



## (*S,S*)-1,1-bis-Ethoxycarbonyl-2,2-bis-*p*-tolylsulfinyl ethene: a highly stereoselective but unexpectedly unreactive dienophile in asymmetric Diels–Alder reactions

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**Abstract:** The synthesis and dienophilic behaviour of (*S,S*)-1,1-bis-ethoxycarbonyl-2,2-bis-*p*-tolylsulfinyl ethene with cyclic and acyclic dienes is reported. The stereoselectivity is high with cyclopentadiene and complete with acyclic dienes, but its reactivity is unexpectedly low, requiring high pressures (13 Kbar) to evolve into the corresponding adducts or their pyrolytic sulfinyl elimination products. © 1997 Elsevier Science Ltd. All rights reserved.

Asymmetric Diels–Alder reactions using enantiopure dienophiles have received an increasing widespread attention during the past two decades and, it has been firmly established that several types of chiral dienophiles react in a highly stereoselective manner.<sup>1</sup> In particular, great attention has recently been paid to the use of enantiopure vinylsulfoxides due to the potential ability of the sulfinyl moiety, directly joined to the dienophilic double bond, to control the stereoselectivity of the cycloaddition process. In order to overcome the unexpectedly very low influence of the sulfinyl group on the reactivity of the double bond,<sup>2</sup> two alternatives have been developed: transformation of the sulfoxide moiety into their corresponding alkoxy-sulfonium salts<sup>3</sup> and the introduction of additional electron-withdrawing groups joined to the double bond. The latter approach has been used to a larger extent and, thus, ester,<sup>4</sup> imide,<sup>5</sup> carbonyl,<sup>6</sup> nitro<sup>7</sup> and sulfone<sup>8</sup> functionalities at  $\alpha$ - or  $\beta$ - (or both) positions of the  $\alpha,\beta$ -unsaturated sulfoxides have afforded satisfactory results.

In this field, in the last few years we have reported some asymmetric Diels–Alder reactions of the mono-,<sup>9</sup> di-,<sup>10</sup> and tri-activated<sup>11</sup> vinylsulfoxides **1**, **2**, and **3**, respectively (Figure 1). The use of appropriate catalysts allowed us to achieve efficient control on the  $\pi$ -facial selectivity of the cycloadditions and to increase the reactivity. Nevertheless, the cycloadditions took place with moderate or even low *endo* selectivity, especially the reactions from dienophiles **1** and **3**, yielding *endo/exo* mixtures of adducts. We reasoned that the use of a dienophile like **4**, a  $C_2$  symmetric bis-sulfoxide,<sup>12</sup> would eliminate the problem of the *endo/exo* selectivity, and, simultaneously, would avoid the formation of mixtures of regioisomers during the sulfinyl elimination step which always takes place after cycloaddition in the reactions with acyclic dienes. Moreover, a very similar molecule, **5**, having both sulfinyl groups incorporated into a five membered ring, had been previously studied<sup>13</sup> and it reacted with cyclopentadiene at room temperature in 12 h, in the absence of catalysts, showing a significant reactivity, similar to that exhibited by dienophile **3**.

Enantiomerically pure dienophile **4** was prepared in two steps from (*S,S*)-bis-*p*-tolylsulfinyl methane<sup>14</sup> (Scheme 1). Deprotonation of (*S,S*)-bis-*p*-tolylsulfinyl methane with *n*-BuLi (1.1 equiv.) in THF and further reaction with diethyl oxomalonate at  $-78^\circ\text{C}$  furnished the alcohol **6**. After some experimentation,<sup>15</sup> successful dehydration of crude **6** was performed by treatment with the Mitsunobu reagents (DEAD, PPh<sub>3</sub>) and pyridine, in CH<sub>2</sub>Cl<sub>2</sub> at rt. Pure **4** was obtained in 73% overall yield after flash chromatography.

