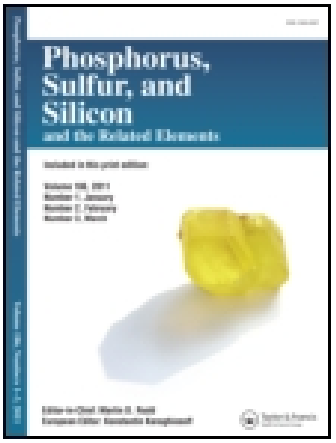

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The Use of Sulfides Derived from Carane, P-Menthane, Pinane, and Bornane in the Synthesis of Optically Active Epoxides

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THE USE OF SULFIDES DERIVED FROM CARANE, *P*-MENTHANE, PINANE, AND BORNANE IN THE SYNTHESIS OF OPTICALLY ACTIVE EPOXIDES

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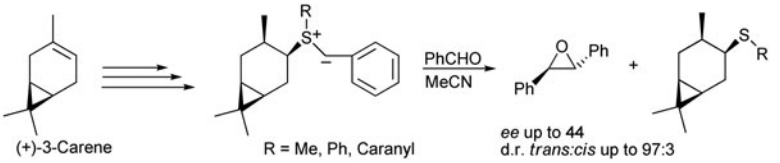
GRAPHICAL ABSTRACT



Abstract *Convenient routes for the synthesis of optically active methyl, phenyl, and dimonoterpenyl sulfides derived from carane,* p-*menthane, pinane, and bornane were developed. Methyl and dimonoterpenyl sulfides have been obtained by the reaction of the corresponding monoterpene thiolates with methyl iodide or monoterpene tosylates. The reactions of monoterpene tosylates with sodium benzenethiolate gave the corresponding phenyl monoterpenyl sulfides. These sulfides were used for the sulfur ylide-mediated reaction to yield epoxides. Good diastereoselectivities up to 99:1 and low to moderate enantioselectivities were observed for the enantioselective synthesis of chiral epoxides.*

Keywords Sulfides; monoterpenes; stereoselective synthesis of epoxides; sulfur ylides

INTRODUCTION

In recent years, an increasing role of chalcogenides in organic synthesis is observed. The specific reactivity of these compounds makes them potential reagents and catalysts for the formation of new carbon–carbon, carbon—nitrogen, and carbon–oxygen bonds.[1] Applications of organosulfur and organoselenium compounds in asymmetric synthesis are particularly interesting, for example, chiral sulfur ylides were used for the synthesis of optically active epoxides aziridines and cyclopropanes.[2,3]

Although the first successful example of using chiral sulfonium ylides for the synthesis of optically active epoxides was reported by Furukawa and coworkers in 1989,[4]

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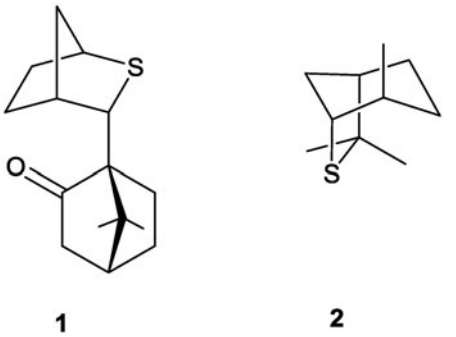


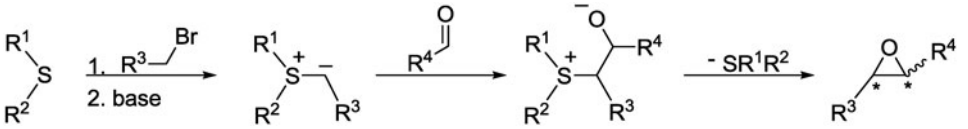
Figure 1 Structures of sulfides **1** and **2**.

searching for new reagents for the synthesis of asymmetric epoxides is still the current direction of modern developments.[5,6] The aim of our investigation was to develop a synthesis of optically active sulfides derived from commercially available monoterpenes [(+)-3-carene, (–)-menthol, (–)-β-pinene, and (–)-borneol] and test them as auxiliaries for the stereoselective synthesis of epoxides. Previous studies on the use of sulfur ylides containing a monoterpene substructure in the sulfide structures were presented for camphor,[4,7–13] pulegone,[14] α-pinene,[15] limonene,[16] and carvone[17] derivatives. Particularly interesting was the use of sulfides **1** and **2** (Figure 1) for the synthesis of quinine and quinidine.[16,18]

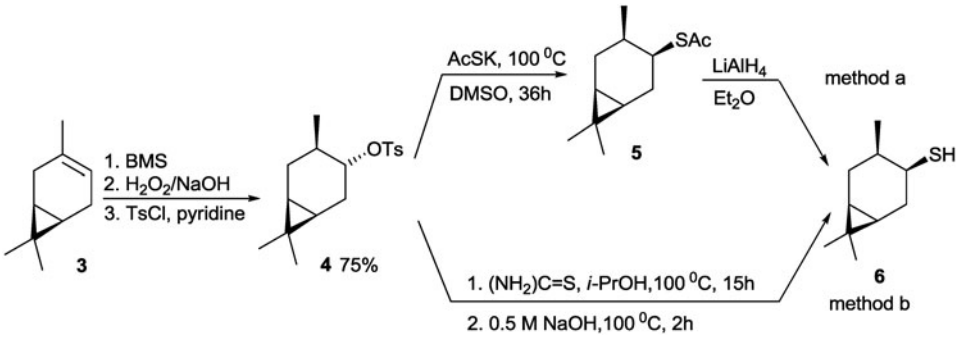
In our previous investigations, we have shown that monoterpene tosylates are convenient substrates for the synthesis of selenium monoterpene derivatives.[19–23] In this work, we present the use of monoterpene tosylates for the synthesis of monoterpene thiols[24,25] and their transformation into methyl, phenyl, and dimonoterpenyl sulfides, precursors for chiral sulfur ylides. We wanted to compare the influence of the methyl and the phenyl group or the additional monoterpene group on the diastereoselectivity and enantioselectivity of the epoxide formation.

