Convenient Approaches towards the Synthesis of Novel Pyrano[2,3-*a*]carbazoles

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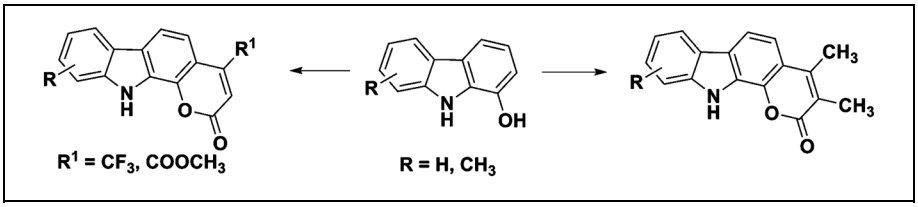

Previously not easily accessible pyrano[2,3-*a*]carbazoles were synthesized in highly convergent syntheses avoiding multistep procedures from readily available 1-hydroxycarbazoles. Substituted pyrano[2,3-*a*]carbazoles were produced by three different methods by treatment of the 1-hydroxycarbazoles with dimethyl acetylene dicarboxylate (DMAD) and triphenylphoshine, by reaction with ethyl 2-methylacetoacetate in the presence of $ZnCl_2/POCl_3$, and by reaction with trifluoroacetic acid followed by Wittig reaction with (carbethoxymethylene) triphenylphosphorane. The article also highlights the optimization of reaction conditions and strategies to avoid formation of byproducts for all three types of reactions.

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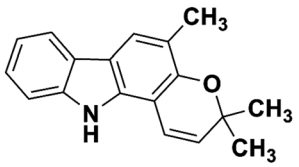
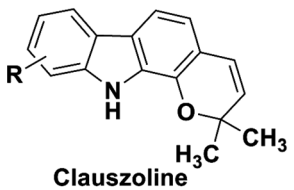
INTRODUCTION

Carbazole alkaloids, both naturally occurring as well as synthetically made, are of great interest not only as attractive targets for synthetic chemists, but especially because of the promising pharmacological properties that many of these compounds confer [1–4]. One family of these biologically active carbazole derivatives that has recently been at the center of attention are naturally occurring 1-oxygenated carbazoles [5]. These alkaloids had initially been extracted from tree and shrub species of the genera *Murraya* and *Clausena*, and in the case of 2- and 3-substituted compounds, their biogenesis has been established [5a,6]. An important milestone in the investigation of this class of natural products had been the isolation of girinimbine, the first pyrano[3,2-*a*]carbazole alkaloid, by Chakraborty *et al*. in 1964 from the stem bark of Murraya koenigii Spreng [7]. Over the following decades a wide range of other 1-oxygenated carbazoles were isolated and described, and new varieties of these compounds continue to be discovered at a regular pace [2a,c]. [2,3-*a*] fused pyranocarbazole alkaloids, for example Clauszolines, were found for the first time in 1996 by Ito *et al.* [8]. After the isolation of these pyranocarbazole alkaloids, from various plant extracts interest into their synthetic manufacture picked up due to the pharmacological potential of these natural products, and in the following years a number of methodologies for the construction of these types of fused carbazoles had been reported [2c,9].



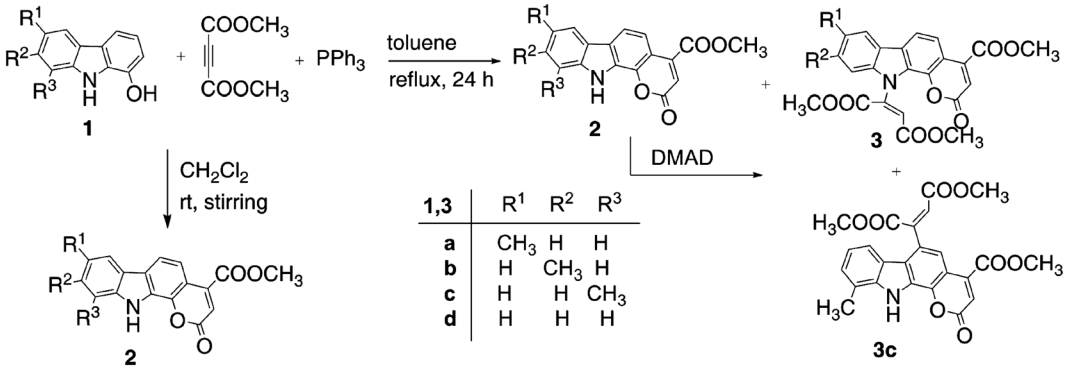
Girinimbine



Clauszoline

Despite of the recent advances in the synthesis of these compounds the development of efficient synthetic routes towards pyranocarbazoles does remain a largely unsolved problem. Most methods are using multiple step sequences with low overall yields, many of the starting materials are not easily accessible, and high cost of catalyst. In our effort to approach this task we would like to herein describe a simple, economical and effective synthetic procedure for the synthesis of pyranocarbazoles utilizing readily accessible 1-hydroxycarbazoles as a starting material, which can be easily prepared from various tetrahydrocarbazol-1-ones [10]. We recently reported the easy conversion of 1-hydroxycarbazole [11] and 1-hydroxycarbazole-2-carbaldehyde [10],[12] into the corresponding pyranocarbazole derivatives, which opened a pathway towards the synthesis of a new pyranocarbazole system. In continuation of this work, we wish to report here several simple and efficient methods for the synthesis of pyrano[2,3-*a*]carbazoles.

Scheme 1



RESULTS AND DISCUSSION

One of the typical features of dimethyl acetylenedicarboxylate (DMAD) is that it forms highly reactive electrophilic vinyltriphenylphosphonium cations when treated with phosphines such as triphenylphosphines (PPh_3) and this reactivity can be readily exploited to activate the DMAD triple bond for many organic synthetic reaction sequences [13].

Treatment of 1-hydroxycarbazoles (**1**) with DMAD and PPh_3 in toluene under refluxing conditions and separation of the reaction mixture by column chromatography afforded the expected products methyl 2-oxo-2,11-dihydropyrano[2,3-*a*]carbazole-4-carboxylate (**2**), but only in low yields, and instead two types of dimethyl maleates (**3**) were isolated in 60-75%, as depicted in **Scheme** 1. The identity of these compounds was deduced from the ^{1}HNMR spectroscopic data which show 3H singlets from methoxy protons and, for **3a**, **3b** and **3d**, they lack the broad singlet typical for an –NH proton. The compounds were thus assigned to be dimethyl 2-(4-(methoxycarbonyl)-2-oxopyrano[2,3-*a*]carbazol-11(2*H*)-yl)maleates **3** resultant from the addition of excess DMAD to the –NH moiety. The NMR spectrum of the reaction product of 1-hydroxy-8-methylcarbazole (**1c**) with DMAD and PPh_3, did, however, still show the broad signal typical for the carbazole –NH moiety. In this case the intermediate compound **2c** did not react by addition of DMAD to the –NH moiety, but yet another compound, dimethyl 2-(4-(methoxycarbonyl)-10-methyl-2-oxo-2,11-dihydropyrano[2,3-*a*]carbazol-6-yl)maleate (**3c**), was obtained by addition of excess DMAD to one of the benzene carbon atoms C_6 as shown in **Scheme** 1. A possible explanation for the different behavior of compounds **1a**, **1b** and **1d** versus **1c** can be found in the steric hindrance provided by the methyl group at C_{10} in the intermediate product **2c** which might have helped to prevent addition of DMAD to the nitrogen atom, leading instead to reaction at C_6. Compounds **1a**, **1b** and **1d** all only carry a hydrogen atom at C_{10}, thus leaving the nitrogen atom less protected against electrophilic attack.

