Expeditious synthesis of helicenes using an improved protocol of photocyclodehydrogenation of stilbenes

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Abstract
An improved procedure has been developed for photodehydrocyclization of stilbenes for the synthesis of phenanthrenes and helicenes. This procedure involves the use of THF as a scavenger of hydriodic acid produced during iodine mediated photodehydrocyclization. The use of THF is advantageous due to its higher boiling point, lower cost and easy availability as compared to propylene oxide. The method is applied to synthesize a number of phenanthrenes and helicenes.

Keywords: Helicenes, HI scavenger tetrahydrofuran, Mizoroki-Heck-reaction, Phenanthrenes, Stilbenes, Wittig-olefination

Introduction

Helicenes\(^1\) constitute a fascinating class of chiral helical molecules comprising ortho-fused aromatic rings having many intriguing features such as extended aromaticity, chirality, a capability to organize into columnar solid state architecture and an ability to behave as organic conductors. Potential applications of helicenes can be found in the fields of non-linear optics\(^2\) and circularly polarized luminescence.\(^3\) The unique structure of functionalized helicenes make them very stable towards acids, bases as well as being stable at high temperature.\(^4\) These type of molecules are considered potentially useful new materials such as discotic liquid crystals\(^5\) or conjugated polymers.\(^6\) Study of helical compounds is an active field of research in supramolecular chemistry due to their self-assembly and physiochemical properties.\(^7\) Also their rigid helical framework, high optical stability and unique chiral array can provide functionalized helicenes such as alcohols,\(^8\) nitriles,\(^9\) amines\(^10\) and phosphines\(^11\) for use as chiral catalysts,\(^12\) ligands\(^13\) and auxiliaries in asymmetric synthesis. Moreover helicenes possessing inherent chirality have attracted attention owing to their extraordinary electronic and optical properties.\(^14\)
A common method for the synthesis of phenanthrene and its derivatives involves the construction of a central ring by photodehydrocyclization of stilbene. This method involves exposure of cis/trans stilbene 1 to UV light, which causes its isomerization to the cis form. This form undergoes electrocyclic ring closure to produce dihydrophenanthrene 2, which on dehydrogenation generates a phenanthrene 3 (Scheme 1).

Scheme 1. Transformation of cis-stilbene 1 into phenanthrene 3.

This classical synthesis of ortho-fused benzene rings has been optimized and widely applied for the syntheses of a number of helical moieties. The required stilbene precursors are obtained either by the Wittig reaction or by the Mizoroki-Heck reaction. In recent years, preparation of heterohelicenes has been extensively studied in order to exploit the unique properties of these compounds.

Results and Discussion

As a part of our ongoing research project, we require a simple an expeditious synthesis of functionalized benzo[c]phenanthrene. In the preliminary communication we have reported an improved method for photocyclodehydrogenation of stilbenes to construct phenanthrenes, helicenes etc. In the classical iodine mediated photocyclodehydrogenation, propylene oxide is used as a scavenger to neutralize the co-product hydrogen iodide. This reagent is slightly expensive and has a low boiling point. In a typical photo reaction even under careful cooling, the reaction mixture warms up which causes the loss of propylene oxide. In our improved procedure we have replaced this scavenger by readily available and cheap tetrahydrofuran which has a higher boiling point and in this paper we present further applications of this modified procedure for the synthesis of a number of helical compounds.

The progress of the neutralization of hydrogen iodide with tetrahydrofuran and propylene oxide is studied by pH measurement of its solution. In this study tetrahydrofuran and propylene oxide neutralizes the HI due to the opening of both cyclic ethers. As a result of the neutralization of HI there is a gradual rise in the pH. We found that the propylene oxide reacts faster than the tetrahydrofuran, Figure 1. This is expected since the propylene oxide has a higher strain compared to tetrahydrofuran, nevertheless this study indicates clearly that even though less efficiently, the later can be used as a scavenger of HI. The ability of tetrahydrofuran to react with HI is also reported in the literature.
In this paper we report several photodehydrocyclization reactions using tetrahydrofuran as scavenger in stead of propylene oxide and hope to establish the generality of this method. With this aim several suitable stilbenes were prepared by various methods and subjected to photodehydrocyclization using the present conditions by which a number of mono- and disubstituted phenanthrenes were prepared in excellent yields\(^\text{17}\) (Scheme 2).

\[
\text{Scheme 2. Improved synthesis of substituted phenanthrenes.}
\]

The photodehydrocyclization of nitrostilbenes is known to offer some difficulty when a catalytic quantity of iodine is used.\(^\text{19}\) In order to test the present method on the nitro containing substrates, stilbenes 1a and 1b were synthesized and subjected to photolysis with I\(_2\)-THF. The corresponding nitro phenanthrenes 2a and 2b were isolated in reasonable yields (Scheme 3). Furthermore, the nitro derivative of styrylnaphthalene (2-[2-(4-nitrophenyl)ethenyl]naphthalene)\(^\text{20}\) 3 was also successfully cyclized to 2-nitrobenzo[c]phenanthrene 4 indicating that the present method also tolerates nitro groups.
**Scheme 3.** Preparation of nitro-substituted angularly fused arene.

The present method was screened for cyclization of 1,2-bis(2-naphthyl)ethylene 5 with the aim to prepare [5]helicene. However, the initially formed [5]helicene 6 was not isolated but underwent further $4\pi+2\pi$ cyclization to form benzo[ghi]perylene 7 in good yield (Scheme 4).

**Scheme 4.** Attempted synthesis of [5]helicene.

Since the photochemical ring closure had proven to be one of the simplest ways to obtain fused aromatics, we decided to study the reaction of different derivatives of ethylene, namely the compounds carrying a fused two- or three-ring aryl on one terminus and a monocyclic aryl on the other terminus of the double bond. The synthesis of these derivatives easily gave the desired helicenes and eventually opened the facile route for the formation of [6]helicenes or larger helicenes.

Encouraged by the previous results, several [6]helicene derivatives have been synthesized as shown in scheme 5. Readily accessible 2-naphthaldehyde 8 was converted into 2-(4-bromostyryl)naphthalene 10 by reaction with the Wittig salt (4-bromobenzyl)triphenylphosphonium
bromide 9 under standard conditions. The photodehydrocyclization of 10 in toluene with iodine-THF gave 2-bromobenzo[c]phenanthrene 11 in high yield.

\[
\begin{align*}
&\text{CHO} \quad + \quad \text{PPh}_3\text{Br}^- \\
&\begin{array}{c}
8 \\
9
\end{array} \quad \text{NaOCH}_3 \\
&\begin{array}{c}
\text{CH}_2\text{OH} \\
\text{RT, 24 h}
\end{array} \quad \text{hv, I}_2, \text{THF} \\
&\begin{array}{c}
\text{Toluene} \\
125W, 20h
\end{array} \quad \text{10 (76%)} \\
&\begin{array}{c}
\text{Br} \\
\text{11 (96%)}
\end{array}
\end{align*}
\]


Reaction of 2-bromobenzo[c]phenanthrene 11 with styrene or 4-methylstyrene using the well-known Pd(OAc)$_2$-1,3-bis(diphenylphosphino)propane (Pd-dppp) catalyzed Heck reaction$^{22}$ resulted into 2-styrylbenzo[c]phenanthrene 12 and 2-(4-methylstyryl)benzo[c]phenanthrene 13 respectively in excellent yield. Further photoirradiation of 12 or 13 under the present reaction conditions furnished [6]helicene 14 and 2-methyl[6]helicene 15 respectively in good yield. Alternatively 14 can be also synthesized by double photodehydrocyclization of 2,7-bis-styrylnaphthalene 18. This new route is presented in scheme 6, where initially 2,7-dihydroxynaphthalene 16 is converted into the corresponding 2,7-dibromonaphthalene 17, which was reacted with styrene under Heck conditions with Pd-dppp to afford 2,7-bis-styrylnaphthalene 18. This was then subjected to the photodehydrocyclization to afford [6]helicene 14 in a single step (Scheme 6).

