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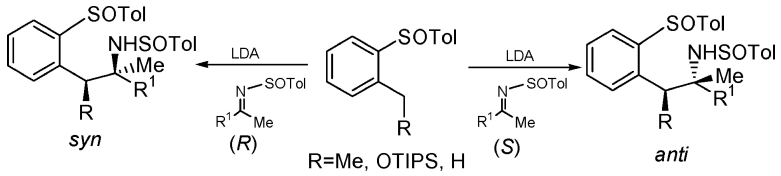

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Highly Stereoselective Benzylation of *N*-Sulfinylketimines

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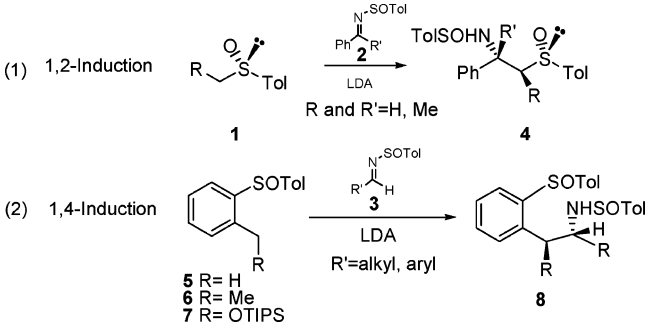
Abstract: The benzylation of *N*-sulfinyl ketimines with 2-(*p*-tolylsulfinyl)ethylbenzene and LDA afford *t*-alkylamines in good yields. The configuration at each one of the new chiral centers simultaneously created in this reaction is controlled by the configuration of the sulfinyl groups at the nucleophile and electrophile, respectively. Thus, the reactions of the (*S*)-sulfoxide **6** with the *N*-(*S*)-sulfinylketimines **3** only yield the *anti* diastereoisomers **18**, whereas the *syn* diastereoisomers **19** are exclusively formed in reactions of (*S*)-**6** with *N*-(*R*)-sulfinylketimines **3**. After a two-step desulfinylation process ((i) TFA, (ii) Ra−Ni), this reaction provides a procedure for synthesizing any epimer of α,α-dibranched β-alkylarylamines in optically pure form by choosing the configuration of the starting materials. A similar behavior is observed for carbanions derived from the O-protected 2-(*p*-tolylsulfinyl) benzyl alcohol **7** thus allowing the synthesis of the optically pure *anti*- and *syn*-1,2-amino alcohols containing a chiral quaternary carbon adjacent to the nitrogen.

Introduction

Nucleophilic addition of organometallics to C=N bonds from chiral aldimines[1] provides one of the most direct and attractive routes to chiral amino derivatives. The moderate reactivities and stereoselectivities associated with the use of *N*-alkyl or aryl aldimines could be substantially improved by using enantiopure *N*-sulfinylimines,[2] as it has been evidenced by several authors, and expecially by the groups of Davis[3] and Ellman.[4] Conversely, the reactions of organometallics with ketimines, affording optically pure α,α-dibranched amines, have been much less explored, mainly due to the lower reactivity of these electrophiles and their propensity to enolization.[5] Moreover, the facile *E*,*Z* isomerization decreases the possibility of diasteroselective processes. These problems justified why only some reactions of limited scope had been reported until 1999,[6] when Ellman[7]

Scheme 1



showed that reactions of organometallics with *N*-*tert*-butanesulfinylketimines in the presence of Me_3Al can be considered a general method to prepare α,α-dibranched amines. One of the problems to be solved in this field concerns the stereoselectivity control in reactions of prochiral carbanions with imines, resulting in the simultaneous formation of two chiral centers in a single step. In this regard we discovered that the organolithium derived from **1**, stabilized by α-sulfinyl groups (eq 1, Scheme 1) reacted with aromatic *N*-sulfinylaldimines **2** with complete control of the stereoselectivity.[8] More recently we reported that carbanions derived from **5**−**7**, and stabilized by γ-sulfinyl groups (eq 2, Scheme 2), were also efficient in this task even in case of the *N*-sulfinyl derivatives of enolizable aliphatic aldimines.[9] With these γ-sulfinyl carbanions it was also possible to solve the problem of the stereoselective benzylation of imines, which had so far proved to be of difficult solution.[10]

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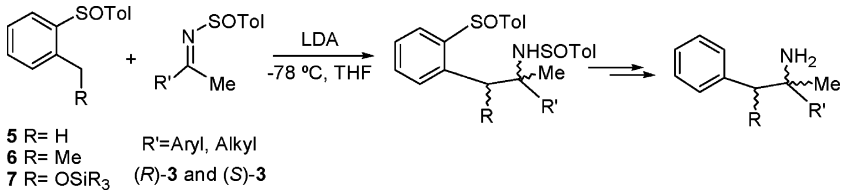
Scheme 2



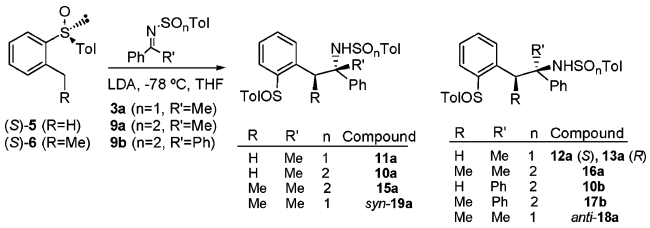
The only report concerning reactions of prochiral carbanions with enolizable *N*-sulfinylketimines **3** involved the use of α-sulfinylated ethyl-lithium to afford the α,α-dibranched *β*-sulfinylamines[11] (eq 1, Scheme 1) in a highly stereoselective manner. These results suggested that stabilized sulfinyl carbanions were able to overcome the problems associated with the enolization of the *N*-sulfinylketimines. This prompted us to investigate the behavior of these electrophiles in their reactions with *ortho*-sulfinylbenzylcarbanions, in the search of a general method for synthesizing *β*-substituted α,α-dibranched amines. In this work we describe the reactions of compounds **5**−**7** with *N*-sulfinylketimines (**3**) as well as the transformation of the resulting compounds into the desired optically pure amines (Scheme 2).

