Pergamon

Tetrahedron: *Asymmetry* 11 (2000) 4737–4752

TETRAHEDRON: *ASYMMETRY*

Stereoselectivity control in Diels–Alder reactions of 4-thiosubstituted 5-alkoxyfuranones: synthesis and reactivity of enantiopure 4-sulfinyl and sulfonyl 5-(*l*-menthyloxy)furan-2(5*H*)-ones

José L. García Ruano,* Fernando Bercial, Alberto Fraile, Ana M. Martín Castro and M. Rosario Martín*

Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

Received 23 October 2000; accepted 21 November 2000

Abstract

The synthesis of enantiomerically pure (*S*)-4-phenylsulfinyl- and 4-phenylsulfonyl-(5*S*)-5-(*l*-menthyloxy)furan-2(5*H*)-ones **5a** and **6** and (5*R*)-5-(*l*-menthyloxy)-4-phenylsulfonylfuran-2(5*H*)-one **8** and the study of their reactions with cyclopentadiene are described. The sulfur substituents at C-4 modify (sulfone **8**, *anti*/*syn* = 78/22) and invert (sulfoxide **5a** and sulfone **6**, *anti*/*syn* ≈ 27/73) the trend imposed by C-5 on the π-facial selectivity and the *syn*-adducts become the favoured ones. The *endo* or *exo* approach mode is favoured for *anti* (*endo*/*exo* ratio ranging between 26 and 5) or *syn* (*exo*/*endo* ratio ranging between 4.5 and 2.3) attack, respectively. © 2001 Published by Elsevier Science Ltd.

1. Introduction

Homochiral 5-alkoxyfuran-2(5*H*)-ones have played an important role as building blocks in the asymmetric synthesis of a number of natural products.[1] In particular, (5*R*)-5-(*l*-menthyloxy)-2(5*H*)-furanone **1**[2] (Fig. 1) is a versatile dienophile in asymmetric Diels–Alder reactions,[1c,2–4] since it has been reported that it controls efficiently both the π-facial and the *endo*/*exo* selectivity (only one *endo* adduct is formed).† The spatial arrangement of the γ-alkoxy substituent, which shields one of the π-faces of the molecule, has usually been presumed as the origin of the high stereocontrol observed in Diels–Alder reactions, as well as in other cycloadditions.[5] As *trans*-addition of the diene relative to the menthyloxy substituent of the furanone was exclusively

* Corresponding authors. E-mail: joseluis.garcia.ruano@uam.es; rosario.martin@uam.es

† Nevertheless, in Ref. 1c there was described one example of low stereoselectivity in the Diels–Alder reaction of the furanone **1** with an arylisobenzofuran.

0957-4166/00/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0957-4166(00)00471-7

observed, the configuration at C-5 was considered as entirely responsible for the π-facial selectivity. The introduction of a sulfonyl group at C-4 strongly enhances the dienophilic reactivity of the furanone but it does not affect its stereoselectivity. Thus, reaction of (5*S*)-5-(*d*-menthyloxy)-4-(phenylsulfonyl)-2(5*H*)-furanone **2** with cyclopentadiene afforded only one *endo*-adduct,[6] which demonstrated once again the important role played by C-5 configuration in determining the stereochemical course of the γ-alkoxybutenolides cycloadditions.

The sulfinyl group has proved to be very efficient in the control of the π-facial selectivity of Diels–Alder reactions on many different dienophiles.[7] In particular, reactions of cyclopentadiene with (*S*)-3-(*p*-tolylsulfinyl)-2(5*H*)-furanone **3**, in the presence of chelating Lewis acids, afforded mixtures of *endo*- and *exo*-adducts,[8] resulting from an almost exclusive approach of the diene to only one of the faces of the dienophile. In the absence of catalysts the observed π-facial selectivity is just the opposite. In order to evaluate the relative influence of the configurations at sulfur and C-5 in the control of the π-facial selectivity of Diels–Alder reactions of 2(5*H*)-furanones, the study of the reactions of (5*R*,S*S*)- and (5*S*,S*S*)-5-ethoxy-3-(*p*-tolylsulfinyl)furan-2(5*H*)-ones **4a** and **4b** with cyclopentadiene[9] was undertaken. The two main stereochemical conclusions of this study were the high predominance of the *endo*-adducts, which indicates that the *endo*/*exo* control is mainly exerted by the lactone moiety, and the fact that, depending on the reaction conditions, the control of the π-facial selectivity is mainly exerted by the configuration at C-5 (under thermal conditions) or by the sulfur configuration (under $ZnBr_2$ catalysis). As a continuation of these studies, we decided to incorporate the sulfinyl moiety at the C-4 position of 5-alkoxyfuran-2(5*H*)-ones and to study the reactions of this dienophile with cyclopentadiene. As the results obtained were unexpectedly contradictory to the previously described ones, it was necessary to carry out the study of other 5-alkoxyfuranones to clarify their behaviour and the actual influence of the configuration at C-5 on the stereoselectivity of the cycloadditions. The synthesis and reactions with cyclopentadiene of 4-thioderivatives of 5-(*l*-menthyloxy)-2(5*H*)-furanones **5a** and **6** (Fig. 1), as well as those of (5*S*)-5-(*l*-menthyloxy)furan-2(5*H*)-one **7**, and the sulfone **8** (enantiomer of compound **2**) are reported herein.

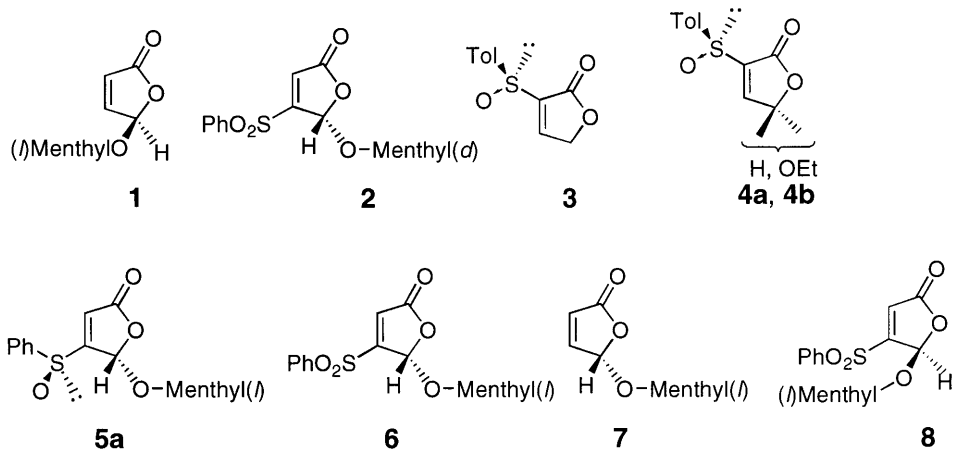
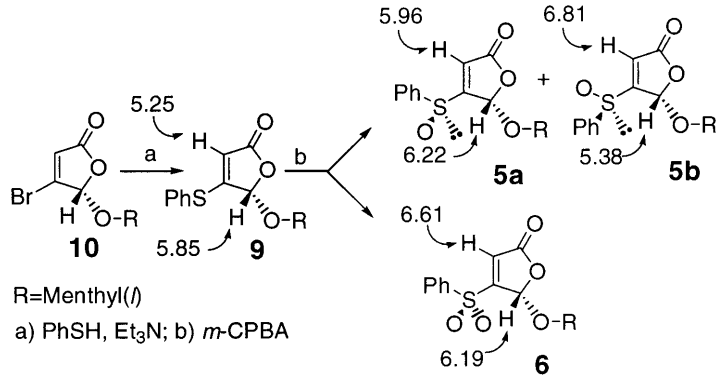


Figure 1.



Scheme 1.

