Novel 13*H*-indolo[3,2-*c*]acridines and their methyl derivatives

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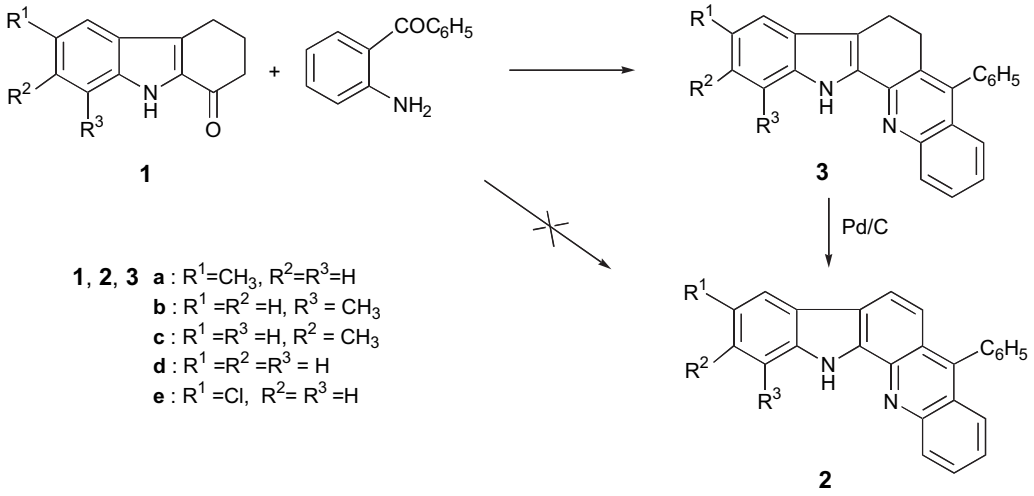
7-Phenyl-13*H*-indolo[3,2-*c*]acridines (**2a–e**) have been prepared from 2,3,4,9-tetrahydro-1*H*-carbazol-1-ones (**1a–e**) *via* the intermediate 5,6-dihydro-derivatives (**3a–e**), and 13*H*-indolo[3,2-*c*]acridines (**8a–e**) from the 1-(*N*-phenylamino)carbazoles (**7a–e**). Methylations of **2** and **8** have been carried out, and UV spectral studies on the title compounds and the methylated products are presented, along with plausible mechanisms for the formation of the final compounds.

Keywords: fused acridines, indoles, carbazoles, methylation, Vilsmeier reagent

Nitrogen containing heterocyclic compounds are the key building blocks used to develop compounds of biological and medicinal interest to chemists. Among the nitrogen heterocycles, indole, its benzo-analog carbazole, and acridine are important structural components in alkaloids and many pharmaceutical agents,[1-15] and also they exhibit a high degree of biological activity including anti-fungal, anti-bacterial, anti-tumour, anti-HIV and DNA interactions.[16-23] Substituted indoles have been referred to as "privileged structures" since they are capable of binding to many receptors with high affinity.[24] Acridine derivatives are well known therapeutic agents, whose mutagenic properties depend on their ability to interact with nucleic acids.[16,17] We expect therefore the combination of indole and acridine structures may play a vital role in biological as well as pharmaceutical systems. In some cases, specific substitution patterns like indoloacridine remain difficult to obtain by standard indole-forming or acridine-forming reactions; thus new methodologies emerge. The present investigation was aimed to devise a viable synthetic route to the hitherto unknown title compounds, the 13*H*-indolo[3,2-*c*]acridines, starting from 1-oxo-1,2,3,4-tetrahydrocarbazoles†[25,26] which may show properties of pharmacological interest.

With the aim to construct indoloacridines we took 1-oxo-1,2,3,4-tetrahydrocarbazoles (**1**) as potential precursors and *o*-aminobenzophenone as reactant as shown in Scheme 1. 6-Methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (**1a**) on treatment with *o*-aminobenzophenone in glacial acetic acid yielded an orange solid. This on purification by column chromatography over silica gel yielded a yellow amorphous solid melting at 156–158°C. Its IR spectrum showed a strong ν_{NH} band at 3275 cm^{-1} and $\nu_{C=N}$ at 1680 cm^{-1}. The UV absorption spectrum in methanol showed an extensive pattern of intense bands peaking between 241 and 339 nm (see Experimental section). Its ^1H NMR spectrum ($CDCl_3$) showed as significant peaks the carbazole NH proton as a broad singlet at δ 10.18, the aromatic protons as a cluster from δ 8.02–6.94, a four proton multiplet in the region δ 2.90–2.54, and a three-proton singlet at δ 2.34 for the CH_3 group. The mass spectrum showed M^+ at *m/z* 360. These spectral details and also the elemental analysis were in good agreement with the molecular formula $C_{26}H_{20}N_2$, corresponding to the structure 5,6-dihydro-3-methyl-7-phenyl-13*H*-indolo[3,2-*c*]acridine (**3a**) and not the desired 3-methyl-7-phenyl-13*H*-indolo[3,2-*c*]acridine (**2a**) (Scheme 1). We reported a similar type of reaction of **1** with *o*-aminoacetophenone that resulted in the formation of the aromatised product[27] in a single step, but in the present case the aerial oxidation did not take place; instead it led to the dihydro derivative **3a**. Similar compounds (**3b–e**) were obtained by repeating the experiment on **1b–e**.

To produce the required product **2** we treated 5,6-dihydro-3-methyl-7-phenyl-13*H*-indolo[3,2-*c*]acridine (**3a**) with 5% palladised charcoal (Pd/C) in diphenyl ether for 5 h to yield a dark brown product. This on purification using column chromatography over silica gel afforded a yellow solid melting at 162–164°C. Its IR spectrum showed a strong ν_{NH} band at 3422 cm^{-1}, and a $\nu_{C=N}$ band at 1667 cm^{-1}. The UV spectrum (see Experimental) was qualitatively similar to that



Scheme 1

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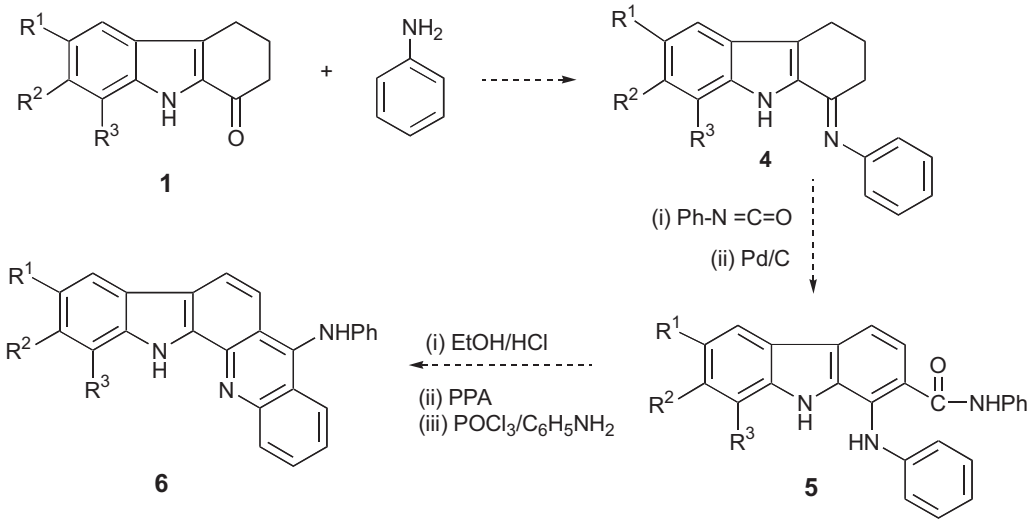
† For simplicity, these compounds are named in the text as oxo- and amino-carbazoles, rather than as carbazolones and carbazolamines.

