Synthetic utility of 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones: syntheses of pyrazolo, isoxazolo, pyrido and pyrimido annelated carbazoles

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2-Furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones were obtained from the mixed aldol condensation of 2,3,4,9-tetrahydrocarbazole-1-ones and furan-2-carbaldehyde (furfural). The corresponding enones were utilised as the synthons to prepare various heteroannulated pyrazolo[3,4-*a*]-, isoxazolo[3,4-*a*]-, pyrido[2,3-*a*]-, and pyrimido[4,5-*a*] carbazoles under different conditions using various reagents. Single crystal X-ray diffraction studies of 2-furylmethylene-6-methyl-2,3,4,9-tetrahydrocarbazol-1-one are discussed.

Keywords: heteroannulated carbazoles, 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones, furan-2-carbaldehyde

Natural products comprising a carbazole skeleton fused with another heterocycle have received significant attention due to the promising antitumour properties of several of their representatives.[1–3] Many total syntheses of these natural compounds have been achieved as well as structural modifications for annulating various heterocyclic systems to carbazole. The rapidly growing class of heteroaryl-condensed carbazoles has begun to attract increasing interest because of their broad spectrum of useful biological activities.[4–9] Most heteroaryl carbazoles reported[10–12] contain a heteroaryl moiety fused with a carbazole; however, there are few reports where the heteroaryl moiety is substituted with a carbazole unit.

Hence, a practical method for the preparation of such compounds is desirable. Simple pyrazole, oxazole, pyrido and pyrimido derivatives have been reported as pharmaceuticals for the treatment of cerebrovascular disorders and for their antiarrhythmic, sedative, and platelet anti-aggregating activities. This promising biological activity prompted us to introduce these types of moieties in the carbazole skeleton. We have reported[13–18] the synthesis of 1-oxo-2-arylidene-2,3,4,9-tetrahydrocarbazoles from potential precursors of the 2,3,4,9-tetrahydrocarbazole-1-one type and these synthons were utilised to derive many heteroannelated carbazoles. Based on these findings we now report the use of 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones (**2a–e**) as effective synthons towards the syntheses of pyrazolo, isoxazolo, pyrido and pyrimido annelated carbazoles.

Results and discussion

For compound **2a** the crystal structure was determined by X-ray diffraction and is discussed below (Fig. 1 and Table 1).

Single crystals of 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2a**), a non-planar molecule, were grown from ethanol, crystallising in the space group P-1. No strong π...π interactions were observed in this compound. Strong N–H...O hydrogen bonds connect the molecules to dimers. The dimers are connected with each other via C–H...O and two pairs of C–H...π(centroid) interactions. The two planes are at an angle of 47.40(3)° to each other. The atoms C5, C6, C7 and C8 are not quite in plane with the other atoms of the planar indole moiety with deviations between 0.12 and 0.38 Å. A few very weak C–H...π(C) interactions are also found. All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon or nitrogen atom.

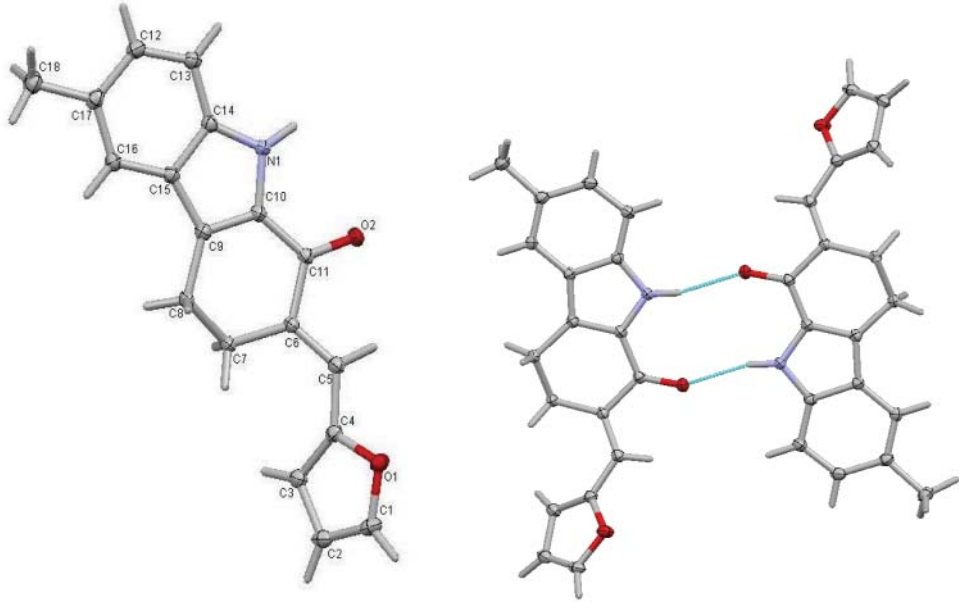

Fig. 1 Ortep diagram for compound 2-furylmethylene-6-methyl-2,3,4,9-tetrahydrocarbazol-1-one (**2a**) with the thermal ellipsoids at 30% probability level.

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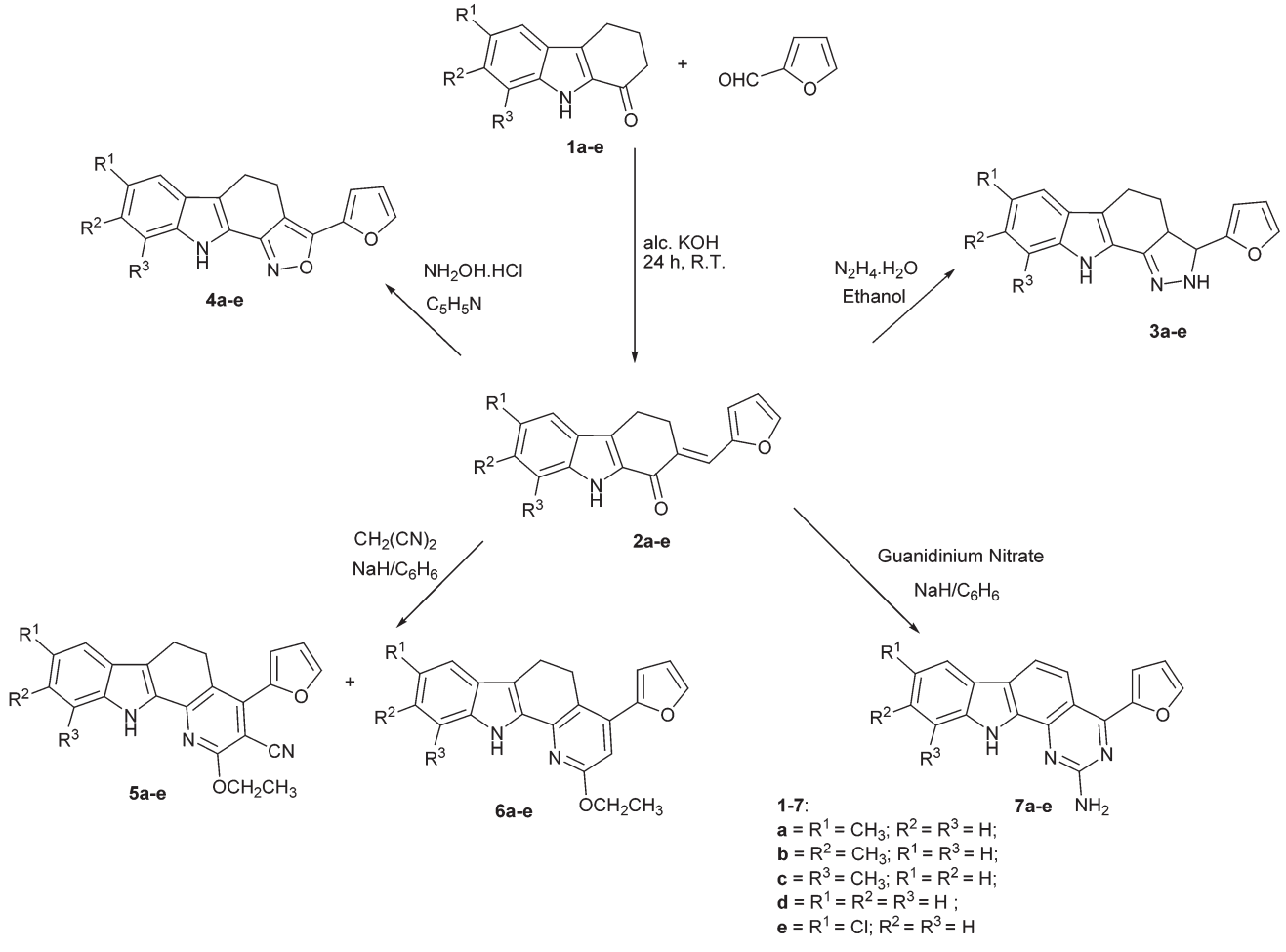
Table 1 Crystal data for 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2a**)