RESULTS AND DISCUSSION

The synthesis of monoterpene thiols **6**, **9**, **12**, **15** was the first step of our investigation. Two methods for the preparation of thiols have been compared: the reaction of monoterpene tosylates with potassium thioacetate and subsequent reduction with lithium alanate (method a),[24] and the one pot reaction of monoterpene tosylate with thiourea and hydrolysis with sodium hydroxide (method b).[25] Monoterpene thioacetates **5**, **8**, **11** were isolated by distillation under reduced pressure. Tosylates **4**, **7**, **10**, **13** were prepared by the reaction of monoterpene alcohols with tosyl chloride in pyridine.[19,20] As an example, the synthesis of the caranyl thiol **6** from (+)-3-carene **3** is presented in Scheme 2.



Scheme 1



Scheme 2

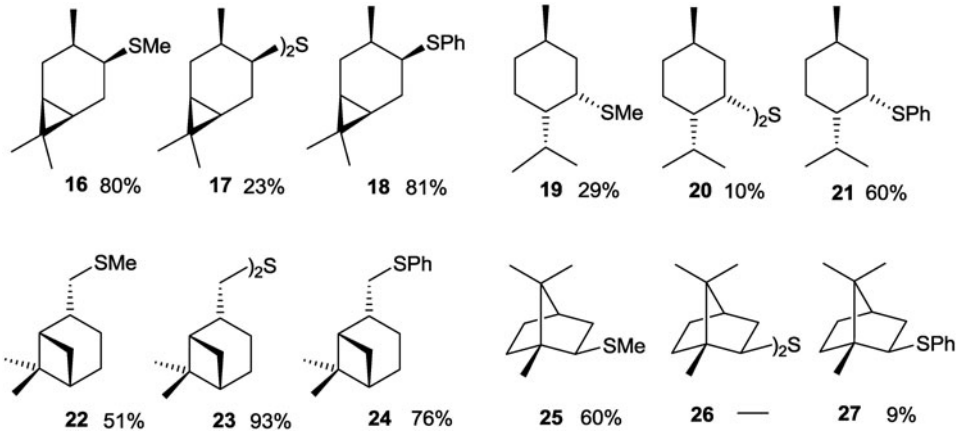


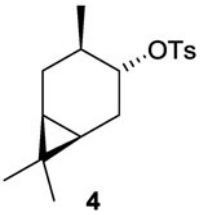
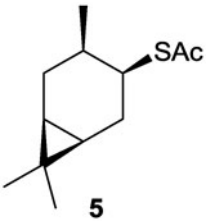
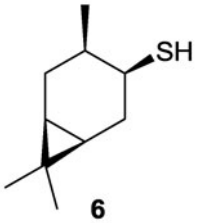
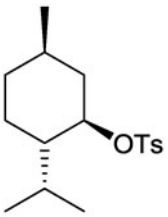
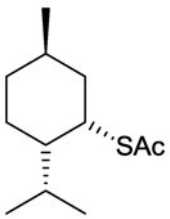
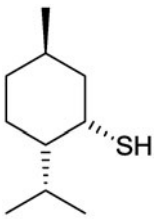
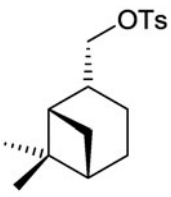
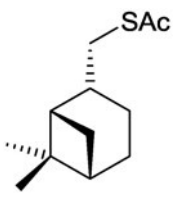
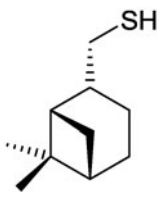
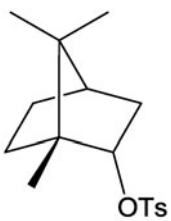
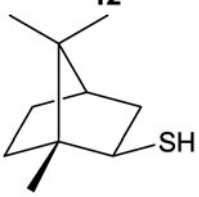
Figure 2 Optically active monoterpene sulfides.

Summaries of the syntheses of thioacetates and monoterpene thiols from derivatives of *p*-menthane, carane, pinane, and bornane are included in Table 1. We could not isolate isobornyl thioacetate **14** by the adopted methodology.

The reaction of thiols **6**, **9**, **12**, and **15** with sodium hydride gave the corresponding thiolates, which upon reaction with methyl iodide or monoterpenyl tosylates were converted into methyl monoterpenyl sulfides **16**, **19**, **22**, **25** and dimonoterpenyl sulfides **17**, **20**, **23**. Using this method, we could not get diisobornyl sulfide **26**. Additionally, the reaction of monoterpene tosylates with sodium benzenethiolate gave the corresponding phenyl monoterpenyl sulfides **18**, **21**, **24**, **27**. Examples for syntheses of methyl-, phenyl-, and dimonoterpenyl sulfides from carane are presented in Scheme 3. Structures of the obtained sulfides and yields are summarized in Figure 2.

