Iodine(III)-Mediated Preparations of Nitrogen-Containing Sulfur Derivatives: Dramatic Influence of the Sulfur Oxidation State

Dominique Leca, Kai Song, Muriel Amatore, Louis Fensterbank, Emmanuel Lacôte, and Max Malacria*[a]

Dedicated to Prof. Pierre Gouzerh on the occasion of his 60th birthday

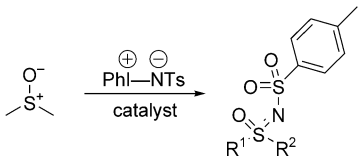
Abstract: Reaction of sulfonamides with iodosobenzene leads to phenyliodinanes. A new catalysis reaction of the decomposition of these products in the presence of sulfoxides that allows the smooth synthesis of sulfoximines has been evidenced and studied: copper(II) salts were used to prepare compounds **4a–j** and **5b, d, f, j, k** from the corresponding, easily prepared, sulfoxides. The reactions proceed with retention of configuration at the sulfur center, and copper(II) triflate is the best candidate for the catalyst for the imination. Switching from sulfonamides to sulfinamides in the preparation of the starting iodinanes completely alters the reaction pathway: iodinanes are no longer accessible, and sulfonimidates **7a–j** are obtained instead. This behavior can be rationalized by the increase in pK_a brought about by the removal of one oxygen atom from the sulfur center. Sulfonimidates are interesting molecules with varied applications. Optimization of their one-pot synthesis has been achieved by carrying out the reaction in acetonitrile. The stereochemical study has shown that the transformation proceeds with global retention of the configuration at the sulfur center, albeit with erosion of the enantiomeric purity. A model accounting for this outcome is proposed. In addition, the presence of oxidized sulfonamide by-products has been explained, and this latter pathway becomes the sole one when alcohol is replaced by water. Good yields of the oxidized products are obtained.

Keywords: iodine · oxidation · sulfonimidates · sulfoximines · sulfur

Introduction

Nitrogen-containing sulfur derivatives are highly important compounds that have found a wide range of applications, for example, as partners for asymmetric synthesis, ligands, bioactive molecules, and bricks for new materials. In particular, sulfonamides,[1] sulfinamides,[2] and sulfoximines[3,4] are among the most prominent members of this family. Thus, the quest for new routes for their preparations is a never-ending challenge that needs to be approached with new perspectives. Some time ago, we reported on our work devoted to asymmetric radical reactions involving chiral sulfoxides.[5,6] Because sulfoximines can be prepared from sulfoxides, we looked for new ways to stereoselectively access to such compounds, and, more generally, most chiral nitrogen-containing sulfur moieties.

When we initiated our work, one of the best syntheses of sulfoximines used phenyliodinane, a hypervalent iodine(III) derivative, as the nitrogen source (Scheme 1). This does not



Scheme 1. General preparation of sulfoximines from sulfoxides.

come as a big surprise because the chemistry of hypervalent iodine compounds has experienced a tremendous development during the last decade.[7,8]

This surging interest is mainly due to their useful mild oxidizing properties and their low toxicity (especially compared to heavy-metal derived oxidizing agents).[7] Among all iodine(III) reagents, iodinanes are very convenient nitrene precursors, whose metal-mediated decomposition is a very powerful tool. Mansuy and co-workers first described the aziridi-

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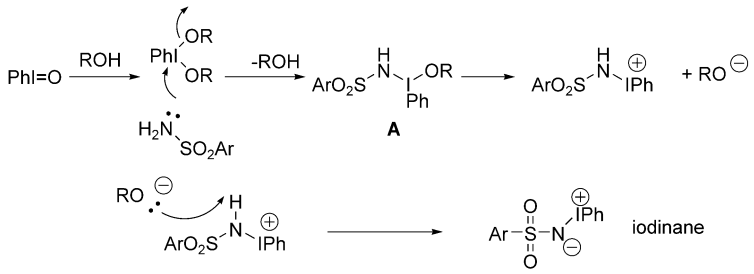
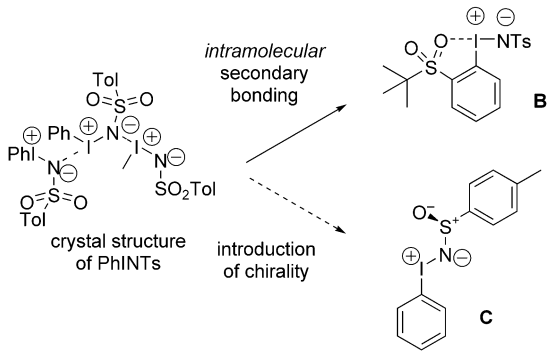
nation of alkenes with phenyliodinane in the presence of iron or manganese porphyrins.[9] The mechanism involves a porphyrin metal–nitrene complex.[10] Evans and co-workers have further investigated the aziridination of alkenes and have made copper salts the catalysts of choice for this reaction.[11] Generally, copper(I) is used. The reaction has been extended to sulfides and sulfoxides as nitrene traps to yield sulfimides[12] and sulfoximines, respectively, by Vogt and Muller[13] and by Bolm and co-workers.[14,15]

Different phenyliodinanes have been prepared[16–18] by coupling the corresponding sulfonamide with iodosobenzene derivatives in KOH/methanol. The initial step is presumably the solvolysis of the initial iodine reagent.[19] Sulfonamides react by nucleophilic substitution on the iodine atom, possibly giving birth to a dissociated intermediate, that would eventually be deprotonated (Scheme 2).



Scheme 2. Possible mechanism for the formation of phenyliodinanes.

The iodinanes are highly polarized molecules. Thorough studies of their structure and solid-state aggregation have shown that these molecules are best described as possessing I–N single bonds with substantial amounts of charge on the I and N atoms.[20] This can lead to varied polymeric assemblies, which can be stabilized through secondary interactions with the oxygen atoms of the sulfonyl moiety.[21] Thus, iodinanes generally are poorly soluble and the catalytic reactions that employ them are heterogeneous and rather slow. This problem can be overcome by the preparation of iodinane **B** in which an additional sulfonyl group is put on the aryl group attached to the iodine center (Scheme 3).[22] Disruption of the electrostatic intermolecular forces on **B** is achieved by the introduction of *intramolecular* secondary bonds. The reactivity is thus much better.



Scheme 3. Routes to modified phenyliodinanes.

In all the latter cases, the iodinanes have been first isolated and subsequently decomposed to yield the desired iminated products. This process has been converted into very elegant one-pot procedures.[23–26]

Chiral ligands were used for asymmetric aziridination[11] and sulfimidation,[12,27] but the *ee* values obtained in the copper-mediated sulfimide synthesis are not satisfactory. Carreira and Tomooka have nicely improved the asymmetric preparation of chiral sulfinimines by using nitridomanganeses complexes.[28] However, a full equivalent of the metal is required to reach high *ee* values. We decided to examine the preparation of chiral iodinanes, in which a sulfinyl group replaced the sulfonyl one, and thus to prepare **C** (Scheme 3). We reasoned that since one oxygen atom of the sulfonyl group always plays no role in the stabilization, sulfinyl moieties could be valid chiral surrogates for the secondary interactions. Precursor **C** could be prepared by a standard procedure starting from a chiral sulfinamide rather than a sulfonamide. We report below the findings we gathered along this path.

Results and Discussion

Catalytic system: Prior to our study, we decided to have a closer look at the catalytic system we would end up using. Several metallic systems can decompose phenyliodinane. Most of them fall into two distinct categories. Porphyrins were the first reported systems: by analogy to the biomimetic oxidations, Mansuy and co-workers reported the aziridination of different aryl-substituted alkenes by iron(III) and manganese(III) porphyrins.[9] It is assumed that these reactions occur via terminal imidoiron(V) and manganese(V) intermediates, as can be inferred from the isolation of an elusive terminal (imido)manganese(V) corrole complex.[10] The second main category contains copper complexes. For aziridination reactions, the oxidation state of the active species has not been clearly identified and a debate is still going on. While Deeth, Scott and co-workers[29] and Norrby and co-workers[30] favor a route involving a copper(I) intermediate, Evans and co-workers reported in their seminal article that UV-monitoring of the aziridination of double bonds showed that "it is reasonable to conclude that these reactions are being catalyzed through Cu^{II} rather than Cu^{I} as originally presumed".[11] The reactions are very likely substrate dependent.

Sulfimides can be obtained from sulfides with both copper(I) and copper(II) salts.[12] However copper(II) derivatives were inferior to copper(I) triflate for asymmetric sulfimidation. The authors attribute this loss to the competition between acetonitrile and the chiral ligand for the ligand sites on copper and/or to the poorer solubility of copper(II) triflate. Formation of sulfoximines was even less examined.[4] To the best of our knowledge, only two groups had focused on the preparation of sulfoximines from sulfoxides and phe-

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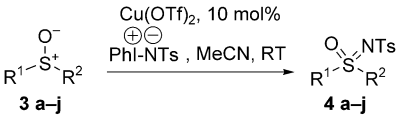
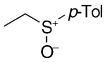
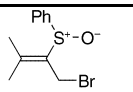
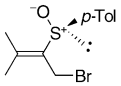
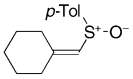
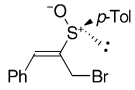
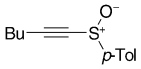
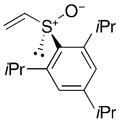
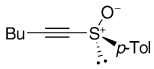
nyliodinane. Both chose to rely on copper(I) catalysts to do the work.[13–15,31] After reviewing the available literature and taking advantage of what was described for alkenes and sulfides, we were confident sulfoximines could be prepared by using copper(II) salts. There are two advantages for such an approach: beyond the economic aspects (copper(II) is generally much less expensive), the practicality of the reaction would be improved, since copper(I) triflate is air-sensitive and must be handled in a glovebox.

The synthesis of sulfoximines was achieved by treatment of suitably substituted sulfoxides with one equivalent of phenyliodinane in acetonitrile, in the presence of 10 mol% of copper(II) triflate.[46] Representative results are summarized in Table 1.

Table 1. Catalytic synthesis of sulfoximines with copper(II) triflate.



