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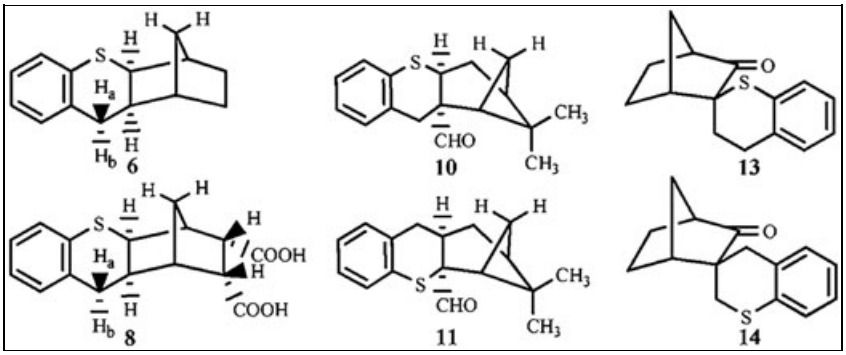

The reaction of benzothiete (**1**) and the bicyclic alkenes **5**, **7**, **9**, or **12** shows a very high π side selectivity (de > 95%) in the formation of the polycyclic thiopyrans **6**, **8**, **10**, **11**, **13**, and **14**.

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INTRODUCTION

Thiochromans (3,4-dihydro-2*H*-1-benzothiopyrans) exhibit various important biological and pharmacological activities [1–10]. An efficient and versatile mode of their preparation makes use of the cycloaddition of benzothiete (**1**) and alkenes **2** (Scheme 1) [11–14]. Thermal or photochemical opening of the four-membered ring in **1** generates the highly reactive *o*-thiobenzoquinonemethide valence isomer **1′**. In the presence of alkenes **2**, competitive cycloadditions, an [8π + 2π] reaction **1′** + **2** → **3**, and a dimerization **1′** + **1/1′** → **4** take place. The yield of **3** depends on the reactivity of **2**. The lower the reactivity of **2** is, the higher is the portion of **4**. However, the portion of **4** is not completely lost. According to Scheme 1, **4** can be reverted to **1** by flash vacuum pyrolysis (FVP).

Because of the different length of the exocyclic CS and CC bond in **1′** and the polarity of **1′**, concerted cycloadditions are less likely. The generation of **3** is only stereoselective, if trans-configured alkenes are used. The retention of the *cis* configuration can be very low [13]. The unsymmetrical transition state of the cycloaddition resembles a biradicaloid with a weakly polar character [15].

Now, we report here on our studies of the reaction of **1/1′** and bicyclic alkenes, which exhibit π side selectivity.

RESULTS AND DISCUSSION

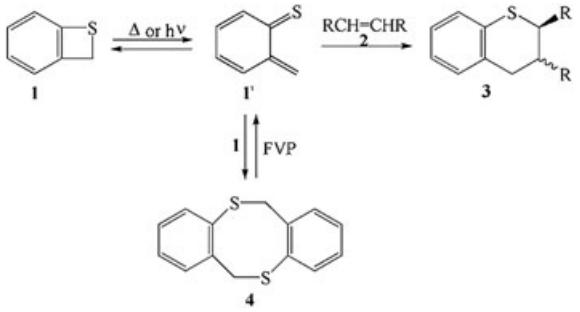
The thermal reaction of **1** in boiling toluene in the presence of norbornene (**5**) yielded 83% cycloadduct **6** as racemate. The intermediate **1′** attacked selectively on the exo side of **5** (Scheme 2). An analogous π side selectivity was observed in the reaction of **1** and bicyclo-[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylic acid anhydride (**7**), the Diels–Alder adduct of cyclopentadiene and maleic acid anhydride. Hydrolysis of the anhydride function in the primary cycloadduct gave the dicarboxylic acid **8** as racemate (yield 71%).

