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

Harish R. Talele, Anju R. Chaudhary, Parthiv R. Patel, and Ashutosh V. Bedekar*

Department of Chemistry, Faculty of Science
The Maharaja Sayajirao University of Baroda, Vadodara 390 002, India
E-mail: avbedekar@yahoo.co.in

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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.

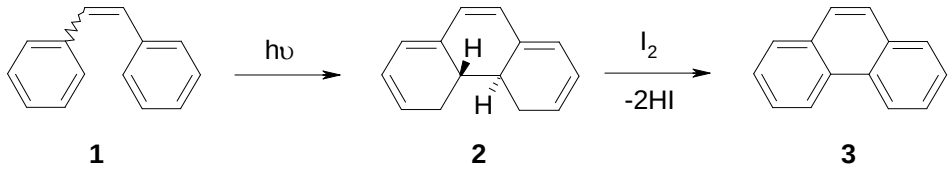
Keywords: Helicenes, HI scavenger tetrahydrofuran, Mizoroki-Heck-reaction, Phenanthrenes, Stilbenes, Wittig-olefination

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]

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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.[15] 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.[16]

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[17] 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.[18]

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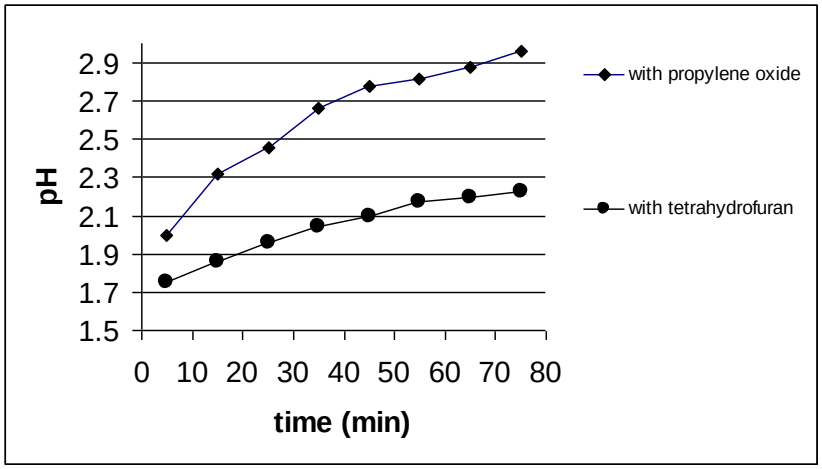
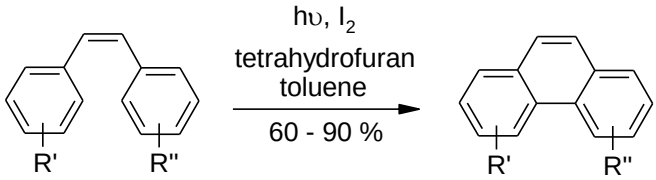


Figure 1. Comparison of propylene oxide and tetrahydrofuran as scavenger of HI.

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 photodehydocyclization using the present conditions by which a number of mono- and di-substituted phenanthrenes were prepared in excellent yields[17] (Scheme 2).

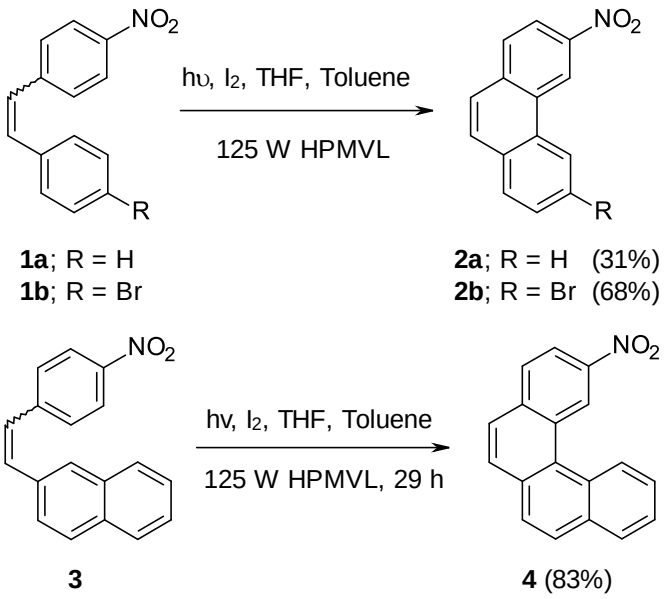


R' and R'' = H, Me, Cl, Br, OMe

Scheme 2. Improved synthesis of substituted phenanthrenes.

