Enethiolizable Thioacylsilanes as Intermediates for the Synthesis of Thietanols, Thiolanols, and Thianols

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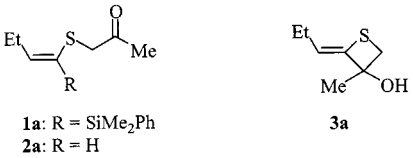
Keywords: Thioacylsilanes / Thietanols / Thiolanols / Thianols / Desilylation / Sulfur

Thietanols, thiolanols, and thianols (tetrahydro-2*H*-thiopyran-3-ols) can be obtained by a fluoride-mediated cyclization of (*Z*)-α-silyl vinyl sulfides containing an ω-carbonyl function in the chain bonded to the sulfur.

Introduction

Cyclic sulfur compounds have interesting synthetic potential.[1] Important applications of cyclic sulfides include the synthesis of biologically active sulfur-containing rings (penicillins, cephalosporins, biotin, etc.)[1−4] and polymers.[5−7] Furthermore, it is possible to obtain sulfur-free rings from cyclic sulfides and such procedures have been applied in natural product synthesis.[1] Among a variety of methodologies developed for the synthesis of cyclic sulfides, the most general routes are the base-[1−4] or acid-induced[8] ring closure of thiols with a good leaving group in a suitable position. Electrophilic cyclization of unsaturated sulfur compounds has also proved to be an efficient method for constructing heterocyclic structures[9−11] and more recently the nickel-catalyzed electroreduction of unsaturated thioacetates and thiosulfonates has been used to prepare four- to six-membered ring systems.[12]

Our ongoing studies on the chemistry of thioacylsilanes[13] showed the potential of these compounds for the preparation of sulfur heterocycles. Silylthiranes,[14,15] silylthietanes,[16] and silyl dihydrothiopyrans[17−20] were obtained from thioacylsilanes by cycloaddition with diazoalkanes, photochemical cycloaddition with olefins and cycloaddition with dienes, respectively. The obtained heterocycles could be further protiodesilylated to give the adducts formally derived from unstable thioaldehydes; in other words, the thioacylsilanes serve as synthetic equivalents of thioaldehydes. More recently we have found that (*Z*)-α-silyl enethiols obtained by thionation of ω-haloalkanoylsilanes can be used for the preparation of silylthiacycloalkenes[21,22] of common to large ring size. Unfunctionalized (*Z*)-α-silyl enethiols react with a variety of halides to give (*Z*)-α-silyl vinyl sulfides.[23,24] During the protiodesilylation of compound **1a** with 1 M tetrabutylammonium fluoride (TBAF) in moist THF, we observed the formation of the cyclic compound **3a** in 18% yield in addition to the expected protiodesilylated derivative **2a** (82% yield).[24] We have now repeated the same reaction using anhydrous THF, which resulted in the thietanol **3a** in 80% yield (Scheme 1).



1a: R = $SiMe_2Ph$
2a: R = H

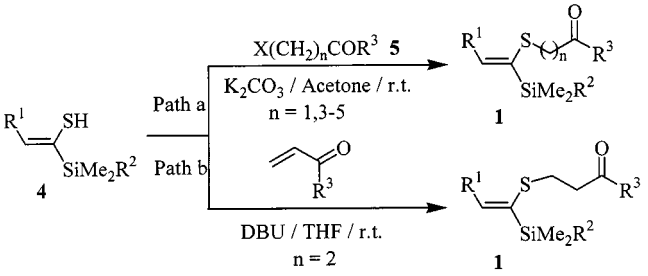
3a

Scheme 1

This reaction represents, therefore, a conceptually new approach to the construction of sulfur heterocycles of different ring size containing an alcohol function and an exocyclic double bond. Accordingly, we undertook a thorough study of the fluoride-promoted cyclization of a variety of (*Z*)-α-silyl vinyl sulfides containing a carbonyl function in a suitable position of the chain bonded to the sulfur in order to establish the scope and the limitations of this process.

Results and Discussion

The starting (*Z*)-α-silyl vinyl sulfides **1a−p** were prepared using the procedures reported previously[24] (Scheme 2). Thus, (*Z*)-α-silyl enethiols **4**, obtained by thionation of enolizable acylsilanes (see Experimental Section), were alkylated with an ω-haloalkylcarbonyl derivative **5** in acetone in the presence of dry potassium carbonate, giving **1** with n = 1, 3, 4, 5 (Path a). Those derivatives in which n = 2 were prepared by a base-induced (DBU), Michael-type



Scheme 2

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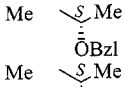
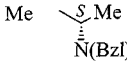
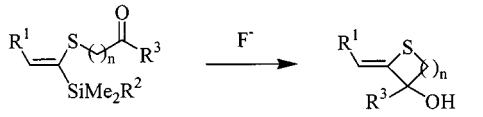
addition of enethiols **4** to methyl vinyl ketone (R^3 = Me) (Path b). In both cases, the stereochemistry of the enethiols was retained and the (*Z*)-α-silyl vinyl sulfides were obtained in satisfactory to excellent yields (Table 1).

Table 1. Synthesis of (*Z*)-α-silyl vinyl sulfides **1**

1	R^1	R^2	R^3	X	n	Yield [%][a]
a	Et	Ph	Me	Cl	1	70
b	*i*Pr	Ph	Me	Cl	1	65
c	*i*Pr	Me	Me	Cl	1	98
d	Ph	Me	Me	Cl	1	91
e	Ph	Me		Cl	1	82
f	Ph	Me		Cl	1	95
g	Et	Ph	Me	-	2	78
h	*i*Pr	Ph	Me	-	2	45
i	*i*Pr	Me	Me	-	2	42
j	Ph	Me	Me	-	2	75
k	Ph	Ph	Me	-	2	68
l	*i*Pr	Ph	Me	Cl	3	54
m	*i*Pr	Me	Me	Cl	3	77
n	Ph	Me	Me	Cl	3	78
o	Ph	Me	Me	Br	4	60
p	Ph	Me	Me	Br	5	65

[a] the yields were determined after chromatography.

For the cyclization step we employed different fluoride ion sources: (A) a commercial 1 M solution of TBAF in anhydrous THF, (B) "anhydrous"[25,26] TBAF in anhydrous THF, and (C) tetrabutylammonium difluorotriphenylstannate, a source of fluoride ion stable up to 210 °C that can be dried without any problems.[27] Usually the reactions were performed at reflux; in a few cases (entries 3 and 5) lower temperatures afforded better yields. Our results are shown in Scheme 3 and Table 2.



1

3 n=1 thietanols
6 n=2 thiolanols
7 n=3 thianols

Scheme 3

The cyclization to thietanols (n = 1) occurs very efficiently in high yields (entry 1−4, Table 2). Variation of R^1 group and of the size of the silyl group did not have any significant effect on the cyclization. Analysis of the crude products by ^{1}H NMR revealed no presence of the protiodesilylated derivative **2**, but a different by-product was observed in very small amount (about 5%), the structure of which was assigned in the case of R^1 = Ph as 2-benzylidene-4-phenyl-1,3-dithiole **8b** (Scheme 4) by comparison with an authentic sample.[28] For the formation of **8b** we speculate that the intermediate carbanion formed by desilylation extrudes the ketone **9** (route *a*), with concomitant formation of an intermediate thioketene **10**, which is known to dimerize to 1,4-dithiafulvenes.[29,30] The route *a* is competitive with the cyclization (route *b*) leading to thietanols **3**. The formation of **10** via an electrocyclic fragmentation of the thietanol anion, obtained by route *b*, can be ruled out because the thietanols are stable in the presence of sodium hydride, excess of F^- and under flash vacuum pyrolysis conditions.

With the aim of expanding this methodology to more functionalized and optically active thietanes, the cyclization was performed with (*Z*)-α-silyl vinyl sulfides **1e** and **1f** prepared from chloromethyl α-hydroxy[31] and α-amino[32] ketones, obtained in turn from *O*-benzyl-protected natural ethyl lactate or *N*,*N*-dibenzyl-protected L-alanine. The thietane **3d** containing a vicinal diol functionality was formed in good yield but with a low *de* (13%) (entry 5, Table 2). The β-amino alcohol **3e** (entry 6, Table 2) was obtained in modest yield, however, as a single diastereoisomer (*de* > 98%) as determined by NMR (see Experimental Section). In both cases the formation of **8b** and of an equimolar amount of 3-benzyloxy-2-butanone **9a**[33] and 3-dibenzylamino-2-butanone **9b**[34] in 18 and 14% yield, respectively, was observed. Presumably, the increase in steric congestion adjacent to the carbonyl reaction center suppresses the efficiency of the cyclization.

The formation of five-membered rings deserves special attention. The reaction of **1j** (R^1 = Ph, R^2 = Me) and **1k** (R^1 = Ph, R^2 = Ph) afforded the expected thiolanol **6a** (entry 10, 11) in 55 and 35% yield, respectively. Substrates **1g**,**h**,**i** with R^1 = alkyl group (entries 7,8,9 Table 2) failed to yield the cyclization product in detectable amounts. Instead, there takes place a competitive retro-Michael reaction followed by the migration of one group from the silicon to the adjacent carbon atom, with the formation of product **11**. (Scheme 5).

