $J=7.3$ Hz, 1H), 6.3 (d, $J=8.7$ Hz, 2H), 6.15–6.12 (m, 2H), 5.26 (dd, $J=10.9$, 10.4 Hz, 1H), 4.49 (d, $J=10.9$ Hz, 1H), 4.16 (dq, $J=10.4$, 7.0 Hz, 1H), 3.95 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 2.44 (s, 3H), 0.96 ppm (d, $J=7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=150.4$, 146.4, 141.6, 141.2, 141.1, 140.9, 133.3, 130.0, 129.8, 128.5, 128.4, 127.4, 127.2, 126.9, 124.4, 120.7, 112.2, 97.1, 64.0, 39.3, 21.1, 18.2 ppm. IR (NaCl): $\tilde{\nu}=3346$, 1603, 1030 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{26}NOS$: C 77.30, H 5.82, N 6.22, S 7.12; found: C 76.96, H 5.83, N 6.22, S 7.12.

(1*R*,2*S*)-*N*-(4-Cyanophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7′b): This compound was obtained as the minor diastereoisomer by using imine **3′b** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 2%; brown solid; m.p. 175.5–177.0°C. $[\alpha]_D^{20}=+143.2$ ($c=0.68$ in $CHCl_3$). ^{1}H NMR (200 MHz): $\delta=7.70$ (d, $J=7.8$ Hz, 2H), 7.60–7.00 (m, 12H), 6.72–6.40 (m, 3H), 4.34–4.20 (m, 1H), 3.00 (dq, $J=6.9$, 6.2 Hz, 1H), 2.38 (s, 3H), 1.05 ppm (d, $J=6.9$ Hz, 1H).

(1*R*/1*S*,2*S*)-*N*-(3-Chlorophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′c/7′c): These compounds were obtained as an inseparable mixture of diastereoisomers; yield: 80%. Major diastereoisomer **7′c**: ^{1}H NMR (200 MHz): $\delta=7.90$ (d, $J=9.1$ Hz, 1H), 7.60–7.00 (m, 11H), 6.80 (t, $J=8.0$ Hz, 1H), 6.45–6.35 (m, 2H), 6.25–6.00 (m,2H), 5.33 (d, $J=7$ Hz, 1H), 4.15 (dd, $J=10.2$, 7.0 Hz, 1H), 3.7 (brs, 1H), 3.66–3.45 (m, 1H), 2.36 (s, 3H), 0.56 ppm (d, J=6.98, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=148.2$, 145.7, 142.1, 141.6, 141.2, 140.9, 134.3, 132.8, 130.2, 130.0, 129.6, 128.5, 127.9, 127.3, 127.0, 125.3, 118.4, 115.9, 112.5, 110.8, 63.9, 40.0, 21.3, 19.0 ppm.

(1*S*,2*S*)-*N*-(4-Chlorophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′e): This compound was obtained as the major diastereoisomer by using imine **3′e** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 49%; yellow solid; m.p. 167–169°C. $[\alpha]_D^{20}=+153.5$ ($c=10$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta=7.91$ (d, $J=7.6$ Hz, 1H), 7.53–7.20 (m, 8H), 6.85 (d, $J=8.6$ Hz, 2H), 6.18 (d, $J=8.9$ Hz, 2H), 5.42 (d, $J=7.2$ Hz, 1H), 4.13 (dd, $J=10.3$, 7.2 Hz, 1H), 3.61 (dq, $J=10.3$, 6.9 Hz, 1H), 2.34 (s, 3H), 0.57 ppm (d, $J=6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=145.8$, 145.7, 142.2, 141.7, 140.9, 132.8 , 129.8, 128.6, 128.6, 128.3 (2C), 127.9, 127.4, 127.2, 126.8, 125.0, 120.4, 113.7, 64.0, 39.8, 21.2, 18.8 ppm. IR (NaCl): $\tilde{\nu}=3311$, 1599, 1492, 1320, 1016, 1012 cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{26}ClNOS$: C 73.10, H 5.70, N 3.04, S 6.97; found: C 72.67, H 5.64, N 3.08, S 6.70.

(1*R*,2*S*)-*N*-(4-Chlorophenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7′e): This compound was obtained as the minor diastereoisomer by using imine **3′e** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 9%; yellow solid; m.p. 93–95°C. $[\alpha]_D^{20}=+26.5$ ($c=0.8$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta=7.62$ (d, $J=9.2$ Hz, 1H), 7.35–7.05 (m, 12H), 6.92 (d, $J=9.0$ Hz, 2H), 6.31 (d, $J=9.0$ Hz, 2H), 5.24–5.12 (m, 1H), 4.45–4.38 (m, 1H), 3.99 (dd, $J=7.2$, 5.2 Hz, 1H), 2.36 (s, 3H), 1.13 ppm (d, $J=7.2$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=147.3$, 143.4, 142.8, 140.5, 131.5, 129.9, 129.8 (2C), 128.9, 128.7, 128.6, 128.5, 128.2, 127.6, 127.5, 127.2, 125.3, 114.6, 63.2, 39.9, 21.3, 18.1 ppm. IR (NaCl): $\tilde{\nu}=3317$, 1599, 1493, 1026 cm^{-1}.