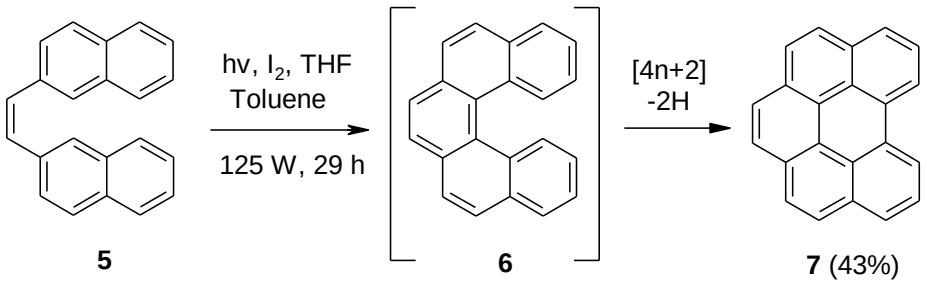
The photodehydrocyclization of nitrostilbenes is known to offer some difficulty when a catalytic quantity of iodine is used.[19] In order to test the present method on the nitro containing substrates, stilbenes **1a** and **1b** were synthesized and subjected to photolysis with I_2-THF. The corresponding nitro phenanthrenes **2a** and **2b** were isolated in reasonable yields (Scheme 3). Furthermore, the nitro derivative of styrylnaphthalene (2-[2-(4-nitrophenyl)ethenyl]naphthalene)[20] **3** was also successfully cyclized to 2-nitrobenzo[*c*]phenanthrene **4** indicating that the present method also tolerates nitro groups.

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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 4π+2π cyclization to form benzo[*ghi*]perylene **7** in good yield (Scheme 4).[21]



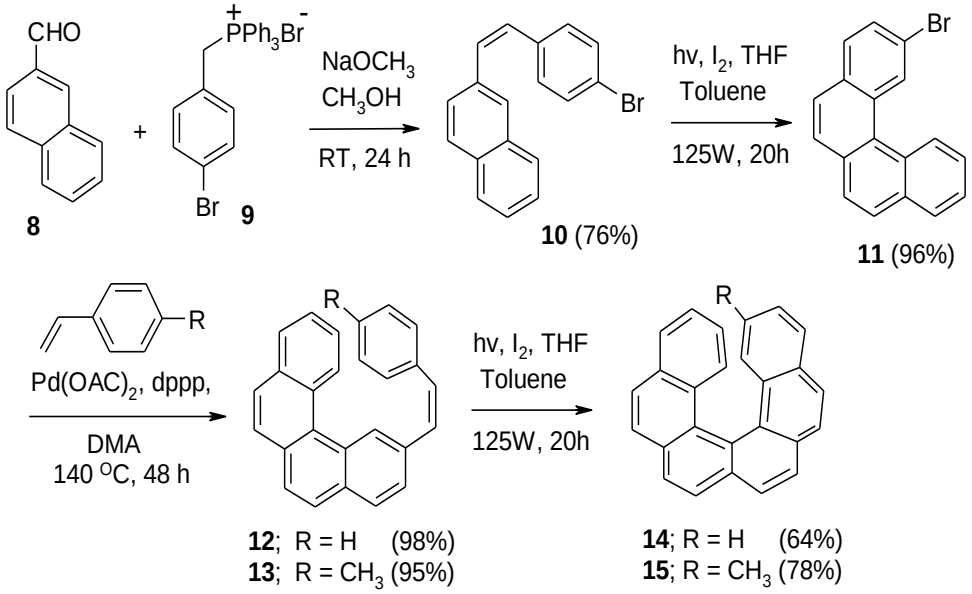
Scheme 4. Attempted synthesis of [5]helicene.

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

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bromide **9** under standard conditions. The photodehydrocyclization of **10** in toluene with iodine-THF gave 2-bromobenzo[*c*]phenanthrene **11** in high yield.



Scheme 5. Synthesis of [6]helicenes.

