Substituent Effect on the Competition between Hetero-*Diels-Alder* and Cheletropic Additions of Sulfur Dioxide to 1-Substituted Buta-1,3-dienes

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The reactivity of sulfur dioxide toward variously substituted butadienes was explored in an effort to define the factors affecting the competition between the hetero-*Diels-Alder* and cheletropic additions. At low temperature ($< -70°$), 1-alkyl-substituted 1,3-dienes **1** that can adopt *s-cis*-conformations add to SO_2 in the hetero-*Diels-Alder* mode in the presence of CF_3COOH as promoter. In the case of (*E*)-1-ethylidene-2-methylidenecyclohexane ((*E*)-**4a**), the [4 + 2] cycloaddition of SO_2 is fast at $-90°$ without acid catalyst. (*E*)-1-(Acyloxy)buta-1,3-dienes (*E*)-**1c**, (*E*)-**1y**, and (*E*)-**1z** with AcO, BzO, and naphthalene-2-(carbonyloxy) substituents, respectively also undergo the hetero-*Diels-Alder* addition with $SO_2 + CF_3COOH$ at low temperatures, giving a 1:10 mixture of the corresponding *cis*- and *trans*-6-(acyloxy)sultines *c*-**2c,y,z** and *t*-**2c,y,z**, respectively). Above $-50°$, the sultines undergo complete cycloreversion to the corresponding dienes and SO_2, which that add in the cheletropic mode at higher temperature to give the corresponding 2-substituted sulfolenes (=2,5-dihydrothiophene 1,1-dioxides) **3**. The hetero-*Diels-Alder* additions of SO_2 follow the *Alder endo* rule, giving first the 6-substituted *cis*-sultines that equilibrate then with the more stable *trans*-isomers. This statement is based on the assumption that the S=O group in the sultine prefers a pseudo-axial rather than a pseudo-equatorial position, as predicted by quantum calculations. The most striking observation is that electron-rich dienes such as 1-cyclopropyl-, 1-phenyl-, 1-(4-methoxyphenyl)-, 1-(trimethylsilyl)-, 1-phenoxy-, 1-(4-chlorophenoxy)-, 1-(4-methoxyphenoxy)-, 1-(4-nitrophenoxy)-, 1-(naphthalen-2-yloxy)-, 1-(methylthio)-, 1-(phenylthio)-, 1-[(4-chlorophenyl)thio]-, 1-[(4-methoxyphenyl)thio]-, 1-[(4-nitrophenyl)thio]-, and 1-(phenylseleno)buta-1,3-diene, as well as 1-(methoxymethylidene)-2-methylidenecyclohexane (**4f**) do not equilibrate with the corresponding sultines between -100 and $-10°$, in the presence of a large excess of SO_2, with or without acidic promoter. The hetero-*Diels-Alder* additions of SO_2 to 1-substituted (*E*)-buta-1,3-dienes are highly regioselective, giving exclusively the corresponding 6-substituted sultines. The 1-substituted (*Z*)-buta-1,3-dienes do not undergo the hetero-*Diels-Alder* additions with sulfur dioxide.

Introduction. – In the preceding report, we have evaluated the thermodynamics and kinetics parameters of the hetero-*Diels-Alder* additions of sulfur dioxide to simple 1,2-dimethylidenecycloalkanes and have compared them with those obtained for the corresponding cheletropic additions [1]. Earlier, we had found that the competition between the hetero-*Diels-Alder* and cheletropic additions of SO_2 is strongly dependent on the substitution of the conjugated dienes [2]. Whereas (*E*)-1-methyl- (**1a**) [3] (*E*)-1-ethyl- (**1b**) [4], and (*E*)-1-acetyloxy)butadiene [5] (**1c**) undergo the hetero-*Diels-Alder* addition with SO_2 below $-50°$ in the presence of CF_3COOH, giving first the

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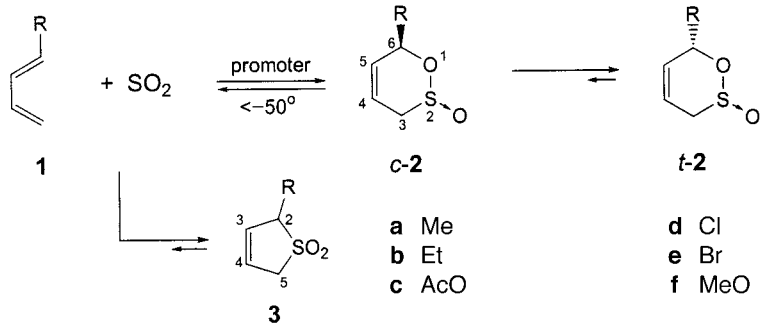
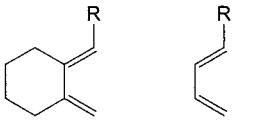
corresponding *cis*- and then the *trans*-6-methyl-, *trans*-6-ethyl-, and *trans*-6-(acetyloxy)-3,6-dihydro-1,2-oxathiin 2-oxides (=6-substituted sultines) **2a**–**c**, respectively, (*E*)-1-chloro-, (*E*)-2-bromo-, and (*E*)-1-methoxybutadienes **1d**–**f**) gave only the corresponding 2-substituted 2,5-dihydrothiophene 1,1-dioxides (=sulfolenes) **3d**–**f**, respectively [2] (*Scheme 1*). Although 1-alkoxy- and 1-(silyloxy)-1,3-dienes equilibrate with sulfolenes rather than with the corresponding sultines at low temperature [5], the latter unstable heterocyclic compounds are believed to be formed as reactive intermediates in our new C–C forming reaction involving the cocondensation of electron-rich 1,3-dienes and alkenes with SO_2 [6][7].

Scheme 1





(*E*)-**4a** R = Me
(*E*)-**4f** R = MeO

(*E*)-**1**

g *t*-Bu
h c-C_6H_{11}
i Bn
j c-C_3H_5
k Ph
l 4-$MeOC_6H_4$
m Me_3Si
n PhO
o 4-ClC_6H_4O
p 4-$MeOC_6H_4O$
q 4-$NO_2C_6H_4O$
r (2-naphthyl)O
s MeS
t PhS
u 4-ClC_6H_4S
v 4-$MeOC_6H_4S$
w 4-$NO_2C_6H_4S$
x PhSe
y PhCOO
z (2-naphthyl)COO

With the hope to learn more about the factors that affect the competition between the hetero-*Diels-Alder* and the cheletropic additions of SO_2, we have explored the behavior of 1-substituted (*E*)- and (*Z*)-1,3-dienes **1g**–**x**, **4a**, and **4f** under various conditions. As we shall see, the formation of sultines is observed only for (*E*)-1-alkyl- and (*E*)-1-(acyloxy)butadienes. In all cases, the sultines are unstable above $-50°$ and undergo *retro-Diels-Alder* reactions, with the formation of the corresponding 1,3-dienes that react then with SO_2 to generate the corresponding sulfolenes **3**. Dienes 1-substituted with electron-rich groups such as cyclopropyl (**1j**), aryl (**1k**,**l**), trimethylsilyl (**1m**), aryloxy (**1n**–**r**), methylthio (**1s**), arylthio (**1t**–**w**), or phenylseleno (**1x**) refuse to equilibrate with the corresponding sultines at low temperature and form exclusively the corresponding sulfolenes **3j**–**x**. Diene (*E*)-**4a** reacts with SO_2 without catalyst, giving the corresponding *cis*-, then *trans*-sultine, whereas the methoxy-substituted analogs (*E*)- and (*Z*)-**4f** equilibrate only with the corresponding sulfolene[4]).

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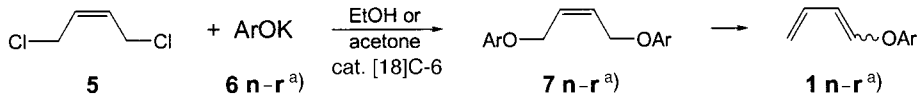
[4]) Sultines fused with benzo groups [8] and other aromatic ring systems are stable compounds [9].

Synthesis of the Dienes. – Pure (*E*)-1-(*tert*-butyl)butadiene (*E*)-**1g** was prepared *via* the acid-catalyzed dehydratation of 2,2-dimethylhex-4-en-3-ol [10]. A 10:1 mixture of (*E*)- and (*Z*)-1-cyclohexylbutadienes **1h** was obtained by treatment of allyldiphenylphosphine oxide with BuLi and quenching of the lithium derivative with cyclohexanecarboxaldehyde, followed by H_2O elimination [11]. A 6:1 mixture of (*E*)- and (*Z*)-1-benzylbutadiene **1i** was prepared by a similar route (*Exper. Part*) since the reported synthesis for the reaction of phenylmagnesium bromide and 5-bromopenta-1,3-diene [12] failed in our hands. The synthesis of 1-cyclopropylbutadiene **1j** was by a method similar to that described in [13]. Bromination of dicyclopropylmethanol [14] with PBr_3, followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-induced HBr elimination provided a 5:1 mixture of (*E*)- and (*Z*)-1-cyclopropylbutadienes **1j**. *Wittig* olefination of (*E*)-cinnamaldehyde produced pure (*E*)-1-phenylbutadiene (*E*)-**1k** [15]. A 4:1 mixture of (*E*)- and (*Z*)-1-(4-methoxyphenyl)butadiene **1l** was obtained in 51% yield by acid-promoted dehydratation of 1-(4-methoxyphenyl)but-3-en-1-ol, a compound resulting from the addition of allylmagnesium chloride to *p*-anisaldehyde [16]. Pure (*E*)-1-(trimethylsilyl)butadiene (*E*)-**1m** was derived from propargyl alcohol (= prop-2-yn-1-ol) following a known procedure [17].

The syntheses of 1-(aryloxy)butadienes **1n**–**r** was according to the general procedure shown in *Scheme 2*. The preparation of the (*Z*)-1,4-bis(aryloxy)but-2-enes **7n**–**r** according to the published procedure [18] from (*Z*)-1,4-dichlorobut-2-ene (**5**) failed in our hands. We obtained **7n**–**r** in good yield (70–95%) by reactions of the corresponding potassium phenolates **6** with **5** in EtOH or acetone [19]. Yields were the highest in the presence of a catalytical amount of [18]crown-6. Base-promoted elimination of 1 equiv. of phenol from **7** afforded the desired dienes with stereoselectivity ((*E*)/(*Z*) ratio) depending on the nature of the base and of the starting 1,4-bis(aryloxy)butene **7** (*Table 1*).

Scheme 2



5 **6 n–r** [a] **7 n–r** [a] **1 n–r** [a]

[a]) See *Scheme 1* for **n**–**r**.

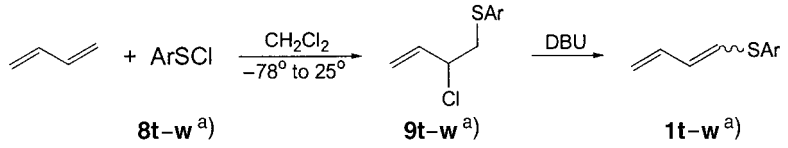
Table 1. *Base-Induced Eliminations* **7n**–**r** → **1n**–**r**

Starting material	Diene	Reaction conditions	(*E*)/(*Z*)	Yield
7n	**1n**	*t*-BuOK [20], neat, sealed tube	< 1:100	40%
7n	**1n**	BuLi, THF, −78 to 25°	> 100:1	78%
7o	**1o**	BuLi, THF, −78 to 25°	3.2:1	63%
7p	**1p**	BuLi, THF, −78 to 25°	12:1	52%
7q	**1q**	Li tetramethylpiperidinide, THF	3:1	18%
7r	**1r**	BuLi, THF, −78 to 25°	> 100:1	26%

Pure (*E*)-1-(methylthio)butadiene (*E*)-**1s** was prepared in a similar way by double displacement of **5** with lithium methanethiolate, followed by BuLi-induced elimination of 1 equiv. of methanethiol, a method that differs slightly from that published for the synthesis of this diene [21]. The 1-(arylthio)butadienes **1t**–**w** were obtained by addition

of the corresponding arylsulfenyl chlorides **8t–w** to butadiene followed by DBU-induced eliminations of HCl from **9t–w** (*Scheme 3*). This produced mixtures of (*E*)- and (*Z*)-1-(arylthio)butadiene ((*E*)/(*Z*) ratio 2:1 to 3.5:1).

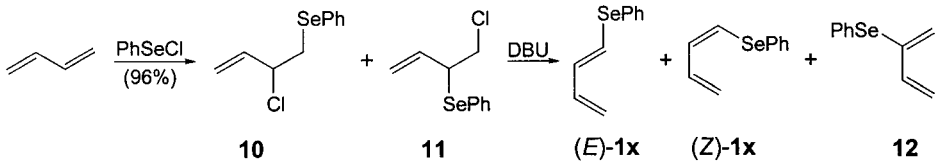
Scheme 3



a) See *Scheme 1* for **t–w**.

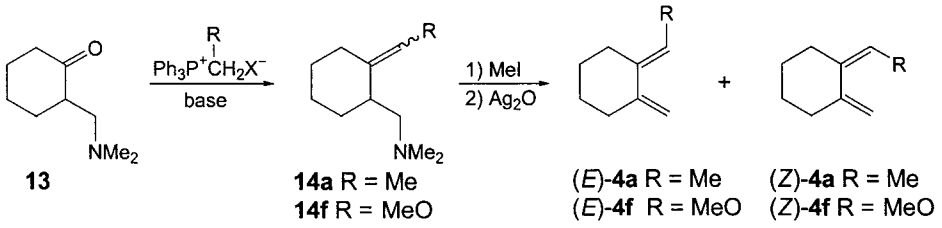
The reaction of benzeneselenyl chloride with butadiene gave a 5:1 mixture of adducts **10** and **11** (*Scheme 4*). Treatment of this mixture with DBU led to a 1:0.8:0.5 mixture of (*E*)-1-(phenylseleno)butadiene (*E*)-**1x**, its (*Z*)-isomer (*Z*)-**1x**, and 2-(phenylseleno)butadiene **12** that was used as such in our exploratory studies with SO_2 (see below).

Scheme 4



The 1-(acyloxy)butadienes **1y** and **1z** were prepared by reaction of (*E*)-1-[(trimethylsilyl)oxy]buta-1,3-diene with benzoyl fluoride and naphthalene-2-carbonyl fluoride in the presence of a catalytical amount of Bu_4NF [22]. This furnished a 10:1 mixture of (*E*)- and (*Z*)-**1y** and a 5:1 mixture of (*E*)- and (*Z*)-**1z**, respectively, in good yield. A 2:1 mixture of (1*E*)- and (1*Z*)-1-ethylidene-2-methylidenecyclohexane ((*E*)- and (*Z*)-**4a**, resp.) was obtained *via* the *Wittig* olefination of 2-[(dimethylamino)-methyl]cyclohexanone (**13**) [23] by [$EtPPh_3$]Br and *t*-BuOK ([18]crown-6, THF) that produced **14a** (*Scheme 5*). When BuLi/LiBr was used [24] as a base for the *Wittig* olefination, (*E*)-**14a** was formed exclusively. Quaternization of **14a** with MeI, followed by treatment with Ag_2O gave the exocyclic dienes (*E*)- and (*Z*)-**4a**. Similarly, a 1:1.5 mixture of (*E*)- and (*Z*)-**4f** was prepared by *Wittig* olefination of **13** with [$MeOCH_2PPh_3$]Cl and lithium diisopropylamide in THF *via* **14f** (*Scheme 5*).

Scheme 5



Competition between the *Diels-Alder* and Cheletropic Additions. – Except for the most reactive diene (*E*)-**4a** (*Scheme 6*), none of the other dienes **1a**–**z** and **4f** did undergo the hetero-*Diels-Alder* addition of SO_2 without an acidic promoter. When SO_2 (10–20 fold excess) was premixed with CF_3COOH (1–2 equiv.), hetero-*Diels-Alder* additions of SO_2 were observed below $-75°$ only for the (*E*)-1-alkylbutadienes (*E*)-**1a** [3], (*E*)-**1b** [4], (*E*)-**1g**, (*E*)-**1h**, and (*E*)-**1i**, and for the (*E*)-1-(acyloxy)butadienes (*E*)-**1c** [2a], (*E*)-**1y**, and (*E*)-**1z** (*Table 2*). Compared with the non-acid-catalyzed *Diels-Alder* addition of SO_2 to 1,2-dimethylidenecyclohexane [1], that of (*E*)-**4a** was at least 60 times faster at $-75°$.

Scheme 6

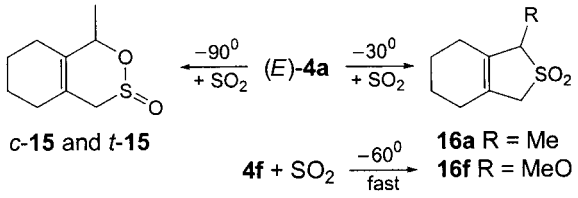


Table 2. *Competition between the Hetero-*Diels-Alder (*D.-A.*) *and Cheletropic* (CHE) *Additions of SO_2 Premixed with CF_3COOH* (1–2 equiv.) *for 1-Substituted (*E*)-Dienes* **1a**–**z**, **4a**, *and* **4f** (0.2–0.4M in $CFCl_3/CDCl_2/SO_2$ 1 : 1.5 : 2): *Temperatures*[a]) *at Which the Reactions are Observed* (half-lives of 0.5–10 h, by ^{1}H-NMR)[b])[c])

	1a [3]	**1b** [4]	**1c** [2a]	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**	**1l**	**1m**	**1y**	**1z**	**4a**	**4f**
D.-A.	−80°	−80°	−75°	–	–	[f])	−70°	−70°	−80°	–[f])	–	–	–	−75°	−75°	<−90°[g])	–[f])
cis ⇄ *trans*[d])	−60°	−60°	−75°	–	–	–	−50°	−50°	−50°	–	–	–	–	−75°	−75°	−85°	–
Cyclo-reversion[e])	−40°	−40°	−20°	–	–	–	−40°	−30°	−40°	–	–	–	–	−30°	−30°	−40°	–
CHE	−40°	−40°	−10°	−50°	−50°	−80°[f])[g])	−25°	−30°	−30°	−50°[g])	−10°	−30°	−10°	25°	25°	−30°	−80°[f])[g])

[a]) ±5°. [b]) All other dienes **1n**–**x** do not undergo the hetero-*Diels-Alder* addition with SO_2. They react with SO_2 to give the corresponding sulfolenes only. None of the 1-substituted (*Z*)-butadienes adds in the hetero-*Diels-Alder* mode. [c]) Butadiene has not reacted yet with SO_2 in the hetero-*Diels-Alder* mode. [d]) Isomerization of the *cis*-sultine formed first to its more stable *trans*-isomer (see text). [e]) Temperature at which less than 5% of sultines are at equilibrium with the diene. [f]) Polymerization in the presence of acids. [g]) Reaction without acidic promoter.

None of the (*Z*)-isomeric dienes added to SO_2 in the *Diels-Alder* mode (for mixtures of (*E*)- and (*Z*)-**1**). In the case of the expectedly highly reactive 1-(cyclopropyl)butadiene **1j**, only polymerization was observed at low temperature in the presence of SO_2 containing CF_3COOH. With $BF_3 \cdot Et_2O$, polymerizaton was even faster. The same behavior was observed for the electron-rich 1-substituted dienes **1n**–**r** (R = ArO), **1s**–**w** (R = MeS or ArS), and **1x** (R = PhSe). All the latter dienes underwent the expected cheletropic additions of SO_2 between -40 and 20°. In the case of the 1-arylbutadienes **1k** (R = Ph) and **1l** (R = 4-$MeOC_6H_4$) and 1-(trimethylsilyl)-butadiene **1m** that were stable under acidic conditions below $-10°$, no hetero-*Diels-Alder* additon of SO_2 (several days at -100 to $-10°$) could be observed before the cheletropic addition. This is surprising, as these dienes are not expected to be less reactive than (*E*)-1-alkylbutadienes in *Diels-Alder* cycloadditions. This suggests that SO_2 is different in nature compared with other dienophiles (see below).

As for the hetero-*Diels-Alder* addition of (*E*)-**1a** [3] and (*E*)-**1b** [4] discussed earlier, the reactions of (*E*)-**1g**, (*E*)-**1h**, (*E*)-**1i**, and (*E*)-**4a** with SO_2 gave first the corresponding *cis*-sultines *c*-**2g**, *c*-**2h**, *c*-**2i**, and *c*-**15**, respectively, in agreement with the *endo-Alder* rule [25] (see *Schemes 1* and *6*). With prolonged reaction times or at higher temperatures, these *cis*-sultines were equilibrated with their more stable *trans*-isomers *t*-**2g**, *t*-**2h**, *t*-**2i**, and *t*-**15**, respectively. In the case of the hetero-*Diels-Alder* additions of the (*E*)-1-(acyloxy)butadienes (*E*)-**1c** [2a], (*E*)-**1y**, and (*E*)-**1z**, 1:10 mixtures of the corresponding *cis*- and *trans*-sultines were formed immediately, and the 1:10 product ratio did not change until their conversion into the corresponding sulfolenes **3c** [2a], **3y**, and **3z**, respectively. The thermodynamic data for the reactions of SO_2 with 1-(acyloxy)butadienes are collected in *Table 3*. They show that the cheletropic additions of these dienes to SO_2 is *ca.* 4 kcal mol^{-1} more exothermic than the corresponding hetero-*Diels-Alder* additions. This is significantly less than (*ca.* 10 kcal mol^{-1}) the difference in exothermicity of hetero-*Diels-Alder* and cheletropic additions of alkyl-subsituted dienes [1][26]. All our attempts to crystallize the sultines presented here failed. Thus their structures were inferred from their ^1H- and ^{13}C-NMR spectra (see below).

Table 3. *Thermodynamic Data for the Hetero*-Diels-Alder *Additions of* **1c**, **1y**, *and* **1z** *and of the Cheletropic Additions of* **1c** *and* **1y** *to* SO_2 (10–20 fold excess, 1 equiv. of CF_3COOH)

Diels Alder	$K(-75°)$ [10^3 l mol^{-1}]	ΔH_r $(-75°)$ [kcal mol^{-1}]	Cheletropic	$K(25°)$ [1 mol^{-1}]	$\Delta H_r(25°)$ [kcal mol^{-1}]
SO_2 + **1c** ⇄ *c*-**2c**	2.3 ± 0.4	−6.0 ± 1.5[a])	SO_2 + **1c** ⇄ **3c**	0.19 ± 0.01	−10.9 ± 0.2[b])
SO_2 + **1c** ⇄ *t*-**2c**	21 ± 3	−6.3 ± 0.2[a])			
SO_2 + **1y** ⇄ *c*-**2y**	0.57 ± 0.08	−5.0 ± 0.2[b])	SO_2 + **1y** ⇄ **3y**	0.092 ± 0.002	−10.5 ± 0.3[b])
SO_2 + **1y** ⇄ *t*-**2y**	5.4 ± 1.2	−5.9 ± 0.2[b])			
SO_2 + **1z** ⇄ *c*-**2z**	0.6 ± 0.2	−5.0 ± 0.2[b])			
SO_2 + **1z** ⇄ *t*-**2z**	5 ± 1	−5.8 ± 0.2[b])			

[a]) See *Van't Hoff* plots, [2a]; $\Delta S_r(SO_2 + \mathbf{1c} \rightleftarrows c\text{-}\mathbf{2c}) = -43 \pm 7$ cal mol^{-1} K^{-1}; $\Delta S_r(SO_2 + \mathbf{1c} \rightleftarrows t\text{-}\mathbf{2c}) = -39.7 \pm 0.8$ cal mol^{-1} K^{-1}. [b]) $\Delta S_r = -40$ cal $mol^{-1}K^{-1}$ used for the calculation.

Except for the 2-oxy-substituted sulfolenes **3n**–**s** and **16f**, the thio analogs **3s**,**r**, and the seleno analog **3x** that were unstable at room temperature, all derivatives **3g**–**m**, **t**, **u**, **w**, **y**, **z** and **16a** were fully characterized by their spectral data and, in the cases of **3u** (*Fig. 1*) and **3y** (*Fig. 2*), by single-crystal X-ray-diffraction studies. Sulfolene **3a** was hydrogenated into sulfolane **17**, the structure of which was also determined by single-crystal X-ray crystallography (*Fig. 3*). The structure of **3m** was confirmed by derivation of this compound from unsubstituted sulfolene (=2,5-dihydrothiophene 1,1-dioxide) *via* lithiation with BuLi and subsequent treatment with Me_3SiCl [26].