The sulfides **16**–**27** were used for the sulfur ylide-mediated enantioselective synthesis of chiral epoxides. The model reaction of benzyl bromide with benzaldehyde yielding epoxystilbene was studied. The reaction was carried out in acetonitrile as a one-pot synthesis, without isolation of the corresponding sulfonium salt (Scheme 4). Yields, enantio- and diastereoselectivities of the epoxide formations are presented in Table 2.

Table 1 Syntheses of monoterpene thioacetates and thiols

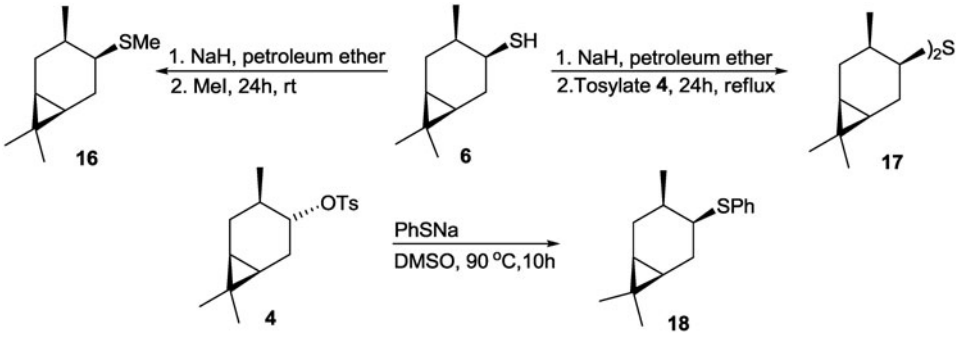
Entry	Tosylate	Thioacetate	Yield [%]	Thiol	Method a yield [%][a]	Method b yield [%]
1	 **4**	 **5**	70	 **6**	48	37
2	 **7**	 **8**	48	 **9**	33	39
3	 **10**	 **11**	63	 **12**	37	40
4	 **13**	 **14**	—	 **15**	—	61

[a]overall yield after two steps.

The best diastereoselectivities were obtained for the reactions of sulfides **16**, **25**, and **27**, while the best enantioselectivity was obtained with sulfide **18**. According to our knowledge, phenyl monoterpenyl sulfides have not yet been tested in this type of reaction.

CONCLUSIONS

We have found that tosylates derived from *p*-menthane, carane, pinane, and bornane can be conveniently used as precursors for the synthesis of optically active monoterpene thiols and sulfides. We have developed and compared two methods for the synthesis of

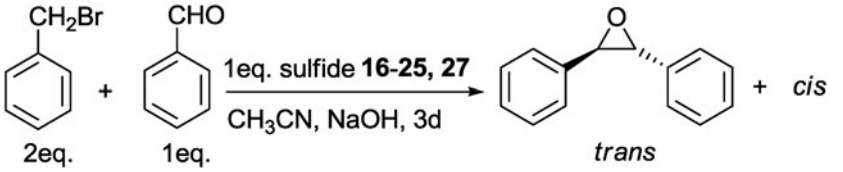


Scheme 3

Table 2 Formation of asymmetric stilbene epoxides by use of monoterpene sulfides

Entry	Sulfide	Yield [%]	Ratio *cis*/*trans*[a]	*ee trans* (%)[b]
1	**16**	53	3/97	8 (*S*,*S*)
2	**19**	30	5/95	2 (*R*,*R*)
3	**22**	74	5/95	6 (*R*,*R*)
4	**25**	50	1/99	0
5	**17**	14	71/29	8 (*S*,*S*)
6	**20**	—	—	—
7	**23**	73	11/89	10 (*R*,*R*)
8	**18**	13	55/45	44 (*S*,*S*)
9	**21**	11	33/67	20 (*S*,*S*)
10	**24**	40	24/76	14 (*R*,*R*)
11	**27**	23	3/97	34 (*S*,*S*)

[a]determined on the basis of the ^{1}H NMR spectra.
[b]determined on the basis of HPLC using a Chiralcel Daicel OD-H column.



Scheme 4

monoterpene thiols. The results are similar, but we regard the method involving thiourea more convenient because of the simplicity of the one pot synthesis. The resulting monoterpene sulfides provided the target epoxides, but low to moderate enantioselectivities were obtained. This is probably caused by the formation of diastereomeric mixtures of sulfonium salts in the first step of the epoxide formation process. We have observed that the introduction of the phenyl group into the structure of sulfides resulted in an increase of the enantioselectivity of the produced epoxides.

EXPERIMENTAL

Melting points were measured with a Büchi Tottoli SPM-20 heating unit and are uncorrected. NMR spectra (solvent $CDCl_3$, chemical shifts δ in /ppm) were recorded on Bruker AM-300, Varian 200, Bruker Avance III/400, or Bruker Avance III/700. Optical rotations were measured in 10-mm cells with a polAAr 3000 polarimeter. Elemental analyses were performed on a Vario MACRO CHN analyzer. TLC was conducted on precoated silica gel plates (Merck 60_{F254}), and the spots were visualized under UV light. Column chromatography was carried out by use of Silica Gel 60 Merck (70–230 mesh) with petroleum ether as eluent. All reactions requiring anhydrous conditions were conducted in a flame-dried apparatus.