The exo attack of **1′** on **5** and **7** could be established by the trans position of 4a-H and 9a-H to the methano bridge C-1−C-11–C-4. The anti proton 11-H shows in **6** and **8** NOEs to the exo-standing protons 2-H and 3-H, the geminal syn-proton 11-H does not show an NOE to 4a-H and 9a-H in **6** and **8**. Very typical is also the small coupling between 4-H and 4a-H (^3J < 1.0 Hz) and the large W coupling between 4a-H and anti-11-H ($|^4J|$ = 1.5 Hz).

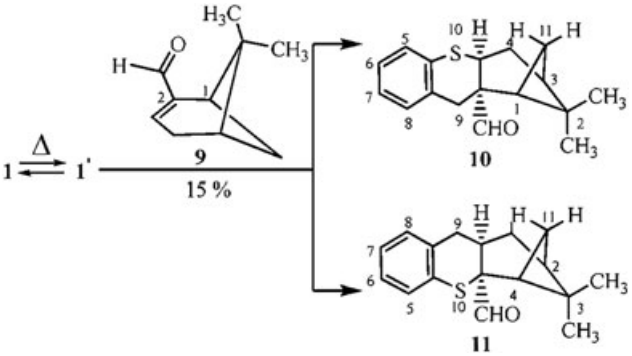
The reactivity of (−)-myrtenal [(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde] (**9**) is low, so that dimer **4** was the major product in the reaction of **1/1′** and **9**. Scheme 3 shows two regioisomeric products **10** and **11** obtained from **1** and **9**. (−)-Myrtenal adds in a strict π side selection (C-2:si, C-3:si), which is based on steric effects, but the cycloaddition is not regioselective (**10**:**11** = 1:1).

The isomers **10** and **11** can be easily distinguished by the AB spin system of 9-H in **10** and the more complicated spin pattern of the geminal 9-H protons in **11**, which exhibit an additional coupling to 9a-H. The configuration of **10** and **11** could be established by the

Scheme 1



Scheme 3



NOE of the aldehyde proton CHO to the endo-methyl group. Figure 1 shows the details of the ^{1}H NMR characterization of the configurations of **10** and **11**, which were studied by one- and two-dimensional NMR techniques (NOE, COSY-45, and HMQC).

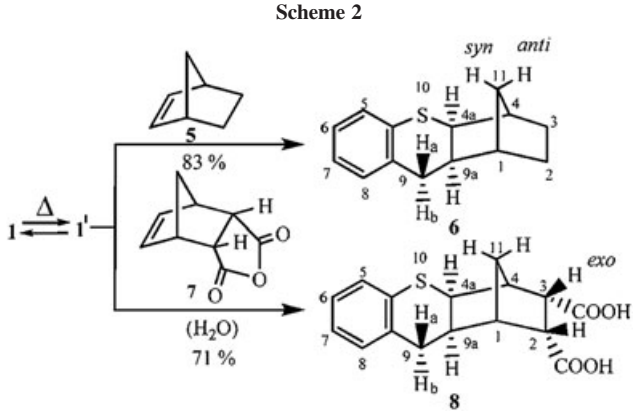
In addition to our studies of reactions of **5**, **7**, and **9**, which have endocyclic CC double bonds, we investigated the behavior of the exocyclic CC double bond in 3-methylene-2-norbornanone (**12**). As found for the attack of **1/1′** on **5**, **7**, and **9**, compound **12** was stereoselectively attacked from the exo side (de $>$ 95%). However, the yield (8%) was very low; dimer **4** was again the major product. The ratio of the regioisomers **13** and **14** was 1:1 (Scheme 4).

The regioisomers **13** and **14** show in the aliphatic region of the ^{1}H NMR spectra an ABCD pattern for 3-H and 4-H in **13**, and two separate AB patterns for 2-H and 4-H in **14**. The identification of the patterns was based on INDOR and NOE measurements. The crystal structure analysis of **14** confirmed the configuration obtained by the exo attack of **1/1′** on **12** (Figs. 2 and 3).

The most interesting structure data of **14** concern the central thiopyran ring. Its molecular parameters are listed in Table 1. The six-membered heterocyclic ring adopts a half-chair conformation in the solid state, which is also presumed for the solution in $CDCl_3$. The very large W-type coupling ($|^4J|$ = 2.7 Hz) between the pseudoequatorial protons 2-H (δ = 2.53) and 4-H proton (δ = 2.69) provides a strong hint for this conformation.

