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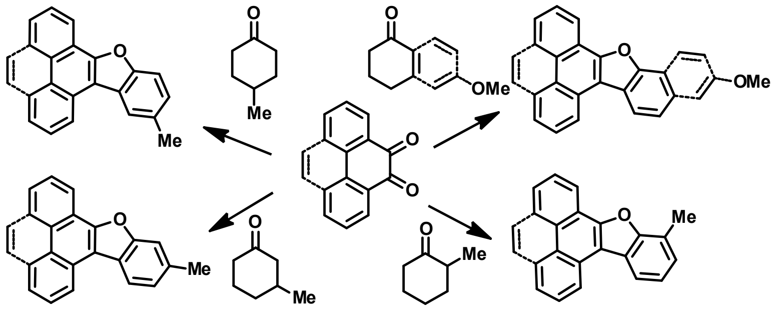
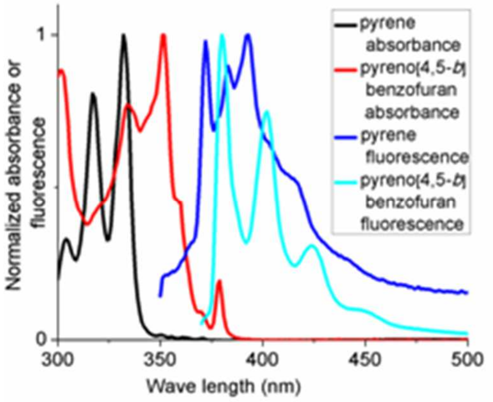


***Reagent and conditions***: **$FeCl_3$ (1 equiv), rt, 12 h.**



# Synthesis and photochromic properties of benzofuran-phenyanthrene and benzofuran-pyrene hybrids

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## Abstract

Iron(III) chloride mediated condensation of phenanthrene-9,10-dione and pyrene-4,5-dione with cyclohexanone and its derivatives furnish benzofuran-phenanthrene and benzofuran-pyrene hybrids. Absorption and emission spectral studies revealed the bathochromic effect of benzofuran annulations on the photophysical properties of the pyrene chromophore. Solvatochromic studies revealed that polarity of solvents did not have noticeable effect on the absorption as well as emission spectra. While benzofuran annulation enhanced the quantum yield in most of the solvents, appending a methyl group, in fact, reduced the quantum yield. Thus, our studies delineated synthesis and photophysical properties of selected PAHs with a furan ring.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAH) represented by common molecules like phenanthrene **1** and pyrene **2** (Figure 1) are a major class of organic compounds.[1] Many PAHs are released into the environment as pollutants primarily due to human intervention. It is well known that PAHs cause cancer, allergies and other ailments.[2] While most of PAHs have a negative impact on nature, some of them, particularly those having more than five rings, have emerged as technologically useful light harvesting materials owing to their unique optoelectronic properties.[3] Although, many PAHs are known and well characterized, PAHs incorporating heteroaromatic rings are rare.[4] However, some of the heteroaromatic ring fused PAHs are naturally occurring and exhibit interesting applications. For example, a few naturally occurring PAHs with fused furan and phenanthrene rings[5] act as non-steroidal anti-inflammatory agents.[6] Some of the heteroaromatic ring annulated phenanthrenes show useful photochromic properties.[7] Therefore, synthesis and structural elucation of PAHs incorporating heterocyclic rings is of high interest.

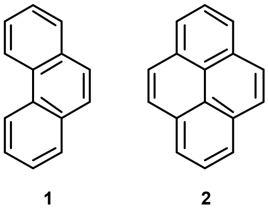
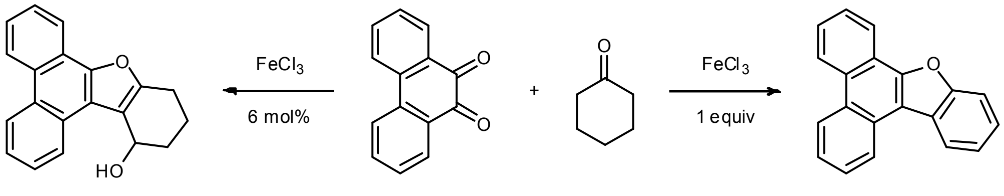


**Figure 1**. Structure of pheanthrene **1**, pyrene **2**.

We have recently disclosed an iron(III) chloride catalyzed synthesis of several furan annulated phenanthrenes from 9,10-phenanthrenequinone (PQ) **3** and aliphatic as well as alicyclic ketones.[8] As an example, condensation of PQ **3** with cyclohexanone **4a** in the presence of 6 mol% of iron(III) chloride under neat conditions provided furan annulated product **5** (Scheme 1). In contrast, when this reaction was conducted under aerobic conditions with one equivalent of iron(III) chloride, we obtained benzofuran annulated phenanthrene **6a** (Scheme 1). Since the reaction provided easy and ready access to benzo[*b*]furan annulated phenanthrene, we explored the reaction further for the synthesis of various benzo[*b*]furans annulated to phenanthrene **6** the details of which we describe herein. We extended the synthetic studies to benzo[*b*]furans annulated to pyrene **8** (Scheme 4) and also evaluated photochromic properties of resulting pyrene-benzofuran hybrids. Furthermore, the spectroscopic properties of the pyrene-benzofuran hybrids were evaluated by theoretical studies.



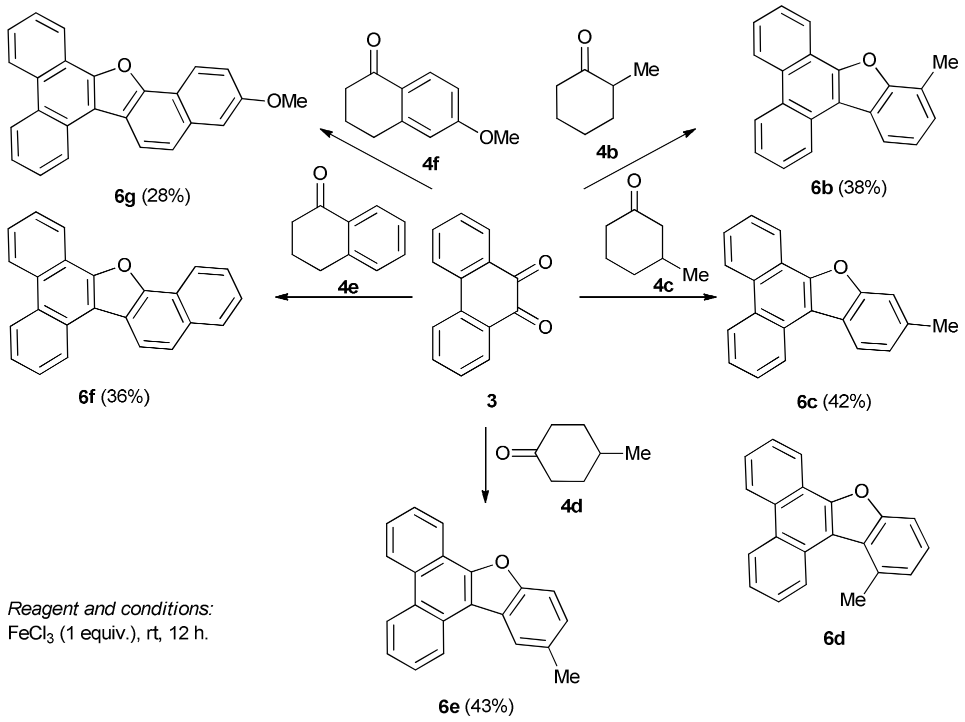
**5** (28%) **3** **4a** **6a** (42%)

**Scheme 1**. $FeCl_3$ mediated reaction of PQ **3** with cyclohexanone to provide furan annulated products **5** or **6**.

## 2. Results and discussion

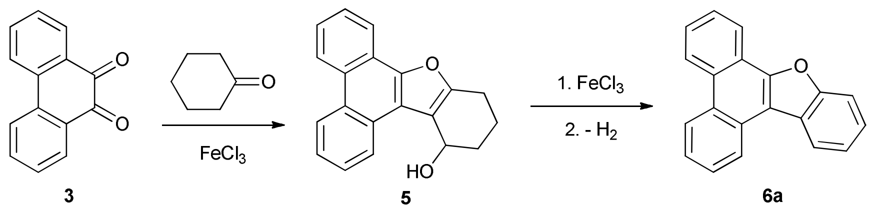
Condensation of PQ **3** with cyclohexanone **4a** was employed as a test case to work out optimal conditions for generation of benzofuran-phenanthrene hybrid **6a** (Scheme 1). The condensation worked well with the stoichiometric amount of iron (III) chloride to provide phenanthrene-benzofuran hybrid **6a** in moderate yield (42%). Unfortunately, when we employed alternate Lewis acids like iron(III) acetylacetonate, iron(III) sulfate, copper(II) sulfate, copper(I) bromide, zinc(II) chloride, titanium(IV) chloride, aluminum(III) chloride, $I_2$ and $Et_2OBF_3$ in catalytic or stoichiometric amounts, no useful product could be isolated. The reaction between PQ **3** and cyclohexanone **4a** to provide **6a** worked well under neat conditions in cyclohexanone (5 equivalents). The product **6a** could be recovered from the reaction mixture by removing cyclohexanone under reduced pressure and isolating the product by chromatographic purification of the residue. Formation of benzofuran-phenanthrene hybrid **6a** was deduced from its characteristic 20 line $^{13}$C NMR and DEPT spectra.