GENERAL PROCEDURE FOR THE PREPARATION OF MONOTERPENE THIOACETATES

A monoterpene tosylate (65.4 mmol) was carefully added to the potassium thioacetate (8.27 g, 72.5 mmol) in anhydrous DMSO (75 mL). The solution was kept at 45°C under Ar for 36 h, subsequently poured into water (100 mL) and extracted with $CHCl_3$ (3×50 mL). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated, and the residue was purified by distillation at reduced pressure.

(1S,3R,4S,6R)-(+)-4-Caranyl Thioacetate (5). Bp: 98–100°C/1.0 mm Hg. Yield 70%; $[\alpha]_D^{22} = +30.10$ (c 4.80, $CHCl_3$); ^{1}H NMR (200 MHz): 0.48–0.79 (m, 3H), 0.85 (d, 3H, CH_3, $J = 6.8$ Hz), 0.96 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.37–1.56 (m, 1H), 1.67–1.91 (m, 2H), 2.30 (s, 3H, CH_3CO), 2.32–2.48 (m, 1H), 3.77–3.88 (m, 1H); ^{13}C NMR (50.3 MHz): 15.8 (CH_3), 17.6 (C), 18.9 (CH_3), 19.0 (CH_3), 19.1 (CH), 22.0 (CH), 25.3 (CH_2), 26.2 (CH_2), 28.6 (CH_3), 30.8 (CH), 43.3 (CH), 195.8 (C). Elemental Anal. Calcd (%) for $C_{12}H_{20}OS$ (212.36): C, 67.87; H, 9.49. Found: C, 68.09; H, 9.45.

(1S,2S,5R)-(+)-Neomenthyl Thioacetate (8). Bp.: 76–78°C/0.5 mm Hg. Yield 48%; $[\alpha]_D^{20} = +72.00$ (c 5.22, $CHCl_3$); Lit.[24] $[\alpha]_D^{20} = +64.00$ (c 2.66, $CHCl_3$); ^{1}H NMR (300 MHz): 0.83 (d, 3H, CH_3, $J = 6.6$ Hz), 0.86 (d, 3H, CH_3, $J = 6.3$ Hz), 0.88 (d, 3H, CH_3, $J = 6.6$ Hz), 0.89–0.94 (m, 2H), 1.04–1.16 (m, 1H), 1.27–1.45 (m, 2H), 1.68–1.75 (m, 2H), 1.82 (dq, 2H, $J = 3.3$, 13.2 Hz), 2.32 (s, 3H, CH_3CO), 4.05–4.09 (m, 1H); ^{13}C NMR (75.5 MHz): 20.7 (CH_3), 20.9 (CH_3), 22.1 (CH_3), 27.7 (CH_2), 28.1 (CH), 30.5 (CH), 31.1 (CH_3), 35.0 (CH_2), 41.9 (CH_2), 45.2 (CH), 47.6 (CH), 195.4 (C). Elemental Anal. Calcd (%) for $C_{12}H_{22}OS$ (214.37): C, 67.23; H, 10.34. Found: C, 67.58; H, 10.37.

(1S,2R,5S)-(–)-cis-Myrtanyl Thioacetate (11). Bp.: 106–108°C/0.8 mm Hg. Yield 63%; $[\alpha]_D^{20} = -75.25$ (c 5.27, $CHCl_3$); ^{1}H NMR (300 MHz): 0.87 (d, 1H, $J = 9.6$ Hz), 1.04 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.43–1.53 (m, 2H), 1.80–2.20 (m, 6H), 2.32 (s, 3H, CH_3CO), 2.96 (dd, 2H, CH_2, $J = 1.8$, 8.1 Hz); ^{13}C NMR (75.5 MHz): 21.8 (CH_2), 23.1 (CH_3), 26.0 (CH_2), 27.9 (CH_3), 30.6 (CH_3), 33.3 (CH_2), 35.7 (CH_2), 38.6 (C), 41.1 (CH), 41.2 (CH), 45.4 (CH), 196.0 (C). Elemental Anal. Calcd (%) for $C_{12}H_{20}OS$ (212.36): C, 67.87; H, 9.49. Found: C, 67.52; H, 9.55.

General Procedure for the Preparation of Thiols

Method a. To the suspension of $LiAlH_4$ (4.00 g, 105.0 mmol) in anhydrous diethyl ether (80 mL), the thioacetate (52 mmol) dissolved in anhydrous diethyl ether (30 mL) was carefully added. The solution was stirred 2 h at reflux under an argon atmosphere,

allowed to cool, and diluted with water (60 mL). The precipitate was dissolved by adding 10% H_2SO_4 (50 mL) and extracted with diethyl ether (3 × 40 mL). The combined ethereal layers were dried over $MgSO_4$, the solvent was evaporated, and the residue was purified by distillation.

Method b. The tosylate (16.0 mmol) and thiourea (32.0 mmol) in propane-2-ol (50 mL) were kept 15 h at 100°C. The mixture was allowed to cool, and 0.5 M NaOH (50 mL) were added. The mixture was kept 2 h at 100°C. The mixture was acidified and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. The crude products were purified by column chromatography.