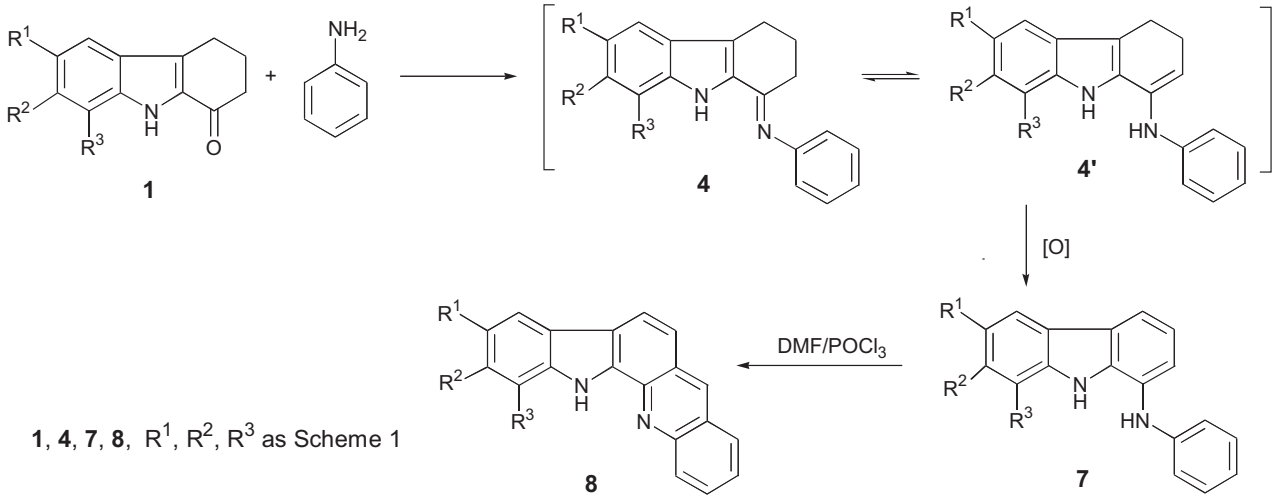


Scheme 2

of **1a**. The ^{1}H NMR was also similar to that of **1a**, but for the 4H high-field multiplet, which was lacking, and the methyl signal, which was shifted to δ 2.66. The molecular ion peak appeared at *m/z* 358 in the MS. The spectral and analytical details attest the compound as 3-methyl-7-phenyl-13*H*-indolo-[3,2-*c*]acridine (**2a**). A series of similar compounds **2b–e** was obtained by dehydrogenating compounds **3b–e**.

As part our program to devise new synthetic avenues to the indoloacridine system, we attempted to prepare the imine **4**, from which the target system **6** can readily be reached, as shown in Scheme 2. 6-Methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (**1a**) was therefore treated with aniline in the presence of a catalytic amount of *p*-toluenesulfonic acid to yield a product which melted at 192–194°C. Its IR spectrum showed two strong bands at 3388 and 3343 cm^{-1} from two N–H groups. Two $\nu_{C=N}$ bands appeared at 1586 and 1582 cm^{-1}. In the ^{1}H NMR spectrum, apart from the carbazole NH proton, a broad singlet at δ 7.71, and a second NH signal at δ 5.65, and the methyl protons at C_6, a 3H singlet at δ 2.45, the remaining signals were all from aromatic protons. The absence of absorption in the region δ 3.25–2.45 clearly demonstrates that the expected product 6-methyl-1-(*N*-phenylimino)-1,2,3,4-tetrahydrocarbazole (**4a**) was not formed Further, the appearance of the molecular ion peak at *m/z* 272 in its MS, and elemental analysis, agreed well with the molecular formula $C_{19}H_{16}N_2$. From the spectral and analytical data, the structure the product was 6-methyl-1-(*N*-phenylamino)carbazole† (**7a**) as shown in Scheme 3 and not **4a** as proposed in Scheme 2. A similar series of compounds was obtained from **1b–e** to form the corresponding derivatives **7b–e**. Evidently the 1-(*N*-phenylimino)-1,2,3,4-tetrahydrocarbazole (**4**), formed *in situ* from the 1-oxo-1,2,3,4-tetrahydrocarbazole (**1**) and aniline, tautomerises to the anilinodihydrocarbazole (**4'**), and this on aerial oxidation yields the aromatised product **7**.

In order to prepare indoloacridines, 6-methyl-1-(*N*-phenylamino)carbazole (**7a**) was treated with DMF/$POCl_3$ (Vilsmeier–Haack reagent) in the ratio 3:7 at room temperature for about 3 h to yield a brown coloured product. This on purification by column chromatography over silica gel afforded a yellow solid which melted at 147–149°C. From the spectral and analytical data, the structure of the product was inferred to be the expected 3-methyl-13*H*-indolo[3,2-*c*]-acridine (**8a**). Its IR spectrum showed strong bands at 3417 and 1665 cm^{-1} (ν_{NH} and $\nu_{C=N}$ respectively). The ^{1}H NMR spectrum exhibited a one proton singlet at δ 8.80 assigned to C_7–H. The indole NH (N_{13}-H) proton appeared as broad singlet at δ 8.65, and C_4–H showed as a singlet at δ 8.26. A three proton singlet at δ 2.50 was due to C_3-CH_3, and the remaining proton signals



Scheme 3

were all doublets or multiplets. The M^+ ion peak at *m/z* 282 in the MS, and the elemental analysis agreed well with the molecular formula $C_{20}H_{14}N_2$. The generality of this reaction was tested with the other carbazoles. A plausible mechanism for the formation of the products **8** is given in Scheme 4. The initial step is the formation of *ortho N*-arylamino-aldehyde intermediate **I** from the substrate **7** by electrophilic *ortho* formylation reaction, which cyclises to intermediate **II**. This on prototropic shift yields the intermediate **III** which eliminates water to give compound **8**.

Further, our interest turned to methylation of title compounds **2** in order to discover whether simple methylation either at the pyrrole N occurs, to afford **9**, or whether, after deprotonation of the pyrrole N, methylation at pyridine N may result in **10**. So we subjected **2a** to methylation using methyl iodide/K_2CO_3. This yielded a single product which melted at 237–238°C. (Scheme 5). Its IR spectrum showed $\nu_{C=N}$ at 1651 cm^{-1} but no ν_{NH} band. The UV (see Experimental) was closely similar to that of the starting material (**2a**). We concluded therefore that the methylation had taken place at the pyrrole N to give **9**, rather than at the pyridine N (forming **10**). Furthermore, the ^1H NMR spectrum showed a fourteen–proton multiplet between δ 8.10 and 7.17, a three-proton singlet at δ 4.20 for N_{13}–CH_3[25] and another at δ 2.66 (C_3–CH_3), all agreed with the proposed structure as 3,13-dimethyl-7-phenylindolo[3,2-*c*]acridine (**9a**). A similar result was obtained with the more sterically-hindered derivative **2b**, which yielded the corresponding product 1,13-dimethyl-7-phenylindolo[3,2-*c*]acridine (**9b**).

We methylated **8a** (Scheme 5) under the same reaction conditions, to yield a single product **11a** or **12a** which melted at 291–294°C. Its IR spectrum showed $\nu_{C=N}$ at 1653 cm^{-1} and absence of ν_{NH}. The possible structure **12a** was ruled out on the basis of the UV spectrum, which showed no major change from that of **8a**. Its ^1H NMR spectrum exhibited the following peaks: a singlet at δ 8.82 (C_7-H), A nine-proton multiplet at δ 8.40–7.30 for aromatic protons, and two three-proton singlets at δ 3.80 and 2.59 accounted for N_{13}–CH_3 and C_3–CH_3 respectively. The elemental analysis was in good agreement with the molecular formula $C_{21}H_{16}N_2$. Based on the above data we conclude the compound to be 3,13-dimethyl-indolo[3,2-*c*]-acridine (**11a**). The generality of the methylation was tested with derivative **8b** which yielded the corresponding derivative 1,13-dimethylindolo[3,2-*c*]acridine (**11b**). Again, from the UV spectrum we infer that the methylation took place at the pyrrole N rather than the pyridine N.