The method is further studied for the syntheses of [7]helicene. Scheme 7 illustrates an attempt for its synthesis. The readily available 2-methylnaphthalene 19 was converted to its Wittig salt 20 via benzylic bromination with NBS, and its reaction with triphenylphosphine. The salt 20, on Wittig reaction with 4-tolualdehyde gave mostly the trans isomer of 2-(4-methylstyryl)naphthalene 21 in good yield, which upon photoirradiation resulted into 2-methylbenzo[c]phenanthrene 22. Similarly 22 was converted to the new Wittig salt 23, via its bromomethyl derivative. Standard Wittig reaction of 23 with 2-naphthaldehyde yielded 2-(2-vinylnaphthyl)benzo[c]phenanthrene 24, predominantly in the trans form. Photodehydrocyclization of 24 led to an unexpected result as the ring closure was directed to the less crowded site yielding the linear derivative, dinaphtho[1,2-
$a:2',1'-h$anthracene 25 instead of the expected [7]helicene 26. The structure of compound 25 was established by comparison of spectroscopic data and its melting point.\textsuperscript{23}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {16};
\node (b) at (2,0) {17 (53\%)};
\node (c) at (2,-2) {18 (65\%)};
\path (a) edge[->] node[anchor=south] {Ph$_3$P - Br$_2$} node[anchor=north] {Acetonitrile 300 \textdegree C 2 h} (b);
\path (b) edge[<-] node[anchor=south] {Pd(OAc)$_2$, dppp, K$_2$CO$_3$} node[anchor=north] {DMA, 140 \textdegree C, 48 h} (c);
\path (c) edge[->] node[anchor=south] {hv, I$_2$, THF Toluene 125W, 20 h} (a);
\end{tikzpicture}
\end{center}


\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {19};
\node (b) at (2,0) {20 (70\%)};
\node (c) at (2,-2) {22 (96\%)};
\node (d) at (4,-4) {24 (54\%)};
\node (e) at (6,-4) {25 (75\%)};
\node (f) at (8,-4) {26 (not detected)};
\node (g) at (2,-2) {21 (86\%)};
\node (h) at (4,-4) {23 (70\%)};
\path (a) edge[->] node[anchor=south] {a) hv, NBS, Bezoyl peroxide CCl$_4$, 8 h \quad b) PPh$_3$, Xylene 12 h} node[anchor=north] {Acetonitrile 300 \textdegree C 2 h} (b);
\path (b) edge[<-] node[anchor=south] {$\rho$-Tolualdehyde NaOCH$_3$, CH$_3$OH RT, 12 h} node[anchor=north] {hv, I$_2$, THF Toluene 125W HPMVL 20 h} (g);
\path (c) edge[->] node[anchor=south] {a) hv, NBS, bezoyl peroxide CCl$_4$, 8 h \quad b) PPh$_3$, Xylene 15 h} node[anchor=north] {Acetonitrile 300 \textdegree C 2 h} (d);
\path (d) edge[<-] node[anchor=south] {hv, I$_2$, THF Toluene 125W HPMVL 24 h} node[anchor=north] {NaOCH$_3$, CH$_3$OH RT, 24 h} (f);
\path (e) edge[->] node[anchor=south] {hv, I$_2$, THF Toluene 125W HPMVL 24 h} node[anchor=north] {Acetonitrile 300 \textdegree C 2 h} (a);
\end{tikzpicture}
\end{center}

The presence of the bulky naphthalene ring may prevent cyclization of 24 at the required angular location. In a modified route the double photocyclization/dehydrogenation was attempted starting from 30 where the bulky naphthyl group (as present in 24) had been replaced by the less bulky phenyl ring (Scheme 8). Accordingly, the required 3,6-(bis-styryl)phenanthrene 30 was synthesized by combination of Witting reaction, photodehydrocyclization and Heck reaction starting from 4-bromobenzaldehyde 27. Photodehydrocyclization of 30 under our improved conditions gave the desired [7]helicene 26 although in moderate yield.

In connection with our project on the synthesis of substituted [7]helicenes, a process for making 9,10-dialkoxy[7]helicenes was needed. With this aim, a commercial sample of phenanthrene 31 was converted to 9,10-phenanthrenequinone by oxidation, followed by conversion to 3,6-dibromo-9,10-phenanthrenequinone 32 by bromination. The required 3,6-dibromo-9,10-dimethoxyphenanthrene 33 was prepared by reduction of 32 using Na2S2O4 followed by an in situ O-methylation using dimethyl sulfate. The desired Pd(OAc)2 catalyzed double Heck reaction of 33 with styrene to get 3,6-(bis-styryl)-9,10-dimethoxyphenanthrene 34 proved to be difficult with dppp but succeeded with an 1-(α-aminobenzyl)-2-naphthol ligand.24 Subsequent photodehydrocyclization of 34 gave 9,10-dimethoxy[7]helicene 35 in moderate yield (Scheme 9).


Table 1. Comparison of photodehydrocyclization of styryl derivatives in presence of tetrahydrofuran and propylene oxide

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>% Yield With I₂-THF</th>
<th>% Yield With I₂-propylene oxide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Compound" /></td>
<td>97</td>
<td>Not mentioned</td>
<td>25a</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Compound" /></td>
<td>84</td>
<td>60-95</td>
<td>25b</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Compound" /></td>
<td>67</td>
<td>70</td>
<td>25b</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Compound" /></td>
<td>96</td>
<td>57</td>
<td>25b</td>
</tr>
</tbody>
</table>
Table 1. (Continued)

<table>
<thead>
<tr>
<th>5</th>
<th><img src="image1" alt="Chemical Structure" /></th>
<th>96</th>
<th>80</th>
<th>25c</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>44</td>
<td>90</td>
<td>25d</td>
</tr>
</tbody>
</table>

**Experimental Section**

Reagents were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens Limited etc. Tetrahydrofuran was refluxed and distilled on sodium benzophenone-ketyl. Toluene was distilled and stored 24 h over molecule sieves 4 Å prior to use. Thin Layer Chromatography was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. Photo reactions were performed in immersion well photo reactor with water jacket for cooling with 125 W or 250 W high pressure mercury vapor lamp made by General Electric (CEMA Electric Lighting Products India Pvt. Ltd).

