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On the Functionalization of [2.2](1,4)Phenanthrenoparacyclophane[‡]

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Dedicated to Professor Manfred Christl on the occasion of his 65th birthday

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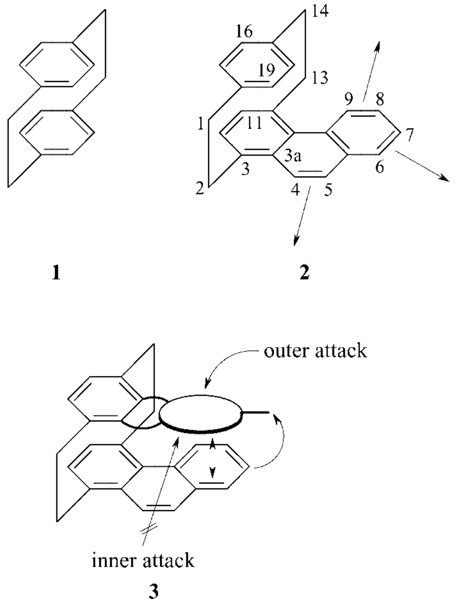
Two routes for preparing functionalized [2.2](1,4)phenanthrenoparacyclophanes are described: either the parent system **2** is subjected to electrophilic substitution (bromination, Friedel–Crafts acylation, Rieche formylation: preparation of **5**, **6**, **7**, **11** and **12**) or the desired substituents are incorporated in the early stages of the synthesis by the preparation of the corresponding functionalized styryl paracyclophanes and their photocyclization to the respective phenanthrenocyclophanes. By these specific routes various bromides (**22a**,**b**), ethers (**28a**–**c**) and phenols (**29a**,**b**) were synthesized. The latter derivatives, on oxidation, furnish *para*- (**31**) and *ortho*-quinonophanes (**30**, **32**, **33**), useful substrates for the preparation of cyclophanes containing phenazine subunits (**36**). The stilbene → phenanthrene photocyclization can also be employed for the preparation of benzothiophenophanes, e.g. **43** and **44**, from the respective precursors.

Introduction

Mono- and polysubstituted derivatives of [2.2]paracyclophane (**1**) carrying all types of functional groups have been prepared by the hundreds during the last decades.[2] Whereas originally these derivatives were prepared and studied largely to learn more about the reactivity of **1**, more recently substituted cyclophanes have become of interest as chiral ligands in stereoselective synthesis[3] and as novel starting materials in material science where they have, inter alia, been used as new mesogenic compounds[4] and as monomers in the CVD production of functionalized surfaces.[5] Compared with these extensive studies little is known about the preparation of [2.2]phane derivatives in which one or both of the benzene decks of **1** have been replaced by an extended aromatic system. We have called these polycondensed cyclophanes PAH-phanes (cyclophanes containing polycondensed aromatic hydrocarbon moieties)[1] and have described the preparation of several of these systems over the years.[6,7] Recently we reported on the preparation of PAH-phanes derived from [2.2](1,4)-phenanthrenoparacyclophane (**2**), hydrocarbons containing a chrysene, a tetrahelicene and other extended aromatic decks as illustrated by the arrows in structure **2** (Scheme 1).[1]



Scheme 1. PAH-Phanes as chiral molecular work-benches.

These compounds interest us primarily for stereochemical reasons because many of them are inherently chiral. Moreover, with one cyclophane deck being smaller (shorter) than the other they possess a "binding pocket" to which a prochiral substrate may be bonded, either by coval-

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ent bonds, e.g. by an ester or amide link, or by noncovalent forces such as hydrogen bonds or salt bridges. This is symbolized in structure **3** by the ellipse for the prochiral substrate and the dotted lines for the noncovalent forces. If the prochiral substrate contains an aromatic system, it could interact with the cyclophane by π stacking (double-headed arrow in **3**). The combination of these different forces may well lead to a clearly defined orientation between the phane "lock" and the substrate "key". If the fit between the two partners is too loose it could be advantageous to introduce other features to stabilize the overall interaction. This is illustrated in structure **3** by a "linking" structural element (bent arrow) which could, for example, possess a polar functional group at its end that could interact with a complementary site at the substrate. Clearly, this combination of rigid and flexible subunits, a chiral "molecular workbench",[8] would prefer to react from only one side, viz. the outer side marked in structure **3**. For an "inside" approach of any reagent the room available would be too limited. Steric hindrance could, furthermore, be increased by extending the PAH unit of the system or by placing voluminous substituents at its rim.

Obviously, this concept can only be realized if the PAH-phane contains functional groups. These can either be introduced into the assembled phane hydrocarbon at the very end of the synthesis by e.g. electrophilic aromatic substitution or be present in the initial phase of the preparation already and be carried through all the way to the very end of the preparation. At either stage of the reaction sequence the functionality present may be altered, of course, by substitution reactions, oxidations, reductions etc.

We will discuss both approaches in this publication and will begin with electrophilic substitution reactions of [2.2](1,4)phenanthrenoparacyclophane (**2**) which we regard as the prototypical example of a chiral PAH-phane.

Results and Discussion

Functionalization of [2.2](1,4)Phenanthrenoparacyclophane by Electrophilic Substitution Reactions

The first reaction of **2** we studied was its bromination. Because all aromatic C–H bonds of the hydrocarbon are different, in principle one could expect up to 12 different monobromination products. As the experiment shows, only one is produced (Scheme 2).

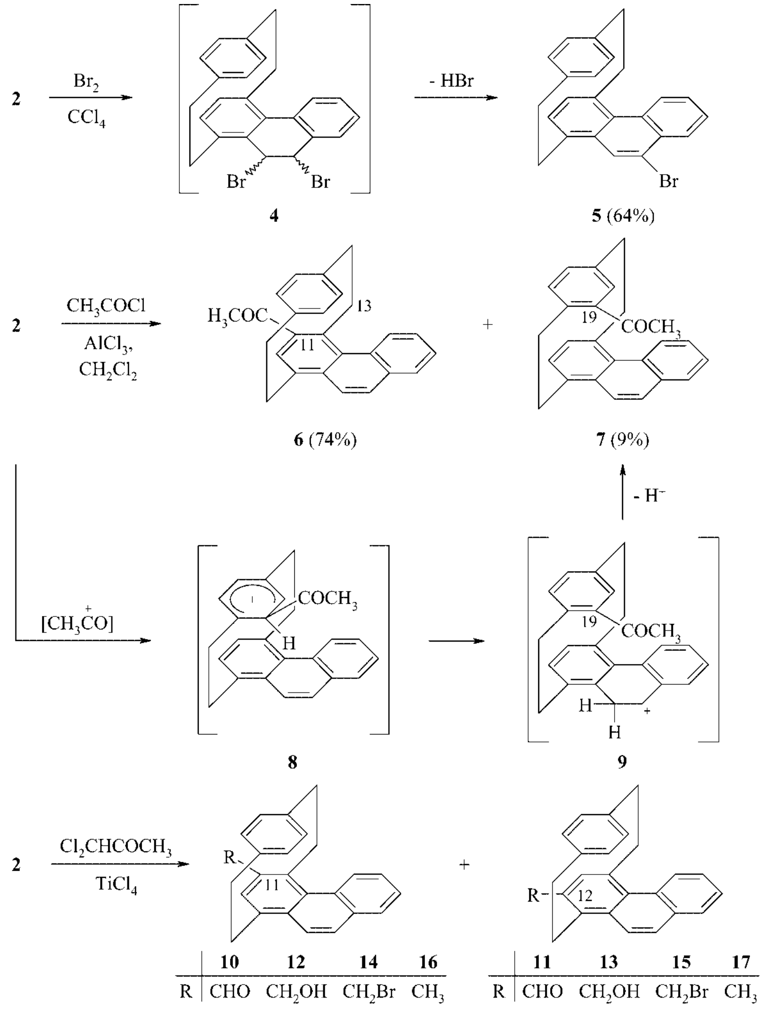
Bromination of **2** with elemental bromine in carbon tetrachloride at room temperature provides 5-bromo[2.2](1,4)phenanthrenoparacyclophane (**5**) in 64% yield, the structure assignment resting on the following observations. The mass spectrum not only shows that a monobromide has been produced (m/z = 388 and 386, ratio 1:1 for $C_{24}H_{19}Br$), but because a strong peak is detected for m/z = 104, signalling the generation of a C_8H_8 (*p*-xylylene) moiety, the bromine must have entered the phenanthrene deck. This conclusion is supported by the ^{1}H NMR spectrum which shows two AB patterns for the isolated benzene ring of **5**. Because an AB system is also displayed by 11-H and 12-H of the condensed aromatic ring, and atoms 6-H to 9-H of the outer phenanthrene benzene ring give rise to multiplets analogous to the parent hydrocarbon **2**,[6] the substitution must have occurred at either C-4 or C-5. The hydrogen directly adjacent to the bromine substituent resonates as a singlet at δ = 7.97 ppm. In the proton spectrum of **2** 6-H resonates at 7.86 ppm, in the spectrum of **5** the corresponding signal is registered at 8.34 ppm. This strong shift to lower field hints that the bromine substituent is very close to 6-H, i.e. at position C-5. In the ^{13}C-NMR spectrum of bromobenzene the substituted carbon atom is shifted by –5.5 ppm as compared to benzene itself.[9] The signals for the C-4 and C-5 atoms in the parent hydrocarbon **2** are at 123.97 and 126.04 ppm, respectively. Should the bromine be attached to C-4 in **5** we would expect a carbon signal at ca. 118.5 ppm, whereas C-5 should resonate at 120.5 ppm. The observed value in **5** is 120.96, i.e. the carbon spectrum confirms the assignment derived from the proton spectrum. The complete spectroscopic and analytical data for **5** can be found in the Experimental Section.

This high regioselectivity is best rationalized by the known high π-bond order of the central double bond in phenanthrene. Halogenations of this hydrocarbon have been shown to involve the addition of the halogenation reagent to this bond leading to the isolation of vicinal dihalides,[10] both *cis*- and *trans* adducts have been observed. These usually are unstable and "rearomatize" under dehydrohalogenation. In the case of **2**, the dibromide **4** would be the respective intermediate.

The bromine substituent in **5** is in a position to allow the introduction of a linker unit as described in general structure **3** by any of the modern C–C coupling reactions.

In the next reaction, a Friedel–Crafts acylation was performed on **2**. Its reaction with acetyl chloride in the presence of aluminium trichloride in dichloromethane at –30 °C furnished a mixture of ketones in a 8:1 ratio: 11-acetyl[2.2](1,4)phenanthrenoparacyclophane (**6**, 74%) and 19-acetyl[2.2](1,4)phenanthrenoparacyclophane (**7**, 9%; Scheme 2). The structure assignment of these two products rests again largely on mass spectral and NMR data. In **6** the unsubstituted benzene ring reveals itself by its two AB patterns for 16-H, 17-H, 19-H and 20-H, respectively, and the *p*-xylylene fragment in the mass spectrum. Because the aromatic region for the protons 5-H to 9-H of **6** is very similar to that of the parent molecule **2**, the acetyl function must either be anchored at C-11 or C-12. That it is the former that is substituted is revealed by the chemical shifts of the ethano bridge protons bonded to C-13. As shown by C,H-correlation these are the bridge protons resonating at lowest field, the downfield shift being caused by the carbonyl group on the one hand, and C-9 of the phenanthrene ring on the other. That substituents with a carbonyl group prefer a conformation in which the oxygen atom points towards the ethano bridge has been observed many times in cyclophane chemistry.[11]

The mass spectrum for **7** shows that the molecules on "horizontal" decomposition yield an acetyl-*p*-xylylene fragment (m/z = 146), and the conclusion that the incoming



Scheme 2. Bromination and Friedel–Crafts chemistry of [2.2](1,4)phenanthrenoparacyclophane (**2**).

substituent has entered the benzene deck is supported by the practically unchanged phenanthrene section of the proton spectrum. The two sets of protons 16-H, 17-H and 19-H, 20-H, respectively, differ significantly from each other in their chemical shifts (see Experimental Section). The protons "above" the phenanthrene deck are – as expected – shifted to higher fields, resonating between δ = 5 and 6 ppm. Because for these protons only a singlet at 5.88 ppm is observed, integrating for one proton, the acetyl group must either be at C-19 or C-20. The distinction between these two alternatives is made by considering the chemical shift of the lone proton (δ = 5.88 ppm). The chemical shifts of 19-H and 20-H in the parent hydrocarbon **2**, δ = 5.86 and 5.24 ppm, respectively, and the chemical shift effect of an acetyl group on its *ortho* proton ($\Delta\delta$ = +0.64 ppm) lead to predictions of the lone proton shift of 5.88 ppm for the 19-acetyl and of 6.50 ppm for the 20-acetyl derivative. The former is in perfect agreement, albeit somewhat fortuitously, with the experimental finding.

To rationalize the observed high selectivity in the Friedel–Crafts acylation reaction of **2** we concentrate on the annelated part first. This reaction has been studied for phenanthrene itself by Girdler and co-workers,[12] who found that in different solvents, mixtures of 1-, 2-, 3-, 4- and 9-acetylphenanthrenes are produced, the composition of which strongly depends on the reaction conditions. Under conditions comparable to ours (see above) they found that at room temperature in chloroform a reactivity order of C-3 > C-9 > C-1 > C-2 > C-4 is observed. This sequence agrees with our observation that C-11 is attacked preferentially. As far as the formation of **7** is concerned we propose that the intraannular directive effect observed by Cram and Reich more than 35 years ago is operative in this example also.[13] Assuming that the acylium cation attacks the phenanthrenophane from the outside only, the substitution at C-19 begins with the formation of the σ complex **8**. By intraannular hydrogen transfer to the "lower" deck this is converted into the isomeric cation **9** while the "upper" deck is rearomatized again. From **9** "external" proton loss to the isolated product **7** is readily achievable. Although the initial electrophilic reaction could have also taken place at C-20, the displaced hydrogen does not have a place to go, because the opposing position is fully substituted. The product ratio of **6**:**7** appears to be slightly temperature dependent: repetition of the acylation experiment at – 70 to –90 °C leads to a ratio of ca. 10:1, i.e. this process as well is highly diastereoselective, although the obtained major isomer **6** cannot be employed to realize the above concept (see structure **3**).