In conclusion, syntheses of indoloacridines and their methylated derivatives were achieved using different synthetic pathways. It remains to be seen whether the compounds thus obtained possess applications in medicine as well as in synthetic chemistry.

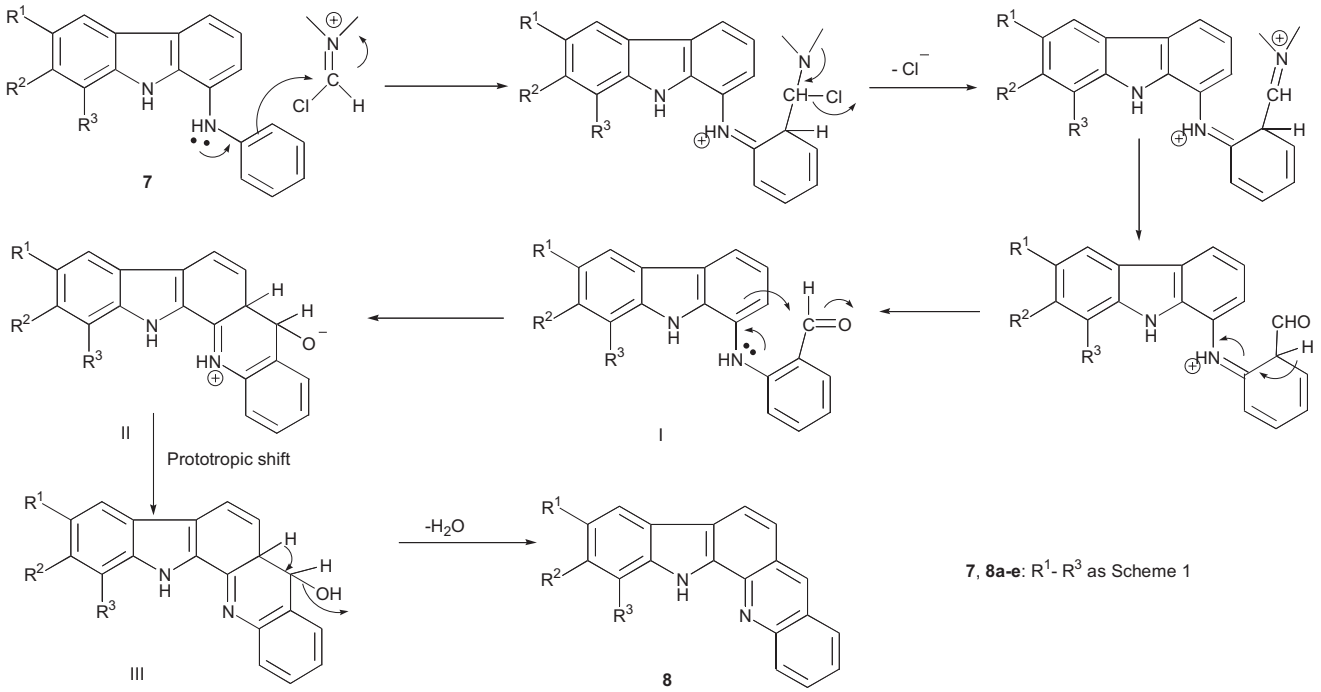
Experimental

Melting points were determined using a Mettler FP 51 apparatus (Mettler Instruments, Switzerland). IR spectra were recorded using KBr discs on a Shimadzu FTIR-8201PC spectrophotometer (Shimadzu, Japan). UV spectra were recorded in UV spectral grade methanol using a Perkin-Elmer UV-VIS spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Varian AMX 400 FT NMR (Varian Australia) using TMS as internal standard. Mass spectra were recorded on JEOL D-300 Mass spectrometer. Micro analyses were performed on a Vario EL III model CHNS analyser (Vario, Germany) at the Department of Chemistry, Bharathiar University. The purity of the products was tested by TLC with plates coated with silica gel-G with petroleum ether and ethyl acetate (85:15) as developing solvents.

5,6-Dihydro-7-phenyl-13H-indolo[3,2-c]acridines (**3a–e**), *general procedure*

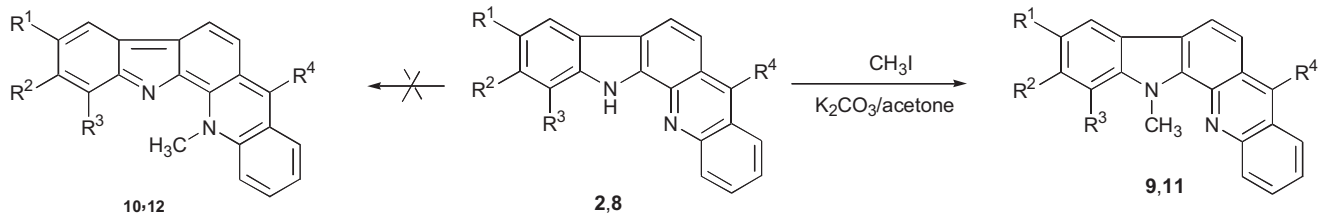
The appropriate 1-oxo-1,2,3,4–tetrahydrocarbazole (**1**, 5 mmol) and *o*-aminobenzophenone (0.985 g, 5 mmol) was refluxed for 8 h in glacial acetic acid (4 ml) containing one drop of sulfuric acid. The reaction was monitored by TLC. After the completion of the reaction, it was poured into crushed ice, extracted with chloroform, and the organic layer dried (Na_2SO_4). The crude product obtained on removal of the solvent was purified by column chromatography over silica gel using pet. ether:ethyl acetate (98:5) to yield the 5,6-dihydro-7-phenyl-13H-indolo[3,2-c]acridine (**3**).

5,6-Dihydro-3-methyl-7-phenyl-13H-indolo[3,2-c]acridine (**3a**): Yellow amorphous solid (1.12 g, 62%), m.p.156–158°C. IR: ν_{max}



A plausible mechanism for the formation of **8a-e** from **7a-e**

Scheme 4



10,**12** **2**,**8** **9**,**11**

2, **9**, **10** **a**: $R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = C_6H_5$ **8**, **11, 12** **a**: $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$
b: $R^1 = R^2 = H$, $R^3 = CH_3$, $R^4 = C_6H_5$ **b**: $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$

Scheme 5

3275, 2980, 2895, 1680, 1581, 1441, 801 cm^{-1}. UV: λ_{max} (log ε) 241 (4.23), 248 (4.89), 282 (3.85), 294 (4.95), 310 (3.97), 326 (3.94), 339 nm (3.92). ^{1}H NMR: δ 10.18 (b s, 1H, N_{13}–H), 8.02–7.15 (m, 10H, C_{11}–, C_{10}–, C_9–, C_8–, C_4–, C_2'–, C_3'–, C_4'–, C_5'–, C_6'–H), 7.10–6.94 (m, 2H, C_2–, C_4–H), 2.90–2.54 (m, 4H, C_6–2H, C_5–2H), 2.34 (s, 3H, C_3–CH_3). ^{13}C NMR: δ 158.3 (C_{12a}), 151.4 (C_7), 150.5 (C_{11a}), 136.1 (C_1'), 131.4 (C_{13a}), 129.6 (C_{12b}), 128.7 (C_3'), 128.4 (C_{10}), 128.1 (C_6'), 128.0 (C_4'), 127.9 (C_5'), 127.7 (C_{11}), 127.6 (C_{6a}), 126.9 (C_3), 126.6 (C_2'), 125.9 (C_9), 125.5 (C_{4a}), 124.3 (C_8), 120.6 (C_4), 120.6 (C_{7a}), 120.4 (C_2), 112.2 (C_{4b}), 109.5 (C_1), 29.3 (C_6), 28.4 (C_3–CH_3), 27.4 (C_5). MS: *m/z* (%) 360 (M^+, 67), 283 (44), 269 (20), 218 (14), 181 (27), 168 (24), 143 (11), 114 (19), 77 (16). Anal. Calc. for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.60; H, 5.45; N, 7.62%.

