Furan-fused 3-sulfolene as a novel building block: intermolecular Diels–Alder reactions of 4*H*,6*H*-thieno[3,4-*c*]furan 5,5-dioxide

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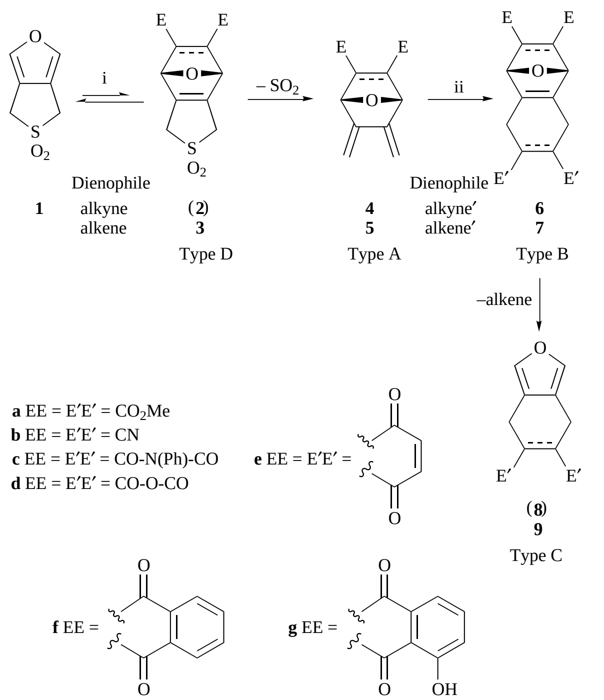
A furan-fused 3-sulfolene 4*H*,6*H*-thieno[3,4-*c*]furan 5,5-dioxide 1, can be used as a bis-diene, reacting sequentially with a variety of dienophiles to construct four types of skeleton, depending on the dienophile and the reaction conditions. The 3-sulfolene moiety of the furansulfolene not only functions as the s-*cis*-diene part in Diels–Alder reactions, but also extends the range of the Diels–Alder reactions of the furan moiety with various dienophiles through its desulfonylation to form the s-*cis*-diene.

Introduction

In the course of our studies on the chemistry of 3-sulfolene,[1] we have been interested in five-membered heteroaromatic ring-fused 3-sulfolenes and have synthesized the previously unknown furan-fused 3-sulfolene, 4*H*,6*H*-thieno[3,4-*c*]furan 5,5-dioxide **1**.[2] This compound contains furan and 3-sulfolene moieties, which can sequentially react with dienophiles to construct four types of skeleton, depending on the dienophile and the reaction conditions (Scheme 1).



Scheme 1 *Reagents:* i, dienophile; ii, dienophile′

In view of the well known weak reactivity of furan as a diene and the retro-Diels–Alder reactions of the adducts of alkenyl dienophiles, such as dimethyl fumarate, dimethyl maleate, and *p*-benzoquinone, due to their inherent thermodynamic instability with respect to either retrocycloaddition or re-aromatization,[3] it is noteworthy that the Diels–Alder adducts of compound **1** with these unfavourable dienophiles (adducts with furan can generally be obtained only under high-pressure conditions[4]) can be isolated in good yields even under thermal conditions. The key to making the equilibrium favourable for the formation of the product is rapid extrusion of SO_2 from the initially formed adducts **3**. Furthermore, the furan and 3-sulfolene moieties of substrate **1** can both be readily functionalized. Thus, the furansulfolene **1** is a useful building block for the construction of polycyclic polyfunctional systems.

Results and discussion

Diels–Alder reaction of the furansulfolene 1

The Diels–Alder reaction of the furansulfolene **1** with a variety of dienophiles has been studied and the results are summarized in Table 1.

The furansulfolene **1** reacted with dimethyl acetylenedicarboxylate (DMAD) (3 mol equiv.) in benzene (sealed tube) at 150 °C (1 h), to give two types of cycloadduct: the monocycloadduct **4a** bearing two methylene groups (type A) and the bis-cycloadduct **6a** (type B) (entry 1). Even at lower temperature (120 °C or room temperature), the same cycloadducts were obtained. Essentially the same type of reaction was observed with dimethyl fumarate as a dienophile. With other ethylenic dienophiles such as dimethyl maleate, cycloaddition proceeded at 150 °C to afford a new type of monocycloadduct **9a** (type C), in addition to the type A monocycloadduct **5a** (entry 10). With fumaronitrile, the formation of the type C adduct predominated over that of the type A adduct. Furthermore, the furansulfolene **1** added to maleic anhydride at room temperature (72 h) to yield the fourth type of cycloadduct (type D), compound **3d**, as the sole product (entry 16).

Thus, the furansulfolene **1** reacts with various dienophiles to give four types of cycloadduct, depending on the dienophiles and the reaction conditions, and even reacts with dimethyl fumarate and dimethyl maleate, whose adducts with furan have not been isolated under thermal conditions, to afford Diels–Alder adducts in good total yields. Both the successful Diels–Alder reaction of the furansulfolene **1** with these unfavourable dienophiles and the current interest in efficient construction of clinically important polycyclic quinones, such as anthracyclinones and pradimicinone A (an anti-HIV agent) prompted us to examine the reaction of compound **1** with quinones, whose Diels–Alder adducts with furan are thermally unstable and either decompose back to furan and the dienophile or are cleaved to Michael-type adducts. At 20 kbar,† furan undergoes cycloaddition to *p*-benzoquinone, to give in addition to the recovered starting materials (71%), a mixture of *endo*- and *exo*-1:1 adducts (14 and 15%), which are unstable and revert to the starting materials at normal pressure.[5] Strikingly, the reaction of compound **1** with *p*-benzoquinone (2 mol equiv.) proceeded at 120 °C (3 h, benzene, sealed tube) and afforded *exo*-**5e** as the single product (78% isolated yield) with recovery of substrate **1** (entry 17). Furthermore, treatment of compound **1** with 1,4-naphthoquinone (2 mol equiv.) at 150 °C for 4 h gave compound **5f** together with a small amount of a type B adduct.

† 1 kbar = 0.1 GPa.