The formylation of **2** by the method of Rieche et al.[14] [dichloromethyl methyl ether, titanium(IV) chloride, dichloromethane, room temp.] leads to a mixture of the two isomeric aldehydes **10** and **11** in 62% total yield. An attempt to separate these isomers by preparative thick-layer chromatography on silica gel failed. Still, that these derivatives have been produced can be inferred from the NMR spectra. The ^{1}H NMR spectrum of the mixture shows two sharp singlets at δ = 10.27 and 10.25 ppm in a ratio of 3:2, i.e. this electrophilic substitution reaction shows hardly any selectivity (not considering that the other 10 positions that also could have been attacked evidently do not react at all). Because the AB systems for 16-H, 17-H and 19-H, 20-H are maintained the formylation has taken place in the annelated part of the substrate. Because, furthermore, the general appearance of the section of the spectrum caused by 4-H to 9-H hardly differs from that of the substrate **2**, the formyl group must either be located at C-11 or C-12. In fact, in this part of the spectrum two singlets are visible at δ = 7.45 and 7.20 ppm, the latter being the more intense. In an attempt to unequivocally assign the structures of the major and minor formylation product, the mixture **10/11** was first reduced with LAH to the alcohols **12/13** and these were converted via the bromides **14/15** (reaction with phosphorus tribromide) to the methyl derivatives **16** and **17** by a second hydride reduction. Disappointingly, none of these isomeric derivatives could be separated. However, because of the different intensities of the respective signals of the two isomers, a structure assignment was possible in the end for **16** and **17**. In the parent compound **2** the signal for 11-H appears at δ = 6.93 ppm whereas 12-H resonates at 6.75 ppm. A substitution of 11-H should cause a change of the chemical shift of the *ortho*-proton 12-H as 11-H is shifted when 12-H is substituted. A singlet at higher frequency (δ = 6.64 ppm, side product) should therefore indicate a substitution at C-12, whereas the singlet at lower frequency (δ = 6.36, main component) is indicative of a substitution at C-11. Thus the main product would be 11- (**16**) and the side product 12-methyl-[2.2](1,4)phenanthrenoparacyclophane (**17**). In the ^{13}C NMR spectrum of **2** the signals for C-13 and C-2 are registered at δ = 38.56 and 33.56 ppm, respectively. In the ^{13}C NMR spectrum of the isomeric mixture **16/17**, the signal of C-13 of the major component appears at δ = 34.38 ppm. The strong upfield shift of 4.18 ppm as compared to the parent system **2** can be explained by postulating that the methyl substituent is attached to C-11. For the side product **17** there is hardly a chemical shift change for C-13 (δ = 38.33 ppm) compared to the reference compound **2**, whereas for C-2 an upfield shift (δ = 27.40, $\Delta\delta$ = 6.16 ppm) is noted, indicating that substitution has occurred at C-12. ^{1}H and ^{13}C NMR spectroscopic data hence lead to a consistent picture. Phenanthrene, incidentally, as investigated by Rieche et al.,[14] reacts with dichloromethyl butyl ether in the presence of tin(IV) chloride in 66% yield to 9-formylphenanthrene.

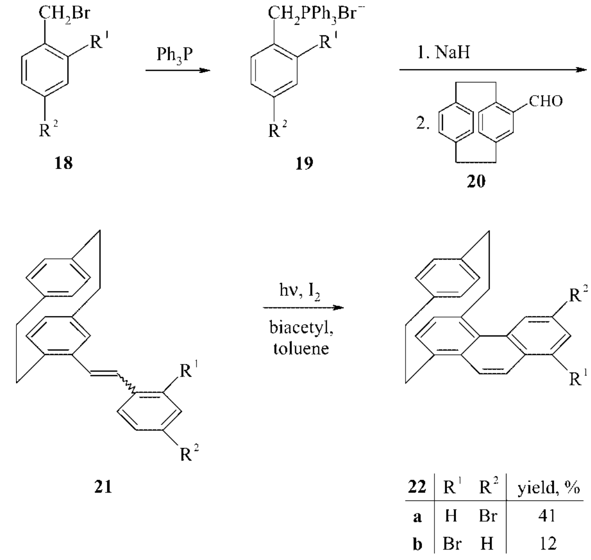
Summarising this section we conclude that although the electrophilic substitution of **2** is highly diastereoselective, only in rare cases are products obtained, viz. **5** and **7**, that can be used to realize the concept discussed above requiring the incorporation of functionality in the intended "active site" of an appropriate PAH-phane (see structure **3**).

We hence decided to explore the second route to these systems which requires the introduction of functionality in the early stages of the synthesis of the chiral ligand. Because we had already shown that the photochemical ring closure/aromatization of stilbenes to phenanthrenes is a particularly convenient route to these systems,[1] we decided to exploit this approach.

Functionalized [2.2](1,4)Phenanthrenoparacyclophanes by Prior Introduction of Functional Groups

According to classical investigations by Katz and coworkers, bromine substitution exhibits a strong influence on the stilbene → phenanthrene cyclization, increasing not only its yield but also its selectivity.[15] Because, furthermore, bromine substitution allows further functionalization to occur readily, we began our studies in this area with the preparation of bromophenanthrenophanes bearing a bromine substituent in other positions of the phenanthrene deck than described above (C-5).

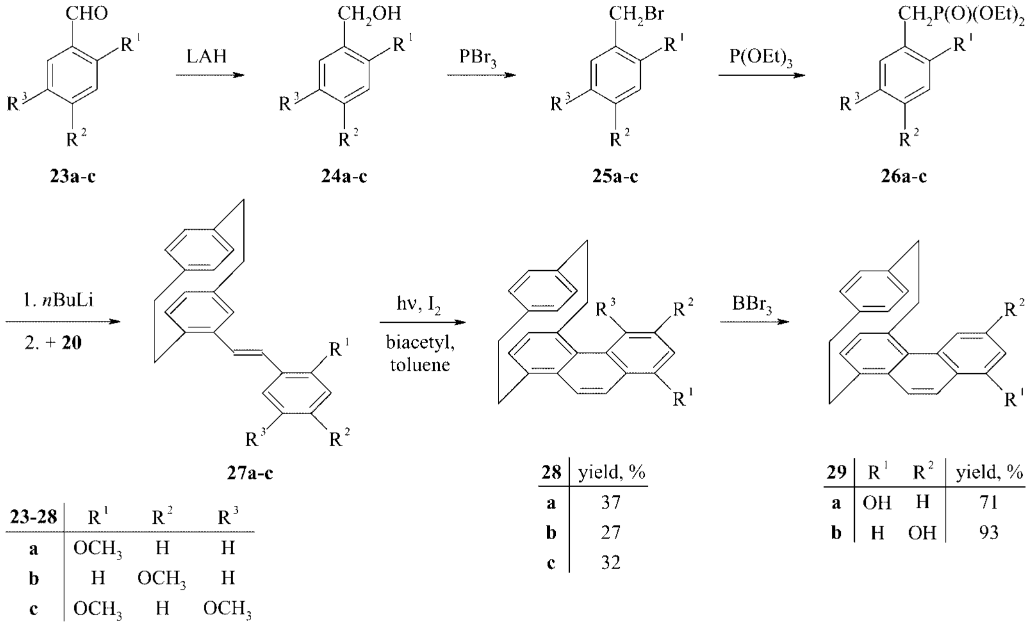
As summarized in Scheme 3 commercial 4-bromobenzyl bromide (**18a**) was first converted into the phosphonium salt **19a** by treatment with triphenylphosphane.



22	R1	R2	yield, %
a	H	Br	41
b	Br	H	12

Scheme 3. Preparation of bromo-phenanthrenoparacyclophanes by photocyclization.

Wittig olefination of 4-formyl[2.2]paracyclophane (**20**) subsequently provided 4-(4-bromostyryl)-[2.2]paracyclophane (**21a**), obtained as *cis*/*trans* mixture (ratio 2:3) in acceptable yield (72%). For analytical purposes the two diastereomers were separated chromatographically and characterized by their spectroscopic and analytical data (see Experimental Section), in particular the coupling constant of



23-28	R^1	R^2	R^3
a	OCH_3	H	H
b	H	OCH_3	H
c	OCH_3	H	OCH_3

28	yield, %
a	37
b	27
c	32

29	R^1	R^2	yield, %
a	OH	H	71
b	H	OH	93

Scheme 4. Preparation of phenanthrenophane phenols.

the olefinic double bond (*cis* isomer: 12.6 Hz, *trans* isomer: 16.2 Hz). Photocyclization took place as expected (formation of **22a**), although an increase of the yield due to bromine substitution was not observed: with 41% the yield is in the typical range observed for **2** and related PAH-phanes.[1]

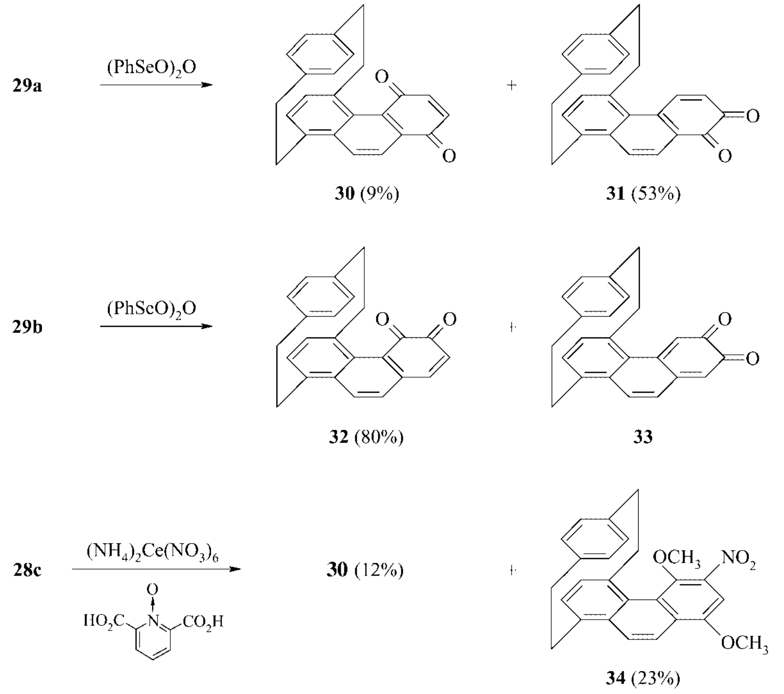
To investigate whether relocation of the bromine substituent has an effect on the process, 2-bromobenzyl bromide (**18b**) was coupled to **20** via **19b** and 4-(2-bromostyryl)[2.2]-paracyclophane (**21b**) obtained in good yield (87%), again as a mixture of diastereomers (ratio 2:3, Scheme 3). After chromatographic separation the two isomers (J_{cis} = 13.0, J_{trans} = 16.0 Hz) could be characterized unambiguously by the usual spectroscopic data (see Experimental Section). Disappointingly the photocyclization yielded 6-bromo[2.2](1,4)phenanthrenoparacyclophane (**22b**) in only 12% yield. Because 2-iodostilbene on irradiation cyclizes to phenanthrene by dehydroiodination,[16] we suspected that the poor outcome of the **21b** → **22b** ring closure could be due to a comparable process. This would lead to the parent hydrocarbon **2**, which, however, could not be detected in the photolysate.

As a second heteroatom directly bonded to the phenanthrene deck we turned to oxygen and prepared the phenols **29a** and **b** by the route summarized in Scheme 4.

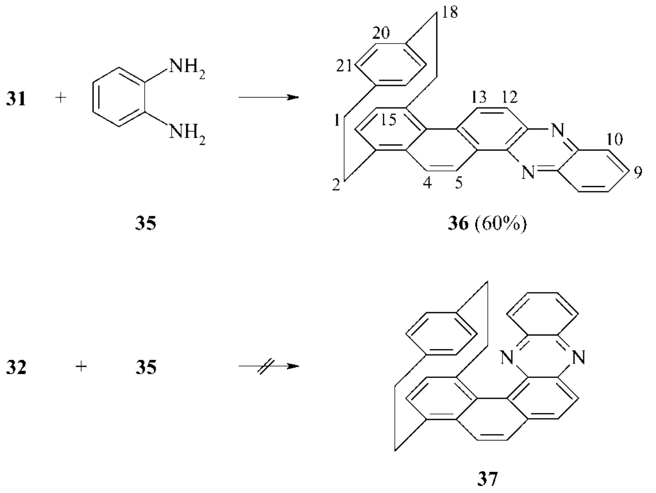
Commercial 2-methoxybenzaldehyde (**23a**) was reduced with lithium aluminium hydride to the benzyl alcohol **24a**, that by reaction with phosphorus tribromide (formation of **25a**) followed by Arbusov reaction with triethyl phosphite furnished the phosphonate **26a**. Wittig–Horner reaction of the latter with 4-formyl[2.2]paracyclophane (**20**) then gave the methoxy stilbene **27a**. Irradiation under the usual conditions (see above) provided 6-methoxy[2.2](1,4)phenanthrenoparacyclophane (**28a**) in moderate yield (37%). Finally, the target molecule 6-hydroxy[2.2](1,4)phenanthrenoparacyclophane (**29a**, 71%) resulted when **28a** was treated with boron tribromide.[17] By practically the same route 4-methoxybenzaldehyde (**23b**) was converted (**24b** → **25b** → **26b** → **27b**) to the 8-methoxyphenanthrenophane derivative **28b** (27% for the photoaromatization step), that, on cleavage with boron tribromide, yielded the isomeric phenol **29b** in practically quantitative yield. To investigate whether two oxygen-containing substituents could also be introduced by the above route the hydroquinone bisether **27c** was prepared by the above sequence (Scheme 4) from 2,5-dimethoxybenzaldehyde (**23c**) and photocyclized to 6,9-dimethoxy[2.2]-(1,4)phenanthrenoparacyclophane (**28c**, 32%); this, however, was not cleaved to the corresponding hydroquinone but was directly oxidatively demethylated to the corresponding quinone (see below).

The phenols **29a/b** are interesting chiral cyclophane derivatives in their own right, but also offer themselves for oxidation to the corresponding quinones. Treating **29a** with benzeneseleninic anhydride[18] indeed affords the *ortho*-quinone **31** in acceptable yield, accompanied by small amounts of its *para* isomer **30** (Scheme 5). The two compounds were separated by plate chromatography and characterized by their spectroscopic data (see Experimental Section); **30** crystallizes in form of beautiful, deep black prisms.

Employing potassium nitroso disulfonate (Fremy's salt)[19] as oxidant leads to **31** exclusively, but in lower yield (31%). The isomer **29b** cannot form a *para*-quinone but, in principle, could give rise to two *ortho*-quinones, **32** and **33**, on oxidation. With Barton's reagent, however, only one isomer **32** is produced in very good yield (80%). Again, this derivative crystallizes in black needles that dissolve in the common organic solvents with a deep red color.[20] The preference of **32** over **33** is probably caused by the greater inherent stability of the former: although it should be sterically more hindered (proximity of an ethano bridge to the



Scheme 5. Oxidation of phenanthrenophane phenols to *ortho*- and *para*-quinones.



Scheme 6. Condensation reactions with *ortho*-quinonophanes.

quinone part), the central ring of its condensed aromatic moiety is benzenoid, whereas this unit is *ortho*-quinoid in isomer **33**, regardless of the resonance structure.