2. Results and discussion

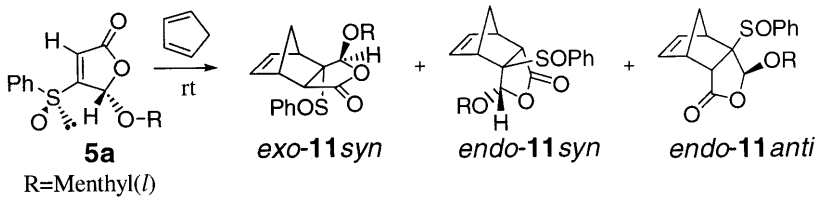
The synthesis of enantiomerically pure (5*S*,S*S*)-5-(*l*-menthyloxy)-4-phenylsulfinylfuran-2(*H*)-one **5a**, as well as that of the sulfone **6** were carried out from the sulfide **9** (Scheme 1). The preparation of **9** was performed following the method previously described by us,[10] consisting in the reaction of the 4-bromo derivative **10** with PhSH and Et_3N (Scheme 1). The oxidation of **9** with *m*-CPBA[‡] (1 equiv., −78°C) afforded a 5:1 mixture of the two sulfoxides, **5a** and **5b**, in 65% yield (after chromatography), easily separated from the sulfone **6** and the starting sulfide **9**, also present in the reaction mixture. The major epimer **5a** could be isolated diastereoisomerically pure (46% yield from **9**) by precipitation with hexane from the epimeric mixture previously dissolved in xylene. When the oxidation of **9** was accomplished at room temperature using 2 equiv. of *m*-CPBA, the sulfone **6** was obtained as a sole product in a 95% yield.

The configuration at C-5 for sulfoxides **5a** and **5b** and sulfone **6** was assigned as *S* on the basis of the known (5*S*)-configuration of starting sulfide **9**.[§] The configuration at sulfur for **5a** and **5b** was initially established from the relative $\Delta\delta$ values ($\delta_{sulfoxide}-\delta_{sulfide}$) for H-3 and H-5 in both epimers. The shielding effect of the phenyl group and the deshielding effect of the sulfinyl one, exerted on the protons adopting a 1,3-parallel arrangement with respect to them, would explain the chemical shifts observed for compounds **5a** and **5b** (see Scheme 1). In this sense, we assume that they exist mainly in the conformations depicted in Scheme 1, which will be favoured by steric and electrostatic grounds. Unequivocal assignment of the absolute configuration at sulfur and C-5 for **5a** was established by X-ray analysis of the adduct *exo*-**11***syn* (see later), resulting from its reaction with cyclopentadiene.

The results obtained in the reactions of sulfoxide **5a** with cyclopentadiene (Scheme 2) are collected in Table 1. In the absence of Lewis acids (entries 1 and 2), the reaction required 24 h at room temperature in CH_2Cl_2 or 0.5 h in refluxing $CHCl_3$ to be completed, affording a mixture of three adducts **11**, easily separated by flash chromatography. The use of $ZnBr_2$ as a catalyst (entry 3) slightly increased the reactivity (lower reaction times at rt are needed) but the proportion of the obtained adducts (determined in all cases by ^1H NMR of the crude mixtures) remained almost unaltered.

[‡] We have unsuccessfully tested other oxidising reagents, such as $NaIO_4$, chlorobenzotriazol, and several hydroperoxides (TBHP, CHP, $H_2O_2/TiCl_3$) and *m*-CPBA under conditions different to those indicated in Section 3, to achieve the oxidation of sulfide into sulfoxides.

[§] Under the conditions used, no epimerisation at C-5 for any of the three thio derivatives was observed. This contrasts with the results reported by Feringa.[6]



Scheme 2.

Table 1
Reactions of **5a** with cyclopentadiene

Entry	Reaction conditions[a]	Yield (%)[b]	Adduct ratio[c]		
			Exo-**11***syn*	*Endo*-**11***syn*	*Endo*-**11***anti*
1	A	88	53	21	26
2	B	86	56	21	23
3	C	76	60	20	20

[a] A: CH_2Cl_2, rt, 24 h; B: CH_3Cl, reflux, 0.5 h; C: $ZnBr_2$ (2.3 equiv.), CH_2Cl_2, rt, 24 h.
[b] Combined yield of pure products after chromatography.
[c] (%) Determined by ^1H NMR.

The *endo* or *exo* geometry for bicyclic adducts **11** was deduced from their ^1H NMR spectra. Compounds *endo*-**11***syn* and *endo*-**11***anti* exhibit coupling constants of 5.7 and 5.8 Hz between H-7 and H-7a, whereas the absence of $J_{7,7a}$ and the existence of a long range coupling constant $^4J_{7a,8x}$ (which was also observed by a COSY experiment) are characteristic features of the major adduct *exo*-**11***syn*. The differentiation between *endo*-**11***syn* and *endo*-**11***anti* was based on the relative δ value of their acetallic proton (it is higher for *endo*-**11***syn* due to the deshielding effect of the sulfinyl group in a *cis* arrangement) and mainly on the NOE enhancement observed for H-3 with H-5 (16%) in *endo*-**11***anti*, which is absent in *endo*-**11***syn*. The unequivocal assignment of *exo*-**11***syn* was established by X-ray analysis (Fig. 2), which, in its turn, allowed us to confirm the absolute configuration at sulfur, as well as that at C-5 of the starting product **5a** (see above).

The results observed in Table 1 clearly contrast with those reported by Feringa for compound **1**[2] (only the *endo*-adduct from the opposite *anti* face to that displayed by the menthyloxy group was formed). Initially, this suggested to us that, in the absence of any catalyst, the role of the sulfinyl group in the control of both *endo*/*exo* and π-facial selectivities was much more important than that of C-5 of the furanone. Thus, the major adduct from **5a** was *exo*-**11***syn*, resulting from the *exo* approach of diene to the same *syn* face bearing the menthyloxy moiety. Moreover, the π-facial selectivity, measured as the *syn*/*anti* adducts ratio ($\geq$3:1), indicated that the approach of the diene from the same face of the alkoxy group was the favoured one, and the *exo*/*endo* ratio (>1) revealed the *exo* addition mode as the slightly preferred one. The comparison between these results and those obtained for **4a** (Fig. 1) in the absence of catalysts, which evidenced the predominant role of the configuration at C-5 of the furanone ring (see above), suggested to us that the position of the sulfinyl group on the furanone skeleton was of utmost importance.

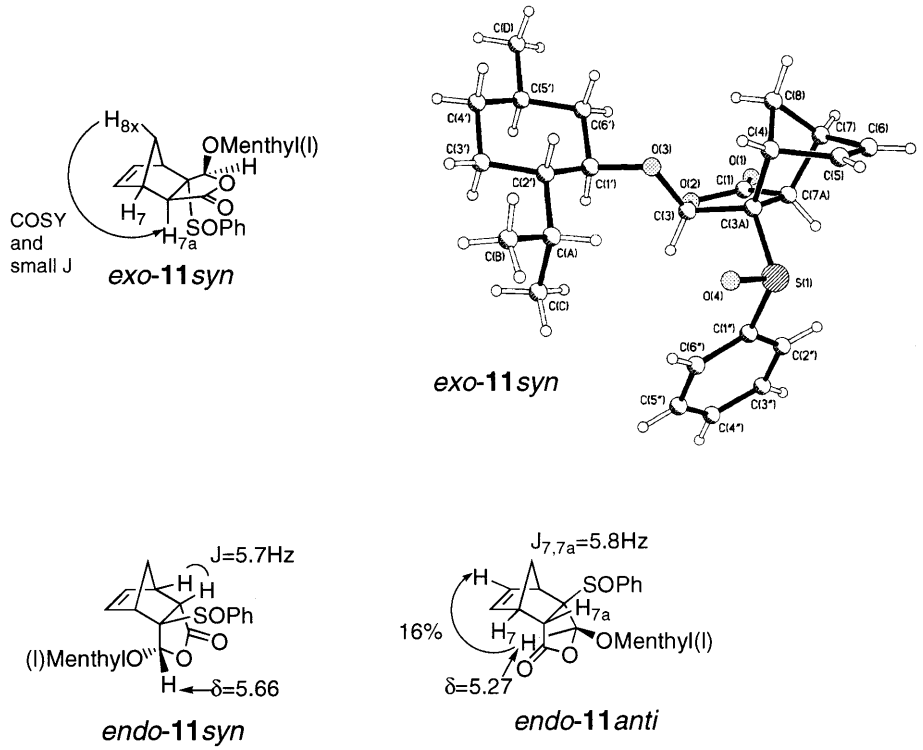
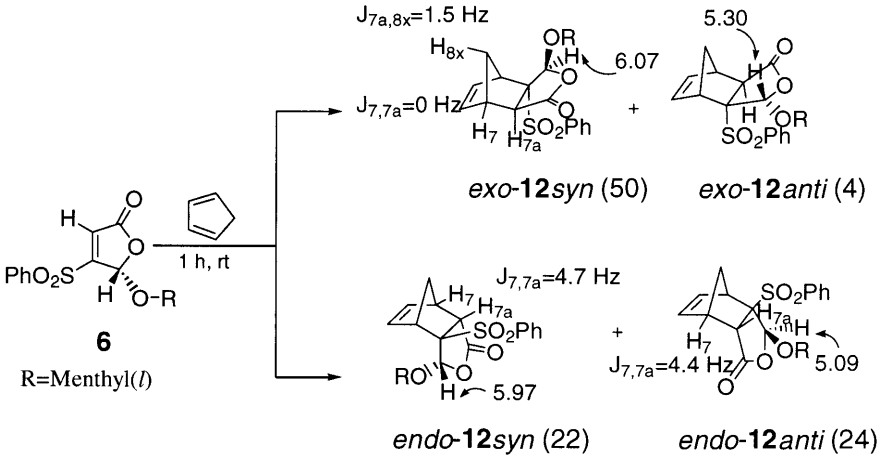


