An Efficient Synthetic Approach to Substituted Penta- and Hexahelicenes

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A two-step synthetic approach to penta- and hexahelicenes substituted at the terminal aromatic rings has been studied. This approach is based on the Diels–Alder reaction of 5,5′,8,8′-tetramethyl-3,3′,4,4′-tetrahydro-[1,1′]-binaphthalene **(2b)**, 3-vinyl-1,2-dihydronaphthalene **(5a)**, 5,8-dimethyl-3-vinyl-1,2-dihydronaphthalene **(5b)** and 3-vinyl-1,2-dihydrophenanthrene **(15)** followed by the aromatization of the cycloadducts. This method is flexible, efficient and of wide application to the synthesis of several benzenoid and nonbenzenoid penta- and hexahelicenes. The racemization energy barriers of helicenes **3**, **9**, **10**, **13**, **14**, **17** and **18** were computed with the semiempirical quantum method AM1. The computed values show that, when methyl groups are introduced at the inner position of the terminal aromatic rings, the racemization barriers increase markedly. A structure analysis of the reaction products by ^{1}H- and ^{13}C-NMR spectroscopy is also presented.

Introduction

There is a great deal of interest in helical structures such as nucleic acids, polysaccharides and helicenes, which are all inherently chiral molecules. Helicenes are a class of small helical molecules that have recently received considerable attention because of their unique helical, nonplanar π-electron system and high optical rotational value.[1] These molecules show extraordinary electronic and optical properties and are of potential interest in the field of new materials as stationary phases, liquid crystals and auxiliaries in asymmetric syntheses. For several years photocyclodehydrogenation of 1,2-diarylethenes followed by *in situ* oxidation (O_2, I_2, TCNE) has been the method extensively used to synthesize carbohelicenes and heterohelicenes.[2] This procedure, however, has severe limitations[2b]: i) it requires very dilute solutions in order to prevent photodimerizations, ii) some functional groups must be absent and, iii) substituted diarylethenes are frequently photoconverted into a mixture of substituted, difficult to separate, helicenes. The development of alternate synthetic strategies that could be adapted for synthesizing compounds with useful functionalities, is therefore a challenging problem.

Recently we have begun a research project with the aim of developing an efficient and flexible approach based on the Diels−Alder cycloaddition of arylethenes to the synthesis of polycyclic aromatic compounds[3] and to helicenes which are a class of polycyclic aromatic compounds characterised by an helical structure. We were interested in studying methods for synthesising them without using light. In previous papers we have reported a two-step synthesis of helical indeno[c]phenanthrene **9a**[3b,3d] (Scheme 1) and hexahelicenes **17a** and **18a**[3f] (Scheme 3) and demonstrated the utility of the use in the cycloaddition reactions of the dihydroarylethenes **5a** and **15**, more reactive than the corresponding aromatic dienes 2-vinyl-naphthalene[3a] and 3-vinyl-phenanthrene.[3c] Furthermore, we have also studied a two−step synthetic approach to pentahelicenequinone **3a** based on the cycloadditions of bis-dialine **2a** with 1,4-benzoquinone[3e] (Scheme 1).

Katz and co-workers[4] have also used the Diels−Alder methodology to prepare helicenequinones, but their strategy differed from ours in that it was based on the cycloaddition of bis-dienes, *p*-divinylbenzenes or 2,7-divinylnaphthalenes to 1,4-benzoquinone. Since the unsubstituted pentahelicenes **3a** and **9a** (Scheme 1) and hexahelicenes **17a** and **18a** (Scheme 3) have low racemization barriers (see Table 1), we have undertaken a study on the synthesis of helicenes substituted at the terminal aromatic rings in order to increase the energy barrier to racemization. For the assembly of the helical frame the Diels−Alder reaction was used, although the presence of methyl groups in the dienes could affect the reactivity of dienes **2b** and **5b** and, in the case of the latter diene, could markedly modify the regioselectivity of the Diels−Alder reaction thus influencing the stability of the transition states by both electronic and steric effects. Furthermore, this paper also wishes to show the potential of the Diels−Alder reactions of the bis-dialines **2** and the dihydro-arylethenes **5** in the synthesis of various substituted helicenes particularly in view of the easy availability of the substituted tetralones **1** from which dienes **2** and **5** can be prepared (Scheme 1). This method is also flexible since it can be used to make helicenes that contain not only benzene rings but also cyclopentane rings, and can be an alternate tool for preparing helicenes in quantity which

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is a requirement for studying their potential applications as new materials.

Here we report the synthesis of the new helicenes **3b**, **9c**, **10b**, **13**, **14**, **18c,** based on the Diels−Alder reaction of tetramethyl-bis-dialine (**2b)**, 5,8-dimethyl-3-vinyl-1,2-dihydronaphthalene **(5b)** or 3-vinyl-1,2-dihydrophenanthrene **(15)**. These helicenes are substituted at the terminal aromatic ring with methyl and methoxy groups in order to increase the energy barrier to racemization and hence have a greater optical stability. The values of the racemization barrier of the above synthesized helicenes, as well as those previously synthesized, are computed in order to compare the energy values and evaluate the substituent effects.

Results and Discussion

Tetramethyl-bis-dialine **(2b)**[3e,5] was prepared according to a previously reported one-pot procedure, based on coupling of the known 5,8-dimethyl-1-tetralone **(1b)**[6] with zinc in protic chlorotrimethylsilane in a 74% overall yield (Scheme 1). The methyl groups at the C(5) and C(8) carbons of **2b** were distinguished by the strong NOE effect observed between H(4) and the methyl group at carbon C(5). A conformational search performed by using the MM2* force field and a MonteCarlo algorithm[7] shows that the *cisoid* form is more stable than the *transoid* by 0.61 kcal/mol. In the case of the unsubstituted bis-dialine **2a**,[3e,8] the *cisoid* form is also the most stable one as the *transoid* form has 0.44 kcal/mol more energy. Comparison of the energy differences between the *cisoid* and *transoid* forms shows that the methyl groups do not markedly affect the conformational equilibrium.

The Diels−Alder cycloaddition[9] of diene **2b** and 1,4-benzoquinone (BQ) (Scheme 1) was investigated under a variety of experimental conditions and the best results were obtained when **2b** was treated with 1,4-benzoquinone (BQ) in toluene solution at reflux temperature for 98 h − a 14:5:1 mixture of three products was obtained in good yield (51%).

The products were isolated by column chromatography and a structure analysis, based on GC-MS measurements and NMR spectroscopy, showed that they were the pentahelicene **3b** and its dihydro- and tetrahydroderivatives **11** and **12** (Scheme 2), derived from the oxidation of the primary cycloadduct. Clearly, 1,4-benzoquinone also act as an oxidant.[3e]

Selective pre-irradiation of the H(12) resonance of compounds **3b** and **11** resulted in signal enhancement of the resonances attributed to the H(11) proton and the methyl group at C(13); in the case of compound **11** mutual enhancement occurred for the resonances of the methyl group at C(5) and H(5), thus supporting the structural assignment for both compounds. Further support was also given by the strongly deshielded shift of the H(11) proton (δ = 9.43 and 9.25 for **3b** and **11**, respectively) due to the anisotropic effect of the carbonyl function. Mutual dipolar contacts for compound **12** were observed between the methyl group at C(4) and both the H(3) and H(5) protons, as well as between the H(2) proton and the methyl group at C(1).