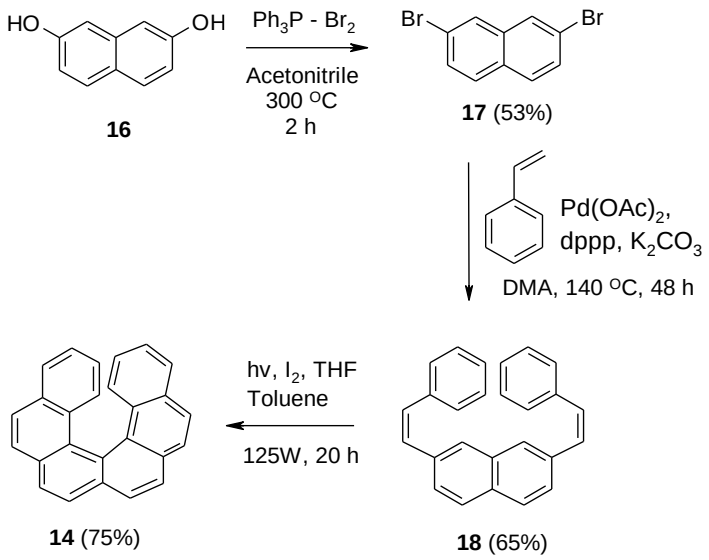
Reaction of 2-bromobenzo[*c*]phenanthrene **11** with styrene or 4-methylstyrene using the well-known $Pd(OAc)_2$-1,3-bis(diphenylphosphino)propane (Pd-dppp) catalyzed Heck reaction[22] resulted into 2-styrylbenzo[*c*]phenanthrene **12** and 2-(4-methylstyryl)benzo[*c*]phenanthrene **13** respectively 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).

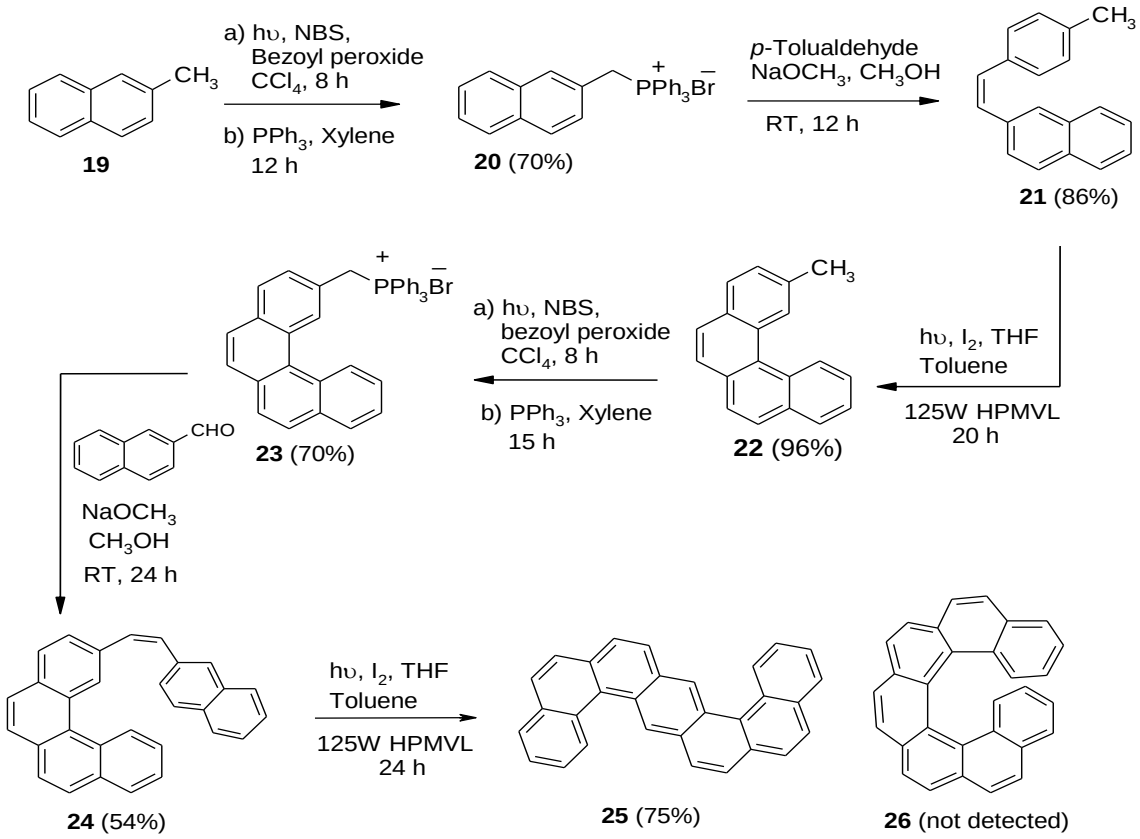
The method is further studied for the syntheses of [7]helicene. Scheme 7 illustrates an attempt for its synthesis. The readily available 2-methylnaphthalene **19** was converted to its Wittig salt **20** *via* benzylic bromination with NBS, and its reaction with triphenylphosphine. The salt **20**, on 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-