All the compounds were purified by column chromatography using SRL silica gel (60-120 mesh). $^1$H NMR spectra were recorded on Bruker Avance 400 Spectrometer and were run in CDCl$_3$ unless otherwise stated. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. IR spectra were recorded on a Perkin-Elmer FTIR RXI spectrometer as KBr pallets. Melting points were recorded in Thiele’s tube using paraffin oil and are uncorrected. Kinetic experiments were run on ELICO L1127 pH meter.

**Comparison of propylene oxide and tetrahydrofuran as scavenger of HI:**

For the comparison of opening of propylene oxide and tetrahydrofuran as scavenger, the HI was synthesized by heating NaI (5.0 g, 0.033 mol) and H$_3$PO$_4$ (3.7 mL, 0.05 mol, 1.5 eq.) in a round bottom flask.$^{18b}$ It was condensed in a dry round bottom flask. From the distilled sample of HI (0.505 g) was taken and diluted with distilled water to 25 mL. For the comparison study two sets were prepared, one for propylene oxide and another for tetrahydrofuran. From this diluted solution (5 mL, 0.103 g of HI, 0.8 mmol) was taken for each set. In one set propylene oxide (0.0935 g, 0.11 mL, 1.6 mmol, 2 equiv) and distilled water was added to adjust the volume of the system to 15 mL. For the second set, tetrahydrofuran (0.1161 g, 0.13 mL, 1.6 mmol, 2 eq.) and distilled water was added to make the volume of the system to 15 mL.

Both sets were stirred at the same speed continuously while the pH was measured using a glass electrode attached to a pH meter at the interval of 5 min. Readings for the comparison are presented below in Table 2 and a graph was plotted (pH vs time in min.) as shown in Figure 1.
Table 2. Comparison of consumption of HI by propylene oxide and tetrahydrofuran

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>HI &amp; propylene oxide pH</th>
<th>HI &amp; tetrahydrofuran pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.00</td>
<td>1.75</td>
</tr>
<tr>
<td>15</td>
<td>2.32</td>
<td>1.86</td>
</tr>
<tr>
<td>25</td>
<td>2.46</td>
<td>1.96</td>
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<tr>
<td>35</td>
<td>2.66</td>
<td>2.04</td>
</tr>
<tr>
<td>45</td>
<td>2.78</td>
<td>2.10</td>
</tr>
<tr>
<td>55</td>
<td>2.82</td>
<td>2.17</td>
</tr>
<tr>
<td>65</td>
<td>2.88</td>
<td>2.20</td>
</tr>
<tr>
<td>75</td>
<td>2.96</td>
<td>2.23</td>
</tr>
</tbody>
</table>

4-Nitrostilbene (1a)

Mizoroki-Heck Reaction (Method A): Preparation of Catalyst Solution

A solution of palladium acetate (0.011 g, 0.00495 mmol, 0.1 mol%) and 1-(α-1-piperidylbenzyl)-2-naphthol (ligand A) (0.0018 g, 0.0059 mmol, 1.2 eq. of Pd(OAc)₂) was prepared in N,N-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature until a homogeneous solution was obtained. This catalyst solution was repeatedly purged by N₂ prior to use.

A two neck r.b. flask was charged with p-bromonitrobenzene (1.0 g, 4.95 mmol), dry potassium carbonate (1.71 g, 12.37 mmol, 2.5 eq.), TBAB (0.319 g, 0.99 mmol, 20 mol%) and N,N-dimethylacetamide (10-15 mL). The solution was repeatedly purged with N₂. Styrene (0.773 g, 7.42 mmol, 1.5 eq.) was added at 60 °C and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 °C for 48 h. After the completion of the reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford pale yellow solid (0.623, 77%), mp. 156 °C (Lit. 154–157 °C).²⁶

IR ν(KBr) cm⁻¹: 3077, 1631, 1589, 1508, 1338, 1185, 1105, 969, 873, 833, 765, 693.

¹H-NMR (400 MHz,CDCl₃): δ 8.21-8.24 (td, J = 9.32 & 2.4 Hz, 2H), 7.62-7.65 (td, J = 9.32 & 2.36 Hz, 2H), 7.38-7.42 (m, 2H), 7.55-7.57 (m, 2H), 7.34-7.36 (m, 1H), 7.25-7.3 (d, J = 16.32 Hz, 1H), 7.12-7.17 (d, J = 16.32 Hz, 1H),

MS (EI): m/z, (%) 226 (15), 225 (100), 208 (6), 195 (6), 180 (7), 179 (43), 178 (99), 177 (19), 152 (25), 151 (10), 89 (13), 76 (6).

3-Nitrophenanthrene (2a)

General procedure for photodehydrocyclization (Method B)

A solution of 4-nitrostilbene 1a (0.250 g, 1.11 mmol), iodine (0.309 g, 1.22 mmol, 1.1 eq.), THF (1.6 g, 1.8 mL, 22.2 mmol) and toluene (1.2 L) was irradiated using a 125W HMPV lamp for 36 h/monitored by tlc. After the reaction was over, the excess of iodine was removed by washing the solution with aqueous Na₂S₂O₃, followed by distilled water. The organic layer was concentrated
under the reduced pressure. The pure product was isolated as a yellow solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.077 g, 31%), mp. 175-177 °C (Lit. 175-177)\(^{\circ}\)C.\(^{27a}\)

IR \(\nu\) (KBr) cm\(^{-1}\): 3433, 1610, 1535, 1503, 1336, 1232, 1199, 1107, 1035, 844, 804, 735.

\(^1\)H-NMR (500 MHz,CDCl\(_3\)): \(\delta\) 9.62-9.62 (d, J = 2.5 Hz, 1H), 8.76-8.78 (d, J = 8.5 Hz, 1H), 8.39-8.39 (dd, J = 9.0, 2.0, 1H), 7.95-7.98 (m, 2H), 7.81-7.83 (d, J = 9.0, 1H), 7.78-7.79 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.22-7.74 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H).

MS (EI): \(m/z\), (%) 224 (16), 223 (100), 193 (27), 177 (62), 176 (72), 167 (21), 165 (43), 151 (51), 150 (28), 149 (81), 88 (25), 81 (34), 57 (49).

\section*{4-Bromo-4′-nitrostilbene (1b)\(^{27a}\)}

\textbf{General procedure for Wittig Reaction (Method C)}

A solution of Na metal (0.083 g, 3.63 mmol) in anhydrous methanol (5 mL) was added dropwise to a suspension of the (4-bromobenzyl)triphenylphosphonium bromide salt (1.685 g, 3.63 mmol) and \(p\)-nitrobenzaldehyde (0.500 g, 3.63 mmol) in anhydrous methanol (10 mL) under \(\text{N}_2\) at room temperature. The color of the solution changed to yellow. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, till no starting material was seen on tlc.

