Water-Accelerated Organometallic Chemistry: Alkyne Carboalumination – Sulfinimine Addition and Asymmetric Synthesis of Allylic Amines

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

Carboalumination of alkynes in the presence of catalytic Cp_2ZrCl_2 and H_2O affords vinyl-alane intermediates, which serve as nucleophiles in the subsequent addition to enantiomerically enriched (*tert*-butyl)- and (*para*-tolyl)sulfinimines. This new *in situ* protocol produces two new C–C bonds. Chiral allylic sulfinamides are obtained in high diastereoselectivity and in good yield. Cleavage of the chiral auxiliary leads to synthetically useful allylic amine building blocks, and facile oxidative degradation of the alkene moiety can be used as an approach toward amino acid derivatives and for assignment of absolute configuration.

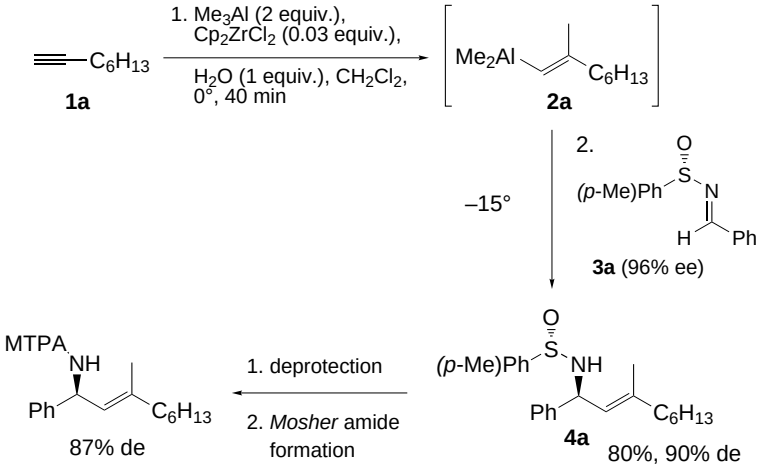
Introduction. – Due to their presence in many biologically important natural products and pharmaceuticals, the synthesis of enantiomerically enriched α-branched amines has attracted considerable interest in the past few years [1]. Allylic amines in particular are useful starting materials for the preparation of amino acids, amino alcohols, and heterocycles [2]. The diastereoselective addition of organometallic reagents to the C=N bond of sulfinimines that are *N*-substituted with chiral auxiliaries is an attractive recent strategy, and enantiomerically pure (*p*-tolyl)sulfinimines [3] and (*t*-butyl)sulfinimines [4] have been successfully employed for asymmetric induction not only for amine [5], but also for α- and β-amino acid [6], and *N*-sulfinylaziridine-2-carboxylic acid synthesis [7]. No application of this methodology in aqueous or in mixed aqueous/organic solvent environments has yet been reported. As an extension of our work on water-accelerated carboaluminations of alkynes [8] and α-olefins [9], and the accelerated aromatic *Claisen* rearrangement [10], we were interested in probing the use of a H_2O/alane reagent mixture for allylic amine formation from sulfinimines[1]). Since the addition of stoichiometric quantities of H_2O to organoaluminum reagents generates powerful *Lewis* acid species, we expected significant rate accelerations for C–C bond formations and a potential for orchestrating consecutive addition processes [13].

Results and Discussion. – Treatment of oct-1-yne (**1a**) with a solution of Me_3Al (2 equiv.), Cp_2ZrCl_2 (0.03 equiv.) and H_2O (1 equiv.) in CH_2Cl_2 at 0° provided the methylaluminated intermediate **2a** within 40 min reaction time (*Scheme 1*) [8]. After

[1]) For related organometallic additions to imines, see [1]; for addition involving Mg, see [11a–e], for Li [11f–k], for Cr [11l], for Zn [11m–z]; for recent reviews of imine addition chemistry, see [12].

addition of (*S*)-(*p*-tolyl)sulfinimine **3a**[2]) at $-15°$, the allylic sulfinamide **4a** was obtained in 80% yield and 90% de after 20 h. Imine **3a** was used in 96% enantiomeric excess, and the transfer of chirality in the addition reaction was essentially complete, as shown by *Mosher*-amide analysis [14] (*Scheme 1*). The addition of H_2O enhanced the rate of carboalumination of **1a** significantly [8][15], but it was less clear whether the transient aluminoxane *Lewis* acid present in the reaction mixture was also capable of activating sulfinimine **3a** toward the 1,2-addition reaction with **2a**, and whether this species had any effect on the diastereoselectivity of the process. As a control experiment, we subjected **1a** to a standard [15] methylalumination mediated by 1 equiv. of Cp_2ZrCl_2 for 3 h at room temperature. When catalytic amounts (0.03 equiv.) of Cp_2ZrCl_2 were used, the methylalumination required 12 h to go to completion at room temperature. In both cases, the addition to sulfinimine **3a** at $-15°$ resulted in formation of sulfinamide **4a** with similar reaction times, yields, and diastereoselectivities as for the reaction with added H_2O. Accordingly, the beneficial effects of stoichiometric H_2O in this process appear to be limited to the acceleration of the alkyne carbometalation step from **1a** to **2a**[3]).

Scheme 1. *H_2O-Accelerated Methylalumination of Oct-1-yne Followed by* In Situ *Asymmetric Imine Addition*

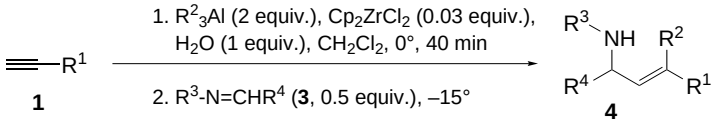


A summary of our investigations of the scope of this new consecutive addition process is shown in the *Table*. When (*S*)-(*p*-tolyl)sulfinimines [3] **3a**–**3e** were used, allylic amides **4a**–**4i** were formed in 72–90% de (*Entries 1–9*). In several cases (*Entries 1*, *5*, *6*, *7*, and *8*), the diastereoselectivity of the imine addition process actually equaled or exceeded 87%. Isolated yields based on sulfinimine ranged from 60% in the ethylalumination process to 85% for the addition to the (naphthalen-2-yl)sulfinimine **3b** [17] (*Entry 2*). The de value of the ethylalumination–sulfinylimine addition product **4c** was slightly lower (78%, *Entry 3*) compared to that of the corresponding

[2]) Prepared in 96% ee according to [3a].