(1S,3R,4S,6R)-(+)-4-Caranyl Thiol (6). *Method a*: bp: 44–46°C/0.3 mm Hg. Yield 48%; *Method b*: Yield 37%; colorless liquid; $[\alpha]_D^{25} = +41.01$ (c 5.02, $CHCl_3$); ^{1}H NMR (200 MHz): 0.47–0.57 (m, 1H), 0.68–0.90 (m, 2H,), 0.92 (d, 3H, CH_3, $J = 6.6$ Hz), 0.98 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.23 (d, 1H, $J = 5.6$ Hz), 1.27–1.36 (m, 1H), 1.60–1.80 (m, 2H), 2.22–2.49 (m, 1H), 3.20–3.32 (m, 1H); ^{13}C NMR (50.3 MHz): 15.8 (CH_3), 17.7 (CH_3), 18.8 (CH), 19.7 (CH), 22.7 (CH_2), 23.6 (C), 28.5 (CH_3), 28.5 (CH_2), 31.6 (CH), 38.8 (CH). Elemental Anal. Calcd (%) for $C_{10}H_{18}S$ (170.31): C, 70.52; H, 10.65. Found: C, 70.13; H, 10.59.

(1S,2S,5R)-(+)-Neomenthyl Thiol (9). *Method a*: bp: 48–50°C/0.7 mm Hg. Yield 33%; *Method b:* Yield 39%; colorless liquid; $[\alpha]_D^{25} = +37.99$ (c 5.3, $CHCl_3$); Lit.[24] $[\alpha]_D^{20} = +53.9$ (c 1.85, $CHCl_3$); ^{1}H NMR (200 MHz) 0.87 (d, 3H, CH_3, $J = 6.2$ Hz), 0.90 (d, 3H, CH_3, $J = 6.6$ Hz), 0.91 (d, 3H, CH_3, $J = 6.8$ Hz), 0.98–1.09 (m, 2H), 1.22 (d, 1H, $J = 6.8$ Hz), 1.29–1.56 (m, 3H), 1.62–1.98 (m, 3H), 3.45–3.53 (m, 1H); ^{13}C NMR (50.3 MHz): 20.3 (CH_3), 20.8 (CH_3), 22.1 (CH_3), 24.2 (CH_2), 25.9 (CH), 30.2 (CH), 35.29 (CH_2), 40.1 (CH), 44.0 (CH_2), 48.2 (CH). Elemental Anal. Calcd (%) for $C_{10}H_{20}S$ (172.33): C, 69.69; H, 11.70. Found: C, 69.99; H, 11.79.

(1S,2R,5S)-(–)-cis-Myrtanyl Thiol (12). *Method a*: bp: 79–81°C/0.3 mm Hg. Yield 37%; *Method b:* Yield 40%; colorless liquid; $[\alpha]_D^{25} = -75.87$ (c 5.18, $CHCl_3$); ^{1}H NMR (200 MHz): 0.89 (d, 1H, $J = 9.4$ Hz), 0.97 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.29 (t, 1H, $J = 7.8$ Hz), 1.43–1.54 (m, 1H), 1.84–2.21 (m, 6H), 2.29–2.41 (m, 1H), 2.57 (t, 2H, $J = 7.6$ Hz); ^{13}C NMR (50.3 MHz): 21.8 (CH_2), 23.2 (CH_3), 26.1 (CH_2), 27.9 (CH_3), 31.4 (CH_2), 32.5 (CH), 33.3 (CH_2), 38.6 (C), 41.3 (CH), 45.3 (CH). Elemental Anal. Calcd (%) for $C_{10}H_{18}S$ (170.31): C, 70.52; H, 10.65. Found: C, 70.77; H, 10.64.

(1R,2R,4R)-(+)-Isobornyl Thiol (15). *Method b*: Yield 61%; colorless liquid; $[\alpha]_D^{22} = +50.00$ (c 4.52, $CHCl_3$); Lit.[26] $[\alpha]_D^{22} = +47.50$ (c 5.06, $CHCl_3$); ^{1}H NMR (700 MHz): 0.83 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.08–1.15 (m, 2H), 1.64–1.74 (m, 3H), 1,78 (d, 1H, $J = 6.3$ Hz), 1.79–1.83 (m, 1H), 1.89 (dd, 1H, $J = 9.1$, 13.3 Hz), 2.96–2.99 (m, 1H); ^{13}C NMR (176.1 MHz): 13.9 (CH_3), 20.3 (CH_3), 20.6 (CH_3), 27.3 (CH_2), 38.2 (CH_2), 41.3 (CH_2), 45.9 (CH), 46.2 (CH), 47.6 (C), 48.4 (C). Elemental Anal. Calcd (%) for $C_{11}H_{18}S$ (170.31): C, 70.52; H, 10.65. Found: C, 70.59; H, 10.68.

General Procedure for the Preparation of Alkyl Methyl Sulfides

The solution of the thiol (5.9 mmol) in anhydrous petroleum ether (15 mL) was carefully added to the suspension of NaH (0.570 g, 23.8 mmol) in anhydrous petroleum ether (15 mL). The mixture was kept 0.5 h at ambient temperature under an argon atmosphere. Methyl iodide (1.70 g, 11.9 mmol) was added and the mixture was stirred for 24 h. The solution was poured into water (75 mL) and extracted with petroleum ether (3 × 50 mL).

The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. The crude products were purified by column chromatography.