Figure 2.

On the other hand, the relative size of the sulfonyl and sulfinyl groups suggested no important differences in their relative *endo* orientating character, thus determining that the *endo*/*exo* adducts ratio should be similar for sulfonyl- and sulfinyl-furanones. Nevertheless, the comparison between the results obtained in reactions of cyclopentadiene with **5a** (*exo*-**11***syn* was obtained as the major adduct) and **2** (only the *endo–anti* adduct was detected)[6] indicated that this was not the case. All these considerations prompted us to study the reaction of the sulfone **6** with cyclopentadiene. It required 1 hour at room temperature to afford a mixture of stereoisomers *exo*-**12***syn*, *exo*-**12***anti*, *endo*-**12***syn* and *endo*-**12***anti*, in a 50:4:22:24 relative ratio (Scheme 3). In our hands their separation could not be achieved successfully.

Characterisation of the compounds was performed by ^{1}H NMR of the crude reaction mixture. The signals corresponding to compounds *exo*-**12***syn*, *endo*-**12***anti* and *endo*-**12***syn* were identified by comparison with those of actual samples of such compounds, independently obtained by *m*-CPBA oxidation of the sulfoxides[¶] *exo*-**11***syn*, *endo*-**11***anti* and *endo*-**11***syn* (the configuration of which had been unequivocally established (see above)), respectively. The remaining signals in the spectra of the crude reaction mixture were assigned to the minor diastereoisomer *exo*-**12***anti*. The coupling constant ($J_{7,7a}$ and $J_{7,8}$) and the chemical shift of the acetallic proton for the sulfonyl adducts **12** (see Scheme 3), as well as those for the sulfinyl adducts **11**, allowed us to assign the *endo–exo* and *syn–anti* stereochemistry and validate the criteria used for the assignment of the stereochemistry of this type of adduct.

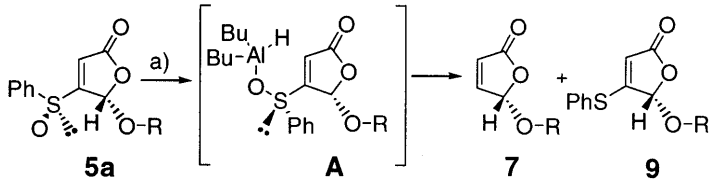
[¶] The formation of sulfonyl epoxides (6 and 8% yield) was observed in the oxidation of the sulfoxides *exo*-**11***syn* and *endo*-**11***syn*.



Scheme 3.

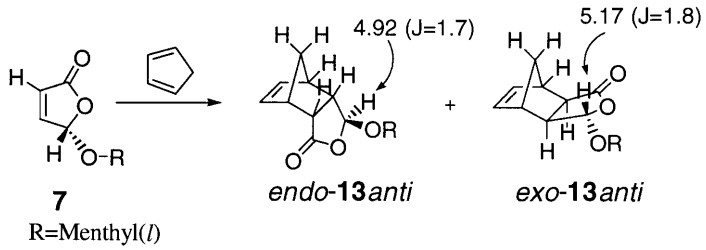
As expected, the proportion of adducts resulting from sulfone **6** (Scheme 3) was quite similar to that obtained from sulfoxide **5a**. The almost identical *endo*/*exo* ratio can be rationalised by assuming a similar *endo* orientating character for the sulfinyl and sulfonyl groups. On the contrary, the fact that the change of sulfur function resulted in no significant variation in the observed π-facial selectivity was unexpected, because it suggests a hardly relevant role of the sulfur configuration on the stereochemical course of these cycloadditions. Additionally, the exclusive formation of the *endo–anti* adduct reported from sulfone **2**[6] strongly contrasted with the behaviour of compound **6**, which yielded a mixture, the *exo*-**12***syn* adduct being the major one. Taking into account that sulfones **2** and **6** only differ in the stereochemistry of their menthyloxy residues (*d*- and *l*-, respectively), the results reported herein suggested that this difference, and not the configuration at C-5 (identical in both substrates), must be responsible for their different stereochemical course. This being the case, the predominant role so far assigned to the configuration at C-5 in cycloadditions of 5-menthyloxyfuranones ought to be reconsidered.

In order to investigate this point we decided to study the reaction of compound **7** (Fig. 1) with cyclopentadiene. Compound **7**, which differs from **1** only in the stereochemistry at the C-5, was studied in order to verify the influence of the relative configuration of the involved stereogenic centres on the π-facial selectivity. The synthesis of **7** was accomplished by DIBALH reduction of **5a** (Scheme 4), which yielded a 1:2 mixture of sulfide **9** and the desired butenolide **7** (54% isolated yield). The formation of the latter compound can be explained as the result of a reduction of the double bond (by 1,4-hydride addition from the associated species **A**, see Scheme 4) followed by desulfinylation of the resulting sulfoxide.



Scheme 4. (a) DIBALH (1.5 equiv.)/THF, −78°C, 30 min, R = menthyl(*l*).

The reaction of **7** with cyclopentadiene (4 equiv.) at room temperature required 12 days to be completed and yielded a 92:8 mixture of two adducts in 82% combined yield (Scheme 5), which could be separated and characterised as *endo*-**13***anti* (77% isolated yield) and *exo*-**13***anti* (5% isolated yield) from their ^{1}H NMR spectra ($J_{3,3a} = 1.7$ and 1.8 Hz) and COSY experiment (*endo*-**13***anti* shows a correlation between H-3a and H-4 but not between H-8 and H-3a or H-7a; however, *exo*-**13***anti* exhibits a correlation signal between H-8 and H-3a and H-7a but not between H-3a and H-4).



Scheme 5.

As we can see, both compounds are the result of the *endo* and *exo* approaches of the diene from the less hindered face of the dienophile (*anti* with respect to the alkoxy group), thus suggesting that configuration at C-5 is totally efficient in the control of the π-facial selectivity. This conclusion agrees with that previously established by Feringa[2,3] from the results obtained from compound **1**. On the other hand, the *endo*/*exo* selectivity is not complete for **7** (84% de), whereas **1** evolved with exclusive (>96%) formation of the *endo* adduct, which suggests that the relative configuration of the stereogenic centres could have some influence on the control of this kind of stereoselectivity. In order to verify this possibility, the study of the reaction of cyclopentadiene with racemic methoxyfuran-2(5*H*)-one, with no stereogenic centre additional to C-5, was undertaken. In our hands the results obtained from the above reaction were quite similar to those from **7** (only *anti* adducts as a 93:7 *endo*/*exo* mixture were formed), which revealed that the *endo*/*exo* selectivity for 5-alkoxyfuran-2(5*H*)-one was high but not complete.

