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Hydrogenation and Dehydrogenation of Pentaphenylcyclopentadienes and Pentaphenylcyclopentenes

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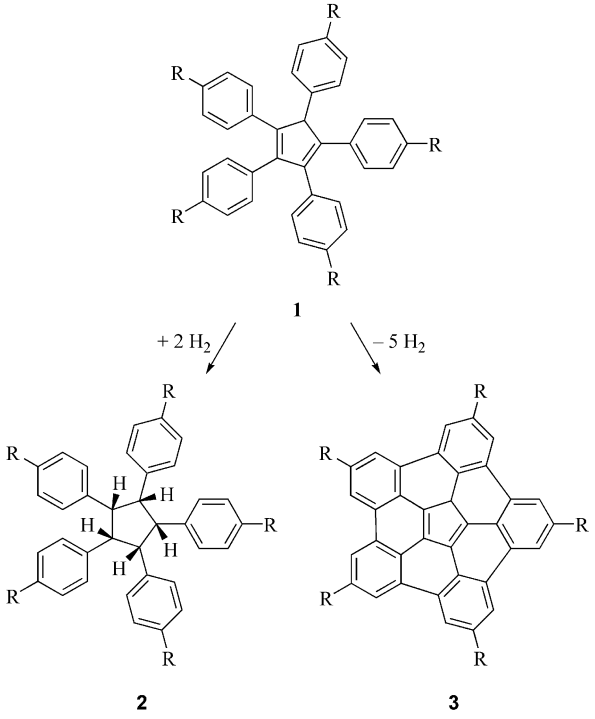
Pentaaryl-substituted cyclopentadienes and cyclopentenes have been employed in catalytic hydrogenation and photochemical cyclodehydrogenation reactions, targeting strained bowl-shaped structures. Both types of reactions generally stop at the monohydrogenation and monocyclization stage, respectively.

Introduction

Non-planar polycyclic compounds with arenes conformationally fixed in a bowl-shaped structure are favourite objects in various fields of chemical research. Calixarenes[1,2] and resorcinarenes[1,3] in supramolecular chemistry are prominent examples, as well as fullerene fragments[4] in material science.



Scheme 1. Spherical target structures **2** and **3** from the reduction and oxidation of cyclopentadiene **1**.

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During our ongoing studies on the synthesis and applications of pentaarylcyclopentadienes[5,6] we noticed that both hydrogenation and dehydrogenation of pentaarylcyclopentadienes **1** should lead to spherical structures with spatially adjusted functional groups. The transformation to the rather strained ultimate target structures (Scheme 1), the circulene **3** and the *all-cis*-cyclopentane **2** with five aryl substituents resembling the fingers of a hand, should be difficult to achieve because of ring and steric strain. However, the corresponding intermediates, monohydrogenated and monocyclized products, deserve attention.

Herein we describe our attempts to hydrogenate pentaarylcyclopentadienes at the central double bonds as well as to oxidatively cyclize them at the aryl moieties and to finally combine these two transformations.

Results and Discussion

Hydrogenation of Cyclopentadienes

We started our investigations with the hydrogenation of cyclopentadienes **1a**–**c** (Scheme 2). The pentamethyl- and pentaester-substituted pentaarylcyclopentadienes **1b** and **1c** were smoothly monohydrogenated with palladium on charcoal at 3 bar within 2 days in 86 and 89% isolated yields, respectively. In comparison, pentaphenylcyclopentadiene (**1a**) reacted rather sluggishly under similar hydrogenation conditions. Because of the poor solubility of **1a** in methanol and ethyl acetate a 1:1 mixture of chloroform and ethyl acetate was chosen as the reaction medium. After 7 days at a hydrogen pressure of 3 bar, with the addition of fresh catalyst after 3 days, only 33% of **1a** was converted into the cyclopentene **4a**. However, an exceptional yield of 60% of **4a** has been reported for the catalytic hydrogenation in acetic acid.[7,8]

We also found that cyclopentene **4a** could also be obtained by the hydrogenation of pentaphenylcyclopentadienol (**5a**), a reaction that was highly dependent on the

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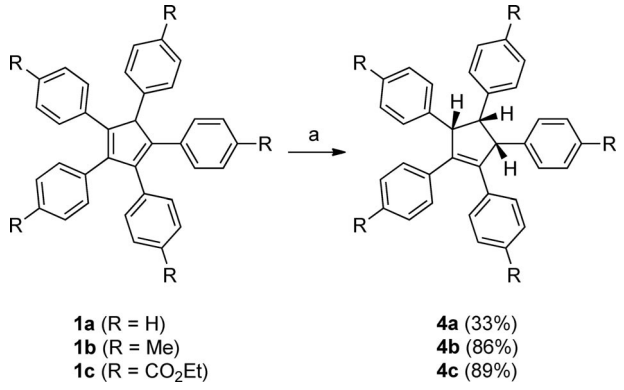
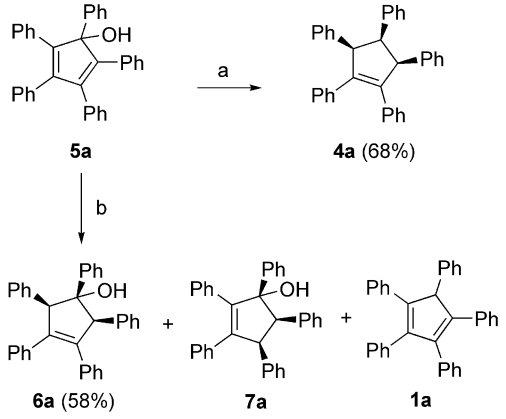


Scheme 2. Catalytic hydrogenation of cyclopentadienes **1a**–**c**. Reagents and condtions: a) Pd/C, H_2, 3 bar, 2 d, EtOAc (**4b** and **4c**), EtOAc/$CHCl_3$ (**4a**), 7 d. The yield of **4a** was estimated by ^{1}H NMR spectroscopy.

choice of solvent and catalyst (Scheme 3). Thus, the hydrogenation of **5a** in the presence of an excess of Raney nickel mainly yielded the dehydroxylated[9] cyclopentene **4a**, whereas palladium on charcoal led to the regio- and stereoselective formation of the symmetrical cyclopentenol **6a** as the main product when a 7:1 mixture of ethyl acetate/methanol was used as solvent. In addition, minor amounts of the regular 1,2-hydrogenated cyclopentenol **7a**, cyclopentene **4a** and pentaphenylcyclopentadiene (**1a**) were observed in the crude reaction mixture, the latter clearly deriving from water elimination from the quite acid-sensitive **7a**. Changing to the acidic ethyl acetate/acetic acid combination as solvent, again in a 7:1 ratio, a 1:1 mixture of the hydrogenation products **4a** and **6a** were obtained according to the ^{1}H NMR spectrum of the crude product.

