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First Asymmetric Cycloaddition of Carbonyl Ylides to Vinyl Sulfoxides and Furan-2(5*H*)-ones

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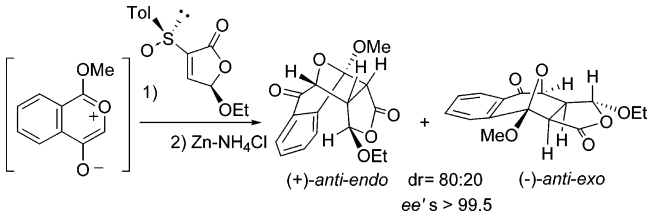

The $Rh_2(OAc)_4$-catalyzed reactions of *o*-(methoxycarbonyl)-α-diazoacetophenone with enantiomerically pure 5-ethoxy-3-*p*-tolylsulfinylfuran-2(5*H*)-ones **1a** and **1b** afford 4,10-epoxybenzo[4,5]cyclohepta[1,2-*c*]furan-3,9-diones **6a** and **6b**, in good or moderate yields and in a completely regioselective way. The *π*-facial selectivity is complete for **1a**, which only yields *anti*-**6a** adducts, and very high for **1b**. The endo stereoisomers are favored with respect to the exo ones in both reactions. The sulfinyl group significantly increases the reactivity of the dipolarophile as it has been demonstrated by studying the behavior of 5-methoxyfuran-2(5*H*)-one (**3**).

Introduction

The generation of carbonyl ylides from diazo compounds and their cycloaddition reactions has gained much attention due to their use in the construction of highly complex polycycles.[1] The main contributions to the development of these reactions in their achiral version were due to Ibata's[2] and Padwa's groups,[3] by using copper or rhodium complexes. The first example of these reactions in their chiral version was provided by Hodgson and co-workers, who reported the enantioselective intramolecular cycloaddition of unsaturated α-diazo-*β*-ketoesters, catalyzed by [Rh(*S*-DOPS)$_4$],[4] which evolved with moderate *ee* (53%). Although these results have been improved up to 90% *ee*,[5] the complete control of the stereoselectivity has not been achieved yet. Enantioselective tandem processes consisting of carbonyl ylide formation−intermolecular cycloaddition have been reported by Suga,[6] Hashimoto,[7] Hodgson,[8] and Doyle.[9] However, as is indicated by Padwa[10] and Hodgson,[8b] the asymmetric induction of these reactions is usually low,[11] providing tetrahydrofuranes with low or moderate *ee* values, which precludes the preparation of optically pure samples by using these

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(11) Some exceptions to this general behavior have been reported. Thus, Hashimoto achieved *ee* values up to 92% by using diazo ketones with DMAD as the dipolarophile (see ref 7a).

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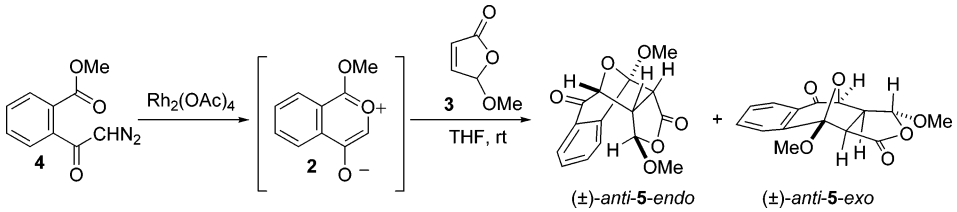
SCHEME 1. Addition of Carbonyl Ylide 2 to Furanone 3



procedures. Furthermore, it should be noted that the degree of asymmetric induction in these intermolecular cycloadditions is very sensitive to the substitution pattern of the dipole and dipolarophile.[8b] Consequently, the search of new and efficient methods giving access to these adducts in their optically pure form is nowadays an unsolved problem that deserves further investigation. In this context, the use of chiral auxiliaries could be a good solution because even if the control of the stereoselectivity is not complete, the separation of the resulting diastereoisomers would provide optically pure samples. Surprisingly, the cycloaddition of carbonyl ylides to dipolarophiles bearing chiral auxiliaries has never been reported.