Results and Discussion

A. Optimization Studies for the Addition of *γ*-Sulfinylcarbanions to Ketimines. We first studied the behavior of (*S*)-**5** with different *N*-sulfinylated benzylideneketimines in the intent to evaluate viability and stereoselectivity of these reactions, as well as the problems emerging from the enolization of the electrophiles. The reactions of (*S*)-**5** with the *N*-sulfonyl methylbenzylidenimine **9a**[12] were completely unfruitful under different conditions, with the starting materials being recovered unaltered (entry 1, Table 1). Quick enolization may be responsible for this behavior as it can be inferred from the fact that diphenylketimine **9b**, lacking enolizable protons, reacts completely under the same conditions and in few minutes, yielding **10b** in 89% yield (entry 2). Sulfinyl derivatives are less prone to enolization, which in turn is dependent on the configuration at the *N*-sulfinyl group. Reaction of (*S*)-**5** with (*S*)-**3a** in the presence of LDA leads to a 67:33 mixture of two diastereoisomers **11a** and **12a** (34% de), readily separated by chromatography (entry 3). Both the low stereoselectivity and moderated conversion observed in this reaction (<60%), which could not be improved by extending the reaction time, could be a consequence of the enolization, fortunately less significant with *N*-sulfonyl ketimines.[13]

To our delight, reaction of (*S*)-**5** with (*R*)-**3a** afforded **13a** as the only isomer and in good yield (entry 4, Table 1). This behavior reveals the existence of a matched and a mismatched pair of reagents, being the first formed by the sulfoxide and the imine with different configurations at the sulfur atom.[14] These results indicate that a completely stereoselective benzylation of the C═N at ketimines can be achieved by using the matched pair *N*-sulfinylketimine/*ortho*-sulfinylbenzylcarbanion because of the favorable balance enolization/nucleophilic addition. The configuration at the chiral carbon of the resulting amine is determined by the configuration of the starting reagents. Hydrogenolysis of the N−S bond at compounds **12a** and **13a** gave the same compound **14a**, thus revealing that they have identical configuration at the chiral carbon (see Supporting Information).

Table 1. Reactions of (*S*)-**5** with Different *N*-Thioderivatives of Benzylideneketimines



entry	nucleophile	ketimine	products ratio (yield, %)	conversion (%)
1	(*S*)-**5**	**9a**	**10a** (0)	−
2	(*S*)-**5**	**9b**	**10b** (89)	100
3	(*S*)-**5**	(*S*)-**3a**	67/33; **11a**/**12a**	58
4	(*S*)-**5**	(*R*)-**3a**	**13a** (75)	100
5	(*S*)-**6**	**9a**	10/90; **15a**/**16a**	10−15
6	(*S*)-**6**	**9b**	**17b** (94)	100
7	(*S*)-**6**	(*S*)-**3a**	*anti*-**18a** (80)	90
8	(*S*)-**6**	(*R*)-**3a**	*syn*-**19a** (70)	90
9	(*S*)-**6**	(*S*)-**3a**	40/60: **20a**/*anti*-**18a**	50

We then studied the reactions with the secondary carbanion derived from **6**. In general, the methyl group at the benzylic position decreases the significance of the enolization and provides better results. Thus, reactions with the *N*-sulfonyl-derivative **9a** gives a mixture of diastereoisomers **15a** and **16a** in low but significant conversions (ranging from 10 to 15% in different experiences, entry 5). As in the case of reactions from (*S*)-**5**, (*S*)-**6** reacts with **9b** yielding **17b** in almost quantitative yield (entry 6) and with complete stereoselectivity (de ≥ 98%), indicating that the configuration at the benzylic carbon is completely controlled by the *ortho*-sulfinyl group.[15] Absolute configuration of **17b** was unequivocally established as R,S_S by X-ray diffraction analysis (see Supporting Information).

We then studied the reaction of **6**-Li with each of the enantiomeric *N*-*p*-tolylsulfinyl derivatives of the phenylmethylketimines (*S*)-**3a** and (*R*)-**3a**. As in the previous case, the change in the sulfur function into sulfinyl improves the conversion, which is now complete with both enantiomeric

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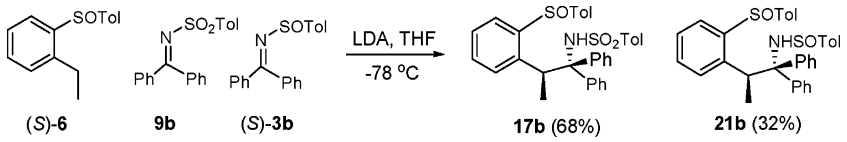
(13) The obtained results in reaction of (*S*)-**5** and (*S*)-**3** suggest that reaction rates for enolization and nucleophilic addition processes must be similar.

(14) A similar situation had been found in reactions of (*S*)-**5** with aldimines (ref 9) but being the reagents with the same configuration at sulphur those conforming the matched pair.

(15) It suggests that **15a** and **16a**, formed from **9a**, must be epimers at the aminic carbon.

Scheme 3



(*S*)-**6** **9b** (*S*)-**3b** **17b** (68%) **21b** (32%)

ketimines. However the most interesting results concern the stereoselectivity, since both reactions are completely stereoselective. Thus, reaction of (*S*)-**6** with (*S*)-**3a**, in the presence of LDA, progressed completely into only one diastereoisomer *anti*-**18a**, which was isolated in 80% yield (entry 7, Table 1), whereas (*R*)-**3a** was transformed into *syn*-**19a** (isolated yield 70%) under similar conditions (entry 8, Table 1). When the latter reaction was performed in the presence of HMPA (5 equiv), the conversion decreased till 50% and a mixture of diastereoisomers, presumably epimers at the benzylic position,[16] was obtained (entry 9).

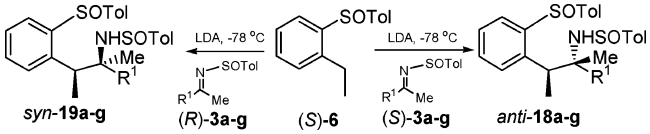
Several conclusions can be deduced from these results, and the first one concerns reactivity. The change of the *N*-sulfonyl into the *N*-sulfinyl group at the imine nitrogen must reduce the enolization rate at a higher level than the reactivity toward the nucleophile, thus allowing the reaction to complete before enolization becomes significant. We were also able to demonstrate that the reactivity of sulfinyl and sulfonyl derivatives is not that different by performing a competitive reaction between *N*-sulfonylketimine **9b** (1 equiv), *N*-sulfinylketimine (*S*)-**3b** (1 equiv), and (*S*)-**6** (1 equiv). As reaction products we could only identify a 68/32 mixture of sulfonylamine **17b** and sulfinylamine **21b** (Scheme 3). The same ratio was also observed for (*S*)-**3b**/**9b**, the unreacted starting materials. This result indicates that **9b** is only two times more reactive than (*S*)-**3b**. On the other hand we have also studied the reaction of (*S*)-**6** with racemic (±)-**3a** (2 equiv). The (*R*) isomer reacts only slightly faster than the (*S*) isomer (a 45/55 mixture of *anti*-**18a**/*syn*-**19a** was obtained) which suggests that the difference in the reaction rates of the *N*-sulfonyl derivative and the (*R*) enantiomer of the *N*-sulfinyl derivative must be even lower.

The second conclusion concerns stereoselectivity. The fact that (*R*)-**3a** only gives the *syn* diastereoisomer *syn*-**19a**, whereas (*S*)-**3a** affords *anti*-**18a**, evidences that the configuration at the quaternary carbon adjacent to nitrogen is mainly controlled by the *N*-sulfinyl group, whereas the configuration at the tertiary benzylic carbon is only dependent on the configuration at carbanion. This behavior allows the synthesis of the four possible diastereoisomers of the α,α′-dibranched *β*-phenyl propylamines by choosing the configuration of the starting reagents.

Finally, the third conclusion concerns the influence of the Li^+ metal on the stereochemical course of the reaction. The results on entry 9 suggest some kind of association between the metal and the reagents that must be determinant for the high stereoselectivity observed.