Structures of Sultines. – We have shown that ^{17}O-NMR chemical shifts of sultines are quite different from those of the isomeric sulfolenes in the case of corresponding alkyl-substituted derivatives [2b]. This method of identification is not practical for systems of high molecular mass because of severe line broadening in the ^{17}O-NMR spectra of sultines that have to be measured at very low temperature ($< -70°$). For instance, with *t*-**15**, two very broad signals at $\delta(^{17}O)$ 141 ($w_{1/2} = 800$ Hz) and 88 ($w_{1/2} = 1200$ Hz) are observed at $-65°$. For the isomeric sulfolene **16**, its ^{17}O-NMR spectrum

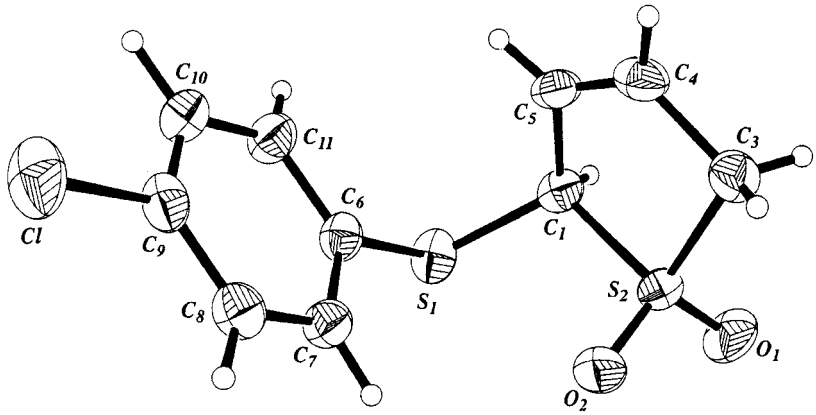


Fig. 1. *ORTEP Representation of 2-[(4-chlorophenyl)thio]-2,5-dihydrothiophene 1,1-dioxide* (**3u**) *showing non-H-atoms with 50% probability*[4])

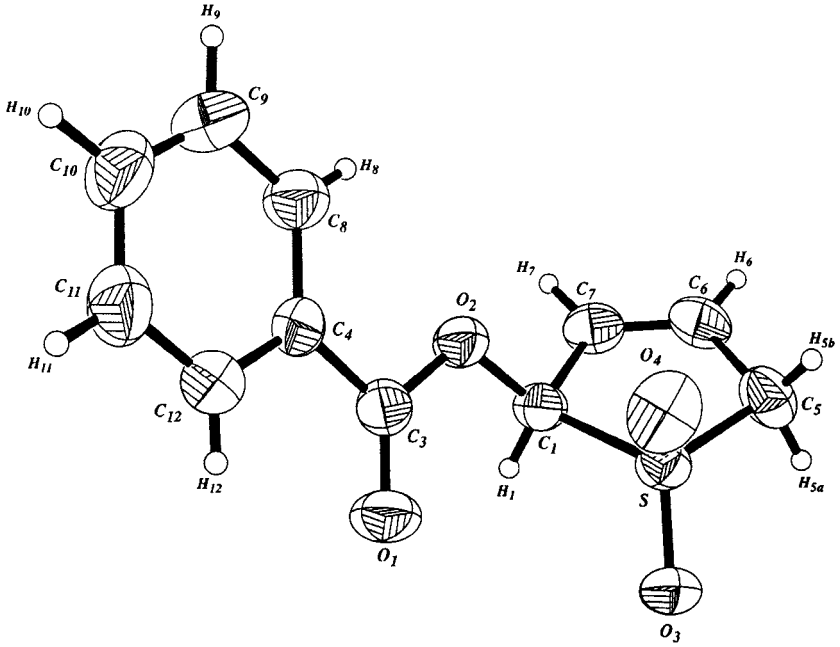


Fig. 2. *ORTEP Representation of 2,5-dihydro-1,1-dioxidothiophen-2-yl benzoate* (**3y**) *showing non-H-atoms with 50% probability*[5])

[5]) The IUPAC numbering of atoms is not followed for reasons of convenience. Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Center* as Supplementary Publication No. 171082 for **3u**, No. 171083 for **3y**, and No. 170963 for **17**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +441223336-033; e-mail: deposit@ccdc.cam.ac.uk.

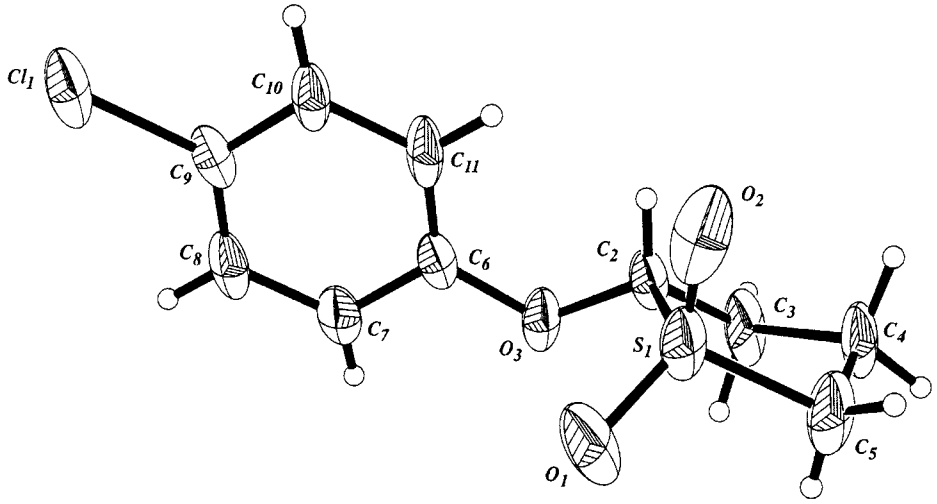
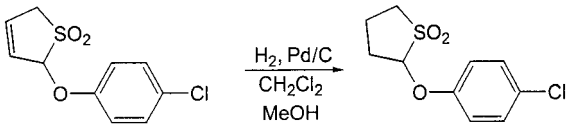


Fig. 3. *ORTEP Representation of 2-(4-chlorophenoxy)-2,3,4,5-tetrahydrothiophene 1,1-dioxide* (**17**) *showing non-H-atoms with 50% probability*[4])

Scheme 7



3o **17**

shows two broad lines also at 25° at $\delta(^{17}O)$ 155.8 and 149.4 ($w_{1/2} = 300$ Hz). Furthermore, and as discussed earlier [26], distinction between sultine and sulfolene structures with alkyloxy and acyloxy substituents based on their ^{17}O-NMR data is not trivial. Comparison of the ^{1}H-NMR data of 6-substituted sultines (*Table 4*) with those of their isomeric 2-substituted sulfolenes (*Table 5*) shows that these compounds can be distinguished by the coupling constants of their vicinal olefinic protons. As expected for cyclohexene ($^{3}J(1,2) = 8.8$ Hz) and cyclopentene ($^{3}J(1,2) = 5.1$ Hz) [27], the vicinal coupling constants $^{3}J(4,5)$ of sultines **2** (11.0–11.8 Hz) are found to be larger than $^{3}J(3,4) = 8.5–8.8$ Hz of sulfolenes **3**.

Comparison of ^{13}C-NMR data of sultines and isomeric sulfolenes show that the C(5) of sulfolenes resonates at lower field (8–10 ppm) than C(6) of the corresponding sultines (see *Exper. Part*).

High-level quantum calculations predicted that unsubstituted sultine and the *cis*- and *trans*-6-methylsultines (*c*- and *t*-**2a**) adopt pseudo-chair conformations in their ground-states with pseudo-axial S=O bonds [2a][28]. Calculations on 6-fluorosultines and preliminary experimental results suggested, however, that sultines substituted at C(6) by polar groups can adopt sofa conformations in which the O-atom lies in the average plane of the four C-atoms [29]. If one assumes that sultine *c*-**2g** adopts a

Table 4. *^{1}H-NMR Data* (400 MHz, $SO_2/CDCl_2/CFCl_3$, $< -70°$) *of 6-Substituted Sultines* **2a–c**, **2g–i**, *and* **2y**. δ(H) in ppm, *J* in Hz.[a])

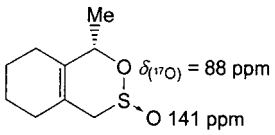
δ(H)	H_a–C(3)[b])	H_e–C(3)[b])	H–C(4)	H–C(5)	H–C(6)	^2J(3a,3e)	^3J(3a,4)	^3J(3e,4)	^3J(4,5)	^3J(5,6)	^5J(3a,6)	^5J(3e,6)[c])	R at C(6)[d])
c-**2a**[e])	3.25	3.37	5.90	6.00	4.60	16.5	2.5	7.0	11.5	2.0	3.0	< 0.5	Me(ax)
t-**2a**	3.45	2.95	5.60	5.80	4.65	17.0	2.0	5.5	11.0	1.0	4.0	2.5	Me(eq)
c-**2b**	3.28	3.38	5.80	6.20	4.45	16.5	3.0	7.0	11.0	2.0	3.5	< 0.5	Et(ax)
t-**2b**	3.45	3.00	5.70	5.80	4.55	17.5	2.5	6.0	?	?	4.5	3.0	Et(eq)
c-**2c**	3.34	3.86	6.17	6.00	6.69	17.3	4.0	4.8	11.2	1.9	2.1	2.1	AcO
t-**2c**	3.61	3.57	6.26	6.14	6.48	17.0	3.3	5.7	?	2.4	?	?	AcO
c-**2g**	3.08	3.56	?	6.18	4.07	15.5	?	6.5	11.0	2.4	?	1.0	*t*-Bu(ax)
t-**2g**	3.41	3.04	5.75	5.95	4.24	17.2	2.7	6.5	11.0	2.1	4.2	2.1	*t*-Bu(eq)
c-**2h**	3.14	3.46	?	?	4.24	16.6	3.3	7.0	?	?	2.3	?	c-Hex(ax)
t-**2h**	3.39	3.03	5.67	?	4.43	17.3	2.6	6.3	11.4	?	4.4	2.6	c-Hex(eq)
c-**2i**	?	?	5.80	6.05	4.64	?	?	?	11.8	?	?	?	Bn(ax)
t-**3i**	3.36	3.00	?	?	?	17.5	2.5	6.2	11.8	?	4.1	2.7	Bn(eq)
c-**1y**	3.87	3.38	6.23	6.16	6.94	17.0	3.8	4.5	*ca.* 12		1.8	1.8	BzO
t-**1y**	3.62	3.58	6.30	6.25	6.69	17.0	?	?	?		?	?	BzO

[a]) See *Exper. Part* for data of other compounds described in this report. Spectral assignments were confirmed by 2D-COSY and NOESY experiments. [b]) H_a–C(3) occupies a pseudo-axial, H_e–C(3) a pseudo-equatorial position in a supposed pseudo-chair conformation of the sultine (*Fig. 4*). [c]) See *Exper. Part* for ^4J values. [d]) Pseudo-axial (ax) and pseudo-equatorial (eq) position of the 6-substituent, average pseudo-chair conformation when assignment was possible. [e]) The *c* corresponds to the sultine of kinetic control, assigned to the *cis* stereoisomer, and *t* corresponds to the more stable stereoisomer, assigned to the *trans*-sultine, see text.

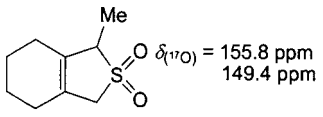
Table 5. *^{1}H-NMR Data* (400 MHz, $SO_2/CDCl_2/CFCl_3$, 0–20°) *of Selected 2-Substituted Sulfolenes* **3a**, **3c–k**, **3m**, **3s**, *and* **3x–y**. δ(H) in ppm, *J* in Hz.

δ(H)	H–C(2)	H–C(3)	H–C(4)	H_a–C(5)[b])	H_b–C(5)[b])	^2J(5a,6b)	^3J(2,3)	^3J(3,4)	^3J(4,5a)	^3J(4,5b)	^4J(2,5a)	^4J(2,5b)	R at C(2)
3a	3.70	5.92	5.96	3.67	3.72			8.8					Me
3c	5.93	6.16	6.43	3.77	3.80	17.2	2.9	8.8	3.0	2.9	1.1	2.4	AcO
3d	5.28	6.26	6.29	3.85	3.85	?	2.0	8.6	3.0	2.5	0.8	2.5	Cl
3e	5.36	6.23	6.32	3.83	3.88	16.9	2.3	8.5	3.0	2.5	1.0	1.5	Br
3f	4.65	5.95	6.18	3.68	3.75	17.5	3.0	8.8	3.0	2.5	0.5	1.0	MeO
3g	3.51	6.13	6.16	3.62	3.67	16.5	2.1	8.8	2.7	2.7	1.1	2.1	*t*-Bu
3h	3.46	6.12	6.09	3.46	3.62	17.3	1.8	8.8	2.3	2.3	?	?	c-Hex
3i	3.94	5.93	6.04	3.74	3.80	16.7	2.3	8.6	2.7	2.7	1.3	2.3	Bn
3j	3.19	6.04	6.09	3.67	3.72	14.5	2.2	8.7	2.9	2.2	1.5	2.2	c-C_3H_5
3k	4.97	6.21	6.31	3.84	3.89	16.6	2.3	8.5	2.7	2.7	2.2	2.2	Ph
3m	3.40	5.95	6.02	3.65	3.74	16.7	2.4	8.5	3.0	2.4	1.3	2.4	Me_3Si
3s	4.61	6.11	6.25	3.77	3.83	17.0	?	8.6	3.2	2.5	1.0	2.2	MeS
3x	4.92	5.95	6.16	3.40	3.65	16.8	2.7	8.5	3.4	2.5	0.6	2.4	PhSe
3y	6.24	6.29	6.46	3.84	3.89	18.0	2.7	8.6	3.0	2.7	0.9	1.8	BzO

[a]) See *Exper. Part* for further data of these sulfolenes and other derivatives. Spectral assignments were confirmed by 2D-COSY and NOESY experiments. [b]) H_a–C(5) is *trans* to H–C(2); H_b–C(5) is *cis* to H–C(2).



t-**15**



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pseudo-chair conformation as shown in *Fig. 4*, both the S=O and *t*-Bu groups reside in pseudo-axial positions, thus making *c*-**2g** less stable than its *trans* isomer *t*-**2g** for steric reasons, as observed. These hypothetical structures and conformations (*Fig. 4*) are consistent with the ^{1}H-NMR data collected for these two sultines (*Table 4*, *Exper. Part*). Assuming the validity of the $^5J(H,H) = 4.99 \sin^2\varphi \sin^2\varphi'$ relationship [30] for the homoallylic coupling constants between proton pairs H–C(3)/H–C(6) (φ and φ' being the angles these protons make with the π-plane C(3)–C(4)–C(5)–C(6)), the ^5J(3,6) coupling constants measured for *c*-**2g** and *t*-**2g** are in agreement with the conformers shown in *Fig. 4*. The proposed conformers are also consistent with the ^3J(3,4) and ^3J(5,6) vicinal coupling constants measured (*Karplus* relationship [31]). The ^{1}H-NMR data (*Table 4*) collected for the other 6-alkyl substituted sultines suggest that similar structures and conformations to those shown in *Fig. 4* can be proposed for **2a**, **2b**, **2h**, and **2i**. Because of ^4J and ^5J coupling constants involving the protons of the cyclohexeno moiety of bicyclic sultines *c*- and *t*-**15**, only complicated *m*s were seen in the ^{1}H-NMR spectra for H–C(1) and 2 H–C(4) of these compounds. Distinction between *c*- and *t*-**15** and signal assignments were based on their 2D ^{1}H,^{1}H-NOESY data obtained at −85°.

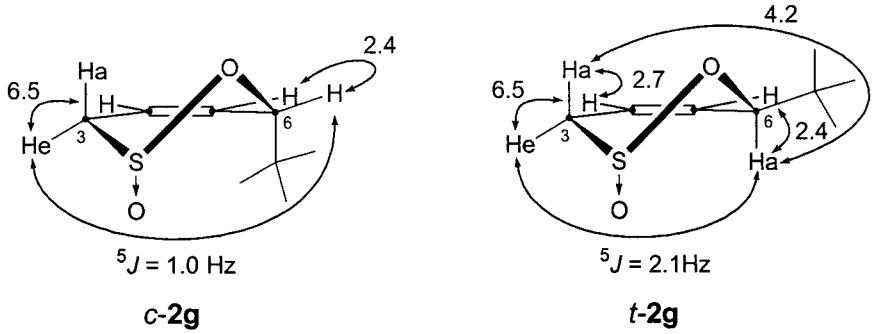

Fig. 4. *Proposed structures and conformations for* cis- *and* trans-*6-(tert-butyl)sultines* **2g** (H,H coupling constants in Hz)

Structures of 6-(acyloxy)sultines **1y** and **1z** were not established unambiguously because of insufficient NMR data. Nevertheless, the coupling constants observed in their ^{1}H-NMR spectra suggested that these sultines adopt similar structures and conformation than those of *c*- and *t*-**2c** for which equilibria of several conformers have been proposed [2a]. Distinction betwen *cis*- and *trans*-sultines **2c**, **2y**, and **2z** relied on 2D ^{1}H,^{1}H-NOESY experiments.

Discussion. – The most surprising result of our exploratory studies is that electron-rich dienes such as 1-alkoxy, 1-(aryloxy)-, 1-thio-, 1-seleno-, 1-cyclopropyl-, and 1-arylbutadiene do not equilibrate with the corresponding sultines at low temperatures, although analogs less reactive towards all kind of dienophiles do add SO_2 in the hetero-*Diels-Alder* mode. These dienes are alkyl-substituted and (*Z*)-1-(acyloxy)butadienes. It is possible that the failure to observe sultines arising from the hetero-*Diels-Alder* additions of SO_2 to electron-rich dienes is due to too low an exothermicity of the [4 + 2] cycloaddition or to too negative an entropy of condensation. Both hypotheses will

have to be tested by further experimentation and, possibly, by high-level calculations. On mixing dienes with SO_2 at low temperature, colors are immediately formed; they vanish once the dienes have reacted with SO_2. These colors are probably due to the formation of charge-transfer complexes between the dienes and SO_2 [32]. The more electronrich the diene is, the deeper the color formed on mixing it with SO_2. It is thus possible that differential solvation effects intervene and affect both the enthalpy and entropy of the equilibria diene + SO_2 = sultines. One is tempted to explain the failure to observe sultine formation with the most electron-rich dienes as being due to specific solvation of the latter by SO_2, which reduces significantly the heat of their hetero-*Diels-Alder* additions. This hypothesis can be tested, in principle, by measuring the heats and entropies of dissolution of dienes and their sultines (or models of them) in solutions containing a large excess of SO_2. No such data is available for closely related systems.

As already demonstrated with (*E*)-piperylene [3], the hetero-*Diels-Alder* addition of SO_2 to (*E*)-1-alkylbutadienes and (*E*)-1-(acyloxy)butadienes are suprafacial and obey the *Alder endo* rule [25]. This affirmation is based on the assumption that the 6-substituted *trans* sultines are more stable than their *cis*-isomers in solution, as predicted by high-level quantum calculations [2b]. To put these conclusions on firmer grounds, X-ray diffraction studies of crystalline sultines are required. This has been possible at the moment for one case only (1*RS*,3*SR*)-1-fluoronaphth[2,1-*d*][2,3]oxathiin 3-oxide, the product of *Diels-Alder* addition of SO_2 to (*Z*)-1-(fluoromethylidene) 1,2,3,4-tetrahydro-2-methylidene naphthalene [29].

The hetero-*Diels-Alder* additions of SO_2 to 1-substituted (*E*)-buta-1,3-dienes are highly regioselective and give exclusively the corresponding 6-substituted sultines. Even after remaining for a prolonged time at equilibrium with their cycloaddents, the 6-substituted sultines were not equilibrated with their 3-substituted isomers. This was the case also with the most reactive system (*E*)-**4a** + SO_2 = *t*-**15** when left at $-60°$ for one week in the presence of CF_3COOH. It appears, therefore, that the activation energy of the hetero-*Diels-Alder* additions of SO_2 to 1-substituted buta-1,2-dienes giving 3-substituted sultines are much higher than those leading to the corresponding 6-substituted sultines. They are higher also than the energy barriers of the corresponding cheletropic additions with SO_2. Alternatively, one can invoke a thermodynamic control that would imply that the 6-substituted sultines are significantly more stable (by at least 2 kcal/mol) than their 3-substituted isomers. This might well be the case for the reactions with (*E*)-1-(acyloxy)buta-1,3-dienes giving 6-(acyloxy)sultines in which a possible enthalpy anomeric effect [2a][33] is expected to stabilize them compared with their 3-(acyloxy)-substituted isomers.

Conclusions. – The 1-substituted (*E*)-butadiene derivatives **1** with Me, Et, *t*-Bu, cyclohexyl and benzyl groups as well as (*E*)-1-(acyloxy) derivatives (AcO, BzO, and (naphthalen-2-ylcarbonyl)oxy) add to SO_2 below $-70°$ in the hetero-*Diels-Alder* mode in the presence of an acidic promoter such as CF_3COOH. These dienes do not undergo the [4 + 2] cycloadditions with SO_2 without acid catalyst, contrary to 1,2-dimethylidenecycloalkanes [1] and (*E*)-1-ethylidene-2-methylidenecyclohexane ((*E*)-**4a**). The uncatalyzed hetero-*Diels-Alder* addition of the latter diene (*E*)-**4a** to SO_2 is at least 60 times more rapid than that of 1,2-dimethylidenecyclohexane. More electron-richer 1,3-dienes such 1-cyclopropyl-, 1-phenyl-, 1-[4-methoxyphenyl)-, 1-(trimethyl-

silyl)-, 1-phenoxy-, 1-(4-chlorophenoxy)-, 1-(4-methoxyphenoxy)-, 1-(4-nitrophenoxy)-, 1-(naphthalen-2-yloxy)-, 1-(methylthio)-, 1-(phenylthio)-, 1-[(4-chlorophenyl)thio], 1-[(4-methoxyphenyl)thio], 1-[(4-nitrophenyl)thio]-, and 1-(phenylseleno)-butadiene did not equilibrate with the corresponding sultines between -100 and $-10°$, in the presence or absence of acidic promoter, but underwent the expected cheletropic additions to give the corresponding 2-substituted sulfolenes. Both (*E*)- and (*Z*)-1-(methoxymethylidene)-2-methylidenecyclohexanes (**4f**) add quickly to SO_2 at $-80°$ in the cheletropic mode exclusively. The failure to observe sultine formation with the most electron-rich 1,3-dienes is a surprise. The reasons for it are unclear at the moment. Perhaps differential solvation effects affect the heat and entropy of the hetero-*Diels-Alder* additions of SO_2 to dienes in excess of SO_2. Based on high-level quantum calculations, the S=O moiety of sultines is assumed to occupy pseudo-axial positions in pseudo-chair conformers. With these hypotheses, all the adducts resulting from the hetero-*Diels-Alder* addition of 1-substituted (*E*)-butadienes under conditions of kinetic control are 6-substituted *cis*-sultines that are then equilibrated with their more stable 6-substituted *trans*-stereoisomers, in agreement with the *Alder endo* rule. These cycloadditions are highly regioselective, and the 6-substituted sultines could not be equilibrated with their 3-substituted isomers.

Experimental Part

General. See [1][34]. ^{17}O-NMR Spectra: *Bruker* spectrometers *DPX-400* and *DRX-400* at 54.2 MHz, and *AMX600* at 81.3 MHz, with 5-mm tubes, see [26].

*(*E*)-1-(*tert*-Butyl)buta-1,3-diene* (=*(3*E*)-5,5-Dimethylhexa-1,3-diene*; (*E*)-**1g**). Obtained in 40% yield, according to [10]. Colorless liquid. UV (MeCN): 226 (10500). IR (film): 2960, 2865, 1780, 1650, 1605, 1475, 1485, 1365, 1265, 1210, 1005, 955, 895, 650. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.33 (*ddd*, $^3J(3,4) = 16.1, 10.2$, $^3J(2,3) = 10.2$, H–C(3)); 6.00 (*dd*, $^3J(1,2) = 15.5$, $^3J(2,3) = 10.2$, H–C(2)); 5.75 (*d*, $^3J(1,2) = 15.5$, H–C(1)); 5.13 (*dm*, $^3J(3,4) = 10.2$, H–C(4)); 4.98 (*dm*, $^3J(3,4) = 16.1$, H–C(4)); 1.05 (*s*, *t*-Bu). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 146.3 (*d*, ^1J(C,H) = 148, C(1)); 137.7 (*d*, ^1J(C,H) = 156, C(3)); 125.7 (*d*, ^1J(C,H) = 149, C(2)); 114.7 (*t*, ^1J(C,H) = 154, C(4)); 33.1 (*s*, Me_3C); 29.4 (*q*, ^1J(C,H) = 134, 3 C, Me_3C).