(1*S*,2*S*)-*N*-(3-Methoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′f): This compound was obtained as the major diastereoisomer by using imine **3′f** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 48%; yellow oil. $[\alpha]_D^{20}=+121.0$ ($c=1.9$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta=7.97$ (d, $J=7.8$ Hz, 1H), 7.58–7.20 (m, 12H), 6.83 (t, $J=8.0$ Hz, 1H), 6.06 (d, $J=8.0$ Hz, 1H), 5.86 (d, $J=8.0$ Hz, 1H), 5.79 (s, 1H), 4.98 (d, $J=6.2$ Hz, 1H), 4.20 (dd, $J=10.0$, 6.8 Hz, 1H), 3.59 (dq, $J=10.0$, 6.9 Hz, 1H), 2.38 (s, 3H), 0.65 ppm (d, $J=6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=160.4$, 148.5, 145.5, 142.7, 141.9, 141.8, 141.4, 132.7, 130.1, 129.3, 128.5, 127.9, 127.5, 127.2, 126.9, 125.5, 106.1, 103.9, 101.5, 98.6, 66.8, 54.8, 40.2, 21.3, 19.3 ppm.

(1*S*,2*S*)-*N*-(4-Methylphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′g): This compound was obtained as the major diastereoisomer by using imine **3′g** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 54%; yellow solid; m.p. 92–94°C. $[\alpha]_D^{20}=+129.5$ ($c=0.8$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta=8.02$ (d, $J=7.5$ Hz, 1H), 7.59 (d, $J=8.3$ Hz, 2H), 7.48–7.26 (m, 10H), 6.78 (d, $J=8.3$ Hz, 2H), 6.16 (d, $J=8.3$ Hz, 2H), 4.61 (brs, 1H), 4.24 (d, $J=10.1$ Hz, 1H), 3.61 (dq, $J=10.1$, 6.9 Hz, 1H), 2.42 (s, 3H), 2.13 (s, 3H), 0.74 ppm (d, $J=6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=145.2$, 144.7, 142.7, 141.9, 141.8, 141.3, 132.4, 130.0 (2C), 129.1, 128.3, 127.5, 127.4, 127.4, 127.1, 126.9, 125.6, 112.7, 63.7, 40.3, 21.2, 20.1, 19.3 ppm. IR (NaCl): $\tilde{\nu}=3322$, 1618, 1453, 1264 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NOS$: C 79.23, H 6.65, N 3.19, S 7.29; found: C 78.99, H 6.55, N 3.27, S 7.11.

(1*R*,2*S*)-*N*-(4-Methylphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7′g): This compound was obtained as the minor diastereoisomer by using imine **3′g** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 27%; yellow solid; m.p. 88–90°C. $[\alpha]_D^{20}=-17.5$ ($c=0.6$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta=7.63$ (dd, $J=7.7$, 1.5 Hz, 1H), 7.53–7.10 (m, 13H), 6.88 (d, $J=8.0$ Hz, 1H), 6.40 (d, $J=8.0$ Hz, 2H), 4.71 (brs, 1H), 4.55 (d, $J=5.8$ Hz, 1H), 4.06 (dq, $J=7.1$, 5.8 Hz, 1H), 2.42 (s, 3H), 2.20 (s, 3H), 1.31 ppm (d, $J=7.1$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=145.1$, 143.9, 143.0, 141.6, 141.1, 140.9, 131.5, 129.9, 129.5, 129.4, 128.9, 128.1, 127.6, 127.4, 126.9, 126.4, 125.6, 113.6, 62.9, 40.5, 21.3, 20.3, 17.9 ppm. IR (NaCl): $\tilde{\nu}=3322$, 1618, 1453, 1264 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NOS$: C 79.23, H 6.65, N 3.19, S 7.29; found: C 79.16, H 6.56, N 3.18, S 7.00.

(1*S*,2*S*)-*N*-(4-Methoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′h): This compound was obtained as the minor diastereoisomer by using imine **3′h** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 28%; brown solid; m.p. 161–162°C. $[\alpha]_D^{20}=+144.7$ ($c=0.5$ in $CHCl_3$). IR (NaCl): $\tilde{\nu}=3321$, 1511, 1237, 1028 cm^{-1}. ^{1}H NMR (300 MHz): $\delta=$ 8.01 (d, $J=7.6$ Hz, 1H), 7.61–7.10 (m, 13H), 6.57 (d, $J=9.0$ Hz, 1H), 6.17 (d, $J=9.0$ Hz, 2H), 4.40 (brs, 1H), 4.20 (d, $J=9.7$ Hz, 1H), 3.64 (s, 3H), 3.59 (dq, $J=10.0$, 7.0 Hz, 1H), 2.41 (s, 3H), 0.74 ppm (d, $J=7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.1$, 145.2, 142.8, 141.0, 141.4, 132.4, 129.9, 128.3, 127.6, 127.5, 127.3, 127.1, 126.9, 125.6, 114.4 (2C), 113.9 (2C), 64.2, 55.6, 40.4, 21.3, 19.4 ppm.