The sulfinyl group has been widely and successfully used as a chiral auxiliary in Diels−Alder reactions.[12] By contrast, vinyl sulfoxides have been used as dipolarophiles only occasionally.[13] Several years ago, we initiated a program to explore the usefulness of vinyl sulfoxides in asymmetric 1,3-dipolar reactions. Their behavior in reactions with diazoalkanes,[14] nitrile oxides,[15] nitrones,[16] and azomethine ylides[17] has evidenced a strong influence of the sulfinyl group on the course of these reactions, significantly enhancing the dipolarophilic reactivity of the double bonds and playing a very important role in the control of the π-facial and endo/exo selectivities. Sulfinyl furanones have been used as dipolarophiles in many of our studies[14a−d,15a−b,16,17c] due to the interest in the resulting highly functionalized adducts. Additionally, the reported behavior of furanones with no sulfinyl group as dienophiles and dipolarophiles allowed us to make the pertinent comparisons. However, to our knowledge, the reactions of carbonyl ylides with vinyl sulfoxides or furanones have never been reported. Therefore, we decided to study the reactions of sulfinyl furanones **1a** and **1b**[18] with the carbonyl ylide **2**. We report herein the results of these reactions, which provide optically pure 4,10-epoxy[4,5]-cyclohepta[1,2-*c*]furan-3,9-diones with suitable substituents to be transformed into new highly functionalized polycyclic condensated systems with a benzoheptane moiety. To determine the role of the sulfinyl group in the course of 1,3-dipolar cycloadditions of carbonyl ylides, it was necessary to compare the results obtained from furanones **1** with those obtained in the reaction of **2** with the racemic 5-methoxyfuran-2(5*H*)-one (**3**),[19] bearing no sulfinyl group, which are also described in this paper.

Results and Discussion

Carbonyl ylide **2** was generated by $Rh_2(OAc)_4$-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**4**).[20] The reaction of **4** (1 equiv) with racemic furanone **3** (3 equiv) in THF at room temperature afforded a 3:2 mixture of *anti*-**5**-*endo*[21] and *anti*-**5**-*exo* (Scheme 1), the former adduct being the major one. The isolated yield was rather low (ca. 17%), probably due to the competitive decomposition of the dipole by different routes under the experimental conditions. It is noteworthy that the anti adducts were the only ones obtained. The predominance of the endo approach mode should also be noticed. The stereoisomers were isolated by column chromatography of the mixture. Diastereomerically pure endo and exo adducts were obtained in 10 and 7% isolated yields, respectively. To find the optimum conditions providing the highest yield and endo selectivity, other metal catalysts and solvents were investigated. The use of dichloromethane, acetonitrile, or an ionic liquid (1-*n*-butyl-3-methylimidazolium tetrafluoroborate)[22] as the solvent did not improve the result obtained with THF. The reaction crude contained, almost exclusively, 1*H*-isochromene-1,4(3*H*)-dione, which results from the hydrolysis of dipole **2**. It is noteworthy that the use of CuCl 10 mol % in THF as the catalyst, instead of $Rh_2(OAc)_4$, did not increase the endo/exo ratio (60:40), in contrast to the results reported by Ibata.[2a]

The reaction of *o*-methoxycarbonyl-α-diazoacetophenone (**4**) with enantiomerically pure sulfinyl furanone **1b** in the presence catalytic amounts of Rh(II) acetate was investigated under different experimental conditions (solvent, **4**/**1b** ratio, temper-

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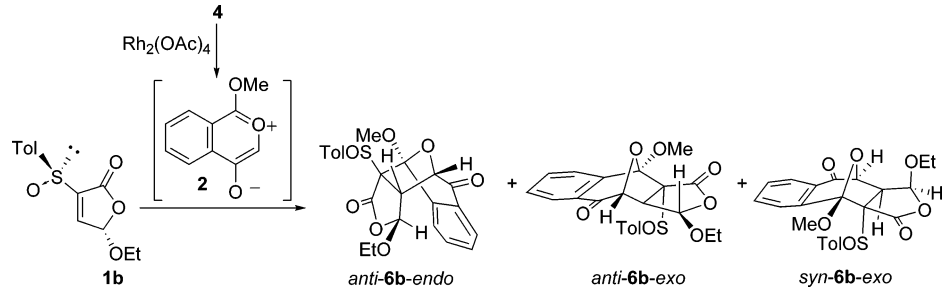
(21) The syn or anti character of the adducts, which indicates the cis or trans relationship between H_1 and H_{10a} (Scheme 1), is related to the face of the dipolarophile that is attacked by the dipole, using as a reference the spatial arrangement of the alkoxy group. The endo or exo terms, indicative of the cis or trans arrangement exhibited by furanone and dihydroisocromone moieties at the tetrahydrofurane ring, are related to the endo and exo addition modes of the dipole, using the ester group at the furanone ring as a reference.