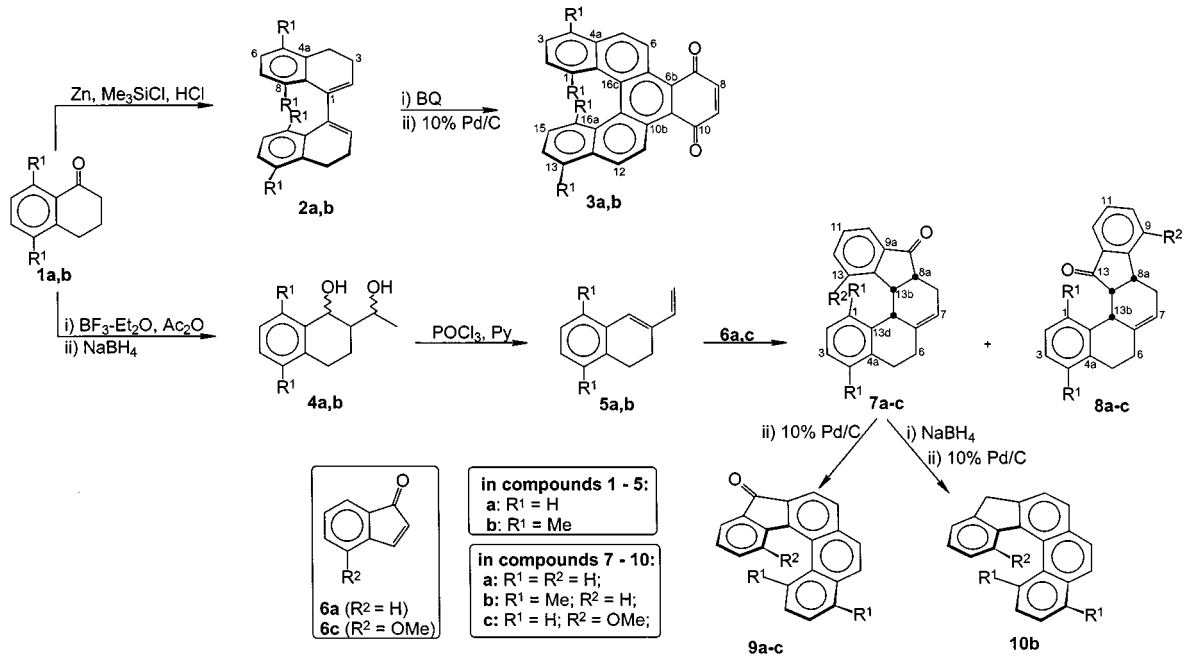
Treatment of the mixture of compounds **3b**, **11** and **12** with 10% Pd/C in triglyme[3b,3c] at reflux temperature afforded the tetramethylpentahelicenequinone **3b** in 62% yield. When **2b** reacted with BQ at 150°C without solvent for 23 h, **3b** was directly obtained, but in very poor yield (7%).

Reaction of the diene **2b** with 1,4-naphthoquinone in toluene solution gave a 1.5:1 mixture of two products which were treated, without purification, with 10% Pd/C in triglyme to afford the tetramethylpentahelicenenaphthoquinone **13** in 26% overall yield (Scheme 2). A GC-Mass spectroscopic analysis of the cycloaddition products indicated that the minor component of the mixture was a cycloadduct and the major one the tetrahydroderivative of **13**. The structural assignment of the pentahelicene **13** followed from the NOE effects observed on the resonances of the H(3) and H(5) protons upon irradiation of the resonance attributed to the methyl group at C(4).

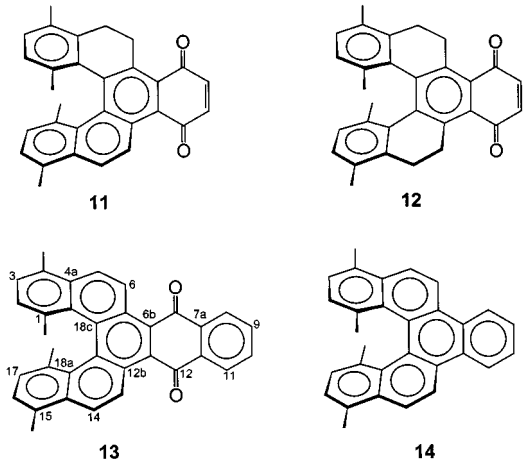
Diene **2b** also reacted with benzyne, generated[10] *in situ*, to give a 7.5:1.5:1 mixture of three products which was directly submitted to aromatization (10% Pd/C) to afford the benzopentahelicene **14** in 33% overall yield (Scheme 2). The assignment of the structure was based on the NOE effects observed between the proton H(2) and the methyl group at C(1), protons H(3) and H(5) with the methyl group at C(4) and between protons H(6) and H(7).

The pentahelicenes **9** and **10b** incorporating a cyclopentane ring were also prepared according to Scheme 1, by the cycloaddition reaction of dienes **5** with indenones **6**. Whereas diene **5a** was available from our previous study,[3b] diene **5b**[11] was prepared from the dimethyl-α-tetralone **1b**[6] by acetylation with the acetic anhydride − boron trifluoride system[3f] and subsequent reduction ($NaBH_4$) of the diketone − catalyst complex, to give a mixture of diols **4b** (75% overall yield), which was then converted into the diene **5b**. The reproducibility and yield of the last step were very low because of the instability of the diene.[11]

Diels−Alder reaction of the diene **5a** with 4-methoxy-2-inden-1-one **(6c)**, generated in *situ* from 3-bromo-4-methoxyindan-1-one,[3f] afforded a 4:1 mixture of the cycloadducts **7c** and **8c** (70% yield) (Scheme 1), which were separated by column chromatography. Compound **7c** was then converted into the fully aromatized pentahelicene **9c** (67%) by the usual treatment with 10% Pd/C. The same method could not be used to synthesize the dimethylpentahelicene **9b** from **5b** because of the marked instability of the diene. Thus, we modified the procedure by directly using the crude mixture of alcohols **4b** in the cycloaddition process to generate, *in situ*, the diene **5b**. When a CCl_4 solution of the crude diols **4b** and 3-bromoindan-1-one was heated in the presence of a small amount of $POCl_3$-pyridine, the diene **5b** and 2-inden-1-one (**6a**) were both generated *in situ* and reacted to afford a 4:1 mixture of the cycloadducts **7b** and **8b** (51% yield, Scheme 1) which were purified by column chromatography. Surprisingly the treatment of the cycloadduct **7b** with 10% Pd/C did not afford the expected aromatized product **9b**. Reduction of the carbonyl function of **7b** by $NaBH_4$, followed by treatment of the crude mixture of



Scheme 1. Synthesis of pentahelicenes **3**, **9** and **10**



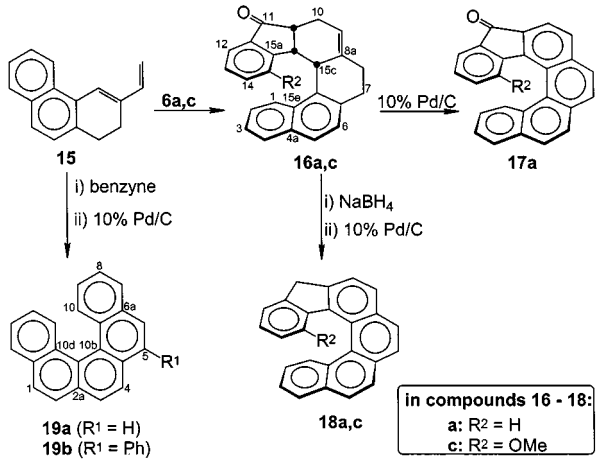
Scheme 2

alcohols with 10% Pd/C, afforded the pentahelicene **10b** in 45% overall yield. The structure of compounds **7b,c**, **8b,c**, **9c** and **10b** was assigned by NMR spectroscopy.

The regiochemistry of the carbonyl function of **7b** followed from the value of the chemical shift of the H(13) proton (5.55 ppm.), the shielding of which is a consequence of the anisotropic effect of the dimethyl-substituted aromatic ring, as well as from the NOE enhancements observed on the H(13) proton upon irradiation of the methyl group at C(1). The regiochemistry of the carbonyl function of **7c** is based on the unusual upfield shift of the methoxy group protons (3.0 ppm) due to the anisotropic effect of the other terminal aromatic ring, as well as on the NOE effect observed between the methoxy group and the H(1) protons. The regiochemistry of the carbonyl function of **8c** was deduced from the NOE effects observed on the H(2), H(13a) and H(13b) protons upon the selective irradiation of H(1). Further support was also given by the NOE effect observed between H(8) and the methoxy group protons. The *cis* relationship of the bridgehead methine protons of ketones **7b,c** and **8b,c** was assigned by the NOE effects observed between them.

The structure of pentahelicene **9c** was confirmed by the NOE effects observed between H(1), H(2), H(12) and the methoxy group protons, and the structure of **10b** from the NOE effects observed between the H(8), H(9) and H(10) protons, between the methyl group at C(1), H(2) and H(13) protons and between the methyl group at C(4), and the H(3) and H(5) protons.

In order to show that this synthetic methodology may have a wide range of applications in the field of helicenes, the synthesis of some hexahelicenes was also studied (Scheme 3).



