1 Synthesis and Reactions of Pyrido[3,2,1-*jk*]carbazole-4,6-diones

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Pyrido[3,2,1-jk]carbazoles 1, synthesized from carbazoles and alkyl- or arylmalonates, gave regioselective electrophilic substitution reactions at position 5 such as chlorination to 5-chloro derivatives 2, nitration to 5-nitro compounds 3, or hydroxylation to 5-hydroxy derivatives 4. 5-Hydroxy compounds 4 gave on treatment with strong bases ring contraction to 5, 6 or the ring opening product 7. Exchange of the chloro group in 2 with azide or amines gave the corresponding azides 8 and the 5-amino derivatives 9 and 10. Alkylation of 1 with benzyl chloride or allyl bromide resulted in the formation of 5-C-alkylated products 11 together with 4-alkyloxy derivatives 12.

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INTRODUCTION

Pyrido [3,2,1-jk]carbazol-6-one, which is part of the heterocyclic skeleton of natural products such as strychnos alkaloids [1], contains the biologically interesting combination of indole and 2-pyridone heterocycles. Some derivatives have found interest in pharmacological investigations [2] and in dye chemistry [3]. Recently, we published the synthesis of 4-hydroxypyrido[3,2,1jk]carbazol-6-ones [4], which possess two reactive positions: the hydroxy group at C-4, which can be substituted by various nucleophiles, and the CH-acidic proton at C-5, which is accessible to electrophilic reactions. In refs. [4] and [5], we published a series of nucleophilic reactions at position 4; in this contribution, we wish to report on regioselective electrophilic substitutions at position 5 to form 5,5-disubstituted pyrido[3,2,1-jk]carbazole-4,6-diones.

RESULTS AND DISCUSSION

Electrophilic substitution of 5-monosubstituted 4hydroxypyridocarbazoles 1 should form regioselectively 5,5-disubstituted pyrido[3,2,1-jk]carbazole-4,6-diones by reaction at the CH-acidic position of C-5, which results in the corresponding dioxo structure of the molecule. Formation of by-products by electrophilic substitution at the two aromatic rings can be avoided because of the different reactivities of C-5 and aromatic positions.

Electrophilic substitution at position 5 in 4-hydroxypyridocarbazoles 1a-f (from its tautomeric dioxo form) by chlorine should be easily achieved by reaction with sulfuryl chloride or elementary chlorine as reagents as described earlier for 4-hydroxyquinolones [6]. A radical process can be ruled out because of the mild reaction conditions. The aspired 5-chloro products 2 were intended to be used in further reactions because of their high reactivity (Scheme 1).

The chlorination of **1** was performed with sulfuryl chloride in dioxane solution at 50°C, followed by a short raise to 90°C to finish the reaction, which gave in excellent yields of 73–83% 5-chloro-5-substituted-pyridocarbazole-4,6-diones **2a–f**. Temperatures and reaction times had to be strictly applied, otherwise unwanted multiple chlorination products were formed. Infrared spectral analysis revealed the additional ketone carbonyl band of C-4 in the region of 1720 cm⁻¹ besides the amide carbonyl band of C-6 at about 1690 cm⁻¹. The aromatic signals in ¹H-NMR showed that no chlorination in the benzo part of the carbazole nucleus had occurred.

Nitration of 1 (again from its tautomeric dioxo form) as an established electrophilic reaction should give 5-



nitro compounds 3 (Scheme 1), which can be further used for reduction to amino groups that is planned to be published in future. The nitration reaction of similar 4hydroxyquinolone systems was reported with nitric acid in boiling acetic acid [7]. However, this reaction sequence could not be applied for 4-hydroxypyridocarbazol-6-one derivatives 1 because a number of by-products were formed by these conditions. To avoid these difficulties, the nitration reaction was carried out under milder conditions, using sodium nitrite as catalyst. Starting with 4-hydroxy-5-substituted pyridocarbazol-6-ones 1a-e, dissolved in glacial acetic acid, the reaction with nitric acid and sodium nitrite led already at room temperature to pure 5-nitro-5-substituted-pyridocarbazole-4,6-diones 3a-e in good yields of 60-85%. The catalytical effect of sodium nitrite can be explained by an initial nitrosation of 1 in position 5 and subsequent oxidation of the nitroso to the desired nitro group [8]. The infrared spectra showed again the ketone carbonyl band of C-4 in the region of 1720 cm^{-1} and the amide carbonyl band of C-6 in the region of 1690 cm^{-1} . The presence of all aromatic ¹H-NMR signals of the carbazole part proved that no further multinitration had occurred.

However, another interesting side reaction was observed, when 4-hydroxypyridocarbazolone **1a** was reacted to the nitro compound **3a** using the nitrite/nitric acid method: in the reaction mixture already at room temperature, traces of 5-hydroxy-5-methylpyrido[3,2,1*jk*]carbazole-4,6-dione (**4a**) were present. When the reaction was performed at higher reaction temperature (60°C), 5-hydroxy-5-methylpyridocarbazoledione **4a** was isolated as the main product (described as method B for the synthesis of **4a**). This can be explained in terms either of a direct oxidation of the CH-acidic position 5 by the oxidative agents present in the reaction mixture, such as nitrous and nitric acid, or by the subsequent exchange of the already formed nitro group in **3a** against the hydroxy group to form **4a**.

5-Hydroxypyrido[3,2,1-*jk*]carbazolediones **4** contain an interesting 2-hydroxy-1,3-diketone structure element with bioactive properties: 3-hydroxy-3-alkylquinolinediones are present in some natural products, e.g., as inherent compounds of bacteria in *Pseudomonas aeruginosa* [9] and some derivatives of 2-hydroxy-2-(2hydroxyphenyl)indane-1,3-diones have anti-inflammatory activity [10].

The direct displacement of the hydrogen atom at position 5 of **1a–e,g,h** (from its tautomeric dioxo form) by a hydroxy group was achieved by oxidation with alkaline hydrogen peroxide in a buffer solution at pH = 8 or in acidic media with peroxycarboxylic acids such as peroxyacetic acid or *m*-chloroperoxybenzoic acid as reagents (Scheme 1). The hydroxylated products, 5-hydroxypyridocarbazolediones **4a–e,g,h**, were obtained in excellent yield of about 70–90% as yellow crystals. For comparison reasons with the natural products [9], the 5-heptyl-(**4g**) and 5-nonyl (**4h**) derivatives were synthesized.

The structure elucidation showed in the infrared spectra a strong, sharp hydroxy band ranging between 3300 and 3500 cm^{-1} together with the additional ketone and amide carbonyl band at about 1720 and 1690 cm^{-1} . The ¹H-NMR spectra of the 5-CH₂ group in the ethyl and benzyl derivatives 4b and 4d gave splitted signals (4b: J = 7.4 and J = 13.7 Hz, 4d: J = 13.3 Hz) because of diastereotopic effects. Mass spectra of hydroxy compounds 4 gave with the APCI (atmospheric pressure chemical ionization) method mass peaks of M-28. Using the ESI (electrospray ionization) mass spectral method for the determination of mass spectra, the spectra of 4 gave the correct masses of the molecule peaks of the hydroxy compounds. Additional signals could be observed that were assigned as adducts of 4 with the cations of sodium and potassium. The formation of such adducts with alkali metal ions in ESI mass spectra are known and were investigated recently by Takayama [11].

As described above, mass spectra of hydroxy compounds **4** gave the APCI (chemical ionization) method mass peaks of M-28, which is derived by the elimination of CO and ring contraction. This matter was already mentioned in literature [9e]. These findings prompted us to investigate the possible synthetic application of such ring contractions. Recently, it was reported that 3hydroxy-2,4-quinolinediones in the presence of a base under nonaqueous conditions form 3-acyloxy-1,3-dihydroindol-2-ones *via* an α -ketol rearrangement [12]. Moreover, it was described that 3-hydroxy-2,4-quinolinediones react with aqueous potassium hydroxide to produce 2-hydroxy-1,2-dihydroindol-3-ones (2-hydroxyindoxyls) and/or isomeric 3-hydroxy-1,3-dihydroindol-2-ones (dioxindoles) in good yield [13]. Similar ring contractions were found in 5-hydroxy-5-alkylbarbituric acids [14].

For our synthetic investigations, we adopted the method described in ref. [13]. When 5-hydroxy-5-methylpyridocarbazoledione **4a** was vigorously stirred in a binary mixture of 1.3*M* aqueous potassium hydroxide and toluene at room temperature, a ring contraction took place under formal loss of CO and 4-hydroxy-4-methylpyrrolo[3,2,1-*jk*]carbazol-5(4*H*)-one (**5a**) was formed in excellent yield (Scheme 2). The structure elucidation based on mass spectral analysis revealed that the correct molecular mass with the APCI method was obtained; the ESI method showed some higher mass fragments from alkali metal complexes. The infrared spectrum showed a carbonyl frequency of a 5-ring amide carbonyl group at 1708 cm⁻¹, and in the ¹H-NMR spectra, one hydroxy signal at 11.91 ppm was visible.

At higher temperatures of about 60-80°C, another reaction sequence was observed in the ring contraction of 4a (Scheme 2). In this case, surprisingly, not the carbonyl group but the 5-methyl group was cleaved, and 4,4-dihydroxypyrrolo[3,2,1-jk]carbazol-5(4H)-one (6) was formed in 55% yield. The structure elucidation showed two hydroxy signals at 10.23 and 11.87 ppm in the ¹H-NMR spectra; the carbonyl bands in the infrared spectra at 1672 cm^{-1} confirm the amide structure. The mass spectral analysis (APCI method) shows an M-2 peak of the dihydroxy structure of 6; the elemental analysis is in accordance with this structure. Both products, 5a and 6, involve a ring opening of the six-membered pyridine part, cleavage of a C-1 ring fragment, and then a recyclization step to a five-membered pyrrole ring. The CO elimination to 5a can be explained by hydrolytic ring opening and subsequent decarboxylation, following the findings outlined in ref. [13]: one possible way leads via a base-catalyzed ring contraction to intermediates A and give ketones B by subsequent hydrolysis of the lactam ring, followed by oxidative decarboxylation. Rearrangement to C and recyclization is a possible way to give 4-hydroxypyrrolo[3,2,1-jk]carbazolones 5. The mechanistic aspects of the cleavage of the Me-C fragment and formation of 6 are not clear until now.