Table 1 Diels–Alder reactions of furansulfolene **1** with dienophiles under thermal conditions

			Products (yield, %)[a]								
Entry	Dienophile (mol equiv.)	Reaction conditions	Type D		Type A		Type B		Type C		Total yield (%)
1	DMAD (3)	sealed tube, 150 °C 1 h, benzene			**4a**	45	**6a**	47			92
2	DMAD (3)	sealed tube, 120 °C 1 h, benzene			**4a**	62	**6a**	29			91
3	DMAD (1)	sealed tube, 120 °C 1 h, benzene			**4a**	40	**6a**	3			43 (51)[b]
4	DMAD (3)	atmosphere, 28 °C 7 days, CH_2Cl_2			**4a**	54	**6a**	39			93
5	DMAD (1)	atmosphere, 28 °C 7 days, CH_2Cl_2			**4a**	35					35 (61)[b]
6	DMAD (3)	atmosphere, 0 °C 90 days, $CDCl_3$			**4a**	100[c]					100[c]
7	Dimethyl fumarate (3)	sealed tube, 150 °C 2 h, benzene			**5a** *trans*[d]	78 78	**7a** *trans*[d]	11 11			89
8	Dimethyl fumarate (1)	sealed tube, 150 °C 2 h, benzene			**5a** *trans*[d]	21 21					21 (72)[b]
9	Dimethyl fumarate (3)	atmosphere, 28 °C 48 h, CH_2Cl_2			no reaction						0 (96)[b]
10	Dimethyl maleate (3)	sealed tube, 150 °C 3 h, benzene			**5a** *endo*[d] *exo*[d]	63 53 10			**9a** *cis*[e]	10 10	73
11	Dimethyl maleate (3)	sealed tube, 120 °C 12 h, benzene			**5a** *endo*[d] *exo*[d]	61 51 10	**7a** *endo*[d] *exo*[d]	29 11 18			90
12	Dimethyl maleate (1)	sealed tube, 120 °C 12 h, benzene			**5a**	72					72 (24)[b]
13	Dimethyl maleate (3)	atmosphere, 28 °C 48 h, CH_2Cl_2			no reaction						0 (94)[b]
14	Fumaronitrile (3)	sealed tube, 150 °C 3 h, benzene			**5b**	36			**9b**	38	74
15	*N*-Phenylmaleimide (3)	sealed tube, 120 °C 1 h, benzene					**7c** *exo*	82 82			82
16	Maleic anhydride (3)	atmosphere, 28 °C 72 h, THF	**3d** *exo*	62 62							62
17	*p*-Benzoquinone (2)	sealed tube, 120 °C 3 h, benzene			**5e** *exo*	78 78					78 (22)[b]
18	1,4-Naphthoquinone (2)	sealed tube, 150 °C 4 h, benzene			**5f** *exo*	58 58			**9f**	4	62
19	1,4-Naphthoquinone (2)	sealed tube, 120 °C 4 h, benzene			**5f** *exo*	50 50					50 (47)[b]
20	Juglone (2)	sealed tube, 120 °C 4 h, benzene			**5g** *exo*	60 60					60 (13)[b]

[a] Isolated yield. [b] Recovery of substrate **1**. [c] Yield determined by ^{1}H NMR spectroscopy. [d] The configuration of the two methoxycarbonyl groups on the 7-oxabicyclo[2.2.1]heptanyl skeleton of **5a** or **7a**. [e] The configuration of the two methoxycarbonyl groups at C-5 and -6 of compound **9**.

Under the same conditions, the reaction of compound **1** with juglone afforded the desired product **5g** (entry 20). The structures of all cycloadducts thus obtained were confirmed by ^{1}H and ^{13}C NMR spectral analysis. The configurations of all cycloadducts could be readily determined by inspection of the ^{1}H NMR spectra; thus, the bridgehead protons of the *cis-exo* isomers of the cycloadducts **5** and **7** appeared as singlets in the expected region, and those of the *cis-endo* isomers appeared as doublets.

Retro-Diels–Alder reaction of type B adducts and formation of type C adducts

A comparison of entries 10 and 11 suggested that the formation of compound **9a** could be explained by a retro-Diels–Alder reaction in which the 7-oxanorbornene skeleton of intermediate **7a** releases the unit alkene to afford the furan ring, driven by both the restoration of aromatic character and the reduction of steric strain. In accord with this, heating of the isolated intermediate *cis-endo*-**7a** in benzene solution at 150 °C for 1 h gave compound **9a** as the exclusive product in 85% yield. Under the same conditions, the retro-Diels–Alder reaction of the *cis-exo* isomer to product **9a** was slow (26% yield; the recovery of *cis-exo*-**7a** was 74%). In both cases, no type A product **5** was observed. In contrast to the ready retro-Diels–Alder reaction of the *cis*-isomers to compound **9a** at reaction temperature higher than 150 °C, the retro-Diels–Alder reactions of intermediates *trans*-**7a** and **6a** to the corresponding type C products were not observed (on heating at 210 °C for 3.5 h and then 240 °C for 2 h, the recovery of substrate **6a** was 96% and that of compound *trans*-**7a** was 99%). The retro-Diels–Alder reaction of tricycle **7a** to compound **9a** seems to be dependent on the configuration of the ester groups on the ethano bridges.

Formation of type D adducts and their desulfonylation

The formation of the type A compounds **4** and **5** is the result of spontaneous desulfonylation of the initially formed type D adducts **2** and **3**, respectively. To examine the formation of the type D adducts, high-pressure conditions were employed (Table 2).

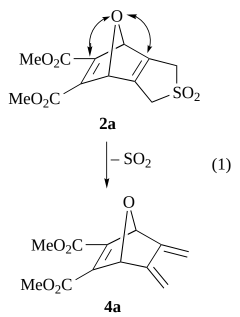
The reaction of compound **1** and 3 mol equiv. of dimethyl maleate in CH_2Cl_2 at 28 °C under a pressure of 12 kbar (1.2 GPa) for 48 h gave a single adduct, the *cis-endo* type D adduct **3a**, in 81% yield. At lower pressures or with a smaller mol ratio (1 : 1) of the dienophile, the yields of product **3** were low and substrate **1** was recovered. Despite our success in the isolation of product **3**, all attempts to detect compound **2a** failed, presumably owing to rapid desulfonylation (Table 1, entries 4–6), but the isolation of the adduct **10** (53%), a 1 : 1 adduct of compounds **1a** and **2a**, when compound **1** was treated with DMAD at 28 °C under a pressure of 1.2 GPa, suggested the formation

