Fe(II)-Catalyzed Imidation of Allyl Sulfides and Subsequent [2,3]-Sigmatropic Rearrangement. Preparation of α-Branched *N*-*tert*-Butyloxycarbonyl (Boc)-Protected *N*-Allylamines

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Allyl aryl sulfides **1** and **5** were shown to undergo an imidation/[2,3]-sigmatropic rearrangement reaction upon treatment with *N*-*tert*-butyloxycarbonyl azide ($BocN_3$) and catalytic amounts of $FeCl_2$ in CH_2Cl_2. The *N*-Boc-protected *N*-allyl sulfenamides **3** and **21** were obtained in yields between 48 and 75% (12 examples). Whereas the reaction is well suited for the transformation of α-unbranched sulfides to α-branched sulfenamides, the enantiomerically pure α-branched sulfides **10** and **13** reacted sluggishly. The corresponding sulfenamides **22** and **23** were obtained in only moderate enantiomeric excess (36−39% ee). A reaction mechanism is proposed that postulates the intermediacy of an *N*-Boc-substituted Fe(IV)−nitrene complex **14** acting as the imidation reagent in the catalytic cycle. Possible side reactions are discussed. The benzenesulfenamides **3** were further converted into *N*-Boc-*N*-allylamines **4** by removal of the phenylsulfanyl group. Bu_3SnH in benzene was found to be the reagent of choice for the deprotection of α-branched amines that bear a secondary allyl substituent (five examples, 71−93% yield). This method failed for the α-branched amines **3i**−**k** with a tertiary allyl substituent. The phenylsulfanyl group was finally removed with $P(OEt)_3/NEt_3$ in CH_2Cl_2 (three examples, 43−62% yield).

Introduction

In recent years, oxygen-transfer reactions to nucleophiles, e.g., to alkenes[1] and sulfides,[2] have been developed into a generally applicable synthetic method. Enantioselective variants have been found that allow the preparation of a variety of epoxides[3] and sulfoxides[4] with significant enantiomeric excess. Analogous nitrogen-transfer reactions have been studied less frequently, and the available methodology for the latter reaction type is limited as compared to what is known in the area of oxygen transfer. Still, there have been major improvements concerning in particular the transfer of a "NTs" (Ts = tosyl) fragment from PhI═NTs or chloramine-T to nucleophiles.[5,6] Despite the excellent yields and stereoselectivities occasionally obtained with these reagents, the somewhat awkward removal of the tosyl group in the product is considered to be a serious drawback. Replacing the tosyl group at the nitrogen atom of the transfer reagent with a more labile protective group is consequently a topic of current interest.[7] Research in our group has centered on the use of *N*-*tert*-butyloxycarbonyl azide ($BocN_3$) as the source of an *N*-Boc-protected nitrene fragment. Indeed, we could show that the imidation of sulfoxides and sulfides with this reagent was possible if $FeCl_2$ was employed as a promoter.[8] For the imidation of sulfides to the corresponding *N*-Boc-protected sulfimines, substoichiometric amounts of $FeCl_2$ (10−20 mol %) were sufficient and the reaction was ligand-accelerated in CH_2Cl_2 at 0 °C. As expected, the removal of the protective group proceeded readily. In this paper, we would like to report on an extension of the sulfide imidation methodology based on an imidation/[2,3]-sigmatropic rearrangement sequence. If applied to allyl sulfides **1**, the reagent combination $BocN_3/FeCl_2$ yielded intermediate sulfimides **2** that rearranged further to *N*-allylamines **3**. The nitrogen atom of these amines is protected by a Boc and a phenylsulfanyl group (Scheme 1), each of which can be readily removed. In this study, we have looked into the selective removal of the phenylsulfanyl group, which yielded the title compounds **4**. The method appears to be particularly useful for the synthesis of α-branched *N*-Boc-*N*-allylamines.

The direct preparation of *N*-Boc-protected *N*-allylamines from allyl sulfides has not yet been reported. However, there has been a study on the Pd(II)-catalyzed nitrene transfer from ethoxycarbonyl azide to allyl sulfides.[9] In addition, the [2,3]-sigmatropic rearrangement

(1) Reviews: (a) Rao, K. A. In *Comprehensive Organic Synthesis*; Trost, B., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 357. (b) Bartók, M.; Láng, K. L. In *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Taylor, E. C., Series Eds.; Hassner, A., Ed.; Wiley: New York 1985; Vol. 42, Part 3, p 15.

(2) Review: Kresze, G. In *Methoden der Organischen Chemie* (*Houben-Weyl*) *4te Aufl.*, Klamann, D., Ed.; Thieme: Stuttgart 1985; Vol. E 11, Part 1, p 702.

(3) Reviews: (a) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, 1991; p 103. (b) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, 1991; p 159.

(4) Review: Kagan, H. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, 1991; p 203.

(5) Transfer to alkenes: (a) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (b) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. (c) Review: Müller, P. In *Advances in Catalytic Processes Vol. 2, Asymmetric Catalysis*; Doyle, M. P., Ed.); JAI, Greenwich 1997; p 131.

(6) Transfer to sulfides: (a) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura,S. *J. Chem. Soc., Chem. Commun.* **1996**, 931. (b) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, S. C. P.; Sparey, T. J.; Taylor, P. C. *J. Org. Chem.* **1997**, *62*, 6512.

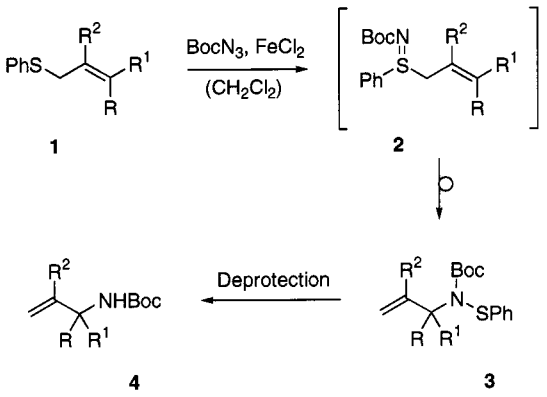
(7) For some recent examples: (a) Dauban, P.; Dodd, R. H. *J. Org. Chem.* **1999**, *64*, 5304. (b) Tomooka, C. S.; LeCloux, D. D.; Sasaki, H.; Carreira, E. M. *Org. Lett.* **1999**, *1*, 149. (c) Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844.

(8) (a) Bach, T.; Körber, C. *Tetrahedron Lett.* **1998**, *39*, 5015. (b) Bach, T.; Körber, C. *Eur. J. Org. Chem.* **1999**, 1033.

(9) Migita, T.; Hongoh, K.; Naka, H.; Nakaido, S.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 931.

10.1021/jo991569p CCC: $19.00
Published on Web 03/28/2000

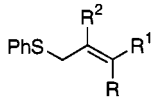
Scheme 1



of other allyl sulfimines is known. Some examples[10] of related, previously reported conversions of allyl sulfides to *N*-allylamines include the reaction with chloramine-T,[11] with PhI=NTs in the presence of a Cu(I)-salt,[6] with *O*-mesitylenesulfonylhydroxylamine (MSH),[12] with *N*-aminophthalimide/$Pb(OAc)_4$,[13] and with ethyl *N*-[(trifluoromethanesulfonyl)oxy]carbamate.[14] The preparation of *N*-allylamines from the corresponding allyl selenides by imidation/[2,3]-sigmatropic rearrangement has been intensively studied.[15]

Results and Discussion

Preparation of the Allyl Sulfides. The structures of the allyl phenyl sulfides **1** employed in this study are shown below.



	R	R^1	R^2
a	H	CH_3	H
b	H	CH_2OH	H
c	H	Ph	H
d	H	COOMe	H
e	H	*t*Bu	H
f	H	$-(CH_2)_4-$	
g	H	CH_3	CH_3
h	H	*i*Pr	CH_3
i	CH_3	CH_3	H
j	CH_3	CH_3	CH_3
k	CH_3	CH_2OBn	H

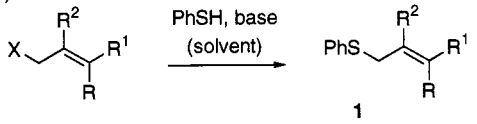
Most of these allyl sulfides were prepared from the corresponding halides by nucleophilic substitution with thiophenolate. The displacement reaction was either conducted with NEt_3 as the base in THF or ether as the solvent[16] or with NaOEt as the base in EtOH as the solvent.[17] Using the NaOEt procedure, the known sulfides **1c**,[17] **1e**,[18] and **1i**[19] were synthesized as depicted in eq 1 and Table 1 (entries 2, 4, and 5).

Table 1. Synthesis of Allyl Sulfides 1 by Nucleophilic Substitution

entry	X	base	solvent	product	yield[a] (%)
1	Br	NEt_3	THF	**1a**	95[b]
2	Br	NaOEt	EtOH	**1c**	88
3	Br	NEt_3	Et_2O	**1d**	82
4	Br	NaOEt	EtOH	**1e**	94
5	Cl	NaOEt	EtOH	**1i**	88
6	Br	NEt_3	THF	**1k**	quant[c]

[a] Yield of isolated product. [b] *E*/*Z* ratio: 86/14. [c] *E*/*Z* ratio: 80/20.

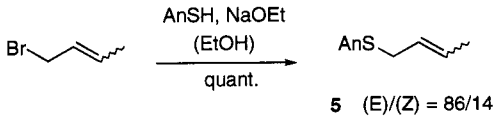
(1)



1

In addition, the anisyl (An = *p*-methoxyphenyl) analogue **5**[20] of compound **1a** was prepared by the very same method starting from *p*-methoxythiophenol (eq 2).

(2)



5 (E)/(Z) = 86/14

Reduction of ester **1d** with Dibal-H in hexane yielded the alcohol **1b**[21] in 46% yield. The nucleophilic substitution reactions of crotyl bromide, of methyl 4-bromocrotonate, and of 1-benzyloxy-4-bromo-2-methyl-2-butene[22] to yield sulfides **1a**,[16] **1d**,[23] and **1k** were carried out with NEt_3 as the base (entries 1, 3, and 6 in Table 1).

