Application of New Camphor-Derived Mercapto Chiral Auxiliaries to the Synthesis of Optically Active Primary Amines

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A series of enantiomerically pure sulfinimines carrying new camphor-based mercapto chiral auxiliaries are subjected to asymmetric alkylation. Such reaction offers an excellent route to the preparation of optically active primary amines. Also reported here is an unprecedented Grignard addition of a chiral sulfenimine leading to a single enantiomer of the corresponding sulfenamide and thence produced enantiopure amine after acidic aqueous workup. The chiral auxiliary can be recovered in high yield.

Introduction

Many biologically important compounds contain chiral amine functionalities.[1] Consequently, the preparation of chiral primary amines is of synthetic significance, and the access by asymmetric synthesis is desirable. Unlike chiral alcohols, however, reactions leading to chiral amines are relatively limited.[2] An attractive approach makes use of diastereoselective addition of organometallic reagents to the C=N bonds of imine and its derivatives containing removable chiral auxiliaries.[3] However, only a few examples of this type, which consist of the reduction or alkylation of *p*-tolylsulfinimines, have been reported.[4,5] A big disadvantage of this strategy is the destruction of the chiral auxiliary in the process of generating the chiral amines. This paper describes the preparation of chiral primary amines through the use of a series of chiral sulfinimines **4** and sulfenimines **3** which are prepared from a group of novel, truly recyclable mercapto chiral auxiliaries derived from camphor.[6]

The synthetic strategy illustated in Scheme 1 was to use the facial differences in the chiral templates **3** and **4** which were prepared from three of our newly developed mercapto chiral auxiliaries, **1a**, **1b**, and **1c**. Asymmetric alkylation of these chiral templates produced the corresponding amides **6** or **7** which gave enantiopure amine **9** and chiral auxiliary **1** after a suitable cleavage process. Our observations indicate that the diastereoselectivity of the asymmetric addition was influenced by several factors. For the reactions of sulfinimines **4**, these factors were the size of the attacking nucleophiles and their metallic counterion, as well as the chirality of the sulfinyl group. But the size difference of 2-alkoxy group of the chiral template seems to have little effect on the diastereoselectivity. With chiral auxiliary **1c** we achieved the first example of a completely diastereoselective addition of the sulfenimines in the literature.[7] It is interest to note that the 2-hydroxyl group of the chiral sulfenimines is critical for obtaining the excellent diastereoselectivity.

Results and Discussions

Synthesis of Chiral Sulfenimines 3 and Sulfinimines 4. According to the results summarized in Table 1, the chiral sulfenimines **3** were prepared by sequential treatment of the chiral thiols **1** with *N*-chlorosuccinimide in a 1:1 mixture of liquid ammonia and dichloromethane at −33 °C, followed by addition of 3 equiv of benzaldehyde, to produce sulfenimines **3** in 85% to 98% overall yields.[8] In addition to obtaining high yields of sulfenimies **3** with this one-pot process, we were also able to isolate the intermediate sulfenamides **2** and synthesize the sulfenimines **3** in a stepwise fashion with reasonable yields (entries 5 and 6). The stereoselective oxidations of sulfenimines **3** can be carried out either with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane or magnesium monoperoxyphthalic acid in methanol. Both procedures gave very good chemical yields of chiral sulfinimines **4**.[9] But MCPBA gave relatively better diastereoselectivity in the case of sulfenimines **3a** (entry 2 vs 7, and entry 3 vs 8). We also found that lowering the reaction temperature to −78 °C improves the stereoselectivity of the oxidation (entry 1 vs 2). Nevertheless, sulfenimine **3c** produced only sulfinimine **4c** using either oxidant, which may be due to the strong chelating effect of the oxidant and the 2-hydroxyl group in the chiral template **3c**.

Asymmetric Additions of Chiral Sulfinimines 4 and Sulfenimines 3. Asymmetric additions were carried out by treatment of sulfinimines **4** in tetrahydrofuran with 3 equiv of Grignard reagents at −10 °C. The resulting

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(1) Scott, J. W. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 1, pp 27-29.

(2) (a) Jiang, Y.-Z.; Guo, P.; Liu, G.-L. *Synth. Commun.* **1990**, *20*, 15-22. (b) Chen, C.-P.; Prasad, K.; Repic, O. *Tetrahedron Lett.* **1991**, *32*, 7175-7178. (c) Chang, Z.-Y.; Coates, R. M. *J. Org. Chem.* **1990**, *55*, 3475-3483.

(3) (a) Denmark, S. E.; Nicaise, O. *Synlett.* **1993**, 359-361. (b) Tomioka, K.; Inoue, I.; Shindo, M.; Koga, K. *Tetrahedron Lett.* **1990**, *31*, 6681-6684. (c) Ukaji, Y.; Watai, T.; Sumi, T.; Fujisawa, T. *Chem. Lett.* **1991**, 1555-1558. (d) Soai, K.; Hatanaka, T.; Miyazawa, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1097-1098. (e) Dieter, R. K.; Datar, R. *Can. J. Chem.* **1993**, *71*, 814-823.

(4) (a) Annunziata, R.; Cinquini, M.; Cozzi, F. *J. Chem. Soc., Perkin Trans. I* **1982**, 339-343. (b) Hua, D. H.; Miao, S. W.; Chen, J. S.; Iguchi, S. *J. Org. Chem.* **1991**, *56*, 4-6. (c) Las chat, S.; Konz, H. *J. Org. Chem.* **1991**, *56*, 5883-5889.

(5) For reactions of ester enolates with sulfenimines, see: Burnett, D. A.; Hart, D. J.; Liu, J. *J. Org. Chem.* **1986**, *51*, 1930-1932, and with sulfinimines see: Davis, F. A.; Reddy, R. T.; Reddy, R. E. *J. Org. Chem.* **1992**, *57*, 6387-6389.

(6) (a) Hung, S.-M.; Lee, D.-S.; Yang, T.-K. *Tetrahedron, Asymmetry* **1990**, *12*, 873-876. (b) Lee, D.-S.; Hung, S.-M.; Lai, M.-C; Chu, H.-Y.; Yang, T.-K. *Org. Prep. Proc. Int.* **1993**, *6*, 673-679.

(7) Davis, F. A.; Mancinelli, P. A. *J. Org. Chem.* **1977**, *42*, 398-399.

(8) Branchund, B. P. *J. Org. Chem.* **1983**, *48*, 3531-3538.

(9) Yang, T.-K.; Teng, T.-F.; Lee, D.-S. *J. Chin. Chem. Soc.* **1991**, *38*, 375-378.

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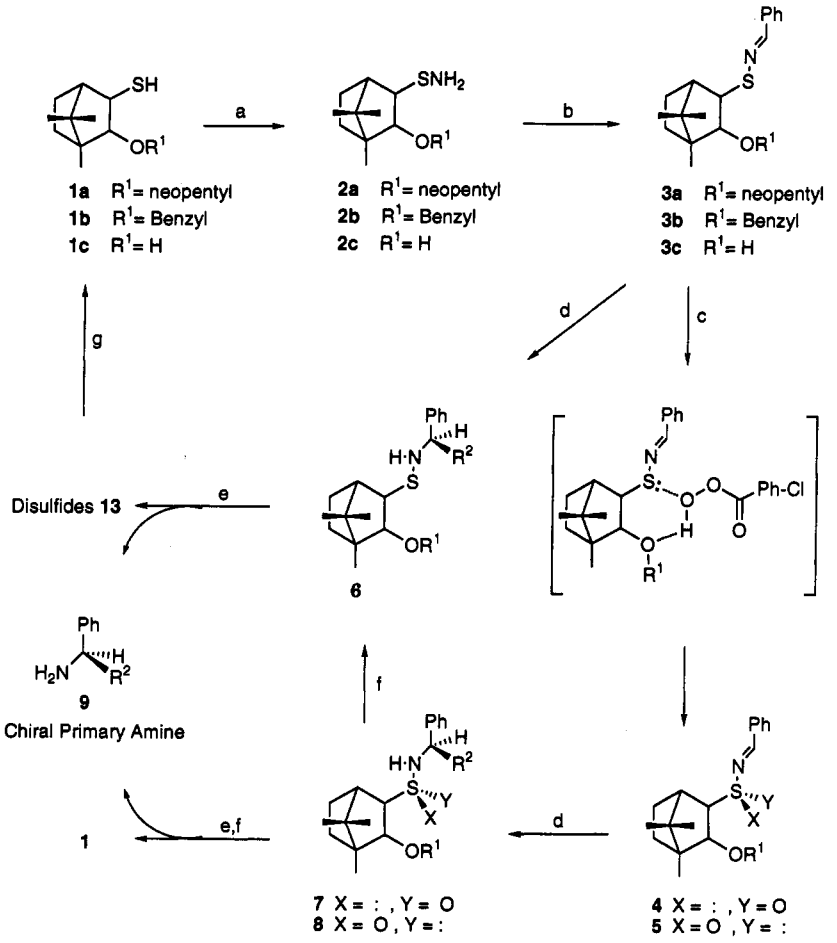
Scheme 1



[a] (a) NCS, NH_3, CH_2Cl_2, −33 °C; (b) PhCHO, CH_2Cl_2, −33 °C; (c) oxidants; (d) alkyl metal reagent; (e) HCl, MeOH; (f) Zn, $TiCl_4$; (g) $LiAlH_4$, THF.