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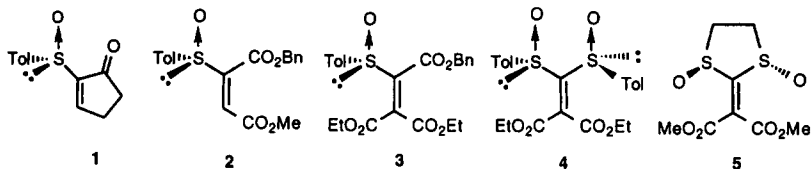
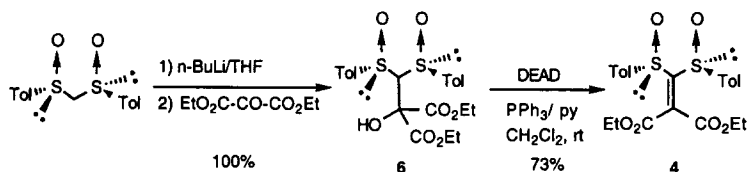
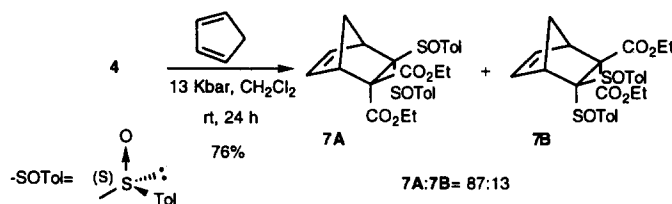


Figure 1.



Scheme 1.



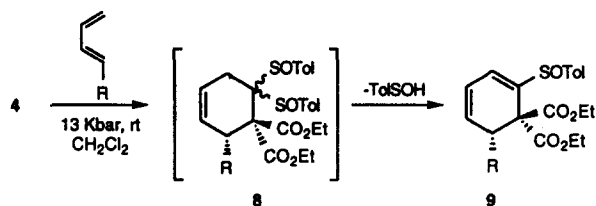
Scheme 2.

Surprisingly, dienophile **4** did not react with cyclopentadiene either in the absence or in the presence of Lewis acids such as  $\text{TiCl}_4$  (1.2 equiv,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ ), or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (1.2 equiv,  $\text{CH}_2\text{Cl}_2$ , rt). Only at high pressures (13 Kbar in  $\text{CH}_2\text{Cl}_2$  at rt) did **4** react with cyclopentadiene to give a 87:13 mixture of adducts **7A/7B** in 76% yield after chromatography (Scheme 2).

Under these harsh conditions **4** reacted also with acyclic dienes, such as piperylene, 1-vinylcycloheptene and Dane's diene. In almost all these cases a single adduct was obtained (Scheme 3), showing that the cycloadditions took place with complete regioselectivity (controlled by the olefinic carbon bearing the ester functions) and  $\pi$ -facial selectivity. Like the cycloadditions of other sulfinyl acrylates, the sulfonylated adducts **8** were not stable at rt, evolving by spontaneous elimination of sulfenic acid to give the 1,3-cyclohexadienes **9**. However, although the cycloadditions were conducted with excess of diene (4–5 equiv.) at 13 Kbar during 3 days at rt the conversions were not higher than 50%.

In order to increase the inherent low reactivity of dienophile **4**, we next studied the same cycloadditions by combining high pressures and Lewis acid catalysis. We observed complete conversions when the reactions were performed at 13 Kbar in the presence of 1.2 equiv. of  $\text{ZnBr}_2$  during 2–3 days (Scheme 3). Under these conditions, the reactions also occurred with very high regio and stereoselectivity leading to the formation of the same adducts (**9a**, 82% yield; **9b+9c**, 58% yield; and **9d**, 74% yield) obtained in the absence of  $\text{ZnBr}_2$ . This result contrasts with the usual inversion of the  $\pi$ -facial selectivity promoted by addition of  $\text{ZnBr}_2$  to the reactions of other sulfinyl acrylates.<sup>16</sup>

The unequivocal assignment of the absolute configuration of the adducts **7** and cyclohexadienes



Scheme 3.

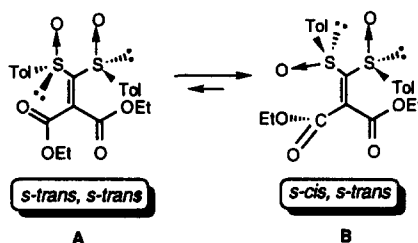


Figure 2.

**9** was not possible by X-ray diffraction studies.<sup>17</sup> Therefore, they have been tentatively assigned according to the following stereochemical model.