Allyl phenyl sulfides with an alkyl group R^2 at the internal carbon atom of the double bond were favorably prepared from the corresponding ketones **6** by a modification of a previously reported procedure.[24] Accordingly, α-lithiated thioanisol was generated from thioanisol by treatment with *n*-butyllithium in THF (0 °C → rt).[25] Subsequent addition of the ketones **6** yielded the tertiary alcohols **7**. These alcohols were not further purified but directly taken into the next step. They underwent a clean elimination to the target compounds **1f**,[26] **1g**,[27] **1h**, and **1j**[28] upon heating with *p*-toluenesulfonic acid (TsOH) in benzene (eq 3). The sulfides **1g** and **1h** were obtained as a mixture of *E*/*Z* isomers. The elimination **7h** → **1h** was not fully regioselective and led to the formation of the

(10) For further references on the preparation of *N*-allylamines, see: (a) Xu, Q.; Dittmer, D. C. *Tetrahedron Lett.* **1999**, *40*, 2255. (b) Johannson, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689.

(11) (a) Ash, A. S. F.; Challenger, F.; Greenwood, D. *J. Chem. Soc.* **1951**, 1877. (b) Johnson, C. R.; Mori, K.; Nakanishi, A. *J. Org. Chem.* **1979**, *44*, 2065. (c) Dolle, R. E.; Li, C.-S.; Shaw, A. N. *Tetrahedron Lett.* **1989**, *30*, 4723.

(12) Tamura, Y.; Matsushima, H.; Minamikawa, J.; Ikeda, M.; Sumoto, K. *Tetrahedron* **1975**, *31*, 3035.

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(16) (a) Babler, J. H.; Haack, R. A. *J. Org. Chem.* **1982**, *47*, 4801. (b) Birkofer, L.; Hartwig, I. *Chem. Ber.* **1954**, *87*, 1189.

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(18) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1981**, *46*, 2837.

(19) Fleming, I.; Paterson, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 256.

(20) Harayama, H.; Kozera, T.; Kimura, M.; Tanaka, S.; Tamaro, Y. *Chem. Lett.* **1996**, 543.

(21) Oswald, A. A.; Griesbaum, K.; Hudson, B. E. *J. Org. Chem.* **1963**, *28*, 2355.

(22) Sato, K.; Inoue, S.; Takagi, Y.; Morii, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3351.

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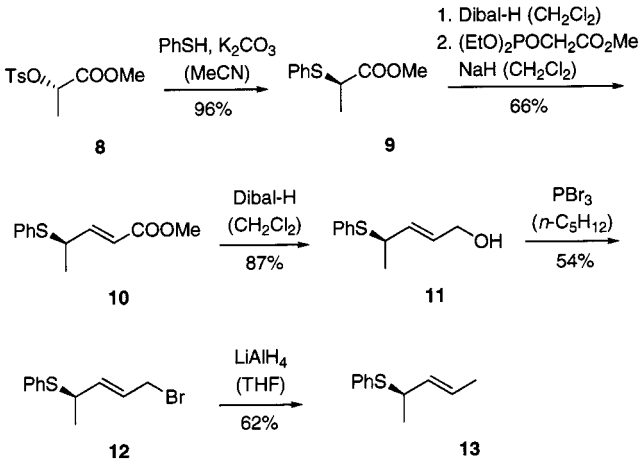
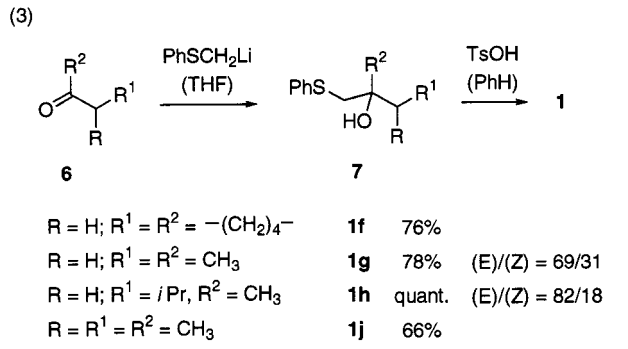
(24) Hiroi, K.; Sato, H.; Kotsuji, K. *Chem. Lett.* **1986**, 743.

(25) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097.

Scheme 2



double-bond isomer 2-(2-methylpropyl)-2-propenyl phenyl sulfide (isomer ratio: 90/10).



As an example for an α-branched allyl sulfide, the enantiomerically pure substrate **13** was prepared starting from the known, lactic acid-derived tosylate **8**.[29] The sequence we followed has been described for the related isopropylsulfanyl-substituted product in a paper by Bellus et al. (Scheme 2).[29] Nucleophilic substitution of tosylate **8** by thiophenolate delivered methyl 2-phenylsulfanylpropionate (**9**), which was converted to acrylate **10** by reduction to the aldehyde and subsequent Horner−Wadsworth−Emmons reaction. Reduction of the ester with Dibal-H at 0 °C in CH_2Cl_2 furnished the allyl alcohol **11**, whose enantiomeric purity was determined by derivatization with (−)-menthyl chloroformate. GLC and ^{1}H NMR analysis revealed the presence of a single diastereoisomer (>95% de). Since the subsequent transformations, i.e., the bromodehydroxylation to the bromide **12** and the reduction to the target compound, obviously did not interfere with the stereogenic center the sulfide **13** was assumed to be enantiomerically pure (>95% ee).

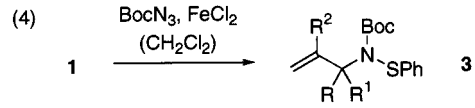
Imidation and [2,3]-Rearrangement. The nitrene-transfer reaction was performed as previously described[8] employing $BocN_3$ as the nitrene source and $FeCl_2$ as the catalyst. The reaction was carried out at room temperature by simply adding the catalyst to a premixed solution of $BocN_3$[30] (CAUTION![31]) and the allyl sulfide in CH_2Cl_2. Nitrogen evolved, and the color of the mixture turned from colorless to red. After the mixture was stirred overnight, the desired protected *N*-allylamines were obtained. Most experiments were conducted with the allyl phenyl sulfides **1**, which gave the corresponding *N*-allylamines **3** (eq 4). It is important to note that in these experiments the reagents $BocN_3$ and sulfide **1** were used in a 1:1 ratio whereas in many related transformations of this type one reagent is used in considerable excess. All yields provided in Table 2 refer to isolated product. In cases in which the conversion of sulfide was incomplete the yield was corrected with regard to the amount of recovered starting material and this value is given in brackets. Obviously, an increase of the sulfide/$BocN_3$ ratio has a beneficial influence on the yield but for reasons of practicability this possibility was not looked into more closely.

Table 2. Synthesis of Protected *N*-Allylamines 3 by Imidation/[2,3]-Rearrangement

entry	sulfide	$FeCl_2$ (equiv)	product	yield[a] (%)
1	**1a**[b]	0.25	**3a**	69
2	**1a**	0.10	**3a**	75
3	**1b**	0.25	**3b**	70
4	**1c**	0.10	**3c**	62 (94)
5	**1d**	0.25	**3d**	22 (−)[c]
6	**1d**	0.10	**3d**	32 (40)
7	**1e**	0.25	**3e**	48
8	**1f**	0.25	**3f**	65 (78)
9	**1g**[d]	0.25	**3g**	70
10	**1h**[e]	0.25	**3h**	70[f]
11	**1i**	0.10	**3i**	66 (75)
12	**1j**	0.25	**3j**	48 (60)
13	**1j**	0.10	**3j**	41 (84)
14	**1k**[g]	0.10	**3k**	52

[a] Yield of isolated product. The yield based on sulfide conversion is given in parentheses. [b] *E*/*Z* ratio: 86/14. [c] Amount of recovered starting material was not determined. [d] *E*/*Z* ratio: 69/31. [e] Used as a 90/10 mixture of double bond isomers (vide infra). *E*/*Z* ratio: 82/18. [f] Obtained as a 84/16-mixture of double bond isomers. [g] *E*/*Z* ratio: 80/20.

(4)



Initial experiments were carried out with a catalyst loading of 25 mol %. It turned out in the course of the study that lower catalyst/substrate ratios led to an increase in yield (entries 1/2, 5/6, 12/13) and were therefore preferred. A catalyst/substrate ratio of 1:10 (0.1 equiv of $FeCl_2$) is recommended. Side reactions (vide infra) are suppressed, and the conversion is still sufficient. Functional groups tolerated include alcohols (entry 3), ethers (entry 14), and esters (entry 6). The reaction makes sterically congested allylamines accessible that bear a tertiary alkyl group at the nitrogen atom (entries 11−14).

Mechanistically, we assume the nitrene transfer to occur via an Fe(IV)−nitrene complex **14**, which is formed from the azide and $FeCl_2$ (Scheme 3). The transfer of the

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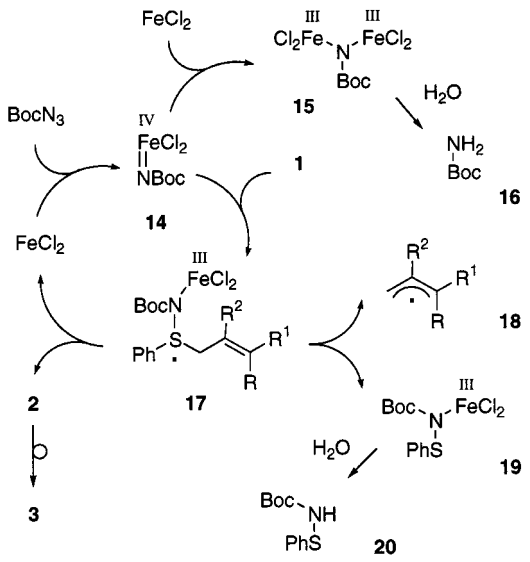
(28) Clennan, G. L.; Chen, X.; Koda, J. J. *J. Am. Chem. Soc.* **1990**, *112*, 5193.
(29) Ernst, B.; Gonda, J.; Jeschke, R.; Nubbemeyer, U.; Oehrlein, R.; Bellus, D. *Helv. Chim. Acta* **1997**, *80*, 876.

(30) $BocN_3$ was prepared according to a published procedure: Carpino, L. A.; Carpino, B. A.; Crowley, P. J.; Giza, C. A.; Terry, P. H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 157.
(31) CAUTION! Explosions have been reported to occur during attempted distillation of $BocN_3$, cf. P. Feyen, P. *Angew. Chem.* **1977**, *89*, 119; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 115. The substance is a potential explosive and is known to be a health hazard. Appropriate safety protections and utmost care are required while handling $BocN_3$.