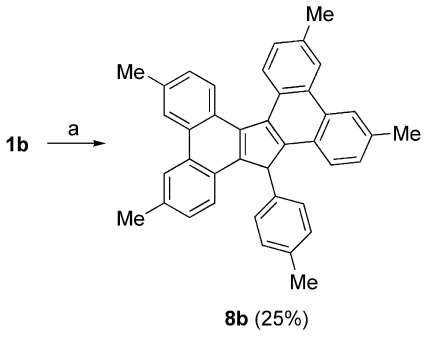


Scheme 3. Catalytic hydrogenation of cyclopentadienol **5a** to cyclopentene **4a** and cyclopentenols **6a** and **7a**, respectively. Reagents and conditions: a) Raney nickel, H_2, 3 bar, 2 d, EtOAc/MeOH 5:1; b) Pd/C, H_2, 3 bar, 2 d, EtOAc/MeOH 7:1.

Most importantly, all hydrogenation reactions of the cyclopentadiene moiety were accompanied by partial reduction of the phenyl rings.[10] Thus, the phenyl rings are much more susceptible to hydrogenation than the isolated but sterically shielded double bond of the cyclopentene. Thus, a complete hydrogenation of the cyclopentadiene to the *all-cis*-cyclopentane will be unfeasible without affecting the phenyl rings even when applying higher pressure. Also, our attempts to reduce the double bond with diimide or by hydroboration failed. Thus, *all-cis* cyclopentanes of type **2** remain a real challenge for synthesis.

Photo-Oxidation of Cyclopentadienes 1 and Cyclopentadienol 5a

To achieve target structure **3** we tried several cyclodehydrogenation reactions, first, by photochemical oxidation of the unsubstituted pentaphenylcyclopentadienol (**5a**) and pentaphenylcyclopentadiene (**1a**). Surprisingly, standard reaction conditions, which reliably convert stilbenes into phenanthrenes,[11] did not lead to any clean reactions. Both model substrates were virtually unreactive towards prolonged irradiation times (7 days). Also, varying the solvent did not improve the result. On the other hand, the pentatolyl-substituted cyclopentadiene **1b**, a derivative of **1a**, was converted into the bis-phenanthrene **8b** in 25% isolated yield in a non-photo-oxidative approach with $AlCl_3$ and $CuCl_2$[12] (Scheme 4). Nevertheless, complete oxidation to circulene **3** was not observed.



Scheme 4. Cyclodehydrogenation of cyclopentadiene **1b** to bisphenanthrene **8b**. Reagents and conditions: a) $AlCl_3/CuCl_2$, CS_2, room temperature, 5 min.

Photo-Oxidation of Cyclopentenes

In contrast to the unreactive cyclopentadiene moiety, we considered the cyclopentenes **4** to be more promising substrates for photochemical phenanthrene formation. The cyclopentenes were thus employed in a photochemical cyclodehydrogenation reaction. Typically, the *all-cis*-pentaphenylcyclopentene (**4a**) was irradiated in oxygen-free toluene with iodine as oxidant (Scheme 5).

Surprisingly, **4a** produced the epimerized asymmetrical phenanthrene **10a** in 71% isolated yield (Table 1). This radical-driven epimerization clearly transfers one phenyl group to a less sterically demanding *trans* position, as shown in Scheme 5. Monitoring the process by ^{1}H NMR spectroscopy suggested that the epimerization is faster than the cyclization to the dihydrophenanthrene. Thus, the isomerized cyclopentene **9a** was observed as an intermediate to the final product **10a** and was isolated from an incomplete reaction for characterization.

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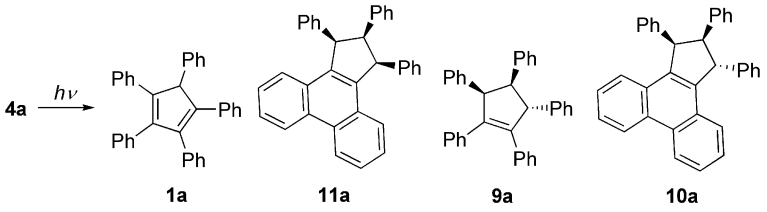
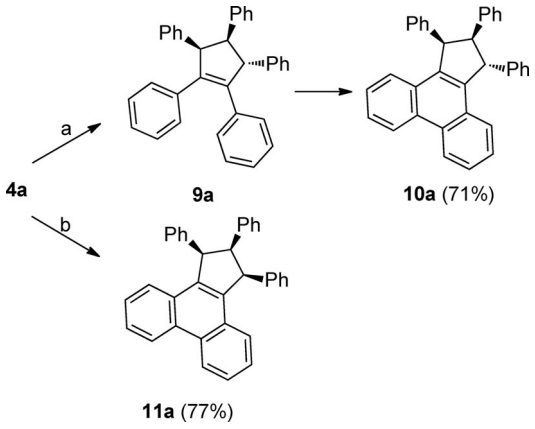
Table 1. Photochemical conversion of cyclopentene **4a**.



Solvent	Ar	Oxidant[a]	*t* [h]	**1a**[b]	**11a**[b]	**9a**[b]	**10a**[b]
$PhCH_3$	+	iodine	15	14	–	43 (23)	43 (33)
$PhCH_3$	+	iodine	33	–	–	Traces	(71)
$PhCH_3$	+	–	4.5	–	–	–	–
MeOH	+	iodine	16	83	17	–	–
$PhCH_3$	–	iodine, air	40	(33)[c]	–	–	–
$PhCH_3$	–	air	38	23[d]	(77)	–	–

[a] Iodine was used in excess (2 equiv.). [b] The ratio of the major components was determined by ^{1}H NMR analysis of the crude reaction mixture. Isolated yields are given in parentheses. [c] Isolated as its oxidation product (diepoxide). [d] The ratio of **1a** was not always well reproducible.

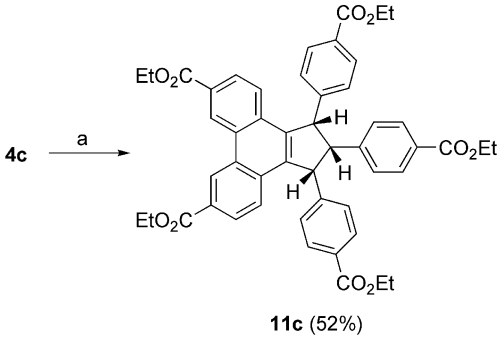


Scheme 5. Formation of the epimeric phenanthrenes **10a** and **11a** from cyclopentene **4a**. Reagents and conditions: a) *hv*, I_2, Ar, toluene, 33 h; b) *hv*, air, toluene, 33 h. The radical-driven formation of **9a** preceeds the photocyclization–oxidation to **10a**.

Unexpectedly, changing from oxygen-free toluene to oxygen-free methanol as solvent, the irradiation of **4a** produced the *all-cis*-phenanthrene **11a** and pentaphenylcyclopentadiene (**1a**), an oxidation product of **4a**, in a preparatively poor ratio (1:5 in favour of the cyclopentadiene **1a**). In addition, the poor solubility of the starting material in methanol rendered any optimization unnecessary.