[3]) However, addition of a small amount of H_2O to a reaction mixture containing $AlCl_3$ has been reported to promote nucleophilic additions to α,β-unsaturated aldimines [16].

Table. *Alkyne Carboalumination – Sulfinimine Addition for the Asymmetric Synthesis of Allylic Amines*



Entry	Alkyne **1**, R^1	Alane, R^2	Imine **3**, R^3, R^4, ee [%][a])	Amide **4**, yield [%][b]) (de [%])[c])
1	**1a**, C_6H_{13}	Me	(*S*)-**3a**, (*S*)-(*p*-Me)C_6H_4S(O), Ph, 96	(S_S,*S*)-**4a**, 80 (90)
2	**1a**, C_6H_{13}	Me	(*S*)-**3b**, (*S*)-(*p*-Me)C_6H_4S(O), Naphthalen-2-yl, 97	(S_S,*S*)-**4b**, 85 (83)
3[d])	**1a**, C_6H_{13}	Et	(*S*)-**3a**, (*S*)-(*p*-Me)C_6H_4S(O), Ph, 96	(S_S,*S*)-**4c**, 60 (78)
4	**1a**, C_6H_{13}	Me	(*S*)-**3c**, (*S*)-(*p*-Me)C_6H_4S(O), (*E*)-Cinnamyl, 90	(S_S,*S*)-**4d**, 65 (72)
5	**1a**, C_6H_{13}	Me	(*S*)-**3d**, (*S*)-(*p*-Me)C_6H_4S(O), (*p*-MeO)C_6H_4, 89	(S_S,*S*)-**4e**, 76 (87)
6	**1a**, C_6H_{13}	Me	(*S*)-**3e**, (*S*)-(*p*-Me)C_6H_4S(O), Cyclohexyl, 89	(S_S,*S*)-**4f**, 72 (87)
7	**1b**, *t*-Bu	Me	(*S*)-**3c**, (*S*)-(*p*-Me)C_6H_4S(O), (*E*)-Cinnamyl, 90	(S_S,*S*)-**4g**, 67 (89)
8	**1c**, Ph	Me	(*S*)-**3a**, (*S*)-(*p*-Me)C_6H_4S(O), Ph, 96	(S_S,*S*)-**4h**, 76 (90)
9	**1d**, TIPSO$(CH_2)_3$[e])	Me	(*S*)-**3a**, (*S*)-(*p*-Me)C_6H_4S(O), Ph, 96	(S_S,*S*)-**4i**, 75 (78)
10	**1a**, C_6H_{13}	Me	(*R*)-**3f**, (*R*)-(*t*-Bu)S(O), Ph, 98	(R_S,*R*)-**4j**, 60 (> 95)
11	**1e**, Bu	Me	(*R*)-**3g**, (*R*)-(*t*-Bu)S(O), (*p*-Cl)C_6H_4, 87	(R_S,*R*)-**4k**, 20 (82)
12	**1e**, Bu	Me	(*R*)-**3h**, (*R*)-(*t*-Bu)S(O), Naphthalen-2-yl, 99	(R_S,*R*)-**4l**, 50 (> 98)
13	**1c**, Ph	Me	(*R*)-**3f**, (*R*)-(*t*-Bu)S(O), Ph, 98	(R_S,*R*)-**4m**, 50 (90)
14	**1d**, TIPSO$(CH_2)_3$[e])	Me	(*R*)-**3f**, (*R*)-(*t*-Bu)S(O), Ph, 98	(R_S,*R*)-**4n**, 67 (90)

[a]) Enantiomeric excess is based on optical rotation comparison with literature values. [b]) Yields are based on sulfinimines **3** and refer to isolated products **4**. [c]) Diastereoselectivity was determined by analysis of the crude reaction mixture by 500-MHz ^{1}H-NMR. [d]) Ethylalumination was complete after 1 h at $-20°$. [e]) TIPS = 2,4,6-Triisopropylsilyl.

methylalumination product **4a** (90%, *Entry 1*), and the reaction mixture had to be kept for 36 h at $-15°$ in order to get a significant turnover of alkyne **1a**. The presence of an electron-donating group (*p*-MeO, *Entry 5*) in **3d** [3a] did not appear to effect the reaction or the selectivity. The presence of a conjugated C=C bond in cinnamate **3c** [5a] led to a slight erosion of diastereoselectivity with alkyne **1a**, but not with the bulkier alkyne **1b**; in contrast, aliphatic *C*-substituents at the sulfoximine such as the cyclohexyl derivative **3e** [18] were well tolerated. Phenylacetylene **1c** reacted in good yield and in excellent diastereoselectivity (*Entry 8*). A more highly functionalized alkyne, silyl ether **1d**, was also converted without loss of protective group or a drop in

yield (*Entry 9*). When the addition of the alkenylalane derived from **1c** to imine **3a** (*Entry 8*) was performed in the absence of H_2O, the yield was greatly reduced: after 24 h, only 31% of the allylic amide **4h** was isolated. However, the diastereoselectivity was not affected.

Use of the bulkier (*R*)-(*t*-Bu)S(O) group [4] in substrates **3f**–**3h** led in some cases to an increase in the facial selectivity of the 1,2-addition process (*Entries 10–14*). For example, **4n** was obtained in 90% de from **3f** [4], whereas the analogous conversion of *p*-tolylsulfinimine **3a** to **4i** proceeded in 78% de. Similarly, naphthylimine addition product **4l** was obtained in >98% de from **3h** [19], compared to 83% de for **4b**. In contrast, the same diastereoselectivity was observed for phenylacetylene addition products **4m** and **4h**. Most noteworthy in the comparisons of (*t*-butyl)sulfinimines and (*p*-tolyl)sulfinimines was the consistent drop of 10–20% in isolated yields of addition products for the former substrates. (*t*-Butyl)sulfinimines **3f**–**3h** were noticeably less reactive toward alkenylalane addition than their *S*-tosyl analogs. It is also remarkable that the yield for the *p*-chlorobenzoyl imine **3g** [19] was only 20% in spite of extending the reaction time to 50 h. Unreacted imine **3g** was the major side product.