When 5-hydroxypyridocarbazolediones such as **4b** with a 5-ethyl substituent or **4e** with a 5-phenyl substituent were treated with aqueous potassium hydroxide and



toluene at room temperature, no reaction took place. At higher temperature, the ring-contracted 4-hydroxypyrrolocarbazolones **5b,c** were obtained, with carbonyl frequencies of 1710 or 1675 cm⁻¹ and one OH-signal at 10.46 (**5b**) or 12.12 ppm (**5c**; Scheme 2). Mass spectra, both with APCI and ESI method, confirm the structures of **5b,c**. Ring contraction of **4b** and **4e** by cleavage of the ethyl- or phenyl-C fragment to form 4,4-dihydroxypyrrolocarbazolone **6** was not observed.

5-Benzyl-5-hydroxypyridocarbazoledione **4d** gave on treatment with potassium hydroxide at $60-80^{\circ}$ C a new ring-opening product, 1-(9H-carbazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (7) instead of a ring-contraction product of type **5** or **6** (Scheme 2). The structure of the



ring-opened product is similar to the products obtained by high pressure-high temperature amination products of recently reported 4-hydroxypyridocarbazolones **1** [5]. Based on the formation of a phenylogous ketone function, the carbonyl band in the infrared spectra shows a low value at 1647 cm⁻¹, ¹H-NMR spectra show one hydroxy signal at 11.76 ppm, and the mass spectra with the APCI method show the molecule peak with 100%.

5-Chloropyrido[3,2,1-jk]carbazole-4,6-diones **2** possess with the 5-chloro substituent a good leaving group at a sp³ carbon which is easily susceptible for a nucleophilic exchange. We introduced in this way nitrogen substituents such as the azido group or primary and secondary amines in position 5.

The exchange of the 5-chloro substituent in 5-chloropyridocarbazol-6-ones $2\mathbf{a}-\mathbf{e}$ against the azide group as the nucleophile to form 5-azido-5-substituted-pyrido[3,2,1-*jk*]carbazole-4,6-diones $8\mathbf{a}-\mathbf{e}$ was of special interest because similar azidoquinolinediones showed inhibition of human blood platelet aggregation [6d]. The reaction was carried out with a solution of 2 in dimethylformamide with sodium azide as reagent at temperatures of 50°C (Scheme 3). Removal of excess sodium azide and formed sodium chloride was achieved by addition of water; this workup effected furthermore the precipitation of the formed azides $8\mathbf{a}-\mathbf{e}$. The yields of the azidation reaction were excellent. Usually, no further purification was necessary; however, it should be noticed that the thin layer chromatography (TLC) $R_{\rm f}$ values of the educts **2** and the products **8** are very similar and separation could be obtained in most cases only with HPLC to allow to recognize the end of the reaction. The infrared spectra showed strong bands of the ketone C-4 frequencies at about 1720 cm⁻¹ and strong azide bands at about 2120 cm⁻¹. The 5-CH₂ group in the ethyl, butyl, and benzyl derivatives **8b–8d** gave again splitted ¹H-NMR signals with J = 7 and J = 13Hz because of diastereotopic effects.

The exchange of the 5-chloro substituent in 5-chloro-5-substituted-pyrido[3,2,1-jk]carbazole-4,6-diones 2 against primary or secondary amines as nucleophiles leads to 5-aminosubstituted pyridocarbazolediones 9 and 10 (Scheme 3). The reaction of a solution of 2a,c,e in dimethylformamide at 50°C with benzylamine or aniline gave the amino compounds 9a-f in good yields. In a similar manner, the secondary aliphatic amines such as morpholine or piperidine led to compounds 10a-e in excellent yields. The infrared spectra both of 9 and 10 showed the bands of the ketone C-4 at about 1720 cm^{-1} and at 1660–1690 cm^{-1} for the amide at C-6. Again the 5-CH₂ group in butyl derivatives 9e,f and 10e gave splitted ¹H-NMR signals with \sim 7 and \sim 13 to 14 Hz because of diastereotopic effects.

The alkylation of 3-alkyl-4-hydroxyquinolones is known to give 3,3-dialkyl products and 4-enolethers depending on the variation of the reaction conditions, because such enolized "malonylheterocycles" can act as ambident anions: the reaction in aqueous sodium hydroxide leads preferable by C-alkylation to 3,3-dialkyl products, whereas polar aprotic solvents such as dimethylformamide favor the formation of 4-enolethers, which could be rearranged thermically to 3,3-dialkyl derivatives [15].

The reaction of 5-butylpyrido[3,2,1-jk]carbazol-6-one 1c with benzylchloride or allylbromide in aqueous sodium hydroxide gave in 60–90% yield the corresponding 5-butylpyrido[3,2,1-*jk*]carbazol-4,6-diones **11a,c**, only with traces of the enolethers 12a,c (Scheme 4), which could not be obtained in a pure form for characterization. ¹H-NMR analyses of impure **12a,c** (as a mixture with 11a,c) showed additional OCH₂ signals at 5.10 ppm (s, benzyl-OCH₂) in **12a** and at 4.45 ppm (m, allyl-OCH₂) in **12c** besides the benzyl-CH₂ signals of 11a at 3.50 ppm and the allyl-CH₂ signals of 11c at 2.70-2.90 ppm, similar to ref. [15d,e]. In the same manner, the 5-benzyl-5-phenyl product 11b was obtained in 64%. All compounds 11 showed infrared bands of the dioxo structure: the C-4 ketone band at about 1700 cm⁻¹ and the C-6 amide band at about 1670 cm^{-1} . Experiments on the thermal rearrangement of 4-allyloxy-5-butylpyridocarbazolone 12c, which was



obtained impure and in traces only during the synthesis of **11c**, showed by TLC tracing of the reaction that on heating in refluxing dimethylformamide **11c** was formed.

CONCLUSIONS

It could be shown that 5-substituted pyrido[3,2,1-jk]carbazol-6-ones **1** can be electrophilic substituted at the CH-acidic position C-5 forming 5-chloro-, 5-nitro-, 5-hydroxy-, and 5-alkyl-pyrido[3,2,1-jk]carbazole-4,6-diones. 5-Hydroxypyrido[3,2,1-jk]carbazole-4,6-diones gave interesting ring-opening structures. 5-Chloropyrido[3,2,1-jk]carbazole-4,6-diones could subsequently be used as starting materials for 5-azido- or 5-aminopyrido[3,2,1-jk]carbazole-4,6-diones.

EXPERIMENTAL

General. Melting points were determined using a Stuart SMP3 melting point apparatus in open capillary tubes. Calorimetric data were obtained on a Rheometric Scientific DSC-Plus instrument with the differential scanning calorimetry software Orchestrator V6.2.2. The differential scanning calorimetry plots were recorded between 25–400°C, with a heating rate of 2-10°C/min, and 1.5-3 mg compound in sealed aluminum crucibles (11 bar). IR spectra were recorded using a Mattson Galaxy Series FTIR 7020 instrument with potassium bromide discs. NMR spectra were recorded on a Bruker AMX 360 instrument (360 MHz ¹H, 90 MHz ¹³C) or on a Bruker Avance DRX 500 instrument (500 MHz¹H, 125 MHz¹³C). Chemical shifts are given in ppm (δ) from the internal tetramethylsilane standard. Elemental analyses were performed at the Microanalytical Laboratory of the University of Vienna, Austria. Mass spectra were obtained from an HP 1100 LC/MSD mass spectral instrument (positive or negative APCI ion source, 50-200 V, nitrogen, or AP-ES electrospray method). Dry-column flash chromatography [16] was carried out on silica gel 60 H (5–40 μ m; Merck, Darmstadt, Germany). All reactions were monitored by TLC on 0.2-mm silica gel F 254 plates (Merck, Darmstadt, Germany) using UV light (254 and 366 nm) for detection. Analytical HPLC was performed on a Shimadzu LC 20 system equipped with a diode array detector (215 and 254 nm) on a Pathfinder AS reversed phase (4.6150 mm, 5 μ m) column, running an acetonitrile/water gradient (30–100% acetonitrile). Common reagent-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

5-Alkyl/Aryl-4-hydroxypyrido[3,2,1-jk]carbazol-6-ones (1ah). These compounds were synthesized from carbazole and the appropriate diethyl alkylmalonates or diethyl phenylmalonate by thermal cyclocondensation as described in ref. [4].

5-Chloro-5-methyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (2a). To a solution of 5-methylpyridocarbazolone 1a (2.00 g, 8 mmol) in dioxane (50 mL), sulfuryl chloride (1.0 mL, 12 mmol) was slowly added and the reaction mixture was heated for 30 min at 50°C, then for 5 min at 90°C. After cooling to room temperature, the reaction mixture was poured onto crushed ice/water (200 mL) and the solid filtered and washed with water. The yield was 1.83 g (81%), yellow needles, mp 145°C (ethanol). IR: 2900–3500 m, 1726 s (4-C=O), 1692 s (6-C=O), 1592 s cm⁻¹. ¹H-NMR (DMSO-d₆): δ 2.07 (s, 3 H, CH₃), 7.57, 7.65, and 7.70 (3 t, *J* = 7.5 Hz, 3 × 1 H, 2-H, 9-H, 10-H), 8.05 and 8.33 (2 d, *J* = 7.6 Hz, 2 × 1 H, 1-H, 11-H), 8.42 (d, *J* = 8.2 Hz, 1 H, 3-H), 8.55 (d, *J* = 7.7 Hz, 1 H, 8-H). Anal Calcd for C₁₆H₁₀ClNO₂ (283.72): C, 67.74; H, 3.55; N, 4.94. Found: C, 67.41; H, 3.45; N, 4.80.