Hence we attempted to change the oxidant to gain access to the symmetrical phenanthrene **11a** in preparatively valuable amounts. We considered air to be more suited than iodine to overcoming the problem of radical-induced epimerization of the starting *all-cis*-pentaphenylcyclopentene (**4a**). Indeed, the irradiation of **4a** in air-saturated toluene in the absence of iodine afforded the desired phenanthrene **11a** in 77% isolated yield (Scheme 5). Attempts to hydrogenate **11a**, targeting a monocyclized derivative of **2**, did not lead to any conversion at the 9,10-double bond of the phenanthrene unit.

In sharp contrast to the unsubstituted system **4a**, the ester-functionalized pentaphenylcyclopentene **4c** furnished the expected symmetrical phenanthrene **11c** in oxygen-free toluene with iodine as oxidant (Scheme 6). This result suggests that the ester functionality in **4c** somehow suppresses the epimerization mechanism that proceeded under identical conditions with **4a**.



Scheme 6. Photochemical oxidation of cyclopentene **4c** to phenanthrene **11c**. Reagents and conditions: a) *hv*, I_2, N_2, toluene, 24 h.

A combination of oxygen and iodine as oxidants, reported to be advantageous[13] for shorter reaction times and cleaner reactions, unfortunately in the case of **4a** gave a complex reaction mixture that included minor amounts of phenanthrene derivatives, as concluded by the diagnostic downfield signals in the ^{1}H NMR spectrum. Only an oxidation product of pentaphenylcyclopentadiene was isolated, the NMR spectra of which were in accord with the structure of the diepoxide, a known photoinduced rearrangement product of the endoperoxide of **1a**.[14]

Photo-Oxidation of Cyclopentenol 6a

Consequently, we were interested in the behaviour of cyclopentenol **6a** under oxidative photocyclization conditions (Table 2). The product distribution turned out to be strongly influenced by the choice of solvent and oxidant. Surprisingly, irradiation of homoallylic alcohol **6a** in oxygen-free toluene as solvent and iodine as oxidant did not

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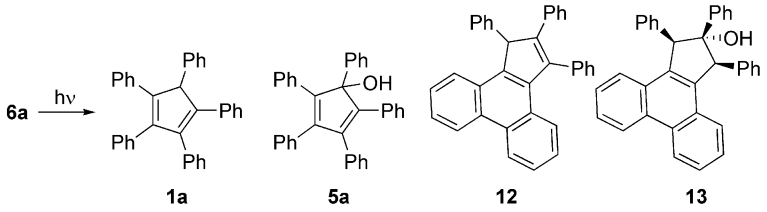
Table 2. Photochemical conversion of cyclopentenol **6a**.

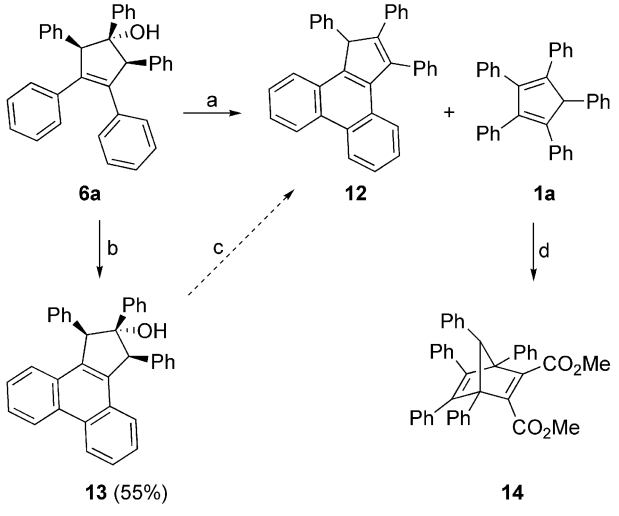


Solvent	Ar	Oxidant[a]	*t* [h]	Additive	**1a**[b]	**5a**[b]	**12**[b]	**13**[b]
$PhCH_3$	+	iodine	15	–	25	75	–	–
$PhCH_3$	+	iodine	12	K_2CO_3	50	50	–	–
$PhCH_3$	+	iodine	15	NEt_3	100	–	–	–
MeOH[c]	+	iodine	19	–	50	–	50	–
MeOH	–	iodine	16	K_2CO_3	–	–	–	20[d]
MeOH	–	iodine	10	–	–	–	–	(41)
$PhCH_3$	–	air	40	–	–	–	–	(55)

[a] Iodine was used in excess (2 equiv.). [b] The ratio of the major components was determined by ^{1}H NMR analysis of the crude reaction mixture. Isolated yields are given in parentheses. [c] In one (not reproducible) experiment **5a** was observed instead of **1a**. [d] 80% unconverted starting material.

give any cyclization products, but yielded the simple oxidation products cyclopentadienol **5a** and cyclopentadiene **1a**, respectively.

Changing to methanol as solvent led to the formation of phenanthrene **12**. The reaction in oxygen-free methanol in the presence of iodine yielded an approximately 1:1 mixture of phenanthrene **12**[15] and pentaphenylcyclopentadiene (**1a**), which were separated by trapping the non-cyclized by-product **1a** as the Diels–Alder adduct with dimethyl acetylenedicarboxylate[16] (Scheme 7). However, the best result with a 55% isolated yield of annulated phenanthrene **13** was obtained by using a toluene/air combination. Although **12** is formally a photocyclization–oxidation product from pentaphenylcyclopentadiene **1a**, we have already proved **1a** to be virtually unreactive towards photocyclization. Therefore we assume that phenanthrene **13** is an intermediate of **12**, obtained then by elimination of water under the acidic conditions provided by the simultaneously formed HI. Indeed, air as oxidant in the absence as well as in the presence of iodine provides less acidic conditions, thus enabling the isolation of the acid-sensitive phenanthrene derivative **13** (Scheme 7).



Scheme 7. Formation of phenanthrenes **12** and **13** from cyclopentenol **6a** in the presence and absence of oxygen, respectively. The transformation d is necessary for the separation of **12** and **1a**. Reagents and conditions. a) *hv*, MeOH, I_2, Ar, 22 h; b) *hv*, toluene, O_2. 68 h; c) *hv*, MeOH, I_2, Ar, **6a**; d) dimethyl acetylenedicarboxylate, toluene, 110 °C, 16 h.

Conclusions

We have investigated the reactivity of pentaarylated cyclopentadienes and cyclopentenes in hydrogenation and dehydrogenation reactions. The product distribution of the hydrogenation of the cyclopentadienes strongly depended on the solvent and catalyst. We also confirmed the complete hydrogenation of the cyclopentadiene moiety to bowl-shaped *all-cis*-cyclopentanes to be unfeasible because the phenyl groups are more susceptible to hydrogenation than the sterically shielded cyclopentene moiety. The aryl-substituted cyclopentadienes did not show clean photo-oxidation to phenanthrenes. Instead we succeeded through a non-photochemical oxidation reaction to synthesize a bis-phenanthrene as a double cyclization product. In contrast, the arylated cyclopentenes exhibited a significant reactivity in the cyclodehydrogenation reactions to phenanthrenes by standard photochemical pathways, the product distribution being highly dependent on the choice of solvent and oxidant.