(1S,3R,4S,6R)-(+)-4-Caranyl Methyl Sulfide (16). Yield 80%; yellow oil; $[\alpha]_D^{22} = +21.42$ (c 7.75, $CHCl_3$); ^1H NMR (700 MHz): 0.55 (ddd, 1H, $J = 6.3, 9.1, 9.1$ Hz), 0.62 (ddd, 1H, $J = 7.0, 9.1, 9.1$ Hz), 0.83 (ddd, 1H, $J = 7.0, 9.1, 16.1$ Hz), 0.92 (d, 3H, CH_3, $J = 7.0$ Hz), 0.96 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.24 (ddd, 1H, $J = 6.3, 8.4, 15.4$ Hz), 1.79 (ddd, 1H, $J = 5.6, 8.4, 14.7$ Hz), 1.85–1.91 (m, 1H), 2.05 (s, 3H, CH_3), 2.14 (ddd, 1H, $J = 6.3, 8.4, 14.7$ Hz), 2.74 (dt, 1H, $J = 6.3, 7.7$ Hz); ^{13}C NMR (100.6 MHz): 15.7 (CH_3), 15.7 (CH_3), 17.6 ©, 18.6 (CH_3), 21.1 (CH), 21.2 (CH), 24.4 (CH_2), 25.2 (CH_2), 28.6 (CH_3), 30.7 (CH), 47.7 (CH). Elemental Anal. Calcd (%) for $C_{11}H_{20}S$ (184.34): C, 71.67; H, 10.94. Found: C, 71.76; H, 10.91.

(1S,2S,5R)-(+)-Methyl Neomenthyl Sulfide (19). Yield 29%; yellow oil; $[\alpha]_D^{23} = +93.10$ (c 7.25, $CHCl_3$); Lit.[24] $[\alpha]_D^{20} = +90.30$ (c 3.85, $CDCl_3$); ^1H NMR (700 MHz): 0.83–0.86 (m, 1H), 0.85 (d, 3H, CH_3, $J = 7.0$ Hz), 0.87 (d, 3H, CH_3, $J = 6.3$ Hz), 0.92 (d, 3H, CH_3, $J = 7.0$ Hz), 1.03–1.23 (m, 3H), 1.59–1.72 (m, 3H), 1.85–1.92 (m, 1H), 1.93 (dq, 1H, $J = 2.8, 14.0$ Hz), 2.04 (s, 3H, CH_3), 2.99 (m, 1H); ^{13}C NMR (176.1 MHz): 15.2 (CH_3), 20.7 (CH_3), 21.1 (CH_3), 22.2 (CH_3), 26.0 (CH_2), 26.4 (CH), 30.1 (CH), 35.4 (CH_2), 39.8 (CH_2), 48.8 (CH), 49.9 (CH). Elemental Anal. Calcd (%) for $C_{11}H_{22}S$ (186.36): C, 70.89; H, 11.90. Found: C, 71.11; H, 11.84.

(1S,2R,5S)-(–)-Methyl Myrtanyl Sulfide (22). Yield 51%; yellow oil; $[\alpha]_D^{24} = -30.00$ (c 5.21, $CHCl_3$); ^1H NMR (700 MHz): 0.87 (d, 1H, $J = 9.1$ Hz), 0.97 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.47–1.53 (m, 1H), 1.80–2.10 (m, 5H), 2.04 (s, 3H, CH_3), 2.18–2.23 (m, 1H), 2.30–3.24 (m, 1H), 2.53 (ddd, 2H, $J = 7.0, 12.6, 24.5$ Hz); ^{13}C NMR (176.1 MHz): 15.8 (CH_3), 22.1 (CH_2), 23.3 (CH_3), 26.2 (CH_2), 28.0 (CH_3), 33.4 (CH_2), 38.7 (C), 40.6 (CH), 41.4 (CH), 41.8 (CH_2), 45.6 (CH). Elemental Anal. Calcd (%) for $C_{11}H_{20}S$ (184.34): C, 71.67; H, 10.94. Found: C, 71.99; H, 10.87.

(1R,2R,4R)-(+)-Isobornyl Methyl Sulfide (25). Yield 60%; yellow oil; $[\alpha]_D^{28} = +72.17$ (c 5.75, $CHCl_3$); ^1H NMR (700 MHz): 0.80 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 0,98 (s, 3H, CH_3), 1.10–1.14 (m, 2H), 1.63–1.78 (m, 4H), 1.86 (dd, 1 H, $J = 9.1, 12.6$ Hz), 2.09 (s, 3H, CH_3), 2.56 (dd, 1H, $J = 5.6, 9.1$ Hz); ^{13}C NMR (176.1 MHz): 13.6 (CH_3), 18.2 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 27.4 (CH_2), 38.5 (CH_2), 40.0 (CH_2), 45.8 (CH), 47.3 (C), 49.5 (C), 56.7 (CH). Elemental Anal. Calcd (%) for $C_{11}H_{20}S$ (184.34): C, 71.67; H, 10.94. Found: C, 72.01; H, 10.90.

General Procedure for the Preparation of Dialkyl Sulfides

To a suspension of NaH (0.660 g, 27.5 mmol) in anhydrous petroleum ether (15 mL) was carefully added a thiol solution (6.6 mmol) in anhydrous petroleum ether (15 mL). The solution was stirred 0.5 h at ambient temperature under an argon atmosphere. The respective tosylate (6.8 mmol) was added, and the mixture was stirred under reflux for 24 h. The solution was poured into water (75 mL) and extracted with petroleum ether (3 × 50 mL). The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography.

