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Reactions of acceptor substituted thiophene-1,1-dioxides with cyclopentadiene: control of selectivity by substitution

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Abstract—Diels–Alder reactions of thiophene-1,1-dioxides with strong electron withdrawing groups (EWG) were studied experimentally and theoretically. Thiophene-1,1-dioxides with two strong EWG behave as dienophiles and regio- and stereoselectively react with cyclopentadiene to give [2+4] cycloadducts **2a–c**, which are derivatives of benzothiophene. In contrast, thiophene-1,1-dioxides with one EWG behave as dienes in the inverse electron demand Diels–Alder reaction yielding dihydro-1*H*-indenes derivatives. Cope [3,3]-sigmatropic rearrangement of adducts **2a–c** was also demonstrated. MP2 calculations successfully rationalize the contrasting regioselectivities of these cycloaddition reactions.
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1. Introduction

Thiophene-1,1-dioxides are useful synthetic precursors for different classes of organic compounds because of their high reactivity in the Diels–Alder and 1,3-dipolar cycloadditions reactions.[1–5] The unique opportunity of SO_2-extrusion allows the creation of various complex multifunctional organic molecules.[5,6]

Diels–Alder reactions of thiophene dioxides have been extensively investigated. It has been reported that halogen- and alkyl- containing thiophene-1,1-dioxides undergo cycloadditions with a variety of dienophiles,[1–4] followed by the loss of sulfur dioxide leading to the formation of substituted cyclohexadienes, aromatics or heterocycles.

Reactions of substituted thiophene-1,1-dioxides with cyclopentadiene are of particular interest because the reaction products can be further transformed to 1*H*-indene derivatives, which are valuable building blocks and precursors in polymer chemistry.[7] Unfortunately, the feasibility of this transformation was only studied for the parent thiophene dioxide and a few halogenated derivatives. It was found that while unsubstituted thiophene dioxide acts as a dienophile, only a [2+4] adduct was isolated,[5b] the reaction with halogen containing thiophene dioxides yields a mixture of [4+2] and [2+4] adducts.[1] Factors controlling these variations in selectivity have not been analyzed theoretically.

2. Results and discussion

We previously reported a convenient method for preparation of thiophene-1,1-dioxides bearing electron-withdrawing groups.[8] Furthermore, we found these compounds to be highly reactive towards cycloaddition with various 1,3-dienes.[9] In particular, thiophene-1,1-dioxides bearing EWG act as strong dienophiles that yield [2+4] cycloadducts in the Diels–Alder reaction under mild conditions with 100% chemo-, regio and stereoselectivity.

The extremely high reactivity of these novel dienophiles motivated us to expand our studies to reactions with cyclopentadiene (CPD). Unusual results were observed when we started our investigation of cycloaddition with thiophene-1,1-dioxides **1a** and **1d**. We found that the chemoselectivity of reaction is different in these two cases. Analysis of the crude reaction mixture shows that thiophene-1,1-dioxide **la** bearing two EWG behaves as a dienophile and gives normal Diels–Alder adduct **2a** stereoselectively and in 85% yield. In contrast, the reaction with compound **1d** bearing only one EWG leads to selective formation of dihydro-1*H*-indene **3d**, which is formed as a result of an inverse electron demand Diels–Alder reaction (Scheme 1).

Keywords: Diels–Alder reaction; Thiophene-1,1-dioxides; EWG-groups; Cyclopentadiene; Dihydro-1*H*-indenes; Cope [3,3]-sigmatropic rearrangement; MP2 calculations; FMO coefficients.
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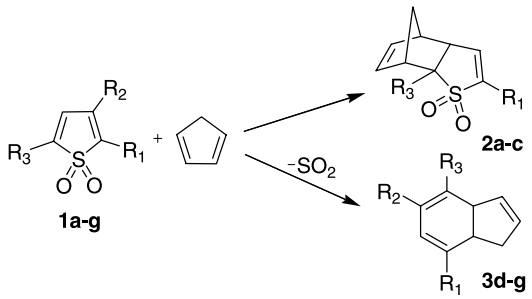


Scheme 1.