5-Chloro-5-ethyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (2b). It was obtained from 5-ethylpyridocarbazolone **1b** (2.10 g, 8 mmol) using the procedure and workup described for **2a**. The yield was 1.87 g (79%), yellow needles, mp 148°C (ethanol). IR: 2900–3500 m, 1723 s (4-C=O), 1695 s (6-C=O), 1603 s cm⁻¹. ¹H-NMR (CDCl₃): $\delta = 0.97$ (t, J = 7.4 Hz, 3 H, CH₃), 2.67 (q, J = 7.3 Hz, 2 H, CH₂), 7.52, 7.58, and 7.62 (3 t, J = 7.5 Hz, 3 × 1 H, 2-H, 9-H, 10-H), 8.07 (d, J = 7.9 Hz, 1 H, 11-H), 8.10 (d, J = 7.9 Hz, 1 H, 1-H), 8.27 (d, J = 7.7 Hz, 1 H, 3-H), 8.60 (d, J = 8.1 Hz, 1 H, 8-H). Anal Calcd for C₁₇H₁₂CINO₂ (297.74): C, 68.58; H, 4.06; N, 4.70. Found: C, 68.90; H, 4.00; N, 4.61.

5-Butyl-5-chloro-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (2c). It was obtained from 5-butylpyridocarbazolone 1c (3.00 g, 10.3 mmol) using the procedure and workup described for **2a**. The yield was 2.70 g (80%), yellow needles, mp 74°C (ethanol). IR: 2957–2341 s, 1718 s (4-C=O), 1693 s (6-C=O), 1604 w cm⁻¹. ¹H-NMR (CDCl₃): δ 0.89 (t, J = 7.3 Hz, 3 H, CH₃), 1.30 and 1.42 (2 q, J = 7.2 Hz, 2 × 2 H, 2 CH₂), 2.67 (t, J = 7.9 Hz, 2 H, 5-CH₂), 7.52–7.67 (m, 3 H, 2-H, 9-H, 10-H), 8.08 and 8.11 (2 d, J = 7.6 Hz, 2 × 1 H, 1-H, 11-H), 8.28 (d, J = 7.7 Hz, 1 H, 3-H), 8.62 (d, J = 8.1 Hz, 1 H, 8-H). Anal Calcd for C₁₉H₁₆CINO₂ (325.80): C, 70.05; H, 4.95; N, 4.30. Found: C, 70.26; H, 5.09; N, 4.27.

5-Benzyl-5-chloro-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (2d). It was obtained from 5-benzylpyridocarbazolone 1d (3.30 g, 10.2 mmol) using the procedure and workup described for 2a. The yield was 2.70 g (74%), yellow needles, mp 167°C (ethanol). IR: 2900–3500 m, 1710 s (4-C=O), 1695 m (6-C=O), 1601 s cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 3.79 (s, 2 H, CH₂), 7.08 (s, 5 H, H at Ph), 7.58, 7.63, and 7.68 (3 t, *J* = 7.7 Hz, 3 × 1 H, 2-H, 10-H, 9-H), 8.00 and 8.28 (2 d, *J* = 7.7 Hz, 2×1 H, 1-H, 11-H), 8.44 (d, J = 8.2 Hz, 1 H, 3-H), 8.50 (d, 7.6 Hz, 1 H, 8-H). Anal Calcd for C₂₂H₁₄ClNO₂ (359.82): C, 73.44; H, 3.92; N, 3.89. Found: C, 73.41; H, 3.87; N, 3.84.

5-Chloro-5-phenyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (2e). It was obtained from 5-phenylpyridocarbazolone 1e (5.00 g, 16 mmol) using the procedure and workup described for 2a. The yield was 4.50 g (81%), yellow needles, mp 171°C (ethanol). IR: 2900–3500 m, 1710 s (4-C=O), 1695 m (6-C=O), 1601 s cm^{-1.} ¹H-NMR (CDCl₃): δ 7.36 (t, J = 3.3 Hz, 3 H, H at Ph), 7.59–7.53 (m, 5 H, 2 H at Ph, 2-H, 9-H, 10-H), 7.62–7.64 and 8.06–8.09 (2 m, 2 × 1 H, 1-H, 11-H), 8.25 (d, J = 7.6 Hz, 1 H, 3-H), 8.60 (d, J = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₂₁H₁₂ClNO₂ (345.79): C, 72.94; H, 3.50; N, 4.05. Found: C, 72.71; H, 3.79; N, 4.01.

5-Chloro-5-hexyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (2f). It was obtained from 5-hexylpyridocarbazolone **1f** (3.19 g, 10.0 mmol) using the procedure and workup described for **2a**. The yield was 2.73 g (77%), yellow needles, mp 65°C (ethanol). IR: 2955–2345 s, 1715 s (4-C=O), 1695 s (6-C=O), 1605 w cm⁻¹. ¹H-NMR (CDCl₃): δ 0.88 (t, J = 7.3 Hz, 3 H, CH₃), 1.30–1.50 (m, 8 H, 4 CH₂), 2.65 (t, J = 7.9 Hz, 2 H, 5-CH₂), 7.55–7.65 (m, 3 H, 2-H, 9-H, 10-H), 8.05–8.15 (m, 2 H, 11-H, 1-H), 8.25 (d, J = 7.7 Hz, 1 H, 3-H), 8.65 (d, J = 8.1 Hz, 1 H, 8-H). Anal Calcd for C₂₁H₂₀ClNO₂ (353.85): C, 71.28; H, 5.70; N, 3.96. Found: C, 70.96; H, 5.49; N, 4.17.

5-Methyl-5-nitro-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (3a). To a mixture of 5-methylpyridocarbazolone 1a (3.30 g, 13 mmol) and sodium nitrite (0.50 g, 7.2 mmol) in glacial acetic acid (50 mL) was slowly dropped concentrated nitric acid (2.5 mL) and stirred for 2 h at 20°C. The reaction mixture was poured onto crushed ice/water (100 mL), the precipitated solid filtered and washed with water. The yield was 3.20 g (84%), yellow crystals, mp 190°C (ethanol). IR: 3600–3400 w, 1721 s (4-C=O), 1688 s (6-C=O), 1561 s cm⁻¹. ¹H-NMR (CDCl₃): δ 2.20 (s, 3 H, CH₃), 7.55–7.67 (m, 3 H, 2-H, 9-H, 10-H), 8.07–8.10 (m, 2 H, 1-H, 11-H), 8.32 (d, *J* = 7.6 Hz, 1 H, 3-H), 8.54 (d, *J* = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₁₆H₁₀N₂O₄ (294.27): C, 65.31; H, 3.43; N, 9.52. Found: C, 65.67; H, 3.82; N, 9.83.

5-Ethyl-5-nitro-4H-pyrido[**3**,**2**,**1**-*j***k**]*carbazole-4*,**6**(5H)-*dione* (**3b**). It was obtained from 5-ethylpyridocarbazolone **1b** (1.50 g, 5.7 mmol) using the procedure and workup described for **3a**. The yield was 1.20 g (68%), yellow needles, mp 162°C (ethanol). IR: 3398 s, 2980 w, 1714 s (4-C=O), 1683 s (6-C=O), 1610 w, 1561 s cm⁻¹. ¹H-NMR (CDCl₃): δ 0.95 (t, *J* = 7.5 Hz, 3 H, CH₃), 2.83 (q, *J* = 7.5 Hz, 2 H, CH₂), 7.55–7.68 (m, 3 H, 2-H, 9-H, 10-H), 8.06–8.09 (m, 2 H, 1-H, 11-H), 8.32 (d, *J* = 7.6 Hz, 1 H, 3-H), 8.57 (d, *J* = 8.6 Hz, 1 H, 8-H). Anal Calcd for C₁₇H₁₂N₂O₄ (308.30): C, 66.23; H, 3.92; N, 9.09. Found: C, 66.47; H, 3.82; N, 8.93.

5-Butyl-5-nitro-4H-pyrido[**3**,**2**,**1**-*j***k**]*carbazole-4*,**6**(**5H**)-*dione (3<i>c*). It was obtained from 5-butylpyridocarbazolone **1***c* (1.50 g, 5.2 mmol) using the procedure and workup described for **3a**. The yield was 1.00 g (57%), yellow needles, mp 155°C (methanol/ethyl acetate). IR: 3600–3300 s, 2950–2800 m, 1722 s (4-C=O), 1692 s (6-C=O), 1605 m, 1565 s cm^{-1. 1}H-NMR (CDCl₃): $\delta = 0.80-0.95$ (m, 3 H, CH₃), 1.15–1.25 and 1.30–1.35 (2 m, 4 H, 2 CH₂), 2.72–2.77 (m, 2 H, 5-CH₂), 7.47–7.68 (m, 3 H, 2-H, 9-H, 10-H), 7.97–8.11 (m, 2 H, 11-H, 1-H), 8.24 (d, *J* = 7.5 Hz, 1 H, 3-H), 8.51 (d, *J* = 7.4 Hz, 1 H, 8-H). Anal Calcd for C₁₉H₁₆N₂O₄ (336.35): C, 67.85; H, 4.79; N, 8.33. Found: C, 67.46; H, 4.41; N, 7.95. **5-Benzyl-5-nitro-4H-pyrido**[**3**,**2**,**1**-*j***k**]*carbazole-4*,**6**(**5H**)-*dione (3<i>d*). It was obtained from 5-benzylpyridocarbazolone **1d** (1.50 g, 4.6 mmol) using the procedure and workup described for **3a**. The yield was 1.00 g (59%), yellow needles, mp 195°C (methanol/ethyl acetate). IR: 3600–3400 m, 3020–2980 w, 1714 s (4-C=O), 1688 s (6-C=O), 1610 w, 1559 s cm⁻¹. ¹H-NMR (CDCl₃): δ 4.10 (s, 2 H, CH₂), 8.85–6.87 (m, 3 H, H at Ph), 7.00–7.02 (m, 2 H, H at Ph), 7.43, 7.51, and 7.63 (3 t, J = 7.2 Hz, 3 × 1 H, 2-H, 9-H, 10-H), 7.91–7.94 (m, 2 H, 1-H, 11-H), 8.07 (d, *J* = 7.6 Hz, 1 H, 3-H), 8.54 (d, *J* = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₂₂H₁₄N₂O₄ (370.37): C, 71.35; H, 3.81; N, 7.56. Found: C, 71.53; H, 3.80; N, 7.60.