We had already observed this behavior previously, during the protiodesilylation with fluoride ion of (*Z*)-α-dimethylphenylsilyl vinyl sulfides containing an electron-withdrawing group β to the sulfur.[24] Apparently, the presence of the phenyl on the double bond is prerequisite for the cyclization when forming the five-membered ring, as it facilitates the Si−C bond cleavage.[35]

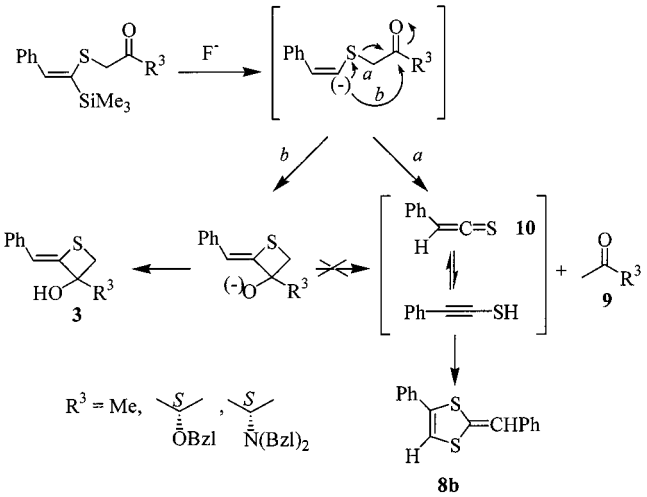
In the case of substrates with n = 3 (entry 12−17 Table 2), it was necessary to work under extremely anhydrous conditions in order to obtain good yields of thianols and minimize protiodesilylation. "Anhydrous" TBAF (method B) and tetrabutylammonium difluorotriphenylstannate (method C)[27] gave better yields than a commercial 1 M solution of TBAF (method A). The thianols **7** and the protiodesilylated products **2** were readily separated by preparative TLC. The size of the silyl group is critical with regard to desilylation when using tetrabutylammonium difluorotriphenylstannate. In fact, no reaction took place with substrates containing the dimethylphenylsilyl group (entry 15). This result can be attributed to steric hindrance of both the desilylating agent and the silyl group.

In order to verify whether this methodology can be used to construct rings with other than four, five, and six members, we investigated the desilylation of substrates with n = 4 and 5 (entry 18,19 Table 2) with anhydrous TBAF under high-dilution conditions. However, only the protiodesilyl-

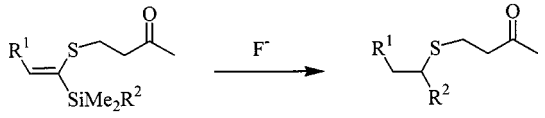
Table 2. Synthesis of thietanols **3**, thiolanols **6**, thianols **7**

Entry	1	R^1	R^3	n	F⁻	*T* [°C]	Cyclic sulfide	Yield [%]	2	Yield [%]
1	**a**	Et	Me	1	A	66	**3a**	80		
2	**b**	*i*Pr	Me	1	A	66	**3b**[a]	76		
3	**c**	*i*Pr	Me	1	A	0	**3b**[a]	80		
4	**d**	Ph	Me	1	A	66	**3c**[b]	86		
5	**e**	Ph		1	A	25	**3d**[c]	55		
6	**f**	Ph		1	A	66	**3e**[d]	30		
7	**g**	Et	Me	2	A	66	[e]	-		
8	**h**	*i*Pr	Me	2	A	66	[e]	-		
9	**i**	*i*Pr	Me	2	A	66	[e]	-		
10	**j**	Ph	Me	2	A	66	**6a**	55		
11	**k**	Ph	Me	2	A	66	**6a**	35		
12	**l**	*i*Pr	Me	3	B		**7a**	55	**b**	45
13	**m**	*i*Pr	Me	3	B		**7a**	73	**b**	27
14	**n**	Ph	Me	3	B		**7b**	78	**c**	22
15	**l**	*i*Pr	Me	3	C		**7a**	-	**b**	-
16	**m**	*i*Pr	Me	3	C		**7a**	70	**b**	15
17	**n**	Ph	Me	3	C	66	**7b**	76	**c**	20
18	**o**	Ph	Me	4	B	66	-	-	**d**	53
19	**p**	Ph	Me	5	B	66	-	-	**e**	91

[a] Besides 5% of **8a**. – [b] Besides 5% of **8b**. – [c] Besides 18% of **8b** and **9a**. – [d] Besides 14% of **8b** and **9b**. – [e] See text and Scheme 5. – A: commercial 1 M solution of TBAF in anhydrous THF, reflux temperature. – B: anhydrous TBAF in anhydrous THF, reflux temperature. – C: tetrabutylammonium difluorotriphenylstannate in anhydrous THF, reflux temperature.



Scheme 4

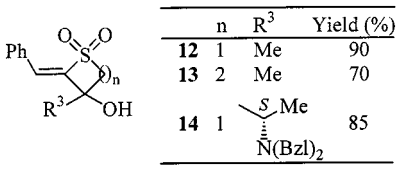


11	R^1	R^2	Yield (%)
a	Et	Ph	48
b	*i*Pr	Ph	60
c	*i*Pr	Me	40

Scheme 5

ated derivatives **2** were obtained. Therefore, the formation of seven- and eight-membered rings is not feasible using this protocol.

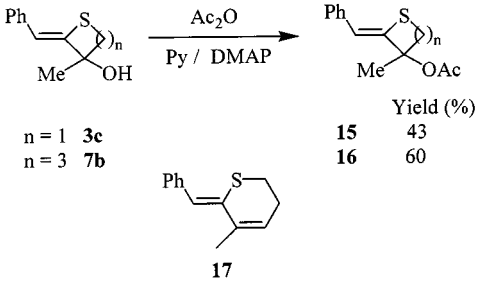
The sulfur heterocycles were oxidized with oxone in very good yields to give the corresponding solid sulfones **12**, **13**, and **14** (Scheme 6), completely characterized by analytical and spectral data. In particular, an X-ray diffraction analysis of product **14** gave the *R* configuration for the newly formed carbinol center.[36]



	n	R^3	Yield (%)
12	1	Me	90
13	2	Me	70
14	1		85

Scheme 6

Furthermore, products **3c** and **7b** were acetylated in 43 and 60% yield, respectively. However, the acetyl derivative **16** was not sufficiently stable to allow purification on silica and was partially transformed into a conjugate diene **17**. Alternatively, this product could also be obtained in quantitative yield by dehydration of **16** in an ethereal solution of hydrogen chloride (Scheme 7).



	Yield (%)
15	43
16	60

Scheme 7

Conclusion

(*Z*)-α-Silyl vinyl sulfides bearing an ω-carbonyl function in the chain bonded to the sulfur can be readily prepared.

Their fluoride-induced intramolecular cyclization is very effective for the synthesis of thietanols and thianols, but this protocol is not suitable for the synthesis of seven- and eight-membered rings. The homochiral substrates derived from L-alanine afforded the thietane **3e** containing the β-amino alcohol functionality as a single diastereoisomer.

Experimental Section

General Remarks: Melting points (uncorrected) were determined with a Büchi melting point apparatus. − ^{1}H-NMR and ^{13}C-NMR spectra were recorded using $CDCl_3$ solutions at 200 and 50.28 MHz respectively, with a Varian Gemini 200 or, at 300 and 75.46 MHz respectively, with a Varian Gemini 300. Chemical shifts (δ) are reported in ppm relative to $CHCl_3$ (δ= 7.26 for ^{1}H and δ = 77.0 for ^{13}C). *J* values are given in Hz. ^{13}C-NMR spectral assignments were made by DEPT experiments. − IR spectra were recorded on a Perkin−Elmer model 257 grating spectrometer. − Mass spectra were obtained using a VG 7070-E spectrometer at an ionizing voltage of 70 eV. − Values for $[\alpha]_D$ were determined with Perkin−Elmer Polarimeter 341. − In the characterization of new compounds, because of the small scale used for preparations, oily products have been characterized by accurate mass measurements. − Reactions were conducted in oven-dried (120 °C) glassware under a positive Ar atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes/septum techniques. THF was distilled from sodium/benzophenone just prior to use and stored under Ar. Et_2O was distilled from phosphorus pentoxide. CH_2Cl_2 was passed through basic alumina and distilled from CaH_2 prior to use. Other solvents were purified by standard procedures. Light petroleum ether refers to the fraction with b.p. 40−60 °C. The reactions were monitored by TLC performed on silica gel plates (Baker-flex IB2-F). Column chromatography was performed with Merck silica gel 60 (70−230 mesh). Preparative thick layer chromatography was carried out on glass plates using a 1-mm layer of Merck silica gel 60 PF_{254}. − All chemicals were used as obtained or purified by distillation as needed. Sodium hydrogen carbonate 99% was purchased from Carlo Erba Reagenti; hydrogen chloride was purchased from Praxair (Belgium). Butanoyl(dimethyl)phenylsilane,[23] 3-methylbutanoyl(dimethyl)phenylsilane,[24] 2-phenyl-1-trimethylsilylethanone,[37] (*Z*)-1-[dimethyl(phenyl)silyl]-but-1-enethiol,[23] (*Z*)-1-[dimethyl(phenyl)silyl]-3-methylbut-1-enethiol,[24] and (*Z*)-1-trimethylsilyl-2-phenylethenethiol[23] were obtained as described previously. 7-Bromo-2-heptanone,[38] 6-bromo-2-hexanone,[38] (3*S*)-3-(benzyloxy)-1-chloro-2-butanone,[31] and (3*S*)-1-chloro-3-(dibenzylamino)-2-butanone[32] were obtained following literature procedures.

