Synthesis of some 3-(1-aryl-9,10-dihydro-4-azaphenanthren-3-yl)coumarins

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Abstract

Various 3-(1-aryl-9,10-dihydro-4-azaphenanthren-9-yl)coumarins **3a-o** were synthesized by reacting various 3-coumarinoyl methyl pyridinium salts **1a-c** with appropriate 2-benzylidene-1-tetralone **2a-e** in the presence of ammonium acetate and acetic acid under the Kröhnke's reaction condition. The structures of all the synthesized compounds were established on the basis of elemental and spectral analysis.

Keywords: Coumarins, 3-azaphenanthrenyl substituted coumarins, Kröhnke's pyridine synthesis

Introduction

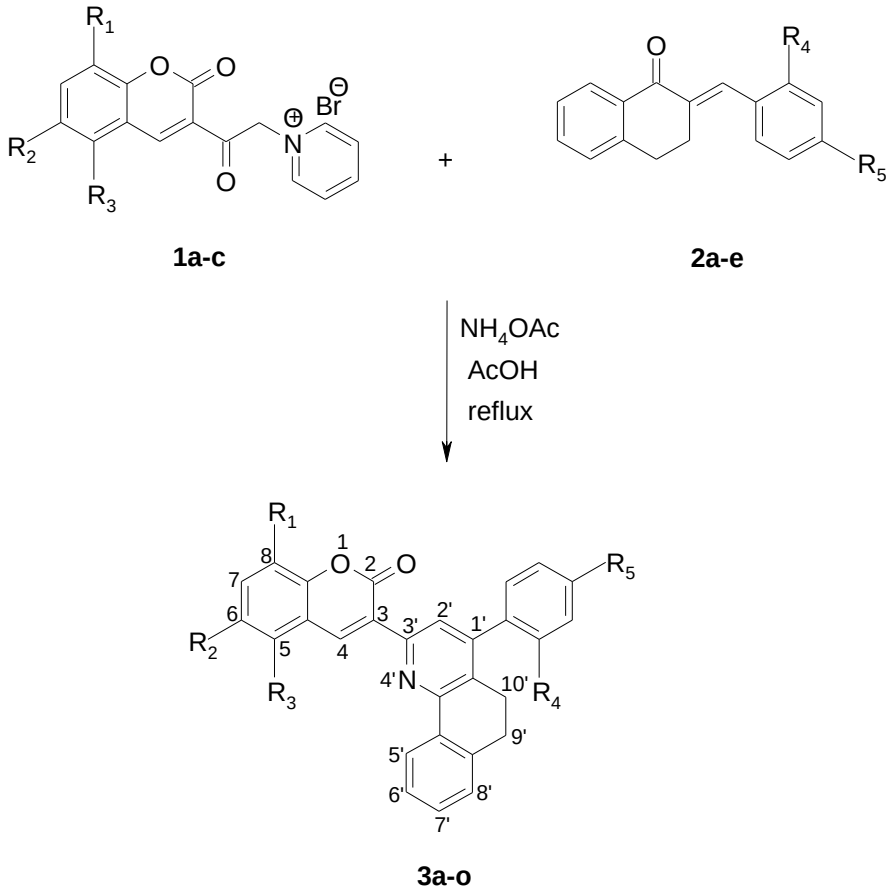
Coumarins (2*H*-1-benzopyran-2-ones) and its derivatives are important heterocyclic compounds that are widely distributed in nature. Many compounds containing the coumarin skeleton have shown antihelmintic, hypnotic, insecticidal, anticoagulant and antifungal properties.[1] Coumarins represent a class of naturally and synthetically obtained compounds that posses a wide variety of biological activities[2-3] often depending on the substituent they bear on their benzopyran skeleton. The incorporation of heterocyclic ring on to the coumarin nucleus can bring about an extensive modification in the biological activities of the parent compound. Among the heterocyclic substituted coumarins, pyridyl coumarins have a special importance due to their diverse physiological actions. A number of coumarin derivatives having pyridine substituted mainly at 3- or 4- position of the coumarin possess CNS depressant activity.[4] Some of the pyridyl substituted coumarins were reported to have fish toxicity and bactericidal activity.[5] Considering the importance of pyridyl substituted coumarins, a variety of pyridyl substituted coumarins were synthesized from our laboratory.[6]