5-Nitro-5-phenyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (3e). It was obtained from 5-phenylpyridocarbazolone 1e (3.11 g, 10 mmol) using the procedure and workup described for 3a. The yield was 2.53 g (71%), yellow needles, mp 175°C (ethanol). IR: 3300 w, 2950 w, 1725 s (4-C=O), 1695 s (6-C=O), 1680 s, 1610 w cm⁻¹. ¹H-NMR (CDCl₃): δ 7.00–7.30 (m, 5 H, H at Ph), 7.50–7.55 and 7.60–7.85 (2 m, 2 + 3 H, 9-H, 10-H, 2-H, 1-H, 11-H), 8.10 (d, J = 7.6 Hz, 1 H, 3-H), 8.50 (d, J = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₂₁H₁₂N₂O₄ (356.34): C, 70.78; H, 3.39; N, 7.86. Found: C, 71.13; H, 3.71; N, 7.60.

5-Hydroxy-5-methyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (4a). Method A: A solution of 5-methylpyridocarbazolone 1a (2.00 g, 8 mmol) was stirred in aqueous sodium hydroxide (0.25*M*, 150 mL) until the solution was complete. The solution was adjusted to pH 8 with aqueous potassium dihydrogenphosphate (1*M*, ~25 mL) and heated to 60°C with intensive stirring. Then hydrogenperoxide (30%, 25 mL) was added and the reaction mixture was stirred for 6 h at 60°C. A solid precipitated and the reaction mixture was cooled to room temperature, filtered by suction, and washed with water. The yield was 1.80 g (85%), yellow needles, mp 147°C (ethanol).

Method B: To a mixture of 5-methylpyridocarbazolone **1a** (2.00 g, 8 mmol) and sodium nitrite (0.50 g, 7.2 mmol) in glacial acetic acid (50 mL) was slowly dropped concentrated nitric acid (2.5 mL) and stirred for 6 h at 60°C. The reaction mixture was poured onto crushed ice/water (100 mL), the precipitated solid filtered and washed with water, and recrystallized from ethanol. The yield was 1.27 g (60%), yellow needles. IR: 3406 s (5-OH), 1711 s (4-C=O), 1681 s (6-C=O), 1632 w, 1605 m cm⁻¹. ¹H-NMR (CDCl₃): δ 1.77 (s, 3 H, CH₃), 3.95 (s, 1 H, OH), 7.48–7.62 (m, 3 H, 2-H, 9-H, 10-H), 8.04 (d, *J* = 7.7 Hz, 2 H, 1-H, 11-H), 8.25 (d, *J* = 8.5 Hz, 1 H, 3-H), 8.49 (d, *J* = 8.1 Hz, 1 H, 8-H). Anal Calcd for C₁₆H₁₁NO₃ (265.27): C, 72.45; H, 4.18; N, 5.28. Found: C, 72.78; H, 4.37; N, 5.02.

5-Ethyl-5-hydroxy-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (4b). It was obtained from 5-ethylpyridocarbazolone 1b (3.00 g, 11.4 mmol) using the procedure and workup described for 4a (method A). The yield was 2.50 g (79%), yellow needles, mp 172°C (ethanol). IR: 3393 s (5-OH), 1710 s (4-C=O), 1681 s (6-C=O), 1604 s cm^{-1.} ¹H-NMR (CDCl₃): δ 1.04 (t, J = 7.4 Hz, 3 H, CH₃), 2.00 and 2.13 (2 qd, J = 7.4 + 13.7 Hz, 2 × 1 H, CH₂), 3.92 (s, 1 H, OH), 7.49–7.63 (m, 3 H, 2-H, 9-H, 10-H), 8.02 and 8.05 (2 d, J = 7.6 Hz, 2 × 1 H, 1-H, 11-H), 8.24 (d, J = 7.6 Hz, 1 H, 3-H), 8.50 (d, J = 8.2 Hz, 1 H, 8-H). ¹³C-NMR: δ 7.4 (CH₃), 35.0 (CH₂), 84.4 (5-C), 116.2, 117.0, 120.8, 124.1, 124.5, 125.1, 125.2, 125.5, 126.9, 128.6, 137.3, 139.7 (12 ArC), 169.3 (6-C), 194.0 (4-C). Anal Calcd for C₁₇H₁₃NO₃ (279.30): C, 73.11; H, 4.69; N, 5.01. Found: C, 72.78; H, 4.62; N, 4.99.

5-Butyl-5-hydroxy-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (4c). Method C: Peroxyacetic acid (32% in acetic acid; 100 mL, 0.48 mol) was added dropwise to a solution of 5-butylpyridocarbazolone 1c (29.1 g, 0.1 mol) in sodium hydroxide (0.5*M*, 960 mL). The reaction mixture was stirred for 1.5 h at 20°C. The formed precipitate was separated by suction filtration, dispersed in sodium bicarbonate solution (5%, 150 mL), filtered again, and washed with water until the filtrate was neutral. The crude product was dissolved in chloroform (200 mL) and extracted with sodium hydroxide $(0.05M, 2 \times 150 \text{ mL})$. The organic layer was dried with sodium sulfate and the solvent evaporated under reduced pressure. The yield was 23.4 g (76%), yellow powder, mp 167°C (ethanol/water). IR: 3480 m (5-OH), 2950 m, 2870 m, 1720 s (4-C=O), 1680 s (6-C=O), 1605 m, 1595 m cm⁻¹; ¹H-NMR (CDCl₃): $\delta = 0.80$ (t, J =7.0 Hz, 3 H, CH₃), 1.05–1.25 (m, 2 H, CH₂), 1.30–1.50 (m, 2 H, CH₂), 1.80–2.05 (m, 2 H, 5-CH₂), 4.15 (s, 1 H, OH), 7.40–7.65 (m, 3 H, 2-H, 9-H, 10-H) 8.05 (t, J = 7.0 Hz, 2 H, 1-H, 11-H), 8.20 (d, J = 8.0 Hz, 1 H, 3-H), 8.45 (d, J = 8.0 Hz, 1 H, 8-H). MS [AP-ES, pos]: m/e (%): 330 ([M + Na]⁺, 100), 308 ([M + H]⁺, 25). Anal Calcd for C₁₉H₁₇NO₃ (307.35): C, 74.25; H, 5.58; N, 4.56. Found: C, 74.35; H, 5.41; N, 4.49.

5-Benzyl-5-hydroxy-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (4d). It was obtained from 5-benzylpyridocarbazolone 1d (3.00 g, 9.2 mmol) using the procedure and workup described for 4a (method A). The yield was 2.70 g (86%), yellow needles, mp 216°C (ethanol). IR: 3433 s (5-OH), 1730 sh, 1715 s (4-C=O), 1684 s (6-C=O), 1605 s cm^{-1.} ¹H-NMR (CDCl₃): δ 3.37 and 3.34 (2 d, *J* = 13.3 Hz, 2 × 1 H, CH₂), 3.93 (s, 1 H, OH), 6.99–7.02 (m, 2 H, H at Ph), 7.10–7.16 (m, 3 H, H at Ph), 7.50–7.56 (m, 2 H, 9-H, 10-H), 7.60–7.64 (m, 1 H, 2-H), 7.98 and 8.03 (2 d, *J* = 7.7 Hz, 2 × 1 H, 1-H, 11-H), 8.20 (d, *J* = 7.7 Hz, 1 H, 3-H), 8.48 (d, *J* = 8.2 Hz, 1 H, 8-H). MS [APCI, neg]: *m/e* (%): 340 ([M - H]⁺, 20), 339 (10), 250 (100). Anal Calcd for C₂₂H₁₅NO₃ (341.37): C, 77.41; H, 4.43; N, 4.10. Found: C, 77.14; H, 4.43; N, 4.04.

5-Hydroxy-5-phenyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (4e). It was obtained from 5-phenylpyridocarbazolone 1e (3.00 g, 9.6 mmol) using the procedure and workup described for 4a (method A). The yield was 2.50 g (80%), yellow needles, mp 234°C (ethanol). IR: 3373 s (5-OH), 1718 s (4-C=O), 1681 s (6-C=O), 1602 s, 1593 s cm⁻¹. ¹H-NMR (CDCl₃): δ 4.45 (s, 1 H, OH), 7.24–7.28 (m, 3 H, H at Ph), 7.40–7.43 (m, 2 H, H at Ph), 7.52–7.58 and 7.61–7.66 (2 m, 2 + 1 H, 9-H, 10-H, 2-H), 8.02 and 8.09 (2 d, *J* = 7.8 Hz, 2 × 1 H, 1-H, 11-H), 8.27 (d, *J* = 7.8 Hz, 1 H, 3-H), 8.57 (d, *J* = 8.2 Hz, 1 H, 8-H). MS [APCI, neg]: *m/e* (%): 326 ([M - H]⁺, 28), 300 (10), 298 (100). Anal Calcd for C₂₁H₁₃NO₃ (327.34): C, 77.06; H, 4.00; N, 4.28. Found: C, 76.77; H, 3.83; N, 4.23.