(1*R*,2*S*)-*N*-(4-Methoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7′h): This compound was obtained as the major diastereoisomer by using imine **3′h** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 50%; brown solid; m.p. 161–163°C. $[\alpha]_D^{20}=-8.5$ ($c=0.6$ in $CHCl_3$). ^{1}H NMR (300 MHz): $\delta=7.63$ (dd, $J=7.7$, 1.5 Hz, 1H), 7.43–7.11 (m, 13H), 6.67 (d, $J=8.9$ Hz, 1H), 6.43 (d, $J=8.9$ Hz, 2H), 4.63 (brs, 1H), 4.50 (d, $J=5.9$ Hz, 1H), 4.07 (dq, $J=7.0$, 5.9 Hz, 1H), 3.70 (s, 3H), 2.41 (s, 3H), 1.31 ppm (d, $J=7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.8$, 143.9, 142.9, 141.6, 141.5, 140.8, 131.4, 129.7, 128.9, 128.0, 127.9, 127.5, 126.8, 127.4, 125.5, 114.8, 114.6, 114.5, 63.5, 55.6, 40.4, 21.2, 17.9 ppm. IR (NaCl): $\tilde{\nu}=3320$, 1511, 1238, 1028 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NO_2S_1$: C 76.45, H 6.42, N 3.07, S 7.02; found: C 76.00, H 6.31, N 3.18, S 6.73.

(1*S*,2*S*)-*N*-(3,4-Dimethoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′n): This compound was obtained as the minor diastereoisomer by using imine **3′n** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 24%; orange solid; m.p. 90–92°C.

$[\alpha]_D^{20}=+128.4$ ($c=0.4$ in $CHCl_3$). ^1H NMR (300 MHz): $\delta=7.93$ (d, $J=8.3$ Hz, 1H), 7.52–7.22 (m, 12H), 6.56 (d, $J=8.6$ Hz, 2H), 5.83 (d, $J=2.5$ Hz, 2H), 5.70 (dd, $J=8.6$, 2.3 Hz, 1H), 4.75 (brs, 1H), 4.13 (d, $J=10.1$ Hz, 1H), 3.65 (s, 3H), 3.59 (dq, $J=10.1$, 6.9 Hz, 1H), 2.34 (s, 3H), 0.64 ppm (d, $J=6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=149.5$, 145.5, 142.9, 142.1, 141.9, 141.1, 140.5, 132.5, 129.9, 128.3, 127.8 (2C), 127.7, 127.4, 127.1 (2C), 126.9, 125.4, 113.0, 103,5, 98.8, 64.5, 56.5, 55.4, 40.2, 21.2, 19.1 ppm. Elemental analysis calcd (%) for $C_{30}H_{31}NO_3S$: C 74.20, H 6.43, N 2.88, S 6.60; found: C 74.00, H 6.31, N 3.18, S 6.73.

(1*R*,2*S*)-*N*-(3,4-Dimethoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7′n): This compound was obtained as the major diastereoisomer by using imine **3′n** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 2:1; yield: 66%; brown solid; m.p. 84–86°C. $[\alpha]_D^{20}=-8.6$ ($c=0.6$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.57$ (dd, $J=7.6$, 1.6 Hz, 1H), 7.43–7.11 (m, 11H), 6.56 (d, $J=8.6$ Hz, 1H), 6.10 (d, $J=2.6$ Hz, 2H), 5.89 (dd, $J=8.6$, 2.6 Hz, 1H), 4.75 (brs, 1H), 4.44 (d, $J=5.8$ Hz, 1H), 4.00 (dq, $J=7.1$, 5.8 Hz, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 2.36 (s, 3H), 1.23 ppm (d, $J=7.1$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 149.6, 143.8, 142.9, 142.3, 141.4, 141.2, 141.0, 140.8, 131.5, 130.0, 129.7, 129.2, 128.1, 127.5, 126.9, 126.0, 125.4, 125.3, 111.9, 104.4, 99.5, 63.7, 56.5, 55.4, 40.2, 21.2, 18.0 ppm. IR (NaCl): $\tilde{\nu}=3323$, 1615, 1596, 1234, 1026 cm^{-1}. Elemental analysis calcd (%) for $C_{30}H_{31}NO_3S$: C 74.20, H 6.43, N 2.88, S 6.60; found: C 74.12, H 6.32, N 2.87, S 6.59.

(1*S*,2*S*)-*N*-(2,4-Dimethoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6′l): This compound was obtained as the minor diastereoisomer by using imine **3′l** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 8%; yellow oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.85$ (d, $J=9.1$ Hz, 1H), 7.48 (d, $J=8.3$ Hz, 2H), 7.42–7.11 (m, 10H), 6.15 (d, $J=3.0$ Hz, 1H), 6.13 (d, $J=8.6$ Hz, 1H), 6.10 (d, $J=8.8$ Hz, 1H), 4.45 (d, $J=7.0$ Hz, 1H), 4.00–4.20 (m, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.35 (s, 3H), 1.21 ppm (d, $J=9.8$ Hz, 3H).