Scheme 3



"NBoc" fragment to sulfur liberates $FeCl_2$, which is available for the next catalytic cycle. If the N−S bond formation is slow, a competition reaction with $FeCl_2$ as the nucleophile can lead to an Fe(III)−μ-imido complex **15**,[32] which is not catalytically active any more and which yields carbamate **16** upon hydrolysis. This sequence of events parallels the reaction course suggested earlier[8b] for simple sulfides. The second reaction step as pointed out in Scheme 1 is the [2,3]-shift (**2** → **3**), which is likely to proceed in a sigmatropic fashion. We have not found an indication for a simple homolysis of the C−S bond in the intermediate sulfimide **2**, which should give a radical pair and which should yield at least partially a 1,2-rearrangement product. However, there is an indication for a C−S bond cleavage as possible side reaction *before* the sulfimide formation is complete. A side product isolated in varying amounts was proven to be *N-tert*-butyloxycarbonyl benzenesulfenamide (**20**), which is likely to be formed from an Fe(III) species **19** upon hydrolysis. If the nitrene transfer from complex **14** to the sulfide **1** is not a two-electron process but occurs via the Fe(III) intermediate **17**, a simple explanation for the occurrence of **19** and **20** can be put forward. Intermediate **17** has two possible reaction pathways, one of which is the homolytic cleavage of the Fe−N bond leading to sulfimide **2** and regenerating $FeCl_2$. The other pathway, however, does not complete the catalytic cycle but rather provides access to the metalated amide **19** and to an allyl radical **18** by C−S bond cleavage. The fate of the transient allyl radical **18** is less clear than the fate of the amide **19**. It might react further either by combining with $FeCl_2$ (giving an alkene after workup), by recombination, by reaction with the solvent, or by other less well-defined events. The tentative mechanistic picture is summarized in Scheme 3. For clarity, possible ligands at the iron atoms have been omitted.

The mechanism depicted in Scheme 3 explains well the unsatisfactory results obtained with the acrylic ester **1d** in the attempted imidation. The cleavage to the stabilized, methoxycarbonyl-substituted allyl radical **18d** could effectively compete with the nitrene transfer. Starting material and catalyst were wasted and the yield diminished. It might also explain why the anisyl reagent **5** despite its higher nucleophilicity delivered a somewhat lower yield of *N*-allylamine **21** (eq 5) than the comparable phenyl sulfide **1a**. The single electron transfer is fast but the higher reactivity might lead to an increased tendency for C−S bond cleavage. Indeed, the *p*-methoxybenzenesulfenamide related to **20** was observed as a byproduct in the transformation of **5** → **21**.

(5) **5** → ($BocN_3$, $FeCl_2$, (CH_2Cl_2), 66%) → **21**

In a final set of experiments, the α-branched allyl sulfides **10** and **13** were used as substrates for the Fe(II)-catalyzed imidation and the subsequent sulfimide rearrangement. It is well established that a chirality transfer occurs in [2,3]-sigmatropic rearrangement reactions[33] and the closely related sulfoxide/allyl alcohol rearrangement has been intensively studied.[34] In the sulfimine series, an efficient chirality transfer was observed by Dolle et al., who successfully employed the imidation of α-branched allyl methyl sulfides with MSH and the concomitant rearrangement in the synthesis of enantiomerically pure alkaloids and *β*-lactams.[35,36] Due to the steric bias on the sulfur atom, the nucleophilicity of α-branched allyl sulfides is significantly reduced. Dolle et al. therefore recommended the use of allyl methyl sulfides instead of allyl phenyl sulfides. On the basis of this precedence and based on our previous experience with methoxycarbonyl substituted allyl sulfides (cf. **1d** → **3d**) the sulfide **10** was certainly not an ideal substrate and it was foreseen that its reaction was sluggish. Indeed, the attempted sulfimidation/rearrangement reaction with substrate **10** (Scheme 2) gave a disappointing low yield of the corresponding *N*-allylamine **22** (eq 6). Even worse,

(6) **10** → ($BocN_3$, $FeCl_2$, (CH_2Cl_2), 6%) → **22**, 39% *ee*

the chirality transfer was insufficient and the enantiomeric excess of **22** was determined to be 39% ee by chiral HPLC (Daicel Chiracel OD). Whereas the low yield of the reaction **10** → **22** can be explained by the weak nucleophilicity of the sulfide and by the facile C−S bond cleavage which shuts down the catalytic cycle (vide supra) we were not sure why the enantiomeric purity of the product was so low. Our initial assumption of a possible racemization of the starting material had to be discarded as the recovered sulfide **10** proved to be still 90% optically pure. A racemization of the product **22**, however, might be possible as a consequence of its substantial CH-acidity. This argument was plausible at first. It worried us, however, that the double bond isomer of **22** which should

(32) A related μ-imido complex has been isolated and structurally characterized: Nichols, P. J.; Falon, G. D.; Murray, K. S.; West, B. O. *Inorg. Chem.* **1988**, *27*, 2795.

(33) Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, part B, p 503.

(34) (a) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (b) Hoffmann, R. W. *Angew. Chem.* **1979**, *91*, 625; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

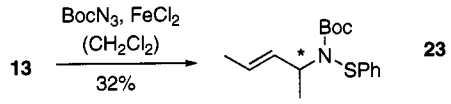
(35) (a) Dolle, R. E.; Osifo, K. I.; Li, C.-S. *Tetrahedron Lett.* **1991**, *32*, 5029. (b) Dolle, R. E.; Li, C.-S.; Novelli, R.; Kruse, L. I.; Eggleston, D. *J. Org. Chem.* **1992**, *57*, 128.

(36) For a related rearrangement, see: Whitesell, J. K.; Yaser, H. K. *J. Am. Chem. Soc.* **1991**, *113*, 3526.

also result from such a process was not detected. We turned toward the other substrate **13** which should yield a configurationally stable product.

Unfortunately, sulfide **13** ($[\alpha]^{25}_D = +46.1$) did not prove much superior to **10** in its reaction with $BocN_3$ and $FeCl_2$. The yield of the protected *N*-allylamine **23** (eq 7) was again unsatisfactory (32%) albeit higher than the yield of amine **22** obtained earlier. With an excess of sulfide

(7)



13 (1.6 equiv), the yield could be improved to 47%. Surprisingly, the recovered sulfide **13** showed a rather strong detoriation of its optical purity ($[\alpha]^{25}_D = +34.5$; 75% ee). The enantiomeric excess of the product **23** was determined after desulfurization (vide supra) to the corresponding *N*-Boc-protected allylamine by chiral HPLC (Daicel Chiracel OD). Although the baseline separation was not fully complete the enantiomeric excess was clearly in the same range (±5% ee) as the one determined for **22** (39% ee). As product **23** is certainly not CH-acidic enough to account for racemization and as the optical purity of product and recovered starting material are not identical additional factors appear to influence the extent of the chirality transfer. It is our current opinion that the stereogenic center in *N*-Boc-substituted sulfimines does have a significant impact on the course of the [2,3]-sigmatropic rearrangement and that it is this impact which renders the stereochemical outcome of the reaction less selective and less predictable than the outcome of related rearrangements. At this point, we stopped looking into the reaction of α-branched allyl sulfides more closely for several reasons. First, the yields of their transformation had not been preparatively useful. Second, the sulfides **10** and **13** were not configurationally stable under the reaction conditions. A possible racemization might be caused by the C−S bond cleavage in intermediates related to **17** (Scheme 3) and subsequent recombination. Third, the facial diastereoselectivity of the imidation with $BocN_3/FeCl_2$ employing chiral α-branched sulfides is low and the stereogenic center at sulfur could therefore not be controlled.[37] The situation would dramatically change if a chiral Fe(II)-catalyst was at hand which allowed the enantioselective preparation of sulfimides. Work along these lines is currently in progress in our laboratories.

Desulfurization of the *N*-Boc-Protected Allylic Sulfenamides 3. The removal of an arylsulfanyl group from the corresponding sulfenamide to yield the unprotected amine is well precedented.[38] In our case, it was of interest to find a method that would leave the *N*-Boc group in place while the phenylsulfanyl group was removed. This premise ruled out the use of many rather drastic deprotection conditions. For the branched *N*-allylamines **3** that bear a secondary branched carbon chain at the nitrogen atom (Scheme 1, R = H), a radical-based method employing Bu_3SnH[39] proved ideal. The removal of the phenylsulfanyl moiety proceeded rapidly

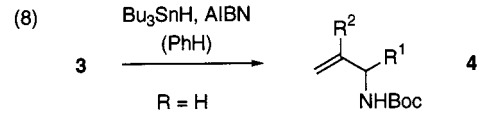
Table 3. Deprotection of Sulfenamides 3 with Tributyl Tinhydride

entry	sulfenamide	R^1	R^2	product	yield[a] (%)
1	**3a**	CH_3	H	**4a**	93
2	**3b**	CH_2OH	H	**4b**	71
3	**3f**	$-(CH_2)_4-$		**4f**	86
4	**3g**	CH_3	CH_3	**4g**	90
5	**3h**[b]	*i*-Pr	CH_3	**4h**	76[c]

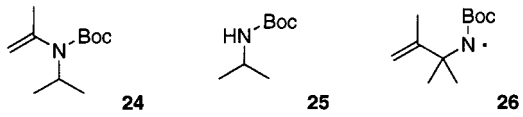
[a] Yield of isolated product. [b] Employed as a 84/16 mixture of double bond isomers (vide infra). [c] Obtained as a 77/23 mixture of double bond isomers.

and cleanly by refluxing the sulfenamide **3**, Bu_3SnH and a catalytic amount of AIBN in benzene (eq 8, Table 3).

(8)

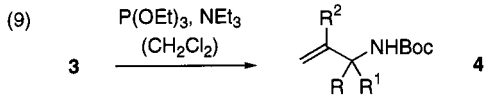


When we attempted to apply the very same conditions to α-branched *N*-allylamines with a tertiary carbon moiety the results were disappointing. There was an array of side products which were difficult to separate and the yield of the desired products remained low. In the case of the sulfenamide **3j** one of the side products was isolated in pure form and its structure was elucidated by spectroscopic methods. It turned out to be the enamide **24** which hydrolyzed upon standing to the amide **25** whose structure was unambiguously proven by comparison with the known compound.[40] To explain the formation of product **24**, we assume that a nitrogen centered radical **26** is formed by attack of the tributyl tin radical at the sulfur. A subsequent 1,2-shift, possibly via an aziridine intermediate, results in the carbon centered radical which abstracts a hydrogen atom from Bu_3SnH to give product **24**.



The failure of the Bu_3SnH-method for the deprotection of the above-mentioned sulfenamides let us return to the nucleophilic displacement reaction with triethyl phosphite which has been used frequently for the deprotection of related *N*-allyl sulfenamides.[11c] In the case of the corresponding benzenesulfenamide its use is a bit hampered by increased steric hindrance at the electrophilic sulfur atom. Methanesulfenamides are certainly better substrates for this reagent. Nonetheless, we were able to achieve a reasonable good yield of *N*-Boc amines **4** by treatment of the sulfenamides **3** with $P(OEt)_3$ and NEt_3 in CH_2Cl_2 at reflux. The reaction is outlined in eq 9 and the results are summarized in Table 4.

