(S*S*)-2-(*p*-Tolylsulfinyl)norborneno-*p*-benzoquinones: A New Type of Facially Perturbed Enantiopure Quinones

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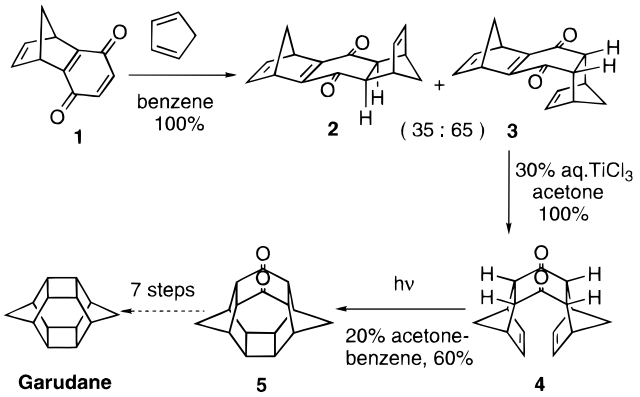
The syntheses and asymmetric Diels−Alder reactions of (S*S*)-2-(*p*-tolylsulfinyl)norborneno-*p*-benzoquinones **10** and **11** with cyclopentadiene are reported. The cycloadditions allowed the highly stereoselective obtention of the four possible *endo* adducts **12**−**15**, optically pure synthetic equivalents of norborneno-*p*-benzoquinone−cyclopentadiene bisadducts. The detailed study of the ^{1}H-NMR spectra of the adducts pointed out the anisotropic effects exerted by the sulfinyl moiety on the spectroscopic behavior of these rigid systems. In all cases, the π-facial selectivities were fully controlled by the sulfinyl group being possible to reverse the diastereoselection in thermal conditions and in the presence of $ZnBr_2$. The stereoselective synthesis of the cage compound **5**, precursor of garudane, was achieved from cycloadduct *endo-syn*-**13**.

Introduction

π-Facial diastereoselectivities in Diels−Alder reactions on π-facially perturbed dienes have been extensively investigated in the past years.[1] The observed results have been rationalized in terms of steric[2] or electronic[3] effects, product stability,[4] orbital interactions,[5] torsional effects,[6] or hyperconjugation.[7] In contrast, a few systematic experiments have been devoted to study the response of facially perturbed dienophiles in cycloadditions with various dienes.[8−13] Several groups have studied the behavior of dienophiles fixed on a norbornadiene skeleton and vinylogous systems. Thus, Edman and Simmons synthesized bicyclo[2.2.1]hepta-2,5-diene-2,3-carboxylic anhydride and observed an unexpected *exo* selectivity in the Diels−Alder reactions.[8] Houk *et al.* studied the cycloadditions of 7-substituted norbornadienes with hexachlorocyclopentadiene[9] and found the selectivity to be dependent on the electronegativity of the substituent. More recently, other sophisticated facially perturbed dienophiles have been prepared and their cycloadditions investigated.[10] With respect to quinones, Mehta and co-workers, following the work initiated by Cookson *et al.*,[11] reported a systematic investigation of the reactions of norbornano- and norbornenobenzoquinone **1** (Scheme 1) with several dienes finding a reversed stereochemical outcome in both systems.[12] The results obtained were applied to the synthesis of the polycyclic strained cage compound "garudane"[13] following the synthetic sequence depicted in Scheme 1.

Scheme 1



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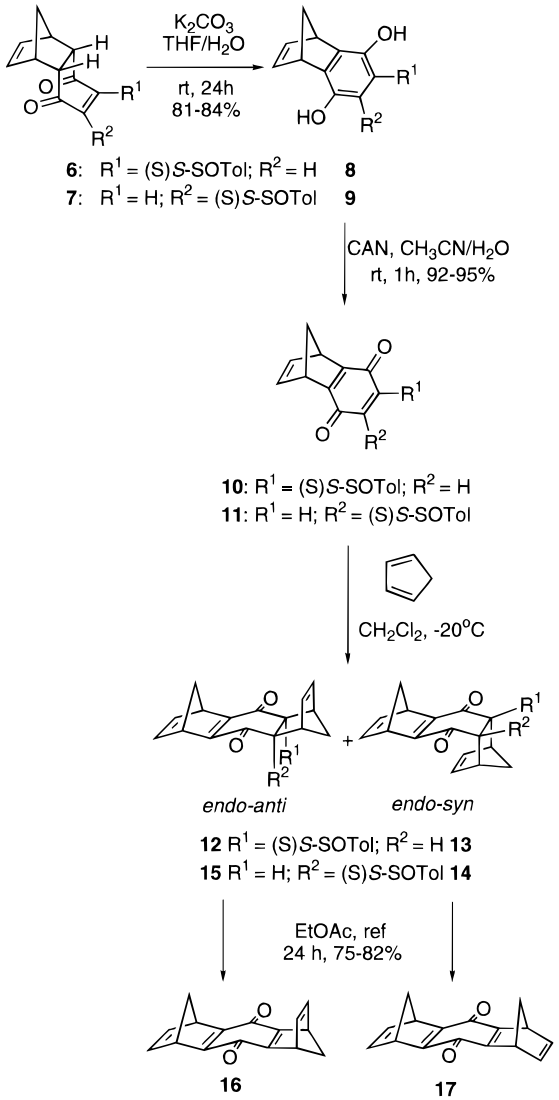
Scheme 2