*10:1 Mixture of (*E*)- and (*Z*)-1-Cyclohexylbuta-1,3-diene* (**1h**). Obtained in 53% yield, according to [11]. Colorless oil. UV (MeCN): 231 (5000). IR (film): 2925, 2850, 1720, 1650, 1605, 1450, 1310, 1260, 1145, 1005, 895, 845. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1h**: 6.31 (*ddd*, $^3J(3,4) = 16.9$, 10.1, $^3J(2,3) = 10.2$, H–C(3)); 6.03 (*dd*, $^3J(1,2) = 15.3$, $^3J(2,3) = 10.2$, H–C(2)); 5.67 (*dd*, $^3J(1,2) = 15.3$, ^3J(1,Chx) = 6.9, H–C(1)); 5.10 (*dm*, $^3J(3,4) = 16.9$, H–C(4)); 4.96 (*dm*, $^3J(3,4) = 10.1$, H–C(4)); 2.20–1.00 (*m*, 11 H, Chx); (*Z*)-**1h**: 6.66 (*ddd*, $^3J(3,4) = 16.8$, 10.8, $^3J(2,3) = 10.8$, H–C(3)); 6.02 (*dd*, $^3J(1,2) = 10.9$, $^3J(2,3) = 10.8$, H–C(2)); 5.31 (*dd*, $^3J(1,2) = 10.9$, ^3J(1,Chx) = 10.8, H–C(1)); 5.23 (*dm*, $^3J(3,4) = 16.8$, H–C(4)); 5.07 (*dm*, $^3J(3,4) = 10.8$, H–C(4)); 2.20–1.00 (*m*, 11 H, Chx). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1h**: 141.1 (*d*, ^1J(C,H) = 148, C(3)); 138.8 (*d*, ^1J(C,H) = 152, C(1)); 128.3 (*d*, ^1J(C,H) = 150, C(2)); 114.6 (*t*, ^1J(C,H) = 159, C(4)); 40.6 (*d*, ^1J(C,H) = 125, CH(Chx)); 32.7 (*t*, ^1J(C,H) = 126, 2 C(Chx)); 27.9 (*t*, ^1J(C,H) = 127, 1 C(Chx)); 25.8 (*t*, ^1J(C,H) = 125, 2 C(Chx)); (*Z*)-**1h**: 138.8 (*d*, ^1J(C,H) = 151, C(3)); 132.5 (*d*, ^1J(C,H) = 151, C(1)); 127.2 (*d*, ^1J(C,H) = 153, C(2)); 116.6 (*t*, ^1J(C,H) = 160, C(4)); 40.6 (*d*, ^1J(C,H) = 125, CH(Chx)); 32.7 (*t*, ^1J(C,H) = 126, 2 C(Chx)); 27.9 (*t*, ^1J(C,H) = 127, 1 C(Chx)); 25.8 (*t*, ^1J(C,H) = 125, 2 C(Chx)).

*6:1 Mixture of (*E*)- and (*Z*)-1-Benzylbuta-1,3-diene* (=*(3*E*)- and (3*Z*)-5-Phenylpenta-1,3-diene*; **1i**). BuLi (1.6M in hexane; 4.5 ml, 7.2 mmol) was added dropwise to a stirred soln. of allyldiphenylphosphine oxide (1.8 g, 7.4 mmol) in THF (25 ml) and hexamethylphosphoric triamide (HMPA; 3 ml) at $-78°$. The resulting soln. was stirred at $-78°$ for 10 min. Phenylacetaldehyde (740 mg, 6.2 mmol) in dry THF (5 ml) was added within 15 min, and the resulting soln. was stirred at $-78°$ for 10 min, at 0° for 30 min, and at 25° for 20 h. THF was evaporated, pentane (25 ml) added to the residue, and the precipitate filtered off (*Celite*). The filtrate was evaporated and the residue purified by FC (petroleum ether): 150 mg (14%) of **1i**. Colorless oil (see [12]). UV (MeCN): 278 (1000), 240 (3400), 200 (2200). IR (film): 3030, 2925, 1650, 1605, 1455, 1430, 1305, 1075, 1030, 1000, 950, 900,

745. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1i**: 7.35–7.20 (*m*, 5 arom. H); 6.38 (*ddd*, $^3J(3,4) = 17.0$, 10.2, $^3J(2,3) = 10.2$, H–C(3)); 6.15 (*dd*, $^3J(1,2) = 16.8$, $^3J(2,3) = 10.2$, H–C(2)); 5.89 (*ddd*, $^3J(1,2) = 16.8$, $^3J(1,Bn) = 6.9$, H–C(1)); 5.17 (*d*, $^3J(3,4) = 17.0$, H–C(4)); 5.01 (*d*, $^3J(3,4) = 10.2$, H–C(4)); 3.46 (*d*, $^3J(1,Bn) = 6.9$, PhCH_2); (*Z*)-**1i**: 7.35–7.20 (*m*, 5 arom. H); 6.81 (*ddd*, $^3J(3,4) = 16.9$, 9.8, $^3J(2,3) = 11.0$, H–C(3)); 6.18 (*m*, H–C(2)); 5.66 (*ddd*, $^3J(1,2) = 8.0$, $^3J(1,Bn) = 7.7$, H–C(1)); 5.32 (*d*, $^3J(3,4) = 16.9$, H–C(4)); 5.21 (*d*, $^3J(3,4) = 9.8$, H–C(4)); 3.58 (*d*, $^3J(1,H(Bn)) = 7.7$, PhCH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1i**: 140.1 (*s*, arom. C); 136.9 (*d*, $^1J(C,H) = 157$, C(3)); 133.4 (*d*, $^1J(C,H) = 147$, C(1)); 132.1 (*d*, $^1J(C,H) = 147$, C(2)); 128.6 (*d*, $^1J(C,H) = 157$, 2 arom. C); 128.4 (*d*, $^1J(C,H) = 158$, 2 arom. C); 126.1 (*d*, $^1J(C,H) = 160$, arom. C); 115.7 (*t*, $^1J(C,H) = 155$, C(4)); 38.9 (*t*, $^1J(C,H) = 127$, Ph*C*H$_2$); (*Z*)-**1i**: detected signals 131.9, 130.6, 129.9 (3 C); 118.0 (*t*, $^1J(C,H) = 159$, C(4)); 33.9 (Ph*C*H$_2$). CI-MS (NH_3): 145 (4, $M^{+\bullet}$), 129 (100), 115 (35), 103 (7), 91 (21).

*5:1 Mixture of (*E*)- and (Z)-1-Cyclopropylbuta-1,3-diene* (**1j**). By syringe, 4-bromo-1-cyclopropylbut-1-ene [14] (1.0 g, 10.6 mmol) was added to DBU (5 ml, 5.1 g, 33.5 mmol) heated to 150°. After 5 min, the mixture was distilled at 35–40°/10 Torr (*Vigreux* column) yielding 240 mg (30%) of (*E*)/(*Z*)-**1j** 5:1. B.p. 107–109°. Colorless liquid [35]. UV (MeCN): 235 (4100). IR (film): 3085, 3010, 1650, 1420, 1200, 1050, 1000, 965, 945, 895, 860, 810. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1j**: 6.29 (*ddd*, $^3J(3,4) = 15.5$, 10.5, $^3J(2,3) = 10.5$, H–C(3)); 6.16 (*dd*, $^3J(1,2) = 14.9$, $^3J(2,3) = 10.5$, H–C(2)); 5.25 (*dd*, $^3J(1,2) = 14.9$, $^3J(1,1') = 9.0$, H–C(1)); 5.07 (*dm*, $^3J(3,4) = 15.5$, H–C(4)); 4.92 (*dm*, $^3J(3,4) = 10.5$, H–C(4)); 1.44 (*m*, H–C(1′)); 0.78 (*m*, 2 H); 0.43 (*m*, 2 H); (*Z*)-**1j**: 6.81 (*ddd*, $^3J(3,4) = 16.9$, 10.2, $^3J(2,3) = 11.2$, H–C(3)); 5.97 (*dd*, $^3J(2,3) = 11.2$, $^3J(1,2) = 10.8$, H–C(2)); 5.14 (*dm*, $^3J(3,4) = 16.9$, H–C(4)); 5.11 (*dm*, $^3J(3,4) = 10.2$, H–C(4)); 4.82 (*dd*, $^3J(1,2) = 10.8$, $^3J(1,1') = 9.5$, H–C(1)); 1.77 (*m*, H–C(1′)); 0.78 (*m*, 2 H); 0.43 (*m*, 2 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1j**: 139.0 (*d*, $^1J(C,H) = 151$, C(1)); 136.9 (*d*, $^1J(C,H) = 153$, C(3)); 128.6 (*d*, $^1J(C,H) = 148$, C(2)); 113.7 (*t*, $^1J(C,H) = 159$, C(4)); 13.9 (*d*, $^1J(C,H) = 158$, C(1′)); 7.21 (*t*, $^1J(C,H) = 162$, C(2′), C(3′)); (*Z*)-**1j**: 136.9 (*d*, $^1J(C,H) = 153$, C(1)); 132.6 (*d*, $^1J(C,H) = 152$, C(3)); 127.5 (*d*, $^1J(C,H) = 149$, C(2)); 116.2 (*t*, $^1J(C,H) = 155$, C(4)); 10.3 (*d*, $^1J(C,H) = 160$, C(1′)); 7.45 (*t*, $^1J(C,H) = 162$, C(2′), C(3′)). CI-MS (NH_3): 95 (35, $[M+1]^+$), 79 (100).

*(*E*)-1-Phenylbuta-1,3-diene* ((*E*)-**1k**). Prepared according to [15][36]. Colorless oil. UV (MeCN): 278 (24200), 232 (8800), 225 (12300), 219 (12500), 209 (13800), 197 (10300). IR (film): 3025, 1600, 1495, 1450, 1000, 945, 890, 755, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42 (*m*, 2 arom. H); 7.32 (*m*, 2 arom. H); 7.22 (*m*, arom. H); 6.81 (*dd*, $^3J(1,2) = 16.8$, $^3J(2,3) = 10.5$, H–C(2)); 6.58 (*d*, $^3J(1,2) = 16.8$, H–C(1)); 6.52 (*ddd*, $^3J(3,4) = 16.8$, 9.9, $^3J(2,3) = 10.5$, H–C(3)); 5.35 (*dm*, $^3J(3,4) = 16.8$, H–C(4)); 5.19 (*dm*, $^3J(3,4) = 9.9$, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 137.3 (*d*, $^1J(C,H) = 153$, C(3)); 137.2 (*s*, arom. C); 132.0 (*d*, $^1J(C,H) = 148$, C(1)); 129.7 (*d*, $^1J(C,H) = 148$, C(2)); 128.7 (*d*, $^1J(C,H) = 160$, arom. C); 127.7 (*d*, $^1J(C,H) = 161$, arom. C); 126.5 (*d*, $^1J(C,H) = 158$, arom. C); 117.7 (*t*, $^1J(C,H) = 151$, C(4)). CI-MS (NH_3): 131 (100, $[M+1]^+$), 115 (17), 103 (50), 77 (84).

*4:1 Mixture of (*E*)- and (Z)-1-(4-Methoxyphenyl)buta-1,3-diene* (**1l**). A mixture of 1-(4-methoxyphenyl)-but-3-en-1-ol [16] (3.6 g, 20 mmol), $KHSO_4$ (0.36 g, 2.6 mmol), and hydroquinone (0.1 g) was heated to 80°. After stirring at 80° for 30 min, the mixture was cooled to 20° and the mixture distilled at 80°/0.5 Torr (*Vigreux* column). The distillate was diluted in pentane (15 ml) and dried ($MgSO_4$). Solvent evaporation gave 1.7 g (51%) of (*E*)/(*Z*)-**1l** 4:1. White solid. M.p. 45–46°. UV (MeCN): 291 (13500), 285 (13500), 256 (1300), 225 (12300). IR (KBr): 3030, 2910, 2835, 1605, 1510, 1245, 1175, 1035, 825, 640. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1l**. 7.40 (*m*, 2 arom. H); 6.90 (*m*, 2 arom. H); 6.76 (*dd*, $^3J(1,2) = 14.9$, $^3J(2,3) = 10.9$, H–C(2)); 6.60 (*d*, $^3J(1,2) = 14.9$, H–C(1)); 6.57 (*ddd*, $^3J(3,4) = 15.4$, 9.2, $^3J(2,3) = 10.9$, H–C(3)); 5.37 (*d*, $^3J(3,4) = 15.4$, H–C(4)); 5.21 (*d*, $^3J(3,4) = 9.2$, H–C(4)); 3.84 (*s*, MeO); (*Z*)-**1l**: 7.35 (*m*, 2 arom. H); 7.00 (*ddd*, $^3J(3,4) = 16.3$, 9.3, $^3J(2,3) = 11.4$, H–C(3)); 6.95 (*m*, 2 arom. H); 6.48 (*d*, $^3J(1,2) = 11.3$, H–C(1)); 6.28 (*dd*, $^3J(2,3) = 11.4$, $^3J(1,2) = 11.3$, H–C(2)); 5.44 (*d*, $^3J(3,4)) = 16.3$, H–C(4)); 5.29 (*d*, $^3J(3,4) = 9.3$, H–C(4)); 3.84 (*s*, MeO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1l**: 159.2 (*s*, arom. C); 137.3 (*d*, $^1J(C,H) = 155$, C(3)); 132.3 (*d*, $^1J(C,H) = 146$, C(1)); 129.8 (*s*, arom. C); 127.7 (*d*, $^1J(C,H) = 158$, arom. C); 127.5 (*d*, $^1J(C,H) = 160$, C(2)); 116.4 (*t*, $^1J(C,H) = 155$, C(4)); 114.0 (*d*, $^1J(C,H) = 161$, arom. C); 55.0 (*q*, $^1J(C,H) = 144$, MeO); (*Z*)-**1l**: 158.6 (*s*, arom. C); 133.2 (*d*, $^1J(C,H) = 153$, C(3)); 130.2 (*d*, $^1J(C,H) = 158$, arom. C); 129.9 (*d*, $^1J(C,H) = 155$, C(1)); 129.2 (*d*, $^1J(C,H) = 157$, C(2)); 128.2 (*s*, arom. C); 118.8 (*t*, $^1J(C,H) = 155$, C(4)); 113.6 (*d*, $^1J(C,H) = 159$, arom. C); 55.0 (*q*, $^1J(C,H) = 144$, MeO). CI-MS (NH_3): 160 (100, $M^{+\bullet}$), 144 (44), 129 (63), 115 (82), 102 (12), 91 (50).

*(*E*)-1-(Trimethylsilyl)buta-1,3-diene* ((*E*)-**1m**). The tetrahydro-2*H*-pyran-2-yl ether derived from prop-2-yn-1-ol was converted [37] into (*E*)-**1m** according to [17]. Colorless liquid. UV (MeCN): 236 (8900). IR (film): 2965, 1815, 1570, 1250, 1125, 1010, 905, 865, 840, 690, 615. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.53 (*dd*, $^3J(1,2) = 18.2$, $^3J(2,3) = 10.1$, H–C(2)); 6.36 (*dddd*, $^3J(3,4) = 16.8$, 10.0, $^3J(2,3) = 10.1$, H–C(3)); 5.89 (*d*, $^3J(1,2) = 18.2$, H–C(1)); 5.24 (*dm*, $^3J(3,4) = 16.8$, H–C(4)); 5.13 (*dm*, $^3J(3,4) = 10.0$, H–C(4)); 0.11 (*s*, Me_3Si). ^{13}C-NMR

(100.6 MHz, $CDCl_3$): 144.5 (C(2)); 139.8 (C(3)); 134.8 (C(1)); 117.6 (C(4)); – 1.4 (3 C, Me_3Si). CI-MS (NH_3): 126 (2, $M^{+\cdot}$), 111 (21), 90 (100).

(Z)-1,4-Di(phenoxy)but-2-ene (**7n**). A mixture of PhOH (21 mmol) and KOH (1.2 g, 21 mmol) was heated under reflux in EtOH (30 ml) for 15 min. Then (*Z*)-1,4-dichlorobut-2-ene (**5**; 1.4 g, 11 mmol) was added slowly under stirring at 0°. After stirring at 0° for 6 h, then at 20° for 15 h, the precipitate was filtered off (*Celite*) and washed with EtOH (5 ml, twice). It was then dissolved in CH_2Cl_2 (60 ml) and the soln. washed with H_2O (3 × 20 ml) and dried ($MgSO_4$). Solvent evaporation gave 3.8 g (75%) of **7n**. White solid. M.p. 31–32°. UV (MeCN): 276 (4500), 269 (5200), 225 (6800), 199 (4800). IR (KBr): 1600, 1495, 1300, 1240, 1170, 1030, 750, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35 (*m*, 4 arom. H); 7.34 (*m*, 6 arom. H); 5.99 (*t*, ^3J = 3.5, H–C(2), H–C(3)); 4.73 (*d*, ^3J = 3.5, CH_2(1), CH_2(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.0 (*s*, arom. C); 129.5 (*d*, ^1J(C,H) = 159, arom. C); 128.5 (*d*, ^1J(C,H) = 164, C(2), C(3)); 121.0 (*d*, ^1J(C,H) = 161, arom. C); 114.6 (*d*, ^1J(C,H) = 159, arom. C); 64.0 (*t*, ^1J(C,H) = 137, C(1), C(4)). CI-MS (NH_3): 258 (100, $[M+18]^+$), 241 (26, $[M+1]^+$), 147 (30), 131 (1), 107 (3), 91 (9). Anal. calc. for $C_{16}H_{16}O_2$ (240.30): C 79.97, H 6.71; found: C 79.88, H 6.68.

(Z)-1,4-Bis(4-chlorophenoxy)but-2-ene (**7o**). As described for **7n**, with 4-chlorophenol (12.9 g, 0.1 mol), KOH (5.6 g, 0.1 mol), and **5** (4.8 g, 38 mmol): 8.0 g (68%) of **7o**. White solid. M.p. 36–38°. UV (MeCN): 280 (4800), 230 (17400), 204 (12400), 187 (2300). IR (KBr): 1595, 1490, 1285, 1235, 1170, 1095, 1005, 825, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.24 (*m*, 4 arom. H); 6.85 (*m*, 4 arom. H); 5.92 (*t*, ^3J = 3.6, H–C(2), H–C(3)); 4.66 (*d*, ^3J = 3.6, CH_2(1), CH_2(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 156.9 (*s*, arom. C); 129.5 (*d*, ^1J(C,H) = 164, arom. C); 128.4 (*d*, ^1J(C,H) = 165, 2 C, C(2), C(3)); 126.0 (*s*, arom. C); 115.9 (*d*, ^1J(C,H) = 161, arom. C); 64.5 (*t*, ^1J(C,H) = 144, C(1), C(4)). CI-MS (NH_3): 326 (100, $[M+18]^+$), 308 (39, $M^{+\cdot}$), 181 (44), 146 (17), 99 (13).

(Z)-1,4-Bis(4-methoxyphenoxy)but-2-ene (**7p**). As described for **7n**, with 4-methoxyphenol (2 g, 16 mmol), KOH (0.87 g, 16 mmol), and **5** (0.74 g, 5.9 mmol): 1.2 g (70%) of **7p**. Brownish solid. M.p. 48–52°. UV (MeCN): 296 (8600), 289 (9500), 226 (26200), 199 (52600). IR (KBr): 2950, 2830, 1510, 1455, 1295, 1230, 1110, 1035, 825, 770. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.86 (*m*, 8 arom. H); 5.93 (*t*, ^3J = 3.5, H–C(2), H–C(3)); 4.63 (*d*, ^3J = 3.5, CH_2(1), CH_2(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.0, 152.5 (2*s*, 2 arom. C); 128.6 (*d*, ^1J(C,H) = 164, C(2), C(3)); 115.7 (*d*, ^1J(C,H) = 160, arom. C); 144.6 (*d*, ^1J(C,H) = 159, arom. C); 64.8 (*t*, ^1J(C,H) = 137, C(1), C(4)); 55.7 (*q*, ^1J(C,H) = 143, MeO). CI-MS (NH_3): 300 (18, $M^{+\cdot}$), 177 (71), 123 (100), 109 (11), 95 (32). Anal. calc. for $C_{18}H_{20}O_4$ (300.35): C 71.98. H 6.71; found: C 71.91, H 6.82.

(Z)-1,4-Bis(4-nitrophenoxy)but-2-ene (**7q**). A mixture of 4-nitrophenol (6.7 g, 48 mmol), KOH (2.7 g, 48 mmol), and [18]crown-6 (0.1 g) in acetone (100 ml) was heated under reflux for 15 min. Then **5** (2.0 g, 2.4 ml, 16 mmol) was added slowly under stirring. After heating under reflux for 24 h, the solvent was evaporated and the residue dissolved in AcOEt (100 ml). The org. phase was washed in 1N NaOH (3 × 30 ml), dried ($MgSO_4$), and evaporated: 3.8 g (95%) of **7q**. White solid. M.p. 133–134°. UV (MeCN): 306 (27900), 226 (17800), 200 (25300), 194 (21300). IR (KBr): 1590, 1505, 1450, 1330, 1260, 1170, 1105, 1025, 850, 750, 650, 495. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.20 (*m*, 4 arom. H); 6.98 (*m*, 4 arom. H); 6.01 (*t*, ^3J = 3.6, H–C(2), H–C(3)); 4.80 (*d*, ^3J = 3.6, CH_2(1), CH_2(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 163.2 (*s*, arom. C); 141.8 (*s*, arom. C); 128.1 (*d*, ^1J(C,H) = 162, C(2), C(3)); 126.0 (*d*, ^1J(C,H) = 168, arom. C); 114.6 (*d*, ^1J(C,H) = 164, arom. C); 64.7 (*t*, ^1J(C,H) = 137, 2 C, C(1), C(4)). CI-MS (NH_3): 348 (100, $[M+18]^+$), 331 (2, $[M+1]^+$), 301 (3), 191 (4), 131 (5). Anal. calc. for $C_{16}H_{14}N_2O_6$ (330.30): C 58.18, H 4.27; found: C 58.22, H 4.15.

(Z)-1,4-Bis(naphthalen-2-yloxy)but-2-ene (**7r**). As described for **7n**, with naphthalen-2-ol (14.4 g, 0.1 mol), KOH (5.6 g, 0.1 mol), and **5** (4.8 g, 38 mmol): 10.4 g (80%) of **7r**. White solid. M.p. 77–80°. UV (MeCN): 327 (6300), 313 (5400), 270 (14800), 232 (47900). IR (KBr): 2920, 1625, 1595,1460, 1390, 1255, 1215, 1180, 1005, 840, 750, 470. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.81–7.20 (*m*, 14 arom. H); 6.08 (*t*, ^3J = 3.5, H–C(2), H–C(3)); 4.88 (*d*, ^3J = 3.5, CH_2(1), CH_2(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 156.4 (*s*, arom. C); 134.5 (*s*, arom. C); 129.6 (*d*, ^1J(C,H) = 159, arom. C); 129.1 (*s*, arom. C); 128.6 (*d*, ^1J(C,H) = 165, C(2), C(3)); 127.6 (*d*, ^1J(C,H) = 164, arom. C); 126.8 (*d*, ^1J(C,H) = 159, arom. C); 126.4 (*d*, ^1J(C,H) = 160, arom. C); 123.8 (*d*, ^1J(C,H) = 158, arom. C); 118.9 (*d*, ^1J(C,H) = 161, arom. C); 106.9 (*d*, ^1J(C,H) = 158, arom. C); 64.2 (*t*, ^1J(C,H) = 144, C(1), C(4)). CI-MS (NH_3): 358 (30, $[M+18]^+$), 341 (100, $[M+1]^+$), 197 (78), 179 (8), 115 (47). Anal. calc. for $C_{24}H_{20}O_2$ (340.42): C 84.68, H 5.92; found: C 84.52, H 5.91.