(9)



As a final remark, it should be mentioned that in the imidation/rearrangement sequence deprotected *N*-Boc N-allylamines **4** can be formed directly from the sulfides **1**. In particular, if larger quantities of $FeCl_2$ (>10 mol

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(39) Bowman, W. R.; Clark, D. N.; Marmon, R. J. *Tetrahedron* **1994**, *50*, 1275.
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Table 4. Deprotection of Sulfenamides 3 with Triethyl Phosphite

entry	sulfenamide	R	R^1	R^2	product	yield[a] (%)
1	**3i**	CH_3	CH_3	H	**4i**	62
2	**3j**	CH_3	CH_3	CH_3	**4j**	50
3	**3k**	CH_3	CH_2OBn	H	**4k**	43

[a] Yield of isolated product.

%) were employed the amount of deprotected product increased in some cases to a significant extent. As an instructive example the sulfide **1i** yielded a 66% yield of the corresponding sulfenamide **3i** upon treatment with $BocN_3$ and 10 mol-% $FeCl_2$ (eq 4, Table 2, entry 11). If 25 mol % of $FeCl_2$ were employed in the very same transformation the yield of sulfenamide **3i** decreased to 32%. Simultaneously, the deprotected amine **4i** was isolated in 30% yield. In separate experiments we showed that $FeCl_2$ can be used to deprotect sulfenamides but the yields obtained never exceeded the yields obtained with the conventional reagents used above.

Conclusion and Outlook

In summary, the synthesis of *N*-Boc-protected α-branched allylic sulfenamides can be readily achieved from the corresponding allyl sulfides by treatment with $BocN_3$ and catalytic amounts of $FeCl_2$. The subsequent removal of the phenylsulfanyl group is facile for α-branched *N*-Boc benzenesulfenamides with a secondary allyl group at the nitrogen atom, the reagent of choice being Bu_3SnH. For *N*-Boc benzenesulfenamides with a tertiary group at the nitrogen atom the deprotection is best conducted with $P(OEt)_3$. The results obtained with the latter procedure are not fully satisfactory but it is likely that methanesulfenamides can be more readily deprotected. The use of a methylsulfanyl instead of a phenylsulfanyl group might also be advantageous for the rearrangement of α-branched allyl sulfides which proceeded sluggishly with the substrates tested in this study. Further work regarding the stereoselectivity of the imidation/[2,3]-sigmatropic rearrangement is currently conducted in our laboratories.

Experimental Section

General Methods. For general remarks see ref 8b. Solvents (P = pentane, MTBE = methyl *tert*-butyl ether) used for chromatography were distilled prior to use. High-pressure liquid chromatography (HPLC) was performed on a Merck-Hitachi L6200A instrument (flow rate: 0.4 mL × min^{-1}, *n*-hexane/2-propanol = 99/1), equipped with an UV spectrometer detector (254 nm). For the determination of ee values a Daicel Chiracel OD column was used. The following compounds were synthesized as described in the literature: 2-butenyl phenyl sulfide (**1a**),[16] (*E*)-1-phenyl-2-propenyl phenyl sulfide (**1c**),[17] methyl (*S*)-*O*-toluenesulfonyl lactate (**8**),[29] 1-chloro-3-methyl-2-butene,[41] (*E*)-4,4-dimethyl-2-pentenyl bromide,[42] methyl 4-bromo-crotonate,[43] 1-benzyloxy-4-bromo-2-methyl-2-butene.[22]

(*E*)-4-Hydroxy-2-butenyl Phenyl Sulfide (1b).[21] A 4.1 g portion of (*E*)-3-methoxycarbonylprop-2-enyl phenyl sulfide (**1d**) (20 mmol) was dissolved in 60 mL of dry toluene and was cooled to −78 °C. 60 mL Dibal-H (60 mmol, 1 N in hexane) was added dropwise. After being stirred for 30 min, 6.5 mL aqueous acetic acid (50%) was added and the mixture was warmed to room temperature. The precipitate was removed by filtration and washed with acetone. The filtrate was concentrated, and the residue was purified by column chromatography (P/MTBE = 55/45). 1.7 g (46%) of **1b** was obtained as a yellow liquid. The NMR data were in agreement with the literature values.[21]

(*E*)-3-Methoxycarbonylprop-2-enyl Phenyl Sulfide (1d).[23] A 3.6 mL portion of methyl 4-bromocrotonate[43] (5.4 g, 30 mmol) and 3.1 mL of thiophenol (3.3 g, 30 mmol) were dissolved in 50 mL of dry diethyl ether and cooled to −10 °C. A 4.1 mL portion of triethylamine (3.0 g, 30 mmol) was added dropwise during 1 h. After being stirred at −10 °C for 30 min, the mixture was refluxed for 1.5 h and stirred overnight at room temperature. The precipitate was removed by filtration and washed with diethyl ether. The filtrate was washed with aqueous NaOH and dried over $MgSO_4$. After the solvent was removed the residue was purified by column chromatography (P/MTBE = 96/4). 5.1 g (82%) of **1d** was obtained as a colorless liquid. The NMR data were in agreement with the literature values.[23]

(*E*)-4,4-Dimethylpent-2-enyl Phenyl Sulfide (1e).[18] **Typical Procedure A.** Sodium (0.50 g, 20 mmol) was dissolved in 20 mL of dry ethanol. Subsequently, 2.1 mL of thiophenol (2.2 g, 20 mmol) and a solution of 3.5 g of (*E*)-4,4-dimethyl-2-pentenyl bromide[42] (20 mmol) in 20 mL of dry ethanol were added. The mixture was stirred for 5 h at room temperature and then poured into 100 mL of water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. After the solvent was removed the residue was purified by column chromatography (P/MTBE = 96/4), 3.9 g (94%) of **1e** was obtained as a colorless liquid. The NMR data were in agreement with the literature values.[18]

3-Methyl-2-butenyl Phenyl Sulfide (1i).[19] As described in typical procedure A, the reaction of 0.50 g of sodium (20 mmol), 2.1 mL of thiophenol (2.2 g, 20 mmol), and 2.1 g of 1-chloro-3-methyl-2-butene[41] (20 mmol) was carried out at reflux temperature (reaction time: 3.5 h). The crude product was purified by column chromatography (P). A total of 3.1 g (88%) of **1i** was obtained as a colorless liquid. The NMR data were in agreement with the literature values.[19]

2-Butenyl *p*-Methoxyphenyl Sulfide (5).[20] As described in typical procedure A, the reaction of 0.25 g of sodium (10 mmol), 1.2 mL of *p*-methoxythiophenol (1.4 g, 10 mmol), and 1.4 g of crotyl bromide (10 mmol) was carried out at room temperature (reaction time: 2 h). The crude product was purified by column chromatography (P/MTBE = 98.5/1.5). A total of 1.9 g (quant) of **5** was obtained as a colorless liquid (*E*/*Z*: 86/14). R_f = 0.37 (P/MTBE = 98.5/1.5). ^{1}H NMR: δ = 1.60−1.64 (m, 3 H), 3.36−3.40 (m, 2 H), 3.77 (s, 3 H), 5.39−5.50 (m, 2 H), 6.79−6.84 (m, 2 H), 7.29−7.38 (m, 2 H). ^{13}C NMR: δ = 17.6, 38.5, 55.2, 114.2, 126.5, 128.5, 136.0, 140.0, 158.9.

4-Benzyloxy-3-methyl-2-butenyl Phenyl Sulfide (1k). A 605 mg portion of 1-benzyloxy-4-bromo-2-methyl-2-butene[22] (2.4 mmol) (*E*/*Z*: 80/20) was dissolved in 8 mL of dry THF and cooled to 0 °C. Subsequently, 0.42 mL of triethylamine (303 mg, 3 mmol) and 0.30 mL of thiophenol (323 mg, 2.9 mmol) were added. The mixture was stirred at 0 °C for 30 min. Stirring was continued at room temperature for an additional 3 h. The mixture was poured into 100 mL of water. After the addition of 50 mL of diethyl ether, the layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed successively with water, aqueous NaOH, aqueous HCl, and aqueous $NaHCO_3$. After drying over $MgSO_4$, the solvent was removed and the residue was purified by column chromatography (P/MTBE = 99/1). A total of 730 mg (quant) of **1k** was obtained as a colorless liquid (*E*/*Z*: 80/20). R_f = 0.19 (P/MTBE = 99/1). IR (film): $\tilde{\nu}$ = 1071 cm^{-1} (s, COC), 738 (s, SC). (*E*)-**1k**. ^{1}H NMR: δ = 1.66 (br s, 3 H), 3.62 (dq, *J* = 7.3, 0.7 Hz, 2 H), 3.91 (d, *J* = 0.7 Hz, 2 H), 4.42 (s, 2 H), 5.64 (tq, *J* = 7.3, 1.5 Hz, 1 H), 7.20−7.40 (m, 10

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(42) de la Mare, P. B. D.; Hughes, E. D.; Merriman, P. C.; Pichat, L.; Vernon, C. A. *J. Chem. Soc.* **1958**, 2563.
(43) Ziegler, K.; Späht, A.; Schaaf, L.; Schumann, W.; Winkelmann, L. *Justus Liebigs Ann. Chem.* **1942**, *551*, 80.

H). ^{13}C NMR: δ = 13.8, 31.7, 71.4, 75.2, 122.7, 126.2, 127.5, 127.7, 128.3, 128.7, 130.1, 136.1, 138.8. (*Z*)-**1k**. ^{1}H NMR: δ = 1.83 (q, *J* = 1.0 Hz, 3 H), 3.57 (br d, *J* = 7.5 Hz, 2 H), 3.91 (d, *J* = 0.7 Hz, 2 H), 4.45 (s, 2 H), 5.56 (tq, *J* = 7.5, 1.0 Hz, 1 H), 7.20−7.40 (m, 10 H). ^{13}C NMR: δ = 21.7, 25.5, 67.9, 71.8, 123.8, 126.2, 127.1, 127.6, 128.4, 129.0, 129.8, 130.1, 136.4. HRMS ($C_{18}H_{20}OS$): calcd 284.1234, found 284.1229.

