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Enantiodivergent, Catalytic Asymmetric Synthesis of γ-Amino Vinyl Sulfones

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A set of diversely substituted *N*-Boc-γ-amino vinyl sulfones has been prepared by a four-step procedure from readily available, highly enantiopure *anti*-*N*-Boc-3-amino-1,2-alkanediols. This new route, which does not depend on the accessibility of α-amino acids as starting materials, is noteworthy for its efficiency, for its generality, and for the fact that both enantiomers of a given γ-amino vinyl sulfone can be obtained with equal ease.

Introduction

Cysteine proteases are a subclass of peptide bond cleaving hydrolases that can be found in viruses, bacteria, protozoa, fungi, plants, and mammals.[1] The biological activity spectrum of these enzymes is very broad: they have been found to be involved in mammalian cellular turnover and apoptosis, in the replication process of human rhinovirus, and in the life cycle of many parasitic protozoa and worms.[2] Inhibition of cysteine proteases constitutes therefore an important strategy to develop new drugs for treatment of tumors, inflammatory diseases, infections with viruses (common cold), and bacterial and protozoa infections (malaria, Chagas' disease, leishmaniasis). In 1995, researchers from Khepri Pharmaceuticals first reported the use of peptidyl vinyl sulfones (Figure 1) as potent and selective inhibitors of cysteine proteases.[3] Further investigations led to the development of a peptidyl vinyl sulfone inhibitor of falcipain that markedly delayed the progression of murine malaria upon in vivo evaluation.[4,5] Peptidyl vinyl sulfones have also been shown to be useful inhibitors of the proteasome and of its bacterial homologue HsIVU.[6]

Despite this remarkable biomedicinal significance, synthetic routes to the requisite enantiopure γ-amino vinyl sulfones are very limited, being invariably based on stereospecific transformations of chiral nonracemic α-amino acids.[3a,7] In particular, these procedures involve the preparation either of α-amino aldehydes[3a] (a class of compounds that can be very prone to racemization)[8] or of α-amino diazoketones[7] and are therefore not easily amenable to scale up or to extensive structural modifications in the final products. We felt, accordingly, that the development of a more general method that would not rely on the availability of a precise α-amino acid and that could afford with equal ease both enantiomers of a given γ-amino vinyl sulfone was a worthy objective and could be instrumental in the optimization of the pharmacological properties of peptidyl vinyl sulfone-based drugs. We wish to report in this paper full details of a short and efficient synthesis of N-protected γ-amino vinyl sulfones that fulfills the above requirements.

Results and Discussion

A simple retrosynthetic analysis of γ-amino vinyl sulfones (Scheme 1) showed that they should be readily accessed from *anti*-*N*-Boc-3-amino-1,2-alkanediols, by a series of synthetic operations that imply the substitution of the primary hydroxyl by an aryl or alkyl thiolate, oxidation of the sulfide to the sulfone level, and elimination of the secondary hydroxyl. The starting 3-amino-1,2-alkanediols, whose chemistry we have been exploring in the past years,[9] can be obtained in a highly enantioselective fashion[10] through catalytic asymmetric Sharpless epoxidation of allylic alcohols[11] and seemed to be ideally suited to our purposes.

We decided to prepare a structurally diverse set of *N*-Boc-γ-amino vinyl sulfones, to assess the generality of our projected method. We selected therefore as starting

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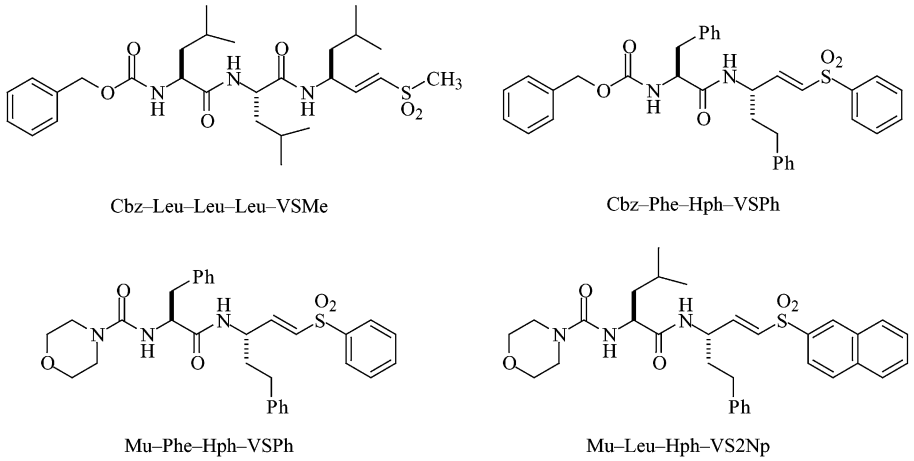

FIGURE 1. Representative peptidyl vinyl sulfone inhibitors.

SCHEME 1

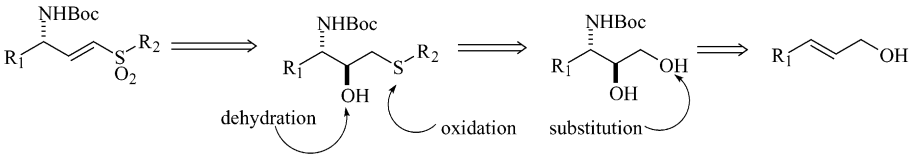

CHART 1

1a (R_1 = Ph)
1b (R_1 = $PhCH_2$)
1c (R_1 = $PhCH_2CH_2$)
1d (R_1 = $(CH_3)_2CHCH_2$)
1e (R_1 = $TBDMSOCH_2CH_2CH_2$)

2a (R_2 = Ph)
2b (R_2 = CH_3)
2c (R_2 = 2-Naphthyl)

materials the amino diols **1a**−**e** and the thiols **2a**−**c** (Chart 1). Whereas most of the R_1 and R_2 residues were chosen on the basis of their occurrence in known peptidyl vinyl sulfone inhibitors (see Figure 1), the phenyl moiety in R_1 was specifically selected in order to provide an entry to γ-aryl-γ-amino vinyl sulfones, a class of compounds that is virtually unknown in the chemical literature,[12] and whose enantioselective preparation through the corresponding stereochemically labile α-amino-α-aryl aldehydes would be particularly challenging. Amino diol **1e**, bearing an alkoxyalkyl residue, was selected to demonstrate the applicability of the method to the preparation of more functionalized compounds.

The required *anti*-*N*-Boc-3-amino-1,2-alkanediols **1a**−**e** were prepared in high enantiomeric purity (ee >95%) according to our previously described procedure (Scheme 2), which involves the catalytic asymmetric Sharpless epoxidation of an (*E*)-allylic alcohol followed by the regio- and stereoselective oxirane ring opening by an ammonia equivalent (azide ion or benzhydrylamine).[10]

The selective replacement of the primary hydroxyl group in **1a**−**e** by an alkyl- or arylsulfonyl moiety was effected by a three-step sequence summarized in Scheme 3 and in Table 1.

In the first place, amino diols **1a**−**e** were submitted to Mitsunobu cyclization conditions (1.07 molar equiv of triphenylphosphine and 1.07 molar equiv of diisopropyl azodicarboxylate in refluxing chloroform) to afford the *anti*-*N*-Boc-(1-aminoalkyl) epoxides **3a**−**e** in good yields after chromatographic purification.[13] Subsequent reaction of these epoxides with 1 molar equiv of thiophenol **2a** in the presence of triethylamine led to the selective formation of the hydroxy sulfides **4aa**−**ea**. In a similar way, the reaction of **3c** with 2-naphthalenethiol (2-NpSH, **2c**) afforded the hydroxy sulfide **4cc**. The introduction of a thiomethyl group was achieved by treatment of the epoxides with sodium methanethiolate in refluxing methanol, to give the hydroxy sulfides **4ab**−**4db**. It is worth noting here that the use of an excess of sodium methanethiolate and of prolonged reaction times completely diverts the course of the process, since in these conditions the initially formed hydroxy sulfide cyclizes to an oxazolidinone (Scheme 4).[14] The oxidation of the hydroxy sulfides **4** with 2.5 molar equiv of *m*-chloroperbenzoic

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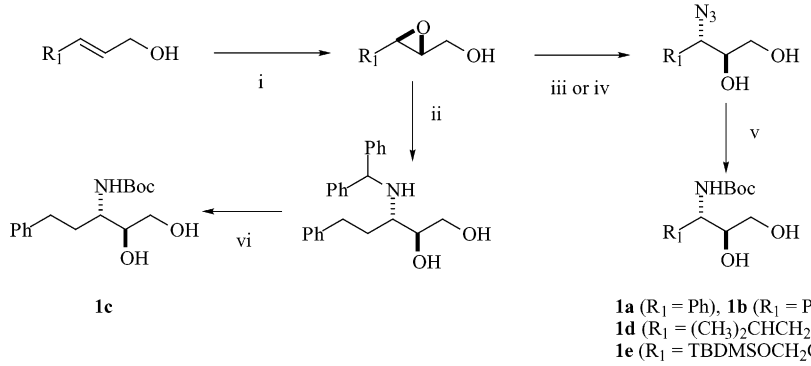
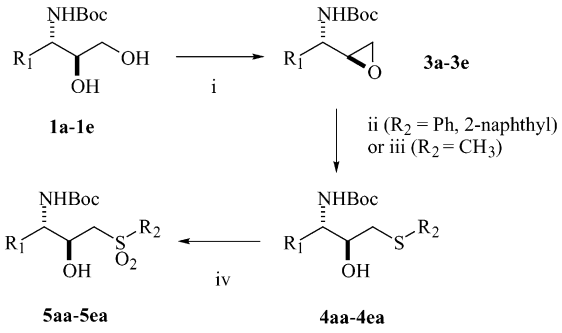
SCHEME 2[a]



