Syntheses of methyl 4,5-dihydro-2*H*-pyrazolo[3,4-*a*]carbazole-3-carboxylates

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The syntheses of methyl 4,5-dihydro-2*H*-pyrazolo[3,4-*a*]carbazole-3-carboxylates (**4a–e**) from 1-oxo-1,2,3,4-tetrahydrocarbazoles (**1a–e**) using the intermediates, methyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetates (**3a–e**) are discussed. The formation of the end products was characterised using spectral and analytical techniques.

Keywords: methyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate, (1,2,3,4-tetrahydrocarbazol-1-ylidene)-hydrazine, methyl 4,5-dihydro-2*H*-pyrazolo-[3,4-*a*]carbazole-3-carboxylate, hydrazine hydrate, semicarbazide hydrochloride

The emerging importance of the various strategies applied to prepare carbazoles and its derivatives is due to their diverse pharmacological properties.[1-3] Development of new methods for the synthesis of functionalised carbazoles, in particular, is attracting organic chemists due to the discovery of many carbazole alkaloids with varied pharmacological properties.[4-8] Identification of promising antineoplastic activity of ellipticine, tetracyclic compounds of the pyridocarbazole type, have stimulated considerable interest in the field of fused systems.[9] In addition, pyrido[3,4-*b*]carbazoles were reported to elicit anti-HIV properties.[10] In this context, we are planning to utilise an intermediate, ethyl 1-oxo-1,2,3,4-tetrahydrocarbazole-2-glyoxalate, to construct newer fused carbazoles.[11,12] The potential precursors, 1-oxo-1,2,3,4-tetrahydrocarbazoles (**1a–e**) prepared in our laboratory have opened new avenues for the synthesis of highly functionalised carbazole derivatives *viz.*, mukonine isomers,[13] oxazolocarbazoles,[14] girinimbine isomers,[15] 2,2-dimethyl-2*H*-pyranocarbazoles,[16] indolo coumarins,[17] carbazolyloxypropanolamines,[18] 3-acetyl-2-hydroxy-1-N,N-diacetylamino carbazoles,[19] benzocarbazoles[20] and pyrazinocarbazoles[21] in excellent yields.

1-Oxo-1,2,3,4-tetrahydrocarbazole (**1a–e**) was treated with diethyl oxalate in the presence of sodium methoxide. When 6-methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (**1a**) was stirred at 0°C with diethyl oxalate in presence of sodium methoxide for 3 h, it yielded a yellow amorphous solid, melted at 162–164°C. Its IR spectrum showed N–H and enolic O–H stretching as a broad band at 3320–3290 cm^{-1}, the ester carbonyl stretching at 1728 cm^{-1} and the ring carbonyl stretching at 1641 cm^{-1}. Its ^{1}H NMR spectrum in $CDCl_3$ showed the following peaks. A one proton singlet at δ 14.81 was due to enolic proton of C_2 =C(O**H**)COOCH$_3$. The enol form and keto form appeared in the ratio of 13:12. A one proton broad singlet at δ 8.75 was due to N_9–H. A one proton singlet at δ 7.43 was due to C_5 proton. A one proton multiplet at δ 7.34–7.26 was due to olefinic proton at C_2 (keto form). A two proton multiplet appeared at δ 7.25–7.16 was due to C_7 and C_8 protons. A three proton singlet at δ 3.93 was due to –OCH$_3$ group. A two proton multiplet centred at δ 3.25 was due to two protons at C_4. A two proton multiplet at δ 3.04–2.95 was due to two protons at C_3. A three proton singlet at δ 2.45 was due to the C_6-methyl group. Its mass spectrum showed the molecular peak at *m/z* 285 (48%). The ^{1}H NMR spectrum clearly indicated the absence of –OCH$_2$CH$_3$ group and the presence of –OCH$_3$ group. Thus, we have concluded that trans esterification reaction has been taking place between the methoxy group of sodium methoxide and the ethoxy group of diethyl oxalate. Our conclusion is well supported by its mass spectrum. The molecular ion peak appeared at *m/z* (%): 285 (46) instead of 299. The major fragments appeared at *m/z* (%): 226 (100), 198 (79), 170 (36), 168 (20), 154 (26), 143 (22) and 115 (24). The elemental analysis was also in good agreement with the calculated value. All these spectral and analytical details attest the compound as methyl 2-(6-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3a**). Therefore, in order to confirm the aforesaid trans esterification reaction we carried out the same reaction in presence of sodium ethoxide, yielded a green solid mass. Its melting point was 155–157°C. Its IR spectrum showed O–H and N–H stretchings as a strong band at 3315 cm^{-1}, the ester carbonyl stretching at 1728 cm^{-1} and the ring carbonyl stretching at 1642 cm^{-1}. Its ^{1}H NMR spectrum in $CDCl_3$ showed a one proton singlet at δ 14.82 was due to enolic proton at C_2 (enolic form- 100%). A one proton broad singlet at δ 8.87 was due to N_9–H. A one proton singlet at δ 7.43 was due to C_5 proton. A one proton doublet at δ 7.34–7.29 (J = 8.5 Hz) was due to C_8 proton. A one proton doublet of doublet appeared at δ 7.26–7.20 (J_{ortho} = 8.5 Hz; J_{meta} = 1.4 Hz) was due to C_7 proton. A two proton quartet appeared at δ 4.44–4.35 (J = 7.1 Hz) was due to –OC**H$_2$** CH$_3$ proton. A two proton multiplet at δ 3.27–3.20 was due to the two proton at C_4. A two proton multiplet appeared at δ 3.04–2.95 was due to two protons at C_3. A three proton singlet at δ 2.45 was due to C_6-methyl protons. A three proton triplet at δ 1.46–1.38 (J = 7.1 Hz) was due to –CH$_2$C**H$_3$**. The molecular ion peak appeared at *m/z* (%): 299 (46). The other fragments appeared at *m/z* (%): 285 (85), 227 (20), 198 (100), 197 (22), 170 (39), 154 (22) and 115 (20). The spectral and analytical results revealed the compound as ethyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**2a**).