The reaction of thiophene dioxide **1a** is strikingly stereoselective. Only one stereoisomer was obtained and the structure of **2a** was unambiguously established from single crystal X-ray analysis. The ORTEP of cycloadduct **2a** is shown in Figure 1. Formation of cycloadduct with the *endo*-orientation of the heterocyclic moiety is consistent with the common *endo*-preference of Diels–Alder reactions known as Alder's rule.[9,10]

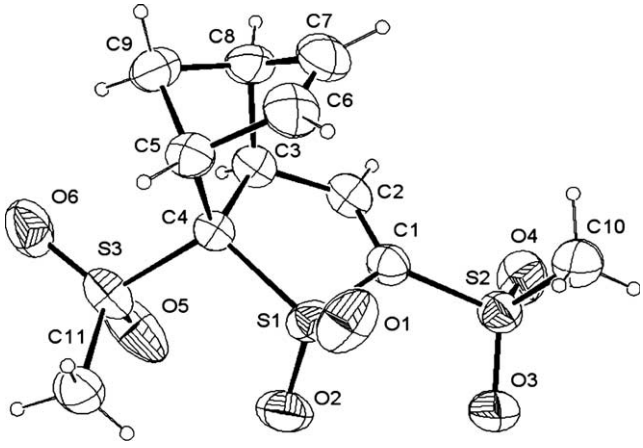
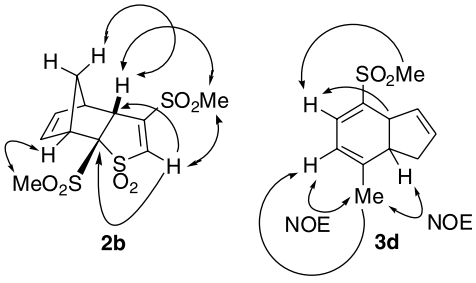


Figure 1. Molecular structure of **2a**.

We investigated a number of thiophene-1,1-dioxides with electron-withdrawing substituents in Diels–Alder reactions with cyclopentadiene. Thiophene-1,1-dioxides **1a–c** having two EWG react with CPD to form norbornene derivatives **2a–c**. On the other hand, the indene derivatives **3d–g** can be prepared exclusively if only one EWG is attached to the thiophene ring. The reaction is carried out in dichloromethane at −10–0 °C to give the respective products **2a–c** and **3d–g** in good yields.

Compounds **1b** and **1c** have been chosen to examine chemo- and regioselectivity in these cycloadditions. Compound **1b** is a very interesting model for the investigation of regiochemistry because it has two $MeSO_2$ groups in the 2,4-positions and, thus, the system contains two differently activated double bonds. Both thiophene dioxides **1b** and **1c** react with CPD 100% selectively to give only one product in each case. Thiophene dioxide **1c** reacts via the more activated double bond bearing the methylsulfonyl substituent. Recently, we found a similar pattern for this compound in reactions with linear 1,3-dienes.[9] We will explain the observed regioselectivity using the FMO theory (see Section 3, vide infra).

The structures of all isolated cycloadducts have been elucidated using ^{13}C, ^{1}H and NOESY NMR spectroscopy. The regiochemistry of **2b** and **2c** was deduced by comparison with ^{1}H NMR spectra of **2a**.[9] All cycloadducts **2a–c** are *exo*-products ($MeSO_2$ orientated towards the bridge). The *exo* stereochemistry was deduced from the value of the coupling constant $J_{3a,4}$, which is in the range 3.5–4.0 Hz for these adducts. Full assignment of the structures of **2b** and **3d** was made by ^{1}H, ^{13}C NMR, COSY, NOE, NOESY, and HMBC measurements. Moreover, NOESY experiments allowed definitive assignment of stereochemistry to the structure **2b**. Scheme 2 shows the important connectivities found in the 1D and 2D spectra of cycloadducts **2b** and **3d**.



Scheme 2. NOE NOESY double pointed arrows and HMBC (single pointed arrows) important correlations in NMR experiments of **2b** and **3d**.

Thus, thiophene-1,1-dioxides containing two strong electron-withdrawing groups (either two methylsulfonyl-or methylsulfonyl- and chloro) **1a–c** give only products **2a–c**, while the thiophene-1,1-dioxides **1d–g** give products **3d–g** (Table 1).