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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.[23]



Scheme 6. Another approach to [6]helicene.

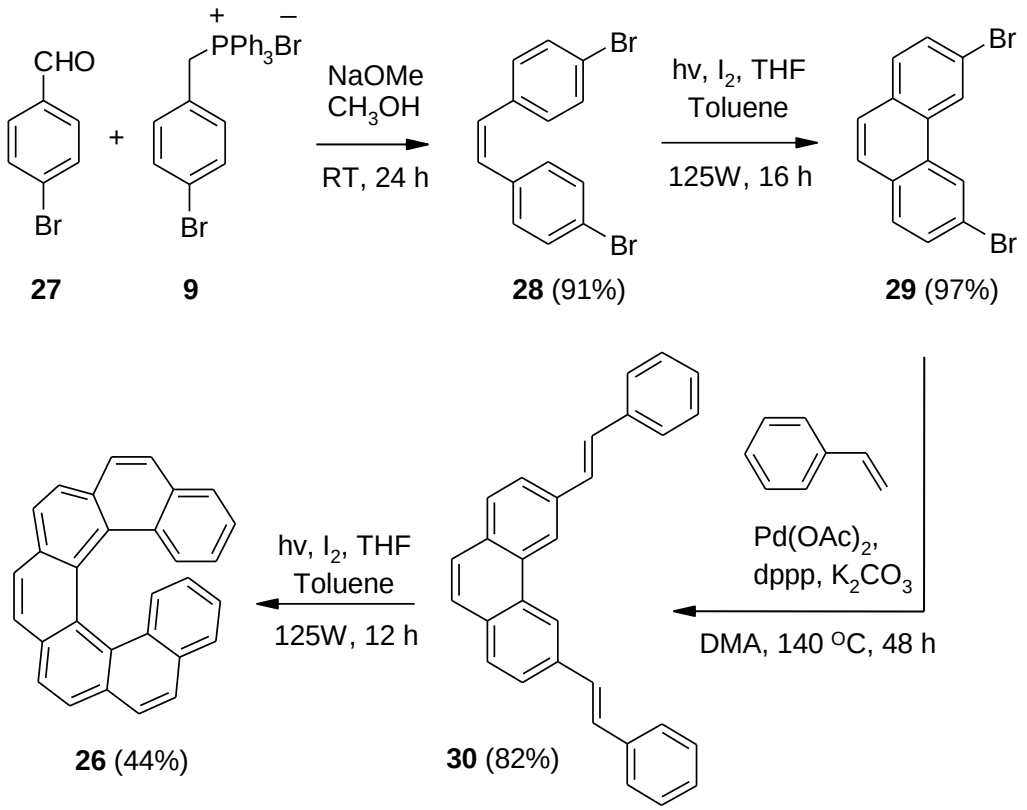


Scheme 7. Towards [7]helicene.

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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 $Na_2S_2O_4$ followed by a *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).

