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A convenient synthesis of partially reduced benzo[*c*]phenanthrenes, its ketals and ketones☆

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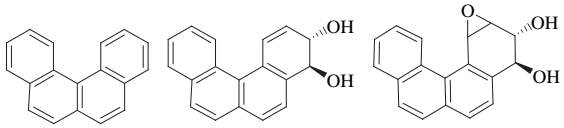
ABSTRACT

A concise and convenient synthesis of various partially reduced 6-*sec*-amino-1,2,3,4,7,8-hexahydro-, 6-*sec*-amino-1,2,7,8-tetrahydrobenzo[*c*]phenanthrene-5-carbonitriles, 6-*sec*-amino-3,4,7,8-tetrahydro-1*H*-benzo[*c*]phenanthrene-2-one-5-carbonitrile cycloalkene ketals, pendant with electron donor and acceptor substituents has been described through base catalyzed ring transformation of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles by cyclohexanone, 2-cyclohexen-1-one, 1,4-cyclohexanedione monocycloalkene ketals. The acid catalyzed deketalation of 6-*sec*-amino-3,4,7,8-tetrahydro-1*H*-benzo[*c*]phenanthrene-2-one-carbonitrile ketals led to yield 6-*sec*-amino-3,4,7,8-tetrahydro-1*H*-benzo[*c*]phenanthrene-3-carbonitrile-2-ones in excellent yield. We also performed the X-ray studies of the molecules **3d** and **6a** to know the degree of non-planarity.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received considerable attention because of their fascinating chemistry and unique physical properties due to highly twisted geometry possibly owing to the over crowding of atoms or groups present in the fjord region. In these molecules, induced strain is relieved by buckling of aromatic ring and bending of bonds, assuming helical conformation. The helicity of polycyclic aromatic hydrocarbons can be further increased through bulky substitution in the fjord region as well as through partial reduction or in combination. There is also a possibility for the reduced distortion if the twisting in the molecule is unidirectional. Small helical molecules are of great significance because of their rich chemistry,[1] physical properties,[2] technological and industrial applications.[1] These molecules have inherent chirality due to their twisted skeletons and racemize by inversion and exhibit chirotopic properties, if resolved. The pure enantiomers are useful as chiral auxiliaries for chiral induction and as shift reagents in NMR spectroscopy.[3]



I II III

Figure 1. Benzo[*c*]phenanthrene and their metabolites.

The high prevalence of various polycyclic aromatic hydrocarbons in the environment and their threat to cause cancer in humans has drawn substantial attention. In vivo these metabolize by the combined action of enzymes P450 and epoxidehydrolase to diolepoxides that covalently bind to purine base of DNA through C–N linkage to form stable adduct involving amino group of deoxyadenosine and deoxyguanosine. When repair enzymes do not excise these lesions, mutation may occur upon DNA replication, resulting initiation of tumorigenesis. Benzo[*c*]phenanthrene (BcP, **I**) is relatively weak carcinogen[4] present in the environment[5] compared to benzo[*a*]pyrene. The 3,4-dihydrodiol (**II**) and the corresponding diolepoxide (**III**) derivatives of BcP are highly potent carcinogenic metabolites (Fig. 1).[6,7]

One of the most intriguing problems in the study of carcinogenic hydrocarbons is to establish the correlation between chemical structure and tumorigenic property. Various theories are proposed

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but none of them is satisfactory in all respect. Based on numerous experimental facts, it has been concluded that partial reduction of polycyclic aromatic hydrocarbons reduces the carcinogenic property, possibly by disrupting the co-planarity of the molecule.[6]

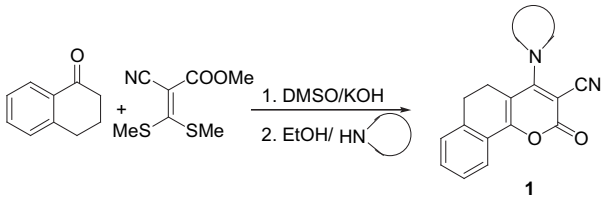
Various approaches to the synthesis of benzo[*c*]phenanthrene ring system are reported[7,8] but none of them devoid from shortfalls of generality, multi-steps sequences with complex work-up and also impractical for the construction of hindered and partially reduced derivatives. The molecules of this ring system are synthesized in multiple steps through the Friedel–Crafts reaction of 1-methallylsuccinic anhydride and benzene followed by reduction and cyclization.[9] Further improvement in the synthetic strategy shorten the reaction steps and also improved the overall yields of the final products. Vilsmeier reaction of 1-(4-anisyl)-2-formyl-6-methoxy-3,4-dihydronaphthalene, which on cyclodehydration and dehydrogenation provided 3,10-dimethoxy-5-methyl-5,6,6a,7,8,12*b*-hexahydrobenzo[*c*]phenanthrene.[10] A novel synthesis of benzo[*c*]phenanthrene and its 3,4-phenolic derivatives via the key intermediate, 4-oxo-1,2,3,4-tetrahydrobenzo[*c*]phenanthrene has been reported.[11] It has also been obtained by alkylation of 1,3-cyclohexanedione by 2-(2-naphthyl)ethyl iodide, which after cyclization and dehydrogenation gave 2-phenyl-4-hydroxybenzo[*c*]phenanthrene.[12] An efficient and convenient route for the synthesis of benzo[*c*]phenanthrene through combined metalation, Suzuki/Grignard cross coupling resimen[13] has been reported. An improved synthesis of benzo[*c*]phenanthrene-3,4-diol-1,2-epoxide has been achieved from 1-(2-naphthyl)-2-(2-methoxyphenyl)ethylene, via photocyclization in five steps in 15% overall yield.[14] Under a new strategy a cross coupling reaction of 2-bromo-5-methoxybenzaldehyde with naphthalene-1-boronic acid produced 2-(1-naphthyl)-5-methoxybenzaldehyde, followed by acid catalyzed cyclization with methanesulfonic acid afforded 3-methoxybenzo[*c*]phenanthrene.[15] It has also been synthesized[15] by the photolysis of 2-naphthylstyrene, obtained from the Wittig reaction of 2-naphthaldehyde and 2,5-dimethylbenzyltriphenylphosphonium chloride. Generally, most of the reported procedures[8c,9,13] for the construction of benzo[*c*]-phenanthrene derivatives suffer from the harsh reaction conditions and commercially non-availability of reagents.

