High-Pressure-Promoted Diels–Alder Reactions between Cycloalkenones and 3-Methylsulfanylfuran and 3-Phenylsulfanylfuran

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3-Methylsulfanylfuran and 3-phenylsulfanylfuran were found to undergo facile, regioselective and stereoselective Diels–Alder (DA) cycloaddition to a variety of cycloalkenones under high pressure to give the corresponding ring-annulated 7-oxabicyclo[2.2.1]heptene derivatives in good yields. The vinyl sulfide groups in the adducts were oxidized to relatively stable vinylsulfones, which were utilized for synthetic transformations such as further DA cycloadditions and epoxidation.

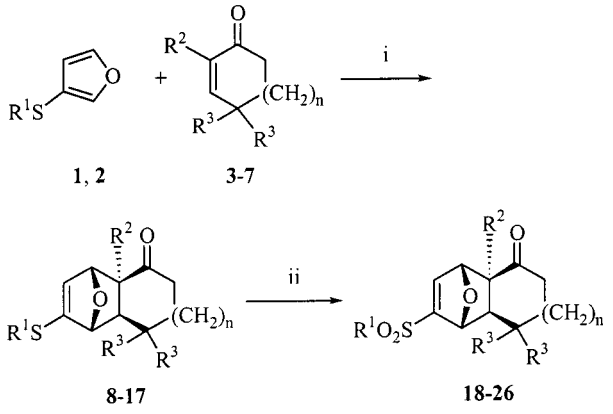
Introduction

The Diels–Alder (DA) reaction between cycloalkenones and dienes is a straightforward method for the construction of polycyclic molecules, which can be promising precursors for natural product synthesis.[1] As cycloalkenones are poorly reactive dienophiles, their DA reaction needs activation by Lewis acids and/or high pressure.[2,3] We became interested in taking advantage of furans as dienes in DA cycloadditions with cycloalkenones in order to provide an easy route to ring-annulated 7-oxabicyclo[2.2.1]heptanes, which might be exploited as precursors in terpene and steroid synthesis. DA reactions between simple furans and even reactive dienophiles already need activation by Lewis acid catalysis or high pressure due to the aromatic nature of furan.[4] Even under high-pressure conditions, however, furan does not react with cyclopentenone, the most reactive of the cycloalkenones. In the presence of Lewis acids, open products are formed.[5] In fact, there are only a very few reports on DA reactions between activated cycloalkenones and furan derivatives in the literature.[4,6] We reasoned that the diene reactivity of the furan reaction component might be enhanced by a strategic placing of electron-donating 3-methylsulfanyl or 3-phenylsulfanyl groups on it.[7] Furthermore, in the cycloadduct these groups can easily be transformed into vinylsulfones by oxidation. As the sulfone group is electron-withdrawing, the alkene reactivity in the adduct for further transformations becomes greatly enhanced. With this in mind, we have studied DA reactions between various cycloalkenones and either 3-methylsulfanylfuran (**1**) or 3-phenylsulfanylfuran (**2**). The DA reactions of both **1** and **2** were evaluated in terms of adduct stability and their further synthetic potential.

Results and Discussion

High-Pressure-Promoted DA Reaction of 3-Methylsulfanylfuran (1) and 3-Phenylsulfanylfuran (2)

The DA cycloaddition of furan derivatives **1** and **2** with cycloalkenones **3**–**7** under 11–15 kbar pressure (50 °C) furnished cycloadducts **8**–**17** in moderate to excellent yields (Scheme 1). As the cycloadducts were found to be thermally labile and generally unstable, they were oxidized to the corresponding more stable sulfones **18**–**26**. The results obtained in this study are presented in Table 1.



Scheme 1. Reagents and conditions: (i) 11–15 kbar, 50 °C; (ii) *m*CPBA, CH_2Cl_2, 20 °C, 15 min to 1 h; **1**: R^1 = Me; **2**: R^1 = Ph; **3**: n = 0, R^2 = R^3 = H; **4**: n = 1, R^2 = R^3 = H; **5**: n = 2, R^2 = R^3 = H; **6**: n = 1, R^2 = H, R^3 = Me; **7**: n = 0, R^2 = Me, R^3 = H; **8**, **18**: R^1 = Me, R^2 = R^3 = H, n = 0; **9**, **19**: R^1 = Me, R^2 = R^3 = H, n = 1; **10**, **20**: R^1 = Me, R^2 = R^3 = H, n = 2; **11**, **21**: R^1 = Ph, R^2 = R^3 = H, n = 0; **12**, **22**: R^1 = Ph, R^2 = R^3 = H, n = 1; **13**, **23**: R^1 = Ph, R^2 = R^3 = H, n = 2; **14**, **24**: R^1 = Me, R^2 = H, R^3 = Me, n = 1; **15**: R^1 = Ph, R^2 = H, R^3 = Me, n = 1; **16**, **25**: R^1 = Me, R^2 = Me, R^3 = H, n = 0; **17**, **26**: R^1 = Ph, R^2 = Me, R^3 = H, n = 0

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Table 1. Cycloaddition of 3-methylsulfanylfuran and 3-phenylsulfanylfuran to cycloalkenones and subsequent oxidation to vinylsulfones

Entry	Furan	Cycloalkenone	Conditions (50 °C)	Sulfide Yield (%)	Sulfone Yield (%)
1	**1**	**3**	11 kbar, 8 h	**8** (95)	**18** (91)
2	**1**	**4**	11 kbar, 15 h	**9** (90)	**19** (95)
3	**1**	**5**	13 kbar, 18 h	**10** (80)	**20** (90)
4	**2**	**3**	15 kbar, 24 h	**11** (81)	**21** (55)
5	**2**	**4**	15 kbar, 48 h	**12** (68)[a]	**22** (43)
6	**2**	**5**	15 kbar, 48 h	**13** (50)[a]	**23** (68)
7	**1**	**6**	15 kbar, 48 h	**14** (45)	**24** (98)
8	**2**	**6**	15 kbar, 72 h	**15**; no reaction	–
9	**1**	**7**	15 kbar, 48 h	**16** (60)	**25** (98)
10	**2**	**7**	15 kbar, 72 h	**17** (4)	**26** (65)

[a] Yield based on recovered starting material; 23% transformation for $n = 1$ and 33% transformation for $n = 2$.

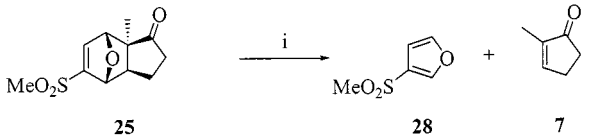
The DA cycloaddition reaction between furan **1** and 2-cyclopentenone (**3**) took place readily at 11 kbar pressure and 50 °C to furnish the regio- and stereospecific adduct **8** in 95% yield (entry 1, Table 1). The ^{1}H NMR spectrum of **8** showed characteristic singlets at $\delta = 4.71$ and $\delta = 5.08$, representing the bridgehead protons, while the olefinic proton appeared as a broad singlet at $\delta = 5.77$. The ^{13}C NMR spectrum showed ten carbon resonances in which the bridgehead carbons were located at $\delta = 84.09$ and $\delta = 88.34$. The regiochemistry of the cycloaddition was also ascertained from 2D NOESY and COLCOC NMR experiments. The NOESY spectrum revealed the steric proximity of the *endo* proton adjacent to the carbonyl group to the olefinic proton. When the cycloaddition was conducted at room temp. and 11 kbar, the reaction was slower (48 h) and, surprisingly, analysis of the reaction mixture revealed the exclusive formation of the *exo* cycloadduct. At lower pressures (8 kbar) the reaction was sluggish, whereas at higher pressures (15 kbar) the yield of the product was lower, due to polymerization. We examined several solvents, such as dichloromethane, chloroform, pentane, acetonitrile, acetone, THF, and toluene, as media for conducting the reaction. Consistent results were obtained when the reaction of **1** was conducted in freshly distilled dry toluene as solvent. The purity of **1** was also found to be very important for its smooth transformation into an adduct, with the presence of impurities resulting either in extensive decomposition or in the formation of conjugate addition products. Moreover, adduct **8** was found to be unstable at room temp., as it reverted to starting materials on standing. It was therefore quantitatively oxidized to the more stable vinyl sulfone **18** with *m*-chloroperbenzoic acid (*m*CPBA) (entry 1, Table 1). The ^{1}H NMR spectrum of the vinyl sulfone **18** revealed an expected downfield shift of the olefinic proton signal, now positioned at $\delta = 7.15$. DA reactions between **1** and other simple cycloalkenones, such as cyclohexenone (**4**) and cycloheptenone (**5**), also took place readily under high-pressure conditions, to furnish the corresponding adducts **9** and **10**, which on further oxidation with *m*CPBA were transformed quantitatively into vinylsulfones **19** and **20** (entry 2, 3; Table 1).