Phenanthrene containing one nitrogen atom is known as azaphenanthrene. During our literature search for azaphenanthrene, we came across some azaphenanthrene derivatives having interesting biological activities. 4-Azaphenanthrene derivatives have been reported to possess wound healing, antibacterial, in vitro antioxidant activity.[7a] The 1,3-amino substituted 4-

azaphenanthrene derivative possesses cytotoxic activity,[7b] where as 1-chloro-2-azaphenanthrene was found to be a novel activator of cystic fibrosis transmembrane conductance regulator.[7c] A 3-(4-methylsufonylphenyl)-4-azaphenanthren-1-carboxylic acid acts as cyclooxygenase-2 inhibitors.[7d] Thus considering the importance of above azaphenanthrene derivatives and in continuation of our interest in synthesizing newer modified pyridyl substituted coumarin derivatives it was thought worthwhile to incorporate azaphenanthrene nucleus into coumarin moiety as a substituent group and therefore in the present work we report the synthesis of various 3-(1-aryl-9,10-dihydro-4-azaphenanthren-3-yl)coumarins **3a-o** (Scheme 1).

Results and Discussion

The compounds **3a-o** have been synthesized in good yield by reacting 3-coumarinoyl methyl pyridinium bromides **1a-c** with appropriate 2-arylidene tetralone **2a-e** under Kröhnke's reaction condition. The formation of pyridine nucleus in compounds **3a-o** involves Kröhnke's reaction mechanism.[8-9]



Scheme 1. Synthetic scheme for 3-(1-aryl-9,10-dihydro-4-azaphenanthren-3-yl)coumarins **3a-o**.

	R_1	R_2	R_3	R_4	R_5		R_1	R_2	R_3	R_4	R_5
3a	H	H	H	H	H	**3i**	OCH_3	H	H	OCH_3	OCH_3
3b	H	H	H	H	CH_3	**3j**	OCH_3	H	H	H	Cl
3c	H	H	H	H	OCH_3	**3k**	H	Benzo		H	H
3d	H	H	H	OCH_3	OCH_3	**3l**	H	Benzo		H	CH_3
3e	H	H	H	H	Cl	**3m**	H	Benzo		H	OCH_3
3f	OCH_3	H	H	H	H	**3n**	H	Benzo		OCH_3	OCH_3
3g	OCH_3	H	H	H	CH_3	**3o**	H	Benzo		H	Cl
3h	OCH_3	H	H	H	OCH_3						

The structures of the synthesized compounds **3a-o** were established on the basis of IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data.

The IR spectrum of **3a** showed a very strong and sharp band at 1716 cm^{-1} which is due to carbonyl stretching of δ-lactone ring present in coumarin nucleus. The strong bands observed at 1607 and 1454 cm^{-1} are due to aromatic C=C and C=N stretching vibrations respectively. The sharp and intense bands observed at 698 and 766 cm^{-1} are due to C-H bending vibrations for mono substituted phenyl ring. The medium bands observed at 2927 and 3057 cm^{-1} are attributed to aliphatic and aromatic C-H stretching vibrations respectively. Its ^{1}H NMR spectrum showed triplet (J = 7.2 Hz) centered at 2.88 δ and poorly resolved triplet centered at 2.99 δ each integrating for two protons. This is due to two protons attached at C_{10}' and two protons attached at C_9' respectively. Total fifteen protons were observed in the region 7.26–9.03 δ. The most downfield signal observed at 9.03 δ as a singlet is due to C_4-H. The singlet appeared at 8.36 δ is due to C_2'-H. The C_5'-H appeared as a poorly resolved doublet of doublet centered at 8.54 δ. The remaining twelve aromatic protons appeared as a multiplet between 7.26–7.75 δ. The C_2' proton of pyridine ring appears in the downfield region due to the peri effect of carbonyl group of δ-lactone. The ^{13}C NMR spectrum of compound **3a** showed twenty five non equivalent carbon signals. However though the compound is having twenty six types of non equivalent carbon atoms, the lack of one signal may be due to overlapping of two carbon signals, which may have identical chemical shifts. The signals observed at 25.5 and 28.1 δ are due to C_{10}' and C_9' respectively. The most downfield signal appeared at 160.0 δ can be assigned to the carbonyl carbon of the δ-lactone ring of coumarin. The signal appeared at 142.0 δ can be attributed to C_4 carbon. The aromatic carbons appeared at 116.4, 119.8, 123.6, 124.5, 125.5, 127.1, 127.7, 128.1, 128.4, 128.8, 129.0, 129.3, 129.6, 131.9, 134.9, 138.4, 139.0, 148.4, 149.1, 152.5 and 153.9 δ. Among these aromatic signals, the most downfield signal at 153.9 δ can be assigned to C_8a carbon as it is attached to the electronegative oxygen atom of δ-lactone ring. The two other downfield signals appearing at 149.1 and 152.5 δ can be assigned to C_3' and C_4'a carbons respectively as they are directly attached to the electronegative nitrogen atom. The DEPT-135 spectrum of compound **3a** showed inverted signals at 25.5 and 28.1 δ which confirms C_{10}' and C_9' methylene carbons respectively. The spectrum showed total thirteen upward carbon signals at

