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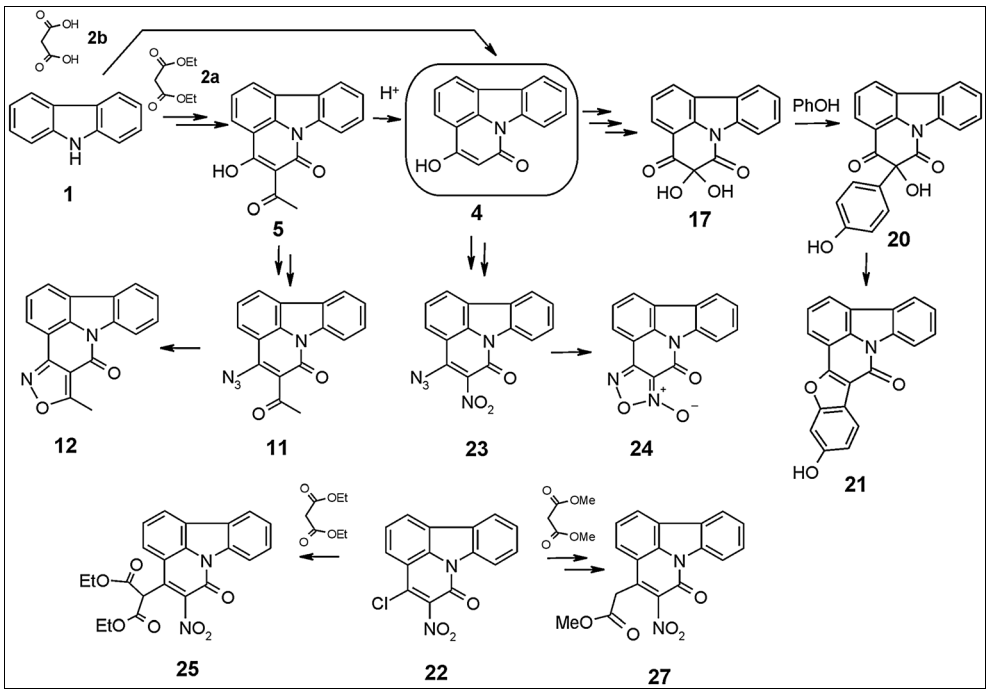
Received December 10, 2012

DOI 10.1002/jhet.1994

Published online 5 May 2014 in Wiley Online Library (wileyonlinelibrary.com).



The synthesis of the 5-unsubstituted pyrido[3,2,1-*jk*]carbazol-6-one **4** can be achieved by the reaction of carbazole (**1**) and malonate derivatives, either in a three-step synthesis via 5-acetyl-pyridocarbazolone **3** or in a one-step reaction from **1** and malonic acid/phosphoryl chloride. The 5-acetyl derivative **5** can be transformed via a tosylate intermediate to 4-azido-pyridocarbazolone **11**, which cyclizes by thermal decomposition to the isoxazolo-pyrido[3,2,1-*jk*]carbazolone **12**. The thermolysis conditions were investigated by DSC. Nitration of pyridocarbazolone **4** and subsequent introduction of azide leads to azido derivative **23**, which cyclizes on thermolysis to furazan-oxide derivative **24**. Again, the thermolysis conditions were investigated by DSC. 5-Chloro-5-nitro-pyrido[3,2,1-*jk*]carbazole-4,6-dione, obtained from **4** by subsequent nitration and chlorination, forms by exchange of both 5-substituents 5,5-dihydroxy-pyridocarbazoledione **17**, which acylates phenol to give 5-hydroxy-5-(*p*-hydroxyphenyl)-pyridocarbazoledione **20**. Acid-catalyzed cyclodehydration of **20** forms a highly fused benzofuro-pyridocarbazole **21**. Another C–C coupling at position 5 starts from 4-chloro-5-nitro-pyridocarbazolone **22** and diethyl malonate **2a**, which forms the diethyl (nitrocarbazolyl)malonate **25**. With dimethyl malonate **2c**, the intermediate dimethyl (nitrocarbazolyl)malonate gives on thermolysis the (nitrocarbazolyl)acetate **27** by loss of one ester group.

J. Heterocyclic Chem., **52**, 114 (2015).

INTRODUCTION

The pyrido[3,2,1-*jk*]carbazol-6-one framework is part of the heterocyclic skeleton of natural products such as Strychnos alkaloids with the biologically interesting combination of an indole and a 2-pyridone structure [2,3]. Furthermore, some pyridocarbazolone derivatives have found interest in pharmacological investigations [4] and in dyestuff chemistry [5].

Recently, we published the syntheses of 5-monosubstituted 4-hydroxypyrido[3,2,1-*jk*]carbazol-6-ones, which were obtained by cyclocondensation of 2-alkyl or 2-aryl malonates and carbazole [6], and studied their reactions [7]. The approach to 5-unsubstituted derivatives was found to require other reaction pathways, which is shown in this contribution. Furthermore, the substitution at C-5 of 4-hydroxypyrido [3,2,1-*jk*]carbazol-6-ones and further reactions lead to new and interesting structures.

RESULTS AND DISCUSSION

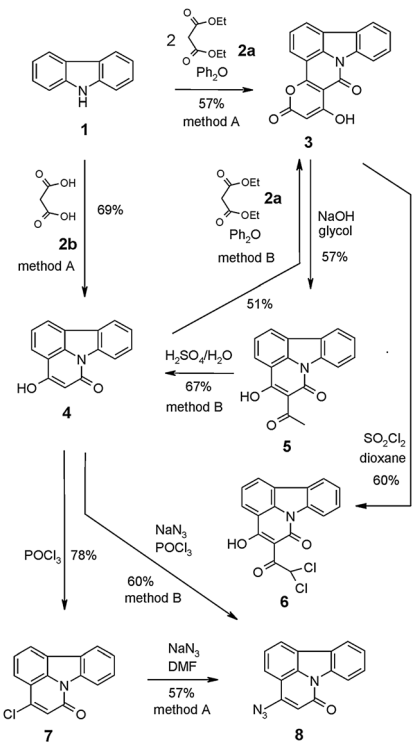
Whereas 2-substituted malonates react in a smooth thermal 1:1 cyclocondensation reaction with carbazole (**1**) in good yields to 5-substituted 4-hydroxy-pyrido [3,2,1-*jk*]carbazol-6-ones [4], 5-unsubstituted derivatives could not be obtained in such an easy way. Attempts to perform a cyclocondensation of 2-unsubstituted diethyl malonate **2a** with carbazole (**1**) give in a 1:1 reaction a mixture of compounds, which cannot be simply separated. In a 2:1 cyclocondensation of **2a** with **1**, however, a single compound **3** is obtained in good yields, which has been shown to consist of one molecule of carbazole (**1**) and two molecules deriving from malonate **2a**. The structure was assigned to 7-hydroxy-5*H*,8*H*-pyrano[2′,3′:4,5]pyrido[3,2,1-*jk*]carbazole-5,8-dione (**3**), a structure similar as obtained from related quinoline systems [8]. We could further show that the use of boiling diphenyl ether (bp 258°C) as solvent gives the best results, when the formed four molecules of ethanol were removed by distillation during the reaction.

Pyrano-pyridocarbazole **3** having a lactone structure reacts as cyclic ester with sodium or potassium hydroxide by hydrolytic ring opening. Best results were obtained when glycol was used as the solvent to obtain a higher reaction temperature and shorter reaction time. Acidification with hydrochloric acid results in the formation of an acetoacetic acid fragment as substituent, which decarboxylates spontaneously at elevated temperatures already in weakly acidic media to give the 5-acetyl-pyridocarbazole **5**. Because strong foaming by evolution of carbon dioxide accompanies this reaction, caution must be taken when performing this reaction.

The 5-acetyl group in pyridocarbazole **5** can be removed in a smooth reaction with 90% sulfuric acid at 140°C by ipso-substitution and results in a moderate overall yield of highly pure 5-unsubstituted pyridocarbazole **4** after three steps (Scheme 1).