Further limitations of the reaction scope were found, when internal alkynes were used. Methylalumination of oct-4-yne in the presence of 0.03 equiv. of Cp_2ZrCl_2 and 1 equiv. of H_2O was accomplished after 1 h at $-20°$. However, no sulfinimine-addition product was detected upon addition of **3a** even after stirring for 36 h at room temperature. The use of additives such as MAO [13a][20] or $Yb(OTf)_3$ [21] for activation of the sulfinimine C=N group toward organometallic addition did not promote the desired reaction. In contrast, the internal alkenylalane produced in the methylaluminaton of oct-4-yne readily attacked benzaldehyde at 0° in good yield, either in the presence or absence of H_2O as an additive.

Trisubstituted alkenes **4a**–**4n** were isolated as (*E*)-isomers in >98% selectivity. This assignment was based on the comparison of the ^{1}H-NMR of the crude addition product **4a** to an authentic sample of the (*Z*)-isomer, prepared by halogen/Li exchange of (*Z*)-iodo-2-methyloct-1-ene, followed by addition to **3a**[4]). Since the stereoselectivity of alkyne carboalumination is generally only *ca.* 92% (*E*)-selective, and the regioselectivity of ethylalumination is <80:20 [8][15], it is likely that the isolation of products **4** as clean regio- and (*E*)-isomers is due to a kinetically disfavored imine-addition reaction of the minor, sterically more-hindered internal and (*Z*)-isomer side products. This hypothesis is supported by the lack of allylic amide formation from the methylalumination product of oct-4-yne.

Nucleophilic attack of an organometallic species on the sulfinimine can occur either at the S-atom or at the imine C-atom. The former side reaction has been observed in the treatment of (*S*)-(*p*-tolyl)sulfinimines with *Grignard* reagents [23]. Careful ^{1}H-NMR analysis of our crude reaction mixtures did not reveal the signal pattern that is typical for *S*-substitution products ($-S-CH=CR^1R^2$, 5.8–6.3 ppm) [24]. The chiral auxiliary, *e.g.*, (*S*)-*p*-tolyl- or (*R*)-(*t*-butyl)sulfinyl, neither affected the regioselectivity of addition nor, instead, led to formation of substitution products. The competition between addition and substitution pathways seems to be strongly related to steric

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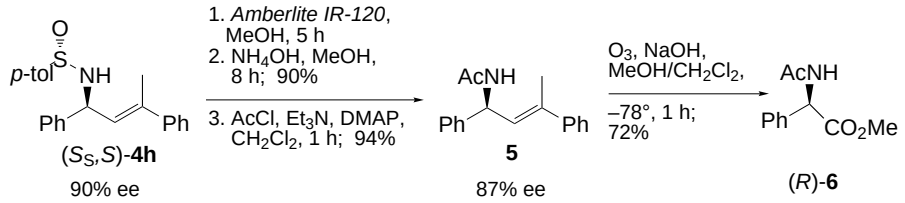
[4]) (*Z*)-1-Iodo-2-methyloct-1-ene was prepared according to [22]. Treatment of this compound with 1 equiv. of BuLi, at $-78°$, followed by the addition of **3a** (0.5 equiv.), afforded the (*Z*)-isomer of **4a**.

interactions in the transition state. Steric hindrance between the bulky organometallic agent and the sulfinyl substituent might prevent an approach to the S-atom, even for the sterically less demanding and more electron-withdrawing *p*-tolylsulfinyl auxiliary.

The absolute configuration of the addition products was determined by oxidative cleavage of the alkene moieties, as shown in *Scheme 2*, which also demonstrated the utility of our approach for α-amino acid synthesis.

Scheme 2. *Oxidative Degradation of Addition Products to Amino Acid Derivatives*

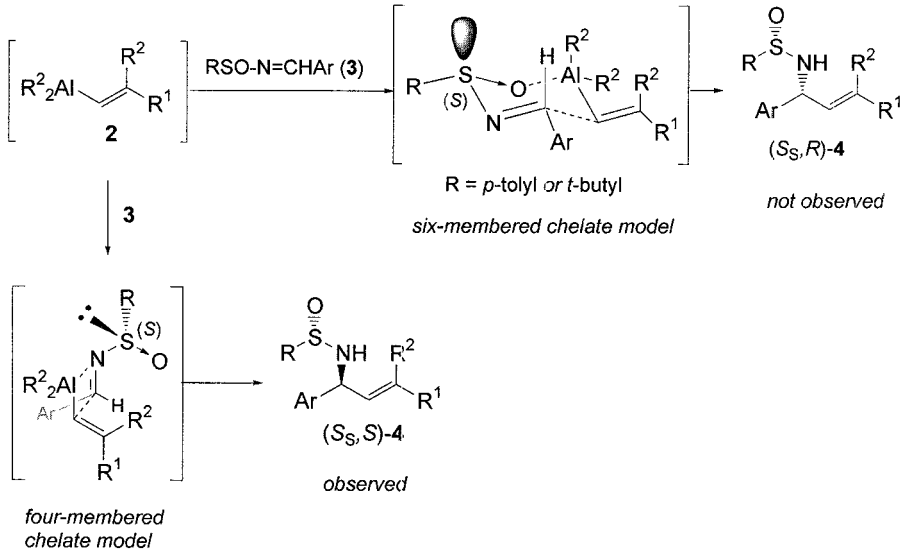


Hydrolysis of the *p*-tolylsulfinyl group of **4h** was readily accomplished by treatment with 3M HCl or 2 equiv. of TFA in MeOH. However, the best yield was achieved with *Amberlite IR-120* suspended in MeOH [25], followed by treatment with NH_4OH to effect release of the product from the resin, affording the free amine in 90% yield and in 87% ee as determined by *Mosher*-amide analysis. *N*-Acetylation furnished 94% of acetamide **5**, which was cleaved under basic ozonolysis conditions [26] to provide the known phenylglycine ester (*R*)-**6**. Interestingly, the specific rotation of (*R*)-**6** was determined as $[\alpha]_D = -164$ ($c = 1.04$, EtOH), which unambiguously indicated the (*R*)-configuration at the stereogenic α-C-atom[5]). Based on the chelating transition state shown in *Scheme 3* and ample literature precedence [1a][3–6], we had expected the (*S*)-configuration in **6** upon usage of the (*S*)-tosylsulfinimine auxiliary. Since the (*R*)-(*t*-butyl)sulfinimine-derived **4m** provided (*S*)-**6** with a specific rotation of $[\alpha]_D = +135$ ($c = 1.05$, EtOH), both chiral auxiliaries favored the same facial selectivity in the addition of the alkenylalane to the imine C-atom. Moreover, we also excluded the possibility that the observed diastereoselectivity was an artifact of the phenylacetylene substrate **1c** used in the synthesis of **4h** and **4m**. When compound **4a** was subjected to ozonolysis, the resulting **6** showed an $[\alpha]_D = -157$ ($c = 1.03$, EtOH), thus further confirming that the initial addition process provided the (*S*)-isomer at the amine α-carbon.