In summary, we can make the statement that benzothiete (**1/1′**) reacts highly diastereoselectively with the bicyclic alkenes **5**, **7**, **9**, and **12** [16]. The exo attack guarantees in all four cases a π side selectivity with a de $>$ 95%, because we could not find any configuration resulting from an endo attack in the ^{1}H and ^{13}C NMR raw spectra. The nonsymmetrical alkenes **9** and **12** give regioisomeric cycloadducts in a 1:1 ratio, each. However, the reactivity of **9** and **12** is low in comparison to that of **5** and **7**. In such cases, the *o*-thiobenzoquinonemethide

Scheme 2



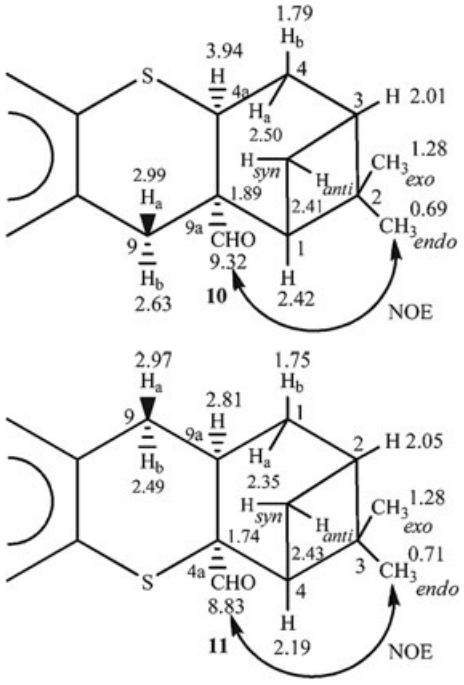
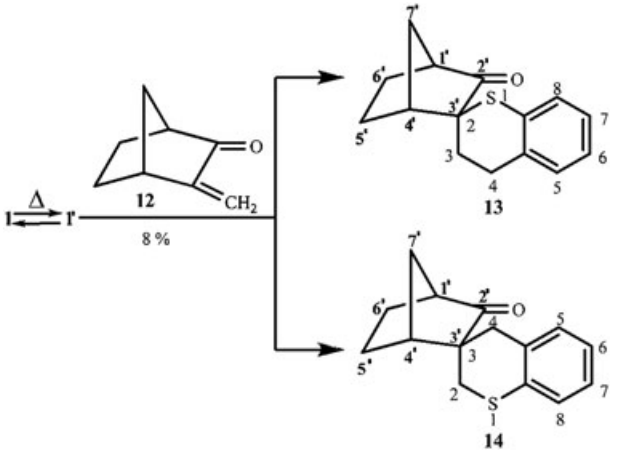


Figure 1. ^{1}H NMR chemical shifts (aliphatic region) of **10** and **11**.

Scheme 4



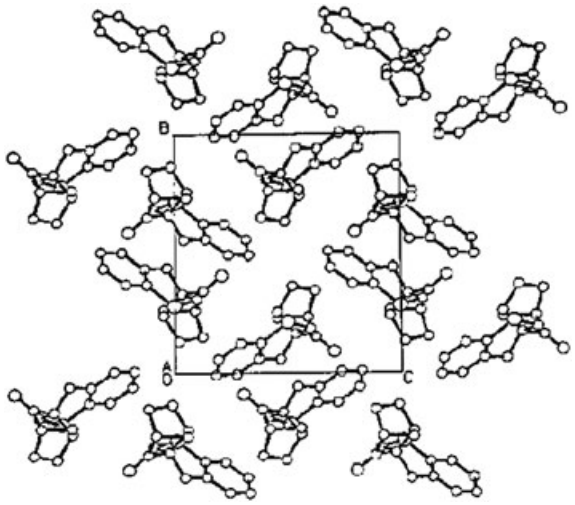


Figure 3. Arrangement of **14** in the elementary cell.

