Direct Synthesis of Allyl Sulfides from Allyl Alcohols and Thiols

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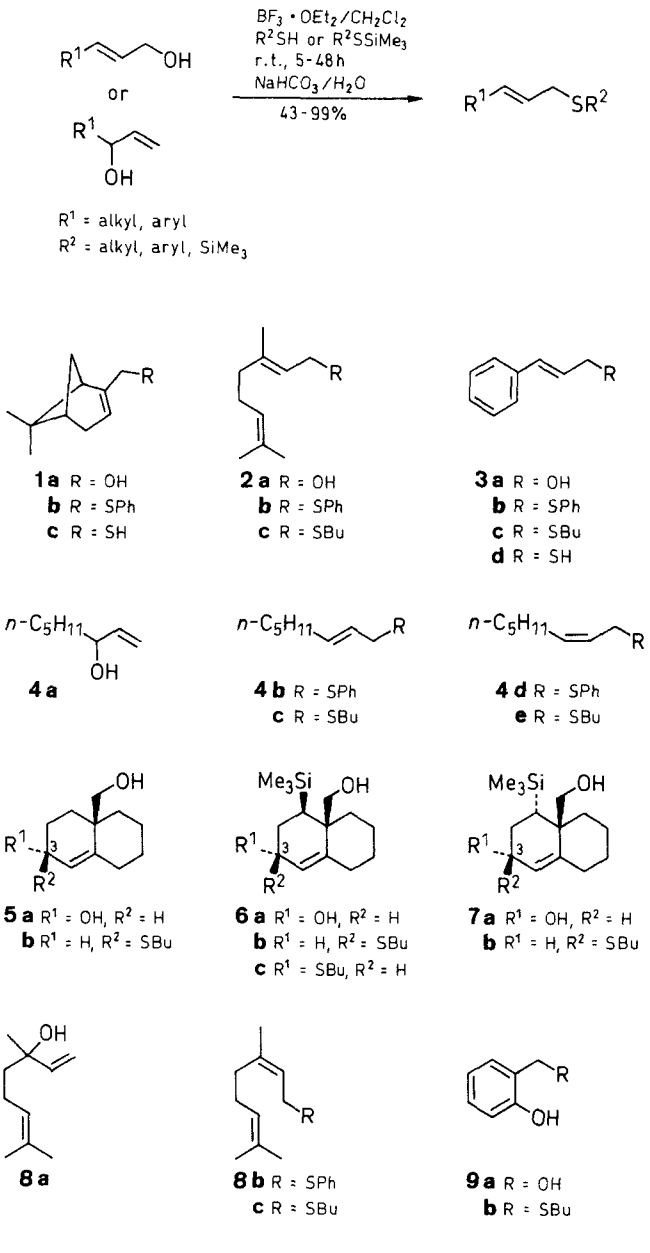
In the presence of boron trifluoride–diethyl ether complex, various allyl alcohols [(−)-myrtenol, geraniol, cinnamyl alcohol, linalool, 1-octen-3-ol, 2-hydroxybenzyl alcohol and bicyclic diols] were reacted with thiophenol, 1-butanethiol, trimethyl(phenylthio)silane or hexamethylsilane in dichloromethane at room temperature to give the corresponding allyl sulfides in good to excellent yields. The mild conditions for this transformation allowed chemoselectivity.

Extensive studies on syntheses of allyl sulfides have been carried out recently. For example, Dunkerton et al.[1] used borone trifluoride–diethyl ether complex ($BF_3 \cdot OEt_2$) to catalyze the reaction of allyl acetates with thiophenol or (phenylthio)trimethylsilane to give allyl sulfides. Trost and Scanlan[2] developed a new way to synthesize allyl sulfides from allyl carbonates by use of trimethylsilyl sulfur nucleophiles and palladium(0) catalyst. Déléris et al.[3] reported that allyl thiols can be prepared by treatment of mono- and sesquiterpenes with *N*-sulfinylbenzenesulfonamide followed by lithium aluminum hydride reduction of the ene adducts. Guindo et al.[4] found that thiophenol reacts with allyl alcohols in the presence of zinc(II) iodide (ZnI_2) to give the corresponding sulfides in 60–86% yields. Volante[5] reported a method for the conversion of an allylic alcohol to the corresponding thiol via thioesters by using triphenylphosphine, diisopropyl azodicarboxylate, and thioacetic acid. Tanigawa et al.[6] prepared unsymmetrical sulfides from allyl alcohols and thiols by utilizing aminophosphonium salts. Herein, we report an efficient procedure for the synthesis of various allyl sulfides directly from allyl alcohols.

We can directly convert aliphatic, alicyclic, benzylic, conjugated, aromatic, and fused ring allyl alcohols to the corresponding sulfides with a sulfur reagent in the presence of the Lewis acid $BF_3 \cdot OEt_2$ (Scheme 1). Thus, a dichloromethane solution of allyl alcohols (1.0 equiv, 0.10–0.17 M) was treated with thiophenol or 1-butanethiol (1.3 equiv) at room temperature and then with $BF_3 \cdot OEt_2$ (1.1–9.1 equiv) for 5–48 hours. After the reaction mixture was worked up and separated by use of radial thin-layer chromatography, the desired allyl sulfides were obtained generally in 70–99% yields.