(E)-1-Phenoxybuta-1,3-diene ((*E*)-**1n**). BuLi (1.6M in hexane; 10 ml, 16 mmol) was added dropwise to a soln. of **7n** (2 g, 8.3 mmol) in dry THF (50 ml) at – 78°. The mixture was stirred at – 78° for 0.5 h, then it was gradually warmed up to 25° and stirred for another 2 h. Et_2O (50 ml) was added, the org. phase washed with brine (3 × 30 ml), dried ($MgSO_4$), and evaporated, and the residue purified by FC (AcOEt/petroleum ether 1:9): 950 mg (78%) of (*E*)-**1n**. Colorless oil. UV (MeCN): 245 (17800), 205 (10900), 187 (2700). IR (film): 3045, 1655, 1590, 1490, 1420, 1230, 1175, 1115, 995, 920, 890, 755, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38 (*m*, 2 arom. H); 7.12 (*m*, arom. H); 7.07 (*m*, 2 arom. H); 6.82 (*d*, ^3J(1,2) = 12.0, H–C(1)); 6.38 (*ddd*, ^3J(3,4) = 16.9, 8.9, ^3J(2,3) = 11.2,

H–C(3)); 6.06 (*dd*, $^3J(1,2) = 12.0$, $^3J(2,3) = 11.2$, H–C(2)); 5.19 (*dm*, $^3J(3,4) = 16.9$, H–C(4)); 5.04 (*dm*, $^3J(3,4) = 8.9$, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 156.9 (*s*, arom. C); 146.2 (*d*, ^1J(C,H) = 181, C(1)); 132.1 (*d*, ^1J(C,H) = 152, C(3)); 129.6 (*d*, ^1J(C,H) = 165, arom. C); 123.2 (*d*, ^1J(C,H) = 160, arom. C); 116.9 (*d*, ^1J(C,H) = 161, arom. C); 114.5 (*t*, ^1J(C,H) = 155, C(4)); 114.3 (*d*, ^1J(C,H) = 154, C(2)). CI-MS (NH_3): 146 (100, $M^{+\bullet}$), 131 (33), 117 (58), 105 (10), 91 (54).

*3.2 : 1 Mixture of (*E*)- and (*Z*)-1-(4-Chlorophenoxy)buta-1,3-diene* (**1o**). As described for (*E*)-**1n**, with **7o** (1 g, 3.2 mmol): 0.35 g (63%) of **1o**. Colorless oil. UV (MeCN): 251 (13000), 212 (9200). IR (film): 2960, 1660, 1590, 1485, 1430, 1240, 1090, 1010, 995, 920, 830, 655. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1o**: 7.28 (*m*, 2 arom. H); 6.96 (*m*, 2 arom. H); 6.72 (*d*, $^3J(1,2) = 11.8$, H–C(1)); 6.31 (*ddd*, $^3J(3,4) = 16.9$, 10.3, $^3J(2,3) = 11.8$, H–C(3)); 6.02 (*dd*, $^3J(1,2) = 11.8$, $^3J(2,3) = 11.8$, H–C(2)); 5.17 (*dm*, $^3J(3,4) = 16.9$, H–C(4)); 5.02 (*dm*, $^3J(3,4) = 10.3$, H–C(4)); (*Z*)-**1o**: 7.27 (*m*, 2 arom. H); 6.96 (*m*, 2 arom. H); 6.81 (*ddd*, $^3J(3,4) = 9.5$, 17.2, $^3J(2,3) = 10.9$, H–C(3)); 6.33 (*d*, $^3J(1,2) = 6.1$, H–C(1)); 5.51 (*dd*, $^3J(2,3) = 10.9$, $^3J(1,2) = 6.1$, H–C(2)); 5.25 (*dm*, $^3J(3,4) =$ 17.2, H–C(4)); 5.09 (*dm*, $^3J(3,4) = 9.5$, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1o**: 155.4 (*s*, arom. C); 145.6 (*d*, ^1J(C,H) = 182, C(1)); 131.8 (*d*, ^1J(C,H) = 153, C(3)); 129.6 (*d*, ^1J(C,H) = 166, arom. C); 128.2 (*s*, arom. C); 118.2 (*d*, ^1J(C,H) = 163, arom. C); 115.2 (*t*, ^1J(C,H) = 154, C(4)); 115.0 (*d*, ^1J(C,H) = 152, C(2)); (*Z*)-**1o**: 155.8 (*s*, arom. C); 140.7 (*d*, ^1J(C,H) = 180, C(1)); 129.5 (*d*, ^1J(C,H) = 165, arom. C); 129.0 (*d*, ^1J(C,H) = 152, C(3)); 128.0 (*s*, arom. C); 117.7 (*d*, ^1J(C,H) = 163, arom. C); 116.6 (*t*, ^1J(C,H) = 153, C(4)); 112.9 (*d*, ^1J(C,H) = 150, C(2)). CI-MS (NH_3): 197 (50), 180 (27), 169 (6), 145 (18), 128 (73), 111 (34), 99 (47), 85 (100).

*12 : 1 Mixture of (*E*)- and (*Z*)-1-(4-Methoxyphenoxy)buta-1,3-diene* (**1p**). As described for (*E*)-**1n**, with **7p** (0.2 g, 0.7 mmol): 60 mg (52%) of **1p**. Colorless oil. UV (MeCN): 247 (54300), 215 (43700). IR (film): 2835, 1655, 1505, 1465, 1440, 1225, 1175, 1115, 1035, 825. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1p**: 6.97 (*m*, 2 arom. H); 6.88 (*m*, 2 arom. H); 6.75 (*d*, $^3J(1,2) = 8.8$, H–C(1)); 6.30 (*ddd*, $^3J(3,4) = 13.0$, 7.9, $^3J(2,3) = 8.6$, H–C(3)); 5.97 (*dd*, $^3J(1,2) = 8.8$, $^3J(2,3) = 8.6$, H–C(2)); 5.18 (*dm*, $^3J(3,4) = 13.0$, H–C(4)); 5.03 (*dm*, $^3J(3,4) = 7.9$, H–C(4)); 3.90 (*s*, MeO); (*Z*)-**1p**: 6.97 (*m*, 2 arom. H); 6.88 (*m*, 2 arom. H); 6.84 (*ddd*, $^3J(3,4) = 17.3$, 10.4, $^3J(2,3) = 10.9$, H–C(3)); 6.30 (*d*, $^3J(1,2) = 6.1$, H–C(1)); 5.47 (*dd*, $^3J(2,3) = 10.9$, $^3J(1,2) = 6.1$, H–C(2)); 5.22 (*dm*, $^3J(3,4) =$ 17.3, H–C(4)); 5.06 (*dm*, $^3J(3,4) = 10.4$, H–C(4)); 3.90 (*s*, MeO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*Z*)-**1p**: 155.6 (*s*, arom. C); 150.6 (*s*, arom. C); 147.6 (*d*, ^1J(C,H) = 181, C(1)); 132.2 (*d*, ^1J(C,H) = 152, C(3)); 118.4 (*d*, ^1J(C,H) = 160, arom. C); 114.6 (*d*, ^1J(C,H) = 161, arom. C); 114.0 (*t*, ^1J(C,H) = 158, C(4)); 113.1 (*d*, ^1J(C,H) = 160, C(2)); 55.6 (*q*, ^1J(C,H) = 135, MeO); (*Z*)-**1p**: 155.6 (*s*, arom. C); 150.6 (*s*, arom. C); 142.4 (*d*, ^1J(C,H) = 181, C(1)); 129.3 (*d*, ^1J(C,H) = 158, C(3)); 115.9 (*d*, ^1J(C,H) = 161, arom. C); 115.3 (*t*, ^1J(C,H) = 158, C(4)); 114.7 (*d*, ^1J(C,H) = 161, arom. C); 111.2 (*d*, ^1J(C,H) = 160, C(2)); 55.6 (*q*, ^1J(C,H) = 135, MeO). CI-MS (NH_3): 176 (100, $M^{+\bullet}$), 159 (69), 144 (31), 124 (80), 105 (55), 91 (30).

*3 : 1 Mixture of (*E*)- and (*Z*)-1-(4-Nitrophenoxy)buta-1,3-diene* (**1q**). BuLi (1.6M in hexane; 3.8 ml, 6.0 mmol) was added slowly under stirring to a soln. of tetramethylpiperidine (0.85 g, 1 ml, 6.0 mmol) in dry THF (30 ml) at 0° (flame-dried flask). After 15 min at 0°, the soln. was added slowly *via* a syringe to **7q** (1 g, 3.0 mmol) in dry THF (50 ml) cooled to −15°. The mixture was then gradually warmed up to 25° and stirred at this temp. for 2 h. Et_2O (30 ml) was added to the dark soln. The org. phase was washed with brine (3 × 30 ml), dried ($MgSO_4$), and evaporated. FC (AcOEt/pentane 1:8) gave 100 mg (18%) of **1q**. Yellow oil. UV (MeCN): 313 (22800), 231 (34000), 203 (26000). IR (film): 2930, 2860, 1655, 1610, 1590, 1520, 1490, 1345, 1255, 1115, 850, 750, 630, 615, 600. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1q**: 8.22 (*m*, 2 arom. H); 7.11 (*m*, 2 arom. H); 6.81 (*d*, $^3J(1,2) = 11.9$, H–C(1)); 6.35 (*ddd*, $^3J(3,4) = 16.7$, 10.3, $^3J(2,3) = 10.6$, H–C(3)); 6.17 (*dd*, $^3J(1,2) = 11.9$, $^3J(2,3) = 10.6$, H–C(2)); 5.26 (*dm*, $^3J(3,4) = 16.7$, H–C(4)); 5.12 (*dm*, $^3J(3,4) = 10.3$, H–C(4)); (*Z*)-**1q**: 8.22 (*m*, 2 arom. H); 7.11 (*m*, 2 arom. H); 6.79 (*ddd*, $^3J(3,4) = 17.2$, 11.9, $^3J(2,3) = 10.1$, H–C(3)); 6.44 (*d*, $^3J(1,2) =$ 6.0, H–C(1)); 5.67 (*dd*, $^3J(2,3) = 10.1$, $^3J(1,2) = 6.0$, H–C(2)); 5.31 (*dm*, $^3J(3,4) = 17.2$, H–C(4)); 5.16 (*dm*, $^3J(3,4) = 11.9$, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1q**: 161.5 (*s*, arom. C); 143.2 (*d*, ^1J(C,H) = 183, C(1)); 142.9 (*s*, arom. C); 131.1 (*d*, ^1J(C,H) = 154, C(3)); 125.9 (*d*, ^1J(C,H) = 169, arom. C); 117.8 (*d*, ^1J(C,H) = 158, C(2)); 117.1 (*t*, ^1J(C,H) = 158, C(4)); 116.3 (*d*, ^1J(C,H) = 169, arom. C); (*Z*)-**1q**: 161.7 (*s*, arom. C); 143.0 (*s*, arom. C); 138.8 (*d*, ^1J(C,H) = 189, C(1)); 128.4 (*d*, ^1J(C,H) = 152, C(3)); 125.9 (*d*, ^1J(C,H) = 169, arom. C); 118.0 (*t*, ^1J(C,H) = 157, C(4)); 116.1 (*d*, ^1J(C,H) = 168, arom. C); 115.4 (*d*, ^1J(C,H) = 149, C(2)). CI-MS (NH_3): 191 (48, $M^{+\bullet}$), 174 (14), 139 (50), 109 (100), 93 (47), 81 (29).

*(*E*)-1-(Naphthalen-2-yloxy)buta-1,3-diene* ((*E*)-**1r**). As described for (*E*)-**1n**, with **7r** (0.1 g, 0.3 mmol): 8 mg (26%) of (*E*)-**1r**. Yellowish solid. M.p. 40–42°. UV (MeCN): 245 (21400). IR (KBr): 2930, 1655, 1630, 1595, 1510, 1465, 1440, 1255, 1215, 1175, 1130, 1095, 995, 850, 820, 750. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.81 (*m*, 2 arom. H); 7.78 (*m*, arom. H); 7.45 (*m*, arom. H); 7.43 (*m*, arom. H); 7.28 (*m*, arom. H); 7.22 (*m*, arom. H); 6.92 (*d*, $^3J(1,2) = 12.0$, H–C(1)); 6.39 (*ddd*, $^3J(3,4) = 16.9$, 10.3, $^3J(2,3) = 11.4$, H–C(3)); 6.10 (*dd*, $^3J(1,2) = 12.0$,

$^3J(2,3) = 11.4$, H–C(2)); 5.19 (*dm*, $^3J(3,4) = 16.9$, H–C(4)); 5.04 (*dm*, $^3J(3,4) = 10.3$, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.7 (*s*, arom. C); 146.0 (*d*, $^1J(C,H) = 182$, C(1)); 134.2 (*s*, arom. C); 132.1 (*d*, $^1J(C,H) =$ 153, C(3)); 130.2 (*s*, arom. C); 129.9 (*d*, $^1J(C,H) = 154$, arom. C); 127.8 (*d*, $^1J(C,H) = 160$, arom. C); 127.1 (*d*, $^1J(C,H) = 159$, arom. C); 126.7 (*d*, $^1J(C,H) = 160$, arom. C); 124.7 (*d*, $^1J(C,H) = 159$, arom. C); 118.7 (*d*, $^1J(C,H) = 162$, arom. C); 114.9 (*d*, $^1J(C,H) = 154$, C(2)); 114.9 (*t*, $^1J(C,H) = 160$, C(4)); 111.4 (*d*, $^1J(C,H) =$ 159, arom. C). CI-MS (NH_3): 197 (28, $[M+1]^+$), 115 (1), 87 (9).

*(*E*)-1-(Methylthio)buta-1,3-diene* ((*E*)-**1s**). As described for (*E*)-**1n**, with (*Z*)-1,4-bis(methylthio)but-2-ene [21] (0.9 g, 8 mmol): 240 mg (30%) of (*E*)-**1s**. Yellowish oil. Data identical with those reported [38].

*2:1 Mixture of (*E*)- and (*Z*)-1-(Phenylthio)buta-1,3-diene* (**1t**). Following [39]. Pale yellow oil. UV (MeCN): 280 (12700), 207 (14200), 203 (14000). IR (film): 3060, 1805, 1620, 1585, 1440, 1230, 1090, 995, 905, 740, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1t**: 7.42–7.20 (*m*, 5 arom. H); 6.47–6.33 (*m*, H–C(1), H–C(2), H–C(3)); 5.17 (*d*, $^3J(3,4) = 17.2$, H–C(4)); 5.08 (*d*, $^3J(3,4) = 9.6$, H–C(4)); (*Z*)-**1t**: 7.42–7.20 (*m*, 5 arom. H); 6.79 (*ddd*, $^3J(3,4) = 16.9$, 10.1, $^3J(2,3) = 10.4$, H–C(3)); 6.41 (*m*, H–C(2)); 6.29 (*d*, $^3J(1,2) = 9.4$, H–C(1)); 5.35 (*d*, $^3J(3,4) = 16.9$, H–C(4)); 5.27 (*d*, $^3J(3,4) = 10.1$, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1t**: 135.5 (*d*, $^1J(C,H) = 154$, C(1)); 134.7 (*s*, arom. C); 132.2 (*d*, $^1J(C,H) = 155$, C(3)); 130.0 (*d*, $^1J(C,H) = 162$, arom. C); 129.0 (*d*, $^1J(C,H) = 161$, arom. C); 127.0 (*d*, $^1J(C,H) = 162$, arom. C); 127.2 (C(2)); 116.3 (*t*, $^1J(C,H) = 157$, C(4)); (*Z*)-**1t**: 134.7 (*s*, arom. C); 132.2 (*d*, $^1J(C,H) = 155$, C(3)); 130.4 (*d*, $^1J(C,H) = 157$, C(2)); 129.2 (*d*, $^1J(C,H) =$ 160, arom. C); 129.1 (*d*, $^1J(C,H) = 160$, arom. C); 126.6 (*d*, $^1J(C,H) = 162$, arom. C); 125.4 (*d*, $^1J(C,H) = 157$, C(1)); 118.8 (*t*, $^1J(C,H) = 155$, C(4)). CI-MS (NH_3): 162 (1, $M^{+\bullet}$), 157 (54), 129 (14), 117 (17), 107 (11), 89 (44).

*2:1 Mixture of (*E*)- and (*Z*)-1-[(4-Chlorophenyl)thio]buta-1,3-diene* (**1u**). Pure 3-chloro-4-[(4-chlorophenyl)thio]but-1-ene (**9u**) [40] (5.8 g, 15 mmol) was added slowly to stirred DBU (7.6 g, 50 mmol) heated to 100°. After 10 min at 100°, the mixture was cooled to 25° and diluted with 2% aq. HCl soln. (100 ml). Extraction with Et_2O (100 ml), washing of the extract with brine (3 × 30 ml), drying ($MgSO_4$), and evaporation gave a residue that was distilled under reduced pressure: 3.6 g (76%) of **1u**. Pale yellow oil. B.p. 80°/0.1 Torr. UV (MeCN): 286 (11600), 201 (11500). IR (film): 2920, 1675, 1475, 1390, 1095, 1010, 815. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1u**: 7.31–7.27 (*m*, 4 arom. H); 6.42–6.34 (*m*, H–C(1), H–C(2), H–C(3)); 5.18 (*d*, $^3J(3,4) = 12.6$, H–C(4)); 5.09 (*d*, $^3J(3,4) = 8.4$, H–C(4)); (*Z*)-**1u**: 7.31–7.27 (*m*, 4 arom. H); 6.76 (*ddd*, $^3J(3,4) = 13.5$, 7.9, $^3J(2,3) = 8.7$, H–C(3)); 6.38 (*m*, H–C(2)); 6.20 (*d*, $^3J(1,2) = 7.2$, H–C(1)); 5.35 (*d*, $^3J(3,4) = 13.5$, H–C(4)); 5.25 $^3J(d, 3,4) = 7.9$, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1u**: 135.2 (*d*, $^1J(C,H) = 156$, C(3)); 133.4 (*s*, arom. C); 133.0 (*d*, $^1J(C,H) = 158$, C(2)); 132.9 (*s*, arom. C); 131.0 (*d*, $^1J(C,H) = 167$, arom. C); 129.2 (*d*, $^1J(C,H) = 168$, arom. C); 126.3 (*d*, $^1J(C,H) = 173$, C(1)); 116.9 (*t*, $^1J(C,H) = 157$, C(4)); (*Z*)-**1u**: 134.3 (*s*, arom. C); 132.5 (*s*, arom. C); 131.9 (*d*, $^1J(C,H) = 156$, C(3)); 131.2 (*d*, $^1J(C,H) = 158$, C(2)); 130.2 (*d*, $^1J(C,H) = 167$, arom. C); 128.8 (*d*, $^1J(C,H) = 168$, arom. C); 124.4 (*d*, $^1J(C,H) = 186$, C(1)); 119.3 (*t*, $^1J(C,H) = 161$, C(4)). CI-MS (NH_3): 196 (2, $M^{+\bullet}$), 166 (88), 129 (37), 119 (17), 97 (74), 84 (100).

*2.3:1 Mixture of (*E*)- and (*Z*)-1-[(4-Methoxyphenyl)thio]buta-1,3-diene* (**1v**). As described for **1u**, with **9v** (17.4 g, 76 mmol) and DBU (22.3 g, 0.15 mmol): 9.9 g (68%) of **1v**. Pale yellow oil. B.p. 100°/0.1 Torr. UV (MeCN): 254 (12000), 228 (14200), 207 (13000), 197 (11000). IR (film): 2955, 2835, 1620, 1590, 1570, 1495, 1460, 1440, 1410, 1290, 1250, 1175, 1030, 930, 900, 825. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1v**: 7.37 (*m*, 2 arom. H); 6.90 (*m*, 2 arom. H); 6.40 (*d*, $^3J(1,2) = 13.0$, H–C(1)); 6.34 (*ddd*, $^3J(3,4) = 13.0$, 8.0, $^3J(2,3) = 7.9$, H–C(3)); 6.14 (*dd*, $^3J(1,2) = 13.0$, $^3J(2,3) = 7.9$, H–C(2)); 5.07 (*d*, $^3J(3,4) = 13.0$, H–C(4)); 4.98 (*d*, $^3J(3,4) = 8.0$, H–C(4)); 3.80 (*s*, MeO); (*Z*)-**1v**: 7.35 (*m*, 2 arom. H); 6.88 (*m*, 2 arom. H); 6.75 (*ddd*, $^3J(3,4) = 13.0$, 7.9, $^3J(2,3) = 7.9$, H–C(3)); 6.22 (*dd*, $^3J(2,3) = 7.9$, $^3J(1,2) = 7.2$, H–C(2)); 6.17 (*d*, $^3J(1,2) = 7.2$, H–C(1)); 5.29 (*d*, $^3J(3,4) = 13.0$, H–C(4)); 5.22 (*d*, $^3J(3,4) = 7.9$, H–C(4)); 3.81 (*s*, MeO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1v**: 159.6 (*s*, arom. C); 135.7 (*d*, $^1J(C,H) = 149$, C(3)); 133.6 (*d*, $^1J(C,H) = 162$, arom. C); 129.6 (*d*, $^1J(C,H) = 160$, C(1), C(2)); 124.0 (*s*, arom. C); 115.2 (*t*, $^1J(C,H) = 156$, C(4)); 114.8 (*d*, $^1J(C,H) = 160$, arom. C); 55.3 (*q*, $^1J(C,H) =$ 144, MeO); (*Z*)-**1v**: 159.2 (*s*, arom. C); 132.3 (*d*, $^1J(C,H) = 162$, arom. C); 132.2 (*d*, $^1J(C,H) = 151$, C(3)); 128.4 (*d*, $^1J(C,H) = 157$, C(2)); 128.0 (*d*, $^1J(C,H) = 168$, C(1)); 126.0 (*s*, arom. C); 118.3 (*t*, $^1J(C,H) = 160$, C(4)); 114.7 (*d*, $^1J(C,H) = 160$, arom. C); 55.3 (*q*, $^1J(C,H) = 144$, MeO). CI-MS (NH_3): 192 (7, $M^{+\bullet}$), 140 (100), 125 (24), 108 (52), 96 (15), 79 (12), 70 (7).

*3.5:1 Mixture of (*E*)- and (*Z*)-1-[(4-Nitrophenyl)thio]buta-1,3-diene* (**1w**). As described for **1u**, with 3-chloro-4-[(4-nitrophenyl)thio]but-1-ene (**9w**; 2.0 g, 8 mmol) and DBU (2.4 g, 16 mmol). FC (Et_2O/light petroleum ether 1:9): 1.2 g (69%) of **1w**. Yellow solid. M.p. 39–40°. UV (MeCN): 340 (9100), 275 (6700), 203 (12400). IR (KBr): 1575, 1510, 1340, 1090, 1000, 850. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1w**: 8.15 (*m*, 2 arom. H); 7.40 (*m*, 2 arom. H); 6.64 (*dd*, $^3J(1,2) = 11.5$, $^3J(2,3) = 8.1$, H–C(2)); 6.43 (*ddd*, $^3J(3,4) = 12.8$, 8.1, $^3J(2,3) = 8.1$, H–C(3)); 6.42 (*d*, $^3J(1,2) = 11.5$, H–C(1)); 5.33 (*d*, $^3J(3,4) = 12.8$, H–C(4)); 5.27 (*d*, $^3J(3,4) = 8.1$, H–C(4)); (*Z*)-**1w**: 8.15 (*m*, 2 arom. H); 7.40 (*m*, 2 arom. H); 6.80 (*ddd*, $^3J(3,4) = 12.9$, 8.5, $^3J(2,3) = 7.2$, H–C(3)); 6.61

(*dd*, ^3J(2,3) = 7.2, ^3J(1,2) = 7.1, H–C(2)); 6.27 (*d*, ^3J(1,2) = 7.1, H–C(1)); 5.51 (*d*, ^3J(3,4) = 12.9, H–C(4)); 5.40 (*d*, ^3J(3,4) = 8.5, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1w**: 146.1 (*s*, arom. C); 145.5 (*s*, arom. C); 138.1 (*d*, ^1J(C,H) = 157, C(2)); 134.8 (*d*, ^1J(C,H) = 161, C(3)); 126.9 (*d*, ^1J(C,H) = 173, arom. C); 124.0 (*d*, ^1J(C,H) = 173, arom. C); 121.7 (*d*, ^1J(C,H) = 154, C(1)); 119.4 (*t*, ^1J(C,H) = 165, C(4)); (*Z*)-**1w**: 146.1 (*s*, arom. C); 145.5 (*s*, arom. C); 135.4 (*d*, ^1J(C,H) = 157, C(2)); 131.50 (*d*, ^1J(C,H) = 160, C(3)); 126.9 (*d*, ^1J(C,H) = 173, arom. C); 124.0 (*d*, ^1J(C,H) = 173, arom. C); 121.3 (*d*, ^1J(C,H) = 154, C(1)); 119.9 (*t*, ^1J(C,H) = 164, C(4)). CI-MS (NH_3): 207 (23, $M^{+\cdot}$), 190 (1), 160 (3), 128 (17), 115 (8), 85 (100). Anal. calc. for $C_{10}H_9NO_2S$ (207.25): C 57.96, H 4.38, N 15.44, S 6.76; found: C 57.85, H 4.33, N 15.45, S 6.71.