B. Reaction Scope for the Addition of *γ*-Sulfinylcarbanion to *N*-Sulfinylketimines. We have studied the behavior of different *N*-sulfinylketimines with (*S*)-**6** in order to check the scope of the reaction. The results are indicated in Table 2. The reaction of (*S*)-**6** with (*S*)-**3c** at −78 °C affords *anti*-**18c** as the only product (entry 2, Table 2). Similar results were obtained

Table 2. Reactions of (*S*)-**6** with *N*-Sulfinylketimines (*S*)- and (*R*)-**3**



syn-**19a-g** (*R*)-**3a-g** (*S*)-**6** (*S*)-**3a-g** *anti*-**18a-g**

entry	R^1	reagent (config)	product (yield %)	% de
1	Ph	(*S*)-**3a**	*anti*-**18a** (80)	≥98
2	*p*-$MeOC_6H_4$	(*S*)-**3c**	*anti*-**18b** (66)	≥98
3	*p*-MeC_6H_4	(*S*)-**3d**	*anti*-**18d** (69)	≥98
4	*p*-BrC_6H_4	(*S*)-**3e**	*anti*-**18e** (64)	≥98
5	*p*-CNC_6H_4	(*S*)-**3f**	*anti*-**18f** (41)	50
6	*i*-Pr	(*S*)-**3g**	*anti*-**18g** (−)	−
7[a]	*i*-Pr	(*S*)-**3′g**[b]	*anti*-**18′g** (58)	≥98
8	*p*-$MeOC_6H_4$	(*R*)-**3c**	*syn*-**19c** (67)	≥98
9	*p*-MeC_6H_4	(*R*)-**3d**	*syn*-**19d** (73)	≥98
10	Ph	(*R*)-**3a**	*syn*-**19a** (70)	≥98
11	*p*-BrC_6H_4	(*R*)-**3e**	*syn*-**19e** (61)	≥98
12	*p*-CNC_6H_4	(*R*)-**3f**	*syn*-**19f** (40)	55
13	*i*-Pr	(*R*)-**3g**	*syn*-**19g** (−)	−
14[a]	*i*-Pr	(*R*)-**3′g**[b]	*syn*-**19′g** (58)	≥98

[a] In the presence of Me_3Al. [b] *N*-*tert*-Butanesulfinylketimine was used.

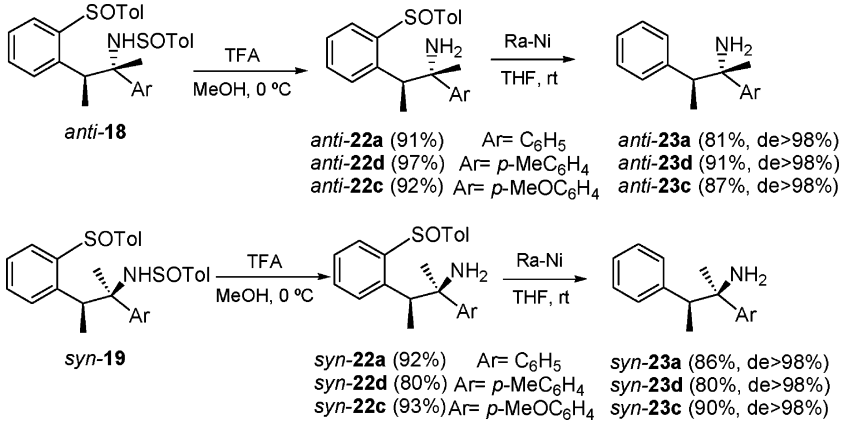
with other (*S*)-ketimines containing electron-donating (*S*)-**3d** or weakly electron-withdrawing groups, (*S*)-**3e**, which allowed us to synthesize the amines *anti*-**18d** and *anti*-**18e** in a completely stereoselective manner (entries 3 and 4, Table 2). The behavior of the corresponding (*R*)-*N*-sulfinyl ketimines, (*R*)-**3c**−**e**, was analogous to that of the (*S*) enantiomers in their reactions with (*S*)-**6**, but now yielding *syn*-**19c**−**e** amines (entries 8−11, Table 2). The yields obtained in all these reactions ranged from 60 to 80%, and the optical purity of the amines is complete (≥98% de). Starting from (*S*)- and (*R*)-**3f** ketimines, which contain a strongly electron-withdrawing group in the aromatic ring, the favored diastereoisomers are the expected *anti*-**18f** and *syn*-**19f**, respectively, but the yield and the stereoselectivity decrease significantly (entries 5 and 12). In these cases the conversion was only 50%. We also studied the behavior of the *N*-*p*-tolylsulfinyldialkylketimines (*S*)-**3g** and (*R*)-**3g** and their corresponding *tert*-butanesulfinylketimines, (*S*)-**3′g** and (*R*)-**3′g**. These compounds do not undergo addition under the reaction conditions used for benzylideneimines (entries 6 and 12). However, the addition of Me_3Al to the reaction mixture[7] determine the transformation of the (*S*)- and (*R*)-*tert*-butanesulfinyl derivatives into *anti*-**18′g** and *syn*-**19′g**, respectively, in a completely stereoselective manner (entries 7 and 14, Table 2).[17]

These results indicate that *ortho*-sulfinylbenzylcarbanions are able to perform the stereoselective benzylation of dialkyl and arylalkyl *N*-sulfinylketimines with complete control of the configuration at the two chiral centers formed in the reaction. This allows the synthesis of all possible amine diastereoisomers

(16) This result it was obtained in the case of the carbanion with ketones. See ref 19.

(17) These reactions were performed on the racemic (±)-**3′g** leading to a 1:1 mixture of the expected *anti*-**18′g** and *syn*-**19′g**, easily separated by chromatography. Imine (±)-**3g** is not stable enough in the presence of Me_3Al and decomposes into the corresponding ketone and *N*-sulfinamide.

Scheme 4. Conversion of Some *anti*-**18** and *syn*-**19** into Free Amines



by choosing the adequate configurations at the sulfoxide (which controls the benzyl center) and at the *N*-sulfinylketimine (controls the aminic carbon). The configurational assignments of **18** and **19** were based on their NMR parameters, chemical correlations, and X-ray diffraction studies (see Supporting Information).