The lack of simple and efficient route necessitated the development of an economical, efficient and regioselective synthesis of partially reduced benzo[*c*]phenanthrenes, their ketals and ketones.

2. Result and discussion

Herein, we report a facile and concise synthesis of functionalized partially reduced benzo[*c*]phenanthrenes through a base catalyzed ring transformation of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles with cyclohexanone, 2-cyclohexen-1-one, 1,4-cyclohexanedione monoethylene- and mono-2,2′-dimethyltrimethylene ketals separately in high yields. The presence of electron-withdrawing and donating substituents at position 3 and 4 of benzo[*h*]chromene ring made it indispensable synthon for the construction of various polycyclic hydrocarbons. The synthetic potential of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles is enormous for generating molecular diversity.

The 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles, have been prepared in two steps. The first step of the reaction involves the synthesis of the 2-oxo-4-methylsulfanyl-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles[16] by stirring a mixture of methyl 2-cyano-3,3-dimethylthioacrylate[17] and 1-tetralone using powdered KOH as a base in DMSO at room temperature. This on amination with a secondary amine in ethanol at reflux temperature produced 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles in good yields[16] and were used for the synthesis of congested diverse polycyclic aromatic hydrocarbons, Scheme 1.



Scheme 1. Two steps synthesis of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles.

As evident from the topography of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles **1** that the C2, C4, and C10b positions are electrophilic in nature. However, the position C10b is more electrophilic compared to other positions due to the presence of an electron-withdrawing CN substituent at position 3 of the chromene ring and extended conjugation that made the position highly prone to nucleophilic attack.

Various cyclic ketones and 1,4-hexanedione monocycloalkene ketals have been used as source of carbanions. The methylene group α- to carbonyl in the cyclic ketones is activated and form carbanion in the presence of base. Thus, stirring an equimolar mixture of **1**, cyclohexanone **2a** and powdered KOH in DMF at room temperature for 2–3 h followed by usual work-up and purification of crude product through column chromatography afforded 6-*sec*-amino-1,2,3,4,7,8-hexahydrobenzo[*c*]phenanthrene-5-carbonitriles **3a**–**d** in excellent yields (Scheme 2).

This reaction possibly proceeds through attack of a carbanion at position C10b of **1** with Michael addition followed by ring closure with loss of water and carbon dioxide to yield **3a**–**d** (Scheme 2). The possibility for the formation of mechanistically obvious product **4** was ruled out on the basis of reduced electrophilicity of the C4 carbon due to the presence of amino group, which does not favor the enolization of Michael adduct formed in the initial step.

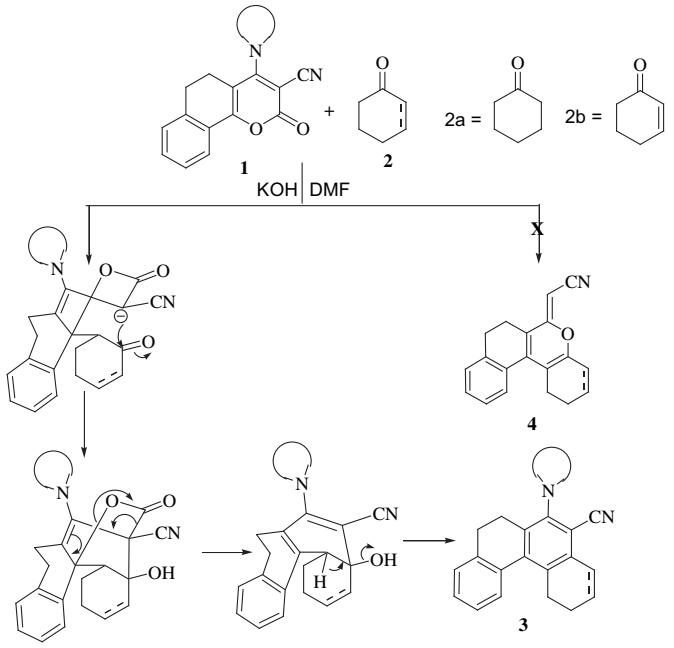
Under analogous conditions, the reaction of **1** with 2-cyclohexen-1-one **2b** followed the similar course of reaction to yield partially reduced benzo[*c*]phenanthrene-3-carbonitriles **3e**–**g** in good yields, Scheme 2.

A similar reaction of **1** with 1,4-cyclohexanedione was carried out to obtain 6-*sec*-amino-3,4,7,8-tetrahydro-1*H*-benzo[*c*]phenanthrene-2-one-5-carbonitrile in single step but finally ended with a complex mixture, possibly due to the side reaction at other carbonyl group. To avoid the complexity of reaction, synthetic strategy was changed by using their monoethylene- and 2,2′-dimethyltrimethylene ketals as a source of carbanion. However, reaction of **1** with 1,4-cyclohexanedione monoalkeneketal **5a** and **5b** separately produced **6a**–**h** in excellent yields, Scheme 3.

Attempts to cleave the cyclic ketal ring of **6e** by amberlyst-15 failed, but easily cleaved by stirring in formic acid at room temperature to yield 6-*sec*-amino-3,4,7,8-tetrahydro-1*H*-benzo[*c*]phenanthrene-2-ones **7** (Scheme 4).

In order to synthesize highly functionalized **7**-helicenes, the ring transformation of **1** was attempted by **7** under analogous reaction conditions, but only **7** was recovered. We tried several base and solvent combinations as KOH/DMSO, NaH/THF, NaH/DMF, KOBu^t/DMF and K_2CO_3/DMF but failed to precede the reaction. We also carried out this reaction at elevated temperature but no positive result was achieved, possibly due to steric hindrance, which restricts the attack of carbanion generated in situ from 7 at C10b of the **1**.

