An Alternative Procedure for the Synthesis of [5]- and [7]Carbohelicenes

Riadh El Abed,[a] Béchir Ben Hassine,*[a] Jean-Pierre Genêt,*[b] Mohamed Gorsane,[a] and Angela Marinetti*[b]

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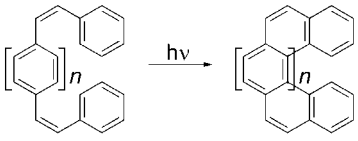
2-Bromo[5]helicene derivatives and substituted [7]helicenes have been prepared through a synthetic sequence relying on Heck-type and photocyclodehydrogenation reactions. This procedure provides a new, versatile and efficient approach to helicene derivatives.

Introduction

Helical compounds currently provide an active field of research in supramolecular chemistry, related to their self-assembly and physicochemical properties.[1] Also, their unique chiral array can provide functionalised helicenes, e.g. alcohols,[2] nitriles,[3] amines,[4] and phosphanes,[5] for use as ligands and auxiliaries in asymmetric syntheses. However, the development of helicene chemistry was long hampered by the lack of convenient synthetic methods and, despite much recent progress, the preparation of helicenes still requires improvement.

During the last decade, intensive efforts have been devoted to the search for new synthetic procedures and improvements of old ones: the first known method, the Friedel−Crafts approach to fused rings introduced by Newman, has rarely been used.[6] The most classical helicene synthesis, Martin's photochemically mediated cyclization of stilbene derivatives, has been optimised and widely applied.[7] It has been complemented recently by the Diels−Alder approach envisioned by Katz, which produces helical quinones from *p*-divinylaryl derivatives and *p*-benzoquinone.[8] Among other synthetic methods,[9] the radical cyclisation of bis(styryl)benzene derivatives,[10] the Co^{I}- or Ni^{0}-catalysed intramolecular [2+2+2] cycloisomerisation of aromatic triynes[11] and the carbenoid coupling of bis(-bromomethyl)biaryls[12] should be mentioned.

Helicene synthesis via photodehydrocyclisation of stilbene derivatives (Scheme 1) is known to have a somewhat restricted application as the scale-up is hampered at the photocyclisation step, which must be performed in dilute hydrocarbon solutions.[7b]



Scheme 1

Nevertheless, it still represents a simple and efficient synthetic method, well suited to the laboratory scale at least. In this paper we suggest a versatile approach to functionalised stilbene derivatives, which are then easily converted into the corresponding helicenes by photolysis.

Results and Discussion

From the beginning, the stilbene precursors to helicenes by photocyclisation (Scheme 1), have been prepared mainly by Wittig reactions between aryl aldehydes and phosphonium salts.[13] The synthetic utility of the photocyclisation reaction could, however, be significantly improved by using alternative approaches to the olefin moiety. In this context, the Mizoroki−Heck reaction suggests itself as an appropriate tool: the functional group tolerance, ready availability and low cost of simple olefins contributes to the well-established utility of this reaction.[14] Heck-coupling has been applied here to the synthesis of the parent heptahelicene as well as to the efficient preparation of functionalised [5]- and [7]helicene derivatives.

Our approach makes use of 3,6-dibromophenanthrene (**1**) as a suitable and versatile starting material for the synthesis of helicenes (Schemes 2 and 3). Either one or both of the bromide functions of **1** can be involved in Heck reactions

[a] Laboratoire de Synthèse Organique Asymétrique et Catalyse Homogène − Faculté des Sciences de Monastir,
Avenue de l'Environnement − 5019 Monastir, Tunisia
[b] Laboratoire de Synthèse Sélective Organique et Produits Naturels − UMR 7573,
E.N.S.C.P. 11, rue Pierre et Marie Curie − 75231 Paris Cedex 06, France
E-mail: marinet@ext.jussieu.Fr

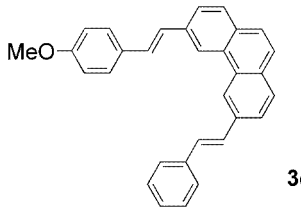
to afford styryl- and bis(styryl)phenanthrenes respectively, which are precursors for [5]- and [7]helicene derivatives.