(**1′**), obtained by thermal ring opening of **1**, exhibits a dimerization to **4** as major process. Starting compound **1** can be recovered from **4** by FVP. Here, the discussed diastereoselective cycloaddition reactions represent an interesting contribution to the versatile applications of benzothiete (**1**) in hetereocyclic synthesis [17,18].

EXPERIMENTAL

Melting points were measured with a Büchi melting point apparatus and uncorrected. NMR spectra were obtained on Bruker AMX 400 and Avance 600 spectrometers. Mass spectra were recorded on a Finnigan MS 95 spectrometer.

The starting compounds **5**, **7**, **9**, and **12** are commercially available, **1** was prepared according to the literature [19,20].

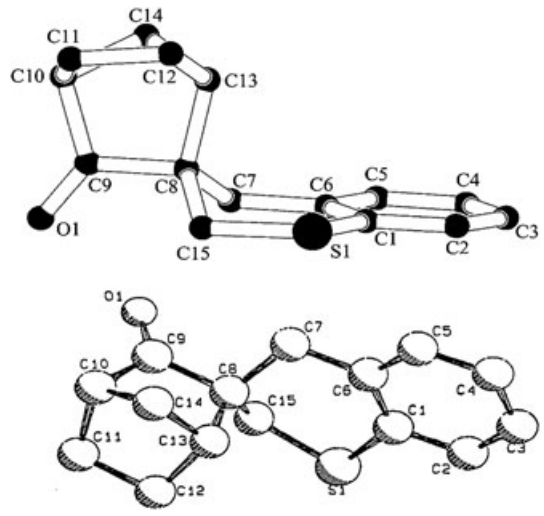


Figure 2. Crystal structure of **14**. Bottom: view from above; top: view from the side. The numbers do not correspond to the nomenclature.

***rac*-1,2,3,4,4a,9a-Hexahydro-1,4-methano-9*H*-thioxanthene (6).** A solution of benzothiete (**1**) (244 mg, 2.0 mmol) and norbornene (**5**) (235 mg, 2.5 mmol) in 15 mL of dry toluene was heated at reflux until the TLC control (SiO_2, toluene) revealed the complete consumption of **1** (about 1–2h). The solvent was removed and the residue purified by column chromatography (3 × 60 cm SiO_2, toluene/ethyl acetate 20:1). After a first fraction of 6*H*,12*H*-5,11-dithia-dibenzo[a,e]cyclooctene (**4**), product **6** could be eluted as colorless, viscous oil.

Yield: 360 mg (83%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (m, 1H, 11-H_{anti}), 1.23–1.29, m, 2H, 1.55–1.70, m, 2H (2-H, 3-H), 1.90 (m, 1H, 9a-H), 2.19–2.29 (m, 3H, 1-H, 4-H, 11-H_{syn}), 2.46 (dd, ^2J = −11.3 Hz, ^3J = 11.2 Hz, 1H, 9-H_a),

Table 1

Selected bond lengths, bond angles, and dihedral angles in the crystal structure of **14**.

Bond lengths	
S1 – C1	1.763 (2) Å
C1 – C6	1.396 (2) Å
C6 – C7	1.516 (2) Å
C7 – C8	1.535 (2) Å
C8 – C15	1.530 (2) Å
C15 – S1	1.804 (2) Å
Bond angles	
S1 – C1 – C6	124.02 (1)°
C1 – C6 – C7	122.67 (1)°
C6 – C7 – C8	113.56 (1)°
C7 – C8 – C15	107.79 (1)°
C8 – C15 – S1	112.88 (1)°
C15 – S1 – C1	102.63 (8)°
Dihedral angles	
S1 – C1 – C6 – C7	−1.2 (2)°[a]
C1 – C6 – C7 – C8	29.8 (2)°
C6 – C7 – C8 – C15	−62.8 (2)°
C7 – C8 – C15 – S1	67.1 (1)°
C8 – C15 – S1 – C1	−37.0 (1)°
C15 – S1 – C1 – C6	4.4(2)°[a]

[a]These small angles are typical for the half-chair conformation.