(3-Methylbutanoyl)trimethylsilane: To a solution of 2-trimethylsilyl-1,3-dithiane (5 g, 26 mmol) in dry THF (0.85 M solution) at 0 °C under argon atmosphere, *n*BuLi (1.6 M in hexane, 18 mL, 29 mmol) was added dropwise. The resulting solution was stirred at 0 °C for 30 min, the temperature was then lowered to −20 °C and a solution of 1-chloro-2-methylpropane (2.8 g, 3.1 mL, 30 mmol) in THF (10 mL) was added. After stirring at −20 °C for 1 h, the reaction mixture was quenched with water and extracted with diethyl ether. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The resulting mixture was dissolved in 15% aqueous THF (0.35 M), and red mercury oxide (12.5 g, 58 mmol) and Celite (12.5 g) were added. Boron trifluoride−diethyl ether (8.2 g, 7.3 mL, 58 mmol) was added and the resulting mixture was stirred at room temperature for 1 h. The reaction mixture was filtered and the filtrate was diluted with diethyl ether, washed with water and brine, and dried (Na_2SO_4). (3-Methylbutanoyl)trimethylsilane was isolated in 72% yield (18.7 mmol, 2.95 g) by distillation as a colorless oil, b.p. 65 °C. The spectroscopic data were in agreement with those reported.[39]

1-Dimethylphenylsilyl-2-phenyl-1-ethanone: To a solution of 1,3-dithiane (2.4 g, 20 mmol) in dry THF (0.85 M solution) at −30 °C under argon atmosphere, *n*BuLi (1.6 M in hexane, 14 mL, 22 mmol) was added dropwise. The resulting solution was stirred at −15 °C for 2 h, the temperature was then lowered to −30 °C and a solution of benzyl bromide (4.1 g, 2.8 mL, 24 mmol) in THF (10 mL) was added. After stirring at room temperature for 15 h, the reaction mixture was cooled to −30 °C and *n*BuLi (1.6 M in hexane, 16 mL, 26 mmol) was added dropwise. The resulting solution was stirred at −15 °C for 2 h, the temperature was then lowered to −30 °C and a solution of dimethylphenylchlorosilane (4.7 g, 4.7 mL, 28 mmol) in THF (10 mL) was added. After stirring at room temperature for 4 h, the reaction mixture was quenched with water and extracted with diethyl ether. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The resulting white solid was dissolved in 15% aqueous THF (0.35 M), and red mercury oxide (8.6 g, 40 mmol) and Celite (8.6 g) were added. Boron trifluoride−diethyl ether (5.6 g, 4.9 mL, 40 mmol) was added and the resulting mixture was stirred at room temperature for 1 h. The reaction mixture was filtered and the filtrate was diluted with diethyl ether, washed with water and brine, and dried (Na_2SO_4). Chromatography on silica gel (light petroleum: diethyl ether, 30:1) gave 1-dimethylphenylsilyl-2-phenyl-1-ethanone in 75% yield (15 mmol, 3.8 g) as a yellow oil. The spectroscopic data were in agreement with those reported.[40]

(*Z*)-3-Methyl-1-trimethylsilylbut-1-enethiol: Hydrogen chloride and hydrogen sulfide were bubbled into a solution of (3-methylbutanoyl)trimethylsilane (0.2 g, 1.3 mmol) in diethyl ether (50 mL) at −20 °C, until the starting acylsilane had disappeared (TLC with light petroleum/Et_2O, 10:1). After the mixture had been allowed to warm to room temperature, it was treated with solid sodium hydrogen carbonate until evolution of carbon dioxide ceased (10 g) and was then left overnight. Filtration and concentration under reduced pressure gave the pure (*Z*)-enethiol as an oil (0.39 g, 1.2 mmol, 94%). − IR (CCl_4): $\tilde{\nu}$ = 2540 cm^{-1} (SH), 1245 ($SiMe_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 1.00 (d, *J* = 6.7 Hz, 6 H, 2× CH_3), 2.50 (s, 1 H, SH), 2.60−2.80 (m, 1 H, *i*Pr−CH), 5.70 (d, *J* = 8.6 Hz, 1 H, vinylic H). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = −2.0 ($SiMe_3$), 21.8 (2× CH_3), 29.6 (CH), 126.9 (vinylic C), 145.4 (vinylic CH). − MS; *m*/*z*: 174 [M^+], 159 [$M^+ - CH_3$], 131 [$M^+ - CH(CH_3)_2$], 73 [$SiMe_3$]. − HR-MS: $C_8H_{18}SSi$ calcd. 174.08985 found 174.0895.

(*Z*)-1-Dimethylphenylsilyl-2-phenyl-1-ethenethiol: Starting from 1-dimethylphenylsilyl-2-phenyl-1-ethanone, the thionation was performed using the same conditions reported for (*Z*)-1-trimethylsilyl-3-methylbut-1-enethiol, yielding the pure (*Z*)-enethiol as an oil (96%); − IR (CCl_4): $\tilde{\nu}$ = 2550 cm^{-1} (SH), 1430, 1110 ($SiMe_2Ph$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.70 (s, 6 H, $SiMe_2$), 3.12 (s, 1 H, SH), 7.06 (s, 1 H, vinylic H), 7.50−7.80 (10 H, m, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = −3.0 ($SiMe_2$), 127.2, 128.0, 128.2, 128.8, 129.6, 134.3, 135.4 (ArCH + vinylic CH), 135.8, 137.4 (ArC + vinylic C). − MS; *m*/*z*: 270 [M^+], 255 [$M^+ - CH_3$], 135 [$SiMe_2Ph$]. − HR-MS: $C_{16}H_{18}SSi$ calcd. 270.08985 found 270.0897.

Synthesis of (*Z*)-α-Silyl Vinyl Sulfides 1. − General Method (Path a): To a solution of (*Z*)-α-silyl enethiol **4** (1.0 mmol) in acetone (4 mL) were added solid K_2CO_3 (1.3 mmol) and the halide

(1.1 mmol). The mixture was stirred at room temperature until the starting enethiol had disappeared (2−5 h). The mixture was then diluted with water and extracted with diethyl ether. The organic layer was dried and concentrated to give the title product. In some cases the product was purified by chromatography on silica (light petroleum/EtOAc, 8:1).

(*Z*)-1-{1-[Dimethyl(phenyl)silyl]but-1-enylsulfanyl}propan-2-one (1a):[24] Starting from (*Z*)-1-[dimethyl(phenyl)silyl]but-1-enethiol and chloroacetone, **1a** was obtained in 70% yield as a colorless oil.

(*Z*)-1-{1-[Dimethyl(phenyl)silyl]-3-methylbut-1-enylsulfanyl}propan-2-one (1b): Starting from (*Z*)-1-[dimethyl(phenyl)silyl]-3-methylbut-1-enethiol and chloroacetone, **1b** was obtained in 65% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1710 cm^{-1} (CO), 1430 (SiPh), 1230 ($SiMe_2$), 1110 (SiPh). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.45 (s, 6 H, $SiMe_2$), 0.98 (d, *J* = 4.0 Hz, 6 H, 2× CH_3), 2.02 (s, 3 H, CH_3), 3.11 (s, 2 H, CH_2), 3.15−3.35 (m, 1 H, *i*Pr−CH), 6.25 (d, *J* = 8.0 Hz, 1 H, vinylic H), 7.35 (m, 3 H, ArH), 7.55 (m, 2 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = −2.3 ($SiMe_2$), 22.2 (2× CH_3), 27.9 (CH_3), 29.7 (CH), 44.6 (CH_2), 127.8, 129.2, 133.9 (ArCH), 137.7 (C), 160.0 (vinylic CH), 202.9 (CO). − MS; *m*/*z*: 292 [M^+], 135 [$SiMe_2Ph$], 43 [CH_3CO]. − HR-MS: $C_{16}H_{24}OSSi$ calcd. 292.1395 found 292.1397.

(*Z*)-1-[1-(Trimethylsilyl)-3-methylbut-1-enylsulfanyl]propan-2-one (1c): Starting from (*Z*)-1-trimethylsilyl-3-methylbut-1-enethiol and chloroacetone, **1c** was obtained in 98% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1710 cm^{-1} (CO), 1250 ($SiMe_3$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 0.95 (d, *J* = 6.7 Hz, 6 H, 2× CH_3), 2.25 (s, 3 H, CH_3), 3.05−3.23 (m, 1 H, *i*Pr−CH), 3.31 (s, 2 H, CH_2), 6.11 (d, *J* = 9.1 Hz, 1 H, vinylic H). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = −0.7 ($SiMe_3$), 22.3 (2× CH_3), 28.0 (CH_3), 29.6 (CH), 45.0 (CH_2), 130.9 (vinylic C), 158.8 (vinylic CH), 203.2 (CO). − MS; *m*/*z*: 230 [M^+], 215 [$M^+ - CH_3$], 157 [$M^+ - SiMe_3$], 73 [$SiMe_3$], 43 [$(CH_3)_2CH$]. − HR-MS: $C_{11}H_{22}OSSi$ calcd. 230.1161 found 230.1163.