Our previous work devoted to the use of sulfinylbenzo-[14] and naphthoquinones[15] as dienophiles had shown that π-facial diastereoselectivities of their Diels−Alder cycloadditions could be controlled by choosing the proper Lewis acid catalyst. Further studies[16] carried out on (S*S*)-4a,5,8,8a-tetrahydro-5,8-methano-2-(*p*-tolylsulfinyl)-1,4-naphthoquinones **6** and **7** (Scheme 2) revealed that both reactivity and *endo*/*exo* selectivity were modulated by the presence of the sulfinyl group, whereas the π-facial selectivity was imposed by the norbornene moiety which hindered diene approach to the bottom face of the dienophile.

Accordingly, we reasoned that the incorporation of a sulfoxide in the norbornenoquinone framework of **1** could substantially increase the π-facial diastereoselection in the cycloadditions of sulfinyl derivatives **10** and **11** compared to that observed for **1**. The study of these rigid substrates, having both faces accessible, should cast light on the role of the sulfoxide vs the norbornene moiety in the control of the π-facial diastereoselection which had not been evaluated in our previous models. Moreover, the cycloadducts obtained would be enantiomerically pure synthetic equivalents of norborneno-*p*-benzoquinone−cyclopentadiene bisadducts already used as key intermediates in the synthesis of bridged polycyclic molecules such as "garudane".[13]

Table 1. Diels−Alder Reactions of 10 and 11 with Cyclopentadiene

entry	dienophile	cat. (equiv)	time (h)	yield (%)	**12**:**13**	**14**:**15**
1	**10**		24	79	90:10	
2	**10**	$ZnBr_2$ (2)	1	87	0:100	
3	**11**		24	92		100:0
4	**11**	$ZnBr_2$ (2)	1	88		0:100

In this paper we describe the synthesis of sulfinylnorborneno-*p*-benzoquinones **10** and **11** and the results of their cycloadditions with cyclopentadiene under thermal conditions and in the presence of $ZnBr_2$. We also report the photochemical obtention of the cage compound **5** and the synthetic efforts made toward the transformation of cycloadduct **13** into a chiral substituted cage derivative of **5**.

Results and Discussion

Enantiomerically pure *p*-tolylsulfinylnorborneno-*p*-benzoquinones **10** and **11** were prepared in two steps from the previously described derivatives **6**[16] and **7**[16] as depicted in Scheme 2.

Thus, the treatment of **6** or **7** with K_2CO_3 in THF/H_2O afforded sulfinylnorbornenohydroquinones **8** (81% yield) and **9** (84% yield), respectively. Upon oxidation of the hydroquinone moiety with ceric ammonium nitrate (CAN) in CH_3CN/H_2O, sulfinylnorborneno-*p*-benzoquinones **10** and **11** were obtained in 92% and 95% yield, respectively.

The Diels−Alder reactions of dienophiles **10** and **11** with cyclopentadiene were carried out under thermal and $ZnBr_2$-catalyzed conditions; the results obtained are collected in Scheme 2 and Table 1.

As can be seen, the cycloaddition of benzoquinone derivative **10** with cyclopentadiene in CH_2Cl_2 at −20 °C afforded two diastereoisomeric adducts *endo-anti*-**12** and *endo-syn*-**13** (Scheme 2) in a 90:10 ratio (Table 1, entry 1). Both adducts resulted from the *endo* approach of the diene on the two diastereotopic faces of the dienophile. In the same conditions, compound **11** evolved to give cycloadduct *endo-syn*-**14** as a sole diastereoisomer (Table 1, entry 3). In the presence of $ZnBr_2$ the Diels−Alder reactions of dienophiles **10** and **11** with cyclopentadiene were faster than in thermal conditions (Table 1, entries 2 and 4) and afforded respectively adducts *endo-syn*-**13** and *endo-anti*-**15** with a total control of the π-facial selectivity. All derivatives **12**−**15** obtained in these reactions could be isolated diastereoisomerically pure by flash chromatography (see Experimental Section).

Configurational assignment of adducts **12**−**15** was based on a simple chemical correlation with the known compounds **16**[12a] and **17**[12a] (Scheme 2). Thus, *endo-anti* cycloadducts **12** and **15** evolved into compound **16** upon heating in EtOAc solution, whereas the same pyrolytic elimination on *endo-syn* sulfoxides **13** and **14** afforded compound **17**. These results allowed us to assign the configurations showed in Scheme 2 to these sulfinyl derivatives. Moreover, the absolute configuration of