Scheme 3. Synthesis of helicenes **17**–**19**

3-Vinyl-1,2-dihydrophenanthrene **(15)** was synthesized from 3-acetyl-1,2-dihydro-(1 H)-phenanthren-1-one according to a previously described procedure.[3f] The Diels–Alder cycloaddition of diene **15** with 4-methoxy-2-inden-1-one (**6c**), generated *in situ* from the reaction of 3-bromo-4-methoxyindan-1-one with triethylamine, afforded a 4:1 mixture of two regioisomer cycloadducts in 65% yield. The major component was shown to have the structure depicted in formula **16c**. The regiochemistry of the carbonyl function is supported by the large upfield shift of the methoxy group protons ($\delta = 2.52$) and by NOE effects observed between these protons and the H(4), H(5) and H(6) protons. The all-*cis* arrangement of the H(10a), H(15b) and H(15c) protons was proposed from the NOE effect observed between these protons. The sodium borohydride reduction of **16c**, followed by treatment of the alcoholic mixture with 10% Pd/C in triglyme at reflux temperature, gave the hexahelicene **18c** in 53% yield. The NOE effects observed between the H(11) methylene protons and the H(10) and H(12) protons, as well as the upfield shift of the methoxy group protons ($\delta = 2.47$) supported the assigned structure.

The cycloaddition of diene **15** with benzyne was also studied. When diene **15** reacted with benzyne generated *in situ*, a 1.5:1 mixture of two products was obtained (57% yield), which was then aromatized by DDQ treatment (Scheme 3). The aromatized compounds were separated by column chromatography and structural analysis showed that the minor component **19a** was the desired pentahelicene,[12] whereas the major component **19b** was the product of the cycloaddition followed by an "ene-reaction" involving a second molecule of dienophile.[13] The structure of **19b** followed from GC-MS and NMR measurements; the regiochemistry of the phenyl group at C(5) was established by comparing the ^{1}H and ^{13}C NMR chemical shifts with those of the pentahelicene **19a**.

The racemization barriers of the helicenes **3, 9, 10, 13, 14, 17** and **18** were calculated with the semiempirical quantum method AM1.[14] By this method, the minima and saddle point structures of the compounds were optimized by focusing on the structures of the ground state (GS) and the pathway for the interconversion of the two enantiomers (racemization). The racemization barriers were estimated as the energy differences between the GS minima and the twisted transition states (TS).

The TS structures found for the racemization of helicenes have terminal aromatic rings oriented face-to-face (Figure 1). The results of the computations for dihedral angles and racemization activation barriers are given in Table 1.

The correspondence between the calculated energy values for compounds **3** (Table 1) and the experimental[2c] and computed[14] ones of [5]helicenes shows that the benzoquinone unit does not affect the energies of **3** and confirms also the reliability of the AM1 method with our compounds. Other interesting facts emerge from the examination of the data reported in Table 1: i) a comparison of the values between compounds **3a** and **9a**, and **17a** and [6]helicene[2c] indicates clearly that the replacement of a benzene unit with a cyclopentane ring markedly decreases the racemization enthalpies [9 and 6 kcal mol−1, respectively], ii) introducing a methoxy group at C(13) of **9a** (as in **9c**) and at C(15) of **18a** (as in **18c**) does not effect markedly the stability of the enantiomers, while a stronger influence (15 kcal mol−1) is observed when methyl groups are introduced at the inner position of the terminal aromatic rings (cf. **3b, 10b**).

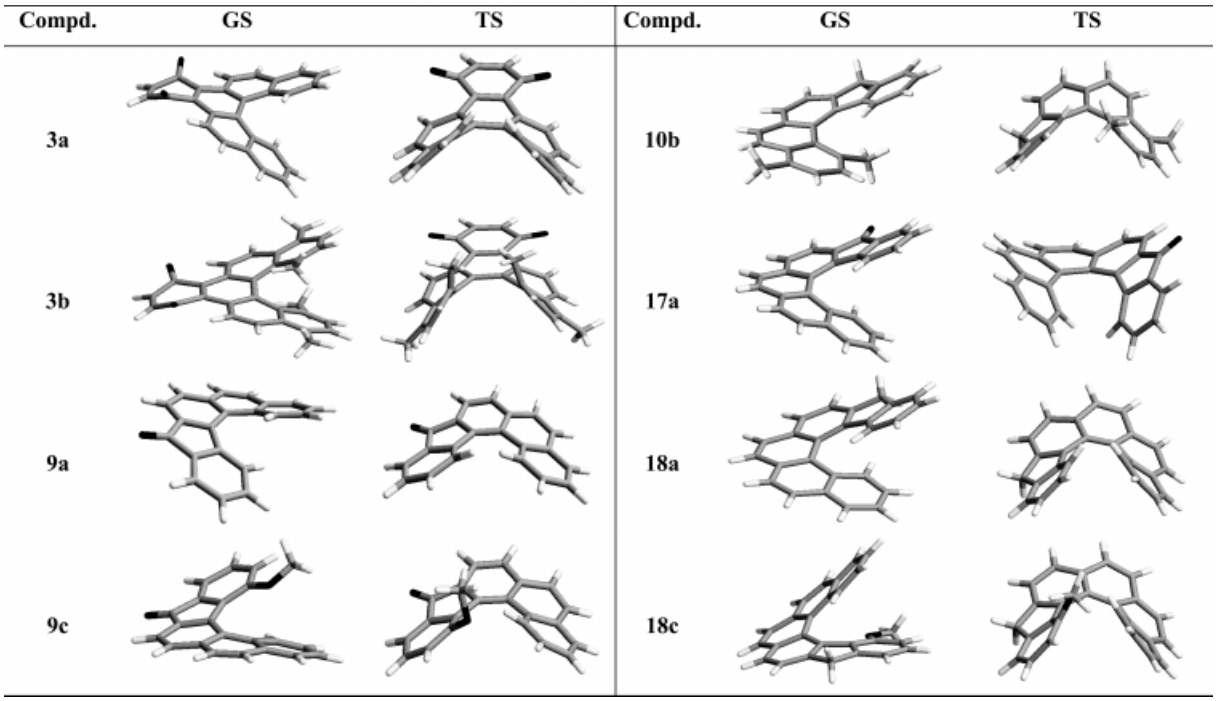


Figure 1. Minima (GS) and transition state (TS) structures of the [n]helicenes, optimized by the semiempirical AM1 method

Table 1. Computed C−C−C−C dihedral angles[a] (degrees) of the GS and TS minima and heat of formation (kcal/mol) for racemization process of helicenes **3**, **9**, **10, 13, 14, 17, 18**

Compd.	C−C−C−C angles GS				C−C−C−C angles TS				AM1, heat of formation (kcal/mol) GS	TS	TS-GS
3a	18.3	30.4	19.7		48.1	2.1	−44.6		73.3	96.0	22.7
3b	27.9	28.9	32.5		15.5	15.9	−2.3		58.9	96.4	37.5
9a	20.8	18.8	9.4		−20.0	3.9	26.7		78.0	91.8	13.8
9c	17.5	21.9	17.3		−31.9	−3.6	38.0		46.5	64.6	18.1
10b	5.7	18.6	31.3		38.0	32.0	−27.4		90.5	119.1	28.6
13	27.3	31.6	29.2		59.0	−4.6	64.0		68.8	103.3	34.5
14	27.5	34.3	25.8		57.2	−6.7	−64.0		108.6	142.3	33.7
17a	15.8	29.7	18.0	5.7	−44.7	−14.8	37.0	37.2	101.5	130.6	29.1
18a	15.7	29.7	18.2	5.1	−45.6	−16.3	36.7	35.5	121.2	150.6	29.4
18c	12.4	29.3	23.5	14.0	−43.0	−26.1	29.7	49.0	90.6	120.2	29.6

[a] The C−C−C−C angles correspond to the atoms of the inner helix; the first angle refers to the first four beginning with C(1) and the following values refer to angles where the first atom is replaced by the second one.