(1*R*,2*S*)-*N*-(2,4-Dimethoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7′l): This compound was obtained as the major diastereoisomer by using imine **3′l** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 68%; brown solid; m.p. 81–83°C. $[\alpha]_D^{20}=+43.2$ ($c=0.6$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.86$ (d, $J=9.2$ Hz, 1H), 7.57 (d, $J=8.3$ Hz, 2H), 7.40–7.11 (m, 10H), 6.28 (d, $J=2.5$ Hz, 1H), 6.13 (dd, $J=8.7$, 2.6 Hz, 1H), 6.07 (d, $J=8.7$ Hz, 1H), 4.42 (brs, 1H), 4.07 (d, $J=6.5$ Hz, 1H), 4.00 (dq, $J=6.9$, 6.5 Hz, 1H), 3.63 (s, 3H), 3.59 (s, 3H), 2.34 (s, 3H), 0.98 ppm (d, $J=7.1$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.5$, 147.7, 144.0, 143.1, 142.4, 141.8, 141.2, 131.7, 131.6, 129.8, 128.2, 127.7, 127.3 (2C), 127.1, 126.3, 125.7, 111.1, 103.5, 99.1, 64.1, 55.5, 55.4, 40.9, 21.3, 19.2 ppm. IR (NaCl): $\tilde{\nu}=3346$, 1596, 1518, 1031 cm^{-1}. Elemental analysis calcd (%) for $C_{30}H_{31}NO_3S$: C 74.20, H 6.43, N 2.88, S 6.60; found: C 74.12, H 6.48, N 3.22, S 6.28.

Products from the reactions of (*S*)-1 and (*S*)-2 with *N*-(2,4,6-trimethoxyphenyl)arylideneamines 3″ (Table 6)

(1*S*/1*R*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-cyanophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (4″b/5″b): These compounds were obtained as an inseparable mixture of diastereoisomers. Chromatography: *n*-hexane/AcOEt, 4:1. Yield: 70%; yellow oil. Minor diastereoisomer: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.62$ (d, $J=6.7$ Hz, 1H), 7.38–7.20 (m, 5H), 6.17–7.10 (m, 6H), 5.93 (s, 2H), 4.85 (t, $J=7.2$ Hz, 1H), 3.76 (s, 6H), 3.68 (s, 3H), 3.22–3.35 (m, 2H), 2.27 ppm (s, 3H). Major diastereoisomer: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.88$ (d, $J=7.4$ Hz, 1H), 7.40–7.22 (m, 5H), 6.19–7.10 (m, 6H), 5.01 (s, 1H), 4.96 (dd, $J=6.9$, 3.0 Hz, 1H), 3.78 (s, 6H), 3.62 (s, 3H), 3.12–3.17 (m, 2H), 2.29 ppm (s, 3H).

(1*R*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(3-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5″f): This compound was obtained as the major diastereoisomer by using imine **3″f** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 68%; yellow oil. $[\alpha]_D^{20}=42.3$ ($c=0.8$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.72$ (d, $J=6.6$ Hz, 1H), 7.58 (d, $J=8.1$ Hz, 2H), 7.25–7.17 (m, 2H), 7.11–7.01 (m, 4H), 6.70 (m, 3H), 5.94 (s, 2H), 4.79 (t, $J=7.4$ Hz, 1H), 3.62 (s, 3H), 3.60 (s, 3H), 3.57 (s, 6H), 3.24–3.16 (m,1H), 3.09–3.04 (m, 1H), 2.34 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.3$, 154.6, 151.8, 144.9, 143.6, 141.9, 141.1, 137.8, 130.6, 130.5, 129.7, 128.9, 127.3, 125.8, 125.6, 124.8, 119.0, 112.3, 112.1, 91.3, 61.3, 55.7, 55.2, 54.9, 39.9, 21.2 ppm.

(1*R*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-chlorophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5″e): This compound was obtained as the major diastereoisomer by using imine **3″e** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 3:1; yield: 72%; yellow oil. $[\alpha]_D^{20}=32.4$ ($c=0.4$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.78$ (dd, $J=3.4$, 2.3 Hz, 1H), 7.48–7.43 (m, 3H), 7.33–7.28 (m, 3H), 7.27–7.14 (m, 5H), 6.02 (s, 2H), 4.85 (t, $J=7.4$ Hz, 1H), 3.72 (s, 3H), 3.65 (s, 6H), 3.31 (dd, $J=7.4$, 3.4 Hz ,1H), 3.14 (dd, $J=7.4$, 3.4 Hz , 1H), 2.34 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154$,8, 152.0, 143.8, 143.3, 142.0, 141.2, 137.9, 130.7, 129.9, 129.8, 128.1, 127.5, 126.9, 125.7, 125.3, 124.9, 118.9, 91.4, 61.6, 55.8, 55.4, 39.9, 21.3 ppm.

