JOC*Note*

An Efficient De Novo Synthesis of Partially Reduced Phenanthrenes through C−C Insertion†

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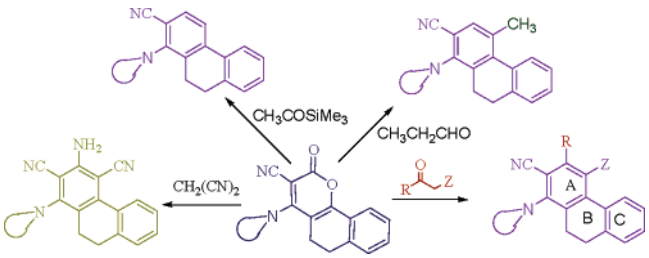

An efficient and novel approach to the synthesis of highly congested 3-alkyl-, 4-alkyl-, 3-aryl-, 3,4-dialkyl-, 4-alkyl-3-aryl-, and 3,4-diaryl-9,10-dihydro-1-*sec*-aminophenanthrene-2-carbonitriles has been delineated through the base-catalyzed ring transformation of 5,6-dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitrile by carbanion derived in situ from various ketones in moderate to good yields. 9,10-Dihydrophenanthrenes with and without substituent in the bay region are efficiently and regioselectively synthesized by using propanal and acetyltrimethylsilane as a source of carbanion. Even the synthesis of bisphenanthrenes has been achieved by the ring transformation of 5,6-dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitrile by 2-acetylphenanthrene in moderate yield. Highly substituted 3-amino-1-*sec*-amino-5,6-dihydrophenanthrene-2,4-dicarbonitriles have also been prepared from the reaction of 2-oxobenzo[*h*]-chromene and malononitrile.

Phenanthrenes represent an important class of compounds abundantly distributed in nature[1] as a substructure that are useful precursors for natural product synthesis[2] and exhibit a broad spectrum of biological activities such as antimalarial,[3] anticancer,[4] antimycotic,[5,6] anti-HIV,[7] and emetic properties.[8] 9,10-Dihydrophenanthrenes with a pendant carboxyl group at position 2 are reported[9] as an inhibitor of 5α-reductase and useful in the treatment of pharmacological disorders associated with elevated levels of dihydrotestosterone. Numerous methods are being reported for the synthesis of phenanthrenes[2] and dihydrophenanthrenes[10−16] through ring annulation[17] and intermolecular[18] and intramolecular[19] cyclization. A majority of the procedures have certain limitations of accessibility of the precursors, require multiple steps, have harsh reaction conditions, are incompatible with the presence of a functional group, have relatively low overall yield, and lack well-defined regiocontrol elements. 2,2′-Disubstituted biphenyls have been used as precursors for the preparation of phenanthrene by intramolecular condensation,[18] cycloisomerization,[20] metal-catalyzed rearrangement of alkene−alkynes,[21] and photocyclization[22] depending upon the functionality present on the biphenyl moiety. Palladium-catalyzed cyclization of arynes with alkynes is also an alternative route[21] for the synthesis of phenanthrene. Recently, 9,10-disubstituted phenanthrenes have been prepared[23] from palladium-catalyzed reaction of o-substituted aryl iodides and diphenyl or alkylphenylacetylenes. These are also prepared through the ring transformation of methyl 6-aryl-4-methylsulfanyl-2*H*-pyran-2-one-3-carboxylates by 1-tetralone in 59−67% yields.[24] The diverse pharmacological activities and limitations of convenient and efficient procedures prompted us to develop a concise, straightforward, and economical route to the synthesis of this class of compounds without use of any catalyst.