116.4, 123.6, 124.5, 125.5, 127.1, 127.7, 128.1, 128.4, 128.8, 129.0, 129.3, 131.9 and 142.0 δ. This supports the presence of thirteen tertiary carbons in the compound. The mass spectrum of **3a** showed molecular ion peak at m/z 401 along with other fragments peaks. It exactly matches with the molecular weight of compound **3a** and thus confirming the structure of **3a**. Similarly all other compounds gave satisfactory spectral analysis.

Experimental Section

General. All the melting points reported are uncorrected. All the IR spectra (KBr disc) were recorded on Shimadzu FT-IR 8400-S spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. The chemical shift (δ) is reported in ppm using chloroform-d as a solvent and calibrated standard solvent signal. Mass spectrum was recorded on Shimadzu QP 2010 spectrometer. 3-Coumarinoyl methyl pyridinium bromides **1a-c** and 2-benzylidene-1-tetralones **2a-e** were prepared according literature procedures.[10-12]

General procedure for the synthesis of 3-(1-aryl-9,10-dihydro-4-azaphenanthren-3-yl) coumarins (3a-o)

In a 100 mL round bottom flask equipped with a dropping funnel, condenser, guard tube and magnetic needle an appropriate 3-coumarinoyl methyl pyridinium salt **1a-c** (0.003 mol) in glacial acetic acid (15 mL) was taken. To this ammonium acetate (0.03 mol) was added with stirring at room temperature. Then a solution of an appropriate 2-arylidene-1-tetralone **2a-e** (0.003 mol) in glacial acetic acid (15 mL) was added with stirring at room temperature during 15 minutes. The reaction mixture was further stirred for 1 hour and then refluxed for 12 hours at 140˚C. It was then allowed to come to room temperature and was poured into ice-cold water (75 mL). A crude solid obtained was extracted with chloroform (3 x 30 mL). The organic layer was washed with 5% sodium bicarbonate solution (3 x 20 mL), water (2 x 20 mL) and dried over anhydrous sodium sulfate. The removal of chloroform under reduced pressure gave crude material which was subjected to column chromatography using silica gel and ethyl acetate-petroleum ether (60-80) (1:9) as an eluent to give products **3a-o**. The compounds were recrystallized from chloroform-hexane.

3-(1-Phenyl-9,10-dihydro-4-azaphenanthren-3-yl)coumarin (3a). Yield 0.62 g (52%); mp 194 ºC; white powder; IR(KBr): 698 (s), 766 (s), 1454 (s), 1607 (s), 1716 (vs), 2927 (m), 3057 (m) cm^{-1}; ^{1}H NMR($CDCl_3$): δ 2.88 (2H, t, protons at C_{10}', J = 7.2 Hz), 2.99 (2H, poorly resolved triplet, protons at C_9'), 7.26–7.75 (12H, m, Ar-H), 8.36 (1H, s, C_2'-H of pyridine ring), 8.54 (1H, poorly resolved dd, C_5'-H), 9.03 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.5 (C_{10}'), 28.1 (C_9'), 116.4 (CH), 119.8 (C), 123.6 (CH), 124.5 (CH), 125.5 (CH), 127.1 (CH), 127.7 (CH), 128.1 (CH), 128.4 (CH), 128.8 (CH), 129.0 (CH), 129.3 (CH), 129.6 (C), 131.9 (CH), 134.9 (C), 138.4 (C), 139.0 (C), 142.0 (C_4), 148.4 (C), 149.1 (C_3'), 152.5 (C_4'a), 153.9 (C_8a), 160.0 (CO of

carbonyl). Anal. Calcd. for $C_{28}H_{19}NO_2$: C, 83.77; H, 4.77; N, 3.49%. Found: C, 83.70; H, 4.87; N, 3.50%.