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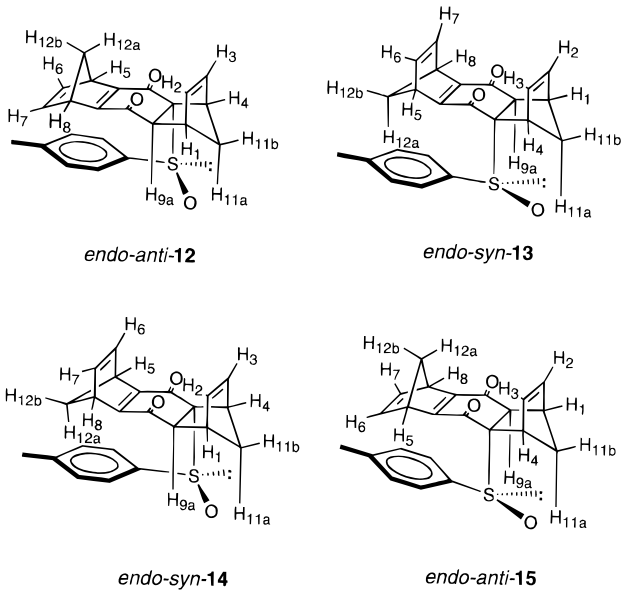

Figure 1.

compound **12** was shown to be (1*S*,4*R*,4a*R*,5*R*,8*S*,9a*S*,S*S*) by X-ray diffraction.[17]

Once known the absolute configuration of **12**, a detailed comparative analysis of the ^{1}H-NMR parameters of derivatives **12**−**15** enabled the unambiguous structural assignments of **13**, **14**, and **15** (See Figure 1 and Table 2).

As can be seen, the *endo* structure of all bisadducts could be assigned from the observed high chemical shifts of H_{11a} (δ 2.33, 2.11, 2.30, and 2.14) if compared to that of H_{11b} (δ 1.48, 1.65, 1.42, and 1.71) as a consequence of the strong deshielding effect exerted by the sulfinylic oxygen[18] on H_{11a}, already observed in similar systems.[15a,16] Other important spectroscopic characteristics of both kinds of adducts are the relative shielding observed in the *endo-anti* adducts **12** and **15** for the H_6 and H_7 olefinic protons (δ 6.1−6.3) with respect to that of the same hydrogens (δ 6.60−6.66) in the *endo-syn* adducts **13** and **14**. This fact must be a consequence of the anisotropic effect exerted by the aromatic ring of the *p*-tolyl group shielding H_6 and H_7 in the *endo-anti* adducts. A similar effect is also evident from the shielding of H_{12a} proton (δ 0.95 and 1.02) in the *endo-syn* adducts **13** and **14** if compared with the chemical shifts of the same hydrogen (δ 1.88 and 1.89) in the *endo-anti* adducts **12** and **15**. Once the *endo-anti* and *endo-syn* relative configurations were known, the most significant parameter to assign the absolute configuration of **12** and **13** is the chemical shift difference observed for H_{9a} protons imposed by the rigid disposition of the sulfinyl group. Thus, H_{9a} appears 0.59 ppm more deshielded in compound **12** than in **15** as a consequence of the strong deshielding effect of the proximal sulfinylic oxygen.[18] The same effect can be observed for adducts **13** and **14** where H_{9a} appeared at 3.82 ppm in **14** and at 3.22 in **13** ($\Delta\delta$ 0.60). All these data reinforce the anisotropic effects of the *p*-tolylsulfinyl group already pointed out by us[15a,16] to assign the stereochemistry of these rigid systems.

The high π-facial diastereoselectivities observed in the cycloadditions of these rigid sulfinylbenzoquinones contrast with those reported for similar reactions on norbornenobenzoquinone **1** lacking the sulfoxide group. As can be seen in Scheme 1, upon reaction with cyclopentadiene, compound **1** gave rise to a 35:65 mixture of adducts **2** and **3** (top to bottom approach).[12,13] Thus, the high stereoselectivities observed in the related sulfinyl-substituted systems **10** and **11** reveal the overwhelming role played by the sulfoxide group with respect to the norbornene moiety in the control of the diene approach. Our results are fully consistent with the stereochemical model on the basis of steric grounds,[19] already proposed to explain similar asymmetric Diels−Alder reactions on sulfinyl dienophiles. The *endo* approach of cyclopentadiene is favored from the less hindered face of the reactive conformation of dienophiles **10** and **11**, which bears the lone electron pair at sulfur.[20] In thermal conditions, such a reactive conformation corresponds to a *s-cis* disposition of the sulfinylic oxygen with respect to the dienophilic double bond. When $ZnBr_2$ is present in the reaction medium, a chelate resulting from metal association with both sulfinylic and carbonylic oxygens (*s-trans* disposition) should be responsible for the reversed diastereoselection observed.[21] Moreover, a complete *endo* selectivity resulted in reactions with quinones **10** and **11**, whereas only a moderate *endo* selectivity was found with the nonplanar ene-diones **6** and **7**.[16] This different behavior suggests that the lack of planarity of the latter is responsible of the formation of the *exo* adduct. The obtention of 10% of the diastereoisomer **13** in the reaction of **10** with cyclopentadiene could be a consequence of the interactions existing in the *endo* approach of cyclopentadiene between the H_2 and H_3 olefinic protons of cyclopentadiene and the methylene group of the norbornadienyl moiety.