To evaluate generality of the above transformation, we subjected PQ **3** to iron(III) chloride mediated condensation with 2-methylcyclohexanone **4b** and the reaction provided phenanthrobenzofuran **6b** as the only product in moderate yield (Scheme 2). The reaction of PQ with 3-methylcyclohexanone **4c** can provide two isomeric phenanthrobenzofurans **6c** and **6d**. The reaction, however, furnished a single product, the structure of which was unambiguously assigned as **6c** on the basis of $^{1}$H and 2D NMR spectral data and in comparison with compounds with 4-alkyldibenzo[*b,d*]furan motif.[9] The reaction of PQ with 4-methylcyclohexanone **4d** provided phenanthrobenzofuran **6e** without any event. The condensation of PQ with α-tetralone **4e** and 6-methoxy-α-tetralone **4f** also took place, albeit in lower yield, to provide corresponding naphthofuran phenanthrene hybrids **6f** and **6g** respectively. It is to be noted that last reaction, however, was required to be conducted in dichloroethane (DCE) as solvent as all the reacting components namely PQ, 6-methoxy-α-tetralone and iron(III) chloride are solids.



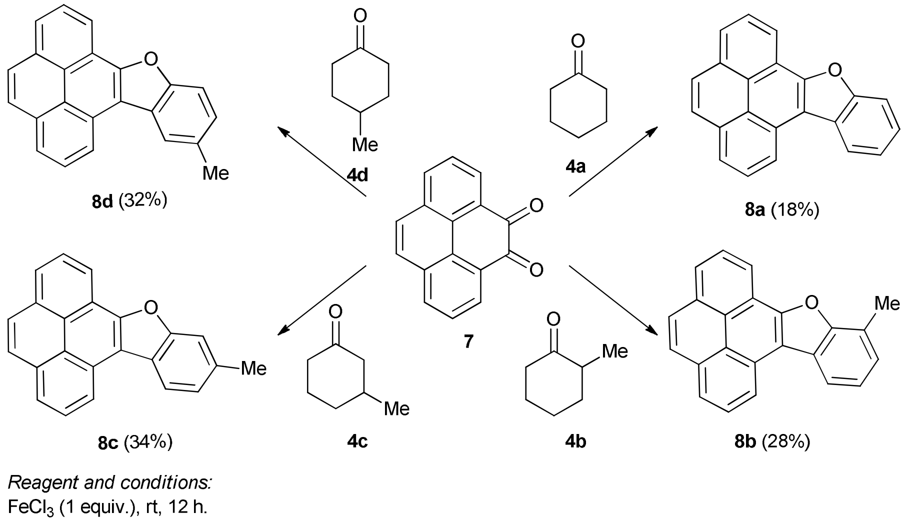
**Scheme 2**. $FeCl_3$ mediated condensation of PQ with substituted cyclohexanones.

Based on above experimental results, the possible pathway for the formation of benzofuran-phenanthrene hybrids **6** is given in Scheme 3. First major intermediate formed is the secondary alcohol **5** generated by cascade steps involving aldol condensation, cyclization and rearrangement.[8] Subsequently, the iron(III) chloride mediated dehydration followed by dehydrogenative aromatization furnished benzofuran-phenanthrene hybrid **6a**. Indeed, when the intermediate **5**, reported by us previously,[8] was treated with iron(III) chloride under present reaction conditions **6a** was formed in quantitative yield. The role of iron(III) chloride appears to be that of being most appropriate Lewis acid facilitating each of the cascade steps like aldol condensation, cyclization, rearrangement of the hydroxyl group, dehydration and dehydrogenative aromatization etc.



**Scheme 3**. Proposed pathway for the formation of furan annulated phenanthrene.

Next, we conducted a series of reactions of iron(III) chloride mediated condensation of pyrene-4,5-dione **7** with cyclohexanone **4a**, 2-methylcyclohexanone **4b**, 3-methylcyclohexanone **4c** and 4-methylcyclohexanone **4d** (Scheme 4) with an intention to study photochromic properties of the resulting benzofuran pyrene hybrids **8a-d**. In each case corresponding benzofuran pyrene hybrids **8a**-**d** formed, albeit in lower yield compared to those formed when PQ **3** was involved. The spectra of **8a-d** compared well with the spectra of benzofuran phenatharene hybrids **6a-e** and the structure of **8b** was confirmed by single crystal X-ray structure analysis (Figure 2). Unfortunately our attempts to induce condensation of pyrene-4,5-dione **7** with α-tetralone **4e** or 6-methoxy-α-tetralone **4f** proved to be futile



**Scheme 4.** $FeCl_3$ mediated condensation of pyrene-4,5-dione with substituted cyclohexanones.

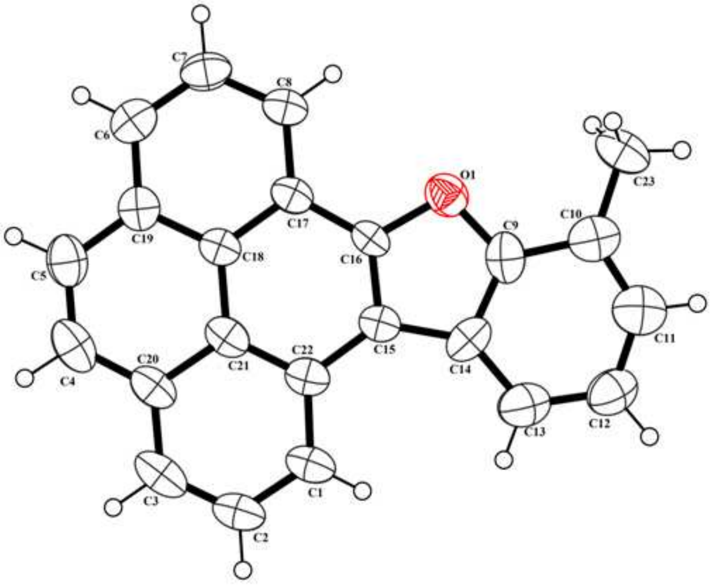
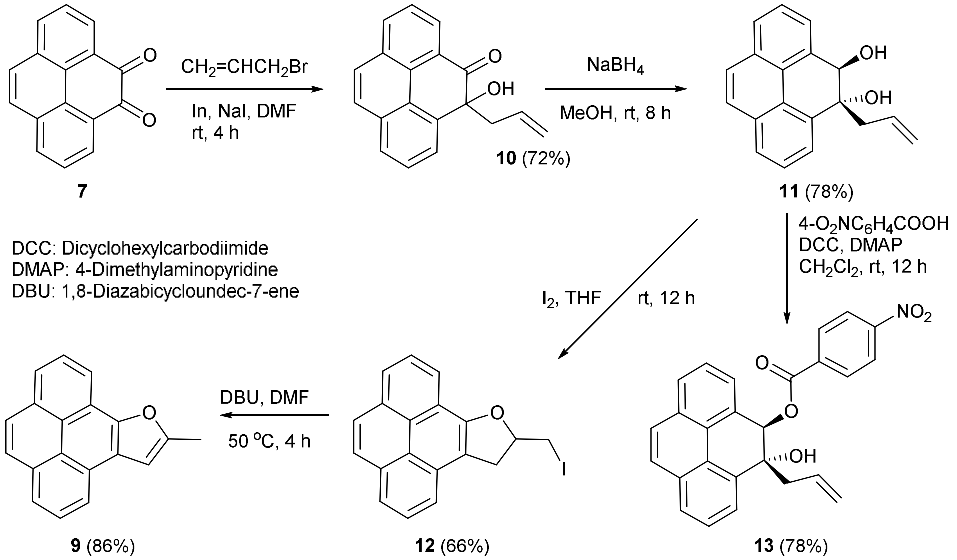


**Figure 2**. ORTEP diagram of 10-methylbenzo[*d*]pyreno[4,5-*b*]furan **8b** (CCDC 929911) with crystallographic numbering.

### 3. Absorption and emission spectra of pyrene appended benzofurans 8a-d.

Of all the polycyclic hydrocarbons, pyrene and its derivatives attracted highest attention owing to their useful photoluminescence properties, high thermal stability and easy synthesis.[10] Several pyrene derivatives exhibit intense fluorescence emission with high sensitivity to their surroundings, which makes them ideal candidates for being micro-environment sensors.[11] Useful photo-luminance properties of pyrene derivatives lead them to be explored for technological applications like organic light-emitting diodes (OLEDs),[12] liquid crystal lasers[13] and dye sensitized solar cells.[14] Previously it was shown that benzo[*b*]furan annulated pyrene **8c**, one of the pyrene derivatives prepared in this study, undergoes self-assembly into nano-wires and consequently exhibit light-emitting diode properties.[15] We have now investigated absorption and emission properties of all the newly prepared pyrene benzofuran hybrids **8a-d** in different solvents and compared the optical properties with the those of parent pyrene and 10-methylpyreno[4,5-*b*]furan **9** which we synthesized according to Scheme 5.



**Scheme 5.** Four-step synthesis of 10-methylpyreno[4,5-*b*]furan **9** from pyrene-4,5-dione **7**.

We achieved synthesis of 10-methylpyreno[4,5-*b*]furan **9** starting from pyrene-4,5-dione **7** in four convenient steps. Indium metal mediated allylation of **7** delivered keto-alcohol **10**.[16] Stereoselective reduction of the carbonyl group in **10** with sodium borohydride furnished trans-diol **11**. Anchimeric assistance provided by the adjacent hydroxyl group allowed syn-facial delivery of hydride ion by sodium borohydride. Structure of **11** was deduced from analysis of the 2D NMR spectra, specially NOESY. Furthermore, the structure of **11** was unequivocally established by single crystal X-ray structure analysis of its 4-nitrobenzoate derivative **13** (Figure 3). The iodine mediated cylization on **11** deliverd the dihydrofuran derivative **12**.[17] Finally dehydroiodination of **12** with non-nucleophilic base 1,8-diazabicycloundec-7-ene (DBU) yielded furan appended pyrene **9**.