The comparison of the results obtained from butenolides **7** (Scheme 5) and **5a** (Table 1) clearly shows the important role of the sulfinyl group in the control of the stereoselectivity of these reactions. The four possible transition states for evolution of **5a** in its presumably most stable conformation are shown in Fig. 3.

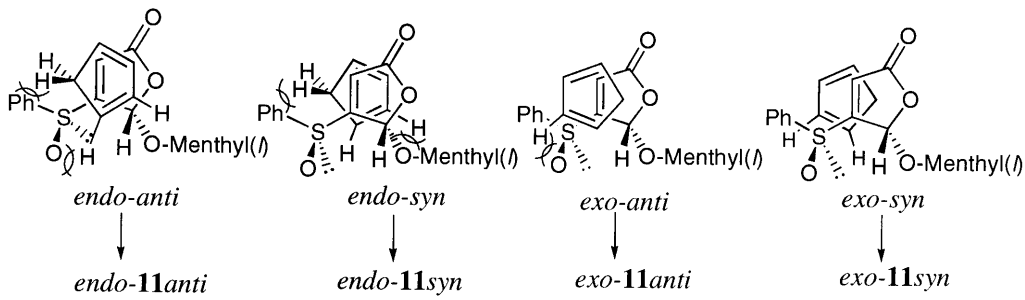
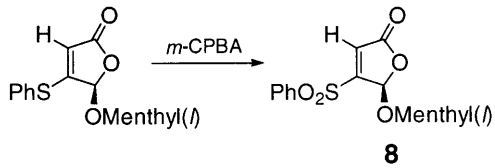


Figure 3.

As we can see, the interaction CH_2/Ph must destabilise the *endo* TSs, thus favouring the *exo* ones. Additionally, the H/O interactions present in each *endo* TS must be similar, thus determining a low facial selectivity for the *endo* approach. By contrast, the two *exo* TSs have different stabilities because of the O/H interaction only exhibited by the *exo–anti* TS (see Fig. 3), thus justifying the complete facial selectivity observed for the *exo* approach (*exo*-**11***anti* was not detected). The comparison of the results observed for compounds **5a** and **7** suggests that the CH_2/Ph interaction of the *endo* adducts (Fig. 3) must be responsible for the significant increase in the proportion in the *exo* ones, observed for sulfoxide **5a**. Moreover, the influence of the sulfinyl group at C-4 in the π-facial selectivity control is clearly higher than that of the configuration at C-5 (*syn* adducts are predominant) and also higher than that exerted by the sulfinyl group when it is at C-3 in the furanone ring (compounds **4a** and **4b**, see above). This behaviour can be explained by assuming that the conformational mobility around the C–S bond is completely restricted for compound **5a** (only the rotamer depicted in Fig. 3 must be present due to the strong electrostatic and steric interactions of the other two possible rotamers).** In this sense, the influence of the SOPh group in **5a** was similar to that observed for SOTol in **4a** in reactions conducted under $ZnBr_2$ catalysis, conditions favouring the chelation of the sulfinyl and lactone oxygens, thus restricting the conformational mobility around the C–S bond.

At this point, the most striking results are the behaviour of sulfones. We decided to study the behaviour of the sulfone **8**. The synthesis of this compound was performed from the corresponding sulfide, as shown in Scheme 6.

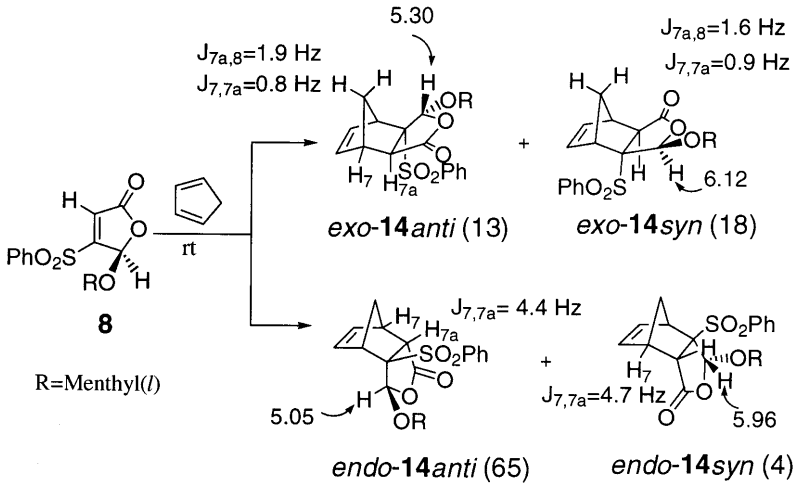


Scheme 6.

The reaction of **8** with cyclopentadiene took place at rt in 5 h, both in CH_2Cl_2 and C_6H_6, and yielded a mixture of four adducts in a 13:18:65:4 ratio (Scheme 7). Chromatographic separation allowed the isolation of the three major ones, the configurational assignment of which was based on their spectroscopic parameters. The stereochemistry of the minor *endo*-**14***syn* was assigned by exclusion.

The stereochemistry of adducts **14** was deduced from their ^{1}H NMR spectra following the same criteria as in adducts **11** and **12**. Thus, compounds *endo*-**14***anti* and *endo*-**14***syn* exhibited coupling constants of 4.4 and 4.7 Hz, respectively, between H-7 and H-7a, whereas the low values of $J_{7,7a}$ and the existence of a long range coupling constant $^4J_{7,8}$ were characteristic of the adducts *exo*-**14***anti* and *exo*-**14***syn*. For adducts **14**, with a configuration at C-3 opposite to that of **12**, the acetallic proton of the *syn*-adducts is deshielded with respect to the corresponding *anti*-adducts, maybe due to the deshielding effect of the sulfone group adopting a *cis* arrangement in the former.

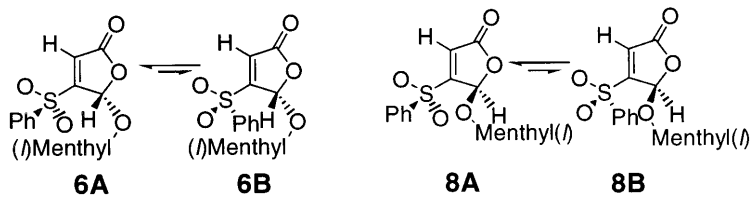
** This explanation suggests that the relative influence of the sulfinyl group and the C-5 configuration could be completely different for compound **5b**, which must exhibit smaller conformational restrictions.



Scheme 7.

The results obtained from sulfone **8** (Scheme 7) revealed that the *endo* addition mode was favoured with respect to the *exo* one (*endo*/*exo* ratio = 69:31) and the π-facial selectivity for the *endo* approach was quite high (88% *de*), but it substantially decreased for the *exo* approach mode (16% *de*). These results indicated that those previously reported by Feringa for compound **2** (enantiomer of **8**) should be reconsidered. The *endo–anti*-adduct is the major one but neither the *endo*/*exo* selectivity nor the π-facial selectivity were complete starting from these sulfones.

The comparison between sulfones **6** and **8**, both epimers at C-5, is also interesting in order to establish the origin of the stereoselectivity of the 5-alkoxy furanones. In these compounds the *endo*/*exo* ratio depends on the relative configuration of both epimers. Thus, compound **8** exhibited a predominance of the *endo*-adducts (*endo*/*exo* = 69:31), whereas it disappeared for compound **6** (*endo*/*exo* = 46:54). A similar but more striking fact was related with the π-facial selectivity. Compound **8** exhibited the expected behaviour, the *anti*-adducts being the major ones (*anti*/*syn* = 78:22); the change in the relative configuration of C-5 or menthyl group determined the inversion of such a selectivity, as observed for compound **6** (*anti*/*syn* = 28:72). These results must be a consequence of the different spatial arrangement of the menthyl moiety in both epimers, which will be able to modify the conformational preferences around the C–S bond (Scheme 8).



Scheme 8.