3,6-Dibromophenanthrene has been prepared by photocyclisation of 4,4′-dibromostyrene, according to the published procedure.[15] The reaction conditions applied to the synthesis of the styryl derivatives **2a**−**f** (Scheme 2) are the following: 1% of Herrmann's palladacycle is used as the catalyst and *N*,*N*-dimethylacetamide as the solvent.[16] The 1:1 mixture of reagents was heated at reflux for about two days to afford the expected coupling products in high yields. The isolated final products are assumed to have an *E*-stereochemistry at the double bond. The *Z*-isomers were neither isolated nor unambiguously identified as minor products in the reaction mixture.

Substitution of both the bromine atoms of **1** to afford the bis(styryl) derivative **3a** (Scheme 3) was performed in analogous reaction conditions, while quite different conditions were used for the synthesis of the disubstituted bis(-styryl)phenanthrene derivative **3b**. The dibromophenanthrene (**1**), an excess amount of the styrene derivative (three equivalents), palladium acetate, potassium carbonate, and tetra-*n*-butylammonium bromide (TBAB) as a solid−liquid phase-transfer agent were heated in DMF for three days under argon to give the desired product.[17]

Disubstituted phenanthrenes were obtained in moderate to good yields by these methods.

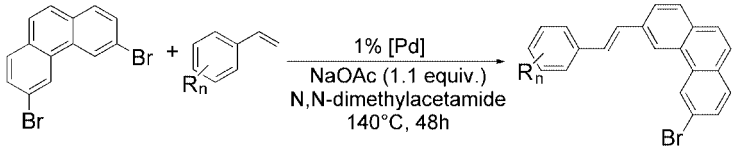
The selective Heck coupling of dibromophenanthrene with a single styrene unit, shown in Scheme 2, should allow the sequential coupling of two different styrene moieties in a two-step procedure. This strategy has been exemplified in this work by the synthesis of the unsymmetrical bis(styryl)-phenanthrene **3c** from **2b** and styrene by applying the reaction conditions (b).



3c (65% yield)

The few examples shown above demonstrate that the Heck reaction is an efficient, simple, and versatile approach to styryl and bis(styryl)phenanthrene derivatives. Of course, many other styrene derivatives as well as other aryl bromides could be involved in analogous reactions to afford helicene precursors for targeted applications.

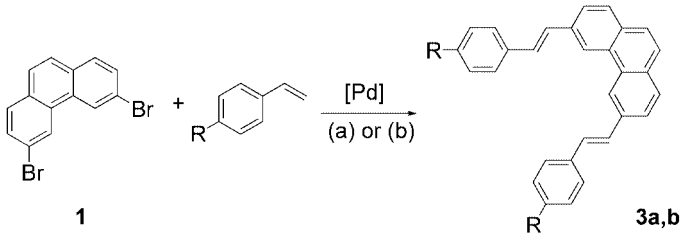
The final step of this work has been the conversion of the phenanthrene derivatives above to the corresponding helicenes by photocyclisation, following a known experimental procedure[7b] (Schemes 4, 5). Photolysis experiments



1 **2a-f**

Reagent	Product	R_n	Yield
styrene	**2a**	H	70%
p-methoxystyrene	**2b**	OMe	83%
p-cyanostyrene	**2c**	CN	78%
p-methylstyrene	**2d**	Me	84%
3,5-dimethoxystyrene	**2e**	OMe, OMe	80%
p-hydroxystyrene	**2f**	OH	70%

Scheme 2



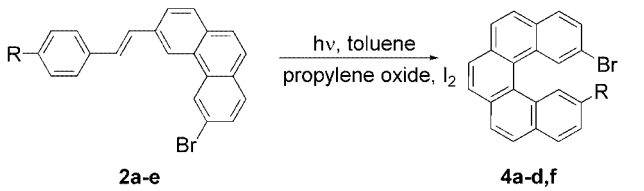
1 **3a,b**

Conditions: (a) Herrmann catalyst (2%), NaOAc (2.2 equiv.), DMA, 140°C, 48h.
(b) 10% $Pd(OAc)_2$, K_2CO_3 (0,6 equiv.), Bu_4NBr (1.2 equiv.), DMF, 140°C, 3 days

Reagent	Conditions	Product	R	Yield
styrene	(a)	**3a**	H	82%
p-methylstyrene	(b)	**3b**	Me	40%

Scheme 3

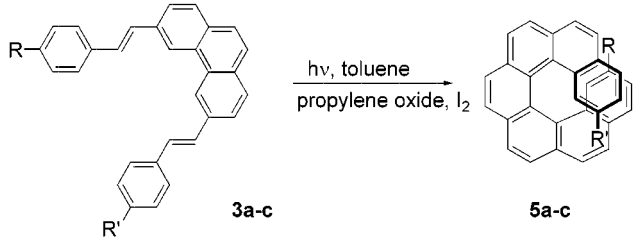
have been performed in the presence of stoichiometric amounts of iodine as an oxidising agent and propylene oxide as an HI scavenger.