2.81 (dd, ^2J = −11.3 Hz, ^3J = 5.3 Hz, 1H, 9-H_b), 3.11 (m, ^3J (4a-H, 9a-H) = 7.5 Hz, $|^4J|$ (4a-H, 11-H_{anti}) = 1.8 Hz, 1H, 4a-H), 7.13–7.34 (m, 4H, 5-H, 6-H, 7-H, 8-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.2, 29.7 (C-2, C-3), 34.0, 36.2 (C-9, C-11), 43.3, 43.6 (C-1, C-4), 48.7, 50.7 (C-4a, C-9a), 126.2, 126.5, 127.6, 129.1 (C-5, C-6, C-7, C-8), 136.1, 140.3 (C-8a, C-10a). EI MS (70 eV): *m/z* (%) = 216 (74) [M^+], 149 (100), 148 (36), 147 (67). Anal. Calcd. for $C_{14}H_{16}S$ (216.3): C, 77.72; H, 7.45. Found: C, 77.63; H, 7.12.

***rac*-1,2,3,4,4a,9a–Hexahydro-1,4-methano-8*H*-thioxanthene-2,3-dicarboxylic acid (8).** The preparation of **8** was accomplished according to the procedure described for **6**. After the evaporation of the solvent, the residue was treated with saturated aqueous $NaHCO_3$ (5 mL). The obtained filtrate was acidified with diluted HCl until **8** as a colorless solid started to precipitate.

Yield: 430 mg (71%); mp 191–194°C (ethanol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.53 (m, 1H, 11-H_{anti}), 2.39 (m, 1H, 11-H_{syn}), 2.46 (dd, ^2J = −12.1 Hz, ^3J = 12.0 Hz, 1H, 9-H_a), 2.52 (m, 2H, 1-H, 4-H), 2.58 (m, 1H, 9a-H), 2.83 (m, 1-H, 9a-H), 3.20 (m, 2H, 2-H_{exo}, 3-H_{exo}), 3.74 (m, ^3J (4a-H, 9a-H) = 8.9 Hz, $|^4J|$ (4a-H, 11-H_{anti}) = 1.5 Hz, 1H, 4a-H), 7.12–7.29 (m, 4H, 5-H, 6-H, 7-H, 8-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ x= 35.6, 36.2 (C-9, C-11), 42.8, 45.7, 47.2, 47.5, 47.8, 48.1 (C-1, C-2, C-3, C-4, C-4a, C-9a), 127.2, 127.4, 128.6, 129.8 (C-5, C-6, C-7, C-8), 136.6, 140.9 (C-8a, C-10a), 172.9, 173.1 (COOH). EI MS (70 eV): *m/z* (%) = 304 (10) [M^+], 286 (81), 186 (38), 185 (71), 149 (34), 148 (39), 147 (100), 71 (57), 57 (88). Anal. Calcd. for $C_{16}H_{16}O_4S$ (304.4): C, 63.14; H, 5.30. Found: C, 62.89; H, 5.01.

1,2,3,4,4a,9a-Hexahydro-1,3-methano-2,2-dimethyl-9*H*-thioxanthene-9a-carbaldehyde (10) and 1,2,3,4,4a,9a-hexahydro-2,4-methano-3,3-dimethyl-9*H*-thioxanthene-4a-carbaldehyde (11). A solution of benzothiete (**1**) (814 mg, 6.66 mmol) and (−)-myrtenal (**9**) (990 mg, 6.58 mmol) in 20 mL of toluene was heated at reflux for 4 h. Column chromatography (2 × 30cm SiO_2, toluene/ethyl acetate 20:1) yielded after a first fraction of **4** the isomeric products **10** and **11** in a 1:1 mixture (270 mg, 15%), which could be separated by another column chromatography with the same conditions.