3-[1-(4-Methylphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3b). Yield 0.75 g (60%); mp 203 ºC; white powder; IR(KBr): 825 (s), 1492 (s), 1600 (s), 1723 (vs), 2955 (m), 3055 (m) cm^{-1}; ^1H NMR: δ 2.46 (3H, s, CH_3), 2.88–2.99 (4H, m, protons at C_9'and C_{10}'), 7.32–7.73 (11H, m, Ar-H), 8.35 (1H, s, C_2'-H of pyridine ring), 8.53 (1H, poorly resolved dd, C_5'-H), 9.01 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 21.3 (CH_3), 25.5 (C_{10}'), 28.1 (C_9'), 116.3 (CH), 119.8 (C), 123.7 (CH), 124.5 (CH), 125.5 (CH), 125.7 (C), 127.1 (CH), 127.7 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 129.2 (CH), 129.6 (C), 131.8 (CH), 135.0 (C), 136.0 (C), 137.9 (C), 138.4 (C), 141.9 (C_4), 148.4 (C), 149.1 (C_3'), 152.4 (C_4'a), 153.9 (C), 160.4 (CO of carbonyl). Anal. Calcd. for $C_{29}H_{21}NO_2$: C, 83.83; H, 5.09; N, 3.37%. Found: C, 83.76; H, 5.09; N, 3.34%.

3-[1-(4-Methoxyphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3c). Yield 0.75 g (58%); mp 181-182 ºC; white powder; IR(KBr): 830 (s), 1465 (s), 1610 (s), 1715 (vs), 2960 (m), 3040 (m) cm^{-1}; ^1H NMR: δ 2.89 (2H, poorly resolved triplet, protons at C_{10}'), 3.01 (2H, poorly resolved triplet, protons at C_9'), 3.90 (3H, s, OCH_3), 7.02–7.75 (11H, m, Ar-H), 8.34 (1H, s, C_2'-H of pyridine ring), 8.52 (1H, poorly resolved dd, C_5'-H), 9.01 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.6 (C_{10}'), 28.1 (C_9'), 55.4 (OCH_3), 113.8 (CH), 116.3 (CH), 119.8 (C), 123.7 (CH), 124.5 (CH), 125.5 (CH), 125.7 (C), 127.1 (CH), 127.6 (CH), 128.8 (CH), 129.2 (CH), 129.6 (C), 130.3 (CH), 131.2 (C), 131.8 (CH), 135.0 (C), 138.4 (C), 141.9 (C_4), 148.4 (C), 148.7 (C_3'), 152.5 (C_4'a), 153.9 (C), 159.5 (C), 160.4 (CO of carbonyl). Anal. Calcd. for $C_{29}H_{21}NO_3$: C, 80.72; H, 4.91; N, 3.25%. Found: C, 80.85; H, 4.90; N, 3.22%.

3-[1-(2,4-Dimethoxyphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3d). Yield 0.85 g (61%); mp 178 ºC; white powder; IR(KBr): 825 (s), 1480 (s), 1605 (s), 1720 (vs), 2960 (m), 3050 (m) cm^{-1}; ^1H NMR: δ 2.72–2.88 (4H, m, protons at C_9'and C_{10}'), 3.78 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 6.58–7.76 (10H, m, Ar-H), 8.29 (1H, s, C_2'-H of pyridine ring), 8.54 (1H, dd, C_5'-H, J = 7.6, 1.2 Hz), 9.02 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.4 (C_{10}'), 28.0 (C_9'), 55.4 (OCH_3), 55.5 (OCH_3), 98.6 (CH), 104.5 (CH), 116.3 (CH), 119.9 (C), 120.7 (C), 124.4 (CH), 124.5 (CH), 125.4 (CH), 125.9 (C), 127.0 (CH), 127.6 (CH), 128.8 (CH), 129.0 (CH), 131.3 (CH), 131.6 (C), 131.7 (CH), 135.2 (C), 138.6 (C), 141.8 (C_4), 146.1 (C), 148.2 (C_3'), 151.8 (C_4'a), 153.9 (C), 157.5 (C), 160.4 (C), 161.2 (CO of carbonyl). Anal. Calcd. for $C_{30}H_{23}NO_4$: C, 78.08; H, 5.02; N, 3.03%. Found: C, 78.17; H, 5.06; N, 3.05%.