Our interest in such reaction further stimulated by the possibility of obtaining methyl 4,5-dihydro-2*H*-pyrazolo[3,4-*a*] carbazole-3-carboxylate (**4**) from methyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3**), we treated methyl 2-(6-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3a**) with hydrazine hydrate in ethanol for 3 h to yield a brown precipitate melted at 162–164°C. Its IR spectrum showed a band at 3300–3230 cm^{-1} was due to three N–H stretchings. A sharp stretching at 1591 cm^{-1} was due to C=N stretching. Its ^{1}H NMR spectrum in $CDCl_3$ showed a one proton broad singlet at δ 8.50 was due to N_9–H. A one proton singlet at δ 7.30 was due to C_5 proton. A one proton doublet at δ 7.23–7.17 (J = 8.1 Hz) was due to C_8 proton. A one proton doublet appeared at δ 7.04–6.98 (J = 8.1 Hz) was due to C_7 proton. A two proton broad singlet at δ 5.21 was due to –NN**H$_2$** protons at C_1. A two proton multiplet at δ 2.85–2.75 was due to two protons at C_2. A two proton multiplet appeared at δ 2.56–2.49 was due to two protons at C_2. A three proton singlet at δ 2.43 was due to C_6-methyl protons. A two proton multiplet centred at δ 2.14–2.02 was due to two protons at C_3. The ^{13}C NMR spectrum in $CDCl_3$ exhibited the presence of thirteen carbon atoms, viz., δ 143.73 (C_1), 135.13 (C_{8a}), 131.72 (C_{5a}), 128.61 (C_6), 127.45 (C_7), 124.93 (C_{9a}), 118.65 (C_5),

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116.12 (C_{4a}), 110.73 (C_8), 22.77 (C_2), 23.03 (C_3), 21.42 (C_4) and 20.61 (C_6-CH_3). The molecular ion peak appeared at *m/z* (%) M^+ 213 (100). The other fragments appeared at *m/z* (%): 199 (37), 183 (68), 182 (80), 181 (64), 180 (52), 168 (40) and 167 (58). All these spectral results afforded that the product realized was not in the expected grounds and characterised as (6-methyl-1,2,3,4-tetrahydrocarbazol-1-ylidene)-hydrazine (**5a**). Similar types of products (**5b–e**) were derived with other carbazole derivatives (**1b–e**, Scheme 1).The formation of the product is also well defended from the literature.[22]

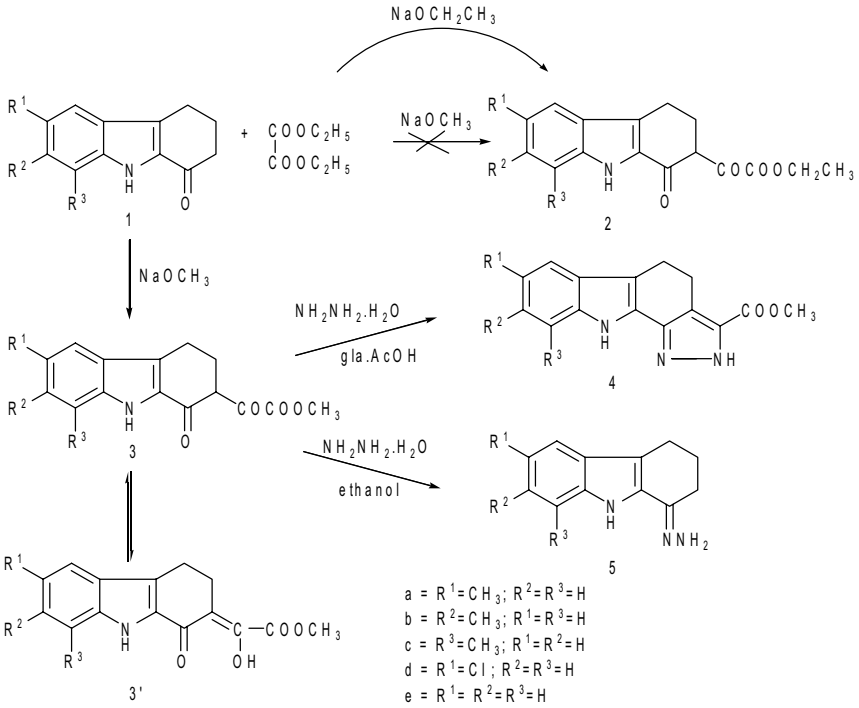
On scrutinising the mechanism, this revealed that the basic condition played a major role to knock out the chain carbonyl moiety over cyclisation. In view of the encouraging results obtained in the above reaction under basic condition, it was considered obligatory to extend the same reaction under acidic condition. We carried out the reaction of methyl 2-(6-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3a**) with hydrazine hydrate in glacial acetic acid at 120°C for 1 h. It yielded a spongy yellow precipitate upon purification by column chromatography over silica gel using petroleum ether: ethyl acetate (85:15) as eluant. It melted at 255–258°C. Its IR spectrum showed peaks at 3410 and 3328 cm^{-1} which were due to two N–H stretchings, a sharp stretching at 1714 cm^{-1} was due to ester carbonyl stretching and the C=N stretching appeared at 1599 cm^{-1}. Its ^{1}H NMR spectrum in DMSO-D_6 showed two each one proton broad singlets at δ 13.56 and δ 11.37 were due to N_2–H and N_{10}–H respectively. A one proton singlet at δ 7.24 was due to C_6 proton. A one proton doublet at δ 7.23–7.17 (J = 8.0 Hz) was due to C_9 proton. A one proton doublet appeared at δ 6.95–6.84 (J = 8.0 Hz) was due to C_8 proton. A three proton singlet at δ 3.86 was due to –OCH_3 group. A two proton multiplet appeared at δ 3.09–3.00 was due to two protons at C_5. A two proton multiplet at δ 2.96–2.87 was due to two protons at C_4. A three proton singlet δ 2.36 was due to C_7-methyl protons. The ^{13}C NMR in DMSO-D_6 showed peaks for 16 carbons, *viz*, δ 159.97 (C_3–C=O), 144.10 (C_3), 135.30 (C_{1a}), 135.22 (C_{9a}), 128.73 (C_{6a}), 127.40 (C_{10a}), 126.87 (C_7), 123.02 (C_6), 120.28 (C_8), 117.85 (C_{3a}), 111.31 (C_{5a}), 110.46 (C_9), 51.81 (C_3-OCH_3), 21.22 (C_4), 20.05 (C_5) and 19.58 (C_7–CH_3). The molecular ion peak appeared at *m/z* (%): M^+ 281 (100). The other fragments appeared at *m/z* (%): 249 (56), 193 (91), 192 (34), 191 (26), 143 (22) and 115 (24). All the spectral and analytical results suggested two possible structures **4a** and **4a'** as shown in Scheme 2. The structure **4a'** was ruled out on the basis of the following points:

(i) In the literature[23] the ^{1}H NMR spectrum of pyrazolo [3,4-*a*]carbazole without a substituent at C_3 showed N_2–H as a broad singlet at δ 12.45. But in our case, the N_2–H appeared as a broad singlet at δ 13.56. This was due to the intra molecular hydrogen bonding between N_2–H and the carbomethoxy group at C_3. Thus, the intra molecular hydrogen bonding shifts the N_2–H peak further to the down field.

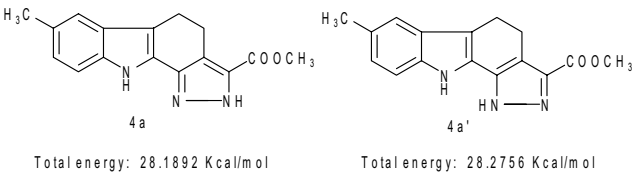
(ii). Further support in favour of the structure **4a** over **4a'** (Scheme 2) was obtained from the molecular mechanics calculations (MM2), The steric energy calculated for structures **4a** and **4a'** are 28.1892 kcal/mol and 28.2756 kcal/mol respectively. The steric energy for structure **4a'** is higher than that for structure **4a**. Therefore, structure **4a** is preferred over structure **4a'**.

(iii) The closer examination of reaction mechanism revealed that the structure **4a** is formed through the intermediate with extending conjugation. Whereas formation of **4a'** does not go through the intermediate with extending conjugation.

All these discussions supported the realised product as methyl 4,5-dihydro-7-methyl-2*H*-pyrazolo[3,4-*a*]carbazole-3-carboxylate (**4a**). Our observation in the above reaction further stimulated us towards the reaction of methyl 2-(6-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3a**) with semicarbazide hydrochloride in glacial acetic acid, in an anticipation to get either methyl 6,7-dihydro-2-hydroxy-9-methyl-4*H*-[1,2,4]triazepino[5,6-*a*]carbazole-5-carboxylate (**6a**) and/or methyl 1-carbamoyl-4,5-dihydro-7-methyl 1H-pyrazolo[3,4-*a*]carbazole-3-carboxylate (**7a**) surprisingly this reaction ended up with the formation of methyl 4,5-dihydro-7-methyl-2*H*-pyrazolo[3,4-*a*]carbazole-3-carboxylate (**4a**), which was the same, we realised in the reaction of hydrazine hydrate (Scheme 3). It is confirmed by mixed m.p., super impossible IR, ^{1}H NMR and mass spectra. The elemental



Scheme 1



Scheme 2

analysis agreed well with our observation. All these reactions were generalised for all carbazole derivatives (Scheme 1).

Conclusion

In conclusion, a novel one-pot synthesis of methyl 4,5-dihydro-2*H*-pyrazolo-[3,4-*a*]carbazole-3-carboxylate (**4**) was developed in moderate yields from the reaction of methyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3**) with hydrazine under acidic conditions. It is noteworthy that a similar type of product was obtained from methyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3**) and semicarbazide hydrochloride. It is conceivable that the compounds described herein may have important applications in medicinal and synthetic organic chemistry.