2a-e **4a-d,f**

	R	yield
4a, 2-bromo[5]helicene	H	96%
4b, 2-bromo-13-methoxy[5]helicene	OMe	68%
4c, 2-bromo-13-cyano[5]helicene	CN	62%
4d, 2-bromo-13-methyl[5]helicene	Me	95%
4f, 2-bromo-13-hydroxy[5]helicene	OH	73%

Scheme 4



3a-c **5a-c**

	R, R'	yield
5a, [7]helicene	H, H	90%
5b, 2,17-dimethyl[7]helicene	Me, Me	70%
5c, 2-methoxy[7]helicene	OMe, H	89%

Scheme 5

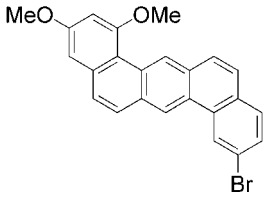
3-Bromo-6-styrylphenanthrenes **2** are precursors for the 2-bromo[5]helicenes **4**, while the bis(styryl)phenanthrenes **3** afford the parent [7]helicene **5a** and the substituted derivatives **5b**,**c**.

The ^{1}H NMR spectra of the [5]helicenes **4** display characteristic signals at low field for both 1-H and 14-H. Among the helicene derivatives above, only [7]helicene (**5a**)[7b,18,11b] and 2-methoxy[7]helicene (**5d**)[2b] are known compounds. The parent [7]helicene (**5a**) was previously prepared by the same photochemical reaction, the starting material being obtained from a Wittig-type reaction.[18b] An alternative, previous photochemical synthesis of the parent [7]helicene from 1,4-bis(2-naphthylvinyl)benzene suffers from lower yields (20%), because of the concurrent photocyclisation into dinaphthoanthracene.[18a]

Compound **5d** was prepared previously through a multistep sequence including several photocyclisation steps.[2h]

On the whole, the synthetic approach to [5]- and [7]helicenes presented here compares favourably with those previously reported, with respect to ease and versatility.

Photocyclisation of 3-bromo-6-(3,5-dimethoxystyryl)-anthracene (**2e**) failed to give the expected [5]helicene: the corresponding 9-bromo-1,3-dimethoxydibenzo[*a*,*h*]anthracene (**6**) was isolated as the major product, in 43% yield. The ^{1}H NMR spectrum of **6** displays the resonance peak of 14-H at δ = 9.9 ppm, a very low-field shift which is characteristic for these structures.



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We argued that the steric hindrance of the *m*-methoxy substituents of the styrene moiety induces preferential cyclisation on the more easily accessible C-7 centre of phenanthrene.

Analogous extended aromatics are well-known side-products of helicene syntheses through both photochemical and radical processes.[10,13c,18a,19]

In summary, a synthetic sequence relying on Heck-type and photocyclodehydrogenation reactions provides an efficient, versatile, and simple approach to helicene derivatives. It has been exemplified here through the preparation of both unsubstituted and functionalised [5]- and [7]helicene derivatives. The same strategy could be easily adapted to the synthesis of a variety of [5]-to-[7]helicenes bearing selected functional groups for various synthetic purposes and applications.

Experimental Section

All reactions were performed under an argon atmosphere. NMR spectra were recorded on either a Bruker AM 400 or a Bruker AM 200 instrument. Photochemical reactions were carried out in a 1-L photoreactor equipped with a high-pressure mercury immersion lamp [Heraeus TQ 150]. 3,6-Dibromophenanthrene was prepared as reported in the literature.[15]

General Procedures for the Heck Reactions between 3,6-Dibromophenanthrene and Styrene Derivatives: Reactions were performed on a 1−2-mmol scale.