(*Z*)-1-[(2-Phenyl-1-trimethylsilylvinyl)sulfanyl]propan-2-one (1d): Starting from (*Z*)-2-phenyl-1-trimethylsilylethenethiol and chloroacetone, **1d** was obtained in 91% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1725 cm^{-1} (CO), 1250, 840 ($SiMe_3$). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.27 (s, 9 H, $SiMe_3$), 2.05 (s, 3 H, $COCH_3$), 3.25 (s, 2 H, SCH_2), 7.12 (s, 1 H, vinylic H), 7.35 (m, 3 H, ArH), 7.65 (m, 2 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = −1.2 ($SiMe_3$), 28.0 (CH_3), 44.2 (CH_2), 127.7, 128.1, 129.2 (ArCH), 136.3 (ArC), 137.1 (vinylic C), 142.6 (vinylic CH), 202.9 (CO). − MS; *m*/*z*: 264 [M^+], 249 [$M^+ - CH_3$], 191 [$M^+ - SiMe_3$], 175 [$M^+ - SCH_2COCH_3$], 73 [$SiMe_3$]. − HR-MS: $C_{14}H_{20}OSSi$ calcd. 264.1004 found 264.1002.

(3*S*)-3-(Benzyloxy)-1-{[(*Z*)-2-phenyl-1-(trimethylsilyl)vinyl]sulfanyl}butan-2-one (1e): Starting from (*Z*)-1-trimethylsilyl-2-phenylethenethiol and (3*S*)-3-(benzyloxy)-1-chloro-2-butanone, **1e** was obtained in 82% yield as a pale yellow oil. − $[\alpha]_D^{20}$ = −12.0 (*c* = 1.23, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO), 1249 ($SiMe_3$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.40 (s, 9 H, $SiMe_3$), 1.32 (d, *J* = 6.8 Hz, 3 H, CH_3), 3.62 (d, *J* = 15.6 Hz, 1 H, CH_2), 3.70 (d, *J* = 15.6 Hz, 1 H, CH_2), 4.02 (q, *J* = 6.8 Hz, 1 H, CH), 4.5 (dd, J_1 = 13.2 Hz, J_2 = 15.0 Hz, 2 H, CH_2), 7.20 (s, 1 H, vinylic H), 7.32−7.55 (m, 8 H, ArH), 7.75 (m, 2 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = −1.1 ($SiMe_3$), 16.8 (CH_3), 39.7, 71.7 (CH_2), 79.0 (CH), 127.6, 127.8, 128.0, 128.3, 128.5, 129.2 (ArCH), 136.7, 137.1, 137.4 (C), 142.2 (vinylic CH), 206.0 (CO). − MS; *m*/*z*: 384 [M^+], 134 [$PhCH_2OC_2H_4$], 91 [$PhCH_2$], 73 [$SiMe_3$]. − HR-MS: $C_{22}H_{28}O_2SSi$ calcd. 384.1579 found 384.1577.

(3*S*)-3-(Dibenzylamino)-1-{[(*Z*)-2-phenyl-1-(trimethylsilyl)vinyl]sulfanyl}butan-2-one (1f): Starting from (*Z*)-1-trimethylsilyl-2-phenylethenethiol and (3*S*)-1-chloro-3-(dibenzylamino)-2-butanone, **1f** was obtained in 95% yield as a yellow oil. − $[\alpha]_d^{20}$ = −85.7 (*c* = 1.22, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 1713 cm^{-1} (CO), 1249 ($SiMe_3$). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 9 H, $SiMe_3$), 0.95 (d, *J* = 6.6 Hz, 3 H, CH_3), 3.29 (d, *J* = 13.7 Hz, 2 H, 2× H_a-CH_2Ph), 3.35 (q, *J* = 6.6 Hz, 1 H, CH), 3.47 (d, *J* = 14.7 Hz, 1 H, H_aCH_2S) 3.53 (d, *J* = 13.7 Hz, 2 H, 2× H_b-CH_2Ph), 3.63 (d, *J* = 14.7 Hz, 1 H, H_bCH_2S), 6.95 (s, 1 H, vinylic H), 7.25−7.33 (m, 13 H, ArH), 7.65 (m, 2 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = −1.2 ($SiMe_3$), 6.5 (CH_3), 41.5, 54.5 (CH_2), 60.5 (CH), 127.1, 127.5, 128.0, 128.3, 128.7, 129.2 (ArCH), 137.0, 137.3, 138.8 (C), 141.7 (vinylic CH), 206.2 (CO). − MS; *m*/*z*: 473 [M^+], 458 [$M^+ - CH_3$], 445 [$M^+ - CO$], 224 [$M^+ - (PhCH_2)NCHCH_3$], 91 [$PhCH_2$], 73 [$SiMe_3$]. − HR-MS: $C_{29}H_{35}NOSSi$ calcd. 473.2209 found 473.2211.

5-{(*Z*)-1-[Dimethyl(phenyl)silyl]-3-methylbut-1-enylsulfanyl}pentan-2-one (1l): Starting from (*Z*)-1-[dimethyl(phenyl)silyl]-3-methylbut-1-enethiol and 5-chloro-2-pentanone, **1l** was obtained in 54% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO), 1430, 1110 (SiPh). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.45 (s, 6 H, $SiMe_2$), 1.01 (d, *J* = 6.6 Hz, 6 H, 2× CH_3), 1.51−1.68 (m, 2 H, CH_2), 2.04 (s, 3 H, $COCH_3$), 2.25 (t, *J* = 7.3 Hz, 2 H, CH_2), 2.35 (t, *J* = 7.0 Hz, 2 H, CH_2), 3.11−3.28 (m, 1 H, *i*Pr−CH), 6.15 (d, *J* = 9 Hz, 1 H, vinylic H), 7.35 (m, 3 H, ArH), 7.55 (m, 2 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = −2.3 ($SiMe_2$), 22.1 (2× CH_3), 23.7 (CH_2), 29.5 (CH_3), 29.7 (CH), 33.5, 41.9 (CH_2), 127.6, 128.9 (ArCH), 129.9 (ArC), 133.7 (ArCH), 138.3 (vinylic C), 158.0 (vinylic CH), 207.7 (CO). − MS; *m*/*z*: 320 [M^+], 235 [$M^+ - (CH_2)_3COCH_3$], 135 [$SiMe_2Ph$], 85 [$(CH_2)_3COCH_3$]. − HR-MS: $C_{18}H_{28}OSSi$ calcd. 320.1630 found 320.1632.

5-[(*Z*)-1-(Trimethylsilyl)-3-methylbut-1-enylsulfanyl]pentan-2-one (1m): Starting from (*Z*)-1-trimethylsilyl-3-methylbut-1-enethiol and 5-chloro-2-pentanone, **1m** was obtained in 77% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1730 (CO) cm^{-1}, 1250 ($SiMe_3$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 0.93 (d, *J* = 6.7 Hz, 6 H, 2× CH_3), 1.70−1.85 (m, 2 H, CH_2), 2.11 (s, 3 H, CH_3), 2.55 (q, *J* = 7.0 Hz, 4 H, 2× CH_2), 3.02−3.21 (m, 1 H, CH), 6.01 (d, *J* = 8 Hz, 1 H, vinylic H). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 0.9 ($SiMe_3$), 22.0 (2× CH_3), 23.5 (CH_2), 29.2 (CH_3), 29.6 (CH), 33.6, 41.7 (CH_2), 131.7 (vinylic C), 159.4 (vinylic CH), 207.4 (CO). − MS; *m*/*z*: 258 [M^+], 173 [$M^+ - (CH_2)_3COCH_3$], 85 [$(CH_2)_3COCH_3$], 73 [$SiMe_3$], 43 [$(CH_3)_2CH$]. − HR-MS: $C_{13}H_{26}OSSi$ calcd. 258.1474 found 258.1472.

5-[(*Z*)-(2-Phenyl-1-trimethylsilylvinyl)sulfanyl]pentan-2-one (1n): Starting from (*Z*)-2-phenyl-1-trimethylsilylethenethiol and 5-chloro-2-pentanone, **1n** was obtained in 78% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.23 (s, 9 H, $SiMe_3$), 1.67 (m, 2 H, CH_2), 2.03 (s, 3 H, CH_3), 2.35 (t, *J* = 7.3 Hz, 2 H, CH_2), 2.52 (t, *J* = 6.9 Hz, 2 H, CH_2), 7.02 (s, 1 H, vinylic H), 7.15−7.63 (m, 5 H, ArCH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 0.9 ($SiMe_3$), 23.1 (CH_2), 29.7 (CH_3), 33.1, 41.8 (CH_2), 127.2, 127.8, 129.1 (ArCH) 137.4, 137.5 (ArC + vinylic C), 141.0 (vinylic CH), 208.0 (CO). − MS; *m*/*z*: 292 [M^+], 277 [$M^+ - CH_3$], 207 [$M^+ - (CH_2)_3COCH_3$], 85 [$(CH_2)_3COCH_3$], 73 [$SiMe_3$], 43 [CH_3CO]. − HR-MS: $C_{16}H_{24}OSSi$ calcd. 292.1317 found 292.1315.