X-ray study of partially reduced benzo[c]phenanthrenes: The helical conformation in the benzo[*c*]phenanthrene has been observed owing to the distortion of aromatic ring in some way.[8c] Effect of partial reduction on acquiring helical conformation in partially reduced benzo[*c*]phenanthrenes is not explored due to non-availability of partially reduced benzo[*c*]phenanthrenes and is the concern for present investigation.



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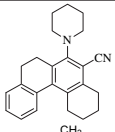
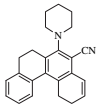
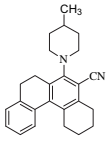
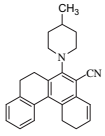
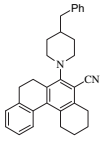
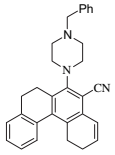
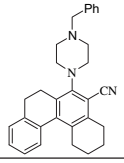
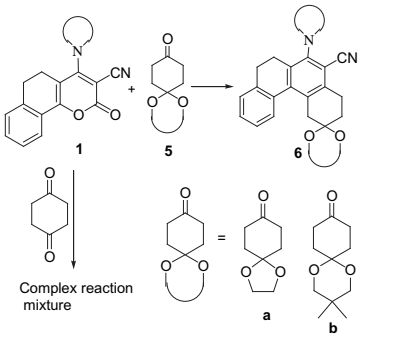
a		89	e		79
b		92	f		84
c		87	g		87
d		95			

Scheme 2. Probable mechanism for the synthesis of 6-*sec*-amino-1,2,3,4,7,8-hexahydrobenzo[*c*]phenanthrene-5-carbonitriles (**3a**–**d**) and 6-*sec*-amino-1,2,7,8-tetrahydrobenzo[*c*]phenanthrene-5-carbonitriles (**3e**–**g**).

For the study of conformational arrangements of the rings of benzo[*c*]phenanthrene, several substituted benzo[*c*]phenanthrenes were crystallized for X-ray structural analysis. Diffraction quality crystals of 6-(4-benzylpiperazin-1-yl)-1,2,3,4,7,8-hexahydrobenzo-[*c*]phenanthrene-5-carbonitrile **3d** and 6-(piperidin-1-yl)-3,4,7,8-tetrahydro-1*H*-benzo[*c*]phenanthrene-2-one-5-carbonitrile-(2,2′-dimethylene ketal) **6a** were obtained in mixture of methanol in chloroform by slow evaporation at room temperature. The conformation of these compounds with arbitrary numbering is shown as ORTEP diagram Figure 2, which indicates a non-planar conformation.

The least square plane calculation from X-ray crystallographic data of **6a** indicates that rings A and C are nearly planar. The average mean plane angle for the twist between the rings A and C is 38.5°. The rings B and D adopt half chair conformation. The ring E adopts



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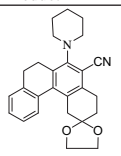
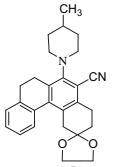
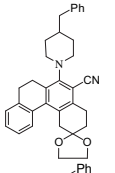
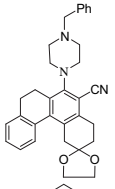
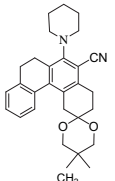
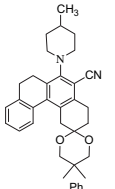
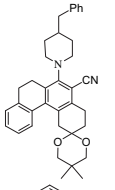
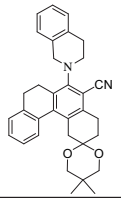
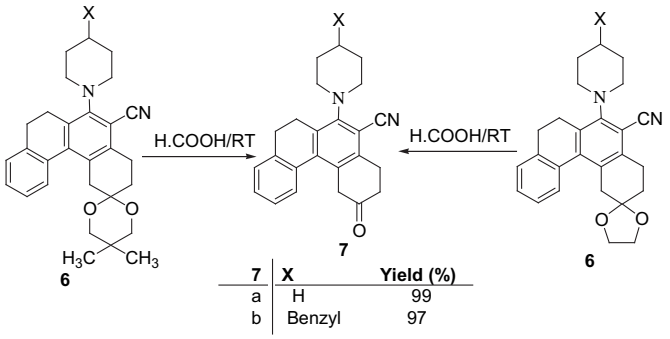
a		91
b		94
c		89
d		81
e		94
f		89
g		91
h		92

Scheme 3. Synthesis of cyclic ethylene ketal of 6-*sec*-amino-3,4,7,8-tetrahydro–1*H*-benzo[*c*]phenanthrene-2-one, cyclic trimethylene ketal of 6-*sec*-amino-3,4,7,8-tetrahydro–1*H*-benzo[*c*]phenanthrene-2-one.



7	X	Yield (%)
a	H	99
b	Benzyl	97

Scheme 4. Deprotection of cyclic trimethylene- and ethylene ketals.

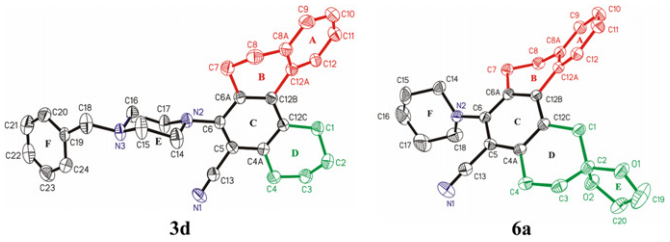


Figure 2. Displacement ellipsoid plot (30% probability) showing the molecular structure of **3d** and **6a** with the atomic-labeling.

an envelope conformation while ring F adopts a full chair conformation. The distance between the non-bonded carbon atoms C1 and C12 is 3 Å, which is shorter than any over crowded molecule and from van der Waals radii of carbon atoms by 0.4 Å, which induces distortion in the molecule. This strain is relieved either through stretching and bending of the chemical bonds or buckling of the aromatic rings.

Similarly the X-ray study of the compound **3d** showed that the average mean plane angle for the twist between the rings A and C is 32.5°. The distance between the non-bonded carbon atoms C1 and C12 is 2.994 Å. The torsion angles (C12-C12A-C12B-C12C and C1-C12C-C12B-C12A) of the compounds **6a** are –40.5 and -9.7°, while for **3d** are 33.28 and 5.9°. The torsion angles of benzo[*c*]phenanthrene and 1,4-dimethyl benzo[*c*]phenanthrene have 17.3 & 19.0 and −29.3 & −18.4°, respectively. Some of the inner C–C bond lengths have been lengthened while the outer bonds are closer to the normal single and double bond lengths. Thus, it is the ring B/C, that accommodates most of the torsional strain.