Experimental

Melting points were determined by using Mettler FP 51 apparatus (Mettler Instruments, Switzerland) and were uncorrected. IR spectra were recorded using KBr on a Shimadzu FTIR-8201PC spectrophotometer (Shimadzu, Japan). ^{1}H NMR spectra were recorded in $CDCl_3$ and DMSO-D_6 on a Varian AMX 400 FT-NMR (Varian Australia, Australia) using tetramethylsilane as internal standard. Mass spectra were recorded on Jeol-JMS-D-300 mass spectrometer (70 eV) (Jeol, Japan). Micro analyses were done on a Vario EL III Model CHNS analyser (Vario, Germany). The purity of the products was tested by TLC using glass plates coated with silica gel G (Hi Media Laboratories, India) and petroleum ether and ethyl acetate (85:15) as the developing solvents. The molecular modeling performed using MM2 by Chem Draw Ultra 7.0.0.

General procedure for the preparation of methyl 2-(1-oxo-2,3,4,9-tetrahydro-1H-carbazol-2-yl)-2-oxoacetate (**3a–e**)

The appropriate 1-oxo-1,2,3,4-tetrahydrocarbazole (**1**, 0.001 mol) in methanol (10 ml) was added diethyl oxalate (1 ml). This was added drop by drop to the stirred solution of sodium methoxide (1 g of sodium in 10 ml methanol) in an ice bath. The stirring was continued for 3–4 h. The reaction was monitored by TLC. After the completion of the reaction the solvent was removed and the residue obtained was poured into crushed ice, and neutralised with 1:1 HCl. The precipitate which separated was filtered off, washed with water and dried. It was pure enough for further reactions.

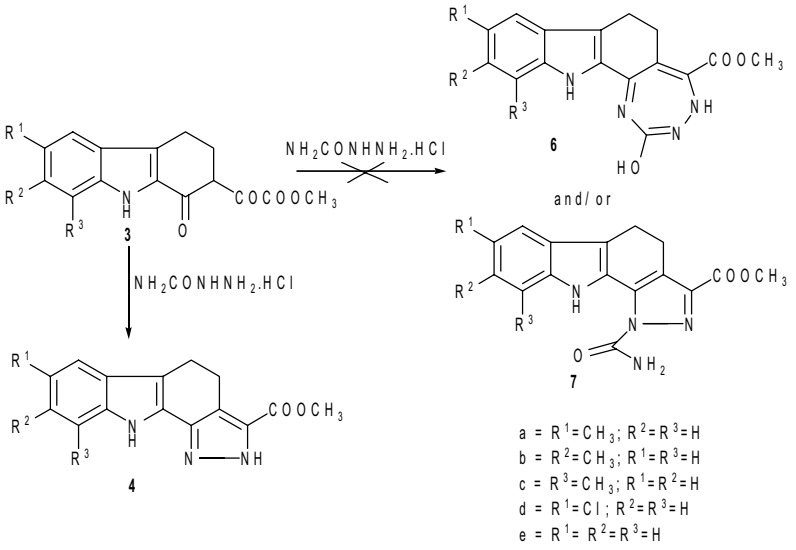
Methyl 2-(6-methyl-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-2-yl)-2-oxoacetate (**3a**): Yellow amorphous solid recrystallised from ethanol; Yield 82%; m.p. 162–164°C; Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.90; Found: C, 67.00; H, 5.23; N, 4.82%; IR: υ_{max}, KBr, 3320–3290, 2922, 1728, 1641, 1609, 1258 cm^{-1}; ^{1}H NMR: δ, $CDCl_3$, 14.81 (s, 1H, enolic proton at C_2, enol: keto form–13:12), 8.75 (b s, 1H, N_9–H), 7.43 (s, 1H, C_5–H), 7.34–7.26 (m, 1H, C_2–H of keto form), 7.25–7.16 (m, 2H, C_7–,C_8 –H), 3.93 (s, 3H, –OCH_3), 3.28–3.22 (m, 2H, C_4–H_2), 3.04–2.95 (m, 2H, C_3–H_2), 2.45 (s, 3H, C_6–CH_3); MS: *m/z* (%), M$^+$ 285 (46), 226 (100), 198 (79), 170 (36), 168 (20), 154 (26), 143 (22), 115 (24).

Methyl 2-(7-methyl-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-2-yl)-2-oxoacetate (**3b**): Yellow crystalline powder recrystallised from ethanol; Yield 83%; m.p. 167–169°C; Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.90; Found: C, 67.88; H, 5.26; N, 4.84%; IR: υ_{max}, KBr, 3315, 2928, 1728, 1640, 1585, 1258 cm^{-1}; ^{1}H NMR: δ, $CDCl_3$, 14.81 (s, 1H, enolic proton at C_2, enol form–100%), 8.93 (b s, 1H, N_9–H), 7.28–6.82 (m, 3H, C_5–, C_6–, C_8–H), 3.93 (s, 3H, –OCH_3), 3.30–3.22 (m, 2H, C_4–H_2), 3.04–2.96 (m, 2H, C_3–H_2), 2.67 (s, 3H, C_7–CH_3); MS: *m/z* (%), M$^+$ 285 (40), 227 (32), 226 (100), 198 (65), 154 (26), 145 (35).