Both types of dimethyl maleates (**3**) are the result of further reaction of initially formed compounds **2** with excess DMAD, which was confirmed by the reaction of isolated compound **2** with DMAD. To be able to isolate **2** we thus repeated the synthesis under milder conditions in methylene chloride at room temperature instead of boiling toluene. When the reaction was carried out this way it indeed yielded exclusively one single product, the target compounds methyl 2-oxo-2,11-dihydropyrano[2,3-*a*]carbazole-4-carboxylate (**2**) in high yield (˜90%) as depicted in Scheme 1. The structures of **2a** and **2c** were unambiguously confirmed by single crystal X-ray analysis [14] as shown in Figure 1.

Next, to transform compound **1** to 3,4-dimethylpyrano [2,3-*a*]carbazoles, the reaction of **1** with ethyl 2-methylacetoacetate was performed in trifluoroacetic acid under reflux conditions for 24 h. TLC showed the presence of three products. Separation of the mixture by column chromatography gave the expected products 3,4-dimethylpyrano [2,3-*a*]carbazole-2-one (**6**) along with 8-hydroxy-4,5-dimethyl-6*H*-pyrido[3,2,1-*j,k*]carbazol-6-ones (**4**) and 1-hydroxy-2-(trifluoroacetyl)carbazoles (**5**) as shown in **Scheme** 2. Compound **1c** afforded **5c** and **6c** without the unexpected product **4c**. The identity of the byproducts **5** was confirmed by a blank reaction of 1-hydroxycarbazole (**1**) with trifluoroacetic acid, which gave the same compound (**Scheme** 3), and the identity of compound **5a** was also confirmed by single crystal X-ray analysis [14] as shown in Figure 2. For the unintended compounds **4** the cyclisation that occurred at C-8 of the carbazole skeleton was attested by its ^{1}H-NMR spectrum, which showed the presence of an OH proton as well as the number and type of signals in the aromatic region expected for compounds **4a**, **4b** and **4d**. Again, similar as for **3c**, the failure of compound **4c** to cyclize can be readily explained by the methyl substituent at carbon atom C10, which prevents reaction at this position.

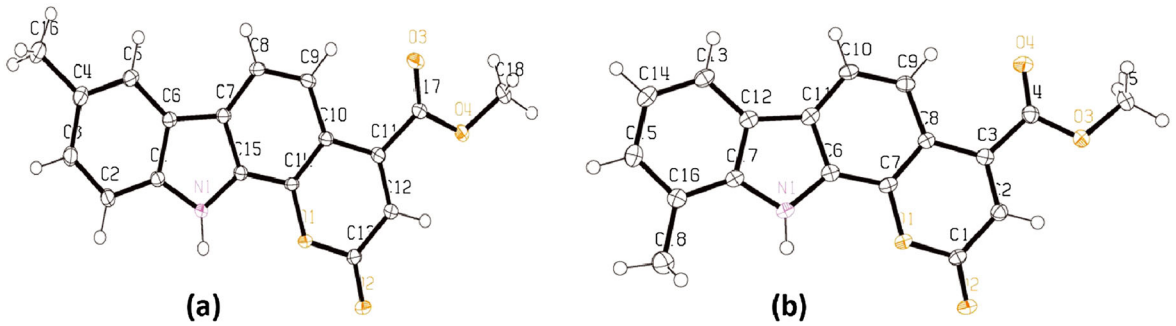


Figure 1. Thermal ellipsoid diagram of (a) methyl 8-methyl-2-oxo-2,11-dihydropyrano[2,3-*a*]carbazole-4-carboxylate (**2a**) and (b) methyl 10-methyl-2-oxo-2,11-dihydropyrano[2,3-*a*]carbazole-4-carboxylate (**2c**). Anistropic displacement parameters are at the 50% probabilty level.

In order to avoid the formation of the trifluoroacetate substituted side product **5**, we then reacted **1** and ethyl 2-methylacetoacetate in the presence of $ZnCl_2/POCl_3$ instead of trifluoroacetic acid. No reaction was observed at room temperature even after 24 h, heating of the mixture to 80°C for 8 h did, however, afford two products (Scheme 1) with the target compounds pyrano[2,3-*a*]carbazole **6** formed in ~80% yield, along with small amounts of the byproduct **4**.

In an earlier report we described the Wittig reaction of 1-hydroxycarbazole-2-carbaldehydes with ylides, which afforded *E*- and *Z*- isomeric products of which only the *Z*- isomer subsequently cyclised to yield pyrano[2,3-*a*] carbazoles in ~40% [12b]. After obtaining product **5** the same idea was adopted utilizing readily available 1-hydroxy-2-(trifluoroacetyl)carbazoles (**5**) as a synthon. Reaction of **5** with (carbethoxymethylene)triphenylphosphorane yielded 4-(trifluoromethyl)pyrano[2,3-*a*]carbazol-2(11*H*)-ones (**7**) in yields of about 90%. The very high yields of the pyranocarbazole in the present case indicates that the 1-hydroxy-2-(trifluoroacetyl)carbazoles form only the *E*-isomers (with the ester group trans to the trifluoromethyl group), which on δ-lactonization afforded the products **7** on intramolecular cyclisation, as it is depicted in Scheme 3. The structures of **7a**, **7b,** and **7c** were confirmed by single crystal X-ray analysis [14] as shown in Figure 3.