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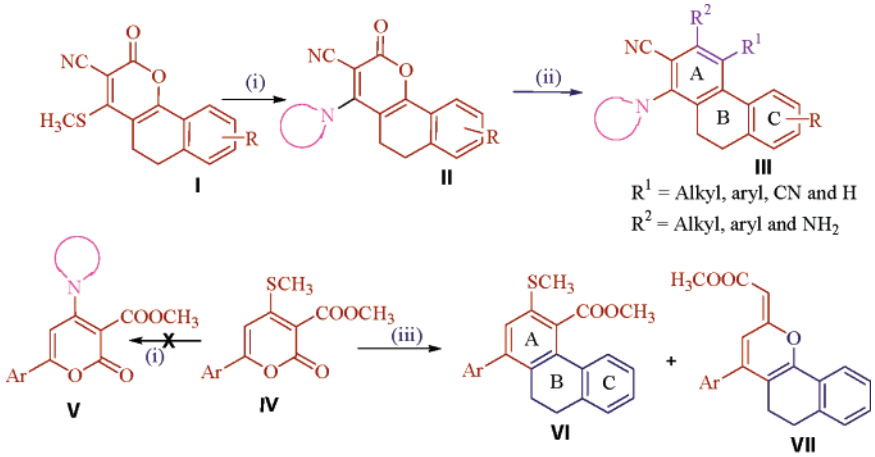
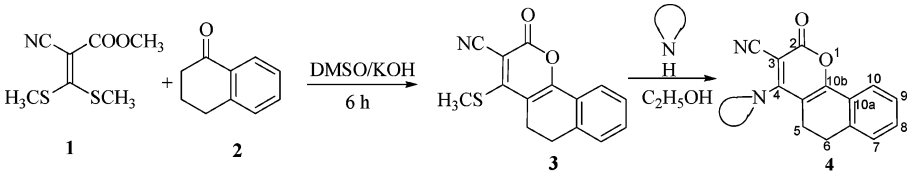
SCHEME 1. Regioselectivity of Benzo[*h*]chromene (II) and Synthetic Limitations of 2*H*-Pyran-2-one-3-carboxylate (IV) for the Synthesis of Congested Phenanthrenes



SCHEME 2. Synthesis and Yields of 5,6-Dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitriles[26] (4)



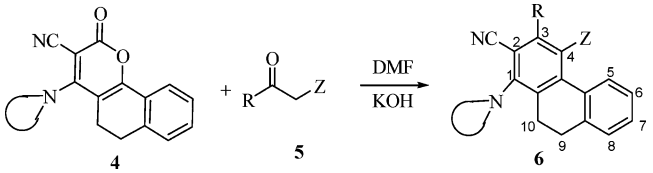
4		Yield (%)
a	piperidin-1-yl	97
b	4-Methylpiperidin-1-yl	94
c	4-Benzylpiperidin-1-yl	87
d	Morpholin-4-yl	76

In search of a novel and efficient synthetic route for the construction of highly congested 9,10-dihydrophenanthrenes, 5,6-dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitrile (**II**) has been considered as a most appropriate precursor to overcome the synthetic limitations of methyl 6-aryl-4-methylsulfanyl-2*H*-pyran-2-one-3-carboxylate (**IV**), which, used earlier as synthon,[24] lacks regioselectivity as it gives a mixture of two products **VI** and **VII** on reaction with 1-tetralone. In addition, it has no option to introduce a group other than ester in the bay region as well as amino functionality at the C-1 and C-3 positions of the phenanthrene ring (Scheme 1).

The synthetic potential of 5,6-dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitriles (**4**) is enormous and obtained by the base-catalyzed condensation−cyclization of 1-tetralone (**2**) and methyl 2-cyano-3,3-dimethylthioacrylate[25] (**1**) followed by amination with *sec*-amine in refluxing ethanol in high yields[26] (Scheme 2). There is no limitation in using the secondary amine for the amination reaction. We have used piperidine, substituted piperidines, and morpholine as secondary amines in the present study. These secondary amines did not influence the course of reaction (Scheme 2).

As evident from the topography of the 5,6-dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitrile (**4**), the positions C-2, C-4, and C-10b are electrophilic in nature. Among these three centers, the latter is highly electrophilic and prone to nucleophilic attack because of extended conjugation and the presence of an electron-withdrawing CN substituent at the C-3 position of the chromene ring.

SCHEME 3. Synthesis of 9,10-Dihydro-3-alkyl-, 3,4-Dialkyl-, 3-Aryl-4-alkyl-, 3-Aryl-, and 3,4-Diarylphenanthrenes (6)



Various ketones such as acetone, ethyl methyl ketone, aryl methyl ketone, propiophenone, deoxyanisoin, 3-acetylphenanthrene, propanal, acetyltrimethylsilane, and malononitrile have been used as source of carbanions.