The two presumably more stable conformations around the C–S bonds in compound **4** are depicted in Figure 2. Rotamer **A**, exhibiting a  $C_2$  symmetry, displays the two sulfinyl oxygens in an *s-trans* arrangement, in order to minimize the electrostatic repulsion between them and the ester group in the *cis* position. The most destabilizing factor of this conformation would probably be the electrostatic repulsion between both sulfinyl oxygens, and/or the strong dipolar repulsion between both parallel S–O bond dipoles. In order to avoid this repulsive interaction, rotamer **B** has both sulfinyl groups in *s-cis* and *s-trans* arrangements, respectively. As a consequence, the ester group in a *cis*-arrangement with respect to the *s-cis* SO group, should be oriented out of the plane to minimize its interactions with the sulfinyl oxygen. We think that rotamer **B** must be the most stable (and therefore the most populated) because the interaction between the two S–O bonds must be quite more destabilizing than that of the ester and sulfinyl groups<sup>18</sup> (Figure 2).

As both aryl groups are placed towards the same face in rotamer **B**, we could assume that the diene approach would take place with high  $\pi$ -facial selectivity from the less hindered face. As we can see in Figure 3 the *endo* orientating character of the ester group coplanar with the dienophilic double bond must be much higher than that of the non conjugated ester group, making the approach 1 (*endo* with respect the sulfinyl group in *s-trans* arrangement and *exo* with respect to the *s-cis*) more favoured than approach 2 (despite the interactions of the methylene bridge of cyclopentadiene with the non conjugated ester). This analysis allows the assignment of the structures **7** (Scheme 2) and **9** (Scheme 3) to the major or sole adducts obtained in the reactions with cyclopentadiene and acyclic dienes, respectively.<sup>19</sup> Finally, the beneficial effect of the  $ZnBr_2$  on the reactivity and the preservation of the sense of the  $\pi$ -facial selectivity, can be easily explained by assuming the chelation of the metal with the *s-cis* sulfinyl group and the ester group in *cis* arrangement, which increases the planarity of the last and thus minimizes its interactions with the dienes.

Despite of the high stereoselectivity observed in the reactions with this dienophile, the most outstanding fact is its lack of reactivity under normal pressure, even in the presence of different catalysts which have proved to be very efficient in many other cases. Taking into account that the

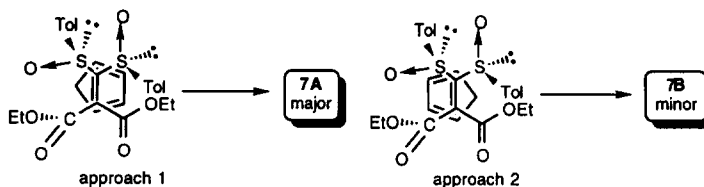


Figure 3.

only apparent difference between substrates **4** and **5** is their acyclic or cyclic structure, which in turn is related to the conformational mobility, the relationship between the conformation around the C–S bond and the dienophilic character of the double bond in vinylsulfoxides emerges as the most likely cause of the different reactivity observed on both substrates. This point is being currently investigated by both theoretical and experimental approaches.

### Experimental

Melting points were determined with a Gallenkamp apparatus in open capillaries and are uncorrected.  $^1\text{H}$ -NMR spectra and  $^{13}\text{C}$ -NMR spectra were recorded in the FT mode on a Bruker WP-200-SY instrument coupled to an ASPECT 2000 computer, transforming 16K data points. Both chemical shifts (ppm downfield from internal tetramethylsilane) and coupling constants (Hz) were obtained by first order analysis of spin patterns. Mass spectra (MS) were recorded on a Hewlett–Packard 5985 spectrometer with electron impact (EI, 70eV). Mass data are reported in mass units ( $m/z$ ) and the values in brackets regard to the relative intensity from base peak (as 100%). Infrared (IR) spectra were recorded on a Philips PU-9716 spectrometer. Elemental analysis were performed in a Perkin–Elmer 2400 CHN Elemental analyzer. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. High pressure data were obtained from a High Pressure Apparatus (Unipressequipment Division), maximum pressure 1.3 GPa.