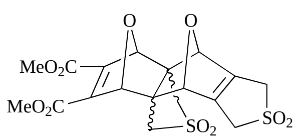
Table 2 Diels–Alder reactions of furansulfolene **1** under high-pressure conditions

Entry	Dienophile (mol equiv.)	Reactions conditions	Products (yield, %)[a] Type D	Type A	Type B	Type C	Total yield (%)
1	Dimethyl maleate (3)	12 kbar, 28 °C 48 h, CH_2Cl_2	**3a** 81 *endo*[b] 81				82
2	Dimethyl maleate (3)	4 kbar, 28 °C 48 h, CH_2Cl_2	**3a** 19 *endo*[b] 19				19 (75)[c]
3	Dimethyl fumarate (3)	12 kbar, 28 °C 48 h, CH_2Cl_2	**3a** 41 *trans*[b] 41	**5a** 37 *trans*[b] 37			78 (12)[c]
4	Dimethyl acetylene-dicarboxylate (DMAD) (3)	4 kbar, 28 °C 24 h, CH_2Cl_2		**4a** 97	**6a**	3	100

[a] Isolated yield. [b] The configuration of the two methoxycarbonyl groups. [c] Recovery of substrate **1**.

of intermediate **2a**. In the rapid desulfonylation of species **2**, release of the high strain arising from two endocyclic olefin-oxabridge repulsions[6] in the oxanorbornadiene moiety of compounds **2** should play an important role [eqn. (1)].





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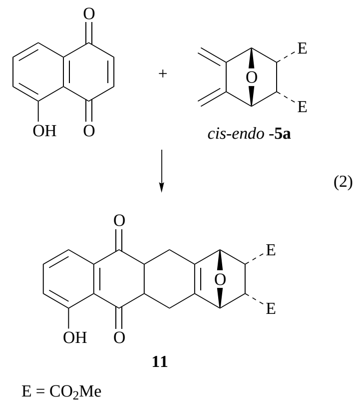
In contrast to the rapid desulfonylation of **2**, desulfonylation of the oxanorbornene fused sulfolenes **3** required moderate heating. Desulfonylation of *cis-endo*-**3a** took place at 80 °C (0.5 h) in benzene, and the desulfonylated product **5a** was obtained in quantitative yield. Even at room temperature, compound *trans*-**3a** underwent desulfonylation to give the corresponding type A product. These desulfonylations of the type D adducts **3** are considered to circumvent the unfavourable equilibrium between compound **1** (furan) and the type D adducts **3** (7-oxanorbornenes).

Reactivity of the type A adducts

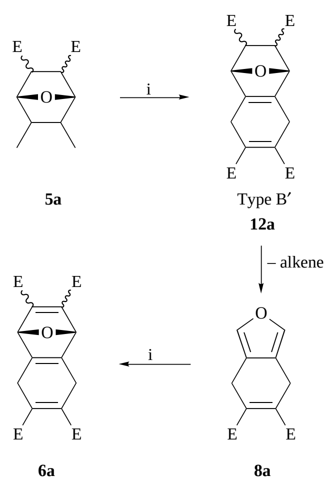
The results shown in Tables 1 and 2 indicate that the cycloaddition of the second equivalent of the dienophile to the monoadduct (type A), giving the corresponding bis-adduct (type B), was slower than the addition of the first equivalent of the dienophile to substrate **1**, which yields the monoadduct (type A). This differentiation would be very useful for constructing polycyclic systems. For example, *cis-endo*-**5a** reacted with juglone (1.1 mol equiv.) at 80 °C for 10 h to give a pentacyclic quinone **11** in 58% isolated yield [eqn. (2)]. This approach to pentacyclic quinones starting from the readily available type A adduct with naphthoquinone may be fruitful in constructing a number of important polycyclic polyfunctional systems, including anthracycline derivatives.

Next, as we had obtained three isomers of compound **5a**, we examined the influence of the ester substituents of the 7-oxanorbornane frame on the Diels–Alder reaction. The reactivity of compound **5a**'s isomers was examined by employing DMAD (1.1 mol equiv.) as a dienophile; DMAD is linear,



so any influence of the secondary orbital effect and steric effects can be avoided.

While compound *cis-endo*-**5a** afforded bicycle **8a** at 150 °C for 3 h, both *cis-exo*- and *trans*-**5a** gave new bis-adducts, *cis-exo*- and *trans*-**12a**, respectively (Scheme 2; Table 3). It is noteworthy that the rate of Diels–Alder reaction of compound *cis-exo*-**5a** with DMAD is as slow as that of compound **4a** with DMAD. The slowness of the latter can be attributed to the formation of a new endocyclic olefin (= another endocyclic olefin–oxabridge repulsion). Thus, when DMAD adds to diene **4a** to afford adduct **6a**, one would expect the new endocyclic double bond to push the oxabridge back to a more symmetrical position. This leads to extra strain. The *cis-exo*-ester groups on diene **5a** seem to play the same role in the reaction of compound **5a** with DMAD. The thermally unstable tricycle *cis-endo*-**12a** was isolated when diene *cis-endo*-**5a** was treated with DMAD under a pressure of 12 kbar (28 °C), and compound *cis-endo*-**12a** underwent a retro-Diels–Alder reaction to give



Scheme 2 *Reagent:* i, DMAD

Table 3 Diels–Alder reaction of the isomers of compound **5a** with 1 mol equiv. of DMAD at 150 °C for 3 h

Entry	5a	Products (yield, %)[a] 12a	8a	6a	Total yield (%)
1	*cis-endo*	0	84	0	84
2	*trans*	*trans* 55	39	0	94
3	*cis-exo*	*cis-exo* 10	0	37	47 (9)[b]
cf.	**4a**		0	34	34 (35)[b]

[a] Isolated yield. [b] Recovery of the diene **5a**.

bicycle **8a** (quant.) at 150 °C (1 h). These results, together with the fact that compound **8a** does not react with the alkene dienophiles to give any trace of adduct **12a** under the same conditions, suggested that the Diels–Alder reactivity of the s-*cis*-butadiene moiety grafted onto 7-oxanorbornane is affected by the remote ester groups of the bicyclic skeleton. The effect of the *cis-exo*-methoxycarbonyl groups of the 7-oxanorbornene skeleton is observed both in the reactions of the type A adducts with the second dienophiles and in the retro-Diels–Alder reactions of the type B adducts to afford the corresponding type C compounds. In these cases, the *cis-exo*-methoxycarbonyl groups of compounds **3a** and **5a** should play the same role as do the endocyclic olefins of **4a** and **6a**.