10. Colorless solid, mp 78–80°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.69 (s, 3H, *endo*−CH_3), 1.28 (s, 3H, *exo*−CH_3), 1.79 (m, 1H, 4-H_b), 1.89 (m, 1H, 11-H_{syn}), 2.01 (m, 1H, 3-H), 2.41 (m, 1H, 11-H_{anti}), 2.42 (m, 1H, 1-H), 2.50 (m, 1H, 4-H_a), 2.63, 9-H_b/2.99, 9-H_a (AB, ^2J = −14.0 Hz, 2H), 3.94 (m, 1H, 4a-H), 7.03–7.50 (m, 4H, 5-H, 6-H, 7-H, 8-H), 9.32 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.5 (*endo*−CH_3), 26.2 (C-11), 26.5 (*exo*-CH_3), 33.4 (C-4), 34.8 (C-4a), 39.2 (C-9), 39.8 (C-3), 49.7 (C-1), 61.2 (C-9a), 126.9, 127.2, 128.2, 128.6 (C-5, C-6, C-7, C-8), 136.8, 136.9 (C-9a, C-10a), 205.0 (CO). EI MS (70 eV): *m/z* (%) = 272 (71) [M^+], 175 (65), 147 (66), 123 (99), 121 (50), 91 (70), 43 (44), 41 (100). Anal. Calcd. for $C_{17}H_{20}OS$ (272.4): C, 74.96; H, 7.39. Found: C, 75.15; H, 7.36.

11. Colorless solid, mp 72–74°C. ^{1}H NMR ($CDCl_3$): δ = 0.71 (s, 3H, *endo*−CH_3), 1.28 (s, 3H, *exo*−CH_3), 1.74 (m, 1H, 11-H_{syn}), 1.75 (m, 1H, 1-H_b), 2.05 (m, 1H, 2-H), 2.19 (m, 1H, 4-H), 2.35 (m, 1H, 1-H_a), 2.43 (m, 1H, 11-H_{anti}), 2.49 (dd, ^2J = −13.2 Hz, ^3J = 13.1 Hz, 1H, 9-H_b), 2.81 (m, 1H, 9a-H), 2.97 (dd, ^2J = −13.2 Hz, ^3J = 4.8 Hz, 7.13–7.25 (m, 4H, 5-H, 6-H, 7-H, 8-H), 8.83 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$,): δ = 22.1 (*endo*−CH_3), 26.7 (*exo*-CH_3), 27.2 (C-11), 29.5 (C-9a), 34.3 (C-1), 40.4 (C-2), 40.7 (C-3), 44.3 (C-9), 46.1 (C-4), 66.9 (C-4a), 126.9, 127.3, 127.7, 130.3 (C-5, C-6, C-7, C-8), 131.3, 141.6 (C-10a), 189.8 (CHO). EI MS (70 eV): *m/z* (%) = 272 (18) [M^+], 147 (21), 123 (48), 91 (34), 79 (29), 77 (27), 69 (100), 45 (35), 43 (69), 41 (97). Anal. Calcd. for $C_{17}H_{20}OS$ (272.4): C, 74.96; H, 7.39. Found: C, 74.82; H, 7.25.

Table 2

Details of the X-ray crystal structure analysis of **14**.

Formular	$C_{15}H_{16}OS$
M_r	244.3 g m^{-1}
Habit	Colorless block
Crystal size	1.00 × 0.87 × 0.62 mm^3
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell constants	
a	8.7296 (3) Å
b	12.3248 (2) Å
c	11.2111 (2) Å
ß	92.034 (3) °
V	1205.44 (5) $Å^3$
Z	4
D	1.346 g cm^{-3}
Radiation	Cu-K_α
μ	2.201 mm^{-1}
F (000)	520
T	298 K
θ_{max}	70°
No of reflections	
Measured	2524
Independent	2280
Observed	2253
$[F_o/\sigma(F_o) > 4.0]$	
R_{int}	0.06
Parameters	166
Restraints	0
ω*R* (F^2, all refl.)	0.1256
R [F^2, >2 σ (F^2)]	0.0481
S	1.076
Max Δδ	0.340
Min Δδ	–0.470