1-Cyclohexenylmethyl Phenyl Sulfide (1f).[26] **Typical Procedure B.**[24] A 2.4 mL portion of thioanisol (2.5 g, 20 mmol) was dissolved in 35 mL of dry THF and cooled to 0 °C. A 12.5 mL portion of *n*-BuLi (20 mmol, 1.6 n in hexane) was slowly added, and the mixture was stirred 15 min at 0 °C. Stirring was continued at room temperature overnight. The mixture was cooled to 0 °C, and a solution of 2.1 mL of cyclohexanone (**6f**) (2.0 g, 20 mmol) in 4 mL of dry THF was added. After the mixture was stirred at room temperature for 2.5 h, 200 mL of water was added. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine. The solution was dried over Na_2CO_3. The solvent was removed and the resulting hydroxy compound **7f** was dissolved in 200 mL of benzene. After addition of a catalytic amount of *p*-toluenesulfonic acid the mixture was refluxed for 4 h. The cold solution was washed with aqueous NaOH and dried over Na_2CO_3. The solvent was removed and the residue was purified by column chromatography (P). A total of 3.1 g (76% over two steps) of **1f** was obtained as a colorless liquid. The NMR data were in agreement with the literature values.[26]

2-Methyl-2-butenyl Phenyl Sulfide (1g).[27] As described in typical procedure B, the reaction was carried out with 8 mL of 2-butanone (**6g**) (1.4 g, 20 mmol). The subsequent elimination reaction of the resulting hydroxy compound **7g** yielded 2.8 g (78% over two steps) of **1g** as a colorless liquid (*E*/*Z* 69/31). The NMR data were in agreement with the literature values. [27]

2,4-Dimethyl-2-pentenyl Phenyl Sulfide (1h). As described in typical procedure B, the reaction was carried out with 2.1 mL of isobutyl methyl ketone (**6h**) (1.7 g, 17 mmol). The subsequent elimination reaction of the resulting hydroxy compound **7h** yielded 3.5 g (quant over two steps) of an isomeric mixture of **1h** (ratio: 90/10) as a colorless liquid (*E*/*Z*: 82/18). R_f = 0.26 (P). IR (film): $\tilde{\nu}$ = 2956 cm^{-1} (s, CH), 740 (s, SC). (*E*)-**1h**. ^{1}H NMR: δ = 0.82 (d, *J* = 6.5 Hz, 6 H), 1.72 (d, *J* = 1.1 Hz, 3 H), 2.31−2.53 (m, 1 H), 3.43 (d, *J* = 1.0 Hz, 2 H), 4.99 (dq, *J* = 9.3, 1.1 Hz, 1 H), 7.10−7.38 (m, 5 H). ^{13}C NMR: δ = 14.9, 22.6, 27.2, 44.5, 126.2, 127.7, 128.5, 131.0, 136.1, 137.2. (*Z*)-**1h**. ^{1}H NMR: δ = 0.87 (d, *J* = 6.5 Hz, 6 H), 1.81 (d, *J* = 1.5 Hz, 3 H), 2.31−2.53 (m, 1 H), 3.50 (d, *J* = 1.0 Hz, 2 H), 4.91−4.92 (m, 1 H), 7.10−7.38 (m, 5 H). HRMS ($C_{13}H_{18}S$): calcd 206.1129, found 206.1132.

2,3-Dimethyl-2-butenyl Phenyl Sulfide (1j).[28] As described in typical procedure B, the reaction was carried out with 2.1 mL of methyl isopropyl ketone (**6j**) (1.7 g, 20 mmol). The subsequent elimination reaction of the resulting hydroxy compound **7j** yielded 2.6 g (66% over two steps) of **1j** as a colorless liquid. The NMR data were in agreement with the literature values.[28]

(*R*)-2-Phenylsulfanylpropionate (9).[44] A 11.3 g portion of finely ground K_2CO_3 (82.0 mmol) and 4.46 mL of thiophenol (4.74 g, 43.0 mmol) were mixed in 100 mL of CH_3CN. Within 1 h, 10.6 g of methyl (*S*)-*O*-toluenesulfonyl lactate[29] (**8**) in 100 mL of CH_3CN was added dropwise. The mixture was vigorously stirred for 5 d at room temperature. The solvent was removed at 30 °C, and the residue was dissolved in 300 mL of diethyl ether. The organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was removed, and the residue was purified by column chromatography (P/MTBE = 98.5/1.5). 7.8 g (96%) of **9** was obtained as a colorless liquid. [α]$^{25}_D$ = +65.5 (*c* = 1.0, acetone). The NMR data were in agreement with the literature values.[44]

(*E*)-(*R*)-3-Methoxycarbonyl-1-methyl-2-butenyl Phenyl Sulfide (10).[45] 2.7 g (*R*)-2-Phenylsulfanylpropionate (**9**) (14 mmol) was dissolved in 50 mL of dry CH_2Cl_2 and cooled to −78 °C. A 16 mL portion of Dibal-H (16 mmol, 1 N in hexane) was added dropwise. To this solution was added a mixture of 530 mg of NaH (80% in white oil, 17 mmol) and 3.2 mL of diethoxyphosphoryl acidic acid methyl ester (3.7 g, 17 mmol) in 10 mL of dry CH_2Cl_2. The mixture was warmed overnight with stirring. After addition of 60 mL of aqueous KNa tartrate (30% w/w), the solution was stirred for an additional hour. An 80 mL portion of water was added, and after separation of the layers, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine and dried over $MgSO_4$. After the removal of the solvent, the residue was purified by flash chromatography (P/MTBE = 96/64). Compound **10** (2.0 g, 66%) was obtained as a colorless liquid (*E*/*Z*: >95/5). [α]$^{25}_D$ = +85.3 (*c* = 1.1, acetone). The NMR data were in agreement with the literature values.[45]

(*E*)-(*R*)-4-Hydroxy-1-methyl-2-butenyl Phenyl Sulfide (11). A 1.5 g portion of (*E*)-(*R*)-3-methoxycarbonyl-1-methyl-2-butenyl phenyl sulfide (**10**) (6.5 mmol) was dissolved in 20 mL of dry THF and cooled to 0 °C. A 22 mL portion of Dibal-H (22 mmol, 1 n in hexane) was added, and after the mixture was stirred for 1 h at 0 °C, 3 mL of methanol, 20 mL of water, 2 mL of aqueous NaOH, and 20 mL of aqueous KNa tartrate (30% w/w) were added successively. The mixture was stirred for 2 h at room temperature, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic layers were washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (P/MTBE = 80/20). Compound **11** (1.1 g, 87%) was obtained as a colorless liquid. R_f = 0.33 (P/MTBE = 60/40), [α]$^{25}_D$ = +37.3 (*c* = 1.1, acetone). IR (film): $\tilde{\nu}$ = 3357 cm^{-1} (w, OH), 1191 (s, COC), 748 (s, SC). ^{1}H NMR: δ = 1.38 (d, *J* = 7.0 Hz, 3 H), 1.59 (br s, 1 H), 3.76 (quint, *J* = 7.0 Hz, 1 H), 3.98 (br d, *J* = 5.2 Hz, 2 H), 5.48 (dt, *J* = 15.6, 5.2 Hz, 1 H), 5.66 (ddt, *J* = 15.6, 7.5, 1.0 Hz, 1 H), 7.18−7.41 (m, 5 H). ^{13}C NMR: δ = 20.7, 48.6, 63.2, 117.7, 129.1, 130.0, 133.4, 133.7, 135.0. HRMS ($C_{11}H_{14}OS$): calcd 194.0765, found 194.0761.

(*E*)-(*R*)-4-Bromo-1-methyl-2-butenyl Phenyl Sulfide (12). A 2.36 g portion of (*E*)-(*R*)-4-hydroxy-1-methyl-2-butenyl phenyl sulfide (**11**) (12.1 mmol) and 0.32 mL of pyridine (0.31 g, 3.8 mmol) were dissolved under argon in 19 mL of pentane. The mixture was cooled to −15 °C. A solution of 0.49 mL of PBr_3 (1.48 g, 5.3 mmol) in 4 mL of pentane was added dropwise during 2 h. Stirring was continued at −10 °C for 2 h and after the addition of 40 mL of water for an additional hour at room temperature. The layers were separated, and the aqueous layer was extracted with pentane. The combined organic layers were washed with water and brine and dried over $MgSO_4$, and the solvent was removed. A total of 1.68 g (54%) of **12** was obtained as a colorless liquid, which was used in the next step without further purification. R_f = 0.76 (P/MTBE = 60/40). ^{1}H NMR: δ = 1.37 (d, *J* = 7.0 Hz, 3 H), 3.72 (quint, *J* = 7.2 Hz, 1 H), 3.84 (d, *J* = 7.2 Hz, 2 H), 5.50 (dt, *J* = 14.9, 7.2 Hz, 1 H), 5.73 (dd, *J* = 14.9, 8.0 Hz, 1 H), 7.20−7.37 (m, 5 H). ^{13}C NMR: δ = 20.0, 32.1, 45.0, 126.2, 127.5, 128.6, 133.0, 136.9.

(*E*)-(*R*)-1-Methyl-2-butenyl Phenyl Sulfide (13).[46] A 0.24 g portion of $LiAlH_4$ (6.3 mmol) was added to 17 mL of dry THF. After the dropwise addition of a solution of 1.41 g of (*E*)-(*R*)-4-bromo-1-methyl-2-butenyl phenyl sulfide (**12**) (5.5 mmol) in 5 mL of dry THF, the mixture was refluxed for 4 h. The mixture was allowed to cool to room temperature. Then, 0.5 mL of water, 0.5 mL of aqueous NaOH, and 0.5 mL of water were successively added to the stirred solution. After the mixture was stirred for an additional hour at room temperature, the resulting slurry was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. The solvent was removed, and the residue was purified by column chromatography (P). Compound **13** (0.61 g, (62%) was obtained as a colorless liquid. [α]$^{25}_D$ = +46.1 (*c* = 1.0, acetone). The NMR data were in agreement with the literature values.[46]

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***N-tert*-Butyloxycarbonyl-*N*-(1-methyl-2-propenyl)benzenesulfenamide (3a). Typical Procedure C.** A 143 mg portion of $BocN_3$ (1.0 mmol) and 165 mg of 2-butenyl phenyl sulfide (**1a**) (1.0 mmol) were dissolved in 1.0 mL of dry CH_2Cl_2. After addition of 32 mg of $FeCl_2$ (0.25 mmol) [12 mg, 0.1 mmol], the mixture stirred at room temperature overnight. The crude reaction mixture was separated by column chromatography (P/MTBE = 98.5/1.5). A total of 187 mg (69%) [207 mg, 75%] of **3a** was obtained as a colorless oil. R_f = 0.18 (P/MTBE = 99/1). IR (film): $\tilde{\nu}$ = 1701 cm^{-1} (s, C=O), 1642 (s, C=C), 1160 (s, C−O−C), 737 (s, S−C). ^1H NMR (373 K, DMSO-d_6): δ = 1.26 (d, J = 6.8 Hz, 3 H), 1.42 (s, 9 H), 4.89 (dtq, J = 6.8, 5.9, 1.4 Hz), 5.07 (dt, J = 10.4, 1.4 Hz, 1 H,), 5.12 (dt, J = 17.3, 1.4 Hz, 1 H), 5.85 (ddd, J = 17.3, 10.4, 5.9 Hz, 1 H), 7.17−7.24 (m, 3 H), 7.32−7.37 (m, 2 H). ^{13}C NMR (373 K, DMSO-d_6): δ = 19.0, 28.5, 58.6, 82.1, 116.0, 124.9, 126.9, 129.5, 139.5, 141.7, 156.5. Anal. Calcd for $C_{15}H_{21}NO_2S$ (279.40): C, 64.48; H, 7.58; N, 5.01. Found: C, 64.38; H, 7.31; N, 5.13.