Here we showed the arrangement of molecules in the unit cell of **3d** and **6a**. In case of **3d** unit cell contain two molecule and in case of **6a** it contains 4 molecules in unit cell (Fig. 3).

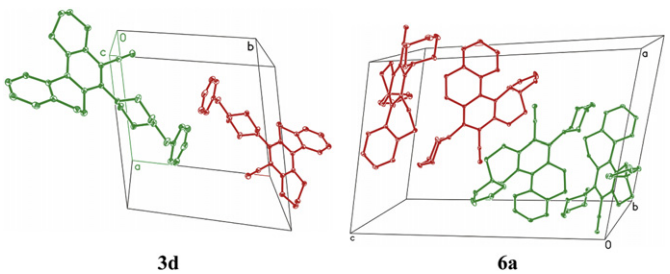


Figure 3. Showing the arrangement of molecules in the unit cell.

The presence of spiro ring at C2 position in **6a** enhances the degree of non-planarity in the compound and thereby induces helicity, by forcing the molecule to deviate from the most favorable planar arrangement by bending out of the plane of the aromatic rings.

The contribution of spiro ring to the helical conformation in **6a** was established by replacing it with hydrogen in **3d**, which reduces the repulsion and thereby torsion angles and degree of induced non-planarity. Because of electronic repulsion between the two rings there is remarkable distortion in the case of **6a** (∼50°) as compared to **3d** (∼39°)(Table 1 and 2).

Table 1
Selected torsion and mean plane twist angles (°)

Comp.	Atoms	Torsion angles (°)	Mean plane angle (Twist angle °)
3d	C4a-C5-C6-N2	−179.04	A, C 32.55
	C6-C5-C13-N1	−102.71	
	C12-C12A-C12B-C12C	33.28	
	C1-C12C-C12B-C12A	5.96	
	C1-C12C-C4A-C5	174.05	
	C12C-C12B-C6A-C7	173.92	
	C12B-C12A-C8A-C9	175.52	
6a	C4a-C5-C6-N2	178.23	A, C 38.55
	C6-C5-C13-N1	−179.53	
	C12-C12A-C12B-C12C	−40.53	
	C1-C12C-C12B-C12A	−9.73	
	C1-C12C-C4A-C5	−175.39	
	C12C-C12B-C6A-C7	−164.43	
	C12B-C12A-C8A-C9	−178.36	

Table 2
Selected bond lengths of **3d** and **6a**

Comp.	Inner C–C Bond lengths	Outer C–C bond lengths
3d	C1-C12C 1.522	C5-C6 1.391
	C12C-C12B 1.412	C6-C6A 1.381
	C12B-C12A 1.500	C6A-C7 1.513
	C12A-C12 1.394	C8-C8A 1.536
6a	C1-C12C 1.518	C5-C6 1.392
	C12C-C12B 1.416	C6-C6A 1.397
	C12B-C12A 1.481	C6A-C7 1.515
	C12A-C12 1.403	C8-C8A 1.500

3. Conclusions

We have developed an innovative and concise protocol for the construction of partially reduced highly functionalized benzo[*c*]-phenanthrenes through base catalyzed ring transformation of 2-oxo-4-*sec*-amino-5,6-dihydro-2H-benzo[*h*]chromene-3-carbonitriles by different alicyclic ketones, using potassium hydroxide as a base and DMF as solvent at room temperature. A methodology for the introduction of a carbonyl group at position 2 of the benzo[c]phenanthrene has also been developed using 1,4-cyclohexanedione mono ketal as an agent for the ring transformation followed by acid cleavage of the resulted ketal, providing 2-oxo-4-*sec*-amino-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene without using any oxidizing agent and catalyst. The conformational study for the selected compounds by X-ray diffraction analysis has also been done.

4. Experimental

4.1. General

All reactions were conducted in flame-dried glassware. Precoated Merck TLC plates were used for monitoring the reaction. Column chromatographic separation was performed on neutral alumina and silica gel (60–120 mesh). IR spectra were recorded on a Shimadzu 8201 PC FTIR Spectrophotometer. ^{1}H NMR spectra were recorded on Bruker DRX 200 as well as Bruker DRX 300 spectrometer in deuterated solvents with TMS as internal reference.

Mass spectra were recorded on JEOL SX-102 (FAB) spectrometer. HRMS were recorded on JEOL JMS-600H (HRMS) spectrometer. Melting points were determined on Büchi-530 capillary melting point apparatus and are uncorrected.

4.2. General procedure for the synthesis of 6-*sec*-amino-1,2,3,4,7,8-hexahydrobenzo[*c*]phenanthrenes (3a–d)

An equimolar mixture of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles, cyclohexanone and KOH in DMF was stirred for 2–3 h. Completion of reaction was monitored by TLC. Thereafter, reaction mixture was poured onto crushed ice with vigorous stirring followed by neutralization with 10% HCl. The precipitate obtained was filtered, washed with water, dried and purified by neutral alumina column using 3% ethyl acetate in hexane as eluent.

*4.2.1. 6-(Piperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-5-carbonitrile (**3a**).* White powder; yield: 89%; mp: 156–158 °C; IR (KBr): 2926, 2855, 2368, 2213, 1596, 1461, 1351 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.62–1.70 (m, 8H, CH_2), 1.84–1.93 (m, 2H, CH_2), 2.63–2.67 (m, 2H, CH_2), 2.73–2.77 (m, 2H, CH_2), 2.93 (t, J=5.97 Hz, 2H, CH_2), 3.01 (t, J=6.80 Hz, 2H, CH_2), 3.21 (br s, 4H, CH_2), 7.21–7.30 (m, 3H, ArH), 7.55–7.59 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.16, 22.01, 22.99, 23.82, 25.61, 27.33, 28.37, 29.50, 51.04, 106.56, 117.18, 124.28, 126.00, 126.43, 127.45, 130.01, 132.70, 134.00, 139.11, 139.20, 150.23; MS m/z 343 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{24}H_{26}N_2$ 342.20960 (M^+) found for m/z 342.20941.