Table 1 lists our results (see entries 1, 4–7, 9, 10, 12–17). The starting materials include (−)-myrtenol (**1a**), geraniol (**2a**), cinnamyl alcohol (**3a**), 1-octen-3-ol (**4a**), bicyclic diol **5a**, silicon-containing diols **6a** and **7a**, linalool (**8a**), and 2-hydroxybenzyl alcohol (**9a**).

We also used silicon-containing reagents trimethyl(phenylthio)silane and hexamethyldisilathiane as the nucleophiles to react with (−)-myrtenol (**1a**), cinnamyl alcohol (**3a**), and 1-octen-3-ol (**4a**). The corresponding allyl sulfides (i.e., **1b**, **4b**, and **4d**) or thiols (i.e., **1c** and **3d**) were obtained in 81–96% yields.



We found that reactions of primary allyl alcohols (i.e., **1a**, **2a**, and **3a**) with a sulfur-containing reagent and $BF_3 \cdot OEt_2$ gave the corresponding primary sulfides without allylic rearrangement (Table 1, entries 1–8). For secondary allyl alcohol **4a** and tertiary alcohol **8a**, the reactions also led to primary allyl sulfides (Table 1, entries 9–11, 15 and 16); these processes involved an S_N2' fashion. On the other hand, secondary allyl alcohols **5a**, **6a**, and **7a** gave **5b**, **6b** + **6c**, and **7b**, respectively (Table 1, entries 12–14); these transformations could proceed by an S_N2 fashion. Consequently, we conclude that the steric effect determines the reaction pathway.

Table 1. Synthesis of Allyl Sulfides or Allyl Thiols from Allyl Alcohols and Sulfur-Containing Reagents

Entry	Allyl Alcohol	Reagent	Product	Yield (%)	Ratio of Isomers
1	**1a**	PhSH	**1b**	97	
2	**1a**	$PhSSiMe_3$	**1b**	92	
3	**1a**	$(Me_3Si)_2S$	**1c**	81	
4	**2a**	PhSH	**2b**	84	
5	**2a**	BuSH	**2c**	74	
6	**3a**	PhSH	**3b**	99	
7	**3a**	BuSH	**3c**	89	
8	**3a**	$(Me_3Si)_2S$	**3d**	81	
9	**4a**	PhSH	**4b** + **4d**	97	**4b/4d** = 1.8/1
10	**4a**	BuSH	**4c** + **4e**	97	**4c/4e** = 1.6/1
11	**4a**	$PhSSiMe_3$	**4b** + **4d**	96	**4b/4d** = 2.6/1
12	**5a**	BuSH	**5b**	96	
13	**6a**	BuSH	**6b** + **6c**	95	**6b/6c** = 13.6/1
14	**7a**	BuSH	**7b**	43	
15	**8a**	PhSH	**2b** + **8b**	99	**2b/8b** = 1.4/1
16	**8a**	BuSH	**2c** + **8c**	70	**2c/8c** = 1.8/1
17	**9a**	BuSH	**9b**	91	

In the conversion of allyl alcohols to allyl sulfides, only the reaction **7a** → **7b** gave a low yield (43%). The cis relationship between the hydroxy and the bulky trimethylsilyl groups in **7a** creates steric hindrance. We believe that the steric hindrance encumbered the coordination of $BF_3 \cdot OEt_2$ with the hydroxy group and retarded the nucleophilic attack of the C-3 carbon by 1-butanethiol.[7]

Guindo et al.[4] provided evidence to show that the ZnI_2-catalyzed conversion of (*S*)-α-phenethyl alcohol to α-methylbenzyl phenyl sulfide proceeds essentially by an S_N1 process. We used $BF_3 \cdot OEt_2$ to catalyze the transformation of allyl alcohols to allyl sulfides or thiols. In the reactions **5a** → **5b**, **6a** → **6b** + **6c**, and **7a** → **7b**, the C-3 hydrogens of products **5b**, **6b**, and **7b** were determined to have α configuration according to the coupling pattern of the adjacent vinylic proton in their ^1H NMR spectra. These vinylic protons unanimously showed a clear doublet, which had a coupling constant of $J = 4.1$ Hz (at $\delta = 5.60$) for **5b**, 5.4 Hz (at $\delta = 5.65$) for **6b**, and 5.7 Hz (at $\delta = 5.77$) for **7b**. This coupling pattern contrasts sharply with that of a single broad peak for the vinylic protons (at $\delta = 5.40$–5.70) of authentic starting materials **5a**,[8–10] **6a**,[7] and **7a**,[7] of which the C-3 hydrogens are known to hold β configuration. We further proved the broad pattern irrelevant to the C-3 hydroxy proton by comparing the ^1H NMR spectra between the parent and the D_2O-exchanged diol **6a**. Both spectra showed the same pattern for the C=CH proton.

We made a direct comparison between the methods developed by Guindo[4] and by us using diol **6a** as the substrate. Following the Guindo's procedure with ZnI_2 as the catalyst, we obtained a diastereomeric mixture of **6b** and **6c** in a ratio of 6.4:1 (determined by GC, see Figure D). The ratio was improved to 13.6:1 by use of our method with $BF_3 \cdot OEt_2$ as the catalyst (Figure, C). We further confirmed the ratios by means of ^1H NMR integration: 6.3:1 by ZnI_2 (Figure B) and 13.8:1 by $BF_3 \cdot OEt_2$ (Figure A). The minor product with $t_R \sim 17.96$ min in both reactions was assigned as the allyl sulfide **6c**, which had a unresolved broad peak at $\delta = 5.61$ for the C=CH proton. The shape of the broad peak is similar to that of **5a**, **6a**, and **7a**.