(1S,3R,4S,6R)-(+)-4-Dicaranyl Sulfide (17). Yield 23%; yellow oil; $[\alpha]_D^{20} = +48.00$ (c 4.84, $CHCl_3$); ^1H NMR (400 MHz): 0.57 (ddd, 2H, $J = 5.2, 8.8, 14.0$ Hz), 0.66 (ddd, 2H, $J = 4.6, 8.4, 15.2$ Hz), 0.85 (ddd, 2H, $J = 5.2, 8.8, 14.0$ Hz), 0.96 (d, 6H, 2 CH_3, $J = 6.8$ Hz), 0.99 (s, 6H, 2 CH_3), 1.04 (s, 6H, 2 CH_3), 1.38 (ddd, 2H, $J = 5.2, 7.2, 14.8$ Hz), 1.79–1.91 (m, 4H), 2.17 (ddd, 2H, $J = 6.8, 8.8, 15.6$ Hz), 2.80 (dd, 2H, $J = 5.2,$

8.8 Hz); ^{13}C NMR (100.6 MHz): 15.9 (2 CH_3), 17.7 (2 C), 19.0 (2 CH_3), 21.0 (2 CH), 21.3 (2 CH), 25.2 (2 CH_2), 25.4 (2 CH_2), 28.7 (2 CH_3), 31.2 (2 CH), 44.8 (2 CH). Elemental Anal. Calcd (%) for $C_{20}H_{34}S$ (306.55): C, 78.36; H, 11.18. Found: C, 78.15; H, 11.12.

(1S,2S,5R)-(+)-Dineomenthyl Sulfide (20). Yield 10%; yellow oil; $[\alpha]_D^{24} = +141.83$ (c 6.04, $CHCl_3$); ^{1}H NMR (400 MHz): 0.83–0.95 (m, 12H), 0.87 (d, 6H, 2 CH_3, $J = 6.4$ Hz), 0.90 (d, 6H, 2 CH_3, $J = 6.4$ Hz), 0.93 (d, 6H, 2 CH_3, $J = 6.8$ Hz), 1.06–1.26 (m, 6H), 1.67–1.77 (m, 6H), 1.93 (dq, 2H, $J = 2.4$, 13.6 Hz), 2.03–2.18 (m, 2H), 3.10 (d, 2H, $J = 2.8$ Hz); ^{13}C NMR (100.6 MHz): 20.4 (2 CH_3), 21.2 (2 CH_3), 22.1 (2 CH_3), 26.2 (2 CH_2), 26.3 (2 CH), 29.8 (2 CH), 35.6 (2 CH_2), 39.9 (2 CH_2), 43.5 (2 CH), 49.0 (2 CH). Elemental Anal. Calcd (%) for $C_{20}H_{38}S$ (310.58): C, 77.34; H, 11.69. Found: C, 77.47; H, 11.70.

(1S,2R,5S)-(–)-Dimyrtanyl Sulfide (23). Yield 93%; yellow oil; $[\alpha]_D^{23} = -67.99$ (c 4.11, $CHCl_3$); ^{1}H NMR (700 MHz): 0.87 (d, 2H, $J = 9.8$ Hz), 0.97 (s, 6H, 2 CH_3), 1.17 (s, 6H, 2 CH_3), 1.47–1.53 (m, 2H), 1.80–2.10 (m, 10H), 2.15–2.20 (m, 2H), 2.30–3.24 (m, 2H), 2.53 (ddd, 4H, $J = 7.7$, 12.6, 23.8 Hz); ^{13}C NMR (176.1 MHz): 22.2 (2 CH_2), 23.3 (2 CH_3), 26.2 (2 CH_2), 28.0 (2 CH_3), 33.4 (2 CH_2), 38.7 (2 C), 39.7 (2 CH_2), 41.2 (2 CH), 41.4 (2 CH), 45.6 (2 CH). Elemental Anal. Calcd (%) for $C_{20}H_{34}S$ (306.55): C, 78.36; H, 11.18. Found: C, 78.72; H, 11.15.

General Procedure for the Preparation of Alkyl Phenyl Sulfides

To a suspension of NaH (1.12 g, 46.5 mmol) in anhydrous DMSO (10 mL) was carefully added thiophenol solution (1.131 g, 6.6 mmol) in DMSO (10 mL). The solution was stirred 0.5 h at ambient temperature under an argon atmosphere. The respective tosylate (11.9 mmol) was added and the mixture was mixed in 90°C for 10 h. The solution was poured into 10% solution NaOH (100 ml) and extracted with diethyl ether (3 × 50 mL). The combined ethereal layers were dried with anhydrous $MgSO_4$, and the solvent was evaporated. The crude product was purified by column chromatography.

(1S,3R,4S,6R)-(+)-4-Caranyl Phenyl Sulfide (18). Yield 81%; yellow oil; $[\alpha]_D^{22} = +36.03$ (c 5.78, $CHCl_3$); ^{1}H NMR (700 MHz): 0.56 (ddd, 1H, $J = 5.6$, 9.1, 14.7 Hz), 0.67 (ddd, 1H, $J = 7.0$, 9.1, 16.1 Hz), 0.90 (ddd, 1H, $J = 7.0$, 9.8, 16.8 Hz), 0.97 (s, 3H, CH_3), 0.98 (d, 3H, CH_3, $J = 7.0$ Hz), 1.03 (s, 3H, CH_3), 1.34 (ddd, 1H, $J = 6.3$, 8.4, 15.4 Hz), 1.85 (ddd, 1H, $J = 6.3$, 9.1, 14.7 Hz), 1.96–2.00 (m, 1H), 2.17 (ddd, 1H, $J = 6.8$, 8.8, 15.6 Hz), 3.45 (dt, 1H, $J = 6.3$, 7.7 Hz), 7.14–7.17 (m, $1H_{arom}$), 7.23–7.26 (m, $2H_{arom}$), 7.34–7.36 (m, $2H_{arom}$); ^{13}C NMR (100.6 MHz): 15.9 (CH_3), 17.8 (C), 19.0 (CH_3), 21.0 (CH), 21.3 (CH), 24.8 (CH_2), 25.4 (CH_2), 28.6 (CH_3), 30.8 (CH), 47.9 (CH), 125.9 (CH_{arom}), 128.8 (2 CH_{arom}), 130.5 (2 CH_{arom}), 137.2 (C_{arom}). Elemental Anal. Calcd (%) for $C_{16}H_{22}S$ (246.41): C, 77.99; H, 9.00. Found: C, 77.81; H, 9.01.