Methyl 2-(8-methyl-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-2-yl)-2-oxoacetate (**3c**): Yellow crystalline powder from ethanol; Yield 77%; m.p. 173–176°C; Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.90; Found: C, 67.38; H, 5.27; N, 4.94%. IR: υ_{max}, KBr, 3213, 2924, 1728, 1640, 1611, 1261 cm^{-1}; ^{1}H NMR: δ, $CDCl_3$, 14.89 (s, 1H, enolic proton at C_2, enol form–100%), 8.73 (b s, 1H, N_9–H), 7.54–7.47 (d, 1H, C_5–H, J = 8.0 Hz), 7.22–7.17 (d, 1H, C_7–H, J = 7.0 Hz), 7.12–7.04 (m, 1H, C_6–H), 3.93 (s, 3H, –OCH_3), 3.29–3.21 (m, 2H, C_4–H_2), 3.08–2.98 (m, 2H, C_3–H_2), 2.50 (s, 3H, C_8–CH_3); MS: *m/z* (%), M$^+$ 285 (48), 226 (100), 198 (78), 170 (34), 168 (20), 154 (22), 115 (20).

Methyl 2-(6-chloro-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-2-yl)-2-oxoacetate (**3d**): Yellow crystalline powder from ethanol; Yield 82%; m.p. 169–171°C; Anal. Calcd. for $C_{15}H_{12}ClNO_4$: C, 58.93; H, 3.96; N, 4.58; Found: C, 58.60; H, 3.88; N, 4.48%; IR: υ_{max}, KBr, 3310, 2870, 1726, 1640, 1611, 1261 cm^{-1}; ^{1}H NMR: δ, $CDCl_3$, 14.69 (s, 1H, enolic proton at C_2, enol: keto form–4: 1), 9.19 (b s, 1H, N_9–H), 7.63 (s, 1H, C_5–H), 7.39–7.28 (m, 3H, C_2–H of keto form, C_7–, C_8–H), 3.93 (s, 3H, –OCH_3), 3.28–3.20 (m, 2H, C_4–H_2), 3.02–2.95 (m, 2H, C_3–H_2); MS: *m/z* (%), M$^+$ 305 (40), 246 (100), 245 (34), 218 (60), 203 (20), 190 (47), 188 (30), 163 (22).

Methyl 2-(1-oxo-2,3,4,9-tetrahydro-1H-carbazol-2-yl)-2-oxoacetate (**3e**): Yellow crystalline powder from ethanol; Yield 78%; m.p. 148–150°C; Anal. Calcd. for $C_{15}H_{13}NO_4$: C, 67.36; H, 5.30; N, 4.90; Found: C, 67.00; H, 5.23; N, 4.82%; IR: υ_{max}, KBr: 3310, 2870, 1728, 1641, 1609, 1257 cm^{-1}; ^{1}H NMR: δ, $CDCl_3$: 14.78 (s, 1H, enolic proton at C_2, (enol: keto form–7: 3)), 8.87 (b s, 1H, N_9–H), 7.70–7.64 (d, 1H, C_8–H, J = 8.0 Hz), 7.46–7.13 (m, 4H, C_2–H of keto form, C_5–, C_6–C_7–H), 3.93 (s, 3H, –OCH_3), 3.30–3.24 (m, 2H,



Scheme 3

C_4–H_2), 3.08–3.01–(m, 2H, C_3–H_2), MS: *m/z* (%), M^+ 271 (38), 212 (100), 211 (22), 169 (32), 156 (56), 115 (46).

Ethyl 2-(6-methyl1-oxo-2,3,4,9-tetrahydro-1H-carbazol-2-yl)-2-oxoacetate (**2a**): Greenish crystalline powder from ethanol; Yield 61%; m.p. 155–157°C; Anal. Calcd. for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.72; N, 4.68; Found: C, 67.67; H, 5.62; N, 4.58%. IR: υ_{max}, KBr, 3315, 2927, 1728, 1642, 1609, 1258 cm^{-1}; ^1H NMR: δ, $CDCl_3$, 14.82 (s, 1H, enolic proton at C_2, enol form–100%), 8.87 (b s, 1H, N_9–H), 7.43 (s, 1H, C_5–H), 7.34–7.29 (d, 1H, C_8–H, *J* = 8.5 Hz), 7.26–7.20 (d, 1H, C_7 –H, *J* = 8.5 Hz), 4.44–4.35 (q, 2H, –OC**H$_2$**CH_3, *J* = 7.1 Hz), 3.27–3.20 (m, 2H, C_4–H_2), 3.04–2.95 (m, 2H, C_3–H_2), 2.45 (s, 3H, C_6–CH_3), 1.46–1.38 (t, 3H, –CH_2C**H$_3$**, *J* = 7.1 Hz); MS: *m/z* (%), M^+ 299 (46), 285 (85), 227 (20), 198 (100), 197 (22), 170 (39), 154 (22), 115 (20).

General procedure for the preparation of (1,2,3,4-tetrahydrocarbazol-1-ylidene)hydrazine (**5a–e**)

The appropriate methyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3**, 0.001 mol) in ethanol (10 ml) was added hydrazine hydrate (0.002 mol) and refluxed on a steam bath for 2–4 h. The reaction was monitored by TLC. After the completion of the reaction the solvent was removed and the residue obtained was poured into crushed ice. The precipitate was filtered, washed with water and dried. It was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (95: 5) as eluant.