While the stereoselectivity of the addition of *Grignard* reagents to sulfinimines usually follows a six-membered chelate model, organolithiums have been found to provide the opposite pairs of diastereoisomers, and a nonchelate, *Felkin-Anh*-type transition-state model has been postulated to explain the latter effect [5a][11i][28]. Reasons for why the nature of the organometallic reagent is intrinsically correlated with the diastereoselectivity preference of sulfinimine attack are not completely understood, and we prefer to rationalize the facial selectivity of alkenylalane addition with the four-membered chelate model shown in *Scheme 3*. This model is in agreement with all our experimental findings. Based on ground-state semi-empirical calculations

[5]) Literature value: $[\alpha]_D = -174$ ($c = 1.00$, EtOH) [27].

Scheme 3. *Possible Transition States for the Addition of Alkenylalane Reagents to Sulfinylimines*



with both PM3 and AM1 parameterizations, sulfinimines prefer an in-plane, *anti*-orientation of imine-aryl and S–O substituents. Attack of the alane opposite to the bulky *p*-tolyl or *t*-Bu groups, minimizing steric interactions between alkene and aryl substituents, and utilizing the *Lewis* acidity of the aluminum to stabilize the emerging negative charge on the N-atom, rationalizes the formation of the observed major diastereoisomer (S_S,*S*)-**4**. An increase in the steric bulk of the R^2 groups or, in particular, the steric crowding around an internal alkenylalane would lead to considerable destabilizing interactions with the aryl group on the imine and slow down the addition process. The internal chelation between the Al- and the N-atom explains the absence of any accelerating effects of *Lewis* acid additives including the H_2O/alane reaction product.

Conclusions. – We have demonstrated a new application for the H_2O-accelerated carboalumination of terminal alkynes. Upon addition of enantiomerically enriched *N*-sulfinylamines to the reaction mixture, 1,2-addition of the alkenylorganometallic intermediate provides allylic sulfinamides in high yields and in good-to-excellent diastereoselectivities. While stoichiometric H_2O considerably enhances the rate of carboalumination, the subsequent imine addition does not appear to be influenced by the increased *Lewis* acidity of the reaction mixture. In these studies, (*p*-tolyl)sulfinimines proved to be more reactive than the analogous (*t*-butyl)sulfinimines, and the product diastereoselectivities obtained with the two chiral auxiliaries were of the same order of magnitude but varied slightly according to the substituents on imine and alkyne. Internal alkenylalanes, however, proved to be unreactive under the reaction conditions, and this steric deactivation as well as the observed facial selectivity of the addition process could be explained by formation of a four-membered-chelate transition-state model. Competitive substitution at the imine S-atom was not observed,

probably due to steric interactions of the auxiliary with the substituents of the bulky alanes and the relative covalent nature of the Al–C bond, which disfavored this undesired side reaction. The sulfinylamide group in addition products **4** was readily cleaved by treatment with *Amberlite* resin in MeOH, and the allylic amine intermediate could be converted to enantiomerically enriched amino acid derivatives by ozonolysis of the alkene moiety.

Experimental Part

General. All reactions were performed under N_2, and all glassware was dried in an oven at 140° prior to use. Dry CH_2Cl_2 was obtained by distillation from CaH_2. Unless otherwise stated, solvents or reagents were used without further purification. All sulfinimines were synthesized according to literature protocols. [4][5a][17–19]. M.p.: *Mel-Temp* aparatus, not corrected. $[\alpha]_D$ Values: *Perkin-Elmer 241* polarimeter. IR Spectra: *Nicolet AVATAR 360 FTIR E.S.P.* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker DPX-300*, at 300 MHz for ^1H and 75 MHz for ^{13}C, in $CDCl_3$ unless otherwise noted; δ in ppm, J in Hz; 500-MHz NMR spectra: *Bruker DPX-500* instrument. High-resolution (HR) EI-MS: *Autospec VG 70-G* or *VG* double-focusing instrument; *m*/*z* (rel. %).

General Procedure (*GP*) *for Additions to Sulfinimines* **3**. A soln. of Me_3Al (90.0 mg, 1.25 mmol) and Cp_2ZrCl_2 (10.0 mg, 0.0600 mmol) in 3 ml of CH_2Cl_2 was treated at −20° under N_2 with H_2O (11.3 µl, 0.625 mmol). *Caution:* The addition of H_2O to organoalane solns. is exothermic and leads to evolution of CH_4, and for larger-scale reactions the rate of addition should be carefully controlled! The cold bath was removed, and the mixture was allowed to warm to rt. After 10 min, the light yellow soln. was cooled to 0° and treated with 0.625 mmol of alkyne **1**. The soln. turned orange, and, after 40 min, the mixture was cooled to −78°, followed by addition of a soln. of 0.313 mmol of sulfinimine **3** in 1 ml of CH_2Cl_2. After 20–50 h stirring at −15°, 10 ml of sat. NH_4Cl was added dropwise, followed by extraction with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$), filtered, and concentrated. The crude residue was analyzed by 500-MHz ^1H NMR to determine the de value. Chromatography (SiO_2, hexanes/CH_2Cl_2 8:2) afforded pure sulfinamides **4**.

(S_S,S*)-4-Methyl*-N-*(3-methyl-1-phenylnon-2-enyl)benzenesulfinamide* (**4a**). According to the *GP*, 92.2 µl (0.625 mmol) of *oct-1-yne* (**1a**) and 78.0 mg (0.321 mmol) of **3a** afforded, after 20 h at −15°, 94.0 mg (0.257 mmol, 80%) of **4a**. Oil. $[\alpha]_D = +189.8$ ($c = 1.19$, $CHCl_3$). IR (neat): 3196, 2959, 2927, 2856, 1491, 1454, 1089, 1064, 809, 698. ^1H-NMR: 7.60 (*d*, *J* = 6.6, 2 H); 7.29–7.23 (*m*, 7 H); 5.40 (*dq*, *J* = 9.3, 1.2, 1 H); 5.28 (*dd*, *J* = 9.3, 2.5, 1 H); 4.13 (*d*, *J* = 2.2, 1 H); 2.37 (*s*, 3 H); 2.05 (*t*, *J* = 7.1, 2 H); 1.84 (*d*, *J* = 1.3, 3 H); 1.45–1.41 (*m*, 2 H); 1.26–0.89 (br. *m*, 6 H); 0.88 (br. *t*, *J* = 6.8, 3 H). ^{13}C-NMR: 142.6; 142.5; 141.2; 140.6; 129.5; 129.2; 128.8; 128.7; 127.7; 127.5; 127.0; 126.4; 125.7; 125.5; 124.5; 55.3; 39.9; 31.8; 29.0; 27.7; 22.9; 22.8; 21.4; 16.9; 14.2. EI-MS: 230 (25, $[M - MePhSO]^+$), 215 (100). HR-MS: 230.1900 ($[M - MePhSO]^+$, $C_{16}H_{24}N$; calc. 230.1909).