Analytical thin-layer chromatography was performed on DC-Alufolien 0.2 mm silica gel 60-F plates (MERCK). Visualization was accomplished with UV light and ethanolic fosfomolybdic acid solution followed by heating. Flash chromatography was performed on silica gel (MN-Kieselgel 60, 230–400 mesh).

All solvents were dried before use. Tetrahydrofuran and ether were distilled from sodium-benzophenone under argon. Dichloromethane and chloroform were distilled from  $\text{P}_2\text{O}_5$ . Cyclopentadiene was freshly distilled. Zinc bromide was dried at  $160^\circ\text{C}$  for 12 h with  $\text{P}_2\text{O}_5$  under *vacuo*. *Trans*-1,3-pentadiene, diethyl oxomalonate and DEAD were purchased from Aldrich and used without further purification. Dane's diene and 1-vinylcycloheptene were prepared according to described procedures.<sup>20</sup>

#### (*S,S*)-1,1-bis-Ethoxycarbonyl-2,2-bis-*p*-tolylsulfinyl-1-ethanol **6**

A 1.0M solution of LHMDS in THF (5.5 ml, 5.5 mmol, 1.2 equiv) was added, under argon atmosphere, to a solution of (*S,S*)-bis-*p*-tolylsulfinylmethane<sup>14</sup> (1.35 g, 4.6 mmol, 1.0 equiv) in THF (25 ml) and cooled to  $-78^\circ\text{C}$ . After being stirred for 15 min, a solution of diethyl oxomalonate (680  $\mu\text{l}$ , 5.5 mmol, 1.2 equiv) was slowly added. Stirring was continued for 2 h at  $-78^\circ\text{C}$ . Then, 10% HCl (20 ml) was added. The organic layer was separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 15$  ml). The combined organic layers was dried ( $\text{MgSO}_4$ ) and concentrated. The residue was purified by chromatography (hexane-ethyl acetate 1:1) to give 2.1 g (100%) of **6** as a white solid. M.p.:  $122\text{--}124^\circ\text{C}$ .  $[\alpha]_{\text{D}}^{20} = +120.5$  ( $c = 1.44$ ,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ ): 3420, 3040, 1730, 1360, 1270, 1200, 1125, 1070, 1035, 840, 990–900.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 1.15 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 1.31 (t, 3H,  $J = 7.1$  Hz,  $\text{CH}_3$ ), 2.31 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 2.40 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 4.13 (m, 2H,  $\text{CH}_2$ ), 4.32 (c, 2H,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 4.77 (s, 1H, CH), 5.10 (bs, 1H, OH), 7.09 (s, 4H, arom), 7.22–7.50 (AA'BB' system, 4H, arom).  $^{13}\text{C}$ -

NMR (CDCl<sub>3</sub>): 13.3 (CH<sub>3</sub>), 13.5 (CH<sub>3</sub>), 20.9 (2CH<sub>3</sub>), 62.5(C), 62.9 (CH<sub>2</sub>), 63.2 (CH<sub>2</sub>), 87.3 (CH), 123.7 (C), 124.0 (CH), 124.9 (CH), 129.3 (CH), 129.5 (CH), 129.9 (C), 140.0 (C), 141.8 (C), 166.5 (C), 167.1 (CO). EM (EI): 468 (29.2, M<sup>+</sup>+2), 467 (100.0, M<sup>+</sup>+1). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>O<sub>7</sub>S<sub>2</sub>: C, 56.64; H, 5.62. Found: C, 56.70; H, 5.57.