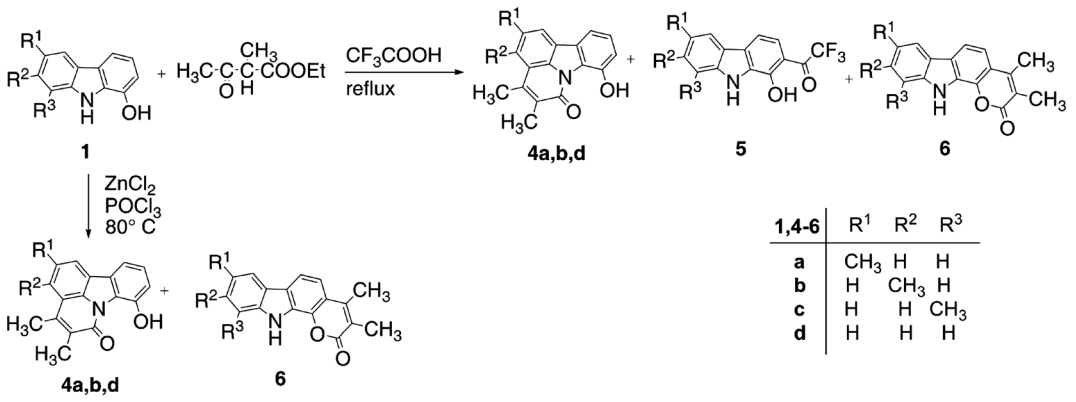
CONCLUSION

In conclusion, we have developed convenient and high yielding methods for the synthesis of a series of pyrano [2,3-*a*]carbazoles in one and two steps, starting from 1-hydroxycarbazoles. A one step synthesis of pyrano[2,3-*a*] carbazole-4-carboxylates and 3,4-dimethylpyrano[2,3-*a*] carbazol-2(11*H*)-ones was achieved with high yield by using DMAD and ethyl 3-methylacetoacetate, respectively. In a two-step procedure, novel trifluoromethyl substituted pyrano[2,3-*a*]carbazoles were synthesized by Wittig reaction through the selective formation of an *E*-isomer intermediate, followed by cyclization.

EXPERIMENTAL

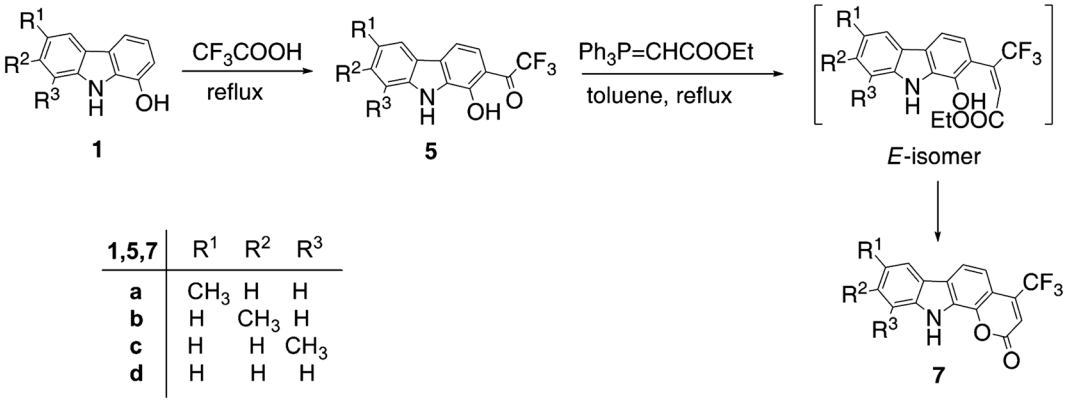
Melting points (mp) were determined on a Mettler FP 51 apparatus (Mettler Instruments, Switzerland) and are uncorrected. They are expressed in degree centigrade (°C). IR spectra were recorded on a Schimadzu FTIR-8201PC spectrophotometer (Schimadzu, Japan) using KBr discs. ^{1}HNMR and ^{13}CNMR spectra were recorded on Bruker AMX 400 and AMX 500 (400 MHz and 500 MHz (^{1}H) and 125 MHz (^{13}CNMR) spectrometer using tetramethylsilane (TMS) as an internal reference. Chemical shifts are expressed in parts per million (ppm). Mass spectra (MS), were recorded on an AutoSpec EI+ shimadzu QP 2010 PLUS GC-MS and LC-MS mass spectrometer. Micro analyses were performed on a Vario EL III model CHNS analyser (Vario, Germany) at

Scheme 2



1,4-6	R^1	R^2	R^3
a	CH_3	H	H
b	H	CH_3	H
c	H	H	CH_3
d	H	H	H

Scheme 3



1,5,7	R^1	R^2	R^3
a	CH_3	H	H
b	H	CH_3	H
c	H	H	CH_3
d	H	H	H

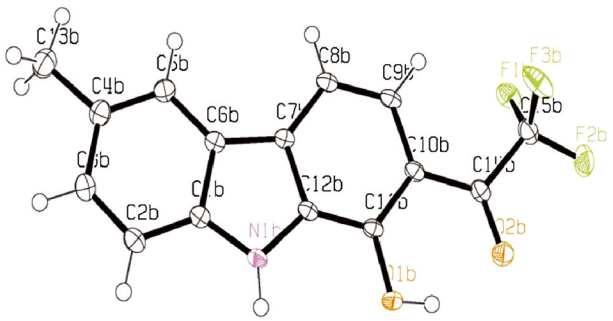


Figure 2. Thermal ellipsoid diagram of 1-hydroxy-6-methyl-2-(trifluoroacetyl)carbazole (**5a**). Anistropic displacement parameters are at the 50% probabilty level. For clarity only one of the two crystallographically independent molecules is shown.

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 as developing solvents. The starting materials **1** were prepared according to a published method [10]. Diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using monochromatic Mo Kα radiation with the omega scan technique. Data were collected, unit cells determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs [15]. The structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL [16]. The crystal of compound **2c** under investigation was found to be nonmerohedrally twinned. The two domains together emulate a three times larger orthorhombic cell with a = 6.659, b = 22.134, and c = 26.577 Å. Further details for this structure are given in the exptl- special- details section of the cif file deposited with the Cambridge Crystallographic Data Centre. Hydrogen atoms for all compounds were placed in calculated positions with X-H bond distances of 0.98 (methyl H), 0.95 (aromatic H), and 0.91 Å (N-H) 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.

General procedure for the preparation of methyl 2-oxo-2,11-dihydropyrano[2,3-a]carbazole-4-carboxylates (2) and dimethyl 2-(4-(methoxycarbonyl)-2-oxo-2,11-dihydropyrano[2,3-a]carbazol-6-yl)-maleate (3). Method: A. To a solution of 1-hydroxycarbazoles **1a-d** (2.5 mmol) and triphenylphosphine (2.5 mmol) in toluene was added dimethyl acetylene dicarboxylate (2.5 mmol) at −5°C. Then, the reaction mixture was heated to reflux for 16 hours. After completion of reaction the excess solvent was removed and the reaction mixture was poured into ice water and extracted with ethylacetate. The organic phase was dried (anhyd. Na_2SO_4), evaporated and purified by column chromatography over silica gel using petroleum ether/ethyl acetate (97:3 and 90:10) as eluent to get the products methyl 2-oxo-2,11-dihydropyrano[2,3-*a*]carbazole-4-carboxylates (**2**) and dimethyl 2-(4-(methoxycarbonyl)-2-oxo-2,11-dihydropyrano[2,3-*a*]carbazol-6-yl)-maleate (**3**) respectively.