(22) Ionic liquids as convenient recyclable media for generation of carbonyl ylides have been reported: Muthusamy, S.; Gnanaprakasam, B. *Tetrahedron* **2005**, *61*, 1309−1315.

TABLE 1. Cycloaddition of Carbonyl Ylide 2 to Furanone 1b



entry	**4**/**1b**	solvent	*T* (°C)	ratio *anti*-**6b**-*endo*/*anti*-**6b**-*exo*/*syn*-**6b**-*exo* (yield (%))
1	1:1	THF	rt	complex mixture
2	1:3	THF	rt	41[a](23):27(20):32(21)
3	1:3	THF	0	61[a]:20:19
4	1:3	CH_2Cl_2	rt	54[b]:28:18
5	1:3	MeCN	rt	58[b]:18:24
6	1:3	MeCN	0	62[a,c]:17:21

[a] Determined by HPLC. [b] Determined by ^{1}H NMR. [c] The conversion of **4** was not complete, and the proportion of adducts **6** in the reaction mixture was very low.

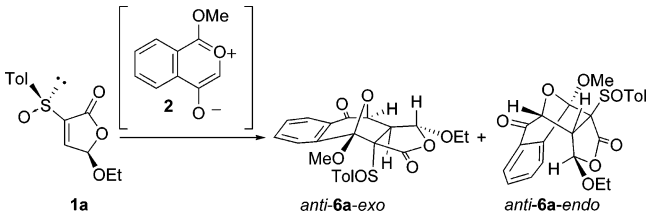
ature, addition speed of **4** to furanone, and catalyst). The best results are collected in Table 1. The reaction of *o*-methoxycarbonyl-α-diazoacetophenone (**4**) with an equimolecular amount of sulfinyl furanone **1b** in dichloromethane or tetrahydrofuran afforded a very complex mixture (entry 1, Table 1). This mixture consisted of three adducts **6b**, such as those depicted in Table 1, along with other adducts resulting from the cycloaddition of dipole **2** to the ketone group of **6b** adducts and 1*H*-isocromene-1,4-dione. The isolation of adducts **6b** as pure compounds was not possible from these mixtures. When the ratio of **1b**/**4** was increased up to 3 (entry 2, Table 1), the chromatographic isolation and purification of the three adducts **6b** (65% combined isolated yield) could be performed, and only traces of the adducts containing two molecules of dipole were detected by ^{1}H NMR of the reaction crude.

The proportion of stereoisomer **6b** depended on the solvent and the reaction temperature. Reactions in dichloromethane are less clean. Stereoselectivity is higher in acetonitrile (compare entries 2, 4, and 5 in Table 1); however, decomposition of **4** into **2** is lower in acetonitrile, which did not allow us to work at lower temperatures in such a solvent (see entry 6, Table 1).

The reaction of **2** (1 equiv) with sulfinyl furanone **1a** (3 equiv) at room temperature in THF provided a 76:24 mixture of only two anti adducts (entry 1, Table 2), the *anti*-**6a**-*endo* being the major one. They were isolated in 51% (exo) and 23% (endo) yields by column chromatography. Higher stereoselectivity (81:19) was attained when the reaction was carried out at 0 °C. However, the use of acetonitrile or dichloromethane instead of THF did not show any substantial change in the stereochemical outcome.

Desulfinylation of adducts **6** with aluminum amalgam gave complex mixtures because the ketone group at the adducts is more sensitive to the reagent than the C−S bond. However, we have found that hydrogenolysis of the C−S bond can be efficiently performed with activated zinc in a mixture of THF and saturated aqueous ammonium chloride solution at room temperature (Scheme 2).[23] Under these mild conditions, the tolylsulfinyl group was completely removed with no competitive process such as reduction, hydrolysis of the acetals, or racemization. The isolated yields of enantiomerically pure compounds **7** obtained in these reactions ranged between 70 and 80%. Compounds obtained from *anti*-**6a**-*exo* and *anti*-**6b**-*exo* have identical NMR spectra but opposite specific rotation since they are enantiomers.[24] The same is true for compounds *anti*-**7**-*endo* resulting from *anti*-**6a**-*endo* and *anti*-**6b**-*endo*.

TABLE 2. Cycloaddition of Carbonyl Ylide 2 to Furanone 1a



entry	solvent	*T* (°C)	ratio *anti*-**6a**-*endo*/*anti*-**6a**-*exo* (yield (%))
1	THF	rt	76[a](51):24(23)
2	THF	0	81[a]:19
3	CH_2Cl_2	rt	68[b]:32
4	MeCN	rt	69[a]:31

[a] Determined by HPLC. [b] Determined by ^{1}H NMR.