(1*R*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}ethylamine (5″h): This compound was obtained as the major diastereoisomer by using imine **3″h** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 3:1; yield: 76%; yellow solid; m.p. 135–137°C; $[\alpha]_D^{20}=72.5$ ($c=1.0$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.73$ (d, $J=6.7$ Hz, 1H), 7.40 (d, $J=8.1$ Hz, 2H), 7.25–7.19 (m, 1H), 7.14–6.97 (m, 4H), 6.66 (t, $J=8.5$ Hz, 2H), 7.02 (d, $J=8.5$ Hz, 2H), 5.97 (s, 2H), 4.78 (t, $J=7.4$ Hz, 1H), 3.65 (s, 3H), 3.63 (s, 6H), 3.60 (s, 3H), 3.25 (dd, $J=6.8$, 6.7 Hz, 1H), 3.07 (dd, $J=7.6$, 7.4 Hz, 1H), 2.26 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=158.2$, 154.6, 152.3, 151.2, 143.5, 141.8, 141.0, 137.9, 135.2, 130.4, 129.7, 127.6, 127.3, 125.6, 124.7, 118.8, 113.2, 91.2, 60.7, 55.6, 55.2, 54.9, 39.7, 21.2 ppm.

(1*S*,2*S*/1*R*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-cyanophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6″b/7″b): These compounds were obtained as an inseparable mixture starting from **3″b** and (*S*)-**2.** Chromatography: *n*-hexane/AcOEt, 4:1; yield: 72%. Minor diastereoisomer: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.48$ (d, $J=9.2$ Hz, 1H), 7.40–7.05 (m, 6H), 7.10–6.95 (m, 3H), 6.90 (d, $J=8.2$ Hz, 2H), 5.82 (s, 2H), 4.62 (d, $J=10.2$, 1H), 3.66 (s, 6H), 3.48 (s, 3H), 3.41–3.22 (m, 1H), 2.28 (s, 3H), 0.72 ppm (d, $J=3.9$ Hz, 3H). Major diastereoisomer: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.92$ (d, J=8.0 Hz, 1H), 7.42–7.34 (m, 5H), 7.15–6.97 (m, 4H), 6.96 (d, $J=8.2$ Hz, 2H), 5.93 (s, 2H), 4.90 (d, $J=9.21$, 1H), 3.82–3.91 (m, 1H), 3.75 (s, 3H), 3.74 (s, 6H), 2.26 (s, 3H), 1.52 ppm (s, $J=6.8$ Hz, 3H).

(1*S*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-trifluoromethylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (6″c): This compound was obtained as the minor diastereoisomer by using imine **3″c** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 3:1; yield: 9%; white solid; m.p. 161–163°C. $[\alpha]_D^{20}=+92.0$ ($c=1.0$ in CHCl3). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.65$ (d, $J=6.7$ Hz, 1H), 7.48–7.34 (m, 5H), 7.29–7.26 (m, 2H), 7.16 (t, $J=9.1$ Hz, 4H), 5.80 (s, 2H), 4.59 (d, $J=10.2$ Hz, 1H), 3.86 (brs, 1H), 3.74–3.69 (m, 1H), 3.54 (s, 3H), 3.49 (s, 6H), 2.25 (s, 3H), 0.70 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.6$, 151.4, 147.9, 145.3, 142.6, 141.9, 140.9, 131.7, 129.8, 128.7 (q, $J_{C,F}=$ 128.7 Hz), 127.7, 127.8, 125.8, 124.7, 124.6, 124.5, 122.4, 119.4, 91.5, 65.4, 55.7, 55.3, 40.1, 21.3, 20.2 ppm.

(1*R*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-trifluoropmethylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7″c): This compound was obtained as the major diastereoisomer by using imine **3″c** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 3:1; yield: 51%; yellow solid; m.p. 142–144°C. $[\alpha]_D^{20}=101.0$ ($c=0.9$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.67$ (d, $J=7.7$ Hz, 1H), 7.46–7.40 (m, 4H), 7.31–7.08 (m, 6H), 6.95 (d, $J=8.1$ Hz, 1H), 5.93 (s, 2H), 4.90 (d, $J=9.1$ Hz, 1H), 4.01 (brs, 1H), 3.88–3.83 (m, 1H), 3.62 (s, 6H), 3.60 (s, 3H), 2.29 (s, 3H), 1.52 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.3$, 151.2, 147.5, 145.0, 142.4, 141.1, 140.3, 129.7, 128.2, 127.9, 127.6 (q, $J_{C,F}=$ 126.3 Hz), 127.5, 126.9, 125.8, 125.4, 124.3, 124.2, 118.9, 91.5, 64.7, 55.7, 55.3, 41.6, 21.2, 19.9 ppm.

(1*S*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(3-chlorophenyl)-2-{2-[(S)-*p*-tolylsulfinyl]phenyl}propylamine (6″d): This compound was obtained as the minor diastereoisomer by using imine **3″d** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 6%; yellow oil. $[\alpha]_D^{20}=+115.1$ ($c=0.4$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.81$ (d, $J=7.8$ Hz, 1H), 7.59–7.36 (m, 4H), 7.41–7.36 (m, 2H), 7.29 (d, $J=4.7$ Hz, 3H), 7.14–7.10 (m, 2H), 5.91 (s, 2H), 4.71 (brs, 1H), 4.62 (d, $J=10.2$ Hz, 1H), 3.78–3.70 (m, 1H), 3.66 (s, 3H), 3.62 (s, 6H), 2.38 (s, 3H), 0.87 ppm (d, $J=7.1$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.3$, 151.5, 145.8, 145.2, 142.2, 142.4, 141.9, 141.2, 133.6, 131.6, 129.9, 128.8,

127.6, 127.3, 126.8, 126.6, 125.9, 125.9.1, 119.3, 91.5, 65.2, 55.8, 55.3, 40.5, 21.4, 20.5 ppm.