The mixture was poured in cold water to separate the precipitate. The aqueous solution along with the precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was removed under reduced pressure and crude product was purified on silica gel column to afford mostly trans form of the title stilbene as yellow solid (0.915 g, 91%), mp. 198-201 °C (lit. 201-203 °C).

IR \(\nu\) (KBr) cm\(^{-1}\): 3436, 1632, 1589, 1505, 1333, 1178, 1103, 1069, 1004, 968, 842, 811, 747.

\(^1\)H-NMR (400 MHz,CDCl\(_3\)): \(\delta\) 8.21-8.24 (ddd, J = 8.88, 2.32, 1.88 Hz, 2H), 7.61-7.65 (ddd, J = 9.32, 2.32, 1.84 Hz, 2H), 7.51-7.54 (ddd, J = 8.88, 2.28, 1.84 Hz, 2H), 7.40-7.43 (ddd, J = 9.00, 2.20, 1.90 Hz, 2H), 7.18-7.22 (d, J = 16.36 Hz, 1H), 7.11-7.15 (d, J = 16.36 Hz, 1H).

MS (EI): \(m/z\), (%) 306(4), 305 (14), 304 (4), 303 (14), 279 (9), 178 (29), 177 (11), 167 (39), 166 (10), 150 (15), 149 (100), 113 (11), 76 (13), 71 (19).

\section*{3-Bromo-6-nitrophenanthrene (2b)\(^{17}\)}

was obtained in 68% yield (0.169 g) on a 0.82 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford pale yellow solid, mp. 198-201 °C (Lit. 201-203 °C).

IR \(\nu\) (KBr) cm\(^{-1}\): 3431, 2922, 1625, 1589, 1509, 1335, 1179, 1105, 965, 861, 831, 745, 688.
1H-NMR (400 MHz, CDCl3): δ 8.22-8.24 (d, J = 8.72 Hz, 2H), 7.87-7.91 (d, J = 16.40 Hz, 1H), 7.82-7.84 (m, 3H), 7.73-7.76 (dd, J = 8.60, 1.24 Hz, 1H), 7.65-7.67 (d, J = 8.36, 2H), 7.47-7.53 (m, 2H), 7.40-7.44 (d, J = 16.30 Hz, 1H), 7.23-7.25 (d, J = 8.32 Hz, 1H).

MS (EI): m/z, (%) 276 (20), 275 (100), 229 (33), 228 (85), 227 (33), 226 (36), 202 (24), 114 (26), 113 (29), 101 (21), 83 (12), 81 (11).

2-Nitrobenzo[c]phenanthrene (4) was obtained in 83% yield (0.165 g) on a 0.91 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford yellow solid, mp. 150-152 °C (Lit. 150-152 °C).17

IR ν(KBr) cm⁻¹: 3052, 3006, 2924, 1601, 1530, 1510, 1378, 1334, 845, 828, 800, 759, 736.

1H-NMR (400 MHz, CDCl3): δ 9.99-10.00 (d, J = 2.00 Hz, 1H), 8.95-8.97 (d, J = 8.50 Hz, 1H), 8.35-8.38 (dd, J = 8.80, 2.20 Hz, 1H), 8.06-8.09 (d, J = 8.90 Hz, 1H), 8.04-8.06 (dd, J = 8.70, 2.40 Hz, 1H), 7.98-8.0 (d, J = 8.50 Hz, 1H), 7.96-7.98 (d, J = 7.80 Hz, 1H), 7.91-7.93 (d, J = 8.50 Hz, 1H), 7.81-7.84 (d, J = 8.50 Hz, 1H), 7.77-7.81 (m, 1H), 7.68-7.72 (m, 1H).

MS (EI): m/z, (%) 278 (3), 277 (25), 311 (41), 310 (61), 309 (15), 308 (70), 230 (15), 229 (89), 228 (100), 226 (33), 202 (15), 152 (66), 128 (07), 114 (57), 101 (26).

1,2-Bis(2-naphthylethylene (5) was obtained in 60% yield (0.540 g) on a 3.52 mmol scale by (method C). It was purified by column chromatography on silica gel to afford mostly trans form of the olefin as colorless solid, mp. 251-252 °C (Lit. 257-258 °C).28

IR ν(KBr) cm⁻¹: 3049, 2361, 1621, 1504, 1439, 1362, 960, 896, 862, 818, 747.

MS (EI): m/z, (%) 281 (23), 280 (100), 279 (72), 278 (33), 265 (17), 152 (14), 140 (34), 139 (43), 126 (20), 97 (23).

Benzo[ghi]perylen (7) was obtained in 43% yield (0.106 g) on a 0.89 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford pale yellow solid, mp. 265-270 °C (Lit. 270 °C).29

IR ν(KBr) cm⁻¹: 3044, 2925, 1612, 1595, 1510, 1445, 844, 811, 767, 753.

1H-NMR (400 MHz, CDCl3): δ 8.98-9.02 (d, J = 7.80, 0.80 Hz, 2H), 8.16-8.21 (dd, J = 7.70, 0.80 Hz, 2H), 8.34 (s, 2H), 8.11-8.15 (d, J = 8.90 Hz, 2H), 8.05-8.09 (d, J = 8.80 Hz, 2H), 7.97-8.05 (d, J = 7.80 Hz, 2H).

MS (EI): m/z, (%) 278 (3), 277 (25), 276 (100), 275 (14), 274 (23), 138 (58), 137 (44), 136 (19), 125 (8), 124 (7).

2-[2-(4-Bromophenyl)ethenyl]naphthalene (10) was obtained in 76% yield (1.575 g) on a 6.7 mmol scale by (method C). It was purified by column chromatography on silica gel to afford mostly trans form of the olefin as colorless solid, mp.192 °C. (Lit. 188.5-189 °C).30

IR ν(KBr) cm⁻¹: 3049, 1583, 1483, 1396, 1072, 965, 853, 820, 741.

1H-NMR (400 MHz, CDCl3): δ 7.80-7.85 (m, 4H), 7.70-7.73 (dd, J = 8.64, 1.68 Hz, 1H), 7.41-7.51 (m, 6H), 7.24-7.28 (d, J = 16.32 Hz, 1H), 7.13-7.17 (d, J = 16.32 Hz, 1H).

MS (EI): m/z, (%) 311 (13), 310 (61), 309 (15), 308 (70), 230 (15), 229 (89), 228 (100), 226 (33), 202 (15), 152 (06), 128 (07), 114 (57), 101 (26).

2-Bromobenzo[c]phenanthrene (11) was obtained in 96% yield (0.953 g) on a 3.2 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford colorless solid, mp. 87-88 °C (Lit. 87-88 °C).30,31
IR ν (KBr) cm⁻¹: 3044, 1600, 1588, 1485, 1440, 1109, 1082, 1039, 781, 746, 599, 570, 529.