The regio- and stereochemistry of adducts **6** were established from their NMR data, after unequivocal assignment of the acetalic and ether CH protons by HMQC.[25] Thus, we assigned the anti stereochemistry to those adducts exhibiting $J_{1,10a}$ values smaller than 3 Hz (they are indicative of a trans relationship), whereas the compound with $J_{1,10a}$ 6.9 Hz was assigned as a syn adduct. The regiochemistry and the cis relationship of the protons at C-10 and C-10a of the *anti*-**6**-*endo* adducts and *anti*-**7**-*endo* was unequivocally established from the large value observed for $J_{10,10a}$ (9−10 Hz).[26] Further evidence for the regiochemistry of primary cycloadducts *anti*-**6a,b**-*endo* and *syn*-

(23) Holton, R. A.; Crouse, D. J.; Williams, A. D.; Kennedy, R. M. *J. Org. Chem.* **1987**, *52*, 2317−2318.

(24) The *ee* values determined by HPLC (Chiracel OD, hexane/*i*-PrOH 90: 10, flow rate = 1 mL/min) for both enantiomers of compounds *anti*-**7**-*endo* and *anti*-**7**-*exo* were higher than 99.5%.

(25) The acetalic carbon at C-1 appears at 101−107 ppm, whereas the chemical shift of C-10 in the α-position with respect to the carbonyl group was ranked at 79−85 ppm.

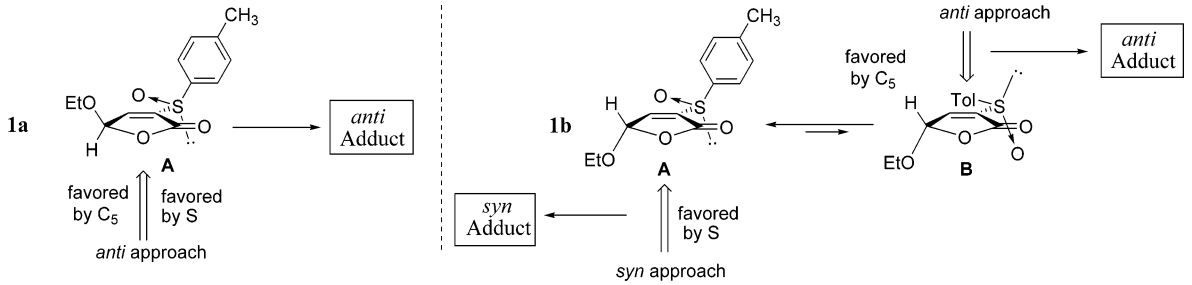
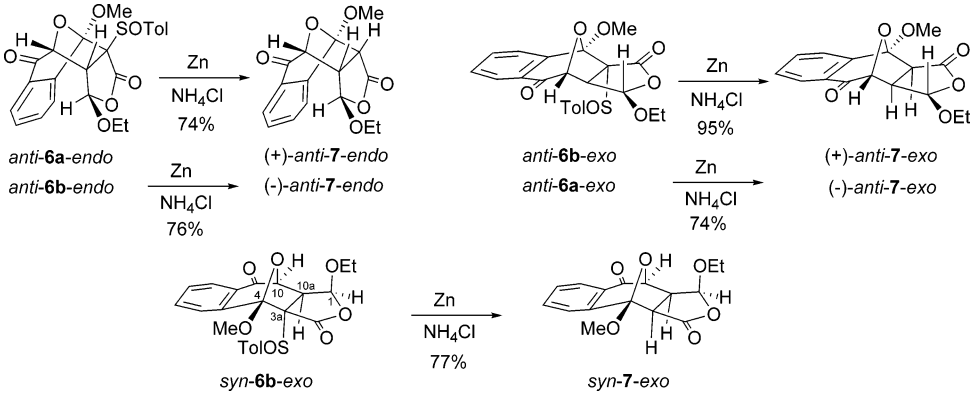


FIGURE 1. π-Facial selectivity for additions of carbonyl ylide to 3-sulfinyl furanones **1**.

SCHEME 2. Desulfinylation of Adducts 6



6b-*exo* is provided by the fact that desulfinylation products showed the proton at C-3a as a doublet. COSY and NOESY experiments with cycloadducts *anti*-**6a,b**-*exo* unequivocally revealed their regiochemistry. Thus, a strong NOE effect was observed between H-1 and H-10 of these compounds, whereas the COSY effect was not observed in *anti*-**6a**-*exo*, and it is very weak in *anti*-**6b**-*exo*.