Method (a): A solution of 3,6-dibromophenanthrene (340 mg, 1 mmol) and dry sodium acetate (90 mg, 1.1 mmol) in *N*,*N*-dimethylacetamide (2 mL) was placed in a Schlenk tube and repeatedly degassed and purged with argon. The styrene derivative (1.4 mmol) was added and the mixture was heated to 100 °C. When this temperature was reached, a solution of *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphanyl)benzyl]dipalladium (Herrmann catalyst, 9.4 mg, 1%) in *N*,*N*-dimethylacetamide (1 mL) was added and the reaction mixture heated to 140 °C. Heating was maintained for about 48 h. The product was worked up by addition of water and extraction of the organic phases with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$. After removal of the solvent, the final product was purified by column chromatography on a silica gel column, as indicated below.

When method (a) was applied to the synthesis of **3a**, 2.2 equivalents of sodium acetate, 3 equivalents of styrene, and 2% of the catalyst were used.

Method (b): A mixture of 3,6-dibromophenanthrene (340 mg, 1 mmol), potassium carbonate (1.2 mmol), tetrabutylammonium

bromide (2.4 mmol), palladium acetate (50 mg, 20 mol%), and styrene derivative (3 mmol) in DMF (20 mL) was heated in a Schlenk tube under argon at 140 °C for three days. After hydrolysis and extraction with dichloromethane, the final product was purified by column chromatography on silica gel, as indicated below.

3-Bromo-6-styrylphenanthrene (2a) was obtained in 70% yield (0.50 g), on a 2-mmol scale, by method (a). A small amount of 3,6-distyrylphenanthrene (**3a**) was also formed in this reaction. Compound **2a** was purified by column chromatography with cyclohexane/ethyl acetate (95:5) as the eluent (R_f = 0.5). Colourless solid. Mass spectrum (E.I.): *m*/*z* = 358 [M, ^{79}Br] (70%), 278 (100%). ^{1}H NMR ($CDCl_3$): δ = 7.2−7.7 (m, 11 H), 7.75 (2H), 8.48 (s, 1 H, 5-H), 8.74 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 120.9 (C-Br), 121.4, 124.8, 125.5, 126.2, 126.6, 127.1, 127.8, 128.8, 129.0, 129.5 (C), 129.5, 129.8, 130.1, 130.8 (C), 131.9 (C), 135.9 (C), 137.2 (C) ppm.

3-Bromo-6-(*p*-methoxystyryl)phenanthrene (2b) was obtained in 83% yield (0.60 g), on a 2-mmol scale, by method (a). It was purified by column chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.5). Colourless solid. M.p. 180 °C. Mass spectrum (E.I.): *m*/*z* = 388 [M, ^{79}Br] (100%), 265 (43%). ^{1}H NMR ($CDCl_3$): δ = 3.78 (s, 3 H, OMe), 6.87 (*AA*′BB′, 2 H, CH-*o*-MeO), 7.47 (AA′*BB*′, *J* = 8.8 Hz, 2 H, CH-*m*-MeO), 7.5−7.7 (m, 6 H), 7.76 (2 H), 8.50 (s, 1 H, 5-H), 8.76 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.3 (OMe), 114.2 (2 × CH-*o*-MeO), 120.8 (C-Br), 120.9, 124.7, 125.5, 126.6, 127.1, 127.9 (2 × CH), 128.9, 129.1, 129.5 (C), 129.8, 130.1, 130.8 (C), 131.5 (C), 131.7 (C), 136.3 (C), 159.5 (*C*-OMe) ppm. $C_{23}H_{17}BrO$ (389.28): calcd. C 70.96, H 4.40; found C 70.50, H, 4.51.

3-Bromo-6-(*p*-cyanostyryl)phenanthrene (2c) was obtained in 78% yield (0.60 g), on a 2-mmol scale, by method (a). It was purified by column chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.3). Colourless solid. M.p. 240 °C. Mass spectrum (E.I.): *m*/*z* = 383 [M, ^{79}Br] (95%), 303 (100%). ^{1}H NMR (CD_2Cl_2): δ = 7.34 (*A*B, *J* = 16.2 Hz, 1 H, CH_{vinyl}), 7.51 (d, *J* = 16.2 Hz, 1 H, CH_{vinyl}), 7.90 (*A*B, *J* = 8.3 Hz, 1 H), 7.92 (d, *J* = 8.3 Hz, 1 H), 8.68 (s, 1 H, 5-H), 8.89 (d, *J* = 1.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 110.8 (C-CN), 119.0 (C-Br), 121.1 (C), 122.2, 124.9, 125.5, 126.9, 127.0, 127.5, 129.2, 129.4 (C), 130.0, 130.2, 130.9 (C), 131.6 (C), 132.4, 132.6, 134.8 (C), 141.7 (C) ppm. $C_{23}H_{14}BrN$ (384.27): calcd. C 71.89, H 3.67; found C 71.65, H, 3.64.