(1*R*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(3-chlorophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7″d): This compound was obtained as the major diastereoisomer by using imine **3″d** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 4:1; yield: 47%; yellow oil. $[\alpha]_D^{20}=-120.0$ ($c=0.6$ in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.94$–7.88 (m, 3H), 7.64–7.48 (m, 4H), 7.39 (d, $J=7.8$ Hz, 2H), 7.28–7.14 (m, 1H), 6.99–6.88 (m, 2H), 6.18 (s, 2H), 4.90 (d, $J=8.5$ Hz, 1H), 3.96–3.89 (m, 1H), 3.73 (s, 6H), 3.70 (s, 3H), 2.39 (s, 3H), 1.60 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.4$, 151.2, 145.7, 145.2, 142.8, 141.0, 140.7, 133.8, 131.4, 130.2, 130.0, 129.8, 129.5, 127.6, 126.9, 126.7, 126.4, 125.7, 119.1, 91.6, 55.9, 55.4, 41.6, 26.9, 21.5, 19.6 ppm.

(1*R*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(3-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7″f): This compound was obtained as a unique diastereoisomer by using imine **3″f** and (*S*)-**2** as the starting materials. Chromatography: n-hexane/AcOEt, 5:1; yield: 71%; white solid; m.p. 92–94 °C. $[\alpha]_D^{20}=-92.3$ ($c=1.0$ in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.77$ (d, $J=7.8$ Hz, 1H), 7.60 (m, $J=7.1$ Hz, 3H), 7.52–7.47 (m, 1H), 7.38–7.33 (m, 1H), 7.27–7.09 (m, 4H), 6.75–6.67 (m, 2H), 5.92 (s, 2H), 4.70 (d, $J=7.5$ Hz, 1H), 3.76–3.89 (m, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.60 (s, 6H), 2.37 (s, 3H), 0.92 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.1$, 154.0, 151.4, 145.7, 144.9, 142.7, 142.0, 140.9, 131.4, 129.7, 128.5, 127.5, 126.9, 126.5, 125.8, 120.1, 119.7, 112.7, 112.1, 91.5, 65.2, 55.8, 55.2, 54.9, 40.5, 21.3, 20.6 ppm.

(1*R*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]-phenyl}propylamine (7″a): This compound was obtained as a unique diastereoisomer by using imine **3″a** and (*S*)-**2** as the starting materials. Chromatography: n-hexane/AcOEt, 1:1; yield: 61%; yellow solid; m.p. 73.5–75.5 °C. $[\alpha]_D^{20}=-63.0$ ($c=0.5$ in EtOH). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 7.80 (dd, $J=7.9$, 1.3 Hz, 1H), 7.62 (d, $J=8.2$ Hz, 2H), 7.52 (td, $J=7.3$, 1.4 Hz, 1H), 7.38 (td, $J=7.8$, 1.2 Hz, 1H), 7.28 (d, $J=8.2$ Hz, 2H), 7.28–7.15 (m, 6H), 5.94 (s, 2H), 4.73 (brs, 1H), 4.00–3.95 (m, 2H), 3.66 (s, 3H), 3.61 (s, 6H), 2.39 (s, 3H), 0.95 ppm (d, $J=6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.0$, 151.4, 145.7, 143.2, 142.7, 142.1, 140.8, 131.4, 129.7, 127.6, 127.5, 127.4, 126.9, 126.5, 126.4, 125.8, 119.8, 91.6, 63.4, 55.7, 55.2, 40.5, 21.2, 20.5 ppm. IR (NaCl): $\tilde{\nu}=3317$, 1604, 1503, 1461, 1411, 1149, 1028 cm^{-1}. Elemental analysis calcd (%) for $C_{31}H_{33}NO_4S$: C 72.20, H 6.45, N 2.72, S 6.22; found: C 71.98, H 6.32, N 2.70, S 6.18.

(1*R*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-methylphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7″g): This compound was obtained as a unique diastereoisomer by using imine **3″g** and (*S*)-**2** as the starting materials. Chromatography: *n*-hexane/AcOEt, 5:1; yield: 72%; yellow oil. $[\alpha]_D^{20}=-35.2$ ($c=0.8$ in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.66$ (d, $J=7.7$ Hz, 1H), 7.48 (d, $J=8.1$ Hz, 3H), 7.39 (t, $J=6.8$ Hz, 1H), 7.30–7.23 (m, 3H), 7.17–7.10 (m, 2H), 6.94–6.92 (m, 2H), 5.82 (s, 2H), 4.60 (d, $J=7.5$ Hz, 1H), 3.79–3.60 (m, 1H), 3.55 (s, 3H), 3.50 (s, 6H), 2.27 (s, 3H), 2.18 (s, 3H), 0.83 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.4$, 145.8, 142.7, 142.0, 140.9, 135.9, 131.5, 129.9, 129.7, 128.4, 127.5, 127.4, 127.2, 127.1, 126.9, 126.3, 125.9, 91.5, 64.9, 55.8, 55.2, 40.7, 21.4, 21.0, 20.6 ppm.

