From Central to Helical Chirality: Synthesis of *P* and *M* Enantiomers of [5]Helicenequinones and Bisquinones from (S*S*)-2-(*p*-Tolylsulfinyl)-1,4-benzoquinone

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Abstract: The reaction of 1,4-divinyl-1,3-cyclohexadiene, 5,8-dimethoxy- or *tert*-butyldimethylsilyloxy-3-vinyl-1,2-dihydrophenanthrene or 6-vinyl-7,8-dihydro-1,4-phenanthrenequinone with an excess of enantiopure (S*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**2**) led to the direct formation of enantioenriched dihydro[5]helicenequinones or bisquinones (50 → 98 % *ee*). A domino Diels – Alder cycloaddition/sulfoxide elimination/partial aromatization process occurs, being the absolute configuration of the final helicene defined in the aromatization step. Both *M* and *P* helimers are accessible through a stepwise enantiodivergent process if the pentacyclic dihydroaromatic intermediate resulting in the two first steps is aromatized in the presence of (±)-**2**, DDQ, CAN or DBU.

Keywords: asymmetric synthesis · cycloadditions · helical structures · quinones · sulfoxides

Introduction

Helicenes are a well-known representative of polycyclic aromatic compounds with a structure characterized by a series of aromatic *ortho* condensed rings.[1] When the number of rings is higher than four, the system can not be planar and adopts a helical structure to liberate the steric congestion. Such helicenes are chiral and, depending on the interconversion barriers,[2] can be resolved into enantiomers and are configurationally stable. These artificial molecules have attracted increasing attention during last years[3] due to the excellent properties they present,[4–9] that are inherently associated to their enantiopurity and are expected to lead to industrial applications.

Although the classical synthesis of helicenes based on the UV light-mediated electrocyclization of stilbene-type precursors[10] is still used nowadays,[11] several new methodologies have emerged during the last decade[12] to provide useful synthetic alternatives to the preparation of this type of helical skeletons. Among them, it is worth to mention the pioneering work by Katz[12a,d] based on Diels – Alder reactions of quinones. Most of the asymmetric approaches reported up to date are based on resolutions[13–15] of the racemic derivatives. Although several enantio- or diastereoselective syntheses have been described so far,[16] moderate asymmetric inductions have been achieved except in a few cases.[16a,d,j] To extend the range of applications of functionalized helicenes, there is still a need for efficient and versatile enantioselective synthetic approaches to both *M* and *P* helimers.

We have recently reported a new asymmetric approach to both enantiomers of [5]helicenebisquinones. The key step in our synthesis was a Diels – Alder reaction between enantiomerically pure 2-(*p*-tolylsulfinyl)-1,4-benzoquinone and vinyl benzenes or naphthalenes.[17] The strategy stems on the well known ability of the sulfoxide situated on a quinone framework to control the regiochemistry, *endo* selectivity and π-facial diastereoselectivity of cycloadditions with a wide range of dienes.[18] The domino[19] Diels – Alder reaction/pyrolytic sulfoxide elimination sequence had already been established as a general one-pot strategy to other enantiomerically enriched polycyclic quinones such as angucyclinones.[20] This domino sequence, with an additional aromatization step carried out in situ by an excess of sulfinylquinone, was utilized in our direct synthesis of fully aromatic pentacyclic systems. Nevertheless, the low reactivity of the aromatic dienes was a serious drawback to the general application of this short synthetic approach to chiral helical bisquinones.

In order to circumvent this problem, we decided to use more reactive dienes such as dihydroarylethenes, already used en route to helicenes.[12o] This slight structural modification of the diene allowed the Diels – Alder reaction between enantiopure (S*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone and vinyl dihydronaphthalenes to proceed under very mild conditions opening an easy access to new helically chiral dihydro[4]helicenes.[21] Moreover, the presence of a central hydroaromatic ring in the resulting helicenes is known to increase the

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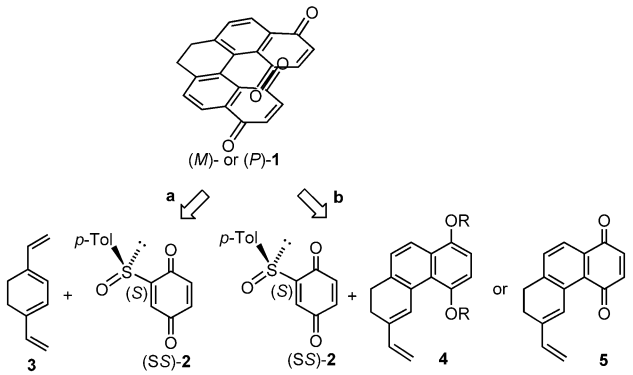
racemization barrier in comparison with that of the whole aromatic derivatives.[22]

In this paper we present a general and efficient approach to dihydro[5]helicenequinones and bisquinones based on the use of appropriately functionalized vinyl dihydrophenanthrenes in the cycloaddition. We have preliminary communicated the first application of this methodology for the enantioselective synthesis of differently substituted [5]helicenequinones.[23] We now report a full account of our results and a new access to enantioenriched dihydro[5]helicenebisquinones featuring our strategy for a convergent one-pot synthesis. The most enantioselective stepwise approach to the pentahelicene system involves as another key feature, the divergent access to both the *M* and *P* helimers from a common centrally chiral pentacyclic precursor.[24] We also disclose the mechanistic pathways which explain our results.

Results and Discussion

Two retrosynthetic analyses for the synthesis of dihydro[5]-helicenebisquinone **1** are outlined in Scheme 1. Firstly, we planned to construct the pentacyclic skeleton from a bis-diene such as 1,4-divinyl-1,3-cyclohexadiene (**3**) by taking advantage of a two-fold domino sequence with an excess of enantiopure (S*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**2**) including cycloaddition, pyrolytic sulfoxide elimination and partial aromatization steps, which presumably could occur in a one-pot process (path **a**). A stepwise retrosynthetic approach requiring a 3-vinyl-5,8-dialkoxy-1,2-dihydrophenanthrene (**4**) or 6-vinyl-7,8-dihydro-1,4-phenanthrenequinone (**5**) as diene partners was also envisaged (path **b**).



Scheme 1. Retrosynthetic analyses for the synthesis of dihydro[5]helicenebisquinone **1**.

Abstract in Spanish: *La reacción de 1,4-divinil-1,3-ciclohexadieno, 5,8-dimetoxi- o terc-butildimetilsililoxi-3-vinil-1,2-dihidrofenantreno o 6-vinil-7,8-dihidro-1,4-fenantrenoquinona con exceso de (SS)-2-(p-tolilsulfinil)-1,4-benzoquinona (**2**) condujo a la formación de dihidro[5]helicenoquinonas o bisquinonas enantioméricamente enriquecidas (50 → 98 % ee) a través de un proceso dominó en el que tiene lugar una reacción de Diels–Alder y una eliminación pirolítica del sulfóxido seguidas de una etapa de aromatización del derivado dihidroaromatico resultante. La configuración absoluta del heliceno final se define en la etapa de aromatización. En un proceso por etapas enantiodivergente, es posible acceder a los dos helímeros (M) y (P) por tratamiento del precursor dihidroaromatico pentacíclico con (±)-**2**, DDQ, CAN o DBU.*

Path **a** was more attractive due to a higher convergency and was first explored. Scheme 2 summarizes the synthesis of bis-diene **3** and the results of its reaction with (S*S*)-**2**. Thus, the enolate derived from commercially available 1,4-cyclohexanedione *mono*-ethylene acetal (**6**), was trapped with Tf_2NPh to afford quantitatively enol triflate **7**. Deketalization of **7** under non acidic conditions ($LiBF_4$, CH_3CN/H_2O, reflux, 20 h)[25] to avoid the conjugation of the double bond, afforded ketone **8**; the latter was treated, without purification, with Tf_2NPh/KHDMS giving bis-triflate **9** in 87 % yield for the two steps. A double Stille coupling of **9** with tributylvinylstannanne in the presence of $[Pd(PPh_3)_4]$ gave a 37 % of bis-diene **3**. Due to its unstability and easy polymerization, compound **3** was immediately submitted to the cycloaddition process. Thus, the Diels–Alder reaction of **3** was carried out with four equivalents of enantiopure sulfinyl quinone (S*S*)-**2**[26] at room temperature in CH_2Cl_2 for 3 d. After flash chromatography, we could isolate a 12 % yield of helicenebisquinone (*M*)-**1** {$[\alpha]_D^{20} = -1810$ ($c = 0.02$ in $CHCl_3$), 50 % *ee*},[27] together with a 7 % of derivative **10**. The one-pot transformation leading to (*M*)-**1** implies six consecutive reactions on bis-diene **3**: first cycloaddition on the sulfinyl substituted C2–C3 double bond of (S*S*)-**2**, elimination of the sulfoxide, partial aromatization and a second analogue domino sequence. With the aim of detecting some intermediates of this interesting process, we followed the reaction by ^1H NMR spectroscopy using $CDCl_3$ as solvent. After 10 min, we could detect compound **11** formed by cycloaddition of **3** with (S*S*)-**2** and spontaneous elimination of the sulfoxide. Aromatization of the B ring of **11** had taken place 24 h later to afford a new diene **5** which finally evolved into the mixture of **1** and **10**. From **5** to **1** and **10** no intermediates could be detected. Derivative **10**, which was obtained as a non-separable mixture of regio- and/or diastereoisomers, proceeded from the attack of the diene on the unsubstituted C_5–C_6 double bond of sulfinyl quinone (S*S*)-**2**.

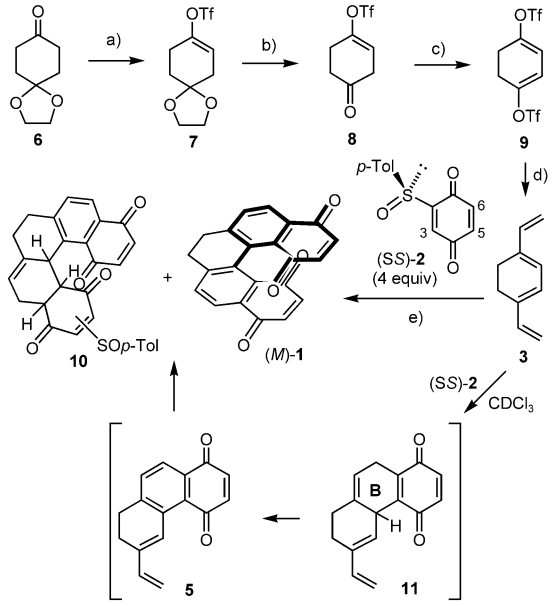
Although the desired [5]helicenebisquinone **1** could be synthesized through this short pathway, both the yield and enantiomeric excess were not satisfactory.

We thus decided to apply the stepwise retrosynthetic pathway **b** (Scheme 1) en route to **1**. The synthetic sequence leading to 5,8-dimethoxy-3-vinyl-1,2-dihydrophenanthrene (**4a**) is outlined in Scheme 3. Enol triflate **7** was submitted to a Stille coupling {tributylvinylstannane, $[Pd(PPh_3)_4]$} to give vinylcyclohexene **12**[29] in 79 % yield. The synthesis of the advanced intermediate **15** from diene **12** was achieved through two alternative routes. Thus, the Diels–Alder reaction (CH_2Cl_2, rt, 6 h) between **12** and racemic 2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**2**)[26] gave quinone **13**, proceeding from the sulfoxide elimination in the initially formed cycloadduct, in 81 % isolated yield. Reduction of **13** to the hydroquinone and subsequent methylation gave rise to **15** in 84 % yield. In the second route, the cycloaddition between **12** and *p*-benzoquinone afforded cycloadduct **14** (RT, 15 d) which, without further purification, was aromatized ($Na_2S_2O_4$)

and methylated (K_2CO_3/Me_2SO_4) to afford **15** (90% yield, two steps). After aromatization of the central ring of **15** with DDQ, tetrahydrophenanthrene derivative **16** was formed in quantitative yield. Acetal deprotection using $CeCl_3/NaI/CH_3CN$[30] afforded ketone **17** (85% yield) whose treatment with Tf_2NPh/KHMDS yielded enol triflate **18**. Finally, a Stille coupling led to dimethoxysubstituted diene **4a** in 82% yield.

With diene **4a** in hand, we performed the Diels–Alder reaction with a two-fold excess[31] of enantiopure (S*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone[26] (**2**) (Scheme 4). The cycloaddition was initially run at room temperature (Table 1, entry 1). After 18 h, we isolated in 72% yield helical quinone (*P*)-**20** showing 72% *ee*,[32] as a result of a one-pot three reactions sequence comprising Diels–Alder reaction and spontaneous sulfoxide elimination, followed by aromatization of the B ring of intermediate **19** effected by the excess of the quinone. According to our previous work,[33] π-facial diastereoselectivity of cycloadditions with sulfinyl quinones improved strongly at low temperatures. Indeed, working at −20 °C (Table 1, entry 2) the optical purity of (*P*)-**20** increased up to 76% *ee*, whereas at −40 °C (entry 3) 84% *ee* was achieved. Moreover, CAN oxidation of the dimethoxy substituted aromatic ring of (*P*)-**20** (Scheme 4) allowed the synthesis of helical bisquinone (*P*)-**1** {$[\alpha]_D^{20} = +2670$ ($c = 0.011$ in $CHCl_3$), 72% *ee*}. Surprisingly, the helicenebisquinone formed under these conditions showed an opposite helicity to that obtained in the one-pot sequence using bisdiene **3** (see Scheme 2).

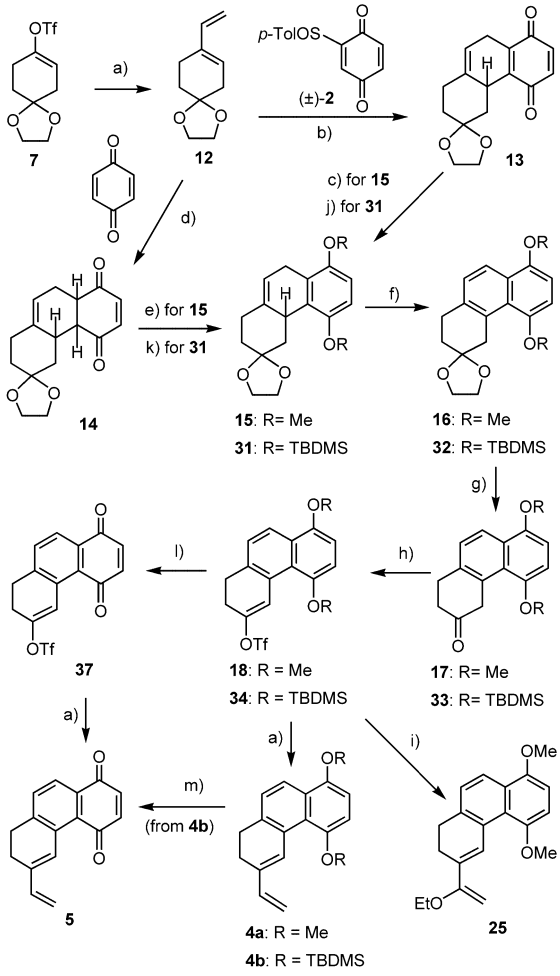
Although we could improve the *ee* of (*P*)-**20** up to 84% by working at −40 °C, the challenge of obtaining the enantiopure product remained. According to the structure of diene **4a**, a 1,2-disusbtituted butadiene system, the opposite regiochemical control exerted by both substituents could be in the origin of the loss of enantiopurity observed.