5-Heptyl-5-hydroxy-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (4g). It was obtained from 5-heptylpyridocarbazolone 1g (3.30 g, 10 mmol) using the procedure and workup described for 4a (method A). The yield was 2.30 g (66%), yellow needles, mp 153°C (ethanol). IR: 3373 s (5-OH), 1719 s (4-C=O), 1681 s, (6-C=O), 1602 w cm⁻¹. ¹H-NMR (DMSO-d₆): δ 0.77 (t, J = 6.5 Hz, 3 H, CH₃), 1.08 (m, 6 H, 3 CH₂), 1.20–1.25 (m, 4 H, 2 CH₂), 1.75–1.90 (m, 2 H, 5-CH₂), 6.07 (s, 1 H, OH), 7.52–7.67 (m, 3 H, 2-H, 9-H, 10-H), 7.93 and 8.30 (2 d, J = 7.7 Hz, 2 × 1 H, 11-H, 1-H), 8.42 (d, J = 7.9 Hz, 1 H, 3-H), 8.50 (d, J = 7.7 Hz, 1 H, 8-H). MS [AP-ES, pos]: *m/e* (%): 372 ([M + Na]⁺, 100) 350 ([M + H]⁺, 30). Anal Calcd for C₂₂H₂₃NO₃ (349.43): C, 75.62; H, 6.63; N, 4.01. Found: C, 75.64; H, 6.59; N, 4.01.

5-Hydroxy-5-nonyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (4h). Method C: To a solution of 5-nonylpyridocarbazolone 1h (2.00 g, 5.5 mmol) in acetic acid (50 mL) at 110°C, peroxyacetic acid (20 mL, 32% in acetic acid) was added. The reaction temperature was lowered to 60°C and the mixture was stirred for 18 h at this temperature. After cooling to room temperature, the reaction mixture was poured onto crushed ice/ water (200 mL), the precipitate filtered by suction, and washed with water. The yield was 1.62 g (78%), colorless powder, mp 95°C (methanol/cyclohexane). IR: 3447 s (5-OH), 2918 s, 2849 s, 1724 s (4-C=O), 1682 s (6-C=O), 1605 s cm⁻¹. ¹H-NMR (CDCl₃): δ 0.85 (t, J = 6.9 Hz, 3 H, CH₃), 1.11–1.24 (m, 14 H, 7 CH₂), 1.85–1.93 and 1.98–2.07 (2 m, 2×1 H, 5-CH₂), 7.49–7.55 and 7.57–7.63 (2 m, 2 + 1 H, 10-H, 9-H, 2-H), 8.01 and 8.05 (2 d, J = 7.7 Hz, 2 \times 1 H, 1-H, 11-H), 8.23 (d, J = 7.7 Hz, 1 H, 3-H), 8.49 (d, J = 8.2 Hz, 1 H, 8-H). MS [AP-ES, pos]: m/e (%) 416 (22, [M + K]⁺), 400 (100, [M + Na^{+}), 378 (34, $[M + H]^{+}$), 333 (10). Anal Calcd for C24H27NO3 (377.49): C, 76.36; H, 7.21; N, 3.71. Found: C, 76.31; H, 7.46; N, 3.54.

4-Hydroxy-4-methylpyrrolo[3,2,1-jk]carbazol-5(4H)-one (5a). A mixture of 5-hydroxy-5-methylpyridocarbazoledione 4a (0.14 g, 0.52 mmol) and aqueous potassium hydroxide solution (1.3M, 10 mL) in toluene (15 mL) was stirred at room temperature for 4 h, then the toluene phase was separated and dried with potassium carbonate (3.0 g), filtered, and the solvent was removed under reduced pressure. The residue was dissolved in acetone (1.0 mL), then water (20 mL) was added. The precipitated solid was filtered by suction and washed with water. The product 5a was separated by dry-column flash chromatography (elution with toluene/acetone). The yield was 0.10 g (80%), yellow crystals, mp 101°C (acetone/water). IR: 3414 s (4-OH), 2923 m, 2853 m, 1708 s (5-C=O), 1639 s, 1621 s, 1588 s cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 2.59 (s, 3 H, CH₃), 7.24–7.33 (m, 2 H, 8-H, 9-H), 7.49 (t, J = 8.1 Hz, 1 H, 2-H), 7.79 and 7.99 (d, J = 8.2, 7.7 Hz, 2 × 1 H, 10-H, 1-H), 8.22 (d, J =7.7 Hz, 1 H, 3-H), 8.56 (d, J = 7.7 Hz, 1 H, 7-H), 11.91 (s, 1 H, OH). MS [API-ES, pos]: m/z (%) = 259 (100, [M + Na]⁺); MS [APCI, neg]: m/z (%) = 236 (100, [M - H]⁺). Anal Calcd for C₁₅H₁₁NO₂ (237.26): C, 75.94; H, 4.67; N, 5.90. Found: C, 75.61; H, 4.47; N, 6.21.

4-Ethyl-4-hydroxypyrrolo[3,2,1-jk]carbazol-5(4H)-one (5b). A mixture of 5-ethyl-5-hydroxypyridocarbazoledione 4b (1.20 g, 4.3 mmol) and aqueous potassium hydroxide (1.3M, 20 mL) in toluene (60 mL) was stirred at 50°C for 8 h, the toluene phase was separated and dried with potassium carbonate (3.0 g), then filtered and the solvent was removed under reduced pressure. The residue was dissolved in acetone (4 mL) and then water (80 mL) was added. The precipitated solid was filtered by suction and washed with water. The product was separated by dry-column flash chromatography (elution with toluene/acetone). The yield was 0.90 g (83%), yellow crystals, mp 115°C (methanol). IR: 3500–3300 s, 1710 s (5-C=O), 1636 s, 1619 m, 1589 m, 1573 m cm⁻¹. ¹H-NMR: δ 1.27 (t, J = 7.0 Hz, 3 H, CH₃), 3.04 (q, J = 7.4 Hz, 2 H, CH₂), 7.31 (t, J = 7.7 Hz, 1 H, 2-H), 7.33–7.36 and 7.52–7.54 (2 m, 2×1 H, 8-H, 9-H), 7.59 and 8.01 (2 d, J = 8.1 and 7.8 Hz, 2 × 1 H, 10-H, 1-H), 8.13 (d, J = 7.8 Hz, 1 H, 3-H), 8.39 (d, J = 7.6 Hz, 1 H, 7-H), 10.46 (s, 1 H, OH). ¹³C-NMR: $\delta = 6.9$ (CH₃), 32.4 (CH₂), 111.5, 114.2, 118.7, 120.5, 120.7, 122.1, 125.3, 126.9, 127.8, 130.0, 139.9, 140.0 (12 ArC of carbazole), 194.2 (4-C), 203.8 (5-C). MS [API-ES, pos]: m/z (%) = 306 (100), 276 (54), 274

(90, $[M + Na]^+ + 1$). MS [APCI, neg]: m/z (%) = 251 (23), 250 (100, $[M - H]^+$), 166 (34). Anal Calcd for $C_{16}H_{13}NO_2$ (251.29): C, 76.48; H, 5.21; N, 5.57. Found: C, 76.87; H, 5.60; N, 5.18.

4-Hydroxy-4-phenylpyrrolo[3,2,1-jk]carbazol-5(4H)-one (5c). A solution of 5-hydroxy-5-phenylpyridocarbazoledione 4e (1.64 g, 5.00 mmol) and aqueous potassium hydroxide (1.3M, 30 mL) in toluene (120 mL) was brought to reaction and worked up as described for 8b. The yield was 1.20 g (80%), yellow crystals, mp 158°C (methanol). IR: 3408 s (4-OH), 1675 s (5-C=O), 1643 s, 1620 m, 1586 s, 1576 s cm⁻¹. ¹H-NMR: δ 7.26–7.31 (m, 2 H, H at Ph), 7.50 (t, J = 7.4 Hz, 1 H, 2-H), 7.62-7.70 (m, 3 H, H at Ph), 7.78-7.83 (m, 2 H, 8-H, 9-H), 8.00 (d, J = 7.4 Hz, 2 H, 1-H, 10-H), 8.26 (d, J = 7.7 Hz, 1 H, 3-H), 8.60 (d, J = 7.4 Hz, 1 H, 7-H), 12.12 (s, 1 H, OH). MS [API-ES, pos]: m/z (%) = 324 (100), 322 (93, $[M + Na]^+$ + 1). MS [APCI, neg]: m/z (%) = 299 (25), 298 (87, [M - H_{1}^{+}), 270 (38), 166 (100). Anal Calcd for $C_{20}H_{13}NO_2$ (299.33): C, 80.25; H, 4.38; N, 4.68. Found: C, 80.64; H, 4.76; N, 4.29.