^1^H-NMR (400 MHz, CDCl₃): δ 9.03-9.05 (d, J = 8.5 Hz, 1H), 9.48 (s, 1H), 8.02-8.04 (d, J = 7.90 Hz, 1H), 7.91-7.93 (d, J = 8.60 Hz, 1H), 7.87-7.90 (d, J = 8.60 Hz, 1H), 7.82-7.85 (d, J = 8.50 Hz, 1H), 7.80-7.82 (d, J = 8.40 Hz, 1H), 7.65-7.67 (d, J = 7.40 Hz, 1H), 7.63-7.65 (d, J = 7.30 Hz, 1H).

MS (EI): m/z, (%) 308 (50), 307 (12), 306 (51), 227 (44), 226 (76), 225 (19), 224 (22), 149 (39), 114 (27), 113 (100), 112 (51), 111 (23), 97 (17).

2-Styrylbenzo[c]phenanthrene (12)
Mizoroki-Heck Reaction (Method D): Preparation of Catalyst Solution
A solution of palladium acetate (0.0015 g, 0.0065 mmol, 1 mol%) and 1,3-bis(diphenylphosphino)propane (0.004 g, 0.0097 mmol, 1.5eq. of Pd(OAc)₂) was prepared in N,N-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature until a homogeneous solution was obtained. This solution was repeatedly purged by N₂ prior to use.

In another r.b. flask, a mixture of 2-bromobenzo[c]phenanthrene (0.2 g, 0.65 mmol), dry potassium carbonate (0.180 g, 1.3 mmol, 2 eq.), TBAB (0.104 g, 0.13 mmol, 20 mol%) was prepared in dry N,N-dimethylacetamide (15 mL) and degassed. This was heated to 60 °C and charged with styrene (0.102 g, 0.97 mmol, 1.5 eq.) and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 °C for 48 h. After completion of the reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel to get pure colorless solid product (0.210 g, 98%), mp. 140-42 °C (Lit. 140 °C).

IR ν (KBr) cm⁻¹: 3023, 2915, 1598, 1508, 1414, 1230, 1181, 961, 838, 802, 747, 671, 610.

^1^H-NMR (400 MHz, CDCl₃): δ 8.98-9.00 (d, J = 8.36 Hz, 1H), 8.14-8.16 (d, J = 8.36 Hz, 1H), 7.84-7.86 (d, J = 8.36 Hz, 1H), 7.79-7.81 (d, J = 8.36 Hz, 1H), 7.76-7.78 (d, J = 8.36 Hz, 1H), 7.61-7.63 (d, J = 8.36 Hz, 1H), 7.48-7.50 (d, J = 8.36 Hz, 1H), 7.32-7.36 (d, J = 8.36 Hz, 1H), 7.24-7.28 (d, J = 8.36 Hz, 1H), 7.19-7.21 (d, J = 8.36 Hz, 1H), 2.37 (s, 3H).

MS (EI): m/z, (%) 345(29), 344 (100), 329 (15), 328 (19), 226 (07), 165 (20), 164 (34), 156 (13).
[6]Helicene (14) was obtained in 64% yield (0.083 g) on a 0.39 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford yellow solid, mp 231-232 °C. (Lit. 231 °C). 33

Same compound was also synthesized by double photodehydrocyclization of 18 (Scheme-6).

A solution of 2,7-distyrylnaphthalene 18 (0.110 g, 0.38 mmol), iodine (0.214 g, 0.84 mmol 2.2 eq.), tetrahydrofuran (1.1 g, 1.23 mL, 15.2 mmol, 40 eq.) and toluene (1.2 L) was irradiate d using 125W HMPV lamp for 22 h and was monitored by tlc. After the reaction was over, the excess of iodine was removed by washing the solution with aqueous Na2S2O3, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained after column chromatography as yellow solid (0.081 g, 75%) (re crystallized from petroleum ether). mp. 231-232 °C (Lit. 231 °C).

IR ν (KBr) cm⁻¹: 3042, 1601, 1500, 1468, 1434, 844, 828, 799, 753.

1H-NMR (400 MHz, CDCl3): δ 7.96-8.01 (m, 4H), 7.90-7.95 (m, 4H), 7.83-7.88 (d, J = 8.0 Hz, 2H), 7.57-7.59 (d, J = 8.60 Hz, 2H), 7.19-7.23 (dd, J = 7.70, 7.20 Hz, 2H), 6.65-6.69 (m, 2H).

MS (EI): m/z, (%) 329 (26), 328 (100), 301 (43), 300 (69), 163 (49), 162 (60), 161 (27), 156 (50), 150 (48), 149 (45), 111 (32), 97 (49), 85 (61), 83 (61).

2-Methyl[6]helicene (15) was obtained in 78% yield (0.193 g) on a 0.75 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford pale yellow solid, recrystallized from ethyl acetate-petroleum ether. mp. 194-196 °C (Lit. 194-198 °C). 34

IR ν (KBr) cm⁻¹: 3045, 2911, 1603, 1475, 1438, 1144, 1036, 951, 848, 833, 794, 747, 733, 618.

1H-NMR (400 MHz, CDCl3): δ 7.92-8.02 (m, 6H), 7.82-7.88 (m, 2H), 7.79-7.81 (dd, J = 8.04, 0.8 Hz, 1H), 7.69-7.71 (d, J = 8.08 Hz, 1H), 7.58-7.60 (d, J = 8.48, Hz, 1H), 7.36 (S, 1H), 7.21-7.23 (dd, J = 7.88, 0.88 Hz, 1H), 7.03-7.05 (dd, J = 8.08, 1.32 Hz, 1H), 1.75 (S, 3H).

MS (EI): m/z, (%) 343 (30), 342 (100), 327 (49), 326 (35), 300 (45), 171 (14), 163 (60), 162 (62), 150 (28).

2,7-Dibromonaphthalene (17). A 250 mL round bottom flask was charged with triphenylphosphine (14.41g, 54.9 mmol, 2.2 eq.) and dry acetonitrile (20 mL). The suspension was cooled to 0 °C and to this mixture dry bromine (8.77 g, 2.8 mL, 54.93 mmol, 2.2 eq.) was added dropwise in such a way that the temperature was maintained below 5 °C. A heavy white precipitate was formed. To this mixture 2,7-dihydroxynaphthalene (16) in acetonitrile (40 mL) was added in one portion. The mixture was carefully stirred even though precipitates gained weight. The mixture was heated to 70-80 °C at which point the precipitate dissolved and the reaction continued for 1.5 h. The flask was fitted with an air cooled distillation assembly and acetonitrile was distilled at atmospheric pressure. The temperature was then gradually increased up to 250 °C. Evolution of HBr appeared with strong heating (~190 °C). This evolved HBr was trapped by a saturated NaOH solution. The temperature was maintained around 280-300 °C for 2 h and a dark oil was obtained which was allowed to cool to 100 °C at which point 50 mL of absolute ethanol was added and the mixture stored at 4 °C overnight. The product was extracted with petroleum ether, and separated by
column chromatography (SiO$_2$, Petroleum ether) to afford a colorless solid (3.76 g, 53%), which was recrystallized from ethanol for further purification.

mp. 138-140 °C (Lit. 140-141 °C).$^{35}$

IR $\nu$(KBr) cm.$^{-1}$: 3052, 1606, 1482, 1344, 1178, 933, 903, 867, 836, 636, 592, 538, 473.