We made several attempts to obtain **4** in a shorter reaction sequence using several reactive malonic acid derivatives (e.g., trichlorophenyl esters or ketene carboxylates) and catalysts [9], but the results were disappointing. The best results we obtained were by the reaction of malonic acid **2c** and carbazole (**1**) with phosphoryl chloride as condensation agent. This method was already described in the literature some decades earlier [10] and was reported to yield **4** in about 57% yield, but the enforcement of this reaction gave often differing yields and purities depending on the accuracy and workup. We adapted this method and optimized the yield to about 70%, but the reaction remained always somehow cumbersome, because product **4** was always contaminated with byproducts such as the diamide of malonic acid (from **2c** and two molecules of carbazole **1**) and further accompanied with small amounts of 4-chloro-pyridocarbazolone **7**.

Scheme 1



For mechanistic studies and to prove the structure of the pyrone **3**, we investigated also the reaction of pyridocarbazolone **4** back to the pyrono derivative **3**. The reaction with 1 equiv of diethyl malonate **2a** gave in moderate yield as main product the pyrone **3**, however with a number of byproducts deriving probably from higher fused derivatives.

A further method for the degradation of the pyrano ring in **3** was found when pyrano-pyridocarbazole **3** was brought to reaction with sulfuryl chloride. In contrast to similar reactions described in the following paragraphs (Scheme 3, reactions to **14** and **16**), not only electrophilic chlorination at the dicarbonyl-methylene group takes place but also the ring opening of the lactone ring and decarboxylation, probably caused by sulfuric acid formed during the reaction. As product, 5-dichloroacetyl-pyridocarbazolone **6** is formed.

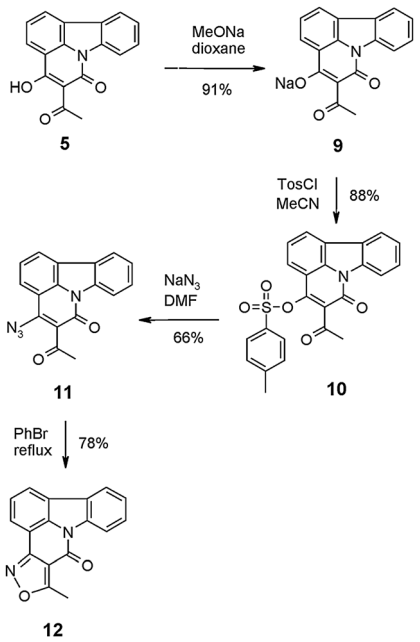
4-Chloro-pyridocarbazolone **7** was obtained in good yields from 4-hydroxypyridocarbazolone **4** by reaction with boiling phosphoryl chloride. The exchange of the chloro atom against the azide group proceeds easily in a nucleophilic reaction with sodium azide in DMF and produces 4-azido-pyridocarbazolone **8**.

Recently, we published a series of electrocyclization reactions of hetaryl azides with reactive ortho-substituents such as acyl or nitro groups [1,8,11,12]. Acetyl-pyridocarbazolone **5** has as precursor of one of these structure elements an acetyl group, together with a hydroxy group in ortho-position. The conversion of the 4-hydroxy group to a reactive intermediate was rather difficult: simple chlorination with phosphoryl chloride or tosylation with tosyl chloride did not work because hydrogen bondings between the acetyl group and the 4-hydroxy group prevented a reaction. A successful way was found by a two-step reaction in a similar manner as shown in [11a], first converting the hydroxy group of **5** with sodium methanolate at room temperature to its sodium salt **9**. The salt can now easily be tosylated under reflux to give tosylate **10**, which proved to be a very reactive intermediate. The tosyloxy group was exchanged against the azido group with sodium azide in DMF at room temperature to form 4-azido compound **11** in very good yields.

The thermal ring closure reaction of the azide **11** was investigated by DSC to obtain the hints on the cyclization temperature and possible further decomposition [13]. The DSC diagram of **11** (Fig. 1) shows that no melting point of **11** appears, but cyclization takes place already at rather low temperatures with an onset temperature of about 85°C and a reaction peak maximum at about 101°C. The reaction enthalpy is rather low with −21 mcal/mg. A small decomposition area is visible at about 170°C, followed by a melting area at 223°C, which is already the melting area of the cyclized species, the isoxazole **12**. A further decomposition can be observed at 330°C. From this information, the decomposition of the azide was performed in refluxing bromobenzene to obtain in good yields 6-methyl-7*H*-isoxazolo[3′,4′:4,5]pyrido[3,2,1-*jk*]carbazol-7-one (**12**). The DSC diagram of isoxazole **12** showed only a melting area with a peak maximum at 226°C (Scheme 2).

In the following part, electrophilic reactions at pyridocarbazolone **4**, directed regioselectively to position 5, were studied. Further electrophilic reactions at the aromatic nuclei should be avoided, which could be accomplished by mild reagents and low temperatures. 4-Hydroxy-pyridocarbazolone **4** reacts at room temperature with nitric acid in acetic acid in the presence of sodium nitrite as a catalyst exclusively at position 5 to give 5-nitro-pyridocarbazolone **13**. An electrophilic chlorination of **13** with sulfuryl chloride in dioxane at about 50°C attacks again position 5 and yields 5-chloro-5-nitro-pyridocarbazoledione **16**. Another pathway to the 5-chloro-5-nitro compound **16** was described in the literature using a reversed order of nitration and chlorination [14,15]. This reaction sequence starts first by 5,5-dichlorination of **4** with sulfuryl chloride, which gives as intermediate 5,5-dichloro-pyridocarbazoledione **14**. Selective reduction with zinc dust leads to the monochloro derivative **15**. In the nitration step to **16**, in literature [14], nitric acid in acetic acid at reflux temperature was applied to attack position 5, which however gives some multinitrated byproducts, already visible by the published melting point. By using again our previously described mild nitration method with sodium nitrite as catalyst at room temperature, the attack takes place exclusively at position 5 and gives pure 5-chloro-5-nitro-pyridocarbazoledione **16**. The total yield leading in our new sequence in two steps from **4** → **13** → **16** is 53%; in the known four-step reaction according to the literature sequence [14,15] from **4** → **14** → **15** → **16**, only 23% is obtained. 5-Chloro-5-nitro-pyridocarbazoledione **16** has recently found interest

Scheme 2



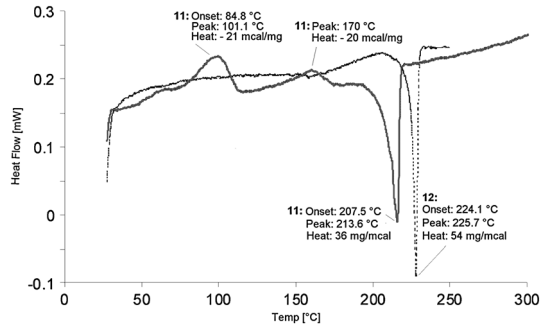


Figure 1. Combined DSC diagram of 5-acetyl-4-azido-pyrido[3,2,1-*jk*]carbazol-6-one (**11**) and 6-methyl-7*H*-isoxazolo[3′,4′:4,5]pyrido[3,2,1-*jk*]carbazol-7-one (**12**) (dotted line).

for anticancer drug development, because it shows a strong inhibitor activity for the enzyme "vaccinia H1-related phosphatase" among a screening of 50 000 tested compounds. In this investigation, only 20 structures have shown a similar strong activity as **16** [16]. Other biological activities of **16** were found by other authors [17] (Scheme 3).

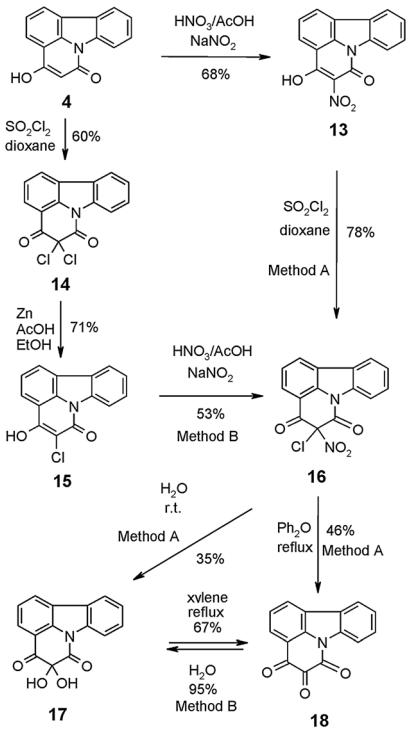
5-Chloro-5-nitro derivative **16** could be shown to be rather sensitive to thermolysis and gives in refluxing diphenyl ether the trioxo derivative, pyrido[3,2,1-*jk*]carbazole-4,5,6-trione **18**. Reaction of **16** with water resulted in a total exchange of both substituents at position 5, the chloro and nitro groups, against hydroxy groups and formed in moderate yields 5,5-dihydroxy-pyridocarbazoledione **17**. Compound **17** can be regarded as the hydrate of the trioxo compound **18**, which is also visible from its reactions: on heating, the yellow dihydroxy compound **17** looses one molecule of water and forms in refluxing xylene the red trioxo compound **18** in good yields. In turn, treating trioxo compound **18** with water forms back the dihydroxy compound **17** nearly quantitatively.