Chemical formula	$C_{18}H_{15}NO_2$
M_r (g mol^{-1})	277.31
Cell setting, space group	Triclinic, *P*-1
Temperature (K)	100(2)
a, *b*, *c* (Å)	6.1600(17), 9.465(3), 12.072(3)
α, β, γ (°)	79.772(4), 83.901(4), 78.223(4)
V (Å^3)	676.3 (3)
Z	2
D_x (Mg m^{-3})	1.362
Radiation type	Mo *K*α
μ (mm^{-1})	0.089
Crystal form, colour	Plate, yellow
Crystal size (mm)	0.49 × 0.44 × 0.26
Absorption correction	Multi-scan
T_{min} and T_{max}	0.858 and 0.977
No. of measured, independent and observed reflections	6680, 3332, 2987
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0157
θ_{max} (°)	28.28
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.040, 0.107, 1.04
No. of relections, restraints, parameters	3332, 0, 191
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.373, –0.227

All estimated standard deviation (ESDs) (except the ESD in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell ESDs are taken into account individually in the estimation of ESDs in distances, angles and torsion angles; correlations between ESDs in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell ESDs is used for estimating ESDs involving l.s. planes. CCDC 749407 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Data Centre via www.ccdc.cam.ac.uk/data_request.cif

Having obtained the key intermediates, 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones (**2a–e**), our aim was to devise a synthetic route to afford the title compounds. Compounds (**2a–e**) were treated with hydrazine hydrate, hydroxylamine hydrochloride, malononitrile and guanidine nitrate, yielding the corresponding pyrazolo[3,4-*a*]- (**3a–e**), isoxazolo[3,4-*a*]- (**4a–e**), pyrido[2,3-*a*]- (**5a–e**) & (**6a–e**), and pyrimido[4,5-*a*]-(**7a–e**) carbazoles respectively (Scheme 1). All the products were examined using IR, NMR and mass spectral analysis. Again the synthetic and spectroscopic details are given here for the compounds of the **'a'** series and the details of other derivatives for compounds of **b**, **c**, **d**, and **e** series are given in experimental section. When **2a** was treated with hydrazine hydrate in ethanol it gave the expected 3-(furan-2-yl)-2,3,3a,4,5,10-hexahydro-7-methylpyrazolo [3,4-a]carbazole (**3a**). Its IR spectrum showed stretching at 1595 cm^{-1} due to the presence of C=N and thereby indicating the absence of a carbonyl moiety. The proton NMR spectrum showed a broad singlet at δ 8.69 due to the presence of indole–NH. The presence of multiplet between δ 7.62 and 6.78 accounted for six aromatic protons *i.e.*, C_6–H, C_8–H, C_9–H, C_3′–H, C_4′–H, C_5′–H respectively. The pyrazolo –NH proton appeared as a broad singlet at δ 5.38. Multiplet at δ 3.20–2.94 belongs to six aliphatic protons at C_3–H, C_{3a}–H, C_4–H_2, C_5–H_2



Scheme 1

in the substrate. The presence C_7–CH_3 was inferred by a singlet at δ 2.53. Mass spectrum and the elemental analysis data supported well with the formation of product **3a**. The generality of this reaction was tested with **2b–e** to yield **3b–e**. Mechanistically the formation of the product is as follows: The lone pair on the nitrogen of the hydrazone intermediate, obtained from the reaction of **2** with hydrazine hydrate in ethanol, attacks the benzylic carbon resulting in the formation of dipolar intermediate which subsequently undergoes 1,3-prototropic shift to yield the expected product **3**.

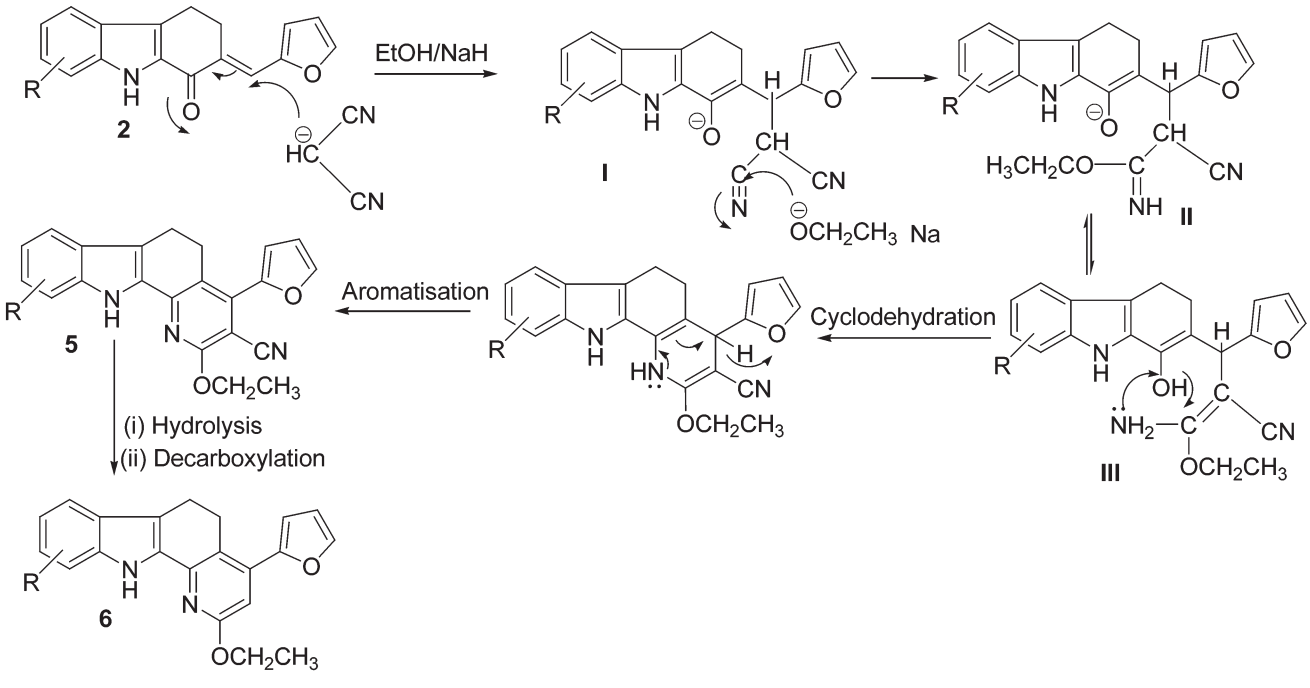
Treatment of 2-furylmethylene-6-methyl-2,3,4,9-tetrahydrocarbazol-1-one (**2a**) with hydroxylamine hydrochloride in dry pyridine yielded a product which was assigned as 3-(furan-2-yl)-4,5-dihydro-7-methylisoxazolo[3,4-*a*]carbazole (**4a**). The generality of this reaction was tested with other carbazole derivatives **2b–e** to yield the corresponding isoxazolo derivatives **4b–e**. The plausible mechanism for the formation of final product is as follows. Hydroxylamine liberated *in situ* from hydroxylamine hydrochloride in the presence of pyridine undergoes 1,4-Michael-type addition to **2** which is followed by further condensation with more hydroxylamine; loss of water molecule from the alkylhydroxylamine group, then the cyclisation and finally deamination, gives the final product **4**. Aerial oxidation of an isoxazoline intermediate can be ruled out since **2** yielded **4** also under a nitrogen atmosphere.