[a] Reagents and conditions: (i) cat. $Ti(O^iPr)_4$, cat. D-(−)-DIPT, ^tBuOOH, CH_2Cl_2, −20 °C, 80−90%; (ii) Ph_2CHNH_2, $Ti(O^iPr)_4$, CH_2Cl_2, rt, 70%; (iii) NaN_3, $LiClO_4$, CH_3CN, reflux, 94% (R_1 = Ph); (iv) $Ti(O^iPr)_2(N_3)_2$, benzene, reflux, 100% (R_1 = $PhCH_2$), 93% (R_1 = $(CH_3)_2CHCH_2$), 55% (R_1 = $TBDMSOCH_2CH_2CH_2$); (v) H_2, cat. 10% Pd/C, Boc_2O, EtAcO, rt, 82% (R_1 = Ph), 92% (R_1 = $PhCH_2$), 80% (R_1 = $(CH_3)_2CHCH_2$), 85% (R_1 = $TBDMSOCH_2CH_2CH_2$); (vi) H_2, cat. 10% $Pd(OH)_2$/C, Boc_2O, EtOAc, rt, 93%.

SCHEME 3[a]



[a] Reagents and conditions: (i) PPh_3, DIAD, $CHCl_3$, reflux; (ii) thiophenol or 2-naphthalenethiol, NEt_3, CH_3OH, reflux; (iii) sodium methanethiolate (1.1 equiv), CH_3OH, reflux; (iv) *m*-CPBA, CH_2Cl_2, rt.

TABLE 1. Synthesis of *N*-Boc-3-amino-2-hydroxy Sulfones 5 from *N*-Boc-3-amino-1,2-alkanediols 1

R_1	epoxide **3** (% yield)	R_2	sulfide **4** (% yield)[a]	sulfone **5** (% yield)[a]
Ph	**3a** (86)	Ph	**4aa** (100)	**5aa** (100)
		CH_3	**4ab** (84)	**5ab** (100)
$PhCH_2$	**3b** (75)	Ph	**4ba** (100)	**5ba** (81)
		CH_3	**4bb** (92)	**5bb** (80)
$PhCH_2CH_2$	**3c** (92)	Ph	**4ca** (78)	**5ca** (100)
		CH_3	**4cb** (78)	**5cb** (79)
		2-naphthyl	**4cc** (87)	**5cc** (87)
$(CH_3)_2CHCH_2$	**3d** (95)	Ph	**4da** (84)	**5da** (97)
		CH_3	**4db** (86)	**5db** (86)
$TBDMSO(CH_2)_3$	**3e** (81)	Ph	**4ea** (89)	**5ea** (85)

[a] Isolated yields of analytically pure products.

acid took place uneventfully, and the corresponding 2-hydroxy sulfones **5** were obtained in good to excellent yields.

We next selected the hydroxy sulfone **5ca** for the evaluation of the reaction conditions for the dehydration step. Contrary to the related precedent of Sengupta et al.,[7] we found that neither pyridine nor triethylamine could effect, at room temperature, the elimination of the mesylate formed in situ. On the other hand, when **5ca** was treated successively with mesyl chloride and 4-(dimethylamino)pyridine in dichloromethane at room temperature, the desired product **6ca** was obtained in quantitative yield and in analytically pure form after a rapid chromatographic purification on triethylamine-pretreated silica gel. Under these optimized conditions, the remaining γ-alkyl-γ-amino vinyl sulfones **6ba**, **6bb**, **6cb**, **6cc**, **6da**, **6db**, and **6ea** were also readily accessed from the corresponding hydroxy sulfones (Scheme 5). In no cases could the presence of the isomer of (*Z*) configuration be detected.

However, when this synthetic protocol was applied to the aryl-substituted hydroxy sulfone **5aa**, the exclusive product was the achiral β,γ-unsaturated sulfone **8**, probably arising from base-catalyzed isomerization of the expected vinyl sulfone **6aa**. Even when 1 molar equiv of triethylamine was used in the mesylate elimination step, a 1:1 mixture of **6aa** and of the rearranged product **8** was obtained (Scheme 6).

To avoid this unwelcome isomerization, a variety of dehydration conditions that take place in the absence of either strong bases or acids[15] were investigated. Best results were obtained by the use of the water-soluble carbodiimide morpho-CDI in the presence of catalytic amounts of copper(II) chloride.[16] Under these conditions, the phenyl-substituted hydroxy sulfones **5aa** and **5ab** were converted into the corresponding vinyl sulfones **6aa** and **6ab** in essentially quantitative yields (Scheme 7).[17] In this way, γ-aryl-γ-amino vinyl sulfones have been enantioselectively prepared for the first time.

In summary, we have developed a short (four steps) and efficient (average yields from 87% to 98% for each one of the steps) route to alkyl- or aryl-substituted *N*-Boc-γ-amino vinyl sulfones **6** from readily available, highly enantiopure *N*-Boc-3-amino-1,2-alkanediols **1**, that takes place without loss of optical purity.[18] Moreover, since the

(15) See: Bartoli, G.; Bellucci, M. C.; Petrini, M.; Marcantoni, E.; Sambri, L.; Torregiani, E. *Org. Lett.* **2000**, *2*, 1791−1793, and references therein.

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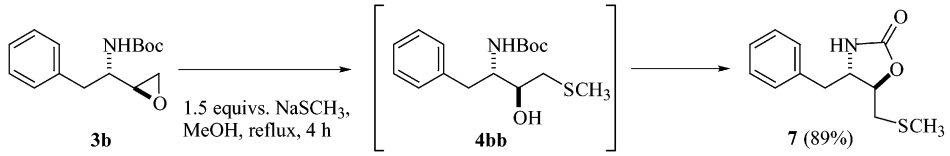
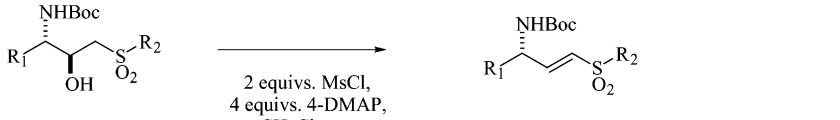
(17) This dehydration procedure can also be applied to the alkyl-substituted β-hydroxy sulfones. Thus, compound **5cc** (3 molar equiv morpho-CDI, cat. $CuCl_2$, CH_3CN, reflux, 11 h) afforded the corresponding vinyl sulfone **6cc** in 92% yield.

(18) Both the melting point and the rotatory power of the known vinyl sulfone **6bb** were higher than those reported in the literature.[19] Moreover, HPLC analysis established a 95% ee for this compound (see Experimental Section).

SCHEME 4

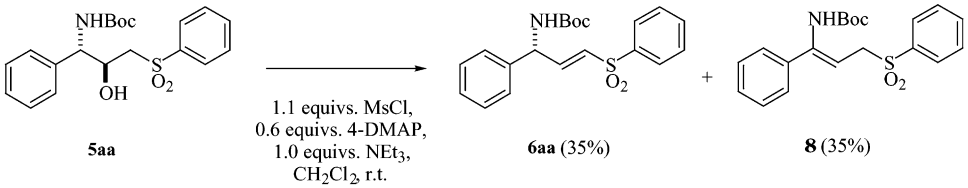


SCHEME 5

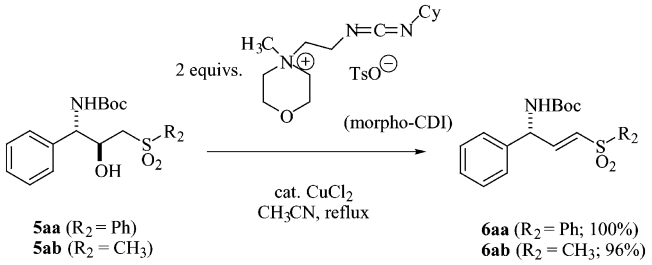


6ba (R_1 = $PhCH_2$, R_2 = Ph; 94%)
6bb (R_1 = $PhCH_2$, R_2 = CH_3; 100%)
6ca (R_1 = $Ph(CH_2)_2$, R_2 = Ph; 100%)
6cb (R_1 = $Ph(CH_2)_2$, R_2 = CH_3; 100%)
6cc (R_1 = $Ph(CH_2)_2$, R_2 = 2-naphthyl; 100%)
6da (R_1 = $(CH_3)_2CHCH_2$, R_2 = Ph; 94%)
6db (R_1 = $(CH_3)_2CHCH_2$, R_2 = CH_3; 89%)
6ea (R_1 = $TBDMSO(CH_2)_3$, R_2 = Ph; 100%)

SCHEME 6



SCHEME 7



starting materials can be obtained from a variety of allyl alcohols in both enantiomeric forms, the present procedure is more flexible and general than those previously described and is therefore particularly well suited for the optimization of the pharmacological properties of peptidyl vinyl sulfone-based protease inhibitors. Contrary to the case of γ-hydroxy vinyl sulfones,[20] the chemistry of γ-amino vinyl sulfones remains practically unexplored. Ongoing work in our laboratory is currently centered on the study of these biologically interesting compounds.