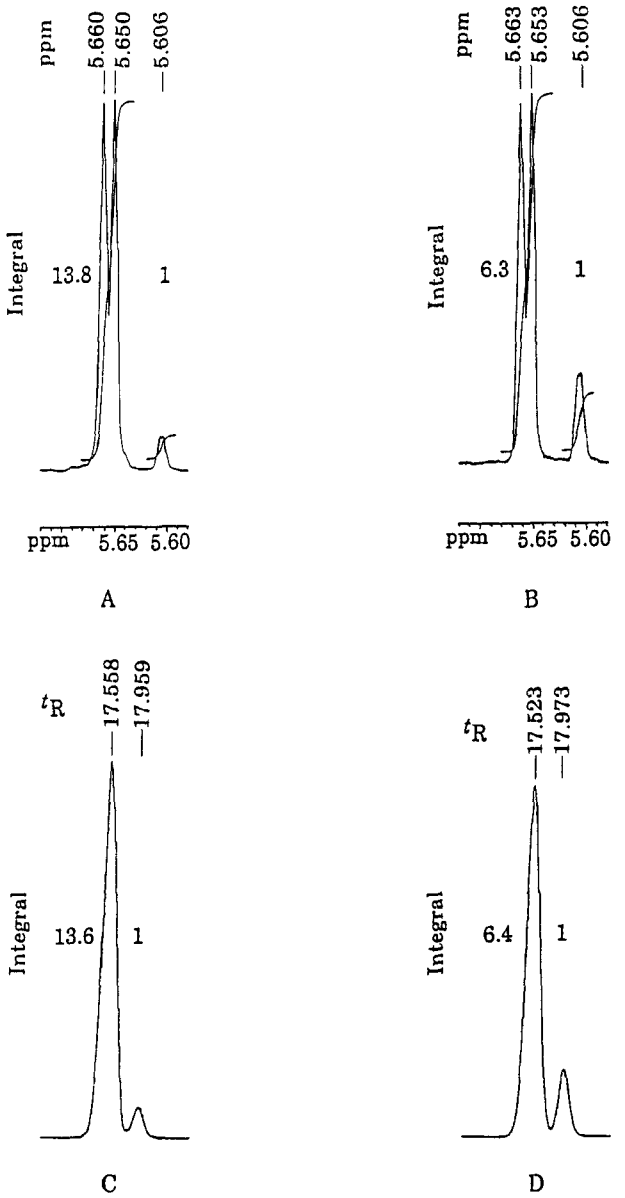


Figure 1. A and C were obtained from the reaction involving $BF_3 \cdot OEt_2$; B and D were obtained from the reaction involving ZnI_2. A and B are part of ^1H NMR spectra from a diastereomeric mixture of allyl sulfides **6b** and **6c**. The doublet in both spectra belonged to the C=CH proton of **6b** and the broad peaks with $\delta = 5.61$ belonged to the C=CH proton of **6c**. C and D are GC chromatograms from a diastereomeric mixture of allyl sulfides **6b** and **6c**. The major peaks with $t_R \sim 17.53$ min in both chromatograms belonged to **6b** and the minor peaks with $t_R \sim 17.96$ min belonged to **6c**.

Our results indicate that neither ZnI_2 nor $BF_3 \cdot OEt_2$ can make the conversion of allyl alcohol **6a** to the corresponding sulfides through an S_N1 or S_N2 process exclusively. Nevertheless, use of $BF_3 \cdot OEt_2$ as the catalyst improved the stereoselectivity from 6.4:1 to 13.6:1. The ratios of **6b** to **6c** greatly derived from unity also indicate that the above transformation involved predominantly an S_N2 process.

The reaction conditions allowed chemoselectivity between allylic and homoallylic alcohols. In the reactions **5a** → **5b**, **6a** → **6b** + **6c**, and **7a** → **7b**, we did not observe any products resulting from the substitution of the primary, homoallylic hydroxy group by 1-butanethiol. We also found that a phenolic hydroxy group remained intact while a benzylic hydroxy group reacted efficiently with 1-butanethiol to give the corresponding benzylic sulfide (i.e., **9a** → **9b**, 91% yield).

We were able to use trimethylsilylated sulfur reagent to convert allyl alcohols to the corresponding sulfides. The efficiency is comparable with that of the reaction by use of the parent thiol: thiophenol and trimethyl(phenylthio)silane were separately reacted with (−)-myrtenol (**1a**) to give sulfide **1b** in 97% and 92% yields, respectively (Table 1, entries 1 and 2); they were also separately reacted with 1-octen-3-ol (**4a**) to give a mixture of sulfides **4b** and **4d** in 97% and 96% overall yields, respectively (Table 1, entries 9 and 11). More importantly, we can convert allyl alcohols to allyl thiols with hexamethyldisilathiane: 81% yield for reactions **1a** → **1c** and **3a** → **3d** (Table 1, entries 3 and 8). Thus, liquid hexamethyldisilathiane can be used to replace notorious hydrogen sulfide gas in the preparation of allyl thiols.

Allyl alcohols are considered as hard bases and sulfur-containing reagents as soft bases.[11] We activated allyl alcohols by a Lewis acid and then utilized sulfur-containing reagents as nucleophiles. According to Pearson's principle of hard and soft acids and bases,[12,13] we chose hard acid $BF_3 \cdot OEt_2$ as the catalyst because it would coordinate preferentially to the hard base, an allyl alcohol. In addition, aprotic solvent dichloromethane was used in those reactions to enhance the nucleophilicity of sulfur-containing reagents.