Table 1. Reaction of thiophene-1,1-dioxides **1a–g** with cyclopentadiene

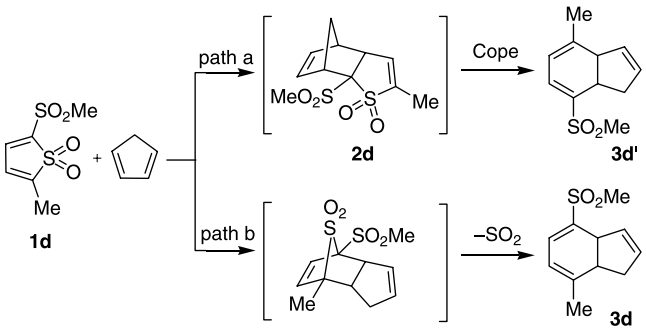
Product	R_1	R_2	R_3	Yield 2 (%)	Yield 3 (%)
a	$MeSO_2$	H	$MeSO_2$	85	
b	H	$MeSO_2$	$MeSO_2$	67	
c	Cl	H	$MeSO_2$	66	
d	Me	H	$MeSO_2$		67
e	Cl	CO_2H	Cl		71
f	Me	H	$MeCO_2$		65
g	Me	H	CN		73

In the first case thiophene dioxides **1a–c** act as dienophiles whereas thiophene-1,1-dioxides **1d–g** behave as dienes. In the latter case, the fast step of the reaction cascade is Diels–Alder reaction with inverse electron demand. In the second step, extrusion of SO_2 gives an unstable intermediate that rearranges to the final dihydro-1*H*-indene products.

Numerous literature precedents for similar electronic systems suggest the probability of [3,3]-Cope rearrangement. For example, vinyl norbomadienes and Diels–Alder adducts of cyclopentadienone undergo the Cope rearrangement to form similar structures.[11] In a similar fashion, substituted cyclopentadiene adducts of

tetrachlorothiophene dioxide (TCTD) also isomerize thermally to dihydro-1*H*-indenes derivatives after SO_2 extrusion.[11b]

Therefore, a very interesting question in the reaction of **1d–g** with cyclopentadiene is the reaction pathway. Two possibilities exist. The first involves Diels–Alder reaction of thiophene dioxide as a dienophile with a subsequent Cope rearrangement (path a). An alternative pathway is cycloaddition with inverse electron demand with thiophene dioxide acting as diene (path b). Detailed investigation of these alternatives was carried out with **1d** as a model compound. Previously, we have demonstrated 100% chemoselectivity of cycloaddition reaction of thiophene dioxide **1d** with non-cyclic dienes towards the more activated double bond. Based on the structure of cycloadduct **3d** and the results of our calculations (see Section 3), it is possible to distinguish between the two possibilities (Scheme 3). If the first mechanism (Diels–Alder reaction followed by Cope rearrangement) takes place, product **3d′** should be formed. Since the exclusive formation of **3d** (structure of which was fully confirmed by 2D NMR study) was observed, the reaction of cyclopentadiene with thiophene dioxide **1d** proceeds along path b. We believe that in all reactions of **1d–g** where indene derivatives **3d–g** are isolated, thiophene dioxides **1d–g** behave as diene components in Diels–Alder reaction.



Scheme 3.

Nevertheless, we found that compounds **2a–c** can also be transformed to indenes **3a–c** since SO_2 can be readily eliminated from adducts **2a–c** even during chromatographic purification of compounds **2a–c** or long-term storage at room temperature. A convenient procedure. for the transformation of **2a–c** into dihydro-1*H*-indenes **4a–c** includes refluxing in acetonitrile for 1–2 min (Table 2). The structure of rearrangement product **3a** was confirmed unambiguously by X-ray analysis (Fig. 2, Scheme 4).

Table 2. Preparation of dihydro-1*H*-indenes **4a–c** by rearrangement of adducts **2a–c**

Products	R_1	R_2	R_3	Yield 4 (%)
a	$MeSO_2$	$MeSO_2$	H	98
b	$MeSO_2$	H	$MeSO_2$	84
c	$MeSO_2$	Cl	H	76

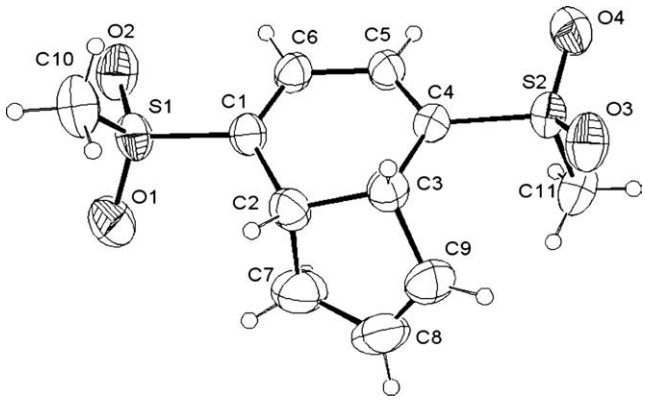
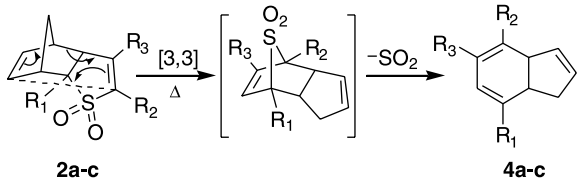


Figure 2. Molecular structure of **4a**.