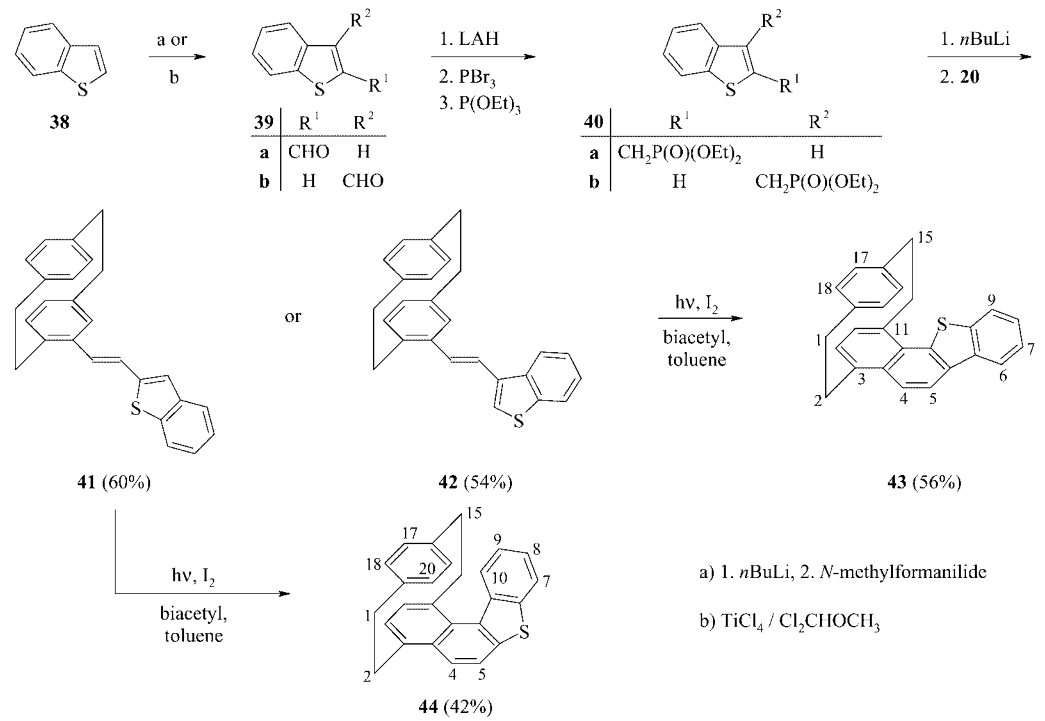
When the bisether **28c** is treated with cerium ammonium nitrate (CAN) in the presence of pyridine-2,6-dicarboxylic acid *N*-oxide, a reagent known to effect oxidative demethylation,[21] the intended product, the *para*-quinone **30**, is obtained, but the yield is poor (12%), and most of the substrate appears to be destroyed by oxidation processes. As the only other product the nitration product **34** of the starting material could be isolated (23%) and be identified by the usual spectroscopic methods (see Experimental Section).

In an exploratory experiment the condensation of the *ortho*-quinones **31** and **32** with *o*-phenylenediamine (**35**) was investigated: if phenazines are produced this would not only lead to a novel class of heteroaromatic cyclophanes, but also extended the "floor" of the receptor unit in **3** and at the same time introduce polar atoms into it, which might be useful for substrate binding. Indeed as shown in Scheme 6 **31** reacts readily with **35** and provides quinoxalino[2,3-*i*][2.2](1,4)phenanthrenoparacyclophane (**36**) in acceptable yield (60%). The elucidation of its structure rests on mass spectral and spectroscopic data, especially on the comparison with literature data for phenazine.[22]

On the other hand the isomer **32** shows no tendency to condense with **35**. It could well be that the compound reacts with the carbonyl group more distant from the ethano bridge and one of the amino groups of **35**, but the second condensation step – leading to **37** – evidently would lead to such an increase in steric strain that it is avoided.

That the incorporation of heteroatoms into the condensed part of a PAH-phane is also possible by photocyclization was shown in a last series of experiments leading to the thiophenophanes **43** and **44**, respectively (Scheme 7).

Beginning with benzo[*b*]thiophene (**38**) this was first converted by a literature procedure[23] to 2-formylbenzo[*b*]thiophene (**39a**). Employing the usual steps (see above) this provided the phosphonate **40a**, which was coupled in a Wittig–Horner step with 4-formyl[2.2]paracyclophane (**20**) to the precursor **41** in acceptable yield, its *trans* configuration being established by the olefinic coupling constant again (J_{trans} = 15.9 Hz). Cyclization proceeded readily and yielded the thiohelicenophane **44** in the expected yield (42%). Switching to the Rieche formylation of **38** gave the isomeric aldehyde **39b**, which was converted to the phosphonate **40b** by the same steps as described for **39a**. Coupling **39b** with



Scheme 7. Preparation of thiophenocyclophanes by photocyclization.

20 gave the expected ring-open 3-benzo[*b*]thiophenylethenyl derivative **42** (J_{trans} = 16.1 Hz), which on exposure to UV light was cyclized/oxidized in good yield (56%) to the corresponding heteroaromatic phane system **43**.

Summary

Having established the stilbene → phenanthrene route as a reliable preparative method in cyclophane chemistry,[1] we now have adopted this approach to the preparation of functionalized PAH-phanes. These may either be obtained by introducing the desired substituent in the early stages of the synthesis already or by functionalising the complete phane system. Subsequent reactions of the new phenanthrenophanes opened the way to a large variety of novel [2.2]cyclophanes possessing one extended, functionalized deck.

Experimental Section

General Remarks: Preparative thick-layer chromatography: silica gel Merck PF 254/366. Column chromatography: silica gel 60 (70–230 mesh, Merck); aluminium oxide, activity II–III (Woelm). Melting points: Kofler hot stage (uncorr. values) NMR: Bruker AC 200 (^{1}H: 200 MHz; ^{13}C: 50.3 MHz); Bruker AM 300 (^{1}H: 300 MHz; ^{13}C: 75.5 MHz); Bruker WM 400 and Bruker AM 400 (^{1}H: 400 MHz; ^{13}C: 100.6 MHz) in CDCl$_3$, TMS as internal standard. IR: Perkin–Elmer 1420 as KBr pellets. MS: Finnigan MAT 84530 (70 eV, EI). UV: Beckman UV 5230. [2.2](1,4)phenanthrenoparacyclophane (**2**) was prepared according to ref.[1]. The ethano bridge protons marked with a prime (′) point towards the condensed annelated ring.

Bromination of [2.2](1,4)Phenanthrenoparacyclophane (2): A dilute solution of bromine in carbon tetrachloride was added to a solution of **2** (92 mg, 0.30 mmol) in carbon tetrachloride (15 mL) until the brown bromine color persisted. After 4 d at room temp excess bromine was removed by washing with aqueous sodium sulfite solution, the phases were separated, and the organic solvent was removed in vacuo: 74.0 mg (64%) of 5-bromo[2.2]phenanthrenoparacyclophane (**5**), colorless needles (hexane), m.p. 197 °C. ^{1}H NMR (400 MHz): δ = 2.69–2.76 (m, 1 H), 2.86–2.93 (m, 1 H), 2.97–3.05 (m, 2 H), 3.17–3.25 (m, 1 H), 3.32–3.40 (m, 1 H), 3.70–3.79 (m, 1 H), 4.21–4.28 (m, 1 H, 1-,2-,13-,14-H), 5.28 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H, 20-H), 5.91 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H, 19-H), 6.51, 6.53 (both dd, J_o = 7.9, J_m = 1.7 Hz, 1 H each, 16-,17-H), 6.74 (d, J_o = 7.5 Hz, 1 H, 12-H), 6.93 (d, J_o = 7.5 Hz, 1 H, 11-H), 7.55–7.64 (m, 2 H, 7-,8-H), 7.97 (s, 1 H, 4-H), 8.34 (m, 1 H, 6-H), 8.47 (m, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz): δ = 33.26 (t, C-2), 34.43, 34.68 (both t, C-1,-14), 38.43 (t, C-13), 126.33, 126.79, 127.57, 127.83, 128.30, 128.40, 129.55, 131.60, 131.99, 132.52, 134.68 (d, C-4,-6,-7,-8,-9,-11,-12,-16,-17,-19,-20), 120.96 (s, C-5), 130.24, 131.77, 132.54, 134.21, 136.17, 136.45, 137.85, 138.65 (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18) ppm. IR (KBr): $\tilde{\nu}$ = 2860 (w), 1590 (m), 1515 (w), 1500 (m), 1440 (m), 1385 (m), 1250 (m), 1100 (m), 940 (m), 910 (m), 870 (s), 780 (m), 770 (vs), 720 (s) cm^{-1}. UV (acetonitrile): $\lambda_{\max}$ (lgε) = 332 nm (sh, 3.89), 286 (4.42), 266 (sh, 4.22), 214 (sh, 4.56), 205 (4.66). MS: *m*/*z* (%) = 388 (9) [M$^+$], 386 (9) [M$^+$], 283 (26), 281 (26), 203 (100), 202 (78), 201 (14), 104 (14). C$_{24}$H$_{19}$Br (387.34): calcd. C 74.42, H 4.95, Br 20.63; found C 74.37, H 4.72, Br 21.29.

Friedel–Crafts Acylation of [2.2](1,4)Phenanthrenoparacyclophane (2): 152 mg (1.14 mmol) of aluminium trichloride was added to anhydrous dichloromethane (20 mL) at –30 °C, followed by acetylchloride (112 mg, 1.43 mmol). To this suspension was added hydrocarbon **2** (170 mg, 0.55 mmol) (color change to red-brown), and the mixture was stirred at –20 to –30 °C for 30 min. For work-up dilute aqueous hydrochloric acid was added, the organic phase was separated and washed with sodium hydrogen carbonate solution and water. After drying with magnesium sulfate the solvent was removed by rotary evaporation; the resulting yellow oil was purified by preparative thick-layer chromatography on silica gel with dichloromethane providing two fractions.

Fraction 1. 11-Acetyl[2.2](1,4)phenanthrenoparacyclophane (6): 143 mg (74%), yellow needles (hexane/ethanol, 3:1), m.p. 116–118 °C. ^{1}H NMR (400 MHz): δ = 2.66 (s, 3 H, CH$_3$CO), 2.72–3.04 (m, 4 H, 1-H or 1-H′, 2-H, 14-H, 14-H′), 3.25 (m$_c$, 1 H, 1-H′ or 1-H), 3.81 (m$_c$, 1 H, 2-H′), 4.09 (m$_c$, 1 H, 13-H), 4.30 (m$_c$, 1 H, 13-H′), 5.49 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H, 20-H), 5.88 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H, 19-H), 6.52 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H, 16-H), 6.63 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H, 17-H), 7.15 (s, 1 H, 12-H), 7.54 (m$_c$, 2 H, 7-,8-H), 7.59 (d, J = 8.9 Hz, 1 H, 4-H), 7.77 (d, J = 8.9 Hz, 1 H, 5-H), 7.87 (m$_c$, 1 H, 6-H), 8.26 (m$_c$, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz): δ = 29.55 (q, CH$_3$), 33.68 (t, C-2), 34.28 (t, C-1), 35.27 (t, C-14), 37.57 (t, C-13), 122.46 (d, C-4), 125.82, 126.29 (both d, C-7,-8), 128.24 (d, C-5), 128.29 (d, C-6), 128.87 (d, C-20), 129.91 (d, C-9), 130.14 (d, C-19), 130.26 (d, C-17), 130.26 (s, C-9a), 130.92 (d, C-16), 132.33 (s, C-5a), 132.72 (d, C-12), 134.94 (s, C-9b), 135.37 (s, C-3a), 135.74 (s, C-3), 138.11 (s, C-11), 138.34 (s, C-18), 139.51 (s, C-15), 141.47 (s, C-10), 199.66 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2920 (m), 1670 (vs), 1570 (m), 1540 (m), 1500 (m), 1400 (m), 1370 (m), 1210 (m), 1130 (m), 950 (m), 820 (s), 760 (m). UV (acetonitrile): λ_{max} (lgε) = 383 nm (sh, 3.15), 345 (3.89), 292 (4.33), 241 (sh, 4.22), 207 (4.66). MS: *m/z* (%) = 350 (36) [M$^+$], 245 (61), 203 (100), 104 (10). C$_{26}$H$_{22}$O (350.48): calcd. C 89.09, H 6.34; found C 89.07, H 6.22.

Fraction 2. 19-Acetyl[2.2](1,4)phenanthrenoparacyclophane (7): 17 mg (9%), colorless prisms (ethanol), m.p. 171–172 °C. ^{1}H NMR (400 MHz): δ = 1.87 (s, 3 H, CH$_3$CO), 2.63 (m$_c$, 1 H), 3.00–3.30 (m, 4 H, 1-,2-,13-,14-H), 3.93 (m$_c$, 1 H, 2-H′), 4.44 (m$_c$, 1 H, 1-H′), 4.54 (m$_c$, 1 H, 13-H′), 5.88 (d, J_m = 1.5 Hz, 1 H, 20-H), 6.57 (d, J_o = 7.8 Hz, 1 H, 17-H), 6.66 (dd, J_o = 7.8, J_m = 1.5 Hz, 1 H, 16-H), 6.87 (d, J_o = 7.5 Hz, 1 H, 12-H), 7.00 (d, J_o = 7.5 Hz, 1 H, 11-H), 7.53–7.60 (m, 3 H, 4-,7-,8-H), 7.64 (d, J = 9.0 Hz, 1 H, 5-H), 7.86 (m$_c$, 1 H, 6-H), 8.76 (m$_c$, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz): δ = 27.69 (q, CH$_3$), 31.74, 33.48, 33.65, 39.86 (t, C-1, -2,-13,-14), 124.43, 125.92, 126.15, 126.83, 127.32, 128.24, 131.13, 131.24, 134.56, 135.00, 135.54 (d, C-4,-5,-6,-7,-8,-9,-11,-12,-16,-17, -20), 130.65, 131.86, 132.00, 134.40, 134.90, 135.61, 138.02, 138.35, 141.50 (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18,-19), 199.18 (s, -CO-) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2940 (m), 1670 (vs), 1550 (m), 1515 (m), 1480 (m), 1460 (m), 1350 (s), 1255 (s), 1190 (m), 960 (m), 810 (s), 755 (s). UV (acetonitrile): λ_{max} (lgε) = 311 nm (sh, 3.86), 270 (4.47), 219 (4.58), 213 (sh, 4.58), 202 (4.57). MS: *m/z* (%) = 350 (38) [M$^+$], 203 (100), 189 (26), 146 (12). C$_{26}$H$_{22}$O (350.48): calcd. C 89.09, H 6.34; found C 88.98, H 6.33. .

Rieche Formylation of [2.2](1,4)Phenanthrenoparacyclophane (2): A solution of **2** (150 mg, 0.49 mmol) in anhydrous dichloromethane (20 mL) was cooled to –30 °C and titanium(IV) chloride (155 mg, 0.82 mmol) was added (color change to violet), followed by 1,1-dichloromethyl methyl ether (103 mg, 0.90 mmol) (color change to black). After stirring for 2 h at –30 °C the reaction mixture was poured on ice, the organic phase was separated, washed with hydrogen carbonate solution and dried (magnesium sulfate). The solvent was removed in vacuo and the remaining oil purified by extensive plate chromatography [first with dichloromethane; main fraction (107 mg), then with hexane/dichloromethane, 1:1], yield: 101 mg (62%), yellow oil. According to NMR analysis the product mixture contained the aldehydes **10** and **11** in a ratio of 3:2.