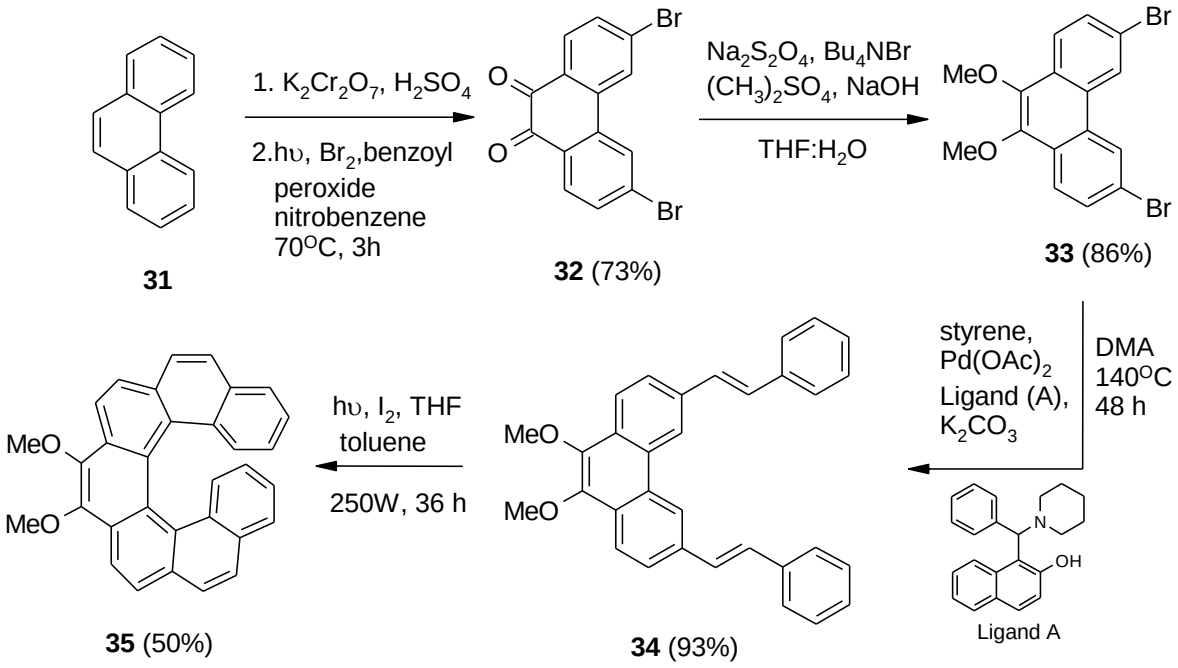


27 **9** **28** (91%) **29** (97%)

30 (82%) **26** (44%)

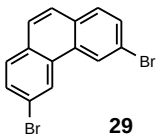
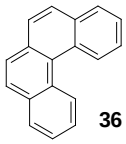
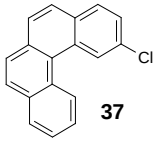
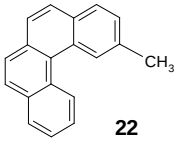
Scheme 8. Synthesis of [7]helicene.

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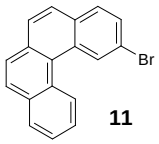
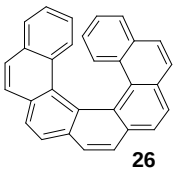
Scheme 9. Synthesis of 9,10-dimethoxy[7]helicene.

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

No.	Compound	% Yield With I_2-THF	% Yield With I_2-propylene oxide	Ref.
1	 **29**	97	Not mentioned	25a
2	 **36**	84	60-95	25b
3	 **37**	67	70	25b
4	 **22**	96	57	25b

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Table 1. (Continued)

5	 **11**	96	80	25c
6	 **26**	44	90	25d

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 F_{254} 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 LI127 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_3PO_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.

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Table 2. Comparison of consumption of HI by propylene oxide and tetrahydrofuran

Time (min)	HI & propylene oxide pH	HI & tetrahydrofuran pH
5	2.00	1.75
15	2.32	1.86
25	2.46	1.96
35	2.66	2.04
45	2.78	2.10
55	2.82	2.17
65	2.88	2.20
75	2.96	2.23

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 N_2 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 N_2. Styrene (0.773 g, 7.42 mmol, 1.5 eq.) was added at 60 ^oC and the mixture was heated up to 100 ^oC. When the temperature reached 100 ^oC, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 ^oC 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 ^oC (Lit. 154–157 ^oC).[26]

IR ν (KBr) $cm.^{-1}$: 3077,1631, 1589, 1508, 1338, 1185, 1105, 969, 873, 833, 765, 693.

^{1}H-NMR (400 MHz,$CDCl_3$): 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 $Na_2S_2O_3$, followed by distilled water. The organic layer was concentrated

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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 ºC (Lit. 175-177ºC).[27a]
IR ν (KBr) cm.$^{-1}$: 3433, 1610, 1535, 1503, 1336, 1232, 1199, 1107, 1035, 892, 844, 804, 735.
^{1}H-NMR (500 MHz,$CDCl_3$): δ 9.62-9.62 (d, J = 2.5 Hz, 1H), 8.76-8.78 (d, J = 8.5 Hz, 1H), 8.39-8.41 (dd, J = 9.0, 2.0, 1H), 8.01-8.03 (d, J = 8.5 Hz, 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).