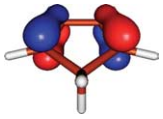
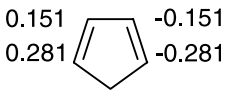
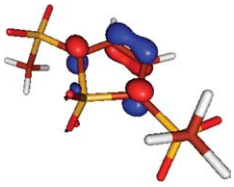
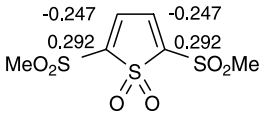
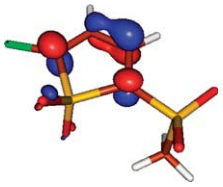
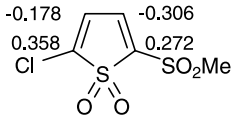
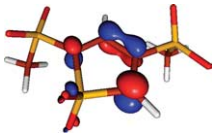
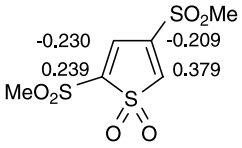
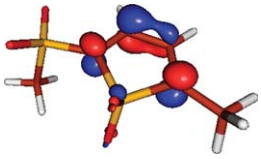
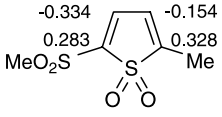
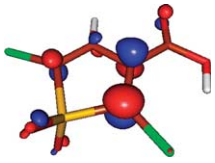
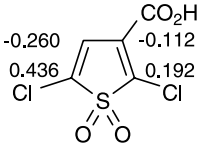
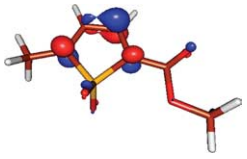
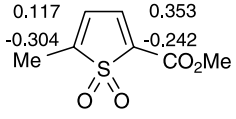
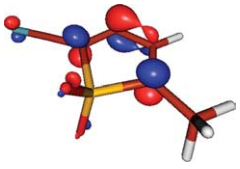
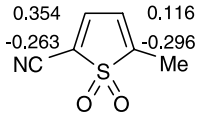
Scheme 4.

3. Computational part

We have used MP2 frontier molecular orbital (FMO) calculation to explain the selectivity of the Diels–Alder reaction of thiophene dioxides.[12] Ab initio all electron correlated resolution of identity second order Moeller–Plesset perturbation theory[13] with B11 basis sets (riMP2(full)/B11//riMP2(full)/B11) has been used to calculate FMOs of thiophene dioxides and cyclopentadiene B11 basis set followed contraction scheme: H-{2,1}/{6,2}; C, N, O-{4,3,1}/{10,7,3}; S,Cl-{5,4,2}/{14,11,6}. All calculations have been performed using PRIRODA-04 quantum chemistry package.[14] Both type of cycloadditions (normal and inverse electron demand Diels–Alder reactions) are HOMO cyclopentadiene-controlled and LUMO thiophene dioxide-controlled. The computer plot of FMO, the corresponding orbital coefficients and HOMO–LUMO energies of cyclopentadiene and thiophene dioxides are presented in Table 3. As can be seen in Table 3 the preferable formation of the **2b** in the case of the reactions of **1b** with CPD is in perfect agreement with 'large–large' molecular orbital overlap in the transition state. The computational data are in very good agreement with experimental results. The regiochemstry of the Diels–Alder reaction is fully controlled by FMO interaction both in the case of normal and in the case of inverse electron demand where the thiophene dioxide plays the role of a diene. For example, the regiochemistry of the Diels–Alder reaction with **1d** can be explained by 'large–large' molecular orbitals overlapping in the transition state (Scheme 5).