Thus, an equimolar mixture of 5,6-dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitrile (**4**) and ketone in the presence of powdered KOH in dry DMF was stirred for 45−90 min and thereafter poured onto crushed ice with vigorous stirring and neutralized with 10% HCl. The precipitate obtained was filtered, dried, and finally purified on silica gel or a neutral alumina column (Scheme 3). All the alkyl-substituted phenanthrenes (**6a**−**d**) prepared by using dialkyl ketones as a source of carbanion are listed in Table 1.

The scope of the reaction was further explored using different kind of ketones such as propiophenone and deoxyanisoin as a source of carbanions for the ring transformation reaction of chromene **4**. Thus, a reaction of **4** with propiophenone and

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TABLE 1. Yields of Various 9,10-Dihydro-3-arylphenanthrenes (6)

6	R	—N◯	Z	yields (%)
a	CH_3	piperidin-1-yl	H	86
b	CH_3	4-methylpiperidin-1-yl	H	78
c	CH_3	piperidin-1-yl	CH_3	81
d	CH_3	4-methylpiperidin-1-yl	CH_3	81
e	C_6H_5	piperidin-1-yl	CH_3	88
f	C_6H_5	4-methylpiperidin-1-yl	CH_3	79
g	4-CH_3O-C_6H_4	piperidin-1-yl	4-CH_3O-C_6H_4	91
h	4-CH_3O-C_6H_4	4-methylpiperidin-1-yl	4-CH_3O-C_6H_4	89
i	C_6H_5	piperidin-1-yl	H	87
j	4-Cl-C_6H_4	piperidin-1-yl	H	91
k	4-Br-C_6H_4	piperidin-1-yl	H	89
l	4-CH_3-C_6H_4	piperidin-1-yl	H	91
m	4-CH_3O-C_6H_4	piperidin-1-yl	H	81
n	3,4-$(Cl)_2$-C_6H_3	piperidin-1-yl	H	88
o	2-thienyl	piperidin-1-yl	H	93
p	1-pyrenyl	piperidin-1-yl	H	76
q	C_6H_5	morpholin-4-yl	H	84
r	C_6H_5	4-methylpiperidin-1-yl	H	73
s	phenanthren-2-yl	4-methylpiperidin-1-yl	H	51

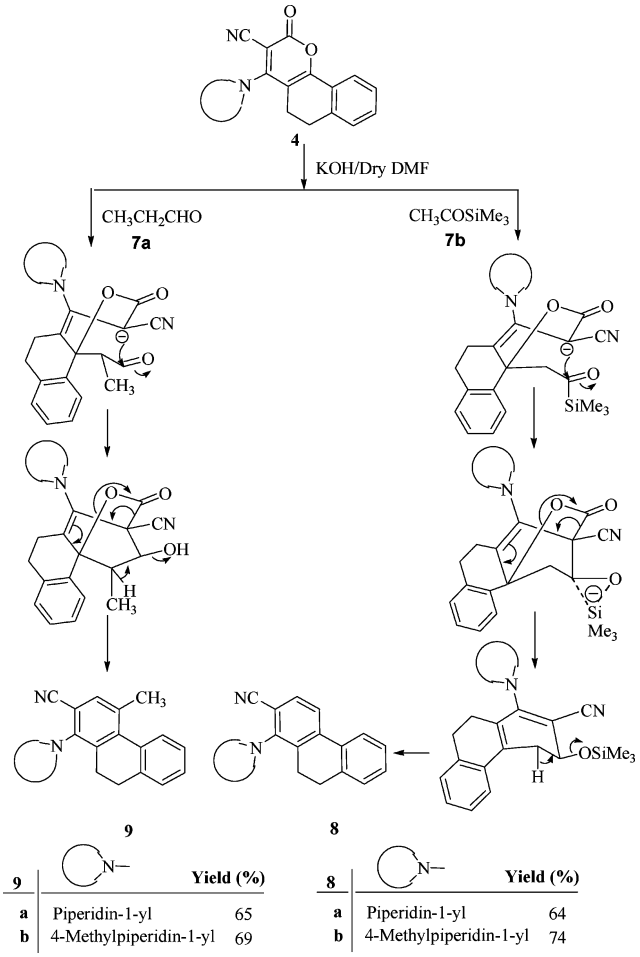
deoxyanisoin separately under analogous reaction conditions produced 3-aryl-4-methyl-1-*sec*-amino-5,6-dihydrophenanthrenes (**6e**,**f**) and 3,4-di(4-anisyl)-1-*sec*-amino-5,6-dihydrophenanthrenes (**6g**,**h**) in very good yields. In these reactions, carbanion generated at either methyl or methylene carbon attacks at C-10b of the chromene **4** with ring closure and concomitant elimination of carbon dioxide and water.