The comparison of the results obtained from compounds **1** and **3** allowed us to know the role of the sulfinyl group in the course of these reactions. The first point concerns the dipolarophilic reactivity of the double bonds toward dipole **2**, which is strongly increased by the presence of the sulfinyl group. Thus, the yields obtained in reactions from **1** (>65%) are higher than those from **3** (<20%) under similar conditions. The regioselectivity of the reactions of **1a** and **1b** with the carbonyl ylide is complete, only affording the adduct with the acetalic carbon of the dipole bonded to C-3 at furanone. Bearing in mind that this is the same regiochemistry as that obtained in the reactions with 5-methoxyfuran-2(5*H*)-one, we can conclude that the regioselectivity was not modified by the sulfinyl group despite the fact that this group could make the formation of this regioisomer difficult by steric grounds. Both reactivity and regiochemistry can be rationalized on the basis of FMO considerations taking into account that the $HOMO_{dipole}$−$LUMO_{dipolarophile}$ interaction is the most relevant reaction of carbonyl ylides with electron deficient dipolarophiles.[3a,27]

The π-facial selectivity observed for reactions of furanone **3**, which only yield *anti* adducts, indicates that the 5-methoxy group is able to exert its complete control. The fact that **1a** only affords the anti adducts, whereas **1b** evolves into a mixture of anti and syn adducts, reveals that the spatial arrangement of the 5-alkoxy group is the main factor controlling the stereoselectivity. The different behavior of **1a** and **1b** can be explained on the basis of the conformational preferences around the C−S bond. Electrostatic repulsion between the negatively charged cabonyl and the sulfinyl oxygens favors conformation A, with both oxygens in an anti arrangement (Figure 1). As we can see, the orientation of the tolyl group in conformation A of compound **1a** reinforces the tendency imposed by the 5-alkoxy group (only the anti adducts are formed). By contrast, in conformation A of compound **1b**, the tolyl group is oriented toward the face opposite to that bearing the ethoxy group, which determines the competence between the directing effects of both groups and therefore justifies the formation of the syn adduct. The predominant influence of the OEt group, despite that its size is smaller than that of the *p*-tolyl one, must be a consequence of the fixed orientation of the former one, contrasting with the variable orientation of the *p*-tolyl group due to its rotation around the C−S bond. The approach of the dipole to conformation B of **1b,** favored by steric grounds but probably less stable than the A conformation, would justify the formation of the anti adduct as the major isomer. The approach to the face bearing the OEt group at the most stable conformation A would explain the formation of the syn adduct. A similar reasoning explains the stereoselectivitiy observed in the reactions of furanones **1** with 3,4-dihydro-2*H*-pyrrole-1-oxide in chloroform under kinetic conditions.[16a]

The complete exo selectivity observed for the approach yielding the syn adduct (from **1b**) can be a consequence of the steric and electrostatic interactions of the dipole with the OEt group, which destabilizes the endo−syn approach to the A conformation (Figure 2). By comparing the endo/exo selectivity of the reactions of **2** with **1** (ca. 70:30 ratio) and **3** (60:40 ratio) for the anti approaches, it can be stated that the sulfinyl group

(26) The coupling constant values between the ether bridgehead proton and the vicinal proton in the adducts of dipole **2** and maleimides (see ref 2b) were higher than 9 Hz or null when these protons were in a cis (endo adduct) or trans relationship (exo adducts), respectively.

(27) Padwa, A.; Sandanayaka, V. P.; Curtis, E. A. *J. Chem. Soc.* **1994**, *116*, 2667−2668.