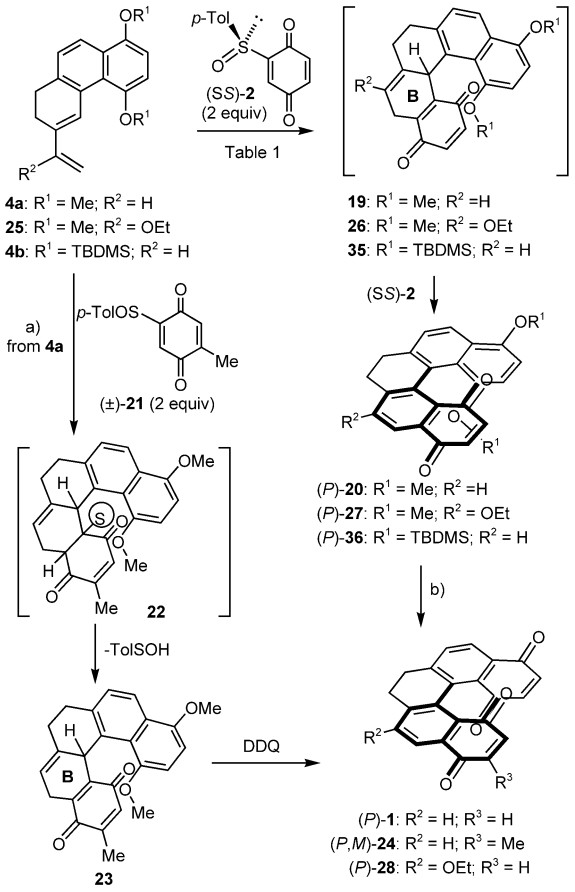
Scheme 2. Enantioselective synthesis of dihydro[5]helicenebisquinone (*M*)-**1** from bisdiene **3**. a) Tf_2NPh, KHMDS, THF, −78 °C, 0.3–4 h, 99%; b) $LiBF_4$, CH_3CN/H_2O, reflux, 20 h; c) Tf_2NPh, KHMDS, −78 °C, 2 h, 87% for the two steps; d) $CH_2{=}CHSnBu_3$, $[Pd(PPh_3)_4]$ LiCl, THF, reflux, 2.5 h, 37%; e) CH_2Cl_2, room temperature, 3 d, 12% for (*M*)-**1** and 7% for **10**.

With the aim of knowing the regiochemical course of the process, we performed the cycloaddition between diene **4a** and racemic 2-(*p*-tolylsulfinyl)-5-methyl-1,4-benzoquinone (**21**)[34] (Scheme 4). After 7 d at −20 °C and further aromatization of the corresponding intermediate **23** with DDQ, we obtained racemic methyl substituted helical quinone (*P*,*M*)-**24** as a sole regioisomer in 67% yield. This result showed that the initial cycloaddition of **4a** took place with complete *ortho* regioselectivity directed by the C-1 substituent of the diene moiety through the cycloadduct **22**, which immediately lost *p*-toluene sulfenic acid to give intermediate **23**. Further DDQ oxidation afforded **24**; its structure was unequivocally established by X-ray diffraction (Figure 1).[35]

With the regiochemical control warranted, we reasoned that the optical purity of the final helicene resulting from reaction of (S*S*)-**2** and diene **4a** could be enhanced working at



Scheme 3. Synthesis of dienes **4a**, **25**, **4b**, and **5**. a) $CH_2{=}CHSnBu_3$, $[Pd(PPh_3)_4]$, LiCl, THF, reflux, 1–4.5 h, 79% for **12**, 82% for **4a**, 74% for **4b** and 26% for **5**; b) CH_2Cl_2, room temperature, 6 h, 81%; c) i) $Na_2S_2O_4$, Et_2O/H_2O; ii) Me_2SO_4, K_2CO_3, acetone, reflux, 5 h, 84%; d) CH_2Cl_2, room temperature, 15 d; e) Me_2SO_4, K_2CO_3, acetone, reflux, 6 h, 90% for the two steps; f) DDQ, CH_2Cl_2, room temperature, 20 min, 99% for **16** and 96% for **32**; g) $CeCl_3 \cdot 7H_2O$, NaI, CH_3CN, reflux, 3 h, 85% for **17** and 95% for **33**; h) Tf_2NPh, KHMDS, THF, −78 °C, 0.3–4 h, 95% for **18** and 72% for **34**; i) $CH_2{=}C(OEt)SnBu_3$, $[Pd(PPh_3)_4]$, LiCl, THF, reflux, 2 h, 67%; j) i) $Na_2S_2O_4$, Et_2O/H_2O; ii) TBDMSCl, imidazole, DMF, RT, overnight, 81%; k) TBDMSCl, imidazole, DMF, RT, overnight, 74% over two steps d) and k); l) CAN, CH_3CN/H_2O, room temperature, 15 min, 72%; m) TBAF, THF, room temperature, 20 min, 58%.



Scheme 4. Enantioselective synthesis of (*P*)-dihydro[5]helicenequinones **20**, **27**, and **36** and bisquinones **1** and **28**. a) i) CH_2Cl_2, $-20\,^{\circ}C$, 7 d; ii) DDQ, room temperature, 30 min, 67%; b) CAN, $CH_2Cl_2/CH_3CN/H_2O$, room temperature, 2 h, 82% from **20**, 90% from **27** and 71% from **36**.

even lower temperatures. We thus thought of using a more reactive diene such as **25** (Scheme 3), bearing an oxygenated substituent at the vinyl moiety. The synthesis of **25** was achieved in 67% yield by a Stille coupling between enol triflate **18** and 1-ethoxyvinyltrybutylstannane in the presence of $[Pd(PPh_3)_4]$. Compound **25** was proven to be very unstable and was immediately submitted to cycloaddition with (S*S*)-**2** (Scheme 4). This reaction could be carried out at $-60\,^{\circ}C$ (Table 1, entry 4) yielding, through intermediate **26**, ethoxy substituted helical quinone (*P*)-**27** with an excellent 92% *ee*.[32] CAN oxidation of (*P*)-**27** led to helical bisquinone (*P*)-**28** $\{[\alpha]_D^{20} = +3370$ ($c = 0.0065$ in $CHCl_3$), 92% *ee*$\}$.[27]

Table 1. Reactions of (S*S*)-**2** (2 equiv) and dienes **4a**, **25** and **4b** in CH_2Cl_2.

Entry	Diene	T [°C]	t [d]	Helicene	Yield [%]	$[\alpha]_D^{20}$ (c in $CHCl_3$)	*ee* [%]
1	**4a**	20	0.75	(*P*)-**20**	72	+2260 (0.002)	72
2	**4a**	−20	2	(*P*)-**20**	53	+2480 (0.004)	76
3	**4a**	−40 to −20	12	(*P*)-**20**	72	+2800 (0.003)	84
4	**25**	−60	6	(*P*)-**27**	62	+2980 (0.0027)	92
5	**4b**	20	1	(*P*)-**36**	50	+2330 (0.0035)	88
6	**4b**	−40 to −20	17	(*P*)-**36**	75	+2690 (0.0033)	>98

In one of the experiments for the one-pot synthesis of helicene **20** from **4a** with two equivalents of (S*S*)-**2** (Scheme 4), the reaction had not been completed. Then, we decided to accelerate the final aromatization of the B ring of the tetrahydroaromatic intermediate **19** by adding a powerful oxidant such as DDQ. After flash chromatography, we isolated helical derivative **20** almost in racemic form. Initially, we reasoned that the achiral nature of DDQ compared with the chiral sulfinyl quinone (S*S*)-**2** acting as oxidant, could be in the origin of the different behaviour observed.

Intrigued by this result, we decided to repeat the reaction with DDQ from pure tetrahydroaromatic derivative **19** (Scheme 5). Thus, the cycloaddition between diene **4a** and a stoichiometric amount of (S*S*)-**2** in CH_2Cl_2 at $-40\,^{\circ}C$ afforded, after spontaneous pyrolytic elimination of the sulfoxide, compound (*R*)-**19**, showing a stereogenic center at C-14c $\{[\alpha]_D^{20} = -736$ ($c = 0.012$, $CHCl_3$)$\}$, in 61% yield after flash chromatography. Treatment of (*R*)-**19** with DDQ in CH_2Cl_2 (Table 2, entry 1) gave rise to optically active helicenequinone (*M*)-**20** with 44% *ee*. Surprisingly, compound **20** showed the opposite helicity to that obtained in the presence of an excess of (S*S*)-**2** (compare entries 1 and 2).

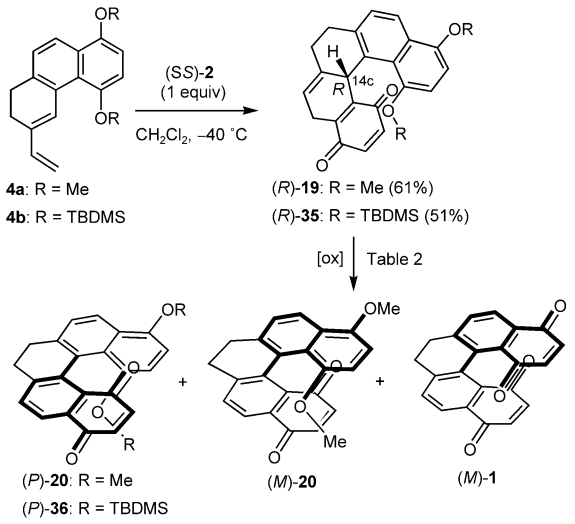
Figure 1. ORTEP drawing of dihydro[5]helicenequinone (*P*,*M*)-**24**.

Table 2. Aromatization reactions of tetrahydro[5]helicenequinones (*R*)-**19** and (*R*)-**35** to dihydro[5]helicenequinones **20**, **36** and bisquinone **1**.

Entry	Compound	Reagent [equiv]	T [°C]	t [h]	Helicene	Yield [%]	$[\alpha]_D^{20}$ (c in $CHCl_3$)	*ee* [%]
1	(*R*)-**19**	DDQ (1.2)	0	1	(*M*)-**20**	95	−1530 (0.003)	44
2[a]	–	(S*S*)-**2**	−20	–	(*P*)-**20**	72	+2800 (0.003)	84
3	(*R*)-**19**	(±)-**2** (2)	−20	240	(*P*)-**20**	85	+2760 (0.003)	80
4	(*R*)-**19**	DBU (1.5)	−20	0.1	(*P*)-**20**	70	+1500 (0.005)	42
5	(*R*)-**19**	CAN (2.5)	RT	1	(*M*)-**20**	67	−3030 (0.003)	90
6[b]	–	(S*S*)-**2**	−20	–	(*P*)-**36**	75	+2690 (0.003)	>98
7	(*R*)-**35**	DDQ (1.2)	RT	1	(*P*)-**36**	88	+2670 (0.003)	96
8	(*R*)-**35**	CAN (2.5)	RT	0.1	(*M*)-**1**	60	−3500 (0.015)	92
9	(*R*)-**35**	nBu$_4$NF (2.5)	RT	0.25	(*M*)-**1**	44	−3250 (0.009)	88

[a] Without isolation of (*R*)-**19** (see Scheme 4). [b] Without isolation of (*R*)-**35** (see Scheme 4).

With this new result at hand, we decided deeply investigate this interesting process by using different aromatizing reagents. The results obtained are summarized in Scheme 5 and Table 2.

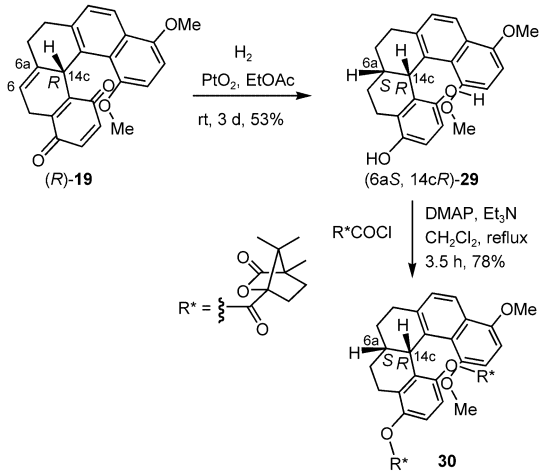


Scheme 5. Synthesis and partial aromatizations of tetrahydro[5]helicenequinones (*R*)-**19** and (*R*)-**35**.

Firstly, we wanted to know if the enantiomeric purity of (S*S*)-**2** acting as oxidant could have an essential role in defining the absolute configuration of the final helicene **20**. We thus performed the aromatization of (*R*)-**19** in the presence of racemic sulfinylquinone **2**[26] (Table 2, entry 3). In this case, the *P* helimer of **20** was again obtained in 80% *ee*, which indicates that the optical purity of the quinone, acting as an oxidant, did not control the helicity of **20** and has little influence in the optical purity (compare entries 2 and 3). At this point we reasoned that the final configuration of the helimer could be dependent on the structure and on the mechanism of aromatization of the corresponding reagent. We then used another method to transform **19** into **20**. Thus, treatment of (*R*)-**19** with DBU (Table 2, entry 4) afforded helicene (*P*)-**20** showing a lower 42% *ee*. Finally, when the aromatization of (*R*)-**19** was carried out with cerium ammoniun nitrate (CAN) in CH_3CN/H_2O (Table 2, entry 5), compound (*M*)-**20** was obtained with an excellent 90% *ee*; this shows that it was possible to gain access to both enantiomers of helicene **20** with very good optical purities by changing the oxidant used.

Although these results increased the versatility of our helicene synthesis, their rationalization was not evident. In order to get insight into a mechanistic explanation it was essential to unequivocally determine the absolute configuration of the stereogenic center created at C-14c in the tetrahydroaromatic derivative **19**. Moreover, this would allow explaining the π-facial diastereoselectivity of the initial cycloaddition. Due to the high tendency to aromatization of compound **19**, we decided to prepare a more stable derivative to get suitable crystals for a X-ray diffraction study.

As depicted in Scheme 6, the catalytic hydrogenation of C6–C6a double bond of **19** with PtO_2 in EtOAc for 3 d



Scheme 6. Configurational assignment for derivative (*R*)-**19**.

afforded the stable *cis*-fused pentacyclic hexahydroaromatic hydroquinone **29** in 53% yield as the unique diastereomer. Compound **29** was later derivatized to the corresponding bis-(−)-camphanate **30** by treatment with (−)-camphanoyl chloride in the presence of DMAP and Et_3N. Fortunately, we could perform the X-ray diffraction study[35] of **30** (Figure 2) and unequivocally assign its structure as well as establish the (6a*S*,14c*R*) absolute configuration for the stereogenic centers of **29** and, as a consequence, the (14c*R*) configuration for the precursor **19**.

Figure 2. ORTEP drawing of hexahydro[5]helicene **30**.

The *R* absolute configuration at the stereogenic center of **19** is in agreement with the formation of the Diels–Alder adduct through the preferred *endo*-approach of the vinyl dihydrophenanthrene **4a** to the less encumbered upper face of sulfinylquinone (S*S*)-**2** adopting the *s-cis* conformation (Figure 3), usually the most stable and reactive of vinyl sulfoxides.[36] According to the (*R*) absolute configuration of **19**, the formation of both *P* and *M* enantiomers of the dihydro[5]helicene **20** depending upon the reagent used in the final aromatization step, is not easy to rationalize. An inspection of molecular models of **19** suggested that the presence of two conformers **I** and **II** (Figure 3), resulting from the boat inversion of the B ring, could be in the origin of the different helicity reached using (S*S*)-**2** or DDQ as oxidants. The evolution of each conformer in the aromatization step

would explain the formation of a different enantiomer of the final dihydro[5]helicene **20**. The intrinsic stability of each conformer as well as the nature of the aromatizing reagent and the reaction mechanism must be defining the preferred evolution.

In accordance with previous conformational studies on 1,4-dihydronaphthalenes[37] and with our own work,[38] tetrahydroaromatic derivative **19** would exist as a more stable boat-like conformation such as **I** with the aryl substituent at C-14c in a pseudoaxial disposition to avoid destabilizing interactions with the methylene group at C-6a and the adjacent carbonyl group,[37b,c] present in conformer **II**. However, a ^{1}H,^{1}H NOESY experiment carried out on (*R*)-**19** evidenced strong NOE enhancements between H-14c and H-5ax as well as with the methoxy group (R = Me) at C-14. This is only possible assuming that conformer **II** is the major in the conformational equilibrium (Figure 3). A detailed inspection of molecular

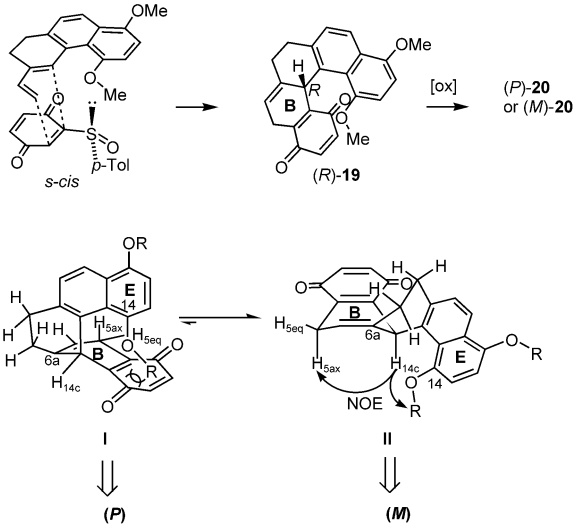


Figure 3. Mechanistic proposal for the enantioselective Diels–Alder reaction between **4a** and (S*S*)-**2** and NOESY enhancements for (*R*)-**19** and (*R*)-**35**.

models revealed that conformation **I** of (*R*)-**19** showed a destabilizing spatial interaction between the methoxy substituent (R = Me) at C-14 and the quinone ring which could explain its lower stability.