3 a–j 4 a–j

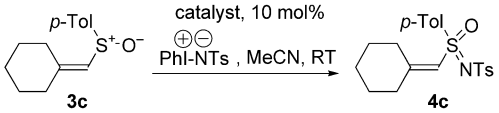
Entry	Sulfoxide	Sulfoximine	Yield [%]	Entry	Sulfoxide	Sulfoximine	Yield [%]
1	**3a** 	**4a**	96	6	**3f** 	**4f**	91
2	**3b** 	**4b**	91	7	**3g** 	**4g**	89
3	**3c** 	**4c**	96	8	**3h** 	**4h**	75
4	**3d** 	**4d**	53	9	**3i** 	**4i**	89
5	**3e** 	**4e**	72	10	**3j** 	**4j**	89

Sulfoximines **4a–j** were obtained in good to excellent yields. We developed our method first with alkylaryl- and dialkyl sulfoxides **3a,b**, which led to their imine counterparts in 96% and 91%, respectively (Table 1, entries 1 and 2). The reaction was almost instantaneous. When stirring is prolonged, a precipitate appears, probably an iodinated byproduct. Versatile vinyl sulfoxides (Table 1, entries 3–5) and allylic bromides (Table 1, entries 6–8) were easily transformed even when reactions were carried out in an open flask with acetonitrile from the bottle. The yield for phenyl vinyl sulfoxide is lower than for all the other derivatives. Phenyl vinyl sulfoxide is prone to anionic polymerization, which is maybe what happens during the imidation. An additional hint for such a behavior is given by entry 5 in Table 1: The triisopropylphenyl derivative **3e** is particularly hindered because of the bulky aromatic ring. This could have prevented or hindered reactions at or near the sulfur atom. Sulfoximine **4e** was obtained in higher yield than its parent compound (72%, entry 5). More interestingly, the imidation occurred as quickly and easily as the sterically less demanding sulfoxides. Entries 9 and 10 in Table 1 show that acetylenic sulfoximines can also be prepared by this method. To the best of our knowledge, this was the first preparation of such compounds, whose reactivity looks promising.[32] Chiral HPLC analysis of **3i** and **3j** showed that the reaction was stereoselective, no loss in *ee* being observed. This is consistent with the earlier studies with copper(I) triflate by Muller and Vogt,[13] who reported complete retention of configuration at the sulfur center. Attack of the sulfur lone pair leads to the formation of the S=N bond. When submitted to our conditions, (*R*)-methyl-*p*-tolyl sulfoxide (*ee* > 98%) yielded the corresponding known (−) sulfoximine (97%, *ee* > 98%), implying an *R* absolute configuration at the sulfur center[33] (we obtained the same specific rotation as the authors. This delivers additional evidence for a good *ee*). The reaction thus proceeds with retention of configuration.

We next turned our attention to the nature of the copper salt (Table 2). We decided to carry out our tests with sulfoxide **1c**, because of the average challenges it poses (one double bond, but no additional potentially problematic functionality, and not too reactive).

Copper(II) triflate appears to be the reagent of choice, both in terms of yields and rates (Table 2, entry 1). Catalyst load could be reduced to 3 mol% without problems (Table 2, entry 2), while further decrease resulted in an important reduction of the rate of the reaction.

Table 2. Optimization of the catalyst.



3c 4c

Entry	Catalyst	Yield [%]
1	$Cu(OTf)_2$	96
2	$Cu(OTf)_2$, 3 mol%	87
3	$CuCl_2$	43 (20% sm)[a]
4	$CuSO_4 \cdot 5H_2O$	no reaction
5	$Cu(acac)_2$	86
6	$Cu(OAc)_2 \cdot H_2O$	77 (7% sm)

[a] PhINTs (1 equiv) and $CuCl_2$ (10 mol%) were added after 1 h. acac = acetylacetonate; sm = starting material.

Copper(II) chloride does not work well (Table 2, entry 3). Copper sulfate gave no reaction at all (Table 2, entry 4), whereas $Cu(acac)_2$ worked well, although it was slightly less active than copper triflate (compare entries 1 and 5, Table 2). Copper(II) acetate monohydrate is also an accepta-

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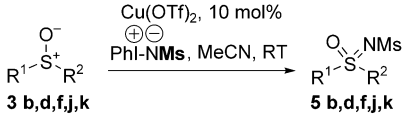
ble catalyst, thus demonstrating that our method is not only compatible with oxygen but also with water (Table 2, entry 6). This quick survey showed that copper(II) triflate is the best catalyst. This has not been further examined but from this point on we have continued with the triflate.

The next step was to examine the nature of the iodinane. In order to know whether the reaction was limited to arylsulfonyliodinane, we introduced the corresponding methylsulfonyl iodinane (Table 3).[18]

Table 3. Catalytic synthesis of *N*-methanesulfonyl sulfoximines with copper(II) triflate.

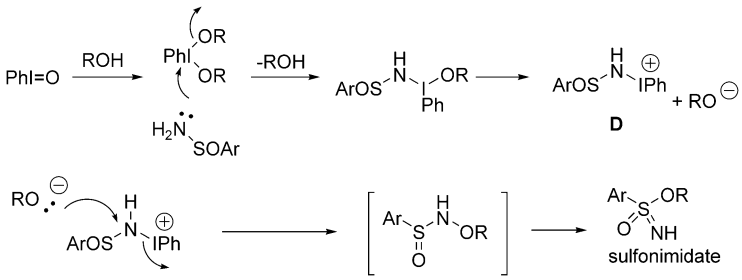


Entry	Sulfoxide	Sulfoximine	Yield [%]
1	**3b**	**5b**	95
2	**3f**	**5f**	70
3	**3k**	**5k**	98
4	**3d**	**5d**	70
5	**3j**	**5j**	40

We tested the sulfoximination with an assay of our sulfoxides. All sulfoximines were obtained in yields similar to those obtained with *p*-toluenesulfonyliodinane except for **5j**, thus demonstrating that the reaction was not limited to the aryl derivatives. This is quite interesting because these new sulfoximines are electronically different from the previous ones and their properties may thus be tuned by the choice of the substituent on the iodinane. In the case of acetylenic sulfoxides **3j**, we did not observe any other by-product than iodobenzene. Since the triple bond is a good ligand for metals, it is possible that it starts interfering with the imination at the sulfur center.

Access to sulfonimidates: With our system in hand, we turned our attention to the preparation of sulfinyl-derived iodinanes. In doing so, we kept in mind that another reaction path was possible. To produce imidoiodinanes, iodosobenzene and iodosobenzene diacetate react with sulfonamides.[9,34] As mentioned before, the initial step is presumably the solvolysis of the initial iodine reagent.[19] Sulfonamides react by nucleophilic substitution on the iodine atom, possibly giving birth to a dissociated intermediate arising from the I–O bond cleavage on **A**. Deprotonation eventually delivers the iminoiodinanes (Scheme 2). Now, switching to sulfinamides implies a strong reduction of the amide function acidity.[35] A methoxide group could substitute the iodobenzene moiety at the nitrogen center on **D** rather than deprotonate it, thus leading to sulfinyl hydroxylamines (Scheme 4).

Maricich and co-workers evidenced in 1973 that, in some cases, sulfinylhydroxylamines underwent spontaneous rearrangement to sulfonimidates, with migration of the alkoxy

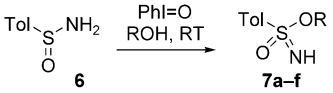


Scheme 4. Possible mechanism for the formation of sulfonimidates.

group from the nitrogen to the sulfur atom.[36] In any case, this alternative route would be of great interest, since sulfonimidates are very interesting chiral and nitrogen-containing compounds. They have also applications in material sciences, as monomers of "inorganic polymers",[37,38] and biochemistry, where they may act as inhibitors of human carbonic anhydrase II.[39] In addition, Johnson and coworkers have shown that they can be used in asymmetric synthesis as chiral enantiopure sulfoximine precursors.[40] Reggelin and co-workers developed these precursors with high levels of sophistication by introducing cyclic sulfonimidates.[41,42]

When submitted to potassium hydroxide in methanol at room temperature, tosylsulfinamide led to the corresponding sulfonimidate after just a few minutes. This not only showed that our assumption was correct, but also that we could prepare sulfonimidates by a one-pot procedure, in contrast to the known reported methods which were multistep procedures.[43,44] Next, we optimized the reaction conditions: it is unnecessary to use a base if PhI=O is used as the starting iodine reagent. This avoids having to work under overly basic conditions. With the optimized procedure in hand, we studied the scope and limitations of this reaction (Table 4).

Table 4. Preparation of sulfonimidates (1): Alcohol as solvent.



Entry	R	Sulfonimidate	Yield [%]
1	Me	**7a**	91
2	Et	**7b**	94
3	*i*Pr	**7c**	73[a]
4		**7d**	71
5		**7e**	92
6		**7f**	85
7	Bn	–	–[b]
8	*t*Bu	–	–[c]

[a] Reaction took 1 h. [b] Tosylbenzylamine (17%) was isolated. [c] Sulfonamide (90%) was obtained.

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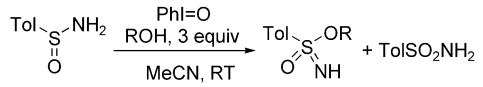
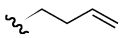
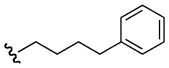
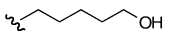
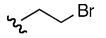
Entries 1, 2, and 4–7 in Table 4 show that the reaction works well with primary alcohols, with the exception of benzyl alcohol. The only isolated product was tosylbenzylamine in low yield. This product arises from the known rearrangement of sulfonimidates.[45] The reaction proved very sensitive to steric hindrance: while the rate diminished with 2-propanol (Table 4, entry 3), no reaction took place in tert-butyl alcohol (Table 4, entry 8). This could be explained by the impossible solvolysis of iodosobenzene, which is an insoluble polymeric material: when alcohols are too sterically demanding, dialkoxyiodosobenzene could not be formed and the reaction could not proceed.