3-Bromo-6-(*p*-methylstyryl)phenanthrene (2d) was obtained in 84% yield (0.30 g), on a 1-mmol scale, by method (a). It was purified by column chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.5). Colourless solid. M.p. 154 °C. Mass spectrum (E.I.): *m*/*z* = 372 [M, ^{79}Br] (100%), 292 (50%), 278 (90%). ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3 H, Me), 7.23 (d, *J* = 8.1 Hz, 2 H, CH), 7.33 (br. s, 2 H), 7.52 (d, *J* = 8.1 Hz, 2 H, CH), 7.66 (d, *J* = 8.7 Hz, 1 H), 7.7 (m, 2 H), 7.61 (d, *J* = 8.7 Hz, 1 H), 7.86 (2 H), 8.61 (s, 1 H, 5-H), 8.86 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.4 (Me), 120.9 (C-Br), 121.3, 124.8, 125.6, 126.2, 126.6 (2 × CH), 127.2, 127.8, 128.3, 129.5 (C), 129.6 (2 × CH), 129.8, 130.2, 130.9 (C), 131.6 (C), 131.7 (C), 134.5 (C), 136.2, 137.9 (*C*-Me) ppm.

3-Bromo-6-(3,5-dimethoxystyryl)phenanthrene (2e) was obtained in 80% yield (0.35 g), on a 1-mmol scale, by method (a). It was purified by column chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.4). Colourless solid. M.p. 133 °C. Mass spectrum (E.I.): *m*/*z* = 418 [M, ^{79}Br] (100%). ^{1}H NMR ($CDCl_3$): δ = 3.88 (s, 6 H, OMe), 6.46 (t, *J* = 2.2 Hz, 1 H, CH-*o*-MeO), 6.78 (d, *J* = 2.2 Hz, 2 H, CH-*o*-MeO), 7.23 (*A*B, *J* = 15.6 Hz, 1 H, CH_{vinyl}), 7.34 (A*B*, *J* = 15.6 Hz, 1 H, CH_{vinyl}), 7.6−7.7 (m, 4 H), 7.84 (2 H), 8.58 (s, 1 H, 5-H), 8.83 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.4 (OMe), 100.4 (CH-*o*-MeO), 104.6 (2 × CH-*o*-MeO), 120.9 (C-Br), 121.5, 124.8, 125.5, 126.3, 127.1, 129.0, 129.2, 129.5 (C), 129.8, 130.1, 130.8 (C), 131.6 (C), 135.7 (C), 139.2 (C), 161.0 (*C*-OMe) ppm. $C_{24}H_{19}BrO_2$ (419.31): calcd. C 68.75, H 4.57 found C 69.88, H, 4.94.

3-Bromo-6-(*p*-hydroxystyryl)phenanthrene (2f) was obtained in 70% yield (0.26 g), on a 1-mmol scale, by method (a). It was purified by column chromatography with cyclohexane/ethyl acetate (70:30) as the eluent (R_f = 0.5). Colourless solid. Mass spectrum (E.I.): *m*/*z* = 374 [M, ^{79}Br] (100%). ^{1}H NMR (CD_2Cl_2): δ = 6.90 (*A*B, *J* = 8.7 Hz, 2 H, CH-*o*-OH), 7.24 (*A*B, *J* = 16.3 Hz, 1 H, CH_{vinyl}), 7.35 (A*B*, *J* = 16.3 Hz, 1 H, CH_{vinyl}), 7.54 (A*B*, *J* = 8.7 Hz, 2 H), 7.6−7.9 (6 H), 8.65 (s, 1 H, 5-H), 8.90 (d, *J* = 1.5 Hz, 1 H, 4-H) ppm.