Reaction of morpholine with 5,5-dihydroxy-pyridocarbazoledione **17** leads to the substitution of one 5-hydroxy group and forms the half-aminal 5-hydroxy-5-morpholinyl-pyridocarbazoledione **19**. In the reaction of the dihydroxy compound **17** with phenol in the presence of concd sulfuric acid as catalyst, a C–C coupling takes place in the manner of an electrophilic acylation at aromatic compounds, which results in a substitution of one hydroxy group by the aromatic ring in para-position of the phenol group, and produces 5-*p*-hydroxyphenyl-5-hydroxy derivative **20**. Such structures having a 1,3-dicarbonyl unit with a 2-alkyl/aryl-2-hydroxy substituent pattern are related to a series of bioactive heterocycles with anti-inflammatory [18] and antibacterial [19] properties (Scheme 4).

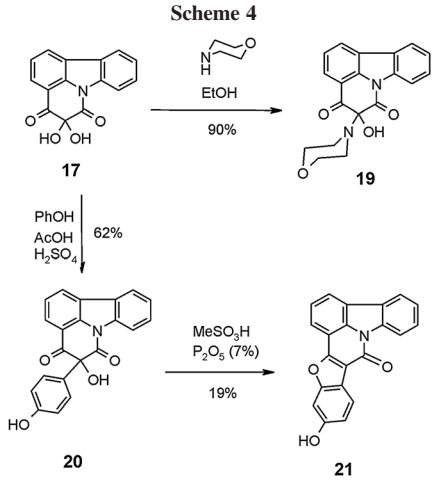
In earlier investigations, we could show that cyclic 1,3-dicarbonyl units possessing a 2-aryl-2-hydroxy moiety can be cyclodehydrated in strongly acidic media to fused benzopyranes [20] containing then the structure of, for example, coumestrols or aza-coumestrols. These structures are known to have potential anti-estrogenic [21] or anti-osteoporotic [22] activities. When 5-*p*-hydroxyphenyl-5-hydroxy-pyridocarbazoledione **20** was treated with Eaton's reagent (methanesulfonic acid, containing 7% phosphorus pentoxide), a cyclodehydration takes place, and 10-hydroxy-[1]benzofuro-pyridocarbazolone **21** was formed in low yields.

As described earlier, electrocyclization reactions of hetaryl azides take place also with reactive ortho-substituents such as nitro groups [1,8,12]. When 5-nitro-pyridocarbazolone **13** as starting material was brought to reaction with phosphoryl chloride to obtain as reactive intermediate 4-chloro-5-nitropyridocarbazolone **22**, again this reaction was hindered by hydrogen bondings between the nitro and hydroxy groups, similarly as observed with the acetyl group in **5**. Addition of TEA destroyed these bondings, and nucleophilic chlorination takes place in excellent yields in position 4 to replace the hydroxy group of **13** against a chloro substituent and formed 4-chloro compound **22**. The exchange of the 4-chloro atom against a 4-azido group was easily achieved with sodium azide in a DMF suspension warming it to 60°C. The isolation of the azide **23** was somewhat cumbersome because the end of the reaction cannot easily be determined from the

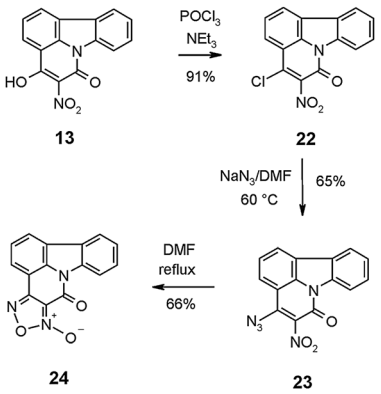
Scheme 3



Scheme 4



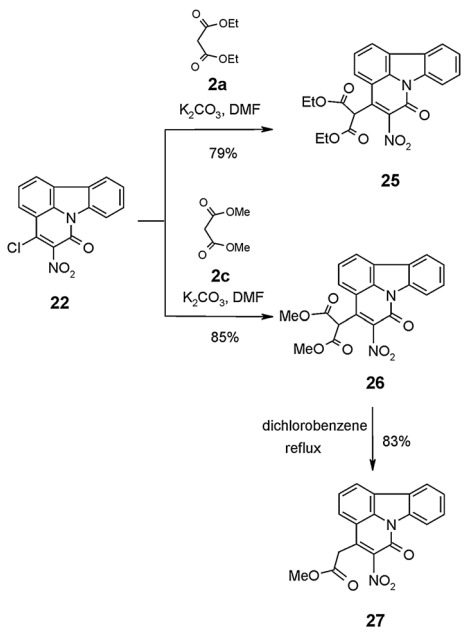
Scheme 5



reaction mixture because both chloro compound **23** and azide **24** have very similar R_f values.

The thermolysis of nitro compounds with ortho-azido groups is known to lead to furoxanes. However, the thermal conditions must be carefully selected; otherwise, decomposition reactions take place [1,8,12]. The thermal conditions for the cyclization of the azide in structure **23** to the furoxane in **24** were again determined by DSC [13]. In this reaction, in the DSC diagram, only a strong exothermic cyclization reaction was visible with an onset at 140°C and 165°C as peak maximum and a reaction enthalpy of −114 mcal/mg. The synthetic thermolysis reaction was carried out in refluxing DMF and produced pure oxadiazolo-pyridocarbazolone oxide **24** in excellent yields. The DSC diagram of furoxane **24** does not show any signals up to the melting area at 275–280°C (Scheme 5).

Scheme 6



4-Chloroquinolines have been recently shown to react with CH-acidic compounds such as malonates, cyanoacetates, malononitriles, or cyclic CH-acidic derivatives (e.g., dimedone) in a nucleophilic C–C coupling reaction to give 4-heteroarylsubstituted 1,3-dicarbonyl compounds [23]. In a similar way, 4-chloro-5-nitro-pyridocarbazolone **22** reacts with diethyl malonate **2a** to form (5-nitro-6-oxopyridocarbazolyl)malonate **25**. When dimethyl malonate **2c** was used, (pyridocarbazolyl)malonate **26** was obtained in excellent yields. Thermolysis of this dimethyl malonate in refluxing dichlorobenzene formed—probably by hydrolytic or substitutive removal of the methyl group followed by a decarboxylation—in excellent yields and purity (pyridocarbazolyl)acetate **27**. A similar elimination with the diethyl malonate **25** could not be observed, because at lower temperatures, no reaction took place and, at higher temperatures, only decomposition products were formed. Attempts to find out a suitable thermolysis temperature failed, because the DSC diagram showed that starting from 150°C, a series of decompositions occur (Scheme 6).

CONCLUSION

This contribution shows that the rarely investigated 5-unsubstituted pyrido[3,2,1-*jk*]carbazol-6-one **4** can be obtained easily via two pathways from carbazole (**1**) and malonic acid derivatives in good yields and purity. The structure of **4** shows two reactive sites: in an electrophilic substitution, position 5 can be attacked easily and regioselectively to give, for example, 5-nitro compound **13** and 5-chloro compound **14**. Further reactions lead to biologically interesting structures such as 5-chloro-5-nitro-pyridocarbazoledione **16**, 5-aryl-5-hydroxy-pyridocarbazoledione **20**, and 10-hydroxy-[1]benzofuro-pyridocarbazolone **21**.

Position 4, which bears in 5-unsubstituted pyrido[3,2,1-*jk*]carbazol-6-one **4** a reactive hydroxy group, can be attacked in a nucleophilic substitution to form tosyloxy, chloro, and azido compounds **10**, **11**, **22**, and **23**, or gives with CH-acidic compounds a C–C coupling reaction to malonates **25** and **26**. The reactive azido intermediates **11** and **23** undergo thermolytic cyclizations to isoxazole **12** and furoxane **24**; the cyclization conditions were investigated by DSC.