Experimental Section

General: Melting points were determined with Reichert Thermovar and Büchi (Dr. Tottoli) instruments. Infrared spectroscopy was performed with a Perkin–Elmer 983 and a Bruker Equinox 55 spectrometer. UV/Vis spectra were recorded with Perkin–Elmer Lambda 40 and Varian Cary 1 spectrophotometers. ^{1}H and ^{13}C

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NMR spectra were recorded with the Bruker DPX 200, DRX 400 and DRX 600 spectrometers. Spectra were calibrated with the residual solvent peak or with TMS as the internal standard. Mass spectrometry was performed with Varian MAT 311A ITD and MATCH5 (70 eV) spectrometers. For analytical TLC, precoated plastic sheets "POLYGRAM SIL G/UV_{254}" from Macherey–Nagel were used. Elemental analyses were determined with a Euro Elemental Analyzer 3000. The irradiations were conducted with a mercury high-pressure lamp (Philips HPK 125 W). For experiments performed under oxygen exclusion, either argon or nitrogen was bubbled through the reaction solution vigorously for 30 min before the irradiation was started. A constant but slow flow of inert gas was sustained throughout the reaction. The procedure was identical when air was used as the oxidant. Pressurized air from the standard laboratory supply was used for this purpose. Solvents for irradiation were distilled prior to use. THF was dried with sodium/benzophenone and freshly distilled prior to use.

Chemicals were used as received. Pentaphenylcyclopentadienes **1b** and **1c** were synthesized by the palladium-catalyzed arylation of cyclopentadiene.[6]

Pentaphenylcyclopentadiene (1a): Tetracyclone (1.40 g, 3.64 mmol) was dissolved in dry THF (50 mL) and phenyllithium (3.0 mL, 2 M in cyclohexane/Et_2O, 6.0 mmol) was added at once at room temperature. The mixture was stirred for 15 min and $LiAlH_4$ was added within 10 min. The mixture was then stirred for 30 min and hydrolyzed with satd. aq. NH_4Cl (40 mL). The layers were separated and the organic layer was extracted with CH_2Cl_2 (2 × 20 mL). The extracts were dried with Na_2SO_4 and the solvents evaporated. The residue was treated in an ultrasonic bath with MeOH (5 mL) until a precipitate formed. Pentaphenylcyclopentadiene (**1a**) was obtained by filtration as an off-white solid (1.27 g, 78%) with m.p. 250 °C (ref.[17] 248–250 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.09 (s, 1 H), 6.94–7.25 (m, 25 H) ppm.

***all-cis*-1,2,3,4,5-Pentaphenylcyclopentene (4a):** Ni–Al alloy (1.5 g) was suspended in H_2O (15 mL) and sodium hydroxide pellets (2.3 g) were added portionwise to keep the mixture boiling. The mixture was left to stand for 10 min and was then placed in a water bath (70 °C) and kept there for 30 min. The water was decanted and the Raney nickel was washed twice each with water, ethanol and ethyl acetate. Alcohol **5a** (500 mg, 1.08 mmol) and the freshly prepared Raney nickel were suspended in ethyl acetate/methanol (5:1, 100 mL) and the mixture was hydrogenated under a hydrogen pressure of 3 bar for 2 d. The nickel catalyst was filtered off and the filtrate was evaporated. The residue was repeatedly crystallized from dichloromethane/methanol to give cyclopentene **4a** as colourless crystals (340 mg, 68%) with m.p. 213 °C (ref.[7] 217 °C). The substance is known in the literature[7] but has not been completely characterized. IR (KBr): $\tilde{\nu}$ = 3102 (w), 3082 (w), 3054 (m), 3028 (m), 2915 (w), 2881 (w), 2861 (w), 1597 (m), 1573 (w), 1491 (s), 1451 (s), 1442 (s), 1345 (w), 1304 (w), 1284 (w), 1266 (w), 1228 (w), 1203 (w), 1176 (m), 1153 (w), 1114 (w), 1074 (m), 1029 (m), 1001 (w), 989 (w), 968 (w), 912 (m), 873 (w), 844 (w), 812 (w), 784 (s), 761 (vs), 724 (s), 706 (vs), 695 (vs) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.61 ("t", J = 9.3 Hz, 1 H, 4-H), 4.75 (d, J = 9.2 Hz, 2 H, 3-H, 5-H), 6.06 (dd, J = 8.1, 1.0 Hz, 2 H, Ph-*o*-H), 6.78 (t, J = 7.7 Hz, 2 H, Ph-*m*-H), 6.93–6.97 (tt, J = 7.4, 1.1 Hz, 1 H, Ph-*p*-H), 7.04 ("s", 10 H, Ph-H), 7.13–7.16 (m, 6 H, Ph-H), 7.29–7.33 (m, 4 H, Ph-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.1 (C-4), 61.2 (C-3, C-5), 126.1, 126.4, 126.7, 127.3, 127.7, 128.4, 129.6, 130.9 (all CH Ph), 132.1 (*o*-CH Ph), 138.1, 138.6, 141.1, 142.0 (all s) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 230 (4.19), 260 (3.98) nm. MS (EI, 70 eV): *m*/*z* (%) = 448 (100) [M]$^+$, 370 (79), 357 (73). $C_{35}H_{28}$ (448.60): calcd. C 93.71, H 6.29; found C 93.66, H 6.28.

***all-cis*-1,2,3,4,5-Pentakis(4-methylphenyl)cyclopentene (4b):** A solution of cyclopentadiene **1b** (258 mg, 0.50 mmol) in EtOAc (100 mL) was hydrogenated with Pd/C (50 mg, 10% Pd) under a hydrogen pressure of 3 bar for 2 d. The catalyst was filtered off and the filtrate was evaporated. The residue was submitted to flash column chromatography (silica, PE, R_f = 0.06; 0.00). The fraction with R_f = 0.06 afforded cyclopentene **4b** (223 mg, 86%) as colourless crystals with m.p. 212 °C. IR (KBr): $\tilde{\nu}$ = 3020 (m), 2920 (m), 2879 (w), 1611 (m), 1509 (s), 1449 (w), 1188 (w), 1182 (w), 1020 (w), 820 (s), 790 (m), 736 (m) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, CH_3), 2.19 (s, 6 H, CH_3), 2.23 (s, 6 H, CH_3), 4.45 (t, J = 9.2 Hz, 1 H, 4-H), 4.58 (d, J = 9.1 Hz, 2 H, 3-H, 5-H), 5.95 (d, J = 8.0 Hz, 2 H, Ph-*o*-H), 6.58 (d, J = 8.0 Hz, 2 H, Ph-*m*-H), 6.81 (d, J = 8.0 Hz, 4 H, Ph-*m*-H), 6.88 (d, J = 8.0 Hz, 4 H, Ph-*o*-H), 6.92 (d, J = 8.0 Hz, 4 H, Ph-*o*-H), 7.16 (d, J = 8.0 Hz, 4 H, Ph-*m*-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.1 (CH_3), 21.2 (CH_3), 21.3 (CH_3), 54.5 (C-4), 60.7 (C-3, C-5), 127.2, 128.1, 128.9, 129.2, 130.6, 131.8 (all CH Ph), 135.0, 135.3, 135.6, 136.5 (all C Ph), 138.1 (C-1, C-2), 141.1 (C Ph) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 209 (3.99), 264 (3.23) nm. MS (FAB): *m*/*z* (%) = 518 (100) [M]$^+$. $C_{40}H_{38}$ (518.73): calcd. C 92.62, H 7.38; found C 92.23, H 6.96.