Conclusions

A short, flexible method for synthesizing substituted pentahelicenes and hexahelicenes has been reported. It shows a further application of the Diels−Alder reaction in organic synthesis. This method could be used to synthesize a variety of helicenes, including nonbenzenoid ones, such as those containing a cyclopentane ring. The replacement of the benzene unit with a five-membered ring is interesting because it modifies both the geometry and the electronic structure of the molecules. A relatively high energy barrier to racemization has been achieved by substituting terminal aromatic rings with methyl and methoxy groups. This methodology is also of interest because it permits synthesis on a preparative scale. It is remarkable that the synthesis of dienes **2** and **5** from the common precursors, tetralones **1**, has been achieved. Further applications of this method to the syntheses of enantiomerically pure carbohelicenes and heterohelicenes are now in progress.

Experimental Section

General: Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. − IR: Perkin−Elmer 983. − NMR: Varian Associates VXR-400 (400 MHz and 100.6 MHz, for ^1H and ^{13}C, respectively). Chemical shifts in $CDCl_3$, are expressed in ppm downfield from internal TMS for ^1H and ^{13}C. The structure of the reaction products were assigned by analysis of ^1H and ^{13}C−NMR spectra. Proton and carbon shift assignments were based on COSY, ^1H- {^1H} NOE and HETCOR experiments; quaternary carbons were assigned by 2D long-range heterocorrelated experiments. − MS: Hewlett Packard 5970 GC-MS (70 eV). All the computations were run on a Silicon Graphics Indigo-2 Workstation R10000 (175 MHz) and on a PC-Pentium MMX (266 MHz). In the conformational analysis, simulations were carried out in the gas phase using the BatchMin V 5.5 simulation programs as implemented in the Macromodel molecular modelling package.[7c] The MM2* force field was used[7a], and the simulation varied all internal degrees of freedom of the molecules. The conformational search was performed by using a Monte Carlo algorithm,[7b] included in the package, and all the conformers with an energy within 3.5 kcal/mol were considered. All semiempirical AM1 calculations of the racemization barriers were performed with both Hyperchem 4.5 (SGI version) and HyperChem 5.1 (PC version), available from Hypercube Inc. Gainesville, Florida.

3,3′,4,4′-Tetrahydro-5,5′,8,8′-tetramethyl-[1,1′]-binaphthalene (2b): This diene was prepared[3e,5] by treating **1b**[6] (6 g, 34.5 mmol) with zinc dust (3.6 g), chlorotrimethylsilane (28.8 mL, 27 mmol) and conc. hydrochloric acid (14 mL) in THF (180 mL). The reaction mixture was stirred at 25°C for 18 h and then worked up as usual to give a residue which was chromatographed on a column (SiO_2). Elution with petroleum ether afforded 4 g of pure diene **2b** (74%), m.p. 129−130°C (methanol). − ^1H NMR: δ = 2.09 (s, 3 H, 8-Me), 2.17 (m, 2 H, H-3), 2.28 (s, 3 H, 5-Me), 2.67 (m, 2 H, H-4), 6.04 (t, 1 H, *J* = 5.2 Hz, H-2), 6.80 (d, 1 H, *J* = 7.8 Hz, H-7), 6.92 (d, 1 H, *J* = 7.8 Hz, H-6). − ^{13}C NMR: δ = 20.2 (5-Me), 22.6 (C-3), 22.8 (8-Me), 25.0 (C-4), 127.1 (C-2), 128.7 (C-6), 129.6 (C-7), 131.9 (C-8), 132.3 (C-5), 134.3 (C-8a), 138.7 (C-1), 141.8 (C-4a). − MS; *m/z* (%): 314 (100) [M^+], 299 (53), 284 (22), 271 (20), 253 (11). − $C_{24}H_{26}$ (314.5): calcd. C 91.67, H 8.33; found C 91.61, H 8.34.

1,4,13,16-Tetramethylpentahelicenebenzoquinone (3b): A solution of diene **2b** (4.5 g, 14.1 mmol) and 1,4-benzoquinone (22.5 g, 141 mmol) in toluene (150 mL) was heated at reflux temperature, under stirring, for 98 h. The excess benzoquinone was removed by steam distillation and the residue extracted with chloroform. The usual work up afforded 3 g of a 14:5:1 mixture of products **11**, **12** and **3b** (GC-MS analysis) which was used for the next step. A small amount of the mixture was chromatographed on silica gel. Elution with toluene gave compounds **11** and **12**, which, although slightly impure, were submitted to structure analysis (GC-MS, IR, NMR). **11:** IR ($CHCl_3$): $\tilde{\nu}$ = 1652 cm^{-1} (C=O). − ^1H NMR: δ = 0.58 (s, 3 H, 1-Me), 1.69 (s, 3 H, 16-Me), 2.44 (s, 3 H, 4-Me), 2.63 (m, 1 H, H-5), 2.65 (m, 1 H, H-6), 2.72 (s, 3 H, 13-Me), 3.24 (m, 1 H, H-5), 4.40 (m, 1 H, H-6), 6.64 (d, 1 H, *J* = 7.7 Hz, H-3), 6.88 (d, 1 H, *J* = 10.1 Hz, H-8), 6.91 (d, 1 H, *J* = 7.3 Hz, H-15), 6.94 (d, 1 H, *J* = 10.1 Hz, H-9), 7.04 (d, 1 H, *J* = 7.7 Hz, H-2), 7.27 (d, 1 H, *J* = 7.3 Hz, H-14), 8.02 (d, 1 H, *J* = 9.5 Hz, H-12), 9.25 (d, 1 H, *J* = 9.5 Hz, H-11). − ^{13}C NMR: δ = 19.4 (13-Me), 19.6 (4-Me), 20.1 (1-Me), 21.4 (16-Me), 25.6 (C-5), 25.9 (C-6), 123.3 (C-11), 125.3 (C-10b), 126.9 (C-12), 128.0 (C-16c), 128.9 (C-15), 129.1 (C-14), 129.2 (C-3), 130.1 (C-16a), 130.3 (C-2), 130.7 (C-13), 131.1 (C-4), 132.2 (C-12a), 132.5 (C-1), 133.6 (C-16b), 134.5 (C-16), 136.8 (C-16d), 138.1 (C-4a), 138.2 (C-8, C-10a), 139.3 (C-9), 140.4 (C-6a), 141.7 (C-6b), 188.5 (C-10), 188.6 (C-7). − MS; *m/z* (%): 416 (79) [M^+], 401 (55), 386 (100), 300 (14), 207 (27), 193 (17), 162 (17), 150 (23). **12:** IR ($CHCl_3$): $\tilde{\nu}$ = 1652 cm^{-1} (C=O). − ^1H NMR:

δ = 1.29 (s, 3 H, 1-Me), 2.34 (dd, 1 H, *J* = 14.5, 14.4 Hz, H-5), 2.38 (s, 3 H, 4-Me), 2.54 (dd, 1 H, *J* = 15.0, 14.4 Hz, H-6), 3.14 (ddd, 1 H, *J* = 14.5, 4.0, 2.8 Hz, H-5), 4.17 (dd, 1 H, *J* = 15.4, 2.8 Hz, H-6), 6.67 (d, 1 H, *J* = 7.8 Hz, H-2), 6.86 (s, 1 H, H-8), 6.98 (d, 1 H, *J* = 7.8 Hz, H-3). − ^{13}C NMR: δ = 19.5 (4-Me), 19.6 (1-Me), 25.8 (C-5), 26.8 (C-6), 128.5 (C-3), 129.2 (C-6a), 129.8 (C-2), 130.7 (C-1), 133.3 (C-4, C-16d), 139.1 (C-8), 139.2 (C-4a), 140.8 (C-16c), 143.7 (C-6b), 187.8 (C-7). − MS; *m/z* (%): 418 (100) [M$^+$], 403 (62), 388 (19), 373 (21), 207 (22), 163 (20), 150 (16). − When diene **2b** and 1,4-benzoquinone were heated at 150°C without solvent for 4.5 h, the same reaction mixture was obtained but the yield dropped to 30%. With a reaction time of 23 h, only pentahelicenebenzoquinone **3b** was obtained in a very low yield (7%). − The aromatization of the reaction mixture obtained by the cycloaddition was accomplished by treating the crude mixture (2 g) in triglyme (100 mL) with 10% Pd/C (2 g) according to a previously reported procedure[3b,3c]. The mixture was refluxed for 18 h and then worked up as usual to afford a residue which was purified by column chromatography on silica gel. Elution with toluene gave 1.24 g of pure **3b** (62%), m.p. 242−243°C (*n*-hexane/ethyl acetate 3:1). IR (nujol): $\tilde{\nu}$ = 1652 cm^{-1} (C=O). − ^{1}H NMR: δ = 0.75 (s, 3 H, 1-Me), 2.83 (s, 3 H, 4-Me), 6.93 (d, 1 H, *J* = 7.3 Hz, H-2), 7.01 (s, 1 H, H-8), 7.38 (d, 1 H, *J* = 7.3 Hz, H-3), 8.30 (d, 1 H, *J* = 9.3 Hz, H-5), 9.43 (d, 1 H, *J* = 9.3 Hz, H-6). − ^{13}C NMR: δ = 19.6 (4-Me), 21.9 (1-Me), 122.5 (C-6), 126.7 (C-5), 127.2 (C-6a), 129.2 (C-2, C-6b, C-3), 131.1 (C-4), 131.5 (C-16d), 131.6 (C-16c), 132.3 (C-4a), 133.5 (C-1), 138.5 (C-8), 189.2 (C-7). − MS; *m/z* (%): 414 (19) [M$^+$], 399 (98), 384 (100), 371 (26), 207 (99), 192 (35), 44 (30). − $C_{30}H_{22}O_2$ (414.5): calcd. C 86.93, H 5.35; found C 86.98, H 5.33.