(6-Methyl-1,2,3,4-tetrahydrocarbazol-1-ylidene)hydrazine (**5a**): Brown amorphous solid; Yield 56%; m.p. 162–164°C; Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70; Found: C, 73.01; H, 7.30; N, 19.64%; IR: υ_{max}, KBr, 3300–3230, 2923, 2858, 2332, 1591, 1481, 1327 cm^{-1}; ^1H NMR: δ, $CDCl_3$, 8.50 (b s, 1H, N_9–H), 7.30 (s, 1H, C_5–H), 7.23–7.17 (d, 1H, C_8 –H, *J* = 8.1 Hz), 7.04–6.98 (d, 1H, C_7 –H, *J* = 8.1 Hz), 5.21 (b s, 2H, –NNH_2), 2.85–2.75 (m, 2H, C_4–H_2), 2.56–2.49 (m, 2H, C_2–H_2), 2.43 (s, 3H, C_6–CH_3), 2.14–2.02 (m, 2H, C_3–H_2); ^{13}C NMR: δ, $CDCl_3$, 143.73 (C_1), 135.13 (C_{8a}), 131.72 (C_{5a}), 128.61 (C_6), 127.45 (C_7), 124.93 (C_{9a}), 118.65 (C_5), 116.12 (C_{4a}), 110.73 (C_8), 22.77 (C_2), 23.03 (C_3), 21.42 (C_4), 20.61 (C_6–CH_3); MS: *m/z* (%), M^+ 213 (100), 199 (37), 183 (68), 182 (80), 181 (64), 180 (52), 168 (40), 167 (58).

(7-Methyl-1,2,3,4-tetrahydrocarbazol-1-ylidene)hydrazine (**5b**): Brown amorphous solid; Yield 58%; m.p. 158–160°C; Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70; Found: C, 73.21; H, 7.36; N, 19.52%; IR: υ_{max}, KBr, 3400–3308, 3198, 2927, 1597, 1331 cm^{-1}; ^1H NMR: δ, $CDCl_3$, 9.21 (b s, 1H, N_9–H), 7.37 (s, 1H, C_8–H), 7.10–7.01 (m, 2H, C_5–, C_6–H), 6.16 (b s, 2H, –NNH_2), 2.72–2.58 (m, 4H, C_4–H_2, C_2–H_2), 2.12–2.00 (m, 2H, C_3–H_2); ^{13}C NMR: δ, $CDCl_3$, 145.43 (C_1), 136.98 (C_{8a}), 132.43 (C_{5a}), 126.48 (C_7), 126.14 (C_6), 125.32 (C_{9a}), 119.87 (C_5), 114.48 (C_{4a}), 111.43 (C_8), 24.05 (C_2), 22.98 (C_3), 22.03 (C_4), 21.33 (C_7–CH_3); MS: *m/z* (%), M^+ 213 (100), 199 (40), 183 (45), 182 (80), 181 (54), 180 (60), 168 (40), 167 (50).

(8-Methyl-1,2,3,4-tetrahydrocarbazol-1-ylidene)hydrazine (**5c**): Brown amorphous solid; Yield 50%; m.p. 170–172°C; Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70; Found: C, 73.01; H, 7.30; N, 19.64%; IR: υ_{max}, KBr, 3360, 3240, 2918, 2852, 1591, 1421, 1330 cm^{-1}; ^1H NMR: δ, $CDCl_3$, 8.41 (b s, 1H, N_9–H), 7.40–6.94 (m, 3H, C_5–, C_6–,C_7–H), 5.22 (b s, 2H, –NNH_2), 2.86–2.78 (m, 2H, C_4–H_2), 2.58–2.51 (m, 2H, C_2–H_2), 2.46 (s, 3H, C_8–CH_3), 2.13–2.03 (m, 2H, C_3–H_2); ^{13}C NMR: δ, $CDCl_3$, 143.47 (C_1), 138.48 (C_{8a}), 130.76 (C_{5a}), 127.47 (C_8), 126.31 (C_7), 125.43 (C_6), 124.73 (C_{9a}) 118.48 (C_5), 116.30 (C_{4a}), 110.73 (C_8), 25.49 (C_2), 23.29 (C_3), 21.47 (C_4), 21.07 (C_8–CH_3); MS: *m/z* (%), M^+ 213 (100), 183 (60), 182 (84), 181 (62), 180 (60), 168 (50), 167 (52).

(6-Chloro-1,2,3,4-tetrahydrocarbazol-1-ylidene)hydrazine (**5d**): Brown amorphous solid; Yield 51%; m.p. 147–149°C; Anal. Calcd. for $C_{12}H_{12}ClN_3$: C, 61.67; H, 5.18; N, 17.98; Found: C, 61.76; H, 5.24; N, 17.79%; IR: υ_{max}, KBr, 3450–3100, 2921, 1592, 1475, 1324 cm^{-1}; ^1H NMR: δ, $CDCl_3$, 8.72 (b s, 1H, N_9–H), 7.46 (s, 1H, C_5–H), 7.22–7.16 (d, 1H, C_8 –H, *J* = 8.6 Hz), 7.13–7.05 (d, 1H, C_7 –H, J_{ortho} = 8.6 Hz; J_{meta} = 1.7 Hz), 5.28 (b s, 2H, –NNH_2), 2.81–2.72 (m, 2H, C_4–H_2), 2.57–2.44 (m, 2H, C_2–H_2), 2.13–2.00 (m, 2H, C_3–H_2); ^{13}C NMR: δ, $CDCl_3$, 144.87 (C_1), 136.13 (C_{8a}), 132.99 (C_{5a}), 132.48 (C_6), 126.48 (C_7), 125.87 (C_{9a}), 120.60 (C_5), 117.87 (C_{4a}), 112.48 (C_8), 22.04 (C_2), 21.48 (C_3), 21.48 (C_4); MS: *m/z* (%), M^+ 233 (100), 219 (45), 203 (70), 202 (65), 201 (48), 198 (40), 187 (45).