By use of $BF_3 \cdot OEt_2$ as catalyst, various primary, secondary, and tertiary allyl alcohols can be directly converted to the corresponding sulfides or thiols with alkyl, aryl, or trimethylsilylated sulfur reagents at room temperature. These reactions gave the desired products in good to excellent yields and proceeded more likely by an S_N2 or S_N2' process.

All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of N_2. Hexanes and EtOAc from Tilley Chemical Co. and CH_2Cl_2 from J. T. Baker Chemical Co. were dried and distilled from CaH_2. MeOH of reagent grade from J. T. Baker Chemical Co. was dried and distilled from Mg turnings and I_2; $BF_3 \cdot OEt_2$ from Aldrich Chemical Co. was distilled from CaH_2 under reduced pressure. The following compounds and reagents were purchased from Aldrich Chemical Co.: (1*R*)-(−)-myrtenol, geraniol, linalool, 1-octen-3-ol, cinnamyl alcohol, 2-hydroxybenzyl alcohol, thiophenol, BuSH, and $PhSSiMe_3$. Hexamethyldisilathiane from Fluka Chemical Co. was stored in serum capped bottles under Ar over molecular sieves 4A. Analytical thin-layer chromatography (TLC) analyses were performed on precoated plates (silica gel GHLF), purchased from Analtech Inc. Gas chromatographic analyses were carried out on a Hewlett-Packard 5794 instrument equipped with a 12.5-m cross-linked methyl silicone gum capillary column (0.2-mm i.d.); the injector temperature was set up at 260 °C. Purification by gravity column chromatography was performed with EM Reagents Silica gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Separations by radial TLC were performed on a model 7924T Chromatotron from Harrison Research. The plates with 1 mm and 2 mm thickness were coated with EM Reagents Silica Gel 60 PF_{254} containing gypsum. IR spectra were measured on a Perkin Elmer 1600 Series FT-IR. ^1H NMR spectra were obtained on a Varian CFT-20 (80 MHz) or a Brüker AMX 500 spectrometer by use of $CDCl_3$ as solvent and TMS as an internal standard. HRMS and electron impact mass spectra (EIMS) were obtained by means of a VG Analytical 70-S mass spectrometer.

Standard Procedure for the Preparation of Allyl Sulfides:
In a one-necked round-bottomed flask with a stirring bar and a rubber septum, $BF_3 \cdot OEt_2$ was added dropwise to a stirring CH_2Cl_2 solution (0.10–0.17 M) containing an allyl alcohol (0.30–3.0 g) and a thiol, $PhSSiMe_3$, or $(Me_3Si)_2S$ at 0 °C. MeOH was added into the mixture when **5a**, **6a**, or **7a** was the substrate. After being stirred under an atmosphere of N_2 at r.t. for 5–48 h, the mixture was diluted by addition of Et_2O (50 mL). This diluted mixture was then washed with sat. aq $NaHCO_3$ (2 × 10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with brine solution (20 mL), dried ($MgSO_4$), filtered, and concentrated to give a yellow oil. The resultant liquid was purified by chromatography to give the desired allyl sulfide. Also, the details for the preparation of sulfide **7b** have been reported previously.[7]

(1*R*)-6,6-Dimethyl-2-[(phenylthio)methyl]bicyclo[3.1.1]hept-2-ene (1b):
Method A: PhSH (172 mg, 1.56 mmol), $BF_3 \cdot OEt_2$ (187 mg, 1.32 mmol), (1*R*)-(−)-myrtenol (**1a**; 183 mg, 1.20 mmol), and CH_2Cl_2 (9.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 16 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **1b** (285 mg, 97%) was obtained as a colorless oil; TLC R_f 0.62 (EtOAc/hexanes, 1:19); GC (column temperature program: initial temperature 55 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 11.97 min.

$C_{16}H_{20}S$	calc.	C 78.65	H 8.26	S 13.10
(244.4)	found	78.51	8.39	13.22

HRMS: *m/z*, $C_{16}H_{20}S$, calc.: 244.1286; found: 244.1291.

IR (neat): ν = 2913, 1585, 1480, 1441, 1385, 1370, 1223, 1030, 890, 745, 695 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 1.04–1.24 (m, 3 H, CH_2CH), 1.27 (s, 3 H, CH_3), 2.18–2.23 (m, 3 H, $CHC{=}CCH_2$), 3.52 (s, 2 H, SCH_2), 5.39–5.55 (br m, 1 H, =CH), 7.11–7.44 (m, 5 H, C_6H_5).

Method B: $PhSSiMe_3$ (285 mg, 1.56 mmol), $BF_3 \cdot OEt_2$ (187 mg, 1.32 mmol), (1*R*)-(−)-myrtenol (**1a**; 183 mg, 1.20 mmol), and CH_2Cl_2 (10 mL) were added into the reaction flask. The mixture was stirred at r.t. for 8 h. After purification by use of a Chromatotron (1 mm plate, hexanes as eluant), sulfide **1b** (270 mg, 92%) was obtained as a colorless oil.