1,4,15,18-Tetramethylpentahelicenenaphthoquinone (13): Diene **2b** (3 g, 9.4 mmol) was added to a toluene solution (100 mL) of 1,4-naphthoquinone (10 g, 63.2 mmol) and the resulting mixture was stirred at reflux temperature for 18 h. Usual work up gave a residue which was chromatographed on column (SiO_2). Elution with toluene afforded a 1.5:1 mixture of two products shown, by GC-Mass spectrometry, to be the cycloadduct and the tetrahydroderivative of **13** formed by oxidation of the cycloadduct by 1,4-naphthoquinone. The reaction mixture (2 g) was aromatized by treatment with 10% Pd/C (2 g) in triglyme (60 mL) at reflux temperature for 30 h[3b,3c] to give a crude product which was purified by column chromatography (SiO_2). Elution with toluene gave 1.14 g of pure **13** (26%), m.p. 253−254°C (hexane/ethyl acetate 3:1). IR (nujol): $\tilde{\nu}$ = 1663 cm^{-1} (C=O). − ^{1}H NMR: δ = 0.77 (s, 3 H, 1-Me), 2.84 (s, 3 H, 4-Me), 6.94 (d, 1 H, *J* = 7.3 Hz, H-2), 7.38 (d, 1 H, *J* = 7.3 Hz, H-3), 7.78 (m, 1 H, H-9), 8.30 (m, 1 H, H-8), 8.31 (d, 1 H, *J* = 9.3 Hz, H-5), 9.52 (d, 1 H, *J* = 9.3 Hz, H-6). − ^{13}C NMR: δ = 19.3 (4-Me), 21.7 (1-Me), 122.7 (C-6), 125.9 (C-5), 126.3 (C-8), 126.6 (C-7a), 127.9 (C-6a), 128.7 (C-3), 128.8 (C-2), 129.5 (C-6b), 130.8 (C-4), 131.4 (C-18d), 131.5 (C-18c), 132.1 (C-4a), 133.3 (C-9), 134.3 (C-1), 186.8 (C-7). − $C_{34}H_{24}O_2$ (464.6): calcd. C 87.91, H 5.21; found C 87.88, H 5.21.

1,4,13,16-Tetramethylbenzopentahelicene (14): A solution of anthranilic acid (3 g, 21.8 mmol) in DME (12 mL)[15] was added to a solution of diene **2b** (2.5 g, 8 mmol) and isoamylnitrite (1.8 g, 15.6 mmol) in DME (20 mL). After that, a DME solution (4 mL) of isoamylnitrite was again added and after usual work up 2.1 g of a 7.5:1.5:1 mixture of three products, as shown by GLC analysis, was obtained. − A triglyme solution (50 mL) of the reaction mixture (2.1 g) was treated with 10% Pd/C (3 g) at reflux temperature for 38 h. Usual work up afforded a crude residue which was chromatographed on column (SiO_2). Elution with toluene gave 1.0 g of pure compound **14** (33% overall yield), m.p. 269−270°C (hexane/chloroform 2:1). − ^{1}H NMR: δ = 0.77 (s, 3 H, 1-Me), 2.89 (s, 3 H, 4-Me), 6.92 (d, 1 H, *J* = 7.2 Hz, H-2), 7.31 (d, 1 H, *J* = 7.2 Hz, H-3), 7.77 (m, 1 H, H-8), 8.28 (d, 1 H, *J* = 8.9 Hz, H-5), 8.75 (d,1 H, *J* = 8.9 Hz, H-6), 8.82 (m, 1 H, H-7). − ^{13}C NMR: δ = 19.7 (4-Me), 22.1 (1-Me), 119.2 (C-6), 123.4 (C-7), 123.7 (C-5), 126.3 (C-16c), 126.8 (C-8), 127.0 (C-3), 127.7 (C-6a), 128.4 (C-2), 129.7 (C-6b), 131.0 (C-4), 132.0 (C-4a), 133.0 (C-1), 133.1 (C-16d). − MS; *m/z* (%): 384 (21) [M$^+$], 369 (39), 354 (100), 177 (20), 169 (18). − $C_{30}H_{24}$ (384.5): calcd. C 93.71, H 6.29; found C 93.73, H 6.30.

Diels−Alder Reaction of 4-Methoxy-2-inden-1-one (6c) with Diene 5a: 3-Bromo-4-methoxyindan-1-one, the precursor of 4-methoxy-2-inden-1-one (**6c**), was prepared from the commercially available 4-methoxyindan-1-one according to a previously described procedure[3b] in 95% yield, m.p.79−80°C (ethyl ether/n-pentane 2:1). − ^{1}H NMR: δ = 3.13 (dd, 1 H, *J* = 20.6, 1.3 Hz, H-2), 3.35 (dd, 1 H, *J* = 20.6, 6.8 Hz, H-2), 3.98 (s, 3 H, OMe), 5.62 (dd, 1 H, *J* = 6.8, 1.3 Hz, H-3), 7.11 (d, 1 H, *J* = 8.5 Hz, H-5), 7.37 (d, 1 H, *J* = 8.5 Hz, H-7), 7.50 (t, 1 H, *J* = 8.5 Hz, H-6). − $C_{10}H_9O_2Br$ (241.1): calcd. C 49.82, H 3.76; found C 49.85, H 3.77. − A solution of 3-bromo-4-methoxyindan-1-one (5.6 g, 23.2 mmol) and diene **5a**[3b] (5.2 g, 33.3 mmol) in 80 mL of CCl_4 was heated at 65°C and added dropwise of a solution of triethylamine (6 g, 59 mmol) in CCl_4 (120 mL). The mixture was then heated at 65°C for 24 h under nitrogen and stirring. The mixture was then cooled to room temperature, poured into ice-cold 5% aqueous H_2SO_4 and extracted with $CHCl_3$. The combined extracts were washed with 5% aqueous H_2SO_4, dried (Na_2SO_4) and evaporated in vacuo. Chromatography on silica gel of the crude product and elution with 95:5 hexane/ethyl acetate gave 4.1 g of pure cycloadducts **7c** (56%) and 1.0 g of pure **8c** (14%).