The main limitation was, of course, the amount of alcohol needed for the transformation. While this posed no problem when methanol or ethanol were used, it became more troublesome when a more expensive alcohol was targeted. We reasoned that if the limiting step was the solvolysis of the starting material, we should be able to reduce the number of equivalents of alcohol used, ideally lowering it to two. Therefore we switched to acetonitrile, anticipating that its polarity could allow the formation of the dialkoxy adducts. Indeed we observed the formation of the desired sulfonimidates, albeit in slightly lower yields. Sulfonamide—arising from the standard oxidation of sulfinamides—was also isolated, and this accounts for the loss in yield (Table 5).

Table 5. Preparation of sulfonimidates (2): Acetonitrile as solvent.



6 7a–j 8

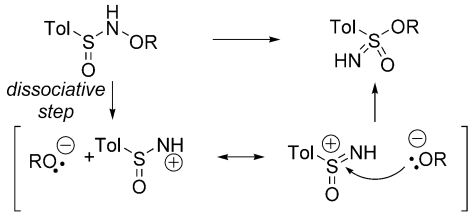
Entry	R	Sulfonimidate	Yield [%]	**8**, Yield [%]
1	Me	**7a**	85	5
2	Et	**7b**	67	23
3	*i*Pr	**7c**	39[a]	30
4		**7d**	60	36
5		**7e**	76	21
6		**7f**	71	13
7		**7g**	57	27
8		**7h**	60	1
9		**7i**	95	3
10		**7j**	62	11
11	Ph	–	–[b]	–[b]

[a] Molecular sieves 3 Å were also used. [b] Immediate degradation was observed.

The reaction was smooth except in the case of secondary alcohols (Table 5, entry 3), which led to a dramatic drop in yield of the desired product. We imagined that the water released during the formation of the dialkoxyiodosobenzene was accountable for this loss, but the addition of molecular sieves in the reaction mixture was not entirely conclusive. It may sometimes slightly improve yields, but not as a general rule.

Nonetheless, the result was quite satisfactory for expensive primary alcohols or for those, whose physical properties would not allow them to be used as solvents (e.g. Table 5, entry 7). Propanediol led to a crystalline compound which was unambiguously proven to be the sulfonimidate by X-ray diffraction (Table 5, entry 8). The ethyl compound was also prepared according to the Roy method; both reactions gave the same product. As stated before, the only observed by-products were sulfonamides. Lowering the amount of alcohol below three equivalents leads to an increase of oxidation at the expense of the desired product. This result is still interesting, since—to the best of our knowledge—no such oxidation involving iodine(III) derivatives has been reported. The scope of the oxidation is presented below. Aromatic alcohols are not suitable: degradation occurs presumably through electrophilic aromatic substitution (Table 5, entry 11).[7,8]

We then turned our attention to the asymmetric version of this reaction (Table 6). Before that, we made sure our reaction was working with other substituents on sulfur and, most importantly, on nitrogen. The reactions work well in both cases and are versatile (Table 6, entries 1, 3 and 5). For better comparison of the stereochemical outcomes, we carried out the reactions in methanol as solvent. As before, reactions work in acetonitrile, but are slower and accompanied by various amounts of oxidized by-products: **9** yielded 52% of **10** and 22% of **26**, while **13** yielded 71% of **14** and 7% of **27**. However, the reaction failed with *N*-acylsulfinamide **21** (see Table 7 for formula). In this case, only oxidation took place (see below). Sulfinamides are chiral compounds. Our first step was to prepare them enantiomerically pure and check the fate of the stereogenic sulfur atom. The proposed mechanism of the rearrangement of sulfinyl hydroxylamines by Maricich and co-workers involves a dissociative step to give a nitrenium cation.[36] One could thus have anticipated a loss of stereochemical information during the rearrangement (Scheme 5).



Scheme 5. Proposed mechanism for the rearrangement of *N*-alkoxybenzenesulfinamides.

We were rather pleased to observe that, when carried out starting from (*S*)-**9** [or (*S*)-**11**], the reaction led to the corresponding sulfonimidates with 62% *ee* [72% *ee*, Table 6, entries 2 and 4, respectively). Products (*R*)-**10** and (*R*)-**12** were resubmitted to the reaction conditions: they neither isomerize nor react in the reaction vessel or on silica for periods of time much longer than the reaction time (but eventually slowly tautomerize into sulfonamides[45]). Thus, maybe the mechanism is slightly different than the one inspired from the literature. To gain more information, we diastereoselectively prepared sulfinamides **15**, **17**, and **19**, which bear

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Table 6. Stereochemical issues associated with the sulfonimidate synthesis.

Entry	Sulfinamide	Sulfonimidate[a]	Yield [%][b]
1	**9**	**10**	74
2	(*S*)-**9**[c]	(*R*)-**10**	96, 62% *ee*[d]
3	**11**	**12**	72
4	(*S*)-**11**[c]	(*R*)-**12**	71, 72% *ee*[d]
5	**13**	**14**	100[e]
6	**15**	**16**	89, 81:19 ds[f]
7	**17**	**18**	90, 88:12 ds[f]
8	**19**	**20**	73, 73:22 ds[f]

[a] Only the major product is shown. [b] All reactions were run in methanol. [c] 100% ee, determined by chiral HPLC. [d] Determined by chiral HPLC. [e] Enantiomers could not be separated. [f] Determined by 400 MHz ^{1}H NMR spectroscopy.

chiral auxiliaries on the nitrogen center (Table 6, entries 6–8). Amazingly, the chiral auxiliaries have no effect on the selectivity: sulfonimidates **16**, **18**, and **20** are cleanly isolated with essentially the same selectivities as before. Once again, those products do not isomerize or tautomerize during the reaction. We were able to isolate a crystal of **16**, whose structure determined by X-ray crystallography indicated that the reaction mainly occurred with retention of configuration (Figure 1).

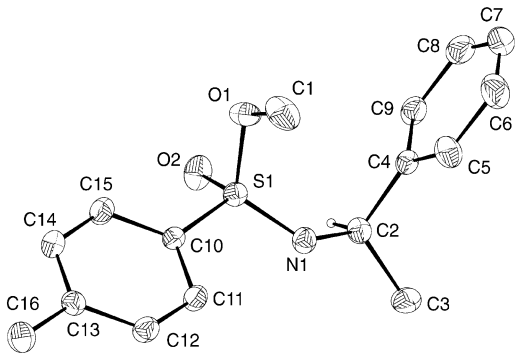
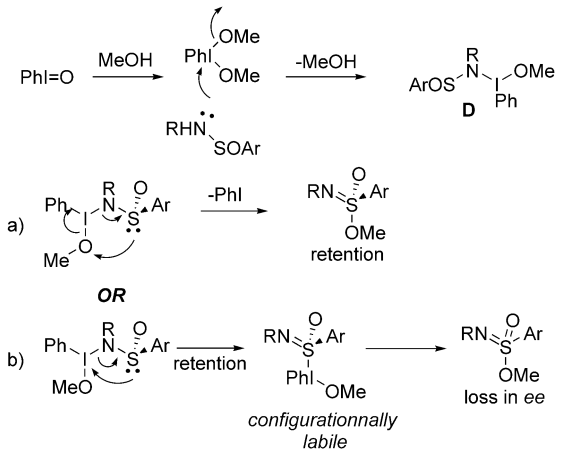


Figure 1. X-ray structure of sulfonimidate **16**.

This prompted us to propose a revised mechanism and a model accounting for the overall retention of configuration (Scheme 6). The reaction would proceed as proposed earlier through intermediate **D**. Because of the difference in the pK_a values between **A** (Scheme 2) and **D**, the latter would not lead to deprotonation, but rather rearrange via a six-electron transition state to afford sulfonimidates with retention of configuration (path a). Sulfinamides are easily oxidized by electrophilic oxidants, which make their lone pair relatively nucleophilic.[47] Alternatively, **D** could undergo a competitive three-atom rearrangement similar to the one evidenced by Reggelin and coworkers (path b).[61] In Reggelin's case, the oxidation of sulfinamides by *tert*-butyl hypochlorite leads to a sulfonimidoyl chloride by initial N-halogenation, which is subsequently substituted by the alcohol with inversion.[42] In our case, the intermediate sulfonimidoyl iodonium derivative would probably be configurationnally labile (contrary to chlorides, bromides are not configurationnally stable), and racemize before trapping by methanol, presumably with inversion too. Thus, if some of the material followed this reaction path, there would be a loss in *ee*. Another possibility is that some competitive reaction occurs following the dissociative pathway proposed by Maricich and co-workers, contributing to the drop in the *ee* value.



Scheme 6. Revised mechanism for the preparation of sulfonimidates.

Oxidation of sulfinamides: When the reactions were run in acetonitrile, the sole by-product was that from the oxidation. To the best of our knowledge, hypervalent iodine reagents had never been used for such a transformation in spite of the discrete reducing power of sulfinamides. Traditionally,

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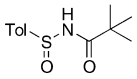
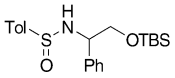
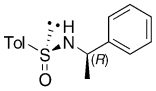
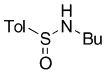
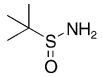
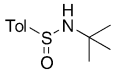
meta-chloroperoxybenzoic acid (MCPBA) is the reagent of choice.[47] However, since it is important to diversify the arsenal available to the chemist, our previous observation prompted us to examine this mild oxidation (Table 7).

Table 7. PhI=O-mediated oxidation of sulfinamides to sulfonamides.

Entry	Sulfinamide	Sulfonamide	Yield [%]
1	**6** 	**8**	84
2	**21** 	**22**	82
3	**23** 	**24**	81
4	**15** 	**25**	78
5	**9** 	**26**	82
6	**13** 	**27**	80
7	**11** 	**28**	81

The best yields were attained when water was added to the mixture of iodosobenzene and sulfinamide in acetonitrile. The reaction proved to be very general: the sulfonamides were isolated in good yields (typically $\geq 80\,\%$) with a broad range of substituents. Their structures were assessed by comparison with published data. Both aryl and alkylsulfinamides work (compare Table 7, entries 1–6). Many different groups can be attached on the nitrogen center, even acyl groups (Table 7, entry 2), and the reaction does not seem sensitive to steric hindrance (compare, for example, Table 7, entries 9 and 11). This contrasts with the sulfonimidates preparation, and this explains the by-products: the oxidation would have a fairly constant rate, so whenever the sulfonimidate formation is quick enough, no oxidation is observed, while it becomes appreciable as soon as the former rate decreases.