4-Bromo-4′-nitrostilbene (1b)
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 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 ºC (lit. 201-203 ºC).[27b]
IR ν (KBr) cm.$^{-1}$: 3436, 1632, 1589, 1505, 1333, 1178, 1103, 1069, 1004, 968, 842, 811, 747.
^{1}H-NMR (400 MHz,$CDCl_3$): δ 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).
3-Bromo-6-nitrophenanthrene (2b) 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. 234-235 ºC (Lit. 234-235 ºC).[17]
IR ν (KBr) cm.$^{-1}$: 3082, 1621, 1591, 1530, 1497, 1437, 1342, 1075, 1028, 845, 736, 588, 509.
^{1}H-NMR (400 MHz,$CDCl_3$): δ 9.52 (d, J = 2.40 Hz, 1H), 8.89 (d, J = 2.20 Hz, 1H), 8.41-8.44 (dd, J = 8.80, 2.20 Hz, 1H), 8.02-8.04 (d, J= 8.80 Hz, 1H), 7.90-7.92 (d, J = 8.80 Hz, 1H), 7.82-7.84 (d, J = 8.80 Hz, 1H), 7.81-7.83 (m, 2H).
MS (EI): *m/z*, (%) = 304 (3), 303 (10), 302 (4), 301 (12), 176 (21), 175 (8), 149 (15), 137 (17), 136 (17), 121 (18), 109 (17), 95 (27), 69 (100).
2-[2-(4 Nitrophenyl)ethenyl]naphthalene (3) was obtained in 90% yield (0.411 g) on a 1.65 mmol scale by (method C). It was purified by column chromatography on silica gel to afford mostly *trans* form of the olefin as yellow solid, mp. 169-171 ºC (Lit. 168-170 ºC).[20]
IR ν (KBr) cm.$^{-1}$: 3431, 2922, 1625, 1589, 1509, 1335, 1179, 1105, 965, 861, 831, 745, 688.

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^{1}H-NMR (400 MHz, $CDCl_3$): 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 ºC (Lit. 150-152 ºC).[17]
IR ν (KBr) cm.$^{-1}$: 3052, 3006, 2924, 1601, 1530, 1510, 1378, 1334, 845, 828, 800, 759, 736.
^{1}H-NMR (400 MHz,$CDCl_3$): 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*, (%) 275 (11), 274 (60), 273 (95), 264 (25), 257 (13), 227 (18), 226 (53), 225 (13), 219 (82), 131 (37), 100 (19).

1,2-Bis(2-naphthyl)ethylene (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 ºC (Lit. 257-258 ºC).[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*]perylene (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 ºC (Lit. 270 ºC).[29]
IR ν (KBr) cm.$^{-1}$: 3044, 2925, 1612, 1595, 1510, 1445, 844, 811, 767, 753.
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.98-9.02 (dd, 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 ºC. (Lit. 188.5-189 ºC).[30]
IR ν (KBr) cm.$^{-1}$: 3049,1583, 1483, 1396, 1072, 965, 853, 820, 741.
^{1}H-NMR (400 MHz, $CDCl_3$): 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 ºC (Lit. 87-88 ºC).[30, 31]