The reaction was further generalized for regioselective introduction of an aryl/heteroaryl group at position 3 of the 9,-10-dihydrophenanthrenes (**6i**−**r**) and bisphenanthrene (**6s**) with 2,3′ linkage by stirring an equimolar mixture of **4**, aryl methyl ketone, or 2-acetylphenanthrene and powdered KOH in DMF for 2 to 3 h. Usual workup and column chromatographic purification produced 3-aryl/heteroarylphenanthrenes (**6i**−**s**). However, use of 1-tetralone as a nucleophile under analogous conditions produced (7,8-dihydro-5-oxabenzo[*c*]chrysene-6-ylidene)acetonitrile[27] following a different course of reaction.

The formation of **6i**−**s** is initiated through attack of carbanion at C-10b of **4** with ring closure followed by elimination of carbon dioxide and water.

The synthetic potential of benzo[*h*]chromene was explored further for the synthesis with or without alkyl substituent in the bay region following a different strategy. Thus, for the synthesis of phenanthrene without any substituent in the bay region, aqueous acetaldehyde was used as a source of carbanion, but the strategy failed to produce the target compound under analogous conditions possibly because of the water content of acetaldehyde. To overcome this difficulty, acetyltrimethylsilane was used as an acetaldehyde equivalent for the ring transformation. This strategy worked very well, and ultimately we succeeded in isolating 1-*sec*-aminophenanthrene-2-carbonitrile in good yield. Thus, a mixture of **4**, acetyltrimethylsilane (**7b**), and powdered KOH in DMF was stirred for 2 to 2.5 h under nitrogen atmosphere in the dark to avoid a side reaction and decomposition. The progress of the reaction was monitored by TLC, and thereafter the mixture was poured onto crushed ice with vigorous stirring and neutralized with 10% HCl. The precipitate obtained was filtered, washed with water several times, and dried. The crude product was purified by column

SCHEME 4. Mechanism Involved in the Synthesis of 1-*sec*-Amino-9,10-dihydrophenanthrene-2-carbonitriles (8) and 1-*sec*-Amino-9,10-dihydrophenanthrene-4-methyl-2-carbonitriles (9)



9		Yield (%)
a	Piperidin-1-yl	65
b	4-Methylpiperidin-1-yl	69

8		Yield (%)
a	Piperidin-1-yl	64
b	4-Methylpiperidin-1-yl	74

chromatography. This reaction was also carried out in aerobic and dark conditions, but the yield of the final product was reduced to half possibly because of decomposition of acetyltrimethylsilane in the presence of light and air. The product isolated was characterized as 9,10-dihydro-1-*sec*-aminophenanthrene-2-carbonitriles (**8**) in place of contemplated product 9,-10-dihydro-1-*sec*-amino-3-trimethylsilylphenanthrene-2-carbonitriles, as the reaction followed a course different from the normal one as shown in Scheme 4. The reaction is possibly initiated by the attack of carbanion generated in situ by base, and it attacks the highly electrophilic center at C-10b with Michael addition followed by intramolecular cyclization involving C-3 of the chromene ring and carbonyl functionality of acetyltrimethylsilane to form an intermediate. The intermediate after elimination of carbon dioxide forms a cyclic transition state, which undergoes Brook rearrangement[28] to form an oxygen silicon bond with elimination of trimethylsilinol, which produces phenanthrene derivatives.

Further synthesis of 4-alkyl-substituted phenanthrenes was directly synthesized through base-catalyzed ring transformation of **4** with propanal **7a** under analogous reaction conditions. The mechanism of these reactions is depicted in Scheme 4.