We next looked for other oxidizing agents. The Koser reagent PhI(OMe)OTs[48] also does the job with comparable yields (100 % and 69 % for the oxidation of **6** and **15**, respectively). It was previously used to oxidize sulfides. Sulfoxides are usually deemed not to be nucleophilic enough to react with this type of reagents.[49] Sulfinamides seem to be in between. We did not pursue the study further because the yields are similar, but the reagent is more difficult to obtain and leads to the formation of an additional by-product (methyl *p*-toluenesulfonate), which has to be removed from the reaction mixture.

Conclusion

Hypervalent iodine derivatives are good reagents for preparing nitrogen-containing sulfur(VI) products. We evidenced an important variation of reactivity between sulfinamides and sulfonamides, which can be explained by their difference in pK_a value. While sulfonamides lead to the corresponding iminoiodinanes, the parent sulfinamides have a very different behavior and yield sulfonimidates. The preparation has a fair degree of retention, which is independent of the substituents on nitrogen. We have proposed a mechanism accounting for these findings. Work to further investigate this model is underway (such as the influence of the solvent, alcohols and aromatic group on the iodine) and will be reported in due course.

Experimental Section

General remarks: Reactions were carried out under an inert gas, with magnetic stirring and degassed solvents when necessary. HPLC grade alcohols were purchased from various manufacturers and were used without further purification. MeCN was dried and distilled from CaH_2. Thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel. Merck Geduran SI 60 A silica gel (35–70 mm) was used for column chromatography. The melting points reported were measured with a Reichert hot-stage apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 1420 and a Bruker Tensor 27 ATR diamant PIKE spectrometer. ^{1}H NMR [^{13}C NMR] spectra were recorded at room temperature with 200 MHz [50 MHz] Bruker AC 200 and ARX 200 spectrometers, 250 MHz [62.5 MHz] Bruker ARX 250 and 400 MHz [100 MHz] Bruker ARX 400 and AVANCE 400 spectrometers. Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents ($\delta = 7.26$ or 77.0, respectively, for $CDCl_3$). Coupling constants (J) are given in Hertz (Hz). Elemental analyses were performed by the Service Régional de Microanalyse de L'Université Pierre et Marie Curie and Exact Mass were recorded at ICSN (CNRS, Gif) on a LCT micromass apparatus (Electrospray source). Optical rotatory powers were recorded on a Perkin Elmer 343 device. The enantiomeric excess (*ee*) values were measured by chiral HPLC (Waters 1525 binary with a Waters 2487 detector) using a CHIRALPAK AD-H stationary phase. The X-ray diffraction study was carried out at the Laboratoire de chimie inorganique et matériaux moléculaires (UMR 7071 CNRS, UPMC). CCDC-219334 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk). The starting sulfinamides were either commercially available and used without further purification or were prepared following reported procedures.[50,51]

General procedure 1 (GP1): *Preparation of N-Tosyl sulfoximines*: Sulfoxides **3a–j** (0.5 mmol; 1 equiv) were added to a solution of $Cu(OTf)_2$ (0.05 mmol; 10 mol %; 18 mg) in acetonitrile (3 mL) at room temperature. PhI=NTs (0.55 mmol; 1.1 equiv; 205 mg) was then added dropwise in one batch. The reaction was monitored by the rapid disappearance of the yellowish powder from the reaction mixture, which turned homogeneous and green generally after two minutes. Acetonitrile was removed in vacuo and the crude material was purified by flash chromatography on silica gel to yield sulfoximines **4a–j**.

General procedure 2 (GP2): *Preparation of N-Mesyl sulfoximines*: Sulfoxides **3 b,d,f,j,k** (0.5 mmol; 1 equiv) were added to a solution of $Cu(OTf)_2$ (0.05 mmol; 10 mol %; 18 mg) in acetonitrile (3 mL) at room temperature. PhI=NMs (0.65 mmol; 1.3 equiv; 193 mg) was then added dropwise in one batch. MeCN was removed in vacuo and the crude material was purified by flash chromatography on silica gel to yield sulfoximines **5b,d,f,j,k**.

General procedure 3 (GP3): *Preparation of sulfonimidates (alcohol as solvent)*: PhI=O[52] (0.75 mmol; 1 equiv; 165 mg) was added at room temperature to a solution of sulfinamide (0.75 mmol; 1 equiv; 116 mg) in alcohol (2 mL). After completion (ranging from 15 min to overnight), the excess alcohol was removed in vacuo. The crude mixture was purified by flash chromatography.

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General procedure 4 (GP4): *Preparation of sulfonimidates in acetonitrile*: Alcohol (2.25 mmol, 3 equiv) and PhI=O (0.75 mmol; 1 equiv; 165 mg) were added at room temperature to a solution of sulfinamide (0.75 mmol; 1 equiv; 116 mg) in MeCN (2 mL). After completion (generally 1 h), the solvent was evaporated. The crude mixture was purified by flash chromatography. When diols were used, the evaporated mixture was diluted in CH_2Cl_2 and washed with water to get rid of excess alcohol before chromatography.

General procedure 5 (GP): *Oxidation of sulfinamides*: PhI=O (0.5 mmol; 1 equiv; 110 mg) was added at room temperature to a solution of sulfinamide (0.5 mmol) and water (5.0 mmol; 10 equiv; 90 μL) in acetonitrile (1.5 mL). After completion, the solvent was removed in vacuo. The crude mixture was purified by flash chromatography.

4a: Following GP1, sulfoximine **4a** was isolated (petroleum ether/ethyl acetate 50:50; 163 mg; 96%) as a white solid. M.p. 79–81°C; IR (neat): $\tilde{\nu}$=3000, 2940, 2220, 1575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.28 (t, J=7.4 Hz, 3H; CH_2Me), 2.41 (s, 3H; Tol), 2.48 (s, 3H; Tol), 3.53 (q, J=7.4 Hz, 2H; CH_2Me), 7.27 (d, J=8.1 Hz, 2H arom.), 7.41 (d, J=8.1 Hz, 2H arom.), 7.86 ppm (d, J=7.9 Hz, 4H arom.); ^{13}C NMR (50 MHz, $CDCl_3$): δ=7.2 (CH_2Me), 21.3 (Tol), 21.5 (Tol), 52.7 (CH_2Me), 126.4 (CH arom.), 128.2 (CH arom.), 129.0 (CH arom.), 130.0 (CH arom.), 132.3 (C arom.), 140.7 (C arom.), 142.4 (C arom.), 145.4 ppm (C arom.); elemental analysis (%) for $C_{16}H_{19}O_3S_2$ (337.45): calcd: C 56.95, H 5.67, N 4.15, found: C 56.79, H 5.82, 4.27.

4b: Following GP1, sulfoximine **4b** was isolated (124 mg; 91%). Analyses were similar to those described by Horner et al.[53] ^1H NMR (400 MHz, $CDCl_3$): δ=2.33 (m, 4H; SCH_2CH_2), 2.41 (s, 3H; Tol), 3.29 (m, 2H; SCH_2), 3.79 (m, 2H; SCH_2), 7.28 (d, J=8.4 Hz, 2H; arom.), 7.87 ppm (d, J=8.4 Hz, 2H; arom.).

4c: Following GP1, sulfoximine **4c** was isolated (petroleum ether/ethyl acetate 70:30; 194 mg; 96%) as a colorless oil. IR (neat): $\tilde{\nu}$=3348, 3262, 3061, 2934, 2858, 1616, 1597 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.32–1.91 (m, 6H; $CH_2(CH_2)_3CH_2$), 2.45 (s, 3H; Tol), 2.50 (s, 3H; Tol), 2.12–2.82 (m, 4H; =CCH_2), 7.29 (d, J=8.5 Hz, 2H; arom.), 7.39 (d, J=8.5 Hz, 2H; arom.), 7.66–7.92 ppm (m, 4H; arom.); ^{13}C NMR (50 MHz, $CDCl_3$): δ=21.6 (Tol), 21.7 (Tol), 25.4 (CH_2), 26.9 (CH_2), 28.2 (CH_2), 29.7 (CH_2), 37.6 (CH_2), 122.8 (=CH), 126.7 (CH arom.), 127.5 (CH arom.), 129.2 (CH arom.), 130.0 (CH arom.), 137.8 (C), 141.1 (C), 142.6 (C), 144.6 (C), 164.6 ppm (C); $C_{21}H_{25}NO_3S_2$ (337.45): HRMS calcd. for $C_{21}H_{25}NNaO_3S_2$ $[M+Na]^+$ 426.1174; found 426.1138.

4d: Following GP1, sulfoximine **4d** was isolated (petroleum ether/ethyl acetate 50:50; 85 mg; 53%) as a white solid. M.p. 136°C; IR (neat): $\tilde{\nu}$=3200, 1580, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.40 (s, 3H; CH_3), 6.20 (br d, J=9.7 Hz, 1H; =C*H*H), 6.48 (br d, J=16.3 Hz, 1H; =CH*H*), 6.84 (dd, J=16.3, 9.7 Hz, 1H; =CHS), 7.26 (d, J=8.1 Hz, 2H; arom.), 7.56–7.69 (m, 3H; arom.), 7.86 (d, J=8.1 Hz, 2H; arom.), 7.96–7.98 ppm (m, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.9 (CH_3), 127.0 (CH arom.), 128.4 (CH arom.), 129.7 (CH arom.+CH_2), 130.1 (CH arom.), 134.7 (CH arom. or *C*H=CH_2), 137.7 (C arom.), 137.9 (CH arom. or *C*H=CH_2), 141.1 (C arom.), 143.3 ppm (C arom.); elemental analysis (%) for $C_{15}H_{15}NO_3S_2$ (321.42): calcd: C 56.05, H 4.70, N 4.36; found: C 55.88, H 4.75, N 4.37.