6-[(*Z*)-(2-Phenyl-1-trimethylsilylvinyl)sulfanyl]hexan-2-one (1o): Starting from (*Z*)-2-phenyl-1-trimethylsilylethenethiol and 6-chloro-2-hexanone, **1o** was obtained in 60% yield as a pale yellow

oil. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.2 (s, 9 H, $SiMe_3$), 1.31−1.50 (m, 4 H, 2× CH_2), 1.96 (s, 3 H, CH_3), 2.21 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.47 (t, *J* = 6.3 Hz, 2 H, CH_2), 6.92 (s, 1 H, vinylic H), 7.08−7.30 (m, 3 H, ArH), 7.54−7.59 (m, 2 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = −0.8 ($SiMe_3$), 22.7, 28.9 (CH_2), 29.7 (CH_3), 33.5, 42.9 (CH_2), 127.2, 127.9, 129.2 (ArCH), 137.7, 137.9 (ArC + vinylic C), 140.1 (vinylic CH), 208.4 (CO). − MS; *m/z*: 306 [M^+], 99 [$(CH_2)_4COCH_3$], 73 [$SiMe_3$]. − HR-MS: $C_{17}H_{26}OSSi$ calcd. 306.1474 found 306.1476.

7-[(*Z*)-(2-Phenyl-1-trimethylsilylvinyl)sulfanyl]heptan-2-one (1p): Starting from (*Z*)-2-phenyl-1-trimethylsilylethenethiol and 7-chloro-2-heptanone, **1p** was obtained in 65% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1725 cm^{-1} (CO). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.22 (s, 9 H, $SiMe_3$), 1.11−1.30 (m, 2 H, CH_2), 1.31−1.48 (m, 4 H, 2× CH_2), 2.06 (s, 3 H, CH_3), 2.31 (t, *J* = 7.3 Hz, 2 H, CH_2), 2.50 (t, *J* = 7.2 Hz, 2 H, CH_2), 6.95 (s, 1 H, vinylic H), 7.13−7.45 (m, 3 H, ArH), 7.53−7.72 (m, 2 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = −0.9 ($SiMe_3$), 23.1, 28.0, 29.2 (CH_2), 29.7 (CH_3), 33.6, 43.3 (CH_2), 127.1, 127.9, 129.1 (ArCH), 137.6, 138.0 (C), 140.0 (vinylic CH), 208.6 (CO). − MS; *m/z*: 320 [M^+], 73 [$SiMe_3$], 43 [CH_3CO]. − HR-MS: $C_{18}H_{28}OSSi$ calcd. 320.1630 found 320.1628.

Synthesis of (*Z*)-α-Silyl Vinyl Sulfides 1. − General Method (Path b): To a solution of (*Z*)-α-silyl enethiol **4** (1.0 mmol) in THF (5 mL) were added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.1 mmol) and the methyl vinyl ketone (1.1 mmol). The mixture was stirred at room temperature until the starting enethiol had disappeared (3 h). The mixture was then quenched with water and extracted with diethyl ether. The organic layer was dried and concentrated to give the title product. The crude products were purified by chromatography on silica (light petroleum/EtOAc, 8:1).

4-{(*Z*)-1-[Dimethyl(phenyl)silyl]but-1-enylsulfanyl}butan-2-one (1g):[24] Starting from (*Z*)-1-[dimethyl(phenyl)silyl]but-1-enethiol, **1g** was obtained in 78% yield as a pale yellow oil.

4-{(*Z*)-1-[Dimethyl(phenyl)silyl]-3-methylbut-1-enylsulfanyl}butan-2-one (1h): Starting from (*Z*)-1-[dimethyl(phenyl)silyl]-3-methylbut-1-enethiol, **1h** was obtained in 45% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO), 1430 (SiPh),1250 ($SiMe_2$), 1110 (SiPh). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.45 (s, 6 H, $SiMe_2$), 1.01 (d, *J* = 5.0 Hz, 6 H, 2× CH_3), 1.95 (s, 3 H, CH_3), 2.35 (m, 2 H, CH_2), 2.68 (m, 2 H, CH_2), 3.05−3.22 (m, 1 H, *i*Pr−CH), 6.15 (d, *J* = 9.0 Hz, 1 H, vinylic H), 7.35 (m, 3 H, ArH), 7.53 (m, 2 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = −1.8 ($SiMe_2$), 22.8 (2× CH_3), 28.6 (CH_2), 30.1 (CH_3), 44.3 (CH_2), 128.3, 129.6 (ArCH), 130.8 (ArC), 134.4 (ArCH), 138.7 (vinylic C), 158.9 (vinylic CH), 207.0 (CO). − MS; *m/z*: 306 [M^+], 235 [M^+ − $CH_2CH_2COCH_3$], 135 [$SiMe_2Ph$], 43 [CH_3CO]. − HR-MS: $C_{17}H_{26}OSSi$ calcd. 306.1474 found 306.1476.

4-[(*Z*)-(3-Methyl-1-trimethylsilyl-1-butenyl)sulfanyl]butan-2-one (1i): Starting from (*Z*)-3-methyl-1-trimethylsilylbut-1-enethiol, **1i** was obtained in 42% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO), 1250 ($SiMe_3$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 0.95 (d, *J* = 6.8 Hz, 6 H, 2× CH_3), 2.15 (s, 3 H, CH_3), 2.61 (m, 2 H, CH_2), 2.75 (m, 2 H, CH_2), 2.98−3.18 (m, 1 H, *i*Pr−CH), 6.05 (d, *J* = 9.0 Hz, 1 H, vinylic H). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 0.7 ($SiMe_3$), 22.3 (2× CH_3), 28.3 (CH_2), 29.5 (CH_3), 30.0 (CH), 43.8 (CH_2), 131.7 (vinylic C), 157.1 (vinylic CH), 206.8 (CO). − MS; *m/z*: 244 [M^+], 173 [M^+ − $CH_2CH_2COCH_3$], 201 [M^+ − $(CH_3)_2CH$], 73 [$SiMe_3$], 43 [$(CH_3)_2CH$]. − HR-MS: $C_{12}H_{24}OSSi$ calcd. 244.1317 found 244.1319.

4-[(*Z*)-(2-Phenyl-1-trimethylsilylvinyl)sulfanyl]butan-2-one (1j): Starting from (*Z*) 2-phenyl-1-trimethylsilylethenethiol, **1j** was obtained in 75% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1730 cm^{-1} (CO). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 9 H, $SiMe_3$), 1.97 (s, 3 H, CH_3), 2.53 (t, *J* = 5.0 Hz, 2 H, CH_2), 2.75 (t, *J* = 5.0 Hz, 2 H, CH_2), 7.00 (s, 1 H, vinylic H), 7.20−7.40 (m, 3 H, ArH), 7.63 (m, 2 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ= 0.3 ($SiMe_3$), 28.1 (CH_2), 30.4 (CH_3), 43.8 (CH_2), 128.0, 128.6, 129.8 (ArCH), 137.9, 138.0, (ArC + vinylic C), 141.5 (vinylic CH), 207.2 (CO). − MS; *m/z*: 278 [M^+], 235 [M^+ − CH_3CO], 221 [M^+ − CH_2COCH_3], 207 [M^+ − $CH_2CH_2COCH_3$], 73 [$SiMe_3$], 43 [CH_3CO]. − HR-MS: $C_{15}H_{22}OSSi$ calcd. 278.1161 found 278.1165.

4-[(*Z*)-(1-Dimethylphenylsilyl-2-phenylvinyl)sulfanyl]butan-2-one (1k): Starting from (*Z*)-1-dimethylphenylsilyl-2-phenylethenethiol, **1k** was obtained in 68% yield as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.59 (s, 6 H, $SiMe_2$), 1.87 (s, 3 H, CH_3), 2.31 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.67 (t, *J* = 7.4 Hz, 2 H, CH_2), 7.12 (s, 1 H, vinylic H), 7.30−7.55 (m, 6 H, ArH), 7.60−7.77 (m, 4 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ= −2.4 ($SiMe_2$), 27.5 (CH_2), 29.5 (CH_3), 43.2 (CH_2), 127.6, 127.8, 128.0, 129.2, 129.3, 133.9 (ArCH), 135.7, 137.3, 137.5 (ArC + vinylic C), 142.4 (vinylic CH), 206.3 (CO). − MS; *m/z*: 340 [M^+], 268 [M^+ − $CH_3CH_2CH_2COCH_3$], 253 [268 − CH_3], 135 [$SiMe_2Ph$]. − HR-MS: $C_{20}H_{24}OSSi$ calcd. 340.1317 found 340.1315.

Desilylation of (*Z*)-α-Silyl Vinyl Sulfides for the Synthesis of Thietanols, Thiolanols, and Thianols. − General Procedure. − Method A: A solution of 1.0 M tetrabutylammonium fluoride (TBAF) in THF (1.2 mmol) was added to a solution of (*Z*)-α-silyl vinyl sulfide **1** (1.0 mmol) in dry THF (2 mL). The reaction mixture was stirred at reflux until complete disappearance of the starting sulfide (2−4 h), then quenched with H_2O and extracted with diethyl ether. The extract was washed several times with aqueous HCl (0.1 M) and with H_2O, then dried with Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^1H NMR and then purified by preparative thick-layer chromatography (light petroleum/EtOAc, 10:1).

Method B: Solid TBAF (1.2 mmol) dried at 40 °C under high vacuum for 48 h[25,26] was dissolved in dry THF (1.2 mL) and added to a solution of (*Z*)-α-silyl vinyl sulfide **1** (1.0 mmol) in dry THF (2 mL). The reaction mixture was stirred at reflux until complete disappearance of the starting sulfide (2−4 h); then for the workup the same procedure as described for method A was followed.