The accessibility of compounds **12**−**15** and their potential as chiral synthons of norborneno-*p*-benzoquinone−cyclopentadiene bisadducts prompted us to undertake their transformation into chiral polycyclic strained derivatives. Thus, compound **13** with an *endo-syn* structure was submitted to treatment with $TiCl_3$ in the conditions reported by Mehta[13] (see Scheme 1). In our case, reduction of the ene-dione moiety did not take place from the *exo* face as expected. Instead, compound **18** (Scheme 3) resulting from the pyrolysis of the sulfinyl group and further reduction of the initially formed quinone was obtained in 75% yield. We reasoned that the transformation of the sulfinyl group in a less labile group such a thioether would avoid the undesirable loss of the sulfur functionality maintaining the chirality in the molecule. So, the treatment of sulfoxide **13** with trifluoroacetic anhydride and sodium iodide in acetone at −40 °C,[22] afforded the corresponding thioether **19** in 75% yield. In this case, the reduction of the ene-dione moiety of **19** took place in the same conditions as above to yield a 82% of the corresponding *endo-syn-endo* compound **20** mantaining the *p*-tolylthio group (Scheme 3).

With compound **20** in hand, a [2 + 2] cycloaddition would afford the desired chiral cage compound. Never-

(17) The authors have deposited atomic coordinates for **12** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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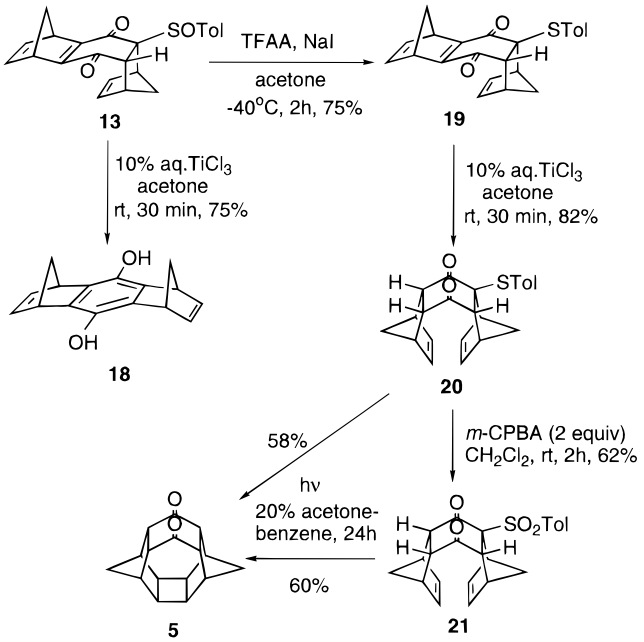
Table 2. ^{1}H-NMR Data for Compounds 12−15

proton	δ (ppm), multiplicity, J (in Hz)			
	endo-anti-**12**	*endo-syn*-**13**	*endo-syn*-**14**	*endo-anti*-**15**
H_1	3.47, m	3.5−3.7, m	3.45, m	3.62, m
H_2	6.14−6.26, m	5.94, dd, 2.9, 5.4	5.93, dd, 2.7, 5.5	6.1−6.3, m
H_3	6.14−6.26, m	5.99, dd, 3.3, 5.4	5.98, dd, 2.7, 5.5	6.1−6.3, m
H_4	3.85, m	4.00, m	3.80, m	4.04, m
H_5	3.72, m	3.5−3.7, m	3.60, m	3.73, m
H_6	6.14−6.26, m	6.60, ddd, 0.3, 3.0, 5.0	6.64, t, 1.9	6.1−6.3, m
H_7	6.14−6.26, m	6.66, ddd, 0.3, 3.0, 5.0	6.64, t, 1.9	6.1−6.3, m
H_8	3.72, m	3.5−3.7, m	3.64, m	3.78, m
H_{9a}	3.80, d, 3.8	3.22, d, 3.8	3.82, d, 3.8	3.21, d, 3.8
H_{11a}	2.33, dt, 9.0, 1.6	2.11, dt, 9.7, 1.5	2.30, dt, 9.1, 1.7	2.14, dt, 9.6, 1.5
H_{11b}	1.48, dt, 9.0, 1.6	1.65, dt, 9.7, 1.8	1.42, dt, 9.1, 1.6	1.71, dt, 9.6, 1.5
H_{12a}	1.88, dt, 7.2, 1.5	0.95, dt, 7.1, 1.6	1.02, dt, 7.1, 1.5	1.89, dt, 7.2, 1.5
H_{12b}	2.05, dt, 7.2, 1.5	1.87, dt, 7.1, 1.5	1.91, dt, 7.1, 1.5	2.04, dt, 7.2, 1.5
CH_3	2.29, s	2.34, s	2.32, s	2.33, s
AA′BB′tolyl system	7.06, 7.17	7.24, 7.46	7.19, 7.37	7.10,7.28

Scheme 3



theless, the irradiation of *endo-syn-endo*-**20** in 20% acetone−benzene at rt for 24 h, produced the cage compound **5** in 58% yield (Scheme 3), showing neither sulfur function nor chirality. When the reaction was stopped before completion, we could detect in the ^{1}H-NMR spectrum of the crude reaction the corresponding intermediate *endo-syn-endo*-**4** (see Scheme 1), lacking the *p*-tolylthio group, in addition to the starting material and final products, **20** and **5**, respectively. This result showed that the loss of the thioether group occurred prior to the [2 + 2] cycloaddition.