4e: Following GP1, sulfoximine **4e** was isolated (petroleum ether/ethyl acetate 80:20; 161 mg; 72%) as a white solid. M.p. 116–118°C; $[\alpha]_D^{25}$=77 (c=1.1, $CHCl_3$); IR (neat): $\tilde{\nu}$=1598, 1230, 1075, 1051 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.31–1.36 (m, 18H; Me_2CH), 2.47 (s, 3H; Tol), 2.98 (sept., J=7.1 Hz, 1H; *p*-C*H*Me_2), 4.21 (sept., J=7.1 Hz, 2H; *m*-C*H*Me_2), 6.23 (d, J=9.7 Hz, 1H; =C*H*H), 6.36 (d, J=16.3 Hz, 1H; =CH*H*), 7.28 (s, 2H; H arom.), 7.28–7.35 (m, 1H; =CH), 7.35 (d, J=8.7 Hz, 2H; arom. Tol), 7.95 ppm (d, J=8.7 Hz, 2H; arom. Tol); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.6 (Tol), 23.6 (Me), 24.3 (Me), 24.9 (Me), 29.5 (C*H*Me_2), 34.3 (C*H*Me_2), 124.8 (CH arom.), 126.8 (CH arom.), 127.4 (=CH_2), 129.3 (CH arom.+C arom.), 140.7 (CHS), 141.4 (C arom.), 142.7 (C arom.), 151.3 (C arom.), 154.6 ppm (C arom.); elemental analysis (%) for $C_{24}H_{33}NO_3S_2$ (447.66): calcd: C 64.39, H 7.43, N 3.13; found: C 64.15, H 7.68, N 3.11.

4f: Following GP1, sulfoximine **4f** was isolated (petroleum ether/ethyl acetate 60:40; 201 mg; 91%) as a white solid. M.p. 107–109°C; IR (neat): $\tilde{\nu}$=1598, 1226, 1150, 1086, 1018 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.89 (s, 3H; =CMe), 2.06 (s, 3H; =CMe), 2.39 (s, 3H; Tol), 4.49 (A of AB, J=12 Hz, 1H; =CC*H*H), 4.76 (B of AB, J=12 Hz, 1H; =CCH*H*), 7.24 (d, J=8.1 Hz, 2H; arom.), 7.51–7.55 (m, 2H; arom.), 7.60–7.63 (m, 1H; arom.), 7.83 (d, J=8.2 Hz, 2H; arom.), 8.10 ppm (d, J=8.1 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.6 (Tol), 23.3 (=C*Me*), 25.0 (=C*Me*), 27.0 (=CCH_2), 126.7 (CH arom.), 127.9 (CH arom.), 129.3 (CH arom.), 129.4 (CH arom.), 134.0 (CH arom.), 139.0, 140.7, 142.9, and 145.2 (4 C arom. and =CCH_3), 157.6 ppm (=CCH_2); $C_{18}H_{2O}BrNO_3S_2$ (442.4): cacld. C 48.87, H 4.56, N 3.17; found: C 48.89, H 4.64, N 3.15.

4g: Following GP1, sulfoximine **4g** was isolated (petroleum ether/ethyl acetate 70:30; 203 mg; 89%) as a white solid. M.p. 117–119°C; $[\alpha]_D^{25}$=156.8 (c=1, $CHCl_3$); IR (neat): $\tilde{\nu}$=3030, 1620, 1600, 1070 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.87 (s, 3H; =CCH_3), 2,03 (s, 3H; =CCH_3), 2.37 (s, 3H; Tol), 2.40 (s, 3H; Tol), 4.47 (B of AB, J=12.3 Hz, 1H; =CCH*H*), 4.73 (A of AB, J=12.3 Hz, 1H; =CC*H*H), 7.21–7.32 (m, 4H arom., S(O)Tol), 7.81 (d, J=8.4 Hz, 2 H arom. SO_2Tol), 7.95 ppm (d, J=8.4 Hz, 2 H arom. SO_2Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ=21.6 (CH_3), 21.7 (CH_3), 23.3 (CH_3), 25.0 (CH_3), 27.1 (=CCH_2), 126.7 (CH, arom.), 128.0 (CH, arom.), 129.3 (CH, arom.), 130.0 (CH, arom.), 133.8 (C), 136.0 (C), 140.9 (C), 142.8 (C), 145.2 (C), 157.1 ppm (C); elemental analysis (%) for $C_{19}H_{22}BrNO_3S_2$ (456.42): calcd: C 50.00, H 4.86, N 3.07; found: C 49.76, H 4.99, N 3.38.

4h: Following GP1, sulfoximine **4h** was isolated (petroleum ether/ethyl acetate 70:30; 188 mg; 75%) as a white solid. M.p. 62°C; $[\alpha]_D^{25}$=−49.9 (c=0.73, $CHCl_3$); IR (neat): $\tilde{\nu}$=3040, 2350, 1600, 1080 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=2.37 (s, 3H; CH_3), 2.44 (s, 3H; CH_3), 4.18 (B of AB, J=12.3 Hz, 1H; =CCH*H*), 4.44 (A of AB, J=12.3 Hz, 1H; =CC*H*H), 7.22–7.67 (m, 9 H arom., Ph+S(O)Tol), 7.83–7.98 ppm (m, 5H; arom. SO_2Tol + =C*H*); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=22.0 (CH_3), 22.1 (CH_3), 24.0 (=CCH_2), 127.1 (CH, arom.), 129.2 (CH, arom.), 129.6 (CH, arom.), 129.7 (CH, arom.), 130.6 (CH, arom.), 130.9 (CH, arom.), 131.5 (CH, arom.), 132.7 (C), 134.9 (C), 136.7 (C), 141.1 (C), 143.4 (C), 144.1 (*C*Ph), 146.2 ppm (C); elemental analysis (%) for $C_{23}H_{22}BrNO_3S_2$ (504.47): calcd: C 54.76, H 4.40, N 2.78; found: C 54.72, H 4.44, N 2.59.

4i: Following GP1, sulfoximine **4i** was isolated (petroleum ether/ethyl acetate 75:25; 173 mg; 89%) as a colorless oil. IR (neat): $\tilde{\nu}$=3064, 2959, 2930, 2197, 1595 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ=0.84 (t, J=7.1 Hz, 3H; CH_2CH_3), 1.24–1.53 (m, 4H; CH_2CH_2Me), 2.32 (t, J=7.4 Hz, 2H; ≡CCH_2), 2.36 (s, 3H; Tol), 2.39 (s, 3H; Tol), 7.25 (d, J=7.9 Hz, 2H; arom.), 7.33 (d, J=8.4 Hz, 2H; arom.), 7.87 (d, J=7.9 Hz, 2H; arom), 7.87 ppm (d, J=8.4 Hz, 2H; arom); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.4 (CH_2CH_3) 19.1 (CH_2), 21.6 (CH_2), 21.7 (Tol), 22.0 (Tol), 28.8 (≡CCH_2), 75.5 (*C*≡CS), 103.2 (C≡*C*S), 127.0 (CH arom.), 127.3 (CH arom.), 129.3 (CH arom.), 130.2 (CH arom.), 136.7 (C arom.), 140.3 (C arom.), 143.0 (C arom.), 146.0 ppm (C arom.); elemental analysis (%) for $C_{20}H_{23}NO_3S_2$ (389.53): calcd: C 61.67, H 5.95, N 3.60; found: C 61.57, H 6.08, N 3.50.**4j**: Sulfoximine **4j** is identical to **4i**. $[\alpha]_D^{25}$ 78.3 (c=1.1, $CHCl_3$).

5b: Following GP2, sulfoximine **5b** was isolated (petroleum ether/ethyl acetate 20:80; 94 mg; 95%) as a white solid. M.p.: 93–95°C; IR (neat): $\tilde{\nu}$=3010, 2700, 2340, 1055 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.17–2.23 (m, 4H; CH_2CH_2S), 2.97 (s, 3H; Me), 3.20–3.25 (m, 2H; CH_2S), 3.58–3.61 ppm (m, 2H; CH_2S); ^{13}C NMR (100 MHz, $CDCl_3$): δ=23.2 (CH_2CH_2S), 45.0 (Me), 54.2 ppm (CH_2S); elemental analysis (%) for $C_5H_{11}NO_3S_2$ (197.28): calcd: C 30.44, H 5.62, N 7.10; found: C 30.46, H 5.73, N 7.16.

5d: Following GP2, sulfoximine **5d** was isolated (petroleum ether/ethyl acetate 60:40; 86 mg; 70%) as a white solid. M.p.: 97–98°C; IR (neat): $\tilde{\nu}$=3020, 2700, 2350, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.09 (s, 3H; Me), 6.19 (dd, J=9.7, 1.5 Hz, 1H; C*H*H=CH), 6.45 (dd, J=16.3, 1.5 Hz, 1H; CH*H*=CH), 6.81 (dd, J=16.3, 9.7 Hz, 1H; CH_2=C*H*), 7.54–7.67 (m, 3H; arom.), 7.92–7.95 ppm (m, 3H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ=45.5 (Me), 128.0 (CH arom.), 129.8 (=CH_2), 129.9 (CH arom.), 134.6 (CH arom. or *C*H=CH_2), 137.1 (C arom.), 137.3 ppm (CH arom. or *C*H=CH_2); elemental analysis (%) for $C_9H_{11}NO_3S_2$ (245.32): calcd: C 44.06, H 4.52, N 5.71; found: C 44.07, H 4.68, N 5.74.

5f: Following GP2, sulfoximine **5f** was isolated (petroleum ether/ethyl acetate 60:40; 128 mg; 70%) as a yellowish solid. M.p.: 97–99°C; IR (neat): $\tilde{\nu}$=3050, 1610, 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.00 (s, 3H; =CMe), 2.10 (s, 3H; =CMe), 3.18 (s, 3H; $MeSO_2$), 4.49 (A of AB, J=12.2 Hz, 1H; =CC*H*H), 4.76 (B of AB, J=12.2 Hz, 1H; =CCH*H*),

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7.59–7.70 (m, 3H; arom.) 8.16–8.19 ppm (m, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.7 (=C*Me*), 25.4 (=C*Me*), 27.2 (CH_2), 45.9 (CH_3SO_2), 128.2 (CH arom.), 129.8 (CH arom.), 133.7 (C arom. or = *C*Me), 134.5 (CH arom.), 139.4 (=*C*Me or C arom.), 157.9 ppm (=*C*CH_2); HRMS calcd for $C_{12}H_{14}BrNO_3S_2$ [*M*+Na, ^{79}Br]$^+$ 387.9653; found 387.9633, [*M*+Na, ^{81}Br]$^+$ 389.9571; found 389.9600.