***N-tert*-Butyloxycarbonyl-*N*-(1-hydroxymethyl-2-propenyl)benzenesulfenamide (3b).** The reaction was carried out on the same scale as described in typical procedure C starting with 170 mg of (*E*)-4-hydroxy-2-butenyl phenyl sulfide (**1b**) (1.0 mmol). A total of 207 mg (70%) of **3b** was obtained as a colorless oil (P/MTBE = 65/35 as eluent). R_f = 0.41 (P/MTBE = 65/35). IR (film): $\tilde{\nu}$ = 3452 cm^{-1} (w, OH), 1701 (s, C=O), 740 (s, SC). ^1H NMR: δ = 1.46 (s, 9 H), 3.20 (br s, 1 H), 3.67 (dd, J = 11.5, 5.5 Hz, 1 H), 3.81 (dd, J = 11.5, 8.2 Hz, 1 H,), 4.85−4.95 (m, 1 H), 5.17 (dd, J = 10.3, 1.2 Hz, 1 H), 5.22 (dd, J = 17.2, 1.2 Hz, 1 H), 5.81 (ddd, J = 17.2, 10.3, 6.8 Hz, 1 H), 7.16−7.30 (m, 5 H). ^{13}C NMR: δ = 28.4, 63.8, 65.1, 82.8, 119.0, 124.9, 126.8, 129.3, 134.2, 140.1, 157.6. Anal. Calcd. for $C_{15}H_{21}NO_3S$ (295.40): C, 60.99; H, 7.17; N, 4.74. Found: C, 60.85, H, 6.84; N, 4.79.

***N-tert*-Butyloxycarbonyl-*N*-(1-phenyl-2-propenyl)benzenesulfenamide (3c).** The reaction was carried out on the same scale as described in typical procedure C starting with 226 mg of (*E*)-1-phenyl-2-propenyl phenyl sulfide[17] (**1c**) (1.0 mmol). A total of 178 mg (52%) [212 mg, 62%] of **3c** was obtained as a colorless oil (P/MTBE = 96/4 as eluent). R_f = 0.46 (P/MTBE = 96/4). IR (film): $\tilde{\nu}$ = 1701 cm^{-1} (s, C=O), 1287 (s, COC), 737 (s, SC). ^1H NMR: δ = 1.42 (s, 9 H), 5.07 (dd, J = 10.3, 1.0 Hz, 1 H), 5.25 (dd, J = 17.0, 1.0 Hz, 1 H), 6.00 (d, J = 6.5 Hz, 1 H), 6.19 (ddd, J = 17.0, 10.3, 6.5 Hz, 1 H), 7.06−7.30 (m, 10 H). ^{13}C NMR: δ = 28.4, 66.5, 82.6, 118.7, 124.8, 126.4, 127.9, 128.3, 128.6, 129.0, 136.2, 140.0, 141.7, 157.0. Anal. Calcd for $C_{20}H_{23}NO_2S$ (341.47): C, 70.35; H, 6.79; N, 4.10. Found: C, 70.38; H, 6.73; N, 4.11.

***N-tert*-Butyloxycarbonyl-*N*-(1-methoxycarbonyl-2-propenyl)benzenesulfenamide (3d).** The reaction was carried out on the same scale as described in typical procedure C starting with 177 mg of (*E*)-3-methoxycarbonyl-2-propenyl phenyl sulfide (**1d**) (1.0 mmol). A total of 72 mg (22%) [94 mg, 32%] of **3d** was obtained as a colorless oil (P/MTBE = 97/3 as eluent). R_f = 0.10 (P/MTBE = 97/3). IR (film): $\tilde{\nu}$ = 1704 cm^{-1} (s, C=O), 1298 (s, COC), 740 (s, SC). ^1H NMR: δ = 1.45 (s, 9 H), 3.70 (s, 3 H), 5.11 (d, J = 7.4 Hz, 1 H), 5.29 (dd, J = 10.0, 1.0 Hz, 1 H), 5.29 (dd, J = 17.2, 1.0 Hz, 1 H), 6.08 (ddd, J = 17.2, 10.0, 7.4 Hz, 1 H), 7.21−7.31 (m, 5 H). ^{13}C NMR: δ = 28.4, 52.8, 67.9, 83.3, 121.0, 125.2, 126.9, 129.1, 131.7, 139.5, 156.4, 170.7. Anal. Calcd for $C_{16}H_{21}NO_4S$ (323.41): C, 59.42; H, 6.54; N, 4.33. Found: C, 59.40; H, 6.58; N, 4.43.

***N-tert*-Butyloxycarbonyl-*N*-(1-*tert*-butyl-2-propenyl)benzenesulfenamide (3e).** The reaction was carried out on the same scale as described in typical procedure C starting with 207 mg of (*E*)-4,4-dimethyl-2-pentenyl phenyl sulfide (**1e**) (1.0 mmol). A total of 154 mg (48%) of **3e** was obtained as a colorless oil (P/MTBE = 96/4 as eluent). R_f = 0.18 (P/MTBE = 96/4). IR (film): $\tilde{\nu}$ = 1749 cm^{-1} (s, C=O), 1287 (s, COC), 739 (s, SC). ^1H NMR: δ = 0.95 (s, 9 H), 1.42 (s, 9 H), 4.66−4.80 (m, 1 H), 5.13 (dd, J = 9.9, 1.5 Hz, 1 H), 5.24 (dd, J = 16.8, 1.5 Hz, 1 H), 6.14 (ddd, J = 16.8, 9.9, 7.5 Hz, 1 H), 7.03−7.28 (m, 5 H). ^{13}C NMR: δ = 27.6, 28.3, 55.7, 81.8, 82.1, 120.2, 123.0, 125.7, 128.8, 129.2, 134.4, 156.9. Anal. Calcd for $C_{18}H_{27}NO_2S$ (321.49): C, 67.25; H, 8.47; N, 4.36. Found: C, 67.07; H, 8.42; N, 4.11.

***N-tert*-Butyloxycarbonyl-*N*-(2-methylene cyclohexyl)benzenesulfenamide (3f).** The reaction was carried out on the same scale as described in typical procedure C starting with 205 mg of 1-cyclohexenylmethyl phenyl sulfide (**1f**) (1.0 mmol). A total of 207 mg (65%) of **3f** was obtained as colorless crystals (P/MTBE = 98.5/1.5 as eluent). R_f = 0.32 (P/MTBE = 98/2). Mp: 57 °C. IR (KBr): $\tilde{\nu}$ = 1700 cm^{-1} (s, C=O), 1292 (s, COC), 851 (s, SN), 737 (s, SC). ^1H NMR: δ = 1.19−1.15 (m, 2 H), 1.44 (s, 9 H), 1.66−2.08 (m, 5 H), 2.42−2.48 (m, 1 H), 4.47 (br s, 1 H), 4.73−4.80 (m, 1 H), 4.79 (br s, 1 H), 7.10−7.20 (m, 3 H), 7.26−7.31 (m, 2 H). ^{13}C NMR: δ = 25.5, 27.0, 27.9, 31.4, 35.1, 63.0, 81.7, 105.0, 123.4, 125.6, 128.6, 140.9, 147.1, 157.0. Anal. Calcd for $C_{18}H_{25}NO_2S$ (319.45): C, 67.67; H, 7.89; N, 4.38. Found: C, 67.42; H, 7.96; N, 4.49.

***N-tert*-Butyloxycarbonyl-*N*-(1,2-dimethyl-2-propenyl)benzenesulfenamide (3g).** The reaction was carried out on the same scale as described in typical procedure C starting with 180 mg of 2-methyl-2-butenyl phenyl sulfide (**1g**) (1.0 mmol). A total of 199 mg (70%) of **3g** was obtained as a colorless oil (P/MTBE = 98/2 as eluent). R_f = 0.27 (P/MTBE = 98/2). IR (film): $\tilde{\nu}$ = 1700 cm^{-1} (s, C=O), 1293 (s, COC), 1163, 853 (s, SN), 737 (s, SC). ^1H NMR: δ = 1.28 (d, J = 6.7 Hz, 3 H), 1.47 (s, 9 H), 1.67 (s, 3 H), 4.82−4.97 (m, 3 H), 7.14−7.20 (m, 5 H). ^{13}C NMR: δ = 16.9, 20.4, 28.0, 59.3, 81.7, 112.0, 124.5, 125.9, 128.5, 140.2, 145.0, 156.9. Anal. Calcd. for $C_{16}H_{23}NO_2S$ (293.43): C, 65.49; H, 7.90; N, 4.77. Found: C, 65.22; H, 7.75; N, 4.79.

***N-tert*-Butyloxycarbonyl-*N*-(2-methyl-1-isopropyl-2-propenyl)benzenesulfenamide (3h).** The reaction was carried out on the same scale as described in typical procedure C starting with 210 mg of 2,4-dimethyl-2-pentenyl phenyl sulfide (**1h**) (1.0 mmol). A total of 226 mg (70%) of an isomeric mixture (ratio: 84/16) was obtained, from which **3h** could be separated from selected chromatography fractions as a colorless oil (P/MTBE = 99/1 as eluent). R_f = 0.34 (P/MTBE = 98.5/1.5). IR (film): $\tilde{\nu}$ = 1701 cm^{-1} (s, C=O), 1281 (s, COC), 736 (s, SC). ^1H NMR: δ = 0.86 (d, J = 6.5 Hz, 3 H), 0.88 (d, J = 6.5 Hz, 3 H), 1.45 (s, 9 H), 1.64 (s, 3 H), 2.27 (dsept, J = 11.0, 6.5 Hz, 1 H), 4.35 (br d, J = 11.0 Hz, 1 H), 4.87 (t, J = 1.5 Hz, 1 H), 5.05 (br s, 1 H), 7.12−7.40 (m, 5 H). ^{13}C NMR: δ = 19.7, 20.0, 21.2, 28.0, 69.8, 81.7, 115.6, 125.0, 126.0, 128.3, 139.6, 142.2, 157.3. Anal. Calcd. for $C_{18}H_{27}NO_2S$ (321.48): C, 67.25; H, 8.46; N, 4.34. Found: C, 67.31; H, 8.32; N, 4.61.