***all-cis*-1,2,3,4,5-Pentakis(4-ethoxycarbonylphenyl)cyclopentene (4c):** A solution of cyclopentadiene **1c** (403 mg, 0.50 mmol) in EtOAc (100 mL) was hydrogenated with Pd/C (50 mg, 10% Pd) under a hydrogen pressure of 3 bar for 2d. The catalyst was filtered off and the filtrate was evaporated. The residue was submitted to flash column chromatography (silica, PE/MTBE, 2:1, R_f = 0.12; 0.00). The fraction with R_f = 0.12 afforded cyclopentene **5c** (360 mg, 89%) as colourless crystals with m.p. 247 °C. IR (KBr): $\tilde{\nu}$ = 2982 (m), 2936 (w), 1719 (s), 1608 (m), 1407 (m), 1367 (m), 1276 (s), 1180 (m), 1106 (s), 1021 (m), 859 (w), 775 (w), 715 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32–1.37 (m, 15 H, CH_3), 4.27–4.35 (m, 10 H, OCH_2), 4.75 ("t", J = 9.0 Hz, 1 H, 4-H), 4.87 (d, J = 9.0 Hz, 2 H, 3-H, 5-H), 6.15 (d, J = 8.3 Hz, 2 H, Ph-H), 7.06 (d, J = 8.2 Hz, 4 H, Ph-H), 7.29 (d, J = 8.3 Hz, 4 H, Ph-H), 7.46 (d, J = 8.4 Hz, 2 H, Ph-H), 7.75 (d, J = 8.2 Hz, 4 H, Ph-H), 7.82 (d, J = 8.4 Hz, 4 H, Ph-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4 (CH_3), 54.5 (C-4), 60.8 (C-3, C-5), 61.0 (OCH_2), 61.1 (OCH_2), 128.3 (CH Ph), 128.9 (C Ph), 129.2 (CH Ph), 129.3 (CH Ph), 129.5 (C Ph), 129.8 (CH Ph), 129.8 (C Ph), 130.3 (CH Ph), 131.5 (CH Ph), 141.2 (C Ph), 142.2 (C Ph), 142.7 (C Ph), 144.9 (C Ph), 166.2 (CO), 166.4 (CO), 166.6 (CO) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 204 (4.30), 244 (4.24), 368 (3.23) nm. MS (EI, 70 eV): *m*/*z* (%) = 808 (34) [M]$^+$, 763 (100) [M – OCH_2CH_3]$^+$. $C_{50}H_{48}O_{10}$ (808.91): calcd. C 74.24, H 5.98; found C 74.29, H 5.56.

Pentaphenylcyclopentadienol (5a): Tetracyclone (1.37 g, 3.57 mmol) was dissolved in dry THF (70 mL) and phenyllithium (3.0 mL, 2 M in cyclohexane/Et_2O, 6.0 mmol) was added at once at room temperature. The mixture was stirred for 15 min and hydrolyzed with water. The mixture was extracted with MTBE (2 × 20 mL) and the organic extracts were dried with Na_2SO_4 and the solvents evaporated. The residue was treated in the ultrasonic bath with methanol/petroleum ether (1:1, 5 mL) until a precipitate formed. Cyclopentadienol **5a** was obtained by filtration as a colourless solid (1.26 g, 76%) with m.p. 174–175 °C (ref.[18] 175–176 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.25 (s, 1 H, OH), 6.96–7.07 (m, 14 H), 7.09–7.17 (m, 6 H), 7.20–7.31 (m, 3 H), 7.57 (dd, J = 8.2, 1.4 Hz, 2 H) ppm.

(1*r,2*R**,5*S**)-1,2,3,4,5-Pentaphenylcyclopent-3-enol (6a):** A solution of pentaphenylcyclopentadienol (**5a**; 440 mg, 0.95 mmol) in ethyl acetate/methanol (7:1, 100 mL) was hydrogenated with Pd/C (50 mg, 10% Pd) under a hydrogen pressure of 3 bar for 2 d. The

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catalyst was filtered off and the filtrate was evaporated. The residue was submitted to flash column chromatography [silica, toluene, R_f = 0.90 (**4a**, hydrogenated derivatives, **1a**), 0.33, 0.19]. The fraction with R_f = 0.33 contained allylic alcohol **7a** (30 mg, 7%) as a colourless solid that easily decomposed to pentaphenylcyclopentadiene (**1a**). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.24 (s, 1 H, OH), 4.48 (d, J = 9.9 Hz, 1 H, 4-H/5-H), 5.08 (d, J = 9.8 Hz, 1 H, 4-H/5-H), 5.99 (d, J = 7.2 Hz, 2 H), 6.76 (t, J = 7.5 Hz, 2 H), 6.87–7.02 (m, 6 H), 7.11–7.17 (m, 6 H), 7.19–7.28 (m, 5 H), 7.34–7.41 (m, 4 H) ppm. MS (EI, 70 eV): m/z (%) = 464 (1) $[M]^+$, 446 (100) $[M - H_2O]^+$. The fraction with R_f = 0.19 afforded the cyclopentenol **6a** (257 mg, 58%) as a colourless solid with m.p. 191 °C. IR (KBr): $\tilde{\nu}$ = 3568 (w), 3082 (w), 3060 (m), 3025 (m), 2923 (w), 2899 (w), 2866 (w), 1597 (m), 1493 (m), 1443 (m), 1381 (w), 1381 (w), 1332 (w), 1280 (w), 1261 (w), 1214 (w), 1180 (m), 1156 (w), 1090 (w), 1076 (w), 1066 (w), 1042 (m), 1027 (m), 1003 (w), 988 (m), 967 (w), 913 (w), 879 (w), 848 (w), 817 (w), 784 (m), 771 (m), 761 (s), 753 (m), 722 (s), 711 (s), 698 (vs), 616 (w), 590 (w), 572 (m), 543 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.97 (s, 1 H, OH), 4.62 (s, 2 H, 2-H, 5-H), 6.40 (dd, J = 8.3, 0.9 Hz, 2 H, Ph-*o*-H), 6.75 ("t", J = 7.8 Hz, 2 H, Ph-*m*-H), 6.90 (tt, J = 7.3, 1.1 Hz, 1 H, Ph-*p*-H), 7.03 (s, 10 H, Ph-H), 7.12–7.15 (m, 6 H, Ph-H), 7.29–7.33 (m, 4 H, Ph-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 77.23 (C-2, C-5), 86.47 (C-1), 125.90 (*m*-CH Ph), 126.16 (*p*-CH Ph), 126.77, 127.44, 127.76, 128.33, 128.36, 129.50, 130.83 (all CH Ph), 137.62, 139.24, 139.37 (all C Ph), 140.51 (C-3, C-4) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 213 (4.42), 263 (sh, 3.56) nm. MS (FAB): m/z (%) = 487 (6) $[M + Na]^+$, 464 (16) $[M]^+$, 447 (69) $[M - OH]^+$, 269 (100). $C_{35}H_{28}O$ (464.60): calcd. C 90.48, H 6.07; found C 90.39, H 5.85.