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IR ν (KBr) cm.$^{-1}$: 3044, 1600, 1588, 1485, 1440, 1109, 1082, 1039, 839, 781, 746, 599, 570, 529.
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.03-9.05 (d, J = 8.50 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), 7.74-7.76 (d, J = 7.20 Hz, 1H), 7.71-7.74 (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(diphenylphospino)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 N_2 prior to use.
In another r.b. flask, a mixture of 2-bromobenzo[*c*]phenanthrene **11** (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 ºC and charged with styrene (0.102 g, 0.97 mmol, 1.5 eq.) and the mixture was heated up to 100 ºC. When the temperature reached 100 ºC, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 ºC 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 ºC (Lit. 140 ºC).[32]
IR ν (KBr) cm.$^{-1}$: 3018,1601, 1497, 1445, 957, 832, 783, 745, 687.
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.18-9.20 d, J = 7.20 Hz, 1H), 9.18 (s, 1H), 8.04-8.07 (m, 2H), 7.89-7.94 (m, 2H), 7.81-7.86 (m, 2H), 7.43-7.78 (m, 1H), 7.63-7.69 (m, 3H), 7.41-7.45 (m, 3H), 7.28-7.35 (m, 3H).
MS (EI): m/z, (%) 331(26), 330 (100), 329 (29), 328 (15), 313 (10), 226 (8), 165 (30), 164 (22), 163 (21), 157 (25), 156 (18), 151 (8).
2-[2-(4-Methylphenyl)ethenyl]benzo[*c*]phenanthrene (13) was obtained in 95% yield (0.531 g), on a 1.62-mmol scale, by (method D). It was purified by column chromatography on silica gel to afford pale yellow solid, mp. 115-116 ºC (Lit. 118-119 ºC).[33]
IR ν (KBr) cm.$^{-1}$: 3023, 2915, 1598, 1508, 1414, 1230, 1181, 961, 838, 802, 747, 671, 610.
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.14-9.16 (d, J = 8.56 Hz, 1H), 9.12 (s, 1H), 8.01-8.03 (dd, J = 8.00, 1.32 Hz, 1H), 7.96-7.98 (d, J = 8.36 Hz, 1H), 7.84-7.90 (m, 3H), 7.79-7.81 (d, J = 8.56 Hz, 1H), 7.76-7.79 (d, J = 8.48 Hz, 2H), 7.70-7.74 (ddd, J = 8.48, 6.96, 1.48 Hz, 1H), 7.61-7.65 (ddd, J = 8.00, 7.00, 1.08 Hz, 1H), 7.48-7.50 (d, J = 8.04 Hz, 2H), 7.32-7.36 (d, J = 16.36 Hz, 1H), 7.24-7.28 (d, J = 16.36 Hz, 1H), 7.19-7.21 (d, J = 7.88 Hz, 1H), 2.37 (s, 3H).
MS (EI): *m/z*, (%) 345(29), 344 (100), 329 (15), 328 (19), 226 (07), 165 (22), 164 (34), 156 (13).

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[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 ºC. (Lit. 231ºC).[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 irradiated 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 $Na_2S_2O_3$, 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%) (recrystallized from petroleum ether).

mp. 231-232 ºC (Lit. 231ºC).[33]

IR ν (KBr) cm.$^{-1}$: 3042, 1601, 1500, 1468, 1434, 844, 828, 799, 753.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.96-8.01 (m, 4H), 7.90-7.95 (m, 4H), 7.83-7.88 (d, J = 8.00 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 ºC (Lit. 194-198 ºC).[34]

IR ν (KBr) cm.$^{-1}$: 3045, 2911, 1603, 1504, 1475, 1438, 1144, 1036, 951, 848, 833, 794, 747, 733, 618.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.92-8.02 (m, 6H), 7.82-7.88 (m, 2H), 7.79-7.81 (dd, J = 8.04, 0.80 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), 6.65-6.69 (ddd, J = 8.36, 6.92, 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 ºC 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 ºC. 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 ºC 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 ºC. Evolution of HBr appeared with strong heating (~190 ºC). This evolved HBr was trapped by a saturated NaOH solution. The temperature was maintained around 280-300 ºC for 2 h and a dark oil was obtained which was allowed to cool to 100 ºC at which point 50 mL of absolute ethanol was added and the mixture stored at 4 ºC overnight. The product was extracted with petroleum ether, and separated by

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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 ºC (Lit. 140-141 ºC).[35]
IR ν (KBr) cm.$^{-1}$: 3052, 1606, 1567, 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-Distyrylnaphthalene (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 ºC (Lit. 260-262 ºC).[36]
IR ν (KBr) cm.$^{-1}$: 3053, 3022, 1619, 1492, 1445, 966, 913, 836, 747, 691.
^{1}H-NMR (400 MHz, d^6-DMSO): δ 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), 7.38-7.41 (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.183-184ºC (Lit. 181-183ºC).[37]
IR ν (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 ºC (Lit. 79-80 ºC).[37]
IR ν (KBr) cm.$^{-1}$: 3047, 3010, 2919, 1598, 1518, 1493, 1417, 838, 785, 754, 669.
^{1}H-NMR (400 MHz, $CDCl_3$): δ 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-Benzo[*c*]phenanthrylmethyltriphenylphosphonium 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 benzoyl 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.