The last step of this methodology involves the synthesis of the free amines by sequential desulfinylation of compounds *anti*-**18** and *syn*-**19**, which can be performed by subsequent reaction of compounds *anti*-**18** and *syn*-**19** with TFA (hydrogenolysis of the N−S bonds) and Ra−Ni (hydrogenolysis of the C−S bond). We have illustrated these desulfinylation processes with the compounds indicated in Scheme 2. Reactions of *anti*-**18** and *syn*-**19** with TFA (MeOH, 0 °C) yielded the amino sulfoxides *anti*-**22** and *syn*-**22**, respectively, in excellent yield (80−97%). These, in turn, react with Ra−Ni (THF, rt) also in high yields (80−91%), affording diastereomeric free amines *anti*-**23** and *syn*-**23** without appreciable epimerization (Scheme 4).[18]

C. Stereochemical Models. The stereochemical model proposed to explain the reactions of (*S*)-**5** and (*S*)-**6** with *N*-sulfinyl aldimines[9] also accounts for the results obtained with ketimines and for the differences observed between both types of electrophiles. The association of the lone electron pair at the imine nitrogen to the benzyllithium, whose presumably most stable conformation is the one depicted in Figure 1,[19] must be previous to the nucleophilic attack. The four most stable transition states (the sub index denotes the configuration of the *N*-sulfinylimine) must display the lone electron pair at the sulfur atom oriented toward the nucleophile thus minimizing steric repulsions (Figure 1). As $\mathbf{B_S}$ and $\mathbf{A_R}$ exhibit the strongly destabilizing $(\text{Tol/Me})_{1,3-p}$ interaction,[20] only $\mathbf{A_S}$ (yielding *syn*-**19**) and $\mathbf{B_R}$ (yielding *anti*-**18**) must be considered to explain the observed results. The fact that the reactivity of the *N*-sulfonyl derivatives is lower than expected (it is only similar to that of the *N*-sulfinyl derivatives) can be due to the low electronic availability of the imine nitrogen, making difficult its association to the lithium and allowing that the competition with the enolization processes to decrease the conversion level. A similar reason could be responsible of the low conversion observed for (*S*)-**3f**. On the other hand, by comparing the transition states in reactions starting from (*S*)-**5** and (*S*)-**6**, we can conclude that the change of Me by H leads to the relative stabilization of $\mathbf{B_R}$ and $\mathbf{B_S}$ with respect to $\mathbf{A_R}$ and $\mathbf{A_S}$, respectively {[(Ar/Me) − (Ar/H)] > [(Me/Me) − (Me/H)]}. As a consequence $\Delta E(\mathbf{B_R} - \mathbf{A_R})$ must be higher and $\Delta E(\mathbf{A_S} - \mathbf{B_S})$ must be lower for (*S*)-**5** than for (*S*)-**6**. This would also explain why the reaction between (*S*)-**5** and (*R*)-**3a**, evolving through TSs $\mathbf{B_R}$ and $\mathbf{A_R}$, is completely stereoselective, whereas that of (*S*)-**5** with (*S*)-**3a**, evolving through TSs $\mathbf{B_S}$ and $\mathbf{A_S}$, is only moderately stereoselective.

D. Synthesis of *Syn* and *Anti* α,a-Dibranched *β*-Phenyl Ethanolamines. The good results obtained in these reactions prompted us to explore the applicability of the method in the synthesis of *β*-amino alcohols in both syn and anti configurations, starting from the protected benzyl alcohol (*S*)-**7**. Amino alcohols are structural subunits with an overspread use as stationary phases in HPLC,[21] as key synthetic intermediates for synthesizing biologically active compounds[22] and as chiral ligands or auxiliaries in asymmetric reactions.[23] In this latter field triorganyl substituted amino ethanol compounds may potentially have a major significance because of their restricted conformational mobility imposed by the quaternary carbon.

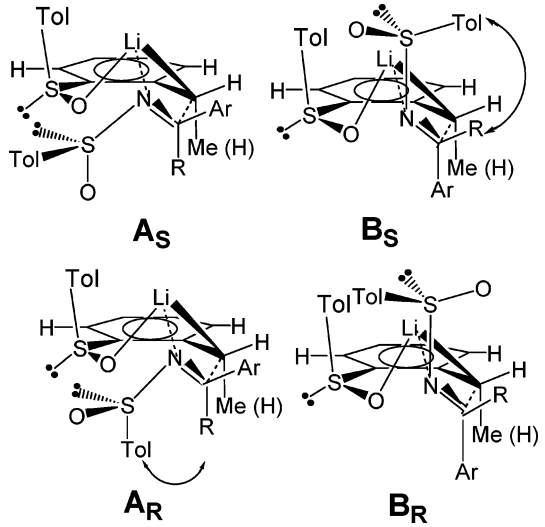


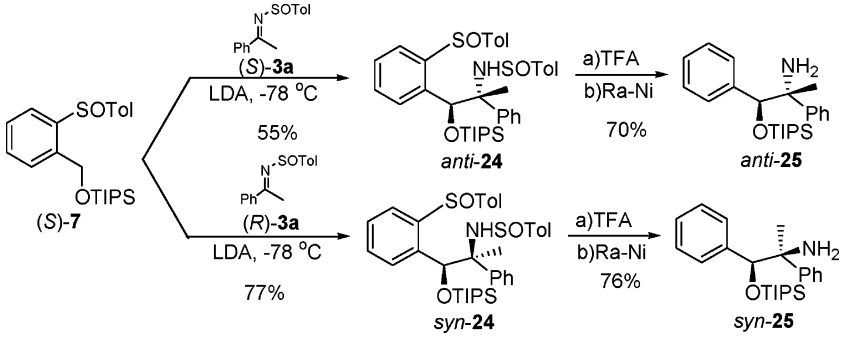
Figure 1. Transition states for reactions of (*S*)-**5** and (*S*)-**6** with (*R*)-**3** ($\mathbf{A_R}$ and $\mathbf{B_R}$) and (*S*)-**3** ($\mathbf{A_S}$ and $\mathbf{B_S}$).

(18) Epimerization at chiral centers in the hydrogenolysis of the C−S bonds with Ra−Ni has been observed in some cases. See: García Ruano, J. L.; Paredes, C. G.; Hamdouchi, C. *Tetrahedron: Asymmetry* **1999**, *10*, 2935 and references therein.

(19) García Ruano, J. L.; Carreño, M. C.; Toledo, M. A.; Aguirre, J. M.; Aranda, M.; Fischer, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2736.

(20) These transition states would not be negligible for *N*-sulfinylaldimines and would explain the differences in their behaviour with respect to the *N*-sulfinylketimines.

Scheme 5. Synthesis of Syn and Anti β-Amino Alcohols



However, to our knowledge, few examples concerning the asymmetric synthesis of these compounds have been reported.[24]

The reaction of (*S*)-**7** with LDA at −78 °C and subsequent treatment with compound (*S*)-**3a** for 15 min yielded the amino alcohol *anti*-**24** (55% yield) as the only diastereoisomer. The cleavage of the N−S and C−S bonds with TFA and Ra−Ni, respectively, afforded the enantiomerically pure 2-aminoethanol derivative (1*S*,2*S*)-*anti*-**25** (Scheme 5). Likewise, the reaction of (*S*)-**7** with (*R*)-**3a** afforded exclusively the *syn*-**24** isomer (77% yield), easily transformed into (1*S*,2*R*)-*syn*-**25** (Scheme 5). Starting from (*S*)-**7** it would be possible to synthesize the other two diastereoisomeric β-amino alcohols.

Conclusion

In summary, we have developed a general and highly stereoselective method to obtain α,α-dibranched β-phenyl propylamines and ethanolamines, in any of their possible configurations, through the reaction of the *ortho*-sulfinylbenzylcarbanions derived from **5**−**7** with the *N*-sulfinylketimines **3**. Configuration at each of the newly formed chiral centers is controlled by the configuration of the sulfinyl groups at the reagents.