Table 1. Preparations of Sulfenimines and Sulfinimines

entry	substrate	R^1	sulfenamide 2 yield,[a] %	sulfenimine 3 yield,[a] %	oxidant	reactn condtn	sulfinimine yield,[a] %	ratio[c] 4:5
1	**1a**	neopentyl		98[b]	MCPBA/CH_2Cl_2	ambient	92	72:28
2	**1a**	neopentyl		98[b]	MCPBA/CH_2Cl_2	−78 °C	95	86:14
3	**1b**	benzyl		90[b]	MCPBA/CH_2Cl_2	−78 °C	96	88:12
4	**1c**	H		85[b]	MCPBA/CH_2Cl_2	−78 °C	97	>99:1
5	**1a**	neopentyl	79	95				
6	**1c**	H	58	31				
7	**1a**	neopentyl			MMPP/CH_3OH	−78 °C	83	70:30
8	**1b**	benzyl			MMPP/CH_3OH	−78 °C	83	80:20
9	**1c**	H			MMPP/CH_3OH	−78 °C	99	>99:1

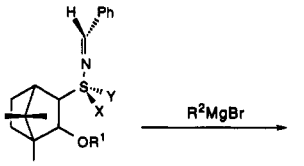
[a] All yields were isolated yields after purification. [b] Overall yields based on the *in situ* process directly from thiol **1** to sulfenimine **3**. [c] The isomeric ratios were determined by isolations after chromatography.

mixtures were stirred for 30 min at the same temperature followed by a regular aqueous workup procedure. The crude sulfenamides **7** were purified by medium pressure column chromatography,[10] and the diastereomeric ratios were determined by NMR analysis of the crude products. The NMR study was confirmed by the isolation of the pure diastereomers. The results of the asymmetric addition reactions described in Table 2 clearly indicate the correspondence of the higher diastereoselectivities (70% to >98%) with the size increments of nucleophiles (entries 6–10). Significantly, sulfenamide **7a(1)** was obtained as the only product in 96% yield from the addition of allylmagnesium bromide to sulfinimine **4a** (entry 4). A plausible explanation for the superior facial selectivity of this process is given in Figure 1. The chairlike transition state **10** illustrates that the allyl anion apparently approaches the imino carbon from the *si* face. On the other hand, the facile aggregation of the methyl Grignard reagent may increase its effective size in the nucleophilic addition, thus the diastereomeric ratio of **7a(2)** is substantially higher than its ethyl analog **7a(3)** (entry 5 vs 6). This hypothesis is also supported by our observation in the nucleophilic addition of **7b(2)** versus **7b(3)** (entry 12 vs 13).

The asymmetric addition of allylmagnesium bromide to the sulfenimines **3a** and **3b** gave a rather low diastereoselectivity (33% and 40% de, entries 1 and 2) in

(10) For a general review of the chemistry of sulfenamides, see (a) Davis, F. A. Nadir, U. K. *Org. Prep. Proc. Int.* **1979**, *11*, 33–51. (b) Craine, L. Raban, M. *Chem. Review* **1989**, *89*, 689–712.

Table 2. Reactions of Sulfenimine and Sulfinimine toward Grignard Reagents



3a X= : , Y= : , R¹ = Neopentyl
3b X= : , Y= : , R¹ = Benzyl
3c X= : , Y= : , R¹ = H
4a X= : , Y= O , R¹ = Neopentyl
4b X= : , Y= O , R¹ = Benzyl

6a(1)R : 6a(1)S X= : , Y= : , R² = Allyl
6b(1)R : 6b(1)S X= : , Y= : , R² = Allyl
6c(1)R : 6c(1)S X= : , Y= : , R² = Allyl
7a(1)R : 7a(1)S X= : , Y= O , R² = Allyl
7a(2)R : 7a(2)S X= : , Y= O , R² = Me
7a(3)R : 7a(3)S X= : , Y= O , R² = Et
7a(4)R : 7a(4)S X= : , Y= O , R² = n-Bu
7a(5)R : 7a(5)S X= : , Y= O , R² = i-Pr
7a(6)R : 7a(6)S X= : , Y= O , R² = t-Bu
7b(1)R : 7b(1)S X= : , Y= O , R² = Allyl
7b(2)R : 7b(2)S X= : , Y= O , R² = Me
7b(3)R : 7b(3)S X= : , Y= O , R² = Et
7b(4)R : 7b(4)S X= : , Y= O , R² = n-Bu
7b(6)R : 7b(6)S X= : , Y= O , R² = t-Bu

entry	substrate	nucleophile	time, min	products yield,[a] %	% de[c] S (confign)
1	**3a**	allylMgBr/THF	30	**6a(1)** 81	34
2	**3b**	allylMgBr/THF	60	**6b(1)** 72	40
3	**3c**	allylMgBr/THF	60	**6c(1)** 75	>98[d]
4	**4a**	allylMgBr/THF	30	**7a(1)** 96	>98[d]
5	**4a**	MeMgI/Et_2O–THF	30	**7a(2)** 96	>97[e]
6	**4a**	EtMgI/Et_2O–THF	30	**7a(3)** 92	70[e]
7	**4a**	*n*-BuMgBr/THF	30	**7a(4)** 96	82[e]
8	**4a**	*n*-BuLi/hexane–THF	30	**7a(4)** 60	50[e]
9	**4a**	*i*-PrMgBr/THF	30	**7a(5)** 83	88[e]
10	**4a**	*t*-BuMgBr/THF	60	**7a(6)** 60[b]	>98[d]
11	**4b**	allylMgBr/THF	30	**7b(1)** 84	>98[d]
12	**4b**	MeMgI/Et_2O–THF	30	**7b(2)** 84	>98[d]
13	**4b**	EtMgI/Et_2O–THF	30	**7b(3)** 54	30[e]
14	**4b**	*n*-BuMgBr/THF	30	**7b(4)** 71	70[e]
15	**4b**	*n*-BuLi/hexane–THF	30	**7b(4)** 90	20[e]
16	**4b**	*t*-BuMgBr/THF	60	**7b(6)** 50[b]	>98[d]

[a] All yields were based on the isolations of products. [b] Yields were not optimized. [c] The diastereomeric ratios were determined by the integration of the 300-MHz ^1H NMR spectra. [d] The other diastereomer was not found. [e] The minor *R* form diastereomer was isolated and identified.

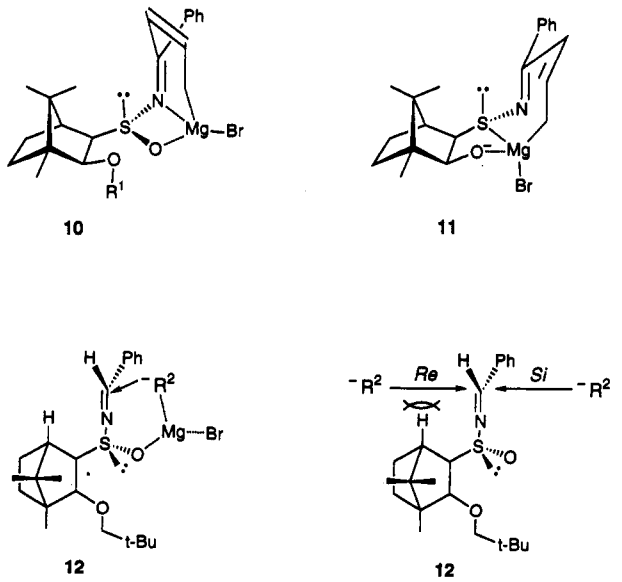


Figure 1.

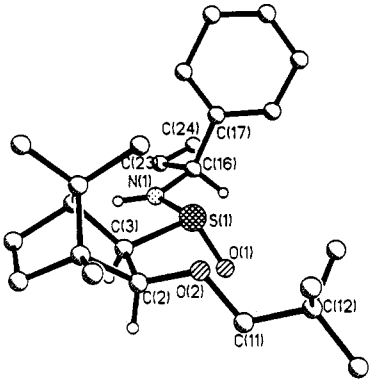
comparison with their sulfinimine analogs **4a** and **4b** (>98% de, entries 4 and 11). The chairlike transition state **10** in Figure 1 suggests the importance of the chelation effect of the sulfinimine to the metal, which brings the allyl group close to the *si* face of the imino group, in obtaining the high diastereoselectivity. Meanwhile, sulfenimine **3c** gave excellent facial selectivity when another chairlike transition state (**11**) could be achieved by chelation of the magnesium ion with both the sulfenimine and the alkoxide oxygen. On the other hand, it is worth mentioning that all of the sulfenimines **3** and sulfinimines **4** we used in the addition reactions produced *S*-form chirality on the amino carbon. Our rationale is that sulfinimine **4** may prefer to adopt the conformation **12**, in which the *si* face is more prone to be attacked by organometallic nucleophiles.[11] This may be due to the association of the sulfinyl oxygen and the metal, or due to the shielding of the *re* face by the camphor skeleton. Another supporting evidence for the importance of the metal complexation is that the replacement of Grignard nucleophile by alkyllithium significantly lowers the stereoselectivity (entry 7 vs 8 and 14 vs 15).