(1*R*,2*S*)-*N*-(2,4,6-Trimethoxyphenyl)-1-(4-methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (7″h): This compound was obtained as a unique diastereoisomer by using imine **3″h** and (*S*)-**2** as the starting materials. Chromatography: n-hexane/AcOEt, 3:1; yield: 78%; yellow solid; m.p. 122–123 °C. $[\alpha]_D^{20}=-175.2$ ($c=1.0$ in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.69$ (dd, $J=6.6$, 1.3 Hz, 1H), 7.52 (d, $J=8.3$ Hz, 3H), 7.41 (t, $J=6.5$ Hz, 1H), 7.27 (t, $J=6.5$ Hz, 1H), 7.19 (d, $J=7.9$ Hz, 2H), 7.97 (d, $J=6.8$ Hz, 2H), 6.66 (d, $J=8.7$ Hz, 2H), 5.85 (s, 2H), 4.60 (d, $J=8.31$ Hz, 1H), 3.65–3.76 (m, 1H), 3.66 (s, 6H), 3.53 (s, 6H), 2.29 (s, 3H), 0.91 ppm (d, J=6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=158.1$, 151.4, 145.8, 142.6, 141.9, 140.8, 135.2, 131.4, 129.7 (2C), 128.2, 127.5, 126.8, 126.3, 125.8, 119.6, 112.9, 91.5, 64.6, 55.7 (2C), 54.9, 40.7, 21.3, 20.5 ppm.

Products from the reaction of (*S*)-1 with imine 8 (Scheme 3)

(1*S*)-*N*-(4-Methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-1-(4-methoxyphenyl)ethylamine (9): This compound was obtained as the minor diastereoisomer by using imine **8** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 4%; brown solid; m.p. 83–85 °C. $[\alpha]_D^{20}=-8.3$ ($c=0.7$ in MeOH). ^{1}H NMR (300 MHz): $\delta=7.91$ (d, $J=$ 9.3 Hz, 1H), 7.46–7.35 (m, 5H), 7.20–7.10 (m, 4H), 6.83 (d, $J=8.4$ Hz, 2H), 6.60 (d, $J=9.0$ Hz, 2H), 6.27 (d, $J=9.0$ Hz, 2H), 4.31 (dd, $J=8.9$, 5.2 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.19 (dd, $J=14.1$, 9.0 Hz, 1H), 2.96 (dd, $J=14.1$, 5.2 Hz, 1H), 2.34 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 141.6, 141.3 (2C), 137.7 (2C), 131.3 (2C), 131.1 (2C), 130.1, 128.3, 127.6, 127.4, 126.4, 125.9, 114.6, 114.4, 114.0, 59.2, 55.7, 55.2, 40.7, 21.4 ppm. IR (NaCl): $\tilde{\nu}=3329$, 1594, 1511, 1301, 1033 cm^{-1}.

(1*R*)-*N*-(4-Methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-1-(4-methoxyphenyl)ethylamine (10): This compound was obtained as the major diastereoisomer by using imine **8** and (*S*)-**1** as the starting materials. Chromatography: *n*-hexane/AcOEt, 1:1; yield: 67%; brown solid; m.p. 88–90 °C. $[\alpha]_D^{20}=-100.9$ ($c=0.3$ in MeOH). ^{1}H NMR (300 MHz): $\delta=7.73$ (d, $J=9.2$ Hz, 1H), 7.36–7.05 (m, 8H), 6.81 (d, $J=8.8$ Hz, 2H), 6.65 (d, $J=9.1$ Hz, 2H), 6.40 (d, $J=8.9$ Hz, 2H), 4.50 (dd, $J=8.2$, 6.2 Hz, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 3.34 (dd, $J=14.2$, 8.2 Hz, 1H), 3.16 (dd, $J=14.2$, 6.2 Hz, 1H), 2.34 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 158.7, 151.9, 143.8, 141.2, 141.0, 137.2, 134.9, 131.2, 130.7, 130.0, 127.8, 127.4, 127.3, 126.0, 125.7, 114.8, 114.5, 114.4, 59.1, 55.6, 55.1, 40.8, 21.3 ppm. IR (NaCl): $\tilde{\nu}=3329$, 1594, 1511, 1301, 1033 cm^{-1}. Elemental analysis calcd (%) for $C_{29}H_{29}NO_3S$; C 73.86, H 6.20, N 2.97, S 6.80; found: C 74.04, H 6.13, N 2.82, S 6.80.

Synthesis of the free amines 12 by oxidation/sulfinylation (Scheme 4)

Synthesis of compounds 11: A solution of CAN (0.8 mmol) in H_20 (0.25 mL) was added to a stirred solution of the corresponding protected amine *syn*-**7″a**,**c**,**h** (0.2 mmol) in CH_3CN/H_2O (1 mL). The reaction mixture was stirred for 2 h. Afterwards CH_2Cl_2 (1 mL) was added and the organic phase separated. A 10% solution of NaOH (2 mL) was added to the aqueous phase which was then extracted with AcOEt (2× 25 mL). The combined organic phases were dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified by chromatography on an SCX column, affording the corresponding pure amine.