Main Fraction. 11-Formyl[2.2](1,4)phenanthrenoparacyclophane (10): ^{1}H NMR (400 MHz): δ = 2.66 (m$_c$, 1 H), 2.92–3.35 (m, 4 H), 3.75 (m$_c$, 1 H), 4.14 (m$_c$, 1 H), 4.28–4.34 (m, 1 H, 1-,2-,13-,14-H), 5.48 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 20-H), 5.82 (dd, J_o = 7.9, J_m = 1.9 Hz, 1 H, 19-H), 6.46 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 16-H), 6.62 (dd, J_o = 7.9, J_m = 1.9 Hz, 1 H, 17-H), 7.20 (s, 1 H, 12-H), 7.51–7.59 (m, 3 H, 4-,7-,8-H), 7.78 (d, J = 8.9 Hz, 1 H, 5-H), 7.86 (m$_c$, 1 H, 6-H), 8.16 (m$_c$, 1 H, 9-H), 10.27 (s, 1 H, CHO) ppm.

Minor Fraction. 12-Formyl[2.2](1,4)phenanthrenoparacyclophane (11): ^{1}H NMR (400 MHz): δ = 2.66 (m$_c$, 1 H), 2.92–3.35 (m, 4 H), 3.75 (m$_c$, 1 H), 4.14 (m$_c$, 1 H), 4.28–4.34 (m, 1 H, 1-,2-,13-,14-H), 5.22 (dd, J_o = 7.8, J_m = 1.8 Hz, 1 H, 20-H), 5.92 (dd, J_o = 7.8, J_m = 1.9 Hz, 1 H, 19-H), 6.37 (d, J = 7.9 Hz, 1 H), 6.45 (d, J = 7.9 Hz, 2 H, 16-,17-H), 7.45 (s, 1 H, 11-H), 7.51–7.59 (m, 2 H, 7-,8-H), 7.73 (br. s, 2 H, 4-,5-H), 7.86 (m$_c$, 1 H, 6-H), 8.54 (m$_c$, 1 H, 9-H), 10.25 (s, 1 H, CHO) ppm. The ^{13}C-NMR signals in the aromatic region of the two components partially overlapped and could not be fully assigned, identifiable were the signals of the aldehydic carbon atoms δ = 190.60 (d) for **10** and 191.00 (d) for **11** and the bridge carbon atoms: **10**: δ = 33.55, 34.30 (2 C), 36.69 (t, C-1,-2, -13,-14); **11**: δ = 26.34, 34.30, 34.73, 38.70 (t, C-1,-2,-13,-14) ppm.

Reduction of 10/11 to the Corresponding Hydroxymethyl[2.2](1,4)-phenanthrenoparacyclophanes 12 and 13: A solution of a mixture of **10** and **11** (101 mg, 0.30 mmol, see above) in THF (5 mL) was added to a suspension of lithium aluminium hydride (10 mg, 0.26 mmol) in anhydrous THF (20 mL) at 0 °C. The reaction mixture was stirred for 1 h and hydrolysed. The THF was removed by rotary evaporation and the obtained residue treated with dilute hydrochloric acid and extracted with dichloromethane. After drying (magnesium sulfate) the solvent was evaporated and the remaining oil purified by thick-layer chromatography on silica gel with dichloromethane: 60 mg (60%) of a mixture of **12** and **13** which was used without further separation in the next step.

Reduction of 12/13 to the Corresponding Methyl[2.2](1,4)phenanthrenoparacyclophanes 16 and 17: Phosphorus(III) bromide (48 mg, 0.18 mmol) was added to a solution of **12** and **13** (60 mg, 0.18 mmol) in anhydrous dichloromethane (20 mL) at 0 °C, and the mixture was stirred for 1 h. After hydrolysis the organic phase was separated, washed with water and dried with potassium carbonate. Solvent removal afforded 70 mg (98%) of a mixture of the bromides **14** and **15** which was subjected to the next step without further purification. A solution of the bromides **14/15** (70 mg, 0.17 mmol) in THF (10 mL) was added to a suspension of lithium aluminium hydride (14 mg, 0.18 mmol) in anhydrous THF (10 mL) at 0 °C. The mixture was stirred for 5 h at room temp. and then hydrolyzed at 0 °C. Work-up as described for the LAH reduction above furnished 53 mg of a yellow oil that was purified by plate chromatography on silica gel (first separation with carbon tetrachloride, second one with cyclohexane): 25 mg (45%) of a mixture of **16** and **17** (colorless oil). The individual isomers were identified by their proton spectra. **16:** ^{1}H NMR (400 MHz): δ = 2.38 (s, 3 H, CH$_3$), 2.77–3.04 (m, 4 H), 3.19 (m$_c$, 1 H), 3.67 (m$_c$, 1 H), 3.78 (m$_c$, 1 H), 4.08 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.40 (dd, J_o = 7.8, J_m = 1.8 Hz, 1 H, 20-H), 5.78 (dd, J_o = 7.8, J_m = 1.9 Hz, 1 H, 19-H), 6.36 (s, 1 H, 12-H), 6.54 (dd, 1 H) and 6.81 (dd, J_o = 7.9, J_m = 1.9 Hz, 1 H, 2 x 1 H, 16-,17-H), 7.44–7.54 (m, 2 H, 7-,8-H), 7.63 (d, 1 H) and 7.65 (d, J = 8.9 Hz, 1 H, 4-,5-H), 7.85 (m$_c$, 1 H, 6-H), 8.20 (m$_c$, 1 H, 9-H) ppm. **17:** ^{1}H NMR (400 MHz): δ = 2.30 (s, 3 H, CH$_3$), 2.71 (m$_c$, 1 H), 2.77–3.04 (m, 3 H) 3.10 (m$_c$, 1 H), 3.30 (m$_c$, 1 H), 3.58 (m$_c$, 1 H), 4.33 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.26 (dd, J_o = 7.8, J_m = 1.8 Hz, 1 H, 20-H), 5.89 (dd, J_o = 7.8, J_m = 1.9 Hz, 1 H, 19-H), 6.41 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 16-H), 6.72 (dd, J_o = 7.9, J_m = 1.9 Hz, 1 H, 17-H), 7.44–7.54 (m, 2 H, 7-,8-H), 7.64 (d, 1 H) and 7.68 (d, J = 9.1 Hz, 1 H, 4-,5-H), 7.85 (m$_c$, 1 H, 6-H), 8.53 (m$_c$, 1 H, 9-H) ppm. The ^{13}C NMR signals in the aromatic region of the two components partially overlapped and could not be fully assigned, identifiable were all saturated carbon atoms of the two isomers; **16:** δ = 21.09 (q, CH_3), 33.22 (t, C-2), 33.30 (t, C-1), 33.78 (t, C-14), 34.38 (t, C-13) ppm. **17**: δ = 21.09 (q, CH_3), 27.40 (t, C-2), 33.41 (t, C-1), 34.38 (t, C-14), 38.33 (t, C-13) ppm.

8-Bromo[2.2](1,4)phenanthrenoparacyclophane (22a). a) (4-Bromobenzyl)triphenylphosphonium Bromide (19a): A solution of 4-bromobenzyl bromide (**18a**) (3.0 g, 12.0 mmol) and triphenylphosphane (3.5 g, 13.5 mmol) in toluene (80 mL) was heated at 110–120 °C for 3 h. After cooling, the precipitate formed was removed by filtration and washed with cyclohexane: 5.86 g (95%) of **19a** a known[24] colorless solid that could be used in the next step without further purification.

b) 4-(4-Bromostyryl)[2.2]paracyclophane (21a): Commercial sodium hydride (60% suspension in oil, 0.47 g, 11.5 mmol) was washed twice with THF under nitrogen; anhydrous THF (70 mL) was added, the suspension cooled to 0 °C, and **19a** (5.86 g, 11.5 mmol) was added in portions (formation of a yellow color). When hydrogen evolution had ceased 4-formyl[2.2]paracyclophane (**20**) (2.36 g, 10.0 mmol) was added, and the reaction mixture was stirred for 2 h at room temp. After hydrolysis, the THF was removed by rotary evaporation and the residue was taken up in dichloromethane. The organic phase was washed with water, dried with magnesium sulfate, and the solvent was removed in vacuo. The raw product was purified by column chromatography (silica gel, carbon tetrachloride) to provide 2.84 g (72%) of **21a** as a mixture of diastereomers (ratio 2:3). For analytical purposes the two geometric isomers were separated by plate chromatography (silica gel, carbon tetrachloride). **(*Z*)-21a:** Colourless needles (hexane), m.p. 104–106 °C. ^{1}H NMR (400 MHz): δ = 2.63 (m_c, 1 H), 2.85 (m_c, 1 H), 2.94–3.08 (m, 5 H), 3.20 (m, 1 H, 1-,2-,9-,10-H), 6.17 (s, 1 H, 5-H), 6.37–6.40 (m, 2 H), 6.44 (dd, J_o = 7.9, J_m = 1.7 Hz, 1 H), 6.48 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H), 6.53 (dd, J_o = 7.7, J_m = 1.7 Hz, 1 H), 6.75 (dd, J_o = 7.8, J_m = 1.6 Hz, 1 H, 7-,8-,12-,13-,15-,16-H), 6.41 (d, 1 H) and 6.55 (d, J = 12.2 Hz, 1 H, 17-,18-H), 6.94 (2 H) and 7.20 (2 H, AA′XX′; 20-,21-,23-,24-H) ppm. ^{13}C NMR (100 MHz): δ = 33.67, 34.25, 34.99, 35.27 (t, C-1,-2,-9,-10), 120.79 (s, C-22), 130.30 (d, 2 C), 131.02 (d, 2 C, C-20,-21,-23,-24), 128.47, 129.11, 130.87, 132.03, 132.18, 133.01, 133.11, 134.62, 134.94 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18), 136.08, 136.13, 138.03, 139.37, 139.47, 139.60 (s, C-3,-4,-6,-11,-14,-19) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2920 (m), 2850 (m), 1580 (m), 1485 (s), 1090 (w), 1070 (m), 1010 (s), 900 (m), 850 (s), 805 (m), 720 (s). UV (acetonitrile): λ_{max} (lgε) = 298 nm (3.96), 249 (4.21), 222 (sh, 4.38), 210 (sh, 4.51), 200 (4.59). MS: m/z (%) = 390 (41) [M^+], 388 (41) [M^+], 309 (28), 285 (80), 283 (77), 271 (18), 269 (18), 205 (100), 203 (48), 202 (35), 189 (30), 139 (10). $C_{24}H_{21}Br$ (389.36): calcd. C 74.03, H 5.45, Br 20.52; found C 74.49, H 5.48, Br 20.68. **(*E*)-21a:** Colourless needles (ethanol), m.p. 178–179 °C. ^{1}H NMR (400 MHz): δ = 2.81–3.19 (m, 7 H), 3.55 (m_c, 1 H, 1-,2-,9-,10-H), 6.40–6.55 (m, 7 H), 6.64–6.66 (m, 2 H, 5-,7-,8-,12-,13-,15-,16-H), 6.80 (d, J = 16.2 Hz, 1 H) and 7.15 (d, J = 16.2 Hz, 1 H, 17-,18-H), 7.39–7.42 (m, 2 H), 7.49–7.51 (m, 2 H, 20-,21-H) ppm. ^{13}C NMR (100 MHz): δ = 33.94, 34.92, 35.22, 35.46 (t, C-1,-2,-9,-10), 121.13 (s, C-22), 127.93 (d, 2 C), 131.81 (d, 2 C, C-20,-21,-23,-24), 127.61, 127.86, 129.84, 130.19, 131.71, 132.07, 133.01, 133.04, 135.00 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18), 136.87, 137.05, 138.46, 139.18, 139.33, 139.99 (s, C-3,-4,-6,-11,-12,-19) ppm. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2920 (m), 1490 (s), 1435 (m), 1400 (m), 1075 (m), 965 (s), 810 (s), 730 (m), 720 (m). UV (acetonitrile): λ_{max} (lgε) = 325 nm (4.32), 262 (4.12), 222 (sh, 4.31), 208 (4.45), 198 (4.49). MS: m/z (%) = 390 (46) [M^+], 388 (44) [M^+], 285 (10), 283 (96), 271 (17), 269 (18), 205 (76), 189 (26), 165 (15). $C_{24}H_{21}Br$ (389.36): calcd. C 74.03, H 5.45, Br 20.52; found C 74.03, H 5.47, Br 20.83.

c) 8-Bromo[2.2](1,4)phenanthrenoparacyclophane (22a): A solution of **21a** (mixture of diastereomers) (1.22 g, 3.15 mmol), iodine (165 mg) and biacetyl (0.4 mL) in anhydrous toluene (250 mL) was irradiated with a mercury high-pressure lamp (Hanau TQ 150) for 40 min. The unreacted iodine was removed by washing with a diluted aqueous sodium hydrogen sulfite solution, the organic phase was separated, washed with water and dried with magnesium sulfate. The solvent was removed by rotary evaporation and the remaining oil purified by thick layer chromatography on silica gel, first with carbon tetrachloride and then with cyclohexane: 504 mg (41%) of **22a**, colorless plates (ethanol), m.p. 190–192 °C. ^{1}H NMR (400 MHz): δ = 2.82 (m_c, 1 H), 2.90–3.05 (m, 3 H), 3.20 (m_c, 1 H), 3.40 (m_c, 1 H), 3.80 (m_c, 1 H), 4.24 (m_c, 1 H, 1-,2-,13-,14-H), 5.26 (d, J_o = 7.9 Hz, 1 H, 20 H), 5.82 (dd, J_o = 7.9, J_m = 1.4 Hz, 1 H, 19-H), 6.52 (m_c, 2 H, 16-,17-H), 6.76 (d, J_o = 7.4 Hz, 1 H, 12-H), 6.93 (d, J_o = 7.5 Hz, 1 H, 11-H), 7.60 (dd, J_o = 8.4, J_m = 1.9 Hz, 1 H, 7-H), 7.64 (br. s, 2 H, 4-,5-H), 7.72 (d, J_o = 8.5 Hz, 1 H, 6-H), 8.66 (d, J_m = 1.8 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz): δ = 33.43, 34.38, 34.73, 38.17 (t, C-1,-2,-13,-14), 124.38, 125.38, 128.44, 128.82, 129.14, 129.71, 130.39, 131.62, 132.05, 132.52, 134.47 (d, C-4,-5,-6,-7,-9,-11,-12,-16,-17,-19,-20), 1 C unresolved, 119.35, 130.63, 131.84, 134.22, 136.32, 136.86, 137.89, 138.68 (s, C-3,-3a,-5a,-8,-9a,-9b,-10,-15,-18) ppm. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2990 (w), 2934 (m), 1590 (m), 1490 (m), 1440 (m), 1080 (m), 930 (m), 890 (m), 870 (m), 845 (s), 830 (vs), 805 (m), 720 (s). UV (acetonitrile): λ_{max} (lgε) = 383 nm (2.78), 315 (3.93), 284 (4.47), 263 (sh, 4.22), 220 (sh, 4.53), 206 (4.65). MS: m/z (%) = 388 (13) [M^+], 386 (13) [M^+], 283 (17), 281 (16), 203 (100), 202 (54), 97 (11). $C_{24}H_{19}Br$ (387.34): calcd. C 74.42, H 4.95, Br 20.63; found C 74.41, H 5.03, Br 20.91.