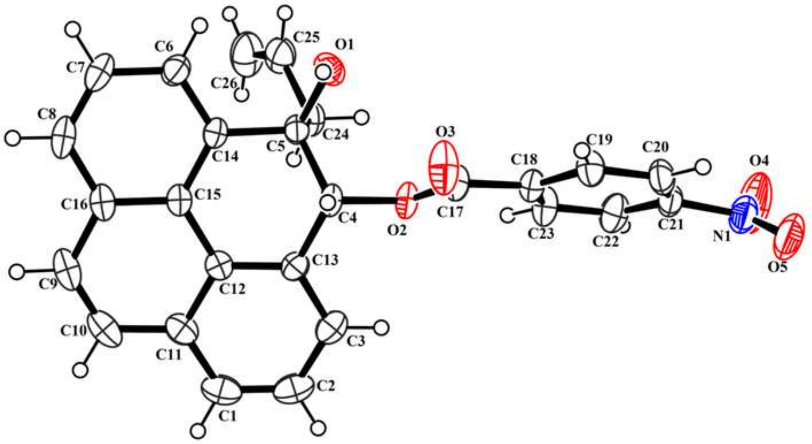


**Figure 3**. ORTEP diagram of (4*RS*,5*RS*)-5-allyl-5-hydroxy-4,5-dihydropyren-4-yl 4-nitrobenzoate **13** (CCDC 988268) with crystallographic numbering.

First, UV-vis spectra of pyrene **2**, 10-methylpyreno[4,5-*b*]furan **9**, benzo[*d*]pyreno[4,5-*b*]furan **8a**, 10-methylbenzo[*d*]pyreno[4,5-*b*]furan **8b**, 11-methylbenzo[*d*]pyreno[4,5-*b*]furan **8c**, 12-methylbenzo[*d*]pyreno[4,5-*b*]furan **8d** were measured as dilute solutions in deaerated MeOH (Figure 4A). As described in Figure 4A, upon the installation of 2-methylfuran ring on the pyrene scaffold most intense band in the UV spectrum showed red shift of 10 nm and upon introduction of benzofuran ring the band further red shift to the extent of 8 nm. The red shift indicates that the entire PAH is flat and the HOMO-LUMO band gaps of pyrene and the benzofuran annulated pyrenes (ΔE = (HOMO-LUMO)) tend to become narrower with increased conjugation. Similar to pyrene which exhibits three broad bands between 300-350 nm in MeOH, the furanopyrene **9** and benzofuranopyrenes **8a-d** exhibit three bands but with much finer structure, In addition, they exhibit a low intensity band at about 385 nm. The UV spectra of pyrene, **9** and **8a-d** recorded in six different solvents namely hexane (non-polar), ethyl acetate (EA, moderately polar aprotic), dichloromethane (DCM, moderately polar aprotic), methanol (MeOH, polar protic), ethanol (EtOH, polar protic) and dimethylformamide (DMF, highly polar aprotic) do not show much variance in the absorption maximum values (Figure 5, Table 1), excepting in EtOH in which the bands show much finer structure and hyperchromic effect.

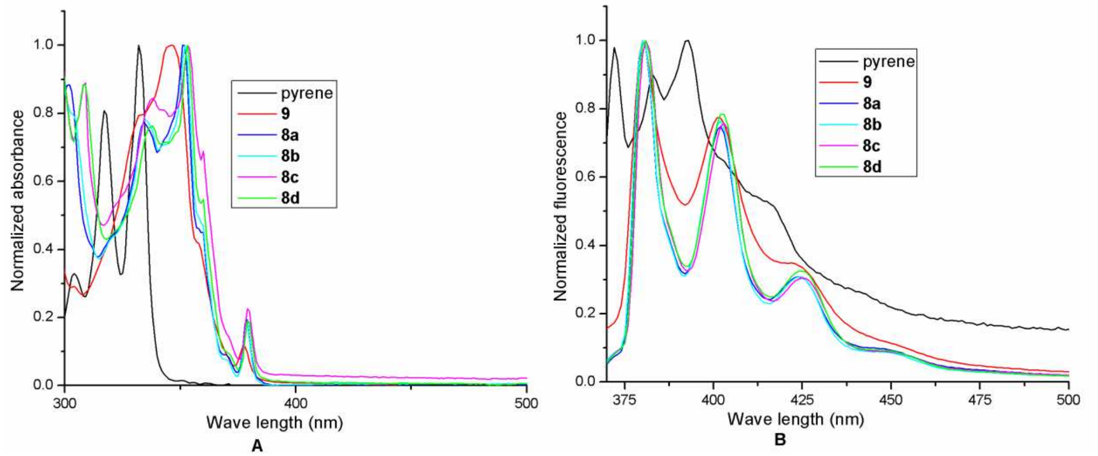


**Figure 4**. Normalized UV-Vis and fluorescence spectra of pyrene, 10-methylpyreno[4,5-*b*]furan **9**, benzo[*d*]pyreno[4,5-*b*]furan **8a**, 10-methylbenzo[*d*]pyreno[4,5-*b*]furan **8b**, 11-methylbenzo[*d*]pyreno[4,5-*b*]furan **8c**, 12-methylbenzo[*d*]pyreno[4,5-*b*]furan **8d** (MeOH, $\lambda_{ex} = \lambda_{abs,\ max}$).

**Table 1**. Absorption characteristics most intense band of the compounds pyrene, **9**, **8a-d** in hexane, ethyl acetate (EtOAc), dichloromethane (DCM), MeOH, EtOH and dimethylformamide (DMF); HOMO and LUMO energies were calculated by TD-DFT/B3LYP/6-311G(d,p) using Gaussian.

| Entry | Compound | Hexane (nm) | EtOAc (nm) | DCM (nm) | MeOH (nm) | EtOH (nm) | DMF (nm) | HOMO (ev) | LUMO (ev) | (LUMO-HOMO) (ev) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Pyrene | 333 | 334 | 336 | 333 | 334 | 336 | -5.67 | -1.86 | 3.81 |
| 2 | **9** | 350 | 347 | 350 | 343 | 347 | 349 | -5.46 | -1.74 | 3.72 |
| 3 | **8a** | 353 | 352 | 354 | 351 | 352 | 353 | -5.62 | -1.97 | 3.65 |
| 4 | **8b** | 354 | 353 | 354 | 352 | 353 | 354 | -5.59 | -1.94 | 3.65 |
| 5 | **8c** | 355 | 354 | 356 | 353 | 354 | 355 | -5.55 | -1.92 | 3.63 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 6 | **8d** | 354 | 353 | 354 | 352 | 353 | 354 | -5.58 | -1.93 | 3.65 |

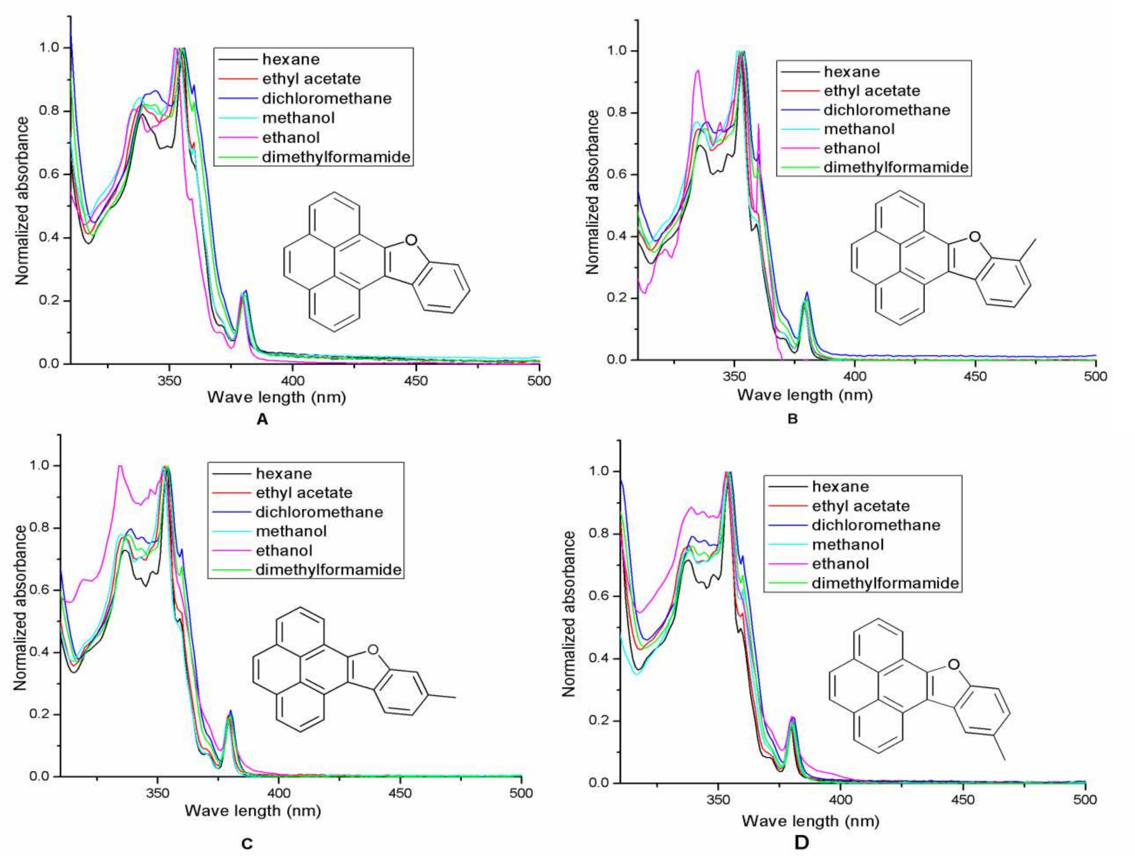


**Figure 5**. Normalized absorbance spectra of pyrene benzofuran hybrids **A: 8a**; **B: 8b**; **C: 8c**; **D: 8d** in hexane (black), EtOAc (red), DCM (blue), MeOH (cyan), EtOH (magenta), DMF (green).