Only in the case of reaction of thiophene dioxide **1c** the predicted regiochemistry differ from experimentally observed. We believe that in this case, steric effects modulate electronic preferences. Both sides of thiophene dioxide **1c** are similarly activated, but the 2,3-side is

Table 3. FMO coefficients and energies of HOMO cyclopentadiene and LUMO of thiophene-1,1-dioxides

FMO coefficients		HOMO	LUMO
		−8.46	3.60
	 **1a**	10.62	−0.18
	 **1b**	−11.47	−0.18
	 **1c**	−11.47	−0.29
	 **1d**	−10.69	0.22
	 **1e**	−10.31	0.31
	 **1f**	−10.52	0.69
	 **1g**	−10.10	0.80

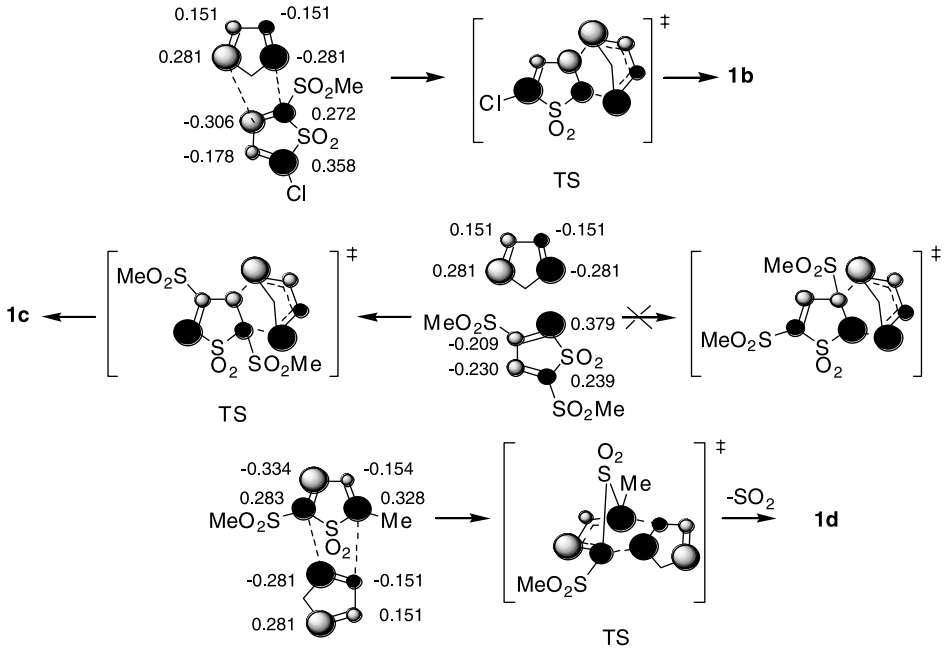
more sterically accessible to the reaction with diene. As a result, the exclusive formation of **2c** is observed.

4. Conclusion

In summary, EWG-containing thiophene-1,1-dioxides were found to be highly active dienophiles in reactions with cyclopentadiene. The reaction pathway depends strongly on the structure of thiophene dioxide, which can behave either as a diene or as a dienophile depending on the substitution pattern. MP2 calculations in conjunction with the FMO analysis successfully rationalize the regioselectivity of cycloaddition.

5. Experimental

All starting materials unless otherwise noted were commercially available. All products unless otherwise noted were identified by comparison NMR spectral and physical data with the data reported in the literature. Melting points are uncorrected. Silica gel 230–400 mesh was used for flash chromatography, all solvents were dried and purified by standard methods. ^{1}H and ^{13}C NMR spectra were recorded on a



Scheme 5.

Varian-400 MHz spectrometer in CD_3COCD_3, $CDC1_3$, and CD_3CN.

5.1. General procedure of preparation of cyclopentadiene adducts 2a–c and 3d–g

To a solution or suspension of corresponding thiophene-1,1-dioxide[5] (1 mmol) in dichloromethane (5 ml) stirred vigorously in an ice-bath was added freshly distilled cyclopentadiene (0.2 ml, 3 mmol). The mixture subsequently was stirred for 1.5 h at −10–0 °C then for an additional hour at room temperature. The clear solution was evaporated in vacuo to afford the crude cycloadducts. The crude products were purified by recrystallization or by flash chromatography using either chloroform or CH_2Cl_2 as eluent to give pure crystalline substances.