A second trial, starting from the corresponding *endo-syn-endo* sulfone **21** obtained by oxidation of thioether **20** with 2 equiv of *m*-CPBA (Scheme 3) was also unsuccessful. The irradiation of **21** in the same conditions as above, yielded again the cage compound **5** in 60% yield, resulting from the [2 + 2] cycloaddition but lacking the sulfone function (Scheme 3). Similar problems had been encountered on other α-substituted ketones structurally related to **20** and **21** with Cl, Br, or Me groups which yielded uncharacterizable materials upon irradiation.[23] These results suggest that only α-unsubstituted ketones are able to undergo efficient [2 + 2] photochemical ring closure.

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Conclusions

We have described a highly stereoselective route to compounds **12**−**15**, enantiomerically pure synthetic equivalents of norborneno-*p*-benzoquinone−cyclopentadiene bisadducts. The success of our approach relies on the high π-facial diastereoselection achieved in the cycloaddition on the sulfinyl substituted quinonic double bond of **10** and **11** which can be inverted in the presence of $ZnBr_2$. The selectivity is exclusively controlled by the sulfoxide group whose steric effects are essential to direct the diene approach. The effect of the norbornene moiety of the dienophile to direct such an approach is circumvented by the sulfinyl group. Finally, the results obtained in the [2 + 2] internal cycloaddition of **20** and **21** showed that the presence of substituents α to the carbonyl group inhibited the reaction which was only possible after the loss of the sulfur substituent.

Experimental Section

Melting points were obtained in open capillary tubes and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 200.1 and 50.3 MHz in $CDCl_3$. Diastereomeric adduct ratios were established by integration of well-separated signals of both diastereomers in the crude reaction mixtures and are listed in Table 1. ^{1}H-NMR data of compounds **12**−**15** are collected in Table 2. All reactions were monitored by TLC that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230−400 mesh) of Macherey-Nagel. Eluting solvents are indicated in the text. The apparatuses for inert atmosphere experiments were dried by flaming in a stream of dry argon. Cyclopentadiene was freshly distilled. CH_2Cl_2 was dried over P_2O_5. $ZnBr_2$ was flamed in the reaction flask, under a stream of dry argon, before using. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2, and solvent drying with Na_2SO_4.

(5*S*,8*R*,S*S*)-1,4-Dihydroxy-5,8-methano-2-*p*-tolylsulfinyl-5,8-dihydronaphthalene (8). To a solution of **6** (936 mg, 3 mmol) in 50 mL of THF was added K_2CO_3 (4.14 g, 30 mmol, 10 equiv) in 50 mL of H_2O. After 1 h at rt, the reaction mixture was hydrolyzed with 10% HCl and extracted with ethyl ether. After workup and flash chromatography (eluent: ethyl ether) compound **8** was obtained as a white solid (81% yield): mp 194−196 °C dec (hexane); $[\alpha]^{20}_D$ = +160 (*c* 0.3, $CHCl_3$); ^{1}H-NMR δ 2.11 and 2.21 (2H, 2dt, J = 7.2 and 1.6 Hz), 2.38 (3H, s), 4.05 and 4.15 (2H, 2m), 6.42 (1H, s), 6.75 and 6.82 (2H, 2dd J = 3.0 and 5.0 Hz), 7.28 and 7.54 (4H, AA′BB′ system), 9.51 (1H, broad s); ^{13}C-NMR δ 21.3, 46.5, 46.9, 69.3, 111.2, 121.3, 124.9 (2C), 130.0 (2C), 139.7, 141.7, 141.8, 142.2, 142.6, 143.8, 144.0, 145.4; Anal. Calcd for $C_{18}H_{16}SO_3$: C, 69.23; H, 5.13. Found: C, 68.98; H, 4.93.

(5*R*,8*S*,S*S*)-1,4-Dihydroxy-5,8-methane-2-*p*-tolylsulfinyl-5,8-dihydronaphthalene (9). Compound **9** was obtained

from **7** as above (84% yield): mp 188−190 °C dec (hexane); $[\alpha]^{20}_D = +31$ (*c* 1.3, $CHCl_3$); ^{1}H-NMR δ 2.15 and 2.21 (2H, 2dt, J = 7.2 and 1.6 Hz), 2.34 (3H, s), 4.06 and 4.15 (2H, 2m), 6.44 (1H, s), 6.67 and 6.74 (2H, 2dd, J = 3.0 and 5.0 Hz), 7.22 and 7.49 (4H, AA′BB′ system), 9.35 (1H, broad s); ^{13}C-NMR δ 21.3, 46.6, 46.9, 69.9, 111.3, 121.6, 124.8 (2C), 130.0 (2C), 139.7, 141.6, 141.8, 142.7, 143.7, 143.8, 143.9, 145.3. Anal. Calcd for $C_{18}H_{16}SO_3$: C, 69.23; H, 5.13. Found: C, 69.02; H, 5.20.