(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]methanethiol (1c):
$(Me_3Si)_2S$ (278 mg, 1.56 mmol), $BF_3 \cdot OEt_2$ (187 mg, 1.32 mmol), (1*R*)-(−)-myrtenol (**1a**; 183 mg, 1.20 mmol), and CH_2Cl_2 (15 mL) were added into the reaction flask. The mixture was stirred at r.t. for 36 h. After purification by use of a Chromatotron (1 mm plate, hexanes as eluant), thiol **1c** (163 mg, 81%) was obtained as a pale yellow oil; TLC R_f 0.46 (100% hexanes).

MS (70 eV): *m/z* (%) = 168 (M^+, 6), 167 (19), 135 (33), 134 (57), 119 (47), 93 (100), 91 (65), 79 (33), 69 (31), 43 (57), 41 (49), 39 (13).

IR (neat): ν = 2919, 2848, 1588, 1460, 1443, 1378, 1360, 1213, 879, 796 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.85 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.31–1.68 (m, 3 H, CH_2CH), 1.95–2.48 (m, 3 H, $CHC{=}CCH_2$), 3.06 (dt, J = 1.2, 6.6 Hz, 2 H, SCH_2), 5.24–5.41 (br s, 1 H, =CH).

The spectroscopic data of this compound were consistent with those in literature.[3]

(*trans*-3,7-Dimethyl-2,6-octadienyl) Phenyl Sulfide (2b) and (*cis*-3,7-Dimethyl-2,6-octadienyl) Phenyl Sulfide (8b):

Method A: PhSH (156 mg, 1.42 mmol), $BF_3 \cdot OEt_2$ (170 mg, 1.20 mmol), linalool (**8a**; 169 mg, 1.09 mmol), and CH_2Cl_2 (8.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 24 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **2b** (153 mg, 57%) and sulfide **8b** (113 mg, 42%) were obtained as yellow oils.

2b: TLC R_f 0.56 (EtOAc/hexanes, 1:9).

HRMS: *m/z*, $C_{16}H_{22}S$, calc.: 246.1442; found: 246.1447.

IR (CCl_4): ν = 3060, 2920, 1587, 1480, 1440, 1390, 1370, 700 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 1.55–1.80 (m, 9H, $3 \times CH_3$), 1.80–2.20 (m, 4H, $2 \times CCH_2C=$), 3.60 (s, 2H, $=CCH_2S$), 5.20–5.65 (m, 2H, $2 \times =CH$), 7.05–7.55 (m, 5H, C_6H_5).

The spectroscopic data of this compound were consistent with those in literature.[6]

8b: TLC R_f 0.65 (EtOAc/hexanes, 1:9).

$C_{16}H_{22}S$	calc.	C 78.00	H 9.01	S 12.99
(246.4)	found	77.89	8.93	13.12

HRMS: *m/z*, $C_{16}H_{22}S$, calc.: 246.1442; found: 246.1447.

IR (CCl_4): ν = 3060, 2920, 1587, 1480, 1440, 1390, 1370, 700 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 1.50–1.70 (m, 9H, $3 \times CH_3$), 1.75–2.05 (m, 4H, $2 \times CCH_2C=$), 3.61 (d, J = 0.7 Hz, 2H, $=CCH_2S$), 5.25–5.50 (m, 2H, $2 \times =CH$), 7.10–7.45 (m, 5H, C_6H_5).

Method B: PhSH (162 mg, 1.47 mmol), $BF_3 \cdot OEt_2$ (176 mg, 1.24 mmol), geraniol (**2a**; 174 mg, 1.13 mmol), and CH_2Cl_2 (9.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 29 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **2b** (234 mg, 84%) was obtained as a colorless oil.

Butyl (*trans*-3,7-Dimethyl-2,6-octadienyl) Sulfide (2c) and Butyl (*cis*-3,7-Dimethyl-2,6-octadienyl) Sulfide (8c):

Method A: BuSH (128 mg, 1.42 mmol), $BF_3 \cdot OEt_2$ (170 mg, 1.20 mmol), linalool (**8a**; 169 mg, 1.09 mmol), and CH_2Cl_2 (8.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 24 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), an inseparable mixture of sulfides **2c** and **8c** (173 mg, 70% overall yield) was obtained as a yellow oil.

Analysis by GC showed that the ratio of **2c/8c** was 1.8:1. For sulfides **2c** and **8c**: TLC R_f 0.70 (EtOAc/hexanes, 1:9).

$C_{14}H_{26}S$	calc.	C 74.28	H 11.59	S 14.14
(226.4)	found	74.44	11.50	14.02

HRMS: *m/z*, $C_{14}H_{26}S$, calc.: 226.1755; found: 226.1758.

IR (CCl_4): ν = 2959, 2935, 2870, 1668, 1465, 1380, 1364, 918, 877 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.1 Hz, 3H, CH_3), 1.15–1.60 (m, 4H, $2 \times CH_2$), 1.61–1.80 (m, 9H, $3 \times CH_3$), 1.81–2.10 (m, 4H, $2 \times =CCH_2$), 2.51 (t, J = 7.1 Hz, 2H, SCH_2), 3.19 (s, 2H, $=CCH_2S$), 5.00–5.70 (br m, 2H, $2 \times =CH$).

Method B: BuSH (133 mg, 1.47 mmol), $BF_3 \cdot OEt_2$ (176 mg, 1.24 mmol), geraniol (**2a**; 174 mg, 1.13 mmol), and CH_2Cl_2 (9.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 24 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **2c** (189 mg, 74%) was obtained as a colorless oil.