The crystal data of **3d**: $C_{30}H_{31}N_3$, M=433.58, triclinic, P-1, a=10.219(6) Å, b=11.256(9) Å, c=11.618(7) Å, α=65.78(7) °, β=81.96(6) °, γ=81.30(5)°, V=1200.2(14) $Å^3$, Z=2, D_c=1.200 gcm^{-3}, μ (Mo-Kα)=0.071 mm^{-1}, F(000)=464, rectangular block, colorless, size=0.175×0.125×0.075 mm, 4868 reflections measured (R_{int}=0.0414), 4109 unique, wR_2=0.2061 for all data, conventional R=0.0674 [$(\Delta/\sigma)_{max}$=000] on F-values of 1525 reflections with $I>2\sigma(I)$, S=0.928 for all data and 299 parameters (deposit No: 3d: 759528).

*4.2.2. 6-(4-Methylpiperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-5-carbonitrile (**3b**).* White powder; yield: 92%; mp: 150–152 °C; IR (KBr): 2951, 2371, 2215, 1596, 1430, 1382, 1352, 1283, 1116, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.0 (d, J=6.12 Hz, 3H, CH_3), 1.41–1.44 (m, 2H, CH_2), 1.56–1.57 (m, 1H, CH), 1.61–1.40 (m, 4H, CH_2), 1.84–1.93 (m, 2H, CH_2), 2.66 (d, J=6.09 Hz, 2H, CH_2), 2.72 (br s, 2H, CH_2), 2.93 (t, J=5.95 Hz, 2H, CH_2), 3.01 (t, J=6.80 Hz, 2H, CH_2), 3.22 (br s, 2H, CH_2), 3.33 (br s, 2H, CH_2), 7.22–7.31 (m, 3H, ArH), 7.55–7.59 (m, 1H, ArH); MS m/z 357 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{25}H_{28}N_2$ 356.22525 (M^+) found for m/z 356.22541.

*4.2.3. 6-(4-Benzylpiperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-5-carbonitrile (**3c**).* White powder; Yield: 87%; mp: 148–150 °C; IR (KBr): 2820, 2378, 2203, 1605, 1434, 1384, 1352, 1197, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.45–1.47 (m, 2H, CH_2), 1.61–1.72 (m, 5H, CH and CH_2), 1.83–1.92 (m, 2H, CH_2), 2.60–2.66 (m, 4H, CH_2), 2.72 (br s, 2H, CH_2), 2.92 (t, J=5.89 Hz, 2H, CH_2), 3.0 (t, J=6.75 Hz, 2H, CH_2), 3.12 (br s, 2H, CH_2), 3.30 (br s, 2H, CH_2), 7.16–7.20 (m, 3H, ArH), 7.23–7.31 (m, 5H, ArH), 7.54–7.57 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 21.33, 21.99, 27.32, 28.37, 29.48, 31.96, 36.64, 42.15, 50.28, 75.98, 117.09, 124.31, 124.56, 126.01, 126.47, 126.94, 127.47, 127.87, 130.19, 132.67, 134.04, 139.18, 139.36, 149.86; MS m/z 433 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{31}H_{32}N_2$ 432.25655 (M^+) found for m/z 432.25617.

*4.2.4. 6-(4-Benzylpiperazin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-5-carbonitrile (**3d**).* White powder; yield: 95%; mp: 154–156 °C; IR (KBr): 2931, 2363, 2214, 1595, 1436, 1351, 1208, 1136, 1006 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.62 (m, 2H, CH_2), 1.84–1.93 (m, 2H, CH_2), 2.62–2.67 (m, 6H, CH_2), 2.72–2.74 (m, 2H, CH_2), 2.93 (t, J=5.94 Hz, 2H, CH_2), 3.01 (t, J=6.78 Hz, 2H, CH_2), 3.29 (br s, 4H, CH_2), 3.58 (s, 2H, CH_2), 7.24–7.39 (m, 8H, ArH), 7.54–7.57 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 21.11, 21.97, 24.13, 27.39, 28.28, 29.50, 49.63, 52.78, 62.02, 107.23, 116.91, 124.35, 125.77, 126.01, 126.53, 126.97, 127.47, 127.94, 130.51, 132.54, 133.92, 137.06, 139.07, 139.18, 139.31, 148.86; MS m/z 434 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{30}H_{31}N_3$ 433.25180 (M^+) found for m/z 433.25200.

4.3. General procedure for the synthesis of 6-*sec*-amino-1,2,7,8-tetrahydrobenzo[*c*]phenanthrene (3e–g)

These were prepared from the reaction of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles and 2-cyclohexenone and work-up as described in the earlier experiment. The crude product was purified by neutral alumina column using 4% ethyl acetate in hexane as eluent.

*4.3.1. 6-(Piperidin-1-yl)-1,2,7,8-tetrahydrobenzo[c]phenanthrene-5-carbonitrile(**3e**).* White powder; yield: 79%; mp: 162–164 °C; IR (KBr): 2957, 2362, 2203, 1584, 1417, 1352, 1300, 1209, 1105 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.64–1.72 (m, 6H, CH_2), 2.32–2.39 (m, 2H, CH_2), 2.67–2.72 (m, 2H, CH_2), 2.74–2.79 (m, 2H, CH_2), 3.01 (t, J=8.05 Hz, 2H, CH_2), 3.22 (br s, 3H, CH_2 and CH), 3.90 (br s, 1H, CH), 6.09–6.15 (m, 1H, CH), 6.77–6.81 (m, 1H, CH), 7.25–7.29 (m, 3H, ArH), 7.48–7.50 (m, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$): 21.75, 24.22, 24.86, 26.85, 27.01, 29.38, 52.26, 52.82, 118.34, 124.76, 125.80, 126.60, 127.29, 127.58, 127.89, 129.50, 133.28, 135.50, 137.52, 139.93, 140.81, 151.32; MS m/z 341 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{24}H_{24}N_2$ 340.19395 (M^+) found for m/z 340.19403.