The Ph/Omenthyl interaction will be more destabilising for compound **6**, thus shifting the conformational equilibrium towards **6A**. The lower magnitude of such an interaction in compound **8** (the menthyl group is far away from the sulfonyl group) would explain the predominance of **8A** with no electrostatic $(O/Omenthyl)_{1,3p}$ interaction. As the Ph group is effectively bulkier than the O-menthyl one, compound **6** must exhibit a *syn* selectivity, whereas **8** will show a net predominance of *anti*-adducts.

In conclusion, we can state that the configuration at C-5 is obviously important in the control of the π-facial selectivity of the cycloadditions to 5-menthyloxyfuran-2(5*H*)-ones (*anti*-adducts were clearly favoured), but its influence in the *endo*/*exo* selectivity is modulated by the relative configuration of C-5 and the menthyl moiety. Substrates bearing a substituent at C-4 can modify (compound **8**) and even invert (compounds **5a** and **6**) the trend imposed by C-5 on the π-facial selectivity, the *syn*-adducts becoming the favoured ones.

3. Experimental

Melting points are uncorrected. Microanalyses were performed with a Perkin–Elmer 2400 CHN analyser. IR spectra were recorded on Perkin–Elmer model 681 and FT 1600 grating spectrophotometers, ν values are in cm^{-1}. ^1H and ^{13}C NMR spectra were determined with Bruker AC-200 and AC-300 spectrometers, in $CDCl_3$ solution. Chemical shifts were reported in ppm (δ) downfield from Me_4Si. Silica gel Merck 60 (230–400 mesh) was used for flash column chromatography. Optical rotation was measured with a Perkin–Elmer model 241 polarimeter at room temperature in the solvent and concentration indicated in each case [g/100 mL]. X-Ray structure was refined by full-matrix least-squares (Sheldrich, G. M., SHELXL96, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, 1996) on F^2. All non-hydrogen atoms were refined anisotropically.

3.1. Oxidation of (5S)-5-(l-menthyloxy)-4-phenylthiofuran-2(5H)-one **9**

Method A: To a stirred solution of (5*S*)-5-(*l*-menthyloxy)-4-(phenylthio)furan-2(5*H*)-one (**9**, 3 g, 8.65 mmol) in dry dichloromethane (150 mL) was added dropwise (1 h) a solution of *m*-CPBA (1.7 g, 90% purity, 8.7 mmol) in dry dichloromethane (250 mL) at −78°C. The mixture was warmed to −10°C and allowed to stand for 3 h, and then washed with saturated aqueous sodium bicarbonate to pH 7. The aqueous layer was extracted several times with dichloromethane. The combined organic layers were dried and the solvent evaporated to dryness. The signals corresponding to three new products **5a** (58%), **5b** (11%) and **6** (8%) and those of the starting material (23%) were observed by ^1H NMR of the crude reaction. The residue was purified by flash chromatography (hexane/dichloromethane, 1:1) to afford, in decreasing order of R_f, compounds **5a**+**5b**, **6** and **9** in 65, 8 and 19% yields, respectively. The pure sulfoxide **5a** was isolated in 46% yield from a solution of a **5a**+**5b** mixture in xylene by precipitation with hexane. An analytical sample of **5b** was obtained by cooling a solution of epimers (**5b**/**5a**>1) in xylene at −33°C.

Method B: To a stirred solution of (5*S*)- or (5*R*)-5-(*l*-menthyloxy)-4-(phenylthio)furan-2(5*H*)-one (150 mg, 0.43 mmol) in dry dichloromethane (6 mL) was added a solution of *m*-CPBA (275 mg, 90% purity, 1.4 mmol) in dry dichloromethane (20 mL) at room temperature. The mixture was allowed to stand for 3 h, and then washed with saturated aqueous sodium bicarbonate to pH 7. The aqueous layer was extracted several times with dichloromethane. The combined organic layers were dried and the solvent evaporated to dryness to afford the sulfone **6** or **8** in quantitative yield.

3.1.1. (5S,SS)-5-(l-Menthyloxy)-4-(phenylsulfinyl)furan-2(5H)-one **5a**

46% Yield. Crystallised from ethyl acetate–hexane (white solid), mp 147–149°C. $[\alpha]_D^{20}=+176$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{20}H_{26}O_4S$: C, 66.27; H, 7.23; S, 8.85. Found: C, 66.28; H, 7.01; S, 9.02. IR (Nujol): 1790, 1760, 1615, 1050. ^{1}H NMR: 7.75–7.54 (m, 5H), 6.22 (d, 1H, *J* 1.1), 5.96 (d, 1H, *J* 1.1), 3.60 (dt, 1H, *J* 10.7 and 4.3), 2.30–0.78 (18H). ^{13}C NMR: 169.7, 166.8, 140.4, 132.8, 129.7, 126.0, 123.5, 102.2, 83.8, 47.9, 42.0, 33.8, 31.5, 25.1, 22.6, 22.0, 21.0, 15.7.

3.1.2. (5S,SS)-5-(l-Menthyloxy)-4-(phenylsulfinyl)furan-2(5H)-one **5b**

6% Yield. Crystallised from ethyl acetate–hexane (white solid), mp 165–167°C. $[\alpha]_D^{20}=-142$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{20}H_{26}O_4S$: C, 66.27; H, 7.23; S, 8.85. Found: C, 66.12; H, 7.12; S, 8.66. IR (KBr): 1799, 1764, 1616, 1050. ^{1}H NMR: 7.75–7.50 (m, 5H), 6.81 (d, 1H, *J* 1.1), 5.38 (d, 1H, *J* 1.1), 3.36 (dt, 1H, *J* 10.2 and 4.7), 2.20–0.65 (18H). ^{13}C NMR: 172.1, 166.6, 140.5, 133.1, 130.2, 126.0, 123.5, 101.4, 83.2, 47.8, 42.1, 33.7, 31.5, 25.0, 22.6, 22.0, 21.0, 16.0.

3.1.3. (5S)-5-(l-Menthyloxy)-4-(phenylsulfonyl)furan-2(5H)-one **6**

95% Yield. Crystallised from ethyl acetate–hexane (white solid), mp 79–80°C. $[\alpha]_D^{20}=+39.4$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{20}H_{26}O_5S$: C, 63.47; H, 6.92; S, 8.47. Found: C, 63.09; H, 6.60; S, 8.17. IR ($CHCl_3$): 1795, 1765, 1585, 1330, 1165, 1130. ^{1}H NMR: 7.92 (m, 2H), 7.72 (m, 1H), 7.64 (m, 2H), 6.61 (d, 1H, *J* 0.8), 6.19 (d, 1H, *J* 0.8), 3.57 (dt, 1H, *J* 10.5 and 4.4), 2.30–0.75 (18H). ^{13}C NMR: 166.2, 161.8, 138.0, 134.9, 129.4, 128.4, 102.0, 83.4, 48.1, 42.0, 33.8, 31.6, 24.5, 22.6, 22.1, 21.1, 15.7.

3.1.4. (5R)-5-(l-Menthyloxy)-4-(phenylsulfonyl)furan-2(5H)-one **8**

95% Yield. $[\alpha]_D^{20}=-124.2$ ($c=1.05$, CH_2Cl_2). ^{1}H NMR: 7.93 (m, 2H), 7.71 (m, 1H), 7.58 (m, 2H), 6.76 (d, 1H, *J* 0.9), 6.28 (d, 1H, *J* 0.9), 3.55 (dt, 1H, *J* 10.6 and 4.1), 2.25–0.57 (18H). ^{13}C NMR: 166.3, 162.2, 138.0, 134.8, 129.2, 128.9, 97.8, 79.4, 47.7, 39.1, 34.1, 31.3, 25.1, 23.1, 22.2, 20.5, 15.6.

3.2. Diels–Alder reactions of sulfoxide **5a** *with cyclopentadiene*

Method A: To a solution of furanone **5a** (350 mg, 0.96 mmol) in dichloromethane (6 mL), cyclopentadiene (383 mg, 5.79 mmol) was added. The mixture was kept at room temperature for 24 h. Then the solvent was removed in vacuo and the resulting residue analysed by ^{1}H NMR and purified by chromatography on silica gel. The first flash chromatography (ether/hexane, 2:3) afforded pure *endo*-**11***syn* (88 mg, 0.21 mmol, 21% yield) and a mixture of *exo*-**11***syn* and *endo*-**11***anti*. The latter compounds were isolated diastereoisomerically pure by a second column chromatography (ether/hexane/dichlorometane, 1:9:3): *exo*-**11***syn* (41%), *endo*-**12***anti* (26%). 88% combined yield.