5j: Following GP2, sulfoximine **5j** was isolated (petroleum ether/ethyl acetate 80:20; 63 mg; 40%) as a colorless oil. $[\alpha]_D^{25}$ = 63.6 (c = 1.2, $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2700, 2360, 2200, 1110 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.6 Hz, 3H; CH_2*Me*), 1.31–1.36 (m, 2H; Me*CH*$_2$*CH*$_2$), 1.49–1.52 (m, 2H; Me*CH*$_2$*CH*$_2$), 2.41 (t, J = 7.1 Hz, 2H; $CH_2C\equiv$), 2.44 (s, 3H; Tol), 3.14 (s, 3H; MeS), 7.38 (d, J = 8.1 Hz, 2H; arom.), 7.93 ppm (J = 8.1 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 (CH_2*Me*), 19.1 (Me*CH*$_2$*CH*$_2$), 21.8 (Tol), 22.0 (Me*CH*$_2$*CH*$_2$), 28.8 (*CH*$_2$C≡), 45.0 (MeS), 75.6 ($CH_2C\equiv$), 103.7 (≡CS), 127.3 (CH arom.), 130.4 (CH arom.), 136.5 (C arom.), 146.2 ppm (C arom.); elemental analysis (%) for $C_{14}H_{19}NO_3S_2$ (313.44): calcd: C 53.65, H 6.11, N 4.47; found: C 54.11, H 6.42, N 4.30.

5k: Following GP2, sulfoximine **5k** was isolated (petroleum ether/ethyl acetate 70:30; 185 mg; 98%) as a white solid. M.p.: 154–157°C; IR (neat): $\tilde{\nu}$ = 3010, 1615, 1095 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96–0.99 (m, 2H; CH_2 of *c*-Pr), 1.25–1.29 (m, 2H; CH_2 of *c*-Pr), 1.81–1.84 (m, 1H; CH of *c*-Pr), 3.17 (s, 3H; $MeSO_2$), 4.33 (A of AB, J = 12.2 Hz, 1H; = CC*H*H), 4.43 (B of AB, J = 12.2 Hz, 1H; =CCH*H*), 6.64 (d, J = 11.2 Hz, 1H; =CH), 7.60–7.70 (m, 3H; arom.), 8.00–8.03 ppm (m, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.8 (CH_2 of *c*-Pr), 10.9 (CH_2 of *c*-Pr), 14.0 (CH of *c*-Pr), 22.3 (=C*CH*$_2$), 45.8 ($MeSO_2$), 128.7 (CH arom.), 129.9 (CH arom.), 133.0 (C arom. or =*C*CH_2), 134.7 (CH arom.), 138.0 (C arom. or =*C*CH_2), 155.9 ppm (=CH); elemental analysis (%) for $C_{13}H_{16}BrNO_3S_2$ (378.31): calcd: C 41.27, H 4.26, N 3.70; found: C 41.19, H 4.42, N 3.69.

7a: Following GP3 [or GP4], sulfonimidate **7a** was isolated (petroleum ether/ethyl acetate 70:30; 126 mg [118 mg]; 91% [85%]) as a white solid. Following GP4, sulfonamide **8** (8 mg; 5%) was also obtained. M.p. 45–47°C; IR (neat): $\tilde{\nu}$ = 3300, 3020, 2905, 1180, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3H; Tol), 3.36 (s, 1H; NH), 3.35 (s, 3H; OMe), 7.25 (d, J = 8.1 Hz, 2H; arom.), 7.81 ppm (d, J = 8.1 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Tol), 55.3 (OMe), 127.6 (CH arom.), 129.4 (CH arom.), 133.9 (C arom.), 143.8 ppm (C arom.); elemental analysis (%) for $C_8H_{11}NO_2S$ (185.24): calcd: C 51.87, H 5.99, N 7.56; found: C 51.84, H 6.17, N 7.45.

7b: Following GP3 [or GP4], sulfonimidate **7b** was isolated (petroleum ether/ethyl acetate 70:30; 140 mg [100 mg]; 94% [67%]) as a pale yellow oil. Following GP4, sulfonamide **8** (30 mg; 23%) was also obtained. IR (neat): $\tilde{\nu}$ = 3280, 2960, 1590 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.1 Hz, 3H; CH_2*Me*), 2.41 (s, 3H; Tol), 3.20 (s, 1H; NH), 3.95 (m, 2H; OCH_2), 7.29 (d, J = 8.2 Hz, 2H; arom.), 7.86 ppm (d, J = 8.4 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (CH_2*Me*), 21.6 (Tol), 65.7 (OCH_2), 127.7 (CH arom.), 129.6 (CH arom.), 135.3 (C arom.), 143.9 ppm (C arom.); NH_3-CIMS m/z (%): 200 ([*M*+1]$^+$, 14), 189 (100); elemental analysis (%) for $C_9H_{13}NO_2S$ (199.27): calcd: C 54.25, H 6.58, N 7.03; found: C 54.17, H 6.87, N 6.75.

7c: Following GP3 [or GP4], sulfonimidate **7c** was isolated (petroleum ether/ethyl acetate 70:30; 115 mg [28 mg]; 73% [18%]) as a colorless oil. Following GP4, sulfonamide **8** (84 mg; 74%) was also obtained. IR (neat): $\tilde{\nu}$ = 3280, 2960, 2920, 1590, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$: δ = 1.03 (d, J = 6.2 Hz, 3H; CH*Me*), 1.07 (d, J = 6.2 Hz, 3H; CH*Me*), 2.28 (s, 3H; Tol), 3.09 (s, 1H; NH), 4.46 (hept, J = 6.2 Hz, 2H; OCH), 7.16 (d, J = 8.2 Hz, 2H; arom.), 7.74 ppm (d, J = 8.2 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (Tol), 22.9 (CH*Me*), 23.9 (CH*Me*), 75.1 (OCH), 127.4 (CH arom.), 129.5 (CH arom.), 136.5 (C arom.), 143.6 ppm (C arom.); elemental analysis (%) for $C_{10}H_{15}NO_2S$ (213.30): calcd: C 56.31, H 7.09, N 6.57; found: C 56.02, H 7.37, N 6.31.

7d: Following GP3 [or GP4], sulfonimidate **7d** was isolated (petroleum ether/ethyl acetate 80:20; 112 mg [95 mg]; 71% [60%]) as a colorless oil. Following GP4, sulfonamide **8** (47 mg; 36%) was also obtained. IR (neat): $\tilde{\nu}$ = 3300, 2920, 1650, 1600, 780 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H; Tol), 3.28 (s, 1H; NH), 4.39 (m, 2H; OCH_2), 5.24 (m, 2H; =CH_2), 5.79 (m, 1H; =CH), 7.30 (d, J = 8.1 Hz, 2H; arom.), 7.87 ppm (d, J = 8.1 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (Tol), 69.9 (OCH_2), 119.3 (=CH_2), 127.6 (CH arom.), 129.6 (CH arom.), 131.2 (=CH), 135.0 (C arom.), 143.6 ppm (C arom.); elemental analysis (%) for $C_{10}H_{13}NO_2S$ (211.28): calcd: C 56.85, H 6.20, N 6.63; found: C 56.92, H 6.19, N 6.58.

7e: Following GP3 [or GP4], sulfonimidate **7e** was isolated (petroleum ether/ethyl acetate 70:30; 145 mg [110 mg]; 92% [70%]) as a pale yellow oil. Following GP4, sulfonamide **8** (5 mg; 4%) was also obtained. IR (neat): $\tilde{\nu}$ = 3280, 2220, 1590, 920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H; Tol), 2.42 (t, J = 2.1 Hz, 1H; ≡CH), 3.43 (s, 1H; NH), 4 .51 (d, J = 2.1 Hz, 2H; OCH_2), 7.29 (d, J = 8.3 Hz, 2H; arom.), 7.87 ppm (d, J = 8.3 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (Tol), 56.7 (CH_2), 76.5 (≡CH), 76.7 (*C*≡CH), 128.0 (CH arom.), 129.8 (CH arom.), 134.5 (C arom.), 144.5 ppm (C arom.); elemental analysis (%) for $C_{10}H_{11}NO_2S$ (209.27): calcd: C 57.39, H 5.30, N 6.69; found: C 57.38, H 5.28, N 6.71.

7f: Following GP3 [or GP4], sulfonimidate **7f** was isolated (petroleum ether/ethyl acetate 80:20; 143 mg [91 mg]; 85% [53%]) as a colorless oil. Following GP4, sulfonamide **8** (50 mg; 39%) was also obtained. IR (neat): $\tilde{\nu}$ = 3300, 2960, 1600, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (m, 2H; OCH_2*CH*$_2$), 2.39 (s, 3H; Tol), 3.30 (s, 1H; NH), 3.90 (m, 2H; OCH_2), 4.09 (m, 2H; =CH_2), 5.63 (m, 1H; =CH), 7.28 (d, J = 8.0 Hz, 2H; arom.), 7.85 ppm (d, J = 8.0 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (Tol), 33.3 (OCH_2*CH*$_2$), 68.5 (OCH_2), 117.8 (=CH_2), 127.7 (CH arom.), 129.6 (CH arom.), 133.1 (=CH), 135.1 (C arom.), 143.9 ppm (C arom.); elemental analysis (%) for $C_{11}H_{15}NO_2S$ (225.31): calcd: C 58.64, H 6.71, N 6.22; found: C 58.72, H 6.81, N 6.04.