3,6,11,14-Tetramethyl-17-(4-methylphenyl)-17*H*-cyclopenta[1,2-*l*:3,4-*l'*]diphenanthrene (8b): $CuCl_2$ (269 mg, 2.00 mmol), $AlCl_3$ (267 mg, 2.00 mmol) and cyclopentadiene **1b** (516 mg, 1.00 mmol) in CS_2 (200 mL) were stirred for 5 min at room temperature. After dilution with ethanol (200 mL) the resulting precipitate was filtered off and washed with ethyl acetate (100 mL). The collected filtrates were concentrated in vacuo and the residue was submitted to flash column chromatography (silica, PE, R_f = 0.06; 0.00). The fraction with R_f = 0.06 gave polycycle **8b** (133 mg, 25%) as bright-yellow crystals with m.p. 246 °C. IR (KBr): $\tilde{\nu}$ = 3022 (w), 2920 (m), 2862 (w), 1606 (w), 1512 (s), 1442 (w), 1407 (w), 1384 (w), 1182 (w), 1129 (w), 1106 (w), 1034 (w), 1021 (w), 819 (s), 771 (w), 738 (w), 723 (w), 699 (m), 692 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 2.56 (s, 6 H, CH_3), 2.67 (s, 6 H, CH_3), 5.75 (s, 1 H, 17-H), 6.93 (d, J = 8.0 Hz, 2 H, Ph-H), 7.15 (d, J = 8.0 Hz, 2 H, Ph-H), 7.29 (d, J = 8.1 Hz, 2 H, 2-H, 15-H), 7.45 (d, J = 8.3 Hz, 2 H, 7-H, 10-H), 7.96 (d, J = 8.1 Hz, 2 H, 1-H, 16-H), 8.47 (s, 2 H, 4-H, 13-H), 8.55 (s, 2 H, 5-H, 12-H), 8.62 (d, J = 8.2 Hz, 2 H, 8-H, 9-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3), 22.15 (CH_3), 22.2 (CH_3), 54.8 (C-17), 123.1 (C-4, C-13), 123.5 (C-5, C-12), 124.4 (C-1, C-16), 126.4 (C-8a, C-8d), 126.7 (C-7, C-10), 127.2 (C-16a, C-17b), 127.8 (C-8, C-9), 128.6 (C-2, C-15), 128.67 (CH Ph), 129.7 (CH Ph), 130.6 (C-4a, C-12b), 131.7 (C-4b, C-12a), 135.3 (C-6, C-11), 135.4 (C-3, C-14), 136.1 (C Ph), 136.1 (C-8b, C-8c), 138.4 (C Ph), 144.4 (C-16b, C-17a) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 214 (4.29), 218 (4.33), 254 (4.27), 340 (3.91) nm. MS (FAB): m/z (%) = 512 (100) $[M]^+$. $C_{40}H_{32}$ (512.68): calcd. C 93.71, H 6.29; found C 93.33, H 6.15.

(3*R,5*R**)-1,2,3,4,5-Pentaphenylcyclopentene (9a):** A solution of pentaphenylcyclopentene (**4a**) (300 mg, 0.65 mmol) and iodine (167 mg, 1.31 mmol) in deoxygenated toluene (250 mL) was irradiated for 15 h under argon. The solution was concentrated and washed with satd. aq. Na_2SO_3 (10 mL). After drying over Na_2SO_4 and evaporation the residue was dissolved in toluene (5 mL) in a screw-capped flask and dimethyl acetylenedicarboxylate (0.02 mL, 0.16 mmol) was added. The mixture was heated at 110 °C for 12 h. Toluene was evaporated and the residue was submitted to flash column chromatography (silica, pentane). The fraction with R_f = 0.22 (pentane, 7 runs) yielded phenanthrene **10a** (100 mg, 33%). The fraction with R_f = 0.26 (PE/EtOAc, 20:1) afforded isomerized cyclopentene **9a** (68 mg, 23%) as a colourless solid. Recrystallization from CH_2Cl_2/MeOH gave colourless crystals with m.p. 176–177 °C. IR (KBr): $\tilde{\nu}$ = 3078 (w), 3057 (w), 3021 (m), 2998 (w), 2896 (m), 2881 (w), 2854 (w), 1600 (m), 1576 (w), 1560 (w), 1541 (w), 1490 (m), 1444 (m), 1385 (w), 1335 (w), 1310 (w), 1223 (w), 1193 (w), 1158 (w), 1111 (w), 1070 (m), 1028 (m), 1002 (w), 983 (w), 960 (w), 907 (w), 874 (w), 857 (w), 806 (w), 790 (m), 777 (m), 764 (s), 726 (m), 692 (s), 659 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.09 ("t", J = 9.1 Hz, 1 H, 4-H), 4.76 (dd, J = 8.5, 1.6 Hz, 1 H, 3-H/5-H), 4.91 (dd, J = 9.7, 1.6 Hz,1 H, 3-H/5-H), 6.87–6.94 (m, 4 H, Ph-H), 7.00–7.15 (m, 19 H, Ph-H), 7.21–7.24 (m, 2 H, Ph-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 59.07 (C-3/C-5), 60.72 (C-3/C-5), 60.93 (C-4), 126.18, 126.31, 126.36, 126.84, 127.02, 127.69, 128.00, 128.10, 128.15, 128.28, 128.83, 129.10, 129.27, 129.35, 129.40 (all CH Ph), 137.12 (C Ph), 137.24 (C Ph), 139.72, 139.74, 141.21, 142.55, 142.84 (all s) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 225 (4.34), 259 (4.16), 265 (4.17) nm. MS (EI, 70 eV): m/z (%) = 448 (100) $[M]^+$, 370 (90) $[M - Ph - 1]^+$, 357 (60). $C_{35}H_{28}$ (448.60): calcd. C 93.71, H 6.29; found C 93.64, H 6.30.