Due to the prominence of their pharmacological activity it was felt worthwhile to devise a simple route for the synthesis of pyridocarbazoles. Hence 2-furylmethylene-6-methyl-2,3,4,9-tetrahydrocarbazol-1-one (**2a**) was reacted with malononitrile to yield a mixture of two products. The products thus obtained were subjected to spectral and analytical data. The product formed was identified as 2-ethoxy-4-(furan-2-yl)-5,6-dihydro-8-methyl-11*H*-pyrido[2,3-*a*]carbazol-3-carbonitrile (**5a**).

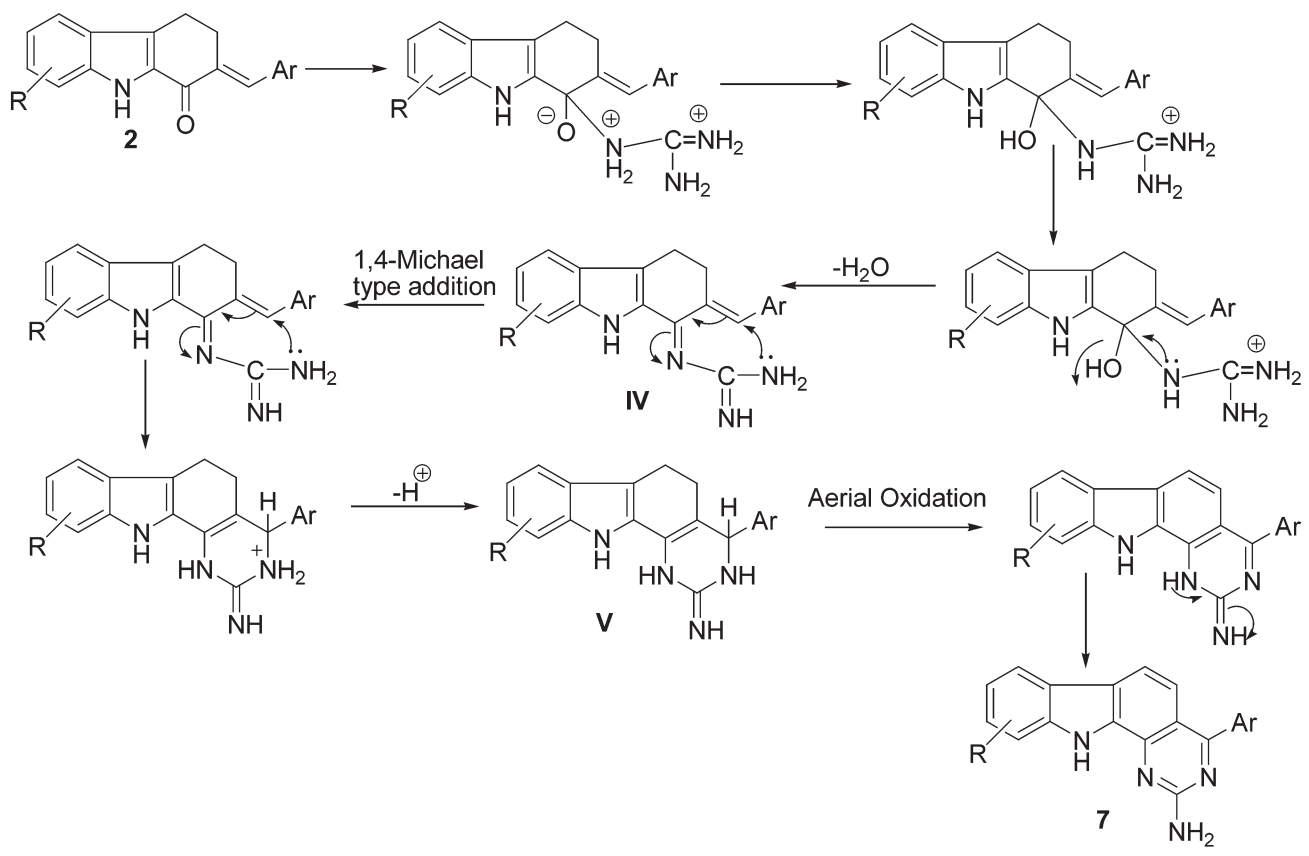
Spectral and analytical data for the compound obtained from the second fraction of petroleum ether: ethyl acetate (95:5) indicated the formation of 2-ethoxy-4-(furan-2-yl)-5,6-dihydro-8-methyl-11H-pyrido[2,3-*a*]carbazole (**6a**). The generality of this reaction was tested with other derivatives (**2b–e**) to obtain the corresponding pyridocarbazoles (**5b–e**) and (**6b–e**) respectively. A plausible mechanism for the formation of product may be the following. In the first step, the carbanion intermediate generated from malononitrile under basic conditions, on 1,4-Michael addition with α,β-unsaturated carbonyl substrate **2** yields the dinitrile intermediate **I**. One of the two symmetric CN-carbons is attacked by the ethoxide ion to give the imino intermediate **II**, which tautomerises to amino intermediate **III**. This amino formed on cyclodehydration followed by aromatisation gioves the product **5**. The product **5** further undergoes hydrolysis and decarboxylation to give the product **6**.