(±)-3-Chloro-4-[(4-methoxyphenyl)thio]but-1-ene (**9v**). To a rapidly stirred suspension of *N*-chlorosuccinimide (9.9 g, 74 mmol) in dry CH_2Cl_2 (70 ml), a soln. of 4-methoxybenzenethiol (10.0 g, 71 mmol) in dry CH_2Cl_2 (30 ml) was added slowly at 25°. Initiation of sulfenyl chloride formation is indicated by the intense orange coloration of the mixture accompanied by gentle boiling of the solvent. Once initiated, the vessel was immersed in an ice bath, and the remaining 4-methoxybenzenethiol was added dropwise at a rate sufficient to maintain the solvent under reflux. When the addition was complete, the ice bath was removed and the orange soln. stirred at 25° for additional 30 min. During this time, *N*-succinimide precipitated. Buta-1,3-diene (30 ml, 18.6 g, 0.34 mol) was condensed in a graduate funnel at −78° and quickly transferred into the above soln. of 4-methoxybenzenesulfenyl chloride (0.71M in CH_2Cl_2; 100 ml, 71 mmol) at −78°. The mixture was allowed to warm to 25°, stirred at 25° for 1 h, and evaporated. The residue was diluted with CCl_4 (40 ml). Filtration and concentration of the filtrate gave 17.4 g (88%) of **9v**. Pale yellow oil. UV (MeCN): 256 (10700), 229 (12600), 203 (18300). IR (film): 2940, 1590, 1495, 1460, 1440, 1285, 1245, 1175, 1030, 930, 830, 720, 640. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40 (*m*, 2 arom. H); 6.90 (*m*, 2 arom. H); 5.88 (*ddd*, ^3J(1,2) = 16.9, 10.1, ^3J(2,3) = 8.6, H–C(2)); 5.35 (*d*, ^3J(1,2) = 16.9, H–C(1)); 5.27 (*d*, ^3J(1,2) = 10.1, H–C(1)); 4.35 (*ddd*, ^3J(3,4) = 8.7, 5.7, ^3J(2,3) = 8.6, H–C(2)); 3.80 (*s*, MeO); 3.29 (*dd*, ^2J = 13.7, ^3J(1,2) = 5.7, H–C(4)); 3.11 (*dd*, ^2J = 13.7, ^3J(1,2) = 8.7, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.5 (*s*, arom. C); 136.7 (*d*, ^1J(C,H) = 161, C(2)); 134.5 (*d*, ^1J(C,H) = 162, arom. C); 124.7 (*s*, arom. C); 118.5 (*t*, ^1J(C,H) = 160, C(1)); 114.7 (*d*, ^1J(C,H) = 160, arom. C); 60.4 (*d*, ^1J(C,H) = 148, C(3)); 55.3 (*q*, ^1J(C,H) = 144, MeO); 43.6 (*t*, ^1J(C,H) = 142, C(4)). CI-MS (NH_3): 228 (20, $M^{+\cdot}$), 193 (62), 139 (100), 108 (26). Anal. calc. for $C_{11}H_{13}ClOS$ (228.74): C 57.76, H 5.73; found: C 57.95, H 5.69.

(±)-3-Chloro-4-[(4-nitrophenyl)thio]but-1-ene (**9w**). As described for **9v**, with 4-nitrobenzenethiol (5.0 g, 32 mmol): 4.8 g (76%) of **9w**. Red oil. UV (MeCN): 336 (13600), 332 (13800), 199 (20500). IR (film): 3095, 1715, 1595, 1580, 1515, 1340, 1185, 1090, 930, 855, 840, 740, 680. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.17 (*m*, 2 arom. H); 7.40 (*m*, 2 arom. H); 5.90 (*ddd*, ^3J(1,2) = 16.8, 10.2, ^3J(1,2) = 8.2, H–C(2)); 5.37 (*d*, ^3J(1,2) = 16.8, H–C(1)); 5.28 (*d*, ^3J(1,2) = 10.2, H–C(1)); 4.50 (*ddd*, ^3J(2,3) = 8.2, ^3J(3,4) = 8.1, 5.8, H–C(3)); 3.53 (*dd*, ^2J = 13.7, ^3J(3,4) = 5.8, H–C(4)); 3.37 (*dd*, ^2J = 13.7, ^3J(3,4) = 8.1, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 145.5 (*s*, arom. C); 135.9 (*d*, ^1J(C,H) = 165, C(2)); 127.1 (*d*, ^1J(C,H) = 165, arom. C); 126.3 (*s*, arom. C); 124.4 (*d*, ^1J(C,H) = 165, arom. C); 119.2 (*t*, ^1J(C,H) = 157, C(1)); 59.6 (*d*, ^1J(C,H) = 158, C(3)); 39.7 (*t*, ^1J(C,H) = 143, C(4)). CI-MS (NH_3): 244 (4, $M^{+\cdot}$), 208 (100), 168 (11), 122 (23). Anal. calc. for $C_{10}H_{10}ClNO_2S$ (243.71): C 49.28, H 4.14; found: C 49.37, H 4.28.

1:0.8:0.5 Mixture of (E)*-1-(Phenylseleno)buta-1,3-diene* ((*E*)-**1x**), (Z)-**1x**, *and 2-(Phenylseleno)buta-1,3-diene* (**12**). As described for **1u**, with **10**/**11** 5:1 (455 mg, 1.9 mmol) and DBU (580 mg, 3.8 mmol): 163 mg (41%). Spectroscopic data identical with those reported for these compounds [41].

5:1 Mixture of (±)-3-Chloro-4-(phenylseleno)but-1-ene (**10**) *and (±)-4-Chloro-3-(phenylseleno)but-1-ene* (**11**). Buta-1,3-diene (0.5 ml, 310 mg, 5.7 mmol) was condensed into a stirred soln. of benzeneselenenyl chloride (0.46 g, 2.4 mmol) in anh. CH_2Cl_2 (3 ml) cooled to −78°. The mixture was allowed to reach 25° in a few hours. After an additional hour of stirring, solvent evaporation gave a residue that was taken up in CCl_4 (2 ml). Filtration and evaporation yielded 565 mg (96%) of **10**/**11** 5:1. Deep orange oil. **10**: UV (MeCN): 198 (15400). IR (film): 3070, 3055, 1580, 1480, 1440, 1020, 1020, 985, 965, 930, 740, 690, 670. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (*m*, 2 arom. H); 7.30 (*m*, 3 arom. H); 5.90 (*ddd*, ^3J(1,2) = 16.9, 10.1, ^3J(2,3) = 8.4, H–C(2)); 5.32 (*d*, ^3J(1,2) = 16.9, H–C(1)); 5.24 (*d*, ^3J(1,2) = 10.1, H–C(1)); 4.50 (*ddd*, ^3J(3,4) = 9.3, 5.4, ^3J(2,3) = 8.4, H–C(3)); 3.39 (*dd*, ^2J = 12.5, ^3J(3,4) = 5.4, H–C(4)); 3.23 (*dd*, ^2J = 12.5, 9.3, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 139.2 (*s*, arom. C); 136.9 (*d*, ^1J(C,H) = 161, C(2)); 133.4 (*d*, ^1J(C,H) = 161, arom. C); 129.3 (*d*, ^1J(C,H) = 161, arom. C); 127.6 (*d*, ^1J(C,H) = 160, arom. C); 118.5 (*t*, ^1J(C,H) = 157, C(1)); 61.2 (*d*, ^1J(C,H) = 159, C(3)); 34.9 (*t*, ^1J(C,H) = 146, C(4)). CI-MS (NH_3): 264 (4, $[M+18]^+$), 246 (57, $M^{+\cdot}$), 211 (100), 157 (25), 89 (25), 78 (31).

9:1 Mixture of (E)*- and* (Z)*-Buta-1,3-dien-1-yl Benzoate* (**1y**). As described for **1z** (see below), with benzoyl chloride instead of naphthalene-2-carbonyl chloride [22]. Colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.1 (*m*, 2 H, H–C(2), H–C(6)); 7.67 (*d*, 0.9 H, ^3J(1′,2′) = 12.0, H–C(1′)); 7.62 (*m*, 1 H, H–C(4)); 7.49 (*m*, 2 H, H–C(3), H–C(5)); 7.34 (*dm*, ^3J(1′,2′) = 6.4, 0.1 H, H–C(1′)); 6.89 (*ddd*, ^3J(3′,4′*cis*) = 17.5, ^3J(2′,3′) = 10.5,

$^3J(3',4'trans) = 10.1$, 0.1 H, H–C(3')); 6.38 (*ddd*, $^3J(3',4'cis) = 17.0$, $^3J(2',3') = 11.1$, $^3J(3',4'trans) = 10.4$, 0.9 H, H–C(3')); 6.25 (*dd*, $^3J(1',2') = 12.0$, $^3J(2',3') = 11.1$, 0.9 H, H–C(2')); 5.67 (*ddm*, $^3J(2',3') = 10.5$, $^3J(1',2') = 6.4$, 0.1 H, H–C(2')); 5.33 (*dm*, $^3J(3',4'cis) = 17.5$, 0.1 H, H_{cis}–C(4')); 5.28 (*dm*, $^3J(3',4'cis) = 17.0$, 0.9 H, H_{cis}–C(4')); 5.19 (*dm*, $^3J(3',4'trans) = 10.1$, 0.1 H, H_{trans}–C(4')); 5.15 (*dm*, $^3J(3',4'trans) = 10.4$, 0.9 H, H_{trans}–C(4')). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1y**: 163.5 (*s*, C=O); 138.9 (*d*, ^1J(C,H) = 195, C(1')); 133.6 (*d*, ^1J(C,H) = 161, C(4)); 131.7 (*d*, ^1J(C,H) = 155, C(3')); 130.0 (*d*, ^1J(C,H) = 163, C(2), C(6)); 128.8 (*s*, C(1)); 128.6 (*d*, ^1J(C,H) = 155, C(3), C(5)); 117.4 (*t*, ^1J(C,H) = 160, C(4')); 116.6 (*d*, ^1J(C,H) = 162, C(2')). ^{17}O-NMR (81.34 MHz, CD_2Cl_2): 359.5 (O=C, (*Z*)); 342.8 (O=C, (*E*)); 186.8 (O–C(1), (*E*)); 171.9 (O–C(1), (*Z*)).

*8:1 Mixture of (*E*)- and (Z)-Buta-1,3-dien-1-yl Naphthalene-2-carboxylate* (**1z**). A mixture of KF (3.66 g), H_2O (6 ml), CH_2Cl_2 (30 ml), naphthalene-2-carbonyl chloride (6 g, 31.5 mmol) and Bu_3N (0.37 ml) was stirred at 0° for 4 h. The aq. layer was extracted with CH_2Cl_2 (2 × 15 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, giving naphthalene-2-carbonyl fluoride (^{19}F-NMR ($CDCl_3$, 376 MHz): 17.5), which was used as such in the next step. To a soln. of this carbonyl fluoride in anh. THF (44 ml); (*E*)/(*Z*)-1-[(trimethylsilyl)-oxy]buta-1,3-diene (5.06 g, 3.07 mmol) and $Bu_3NF \cdot 3\ H_2O$ (225 mg) were added, and the mixture was stirred at 0° for 3 h under Ar. Sat. aq. $NaHCO_3$ soln. (50 ml) was added (pH 7), the org. phase washed with sat. aq. $NaHCO_3$ soln. (2 × 20 ml), then with H_2O (2 × 20 ml), dried ($MgSO_4$), and evaporated. FC (AcOEt/light petroleum ether 1:12): 5.45 g (76%) of **1z**. White solid. M.p. 37–40°. UV (MeCN): 281 (40000), 241 (140000), 193 (88000). IR (KBr): 3085, 1725, 1650, 1630, 1600, 1265, 1225, 1195, 1135, 1115, 1005, 930, 890, 775, 760, 475. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**1z**: 8.69 (*s*, H–C(1)); 8.11 (*dm*, $^3J(3,4) = 8.3$, H–C(3)); 7.99 (*dm*, $^3J(7,8) = 7.7$, H–C(8)); 7.74 (*d*, $^3J(1',2') = 11.7$, H–C(1')); 7.94–7.90 (*m*, H–C(4), H–C(5)); 7.56–7.65 (*m*, H–C(6), H–C(7)); 6.41 (*ddd*, $^3J(2',3') = 11.1$, $^3J(3',4'cis)) = 16.5$, $^3J(3',4'trans) = 10.2$, H–C(3')); 6.32 (*dd*, $^3J(2',3') = 11.1$, $^3J(1',2') = 11.7$, H–C(2')); 5.32 (*d*, $^3J(3',4'cis) = 16.5$, H_{cis}–C(4')); 5.32 (*ddm*, $^3J(3',4'trans) = 10.2$, $^2J(4'cis,4'trans) = 1.8$, H_{trans}–C(4')); (*Z*)-**1z**: 8.71 (*s*, H–C(1)); 8.14 (*dm*, $^3J(3,4) = 8.3$, H–C(3)); 8.01 (*dm*, $^3J(7,8) = 7.7$, H–C(8)); 7.90–7.94 (*m*, H–C(4), H–C(5)); 7.65–7.56 (*m*, H–C(6), H–C(7)); 7.40 (*dddd*, $^3J(1',2') = 6.2$, $^5J(1',4'trans) = 1.7$, $^4J(1',3') = 1.0$, $^5J(1',4'cis) = 0.9$, H–C(1')); 6.99 (*dddd*, $^3J(2',3') = 10.7$, $^3J(3',4'cis) = 17.3$, $^3J(3',4'trans) = 10.5$, $^4J(1',3') = 1.0$, H–C(3')); 5.70 (*dddd*, $^3J(2',3') = 10.7$, $^3J(1',2'cis) = 6.2$, $^4J(2',4'cis) = 0.8$, $^4J(2',4'trans) = 0.8$, H–C(2')); 5.37 (*dddd*, $^3J(3',4'cis) = 17.3$, $^2J(4'cis,4'trans) = 1.8$, $^5J(1',4'cis) = 0.9$, $^4J(2',4'trans) = 0.8$, H_{cis}–C(4')); 5.24 (*dddd*, $^3J(3',4'trans) = 10.5$, $^2J(4'cis,4'trans) = 1.8$, $^5J(1',4'trans) = 1.7$, $^4J(2',4'trans) = 0.8$, H_{trans}–C(4')). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**1z**: 163.6 (*s*, C=O); 139.0 (*d*, ^1J(C,H) = 190, C(1')); 135.8 (*s*, C(4a)); 132.4 (*s*, C(8a)); 131.8 (*d*, ^1J(C,H) = 158, C(1), C(3')); 129.4 (*d*, ^1J(C,H) = 161, C(8)); 128.7 (*d*, ^1J(C,H) = 160, C(6)); 128.4 (*d*, ^1J(C,H) = 160, C(4)); 127.8 (*d*, ^1J(C,H) = 160, C(5)); 126.8 (*d*, ^1J(C,H) = 161, C(7)); 125.9 (*s*, C(2)); 125.1 (*d*, ^1J(C,H) = 164, C(3)); 117.4 (*d*, ^1J(C,H) = 158, C(4')); 116.6 (*d*, ^1J(C,H) = 158, C(2')); (*Z*)-**1z**: 163.6 (*s*, C=O); 139.0 (*d*, ^1J(C,H) = 190, C(1')); 135.8 (*s*, C(4a)); 134.4 (*d*, ^1J(C,H) = 194, C(2')); 132.4 (*s*, C(8a)); 131.8 (*d*, ^1J(C,H) = 158, C(1)); 129.4 (*d*, ^1J(C,H) = 161, C(8)); 129.0 (*d*, ^1J(C,H) = 156, C(3')); 128.7 (*d*, ^1J(C,H) = 160, C(6)); 128.4 (*d*, ^1J(C,H) = 160, C(4)); 127.8 (*d*, ^1J(C,H) = 160, C(5)); 126.8 (*d*, ^1J(C,H) = 161, C(7)); 126.1 (*s*, C(2)); 125.1 (*d*, ^1J(C,H) = 164, C(3)); 118.0 (*d*, ^1J(C,H) = 158, C(4')); 114.0 (*d*, ^1J(C,H) = 158, C(2')). CI-MS (NH_3): 242 (9, $[M + NH_4]^+$), 225 (32, $[M + H]^+$), 172 (11, $[M + H - C_4H_5]^+$), 156 (44, $[M + H - OC_4H_5]^+$), 155 (100, $[M - OC_4H_5]^{+\bullet}$), 127 (27, $[M - C(O)OC_4H_5]^{+\bullet}$), 99 (16), 76 (58). Anal. calc. for $C_{15}H_{12}O_2 \cdot 0.5\ H_2O$ (224.26 + 9.01): C 77.24, H 5.62; found: C 77.05, H 5.63.

*2:1 Mixture of (1*E*)- and (1*Z*)-Ethylidene-2-methylidenecyclohexane* (**4a**). At 0°, 2-[(dimethylamino)-methyl]cyclohexanone (**13**) [23] (5 g, 32.5 mmol) was added dropwise to a stirred soln. of $(EtPPh_3)Br$ (13.2 g, 35.5 mmol), *t*-BuOK (3.98 g, 35.5 mmol), and [18]crown-6 (30 mg) in anh. THF (50 ml) under Ar. After stirring at 25° for 5.5 h, the solvent was evaporated. The oily residue was filtered through a pad of silica gel, rinsing with light petroleum ether, the filtrate evaporated, and the oily residue added dropwise to a stirred soln. of MeI (3.85 ml) in anh. Et_2O (55 ml) under Ar. After stirring at 25° for 12 h, the precipitate was collected and washed with Et_2O. The white solid so obtained was dissolved in H_2O (171 ml), then Ag_2O (10 g, 43 mmol) was added portionwise under stirring and Ar. After stirring at 25° for 6 h, the brownish soln. was filtered, the filtrate evaporated (< 40°), and the residue heated in a *Büchi* 'Kugelrohr' (150°/130 Torr) for 1 h. The residue was extracted with pentane (2 × 15 ml), the combined extract washed with 0.7N aq. HCl (15 ml), then with H_2O (2 × 20 ml), dried ($MgSO_4$), and evaporated at 30°/600 mbar, and the residue distilled bulb-to-bulb (*Büchi* 'Kugelrohr') at 70–80°/30 mbar: 1.97 g (585) of (*E*)/(*Z*)-**4a** 2:1. Colorless liquid. UV (MeCN): 227 (5700). IR (film): 3080, 2930, 2855, 1625, 1440, 890, 830. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**4a**: 5.54 (*q*, $^3J = 6.9$, H–C(1')); 4.79 (*d*, $^2J = 2.7$, H_{cis}–C(1'')); 4.56 (*dm*, $^2J = 2.7$, H_{trans}–C(1'')); 2.25–2.22 (*m*, CH_2(3), CH_2(6)); 1.64 (*d*, $^3J = 6.9$, Me(2')); 1.67–1.59 (*m*, CH_2(4), CH_2(5)); (*Z*)-**4a**: 5.29 (*q*, $^3J = 6.9$, H–C(1')); 4.96 (*dm*, $^2J = 2.7$, H_{cis}–C(1'')); 4.65 (*d*, $^2J = 2.7$, H_{trans}–C(1'')); 2.20–2.16 (*m*, CH_2(3), CH_2(6)); 1.70 (*d*, $^3J = 6.9$, Me(2')); 1.67–1.59 (*m*, CH_2(4), CH_2(5)); distinctions between (*E*)- and (*Z*)-**4a** and signal assignments based on 2D ^{1}H,^{1}H-NOESY. ^{13}C-NMR

(100.6 MHz, $CDCl_3$): (*E*)-**4a**: 151.4 (*s*, C(2)); 140.7 (*s*, C(1)); 117.2 (*d*, ^1J(C,H) = 150, *C*H=C(1)); 106.8 (*t*, ^1J(C,H) = 156, *C*H_2=C(2)); 35.5 (*t*, ^1J(C,H) = 126, C(3)); 28.1 (*t*, ^1J(C,H) = 128, C(6)); 27.2 (*t*, ^1J(C,H) = 128, C(4) or C(5)); 26.1 (*t*, ^1J(C,H) = 128, C(5) or C(4)); 13.0 (*q*, ^1J(C,H) = 126, Me); (*Z*)-**4a**: 151.4 (*s*, C(2)); 140.7 (*s*, C(1)); 117.8 (*d*, ^1J(C,H) = 151, *C*H=C(1)); 110.2 (*t*, ^1J(C,H) = 156, *C*H_2=C(2)); 37.9 (*t*, ^1J(C,H) = 126, C(3) or C(6)); 36.8 (*t*, ^1J(C,H) = 126, C(6) or C(3)); 28.0 (*t*, ^1J(C,H) = 128, C(4) or C(5)); 27.7 (*t*, ^1J(C,H) = 128, C(5) or C(4)); 14.3 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 140 (100, $[M+NH_4]^+$), 123 (17, $[M+H]^+$), 122 (15, $M^{+\cdot}$), 110 (34), 83 (56).

*1.5 : 1 Mixture of (1*E*)- and (1*Z*)-1-(Methoxymethylidene)-2-methylidenecyclohexane* (**4f**). Ag_2O (3.5 g, 15 mmol) and (*E*)/(*Z*)-**14f** 1.5 : 1 (3.9 g, 12 mmol) in H_2O (100 ml) were stirred at 25° for 4 h. The precipitate was filtered off and the solvent evaporated (40°/1 mbar). The yellow residue was heated in a *Büchi* 'Kugelrohr' at 150°/0.1 mbar yielding 620 mg (38%) of (*E*)/(*Z*)-**4f** 1.5 : 1. Colorless oil. UV (MeCN): 202 (3900), 198 (4300). IR (film): 2930, 2860, 1655, 1620, 1445, 1225, 1130, 985, 885, 715. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**4f**: 6.13 (*t*, *J* = 1.4, MeOC*H*); 4.71, 4.49 (2 br. *s*, CH_2=C(2)); 3.63 (*s*, MeO); 2.24 (*m*, CH_2(3), H–C(6)); 2.03 (*m*, H–C(6)); 1.60 (*m*, CH_2(5), CH_2(4)); (*Z*)-**4f**: 5.88 (*s*, MeOC*H*); 5.06, 5.05 (2*m*, CH_2=C(2)); 3.60 (*s*, MeO); 2.24 (*m*, CH_2(6), CH_2(3)); 1.60 (*m*, CH_2(5), CH_2(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**4f**: 146.8 (*s*, C(2)); 140.6 (*d*, ^1J(C,H) = 184, MeO*C*H); 119.5 (*s*, C(1)); 105.3 (*t*, ^1J(C,H) = 156, *C*H_2=C(2)); 59.6 (*q*, ^1J(C,H) = 143, MeO); 35.2 (*t*, ^1J(C,H) = 128, C(3)); 26.9 (*t*, ^1J(C,H) = 128); 25.5 (*t*, ^1J(C,H) = 127); 25.2 (*t*, ^1J(C,H) = 127); (*Z*)-**4f**: 143.1 (*s*, C(2)); 141.6 (*d*, ^1J(C,H) = 176, MeO*C*H); 116.4 (*s*, C(1)); 111.5 (*t*, ^1J(C,H) = 159, *C*H_2=C(2)); 59.9 (*q*, ^1J(C,H) = 143, MeO); 35.7 (*t*, ^1J(C,H) = 131, C(3)); 31.0 (*t*, ^1J(C,H) = 126); 26.9 (*t*, ^1J(C,H) = 127); 26.8 (*t*, ^1J(C,H) = 128). CI-MS (NH_3): 139 (100, $[M+1]^+$), 125 (43), 109 (50), 95 (40), 81 (46), 75 (37).