5,6-Dihydro-1-methyl-7-phenyl-13H-indolo[3,2-c]acridine (**3b**): Spongy yellow solid (1.15 g, 64%), m.p. 268–270°C. IR: ν_{max} 3461, 2962, 2923, 1672, 1547, 801 cm^{-1}. UV: λ_{max} (log ε) 226 (4.61), 248 (4.68), 285 (3.93), 295 (4.16), 310 (3.97), 333 (3.71), 346 nm (3.67). ^{1}H NMR: δ 8.68 (b s, 1H, N_{13}–H), 7.68–7.06 (m, 10H, C_{11}–, C_{10}–, C_9–, C_8–, C_3–, C_2'–, C_3'–, C_4'–, C_5'–, C_6'–H), 7.00–6.94 (m, 2H, C_4–, C_2–H), 2.90–2.54 (m, 4H, C_6–2H, C_5–2H), 2.41 (s, 3H, C_1–CH_3). ^{13}C NMR: δ 156.3 (C_{12a}), 152.0 (C_7), 149.3 (C_{11a}), 136.2 (C_1'), 131.4 (C_{13a}), 129.1 (C_{12b}), 128.7 (C_3'), 128.5 (C_6'), 128.4 (C_{10}), 127.9 (C_4'), 127.9 (C_{11}), 127.6 (C_5'), 127.4 (C_{6a}), 126.1 (C_2'), 125.9 (C_9), 125.2 (C_{4a}), 124.3 (C_8), 122.4 (C_3), 122.3 (C_1), 121.3 (C_2), 120.9 (C_4), 120.5 (C_{7a}), 112.2 (C_{4b}), 29.3 (C_6), 27.6 (C_5), 24.3 (C_1–CH_3). MS: *m/z* (%) M^+ 360 (57), 283 (39), 269 (24), 218 (19), 181 (17), 168 (28), 143 (17), 114 (22), 77 (10). Anal. Calc. for $C_{26}H_{20}N_2$: C, 86.64; H, 5.58; N, 7.71%.

5,6-Dihydro-2-methyl-7-phenyl-13H-indolo[3,2-c]acridine (**3c**): Yellow amorphous solid (1.04 g, 58%), m.p. 138–141°C. IR: ν_{max} 3431, 2962, 2360, 1679, 1579, 1443, 800 cm^{-1}. UV: λ_{max} (log ε) 238 (4.64), 250 (4.85), 282 (3.87), 296 (4.05), 307 (3.98), 328 (3.59), 339 nm (3.54). ^{1}H NMR: δ 10.07 (b s, 1H, N_{13}–H), 8.03–6.92 (m, 10H, C_{11}–, C_{10}–, C_9–, C_8–, C_1–, C_2'–, C_3'–, C_4'–, C_5'–, C_6'–H), 6.84–6.67 (m, 2H, C_4–, C_3–H), 2.83–2.52 (m, 4H, C_6–2H, C_5–2H), 2.32 (s, 3H, C_2–CH_3). ^{13}C NMR: δ 155.8 (C_{12a}), 150.4 (C_7), 150.1 (C_{11a}), 135.6 (C_1'), 131.0 (C_{13a}), 129.4 (C_{12b}), 128.7 (C_6'), 128.3 (C_{10}), 128.2 (C_3'), 128.1 (C_4'), 127.9(C_{6a}), 127.6 (C_{11}), 127.1 (C_5'), 125.9 (C_2'), 125.4 (C_9), 125.0 (C_{4a}), 123.9 (C_8), 121.4 (C_3), 120.9 (C_2), 120.6 (C_4), 119.9 (C_{7a}), 111.9 (C_{4b}), 109.9 (C_1), 29.4 (C_6), 28.0 (C_5), 26.2 (C_2–CH_3). MS: *m/z* (%) 360 (M^+, 61), 283 (34), 269 (27), 218 (11), 181 (26), 168 (20), 143 (19), 114 (11), 77 (16). Anal. Calc. for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.39; H, 5.63; N, 7.81%.

5,6-Dihydro-7-phenyl-13H-indolo[3,2-c]acridine (**3d**): Yellow amorphous solid (1.07 g, 62%), m.p. >300°C. IR: ν_{max} 3413, 2922, 2360, 1689, 1548 cm^{-1}. UV: λ_{max} (log ε) 229 (4.44), 243 (4.62), 250 (4.46), 261 (4.34), 295 (4.21), 306 (3.96), 322 (3.94), 335 nm (3.92). ^{1}H NMR: δ 12.30 (b s, 1H, N_{13}–H), 8.57–6.96 (m, 13H, C_{11}–, C_{10}–, C_9–, C_8–, C_4–, C_3–, C_2–, C_1–, C_2'–, C_3'–, C_4'–, C_5'–, C_6'–H), 3.08–2.93 (m, 4H, C_6–2H, C_5–2H). ^{13}C NMR: δ 157.2 (C_{12a}), 151.1 (C_7), 150.4 (C_{11a}), 136.9 (C_1'), 131.5 (C_{13a}), 129.9 (C_{12b}), 128.9 (C_{10}), 128.4 (C_4'), 128.3 (C_3'), 128.2 (C_5'), 128.0 (C_{11}), 127.9 (C_6'), 127.6 (C_{6a}), 126.5 (C_2'), 125.3 (C_{4a}), 124.9 (C_9), 124.2 (C_3), 124.1 (C_8), 123.0 (C_2), 120.9 (C_4), 120.5 (C_{7a}), 111.9 (C_{4a}), 111.5 (C_1), 29.4 (C_6), 27.4 (C_5). MS: *m/z* (%) 346 (M^+, 44), 269 (57), 219 (16), 197(21), 181 (23), 143 (11), 114 (16), 77 (12). Anal. Calc. for $C_{25}H_{18}N_2$: C, 86.68; H, 5.24; N, 8.08. Found: C, 86.51; H, 5.19; N, 8.03%.

3-Chloro-5,6-dihydro-7-phenyl-13H-indolo[3,2-c]acridine (**3e**): Greenish yellow solid (1.20 g, 63%), m.p. >300°C. IR: ν_{max} 3434, 2962, 2923, 2360, 1668, 1463, 801 cm^{-1}. UV: λ_{max} (log ε) 229 (4.65), 251 (4.69), 288 (3.96), 298 (4.18), 318 (3.99), 338 (3.74), 354 nm (3.70). ^{1}H NMR: δ 10.58 (b s, 1H, N_{13}–H), 8.01–7.20 (m, 10H, C_{11}–, C_{10}–, C_9–, C_8–, C_4–, C_2'–, C_3'–, C_4'–, C_5'–, C_6'–H), 7.12–7.04 (m, 2H, C_2–, C_1–H), 2.97–2.85 (m, 4H, C_6–2H, C_5–2H). ^{13}C NMR: δ 159.8 (C_{12a}), 153.4 (C_7), 151.8 (C_{11a}), 134.9 (C_1'), 130.9 (C_{13a}), 129.5 (C_{12b}), 128.5 (C_6'), 128.9 (C_4'), 128.4 (C_{6a}), 128.1 (C_3'), 127.9 (C_{10}), 127.7 (C_5'), 127.4 (C_{11}), 126.5 (C_2'), 126.1 (C_{4a}), 125.7 (C_9), 125.6 (C_3), 124.4 (C_8), 121.5 (C_4), 120.3 (C_2), 120.0 (C_{7a}), 119.5 (C_1), 112.4 (C_{4b}), 30.1 (C_5), 30.0 (C_6). MS: *m/z* (%) 382/380 (M^+, 14/46), 303 (16), 269 (32), 244 (17), 219 (27), 194 (37), 181 (20), 168 (13), 91 (15). Anal. Calc. for $C_{25}H_{17}ClN_2$: C, 78.84; H, 4.50; N, 7.35. Found: C, 78.78; H, 4.56, N, 7.33%.