3,6-Distyrylphenanthrene (3a) was obtained in 82% yield (0.32 g), on a 1-mmol scale, by method (a), by treating 3,6-dibromophenanthrene (1 mmol) with excess styrene (3 mmol) in the presence of sodium acetate (2.2 mmol). A catalyst amount of 19 mg (2%) was used. The final product was purified by column chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.4). Colourless solid. ^{1}H NMR ($CDCl_3$): δ = 7.2−7.8 (18 H), 7.75 (4 H), 8.64 (s, 2 H, 4,5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.6, 124.2, 126.6, 127.7, 128.8, 129.0, 129.1, 129.2, 130.5 (C), 131.9 (C), 135.6 (C), 137.4 (C) ppm.

3,6-Bis(*p*-methylstyryl)phenanthrene (3b) was obtained in 40% yield (0.16 g), on a 1-mmol scale, by method (b). It was purified by column chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.6). Colourless solid. Mass spectrum (E.I.): *m*/*z* = 410 [M] (100%). ^{1}H NMR (CD_2Cl_2): δ = 2.30 (s, 6 H, Me), 7.14 (d, *J* = 9.0 Hz, 4 H), 7.25 (d, *J* = 15 Hz, 2 H, CH_{vinyl}), 7.32 (d, *J* = 15 Hz, 2 H, CH_{vinyl}), 7.44 (d, *J* = 9.0 Hz, 4 H), 7.61 (s, 2 H), 7.75 (d, *J* = 9.0 Hz, 2 H), 7.78 (d, *J* = 9.0 Hz, 2 H) 8.69 (s, 2 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.4 (Me), 121.6, 124.6, 126.8, 128.2, 129.4, 129.6, 129.9, 130.8 (C), 132.2 (C), 134.9 (C), 136.3 (C), 138.3 (C) ppm.

3-(*p*-Methoxystyryl)-6-styrylphenanthrene (3d) was obtained in 65% yield (0.27 g) by method (b) starting from 3-bromo-6-(*p*-methoxystyryl)phenanthrene (**2b**, 1 mmol) and styrene. It was purified by column chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.5). Colourless solid. M. p. 178 °C. Mass spectrum (E.I.): *m*/*z* = 412 [M] (100%). ^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 3 H, OMe), 6.84 (*AA*′BB′, *J* = 8.8 Hz, 2 H, CH-*o*-MeO), 7.2−7.6 (13 H), 7.74 (2 H), 7.76 (2 H), 8.62 (1 H), 8.64 (1 H) ppm. ^{13}C NMR ($CDCl_3$), selected data: δ = 55.3 (OMe), 114.2 (2 × CH-*o*-MeO), 121.1, 121.6, 124.1 (CH), 131.6 (C), 131.9 (C), 135.5 (C), 135.9 (C), 137.4 (C), 159.4 (C-OMe) ppm.

General Procedure for the Photocyclisation Reactions: Photocyclisations were performed on a 0.5-mmol scale, in a 1-L apparatus (10^{-3} M solutions). The styrylphenanthrenes **2** (or **3**) (0.5 mmol) and iodine (140 mg, 1.1 equiv.) (or 2.2 equiv.) were dissolved in 1 L of toluene and placed in the photoreactor equipped with an immersion lamp (150 W). Propylene oxide (1.8 mL, 25 mmol) was added and the mixture was irradiated for about 40 min. After evaporation of the solvent, the final product was purified by column chromatography on silica gel.

2-Bromo[5]helicene (4a) was obtained from **2a** in 96% yield (0.17 g), on a 0.5-mmol scale, after chromatography with cyclohexane/ethyl acetate (95:5) as the eluent (R_f = 0.5). Colourless solid. M.p. 143 °C. Mass spectrum (E.I.): *m*/*z* = 356 [M] (30%), 276 (100%). ^{1}H

NMR ($CDCl_3$): δ = 7.26 (ddd, *J* = 8.4, *J* = 6.8, *J* = 2.0 Hz, 1 H, 13-H), 7.47 (ddd, *J* = 8.0, *J* = 7.0, *J* = 1.2 Hz, 1 H, 12-H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.7−7.9 (8 H), 8.43 (d, *J* = 8.4 Hz, 14-H), 8.61 (s, 1-H); 118.6 (C-Br), 124.6, 126.0, 126.3, 126.6, 126.9, 127.0, 127.8, 127.9, 128.0, 128.5, 129.4, 130.2, 131.2, 132.0 (C), 132.3 (C), 132.6 (C) ppm.