The DFT studies were conducted on pyrene, furan annulated pyrene **9** and benzofuran annulated pyrenes **8a-d** to determine HOMO-LUMO energy gaps (Table 1). Decrease in HOMO-LUMO energy difference (ΔE) upon moving from pyrene to furan annulated pyrene **9** (entries 1 and 2, Table 1) and as a consequence the red shift of the $\lambda_{max,}$ is due to increase of delocalization in **9** arising from annulation of the furan ring. Similarly, further red-shift in benzofuran annulated pyrene **8a** (entry 3) in all the solvents is due to increase in delocalization. Among the three isomeric methylpyreno[4,5-*b*]benzofurans **8b-d** (entries 4-6) lowest HOMO-LUMO energy gap was noticed for 11-methylpyreno[4,5-*b*]benzofuran **8c** (entry 5). This observation indicates that compared to a methyl group located on C10 (**8b**) or C12 (**8d**), one on C11 (**8c**) participates in the resonance better, possibly through σ-π conjugation (hyperconjugation).

**Table 2.** Emission characteristic of the compounds pyrene, 10-methylpyreno[4,5-*b*]furan **9**, **8a-d** in hexane, EtOAc, DCM, MeOH, EtOH and DMF.

| Entry | Compound | Hexane | EtOAc | DCM | MeOH | EtOH | DMF |
|---|---|---|---|---|---|---|---|
| 1 | Pyrene | 372, 383, 393 | 372, 384, 393 | 373, 384, 394 | 372, 383, 393 | 372, 383, 393 | 373, 384, 394 |
| 2 | **9** | 379, 400, 418 | 380, 402, 423 | 382, 404, 427 | 380, 401, 420 | 380, 402, 424 | 382, 403, 425 |
| 3 | **8a** | 380, 402, 424 | 381, 402, 424 | 381, 403, 426 | 380, 402, 424 | 381, 403, 426 | 382, 403, 425 |
| 4 | **8b** | 380, 402, 425 | 381, 402, 425 | 382, 403, 426 | 380, 402, 424 | 380, 402, 425 | 382, 403, 426 |
| 5 | **8c** | 381, 403, 425 | 381, 403, 426 | 383, 404, 427 | 381, 403, 425 | 380, 402, 426 | 382, 404, 427 |
| 6 | **8d** | 381, 403, 425 | 381, 403, 425 | 382, 404, 426 | 381, 402, 425 | 381, 403, 426 | 382, 404, 427 |

Similar to pyrene which exhibits three bands (I, II and III) in its fluorescence spectrum in MeOH, **9** and **8a-d**, exhibit three bands in their respective spectra (Figure 4B, Table 2). Interestingly, highly structured fluorescence of pyrene, known as the Ham effect,[18] was not retained after introduction appended furan or benzofuran ring which indicates clear vibrational structures for **9** and **8a-d**. While the red shift owing to introduction of furan ring is clearly discernible in **9** for all the bands including (0 – 0) band, further red shifts anticipated after benzofruan annulation **8a-d** nearly absent (Figure 4B).

We calculated relative fluorescence quantum yields ($\Phi_f$) for the furan annulated pyrene **9** and benzofuran annulated pyrenes **8a-d** by taking 9,10-diphenylanthracene in EtOH ($\Phi_f = 0.95$) as standard (Table 3).[19] The analysis showed that compared to furan annulated pyrene **9** the quantum yields of benzofuran annulated pyrenes **8a-d** increased in all the solvents employed. Among benzofuran annulated pyrenes, **8a** displayed higher quantum yields compared to **8b-d** in all solvents excepting in dicholoromethane (DCM; Table 3). In DCM however, quantum yield of **8d** is more than rest of benzofuran annulated pyrenes, which indicates that in DCM methyl group at C12 position has highest influence on fluorescence possibly due to better σ-π conjugation in the excited state.[20] The fluorescence spectra recorded in six solvents of different polarities (Figure 6) did not show much variance which make the benzofuran pyrene hybrids **9** and **8a-d** Acree's non-probe PAHs.[21]

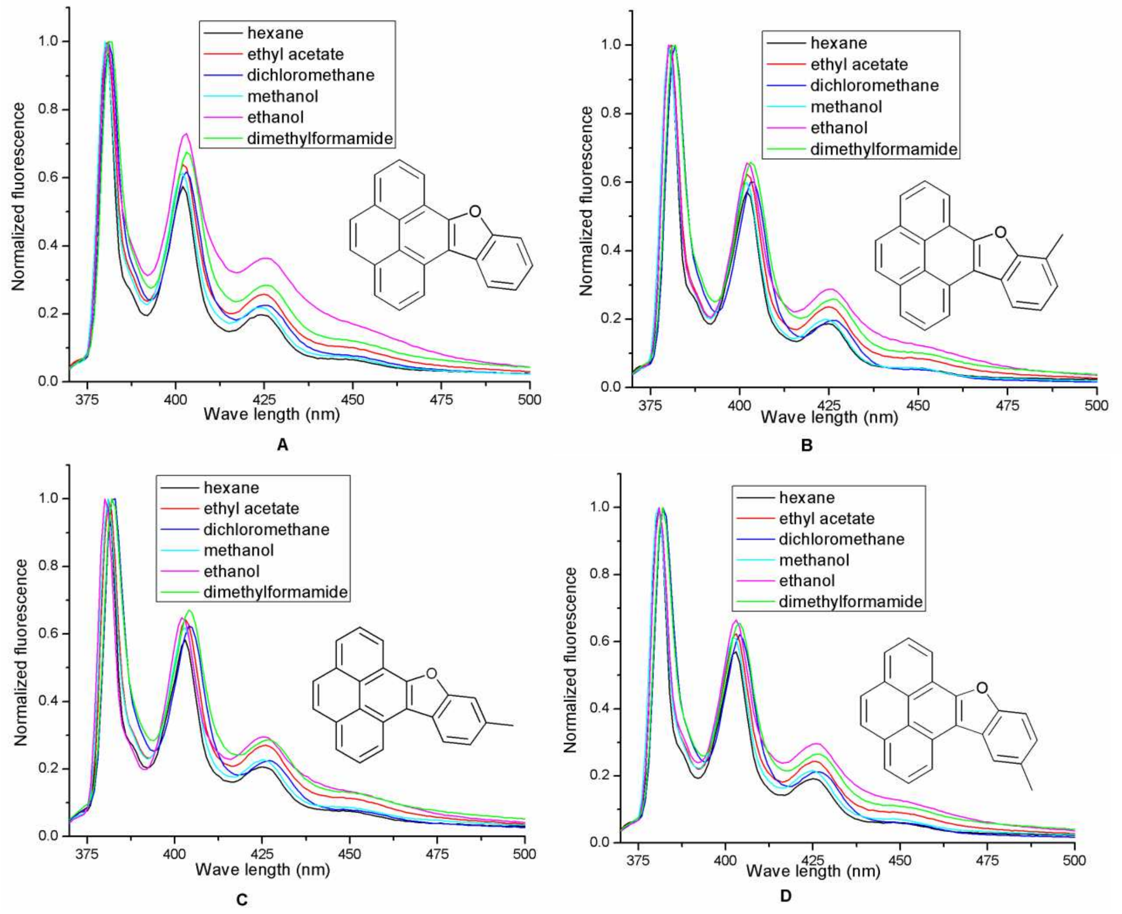


**Figure 6**. Normalized emission spectra of compounds **A: 8a**; **B: 8b**; **C: 8c**; **D: 8d** in hexane (black), EtOAc (red), DCM (blue), MeOH (cyan), EtOH (magenta), DMF (green).

**Table 3**. Quantum yields of **9**, **8a-d** in hexane, EtOAc, DCM, MeOH, EtOH and DMF.

| Entry | Compound | Hexane | EtOAc | DCM | MeOH | EtOH | DMF |
|---|---|---|---|---|---|---|---|
| 1 | **9** | 0.17 | 0.23 | 0.38 | 0.18 | 0.28 | 0.40 |
| 2 | **8a** | 0.24 | 0.37 | 0.41 | 0.33 | 0.43 | 0.51 |
| 3 | **8b** | 0.22 | 0.35 | 0.41 | 0.28 | 0.34 | 0.47 |
| 4 | **8c** | 0.22 | 0.34 | 0.39 | 0.29 | 0.38 | 0.45 |
| 5 | **8d** | 0.21 | 0.34 | 0.49 | 0.32 | 0.43 | 0.43 |

## 4. Conclusion

In summary we have delineated a facile $FeCl_3$ mediated synthesis of benzofuran phenanthrene and benzofuran pyrene hybrid PAHs by condensation of 9,10-phenanthrenequinone or pyrene-4,5-dione with cyclohexanone and its derivatives. Absorption and emission properties of benzofuran pyrene hybrids were studied which reflect expanded conjugation owing to annulations of furan or benzofuran ring to pyrene. Among the benzofuran annulated pyrenes one without any methyl appendage exhibited high quantum yield in most of the solvents compared to those which had a methyl group. Solvatochromic studies revealed that polarity of solvents did not have noticeable effect on the absorption as well as emission spectra.