The reactivity of 3-phenylsulfanylfuran **2** towards cycloaddition was found to be lower than that of its methylsulfanyl analogue **1**. Treatment of **1** with 2-cyclopentenone (**3**), for example, required higher pressure and longer reaction times for completion. However, similarly to what was observed in the cycloaddition reaction of **1**, this reaction also regio- and stereoselectively furnished the *exo* adduct **11** (entry 4, Table 1). Cycloadditions of 2-cyclohexenone (**3**) and 2-cycloheptenone (**4**) to furan derivative **2** were found to be difficult, even under 15 kbar pressure. Substantial amounts of **2** were recovered unreacted even after 48 h of compression (see Exp. Sect.). Furthermore, oxidation of the vinyl sulfides **11**–**13** to the corresponding vinylsulfones **21**–**23** was also found to be difficult. A variety of oxidizing agents, such as ozone, *m*CPBA, monomethoxyperphthalic acid (MMPA), and hydrogen peroxide, were tried for this purpose. Controlled oxidation was achieved with *m*CPBA when the reaction was performed at 20 °C over 15 min. Prolonged reaction times resulted in epoxidation of the vinyl sulfone moiety and further oxidative cleavage of the carbonyl group. When the reaction was conducted at 0 °C, the corresponding diastereomeric mixture of sulfoxides was isolated as the major product.

Treatment of 3-methylsulfanylfuran (**1**) with 4,4-dimethylcyclohexenone (**6**) at 15 kbar and 50 °C resulted in the *exo* cycloadduct **14** in moderate yield. The presence of the sterically demanding *gem* dimethyl group is obviously responsible for the lower yield in this reaction. Further oxidation of the vinyl sulfide moiety in **14** produced vinyl sulfone **24** in excellent yield. The geminal dimethyl group on the cyclohexane ring in **24** can readily be recognized as a structural motif in several terpenoid natural products. Under the reaction conditions employed, 3-phenylsulfanylfuran (**2**) did not react with cycloalkenone **6** to give adduct **15**.

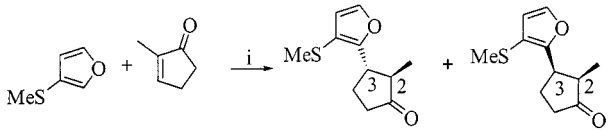
The cycloaddition between 2-methyl-2-cyclopentenone (**7**) and furan derivatives **1** or **2** permits the regioselective construction of CD rings of steroid-type systems, although a *cis* ring junction is also formed in the process. Treatment of 3-methylsulfanylfuran (**1**) with 2-methyl-2-cyclopentenone (**7**) proceeded smoothly at 15 kbar and 50 °C to furnish cycloadduct **16** in 60% yield; this compound was further transformed to vinyl sulfone **25**. However, we found that the sulfone **25** is not very stable at room temp. and slowly undergoes a retro-DA reaction to give 3-methylsulfonylfuran (**28**) and 2-methyl-2-cyclopentenone (**7**; Scheme 2). The retro-DA transformation at 65 °C was complete within 1 h. Interestingly, when the cycloaddition reaction between **1** and cycloalkenone **7** was conducted in the presence of a catalytic amount of zinc iodide, in dichloromethane as solvent, a diastereomeric mixture of conjugate addition products **29** and **30** was formed regioselectively, in a ratio of 80:20. The former compound was isolated and characterized (Scheme 3). These results again illustrate that Lewis acid catalysis is no alternative for the use of high pressure in DA reactions of **1** and **2** with cycloalkenones. The ^{1}H NMR spectrum of **29** revealed a doublet for the

methyl group at δ = 1.07. The C^3-H appeared as a triplet of doublets, with coupling constants of 12.3 Hz and 6.1 Hz, representing two equal diaxial and one axial–equatorial coupling, thus indicating a *trans* stereochemistry for the C^2 and C^3 substituents. The regiochemistry of the furan ring substituents was ascertained from NOESY contacts between the aromatic protons.



25 **28** **7**

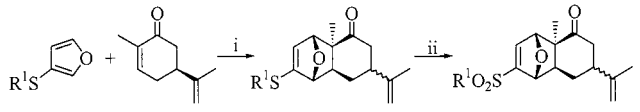
Scheme 2. Conditions: i. $CDCl_3$, 65 °C, 1 h



1 **7** **29** **30**

Scheme 3. Reagents and conditions: i. cat. ZnI_2, CH_2Cl_2, 15 kbar, 50 °C, 48 h

High-pressure-mediated cycloaddition reactions between **1** and **2** and D-(+)-carvone **27** were studied next in order to examine the cycloaddition potential of the 2-methyl-2-cyclohexenone moiety and also possible chiral induction from the isopropenyl group. Treatment of 3-methylsulfanylfuran (**1**) with carvone at 15 kbar and 50 °C gave a diastereomeric mixture of cycloaddition products **31** in 23% yield (Scheme 4). Although this reaction displayed high regioselectivity and *exo* stereoselectivity in the cycloaddition step, remote diastereoselectivity from the isopropenyl group was absent. The adducts were oxidized to the corresponding sulfones **32** in quantitative yield. The furan derivative **2** did not undergo cycloaddition with carvone **27** even after 72 h at 15 kbar and 50 °C, which reflects its lower reactivity.



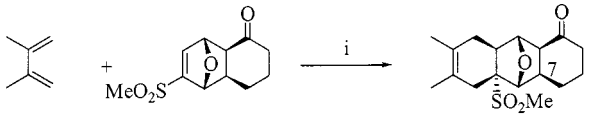
1, 2 **27** **31** **32**

Scheme 4. **1**, **31**, **32**: R^1 = Me; **2**: R^1 = Ph. – Conditions: i. 15 kbar, 50 °C, 48 h; ii. *m*CPBA, CH_2Cl_2, 20 °C, 1 h

The regioselectivity in all the cycloadditions is in accordance with predictions based on FMO theory.[8] The strongly donating *S*-alkyl or *S*-phenyl groups put the highest HOMO coefficient in the furan at C-2, whereas the highest LUMO coefficients in the cycloalkenones are at the β-carbon of the enone function.

Further DA Reactions of Vinylsulfone Adducts

Oxidation of a vinylsulfide moiety to a vinylsulfone converts the double bond from an electron-rich group to an electron-deficient one. The vinylsulfones generated in this step are well suited for such synthetic applications as further cycloadditions and conjugate addition reactions. We have examined their DA reactivity as dienophiles with a few dienes. The electron-rich 2,3-dimethylbutadiene (**33**) added to vinyl sulfone **19** exclusively from the *exo* face, both under high pressure conditions (15 kbar) at room temp. and in refluxing toluene, to produce the tetracyclic ketone **34** in good yields (Scheme 5). The stereoselectivity of the cycloaddition was deduced from an unusual downfield shift of the C^7-*endo* hydrogen, which appeared as a multiplet at δ = 3.45. The C^7-H most probably forms a hydrogen bond with a sulfone oxygen, by way of a six-membered cyclic structure.