2-Bromo-13-methoxy[5]helicene (4b) was obtained from **2b** in 68% yield (0.13 g) after chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.6). Colourless solid. M.p. 165 °C. Mass spectrum (E.I.): *m*/*z* = 386 (M, ^{79}Br, 35%), 276 (73%), 263 (65%), 131 (100%). ^{1}H NMR ($CDCl_3$): δ = 3.52 (s, OMe), 7.13 (dd, *J* = 8.8, *J* = 2.6 Hz, 12-H), 7.50 (dd, *J* = 8.6, *J* = 1.8 Hz, 1 H), 7.6−7.9 (m, 9 H), 8.60 (d, *J* = 1.6 Hz, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.0 (OMe), 108.7 (CH-*o*-OMe), 118.3 (C-Br), 118.6 (CH-*o*-OMe), 124.0, 126.0 (C), 126.7, 127.0, 127.5, 127.9 (C), 128.2, 129.1, 129.5, 129.6, 131.0 (C), 131.4 (C), 131.5 (C), 131.8, 132.6 (C), 132.9 (C), 156.9 (C-OMe) ppm. $C_{23}H_{15}BrO$ (384.27): calcd. C 71.33, H 3.90; found C 71.05, H, 4.05.

2-Bromo-13-cyano[5]helicene (4c) was obtained from **2c** in 62% yield (0.12 g) after chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.4). Colourless solid. M.p. 288 °C. Mass spectrum (E.I.): *m*/*z* = 381 [M, ^{79}Br] (30%), 301 (100%). ^{1}H NMR ($CDCl_3$): δ = 7.56 (dd, *J* = 8.6, *J* = 1.8 Hz, 1 H), 7.61 (dd, *J* = 8.4, *J* = 1.6 Hz, 1 H), 7.7−8.0 (m, 8 H), 8.45 (d, *J* = 1.6 Hz, 1-H), 8.79 (d, *J* = 0.8 Hz, 14-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 107.8 (*C*-CN), 119.1 (C-Br), 119.4 (C), 125.4 (C), 126.2 (C), 126.7, 127.0, 127.4, 127.7, 127.8, 128.4, 129.2, 129.6, 129.8, 130.1, 130.3 131.2 (C), 131.4 (C), 132.7 (C), 133.0 (C), 133.8, 134.4 (C) ppm. $C_{23}H_{12}BrN$ (382.25): calcd. C 72.27, H 3.16; found C 72.12, H 3.84.

2-Bromo-13-methyl[5]helicene (4d) was obtained from **2d** in 95% yield (0.18 g) after chromatography with cyclohexane/ethyl acetate (95:5) as the eluent (R_f = 0.6). Colourless solid. M. p. 161 °C. Mass spectrum (E.I.): *m*/*z* = 370 [M, ^{79}Br] (40%), 276 (93%), 138 (100%). ^{1}H NMR ($CDCl_3$): δ = 7.29 (dd, *J* = 8.0, *J* = 1.4 Hz, 1 H), 7.49 (dd, *J* = 8.6, *J* = 2.0 Hz, 1 H), 7.6−7.8 (8 H), 8.22 (d, *J* = 0.6 Hz, 1 H, 14-H), 8.64 (d, *J* = 1.6 Hz, 1 H, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.7 (Me), 118.3 (C-Br), 125.4, 126.1 (C), 126.5 (C), 126.8, 127.0, 127.6, 127.9, 128.0, 128.3, 128.5, 129.2, 129.3, 130.3 (C), 130.8 (C), 131.0 (C), 131.4, 131.9 (C), 132.6, 134.5 ppm.

2-Bromo-13-hydroxy[5]helicene (4f) was obtained from **2f** in 73% yield (0.15 g) after chromatography with cyclohexane/ethyl acetate (70:30) as the eluent (R_f = 0.6). Colourless solid. Mass spectrum (E.I.): *m*/*z* = 372 [M, ^{79}Br] (17%), 293 [M − Br] (87%), 275 (100%). ^{1}H NMR ($CDCl_3$): δ = 5.9 (OH), 7.19 (dd, *J* = 8.7, *J* = 2.3 Hz, 1 H, CH-*o*-OH), 7.56 (dd, *J* = 8.5, *J* = 1.9 Hz, 1 H), 7.71 (*A*B, *J* = 8.5 Hz, 1 H), 7.76 (A*B*, *J* = 8.5 Hz, 1 H), 7.8−7.9 (7 H), 8.74 (d, *J* = 1.5 Hz, 1 H, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 112.2 (C12), 117.4 (C14), 118.4 (C-Br), 123.9, 125.8 (C), 126.1 (C), 126.7, 127.0, 127.1, 127.6, 127.8 (C), 128.0, 129.2, 129.4, 129.9, 131.1 (C), 131.5, 131.7 (C), 132.5 (C), 132.9 (C), 153.1 (C-OH) ppm.