Spiro[1-benzothiopyran-2,3′-bicyclo[2.2.1]heptan-2′-one] (13) and spiro[1-benzothiopyran-3,3′-bicyclo[2.2.1.]heptan-2′-one] (14). A solution of benzothiete (**1**) (812 mg, 6.66 mmol) and 3-methylene-norbornan-2-one (**12**) (805 mg, 6.58 mmol) in 20 mL of dry toluene was heated at reflux for 4–5 h. Column chromatography (2 × 75 cm SiO_2, toluene/ethyl acetate 10:1) yielded 128 mg (8%) of a 1:1 mixture of the isomers **13** and **14**. EI MS (70 eV): *m/z* (%) = 244 (56) [M^+], 216 (29), 176 (23), 175 (100), 147 (58). Anal. Calcd. for $C_{15}H_{16}OS$ (244.4): C, 73.73; H, 6.60. Found: C, 73.68; H, 6.51.

Repeated column chromatography under the same conditions permitted the separation of the isomers: **13** was obtained as a highly viscous, colorless oil and **14** as colorless crystals, mp 158°C.

13. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.55 (m, 1H, 6′-H), 1.61 (d, ^2J = −11.3 Hz, 1H, 7′-H), 1.69 (m, 1H, 5′-H), 1.81 (m, 1H, 5′-H), 1.89 (m, 1H, 6′-H), 1.99 (m, 1H, 3-H), 2.15 (m, 1H, 3-H), 2.29 (d, ^2J = −11.3 Hz, 1H, 7′-H), 2.65 (m, 1H, 4′-H), 2.71 (m, 1H, 1′-H), 2.76 (m, 1H, 4-H), 3.10 (m, 1H, 4-H), 6.98–7.12 (m, 4H, 5-H, 6-H, 7-H, 8-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7, 25.3 (C-5′, C-6′), 27.3, 27.7 (C-3, C-4), 35.6 (C-7′),

47.0 (C-4′), 49.7 (C-1′), 57.3 (C-2), 124.8, 126.5, 126.8, 129.2 (C-5, C-6, C-7, C-8), 131.7, 134.3 (C-4a, C-8a), 215.2 (C-2′).

14. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.53 (d, ^2J = −11.5 Hz, 1H, 7′-H), 1.59 (m, 1H, 6′-H), 1.70 (m, 1H, 5′-H), 1.78 (m, 1H, 5′-H), 1.95 (m, 1H, 6′-H), 1.98 (d, ^2J = −11.5 Hz, 1H, 7′-H), 2.38 (m, 1H, 4′-H), 2.53 (dd, ^2J = −13.2 Hz, ^4J = 2.7 Hz, 1H, 2-H), 2.69 (dd, ^2J = −16.3 Hz, ^4J = 2.7 Hz, 1H, 4-H), 2.71 (m, 1H, 1′-H), 2.81 (d, ^2J = −16.3 Hz, 1H, 4-H, 3.26 (d, ^2J = −13.2 Hz, 2H, 2-H), 6.95–7.10 (m, 4H, 5-H, 6-H, 7-H, 8-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.1, 25.5 (C-5′, C-6′), 31.3, 34.1 (C-2, C-4), 35.1 (C-7′), 40.6 (C-4′), 48.1 (C-3), 50.5 (C-1′), 124.0, 126.1, 126.7, 130.9 (C-5, C-6, C-7, C-8), 131.2, 132.1 (C-4a, C-8a), 219.6 (C-2′).

FVP of 6H, 12H-dibenzo[b,f][1,5]dithiocin (4). FVP pyrolysis of gathered samples of **4** at 700°C and 10^{-3} kPa yielded **1**, which was purified by distillation. Yield: 67%, bp 32–36°C (2.7 Pa). Identification by comparison with an authentic probe.

Crystal structure analysis of compound 14. Structure solution, refinement, and data output were carried out with SHELXS/L. H atoms were places at calculated positions. Details of the X-ray crystal structure analysis are summarized in Table 2. Crystallographic data for **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 149386.

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[1] See for example ref. [2–10] and the references cited therein.

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[16] Monocyclic alkenes containing a chiral center, for example *R*-(−)carvone [(*R*)-2-methyl-5-propen-2-yl-cyclohex-2-en-1-one] do not give a diastereoselective cycloaddition of **1/1′**. Unpublished result.

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