5.1.1. 2,7a-Bis(methylsulfonyl)-3a,4,7,7a-tetrahydro-4,7-methano-1-benzothiophene 1,1-dioxide (2a). Yield 85%, mp 231 °C, colorless prisms. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2). ^1H NMR (δ ppm, CD_3COCD_3): 1.76 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 2.76 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 3.21 (s, 3H, SO_2CH_3); 3.43 (s, 3H, SO_2CH_3); 3.47 (m, 1H, H-10); 3.83 (m, 1H, H-6); 4.33 (ddd, 1H, H-7, $J=7.1$, 3.5 Hz); 6.34 (dd, 1H, CH═CH, $J=8.5$, 3.2 Hz); 6.49 (dd, 1H, CH═CH, $J=8.5$, 3.2 Hz); 7.66 (d, 1H, H-5, $J=3.5$ Hz). ^{13}C NMR (δ ppm, CD_3COCD_3): 40.6; 43.1; 43.7; 44.0; 115.7; 131.0; 131.4; 132.2; 133.9; 147.4. Anal. Calcd for: $C_{11}H_{14}O_6S_3$ C, 39.04; H, 4.17%. Found: C, 38.79; H, 3.99%.

Crystal data of **2a**. $C_{11}H_{14}O_6S_3$, $M=338.40$, monoclinic, space group $C2/c$, $a=21.067(4)$ Å, $b=12.031(2)$ Å, $c=12.688(3)$ Å, $\beta=120.86(3)°$, $V=2760.6(10)$ $Å^3$, $Z=8$, $D_{calcd}=1.628$ g/cm^3, monochromated Mo K_α radiation, $\lambda=0.71073$ Å. A colorless prism of compound **2a** (from approximate dimensions $0.35\times0.26\times0.14$ mm), mounted on a glass fiber in random orientation, was used for X-ray data collection. Data were collected on Enraf-Nonius CAD-4 diffractometer using $\theta/2\theta$ at a temperature of 20 ± 1 °C. A total of 2270 reflections were collected of which 1624 were unique. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 calculations to give R indices (all data) $R1=0.0578$, $wR2=0.0979$ for 2270 observed independent reflections [$|F_0^2|>3\sigma(F_0)^2$, $2.03°<\Theta<24.97°$]. Crystallographic data for the structure have been deposited with Cambridge Crystallographic Database as supplementary publication number CCDC 293745.[15]

5.1.2. 3,7a-Bis(methylsulfonyl)-3a,4,7,7a-tetrahydro-4,7-methano-1-benzothiophene 1,1-dioxide (2b). Yield 67%, mp 215 °C, colorless prisms. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2). ^1H NMR (δ ppm, CD_3CN): 1.77 d (1H, CH_2, $J=9.7$ Hz); 2.32 (d, 1H, CH_2, $J=9.7$ Hz); 3.13 (s, 3H, SO_2CH_3); 3.18 (s, 3H, SO_2CH_3); 3.65 (br s, 1H); 3.73 (br s, 1H); 4.49 (d, 1H, $J=3.8$ Hz); 6.31 (dd, 1H, CH═CH, $J=5.4$, 3.3 Hz); 6.46 (dd, 1H, CH═CH, $J=5.4$, 3.3 Hz); 7.45 (s, 1H, CH═C). ^{13}C NMR (δ ppm, CD_3CN): 40.9; 46.2; 48.3; 50.2; 50.8; 69.4; 136.7; 139.4; 143.5; 146.8; 147.1. Anal. Calcd for: $C_{11}H_{14}O_6S_3$ C, 39.04; H, 4.17%. Found: C, 39.01; H, 4.08%.

5.1.3. 2-Chloro-1,1-dioxido-4,7-dihydro-4,7-methano-1-benzothien-7a(3a*H*)-yl methyl sulfone (2c). Yield 66%, mp 203 °C, pale yellow crystalline solid. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2). ^1H NMR (δ ppm, CD_3COCD_3): 2.09 (d, 1H, CH_2, $J=9.3$ Hz); 2.29 (d, 1H, CH_2, $J=9.3$ Hz); 3.12 (s, 3H, SO_2CH_3); 3.30 (m, 1H); 3.47 (s, 1H); 3.76 (t, 1H, $J=3.5$ Hz); 6.05 (dd, 1H, CH═CH, $J=5.6$, 3.1 Hz); 6.39 (dd, 1H, CH═CH, $J=5.6$, 3.1 Hz); 7.17 (d, 1H, ═C, $J=2.9$ Hz). ^{13}C NMR (δ ppm; CD_3COCD_3): 40.5; 43.2; 44.9; 45.1; 118.1; 129.8; 130.4; 131.1; 135.4; 145.0. Anal. Calcd for: $C_{10}H_{11}ClO_4S_2$ C, 40.75; H, 3.76%. Found: C, 40.79; H, 3.87%.