(1,2,3,4-Tetrahydrocarbazol-1-ylidene)hydrazine (**5e**): Brown amorphous solid; Yield 64%; m.p. 141–143°C; Anal. Calcd. for $C_{12}H_{13}N_3$: C, 73.33; H, 6.58; N, 21.09; Found: C, 73.01; H, 6.60; N, 21.00%; IR: υ_{max}, KBr, 3307, 3290, 3194, 2852, 1597, 1331 cm^{-1}; ^1H NMR: δ, $CDCl_3$, 8.67 (b s, 1H, N_9–H), 7.53–7.49 (d, 1H, C_8–H, *J* = 7.8 Hz), 7.40–7.35 (d, 1H, C_5 –H, *J* = 8.1 Hz), 7.14–7.02 (m, 2H, C_6–, C_7–H), 5.24 (b s, 2H, –NNH_2), 2.86–2.76 (m, 2H, C_4–H_2), 2.58–2.47 (m, 2H, C_2–H_2), 2.18–2.01 (m, 2H, C_3–H_2); ^{13}C NMR: δ, $CDCl_3$, 146.48 (C_1), 134.87 (C_{8a}), 130.68 (C_{5a}), 127.45 (C_7), 127.00 (C_6), 123.48 (C_{9a}), 119.48 (C_5), 116.97 (C_{4a}), 113.78 (C_8), 22.04 (C_2), 21.67 (C_3), 21.07 (C_4); MS: *m/z* (%), M^+ 199 (100), 169 (68), 168 (80), 167 (64), 166 (48), 155 (38), 154 (34).

General procedure for the preparation of methyl 4,5-dihydro-2H-pyrazolo-[3,4-a]carbazole-3-carboxylate (**4a–e**)

The appropriate methyl 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)-2-oxoacetate (**3**, 0.001 mol) in glacial acetic acid (15 ml) was added hydrazine hydrate (0.002 mol)/semicarbazide hydrochloride (0.002 mol) and refluxed on oil bath for 1 h. The reaction was monitored by TLC. After the completion of the reaction it was poured into crushed ice. The precipitate was filtered, washed with water and dried. It was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (85: 15) as eluant.

Methyl 4,5-dihydro-7-methyl-2H-pyrazolo[3,4-a]carbazole-3-carboxylate (**4a**): Yellow spongy mass; Yield 65%; m.p. 255–258°C; Anal. Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.37; N, 14.94; Found: C, 68.20; H, 5.44; N, 14.88%; IR: υ_{max}, KBr, 3410, 3328, 2922, 1714, 1599, 1438, 1310, cm^{-1}; ^1H NMR: δ, DMSO–D_6, 13.56 (b s, 1H, N_2–H), 11.37 (b s, 1H, N_{10}–H), 7.24 (s, 1H, C_6–H), 7.23–7.17 (d, 1H, C_9–H, *J* = 8.0 Hz), 6.95–6.84 (d, 1H, C_8 –H, *J* = 8.0 Hz), 3.86 (s, 3H, –OCH_3), 3.09–3.00 (m, 2H, C_5–H_2), 2.96–2.87 (m, 2H, C_4–H_2), 2.36 (s, 3H, C_7–CH_3); ^{13}C NMR: δ, DMSO–D_6, 159.97 (C_3–C=O), 144.10 (C_3), 135.30 (C_{1a}), 135.22 (C_{9a}), 128.73 (C_{6a}), 127.40 (C_{10a}), 126.87 (C_7), 123.02 (C_6), 120.28 (C_8), 117.85 (C_{3a}), 111.31 (C_{5a}), 110.46 (C_9), 51.81 (C_3–OCH_3), 21.22 (C_4), 20.05 (C_5), 19.58 (C_7–CH_3); MS: *m/z* (%), M^+ 281 (100), 249 (56), 193 (91), 192 (34), 191 (26), 143 (22), 115 (24).

Methyl 4,5-dihydro-8-methyl-2H-pyrazolo[3,4-a]carbazole-3-carboxylate (**4b**): Pale yellow spongy mass; Yield 58%; m.p. 250–252°C; Anal. Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.37; N, 14.94; Found: C, 68.40; H, 5.44; N, 14.82%; IR: υ_{max}, KBr, 3432, 3313, 1701, 1600, 1437, 1301 cm^{-1}; ^1H NMR: δ, DMSO–D_6, 13.74 (b s, 1H, N_2–H), 11.17 (b s, 1H, N_{10}–H), 7.53 (s, 1H, C_9–H), 7.10–6.99 (m, 2H, C_6–,C_7–H), 3.95 (s, 3H, –OCH_3), 3.10–2.89 (m, 4H, C_4–H_2, C_5–H_2), 2.49 (s, 3H, C_8–CH_3); ^{13}C NMR: δ, DMSO–D_6, 162.22 (C_3–C=O), 146.73 (C_3), 134.40 (C_{1a}), 133.38 (C_{9a}), 129.43 (C_{6a}), 128.47 (C_{10a}), 124.87 (C_8),121.12 (C_7), 121.01 (C_6), 118.44 (C_{3a}), 113.32 (C_{5a}), 111.38 (C_9), 54.97 (C_3–OCH_3), 22.49 (C_4), 21.68 (C_5), 20.74 (C_8–CH_3); MS: *m/z* (%), M^+ 281 (100), 249 (50), 193 (88), 192 (45), 115 (24).