(S_S,S*)-4-Methyl*-N-*[3-methyl-1-(naphthalen-2-yl)non-2-enyl]benzenesulfinamide* (**4b**). According to the *GP*, 92.2 µl (0.625 mmol) of **1a** and 91.0 mg (0.313 mmol) of **3b** afforded, after 24 h at −15°, 0.111 g (0.266 mmol, 85%) of **4b**. Oil. $[\alpha]_D = +128.0$ ($c = 1.09$, $CHCl_3$). IR (neat): 3201, 3053, 2953, 2926, 2855, 1090, 1062, 1017, 810. ^1H-NMR: 7.76 (*d*, *J* = 7.3, 3 H); 7.64–7.54 (*m*, 3 H); 7.48–7.38 (*m*, 3 H); 7.18 (*d*, *J* = 8.1, 2 H); 5.47 (*dq*, *J* = 8.6, 0.7, 1 H); 5.44 (*dd*, *J* = 9.3, 2.0, 1 H); 4.24 (*d*, *J* = 1.8, 1 H); 2.30 (*s*, 3 H); 2.07 (*t*, *J* = 7.4, 2 H); 1.88 (*d*, *J* = 0.7, 3 H); 1.43–1.41 (*m*, 2 H); 1.31–1.16 (br. *m*, 6 H); 0.85 (br. *t*, *J* = 6.5, 3 H). ^{13}C-NMR: 142.2; 141.3; 140.9; 139.9; 133.3; 132.8; 129.5; 128.5; 127.9; 127.7; 126.2; 125.9; 125.7; 125.5; 125.6; 124.3; 55.1; 39.9; 31.8; 29.0; 27.7; 22.8; 21.4; 17.0; 16.9; 14.2. EI-MS: 401 ($[M - H_2O]^+$, 27), 264 (40), 193 (77), 179 (100).

(S_S,S*)-4-Methyl*-N-*(3-ethyl-1-phenylnon-2-enyl)benzenesulfinamide* (**4c**). According to the *GP*, 92.2 µl (0.625 mmol) of **1a** and 76.0 mg (0.313 mmol) of **3a** afforded, after 36 h at −15°, 71.2 mg (0.188 mmol, 60%) of **4c**. Oil. $[\alpha]_D = +144.7$ ($c = 1.69$, $CHCl_3$). IR (neat): 3196, 2959, 2927, 2856, 1491, 1454, 1089, 1064, 809, 698. ^1H-NMR: 7.61 (*d*, *J* = 8.2, 2 H); 7.33–7.21 (*m*, 7 H); 5.40–5.30 (*m*, 2 H); 4.12 (*s*, 1 H); 2.39 (*s*, 3 H); 2.24–2.17 (*m*, 2 H); 2.08 (*t*, *J* = 7.4, 2 H); 1.47–1.42 (*m*, 2 H); 1.30–1.25 (br. *m*, 6 H); 1.06 (*t*, *J* = 7.6, 3 H); 0.87 (br. *t*, *J* = 6.5, 3 H). ^{13}C-NMR: 146.3; 12.7; 141.2; 138.0; 129.5; 128.7; 127.5; 127.1; 125.5; 123.8; 55.0; 36.6; 31.8; 29.1; 27.9; 23.9; 22.7; 21.4; 14.2; 13.3. EI-MS: 244 ($[M - MePhSO]^+$, 20); 229 (100). HR-MS: 244.2046 ([*M* − MePhSO], $C_{18}H_{26}N$; calc. 244.265).

(S_S,R*)-4-Methyl*-N-*[3-methyl-1-(2-phenylethenyl)non-2-enyl]benzenesulfinamide* (**4d**). According to the *GP*, 92.2 µl (0.625 mmol) of **1a** and 84.0 mg (0.313 mmol) of **3c** afforded, after 24 h at −15°, 80.0 mg (0.203 mmol, 65%) of **4d**. Oil. $[\alpha]_D = +115.9$ ($c = 1.01$, $CHCl_3$). IR (neat): 3199, 3025, 2927, 2855, 1492, 1448,

1090, 1066. ^{1}H-NMR: 7.60 (*d*, *J* = 8.2, 2 H); 7.27–7.22 (*m*, 7 H); 6.40 (*d*, *J* = 15.8, 1 H); 6.02 (*dd*, *J* = 15.8, 7.2, 1 H); 5.23 (*dq*, *J* = 8.9, 1.1, 1 H); 4.89 (*ddd*, *J* = 9.3, 7.0, 2.6, 1 H); 3.97 (*d*, *J* = 2.7, 1 H); 2.34 (*s*, 3 H); 2.07 (*t*, *J* = 6.9, 2 H); 1.79 (*d*, *J* = 1.1, 3 H); 1.47–1.36 (*m*, 2 H); 1.28–1.25 (br. *m*, 6 H); 0.87 (br. *t*, *J* = 6.9, 3 H). ^{13}C-NMR: 142.5; 141.3; 141.2; 136.7; 130.8; 129.8; 129.5; 128.6; 127.7; 126.5; 125.6; 122.7; 53.8; 39.9; 31.8; 29.0; 27.7; 22.7; 21.4; 16.9; 14.2. EI-MS: 256 ([*M* – MePhSO]$^+$, 11), 240 (20), 169 (43), 139 (50), 91 (100). HR-MS: 256.2039 ([*M* – MePhSO], $C_{18}H_{26}N$; calc. 256.2065).