According to the mechanisms proposed for the quinone mediated dehydrogenation of hydroaromatic compounds, two possibilities may be considered. The reaction can be initiated by the transfer of a hydride ion to one of the oxygens of the oxidant quinone to generate an ion-pair in the rate-determining step followed by a rapid proton transfer from the resulting intimate ion-pair to the hydroquinone anion.[39] A one-step sequence with the 1,4-transfer of the hydride to the quinone and simultaneous protonation in an almost synchronous process can also be considered.[40] In both cases, the powerful oxidant quinone should approach the 1,4-cyclohexadiene moiety of **19** in a parallel direction to produce the *cis*-1,4-elimination of H-5 and H-14c as shown in Figure 4 (the approaching quinone is represented without substituents for simplicity). The ease of hydride transfer from the substrate is

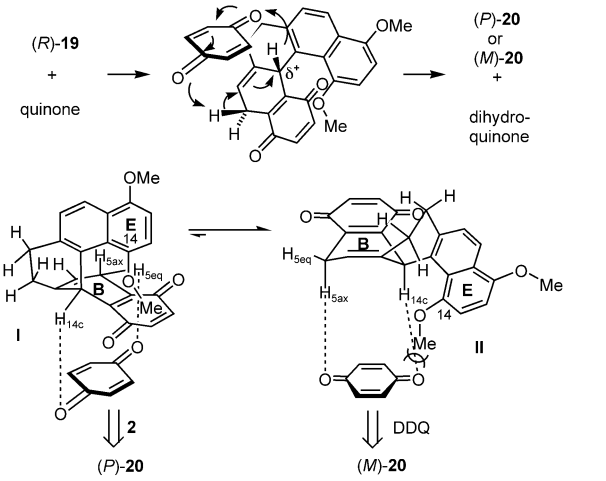


Figure 4. Mechanistic proposal for quinone-mediated aromatizations of compounds (*R*)-**19** and (*R*)-**35**.

dependent upon the degree of stabilization of the incipient positive charge in the transition state. In our case, H-14c, situated at a tertiary carbon, must be the hydride involved in the quinone-mediated aromatization process. The attack of DDQ to the reactive conformer **II** of **19** must occur from the bottom face to take H-14c (Figure 4) giving rise to the *M* enantiomer of dihydro[5]helicene **20** with a 44% *ee*. The moderate *ee* obtained suggested that the evolution through the less favored conformer **I** was not negligible. Probably, the approach of DDQ to conformer **II** is slightly hindered by the presence of steric and/or stereoelectronic interactions between the approaching quinone and the methoxy group at C-14. When quinone **2** bearing the bulky sulfoxide acts as the oxidant, these interactions become greater and the evolution through conformer **I** is preferred affording in this case the *P* enantiomer of **20** in ca. 80% *ee*.

The stereoselectivity of DBU and CAN aromatizations is more difficult to rationalize, but, in accordance with this reasoning, the major formation of the *P* enantiomer of **20** when DBU was used (*er* 71:29) should result from the preferred evolution through conformer **I** whereas the CAN mediated aromatization giving rise to the *M* enantiomer of **20** (90% *ee*), suggested the evolution of a conformer such as **II** of **19**.

In light of the above-mentioned discussion, we reasoned that the incorporation of a bulkier substituent (R = TBDMS) into the hydroquinone E ring of the tetrahydroaromatic derivative **19** could enhance the steric congestion of the bottom face of conformer **II** (Figure 4). This would favour the aromatization process through conformer **I** to afford the *P* enantiomer of the corresponding dihydro[5]helicenequinones in a more stereoselective manner. For this purpose, it was necessary to prepare OTBDMS-substituted diene **4b**, which was synthesized as depicted in Scheme 3.

Starting from compound **13**, reduction of the quinone ring ($Na_2S_2O_4$) followed by TBDMS protection (TBDMSCl/imidazole) gave compound **31** in a 81% yield. In a similar way, **31** could be synthesized from **14** in 74% yield (two steps). Partial aromatization of **31** with DDQ yielded a 96% of derivative

32; subsequent ketal deprotection ($CeCl_3$/NaI/CH_3CN) gave ketone **33** in 95% yield. After formation of the enol triflate **34** (Tf_2NPh/KHMDS, 72%) and Stille coupling, OTBDMS substituted diene **4b** was obtained in 74% yield.

The cycloaddition between **4b** and two equivalents of enantiopure sulfinylquinone (S*S*)-(+)-**2** at RT for 24 h (Scheme 4, Table 1, entry 5) afforded, through intermediate **35**, helical quinone (*P*)-**36** with 88% *ee*,[41] indicating a notable increase in the diastereoselectivity of the process if compared with the results obtained from dimethoxy substituted diene **4a** under the same conditions (Table 1, entry 1, 72% *ee*). When the reaction of **4b** was performed at -40 to $-20\,^{\circ}C$ (Table 1, entry 6) the resulting (*P*)-**36** was obtained in optically pure form. Moreover, enantiopure helical bisquinone (*P*)-**1** {$[\alpha]_D^{20} = +3700$ ($c = 0.015$, $CHCl_3$), *ee* > 98} (Scheme 4) could be obtained by CAN oxidation of (*P*)-**36**.

On the other hand, the cycloaddition between diene **4b** and one equivalent of (S*S*)-**2** in CH_2Cl_2 at $-40\,^{\circ}C$, allowed isolating compound (*R*)-**35** {$[\alpha]_D^{20} = -240$ ($c = 0.02$, $CHCl_3$)} in 51% yield (Scheme 5). The structure of **35** was established on the basis of its spectroscopic parameters including a $^1H,^1H$ NOESY experiment (Figure 3) which revealed strong NOE enhancements between H-14c and H-5ax as well as between these two hydrogens and the substituents (R = TBDMS) at C-14. This suggested that conformer **II** was also the major in the conformational equilibrium of **35** (Figure 3). The aromatization of the B ring of compound (*R*)-**35** by using DDQ as the oxidant reagent (Table 2, entry 7) afforded the *P* enantiomer of helicene **36** with an excellent 96% *ee*. The helicity of this TBDMS disubstituted helicenequinone was the opposite to that of the methoxy substituted analogue (*M*)-**20** obtained with this oxidant (Table 2, entry 1).

The formation of the same *P* helimer by oxidation of (*R*)-**35** with (S*S*)-**2** and DDQ (compare entries 6 and 7) suggested that the bulkier OTBDMS substituent at C-14 was completely hindering the approach of any quinone oxidant from the bottom face of the major conformer **II** (Figure 4). These different results showed that the substitution (R = Me or TBDMS) on the E ring of derivatives **19** and **35** played an important role in defining the final helicity, as anticipated.

The treatment of (*R*)-**35** with CAN in CH_3CN/H_2O (Table 2, entry 8) did not yield the expected helicenequinone **36** but the helicenebisquinone (*M*)-**1**, showing the opposite absolute configuration and an excellent 92% *ee*. This suggests that, under these conditions the OTBDMS groups are broken first and the resulting hydroquinone is further transformed into **1**. The non-isolated intermediate hydroquinone can evolve either through the oxidation to the corresponding bisquinone followed by aromatization of the B ring or through the inverse sequence. In any case, the elimination of the R group at C-14 in conformer **II** (Figure 4) clearly favours the evolution of this rotamer to afford the *M* enantiomer of the final dihydro[5]helicenebisquinone (*M*)-**1**.

Finally, when tetrahydroaromatic derivative (*R*)-**35** was treated with nBu_4NF (Scheme 5, Table 2, entry 9), the only isolated product was again dihydro[5]helicenebisquinone (*M*)-**1** showing 88% *ee*, thus confirming the previous elimination of the TBDMS group followed by partial aromatization and hydroquinone oxidation.

The above results clearly demonstrate that the absolute configuration of the final helicenequinones is defined in the oxidation step and not in the Diels–Alder cycloaddition, as we had previously suggested.[23]

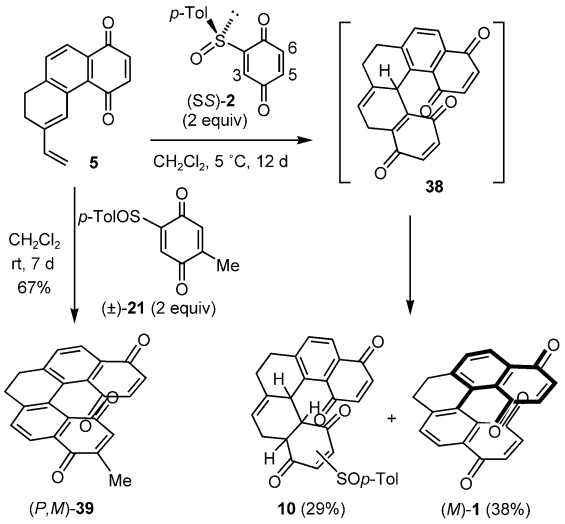
In order to evaluate the alternative approach to **1** using 6-vinyl-7,8-dihydro-1,4-phenanthrenequinone (**5**), (Scheme 1, pathway **b**) we tried to synthesize such diene from compound **18** (Scheme 3). So, CAN oxidation of the terminal aromatic ring of **18** gave quinone **37** (72% yield), which was further submitted to a Stille coupling with vinyltributylstannane yielding only a 26% of the desired vinyl derivative **5**. We thus tried the direct oxidation of **4a** with CAN but, unfortunately, this oxidation afforded a complex mixture of products. Finally, diene **5** could be obtained in a more satisfactory yield starting from OTBDMS substituted diene **4b** by desilylation with TBAF which led directly to vinyl phenanthrenequinone **5** after spontaneous oxidation of the hydroquinone ring, in a 58% isolated yield.

Reaction of diene **5** with an excess of enantiopure sulfinyl quinone (S*S*)-**2** (Scheme 7) gave, through intermediate **38**, helicenebisquinone (*M*)-**1** {$[\alpha]_D^{20} = -1940$ ($c = 0.02$ in $CHCl_3$), 74% *ee*}[27] in 38% yield together with a 29% of derivative **10**. The long reaction time necessary to complete this process evidenced a lower reactivity of the quinone substituted diene **5** if compared with **4a–b**, bearing a protected hydroquinone moiety. The higher reactivity of the later must be due to the electron donating character of the alkoxy or silyloxy substituted aromatic group of **4**. The different *M* helicity obtained in the reaction with **5** when compared with that resulting from dienes **4a–b** is again in agreement with our mechanistic proposal since the lack of any R group at C-14 of conformer **II** in Figure 4, which is hindering the oxidant approach to H-14c and H-5, favours the evolution through this rotamer to give the *M* enantiomer.

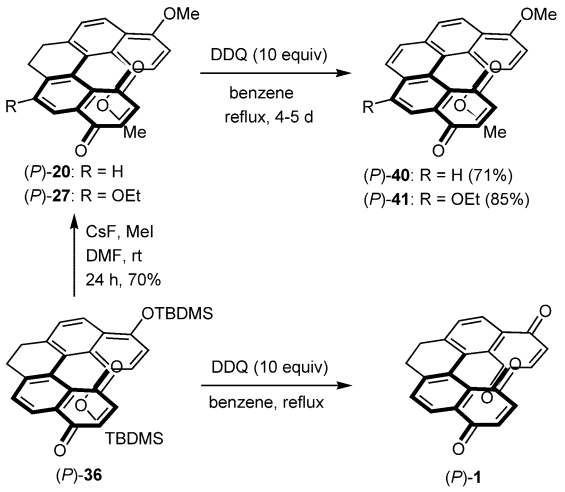
With the aim of confirming the regioselectivity of the cycloaddition process on the sulfinyl substituted C_2–C_3 double bond, we performed the Diels–Alder reaction of diene **5** with racemic methyl-substituted sulfinylquinone **21** (Scheme 7). After 7 d at room temperature, only compound (*P,M*)-**39** was isolated, demonstrating again the *ortho*-regioselectivity of the initial cycloaddition.

Although helicenebisquinone (*M*)-**1** could be also synthesized from quinone-substituted diene **5**, both chemical and optical yields were not competitive with the sequence starting from dienes **4a** and **4b**.

Finally, we were interested in performing the full aromatization of the central ring of dihydro[5]helicenequinones **20**, **27** and **36** and bisquinone **1** prepared by us. Fully aromatic helicene[5]bisquinones have been already synthesized by Katz and coworkers which have demonstrated to possess excellent chiroptical properties and usefulness as new materials.[42] After several trials, the best conditions for the full aromatization[39b] of (*P*)-**20** corresponded to the use of an excess of DDQ (10 equiv) in benzene (4 d) or toluene (2 d) heated under reflux (Scheme 8), affording [5]helicenequinone (*P*)-**40** in 71 and 65% yield, respectively, without loss of its optical integrity. When similar conditions were applied to dihydroaromatic derivative (*P*)-**36**, only dihydro helicenebisquinone (*P*)-**1** was obtained, which did not evolve to the



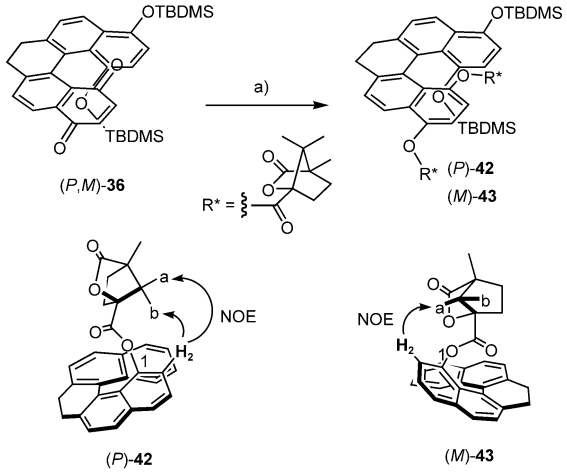
Scheme 7. Synthesis of dihydro[5]helicenes (*M*)-**1** and (*P*,*M*)-**39** from diene **5**.



Scheme 8. Enantioselective synthesis of fully aromatized (*P*)-[5]helicenequinones **40** and **41**.

corresponding fully aromatic compound. Nevertheless, OTBDMS-substituted compound (*P*)-**36** (*ee* >98%) could be fully aromatized, previous transformation (CsF/MeI)[43] into its dimethoxy substituted derivative (*P*)-**20** {$[\alpha]_D^{20} = +3200$ ($c = 0.004$ in $CHCl_3$), *ee* >95%}[32] and subsequent treatment with an excess of DDQ in benzene heated under reflux. [5]Helicenequinone (*P*)-**40** {$[\alpha]_D^{20} = +1430$ ($c = 0.009$ in $CHCl_3$), *ee* >95%}[32] was thus obtained in enantiomerically pure form in 71% yield. We also performed the full aromatization of ethoxy substituted dihydroaromatic derivative (*P*)-**27** (92% *ee*) with an excess of DDQ in benzene heated under reflux for 5 d to obtain [5]helicenequinone (*P*)-**41** {$[\alpha]_D^{20} = +910$ ($c = 0.004$ in $CHCl_3$), 92% *ee*}.[32]

The absolute configuration of all helicenes prepared by us was initially assigned by comparison with the sign of the optical rotation of other helicenes.[44] This configurational assignment was later confirmed by applying the methodology described by Katz[14a] based on the different O=C–C–O conformations of (*M*)- and (*P*)-helicenol camphanates which bring about a different polarity and NMR behaviour of each diastereoisomer. Thus, as depicted in Scheme 9, we prepared



Scheme 9. Synthesis and characteristic NOESY enhancements of bis-camphanates (*P*)-**42** and (*M*)-**43**. a) Zn, (–)-camphanoyl chloride, DMAP, Et_3N, CH_2Cl_2, reflux, 1 h, 48% for (*P*)-**42** and 45% for (*M*)-**43** from (*P*,*M*)-**36**, 92% for (*P*)-**42** from (*P*)-**36**.

bis-(–)-camphanates (*P*)-**42** and (*M*)-**43** from racemic (*P*,*M*)-**36** and the diastereoisomer (*P*)-**42** from enantiopure (*P*)-**36** (Zn, (–)-camphanoyl chloride, DMAP, Et_3N). The lower R_f (0.42) shown by diastereoisomer (*P*)-**42** in TLC on silica gel (hexane/EtOAc 2:1) with respect to that of (*M*)-**43** ($R_f = 0.49$), as well as the differentiated NOESY enhancements shown in Scheme 9 between H_2 and methyl groups *a* and *b* of the inside camphanate at C-1 in the *P* isomer and only methyl group *a* in the *M* one, are consistent with the data reported[14a] for determining the absolute configuration of these derivatives. Moreover, the absolute configuration of dihydro[5]helicene (*M*)-**43** could be unequivocally established by X-ray structural analysis (Figure 5).[35]

Figure 5. ORTEP drawing of dihydro[5]helicenequinone (*M*)-**43**. Hydrogens are omitted for clarity.