6-Bromo[2.2](1,4)phenanthrenoparacyclophane (22b). a) (4-Bromobenzyl)triphenylphosphonium Bromide (19b): As described above for **19a**, **19b** was prepared from 2-bromobenzyl bromide (**18b**) (3.0 g, 12.0 mmol) and triphenylphosphane (3.5 g, 13.5 mmol) in toluene (80 mL): yield 6.1 g (99%), a known phosphonium bromide.[25]

b) 4-(2-Bromostyryl)[2.2]paracyclophane (21b): By the procedure described above for **21a** the isomer **21b** was prepared from sodium hydride (0.48 g, 11.9 mmol), **19b** (6.1 g, 11.9 mmol) and 4-formyl[2.2]paracyclophane (**20**) (2.13 g, 9.0 mmol). After work-up (see above) 3.07 g (87%) of **21b** was isolated as a mixture of isomers that can be used for the photocyclization (see below) without further purification. For analytical purposes the two diastereomers (ratio 2:3) were separated by thick-layer chromatography on silica gel with carbon tetrachloride. **(*Z*)-21b:** Colourless leaflets (hexane), m.p. 108–110 °C. ^{1}H NMR (400 MHz): δ = 2.57 (m_c, 1 H), 2.80 (m_c, 1 H), 2.93–3.07 (m, 5 H), 3.21 (m_c, 1 H, 1-,2-,9-,10-H), 6.60 and 6.63 (AB, J = 13.0 Hz, 2 H, 17-,18-H), 6.11 (s, 1 H, 5-H), 6.33 (d, J_o = 7.8 Hz, 1 H), 6.38–6.41 (m, 2 H), 6.47 (d, J_o = 7.9 Hz, 1 H), 6.51 (d, J_o = 7.9 Hz, 1 H), 6.77 (d, J_o = 7.8 Hz, 1 H), 6.85–6.87 (m, 2 H, 7-,8-,12-,13-,15-,16-,21-,22- or 23-H), 6.96 (m_c, 1 H, 22- or 23-H), 7.53 (d, J_o = 7.9 Hz, 1 H, 24-H) ppm. ^{13}C NMR (100 MHz): δ = 33.78, 34.39, 35.01, 35.28 (t, C-1,-2,-9,-10), 123.87 (s, C-20), 126.57, 128.38, 129.19, 129.69, 130.87, 131.11, 132.07, 132.11, 132.42, 132.97, 133.01, 134.90, 135.02 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18,-21,-22,-23,-24), 135.77, 137.72, 138.36, 139.31 (2 C), 139.55 (s, C-3,-4,-6,-11,-14,-19) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2920 (m), 2840 (m), 1580 (m), 1495 (m), 1460 (m), 1040 (w), 1020 (s), 900 (m), 795 (m), 765 (s), 750 (s), 725 (s), 715 (s). UV (acetonitrile): λ_{max} (lgε) = 298 nm (3.89), 237 (sh, 4.21), 223 (sh, 4.37), 202 (4.59). MS: m/z (%) = 390 (16) [M^+], 388 (16) [M^+], 309

(32), 285 (34), 283 (34), 205 (100), 189 (38), 104 (22). $\mathrm{C_{24}H_{21}Br}$ (389.36): calcd. C 74.03, H 5.45, Br 20.52; found C 74.12, H 5.38, Br 20.05. **(*E*)-21b:** Colourless leaflets (hexane), m.p. 108–110 °C. ^{1}H NMR (400 MHz): δ = 2.81–3.17 (m, 7 H), 3.53 (m$_c$, 1 H, 1-,2-,9-,10-H), 6.68 (J_m = 1.4 Hz, 1 H, 5-H), 6.46–6.63 (m, 5 H), 6.80 (dd, J_o = 7.8, J_m = 1.8 Hz, 1 H, 7-,8-,12-,13-,15-,16-H), 7.05 (d, J = 16.0 Hz, 1 H), 7.23 (d, J = 16.0 Hz, 1 H, 17-,18-H), 7.14 (m$_c$, 1 H), 7.34 (m$_c$, 1 H, 22-,23-H), 7.62 (dd, J_o = 8.0, J_m = 1.1 Hz, 1 H), 7.67 (dd, J_o = 7.8, J_m = 1.5 Hz, 1 H, 21-,24-H) ppm. ^{13}C NMR (100 MHz): δ = 34.00, 34.83, 35.20, 35.44 (t, C-1,-2,-9,-10), 124.21 (s, C-20), 126.88, 127.61, 128.53, 128.67, 129.58, 129.94, 130.41, 131.67, 132.19, 132.98, 133.04, 133.13, 134.90 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18,-21,-22,-23,-24), 137.21, 137.86, 138.69, 139.14, 139.39, 140.04 (s, C-3,-4,-6,-11,-14,-19) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2950 (w), 2920 (m), 1495 (m), 1480 (m), 1460 (s), 10120 (s), 965 (s), 955 (m), 800 (s), 755 (s), 730 (m). UV (acetonitrile): $\lambda_{\max}$ (lgε) = 306 nm (4.02), 237 (sh, 4.21), 200 (4.57). MS: *m*/*z* (%) = 390 (22) [M$^+$], 388 (22) [M$^+$], 309 (16), 285 (99), 283 (94), 205 (100), 202 (77), 189 (42), 178 (13). $\mathrm{C_{24}H_{21}Br}$ (389.36): calcd. C 74.03, H 5.45, Br 20.52; found C 74.31, H 5.51, Br 20.83.

c) 6-Bromo[2.2](1,4)phenanthrenoparacyclophane (22b): The photocyclization was carried out as described above for **21a**; from **21b** (mixture of diastereomers) (1.34 g, 3.43 mmol) iodine (220 mg) and of biacetyl (0.4 mL) in anhydrous toluene (250 mL) after 50 min irradiation and plate chromatography on silica gel with cyclohexane 383 mg of a colorless oil was obtained that provided 158 mg (12%) of **22b** after recrystallization from hexane; colorless plates, m.p. 191–192 °C. ^{1}H NMR (400 MHz): δ = 2.77 (m$_c$, 1 H), 2.88 (m$_c$, 1 H), 2.94–3.06 (m, 2 H), 3.20 (m$_c$, 1 H), 3.40 (m$_c$, 1 H), 3.82 (m$_c$, 1 H), 4.19 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.26 (dd, J_o = 7.8, J_m = 1.5 Hz, 1 H, 20-H), 5.83 (dd, J_o = 7.8, J_m = 1.5 Hz, 1 H, 19-H), 6.51 (dd, J_o = 7.8, J_m = 1.5 Hz, 1 H, 16-H), 6.55 (dd, J_o = 7.9, J_m = 1.5 Hz, 1 H, 17-H), 6.76 (d, J_o = 7.4 Hz, 1 H, 12-H), 6.93 (d, J_o = 7.4 Hz, 1 H, 11-H), 7.34 (m, 1 H, 8-H), 7.72 (d, J = 9.2 Hz, 1 H, 4-H), 7.81 (dd, J_o = 7.4, J_m = 0.8 Hz, 1 H, 7-H), 8.17 (d, J = 9.2 Hz, 1 H, 5-H), 8.42 (d, J_o = 8.4 Hz, 1 H, 8-H) ppm. ^{13}C NMR (100 MHz): δ = 33.33, 34.42, 34.87, 38.26 (t, C-1,-2,-13,-14), 123.21 (s, C-6), 124.29, 125.39, 125.63, 127.97, 128.55, 129.40, 129.90, 131.45, 132.01, 132.63, 134.60 (d, C-4,-5,-7,-8,-9,-11,-12,-16,-17,-19,-20), 130.57, 132.21, 132.68, 133.86, 136.48, 136.89, 137.96, 138.68 (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18) ppm. IR (KBr): $\tilde{\nu}$ = 3005 cm^{-1} (w), 2820 (m), 1590 (m), 1555 (m), 1435 (vs), 1390 (m), 935 (m), 870 (m), 820 (vs), 810 (s), 800 (s), 760 (vs), 720 (vs). UV (acetonitrile): $\lambda_{\max}$ (lgε) = 375 nm (2.70), 320 (sh, 3.92), 286 (4.45), 260 (sh, 4.19), 212 (sh, 4.61), 207 (4.66). MS: *m*/*z* (%) = 388 (8) [M$^+$], 386 (8) [M$^+$], 283 (14), 281 (14), 203 (100), 202 (55). $\mathrm{C_{24}H_{19}Br}$ (387.34): calcd. C 74.42, H 4.95, Br 20.63; found C 74.34, H 5.04, Br 20.77.

6-Hydroxy[2.2](1,4)phenanthrenoparacyclophane (29a). a) *trans*-4-(2-Methoxystyryl)[2.2]paracyclophane (27a): By methods described in the literature 2-methoxybenzaldehyde (**23a**) was reduced to benzyl alcohol (**24a**),[26] and this was converted via the bromide **25a**[26] to the phosphonate **26a**.[27] A solution of **26a** (2.32 g, 9.00 mmol) in anhydrous THF (50 mL) was cooled to 0 °C under nitrogen. After the addition of *n*-butyllithium (10 mmol, THF; color change to yellow) solid 4-formyl[2.2]paracyclophane (**20**) (1.90 g, 8.04 mmol) was added in portions. Stirring was continued for 4 h at room temp., and the reaction mixture was hydrolysed. The THF was removed by rotary evaporation, dilute hydrochloric acid was added, and the residue was extracted with dichloromethane. The organic phase was separated, washed with water and dried with magnesium sulfate. Solvent removal and column chromatography (silica gel, carbon tetrachloride) provided 1.80 g (66%) of **27a** as an oily raw product, that soon solidified: colorless needles (ethanol), m.p. 117–119 °C. ^{1}H NMR (400 MHz): δ = 2.83 (m$_c$, 1 H), 2.92–3.17 (m, 6 H), 3.57 (m$_c$, 1 H, 1-,2-,9-,10-H), 3.92 (s, 3 H, OCH$_3$), 6.68 (br. s, 1 H, 5-H), 6.43–6.55 (m, 5 H), 6.76 (dd, J_o = 7.8, J_m = 1.5 Hz, 1 H, 7-,8-,12-,13-,15-,16-H), 6.93 (d, J_o = 8.3 Hz, 1 H, 21-H), 7.17 (d, J = 16.3 Hz, 1 H), 7.24 (d, J = 16.3 Hz, 1 H, 17-,18-H), 7.01 (pseudo-t, J = 7.5 Hz, 1 H), 7.26 (m$_c$, 1 H, 22-,23-H), 7.64 (dd, J_o = 7.7, J_m = 1.4 Hz, 1 H, 24-H) ppm. ^{13}C NMR (100 MHz): δ = 34.04, 34.80, 35.22, 35.47 (t, C-1,-2,-9,-10), 55.63 (q, OCH$_3$), 120.77, 124.21, 126.46, 127.53, 128.48, 129.73, 130.36, 131.49, 131.75, 132.95, 133.00, 134.81 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18,-22,-23,-24), 127.13 (s, C-19), 138.10, 138.23, 139.29, 139.32, 139.83 (s, C-3,-4,-6,-11,-14), 157.00 (s, C-20) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2920 (m), 1590 (m), 1490 (m), 1330 (m), 1290 (m), 1250 (vs), 1105 (m), 1030 (m), 970 (m), 960 (m), 800 (m), 750 (s). UV (acetonitrile): $\lambda_{\max}$ (lgε) = 330 nm (4.19), 238 (sh, 4.17), 227 (sh, 4.31), 212 (4.50), 220 (4.49). MS: *m*/*z* (%) = 340 (41) [M$^+$], 235 (100), 221 (19), 205 (14), 202 (11), 97 (10). $\mathrm{C_{25}H_{24}O}$ (340.49): calcd. C 88.18, H 7.12; found C 88.22, H 7.11.

b) 6-Methoxy[2.2](1,4)phenanthrenoparacyclophane (28a): The photocyclization of **27a** was carried out as described above for the **21** → **22** interconversion using **27a** (840 mg, 2.48 mmol), iodine (215 mg) and biacetyl (0.4 mL) in toluene (250 mL). After 1 h irradiation and work-up (see above) 309 mg (37%) of **28a** was isolated; colorless prisms (ethanol), m.p. 183–184 °C. ^{1}H NMR (400 MHz): δ = 2.76 (m$_c$, 1 H), 2.90 (m$_c$, 1 H), 2.95–3.04 (m, 2 H), 3.17 (m$_c$, 1 H), 3.35 (m$_c$, 1 H), 3.83 (m$_c$, 1 H), 4.27 (m$_c$, 1 H), 4.03 (s, 3 H, OCH$_3$), 5.26 (d, J_o = 7.8 Hz, 1 H, 20-H), 5.85 (d, J_o = 7.8 Hz, 1 H, 19-H), 6.46–6.57 (m, 2 H, 16-,17-H), 6.74 (d, J_o = 7.4 Hz, 1 H, 12-H), 6.91 (m$_c$, 2 H, 7-,11-H), 7.43 (m$_c$, 1 H, 8-H), 7.64 (d, J = 8.8 Hz, 1 H, 4-H), 8.08 (d, J = 8.8 Hz, 1 H, 5-H), 8.21 (d, J = 9.2 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz): δ = 33.44, 34.38, 34.76, 38.56 (t, C-1,-2,-13,-14), 55.62 (q, OCH$_3$), 104.83 (d, C-7), 119.31, 120.54, 123.20, 125.39, 128.37, 129.07, 131.54, 131.83, 131.96, 134.04 (d, C-4,-5,-8,-9,-11,-12,-16,-17,-19,-20), 123.43 (s, C-5a), 131.77, 132.61, 134.19, 136.59, 136.68, 137.88, 138.75 (s, C-3,-3a,-9a,-9b,-10,-15,-18), 155.53 (s, C-6) ppm. IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2960 (m), 1600 (s), 1560 (m), 1510 (m), 1430 (m), 1400 (m), 1255 (vs), 1235 (s), 835 (m), 820 (m), 760 (m). UV (acetonitrile): $\lambda_{\max}$ (lgε) = 375 nm (2.70), 355 (2.85), 328 (4.03), 305 (sh, 4.10), 292 (sh, 4.26), 277 (4.40), 237 (sh, 4.18), 213 (4.63). MS: *m*/*z* (%) = 338 (40) [M$^+$], 233 (100), 219 (24), 203 (44), 202 (23), 189 (21). $\mathrm{C_{25}H_{22}O}$ (338.47): calcd. C 88.71, H 6.56; found C 88.78, H 6.56.