Heterocyclic pyrimidines with an amino group have pharmacological as well as chemotherapeutic properties; hence based on the above mentioned facts we decided to synthesise several new amino substituted pyrimidocarbazoles. To achieve our target we utilised the present synthon, 2-furylmethylene-6-methyl-2,3,4,9-tetrahydrocarbazol-1-one (**2a**) with guanidine nitrate in the presence of sodium hydride/benzene under reflux to give a brown solid. It was concluded that the product formed was 2-amino-4-(furan-2-yl)-8-methyl-11*H*-pyrimido [4,5-*a*]carbazole (**7a**). A series of similar reactions were carried out with (**2b–e**) and the corresponding pyrimido[4,5-*a*] carbazoles (**7b–e**) realised Mechanistically the amino group of the guanidine nitrate reacts with the carbonyl group of the enone to give the Schiff's base intermediate **IV** which subsequently undergoes intramolecular 1,4-Michael addition to give intermediate **V**, which further on aerial oxidation to yield the aromatised product **7** (Scheme 3).

In conclusion, pyrazolo[3,4-*a*]-, isoxazolo[3,4-*a*], pyrido [2,3-*a*]- and pyrimido[4,5-*a*]- carbazoles were synthesised from the newly developed synthons 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1ones **2**, thus opening an easy access to fused carbazoles with hoped-for biological and pharmacological activities. Compound **2a** was also analysed by single crystal X-ray diffraction, providing knowledge about the exact geometry of the molecule.



Scheme 2



Scheme 3

Experimental

Melting points (m.p.) were determined on a Mettler FP 51apparatus (Mettler Instruments, Switzerland) and are uncorrected. IR spectra were recorded on a Schimadzu FTIR-8201PC spectrophotometer (Schimadzu, Japan) from KBr pellets. 1H NMR spectra were recorded on a Bruker AMX 400 (400 MHz) spectrometer using tetramethylsilane (TMS) as an internal reference. The chemical shifts are expressed in ppm. Microanalyses were done on a Vario EL III model CHNS analyzer (Vario, Germany). Diffraction data for all the compound were collected using a Bruker AXS SMART APEX CCD diffractometer at 100(2) K with monochromatic Mo Kα radiation using the omega scan technique. Data were collected, the unit cell determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs. The structure was solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL. The purity of the products was tested by TLC with plates coated with silicagel-G with petroleum ether and ethyl acetate as developing solvents. All chemicals were purchased from Sigma–Aldrich, Bangalore, India.

Preparation of 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones (**2**)*; general procedure*

An equimolar mixture of the appropriate 2,3,4,9-tetrahydrocarbazol-1-one (**1a–e**, 0.005 mol) and furan-2-carbaldehyde (0.005 mol) was treated with 25 mL of a 5% ethanolic potassium hydroxide solution and stirred for 6 h at room temperature. The product precipitated as a yellow crystalline mass, was filtered off and washed with 50% ethanol. A further crop of condensation product was obtained on neutralisation with acetic acid and dilution with water. The product was recrystallised from methanol to yield the 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones (**2a–e**).

2-furylmethylene-6-methyl-2,3,4,9-tetrahydrocarbazol-1-one (**2a**): Yellow solid (1.27 g, 92%), m.p. 217–219 °C. IR: ν_{max} 3235, 2923, 2856, 1633, 1580, 1451, 747 cm^{-1}. ^1H NMR: δ 8.80 (b s, 1H, N_9-H), 7.56–6.54 (m, 7H, C_2–H, C_5–H, C_7–H, C_8–H, C_3'–H, C_4'–H, C_5'–H), 3.47 (m, 2H, C_3–H_2), 3.09 (m, 2H, C_4–H_2), 2.46 (s, 3H, C_6–CH_3). MS: *m/z* (%) 277 (M^+, 100) 262 (20), 196 (17), 183 (12), 169 (14), 115 (20), 91(18). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.64; H, 5.39; N, 4.93%.

2-furylmethylene-7-methyl-2,3,4,9-tetrahydrocarbazol-1-one (**2b**): Yellow solid (1.23 g, 89%), m.p. 186–188 °C. IR: ν_{max} 3241, 2922, 1631, 1575, 1473, 751 cm^{-1}. ^1H NMR: δ 8.75 (b s, 1H, N_9-H), 7.57–6.51 (m, 7H, C_2–H, C_5–H, C_6–H, C_8–H, C_3'–H, C_4'–H, C_5'–H), 3.49 (m, 2H, C_3–H_2), 3.11 (m, 2H, C_4–H_2), 2.48 (s, 3H, C_7–CH_3). MS: *m/z* (%) 277 (M^+, 87) 262 (24), 195 (19), 184 (19), 169 (27), 115 (16), 91(14). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.52; H, 5.31; N, 5.10%.

2-furylmethylene-8-methyl-2,3,4,9-tetrahydrocarbazol-1-one (**2c**): Yellow solid (1.24 g, 90%), m.p. 231–233 °C. IR: ν_{max} 3280, 2924, 1640, 1585, 1474, 746 cm^{-1}. ^1H NMR: δ 8.84 (b s, 1H, N_9-H), 7.59–6.55 (m, 7H, C_2–H, C_5–H, C_6–H, C_7–H, C_3'–H, C_4'–H, C_5'–H), 3.51 (m, 2H, C_3–H_2), 3.13 (m, 2H, C_4–H_2), 2.42 (s, 3H, C_8–CH_3). MS: *m/z* (%) 277 (M^+, 100), 262 (27), 247 (18), 195 (26), 168 (17), 107 (20), 91 (24). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.49; H, 5.33; N, 5.12%.

2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2d**): Yellow solid (1.17 g, 89%), m.p. 219–221 °C. IR: ν_{max} 3238, 2924, 1636, 1580, 1475, 1387, 737 cm^{-1}. ^1H NMR: δ 8.86 (b s, 1H, N_9-H), 7.70–6.69 (m, 8H, C_2–H, C_5–H, C_6–H, C_7–H, C_8–H, C_3'–H, C_4'–H, C_5'–H), 3.50 (m, 2H, C_3–H_2), 3.14 (m, 2H, C_4–H_2). MS: *m/z* (%) 263 (M^+, 100), 196 (30), 183 (24), 169 (17), 114 (11), 91 (18). Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.09; H, 4.88; N, 5.29%.

6-Chloro-2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2e**): Yellow solid (1.31 g, 90%), m.p. 227–229 °C. IR: ν_{max} 3228, 2924, 1632, 1577, 1378, 1238, 753 cm^{-1}. ^1H NMR: δ 8.98 (b s, 1H, N_9-H), 7.67–6.55 (m, 7H, C_2–H, C_5–H, C_7–H, C_8–H, C_3'–H, C_4'–H, C_5'–H), 3.49 (m, 2H, C_3–H_2), 3.10 (m, 2H, C_4–H_2). MS: *m/z* (%) 279/277 (M^+, 23/71), 262 (21), 217(19), 184 (16), 169 (18), 115 (13), 91(15). Anal. Calcd for $C_{17}H_{12}ClNO_2$: C, 68.58; H, 4.06; N, 4.70. Found: C, 68.13; H, 4.01; N, 4.61%.