Conclusions

The 3-sulfone function of the furansulfolene **1** not only acts as an s-*cis*-diene in Diels–Alder reactions, but also extends the scope of the Diels–Alder reactions of the furan moiety with various dienophiles through its desulfonylation to form an s-*cis*-diene. So, the furansulfolene, 4*H*,6*H*-thieno[3,4-*c*]furan 5,5-dioxide **1**, can be used as a bis-diene which can sequentially react with two different dienophiles to afford polycyclic polyfunctional systems. Remote substituent effects are caused by methoxycarbonyl groups in compounds **5a** and **7a**, and the largest retardation effect is seen with *cis-exo*-methoxycarbonyl groups.

Experimental

Mps (Yanaco Micro Melting Point apparatus) are uncorrected. The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were determined for $CDCl_3$ solutions containing ~1% $SiMe_4$ as internal standard with a JEOL GSX-400 spectrometer while ^{1}H NMR (90 MHz) and ^{13}C (22.5 MHz) were determined with a JEOL GSX-90 spectrometer. *J* Values are given in Hz. Infrared spectra were taken on a JASCO A-302 diffraction grating infrared spectrophotometer. Column chromatography was performed on silica gel (Wakogel C-200). All reactions were conducted under argon unless otherwise stated. High-pressure equipment: a double-walled cylindrical pressure vessel (Hikari Koattu Ltd., Hiroshima, Japan) was fitted with a piston powered by a hydraulic ram, the whole being contained in a press frame. Samples of up to 1.8 cm^3 were placed in a poly(tetrafluoroethylene) (PTFE) cylindrical cell closed by a sliding stopper. This was placed within the cylinder which was filled with kerosene and the desired pressure was applied, monitored by a calibrated strain gauge directly connected to the cylinder. The temperature was controlled by an external heating jacket. CH_2Cl_2 was distilled from CaH_2 under argon.

Diels–Alder reactions of sulfolene 1 with dienophiles under thermal conditions; general method

A solution of sulfolene **1** (50.0 mg, 0.32 mmol), 4-methoxyphenol (10 mg, 0.25 mol equiv., as a polymerization inhibitor) and the dienophile (3 mol equiv.) in benzene (1 cm^3) was heated in a sealed tube. After concentration, the residue was subjected to column chromatography on silica gel and eluted with a mixture of hexane and AcOEt (9:1).

Diels–Alder reaction of sulfolene 1 with DMAD at 150 °C (entry 1 of Table 1). After column chromatography, compound **4a** (48.2 mg, 45%) was obtained as needles, mp 86–87 °C [from AcOEt–hexane (1:4)] together with compound **6a** (61.1 mg, 47%) also as needles, mp 71–72 °C [from AcOEt–hexane (1:4)] from substrate **1** and DMAD (0.12 cm^3, 3 mol equiv.) at 150 °C for 1 h by the general method.

Dimethyl 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate **4a**, δ_H 3.83 (6 H, s), 5.35 (2 H, s, bridgehead H), 5.44 (2 H, s) and 5.45 (2 H, s); δ_C 52.37 (q), 85.16 (d), 106.00 (t), 140.14 (s), 143.27 (s) and 162.35 (s); *m/z* 236 (M$^+$), 205 (M$^+$ − OCH_3, 3.0%), 176 (M$^+$ − CO_2CH_3, 24.7) and 145 (M$^+$ − CO_2CH_3 − OCH_3, base) (Found: M$^+$, 236.0689. Calc. for $C_{12}H_{12}O_5$: M, 236.0684).

Tetramethyl 1,4-epoxy-1,4,5,8-tetrahydronaphthalene-2,3,6,7-tetracarboxylate **6a**, δ_H 3.15 (2 H, m), 3.44 (2 H, m), 3.79 (6 H, s), 3.83 (6 H, s) and 5.54 (2 H, s, bridgehead H); δ_C 27.02 (t), 52.35 (q), 52.39 (q), 86.33 (d), 132.57 (s), 145.33 (s), 152.56 (s), 163.13 (s) and 167.93 (s); *m/z* 347 (M$^+$ − OCH_3, 2.2%), 285 (M$^+$ − OCH_3 × 3, 24.1) and 205 (M$^+$ − $C_6H_6O_4$ − OCH_3, base) (Found: M$^+$, 378.0986. Calc. for $C_{18}H_{18}O_9$; M, 378.0949).

Diels–Alder reaction of sulfolene 1 with dimethyl fumarate at 150 °C (entry 7 of Table 1). After column chromatography, compound *trans*-**5a** (59.3 mg, 78%) and compound *trans*-**7a** (13.9 mg, 11%) were both obtained as oils from sulfolene **1** and dimethyl fumarate (138.0 mg) at 150 °C for 1 h by the general method.

Dimethyl 5,6-dimethylene-7-oxabicyclo[2.2.1]heptane-*trans*-2,3-dicarboxylate *trans*-**5a**, δ_H 3.29 (1 H, d, *J* 4.88), 3.68 (3 H, s), 3.72 (1 H, s), 3.75 (3 H, s), 4.99 (1 H, s, bridgehead H), 5.07 (1 H, d, *J* 4.88, bridgehead H), 5.13 (1 H, s), 5.15 (1 H, s), 5.30 (1 H, s) and 5.32 (1 H, s); δ_C 50.19 (d), 51.17 (d), 52.21 (q), 52.54 (q), 82.36 (d), 84.54 (d), 103.00 (t), 104.46 (t), 143.66 (s), 145.28 (s), 170.31 (s) and 172.12 (s); *m/z* 238 (M$^+$, 2.2%), 207 (M$^+$ − OCH_3, 5.0), 179 (M$^+$ − CO_2CH_3, 7.0) and 94 (M$^+$ − $C_6H_8O_4$, base) (Found: M$^+$, 238.0848. Calc. for $C_{12}H_{14}O_5$: M, 238.0841).