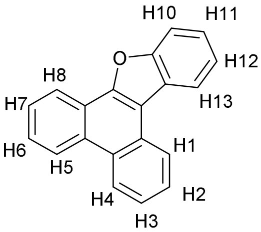
## 5. Experimental section

### 5.1 General

All melting points were uncorrected and were determined using open-ended capillary tubes on VEEGO VMP-DS instrument. The reactions and chromatographic separations were monitored by thin layer chromatography. Glass plates coated with silica gel (60–120 mesh SRL chemicals) were used for thin layer chromatography. Column chromatography was carried on silica gel (100-200 mesh) using hexane and ethyl acetate as eluent. IR spectra were recorded as KBr pellets on a Nicolet-6700 spectrometer. Electronic absorption spectra were obtained on a Shimadzu UV-2450 spectrophotometer. Emission spectra were recorded on a Fluoromax-4 spectrofluorometer. Solvents used for UV–vis and fluorescence spectroscopic experiments were of spectral grade. $^1$H-NMR (400 MHz), $^{13}$C-

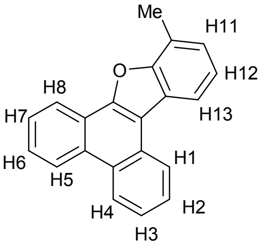
NMR (100 MHz) and DEPT-135 spectra were recorded for ($CDCl_3$ or $CDCl_3 + CCl_4$, 1:1) solutions on a Bruker-400 spectrometer with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. $^1$H-NMR data are reported as follows: chemical shift (multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet and m = multiplet), coupling constant, integrations, type of proton). $^{13}$C NMR spectra were determined with $^1$H decoupling. Elemental analysis (C, H and N) was performed using Thermo Scientific FLASH 2000 Organic Elemental Analyzer. High resolution mass spectra were recorded on a Water Q-TOF micro mass spectrometer using the electron spray ionization mode. The X-ray diffraction measurements were carried out at 298 K on an Oxford CrysAlis CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda$ = 0.71073 Å). PQ **3**, pyrene, cyclohexanones and $FeCl_3$ were procured from commercial sources and used as received. Pyrene-4,5-dione **7** was prepared according to literature procedure.[22] The equilibrium structures of the benzofuran-pyrene hybrids were fully optimized by the B3LYP method with 6-311G(d,p) basis set. All calculations were performed by using Gaussian program.

**5.2. General procedure for iron(III) chloride mediated reactions of PQ or pyrene 4,5-dione with ketones**: To 9,10-phenanthrenequinone or pyrene-4,5-dione (1 equiv) taken in a covered 10 mL test tube cyclic ketone (5 equiv) was added and stirred at rt for 5 min. To the resulting mixture anhydrous $FeCl_3$ (1 equiv) was added and stirring continued at rt for 12 h. After completion of the reaction (absence of PQ or pyrene-4,5-dione by TLC) excess ketone was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel (100-200 mesh) and 100% hexane as eluent.



**6a**

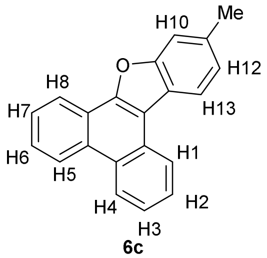
**5.2.1. Benzo[*d*]phenanthro[9,10-*b*]furan (6a)**. Following the general procedure, the reaction of 9,10-phenanthrenequinone (200.2 mg, 0.96 mmol), cyclohexanone (471.3 mg, 4.80 mmol) and iron(III) chloride (154.6 mg, 0.96 mmol) afforded benzo[*d*]phenanthro[9,10-*b*]furan **6a** as a white solid in 42% yield, mp 153-154 ºC, reported 156-158 °C;[23] IR (KBr) $\nu_{max}$ 3021, 1612, 1582, 1519, 1447, 1359, 1322, 1219, 1163, 1113, 1065, 1034, 960, 748, 721, 691, 663 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$ + $CCl_4$) δ 8.72-8.68 (m, 2H, ArH4, H5), 8.58 (dd, *J* = 8.0, 1.0 Hz, 1H, ArH1), 8.49-8.47 (m, 1H, ArH8), 8.35-8.33 (m, 1H, ArH13), 7.75-7.60 (m, 5H, ArH2, H3, H6, H7 and H10), 7.50-7.43 (m, 2H, ArH11, H12) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$ + $CCl_4$) 156.0 (C), 151.4 (C), 130.8 (C), 128.8 (C), 128.4 (C), 127.5 (CH), 127.20 (CH), 127.15 (CH), 125.9 (C), 125.5 (CH), 125.2 (CH), 124.3 (CH), 123.9 (CH), 123.54 (CH), 123.49 (CH), 122.4 (C), 121.9 (2 × CH), 114.6 (C), 112.1 (CH) ppm; Anal. Calcd for $C_{20}H_{12}O$: C, 89.53; H, 4.51. Found: C, 89.19; H, 4.50.



**6b**

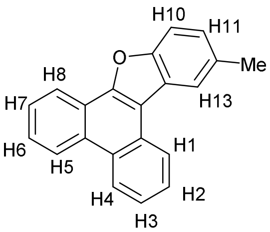
**5.2.2. 10-Methylbenzo[*d*]phenanthro[9,10-*b*]furan (6b)**. Following the general procedure, the reaction of 9,10-phenanthrenequinone (201.2 mg, 0.96 mmol), 2-

methylcyclohexanone (538.4 mg, 4.80 mmol) and iron(III) chloride (156.2 mg, 0.96 mmol) afforded 10-methylbenzo[*d*]phenanthro[9,10-*b*]furan **6b** as a white solid in 38% yield, mp 195-196 ºC, reported 197-198 ºC;[24] IR (KBr) $\nu_{max}$ 3057, 2916, 2852, 1612, 1585, 1513, 1450, 1422, 1356, 1317, 1219, 1197, 1143, 1088, 1030, 932, 854, 761, 735, 690 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$ + $CCl_4$) δ 8.76-8.72 (m, 2H, ArH4, H5), 8.61 (dd, *J* = 8.1, 1.1 Hz, 1H, ArH1), 8.55-8.52 (m, 1H, ArH8), 8.18 (d, *J* = 7.7 Hz, 1H, ArH13), 7.76-7.62 (m, 4H, ArH2, H3, H6 and H7), 7.35 (t, *J* = 7.6 Hz, 1H, ArH12), 7.28 (d, *J* = 7.5 Hz, 1H, ArH11), 2.75 (s, 3H, $CH_3$) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$ + $CCl_4$) δ 154.9 (C), 151.1 (C), 130.7 (C), 129.0 (C), 128.4 (C), 127.5 (CH), 127.2 (CH), 127.1 (CH), 126.7 (CH), 125.3 (C), 125.1 (CH), 124.4 (CH), 123.9 (CH), 123.58 (CH), 123.55 (CH), 122.6 (C), 122.2 (C), 122.0 (CH), 119.5 (CH), 115.0 (C), 15.7 ($CH_3$) ppm; Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.09; H, 4.98.



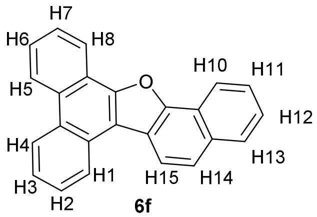
6c

**5.2.3. 11-Methylbenzo[*d*]phenanthro[9,10-*b*]furan (6c)**. Following the general procedure, the reaction of 9,10-phenanthrenequinone (101.8 mg, 0.48 mmol), 3-methylcyclohexanone (268.2 mg, 2.40 mmol) and iron(III) chloride (78.1 mg, 0.48 mmol) afforded 11-methylbenzo[*d*]phenanthro[9,10-*b*]furan **6c** as a white solid in 42% yield, mp 202-203 ºC; IR (KBr) $\nu_{max}$ 3075, 3028, 2919, 2852, 1616, 1517, 1449, 1354, 1227, 1190, 1113, 1066, 1037, 999, 959, 861, 802, 755, 719, 678 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$ + $CCl_4$) δ 8.77-8.72 (m, 2H, ArH4, H5), 8.60 (dd, *J* = 8.1, 1.1 Hz, 1H, ArH1), 8.50-8.47 (m, 1H, ArH8), 8.21 (d, *J* = 8.0 Hz, 1H, ArH13), 7.77-7.64 (m, 5H, ArH2, H3, H6, H7 and H12), 7.54 (s, 1H, ArH10), 2.59 (s, 3H, $CH_3$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$ + $CCl_4$) δ 156.2 (C), 150.8 (C), 135.6 (C), 130.2 (C), 128.5 (C), 128.0 (C), 127.2 (CH), 126.9 (CH), 126.6 (CH), 124.8 (CH), 124.5 (CH), 124.1 (CH), 123.6 (CH), 123.3 (CH), 123.0 (C), 122.2 (C), 121.5 (CH), 121.1 (CH), 114.4 (C), 112.1 (CH), 21.8 ($CH_3$) ppm; Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.29; H, 4.99.