9-Bromo-1,3-dimethoxydibenzo[*a*,*h*]anthracene (6) was obtained from **4e** in 43% yield (90 mg) after chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.3). Colourless solid. Mass spectrum (E.I.): *m*/*z* = 416 [M] (78%), 322 (71%), 125 (100%). ^{1}H NMR ($CDCl_3$): δ = 3.99 (s, OMe), 4.19 (s, OMe), 6.84 (d, *J* = 2.4 Hz, 2-H), 6.94 (d, *J* = 2.5 Hz, 4-H), 7.5−7.7 (m, 4 H), 7.90 (d, *J* = 8.9 Hz, 1 H), 7.94 (d, *J* = 8.9 Hz, 1 H), 8.92−8.94 (2 H, 7-H, 8-H), 9.99 (s, 1 H, 14-H) ppm. ^{13}C NMR ($CDCl_3$) selected data: δ = 55.6 (OMe), 55.9 (OMe), 99.4 (CH-*o*-MeO), 102.3 (CH-*o*-MeO) ppm.

[7]Helicene (5a) was obtained from **3a** in 90% yield after chromatography with cyclohexane/ethyl acetate (99:1) as the eluent. NMR spectroscopic data are in agreement with those previously reported.[7a,20]

2,17-Dimethyl[7]helicene (5c) was obtained from **3c** in 70% yield (140 mg) after chromatography with cyclohexane/ethyl acetate (90:10) as the eluent (R_f = 0.7). Mass spectrum (E.I.): *m*/*z* = 406 [M] (63%), 187 (100%). ^{1}H NMR ($CDCl_3$): δ = 1.77 (s, 6 H, Me), 6.75 (dd, *J* = 8.1, *J* = 1 Hz, 2 H, 3-H, 16-H), 6.94 (d, *J* = 1 Hz, 2 H, 1-H, 18-H), 7.22 (d, *J* = 8.0 Hz, 2 H, 4-H, 15-H), 7.49 (*A*B, *J* = 8.5 Hz, 2 H), 7.67 (A*B*, *J* = 8.5 Hz, 2 H), 7.93 (AB, *J* = 8.2 Hz, 2 H), 8.00 (AB, *J* = 8.2 Hz, 2 H), 8.03 (s, 2 H, 9-H, 10-H) ppm. ^{13}C NMR ($CDCl_3$) δ = 20.1 (Me) 123.6, 123.9, 124.2 (C), 125.2, 125.5, 125.7, 125.8, 126.3, 127.2 (C), 128.2 (C), 128.9 (C), 130.0 (C), 130.7 (C),132.6 (C) ppm.

2-Methoxy[7]helicene (5d) was obtained from **3d** in 89% yield (180 mg) after chromatography with cyclohexane/ethyl acetate as the eluent (R_f = 0.5). Mass spectrum (E.I.): *m*/*z* = 408 [M] (100%). ^{1}H NMR ($CDCl_3$): δ = 3.04 (s, 3 H, OMe), 6.32 (ddd, *J* = 8.4, *J* = 7.0, *J* = 1.4 Hz, 1 H, 17-H), 6.5 (m, 2 H), 6.84 (ddd, *J* = 8.0, *J* = 7.0, *J* = 1.2 Hz, 1 H, 16-H), 7.02 (d, *J* = 8.6 Hz, 1 H), 7.13 (d, *J* = 8.6 Hz, 1 H), 7.27 (d, *J* = 7.2 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 7.50 (d, *J* = 8.4 Hz, 1 H), 7.56 (d, *J* = 8.4 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.81 (*A*B, *J* = 8.1 Hz, 1 H), 7.84 (d, *J* = 8.1 Hz, 1 H), 7.90 (A*B*, *J* = 8.1 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.95 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$) selected data: δ = 52.8 (OMe), 103.4 (*C*H-3), 115.9 (CH-1), 155.4 (C-OMe) ppm.

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