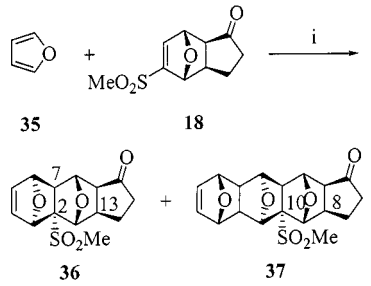


33 **19** **34**

Scheme 5. Conditions: i. 15 kbar, room temp., 24 h; or toluene reflux, 18 h

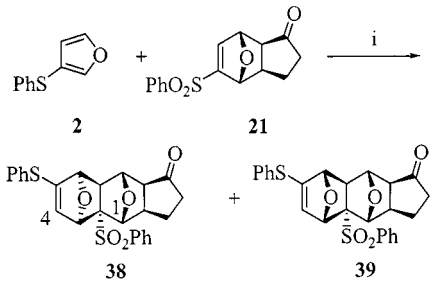
The treatment of sulfone **18** with an excess of furan under high-pressure conditions (13 kbar, 50 °C) yielded two major products after chromatographic purification: the *exo-anti* adduct **36** and the *exo-anti-anti* adduct **37** in an 8:1 ratio, formed by addition of one and two furan units to **18**, respectively (Scheme 6). The ^1H NMR spectrum of the major product **36** showed four signals in the range δ = 4.6–5.1 for the bridgehead protons. C^{13}-H appeared as a multiplet at δ = 3.7 indicating an *exo* addition of furan. The ^{13}C NMR spectrum of **36** showed four signals at δ = 83–86, corresponding to four bridgehead carbons. Cycloadducts and domino cycloadducts such as these have previously been reported in high-pressure-mediated DA reactions between furan and reactive dienophiles.[9] As in earlier findings, C^7-H appeared as a doublet at δ = 2.60 with a coupling constant of 8.5 Hz, indicating an *anti* positioning of the bridgehead oxygens. The ^1H NMR spectrum of the *exo-anti-anti* adduct **37** showed six bridgehead proton signals in the range δ = 4.3–4.9. The ^{13}C NMR spectrum of **37** also showed six signals between δ = 78 and 84 for the bridgehead carbons. The ^1H NMR spectrum of the crude product indicated the presence of other bis, tris and tetrakis adducts; however, we were not able to isolate them in pure form. When the cycloaddition between sulfone **18** and furan was attempted in 1,2-dichloroethane under reflux conditions, only the retro-DA product 3-methylsulfonylfuran **28** was obtained from the reaction.

The treatment of 3-phenylsulfanylfuran (**2**) with sulfone **21** was attempted next in order to determine the regio- and stereoselectivity in the domino-DA cycloaddition reaction. This reaction at 15 kbar pressure resulted in the formation of two diastereomeric adducts **38** and **39**, in 3:2 ratio and 93% yield (Scheme 7). The ^1H NMR spectrum of the major product **38** showed four signals for the bridgehead protons between δ = 4.3 and 4.9. The NOESY spectrum showed



Scheme 6. Conditions: i. 13 kbar, 50 °C, 36 h

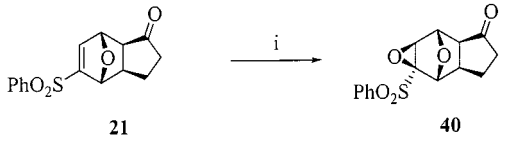
steric contacts between the bridgehead C^1-H and the olefinic C^4-H, which showed that the product had *anti* stereochemistry for the bridgehead oxygen atoms. As in earlier cases, the C^{13}-H of **38** appeared downfield, at δ = 3.93, revealing hydrogen-bonding interactions with the sulfonyl oxygen atom and also the *exo* nature of the cycloaddition. The stereochemistry of the adduct **39** was similarly deduced from its spectroscopic data (see Exp. Sect.).



Scheme 7. Conditions: i. 15 kbar, 50 °C, 18 h

Stereoselective Epoxidation of Vinyl Sulfone Adducts

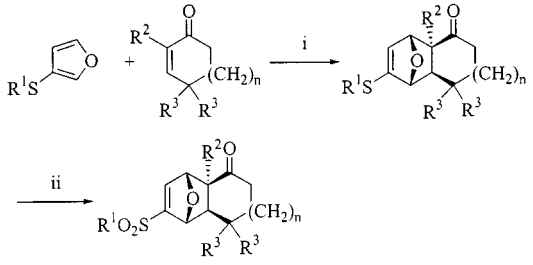
Having established a simple methodology for the production of highly functionalized, ring-annulated, 7-oxabicyclo[2.2.1]heptane-derived vinyl sulfones, we focused our attention on further functionalization of the carbon−carbon double bond. In a preliminary study, vinylsulfone **21** was treated with *m*CPBA to provide the *exo* epoxide **40** in quantitative yield (Scheme 8). Under the conditions employed, no Baeyer−Villiger oxidation product was observed. It was recently shown that epoxysulfones incorporated in 7-oxabicyclo[2.2.1]heptane skeletons are useful starting materials for base-induced rearrangement reactions.[10] In addition, the epoxide could be further transformed into synthetically useful intermediates by opening with various nucleophiles.



Scheme 8. Reagents and conditions: i. *m*CPBA, CH_2Cl_2, 20 °C, 4 h

Conclusions

In conclusion, we have shown that a variety of simple and alkyl-substituted cycloalkenones undergo facile cycloaddition reactions with 3-methylsulfanylfuran (**1**) and, to a lesser extent, with 3-phenylsulfanylfuran (**2**) under high-pressure mediation to furnish ring-annulated 7-oxabicyclo[2.2.1]heptane adducts in good yields (Scheme 9). Although adducts from **2** were found to be more difficult to obtain, they were also found to be more stable than adducts derived from **1**. The application of high pressure appeared to be essential in this study, because only conjugate addition products were formed in the reaction in the presence of Lewis acids. The selective oxidation of the vinyl sulfide moiety in the adduct resulted in stable vinyl sulfones. The vinyl sulfones were shown to be good synthons for further synthetic manipulations such as DA cycloadditions, and epoxidation. We are currently exploiting these products for the synthesis of *cis*-hydrindanone and *cis*-decalone systems, the results of which will be reported in due course.



Scheme 9. Reagents and conditions: i. 11−15 kbar, 50 °C; ii. *m*CPBA, CH_2Cl_2, 20 °C, 15 min to 1 h

Experimental Section

General: The FTIR spectra were recorded on a Genesis Series Mattson instrument. − The ^{1}H NMR, ^{13}C NMR, and DEPT spectra were recorded using a Bruker AM 300 (300 MHz and 75 MHz) spectrometer in $CDCl_3$ solutions. The 2D NOESY spectra were recorded on a Bruker AM 400 (400 MHz) spectrometer. Chemical shift values are reported as δ values in parts per million (ppm) relative to tetramethylsilane as an internal standard. − Mass spectra were determined using a double focusing VG 7070E spectrometer. − Melting points were measured on a Reichert Thermopan microscope and are uncorrected. − All reactions were monitored for completion by thin layer chromatography (TLC), which was performed using glass-baked silica gel ($60F_{254}$) plates and detection was achieved with the aid of UV light, iodine vapour, anisaldehyde spray, or basic potassium permanganate solution. − Column chromatography was performed using Baker silica gel (70−230 mesh) with heptane/ethyl acetate solvent mixtures. − 3-Methylsulfanylfuran,[11] 3-phenylsulfanylfuran,[10] and 4,4-dimethylcyclohexenone[12] were prepared according to literature procedures and were distilled under reduced pressure prior to use. For consistent results, 3-methylsulfanylfuran was dried as a toluene azeotrope before distillation under reduced pressure (73 °C/80 mm) immediately before subjection to high-pressure-mediated cycloaddition reactions. The other cycloalkenones used in this study were procured from commercial sources. The solvents were distilled prior to use. − The high-pressure apparatus used in this study has been described be-

fore.[13] Reactions were carried out in sealed 1.5 mL, 2.5 mL, or 7.5 mL Teflon vessels.