(S_S,S*)-4-Methyl*-N-*[1-(4-methoxyphenyl)-3-methylnon-2-enyl]benzenesulfinamide* (**4e**). According to the *GP*, 92.2 µl (0.625 mmol) of **1a** and 86.0 mg (0.313 mmol) of **3d** afforded, after 24 h at −15°, 91.0 mg (0.238 mmol, 76%) of **4e**. Oil. $[\alpha]_D = +113.3$ (*c* = 1.68, $CHCl_3$). IR (neat): 3437, 3224, 2927, 2851, 1611, 1511, 1461, 1245, 1088, 1035, 808, 490. ^{1}H-NMR: 7.58 (*d*, *J* = 8.2, 2 H); 7.24 (*d*, *J* = 8.0, 2 H); 7.22 (*d*, *J* = 6.7, 2 H); 6.80 (*d*, *J* = 6.8, 2 H); 5.35 (*dq*, *J* = 9.2, 0.9, 1 H); 5.23 (*dd*, *J* = 9.2, 2.4, 1 H); 4.07 (*d*, *J* = 2.3, 1 H); 3.76 (*s*, 3 H); 2.38 (*s*, 3 H); 2.05 (*t*, *J* = 7.2, 2 H); 1.81 (*d*, *J* = 1.2, 3 H); 1.45–1.40 (*m*, 2 H); 1.30–1.26 (br. *m*, 6 H); 0.84 (br. *t*, *J* = 6.3, 3 H). ^{13}C-NMR: 159.0; 142.6; 141.2; 140.3; 134.7; 129.5; 128.2; 125.5; 124.6; 114.1; 55.4; 54.8; 39.9; 31.8; 29.0; 27.7; 22.7; 21.4; 16.8; 14.2. EI-MS: 244 ([*M* – MePhSO]$^+$, 25); 215 (100). HR-MS: 244.1846 ([*M* – MePhSO], $C_{14}H_{28}OS$; calc. 244.1861).

(S_S,R*)-4-Methyl*-N-*(1-cyclohexyl-3-methylnon-2-enyl)benzenesulfinamide* (**4f**). According to the *GP*, 92.2 µl (0.625 mmol) of **1a** and 78.0 mg (0.313 mmol) of **3e** afforded, after 20 h at −15°, 84.0 mg (0.225 mmol, 72%) of **4f**. Oil. $[\alpha]_D = +86.3$ (*c* = 1.18, $CHCl_3$). IR (neat): 3203, 2925, 2853, 1450, 1089, 1058, 1016, 810, 443. ^{1}H-NMR: 7.57 (*d*, *J* = 8.5, 2 H); 7.28 (*d*, *J* = 8.0, 2 H); 5.09 (*dq*, *J* = 9.7, 1.2, 1 H); 3.98–3.92 (*m*, 1 H); 3.84 (*d*, *J* = 2.7, 1 H); 2.40 (*s*, 3 H); 2.07 (*t*, *J* = 7.2, 2 H); 1.72 (*d*, *J* = 1.3, 3 H); 1.70–1.60 (br. *m*, 4 H); 1.47–1.42 (*m*, 2 H); 1.34 (br. *m*, 6 H); 1.19–1.09 (*m*, 3 H); 1.00–0.92 (*m*, 2 H); 0.87 (br. *t*, *J* = 6.8, 3 H). ^{13}C-NMR: 143.4; 141.1; 140.9; 129.5; 125.6; 124.7; 122.9; 56.7; 43.9; 40.0; 31.8; 29.8; 28.9; 28.3; 27.8; 26.5; 26.3; 26.2; 22.8; 21.4; 16.9; 14.2. EI-MS: 375 (*M*$^+$, 27), 357 (20), 292 (100). HR-MS: 375.2595 ($C_{23}H_{37}NOS$; calc. 375.2596).

(S_S,R*)-4-Methyl*-N-*[3,4,4-trimethyl-1-(2-phenylethenyl)pent-2-enyl]benzenesulfinamide* (**4g**). According to the *GP*, 77.0 µl (0.625 mmol) of *3,3-dimethylbut-1-yne* (**1b**) and 84.0 mg (0.313 mmol) of **3c** afforded, after 20 h at −15°, 72.0 mg (0.210 mmol, 67%) of **4g**. Colorless solid. M.p. 11°. $[\alpha]_D = +141.8$ (*c* = 1.27, $CHCl_3$). IR (neat): 3196, 2963, 1089, 1063, 693. ^{1}H-NMR: 7.61 (*d*, *J* = 8.2, 2 H); 7.30–7.22 (br. *m*, 7 H); 6.36 (*d*, *J* = 15.9, 1 H); 6.02 (*dd*, *J* = 15.9, 7.4, 1 H); 5.28 (*q*, *J* = 8.7, 0.9, 1 H); 4.88 (*ddd*, *J* = 8.1, 6.9, 2.9, 1 H); 3.99 (*d*, *J* = 2.6, 1 H); 2.33 (*s*, 3 H); 1.80 (*d*, *J* = 0.9, 3 H); 1.09 (*s*, 9 H). ^{13}C-NMR: 148.5; 142.5; 141.3; 136.7; 130.8; 129.8; 129.5; 128.6; 127.7; 126.5; 125.6; 119.9; 54.0; 36.7; 29.0; 21.4; 13.7. EI-MS: 349 ([*M* – H_2O]$^+$, 10), 155 (45), 139 (35), 91 (100).

(S_S,S*)-4-Methyl*-N-*(1,3-diphenylbut-2-enyl)benzenesulfinamide* (**4h**)**.** According to the *GP*, 70.6 µl (0.625 mmol) of *phenylacetylene* (**1c**) and 76.0 mg (0.313 mmol) of **3a** afforded, after 24 h at −15°, 86.0 mg (0.238 mmol, 76%) of **4h**. Oil. $[\alpha]_D = +119.4$ (*c* = 1.35, $CHCl_3$). IR (neat): 3196, 3056, 3027, 2920, 1492, 1447, 1089, 1063, 1015, 810, 755, 698. ^{1}H-NMR: 7.71 (*d*, *J* = 8.2, 2 H); 7.52 (*d*, *J* = 7.0, 2 H); 7.44–7.30 (*m*, 10 H); 6.09 (*dq*, *J* = 9.2, 0.4, 1 H); 5.53 (*dd*, *J* = 9.2, 2.8, 1 H); 4.37 (*d*, *J* = 2.4, 1 H); 2.47 (*s*, 3 H); 2.34 (*d*, *J* = 1.0, 3 H). ^{13}C-NMR: 143.2; 142.3; 141.9; 141.5; 138.8; 129.6; 128.9; 128.4; 127.9; 127.6; 127.3; 126.2; 125.6; 55.8; 21.5; 16.9. EI-MS: 222 ([*M* – MePhSO]$^+$, 22), 206 (95), 139 (55), 91 (100). HR-MS: 222.3157 ([*M* – MePhSO], $C_{16}H_{16}N$; calc. 222.3139).