*4.3.2. 6-(4-Methylpiperidin-1-yl)-1,2,7,8-tetrahydrobenzo[c]phenanthrene-5-carbonitrile (**3f**).* White powder; yield: 84%; mp: 130–132 °C; IR (KBr): 3018, 2934, 2363, 2222, 1655, 1560, 1429, 1217, 1009 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (d, J=4.77 Hz, 3H, CH_3), 1.28–1.42 (m, 2H, CH_2), 1.55–1.62 (m, 1H, CH), 1.69 (d, J=11.61 Hz, 2H, CH_2), 2.31–2.39 (m, 2H, CH_2), 2.71 (br s, 4H, CH_2), 3.01 (t, J=8.05 Hz, 2H, CH_2), 3.13 (br s, 2H, CH_2), 3.34 (br s, 2H, CH_2), 6.08–6.15 (m, 1H, CH), 6.77–6.81 (m, 1H, CH), 7.24–7.29 (m, 3H, ArH), 7.47–7.50 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 20.50, 20.93, 25.76, 28.13, 28.42, 29.42, 33.93, 50.31, 124.55, 125.35, 125.70, 126.04, 126.31, 126.65, 128.25, 132.03, 134.20, 136.28, 138.68, 139.52, 149.90; MS m/z 355 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{25}H_{26}N_2$ 354.20960 (M^+) found for m/z 354.20911.

*4.3.3. 6-(4-Benzylpiperazin-1-yl)-1,2,7,8-tetrahydrobenzo[c]phenanthrene-5-carbonitrile (**3g**).* White powder; yield: 87%; mp: 164–166 °C; IR (KBr): 2935, 2365, 2204, 1597, 1478, 1384, 1351, 1248, 1201 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.32–2.39 (m, 2H, CH_2), 2.62 (br s, 4H, CH_2), 2.67–2.78 (m, 4H, CH_2), 3.01 (t, J=8.04 Hz, 2H, CH_2), 3.31 (br s, 4H, CH_2), 3.59 (s, 2H, CH_2), 6.11–6.16 (m, 1H, CH), 6.77–6.81 (m, 1H, CH), 7.24–7.39 (m, 8H, ArH), 7.47–7.49 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 20.48, 23.86, 25.79, 28.05, 49.59, 52.75, 62.0, 116.81, 124.61, 125.28, 125.78, 126.05, 126.63, 126.74, 126.97, 127.93, 128.27, 131.87, 134.24, 138.56; MS m/z 432 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{30}H_{29}N_3$ 431.23615 (M^+) found for m/z 431.23635.

4.4. General procedure for the synthesis of protected 5-cyano-6-*sec*-amino-1,2,3,4,7,8-hexahydro-2-oxobenzo[*c*]phenanthrene (6)

These were obtained by stirring an equimolar mixture of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles, cyclohexan-1,4-dionemonoalkyleneketal and KOH in DMF for

1–2 h. After completion of reaction, excess of DMF was removed under reduced pressure. The reaction mixture was poured onto crushed ice with vigorous stirring. Neutralization with 10% HCl gave a precipitate, which was filtered, washed with water, dried and purified on neutral alumina column using 3% ethyl acetate in hexane as eluent.

*4.4.1. 5-Cyano-6-(piperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-ethylene ketal (**6a**).* White powder; yield: 91%; mp: 216–218 °C; IR (KBr): 2941, 2363, 2210, 1607, 1452, 1291, 1252, 1095 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.62–1.70 (m, 6H, CH_2), 2.05 (t, J=7.04 Hz, 2H, CH_2) 2.63–2.67 (m, 2H, CH_2), 2.71–2.74 (m, 2H, CH_2), 3.16 (s, 2H, CH_2), 3.21 (t, J=6.94 Hz, 6H, CH_2), 3.87–3.92 (m, 2H, CH_2), 3.94–3.99 (m, 2H, CH_2), 7.22–7.30 (m, 3H, ArH), 7.49–7.52 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.97, 23.88, 25.57, 26.60, 28.24, 29.65, 38.47, 51.01, 63.33, 106.33, 106.03, 106.96, 117.03, 124.53, 126.08, 126.40, 126.59, 127.07, 132.36, 134.77, 137.48, 139.30, 139.48, 150.80; MS m/z 401 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{26}H_{28}N_2O_2$ 400.21508 (M^+) found for m/z 400.21493.

The crystal data of **6a**: $C_{26}H_{28}N_2O_2$, M=400.50, monoclinic, $P2(1)/n$, a=12.452(1) Å,b=9.378(2) Å, c=18.631(4) Å, β=103.800(1) °, V=2112.8(7) $Å^3$, Z=4, D_c=1.259 gcm^{-3}, μ (Mo-Kα)=0.080 mm^{-1}, F(000)=856, rectangular block, yellow, size=0.25×0.175×0.125 mm, 4843 reflections measured (R_{int}=0.0387), 3723 unique, wR_2=0.1564 for all data, conventional R=0.0527 [$(\Delta/\sigma)_{max}$=000] on F-values of 1534 reflections with $I>2\sigma(I)$, S=0.964 for all data and 272 parameters.

Unit cell determination and intensity data collection (2θ=50°) was performed on a Bruker P4 diffractometer at 293(2) K. Structure solutions by direct methods and refinements by full-matrix least-squares methods on F^2. Programs: XSCANS [Siemens Analytical X-ray Instrument Inc.: Madison, Wisconsin, USA 1996], SHELXTL-NT [Bruker AXS Inc.: Madison, Wisconsin, USA 1997], MERCURY [Version 1.4.1, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U. K]. CCDC (deposit No: 6a: 759529) contains the supplementary crystallographic data. These data can be obtained free of charge from www.ccdc.cam.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U. K; Fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk.