Tetramethyl 1,4-epoxy-1,2,3,4,5,6,7,8-octahydronaphthalene-*trans*-2,3-*trans*,6,7-tetracarboxylate *trans*-**7a**, δ_H 2.45–2.52 (2 H, m), 2.67–2.94 (4 H, m), 3.64–3.66 (1 H, m), 3.68 (1 H, s), 3.74 (6 H, s), 3.75 (3 H, s), 3.81 (3 H, s) and 5.02–5.04 (2 H, s, bridgehead H); δ_C 23.81 (t), 23.97 (t), 24.90 (t), 26.24 (t), 40.81 (d), 41.03 (d), 41.15 (d), 41.61 (d), 47.57 (d), 47.82 (d), 48.82 (d), 48.97 (d), 51.94 (q), 51.99 (q), 52.05 (q), 52.09 (q), 52.11 (q), 52.45 (q), 52.47 (q), 81.45 (d), 81.69 (d), 84.08 (d), 84.43 (d), 138.70 (s), 139.35 (s), 140.72 (s), 140.89 (s), 170.59 (s), 170.79 (s), 172.47 (s), 174.14 (s), 174.16 (s), 174.32 (s) and 174.43 (s); *m/z* 351 (M$^+$ − OCH_3, 2.9%), 323 (M$^+$ − CO_2CH_3, 1.1), 238 (M$^+$ − $C_6H_8O_4$, 34.4) and 94 (M$^+$ − $C_6H_8O_4$ × 2, base) (Found: M$^+$, 382.1257. Calc. for $C_{18}H_{22}O_9$: M, 382.1263).

Diels–Alder reaction of sulfolene 1 with dimethyl maleate at 150 °C (entry 10 of Table 1). After column chromatography, compounds *cis-endo*-**5a** (40.4 mg, 53%), *cis-exo*-**5a** (7.4 mg, 10%) and **9a** (7.8 mg, 10%) were all obtained as oils from sulfolene **1** and dimethyl maleate (0.12 cm^3) at 150 °C for 3 h by the general method.

Dimethyl 5,6-dimethylene-7-oxabicyclo[2.2.1]heptane-2-*endo*,3-*endo*-dicarboxylate *cis-endo*-**5a**, δ_H 3.43 (2 H, d, *J* 2.44), 3.63 (6 H, s), 4.98 (2 H, d, *J* 2.44, bridgehead H), 5.10 (2 H, s) and 5.42 (2 H, s); δ_C 48.50 (d), 51.74 (q), 82.00 (d), 105.02 (t), 143.79 (s) and 169.82 (s); *m/z* 238 (M$^+$, 3.3%), 207 (M$^+$ − OCH_3, 7.5), 179 (M$^+$ − CO_2CH_3, 7.0) and 94 (M$^+$ − $C_6H_8O_4$, base) (Found: M$^+$, 238.0847. Calc. for $C_{12}H_{14}O_5$: M, 238.0841).

Dimethyl 5,6-dimethylene-7-oxabicyclo[2.2.1]heptane-2-*exo*,3-*exo*-dicarboxylate *cis-exo*-**5a**, δ_H 3.15 (2 H, s), 3.71 (6 H, s), 5.09 (2 H, s, bridgehead H), 5.16 (2 H, s) and 5.29 (2 H, s); δ_C 51.56 (d), 52.30 (q), 83.03 (d), 103.10 (t), 145.71 (s) and 171.02 (s); *m/z* 238 (M$^+$), 207 (M$^+$ − OCH_3, 0.8%) and 94 (M$^+$ − $C_6H_8O_4$, base) (Found: M$^+$, 238.0849).

Dimethyl 4,5,6,7-tetrahydrobenzo[*c*]furan-*cis*-5,6-dicarboxylate **9a**, δ_H 2.85 (2 H, dd, *J* 0.91 and 5.19), 2.88 (2 H, dd, *J* 0.91 and 5.19), 3.18 (2 H, m), 3.70 (6 H, s) and 7.19 (2 H, s); δ_C 20.62 (t), 40.95 (d), 51.96 (q), 118.80 (s), 137.75 (d) 173.14 (s); *m/z* 238 (M^+, 11.5%) and 119 ($M^+ - CO_2CH_3 \times 2$, base) (Found: M^+, 238.0846).

Diels–Alder reaction of sulfolene 1 with dimethyl maleate at 120 °C (entry 11 of Table 1). After column chromatography, compounds *cis-endo*-**5a** (39.2 mg, 51%), *cis-exo*-**5a** (7.2 mg, 10%), *cis-endo*-**7a** (13.0 mg, 11%) as an oil and *cis-exo*-**7a** (21.8 mg, 18%) as another oil were obtained from sulfolene **1** and dimethyl maleate (0.12 cm^3) at 120 °C for 12 h by the general method.

Tetramethyl 1,4-epoxy-1,2,3,4,5,6,7,8-octahydronaphthalene-2-*endo*,3-*endo*,6,7-tetracarboxylate *cis-endo*-**7a**, δ_H 2.49 (2 H, m), 2.82 (2 H, m), 3.06 (2 H, m), 3.47 (2 H, d, *J* 1.53), 3.62 (6 H, s), 3.67 (6 H, s) and 4.89 (2 H, d, *J* 1.53, bridgehead H); δ_C 24.52 (t), 40.15 (d), 47.90 (d), 51.94 [q, the signals of the methyl groups of the methoxycarbonyl groups on C-2(3) and C-7(6) overlappped], 81.98 (d), 140.04 (s), 170.74 (s) and 173.45 (s); *m/z* 382 (M^+, 4.2%), 351 ($M^+ - OCH_3$, 14.4) and 238 ($M^+ - C_6H_8O_4$, base) (Found: M^+, 382.1267. Calc. for $C_{18}H_{22}O_9$: M, 382.1263).

Tetramethyl 1,4-epoxy-1,2,3,4,5,6,7,8-octahydronaphthalene-2-*exo*,3-*exo*, 6,7-tetracarboxylate *cis-exo*-**7a**, δ_H 2.36 (2 H, dd, *J* 6.10 and 15.60), 2.57 (2 H, dd, *J* 5.00 and 15.60), 2.83 (2 H, s), 3.11 (2 H, m), 3.68 (6 H, s), 3.70 (6 H, s) and 5.06 (2 H, s, bridgehead H); δ_C 22.76 (d), 40.40 (d), 47.84 (d), 52.06 (q), 52.19 (q), 82.55 (d), 140.31 (s), 171.99 (s) and 172.94 (s); *m/z* 382 (M^+, 0.9%), 351 ($M^+ - OCH_3$, 4.8), 238 ($M^+ - C_6H_8O_4$, 27.9) and 178 ($M^+ - CO_2CH_3 \times 3$, base) (Found: M^+, 382.1269).