Method C: (*Z*)-α-Silyl vinyl sulfide **1** (1.0 mmol) and tetrabutylammonium difluorotriphenylstannate[27] ($Bu_4NPh_3SnF_2$) (1.5 mmol) were dissolved in THF (3 mL). The reaction mixture was stirred at reflux until complete disappearance of the starting sulfide (30−48 h). The same workup procedure as described for method A was followed.

3-Methyl-2-[(*Z*)-propylidene]-3-thietanol (3a):[24] Following method A, **1a** gave **3a** in 80% yield as a colorless oil.

3-Methyl-2-[(*Z*)-2-methylpropylidene]-3-thietanol (3b): Following method A, **1b** gave **3b** in 76% yield as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 3400 cm^{-1} (OH). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.01 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 2.06−2.24 (m, 1 H, *i*Pr-CH), 2.50 (s, 1 H, OH), 3.15 (d, *J* = 9.0 Hz, 1 H, H_aCH), 3.34 (d, *J* = 9.0 Hz, 1 H, H_bCH),

5.47 (d, J = 8.4 Hz, 1 H, vinylic H). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 22.7, 22.8, 27.4 (CH_3), 28.4 (CH), 42.5 (CH_2), 82.1 (COH), 124.4 (vinylic CH), 143.8 (vinylic C). − MS; *m/z*: 158 [M^+], 143 [$M^+ - CH_3$], 58 [CH_3COCH_3], 43 [$(CH_3)_2CH$]. − HR-MS: $C_8H_{14}OS$ calcd. 158.0765 found 158.0762. Following method A, **1c** gave **3b** in 80% yield.

In both cases **8a** was obtained as by-product in about 5% yield as a mixture of (*E*) and (*Z*) isomers. − **8a**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.02 (2d, J = 6.7 Hz, 6 H, 2× CH_3), 1.65 (2d, J = 6.7 Hz, 6 H, 2× CH_3), 2.10−2.40 (m, 1 H, *i*Pr−CH), 2.55−2.70 (m, 1 H, *i*Pr-CH), 5.2 (m, 1 H, vinylic H), 5.7 (m, 1 H, vinylic H). − MS; *m/z*: 200 [M^+], 185 [$M^+ - CH_3$], 170 [$M^+ - 2\times CH_3$].

3-Methyl-2-[(*Z*)-phenylmethylidene]-3-thietanol (3c): Following method A, **1d** gave **3c** in 86% yield as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 3500 br. s (OH) cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (s, 3 H, CH_3), 2.90 (br. s, 1 H, OH), 3.40 (d, J = 9.2 Hz, 1 H, H_a-CH_2), 3.60 (d, J = 9.2 Hz, 1 H, H_b-CH_2), 6.60 (s, 1 H, vinylic H), 7.20−7.41 (m, 5 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 27.1 (CH_3), 45.1 (CH_2), 82.3 (C), 116.3 (vinylic CH), 126.4, 127.53, 128.54 (ArCH), 136.1, 147.3 (C). − MS; *m/z*: 192 [M^+], 177 [$M^+ - CH_3$], 149 [$M^+ - COCH_3$], 134 [PhCHCS], 59 [C_3H_6OH]. − HR-MS: $C_{11}H_{12}OS$ calcd. 192.0609 found 192.0608.

In some cases **8b** was obtained as a by-product in about 5% yield as a solid mixture of *E* and *Z* isomers. − m.p. 190−195 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.45 (s, 2 H, vinylic H), 6.62 (s, 2 H, vinylic H), 7.2−7.5 (m, 20 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 111.7, 111.8, 113.2, 113.7, (vinylic CH), 125.6, 126.21, 126.25, 126.6, 128.3, 128.4, 128.5, 128.9 (ArCH), 134.0, 136.8 (ArC). − MS; *m/z*: 268 [M^+], 234 [$M^+ - H_2S$], 134 [PhCHCS]. − UV ($CHCl_3$): λ_{max} (ε) = 350 nm (25120). Product **8b** was compared with an authentic sample prepared according to the procedure reported in the literature.[28,29]

3-[(1*S*)-1-(Benzyloxy)ethyl]-2-[(*Z*)-phenylmethylidene]-3-thietanol (3d): Product **1e** was desilylated according to method A at room temperature. The crude reaction mixture was analyzed by ^{1}H- and ^{13}C NMR and showed the presence of two diastereoisomers in a 1.3:1 ratio (*de* = 13%). The crude mixture was then filtered to give **8b** (18%) as a yellow solid. The filtrate was purified by chromatography (light petroleum/EtOAc, 10:1), to yield, as the higher R_f product, 3-benzyloxy-2-butanone **9a**[33] in 18% yield and, as the lower R_f product, **3d** as a mixture of diastereoisomers in 55% yield as a yellow oil. **3d:** − IR (CCl_4): $\tilde{\nu}$ = 3550 cm^{-1} (OH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (d, J = 6.2 Hz, 3 H, CH_3 major), 1.39 (d, J = 6.2 Hz, 3 H, CH_3 minor), 3.38−3.58 (2m, 4 H, 2× CH_2 major + minor), 3.78 (q, J = 6.2 Hz, 1 H, CH minor), 3.82 (q, J = 6.2 Hz, 1 H, CH major), 4.50 (d, J = 11.4 Hz, 2 H, 2× CH−O), 4.70 (d, J = 11.4 Hz, 1 H, 1× CH−O), 4.74 (d, J = 11.4 Hz, 1 H, 1× CH−O), 6.62 (s, 1 H, vinylic H major), 6.64 (s, 1 H, vinylic H minor), 7.3−7.6 (m, 10 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 13.2 (CH_3 major), 13.8 (CH_3 minor), 38.1 (CH_2 minor), 40.4 (CH_2 major), 71.4 (CH_2 minor), 71.8 (CH_2 major), 78.2 (CH major), 78.6 (CH minor), 85.59 (C major), 85.60 (C minor), 118.2 (vinylic CH minor), 118.8 (vinylic CH major), 126.4, 127.6, 127.9, 128.0, 128.5 (ArCH), 136.2, 136.3, 137.9, 142.1, 142.4 (C). − MS; *m/z*: 312 [M^+], 177 [$M^+ - CH(CH_3)OBzl$], 159 [177 − H_2O], 91 [C_7H_7]. − HR-MS: $C_{19}H_{20}O_2S$ calcd. 312.1184 found 312.1181.

(3*R*)-3-[(1*S*)-1-(Dibenzylamino)ethyl]-2-[(*Z*)-phenylmethylidene]-3-thietanol (3e): The crude reaction mixture obtained by desilylation (method A) of **1f** was analyzed by ^{1}H- and ^{13}C NMR and showed the presence of a single diastereoisomer (*de* > 98%). The crude mixture was then filtered to give **8b** (14%) as a yellow solid. The filtate was purified by chromatography (light petroleum/EtOAc, 10:1), to yield, as the higher R_f product, 3-dibenzylamino-2-butanone **9b**[34] in 15% yield and, as the lower R_f product, **3e** in 30% yield as a yellow oil. **3e:** $[\alpha]_d^{20}$ = +69.3 (c = 1.01, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3589 cm^{-1} (OH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (d, J = 6.9 Hz, 3 H, CH_3), 3.01 (q, J = 6.9 Hz, 1 H, CH), 3.10 (br. s, 1 H, OH), 3.23 (d, J = 8.8 Hz, 1 H, H_a-CH_2S), 3.36 (d, J = 13.5 Hz, 2 H, 2× H_a-CH_2Ph), 3.56 (d, J = 8.8 Hz, 1 H, H_b-CH_2S), 4.05 (d, J = 13.5 Hz, 2 H, 2× H_b-CH_2Ph), 6.61 (s, 1 H, vinylic H), 7.02−7.41 (m, 15 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 7.0 (CH_3), 42.7, 55.5 (CH_2), 59.4 (CH), 85.7 (C), 118.4 (vinylic CH), 126.2, 127.6, 127.3, 127.6, 128.4, 128.5, 128.9 (ArCH), 136.09, 139.11, 145.6 (C). − MS; *m/z*: 401 [M^+], 224 [M^+ − PhCH=CSCH$_2$COH], 210 [224 − CH_2], 91 [C_7H_7]. − HR-MS: $C_{26}H_{27}NOS$ calcd. 401.1813 found 401.1815.

3-Methyl-2-[(*Z*)-phenylmethylidene]-3-thiolanol (6a): Following method A, **1j** gave **6a** in 55% yield as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 3610 cm^{-1} (OH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58 (s, 3 H, CH_3), 1.94 (br. s, 1 H, OH), 2.03−2.22 (m, 2 H, CH_2), 2.98−3.06 (m, 2 H, CH_2), 3.16−3.26 (m, 2 H, CH_2), 6.65 (s, 1 H, vinylic H), 7.17−7.62 (m, 5 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 26.1 (CH_3), 29.2, 42.7 (CH_2), 82.5 (C), 116.9 (vinylic CH), 126.5, 128.2, 128.4 (ArCH), 136.9 (ArC), 146.3 (vinylic C). − MS; *m/z*: 206 [M^+], 191 [$M^+ - CH_3$], 188 [$M^+ - H_2O$], 173 [$M^+ - SH$], 163 [$M^+ - COCH_3$], 129 [$M^+ - C_6H_5$], 77 [C_6H_5], 43 [$COCH_3$]. − HR-MS: $C_{12}H_{14}OS$ calcd. 206.0765 found 206.0768. With the same procedure, **1k** gave **6a** in 35% yield as a colorless oil.