Preparation of 3-(furan-2-yl)-2,3,3a,4,5,10-hexahydropyrazolo[3,4-a] carbazoles (**3**)*: general procedure*

The respective 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2a–e**, 0.001 mol) was dissolved in absolute ethanol (20 mL). Hydrazine hydrate (0.5 mL, 0.01 mol) was added to this mixture, it was refluxed for 6 h and the reaction was monitored by TLC. After

completion of the reaction, the solvent was removed under reduced pressure. The crude mixture was poured into ice cold water and extracted with ethyl acetate, washed with water and the combined organic layers were dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica gel column chromatography using petroleum ether: ethyl acetate (95:5) as eluent yielded the corresponding 3-(furan-2-yl)-2,3,3a,4,5,10-hexahydropyrazolo[3,4-a]carbazole (**3**) The product thus obtained was recrystallised from ethanol.

3-(Furan-2-yl)-2,3,3a,4,5,10-hexahydro-7-methylpyrazolo[3,4-a] carbazole (**3a**): Yellow solid (0.201g, 69%), m.p. 142–144 °C. IR: ν_{max} 3436, 2926, 1595, 1452, 1350, 1143, 801 cm^{-1}. ^{1}H NMR: δ 8.69 (b s, 1H, N_{10}–H), 7.62–6.78 (m, 6H, C_6–H, C_8–H, C_9–H, C_3'–H, C_4'–H, C_5'–H), 5.38 (s, 1H, pyrazolo –NH), 3.20–2.94 (m, 6H, C_3–H, C_{3a}–H, C_4–H_2, C_5–H_2), 2.53 (s, 3H, C_7–CH_3). MS: *m/z* (%) 291(M$^+$, 84), 276 (20), 224 (18), 210 (16), 168 (14), 115 (10), 76 (12), 67 (17). Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.09; H, 5.65; N, 14.22%.

3-(Furan-2-yl)-2,3,3a,4,5,10-hexahydro-8-methylpyrazolo[3,4-a] carbazole (**3b**): Yellow solid (0.212g, 73%), m.p. 131–133 °C. IR: ν_{max} 3404, 2925, 1617, 1450, 1255, 1136, 806 cm^{-1} ^{1}H NMR: δ 8.57 (b s, 1H, N_{10}–H), 7.67–6.55 (m, 6H, C_6–H, C_7–H, C_9–H, C_3'–H, C_4'–H, C_5'–H), 5.63 (s, 1H, pyrazolo –NH), 3.07–2.76 (m, 6H, C_3–H, C_{3a}–H, C_4–H_2, C_5–H_2), 2.47 (s, 3H, C_8–CH_3). MS: *m/z* (%) 291(M$^+$, 100), 276 (15), 223 (17), 209 (19), 168 (20), 114 (16), 76 (14), 67 (18). Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.11; H, 5.75; N, 14.31%.

3-(Furan-2-yl)-2,3,3a,4,5,10-hexahydro-9-methylpyrazolo[3,4-a] carbazole (**3c**): Yellow solid (0.189g, 65%), m.p. 137–139 °C. IR: ν_{max} 3422, 2923, 2855, 1592, 1450, 1260, 1137, 1025 cm^{-1}. ^{1}H NMR: δ 8.73 (b s, 1H, N_{10}–H), 7.66–6.32 (m, 6H, C_6–H, C_7–H, C_8–H, C_3'–H, C_4'–H, C_5'–H), 5.44 (s, 1H, pyrazolo –NH), 3.17–2.88 (m, 6H, C_3–H, C_{3a}–H, C_4–H_2, C_5–H_2), 2.50 (s, 3H, C_9–CH_3). MS: *m/z* (%) 291(M$^+$, 68), 276 (21), 248 (10), 170 (16), 115 (10), 76 (13), 67 (15). Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.24; H, 5.69; N, 14.27%.

3-(Furan-2-yl)-2,3,3a,4,5,10-hexahydropyrazolo[3,4-a]carbazole (**3d**): Yellow solid (0.196g, 71%), m.p. 144–146 °C. IR: ν_{max} 3330, 2924, 1620, 1513, 1454, 1261, 807 cm^{-1}. ^{1}H NMR: δ 8.52 (b s, 1H, N_{10}–H), 7.49–6.69 (m, 7H, C_6–H, C_7–H, C_8–H, C_9–H, C_3'–H, C_4'–H, C_5'–H), 5.68 (s, 1H, pyrazolo –NH), 3.13–2.99 (m, 6H, C_3–H, C_{3a}–H, C_4–H_2, C_5–H_2). MS: *m/z* (%) 277 (M$^+$, 100), 277 (22), 211 (22), 210 (15), 169 (17), 116 (18), 76 (15), 67 (14). Anal. Calcd for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.44; H, 5.35; N, 15.04%.

7-Chloro-3-(furan-2-yl)-2,3,3a,4,5,10-hexahydropyrazolo[3,4-a] carbazole (**3e**): Yellow solid (0.217 g, 70%), m.p. 157–159 °C. IR: ν_{max} 3412, 2922, 1617, 1459, 1376, 1266, 808 cm^{-1}. ^{1}H NMR: δ 8.80 (b s, 1H, N_{10}–H), 7.62–6.48 (m, 6H, C_6–H, C_7–H, C_8–H, C_9–H, C_3'–H, C_4'–H, C_5'–H), 5.46 (s, 1H, pyrazolo –NH), 3.19–2.91 (m, 6H, C_3–H, C_{3a}–H, C_4–H_2, C_5–H_2). MS: *m/z* (%) 313/311 (M$^+$, 16/56), 276 (22), 244 (18), 210 (12), 184 (10), 114 (15), 76 (16), 67 (10). Anal. Calcd for $C_{17}H_{14}ClN_3O$: C, 65.49; H, 4.53; N, 13.48. Found: C, 65.04; H, 4.45; N, 13.24%.

*Preparation of 3-(furan-2-yl)-4,5-dihydroisoxazolo[3,4-a]carbazoles (**4**): general procedure*

The respective 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2a–e**, 0.001 mol) was treated with hydroxylamine hydrochloride (1 g, 0.014 mol) in pyridine (5 mL) at 130°C for 8 h. After completion of the reaction, the crude mixture was poured into ice cold water and neutralised with 1:1 HCl, and the resulting semi-solid separated was extracted with chloroform (3x10 mL). The combined organic layers were dried over anhydrous sodium sulfate. After the removal of solvent it was purified by silica gel column chromatography using petroleum ether: ethyl acetate (98:2) as eluent to yield the respective 3-(furan-2-yl)-4,5-dihydroisoxazolo[3,4-a]carbazole (**4a–e**). The product thus obtained was recrystallised from ethanol.

3-(Furan-2-yl)-4,5-dihydro-7-methylisoxazolo[3,4-a]carbazole (**4a**): Yellow solid (0.205g, 71%), m.p. 131–133 °C. IR: ν_{max} 3454, 2915, 1586, 1433, 1206, 1107, 737 cm^{-1}. ^{1}H NMR: δ 9.75 (b s, 1H, N_{10}–H), 7.51–7.05 (m, 5H, C_6–H, C_8–H, C_9–H, C_3'–H, C_5'–H), 6.46 (m, 1H, C_4'–H), 3.28 (m, 2H, C_4–H_2), 2.98 (m, 2H, C_5–H_2), 2.46 (s, 3H, C_7–CH_3). MS: *m/z* (%) 290 (M$^+$, 100), 275 (16), 209 (18), 195 (16), 167 (14), 115 (20), 91 (20), 67 (14). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.19; H, 4.79; N, 9.52%.