Experimental Section

General Materials and Methods. Melting points were determined in an open capillary tube and are uncorrected. Optical rotations were measured at room temperature (23 °C); concentrations are given in g 100 mL^{-1}. Infrared spectra were recorded in a Fourier transform mode, using the NaCl film technique. Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ solution. Chemical shifts are given in ppm and referenced to TMS or $CHCl_3$. Carbon multiplicities were established by DEPT experiments. Elemental analyses were performed by the "Servicios Xerais de Apoio á Investigación, Universidade da Coruña". Exact mass measurements (HRMS) were performed by the "Unidad de Espectrometría de Masas de la Universidad de Santiago de Compostela". Reactions were generally run in flame- or oven-dried glassware under a N_2 atmosphere. Commercially available reagents were used as received. Diethyl ether used in the reactions was dried by distillation over metallic sodium and benzophenone. Dichloromethane, chloroform, acetonitrile, and triethylamine were distilled from calcium hydride. *N*-Boc-3-amino-1,2-alkanediols **1a**−**e** were prepared according to our previously described procedures.[10b,21]

Typical Procedure for the Preparation of *N*-Boc-1-(1-aminoalkyl)epoxides: (*S*)-[(*S*)-1-(*tert*-Butoxycarbonylamino)-3-phenylpropyl]oxirane (3c). To a solution of (2*S*,3*S*)-*N*-Boc-3-amino-5-phenylpentane-1,2-diol **(1c)** (0.10 g, 0.34 mmol) and of triphenylphosphine (95 mg, 0.36 mmol) in anhydrous chloroform (2 mL), a solution of diisopropyl azodicarboxylate (71 μL, 0.36 mmol) in anhydrous chloroform (1 mL) was added in one portion. The resulting mixture was heated to reflux for 20 h, after which time TLC analysis showed the complete disappearance of the starting product **1c**. Elimination of the solvent followed by chromatographic purification (silica gel, hexanes−ethyl acetate mixtures as eluents) gave 86 mg

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(20) See, inter alia: (a) Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903−917. (b) Isobe, M. In *Perspectives in the Organic Chemistry of Sulphur*; Zwanenburg, D., Klunder, A. J. H., Eds.; Elsevier: New York, 1987; Vol. 28, pp 209−229. (c) Nájera, C.; Yus, M. *J. Org. Chem.* **1989**, *54*, 1491−1499. (d) Trost, B. M.; Seoane, P.; Mignani, P.; Acemoglu, J. *J. Am. Chem. Soc.* **1989**, *111*, 7487−7500. (e) Corey, E. J.; Bakshi, R. K. *Tetrahedron Lett.* **1990**, *31*, 611−614. (f) Domínguez, E.; Carretero, J. L. *Tetrahedron* **1990**, *46*, 7197−7206. (g) Carretero, J. C.; Domínguez, E. *J. Org. Chem.* **1993**, *58*, 1596−1600. (h) Enders, D.; Jandeleit, B.; von Berg, S. *Synlett* **1997**, 421−431. (i) de Vicente, J.; Gómez Arrayás, J.; Cañada, J. C.; Carretero, J. C. *Synlett* **2000**, 53−56. (j) Adrio, J.; Rodríguez Rivero, M.; Carretero, J. C. *Chem. Eur. J.* **2001**, *7*, 2435−2448.

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(92% yield) of the title compound **3c** as a colorless solid. Mp: 68−70 °C. $[\alpha]_D^{23} = -8.5$ ($c = 1.02$, $CHCl_3$). IR (NaCl film): ν_{max} = 2979, 1696, 1522, 1427, 1366, 1248, 1171 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.46 (s, 9H), 1.70−1.80 (m, 1H), 1.90−2.02 (m, 1H), 2.66−2.78 (m, 4H), 2.90 (m, 1H), 3.50 (m, 1H), 4.52 (br s, 1H), 7.18−7.28 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.4 (CH_3), 31.9 (CH_2), 33.8 (CH_2), 46.1 (CH_2), 52.1 (CH), 54.1 (CH), 79.8 (Cq), 126.0 (CH), 128.3 (CH), 128.4 (CH), 141.6 (Cq), 155.7 (Cq) ppm. MS (CI, NH_3) *m/e*: 295 (M + 18, 45%), 278 (M + 1, 46%), 240 (M − 37, 100%). HRMS (CI, NH_3) $C_{16}H_{24}NO_3$ (M + 1): calcd 278.1756, found 278.1760.

(*S*)-[(*S*)-1-(*tert*-Butoxycarbonylamino)-4-(*tert*-butyldimethylsilyloxy)butyl]oxirane (3e). Obtained in 81% yield, after chromatographic purification, from *N*-Boc-3-amino-1,2-alkanediol **1e** (0.29 g, 0.80 mmol), diisopropyl azodicarboxylate (0.17 mL, 0.86 mmol), and triphenylphosphine (0.22 g, 0.86 mmol) in refluxing chloroform (4 mL, 7 h). Colorless oil. $[\alpha]_D^{23} = -5.15$ ($c = 1.04$, $CHCl_3$). IR (NaCl film): ν_{max} = 2930, 2859, 1702, 1522, 1254, 1173, 1100, 836 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.89 (s, 9H), 1.43 (s, 9H), 1.50−1.71 (m, 4H), 2.76 (d, J = 3.6 Hz, 2H), 2.86 (m, 1H), 3.38 (m, 1H), 3.62 (t, J = 5.4 Hz, 2H), 4.71 (br s, 1H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ −5.3 (CH_3), 18.4 (Cq), 26.0 (CH_3), 28.3 (CH_2), 28.4 (CH_3), 28.6 (CH_2), 46.5 (CH_2), 52.0 (CH), 54.1 (CH), 62.6 (CH_2), 79.8 (Cq), 155.5 (Cq) ppm. MS (FAB+, NBA) *m/e*: 346 (M + 1, 100%), 468 (M + 23, 61%). HRMS (FAB+) $C_{17}H_{36}NO_4Si$ (M + 1): calcd 346.2413, found 346.2397.

The known *N*-Boc-1-(1-aminoalkyl)epoxides **3a**[13] (86% yield, 0.4 mmol scale), **3b**[22] (77% yield, 7.1 mmol scale), and **3d**[14] (95% yield, 5.3 mmol scale) were obtained in a similar way.

Typical Procedure for the Preparation of *N*-Boc-3-amino-1-phenylthio-2-alkanols: (2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1-phenylthio-2-propanol (4aa). To a solution of the epoxide **3a** (0.10 g, 0.40 mmol) in anhydrous methanol (4 mL), triethylamine (57 μL, 0.40 mmol) and thiophenol **2a** (41 μL, 0.40 mmol) were added sequentially via syringe. The resulting mixture was heated to reflux until TLC analysis showed the complete disappearance of the starting product (1 h). Elimination of the solvent followed by chromatographic purification (triethylamine-pretreated silica gel, 2.5% v/v, hexanes−ethyl acetate mixtures as eluents) gave 143 mg (100% yield) of the title compound **4aa** as a colorless solid. Mp 119−120 °C. $[\alpha]_D^{23} = +6.4$ (c = 1.02, $CHCl_3$). IR (NaCl film): ν_{max} = 1684, 1497, 1457, 1368, 1167 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.39 (s, 9H), 2.54−2.65 (m, 1H), 2.98−3.10 (m, 1H), 3.98 (m, 1H), 4.76 (br s, 1H), 5.50 (br s, 1H), 7.23−7.33 (m, 10H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.6 (CH_3), 39.0 (CH_2), 58.1 (CH), 72.0 (CH), 80.1 (Cq), 127.0 (CH), 128.1 (CH), 128.2 (CH), 128.8 (CH), 129.4 (CH), 130.4 (CH), 135.0 (Cq), 138.2 (Cq), 155.8 (Cq) ppm. MS (CI, NH_3) *m/e*: 360 (M + 1, 22%), 359 (M, 100%), 321 (M − 38, 56%), 304 (M − 55, 43%). Anal. ($C_{20}H_{25}NO_3S$) (calcd, found): C (66.82, 66.99), H (7.01, 7.18), N (3.90, 3.64), S (8.92, 8.60).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-4-phenyl-1-phenylthio-2-butanol (4ba). The known *N*-Boc-3-amino-2-hydroxy sulfide **4ba**[23] (100% yield, 0.8 mmol scale) was obtained in a similar way. Mp 148−149 °C. $[\alpha]_D^{23} = -26.6$ (c = 1.0, $CHCl_3$). IR (NaCl film): ν_{max} = 3747, 3359, 1686, 1654, 1559, 1522, 1457, 1173, 741 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.34 (s, 9H), 2.83−3.02 (m, 2H), 3.16−3.30 (m, 2H), 3.30 (br s, 1H, OH), 3.68 (m, 1H), 3.87 (m, 1H), 4.60 (br s, 1H, NH), 7.16−7.36 (m, 10H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.3 (CH_3), 35.8 (CH_2), 38.8 (CH_2), 55.9 (CH), 71.6 (CH), 80.0 (Cq), 126.4 (CH), 126.7 (CH), 128.4 (CH), 129.3 (CH), 129.5 (CH), 130.1 (CH), 138.0 (Cq), 141.4 (Cq), 156.0 (Cq) ppm.