4,4-Dihydroxypyrrolo[3,2,1-jk]carbazol-5(4H)-one (6). A solution of 5-hydroxy-5-methylpyridocarbazoledione 4a (0.40 g, 1.50 mmol) and aqueous potassium hydroxide solution (1.3M, 30 mL) in toluene (80 mL) was brought to reaction and worked up as described for 5b. The yield was 0.20 g (55%), vellow crystals, mp 138°C (methanol). IR: 3383 s (4-OH), 3056 w, 2815 w, 1672 s (5-C=O), 1598 s cm⁻¹. ¹H-NMR (DMSO- d_6): δ 7.26, 7.39, and 7.42 (3 t, J = 7.6 Hz, 3 × 1 H, 2-H, 8-H, 9-H), 7.76 and 8.01 (2 d, J = 7.4 Hz, 2 \times 1 H, 1-H, 10-H), 8.20 (d, J = 7.8 Hz, 1 H, 3-H), 8.50 (d, J = 7.6 Hz, 1 H, 7-H), 10.23 (s, 1 H, OH), 11.87 (s, 1 H, OH). ¹³C-NMR (DMSO-d₆): δ 112.9, 118.8, 120.2, 120.3, 120.7, 121.7, 124.6, 126.8, 127.4, 132.0, 137.3, 141.1 (12 ArH), 193.5 (4-C), 211.8 (5-C). MS [APCI, neg]: m/z (%) = 236 (30, [M - H]⁺ - 2), 194 (100). Anal Calcd for C14H9NO3 (239.23): C, 70.29; H, 3.79; N, 5.85. Found: C, 70.02; H, 3.95; N, 5.93.

1-(9H-Carbazol-1-yl)-2-hydroxy-3-phenylpropan-1-one (7). A solution of 5-hydroxy-5-methylpyridocarbazoledione **4d** (0.40 g, 1.17 mmol) and potassium hydroxide (1.3*M*, 30 mL) in toluene (120 mL) was brought to reaction and worked up as described for **5a**. The yield was 0.23 g (62%), yellow crystals, mp 147°C (acetone/water). IR: 3522 s, 3428 s, 3368 s, 1647 (C=O) s, 1622 s, 1597 s, 1572 s cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 2.95 and 3.17 (2 qd, *J* = 7.0 and 13.0 Hz, 2 × 1 H, CH₂), 5.32 (q, *J* = 7.0 Hz, 1 H, CH), 5.61 (d, *J* = 7.0 Hz, 1 H, OH), 7.15–7.30 (m, 7 H, 7-H, 6-H, 5 H at Ph), 7.45 (t, *J* = 7.6 Hz, 1 H, 3-H), 7.77 (d, *J* = 8.0 Hz, 1 H, 8-H), 8.18 (d, *J* = 7.7 Hz, 1 H, 5-H), 8.28 (d, *J* = 7.6 Hz, 1 H, 4-H), 8.45 (d, *J* = 7.5 Hz, 1 H, 2-H), 11.76 (s, 1 H, NH). MS [APCI, pos]: *m/z* (%) = 316 (100, [M + H]⁺). MS [APCI, neg]: *m/z* (%) = 314 (100, [M - H]⁺). Anal Calcd for C₂₁H₁₇NO₂ (315.38): C, 79.98; H, 5.43; N, 4.44. Found: C, 79.59; H, 5.82; N, 4.05.

5-Azido-5-methyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (8a). A mixture of 5-chloro-5-methylpyridocarbazoledione 2a (3.00 g, 10.5 mmol) and sodium azide (1.00 g, 15.3 mmol) in dimethylformamide (50 mL) was stirred and heated for 60 min at 50°C. The reaction mixture was cooled to room temperature and poured onto crushed ice/water (100 mL), filtered, and washed with water. The yield was 2.30 g (75%), yellow needles, mp 155°C (ethanol). IR: 3500–2900 m, 2116 s (N₃), 1711 s (4-C=O), 1684 s (6-C=O), 1600 s cm⁻¹. ¹H-NMR (CDCl₃): δ 1.98 (s, 3 H, CH₃), 7.55, 7.59 and 7.63 (3 t, *J* =

7.3 Hz, 3 × 1 H, 2-H, 9-H, 10-H), 8.07 (d, J = 7.7 Hz, 2 H, 1-H, 11-H), 8.26 (d, J = 7.7 Hz, 1 H, 3-H), 8.55 (d, J = 8.3 Hz, 1 H, 8-H). Anal Calcd for C₁₆H₁₀N₄O₂ (290.28): C, 66.20; H, 3.47; N, 19.30. Found: C, 66.34; H, 3.39; N, 19.10.

5-*Azido*-**5**-*ethyl*-*4H*-*pyrido*[*3*,2,1-*jk*]*carbazole*-*4*,6(5*H*)-*dione* (*8b*). It was obtained from 5-chloro-5-ethylpyridocarbazoledione **2b** (3.04 g, 10.2 mmol) using the procedure and workup described for **5a**. The yield was 2.60 g (84%), yellow needles, mp 136°C (ethanol). IR: 3500–2900 m, 2126 s (N₃), 1722 s (4-C=O), 1689 s (6-C=O), 1600 s cm⁻¹. ¹H-NMR (CDCl₃): δ 1.02 (t, *J* = 7.4 Hz, 3 H, CH₃), 2.36 (qd, *J* = 7.0 and 13.0 Hz, 2 H, CH₂), 7.54–7.57 and 7.62–7.64 (2 m, 2 + 1 H, 2-H, 9-H, 10-H), 8.04 and 8.06 (2 d, *J* = 7.4 Hz, 2 × 1 H, 1-H, 11-H), 8.25 (d, *J* = 7.6 Hz, 1 H, 3-H), 8.55 (d, *J* = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₁₇H₁₂N₄O₂ (304.31): C, 67.10; H, 3.97; N, 18.41. Found: C, 67.20; H, 4.00; N, 18.08.

5-Azido-5-butyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (8c). It was obtained from 5-butyl-5-chloropyridocarbazoledione 2c (3.25 g, 10 mmol) using the procedure and workup described for 5a. The yield was 3.19 g (96%), yellow powder, mp 93–96°C (ethanol). DSC: mp 81.2°C onset, 91.1°C peak max. (5 mcal/mg); decomposition 172.4°C onset, 208.5°C peak max (-100 mcal/mg). IR: 3600–3400 s, 2927 w, 2118 s (N₃), 1719 s (4-C=O), 1688 s (6-C=O), 1637 m, 1606 s cm⁻¹. ¹H-NMR (CDCl₃): δ 0.85 (t, *J* = 7.0 Hz, 3 H, CH₃), 1.30 and 1.40 (2 q, *J* = 7.0 Hz, 2 × 2 H, 2 CH₂), 2.65 (dt, *J* = 7.5 and 13.1 Hz, 2 H, 5-CH₂), 7.55–7.65 (m, 3 H, 2-H, 9-H, 10-H), 8.05 and 8.10 (2 d, *J* = 7.5 Hz, 2 × 1 H, 1-H ,11-H), 8.25 (d, *J* = 7.5 Hz, 1 H, 3-H), 8.62 (d, *J* = 8.1 Hz, 1 H, 8-H). Anal Calcd for C₁₉H₁₆N₄O₂ (332.36): C, 68.66; H, 4.85; N, 16.86. Found: C, 68.27; H, 5.05; N, 16.54.

5-Azido-5-benzyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (8d). It was obtained from 5-benzyl-5-chloropyridocarbazoledione 2d (3.60 g, 10 mmol) using the procedure and workup described for 2a. The yield was 2.70 g (74%), yellow needles, mp 162°C (ethanol). IR: 2600 w, 2116 s (N₃), 1721 s (4-C=O), 1687 s (6-C=O), 1602 s cm⁻¹. ¹H-NMR (CDCl₃): δ 4.05 and 4.15 (2 d, J = 13.3 Hz, 2 × 1 H, CH₂), 6.92–6.94 (m, 2 H, H at Ph), 7.02–7.08 (m, 3 H, H at Ph), 7.46–7.59 and 7.68 (2 m, 3 H, 2-H, 9-H, 10-H), 7.90 and 8.27 (2 d, J = 7.7 Hz, 1 H, 11-H), 8.35 (d, J = 8.2 Hz, 1 H, 3-H), 8.44 (d, 7.6 Hz, 1 H, 8-H). Anal Calcd for C₂₂H₁₄N₄O₂ (366.38): C, 72.12; H, 3.85; N, 15.29. Found: C, 72.10; H, 4.02; N, 14.90.

5-Azido-5-phenyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (8e). It was obtained from 5-chloro-5-phenylpyridocarbazoledione **2e** (3.45 g, 10 mmol) using the procedure and workup described for **2a**. The yield was 2.39 g (68%), yellow needles, mp 165–170°C (ethanol). DSC: mp: 167.7°C onset, 173.5°C peak max. (2 mcal/mg); decomposition: 167.0°C onset, 199.6°C peak max., -86 mcal/mg. IR: 3500–3300 s, 2117 s (N₃), 1725 s (4-C=O), 1697 s (6-C=O), 1632 s cm⁻¹. ¹H-NMR (CDCl₃): δ 7.30–7.50 (m, 5 H, H at Ph), 7.50, 7.55, and 7.60 (3 t, *J* = 7.5 Hz, 3 × 1 H, 2-H, 9-H, 10-H), 8.00 and 8.10 (2 d, *J* = 7.6 Hz, 1 H, 1-H, 11-H), 8.20 (d, *J* = 7.2 Hz,1 H, 3-H), 8.70 (d, *J* = 7.9 Hz, 1 H, 8-H). Anal Calcd for C₂₁H₁₂N₄O₂ (352.36): C, 71.59; H, 3.43; N, 15.90. Found: C, 71.90; H, 3.72; N, 15.53.