Experimental Section

General Procedures. All flasks were flame-dried under a stream of argon and cooled before use. Solvents and solutions were transferred with syringes and cannulas using standard inert atmosphere techniques. ^{1}H NMR spectra were acquired at either 200 or 300 MHz, and ^{13}C NMR were acquired at 50 or 75 MHz (unless otherwise indicated). Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm). Mass spectra (MS) were determined by FAB. All reactions were carried out in anhydrous solvents and under argon atmosphere. THF and Et_2O were distilled from sodium-benzophenone under argon. Dichloromethane was distilled with calcium hydride. *i*-Pr_2NH was distilled with KOH. Flash silica gel column chromatography was performed using silica gel Merk-60 (230−400 mesh). *n*-BuLi (2.5 M solution in hexane) was purchased from Aldrich. Compounds **5**, **6**, and **7**[9] were previously synthesized. All *N*-sulfinylketimines **3a**−**g** were synthesized using Davis' methodology. *N*-Sulfinylketimine **3b** was described by Annunziata;[25] **3c** (R = *p*-$MeOC_6H_4$), **3d** (R = *p*-MeC_6H_4), and **3a** (R = Ph) were described by Davis;[26] **3f** (*R* = *p*-CNC_6H_4) was described by García Ruano;[12] and **3e** (R = *p*-Br−C_6H_4) is described in the Supporting Information. The *N*-*tert*-butylsulfinylketimine **3g′** was synthesized following Ellman' procedure.[7]

General Procedure for Benzylation of *N*-Sulfinylketimines. A solution of *n*-BuLi (0.6 mmol, 2.3 M in hexane) was added to ^{i}Pr$_2$NH (0.9 mmol) in THF (3 mL) at 0 °C. After stirring for 20 min the mixture was cooled to −78 °C. A solution of sulfoxide (*S*)-**6** (0.5 mmol) in THF (2 mL) was added. After stirring for 30 min, the corresponding sulfinylketimine **3a**−**g** (0.5 mmol) was added at −78 °C. When the reaction completed (20−30 min), the mixture was hydrolyzed (saturated NH_4Cl), extracted (3 × 10 mL Et_2O), washed (2 × 10 mL sat NH_4Cl), and dried ($MgSO_4$) and the solvent was removed under reduced pressure. Compounds were purified by flash silica gel column (eluent is indicated in each case).

***N*-{1,2-Diphenyl-[(*S*)-3-(*p*-toluenesulfinyl)phenyl]ethyl}-*p*-toluenesulfonamide (10b):** *N*-Sulfonylketimine **9b** was used as electrophile. Chromatography: *n*-hexane−AcOEt 2:1; yield: 89%; white solid; mp: 92−94 °C; $[\alpha]_D^{20}$ −43.5 (*c* 0.3, $CHCl_3$); IR (NaCl): 3110, 1493, 1331, 1158, 1055, 1032 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.25−6.82 (m, 20H), 6.39 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 13.6 Hz, 1H), 4.15 (d, *J* = 13.5 Hz, 1H), 3.30 (d, *J* = 13.5 Hz, 1H), 2.29 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 141.9, 141.4, 141.2 (2C), 141.1, 139.5, 135.3, 133.7, 131.0, 129.9(2C), 129.5, 129.1, 128.6, 127.6, 127.4(2C), 127.3, 127.2, 126.4, 125.0, 67.6, 42.9, 30.9, 21.4. Anal. Calcd for $C_{32}H_{27}NO_2S_2$: C, 73.67; H, 5.22; N, 2.68; S, 12.29. Found: C, 73.51; H, 5.13; N, 2.68; S, 12.67.

[1*R*,(*S*)*R*]-*N*-(1-Methyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethyl)-*p*-toluenesulfinamide (13a): (*R*)-*N*-Sulfinylketimine **3a** was used as electrophile. Chromatography: *n*-hexane−AcOEt 2:1; yield: 75%; white solid; $[\alpha]_D^{20}$ −84.4 (*c* 0.45, acetone); IR (NaCl): 3181, 1493, 1470, 1118, 1085 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 6.2, 1.5 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.43 (dd, *J* = 7.0, 1.1 Hz, 2H), 7.34−7.14 (m, 9H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.84 (dd, *J* = 6.4, 1.1 Hz, 1H), 4.80 (bs, 1H), 3.40 (d, *J* = 13.9 Hz, 1H), 3.20 (dd, *J* = 13.9 Hz, 1H), 2.31 (s, 3H), 2.24 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.2, 144.1, 143.4, 141.3, 141.2, 140.9, 135.3, 132.3, 130.8, 129.9, 129.6, 128.5, 128.3, 127.7, 127.2, 126.6, 125.5, 125.4, 62.2, 53.5, 46.6, 27.5, 21.4. Anal. Calcd for $C_{29}H_{29}NO_2S_2$: C, 71.42; H, 5.99; N, 2.87; S, 13.15. Found: C, 71.50; H, 6.01; N, 2.90; S, 13.40.

[1*S*,(*S*)*R*]-*N*-(1-Methyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethyl)-*p*-toluenesulfinamide (11a). (*S*)-*N*-Sulfinylketimine **3a** was used as electrophile. This compound was obtained as a major diastereoisomer. Chromatography: *n*-hexane−AcOEt 3:1; yield: 34%; white solid;

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(26) Davis, F. A.; Seung, L.; Zhang, H.; Fanelli, D. L. *J. Org. Chem*. **2000**, *65*, 8704.

mp: 75−77 °C; $[\alpha]_D^{20}$ −115.9 (*c* 0.71, acetone); IR (NaCl): 3186, 1493, 1472, 1086, 1085, 1058, 1038 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (dd, J = 6.2, 1.5 Hz, 1H), 7.49 (dd, J = 7.3, 1.3 Hz, 2H), 7.36−7.31 (m, 6H), 7.21−7.15 (m, 6H), 7.07 (d, J = 8.1 Hz, 2H), 5.02 (bs, 1H), 3.46 (d, J = 13.7, 1H), 3.29 (d, J = 13.7 Hz, 1H), 2.32 (s, 3H), 2.24 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 144.9, 143.3, 141.5, 141.4, 141.1, 135.7, 132.6, 130.8, 129.9, 129.5, 128.5, 127.9, 127.5, 126.4, 126.2, 125.5, 125.4, 61.9, 43.8, 27.6, 21.4 (2C). Anal. Calcd for $C_{29}H_{29}NO_2S_2$: C, 71.42; H, 5.99; N, 2.87; S, 13.15. Found: C, 71.65; H, 6.11; N, 2.73; S, 12.67.