*1.5 : 1 Mixture of (2*E*)- and (2*Z*)-*N,N-*Dimethyl-2-(methoxymethylidene)cyclohexanemethanamine* (**14f**). BuLi (1.6M in hexane; 4.4 ml, 7 mmol) was added slowly to a stirred soln. of $(i\text{-Pr})_2$NH (708 mg, 1 ml, 7 mmol) in anh. THF (5 ml) under Ar at 0°. After stirring at 0° for 15 min, this soln. was cooled to −78° and added dropwise to a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (2.0 g, 6 mmol) in anh. THF (40 ml) cooled to −78° under Ar. The resulting orange soln. was allowed to warm to 0° and stirred at 0° for 1 h. Then a soln. of **13** [23] (1 g, 6 mmol) in anh. THF (5 ml) was added slowly (syringe). After stirring at 25° for 1 h, the precipitate was filtered off, the solvent evaporated, the residue extracted with Et_2O (10 ml, 5 ×), the combined Et_2O extract dried ($MgSO_4$) and evaporated, and the residue distilled bulb-to-bulb in a *Büchi* oven at 90°/0.02 mbar : 1.2 g (89%) of (*E*)/(*Z*)-**14f** 1.5 : 1. Colorless liquid. UV (MeCN): 204 (6500). IR (film): 2925, 2855, 2765, 1680, 1460, 1235, 1200, 1130, 1010, 835. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-**14f**: 5.79 (*s*, MeOC*H*); 3.55 (*s*, MeO); 2.34 (*dd*, ^2J = 11.9, ^3J(CH_2N,1) = 8.5, 1 H, CH_2N); 2.21 (*s*, Me_2N); 2.24–1.38 (*m*, 1 H of CH_2N, H–C(1), CH_2(3), CH_2(4), CH_2(5), CH_2(6)); (*Z*)-**14f**: 5.84 (*d*, *J* = 1.6, MeOC*H*); 3.53 (*s*, MeO); 3.06 (*m*, H–C(1)); 2.46 (*dd*, ^2J = 11.9, ^3J = 9.0, 1 H, CH_2N); 2.24 (*s*, Me_2N); 2.24–1.38 (*m*, 1 H of CH_2N, CH_2(3), CH_2(4), CH_2(5), CH_2(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (*E*)-**14f**: 139.3 (*d*, ^1J(C,H) = 171, MeO*C*H); 119.5 (*s*, C(2)); 59.1 (*q*, ^1J(C,H) = 143, MeO); 61.9 (*t*, ^1J(C,H) = 130, CH_2N); 45.8 (*q*, ^1J(C,H) = 133, 2 CMe_2N); 36.8 (*d*, ^1J(C,H) = 124, C(1)); 31.2 (*t*, ^1J(C,H) = 128); 27.2 (*t*, ^1J(C,H) = 126); 23.3 (*t*, ^1J(C,H) = 127); 23.2 (*t*, ^1J(C,H) = 127); (*Z*)-**14f**: 139.9 (*d*, ^1J(C,H) = 181, MeO*C*H); 119.0 (*s*, C(2)); 60.8 (*t*, ^1J(C,H) = 130, CH_2N); 59.0 (*q*, ^1J(C,H) = 143, MeO); 45.8 (*q*, ^1J(C,H) = 133, 2 C, Me_2N); 30.8 (*d*, ^1J(C,H) = 124, C(1)); 28.4 (*t*, ^1J(C,H) = 126); 28.8 (*t*, ^1J(C,H) = 126); 26.6 (*t*, ^1J(C,H) = 125); 21.5 (*t*, ^1J(C,H) = 127). CI-MS (NH_3): 184 (100, $[M+1]^+$), 157 (7), 139 (16), 123 (10), 107 (5), 91 (10), 77 (7). Anal. calc. for $C_{11}H_{21}NO$ (183.29): C 72.08, H 11.55; found: C 72.31, H 11.22.

*(2*RS*,6*SR*)-*cis*-6-(*tert*-Butyl)-3,6-dihydro-1,2-oxathiin 2-Oxide* (*c*-**2g**) *and (2*RS*,6*RS*)-*trans*-6-(*tert*-Butyl)-3,6-dihydro-1,2-oxathiin 2-Oxide* (*t*-**2g**). In a 5-mm NMR *Pyrex* tube, pure (*E*)-**1g** (40 mg, 0.4 mmol), CD_2Cl_2 (0.15 ml), and $CFCl_3$ (100 mg) were mixed at 25°. After degassing by several freeze-thaw cycles at 10^{-2} mbar on the vacuum line, degassed SO_2 (*ca.* 0.2 ml, 4–6 mmol) and CF_3COOH (23 mg, 0.2 mmol) were transferred to the above mixture. The NMR tube was sealed under vacuum at −196°, warmed to −80°, and left at −80° for 6 h. The tube was then transferred to a *Bruker ARX-400* spectrometer probe cooled to −80° and analyzed: traces of *c*-**2g** could be detected. After additional 12 h at −80°, isomerization to *t*-**2g** took place. ^{1}H-NMR (400 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 193 K): *c*-**2g**, detected signals: 6.18 (*dd*, ^3J(4,5) = 11.0, ^4J(3ax,5) = 2.4, H–C(5)); 4.07 (*m*, H–C(6)); 3.56 (*ddd*, ^2J = 16.4, ^3J(3eq,4) = 6.5, *J* = 1.0, H_{eq}–C(3)); 3.08 (*m*, H_{ax}–C(3)); *t*-**2g**: 5.95 (*dm*, ^3J(4,5) = 11.7, H–C(5)); 5.75 (*m*, H–C(4)); 4.24 (*dddd*, ^5J(3ax,6)) = 4.2, ^5J(3eq,6) = 2.8, ^3J(5,6) = 2.1, ^4J(4,6) = 2.1, H–C(6)); 3.41 (*dddd*, ^2J = 17.2, ^5J(3ax,6) = 4.2, ^3J(3ax,4) = 2.7, ^4J(3ax,5) = 2.7, H_{ax}–C(3)); 3.04 (*dddd*, ^2J = 17.2, ^3J(3eq,4) = 6.5, ^5J(3eq,6) = 2.8, ^4J(3eq,5) = 1.1, H_{eq}–C(3)); 0.86 (*s*, Me_3C). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 223 K): *t*-**2g**, detected signals: 125.9 (*d*, ^1J(C,H) = 161, C(5)); 125.7 (*d*, ^1J(C,H) = 151, C(4)); 77.6 (*d*, ^1J(C,H) = 150, C(6)); 45.3 (*t*, ^1J(C,H) = 141, C(3)).

*(2*RS,*6*RS*)*-cis-*6-Cyclohexyl-3,6-dihydro-1,2-oxathiin 2-Oxide* (*c*-**2h**) *and (2*RS,*6*SR*)*-trans-*6-Cyclohexyl-3,6-dihydro-1,2-oxathiin 2-Oxide* (*t*-**2h**). As described for **2g**, with (*E*)/(*Z*)-**1h** 10:1 (40 mg, 0.3 mmol). After 15 h at 80°, traces of *c*/*t*-**2h** 1:2 were observed by ^{1}H-NMR. After 12 h at −50°, complete isomerization of *c*-**2h** to *t*-**2h** occurred. ^{1}H-NMR (400 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 193 K): *c*-**2h**, detected signals: 4.24 (br. *s*, H−C(6)); 3.46 (*dd*, ^2J = 16.6, ^3J(3ax,4) = 4.2, H_{ax}−C(3)); 3.14 (*dddd*, ^2J = 16.6, ^5J(3eq,6) = 2.3, ^3J(3eq,4) = 2.3, ^4J(3eq,5) = 2.3, H_{eq}−C(3)); 1.90–0.80 (*m*, 11 H, Chx); *t*-**2h**, detected signals: 5.12 (*dm*, ^3J(4,5) = 11.5, H−C(5)); 4.43 (br. *s*, H−C(6)); 3.39 (*dddd*, ^2J = 17.3, ^5J(3ax,6) = 4.4, ^3J(3ax,4) = 2.6, ^4J(3ax,5) = 2.6, H_{ax}−C(3)); 3.03 (*ddd*, ^2J = 17.3, ^3J(3eq,4) = 6.3, ^5J(3eq,6) = 2.6, H_{eq}−C(3)); 1.90–0.80 (*m*, 11 H, Chx). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 223 K): *t*-**2h** detected signals: 130.5 (*d*, ^1J(C,H) = 151, C(5)); 119.3 (C(4)); 74.8 (*d*, ^1J(C,H) = 146, C(6)); 46.2 (*t*, ^1J(C,H) = 143, C(3)).

*(2*RS,*6*RS*)*-cis-*6-Benzyl-3,6-dihydro-1,2-oxathiin 2-Oxide* (*c*-**2i**) *and (2*RS,*6*SR*)*-trans-*6-Benzyl-3,6-dihydro-1,2-oxathiin 2-Oxide* (*t*-**2i**). As described for **2g**, with (*E*)/(*Z*)-**1i** 6:1 (20 mg, 0.14 mmol). After 6 h at −80°, traces of *c*-**2i** were detected by ^{1}H-NMR. After 12 h at −50°, total isomerization of *c*-**2i** into *t*-**2i** was observed. ^{1}H-NMR (400 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 193 K): *c*-**2i**: 7.50–7.10 (*m*, 5 arom. H), 6.05 (*dm*, ^3J(4,5) = 11.8, H−C(5)); 5.80 (*dm*, ^3J(4,5) = 11.8, H−C(4)); 4.64 (*m*, H−C(6)); 3.50–2.80 (*m*, CH_2(3)); 2.94 (*dd*, ^2J = 14.0, ^3J = 9.6, 1 H, PhCH_2); 2.88 (*dd*, ^2J = 14.0, ^3J = 5.9, 1 H, PhCH_2); *t*-**2i**: 7.50–7.10 (*m*, 5 arom. H); 5.88 (*dm*, ^3J(4,5) = 11.8, H−C(5)); 5.67 (*dddd*, ^3J(4,5) = 11.8, ^3J(3eq,4) = 6.2, ^3J(3ax,4) = 2.5, ^4J(4,6) = 2.1, H−C(4)); 4.82 (*m*, H−C(6)); 3.36 (*dddd*, ^2J = 17.5, ^5J(3ax,6) = 4.1, ^3J(3ax,4) = 2.5, ^4J(3ax,5) = 2.5, Hax−C(3)); 3.00 (*dddd*, ^2J = 17.5, ^3J(3eq,4) = 6.2, ^5J(3eq,6) = 2.7, ^4J(3eq,5) = 1.1, H_{eq}−C(3)); 2.96 (*dd*, ^2J = 14.1, ^3J = 5.3, 1 H, PhCH_2); 2.86 (*dd*, ^2J = 14.1, ^3J = 7.9, 1 H, PhCH_2). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 193 K): *c*-**2i**: 145–110 (6 arom. C); 129.4 (C(5)); 120.6 (C(4)); 78.2 (C(6)); 45.4 (C(3)); 42.5 (CH_2Ph); *t*-**2i**: 145–110 (6 arom. C); 129.8 (C(5)); 117.1 (C(4)); 70.5 (C(6)); 45.0 (C(3)); 39.7 (PhCH_2).

*(2*RS,*6*SR*)*-cis-*3,6-Dihydro-2-oxido-1,2-oxathiin-6-yl Benzoate* (*c*-**2y**) *and (2*RS,*6*SR*)*-trans-*3,6-Dihydro-2-oxido-1,2-oxathiin-6-yl Benzoate* (*t*-**2y**). As described for **2g**, with (*E*)/(*Z*)-**1y** 9:1 (54 mg, 0.31 mmol), CD_2Cl_2 (248 mg), CF_3COOH (25.7 mg, 0.23 mmol), $CFCl_3$ (268 mg), SO_2 (218 mg, 3.4 mmol), and MeCN (5.6 mg) as internal reference. Both sultines *c*- and *t*-**2y** were formed simultaneously at −75° in a 1:10 ratio. Equilibrium with diene (*E*)-**1y** (K((*E*)-**1y** + SO_2 ⇄ *t*-**2y**) = 6.58 · 10^{-3} lmol^{-1} and K((*E*)-**1y** + SO_2 ⇄ *c*-**2y**) = 6.4 · 10^{-4} lmol^{-1} at −75°) was reached after 10 h at −75°. Diene (*Z*)-**1y** did not add to SO_2 at −75°. ^{1}H-NMR (400 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 198 K): *c*-**2y**, detected signals: 6.94 (*m*, H−C(6′)); 6.23 (*dm*, ^3J(4,5) ≈ 12, H−C(4)); 6.16 (*dm*, ^3J(4,5) ≈ 12, H−C(3), H−C(5)); 3.87 (*dddd*, ^2J = 17.0, ^3J(3′a,4′) = 3.8, ^4J(3′a,5′) = 2.0, ^5J(3′a,6′) = 1.8, H_a−C(3′)); 3.38 (*dddd*, ^2J = 17.0, ^3J(3′,4′) = 4.5, ^4J(3′b,5′) = 2.4, ^5J(3′b,6′) = 1.8, H_b−C(3′)). 2D ^{1}H,^{1}H-NOESY of *c*-**2y**: correlation peaks for signals H_a−C(3′)/H_b−C(3′), H_a−C(3′)/H−C(4′), H_a−C(3′)/H−C(5′), H_b−C(3′)/H−C(4′), H−C(4′)/H−C(6′), H−C(5′)/H−C(6′)). ^{1}H-NMR (600 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 198 K): *t*-**2y**: 8.08 (*dm*, ^3J = 8.0, 7.9, H−C(2), H−C(6)); 7.70 (*m*, H−C(4)); 7.56 (*m*, H−C(3), H−C(5)); 6.69 (*m*, H−C(6′)); 6.30 (*m*, H−C(4′)); 6.25 (*m*, H−C(5′)); 3.62 (*dm*, ^2J = 17.0, H_a−C(3′)); 3.58 (*dm*, ^2J = 17.0, H_b−C(3′)); signals for H−C(4′) and H−C(5′) were detected by 1D-COSY-DQF and TOCSY measurements with selective irradiation of the signals of CH_2(3′) and H−C(6′). 2D ^{1}H,^{1}H-NOESY of *t*-**2y**: correlation peaks for signal pairs H_a−C(3′)/H−C(6′). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 198 K): *c*-**2y**, detected signals: 124.3 (C(5′)); 121.8 (C(4′)); 84.1 (C(6′)); 45.5 (C(3′)); *t*-**2y**: 165.5 (*s*, C=O); 134.8 (*d*, ^1J(C,H) = 162, C(4)); 130.4 (*d*, ^1J(C,H) = 162, C(2), C(6)); 129.1 (*d*, ^1J(C,H) = 162, C(3), C(5)); 128.0 (*s*, C(1)); 123.3 (*d*, ^1J(C,H) = 170, C(5′)); 119.3 (*d*, ^1J(C,H) = 175, C(4′)); 84.1 (*d*, ^1J(C,H) = 180, C(6′)); 45.5 (*t*, ^1J(C,H) = 139, C(3′)).

*(2*RS,*6*SR*)*-cis-*3,6-Dihydro-2-oxido-1,2-oxathiin-6-yl Naphthalene-2-carboxylate* (*c*-**2z**) *and (2*RS,*6*RS*)*-trans-*3,6-Dihydro-2-oxido-1,2-oxathiin-6-yl Naphthalene-2-carboxylate* (*t*-**2z**). As described for **2y**, with (*E*)/(*Z*)-**1z** 8:1 (49 mg, 0.22 mmol), CD_2Cl_2 (248 mg), CF_3COOH (25 mg, 0.22 mmol), $CFCl_3$ (250 mg), and SO_2 (0.3 ml, 400 mg, 6.2 mmol). ^{1}H-NMR (400 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 198 K): *c*-**2z**, detected signals: 6.94 (*m*, H−C(6′)); 3.88 (*dm*, ^2J = 17.0, H_a−C(3′)); 3.37 (*dm*, ^2J = 17.0, H_b−C(3′)); *t*-**2z**, detected signals: 6.72 (*m*, H−C(6′)); 6.30 (*m*, H−C(4′)); 6.25 (*m*, H−C(5′)); 3.63 (*dm*, ^2J = 16.5, H_a−C(3′)); 3.58 (*dm*, ^2J = 16.5, H_b−C(3′)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/$CFCl_3$/SO_2, 198 K): *t*-**2z**, detected signals: 84.2 (*d*, ^1J(C,H) = 180, C(6′)); 45.5 (*t*, ^1J(C,H) = 139, C(3′)). *(±)-2-(*tert*-Butyl)-2,5-dihydrothiophene 1,1-Dioxide* (**3g**). A mixture of **1g** (40 mg, 0.36 mmol) and SO_2 (*ca.* 0.2 ml, 4–6 mmol) was placed in a *Pyrex* tube and degassed on the vacuum line. After sealing the tube under vacuum, the mixture was left at 25° for 15 h. After cooling in liq. N_2, the tube was opened and SO_2 evaporated. The residue was purified by FC (silica gel, CH_2Cl_2) affording 36 mg (57%) of **3g**. Colorless oil. UV (MeCN): 270 (350), 195 (1800). IR (film): 2965, 1370, 1310, 1255, 1235, 1135, 1120, 770. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.16 (*dtd*, ^3J(3,4) = 8.8, ^3J(4,5) = 2.7, ^4J(2,4) = 2.7, H−C(4)); 6.13 (*dtd*, ^3J(3,4) = 8.8, ^3J(2,3) = 2.1, ^4J(3,5) = 2.1, 2.0, H−C(3)); 3.67 (*dddd*, ^2J = 16.5, ^3J(4,5) = 2.7, ^4J(3,5) = 2.1, ^4J(2,5) = 2.1, H−C(5)); 3.62 (*dddd*, ^2J = 16.5, ^3J(4,5) = 2.7, ^4J(3,5) = 2.0, ^4J(2,5) = 1.1, H−C(5)); 3.51 (*m*, H−C(2)); 1.17 (*s*, *t*-Bu). ^{13}C-NMR

(100.6 MHz, $CDCl_3$): 128.9 (*d*, ^1J(C,H) = 171, C(3)); 124.0 (*d*, ^1J(C,H) = 174, C(4)); 74.2 (*d*, ^1J(C,H) = 144, C(2)); 56.3 (*t*, ^1J(C,H) = 136, C(5)); 34.4 (*s*, Me_3C); 26.92 (*q*, ^1J(C,H) = 131, 3 C, Me_3C). ^{17}O-NMR (54 MHz, $CDCl_3$, 295 K): 167, 158. CI-MS (NH_3): 192 (100, $[M+18]^+$), 175 (3, $[M+1]^+$), 128 (26), 110 (95), 95 (92), 82 (26). Anal. calc. for $C_8H_{14}O_2S$ (174.26): C 55.14, H 8.10; found: C 55.15, H 8.05.

(±)-2-Cyclohexyl-2,5-dihydrothiophene 1,1-Dioxide (**3h**). As described for **3g**, with (*E*)/(*Z*)-**1h** 10:1 (40 mg, 0.29 mmol). FC (CH_2Cl_2): 32 mg (55%) of **3h**. Yellowish oil. UV (MeCN): 277 (500), 197 (2200). IR (film): 2925, 1440, 1295, 1250, 1135, 1110, 890, 735, 655, 615, 580, 480, 410. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.11 (*m*, H−C(4), H−C(3)); 3.69 (*dm*, ^2J = 17.3, H−C(5)); 3.62 (*dm*, ^2J = 17.3, H−C(5)); 3.46 (*dm*, ^3J = 7.2, H−C(2)); 2.00–1.13 (*m*, 11 H, Chx). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 128.7 (*d*, ^1J(C,H) = 169, C(3)); 124.1 (*d*, ^1J(C,H) = 175, C(4)); 70.4 (*d*, ^1J(C,H) = 140, C(2)); 56.3 (*t*, ^1J(C,H) = 144, C(5)); 37.9 (*d*, ^1J(C,H) = 135, CH(Chx)); 31.9 (*t*, ^1J(C,H) = 125, CH_2(Chx)); 29.7 (*t*, ^1J(C,H) = 117, CH_2(Chx)); 26.4, 26.30, 26.27 (3*t*, ^1J(C,H) = 122, 3 CH_2(chx)). ^{17}O-NMR (54 MHz, CD_2Cl_2/SO_2, 295 K): 169, 156. CI-MS (NH_3): 218 (100, $[M+18]^+$), 201 (1, $[M+1]^+$), 154 (13), 136 (83), 121 (35), 107 (53), 94 (45), 81 (49). Anal. calc. for $C_{10}H_{16}O_2S$ (200.30): C 59.97, H 8.06; found: C 59.95, H 8.11.

(±)-2-Benzyl-2,5-dihydrothiophene 1,1-Dioxide (**3i**). As described for **3g**, with (*E*)/(*Z*)-**1i** 6:1 (20 mg, 0.14 mmol). FC (CH_2Cl_2): 20 mg (69%) of **3i**. Yellowish oil. UV (MeCN): 193 (11200), 198 (11400). IR (film): 3065, 3030, 1495, 1455, 1405, 1305, 1245, 1135, 1080, 920, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36 (*m*, 2 arom. H); 7.27 (*m*, 3 arom. H); 6.04 (*dddd*, ^3J(3,4) = 8.6, ^3J(4,5) = 2.7, 2.7, ^4J(2,4) = 2.7, H−C(4)); 5.93 (*dddd*, ^3J(3,4) = 8.6, ^3J(2,3) = 2.3, ^4J(3,5) = 2.3, 2.3, H−C(3)); 3.94 (*m*, H−C(2)); 3.80 (*dddd*, ^2J = 16.7, ^3J(4,5) = 2.7, ^4J(3,5) = 2.3, ^4J(2,5) = 2.3, H−C(5)); 3.74 (*dddd*, ^2J = 16.7, ^3J(4,5) = 2.7, ^4J(3,5) = 2.3, ^4J(2,5) = 1.3, H−C(5)); 3.38 (*dd*, ^2J = 14.0, ^3J = 5.7, 1 H, PhCH_2); 2.82 (*dd*, ^2J = 14.0, ^3J = 9.9, 1 H, PhCH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 136.3 (*s*, arom. C); 129.7 (*d*, ^1J(C,H) = 177, C(3)); 129.0 (*d*, ^1J(C,H) = 153, arom. C); 128.8 (*d*, ^1J(C,H) = 169, arom. C); 127.1 (*d*, ^1J(C,H) = 169, arom. C); 123.2 (*d*, ^1J(C,H) = 175, C(4)); 65.2 (*d*, ^1J(C,H) = 144, C(2)); 55.7 (*t*, ^1J(C,H) = 134, C(5)); 34.5 (*t*, ^1J(C,H) = 132, PhCH_2). CI-MS (NH_3): 226 (100, $[M+18]^+$), 209 (6, $[M+1]^+$), 143 (98), 128 (73), 115 (63), 91 (84). Anal. calc. for $C_{11}H_{12}O_2S$ (208.28): C 63.44, H 5.81; found: C 63.52, H 5.87.

(±)-2-Cyclopropyl-2,5-dihydrothiophene 1,1-Dioxide (**3j**). As described for **3g**, with (*E*)/(*Z*)-**1j** 5:1 (30 mg, 0.32 mmol). FC (CH_2Cl_2): 50 mg (99%) of **3j**. White solid. M.p. 66–67°. UV (MeCN): 193 (1100). IR (KBr): 3070, 3010, 2960, 1620, 1470, 1435, 1420, 1355, 1305, 1255, 1130, 1105, 1050, 1020, 675. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.09 (*dddd*, ^3J(3,4) = 8.7, ^3J(4,5) = 2.9, 2.2, ^4J(2,4) = 2.7, H−C(4)); 6.04 (*dddd*, ^3J(3,4) = 8.7, ^3J(2,3) = 2.2, ^4J(3,5) = 2.2, 2.0, H−C(3)); 3.72 (*dddd*, ^2J = 14.5, ^3J(4,5) = 2.2, ^4J(3,5) = 2.0, ^4J(2,5) = 1.5, H−C(5)); 3.67 (*dddd*, ^2J = 14.5, ^3J(4,5) = 2.9, ^4J(3,5) = 2.2, ^4J(2,5) = 2.2, H−C(5)); 3.19 (*dm*, ^3J = 9.0, H−C(2)); 1.03 (*m*, 1 H); 0.73 (*m*, 2 H); 0.51 (*m*, 1 H); 0.36 (*m*, 1 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 129.5 (*d*, ^1J(C,H) = 178, C(3)); 124.1 (*d*, ^1J(C,H) = 175, C(4)); 69.5 (*d*, ^1J(C,H) = 143, C(2)); 55.5 (*t*, ^1J(C,H) = 144, C(5)); 8.9 (*d*, ^1J(C,H) = 169, CH(cycloprop.)); 3.5 (*t*, ^1J(C,H) = 163, CH_2(cycloprop.)); 2.5 (*t*, ^1J(C,H) = 161, CH_2(cycloprop.)). ^{17}O-NMR (54 MHz, $CDCl_3$, 295 K): 164, 157. CI-MS (NH_3): 94 (32), 79 (100). Anal. calc. for $C_7H_{10}O_2S$ (158.22): C 53.14, H 6.37; found: C 53.13, H 6.23.