General Procedure for the Cycloaddition of 3-Methylsulfanylfuran or 3-Phenylsulfanylfuran with Cycloalkenones and Subsequent Oxidation to Sulfones

Compound 18: Cyclopentenone **3** (1.07 g, 13.05 mmol) was added to 3-methylsulfanylfuran (**1**) (1.19 g, 10.43 mmol) in a 7.5 mL Teflon vessel and mixed well. The resulting solution was diluted with distilled toluene (5.5 mL) until the vessel was full and then closed tightly with a cap. The vessel was pressurized at 11 kbar and 50 °C for 8 h. After the release of pressure, the progress of the reaction was checked by TLC. Anisaldehyde spray gave a diagnostic violet coloration for the product, turning black on standing. After concentration of the reaction mixture at reduced pressure below 30 °C, it was subjected to rapid column chromatography on silica gel, eluting with heptane/ethyl acetate (5:1) solvent mixtures. Concentration of the pooled fractions produced 1.94 g (95%) of compound **8** as a colourless oil. − IR (neat): $\tilde{\nu}$ = 2954, 2939, 1733, 1560, 1173, 1139, 1013, 909, 889 cm^{-1}. − ^1H NMR: δ = 1.85−2.00 (m, 1 H), 2.15−2.70 (m, 5 H), 2.28 (s, 3 H), 4.71 (s, 1 H), 5.08 (s, 1 H), 5.77 (br. s, 1 H). − ^{13}C NMR: δ = 15.21, 24.90, 40.15, 42.19, 56.45, 84.09, 88.34, 123.68, 148.99, 217.95. The vinyl sulfide **8** was immediately subjected to oxidation with *m*CPBA, as it was found that the adduct was slowly undergoing a retro-DA reaction on standing. Potassium carbonate (1.34 g, 9.7 mmol) was added to the stirred solution of the adduct **8** (1.9 g, 9.7 mmol) in 25 mL dichloromethane at 20 °C, followed by freshly purified *m*CPBA (3.68 g, 21.3 mmol) in five portions over 5 min. The reaction mixture was stirred for 1 h, by which time the reaction was complete (TLC; anisaldehyde spray gave light brown spots for the sulfone and basic $KMnO_4$ spray gave yellow spots). The reaction mixture was diluted with 25 mL dichloromethane and stirred with 50 mL water for 30 min. The aqueous phase was separated and then extracted with dichloromethane (2 × 20 mL). The combined organic fractions were washed with saturated sodium bicarbonate solution (2 × 20 mL) and brine (2 × 20 mL), and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure to yield 2.01 g (91%) of sulfone **18**, which was purified by recrystallization from ethyl acetate and heptane; m.p. 132 °C. − IR (neat): $\tilde{\nu}$ = 3004, 2973, 2932, 2921, 1740, 15.92, 1300, 1142, 1085, 1004, 901, 760 cm^{-1}. − ^1H NMR: δ = 1.85−2.10 (m, 1 H), 2.20−2.37 (m, 1 H), 2.45−2.60 (m, 3 H), 2.28−2.92 (m, 1 H), 3.09 (s, 3 H), 5.14 (s, 1 H), 5.26 (br. s, 1 H), 7.15 (br. s, 1 H). − ^{13}C NMR: δ = 24.49, 40.58, 42.61 (2 × C), 52.49, 83.79, 85.13, 144.97, 150.78, 215.31. − MS (EI): *m*/*z* (%) = 228 (0.3) [M^+], 147, 131 (100), 115, 83 etc. − HRMS calcd. for $C_{10}H_{12}O_4S$: 196.05580; found 196.05563.

Compound 19: Treatment of 3-methylsulfanylfuran **1** (138 mg, 1.21 mmol) with cyclohexenone **4** (145 mg, 1.51 mmol) in toluene (1.1 mL), following the general procedure described above, in a 2.5 mL Teflon reaction vessel at 11 kbar and 50 °C for 15 h, produced 208 mg (90%) of cycloadduct **9**, which on oxidation with *m*CPBA (450 mg) furnished 227 mg (95%)of sulfone **19**.

Compound 9: Viscous oil. − IR (neat): $\tilde{\nu}$ = 2937, 1710, 1554, 1220, 1005, 925, 875 cm^{-1}. − ^1H NMR: δ = 1.30−1.45 (m, 1 H), 1.65−1.80 (m, 1 H), 1.90−2.00 (m, 1 H), 2.05−2.20 (m, 1 H), 2.25−2.45 (m, 4 H), 2.28 (s, 3 H), 4.52 (s, 1 H), 5.30 (br. s, 1 H), 5.78 (d, *J* = 1.8 Hz, 1 H). − ^{13}C NMR: δ = 15.23, 20.54, 28.11, 39.28, 39.67, 52.41, 83.38, 85.97, 123.03, 147.27, 212.27.

Compound 19: M.p.: 151 °C. − IR (KBr): $\tilde{\nu}$ = 3030, 2923, 2852, 1706, 1292, 1137, 1081, 767 cm^{-1}. − ^1H NMR: δ = 1.20−1.40 (m, 1 H), 1.70−1.85 (m, 1 H), 1.90−2.05 (m, 1 H), 2.20−2.40 (m, 3 H), 2.40−2.60 (m, 2 H), 3.08 (s, 3 H), 4.95 (s, 1 H), 5.54 (br. s, 1 H), 7.15 (d, *J* = 1.8 Hz, 1 H). − ^{13}C NMR: δ = 20.39, 27.67, 38.86, 40.15, 42.69, 48.26, 82.81 (2×C), 144.24, 149.08, 210.18. − MS (EI): *m*/*z* (%) = 242 (0.6) [M^+], 147, 131, 115 (110), 96, 83 etc. − HRMS calcd. for $C_{11}H_{14}O_4S$: 242.06128; found 242.06107.

Compound 20: Treatment of 3-methylsulfanylfuran **1** (390 mg, 3.42 mmol) with cycloheptenone **5** (470 mg, 4.27 mmol) in toluene (0.5 mL), following the general procedure, in a 2.5 mL Teflon reaction vessel at 13 kbar, and 50 °C for 18 h, produced the crude adduct **10**, which was subjected, without further purification, to oxidation with *m*CPBA (1.18 g, 6.84) in the presence of potassium carbonate (472 mg) to furnish 630 mg (90%) of the sulfone **20**. M.p.: 195 °C. − IR (KBr): $\tilde{\nu}$ = 3016, 3005, 2936, 2858, 1697, 1593, 1453, 1297, 1138, 1091, 1065, 973 cm^{-1}. − ^1H NMR: δ = 1.20−1.40 (m, 1 H), 1.55−1.70 (m, 2 H), 1.75−2.0 (m, 2 H), 2.05−2.24 (m,1 H), 2.25−2.40 (m, 1 H), 2.42−2.44 (m, 2 H), 2.79 (d, *J* = 8.7 Hz, 1 H), 3.08 (s, 3 H), 4.82 (s, 1 H), 5.56 (br. s, 1 H), 7.26 (d, 1.2 Hz, 1 H). − ^{13}C NMR: δ = 23.47, 26.42, 30.23, 40.39, 42.67, 43.96, 53.26, 80.26, 83.95, 145.20, 150.32, 209.42. − MS (EI): *m*/*z* (%) = 256 (3.7) [M^+], 227, 176, 159, 146, 131, 110 (100), 81, 66 etc. − HRMS calcd. for $C_{12}H_{16}O_4S$: 256.07693; found 256.07688.

Compound 21: Treatment of 3-phenylsulfanylfuran **2** (129 mg, 0.73 mmol) with cyclopentenone **3** (120 mg, 1.4 mmol) in THF (about 1.5 mL), following the general procedure described above, in a 2.5 mL Teflon reaction vessel at 15 kbar and 50 °C for 24 h, produced 153 mg (81%) of cycloadduct **11**, which on controlled oxidation with *m*CPBA (450 mg) after 15 min at 20 °C and further purification by column chromatography furnished 95 mg (55%)of the sulfone **21**.