[1*R*,(*S*)*R*]-*N*-(1-Methyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-ethyl)-*p*-toluensulfinamide (12a): (*S*)-*N*-Sulfinylketimine **3a** was used as electrophile. This compound was obtained as minor diastereoisomer. Chromatography: *n*-hexane−AcOEt 3:1; yield: 17%; white solid; mp: 80−82 °C; $[\alpha]_D^{20}$ −135.9 (*c* 0.64, acetone); IR (NaCl): 3175, 3057, 2984, 2924, 1493, 1471,1085, 1058, 1031, 809, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (dd, J = 6.6, 1.2 Hz, 1H), 7.52 (d, J = 8.2 Hz, 2H), 7.38−7.19 (m, 10H), 7.12−7.04 (m, 3H), 6.40 (d, J = 7.7 Hz, 1H), 4.69 (bs, 1H), 3.33 (d, J = 13.6 Hz, 1H), 3.15 (d, J = 13.6 Hz, 1H), 2.33 (s, 3H), 2.26 (s, 3H), 1.95 (s, 3H);^{13}C NMR (75 MHz, $CDCl_3$): δ 145.2, 143.3, 143.2, 141.7, 141.5, 141.2, 134.3, 131.9, 130.6, 129.9, 129.6, 128.4, 128.2, 127.8, 127.5, 125.5, 125.4, 125.3, 62.5, 46.9, 27.7, 21.4 (2C). Anal. Calcd for $C_{29}H_{29}NO_2S_2$: C, 71.42; H, 5.99; N, 2.87; S, 13.15. Found: C, 71.36; H, 6.28; N, 2.77; S, 13.05.

[3*S*,(*S*)*S*]-*N*-{2,2-Diphenyl-[(*S*)-3-(*p*-toluenesulfinyl)phenyl]butyl}-*p*-toluenesulfinamide (21b): (*S*)-*N*-Sulfinylketimine **3b** was used as electrophile. Chromatography: *n*-hexane−AcOEt 1:1; yield: 73%; white solid; mp: 171−173 °C; $[\alpha]_D^{20}$ −4.4 (*c* 1.0, $CHCl_3$); IR (NaCl): 3134, 1656, 1599, 1085 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, J = 7.7, 1.3 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.50−7.25 (m, 17H), 7.18 (d, J = 8.5 Hz, 2H), 7.08 (bs, 1H), 5.86 (d, J = 6.9 Hz, 1H), 4.82 (q, J = 7.0 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 0.68 (d, J = 7.0 Hz, 3H);^{13}C NMR (75 MHz, CD_3OD): δ 147.2, 143.8, 131.4, 130.0, 129.9 (2C), 128.9 (2C), 128.8 (2C), 128.1 (2C), 61.0, 52.9, 31.7, 25.1, 17.1; MS (FAB^+) *m*/*z* 564 (M + 1, 95), 409 (100), 320 (33), 182 (76).

[2*S*,3*S*,(*S*)*S*]-*N*-{2-Phenyl-3-[(*S*)-2-(*p*-toluenesulfinyl)phenyl]butyl}-*p*-toluenesulfinamide (*anti*-18a): (*S*)-*N*-Sulfinylketimine **3a** was used as electrophile Chromatography: *n*-hexane−AcOEt 1:1; yield: 80%; white solid; mp: 197−199 °C; $[\alpha]_D^{20}$ +25.7 (*c* 0.56, $CHCl_3$); IR (NaCl): 3417, 3194, 1492, 1450, 1438 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, J = 6.4 Hz, 2.0 Hz, 1H), 7.65−7.58 (m, 4H), 7.49−7.44 (m, 2H), 7.38−7.33 (m, 2H), 7.24 (d, J = 8.3 Hz, 1H), 7.17−7.14 (m, 1H), 7.09 (d, J = 7.0 Hz, 4H), 6.95 (d, J = 8.3 Hz, 2H), 3.86 (q, J = 7.1 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H), 1.87 (s, 3H), 0.49 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.0, 145.0, 143.6, 142.8, 140.9, 140.3, 140.0, 132.0, 130.5, 129.9, 129.7, 129.4, 128.9, 127.9, 126.7, 126.6, 125.6, 124.3, 63.1, 43.8, 21.2, 21.0, 18.7, 14.8; MS (FAB^+) *m*/*z* 502 (M + 1, 100), 495 (7), 473 (28), 429 (25); HRMS calcd for $C_{30}H_{31}NO_2S_2$ [M + 1] 502.1874, found 502.1874.

[2*S*,3*S*,(*S*)*S*]-*N*-{2-(4-Methoxyphenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*anti*-18b): (*S*)-*N*-Sulfinylketimine **3b** was used as electrophile. Chromatography: *n*-hexane−AcOEt 2:1; yield: 66%; white solid; mp: 172−175 °C; $[\alpha]_D^{20}$ +106.0 (*c* 1.0, acetone); IR (NaCl): 3424, 3196, 2970, 1612, 1514 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 7.7 Hz, 1H), 7.61−7.53 (m, 3H), 7.47−7.42 (m, 2H), 7.16 (d, J = 8.4 Hz, 4H), 7.10 (d, J = 6.8 Hz, 2H), 6.96 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 6.83 (bs, 1H), 3.88 (q, J = 7.1 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H), 1.83 (s, 3H), 0.50 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 145.1, 143.6, 142.7, 140.9, 140.2, 139.9, 139.2, 131.9, 130.4, 129.9, 129.4, 128.8, 127.7, 126.5, 125.6, 124.3, 113.2, 62.7, 55.0, 43.9, 21.2, 21.1, 18.9, 14.8; MS (FAB^+) *m*/*z* 532 (M + 1, 100), 504 (18), 503 (81), 481 (6); Anal. Calcd for $C_{31}H_{33}NO_3S_2$: C, 70.02; H, 6.26; N, 2.63; S, 12.06. Found: C, 69.94; H, 6.45; N, 2.45; S, 11.95.

[2*S*,3*S*,(*S*)*S*]-*N*-{2-(4-Methylphenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*anti*-18d): (*S*)-*N*-Sulfinylketimine **3d** was used as electrophile. In this case 2 equiv of the carbanion derivate from **6** were used. Chromatography: *n*-hexane−AcOEt 3:2; yield: 69%; white solid; mp: 172−175 °C; $[\alpha]_D^{20}$ +67.6 (*c* 2.0, $CHCl_3$); IR (NaCl): 3423, 3243, 2950, 1638, 1440, 1064, 810, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (dd, J = 7.6, 1.1 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 8.3 Hz, 1H), 7.56−7.52 (m, 1H), 7.53−7.51 (m, 2H), 7.21 (d, J = 6.9 Hz, 4H), 7.14 (d, J = 6.8 Hz, 4H), 7.01 (d, J = 8.2 Hz, 2H), 6.92 (bs, 1H), 3.90 (q, J = 7.1 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 2.30 (s, 3H), 1.90 (s, 3H), 0.57 (d, J = 7.1 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$): δ 145.0, 144.1, 143.5, 142.7, 140.8, 140.1, 139.9, 136.1, 131.9, 130.4, 129.8, 129.4, 128.8, 128.5, 126.3 (2C), 125.5, 124.2, 62.8, 47.7, 21.1, 21.0, 20.8, 18.7, 14.8; MS (FAB^+) *m*/*z* 516 (M + 1, 28), 504 (28), 503 (100), 497 (10), 481 (18); Anal. Calcd for $C_{31}H_{33}NO_2S_2$: C, 72.19; H, 6.45; N, 2.72; S, 12.44. Found: C, 72.10; H, 6.45; N, 2.61; S, 12.42.