*4.4.2. 5-Cyano-6-(4-methylpiperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-ethylene ketal (**6b**).* White powder; yield: 94%; mp: 220–222 °C; IR (KBr): 2919, 2362, 2208, 1592, 1522, 1477, 1351, 1194 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.0 (d, J=6.21 Hz, 3H, CH_3), 1.34–1.41 (m, 2H, CH_2), 1.50–1.55 (m, 1H, CH), 1.68 (d, J=11.82 Hz, 2H, CH_2), 2.05 (t, J=7.0 Hz, 2H, CH_2), 2.65–2.71 (m, 4H, CH_2), 3.16–3.24 (m, 6H, CH_2), 3.31 (br s, 2H, CH_2), 3.87–3.92 (m, 2H, CH_2), 3.94–3.99 (m, 2H, CH_2), 7.24–7.31 (m, 3H, ArH), 7.49–7.53 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 20.90, 26.60, 28.24, 29.41, 29.64, 33.94, 38.47, 50.30, 63.32, 106.96, 117.02, 124.53, 126.07, 126.36, 126.58, 127.07, 132.37, 134.75, 137.48, 139.38, 150.63; MS m/z 415 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{27}H_{30}N_2O_2$ 414.23073 (M^+) found for m/z 414.23091.

*4.4.3. 5-Cyano-6-(4-benzylpiperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-ethylene ketal (**6c**).* White powder; yield: 89%; mp: 146–148 °C; IR (KBr): 2928, 2363, 2216, 1596, 1458, 1354, 1119, 1060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.45 (br s, 1H, CH), 1.60 (br s, 1H, CH), 1.70 (d, J=10.38 Hz, 3H, CH and CH_2), 2.05 (t, J=7.04 Hz, 2H, CH_2), 2.61 (d, J=6.66 Hz, 2H, CH_2), 2.65–2.70 (m, 4H, CH_2), 3.16–3.24 (m, 8H, CH_2), 3.87–3.92 (m, 2H, CH_2), 3.94–3.96 (m, 2H, CH_2) 7.16–7.23 (m, 3H, ArH), 7.24–7.31 (m, 5H, ArH), 7.48–7.51 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 26.61, 28.21, 29.61, 31.90, 36.64, 38.49, 42.13, 50.26. 63.34, 106.93, 117.50, 124.56, 126.09, 126.62, 126.93, 127.08, 127.86, 132.31, 134.80, 137.49, 139.31, 150.45; MS m/z 491 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{33}H_{34}N_2O_2$ 490.26203 (M^+) found for m/z 490.26213.

*4.4.4. 5-Cyano-6-(4-benzylpiperazin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-ethylene ketal (**6d**).* White powder; yield: 81%; mp: 180–182 °C; IR (KBr): 2923, 2373, 2210, 1595, 1438, 1378, 1352, 1279, 1127 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.05 (t, J=7.02 Hz, 2H, CH_2), 2.61–2.66 (m, 6H, CH_2), 2.71–2.73 (m, 2H, CH_2), 3.16 (s, 2H, CH_2), 3.21 (t, J=7.05 Hz, 2H, CH_2), 3.28 (br s, 4H, CH_2), 3.58 (s, 2H, CH_2), 3.87–3.92 (m, 2H, CH_2), 3.93–3.99 (m, 2H, CH_2), 7.22–7.38 (m, 8H, ArH), 7.48–7.51 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 24.16, 26.66, 28.15, 28.42, 29.61, 38.50, 49.59, 52.73, 61.99, 63.34, 106.70, 106.91, 116.76, 124.60, 125.79, 126.10, 126.69, 126.96, 127.10, 127.93, 132.19, 134.69, 136.98, 137.67, 139.18, 139.49, 149.43; MS m/z 492 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{32}H_{33}N_3O_2$ 491.25728 (M^+) found for m/z 491.25709.

*4.4.5. 5-Cyano-6-(piperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-(2,2-dimethyltrimethylene)ketal (**6e**).* White powder; yield: 94%; mp: 238–240 °C; IR (KBr): 2944, 2849, 2205, 1594, 1437, 1354, 1277, 1114, 1089 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.83 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.65–1.70 (m, 6H, CH_2), 2.28 (t, J=6.72 Hz, 2H, CH_2), 2.64–2.74 (m, 4H, CH_2), 3.08 (t, J=6.93 Hz, 2H, CH_2), 3.21–3.24 (m, 6H, CH_2), 3.37 (d, J=11.58 Hz, 2H, CH_2), 3.63 (d, J=11.49 Hz, 2H, CH_2), 7.23–7.31 (m, 3H, ArH), 7.52–7.57 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 21.00, 21.56, 22.96, 23.84, 24.0, 25.57, 25.76, 28.23, 28.90, 39.43, 51.0, 69.19, 96.33, 105.86, 117.13, 124.61, 125.78, 126.06, 126.57, 127.11, 132.37, 134.75, 137.72, 139.26, 139.44, 150.62; MS m/z 443 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{29}H_{34}N_2O_2$ 442.26203 (M^+) found for m/z 442.26188.

*4.4.6. 5-Cyano-6-(4-benzylpiperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-(2,2-dimethyltrimethylene)ketal (**6f**).* White powder; yield: 89%; mp: 230–232 °C; IR (KBr): 3031, 2861, 2219, 1253, 1209, 1156, 1021, 1000, 954, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.83 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.02 (d, J=4.81 Hz, 3H, CH_3), 1.29–1.47 (m, 2H, CH_2), 1.50–1.61 (m, 1H, CH), 1.68 (d, J=11.70 Hz, 2H, CH_2), 2.27 (t, J=6.78 Hz, 2H, CH_2), 2.67–2.70 (m, 4H, CH_2), 3.08 (t, J=6.84 Hz, 4H, CH_2), 3.23 (s, 2H, CH_2), 3.31 (br s, 2H, CH_2), 3.37 (d, J=11.22 Hz, 2H, CH_2), 3.63 (d, J=11.49 Hz, 2H, CH_2), 7.22–7.30 (m, 3H, ArH), 7.52–7.55 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 20.90, 21.01, 21.56, 24.12, 25.77, 28.24, 28.89, 29.41, 33.95, 39.36, 50.29, 69.19, 96.35, 117.09, 124.60, 125.81, 126.06, 126.56, 127.12, 132.39, 134.75, 137.78, 139.25, 139.44, 150.41; MS m/z 533 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{30}H_{36}N_2O_2$ 456.27768 (M^+) found for m/z 456.27770.