EXPERIMENTAL

General. Melting points were determined using a Stuart SMP3 melting point apparatus (Bibby Scientific Limited, Stone, Staffordshire, UK) in open capillary tubes. Calorimetric data (DSC data) were obtained on a Perkin Elmer Pyris 1 DSC instrument (Perkin Elmer Corp., Waltham, MA, USA) with the Pyris Software for Windows (Pyris Thermal Analysis System) version 3.72. The DSC plots were recorded between 25°C and 600°C, with a heating rate of 2–10°C/min, and 1.5–3.0 mg of compound in sealed aluminum crucibles (11 bar). IR spectra

were recorded with a Mattson Galaxy Series FTIR 7020 instrument (Mattson Instruments, Ltd., Milton Keynes, England) in potassium bromide (KBr) discs or with a Bruker Alpha-P instrument (Bruker GmbH, Karlsruhe, Germany) with ATR measurement, using a reflection method. NMR spectra were recorded on a Bruker AMX 360 instrument (Bruker GmbH) (360 MHz ^{1}H, 90 MHz ^{13}C), on a Bruker Avance III instrument (Bruker GmbH) (300 MHz ^{1}H), or on a Bruker Avance DRX 500 instrument (Bruker GmbH) (500 MHz ^{1}H, 125 MHz ^{13}C). Chemical shifts are given in parts per million (δ) from the internal TMS 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 (Agilent Technologies, Santa Clara, CA, USA) with either positive or negative atmospheric pressure chemical ionization (APCI) ion source, 50–200 V, nitrogen, or atmospheric pressure electrospray method. Dry column flash chromatography [24] was carried out on silica gel 60 H (5–40 μm) (Merck, Darmstadt, Germany). All reactions were monitored by TLC on 0.2-mm silica gel F254 plates (Merck) using UV light (254 and 366 nm) for detection. Analytical HPLC was performed on a Shimadzu LC 20 system (Shimadzu Corp., Kyoto, Japan) equipped with a diode array detector (215 and 254 nm) on a Pathfinder AS reversed-phase (4.6150 mm, 5 μm) 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.

7-Hydroxy-5*H*,8*H*-pyrano[2′,3′:4,5]pyrido[3,2,1-*jk*]carbazole-5,8-dione (3).

Method A. A mixture of carbazole (**1**) (3.34 g, 20 mmol), diethyl malonate (**2a**) (9.60 g, 60 mmol), and diphenyl ether (40 mL) was stirred for 7 h at 250–260°C. The formed ethanol (about 2 mL) was removed by distillation from the reaction mixture. After cooling to 50°C, the reaction mixture was poured into dioxane (30 mL), and then, methanol (20 mL) was slowly added until a solid precipitated. The product was kept 12 h at 5°C, then filtered by suction, and washed with cold methanol (~50 mL). The yield was 3.45 g (57%), orange prisms, mp 252°C (1-butanol).

Method B. A mixture of 4-hydroxy-pyridocarbazolone **4** (4.70 g, 20 mmol) and diethyl malonate (**2a**) (4.80 g, 30 mmol) in diphenyl ether (20 mL) was brought to reaction and worked up as described for method A. The yield was 3.07 g (51%), orange prisms, mp 246°C (*n*-butanol). IR (KBr): 2955 s, 1744 s (8-CO), 1661 s (5-CO), 1633 s, 1546 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.74 (s, 1H, 6-H), 7.59 (t, J = 7.3 Hz, 1H, 2-H), 7.63–7.74 (m, 2H, 11-H, 12-H), 8.10, 8.26, and 8.30 (3 d, J = 7.5 Hz, 3 × 1H, 1-H, 3-H, 13-H), 8.61 (d, J = 8.0 Hz, 1H, 10-H), 12.59 (s, 1H, 7-OH). MS [APCI, neg]: *m*/*z* (%) = 303 (20, M), 302 (100, M − 1). *Anal*. Calcd for $C_{18}H_9NO_4$ (303.28): C, 71.29; H, 2.99; N, 4.62. Found: C, 71.47; H, 3.29; N, 4.35.

4-Hydroxy-6*H*-pyrido[3,2,1-*jk*]carbazole-6-one (4).

Method A. To a stirred mixture of carbazole (**1**) (1.83 g, 11 mmol), malonic acid (**2a**) (3.02 g, 29 mmol), and naphthalene (3.00 g), phosphoryl chloride (16.8 g, 10 mL, 110 mmol) was slowly added. The reaction mixture was heated to 70–80°C under stirring until the mixture dissolved. The solution was kept for 45 min at this temperature, and then, the mixture was heated for further 10 min to 120°C (attention: strong foaming occurs). The bright brown color of the reaction mixture changed to dark brown. After cooling to 20°C, excess phosphoryl chloride was removed by distillation *in vacuo*, and the residue was poured onto crushed ice/water (100 mL) and stirred for 3 h at 20°C until the solid precipitated. The solid was filtered by suction and dissolved in 0.5*M* aq sodium hydroxide solution (250 mL), and the remaining insoluble byproducts were filtered off. The mother liquor was acidified with 2*M* hydrochloric acid to pH 2, and the formed solid was filtered by suction, washed with water (100 mL), and dried at 40°C. The yield was 1.80 g (70%), yellowish prisms, mp 315°C (ethanol).

Method B. A solution of 5-acetyl-pyridocarbazolone **5** (1.50 g, 5.4 mmol) in sulfuric acid (86%, 60 mL) was heated for 5 min to 140°C. The solution was cooled to room temperature, poured onto crushed ice/water (500 mL), and then stirred for 2 min until a yellowish solid precipitated. The mixture was stirred at room temperature for 3 h, and the solid was filtered by suction and washed with water (250 mL) until the filtrate was neutral. The yield was 0.85 g (67%), yellowish prisms, mp 321°C (ethanol); lit. mp 320°C (nitrobenzene) [10]. IR (KBr): 3059–2918 s, 1669 s (6-CO), 1630 s, 1547 s cm^{-1}. ^{1}H NMR (360 MHz, DMSO-d_6): δ 5.94 (s, 1H, 5-H), 7.50, 7.61 and 7.95 (3t, J = 7.7 Hz, 3 × 1H, 2-H, 9-H, 10-H), 8.27 and 8.39 (2d, J = 7.5 Hz, 2 × 1H, 1-H, 11-H), 8.53 (d, J = 8.0 Hz, 1H, 8-H), 12.03 (s, 1H, OH).

5-Acetyl-4-hydroxy pyrido[3,2,1-*jk*]carbazol-6-one (5). A solution of pyrano-pyridocarbazolone **3** (3.03 g, 10 mmol) in 1.6*M* aq sodium hydroxide solution (30 mL) and 1,2-ethanediol (30 mL) was heated under reflux for 3 h at 180°C (bath temperature). After cooling to room temperature, the reaction mixture was poured onto crushed ice/water (100 mL) and neutralized with 2*M* hydrochloric acid (5 mL), which formed a precipitate (attention: strong foaming occurs). The solid was filtered by suction and washed with water until the filtrate was acid free (~200 mL). The yield was 1.58 g (57%), brown powder, mp 177°C (ethanol/toluene). IR (ATR): 3434 s, 1672 s (6-CO), 1607 s, 1547 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.94 (s, 3H, Me), 7.51 (t, J = 7.5 Hz, 1H, 2-H), 7.55–7.63 (m, 2H, 9-H, 10-H), 8.08, 8.17 and 8.26 (3d, J = 7.5 Hz, 3 × 1H, 1-H, 3-H, 11-H), 8.71 (d, J = 8.0 Hz, 1H, 8-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.6 (acetyl-CH_3), 105.6 (5-C), 115.5 (ArC), 118.6 (ArC), 123.0 (ArC), 123.1 (ArC), 124.3 (ArC), 125.6 (ArC), 128.8 (ArC), 132.6 (ArC), 135.8 (ArC), 137.0 (ArC), 138.5 (ArC), 156.0 (6-amide-CO), 175.2 (4-C–OH), 198.9 (acetyl-CO). MS [APCI, neg]: *m*/*z* (%) = 277 (15, M), 276 (100, M − 1), 234 (12). *Anal*. Calcd for $C_{17}H_{11}NO_3$ (277.28): C, 73.64; H, 4.00; N, 5.05. Found: C, 73.78; H, 3.97; N, 4.85.