[2*S*,3*S*,(*S*)*S*]-*N*-{2-(4-Bromophenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*anti*-18e): (*S*)-*N*-Sulfinylketimine **3e** was used as electrophile. Chromatography: *n*-hexane−AcOEt 5:2; yield: 64%; white solid; mp: 141−143 °C; $[\alpha]_D^{20}$ +103.8 (*c* 2.0, $CHCl_3$); IR (NaCl): 3168, 1590, 1491, 1083 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.72−7.43 (m, 8H), 7.17−7.06 (m, 6H), 6.90 (d, J = 8.1 Hz, 2H), 3.73 (q, J = 7.1 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 1.83 (s, 3H), 0.42 (d, J = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 146.5, 144.6, 143.0, 142.3, 140.7, 140.2, 132.2, 131.4, 130.9, 130.5, 130.2, 129.5, 128.8, 128.4, 126.6, 125.5, 123.9, 120.7, 62.6, 43.5, 21.1, 20.9, 17.9, 14.3; Anal. Calcd for $C_{30}H_{30}BrNO_2S_2$: C, 62.06; H, 5.21; N, 2.41; S, 11.05. Found: C, 62.08; H, 5.26; N, 2.34; S, 10.51.

[2*S*,3*S*,(*S*)*S*]-*N*-{2-(4-Nitrilephenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*anti*-18f): (*S*)-*N*-Sulfinylketimine **3f** was used as electrophile. Chromatography: *n*-hexane−AcOEt 1:1; yield: 31%; yellow solid; mp: 200−201 °C; $[\alpha]_D^{20}$ +54.6 (*c* 1.0, acetone); IR (NaCl): 3442, 3127, 2980, 2230, 1607, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 8.6 Hz, 2H), 7.75−7.72 (m, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.54−7.49 (m, 2H), 7.64 (bs, 1H), 7.10 (s, 4H), 7.09 (d, J = 7.8 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 3.79 (q, J = 7.2 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 1.92 (s, 3H), 0.43 (d, J = 7.2 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 144.4, 142.9, 142.5, 140.8, 140.7, 140.3, 132.4, 131.8, 130.7, 130.4, 129.6, 129.0, 127.5, 126.8, 125.6, 124.0, 118.9, 110.7, 62.9, 43.4, 21.2, 21.0, 17.7, 14.2; MS (FAB^+) *m*/*z* 527 (M + 1, 11), 504 (24), 503 (100), 481 (5); HRMS calcd for $C_{31}H_{30}N_2O_2S_2$ 527.1846, found 527.1827.

[2*R*,3*S*,(*S*)*S*]-*N*-{2-(4-Nitrilephenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*syn*-18f): (*S*)-*N*-Sulfinylketimine **3f** was used as electrophile. This compound was obtained as a minority diastereoisomer. Chromatography: *n*-hexane−AcOEt 1:1; yield: 10%; yellow solid; mp: 205−206 °C; $[\alpha]_D^{20}$ −175.0 (*c* 1.0, $CHCl_3$); IR (NaCl): 3441, 3157, 2974, 2925, 2855, 1497, 1084, 1044, 731 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (dd, J = 7.6, 2.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.41−7.17 (m, 12H), 6.66 (bs, 1H), 6.47 (dd, J = 7.3, 1.4 Hz, 1H), 3.82 (q, J = 7.1 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.03 (s, 3H), 0.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1, 140.8, 131.6, 131.3, 131.0, 130.1, 129.7, 129.6, 129.4 (2C), 127.2 (2C), 125.4, 125.3 (2C), 124.4 (2C), 118.7, 111.3, 64.9, 43.6, 29.3, 21.4, 21.2, 15.5; MS (FAB) *m*/z 527 (M + 1, 33), 497 (20), 459 (100), 453 (17); HRMS calcd for $C_{31}H_{30}N_2O_2S_2$ 527.1826, found 527.1845.

[2*S*,3*S*,(*S*)*S*]-*N*-{2-(Isopropyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)phenyl]-butyl}-*tert*-butanesulfinamide (*anti*-18′g): In this case the *ortho*-sulfinylcarbanion derivate from (*S*)-**6** using the standard procedure was added over a solution of the *N*-*tert*-butanesulfinylketimine **3′g** and 110 mol % of $AlMe_3$ (2 M, toluene) in 1 mL of toluene at −78 °C. Chromatography: *n*-hexane−AcOEt 1:1; yield: 58%; colorless oil; $[\alpha]_D^{20}$ +58.2 (*c* 1.0, acetone); IR (NaCl): 3343, 1494, 1471, 1378 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.82 (d, J = 8.2 Hz, 2H), 7.60−7.10 (m, 6H), 3.80 (q, J = 7.0 Hz, 1H), 3.33 (bs, 1H), 2.37 (s, 3H), 2.33−

2.19 (m, 1H), 1.24 (s, 9H), 1.17 (d, $J = 7.0$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 3H), 0.92 (d, $J = 7.1$ Hz, 3H), 0.82 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.1, 143.9, 141.0, 131.5, 130.8, 129.9, 129.7, 128.2, 127.3, 125.5, 65.0, 63.7, 39.7, 32.6, 23.4, 23.1, 21.3, 20.6, 17.9, 17.7.

[2*R*,3*S*,(*S*)*S*]-*N*-{2-Phenyl-3-[(*S*)-2-(*p*-toluenesulfinyl)phenyl]butyl}-*p*-toluenesulfinamide (*syn*-19a): (*R*)-*N*-Sulfinylketimine **3a** was used as electrophile. Chromatography: *n*-hexane−AcOEt 1:1; yield: 70%; white solid; mp: 135−138 °C; $[\alpha]_D^{20}$ −60.1 (*c* 1.0, $CHCl_3$); IR (NaCl): 3186, 3088, 1492, 1469, 1085 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, $J = 8.6$ Hz, 2H), 7.45−7.14 (m, 12H), 7.06 (s, 4H), 5.38 (bs, 1H), 4.22 (q, $J = 7.3$ Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 1.94 (s, 3H), 0.76 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.2, 144.3, 143.2, 140.6, 140.3, 139.8, 135.2, 131.9, 130.4 (2C), 129.3, 129.1, 128.4, 127.8, 127.5, 127.2, 125.2, 124.8, 64.3, 44.7, 21.7, 21.3, 21.2 16.3; Anal. Calcd for $C_{30}H_{31}NO_2S_2$: C, 71.82; H, 6.23; N, 2.79; S, 12.78. Found: C, 71.79; H, 6.26; N, 2.70; S, 12.82.