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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 ºC. (Lit. mp. 308 ºC).[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 *trans* form of the olefin as colorless solid, mp**.** 198-200 ºC (Lit. 200-201ºC).[23]

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

^{1}H-NMR (500 MHz, $CDCl_3$): δ 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 ºC (Lit. 230-231 ºC).[23]

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

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.66 (S, 2H), 9.36- 9.38 (d, J = 8.52, 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, 1.40 Hz, 2H), 7.67-7.71 (ddd, 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 *trans* form of the olefin as colorless solid, mp. 210-212 ºC (Lit. 215-6 ºC).[25d]

IR ν (KBr) cm.$^{-1}$: 3049, 1901, 1721, 1584, 1494, 1405, 1379, 1230, 1151, 1104, 1070, 1018, 837, 769, 695, 607, 575, 517.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 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. 194ºC (Lit.- 194ºC).[25d]

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

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.75-8.76 (d, J = 1.56 Hz, 2H), 7.80-7.83 (d, J = 8.48 Hz, 2H), 7.71-7.75 (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).

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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, [38] mp.198-200 ºC.
IR ν (KBr) cm.$^{-1}$: 3022, 1802, 1601, 1494, 1446, 1154, 958, 886, 840, 788, 750, 688.
^{1}H-NMR (500 MHz, $CDCl_3$): 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, 2.2 eq.), THF (1.32 g, 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 $Na_2S_2O_3$, 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 ºC (Lit. 254-255ºC.).[15a, 38]
IR ν (KBr) cm.$^{-1}$: 2925, 2364, 1610, 1049, 839, 608.
^{1}H-NMR (500 MHz, $CDCl_3$): 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 H_2SO_4 (30 mL, conc. H_2SO_4 in 60 mL H_2O), $K_2Cr_2O_7$ (18 g) was added at 90-95 ºC (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 ºC. The temperature of the reaction mixture was not allowed to drop below 85 ºC (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 ºC (Lit. 208.5-210 ºC).[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. H_2SO_4) 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 ºC. 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 ºC (Lit. 259-276 ºC).[39b]

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IR ν (KBr) cm.$^{-1}$: 3101, 3034, 2921, 2852, 1677, 1583, 1545, 1470, 1225, 967, 903, 828, 701.
^{1}H-NMR (200 MHz, $CDCl_3$): 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 H_2O (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 ^{o}C.[39c]
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, 1023, 985, 861, 820, 707, 601.
^{1}H-NMR (400 MHz, $CDCl_3$): 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 ^{o}C.
IR ν (KBr) cm.$^{-1}$: 3438, 3024, 2931, 2835, 1602, 1503, 1446, 1419, 1364, 1327, 1243, 1202, 1121, 1062, 986, 954, 816, 751.
^{1}H-NMR (400 MHz, $CDCl_3$): 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).
^{13}C-NMR (50 MHz, $CDCl_3$): δ 61.69 (-OCH_3, 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 $Na_2S_2O_3$, followed by distilled water. The organic layer was

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concentrated under reduced pressure. After column chromatography, the pure product was obtained as orange-yellow crystals (0.225 g, 50%), mp. 270-272 ºC, (Lit. > 250 ºC).[40]
IR ν (KBr) cm.$^{-1}$: 3435, 3045, 2977, 2941, 2362, 1600, 1571, 1519, 1469, 1418, 1375, 1277, 1096, 1048, 987, 828, 749.
^{1}H-NMR (500 MHz, $CDCl_3$): 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), 7.28-7.29 (dd, J = 8.50, 1.00 Hz, 2H), 7.12-7.14 (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 ºC (Lit. 67-68 ºC).[41]
IR ν (KBr) cm.$^{-1}$: 3042, 3007, 2926, 1618, 1599, 1518, 1494, 1458, 1418, 832, 806, 744.
^{1}H-NMR (200 MHz, $CDCl_3$): δ 9.12-9.16 (d, J = 8.00 Hz, 2H), 8.01-8.05 (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 ºC (Lit. 61.4-61.8 ºC).[41]
IR ν (KBr) cm.$^{-1}$: 3046, 2924, 1596, 1487, 1440, 1419, 1110, 1092, 1039, 838, 779, 747.
^{1}H-NMR (200 MHz, $CDCl_3$): 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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