Phenyl *trans*-(3-Phenyl-2-propenyl) Sulfide (3b):

PhSH (218 mg, 1.98 mmol), $BF_3 \cdot OEt_2$ (238 mg, 1.68 mmol), cinnamyl alcohol (**3a**; 205 mg, 1.52 mmol), and CH_2Cl_2 (10 mL) were added into the reaction flask. The mixture was stirred at r.t. for 24 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **3b** (340 mg, 99%) was obtained as a yellow solid; TLC R_f 0.58 (EtOAc/hexanes, 1:9); GC (column temperature program: initial temperature 55°C, duration 2.00 min; increment rate 15°C/min; final temperature 250°C) t_R 12.62 min.

HRMS: *m/z*, $C_{15}H_{14}S$, calc.: 226.0816; found: 226.0819.

IR (CCl_4): ν = 3080, 3025, 2920, 1585, 1480, 1440, 970, 710 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 3.70 (d, J = 6.0 Hz, 2H, $=CCH_2S$), 6.22 (dt, J = 15.7, 6.0 Hz, 1H, $=CHCS$), 6.44 (d, J = 15.7 Hz, 1H, ArCH=), 7.00–7.60 (m, 10H, $2 \times C_6H_5$).

The spectroscopic data of this compound were consistent with those in literature.[4]

Butyl *trans*-(3-Phenyl-2-propenyl) Sulfide (3c):

BuSH (179 mg, 1.98 mmol), $BF_3 \cdot OEt_2$ (238 mg, 1.68 mmol), cinnamyl alcohol (**3a**; 205 mg, 1.52 mmol), and CH_2Cl_2 (10 mL) were added into the reaction flask. The mixture was stirred at r.t. for 43 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **3c** (279 mg, 89%) was obained as a yellow oil; TLC R_f 0.71 (EtOAc/hexanes, 1:9); GC (column temperature program: initial temperature 55°C, duration 2.00 min; increment rate 15°C/min; final temperature 250°C) t_R 10.76 min.

$C_{13}H_{18}S$	calc.	C 75.69	H 8.80	S 15.51
(206.34)	found	75.81	8.89	15.37

HRMS: *m/z*, $C_{13}H_{18}S$, calc.: 206.1129; found: 206.1130.

IR (CCl_4): ν = 3084, 3025, 2931, 2872, 1649, 1596, 1578, 1496, 1467, 1420, 1378, 961, 691 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.7 Hz, 3H, CH_3), 1.15–1.88 (m, 4H, $2 \times CH_2$), 2.49 (t, J = 6.9 Hz, 2H, SCH_2C), 3.28 (d, J = 6.3 Hz, 2H, $=CCH_2S$), 6.13 (dt, J = 15.7, 6.7 Hz, 1H, $=CHCS$), 6.43 (d, J = 15.7 Hz, 1H, ArCH=), 7.10–7.55 (m, 5H, C_6H_5).

3-Phenyl-2-propene-1-thiol (3d):

$(Me_3Si)_2S$ (353 mg, 1.98 mmol), $BF_3 \cdot OEt_2$ (238 mg, 1.68 mmol), cinnamyl alcohol (**3a**; 205 mg, 1.52 mmol), and CH_2Cl_2 (10 mL) were added into the reaction flask. The mixture was stirred at r.t. for 40 h. After purification by use of a Chromatotron (1 mm plate, EtOAc/hexanes, 1:19 as eluant), thiol **3d** (185 mg, 81%) was obtained; TLC R_f 0.48 (EtOAc/hexanes, 1:19).

MS (70 eV): *m/z* (%) = 150 (M^+, 7), 149 (3), 117 (100), 116 (9), 115 (32), 91 (21), 85 (6), 59 (11), 57 (15), 43 (13), 41 (14), 39 (9).

IR (neat): ν = 3080, 3020, 2933, 1585, 1482, 1440, 971, 710 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 3.33 (dd, J = 7.5, 6.0 Hz, 2H, $=CCH_2S$), 6.20 (dt, J = 15.6, 6.0 Hz, 1H, $=CHCS$), 6.43 (d, J = 15.6 Hz, 1H, ArCH=), 7.15–7.34 (m, 5H, C_6H_5).

The spectroscopic data of this compound were consistent with those in literature.[5]

(*trans*-Oct-2-enyl) Phenyl Sulfide (4b) and (*cis*-Oct-2-enyl) Phenyl Sulfide (4d):

Method A: PhSH (182 mg, 1.65 mmol), $BF_3 \cdot OEt_2$ (198 mg, 1.40 mmol), 1-octen-3-ol (**4a**, 163 mg, 1.27 mmol), and CH_2Cl_2 (8.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 8 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **4b** (174 mg, 62%) and sulfide **4d** (98 mg, 35%) were obtained as yellow oils.

4b: TLC R_f 0.68 (EtOAc/hexanes, 1:10); GC (column temperature program: initial temperature 55°C, duration 2.00 min; increment rate 15°C/min; final temperature 250°C) t_R 10.82 min.

$C_{14}H_{20}S$	calc.	C 76.32	H 9.16	S 14.52
(220.4)	found	76.42	9.27	14.38

HRMS: *m/z*, $C_{14}H_{20}S$, calc.: 220.1286; found: 220.1292.