(5*S*,8*R*,S*S*)-5,8-Methano-2-*p*-tolylsulfinyl-5,8-dihydro-1,4-naphthoquinone (10). An aqueous solution (50 mL) of CAN (2.1 g, 4 mmol, 2 equiv) was added to a solution of **8** (624 mg, 2 mmol) in 50 mL of CH_3CN and the mixture was stirred for 2 h. After evaporation of the solvent and workup compound **10** was obtained as an orange solid (92% yield): mp 173−175 °C (ethyl ether); $[\alpha]^{20}_D = +656$ (*c* 0.25, $CHCl_3$); ^{1}H-NMR δ 2.33 (2H, m), 2.38 (3H, s), 4.03 and 4.09 (2H, 2m), 6.78 (2H, m), 7.23 (1H, s), 7.27 and 7.65 (4H, AA′BB′ system); ^{13}C-NMR δ 21.4, 48.2, 48.4, 74.4, 125.7 (2C), 130.1 (2C), 131.3, 138.6, 142.1, 142.2, 142.6, 154.1, 160.8, 162.7, 179.9, 181.5. Anal. Calcd for $C_{18}H_{14}SO_3$: C, 69.66; H, 4.54. Found: C, 69.81; H, 4.39.

(5*R*,8*S*,S*S*)-5,8-Methano-2-*p*-tolylsulfinyl-5,8-dihydro-1,4-naphthoquinone (11). Compound **11** was obtained from **9** as above (95% yield): mp 168−170 °C (ethyl ether); $[\alpha]^{20}_D = +506$ (*c* 0.5, $CHCl_3$); ^{1}H-NMR δ 2.19 and 2.30 (2H, 2dt, J = 7.2 and 1.5 Hz), 2.39 (3H, s), 3.98 and 4.08 (2H, 2m), 6.86 (2H, t, J = 1.9 Hz), 7.21 (1H, s), 7.30 and 7.68 (4H, AA′BB′ system); ^{13}C-NMR δ 21.2, 48.0, 48.1, 73.4, 125.6 (2C), 129.9 (2C), 130.9, 138.4, 142.1, 142.2, 142.4, 154.0, 160.7, 162.4, 179.8, 181.3. Anal. Calcd for $C_{18}H_{14}SO_3$: C, 69.66; H, 4.54. Found: C, 69.53; H, 4.65.

***endo-anti*-(1*S*,4*R*,4a*R*,5*R*,8*S*,9a*S*,S*S*)-1,4,4a,5,8,9a-Hexahydro-1,4:5,8-dimethano-4a-*p*-tolylsulfinylanthracene-9,10-dione (12).** To a solution of **10** (122 mg, 0.4 mmol) in 10 mL of dry CH_2Cl_2 at −20 °C was added cyclopentadiene (100 μL, 1.6 mmol, 4 equiv) under argon. After 24 h, the solvent was evaporated, the residue chromatographed on silica gel (eluent: CH_2Cl_2/EtOAc 90:10), and compound **12** was obtained as a yellow solid (79% yield): mp 131−132 °C (ethyl ether); $[\alpha]^{20}_D = -37$ (*c* 1, $CHCl_3$); ^{13}C-NMR δ 21.1, 45.4, 47.5, 47.8, 48.1, 48.2, 53.5, 73.4, 79.9, 124.8 (2C), 129.5 (2C), 136.9, 137.5, 138.7, 140.1, 141.4, 142.1, 164.9, 165.5, 190.8, 193.3. Anal. Calcd for $C_{23}H_{20}SO_3$: C, 73.38; H, 5.35. Found: C, 73.55; H, 5.41.

***endo-syn*-(1*R*,4*S*,4a*S*,5*S*,8*R*,9a*R*,S*S*)-1,4,4a,5,8,9a-Hexahydro-1,4:5,8-dimethano-4a-*p*-tolylsulfinylanthracene-9,10-dione (14).** Compound **14** was obtained from **11** as above as a yellow oil (92% yield): $[\alpha]^{20}_D$ −22 (*c* 0.7, $CHCl_3$); ^{13}C-NMR δ 21.9, 45.7, 48.4, 48.6, 48.7, 48.8, 53.7, 72.2, 78.4, 125.9, 130.3, 137.5 (2C), 138.7, 139.3, 142.8 (2C), 143.0, 143.1, 165.8, 166.9, 191.7, 194.3. Anal. Calcd for $C_{23}H_{20}SO_3$: C, 73.38; H, 5.35. Found: C, 73.20; H, 5.19.

***endo-syn*-(1*R*,4*S*,4a*S*,5*R*,8*S*,9a*R*,S*S*)-1,4,4a,5,8,9a-Hexahydro-1,4:5,8-dimethano-4a-*p*-tolylsulfinylanthracene-9,10-dione (13).** A solution of **10** (122 mg, 0.4 mmol) in 10 mL of dry CH_2Cl_2 was added to $ZnBr_2$ (180 mg, 0.8 mmol, 2 equiv) under argon and the mixture was stirred for 1 h at rt. After the solution was cooled at −20 °C, cyclopentadiene (100 μL, 1.6 mmol, 4 equiv) was added and the reaction was continued for 1 h. After workup, the residue was chromatographed on silica gel (eluent: CH_2Cl_2/EtOAc 90:10) and compound **13** obtained as a yellow oil (87% yield): $[\alpha]^{20}_D = -195$ (*c* 0.6, $CHCl_3$); ^{13}C-NMR δ 21.3, 45.0, 47.8, 48.3, 48.4, 48.6, 53.2, 70.2, 78.2, 125.2, 129.9, 136.7 (2C), 137.1, 137.4, 142.3, 142.4 (2C), 142.7, 164.6, 168.5, 187.3, 192.3. Anal. Calcd for $C_{23}H_{20}SO_3$: C, 73.38; H, 5.35. Found: C, 73.26; H, 5.50.