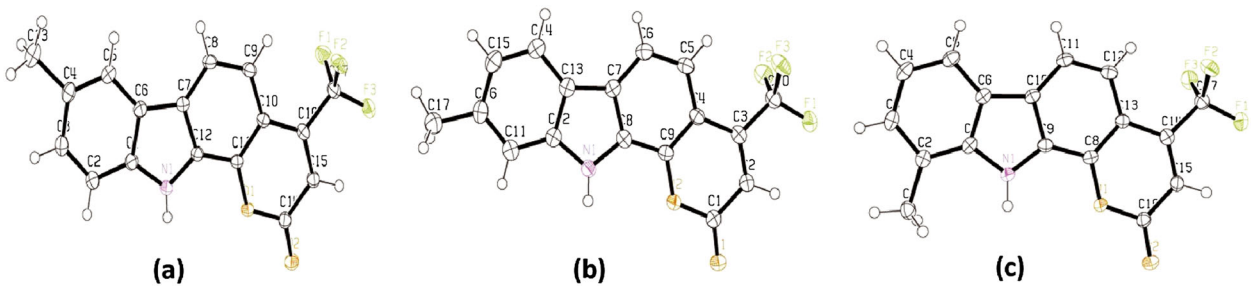


Figure 3. Thermal ellipsoid diagram of (a) 8-methyl-4-(trifluoromethyl)pyrano[2,3-*a*]carbazol-2(11*H*)-one (**7a**); (b) 9-methyl-4-(trifluoromethyl)pyrano [2,3-*a*]carbazol-2(11*H*)-one (**7b**) and (c) 10-methyl-4-(trifluoromethyl)pyrano[2,3-*a*]carbazol-2(11*H*)-one (**7c**). Anistropic displacement parameters are at the 50% probabilty level.

Methyl 8-methyl-2-oxo-2,11-dihydropyrano[2,3-a]carbazole-4-carboxylate (2a). Yellow solid; mp: 283°C; yield: (0.092 g; 12%); IR (KBr): 3382 (vNH), 1740(vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.52 (s, 3H, CH_3), 4.08 (s, 3H, OCH_3), 6.84 (s, 1H, 3-H), 7.32 (d, 1H, 6-H, *J* = 8.0 Hz), 7.40 (d, 1H, 9-H, *J* = 8.0 Hz), 7.82-7.94 (m, 3H, 5-, 7-, and 10-H), 8.64 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 21.67 (CH_3), 53.55 (OCH_3), 110.32, 113.25, 116.12, 116.65, 118.68, 120.68, 123.00, 125.45, 127.68, 130.98, 131.20, 135.14, 137.18, 144.06, 158.64 (C═O), 164.48 (C═O); MS (EI) *m/z*: 307 (M^+); Anal. Calcd. for: $C_{18}H_{13}NO_4$: C, 70.35; H, 4.23; N, 4.56. Found: C, 70.40; H, 4.26; N, 4.52%.

Dimethyl 2-(4-(methoxycarbonyl)-8-methyl-2-oxopyrano [2,3-a]carbazol-11(2H)-yl)-maleate (3a). Yellow solid; mp: 208°C; yield: (0.673 g, 60%); IR (KBr): 1733 cm^{-1} (vOC═O); ^{1}HNMR (δ, $CDCl_3$): 2.54 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.68 (s, 1H, N-C═CH), 6.84 (s, 1H, 3-H), 7.37 (d, 1H, 6-H, *J* = 8.4 Hz), 7.46 (d, 1H, 9-H, *J* = 8.5 Hz), 7.91 (s, 1H, 7-H), 7.93 (d, 1H, 10-H, *J* = 8.5 Hz), 8.04 (d, 1H, 5-H, *J* = 8.4 Hz); ^{13}CNMR (δ, $CDCl_3$): 21.22 (CH_3), 52.08 (OCH_3), 53.07 (OCH_3), 53.39 (OCH_3), 109.70, 113.02, 116.37, 116.47, 118.29, 120.95, 123.06, 125.51, 127.09, 128.02, 129.25, 131.11, 137.14, 139.68, 141.94, 144.15, 158.83 (C═O), 163.44 (C═O), 163.90 (C═O), 164.63 (C═O); MS (EI) *m/z*: 449 (M^+); Anal. Calcd. for: $C_{24}H_{19}NO_8$: C, 64.14; H, 4.23; N, 3.12. Found: C, 64.26; H, 4.21; N, 3.15%.

Methyl 9-methyl-2-oxo-2,11-dihydropyrano[2,3-a]carbazole-4-carboxylate (2b). Yellow solid; mp: 267°C; yield: (0.115 g, 15%); IR (KBr): 3377 (vNH), 1715 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.54 (s, 3H, CH_3), 4.06 (s, 3H, OCH_3), 6.91 (s, 1H, 3-H), 7.17 (d, 1H, 8-H, *J* = 8.5 Hz), 7.36 (s, 1H, 10-H), 7.94 (d, 1H, 6-H, *J* = 8.5 Hz), 7.99 (d, 1H, 5-H, *J* = 8.5 Hz), 8.03 (d, 1H, 7-H, *J* = 8.5 Hz), 8.65 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 21.2 (CH_3), 53.5 (OCH_3), 111.1, 113.5, 116.0, 116.8, 118.9, 120.4, 121.3, 121.8, 122.8, 131.0, 131.2, 132.4, 135.0, 144.5, 158.3 (CO), 164.1 (CO); MS (EI) *m/z*: 307 (M^+); Anal. Calcd. for: $C_{18}H_{13}NO_4$: C, 70.35; H, 4.23; N, 4.56. Found: C, 70.38; H, 4.21; N, 4.59%.

Dimethyl 2-(4-(methoxycarbonyl)-9-methyl-2-oxopyrano [2,3-a]carbazol-11(2H)-yl)- maleate (3b). Yellow solid; mp: 205°C; yield: (0.841 g, 75%); IR (KBr):1738 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.51 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 6.55 (s, 1H, 2′-H), 6.99 (s, 1H, 3-H), 7.22 (d, 1H, 8-H, *J* = 7.8 Hz), 7.38 (d, 1H, 6-H, *J* = 8.1 Hz), 7.94 (d, 1H, 7-H, *J* = 7.8 Hz), 7.96 (s,1H, 10-H), 8.02 (d, 1H, 5-H, *J* = 8.1 Hz); ^{13}CNMR (δ, $CDCl_3$): 21.5 (CH_3), 52.3 (OCH_3), 53.1 (OCH_3), 53.5 (OCH_3), 111.3, 113.4, 116.1, 117.1, 118.9, 120.0, 120.4, 121.5, 123.4, 129.0, 130.5, 130.8, 132.1, 137.5, 141.5, 144.0, 158.7 (CO), 163.1 (CO), 163.5 (CO), 164.3 (CO); MS (EI) *m/z*: 449 (M^+); Anal. Calcd. for: $C_{24}H_{19}NO_8$: C, 64.14; H, 4.23; N, 3.12. Found: C, 64.26; H, 4.22; N, 3.15%.