Cleavage of Chiral Amine and Recycle of Chiral Auxiliary. The X-ray crystallographic studies of **7a(3)S** and **7b(4)S** shown in Figure 2 confirmed our assignments on the absolute configuration of the α-amino carbon as well as the sulfur chiral center.[12] The chirality of the α-amino carbon atoms in some adducts was confirmed by converting them into the corresponding known amines **9(1)–(6)** in 85% to 90% yields with higher than 99% optical purity.[13–16] Sulfinamides **7** were treated with zinc

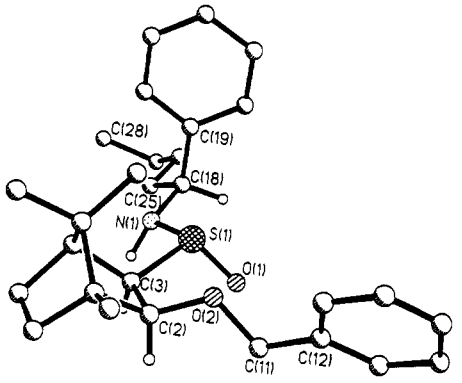
(11) The proposed conformation of sulfinimine **4** was based the computer aid conformation analysis program from *Biosym* and the X-ray structure of **7a(3)S**.

(12) Crystal data of **7a(3)S** and **7b(4)S** supplied as supplementary material.

(13) Deng, J.-G.; Hu, W.-H.; Liu, G.-L.; Mi, A.-Q.; Jiang, Y.-Z. *Chin. J. Chem.* **1990**, *6*, 542–549.
(14) Wu, M.-J.; Pridgen, L. N. *J. Org. Chem.* **1991**, *56*, 1340–1344.
(15) Smith, H. E.; Gordon, A. W.; Bridges, A. F. *J. Org. Chem.* **1974**, *39*, 2309–2311.



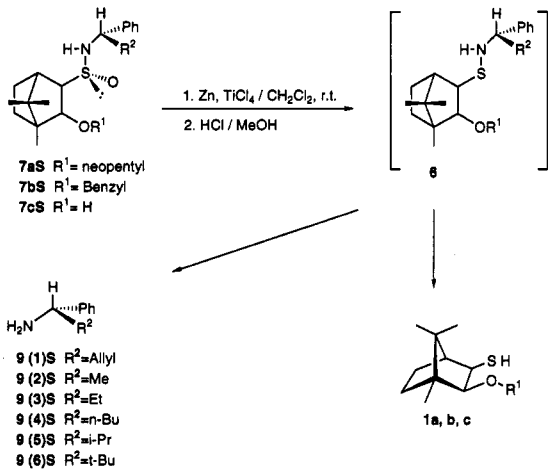
X-ray plot of (3R)-*exo*-[[(1"S)-1-phenylpropyl]amino-(1'R)-sulfinyl]-(1R,2S)-1,7,7-trimethyl-2-*exo*-(2,2-dimethylpropoxy)-bicyclo[2.2.1]heptane **7a(3)S**



X-ray plot of (3R)-*exo*-[[(1"S)-1-phenylpentyl]amino-(1'R)-sulfinyl]-(1R,2S)-1,7,7-trimethyl-2-*exo*-benzyloxy-bicyclo[2.2.1]heptane **7b(4)S**

Figure 2.

Scheme 2



powder and 1.0 M titanium tetrachloride in dichloromethane at ambient temperature to produce sulfenamides **6**,[17] which were hydrolyzed in a 1 N hydrochloric acid solution of methanol to give free amines and the mercapto chiral auxiliaries in good chemical and optical yields (Scheme 2 and Table 3). When sulfenamides **6** were hydrolyzed in 6 N aqueous hydrochloric acid without zinc,[7] disulfide **13** was the major product, which when reduced by LAH in tetrahydrofuran gave thiol **1** in high yield.

(16) Johnson, W. C., Jr.; Fontana, L. P.; Smith, H. E. *J. Am. Chem. Soc.* **1987**, *109*, 3361–3369.
(17) Drabowicz, J.; Mikolajczyk, M. *Synthesis* **1978**, 138–139.
(18) Goodridge, R. J.; Hambley, T. W.; Haynes, R. K.; Ridley, D. D. *J. Org. Chem.* **1988**, *53*, 2881–2889.

Conclusion

In summary, we present here the use of three new mercapto chiral auxiliaries **1a–c** which can direct the asymmetric addition of Grignard reagents to optically active sulfinyl aldimines, hence providing an efficient preparation of chiral α-alkylbenzylamines. More significantly, it is the unique feature of our new chiral auxiliary **1c** which allows us to demonstrate the first example of completely diastereoselective addition to the chiral sulfenimine **3c**.[7] Our observation suggests that these mercapto chiral templates rely not only on the chirality at the sulfur atom but also on the camphor skeleton to provide a chiral environment that ensures the asymmetric facial selectivity. This methodology can also be used in the ketimines and nonaromatic aldimine[3a] systems; however, our present results indicate that the chemical yields of such reactions were still too low (<15%) to be synthetically useful. Applications of these mercapto chiral auxiliaries to the synthesis of amino acids will be reported in due course.

Experimental Section

General Aspects. Melting points were determined with a Buchi 535 digital melting point apparatus and are uncorrected. Optical rotations were recorded on a Perkin-Elmer Model 241 polarimeter using a 1.0-dm cell at specific temperatures. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-300 and Gemini-200 spectrometers with chemical shifts (δ) given in ppm from internal TMS. Infrared spectra were measured on a Hitachi 270-30 IR spectrometer. High-resolution mass spectra were recorded on a Jeol Jms-SX/SX 102A mass spectrometer. Microanalyses were performed by the NSC Central Instrumental Center on Heraeus CHN-O-Rapid and Tacussel Coulomax 78 instruments. *n*-Butyllithium was purchased from Aldrich Chemical Co. and standardized by titration. Merck silica gel 60 (70–230 mesh) was used for chromatography. Solvent systems are described as volume ratios before mixing. Merck 5715 glass-backed TLC plates were used for analysis of reactions and fractions.

Preparation of (1*R*,2*S*,3*R*)-3-Mercapto-2-(benzyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (1b). A solution of 3-mercapto-2-camphanol (**1c**)[6b,18] (3.00 g, 16.0 mmol) in 100 mL of benzene was added slowly to a solution of benzaldehyde (1.89 g, 1.89 mmol) and *p*-toluenesulfonic acid monohydrate (0.30 g, 1.60 mmol) in 60 mL of benzene at room temperature. The resulting mixture was stirred for 1 h and then diluted with 50 mL of saturated aqueous sodium bicarbonate. The aqueous layer was extracted with three 100-mL portions of dichloromethane. The combined organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to give a pale yellow oil. The crude product was purified through silica gel eluted with 1:60 ethyl acetate–hexane to yield 4.30 g (98%) of the desired oxathiolane as a white crytalline solid.

A mixture of diphenylsilane (1.82 g, 9.88 mol), bis(tributyltin) oxide (5.89 g, 9.88 mol), and azobis(isobutyronitrile) (185 mg, 1.14 mmol) in 30 mL of toluene was added to a refluxing solution of the oxathiolane (1.35 g, 4.94 mol) obtained from the above process in 20 mL of toluene. Upon the completion of addition, the reaction temperature was kept at 110 °C for another 3 h followed by addition of 100 mL of aqueous saturated ammonium chloride. The reaction pot was allowed to reach ambient temperature, and the aliquot was extracted with three 100-mL portions of hexane. The combined organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to give a pale yellow oil. The crude products were purified through silica gel eluted with 1:25 dichloromethane–hexane to yield 1.25 g (92%) of the desired thiol **1b** as a white crytalline solid: mp = 74–75 °C; $[\alpha]^{20}_D$ = −100.4° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3024, 2964, 1234, 1204 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (s, 3H), 0.93 (s, 3H), 1.00–1.15 (m, 2H), 1.22 (s, 3H), 1.40–1.60 (m, 2H), 1.65–1.80 (m, 2H), 1.94 (d, J = 8.4 Hz, 1H), 3.24 (t, J = 7.8 Hz, 1H), 3.41 (d, J = 7.8 Hz, 1H), 4.45 (d, J = 12.3 Hz, 1H), 4.84 (d, J = 12.3 Hz, 1H), 7.20–7.45

Table 3

entry	sulfenamide or sulfinamide	R^1	R^2	amine yield,[a] %	optical purity, %	amine[b] $[\alpha]_D$, deg	amine lit. $[\alpha]_D$, deg	recycled thiol yield,[a] %
1	**6c(1)S**	H	allyl	**9(1)S** 80	>99	−31.8 (*c* 1.50)	5.5 (*c* 1.89)[c]	
2	**7a(1)S**	neopentyl	allyl	**9(1)S** 80	99	−31.5 (*c* 1.50)	5.5 (*c* 1.89)[c]	86
3	**7a(2)S**	neopentyl	Me	**9(2)S** 56	>99	−30.4 (*c* 1.00)	28.8 (*c* 1.00)[d]	89
4	**7a(3)S**	neopentyl	Et	**9(3)S** 78	99	−36.6 (*c* 1.00)	35.2 (*c* 1.20)[e]	87
5	**7a(4)S**	neopentyl	*n*-Bu	**9(4)S** 79	>99	−12.7 (*c* 2.50)	11.7 (*c* 1.00)[f]	90
6	**7a(5)S**	neopentyl	*i*-Pr	**9(5)S** 86	>98	−11.5 (*c* 1.00)	8.5 (*c* 1.00)[g]	90
7	**7a(6)S**	neopentyl	*t*-Bu	**9(6)S** 86		−5.5 (*c* 1.00)	−5.4 (neat)[h]	85
8	**7b(1)S**	benzyl	allyl	**9(1)S** 80	>98	−31.2 (*c* 1.50)	5.5 (*c* 1.89)[c]	87