(1*R*,2*S*)-1-Phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (*syn*-11a): Yield: 96%; yellow oil. $[\alpha]_D^{20}=-16.2$ ($c=1.0$ in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.85$ (d, $J=7.7$ Hz, 1H), 7.63 (d, $J=8.1$ Hz, 2H), 7.50–7.26 (m, 10H), 3.95 (d, $J=9.8$ Hz, 1H), 3.67–3.59 (m, 1H), 2.36 (s, 3H), 1.60 (brs, 2H), 0.82 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.9$, 144.6, 143.7, 142.0, 142.3, 132.1, 129.9, 128.5, 128.5 (2C), 127.4, 127.4, 127.2, 127.1, 62.2, 42.1, 21.4, 19.9 ppm.

(1*R*,2*S*)-1-(4-Trifluorophenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (*syn*-11c): Yield: 82%; yellow oil. $[\alpha]_D^{20}=-122.3$ ($c=0.4$ in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.58$–7.06 (m, 12H), 4.28 (d, $J=$ 7.2 Hz, 1H), 4.02–3.94 (m, 1H), 2.37 (s, 3H), 1.32 ppm (d, $J=6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.2$, 141.3, 132.4, 131.5, 129.8, 128.1, 128.0, 127.9, 127.7, 126.0, 125.8, 125.2, 125.5 (q, $J_{C,F}=121.2$ Hz), 124.9, 124.8, 60.1, 41.3, 21.3, 19.1 17.9 ppm.

(1*R*,2*S*)-1-(4-Methoxyphenyl)-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}propylamine (*syn*-11h): Yield: 80%; yellow oil. $[\alpha]_D^{20}=-112.2$ ($c=1.0$ in $CHCl_3$). ^{1}H NMR (300 MHz, CDCl3): $\delta=7.86$ (d, $J=7.7$ Hz, 1H), 7.63 (d, $J=8.1$ Hz, 2H), 7.47–7.42 (m, 3H), 3.30–7.25 (m, 4H), 6.90 (d, $J=$ 8.6 Hz, 2H), 3.93 (d, $J=9.7$ Hz, 1H), 3.83 (s, 3H), 3.63–3.60 (m, 1H), 2.38 (s, 3H), 0.85 ppm (d, $J=6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=158.9$, 144.9, 143.6, 141.9, 141.2, 132.1, 129.9, 129.7, 129.7, 128.9, 128.2, 127.4, 125.7, 113.9, 61.4, 55.3 (2C), 21.4, 19.8 ppm.

Synthesis of compounds 12a,c,h: A solution of the corresponding compounds *syn*-**11a**,**c**,**h** (0.18 mmol) in THF (2 mL) was added to activated Raney nickel (1.2 g) in THF (3 mL). The reaction was monitored by TLC and then the mixture was stirred for 2 h, filtered and the residue was purified by chromatography on a SCX column, affording the pure free amine.

(1*R*,2*S*)-1,2-Diphenylpropylamine (*syn*-12a): Yield: 98%; yellow oil. $[\alpha]_D^{20}=60.2$ ($c=0.2$ in $CHCl_3$). ^{1}H NMR (300 MHz, CD_3OD): $\delta=7.38$–7.21 (m, 10H), 3.92 (d, $J=9.8$ Hz, 1H), 2.90 (dd, $J=7.0$, 2.6 Hz, 1H), 0.93 ppm (d, $J=7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.9$, 128.6, 128.4, 128.0, 127.8, 127.3, 126.7, 126.6, 62.2, 48.2, 19.5 ppm.

(1*R*,2*S*)-1-(4-Trifluorophenyl)-2-phenylpropylamine (*syn*-12c): Yield: 81%; yellow oil. $[\alpha]_D^{20}=22.3$ ($c=0.3$ in $CHCl_3$). ^{1}H NMR (300 MHz,

$CDCl_3$): $\delta = 7.49$ (d, $J = 7.9$ Hz, 2H), 7.43–7–16 (m, 5H), 7.04 (d, $J = 5.8$ Hz, 2H), 4.21 (d, $J = 6.6$ Hz, 1H), 3.15–3.10 (m, 1H), 1.34 ppm (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.9$, 128.3 (2C), 127.9 (2C), 127.5 (2C), 126.6, 124.8 (q, $J_{C,F} = 125.3$ Hz), 61.3, 50.8, 15.9 ppm.

(1*R*,2*S*)-1-(4-Methoxyphenyl)-2-phenylpropylamine (*syn*-12h): Yield: 85%; yellow oil. $[\alpha]_D^{20} = 123.5$ ($c = 0.82$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.32–7.29$ (m, 7H), 6.86 (d, $J = 8.8$ Hz, 2H), 3.93 (d, $J = 9.4$ Hz, 1H), 3.82 (s, 3.H), 2.90–2.80 (m, 1H), 1.01 ppm (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.8$, 144.8, 136.5, 128.6, 128.4, 127.8, 126.6, 113.7, 62.1, 55.3, 48.3, 19.5 ppm.

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