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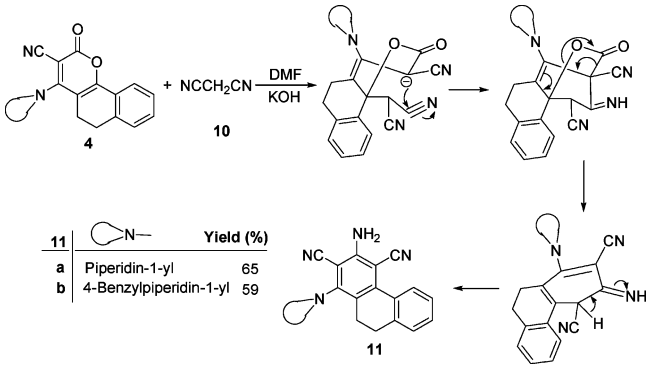
SCHEME 5. Mechanism Involved in the Synthesis of 3-Amino-1-*sec*-amino-9,10-dihydrophenanthrene-2, 4-dicarbonitriles (11)



The synthetic potential of 2-oxo-5,6-dihydrobenzo[*h*]chromene (**4**) was explored further using malononitrile as a source of carbanion for the synthesis of highly congested phenanthrenes (**11**) through ring transformation reactions. Thus, under analogous conditions, stirring of an equimolar mixture of **4** and malononitrile (**10**) in the presence of powdered KOH in DMF for 2 to 3 h and followed by usual workup and column chromatographic purification produced highly congested 3-amino-1-*sec*-amino-9,10-dihydrophenanthrene-2,4-dicarbonitriles (**11**) in moderate yields.

This reaction is also initiated by the attack of carbanion, formed in situ from activated methylene of malononitrile, at C-10b with ring closure involving a cyano group and C-3 of benzo[*h*]chromene ring followed by elimination of carbon dioxide to yield 3-amino-1-*sec*-amino-9,10-dihydrophenanthrene-2,4-dicarbonitriles (**9**) in moderate yields. The plausible mechanism of the reaction is shown in Scheme 5.

In summary, this is the first report of the straightforward synthesis of congested 9,10-dihydrophenanthrenes from 5,6-dihydro-2-oxo-4-*sec*-amino-2*H*-benzo[*h*]chromene-3-carbonitriles through base-catalyzed ring transformation by carbanion generated from various ketones, acetyltrimethylsilane, malononitrile, and aldehyde in the shortest possible step in moderate to high yields. This procedure provides an option to introduce various substituents in the A and C rings of the phenanthrene.

Experimental Section

Typical Procedure for the Synthesis of 3-Alkyl-, 3,4-Dialkyl-, 3-Aryl-, 3-Aryl-4-alkyl-, 3,4-Diaryl-, 4-Alkyl-1-*sec*-amino-9,10-dihydrophenanthrene-2-carbonitriles (6a−s and 9a,b). A mixture of 2-oxo-4-*sec*-amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile (0.5 mmol) and acetone/ethyl methyl ketone/propiophenone/deoxyanisoin/arylmethylketone/propanal (0.6 mmol) in dry DMF (4 mL) was stirred in the presence KOH (0.8 mmol) for 1−3 h. After consumption of starting material, excess of DMF was removed under reduced pressure and the reaction mixture was poured onto crushed ice with vigorous stirring and acidified with 10% HCl to neutral pH. The product separated was filtered while in situation of oily compound it was extracted with chloroform (3 × 20 mL) and dried over sodium sulfate, and the solvent was removed under vacuum. The crude product obtained was purified by silica gel/neutral alumina column chromatography.

3-Methyl-1-(piperidin-1-yl)-9,10-dihydrophenanthrene-2-carbonitrile (6a): Viscous oil; yield: 86%; IR (neat): 2928, 2851, 2365, 2216, 1596, 1382, 1352, 1029 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.70−1.72 (m, 6H), 2.50 (s, 3H) 2.72−2.88 (m, 4H), 3.21 (bs, 4H), 7.23−7.34 (m, 3H), 7.39 (s, 1H), 7.69 (dd, $J = 6.54$ and 4.59 Hz, 1H); MS *m*/*z* 303 ($M^+ + 1$); HRMS (EI, 70 eV) calcd for $C_{21}H_{22}N_2$, 302.17830 (M^+); found for *m*/*z*, 302.17856.