(1*R,3*R**)-1,2,3-Triphenyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (10a):** A solution of cyclopentene **4a** (135 mg, 0.30 mmol) and iodine (78 mg, 0.6 mmol) in deoxygenated toluene (250 mL) was irradiated for 33 h under argon. The solvent was evaporated and the residue was dissolved in dichloromethane and washed with aq. satd. Na_2SO_3 to remove iodine. The organic layer was dried with Na_2SO_4 and dichloromethane was removed in vacuo. The residue was subjected to flash column chromatography (silica, pentane, 7 runs; R_f = 0.22, 0.26, 0.32). The fraction with R_f = 0.22 gave phenanthrene **10a** (95 mg, 71%) as a colourless solid. Recrystallization from dichloromethane/petroleum ether afforded colourless crystals with m.p. 199–200 °C. IR (KBr): $\tilde{\nu}$ = 3101 (w), 3073 (w), 3059 (w), 3023 (m), 3002 (w), 2982 (w), 2856 (w), 1599 (m), 1489 (m), 1450 (m), 1429 (w), 1393 (w), 1336 (w), 1312 (w), 1264 (w), 1238 (w), 1180 (w), 1167 (w), 1154 (w), 1109 (w), 1080 (w), 1066 (w), 1045 (w), 1030 (m), 1001 (w), 987 (w), 960 (w), 945 (w), 918 (w), 894 (w), 875 (w), 856 (w), 838 (w), 812 (m), 756 (s), 726 (s), 701 (s), 613 (w), 577 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.17 ("t", J = 9.0 Hz, 1 H, 2-H), 5.27 (d, J = 9.4 Hz, 1 H, 1-H/3-H), 5.30 (d, J = 8.6 Hz,1 H, 1-H/3-H), 6.65 (dd, J = 7.8, 1.3 Hz, 2 H, Ph-H), 6.88–6.91 (m, 2 H, Ph-H), 6.95–7.06 (m, 6 H, Ph-H), 7.09–7.12 (m, 2 H, Ph-H), 7.16–7.21 (m, 3 H, Ph-H), 7.37 (ddd, J = 8.1, 7.0, 1.0 Hz, 1 H, 5-H/10-H), 7.47 (ddd, J = 8.0, 7.1, 1.0 Hz, 1 H, 5-H/10-H), 7.51 (dd, J = 8.0, 0.8 Hz, 1 H, 4-H/11-H), 7.58–7.63 (m, 2 H, 6-H, 9-H), 7.70 (d, J = 8.0, 0.8 Hz, 1 H, 4-H/11-H), 8.77 ("t", J = 7.7 Hz, 2 H, 7-H, 8-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 56.04 (C-1/C-3), 56.28 (C-1/C-3), 63.72 (C-2), 123.29 (C-7/C-8), 123.47 (C-7/C-8), 126.06 (C-4/C-11), 126.10 (C-6/C-9), 126.32 (C-4/C-11), 126.36 (C-5/C-10), 126.42 (CH Ph), 126.44 (CH Ph), 126.48 (CH Ph), 126.58 (CH Ph), 126.97 (C-5/C-10), 127.73 (CH Ph), 128.06 (CH Ph), 128.20 (CH Ph), 128.77 (CH Ph), 129.09 (CH Ph), 129.44 (two overlapping signals, C-3b, C-11a), 129.50 (CH Ph), 131.59 (C-7a/C-7b), 131.73 (C-7a/C-7b), 139.14 (C-3a, C-11b), 139.40 (C-3a, C-11b), 139.83 (C Ph), 140.69 (C Ph), 144.82 (C Ph) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 217 (4.51), 247 (4.52, br), 271 (4.23, sh), 279 (4.06), 290 (4.03), 302 (4.08), 352 (2.70) nm. MS (EI, 70 eV): m/z (%) = 446 (100) $[M]^+$,

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368 (43), 355 (41). $C_{35}H_{26}$ (446.58): calcd. C 94.13, H 5.87; found C 93.72, H 5.67.

***all-cis*-1,2,3-Triphenyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (11a):** A solution of cyclopentene **4a** (95 mg, 0.2 mmol) in air-saturated toluene (250 mL) was irradiated for 33 h. The solvent was evaporated and the residue was dissolved directly in toluene in a screw-capped flask and dimethyl acetylenedicarboxylate was added. The mixture was heated to 110 °C for 16 h. After cooling to room temperature the solution was submitted directly to a short plug of silica and eluted with toluene. The fraction with $R_f \approx 1$ gave phenanthrene **11a** (72 mg, 77%) as a colourless solid. Recrystallization from dichloromethane/petroleum ether gave colourless crystals with m.p. 261–264 °C. IR (KBr): $\tilde{\nu}$ = 3102 (w), 3080 (w), 3058 (m), 3024 (m), 3001 (w), 2929 (w), 2870 (w), 1620 (w), 1600 (m), 1492 (m), 1452 (m), 1432 (w), 1395 (w), 1338 (w), 1301 (w), 1262 (w), 1239 (w), 1224 (w), 1203 (w), 1174 (w), 1156 (w), 1077 (w), 1032 (m), 1000 (w), 985 (w), 966 (w), 951 (w), 915 (w), 873 (w), 845 (w), 814 (w), 793 (w), 778 (w), 759 (s), 739 (m), 725 (s), 700 (vs), 630 (w), 616 (w), 592 (w), 549 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.75 (t, J = 9.5 Hz, 1 H, 2-H), 5.29 (d, J = 9.5 Hz, 2 H, 1-H, 3-H), 6.10 (d, J = 7.3 Hz, 2 H, Ph-*o*-H), 6.77 ("d", J = 7.1 Hz, 4 H, Ph-*o*-H), 6.83 (t, J = 7.7 Hz, 2 H, Ph-H), 6.95–7.05 (m, 7 H, Ph-H), 7.45 (ddd, J = 8.0, 7.0, 0.9 Hz, 2 H, 5-H, 10-H), 7.60–7.66 (m, 4 H, 4-H, 6-H, 9-H, 11-H), 8.81 (d, J = 8.3 Hz, 2 H, 7-H, 8-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 56.25 (C-1, C-3), 56.50 (C-2), 123.36 (C-7, C-8), 126.21 (CH Ph), 126.35 (C-4, C-6, C-9, C-11, overlapping), 126.64 (CH Ph), 126.75 (CH Ph), 126.97 (C-5, C-10), 127.65 (CH Ph), 129.83 (C-3b, C-11a), 130.41 (*o*-CH Ph), 131.44 (C-7a, C-7b), 132.29 (*o*-CH Ph), 138.13 (C Ph), 139.56 (C-3a, C-11b), 141.36 (C Ph) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 209 (sh, 4.45), 247 (4.37), 255 (4.47), 278 (3.79), 288 (3.73), 300 (3.82) nm. MS (EI, 70 eV): m/z (%) = 446 (100) $[M]^+$, 368 (35) $[M - Ph + 1]^+$, 355 (51). $C_{35}H_{26}$ (446.58): calcd. C 94.13, H 5.87; found C 94.17, H 5.72.