IR (neat): ν = 3080, 2920, 2860, 1585, 1483, 1440, 1380, 970, 745, 695 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.0 Hz, 3H, CH_3), 1.10–1.55 (m, 6H, $3 \times CH_2$), 1.80–2.10 (m, 2H, $=CCH_2$), 3.50 (dd, J = 0.8, 4.8 Hz, 2H, $=CCH_2S$), 5.23–5.58 (m, 2H, $2 \times =CH$), 7.10–7.45 (m, 5H, C_6H_5).

4d: TLC R_f 0.74 (EtOAc/hexanes, 1:10); GC (column temperature program: initial temperature 55°C, duration 2.00 min; increment rate 15°C/min; final temperature 250°C) t_R 10.01 min.

$C_{14}H_{20}S$	calc.	C 76.32	H 9.16	S 14.52
(220.4)	found	76.24	9.30	14.55

HRMS: *m/z*, $C_{14}H_{20}S$, calc.: 220.1286; found: 220.1292.

IR (neat): ν = 3070, 2960, 2930, 2860, 1585, 1545, 1480, 1440, 1380, 970, 745, 695 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.0 Hz, 3 H, CH_3), 1.05–1.70 (m, 6 H, 3 × CH_2), 1.80–2.10 (m, 2 H, $=CCH_2$), 3.49 (dd, J = 1.4, 3.4 Hz, 2 H, $=CCH_2S$), 5.20–5.55 (m, 2 H, 2 × =CH), 7.05–7.40 (m, 5 H, C_6H_5).

Method B: $PhSSiMe_3$ (301 mg, 1.65 mmol), $BF_3 \cdot OEt_2$ (198 mg, 1.40 mmol), 1-octen-3-ol (**4a**; 163 mg, 1.27 mmol), and CH_2Cl_2 (11 mL) were added into the reaction flask. The mixture was stirred at r.t. for 24 h. After purification by use of a Chromatotron (1 mm plate, hexanes as eluant), sulfide **4b** (193 mg, 69%) and sulfide **4d** (76 mg, 27%) were obtained as yellow oils.

Butyl (*trans*-Oct-2-enyl) Sulfide (4c) and Butyl (*cis*-Oct-2-enyl) Sulfide (4e):

BuSH (149 mg, 1.65 mmol), $BF_3 \cdot OEt_2$ (198 mg, 1.40 mmol), 1-octen-3-ol (**4a**; 163 mg, 1.27 mmol), and CH_2Cl_2 (8.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 24 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **4c** (153 mg, 60%) and sulfide **4e** (94 mg, 37%) were obtained as yellow oils.

4c: TLC R_f 0.75 (EtOAc/hexanes, 1:10); GC (column temperature program: initial temperature 55°C, duration 2.00 min; increment rate 15°C/min; final temperature 250°C) t_R 8.85 min.

$C_{12}H_{24}S$	calc.	C 71.94	H 12.08	S 15.97
(200.4)	found	72.08	11.98	16.09

HRMS: *m/z*, $C_{12}H_{24}S$, calc.: 200.1599; found: 200.1601.

IR (CCl_4): ν = 2924, 2865, 1545, 1470, 1380, 970 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.50–1.05 (m, 6 H, 2 × CH_3), 1.05–1.75 (m, 10 H, 5 × CH_2), 1.75–2.15 (m, 2 H, $=CCH_2$), 2.45 (t, J = 7.1 Hz, 2 H, SCH_2), 3.08 (d, J = 5.7 Hz, 2 H, $=CCH_2S$), 5.15–5.50 (m, 2 H, 2 × =CH).

4e: TLC R_f 0.79 (EtOAc/hexanes, 1:10); GC (column temperature program: initial temperature 55°C, duration 2.00 min; increment rate 15°C/min; final temperature 250°C) t_R 8.10 min.

$C_{12}H_{24}S$	calc.	C 71.94	H 12.08	S 15.97
(200.4)	found	71.82	11.92	15.90

HRMS: *m/z* $C_{12}H_{24}S$, calc.: 200.1599; found: 200.1601.

IR (CCl_4): ν = 2924, 2865, 1545, 1470, 1380, 970 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.75–1.05 (m, 6 H, 2 × CH_3), 1.06–1.70 (m, 10 H, 5 × CH_2), 1.75–2.15 (m, 2 H, $=CCH_2$), 2.45 (t, J = 6.9 Hz, 2 H, SCH_2), 3.08 (d, J = 5.3 Hz, 2 H, $=CCH_2S$), 5.15–5.50 (m, 2 H, 2 × =CH).

Butyl [*cis*-6-(Hydroxymethyl)bicyclo[4.4.0]dec-1(2)-en-3-yl] Sulfide (5b):

BuSH (77 mg, 0.86 mmol), $BF_3 \cdot OEt_2$ (103 mg, 0.72 mmol), diol **5a** (121 mg, 0.66 mmol), CH_2Cl_2 (4.0 mL), and MeOH (4.0 mL) were added into the reaction flask. The mixture was stirred at r.t. for 18 h. After purification by use of a Chromatotron (1 mm plate, EtOAc/hexanes, 1:4 as eluant), sulfide **5b** (161 mg, 96%) as a colorless oil was obtained; TLC R_f 0.33 (EtOAc/hexanes, 1:4), GC (column temperature program: initial temperature 100°C, duration 2.00 min; increment rate 10°C/min; final temperature 250°C) t_R 13.12 min.

$C_{15}H_{26}OS$	calc.	C 70.82	H 10.31	S 12.58
(254.4)	found	70.97	10.19	12.69

HRMS: *m/z*, $C_{15}H_{26}OS$, calc.: 254.1704; found: 254.1709.