***endo-anti*-(1*S*,4*R*,4a*R*,5*S*,8*R*,9a*S*,S*S*)-1,4,4a,5,8,9a-Hexahydro-1,4:5,8-dimethano-4a-*p*-tolylsulfinylanthracene-9,10-dione (15).** Compound **15** was prepared from **11** as above as a yellow solid (88% yield): mp 125−126 °C (ethyl ether); $[\alpha]^{20}_D = -246$ (*c* 0.5, $CHCl_3$); ^{13}C-NMR δ 21.1, 45.2, 47.5, 47.6, 48.8, 48.9, 53.3, 74.4, 77.4, 124.5 (2C), 129.7 (2C), 136.5, 137.0, 137.2, 140.0, 141.2, 142.1, 164.4, 167.4, 186.9, 191.7. Anal. Calcd for $C_{23}H_{20}SO_3$: C, 73.38; H, 5.35. Found: C, 73.55; H, 5.41.

1α,4α,5*β*,8*β*-Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (16). Compound **16** was obtained as a yellow solid from 40 mg (0.1 mmol) of **12** (75% yield) or **15** (78% yield) by refluxing in 5 mL of EtOAc for 24 h, evaporation of the solvent, and flash chromatography (eluent: hexane/EtOAc 20:1): mp 245−246 °C (lit.[12a] mp 250 °C); ^{1}H-NMR δ 2.24 (4H, m), 4.00 (4H, m), 6.84 (4H, t, J = 1.5 Hz).

1α,4α,5α,8α-Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (17). Compound **17** was obtained as above, from **13** (82% yield) or **14** (77% yield) as a yellow solid: mp 202−203 °C (lit.[12a] mp 205 °C); ^{1}H-NMR δ 2.28 (4H, m), 4.04 (4H, m), 6.80 (4H, t, J = 1.5 Hz).

1α,4α,5α,8α-Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-diol (18). To a stirred solution of *endo-syn*-**13** (110 mg, 0.3 mmol) in 5 mL of acetone was added 10% aqueous $TiCl_3$ solution dropwise until a pale purple color persisted. After workup and flash chromatography (eluent: CH_2Cl_2/ethyl ether 90:10) compound **18** was obtained as a white solid (75% yield): mp > 300 °C ($CHCl_3$); ^{1}H-NMR (acetone-d_6) δ 2.04 and 2.11 (4H, 2dt, J = 6.6 and 1.7 Hz), 2.97 (2H, broad s), 4.03 (4H, m), 6.68 (4H, t, J = 1.9 Hz); ^{13}C-NMR (acetone-d_6) δ 47.36 (4C), 70.30 (2C), 134.38 (4C), 141.06 (2C), 143.49 (4C). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.66; H, 5.92. Found: C, 80.40; H, 6.19.

***endo-syn*-(1*R*,4*S*,4a*S*,5*R*,8*S*,9a*R*,S*S*)-1,4,4a,5,8,9a-Hexahydro-1,4:5,8-dimethano-4a-*p*-tolylthioanthracene-9,10-dione (19).** Trifluoroacetic anhydride (212 μL, 1.5 mmol, 5 equiv) was added dropwise into a stirred suspension of the sulfoxide *endo-syn*-**13** (113 mg, 0.3 mmol) and sodium iodide (134 mg, 9 mmol, 3 equiv) in 10 mL of acetone at −40 °C under an argon atmosphere. The reaction mixture was stirred for 2 h at the same temperature, and an excess of saturated aqueous Na_2SO_3 and Na_2CO_3 was added. Acetone was removed under reduced pressure and the aqueous layer was extracted with diethyl ether. After workup, the residue was flash chromatographed (eluent: ethyl ether/hexane 20:80) to give compound **19** as a yellow oil (75% yield): $[\alpha]^{20}_D$ −74 (*c* 0.6, $CHCl_3$); ^{1}H-NMR δ 1.64 (dt, 1H, J = 9.0 and 1.8 Hz), 1.84 (dt, 1H, J = 7.2 and 1.6 Hz), 2.13 (dt, 1H, J = 7.2 and 1.5 Hz), 2.23 (dt, 1H, J = 9.0 and 1.5 Hz), 2.34 (s, 3H), 3.26 (m, 1H), 3.37 (d, 1H, J = 3.9 Hz), 3.50 (m, 1H), 3.8−3.9 (m, 2H), 5.85 (m, 2H), 6.69 and 6.74 (2ddd, 2H, J = 0.8, 3.0, and 5.0 Hz), 7.20 and 7.33 (AA′BB′ system, 4H); ^{13}C-NMR δ 21.1, 46.4, 47.9, 48.0, 48.7, 50.3, 60.5, 64.8, 70.7, 127.1, 129.7 (2C), 136.2, 136.4, 136.7 (2C), 139.9, 141.9, 142.3, 164.6, 167.8, 191.4, 193.8. Anal. Calcd for $C_{23}H_{20}SO_2$: C, 76.64; H, 5.59. Found: C, 76.54; H, 5.41.