Retro-Diels–Alder reaction of *cis-endo*-7a. A solution of adduct *cis-endo*-**7a** (21.8 mg, 0.056 mmol) in benzene (1 cm^3) was heated at 150 °C for 1 h in a sealed tube. After removal of the solvent, the residue was purified by column chromatography (silica gel; hexane–AcOEt 19 : 1) to give compound **9a** (11.3 mg, 84%).

Diels–Alder reaction of sulfolene 1 with fumaronitrile at 150 °C (entry 14 of Table 1). After column chromatography (hexane–AcOEt 4 : 1), compounds *trans*-**5b** (20.1 mg, 36%) and **9b** (21.2 mg, 38%) were both obtained as oils from sulfolene **1** and fumaronitrile (74.0 mg) at 150 °C for 3 h by the general method.

5,6-Dimethylene-7-oxabicyclo[2.2.1]heptane-*trans*-2,3-dicarbonitrile *trans*-**5b**, δ_H(90 MHz) 3.09 (1 H, m), 3.38 (1 H, m), 5.26 (3 H, m), 5.34 (1 H, s), 5.43 (1 H, s) and 5.61 (1 H, s); δ_C 37.61 (d), 38.59 (d), 82.12 (d), 84.40 (d), 106.06 (t), 108.34 (t), 116.39 (d), 118.01 (s), 140.13 (s) and 142.67 (t); *m/z* 172 (M^+, 4.2%) and 146 ($M^+ - CN$, base) (Found: M^+, 172.0639. $C_{10}H_8N_2O$ requires M, 172.0637).

4,5,6,7-Tetrahydrobenzo[*c*]furan-*trans*-5,6-dicarbonitrile **9b**, δ_H(90 MHz) 3.01 (2 H, m), 3.20–3.28 (4 H, m) and 7.37 (2 H, m); δ_C(22.5 MHz) 22.28 (t), 28.57 (d), 114.93 (s), 118.20 (s) and 138.88 (d); *m/z* 172 (M^+, 4.8%) and 94 ($M^+ - C_4H_2N_2$, base) (Found: M^+, 172.0642. $C_{10}H_8N_2O$ requires M, 172.0637).

Diels–Alder reaction of sulfolene 1 with *N*-phenylmaleimide at 120 °C (entry 15 of Table 1). After column chromatography, adduct *cis-exo*-**7c** (115.9 mg, 82%) was obtained as an oil from sulfolene **1** and *N*-phenylmaleimide (166.0 mg) at 120 °C for 1 h by the general method.

N,*N′*-Diphenyl-1,4-epoxy-1,2,3,4,5,6,7,8-octahydronaphthalene-2-*exo*,3-*exo*,6,7-tetracarboximide *cis-exo*-**7c**, δ_H 2.49 (2 H, m), 3.01 (2 H, s), 3.03 (2 H, d, *J* 14.8), 3.38 (2 H, m), 5.25 (2 H, s, bridgehead H) and 7.25–7.50 (10 H, m, ArH); δ_C 20.50 (t), 37.51 (d), 48.32 (d), 83.62 (d), 126.32 (d), 126.55 (d), 128.78 (d), 128.92 (d), 129.19 (d), 131.59 (s), 131.72 (s), 140.76 (s), 174.98 (s) and 177.87 (s); *m/z* 267 ($M^+ - C_{10}H_7NO_2$ base) (Found: $M - C_{10}H_7NO_2$, 267.0909. Calc. for $C_{16}H_{13}NO_3$: *m/z* 267.0894).

Diels–Alder reaction of sulfolene 1 with maleic anhydride at room temperature (entry 16 of Table 1). A solution of sulfolene **1** (50.0 mg, 0.32 mmol), 4-methoxyphenol (10 mg) and maleic anhydride (94.1 mg, 3 mol equiv.) in absolute tetrahydrofuran (THF) (1 cm^3) was stirred at room temperature for 72 h. After concentration, the residue was purified by column chromatography (silica gel; hexane–AcOEt 1 : 1) to give adduct *cis-exo*-**3d** (51.3 mg, 62%) as an oil.

4,7-Epoxy-2,2-dioxo-1,3,4,5,6,7-hexahydrobenzo[*c*]thiophene-5-*exo*,6-*exo*-dicarboxylic acid anhydride *cis-exo*-**3d**, δ_H 3.29 (2 H, s), 3.86 (4 H, s) and 5.20 (2 H, s, bridgehead H); δ_C 49.02 (d), 56.51 (t), 84.30 (d), 116.51 (s) and 168.21 (s); *m/z* 256 (M^+, 2.2%), 192 ($M^+ - SO_2$, 8.9) and 96 (base) (Found: $M - SO_2$, 192.0419. $C_{10}H_8O_4$ requires 192.0422).

Diels–Alder reaction of sulfolene 1 with *p*-benzoquinone at 120 °C (entry 17 of Table 1). After column chromatography, adduct *cis-exo*-**5e** (50.5 mg, 78%) as a yellow oil and sulfolene **1** (11.0 mg, 22% recovery) were obtained from sulfolene **1** and *p*-benzoquinone (69.0 mg, 2 mol equiv.) at 120 °C for 3 h by the general method.

cisoid-4a,5-*cis*-4a,8a-5,8-Epoxy-6,7-dimethylene-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone *cis-exo*-**5e**, δ_H 3.13 (2 H, s), 5.15 (2 H, s, bridgehead H), 5.20 (2 H, s), 5.35 (2 H, s) and 6.81 (2 H, s); δ_C 53.40 (d), 86.26 (d), 103.48 (t), 142.20 (t), 145.29 (s) and 196.01 (s); *m/z* 202 (M^+) (Found: M^+, 202.0634. Calc. for $C_{12}H_{10}O_3$: M, 202.0630).