Compound 11: Viscous oil. − IR (neat): $\tilde{\nu}$ = 3138, 3120, 3056, 1742, 1583, 1477, 1439, 1191, 1141, 1010, 868, 702, 689 cm^{-1}. − ^1H NMR: δ = 1.80−1.86 (m, 1 H), 2.10−2.30 (m, 5 H), 4.64 (s, 1 H), 5.08 (s, 1 H), 6.13 (br. s, 1 H), 7.20−7.40 (m, 5 H). − ^{13}C NMR: δ = 24.56, 40.09, 41.65, 55.74, 84.07, 87.48, 127.57, 129.22, 130.77, 132.05, 132.52, 144.61, 217.30.

Compound 21: M.p.: 128 °C. − IR (neat): $\tilde{\nu}$ = 3083, 3068, 2973, 2950, 1724, 1585, 1444, 1307, 1153, 1105, 1076, 1010, 857 cm^{-1}. − ^1H NMR: δ = 1.80−1.95 (m, 1 H), 2.20−2.55 (m, 4 H), 2.75−2.90 (m, 1 H), 4.92 (s, 1 H), 5.12 (br. s, 1 H), 7.07 (d, *J* = 1.7 Hz, 1 H), 7.55−7.61 (m, 2 H), 7.66−7.72 (m, 1 H), 7.91−7.96 (m, 2 H). − ^{13}C NMR: δ = 24.60, 40.61, 42.62, 52.98, 83.79, 85.29, 127.87, 129.57, 134.15, 139.11, 143.94, 151.72, 215.59. − MS (EI): *m*/*z* (%) = 290 (0.4) [M^+], 208, 149, 125, 115 (100), 115, 83, 77 etc. − HRMS calcd. for $C_{15}H_{14}O_4S$: 290.06128; found 290.06147.

Compound 22: Treatment of 3-phenylsulfanylfuran **2** (133 mg, 0.75 mmol) with cyclohexenone **4** (145 mg, 1.5 mmol) in THF (about 0.5 mL), following the general procedure described above, in a 1.5 mL Teflon reaction vessel at 15 kbar and 50 °C for 48 h, produced crude product **12**, which was purified by column chromatography; yield: 48 mg (23%); recovered 3-phenylsulfanylfuran: 87 mg. Controlled oxidation (15 min, 20 °C) of the adduct **12** (19 mg, 0.07 mmol) with *m*CPBA (24 mg, 0.14 mmol) in the presence of potassium carbonate (19.3 mg, 0.14 mmol) and further purification of the product by column chromatography furnished 9 mg (43%) of the sulfone **22**.

Compound 12: Viscous oil. − IR (neat): $\tilde{\nu}$ 3010, 2935, 1700, 1590, 1581, 1560, 1477, 1438, 1174, 1022, 900, 736 cm^{-1}. − ^1H NMR: δ = 1.20−2.50 (m, 8 H), 4.48 (s, 1 H), 5.35 (br. s, 1 H), 6.17 (d, *J* = 1.7 Hz, 1 H), 7.28−7.42 (m, 5 H). − ^{13}C NMR: δ = 20.45,

27.98, 39.16, 39.20, 51.74, 83.44, 85.23, 127.59, 129.32, 130.90, 131.73, 132.86, 142.80, 211.90. − MS (EI): *m/z* (%) = 272 (19) [M$^+$], 215, 177 (100), 148, 115, 96, 77 etc.

Compound 22: M.p.: 139 °C. − IR (KBr): $\tilde{\nu}$ = 3081, 2956, 2873, 1700, 1585, 1446, 1313, 1151, 1101, 1020 cm^{-1}. − ^{1}H NMR: δ = 1.25−1.35 (m, 1 H), 1.05−1.72 (m, 1 H), 1.90−2.00 (m, 1 H), 2.15−2.55 (m, 5 H), 4.73 (s, 1 H), 5.47 (s, 1 H), 7.08 (s, 1 H), 7.55−7.61 (m, 2 H), 7.62−7.68 (m, 1 H), 7.90−7.96 (m, 2 H). − ^{13}C NMR: δ = 20.40, 2771, 38.89, 40.13, 48.74, 82.12, 82.90, 127.83, 129.54, 134.05, 139.22, 143.12, 149.90, 210.31. − MS (EI): *m/z* (%) = 304 (0.3) [M$^+$], 147, 131, 115 (100), 96, 83 etc. − HRMS calcd. for $C_{16}H_{16}O_4S$: 304.07692; found 304.07681.

Compound 23: High-pressure treatment of 3-phenylsulfanylfuran **2** (88 mg, 0.5 mmol) with cycloheptenone **5** (110 mg, 1 mmol) in THF (0.7 mL), following the general procedure described above, in a 1.5 mL Teflon reaction vessel at 15 kbar and 50 °C for 48 h, produced crude product **13**, which was purified by column chromatography; yield: 48 mg (33%); recovered 3-phenylsulfanylfuran: 28 mg. Controlled oxidation (15 min) of the adduct (42 mg, 0.15 mmol) with *m*CPBA (52 mg, 0.3 mmol) in the presence of potassium carbonate (41 mg, 0.3 mmol) and further purification of the product by column chromatography furnished 35 mg (68%)of the sulfone **23**.

Compound 13: M.p.: 107−108 °C. − IR (KBr): $\tilde{\nu}$ = 3014, 2923, 2848, 1697, 1558, 1475, 1440, 1359, 1234, 1155 cm^{-1}. − ^{1}H NMR: δ = 1.20−1.35 (m, 2 H), 1.55−1.70 (m, 2 H), 1.75−1.95 (m, 2 H), 2.05−2.15 (m, 1 H), 2.4−2.5 (m, 2 H) 2.75 (d, *J* = 8.0 Hz, 1 H), 4.36 (s, 1 H), 5.39 (s, 1 H), 6.15 (s, 1 H), 7.2−7.4 (m, 5 H). − ^{13}C NMR: δ = 23.59, 26.61, 30.45, 39.92, 42.88, 56.59, 80.05, 85.88, 127.51, 129.78, 130.69, 131.98, 132.88, 143.63, 210.87.

Compound 23: M.p.: 163 °C. − IR (KBr): $\tilde{\nu}$ = 3015, 1714, 1587, 1448, 1307, 1153, 1105, 1076 cm^{-1}. − ^{1}H NMR: δ = 1.20−1.60 (m, 1 H), 1.50−1.70 (m, 2 H), 1.75−2.00 (m, 2 H), 2.02−2.20 (m,1 H), 2.25−2.35 (m, 1 H), 2.40−2.50 (m, 2 H), 2.79 (d, *J* = 8.7 Hz, 1 H), 4.60 (s, 1 H), 5.50 (br. s, 1 H), 7.11 (d, 1.2 Hz, 1 H), 7.55−7.61 (m, 2 H), 7.63−7.68 (m, 1 H), 7.89−7.95 (m, 2 H). − ^{13}C NMR: δ = 23.52, 26.52, 30.32, 40.47, 42.98, 53.79, 80.15, 84.00, 127.81, 129.52, 134.04, 139.22, 144.00, 151.11, 209.45. − MS (EI): *m/z* (%) = 318 (0.8) [M$^+$], 221, 208, 125, 115, 110 (100), 81 etc. − HRMS calcd. for $C_{17}H_{18}O_4S$: 318.09256; found 318.09237.

Compound 24: Treatment of 3-methylsulfanylfuran **1** (245 mg, 2.15 mmol) with 4,4-dimethyl-2-cyclohexenone **6** (333 mg, 2.68 mmol) in toluene (0.5 mL), following the general procedure described above, in a 2.5 mL Teflon reaction vessel at 15 kbar and 50 °C for 48 h, produced 230 mg (45%) of cycloadduct **14**. Oxidation of 67 mg (0.29 mmol) of the adduct with *m*CPBA (121.5 mg, 0.7 mmol) furnished 75 mg (98%)of the sulfone **24**.