5.1.4. 4-Methyl-7-(methylsulfonyl)-3a,7a-dihydro-1*H*-indene (3d). Yield 67%, mp 175 °C, colorless crystalline

solid. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2). ^1H NMR (δ ppm, $CDCl_3$): 1.89 (s, 3H, CH_3); 2.42 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 2.85 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 2.95 (s, 3H, SO_2CH_3); 3.15 (m, 1H, CH); 3.94 (d, 1H, CH, $J=4.8$ Hz); 5.73 (d, 1H, CH=CH, $J=2.4$ Hz); 5.99 (m, 1H, CH=CH); 6.10 (m, 1H, CH=CH); 7.78 (d, 1H, CH=CH, $J=2.4$ Hz). ^{13}C NMR (δ ppm, $CDCl_3$): 22.4; 40.6; 43.1; 43.7; 44.0; 115.7; 131.0; 131.4; 132.2; 133.9; 147.4. Anal. Calcd for: $C_{11}H_{14}O_2S$ C, 62.83; H, 6.71%. Found: C, 61.80; H, 6.87%.

5.1.5. 4,7-Dichloro-3a,7a-dihydro-1*H*-indene-5-carboxylic acid (3e). Yield 71%, mp 183 °C, yellow crystalline solid. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2); 3000, 1720 (COOH). ^1H NMR (δ ppm, CD_3COCD_3): 1.76 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 2.76 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 3.47 (m, 1H, H-10); 3.83 (m, 1H); 4.33 (ddd, 1H, $J=7.1$, 3.5 Hz); 6.34 (dd, 1H, CH=CH, $J=8.5$, 3.2 Hz); 6.49 (dd, 1H, CH=CH, $J=8.5$, 3.2 Hz); 7.66 (d, 1H, $J=3.5$ Hz). ^{13}C NMR (δ ppm, CD_3COCD_3): 32.7; 44.8; 46.0; 120.9; 124.5; 132.1; 133.2; 135.1; 141.9; 166.8. Anal. Calcd for: $C_{10}H_8Cl_2O_2$ C, 51.98; H, 3.49. Found: C, 51.80; H, 3.52.

5.1.6. Methyl 4-methyl-3a,7a-dihydro-1*H*-indene 7-carboxylate (3f). Yield 65%, mp 191 °C, pale yellow crystalline solid. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2); 1750 (CO_2Me). ^1H NMR (δ ppm, CD_3COCD_3): 1.73 (s, 3H, CH_3), 1.93 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 2.76 (dd, 1H, CH_2, $J=9.4$, 3.2 Hz); 3.21 (s, 3H, CO_2CH_3); 3.47 (m, 1H, H-10); 3.83 (m, 1H, H-6); 4.30 (ddd, 1H, H-7, $J=7.0$, 3.2 Hz); 6.31 (dd, 1H, CH=CH, $J=8.5$, 3.2 Hz); 6.51(dd, 1H, CH=CH, $J=8.5$, 3.2 Hz); 7.66 (d, 1H, H-5, $J=$ 3.5 Hz). ^{13}C NMR (δ ppm, CD_3COCD_3): 21.1; 34.0; 39.6; 41.3; 52.1; 115.4; 122.5; 129.3; 131.4; 131.9; 140.7; 169.6. Anal. Calcd for: $C_{12}H_{14}O_{14}$ C, 75.76; H, 7.42%. Found: C, 75.90; H, 7.57%.

5.1.7. 4-Methyl-3a,7a-dihydro-1*H*-indene-7-carbonitrile (3g). Yield 73%, mp 211 °C, colorless prisms. IR (υ, cm^{-1}): 1330, 1100 (SO_2); 2240 (CN). ^1H NMR (δ ppm) (CD_3COCD_3): 1.76 (s, 3H, CH_3); 2.79 (d, IH, CH_2, $J=9.0$, 3.1 Hz); 3.52 (m, 1H); 3.83 (m, 1H); 4.40 (ddd, 1H, $J=6.9$, 3.1 Hz); 6.39 (dd, 1H, CH=CH, $J=8.5$, 3.1 Hz); 6.51 (dd, 1H, CH=CH, $J=8.5$, 3.1 Hz); 7.72 (d, 1H, H-5, $J=$ 3.8 Hz). ^{13}C NMR (δ ppm, CD_3COCD_3): 20.1; 33.4; 36.9; 43.3; 103.7; 115.2; 116.5; 121.0; 129.8; 141.3; 142.9. Anal. Calcd for: $C_{11}H_{11}N$ C, 84.04; H, 7.05. Found: C, 84.43; H, 7.37