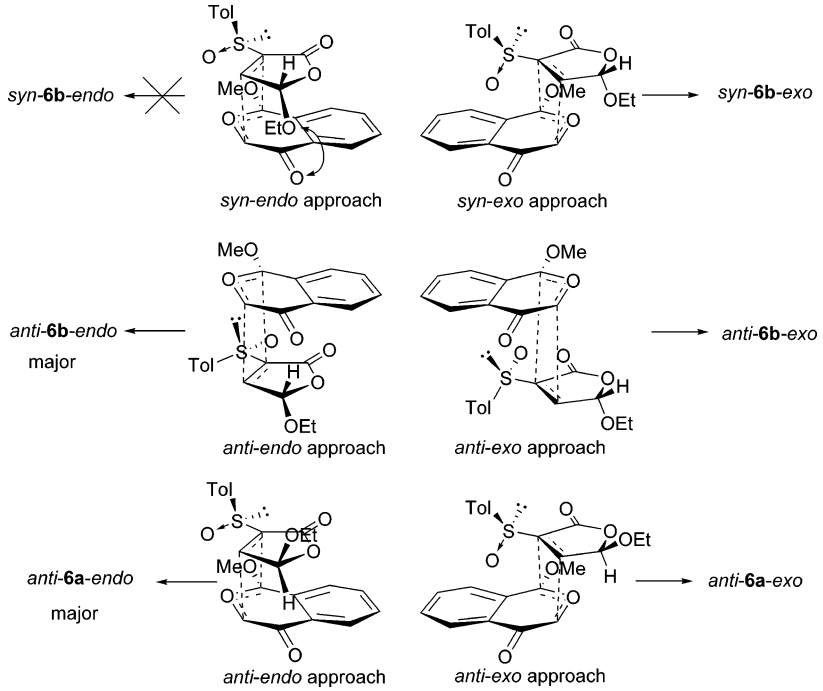


FIGURE 2. Endo/exo selectivity for additions of carbonyl ylide **2** to 3-sulfinyl furanones **1**.

slightly favors the formation of the endo adducts. It could be explained by assuming that steric interactions of the dipole with the sulfinyl group at the exo approach slightly favor the formation of the endo adducts (Figure 2).

In summary, the first asymmetric carbonyl ylide cycloaddition to alkenes bearing a chiral auxiliary, such as vinyl sulfoxide and furan-2(5*H*)-ones, is reported. High diastereoselectivity and complete enantioselectivity have been achieved. The level of stereoselectivity achieved in the current study with sulfinylfuranones correlates well with those that we have previously observed in cycloadditions of 3,4-dihydro-2*H*-pyrrole-1-oxide; however, the endo/exo selectivity in the addition of carbonyl ylide **2** to 5-methoxyfuran-2(5*H*)-one is opposite to that reported with the cited nitrone. Further studies are currently in progress to investigate the factors affecting the stereoselectivity of such cycloaddition processes.

Experimental Procedures

Cycloadditions of 2-Benzopyrylium-4-olate. General Procedure. A solution of 138 mg (0.68 mmol) of *o*-methoxycarbonyl-α-diazoacetophenone (**4**) in THF (2.2 mL) was added to a suspension of $Rh_2(OAc)_4$ (7.5 mg, 0.017 mmol) and furanone **1a**, **1b** (5.43 mg, 2.04 mmol), or **3** (233 mg, 2.04 mmol) in 18 mL of the same solvent over a period of 2 h at room temperature. After the time indicated in each case, the solvent was removed in vacuo to give a mixture, which was purified by column chromatography to provide diastereoisomerically pure adducts. The ratio of stereoisomeric adducts was determined by ^{1}H NMR of the crude reaction mixture. The reported yields correspond to isolated products and are calculated from the amount of starting diazoketone **4**.

(R_1,S_S)-1-Ethoxy-4-methoxy-3a-(*p*-tolylsulfinyl)-3a,4,10,10a-tetrahydro-1*H*-4,10-epoxybenzo[4,5]cyclohepta[1,2-*c*]furan-3,9-diones (**6a**). This was obtained as a 24:76 mixture of *anti*-**6a**-*exo*/*anti*-**6a**-*endo* after 5 min once the addition of diazoketone to (R_5,S_S)-5-ethoxy-3-(*p*-tolylsulfinyl)furan-2(5*H*)-one (**1a**) was complete. They were isolated as pure isomers by column chromatography (hexane/ethyl acetate 2:1).

(R_1,S_{3a},S_4,S_{10},S_{10a},S_S)-(*anti*-6a-*exo*). This compound was obtained as a minor product from **1a** in 23% yield; it recrystallized from ether−hexane, mp 182−184 °C (white solid). $[\alpha]_D^{20}$ −42.9 (*c* 0.51, $CHCl_3$). Anal. calcd. for $C_{23}H_{22}O_7S$: C, 62.43; H, 5.01; S, 7.25. Found: C, 62.03; H, 5.08; S, 7.20. IR (KBr): 1771, 1703, 1599, 1585, 1258, 1173, 1013. ^{1}H NMR δ: 8.11 (m, 1H), 7.79 (m, 2H), 7.63 (m, 1H), 7.48 and 7.20 (AA′BB′ system, 4H), 5.41 (d, 1H, *J* 1.7), 4.90 (d, 1H, *J* 0.8), 3.59 (s, 3H), 3.41 (q, 2H, *J* 7.1), 3.33 (dd, 1H, *J* 1.7 and 0.8), 2.35 (s, 3H), 0.98 (t, 3H, *J* 7.1). ^{13}C NMR δ: 190.8, 167.0, 143.1, 137.5, and 135.3 (C), 134.7 (CH), 132.0 (C), 130.8, 129.2, 127.8, 127.4, and 125.5 (CH), 109.3 (C), 106.5 and 84.5 (CH), 82.8 (C), 65.7 (CH_2), 54.5 (CH_3), 47.0 (CH), 21.4, 14.5 (CH_3).