Methyl 4,5-dihydro-9-methyl-2H-pyrazolo[3,4-a]carbazole-3-carboxylate (**4c**): Dirty white spongy mass; Yield 66%; m.p. 255–257°C; Anal. Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.37; N, 14.94; Found: C, 68.33; H, 5.34; N, 14.99%; IR: υ_{max}, KBr, 3408, 3341, 2924, 1716, 1620, 1446, 1318 cm^{-1}; ^1H NMR: δ, DMSO–D_6, 13.59 (b s, 1H, N_2–H), 11.41 (b s, 1H, N_{10}–H), 7.31–7.26 (d, 1H, C_6–H, *J* = 7.6 Hz), 6.95–6.82 (m, 2H, C_7–, C_8–H), 3.87 (s, 3H, –OCH_3), 3.12–3.00 (m, 2H, C_5–H_2), 3.00–2.88 (m, 2H, C_4–H_2), 2.49 (s, 3H, C_9–CH_3); ^{13}C NMR: δ, DMSO–D_6, 159.75 (C_3–C=O), 147.03 (C_3), 137.43 (C_{1a}), 135.78 (C_{9a}), 130.46 (C_{6a}), 129.71 (C_{10a}), 122.46 (C_9), 122.38 (C_7), 122.13 (C_6), 121.07 (C_8), 120.57 (C_{3a}), 115.68 (C_{5a}), 52.47 (C_3–OCH_3), 24.23 (C_4), 23.47 (C_5), 21.48 (C_9–CH_3); MS: *m/z* (%), M^+ 281 (100), 249 (44), 194 (24), 193 (96), 192 (33), 143 (22), 115 (20).

Methyl 6-chloro-4,5-dihydro-2H-pyrazolo[3,4-a]carbazole-3-carboxylate (**4d**): Yellow powder; Yield 50%; m.p. 248–250°C; Anal. Calcd. for $C_{15}H_{12}ClN_3O_2$: C, 59.71; H, 4.01; N, 13.93; Found: C, 59.66; H, 4.11; N, 13.83%; IR: υ_{max}, KBr, 3400–3235, 2924, 1703, 1614, 1437, 1312 cm^{-1}; ^1H NMR: δ, DMSO–D_6, 13.67 (b s, 1H, N_2–H), 11.74 (b s, 1H, N_{10}–H), 7.52 (s, 1H, C_6–H), 7.39–7.27 (d, 1H, C_9–H, *J* = 8.5 Hz), 7.13–6.97 (d d, 1H, C_8 –H, J_{ortho} = 8.5 Hz, J_{meta} = 1.5 Hz), 3.87 (s, 3H, –OCH_3), 3.10–3.01 (m, 2H, C_5–H_2), 2.99–2.90 (m, 2H, C_4–H_2); ^{13}C NMR: δ, DMSO–D_6, 161.47 (C_3–C=O), 143.17 (C_3), 135.36 (C_{1a}), 135.14 (C_{9a}), 132.01 (C_7),126.73 (C_{6a}), 126.44 (C_{10a}), 122.94 (C_6), 120.12 (C_8), 118.43 (C_{3a}), 112.43 (C_{5a}), 110.98 (C_9), 52.47 (C_3–OCH_3), 22.22 (C_4), 20.05 (C_5); MS: *m/z* (%), M^+ 301 (100), 299 (32), 269 (56), 213 (80), 193 (26), 163 (22), 135 (24).

Methyl 4,5-dihydro-2H-pyrazolo[3,4-a]carbazole-3-carboxylate (**4e**): White spongy mass; Yield 68%; m.p. 238–240°C; Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72; Found: C, 67.34; H, 4.98; N, 15.64%; IR: υ_{max}, KBr, 3403, 3343, 1708, 1622, 1444, 1332 cm^{-1}; ^1H NMR: δ, DMSO–D_6, 13.57 (b s, 1H, N_2–H), 11.50 (b s, 1H, N_{10}–H), 7.51–7.44 (d, 1H, C_9–H, *J* = 7.68 Hz,), 7.36–7.31 (d, 1H, C_6–H, *J* = 7.88 Hz), 7.10–7.03 (m, 1H, C_8 –H), 7.01–6.95 (m, 1H, C_7 –H), 3.87 (s, 3H, –OCH_3), 3.14–3.02 (m, 2H, C_5–H), 2.98–2.92

(m, 2H, C_4–H); ^{13}C NMR: δ, DMSO–D_6, 158.73 (C_3–C=O), 142.64 (C_3), 134.97 (C_{1a}), 133.22 (C_{9a}), 128.64 (C_{6a}), 126.32 (C_{10a}), 123.02 (C_6), 122.47 (C_7), 120.17 (C_8), 117.43 (C_{3a}), 112.25 (C_{5a}), 110.96 (C_9), 52.44 (C_3–OCH_3), 20.47 (C_4), 19.99 (C_5); MS: *m/z* (%), M^+ 267 (100), 255 (50), 199 (92), 159 (24), 121 (32).

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