Method B: To a stirred solution of $ZnBr_2$ (140 mg, 0.62 mmol) in 0.5 mL of THF was added at room temperature to a solution of **5a** (100 mg, 0.27 mmol) in dichloromethane (2 mL). The mixture was stirred for 1 h and then cyclopentadiene (91 mg, 1.38 mmol) was added and stirring was continued for 5 h. Water was added to the reaction mixture and the aqueous layer was extracted several times with dichloromethane. The combined organic layers were dried over dry magnesium sulfate and the solvent removed in vacuo. The resulting residue was analysed by ^{1}H NMR (Table 1) and purified by chromatography on silica gel following the above procedure.

3.2.1. Adduct-exo-***11***syn*

42% (Method B) and 41% (method A) yield. Crystallised from ethyl acetate–hexane (white solid), mp 154–156°C. $[\alpha]_D^{20}=+213$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_4S$: C, 70.06; H, 7.53; S, 7.48. Found: C, 70.03; H, 7.42; S, 7.50. IR (Nujol): 1765, 1650, 1080, 1050. ^{1}H NMR: 7.54 (m, 5H), 6.70 (dd, 1H, *J* 5.6 and 2.9), 6.54 (dd, 1H, *J* 5.6 and 3.1), 5.80 (s, 1H), 3.69 (m, 1H), 3.55 (dt, 1H, *J* 10.6 and 4.4), 3.36 (m, 1H), 2.42 (m, 1H), 2.40–2.00 (m, 2H), 1.95 (m, 1H), 1.80 (m, 1H), 1.75–0.85 (16H). ^{13}C NMR: 172.6, 139.9, 139.4, 138.0, 131.9, 129.4, 125.0, 102.0, 82.6, 78.7, 52.8, 48.0, 47.8, 47.5, 46.9, 42.1, 34.0, 31.4, 25.2, 22.4, 22.0, 21.1, 15.7.

3.2.2. Adduct-endo-***11***syn*

21% (Method A) and 17% (method B) yield. Crystallised from ethyl acetate–hexane (white solid), mp 169–171°C. $[\alpha]_D^{20}=+97.4$ ($c=0.50$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_4S$: C, 70.06; H, 7.53; S, 7.48. Found: C, 69.77; H, 7.45; S, 7.62. IR (Nujol): 1775, 1760, 1085, 1055. ^{1}H NMR: 7.70–7.53 (m, 5H), 6.43 (dd, 1H, *J* 5.5 and 3.1), 6.17 (dd, 1H, *J* 5.5 and 3.1), 5.66 (s, 1H), 3.60 (m, 1H), 3.50 (dt, 1H, *J* 10.6 and 4.3), 3.31 (m, 1H), 3.07 (d, 1H, *J* 4.8), 2.40–0.84 (m, 20H). ^{13}C NMR: 172.6, 139.4, 138.4, 134.1, 132.3, 129.6, 125.4, 102.1, 82.3, 77.5, 52.5, 50.2, 48.7, 48.1, 45.7, 42.0, 34.1, 31.4, 25.3, 22.6, 22.1, 21.2, 15.8.

3.2.3. Adduct-endo-***11***anti*

26% (Method A) and 17% (method B) yield. Crystallised from ethyl acetate–hexane (white solid), mp 175–176°C. $[\alpha]_D^{20}=-12$ ($c=0.45$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_4S$: C, 70.06; H, 7.53; S, 7.48. Found: C, 69.67; H, 7.34; S, 7.45. IR ($CHCl_3$): 1760, 1070, 1040. ^{1}H NMR: 7.82 (m, 2H), 7.50 (m, 3H), 6.42 (m, 2H), 5.27 (s, 1H), 3.59 (m, 1H), 3.50 (dt, 1H, *J* 10.7 and 4.3), 3.11 (m, 1H), 2.82 (d, 1H, *J* 4.7), 2.50–2.10 (m, 3H), 1.75–0.82 (m, 17H).^{13}C NMR: 174.3, 143.0, 140.8, 137.2, 131.1, 129.3, 125.2, 107.4, 85.2, 77.5, 53.6, 51.5, 50.2, 48.4, 44.0, 42.5, 33.9, 31.7, 25.4, 22.6, 22.0, 21.1, 15.7.

*3.3. Diels–Alder reaction of sulfone **6** with cyclopentadiene*

To a solution of furanone **6** (250 mg, 0.66 mmol) in dichloromethane (4 mL), cyclopentadiene (174 mg, 2.64 mmol) was added. The mixture was kept at room temperature for 1 h. The solvent was removed in vacuo. ^{1}H NMR analysis of the crude reaction showed the presence of adducts *exo*-**12***syn*, *exo*-**12***anti*, *endo*-**12***syn* and *endo*-**12***anti* in a 50:4:22:24 ratio. By flash chromatography (ethyl acetate/hexane, 5:1) a mixture of adducts was obtained in 94% yield. All attempts to separate the adducts by column chromatography on silica gel or crystallisation were unsuccessful.

3.3.1. Oxidation of sulfinyl adducts

To a stirred solution of the adducts: *exo*-**11***syn*, *endo*-**11***syn*, *endo*-**11***anti* (0.31 mmol) in dry dichloromethane (3 mL) was added dropwise a solution of *m*-CPBA (62 mg, of 90% purity) in dry dichloromethane (3 mL) at −78°C. The mixture was warmed to −33°C and allowed to stand for the time indicated in Table 2, and then washed with saturated aqueous sodium bicarbonate to pH 7. The aqueous layer was extracted several times with dichloromethane. The combined organic layers were dried and the solvent evaporated to dryness. The compounds obtained from *exo*-**11***syn* and *endo*-**11***syn* were isolated by column chromatography (ether/hexane/dichlorometane, 1:4:1).

Table 2
Oxidation of the sulfinyl adducts

Adduct	Time (h)	Products (%)[a]	Yield (%)[b]
Exo-**11***syn*	72	*Exo*-**12***syn* (94): epoxide (6)	**12** (78): epoxide (6)
Endo-**11***syn*	96	*Endo*-**12***syn* (92): epoxide (8)	**12** (76): epoxide (8)
Endo-**11***anti*	24	*Endo*-**12***anti* (100)	**12** (92)

[a] Determined by ^{1}H NMR from the crude reaction mixture.
[b] Of pure products.

3.3.2. *Adduct*-exo-***12***syn

78% Yield, from oxidation of sulfinyl adduct *exo*-**11***syn* (ether/hexane/dichloromethane, 1:4:1). White solid, mp 146–147°C. $[\alpha]_D^{20}=+106$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_5S$: C, 67.54; H, 7.25; S, 7.21. Found: C, 67.66; H, 7.16; S, 7.16. IR (Nujol): 1780, 1325, 1315, 1150, 1140. ^{1}H NMR: 7.86 (m, 2H), 7.75–7.55 (m, 3H), 6.36 (m, 2H), 6.07 (s, 1H), 3.39 (m, 1H), 3.30–3.23 (m, 2H), 3.18 (d, 1H, *J* 1.5), 2.20–0.45 (m, 20H). ^{13}C NMR: 172.8, 137.7, 137.0, 136.6, 134.5, 129.6, 129.1, 103.3, 82.5, 81.5, 52.5, 48.8, 48.2, 47.9, 47.6, 42.0, 33.8, 31.4, 25.0, 22.6, 22.0, 21.0, 15.7.