3-[1-(4-Chlorophenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3e). Yield 0.63 g (48%); mp 222 ºC; light yellow powder; IR(KBr): 840 (s), 1485 (s), 1610 (s), 1725 (vs), 2940 (m), 3070 (m) cm^{-1}; ^1H NMR: δ 2.89–2.95 (4H, m, protons at C_9'and C_{10}'), 7.37–7.76 (11H, m, Ar-H), 8.33 (1H, s, C_2'-H of pyridine ring), 8.53 (1H, poorly resolved dd, C_5'-H), 9.03 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.9 (C_{10}'), 28.1 (C_9'), 116.4 (CH), 119.7 (C), 123.3 (CH), 124.6 (CH), 125.4 (C), 125.6 (CH), 127.2 (CH), 127.7 (CH), 128.7 (CH), 128.9 (CH), 129.4 (CH), 130.4 (CH), 132.0 (CH), 134.3 (C), 134.8 (C), 137.4 (C), 138.3 (C), 142.1 (C_4), 147.9 (C), 148.6 (C_3'), 152.4 (C_4'a), 152.7 (C), 153.9 (C), 160.4 (CO of carbonyl). Anal. Calcd. for $C_{28}H_{18}ClNO_2$: C, 77.15; H, 4.16; N, 3.21%. Found: C, 77.23; H, 4.12; N, 3.19%.

8-Methoxy-3-(1-phenyl-9,10-dihydro-4-azaphenanthren-3-yl)coumarin (3f). Yield 0.81 g (62%); mp 270-272 ºC; white powder; IR(KBr): 710 (s), 740 (s), 1480 (s), 1605 (s), 1725 (vs), 2940 (m), 3060 (m) cm^{-1}; ^1H NMR: δ 2.89 (2H, poorly resolved triplet, protons at C_{10}'), 2.98 (2H, poorly resolved triplet, protons at C_9'), 4.02 (3H, s, OCH_3), 7.12–7.50 (11H, m, Ar-H), 8.38 (1H, s, C_2'-H of pyridine ring), 8.54 (1H, poorly resolved dd, C_5'-H), 9.01 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.5 (C_{10}'), 28.1 (C_9'), 56.3 (OCH_3), 113.6 (CH), 120.3 (CH), 120.4 (C), 123.6 (CH), 124.3 (CH), 125.5 (CH), 125.8 (C), 127.1 (CH), 127.7 (CH), 128.1 (CH), 128.4 (CH), 129.0 (CH), 129.3 (CH), 129.6 (C), 134.9 (C), 138.4 (C), 138.9 (C), 142.1 (C_4), 143.5 (C), 146.9 (C), 148.4 (C), 149.1 (C_3'), 152.4 (C_4'a), 159.8 (CO of carbonyl). Anal. Calcd. for $C_{29}H_{21}NO_3$: C, 80.72; H, 4.91; N, 3.25%. Found: C, 80.68; H, 4.87; N, 3.23%.

8-Methoxy-3-[1-(4-methylphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3g). Yield 0.76 g (57%); mp 260-262 ºC; light yellow powder; IR(KBr): 825 (s), 1485 (s), 1595 (s), 1715 (vs), 2945 (m), 3065 (m) cm^{-1}; ^1H NMR: δ 2.46 (3H, s, CH_3), 2.88 (2H, t, protons at C_{10}', J = 7.6 Hz), 3.00 (2H, t, protons at C_9', J = 7.6 Hz), 4.02 (3H, s, OCH_3), 7.12–7.47 (10H, m, Ar-H), 8.36 (1H, s, C_2'-H of pyridine ring), 8.52 (1H, poorly resolved dd, C_5'-H), 9.00 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 21.3 (CH_3), 25.5 (C_{10}'), 28.1 (C_9'), 56.3 (OCH_3), 113.6 (CH), 120.3 (CH), 120.4 (C), 123.7 (CH), 124.3 (CH), 125.5 (CH), 125.9 (C), 127.1 (CH), 127.6 (CH), 128.9 (CH), 129.1 (CH), 129.2 (CH), 129.6 (C), 135.0 (C), 136.0 (C), 137.9 (C), 138.4 (C), 142.0 (C_4), 143.6 (C), 146.9 (C), 148.4 (C), 149.1 (C_3'), 152.4 (C_4'a), 159.8 (CO of carbonyl). Anal. Calcd. for $C_{30}H_{23}NO_3$: C, 80.88; H, 5.20; N, 3.14%. Found: C, 80.80; H, 5.23; N, 3.16%.