*(S,S)-1,1-bis-Ethoxycarbonyl-2,2-bis-p-tolylsulfinyl ethene 4*

To a solution of **6** (488 mg, 1.05 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) cooled at 0°C were added PPh<sub>3</sub> (686 mg, 2.6 mmol, 2.5 equiv), DEAD (412 μl, 2.6 mmol, 2.5 equiv) and pyridine (170 μl, 2.1 mmol, 2.0 equiv). The mixture was allowed to stand at rt for 2 h. Then, the reaction mixture was concentrated and the residue was purified by chromatography (hexane-ethyl acetate 4:1) to give 367 mg (73%) of **4** as a yellow solid. M.p.: 118–119°C. [α]<sub>D</sub><sup>20</sup>=+134.2 (c=1.5, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>): 3150, 1705, 1360, 1240, 1210, 1100, 1010, 910. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.35 (t, 3H, J=7.1 Hz, 2CH<sub>3</sub>), 2.31 (s, 6H, 2CH<sub>3</sub>Ar), 4.38 (m, 4H, 2CH<sub>2</sub>), 6.99 and 7.36 (AA'BB' system, 8H, arom). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 13.8 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>), 21.0 (2C, CH<sub>3</sub>), 62.9 (2C, CH<sub>2</sub>), 126.6 (2C, CH), 129.3 (2C, CH), 138.3 (C), 141.9 (C), 161.6 (CO) and 167.6 (CO). EM (EI): 448 (0.4, M<sup>+</sup>), 403 (6.1), 388 (2.9), 342 (60.6), 139 (77.9), 123 (47.3), 92 (51.2), 91 (100.0) and 65 (29.3). Anal. Calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>6</sub>S<sub>2</sub>: C, 57.13; H, 4.80. Found: C, 56.74; H, 5.08.

*Diels–Alder reaction of 4 with cyclopentadiene under high pressure*

In a high pressure reaction tube was placed a solution of **4** (55 mg, 0.1 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (1 ml) and cyclopentadiene (102 μl, 1.2 mmol, 10.0 equiv). After standing the mixture at rt for 24 h at 13 Kbar, the reaction was allowed to reach atmospheric pressure and the solvent and the excess of cyclopentadiene were evaporated *in vacuo*. The residue was washed with water (2 ml) and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×5 ml). The combined organic layers were dried (MgSO<sub>4</sub>) and concentrated. The residue was analyzed by <sup>1</sup>H NMR (isomer ratio: **7A**:**7B**=87:13) and purified by flash chromatography (hexane-ethyl acetate 3:1) to give 47.6 mg of major isomer **7A** (76%).

*(R<sub>1</sub>,S<sub>4</sub>,S<sub>5</sub>,S<sub>5</sub>)-3,3-bis-Ethoxycarbonyl-2,2-bis-p-tolylsulfinylbicyclo[2.2.1]-5-heptene 7A (major isomer)*

[α]<sub>D</sub><sup>20</sup>=+118.9 (c=2.06, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>): 2980, 1725, 1600, 1445, 1360, 1260, 1200, 1090 and 860. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.30 (t, 3H, J=7.1 Hz, CH<sub>3</sub>), 1.36 (t, 3H, J=7.1 Hz, CH<sub>3</sub>), 1.67 (dt, 1H, J=1.68 y 9.9 Hz, H<sub>7</sub>), 2.24 (bd, 1H, J=9.8 Hz, H<sub>7</sub>), 2.36 (s, 3H, CH<sub>3</sub>Ar), 2.42 (s, 3H, CH<sub>3</sub>Ar), 3.66 (m, 2H, H<sub>1</sub> y H<sub>4</sub>), 4.18–4.36 (m, 4H, 2CH<sub>2</sub>), 6.47 (dd, 1H, J=3.0 and 5.5, H<sub>6</sub>), 6.79 (dd, 1H, J=3.0 and 5.4 Hz, H<sub>5</sub>), 7.08–7.23 (AA'BB' system, 4H, J=8.3 Hz, arom) and 7.24–7.94 (AA'BB' system, 4H, J=8.3 Hz, arom).




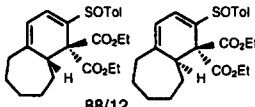
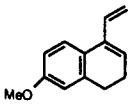
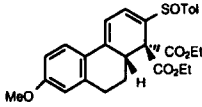
*(S<sub>1</sub>,R<sub>4</sub>,S<sub>5</sub>,S<sub>5</sub>)-3,3-Diethoxycarbonyl-2,2-bis-p-tolylsulfinylbicyclo[2.2.1]-5-heptene 7B (minor isomer)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.62 (bs, 1H, H<sub>4</sub>), 3.55 (bs, 1H, H<sub>1</sub>), 5.37 (dd, 1H, J=3.0 and 5.5 Hz, H<sub>6</sub>) and 6.15 (dd, 1H, J=3.0 and 5.4 Hz, H<sub>5</sub>).