c) 6-Hydroxy[2.2](1,4)phenanthrenoparacyclophane (29a): A solution of **28a** (309 mg, 0.91 mmol) in 10 mL of anhydrous dichloromethane was cooled to 0 °C under nitrogen, and boron tribromide (1.0 mL, 10.6 mmol) was added (color change to violet). The reaction mixture was kept in the refrigerator for 2 d and then hydrolysed. The organic phase was separated, washed with water and dried with sodium sulfate. The solvent was removed in vacuo and the raw product purified by thick-layer chromatography on silica gel with dichloromethane: 211 mg (71%) of **29a**, colorless needles (hexane), m.p. 143–145 °C. ^{1}H NMR (400 MHz): δ = 2.80 (m$_c$, 1 H), 2.92 (m$_c$, 1 H), 2.97–3.07 (m, 2 H), 3.23 (m$_c$, 1 H), 3.37 (m$_c$, 1 H), 3.85 (m$_c$, 1 H), 4.30 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.29 (br. d, J_o = 7.9 Hz, 1 H, 20-H), 5.41 (s, 1 H, OH), 5.88 (dd, J_o = 7.9, J_m = 1.5 Hz, 1 H, 19-H), 6.54 (m$_c$, 2 H, 16-,17-H), 6.77 (d, J_o = 7.4 Hz, 1 H, 12-H), 6.89 (d, J_o = 7.4 Hz, 1 H, 11-H), 6.93 (d, J_o = 7.4 Hz, 1 H, 7-H), 7.34 (m$_c$, 1 H, 8-H), 7.66 (d, J = 9.2 Hz, 1 H, 4-H), 8.09 (d, J_o = 8.6 Hz, 1 H, 9-H), 8.13 (d, J = 9.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz): δ = 33.47, 34.40, 34.78, 38.52 (t, C-1,-2,-13,-14), 109.69 (d, C-7), 118.94, 121.04, 123.31, 125.38, 128.46, 129.15, 131.57, 131.90, 132.11, 134.18 (d, C-4,-5,-8,-9,-11,-12,-16,-17,-19,-20), 122.17 (s, C-5a), 132.15, 132.65, 136.65, 136.77, 137.93, 138.81 and 1 hidden signal (s, C-3,-3a,-9a,-9b,-10,-15,-18), 151.56 (s, C-6) ppm. IR (KBr): $\tilde{\nu}$ = 3490 cm^{-1} (vs), 3420 (vs), 2920 (m), 1600 (vs), 1565 (m), 1520 (m), 1445 (vs), 1350 (m), 1265 (vs), 1230 (m), 1115 (s), 920 (m), 810 (vs), 760 (s), 715 (s). UV (acetonitrile): λ_{max} (lgε) = 378 nm (2.90), 362 (3.04), 328 (3.96), 308 (sh, 4.08), 285 (sh, 4.31), 278 (4.36), 251 (4.18), 211 (sh, 4.59), 207 (4.60). MS: m/z (%) = 324 (25) [M$^+$], 219 (100), 205 (21), 189 (15). C$_{24}$H$_{20}$O (324.44): calcd. C 88.84, H 6.23; found C 88.84, H 6.17.

8-Hydroxy[2.2](1,4)phenanthrenoparacyclophane (29b). a) *trans*-4-(4-Methoxystyryl)[2.2]paracyclophane (27b): By methods described in the literature 4-methoxybenzaldehyde (**23b**) was reduced to benzyl alcohol **24b**,[28] and this was converted via the bromide **25b**[29] to the phosphonate **26b**.[30] A solution of **26b** (2.32 g, 9.00 mmol) in anhydrous THF (100 mL) was cooled to 0 °C under nitrogen. After the addition of *n*-butyllithium (10 mmol, THF; color change to yellow) solid 4-formyl[2.2]paracyclophane (**20**) (1.90 g, 8.04 mmol) was added in portions. Work-up as above for **27a** provided 1.7 g (62%) of **27b**, colorless needles (ethanol), m.p. 160–161 °C. ^{1}H NMR (400 MHz): δ = 2.74–3.20 (m, 7 H), 3.56 (m$_c$, 1 H, 1-,2-,9-,10-H), 3.82 (s, 3 H, OCH$_3$), 6.61 (s, 1 H, 5-H), 6.39–6.56 (m, 5 H), 6.70 (dd, J_o = 7.8, J_m = 1.6 Hz, 1 H, 7-,8-,12-,13-,15-,16-H), 6.93 (m$_c$, 2 H, 21-,22-H), 6.82 (d, J = 16.1 Hz, 1 H), 7.04 (d, J = 16.1 Hz, 1 H, 17-,18-H), 7.50 (m$_c$, 2 H, 20-,24-H) ppm. ^{13}C NMR (100 MHz): δ = 33.99, 34.83, 35.24, 35.47 (t, C-1,-2,-9,-10), 55.35 (q, OCH$_3$), 114.19 (d, 2 C, C-21,-23), 124.92, 127.66 (2 C), 128.67, 129.72, 129.99, 131.38, 131.70, 132.98 (2 C), 134.89 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18,-20,-24), 130.75, 137.68, 138.05, 139.29 (2 C), 139.83 (s, C-3,-4,-6,-11,-14,-19), 159.22 (s, C-22) ppm. IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2920 (m), 1605 (m), 1580 (m), 1510 (vs), 1450 (m), 1290 (m), 1255 (s), 1170 (s), 850 (m). UV (acetonitrile): λ_{max} (lgε) = 324 nm (4.24), 308 (sh, 4.19), 259 (4.06), 211 (4.45), 199 (4.51). MS: m/z (%) = 340 (40) [M$^+$], 235 (100), 221 (27), 205 (16), 178 (12), 125 (12), 97 (21). C$_{25}$H$_{24}$O (340.49): calcd. C 88.18, H 7.12; found C 88.18, H 7.16.

b) 8-Methoxy[2.2](1,4)phenanthrenoparacyclophane (28b): The photocyclization of **27b** was carried out as described above for the **21** → **22** interconversion using **27b** (408 mg, 1.20 mmol), iodine (108 mg) and biacetyl (0.4 mL) in toluene (250 mL). After 30 min irradiation and work-up (see above) 111 mg (27%) of **28b** was isolated; colorless leaflets (ethanol), m.p. 197–198 °C. ^{1}H NMR (400 MHz): δ = 2.79, (m$_c$, 1 H), 2.91–3.05 (m, 3 H), 3.17 (m$_c$, 1 H), 3.37 (m$_c$, 1 H), 3.82 (m$_c$, 1 H), 4.33 (m$_c$, 1 H, 1-,2-,13-,14-H), 3.96 (s, 3 H, OCH$_3$), 5.25 (d, J_o = 7.9 Hz, 1 H, 20-H), 5.87 (d, J_o = 7.9 Hz, 1 H, 19-H), 6.52 (m$_c$, 2 H, 16-,17-H), 6.74 (d, J_o = 7.4 Hz, 1 H, 12-H), 6.91 (d, J_o = 7.4 Hz, 1 H, 11-H), 7.19 (dd, J_o = 8.6, J_m = 2.5 Hz, 1 H, 7-H), 7.51 (d, J = 8.9 Hz, 1 H, 4-H), 7.65 (d, J = 8.9 Hz, 1 H, 5-H), 7.79 (d, J_o = 8.6 Hz, 1 H, 6-H), 7.91 (d, J_m = 2.5 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz): δ = 33.50, 34.33, 34.68, 38.15 (t, C-1,-2,-13,-14), 55.47 (q, OCH$_3$), 109.12, 116.07 (d, C-7,-9), 121.77, 125.65, 128.29, 128.83, 129.53, 131.64, 131.77, 131.94, 133.95 (d, C-4,-5,-6,-11,-12,-16,-17,-19,-20), 127.03, 131.91, 132.35, 134.37, 136.14, 136.85, 137.89, 138.57 (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18), 157.31 (s, C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2940 (m), 2920 (m), 1610 (vs), 1515 (m), 1460 (s), 1435 (s), 1220 (vs), 1040 (s), 860 (m), 840 (vs), 795 (m), 720 (s). UV (acetonitrile): λ_{max} (lgε) = 381 nm (3.11), 362 (3.04), 318 (sh, 3.90), 283 (4.50), 242 (sh, 4.22), 219 (sh, 4.49), 206 (4.64). MS: m/z (%) = 338 (37) [M$^+$], 233 (100), 219 (17), 203 (62), 202 (34), 189 (20). C$_{25}$H$_{24}$O (338.47): calcd. C 88.71, H 6.56; found C 88.79, H 6.60.

c) 8-Hydroxy[2.2](1,4)phenanthrenoparacyclophane (29b): The ether cleavage was performed as described above for **29a**; from **28b** (92 mg, 0.21 mmol) and boron tribromide (500 mg, 2.00 mmol) after work-up and purification (see above) 64 mg (93%) of **29b** were obtained, colorless needles (hexane), m.p. 146–148 °C. ^{1}H NMR (400 MHz): δ = 2.78 (m$_c$, 1 H), 2.86–3.04 (m, 3 H), 3.17 (m$_c$, 1 H), 3.31 (m$_c$, 1 H), 3.80 (m$_c$, 1 H), 4.25 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.18 (s, 1 H, OH), 5.27 (dd, J_o = 7.9, J_m = 1.3 Hz, 1 H, 20-H), 5.87 (dd, J_o = 7.8, J_m = 1.3 Hz, 1 H, 19-H), 6.52 (m$_c$, 2 H, 16-,17-H), 6.73 (d, J_o = 7.4 Hz, 1 H, 12-H), 6.87 (d, J_o = 7.4 Hz, 1 H, 11-H), 7.07 (dd, J_o = 8.5, J_m = 2.5 Hz, 1 H, 7-H), 7.49 (d, J = 8.9 Hz, 1 H, 4-H), 7.63 (d, J = 8.9 Hz, 1 H, 5-H), 7.75 (d, J_o = 8.5 Hz, 1 H, 6-H), 7.87 (d, J_m = 2.5 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz): δ = 33.50, 34.33, 34.69, 38.22 (t, C-1,-2,-13,-14), 111.87, 115.92 (d, C-7,-9), 121.76, 125.69, 128.38, 128.90, 129.90, 131.62, 131.87, 132.07, 133.88 (d, C-4,-5,-6,-11,-12,-16,-17,-19,-20), 127.10, 132.12, 134.37, 136.39, 136.74, 137.92, 138.67, 1 C unresolved (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18), 153.10 (s, C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3480 cm^{-1} (vs), 2920 (m), 1610 (vs), 1520 (m), 1450 (m), 1350 (m), 1200 (vs), 1175 (vs), 940 (m), 835 (vs), 800 (m), 715 (vs). UV (acetonitrile): λ_{max} (lgε) = 382 nm (3.18), 363 (3.08), 317 (sh, 3.91), 282 (4.49), 241 (sh, 4.21), 218 (sh, 4.51), 205 (4.65). MS: m/z (%) = 324 (22) [M$^+$], 219 (100), 205 (24), 202 (15), 189 (14), 104 (6). C$_{24}$H$_{20}$O (324.44): calcd. C 88.84, H 6.23; found C 88.95, H 6.27.

6,9-Dimethoxy[2.2](1,4)phenanthrenoparacyclophane (28c). a) *trans*-4-(2,5-Dimethoxystyryl)[2.2]paracyclophane (27c): By methods described in the literature 2,5-(dimethoxy)benzaldehyde (**23c**) was reduced to benzyl alcohol **24c**,[31] and this was converted via the bromide **25c**[32] to the phosphonate **26c**.[33] According to the procedure described above for **27a** and **27b** **26c** (2.10 g, 5.82 mmol) was coupled with **20** (1.54 g, 6.52 mmol) to provide after work-up and purification (see above) 1.54 g (71%) of **27c**, colorless prisms (ethanol), m.p. 161–162 °C. ^{1}H NMR (400 MHz): δ = 2.77–3.18 (m, 7 H), 3.57 (m$_c$, 1 H, 1-,2-,9-,10-H), 3.84 (s, 3 H, OCH$_3$), 3.87 (s, 3 H, OCH$_3$), 6.68 (d, J_m = 1.4 Hz, 1 H, 5-H), 6.42–6.50 (m, 4 H), 6.53 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H), 6.74 (dd, J_o = 7.8, J_m = 1.7 Hz, 1 H, 7-,8-,12-,13-,15-,16-H), 6.80 (dd, J_o = 8.9, J_m = 2.9 Hz, 1 H, 22-H), 6.86 (d, J_o = 8.9 Hz, 1 H, 21-H), 7.15 (d, J = 16.4 Hz, 1 H), 7.21 (d, J = 16.4 Hz, 1 H, 17-,18-H), 7.20 (d, J_m = 2.9 Hz, 1 H, 24-H) ppm. ^{13}C NMR (100 MHz): δ = 34.07, 34.92, 35.31, 35.57 (t, C-1,-2,-9,-10), 55.92 (q, OCH$_3$), 56.59 (q, OCH$_3$), 112.55, 112.76, 113.21 (d, C-21,-22,-24), 124.29, 128.10, 129.84, 130.53, 131.71, 131.84, 132.97, 133.06, 134.88 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18), 138.07, 138.33, 139.31, 139.33, 139.87, 1 quat. C not observed (s, C-3,-4,-6,-11,-12,-19), 151.84, 154.08 (s, C-20,-23) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2940 (m), 2920 (m), 1600 (w), 1500 (vs), 1465 (m), 1280 (m), 1240 (m), 1220 (vs), 1050 (s), 1025 (m), 970 (s). UV (acetonitrile): λ_{max} (lgε) = 346 nm (4.21), 306 (sh, 4.08), 248 (sh, 4.10), 215 (4.51), 201 (sh, 4.43). MS: m/z (%) = 370 (43) [M$^+$], 265 (100), 251 (19), 235 (26), 104 (5). C$_{26}$H$_{26}$O$_2$ (370.52): calcd. C 84.28, H 7.09; found C 84.18, H 7.15.

b) 6,9-Dimethoxy[2.2](1,4)phenanthrenoparacyclophane (28c): By the procedure described above for **28a** and **28b**, **27c** (542 mg, 1.46 mmol) was photocyclized in the presence of iodine (116 mg) and biacetyl (0.4 mL) in toluene (250 mL). After 1 h irradiation and work-up and purification (see above) 170 mg (32%) of **28c** were obtained, colorless needles (ethanol), m.p. 184–185 °C. ^{1}H NMR (400 MHz): δ = 2.61 (m$_c$, 1 H), 2.86–3.04 (m, 3 H), 3.16–3.29 (m, 2 H), 3.50 (m$_c$, 1 H), 3.81 (m$_c$, 1 H), 3.82 (s, 3 H, OCH$_3$), 4.02 (s, 3 H, OCH$_3$), 5.34 (m$_c$, 1 H, 20-H), 5.82 (dd, J_o = 7.9, J_m = 1.5 Hz, 1 H, 19-H), 6.58 (dd, J_o = 8.0, J_m = 1.5 Hz, 1 H, 16-H), 6.66 (dd, J_o = 8.0, J_m = 1.5 Hz, 1 H, 17-H), 6.70 (d, J_o = 7.5 Hz, 1 H, 12-H), 6.80 (d, J_o = 7.5 Hz, 1 H, 11-H), 6.89 (m$_c$, 2 H, 7-,8-H), 7.64 (d, J = 9.2 Hz, 1 H, 4-H), 8.15 (d, J = 9.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz): δ = 34.14, 34.82, 35.57, 37.03 (t, C-1,-2,-13,-14), 56.05 (q, OCH_3), 56.22 (q, OCH_3), 105.84, 107.27 (d, C-7,-8), 118.89, 123.78, 128.11, 129.72, 130.51, 131.17, 132.57, 133.16 (d, C-4,-5,-11,-12,-16,-17,-19,-20), 122.81, 124.88 (s, C-5a, -9a), 128.31, 134.01, 134.42, 138.34, 139.81, 140.59 (s, C-3,-3a,-9b, -10,-15,-18), 149.91, 150.58 (s, C-6,-9) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2940 (m), 2920 (m), 1600 (m), 1500 (m), 1450 (s), 1425 (s), 1260 (vs), 1125 (m), 1100 (vs), 815 (m), 805 (s), 720 (m). UV (acetonitrile): λ_{max} (lgε) = 388 nm (3.36), 370 (3.34), 340 (4.02), 315 (4.22), 297 (sh, 4.11), 274 (4.31), 243 (4.27), 209 (4.61). MS: *m/z* (%) = 368 (76) [M$^+$], 264 (66), 249 (100), 233 (71), 218 (15), 189 (13). $C_{26}H_{24}O_2$ (368.50): calcd. C 84.74, H 6.58; found C 84.67, H 6.60.