Conclusion

We have established two complementary ways to chiral dihydro[5]helicenequinones based on the domino asymmetric Diels–Alder reaction/pyrolytic sulfoxide elimination and in situ oxidation as key steps. The one-pot procedure stems on the use of 1,4-divinyl-1,3-cyclohexadiene and (S*S*)-2-*p*-tolylsulfinyl-1,4-benzoquinone (**2**) as cycloaddition partners. This shortest approach gave dihydro[5]helicenebisquinone (*M*)-**1** in 3.8% overall yield and 50% *ee*. In the stepwise approach, vinyl substituted dihydrophenanthrenequinone **5**, phenanthrenehydroquinone dimethyl ethers **4a** and **25** or di-*tert*-butyldimethylsilyl ether **4b** were used as dienes, to obtain dihydro[5]helicenebisquinone (*M*)-**1** (4.6% overall yield and 74% *ee*), dihydro[5]helicenequinone (*P*)-**20** (34% overall yield and 84% *ee*), dihydro[5]helicenequinone (*P*)-**27** (23% overall yield and 92% *ee*) and dihydro[5]helicenequinone (*P*)-**36** (21% overall yield and >98% *ee*), respectively. In turn, this access to dihydro[5]helicenequinones allows, after isolation of the cycloaddition/pyrolytic elimination products (*R*)-**19** or (*R*)-**35** from dienes **4a** and **4b**, the divergent synthesis of either *P* or *M* enantiomeric helimers from such common intermediates by simply selecting the oxidant reagent [best results: (*M*)-**20** (19% overall yield and 90% *ee*, CAN), (*P*)-**36** (12.6% overall yield and 96% *ee*, DDQ) and (*M*)-**1** (8.6% overall yield and 92% *ee*, CAN).

The maximum optical yield is defined in the cycloaddition step, but the absolute configuration of the helicene is selected in the oxidation step. Our method illustrates the possibility of transforming centrally chiral compounds, a sulfinyl quinone, into the corresponding helically chiral dihydro[5]helicenequinones and bisquinones in excellent optical yields. This study also revealed the strong influence of the electron donating or electron withdrawing aromatic substituent of the diene in its reactivity and led not only to the efficient synthesis of the desired targets but also to the unequivocal configurational assignment and full comprehension of the regio- and stereochemistry of the cycloaddition step.

Experimental Section

General methods: Melting points were obtained in open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. All reactions were monitored by thin-layer chromatography which was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230–400 mesh). Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. CH_2Cl_2 was dried over P_2O_5. Dry THF was distilled from sodium/benzophenone. All other reagent quality solvents were used without purification. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2, and solvent drying with Na_2SO_4.

General procedure I—Enol triflate formation: A solution of 0.5 M KHMDS in toluene (4.7 mL, 2.34 mmol) was added to a solution of the corresponding ketone (1.80 mmol) and *N*-phenyltrifluoromethanesulfonimide (2.34 mmol) in dry THF (18 mL) at −78 °C under argon. After stirring at −78 °C for the time indicated, the mixture was quenched with H_2O, extracted with diethyl ether and dried with $MgSO_4$. After workup and flash chromatography pure enol triflate was obtained.

8-[(Trifluoromethanesulfonyl)oxy]-1,4-dioxaspiro[4.5]dec-7-ene (7): Compound **7** was obtained according to GP I (4 h) from ketone **6** (hexane/EtOAc 90:10) in quantitative yield: ^{1}H NMR: $\delta = 1.90$ (t, $J = 6.5$ Hz, 2H), 2.40 (m, 2H), 2.53 (m, 2H), 3.98 (m, 4H), 5.66 ppm (tt, $J = 1.2$, 4.0 Hz, 1H); ^{13}C NMR: $\delta = 26.2$, 30.9, 34.0, 64.5 (2C), 105.9, 108.9–115.2–121.6–128.0 (q, $J = 321$ Hz, CF_3), 115.8, 148.1 ppm; MS (EI) *m*/*z* (%): 155 (100) $[M - SO_2CF_3]^+$.

1,4-Bis[(trifluoromethanesulfonyl)oxy]-1,3-cyclohexadiene (9): Compound **7** (665 mg, 2.27 mmol) in admixture dissolved in a mixture of CH_3CN (21 mL) and H_2O (40 drops) was added to a solution of 1 M $LiBF_4$ in CH_3CN (5.70 mL, 5.70 mmol) under argon. After refluxing for 20 h and workup, 4-[(trifluoromethanesulfonyl)oxy]-3-cyclohexenone (**8**) was obtained as a very unstable solid which was used immediately in the next step without further purification. ^{1}H NMR: $\delta = 2.67$ (m, 2H), 2.79 (m, 2H), 3.04 (m, 2H), 5.87 ppm (t, $J = 4.0$ Hz, 1H). Compound **9** was obtained according to GP I (2 h) from ketone **8** (hexane/EtOAc 40:1) over two steps (87%). M.p. 30–33 °C (hexane); ^{1}H NMR: $\delta = 2.81$ (s, 4H), 5.91 ppm (s, 2H); ^{13}C NMR: $\delta = 26.6$, 112.5, 112.1/116.3/120.6/124.8 (q, $J = 320$ Hz, CF_3), 147.1 ppm; MS (EI): calcd for $C_8H_6S_2O_6F_6$: 375.95100; found: 375.95081 $[M]^+$; *m*/*z* (%): 376 (11) $[M]^+$, 69 (100).

1,4-Divinyl-1,3-cyclohexadiene (3): Vinyltributylstannane (1.26 mL, 4.32 mmol) was added under argon to a well-stirred mixture of **9** (812 mg, 2.16 mmol) in dry THF (40 mL), containing LiCl (918 mg, 21.6 mmol) and $[Pd(PPh_3)_4]$ (210 mg, 0.18 mmol). The mixture was heated under reflux for 2.5 h, diluted with hexane and washed with 10% aqueous NH_4OH solution, water and brine. After workup and flash chromatography (hexane), compound **3** was obtained. ^{1}H NMR: $\delta = 2.43$ (s, 4H), 5.08 (d, $J = 10.5$ Hz, 2H), 5.26 (d, $J = 17.4$ Hz, 2H), 5.98 (s, 2H), 6.45 ppm (dd, $J =$ 17.4, 10.5 Hz, 2H); ^{13}C NMR: $\delta = 21.8$, 112.3, 125.6, 136.6, 138.2 ppm; MS (EI): calcd for $C_{10}H_{12}$: 132.09390; found: 132.09393 $[M]^+$; *m*/*z* (%): 132 (100) $[M]^+$.

Dihydro[5]helicenebisquinone (*M*)-1 from 3: Bis-diene **3** (60 mg, 0.45 mmol) in CH_2Cl_2 (4 mL) was slowly added to a solution of (S*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone [(+)-**2**][26] (442 mg, 1.80 mmol) in CH_2Cl_2 (4 mL) under argon. The mixture was stirred at room temperature for 3 d, and the solvent was evaporated. After flash chromatography (hexane/EtOAc 6:1), two compounds were isolated: derivative **10** as a mixture of regio- and/or diastereoisomers which could not be separated, in 7% yield, and helicene (*M*)-**1**, in 12% yield. {$[\alpha]_D^{20} = -1810$ ($c = 0.02$ in $CHCl_3$), 50% *ee*}; ^{1}H NMR: $\delta = 2.79$ (m, 4H), 6.74/6.90 (AB system, $J =$ 10.0 Hz, 4H), 7.64 (d, $J = 8.1$ Hz, 2H), 8.06 ppm (d, $J = 8.1$ Hz, 2H); ^{13}C NMR: $\delta = 30.4$, 126.6, 131.2, 131.4, 132.2, 132.4, 137.3, 139.8, 147.7, 184.7, 186.9 ppm; MS (EI): calcd for $C_{22}H_{12}O_4$: 340.07356; found: 340.07318 $[M]^+$; *m*/*z* (%): 340 (63) $[M]^+$, 258 (100).

General procedure II—Stille couplings: To a stirred solution of the enol triflate (0.30 mmol) in dry THF (3 mL), containing LiCl (64 mg, 1.50 mmol) and $[Pd(PPh_3)_4]$ (15 mg, 0.013 mmol), the corresponding vinyltributylstannane (0.30 mmol) was added under argon. The mixture was heated under reflux for the time indicated, diluted with CH_2Cl_2 and washed with 10% aqueous NH_4OH solution, water and brine. After workup and flash chromatography, pure diene was obtained.

8-Ethenyl-1,4-dioxaspiro[4.5]dec-7-ene (12): Compound **12**[29] was obtained (79%) according to GP II (1.5 h) from enol triflate **7** and vinyltributylstannane (hexane/EtOAc 90:10). ^{1}H NMR: $\delta = 1.83$ (m, 2H), 2.38 (m, 4H), 3.99 (s, 4H), 4.95 (d, $J = 10.7$ Hz, 1H), 5.09 (d, $J = 17.2$ Hz, 1H), 5.65 (m, 1H), 6.36 ppm (dd, $J = 17.2$, 10.7 Hz, 1H); ^{13}C NMR: $\delta = 22.8$, 30.6, 35.9, 64.3 (2C), 107.9, 111.0, 126.0, 135.4, 138.8 ppm; MS (EI): calcd for $C_{10}H_{14}O_2$: 166.09938; found: 166.09953 $[M]^+$; *m*/*z* (%): 166 (30) $[M]^+$, 86 (100).

Spiro[1,3-dioxolane-2,3′-1′,4′,4a′,9′-tetrahydro-(2′H)-phenanthrene-5′,8′-dione] (13): Diene **12** (450 mg, 2.7 mmol) was added to a solution of racemic 2-(*p*-tolylsulfinyl)-1,4-benzoquinone [(±)-**2**][26] (1.07 g, 4.3 mmol) in dry CH_2Cl_2 (25 mL) under argon. The mixture was stirred at room temperature for 6 h, and the solvent was evaporated. After flash chromatography (hexane/EtOAc 6:1), compound **13** was obtained (81%). M.p. 199–200 °C (EtOAc/hexane); ^{1}H NMR: $\delta = 1.29$ (t, $J = 12.4$ Hz, 1H), 1.64 (m, 1H), 1.88 (m, 1H), 2.30 (m, 3H), 3.06 (m, 2H), 3.48 (m, 1H), 3.9–4.2 (m, 4H), 5.50 (br s, 1H), 6.69 ppm (AB system, $J = 10.5$ Hz, 2H); ^{13}C NMR: $\delta = 24.8$, 32.0, 33.8, 36.9, 41.7, 64.4 (2C), 108.4, 114.5, 135.9, 136.2, 136.7, 141.3, 186.7, 187.1 ppm; MS (EI): *m*/*z* (%): 272 (100) $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{16}O_4$ (272.3): C 70.57, H 5.92; found: C 70.77, H 6.19.

Spiro[1,3-dioxolane-2,3′-5′,8′-dimethoxy-1′,4′,4a′,9′-tetrahydro-(2′H)-phenanthrene] (15): ***From 13***: A solution of $Na_2S_2O_4$ (1.91 g, 11.0 mmol) in H_2O (25 mL) was added to a solution of quinone **13** (529 mg, 1.94 mmol) in EtOAc (25 mL). The mixture was vigorously shaken in a separatory funnel for 5 min. The organic layer was separated and washed with brine. After workup, the corresponding hydroquinone was obtained and, without further purification, was immediately dissolved in acetone (45 mL) and treated with K_2CO_3 (3.84 g, 27.8 mmol) and Me_2SO_4 (787 μL, 8.3 mmol). After the solution was heated under reflux for 5 h, the mixture was hydrolyzed with water, extracted with diethyl ether and dried with $MgSO_4$. After workup and flash chromatography (hexane/EtOAc 6:1), compound **15** was obtained (84%). M.p. 107–109 °C; ^{1}H NMR: $\delta = 1.35$ (t, $J =$ 12.3 Hz, 1H), 1.72 (dt, $J = 6.8$, 12.3 Hz, 1H), 1.96 (m, 1H), 2.36 (m, 2H), 2.63 (dt, $J = 12.3$, 3.2 Hz, 1H), 3.30 (m, 2H), 3.72 (m, 1H), 3.77 (s, 3H), 3.80 (s, 3H), 3.91–4.16 (m, 4H), 5.62 (t, $J = 3.0$ Hz, 1H), 6.62/6.67 ppm (AB system, $J = 8.9$ Hz, 2H); ^{13}C NMR: $\delta = 24.9$, 32.3, 34.1, 37.1, 41.7, 55.1, 55.2, 63.9, 64.0, 106.7, 107.4, 108.9, 115.4, 123.7, 126.9, 136.7, 150.7, 150.9 ppm; MS (EI): *m*/*z* (%): 302 (100) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{22}O_4$ (302.4): C 71.50, H 7.33; found: C 71.26, H 7.12.

From 14: Diene **12** (623 mg, 3.75 mmol) was added to a solution of 1,4-benzoquinone (405 mg, 3.75 mmol) in dry CH_2Cl_2 (15 mL) under argon. After the reaction mixture was stirred at room temperature for 15 d, the solvent was evaporated to afford spiro[1,3-dioxolane-2,3′-1′,4′,4a′,4b′,8a′,9′-hexahydro-(2′H)-phenanthrene-5′,8′-dione] (**14**) which, without further purification, was dissolved in acetone (50 mL) and treated with K_2CO_3 (7.76 g, 56.00 mmol) and Me_2SO_4 (1.60 mL, 17.00 mmol). The mixture was refluxed for 6 h, and hydrolyzed with water. After workup and flash chromatography (hexane/EtOAc 6:1), compound **15** was obtained (90%).

Spiro[1,3-dioxolane-2,3′-5′,8′-dimethoxy-1′,4′-dihydro-(2′*H*)-phenanthrene] (16): DDQ (794 mg, 3.50 mmol) in CH_2Cl_2 (20 mL) was added to a solution of **15** (874 mg, 2.90 mmol) in CH_2Cl_2 (60 mL). The mixture was stirred at room temperature for 20 min, diluted with CH_2Cl_2, and washed several times with water. After workup and flash chromatography (hexane/EtOAc 6:1), compound **16** was obtained in quantitative yield. M.p. 142–143 °C; ^{1}H NMR: $\delta = 1.99$ (t, $J = 6.9$ Hz, 2H), 3.13 (t, $J = 6.9$ Hz, 2H), 3.72 (s, 2H), 3.86 (s, 3H), 3.93 (s, 3H), 4.06 (m, 4H), 6.66/6.72 (AB system, $J =$ 8.5 Hz, 2H), 7.21 (d, $J = 8.9$ Hz, 1H), 8.03 ppm (d, $J = 8.9$ Hz, 1H); ^{13}C NMR: $\delta = 29.4$, 30.5, 40.1, 55.8, 55.9, 64.4 (2C), 103.0, 105.8, 108.8, 119.8, 125.9, 126.2, 127.4, 130.0, 133.4, 149.7, 151.9 ppm; MS (EI): *m*/*z* (%): 300 (100) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{20}O_4$ (300.3): C 71.98, H 6.71; found: C 71.76, H 6.57.