7g: Following GP4, sulfonimidate **7g** was isolated (petroleum ether/ethyl acetate 60:40; 130 mg; 57%) as a white oil, along with sulfonamide **8** (35 mg; 27%). IR (neat): $\tilde{\nu}$ = 3300, 3040, 2950, 1600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59–1.63 (m, 4H; -$(CH_2)_2$-), 2.40 (s, 3H; Tol), 2.53 (t, J = 6.9 Hz, 2H; CH_2Ph), 3.19 (s, 1H; NH), 3.88 (m, 2H; OCH_2), 7.09 (d, J = 7.1 Hz, 2H; arom.), 7.16 (t, J = 7.1 Hz, 1H; arom.), 7.24 (t, J = 7.1 Hz, 2H; arom.), 7.28 (d, J = 8.1 Hz, 2H; arom.), 7.87 ppm (d, J = 8.1 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (Tol), 27.3 (OCH_2*CH*$_2$), 28.6 (*CH*$_2$CH$_2$Ph), 35.3 (OCH_2), 69.4 (*CH*$_2$Ph), 125.9 (CH arom.), 127.7 (CH arom.), 128.4 (CH arom.), 129.6 (CH arom.), 135.2 (C arom.), 141.8 (C arom.), 143.9 ppm (C arom.); elemental analysis (%) for $C_{17}H_{21}NO_2S$ (303.42): calcd: C 67.29, H 6.98, N 4.62; found: C 67.44, H 7.06, N 4.53.

7h: Following GP4, sulfonimidate **7h** was isolated (petroleum ether/ethyl acetate 20:80; 116 mg; 68%) as white crystals, along with sulfonamide **8** (3 mg; 1%). M.p. 52–54°C; IR (neat): $\tilde{\nu}$ = 3300, 2960, 2950, 1600, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.82 (m, 2H; OCH_2*CH*$_2$), 2.42 (s, 3H; Tol), 2.48 (t, J = 5.6 Hz, OH), 3.34 (s, 1H; NH), 3.61 (m, 2H; *CH*$_2$OH), 4.08 (m, 2H; $SOCH_2$), 7.31 (d, J = 7.6 Hz, 2H; arom.), 7.86 ppm (d, J = 7.6 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (Tol), 31.6 (OCH_2*CH*$_2$), 57.8 (CH_2OH), 66.3 ($SOCH_2$), 127.4 (CH arom.), 129.5 (CH arom.), 134.8 (C arom.), 143.9 ppm (C arom.); elemental analysis (%) for $C_{10}H_{15}NO_3S$ (229.30): calcd: C 52.38, H 6.59, N 6.11; found: C 52.51, H 6.57, N 6.18.

7i: Following modified GP4 (5 equiv alcohol), sulfonimidate **7i** was isolated (petroleum ether/ethyl acetate 70:30; 184 mg; 95%) as a colorless oil, along with sulfonamide **8** (4 mg; 3%). IR (neat): $\tilde{\nu}$ = 3250, 2900, 2840, 1580 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (m, 2H; CH_2(*CH*$_2$)$_3$$CH_2$), 1.40 (m, 2H; CH_2(*CH*$_2$)$_3$$CH_2$), 1.52 (m, 2H; CH_2(*CH*$_2$)$_3$$CH_2$), 2.34 (s, 3H; Tol), 3.09 (s, 1H; NH), 3.45 (t, J = 6.4 Hz, 2H; *CH*$_2$OH), 3.82 (m, 2H; $SOCH_2$), 7.24 (d, J = 8.1 Hz, 2H; arom.), 7.78 ppm (d, J = 8.1 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (Tol), 21.7 (CH_2(*CH*$_2$)$_3$$CH_2$), 28.5 ($CH_2$(*CH*$_2$)$_3$$CH_2$), 31.8 ($CH_2$(*CH*$_2$)$_3$$CH_2$), 61.9 (HO*CH*$_2$), 69.3 ($SOCH_2$), 127.4 (CH arom.), 129.5 (CH arom.), 134.9 (C arom.), 143.9 ppm (C arom.); elemental analysis (%) for $C_{12}H_{19}NO_3S$ (257.35): calcd. C 56.00, H 7.44, N 5.44; found: C 55.58, H 7.58, N 5.31.

7j: Following GP4, sulfonimidate **7j** was isolated (petroleum ether/ethyl acetate 70:30; 129 mg; 62%) as a colorless oil, along with sulfonamide **8** (14 mg; 11%). IR (neat): $\tilde{\nu}$ = 3280, 1590 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H; Tol), 3.41 (t, J = 6.1 Hz, 2H; CH_2Br), 3.41 (s, 1H; NH), 4.14 (t, J = 6.1 Hz, 2H; OCH_2), 7.31 (d, J = 8.6 Hz, 2H; arom.), 7.88 ppm (d, J = 8.6 Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

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21.7 (Tol), 28.2 (CH_2Br), 68.1 (OCH_2), 127.7 (CH arom.), 129.8 (CH arom.), 134.4 (C arom.), 144.4 ppm (C arom.).

(*R*)-10: Following GP3 starting from sulfinamide (*S*)-**9**,[54] sulfonimidate (*R*)-**10** was isolated (petroleum ether/ethyl acetate 90:10; 164 mg; 96%) as a colorless oil. $[\alpha]_D^{25}=-37$ ($c=1$, $CHCl_3$); IR (neat): $\tilde{\nu}=2920$, 2850, 1450, 980, 810, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=0.92$, (t, $J=7.4$ Hz, 3H; CH_2Me), 1.41 (m, 2H; CH_2CH_2Me), 1.60 (m, 2H; CH_2CH_2Me), 2.40 (s, 3H; Tol), 3.19 (m, 1H; NC*H*H), 3.29 (m, 1H; NCH*H*), 3.54 (s, 3H; OMe), 7.28 (d, $J=8.1$ Hz, 2H; arom.), 7.83 ppm (d, $J=8.1$ Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.9$ (CH_2Me), 20.4 (CH_2CH_2Me), 21.6 (Tol), 34.7 (CH_2CH_2Me), 42.5 (NCH_2), 55.4 (OMe), 127.9 (CH, arom.), 129.2 (CH, arom.), 134.2 (C, arom.), 143.6 ppm (C, arom.); elemental analysis (%) for $C_{10}H_{15}NO_3S$ (229.30): calcd: C 59.72, H 7.93, N 5.80; found: C 59.71, H 7.89, N 5.78.

(*R*)-12: Following GP3 starting from sulfinamide (*S*)-**11**,[55] sulfonimidate (*R*)-**12** was isolated (petroleum ether/ethyl acetate 90:10; 130 mg; 72%) as a colorless oil. $[\alpha]_D^{25}=0$ ($c=1$, $CHCl_3$). IR (neat): $\tilde{\nu}=2970$, 2870, 2360, 984 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.43$ (s, 9H; *t*Bu), 2.41 (s, 3H; Tol), 3.52 (s, 3H; OMe), 7.27 (d, $J=8.6$ Hz, 2H; arom.), 7.83 ppm (d, $J=8.6$ Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.5$ (Tol), 32.8 (CMe_3), 55.3 (CMe_3), 55.5 (OMe), 127.8 (CH, arom.), 129.4 (CH, arom.), 143.0 (C, arom.), 145.6 ppm (C, arom.); elemental analysis (%) for $C_{12}H_{19}NO_2S$ (141.35): calcd: C 59.72, H 7.93, N 5.80; found: C 59.70, H 8.06, N 5.73.

14: Following GP3 starting from commercially available sulfinamide **13**, sulfonimidate **14** was isolated (petroleum ether/ethyl acetate 90:10; 113 mg; 100%) as a colorless oil. IR (neat): $\tilde{\nu}=3295$, 2981, 2952, 1152 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.44$ (s, 9H; *t*Bu), 2.70 (s, 1H; NH), 3.75 ppm (s, 3H; OMe); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=24.7$ (CMe_3), 52.3 (OMe), 52.7 ppm (CMe_3); elemental analysis (%) for $C_5H_{13}NO_2S$ (151.23): calcd: C 39.71, H 8.66, N 9.26; found: C 39.48, H 8.88, N 9.35.

16: Following GP3 starting from sulfinamide **15**,[50] sulfonimidate **16** was isolated (petroleum ether/ethyl acetate 90:10; 193 mg; 89%) as a mixture of two diastereomers in a 81:19 ratio (determined by ^1H NMR spectroscopy). The major diastereomer crystallized out (it corresponds to the enantiomer of the minor diastereomer of **18**). M.p. 55–56 °C. $[\alpha]_D^{25}=-56$ ($c=0.99$, $CHCl_3$). IR (neat): $\tilde{\nu}=3054$, 2986, 896 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.60$ (d, $J=6.6$ Hz, 3H; CH*Me*), 2.45 (s, 3H; Tol), 3.32 (s, 3H; OMe), 4.91 (q, $J=6.6$ Hz, 1H; C*H*Me), 7.27 (m, 4H; arom.), 7.53 (d, $J=7.6$ Hz, 2H; arom.), 7.93 ppm (d, $J=8.1$ Hz, 1H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.6$ (Tol), 27.3 (CH*Me*), 52.6 (NCH), 55.3 (OMe), 126.3 (CH arom.), 126.7 (C arom.), 128.0 (CH arom.), 128.3 (CH arom.), 129.6 (CH arom.), 134.3 (C arom.), 143.6 (C arom.), 146.7 ppm (C arom.); elemental analysis (%) for $C_{16}H_{19}NO_2S$ (289.39): calcd: C 66.40, H 6.62, N 4.84; found: C 66.22, H 6.70, N 5.01.

18: Following GP3 starting from sulfinamide **17**,[50] sulfonimidate **18** was isolated (petroleum ether/ethyl acetate 90:10; 198 mg; 90%) as a mixture of two diastereomers in a 88:12 ratio (determined by ^1H NMR). The major diastereomer was separated (it corresponds to the enantiomer of the minor diastereomer of **16**). Colorless oil. $[\alpha]_D^{25}=-60$ ($c=0.98$, $CHCl_3$). IR (neat): $\tilde{\nu}=3062$, 3027, 2971, 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.58$ (d, $J=6.6$ Hz, 3H; CH*Me*), 2.42 (s, 3H; Tol), 3.60 (s, 3H; OMe), 4.88 (q, $J=6.6$ Hz, 1H; C*H*Me), 7.21–7.33 (m, 5H; arom.), 7.46 (d, $J=7.1$ Hz, 2H; arom.), 7.87 ppm (d, $J=8.1$ Hz, 1H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.6$ (Tol), 26.7 (CH*Me*), 52.9 (NCH), 55.3 (OMe), 126.3 (CH arom.), 126.6 (C arom.), 128.0 (CH arom.), 128.3 (CH arom.), 129.6 (CH arom.), 143.6 (C arom.), 146.7 ppm (C arom.); elemental analysis (%) for $C_{16}H_{19}NO_2S$ (289.39): calcd: C 66.40, H 6.62, N 4.84; found: C 66.22, H 6.70, N 5.01.