IR (neat): ν = 3355 br, 2967, 2820, 1716, 1379, 1170, 1054, 1011, 958, 897, 761 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$): δ = 0.80–2.20 (m, 19 H, CH_3 + 8 × CH_2), 1.54 (s, 1 H, OH), 2.46–2.65 (m, 2 H, H_2CS), 3.25–3.36 (m, 1 H, HCS), 3.63 (s, 2 H, CH_2O), 5.60 (d, J = 4.1 Hz, 1 H, HC=).

Butyl [*c*-6-Hydroxymethyl-*c*-5-(trimethylsilyl)bicyclo[4.4.0]-dec-1-en-*r*-3-yl] Sulfide (6b) and Butyl [*t*-6-Hydroxymethyl-*t*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-*r*-3-yl] Sulfide (6c):

Method A: BuSH (69 mg, 0.77 mmol), $BF_3 \cdot OEt_2$ (92 mg, 0.65 mmol), diol **6a** (150 mg, 0.59 mmol), CH_2Cl_2 (5.0 mL), and MeOH (5.0 mL) were added into the reaction flask. This mixture was stirred at r.t. in a sealed, round-bottomed flask for 5 h. After purification by use of a Chromatotron (1 mm plate, EtOAc/hexanes, 1:10 as eluant), a mixture of diastereomeric sulfides **6b** and **6c** (183 mg, 95% overall yield) was obtained as a colorless oil. The ratio of **6b/6c** was determined by GC as 13.6:1. TLC R_f 0.32 (EtOAc/hexanes, 1:10); GC (column temperature 210°C) t_R 17.56 min for **6b** and 17.96 min for **6c**.

HRMS: *m/z*, $C_{18}H_{34}OSSi$, calc.: 326.2100; found: 326.2105.

IR (neat): ν = 3500 br, 2940, 2855, 1645, 1440, 1245, 1040, 850, 825, 750 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) for the mixture of **6b** and **6c**: δ = 0.10 [s, 9 H, $Si(CH_3)_3$ of **6c**], 0.11 [s, 9 H, $Si(CH_3)_3$ of **6b**], 0.86–2.23 (m, 18 H, **6b** + **6c**), 1.52 (s, 1 H, OH, **6b** + **6c**), 2.30–2.62 (m, 2 H, H_2CS, **6b** + **6c**), 3.33–3.44 (m, 1 H, HCS, **6b** + **6c**), 3.66 (dd, J = 11.3, 1.7 Hz, 1 H, CHO, **6b** + **6c**), 3.85 (d, J = 11.3 Hz, 1 H, CHO, **6b** + **6c**), 5.61 (m, 1 H, HC=C of **6c**), 5.66 (d, J = 5.4 Hz, 1 H, HC=C of **6b**).

Method B: The procedure developed by Guindon et al.[4] was followed. ZnI_2 (16.6 mg, 0.052 mmol) was added to a stirred solution containing BuSH (46.4 mg, 0.515 mmol), diol **6a** (26.2 mg, 0.103 mmol), and CH_2Cl_2 (3.0 mL) at r.t. This mixture was stirred at r.t. in a sealed, round-bottomed flask for 24 h. The mixture was quenched with H_2O and the solution was extracted with CH_2Cl_2 (30 mL). The organic layers were washed with H_2O (2 × 30 mL) and brine (30 mL), dried ($MgSO_4$), filtered, and concentrated to give a mixture of diastereomeric sulfides **6b** and **6c** (20.0 mg, 61% overall yield) as a yellow oil. The yield was not optimized; the ratio of **6b/6c** was determined by GC as 6.4:1. GC (column temperature 210°C) t_R 17.52 min for **6b** and 17.97 min for **6c**.

Butyl 2-Hydroxybenzyl Sulfide (9b):

BuSH (186 mg, 2.07 mmol), $BF_3 \cdot OEt_2$ (249 mg, 1.75 mmol), 2-hydroxybenzyl alcohol (**9a**; 198 mg, 1.59 mmol), and CH_2Cl_2 (10 mL) were added into the reaction flask. The mixture was stirred at r.t. for 48 h. After purification by use of a Chromatotron (2 mm plate, hexanes as eluant), sulfide **9b** (284 mg, 91%) was obtained as a colorless oil; TLC R_f 0.30 (EtOAc/hexanes, 1:10); GC (column temperature program: initial temperature 130°C, duration 2.00 min; increment rate 15°C/min; final temperature 250°C) t_R 4.59 min.

$C_{11}H_{16}OS$	calc.	C 67.32	H 8.22	S 16.30
(196.3)	found	67.49	8.09	16.37

HRMS: *m/z*, $C_{11}H_{16}OS$, calc.: 196.0922; found: 196.0927.

IR (CCl_4): ν = 3613, 3331 br, 3073, 2955, 2931, 2872, 1690, 1614, 1584, 1549, 1490, 1467, 1420, 1378, 1173, 1155, 1091, 1038, 1008, 978, 938, 920, 861 cm^{-1}.

^1H NMR (80 MHz, $CDCl_3$ and D_2O): δ = 0.86 (t, J = 6.9 Hz, 3 H, CH_3), 1.06–1.75 (m, 4 H, 2 × CH_2), 2.40 (t, J = 6.8 Hz, 2 H, SCH_2C), 3.78 (s, 2 H, $ArCH_2S$), 6.65–7.30 (m, 4 H, C_6H_4).

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