***N-tert*-Butyloxycarbonyl-*N*-(1,1-dimethyl-2-propenyl)benzenesulfenamide (3i).** The reaction was carried out on the same scale as described in typical procedure C starting with 180 mg of 3-methyl-2-butenyl phenyl sulfide (**1i**) (1.0 mmol). A total of 97 mg (32%) [198 mg, 66%] of **3i** was obtained as colorless crystals (P/MTBE = 99/1 as eluent). R_f = 0.33 (P/MTBE = 98.5/1.5). Mp: 29 °C. IR (KBr): $\tilde{\nu}$ = 1710 cm^{-1} (s, C=O), 1283 (s, COC), 740 (s, SC). ^1H NMR: δ = 1.44 (s, 9 H), 1.51 (s, 6 H), 4.96 (dd, J = 10.8, 0.7 Hz, 1 H), 5.00 (br d, J = 17.5 Hz, 1 H), 6.10 (dd, J = 17.5, 10.8 Hz, 1 H), 7.09−7.19 (m, 5 H). ^{13}C NMR: δ = 28.0, 28.1, 64.5, 81.7, 110.3, 127.1, 127.4, 129.0, 136.9, 145.8, 156.6. Anal. Calcd. for $C_{16}H_{23}NO_2S$ (293.43): C, 65.49; H, 7.90; N, 4.77. Found: C, 65.24; H, 8.03; N, 4.59.

***N-tert*-Butyloxycarbonyl-*N*-(1,1,2-trimethyl-2-propenyl)benzenesulfenamide (3j).** The reaction was carried out on the same scale as described in typical procedure C starting with 195 mg of 2,3-dimethyl-2-butenyl phenyl sulfide (**1j**) (1.0 mmol). A total of 147 mg (48%) [126 mg, 41%] of **3j** was obtained as a colorless oil (P/MTBE = 98.5/1.5 as eluent). R_f = 0.21 (P/MTBE = 98.5/1.5). IR (film): $\tilde{\nu}$ = 1711 cm^{-1} (s, C=O), 1288 (s, COC), 848 (s, SN), 737 (s, SC). ^1H NMR: δ = 1.45 (s, 9 H), 1.51 (s, 6 H), 1.70 (s, 3 H), 4.75 (br s, 1 H), 4.80 (br s, 1 H), 7.15−7.26 (m, 5 H). ^{13}C NMR: δ = 19.5, 28.1, 28.4, 67.1, 81.8, 108.2, 124.7, 126.1, 128.2, 141.3, 151.2, 156.8. Anal. Calcd for $C_{17}H_{25}NO_2S$ (307.45): C, 66.41; H, 8.19; N, 4.55. Found: C, 66.61; H, 8.11; N, 4.77.

***N-tert*-Butyloxycarbonyl-*N*-(1-benzyloxymethyl-1-methyl-2-propenyl)benzenesulfenamide (3k).** The reaction was carried out on the same scale as described in typical procedure

C starting with 290 mg of 4-benzyloxy-3-methyl-2-butenyl phenyl sulfide (**1k**) (1.0 mmol). A total of 208 mg (52%) of **3k** was obtained as a colorless oil (P/MTBE = 99/1 as eluent). R_f = 0.15 (P/MTBE = 99/1). IR (film): $\tilde{\nu}$ = 1706 cm^{-1} (s, C=O), 1285 (s, COC), 855 (s, SN), 737 (s, SC). ^{1}H NMR: δ = 1.31 (s, 9 H), 1.47 (s, 3 H), 3.75 (br s, 2 H), 4.42 (s, 2 H), 4.96 (d, J = 16.9 Hz, 1 H), 4.99 (d, J = 11.3 Hz), 6.11 (dd, J = 16.9, 11.3 Hz, 1 H), 6.97−7.22 (m, 10 H).^{13}C NMR: δ = 23.4, 27.9, 66.8, 73.1, 75.2, 81.6, 112.2, 123.1, 125.3, 127.3, 127.4, 128.2, 128.4, 138.3, 141.6, 156.5. Anal. Calcd for $C_{23}H_{29}NO_3S$ (399.56): C, 69.14; H, 7.31; N, 3.50. Found: C, 69.16; H, 7.41; N 3.75.

***N*-*tert*-Butyloxycarbonyl-*N*-(1-methyl-2-propenyl)-*p*-methoxybenzenesulfenamide (21).** The reaction was carried out on the same scale as described in typical procedure C starting with 195 mg of 2-butenyl *p*-methoxyphenyl sulfide (**5**) (1.0 mmol). A total of 160 mg (51%) [205 mg, 66%] of **21** was obtained as a colorless oil (P/MTBE = 98/2 as eluent). R_f = 0.20 (P/MTBE = 98/2). IR (film): $\tilde{\nu}$ = 1700 cm^{-1} (s, C=O), 1292 (s, COC), 828 (s, SN), 737 (s, SC). ^{1}H NMR: δ = 1.23 (d, J = 6.8 Hz, 3 H), 1.45 (s, 9 H), 3.74 (s, 3 H), 4.82−4.90 (m, 1 H), 5.01 (dt, J = 10.4, 1.4, 10.4 Hz, 1 H,), 5.04 (dt, J = 17.3, 1.4 Hz, 1 H), 5.85 (ddd, J = 17.3, 10.4, 5.7 Hz, 1 H), 6.76−6.84 (m, 2 H), 7.28−7.35 (m, 2 H). ^{13}C NMR: δ = 18.5, 28.1, 55.3, 57.9, 81.5, 114.4, 115.0, 129.8, 131.2, 139.0, 156.8, 159.2. Anal. Calcd for $C_{16}H_{23}NO_3S$ (309.43): C, 62.11; H, 7.49; N, 4.53. Found: C, 61.83; H, 7.56; N, 4.90.

***N*-*tert*-Butyloxycarbonyl-*N*-[(*E*)-1-methoxycarbonyl-2-butenyl]benzenesulfenamide (22).** The reaction was carried out as described in typical procedure C starting with 333 mg of (*E*)-(*R*)-3-methoxycarbonyl-2-butenyl phenyl sulfide (**10**) (1.5 mmol), 143 mg of $BocN_3$ (1.0 mmol), and 12 mg of $FeCl_2$ (0.1 mmol). A total of 20 mg (6%) of **22** was obtained as a colorless oil (39% ee) (P/MTBE = 96/4 as eluent). R_f = 0.08 (P/MTBE = 96/4). [α]$^{25}_D$ = −11.5 (c = 2.0, acetone). HPLC: t_R = 11.63, 12.30 min. IR (film): $\tilde{\nu}$ = 1702 cm^{-1} (s, C=O), 1200 (s, COC), 856 (s, SN), 739 (s, SC). ^{1}H NMR: δ = 1.42 (s, 9 H), 1.62 (d, J = 5.3 Hz, 3 H), 3.67 (s, 3 H), 5.01−5.10 (m, 1 H), 5.67 (dd, J = 15.5, 6.7 Hz, 1 H), 5.71 (dq, J = 15.5, 5.3 Hz, 1 H), 7.13−7.15 (m, 1 H), 7.24−7.28 (m, 4 H). ^{13}C NMR: δ = 17.7, 27.8, 52.1, 66.4, 82.5, 124.2, 124.7, 126.2, 128.4, 132.7, 139.3, 156.0, 170.7. Anal. Calcd for $C_{17}H_{23}NO_4S$ (337.44): C, 60.51; H, 6.87; N, 4.15. Found: C, 60.29; H, 7.20; N, 4.35.

***N*-*tert*-Butyloxycarbonyl-*N*-[(*E*)-1-methyl-2-butenyl]benzenesulfenamide (23).** The reaction was carried out as described in typical procedure C starting with 179 mg of (*E*)-(*R*)-1-methyl-2-butenyl phenyl sulfide (**13**) (1.0 mmol), 143 mg of $BocN_3$ (1.0 mmol), and 12 mg of $FeCl_2$ (0.1 mmol). A total of 97 mg (32%) of **23** was obtained as a colorless oil (P/MTBE = 98.5/1.5 as eluent). R_f = 0.25 (P/MTBE = 98.5/1.5). [α]$^{25}_D$ = −10.7 (c = 1.0, acetone). IR (film): $\tilde{\nu}$ = 1699 cm^{-1} (s, C=O), 1293 (s, COC), 736 (s, SC). ^{1}H NMR: δ = 1.16 (d, J = 6.8 Hz, 3 H), 1.37 (s, 9 H), 1.52 (d, J = 5.8 Hz, 3 H), 4.86 (quint, J = 5.8 Hz, 1 H), 5.32−5.58 (m, 2 H), 7.01−7.24 (m, 5 H). ^{13}C NMR: δ = 17.5, 18.9, 28.0, 68.0, 81.5, 123.9, 125.6, 126.7, 128.4, 131.6, 139.3, 156.5. Anal. Calcd for $C_{16}H_{23}NO_2S$ (293.43): C, 65.49; H, 7.90; N, 4.77. Found: C, 65.30; H, 8.04; N, 5.14.