7-Phenyl-13H-indolo[3,2-c]acridines (**2a–e**), *general procedure*

The appropriate 5,6-dihydro-7-phenyl-13*H*-indolo[3,2-*c*]acridine (**3**, 1 mmol) and Pd/C (0.050 g) was refluxed in diphenyl ether (3 ml) for about 5 h. The reaction was monitored by TLC. It was then filtered through Whatman-41 filter paper to remove Pd/C. After removal of solvent the mixture was poured into crushed ice, extracted with ethyl acetate, and dried (Na_2SO_4). The crude product obtained by removal of solvent was purified by column chromatography over silica gel using pet. ether: ethyl acetate (98:2) to yield the corresponding 7-phenyl-13*H*-indolo[3,2-*c*]acridine (**2**).

3-Methyl-7-phenyl-13H-indolo[3,2-c]acridine (**2a**): Pale yellow solid (0.23 g, 64%), m.p. 162–164°C. IR: ν_{max} 3422, 2965, 2783, 1667, 1589, 743 cm^{-1}. UV: λ_{max} (log ε) 255 (4.89), 263 (4.34), 270 (3.86), 290 (4.82), 304 (3.66), 320 (3.87), 334 nm (3.84). ^{1}H NMR: δ 10.13 (b s, 1H, N_{13}–H), 8.34–7.35 (m, 14H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_2–, C_1–, C_2'–, C_3'–, C_4'–, C_5'–, and C_6'–H), 2.66 (s, 3H, C_3–CH_3). ^{13}C NMR: δ 150.5 (C_{12a}), 147.4 (C_{11a}), 139.5 (C_1'), 138.2 (C_7), 133.5 (C_4'), 132.5 (C_5'), 131.6 (C_3'), 130.4 (C_{11}), 130.3 (C_2'), 130.1 (C_{4b}), 129.7 (C_6'), 129.6 (C_{10}), 129.4 (C_6), 128.8 (C_9), 128.4 (C_8), 127.6 (C_{12b}), 127.1 (C_5), 125.3 (C_{13a}), 125.1 (C_2), 124.6 (C_3), 123.6 (C_{7a}), 121.1 (C_4), 118.1 (C_{6a}), 113.4 (C_1), 111.2 (C_{4a}) and 25.0 (C_3–CH_3). MS: *m/z* (%) 358 (M^+, 49), 281 (23), 267(31), 197 (27), 166 (17), 116 (28), 77 (17). Anal. Calc. for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.09; H, 5.04; N, 7.80%.

1-Methyl-7-phenyl-13H-indolo[3,2-c]acridine (**2b**): Yellow spongy mass (0.243 g, 68%), m.p. >300°C. IR: ν_{max} 3276, 2922, 2358, 1672, 746 cm^{-1}. UV, λ_{max} (log ε) 265 (4.71), 254 (4.34), 239 (4.84), 244 (4.13), 264 (3.89), 288 (4.04), 302 (3.45) 341 (3.14), 352 (3.15), 347 (3.84). ^{1}H NMR: δ 10.14 (b s, 1H, N_{13}–H), 8.72–7.03 (m, 14H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_3–, C_2–, C_2'–, C_3'–, C_4'–, C_5'–, and C_6'–H), 2.47 (s, 3H, C_1–CH_3). ^{13}C NMR: δ 150.4 (C_{12a}), 147.4(C_{11a}), 138.5 (C_1'), 137.9 (C_7), 133.4 (C_4'), 131.5 (C_3'), 131.0 (C_{4b}), 130.9 (C_5'), 130.1 (C_2'), 129.5 (C_{10}), 129.1 (C_{11}), 128.8 (C_6), 128.4 (C_6'), 128.3 (C_8), 127.9 (C_9), 127.6 (C_5), 126.9 (C_{12b}), 125.5 (C_{13a}), 124.1 (C_3), 123.4 (C_{7a}), 120.1 (C_2), 118.9 (C_1), 118.5 (C_4), 117.9 (C_{6a}), 110.9 (C_{4a}), 21.6 (C_1–CH_3). MS: *m/z* (%) 358 (M^+, 51), 281 (20), 267(28), 197 (30), 166 (15), 116 (21), 77 (14). Anal. Calc. for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.15; H, 5.00; N, 7.77%.

2-Methyl-7-phenyl-13H-indolo[3,2-c]acridine (**2c**): Yellow amorphous solid (0.215 g, 60%), m.p. 228–230°C. IR: ν_{max} 3417, 2781, 2359, 1665, 743 cm^{-1}. UV: λ_{max} (log ε) 267 (4.74), 254 (4.36), 240 (4.27), 250 (4.13), 266 (3.84), 291 (4.46), 309 (3.56) 326 (3.84), 334 (3.14), 346 nm (3.88). ^{1}H NMR: δ 10.80 (b s, 1H, N_{13}–H), 8.35–6.98 (m, 14H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_3–, C_1–, C_2'–, C_3'–, C_4'–, C_5'–, and C_6'–H), 2.46 (s, 3H, C_2–CH_3). ^{13}C NMR: δ 149.9 (C_{12a}), 147.5 (C_{11a}), 139.4 (C_1'), 138.5 (C_7), 133.6 (C_4'), 131.9 (C_5'), 131.5 (C_3'), 130.5 (C_{11}), 129.9 (C_{4b}), 129.4 (C_2'), 129.1 (C_6'), 128.9 (C_{10}), 128.7 (C_6), 128.5 (C_9), 128.1 (C_8), 127.6 (C_{12b}), 127.1 (C_5), 126.2 (C_2), 124.9 (C_{13a}), 122.9 (C_{7a}), 121.5 (C_3), 120.6 (C_4), 118.5 (C_{6a}), 115.4 (C_1), 111.5 (C_{4a}), 27.7 (C_2–CH_3). MS: *m/z* (%) 358 (M^+, 40), 281 (19), 267(33), 197 (29), 166 (14), 116 (24), 77 (10). Anal. Calc. for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06, N, 7.82. Found: C, 86.95; H, 5.10; N, 7.76%.

7-Phenyl-13H-indolo[3,2-c]acridine (**2d**): Yellow amorphous solid (0.206 g, 60%), m.p. >300°C. IR: ν_{max} 3415, 2783, 2359, 1668, 1592, 746 cm^{-1}. UV, λ_{max} (log ε) 265 (4.65), 250 (4.14), 242 (4.77), 254 (4.34), 260 (3.46), 291 (3.87), 330 (3.84), 340 nm (3.94).^{1}H NMR: δ 11.30 (b s, 1H, N_{13}–H), 8.28–7.23 (m, 15H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_3–, C_2–, C_1–, C_2'–, C_3'–, C_4'–, C_5'–, and C_6'–H). ^{13}C NMR: δ, $CDCl_3$ 150.9 (C_{12a}), 148.0 (C_{11a}), 139.4 (C_1'), 138.2 (C_7), 133.5 (C_4'), 131.4 (C_5'), 130.9 (C_3'), 130.5 (C_{4b}), 130.2 (C_2'), 129.9 (C_2), 129.8 (C_6), 129.6 (C_6'), 129.3 (C_{10}), 128.2 (C_9), 127.9 (C_8), 127.3 (C_5), 127.1 (C_{12b}), 125.6 (C_{13a}), 124.3 (C_3), 123.6 (C_{7a}), 121.3 (C_2), 119.4 (C_4), 118.3 (C_{6a}), 112.4 (C_1), 111.3 (C_{4a}). MS: *m/z* (%) 344 (M^+, 42), 343 (16), 267 (31), 197 (27), 166 (17), 116 (28), 77 (17). Anal. Calc. for $C_{25}H_{16}N_2$: C, 87.18; H, 4.68; N, 8.13. Found: C, 87.15; H, 4.68; N, 8.12%.