[a] All yields were based on the isolations of products. [b] All of the optical rotation data of amines were taken in $CHCl_3$. [c] The optical rotation data of the corresponding 92% ee *R*-form amines were taken in EtOH in ref 13. [d] The optical rotation data of the corresponding 94% ee *R*-form amines were taken in $CHCl_3$ in ref 14. [e] The optical rotation data of the corresponding 95% ee *R*-form amines were taken in $CHCl_3$ in ref 14. [f] The optical rotation data of the corresponding 92% ee *R*-form amines were taken in $CHCl_3$ in refs 14 and 3e. [g] The optical rotation data of the corresponding *R*-form amines were taken in benzene in refs 15 and 3e. [h] The optical rotation data of the corresponding 96% ee *S*-form amines were taken in neat form in ref 16.

(m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.21, 21.53, 21.68, 28.68, 33.57, 47.34, 47.41, 50.39, 55.36, 74.46, 88.33, 127.24, 127.42, 128.41, 138.83. Anal. Calcd for $C_{17}H_{24}OS$: C, 73.87; H, 8.75; S, 11.60. Found: C, 73.78; H, 8.75; S, 11.56.

Typical Procedure for the Preparation of Sulfenamides 2. To a 50-mL three-neck flask fitted with a dry ice condenser containing *N*-chlorosuccinimide (178 mg, 1.34 mmol) in 12 mL of liquid ammonia was slowly added a solution of thiol **1a**[6b] (268 mg, 1.04 mmol) in 2 mL of tetrahydrofuran at −33 °C. The reaction mixture was stirred for 30 min and then was warmed up to room temperature for evaporation of liquid ammonia. The residue was concentrated *in vacuo* and purified through 20 g of silica gel eluted with 1:20 ethyl acetate–hexane to give 210 mg (79%) of the desired sulfenamide **2a** as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 0.79 (s, 3H), 0.89 (s, 3H), 0.92 (s, 9H), 1.00–1.10 (m, 2H), 1.15 (s, 3H), 1.40–1.55 (m, 1H), 1.70–1.85 (m, 1H), 1.92 (d, *J* = 4.5 Hz, 1H), 2.27 (br s, 2H), 3.05 (d, *J* = 7.8 Hz, 1H), 3.18 (d, *J* = 7.8 Hz, 1H), 3.34 (d, *J* = 7.8 Hz, 1H), 3.37 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.88, 21.09, 21.44, 26.85, 28.70, 32.72, 33.48, 46.95, 49.85, 50.62, 66.19, 83.90, 89.01; HRMS (EI) for $C_{15}H_{29}NOS$ calcd 271.1972, found 271.1976.

Typical Procedure for the Preparation of Sulfenimines 3. To a 50-mL three-neck flask fitted with a dry ice condenser containing *N*-chlorosuccinimide (552 mg, 4.14 mmol) in 40 mL of liquid ammonia was slowly added a solution of thiol **1a**[6b] (533 mg, 2.08 mmol) in 2 mL of tetrahydrofuran at −33 °C. The reaction mixture was stirred for 30 min followed by the addition of benzaldehyde (315 mg, 2.97 mmol) in 5 mL of dichloromethane. The resulting mixture was warmed up to room temperature and stirred for another 28 h. It was then poured into 20 mL of distilled water. The aqueous layer was extracted with three 20-mL portions of dichloromethane. The combined organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to give a pale yellow oil. The crude product was chromatographed through 30 g of silica gel eluted with hexane to yield 731 mg (98%) of the desired sulfenimine **3a** as a light yellow oil: $[\alpha]_D$ = +44.4° (*c* 5.9, $CHCl_3$); IR ($CHCl_3$) 1450 (s, N=C); ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (s, 3H), 0.90 (s, 9H), 0.94 (s, 3H), 1.14 (s, 3H), 1.11–1.30 (m, 2H), 1.48–1.62 (m, 1H), 1.76–1.90 (m, 1H), 2.05 (d, *J* = 4.5 Hz, 1H), 3.01 (d, *J* = 7.8 Hz, 1H), 3.38 (d, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 7.8 Hz, 1H), 3.88 (d, *J* = 7.8 Hz, 1H), 7.30–7.40 (m, 3H), 7.58–7.61 (m, 2H), 8.37 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.84, 21.10, 21.18, 26.89, 28.35, 32.77, 33.61, 47.08, 50.67, 51.68, 61.55, 83.87, 89.26, 126.77, 128.51, 129.42, 136.92, 154.28; HRMS (EI) for $C_{22}H_{33}NOS$ calcd 359.2283, found 359.2285. Anal. Calcd for $C_{22}H_{33}NOS$: C, 73.49; H, 9.25; N, 3.89; S, 8.92. Found: C, 73.56; H, 9.30; N, 3.87; S, 9.02.

3b: $[\alpha]_D$ = +84.0° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 1454 (s, N=C); ^1H NMR (300 MHz, $CDCl_3$) δ 0.83 (s, 3H), 0.94 (s, 3H), 1.13 (s, 3H), 1.23–1.32 (m, 1H), 1.49–1.61 (m, 2H), 1.78–1.92 (m, 1H), 2.09 (d, *J* = 4.5 Hz, 1H), 3.67 (d, *J* = 7.8 Hz, 1H), 3.94 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.78 (d, *J* = 11.7 Hz, 1H), 7.20–7.40 (m, 8H), 7.58–7.61 (m, 2H), 8.40 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.94, 20.97, 21.35, 28.37, 33.74, 47.12, 50.43, 52.27, 61.86, 74.49, 88.72, 126.81, 127.15, 127.36, 128.08, 128.55, 129.57, 136.77, 138.94, 154.71; HRMS (EI) for $C_{24}H_{29}NOS$ calcd 379.1970, found 379.1971. Anal. Calcd for $C_{24}H_{29}NOS$: C, 75.95; H, 7.70; N, 3.69; S, 8.45. Found: C, 76.01; H, 7.75; N, 3.71; S, 8.49.

3c: $[\alpha]_D$ = +117.7° (*c* 6.9, $CHCl_3$); IR ($CHCl_3$) 3484 (br, OH), 1450 (s, N=C); ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (s, 3H), 0.99 (s, 3H), 1.02 (s, 3H), 1.14–1.25 (m, 1H), 1.25–1.36 (m, 1H), 1.51–1.60 (m, 1H), 1.80–1.92 (m, 1H), 2.05 (d, *J* = 4.5 Hz, 1H), 2.48 (d, *J* = 3.0 Hz, 1H), 3.90 (d, *J* = 7.8 Hz, 1H), 3.96 (dd, *J* = 7.8, 3.0 Hz, 1H), 7.30–7.40 (m, 3H), 7.58–7.62 (m, 2H), 8.45 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.52, 21.07, 21.38, 28.77, 33.47, 47.02, 49.84, 52.14, 62.52, 80.30, 127.04, 128.61, 130.09, 136.27, 156.66. Anal. Calcd for $C_{17}H_{23}NOS$: C, 70.54; H, 8.01; N, 4.84; S, 11.08. Found: C, 70.39; H, 8.12; N, 4.46; S, 11.07.

Typical Procedure for the Preparation of Sulfinimines 4 and 5. To a solution of sulfenimine **3a** (1.05 g, 2.92 mmol) in 8 mL of tetrahydrofuran was slowly added a solution of 85% *m*-chloroperoxybenzoic acid (0.66 g, 3.24 mmol) in 2 mL of tetrahydrofuran at −78 °C over a period of 10 min. Upon completion of the addition, the reaction mixture was stirred for another 10 min, and then 20 mL of saturated aqueous sodium bicarbonate was added. The resulting mixture was extracted with three 20-mL portions of ether. The combined organic layer was dried ($MgSO_4$) and concentrated in vacuo to give a pale yellow oil. The crude products were chromatographied through 30 g of silica gel eluted with 1:15 ethyl acetate–hexane to yield 895 mg (82%) of sulfenimine **4a** as a colorless oil and 142 mg (13%) of sulfenimine **5a** as a pale yellow oil.