5-Methyl-5-phenylamino-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)dione (9a). A solution of 5-chloro-5-methylpyridocarbazoledione 2a (2.00 g, 7 mmol) and aniline (5.5 mL, 60 mmol) in dimethylformamide (20 mL) was heated and stirred for 5 h at 50°C. After cooling to room temperature, the reaction mixture was poured onto crushed ice/water (100 mL), filtered by suction, and washed with water. The yield was 1.50 g (63%), yellow crystals, mp 230°C (ethanol). IR: 3389 s, 2980 w, 1722 s (4-C=O), 1689 s (6-C=O), 1602 s cm⁻¹. ¹H-NMR (CDCl₃): δ 1.87 (s, 3 H, CH₃), 3.50 (s, 1 H, NH), 6.37 (d, J = 8.0 Hz, 2 H, H at Ph), 6.72 (t, J = 7.3 Hz, 1 H, H at Ph), 7.05 (t, J = 8.0 Hz, 2 H, H at Ph), 7.52–7.64 (m, 3 H, 2-H, 9-H, 10-H), 8.10–8.14 (m, 2 H, 1-H, 11-H), 8.34 (d, J = 7.7 Hz, 1 H, 3-H), 8.60 (d, J = 8.1 Hz, 1 H, 8-H). Anal Calcd for C₂₂H₁₆N₂O₂ (340.39): C, 77.63; H, 4.74; N, 8.23. Found: C, 77.71; H, 4.98; N, 8.27.

5-Methyl-5-benzylamino-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)dione (9b). It was obtained from 5-chloro-5-methylpyridocarbazoledione **2a** (3.00 g, 10.6 mmol) and benzylamine (10 mL, 91 mmol) in dimethylformamide (20 mL) using the procedure and workup described for **9a**. The yield was 3.00 g (80%), yellow crystals, mp 159°C (ethanol). IR: 3298 s, 2950–2850 w, 1722 s (4-C=O), 1664 s (6-C=O), 1600 w cm⁻¹. ¹H-NMR (CDCl₃): δ 1.72 (s, 3 H, CH₃), 3.69–3.71 (m, 2 H, CH₂), 7.17–7.26 (m, 3 H, H at Ph), 7.41 (d, *J* = 7.2 Hz, 2 H, H at Ph), 7.51–7.58 and 7.65–7.67 (2 m, 1 + 2 H, 2-H, 9-H, 10-H), 8.09 (d, *J* = 7.7 Hz, 2 H, 1-H, 11-H), 8.27 (d, *J* = 7.6 Hz, 1 H, 3-H), 8.65 (d, *J* = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₂₃H₁₈N₂O₂ (354.41): C, 77.95; H, 5.12; N, 7.90. Found: C, 77.56; H, 5.30; N, 7.60.

5-Phenyl-5-phenylamino-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)dione (9c). It was obtained from 5-chloro-5-phenylpyridocarbazoledione **2e** (2.00 g, 5.8 mmol) and aniline (5.5 mL, 60 mmol) according to the procedure and workup described for **9a**. The yield was 1.94 g (83%), yellow crystals, mp 165°C (ethanol). IR: 3415 s, 3010 m, 1720 s (4-C=O), 1688 s (6-C=O), 1600 s cm^{-1.} ¹H-NMR (CDCl₃): δ 4.99 (s, 1 H, NH), 6.49 (d, *J* = 7.7 Hz, 2 H, H at Ph), 6.75 (t, *J* = 7.3 Hz, 1 H, H at Ph), 7.10 (t, *J* = Hz, 2 H, H at Ph), 7.29–7.32 (m, 3 H, H at Ph), 7.53–7.66 (m, 5 H, 2 H at Ph, 2-H, 9-H, 10-H), 8.11 (t, *J* = 7.0 Hz, 2 H, 1-H, 11-H), 8.27 (d, *J* = 7.0 Hz, 1 H, 3-H), 8.67 (d, *J* = 8.1 Hz, 1 H, 8-H). Anal Calcd for C₂₇H₁₈N₂O₂ (402.46): C, 80.58; H, 4.51; N, 6.96. Found: C, 80.37; H, 4.71; N, 6.97.

5-Benzylamino-5-phenyl-4H-pyrido[3,2,1-jk]carbazol-4,6(5H)dione (9d). It was obtained from 5-chloro-5-phenylpyridocarbazoledione **2e** (3.00 g, 8.7 mmol) and benzylamine (10.00 mL, 91 mmol) in dimethylformamide (20 mL) according to the procedure and workup described for **9a**. The yield was 3.00 g (83%), yellow crystals, mp 165°C (ethanol). IR: 3288 s, 3010– 2920 w, 1700 m (4-C=O), 1667 s (6-C=O), 1611 s cm⁻¹. ¹H-NMR (CDCl₃): δ 3.79 and 3.88 (2 d, *J* = 13.0 Hz, 2 × 1 H, CH₂), 5.72 (m, 1 H, NH), 7.24–7.27, 7.30–7.34, and 7.51– 7.55 (3 m, 4 + 2 + 6 H, 10 H at Ph, 9-H, 10-H), 7.67 (t, *J* = 7.7 Hz, 1 H, 2-H), 8.05 and 8.10 (2 d, *J* = 7.7 Hz, 1 H, 1-H, 11-H), 8.22 (d, *J* = 7.6 Hz, 1 H, 3-H), 8.71 (d, *J* = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₂₈H₂₀N₂O₂ (416.48): C, 80.75; H, 4.84; N, 6.73. Found: C, 80.36; H, 4.68; N, 6.68.

5-Butyl-5-phenylamino-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)dione (9e). It was obtained from 5-butyl-5-chloropyridocarbazoledione 2c (1.50 g, 4.6 mmol) and aniline (2.00 mL, 22 mmol) in dimethylformamide (20 mL) using the procedure and workup described for 9a. The yield was 1.30 g (74%), yellow crystals, mp 201°C (ethanol). IR: 3357 s, 2950–2800 w, 1715 s (4-C=O), 1675 s (6-C=O), 1599 s cm⁻¹. ¹H-NMR (CDCl₃): δ 0.82 (t, J = 7.2 Hz, 3 H, CH₃), 1.19–1.29 and 1.33–1.42 (2 m, 4 H, 2 CH₂), 2.18 (dt, J = 7.5 + 14.3 Hz, 2 H, ArCH₂), 4.71 (s, 1 H, NH), 6.38 (d, J = 7.7 Hz, 2 H, H at Ph), 6.70 (t, J = 7.4 Hz, 1 H, H at Ph), 6.99–7.03 (m, 2 H, H at Ph), 7.52–7.64 (m, 3 H, 2-H, 9-H, 10-H), 8.10–8.13 (m, 2 H, 1-H, 11-H), 8.32 (d, J = 7.6 Hz, 1 H, 3-H), 8.61 (d, J = 7.9 Hz, 1 H, 8-H). Anal Calcd for C₂₅H₂₂N₂O₂ (382.47): C, 78.51; H, 5.80; N, 7.32. Found: C, 78.71; H, 5.91; N, 7.34.

5-Benzylamino-5-butyl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)dione (9f). It was obtained from 5-butyl-5-chloropyridocarbazoledione **2c** (3.26 g, 10 mmol) and benzylamine (3.2 mL, 30 mmol) in dimethylformamide (20 mL) after 24 h using the procedure and workup described for **9a**. The yield was 3.09 g (78%), yellow crystals, mp 154–155°C (methanol). IR: 3445 m, 380 m, 2800–2970 w, 1710 m (4-C=O), 1660 s (6-C=O), 1595 w cm⁻¹. ¹H-NMR (CDCl₃): δ 0.90 (t, *J* = 7 Hz, 3 H, CH₃), 1.20–1.45 (m, 4 H, 2 butyl-CH₂), 2.20–2.30 (m, 2 H, ArCH₂), 3.55 (s, 1 H, NH), 4.49–4.51 (m, 2 H, benzyl-CH₂), 7.05–7.35 (m, 8 H, 5 H at Ph, 2-H, 9-H, 10-H), 8.10 (d, *J* = 7.5 Hz, 2H, 1-H, 11-H), 8.30 (d, *J* = 7.0 Hz, 1 H, 3-H), 8.50 (d, *J* = 7.0 Hz, 1 H, 8-H). Anal Calcd for C₂₆H₂₄N₂O₂ (396.49): C, 78.76; H, 6.10; N, 7.07. Found: C, 78.91; H, 5.95; N, 7.35.

5-Methyl-5-morpholin-4-yl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (10a). It was obtained from 5-chloro-5-methylpyridocarbazoledione 2a (1.00 g, 3.5 mmol) and morpholine (3.0 mL, 35 mmol) in dimethylformamide (20 mL) using the procedure and workup described for 9a. The yield was 1.02 g (87%), yellow crystals, mp 165°C (ethanol). IR: 3600–3400 m, 2950–2830 s, 1719 s (4-C=O), 1684 s (6-C=O), 1600 w cm⁻¹. ¹H-NMR (CDCl₃): δ 1.72 (s, 3 H, CH₃), 2.88 (t, J =4.5 Hz, 4 H, 2 CH₂), 3.73 (t, J = 4.5 Hz, 4 H, 2 CH₂), 7.50– 7.55 and 7.63–7.65 (2 m, 2 + 1 H, 2-H, 9-H, 10-H), 8.04 and 8.08 (2 d, J = 7.7 Hz, 2 × 1 H, 1-H, 11-H), 8.25 (d, J = 7.6 Hz, 1 H, 3-H), 8.64 (d, J = 7.8 Hz, 1 H, 8-H). Anal Calcd for C₂₀H₁₈N₂O₃ (334.38): C, 71.84; H, 5.43; N, 8.38. Found: C, 71.63; H, 5.61; N, 8.30.