5,6,8,8a,13b,13c-Hexahydro-13-methoxy-9*H*-indeno[2,1-*c*]-phenanthren-9-one (7c): m.p. 131−132°C (diethyl ether). − IR (nujol): $\tilde{\nu}$ = 1702 cm^{-1} (C=O). − ^{1}H NMR: δ = 1.22−2.94 (m, 6 H, H-5, H-6, H-8), 2.97 (ddd, 1 H, *J* = 7.0, 2.4, 2.0 Hz, H-8a), 3.0 (s, 3 H, OMe), 3.84 (ddd, 1 H, J = 7.3, 2.5, 1.5 Hz, H-13c), 4.26 (dd, 1 H, *J* = 7.3, 7.0 Hz, H-13b), 5.75 (m, 1 H, H-7), 6.66 (m, 1 H, H-12), 6.93 (d, 1 H, *J* = 7.6 Hz, H-4), 7.12 (d, 1 H, *J* = 7.6, 7.2 Hz, H-3), 7.22−7.24 (m, 2 H, H-10, H-11), 7.28 (dd, 1 H, *J* = 7.8, 7.6 Hz, H-2), 7.48 (d, 1 H, *J* = 7.8 Hz, H-1). − ^{13}C NMR: δ = 25.1 (C-8), 29.1 (C- 5), 30.8 (C-6), 43.7 (C-13c), 44.9 (C-13b), 49.3 (C-8a), 54.8 (OMe), 114.2 (C-10), 114.3 (C-12), 121.6 (C-7), 125.9 (C-2, C-3), 127.2 (C-4), 129.2 (C-11), 130.4 (C-1), 137.7 (C-13d), 139.8 (C-6a), 139.9 (C-9a), 140.4 (C-4a), 143.2 (C-13a), 157.8 (C-13), 209.3 (C-9). − MS; *m/z* (%): 316 (9) [M$^+$], 157 (22), 156 (100), 141 (26), 128 (23). − $C_{22}H_{20}O_2$ (316.4): calcd. C 83.52, H 6.37; found C 83.42, H 6.29.

5,6,8,8a,13a,13b-Hexahydro-9-methoxy-13*H*-indeno[1,2-*c*]-phenanthren-13-one (8c): m.p. 211−212°C (diethyl ether). IR (nujol): $\tilde{\nu}$ = 1700 cm^{-1} (C=O). − ^{1}H NMR: δ = 2.32−2.85 (m, 6 H, H-5, H-6, H-8), 3.24 (dd, 1 H, *J* = 7.4, 5.8 Hz, H-13a), 3.72 (dd, 1 H, *J* = 5.8, 2.2 Hz, H-13b), 3.92 (s, 3 H, OMe), 4.01 (dd, 1 H, *J* = 8.0, 7.4 Hz, H-8a), 5.38 (m, 1 H, H-7), 7.01 (d, 1 H, *J* = 8.0 Hz, H-10), 7.13 (d, 1 H, *J* = 7.6 Hz, H-12), 7.16 (d, 1 H, *J* = 7.6 Hz, H-4), 7.19−7.28 (m, 3 H, H-2, H-3, H-11), 7.37 (d, 1 H, *J* = 7.6 Hz, H-1). − ^{13}C NMR: δ = 26.4 (C-8), 29.5 (C-5), 30.7 (C-6), 40.3 (C-8a, C-13b), 52.9 (C-13a), 55.4 (OMe), 114.4 (C-12), 115.1 (C-10), 119.2 (C-7), 125.8 (C-3), 126.4 (C-11), 128.0 (C-1), 128.1 (C-4), 128.9 (C-2), 136.7 (C-13c), 139.9 (C-6a), 140.2 (C-12a), 140.8 (C-4a), 145.4 (C-8b), 156.9 (C-9), 206.7 (C-13). − MS; *m/z* (%): 316 (70) [M$^+$], 166 (88), 156 (100), 141 (38), 128 (37). − $C_{22}H_{20}O_2$ (316.4): calcd. C 83.52, H 6.37; found C 83.59, H 6.41.

13-Methoxy-9*H*-indeno[2,1-*c*]phenanthren-9-one (9c): A mixture **7c** (3.9 g, 12.3·mmol) and 10% Pd/C (4.2 g) in 170 mL of triglyme was

stirred at 200°C for 24 h under nitrogen. The reaction mixture was then cooled to room temperature, more catalyst was added (2.1 g) and the heating (200°C) continued for another 24 h. Usual work up gave a residue which was chromatographed on a column. Elution with 49:1 hexane/ethyl acetate afforded 2.5 g of **9c** (67%), m.p. 178−179°C (ethyl acetate). − IR (nujol): $\tilde{\nu}$ = 1704 cm^{-1} (C=O). − ^1H NMR: δ = 3.48 (s, 3 H, OMe), 7.06 (d, 1 H, *J* = 8.2 Hz, H-12), 7.32 (dd, 1 H, *J* = 8.2, 7.1 Hz, H-11), 7.37 (dd, 1 H, *J* = 8.2, 7.4 Hz, H-2), 7.42 (d, 1 H, *J* = 7.1 Hz, H-10), 7.57 (dd, 1 H, *J* = 7.6, 7.4 Hz, H-3), 7.60 (d, 1 H, *J* = 8.7 Hz, H-6), 7.67 (d, 1 H, *J* = 7.8 Hz, H-7), 7.73 (d, 1 H, *J* = 8.7 Hz, H-5), 7.79 (d, 1 H, *J* = 7.6 Hz, H-4), 7.82 (d, 1 H, *J* = 8.2 Hz, H-8), 8.02 (d, 1 H, *J* = 8.2 Hz, H-1). − ^{13}C NMR: δ = 53.5 (OMe), 116.8 (C-10), 118.3 (C-12), 120.8 (C-8), 122.9 (C-2), 126.3 (C-4, C-6), 126.8 (C-2), 128.0 (C-13c), 128.3 (C-7), 129.3 (C-1), 129.4 (C-5), 130.2 (C-11), 130.5 (C-13d), 132.3 (C-4a), 134.2 (C-6a, C-13a), 136.6 (C-9a), 138.7 (C-8a), 141.8 (C-13b), 154.0 (C-13), 193.5 (C-9). − MS; *m*/*z* (%): 310 (100) [M^+], 295 (23), 250 (18), 239 (26), 118 (18). − $C_{22}H_{14}O_2$ (310.3): calcd. C 85.15, H 4.55; found C 85.15, H 4.61.

1,2-Dihydro-5,8-dimethyl-3-vinylnaphthalene (5b): $BF_3{\cdot}Et_2O$ (2.8 mL, 20·mmol) was added to a mixture of **1b** (2.5 g, 14.5·mmol) and anhydrous Ac_2O (5.5 mL, 58·mmol) whilst stirring under nitrogen. Stirring was continued at 60°C for 21 h and then at reflux temperature for 1.5 h, after which time the reaction mixture was left standing at room temperature for 12 h. The resultant precipitate was triturated with cold Et_2O, filtered and washed with cold Et_2O to give 2.9 g (76%) of a yellow crystalline complex BF_2-diketone, m.p. 131−132°C . − ^1H NMR: δ = 2.30 (s, 3 H, Me), 2.38 (s, 3 H, Me), 2.6 (m, 2 H), 2.83 (m, 2 H), 7.05 (d, 1 H), 7.30 (d, 1 H), 9.10 (s, 1 H). − MS; *m*/*z* (%): 264 (100) [M^+], 249 (38), 221 (44). − A solution of 2.75 g (73 mmol) of $NaBH_4$ in 44 mL of H_2O was added to a refluxing solution of BF_2-diketone complex (2.9 g, 10.9 mmol) in 110 mL of EtOH, and the reflux continued for 1.5 h. Half of the solvent was then evaporated under vacuum and the residue extracted with $CHCl_3$. The combined extracts were washed with saturated brine, dried (Na_2SO_4) and evaporated under vacuum to afford 2.4 g of a mixture of diols **4b** (98%) which was used, without purification, for the next step. − To a solution of 2.4 g of the diols **4b** in 330 mL of dry pyridine, was added $POCl_3$ (1.8 mL, 1.9 mmol), and the reaction mixture was refluxed for 2.5 h under nitrogen. Usual work up gave 0.1 g of **5b** (5%) having ^1H NMR spectroscopic data identical to those reported in the literature[11].

Reaction of 2-Inden-1-one (6a) with Diols 4b: A solution of 1.5 mL of pyridine and 1.2 mL of $POCl_3$ in 20 mL of CCl_4 was added to a solution of 2.4 g (10.9 mmol) of the crude mixture of diols **4b** and 3.2 g (15.2 mmol) of 3-bromo-indan-1-one in 60 mL of CCl_4 whilst stirring under nitrogen. The mixture was refluxed for 24 h and then worked up as usual to give a residue which was chromatographed on silica gel. Elution with 49:1 hexane/ethyl acetate afforded 1.4 g of pure **7b** (41%) and 0.36 g of **8b** (10%).