Compound 14: IR (KBr): $\tilde{\nu}$ = 2954, 2920, 2868, 1705, 1692, 1561, 1468, 1313, 1211, 1024, 905 cm^{-1}. − ^{1}H NMR: δ = 0.98 (s, 3 H), 1.05 (s, 3 H), 1.56−1.63 (m, 1 H), 1.77−1.89 (m, 2 H), 2.28 (s, 3 H), 2.32−2.40 (m, 3 H),4.73 (s, 1 H), 5.20 (br. s, 1 H), 5.76 (d, *J* = 1.8 Hz, 1 H). − ^{13}C NMR: δ = 14.13, 24.31, 28.68, 30.72, 32.12, 34.42, 50.04, 51.16, 81.15, 81.90, 122.22, 147.75, 212.28. − MS (EI): *m/z* (%) = 238 [M$^+$], 223, 171, 115 (100), 124 etc.

Compound 24: M.p.: 123 °C. − IR (KBr): $\tilde{\nu}$ = 3109, 2957, 2923, 2872, 1700, 1590, 1469, 1409, 1372, 1304, 1215, 1142, 1090, 976 cm^{-1}. − ^{1}H NMR: δ = 0.86 (s, 3 H), 1.09 (s, 3 H), 1.70 (t, *J* = 7.5 Hz, 2 H), 2.17 (d, *J* = 9.1 Hz, 1 H), 2.33 (d, *J* = 9.2 Hz, 1 H), 2.37 (m, 2 H), 3.04 (s, 3 H), 5.09 (s, 1 H), 5.47 (br. s, 1 H), 7.01 (d, *J* = 1.8 Hz, 1 H). − ^{13}C NMR: δ = 22.89, 30.16, 31.83, 33.96, 35.38, 42.73, 47.32, 50.42, 79.51, 81.40, 144.40, 150.23, 210.99. − MS (EI): *m/z* (%) = 270 (0.5) [M$^+$], 214, 159, 146, 131, 124, 96 (100), 82, 67 etc. − HRMS calcd. for $C_{13}H_{18}O_4S$: 270.09258; found 270.09239.

Compound 25: Treatment of 3-methylsulfanylfuran **1** (532 mg, 4.66 mmol) with 2-methyl-2-cycloptenone **7** (560 mg, 5.83 mmol) in toluene (0.5 mL), following the general procedure, in a 2.5 mL Teflon reaction vessel at 15 kbar and 50 °C for 48 h, produced the crude adduct **16**, which was subjected without further purification to oxidation with *m*CPBA (1.61 g, 9.3 mmol) in the presence of potassium carbonate (645 mg, 4.67 mmol) to furnish 580 mg (60%) of sulfone **25** and 30 mg of 3-(methylsulfonyl)furan. The yield of **16** was estimated on the basis of the NMR spectrum of the crude product. The sulfone **25** was found to decompose to retro-DA products on standing. Furthermore, heating of **25** in $CDCl_3$ in a NMR tube at 65 °C resulted in quantitative generation of the retro-DA product **28**; viscous oil. − IR (neat): $\tilde{\nu}$ = 3089, 2927, 1781, 1735, 1722, 1589, 1456, 1409, 1303, 1147, 1066, 996 cm^{-1}. − ^{1}H NMR: δ = 1.08 (s, 3 H), 1.95−2.05 (m, 1 H), 2.2−2.65 (m, 4 H), 3.10 (s, 3 H), 4.94 (s, 1 H), 5.10 (s, 1 H), 7.22 (d, *J* = 1.5 Hz, 1 H). − ^{13}C NMR: δ = 18.21, 23.64, 39.80, 42.87, 49.52, 57.69, 86.60, 86.85, 145.14, 151.59, 219.51. − MS (EI): *m/z* (%) = 242 (0.3) [M$^+$], 158, 156, 146, 131, 115, 96, 83, 67 etc. − HRMS calcd. for $C_{11}H_{14}O_4S$: 242.06128; found 242.06109.

Compound 28: M.p. 136 °C. − IR (KBr): $\tilde{\nu}$ = 3139, 3018, 2926, 1549, 1498, 1304, 1221, 1151, 1133, 1080, 1010, 972, 936 cm^{-1}. − ^{1}H NMR: δ = 3.10 (s, 3 H), 6.71 (d, *J* = 2.1 Hz, 1 H), 7.52 (t, 2.1 Hz, 1 H), 8.01 (br. s, 1 H). − ^{13}C NMR: δ = 45.05, 108.32, 133.63, 144.99, 146.42. − MS (EI): *m/z* (%) = 146 (76) [M$^+$], 131 (100), 115 etc. − HRMS calcd. for $C_5H_6O_3S$: 146.00381; found 146.00369.

Compound 26: High-pressure treatment of 3-phenylsulfanylfuran **2** (352 mg, 2 mmol) with 2-methyl-2-cycloheptenone **7** (288 mg, 3 mmol) in THF (1.0 mL), following the general procedure described above, in a 2.5 mL Teflon reaction vessel at 15 kbar and 50 °C for 72 h, resulted in the crude adduct **17**, which was purified by column chromatography; yield: 20 mg (4%); recovered starting material: 232 mg. Controlled oxidation of the adduct **27** (18 mg, 0.06 mmol) over 15 min with *m*CPBA (24 mg, 0.12 mmol) in the presence of potassium carbonate (18 mg, 0.12 mmol) and further purification of the product by column chromatography furnished 13 mg (65%)of the sulfone **26**.

Compound 17: Viscous oil. − IR (neat): $\tilde{\nu}$ = 3018, 2962, 1731, 1477, 1456, 1215 cm^{-1}. − ^{1}H NMR: δ = 1.00 (s, 3 H), 1.80−1.87 (m, 1 H), 2.2−2.6 (m, 4 H), 4.63 (s, 1 H), 4.75 (br. s, 1 H), 6.17 (s, 1 H), 7.3−7.44 (m, 5 H). − ^{13}C NMR: δ = 18.26, 23.45, 39.64, 48.80, 59.62, 86.83, 89.06, 127.96, 129.44, 130.34, 131.32, 132.48, 145.89, 221.46.

Compound 26: M.p.: 70 °C. − IR (KBr): $\tilde{\nu}$ = 3076, 2957, 2877, 1735, 1583, 1440, 1307, 1152, 1098, 1073, 997 cm^{-1}. − ^{1}H NMR: δ = 1.05 (s, 3 H), 1.88−2.30 (m, 1 H), 2.20−2.35 (m, 1 H), 2.40−2.60 (m, 3 H), 4.87 (br. s, 1 H), 4.90 (s, 1 H), 7.10 (d, *J* = 1.2 Hz, 1 H), 7.59−7.65 (m, 2 H), 7.79−7.85 (m, 1 H), 7.92−7.97 (m, 2 H). − ^{13}C NMR: δ = 17.99, 23.46, 39.57, 49.31, 57.81, 86.32, 86.67, 127.92, 129.57, 134.18, 139.11, 143.70, 152.22, 219.43. − MS (EI): *m/z* (%) = 304 (1) [M$^+$], 291, 208, 179, 125, 115 (100), 96, 77 etc. − HRMS calcd. for $C_{16}H_{16}O_4S$: 304.07693; found 304.07617.