3.3.3. *Adduct*-endo-***12***syn

76% Yield, from oxidation of sulfinyl adduct *endo*-**11***syn* (ether/hexane/dichloromethane, 1:4:1). White solid, mp 136–138°C. $[\alpha]_D^{20}=+3.8$ ($c=0.50$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_5S$: C, 67.54; H, 7.25; S, 7.21. Found: C, 67.63; H, 7.28; S, 7.03. IR (KBr): 1772, 1320, 1175, 1148. ^{1}H NMR: 7.95 (m, 2H), 7.75–7.60 (m, 3H), 6.36 (dd, 1H, *J* 5.4 and 2.9), 6.23 (dd, 1H, *J* 5.4 and 3.0), 5.97 (s, 1H), 3.78 (d, 1H, *J* 4.7), 3.37 (m, 2H), 3.23 (dt, 1H, *J* 10.6 and 4.3), 2.40 (m, 1H), 2.10–0.55 (m, 19H). ^{13}C NMR: 172.5, 139.8, 136.8, 135.3, 134.7, 129.7, 129.6, 103.1, 82.8, 81.8, 52.6, 50.5, 49.5, 48.1, 45.6, 41.7, 33.9, 31.4, 25.1, 22.7, 22.1, 21.2, 15.9.

3.3.4. *Adduct*-endo-***12***anti

92% Yield, from oxidation of *endo*-**11***anti*. Crystallised from ethyl acetate–hexane (white solid), mp 147–148°C. $[\alpha]_D^{20}=+58.4$ ($c=0.50$, $CHCl_3$). Anal. calcd for: $C_{25}H_{32}O_5S$: C, 67.54; H, 7.25; S, 7.21. Found: C, 67.70; H, 7.19; S, 7.12. IR (Nujol): 1780, 1320, 1305, 1190, 1150. ^{1}H NMR: 7.93 (m, 2H), 7.70–7.45 (m, 3H), 6.51 (dd, 1H, *J* 5.6 and 3.0), 6.35 (dd, 1H, *J* 5.6 and 3.3), 5.09 (s, 1H), 4.06 (d, 1H, *J* 4.4), 3.81 (m, 1H), 3.47 (m, 1H), 3.20 (dt, 1H, *J* 10.8 and 4.4), 2.87 (m, 1H), 1.90–0.60 (m, 19H). ^{13}C NMR: 173.1, 141.4, 140.4, 137.7, 133.4, 129.9, 128.4, 106.0, 82.3, 81.3, 54.0, 52.0, 50.2, 48.3, 46.3, 42.0, 33.9, 31.6, 24.6, 22.5, 21.9, 21.2, 15.7.

3.3.5. *Epoxide of adduct*-exo-***12***syn

Isolated by chromatography (ether/hexane/dichlorometane, 1:4:1). Yield 6%. Crystallised from ethyl acetate–hexane (white solid), mp 198–199°C. $[\alpha]_D^{20}=+58.6$ ($c=1$, $CHCl_3$). Anal. calcd $C_{25}H_{32}O_6S$: C, 65.19; H, 7.00; S, 6.96. Found: C, 65.03; H, 6.85; S, 6.48. IR (KBr): 1782, 1374, 1324, 1191, 1143. ^{1}H NMR: 7.91 (m, 2H), 7.75–7.62 (m, 3H), 5.79 (s, 1H), 3.93 (d, 1H, *J* 3.5), 3.53 (d, 1H, *J* 3.5), 3.36 (d, 1H, *J* 2), 3.11 (dt, 1H, *J* 10.6 and *J* 4.4), 3.04 (m, 2H), 2.06–0.36 (m, 20H). ^{13}C NMR: 172.8, 136.4, 134.9, 129.9, 128.9, 103.8, 82.9, 80.7, 50.5, 49.8, 48.7, 47.8, 43.7, 42.3, 41.9, 33.7, 31.4, 25.1, 24.9, 22.6, 22.0, 21.0, 15.6.

3.3.6. Epoxide of adduct-endo-***12***syn

Isolated by chromatography (ether/hexane/dichlorometane, 1:4:1). Yield 8%. Crystallised from ethyl acetate–hexane (white solid), mp 117–119°C. $[\alpha]_D^{20}=+24.7$ ($c=0.70$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_6S$: C, 65.19; H, 7.00; S, 6.96. Found: C, 65.04; H, 6.70; S, 6.53. IR (KBr): 1776, 1368, 1312, 1224, 1152. ^{1}H NMR: 7.91 (m, 2H), 7.80–7.62 (m, 3H), 6.12 (s, 1H), 3.92 (d, 1H, *J* 3.6), 3.65 (d, 1H, *J* 5.4), 3.36 (d, 1H, *J* 3.6), 3.31 (dt, 1H, *J* 10.6 and 4.3), 3.10 (m, 1H), 3.01 (m, 1H), 2.12–0.55 (m, 20H). ^{13}C NMR: 170.8, 136.2, 135.0, 129.9, 129.8, 103.4, 83.5, 81.1, 50.9, 48.7, 48.4, 48.2, 44.8, 41.8, 40.1, 33.9, 31.5, 26.7, 25.3, 22.8, 22.1, 21.3, 16.0.

*3.4. (5*S*)-5-(-*l*-Menthyloxy)furan-2(5*H*)-one* ***7****: desulfinylation of (5*S*)-5-(-*l*-menthyloxy)-4-(phenylsulfinyl)furan-2(5*H*)-one* ***5a***

To a solution of **5a** (300 mg, 0.83 mmol) in THF (15 mL) at −78°C, under an argon atmosphere, DIBALH (1.25 mL of 1.0 M in hexane, 1.25 mmol) was added dropwise and the mixture was further stirred for 30 min at the same temperature. Then ethanol (2 mL), ethyl acetate (10 mL) and a sodium/potassium tartrate solution (5 mL) were added and the mixture was stirred for 15 min. The aqueous layer was extracted with ethyl acetate and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude mixture was analysed by ^{1}H NMR (**7**/**9** = 67:33) and the products were separated by column chromatography (hexane/ethyl acetate, 10:1).

*3.4.1. (5*S*)-5-(-*l*-Menthyloxy)furan-2(5*H*)-one* ***7***

54% Yield. ^{1}H NMR: 7.19 (dd, 1H, *J* 5.7 and 1.3), 6.21 (dd, 1H, *J* 5.7 and 1.3), 5.95 (t, 1H, *J* 1.3), 3.52 (dt, 1H, *J* 10.6 and 4.4), 2.25 (m, 1H), 2.12 (m, 1H), 1.66 (m, 2H), 1.56–1.25 (m, 2H), 1.12–0.79 (m, 12H).

*3.5. Diels–Alder reaction of (5*S*)-5-(-*l*-menthyloxy)furan-2(5*H*)-one* ***7*** *with cyclopentadiene*

To a solution of furanone **7** (94 mg, 0.39 mmol) in dichloromethane (2.5 mL), cyclopentadiene (103 mg, 1.56 mmol) was added. The mixture was kept at room temperature under inert atmosphere for 12 days. The solvent was removed in vacuo. ^{1}H NMR analysis showed the presence of *endo*-**13***anti*, *exo*-**13***anti* and **7** in a 85:7:8 ratio. The residue was purified by flash chromatography (hexane/ethyl acetate, 14:1) to afford, in decreasing order of R_f, compounds *exo*-**13***anti* and *endo*-**13***anti* in 5 and 77% yields, respectively.

3.5.1. Adduct-endo-***13***anti

77% Yield. White solid, mp 62–63°C. $[\alpha]_D^{20}=+11.9$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.99; H, 9.33. IR (KBr): 1757, 1358, 1180, 1118. ^{1}H NMR: 6.24 (dd, 1H, *J* 5.7 and 2.8), 6.18 (dd, 1H, *J* 5.7 and 2.9), 4.92 (d, 1H, *J* 1.7), 3.31 (m, 3H), 3.16 (m, 1H), 2.95 (ddd, 1H, *J* 8.5, 4.3 and 1.7), 2.16–2.03 (m, 2H), 1.65–1.57 (m, 3H), 1.45–1.17 (m, 3H), 1.02–0.78 (m, 12H). ^{13}C NMR: 177.4, 136.5, 134.2, 107.6, 82.3, 51.9, 48.6, 48.2, 47.9, 45.5, 44.8, 42.7, 34.1, 31.6, 25.9, 23.3, 22.0, 20.9 and 16.3.