Diels–Alder reaction of sulfolene 1 with 1,4-naphthoquinone at 150 °C (entry 18 of Table 1). After column chromatography, adducts *cis-exo*-**5f** (46.7 mg, 58%) and **9f** (3.4 mg, 4%) were obtained from sulfolene **1** and 1,4-naphthoquinone (100.0 mg, 2 mol equiv.) at 150 °C for 4 h by the general method.

cisoid-4,4a-*cis*-4a,9a-1,4-Epoxy-2,3-dimethylene-1,2,3,4,4a,9a-hexahydroanthraquinone *cis-exo*-**5f**, δ_H 3.34 (2 H, s), 5.24 (2 H, s, bridgehead H), 5.28 (2 H, s), 5.37 (2 H, s), 7.76 (2 H, s) and 8.12 (2 H, s); δ_C 54.46 (d), 86.85 (d), 103.30 (t), 127.20 (d), 134.45 (d), 138.67 (s), 145.70 (s) and 194.66 (s); *m/z* 252 (M^+) (Found: M^+, 252.0781. Calc. for $C_{16}H_{12}O_3$: M, 252.0786).

4,11-Dihydroanthro[2,3-*c*]furan-5,10-dione **9f**, δ_H 2.78 (2 H, dd, *J* 5.80 and 16.20), 3.10 (2 H, dd, *J* 5.80 and 16.20), 3.51 (2 H, m), 7.36 (2 H, s), 7.75 (2 H, m) and 8.10 (2 H, m); δ_C 19.76 (t), 47.43 (d), 117.00 (s), 126.45 (d), 131.95 (s), 133.95 (d), 138.70 (d) and 185.05 (s); *m/z* 252 (M^+) (Found: M^+, 252.0785. Calc. for $C_{16}H_{12}O_3$: M, 252.0786).

Diels–Alder reaction of sulfolene 1 with 5-hydroxy-1,4-naphthoquinone (juglone) at 150 °C (entry 20 of Table 1). After column chromatography, adduct *cis-exo*-**5g** (51.5 mg, 58%) as a yellow oil and unchanged substrate **1** (6.2 mg, 13% recovery) were obtained from sulfolene **1** and 5-hydroxy-1,4-naphthoquinone (juglone) (111.0 mg, 2 mol equiv.) at 120 °C for 4 h by the general method.

cisoid-4,4a-*cis*-4a,9a-1,4-Epoxy-5-hydroxy-2,3-dimethylene-1,2,3,4,4a,9a-hexahydroanthraquinone *cis-exo*-**5g**, δ_H 3.30 (1 H, d, *J* 1.37), 3.35 (1 H, d, *J* 1.37), 5.26 (2 H, s, bridgehead H), 5.27 (2 H, s), 5.37 (2 H, s), 6.12 (1 H, br s), 7.27 (1 H, m) and 7.66 (2 H, m); δ_C 53.96 (d), 54.43 (d), 87.15 (d), 87.20 (d), 103.52 (t, the signals of the two methylene groups for C-2 and C-3 overlapped), 118.22 (s), 118.78 (d), 123.93 (d), 135.19 (s), 137.50 (d), 145.39 (s), 145.50 (s), 162.18 (s), 194.02 (s) and 201.24 (s); *m/z* 268 (M^+) (Found: M^+, 268.0729. Calc. for $C_{16}H_{12}O_4$: M, 268.0735).

Diels–Alder reaction of sulfolene 1 with dimethyl maleate under high-pressure conditions (entry 1 of Table 2)

A typical procedure was as follows: furansulfolene **1** (50.0 mg, 0.32 mmol), 4-methoxyphenol (10 mg) and dimethyl maleate (0.12 cm^3, 3 mol equiv.) were dissolved in CH_2Cl_2 (1.8 cm^3) and the solution was placed in a PTFE cylinder and allowed to react at the temperature, the pressure and for the time indicated in Table 2. After evaporation of the mixture, the crude product was purified by column chromatography (silica gel; hexane–AcOEt 4 : 1) to afford adduct *cis-endo*-**3a** (78.3 mg, 81%).

Dimethyl 4,7-epoxy-2,2-dioxo-1,3,4,5,6,7-hexahydrobenzo-[*c*]thiophene-5-*endo*,6-*endo*-dicarboxylate *cis-endo*-**3a**, ν_{max}-

($CHCl_3$)/cm^{-1} 1744, 1324 and 1175; δ_H 3.61 (1 H, d, *J* 2.45), 3.62 (1 H, d, *J* 2.45), 3.63 (6 H, s), 3.99 (2 H, s), 4.00 (2 H, s) and 5.18 (2 H, d, *J* 2.45, bridgehead H); δ_C 48.40 (d), 52.24 (q), 56.58 (t), 79.97 (d), 141.03 (s) and 169.93 (s); *m/z* 238 ($M^+ - SO_2$, 3.7%) and 94 ($M^+ - SO_2 - C_6H_8O_4$, base) (Found: M^+, 238.0844. Calc. for $C_{12}H_{14}O_5$: M, 238.0841).

Other products were obtained in an analogous way. The adduct *trans*-**3a** from dimethyl fumarate was a thermally unstable powder.

Dimethyl 4,7-epoxy-2,2-dioxo-1,3,4,5,6,7-hexahydrobenzo-[*c*]thiophene-*trans*-5,6-dicarboxylate *trans*-**3a**, ν_{max}($CHCl_3$)/cm^{-1} 1735, 1319 and 1181; δ_H 2.91 (1 H, d, *J* 4.0), 3.67 (3 H, s), 3.76 (1 H, s), 3.80 (3 H, s), 3.99 (2 H, d, *J* 15.2), 4.02 (2 H, d, *J* 15.2), 5.30 (1 H, s, bridgehead H) and 5.35 (1 H, d, *J* 4.00, bridgehead H); *m/z* 243 ($M^+ - CO_2CH_3$), 238 ($M^+ - SO_2$, 0.4), 178 ($M^+ - SO_2 - CO_2CH_3$, 26.5) and 94 ($M^+ - SO_2 - C_6H_8O_4$, base) (Found: M^+, 238.0842).

Diels–Alder reaction of adduct *cis-endo*-5a with DMAD under high-pressure conditions

The type A adduct *cis-endo*-**5a** (50.0 mg, 0.21 mmol), 4-methoxyphenol (10 mg) and DMAD (0.028 cm^3, 1.1 mol equiv.) were dissolved in CH_2Cl_2 (1.8 cm^3) and the solution was placed in a PTFE cylinder and allowed to react at 12 kbar for 48 h (28 °C). After removal of the solvent, the residue was purified by column chromatography (silica gel; hexane–AcOEt 4:1) to give *cis-endo*-**12a** (79 mg, quant.) as a pale yellow oil.