5,6,8,8a,13b,13c,-Hexahydro-1,4-dimethyl-9*H*-indeno[2,1-*c*]-phenanthren-9-one (7b): m.p. 155−156°C (diethyl ether). − IR (nujol): $\tilde{\nu}$ = 1705 cm^{-1} (C=O). − ^1H NMR: δ = 0.84 (m, 1 H, H-5), 2.01 (m, 1 H, H-6), 2.12 (s, 3 H, 4-Me), 2.15 (m, 1 H, H-6), 2.28 (m, 1 H, H-8), 2.45 (m, 1 H, H-5), 2.56 (s, 3 H, 1-Me), 2.93 (ddd, 1 H, *J* = 14.5, 7.1, 2.2 Hz, H-8), 3.03 (ddd, 1 H, *J* = 7.0, 6.6, 2.2 Hz, H-8a), 4.03 (dd, 1 H, *J* = 7.0, 6.6 Hz, H-13b), 4.05 (dd, 1 H, *J* = 7.0, 2.2 Hz, H-13c), 5.55 (d, 1 H, *J* = 7.8 Hz, H-13), 5.69 (d, 1 H, *J* = 7.9 Hz, H-7), 7.04 (d, 1 H, *J* = 7.5 Hz, H-3), 7.08 (m, 1 H, H-12), 7.10 (d, 1 H, *J* = 7.5 Hz, H-2), 7.23−7.62 (m, 2 H, H-10, H-11). − ^{13}C NMR: δ = 19.3 (1-Me), 19.7 (4-Me), 24.6 (C-8), 25.5 (C-5), 30.1 (C-6), 39.7 (C-13c), 42.7 (C-13b), 48.5 (C-8a), 119.8 (C-7), 122.4 (C-10), 127.4 (C-11), 127.6 (C-13), 127.8 (C-3), 128.3 (C-2), 132.8 (C-1), 133.2 (C-12), 133.4 (C-4), 134.6 (C-13d), 138.7 (C-9a), 140.1 (C-4a), 140.3 (C-6a), 154.6 (C-13a), 209.5 (C-9). − MS; *m*/*z* (%): 314 (16) [M^+], 184 (100), 169 (32), 143 (31). − $C_{23}H_{22}O$ (314.4): calcd. C 87.86, H 7.05; found C 86.91, H 7.11.

5,6,8,8a,13a,13b-Hexahydro-1,4-dimethyl-13*H*-indeno[1,2-*c*]-phenanthren-13-one (8b): m.p. 137−138°C (diethyl ether). − IR (nujol): $\tilde{\nu}$ = 1707 cm^{-1} (C=O). − ^1H NMR: δ = 2.14−2.18 (m, 2 H, H-5, H-6), 2.29 (s, 3 H, 4-Me), 2.33 (m, 1 H, H-6), 2.42 (s, 3 H, 1-Me), 2.54−2.64 (m, 2 H, H-8), 2.79 (m, 1 H, H-5), 3.19 (dd, 1 H, *J* = 7.1, 6.5 Hz, H-13a), 3.85 (dd, 1 H, *J* = 6.5, 2.2 Hz, H-13b), 3.86 (dd, 1 H, *J* = 7.1, 6.8 Hz, H-8a), 5.38 (dd, 1 H, *J* = 7.0, 3.0 Hz, H-7), 7.02 (s, 2 H, H-2, H-3), 7.30 (m, 1 H, H-11), 7.52 (d, 1 H, *J* = 7.4 Hz, H-9), 7.54 (d, 1 H, *J* = 7.5 Hz, H-12), 7.58 (m, 1 H, H-10). − ^{13}C NMR: δ = 19.4 (1-Me), 20.0 (4-Me), 25.6 (C-5), 28.8 (C-8), 30.6 (C-6), 38.9 (C-13b), 39.5 (C-8a), 49.9 (C-13a), 117.7 (C-7), 122.6 (C-12), 125.3 (C-9), 127.3 (C-11), 127.9 (C-3), 128.1 (C-2), 132.4 (C-4), 132.7 (C-1), 133.9 (C-13c), 134.6 (C-10), 139.0 (C-4a, C-12a), 141.7 (C-6a), 157.6 (C-8b), 206.1 (C-13). − MS; *m*/*z* (%): 314 (100) [M^+], 281 (9), 185 (9), 183 (29), 169 (9). − $C_{23}H_{22}O$ (314.4): calcd. C 87.86, H 7.05; found C 88.09, H 6.99.

1,4-Dimethyl-9*H*-indeno[2,1-*c*]-phenanthrene (10b): $NaBH_4$ (2.3 g) was added to a solution of 1.5 g (4.6 mmol) of cycloadduct **7b** dissolved in 150 mL of $MeOH/CH_2Cl_2$ (1:1). The mixture was stirred at room temperature for 5 h and then worked up as usual. The crude product obtained (1.4 g) was dissolved in 75 mL of triglyme and treated with 2.5 g of 10% Pd/C at 200°C for 24 h under nitrogen. Then the resulting mixture was cooled to room temperature, more catalyst (1.1 g) was added and the heating (200°C) continued for a further 24 h. Usual work up gave a residue which was purified by column chromatography on silica gel. Elution with 99:1 hexane/ethyl acetate gave 0.6 g of **10b** (45%), m.p. 101−102°C (MeOH). − ^1H NMR: δ = 2.44 (s, 3 H, 1-Me), 2.77 (s, 3 H, 4-Me), 3.27 (d, 1 H, *J* = 22.0 Hz, H-9), 3.93 (d, 1 H, *J* = 22 Hz, H-9), 7.18 (m, 1 H, H-12), 7.24 (m, 1 H, H-11), 7.30 (d, 1 H, *J* = 7.25 Hz, H-2), 7.41 (d, 1 H, *J* = 7.3 Hz, H-3), 7.56 (m, 1 H, H-10), 7.67 (d, 1 H, *J* = 8.8 Hz, H-6), 7.75 (s, 2 H, H-7, H-8), 7.84 (d, 1 H, *J* = 8.8 Hz, H-5), 7.73 (d, 1 H, *J* = 7.4 Hz, H-13). − ^{13}C NMR: δ = 19.6 (4-Me), 23.2 (1-Me), 37.6 (C-9), 122.1 (C-13), 122.2 (C-5), 123.4 (C-8), 124.4 (C-10), 125.8 (C-7, C-12), 125.9 (C-6a), 126.0 (C-6), 126.1 (C-11), 127.6 (C-2), 127.7 (C-3), 130.1 (C-13c), 130.6 (C-4), 132.5 (C-1), 132.7 (C-4a), 134.9 (C-13d), 139.3 (C-13b), 142.0 (C-8a), 143.2 (C-13a), 144.1 (C-9a). − MS; *m*/*z* (%): 294 (100) [M^+], 293 (21), 279 (67), 277 (29), 276 (29) 138 (40), 132 (47). − $C_{23}H_{18}$ (294.4): calcd. C 93.84, H 6.16; found C 93.1, H 6.21.

15-Methoxycyclopentahexahelicene (18c): A solution of 3-bromo-4-methoxyindan-1-one (6 g, 24.9 mmol) and diene **15**[3f] (5 g, 24.3 mmol) in CCl_4 (200 mL) was heated at reflux temperature whilst stirring under nitrogen. A CCl_4 solution of triethylamine (3.5 g) was then added dropwise and reflux continued for 48 h. The mixture was then cooled and worked up as usual to afford a 4:1 mixture of two cycloadducts (5.8 g) as shown by GC-MS measurements. Column chromatography using a Merk Lichoprep Si 60 prepacked column (elution with hexane/ethyl acetate 9:1) gave 4.4 g of pure cycloadduct **16c** (50%), m.p. 195°−196°C (ethyl acetate). − IR ($CHCl_3$): $\tilde{\nu}$ = 1700 cm^{-1} (C=O). − ^1H NMR: δ = 1.32 (ddd, 1 H, *J* = 14.3, 13.9, 4.2 Hz, H-7), 2.07 (ddd, 1 H, *J* = 14.4, 13.9, 3.8 Hz, H-8), 2.28 (ddd, 1 H, *J* = 14.3, 3.8, 2.4 Hz, H-7), 2.33 (ddd, 1 H, *J* = 14.4, 4.2, 2.4 Hz, H-8), 2.37 (m, 1 H, H-10), 2.51 (s, 3 H, OMe), 3.04 (ddd, 1 H, *J* = 14.1, 7.3, 2.4 Hz, H-10), 3.06 (ddd, 1 H, *J* = 7.1, 2.4, 2.2 Hz, H-10a), 4.56 (dd, 1 H, *J* = 7.1, 7.0 Hz, H-15b), 4.64 (ddd, 1 H, *J* = 7.0, 2.8, 1.5 Hz, H-15c), 5.89 (ddd, 1 H,