3-(Furan-2-yl)-4,5-dihydro-8-methylisoxazolo[3,4-a]carbazole (**4b**): Yellow solid (0.208g, 72%), m.p. 156–158 °C. IR: ν_{max} 3406, 2922, 1594, 1451, 1261, 1095, 801 cm^{-1}. ^{1}H NMR: δ 9.88 (b s, 1H, N_{10}–H), 7.53–6.98 (m, 5H, C_6–H, C_7–H, C_9–H, C_3'–H, C_5'–H), 6.47 (m, 1H, C_4'–H), 3.30 (m, 2H, C_4–H_2), 2.99 (m, 2H, C_5–H_2), 2.48 (s, 3H, C_8–CH_3). MS: *m/z* (%) 290 (M$^+$, 63), 275 (26), 209 (14), 197 (18), 114 (10), 91 (11), 67 (13). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.20; H, 4.71; N, 9.60%.

3-(Furan-2-yl)-4,5-dihydro-9-methylisoxazolo[3,4-a]carbazole (**4c**): Yellow solid (0.201g, 69%), m.p. 160–162 °C. IR: ν_{max} 3459, 2931, 1601, 1413, 1318, 1010, 738 cm^{-1}. ^{1}H NMR: δ 9.73 (b s, 1H, N_{10}–H), 7.50–7.08 (m, 5H, C_6–H, C_7–H, C_8–H, C_3'–H, C_5'–H), 6.48 (m, 1H, C_4'–H), 3.31 (m, 2H, C_4–H_2), 3.03 (m, 2H, C_5–H_2), 2.53 (s, 3H, C_9–CH_3). MS: *m/z* (%) 290 (M$^+$, 77), 275 (26), 209 (19), 184 (12), 115 (10), 91 (12), 67 (16). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.41; H, 4.69; N, 9.57%.

3-(Furan-2-yl)-4,5-dihydroisoxazolo[3,4-a]carbazole (**4d**): Yellow solid (0.207 g, 75%), m.p. 154–156 °C. IR: ν_{max} 3456, 2929, 1595, 1457, 1334, 1208, 740 cm^{-1}.. ^{1}H NMR: δ 9.81 (b s, 1H, N_{10}–H), 7.63–7.10 (m, 6H, C_6–H, C_7–H, C_8–H, C_9–H, C_3'–H, C_5'–H), 6.46 (m, 1H, C_4'–H), 3.28 (m, 2H, C_4–H_2), 2.99 (m, 2H, C_5–H_2). MS: *m/z* (%) 290 (M$^+$, 91), 276 (33), 209 (11), 195 (19), 167 (19), 91 (11), 67 (10). Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.75; H, 4.22; N, 10.07%.

7-Chloro-3-(furan-2-yl)-4,5-dihydroisoxazolo[3,4-a]carbazole (**4e**): Yellow solid (0.238g, 77%), m.p. 147–149 °C. IR: ν_{max} 3460, 2988, 1594, 1469, 1204, 1056, 735 cm^{-1}.^{1}H NMR: δ 9.86 (b s, 1H, N_{10}–H), 7.59–7.05 (m, 6H, C_6–H, C_7–H, C_8–H, C_9–H, C_3'–H, C_5'–H), 6.47 (m, 1H, C_4'–H), 3.24 (m, 2H, C_4–H_2), 2.96 (m, 2H, C_5–H_2). MS: *m/z* (%) 312/310 (M$^+$, 22/79), 275 (10), 243 (13), 201 (17), 169 (14), 115 (16), 91 (19), 67 (12). Anal. Calcd for $C_{17}H_{11}ClN_2O_2$: C, 65.71; H, 3.57; N, 9.02. Found: C, 65.12; H, 3.42; N, 8.98%.

Reaction of 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-ones with malononitrile: general procedure

A solution of the appropriate 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2a–e**, 0.001 mol) in dry ethanol (20 mL) was added to an ice-cooled solution of 1.00 g of sodium hydride (degreased with petroleum ether) in dry benzene (10 mL). To this, malononitrile (0.005 mol) was added and the mixture was refluxed on an oil bath for five hours. The reaction monitored by TLC indicated the formation of two products. The excess solvent was removed by distillation and the mixture was poured into ice-water. The brown solid separated was then neutralised, filtered and dried. It was then purified by column chromatography over silica gel using petroleum ether: ethyl acetate as eluants (98:2) and (95:5) to yield corresponding pyridocarbazoles 2-ethoxy-4-(furan-2-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (**5**) and 2-ethoxy-4-(furan-2-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole (**6**).

2-Ethoxy-4-(furan-2-yl)-5,6-dihydro-8-methyl-11H-pyrido[2,3-a] carbazole-3-carbonitrile (**5a**): Yellow prisms (0.148 g, 40%), m.p. 216–218 °C. IR: ν_{max} 3356, 2921, 2212, 1587, 1494, 1341, 1028, 801 cm^{-1}. ^{1}H NMR: δ 8.66 (b s, 1H, N_{11}–H), 7.66–6.95 (m, 5H, C_7–H, C_9–H, C_{10}–H, C_3'–H, C_5'–H), 6.62 (m,1H, C_4'–H), 4.61 (q, 2H, C_2–O–**CH_2**CH_3, *J* = 8.80 Hz), 3.15 (m, 2H, C_5–H_2), 2.98 (m, 2H, C_6–H_2), 2.46 (s, 3H, C_8–CH_3), 1.49 (t, 3H, C_2–O–CH_2**CH_3**, *J* = 8.80 Hz). MS: *m/z* (%) 369 (M$^+$, 80), 354 (15), 343 (22), 263 (16), 218 (19), 168 (12), 107 (18), 67 (19). Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.67; H, 5.10; N, 11.22%.

2-Ethoxy-4-(furan-2-yl)-5,6-dihydro-8-methyl-11H-pyrido[2,3-a] carbazole (**6a**): Yellow prisms (0.124 g, 36%), m.p. 197–199 °C. IR: ν_{max} 3423, 2926, 1591, 1486, 1327, 1040, 802 cm^{-1}. ^{1}H NMR: δ 9.15 (b s, 1H, N_{11}–H), 7.57 (d, 1H, C_3'–H, $J_{\alpha\beta}$ =1.08 Hz), 7.36 (s, 1H, C_7–H), 7.29 (d, 1H, C_9–H, *J* = 7.76 Hz), 7.05 (d, 1H, C_{10}–H, *J* = 7.76 Hz), 6.82 (s, 1H, C_3–H), 6.70 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.12 Hz), 6.55 (m,1H, C_4'–H), 4.68 (q, 2H, C_2–O–**CH_2**CH_3, *J* = 7.04 Hz), 3.28 (m, 2H, C_5–H_2), 3.02 (m, 2H, C_6–H_2), 2.47 (s, 3H, C_8–CH_3), 1.46 (t, 3H, C_2–O–CH_2**CH_3**, *J* = 7.04 Hz). MS: *m/z* (%) 344 (M$^+$, 100), 329 (27), 285 (19), 221 (17), 197 (19), 131 (11), 116 (19), 67 (12). Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.57; H, 5.75; N, 8.01%.