5-(2,2-Dichloroacetyl)-4-hydroxy-6*H*-pyrido[3,2,1-*jk*] carbazol-6-one (6). To a solution of pyrano-pyridoquinoline **3** (1.61 g, 5.3 mmol) in dioxane (50 mL), sulfuryl chloride (1.35 g, 0.81 mL, 10 mmol) was slowly added. The reaction mixture was heated for 30 min to 50°C and then for 5 min to 90°C. The mixture was cooled to room temperature and then poured onto ice/water (200 mL). The obtained solid was filtered by suction and washed with water (250 mL) until neutral. The yield was 1.10 g (60%), yellow needles, mp 317°C (ethanol/toluene). IR (KBr): 3439 s, 3040 s, 1754 s, 1730 s (dichloroacetyl-CO), 1672 s (6-CO), 1631 s, 1580 s cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.54 (s, 1H, $CHCl_2$), 7.64–7.60 (m, 2H, 2-H, 9-H), 8.08 (d, J = 7.9 Hz, 2H, 10-H, 11-H), 8.20 (d, J = 7.9 Hz, 1H, 1-H), 8.31 (d, J = 7.5 Hz, 1H, 3-H), 8.70 (d, J = 8.0 Hz, 1H, 8-H), 16.02 (s, 1H, OH). ^{13}C NMR (125 MHz, $CHCl_2$): δ 68.5 (acetyl-$CHCl_2$), 104.5 (5-C), 112.5 (ArC), 117.2 (ArC), 121.1 (ArC), 121.8 (ArC), 123.5 (ArC), 124.4 (ArC),

125.4 (ArC), 127.4 (ArC), 128.9 (ArC), 130.8 (ArC), 137.0 (ArC), 138.0 (ArC), 159.5 (6-amide–CO), 189.1 (4-C–OH), 193.5 (dichloroacetyl-CO). *Anal*. Calcd for $C_{17}H_9Cl_2NO_3$ (346.17): C, 58.98; H, 2.62; N, 4.05. Found: C, 58.56; H, 2.47; N, 3.96.

4-Chloropyrido[3,2,1-*jk*]carbazole-6-one (7). A mixture of 4-hydroxy-pyridocarbazolone **4** (1.60 g, 6.8 mmol) in excess phosphoryl chloride (20 mL) was heated under reflux for 1 h. After cooling to room temperature, the reaction mixture was poured onto ice/water (500 mL) and neutralized with 1*M* aq sodium hydroxide solution. The precipitated solid was filtered off by suction and washed with water (200 mL) until neutral. The yield was 1.35 g (78%), pale blue prisms, mp 246°C (ethanol). IR (ATR): 3447 s, 1672 s (6-CO), 1603 s, 1554 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.69 (s, 1H, 5-H), 7.52 (t, J = 7.0 Hz, 1H, 2-H), 7.60–7.63 (m, 2H, 9-H, 10-H), 8.03 (d, J = 7.4 Hz, 1H, 11-H), 8.09 (d, J = 7.6 Hz, 1H, 1-H), 8.22 (d, J = 6.8 Hz, 1H, 3-H), 8.73 (d, J = 8.0 Hz, 1H, 8-H). *Anal*. Calcd for $C_{15}H_8ClNO$ (253.69): C, 71.02; H, 3.18; N, 5.52. Found: C, 71.23; H, 3.39; N, 5.26.

4-Azidopyrido[3,2,1-*jk*]carbazol-6-one (8).

Method A. A mixture of 4-chloro-pyridocarbazolone **7** (2.03 g, 8 mmol) and sodium azide (1.04 g, 16 mmol) in DMF (30 mL) was stirred and warmed for 12 h at 60°C. Then, ice/water (100 mL) was added, the mixture stirred for 1 h and warmed to room temperature, and the formed precipitate filtered by suction. The yield was 1.19 g (57%), yellowish prisms, mp 252°C dec (methanol).

Method B. A mixture of 4-hydroxy-pyridocarbazolone **4** (0.19 g, 0.8 mmol) and sodium azide (1.00 g, 15.4 mmol) in excess phosphoryl chloride (10 mL) was vigorously stirred and warmed for 12 h at 60°C. The excess phosphoryl chloride was removed by vacuum distillation, the residue cooled to room temperature, poured onto ice/water (50 mL), and stirred for 2 h, and the precipitated solid filtered by suction. The yield was 0.12 g (60%), yellowish prisms, mp 250°C dec (methanol). IR (ATR): 3433 s, 2126 s (N_3), 1673 s (6-CO), 1605 s, 1555 m cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.57 (s, 1H, 5-H), 7.55 (t, J = 7.0 Hz, 1H, 2-H), 7.61–7.69 (m, 2H, 9-H, 10-H), 7.94 (d, J = 7.9 Hz, 1H, 11-H), 8.29 (d, J = 7.6 Hz, 1H, 1-H), 8.45 (d, J = 7.5 Hz, 1H, 3-H), 8.51 (d, J = 8.0 Hz, 1H, 8-H). *Anal*. Calcd for $C_{15}H_8N_4O$ (260.26): C, 69.23; H, 3.10; N, 21.53. Found C, 68.85; H, 3.47; N, 21.15.

Sodium 5-acetyl-6-oxo-6*H*-pyrido[3,2,1-*jk*]carbazol-4-olate (9). To a mixture of 4-acetylpyridocarbazolone **5** (10.00 g, 36 mmol) and sodium methoxide (70 mL) prepared from sodium (2.76 g, 120 mmol) and methanol (70 mL), dioxane (270 mL) was added. The reaction mixture was stirred for 5 min at room temperature, and the formed solid was filtered by suction and washed with methanol (20 mL). The yield was 9.66 g (9 1%), yellowish powder, mp > 300°C (methanol). This product was used without further purification for the synthesis of **10**.

5-Acetyl-6-oxo-6*H*-pyrido[3,2,1-*jk*]carbazol-4-yl 4-methylbenze nesulfonate (10). A mixture of the sodium salt **9** (4.94 g, 16.7 mmol) in dry acetonitrile (70 mL) and *p*-toluenesulfonylchloride (4.00 g, 21 mmol) was stirred and heated under reflux for 8 h. After cooling to room temperature, the mixture was poured onto ice/water (100 mL). A solid precipitated, which was then filtered by suction and washed with water (200 mL). The yield was 6.34 g (88%), yellowish needles, mp 189°C (ethanol). IR (ATR): 1696 s (6-CO), 1607 m, 1560 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.52 (s, 3H, tosyl-CH_3), 2.67 (s, 3H, acetyl-CH_3), 7.45 (d, J = 8.0 Hz, 2H, ArH), 7.62–7.50 (m, 3H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 7.94 (d, J = 8.0 Hz, 2H, ArH), 8.07 and 8.20 (2d, J = 7.5 Hz, 2 × 1H, 3-H, 11-H), 8.67 (d, J = 8.0 Hz, 1H, 8-H). *Anal*. Calcd for $C_{24}H_{17}NO_5S$ (431.47): C, 66.81; H, 3.97; N, 3.25. Found: C, 66.58; H, 3.91; N, 3.08.

5-Acetyl-4-azido-pyrido[3,2,1-*jk*]carbazol-6-one (11). A mixture of tosylate **10** (0.45 g, 1.0 mmol) and sodium azide (0.18 g, 2.8 mmol) in DMF (15 mL) was stirred for 5 h at room temperature and then poured onto ice/water (100 mL). The formed precipitate was filtered by suction, washed with water, and dried *in vacuo* at ambient temperature. The yield was 0.20 g (66%), yellowish prisms, mp 206°C dec (methanol). DSC: reaction onset 84.8°C, peak maximum 101.1°C (−21 mcal/mg); decomposition peak maximum 170°C (−20 mcal/mg); mp onset 207.5°C, peak maximum 213.6°C (36 mcal/mg); decomposition onset 330.7°C, peak maximum 334.1°C (−110 mcal/mg). IR (ATR): 3433 m, 2136 s (N_3), 1688 s (6-CO), 1645 s, 1640 s, 1607 s, 1536 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.90 (s, 3H, Me), 7.52 (t, J = 7.6 Hz, 1H, 2-H), 7.58–7.62 (m, 2H, 9-H, 10-H), 8.04, 8.24 and 8.34 (3d, J = 7.6 Hz, 3 × 1H, 1-H, 3-H, 11-H), 8.49 (d, J = 8.0 Hz, 1H, 8-H). *Anal*. Calcd for $C_{17}H_{10}N_4O_2$ (302.29): C, 67.55; H, 3.33; N, 18.53. Found: C, 67.91; H, 3.71; N, 18.13.