4a: $[\alpha]_D$ = −34.5° (*c* 3.4, $CHCl_3$); IR ($CHCl_3$) 1080 (s, SO); ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 3H), 1.00 (s, 9H), 1.01 (s, 3H), 0.90–1.10 (m, 2H, CH_2), 1.32 (s, 3H), 1.45–1.60 (m, 1H), 1.70–1.83 (m, 1H), 2.52 (d, *J* = 4.5 Hz, 1H), 2.71 (d, *J* = 7.8 Hz, 1H), 3.15 (d, *J* = 7.8 Hz, 1H), 3.52 (d, *J* = 7.8 Hz, 1H), 3.59 (d, *J* = 7.8 Hz, 1H), 7.42–7.53 (m, 3H), 7.85–7.88 (m, 2H), 8.67 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.65, 20.72, 21.45, 26.86, 28.38, 32.60, 32.83, 46.87, 49.50, 50.86, 82.16, 84.09, 87.57, 128.86, 129.34, 132.08, 134.55, 161.29; HRMS (EI) for $C_{22}H_{33}NO_2S$ calcd 375.2232, found 375.2224. Anal. Calcd for $C_{22}H_{33}NO_2S$: C, 70.36; H, 8.87; N, 3.73; S, 8.54. Found: C, 69.97; H, 8.87; N, 3.76; S, 8.53.

5a: mp = 96–97 °C; $[\alpha]_D$ = +136.0° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 1080 (s, SO); ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 3H), 0.95 (s, 9H), 1.00 (s, 3H), 0.94–1.04 (m, 2H), 1.43 (s, 3H), 1.44–1.60 (m, 1H), 1.78–1.90 (m, 1H), 2.39 (d, *J* = 4.5 Hz, 1H), 2.82 (d, *J* = 7.8 Hz, 1H), 3.16 (d, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 7.8 Hz, 1H), 3.73 (d, *J* = 7.8 Hz, 1H), 7.44–7.48 (m, 3H), 7.85–7.89 (m, 2H), 8.64 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.61, 20.83, 21.05, 26.98, 28.36, 32.79, 32.94, 47.05, 47.29, 51.39, 78.93, 83.61, 87.66, 128.93, 129.30, 132.15, 134.53, 160.03; HRMS (EI) for $C_{22}H_{33}NO_2S$ calcd 375.2232, found 375.2224. Anal. Calcd for $C_{22}H_{33}NO_2S$: C, 70.36; H, 8.87; N, 3.73; S, 8.54. Found: C, 69.97; H, 8.87; N, 3.76; S, 8.53.

4b: $[\alpha]_D$ = +18.08° (*c* 2.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 3H), 0.98 (s, 3H), 0.92–1.06 (m, 2H), 1.31 (s, 3H), 1.48–1.59 (m, 1H), 1.70–1.83 (m, 1H), 2.53 (d, *J* = 4.5 Hz, 1H), 2.80 (d, *J* = 7.8 Hz, 1H), 3.73 (d, *J* = 7.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 7.26–7.38 (m, 3H), 7.40–7.51 (m, 5H), 7.86–7.89 (m, 2H), 8.69 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.62, 20.70, 21.64, 28.32, 32.96, 46.93, 49.48, 50.69, 76.56, 81.77, 88.09, 127.41, 127.97, 128.16, 128.87, 129.36, 132.16, 134.51, 138.60, 161.44; HRMS (EI) for $C_{24}H_{29}NO_2S$ calcd 395.1919, found 395.1926. Anal. Calcd for $C_{24}H_{29}NO_2S$: C, 72.87; H, 7.39; N, 3.54; S, 8.11. Found: C, 72.48; H, 7.44; N, 3.57; S, 8.10.

5b: mp = 103–104 °C; $[\alpha]_D$ = +250.52° (*c* 2.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (s, 3H), 0.99 (s, 3H), 0.95–1.15 (m, 2H), 1.42 (s, 3H), 1.46–1.68 (m, 1H), 1.80–1.96 (m, 1H), 2.43 (d, *J* = 4.6 Hz, 1H), 2.89 (d, *J* = 7.8 Hz, 1H), 3.70 (d, *J* = 7.8 Hz, 1H), 4.59 (d, *J* = 10.8 Hz, 1H), 5.09 (d, *J* = 10.8 Hz, 1H), 7.26–7.55 (m, 8H), 7.81–7.86 (m, 2H), 8.69 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.56, 21.00, 28.34, 33.05, 47.17, 47.33, 51.24, 75.47, 78.64, 88.31, 127.47, 128.20, 128.24, 128.94, 129.36, 132.26, 134.40, 138.75, 160.69; HRMS (EI) for $C_{24}H_{29}NO_2S$ calcd 395.1919, found 395.1926.

4c: mp = 108–109 °C, $[\alpha]_D$ = −32.60° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 3H), 1.03 (s, 3H), 0.94–1.12 (m, 2H), 1.37 (s, 3H), 1.52–1.58 (m, 1H), 1.76–1.86 (m, 1H), 2.47 (d, *J* = 4.5 Hz, 1H), 2.69 (d, *J* = 7.2 Hz, 1H), 3.45 (br s, 1H), 4.08 (d, *J* = 7.2 Hz, 1H), 7.48–7.53 (m, 3H), 7.87–7.90 (m, 2H), 8.67 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.36, 21.01, 21.60, 28.34, 33.14, 47.16, 49.02, 49.97, 80.01, 81.10, 128.88, 129.39, 132.35, 134.28, 161.86; HRMS (EI) for $C_{17}H_{23}NO_2S$ calcd 305.1449, found 305.1446. Anal. Calcd for $C_{17}H_{23}NO_2S$: C, 66.85; H, 7.59; N, 4.59. Found: C, 66.35; H, 7.59; N, 4.59.

Typical Procedure for the Grignard Reagent Addition of Sulfinimines 3 and Sulfinimines 4. To a solution of sulfinimine **4a** (153 mg, 0.41 mmol) in 2 mL of tetrahydrofuran was added a 0.5 M tetrahydrofuran solution of allylmagnesium bromide (6 mL, 3.0 mmol). The mixture was stirred for another 30 min and then was poured into 20 mL of aqueous saturated ammonium chloride. The aqueous layer was extracted with three 20-mL portions of ether. The combined organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to give a pale yellow oil. The crude product was purified by chromatography through silica gel eluted with 1:2 ethyl acetate–hexane to give 164 mg (96%) of sulfinamide **7a(1)S** as a white crystalline solid: mp = 126–127 °C; $[\alpha]_D$ = −82.74° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 3300 (w, NH), 1082 (s, SO); ^1H NMR (300 MHz, $CDCl_3$) δ 0.75 (s, 3H), 0.86 (s, 9H), 0.87 (s, 3H), 0.90 (s, 3H), 0.98–1.18 (m, 2H), 1.44–1.58 (m, 1H), 1.70–1.84 (m, 1H), 2.18 (d, *J* = 4.5 Hz, 1H), 2.45–2.65 (m, 2H), 2.96 (d, *J* = 7.8 Hz, 1H), 2.98 (d, *J* = 7.8 Hz, 1H), 3.43 (d, *J* = 7.8 Hz, 1H), 3.45 (d, *J* = 7.8 Hz, 1H), 3.76 (br s, 1H), 4.51 (t, *J* = 6.9 Hz, 1H), 5.12–5.19 (m, 2H), 5.64–5.78 (m, 1H), 7.25–7.33 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.60, 20.70, 20.90, 26.75, 28.40, 32.45, 32.88, 43.08, 46.70, 50.18, 50.94, 56.89, 79.94, 83.86, 87.22, 118.92, 127.41, 127.47, 128.29, 134.12, 142.01; HRMS (EI) for $C_{25}H_{39}NO_2S$, calcd 417.2701, found 417.2691. Anal. Calcd for $C_{25}H_{39}NO_2S$: C, 71.90; H, 9.41; N, 3.35; S, 7.68. Found: C, 71.79; H, 9.46; N, 3.38; S, 7.56.

6a(1)S+6a(1)R: IR ($CHCl_3$) 3400 (br, NH); ^1H NMR (300 MHz, $CDCl_3$) δ 0.72 (s, CH_3), 0.74 (s, CH_3), 0.80–0.90 (s, Bu^t, CH_2, CH_3), 0.93 (s, CH_3), 1.00 (s, CH_3), 1.36–1.46 (m, CH_2), 1.47–1.78 (m, CH, CH_2), 1.81 (d, *J* = 4.5 Hz, CH), 2.39–2.60 (m, C=CCH_2), 2.86 (d, *J* = 7.8 Hz, SCH), 2.88 (d, *J* = 7.8 Hz, SCH), 3.02 (d, *J* = 7.8 Hz, OCH_2), 3.04 (d, *J* = 7.8 Hz, OCH_2), 3.18 (d, *J* = 7.8 Hz, OCH), 3.22 (d, *J* = 7.8 Hz, OCH), 3.26 (d, *J* = 7.8 Hz, OCH_2), 3.29 (d, *J* = 7.8 Hz, OCH_2), 3.90 (t, *J* = 6.9 Hz, NCHPh), 5.03–5.10 (m, C=CH_2), 5.61–5.75 (m, CH=C), 7.20–7.32 (m, PhH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.86, 21.09, 21.22, 26.85, 26.92, 27.03, 28.42, 32.63, 33.58, 41.84, 46.77, 50.41, 51.11, 51.84, 61.65, 64.44, 83.54, 89.26, 117.49, 117.58, 127.15, 127.49, 127.63, 128.18, 128.24, 135.17, 143.52. Anal. Calcd for $C_{25}H_{39}NOS$: C, 74.76; H, 9.79; N, 3.49; S, 7.98. Found: C, 74.59; H, 9.86; N, 3.24; S, 8.05.