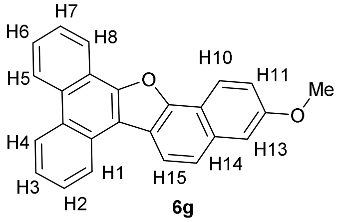
**6e**

**5.2.4. 12-Methylbenzo[*d*]phenanthro[9,10-*b*]furan (6e)**. Following the general procedure, the reaction of 9,10-phenanthrenequinone (101.2 mg, 0.48 mmol), 4-methylcyclohexanone (271.2 mg, 2.40 mmol) and iron(III) chloride (78.4 mg, 0.48 mmol) afforded 12-methylbenzo[*d*]phenanthro[9,10-*b*]furan **6e** as a white solid in 43% yield, mp 166-167 ºC, reported 168-169 ºC;[25] IR (KBr) $\nu_{max}$ 3069, 2921, 2856, 1611, 1515, 1458, 1375, 1325, 1219, 1157, 1114, 1069, 1037, 936, 859, 798, 755, 722, 669 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.77-8.71 (m, 2H, ArH$_4$, H$_5$), 8.59 (dd, *J* = 8.1, 1.0 Hz, 1H, ArH$_1$), 8.48-8.46 (m, 1H, ArH$_8$), 8.12 (s, 1H, ArH$_{13}$), 7.77-7.61 (m, 5H, ArH$_2$, H$_3$, H$_6$, H$_7$ and H$_{10}$), 7.29 (dd, *J* = 8.3, 1.1 Hz, 1H, ArH$_{11}$), 2.61 (s, 3H, $CH_3$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.2 (C$_{9a}$), 151.3 (C$_{8b}$), 132.7 (C$_{12}$), 130.4 (C$_{4a}$), 128.6 (C$_{4b}$), 128.1 (C$_{13c}$), 127.3 (C$_1$), 127.0 (C$_8$), 126.9 (C$_2$), 126.5 (C$_7$), 125.6 (C$_{13b}$), 124.9 (C$_{11}$), 124.1 (C$_3$), 123.7 (C$_6$), 123.3 (C$_{13}$), 122.3 (C$_{13a}$), 121.7 (C$_4$), 121.6 (C$_5$), 114.2 (C$_{8a}$), 111.3 (C$_{10}$), 21.7 ($CH_3$) ppm; Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.61; H, 4.99.



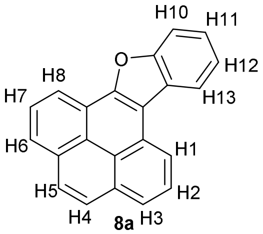
**6f**

**5.2.5. Naphtho[2,1-*d*]phenanthro[9,10-*b*]furan (6f)**. Following the general procedure, the reaction of 9,10-phenanthrenequinone (100.3 mg, 0.48 mmol), α-tetralone (351.2 mg, 2.40 mmol) and iron(III) chloride (79.1 mg, 0.48 mmol) afforded naphtho[2,1-*d*]phenanthro[9,10-*b*]furan as a white solid **6f** in 36% yield, mp 205-206 ºC, reported 208-210 ºC;[26] IR (KBr) $\nu_{max}$ 3055, 1611, 1521, 1450, 1376, 1290, 1218, 1112, 1074, 1023, 938, 871, 803, 757, 719, 674 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.82-8.73 (m, 3H, ArH4, H5, H10), 8.67-8.61 (m, 2H, ArH1, H8), 8.45 (d, *J* = 8.4 Hz, 1H, ArH13), 8.04 (d, *J* = 7.7 Hz, 1H, ArH15), 7.90 (d, *J* = 7.7 Hz, 1H, ArH14), 7.80-7.59 (m, 6H, ArH2, H3, H6, H7, H11 and H12) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.6 (C), 150.8 (C), 132.0 (C), 130.2 (C), 128.7 (C), 128.53 (C), 128.49 (CH), 127.5 (CH), 127.4 (CH), 126.9 (CH), 126.8 (CH), 126.0 (CH), 125.4 (CH), 124.4 (CH), 124.1 (CH), 124.0 (CH), 123.6 (CH), 122.6 (C), 121.7 (C), 121.6 (CH), 121.0 (C), 120.8 (CH), 120.0 (CH), 115.7 (C) ppm; Anal. Calcd for $C_{24}H_{14}O$: C, 90.54; H, 4.43. Found: C, 89.99; H, 4.43.



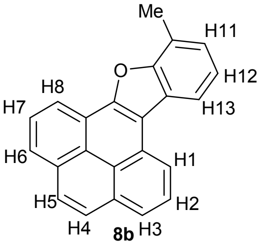
**6g**

**5.2.6. 12-Methoxynaphtho[2,1-*d*]phenanthro[9,10-*b*]furan (6g)**. Following the general procedure, the reaction of 9,10-phenanthrenequinone (100.2 mg, 0.48 mmol), 6-methoxy α-tetralone (169.8 mg, 0.96 mmol) and iron(III) chloride (78.8 mg, 0.48 mmol) in 0.5 mL dry dichloroethane (DCE) as sovent afforded 12-methoxynaphtho[2,1-*d*]phenanthro[9,10-*b*]furan **6g** as a white solid in 28% yield, mp 220-221 ºC; IR (KBr) $\nu_{max}$ 3057, 3010, 2933, 2833, 1639, 1600, 1473, 1453, 1416, 1371, 1328, 1266, 1244, 1218, 1187, 1164, 1142, 1075, 1030, 936, 844, 819, 792, 755, 719, 689, 671 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.3 Hz, 2H, ArH4, H5), 8.69 (d, *J* = 7.8 Hz, 1H, ArH1), 8.60 (dd, *J* = 8.0, 1.0 Hz, 1H, ArH8), 8.49 (d, *J* = 8.7 Hz, 1H, ArH15), 8.38 (d, *J* = 8.7 Hz, 1H, ArH14), 7.79-7.66 (m, 5H, ArH2, H3, H6, H7 and H10), 7.36-7.33 (m, 2H, ArH11, H13), 3.99 (s, 3H, $OCH_3$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.9 (C), 152.0 (C), 150.3 (C), 134.2 (C), 133.4 (C), 129.9 (C), 128.7 (C), 128.5 (C), 127.4 (CH), 127.3 (CH), 126.6 (CH), 125.2 (CH), 124.3 (CH), 123.9 (CH), 123.6 (CH), 123.0 (CH), 122.5 (CH), 121.4 (CH), 120.6 (CH), 119.2 (CH), 119.1 (C), 116.9 (C), 115.7 (C), 107.1 (CH), 55.5 ($CH_3$) ppm; Anal. Calcd for $C_{25}H_{16}O_2$: C, 86.19; H, 4.63. Found: C, 86.13; H, 4.61.



**8a**

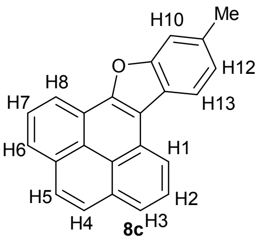
**5.2.7. Benzo[*d*]pyreno[4,5-*b*]furan (8a)**. Following the general procedure, the reaction of pyrene-4,5-dione (100.2 mg, 0.43 mmol), cyclohexanone (211.2 mg, 2.15 mmol) and iron(III) chloride (69.8 mg, 0.43 mmol) afforded benzo[*d*]pyreno[4,5-*b*]furan **8a** as a white solid in 18% yield, mp 198-199 ºC; IR (KBr) $\nu_{max}$ 1593, 1448, 1357, 1276, 1217, 1175, 1105, 1062, 894, 869, 821, 767, 741, 710 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH3), 8.70 (dd, *J* = 7.7, 1.1 Hz, 1H, ArH6), 8.47-8.45 (m, 1H, ArH13), 8.21 (dd, *J* = 7.7, 1.0 Hz, 1H, ArH4), 8.16 (dd, *J* = 7.7, 1.2 Hz, 1H, ArH5), 8.12-8.06 (m, 4H, ArH1, H2, H7 and H8), 7.83-7.81 (m, 1H, ArH10), 7.55-7.52 (m, 2H, ArH11, H12) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.1 (C), 151.8 (C), 132.0 (C), 131.7 (C), 128.2 (CH), 127.7 (C), 127.5 (CH), 126.5 (CH), 126.2 (CH), 125.9 (CH + C), 125.7 (CH), 124.44 (C), 124.42 (CH), 123.6 (CH), 122.7 (C), 122.0 (CH), 121.38 (C), 121.36 (CH), 118.8 (CH), 115.1 (C), 112.1 (CH) ppm; Anal. Calcd for $C_{22}H_{12}O$: C, 90.39; H, 4.14. Found: C, 89.82; H, 4.14.