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-phenylthio-2-pentanol (4ca). Obtained in 78% yield, after chromatographic purification, from epoxide **3c** (0.50 g, 1.8 mmol), thiophenol **2a** (184 μL, 1.8 mmol), and triethylamine (255 μL, 1.8 mmol) in refluxing methanol (18 mL, 4 h). Mp 118−119 °C. $[\alpha]_D^{23} = -11.6$ (c = 0.7, $CHCl_3$). IR (NaCl film): ν_{max} = 3347, 1681, 1528, 1299, 1248, 1169, 1017 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.45 (s, 9H), 1.65−1.93 (m, 2H), 2.57−2.92 (m, 2H), 3.02 (m, 1H), 3.13 (dd, J = 13.6 Hz, J' = 3.2 Hz, 2H), 3.72 (br s, 2H), 4.72 (br s, 1H), 7.19−7.36 (m, 10H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 29.4 (CH_3), 31.7 (CH_2), 32.4 (CH_2), 38.8 (CH_2), 54.3 (CH), 72.4 (CH), 79.8 (Cq), 126.0 (CH), 126.7 (CH), 128.3 (CH), 128.4 (CH), 129.1 (CH), 130.1 (CH), 141.6 (Cq), 142.3 (Cq), 157.7 (Cq) ppm. MS (CI, NH_3) *m/e*: 388 (M + 1, 100%), 349 (M − 38, 55%), 332 (M − 55, 34%). Anal. ($C_{22}H_{29}NO_3S$) (calcd, found): C (68.18, 68.30), H (7.54, 7.78), N (3.61, 3.23), S (8.27, 7.81).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-methyl-1-phenylthio-2-hexanol (4da). Obtained in 84% yield, after chromatographic purification, from epoxide **3d** (0.30 g, 1.3 mmol), thiophenol **2a** (135 μL, 1.3 mmol), and triethylamine (185 μL, 1.3 mmol) in refluxing methanol (10 mL, 1 h). Mp 83−85 °C. $[\alpha]_D^{23} = -25.3$ (c = 1.02, $CHCl_3$). IR (NaCl film): ν_{max} = 1684, 1654, 1559, 1507, 1368, 1167, 737, 668 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 1.30−1.40 (m, 2H), 1.43 (s, 9H), 1.56−1.74 (m, 1H), 2.84−2.96 (m, 1H), 3.00−3.20 (m, 1H), 3.68 (br m, 2H), 4.62 (br s, 1H, NH), 7.21−7.39 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.6 (CH_3), 23.7 (CH_3), 24.7 (CH), 28.4 (CH_3), 38.6 (CH_2), 38.9 (CH_2), 52.9 (CH), 72.8 (CH), 79.8 (Cq), 126.5 (CH), 129.0 (CH), 129.9 (CH), 135.4 (Cq), 156.2 (Cq) ppm. MS (CI, NH_3) *m/e*: 340 (M + 1, 6%), 339 (M, 32%), 284 (M − 55, 100%). HRMS (CI, NH_3) $C_{18}H_{30}NO_3S$ (M + 1): calcd 340.1946, found 340.1936.

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-6-(*tert*-butyldimethylsiloxy)-1-phenylthio-2-hexanol (4ea). Obtained in 89% yield, after chromatographic purification, from epoxide **3e** (0.17 g, 0.50 mmol), thiophenol **2a** (51 μL, 0.50 mmol) and triethylamine (71 μL, 0.51 mmol) in refluxing methanol (5 mL, 1.5 h). Colorless oil. $[\alpha]_D^{23} = -10.0$ (c = 1.1, $CHCl_3$). IR (NaCl film): ν_{max}= 2931, 1696, 1654, 1507, 1252, 1169, 1100, 836 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.89 (s, 9H), 1.43 (s, 9H), 1.50−1.71 (m, 4H), 2.91 (dd, J = 13.4 Hz, J' = 9.0 Hz, 1H), 3.16 (dd, J = 13.4 Hz, J' = 3.4 Hz, 1H), 3.62 (t, J = 5.5 Hz, 2H), 3.70 (br m, 1H), 4.84 (br s, 1H, NH), 7.18−7.40 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ −5.3 (CH_3), 18.4 (Cq), 26.0 (CH_3), 26.3 (CH_2), 28.4 (CH_3), 29.1 (CH_2), 38.7 (CH_2), 54.6 (CH), 62.7 (CH_2), 72.5 (CH), 79.7 (Cq), 126.5 (CH), 129.0 (CH), 129.5 (CH), 135.7 (Cq), 156.2 (Cq) ppm. MS (FAB+, NBA) *m/e*: 456 (M + 1, 100%), 478 (M + 23, 39%). HRMS (FAB+) $C_{23}H_{42}NO_4SSi$ (M + 1): calcd 456.2604, found 456.2626.

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-2-naphthylthio-2-pentanol (4cc). To a solution of the epoxide **3c** (0.50 g, 1.80 mmol) in anhydrous methanol (18 mL), triethylamine (255 μL, 1.82 mmol) and 2-naphthalenethiol **2c** (0.29 g, 1.80 mmol) were added sequentially via syringe. The resulting solution was heated to reflux for 4 h, at which point TLC analysis showed that no starting epoxide **3c** was present in the reaction mixture. Elimination of the solvent and chromatographic purification (triethylamine-pretreated silica gel, 2.5% v/v, hexanes−ethyl acetate mixtures as eluents) afforded 0.68 g (87% yield) of the title compound **4cc** as a colorless solid. Mp 125−127 °C. $[\alpha]_D^{23} = -23.0$ (c = 1.01, $CHCl_3$). IR (NaCl film): ν_{max} = 3357, 1683, 1524, 1297, 1248, 1173, 1021 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.44 (s, 9H), 1.62−1.96 (m, 2H), 2.58−3.27 (m, 5H), 3.72 (br s, 2H), 4.71 (br s, 1H), 7.15−7.81 (m, 12H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.4 (CH_3), 31.8 (CH_2), 32.4 (CH_2), 38.6 (CH_2), 54.4 (CH), 72.5 (CH), 79.8 (Cq), 125.9 (CH), 126.6 (CH), 127.1 (CH), 127.6 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 131.4 (Cq), 133.6 (Cq), 141.4 (Cq), 156.1 (Cq) ppm. MS (CI, NH_3) *m/e*: 455 (M + 18, 69%), 438 (M + 1, 36%), 437 (M,

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100%). Anal. ($C_{26}H_{31}NO_3S$), (calcd, found): C (71.36, 71.47), H (7.14, 7.29), N (3.20, 2.97), S (7.33, 7.48).

Typical Procedure for the Preparation of *N*-Boc-3-amino-1-methylthio-3-alkanols: (2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1-methylthio-2-propanol (4ab). A solution of epoxide **3a** (0.10 g, 0.40 mmol) and of sodium methanethiolate (34 mg, 0.50 mmol) in anhydrous methanol (5 mL) was heated to reflux until TLC analysis showed the disappearance of the starting epoxide (4 h). Elimination of the solvent and chromatographic purification (triethylamine-pretreated silica gel, 2.5% v/v, hexanes−ethyl acetate mixtures as eluents) afforded 0.10 g (84% yield) of the title compound **4ab** as a colorless solid. Mp 129−130 °C. $[\alpha]_D^{23} = +29.2$ (c = 1.05, $CHCl_3$). IR (NaCl film): ν_{max} = 3377, 1684, 1654, 1522, 1457, 1246, 1171, 1015 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.41 (s, 9H), 2.09 (s, 3H), 2.16−2.28 (m, 1H), 2.56−2.62 (m, 1H), 4.03 (m, 1H), 4.72 (br m, 1H), 5.53 (br s, 1H), 7.31−7.33 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.8 (CH_3), 28.4 (CH_3), 38.6 (CH_2), 58.1 (CH), 72.0 (CH), 80.1 (Cq), 127.7 (CH), 127.9 (CH), 128.3 (CH), 138.1 (Cq), 155.4 (Cq) ppm. MS (CI, NH_3) *m/e*: 315 (M + 18, 9%), 298 (M + 1, 100%), 259 (M − 38, 75%), 242 (M − 55, 23%). Anal. ($C_{15}H_{23}NO_3S$) (calcd, found): C (60.58, 60.61), H (7.79, 7.78), N (4.71, 4.24), S (10.78, 10.41).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-4-phenyl-1-methylthio-2-butanol (4bb). 4bb was obtained in 92% yield, after chromatographic purification, from epoxide **3b** (0.20 g, 0.76 mmol) and sodium methanethiolate (60 mg, 0.84 mmol) in refluxing methanol (10 mL, 0.5 h). Mp 134.5−135.5 °C. $[\alpha]_D^{23} = -7.0$ (c = 1.0, $CHCl_3$). IR (NaCl film): ν_{max} = 3357, 1685, 1527, 1316, 1250, 1171, 1015, 702 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.35 (s, 9H), 2.11 (s, 3H), 2.49−3.03 (m, 4H), 3.20 (m, 1H), 3.71 (m, 1H), 3.88 (br s, 1H), 4.59 (br s, 1H), 7.20−7.30 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.5 (CH_3), 28.3 (CH_3), 35.7 (CH_2), 38.8 (CH_2), 55.3 (CH), 70.6 (CH), 80.0 (Cq), 126.3 (CH), 128.3 (CH), 129.4 (CH), 137.7 (Cq), 155.6 (Cq) ppm. MS (CI, NH_3) *m/e*: 312 (M + 1, 76%), 273 (M − 38, 100%), 256 (M − 55, 99%). HRMS (CI, NH_3) $C_{16}H_{26}NO_3S$ (M + 1): calcd 312.1633, found 312.1631.