*General procedure for the Diels–Alder reactions of 4 catalyzed by ZnBr<sub>2</sub> under high pressure*

In a high pressure reaction tube was placed ZnBr<sub>2</sub> (39 mg, 0.17 mmol, 1.1 equiv) and a solution of **4** (70 mg, 0.16 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (1 ml). Then, the diene is added (piperylene, 1-vinylcycloheptene or Dane's diene) (0.64 mmol, 4–5 equiv), and the reaction was pressurized (13 Kbar) at room temperature. After the reaction times indicated in Table 1, the reaction was allowed to reach atmospheric pressure and the solvent and the excess of diene were evaporated *in vacuo*. Then, 10% NaHCO<sub>3</sub> was added (1 ml). The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×2 ml). The combined organic layers was dried (MgSO<sub>4</sub>) and concentrated. The residue was analyzed by <sup>1</sup>H NMR and purified by flash chromatography (eluents and yields are indicated below for each case).

Table 1. Diels–Alder reactions of **4** with acyclic dienes

Entry	Diene	Catalyst	P (kbar)	t (h)	Products	Yield (%) <sup>a</sup>
1		---	12	43	 <b>9a</b>	10 <sup>b</sup>
2	"	---	13	72	<b>9a</b>	50 <sup>b</sup>
3	"	ZnBr <sub>2</sub> <sup>c</sup>	13	68	<b>9a</b>	82
4		ZnBr <sub>2</sub> <sup>c</sup>	13	48	 <b>9b / 9c</b>	58
5		---	13	68	 <b>9d</b>	56 <sup>d</sup>
6	"	ZnBr <sub>2</sub> <sup>c</sup>	13	46	<b>9d</b>	74

<sup>a</sup>In pure product after chromatography. <sup>b</sup>Calculated from the crude reaction. <sup>c</sup>1.2 equivalents. <sup>d</sup>40% of **4** was recovered.

**(R<sub>6</sub>,S<sub>5</sub>)-1,1-Diethoxycarbonyl-6-Methyl-2-p-tolylsulfinyl-2,4-cyclohexadiene 9a**

Yield: 82%. Eluent: Hexane–AcOEt 3:1.  $[\alpha]_D^{20} = -323.9$  ( $c=2.24$ , CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>): 2970, 1720, 1440, 1250, 1210, 1080 and 1010. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.02 (t, 3H,  $J=7.1$  Hz, CH<sub>3</sub>), 1.16 (d, 3H,  $J=7.3$  Hz, CH<sub>3</sub>), 1.28 (t, 3H,  $J=7.1$  Hz, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>Ar), 3.35 (ddc, 1H,  $J=1.5, 5.5$  and 7.3 Hz), 3.70 (m, 2H, CH<sub>2</sub>), 4.25 (c, 2H, CH<sub>2</sub>,  $J=7.1$  Hz), 6.07 (m, 2H, H<sub>4</sub> and H<sub>5</sub>), 7.04 (d, 1H,  $J=5.1$ , H<sub>3</sub>), 7.23 and 7.63 (AA'BB' system, 4H,  $J=8.2$  Hz, arom). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 13.6 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 14.5 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 36.8 (CH), 61.2 (C), 61.8 (CH<sub>2</sub>), 62.0 (C, CH<sub>2</sub>), 121.4 (C, CH), 126.7 (C, CH), 129.5 (3C, CH), 136.7 (CH), 139.6 (C), 141.5 (C), 167.6 (CO) and 168.0 (CO). EM (EI): 377 (M<sup>+</sup>+1, 0.6), 376 (M<sup>+</sup>, 2.9), 360 (5.3), 331 (5.2), 286 (13.3), 257 (65.7), 241 (100.0), 209 (32.3), 135 (79.5), 92 (17.8), 91 (57.8) and 65 (28.8). HMRS: exact mass calcd for C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>S (M<sup>+</sup>) 376.1345, found 376.1349.