MS (EI): $m/z$ (%) 288 (42), 286 (100), 284 (46), 207 (21), 205 (23), 144 (09), 143 (18), 142 (09), 126 (84), 125 (10), 103 (08), 74 (11), 63 (38).

2,7-Distyrlynaphthalene (18) was obtained in 65% yield (0.377 g) on a 1.74 mmol scale by (method D). It was purified by column chromatography on silica gel to afford colorless solid, mp. 262-264 °C (Lit. 260-262 °C).$^{36}$

IR $\nu$(KBr) cm.$^{-1}$: 3053, 3022, 1619, 1492, 1445, 966, 913, 836, 747, 691.

$^1$H-NMR (400 MHz, d$_6$-DMSO): $\delta$ 7.92-7.98 (m, 12H including 1 olefin H), 7.79-7.83 (m, 2H, for olefin $J = 17.6$ Hz), 7.60-7.62 (m, 2H), 7.28-7.32 (m, 2H).

MS (EI): $m/z$, (%) 333 (27) 332 (100), 254 (7), 253 (26), 229 (11), 228 (20), 226 (09), 166 (12), 164 (9), 158 (26), 151 (13).

2-[2-(4-Methylphenyl)ethenyl]naphthalene (21) was obtained in 86% yield (3.552 g) on a 16.96 mmol scale by (method C). It was purified by column chromatography on silica gel to afford mostly trans form of the olefin as colorless solid, mp. 183-184 °C (Lit. 181-183 °C).$^{37}$

IR $\nu$(KBr) cm.$^{-1}$: 3016, 2913, 2361, 1907, 1591, 1508, 1411, 1363, 1274, 1112, 965, 901, 853, 821, 740.

MS (EI): $m/z$, (%) 245 (21), 244 (100), 243 (23), 230 (18), 229 (85), 228 (60), 167 (28), 148 (69), 129 (16), 122 (15), 121 (22), 114 (22), 113 (23), 101 (15), 83 (20), 71 (20).

2-Methylbenzo[c]phenanthrene (22) was obtained in 96% yield (0.236 g) on a 1.02 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford colorless solid, mp. 79-81 °C (Lit. 79-80 °C).$^{37}$

IR $\nu$(KBr) cm.$^{-1}$: 3047, 3010, 2919, 1598, 1518, 1493, 1417, 838, 785, 754, 669.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 9.13-9.15 (d, $J = 8.44$ Hz, 1H), 8.93-8.93 (d, $J = 0.64$ Hz, 1H), 7.99-8.02 (dd, $J = 7.96$, 1.40 Hz, 1H), 7.90-7.92 (d, $J = 8.12$ Hz, 1H), 7.84-7.88 (t, $J = 8.28$ Hz, 2H), 7.79-7.81 (d, $J = 8.52$ Hz, 1H), 7.74-7.76 (d, $J = 8.48$ Hz, 1H), 7.66-7.70 (ddd, $J = 8.40$, 6.84, 1.52 Hz, 1H), 7.59-7.63 (ddd, $J = 8.00$, 7.00, 1.16 Hz, 1H), 7.44-7.47 (dd, $J = 8.08$, 1.32 Hz, 1H), 2.65 (S, 3H).

MS (EI): $m/z$, (%) 243 (22), 242 (100), 241 (17), 227 (29), 226 (31), 167 (8), 149 (27), 121 (12), 120 (15), 119 (31), 113 (25), 106 (10), 81 (8).

2-Benzocphcalmethytriphenylphosphonium bromide (23)

A solution of 2-methylbenzo[c]phenanthrene 22 (0.250 g, 1.03 mmol), N-bromosuccinimide (0.184 g, 1.03 mmol) and benzyol peroxide (0.025 g, 0.1 mmol) in carbon tetrachloride (10 mL) was heated to reflux and stirred for 8 h. At the end of this time the reaction mixture was cooled and the succinimide produced was removed by filtration. The filtrate was washed with a sodium thiosulphate solution, water and was dried over sodium sulfate. The solvent was then removed under reduced pressure.
The crude product (0.330 g) and triphenylphosphine (0.295 g, 1.12 mmol) was dissolved in xylene and refluxed with stirring for 8 h. The precipitates formed were collected, washed with petroleum ether and dried in vacuum affording a white solid (0.61 g, 98%), mp. 298-302 °C. (Lit. mp. 308 °C).\(^{37}\)

2-[2-(Naphthyl)ethenyl]benzo[c]phenanthrene (24) was obtained in 54% yield (0.660 g) on a 3.2 mmol scale by (method C). It was purified by column chromatography on silica gel to afford mostly \textit{trans} form of the olefin as colorless solid, mp. 198-200 °C (Lit. 200-201°C).\(^{23}\)

IR \(\nu\) (KBr) cm\(^{-1}\): 3046, 2364, 1919, 1595, 1500, 1426, 1237, 959, 895, 820, 811, 744, 621.

\(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 9.18-9.20 (d, \(J = 8.50\) Hz, 1H), 9.18 (s, 1H), 8.02-8.06 (m, 2H), 7.81-7.85 (m, 10 H), 7.75-7.78 (m, 1H), 7.65-7.68 (m, 1H), 7.45-7.55 (m, 4 H, 2-aromatic & 2-olefinic protons, \(J = 16.50\) Hz for olefinic H).

MS (EI): \(m/z\), (%) 381 (31), 380 (100), 379 (36), 378 (16), 363 (11), 226 (7), 190 (37), 189 (38), 188 (27), 182 (26), 176 (6).

Dinaphtho[1,2-a:2',1'-h]anthracene (25) was obtained in 75% yield (0.093 g) on a 1.02 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford yellow solid, mp. 230-231 °C (Lit. 230-231°C).

IR \(\nu\) (KBr) cm\(^{-1}\): 3047, 1596, 1501, 1419, 1387, 1223, 902, 841, 797, 753.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.66 (S, 2H), 9.36-9.38 (d, \(J = 8.52\) Hz, 2H), 8.09-8.12 (m, 4H), 8.00-8.02 (d, \(J = 8.48\) Hz, 2H), 7.86-7.92 (dd, \(J = 8.68\), 8.48 Hz, 4H), 7.78-7.82 (ddd, \(J = 6.92\), 1.48, 1.00 Hz, 2H), 7.67-7.71 (dd, \(J = 7.92\), 1.00, 0.96 Hz, 2H).

MS (EI): \(m/z\), (%) 379 (30), 378 (91), 376 (22), 256 (16), 189 (48), 188 (44), 187 (48), 129 (34), 111 (49), 98 (58), 97 (81), 85 (90), 83 (100), 82 (49), 71 (98).

4,4’-Dibromostilbene (28) was obtained in 91 % yield (0.826 g) on a 2.7 mmol scale by (method C). It was purified by column chromatography on silica gel to afford mostly \textit{trans} form of the olefin as colorless solid, mp. 210-212 °C (Lit. 215-6 °C).