(±)-2,5-Dihydro-2-phenylthiophene 1,1-Dioxide (**3k**). As described for **3g**, with (*E*)-**1k** (80 mg, 0.62 mmol). FC (CH_2Cl_2): 50 mg (42%) of **3k**. Colorless oil. UV (MeCN): 281 (1500), 216 (9800). IR (film): 3630, 3030, 1495, 1455, 1405, 1310, 1240, 1135, 1115, 910, 775, 735, 700, 640, 615. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45 (*m*, 3 arom. H); 7.31 (*m*, 2 arom. H); 6.31 (*dddd*, ^3J(3,4) = 8.5, ^3J(4,5) = 2.7, 2.7, ^4J(2,4) = 2.7, H−C(4)); 6.21 (*dddd*, ^3J(3,4) = 8.5, ^3J(2,3) = 2.3, ^4J(3,5) = 2.3, 2.3, H−C(3)); 4.96 (*m*, H−C(2)); 3.87 (*dddd*, ^2J = 16.6, ^3J(4,5) = 2.7, ^4J(3,5) = 2.3, ^4J(2,5) = 2.2, H−C(5)); 3.81 (*dddd*, ^2J = 16.6, ^3J(4,5) = 2.7, ^4J(3,5) = 2.3, ^4J(2,5)) = 2.2, H−C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 130.0 (*s*, arom. C); 129.4 (*d*, ^1J(C,H) = 174, C(3)); 129.2 (*d*, ^1J(C,H) = 161, arom. C); 129.0 (*d*, ^1J(C,H) = 161, arom. C); 128.8 (*d*, ^1J(C,H) = 161, arom. C); 124.8 (*d*, ^1J(C,H) = 175, C(4)); 69.7 (*d*, ^1J(C,H) = 143, C(2)); 54.8 (*t*, ^1J(C,H) = 137, C(5)). ^{17}O-NMR (54 MHz, $CDCl_3$): 162, 158. CI-MS (NH_3): 212 (65, $[M+18]^+$), 130 (100), 115 (56).

(±)-2,5-Dihydro-2-(4-methoxyphenyl)thiophene 1,1-Dioxide (**3l**). As described for **3g**, with (*E*)/(*Z*)-**1l** 4:4 (20 mg, 0.13 mmol). FC (CH_2Cl_2): 16 mg (55%) of **3l**. Colorless oil. UV (MeCN): 266 (4400), 230 (7400), 200 (13400). IR (film): 2900, 1610, 1515, 1465, 1315, 1250, 1175, 1035, 835. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.24 (*m*, 2 arom. H); 6.95 (*m*, 2 arom. H); 6.29 (*dddd*, ^3J(3,4) = 8.5, ^3J(4,5) = 2.7, 2.7, ^4J(2,4) = 2.7, H−C(4)); 6.19 (*dddd*, ^3J(3,4) = 8.5, ^3J(2,3) = 2.2, 2.2, ^4J(3,5) = 2.2, H−C(3)); 4.46 (*m*, H−C(2)); 3.86 (*m*, CH_2(5)); 3.82 (*s*, MeO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.4 (*s*, arom. C); 130.3 (*d*, ^1J(C,H) = 158, arom. C); 129.9 (*d*, ^1J(C,H) = 174, C(3)); 124.5 (*d*, ^1J(C,H) = 174, C(4)); 121.8 (*s*, arom. C); 114.4 (*d*, ^1J(C,H) = 160, arom. C); 69.4 (*d*, ^1J(C,H) = 143, C(2)); 55.3 (*q*, ^1J(C,H) = 144, MeO); 54.7 (*t*, ^1J(C,H) = 137, C(5)). CI-MS (NH_3): 224 (3, $M^{+\bullet}$), 199 (14), 161 (85), 135 (34), 121 (100).

(±)-2,5-Dihydro-2-(trimethylsilyl)thiophene 1,1-Dioxide (**3m**). As described for **3g**, with (*E*)-**1m** [17]. Yield 75%. Identical to **3m** obtained by silylation of 2,5-dihydrothiophene 1,1-dioxide [26].

(±)-2,5-Dihydro-2-(phenoxy)thiophene 1,1-Dioxide (**3n**). As described for **3g**, with (*E*)-**1n** (23 mg, 0.31 mmol), CD_2Cl_2 (0.15 ml), $CFCl_3$ (100 mg), and SO_2 (0.2 ml) in a 5-mm NMR tube, reaction followed by ^{1}H-NMR, complete reaction after 24 h at −10°. Sulfolene **3n** was unstable at 20° after SO_2 evaporation. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 263 K): 7.40 (*m*, arom. H); 6.80 (*m*, 4 arom. H); 6.41 (*dddd*, $^3J(3,4)=8.8$, $^3J(4,5)=3.0$, 2.5, $^4J(2,4)=1.5$, H−C(4)); 6.26 (*dddd*, $^3J(3,4)=8.8$, $^3J(2,3)=2.5$, $^4J(3,5)=2.5$, 2.5, H−C(3)); 5.63 (*m*, H−C(2)); 3.87 (*dddd*, $^2J=17.1$, $^3J(4,5)$, H−C(4))$=2.5$, $^4J(3,5)=2.5$, $^4J(2,5)=2.5$, H−C(5)); 3.80 (*dddd*, $^2J=17.1$, $^3J(4,5)=3.0$, $^4J(3,5)=2.5$, $^4J(2,5)=0.8$, H−C(5)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/SO_2, 263 K): 157.2 (*s*, arom. C); 130.5 (*d*, ^1J(C,H) = 161, arom. C); 129.6 (*d*, $^1J(C,H)=177$, C(4)); 126.0 (*d*, $^1J(C,H)=175$, C(3)); 123.7 (*d*, ^1J(C,H) = 161, arom. C); 115.8 (*d*, $^1J(C,H)=158$, arom. C); 89.7 (*d*, $^1J(C,H)=166$, C(2)); 54.8 (*t*, $^1J(C,H)=138$, C(5)).

(±)-2-(4-Chlorophenoxy)-2,5-dihydrothiophene 1,1-Dioxide (**3o**). As described for **3n**, with (*E*)/(*Z*)-**1o** 3.2:1 (23 mg, 0.31 mmol). Sulfolene **3o** was unstable at 20°. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 263 K): 7.38 (*m*, 2 arom. H); 7.12 (*m*, 2 arom. H); 6.42 (*dddd*, $^3J(3,4)=8.8$, $^3J(4,5)=3.0$, 2.5, $^4J(2,4)=1.5$, H−C(4)); 6.22 (*dddd*, $^3J(3,4)=8.8$, $^3J(2,3)=2.5$, $^4J(3,5)=2.5$, 2.5, H−C(3)); 5.57 (*m*, H−C(2)); 3.87 (*dddd*, $^2J=17.2$, $^3J(4,5)=2.5$, $^4J(3,5)=2.5$, $^4J(2,5)=2.5$, H−C(5)); 3.81 (*dddd*, $^2J=17.2$, $^3J(4,5)=3.0$, $^4J(3,5)=2.5$, $^4J(2,5)=0.7$, H−C(5)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/SO_2, 263 K): 155.9 (*s*, arom. C); 130.2 (*d*, $^1J(C,H)=173$, arom. C); 129.9 (*d*, $^1J(C,H)=177$, C(4)); 129.7 (*s*, arom. C); 126.1 (*d*, $^1J(C,H)=183$, C(3)); 116.4 (*d*, $^1J(C,H)=163$, arom. C); 90.1 (*d*, $^1J(C,H)=173$, C(2)); 54.9 (*t*, $^1J(C,H)=138$, C(5)). ^{17}O-NMR (48.9 MHz, CD_2Cl_2/SO_2, 253 K): 161.

(±)-2,5-Dihydro-2-(4-methoxyphenoxy)thiophene 1,1-Dioxide (**3p**). As described for **3n**, with (*E*)/(*Z*)-**1p** 3:1. Complete reaction after 24 h at −10° (NMR). Sulfolene **3p** decomposed at 25°. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 263 K): 7.00 (*m*, 2 arom. H); 6.83 (*m*, 2 arom. H); 6.38 (*dddd*, $^3J(3,4)=8.8$, $^3J(4,5)=3.0$, 2.5, $^4J(2,4)=1.5$, H−C(4)); 6.23 (*dddd*, $^3J(3,4)=8.8$, $^3J(2,3)=2.5$, $^4J(3,5)=2.5$, 2.5, H−C(3)); 5.53 (*m*, H−C(2)); 3.86 (*dddd*, $^2J=17.2$, $^3J(4,5)=2.5$, $^4J(3,5)=2.5$, $^4J(2,5)=2.5$, H−C(5)); 3.79 (*dddd*, $^2J=17.2$, $^3J(4,5)=3.0$, $^4J(3,5)=2.5$, $^4J(2,5)=0.7$, H−C(5)); 3.73 (*s*, MeO). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/SO_2, 263 K): 156.9, 153.0 (2*s*, arom. C); 129.5 (*d*, $^1J(C,H)=176$, C(4)); 126.5 (*d*, $^1J(C,H)=177$, C(3)); 117.4 (*d*, $^1J(C,H)=162$, arom. C); 115.2 (*d*, ^1J(C,H) = 157, arom. C); 91.0 (*d*, $^1J(C,H)=164$, C(2)); 55.2 (*q*, $^1J(C,H)=145$, MeO); 54.8 (*t*, $^1J(C,H)=145$, C(5)). ^{17}O-NMR (48.9 MHz, CD_2Cl_2/SO_2, 253 K): 158, 76, 43.

(±)-2,5-Dihydro-2-(4-nitrophenoxy)thiophene 1,1-Dioxide (**3q**). As described for **3n**, with (*E*)/(*Z*)-**1q** 3:1 (17 mg, 0.09 mmol). Complete conversion into **3q** at 10° after 24 h. Sulfolene **3q** was unstable at 20°. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 273 K): 8.25 (*m*, 2 arom. H); 7.13 (*m*, 2 arom. H); 6.51 (*dddd*, $^3J(3,4)=8.8$, $^3J(4,5)=3.0$, 2.5, $^4J(2,4)=1.5$, H−C(4)); 6.28 (*dddd*, $^3J(3,4)=8.8$, $^3J(2,3)=2.5$, $^4J(3,5)=2.5$, 2.5, H−C(3)); 5.77 (*m*, H−C(2)); 3.96 (*dddd*, $^2J=17.4$, $^3J(4,5)=2.5$, $^4J(3,5)=2.5$, $^4J(2,5)=2.5$, H−C(5)); 3.90 (*dddd*, $^2J=17.4$, $^3J(4,5)=3.0$, $^4J(3,5)=2.5$, $^4J(2,5)=0.9$, H−C(5)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/SO_2, 273 K): detected signals: 130.6 (*d*, $^1J(C,H)=177$, C(4)); 125.9 (*d*, $^1J(C,H)=178$, C(3)); 89.4 (*d*, $^1J(C,H)=164$, C(2)); 55.3 (*t*, $^1J(C,H)=145$, C(5)).

(±)-2,5-Dihydro-2-(naphthalen-2-yloxy)thiophene 1,1-Dioxide (**3r**). As described for **3n**, with (*E*)-**1r** (12 mg, 0.04 mmol). Sulfolene **3r** was unstable at 25°. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 263 K): 7.85–7.23 (*m*, 7 arom. H); 6.44 (*dddd*, $^3J(3,4)=8.8$, $^3J(4,5)=3.0$, 2.5, $^4J(2,4)=1.5$, H−C(4)); 6.29 (*dddd*, $^3J(3,4)=8.8$, $^3J(2,3)=2.5$, $^4J(3,5)=2.5$, 2.5, H−C(3)); 5.77 (*m*, H−C(2)); 3.91 (*dddd*, $^2J=17.1$, $^3J(4,5)=2.5$, $^4J(3,5)=2.5$, $^4J(2,5)=2.5$, H−C(5)); 3.85 (*dddd*, $^2J=17.1$, $^3J(4,5)=3.0$, $^4J(3,5)=2.5$, $^4J(2,5)=0.8$, H−C(5)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/SO_2, 263 K): 155.4, 134.5 (2*s*, arom. C); 130.8 (*d*, $^1J(C,H)=162$, arom. C); 129.9 (*d*, $^1J(C,H)=170$, C(4)); 128.5, 127.9, 127.8 (3 arom. C); 126.4 (*d*, $^1J(C,H)=151$, C(3)); 125.8 (*d*, $^1J(C,H)=161$, arom. C); 125.6 (*s*, arom. C); 119.0 (*d*, $^1J(C,H)=163$, arom. C); 109.6 (*d*, $^1J(C,H)=159$, arom. C); 90.0 (*d*, $^1J(C,H)=165$, C(2)); 55.0 (*t*, $^1J(C,H)=146$, C(5)).

(±)-2,5-Dihydro-2-(methylthio)thiophene 1,1-Dioxide (**3s**). As described for **3g**, with (*E*)-**1s** (124 mg, 1.2 mmol). FC (CH_2Cl_2): 94 mg (48%) of **3s**. Pale yellow oil that decomposed on staying at 20°. UV (MeCN): 202 (2400). IR (film): 2920, 1715, 1680, 1435, 1305, 1245, 1175, 1135, 970. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.25 (*dddd*, $^3J(3,4)=8.6$, $^3J(4,5)=3.2$, 2.5, $^4J(2,4)=2.0$, H−C(4)); 6.11 (*dddd*, $^3J(3,4)=8.6$, $^3J(2,3)=3.0$, $^4J(3,5)=2.3$, 2.3, H−C(3)); 4.61 (*dddd*, $^3J(2,3)=3.0$, $^4J(2,5)=2.0$, 1.0, H−C(2)); 3.83 (*dddd*, $^2J=17.0$, $^3J(4,5)=3.2$, $^4J(3,5)=2.3$, $^4J(2,5)=1.0$, H−C(5)); 3.77 (*dddd*, $^2J=17.0$, $^3J(4,5)=2.5$, $^4J(3,5)=2.3$, $^4J(2,5)=2.0$, H−C(5)); 2.20 (*s*, MeS). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 127.7 (*d*, $^1J(C,H)=177$, C(4)); 125.4 (*d*, $^1J(C,H)=169$, C(3)); 68.0 (*d*, $^1J(C,H)=155$, C(2)); 53.4 (*t*, $^1J(C,H)=144$, C(5)); 13.7 (*q*, $^1J(C,H)=136$, MeS). ^{17}O-NMR (54 MHz, $CDCl_3$, 295 K): 162, 160. CI-MS (NH_3): 163 (3, $M^{+\bullet}$), 147 (19), 133 (17), 96 (9), 83 (3).

(±)-2,5-Dihydro-2-(phenylthio)thiophene 1,1-Dioxide (**3t**). As described for **3g**, with (*E*)/(*Z*)-**1t** 2:1 [39] (1.0 g, 6.2 mmol) and SO_2 (10 g, 0.16 mol), without solvent. FC (CH_2Cl_2): 550 mg (39%) of **3t**. White solid. M.p. 55–56° (pentane). UV (MeCN): 204 (17600), 199 (20200). IR (KBr): 3070, 2935, 1575, 1480, 1400, 1320, 1250, 1185, 1145, 1110, 1095, 815, 740, 685. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60 (*m*, 2 arom. H); 7.30 (*m*, arom. H); 7.16 (*m*, 2 arom. H); 6.10 (*dddd*, $^3J(3,4) = 8.6$, $^3J(4,5) = 3.2$, 2.5, $^4J(2,4) = 1.9$, H–C(4)); 6.00 (*dddd*, $^3J(3,4) = 8.6$, $^3J(3,5) = 2.5$, $^3J(2,3) = 2.2$, $^4J(3,5) = 1.8$, H–C(3)); 4.80 (*m*, H–C(2)); 3.70 (*dddd*, $^2J = 17.0$, $^3J(4,5) = 3.2$, $^4J(3,5) = 1.8$, $^4J(2,5) = 1.0$, H–C(5)); 3.50 (*dddd*, $^2J = 17.0$, $^3J(4,5) = 2.5$, $^4J(3,5) = 2.5$, $^4J(2,5) = 2.2$, H–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 133.7 (*d*, ^1J(C,H) = 161, arom. C); 130.5 (*s*, arom. C); 129.1 (*d*, ^1J(C,H) = 161, arom. C); 128.8 (*d*, ^1J(C,H) = 161, arom. C); 127.4 (*d*, ^1J(C,H) = 177, C(4)); 125.4 (*d*, ^1J(C,H) = 175, C(3)); 70.4 (*d*, ^1J(C,H) = 157, C(2)); 54.1 (*t*, ^1J(C,H) = 144, C(5)). ^{17}O-NMR (48.9 MHz, $CDCl_3$, 295 K): 160. CI-MS (NH_3): 226 (6, $M^{+\bullet}$), 162 (53), 129 (92), 104 (14), 85 (100). Anal. calc. for $C_{10}H_{10}O_2S_2$ (226.31): C 53.07, H 4.45, S 28.33; found: C 53.15, H 4.55, S 28.15.

(±)-2-[(4-Chlorophenyl)thio]-2,5-dihydrothiophene 1,1-Dioxide (**3u**). As described for **3g**, with (*E*)/(*Z*)-**1u** 2:1 (1.2 g, 6.1 mmol) and SO_2 (9.9 g, 0.15 mol), without solvent. FC (CH_2Cl_2): 1.2 g (60%) of **3u**. White solid. M.p. 86–87° (pentane). UV (MeCN): 263 (4300), 260 (4300), 223 (9500), 201 (18300). IR (KBr): 1475, 1310, 1240, 1140, 1120, 740, 650, 625, 580, 475. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.51 (*m*, 2 arom. H); 7.24 (*m*, 2 arom. H); 6.13 (*dddd*, $^3J(3,4) = 8.6$, $^3J(4,5) = 3.0$, 2.3, $^4J(2,4) = 1.9$, H–C(4)); 6.08 (*dddd*, $^3J(3,4) = 8.6$, $^3J(2,3) = 2.5$, $^4J(3,5) = 1.8$, 1.5, H–C(3)); 4.80 (*m*, H–C(2)); 3.70 (*dddd*, $^2J = 16.9$, $^3J(4,5) = 3.0$, $^4J(3,5) = 1.8$, $^4J(2,5) = 1.0$, H–C(5)); 3.60 (*dddd*, $^2J = 16.9$, $^3J(4,5) = 2.3$, $^4J(3,5) = 2.5$, $^4J(2,5) = 2.3$, H–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): detected signals: 135.6 (*d*, ^1J(C,H) = 165, arom. C); 129.4 (*d*, ^1J(C,H) = 166, arom. C); 128.8 (*s*, arom. C); 127.4 (*d*, ^1J(C,H) = 175, C(4)); 125.7 (*d*, ^1J(C,H) = 165, C(3)); 70.1 (*d*, ^1J(C,H) = 157, C(2)); 54.2 (*t*, ^1J(C,H) = 137, C(5)). ^{17}O-NMR (48.9 MHz, CD_2Cl_2, 295 K): 161. CI-MS (NH_3): 196 (33), 144 (31), 108 (36), 85 (100). Anal. calc. for $C_{10}H_9ClO_2S_2$ (260.75): C 46.06, H 3.48, Cl 13.60, S 24.59; found: C 46.11, H 3.47, Cl 13.67, S 24.68.

(±)-2,5-Dihydro-2-[(4-methoxyphenyl)thio]thiophene 1,1-Dioxide (**3v**). As described for **3g**, with (*E*)/(*Z*)-**1v** 2.3:1 (2.0 g, 10 mmol) and SO_2 (20 g, 0.31 mol), without solvent. FC (CH_2Cl_2): 1.0 g (39%) of **3v**. Pale yellow oil, unstable at 25°. UV (MeCN): 263 (11200), 257 (11400), 232 (16000), 202 (23300). IR (film): 2835, 1590, 1570, 1495, 1465, 1440, 1315, 1290, 1250, 1175, 1135, 1105, 1030, 830, 790, 735, 640. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60 (*m*, 2 arom. H); 6.86 (*m*, 2 arom. H); 6.09 (*dddd*, $^3J(3,4) = 8.5$, $^3J(4,5) = 3.2$, 2.5, $^4J(2,4) = 2.4$, H–C(4)); 6.02 (*dddd*, $^3J(3,4) = 8.5$, $^3J(2,3) = 3.4$, $^4J(3,5) = 2.4$, 1.8, H–C(3)); 4.71 (*m*, H–C(2)); 3.81 (*s*, MeO); 3.64 (*dddd*, $^2J = 16.9$, $^3J(4,5) = 3.2$, $^4J(3,5) = 1.8$, $^4J(2,5) = 0.7$, H–C(5)); 3.44 (*dddd*, $^2J = 16.9$, $^3J(4,5) = 2.4$, $^4J(3,5) = 2.4$, $^4J(2,5) = 2.4$, H–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 137.4 (*d*, ^1J(C,H) = 164, arom. C); 133.5 (*s*, arom. C); 127.8 (*d*, ^1J(C,H) = 177, C(4)); 125.2 (*d*, ^1J(C,H) = 175, C(3)); 119.9 (*s*, arom. C); 114.7 (*d*, ^1J(C,H) = 161, arom. C); 71.0 (*d*, ^1J(C,H) = 156, C(2)); 55.3 (*q*, ^1J(C,H) = 144, MeO); 54.0 (*t*, ^1J(C,H) = 145, C(5)). ^{17}O-NMR (48.9 MHz, $CDCl_3$, 295 K): 162, 53. CI-MS (NH_3): 274 (8, $[M+18]^+$), 144 (31), 209 (14), 193 (94), 159 (17), 139 (100), 124 (13), 96 (17), 85 (10).

(±)-2,5-Dihydro-2-[(4-nitrophenyl)thio]thiophene 1,1-Dioxide (**3w**). As described for **3g**, with (*E*)/(*Z*)-**1w** 3.5:1 (0.8 g, 3.9 mmol) and SO_2 (5 g, 0.08 mol), without solvent, left at 25° for 7 days. FC (CH_2Cl_2): 240 mg (23%) of **3w**. Yellow solid. M.p. 109–110°. UV (MeCN): 321 (9100), 260 (4200), 217 (7100), 197 (16400). IR (KBr): 1505, 1340, 1335, 1300, 1140, 855, 840, 740, 640, 595. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.21 (*m*, 2 arom. H); 7.65 (*m*, 2 arom. H); 6.30 (*dddd*, $^3J(3,4) = 8.6$, $^3J(4,5) = 3.2$, 2.7, $^4J(2,4) = 2.0$, H–C(4)); 6.10 (*dddd*, $^3J(3,4) = 8.6$, $^3J(2,3) = 2.8$, $^4J(3,5) = 2.3$, 2.0, H–C(3)); 5.08 (*m*, H–C(2)); 3.87 (*dddd*, $^2J = 17.0$, $^3J(4,5) = 3.2$, $^4J(3,5) = 2.0$, $^4J(2,5) = 1.0$, H–C(5)); 3.85 (*dddd*, $^2J = 17.0$, $^3J(4,5) = 2.7$, $^4J(3,5) = 2.3$, $^4J(2,5) = 2.3$, H–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 146.9 (*s*, arom. C); 141.2 (*s*, arom. C); 130.7 (*d*, ^1J(C,H) = 167, arom. C); 126.8 (*d*, ^1J(C,H) = 170, C(4)); 126.3 (*d*, ^1J(C,H) = 172, C(3)); 124.2 (*d*, ^1J(C,H) = 170, arom. C); 68.9 (*d*, ^1J(C,H) = 158, C(2)); 54.5 (*t*, ^1J(C,H) = 145, C(5)). ^{17}O-NMR (48.9 MHz, $CDCl_3$, 295 K): 570, 161. CI-MS (NH_3): 271 (1, $M^{+\bullet}$), 207 (29), 128 (11), 115 (6), 85 (100). Anal. calc. for $C_{10}H_9NO_4S_2$ (271.31): C 44.27, H 3.34, N 5.16, S 23.63; found: C 44.31, H 3.35, N 5.11, S 23.64.