5,8-Dimethoxy-1,4-dihydro-(2*H*)-phenanthren-3-one (17): Solid $CeCl_3 \cdot 7H_2O$ (1.90 g, 5.1 mmol) was added to a solution of **16** (903 mg, 3.00 mmol) and NaI (90 mg, 0.6 mmol) in CH_3CN (70 mL). The mixture was heated under reflux for 3 h, filtered and washed with CH_2Cl_2. After elimination of the solvent and flash chromatography (hexane/EtOAc 4:1), compound **17** was obtained (85%). M.p. 99–100 °C; ^{1}H NMR: $\delta = 2.60/3.14$ (2t, $J =$ 6.5 Hz, 4H), 3.83 (s, 3H), 3.92 (s, 3H), 4.43 (s, 2H), 6.63/6.69 (AB system, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 8.6$ Hz, 1H), 8.11 ppm (d, $J = 8.6$ Hz, 1H); ^{13}C NMR: $\delta = 29.8$, 38.0, 44.5, 55.5, 55.6, 103.0, 105.6, 120.6, 124.7, 124.8, 126.5, 129.0, 134.4, 149.6, 151.3, 211.9 ppm; MS (EI): calcd for $C_{16}H_{16}O_3$: 256.10994; found: 256.11026 $[M]^+$; *m*/*z* (%): 256 (100) $[M]^+$.

5,8-Dimethoxy-3-[(trifluoromethanesulfonyl)oxy]-1,2-dihydrophenanthrene (18): Compound **18** was obtained according to GP I (20 min) from ketone **17** (hexane/EtOAc 9:1) in 95% yield. M.p. 102–103 °C; ^{1}H NMR: $\delta = 2.69$ (t, $J = 8.5$ Hz, 2H), 3.15 (t, $J = 8.5$ Hz, 2H), 3.91 (s, 3H), 3.95 (s, 3H), 6.67/6.78 (AB system, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 1H), 8.16 (d, $J = 8.5$ Hz, 1H), 8.23 ppm (s, 1H); ^{13}C NMR: $\delta = 25.5$, 30.2, 55.7, 55.8, 103.0, 106.6, 119.8, 122.5, 122.8, 126.0, 126.2, 126.7, 132.8, 148.7, 149.8, 150.9 ppm; MS (EI): calcd for $C_{17}H_{15}F_3O_5S$: 388.05923; found: 388.05859 $[M]^+$; *m*/*z* (%): 388 (47) $[M]^+$, 255 (100).

5,8-Dimethoxy-3-vinyl-1,2-dihydrophenanthrene (4a): Compound **4a** was obtained according to GP II (1 h) from enol triflate **18** and vinyltributylstannane (hexane/EtOAc 20:1) in 82% yield. M.p. 110–112 °C; ^{1}H NMR: $\delta = 2.47/2.97$ (2dd, $J = 8.9$, 7.7 Hz, 4H), 3.92 (s, 3H), 3.95 (s, 3H), 5.17 (d, $J = 10.5$ Hz, 1H), 5.39 (d, $J = 17.3$ Hz, 1H), 6.65/6.77 (AB system, $J =$ 8.5 Hz, 2H), 6.73 (dd, $J = 17.3$, 10.5 Hz, 1H), 7.32 (d, $J = 8.5$ Hz, 1H), 8.09 (s, 1H), 8.11 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = 21.0$, 29.6, 55.7, 56.1, 102.6, 106.6, 111.8, 120.9, 122.8, 126.4, 126.8, 129.5, 129.9, 135.6, 136.7, 139.6, 150.0, 151.6 ppm; MS (EI): calcd for $C_{18}H_{18}O_2$: 266.13068; found: 266.13055 $[M]^+$; *m*/*z* (%): 266 (100) $[M]^+$.

General procedure III—Synthesis of dihydro[5]helicenequinones by Diels–Alder reactions: To a solution of (*SS*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (+)-**2**[26] (74 mg, 0.30 mmol) in CH_2Cl_2 (3 mL) under argon at the temperature indicated (see Table 1 for reaction conditions), the corresponding diene (0.15 mmol) in CH_2Cl_2 (3 mL) was slowly added. After the time required and evaporation of the solvent, crude dihydro[5]helicenequinones were obtained and purified by flash chromatography.

Dihydro[5]helicenequinone (*P*)-20 from 4a: Compound (*P*)-**20** was obtained according to GP III (see Table 1 for reaction conditions) from diene **4a** (CH_2Cl_2). M.p. 180–181 °C (methanol); ^{1}H NMR: $\delta = 2.7–3.0$ (m, 4H), 3.42 (s, 3H), 3.99 (s, 3H), 6.68/6.73 (AB system, $J = 8.5$ Hz, 2H), 6.69 (d, $J = 10.0$ Hz, 1H), 6.87 (d, $J = 10.0$ Hz, 1H), 7.47 (d, $J = 8.5$ Hz, 1H), 7.57 (dd, $J = 7.7$, 1.0 Hz, 1H), 8.01 (d, $J = 7.7$ Hz, 1H), 8.33 ppm (d, $J =$ 8.5 Hz, 1H); ^{13}C NMR: $\delta = 30.5$, 31.0, 55.4, 55.7, 102.8, 106.3, 123.4, 124.0, 124.6, 125.8, 125.9, 127.7, 129.5, 129.7, 132.7, 135.2, 136.4, 140.1, 141.5, 147.5, 148.3, 150.9, 183.6, 185.9 ppm; MS (EI): *m*/*z* (%): 370 (28) $[M]^+$, 258 (100); elemental analysis calcd (%) for $C_{24}H_{18}O_4$ (370.4): C 77.82, H 4.90; found: C 77.70, H 5.05.

General procedure IV—Synthesis of dihydro[5]helicenebisquinones by CAN oxidation: A solution of the corresponding dihydro[5]helicenequinone (0.048 mmol) in CH_2Cl_2 (2 mL) was slowly added to a rapidly stirring solution of ammonium cerium nitrate (132 mg, 0.24 mmol) in H_2O (2 mL) and CH_3CN (2 mL). The mixture was stirred for 2 h, diluted with CH_2Cl_2 and washed several times with H_2O. After workup and flash chromatography, pure dihydro[5]helicenebisquinones were obtained.

Dihydro[5]helicenebisquinone (*P*)-1 from (*P*)-20: Compound (*P*)-**1** was obtained according GP IV from (*P*)-**20** (72% *ee*) (CH_2Cl_2/EtOAc 15:1) in 82% yield. M.p. 283–284 °C (methanol); $[\alpha]_D^{20} = +2670$ ($c = 0.011$ in $CHCl_3$), 72% *ee*.

3-Methyl-dihydro[5]helicenequinone (*P,M*)-24: Diene **4a** (32 mg, 0.12 mmol) was added to a solution of racemic 2-(*p*-tolylsulfinyl)-5-methyl-1,4-benzoquinone (**21**)[34] (62 mg, 0.24 mmol) in dry CH_2Cl_2 (3 mL) under argon. The mixture was stirred at −20 °C for 7 d, and then DDQ (54 mg, 0.24 mmol) was added at room temperature. After 30 min, the mixture was diluted with CH_2Cl_2, and washed several times with water. After workup and flash chromatography (CH_2Cl_2), compound (*P,M*)-**24** was obtained in 67% yield. M.p. 217–218 °C (methanol); ^{1}H NMR: $\delta =$ 2.16 (d, $J = 1.2$ Hz, 3H), 2.66–2.94 (m, 4H), 3.39 (s, 3H), 3.98 (s, 3H), 6.55 (d, $J = 1.2$ Hz, 1H), 6.68/6.72 (AB system, $J = 8.5$ Hz, 2H), 7.46 (d, $J =$ 8.5 Hz, 1H), 7.55 (d, $J = 7.7$ Hz, 1H), 8.03 (d, $J = 7.7$ Hz, 1H), 8.32 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = 15.9$, 30.5, 30.9, 55.4, 55.7, 102.7, 106.4, 123.2, 123.3, 124.2, 124.7, 125.8, 127.8, 129.4, 129.8, 132.9, 135.0, 136.7, 141.3, 145.3, 147.1, 148.5, 150.8, 183.6, 186.3 ppm; MS (EI): *m*/*z* (%): 384 (100) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{20}O_4$ (384.4): C 78.11, H 5.24; found: C 77.84, H 5.40.

3-(1-Ethoxyvinyl)-5,8-Dimethoxy-1,2-dihydrophenanthrene (25): Compound **25** was obtained according to GP II (2 h) from enol triflate **18** and (1-ethoxyvinyl)tributylstannane (Al_2O_3, hexane/EtOAc 20:1) as a very unstable oil (67%). ^{1}H NMR: $\delta = 1.48$ (t, $J = 7.0$ Hz, 3H), 2.46 (dd, $J = 9.5$, 7.0 Hz, 2H), 2.95 (dd, $J = 9.5$, 7.0 Hz, 2H), 3.93 (s, 3H), 3.93 (q, $J = 7.0$ Hz, 2H), 3.94 (s, 3H), 4.24 (d, $J = 2.4$ Hz, 1H), 4.47 (d, $J = 2.4$ Hz, 1H), 6.65, 6.78 (AB system, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.6$ Hz, 1H), 8.09 (d, $J =$ 8.6 Hz, 1H), 8.67 ppm (s, 1H).

6-Ethoxy-dihydro[5]helicenequinone (*P*)-27: Compound (*P*)-**27** was obtained according to GP III (see Table 1 for reaction conditions) from diene **25** (CH_2Cl_2). M.p. 257–258 °C (methanol); ^{1}H NMR: $\delta = 1.53$ (t, $J = 7.0$ Hz, 3H), 2.22 (dt, $J = 4.8$, 15.0 Hz, 1H), 2.75 (dt, $J = 4.2$, 15.0 Hz, 1H), 2.89 (ddd, $J = 2.2$, 5.0, 15.0 Hz, 1H), 3.42 (s, 3H), 3.45 (ddd, $J = 2.2$, 4.2, 15.0 Hz, 1H), 3.98 (s, 3H), 4.26 (dq, $J = 9.5$, 7.0 Hz, 1H), 4.30 (dq, $J = 9.5$, 7.0 Hz, 1H), 6.63 (d, $J = 10.3$ Hz, 1H), 6.65/6.71 (AB system, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 10.3$ Hz, 1H), 7.47 (d, $J = 8.5$ Hz, 1H), 7.54 (s, 1H), 8.31 ppm (d, $J =$ 8.5 Hz, 1H); ^{13}C NMR: $\delta = 14.8$, 22.0, 30.6, 55.3, 55.7, 64.4, 102.6, 106.0, 106.1, 123.1, 125.5, 125.8, 126.9, 128.0, 130.1, 136.0, 136.3, 137.5, 140.3, 141.4, 148.5, 150.7, 157.2, 182.9, 186.2 ppm; MS (EI): *m*/*z* (%): calcd for $C_{26}H_{22}O_5$: 414.14672; found: 414.14621 (100) $[M]^+$.

6-Ethoxy-dihydro[5]helicenebisquinone (*P*)-28: Compound (*P*)-**28** was obtained from (*P*)-**27** (92% *ee*) according to GP IV (CH_2Cl_2/EtOAc 12:1) in 90% yield: M.p. >300 °C (methanol); $[\alpha]_D^{20} = +3370$ ($c = 0.0065$ in

$CHCl_3$), 92% *ee*; ^{1}H NMR: $\delta = 1.52$ (t, $J = 6.9$ Hz, 3H), 2.19 (dt, $J = 4.5$, 15.5 Hz, 1H), 2.58 (dt, $J = 4.4$, 15.3 Hz, 1H), 2.85 (ddd, $J = 2.0$, 4.5, 15.0 Hz, 1H), 3.42 (ddd, $J = 2.0$, 4.5, 15.0 Hz, 1H), 4.25 (dq, $J = 9.3$, 6.9 Hz, 1H), 4.32 (dq, $J = 9.3$, 6.9 Hz, 1H), 6.65 (d, $J = 10.1$ Hz, 1H), 6.74 (d, $J = 10.1$ Hz, 1H), 6.83 (d, $J = 10.1$ Hz, 1H), 6.88 (d, $J = 10.1$ Hz, 1H), 7.54 (s, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 8.04 ppm (d, $J = 7.7$ Hz, 1H); ^{13}C NMR: $\delta = 14.7$, 22.0, 29.9, 64.6, 107.5, 124.1, 126.3, 130.6, 131.7, 132.3, 132.4, 132.7, 135.0, 136.6, 136.9, 137.3, 139.8, 140.2, 147.8, 159.3, 184.8, 185.1, 185.8, 186.7 ppm; MS (EI): *m*/*z* (%): calcd for $C_{24}H_{16}O_5$: 384.09977; found: 384.09961 (100) $[M]^+$.

General procedure V--Synthesis of tetrahydro[5]helicenequinones by Diels – Alder reactions: To a solution of (*SS*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone [(+)-**2**][26] (37 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) under argon at $-40\,^\circ$C, the corresponding diene (0.15 mmol) in CH_2Cl_2 (3 mL) was slowly added. After the solution was stirred for 5 d at the same temperature, the solvent was evaporated, and the residue purified by flash chromatography (CH_2Cl_2). Pure tetrahydro[5]helicenequinones were obtained as unstable brown solids, which were used immediately in the next reactions without any purification.

Tetrahydro[5]helicenequinone (*R*)-19: Compound **19** was obtained according to GP V from **4a** in 61% yield: $[\alpha]_D^{20} = -736$ ($c = 0.0012$ in $CHCl_3$); ^{1}H NMR: $\delta = 2.37 - 2.95$ (m, 5H), 3.62 (s, 3H), 3.71 (m, 1H), 3.95 (s, 3H), 5.38 (m, 1H), 5.85 (m, 1H), 6.38/6.64 (AB system, $J = 10.2$ Hz, 2H), 6.61/6.66 (AB system, $J = 8.6$ Hz, 2H), 7.29, 8.17 ppm (AB system, $J = 8.6$ Hz, 2H).

General procedure VI—Partial aromatizations of tetrahydro[5]helicenequinones: To a solution of tetrahydro[5]helicenequinones **19** or **35** (0.03 mmol) in CH_2Cl_2 (0.5 mL), the corresponding oxidant reagent in CH_2Cl_2 (0.5 mL) was slowly added (see Table 2 for experimental conditions). After the time required in each case, workup and flash chromatography (CH_2Cl_2), pure dihydro[5]helicenequinones or bisquinones were obtained.

Dihydro[5]helicenequinone (*M*)-20 from tetrahydro[5]helicenequinone (*R*)-19: Compound (*M*)-**20** was obtained according to GP VI from (*R*)-**19**, by using DDQ (Table 2, entry 1) or CAN (Table 2, entry 5).

Dihydro[5]helicenequinone (*P*)-20 from tetrahydro[5]helicenequinone (*R*)-19: Compound (*P*)-**20** was obtained according to GP VI from (*R*)-**19**, by using (±)-**2**[26] (Table 2, entry 3) or DBU (Table 2, entry 4).

Tetrahydro[5]helicene (6a*S*,14c*R*)-29: Compound (*R*)-**19** (34 mg, 0.09 mmol) in EtOAc (1 mL) was added via syringe to a suspension of PtO_2 (2 mg, 0.009 mmol, 0.1 equiv) in EtOAc (1 mL) under a hydrogen atmosphere. After 3 d at room temperature the mixture was filtered on Celite and washed with EtOAc, and the solvent was evaporated. After flash chromatography (CH_2Cl_2), compound **29** was obtained as a white solid (53%). $[\alpha]_D^{20} = -226$ ($c = 0.34$ in $CHCl_3$); ^{1}H NMR: $\delta = 1.64$ (m, 3H), 2.21 (m, 2H), 2.61 (m, 1H), 2.79 (m, 2H), 3.02 (m, 2H), 3.67 (s, 3H), 3.96 (s, 3H), 4.47 (s, 1H), 5.26 (s, 1H), 5.54 (d, $J = 4.0$ Hz, 1H), 6.42/6.53 (AB system, $J = 8.5$ Hz, 2H), 6.70/6.81 (AB system, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 1H), 8.18 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = 20.0$, 26.3, 27.9, 30.7, 33.1, 40.3, 55.8, 56.0, 103.0, 106.9, 112.9, 114.5, 121.5, 125.2, 125.4, 126.4, 127.0, 128.1, 134.1, 139.1, 145.5, 149.3, 150.2, 150.9 ppm; MS (EI): *m*/*z* (%): calcd for $C_{24}H_{24}O_4$: 376.16746; found: 376.16769 (100) $[M]^+$.