***endo-syn-endo*-(1*R*,4*S*,4a*S*,5*R*,8*S*,8a*R*,9a*R*,10a*S*,S*S*)-1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-4a-*p*-tolylthioanthracene-9,10-dione (20).** To a stirred solution of compound **19** (110 mg, 0.3 mmol) in 5 mL of acetone was added 10% aqueous $TiCl_3$ solution dropwise until a pale purple color persisted. After 30 min and workup compound **20** was obtained as a white solid (82% yield): mp 154−156 °C (MeOH); $[\alpha]^{20}_D$ +179 (*c* 0.3, $CHCl_3$); ^{1}H-NMR δ 1.30 (dt, 1H, J = 8.6 and 1.4 Hz), 1.41 (dt, 1H, J = 8.6 and 1.9 Hz), 1.48 (dt, 1H, J = 8.9 and 1.9 Hz), 2.11 (dt, 1H, J = 8.9 and 1.4 Hz), 2.37 (s, 3H), 2.94 (m, 1H), 2.96 (dd, 1H, J = 1.3 and 3.7 Hz), 3.29 (m, 3H, H_1), 3.47 (ddd, 1H, J = 1.3, 3.5 and 11.7 Hz), 4.28 (dd, 1H, J = 3.5 and 11.7 Hz), 5.70 (dd, 1H, J = 3.0 and 5.6 Hz), 5.84 and 5.95 (2dd, 2H, J = 3.3, and 5.7 Hz), 5.99 (dd, 1H, J = 2.9 and 5.6 Hz), 7.18 and 7.32 (AA′BB′ system, 4H); ^{13}C-NMR δ 21.3, 43.9, 44.0, 44.4, 44.6, 46.9, 47.6, 50.0, 53.5, 61.6, 67.3, 126.9, 129.8 (2C), 135.8 (2C), 136.1, 136.2, 136.8, 138.4, 140.3, 203.7, 208.2. Anal. Calcd for $C_{23}H_{22}SO_2$: C, 76.21; H, 6.11. Found: C, 75.98; H, 6.30.

***endo-syn-endo*-(1*R*,4*S*,4a*S*,5*R*,8*S*,8a*R*,9a*R*,10a*S*,S*S*)-1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-4a-*p*-tolylsulfonylanthracene-9,10-dione (21).** To a solution of **20** (108 mg, 0.3 mmol) in 5 mL of CH_2Cl_2 cooled at 0 °C, *m*-CPBA (200 mg, 0.6 mmol, 2 equiv) in 5 mL of CH_2Cl_2 was added. After the addition, the temperature was raised to rt and the reaction was continued for 2 h. The mixture was then treated with $NaHCO_3$ saturated solution, and after workup, the residue was purified by flash chromatography (eluent: ethyl ether/hexane 40:60) to afford compound **21** as a colorless oil (62% yield): $[\alpha]^{20}_D$ +192° (*c* 0.5, $CHCl_3$); ^{1}H-NMR δ 1.25 (dt, 1H, J = 9.3 and 1.7 Hz), 1.30 (dt, 1H, J = 8.7 and 1.9 Hz), 1.38 (dt, 1H, J = 8.7 and 1.9 Hz), 2.23 (dt, 1H, J = 9.3 and 1.4

Hz), 2.48 (s, 3H), 2.97 (m, 1H), 3.33 (m, 1H), 3.36 (m, 1H), 3.47 (m, 1H), 3.55 (ddd, 1H, J = 1.0, 3.7 and 11.6 Hz), 3.97 (dd, 1H, J = 1.0 and 4.8 Hz), 4.03 (dd, 1H, J = 3.7 and 11.6 Hz), 5.61 (dd, 1H, J = 3.1 and 5.5 Hz), 5.77 (d, 1H, J = 2.8 and 5.6 Hz), 5.96 (dd, 1H, J = 2.8, and 5.6 Hz), 6.02 (dd, 1H, J = 2.8 and 5.5 Hz), 7.39 and 7.66 (AA′BB′ system, 4H); ^{13}C-NMR δ 21.7, 43.6, 44.5, 44.6, 45.1, 46.9, 50.1, 53.4, 54.1, 55.4, 83.8, 129.6 (2C), 129.8 (2C), 131.7, 135.7, 137.1, 137.6, 140.6, 145.7, 204.2, 207.7. Anal. Calcd for $C_{23}H_{22}SO_4$: C, 70.03; H, 5.62. Found: C, 69.96; H, 5.49.

Heptacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{4,13}.0^{6,12}.0^{10,15}]hexadecane-11,14-dione (5). A solution of compounds **20** (140 mg, 4 mmol) or **21** (158 mg, 2 mmol) in 20% acetone−benzene (50 mL) was irradiated under argon with an OSRAM HQL-125 W lamp. After 24 h the solvent was evaporated and the residue purified by flash chromatography (eluent: EtOAc/hexane 40:60) to afford compound **5** as a white solid (58% yield from **20** and 60% from **21**): mp 245−246 °C (lit.[13] mp 247−248 °C); ^{1}H-NMR δ 1.55 (4H, m), 2.68 (4H, m), 2.84 (4H, m), 3.08 (4H, m).

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