5-Methyl-5-piperidin-1-yl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)dione (10b). It was obtained from 5-chloro-5-methylpyridocarbazoledione **2a** (1.00 g, 3.5 mmol) and piperidine (3.0 mL, 35 mmol) in dimethylformamide (20 mL) using the procedure and workup described for **9a**. The yield was 1.01 g (86%), yellow crystals, mp 116°C (ethanol). IR: 2940–2820 s, 1704 s (4-C=O), 1677 s (6-C=O), 1605 m cm⁻¹. ¹H-NMR (CDCl₃): δ 1.48 (q, J = 5.4 Hz, 2 H, CH₂), 1.60 (q, J = 5.4 Hz, 4 H, 2 CH₂), 1.69 (s, 3 H, CH₃), 2.81 (q, J = 5.3 Hz, 4 H, 2 CH₂), 7.47–7.53 and 7.61–7.63 (2 m, 2 + 1 H, 2-H, 9-H, 10-H), 8.06 and 8.07 (2 d, J = 7.8 Hz, 2 × 1 H, 1-H, 11-H), 8.21 (d, J =7.4 Hz, 1 H, 3-H), 8.64 (d, J = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₂₁H₂₀N₂O₂ (332.41): C, 75.88; H, 6.06; N, 8.43. Found: C, 75.85; H, 6.19; N, 8.36.

5-Morpholin-4-yl-5-phenyl-4H-pyrido[3,2,1-jk]carbazol-4,6(5H)dione (10c). It was obtained from 5-chloro-5-phenylpyridocarbazoledione **2e** (2.00 g, 5.8 mmol) and morpholine (5.50 mL, 60 mmol) in dimethylformamide (20 mL) using the procedure and workup described for **9a**. The yield was 1.80 g (78%), yellow crystals, mp 230°C (ethanol). IR: 3600–3400 m, 2970– 2830 s, 1715 s (4-C=O), 1681 s (6-C=O), 1605 s, 1596 s cm⁻¹. ¹H-NMR (CDCl₃): δ 3.01 (m, 4 H, CH₂), 3.78 (m, 4 H, CH₂), 7.44–7.67 (m, 8 H, 5 H at Ph, 2-H, 9-H, 10-H), 7.97 and 8.06 (2 d, *J* = 7.8 Hz, 2 × 1 H, 1-H, 11-H), 8.18 (d, *J* = 7.8 Hz, 1 H, 3-H), 8.71 (d, *J* = 7.6 Hz, 1 H, 8-H). Anal Calcd for C₂₅H₂₀N₂O₃ (396.45): C, 75.73; H, 5.08; N, 7.07. Found: C, 75.70; H, 5.19; N, 7.08. **5-Phenyl-5-piperidin-1-yl-4H-pyrido**[3,2,1-jk]carbazol-4,6(5H)dione (10d). It was obtained from 5-chloro-5-phenylpyridocarbazoledione **2e** (3.00 g, 8.7 mmol) and piperidine (10 mL, 91 mmol) in dimethylformamide (20 mL) using the procedure and workup described for **9a**. The yield was 3.02 g (88%), yellow crystals, mp 165°C (ethanol). IR: 3100 w, 2938 s, 2860–2800 m, 1718 s (4-C=O), 1686 s (6-C=O), 1593 s cm⁻¹. ¹H-NMR (CDCl₃): δ 1.53–1.64 (m, 6 H, 3 CH₂), 2.74–2.87 (m, 4 H, 2 CH₂), 7.26–7.29 (m, 3 H, H at Ph), 7.45–7.54 and 7.62–7.66 (2 m, 2 + 3 H, 2-H at Ph, 2-H, 9-H, 10-H), 7.98 and 8.07 (2 d, *J* = 8.3 Hz, 2 × 1 H, 1-H, 11-H), 8.18 (d, *J* = 7.6 Hz, 1 H, 3-H), 8.73 (d, *J* = 8.2 Hz, 1 H, 8-H). Anal Calcd for C₂₆H₂₂N₂O₂ (394.48): C, 79.17; H, 5.62; N, 7.10. Found: C, 78.88; H, 5.84; N, 7.10.

5-Butyl-5-morpholin-4-yl-4H-pyrido[3,2,1-jk]carbazole-4,6(5H)dione (10e). It was obtained from 5-butyl-5-chloropyridocarbazoledione **2c** (3.26 g, 0.01 mol) and morpholine (27 mL, 30 mmol) in dimethylformamide (8 mL) after 24 h using the procedure and workup described for **9a**. The yield was 3.19 g (85%), brown powder, mp 40–45°C. IR: 3600–3400 m, 2950– 2850 s, 1720 s (4-C=O), 1680 s (6-C=O), 1600 s cm⁻¹. ¹H-NMR (CDCl₃): δ 0.75 (t, *J* = 7.0 Hz, 3 H, CH₃), 1.00–1.35 (m, 4 H, 2 butyl-CH₂), 2.20–2.28 (m, 2 H, ArCH₂), 2.80 (t, *J* = 5.0 Hz, 4 H, 2 morpholine-CH₂), 3.65 (t, *J* = 5.0 Hz, 4 H, 2 morpholine-CH₂), 7.45–7.70 (m, 3 H, 2-H, 9-H, 10-H), 8.05 (t, *J* = 7.0 Hz, 2 H, 1-H, 11-H), 8.25 (d, *J* = 7.5 Hz, 1 H, 3-H), 8.65 (d, *J* = 7 Hz, 1 H, 8-H). Anal Calcd for C₂₃H₂₄N₂O₃ (376.46): C, 73.38; H, 6.43; N, 7.44. Found: C, 73.76; H, 6.70; N, 7.07.

5-Benzyl-5-butylpyrido[3,2,1-jk]carbazol-4,6(5H)-dione (11a). A solution of 5-butyl-4-hydroxypyridocarbazolone 1c (10.27 g, 0.035 mol) in aqueous sodium hydroxide (2.92 g, 0.073 mol in 150 mL water) was heated to 80°C. Benzylchloride (9.0 mL, 0.078 mol) was added dropwise under vigorous stirring and the obtained suspension was stirred for 12 h at 80°C. After cooling, chloroform (80 mL) was added, the layers were separated, and the aqueous layer was extracted with chloroform (2 \times 30 mL). The combined organic layers were washed with water and dried with sodium sulfate. The solvent was removed under reduced pressure, the solid product washed with ice-cold petroleum ether, and dried at room temperature. The yield was 11.68 g (87%), yellowish powder, mp 132-133°C (ethanol); IR : 3080–2760 m, 1705 s, 1670 s, 1595 m cm⁻¹. ¹H-NMR(CDCl₃): δ 0.80 (t, J = 7.0 Hz, 3 H, CH₃), 1.05–1.40 (m, 4 H, 2 butyl-CH₂), 2.35 (t, J = 7.1 Hz, 2 H, butyl-CH₂), 3.50 (s, 2 H, benzyl-CH₂), 6.80-6.95 (m, 3 H, H at Ph), 6.95-7.15 (m, 2 H, H at Ph), 7.30-7.65 (m, 3 H, 2-H, 9-H, 10-H), 7.85–8.10 (m, 3 H, 1-H, 11-H, 3-H), 8.60 (dd, J = 7.0 + 1.5Hz, 1 H, 8-H). Anal Calcd for C₂₆H₂₃NO₂ (381.48): C, 81.86; H, 6.08; N, 3.67. Found: C, 81.90; H, 6.16; N, 3.59.

5-Benzyl-5-phenylpyrido[3,2,1-jk]carbazol-4,6(5H)-dione (11b). 5-Phenyl-4-hydroxypyridocarbazolone 1e (10.85g, 0.035 mol) and benzylchloride (9.0 mL, 0.078 mol) were brought to reaction and worked up as described for 11a. The yield was 8.98 g (64%), yellow brownish powder, mp 201°C (cyclohexane); lit. mp 201°C [17]. IR: 3040 w, 1705 s, 1670 s, 1600 m, 1490 m cm⁻¹. ¹H-NMR (DMSO- d_6): δ 3.62 (s, 2 H, CH₂), 6.85–7.25 (m, 10 H, H at Ph), 7.35–7.70 (m, 3 H, 2-H, 9-H, 10-H), 7.90–8.25 (m, 3 H, 1-H, 11-H, 3-H), 8.70 (dd, J = 7.0 + 1.5 Hz, 1 H, 8-H). MS (EI): m/z (%) = 401 (36, M⁺), 310 (76), 309 (67), 194 (51), 193 (26), 166 (36), 165 (27), 92 (20), 91 (100). Anal Calcd for C₂₈H₁₉NO₂ (401.47): C, 83.77; H, 4.77; N, 3.49. Found: C, 83.99; H, 4.98; N, 3.88.

5-Allyl-5-butylpyrido[3,2,1-jk]carbazol-4,6(5H)-dione (11c). 5-Butyl-4-hydroxypyridocarbazolone 1c (3.11 g, 0.01 mol) and allylbromide (5.5 mL, 0.064 mol) were brought to reaction at 40°C and worked up as described for 11a. The yield was 1.95 g (59%), yellowish powder, mp 96–99°C (ethanol/ water). IR: 2980–2750 w, 1700 s, 1665 s, 1630 w, 1600 s. ¹H-NMR (CDCl₃): δ 0.85 (t, J = 7.0 Hz, 3 H, CH₃), 1.10– 1.35 (m, 4 H, 2 butyl-CH₂), 2.00–2.20 (m, 2 H, butyl-CH₂), 2.70–2.90 (m, 2 H, allyl-CH₂), 4.95–5.10 (m, 2 H, =CH₂), 5.55–5.80 (m, 1 H, –CH=), 7.30–7.65 (m, 3 H, 2-H, 9-H, 10-H), 7.85–8.10 (m, 3 H, 1-H, 11-H, 3-H), 8.60 (dd, J =7.0 + 1.5 Hz, 1 H, 8-H). Anal Calcd for C₂₂H₂₁NO₂ (331.42) C, 79.73; H, 6.39; N, 4.23. Found: C, 79.46; H, 6.75; N, 3.88.

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