(1S,2S,5R)-(+)-Neomenthyl Phenyl Sulfide (21). Yield 60%; yellow oil; $[\alpha]_D^{24} = +82.21$ (c 6.79, $CHCl_3$); ^{1}H NMR (400 MHz): 0.86 (d, 3H, CH_3, $J = 6.4$ Hz), 0.90–0.92 (m, 1H), 0.95 (d, 3H, CH_3, $J = 2.4$ Hz), 0.96 (d, 3H, CH_3, $J = 2.8$ Hz), 1.15–1.33 (m, 3H), 1.72–1.82 (m, 3H), 1.92 (dq, 1H, $J = 2.0$, 13.6 Hz), 2.01–2.09 (m, 1H), 3.65 (d, 1H, $J = 2.0$ Hz), 7.18–7.23 (m, $1H_{arom}$), 7.27–7.31 (m, $2H_{arom}$), 7.40–7.43 (m, $2H_{arom}$); ^{13}C NMR (100.6 MHz): 20.7 (CH_3), 21.2 (CH_3), 22.2 (CH_3), 26.2 (CH_2), 26.5 (CH), 30.2 (CH), 35.4 (CH_2), 40.6 (CH_2), 48.9 (CH), 49.8 (CH), 126.1 (CH_{arom}), 128.8 (2 CH_{arom}), 131.1 (2 CH_{arom}), 136.9 (C_{arom}). Elemental Anal. Calcd (%) for $C_{16}H_{24}S$ (248.43): C, 77.36; H, 9.72. Found: C, 77.35; H, 9.70.

(1S,2R,5S)-(–)-Myrtanyl Phenyl Sulfide (24). Yield 76%; yellow oil; $[\alpha]_D^{21} = -29.71$ (c 6.83, $CHCl_3$); ^1H NMR (400 MHz): 0.85–0.89 (m, 1H), 0.90 (d, 1H, $J = 9.6$ Hz), 1.05 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.60–1.64 (m, 1H), 1.81–2.10 (m, 4H), 2.26–2.39 (m, 2H), 3.02 (ddd, 2H, $J = 7.2$, 12.4, 26.4 Hz), 7.14–7.19 (m, $1H_{arom}$), 7.25–7.30 (m, $2H_{arom}$), 7.35–7.40 (m, $2H_{arom}$); ^{13}C NMR (100.6 MHz): 22.1 (CH_2), 23.3 (CH_3), 26.2 (CH_2), 28.0 (CH_3), 33.3 (CH_2), 38.7 Ⓒ, 40.6 (CH), 40.8 (CH_2), 41.3 (CH), 45.6 (CH), 125.6 (CH_{arom}), 128.8 (2 CH_{arom}), 128.9 (2 CH_{arom}), 137.3 (C_{arom}). Elemental Anal. Calcd (%) for $C_{16}H_{22}S$ (246.41): C, 77.99; H, 9.00. Found: C, 78.25; H, 8.97.

(1R,2R,4R)-(+)-Isobornyl Phenyl Sulfide (27). Yield 9%; yellow oil; $[\alpha]_D^{28} = +82.88$ (c 5.92, $CHCl_3$); ^1H NMR (700 MHz): 0.89 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.20–1.32 (m, 2H), 1.70–1.80 (m, 3H), 2.05 (dt, 2H, $J = 2.0$, 7.6 Hz), 3.25 (t, 1H, $J = 7.6$ Hz), 7.14–7.19 (m, $1H_{arom}$), 7.25–7.30 (m, $2H_{arom}$), 7.35–7.40 (m, $2H_{arom}$); ^{13}C NMR (100.6 MHz): 14.9 (CH_3), 21.2 (CH_3), 21.5 (CH_3), 28.4 (CH_2), 39.5 (CH_2), 42.0 (CH_2), 46.9 (CH), 48.6 (C), 50.9 (C), 57.2 (CH), 126.5 (CH_{arom}), 129.7 (2 CH_{arom}), 130.3 (2 CH_{arom}), 140.3 (C_{arom}). Elemental Anal. Calcd (%) for $C_{16}H_{22}S$ (246.41): C, 77.99; H, 9.00. Found: C, 78.44; H, 8.92.

Stilbene Epoxide. A mixture of a sulfide (2.18 mmol), benzyl bromide (0.749 g, 4.38 mmol), sodium hydroxide (0.088 g, 2.20 mmol) and benzaldehyde (0.231 g, 2.18 mmol) in 10 mL of acetonitrile was stirred for 3 d. Acetonitrile was evaporated, and water (50 mL) was added. The mixture was extracted with petroleum ether (3 × 50 mL) and the combined organic layers were dried with anhydrous magnesium sulfate. The solvent was evaporated. The crude products were purified by column chromatography. Using petroleum ether:ethyl acetate 95:5 as the mobile phase gave pure *trans*-stilbene oxide. For the detailed results see Table 2.

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