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-methylthio-2-pentanol (4cb). 4cb was obtained in 78% yield, after chromatographic purification, from epoxide **3c** (0.50 g, 1.8 mmol) and sodium methanethiolate (150 mg, 2.2 mmol) in refluxing methanol (20 mL, 4 h). Mp 108−109 °C. $[\alpha]_D^{23} = -7.6$ (c = 1.02, $CHCl_3$). IR (NaCl film): ν_{max} = 3357, 1685, 1522, 1248, 1173, 1019, 699 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.46 (s, 9H), 1.70−1.92 (m, 2H), 2.09 (s, 3H), 2.49−2.78 (m, 4H), 3.02 (m, 1H), 3.68 (br s, 2H), 4.78 (br s, 1H), 7.18−7.28 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.4 (CH_3), 28.4 (CH_3), 31.5 (CH_2), 32.4 (CH_2), 38.6 (CH_2), 54.2 (CH), 71.5 (CH), 80.0 (Cq), 125.9 (CH), 128.3 (CH), 128.4 (CH), 141.6 (Cq), 156.0 (Cq) ppm. MS (CI, NH_3) *m/e*: 343 (M + 18, 100%), 326 (M + 1, 15%), 325 (M, 83%), 287 (M − 38, 32%). Anal. ($C_{17}H_{27}NO_3S$) (calcd, found): C (62.74, 62.85), H (8.36, 8.49), N (4.30, 4.14), S (9.85, 9.96).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-methyl-1-methylthio-2-hexanol (4db). 4db was obtained in 86% yield, after chromatographic purification, from epoxide **3d** (0.30 g, 1.31 mmol) and sodium methanethiolate (101 mg, 1.44 mmol) in refluxing methanol (20 mL, 1 h). Mp 109−110 °C. $[\alpha]_D^{23} = -24.4$ (c = 1.0, $CHCl_3$). IR (NaCl film): $\nu_{màx}$ = 3359, 2952, 1679, 1530, 1329, 1254, 1171, 1057 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 1.25−1.37 (m, 2H), 1.45 (s, 9H), 1.61−1.76 (m, 1H), 2.12 (s, 3H), 2.45−2.71 (m, 2H), 3.68 (m, 2H), 4.63 (br s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.5 (CH_3), 21.6 (CH_3), 23.7 (CH_3), 24.7 (CH), 28.4 (CH_3), 38.4 (CH_2), 38.6 (CH_2), 52.7 (CH), 72.0 (CH), 79.8 (Cq), 156.0 (Cq) ppm. MS (CI, NH_3) *m/e*: 295 (M + 18, 8%), 278 (M + 1, 100%), 239 (M − 38, 23%), 223 (M − 54, 58%). Anal. ($C_{13}H_{27}NO_3S$), (calcd, found): C (56.28, 56.48), H (9.81, 9.80), N (5.05, 4.99), S (11.56, 11.49).

(4*S*,5*S*)-4-Benzyl-5-(methylthio)methyl-1,3-oxazolidin-2-one (7). A solution of epoxide **3b** (0.20 g, 0.76 mmol) and of sodium methanethiolate (80 mg, 1.15 mmol) in anhydrous methanol (10 mL) was heated to reflux. After 1 h, TLC analysis showed that no starting epoxide remained and that the hydroxy sulfide **4bb** was the almost exclusive product; at this point, only a trace of **7** was present in the reaction mixture. The reflux was maintained for 4 h, after which time the conversion of **4bb** to **7** was essentially complete. Elimination of the solvent and chromatographic purification (triethylamine-pretreated silica gel, 2.5% v/v, hexanes−ethyl acetate mixtures as eluents) afforded 0.16 g (89% yield) of the title compound **7** as a colorless dense oil. $[\alpha]_D^{23} = -112.5$ (c = 1.0, $CHCl_3$). IR (NaCl film): ν_{max} = 3286, 2921, 1758, 1495, 1457, 1366, 1233, 1081 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.58−3.04 (m, 4H), 4.06 (m, 1H), 4.81 (q, J = 7 Hz, 1H), 5.15 (br s, 1H, NH), 7.16−7.35 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.6 (CH_3), 32.7 (CH_2), 36.0 (CH_2), 56.5 (CH), 78.5 (CH), 127.2 (CH), 128.9 (CH), 129.0 (CH), 136.2 (Cq), 157.9 (Cq) ppm. MS (CI, NH_3) *m/e*: 255 (M + 18, 100%), 238 (M + 1, 28%). HRMS (CI, NH_3) $C_{12}H_{17}NO_2S$ (M + 1): calcd 238.0902, found 238.0903.

Typical Procedure for the Preparation of *N*-Boc-3-amino-1-aryl(alkyl)sulfonyl-2-alkanols: (2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1-phenylsulfonyl-2-propanol (5aa). To a solution of the sulfide **4aa** (0.107 g, 0.30 mmol) in dry dichloromethane (6 mL), a solution of *m*-chloroperbenzoic acid (0.130 g, 0.75 mmol) in dry dichloromethane (6 mL) was added dropwise. Stirring was maintained at rt until TLC analysis showed that the reaction was complete (3 h). The reaction mixture was then cooled to 0 °C and treated with 10% aqueous sodium sulfite (4 mL). After 15 min of stirring, the aqueous layer was separated. The organic phase was then washed with saturated aqueous sodium bicarbonate (5 mL) and with brine (5 mL) and dried over magnesium sulfate. Elimination of the solvent and chromatographic purification (triethylamine-pretreated silica gel, 2.5% v/v, hexanes−ethyl acetate mixtures as eluents) afforded 0.115 g (100% yield) of the title compound **5aa** as a colorless solid. Mp 158−160 °C. $[\alpha]_D^{23} = +3.2$ (c = 1.1, $CHCl_3$). IR (NaCl film): ν_{max} = 3504, 1702, 1497, 1366, 1308, 1153 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.37 (s, 9H), 2.87−3.25 (m, 2H), 3.48 (m, 1H, OH), 4.45−4.58 (m, 2H), 5.50 (br s, 1H, NH), 7.26−7.32 (m, 5H), 7.56−7.70 (m, 3H), 7.86−7.91 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.3 (CH_3), 58.2 (CH), 59.7 (CH_2), 68.2 (CH), 80.2 (Cq), 127.9 (CH), 128.1 (CH), 128.6 (CH), 129.4 (CH), 134.0 (CH), 134.1 (CH), 137.8 (Cq), 138.8 (Cq), 155.0 (Cq) ppm. MS (CI, NH_3) *m/e*: 409 (M + 18, 100%), 354 (M − 37, 74%), 335 (M − 55, 82%). Anal. ($C_{20}H_{25}NO_5S$) (calcd, found): C (61.36, 61.08), H (6.44, 6.43), N (3.58, 3.37), S (8.19, 8.08).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1-methylsulfonyl-2-propanol (5ab). Obtained in 100% yield, after chromatographic purification, from sulfide **4ab** (55 mg, 0.3 mmol). IR (NaCl film): ν_{max} = 1719, 1685, 1507, 1366, 1283, 1121, 1071 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.42 (s, 9H), 3.00 (s, 3H), 3.02−3.33 (m, 2H), 3.32 (br s, 1H, OH), 4.53 (m, 1H), 4.69 (m, 1H), 5.29 (br s, 1H, NH), 7.33−7.39 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.6 (CH_3), 43.0 (CH_3), 58.4 (CH_2), 59.3 (CH), 69.7 (CH), 80.9 (Cq), 127.9 (CH), 128.8 (CH), 129.3 (CH), 137.8 (Cq), 156.0 (Cq) ppm. MS (CI, NH_3) *m/e*: 347 (M + 18, 9%), 330 (M + 1, 88%), 291 (M − 38, 18%), 274 (M − 55, 100%). HRMS (CI, NH_3) $C_{15}H_{24}NO_5S$ (M + 1): calcd 330.1375, found 330.1363.