IR \(\nu\) (KBr) cm\(^{-1}\): 3047, 1901, 1721, 1584, 1494, 1405, 1379, 1230, 1151, 1104, 1070, 1018, 837, 769, 695, 607, 517.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.46-7.50 (d, \(J = 8.55\) Hz, 4H), 7.35-7.38 (d, \(J = 8.55\) Hz, 4H), 7.02 (s, 2H).

MS (EI): \(m/z\), (%) 340 (23), 339 (8), 338 (47), 336(27), 179 (16), 178 (100), 177 (16), 176 (21), 152 (10), 151 (10), 89 (48), 88 (33).

3,6-Dibromophenanthrene (29) was obtained in 97% yield (0.241 g) on a 0.81 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford colorless solid, mp. 194°C (Lit.- 194°C).

IR \(\nu\) (KBr) cm\(^{-1}\): 3049, 2918, 1583, 1494, 1405, 1379, 1069, 1017, 948, 837, 769, 732, 606, 517.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.75-8.76 (d, \(J = 1.56\) Hz, 2H), 7.80-7.83 (d, \(J = 8.48\) Hz, 2H), 7.17-7.75 (m, with overlapping d, \(J = 8.48\) Hz, 4 H).

MS (EI): \(m/z\), (%) 338 (30), 336 (61), 334 (33), 177 (17), 176 (100), 175 (20), 174 (17), 168 (18), 167 (38), 150 (26), 149 (99), 88 (63), 87 (25), 71 (26).
**3,6-Distyrylphenanthrene (30)** was obtained in 82% yield (0.233 g) on a 0.74 mmol scale by (method D). It was purified by column chromatography on silica gel to afford colorless solid, mp.198-200 °C.

IR ν (KBr) cm.−1: 3022, 1675, 1593, 1478, 1451, 1229, 972, 893, 766, 716.

1H-NMR (500 MHz, CDCl3): δ 8.76 (s, 2H), 7.85-7.89 (m, 4H), 7.70 (s, 2H), 7.63-7.64 (d, J = 7.0 Hz, 4H), 7.40-7.45 (m, 6H), 7.32-7.36 (d, J = 16.5 Hz, 2H), 7.29-7.31 (d, J = 7.5 Hz, 2H).

MS (EI): m/z, (%) = 384 (4), 383 (32), 382 (100), 303 (13), 302 (9), 289 (8), 278 (8), 277 (6), 276 (10), 191 (19), 183 (10), 182 (17), 151 (13).

**[7]Helicene (26)** was obtained by method B. A solution of 3,6-distyrylphenanthrene 30 (0.150 g, 0.39 mmol), iodine (0.219 g, 8.64 mmol, 20 eq.), THF (1.27 mL, 15.71 mmol, 40 eq.) and toluene (1.2 L) was irradiated using 125W HMPV lamp for 9 h. After the reaction was over the excess of iodine was removed by washing the solution with aqueous Na2S2O3, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product as yellow solid was obtained after column chromatography (0.066 g, 44%), mp. 254-256 °C (Lit. 254-255 °C).15a, 38

IR ν (KBr) cm.−1: 2925, 2364, 1610, 1049, 839, 608.

1H-NMR (500 MHz, CDCl3): δ 8.03 (s, 2H), 7.99-8.01 (d, J = 8.50 Hz, 2H), 7.92-7.93 (d, J = 8.00 Hz, 2H), 7.73-7.75 (d, J = 8.50 Hz, 2H), 7.49-7.51 (d, J = 8.50 Hz, 2H), 7.29-7.31 (d, J = 7.50 Hz, 2H), 7.15-7.17 (d, J = 8.50 Hz, 2H), 6.89-6.92 (t, J = 7.50 Hz, 2H), 6.38-6.41 (t, J = 7.00 Hz, 2H).

MS (EI): m/z, (%) = 378 (31), 377 (12), 351 (10), 350 (8), 256 (18), 187 (26), 129 (31), 111 (46), 98 (59), 97 (76), 83 (96), 71 (100).

**3,6-Dibromo-9,10-phenanthrenequinone (32)**

To a suspension of phenanthrene 31 (3.0 g, 17 mmol) in dilute H2SO4 (30 mL, conc. H2SO4 in 60 mL H2O), K2Cr2O7 (18 g) was added at 90-95 °C (water bath) in small portions (0.5-1 g) until a vigorous reaction sets in. The external heating was removed and the temperature of the mixture was kept approximately 110-115 °C. The temperature of the reaction mixture was not allowed to drop below 85 °C (hot water bath can be used if necessary). Finally the mixture was heated on a boiling water bath for 30 min, cooled, then water (200 mL) was added and the crude product was filtered, washed with water, purified by suspending in ethanol (30 mL) and stirred with saturated sodium bisulphate solution (30 mL). The mixture was stirred for 10 min, diluted with water (175 mL) and filtered. The filtrate was treated with a saturated sodium carbonate solution. The precipitated 9,10-phenanthrenequinone was filtered, washed with water, crystallized from glacial acetic acid, to obtain an orange solid. (4.046 g, 57.7%), mp. 207-209 °C (Lit. 208.5-210 °C).39a

IR ν (KBr)/cm.−1: 3067, 1675, 1593, 1478, 1451, 1229, 972, 893, 766, 716.

A mixture of 9,10-phenanthrenequinone (0.5 g, 2.4 mmol), dry nitrobenzene (3.0 mL) and dry bromine (1.35 mL, 26.4 mmol, dried over conc. H2SO4) and benzoyl peroxide (0.029 g, 0.12 mmol) was exposed to a coiled coil 200W tungsten lamp made by Edison India. Within about 10 min, evolution of gas bubbles could be seen. The temperature of the reaction was kept at 75 °C. After about 1 hr, the evolution of gas became imperceptible and cluster of needles gradually separated. The crude product was filtered, dried and recrystallized from absolute ethanol to obtain orange needles (0.50 g, 72.5%). mp. 258-260 °C (Lit. 259-276 °C).39b
IR ν (KBr) cm.⁻¹: 3101, 3034, 2921, 1677, 1583, 1545, 1470, 1225, 967, 903, 828, 701.

¹H-NMR (200 MHz, CDCl₃): δ 8.11 (s, 2H), 8.04-8.08 (d, J = 8.00 Hz, 2H), 7.64-7.68 (d, J = 8.00 Hz, 2H).

MS (EI): m/z, (%) = 368 (8), 367 (4), 366 (14), 339 (28), 337 (55), 335 (30), 230 (21), 228 (22), 150 (100), 149 (24), 129 (20), 115 (23), 83 (26), 81 (18), 75 (56), 74 (25), 71 (24).