4-[(1-Phenylbutyl)sulfanyl]-2-butanone (11a):[24] The desilylation of **1g** by method A gave **11a** in 48% yield as a colorless oil.

4-[(3-Methyl-1-phenylbutyl)sulfanyl]-2-butanone (11b): The desilylation of **1h** by method A gave **11b** in 60% yield as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 1725 cm^{-1} (CO). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 6 H, 2× CH_3), 1.20−1.80 (m, 4 H, 2× CH_2), 2.40−2.55 (m, 2 H, CH_2), 2.05 (s, 3 H, $COCH_3$), 3.75 (m, 1 H, *i*Pr-CH), 3.85 (dd, J_1 = J_2 = 7.5 Hz, 1 H, CH), 7.20−7.40 (m, 5 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 22.0, 22.8 (3× CH_3), 24.8 (CH_2), 25.7 (CH), 29.9 (CH_3), 43.4, 45.4 (CH_2), 48.2 (CHPh), 127.1, 127.8, 128.5 (ArCH), 142.8 (ArC), 206.9 (CO) − MS; *m/z*: 250 [M^+], 207 [$M^+ - (CH_3)_2CH$], 193 [$M^+ - CH_2COCH_3$], 179 [$M^+ - (CH_2)_2COCH_3$], 103 [$S(CH_2)_2COCH_3$], 71 [$(CH_2)_2COCH_3$], 43 [$(CH_3)_2CH$]. − HR-MS: $C_{15}H_{22}OS$ calcd. 250.1391 found 250.1396.

4-[(1,3-Dimethylbutyl)sulfanyl]-2-butanone (11c): The desilylation of **1i** by method A gave **11c** in 40% yield as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (2d, J = 6.3 Hz, 6 H, 2× CH_3), 1.21 (d, J = 6.2 Hz, 3 H, CH_3), 1.30−1.45 (m, 2 H, CH_2), 1.75 (m, 1 H, CH), 2.13 (s, 3 H, $COCH_3$), 2.65 (m, 5 H, 2× CH_2, 1× CH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.6, 22.3, 22.6 (CH_3), 23.7 (CH_2), 22.5 (CH), 30.1 (CH_3), 38.2 (CH), 43.8, 46.2 (CH_2), 207.0 (CO). − MS; *m/z*: 188 [M^+], 145 [$M^+ - CH(CH_3)_2$], 131 [$M^+ - CH_2COCH_3$], 117 [$M^+ - (CH_2)_2COCH_3$], 57 [CH_2COCH_3], 43 [$CH(CH_3)_2$]. − HR-MS: $C_{10}H_{20}OS$ calcd. 188.1235 found 188.1237.

3-Methyl-2-[(*Z*)-2-methylpropylidene]tetrahydro-2*H*-thiopyran-3-ol (7a): Following method B, **1m** gave, after chromatography (light petroleum/EtOAc, 5:1), **7a** as the higher R_f fraction in 73% yield as a colorless oil and, as the second R_f fraction, **2b** in 27% yield as a colorless oil. − **7a**: IR (CCl_4): $\tilde{\nu}$ = 3610 cm^{-1} (OH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (2d, J = 8.5 Hz, 6 H, 2× CH_3), 1.45

(s, 3 H, CH_3), 1.60−1.75 (m, 2 H, CH_2), 1.85−2.20 (m, 2 H, CH_2), 2.50 (br. s, 1 H, OH), 2.58 (t, J = 8.7 Hz, 2 H, CH_2), 2.80−2.95 (m, 1 H, *i*Pr-CH), 5.75 (d, J = 9.0 Hz, 1 H, vinylic H). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 22.7 (2× CH_3), 24.8 (CH_2), 27.4 (CH_3), 28.4 (CH), 30.8 (CH_2), 41.4 (CH_2), 70.7 (COH), 135.4 (vinylic CH), 136.1 (vinylic C). − MS; *m*/*z*: 186 [M^+], 168 [$M^+ - H_2O$], 153 [M^+ − SH], 143 [$M^+ - CH(CH_3)_2$], 43 [$CH(CH_3)_2$]. − HR-MS: $C_{10}H_{18}OS$ calcd. 186.1078 found 186.1076.

2b: IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95 (d, J = 6.5 Hz, 6 H, 2× CH_3), 1.79−1.91 (m, 2 H, CH_2), 2.15 (s, 3 H, CH_3), 2.58 (t, J = 7.1 Hz, 2 H, CH_2), 2.66 (t, J = 7.0 Hz, 2 H, CH_2), 2.60 (m, 1 H, *i*Pr-CH), 5.42 (dd, J_1 = J_2 = 9.2 Hz, 1 H, vinylic H), 5.76 (dd, J_1 = 9.3 Hz, J_2 = 0.8 Hz, 1 H, vinylic SCH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 22.2 (2× CH_3), 23.8 (CH_2), 28.7 (CH), 30.0 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 122.0 (vinylic CH), 137.4 (vinylic CH), 208.0 (CO). − MS; *m*/*z*: 188 [M^+], 117 [$M^+ - (CH_2)_2COCH_3$], 85 [$(CH_2)_3COCH_3$], 71 [$(CH_2)_2COCH_3$], 43 [$CH(CH_3)_2$]. − HR-MS: $C_{10}H_{18}OS$ calcd. 186.1078 found 186.1072.

With procedure B, **1l** gave **7a** in 55% yield and **2b** in 45% yield. Following procedure C, **1m** gave **7a** in 70% yield and **2b** in 15% yield. Following method C, **1l** was recovered unchanged.

3-Methyl-2-[(*Z*)-phenylmethylidene]tetrahydro-2*H*-thiopyran-3-ol (7b): Following method B, **1n** gave, after chromatography (light petroleum/EtOAc, 5:1), **7b** as the higher R_f fraction in 78% yield as a colorless oil and, as the second R_f fraction, **2c** in 22% yield as a colorless oil. − **7b**: IR (CCl_4): $\tilde{\nu}$ = 3610 cm^{-1} bs (OH). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.65 (s, 3 H, CH_3), 1.75−1.90 (m, 2 H, CH_2), 2.01−2.25 (m, 2 H, CH_2), 2.40 (br. s, 1 H, OH), 2.62−2.73 (m, 2 H, CH_2) 7.11 (s, 1 H, vinylic H), 7.20−7.60 (m, 5 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 24.9 (CH_2), 28.3 (CH_3), 30.8, 41.5 (CH_2), 71.9 (C), 126.1, 127.1 127.8, 129.6 (3 ArCH + vinylic CH), 136.4, 140.4 (ArC + vinylic C). − MS; *m*/*z*: 220 [M^+], 202 [$M^+ - H_2O$], 134 [$M^+ - CH_3CH_2CH_2COCH_3$]. − HR-MS: $C_{13}H_{16}OS$ calcd. 220.0922 found 220.0925.

2c: IR (CCl_4): $\tilde{\nu}$ = 1730 cm^{-1} (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.96 (m, 2 H, CH_2), 2.15 (s, 3 H, CH_3), 2.61 (t, J = 7.0 Hz, 2 H, CH_2CO), 2.82 (t, J = 6.9 Hz, 2 H, CH_2S), 6.21(d, J = 11.0 Hz, 1 H, vinylic H), 6.47 (d, J = 11.0 Hz, 1 H, vinylic SCH), 7.15−7.51 (m, 5 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 23.8 (CH_2), 30.0 (CH_3), 35.0, 41.5 (CH_2), 126.0, 126.7, 126.9, 128.2, 128.6, (3 ArCH + 2 vinylic CH), 136.9 (ArC), 207.6 (CO). − MS; *m*/*z*: 220 [M^+], 135 [$M^+ - (CH_2)_3COCH_3$], 85 [$(CH_2)_3COCH_3$], 43 [$COCH_3$]. − HR-MS: $C_{13}H_{16}OS$ calcd. 220.0922 found 220.0920. Following the procedure C, **1n** gave **7b** in 76% yield and **2c** in 20% yield.

6-[(*Z*)-2-Phenylvinyl]sulfanyl-2-hexanone (2d): Following procedure B, **1o** gave, after chromatography (light petroleum/EtOAc, 5:1), **2d** as a colorless oil in 53% yield. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.66−1.74 (m, 4 H, 2× CH_2), 2.13 (s, 3 H, CH_3), 2.42−2.50 (m, 2 H, CH_2), 2.74−2.83 (m, 2 H, CH_2), 6.21 (d, J = 11.0 Hz, 1 H, vinylic H), 6.42 (d, J = 11.0 Hz, 1 H, vinylic H), 7.1−7.5 (m, 5 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 22.5, 29.6 (CH_2), 29.7 (CH_3), 35.5, 43.0 (CH_2), 125.5, 126.6, 127.2, 128.1, 128.5 (3 ArCH + 2 vinylic CH), 134.0, 137.2 (C), 208.1 (CO). − MS; *m*/*z*: 234 [M^+], 135 [$M^+ - (CH_2)_4COCH_3$], 99 [$(CH_2)_4COCH_3$], 77 [C_6H_5], 71 [$(CH_2)_2COCH_3$]. − HR-MS: $C_{14}H_{18}OS$ calcd. 234.1078 found 234.1075.