3.5.2. Adduct-exo-***13***anti

5% Yield. Colourless oil. ^{1}H NMR: 6.21 (m, 2H), 5.17 (d, 1H, *J* 1.8), 3.40 (dt, 1H, *J* 10.7 and 4.4), 3.24 (m, 1H), 2.96 (m, 1H), 2.74 (dt, 1H, *J* 8.0 and 1.4), 2.36 (m, 1H), 2.23–2.05 (m, 2H), 1.63 (m, 2H), 1.50 (m, 1H), 1.37–1.21 (m, 3H), 1.08–0.80 (m, 12H).

3.6. Diels–Alder reaction of (5R)-5-(-l-menthyloxy)-4-(phenylsulfonyl)furan-2(5H)-one **8** with cyclopentadiene

To a solution of furanone **8** (850 mg, 2.25 mmol) in dichloromethane (15 mL), cyclopentadiene (594 mg, 9 mmol) was added. The mixture was kept at room temperature under an inert atmosphere for 5 h. The solvent was removed in vacuo. ^{1}H NMR analysis showed the presence of *endo*-**14***anti*, *exo*-**14***anti*, *exo*-**14***syn* and *endo*-**14***syn* in a 65:13:18:4 ratio. The residue was purified by flash chromatography (hexane/ethyl acetate, 8:1) to afford, in decreasing order of R_f, compounds *exo*-**14***syn*+*endo*-**14***syn*, *endo*-**14***anti* and *exo*-**14***anti* in 22, 61 and 8%, respectively. An analytical sample of *exo*-**14***syn* was obtained by precipitation with ethyl acetate–hexane.

3.6.1. *Adduct*-endo-***14***anti

61% Yield. White solid, mp 57–58°C. $[\alpha]_D^{20}=-137.4$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_5S$: C, 67.54; H, 7.25; S, 7.21. Found: C, 67.70; H, 7.23; S, 6.93. IR (KBr): 1777, 1308, 1146. ^{1}H NMR: 7.92 (m, 2H), 7.60 (m, 1H), 7.49 (m, 2H), 6.48 (dd, 1H, *J* 5.5 and 2.9), 6.43 (dd, 1H, *J* 5.5 and 3.2), 5.05 (s, 1H), 4.00 (d, 1H, *J* 4.4), 3.84 (m, 1H), 3.48 (m, 1H), 3.22 (dt, 1H, *J* 10.9 and 4.2), 2.84 (m, 1H), 1.74 (m, 2H), 1.56 (m, 3H), 1.27–0.55 (m, 14H). ^{13}C NMR: 173.3, 141.9, 140.8, 137.0, 133.2, 129.6, 128.4, 102.4, 80.8, 80.6, 53.6, 51.6, 50.7, 47.2, 46.6, 39.4, 34.1, 31.3, 24.4, 22.5, 22.0, 21.0, 14.9.

3.6.2. *Adduct*-exo-***14***anti

8% Yield. White solid, mp 66–67°C. $[\alpha]_D^{20}=-46.6$ ($c=1$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_5S$: C, 67.54; H, 7.25; S, 7.21. Found: C, 67.27; H, 7.02; S, 7.02. IR (KBr): 1773, 1316, 1149. ^{1}H NMR: 7.79 (m, 2H), 7.59 (m, 1H), 7.50 (m, 2H), 6.50 (dd, 1H, *J* 5.6 and 2.9), 6.40 (dd, 1H, *J* 5.6 and 3.2), 5.30 (s, 1H), 3.43 (m, 2H), 3.37 (m, 1H), 3.30 (dt, 1H, *J* 10.8 and 4.3), 1.77–1.56 (m, 6H), 1.24 (m, 1H), 1.05 (m, 1H), 0.93–0.63 (m, 11H), 0.50 (m, 1H). ^{13}C NMR: 172.6, 142.2, 135.7, 133.0, 128.8, 128.5, 104.5, 81.3, 80.3, 53.1, 51.3, 48.8, 47.2, 46.5, 39.4, 34.1, 31.3, 24.4, 22.6, 22.0, 21.1, 15.0.

3.6.3. *Adduct*-exo-***14***syn

White solid, mp 168–170°C. $[\alpha]_D^{20}=-190.8$ ($c=0.5$, $CHCl_3$). Anal. calcd for $C_{25}H_{32}O_5S$: C, 67.54; H, 7.25; S, 7.21. Found: C, 67.31; H, 7.17; S, 7.19. IR (KBr): 1774, 1321, 1152, 1122. ^{1}H NMR: 7.89 (m, 2H), 7.73 (m, 1H), 7.62 (m, 2H), 6.40 (m, 1H), 6.12 (s, 1H), 3.44 (m, 2H), 3.26 (m, 1H), 3.23 (m, 1H), 1.94 (m, 2H), 1.60 (m, 4H), 1.26 (m, 1H), 1.10–0.67 (m, 12H), 0.28 (m, 1H). ^{13}C NMR: 172.7, 137.6, 137.2, 136.7, 134.4, 129.5, 129.2, 100.1, 80.6, 79.0, 52.9, 48.7, 48.3, 47.8, 47.7, 39.1, 33.9, 31.1, 25.3, 22.4, 22.1, 21.0, 15.1.

3.6.4. *Adduct*-endo-***14***syn

^{1}H NMR: 7.95 (m, 2H), 6.30 (dd, 1H, *J* 5.5 and 3.2), 6.23 (dd, 1H, *J* 5.5 and 3.0), 5.96 (s, 1H), 3.92 (d, 1H, *J* 4.7), 2.53 (m, 1H), 0.66 (d, 3H, *J* 6.9), 0.34 (m, 1H) (the remaining signals were not included because they overlap with the signals of the adduct-*exo*-**14***syn*).

Acknowledgements

We thank Dirección General de Investigación Científica y Técnica (grant PB98-0078) for financial support.

References

1. (a) Bertrand, S.; Hoffmann, N.; Pete, J.-P. *Eur. J. Org. Chem.* **2000**, 2227; (b) Van Oeveren, A.; Jansen, J. F. G. A.; Feringa, B. L. *J. Org. Chem.* **1994**, *59*, 5999; (c) Pelter, P.; Ward, R. S.; Qianrong, L.; Pis, J. *Tetrahedron*: *Asymmetry* **1994**, *5*, 909.
2. Feringa, B. L.; de Jong, J. C. *J. Org. Chem.* **1988**, *53*, 1125.
3. (a) de Jong, J. C.; Jansen, J. F. G. A; Feringa, B. L. *Tetrahedron Lett.* **1990**, *31*, 3047; (b) de Jong, J. C.; Feringa, B. L. *Tetrahedron Lett.* **1989**, *30*, 7239.
4. de Jong, J. C.; van Bolhuis, F.; Feringa, B. L. *Tetrahedron*: *Asymmetry* **1991**, *2*, 1247.
5. (a) de Lange, B.; Feringa, B. L. *Tetrahedron Lett.* **1988**, *29*, 5317; (b) Rispens, T. M.; Keller, E.; de Lange, B.; Zijlstra, W. J.; Feringa, B. L. *Tetrahedron*: *Asymmetry* **1994**, *5*, 607.
6. de Jong, J. C.; van den Berg, K. J.; van Leusen, M.; Feringa, B. L. *Tetrahedron Lett.* **1991**, *32*, 7751.
7. (a) Carreño, M. C. *Chem. Rev.* **1995**, *95*, 1717; (b) Cid, M. B.; García Ruano, J. L. In *Topics in Current Chemistry*. *Organosulfur Chemistry*; Page, P. C. B., Ed.; Springer: Berlin, 1999; p. 1.
8. Carretero, J. C.; García Ruano, J. L.; Martín, M. L. *Tetrahedron*: *Asymmetry* **1997**, *53*, 14115.
9. Carretero, J. C.; García Ruano, J. L.; Lorente, A.; Yuste, F. *Tetrahedron*: *Asymmetry* **1993**, *4*, 177.
10. Martín, M. R.; Mateo, A. I. *Tetrahedron*: *Asymmetry* **1994**, *5*, 1385.