Methyl 10-methyl-2-oxo-2,11-dihydropyrano[2,3-a]carbazole-4-carboxylate (2c). Yellow solid; mp: 291°C; yield: (0.145 g, 19%); IR (KBr): 3334 (vNH), 1735 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.60 (s, 3H, CH_3), 4.03 (s, 3H, OCH_3), 6.89 (s, 1H, 3-H), 7.22 (t, 1H, 8-H, *J* = 8.5 Hz), 7.32 (d, 1H, 6-H, *J* = 8.0 Hz), 7.92 (d, 1H, 9-H, *J* = 8.5 Hz), 7.94 (d, 1H, 5-H, *J* = 8.0 Hz), 7.96 (d, 1H, 7-H, *J* = 8.5 Hz), 8.69 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 16.3 (CH_3), 53.4 (OCH_3), 113.1, 116.6, 116.9, 118.2, 118.7, 120.4, 121.6, 123.4, 126.1, 128.4, 130.8, 131.3, 135.7, 144.2, 158.2 (CO), 164.0 (CO); MS (EI) *m/z* : 307 (M^+); Anal. Calcd. for: $C_{18}H_{13}NO_4$: C, 70.35; H, 4.23; N, 4.56. Found: C, 70.42; H, 4.25; N, 4.49%.

Dimethyl 2-(4-(methoxycarbonyl)-10-methyl-2-oxo-2,11-dihydropyrano[2,3-a]carbazol-6-yl)- maleate (3c). Yellow solid; mp: 222°C; yield: (0.774 g, 69%); IR (KBr): 3335 (vNH), 1740 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.62 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.67 (s, 1H, 2′-H), 6.90 (s, 1H, 3-H), 7.23 (t, 1H, 8-H, *J* = 7.8 Hz), 7.91 (d, 1H, 9-H, *J* = 7.7 Hz), 7.93 (s, 1H, 5-H), 7.98 (d, 1H, 7-H, *J* = 7.8 Hz), 8.63 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 16.5 (CH_3), 52.0 (OCH_3), 53.3 (OCH_3), 53.6 (OCH_3), 108.6, 116.0, 117.3, 117.8, 118.2, 120.6, 121.8, 122.4, 122.7, 127.1, 129.0, 129.4, 130.5, 136.6, 143.8, 145.6, 158.3 (CO), 164.2 (CO), 165.3 (CO), 166.1 (CO); MS (EI) *m/z*: 449 (M^+); Anal. Calcd. for: $C_{24}H_{19}NO_8$: C, 64.14; H, 4.23; N, 3.12. Found: C, 64.18; H, 4.20; N, 3.19%.

Methyl 2-oxo-2,11-dihydropyrano[2,3-a]carbazole-4-carboxylate (2d). Yellow solid; mp: 296°C; yield: (0.095 g, 13%); IR (KBr): 3395 (vNH), 1715 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 4.04 (s, 3H, OCH_3), 6.86 (s, 1H, 3-H), 7.28 (t, 1H, 8-H, *J* = 8.2 Hz), 7.31 (d, 1H, 6-H, *J* = 7.8 Hz), 7.48 (t, 1H, 9-H, *J* = 7.6 Hz), 7.65 (d, 1H, 10-H, *J* = 7.7 Hz), 7.94 (d, 1H, 5-H, *J* = 7.8 Hz), 7.03 (d, 1H, 7-H, *J* = 8.2 Hz), 8.63 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 53.5 (OCH_3), 111.4, 113.0. 116.2, 117.2, 119.1, 119.4, 120.6, 123.2, 125.5, 126.1, 131.5, 135.8, 141.2, 144.0, 158.1 (CO), 164.4 (CO); MS (EI) *m/z*: 293 (M^+); Anal. Calcd. for: $C_{17}H_{11}NO_4$: C, 69.62; H, 3.75; N, 4.78. Found: C, 69.53; H, 3.72; N, 4.69%.

Dimethyl 2-(4-(methoxycarbonyl)-2-oxopyrano[2,3-a] carbazol-11(2H)-yl)-maleate (3d). Yellow solid; mp: 198°C; yield: (0.708 g, 65%); IR (KBr): 3309 (vNH), 1746 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 3.87 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.65 (s, 1H, 2′-H), 6.86 (s, 1H, 3-H), 7.29 (t, 1H, 8-H, *J* = 7.9 Hz), 7.34 (d, 1H, 6-H, *J* = 8.2 Hz), 7.46 (t, 1H, 9-H, *J* = 7.8 Hz), 7.98 (d, 1H, 5-H, *J* = 8.2 Hz), 8.04 (d, 1H, 10-H, *J* = 7.8 Hz), 8.12 (d, 1H, 7-H, *J* = 7.9 Hz,); ^{13}CNMR (δ, $CDCl_3$): 52.4 (OCH_3), 53.2 (OCH_3), 53.6 (OCH_3), 111.2, 112.8, 116.0, 117.0, 118.4, 118.9, 120.5, 122.9, 123.4, 126.2, 129.5, 131.6, 137.1, 141.1, 142.1, 144.7, 158.4 (CO), 163.2 (CO), 163.8 (CO), 164.9 (CO); MS (EI) *m/z*: 435 (M^+); Anal. Calcd. for: $C_{23}H_{17}NO_8$: C, 63.45; H, 3.91; N, 3.22. Found: C, 63.36; H, 3.88; N, 3.17%.

Method: B. To a solution of the respective 1-hydroxy carbazoles (2.5 mmol) and triphenylphosphine (2.5 mmol) in dichloromethane was added dimethyl acetylene dicarboxylate (2.5 mmol) at −5°C. Then, the reaction mixture was stirred 24 h at room temperature. After completion of reaction the excess solvent was removed and the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic phase was dried (anhyd.Na_2SO_4) evaporated and purified by column chromatography over silica gel using petroleum ether/ethyl acetate (97:3) to afford the single product methyl 2-oxo-2,11-dihydropyrano[2,3-*a*]carbazole-4-carboxylates (**2**) [yield: **2a** (0.698 g, 91%); **2b** (0.714 g, 93%); **2c** (0.690 g, 90%); **2d** (0.696 g, 95%)].