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-4-phenyl-1-phenylsulfonyl-2-butanol (5ba). Obtained in 81% yield, after chromatographic purification, from sulfide **4ba** (0.20 g, 0.55 mmol). Mp 154−155 °C. $[\alpha]_D^{23} = +3.0$ (c = 1.04, $CHCl_3$). IR (NaCl film): ν_{max} = 3355, 1692, 1526, 1316, 1148, 1013, 739 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.30 (s, 9H), 2.83−3.02 (m, 2H), 3.19−3.38 (m, 2H), 3.82 (br s, 1H, OH), 3.98 (m, 1H), 4.14 (m, 1H), 4.60 (br s, 1H, NH), 7.19−7.26 (m, 5H), 7.57−7.72 (m, 3H), 7.89−7.93 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.2 (CH_3), 35.9 (CH_2), 55.3 (CH), 59.9 (CH_2), 68.1 (CH), 80.2 (Cq), 126.6 (CH), 127.9 (CH), 128.5 (CH), 129.3

(CH), 129.4 (CH), 134.1 (CH), 136.9 (Cq), 139.0 (Cq), 155.6 (Cq) ppm. MS (CI, NH_3) *m/e*: 423 (M + 18, 7%), 406 (M + 1, 5%), 405 (M, 19%), 366 (M − 39, 100%), 349 (M − 56, 41%). Anal. ($C_{21}H_{27}NO_5S$), (calcd, found): C (62.20, 62.10), H (6.71, 6.77), N (3.45, 3.44), S (7.91, 7.78).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-4-phenyl-1-methylsulfonyl-2-butanol (5bb). Obtained in 80% yield, after chromatographic purification, from sulfide **4bb** (0.20 g, 0.64 mmol). Mp 155−156 °C. $[\alpha]_D^{23} = -23.1$ (*c* = 0.9, $CHCl_3$). IR (NaCl film): ν_{max} = 3359, 1686, 1521, 1301, 1254, 1169, 1129, 1013 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.36 (s, 9H), 2.72−2.95 (m, 2H), 3.03 (s, 3H), 3.18 (br d, 2H), 3.86 (br s, 1H, OH), 4.24 (m, 1H), 4.37 (br m, 1H), 4.65 (br s, 1H, NH), 7.20−7.33 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.3 (CH_3), 36.3 (CH_2), 42.6 (CH_3), 56.5 (CH), 58.4 (CH_2), 69.2 (CH), 80.6 (Cq), 126.9 (CH), 128.7 (CH), 129.2 (CH), 136.7 (Cq), 156.6 (Cq) ppm. MS (CI, NH_3) *m/e*: 344 (M + 1, 2%), 343 (M, 11%), 305 (M − 38, 100%), 288 (M − 55, 19%). Anal. ($C_{16}H_{25}NO_5S$), (calcd, found): C (55.95, 55.85), H (7.34, 7.21), N (4.08, 3.96), S (9.34, 9.17). A 95% ee was determined for this compound by ^1H NMR spectroscopy of the corresponding Mosher's ester.

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-phenylsulfonyl-2-pentanol (5ca). 5ca was obtained in 100% yield, after chromatographic purification, from sulfide **4ca** (0.155 g, 0.40 mmol). Mp 129−130 °C. $[\alpha]_D^{23} = -13.5$ (*c* = 1.0, $CHCl_3$). IR (NaCl film): ν_{max} = 2362, 2341, 1717, 1507, 1289, 1144 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.42 (s, 9H), 1.71−1.86 (m, 2H), 2.56−2.74 (m, 2H), 3.22 (d, *J* = 5 Hz, 2H), 3.55 (br s, 1H, OH), 3.72 (m, 1H), 4.13 (m, 1H,), 4.71 (br s, 1H, NH), 7.13−7.92 (m, 10H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.3 (CH_3), 31.7 (CH_2), 32.1 (CH_2), 54.2 (CH), 60.0 (CH_2), 68.8 (CH), 80.0 (Cq), 125.9 (CH), 127.8 (CH), 128.3 (CH), 128.4 (CH), 129.4 (CH), 134.0 (CH), 139.0 (Cq), 141.2 (Cq), 157.8 (Cq) ppm. MS (CI, NH_3) *m/e*: 437 (M + 18, 16%), 420 (M + 1, 15%), 381 (M − 38, 22%), 380 (M − 39, 100%). Anal. ($C_{22}H_{29}NO_5S$) (calcd, found): C (62.98, 62.84), H (6.97, 7.38), N (3.34, 3.28).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-methylsulfonyl-2-pentanol (5cb). 5cb was obtained in 80% yield, after chromatographic purification, from sulfide **4cb** (0.20 g, 0.62 mmol). Mp 125−127 °C. $[\alpha]_D^{23} = -11.6$ (*c* = 1.0, $CHCl_3$). IR (NaCl film): ν_{max} = 1685, 1522, 1457, 1299, 1129, 473 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.46 (s, 9H), 1.67−1.92 (m, 2H), 2.63−3.21 (m, 4H), 3.01 (s, 3H), 3.63 (m, 1H), 4.17 (br m, 1H), 4.69 (br s, 1H, NH), 7.18−7.31 (m, 5H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.3 (CH_3), 31.9 (CH_2), 32.2 (CH_2), 42.6 (CH_3), 55.0 (CH), 58.2 (CH_2), 70.0 (CH), 80.3 (Cq), 126.2 (CH), 128.3 (CH), 128.5 (CH), 140.6 (Cq), 156.7 (Cq) ppm. MS (CI, NH_3) *m/e*: 374 (M + 18, 100%). HRMS (CI, NH_3) $C_{17}H_{28}NO_5S$ (M + 1): calcd 358.1688, found 358.1677. Anal. ($C_{17}H_{27}NO_5S{\cdot}0.5H_2O$) (calcd, found): C (55.72, 56.19), H (7.70, 7.58), N (3.82, 3.51), S (8.75, 8.93).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-(2-naphthylsulfonyl)-2-pentanol (5cc). **5cc** was obtained in 87% yield, after chromatographic purification, from sulfide **4cc** (0.30 g, 0.69 mmol). M.p 158−159 °C. $[\alpha]_D^{23} = -17.7$ (*c* = 1.03, $CHCl_3$). IR (NaCl film): ν_{max} = 1696, 1507, 1368, 1304, 1246, 1144, 1127, 1019, 749 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.40 (s, 9H), 1.69−1.92 (m, 2H), 2.49−2.73 (m, 2H), 3.30 (d, *J* = 4.6 Hz, 2H), 3.57 (br s, 1H, OH), 3.73 (m, 1H), 4.17 (m, 1H), 4.67 (br s, 1H, NH), 7.11−7.26 (m, 5H), 7.67−8.08 (m, 6H), 8.47 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.3 (CH_3), 31.7 (CH_2), 32.1 (CH_2), 54.3 (CH), 59.9 (CH_2), 68.9 (CH), 80.1 (Cq), 122.3 (CH), 126.0 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 129.4 (CH), 129.5 (CH), 129.8 (CH), 132.0 (Cq), 135.4 (Cq), 141.1 (Cq), 156.0 (Cq) ppm. MS (CI, NH_3) *m/e*: 487 (M + 18, 100%), 431 (M − 38, 5%). HRMS (CI, NH_3) $C_{26}H_{32}NO_5S$ (M + 1): calcd 470.2001, found 470.2011. Anal. ($C_{26}H_{31}NO_5S{\cdot}0.5H_2O$), (calcd, found): C (65.25, 65.67), H (6.74, 6.72), N (2.93, 2.71), S (6.70, 6.74).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-methyl-1-phenylsulfonyl-2-hexanol (5da). 5da was obtained in 97% yield, after chromatographic purification, from sulfide **4da** (0.20 g, 0.60 mmol). Mp 106−107 °C $[\alpha]_D^{23} = -16.2$ (*c* = 1.03, $CHCl_3$). IR (NaCl film): ν_{max} = 2960, 1962, 1521, 1449, 1368, 1304, 1144 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 1.30−1.40 (m, 2H), 1.40 (s, 9H), 1.56−1.74 (m, 1H), 3.26 (d, *J* = 5.5 Hz, 2H), 3.62 (m, 1H), 3.78 (br s, 1H, OH), 4.11 (m, 1H), 4.62 (br s, 1H, NH), 7.54−7.69 (m, 3H), 7.90−7.98 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.5 (CH_3), 23.6 (CH_3), 24.6 (CH), 28.3 (CH_3), 38.9 (CH_2), 52.9 (CH), 59.8 (CH_2), 69.3 (CH), 80.1 (Cq), 127.9 (CH), 129.3 (CH), 133.9 (CH), 139.4 (Cq), 156.0 (Cq) ppm. MS (CI, NH_3) *m/e*: 372 (M + 1, 18%), 371 (M, 86%), 316 (M − 55, 100%). HRMS (CI, NH_3) $C_{18}H_{30}NO_5S$ (M + 1): calcd 372.1845, found 372.1842. Anal. ($C_{18}H_{29}NO_5S{\cdot}0.25H_2O$) (calcd, found): C (57.50, 57.26), H (7.91, 7.72), N (3.73, 3.89), S (8.53, 8.97).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-5-methyl-1-methylsulfonyl-2-hexanol (5db). 5db was obtained in 86% yield, after chromatographic purification, from sulfide **4db** (0.10 g, 0.36 mmol). Mp 137−138 °C. $[\alpha]_D^{23} = -22.8$ (*c* = 1.0, $CHCl_3$). IR (NaCl film): ν_{max} = 2960, 1686, 1522, 1393, 1368, 1295, 1167, 1133 cm^{-1}.^1H NMR (200 MHz, $CDCl_3$): δ 0.96 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 1.29−1.37 (m, 2H), 1.45 (s, 9H), 1.58−1.75 (m, 1H), 2.98−3.23 (m, 2H), 3.05 (s, 3H), 3.74 (br s, 1H, OH), 4.17 (m, 1H), 4.29 (br m, 1H), 4.60 (br s, 1H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.6 (CH_3), 23.3 (CH_3), 24.8 (CH), 28.3 (CH_3), 39.4 (CH_2), 42.7 (CH_3), 53.9 (CH), 58.1 (CH_2), 70.5 (CH), 80.6 (Cq), 157.2 (Cq) ppm. MS (CI, NH_3) *m/e*: 327 (M + 18, 29%), 310 (M + 1, 23%), 271 (M − 38, 100%), 254 (M − 55, 15%). Anal. ($C_{13}H_{27}NO_5S$), (calcd, found): C (50.46, 50.89), H (8.80, 8.92), N (4.53, 4.52), S (10.36, 10.35).

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-6-(*tert*-butyldimethylsilyloxy)-1-phenylsulfonyl-2-hexanol (5ea). 5ea was obtained in 85% yield, after chromatographic purification, from sulfide **4ea** (80 mg, 0.18 mmol). Colorless oil. $[\alpha]_D^{23} = -4.1$ (*c* = 1.7, $CHCl_3$). IR (NaCl film): ν_{max} = 2931, 1685, 1507, 1366, 1306, 1252, 1146, 1086, 836 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.89 (s, 9H), 1.40 (s, 9H), 1.47−1.71 (m, 4H), 3.25 (m, 2H), 3.53 (br, 1H, OH), 3.60 (t, *J* = 5.5 Hz, 2H), 3.82 (m, 1H), 4.10 (m, 1H), 4.88 (br s, 1H, NH), 7.54−7.72 (m, 3H), 7.90−7.95 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ −5.3 (CH_3), 18.3 (Cq), 26.0 (CH_3), 26.3 (CH_2), 28.3 (CH_3), 28.6 (CH_2), 54.4 (CH), 60.0 (CH_2), 62.5 (CH_2), 69.0 (CH), 79.9 (Cq), 127.9 (CH), 129.3 (CH), 133.9 (CH), 139.2 (Cq), 156.1 (Cq) ppm. MS (FAB+, NBA) *m/e*: 488 (M + 1, 47%), 510 (M + 23, 100%). HRMS (FAB+) $C_{23}H_{42}NO_6SSi$ (M + 1): calcd 488.2502, found 488.2504.

Typical Procedure for the Preparation of *N*-Boc-γ-alkyl-γ-amino Vinyl Sulfones: (3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-4-phenyl-1-phenylsulfonyl-1-butene (6ba). To a cold (0 °C) solution of the 2-hydroxy sulfone **5ba** (85 mg, 0.21 mmol) and of 4-(*N*,*N*-dimethylamino)pyridine (105 mg, 0.86 mmol) in anhydrous dichloromethane (2 mL), a solution of mesyl chloride (33 mL, 0.43 mmol) in anhydrous dichloromethane (1 mL) was added via syringe. The resulting mixture was stirred at rt for 30 min., at which time TLC analysis showed that the reaction was complete. After dilution with dichloromethane (3 mL), the reaction mixture was successively washed with a cold (0 °C) 10% aqueous HCl solution (10 mL) and with aqueous saturated sodium bicarbonate (2 × 5 mL). The organic phase was dried over magnesium sulfate. Following evaporation of the solvent at reduced pressure, column chromatography of the crude producte (triethylamine-pretreated silica gel, 2.5% v/v, hexanes−ethyl acetate mixtures as eluent) gave 76 mg (94% yield) of the title compound **6ba** as a colorless solid. Mp 139.0−140.5 °C. $[\alpha]_D^{23} = +3.2$ (*c* = 1.05, $CHCl_3$). IR (NaCl film): ν_{max} = 1702, 1507, 1447, 1368, 1308, 1148, 1086, 753 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.34 (s, 9H), 2.90 (d, *J* = 6.6 Hz, 2H), 4.53 (br m, 1H), 4.64 (br s, 1H, NH), 6.32 (dd, *J* = 15.0 Hz, *J′* = 1.2 Hz, 1H), 6.94 (dd, *J* = 15.0 Hz, *J′* = 5.0 Hz, 1H), 7.13−7.26 (m, 5H), 7.51−7.59 (m, 3H), 7.81 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.2 (CH_3), 40.5 (CH_2), 52.1 (CH), 80.2

(Cq), 127.0 (CH), 127.5 (CH), 128.6 (CH), 129.2 (CH), 129.3 (CH), 130.7 (CH), 133.3 (CH), 135.5 (Cq), 140.0 (Cq), 145.7 (CH), 154.6 (Cq) ppm. MS (CI, NH_3) *m/e*: 405 (M + 18, 100%), 348 (M − 39, 30%). Anal. ($C_{21}H_{25}NO_4S$), (calcd, found): C (65.09, 64.97), H (6.50, 6.55), N (3.61, 3.54), S (8.28, 8.25).

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-4-phenyl-1-methylsulfonyl-1-butene (6bb). 6bb was obtained in 100% yield, after chromatographic purification, from sulfone **5bb** (18 mg, 0.052 mmol). Mp 145−146 °C (lit. 143−144 °C).[19] $[\alpha]_D^{23} = +8.4$ ($c = 0.83$, $CHCl_3$) (lit: $[\alpha]_D^{25} = +6.7$ ($c = 0.9$, $CHCl_3$)).[19] ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40 (s, 9H), 2.87 (s, 3H), 2.92 (d, $J = 6.2$ Hz, 2H), 4.63 (br m, 2H), 6.37 (dd, $J = 15$ Hz, $J' = 1.6$ Hz, 1H), 6.89 (dd, $J = 15$ Hz, $J' = 5.0$ Hz, 1H), 7.15−7.19 (m, 2H), 7.27−7.35 (m, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.3 (CH_3), 40.5 (CH_2), 42.8 (CH_3), 52.1 (CH), 80.2 (Cq), 127.1 (CH), 128.7 (CH), 129.3 (CH), 129.8 (CH), 135.5 (Cq), 147.2 (CH), 154.6 (Cq) ppm. A 95% ee was determined for this compound by HPLC (Chiralpak AS column, 80:20 hexane/isopropyl alcohol; $t_R(R) = 25.3$ min, $t_R(S) = 29.2$ min).

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-phenylsulfonyl-1-pentene (6ca). 6ca was obtained in 100% yield, after chromatographic purification, from sulfone **5ca** (100 mg, 0.24 mmol). Mp 78−80 °C. $[\alpha]_D^{23} = -1.3$ ($c = 0.9$, $CHCl_3$). IR (NaCl film): $\nu_{max} = 1702$, 1517, 1368, 1308, 1250, 1148, 1086 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40 (s, 9H), 1.67−1.99 (m, 2H), 2.67 (t, $J = 7.6$ Hz, 2H), 4.37 (br m, 1H), 4.58 (br s, 1H, NH), 6.43 (dd, $J = 15.2$ Hz, $J' = 1.2$ Hz, 1H), 6.90 (dd, $J = 15.2$ Hz, $J' = 5.0$ Hz, 1H), 7.15−7.85 (m, 10H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.2 (CH_3), 31.9 (CH_2), 35.9 (CH_2), 50.7 (CH), 80.1 (Cq), 126.3 (CH), 127.5 (CH), 128.2 (CH), 128.5 (CH), 129.2 (CH), 130.5 (CH), 133.4 (CH), 140.1 (Cq), 141.2 (Cq), 146.2 (CH), 154.8 (Cq) ppm. MS (CI, NH_3) *m/e*: 419 (M + 18, 100%), 363 (M − 38, 33%), 345 (M − 56, 19%). HRMS (CI, NH_3) $C_{22}H_{28}NO_4S$ (M + 1): calcd 402.1739, found 402.1736. Anal. ($C_{22}H_{27}NO_4S \cdot 0.5H_2O$) (calcd, found): C (64.36, 64.42), H (6.87, 7.02), N (3.41, 3.27), S (7.81, 7.24).

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-methylsulfonyl-1-pentene (6cb). 6cb was obtained in 100% yield, after chromatographic purification, from sulfone **5cb** (100 mg, 0.28 mmol). Mp 118−120 °C. $[\alpha]_D^{23} = +5.6$ ($c = 1.04$, $CHCl_3$). IR (NaCl film): $\nu_{max} = 1700$, 1521, 1310, 1248, 1167, 1135, 1048, 967, 668 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.46 (s, 9H), 1.77−1.98 (m, 2H), 2.71 (t, $J = 7.6$ Hz, 2H), 2.93 (s, 3H), 4.38 (br m, 1H), 4.60 (br s, 1H, NH), 6.48 (dd, $J = 15.2$ Hz, $J' = 1.6$ Hz, 1H), 6.85 (dd, $J = 15.2$ Hz, $J' = 5.0$ Hz, 1H), 7.15−7.35 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.3 (CH_3), 31.9 (CH_2), 35.8 (CH_2), 42.9 (CH_3), 50.6 (CH), 80.2 (Cq), 126.3 (CH), 128.3 (CH), 128.6 (CH), 129.5 (CH), 140.1 (Cq), 147.8 (CH), 154.8 (Cq) ppm. MS (CI, NH_3) *m/e*: 357 (M + 18, 100%), 301 (M − 38, 9%). Anal. ($C_{17}H_{25}NO_4S$) (calcd, found): C (60.15, 59.92), H (7.42, 7.53), N (4.13, 3.86), S (9.45, 9.82).

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-5-phenyl-1-(2-naphthylsulfonyl)-1-pentene (6cc). **6cc** was obtained in 100% yield, after chromatographic purification, from sulfone **5cc** (100 mg, 0.28 mmol). Mp 123−126 °C (dec). $[\alpha]_D^{23} = +0.6$ ($c = 1.02$, $CHCl_3$). IR (NaCl film): $\nu_{max} = 3855$, 1702, 1654, 1559, 1507, 1457, 1148, 1127, 668 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.37 (s, 9H), 1.77−1.97 (m, 2H), 2.67 (t, $J = 7.2$ Hz, 2H), 4.38 (br m, 1H), 4.53 (br s, 1H, NH), 6.49 (dd, $J = 15$ Hz, $J' = 1.2$ Hz, 1H), 6.95 (dd, $J = 15$ Hz, $J' = 4.8$ Hz, 1H), 7.11−7.28 (m, 5H), 7.61−8.00 (m, 6H), 8.48 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.2 (CH_3), 31.9 (CH_2), 35.8 (CH_2), 50.7 (CH), 80.1 (Cq), 122.4 (CH), 126.2 (CH), 127.6 (CH), 127.9 (CH), 128.2 (CH), 128.5 (CH), 129.1 (CH), 129.2 (CH), 129.3 (CH), 129.6 (CH), 130.6 (Cq), 132.1 (Cq), 135.1 (Cq), 136.8 (Cq), 146.2 (CH), 154.7 (Cq) ppm. MS (CI, NH_3) *m/e*: 469 (M + 18, 100%). HRMS (CI, CH_4) $C_{26}H_{29}NO_4S + C_2H_5$: calcd 480.2208, found 480.2200.

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-5-methyl-1-phenylsulfonyl-1-hexene (6da). 6da was obtained in 94% yield, after chromatographic purification, from sulfone **5da** (100 mg, 0.28 mmol). Mp 74−75 °C. $[\alpha]_D^{23} = -6.0$ ($c = 1.0$, $CHCl_3$). IR (NaCl film): $\nu_{max} = 3363$, 2959, 1702, 1517, 1368, 1308, 1148, 1086 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, $J = 6.6$ Hz, 3H), 0.92 (d, $J = 6.6$ Hz, 3H), 1.30−1.43 (m, 2H), 1.37 (s, 9H), 1.63−1.75 (m, 1H), 4.46 (br m, 2H), 6.42 (dd, $J = 15$ Hz, $J' = 1.4$ Hz, 1H), 6.88 (dd, $J = 15$ Hz, $J' = 5.0$ Hz, 1H), 7.53−7.62 (m, 3H), 7.88 (dd, $J = 8.5$ Hz, $J' = 1.8$ Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.0 (CH_3), 22.8 (CH_3), 24.7 (CH), 28.2 (CH_3), 43.3 (CH_2), 49.4 (CH), 80.1 (Cq), 127.5 (CH), 129.2 (CH), 129.8 (CH), 133.4 (CH), 140.3 (Cq), 147.0 (CH), 154.8 (Cq) ppm. MS (CI, NH_3) *m/e*: 371 (M + 18, 100%), 315 (M − 38, 33%). Anal. ($C_{18}H_{27}NO_4S$) (calcd, found): C (61.16, 61.37), H (7.70, 7.78), N (3.96, 3.81), S (9.07, 8.93).

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-5-methyl-1-methylsulfonyl-1-hexene (6db). 6db was obtained in 89% yield, after chromatographic purification, from sulfone **5db** (50 mg, 0.16 mmol). Mp 69−70 °C. $[\alpha]_D^{23} = -20.3$ ($c = 1.0$, $CHCl_3$). IR (NaCl film): $\nu_{max} = 3357$, 2960, 1702, 1521, 1393, 1368, 1310, 1252, 1169, 1136 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, $J = 6.6$ Hz, 3H), 0.92 (d, $J = 6.6$ Hz, 3H), 1.40−1.44 (m, 2H), 1.45 (s, 9H), 1.60−1.75 (m, 1H), 2.95 (s, 3H), 4.41 (br m, 1H), 4.55 (br s, 1H, NH), 6.49 (dd, $J = 15$ Hz, $J' = 1.4$ Hz, 1H), 6.81 (dd, $J = 15$ Hz, $J' = 5.2$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9 (CH_3), 22.7 (CH_3), 24.7 (CH), 28.3 (CH_3), 42.9 (CH_3), 43.3 (CH_2), 49.5 (CH), 80.2 (Cq), 128.9 (CH), 148.5 (CH), 154.9 (Cq) ppm. MS (CI, NH_3) *m/e*: 309 (M + 18, 100%), 253 (M − 38, 97%). HRMS (CI, CH_4) $C_{13}H_{25}NO_4S + C_2H_5$: calcd 320.1895, found 320.1890.

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-6-(*tert*-butyldimethylsilyloxy)-1-phenylsulfonyl-1-hexene (6ea). 6ea was obtained in 100% yield, after chromatographic purification, from sulfone **5ea** (67 mg, 0.17 mmol). Colorless oil. $[\alpha]_D^{23} = -3.0$ ($c = 1.2$, $CHCl_3$). IR (NaCl film): $\nu_{max} = 2931$, 1702, 1507, 1252, 1148, 1086, 1017, 836 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.89 (s, 9H), 1.38 (s, 9H), 1.52−1.74 (m, 4H), 3.62 (t, $J = 5.5$ Hz, 2H), 4.35 (m, 1H), 4.96 (br s, 1H, NH), 6.42 (dd, $J = 15.0$ Hz, $J' = 1.6$ Hz, 1H), 6.90 (dd, $J = 15.0$ Hz, $J' = 5.0$ Hz, 1H), 7.48−7.62 (m, 3H), 7.85−7.90 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ −5.3 (CH_3), 18.3 (Cq), 26.0 (CH_3), 28.2 (CH_3), 28.5 (CH_2), 30.6 (CH_2), 50.8 (CH), 62.3 (CH_2), 79.9 (Cq), 127.5 (CH), 129.2 (CH), 130.2 (CH), 133.3 (CH), 140.2 (Cq), 146.8 (CH), 154.9 (Cq) ppm. MS (FAB+, NBA) *m/e*: 492 (M + 23, 46%). HRMS (FAB+) $C_{23}H_{40}NO_5SSi$ (M + 1): calcd 470.2396, found 470.2376.

Typical procedure for the Preparation of *N*-Boc-γ-amino-γ-aryl Vinyl Sulfones: (3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1-phenylsulfonyl-1-propene (6aa). A solution of the 2-hydroxy sulfone **5aa** (50 mg, 0.13 mmol), of the carbodiimide morpho-CDI (110 mg, 0.26 mmol), and of anhydrous cupric chloride (2 mg) in dry acetonitrile (2 mL) was heated to 70 °C for 1 h. After cooling to rt, the reaction mixture was filtered through a short pad of Celite and silica gel, which was thoroughly washed with dichloromethane. Elimination of the solvents at reduced pressure afforded the title compound **6aa** (48 mg, 100% yield) as a colorless solid. Mp 88−89 °C. $[\alpha]_D^{23} = +31.5$ ($c = 1.04$, $CHCl_3$). IR (NaCl film): $\nu_{max} = 1700$, 1507, 1320, 1148, 1086, 753, 689 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.38 (s, 9H), 4.89 (br s, 1H, NH), 5.47 (br m, 1H), 6.50 (dd, $J = 15$ Hz, $J' = 1.8$ Hz, 1H), 7.11 (dd, $J = 15$ Hz, $J' = 5.0$ Hz, 1H), 7.23−7.37 (m, 5H), 7.54−7.62 (m, 3H), 7.86−7.91 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.2 (CH_3), 55.0 (CH), 80.5 (Cq), 127.1 (CH), 127.6 (CH), 128.5 CH), 129.1 (CH), 129.2 (CH), 131.0 (CH), 133.4 (CH), 137.9 (Cq), 140.0 (Cq), 145.3 (CH), 154.4 (Cq) ppm. MS (CI, NH_3) *m/e*: 391 (M + 18, 99%), 374 (M + 1, 4%), 335 (M − 38, 100%), 318 (M − 55, 9%). HRMS (CI, NH_3) $C_{20}H_{42}NO_4S$ (M + 1): calcd 374.1426, found 374.1410. Anal. ($C_{20}H_{23}NO_4S \cdot 0.25H_2O$) (calcd, found): C (63.55, 63.69), H (6.27, 6.25), N (3.71, 3.26), S (8.48, 8.18).

(3*S*,*E*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1-methylsulfonyl-1-propene (6ab). 6ab was obtained in 96% yield from the 2-hydroxy sulfone **5ab** (45 mg, 0.14 mmol). Mp 128−130 °C. $[\alpha]_D^{23} = +50.3$ ($c = 0.30$, $CHCl_3$). IR (NaCl film): ν_{max}

= 1702, 1654, 1559, 1507, 1457, 1312, 1165, 1135, 969, 700 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.26 (s, 9H), 2.97 (s, 3H), 4.95 (br s, 1H, NH), 5.47 (br m, 1H), 6.51 (dd, J = 15.0 Hz, J' = 1.8 Hz, 1H), 7.10 (dd, J = 15.0 Hz, J' = 4.5 Hz), 7.24−7.40 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.7 (CH_3), 42.9 (CH_3), 55.2 (CH), 80.9 (Cq), 127.1 CH), 128.6 (CH), 129.2 (CH), 130.0 (CH), 138.8 (Cq), 146.9 (CH), 154.4 (Cq) ppm. MS (CI, NH_3) *m/e*: 329 (M + 18, 100%), 274 (M − 37, 13%). HRMS (CI, NH_3) $C_{15}H_{22}NO_4S$ (M + 1): calcd 312.1269, found 312.1263.

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Supporting Information Available: Copies of the ^1H- and ^{13}C NMR spectra of compounds **3c**, **3e**, **4da**, **4ea**, **4bb**, **7**, **5ab**, **5da**, **5ea**, **6cc**, **6db**, **6ea**, and **6ab**. This material is available free of charge via the Internet at http://pubs.acs.org.

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