6-Methyl-7*H*-isoxazolo[3′,4′:4,5]pyrido[3,2,1-*jk*]carbazol-7-one (12). A mixture of 4-azido-pyridocarbazolone **10** (0.10 g, 0.33 mmol) in bromobenzene (3 mL) was heated under reflux for 3 h. After cooling to room temperature, the mixture was poured onto ice/water (50 mL). The formed solid was filtered, washed with water (50 mL), and dried. The yield was 0.071 g (78%), yellow prisms, mp 223°C (methanol). DSC: mp onset 224.1°C; peak maximum 225.7°C (54 mcal/mg). IR (ATR): 3396 m, 1694 s (amide-CO), 1669 m, 1637 s, 1612 s, 1574 w cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.92 (s, 3H, Me), 7.53 (t, J = 7.5 Hz, 1H, 2-H), 7.64 (t, J = 7.6 Hz, 2H, 9-H, 10-H), 8.07, 8.27 and 8.37 (3d, J = 7.7 Hz, 3 × 1H, 1-H, 3-H, 11-H), 8.52 (d, J = 8.1 Hz, 1H, 8-H). *Anal*. Calcd for $C_{17}H_{10}N_2O_2$ (274.28): C, 74.45; H, 3.67; N, 10.21. Found: C, 74.55; H, 3.70; N, 10.03.

4-Hydroxy-5-nitropyrido[3,2,1-*jk*]carbazol-6-one (13). To a stirred mixture of 4-hydroxypyridocarbazolone **4** (1.48 g, 6.3 mmol) in glacial acetic acid (50 mL) at room temperature, concentrated nitric acid (4.0 mL, 60 mmol) was slowly added. Then, sodium nitrite (0.25 g, 3.6 mmol) was added as catalyst, which starts a slightly exothermic reaction. The starting material dissolved, and then, a precipitation of the product can be observed. The mixture was stirred for further 30 min and then poured onto crushed ice/water (100 mL). The precipitated solid was filtered by suction and washed with water until acid free. The yield was 1.20 g (68%), yellow needles, mp 192°C (ethanol). IR (ATR): 3456 m, 1671 s (6-CO), 1648 s, 1549 m cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.49 (t, J = 7.5 Hz, 1H, 2-H), 7.57–7.62 (m, 2H, 9-H, 10-H), 8.14 (d, J = 7.8 Hz, 1H, 11-H), 8.26 (d, J = 7.7 Hz, 1H, 1-H), 8.42 (d, J = 7.6 Hz, 1H, 3-H), 8.50 (d, J = 8.1 Hz, 1H, 8-H). MS [APCI, pos]: m/z (%) = 282 (15, M + 2), 281 (100, M + 1), 249 (25), 233 (15). *Anal*. Calcd for $C_15H_8N_2O_4$ (280.24): C, 64.29; H, 2.88; N, 10.00. Found: C, 64.02; H, 3.11; N, 9.74.

5,5-Dichloropyrido[3,2,1-*jk*]carbazole-4,6-dione (14). To a stirred solution of 4-hydroxy-pyridocarbazolone **4** (1.50 g, 6.4 mmol) in dioxane (20 mL), sulfuryl chloride (1.35 g, 0.81 mL, 10 mmol) was slowly added. The reaction mixture was heated for 30 min to 50°C, then for 5 min to 90°C. After cooling to room temperature, the reaction mixture was poured onto ice/water (100 mL). This solution was extracted with ethyl

acetate (50 mL), and the organic layer was dried with sodium sulfate and taken to dryness *in vacuo* to give a solid. The yield was 1.17 g (60%), yellow needles, mp 183°C (ethanol), lit. mp 181–183°C (benzene) [15]. IR (ATR): 3425 m 1733 s (4-CO), 1708 s (6-CO), 1607 s, 1590 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54–7.63 (m, 3H, 2-H, 9-H, 10-H), 8.04 (d, $J = 7.1$ Hz, 1H, 11-H), 8.14 (d, $J = 7.2$ Hz, 1H, 1-H), 8.27 (d, $J = 7.1$ Hz, 1H, 3-H), 8.51 (d, $J = 7.8$ Hz, 1H, 8-H).

5-Chloro-4-hydroxypyrido[3,2,1-*jk*]carbazol-6-one (15). A solution of 5,5-dichloro-pyridocarbazolone **14** (1.00 g, 3.3 mmol) in ethanol (30 mL) in glacial acetic acid (20 mL) was heated under reflux. Zinc dust (0.60 g, 9.2 mmol) was slowly added to the boiling mixture in small portions under vigorous stirring, and then the reaction mixture heated under reflux for further 30 min. The color of the mixture turned from yellow to colorless greenish during this time. After cooling to room temperature, the reaction mixture was filtered by suction and washed with ethanol (10 mL). The filtrate was taken to dryness under reduced pressure. To both solids, ethanol (each 20 mL) was added, the mixtures were heated to reflux, and the insoluble solids were filtered off while still hot. The ethanol filtrates were combined and cooled to room temperature, which formed a crystalline precipitate. The yield was 0.63 g (71%), pale yellowish needles, mp 258°C (ethanol), lit. mp 259–260°C (1-butanol, acetic acid, or nitrobenzene) [15]. IR (ATR): 3057 m, 2925 m, 1634 s (6-CO), 1603 s, 1512 s cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.53 (t, $J = 7.5$ Hz, 1H, 2-H), 7.60–7.66 (m, 2H, 9-H, 10-H), 8.12 (d, $J = 7.8$ Hz, 1H, 11-H), 8.28 (d, $J = 7.8$ Hz, 1H, 1-H), 8.41 (d, $J = 5.5$ Hz, 1H, 3-H), 8.53 (d, $J = 8.0$ Hz, 1H, 8-H). MS [APCI, pos]: *m/z* (%) = 272 (45, M + 3), 270 (100, M + 1). MS [APCI, neg]: *m/z* (%) = 270 (25, M + 1), 268 (100, M − 1), 234 (5). *Anal*. Calcd for $C_{15}H_8ClNO_2$ (269.69): C, 66.81; H, 2.99; N, 5.19. Found: C, 66.45; H, 3.06; N, 5.13.

5-Chloro-5-nitro-pyrido[3,2,1-*jk*]carbazole-4,6-dione (16).

Method A. To a solution of 5-nitro-pyridocarbazolone **13** (0.50 g, 1.6 mmol) in dioxane (15 mL) at 50°C, sulfuryl chloride (0.42 mL, 0.71 g, 3.7 mmol) was added slowly in small portions and the mixture kept at this temperature. The color of the mixture changed from yellow to brown. The temperature was kept at 50°C for further 10 min and the complete conversion checked by TLC comparison. Then, the mixture was heated for 5 min to 60°C and then cooled in an ice bath. The precipitated solid was filtered by suction and washed with a small amount of cold water. The yield was 0.39 g (78%), yellow powder, mp 164–166°C dec (ethanol).

Method B. To a stirred mixture of 5-chloro-pyridocarbazolone **15** (1.69 g, 6.3 mmol) in glacial acetic acid (50 mL) at room temperature, concentrated nitric acid (4.0 mL, 60 mmol) was slowly added. Then, sodium nitrite (0.25 g, 3.6 mmol) was added as catalyst, which starts a slightly exothermic reaction. The starting material dissolved, and then, a precipitation of the product can be observed. The mixture was stirred for further 30 min and then poured onto crushed ice/water (50 mL), the solid filtered by suction, and the filtrate kept for the synthesis of **17**. The solid was washed with water until acid free. The yield was 1.05 g (53%), yellow prisms, mp 165–166°C dec (ethanol); lit. mp 135–140°C dec (benzene) [14]. IR (ATR): 3100 w, 1729 s (4-CO), 1698 s (6-CO), 1583 s cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 7.65–7.80 (m, 3H, 2-H, 9-H, 10-H), 8.16 and 8.39 (2d, $J = 8.2$ Hz, 3H, 1-H, 3-H, 11-H), 8.72 (d, 1H, $J = 7.7$ Hz, 8-H).

5,5-Dihydroxypyrido[3,2,1-*jk*]carbazole-4,6-dione (17).