(R_1,S_{3a},R_4,R_{10},S_{10a},S_S)-(*anti*-6a-*endo*). This compound was obtained as the major adduct from **1a** following the general procedure. It was isolated by column chromatography (hexanes−ethyl acetate 2:1) with a 51% yield; mp 112−114 °C (white solid). $[\alpha]_D^{20}$ +103.0 (*c* 0.11, $CHCl_3$). IR (KBr): 1771, 1703, 1599, 1258, 1141, 1085, 1013. ^{1}H NMR δ: 8.01 (dd, 1H, *J* 7.8 and 0.9), 7.71 (td, 1H, *J* 7.8 and 1.3), 7.62 (dd, 1H, *J* 7.8 and 0.9), 7.54 (m, 1H), 7.55 and 7.26 (AA′BB′ system, 4H), 5.07 (d, 1H, *J* 9.5), 4.75 (d, 1H, *J* 1.8), 3.84 (dd, 1H, *J* 9.5 and 1.8), 3.65 (s, 3H), 3.03 (m, 2H), 2.35 (s, 3H), 0.70 (t, 3H, *J* 7.1). ^{13}C NMR δ: 192.2, 168.0, 142.4, 139.3, and 135.6 (C), 135.0 and 130.5 (CH), 130.2 (C), 129.5, 127.1, 126.7, and 126.1 (CH), 108.1 (C), 101.7 (CH), 84.3 (C), 80.8 (CH), 65.4 (CH_2), 54.4 (CH_3), 46.3 (CH), 21.3, 14.3 (CH_3). HRMS Calcd for $C_{23}H_{23}O_7S$ [M + H] 443.11645, found 443.11631.

(S_1,S_S)-1-Ethoxy-4-methoxy-3a-(*p*-tolylsulfinyl)-3a,4,10,10a-tetrahydro-1*H*-4,10-epoxybenzo[4,5]cyclohepta[1,2-c]furan-3,9-diones (**6b**). This was obtained from (S_5,S_S)-5-ethoxy-3-(*p*-tolylsulfinyl)furan-2(5*H*)-one (**1b**), as a mixture of *syn*-**6b**-*exo*/*anti*-**6b**-*exo*/*anti*-**6b**-*endo* in THF, and isolated as pure isomers by a difficult chromatography process after removing a part of **1b** by filtration of the product precipitated by adding hexane to the solution of the crude reaction mixture in ethyl acetate.

(S_1,S_{3a},R_4,S_{10},S_{10a},S_S)-(*syn*-6b-*exo*). This was purified by column chromatography (hexane−dichloromethane−diethyl ether, 6:4:1). Yield 21%. White solid, mp 184 °C. $[\alpha]_D^{20}$ + 86.9 (*c* 0.51, $CHCl_3$). Anal. calcd. for $C_{23}H_{22}O_7S$: C, 62.43; H, 5.01; S, 7.25. Found: C, 62.17; H, 5.03; S, 7.09. IR (KBr): 1772, 1705, 1598, 1248, 1172,

1084. ^{1}H NMR δ: 8.10 (m, 1H), 7.79 (m, 2H), 7.63 (m, 1H), 7.45 and 7.27 (AA′BB′ system, 4H), 5.41 (d, 1H, *J* 0.8), 4.80 (d, 1H, *J* 6.9), 3.80 (m, 1H), 3.58 (s, 3H), 3.53 (m, 1H), 3.49 (dd, 1H, *J* 6.9 and 0.8), 2.38 (s, 3H), 1.24 (t, 3H, *J* 7.1). ^{13}C NMR δ: 192.3, 165.7, 143.7, 138.0, and 135.7 (C), 134.7 (CH), 132.0 (C), 130.6, 130.0, 127.7, 125.7, and 125.3 (CH), 109.1 (C), 101.1 (CH), 83.6 (C), 79.2 (CH), 67.4 (CH_2), 54.3 (CH_3), 43.3 (CH), 21.5 and 14.7 (CH_3).