3-Phenyl-1-(piperidin-1-yl)-9,10-dihydrophenanthrene-2-carbonitrile (6i): White powder; yield: 87%; mp: 128−130 °C; IR (KBr): 2938, 2815, 2369, 2341, 2219, 1592, 1351, 1211, 1157, 1116, 1029, 948, 889, 834, 763, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.67−1.75 (m, 6H), 2.82−2.87 (m, 2H), 2.92−2.97 (m, 2H), 3.27 (bs, 4H), 7.27−7.32 (m, 3H), 7.40−7.51 (m, 3H), 7.54−7.58 (m, 3H), 7.71−7.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1, 22.9, 25.6 (2C), 27.3, 50.8 (2C), 105.7, 117.5, 120.1, 123.5, 125.9, 126.7, 127.1, 127.2 (2C), 127.4, 127.7 (2C), 132.6, 133.2, 136.7, 137.7, 138.6, 144.3, 153.5; MS *m*/*z* 365 ($M^+ + 1$); HRMS (EI, 70 eV) calcd for $C_{26}H_{24}N_2$, 364.19395 (M^+); found for *m*/*z*, 364.19394.

Typical Procedure for the Synthesis of 9,10-Dihydro-1-*sec*-aminophenanthrene-2-carbonitriles (8a,b). 8a,**b** were obtained by stirring a mixture of **4** (0.5 mmol), acetyltrimethylsilane **7b** (0.6 mmol), and KOH (0.8mmol) in dry DMF under nitrogen atmosphere in dark. The reaction was monitored by TLC. After completion of reaction, excess DMF was removed under reduced pressure. Thereafter, the reaction mixture was poured onto crushed ice with vigorous stirring followed by neutralization with 10% aqueous HCl. The precipitate obtained was filtered, washed with water, dried, and purified by neutral alumina column chromatography using 40% chloroform in hexane as eluent.

1-Piperidin-1-yl-9,10-dihydrophenanthrene-2-carbonitrile (8a): Viscous oil; yield: 64%; IR (neat): 2208 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.70−1.75 (m, 6H), 2.78−2.83 (m, 2H), 2.87−2.92 (m, 2H), 3.22 (bs, 4H), 7.25−7.37 (m, 3H), 7.47 (d, $J = 8.37$ Hz, 1H), 7.50 (d, $J = 8.37$ Hz, 1H), 7.67−7.70 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1, 22.9, 25.5, 27.2, 51.0, 105.3, 118.7, 123.4, 125.8, 126.7, 127.3, 131.4, 132.6, 136.6; MS *m*/*z* 291 ($M^+ + 1$); HRMS (EI, 70 eV) calcd for $C_{20}H_{20}N_2$, 288.16265 (M^+); found for *m*/*z*, 288.16244.

3-Amino-1-(piperidin-1-yl)-9,10-dihydrophenanthrene-2,4-dicarbonitriles (11). These were prepared by stirring an equimolar mixture of **4**, malononitrile **10**, and KOH in DMF. The usual workup and neutral alumina column chromatographic purification using 3% ethyl acetate in hexane as eluent gave **11**.

3-Amino-1-piperidin-1-yl-9,10-dihydrophenanthrene-2,4-dicarbonitrile (11a): Light yellow powder; yield: 65%; mp: 182−184 °C; IR (KBr): 3419, 2862, 2213, 1601, 1555, 1498, 1401, 1330, 1007, 951, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.69−1.73 (m, 6H), 2.58−2.63 (m, 2H), 2.68−2.73 (m, 2H), 3.29 (t, $J = 4.80$ Hz, 4H), 5.13 (bs, 2H, NH_2), 7.28−7.32 (m, 1H), 7.34−7.39 (m, 2H), 8.06−8.09 (m, 1H); MS *m*/*z* 329 ($M^+ + 1$); HRMS (EI, 70 eV) calcd for $C_{21}H_{20}N_4$, 328.16880 (M^+); found for *m*/*z*, 328.16891.

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Supporting Information Available: Experimental details and chemical characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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