General procedure for the preparation of 8-hydroxy-4,5-dimethyl-6*H*-pyrido[3,2,1-*jk*]carbazol-6-ones (4) and 3,4-dimethylpyrano[2,3-*a*]carbazol-2(11*H*)-ones (5). Method: A. An appropriate mixture of the respective 1-hydroxycarbazoles (2.5 mmol) and ethyl 2-methylacetoacetate (2.5 mmol) was refluxed in trifluoroacetic acid (10 mL) at steam bath temperature for 24 h. The reaction was monitored by TLC. After completion of the reaction the mixture was poured onto crushed ice and extracted with ethyl acetate. The organic phase was dried (anhydrous Na_2SO_4),

evaporated and purified by column chromatography over silica gel using petroleum ether/ethyl acetate (100:0, 99:1, and 95:5) as eluent to get the products 8-hydroxy-4,5-dimethyl-6*H*-pyrido[3,2,1-*j,k*] carbazol-6-one (**4**), 1-hydroxy-2-(trifluoroacetyl) carbazole (**5**) and 3,4-dimethylpyrano[2,3-*a*]carbazol-2(11*H*)-one (**6**), respectively.

8-Hydroxy-2,4,5-trimethyl-6H-pyrido[3,2,1-j,k]carbazol-6-one (4a). Yellow solid; mp: 189°C; yield: (0.214 g, 31%); IR (KBr): 3424 (vOH), 1628 (vC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.34 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 7.05 (d, 1H, 9-H, *J* = 8.0 Hz), 7.32 (t, 1H, 10-H, *J* = 7.7 Hz), 7.41 (d, 1H, 11-H, *J* = 7.4 Hz), 7.55 (s, 1H, 3-H), 7.82 (s, 1H, 1-H), 12.58 (s, 1H, OH); ^{13}CNMR (δ, $CDCl_3$): 13.24 (CH_3), 14.68 (CH_3), 21.87 (CH_3), 111.03, 116.21, 118.93, 119.00, 122.63, 122.78, 124.53, 126.77, 127.47, 128.48, 131.06, 134.37, 143.87, 146.60, 160.58 (C=O); LC-MS *m/z*: 278 ($M+H^+$); Anal. Calcd. for: $C_{18}H_{15}NO_2$: C, 77.98; H, 5.41; N, 5.05. Found: C, 77.87; H, 5.43; N, 5.00%.

1-Hydroxy-6-methyl-2-(trifluoroacetyl)carbazole (5a). Yellow solid; m. p. 192°C; yield: (0.088 g, 12%); IR (KBr): 3391(vNH overlapped with OH), 1654 (vC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.55 (s, 3H, CH_3), 7.38 (dd, 1H, 7-H, J_m = 1.5 Hz, J_o = 8.5 Hz), 7.43 (d, 1H, 8-H, *J* = 8.5 Hz), 7.58-7.62 (m, 2H, 3- and 4-H), 7.88 (s, 1H, 5-H), 8.55 (br s, 1H, NH), 11.87 (s, 1H, OH); ^{13}CNMR (δ, $CDCl_3$): 21.38 (CH_3), 109.74, 111.41, 111.74, 112.28, 115.21, 120.19, 121.28, 122.81, 128.16, 130.15, 130.38, 130.54, 139.35, 152.63 (C=O); MS (EI) *m/z* (%): 293 (M^+, 100); Anal. Calcd. for: $C_{15}H_{10}F_3NO_2$: C, 61.43; H, 3.41; N, 4.78. Found: C, 61.38; H, 3.39; N, 4.76%.

3,4,8-Trimethylpyrano[2,3-a]carbazol-2(11H)-one (6a). Yellowish white solid; mp: >300°C; yield: (0.305 g, 44%); IR (KBr): 3272 (vNH), 1688 (vOC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.28 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 7.31 (dd, 1H, 9-H, J_m = 1.2 Hz, J_o = 7.4 Hz), 7.40-7.43 (m, 2H, 6- and 10-H), 7.88-7.90 (m, 2H, 5- and 7-H), 8.61 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 13.34 (CH_3), 14.68 (CH_3), 21.66 (CH_3), 111.50, 112.51, 118.25, 118.92, 119.84, 122.14, 122.98, 126.30, 127.36, 127.54, 133.72, 134.45, 137.18, 142.96, 158.14 (C=O); LC-MS *m/z*: 278 ($M+H^+$); Anal. Calcd. for: $C_{18}H_{15}NO_2$: C, 77.98; H, 5.41; N, 5.05. Found: C, 77.92; H, 5.43; N, 5.01%.

8-Hydroxy-3,4,5-trimethyl-6*H*-pyrido[3,2,1-*j,k*]carbazol-6-one (4b):. Yellow solid; mp: 194°C; yield: (0.194 g, 28%); IR (KBr): 3426 (vOH), 1621 (vC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.35 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 7.08 (d, 1H, 9-H, *J* = 8.0 Hz), 7.31(d, 1H, 2-H, *J* = 8.0 Hz), 7.37 (t, 1H, 10-H, *J* = 8.0 Hz,), 7.51 (d, 1H, 11-H, *J* = 8.0 Hz), 7.66 (d, 1H, 1-H, *J* = 8.0 Hz), 12.84 (s, 1H, OH); ^{13}CNMR (δ, $CDCl_3$): 13.3, (CH_3), 14.5 (CH_3), 20.8 (CH_3), 110.8, 116.0, 118.3, 119.5, 119.8, 120.2, 123.3, 125.2, 126.5, 128.3, 128.6, 131.6, 144.1, 146.8, 160.8 (CO); LC-MS *m/z*: 278 ($M+H^+$); Anal. Calcd. for: $C_{18}H_{15}NO_2$: C, 77.98; H, 5.41; N, 5.05. Found: C, 77.89; H, 5.38; N, 5.10%.

1-Hydroxy-7-methyl-2-(trifluoroacetyl)carbazole (5b). Yellow solid; mp: 216°C; yield: (0.073 g, 10%); IR (KBr): 3393 (vNH overlapped with OH), 1654 (vC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.58 (s, 3H, CH_3), 7.15 (d, 1H, 6-H, *J* = 8.0 Hz), 7.34 (s, 1H, 8-H), 7.61-7.62 (m, 2H, 3- and 4-H), 7.98 (d, 1H, 5-H, *J* = 8.0 Hz), 8.54 (br s, 1H, NH), 11.89 (s, 1H, OH); ^{13}CNMR (δ, $CDCl_3$): 21.2 (CH_3), 109.3, 111.0, 111.6, 112.4, 115.5, 120.0, 120.4, 121.1, 121.6, 130.4, 130.9, 132.7, 140.1, 152.8 (CO); MS (EI) *m/z* (%): 293 (M^+, 100); Anal. Calcd. for: $C_{15}H_{10}F_3NO_2$: C, 61.43; H, 3.41; N, 4.78. Found: C, 61.36; H, 3.37; N, 4.73%.