(S_1,R_{3a},R_4,R_{10},R_{10a},S_S)−(*anti*-6b-*exo*). It was purified by column chromatography (hexanes−ethyl acetate, 3:2). Yield 20%. White solid, mp 118−120 °C with descomposition. $[\alpha]_D^{20}$ +131.8 (*c* 0.38, $CHCl_3$). Anal. calcd. for $C_{23}H_{22}O_7S$: C, 62.43; H, 5.01; S, 7.25. Found: C, 62.14; H, 5.12; S, 7.07. IR (KBr): 1772, 1707, 1598, 1260, 1172, 1090. ^{1}H NMR δ: 8.15 (ddd, 1H, *J* 7.7, 1.4 and 0.6), 8.04 (ddd, 1H, *J* 7.8, 1.2 and 0.6), 7.33 (dt, 1H, *J* 7.7 and 1.4), 7.67 (dt, 1H, *J* 7.7 and 1.2) 7.50 and 7.23 (AA′BB′ system, 4H), 5.24 (d, 1H, *J* 1.6), 4.83 (d, 1H, *J* 0.8), 3.58 (s, 3H,), 3.28 (q, 2H, *J* 7.0), 2.54 (dd, 1H, *J* 1.6 and 0.8), 2.36 (s, 3H), 0.82 (t, 3H, *J* 7.0). ^{13}C NMR δ: 191.3, 164.7, 143.4, 138.5, and 135.2 (C), 135.0 and 130.8 (CH), 130.2 (C), 129.7, 128.0, 127.7, and 127.1 (CH), 110.5 (C), 104.7 and 83.8 (CH), 77.2 (C), 65.4 (CH_2), 54.5 (CH_3), 51.8 (CH), 21.5, 14.3 (CH_3). ^{13}C NMR (C_6D_6) δ: 191.6, 164.0, 142.6, 139.3, and 136.9 (C), 134.6 (CH), 131.0 (C) 130.7 129.5, 128.7, 127.7, and 127.3 (CH), 111.0 (C), 104.4 and 84.0 (CH), 77.6 (C), 65.0 (CH_2), 54.0 (CH_3), 52.3 (CH), 21.1, 14.5 (CH_3).

(S_1,R_{3a},S_4,S_{10},R_{10a},S_S)-(*anti*-6b-*endo*). This was purified by column chromatography (hexane−dichloromethane−diethyl ether, 6:4:1). Yield 23%. White solid, mp 164−166 °C. $[\alpha]_D^{20}$ +66.9 (*c* 0.44, $CHCl_3$). IR (KBr): 1771, 1708, 1597, 1177, 1141, 1052. ^{1}H NMR δ: 8.00 (dd, 1H, *J* 7.8 and 0.8), 7.77 and 7.37 (AA′BB′ system, 4H), 7.71 (dd, 1H, *J* 7.3 and 1.2), 7.59 (m, 2H), 4.82 (d, 1H, *J* 2.2), 4.54 (d, 1H, *J* 9.6), 3.83 (dd, 1H, *J* 9.6 and 2.2), 3.64 (m, 1H), 3.41 (m, 1H), 3.41 (s, 3H), 2.45 (s, 3H), 1.13 (t, 3H, *J* 7.0). ^{13}C NMR δ: 191.2, 168.4, 143.1, 138.6, and 137.9 (C), 135.3 and 130.8 (CH), 130.2 (C), 129.6, 127.2, 127.0, and 126.3 (CH), 108.5 (C), 101.8 (CH), 84.8 (C), 80.2 (CH), 66.1 (CH_2), 53.5 (CH_3), 48.5 (CH), 26.5 and 14.4 (CH_3). HRMS Calcd for $C_{23}H_{23}O_7S$ [M + H] 443.11645, found 443.11822.

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Supporting Information Available: Experimental procedures and characterization data of compounds [(±)-*anti*-**5**-*exo*, (±)-*anti*-**5**-*endo*, and enantiomerically pure stereoisomers **7**], as well as ^{1}H and ^{13}CNMR spectra of compounds lacking CHN analyses together with HMQC (all adducts **6** and (−)-*anti*-**7**-*exo*), COSY (adducts **6b** and *anti*-**6a**-*exo*), and NOESY (adducts **6b** and *anti*-**6a**-*exo*). This material is available free of charge via the Internet at http://pubs.acs.org.

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