3,6-Dibromo-9,10-dimethoxyphenanthrene (33)
A mixture of 3,6-dibromo-9,10-phenanthrenequinone 32 (2.5 g, 6.83 mmol), tetrabutylbutyl ammonium bromide (0.704 g, 2.186 mmol), sodium dithionite (3.567 g, 20.49 mmol), THF (30 mL) and H₂O (30 mL) in a round bottom flask was stirred for 30 min, then dimethyl sulfate (3.36 mL, 35.52 mmol) was added, followed by aqueous NaOH (3.56 g in 20 mL water). The mixture was stirred for 15 min, while after 3 min, 5-6 g of ice was added to keep mixture at ambient temperature. The aqueous layer was separated and extracted with ethyl acetate, the combined organic layer was washed with water, dilute ammonia, brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate: petroleum ether as eluent to obtain a colorless solid (2.46 g, 86%), mp. 134-136 °C.

IR ν (KBr) cm.⁻¹: 3438, 2932, 2837, 2366, 2340, 1906, 1720, 1614, 1587, 1482, 1458, 1422, 1394, 1345, 1311, 1229, 1202, 1121, 1091, 1064, 985, 861, 820, 707, 601.

¹H-NMR (400 MHz, CDCl₃): δ 8.56-8.57 (d, J = 1.44 Hz, 2H), 8.00-8.02 (d, J = 8.72 Hz, 2H), 7.63-7.65 (dd, J = 8.72, 1.44 Hz, 2H), 3.99 (s, 6H).

MS (EI): m/z, (%) = 398 (43), 396 (91), 394 (53), 382 (35), 380 (75), 378 (43), 352 (33), 337 (24), 273 (56), 271 (57), 165 (42), 163 (22), 150 (100), 148 (95), 81 (28).

9,10-Dimethoxy-3,6-distyrylphenanthrene (34) was obtained in 93% yield (0.52 g), on a 1.26-mmol scale, by (method A). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford pale yellow solid, mp. 116-120 °C.

IR ν (KBr) cm.⁻¹: 3438, 3024, 2931, 2835, 1602, 1503, 1446, 1419, 1364, 1327, 1243, 1202, 1121, 1062, 986, 954, 816, 751.

¹H-NMR (400 MHz, CDCl₃): δ 8.71-8.71 (d, J = 1.20 Hz, 2H), 8.21-8.23 (d, J = 8.40 Hz, 2H), 7.87-7.89 (dd, J = 8.80, 1.60 Hz, 2H), 7.62-7.64 (m, 4H), 7.28-7.44 (m, 10 H, overlapping the trans coupling proton signals d, J = 16.40 Hz), 4.11 (s, 6H).

MS (EI): m/z, (%) = 443 (33), 442 (100), 428 (13), 427 (41), 399 (23), 221 (53), 213 (10), 192 (10), 191 (14), 184 (15), 183 (13), 182 (18), 177 (23), 176 (34), 175 (12), 169 (32), 163 (11).

¹³C-NMR (50 MHz, CDCl₃): δ 61.69 (-OCH₃, 2C), 122.25 (-CH, 2C), 123.29 (-CH, 2C), 125.17 (-CH, 2C), 127.25 (-CH, 4C), 128.37 (-CH, 2C), 129.43 (-CH, 4C), 129.43 (-C, 4C) [DEPT 90 & 135 analysis shows the decrease in the intensity of signal due to overlapping quaternary carbon.], 135.49 (-C, 2C), 138.04 (-C, 2C), 144.79 (-C, 2C).

9,10-Dimethoxy[7]helicene (35) by (method B). A solution of 3,6-distyryl-9,10-dimethoxyphenanthrene 37 (0.450 g, 1.02 mmol), iodine (0.568 g, 2.24 mmol, 2.2 eq.), tetrahydrofuran (7.34 g, 8.25 mL, 10.18 mmol, 100 eq.) and toluene (1.2 L) was irradiated using a 250W HMPV lamp for 36 h. After the reaction was over, the excess of iodine was removed by washing the solution with aqueous Na₂S₂O₃, followed by distilled water. The organic layer was
concentrated under reduced pressure. After column chromatography, the pure product was obtained as orange-yellow crystals (0.225 g, 50%), mp. 270-272 °C, (Lit. > 250 °C).

IR ν (KBr) cm⁻¹: 3435, 3045, 2977, 2941, 2362, 1600, 1571, 1519, 1469, 1418, 1375, 1277, 1096, 1048, 987, 828, 749.

1H-NMR (500 MHz, CDCl₃): δ 8.37-8.39 (d, J = 8.00 Hz, 2H), 7.94-7.95 (d, J = 8.50 Hz, 2H), 7.71-7.73 (d, J = 8.50 Hz, 2H), 7.46-7.48 (d, J = 8.00 Hz, 2H), 6.88-6.91 (ddd, J = 8.50, 8.00, 1.50 Hz, 2H), 6.37-6.41 (ddd, J = 8.50, 7.00, 1.50 Hz, 2H), 4.25 (s, 6H).

MS (EI): m/z, (%) 439 (21), 438 (63), 423 (28), 395 (28), 380 (24), 350 (25), 203 (22), 195 (30), 181 (36), 180 (34), 175 (100), 174 (40), 168 (24), 111 (22), 97 (33), 85 (43), 84 (22), 83 (43), 71 (43).

Benzo[c]phenanthrene (36) was obtained in 84 % yield (0.125 g) on a 0.65 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford colorless solid, mp. 68-69 °C (Lit. 67-68 °C).

IR ν (KBr) cm⁻¹: 3042, 3007, 2926, 1618, 1599, 1518, 1494, 1458, 1418, 832, 806, 744.

1H-NMR (200 MHz, CDCl₃): δ 9.12-9.16 (d, J = 8.00 Hz, 2H), 8.01-8.03 (dd, J = 8.00, 2.00 Hz, 2H), 7.81-7.89 (dd, J = 8.00 Hz, 4H), 7.58-7.73 (m, 4H).

MS (EI): m/z, (%) 230 (02), 229 (19), 228 (100), 227 (48), 226 (43), 113 (17), 112 (06).

2-Chlorobenzo[c]phenanthrene (37) was obtained in 67% yield (0.10 g) on a 0.567 mmol scale by (method B). It was purified by column chromatography on silica gel using petroleum ether as eluent to afford colorless solid, mp. 62-64 °C (Lit. 61.4-61.8 °C).

IR ν (KBr) cm⁻¹: 3046, 2924, 1596, 1487, 1440, 1419, 1110, 1092, 1039, 838, 779, 747.

1H-NMR (200 MHz, CDCl₃): δ 9.11 (d, J = 1.30 Hz, 1H), 9.03-9.06 (d, J = 9.70 Hz, 1H), 8.01-8.03 (dd, J = 7.70, 0.80 Hz, 1H), 7.93-7.95 (d, J = 8.50 Hz, 1H), 7.90-7.93 (d, J = 8.50 Hz, 1H), 7.80-7.87 (m, 3H), 7.71-7.75 (m, 1H), 7.63-7.66 (m, 1H), 7.56-7.58 (dd, J = 8.50, 2.00 Hz, 1H).

MS (EI): m/z, (%) 265 (06), 264 (32), 263 (20), 262 (100), 228 (10), 227 (57), 226 (84), 225 (21), 224 (23), 113 (72), 112 (33).

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References