(±)-2,5-Dihydro-2-(phenylseleno)thiophene 1,1-Dioxide (**3x**) *and (±)-2,5-Dihydro-3-(phenylseleno)thiophene 1,1-Dioxide.* As described for **3g**, with (*E*)-**1x**/(*Z*)-**1x**/**12** 1:0.8:0.5 (270 mg, 1.29 mmol) and SO_2 (1.4 g, 22 mmol). FC (CH_2Cl_2) gave 40 mg (19%) of **3x** and 25 mg (19%) of 2,5-dihydro-3-(phenylseleno)thiophene 1,1-dioxide.

Data of **3x**: Yellow oil that decomposed at 25°. UV (MeCN): 224 (26900), 208 (17300). IR (film): 3060, 1580, 1480, 1320, 1245, 1140, 1100, 740, 690, 645. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.73 (*m*, 2 arom. H); 7.35 (*m*, 3 arom. H); 6.16 (*dddd*, $^3J(3,4) = 8.5$, $^3J(2,3) = 2.7$, $^4J(3,5) = 2.5$, 1.8, H–C(3)); 5.95 (*dddd*, $^3J(3,4) = 8.5$, $^3J(4,5) = 3.4$, 2.5, $^4J(2,4) = 1.9$, H–C(4)); 4.92 (*m*, H–C(2)); 3.65 (*dddd*, $^2J = 16.8$, $^3J(4,5) = 3.4$, $^4J(3,5) = 2.5$,

$^4J(2,5) = 2.5$, H–C(5)); 3.40 (*dddd*, $^2J = 16.8$, $^3J(4,5) = 2.5$, $^3J(3,5) = 2.5$, $^4J(2,5) = 2.5$, H–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 136.5 (*t*, ^1J(C,H) = 165, arom. C); 129.3 (*d*, ^1J(C,H) = 161, arom. C); 129.2 (*d*, ^1J(C,H) = 161, arom. C); 128.8 (*d*, ^1J(C,H) = 178, C(4)); 124.2 (*d*, ^1J(C,H) = 164, C(3)); 63.0 (*d*, ^1J(C,H) = 158, C(2)); 53.7 (*t*, ^1J(C,H) = 144, C(5)). ^{17}O-NMR (54 MHz, $CDCl_3$): 163, 157.

Data of 2,5-Dihydro-3-(phenylseleno)thiophene 1,1-Dioxide: Yellow solid. M.p. 49–50°. UV (MeCN): 251 (7100), 198 (14300). IR (film): 1580, 1450, 1435, 1315, 1300, 1125, 1020, 905, 735, 590. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39 (*m*, 2 arom. H); 7.30 (*m*, 3 arom. H); 6.00 (*dddd*, $^3J(4,5) = 2.0, 2.0$, $^4J(2,4) = 2.0, 2.0$, H–C(4)); 3.86 (*m*, CH_2); 3.74 (*m*, CH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 134.9 (*d*, ^1J(C,H) = 160, arom. C); 129.8 (*d*, ^1J(C,H) = 163, arom. C); 129.1 (*d*, ^1J(C,H) = 162, arom. C); 127.1 (*s*); 125.5 (*s*); 123.4 (*d*, ^1J(C,H) = 176, C(4)); 59.1 (*t*, ^1J(C,H) = 139, CH_2); 58.3 (*t*, ^1J(C,H) = 151, CH_2). ^{17}O-NMR (54 MHz, $CDCl_3$): 168. CI-MS (NH_3): 292 (18, $[M+1+18]^+$), 274 (45, $[M+1]^+$), 210 (57), 158 (35), 129 (100). Anal. calc. for $C_{10}H_{10}O_2SSe$ (273.21): C 43.96; H 3.69; found: C 44.11, H 3.74.

(±)-2,5-Dihydro-1,1-dioxidothiophen-2-yl Benzoate (**3y**). A mixture of (*E*)/(*Z*)-**1y** 10:1 (597 mg, 3.43 mmol) and pure SO_2 (3.52 g, 54.9 mmol) was placed in a sealed *Pyrex* tube and left at 25° for 7 days. After freezing the tube in liq. N_2 and opening, SO_2 was evaporated. The residue was purified by FC (AcOEt/light petroleum ether 1:1, then gradually up to 4:1): 446 mg (55%) of **3y**, soluble in $CHCl_3$ only. Recrystallization from $CHCl_3$/pentane gave colorless needles submitted to X-ray analysis. M.p. 112–115° (dec.). UV (MeCN): 271 (2600), 236 (9800). IR (KBr): 3090, 3070, 3000, 2940, 1730, 1600, 1455, 1405, 1315, 1255, 1185, 1130, 1085, 1070, 755, 710. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.11 (*dm*, $^3J = 8.0$, H–C(2), H–C(6)); 7.63 (*tm*, $^3J = 8.0$, H–C(4)); 7.48 (*tm*, $^3J = 8.0$, H–C(3), H–C(5)); 6.46 (*dddd*, $^3J = 8.6$, ^3J(4′,5b)) = 3.0, ^3J(4′,5a) = 2.7, $^4J(2,4') = 0.9$, H–C(4′)); 6.29 (*dddd*, $^3J(3',4') = 8.6$, $^3J(2',3') = 2.7$, $^4J(3',5'a) = 2.7$, $^4J(3',5'b) = 2.1$, H–C(3′)); 6.24 (*dddd*, $^3J(2',3') = 2.7$, $^5J(2',5'a) = 1.8$, $^4J(2',4') = 0.9$, $^5J(2',5'b) = 0.9$, H–C(2′)); 3.89 (*dddd*, $^2J(5'a,5'b) = 18.0$, $^3J(4',5'a) = 2.7$, $^4J(3',5'a) = 2.7$, $^5J(2',5'a) = 1.8$, H_a–C(5′)); 3.84 (*dddd*, $^2J(5'a,5'b) = 18.0$, $^3J(4',5'b) = 3.0$, $^4J(3',5'b) = 2.1$, $^5J(2',5'b) = 0.9$, H_b–C(5′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.0 (*s*, C=O); 134.0 (*d*, ^1J(C,H) = 162, C(4)); 130.2 (*d*, ^1J(C,H) = 170, C(4′)); 130.2 (*d*, ^1J(C,H) = 162, C(2), C(6)); 128.6 (*d*, ^1J(C,H) = 162, C(3), C(5)); 128.1 (*s*, C(1)); 125.5 (*d*, ^1J(C,H) = 177, C(3′)); 83.9 (*d*, ^1J(C,H) = 168, C(2′)); 54.4 (*t*, ^1J(C,H) = 145, C(5′)). ^{17}O-NMR (81.3 MHz, MeCN/$CDCl_3$/$CHCl_3$, 25°): 341 (C=O); 161.5 (O–C(2)); 153.5 (O(a)=S); 152.1 (O(b)=S). CI-MS (NH_3): 238 (0.1, $M^{+\bullet}$), 174 (1.1, $[M-SO_2]^{+\bullet}$), 166 (3), 164 (2), 122 (2), 106 (13), 105 (100), 78 (5), 77 (24). Anal. calc. for $C_{11}H_{10}O_4S$ (238.26): C 55.45, H 4.23, S 13.46; found: C 55.39, H 4.20, S 13.38.

(±)-2,5-Dihydro-1,1-dioxidothiophen-2-yl Naphthalene-2-carboxylate (**3z**). As described for **3y**, with (*E*)/(*Z*)-**1z** 8:1 (2.0 g, 8.9 mmol) and pure SO_2 (5 ml), at 0° for 4 days. FC (CH_2Cl_2/light petroleum ether 1:1, then pure CH_2Cl_2): 770 mg of (*E*)/(*Z*)-**1z** and 563 mg (22%) of **3z** as colorless needles. M.p. 128–130° (dec.). UV (MeCN): 337 (8600), 325 (8600), 290 (23000), 281 (31000), 274 (26000), 240 (118000), 211 (63000). IR (KBr): 3070, 2985, 1725, 1305, 1195, 1145, 1080, 780, 675, 585, 470, 410. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.69 (br. *s*, H–C(1)); 8.10 (*dd*, $^3J(3,4) = 8.6$, $^4J(1,3) = 1.7$, H–C(3)); 7.98 (*ddm*, $^3J(7,8) = 8.1$, $^4J(6,8) = 1.4$, H–C(8)); 7.92 (*d*, $^3J(3,4) = 8.6$, H–C(4)); 7.90 (*ddm*, $^3J(5,6) = 8.1$, $^4J(5,7) = 1.3$, H–C(5)); 7.64 (*ddd*, $^3J(5,6) = 8.1$, $^3J(6,7) = 6.9$, $^4J(6,8) = 1.4$, H–C(6)); 7.57 (*ddd*, $^3J(7,8) = 8.1$, $^3J(6,7) = 6.9$, $^4J(5,7) = 1.3$, H–C(7)); 6.49 (*ddm*, $^3J(3',4') = 8.6$, $^4J(2',4') = 1.0$, H–C(4′)); 6.34 (*ddm*, $^3J(3',4') = 8.6$, $^3J(2',3') = 3.0$, H–C(3′)); 6.32 (*ddm*, $^3J(2',3') = 3.0$, $^4J(2',4') = 1.0$, H–C(2′)); 3.93 (*dm*, $^2J(5'a,5'b) = 17.0$, H_a–C(5′)); 3.86 (*dm*, $^2J(5'a,5'b) = 17.0$, H_b–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.6 (*s*, C=O); 136.0 (*s*, C(4a)); 132.3 (*s*, C(8a)); 132.2 (*d*, ^1J(C,H) = 162, C(1)); 130.3 (*d*, ^1J(C,H) = 173, C(4′)); 129.5 (*d*, ^1J(C,H) = 161, C(8)); 128.9 (*d*, ^1J(C,H) = 162, C(4)); 128.5 (*d*, ^1J(C,H) = 162, C(6)); 127.8 (*d*, ^1J(C,H) = 162, C(5)); 126.9 (*d*, ^1J(C,H) = 162, C(7)); 125.6 (*d*, ^1J(C,H) = 177, C(3′)); 125.2 (*d*, ^1J(C,H) = 172, C(3)); 125.1 (*s*, C(2)); 84.0 (*d*, ^1J(C,H) = 168, C(2′)); 54.5 (*t*, ^1J(C,H) = 144, C(5′)). CI-MS (NH_3): 306 (15, $[M+NH_4]^+$), 289 (3, $[M+H]^+$), 288 (0.2, $M^{+\bullet}$), 242 (5, $[M+NH_4-SO_2]^+$), 225 (34, $[M+H-SO_2]^+$), 172 (9), 156 (37), 155 (100), 127 (38), 98 (18).

*(1*RS*,3*RSi*)*-cis-*1,4,5,6,7,8-Hexahydro-1-methyl-2,3-benzoxathiin 3-Oxide* (*c*-**15**) *and (1*RS*,3*SR*)*-trans-*1,4,5,6,7,8-Hexahydro-1-methyl-2,3-benzoxathiin 3-Oxide* (*t*-**15**). As described for **2g**, with (*E*)/(*Z*)-**4a** 2:1, without CF_3COOH. After 5 min at −75°, the equilibrium (*E*)-**4a** + SO_2 ⇄ *cis*-sultine *c*-**15** was reached. After 14 h at −75°, *c*/*t*-**15** 5:95 was obtained.

Data of c-**15**: ^{1}H-NMR (400 MHz, CD_2Cl_2/$CFCl_3$/SO_2, −85°): 4.51 (*qm*, $^3J = 7.0$, H–C(1)); 3.32 (*dm*, $^2J = 15.7$, H_a–C(4)); 2.99 (*dm*, $^2J = 15.7$, H_b–C(4)); 2.08–1.99 (*m*, H_a–C(8)); 2.04–1.93 (*m*, CH_2(5)); 1.82–1.75 (*m*, H_b–C(8)); 1.80–1.75 (*m*, H_a–C(7) or H_a–C(6)); 1.76 (*m*, H_a–C(6) or H_a–C(7)); 1.57–1.44 (*m*, H_b–C(6) or H_b–C(7)); 1.55–1.45 (*m*, H_b–C(7) or H_b–C(6)); 1.43 (*d*, $^3J = 7.0$, Me). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/$CFCl_3$/SO_2, −85°): 130.6 (*s*, C(8a)); 117.3 (*s*, C(4a)); 76.1 (*d*, ^1J(C,H) = 150, C(1)); 51.7 (*t*, ^1J(C,H) = 139, C(4));

30.3 (t, ^1J(C,H) = 127, C(5)); 25.9 (t, ^1J(C,H) = 127, C(8)); 22.1 (t, ^1J(C,H) = 127, C(6) or C(7)); 21.9 (t, ^1J(C,H) = 127, C(7) or C(6)); 20.7 (q, ^1J(C,H) = 130, Me).

Data of t-**15**: ^{1}H-NMR (400 MHz, $CD_2Cl_2/CFCl_3/SO_2$, −65°): 4.46 (qm, ^3J = 6.8, H−C(1)); 3.39 (dm, ^2J = 16.7, H_a−C(4)); 2.74 (dm, ^2J = 16.7, H_b−C(4)); 1.94–1.90 (m, H_a−C(8)); 1.91–1.80 (m, CH_2(5)); 1.72 (m, H_a−C(6), H_a−C(7)); 1.72–1.67 (m, H_b−C(8)); 1.41 (m, H_b−C(6), H_b−C(7)); 1.38 (d, ^3J = 6.8, Me); 1.53–1.43 (m, H_b−C(6), H_b−C(7)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, −65°): 129.8 (s, C(8a)); 117.4 (s, C(4a)); 68.8 (d, ^1J(C,H) = 149, C(1)); 49.9 (t, ^1J(C,H) = 138, C(4)); 30.0 (t, ^1J(C,H) = 127, C(5)); 25.4 (t, ^1J(C,H) = 127, C(8)); 22.1, 22.0 (2t, ^1J(C,H) = 127, C(6), C(7)); 18.3 (q, ^1J(C,H) = 129, Me): ^{17}O-NMR (54.2 MHz, $CD_2Cl_2/CFCl_3/SO_2$, −65°): 141 (br. s, $w_{1/2}$ = 800, O=S(3)); 88 (br. s, $w_{1/2}$ = 1200, O(2)).

(±)-1,3,4,5,6,7-Hexahydro-1-methylbenzo[c]thiophene 2,2-Dioxide (**16a**). As described for **3g**, with (*E*)/(*Z*)-**4a** 2:1 (200 mg, 1.03 mmol), SO_2 (2 ml), no solvent (25°, 14 h). FC (CH_2Cl_2): 300 mg (98%) of **16a**. Colorless oil. UV (MeCN): 202 (4000). IR (KBr): 2935, 2860, 2840, 1450, 1410, 1380, 1305, 1240, 1145, 1105, 785. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.64 (dm, ^2J = 17.7, H_a−C(3)); 3.60 (dm, ^2J = 17.7, H_b−C(3)); 3.59 (qm, ^3J = 7.2, H−C(1)); 2.08–1.90 (m, CH_2(7)); 2.02 (m, CH_2(4)); 1.73–1.62 (m, CH_2(5), CH_2(6)); 1.35 (d, ^3J = 7.2, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 133.0 (s, C(7a)); 126.3 (s, C(3a)); 62.8 (d, ^1J(C,H) = 141, C(1)); 57.8 (t, ^1J(C,H) = 142, C(3)); 25.6 (t, ^1J(C,H) = 127, C(7)); 23.8 (t, ^1J(C,H) = 127, C(4)); 21.7 (2t, ^1J(C,H) = 129, C(5), C(6)); 12.0 (q, ^1J(C,H) = 130, Me). ^{17}O-NMR (54.2 MHz, $CDCl_3$, 298 K): 155.8 (br. s, $w_{1/2}$ = 300, O(a)=S); 149.4 (br. s, $w_{1/2}$ = 300, O(b)=S). CI-MS (NH_3): 205 (28, $[M+H+NH_4]^+$), 204 (100, $[M+NH_4]^+$), 122 (15, $[M-SO_2]^+$), 107 (4), 93 (5), 76 (3).

(±)-1,3,4,5,6,7-Hexahydro-1-methoxybenzo[c]thiophene 2,2-Dioxide (**16f**). As described for **2g**, with (*E*)/(*Z*)-**4f** 1.5:1 (36 mg, 2.6 mmol), without CF_3COOH. By ^{1}H-NMR the cheletropic addition was complete after 15 h at −80°. Sulfolene **16f** was decomposed as a result of attempts to eliminate the excess SO_2 or raising the temp. above −10°. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 203 K): 4.55 (br. s, H−C(2)); 3.68 (dm, ^2J = 16.6, H−C(4)); 3.57 (s, MeO); 3.52 (dm, ^2J = 16.6, H−C(4)); 2.05 (m, CH_2(6), CH_2(9)); 1.68 (m, CH_2(7), CH_2(8)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2/SO_2, 203 K): 133.9 (s, C(1)); 129.6 (s, C(5)); 96.8 (d, ^1J(C,H) = 162, C(2)); 59.1 (q, ^1J(C,H) = 140, MeO); 59.5 (t, ^1J(C,H) = 144, C(4)); 25.8 (t, ^1J(C,H) = 128); 23.7 (t, ^1J(C,H) = 128); 21.4 (t, ^1J(C,H) = 144); 21.2 (t, ^1J(C,H) = 144). ^{17}O-NMR (54 MHz, CD_2Cl_2/SO_2, 263 K): 159, 156.

(±)-2-(4-Chlorophenoxy)-2,3,4,5-tetrahydrothiophene 1,1-Dioxide (**17**). A mixture of (*E*)/(*Z*)-**1o** 3.2:1 (0.2 g, 0.9 mmol), CD_2Cl_2 (0.3 ml), and SO_2 (0.3 ml) was kept at −15° for 12 h. After cooling to −30°, the solvent was evaporated and dry MeOH (4 ml) added slowly. After the addition of 10% Pd/C (30 mg), the mixture was degassed at −30° and pressurized with H_2 (1 atm). After shaking at −30° for 1 h, the precipitate (catalyst) was filtered off and the filtrate evaporated. The residue was triturated with dry pentane at 20° for 3 h: 30 mg (14%) of **17**. White solid. M.p. 77–78°. IR (KBr): 2950, 1585, 1490, 1310, 1230, 1140, 1100, 1000, 720, 660. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.28 (m, 2 arom. H); 7.00 (m, 2 arom. H); 5.08 (dd, ^3J(2,3) = 6.3, 4.2, H−C(2)); 3.12 (m, CH_2(5)); 2.59 (m, 1 H, H−C(3)); 2.37 (m, 2 H, H−C(4), H−C(3)); 2.21 (m, 1 H, H−C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 155.5 (s, arom. C); 129.6 (d, ^1J(C,H) = 166, arom. C); 128.0 (s, arom. C); 117.0 (d, ^1J(C,H) = 162, arom. C); 88.9 (d, ^1J(C,H) = 164, C(2)); 50.0 (t, ^1J(C,H) = 142, C(5)); 29.8 (t, ^1J(C,H) = 136, C(3)); 18.6 (t, ^1J(C,H) = 139, C(4)). CI-MS (NH_3): 248 (6, $[M+2]^+$), 246 (15, $M^{+\cdot}$), 182 (13), 154 (63), 128 (100), 119 (56), 99 (13), 91 (48). Anal. calc. for $C_{10}H_{11}ClO_3S$ (246.71): C 48.68, H 4.49, Cl 14.27, S 13.00; found: C 48.6, H 4.40, Cl 14.27, S 12.89.

X-Ray Crystal-Structure Determinations[4]). For (±)-2-[(4-chlorophenyl)thio]-2,5-dihydrothiophene 1,1-dioxide (**3u**), see *Table 6*; for (±)-2,5-dihydro-1,1-dioxidothiophen-2-yl benzoate (**3y**), see *Table 7*; for 2-(4-chlorophenoxy)-2,3,4,5-tetrahydrothiophene 1,1-dioxide (**17**), see *Table 8*.

Table 6. *Crystal Data and Structure Refinement of (±)-***3u**

Empirical formula	$C_{10}H_9ClO_2S_2$	Morphology	Pinacoids	{010}, {001}
M_r	260.74		Pedions	($^-$, 1 01)
Temperature [K]	203 (2)		Fracture plane	(314)
Wavelength [Å]	0.71073	θ Range [°]		2.95 to 27.81
Crystal system	triclinic	Index ranges		$-8 \le h \le 8$, $-9 \le k \le 9$, $-14 \le l \le 15$
Space group	$P\bar{1}$	Reflect. collected		4997
Unit-cell dimensions a [Å]	6.9453(12)	Independent reflect.		2325 (R(int) = 0.0280)
b [Å]	7.1057(13)	Refinement method		Full-matrix least-squares on F^2
c [Å]	11.463(2)	Data/restraints/parameters		2325/0/172
α [°]	102.43(2)	Goodness-of-fit on F^2		0.712
β [°]	92.67(2)	Final R indices ($I > 2\sigma(I)$)		$R_1 = 0.0313$, $wR_2 = 0.900$
γ [°]	94.85(2)	R indices (all data)		$R_1 = 0.0388$,$wR_2 = 0.0982$
V [Å^3]	549.3(2)	Weights		$[\sigma^2(F^2)]^{-1}$
Z	2	R indices (all data)		$R_1 = 0.0592$, $wR_2 = 0.1918$
Density calc. [Mgm^{-3}]	1.577	Weights		$[\sigma^2(F_o,^2) + (0.1 \cdot P)^2 + 0.00 \cdot P]^{-1}$
Absorption coeff. [mm^{-1}]	0.702	where P =		$(\mathrm{Max}(F_o^20) + 2 \cdot F_c,^2)/3$
F(000)	268	Largest difference peak		0.794 and −0.442
Crystal size [mm]	$0.6 \times 0.2 \times 0.14$	and hole [e·A^{-3}]		

Table 7. *Crystal Data and Structure Refinement of (±)-***3y**

Empirical formula	$C_{11}H_{10}O_4S$	θ Range [°]	1.81 to 23.29
M_r	238.25	Index ranges	$-7 \le h \le 7$, $-24 \le k \le 24$, $-8 \le l \le 5$
Temperature [K]	293 (2)	Reflect. collected	4102
Wavelength [Å]	0.71073	Independent reflect.	1548 (R(int) = 0.0234)
Crystal system	monoclinic	Absorption correction	none
Space group	$P2_1/n$	Refinement method	Full-matrix least-squares on F^2
Unit cell dimensions a [Å]	6.9190(7)	Data/restraints/parameters	1548/0/187
b [Å]	22.441(2)	Goodness-of-fit on F^2	3.236
c [Å]	7.2236	Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0219$, $wR_2 = 0.0711$
α [°]	90	R indices (all data)	$R_1 = 0.0318$, $wR_2 = 0.0716$
β [°]	105.138(2)	Weights	$[\sigma^2(F_o,^2)]^{-1}$
γ [°]	90	Extinction coeff.	0.022(2)
V [Å^3]	1082.7(2)	Largest difference peak and hole [e·A^{-3}]	0.177 and −0.239
Z	4		
Density calc. (Mgm^{-3}]	1.462		
Absorption coeff. [mm^{-1}]	0.294		
F(000)	496		
Crystal size [mm]	$0.6 \times 0.4 \times 0.2$		

Table 8. *Crystal Data and Structure Refinement of (±)-***17**

Empirical formula	$C_{10}H_{11}ClO_3S$	θ Range [°]	2.12 to 22.5
M_r	246.70	Index ranges	$-6 \le h \le 6$, $-12 \le k \le 12$, $-16 \le l \le 16$
Temperature [K]	293 (2)	Reflect. collected	5786
Wavelength [Å]	0.71073	Independent reflect.	2893 (R(int) = 0.032)
Crystal system	triclinic	Absorption correction	none
Space group	$P\bar{1}$	Refinement method	Full-matrix least-squares on F^2
Unit-cell dimensions a [Å]	6.387(1)	Data/restraints/parameters	1896/0/359
b [Å]	11.500(2)	Goodness-of-fit on F^2	0.839
c [Å]	15.377(2)	Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0407$, $wR_2 = 0.1006$
α [°]	84.14(1)	R indices (all data)	$R_1 = 0.0644$, $wR_2 = 0.1095$
β [°]	81.20(1)	Weights	$\{\sigma^2(F_o^2) + [0.075(F_o^2 + 2F_c^2)/3]^2\}^{-1}$
γ [°]	88.56(1)	Extinction coeff.	none
Volume [Å^3]	1110	Largest difference peak and hole [e · A^{-3}]	0.2 [e · A^{-3}] −0.3 [e · A^{-3}]
Z	4		
Density calc. (Mgm^{-3}]	1.476		
Absorption coeff. [mm^{-1}]	0.51		
F(000)	512		
Crystal size [mm]	0.4 × 0.3 × 0.2		

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