2-ethoxy-4-(furan-2-yl)-5,6-dihydro-9-methyl-11H-pyrido[2,3-a] carbazole-3-carbonitrile (**5b**): Yellow prisms (0.156 g, 42%), m.p. 203–205 °C. IR: ν_{max} 3343, 2923, 2214, 1585, 1495, 1342, 1264, 736 cm^{-1}. ^{1}H NMR: δ 8.63 (b s, 1H, N_{11}–H), 7.67–6.97 (m, 5H, C_7–H,

C_8–H, C_{10}–H, C_3'–H, C_5'–H), 6.60 (m,1H, C_4'–H), 4.63 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.84 Hz), 3.19 (m, 2H, C_5–H_2), 3.02 (m, 2H, C_6–H_2), 2.50 (s, 3H, C_9–CH_3), 1.51 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.84 Hz). MS: *m/z* (%) 369 (M^+, 69), 354 (19), 341 (29), 262 (15), 218 (11), 157 (15), 130 (13), 67 (11). Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.43; H, 5.08; N, 11.19%.

2-Ethoxy-4-(furan-2-yl)-5,6-dihydro-9-methyl-11H-pyrido[2,3-a] carbazole (**6b**): Yellow prisms (0.121 g, 35%), m.p. 101–103 °C. IR: ν_{max} 3337, 2965, 1595, 1486, 1331, 1261, 801 cm^{-1}. ^1H NMR: δ 8.70 (b s, 1H, N_{11}–H), 7.59–6.81 (m, 6H, C_3–H, C_7–H, C_8–H, C_{10}–H, C_3'–H, C_5'–H), 6.55 (m,1H, C_4'–H), 4.42 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.00 Hz), 3.29 (m, 2H, C_5–H_2), 3.04 (m, 2H, C_6–H_2), 2.48 (s, 3H, C_9–CH_3), 1.46 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.00 Hz). MS: *m/z* (%) 344 (M^+, 100), 329 (16), 285 (14), 219 (23), 195 (20), 155 (13), 116 (12), 67 (17). Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.09; H, 5.70; N, 8.07%.

2-Ethoxy-4-(furan-2-yl)-5,6-dihydro-10-methyl-11H-pyrido[2,3-a] carbazole-3-carbonitrile (**5c**): Yellow prisms (0.143 g, 39%), m.p. 179–181 °C. IR: ν_{max} 3356, 2855, 2216, 1548, 1458, 1336, 1028, 743 cm^{-1}. ^1H NMR: δ 8.57 (b s, 1H, N_{11}–H), 7.63–6.98 (m, 5H, C_7–H, C_8–H, C_9–H, C_3'–H, C_5'–H), 6.61 (m, 1H, C_4'–H), 4.64 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.08 Hz), 3.17 (m, 2H, C_5–H_2), 3.03 (m, 2H, C_6–H_2), 2.57 (s, 3H, C_{10}–CH_3), 1.49 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.08 Hz). MS: *m/z* (%) 369 (M^+, 72), 354 (18), 343 (24), 263 (19), 219 (20), 156 (19), 131 (12), 67 (12). Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.54; H, 5.18; N, 11.34%.

2-Ethoxy-4-(furan-2-yl)-5,6-dihydro-10-methyl-11H-pyrido[2,3-a] carbazole (**6c**): Yellow prisms (0.106 g, 31%), m.p. 122–124 °C. IR: ν_{max} 3465, 2925, 1592, 1439, 1330, 1028, 739 cm^{-1}. ^1H NMR: δ 8.74 (b s, 1H, N_{11}–H), 7.59 (d, 1H, C_3'–H, $J_{\alpha\beta}$ =1.40 Hz), 7.44–7.12 (m, 3H, C_7–H, C_8–H, C_9–H), 6.84 (s, 1H, C_3–H), 6.71 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.08 Hz), 6.56 (m, 1H, C_4'–H), 4.61 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.24 Hz), 3.31 (m, 2H, C_5–H_2), 3.05 (m, 2H, C_6–H_2), 2.55 (s, 3H, C_{10}–CH_3), 1.45 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.24 Hz). MS: *m/z* (%) 344 (M^+, 76), 329 (31), 285 (19), 220 (20), 195 (17), 154 (15), 114 (12), 67 (11). Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 75.97; H, 5.69; N, 8.09%.

2-Ethoxy-4-(furan-2-yl)-5,6-dihydro-11H-pyrido[2,3-a]carbazole-3-carbonitrile (**5d**): Yellow prisms (0.131 g, 37%), m.p. 167–169 °C. IR: ν_{max} 3352, 2923, 2214, 1586, 1549, 1338, 1341, 1031, 799 cm^{-1}. ^1H NMR: δ 8.76 (b s, 1H, N_{11}–H), 7.67–6.90 (m, 6H, C_7–H, C_8–H, C_9–H, C_{10}–H, C_3'–H, C_5'–H), 6.61 (m, 1H, C_4'–H), 4.62 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.10 Hz), 3.19 (m, 2H, C_5–H_2), 3.01 (m, 2H, C_6–H_2), 1.51 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.10 Hz). MS: *m/z* (%) 355 (M^+, 69), 310 (13), 285 (18), 220 (11), 269 (17), 129 (19), 114 (13), 67 (12). Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.11; H, 4.61; N, 11.66%.

2-Ethoxy-4-(furan-2-yl)-5,6-dihydro-11H-pyrido[2,3-a]carbazole (**6d**): Yellow prisms (0.105 g, 32%), m.p. 128–130 °C. IR: ν_{max} 3417, 2963, 1596, 1332, 1187, 1037, 803 cm^{-1}. ^1H NMR: δ 8.83 (b s, 1H, N_{11}–H), 7.61 (d, 1H, C_3'–H, $J_{\alpha\beta}$ =1.36 Hz), 7.59–7.12 (m, 4H, C_7–H, C_8–H, C_9–H, C_{10}–H), 6.84 (s, 1H, C_3–H), 6.71 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.24 Hz), 6.56 (m, 1H, C_4'–H), 4.47 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.04 Hz), 3.28 (m, 2H, C_5–H_2), 3.05 (m, 2H, C_6–H_2), 1.46 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.04 Hz). MS: *m/z* (%) 330 (M^+, 59), 285 (17), 263 (20), 219 (22), 168 (19), 129 (19), 114 (14), 67 (12). Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.19; H, 5.40; N, 8.34%.

8-Chloro-2-ethoxy-4-(furan-2-yl)-5,6-dihydro-11H-pyrido[2,3-a] carbazole-3-carbonitrile (**5e**): Yellow prisms (0.136 g, 35%), m.p. 227–229 °C. IR: ν_{max} 3346, 2289, 2211, 1546, 1497, 1336, 1026, 884 cm^{-1}. ^1H NMR: δ 8.79 (b s, 1H, N_{11}–H), 7.67–6.92 (m, 5H, C_7–H, C_9–H, C_{10}–H, C_3'–H, C_5'–H), 6.63 (m, 1H, C_4'–H), 4.63 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.04Hz), 3.21 (m, 2H, C_5–H_2), 3.00 (m, 2H, C_6–H_2), 1.52 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.04 Hz). MS: *m/z* (%) 391/389 (M^+, 20/64), 354 (11), 319 (23), 310 (10), 219 (17), 168 (19), 109 (12), 67 (16). Anal. Calcd for $C_{22}H_{16}ClN_3O_2$: C, 67.78; H, 4.14; N, 10.78. Found: C, 67.51; H, 4.11; N, 10.63%.