Compound 29: 2-Methyl-2-cyclopentenone **7** (145 mg, 1.5 mmol) and zinc iodide (6 mg, 2.5mol %) were added to 3-methylsulfanyl-

furan **1** (114 mg, 1 mmol) in dichloromethane (2 mL) and the resulting solution was pressurized to 15 kbar at 50 °C for 48 h. TLC of the reaction mixture after depressurization indicated the presence of two diastereomeric products, of which the faster moving component **29** was obtained in pure form by column chromatography; yield 101 mg (48%); viscous oil. − IR (KBr): $\tilde{\nu}$ = 3010, 2966, 2923, 2871, 1740, 1455, 1373, 1146 cm^{-1}. − ^1H NMR: δ = 1.04 (d, *J* = 7.02 Hz, 3 H), 2.1−2.3 (m, 3 H), 2.30 (s, 3 H), 2.40−2.60 (m, 2 H), 3.25 (td, *J* = 12.3, 6.2 Hz, 1 H), 6.42 (d, *J* = 1.7 Hz, 1 H), 7.35 (d, *J* = 1.7 Hz, 1 H). − ^{13}C NMR: δ = 12.33, 19.84, 26.59, 37.34, 41.86, 48.81, 113.89, 114.02, 141.41, 155.19, 218.66. − MS (EI): *m*/*z* (%) = 210 (100) [M^+], 195, 177, 163, 153, 139, 125, 111 etc. − HRMS calcd. for $C_{11}H_{14}O_2S$: 210.07146; found 210.07129.

Compound 32 (mixture of diastereomers): Treatment of 3-methylsulfanylfuran **1** (207 mg, 1.81 mmol) with D-(+)-carvone **27** (340 mg, 2.26 mmol) in toluene (0.5 mL), following the general procedure described above, in a 2.5 mL Teflon reaction vessel at 15 kbar and 50 °C for 48 h, produced 110 mg (23%) of a diastereomeric mixture of cycloadducts **31**. Oxidation of the adducts **31** (57 mg, 0.21 mmol) with *m*CPBA (75 mg, 0.43 mmol) in the presence of potassium carbonate (30 mg, 0.21 mmol) furnished 63 mg (98%)of a diastereomeric mixture of sulfones **32**.

Compound 31 (mixture of diastereomers): ^1H NMR: δ = 1.03 (s, 3 H), 1.04 (s, 3 H), 1.20 (dd, *J* = 18.9, 12.5 Hz, 1 H), 1.72 (s, 3 H), 1.73 (br. d, *J* = 6.3 Hz, 1 H), 1.75 (s, 3 H), 1.77 (dd, *J* = 5.7, 2.4 Hz), 1.81 (dd, *J* = 12.4, 6.9 Hz, 1 H), 1.85−1.95 (m, 1 H), 2.07−2.14 (m, 2 H), 2.16 (dd, *J* = 18.6, 11.4 Hz, 1 H), 2.31 (s, 3 H), 2.32 (s, 3 H), 2.5−2.58 (m 3 H), 2.71 (ddd, 18.6, 6.3, 2.7 Hz, 1 H), 4.38 (s, 1 H), 4.47 (s, 2 H), 4.73 (s, 1 H), 4.76 (q, *J* = 1.2 Hz), 4.79 (q, *J* = 1.2 Hz, 1 H), 5.01 (s, 1 H), 5.28 (br. s, 1 H), 5.78 (d, *J* = 1.8 Hz, 1 H), 5.81 (d, *J* = 1.8 Hz, 1 H). − ^{13}C NMR: δ = 15.32, 15.34, 20.14, 20.62, 22.58, 23.55, 32.29, 34.20, 37.30, 39.77, 42.84, 44.95, 45.78, 47.73, 55.47, 55.50, 84.43, 88.02, 88.35, 86.19, 109.85, 110.07, 120.82, 120.97, 147.20, 147.54, 147.79, 150.64, 214.0, 215.58.

Compound 32 (mixture of diastereomers): IR (KBr): $\tilde{\nu}$ = 3002, 2920, 1695, 1648, 1554, 1454, 1323, 1320, 1147, 1077, 958 cm^{-1}. − ^1H NMR: δ = 1.08 and 1.10 (s, 3 H), 1.1−1.3 (m, 1 H), 1.73 and 1.75 (s, 3 H), 1.9−2.85 (m, 5 H), 3.09 (s, 3 H), 4.75 and 4.82 (s, 2 H), 4.78 and 4.92 (s, 1 H), 5.27 and 5.52 (s, 1 H), 7.16 (s, 1 H). − ^{13}C NMR: δ = 20.13, 20.63, 21.90, 22.42, 32.07, 33.70, 37.32, 39.33, 42.25, 42.57, 42.63, 44.56, 45.81, 47.91, 52.63, 53.48, 83.31, 84.38, 85.79, 87.61, 110.39 (2 × C), 143.23, 143.93, 146.59, 146.72, 149.98, 152.24, 211.77, 213.47. − MS (EI): *m*/*z* (%) = 296 (0.01) [M^+], 150, 146, 135, 131, 115, 108, 107, 93, 82, 77, 67, 54, 34 (100) etc. − HRMS calcd. for $C_{15}H_{20}O_4S$ + H: 297.11605; found 297.11572.

Compound 34, High-Pressure Conditions: 2,3-Dimethylbutadiene **33** (113 mg, 1.37 mmol) was added to the vinyl sulfone **19** (111 mg, 0.46 mmol) in 1.5 mL dichloromethane in a 2.5 mL Teflon vessel and the resulting solution was pressurized to 15 kbar at room temp. for 24 h. After depressurization, the product was purified by column chromatography to furnish 87 mg (59%) of the adduct **34**.

Reaction under Thermal Conditions: 2,3-Dimethylbutadiene **33** (25 mg, 0.3 mmol) was added to the vinyl sulfone **19** (24 mg, 0.1 mmol) in toluene (10 mL) and the resulting solution was refluxed in an oil bath maintained at 110 °C for 18 h, by which time the reaction was complete (TLC). After removal of solvent and excess 2,3-dimethylbutadiene, the reaction mixture was purified by column chromatography to yield 31 mg (95%) of the adduct **34**; mp: 106 °C. − IR (KBr): $\tilde{\nu}$ = 2978, 2938, 2874, 1701, 1448, 1286, 1146, 1119, 913 cm^{-1}. − ^1H NMR: δ = 1.20−1.35 (m, 2 H), 1.69 (s, 3 H), 1.73 (s, 3 H), 1.90−2.1 (m, 4 H), 2.20−2.65 (m, 5 H), 2.71 (s, 3 H), 2.79 (d, *J* = 8.5 Hz, 1 H), 3.40−3.50 (m, 1 H), 4.08 (s, 1 H), 4.64 (s, 1 H). − ^{13}C NMR: δ = 18.89, 19.33, 20.29, 26.41, 33.96, 36.46, 38.07, 40.32, 41.64, 44.77, 53.78, 74.90, 88.42, 89.19, 123.94, 127.42, 211.67. − MS (EI): *m*/*z* (%) = 324 (0.5) [M^+], 246, 229, 225, 217, 208, 201, 193, 188, 167, 165 (100), 158, 149, 127, 121, 116 etc. − HRMS calcd. for $C_{17}H_{24}SO_4$: 324.13953; found: 324.13911.

Cycloaddition Reaction between Sulfone 18 and Furan 35: Freshly distilled furan (170 mg, 2.5 mmol) was added to the sulfone **18** (114 mg, 0.5 mmol) in dichloromethane (2.3 mL) and the resulting solution was pressurized to 13 kbar at 50 °C for 36 h. After depressurization, purification of the resulting product by column chromatography yielded two products, **36** and **37**, in a 1:8 ratio and 45% combined yield. This cycloaddition reaction did not take place under thermal conditions in refluxing 1,2-dichloroethane: only retro-DA reaction product 3-methylsulfonylfuran **28** was isolated.