6b(1)S+6b(1)R: IR ($CHCl_3$) 3400 (w, NH); ^1H NMR (300 MHz, $CDCl_3$) δ 0.72 (s, CH_3), 0.75 (s, CH_3), 0.84 (s, CH_3), 0.85–0.95 (m, CH_3), 1.00 (s, CH_3), 1.04 (s, CH_3), 1.38–1.46 (m, CH_2), 1.55–1.75 (m, CH, CH_2), 1.87 (d, *J* = 4.2 Hz, CH), 2.35–2.60 (m, C=CCH_2, NH), 2.93 (br, NH), 3.01 (d, *J* = 7.8 Hz, SCH), 3.04 (d, *J* = 7.8 Hz, SCH), 3.35 (d, *J* = 7.8 Hz, OCH), 3.41 (d, *J* = 7.8 Hz, OCH), 3.88–3.93 (m, NCHPh), 4.32 (d, *J* = 12 Hz, OCH_2Ph), 4.35 (d, *J* = 12 Hz, OCH_2Ph), 4.66 (d, *J* = 12 Hz, OCH_2Ph), 5.00–5.10 (m, C=CH_2), 5.60–5.75 (m, CH=C), 7.20–7.35 (m, PhH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.92, 20.99, 21.11, 21.38, 28.41, 28.46, 33.82, 41.86, 41.96, 46.83, 46.91, 50.28, 51.78, 52.19, 62.00, 62.11, 64.96, 65.38, 74.49, 89.03, 117.45, 117.58, 127.06, 127.21, 127.25, 127.30, 127.38, 127.55, 127.68, 128.06, 128.08, 128.25, 128.28, 135.06, 135.10, 139.24, 143.59; HRMS (EI) for $C_{27}H_{35}NOS$ calcd 421.2440, found 421.2429.

6c(1)S: $[\alpha]_D$ = −30.74° (*c* 1.9, $CHCl_3$); IR ($CHCl_3$) 3400 (br, OH); ^1H NMR (300 MHz, $CDCl_3$) δ 0.69 (s, 3H), 0.72 (s, 3H), 0.89 (s, 3H), 0.90–1.15 (m, 2H), 1.32–1.45 (m, 1H), 1.60–1.70 (m, 1H), 1.71 (d, *J* = 3.9 Hz, 1H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.90 (d, *J* = 7.5 Hz, 1H), 3.62 (d, *J* = 7.5 Hz, 1H), 3.88 (t, *J* = 6.9 Hz, 1H), 5.08 (d, *J* = 9.9 Hz, 1H), 5.09 (d, *J* = 17.4 Hz, 1H), 5.61–5.75 (m, 1H), 7.26–7.36 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.49, 20.82, 21.30, 28.75, 33.38, 42.24, 46.29, 49.56, 53.03, 65.00, 65.80, 79.65, 118.08, 127.47, 127.59, 128.38, 134.65, 142.74. Anal. Calcd for $C_{20}H_{28}NOS$: C, 72.68; H, 8.54; N, 4.24; S, 9.70. Found: C, 72.81; H, 8.81; N, 4.14; S, 9.39.

7a(2)S: mp = 147–148 °C; $[\alpha]_D$ = −64.78° (*c* 2.1, $CHCl_3$); IR ($CHCl_3$) 3350 (w, NH), 1090 (s, SO); ^1H NMR (300 MHz, $CDCl_3$) δ 0.76 (s, 3H), 0.89 (s, 9H), 0.92 (s, 3H), 0.94 (s, 3H), 1.03–1.10 (m, 1H), 1.44–1.51 (m, 1H), 1.54 (d, *J* = 6.9 Hz, 1H), 1.70–1.82 (m, 2H), 2.17 (d, *J* = 3.9 Hz, 1H), 2.98 (d, *J* = 7.8 Hz, 1H), 3.00 (d, *J* = 7.8 Hz, 1H), 3.45 (d, *J* = 7.8 Hz, 1H), 3.47 (d, *J* = 7.8 Hz, 1H), 3.61 (br s, 1H), 4.55–4.65 (m, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.62, 20.69, 20.98, 24.90, 26.76, 28.36, 32.48, 32.84, 46.70, 50.23, 50.98, 53.39, 79.84, 83.77, 87.17, 126.86, 127.29, 128.38, 143.81; HRMS (EI) for $C_{23}H_{37}NO_2S$ calcd 391.2545, found 391.2551. Anal. Calcd for $C_{23}H_{37}NO_2S$: C, 70.54; H, 9.52; N, 3.58; S, 8.19. Found: C, 70.14; H, 9.52; N, 3.52; S, 8.15.

7a(2)R: mp = 111–112 °C; $[\alpha]_D$ = +3.40° (*c* 2.0, $CHCl_3$); IR ($CHCl_3$) 3370 (w, NH), 1095 (s, SO); ^1H NMR (300 MHz, $CDCl_3$) δ 0.46–0.55 (m, 1H), 0.76 (s, 3H), 0.92 (s, 9H), 0.95 (s, 3H), 1.13 (s, 3H), 1.35–1.45 (m, 1H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.92 (d, *J* = 3.9 Hz, 1H), 2.87 (d, *J* = 7.5 Hz, 1H), 3.03 (d, *J* = 7.5 Hz, 1H), 3.38 (d, *J* = 7.5 Hz, 1H), 3.50 (d, *J* = 7.5 Hz, 1H), 3.78 (br s, 1H), 4.66–4.76 (m, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.63, 20.73, 21.18, 24.35, 26.82, 27.70, 32.52, 32.72, 46.65, 50.06, 51.04, 77.82, 83.74, 87.17, 126.76, 127.43, 128.46, 144.74; HRMS (EI) for $C_{23}H_{37}NO_2S$ calcd 391.2545, found 391.2546. Anal. Calcd for $C_{23}H_{37}NO_2S$: C, 70.54; H, 9.52; N, 3.58; S, 8.19. Found: C, 70.55; H, 9.49; N, 3.62; S, 8.15.

7a(3)S: mp = 144–146 °C; $[\alpha]_D$ = −74.57° (*c* 2.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.73 (s, 3H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.86 (s, 12H), 0.90 (s, 3H), 1.00–1.14 (m, 2H), 1.40–1.52 (m, 1H), 1.70–1.90 (m, 3H), 2.14 (d, *J* = 3.9 Hz, 1H), 2.99 (d, *J* = 7.8 Hz, 1H), 3.02 (d, *J* = 7.8 Hz, 1H), 3.43 (d, *J* = 7.8 Hz, 1H), 3.45 (d, *J* = 7.8 Hz, 1H), 3.80 (br s, 1H), 4.32 (t, *J* = 6.9 Hz, 1H), 7.20–7.32 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.52, 11.62, 20.68, 20.89, 26.77, 28.42, 31.53, 32.47, 32.93, 46.69, 50.20, 50.99, 59.85, 80.05, 83.85, 87.30, 127.32, 127.65, 128.25, 142.22; HRMS (EI) for $C_{24}H_{39}NO_2S$ calcd 405.2702, found 405.2700. Anal. Calcd for $C_{24}H_{39}NO_2S$: C, 71.06; H, 9.69; N, 3.45; S, 7.90. Found: C, 71.13; H, 9.65; N, 3.46; S, 7.65.

7a(3)R: mp = 133–135 °C; $[\alpha]_D$ = +4.81° (*c* 1.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.33 (t, *J* = 9.3 Hz, 1H), 0.71 (s, 3H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 3H), 0.95–1.12 (m, 13H), 1.20–1.40 (m, 2H), 1.69–2.00 (m, 3H), 2.83 (d, *J* = 7.5 Hz, 1H), 3.01 (d, *J* = 7.5 Hz, 1H), 3.36 (d, *J* = 7.5 Hz, 1H), 3.50 (d, *J* = 7.5 Hz, 1H), 3.86 (d, *J* = 3 Hz, 1H), 4.48 (m, 1H), 7.20–7.34 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.38, 11.66, 20.74, 21.27, 26.86, 27.58, 31.09, 32.51, 32.78, 46.58, 50.10, 51.08, 55.37, 77.67, 83.81, 87.32, 127.31, 127.52, 128.48, 143.25; HRMS (EI) for $C_{24}H_{39}NO_2S$ calcd 405.2702, found 405.2702. Anal. Calcd for $C_{24}H_{39}NO_2S$: C, 71.06; H, 9.69; N, 3.45; S, 7.90. Found: C, 71.11; H, 9.66; N, 3.47; S, 7.65.

7a(4)S: mp = 104–105 °C; $[\alpha]_D$ = −71.20° (*c* 2.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.73 (s, 3H), 0.85 (s, 3H), 0.86 (s, 9H), 0.90 (s, 3H), 0.84–1.00 (m, 2H), 1.00–1.20 (m, 3H), 1.20–1.35 (m, 3H), 1.40–1.54 (m, 2H), 1.70–1.85 (m, 3H), 2.14 (d, *J* = 4.2 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 1H), 2.98 (d, *J* = 7.5 Hz, 1H), 3.43 (d, *J* = 7.5 Hz, 1H), 3.45 (d, *J* = 7.5 Hz, 1H), 4.39 (t, *J* = 6.9 Hz, 1H), 7.20–7.35 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.62, 13.89, 20.69, 20.86, 22.47, 26.76, 28.21, 28.40, 32.47, 32.88, 38.37, 46.68, 50.17, 50.98, 58.26, 79.84, 83.77, 87.20, 127.31, 127.61, 128.27, 142.54; HRMS (EI) for $C_{26}H_{43}NO_2S$ calcd 433.3015, found 433.302. Anal. Calcd for $C_{26}H_{43}NO_2S$: C, 71.92; H, 9.98; N, 3.25; S, 7.27. Found: C, 71.11; H, 9.66; N, 3.47; S, 7.65.