Tetramethyl 1,4-epoxy-1,2,3,4,5,8-hexahydronaphthalene-2-*endo*,3-*endo*,6,7-tetracarboxylate, *cis-endo*-**12a**, δ_H 3.25 (4 H, m), 3.53 (2 H, d, *J* 2.44), 3.63 (6 H, s), 3.78 (6 H, s) and 4.96 (2 H, d, *J* 2.44, bridgehead H); δ_C 27.15 (q), 47.89 (d), 51.84 (q), 52.28 (q), 81.59 (d), 132.69 (s), 138.21 (s), 168.28 (d) and 170.38 (s); *m/z* 349 ($M^+ - OCH_3$, 1.1%), 268 ($M^+ - C_6H_8O_2$), 204 ($M^+ - CO_2CH_3 \times 3$, 49.7) and 94 ($M^+ - C_6H_6O_4 - C_6H_8O_6$, base) (Found: $M - OCH_3$, 349.0924. Calc. for $C_{17}H_{17}O_8$: *m/z* 349.0922).

Retro-Diels–Alder reaction of adduct *cis-endo*-12a

A solution of compound *cis-endo*-**12a** (10.1 mg, 0.03 mmol) in benzene (0.56 cm^3) was heated at 150 °C for 3 h in a sealed tube. After removal of the solvent, the residue was purified by column chromatography (silica gel; hexane–AcOEt 4:1) to give compound **8a** (7.0 mg, quant.) as an oil.

Dimethyl 4,7-dihydrobenzo[*c*]furan-5,6-dicarboxylate **8a**, δ_H 3.54 (4 H, s), 3.82 (6 H, s) and 7.29 (2 H, s); δ_C 22.57 (t), 52.37 (q), 116.68 (s), 133.02 (s), 137.57 (d) and 168.49 (s); *m/z* 236 (M^+, 27.1%), 221 ($M^+ - CH_3$, 8.5) and 118 ($M^+ - C_4H_6O_4$, base) (Found: M^+, 236.0685. Calc. for $C_{12}H_{12}O_5$: M, 236.0684).

Diels–Alder reaction of compound *trans*-5a with DMAD under thermal conditions

A solution of compound *trans*-**5a** (24.4 mg, 0.103 mmol) and DMAD (0.014 cm^3, 1.1 mol equiv.) in benzene (0.5 cm^3) was heated at 150 °C for 3 h in a sealed tube. After concentration, the residue was purified by column chromatography (silica gel; hexane–AcOEt 9:1) to give adduct *trans*-**12a** (21.9 mg, 55%) as an oil and substrate **8a** (9.5 mg, 39% recovery).

Tetramethyl 1,4-epoxy-1,2,3,4,5,8-hexahydronaphthalene-*trans*-2,3,6,7-tetracarboxylate, *trans*-**12a**, δ_H 2.91 (1 H, m), 3.37 (4 H, m), 3.69 (3 H, s), 3.71 (1 H, s), 3.77 (6 H, s), 3.83 (3 H, s), 5.07 (1 H, m, bridgehead H) and 5.51 (1 H, s, bridgehead H); *m/z* 349 ($M^+ - OCH_3$, 2.3%) and 94 ($M^+ - C_6H_6O_4 - C_6H_8O_6$, base) (Found: $M^+ - OCH_3$, 349.0925. $C_{17}H_{17}O_8$ requires 349.0922).

Diels–Alder reaction of adduct *cis-endo*-5a with DMAD under thermal conditions

A solution of compound *cis-endo*-**5a** (24.2 mg, 0.103 mmol) and DMAD (0.014 cm^3, 1.1 mol equiv.) in benzene (0.5 cm^3) was heated at 150 °C for 3 h in a sealed tube. After concentration, the residue was purified by column chromatography (silica gel; hexane–AcOEt 9:1) to give compound **8a** (20.5 mg, 84%).

Diels–Alder reaction of compound *cis-exo*-5a with DMAD under thermal conditions

A solution of compound *cis-exo*-**5a** (24.3 mg, 0.103 mmol) and DMAD (0.014 cm^3, 1.1 mol equiv.) in benzene (0.5 cm^3) was heated at 150 °C for 3 h in a sealed tube. After concentration, the residue was purified by column chromatography (silica gel; hexane–AcOEt 9:1) to give adduct *cis-exo*-**12a** (4.0 mg, 10%) as an oil, compound **8a** (9.0 mg, 37%) and the recovery of substrate *cis-exo*-**5a** (2.2 mg, 9%).

Tetramethyl 1,4-epoxy-1,2,3,4,5,8-hexahydronaphthalene-2-*exo*,3-*exo*,6,7-tetracarboxylate *cis-exo*-**12a**, δ_H 3.19 (4 H, m), 3.42 (2 H, m), 3.68 (6 H, s), 3.79 (6 H, s) and 5.12 (2 H, s, bridgehead H); *m/z* 349 ($M^+ - OCH_3$, 0.9%), 268 ($M^+ - C_6H_8O_2$), 204 ($M^+ - CO_2CH_3 \times 3$, 35.5) and 94 ($M^+ - C_6H_6O_4 - C_6H_8O_6$, base) (Found: $M - OCH_3$, 349.0928. Calc. for $C_{17}H_{17}O_8$: *m/z* 349.0922).

Diels–Alder reaction of compound *cis-endo*-5a with 5-hydroxy-1,4-naphthoquinone (juglone)

A solution of compound *cis-endo*-**5a** (50.0 mg, 0.21 mmol) and 5-hydroxy-1,4-naphthoquinone (juglone) (40.1 mg, 1.1 mol equiv.) in CH_2Cl_2 (2 cm^3) was heated at 80 °C for 10 h in a sealed tube. After concentration, the residue was purified by column chromatography (benzene–CH_2Cl_2 9:1) to give compound **11** (50.5 mg, 58%) as a yellow oil.

1,4-Epoxy-7-hydroxy-6,11-dioxo-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-2-*endo*,3-*endo*-dicarboxylate **11**, δ_H(90 MHz) 2.52 (2 H, m), 2.78 (2 H, m), 3.10 (2 H, m), 3.51 (2 H, d, *J* 1.51), 3.61 (3 H, s), 3.65 (3 H, s), 4.89 (2 H, d, *J* 1.51), 7.32 (1 H, m) and 7.64 (2 H, m); *m/z* 412 (M^+) (Found: M^+, 412.1152. Calc. for $C_{22}H_{20}O_8$: M, 412.1157).

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