3,4,9-Trimethylpyrano[2,3-*a*]carbazol-2(11*H*)-one (6b). Yellowish white solid; mp: >300°C; yield: (0.284 g, 41%); IR (KBr): 3269 (vNH), 1685 (vOC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.29 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 7.13 (d, 1H, 6-H, *J* = 8.5 Hz), 7.34 (s, 1H, 10-H), 7.43 (d, 1H, 8-H, *J* = 8.0 Hz), 7.89 (d, 1H, 5-H, *J* = 8.5 Hz), 7.97 (d, 1H, 7-H, *J* = 8.0 Hz), 8.63 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 13.7 (CH_3), 14.5 (CH_3), 21.7 (CH_3), 111.2, 111.9, 117.8, 119.1, 119.4, 120.1, 120.7, 121.8, 126.0, 128.2, 130.8, 132.6, 137.1, 143.2, 158.6 (CO); LC-MS *m/z*: 278 ($M+H^+$); Anal. Calcd. for: $C_{18}H_{15}NO_2$: C, 77.98; H, 5.41; N, 5.05. Found: C, 78.04; H, 5.45; N, 4.99%.

1-Hydroxy-8-methyl-2-(trifluoroacetyl)carbazole (5c). Yellow solid; mp: 162°C; yield: (0.059 g, 8%); IR (KBr): 3377 (vNH overlapped with OH), 1647 (vC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.61 (s, 3H, CH_3), 7.25 (t, 1H, 6-H, *J* = 7.5 Hz), 7.38 (d, 1H, 7-H, *J* = 7.5 Hz), 7.64-7.67 (m, 2H, 3- and 4-H), 7.96 (d, 1H, 5-H, *J* = 8.0 Hz), 8.55 (br s, 1H, NH), 11.95 (s, 1H, OH); ^{13}CNMR (δ, $CDCl_3$): 16.9 (CH_3), 109.2, 111.8, 112.1, 115.4, 118.7, 120.5, 120.7, 121.9, 127.6, 129.2, 130.0, 130.6, 140.3, 152.5 (CO); MS (EI) *m/z* (%): 293 (M^+, 100); Anal. Calcd. for: $C_{15}H_{10}F_3NO_2$: C, 61.43; H, 3.41; N, 4.78. Found: C, 61.48; H, 3.44; N, 4.76%.

3,4,10-Trimethylpyrano[2,3-*a*]carbazol-2(11*H*)-one (6c). Yellow solid; mp: >300°C; yield: (0.270 g, 39%); IR (KBr): 3309 (vNH), 1691 (vOC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.31 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 7.23 (t, 1H, 8-H, *J* = 8.5 Hz), 7.32 (d, 1H, 6-H, *J* = 7.5 Hz), 7.45 (d, 1H, 9-H, *J* = 8.5 Hz), 7.92-7.96 (m, 2H, 5- and 7-H), 8.69 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 13.4 (CH_3), 14.8 (CH_3), 16.8 (CH_3), 112.8, 118.0, 118.3, 118.7, 119.6, 120.3, 121.2, 126.5, 127.3, 128.4, 129.0, 130.2, 137.4, 142.8, 158.0 (CO); LC-MS *m/z*: 278 ($M+H^+$); Anal. Calcd. for: $C_{18}H_{15}NO_2$: C, 77.98; H, 5.41; N, 5.05. Found: C, 77.99; H, 5.40; N, 5.12%.

8-Hydroxy-4,5-dimethyl-6*H*-pyrido[3,2,1-*j,k*]carbazol-6-one (4d). Yellow solid; mp: 191°C; yield: (0.204 g, 31%); IR (KBr): 3425 (vOH), 1635 (vC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.39 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 7.09 (d, 1H, 3-H, *J* = 8.0 Hz), 7.37 (t, 1H, 10-H, *J* = 8.0 Hz), 7.49 (d, 1H, 9-H, *J* = 8.0 Hz), 7.57 (t, 1H, 2-H, *J* = 8.0 Hz), 7.82 (d, 1H, 11-H, *J* = 8.0 Hz), 8.07 (d, 1H, 1-H, *J* = 8.0 Hz), 12.59 (s, 1H, OH); ^{13}CNMR (δ, $CDCl_3$): 13.4 (CH_3), 14.5 (CH_3), 110.0, 111.5, 116.5, 118.8, 119.2, 119.7, 120.9, 122.7, 126.2, 128.1, 128.7, 131.4, 144.2, 146.5, 160.6 (CO); LC-MS *m/z*: 264 ($M+H^+$); Anal. Calcd. for: $C_{17}H_{13}NO_2$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.49; H, 4.97; N, 5.25%.

1-Hydroxy-2-(trifluoroacetyl)carbazole (5d). Yellow solid; mp: 206°C; yield: (0.091 g, 13%); IR (KBr): 3388 (vNH overlapped with OH), 1650 (vC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 7.32 (t, 1H, 6-H, J_m = 2.0 Hz, J_o = 7.8 Hz), 7.55-7.59 (m, 2H, 3- and 4-H), 7.63-7.68 (m, 2H, 7- and 8-H), 8.11 (d, 1H, 5-H, *J* = 7.8 Hz), 8.64 (br s, 1H, NH), 11.89 (s, 1H, OH); ^{13}CNMR (δ, $CDCl_3$): 109.8, 111.1, 111.4, 112.9, 115.1, 118.3, 120.2, 120.5, 123.4, 127.0, 130.2, 139.8, 140.7, 152.6 (CO); MS (EI) *m/z* (%): 279 (M^+, 100); Anal. Calcd. for: $C_{14}H_8F_3NO_2$: C, 60.21; H, 2.87; N, 5.02. Found: C, 60.24; H, 2.83; N, 5.05%.

3,4-Dimethylpyrano[2,3-*a*]carbazol-2(11*H*)-one (6d). Yellow solid; mp: >300°C; yield: (0.289 g, 44%); IR (KBr): 3278 (vNH), 1688 (vOC=O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.30 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 7.31 (t, 1H, 8-H, *J* = 8.0 Hz), 7.46 (d, 1H, 6-H, *J* = 8.5 Hz), 7.51 (t, 1H, 9-H, *J* = 8.0 Hz), 7.55 (d,

1H, 10-H, *J* = 8.0 Hz), 7.95 (d, 1H, 5-H, *J* = 8.5 Hz), 8.11 (d, 1H, 7-H, *J* = 8.0 Hz), 8.78 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 13.3 (CH_3), 14.6 (CH_3), 111.0, 112.5, 118.3, 118.8, 119.0, 120.1, 120.7, 123.2, 126.1, 126.6, 128.1, 137.3, 141.4, 143.5, 158.4 (CO); LC-MS *m/z*: 264 ($M+H^+$); Anal. Calcd. for: $C_{17}H_{13}NO_2$: C, 77.49; H, 4.97; N, 5.25. Found: C, 77.54; H, 4.95; N, 5.19%.