**(R<sub>9a</sub>,S<sub>5</sub>)-1,1-Diethoxycarbonyl-2-p-tolylsulfinylbicyclo[4.5.0]-3,4-undecadiene 9b**

Dates from a mixture of **9b**+**9c** (ratio 88:12). Yield: 56%. Eluent: Hexane–AcOEt 3:1.  $[\alpha]_D^{20} = -322.25$  ( $c=2.3$ , CHCl<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.97 (t, 3H,  $J=7.1$  Hz, CH<sub>3</sub>), 1.16 (d, 3H,  $J=7.1$  Hz, CH<sub>3</sub>), 1.32–1.86 (m, 7H, cyclo), 2.33–2.45 (m, 3H, cyclo), 2.37 (3H, s, CH<sub>3</sub>Ar), 3.03 (dd, 1H,  $J=2.9$  and 10.8 Hz), 3.81 (m, 2H, CH<sub>2</sub>), 4.24 (m, 2H, CH<sub>2</sub>), 5.82 (d, 1H,  $J=5.7$  Hz, H<sub>4</sub>), 6.91 (d, 1H,  $J=5.7$  Hz, H<sub>3</sub>), 7.23 (AA'BB' system, 2H,  $J=8.2$  Hz, arom.) and 7.60 (AA'BB' system, 2H,  $J=8.2$  Hz, arom). EM (EI): 430 (M<sup>+</sup>, 1.2), 414 (8.9), 357 (8.6), 312 (18.1), 311 (75.3), 295 (100), 285 (11.4), 263 (19.6), 235 (17.3), 217 (23.7), 189 (56.5), 139 (19.0) and 91 (44.0). HMRS: exact mass calcd for C<sub>24</sub>H<sub>30</sub>O<sub>5</sub>S (M<sup>+</sup>) 430.1814, found 430.1808.

**(R<sub>10a</sub>,S<sub>5</sub>)-1,1-Diethoxycarbonyl-7-methoxy-2-p-tolylsulfinyl-1,9,10,10a-tetrahydropheanthrene 9d**

Yield: 74%. Eluent: Hexane–AcOEt 2:1  $[\alpha]_D^{20} = -192.2$  ( $c=1$ , CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>): 2960, 1720, 1600, 1570, 1490, 1230, 1210, 1090 and 1040. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.19 (t, 3H,  $J=7.1$  Hz, CH<sub>3</sub>), 1.23

(d, 3H,  $J=7.3$  Hz,  $\text{CH}_3$ ), 1.96 (m, 1H,  $\text{H}_{10}$ ), 2.28 (m, 1H,  $\text{H}_{10}$ ), 2.40 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 2.72 (m, 2H,  $\text{H}_9$ ), 3.59 (m, 1H,  $\text{H}_{10a}$ ), 3.81 (s, 3H, OMe), 3.94 (m, 2H,  $\text{CH}_2$ ), 4.16 (m, 2H,  $\text{CH}_2$ ), 6.6 (d, 1H,  $J=3.0$  Hz,  $\text{H}_4$ ), 6.63 (d, 1H,  $J=2.3$  Hz,  $\text{H}_8$ ), 7.22 and 7.28 (AA'BB' system, 4H,  $J=1$  Hz, arom), 7.63 (d, 1H,  $J=9.2$ ,  $\text{H}_3$ ) and 7.67 (d, 1H,  $J=8.4$  Hz,  $\text{H}_5$ ). EM (EI): 496 (0.7,  $\text{M}^+ + 2$ ), 495 (3.5,  $\text{M}^+ + 1$ ), 494 (13.0,  $\text{M}^+$ ), 478 (32.1), 404 (31.8), 376 (17.8), 375 (70.7), 360 (26.1), 359 (100.0), 283 (22.4), 282 (87.9), 253 (43.1), 252 (42.7), 209 (41.0), 165 (58.6), 92 (18.1) and 91 (35.8). HMRS: exact mass calcd for  $\text{C}_{28}\text{H}_{30}\text{O}_6\text{S}$  ( $\text{M}^+$ ) 494.1763, found 494.1765.

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17. We failed in all the trials to obtain crystals from **9a** and **9d**, suitable for X-ray diffraction studies. We had the same problem with sulfone **10** (obtained by MCPBA oxidation of **9a**) and alcohol **11**, (resulting in the stereoselective hydroboration of **9d**) which were prepared with this aim.
18. We must also consider that the stereoelectronic interactions between the geminal ester groups in rotamer **A**, should produce distortions in the coplanarity decreasing its relative stability.
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