Compound 37: Yield: 5%; faster moving component; m.p.: 233 °C. − IR (KBr): $\tilde{\nu}$ = 3005, 2936, 1736, 1458, 1406, 1288, 1224, 1016, 916 cm^{-1}. − ^1H NMR: δ = 1.60−1.66 (m, 1 H), 2.23−2.31 (m, 3 H), 2.52 (d, *J* = 8.1 Hz, 1 H), 2.62 (d, *J* = 6.8 Hz, 1 H), 2.74 (dd, *J* = 7.56, 5.1 Hz, 1 H), 2.83 (dd, *J* = 5.56, 5.1 Hz, 1 H), 2.91 (s, 3 H), 3.67 (dd, *J* = 15.1, 8.1 Hz, 1 H), 4.30 (d, *J* = 6.8 Hz, 1 H), 4.48 (s, 1 H), 4.51 (s, 1 H), 4.62 (s, 1 H), 4.86 (br. t, *J* = 5.1 Hz, 2 H), 6.27 (dd, *J* = 8.9, 1.5 Hz, 1 H), 6.30 (dd, *J* = 8.9, 1.5 Hz, 1 H). − ^{13}C NMR: δ = 24.85, 39.42, 41.78, 42.60, 45.47, 45.75, 55.30, 57.05, 78.63, 79.36, 79.53, 79.69, 81.26, 84.05, 134.36, 134.97, 217.96 (SO_2C was not found). − MS (EI): *m*/*z* (%) = 364 (5.1) [M^+], 285, 267, 239, 217, 199, 191, 171, 157, 128, 115, 68 (100) etc. − HRMS calcd. for $C_{18}H_{20}O_6S$: 364.09806; found 364.09726.

Compound 36: Yield: 40%, slower moving component; m.p.: 182 °C (dec). − IR (KBr): $\tilde{\nu}$ = 3004, 2930, 1742, 1295, 1137, 1036, 942 cm^{-1}. − ^1H NMR: δ = 1.68−1.73 (m, 1 H), 2.18−2.40 (m, 3 H), 2.44 (s, 1 H), 2.60 (d, *J* = 8.5 Hz, 1 H), 2.99 (s, 3 H), 3.68−3.75 (m, 1 H), 4.61 (s, 1 H), 4.77 (s, 1 H), 4.95 (d, *J* = 1.5 Hz, 1 H), 5.06 (br. s, 1 H), 6.50 (dd, *J* = 5.7, 1.9 Hz, 1 H), 6.71 (dd, *J* = 5.7, 1.5 Hz, 1 H). − ^{13}C NMR: δ = 24.90, 39.14, 42.53, 42.63, 52.84, 55.16, 83.52, 84.08, 84.20, 86.82, 135.15, 139.88, 217.55 (SO_2C was not found). − MS (EI): *m*/*z* (%) = 296 (0.3) [M^+], 278, 217, 199, 146, 131, 82, 68 (100) etc. − HRMS calcd. for $C_{14}H_{16}O_5S$: 296.07183; found 296.07159.

Cycloaddition Reaction between Sulfone 21 and 3-Phenylsulfanylfuran 2: Freshly purified 3-phenylsulfanylfuran **2** (52 mg, 0.3 mmol) was added to the vinylsulfone **21** (48 mg, 0.15 mmol) in dichloromethane (0.5 mL) and the resulting solution was pressurized to 15 kbar at 50 °C for 18 h. After depressurization, purification of the resulting reaction mixture by column chromatography yielded two diastereomeric products **38** and **39** in a 3:2 ratio and 93% (combined) yield.

Compound 38: Yield: 57%; faster moving component in TLC; m.p.: 113 °C. − IR (KBr): $\tilde{\nu}$ = 3058, 2991, 1735, 1581, 1475, 1444, 1249, 1209, 1168, 1081, 1022 cm^{-1}. − ^1H NMR: δ = 1.60−1.75 (m, 1 H), 2.20−2.40 (m, 3 H), 2.63 (d, *J* = 7.8 Hz, 1 H), 2.88 (d, *J* = 5.5 Hz, 1 H), 3.95 (br. q, *J* = 7.8 Hz, 1 H), 4.32 (s, 1 H), 4.55 (d, *J* = 1.2 Hz, 1 H), 4.74 (s, 1 H), 4.94 (br. s, 1 H), 6.01 (br. s, 1 H), 7.36−7.26 (m, 5 H), 7.48−7.54 (m, 2 H), 7.66−7.60 (m, 1 H), 7.85−7.90 (m, 2 H). − ^{13}C NMR: δ = 24.86, 39.46, 43.44, 52.97, 56.35, 79.71, 79.89, 82.31, 82.74, 127.62, 127.95, 128.64, 129.33, 129.85, 131.50, 131.72, 133.96, 138.61, 143.87, 218.22 (SO_2C was not found). − MS (EI): *m*/*z* (%) = 466 (0.1) [M^+], 208, 176, 147,

125, 115(100), 97, 77 etc. − HRMS calcd. for $C_{25}H_{22}O_5S_2$ + H: 467.04729; found 467.04715.

Slower Moving Component (39): Yield: 36%; m.p.: 98 °C. − IR (KBr): $\tilde{\nu}$ = 3058, 2975, 1732, 1586, 1475, 1444, 1301, 1147, 1085, 898, 748, 690 cm^{-1}. − ^1H NMR: δ = 1.60−1.70 (m, 2 H), 2.10−2.40 (m, 1 H), 2.22 (d, *J* = 9.6 Hz, 1 H), 2.48 (s, 1 H), 2.64 (d, *J* = 7.8 Hz, 1 H), 3.95 (br. q, *J* = 7.3 Hz, 1 H), 4.45 (s, 1 H), 4.57 (s, 1 H), 4.63 (s, 1 H), 5.06 (br. s, 1 H), 5.36 (br. s, 1 H), 7.32−7.40 (m, 5 H), 7.61−7.67 (m, 2 H), 7.69−7.75 (m, 1 H), 7.80−7.85 (m, 2 H). − ^{13}C NMR: δ = 24.88, 39.18, 43.46, 52.84, 55.00, 84.10, 84.40, 84.91, 87.23, 128.16, 128.54, 129.46, 129.63, 129.99, 131.44, 133.96, 134.45, 140.08, 142.38, 218.19(SO_2C was not found). − MS (EI): *m*/*z* (%) = 466 (0.05) [M^+], 208, 176, 147, 125, 115 (100), 77 etc. − HRMS calcd. for $C_{25}H_{22}O_5S_2$ + H: 467.04729; found 467.04708.

Compound 40: *m*CPBA (35 mg, 0.2 mmol) was added to the vinyl sulfone **21** (29 mg, 0.1 mmol) in dichloromethane (3 mL). The reaction mixture was stirred at 20 °C and the progress of the reaction was monitored by TLC. After completion of the reaction (4 h), a saturated bicarbonate solution (10 mL) and dichloromethane (15 mL) were added and the aqueous solution was extracted with dichloromethane (15 mL). The recombined organic phase was washed with saturated sodium bicarbonate solution (2 × 15 mL) and brine (2 × 15 mL) and the solvent was evaporated. The resulting solid (27 mg, 88) was recrystallized from a dichloromethane/heptane solvent mixture (1:15). M.p.: 196−197 °C. − IR (KBr): $\tilde{\nu}$ = 3073, 3006, 2985, 2940, 1736, 1445, 1322, 1290, 1240, 1176, 1126, 1087 cm^{-1}. − ^1H NMR: δ = 1.78−1.85 (m, 1 H), 2.3−2.4 (m, 3 H), 2.63 (d, *J* = 8.9 Hz, 1 H), 3.65−3.8 (m, 1 H, 3.94 (s, 1 H), 4.42 (s, 1 H), 4.68 (s, 1 H), 7.59−7.66 (m, 2 H), 7.71−7.77 (m, 1 H), 7.93−7.98 (m, 2 H). − ^{13}C NMR: δ = 24.84, 39.18, 43.24, 52.38, 57.96, 72.10, 78.60, 81.03, 128.77, 129.57, 136.97, 212.46. − MS (EI): *m*/*z* (%) = 306 (1.9) [M^+], 277, 211, 165, 137, 125, 109, 95, 81, 77, 55 (100) etc. − HRMS calcd. for $C_{15}H_{14}O_5S$: 306.05619; found 306.05622.

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