***N*-*tert*-Butyloxycarbonyl-*N*-(1-methyl-2-propenyl)amine (4a).**[47] **Typical Procedure D.** A 190 mg portion of *N*-*tert*-butyloxycarbonyl-*N*-(1-methyl-2-propenyl)benzenesulfenamide (**3a**) (0.68 mmol), 0.27 mL of Bu_3SnH (320 mg, 1.1 mmol), and a catalytic amount of AIBN were dissolved in 50 mL of dry benzene and refluxed for 1 h. The solvent was removed, and the residue was purified by column chromatography (P/MTBE = 94/4). A total of 108 mg (93%) of **4a** was obtained as a colorless oil. The NMR data were in agreement with the literature values.[47]

***N*-*tert*-Butyloxycarbonyl-*N*-(1-hydroxymethyl-2-propenyl)amine (4b).**[48] A 124 mg portion of *N*-*tert*-butyloxycarbonyl-*N*-(1-hydroxymethyl-2-propenyl)benzenesulfenamide (**3b**) (0.42 mmol) and 0.19 mL of Bu_3SnH (209 mg, 0.71 mmol) were converted as described in typical procedure D. A total of 56 mg (71%) of **4b** was obtained as a colorless oil (P/MTBE = 50/50 as eluent). The NMR data were in agreement with the literature values.[48]

***N*-*tert*-Butyloxycarbonyl-*N*-(2-methylenecyclohexyl)amine (4f).** A 234 mg portion of *N*-*tert*-butyloxycarbonyl *N*-(2-methylenecyclohexyl)benzenesulfenamide (**3f**) (0.73 mmol) and 0.28 mL of Bu_3SnH (349 mg, 1.2 mmol) were converted as described in typical procedure D. A total of 133 mg (86%) of **4f** was obtained as colorless crystals. R_f = 0.23 (P/MTBE = 96/4). Mp: 55 °C, IR (KBr): $\tilde{\nu}$ = 3330 cm^{-1} (w, NH), 1687 (s, C=O), 1273 (s, COC). ^{1}H NMR (373 K, DMSO-d_6): δ = 1.22−1.45 (m, 4 H), 1.39 (s, 9 H), 1.64−1.67 (m, 1 H), 1.73−1.79 (m, 2 H), 1.96−2.00 (m, 1 H), 2.33−2.36 (m, 1 H), 3.82−3.88 (m, 1 H), 4.65 (s, 1 H), 4.68 (br s, 1 H). ^{13}C NMR: δ = 25.2, 27.6, 28.4, 34.6, 35.2, 53.2, 79.2, 105.0, 149.3. Anal. Calcd for $C_{12}H_{21}NO_2$ (211.30): C, 68.21; H, 10.02; N, 6.63. Found: C, 67.89; H, 9.68; N, 6.64.

***N*-*tert*-Butyloxycarbonyl-*N*-(1,2-dimethyl-2-propenyl)amine (4g).** A 140 mg portion of *N*-*tert*-butyloxycarbonyl-*N*-(1,2-dimethyl-2-propenyl)benzenesulfenamide (**3g**) (0.48 mmol) and 0.22 mL of Bu_3SnH (247 mg, 0.85 mmol) were converted as described in typical procedure D. A total of 80 mg (90%) of **4g** was obtained as colorless crystals. R_f = 0.34 (P/MTBE = 90/10). Mp: 53 °C. IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} (w, NH), 1683 (s, C=O), 1253 (s, COC). ^{1}H NMR: δ = 1.17 (d, J = 7.0 Hz, 3 H), 1.40 (s, 9 H), 1.67 (s, 3 H), 3.98−4.14 (m, 1 H), 4.50 (br s, 1 H), 4.75 (br s, 1 H), 4.82 (br s, 1 H). ^{13}C NMR: δ = 19.3, 19.9, 28.3, 51.1, 79.1, 109.7, 146.7, 155.1. Anal. Calcd for $C_{10}H_{19}NO_2$ (185.29): C, 64.82; H, 10.34; N, 7.56. Found: C, 64.66; H, 10.12, N, 7.24.

***N*-*tert*-Butyloxycarbonyl-*N*-(2-methyl-1-isopropyl-2-propenyl)amine (4h).** A 202 mg portion of *N*-*tert*-butyloxycarbonyl-*N*-(2-methyl-1-isopropyl-2-propenyl)benzenesulfenamide (**3h**) (0.63 mmol) and 0.26 mL of Bu_3SnH (285 mg, 0.98 mmol) were converted as described in typical procedure D. A total of 102 mg (76%) of a mixture of **4h** and its double-bond isomer (ratio: 77/23) was obtained as colorless crystals that could not be separated. R_f = 0.18 (P/MTBE = 96/4). Mp: 34 °C. IR (KBr): $\tilde{\nu}$ = 3337 cm^{-1} (w, NH), 1686 (s, C=O), 1246 (s, COC). ^{1}H NMR: δ = 0.81 (d, J = 6.7 Hz, 3 H), 0.86 (d, J = 6.2 Hz, 3 H), 1.38 (s, 9 H), 1.64 (s, 3 H), 1.74−1.83 (m, 1 H), 3.49 (d, J = 6.0 Hz, 1 H), 4.53 (br s, 1 H), 4.73−4.81 (m, 2 H). ^{13}C NMR: δ = 19.1, 19.9, 22.3, 28.3, 29.5, 45.3, 79.0, 111.7, 144.3.

***N*-*tert*-Butyloxycarbonyl-*N*-isopropyl-*N*-2-propenylamine (24).** A 151 mg portion of *N*-*tert*-butyloxycarbonyl-*N*-(1,1,2-trimethyl-2-propenyl)benzenesulfenamide (**3k**) (0.47 mmol) and 0.20 mL of Bu_3SnH (221 mg, 0.76 mmol) were converted as described in typical procedure D. A total of 72 mg (77%) of **24** was obtained as a colorless oil. R_f = 0.21 (P/MTBE = 96/4). IR (film): $\tilde{\nu}$ = 1698 cm^{-1} (s, C=O), 1272 (s, COC). ^{1}H NMR: δ = 1.14 (d, J = 6.8 Hz, 6 H), 1.41 (s, 9 H), 1.80 (s, 3 H), 4.20 (sept, J = 6.8 Hz, 1 H), 4.68 (br s, 1 H), 4.90 (br s, 1 H). ^{13}C NMR: δ = 21.1, 20.3, 27.2, 48.0, 79.2, 113.1, 142.3, 153.8. MS (70 eV): m/z 143 (15) [$M^+ - C_4H_8$], 98 (15) [M^+ − Boc], 84 (22) [$M^+ - C_4H_8 - CO_2 - CH_3$], 57 (100) [$C_4H_9^+$].

Hydrolysis of enecarbamate **24** yielded compound **25**, the NMR data of which were in agreement with the literature values.[40]

***N*-*tert*-Butyloxycarbonyl-*N*-(1,1-dimethyl-2-propenyl)amine (4i).**[15] **Typical Procedure E.** A 136 mg portion of *N*-*tert*-butyloxycarbonyl-*N*-(1,1-dimethyl-2-propenyl)benzenesulfenamide (**3i**) (0.46 mmol), 0.27 mL of triethylamine (189 mg, 1.8 mmol), and 0.12 mL of triethyl phosphite (113 mg, 0.69 mmol) were dissolved in 5 mL of dry CH_2Cl_2 and refluxed for 3.5 h. The mixture was poured into 5 mL of water, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with aqueous HCl and saturated aqueous $NaHCO_3$. After drying over $MgSO_4$, the solvent was removed and the residue was purified by column chromatography (P/MTBE = 96/4). A total of 53 mg (62%) of **4i** was

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obtained as a colorless oil. R_f = 0.21 (P/MTBE = 96/4). ^{1}H NMR: δ = 1.32 (s, 6 H), 1.39 (s, 9 H), 4.55 (br s, 1 H), 4.98 (d, J = 10.5 Hz, 1 H), 5.04 (d, J = 17.4 Hz, 1 H), 5.93 (dd, J = 17.4, 10.5 Hz, 1 H). ^{13}C NMR: δ = 27.8, 28.8, 53.3, 78.9, 111.3, 144.4, 154.8.

***N-tert*-Butyloxycarbonyl-*N*-(1,1,2-trimethyl-2-propenyl)-amine (4j).** A 133 mg portion of *N-tert*-butyloxycarbonyl-*N*-(1,1,2-trimethyl-2-propenyl)benzenesulfenamide (**3j**) (0.43 mmol), 0.27 mL of triethylamine (189 mg, 1.8 mmol), and 0.12 mL of triethyl phosphite (113 mg, 0.69 mmol) were converted as described in typical procedure E. A total of 43 mg (50%) of **4j** was obtained as colorless oil, which crystallized slowly. R_f = 0.13 (P/MTBE = 96/4). Mp: 49 °C. IR (film): $\tilde{\nu}$ = 3332 cm^{-1} (w, NH), 1698 (s, C=O), 1250 (s, COC), 1164 (s, COC). ^{1}H NMR: δ = 1.35 (s, 6 H), 1.39 (s, 9 H), 1.72 (br s, 3 H), 4.56 (br s, 1 H), 4.80 (br s, 1 H), 4.85 (br s, 1 H). ^{13}C NMR: δ = 19.0, 27.4, 28.4, 55.5, 78.9, 109.7, 149.7. MS (70 eV): m/z 143 (28) [$M^+ - C_4H_8$], 128 (29) [$M^+ - C_4H_8 - CH_3$], 83 (38) [$C_6H_{11}^+$], 57 (100) [$C_4H_9^+$].

***N-tert*-Butyloxycarbonyl-*N*-(1-benzyloxymethyl-1-methyl-2-propenyl)amine (4k).** A 200 mg portion of *N-tert*-butyloxycarbonyl-*N*-(1-benzyloxymethyl-1-methyl-2-propenyl)-benzenesulfenamide (**3k**) (0.5 mmol), 0.32 mL of triethylamine (222 mg, 2.2 mmol), and 0.14 mL of triethyl phosphite (134 mg, 0.81 mmol) were converted as described in typical procedure E. A total of 62 mg (43%) of **4k** was obtained as a colorless oil. R_f = 0.11 (P/MTBE = 96/4). IR (film): $\tilde{\nu}$ = 3431 cm^{-1} (w, NH), 3359 (w, NH), 1723 (s, C=O), 1248 (s, COC). ^{1}H NMR: δ = 1.35 (s, 12 H), 3.29 (d, J = 9.0 Hz, 1 H), 3.38 (d, J = 9.0 Hz, 1 H), 4.46 (s, 2 H), 4.94 (br s, 1 H), 5.06 (d, J = 11.2 Hz, 1 H), 5.07 (d, J = 17.0 Hz, 1 H), 5.89 (dd, J = 17.0, 11.2 Hz), 7.25 (s, 5 H, arom. H).^{13}C NMR: δ = 21.8, 28.3, 56.4, 73.3, 75.8, 79.0, 113.5, 127.5, 127.6, 128.4, 138.0, 141.0, 154.7. MS (70 eV): m/z 235 (1) [$M^+ - C_4H_8$], 114 (38) [$C_6H_{12}NO^+$], 91 (79) [$C_7H_7^+$], 57 (100) [$C_4H_9^+$].

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Supporting Information Available: NMR spectra (^{1}H, ^{13}C) of compounds **1h** (mixture of isomers), **1k** (mixture of isomers), **11**, **4h** (mixture of isomers), **4j**, **4k**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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