Oxidation of 6-Hydroxy[2.2](1,4)phenanthrenoparacyclophane (29a): Compound **29a** (300 mg, 0.93 mmol) in THF (15 mL) was added to a solution of benzeneseleninic anhydride (504 mg, 1.4 mmol) in anhydrous THF (15 mL) at 50 °C under nitrogen (color change to red). After stirring for 15 min at this temperature, the reaction mixture was cooled to room temp., the THF was removed in vacuo, and the residue was dissolved in dichloromethane. The solution was washed with satd. hydrogencarbonate solution, dried (magnesium sulfate), the solvent was removed by rotary evaporation and thick-layer chromatography (silica gel, dichloromethane) to provide two fractions.

Fraction 1. [2.2](1,4)Phenanthrenoparacyclophane-6,9-quinone (30): 28 mg (9%), red prisms (ethanol), m.p. 215–217 °C. ^{1}H NMR (400 MHz): δ = 2.78–2.82 (m, 2 H), 2.92 (m$_c$, 1 H), 3.00–3.13 (m, 2 H), 3.23 (m$_c$, 1 H), 3.38 (m$_c$, 1 H), 3.80 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.52 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 20-H), 5.62 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 19-H), 6.58 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 16-H), 6.64 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 17-H), 6.83 (d, J_o = 7.3 Hz, 1 H, 12-H), 6.95 (d, J_o = 7.3 Hz, 1 H, 11-H), 6.96 (d, J = 10.3 Hz, 1 H), 7.04 (d, J = 10.3 Hz, 1 H, 7-,8-H), 8.04 (d, J = 8.6 Hz, 1 H), 8.12 (d, J = 8.6 Hz, 1 H, 4-,5-H) ppm. ^{13}C NMR (100 MHz): δ = 33.31, 34.49, 35.09, 37.66 (t, C-1,-2,-13,-14), 121.05, 128.18, 130.42, 130.49, 131.15, 132.37, 134.77, 135.21, 136.22, 139.76 (d, C-4, -5,-7,-8,-11,-12,-16,-17,-19,-20), 130.38, 131.30, 131.48, 135.56, 138.06, 139.09, 139.15, 139.68 (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18), 185.78, 186.42 (s, C-6,-9) ppm. IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (w), 2940 (m), 2920 (m), 1660 (vs), 1650 (vs), 1610 (s), 1585 (m), 1435 (s), 1310 (vs), 1085 (s), 1060 (s), 1020 (m), 820 (s), 800 (s), 740 (m). UV (acetonitrile): λ_{max} (lgε) = 409 nm (3.48), 329 (3.95), 288 (3.79), 247 (4.39), 208 (4.52). MS: *m/z* (%) = 338 (19) [M$^+$], 234 (100), 176 (6), 151 (5), 104 (8). $C_{24}H_{18}O_2$ (338.42): calcd. C 85.17, H 5.37; found C 85.09, H 5.30.

Fraction 2. [2.2](1,4)Phenanthrenoparacyclophane-6,7-quinone (31): 165 mg (53%), black prisms (ethanol), 250 °C (decomp.). ^{1}H NMR (400 MHz): δ = 3.08–3.21 (m, 4 H), 3.22 (m$_c$, 1 H), 3.45–3.60 (m, 2 H), 3.75 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.69 (dd, J_o = 7.9, J_m = 1.6 Hz, 1 H, 20-H), 5.73 (dd, J_o = 7.9, J_m = 1.6 Hz, 1 H, 19-H), 6.43 (d, J = 10.5 Hz, 1 H, 8-H), 6.61 (dd, J_o = 7.9, J_m = 1.6 Hz, 1 H, 16-H), 6.65 (dd, J_o = 7.9, J_m = 1.6 Hz, 1 H, 17-H), 6.81 (d, J_o = 7.3 Hz, 1 H, 12-H), 6.89 (d, J_o = 7.3 Hz, 1 H, 11-H), 7.79 (d, J = 8.5 Hz, 1 H, 4-H), 8.00 (d, J = 10.5 Hz, 1 H, 9-H), 8.10 (d, J = 8.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz): δ = 33.22, 34.27, 35.41, 39.08 (t, C-1,-2,-13,-14), 124.07, 125.81, 127.03, 128.75, 130.90, 131.08, 132.42, 134.90, 135.71, 144.53 (d, C-4,-5,-8,-9,-11,-12,-16,-17,-19, -20), 129.55, 131.85, 133.96, 136.79, 137.44, 138.24, 138.50, 140.13 (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18), 179.79, 181.78 (s, C-6,-7) ppm. IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (w), 1690 (s), 1665 (vs), 1580 (m), 1500 (m), 1410 (s), 1340 (m), 1285 (s), 1045 (m), 800 (m), 745 (m). UV (dichloromethane): λ_{max} (lgε) = 522 nm (sh, 3.18), 423 (3.70), 330 (4.15), 291 (4.18), 254 (4.35), 229 (4.25). MS: *m/z* (%) = 338 (16) [M$^+$], 310 (8), 206 (8), 178 (11), 152 (8), 104 (100), 77 (8). $C_{26}H_{24}O_2$ (338.42): calcd. C 85.17, H 5.37; found C 85.12, H 5.36.

Oxidation of 8-Hydroxy[2.2](1,4)phenanthrenoparacyclophane (29b): Under the conditions described for isomer **29a**, **29b** (120 mg, 0.37 mmol) in anhydrous THF (20 mL) was oxidized with benzeneseleninic anhydride (200 mg, 0.56 mmol) in THF (40 mL). Work-up and purification as above furnished 100 mg (80%) of **32**, black needles (ethanol), m.p. 189–190 °C. ^{1}H NMR (400 MHz): δ = 2.72–2.92 (m, 3 H), 2.98–3.11 (m, 2 H), 3.18–3.33 (m, 2 H), 3.73 (m$_c$, 1 H, 1-,2-,13-,14-H), 5.65 (m$_c$, 2 H, 19-,20-H), 6.45 (d, J = 9.9 Hz, 1 H, 7-H), 6.59 (dd, J_o = 7.9, J_m = 1.5 Hz, 1 H, 16-H), 6.64 (dd, J_o = 7.9, J_m = 1.5 Hz, 1 H, 17-H), 6.74 (d, J_o = 7.3 Hz, 1 H, 12-H), 6.89 (d, J_o = 7.3 Hz, 1 H, 11-H), 7.35 (d, J = 8.3 Hz, 1 H, 4-H), 7.53 (d, J = 9.9 Hz, 1 H, 6-H), 7.96 (d, J = 8.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz): δ = 33.13, 34.44, 34.80, 36.97 (t, C-1,-2,-13, -14), 125.68, 127.52, 128.10, 130.49, 131.25, 132.39, 132.47, 133.84, 136.20, 147.21 (d, C-4,-5,-6,-7,-11,-12,-16,-17,-19,-20), 133.63, 134.95, 135.78, 137.49, 137.77, 138.67, 139.32, one signal not resolved (s, C-3,-3a,-5a,-9a,-9b,-10,-15,-18), 182.59, 184.25 (s, C-8, -9) ppm. IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (m), 2920 (m), 1680 (vs), 1660 (vs), 1570 (m), 1500 (m), 1320 (m), 1240 (s), 1180 (m), 880 (m), 845 (s), 835 (s), 745 (m). UV (acetonitrile): λ_{max} (lgε) = 447 nm (3.72), 332 (4.01), 291 (3.86), 252 (4.26), 212 (4.55). MS: *m/z* (%) = 338 (39) [M$^+$], 234 (100), 206 (95), 176 (26), 152 (13), 104 (18). $C_{24}H_{18}O_2$ (338.42): calcd. C 85.17, H 5.37; found C 85.32, H 5.34.

Oxidative Demethylation of 6,9-Dimethoxy[2.2](1,4)phenanthrenoparacyclophane (28c): A solution of cerium(IV) ammonium nitrate (685 mg, 1.25 mol) in acetonitrile (1.5 mL) and water (1.5 mL) was added to a suspension of **28c** (184 mg, 0.50 mmol) and pyridine-2,6-dicarboxylic acid-*N*-oxide[21] (230 mg, 1.25 mmol) in acetonitrile (20 mL) and water (1 mL) at 0 °C . The reaction mixture was stirred for 5 h at 0 °C and overnight at room temp., water (50 mL) was added and the hydrolysis mixture extracted with dichloromethane. The organic phase was separated, dried (magnesium sulfate), and the solvent was removed in vacuo. Separation by thick layer chromatography on silica gel with dichloromethane provided two fractions, one of which was the *para*-quinone **30** (20 mg, 12%). **6,9-Dimethoxy-8-nitro[2.2](1,4)phenanthrenoparacyclophane (34):** 48 mg (23%), yellow prisms (ethanol), m.p. 246–248 °C. ^{1}H NMR (400 MHz): δ = 2.64 (m$_c$, 1 H), 2.89–3.07 (m, 3 H), 3.24–3.40 (m, 2 H), 3.56 (m$_c$, 1 H), 3.87 (m$_c$, 1 H, 1-,2-,13,-14-H), 3.34 (s, 3 H, OCH_3), 4.10 (s, 3 H, OCH_3), 5.29 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 20-H), 5.76 (dd, J_o = 7.9, J_m = 1.8 Hz, 1 H, 19-H), 6.00 (dd, J_o = 7.8, J_m = 1.8 Hz, 1 H, 16-H), 6.68 (dd, J_o = 7.8, J_m = 1.8 Hz, 1 H, 17-H), 6.83 (d, J_o = 7.4 Hz, 1 H, 12-H), 6.90 (d, J_o = 7.4 Hz, 1 H, 11-H), 7.35 (s, 1 H, 7-H), 7.81 (d, J = 9.2 Hz, 1 H, 4-H), 8.18 (d, J = 9.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz): δ = 33.95, 34.76, 35.45, 37.18 (t, C-1,-2,-13,-14), 56.31 (q, OCH_3), 62.21 (q, OCH_3), 100.76 (d, C-7), 118.52, 126.75, 128.19, 129.90, 130.48, 132.65, 132.71, 132.42 (d, C-4,-5,-11,-12,-16,-17,-19,-20), 125.45, 127.44, 128.30, 134.38, 135.33, 138.16, 139.87, 140.32, 141.22, 145.63, 151.42 (s, C-3,-3a,-5a,-6,-8,-9,-9a,-9b,-10,-15,-18) ppm. IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (m), 2910 (m), 1570 (m), 1505 (vs), 1450 (m), 1400 (m), 1350 (s), 1335 (s), 1200 (m), 1060 (s), 975 (m), 820 (m). UV (acetonitrile): λ_{max} (lgε) = 392 nm (3.86), 332 (3.78), 273 (4.34), 133 (sh, 4.26), 206 (4.65). MS: *m/z* (%) = 413 (100) [M$^+$], 367 (17), 294 (99), 278 (93), 263 (15), 248 (22), 233 (24), 231 (24), 217 (16). $C_{26}H_{23}NO_4$ (413.50): calcd. C 75.52, H 5.62, N 3.39; found C 75.53, H 5.60, N 3.32.

Condensation of [2.2](1,4)Phenanthrenoparacyclophane-6,7-quinone (31) with *o*-Phenylenediamine (35): A solution of **31** (165 mg, 0.49 mmol) and **35** (55 mg, 0.51 mmol) in ethanol (70 mL) was treated with a drop of hydrochloric acid (37%), and the mixture was heated under reflux for 2 h. After cooling to room temp. the solvent was removed in vacuo and the remainder purified by thick-layer chromatography on silica gel with dichloromethane: 120 mg (60%) of the quinoxalinophane **36**; yellow needles (ethanol), m.p. 246–247 °C. ^{1}H NMR (400 MHz): δ = 2.78 (m$_c$, 1 H), 2.94 (m$_c$, 1 H), 3.00–3.12 (m, 2 H), 3.24 (m$_c$, 1 H), 3.50 (m$_c$, 1 H), 3.94 (m$_c$, 1 H), 4.22 (m$_c$, 1 H, 1-,2-,17-,18-H), 5.24 (d, J_o = 7.8 Hz, 1 H, 24-H), 5.79 (d, J_o = 7.8 Hz, 1 H, 23-H), 6.53 (d, J_o = 7.9 Hz, 1 H, 20-H), 6.58 (d, J_o = 7.9 Hz, 1 H, 21-H), 6.84 (d, J_o = 7.3 Hz, 1 H, 16-H), 7.01 (d, J_o = 7.3 Hz, 1 H, 15-H), 7.87 (m$_c$, 2 H, 8-,9-H), 8.01 (d, J_o = 9.0 Hz, 1 H, 13-H), 8.09 (d, J = 9.6 Hz, 1 H, 4-H), 8.31 (m, 1 H) 8.42 (m, 1 H, 7-,10-H), 8.74 (d, J = 9.6 Hz, 1 H, 5-H), 9.43 (d, J_o = 9.0 Hz, 1 H, 12-H) ppm. ^{13}C NMR (100 MHz): δ = 33.44, 34.43, 35.07, 38.78 (t, C-1,-2,-17,-18), 121.71, 125.36, 125.63, 128.20, 129.20, 129.70, 129.80, 129.86, 130.06, 131.40, 131.97, 132.72, 132.74, 134.66 (d, C-4,-5,-7,-8,-9,-10,-12,-13,-15,-16,-20,-21,-23,-24), 129.44, 130.14, 132.90, 136.17, 136.37, 137.18, 137.96, 138.55 (s, C-3,-3a,-5a,-13a,-13b,-14,-19,-22), 142.32, 142.37, 142.81, 142.93 (s, C-5b,-6a,-10a,-11a) ppm. IR (KBr): $\tilde{\nu}$ = 300 cm^{-1} (w), 2920 (m), 2850 (m), 1500 (m), 1470 (m), 1430 (m), 1360 (s), 1120 (m), 935 (m), 890 (m), 840 (s), 800 (s), 760 (s), 740 (s). UV (acetonitrile): $\lambda_{\max}$ ($\lg\varepsilon$) = 411 nm (12900), 344 (25700), 308 (sh, 23300), 299 (25000), 280 (56600), 243 (25400), 226 (30200), 201 (47600). MS: m/z (%) = 388 (34) [M$^+$], 306 (100), 291 (18), 152 (8), 104 (8). $C_{30}H_{22}N_2$ (410.54): calcd. C 87.76, H 5.41, N 6.83; found C 87.60, H 5.24, N 6.69.