(S_S,S*)-4-Methyl*-N-*[3-methyl-1-phenyl-6-(triisopropylsilyloxy)hex-2-enyl]benzenesulfinamide* (**4i**). According to the *GP*, 150 µl (0.625 mmol) of *5-(triisopropylsilyloxy)pent-1-yne* (**1d**) and 76.0 mg (0.313 mmol) of **3a** afforded, after 20 h at −15°, 0.113 g (0.235 mmol, 75%) of **4i**. Oil. $[\alpha]_D = +102.4$ (*c* = 1.47, $CHCl_3$). IR (neat): 3195, 2941, 2865, 1462, 1093, 1067, 882, 681. ^{1}H-NMR: 7.60 (*d*, *J* = 6.6, 2 H), 7.30–7.20 (*m*, 7 H); 5.43 (*dq*, *J* = 9.3, 1.2, 1 H); 5.28 (*dd*, *J* = 9.3, 2.4, 1 H); 4.12 (*d*, *J* = 2.3, 1 H); 3.65 (*t*, *J* = 6.5, 2 H); 2.37 (*s*, 3 H); 2.15 (*t*, *J* = 6.9, 2 H); 1.87 (*d*, *J* = 1.2, 3 H); 1.73–1.61 (*m*, 3 H); 1.05–1.00 (*m*, 18 H). ^{13}C-NMR: 142.5; 141.2; 140.1; 129.5; 128.8; 128.7; 127.7; 127.5; 127.1; 125.5; 124.7; 62.9; 55.3; 36.1; 31.0; 21.4; 18.1; 16.9; 12.1. EI-MS: 345 ([*M* – MePhSONH]$^+$, 45), 171 (100).

(R_S,R*)-1,1-Dimethyl*-N-*(3-methyl-1-phenylnon-2-enyl)ethanesulfinamide* (**4j**). According to the *GP*, 92.2 µl (0.625 mmol) of **1a** and 65.0 mg (0.313 mmol) of **3f** afforded, after 24 h at −15°, 63.0 mg (0.188 mmol, 60%) of **4j**. Oil. $[\alpha]_D = -17.7$ (*c* = 1.00, $CHCl_3$). IR (neat): 3199, 2956, 2928, 2857, 1455, 1363, 1063, 699. ^{1}H-NMR: 7.55 (*d*, *J* = 8.3, 2 H); 7.36–7.18 (*m*, 5 H); 5.63 (*dq*, *J* = 8.9, 1.2, 1 H); 5.54 (*dd*, *J* = 8.9, 2.7, 1 H); 3.41 (*d*, *J* = 1.9, 1 H); 2.01 (*t*, *J* = 7.1, 2 H); 1.82 (*d*, *J* = 1.0, 3 H); 1.44–1.28 (*m*, 6 H); 1.14 (*s*, 9 H); 1.01 (*t*, *J* = 6.7, 3 H). ^{13}C-NMR: 142.4; 139.5; 128.6; 127.6; 127.5; 125.9; 56.5; 55.7; 39.7; 31.8; 29.0; 27.7; 22.7; 16.8; 14.2. EI-MS: 260 ([*M* – H_2O]$^+$, 47), 215 (100). HR-MS: 260.1467 ([*M* – H_2O], $C_{16}H_{22}NS$; calc. 260.1473).

(R_S,R*)-1,1-Dimethyl*-N-*[1-(4-chlorophenyl)-3-methylhept-2-enyl]ethanesulfinamide* (**4k**). According to the *GP*, 74.6 µl (0.625 mmol) of hex-1-yne (**1e**) and 76.0 mg (0.313 mmol) of **3g** afforded, after 50 h at −15°, 22.0 mg (0.0630 mmol, 20%) of **4k**. Oil. $[\alpha]_D = -14.1$ (*c* = 1.20, $CHCl_3$). IR (neat): 3194, 2956, 2928, 2870, 1489,

1456, 1363, 1062, 1014, 822. ^{1}H-NMR: 7.29 (*s*, 4 H); 5.28 (*dq*, *J* = 8.8, 1.2, 1 H); 5.17 (*dd*, *J* = 8.8, 2.2, 1 H); 3.28 (*d*, *J* = 2.1, 1 H); 2.00 (*t*, *J* = 7.1, 2 H); 1.76 (*d*, *J* = 1.3, 3 H); 1.38–1.23 (*m*, 4 H); 1.19 (*s*, 9 H); 0.85 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR: 140.9; 140.1; 133.2; 128.9; 128.8; 125.4; 55.9; 55.7; 39.4; 29.9; 22.7; 22.5; 16.9; 14.1. EI-MS: 323 ([*M* – H_2O]$^+$, 40), 237 (100). HR-MS: 323.1485 ([*M* – H_2O], $C_{18}H_{26}NSCl$; calc. 323.1474).

(R_S,R*)-1,1-Dimethyl*-N-*[3-methyl-1-(naphthalen-2-yl)hept-2-enyl]ethanesulfinamide* (**4l**). According to the *GP*, 74.6 µl (0.625 mmol) of **1e** and 80.0 mg (0.313 mmol) of **3h** afforded, after 50 h at −15°, 55.0 mg (0.156 mmol, 50%) of **4l**. Oil. $[\alpha]_D = -18.2$ (*c* = 2.1, $CHCl_3$). IR (neat): 3444, 3200, 3054, 2956, 2928, 2869, 1456, 1379, 1363, 1062, 817, 745. ^{1}H-NMR: 7.83–7.70 (*m*, 4 H); 7.49–7.44 (*m*, 3 H); 5.45 (*dq*, *J* = 8.8, 1.2, 1 H); 5.36 (*dd*, *J* = 8.7, 1.5, 1 H); 3.38 (br. *s*, 1 H); 2.00 (*t*, *J* = 6.7, 2 H); 1.81 (*d*, *J* = 1.2, 3 H); 1.40–1.33 (*m*, 2 H); 1.23 (*s*, 9 H); 0.87 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR: 139.9; 139.6; 133.4; 132.9; 128.5; 128.0; 127.8; 126.5; 126.2; 125.9; 125.6; 125.6; 56.7; 55.6; 39.4; 29.9; 22.7; 22.5; 16.9; 14.0. EI-MS: 282 ([*M* – (*t*-Bu)OH]$^+$, 15), 237 (100). HR-MS: 282.1317 ([*M* – (*t*-Bu)OH], $C_{18}H_{20}NS$; calc. 282.1316).