8-Chloro-2-ethoxy-4-(furan-2-yl)-5,6-dihydro-11H-pyrido[2,3-a] carbazole (**6e**): Yellow prisms (0.120 g, 33%), m.p. 158–160 °C. IR: ν_{max} 3427, 2925, 1599, 1451, 1324, 1190, 803 cm^{-1}. ^1H NMR: δ 8.86 (b s, 1H, N_{11}–H), 7.60 (s, 1H, C_7–H), 7.53 (d, 1H, C_3'–H, $J_{\alpha\beta}$ =1.36 Hz), 7.32 (d, 1H, C_{10}–H, J = 8.60 Hz), 7.15 (dd, 1H, C_9–H, J_m = 2.00 Hz, J_{ortho} = 8.08 Hz), 6.86 (s, 1H, C_3–H), 6.71 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.32 Hz), 6.56 (m, 1H, C_4'–H), 4.46 (q, 2H, C_2–O–**CH_2**CH_3, J = 7.06 Hz), 3.29 (m, 2H, C_5–H_2), 3.03 (m, 2H, C_6–H_2), 1.46 (t, 3H, C_2–O–CH_2**CH_3**, J = 7.06 Hz). MS: *m/z* (%) 371/369 (M^+, 20/69), 319 (11), 297 (17), 285 (13), 167 (12), 105 (10), 67 (10). Anal. Calcd for $C_{21}H_{17}ClN_2O_2$: C, 69.14; H, 4.70; N, 7.68. Found: C, 69.04; H, 4.62; N, 7.55%.

*Preparation of 2-amino-4-(furan-2-yl)-11H-pyrimido[4,5-a]carbazole (**7**): general procedure*

To 1.00 g of sodium hydride (degreased with petroleum ether) in dry benzene (10 mL), a mixture of the respective 2-furylmethylene-2,3,4,9-tetrahydrocarbazol-1-one (**2a–e**, 0.001 mol) and guanidine nitrate (0.01 mol) was added and refluxed for 24 h. The reaction was monitored by TLC. After completion of the reaction, the excess of solvent was boiled off and the mixture was poured into crushed ice. The reaction mixture was then neutralised and extracted with chloroform (3 × 40 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. Upon removal of the solvent a brown crude mixture was obtained. It was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (75:25) to yield the corresponding 2-amino-4-(furan-2-yl)-11*H*-pyrimido[4,5-a] carbazole (**7a–e**) and crystallised form the same solvent mixture.

2-Amino-4-(furan-2-yl)-8-methyl-11H-pyrimido[4,5-a]carbazole (**7a**): Yellow solid (0.141 g, 45%), m.p. 244–246 °C. IR: ν_{max} 3437, 3162, 3114, 1601, 1544, 1356, 1214, 781 cm^{-1}. ^1H NMR: δ 9.74 (b s, 1H, N_{11}–H), 7.91–6.93 (m, 6H, C_5–H, C_6–H, C_7–H, C_9–H, C_{10}–H, C_3'–H), 6.63 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.48 Hz), 6.49 (m,1H, C_4'–H), 5.17 (b s, 2H, –NH_2), 2.44 (s, 3H, C_8 –CH_3). MS: *m/z* (%) 314 (M^+, 41). Anal. Calcd for $C_{19}H_{14}N_4O$: C, 72.60; H, 4.49; N, 17.82. Found: C, 72.22; H, 4.39; N, 17.39%.

2-Amino-4-(furan-2-yl)-9-methyl-11H-pyrimido[4,5-a]carbazole (**7b**): Yellow solid (0.160 g, 51%), m.p. 291–293 °C. IR: ν_{max} 3361, 3197, 3146, 1604, 1418, 1376, 1107, 807 cm^{-1}. ^1H NMR: δ 9.85 (b s, 1H, N_{11}–H), 7.83–6.89 (m, 6H, C_5–H, C_6–H, C_7–H, C_8–H, C_{10}–H, C_3'–H), 6.73 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.12 Hz), 6.51 (m,1H, C_4'–H), 5.09 (b s, 2H, –NH_2), 2.50 (s, 3H, C_9–CH_3). MS: *m/z* (%) 314 (M^+, 53). Anal. Calcd for $C_{19}H_{14}N_4O$: C, 72.60; H, 4.49; N, 17.82. Found: C, 72.47; H, 4.41; N, 17.52%.

2-Amino-4-(furan-2-yl)-10-methyl-11H-pyrimido[4,5-a]carbazole (**7c**): Yellow solid (0.116 g, 37%), m.p. 176–178°C. IR: ν_{max} 3372, 3144, 3109, 1596, 1384, 1272, 737 cm^{-1}. ^1H NMR: δ 10.07 (b s, 1H, N_{11}–H), 7.84–7.07 (m, 6H C_5–H, C_6–H, C_7–H, C_8–H, C_9–H, C_3'–H,), 6.70 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.08 Hz), 6.49 (m,1H, C_4'–H), 5.11 (b s, 2H, –NH_2), 2.49 (s, 3H, C_{10} –CH_3). MS: *m/z* (%) 314 (M^+, 47). Anal. Calcd for $C_{19}H_{14}N_4O$: C, 72.60; H, 4.49; N, 17.82. Found: C, 72.17; H, 4.29; N, 17.41%.

2-Amino-4-(furan-2-yl)-11H-pyrimido[4,5-a]carbazole (**7d**): Yellow solid (0.123 g, 41%), m.p. 231–237°C. IR: ν_{max} 3437, 3131, 3104, 1598, 1408, 1237, 808 cm^{-1}. ^1H NMR: δ 9.86 (b s, 1H, N_{11}–H), 7.88–6.99 (m, 7H, C_5–H, C_6–H, C_7–H, C_8–H, C_9–H, C_{10}–H, C_3'–H), 6.59 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.32 Hz), 6.54 (m, 1H, C_4'–H), 5.21 (b s, 2H, –NH_2). MS: *m/z* (%) 300 (M^+, 57). Anal. Calcd for $C_{18}H_{12}N_4O$: C, 71.99; H, 4.03; N, 18.66. Found: C, 71.61; H, 3.94; N, 18.53%.

2-Amino-8-chloro-4-(furan-2-yl)-9-methyl-11H-pyrimido[4,5-a] carbazole (**7e**): Yellow solid (0.116 g, 35%), m.p. 245–247 °C. IR: ν_{max} 3397, 3156, 3119, 1589, 1459, 1381, 1039, 747 cm^{-1}. ^1H NMR: δ 8.90 (b s, 1H, N_{11}–H), 8.03–7.07 (m, 6H, C_5–H, C_6–H, C_7–H, C_9–H, C_{10}–H, C_3'–H), 6.67 (d, 1H, C_5'–H, $J_{\beta\beta'}$ = 3.12 Hz), 6.41 (m,1H, C_4'–H), 5.10 (b s, 2H, –NH_2). MS: *m/z* (%) 336/334 (M^+, 14/ 48). Anal. Calcd for $C_{18}H_{11}ClN_4O$: C, 64.58; H, 3.31; N, 16.74. Found: C, 64.13; H, 3.14; N, 16.48%.

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