3-Chloro-7-phenyl-13H-indolo[3,2-c]acridine (**2e**): Pale yellow powder (0.234 g, 62%), m.p. 178–180°C. IR: ν_{max} 3415, 2783, 2359, 1668, 1590, 1492, 746 cm^{-1}. UV, λ_{max} (log ε) 265 (4.65), 251 (4.34), 244 (4.84), 257 (4.18), 267 (3.76), 284 (4.04), 331 (3.80), 341 nm (3.24). ^{1}H NMR: δ 10.40 (b s, 1H, N_{13}–H), 6.98–8.25 (m, 14H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_2–, C_1–, C_2'–, C_3'–, C_4'–, C_5'–, and C_6'–H). ^{13}C NMR: δ 151.7 (C_{12a}), 147.5 (C_{11a}), 139.3 (C_1'), 138.5 (C_7), 133.1 (C_4'), 132.4 (C_5'), 131.5 (C_3'), 130.3 (C_{11}), 130.1 (C_{4b}), 129.9 (C_2'), 129.5 (C_6), 129.4 (C_6'), 129.0 (C_9), 128.9 (C_{10}), 128.0 (C_8), 127.4 (C_5), 127.3 (C_{12b}), 124.9 (C_{13a}), 123.5 (C_{7a}), 121.0 (C_3), 120.9 (C_4), 118.0 (C_{6a}), 117.6 (C_2), 116.5 (C_1), 110.4 (C_{4a}). MS: *m/z* (%) 380/378 (M^+, 21/61), 343 (17), 267 (28), 216 (23), 201 (12), 161 (9), 116 (21), 77 (13). Anal. Calc. for $C_{25}H_{15}ClN_2$: C, 79.26; H, 3.99; N, 7.39. Found: C, 78.98; H, 4.05; N, 7.40%.

1-(N-phenylamino)carbazoles (**7a–e**), *general procedure*

To the appropriate 1-oxo-1,2,3,4-tetrahydrocarbazole (**1**, 5 mmol) and aniline (5 mmol) in dry *o*-xylene (20 ml) was added a catalytic amount of *p*-toluenesulfonic acid, and the whole was refluxed for 10 h in an oil bath at 160°C. The reaction was monitored by TLC. After the completion of the reaction the solvent was removed. The residue was poured into crushed ice, neutralised with dil. HCl, extracted with ethyl acetate and the extracts dried (Na_2SO_4). The crude product was purified by column chromatography over silica gel using pet.ether: ethyl acetate (98:2) to yield the 1-(*N*-phenylamino)carbazole.

6-Methyl-1-(N-phenylamino)carbazole (**7a**): White crystalline material (0.6 g, 44%); m.p. 192–194°C. IR: ν_{max} 3388, 3343, 2923, 2855, 1586, 1582, 1458, 798 cm^{-1}. ^{1}H NMR: δ 7.83–7.79 (m, 2H, C_2–, C_4–H), 7.71 (b s, 1H, N_9–H), 7.23–7.12 (m, 6H, C_5–, C_7–, C_8–, C_3'–, C_4'–, C_5'–H), 6.82–6.75 (m, 1H, C_3–H), 6.69–6.64 (d, 2H, C_2'–, C_6'–H, *J* = 7.60 Hz), 5.65 (b s, 1H, C_1–NH), 2.45 (s, 3H, C_6–CH_3). ^{13}C NMR: δ, $CDCl_3$ δ, 137.5 (C_1'), 135.0 (C_{9a}), 129.4 (C_{4a}), 128.9 (C_3'), 127.3 (C_5'), 125.6 (C_6), 124.8 (C_1), 122.4 (C_{8a}) 119.8 (C_3), 119.6 (C_5), 118.9 (C_6') 118.5 (C_2'), 117.0 (C_4'), 115.2 (C_7), 112.4 (C_2), 110.5 (C_8), 106.9 (C_4), 106.1 (C_{5a}), and 24.1 (C_6–CH_3). MS: *m/z* (%), M^+ 272 (100), 256 (46), 205 (11), 195 (18), 180 (17), 168 (11), 152 (10), 128 (24), 77 (8). Anal. Calc. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.28. Found: C, 83.70; H, 5.83; N, 10.21%.

8-Methyl-1-(N-phenylamino)carbazole (**7b**): White spongy mass (0.612 g, 45%); m.p. 161–163°C. IR: ν_{max} 3417, 3365, 3053, 2924, 1603, 1582, 1445, 746 cm^{-1}. ^{1}H NMR: δ 8.09–8.05 (d, 1H, C_5–H, *J* = 7.76), 7.97–7.85 (m, 2H, C_2–, C_4–H), 7.77 (b s, 1H, N_9–H), 7.42–7.32 (m, 5H, C_6–, C_7–, C_3'–, C_4'–, C_5'–H), 6.90–6.73 (m, 3H, C_3–, C_2'–, C_6'–H), 5.69 (br s, 1H, C_1–NH), 2.45 (s, 3H, C_8–CH_3). ^{13}C NMR: δ 137.1 (C_1'), 134.8 (C_{9a}), 129.2 (C_{4a}), 129.1 (C_3'), 127.3 (C_5'), 126.0 (C_6), 125.2 (C_1), 121.3 (C_{8a}), 120.1 (C_3), 119.1 (C_5), 118.2 (C_6'), 117.1 (C_2'), 116.9 (C_4'), 115.9 (C_7), 112.9 (C_2), 110.9 (C_8), 107.1 (C_4), 106.7 (C_{5a}), 20.4 (C_8–CH_3). MS: *m/z* (%), 272 (M^+, 100), 256 (41), 205 (19), 195 (19), 180 (11), 168 (19), 152 (17), 128 (30), 77 (14). Anal. Calc. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.28. Found: C, 83.53; H, 5.89; N, 10.21%.

7-Methyl-1-(N-phenylamino)carbazole (**7c**): Dirty white powder (0.6 g, 44%), m.p. 172–173°C. IR: ν_{max} 3410, 3363, 3046, 2922, 1600, 1404, 798 cm^{-1}. ^{1}H NMR: δ 7.98–7.83 (m, 2H, C_2–, C_4–H), 7.79 (b s, 1H, N_9–H), 7.28–7.14 (m, 6H, C_5–, C_6–, C_8–, C_3'–, C_4'–, C_5'–H), 6.84–6.74 (m, 3H, C_3–, C_2'–, C_6'–H), 5.75 (b s, 1H, C_1–NH), 2.51 (s, 3H, C_7–CH_3). ^{13}C NMR: δ 137.6 (C_1'), 134.9 (C_{9a}), 129.2 (C_3'), 128.9 (C_{4a}), 128.1 (C_5'), 124.1 (C_1), 123.8 (C_7), 122.9 (C_{8a}), 119.8 (C_6), 119.5 (C_3), 119.2 (C_5), 118.3 (C_6'), 118.1 (C_4'), 117.9 (C_2'), 111.9 (C_2), 111.5 (C_8), 107.2 (C_4), 106.5 (C_{5a}), 24.9 (C_7–CH_3). MS: *m/z* (%) 272 (M^+, 100), 256 (42), 205 (17), 197 (21), 180 (19), 168 (16), 152 (14), 128 (24), 77 (10). Anal. Calc. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.28. Found: C, 83.74; H, 5.83; N, 10.24%.