7-[(*Z*)-2-Phenylvinyl]sulfanyl-2-heptanone (2e): Following method B, **1p** gave, after chromatography (light petroleum/EtOAc, 5:1), **2e** as a colorless oil in 91%. − IR (CCl_4): $\tilde{\nu}$ = 1720 cm^{-1} (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.42 (m, 2 H, CH_2), 1.55 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 2.11 (s, 3 H, CH_3CO), 2.45 (t, J = 7.0 Hz, 2 H, CH_2), 2.75 (t, J = 7.2 Hz, 2 H, CH_2), 6.20 (d, J = 11.0 Hz, 1 H, vinylic H), 6.45 (d, J = 11.0 Hz, 1 H, vinylic H), 7.12−7.58 (m, 5 H, ArH). − ^{13}C NMR (50.28 MHz, $CDCl_3$): δ = 23.1, 27.8 (CH_2), 29.7 (CH_3), 29.8, 35.5, 43.3 (CH_2), 125.3, 126.5, 127.4 128.1, 128.5 (3 ArCH + 2 vinylic CH), 136.9 (ArC), 208.6 (CO). − MS; *m*/*z*: 248 [M^+], 149 [$M^+ - (CH_2)_4COCH_3$], 135 [$M^+ - (CH_2)_5COCH_3$], 77 [C_6H_5], 43 [CH_3CO]. − HR-MS: $C_{15}H_{20}OS$ calcd. 248.1235 found 248.1239.

General Procedure for the Oxidation of Thietanols and Thiolanols to the Corresponding Sulfones: To a solution of the cyclic sulfides (**3c**, **7a**, **3e**) (1.0 mmol) in methanol (6 mL) cooled to 0 °C was added a solution of oxone® (3.0 mmol) in water (6 mL). The mixture was allowed to warm to room temperature and after 5 h was diluted with water and extracted with chloroform. The organic layer was dried and concentrated under reduced pressure to give the corresponding sulfone.

3-Hydroxy-3-methyl-2-[(*Z*)-phenylmethylidene]-1λ⁶-thietane-1,1-dione (12): Yield 90% − m.p. 112−114 °C. − IR (CCl_4): $\tilde{\nu}$ = 1110, 1310 cm^{-1} (SO_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH_3), 2.30 (br. s, 1 H, OH), 4.08 (dd, J_1 = J_2 = 13.7 Hz, 2 H, CH_2), 6.84 (s, 1 H, vinylic H), 7.41 (m, 3 H, ArH), 7.65 (m, 2 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 27.5 (CH_3), 65.5 (CH_2), 75.7 (COH), 129.2, 129.6, 131.0, 132.7, (3× ArCH + vinylic CH), 131.2 (ArC), 156.0 (vinylic C). − MS; *m*/*z*: 224 [M^+], 207 [M^+ − OH], 91 [C_7H_7]. − $C_{11}H_{12}O_3S$ (224.0507): calcd. C, 74.97 H, 6.87 S, 18.16 found C, 74.99 H, 6.83 S, 18.18.

4-Hydroxy-4-methyl-5-[(*Z*)-phenylmethylidene]dihydro-1*H*-1λ⁶-thiophene-1,1(2*H*)-dione (13): Yield 70% − m.p. 115−117 °C − IR (CCl_4): $\tilde{\nu}$ = 1130, 1300 cm^{-1} (SO_2), 3590 (OH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s, 3 H, CH_3), 2.31 (m, 3 H, OH + CH_2), 3.12 (m, 1 H, H_aCH_2), 3.40 (m, 1 H, H_bCH_2), 7.05 (s, 1 H, vinylic H), 7.40 (m, 3 H, ArH), 7.60 (m, 2 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 28.2 (CH_3), 35.2, 49.6 (CH_2), 75.2 (COH), 128.6, 130.2, 130.4, 134.1, (3× ArCH + vinylic CH), 131.7 (ArC), 144.0 (vinylic C). − MS; *m*/*z*: 238 [M^+], 223 [$M^+ - CH_3$], 146 [$M^+ - C_2H_4SO_2$], 91 [C_7H_7]. − $C_{12}H_{14}O_3S$ (238.0664): calcd. C, 75.76 H, 7.42 S, 16.82 found C, 75.72 H, 7.44 S, 16.84.

(3*R*)-3-[(1*S*)-1-(Dibenzylamino)ethyl]-3-hydroxy-2-[(*Z*)-phenylmethylidene]-1λ⁶-thietane-1,1-dione (14): Yield 85% − Colorless solid − m.p. 121−124 °C − IR (CCl_4): $\tilde{\nu}$ = 1150, 1300 cm^{-1} (SO_2), 3480 (OH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, J = 6.9 Hz, 3 H, CH_3), 3.05 (q, J = 6.9 Hz, 1 H, CH), 3.33 (d, J = 13.7 Hz, 2 H, 2× H_a-CH_2Ph), 4.03 (m, 4 H, 2× H_b-CH_2Ph + CH_2S), 4.20 (br. s, 1 H, OH), 6.82 (s, 1 H, vinylic H), 7.22−7.40 (m, 13 H, ArH), 7.53 (m, 2 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 6.6 (CH_3), 55.5 (CH_2), 59.6 (CH), 71.3 (COH), 72.6 (CH), 127.4, 128.6, 128.9, 129.5, 130.7, 134.2, 138.8 (6× ArCH + vinylic CH), 131.4 (ArC), 154.9 (vinylic C). − MS; *m*/*z*: 433 [M^+], 353 [M^+ − SO_3], 91 [C_7H_7]. − $C_{26}H_{27}NO_3S$ (433.1712): calcd. C, 81.00 H, 7.06 N, 3.64 S, 8.30 found C, 80.89 H, 7.10 N, 3.60 S, 8.41. Suitable crystals for X-ray diffraction analysis were grown from diethyl ether − pentane: the product crystallized as colorless thin needles.

3-Methyl-2-[(*Z*)-phenylmethylidene]-3-thietanyl Acetate (15): To a solution of **3c** (0.15 g, 0.78 mmol) in pyridine (2 mL) were added 4-(dimethylamino)pyridine (DMAP) (0.19 g, 1.56 mmol) and acetic anhydride (0.15 mL, 1.56 mmol). After 12 h the mixture was diluted with diethyl ether, the organic layer was separated and washed with aqueous HCl (1 M) and 10% $NaHCO_3$ solution, then dried

over Na_2SO_4. After evaporation of the solvent in vacuo **15** was obtained in 43% as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 1740 cm^{-1} (CO). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.89 (d, *J* = 0.7 Hz, 3 H, CH_3), 2.11 (s, 3 H, CH_3CO), 3.55 (d, *J* = 9.7 Hz, 1 H, H_aCH), 3.98 (d, *J* = 9.7 Hz, 1 H, H_bCH), 6.72 (s, 1 H, vinylic H), 7.15−7.40 (m, 5 H, ArH). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.7 (CH_3), 24.7 (CH_3), 41.4 (CH_2), 86.6 (C), 117.6 (vinylic CH), 126.4, 127.5, 128.5 (ArCH), 136.0, 141.2 (ArC + vinylic C), 169.5 (CO). − MS; *m/z*: 234 [M^+], 174 [M^+ − AcOH], 59 [AcO]. − HR-MS: $C_{13}H_{14}O_2S$ calcd. 234.07145 found 234.07146.

3-Methyl-2-[(*Z*)-phenylmethylidene]tetrahydro-2*H*-thiopyran-3-yl Acetate (16): To a solution of **7b** (0.1 g, 0.45 mmol) in pyridine (1 mL) were added 4-(dimethylamino)pyridine (DMAP) (0.1 g, 0.9 mmol) and acetic anhydride (0.09 mL, 0.9 mmol). After 12 h the mixture was diluted with diethyl ether, the organic layer was separated and washed with aqueous HCl (1 M) and 10% $NaHCO_3$ solution, then dried over Na_2SO_4. The crude reaction mixture was purified by preparative TLC (light petroleum/Et_2O 10:1) to furnish 70 mg of **16** (60%) and 32 mg of 3-methyl-2-[(*Z*)-phenylmethylidene]-5,6-dihydro-2*H*-thiopyran (**17**) (35%). Compound **16** was converted quantitatively into **17** by treating with HCl dissolved in diethyl ether. **16:** ^1H NMR (200 MHz, $CDCl_3$): δ = 1.84 (s, 3 H, CH_3), 1.85−2.00 (m, 2 H, CH_2), 2.11−2.28 (m, 2 H, CH_2), 2.08 (s, 3 H, CH_3CO), 2.65 (m, 2 H, CH_2), 6.90 (1 H, s, vinylic H), 7.15−7.55 (m, 5 H, ArH). **17**: ^1H NMR (200 MHz, $CDCl_3$): δ = 2.1 (s, 3 H, CH_3), 2.50 (m, 2 H, CH_2), 2.78 (t, *J* = 5.0 Hz, 2 H, CH_2), 5.89 (t, *J* = 3.8 Hz, 1 H, vinylic H), 6.70 (s, 1 H, vinylic H), 7.22−7.61 (m, 5 H, ArH). − MS; *m/z*: 202 [M^+], 77 [C_6H_5]. − HR-MS: $C_{13}H_{14}S$ calcd. 202.0816 found 202.0813.

Acknowledgments

Thanks are due to Dr. Cristina Femoni, University of Bologna, for providing the X-ray diffraction structure. Financial support was received from MURST (national project "Stereoselection in Organic Synthesis 1999").

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Received December 9, 1999
[O99681]