7a(4)R: mp = 170–171 °C; $[\alpha]_D$ = −1.60° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.31 (t, *J* = 9 Hz, 1H), 0.70 (s, 3H), 0.83 (t, *J* = 7 Hz, 3H), 0.90 (s, 3H), 0.94 (s, 9H), 0.80–0.95 (m, 1H), 1.12 (s, 3H), 1.20–1.40 (m, 6H), 1.68–1.78 (m, 1H), 1.78–1.90 (m, 2H), 2.83 (d, *J* = 7.8 Hz, 1H), 3.00 (d, *J* = 7.2 Hz, 1H), 3.35 (d, *J* = 7.8 Hz, 1H), 3.49 (d, *J* = 7.2 Hz, 1H), 3.86 (d, *J* = 3 Hz, 1H), 4.54 (m, 1H), 7.20–7.33 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$)

δ 11.66, 13.91, 20.75, 21.26, 22.46, 26.84, 27.49, 28.08, 32.52, 32.70, 38.09, 46.55, 50.04, 51.05, 53.82, 83.73, 87.20, 87.22, 127.28, 127.45, 128.50, 143.64; HRMS (EI) for $C_{26}H_{43}NO_2S$ calcd 433.3015, found 433.3025.

7a(5)S: mp = 104–105 °C; $[\alpha]_D$ = −57.2° (*c* 2.9, $CHCl_3$); IR ($CHCl_3$) 3312 (w, NH), 1078 (s, SO); ^1H NMR (300 MHz, $CDCl_3$) 0.73 (s, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.84 (s, 12H), 0.89 (s, 3H), 0.99 (d, *J* = 6.6 Hz, 3H), 1.00–1.16 (m, 2H), 1.20–1.82 (m, 2H), 1.92–2.05 (m, 1H), 2.15 (d, *J* = 4.2 Hz, 1H), 2.96 (d, *J* = 7.8 Hz, 1H), 2.97 (d, *J* = 7.5 Hz, 1H), 3.42 (d, *J* = 7.8 Hz, 1H), 3.43 (d, *J* = 7.5 Hz, 1H), 3.66 (br s, 1H), 4.17 (d, *J* = 6.6 Hz, 1H), 7.20–7.36 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.52, 18.92, 19.28, 20.61, 20.77, 26.66, 28.37, 32.38, 32.79, 34.68, 46.63, 50.02, 50.86, 64.22, 80.04, 83.75, 87.18, 127.24, 127.88, 128.47, 140.78; HRMS (EI) for $C_{25}H_{41}NO_2S$ calcd 419.2860, found 419.2865. Anal. Calcd for $C_{25}H_{41}NO_2S$: C, 71.55; H, 9.85; N, 3.34; S, 7.64. Found: C, 71.39; H, 9.83; N, 3.34; S, 7.64.

7a(5)R: mp = 137–138 °C; $[\alpha]_D$ = +10.60° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.18–0.22 (m, 1H), 0.69 (s, 3H), 0.81 (d, *J* = 6.3 Hz, 3H), 0.89 (s, 3H), 0.94 (s, 9H), 0.96 (d, *J* = 6.3 Hz, 3H), 1.12 (s, 3H), 1.25–1.35 (m, 3H), 1.79 (d, *J* = 3.5 Hz, 1H), 1.95–2.10 (m, 1H), 2.80 (d, *J* = 7.5 Hz, 1H), 2.98 (d, *J* = 7.5 Hz, 1H), 3.32 (d, *J* = 7.5 Hz, 1H), 3.50 (d, *J* = 7.5 Hz, 1H), 3.98 (d, *J* = 4.5 Hz, 1H), 4.40 (dd, *J* = 6.3 Hz, 4.5 Hz, 1H), 7.20–7.30 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.65, 18.63, 19.45, 20.72, 21.32, 26.86, 27.55, 32.49, 32.83, 34.25, 46.53, 50.15, 51.10, 59.14, 77.80, 83.82, 87.52, 127.08, 128.10, 128.14, 142.11; HRMS (EI) for $C_{25}H_{41}NO_2S$ calcd 419.2860, found 419.2865. Anal. Calcd for $C_{25}H_{41}NO_2S$: C, 71.55; H, 9.85; N, 3.34; S, 7.64. Found: C, 71.58; H, 9.82; N, 3.35; S, 7.60.

7a(6)S: $[\alpha]_D$ = −62.51° (*c* 4.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.74 (s, 3H), 0.82 (s, 12H), 0.89 (s, 3H), 0.95 (s, 9H), 1.0–1.35 (m, 2H), 1.40–1.55 (m, 1H), 1.70–1.85 (m, 1H), 2.18 (d, *J* = 4.5 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 1H), 2.99 (d, *J* = 7.5 Hz, 1H), 3.43 (d, *J* = 7.5 Hz, 2H), 3.72 (br, 1H), 4.15 (s, 1H), 7.26 (s, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.59, 20.70, 20.88, 26.71, 26.86, 28.48, 32.42, 32.89, 35.01, 46.70, 50.03, 50.86, 67.33, 80.22, 83.82, 87.26, 127.22, 127.32, 129.66, 139.43; HRMS (EI) for $C_{26}H_{43}NO_2S$ calcd 433.3015, found 433.3021.

7b(1)S: mp = 125–127 °C; $[\alpha]_D$ = −100.20° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.75 (s, 3H), 0.85 (s, 3H), 0.87 (s, 3H), 1.00–1.20 (m, 2H), 1.45–1.54 (m, 1H), 1.76–1.86 (m, 1H), 2.20 (d, *J* = 4.5 Hz, 1H), 2.40–2.70 (m, 2H), 3.07 (d, *J* = 7.8 Hz, 1H), 3.65 (d, *J* = 7.8 Hz, 1H), 3.88 (br, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.52 (t, *J* = 6.9 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 5.10–5.22 (m, 2H), 5.60–5.90 (m, 1H), 7.20–7.33 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.59, 20.66, 21.09, 28.34, 33.00, 43.14, 46.74, 50.16, 50.73, 57.13, 57.16, 75.68, 79.54, 87.75, 118.95, 127.21, 127.49, 127.92, 128.03, 128.34, 134.06, 138.67, 141.87. Anal. Calcd for $C_{27}H_{35}NO_2S$: C, 74.10; H, 8.06; N, 3.20; O, 7.31; S, 7.33. Found: C, 73.80; H, 8.10; N, 3.21; O, 7.09; S, 7.27.

7b(2)S: mp = 114–115 °C; $[\alpha]_D$ = −110.1° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3350 (w, NH), 1070 (s, SO); ^1H NMR (300 MHz, $CDCl_3$) δ 0.76 (s, 3H), 0.87 (s, 3H), 0.94 (s, 3H), 1.00–1.15 (m, 1H), 1.45–1.50 (m, 1H), 1.55 (d, *J* = 6.9 Hz, 3H), 1.75–1.85 (m, 2H), 2.19 (d, *J* = 4.5 Hz, 1H), 3.05 (d, *J* = 7.8 Hz, 1H), 3.63 (d, *J* = 3.9 Hz, 1H), 3.66 (d, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 11.1 Hz, 1H), 4.58–4.68 (m, 1H), 4.87 (d, *J* = 11.1 Hz, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.61, 20.68, 21.19, 24.96, 28.36, 33.02, 46.76, 50.24, 50.79, 53.59, 75.68, 79.61, 87.79, 126.89, 127.21, 127.36, 127.89, 128.04, 128.44, 138.74, 143.74; HRMS (EI) for $C_{25}H_{33}NO_2S$ calcd 411.2232, found 411.2222. Anal. Calcd for $C_{25}H_{33}NO_2S$: C, 72.95; H, 8.08; N, 3.40; S, 7.79. Found: C, 72.72; H, 8.06; N, 3.48; S, 7.49.

7b(3)S: mp = 107–108 °C; $[\alpha]_D$ = −96.2° (*c* 1.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.74 (s, 3H), 0.85 (s, 3H), 0.86 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 3H), 1.00–1.16 (m, 2H), 1.44–1.55 (m, 1H), 1.75–1.91 (m, 3H), 2.16 (d, *J* = 4.5 Hz, 1H), 3.04 (d, *J* = 7.8 Hz, 1H), 3.64 (d, *J* = 7.8 Hz, 1H), 3.69 (d, *J* = 2.7 Hz, 1H), 4.33 (m, 1H) 4.38 (d, *J* = 11.1 Hz, 1H), 4.85 (d, *J* = 11.1 Hz, 1H), 7.24–7.32 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.51, 11.60, 20.65, 21.05, 28.34, 31.58, 32.99, 46.72, 50.13, 50.77, 60.12, 75.64, 79.40, 87.72, 127.21, 127.41, 127.67, 127.90, 128.03, 128.29, 138.69, 141.98; HRMS (EI) for $C_{26}H_{35}NO_2S$ calcd 425.2390, found 425.2397. Anal. Calcd for $C_{26}H_{35}NO_2S$: C, 73.37; H, 8.29; N, 3.29; S, 7.52. Found: C, 73.23; H, 8.32; N, 3.30; S, 7.50.