*4.4.7. 5-Cyano-6-(4-benzylpiperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-(2,2-dimethyltrimethylene)ketal (**6g**).* White powder; yield: 91%; mp: 182–184 °C; IR (KBr): 2949, 2872, 2371, 2215, 1596, 1429, 1283, 1209, 1116, 1068, 1029, 936, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.83 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.42–1.45 (m, 1H, CH), 1.56 (s, 2H, CH_2), 1.70 (d, J=10.53 Hz, 3H, CH and CH_2), 2.26 (t, J=6.76 Hz, 2H, CH_2), 2.61 (d, J=6.66 Hz, 2H, CH_2), 2.67 (br s, 4H, CH_2), 3.07 (t, J=6.84 Hz, 4H, CH_2), 3.22 (br s, 4H, CH_2), 3.36 (d, J=11.46 Hz, 2H, CH_2), 3.62 (d, J=11.43 Hz, 2H, CH_2), 7.16–7.20 (m, 3H, ArH), 7.24–7.31 (m, 5H, ArH), 7.53–7.55 (m, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$): 22.21, 22.77, 25.20, 26.98, 29.42, 30.09, 33.11, 37.84, 40.67, 43.33, 51.45, 70.34, 97.51, 118.23, 125.76, 125.84, 127.29, 127.81, 128.13, 128.33, 127.05, 133.53, 135.97, 138.99, 140.49, 140.64, 151.43; MS m/z 533 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{36}H_{40}N_2O_2$ 532.30898 (M^+) found for m/z 532.30909.

4.4.8. 5-Cyano-6-(tetrahydroisoquinolin-2-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-2-one-(2,2-dimethyltrimethylene)ketal

(***6h***). White powder; yield: 99%; mp: 170–172 °C; IR (KBr): 2820, 2734, 2210, 1595, 1437, 1382, 1352 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.84 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.55 (s, 2H, CH_2), 2.30 (br s, 2H, CH_2), 2.62 (t, J=6.30 Hz, 2H, CH_2), 2.74 (br s, 2H, CH_2), 2.95–3.01 (m, 2H, CH_2), 3.12 (t, J=6.90 Hz, 2H, CH_2), 3.27 (s, 2H, CH_2), 3.39 (d, J=11.52 Hz, 2H, CH_2), 3.64 (d, J=11.52 Hz, 2H, CH_2), 4.35 (s, 2H, CH_2), 7.0–7.03 (m, 1H, ArH), 7.13–7.18 (m, 3H, ArH), 7.24–7.29 (m, 3H, ArH), 7.56–7.60 (m, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.15, 22.71, 24.82, 25.14, 26.94, 29.24, 30.03, 30.46, 40.64, 48.66, 52.70, 70.32, 97.42, 107.56, 117.89, 125.50, 125.80, 125.97, 127.32, 127.88, 127.93, 128.29, 129.08, 133.34, 134.43, 134.68, 136.50, 139.28, 140.48, 140.76, 150.13; MS m/z 491 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{33}H_{34}N_2O_2$ 490.26203 (M^+) found for m/z 490.26189.

4.5. General Procedure for the synthesis of 2-oxo-6-*sec*-amino-1,2,3,4,7,8-hexahydrobenzo[*c*]phenanthrene-3-carbonitriles (7)

These were obtain through deprotection of ketal by stirring in 80% formic acid for 1 h at room temperature. After completion of the reaction, excess of formic acid was removed and reaction mixture was poured onto ice cold water. The precipitate obtained was filtered washed with water and purified by crystallization with 1:1 chloroform and methanol.

*4.5.1. 2-Oxo-6-(piperidin-1-yl)-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-5-carbonitrile (**7a**).* White powder; yield: 97%; mp: 198–200 °C; IR (KBr): 2926, 2821, 2372, 2213, 1716, 1595, 1435, 1383, 1351, 1282, 1232, 1199, 1025 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.66–1.73 (m, 6H, CH_2), 2.53 (t, J=6.60, 2H, CH_2), 2.68–2.70 (m, 2H, CH_2), 2.76–2.78 (m, 2H, CH_2), 3.24 (br s, 4H, CH_2), 3.36 (t, J=6.60 Hz, 2H, CH_2), 3.88 (s, 2H, CH_2), 7.26–7.29 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.89, 23.85, 25.54, 25.76, 28.08, 35.24, 43.27, 51.11, 105.18, 116.83, 124.31, 124.82, 126.28, 127.06, 127.28, 131.52, 135.22, 138.95, 139.52, 150.66, 208.44; MS m/z 357 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{24}H_{24}N_2O$ 356.18886 (M^+) found for m/z 356.18897.

*4.5.2. 6-(4-Benzylpiperidin-1-yl)-2-oxo-1,2,3,4,7,8-hexahydrobenzo[c]phenanthrene-5-carbonitrile (**7b**).* White powder; Yield: 97%; mp: 140–142 °C; IR (KBr): 2927, 2826, 2365, 2214, 1718, 1594, 1436, 1382, 1350, 1231, 1116, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.54–1.57 (m, 2H, CH_2), 1.73 (d, J=10.23 Hz, 3H, CH and CH_2), 2.52 (t, J=6.67 Hz, 2H, CH_2), 2.63 (d, J=6.66 Hz, 2H, CH_2), 2.69 (d, J=5.10 Hz, 2H, CH_2), 2.74 (br s, 2H, CH_2), 3.14–3.22 (m, 2H, CH_2), 3.35 (t, J=6.63 Hz, 4H, CH_2), 3.88 (s, 2H, CH_2), 7.17–7.22 (m, 3H, ArH), 7.27–7.32 (m, 6H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.97, 29.28, 33.09, 36.43, 37.81, 43.31, 44.50, 51.59, 125.70, 125.83, 126.06, 127.52, 128.52, 128.18, 128.31, 128.51, 132.70, 140.03, 140.43, 140.78, 151.51, 209.59; MS m/z 447 (M^++1); HRMS: (EI, 70 eV) calcd for $C_{31}H_{30}N_2O$ 446.23581 (M^+) found for m/z 446.23564.

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