Method A. To the filtrate of the reaction mixture of 5-chloro-5-nitro-pyridocarbazoledione **16** (obtained from **15** in method B), water (50 mL) was added and the mixture kept overnight at room temperature. Colorless needles of dihydroxy compound **17** were formed, which were then filtered by suction. The yield was 0.52 g (31%), colorless prisms, decomposition starting at 120–140°C.

Method B. Pyridocarbazoletrione **18** (25 mg, 0.1 mmol) was heated in water (5 mL) to 80°C for 15 min. The reaction mixture was cooled to 10°C, filtered by suction, and dried under reduced pressure at 40°C. The yield was 27 mg (95%), colorless prisms, decomposition starting at 120–140°C, then melting between 220°C and 223°C dec by forming back the red tricarbonyl compound **18**; lit. mp 215–223°C [15]. IR (ATR): 3435 m, 3240 s, 1708 m (4-CO), 1660 s (6-CO), 1605 m, 1587 m cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 7.04–7.12 (m, 3H, 2-H, 9-H, 10-H), 7.26, 7.44 and 7.58 (3 d, $J = 7.1$ Hz, 3 × 1H, 1-H, 3-H, 11-H), 7.65 (d, $J = 7.8$ Hz, 1H, 8-H).

Pyrido[3,2,1-*jk*]carbazole-4,5,6-trione (18).

Method A. A solution of 5-chloro-5-nitropyridocarbazoledione **16** (0.10 g, 0.32 mmol) in diphenyl ether (4 mL) was heated slowly to 190–200°C. The color of the reaction mixture changed from yellow to red, and the formation of nitrous gases was observed. The reaction mixture was cooled to 0°C, and dry cyclohexane (4 mL) was added. The formed precipitate was filtered by suction and washed with dry cyclohexane. The yield was 37 mg (46%), red powder, mp 218–223°C.

Method B. A solution of 5,5-dihydroxy-pyridocarbazoledione **16** (86 mg, 0.32 mmol) in dry xylene (4 mL) was heated for 30 min under reflux, and the yellow color of the reaction mixture changed during this time to red. After cooling to 0°C, a precipitate was formed, which was then filtered by suction. The yield was 54 mg (67%), red powder, mp 220–223°C; lit. mp 215–223°C [15] IR (ATR): 3083 w, 1711 s (4-CO, 5-CO), 1687 s (6-CO), 1591 s cm^{-1}. ^1H NMR(300 MHz, DMSO-d_6): δ 7.55–7.71 (m, 3H, 2-H, 9-H, 10-H), 8.02 and 8.32 (2d, $J = 7.4$, 2 × 1H, 1-H, 11-H), 8.50 (d, $J = 7.3$ Hz, 2H, 3-H, 8-H).^{13}C NMR (75 MHz, DMSO-d_6): 116.2 (ArC), 121.1 (ArC), 122.0 (ArC), 124.4 (ArC), 124.8 (ArC), 124.9 (ArC), 125.7 (ArC), 127.3 (ArC), 129.1 (ArC), 137.0 (ArC), 139.7 (ArC), 155.7 (4-CO), 170.9 (6-CO), 176.4 (5-CO).

5-Hydroxy-5-morpholin-4-yl-pyrido[3,2,1-*jk*]carbazole-4,6-dione (19). To a solution of 5,5-dihydroxy-pyridocarbazoledione **17** (1.34 g, 5 mmol) in ethanol (10 mL), morpholine (0.61 g. 7 mmol) was added, and the mixture was heated under reflux for 30 min. Then, the mixture was cooled to room temperature, and the precipitated crystals were filtered by suction and washed with a small amount of cold ethanol. The yield was 1.51 g (90%) light yellow-brownish prisms, mp 167°C (ethanol). IR (KBr): 3450 m, 3250–2900 m, 1715 s (4-CO), 1705 s, 1670 s (6-CO), 1620 s, 1545 s cm^{-1}. ^1H NMR (360 MHz, DMSO-d_6): δ 2.60–2.70 (m, 4H, NCH_2), 3.55–3.60 (m, 4H, OCH_2), 5.60 (s, 1H, 5-OH), 7.50–7.70 (m, 3H, 2-H, 9-H, 10-H), 8.00 and 8.30 (2d, $J = 7.4$, 2 × 1H, 1-H, 11-H), 8.50–8.55 (m, 2H, 3-H, 8-H). *Anal*. Calcd for $C_{19}H_{16}N_2O_4$ (336.35): C, 67.85; H, 4.79; N, 8.33. Found: C, 68.21; H, 5.12; N, 7.95.

5-Hydroxy-5-(4-hydroxyphenyl)pyrido[3,2,1-*jk*]carbazole-4,6-dione (20). A solution of 5,5-dihydroxy-pyridocarbazoledione **17** (1.34 g, 5 mmol) in glacial acetic acid (13 mL) and water (0.03 mL) was cooled to 0–5°C. To this mixture, concd sulfuric acid (2.1 mL) was added and the mixture kept at this temperature. Then, phenol (0.94 g, 10 mmol) was added in small portions and the mixture warmed to room temperature and stirred for 2 h. A solid precipitated, which was then filtered by suction. The yield was 1.00 g (58%), brownish prisms, mp 209–210°C. IR (KBr): 3400 m, 1710 s (4-CO), 1680 s (6-CO), 1610 s, 1580 s cm^{-1}. ^1H

NMR (360 MHz, DMSO-d_6): δ 5.55 (s, 1H, 5-OH), 6.60–7.10 (m, 4H, PhH), 7.50–7.70 (m, 3H, 2-H, 9-H, 10-H), 8.00 and 8.30 (2 d, 2 × 1H, J = 7.4, 2 H, 1-H, 11-H), 8.50–8.55 (m, 2H, 3-H, 8-H) 9.10 (s, 1H, 4′-OH). *Anal*. Calcd for $C_{21}H_{13}NO_4$ (343.34): C, 73.46; H, 3.82; N, 4.08. Found: C, 73.84; H, 4,19; N, 3.70.

10-Hydroxy-13*H*-[1]benzofuro[2′,3′:4,5]pyrido[3,2,1-*jk*]carbazol-13-one (21). A solution of 5-hydroxy-5-(4-hydroxyphenyl)-pyridocarbazoledione **20** (0.034 g, 0.1 mmol) in Eaton's reagent (methanesulfonic acid/7% phosphorus pentoxide) (10 mL) was heated for 20 min to 150°C. Then, the reaction mixture was poured onto crushed ice/water (50 mL), and the precipitate filtered by suction, washed with water until neutral, dried, and recrystallized several times from DMF/methanol using charcoal for purification. The yield was 6.3 mg (19%), yellowish prisms, mp 285°C dec mp (DMF/methanol). IR (KBr): 3380 s, 3050 w, 1655 m (13-CO), 1640 s, 1595 w cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.30, 7.45 and 7.55 (3t, J = 7.3 Hz, 3H, 2-H, 3-H, 6-H), 7.65–7.75 (m, 2H, 9-H, 11-H), 8.30–8.40 (m, 4H, 4-H, 5-H, 7-H, 12-H), 8.77 (d, J = 8.1 Hz, 1H, 1-H), 9.02 (s, 1H, 10-OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 98.9 (ArC), 99.7 (ArC), 112.1 (ArC), 112.2 (ArC), 115.6 (ArC), 116.3 (ArC), 122.3 (ArC), 122.5 (ArC), 124.3 (ArC), 124.6 (ArC), 125.0 (ArC), 126.0 (ArC), 127.0 (ArC), 128.1 (ArC), 133.4 (ArC), 135.3 (ArC), 139.9 (ArC), 150.1 (4a-C–O), 155.6 (3b-C–O), 156.7 (6-C–OH), 159.7 (13-amide-CO). MS [APCI, pos]: *m/z* (%) = 326 (M + 1, 80), 325 (M, 25). *Anal*. Calcd for $C_{21}H_{11}NO_3$ (325.33): C, 77.53; H, 3.41; N, 4.31. Found: C, 77.85; H, 3.79; N, 3.95.