7b(3)R: mp = 140–142 °C; $[\alpha]_D$ = −3.0° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.42–0.47 (m, 1H), 0.72 (s, 3H), 0.83 (t, *J* = 6.6 Hz, 3H), 0.87 (s, 3H), 1.12 (s, 3H), 1.37–1.48 (m, 2H), 1.70–1.82 (m, 2H), 1.88 (d, *J* = 3.3 Hz, 1H), 1.90–2.00 (m, 1H), 2.93 (d, *J* = 7.8 Hz, 1H), 3.58 (d, *J* = 7.8 Hz, 1H), 3.89 (br s, 1H), 4.40 (d, *J* = 10.8 Hz, 1H), 4.47 (t, *J* = 6.6 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 7.20–7.34 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.38, 11.60, 20.69, 21.43, 27.57, 30.97, 32.85, 46.62, 50.06, 50.83, 55.94, 75.64, 77.04, 87.85, 127.18, 127.38, 127.42, 127.88, 128.05, 128.29, 138.85, 143.17; HRMS (EI) for $C_{26}H_{35}NO_2S$ calcd 425.2390, found 425.2386. Anal. Calcd for $C_{26}H_{35}NO_2S$: C, 73.37; H, 8.29; N, 3.29; S, 7.52. Found: C, 73.25; H, 8.32; N, 3.32; S, 7.57.

7b(4)S: mp = 142–144 °C; $[\alpha]_D$ = −103.0° (*c* 2.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.73 (s, 3H), 0.84 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.85 (s, 3H), 1.00–1.40 (m, 6H), 1.42–1.54 (m, 1H), 1.76–1.82 (m, 4H), 2.16 (d, *J* = 4.2 Hz, 1H), 3.04 (d, *J* = 7.8 Hz, 1H), 3.64 (d, *J* = 7.5 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.40 (t, *J* = 7.8 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 7.24–7.32 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.61, 13.87, 20.65, 21.06, 22.45, 28.20, 28.37, 33.03, 38.45, 46.72, 50.15, 50.78, 58.49, 75.66, 79.64, 87.77, 127.21, 127.37, 127.61, 127.92, 128.03, 128.31, 138.74, 142.47; HRMS (EI) for $C_{28}H_{39}NO_2S$ calcd 453.2702, found 453.2701. Anal. Calcd for $C_{28}H_{39}NO_2S$: C, 74.13; H, 8.66; N, 3.09; S, 7.07. Found: C, 73.89; H, 8.64; N, 3.16; S, 7.03.

7b(4)R: mp = 111–112 °C; $[\alpha]_D$ = −7.9° (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.41 (m, 1H), 0.71 (s, 3H), 0.82 (t, *J* = 7.5 Hz, 3H), 0.86 (s, 3H), 0.81–0.96 (m, 1H), 1.11 (s, 3H), 1.20–1.35 (m, 2H), 1.36–1.42 (m, 2H), 1.50–1.80 (m, 4H), 1.86 (d, *J* = 2.7 Hz, 1H), 2.93 (d, *J* = 7.8 Hz, 1H), 3.57 (d, *J* = 7.5 Hz, 1H), 3.92 (br s, 1H), 4.40 (d, *J* = 10.8 Hz, 1H), 4.54 (m, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 7.25–7.38 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.64, 13.92, 20.72, 21.46, 22.45, 27.54, 28.13, 32.83, 37.97, 46.62, 50.05, 50.86, 54.50, 75.62, 77.28, 87.83, 127.21, 127.36, 127.88, 128.08, 128.55, 138.87, 143.61; HRMS (EI) for $C_{28}H_{39}NO_2S$ calcd 453.2702, found 453.2697.

7b(6)S: $[\alpha]_D$ = −90.7° (*c* 2.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.74 (s, 3H), 0.74 (s, 12H), 0.82 (s, 3H), 0.83 (s, 3H), 0.96 (s, 9H), 1.00–1.35 (m, 2H), 1.40–1.55 (m, 1H), 1.75–1.90 (m, 1H), 2.19 (d, *J* = 4.5 Hz, 1H), 3.06 (d, *J* = 7.5 Hz, 1H), 3.64 (d, *J* = 7.5 Hz, 1H), 3.69 (br s, 1H), 4.17 (s, 1H), 4.36 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 10.5 Hz, 1H), 7.20–7.34 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.63, 20.68, 21.09, 26.87, 28.45, 33.04, 35.05, 46.75, 50.02, 50.66, 67.42, 75.69, 79.92, 87.75, 127.24, 127.33, 127.42, 128.03, 129.66, 139.33; HRMS (EI) for $C_{28}H_{39}NO_2S$ calcd 453.2702, found 453.2702.

Typical Procedure for Redutive Cleavage of Sulfenamide 6 to Chiral Amine 9. To a solution of sulfenamide **6c(1)S** (147 mg, 0.44 mmol) in 5 mL of tetrahydrofuran was added 10 mL of 6 N hydrochloric acid, and the resulting mixture was stirred vigorously for 3 h. The aqueous layer was separated and extracted with 20 mL of ether. The combined organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow solid. The crude product was purified by chromatography through silica gel eluted with hexane to give 82 mg (>99%) of disulfide **13c** as a pale yellow crystalline solid. The aqueous layer was treated with saturated sodium hydroxide solution until the solution turned basic. It was then extracted with two 30-mL portions of ether. After the solvent was evaporated, the residual oil was purified by bulb-to-bulb distillation to give 52 mg (80%) of amine **9(1)S** as a colorless oil: mp = 115–116 °C; $[\alpha]_D$ = −85.0° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 2950 (m), 1600 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (s, 6H), 0.95 (s, 6H), 1.03 (s, 6H), 1.03–1.30 (m, 4H), 1.49 (td, *J* = 12.6, 3.0 Hz, 2H), 1.72–1.85 (m, 2H), 1.96 (d, *J* = 4.5 Hz, 2H), 2.45 (br s, 2H), 3.35 (d, *J* = 7.5 Hz, 2H), 3.83 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.49, 21.06, 21.64, 28.83, 33.21, 46.78, 49.85, 53.34, 67.04, 79.80; HRMS (EI) for $C_{20}H_{34}O_2S_2$ calcd 370.2003, found 370.2006. Anal. Calcd for $C_{20}H_{34}O_2S_2$: C, 64.82; H, 9.25; O, 8.63; S, 17.3. Found: C, 64.83; H, 9.26; O, 8.64; S, 17.27.

Typical Procedure for Redutive Cleavage of Sulfinamide 7 to Chiral Amine 9. To a solution of sulfenamide **7a(1)S** (136 mg, 0.33 mmol) in 2 mL of dichloromethane was added a 1.0 M dichloromethane solution of titanium tetrachloride (1 mL, 1.0 mmol) at ambient temperature, followed by the addition of zinc powder (136 mg, 1.40 mmol) and 2 mL of ether. The resulting greenish yellow solution changed to deep purple while being

stirred at ambient temperature for 10 min. To this solution was added 6 mL of 6 N hydrochloric acid, and the resulting mixture was stirred vigorously for 3 h. The aqueous layer was separated and extracted with 20 mL of ether. The combined organic layer was dried with $MgSO_4$ and evaporated under reduced pressure to give a yellow solid. The crude product was purified by chromatography through silica gel eluted with hexane to give 72 mg (86%) of thiol **1a** as a pale yellow crystalline solid. The aqueous layer was adjusted to basic with saturated sodium hydroxide solution and extracted with two 30-mL portions of ether. After the solvent was evaporated, the residual oil was purified by bulb-to-bulb distillation to give 39 mg (80%) of amine **9(1)S** as a colorless oil: $[\alpha]_D = -31.8°$ (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 2950 (m), 1600 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 1.88 (br s, 2H), 2.28–2.55 (m, 2H), 3.98 (dd, J = 10.5, 7.5 Hz, 1H), 5.03–5.18 (m, 2H), 5.65–5.85 (m, 1H), 7.18–7.42 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.49, 21.06, 21.64, 28.83, 33.21, 46.78, 49.85, 53.34, 67.04, 79.80. Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.79; H, 8.80; N, 9.41.

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Supplementary Material Available: ^1H NMR data for **1b**, **2a**, **3a–c**, **4a–c**, **5a**, **5b**, **6a(1)S+6a(1)R**, **6b(1)S+6b(1)R**, **6c**, **7a(1)S–7a(6)S**, **7a(2)R–7a(5)R**, **7b(1)S–7b(4)S**, **7b(3)S**, **7b(4)S**, **7b(6)S**, **7b(3)R**, **7b(4)R**, **13c**, and **9(1)S** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see current masthead page for ordering information. The authors have deposited atomic coordinates for compounds **7a(3)S** and **7b(4)S** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK.