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A Sulfinyl Trialkoxycarbonyl Ethene as a New Enantiopure Dienophile in Asymmetric Diels-Alder Reactions

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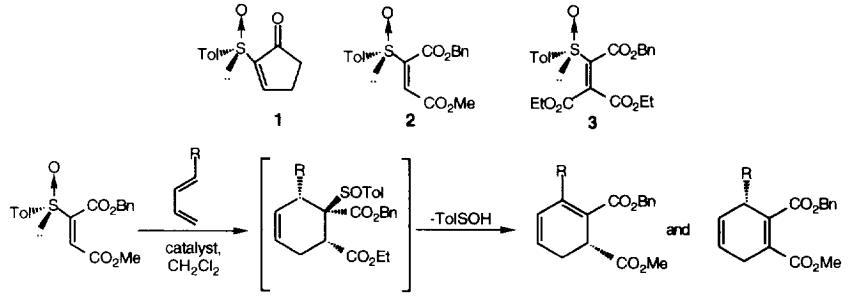
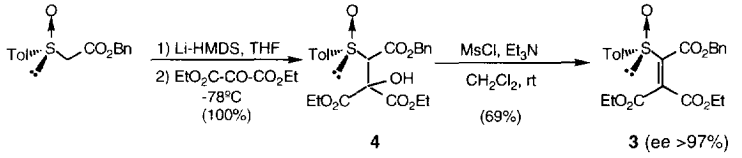
Abstract: The synthesis and the asymmetric Diels-Alder reactions of the enantiomerically pure (*S*)-*p*-tolylsulfinyl trialkoxycarbonyl ethene **3** with cyclic and acyclic dienes are reported. π-Facial selectivity and regioselectivity are very high in all studied cases. Reactions with cyclopentadiene exhibit moderated or high *exo*-selectivity, which disappears with acyclic dienes. The use of high pressure improves the π-facial selectivity but does not substantially modify the *endo-exo* selectivity.

During the last two decades the asymmetric Diels-Alder reaction from enantiopure dienophiles has known an impressive development, showing that several types of chiral dienophiles react in a highly and predictable stereoselective manner.[1] In particular, the use of vinylsulfoxides in asymmetric Diels-Alder reactions is receiving an increasing attention due to the potential ability of the sulfinyl group, directly joined to the dienophilic double bond, to control efficiently the stereoselectivity of the cycloadditions. However, the low dienophilic reactivity of vinylsulfoxides determines that other activating groups must be attached to the double bond.[1] In this field, we have recently described that the Diels-Alder reactions of mono- and diactivated vinylsulfoxides[2], (*S*)-*p*-tolylsulfinyl-2-cyclopentenone (**1**)[3] and (*S*)-2-*p*-tolylsulfinyl maleates **2**[4], catalyzed by Lewis acids, take place with very high regioselectivity, *endo* selectivity and π-facial selectivity. The cyclohexenes resulting from the reactions of diesters **2** with acyclic dienes evolve quickly at rt into cyclohexadienes by pyrolytic elimination of the sulfinyl group. The problems associated to the use of these diesters derive from its moderated reactivity (they require acid catalysts) and mainly from the fact that the pyrolytic elimination is not regioselective in the case of the adducts resulting from 1-substituted dienes (scheme 1). In order to avoid these problems, we decide to study the behavior as a dienophile of a triactivated enantiopure vinylsulfoxide, the (*S*)-*p*-tolylsulfinyl trialkoxycarbonyl ethene **3**, the adducts of which could only evolve into the conjugated cyclohexadienes. In this paper we report the results obtained from this study.



Scheme 1

Dienophile **3** was readily prepared in two steps (scheme 2). Deprotonation of (*R*)-benzyl *p*-tolylsulfinyl acetate[4b] with Li-HMDS (1.2 equiv) in THF and further reaction at -78°C with diethyl oxomalonate furnished quantitatively the corresponding alcohol **4**. Dehydration of crude **4** was performed by reaction with MsCl/Et_3N in CH_2Cl_2 at rt, affording pure olefin **3** in 69% yield after flash chromatography. The optical purity of **3** (ee> 97%) was established by ^{1}H-NMR analysis of both **3** and its racemic (±)-**3** (prepared from the corresponding racemic sulfinyl acetate) in the presence of 0.2 equiv of Yb(hfc)$_3$.

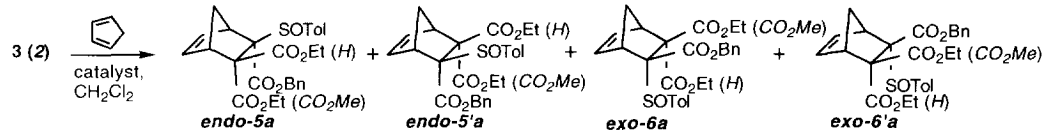


Scheme 2

In Table 1 are shown the results obtained in the reaction of **3** with an excess of cyclopentadiene under different conditions. We have also included the results obtained from diester **2** under similar conditions taken from reference 4b. The *endo* or *exo* denominations used in this paper are related to the stereochemistry of the two ester groups displaying a *cis*-arrangement in the dienophile, which is valid for the adducts resulting from both dienophiles **2** and **3**.

All the cycloadditions occurred in high yields (76-89%), affording mixtures of three adducts: the two possible *exo* adducts, *exo*-**6a** and *exo*-**6'a**, and only one *endo* adduct, *endo*-**5'a**. After flash chromatography, the *endo*-**5'a** adduct could be conveniently separated and its absolute configuration was unequivocally determined by X-ray diffraction (Fig 1).[5]

Table 1. Diels Alder reactions of dienophiles **3** and **2** (values in brackets taken from reference 4b) with cyclopentadiene.



				Isomer ratio[b]			
Entry	Catalyst (equiv)	Conditions	Yield (%)[a]	*endo*-**5a**	*endo*-**5'a**	*exo*-**6a**	*exo*-**6'a**
1	----	20°C, 72h	83	-- (73)	30 (8)	8 (19)	62 (--)
2	Eu(fod)$_3$ (1.2)	0°C, 2h	77	-- (66)	30 (3)	8 (31)	62 (--)
3	$ZnBr_2$ (1.8)	-10°C, 2h	89	-- (6)	45 (91)	-- (3)	55 (--)
4	$TiCl_4$ (1.2)	-78°C, 1h	76	-- (83)	6 (13)	4 (4)	90 (--)

[a] In pure product after chromatographic purification. [b]Determined by ^{1}H-NMR.

The mixture **6a+6'a** was oxidized with MCPBA into their corresponding sulfones **8** and **8'**, which exhibit the same ^{1}H-NMR spectrum (only one set of signals was observed). This demonstrates that both sulfones are enantiomers, and therefore they, as well as the starting sulfoxides **6a** and **6'a**, must exhibit the same *endo*- or *exo*-configuration. As the stereochemistry of **5'a** had been unequivocally established as *endo*, the *exo* configuration must be assigned to **6a** and **6'a**, as well as the enantiomeric sulfones **8** and **8'**. This was

confirmed by oxidation of the sulfoxide *endo*-**5'a** into the sulfone *endo*-**7**, which shows ^{1}H-NMR spectrum different to that of the sulfone *exo*-**8**. Finally, the results obtained from compounds **2** and **3** allowed us the stereochemical assignment of the exo adducts **6a** and **6a'**. As it can be seen in Table 1, both dienophiles showed an opposite π-facial selectivity for the *endo* approach, (starting from **3** the adduct **5'a** is exclusively formed, whereas in the reactions from dienophile **2** the *endo* adduct with similar stereochemistry to that of **5'a** is the minor, except in reaction catalyzed by $ZnBr_2$), and this should also be the case for the *exo* approach. Therefore, we have assigned to the major *exo*-adduct (*exo*-**6'a**) obtained from **3** the same stereochemistry to that of the *exo*-adduct,which is not formed from dienophile **2**.

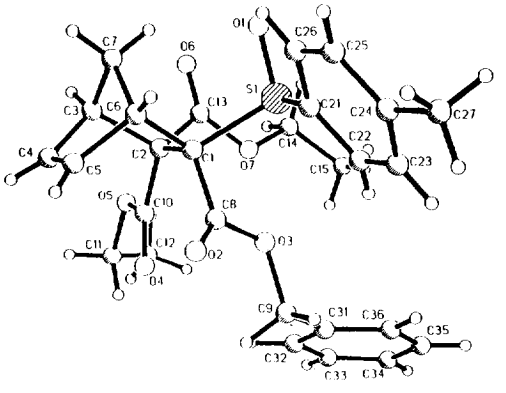


Fig1: X-ray crystal structure of compound *endo-5'a.*

The comparison of the results obtained from diester **2** with those from triester **3** (see Table 1 and reference 4b) shows that the reactivity of **3** is only slightly higher than that of **2**, which indicates a low influence of the third activating group, perhaps due to the steric resonance inhibition. On the other hand, both π-facial and *endo/exo* selectivities are the opposite from each dienophile, and thus *exo*-**6'a** (the major diastereoisomer obtained from **3**) is not observed starting from **2**, whereas *endo*-**5a** (the major component of the mixture obtained from **2** in the most of the conditions) is not detected in the reactions from **3**. Moreover, the proportion of diastereoisomers obtained from **3** was less dependent on the nature of the catalyst than that derived from **2**. The uncatalyzed reaction of **3** (entry 1) as well as those performed under $Eu(fod)_3$ (entry 2) and $ZnBr_2$ (entry 3) catalysis, took place with low *exo/endo* selectivity (*exo/endo* < 2.5). Only the reaction catalyzed by $TiCl_4$ (entry 4) is highly *exo* selective (*exo/endo* = 15). Additionally, the π-facial selectivity is complete for the *endo* approach on dienophile **3** and very high for the *exo* one.

The observed differences in the behavior of both dienophiles (**2** and **3**) can be explained on the basis of the conformational preferences around the C-S bond. Thus, in Fig 2 are depicted the presumably favored conformations for **2** and **3**. Rotamer **A-2**, exhibiting the *s-cis* arrangement of the sulfinyl oxygen, was suggested as the most reactive conformation for compound **2**.[4b] By the contrary, conformation **A-3** must be strongly unstabilized due to the interaction SOTol/CO_2Me, which precludes the ester group and the sulfinyl oxygen became coplanar with the double bond. It suggests that **B-3** or **C-3** were the most stable rotamers for compound **3**.[6] If we assume that the favored approach of the diene takes place from the less hindered face of the dienophile, the fact that such face was the opposite in conformations **A-2** than in **B-3** or **C-3**, would explain the observed changes in the π-facial selectivity. These conformational preferences could also be related to the different *endo/exo* selectivity exhibited by both dienophiles, although this could be attributed to the *endo* orientating character of the substituents[7]. On the other hand, the fact that the third ester group was not conjugated would explain its moderate influence on the dienophilic reactivity.

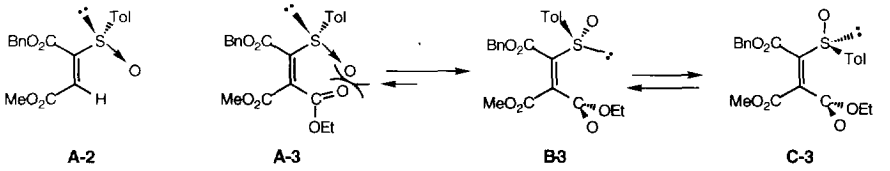
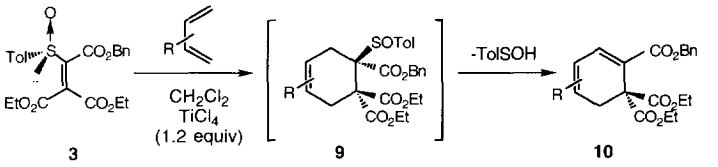
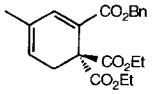
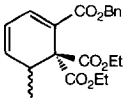
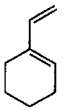
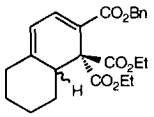
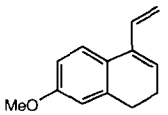
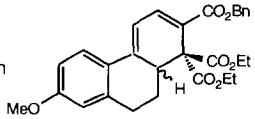


Fig 2. Presumably favored conformations for dienophiles **2** and **3**.

In a second step, we have studied the reactions of **3** with several acyclic dienes. The reactions were studied under $TiCl_4$ catalysis due to the low conversion obtained under thermal conditions or under $ZnBr_2$ or $Eu(fod)_3$ catalysis. The results are given in Table 2.

Table 2. Diels-Alder reaction of **3** with acyclic dienes catalyzed by $TiCl_4$ in CH_2Cl_2 at -78°C.



Entry	Diene	Reaction times	Product	Yield (%)[a]	ee (%)[b]
1		1 h	 **10a**	78	–
2		1 h	 **10b**	87	16
3		30 min	 **10c**	87	18
4		30 min	 **10d**	89	8

[a] In pure product after flash chromatography. [b] Determined by ^{1}H-NMR in the presence of $Pr(hfc)_3$.

As in the case of the reactions of **2** with acyclic dienes,[4b] the adducts **9**, derived from **3**, were not stable (they could not be detected by ^{1}H-NMR) and rapidly evolved by clean elimination of the sulfinyl group to give 1,3-cyclohexadienes **10**, which were isolated after chromatography in 78-89% yield. The reactions took place in

very mild conditions (-78°C, < 1 h in CH_2Cl_2) with 80-90% yields, and afforded only one regioisomer. From the structure of compounds **10** we can conclude that the regioselectivity of the cycloaddition is controlled by the olefinic carbon supporting the *gem*-diester group, (the *gem*-diester group adopts the "*ortho*" and "*para*" positions with respect to the diene substituents at C-1 (entry 2) and C-2 (entry 1) respectively). For 1,2-disubstituted dienes (entries 3 and 4) the favored orientation is that determined by substituents at C-1. Interestingly the observed regioselectivity for dienophiles **3** and **2**[4b] is the opposite, because in the last one, it was controlled by the olefinic carbon bearing the CO_2Bn and SOTol groups. These results suggest that the orientating effect of a CO_2R group is larger than that of a SOTol one.

Unfortunately, the optical purity of dienes **10**, determined by ^{1}H-NMR in the presence of $Pr(hfc)_3$, is very low (8-18 % *ee*). This suggests that the use of acyclic dienes determines a strong decrease of either the π-facial selectivity or the *endo/exo* selectivity (or both). Taking into account the behavior of compound **2** (the π-facial selectivity increased with the use of acyclic dienes and only one *endo* and one *exo* adducts were isolated) we propose that the low optical purity of compounds obtained from **3** must be attributed to the strong decrease of the *endo/exo* selectivity, determining the initial formation of nearly 1:1 mixtures of *endo*-**9** and *exo*-**9** adducts, which respectively evolve into a different enantiomer of compound **10**. As the reactions of **2** with acyclic dienes catalyzed by $TiCl_4$ were more *endo* selective than those with cyclopentadiene,[4b] and the reaction of **3** with cyclopentadiene takes place with high *exo*-selectivity (see Table 1), the increase of the *endo* adduct proportion in reaction of **3** with acyclic dienes, and therefore the decrease of the *endo/exo* selectivity, is not unexpected.[8]

Finally, we have studied the effect of the high pressures on some of these reactions, with the aim of improving the stereochemical results (Table 3).

Table 3. Effect of the presence in the Diels-Alder reactions of **3** with cyclopentadiene and piperylene.

Entry	Diene	Catalyst	Pressure	Reaction Time	Product	Yield (%)
1	Cyclopentadiene	--	10 Kbar	22 h	*exo*-**6'a** (60%)+*endo*-**5'a** (40%)[a]	89
2			1 bar	3 days	*exo*-**6'a** (62%)+ *exo*-**6a** (8%) +*endo*-**5'a** (30%)[a]	83
3	Piperylene	--	8 Kbar	48 h	**10b** (26% *ee*)	72[b]
4			1 bar	7 days	---[c]	---[c]
5	Piperylene	$ZnBr_2$	12 Kbar	36 h	**10b** (17% *ee*)	60
6			1 bar	7 days	**10b** (24% *ee*)	19[d]
7	Piperylene	$Eu(fod)_3$	11 Kbar	48 h	**10b** (4% *ee*)	85
8			1 bar	7 days	---[e]	---[e]

[a] Determined by ^{1}H-NMR on the crude mixtures. [b] 38% of starting dienophile was recovered. [c] No reaction was observed. [d] 81% of starting dienophile was recovered. [e] Complex mixture was obtained.

We have studied only those reactions which at room temperature require long reaction times or do not work. As a consequence of the high pressure, the reactivity is substantially increased. Thus, piperylene reacted under high pressure without catalyst (entry 3) or under $Eu(fod)_3$ or $ZnBr_2$ catalysis (entries 5 and 7), whereas all these transformations were not satisfactory at normal pressure (entries 4, 6 and 8). The influence of the pressure on the stereoselectivity can be deduced from the results obtained in the reaction with cyclopentadiene. At normal

pressure, the π-facial selectivity is high but not complete for the *exo* approach (two *exo* adducts are obtained, entry 2), whereas at 10 Kbar, only one *exo* adduct was detected (entry 1). The *endo* approach is completely stereoselective in both conditions. This behavior suggests that the high pressure increases the π-facial selectivity. Nevertheless, the *exo/endo* selectivity is scarcely modified by the pressure and it varies from *exo /endo*= 1.5 at high pressure (entry 1) to *exo /endo*= 2.3 at normal pressure (entry 2). This is also the case in reactions with piperylene. The *ee* of the isolated cyclohexadienes are low and similar to that observed at normal pressure. These results support the assumption that the decrease of the *endo/exo* selectivity must be the main responsible of the low optical purity of the compounds **10** obtained by reaction of triester **3** with acyclic dienes (see above).

From these studies we can conclude that the incorporation of a third ester group into the maleates **2** has scarce influence on its reactivity, but it inverts both the regioselectivity and the π-facial selectivity of their cycloadditions. The *exo* selectivity is also increased which determines that almost equimolecular mixtures of *endo* and *exo* adducts were obtained from acyclic dienes.

EXPERIMENTAL

Melting points were determined with a Gallenkamp apparatus in open capillaries and are uncorrected. ^{1}H-NMR spectra and ^{13}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 the relative intensity from base peak (as 100%). High-resolution mass spectra were determined at an ionizing voltage of 70 eV. Infrared (IR) spectra were recorded on a Philips PU-9716 spectrometer. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. High pressure data were obtained from a High Pressure Apparatus (Unipressequipment Division), maximun pressure 1.3GPa.

Analytical thin-layer chromatography was performed on DC-Alufolien 0.2 mm silica gel 60-F plates (MERCK). Visualization was accomplished with UV light, iodine and ethanolic fosfomolybdic acid solution followed by heating. Flash chromatography was performed by use of 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 P_2O_5. Diisopropylamine was distilled from sodium hydroxide. Cyclopentadiene was freshly distilled. Zinc bromide was dried at 160°C for 12h with P_2O_5 under vacuo. Eu(fod)$_3$, $TiCl_4$, isoprene, *trans*-1,3-pentadiene, were purchased from Aldrich and used without further purification. Vinylcyclohexene and Dane's diene were prepared according to described procedures.[9] (+)-(*R*)-Benzyl *p*-tolylsulfinylacetate was described according to reference 4b.

(+)-(*S*)-Benzyl 3,3-diethoxycarbonyl-2-*p*-Tolylsulfinylpropenoate (3).

A solution of (+)-(*R*)-benzyl *p*-tolylsulfinylacetate (1.0 g, 3.5 mmol, 1.0 equiv) in THF (17 ml) was added, under argon atmosphere, to a solution of Li-HMDS 1M in THF (4.2ml, 4.2 mmol, 1.2 equiv), cooled to -78°C. After being stirred for 30 min, a solution of diethyl oxomalonate (587 µl, 3.8 mmol, 1.1 equiv) was slowly added. Stirring was continued for 4 h. Then, a solution of saturated NH_4Cl (10 ml) was added, and the mixture was extracted with CH_2Cl_2 (2x20 ml). The combined organic layers were dried ($MgSO_4$), and concentrated to give crude **4** (^{1}H NMR δ: 1.15 (t, 3H, J = 7.3Hz), 1.16 (t, 3H, J = 7.3 Hz), 1.36 (t, 3H, J =

7.3 Hz), 1.37 (t, 3H, J = 7.3 Hz), 2.38 (s, 3H), 4.16 (m, 4H), 4.37 (m, 4H), 4.70 (s, 1H), 4.85 (s, 1H), 4.90 (AB system, 2H, J = 11.9 Hz), 5.16 (AB system , 2H, J = 12.1 Hz), 7.14-7.36 (m, 14H), 7.55-7.59 (half on an AA'BB' system, 2H), 7.57-7.61 (half on an AA'BB' system, 2H). Crude **4** was dissolved in dry CH_2Cl_2 (14 ml), and Et_3N (1.9 ml, 14 mmol, 4.0 equiv) and MsCl (1.1 ml, 14 mmol, 4.0 equiv) were added at 0°C. The mixture was allowed to stand at rt for 1 h. The mixture was treated with 10% HCl (10 ml) and extracted with CH_2Cl_2 (2x20 ml). The combined organic layers were washed with water (15 ml), dried ($MgSO_4$), and concentrated. The residue was purified by chromatography (hexane-ethyl acetate 4:1) to give 1.08g (69%) of **3**. $[\alpha]^{20}_D$= +71.69 (c = 1.06, $CHCl_3$), ee ≥ 97% . IR ($CHCl_3$): 2990, 1725, 1495, 1455, 1370, 1260, 1090, and 1020 cm^{-1}.^{1}H NMR δ: 1.21 (t, 2H, J = 7.1 and 7.3 Hz), 1.38 (t, 2H, J = 7.1 and 7.3 Hz), 2.38 (s, 3H), 4.15 (q, 3H, J = 7.1 Hz), 4.40 (q, 3H, J = 7.1 Hz), 5.11 (s, 2H), 7.18-7.34 (m, 7H), and 7.59-7.63 (half on an AA'BB' system , 2H).^{13}C NMR δ: 13.6, 13.8, 21.3, 62.7, 68.0, 125.8, 128.3, 128.4, 128.5, 129.9, 134.1, 137.3, 142.7, 151.3, 160.5, 160.7, and 162.0. MS (EI):444 (5.6, M^+), 399 (7.8), 337 (14.2), 289 (7.2), 215 (14.5), 171 (14.4), 139 (32.8), 123 (11.9), and 91 (100). HRMS: exact mass calcd for $C_{23}H_{24}O_7S$-(M^+) 444.124275, found 444.124050.

Diels-Alder reaction of 3 with cyclopentadiene catalyzed by Eu(fod)$_3$.

A solution of **3** (50.0 mg, 0.11 mmol, 1.0 equiv) in 0.3 ml CH_2Cl_2 was added, under an argon atmosphere, to a solution of Eu(fod)$_3$ (136.9 mg, 0.13 mmol, 1.2 equiv) in 0.3 ml of CH_2Cl_2 at 0°C. The mixture was stirred for 10 min, and then 55 µl (0.66 mmol, 6 equiv) of cyclopentadiene was added. Stirring was continued for 2h. Then, 5% HCl (3 ml) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2x10 ml). The combined organic layer were washed with water (2 ml), dried ($MgSO_4$), and concentrated. The mixture was analyzed by ^{1}H NMR (isomer ratio: 30% *endo-**5'a***, 8% *exo-**6a***, and 62% *exo-6'a),* and purified by flash cromatgraphy (CH_2Cl_2-Et_2O 40:1) to give 43.2 mg (77% yield) of adducts.

Diels-Alder reaction of 3 with cyclopentadiene catalyzed by ZnBr$_2$.

A solution of **3** (91.0 mg, 0.20 mmol, 1.0 equiv) in 0.5 ml CH_2Cl_2 was added, under an argon atmosphere, to a suspension of $ZnBr_2$ (81.1 mg, 0.36 mmol, 1.8 equiv) in 0.5 ml of CH_2Cl_2 at -10°C. The mixture was stirred for 10 min, and then 102 µl (1.2 mmol, 6 equiv) of cyclopentadiene was added. Stirring was continued for 2h at -10°C. Then, 10% $NaHCO_3$ (5 ml) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2x15 ml). The combined organic layer were washed with water (5 ml), dried ($MgSO_4$), and concentrated. The mixture was analyzed by ^{1}H NMR (isomer ratio: 45% *endo-**5'a***, 8% *exo-**6a***, and 55% *exo-**6'a**),* and purified by flash cromatography (CH_2Cl_2-Et_2O 40:1) to give 90.8 mg (89% yield) of adducts.

General procedure for the Diels-Alder reaction of 3 catalyzed by TiCl$_4$.

$TiCl_4$ (0.30 mmol, 1.2 equiv from a solution 1.0 M in CH_2Cl_2) was added dropwise, under argon atmosphere, to a solution of dienophile **3** (110 mg, 0.25 mmol, 1.0 equiv) in 1.2 ml of CH_2Cl_2 at -78°C. The mixture was stirred for 10 min, and then 6 equiv (1.5 mmol) of the corresponding diene was added. Stirring was continued until dienophile disappered by TLC (the reaction times are indicated in tables 1-2). Then, 10% $NaHCO_3$ (4 ml) was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2x10 ml). The combined organic layers were washed with water (5 ml), dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography (eluents are indicated below for each case and yields are indicated in tables 1 and 2).

General procedure for the Diels-Alder Reactions of 3 under high pressure.

In a high pressure reaction tube was placed a solution of **3** (35 mg, 0.08 mmol, 1.0 equiv) and cyclopentadiene or piperylene (10 equiv) and the catalyst (1.5 equiv of $ZnBr_2$ or $Eu(fod)_3$) in 1.7 ml CH_2Cl_2. After standing at rt for the reaction times and pressures indicated in table 3, the reactions were allowed to reach atmospheric pressure and were treated and isolated as in the case of the reactions conducted under normal pressure (yields are indicated in table 3)

(*S*$_1$,*S*$_2$,*R*$_4$,*S*$_S$)-Benzyl 3,3-diethoxycarbonyl-2-(*p*-tolylsulfinyl)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (*endo-5'a*).

Diene: Cyclopentadiene. Eluent: CH_2Cl_2-Et_2O 40:1. MP: 117-123°C. $[\alpha]^{20}_D$ = +20.6 (c = 2.0, $CHCl_3$). IR ($CHCl_3$): 2990, 1730, 1460, 1255, 1080, and 1060 cm^{-1}. ^1H NMR δ: 1.19 (t, 3H, J = 7.1 Hz), 1.37 (t, 3H, J = 7.1 Hz), 1.41 (dt, 1H, J = 1.63 and 3.29 Hz), 2.39 (s, 3H), 2.68 (dt, 1H, J = 1.63 and 3.29 Hz), 3.08 (m, 1H), 3.57 (m, 1H), 4.07 (m, 2H), 4.41 (m, 2H), 5.01 and 5.08 (AB system, 2H, J = 3.2 and 5.4 Hz), 7.21-7.23 (half of an AA'BB' system, 2H), and 7.32-7.39 (m, 7H). ^{13}C NMR δ: 13.9, 21.5, 45.4, 47.31, 51.6, 61.9, 62.4, 66.9, 67.6, 82.4, 126.2, 126.4, 127.8, 128.1, 128.4, 129.6, 135.2, 136.4, 137.5, 141.9, 142.5, 167.6, 167.9, and 168.7. MS (EI): 510 (0.1, M^+), 494 (3.6), 403 (8.2), 371 (14.7), 139 (12.5), 91 (100), and 65 (16.1).

(*R*$_1$,*S*$_2$,*S*$_4$,*S*$_S$)-Benzyl 3,3-diethoxycarbonyl-2-(*p*-tolylsulfinyl)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (*exo-6'a*).

Diene: Cyclopentadiene. Eluent: CH_2Cl_2-Et_2O 40:1. $[\alpha]^{20}_D$ = +7.98 (c = 2.77, $CHCl_3$). IR ($CHCl_3$): 2290, 1730, 1460, 1255, 1080, and 1060 cm^{-1}. ^1H NMR δ: 1.16 (t, 2H, J = 7.1 Hz), 1.35 (t, 2H, J = 7.1 Hz), 1.57 (dt, 1H, J = 1.7 and 9.7 Hz), 2.15 (bd, 1H, J = 6.3 Hz), 2.37 (s, 3H), 3.36 (bs, 1H), 3.47 (bs, 1H), 3.91 (m, 3H), 4.18 (m, 3H), 4.81 (AB system, 2H, J = 13.6 Hz), 6.44 (dd, 1H, J = 3.0 and 5.5 Hz), 6.70 (dd, 1H, J = 3.0 and 5.5 Hz), 7.20-7.37 (m, 7H) and 7.58-7.63 (half on an AA'BB' system, 2H). ^{13}C-NMR: 13.7, 13.9, 21.3, 46.7, 53.4, 61.9, 62.1, 67.1, 85.9, 126.3, 127.7, 128.0, 128.4, 129.2, 129.6, 136.8, 137.6, 138.9, 141.5, 141.8, 167.2, 168.1, and 169.9. MS (EI): 510 (0.2, M^+), 494 (3.1), 403 (7.0), 371 (14.2), 139 (15.9), 91 (100), and 65 (15.7).

Benzyl 6,6-diethoxycarbonyl-3-methyl-1,3-cyclohexadien-1-carboxylate (10a).

Diene: isoprene. Eluent: CH_2Cl_2. IR ($CHCl_3$): 2980, 1720, 1450, 1370, 1255, 1200, 1040, 1020, and 860 cm^{-1}. ^1H NMR δ: 1.18 (t, 6H, J = 7.1 Hz), 1.82 (q, 3H, J = 1.9 Hz), 3.01 (m, 2H), 4.13 (dq, 4H, J = 2.3 and 7.2 Hz), 5.22 (s, 2H), 5.83 (m, 1H), 7.14 (d, 1H, J = 1.3 Hz), and 7.29-7.39 (m, 5H). MS (EI): 313 (16.0), 281 (2.5), 271 (25.0), 252 (16.9), 237 (3.9), 224 (21.5), 208 (13.4), 167 (4.8), 135 (19.4), 119 (35.6), 91 (100), and 65 (5.8).

Benzyl 6,6-diethoxycarbonyl-5-methyl-1,3-cyclohexadien-1-carboxylate (10b).

Diene: piperylene. Eluent: hexane- ethyl acetate 4:1. ee=24% ($ZnBr_2$). $[\alpha]^{20}_D$ = -21.0 (c = 1.42, $CHCl_3$). IR ($CHCl_3$): 2980, 2940, 1720, 1450, 1375, 1260, 1210, 1100, and 1030 cm^{-1}. ^1H NMR δ: 1.16 (t, 2H, J = 7.0 Hz), 1.18 (t, 3H, J = 7.0 Hz), 1.24 (d, 2H, J = 7.4 Hz), 3.37 (m, 1H), 4.13 (m, 6H), 5.21 (s, 2H), 6.07 (m, 2H), 7.21 (dd, 1H, J = 1.3 and 5.2), and 7.31-7.38 (m, 5H).^{13}C NMR δ: 13.9, 14.0, 15.3, 37.4, 61.3, 61.9, 66.5, 122.0, 128.2, 128.4, 128.5, 129.9, 134.5, 135.9, 139.7, 166.7, 168.6, and 168.9. MS (EI): 327 (0.2), 253 (6.7), 191 (10.0), 163 (18.5), 119 (6.8), 91 (100), and 65 (6.1).

Benzyl 1,1-diethoxycarbonyl-1,5,6,7,8,8a-hexahydronaphtalene-2-carboxylate (10c).

Diene: Vinylcyclohexene. Eluent: hexane-ethyl acetate 4:1. ee=18%. $[\alpha]^{20}_D$ = + 60.06 (c = 1.7, $CHCl_3$). IR ($CHCl_3$): 2920, 1710, 1580, 1440, 1360, 1240, 1200, 1130, 1060, and 1020 cm^{-1}. ^1H NMR δ: 1.15 (t, 3H, J = 7.1 Hz), 1.16 (t, 3H, J = 7.1 Hz), 1.29-2.45 (m, 8H), 3.31 (m, 1H), 4.11 (m, 4H), 5.20 (s, 2H), 5.76 (1H, bd, J = 6.1 Hz), and 7.16 (1H, d, J =6.1 Hz). ^{13}C NMR δ: 13.8, 26.4, 29.2, 30.8, 35.8, 46.1, 59.0, 61.2, 61.8, 66.2, 114.6, 122.8, 128.0, 128.1, 128.4, 135.1, 136.3, 152.4, and 168.7. MS (EI): 412 (0.2), 3.39 (1.6), 293 (7.0), 231 (10.1), 203 (21.3), and 91 (100). HRMS: exact mass calcd for $C_{24}H_{28}O_6$-(M^+) 412.188589, found 412.187350.

Benzyl 1,1-diethoxycarbonyl-7-methoxy-1,9,10,10a-tetrahydrophenanthrene-2-carboxylate (10d).

Diene: Dane's Diene. Eluent: hexane-ehtyl acetate 10:1. ee = 8%. $[\alpha]^{20}_D$ = + 2.1 (c = 2.5, $CHCl_3$). IR ($CHCl_3$): 2980, 2920, 2820, 1710, 1600, 1530, 1490, 1445, 1365, 1260, 1200, 1120, and 1050 cm^{-1}. ^1H NMR δ: 1.09 (t, 2H, J = 7.2 Hz), 1.89 (t, 2H, J = 7.2 Hz), 1.86 (m, 1H), 2.51-3.29 (m, 4H), 3.42 (m, 1H), 3.83 (3H, s), 4.18 (m, 6H), 5.28 (AB system, 2H, J = 12.5 Hz), 6.49 (dd, 1H, J = 2.84 and 6.23 Hz), 6.78 (dd, 1H, J = 2.7 and 8.78 Hz), 7.38-7.41 (m, 5H), 7.39 (d, 1H, J= 7.4 Hz), and 7.60 (d, 1H, J = 8.7 Hz). ^{13}C NMR δ: 13.8, 13.9, 24.1, 31.2, 45.2, 55.3, 59.3, 61.1, 61.8, 66.3, 112.9, 113.3, 113.4, 125.5, 125.8, 126.2, 127.9, 128.1, 128.4, 136.3, 141.1, 143.9, 160.2, 165.1, 168.3, and 171.4. MS (EI): 490 (3.0, M^+), 445 (0.3), 371 (8.2), 3094 (16.1), 281 (20.8), 237 (7.7), 165 (5.3) and 91 (100). HRMS: exact mass calcd for $C_{29}H_{30}O_7$-(M^+) 490.199154, found 490.198850.

General procedure for the oxidation of sulfoxides *endo-5'a* and *exo-6'a*.

A solution of sulfoxide (*endo-5'a* or *exo-6'a*) (93mg, 0.182 mmol, 1.0 equiv) in 0.7 ml CH_2Cl_2 was added to a solution of MCPBA (50-60%) (126mg, 0.728 mmol, 2.0 equiv) in 1.5 ml of CH_2Cl_2 at 0°C. The mixture was stirred at 0°C for 1h, and then 10% $Na_2S_2O_3$ (5 ml) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 ml). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2x10 ml). The combined organic layers were washed with water (2 ml), dried ($MgSO_4$), and concentrated. The mixture was analyzed by ^1H NMR and purified by flash cromatography (CH_2Cl_2-hexane 3:1) to give 77.5 mg (81% yield) of sulfone **7** or **8**.

(*S1,S2,R4*)-Benzyl 3,3-diethoxycarbonyl-2-(*p*-tolylsulfonyl)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (7).

Eluent: CH_2Cl_2-hexane 3:1. IR ($CHCl_3$): 2980, 1720, 1330, 1260, 1220, 1140, and 1080 cm^{-1}. ^1H NMR δ: 1.15 (t, 3H, J= 7.2 Hz), 1.35 (t, 3H, J = 7.2 Hz), 1.08 (dt, 1H, J = 1.6 and 9.7 Hz), 2.75 (bd, 1H, J = 9.9 Hz), 2.36 (s , 3H), 3.09 (bs, 1H), 3.89 (bs, 1H), 3.99 (m, 2H), 4.30 (m, 2H), 4.83 (AB system, 2H), 6.43 (dd, 1H, J = 2.8 and 5.4 Hz), 6.69 (dd, 1H, J = 3.1 and 5.4 Hz), 7.19-7.40 (m, 7H), and 7.58-7.62 (half on an AA'BB' system, 2H).

(*R1,S2,R4*)-Benzyl 3,3-diethoxycarbonyl-2-(*p*-tolylsulfonyl)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (8).

Eluent: CH_2Cl_2-hexane 3:1. MP: 128-130°C. $[\alpha]^{20}_D$ = -2.1 (c =2.86, $CHCl_3$).IR ($CHCl_3$): 2980, 1720, 1330, 1260, 1220, 1140, and 1080 cm^{-1}. ^1H NMR δ: 1.05 (t, 3H, J = 7.2 Hz), 1.35 (t, 3H, J = 7.2 Hz), 1.47 (dt, 1H, J = 1.6 and 9.7 Hz), 2.26 (bd, 1H, J = 9.9 Hz), 2.31 (s, 3H), 3.21 (bs, 1H), 3.88 (m, 2H), 4.39 (m, 2H), 4.95 (AB system, 2H, J = 12.9 Hz), 6.43 (dd, 1H, J = 2.8 and 5.4 Hz), 6.67 (dd, 1H, J = 3.1 and 5.4

Hz), 7.15-7.40 (m, 7H) and 7.58-7.62 (half on an AA'BB' system, 2H).^{13}C NMR δ: 13.6, 21.5, 45.4, 51.5, 53.8, 61.8, 62.3, 67.6, 69.9, 88.5, 127.5, 127.8, 128.1, 129.1, 129.4, 134.7, 135.7, 137.5, 138.8, 144.7, 167.3, 167.6, and 170.2. MS (EI): 526 (15.8), 415 (20.8), 371 (44.2), 326 (7.8), 279 (18.3), 139 (14.6), 91 (100), and 65 (13.9).

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