8-Methoxy-3-[1-(4-methoxyphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3h). Yield 0.83 g (60%); mp 275-276 ºC; white powder; IR(KBr): 825 (s), 1480 (s), 1610 (s), 1720 (vs), 2940 (m), 3055 (m) cm^{-1}; ^1H NMR: δ 2.89 (2H, poorly resolved triplet, protons at C_{10}'), 3.01 (2H, poorly resolved triplet, protons at C_9'), 3.90 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 7.02–7.47 (10H, m, Ar-H), 8.35 (1H, s, C_2'-H of pyridine ring), 8.52 (1H, poorly resolved dd, C_5'-H), 8.99 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.6 (C_{10}'), 28.1 (C_9'), 55.4 (OCH_3), 56.3 (OCH_3), 113.6 (CH), 113.8 (CH), 120.3 (CH), 120.4 (C), 123.7 (CH), 124.3 (CH), 125.5 (CH), 125.9 (C), 127.1 (CH), 127.6 (CH), 129.2 (CH), 129.6 (C), 130.3 (CH), 131.2 (C), 135.0 (C), 138.4 (C), 142.1 (C_4), 143.5 (C), 146.9 (C), 148.4 (C), 148.8 (C_3'), 152.4 (C_4'a), 159.5 (C), 159.8 (CO of carbonyl). Anal. Calcd. for $C_{30}H_{23}NO_4$: C, 78.08; H, 5.02; N, 3.03%. Found: C, 78.19; H, 5.04; N, 3.03%.

8-Methoxy-3-[1-(2,4-dimethoxyphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3i). Yield 0.94 g (64%); mp 271 ºC; white powder; IR(KBr): 830 (s), 1480 (s), 1600 (s), 1715 (vs), 2940 (m), 3055 (m) cm^{-1}; ^1H NMR: δ 2.73–2.88 (4H, m, protons at $C_9'$and C_{10}'), 3.78 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 6.58–7.45 (9H, m, Ar-H), 8.31 (1H, s, C_2'-H of pyridine ring), 8.53 (1H, poorly resolved dd, C_5'-H), 9.00 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.4 (C_{10}'), 28.0 (C_9'), 55.4 (OCH_3), 55.5 (OCH_3), 56.3 (OCH_3), 98.6 (CH), 104.5 (CH), 113.4 (CH), 120.2 (CH), 120.5 (C), 120.7 (C), 124.3 (CH), 124.5 (CH), 125.4 (CH), 126.1 (C), 127.0 (CH), 127.6 (CH), 129.0 (CH), 131.4 (CH), 131.6 (C), 135.2 (C), 138.6 (C), 141.9 (C_4), 143.5

(C), 146.1 (C), 146.9 (C), 148.1 (C_3'), 151.7 (C_4′a), 157.5 (C), 159.8 (C), 161.2 (CO of carbonyl). Anal. Calcd. for $C_{31}H_{25}NO_5$: C, 75.75; H, 5.13; N, 2.85%. Found: C, 75.62; H, 5.09; N, 2.83%.

8-Methoxy-3-[1-(4-chlorophenyl)-9,10-dihydro-4-azaphenanthren-3-yl]coumarin (3j). Yield 0.74 g (53%); mp 292 ºC; white powder; IR(KBr): 830 (s), 1480 (s), 1610 (s), 1725 (vs), 2955 (m), 3050 (m) cm^{-1}; ^{1}H NMR: δ 2.88–2.93 (4H, m, protons at C_9'and C_{10}'), 4.01 (3H, s, OCH_3), 7.12–7.48 (10H, m, Ar-H), 8.34 (1H, s, C_2'-H of pyridine ring), 8.51 (1H, poorly resolved dd, C_5'-H), 9.00 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.4 (C_{10}'), 28.0 (C_9'), 56.3 (OCH_3), 113.7 (CH), 120.3 (CH), 123.4 (CH), 124.4 (CH), 125.5 (CH), 127.1 (CH), 127.7 (CH), 128.7 (CH), 129.4 (CH), 130.4 (CH), 134.2 (C), 134.7 (C), 137.3 (C), 138.3 (C), 142.2 (C_4), 143.5 (C), 146.9 (C), 147.9 (C), 148.5 (C_3'), 152.5 (C_4′a), 159.8 (CO of carbonyl). Anal. Calcd. for $C_{29}H_{20}ClNO_3$: C, 74.76; H, 4.33; N, 3.01%. Found: C, 74.68; H, 4.37; N, 3.01%.