**8b**

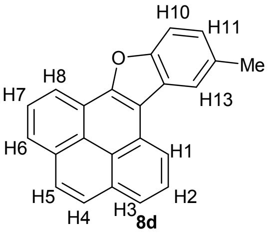
**5.2.8. 10-Methylbenzo[*d*]pyreno[4,5-*b*]furan (8b)** .Following the general procedure, the reaction of pyrene-4,5-dione (100.8 mg, 0.43 mmol), 2-methylcyclohexanone (241.6 mg, 2.15 mmol) and iron(III) chloride (69.7 mg, 0.43 mmol) afforded 10-methylbenzo[*d*]pyreno[4,5-*b*]furan **8b** as a white solid in 28% yield, mp 188-189 ºC; IR (KBr) $\nu_{max}$ 3040, 2923, 2857, 1594, 1456, 1364, 1311, 1266, 1179, 1092, 1029, 965, 896, 832, 781, 746, 712 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH3), 8.73 (dd, *J* = 7.7, 1.1 Hz, 1H, ArH6), 8.29 (d, *J* = 7.6 Hz, 1H, ArH4), 8.21 (dd, *J* = 7.7, 1.1 Hz, 1H, ArH5), 8.18-8.05 (m, 5H, ArH1, H2, H7, H8 and H13), 7.42 (t, *J* = 7.5 Hz, 1H, ArH12), 7.33 (d, *J* = 7.2 Hz, 1H, ArH11), 2.78 (s, 3H, $CH_3$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.0 (C), 151.6 (C), 132.0 (C), 131.7 (C), 128.2 (CH), 127.8 (C), 127.4 (CH), 126.7 (CH), 126.5 (CH), 126.1 (CH), 125.8 (CH), 125.3 (C), 124.4 (C), 124.3 (CH), 123.5 (CH), 122.7 (C), 122.3 (C), 121.5 (C), 121.4 (CH), 119.4 (CH), 118.8 (CH), 115.5 (C), 15.5 ($CH_3$) ppm; Anal. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61. Found: C, 89.89; H, 4.63. **Crystal data for 8b**: Empirical formula, $C_{23}H_{14}O$; Formula weight, 306.35; Crystal color, habit: colorless, rectangular block; Crystal system, orthorhombic; Crystal dimensions, 0.45

× 025 × 0.20 mm$^3$; Lattice parameters, a = 4.8868(5) Å, b = 16.136(3) Å, c = 19.0524(16) Å; α = 90.00, β = 90.00, γ = 90.00; V = 1502.3(3) A$^3$; Space group P2-1; Z = 4; $D_{calcd}$ = 1.354 g/cm$^3$; $F_{000}$ = 640; λ(Mo Kα) = 0.7107 Å; R ($I \geq 2\sigma_1$) = 0.0745, wR$^2$ = 0.2324. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **8b** CCDC # 929911).



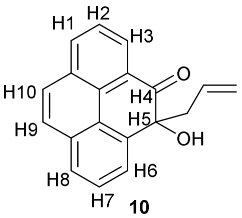
**8c**

**5.2.9. 11-Methylbenzo[*d*]pyreno[4,5-*b*]furan (8c)**. Following the general procedure, the reaction of pyrene-4,5-dione (100.8 mg, 0.43 mmol), 3-methylcyclohexanone (241.2 mg, 2.15 mmol) and iron(III) chloride (69.9 mg, 0.43 mmol) afforded 11-methylbenzo[*d*]pyreno[4,5-*b*]furan **8c** as a white solid in 32% yield, mp 193-194 ºC; IR (KBr) $\nu_{max}$ 3052, 2917, 2852, 1593, 1512, 1430, 1356, 1307, 1250, 1172, 1107, 1054, 953, 894, 829, 751, 711 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 7.5, 1.1 Hz, 1H, ArH3), 8.65 (dd, *J* = 7.7, 1.0 Hz, 1H, ArH6), 8.25 (d, *J* = 8.0 Hz, 1H, ArH4), 8.17 (dd, *J* = 7.6, 0.9 Hz, 1H, ArH5), 8.18-8.02 (m, 5H, ArH1, H2, H7, H8 and H13), 7.56 (s, 1H, ArH10), 7.29 (d, *J* = 7.9 Hz, 1H, ArH12), 2.60 (s, 3H, $CH_3$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.5 (C), 151.4 (C), 136.1 (C), 132.0 (C), 131.7 (C), 128.2 (CH), 127.6 (C), 127.4 (CH), 126.4 (CH), 126.1 (CH), 125.6 (CH), 124.8 (CH), 124.23 (CH), 124.20 (C), 123.3 (C), 122.6 (C), 121.5 (C), 121.34 (CH), 121.32 (CH), 118.6 (CH), 115.2 (C), 112.3 (CH), 22.0 ($CH_3$) ppm; Anal. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61. Found: C, 89.96; H, 4.60.



**8d**

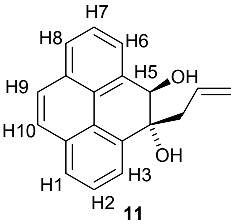
**5.2.10. 12-Methylbenzo[*d*]pyreno[4,5-*b*]furan (8d)**. Following the general procedure, the reaction of pyrene-4,5-dione (100.2 mg, 0.43 mmol), 4-methylcyclohexanone (240.8 mg, 2.15 mmol) and iron(III) chloride (70.1 mg, 0.43 mmol) afforded 12-methylbenzo[*d*]pyreno[4,5-*b*]furan **8d** as a white solid in 34% yield, mp 182-183 ºC; IR (KBr) $\nu_{max}$ 3045, 2920, 2860, 1596, 1454, 1373, 1310, 1217, 1175, 1109, 823, 761, 714 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 8.72 (dd, *J* = 7.5, 1.1 Hz, 1H, ArH3), 8.64 (dd, *J* = 7.7, 1.1 Hz, 1H, ArH6), 8.17-8.14 (m, 2H, ArH4, H5), 8.10-8.00 (m, 5H, ArH1, H2, H7 and H8, H13), 7.62 (d, *J* = 8.3 Hz, 1H, ArH10), 7.28 (dd, *J* = 8.3, 1.1 Hz, 1H, ArH11), 2.63 (s, 3H, $CH_3$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 154.5 (C), 152.1 (C), 132.8 (C), 132.1 (C), 131.8 (C), 128.2 (CH), 127.9 (C), 127.4 (CH), 126.8 (CH), 126.4 (CH), 126.08 (CH), 126.05 (C), 125.8 (CH), 124.5 (C), 124.3 (CH), 122.8 (C), 122.0 (CH), 121.6 (C), 121.4 (CH), 118.8 (CH), 115.1 (C), 111.6 (CH), 22.0 ($CH_3$) ppm; Anal. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61. Found: C, 89.91; H, 4.59.



**10**

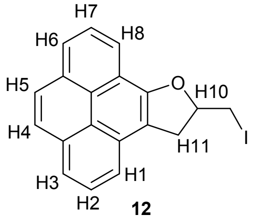
**5.2.11. 5-Allyl-5-hydroxypyren-4(5*H*)-one (10)**. Pyrene-4,5-dione (501.2 mg, 2.16 mmol) was dissolved in 5 mL dry dimethylformamide and to this solution allyl bromide (406.3 mg, 3.35 mmol), indium powder (258.6 mg, 2.26 mmol), sodium iodide (501.8 mg, 3.35

mmol) was added and stirred at rt for 4 h. The reaction mixture was quenched with 1N HCl solution (1 mL) and extracted the organic layer using dichloromethane (30 mL). The DCM layer was washed with water (2 × 30 mL), brine solution (2 ×30 ml) and then dried over anhydrous sodium sulfate. The concentrated crude product was purified by column chromatography using silica (100-200 mesh) and increasing amounts of (2 to 5%) EtOAc in hexanes to afford 5-allyl-5-hydroxypyren-4(5*H*)-one **10** as a white solid in 72% yield; mp. 152-153 ºC; IR (KBr) $\nu_{max}$ 3488, 3054, 3012, 2958, 2924, 2854, 1690, 1638, 1620, 1587, 1494, 1459, 1429, 1379, 1342, 1296, 1228, 1172, 1092, 1069, 1034, 997, 920, 871, 837, 780, 760, 723, 652 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 8.24 (dd, *J* = 7.3, 1.2 Hz, 1H, ArH3), 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH1), 7.93 (dd, *J* = 7.4, 1.2 Hz, 1H, ArH10), 7.83-7.66 (m, 5H, ArH2, H6, H7, H8 and H9), 5.68-5.58 (m, 1H, alkene CH), 5.01 (dd, *J* = 9.2, 0.9 Hz, 1H, alkene $CH_2$), 4.84 (dd, *J* = 17.0, 1.7 Hz, 1H, alkene $CH_2$), 4.20 (s, 1H, OH), 2.58-2.48 (m, 2H, allyl $CH_2$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 202.7 (C=O), 140.5 (C), 134.3 (CH), 131.9 (C), 131.3 (C), 131.2 (CH), 129.9 (C), 128.0 (C), 127.9 (CH), 127.7 (CH), 127.2 (CH), 127.0 (CH), 126.23 (CH), 126.18 (CH), 124.4 (CH), 123.6 (C), 119.9 ($CH_2$), 80.5 (C), 49.7 ($CH_2$) ppm; HRMS (ESI) calcd for $C_{19}H_{14}O_2Na$ $[M + Na]^+$ 297.0891, found 297.0891; Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 82.39; H, 5.15.