Benzo[*b*]thiopheno[3,2-*f*]-[2.2](1,4)naphthalenoparacyclophane (44). a) *trans*-4-(2-Benzo[*b*]thiophenylethenyl)[2.2]paracyclophane (41): From benzo[*b*]thiophene (**38**) the 2-formyl derivative **39a** was prepared according to a published procedure.[34] This was converted into the phosphonate **40a**, a known compound,[35] via the corresponding alcohol[36] and bromide.[37] As described above for **27**, the paracyclophane derivative **41** was prepared from **40a** (0.94 g, 3.33 mmol) and 4-formyl[2.2]paracyclophane (**20**) (0.79 g, 3.33 mmol). After work-up and chromatographic separation (see above) 730 mg (60%) of **41** were obtained, colorless needles (ethanol), m.p. 175–176 °C. ^{1}H NMR (400 MHz): δ = 2.85 (m$_c$, 1 H), 2.93–3.20 (m, 6 H), 3.58 (m$_c$, 1 H, 1-,2-,9-,10-H), 6.64 (d, J_m = 1.5 Hz, 1 H, 5-H), 6.41–6.54 (m, 5 H), 6.70 (dd, J_o = 7.8, J_m = 1.8 Hz, 1 H, 7-,8-,12-,13-,15-,16-H), 7.06, 7.09 (2 d, J = 15.9 Hz, 2 H, 17-,18-H), 7.27 (s, 1 H, 20-H), 7.28–7.35 (m, 2 H, 22-,23-H), 7.71 (m$_c$, 1 H), 7.79 (m$_c$, 1 H, 21-,24-H) ppm. ^{13}C NMR (100 MHz): δ = 34.04, 34.98, 35.28, 35.51 (t, C-1,-2,-9,-10), 122.23, 122.64, 122.93, 123.39, 124.58, 124.74, 129.25, 130.00, 130.24, 131.74, 132.26, 133.07 (2 C), 135.10 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18,-20,-21,-22,-23,-24), 136.75, 138.67, 138.85, 139.27, 139.32, 140.05, 140.41, 143.66 (s, C-3,-4,-6,-11,-14,-19,-20a,-24a) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2920 (m), 1580 (m), 1500 (m), 1455 (m), 1200 (w), 950 (vs), 985 (m), 880 (m), 810 (s), 800 (s), 740 (vs), 720 (vs). UV (acetonitrile): $\lambda_{\max}$ ($\lg\varepsilon$) = 367 nm (sh, 4.20), 348 (4.37), 338 (4.37), 225 (4.47), 203 (4.49). MS: m/z (%) = 366 (74) [M$^+$], 261 (100), 247 (16), 229 (11), 128 (10). $C_{26}H_{22}S$ (366.54): calcd. C 85.19, H 6.06, S 8.75; found C 84.87, H 5.96, S 8.74.

b) Benzo[*b*]thiopheno[3,2-*f*][2.2](1,4)naphthalenoparacyclophane (44): As described for the photocyclization of **27** above, **41** (418 mg, 1.14 mmol) was irradiated (room temp., 60 min) in the presence of iodine (110 mg) and biacetyl (0.4 mL) in anhydrous toluene (250 mL). After work-up and preparative thick-layer chromatography (silica gel, cyclohexane) 176 mg (42%) of **44** were isolated, colorless needles (chloroform), m.p. 206–208 °C. ^{1}H NMR (400 MHz, iterative analysis): δ = 2.67 (m, 1 H, 15-H), 2.79 (m, 1 H, 15-H′), 3.01 (m, 1 H, 1-H′), 3.03 (m, 1 H, 2-H), 3.25 (m, 1 H, 1-H), 3.53 (m, 1 H, 14-H′), 3.57 (m, 1 H, 14-H), 3.84 (m, 1 H, 2-H′), [$J_{1,1'}$ = –13.0, $J_{1,2}$ = 10.2, $J_{1,2'}$ = 1.2, $J_{1',2}$ = 8.0, $J_{1',2'}$ = 9.6, $J_{2,2'}$ = –13.6, $J_{14,14'}$ = –14.2, $J_{14,15}$ = 9.5, $J_{14,15'}$ = 2.5, $J_{14',15}$ = 7.5, $J_{14',15'}$ = 9.4, $J_{15,15'}$ = –13.4 Hz] 5.31 (ddd, J_o = 7.8, J_m = 2.0, $J_{15',21}$ = 0.8 Hz, 1 H, 21-H), 5.73 (dd, J_o = 7.8, J_m = 2.0 Hz, 1 H, 20-H), 6.55 (dd, J_o = 7.9, J_m = 2.0 Hz, 1 H, 17-H), 6.68 (dd, J_o = 7.9, J_m = 2.0 Hz, 1 H, 18-H), 6.76 (d, J_o = 7.3 Hz, 1 H, 13-H), 6.95 (dd, J_o = 7.3, $J_{2',12'}$ = 0.8 Hz, 1 H, 12-H), 7.44 (m, 1 H, 8-H), 7.47 (m, 1 H, 9-H), 7.74 (d, J = 8.8 Hz, 1 H, 4-H), 7.87 (d, J = 8.8 Hz, 1 H, 5-H), 7.95 (m, 1 H, 7-H), 8.15 ppm (m, 1 H, 10-H), [$J_{7,8}$ = 8.0, $J_{7,9}$ = 1.2, $J_{7,10}$ = 0.7, $J_{8,9}$ = 7.1, $J_{8,10}$ = 1.2, $J_{9,10}$ = 8.2 Hz]; important NOE at 14-H′ (13%) when saturating 10-H. ^{13}C NMR (100 MHz): δ = 34.34 (t, C-2), 34.82 (t, C-1), 35.60 (t, C-15), 36.92 (t, C-14), 119.78 (d, C-5), 122.65 (d, C-7), 123.61 (d, C-9), 124.27 (d, C-4), 125.18 (d, C-8), 125.86 (d, C-10), 127.58 (d, C-21), 129.99 (d, C-20), 130.36 (s, C-10b), 130.41 (s, C-10c), 130.77 (d, C-18), 132.11 (d, C-13), 132.44 (d, C-17), 133.60 (d, C-12), 133.86 (s, C-3a), 134.67 (s, C-11), 136.38 (s, C-10a), 136.63 (s, C-3), 138.21 (s, C-5a), 138.38 (s, C-19), 138.91 (s, C-16), 139.23 (s, C-6a) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2940 (m), 2900 (m), 2850 (m), 1585 (m), 1500 (m), 1440 (s), 1390 (m), 1205 (m), 1030 (m), 935 (s), 845 (m), 800 (vs), 750 (vs), 730 (vs), 715 (s). UV (acetonitrile): $\lambda_{\max}$ ($\lg\varepsilon$) = 375 nm (3.28), 340 (4.05), 330 (4.01), 310 (4.05), 282 (4.48), 242 (sh, 4.26), 230 (sh, 4.31), 204 (4.71). MS: m/z (%) = 364 (28) [M$^+$], 259 (100), 245 (39), 104 (4). $C_{26}H_{20}S$ (364.52): calcd. C 85.66, H 5.54, S 8.80; found C 85.81, H 5.68, S 9.40.

Benzo[*b*]thiopheno[2,3-*f*][2.2](1,4)naphthalenoparacyclophane (43). a) *trans*-4-(3-Benzo[*b*]thiophenylethenyl)[2.2]paracyclophane (42): The 3-formyl derivative **39b** was prepared from benzo[*b*]thiophene (**38**) according to a published procedure.[38] This was converted into the phosphonate **40a**, a known compound,[39] via the corresponding alcohol[36] and bromide.[23] As described above for **27**, the paracyclophane derivative **42** was prepared from **40b** (0.77 g, 2.70 mmol) and 4-formyl[2.2]paracyclophane (**20**) (0.64 g, 2.70 mmol). After work-up and chromatographic separation (see above) 532 mg (54%) of **42** were obtained, colorless needles (ethanol), m.p. 121–123 °C. ^{1}H NMR (400 MHz): δ = 2.85 (m$_c$, 1 H), 2.93–3.18 (m, 6 H), 3.57 (m$_c$, 1 H, 1-,2-,9-,10-H), 6.70 (s, 1 H, 5-H), 6.45–6.65 (m, 5 H), 6.76 (dd, J_o = 7.8, J_m = 1.6 Hz, 1 H, 7-,8-,12-,13-,15-,16-H), 7.14 (d, J = 16.1 Hz, 1 H), 7.24 (d, J = 16.1 Hz, 1 H, 17-,18-H), 7.41 (m$_c$, 1 H), 7.47 (m$_c$, 1 H, 23-,24-H), 7.57 (s, 1 H, 20-H), 7.90 (d, J_o = 8.0 Hz, 1 H), 8.06 (d, J_o = 8.0 Hz, 1 H, 22-,25-H) ppm. ^{13}C NMR (100 MHz): δ = 33.97, 34.85, 35.22, 35.45 (t, C-1,-2,-9,-10), 121.30, 121.54, 121.94, 123.03, 124.39, 124.60, 128.60, 129.66, 130.09, 131.67, 131.89, 133.05, 133.08, 134.96 (d, C-5,-7,-8,-12,-13,-15,-16,-17,-18,-20,-22,-23,-24,-25), 134.75, 137.45, 137.88, 138.30, 139.23, 139.35, 139.99, 140.56 (s, C-3,-4,-6,-11,-14,-19,-21a,-25a) ppm. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2950 (m), 2860 (m), 1500 (m), 1430 (m), 1025 (w), 965 (vs), 940 (m), 760 (vs), 740 (vs), 725 (s). UV (acetonitrile): $\lambda_{\max}$ ($\lg\varepsilon$) = 301 nm (3.88), 268 (3.98), 219 (4.60), 200 (4.60). MS: m/z (%) = 366 (48) [M$^+$], 261 (100), 247 (17), 229 (12), 97 (11). $C_{26}H_{22}S$ (366.54): calcd. C 85.19, H 6.06, S 8.75; found C 85.08, H 6.09, S 8.74.

b) Benzo[*b*]thiopheno[2,3-*f*][2.2](1,4)naphthalenoparacyclophane (43): As described for **44** above, **42** (0.53 g, 1.44 mmol) was photocyclized (30 min, room temp.) in the presence of iodine (0.15 g) and biacetyl (0.4 mL) in toluene (250 mL). After work-up (see above) 0.29 g (56%) of **43** were isolated as colorless needles (chloroform), m.p. 198–199 °C. ^{1}H NMR (300 MHz, iterative analysis): δ = 2.96 (m, 1 H, 1-H′), 3.05 (m, 1 H, 15-H′), 3.13 (m, 1 H, 2-H), 3.16 (m, 1 H, 1-H), 3.19 (m, 1 H, 14-H), 3.20 (m, 1 H, 15-H), 3.88 (m, 1 H, 2-H′), 4.44 (m, 1 H, 14-H′), [$J_{1,1'}$ = –13.3, $J_{1,2}$ = 10.7, $J_{1,2'}$ = 1.7,

$J_{1',2}$ = 6.4, $J_{1',2'}$ = 10.2, $J_{2,2'}$ = –13.8, $J_{14,14'}$ = –14.7, $J_{14,15}$ = 10.3, $J_{14,15'}$ = 7.7, $J_{14',15}$ = 1.4, $J_{14',15'}$ = 9.7, $J_{15,15'}$ = –13.2 Hz,] 5.36 (m, 1 H, 21-H), 5.65 (m, 1 H, 20-H), 6.47 (m, 2 H, 17-,18-H), [$J_{17,18}$ = undetermined, $J_{17,20}+J_{18,20}$ = 2.3, $J_{17,21}+J_{18,21}$ = 2.3, $J_{20,21}$ = 7.8 Hz], 6.80 (d, J_o = 7.3 Hz, 1 H, 13-H), 6.87 (d, J_o = 7.3 Hz, 1 H, 12-H), 7.49 (m, 1 H, 8-H), 7.51 (m, 1 H, 7-H), 7.75 (d, J = 8.7 Hz, 1 H, 4-H), 7.96 (m, 1 H, 9-H), 8.13 (d, J = 8.7 Hz, 1 H, 5-H), 8.22 (m, 1 H, 6-H), [$J_{6,7}$ = 8.0, $J_{6,8}$ = 1.2, $J_{6,9}$ = 0.7, $J_{7,8}$ = 7.2, $J_{7,9}$ = 1.1, $J_{8,9}$ = 8.0 Hz] ppm. ^{13}C NMR (100 MHz): δ = 33.81 (t, C-2), 34.29 (t, C-15), 34.42 (t, C-1), 36.75 (t, C-14), 118.68 (d, C-5), 121.47 (d, C-6), 122.38 (d, C-9), 122.91 (d, C-4), 124.48 (d, C-7), 126.21 (d, C-8), 127.96 (d, C-21), 128.48 (d, C-20), 130.91 (s, C-10b), 130.96 (d, C-13), 131.74 (d, C-17), 132.27 (d, C-18), 132.88 (s, C-5a), 133.77 (d, C-12), 135.15 (s, C-3a), 135.56 (s, C-5b), 135.68 (s, C-11), 136.14 (s, C-10a), 137.99 (s, C-19), 138.48 (s, 2 C, C-3, -16), 139.49 (s, C-9a) ppm. IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2920 (m), 1500 (m), 1450 (m), 1345 (m), 1075 (m), 930 (m), 800 (vs), 740 (vs), 720 (vs). UV (acetonitrile): $\lambda_{\max}$ (lgε) = 371 nm (3.25), 353 (3.20), 330 (sh, 3.75), 315 (4.15), 288 (4.56), 234 (4.50), 208 (4.39). MS: *m/z* (%) = 364 (13) [M$^+$], 260 (100), 104 (2). $C_{26}H_{20}S$ (364.52): calcd. C 85.66, H 5.54, S 8.80; found C 85.39, H 5.65, S 8.79.

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