3-(1-Phenyl-9,10-dihydro-4-azaphenanthren-3-yl)benzo[*f*]coumarin (3k). Yield 0.82 g (61%); mp 274 ºC; yellow powder; IR(KBr): 705 (s), 760 (s), 1480 (s), 1595 (s), 1715 (vs), 2950 (m), 3055 (m) cm^{-1}; ^{1}H NMR: δ 2.91 (2H, t, protons at C_{10}', J = 7.6 Hz), 3.03 (2H, t, protons at C_9', J = 7.6 Hz), 7.10–8.06 (13H, m, Ar-H), 8.45 (1H, s, C_2'-H of pyridine ring), 8.55 (1H, poorly resolved dd, C_5-H of phenyl ring), 8.62 (1H, poorly resolved dd, C_5'-H), 9.87 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.5 (C_{10}'), 28.1 (C_9'), 114.0 (C), 116.7 (CH), 122.0 (CH), 123.6 (CH), 124.3 (C), 125.5 (CH), 126.1 (CH), 127.2 (CH), 127.7 (CH), 128.1 (CH), 128.4 (CH), 128.5 (CH), 129.0 (CH), 129.1 (CH), 129.3 (CH), 129.5 (C), 129.6 (C), 130.4 (C), 133.4 (CH), 135.0 (C), 137.7 (C_4), 138.5 (C), 139.0 (C), 148.7 (C), 149.2 (C_3'), 152.5 (C_4'a), 153.7 (C), 160.5 (CO of carbonyl). Anal. Calcd. for $C_{32}H_{21}NO_2$: C, 85.12; H, 4.69; N, 3.10%. Found: C, 85.24; H, 4.66; N, 3.08%.

3-[1-(4-Methylphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]benzo[*f*]coumarin (3l). Yield 0.90 g (64 %); mp 296 ºC; yellow powder; IR(KBr): 820 (s), 1475 (s), 1600 (s), 1715 (vs), 2960 (m), 3060 (m) cm^{-1}; ^{1}H NMR: δ 2.47 (3H, s, CH_3), 2.91 (2H, m, protons at C_{10}'), 3.03 (2H, m, protons at C_9'), 7.29–8.06 (12H, m, Ar-H), 8.44 (1H, s, C_2'-H of pyridine ring), 8.55 (1H, poorly resolved dd, C_5-H of phenyl ring), 8.61 (1H, dd, C_5'-H, J = 7.6, 0.8 Hz), 9.86 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 21.3 (CH_3), 25.6 (C_{10}'), 28.2 (C_9'), 114.0 (C), 116.7 (CH), 122.0 (CH), 123.7 (CH), 124.4 (C), 125.5 (CH), 126.1 (CH), 127.2 (CH), 127.7 (CH), 128.4 (CH), 128.9 (CH), 129.0 (CH), 129.1 (CH), 129.2 (CH), 129.6 (C), 130.4 (C), 133.3 (CH), 135.0 (C), 136.0 (C), 137.7 (C_4), 138.0 (C), 138.5 (C), 148.7 (C), 149.2 (C_3'), 152.5 (C_4'a), 153.7 (C), 160.5 (CO of carbonyl). Anal. Calcd. for $C_{33}H_{23}NO_2$: C, 85.14; H, 4.98; N, 3.01%. Found: C, 85.22; H, 4.95; N, 3.02%.

3-[1-(4-Methoxyphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]benzo[*f*]coumarin (3m). Yield 0.86 g (60%); mp 235 ºC; yellow powder; IR(KBr): 830 (s), 1470 (s), 1603 (s), 1717 (vs), 2940 (m), 3060 (m) cm^{-1}; ^{1}H NMR: δ 2.91(3H, t, protons at C_{10}', J = 7.6 Hz), 3.04 (2H, t, protons at C_9', J = 7.6 Hz), 3.91 (3H, s, OCH_3), 7.04–8.05 (12H, m, Ar-H), 8.43 (1H, s, C_2'-H of pyridine ring), 8.54 (1H, poorly resolved dd, C_5-H of phenyl ring), 8.61 (1H, poorly resolved dd, C_5'-H), 9.86 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.6 (C_{10}'), 28.2 (C_9'), 55.4 (OCH_3), 113.9 (CH), 114.0 (C), 116.6 (CH), 122.0 (CH), 123.7 (CH), 124.3 (C), 125.5 (CH), 126.1 (CH), 127.2 (CH),