[2*R*,3*S*,(*S*)*S*]-*N*-{2-(4-Methoxyphenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*syn*-19c): (*R*)-*N*-Sulfinylketimine **3b** was used as electrophile. Chromatography: *n*-hexane−AcOEt 1:2; yield: 67%; white solid; mp: 180−182 °C; $[\alpha]_D^{20}$ −51.6 (*c* 1.0, $CHCl_3$); IR (NaCl): 3188, 1609, 1512, 1464 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.60 (d, $J = 8.9$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 2H), 7.37−7.05 (m, 10H), 6.97 (d, $J = 8.9$ Hz, 2H), 5.01 (bs, 1H), 4.24 (q, $J = 6.9$ Hz, 1H), 3.86 (s, 3H), 2.35 (s, 6H), 1.92 (s, 3H), 0.85 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.3, 143.2, 140.6, 140.3, 139.7, 136.7, 136.6, 131.7, 130.2, 129.3 (2C), 128.7 (2C), 127.6, 125.1 (2C), 124.8 (2C), 113.3, 63.9, 54.9, 44.8, 22.3, 21.1, 16.4, 13.9. MS (FAB$^+$) *m*/*z* 532 (M + 1, 22), 503 (21), 377 (100); HRMS (FAB$^+$) calcd for $C_{31}H_{34}N_1O_3S_2$ [M + 1] 532.1980, found 532.1997.

[2*R*,3*S*,(*S*)*S*]-*N*-{2-(4-Methylphenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*syn*-19d): (*R*)-*N*-Sulfinylketimine **3c** was used as electrophile. In this case 2 equiv of the carbanion derivate from **5** were used. Chromatography: *n*-hexane−AcOEt 5:2; yield: 73%; white solid; mp: 179−181 °C; $[\alpha]_D^{20}$ +105.6 (*c* 1.0, $CHCl_3$); IR (NaCl): 3187, 1595, 1513, 1442 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.54 (d, $J = 7.6$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 1H), 7.38−7.00 (m, 13H), 5.09 (bs, 1H), 4.23 (q, $J = 6.9$ Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 1.92 (s, 3H), 0.82 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.6, 143.3, 141.9, 140.7, 140.4, 139.7, 136.9, 131.9, 130.3, 129.4, 129.3, 128.9, 128.8, 127.8, 127.5, 125.3, 124.9, 124.8, 64.2, 44.8, 22.2, 21.2, 21.1, 20.9, 16.5. Anal. Calcd for $C_{31}H_{33}NO_2S_2$: C, 72.19; H, 6.45; N, 2.72; S, 12.44. Found: C, 72.24; H, 6.60; N, 2.48; S, 12.51.

[2*S*,3*S*,(*S*)*S*]-*N*-{2-(4-Bromophenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*syn*-19e): (*R*)-*N*-Sulfinylketimine **3e** was used as electrophile. Chromatography: *n*-hexane−AcOEt 5:2; yield: 61%; white solid; mp: 131−133 °C; $[\alpha]_D^{20}$ −4.6 (*c* 1.0, $CHCl_3$); IR (NaCl): 3180, 1711, 1589, 1589, 1490, 1083 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.52 (s, 4H), 7.46−7.05 (m, 12H), 5.75 (bs, 1H), 4.08 (q, $J = 7.0$ Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 1.89 (s, 3H), 0.67 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.9, 143.7, 143.1, 143.0, 140.6, 140.4, 139.8, 132.0, 131.0, 130.4, 129.4, 129.3, 129.2, 129.1, 127.6, 125.0, 124.5, 121.2, 63.8, 44.3, 29.5, 21.2, 21.1, 15.8; Anal. Calcd for $C_{30}H_{30}BrNO_2S_2$: C, 62.06; H, 5.21; N, 2.41; S, 11.05. Found: C, 61.82; H, 5.26; N, 2.34; S, 10.51.

[2*R*2*S*,3*S*,(*S*)*S*]-*N*-{2-(4-Nitrilephenyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)-phenyl]butyl}-*p*-toluenesulfinamide (*syn*-19f/*anti*-19f): These compounds were obtained as an unseparated mixture of diastereoisomers. Chromatography: *n*-hexane−AcOEt 1:1; combined yield: 40%; yellow oil; Major isomer *syn*-**4′e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, $J = 8.6$ Hz, 2H), 7.75−7.22 (m, 14H), 3.94 (q, $J = 7.0$ Hz, 1H), 2.30 (s, 6H), 2.05 (s, 3H), 0.48 (d, $J = 7.2$ Hz, 3H). Minor isomer *anti*-**4′e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, $J = 8.7$ Hz, 2H), 7.75−7.22 (m, 14H), 4.03 (q, $J = 7.2$ Hz, 1H), 2.28 (s, 6H), 2.02 (s, 3H), 0.32 (d, $J = 7.2$ Hz, 3H).

[2*R*,3*S*,(*S*)*S*]-*N*-{2-(Isopropyl)-3-[(*S*)-2-(*p*-toluenesulfinyl)phenyl]-butyl}-*tert*-butanesulfinamide (*syn*-19′g): In this case the *ortho*-sulfinylcarbanion derivate from (*S*)-**6** using the stardard procedure was added to a solution of the *N*-*tert*-butanesulfinylketimine **3′g** and 110 mol % of $AlMe_3$ (2 M, toluene) in 1 mL of toluene at −78 °C. Chromatography: *n*-hexane−AcOEt 1:1; yield: 58%; colorless oil; $[\alpha]_D^{20}$ +12.5 (*c* 1.0, acetone); IR (NaCl): 3348, 1493, 1472, 1378 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.83 (d, $J = 8.6$ Hz, 2H), 7.55−7.20 (m, 6H), 3.89 (q, $J = 7.0$ Hz, 1H), 3.45 (bs, 1H), 2.39 (s, 3H), 1.93 (pent, $J = 7.1$ Hz, 1H), 1.28−1.24 (m, 12H), 1.06 (s, 3H), 0.93 (d, $J = 7.1$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.0, 143.4, 141.2, 140.6, 131.9, 130.0, 129.7, 127.9, 127.6, 125.9, 63.5, 56.9, 40.4, 37.3, 23.1, 21.3, 20.5, 18.5, 18.0, 17.4.

(2*S*)-*N*-{1,1-Diphenyl-[(*S*)-3-(*p*-toluenesulfinyl)phenyl]propyl}-*p*-toluenesulfonamide (17b): In this case *N*-sulfonylketimine **9b** was used as electrophile. Chromatography: *n*-hexane−AcOEt 1:1; yield: 94%; white solid; mp: 247−248 °C; $[\alpha]_D^{20}$ +23.8 (*c* 1.0, $CHCl_3$); IR (NaCl): 3529, 3509, 1493, 1378 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (bs, 1H), 7.81 (dd, $J = 6.8$, 1.3 Hz, 1H), 7.39−7.23 (m, 13H), 7.13−7.10 (m, 1H), 7.00−6.90 (m, 6H), 5.47 (d, $J = 8.1$ Hz, 1H), 5.51 (q, $J = 7.0$ Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 0.39 (d, $J = 7.0$ Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 141.7, 141.2, 140.6, 139.9, 138.7, 137.7, 133.5, 131.7, 130.3, 129.8, 129.7, 128.3, 127.6, 127.1, 126.9, 126.1, 123.9, 70.9, 42.3, 21.3, 21.2, 16.9. MS (FAB$^+$) *m*/*z* 564 (M + 1, 94), 409 (100), 182 (76).

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Supporting Information Available: Experimental procedures and spectroscopic data for all new additional compounds, X-ray data for **17b** and *anti*-**18b**, and the NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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