Diethyl *all-cis*-1,2,3-Tris(4-ethoxycarbonylphenyl)-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-6,9-dicarboxylate (11c): A solution of cyclopentene **4c** (404 mg, 0.50 mmol) and iodine (127 mg, 1.00 mmol) in toluene (150 mL) was irradiated under nitrogen for 24 h. The solvent was removed in vacuo and the residue was submitted to flash column chromatography (silica, PE/MTBE 2:1, R_f = 0.12; 0.10). The fraction with R_f = 0.10 afforded polycycle **11c** (210 mg, 52%) as colourless crystals with m.p. 258 °C. IR (KBr): $\tilde{\nu}$ = 2981 (w), 2934 (w), 1715 (s), 1610 (m), 1464 (w), 1417 (w), 1367 (m), 1277 (s), 1180 (w), 1105 (s), 1021 (m), 865 (w), 772 (w), 715 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.0 Hz, 6 H, CH_3), 1.36 (t, J = 7.0 Hz, 3 H, CH_3), 1.47 (t, J = 7.5 Hz, 6 H, CH_3), 4.30 (q, J = 7.5 Hz, 4 H, OCH_2), 4.32 (q, J = 7.0 Hz, 2 H, OCH_2), 4.50 (q, J = 7.0 Hz, 4 H, OCH_2), 4.92 (t, J = 9.5 Hz, 1 H, 2-H), 5.40 (d, J = 9.5 Hz, 2 H, 1-H, 3-H), 6.17 (d, J = 8.0 Hz, 2 H, Ph-*o*-H), 6.79 (d, J = 8.5 Hz, 4 H, Ph-*o*-H), 7.52 (d, J = 8.5 Hz, 2 H, 4-H, 11-H), 7.53 (d, J = 8.5 Hz, 2 H, Ph-*m*-H), 7.68 (d, J = 8.0 Hz, 4 H, Ph-*m*-H), 8.09 (dd, J = 8.5, 1.4 Hz, 2 H, 5-H, 10-H), 9.61 (d, J = 1.4 Hz, 2 H, 7-H, 8-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4 (two overlapping signals, CH_3), 14.6 (CH_3), 55.9 (C-2), 56.1 (C-1, C-3), 61.1 (two overlapping signals, OCH_2), 61.6 (OCH_2), 126.0 (C-7, C-8), 126.6 (C-4, C-11), 127.7 (C-5, C-10), 128.3 (CH Ph), 129.0 (C-3a, C-11b), 129.1 (C Ph), 129.3 (C Ph), 129.4 (CH Ph), 130.0 (CH Ph), 131.4 (C-7a, C-7b), 131.9 (CH Ph), 132.1 (C-3b, C-11a), 141.1 (C-6, C-9), 141.9 (C Ph), 145.3 (C Ph), 166.4 (two overlapping signals, CO), 166.7 (CO) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 204 (4.21), 250 (4.25), 276 (3.85, sh), 314 (3.59), 328 (3.53) nm. MS (EI, 70 eV): m/z (%) = 806 (45) $[M]^+$, 761 (100) $[M - OCH_2CH_3]^+$. $C_{50}H_{46}O_{10}$ (806.89): calcd. C 74.43, H 5.75; found C 74.56, H 5.44.

1,2,3-Triphenyl-1*H*-cyclopenta[*l*]phenanthrene (12): A solution of cyclopentenol **6a** (215 mg, 0.46 mmol) and iodine (117 mg, 0.92 mmol) in deoxygenated methanol was irradiated for 22 h under argon. MeOH was evaporated and the residue was dissolved in CH_2Cl_2 and washed with aq. satd. Na_2SO_3 (1 × 5 mL). The organic layer was filtered through a short plug of silica (CH_2Cl_2, EtOAc) and the filtrate was evaporated. Dimethyl acetylenedicarboxylate (0.03 mL, 0.24 mmol) was added to a solution of a sample of the crude product (90 mg) in toluene (3 mL) and the mixture was stirred for 16 h at 110 °C. After evaporation of the solvent the residue was subjected to flash column chromatography (silica, pentane, 4 runs, R_f = 0, 0.14, 0.24, 0.33, 0.47). The fraction with R_f = 0.14 afforded phenanthrene **12** (20 mg, 27%) as an off-white solid. Crystallization from CH_2Cl_2/PE afforded slightly yellow crystals with m.p. 217–219 °C (ref.[15] 224–225 °C). The substance has been described in the literature[15] but the reported NMR data do not fit our observations. ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.47 (s, 1 H), 7.02–7.11 (m, 6 H), 7.13–7.19 (m, 4 H), 7.26–7.31 (m, 2 H), 7.38–7.44 (m, 3 H), 7.50–7.66 (m, 5 H), 7.87 (d, J = 8.0 Hz, 1 H), 8.70 (d, J = 8.3 Hz, 1 H), 8.76 (d, J = 8.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 58.75, 123.46, 123.53, 124.66, 125.37, 125.72, 125.87, 126.12, 126.73, 126.85, 126.91, 127.71, 127.77, 128.45, 128.62, 128.69, 128.91, 129.17, 129.64, 129.80, 131.02, 131.62, 136.79, 138.59, 129.06, 139.66, 141.44, 142.97, 150.35 ppm.

(1*R,2*r**,3*S**)-1,2,3-Triphenyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-2-ol (13):** A solution of cyclopentenol **6a** (111 mg, 0.24 mmol) in air-saturated toluene was irradiated for 68 h. The solvent was evaporated and the residue was subjected to flash column chromatography (silica, toluene, R_f = 0.06, 0.23, 0.34, 0.39, 0.55, 0.90). The fraction with R_f = 0.23 yielded phenanthrene **13** as a colourless solid (61 mg, 55%). Crystallization with dichloromethane/petroleum ether yielded colourless crystals with m.p. 277–279 °C. IR (KBr): $\tilde{\nu}$ = 3545 (m), 3064 (w), 3024 (w), 2923 (w), 2877 (w), 1494 (m), 1448 (m), 1433 (w), 1360 (w), 1333 (m), 1316 (m), 1261 (w), 1251 (w), 1225 (w), 1188 (w), 1169 (m), 1110 (w), 1086 (w), 1076 (w), 1032 (m), 1023 (m), 999 (m), 953 (w), 942 (w), 915 (w), 882 (w), 846 (w), 806 (w), 791 (w), 778 (m), 751 (s), 733 (m), 722 (s), 704 (s), 658 (w), 634 (w), 616 (w), 595 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.98 (s, 1 H, OH), 5.14 (s, 2 H, 1-H, 3-H), 6.40 (d, J = 7.6 Hz, 2 H, Ph-*o*-H), 6.85–6.76 (m, 6 H, Ph-H), 6.96–7.09 (m, 7 H, Ph-H), 7.48 (ddd, J = 8.0, 7.0, 0.9 Hz, 2 H, 5-H, 10-H), 7.59 (dd, J = 8.0, 0.9 Hz, 2 H, 4-H, 11-H), 7.68 (ddd, J = 8.3, 7.1, 1.2 Hz, 2 H, 6-H, 9-H), 8.84 (d, J = 8.3 Hz, 2 H, 7-H, 8-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 68.05 (C-1, C-3), 88.57 (C-2), 123.44 (C-7, C-8), 125.87 (CH Ph), 126.28 (C-6, C-9), 126.62, 126.76, 126.84, 127.10, 127.84, 128.64, 130.00 (all CH Ph), 130.50 (C-3b, C-11a), 131.66 (C-7a, C-7b), 138.15 (C-3a, C-11b), 138.96 (C Ph), 139.91 (C Ph) ppm. UV/Vis (MeCN): λ_{max} (log ε) = 223 (4.48), 245 (4.49), 278 (4.09), 287 (4.09), 299 (4.15), 350 (2.66) nm. MS (EI, 70 eV): m/z (%) = 462 (3) $[M]^+$, 444 (100) $[M - OH + 1]^+$, 368 (27), 355 (22). $C_{35}H_{26}O$ (462.58): calcd. C 90.88, H 5.67; found C 90.78, H 5.53.

Supporting Information (see also the footnote on the first page of this article): ^1H and ^{13}C NMR spectra of new compounds.

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