5.1.8. 4,7-Bis(methylsulfonyl)-3a,7a-dihydro-1*H*-indene (4a). Yield 98%, mp 221 °C, colorless prisms. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2). ^1H NMR (δ ppm, CD_3COCD_3): 2.50–2.59 (m, 1H); 2.97–3.04 (m, 1H); 3.01(s, 3H, SO_2CH_3); 3.09 (s, 3H, SO_2CH_3); 3.62–3.72 (m, 1H); 4.15–4.20 (m, 1H); 6.10–6.13 (m, 1H); 6.19–6.22 (m, 1H); 6.97 (br s, 1H); 6.98 (d, 1H, $J=0.7$ Hz). ^{13}C NMR (δ ppm, CD_3COCD_3): 37.4; 41.2; 45.1; 45.8; 128.7; 131.1; 132.0; 132.6; 136.8; 149.2. Anal. Calcd for: $C_{11}H_{14}O_4S_2$ C, 48.16; H, 5.14%. Found: C, 48.13; H, 5.09%.

Crystal data of **4a**. $C_{11}H_{14}O_4S_2$, $M=274.34$, monoclinic, space group $P2_1/n$, $a=10.436(2)$ Å, $b=11.421(2)$ Å, $c=10.691(2)$ Å, $\beta=105.71(3)°$, $V=1226.7(4)$ $Å^3$, $Z=4$, $D_{calcd}=1.486$ g/cm, monochromated Mo K_α radiation, $\lambda=0.71073$ Å. A colorless prism of compound **4a** (from approximate dimensions $0.35\times0.20\times0.17$ mm), mounted on a glass fiber in random orientation, was used for X-ray data collection. Data were collected on Enraf-Nonius CAD-4 diffractometer using $\theta/2\theta$ at a temperature of 20 ± 1 °C. A total of 1396 reflections were collected of which 1314 were unique. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 calculations to give R indices (all data) $R1=0.0261$, $wR2=0.0726$ for 1396 observed independent reflections [$|F_0^2|>3\sigma(F_0)^2$, $2.42°<\Theta<24.97°$] Crystallographic data for the structure have been deposited with Cambridge Crystallographic Database as supplementary publication number CCDC 293746.[15]

5.1.9. 5,7-Bis(methylsulfonyl)-3a,7a-dihydro-1*H*-indene (4b). Yield 84%, mp 203 °C, colorless prisms. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2). ^1H NMR (δ ppm) ($CDCl_3$): 2.50–2.57 (m, 1H); 2.93 (s, 3H, SO_2CH_3); 3.00 (s, 3H, SO_2CH_3); 3.59–3.66 (m, 1H); 3.91–3.94 (m, 1H); 5.88–5.90 (m, 1H); 6.01–6.04 (m, 1H); 6.97 (d, 1H, $J=3.6$ Hz); 7.13 (s, 1H). ^{13}C NMR (δ ppm, CD_3COCD_3): 36.4; 36.6; 41.6; 44.9; 52.3; 111.4; 121.2, 130.5; 135.7; 143.8; 148.9. Anal. Calcd for: $C_{11}H_{14}O_4S_2$ C, 48.16; H, 5.14%. Found: C, 48.20; H, 5.17%.

5.1.10. 4-Chloro-7-(methylsulfonyl)-3a,7a-dihydro-1*H*-indene (4c). Yield 76%, mp 188°C, pale yellow needles. IR (neat, υ, cm^{-1}): 1330, 1100 (SO_2). ^1H NMR (δ ppm) ($CDCl_3$): 2.71–2.78 (m, 1H); 2.88–2.96 (m, 1H); 2.93 (s, 3H, SO_2CH_3); 3.42–3.49 (m, 1H); 4.04 (dd, 1H, $J=10.1$, 1.7 Hz); 5.95–6.01 (m, 2H); 6.09 (dd, 1H, $J=5.3$, 1.2 Hz); 6.75 (dd, 1H, $J=5.3$, 1.4 Hz). ^{13}C NMR (δ ppm, CD_3COCD_3): 36.4; 41.1; 43.6; 47.3; 125.2; 131.0, 131.8; 132.6; 139.3; 140.1. Anal. Calcd for: $C_{10}H_{11}ClO_2S$ C, 52.06; H, 4.81%. Found: C, 52.1 1; H, 4.77%.

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15. Crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.