127.7 (CH), 128.3 (CH), 129.0 (CH) 129.2 (CH), 129.5 (C), 129.6 (C), 130.3 (CH), 130.4 (C), 131.3 (CH), 133.3 (C), 135.1 (C), 137.6 (C_4), 138.4 (C), 148.6 (C), 148.8 (C_3'), 152.5 (C_4'a), 153.7 (C), 159.5 (C), 160.5 (CO of carbonyl). Anal. Calcd. for $C_{33}H_{23}NO_3$: C, 82.31; H, 4.81; N, 2.91%. Found: C, 82.21; H, 4.84; N, 2.92%.

3-[1-(2,4-Dimethoxyphenyl)-9,10-dihydro-4-azaphenanthren-3-yl]benzo[*f*]coumarin (3n). Yield 0.90 g (59%); mp 292-294 ºC; yellow powder; IR(KBr): 820 (s), 1470 (s), 1590 (s), 1720 (vs), 2940 (m), 3060 (m) cm^{-1}; ^{1}H NMR: δ 2.76–2.91 (4H, m, protons at C_9'and C_{10}'), 3.79 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 6.59–8.05 (11H, m, Ar-H), 8.37 (1H, s, C_2'-H of pyridine ring), 8.55 (1H, poorly resolved dd, C_5-H of phenyl ring), 8.62 (1H, poorly resolved dd, C_5'-H), 9.86 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.4 (C_{10}'), 28.1 (C_9'), 55.4 (OCH_3), 55.5 (OCH_3), 98.6 (CH), 104.6 (CH), 114.0 (C), 116.6 (CH), 120.8 (C), 122.0 (CH), 124.5 (CH), 124.6 (C), 125.4 (CH), 126.1 (CH), 127.1 (CH), 127.7 (CH), 128.3 (CH), 129.0 (CH), 129.1 (CH), 129.6 (C), 130.4 (C), 131.4 (CH), 131.6 (C), 133.1 (CH), 135.2 (C), 137.4 (C_4), 138.7 (C), 146.2 (C), 148.4 (C_3'), 151.8 (C_4'a), 153.6 (C), 157.6 (C), 160.5 (C), 161.2 (CO of carbonyl). Anal. Calcd. for $C_{34}H_{25}NO_4$: C, 79.83; H, 4.94; N, 2.74%. Found: C, 79.85; H, 4.98; N, 2.73%.

3-[1-(4-Chlorophenyl)-9,10-dihydro-4-azaphenanthren-3-yl]benzo[*f*]coumarin (3o). Yield 0.75 g (51%); mp 249 ºC; yellow powder; IR(KBr): 830 (s), 1475 (s), 1600 (s), 1725 (vs), 2950 (m), 3055 (m) cm^{-1}; ^{1}H NMR: δ 2.90–3.01 (4H, m, protons at C_9'and C_{10}'), 7.29–8.06 (12H, m, Ar-H), 8.42 (1H, s, C_2'-H of pyridine ring), 8.54 (1H, poorly resolved dd, C_5-H of phenyl ring), 8.61 (1H, poorly resolved dd, C_5'-H), 9.87 (1H, s, C_4-H of coumarin); ^{13}C NMR: δ 25.5 (C_{10}'), 28.1 (C_9'), 114.0 (C), 116.7 (CH), 122.0 (CH), 123.3 (CH), 124.1 (C), 125.5 (CH), 126.2 (CH), 127.3 (CH), 127.8 (CH), 128.4 (CH), 128.7 (CH), 129.1 (CH), 129.3 (C), 129.4 (CH), 129.6 (C), 130.3 (CH), 130.4 (C), 133.5 (CH), 134.3 (C), 134.8 (C), 137.4 (C), 137.8 (C_4), 138.4 (C), 148.0 (C), 148.8 (C_3'), 152.6 (C_4'a), 153.8 (C), 160.5 (CO of carbonyl). Anal. Calcd. for $C_{32}H_{20}ClNO_2$: C, 79.09; H, 4.15; N, 2.88%. Found: C, 79.03; H, 4.13; N, 2.89%.

It is important to note that in case of compounds **3j** and **3l**, the number of non equivalent carbon signals in ^{13}C NMR spectra are less than expected (in case of compound **3j**, three signals and in case of compound **3l**, one signal). This may be due to identical chemical shifts of certain carbons which may appear at the same position.

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