19: Sulfinamide **19** was prepared from (−)-menthyl sulfinate and (*R*)-(+)-1-naphthyl-1-ethylamine according to the abovementioned procedure (2.3 mmol scale; 217 mg; 28%). Colorless crystals. M.p. 141–143 °C; $[\alpha]_D^{25}=-26$ ($c=1$, $CHCl_3$); IR (neat): $\tilde{\nu}=3179$, 3080, 2974, 2925, 1087 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.68$ (d, J = 6.6 Hz, 3H; CH*Me*), 2.40 (s, 3H; Tol), 4.21 (s, 1H; NH), 5.52 (m, 1H; C*H*Me), 7.28 (d, $J=8.1$ Hz, 2H; arom.), 7.48–7.66 (m, 6H; arom.), 7.82 (d, $J=8.1$ Hz, 1H; arom.), 7.86 (d, $J=7.6$ Hz, 1H; arom.), 8.27 ppm (d, $J=8.1$ Hz, 1H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.4$ (Tol), 24.7 (CH*Me*), 50.7 (NCH), 123.9 (CH arom.), 124.4 (CH arom.), 125.5 (CH arom.), 125.8 (CH arom.), 126.3 (CH arom.), 128.4 (CH arom.), 129.1 (CH arom.), 129.6 (CH arom), 130.8 (C arom.), 134.1 (C arom), 138.9 (C arom.), 141.4 (C arom.), 142.7 ppm (C arom.); elemental analysis (%) for $C_{19}H_{19}NOS$ (339.43): calcd: C 73.75, H 6.19, N 4.53; found: C 73.74, H 6.16, N 4.46.

20: Following GP3 starting from sulfinamide **19**, sulfonimidate **20** was isolated (petroleum ether/ethyl acetate 80:20; 186 mg; 73%) as a mixture of two diastereomers in a 78:22 ratio (determined by ^1H NMR spectroscopy). The major diastereomer crystallized out but the minor diastereomer could not be obtained pure. Major diastereomer: colorless crystals. M.p. 115–117 °C; $[\alpha]_D^{25}=-96$ ($c=0.95$, $CHCl_3$). IR (neat): $\tilde{\nu}=3050$, 2971, 2927, 1160, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.73$ (d, $J=6.6$ Hz, 3H; CH*Me*), 2.46 (s, 3H; Tol), 3.28 (s, 3H; OMe), 5.67 (q, $J=6.6$ Hz, 1H; C*H*Me), 7.34 (d, $J=8.6$ Hz, 2H; arom.), 7.49–7.58 (m, 3H; arom.), 7.78 (d, $J=8.1$ Hz, 1H; arom.), 7.90 (t, $J=6.6$ Hz, 2H; arom.), 7.96 (d, $J=8.2$ Hz, 2H; arom.), 8.35 ppm (d, $J=8.6$ Hz, 1H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.7$ (Tol), 27.0 (CH*Me*), 49.7 (NCH), 55.5 (OMe), 123.7 (CH arom.), 123.9 (CH arom.), 125.4 (CH arom.), 125.8 (CH arom.), 127.3 (CH arom.), 128.1 (CH arom.), 129.0 (CH arom), 129.7 (CH arom.), 130.5 (C arom), 134.1 (C arom), 134.4 (C arom.), 142.6 (C arom.), 143.8 ppm (C arom.); elemental analysis (%) for $C_{20}H_{21}NO_2S$ (339.45): calcd: C 70.77, H 6.24, N 4.13; found: C 70.80, H 6.24, N 3.99. Minor diastereomer: ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.74$ (d, $J=6.6$ Hz, CH*Me*), 2.41 (s, 3H; Tol), 3.63 (s, 3H; OMe), 5.67 (q, $J=6.6$ Hz, 1H; C*H*Me), 7.28 (d, $J=8.6$ Hz, 2H; arom.), 7.49–7.58 (m, 3H; arom.), 7.74 (d, $J=8.1$ Hz, 1H; arom.), 7.85–7.97 (m, 4H; arom.), 8.26 ppm (d, $J=8.6$ Hz, 1H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 21.7 (Tol), 26.3 (CH*Me*), 49.9 (NCH), 55.5 (OMe), 123.4 (CH arom.), 123.8 (CH arom.), 125.3 (CH arom.), 125.7 (CH arom.), 127.4 (CH arom.), 127.9 (CH arom.), 128.9 (CH arom), 129.6 (CH arom.), 130.6 (C arom), 134.1 (C arom), 134.6 (C arom.), 142.4 (C arom.), 143.7 ppm (C arom.).

21: Sulfinamide **21**[56] was prepared from sulfinamide **6** and trimethyl acetic anhydride according to the literature (41% yield).[51] White solid. M. p. 110–112 °C; IR (neat): $\tilde{\nu}=3380$, 3054, 2986, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.18$ (s, 9H; *t*Bu), 2.38 (s, 3H; Tol), 7.26 (d, $J=7.9$ Hz, 2H; arom.), 7.47 (d, $J=7.9$ Hz, 2H; arom.), 8.40 ppm (bs, 1H; NH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.41$(Tol), 26.9 (Me of *t*Bu), 39.6 (C of *t*Bu), 124.8 (CH arom.), 129.9 (CH arom.), 132.6 (C arom.), 142.3 (C arom.), 179.1 ppm (C=O); elemental analysis (%) for $C_{12}H_{17}NO_2S$ (239.33): calcd: C 60.22, H 7.16, N 5.85; found: C 60.10, H 7.26, N 6.00.

22: Following GP5 starting from sulfinamide **21**, sulfonamide **22** was isolated (petroleum ether/ethyl acetate 90:10; 105 mg; 82%). Data corresponded to those described in the literature.[57]

23: Sulfinamide **23** was synthesized from (−)-menthyl sulfinate and 2-(*tert*-butyldimethylsilanyloxy)-1-phenyl-ethylamine according to the above-mentioned reference (68% yield). White solid. M.p. 77–79 °C; IR (neat): $\tilde{\nu}=3209$, 2954, 2928, 2856, 1088 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=-0.09$ (s, 3H; Si*Me*Me), −0.05 (s, 3H; SiMe*Me*), 0.84 (s, 9H; *t*Bu), 2.30 (s, 3H; Tol), 3.78 (A of ABX, $J=9.9$, 5.1 Hz, 1H; C*H*HOSi), 3.91 (B of ABX, $J=9.9$, 4.6 Hz, 1H; CH*H*OSi), 4.45 (m, 1H; NCH), 5.05 (bs, 1H; NH), 7.08–7.26 (m, 7H; arom.), 7.46 ppm (d, $J=8.6$ Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ −5.5 (SiMe), 18.3 (SiC), 21.3 (Tol), 25.9 (Me of *t*-Bu), 56.3 (CH_2), 68.0 (NCH), 126.0 (CH arom.), 127.2 (CH arom.), 127.4 (CH arom.), 128.0 (CH arom.), 129.2 (CH arom.), 140.4 (C arom.), 141.0 (C arom.), 141.2 ppm (C arom.); elemental analysis (%) for $C_{21}H_{31}NO_2SSi$ (389.63): calcd: C 64.73, H 8.02, N 3.59; found: C 64.61, H 8.12, N 3.69.

24: Following GP5 starting from substituted sulfinamide **23**, sulfonamide **24** was isolated (petroleum ether/ethyl acetate 90:10; 164 mg, 81%) as a colorless oil. IR (neat): $\tilde{\nu}=3278$, 2929, 2857, 2361, 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=-0.10$ (s, 3H; Si*Me*Me), −0.09 (s, 3H; SiMe*Me*), 0.81 (s, 9H; *t*Bu), 2.73 (s, 3H; Tol), 3.57 (A of ABX, $J=10.2$, 6.8 Hz, 1H; C*H*HOSi), 3.67 (B of ABX, $J=10.2$, 4.4 Hz, 1H; CH*H*OSi), 4.29 (m, 1H; NCH), 5.33 (bs, NH), 7.15–7.21 (m, 7H; arom.), 7.58 ppm (d, $J=8.0$ Hz, 2H; arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=-5.5$(SiMe), 18.3 (C), 21.6 (Tol), 25.9 (Me of *t*Bu), 59.4 (CH_2), 66.7 (NCH), 127.3 (CH arom.), 127.4 (CH arom.), 127.8 (CH arom.), 128.3 (CH arom.), 129.5 (CH arom.), 137.2 (C arom.), 138.2 (C arom.), 143.3 ppm (C arom.); elemental analy-

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sis (%) for $C_{21}H_{31}NO_3SSi$ (405.63): calcd: C 62.18, H 7.70, N 3.45; found: C 62.04, H 7.85, N 3.60.

25: Following GP5 starting from substituted sulfinamide **15**, sulfonamide **25** was isolated (petroleum ether/ethyl acetate 90:10; 107 mg; 78%). Data corresponded to those described in the literature.[58,59]

26: Following GP5 starting from substituted sulfinamide **9**, sulfonamide **26** was isolated (petroleum ether/ethyl acetate 90:10; 93 mg; 82%). Data corresponded to those of an authentic sampled which could be purchased from Aldrich.

27: Following GP5 starting from commercially available sulfinamide **13**, sulfonamide **27** was isolated (petroleum ether/ethyl acetate 90:10; 55 mg; 80%). Data corresponded to those described in the literature.[60]

28: Following GP5 starting from substituted sulfinamide **11**, sulfonamide **28** was isolated (petroleum ether/ethyl acetate 90:10; 92 mg; 81%). Data corresponded to those described in the literature.[57]

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