(R_S,R*)-1,1-Dimethyl*-N-*(1,3-diphenylbut-2-enyl)ethanesulfinamide* (**4m**). According to the *GP*, 70.6 µl (0.625 mmol) of **1c** and 65.0 mg (0.313 mmol) of **3f** afforded, after 36 h at −15°, 51.0 mg (0.156 mmol, 50%) of **4m**. Oil. $[\alpha]_D = -44.4$ (*c* = 1.14, $CHCl_3$). IR (neat): 3193, 3028, 2956, 1492, 1452, 1059, 757, 698. ^{1}H-NMR: 7.47–7.40 (*m*, 10 H); 6.03 (*dq*, *J* = 9.0, 1.4, 1 H); 5.47 (*dd*, *J* = 9.0, 3.1, 1 H); 3.56 (*d*, *J* = 3.0, 1 H); 3.30 (*d*, *J* = 1.4, 3 H); 1.32 (*s*, 9 H). ^{13}C-NMR: 142.7; 141.6; 137.7; 128.9; 128.8; 128.4; 127.8; 127.7; 127.6; 126.1; 57.2; 55.8; 22.7; 16.7. EI-MS: 309 ([*M* – H_2O]$^+$, 30), 238 (35), 207 (100). HR-MS: 309.1554 ([*M* – H_2O], $C_{20}H_{23}NS$; calc. for 309.1551).

(R_S,R*)-1,1-Dimethyl*-N-*[3-methyl-1-phenyl-6-(triisopropylsilyloxy)hex-2-enyl]ethanesulfinamide* (**4n**). According to the *GP*, 150 µl (0.625 mmol) of **1d** and 65.0 mg (0.313 mmol) of **3f** afforded, after 48 h at −15°, 93.0 mg (0.210 mmol, 67%) of **4n**. Oil. $[\alpha]_D = -16.2$ (*c* = 1.20, $CHCl_3$). IR (neat): 2942, 2865, 1461, 1104, 1066, 882, 697, 681. ^{1}H-NMR: 7.34–7.29 (*m*, 5 H); 5.37 (*dq*, *J* = 9.0, 1.2, 1 H); 5.20 (*dd*, *J* = 9.0, 2.6, 1 H); 3.61 (*td*, *J* = 6.4, 2.4, 2 H); 3.29 (*d*, *J* = 2.5, 1 H); 2.07 (*t*, *J* = 7.9, 2 H); 1.79 (*d*, *J* = 1.3, 3 H); 1.67–1.60 (*m*, 3 H); 1.20 (*s*, 9 H); 1.05–1.00 (*m*, 18 H). ^{13}C-NMR: 142.3; 138.9; 128.6; 127.6; 127.5; 126.3; 62.8; 56.5; 55.6; 35.9; 31.0; 22.7; 18.1; 16.9; 12.0. EI-MS: 466 (M^+, 15), 171 (100).

*Methyl (*R*)-2-(Acetylamino)-2-phenylacetate* (**6**). A soln. of **4h** (180 mg, 0.500 mmol) in 15.0 ml of MeOH was treated with *Amberlite IR-120* ion-exchange resin (500 mg) in one portion at r.t.[6]). The resulting heterogeneous mixture was slowly stirred at r.t. for 5 h. Analysis by TLC (AcOEt/hexanes 1:2) showed complete disappearance of the starting material. The resin, which contained the deprotected product, was separated by filtration and then washed with MeOH (3 × 15 ml). The free amine was released from the resin by immersion in 15% NH_4OH/MeOH soln. (15 ml) for 8 h. The resin was filtered off and washed with MeOH (3 × 10 ml). The combined filtrates were concentrated to dryness to give the free amine derivative of **4h** (100 mg, 90%): ^{1}H-NMR: 7.44–7.25 (*m*, 10 H); 5.93 (*dq*, *J* = 8.8, 1.3, 1 H); 4.94 (*d*, *J* = 8.8, 1 H); 2.16 (*d*, *J* = 1.3, 3 H); 1.61 (*s*, 2 H). This amine (100 mg, 0.450 mmol) was dissolved in 5 ml of CH_2Cl_2 and cooled to 0°. Et_3N (95.0 µl, 0.680 mmol), AcCl (48.0 µl, 0.680 mmol), and one small crystal of 4-(dimethylamino)pyridine were added, and the reaction was allowed to proceed for 1 h. H_2O was added, and the org. layer was separated, dried ($MgSO_4$), concentrated and purified by chromatography (SiO_2; CH_2Cl_2/AcOEt 1:1). Compound **5** was obtained as an oil (101 mg, 94%): ^{1}H-NMR: 7.48–7.33 (*m*, 10 H); 6.60 (*d*, *J* = 7.9, 1 H); 6.11 (*t*, *J* = 8.6, 1 H); 5.97 (*d*, *J* = 8.7, 1 H); 2.26 (*s*, 3 H); 2.08 (*s*, 3 H). A mixture of **5** (101 mg, 0.420 mmol) dissolved in 10 ml of CH_2Cl_2 and 2 ml of a NaOH soln. in MeOH (2.5M, 4.20 mmol) was bubbled, for 1 h at −8°, with a stream of O_3. The soln. turned from orange to light blue at the end of the reaction. H_2O was added, and the org. layer was separated. The aq. layer was extracted with CH_2Cl_2, and the combined org. layers were dried ($MgSO_4$), filtered, concentrated, and purified by chromatography (SiO_2; AcOEt/hexanes 20:80) to afford pure **6** [27] as a colorless solid (62.3 mg, 72%). $[\alpha]_D = -164$ (*c* = 1.04, EtOH); ^{1}H- NMR: 7.35–7.28 (*m*, 5 H); 6.63 (br. *d*, *J* = 7.3, 1 H); 5.57 (*d*, *J* = 7.3, 1 H); 3.71 (*s*, 3 H); 2.00 (*s*, 3 H).

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6) For the analogous hydrolysis of the (*t*-butyl)sulfinyl group of **4m**, TFA (2 equiv.) in MeOH was used instead.

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