1-(N-phenylamino)carbazole (**7d**): Dirty white solid (0.541 g, 42%); m.p. 143–145°C. IR: ν_{max} 3392, 3365, 3033, 2841, 1599, 1579, 1404, 755 cm^{-1}. ^{1}H NMR: δ 8.12–8.08 (m, 2H, C_2–, C_4–H), 7.92 (b s, 1H, N_9–H), 7.31–7.18 (m, 7H, C_5–, C_6–, C_7–, C_8–, C_3'–, C_4'–, C_5'–H), 6.90–6.74 (m, 3H, C_3–, C_2'–, C_6'–H), 5.78 (br. s, 1H, C_1–NH). ^{13}C NMR: δ 138.5 (C_1'), 134.7 (C_{9a}), 130.2 (C_{4a}), 129.2 (C_3'), 128.1 (C_5'), 125.6 (C_6), 125.2 (C_1), 121.9 (C_{8a}), 120.9 (C_3), 118.9 (C_6'), 118.5 (C_5), 117.3 (C_2'), 116.9 (C_4'), 114.9 (C_7), 111.8 (C_2), 111.5 (C_8), 107.0 (C_{5a}), 104.7 (C_4). MS: *m/z* (%) 258 (M^+, 100), 205 (11), 195 (18), 180 (17), 167 (11), 151 (10), 128 (24), 77 (9). Anal. Calc. for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.68; H, 5.48; N, 10.88%.

6-Chloro-1-(N-phenylamino)carbazole (**7e**): Dirty white solid (0.584 g, 40%); m.p. 152–154°C. IR: ν_{max} 3408, 3361, 2923, 2854, 1601, 1589, 1499, 748 cm^{-1}. ^{1}H NMR: δ 8.04 (b s, 1H, N_9–H), 7.96–7.84 (m, 2H, C_2–, C_4–H), 7.38–7.20 (m, 6H, C_5–, C_7–, C_8–, C_2'–, C_4'–, C_5'–H), 6.93–6.74 (m, 3H, C_3–, C_2'–, C_6'–H), 5.60 (b s, 1H, C_1–NH). ^{13}C NMR: δ 136.1 (C_1'), 135.9 (C_{9a}), 129.4 (C_{4a}), 129.3 (C_6), 128.1 (C_3'), 126.8 (C_5'), 125.8 (C_1), 123.1 (C_{8a}), 120.4 (C_3), 119.0 (C_5), 117.9 (C_6'), 117.7 (C_4'), 117.5 (C_2'), 114.8 (C_7), 112.3 (C_2), 110.2 (C_8), 107.2 (C_4), 106.2 (C_{5a}). MS: *m/z* (%) 294/292 (M^+, 17/57), 205 (15), 195 (21), 181 (17), 169 (13), 152 (19), 128 (16), 77 (8). Anal. Calc. for $C_{18}H_{13}ClN_2$: C, 73.85; H, 4.48; N, 9.56. Found: C, 73.81; H, 4.51; N, 9.50%.

13H-indolo[3,2-c]acridine (**8a–e**), *general procedure*

A 1-(*N*-phenylamino)carbazole (**7**, 1 mmol) was taken up in DMF (1.8 ml) and $POCl_3$ (4.2 ml) and kept at room temperature for 4 h. The reaction was monitored by TLC. After completion of the reaction the mixture was poured into crushed ice and extracted with chloroform. The organic solution was dried (Na_2SO_4). Removal of solvent gave a crude residue which was purified by column chromatography over silica gel, eluting with chloroform:methanol (98:2), to yield the corresponding 13*H*-indolo[3,2-*c*]acridine (**8**).

3-Methyl-13H-indolo[3,2-c]acridine (**8a**): Yellow amorphous solid (93 mg, 33%), m.p. 147–149°C. IR: ν_{max} 3417, 2930, 2781, 1665, 738 cm^{-1}. UV: λ_{max} (log ε) 225 (4.50), 247 (4.84), 285 (3.85), 296 (4.10), 313 (3.97), 328 (3.93), 338 nm (3.94). ^{1}H NMR: δ 8.80 (s, 1H, C_7–H), 8.65 (s, 1H, N_{13}–H), 8.26 (s, 1H, C_4–H), 8.08–7.05 (m, 8H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_2–, C_1–H), 2.50 (s, 3H, C_3–CH_3). ^{13}C NMR: δ 162.6 (C_{12a}), 161.5 (C_{11a}), 134.5 (C_7), 129.9 (C_{11}), 129.3 (C_{10}), 128.9 (C_3), 128.0 (C_9), 127.8 (C_8), 126.4 (C_6), 125.9 (C_{4b}), 125.3 (C_{7a}), 124.7 (C_5), 124.4 (C_{12b}), 124.3 (C_4), 120.3 (C_{6a}), 119.5 (C_{13a}), 116.4 (C_2), 111.1 (C_1), 110.9 (C_{4a}) and 29.7 (C_3–CH_3). MS: *m/z* (%) 282 (M^+, 65), 271 (23), 267 (17), 225 (19), 211 (28), 197 (21), 181 (12), 157 (21) 143 (18), 130 (19), 115 (15), 77 (12). Anal. Calc. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00, N, 9.92. Found: C: 84.98, H: 5.09, N: 9.84%.

1-Methyl-13H-indolo[3,2-c]acridine (**8b**): Yellow amorphous solid (0.127 g, 45%), m.p. 174–176°C. IR: ν_{max} 3276, 2922, 2358, 1672, 746 cm^{-1}. UV: λ_{max} (log ε) 229 (4.68), 254 (4.70) 288 (3.94), 299 (4.18), 318 (3.99), 338 (3.78), 349 nm (3.69). ^{1}H NMR: δ 8.79 (s, 1H, C_7–H), 8.68 (b s, 1H, N_{13}–H), 8.10–7.00 (m, 9H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_3–, C_2–H), 2.33 (s, 3H, C_1–CH_3). ^{13}C NMR: δ 161.9 (C_{12a}), 161.5 (C_{11a}), 134.5 (C_7), 129.8 (C_{11}), 129.3 (C_{10}), 128.0 (C_9), 127.8 (C_8), 126.4 (C_6), 125.9 (C_{4b}), 125.3 (C_{7a}), 124.4 (C_5), 124.3 (C_4), 123.3 (C_{12b}), 122.5 (C_3), 120.9 (C_{4a}), 120.3 (C_{6a}), 120.1 (C_{13a}), 118.4 (C_2), 111.2 (C_1), 23.7 (C_1–CH_3). MS: *m/z* (%) 282 (M^+, 41), 271 (23), 267 (17), 225 (19), 211 (28), 197 (21), 181 (12), 141 (18), 128(9), 115 (15), 77 (7). Anal. Calc. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.06; H, 5.03; N, 10.11%.

2-Methyl-13H-indolo[3,2-c]acridine (**8c**): Yellow amorphous solid (0.113 g, 40%), m.p. 104–105°C. IR: ν_{max} 3422, 2965, 2359, 1667, 743 cm^{-1}. UV: λ_{max} (log ε) 238 (4.64), 250 (4.85), 282 (3.87), 296 (4.05), 307 (3.98), 328 (3.59), 339 nm (3.54). ^{1}H NMR: δ 8.73 (s, 1H, C_7–H), 8.61 (b s, 1H, N_{13}–H), 8.31 (s, 1H, C_4–H), 8.18–6.65 (m, 8H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_3–, C_1–H), 2.45 (s, 3H, C_2–CH_3). ^{13}C NMR: δ 162.0 (C_{12a}), 161.9 (C_{11a}), 133.3 (C_7), 130.2 (C_{11}), 129.5 (C_{10}), 127.4 (C_9), 127.1 (C_8), 126.4(C_{7a}), 126.3 (C_6), 125.8 (C_{4b}), 125.4 (C_2), 125.1 (C_5), 124.1 (C_{12b}), 123.1 (C_3), 121.1 (C_{6a}), 120.2 (C_4), 120.0 (C_{13a}), 112.1 (C_1), 111.2 (C_{4a}), 27.1 (C_2–CH_3). MS: *m/z* (%) 282 (M^+, 58), 271 (26), 267 (24), 225 (12), 211 (34), 197 (27), 181 (12), 141 (17), 128 (10), 115 (15), 77 (8). Anal. Calc. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.08; H, 4.98; N, 9.89%.