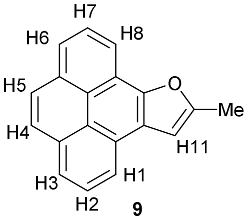
**11**

**5.2.12. (4*R*,5*R*)-4-Allyl-4,5-dihydropyrene-4,5-diol (11)**. 5-allyl-5-hydroxypyren-4(5*H*)-one (100.3 mg, 0.37 mmol) was dissolved in 3 mL MeOH and cool to 0 $^{o}$C and then sodium borohydride (28.1 mg, 0.74 mmol) was added under nitrogen atmosphere at 0 °C and stirred for 10 min and then temperature raised to room temperature and stirred at rt for 8 h. After the completion of reaction (by TLC) MeOH was evaporated. Then the crude product was extracted using dichloromethane (30 mL). The DCM layer was washed with water (2 × 30 mL), brine solution (2 × 30 ml) and then dried over anhydrous sodium sulfate. Then concentrated crude product purified by recrystalization using hexane to afford (4*R*,5*R*)-4-allyl-4,5-dihydropyrene-4,5-diol **11** as a white solid in 78% yield; mp. 113-114 °C; IR (KBr) $\nu_{max}$: 3421, 3052, 3012, 2925, 2854, 1638, 1592, 1430, 1291, 1239, 1169, 1100, 1058, 1000, 916, 864, 834, 810, 773, 729 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 7.87 (d, *J* = 7.2 Hz, 1H, ArH6), 7.78 (d, *J* = 7.9 Hz, 2H, Ar H9, H10), 7.74-7.69 (m, 3H, ArH1, H3 and H8), 7.61-7.52 (m, 2H, ArH2, H7), 5.54-5.44 (m, 2H, H5, alkene CH ), 4.99 (d, *J* = 10.1 Hz, 1H, alkene $CH_2$), 4.92 (d, *J* = 17.1 Hz, 1H, alkene $CH_2$), 3.76 (s, 1H, OH), 3.37 (s, 1H, OH), 2.78 (dd, *J* = 14.1, 8.8 Hz, 1H, allyl $CH_2$), 2.28 (dd, *J* = 14.0, 6.0 Hz, 1H, allyl $CH_2$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 139.0 (C), 135.8 (C), 133.4 (CH), 131.2 (C), 130.9 (C), 127.15 (CH), 127.13 (CH), 126.78 (CH), 126.75 (CH), 126.7 (CH), 126.5 (CH), 125.9 (C), 125.7 (C), 123.1 (CH), 122.5 (CH), 119.6 ($CH_2$), 77.9 (C), 76.5 (CH), 38.2 ($CH_2$) ppm; HRMS (ESI) calcd for $C_{19}H_{16}O_2Na$ $[M + Na]^+$ 299.1048, found 299.1045; Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.97; H, 5.79.



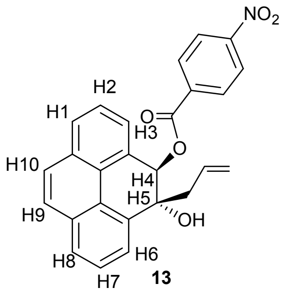
**12**

**5.2.13. 10-(Iodomethyl)-10,11-dihydropyreno[4,5-*b*]furan (12)**. To the solution of (4*R*,5*R*)-4-allyl-4,5-dihydropyrene-4,5-diol (100.3 mg, 0.37 mmol) in tetrahydrofuran (2 mL), iodine (143.1 mg, 1.11 mmol) was added and stirred at rt for 12 h. After the completion of the reaction (by TLC) evaporated THF and the crude product was extracted using dichloromethane (20 mL). The organic layer was washed with hypo solution (2 × 20 mL), brine solution (2 × 20 ml) and then dried over anhydrous sodium sulfate. The concentrated crude product was purified by column chromatography using silica (100-200 mesh) and hexane as eluent to afford 10-(iodomethyl)-10,11-dihydropyreno[4,5-*b*]furan **12** as a white solid in 66% yield; mp. 130-131 ºC; IR (KBr) $\nu_{max}$: 3044, 2923, 2850, 1639, 1593, 1473, 1404, 1347, 1299, 1240, 1200, 1173, 1082, 1024, 973, 946, 887, 827, 761, 716, 624 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.6 Hz, 1H, ArH3), 8.18 (d, *J* = 7.4 Hz, 1H, ArH6), 8.07-7.96 (m, 5H, ArH1, H2, H4, H5 and H7), 7.87 (d, *J* = 7.6 Hz, 1H, ArH8), 5.34-5.26 (m, 1H, H10), 3.83 (dd, *J* = 15.5, 7.6 Hz, 1H, H11), 3.67 (dd, *J* = 10.0, 4.7 Hz, 1H, H11), 3.55-3.45 (m, 2H, $CH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.3 (C), 131.7 (C), 131.5 (C), 129.1 (C), 127.9 (CH), 127.4 (CH), 126.4 (CH), 125.8 (CH), 125.6 (CH), 125.1 (C), 122.9 (CH), 121.6 (C), 121.2 (C), 120.0 (CH), 119.3 (CH), 113.7 (C), 82.7 (CH), 36.1 ($CH_2$), 9.6 ($CH_2$) ppm; Anal. Calcd for $C_{19}H_{13}IO$: C, 59.40; H, 3.41. Found: C, 59.46; H, 3.42.



**9**

**5.2.14. 10-Methylpyreno[4,5-*b*]furan (9).** To the solution of 10-(iodomethyl)-10,11-dihydropyreno[4,5-*b*]furan (100.2 mg, 0.26 mmol) in DMF (2 mL), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (39.6 mg, 0.26 mmol) was added and stirred at 50 ºC for 4 h. After the completion of the reaction (by TLC) evaporated DMF and the crude product was extracted using dichloromethane (20 mL). The organic layer was washed with 0.01N HCl solution (2 × 20 mL), brine solution (2 × 20 ml) and then dried over anhydrous sodium sulfate. The concentrated crude product was purified by crystallization using hexane and ethyl acetate to afford 10-methylpyreno[4,5-*b*]furan **9** as a white solid in 86% yield; mp. 170-171 ºC; IR (KBr) $\nu_{max}$: 1595, 1577, 1423, 1063, 1020, 937, 824, 800, 759, 711 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.52 (dd, *J* = 7.6, 1.1 Hz, 1H, ArH3), 8.31 (dd, *J* = 7.6, 1.0 Hz, 1H, ArH6), 8.12-8.10 (m, 2H, ArH4, H5), 8.05-7.99 (m, 4H, ArH1, H2, H7 and H8), 6.99 (s, 1H, ArH11), 2.69 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.6 (C), 148.9 (C), 132.1 (C), 131.9 (C), 128.0 (CH), 127.7 (CH), 126.9 (C), 126.1 (CH), 126.0 (CH), 124.2 (2 x CH), 123.1 (C), 122.7 (C), 122.2 (C), 121.8 (C), 121.0 (CH), 117.1 (CH), 103.0 (CH), 14.0 (CH$_3$). ppm; Anal. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72. Found: C, 89.21; H, 4.69.



13

**5.2.15. (4*R*,5*R*)-5-Allyl-5-hydroxy-4,5-dihydropyren-4-yl 4-nitrobenzoate (13)**.

(4*R*,5*R*)-4-allyl-4,5-dihydropyrene-4,5-diol (101.2 mg, 0.37 mmol) was dissolved in 3 mL dichloromethane, then added 4- nitro benzoic acid (61.8 mg, 0.37 mmol), dicyclohexylcarodiimide (DCC) (71.2 mg, 0.37 mmol), 4-dimethylaminopyridine (DMAP) (45.3 mg, 0.37 mmol) and stir at rt for 12 h. Then the crude product was extracted using dichloromethane (30 mL). The DCM layer was washed with water (2 × 30 mL), brine solution (2 × 30 ml) and then dried over anhydrous sodium sulfate. The concentrated crude product was purified by crystallization using hexane and ethyl acetate to afford (4*R*,5*R*)-5-allyl-5-hydroxy-4,5-dihydropyren-4-yl 4-nitrobenzoate **13** as a light yellow color solid in 78% yield; mp. 192-193 ºC; IR (KBr) $\nu_{max}$: 3331, 2929, 2853, 1728, 1645, 1601, 1562, 1527, 1445, 1379, 1342, 1270,1218, 1103, 836, 809, 724 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.41-8.35 (m, 4H, 4-nitrobenzoate ArH), 7.90-7.78 (m, 5H, ArH1, H3, H6, H9 and H10), 7.68-7.61 (m, 1H, ArH8), 7.59-7.54 (m, 2H, ArH2, H7), 6.97 (s, 1H, H4), 5.61-5.57 (m, 1H, alkene CH), 4.99 (d, *J* = 10.0 Hz, 1H, alkene $CH_2$), 4.86 (d, *J* = 17.2 Hz, 1H, alkene $CH_2$), 2.87-2.81 (m, 1H, allyl $CH_2$), 2.62-2.57 (m, 2H, 1H in allyl $CH_2$, OH) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ δ 164.9 (C), 151.0 (C), 138.2 (C), 135.4 (C), 132.7 (CH), 131.9 (C), 131.3 (2 × C), 131.2 (2 × CH), 127.9 (CH), 127.8 (2 × CH), 127.3 (CH), 127.0 (CH), 126.7 (CH), 126.1 (C), 125.6 (C), 124.0 (2 × CH), 123.5 (CH), 122.8 (CH), 119.4 ($CH_2$), 78.8 (CH), 76.7 (C), 39.6 ($CH_2$) ppm; Anal. Calcd for $C_{26}H_{19}NO_5$: C, 73.40; H, 4.50; N, 3.29. Found: C, 73.97; H, 4.48; N, 3.29.

**Crystal data for 13**: Empirical formula, $C_{26}H_{19}NO_5$; Formula weight, 425.43; Crystal color, habit: light yellow, needle; Crystal system, triclinic; Crystal dimensions, 0.35 × 025 × 0.20 $mm^3$; Lattice parameters, a = 8.6817(5) Å, b = 10.0211(6) Å, c = 12.9825(9) Å; α = 109.18(6), β = 97.30(5), γ = 99.85(5); V = 1030.43(12) $A^3$; Space group P-1; Z = 2; $D_{calcd}$ = 1.381 g/$cm^3$; $F_{000}$ = 444; λ(Mo Kα) = 0.7107 Å; R ($I \geq 2\sigma_1$) = 0.0547, $wR^2$ = 0.1535. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **13** CCDC # 988268).

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