Tetrahydro[5]helicene 30: Et_3N (132 μL) and CH_2Cl_2 (2 mL) were added to a mixture of tetrahydro[5]helicene **29** (17 mg, 0.045 mmol), (−)-camphanoyl chloride (49 mg, 0.23 mmol) and DMAP (3 mg, 0.023 mmol) under argon. After refluxing for 3.5 h, the mixture was filtered through Celite, aided by several ethyl acetate washes, in order to remove remaining Zn. The organic solution was washed with saturated aqueous $NaHCO_3$, 2% HCl and water. After workup and flash chromatography (hexane/EtOAc 70:30), compound **30** was obtained as a yellowish solid (78%). M.p. 228 – 230 °C (methanol); $[\alpha]_D^{20} = -133$ ($c = 0.18$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.53$ (ddd, $J = 4.4$, 9.3, 13.7 Hz, 1H), 0.77, 0.83/0.94 (3s, 9H), 1.05 – 1.42 (m, 4H), 1.16 (s, 3H), 1.19 (s, 6H), 1.47 – 1.69 (m, 2H), 1.80 (ddd, $J = 4.4$, 9.3, 13.0 Hz, 1H), 1.96 – 2.19 (m, 2H), 2.20 – 2.34 (m, 2H), 2.47 – 2.97 (m, 5H), 3.47/3.93 (2s, 6H), 5.31 (br d, $J = 4.8$ Hz, 1H), 6.61 (d, $J = 8.9$ Hz, 1H), 6.69 (s, 2H), 6.90 (dd, $J = 8.9$, 0.8 Hz, 1H), 7.18 (d, $J = 8.5$ Hz, 1H), 8.05 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = 9.5$, 9.7, 16.5, 16.7, 16.9, 17.0, 21.3, 26.5, 27.6, 28.4, 28.5, 28.9, 30.4, 31.0, 33.4, 41.2, 54.3, 54.5, 54.6, 54.9, 55.4, 56.0, 90.0, 90.9, 103.4, 106.0, 118.8, 120.5, 120.9, 126.2, 126.4, 127.6, 133.1, 135.0, 135.8, 136.1, 144.2, 147.6, 149.5, 151.7, 166.2, 166.3, 177.8, 177.9 ppm; MS (EI): *m*/*z* (%): calcd for $C_{44}H_{48}O_{10}$: 736.32475; found: 736.32599 (100) $[M]^+$.

Spiro[1,3-dioxolane-2,3′-5′,8′-bis[(*tert*-butyldimethylsilyl)oxy]-1′,4′,4a′,9′-tetrahydro-(2′H)-phenanthrene] (31): ***From 13***: A solution of $Na_2S_2O_4$ (2.18 g, 12.5 mmol) in H_2O (30 mL) was added to a solution of **13** (602 mg, 2.2 mmol) in EtOAc (30 mL). The mixture was vigorously shaken in a separatory funnel for 5 min. The organic layer was separated, washed with brine, dried with $MgSO_4$ and the solvent evaporated to afford the corresponding hydroquinone, which without purification was immediately dissolved in DMF (10 mL) and treated with TBDMSCl (829 mg, 5.5 mmol) and imidazole (751 mg, 11.0 mmol). The mixture was stirred at room temperature overnight, hydrolyzed with an aqueous saturated solution of NH_4Cl and extracted with diethyl ether. The organic layer was washed with a saturated solution of NH_4Cl and brine. After workup and flash chromatography (hexane/EtOAc 40:1), compound **31** was obtained (81%). ^{1}H NMR: $\delta = 0.19$ (s, 6H), 0.23 (s, 3H), 0.25 (s, 3H), 1.00 (s, 9H), 1.03 (s, 9H), 1.38 (t, $J = 12.1$ Hz, 1H), 1.60 (m, 1H), 1.90 (m, 1H), 2.31 (m, 2H), 2.56 (dt, $J = 12.1$, 3.2 Hz, 1H), 3.24 (m, 2H), 3.64 (dq, $J = 12.1$, 4 Hz, 1H), 3.88 – 4.06 (m, 4H), 5.60 (t, $J = 3.2$ Hz, 1H), 6.50/6.54 ppm (AB system, $J = 8.5$ Hz, 2H); ^{13}C NMR: $\delta = -4.07$ (2C), −3.79 (2C), 18.2, 18.3, 25.8 (6C), 26.2, 32.7, 34.9, 37.7, 43.4, 64.4, 64.5, 109.3, 115.1, 115.7, 115.9, 126.2, 129.2, 137.4, 146.8, 147.3 ppm; MS (EI): *m*/*z* (%): calcd for $C_{28}H_{46}O_4Si_2$: 502.29347; found: 502.29245 (21) $[M]^+$, 73 (100).

From 14: Diene **12** (930 mg, 5.6 mmol) was added to a solution of 1,4-benzoquinone (605 mg, 5.6 mmol) in dry CH_2Cl_2 (20 mL) under argon. After stirring at room temperature for 15 d, the solvent was evaporated to afford spiro[1,3-dioxolane-2,3′-1′,4′,4a′,4b′,8a′,9′-hexahydro-(2′H)-phenanthrene-5′,8′-dione] (**14**) which, without further purification, was dissolved in DMF (25 mL) and treated with TBDMSCl (2.10 g, 14.00 mmol) and imidazole (1.90 g, 28.00 mmol). After stirring overnight at room temperature under argon, the mixture was hydrolyzed with an aqueous saturated solution of NH_4Cl and extracted with diethyl ether. The organic layer was washed with saturated solution of NH_4Cl and brine. After workup and flash chromatography (hexane/EtOAc 20:1), compound **31** was obtained (74% over the two steps.

Spiro[1,3-dioxolane-2,3′-5′,8′-bis[(*tert*-butyldimethylsilyl)oxy]-1′,4′-dihydro-(2′H)-phenanthrene] (32): Aromatization of compound **31** in a similar way that for **15** afforded **32** (96%). ^{1}H NMR: $\delta = 0.25$ (s, 6H), 0.37 (s, 6H), 1.06 (s, 9H), 1.10 (s, 9H), 2.02 (t, $J = 6.7$ Hz, 2H), 3.15 (t, $J = 6.7$ Hz, 2H), 3.77 (s, 2H), 4.06 (m, 4H), 6.66/6.71 (AB system, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.5$ Hz, 1H), 7.97 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = -4.1$ (2C), −3.6 (2C), 18.4, 18.9, 25.9 (3C), 26.3 (3C), 29.4, 30.8, 40.5, 64.5 (2C), 108.8, 111.6, 113.6, 120.8, 127.0, 127.4, 128.5, 129.9, 132.6, 145.5, 147.4 ppm; MS (EI): *m*/*z* (%): calcd for $C_{28}H_{44}O_4Si_2$: 500.27782; found: 500.27628 (100) $[M]^+$.

5,8-Bis[(*tert*-butyldimethylsilyl)oxy]-1,4-dihydro-2*H*-phenanthren-3-one (33): Ketal deprotection of **32** in a similar way that for preparation of **17** gave compound **33** (hexane/EtOAc 9:1) (95%). ^{1}H NMR: $\delta = 0.29$ (s, 6H), 0.38 (s, 6H), 1.06 (s, 9H), 1.12 (s, 9H), 2.64 (t, $J = 6.5$ Hz, 2H), 3.20 (t, $J = 6.5$ Hz, 2H), 4.51 (s, 2H), 6.72/6.77 (AB system, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 1H), 8.09 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = -4.2$ (2C), −3.6 (2C), 18.3, 18.8, 25.9 (3C), 26.2 (3C), 29.7, 37.9, 44.5, 111.7, 114.2, 121.5, 126.1, 126.4, 128.8, 129.0, 134.4, 145.7, 146.9, 211.2 ppm; MS (EI): *m*/*z* (%): calcd for $C_{26}H_{40}O_3Si_2$: 456.25160; found: 456.25122 (98) $[M]^+$, 73 (100).

5,8-Bis[(*tert*-butyldimethylsilyl)oxy]-3-[(trifluoromethanesulfonyl)oxy]-1,2-dihydrophenanthrene (34): Compound **34** was obtained according to GP I (20 min) from ketone **33** (hexane/EtOAc 40:1) in 72% yield. M.p. 71 – 73 °C; ^{1}H NMR: $\delta = 0.29$ (s, 6H), 0.32 (s, 6H), 1.05 (s, 9H), 1.12 (s, 9H), 2.74 (t, $J = 8.5$ Hz, 2H), 3.19 (t, $J = 8.5$ Hz, 2H), 6.73/6.81 (AB system, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 1H), 8.24 ppm (s, 1H); ^{13}C NMR: $\delta = -4.0$ (2C), −3.9 (2C), 18.4, 18.7, 25.5, 25.9 (3C), 26.0 (3C), 30.0, 111.8, 112.3/116.5/120.8/125.0 (q, $J = 320$ Hz, CF_3), 115.4, 120.3, 123.4, 124.8, 125.6, 126.3, 129.0, 132.7, 146.0, 146.5, 147.7 ppm; MS (EI): *m*/*z* (%): calcd for $C_{27}H_{39}F_3O_5SSi_2$: 588.20089; found: 588.19965 (33) $[M]^+$, 73 (100).

5,8-Bis[(*tert*-butyldimethylsilyl)oxy]-3-vinyl-1,2-dihydrophenanthrene (4b): Compound **4b** was obtained according to GP II (4.5 h) from enol triflate **34** and vinyltributylstannane (hexane/EtOAc 60:1) in 74% yield. M.p. 49 – 52 °C; ^{1}H NMR: $\delta = 0.27$ (s, 6H), 0.29 (s, 6H), 1.04 (s, 9H), 1.12 (s, 9H), 2.48 (t, $J = 8.3$ Hz, 2H), 2.96 (t, $J = 8.3$ Hz, 2H), 5.18 (d, $J = 11.0$ Hz, 1H), 5.38 (d, $J = 17.0$ Hz, 1H), 6.69/6.77 (AB system, $J = 8.5$ Hz, 2H), 6.72

(dd, $J = 11.0, 17.0$ Hz, 1H), 7.29 (d, $J = 8.5$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 8.04 ppm (s, 1H); ^{13}C NMR: $\delta = -4.1$ (2C), -3.8 (2C), 18.4, 18.7, 21.1, 25.9 (3C), 26.1 (3C), 29.4, 111.3, 111.7, 115.0, 121.8, 124.9, 126.0, 129.1, 129.6, 130.1, 135.1, 135.4, 139.2, 145.9, 147.0 ppm; MS (EI): *m/z* (%): calcd for $C_{28}H_{42}O_2Si_2$: 466.27234; found: 466.27054 (100) $[M]^+$.

Dihydro[5]helicenequinone (*P*)-36 from 4b: Compound (*P*)-**36** was obtained according to GP III (see Table 1 for reaction conditions) from diene **4b** (CH_2Cl_2). M.p. 151–153 °C; ^{1}H NMR: $\delta = -0.48$ (s, 3H), -0.26 (s, 3H), 0.29 (s, 3H), 0.30 (s, 3H), 0.51 (s, 9H), 1.10 (s, 9H), 2.7–3.0 (m, 4H), 6.67/6.73 (AB system, $J = 8.1$ Hz, 2H), 6.75/6.82 (AB system, $J = 10.1$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 1H), 7.57 (dd, $J = 7.7$, 0.8 Hz, 1H), 8.01 (d, $J = 7.7$ Hz, 1H), 8.23 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = -4.1$, -3.9, -3.7, -3.4, 18.5, 18.6, 26.0 (6C), 30.7, 30.8, 111.5, 116.0, 124.2, 124.7, 125.3, 126.9, 127.5, 127.8, 129.8, 130.7, 130.9, 132.5, 135.0, 135.8, 140.6, 141.4, 144.8, 147.2, 183.7, 185.9 ppm; MS (EI): *m/z* (%): calcd for $C_{34}H_{42}O_4Si_2$: 570.26217; found: 570.26160 (100) $[M]^+$.

Dihydro[5]helicenebisquinone (*P*)-1 from (*P*)-36: Compound (*P*)-**1** was obtained according to GP IV from (*P*)-**36** (>98% *ee*) (CH_2Cl_2/EtOAc 15:1) in 71% yield. $[\alpha]_D^{20} = +3700$ ($c = 0.015$ in $CHCl_3$), >95% *ee*.

Tetrahydro[5]helicenequinone (*R*)-35: Compound **35** was obtained according to GP V from **4b** in 51% yield: $[\alpha]_D^{20} = -240$ ($c = 0.02$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.12$ (s, 3H), 0.24 (s, 3H), 0.26 (s, 3H), 0.29 (s, 3H), 0.86 (s, 9H), 1.10 (s, 9H), 2.42–2.92 (m, 5H), 3.67 (ddd, $J = 3.2$, 6.4, 20.4 Hz, 1H), 5.83 (m, 1H), 5.85 (m, 1H), 6.35/6.60 (AB system, $J = 10.2$ Hz, 2H), 6.62 (s, 2H), 7.24/8.13 ppm (AB system, $J = 8.6$ Hz, 2H).

Dihydro[5]helicenequinone (*P*)-36 from tetrahydro[5]helicenequinone (*R*)-35: Compound (*P*)-**36** was obtained according to GP VI from (*R*)-**35**, by using DDQ (Table 2, entry 7).

Dihydro[5]helicenebisquinone (*M*)-1 from tetrahydro[5]helicenequinone (*R*)-35: Compound (*M*)-**1** was obtained according to GP VI from (*R*)-**35**, by using CAN (Table 2, entry 8) or nBu$_4$NF in THF (Table 2, entry 9), after flash chromatography (CH_2Cl_2/EtOAc 10:1).

6-[(Trifluoromethanesulfonyl)oxy]-7,8-dihydrophenanthrene-1,4-dione (37): Ammonium cerium nitrate (559 mg, 1.02 mmol) in H_2O (15 mL) was added to a solution of **18** (200 mg, 0.51 mmol) in CH_3CN (15 mL) at 0 °C. The mixture was stirred for 15 min, diluted with CH_2Cl_2 and washed twice with water. After workup and flash chromatography (hexane/EtOAc 80:20), compound **37** was obtained (72%). M.p. 110–112 °C; ^{1}H NMR: $\delta =$ 2.74 (dt, $J = 1.2$, 8.5 Hz, 2H), 3.15 (dd, $J = 7.7$, 8.5 Hz, 2H), 6.89/6.93 (AB system, $J = 10.1$ Hz, 2H), 7.53 (d, $J = 7.7$ Hz, 1H), 8.00 (d, $J = 7.7$ Hz, 1H), 8.17 ppm (s, 1H); ^{13}C NMR: $\delta = 25.7$, 29.4, 116.3, 112.2/116.4/120.7/125.9 (q, $J = 320$ Hz, CF_3), 126.0, 127.0, 131.9, 132.0, 132.5, 136.9, 140.3, 141.1, 154.2, 184.5, 187.2 ppm; MS (EI): *m/z* (%): calcd for $C_{15}H_9O_5SF_3$: 358.01228; found: 358.01285 (33) $[M]^+$, 197 (100).

6-Vinyl-7,8-dihydrophenanthrene-1,4-dione (5): ***From 37***: Compound **5** was obtained according to GP II (3.5 h) from enol triflate **37** and vinyltributylstannane (hexane/EtOAc 80:20) in 26% yield.

From 4b: A solution of 1M tetrabutylammonium fluoride in THF (280 µL, 0.28 mmol) was added to a solution of **4b** (50 mg, 0.11 mmol) in dry THF (2 mL) under argon. The mixture was stirred at room temperature for 20 min and quenched with H_2O. After workup and flash chromatography (hexane/EtOAc 4:1), compound **5** was obtained (58%). ^{1}H NMR: $\delta = 2.49$ (t, $J = 7.7$ Hz, 2H), 2.94 (t, $J = 7.7$ Hz, 2H), 5.30 (d, $J = 10.5$ Hz, 1H), 5.48 (d, $J = 17.4$ Hz, 1H), 6.70 (dd, $J = 17.4$, 10.5 Hz, 1H), 6.87 (s, 2H), 7.47 (dd, $J = 7.7$, 0.8 Hz, 1H), 7.91 (d, $J = 7.7$ Hz, 1H), 8.00 ppm (br s, 1H); ^{13}C NMR: $\delta = 21.3$, 29.1, 115.4, 125.3, 125.4, 125.8, 131.9, 132.1, 135.7, 136.6, 138.8, 140.7, 143.6, 144.3, 185.2, 187.8 ppm; MS (EI): *m/z* (%): calcd for $C_{16}H_{12}O_2$: 236.08373; found: 236.08392 (93) $[M]^+$, 57 (100).