13H-Indolo[3,2-c]acridine (**8d**): Yellow amorphous solid, (0.105 g, 39%), m.p. 155–156°C. IR: ν_{max} 3413, 2359, 1668, 1492, 746 cm^{-1}. UV, λ_{max} (log ε) 222 (4.43), 246 (4.65), 250 (4.48), 261 (4.32), 298 (4.26), 318 (3.99), 325 (3.96), 336 nm (3.96). ^{1}H NMR: δ 8.86 (s, 1H, C_7–H), 8.69 (s, 1H, N_{13}–H), 8.38–7.10 (m, 10H, C_{11}–, C_{10}–,

C_9–, C_8–, C_6–, C_5–, C_4–, C_3–, C_2–, C_1–H). ^{13}C NMR: δ 162.1 (C_{12a}), 161.1 (C_{11a}), 133.9 (C_7), 129.5 (C_{11}), 129.3 (C_{10}), 127.9 (C_9), 127.8 (C_8), 126.1 (C_{4b}), 125.8 (C_6), 125.3 (C_{7a}), 125.1 (C_{12b}), 124.9 (C_5), 124.4 (C_3), 122.3 (C_2), 120.3 (C_{6a}), 119.6 (C_{13a}), 119.4 (C_4), 110.8 (C_{4a}), 109.6 (C_1). MS: *m/z* (%) 268 (M^+, 60), 267 (17), 225 (12), 211 (21), 197 (32), 141 (12), 128 (9), 115 (15), 77 (7). Anal. Calc. for $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44. Found: C, 85.01; H, 4.49; N, 10.45%.

3-Chloro-13H-indolo[3,2-c]acridine (**8e**): Yellow amorphous solid (0.127 g, 42%), m.p. 164–167°C. IR: ν_{max} 3415, 2783, 2359, 1668, 1022, 748 cm^{-1}. UV, λ_{max} (log ε) 231 (4.61), 258 (4.72), 290 (3.96), 299 (4.18), 320 (4.01), 339 (3.75), 358 nm (3.72). ^{1}H NMR: δ 8.83 (s, 1H, C_7–H), 8.73 (s, 1H, N_{13}–H), 8.00–7.04 (m, 9H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_2–, C_1–H). ^{13}C NMR: δ 162.0 (C_{12a}), 159.5 (C_{11a}), 134.5 (C_7), 129.3 (C_{10}), 129.1 (C_{11}), 128.6 (C_3), 128.0 (C_9), 128.1 (C_8), 126.5 (C_6), 125.8 (C_{4b}), 125.3 (C_{7a}), 124.5 (C_{12b}), 124.4 (C_5), 121.6 (C_4), 121.1 (C_{6a}), 120.0 (C_{13a}), 111.4 (C_2), 110.8 (C_{4a}), 109.5 (C_{12}). MS: *m/z* (%) 304/302 (M^+, 19/58), 267 (21), 256 (13), 195 (21), 180 (12), 168 (13), 152 (19), 128 (16), 77 (8). Anal. Calc. for $C_{19}H_{11}ClN_2$: C, 75.38; H, 3.66; N, 9.25. Found: C, 75.19; H, 3.69; N, 9.23%.

Methylation of indolo[3,2-c]acridines (**2** and **8**), *general procedure*
A mixture of the 13*H*-indolo[3,2-*c*]acridine (1 mmol) methyl iodide (2 ml, 0.03 mol) and ignited potassium carbonate (0.55 g) in dry acetone (10 ml) was refluxed for *ca* 10 h. The reaction was monitored by TLC. After completion of the reaction the solvent was removed and the mixture was poured onto crushed ice and extracted with chloroform which was then dried (Na_2SO_4). The crude product after solvent removal was purified by column chromatography over silica gel using chloroform:methanol (98:2) to yield the corresponding 13-methylindolo[3,2-*c*]acridine (**9**, **11**).

3,13-Dimethyl-7-phenylindolo[3,2-c]acridine (**9a**): Pale yellow solid (0.164 g, 44%), m.p. 237–238°C. IR: ν_{max} 2963, 2360, 1651, 1577, 1414, 1261, 1095 cm^{-1}. UV, λ_{max} (log ε) 254 (4.58), 262 (4.11), 267 (3.46), 294 (4.80), 303 (3.67), 318 (3.46), 337 nm (3.97). ^{1}H NMR: δ 8.10–7.17 (m, 14H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_2–, C_1–, C_2'–, C_3'–C_4'–, C_5'–, and C_6'–H), 4.20 (s, 3H, N_{13}–CH_3), 2.66 (s, 3H, C_3–CH_3). Anal. Calc. for $C_{27}H_{20}N_2$: C: 86.85, H: 5.40, N: 7.54. Found: C: 86.91, H: 5.34, N: 7.51%.

1,13-Dimethyl-7-phenylindolo[3,2-c]acridine (**9b**): Yellow amorphous solid (0.178 g, 48%), m.p. >300°C. IR: ν_{max} 2910, 2347, 1679, 1549, 1430, 1280, 1089 cm^{-1}. UV, λ_{max} (log ε) 240 (4.47), 250 (4.17), 267 (4.84), 264 (3.66), 280 (4.17), 304 (3.66) 349 (3.76), 340 nm (3.98).^{1}H NMR: δ 8.10–7.17 (m, 14H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_2–, C_1–, C_2'–, C_3'–C_4'–, C_5'–, and C_6'–H), 4.14 (s, 3H, N_{13}–H), 2.58 (s, 3H, C_1–CH_3). Anal. Calc. for $C_{27}H_{20}N_2$: C: 86.85, H: 5.40, N: 7.54. Found: C: 86.88, H: 5.30, N: 7.56%.

3,13-Dimethylindolo[3,2-c]acridine (**11a**): Yellow amorphous solid (0.15 g, 51%), m.p. 291–294°C. IR: ν_{max} 2954, 2352, 1653, 1541, 1410, 1230, 1100 cm^{-1}. UV: λ_{max} (log ε) 224 (4.17), 245 (4.81), 289 (3.67), 318 (3.88), 327 (3.49), 337 (3.94), 341 nm (3.21). ^{1}H NMR: δ 8.82 (s, 1H, C_7–H), 8.40–7.30 (m, 9H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_2–, C_1–H), 3.80 (s, 3H, N_{13}–CH_3) 2.59 (s, 3H, C_3–CH_3). Anal. Calc. for $C_{21}H_{16}N_2$: C: 85.10, H: 5.42, N: 9.37; Found: C: 85.04, H: 5.46, N: 9.39%.

1,13-Dimethylindolo[3,2-c]acridine (**11b**): Yellow amorphous solid (0.16 g, 53%), m.p. >300°C. IR: ν_{max} 2985, 2367, 1644, 1587, 1421, 1180, 1046 cm^{-1}. UV, λ_{max} (log ε) 229 (4.60), 250 (4.10) 284 (3.67), 280 (4.34), 307 (3.84), 324 (3.16), 354 nm (3.89). ^{1}H NMR: δ 8.88 (s, 1H, C_7–H), 8.35–7.43 (m, 9H, C_{11}–, C_{10}–, C_9–, C_8–, C_6–, C_5–, C_4–, C_2–, C_1–H), 3.73 (s, 3H, N_{13}–CH_3) 2.63 (s, 3H, C_1–CH_3). Anal. Calc. for $C_{21}H_{16}N_2$: C: 85.10, H: 5.42, N: 9.37. Found: C: 84.94, H: 5.40, N: 9.29%.

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