4-Chloro-5-nitropyrido[3,2,1-*jk*]carbazol-6-one (22). A mixture of 5-nitro-pyridocarbazolone **13** (1.29 g, 4.6 mmol) in phosphoryl chloride (11.03 g, 6.6 mL, 72 mmol) and TEA (0.5 mL) as catalyst was heated under reflux for 2 h. The reaction mixture was then cooled to room temperature and poured onto crushed ice/water (100 mL). The solid product was filtered by suction and washed with water. The yield was 1.25 g (91%), pale blue powder, mp 261°C (ethanol). IR (ATR): 1684 s (6-CO), 1604 m, 1538 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.60 (t, J = 7.6 Hz, 1H, 2-H), 7.67 (t, J = 7.6 Hz, 1H, 10-H), 7.75 (t, J = 7.8 Hz, 1H, 9-H), 8.11 (m, 2H, 1-H, 11-H), 8.33 (d, J = 7.6 Hz, 1H, 3-H), 8.65 (d, J = 8.1 Hz, 1H, 8-H). *Anal*. Calcd for $C_{15}H_7ClN_2O_3$ (298.69): C, 60.32; H, 2.36; N, 9.38. Found: C, 59.95; H, 2.55; N, 9.04.

4-Azido-5-nitropyrido[3,2,1-*jk*]carbazol-6-one (23). A stirred mixture of 4-chloropyridocarbazolone **22** (1.20 g, 4 mmol) and sodium azide (6.00 g, 92 mmol) in DMF (40 mL) was heated for 3 h at 60°C. The reaction mixture was then poured onto crushed ice/water (200 mL) and kept for 5 h at room temperature. The precipitate was filtered by suction and washed with water. The yield was 0.79 g (65%), yellow powder, mp 210°C dec (ethanol). DSC: reaction onset 139.8°C, peak maximum 164.7°C (−114 mcal/mg). IR (ATR): 3435 s, 2141 s (N_3), 1642 s (6-CO), 1601 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56–7.63 (m, 1H, 2-H), 7.65–7.85 (m, 2H, 9-H, 10-H), 8.00 (d, J = 7.2 Hz, 1H, 3-H), 8.10–8.14 (m, 2H, 1-H, 11-H), 8.68 (d, J = 7.7 Hz, 1H, 8-H). *Anal*. Calcd for $C_{15}H_7N_5O_3$ (305.25): C, 59.02; H, 2.31; N, 22.94. Found: C, 59.34; H, 2.70; N, 22.55.

7*H*-[1, 2, 5]Oxadiazolo[3′,4′: 4,5]pyrido[3,2,1-*jk*]carbazol-7-one 6-oxide (24). A solution of 4-azidopyridocarbazolone **23** (0.10 g, 0.32 mmol) in DMF (20 mL) was heated under reflux for 2 h. After cooling to room temperature, the mixture was poured onto crushed ice/water (100 mL). The formed solid was filtered by suction, washed with water, and dried. The yield was 0.08 g (89%), yellow prisms, mp 278°C (methanol). DSC: mp onset 275.1°C, peak maximum 279.5°C (28 mcal/mg). IR (ATR): 3369 m, 1694 s (7-CO), 1648 m, 1608 s, 1598 s cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.68 (t, J = 7.6 Hz, 1H, 2-H), 7.76 and 7.83 (2t, J = 7.6 Hz, 2 × 1H, 10-H, 11-H), 8.17 (d, J = 8.0 Hz, 1H, 12-H), 8.42 (d, J = 7.6 Hz, 1H, 1-H), 8.51 (d, J = 8.0 Hz, 1H, 3-H), 8.76 (d, J = 7.6 Hz, 1H, 9-H). *Anal*. Calcd for $C_{15}H_7N_3O_3$ (277.24): C, 64.99; H, 2.54; N; 15.16. Found: C, 65.31; H, 2.59; N; 14.89.

Diethyl (5-nitro-6-oxopyrido[3,2,1-*jk*]carbazol-4-yl)malonate (25). To a solution of 4-chloro-5-nitro-pyridocarbazolone **22** (1.79 g, 6 mmol) in DMF (30 mL), anhydrous potassium carbonate (2.00 g, 14 mmol) and diethyl malonate (**2a**) (16.0 g, 100 mmol) were added. The reaction mixture was stirred for 6 h at room temperature, poured onto crushed ice/water (100 mL), and neutralized with concd hydrochloric acid (2 mL) in crushed ice. After standing for 3 h, the solid was filtered by suction and washed with water until acid free. The yield was 1.99 g (79%), pale blue prisms, mp 230°C (ethanol). IR (ATR): 3457 m, 1757 s (ester-CO), 1743 s (ester-CO), 1685 s (6-CO), 1538 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (t, J = 7.1 Hz, 6H, 2 Me), 4.33 (q, J = 7.1 Hz, 4H, 2 CH_2), 4.95 (s, 1H, CH), 7.58 (t, J = 7.5 Hz, 1H, 2-H), 7.60–7.64 (m, 2H, 9-H, 10-H), 8.04 (d, J = 8.1 Hz, 1H, 11-H), 8.09 (d, J = 7.5 Hz, 1H, 1-H), 8.26 (d, J = 7.5 Hz, 1H, 3-H), 8.68 (d, J = 8.0 Hz, 1H, 8-H). MS [APCI, pos]: *m/z* (%) = 423 (85, M + 1), 377 (30), 333 (15), 305 (30), 261 (25), 235 (100). MS [APCI, neg]: *m/z* (%) = 422 (27, M), 421 (100, M − 1). *Anal*. Calcd for $C_{22}H_{18}N_2O_7$ (422.40): C, 62.56; H, 4.30; N, 6.63. Found: C, 62.28; H, 4.44; N, 6.57.

Dimethyl (5-nitro-6-oxopyrido[3,2,1-*jk*]carbazol-4-yl) malonate (26). To a solution of 4-chloro-5-nitro-pyridocarbazolone **22** (1.80 g, 6 mmol) in DMF (30 mL), anhydrous potassium carbonate (2.00 g, 14 mmol) and dimethyl malonate (**2c**) (11.9 g, 90 mmol) were added. The reaction mixture was stirred for 6 h at room temperature and poured onto crushed ice/water (100 mL). The solution was neutralized with concentrated hydrochloric acid (2 mL) in crushed ice. After standing for 3 h, the solid was filtered by suction and washed with water until acid free. The yield was 2.05 g (85%), pale blue prisms, mp 205°C (ethanol/toluene). IR (ATR): 3478 m, 1761 s (ester-CO), 1740 s (ester-CO), 1680 m (6-CO), 1540 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 6H, 2 Me), 4.99 (s, 1H, CH), 7.55 (t, J = 7.5 Hz, 1H, 2-H), 7.60–7.65 (m, 2H, 9-H, 10-H), 8.00 (d, J = 8.1 Hz, 1H, 11-H), 8.07 (d, J = 7.5 Hz, 1H, 1-H), 8.25 (d, J = 7.5 Hz, 1H, 3-H), 8.65 (d, J = 8.1 Hz, 1H, 8-H). *Anal*. Calcd for $C_{20}H_{14}N_2O_7$ (394.34): C, 60.92; H, 3.58; N, 7.10. Found: C, 60.96; H, 3.40; N, 7.13.

Methyl (5-nitro-6-oxopyrido[3,2,1-*jk*]carbazol-4-yl)acetate (27). A solution of dimethyl (5-nitro-pyridocarbazolyl) malonate **26** (1.00 g, 2.5 mmol) in dichlorobenzene (30 mL) was stirred and heated under reflux for 12 h. The reaction mixture was cooled to room temperature, and cyclohexane (50 mL) was added. The precipitated solid was filtered by suction and washed with cyclohexane. The yield was 0.70 g (83%), yellow prisms, mp 210°C (ethanol). IR (ATR): 3459 m, 1734 s (ester-CO), 1686 s (6-CO), 1535 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 3H, Me), 4.02 (s, 2H, CH2), 7.53 (t, J = 7.5 Hz, 1H, 2-H), 7.58–7.66 (m, 2H, 9-H, 10-H), 7.86 (d, J = 8.0 Hz, 1H, 11-H), 8.05 (d, J = 7.5 Hz, 1H, 1-H), 8.23 (d, J = 7.5 Hz, 1H, 3-H), 8.62 (d, J = 8.0 Hz, 1H, 8-H). MS [APCI, pos]: *m/z* (%) = 337 (32, M + 1), 235 (100), 148 (10), 112 (10). MS

[APCI, neg]: *m/z* (%) = 336 (25, M), 335 (100, M − 1), 268 (18), 215 (15). *Anal*. Calcd for $C_{18}H_{12}N_2O_5$ (336.31): C, 64.29; H, 3.60; N, 8.33. Found: C, 64.58; H, 3.71; N, 8.12.

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