Dihydro[5]helicenebisquinone (*M*)-1 from 5: Diene **5** (15 mg, 0.064 mmol) in CH_2Cl_2 (1 mL) was slowly added to a solution of (*SS*)-**2** (31 mg, 0.128 mmol) in CH_2Cl_2 (1 mL) at 5 °C under argon. The mixture was stirred for 12 d at 5 °C, and the solvent was evaporated. After flash chromatography (hexane/EtOAc 6:1), compound (*M*)-**1** {$[\alpha]_D^{20} = -1940$ ($c = 0.02$ in $CHCl_3$), 74% *ee*} was obtained in 38% yield together with a 29% yield of derivative **27** as a mixture of regio- and/or diastereoisomers which could not be separated.

3-Methyl-dihydro[5]helicenebisquinone (*P,M*)-39: Diene **5** (10 mg, 0.042 mmol) was added to a solution of racemic sulfinylquinone **21**[34] (22 mg, 0.085 mmol) in CH_2Cl_2 (2 mL) under argon. The mixture was stirred at room temperature for 7 d, and the solvent was evaporated. After flash chromatography (hexane/EtOAc 6:1), compound **39** was obtained (67%). M.p. 228–231 °C; ^{1}H NMR: $\delta = 2.15$ (d, $J = 1.6$ Hz, 3H), 2.79 (m, 4H), 6.58 (q, $J = 1.6$ Hz, 1H), 6.75/6.89 (AB system, $J = 10.1$ Hz, 2H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H), 8.04 (d, $J = 8.1$ Hz, 1H), 8.07 ppm (d, $J = 7.7$ Hz, 1H); ^{13}C NMR: $\delta = 16.0$, 30.4 (2C), 126.4, 126.7, 130.2, 131.0, 131.4, 131.6, 132.0, 132.3, 132.5, 136.7, 137.3, 139.8 (2C), 146.9, 147.3, 147.7, 184.8, 185.2, 186.9, 187.0 ppm; MS (EI): *m/z* (%): calcd for $C_{23}H_{14}O_4$: 354.08921; found: 354.08969 (100) $[M]^+$.

Dihydro[5]helicenequinone (*P*)-20 from (*P*)-36: A solution of enantiomerically pure helicene (*P*)-**36** (30 mg, 0.066 mmol) in DMF (2 mL) was added via cannula to a vigorously stirred suspension of CsF (51 mg, 0.33 mmol) and MeI (42 µL, 0.66 mmol) in DMF (1 mL) under argon. The mixture was stirred for 24 h at room temperature, quenched with water and extracted several times with diethyl ether. After workup and flash chromatography (hexane/EtOAc 65:35), compound (*P*)-**20** {$[\alpha]_D^{20} = +3200$ ($c = 0.004$, $CHCl_3$), >95% *ee*} was obtained (70%).

General procedure VII (GP VII)—Aromatizations of dihydro[5]helicenequinones to [5]-helicenequinones: A solution of the corresponding dihydro[5]helicenequinone (0.046 mmol) and DDQ (104 mg, 0.46 mmol, 10 equiv) in benzene (2 mL) was heated under reflux for the time indicated. After evaporation of the solvent, the residue was passed through a short column of silica gel eluting with CH_2Cl_2, and finally purified by flash chromatography.

[5]Helicenequinone (*P*)-40: Compound **40** was obtained according to GP VII (4 d) from enantiopure **20** (hexane/EtOAc 65:35) in 71% yield. M.p. 231–232 °C (methanol); $[\alpha]_D^{20} = +1430$ ($c = 0.009$, $CHCl_3$), >95% *ee*}; ^{1}H NMR $\delta = 8.54/7.85$ (AB system, $J = 8.9$ Hz, 2H), 8.26, 7.97 (AB system, $J = 8.1$ Hz, 2H), 8.13/7.88 (AB system, $J = 8.5$ Hz, 2H), 6.98/6.89 (AB system, $J = 8.5$ Hz, 2H), 6.93, 6.81 (AB system, $J = 10.1$ Hz, 2H), 4.05/3.55 ppm (2s, 6H); ^{13}C NMR $\delta = 55.6$, 56.0, 105.4, 107.1, 122.0, 123.3, 123.7, 124.5, 124.6, 125.9, 126.0, 127.1, 127.5, 130.3, 131.4, 134.5, 135.6, 136.1, 140.1, 140.2, 148.5, 150.6, 182.2, 186.2 ppm; MS (EI): *m/z* (%): calcd for $C_{24}H_{16}O_4$: 368.10486; found: 368.10559 (100) $[M]^+$.

[5]Helicenequinone (*P*)-41: Compound **41** was obtained according to GP VII (5 d) from **27** (92% *ee*) (hexane/EtOAc 80:20) in 85% yield. M.p. 229–231 °C (methanol); $[\alpha]_D^{20} = +910$ ($c = 0.004$ in $CHCl_3$), 92% *ee*}; ^{1}H NMR: $\delta = 1.64$ (t, $J = 6.9$ Hz, 3H), 3.55 (s, 3H), 4.04 (s, 3H), 4.40 (dq, $J = 9.3$, 6.9 Hz, 1H), 4.46 (dq, $J = 9.3$, 6.9 Hz, 1H), 6.73/6.88 (AB system, $J = 10.1$ Hz, 2H), 6.84/6.96 (AB system, $J = 8.5$ Hz, 2H), 7.57 (s, 1H), 7.83 (d, $J = 8.5$ Hz, 1H), 7.94 (d, $J = 8.5$ Hz, 1H), 8.46 (d, $J = 8.5$ Hz, 1H), 8.51 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = 14.7$, 55.5, 55.9, 64.7, 100.6, 105.4, 106.8, 120.5, 123.1, 124.0, 124.4, 125.9, 127.6, 128.0, 128.8, 129.3, 134.5, 135.2, 140.4, 148.7, 150.3, 157.2, 181.7, 186.5 ppm; MS (EI): *m/z* (%): calcd for $C_{26}H_{20}O_5$: 412.13107; found: 412.13058 (100) $[M]^+$.

Dihydro[5]helicenes (*P*)-42 and (*M*)-43: Et_3N (200 µL) and CH_2Cl_2 (3 mL) were added to a mixture of helicene (*P,M*)-**36** (39 mg, 0.068 mmol), activated Zn (58 mg, 0.89 mmol), (−)-camphanoyl chloride (74 mg, 0.34 mmol) and DMAP (4 mg, 0.034 mmol) under argon. The mixture was heated under reflux for 1 h. Filtration through Celite, aided by several ethyl acetate washes, removed remaining Zn. The organic solution was washed with saturated aqueous $NaHCO_3$, 2% HCl and water. Workup and flash chromatography (hexane/EtOAc 80:20) yielded 48% of the low R_f isomer (*P*)-**42** and 45% of the high R_f isomer (*M*)-**43**. Dihydro[5]helicene (*P*)-**42** was exclusively obtained in 92% yield from enantiomerically pure (*P*)-**36**. (*P*)-**42**: M.p. 253–254 °C ($CHCl_3$/hexane); $[\alpha]_D^{20} = +210$ ($c = 0.27$, $CHCl_3$); ^{1}H NMR: $\delta = -0.74$ (s, 3H), -0.43 (s, 3H), 0.27 (s, 3H), 0.31 (s, 3H), 0.32 (s, 9H), 0.68 (s, 3H), 0.77 (s, 3H), 0.96 (s, 3H), 1.10 (s, 9H), 1.12 (m, 1H), 1.20 (s, 3H), 1.21 (m, 1H), 1.22 (s, 3H), 1.23 (s, 3H), 1.42 (m, 1H), 1.62 (ddd, $J = 5.0$, 11.0, 13.5 Hz, 1H), 1.85 (ddd, $J = 4.0$, 9.5, 13.0 Hz, 1H), 2.07 (ddd, $J = 4.5$, 9.5, 10.5 Hz, 1H), 2.35 (ddd, $J = 4.5$, 9.0, 13.5 Hz, 1H), 2.70 (ddd, $J = 4.0$, 10.5, 13.0 Hz, 1H), 2.72–2.92 (m, 4H), 6.52/6.57 (AB system, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 8.5$ Hz, 1H), 7.51 (d, $J = 8.5$ Hz, 1H), 7.94 (d, $J = 8.5$ Hz, 1H), 8.11 ppm (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: $\delta = -3.8$, -3.5, -3.2, 9.6, 9.8, 16.7, 16.8, 16.9, 17.0, 18.3, 25.9 (6C), 28.4, 28.9, 29.0, 30.5, 30.6, 31.0, 54.4, 54.5, 54.6, 55.0, 77.2, 90.5, 91.2, 110.0, 114.8, 115.2, 117.0, 120.1, 122.5, 125.2, 126.6, 127.0, 127.5, 128.6, 129.1, 129.4, 131.7, 139.8, 140.0, 144.1, 144.5, 145.8, 145.9, 164.7, 165.6, 177.8, 178.1 ppm; MS (EI): *m/z* (%): calcd for $C_{54}H_{68}O_{10}Si_2$: 932.43511; found: 932.43329 (18) $[M]^+$, 83 (100).

(*M*)-**43**: M.p. >300 °C ($CHCl_3$/hexane); $[\alpha]_D^{20} = -260$ ($c = 0.26$, $CHCl_3$); ^{1}H NMR: $\delta = -0.71$ (s, 3H), −0.47 (s, 3H), 0.32 (s, 3H), 0.35 (s, 9H), 0.38 (s, 3H), 0.64 (s, 3H), 0.75 (s, 3H), 0.94 (s, 3H), 1.09 (s, 9H), 1.12 (m, 1H), 1.20 (s, 3H), 1.22 (s, 3H), 1.24 (s, 3H), 1.40 (m, 2H), 1.61 (m, 1H), 1.85 (ddd, $J = 4.1$, 9.3, 13.3 Hz, 1H), 2.07 (ddd, $J = 4.4$, 10.5, 13.0 Hz, 1H), 2.35 (ddd, $J = 4.4$, 9.3, 13.6 Hz, 1H), 2.70 (ddd, $J = 4.3$, 10.7, 13.4 Hz, 1H), 2.76–2.90 (m, 4H), 6.59/6.66 (AB system, $J = 8.2$ Hz, 2H), 6.86 (d, $J = 8.2$ Hz, 1H), 7.25 (d, $J = 8.2$ Hz, 1H), 7.37 (d, $J = 8.3$ Hz, 1H), 7.52 (d, $J = 8.3$ Hz, 1H), 7.92 (d, $J = 8.3$ Hz, 1H), 8.16 ppm (d, $J = 8.3$ Hz, 1H); ^{13}C NMR: $\delta = -4.0$, −3.8, −3.7, −3.1, 9.6, 9.8, 16.3, 16.5, 17.0, 18.3, 18.4, 25.9 (6C), 28.8, 29.1, 29.8, 30.8, 30.9, 31.1, 54.2, 54.6, 54.9, 55.0, 77.2, 89.7, 91.2, 110.2, 115.5, 115.7, 117.0, 120.0, 122.8, 124.1, 126.7, 127.1, 128.1, 129.0, 129.2, 132.1, 139.4, 139.9, 144.0, 144.9, 145.3, 146.0, 165.4, 165.6, 177.6, 178.1 ppm; MS (EI): *m*/*z* (%): calcd for $C_{54}H_{68}O_{10}Si_2$: 932.43511; found: 932.43695 (61) $[M]^+$, 73 (100).

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[1] a) F. Vögtle, *Fascinating Molecules in Organic Chemistry*, Wiley, New York, **1992**, 156–180, and references therein; b) H. Osuga, H. Suzuki, *J. Synth. Org. Chem. Jpn.* **1994**, *52*, 1020–1031.

[2] a) R. H. Janke, G. Haufe, E. U. Würthwein, J. H. Borkent, *J. Am. Chem. Soc.* **1996**, *118*, 6031–6035; b) S. Grimme, S. D. Peyerimhoff, *Chem. Phys.* **1996**, *204*, 411–417; c) A. Ferrarini, G. Gottarelli, P. L. Nordio, G. P. Spada, *J. Chem. Soc. Perkin Trans. 2* **1999**, 411–417; d) O. Katzenelson, J. Edelstein, D. Avnir, *Tetrahedron: Asymmetry* **2000**, *11*, 2695–2704.

[3] a) S. Grimme, J. Harren, A. Sohanski, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 1491–1509; b) T. J. Katz, *Angew. Chem.* **2000**, *112*, 1997–1999; *Angew. Chem. Int. Ed.* **2000**, *39*, 1921–1923; c) K. Tanaka, H. Osuga, Y. Kitahara, *J. Org. Chem.* **2002**, *67*, 1795–1801.

[4] Chiroptical and photochromic properties: a) D. J. Weix, S. D. Dreher, T. J. Katz, *J. Am. Chem. Soc.* **2000**, *122*, 10027–10032; b) F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle, S. Grimme, *J. Am. Chem. Soc.* **2000**, *122*, 1717–1724; c) J. Nishida, T. Suzuki, M. Ohkita, T. Tsuji, *Angew. Chem.* **2001**, *113*, 3351–3354; *Angew. Chem. Int. Ed.* **2001**, *40*, 3251–3254; d) T. B. Norsten, A. Peters, R. McDonald, M. Wang, N. R. Branda, *J. Am. Chem. Soc.* **2001**, *123*, 7447–7448; e) T. Caronna, M. Catellani, S. Luzzati, L. Malpezzi, S. V. Meille, A. Mele, C. Richter, R. Sinisi, *Chem. Mater.* **2001**, *13*, 3906–3914; f) J. Autschbach, T. Ziegler, S. J. A. van Gisbergen, E. J. Baerends, *J. Chem. Phys.* **2002**, *116*, 6930–6940.

[5] Nonlinear optical materials: a) T. Verbiest, S. Van Elshocht, M. Kauranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T. J. Katz, A. Persoons, *Science* **1998**, *282*, 913–915; b) F. Feng, T. Miyashita, H. Okubo, M. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 10166–10170; c) S. Sioncke, S. Van Elshocht, T. Verbiest, A. Persoons, M. Kauranen, K. E. S. Phillips, T. J. Katz, *J. Chem. Phys.* **2000**, *113*, 7578–7581; d) T. Verbiest, S. Van Elshocht, A. Persoons, C. Nuckolls, K. E. S. Phillips, T. J. Katz, *Langmuir* **2001**, *17*, 4685–4687; e) C. Nuckolls, R. Shao, W.-G. Jang, N. A. Clark, D. M. Walba, T. J. Katz, *Chem. Mater.* **2002**, *14*, 773–776; f) T. Verbiest, S. Sioncke, A. Persoons, L. Vyklický, T. J. Katz, *Angew. Chem.* **2002**, *114*, 4038–4040; *Angew. Chem. Int. Ed.* **2002**, *41*, 3882–3884.

[6] Self-assembling properties: a) K. Tanaka, Y. Kitahara, *Chem. Commun.* **1998**, 1141–1142; b) C. Nuckolls, T. J. Katz, *J. Am. Chem. Soc.* **1998**, *120*, 9541–9544; c) J. M. Fox, T. J. Katz, S. Van Elshocht, T. Verbiest, M. Kauranen, A. Persoons, T. Thongpanchang, T. Krauss, L. Brus, *J. Am. Chem. Soc.* **1999**, *121*, 3453–3459; d) C. Nuckolls, T. J. Katz, G. Katz, P. J. Collings, L. Castellanos, *J. Am. Chem. Soc.* **1999**, *121*, 79–88; e) K. Tanaka, H. Osuga, Y. Kitahara, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2492–2497; f) K. Nakamura, H. Okubo, M. Yamaguchi, *Org. Lett.* **2001**, *3*, 1097–1099; g) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, *J. Am. Chem. Soc.* **2001**, *123*, 11899–11907; h) Y. Kitahara, K. Tanaka, *Chem. Commun.* **2002**, 932–933.