J = 7.3, 3.5, 2.8 Hz, H-9), 6.52 (dd, 1 H, *J* = 7.5, 1.4 Hz, H-14), 7.07 (d, 1 H, *J* = 8.4 Hz, H-6), 7.19 (t, 1 H, *J* = 7.5 Hz, H-13), 7.22 (d, 1 H, *J* = 7.5 Hz, H-12), 7.51 (dd, 1 H, *J* = 8.0, 6.8 Hz, H-3), 7.62 (dd, 1 H, J = 8.4, 6.8 Hz, H-2), 7.65 (d, 1 H, J = 8.4 Hz, H-5), 7.89 (d, 1 H, *J* = 8.0 Hz, H-4), 8.35 (d, 1 H, *J* = 8.4 Hz, H-1). − ^{13}C NMR: δ = 24.4 (C-10), 29.6 (C-7), 30.3 (C-8), 39.0 (C-15c), 42.4 (C-15b), 49.5 (C-10a), 53.9 (OMe), 113.8 (C-14), 113.9 (C-12), 121.9 (C-9), 122.2 (C-1), 124.3 (C-3), 125.7 (C-2), 126.2 (C-5), 126.8 (C-6), 128.3 (C-4), 129.0 (C-13), 132.0 (C-15e), 132.5 (C-15d), 133.2 (C-4a), 137.7 (C-6a), 139.7 (C-8a), 140.0 (C-11a), 143.1 (C-15a), 157.4 (C-15), 209.0 (C-11). − MS; *m/z* (%): 366 (6) [M$^+$], 206 (100), 178 (12), 165 (14). − $C_{26}H_{22}O_2$ (366.5): calcd C 85.22; H 6.05; found C 85.18, H 6.06. − Treatment[3c] of ketone **16c** (3 g, 8.2 mmol) in 1:1 methanol/dichloromethane solution (200 mL) with $NaBH_4$ (3 g) at room temperature for 3 h gave a mixture of alcohols, a solution of which in triglyme (200 mL), was treated over 10% Pd/C catalyst (6 g) at 160°C for 24 h. Then, more catalyst (1.4 g) was added and the mixture heated for 24 h. Usual work up afforded a residue which was purified by chromatography using a Merk Lichoprep Si 60 prepacked column. Elution with petroleum ether/ethyl acetate 49:1 gave 1.5 g of compound **18c** (53%), m.p. 207°−208°C (ethyl acetate). − ^{1}H NMR: δ = 2.47 (s, 3 H, OMe), 4.15 (bd, 1 H, *J* = 22.1 Hz, H-11), 4.45 (bd, 1 H, *J* = 22.1 Hz, H-11), 6.37 (d, 1 H, *J* = 8.0 Hz, H-14), 7.07 (dd, 1 H, *J* = 8.6, 6.8 Hz, H-2), 7.20 (dd 1 H, *J* = 8.0, 7.7 Hz, H-13), 7.26 (d, 1 H, *J* = 7.7 Hz, H-12), 7.37 (dd, 1 H, *J* = 8.1, 6.8, Hz, H-3), 7.83 (d, 1 H, *J* = 8.2 Hz, H-7), 7.84 (d, 1 H, *J* = 8.0 Hz, H-10), 7.89 (d, 1 H, *J* = 8.6 Hz, H-1), 7.91 (d, 1 H, *J* = 8.0 Hz, H-9), 7.92 (d, 1 H, *J* = 8.4 Hz, H-6), 7.94 (d, 1 H, *J* = 8.2 Hz, H-8), 7.96 (d, 1 H, *J* = 8.1 Hz, H-4), 8.0 (d, 1 H, *J* = 8.4 Hz, H-5). − ^{13}C NMR: δ = 38.3 (C-11), 53.5 (OMe), 108.3 (C-14), 116.5 (C-12), 122.4 (C-10), 124.3 (C-8a), 124.7 (C-3), 124.9 (C-2), 125.5 (C-6), 126.0 (C-7), 126.6 (C-1), 126.8 (C-9), 127.0 (C-8), 127.1 (C-5), 127.3 (C-4), 127.5 (C-13), 129.1 (C-15d), 130.5 (C-6a), 130.8 (C-4a), 132.3 (C-15e), 132.7 (C-15c), 133.1 (C-15a), 137.5 (C-15b), 142.5 (C-10a), 144.4 (C-11a), 153.9 (C-15). − MS; *m/z* (%): 346 (100) [M$^+$], 331 (18), 150 (20), 276 (8). − $C_{26}H_{18}O$ (346.4): calcd. C 90.15, H 5.24; found C 90.17, H 5.24.

Diels−Alder Reaction of 1,2-Dihydro-3-vinylphenanthrene (15) with Benzyne: The reaction was carried out according to the procedure described above for compound **14** using: diene **15** (2.5 g, 12.1 mmol), isoamylnitrite (1.6 g, 13 mmol), in DME (30 mL). The reaction mixture was heated at reflux temperature and was then added to a DME (15 mL) solution of anthranilic acid (2.5 g, 18 mmol). After that, a DME solution of isoamylnitrite (1.6 g, 13 mmol) was again added. Usual work up gave a residue (1.5 g) which was shown (GLC) to be a 1.5:1 mixture of two products. A benzene solution (150 mL) of the crude mixture (1.5 g) was treated with DDQ (6 g) at reflux temperature for 24 h. Then, the reaction mixture was worked up as usual to afford a 1.5:1 mixture of compounds **19b** and **19a** which were purified by column chromatography using a Merk Lichoprep Si 60 prepacked column (elution with hexane).

Pentahelicene (19a): Overall yield 0.57 g (17%), m.p. 178−179°C (EtOH) [Lit.[12]: 178°C (EtOH)]. − MS; *m/z* (%): 278 (100) [M$^+$], 206 (26), 94 (11).

5-Phenylpentahelicene (19b): Overall yield 1 g (25%), m.p. 182−183°C (EtOH). − ^{1}H NMR: δ = 7.25 (dd, 1 H, *J* = 8.6, 7.2 Hz, H-12), 7.29 (dd, 1 H, *J* = 7.8, 7.1 Hz, H-9), 7.52 (dd, *J* = 7.6, 7.2 Hz, H-13), 7.52 (dd, 1 H, *J* = 8.4, 7.1 Hz, H-8), 7.53 (m, 1 H, H-4′), 7.54 (m, 2 H, H-3′, H-5′), 7.62 (m, 2 H, H-2′, H-6′), 7.77 (d, 1 H, *J* = 8.5 Hz, H-3), 7.86 (d, 1 H, *J* = 8.6 Hz, H-2), 7.87 (d, 1 H, *J* = 8.5 Hz, H-4), 7.88 (br. s, 1 H, H-6), 7.94 (d, 1 H, *J* = 8.6 Hz, H-1), 7.96 (ddd, 2 H, *J* = 8.4, 7.6, 1.3 Hz, H-7, H-14), 8.47 (d, 1 H, *J* = 8.6 Hz, H-11), 8.52 (d, 1 H, *J* = 7.8 Hz, H-10). − ^{13}C NMR: δ = 124.4 (C-12), 124.5 (C-9), 125.5 (C-4), 126.1 (C-6), 126.2 (C-13), 126.5 (C-8), 126.8 (C-3), 126.9 (C-10c), 127.5 (C-4′), 127.7 (C-2), 127.7 (C-14), 127.8 (C-10c), 127.8 (C-1), 127.9 (C-7), 128.4 (C-3′, C-5′), 129.0 (C-11), 129.2 (C-10), 130.4 (C-10d), 130.5 (C-2′, C-6′), 131.1 (C-2a, C-10a), 131.9 (C-14a), 131.9 (C-4a), 132.6 (C-6a), 138.2 (C-5), 140.8 (C-1′). − MS; *m/z* (%): 354 (100) [M$^+$], 278 (16), 206 (16), 195 (35), 178 (21). − $C_{28}H_{18}$ (354.4): calcd. C 94.88, H 5.12; found C 94.92, H 5.12.

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