Method: B. To an appropriate mixture of the respective 1-hydroxycarbazole (2.5 mmol), ethyl 2-methylacetoacetate (2.5 mmol) and fused $ZnCl_2$ (1.5 g), $POCl_3$ (6 mL) was added drop by drop at 0°C with constant stirring for 1 hour and then temperature was raised to 80°C for 8 h. The reaction was monitored by TLC. After completion of the reaction, the mixture was poured onto crushed ice with continuous stirring and extracted with ethyl acetate. The organic phase was dried (anhydrous Na_2SO_4), evaporated and purified by column chromatography over silica gel using petroleum ether/ethyl acetate (100:0 and 95:5) as eluent to get the products 8-hydroxy-4,5-dimethyl-6*H*-pyrido[3,2,1-*j,k*] carbazol-6-one (**4**), and 3,4-dimethylpyrano[2,3-*a*]carbazol-2(11*H*)-one (**6**) respectively. (Yield: **4a** (0.055 g, 8%); **6a** (0.568 g, 82%); **4b** (0.069 g, 10%); **6b** (0.554 g, 80%); **6c** (0.540 g, 78%); **4d** (0.066 g, 10%); **6d** (0.552 g, 84%)).

General procedure for the preparation of 4-(trifluoromethyl) pyrano[2,3-a]carbazol-2(11*H*)-ones (7). A mixture of an appropriate 1-hydroxy-2-(trifluoroacetyl)carbazoles (1 mmol), (carbethoxymethylene)triphenylphosphorane (1 mmol) was heated to reflux in 5 mL toluene at 120°C for 6 h. The reaction was monitored by TLC. After the removal of excess solvent, the obtained crude product was purified by column chromatography over silica gel using petroleum ether : ethyl acetate (97:3) to yield the corresponding 4-(trifluoromethyl) pyrano[2,3-*a*]carbazol-2(11*H*)-ones (**7**).

8-Methyl-4-(trifluoromethyl)pyrano[2,3-a]carbazol-2(11H)-one (7a). Yellow solid; mp: 269°C; yield: (0.304 g, 96%); IR (KBr): 3311 (vNH), 1733 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.55(s, 3H, CH_3), 6.79 (s, 1H, 3-H), 7.38 (d, 1H, 6-H, *J* = 8.4 Hz), 7.46 (d, 1H, 9-H, *J* = 8.1 Hz), 7.51 (d, 1H, 10-H, *J* = 8.1 Hz), 7.91 (s, 1H, 7-H), 7.96 (d, 1H, 5-H, *J* = 8.4 Hz), 8.72 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 21.31 (CH_3), 109.80, 111.22, 114.14, 115.13, 116.93, 116.98, 120.79, 122.46, 124.72, 127.35, 128.88, 129.52, 130.30, 138.68, 152.12, 158.62 (C=O); MS (EI) *m/z*: 317 (M^+); Anal. Calcd. for: $C_{17}H_{10}F_3NO_2$: C, 64.35; H, 3.15; N, 4.41. Found: C, 64.31; H, 3.12; N, 4.45%.

9-Methyl-4-(trifluoromethyl)pyrano[2,3-*a*]carbazol-2(11*H*)-one (7b). Yellow solid; mp: 252°C; yield: (0.301 g, 95%); IR (KBr): 3311 (vNH), 1734 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.57(s, 3H, CH_3), 6.81 (s, 1H, 3-H), 7.18 (d, 1H, 6-H, *J* = 8.0 Hz), 7.38 (s, 1H, 10-H), 7.54 (d, 1H, 8-H, *J* = 8.5 Hz), 7.97 (d, 1H, 7-H, *J* = 8.5 Hz), 8.01 (d, 1H, 5-H, *J* = 8.0 Hz), 8.71(br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 21.4 (CH_3), 110.2, 111.1, 114.4, 115.7, 116.2, 116.8, 120.3, 121.7, 122.3, 122.8, 129.1, 130.9, 132.4, 136.2, 152.5, 158.8 (CO); MS (EI) *m/z*: 317 (M^+); Anal. Calcd. for: $C_{17}H_{10}F_3NO_2$: C, 64.35; H, 3.15; N, 4.41. Found: C, 64.38; H, 3.17; N, 4.38%.

10-Methyl-4-(trifluoromethyl)pyrano[2,3-*a*]carbazol-2(11*H*)-one (7c). Yellow solid; mp: 285°C; yield: (0.295 g, 93%); IR (KBr): 3320 (vNH), 1738 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 2.56 (s, 3H, CH_3), 6.74 (s, 1H, 3-H), 7.19 (t, 1H, 8-H, *J* = 8.5 Hz), 7.29 (d, 1H, 6-H, *J* =8.0 Hz), 7.47 (d, 1H, 9-H, *J* = 8.5 Hz), 7.90 (d, 1H, 5-H, *J* = 8.0 Hz), 7.92 (d, 1H, 7-H, *J* = 8.5 Hz), 8.66 (br s, 1H, NH); ^{13}CNMR (δ, $CDCl_3$): 16.9 (CH_3), 109.9, 114.0, 115.4, 116.3, 116.6, 118.3, 120.0, 121.6, 122.1, 127.8, 129.2, 129.9, 131.1, 136.7, 152.3, 158.4 (CO); MS (EI) *m/z*: 317 (M^+); Anal. Calcd. for: $C_{17}H_{10}F_3NO_2$: C, 64.35; H, 3.15; N, 4.41. Found: C, 64.30; H, 3.19; N, 4.39%.

4-(Trifluoromethyl)pyrano[2,3-*a*]carbazol-2(11*H*)-one (7d). Yellow solid; mp: 271°C; yield: (0.287 g, 95%); IR (KBr): 3318 (vNH), 1733 (vOC═O) cm^{-1}; ^{1}HNMR (δ, $CDCl_3$): 6.72 (s, 1H, 3-H), 7.27 (t, 1H, 8-H, *J* = 8.5 Hz), 7.30 (d, 1H, 10-H, *J* = 8.5 Hz), 7.38 (d, 1H, 6-H, *J* = 8.5 Hz), 7.44 (t, 1H, 9-H, *J* = 8.5 Hz), 7.88 (d, 1H, 5-H, *J* = 8.5 Hz), 7.93 (d, 1H, 7-H, *J* = 8.5 Hz), 8.62 (br s, 1H, N_{11}-H); ^{13}CNMR (δ, $CDCl_3$): 109.6, 111.2, 114.2, 115.7, 116.1, 116.9, 118.6, 120.5, 122.7, 123.1, 126.3, 128.8, 136.1, 140.3, 152.1, 158.6 (CO); MS (EI) m/z: 303 (M^+); Anal. Calcd. for: $C_{16}H_8F_3NO_2$: C, 63.36; H, 2.64; N, 4.62. Found: C, 63.32; H, 2.68; N, 4.65%.

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[14] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 796520 - 796525. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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