[7] Asymmetric molecular recognition: a) K. Yamamoto, T. Ikeda, T. Kitsubki, Y. Okamoto, H. Chikamatsu, M. Nakazaki, *J. Chem. Soc. Perkin Trans. 1* **1990**, 271–276; b) L. Owens, C. Thilgen, F. Diederich, C. B. Knobler, *Helv. Chim. Acta* **1993**, *76*, 2757–2774; c) K. Kano, H. Kamo, S. Negi, T. Kitae, R. Takaoka, M. Yamaguchi, H. Okubo, M. Hirama, *J. Chem. Soc. Perkin Trans. 2* **1999**, 15–21; d) K. Yamada, Y. Kobori, H. Nakagawa, *Chem. Commun.* **2000**, 97–98; e) E. Murguly, R. McDonald, N. R. Branda, *Org. Lett.* **2000**, *2*, 3169–3172; f) H. Okubo, D. Nakano, S. Anzai, M. Yamaguchi, *J. Org. Chem.* **2001**, *66*, 557–563; g) M. T. Reetz, S. Sostmann, *Tetrahedron* **2001**, *57*, 2515–2520.

[8] Asymmetric catalysis: a) M. T. Reetz, E. W. Beuttenmüller, R. Goddard, *Tetrahedron Lett.* **1997**, *38*, 3211–3214; b) H. Okubo, M. Yamaguchi, C. Kabuto, *J. Org. Chem.* **1998**, *63*, 9500–9509; c) S. D. Dreher, T. J. Katz, K.-C. Lang, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 815–822; d) M. T. Reetz, S. Sostmann, *J. Organomet. Chem.* **2000**, *603*, 105–109; e) I. Sato, R. Yamashima, K. Kadowaki, J. Yamamoto, T. Shibata, K. Soai, *Angew. Chem.* **2001**, *113*, 1130–1132; *Angew. Chem. Int. Ed.* **2001**, *40*, 1096–1098.

[9] Molecular machinery: a) T. R. Kelly, R. A. Silva, H. De Silva, S. Jasmin, Y. Zhao, *J. Am. Chem. Soc.* **2000**, *122*, 6935–6949; b) T. R. Kelly, *Acc. Chem. Res.* **2001**, *34*, 514–522.

[10] a) W. H. Laarhoven, W. J. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–120; b) K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1–76; c) L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769–3775.

[11] See references [4b, d, 6h, 7e, g] and the following: a) M. Sato, K. Yamamoto, H. Sonobe, K. Yano, H. Matsubara, H. Fujita, T. Sujimoto, K. Yamamoto, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1909–1913; b) J. M. Fox, D. Lin, Y. Itagaki, T. Fujita, *J. Org. Chem.* **1998**, *63*, 2031–2038; c) K. Tanaka, H. Osuga, H. Suzuki, Y. Shogase, Y. Kitahara, *J. Chem. Soc. Perkin Trans. 1* **1998**, 935–940; d) H. Meier, M. Schwertel, D. Schollmeyer, *Angew. Chem.* **1998**, *110*, 2224–2226; *Angew. Chem. Int. Ed.* **1998**, *37*, 2110–2113; e) S. Arai, M. Ishikura, T. Yamagishi, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1561–1567; f) C. Stammel, R. Fröhlich, C. Wolff, H. Wenck, A. de Meijere, J. Mattay, *Eur. J. Org. Chem.* **1999**, 1709–1718; g) T. Caronna, R. Sinisi, M. Catellani, L. Malpezzi, S. V. Meille, A. Mele, *Chem. Commun.* **2000**, 1139–1140; h) T. Caronna, R. Sinisi, M. Catellani, S. Luzzati, S. Abbate, G. Longhi, *Synth. Met.* **2001**, *119*, 79–80.

[12] See ref. [4c] and the following: a) L. Liu, T. J. Katz, *Tetrahedron Lett.* **1990**, *31*, 3983–3986; b) D. E. Pereira, Neelima, N. J. Leonard, *Tetrahedron* **1990**, *46*, 5895–5908; c) R. Fritsch, E. Hartmann, D. Andert, A. Mannschreck, *Chem. Ber.* **1992**, *125*, 849–855; d) N. D. Willmore, L. Liu, T. J. Katz, *Angew. Chem.* **1992**, *104*, 1081–1082; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1093–1095; e) I. G. Stará, I. Starý, M. Tichý, J. Závada, V. Hanus, *J. Am. Chem. Soc.* **1994**, *116*, 5084–5088; f) G. Bringmann, B. Schönner, O. Schupp, K. Peters, E. Peters, H. G. Von Schnering, *Liebigs Ann. Chem.* **1994**, 91–97; g) A. Dore, D. Fabbri, S. Gladiali, G. Valle, *Tetrahedron: Asymmetry* **1995**, *6*, 779–788; h) I. Pischel, S. Grimme, S. Kotila, M. Nieger, F. Vögtle, *Tetrahedron: Asymmetry* **1996**, *7*, 109–116; i) J. Larsen, K. Bechgaard, *J. Org. Chem.* **1996**, *61*, 1151–1152; j) K. Tanaka, H. Suzuki, H. Osuga, *J. Org. Chem.* **1997**, *62*, 4465–4470; k) S. Cossu, O. de Lucchi, D. Fabbri, S. Gladiali, G. Valle, G. F. Painter, A. J. Smith, *Tetrahedron* **1997**, *53*, 6873–6878; l) J. P. Gao, X. S. Meng, T. P. Bender, S, MacKinnon, V. Grand, Z. Y. Wang, *Chem. Commun.* **1999**, 1281–1282; m) M. Gingras, F. Dubois, *Tetrahedron Lett.* **1999**, *40*, 1309–1312; n) I. G. Stará, I. Starý, A. Kollárovic, F. Teplý, S. Vyskocil, D. Saman, *Tetrahedron Lett.* **1999**, *40*, 1993–1996; o) L. Minuti, A. Taticchi, A. Marrocchi, E. Gacs-Baitz, R. Galeazzi, *Eur. J. Org. Chem.* **1999**, 3155–3163; p) A. Modler-Spreitzer, R. Fritsch, A. Mannschreck, *Collect. Czech. Chem. Commun.* **2000**, *65*, 555–560; q) K. Miyawaki, T. Kawano, I. Ueda, *Polycyclic Aromat. Compd.* **2000**, *19*, 133–154; r) J. Eskildsen, F. C. Krebs, A. Faldt, P. Sommer-Larsen, K. Bechgaard, *J. Org. Chem.* **2001**, *66*, 200–205; s) Y. Yamamoto, R. Hattori, T. Miwa, Y. Nakagai, T. Kubota, C. Yamamoto, Y. Okamoto, K. Itoh, *J. Org. Chem.* **2001**, *66*, 3865–3870; t) A. Marrocchi, L. Minuti, A. Taticchi, I. Dix, H. Hopf, E. Gacs-Baitz, P. G. Jones, *Eur. J. Org. Chem.* **2001**, *66*, 4259–4268; u) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Lett.* **2002**, *43*, 3189–3191; v) F. Teply, I. G. Stara, I. Stary, A. Kollarovic, D. Saman, L. Rulisek, P. Fiedler, *J.*

Am. Chem. Soc. **2002**, *124*, 9175–9180; w) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Lett.* **2002**, *43*, 7345–7347; x) Y. Ogawa, T. Ueno, M. Karikomi, K. Seki, K. Haga, T. Uyehara, *Tetrahedron Lett.* **2002**, *43*, 7827–7829; y) T. Caronna, S. Gabiaddini, A. Mele, F. Recupero, *Helv. Chim. Acta* **2002**, *85*, 1–8; z) M. M. Real, J. Pérez Sestelo, L. A. Sarandeses, *Tetrahedron Lett.* **2002**, *43*, 9111–9114; aa) T. Sooksimuang, B. K. Mandal, *J. Org. Chem.* **2003**, *68*, 652–655.

[13] For recent work on chromatographic resolutions see refs. [4b, 7g, 8a, 11d, f, 12f, h, l].

[14] For recent work on chemical resolutions see refs. [6d, g, 8b, 11b and 12l] and the following: a) T. Thongpanchang, K. Paruch, T. J. Katz, A. L. Rheingold, K. Lam, L. Liable-Sands, *J. Org. Chem.* **2000**, *65*, 1850–1856, and references therein.

[15] For recent work on enzymatic resolutions see refs. [7d, 11c] and the following: K. Tanaka, Y. Shogase, H. Osuga, H. Suzuki, K. Nakamura, *Tetrahedron Lett.* **1995**, *36*, 1675–1678.

[16] See refs. [4c, 12e–g, j, m, n, s] and the following: a) A. Sudhakar, T. J. Katz, *J. Am. Chem. Soc.* **1986**, *108*, 179–181; b) A. Sudhakar, T. J. Katz, B. W. Yang, *J. Am. Chem. Soc.* **1986**, *108*, 2790–2791; c) K. Tanaka, H. Osuga, H. Suzuki, *Tetrahedron*: *Asymmetry* **1993**, *4*, 1843–1856; d) T. J. Katz, A. Sudhakar, M. F. Teasley, A. M. Gilbert, W. E. Geiger, M. P. Robben, M. Wuensch, M. D. Ward, *J. Am. Chem. Soc.* **1993**, *115*, 3182–3198; e) A. M. Gilbert, T. J. Katz, W. E. Geiger, M. P. Robben, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 3199–3211; f) K. Tanaka, H. Osuga, Y. Shogase, H. Suzuki, *Tetrahedron Lett.* **1995**, *36*, 915–918; g) K. Tanaka, Y. Kitahara, H. Suzuki, H. Osuga, Y. Kawai, *Tetrahedron Lett.* **1996**, *37*, 5925–5928; h) K. Tanaka, H. Osuga, K. Koyama, H. Suzuki, K. Imai, Y. Yoshida, *Enantiomer* **1997**, *2*, 193–201; i) H. Osuga, H. Suzuki, K. Tanaka, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 891–897; j) G. Bringmann, J. Hinrichs, J. Kraus, A. Wuzik, T. Schulz, *J. Org. Chem.* **2000**, *65*, 2517–2527.

[17] M. C. Carreño, R. Hernández-Sánchez, J. Mahugo, A. Urbano, *J. Org. Chem.* **1999**, *64*, 1387–1390.

[18] For an overview of our work, see: a) M. C. Carreño, *Chem. Rev.* **1995**, *95*, 1717–1760; for more recent references, see: b) M. C. Carreño, J. Mahugo, A. Urbano, *Tetrahedron Lett.* **1997**, *38*, 3047–3050; c) M. C. Carreño, S. García-Cerrada, A. Urbano, C. Di Vitta, *Tetrahedron*: *Asymmetry* **1998**, *9*, 2965–2969; d) M. C. Carreño, A. Urbano, *Tetrahedron Lett.* **2000**, *41*, 4117–4121; e) M. C. Carreño, M. Ribagorda, A. Somoza, A. Urbano, *Chem. Commun.* **2002**, 3052–3053.

[19] a) L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137–170; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131–163; b) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–36.

[20] a) M. C. Carreño, A. Urbano, J. Fischer, *Angew. Chem.* **1997**, *109*, 1695–1697; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1621–1623; b) M. C. Carreño, A. Urbano, C. Di Vitta, *J. Org. Chem.* **1998**, *63*, 8320–8330; c) M. C. Carreño, A. Urbano, C. Di Vitta, *Chem. Commun.* **1999**, 817–818; d) M. C. Carreño, A. Urbano, C. Di Vitta, *Chem. Eur. J.* **2000**, *6*, 906–913; e) M. C. Carreño, M. Ribagorda, A. Somoza, A. Urbano, *Angew. Chem.* **2002**, *114*, 2879–2881; *Angew. Chem. Int. Ed.* **2002**, *41*, 2755–2757.

[21] M. C. Carreño, S. García-Cerrada, M. J. Sanz-Cuesta, A. Urbano, *Chem. Commun.* **2001**, 1452–1453.

[22] C. Goedicke, H. Stegemeyer, *Tetrahedron Lett.* **1970**, 937–940.

[23] M. C. Carreño, S. García-Cerrada, A. Urbano, *J. Am. Chem. Soc.* **2001**, *123*, 7929–7930.

[24] M. C. Carreño, S. García-Cerrada, A. Urbano, *Chem. Commun.* **2002**, 1412–1413.

[25] B. H. Lipshutz, D. F. Harvey, *Synth. Commun.* **1982**, *12*, 267–277.

[26] M. C. Carreño, J. L. García Ruano, A. Urbano, *Synthesis* **1992**, 651–653.

[27] The *ee* values were evaluated by ^{1}H NMR analysis using 2,2,2-trifluoro-1-(9-anthryl)ethanol as chiral solvating agent.[28] The racemic compounds necessary for such evaluation were obtained starting from racemic 2-(*p*-tolylsulfinyl)-1,4-benzoquinone.[26]

[28] W. H. Pirkle, D. J. Hoover, *Top. Stereochem.* **1982**, *13*, 263–331.

[29] M. A. Tius, M. A. Kerr, *J. Am. Chem. Soc.* **1992**, *114*, 5959–5966.

[30] E. Marcantoni, F. Nobili, G. Bartoli, M. Bosco, L. Sambri, *J. Org. Chem.* **1997**, *62*, 4183–4184.

[31] An excess of (*SS*)-**2** was used to aromatize in situ the product resulting from the elimination of the sulfoxide in the initially formed cycloadduct.

[32] The *ee* were evaluated by ^{1}H-NMR analysis using [Pr(hfc)$_3$] as chiral lantanide shift reagent. The racemic compounds necessary for such evaluation were obtained starting from racemic 2-(*p*-tolylsulfinyl)-1,4-benzoquinone.[26]

[33] M. C. Carreño, J. L. García Ruano, M. A. Toledo, A. Urbano, C. Z. Remor, V. Stefani, J. Fischer, *J. Org. Chem.* **1996**, *61*, 503–509.

[34] M. C. Carreño, J. L. García Ruano, M. A. Toledo, A. Urbano, *Tetrahedron*: *Asymmetry* **1997**, *8*, 913–921.

[35] CCDC-100127 (**24**), -187346 (**30**) and -187097 (**42**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[36] S. D. Kahn, W. J. Hehre, *J. Am. Chem. Soc.* **1986**, *108*, 7399–7400.

[37] a) P. W. Rabideau, *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*, VCH, New York, **1989**; b) D. J. Raber, L. E. Hardee, P. W. Rabideau, K. B. Lipkowitz, *J. Am. Chem. Soc.* **1982**, *104*, 2843–2847; c) P. W. Rabideau, *Acc. Chem. Res.* **1978**, *11*, 141–147.

[38] M. C. Carreño, S. García-Cerrada, A. Urbano, C. Di Vitta, *J. Org. Chem.* **2000**, *65*, 4355–4363.

[39] a) B. M. Trost, *J. Am. Chem. Soc.* **1967**, *89*, 1847–1851; b) P. P. Fu, R. G. Harvey, *Chem. Rev.* **1978**, *78*, 317–361.

[40] F. Stoos, J. Rocek, *J. Am. Chem. Soc.* **1972**, *94*, 2719–2722.

[41] The enantiomeric purities were determined by chiral HPLC (Chiralcel OD, hexane/isopropanol 99:1, 0.2 mL min^{-1}, $t_R = 35.9$ min (*P* enantiomer) and 38.9 min (*M* enantiomer).

[42] See refs. [3b, 4a, 5a,c,d, 6b,c,d,g] and the following: a) C. Nuckolls, T. J. Katz, L. Castellanos, *J. Am. Chem. Soc.* **1996**, *118*, 3767–3768; b) C. Nuckolls, T. J. Katz, T. Verbiest, S. Van Elshocht, H.-G. Kuball, S. Kiesewalter, A. J. Lovinger, A. Persoons, *J. Am. Chem. Soc.* **1998**, *120*, 8656–8660; c) A. J. Lovinger, C. Nuckolls, T. J. Katz, *J. Am. Chem. Soc.* **1998**, *120*, 264–268.

[43] a) T. Oriyama, K. Noda, K. Yatabe, *Synlett* **1997**, 701–703; b) K. Paruch, T. J. Katz, C. Incarvito, K.-C. Lam, B. Rhatigan, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 7602–7608.

[44] a) W. H. Laarhoven, W. J. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–130. We assigned the *M* absolute configuration to (−)-helicenes and *P* to (+)-helicenes: (*M*) = left-handed and (*P*) = right-handed helix: b) R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem.* **1966**, *78*, 413–447; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 385–415.

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