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Heterocycles [*h*]-fused onto 4-oxoquinoline-3-carboxylic acid, Part VI [1]. Synthesis and X-ray structure of model indolo[3,2-*b*]- and [2,3-*b*]pyrido[2,3-*f*]-quinoxaline-3-carboxylic esters

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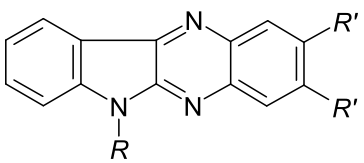
Abstract Cyclocondensation reaction of ethyl 7,8-diamino-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate with 1-methylisatin produced a separable mixture of the corresponding indolo[3,2-*b*]- and [2,3-*b*]pyrido[2,3-*f*]quinoxaline-3-carboxylates, of which the latter isomer predominates. On the other hand, interaction with 1*H*-isatin or 5-chloroisatin gave the respective indolo[2,3-*b*]pyrido[2,3-*f*]quinoxaline-3-carboxylates as the sole regiospecific products. The structures of these new pentacyclic derivatives are based on microanalytical, spectral (IR, MS, and NMR) and X-ray crystal structure data.

Keywords Ethyl 7,8-diamino-4-oxoquinoline-3-carboxylate; Isatins; Cyclocondensation; Regioselectivity; X-Ray crystal data.

Introduction

The parent 6*H*-indolo[2,3-*b*]quinoxaline (**1**/Fig. 1) has been synthesized [2] in 1895 *via* cyclocondensation of isatin with *o*-phenylenediamine. Following this versatile route, several derivatives of **1** have been prepared and intensely studied [3–12]. An alternate synthesis route towards **1** (and derivatives thereof) involves initial interaction between *o*-phenylenediamines and 1-acetyl-2-bromo-3-indolinone [13]. Derivatives of this tetracyclic heteroaromatic system are important *DNA* interchelators [5–7], some of which display antitumor activity [6, 8], while others are useful agents for the treatment of autoimmune disease [9], and multiple sclerosis [10]. Certain derivatives with basic appendages at the N(6)-position, such as **2** (Fig. 1), exhibit potent antiviral activity [11] against *e.g.*, *Herpes simplex* virus type 1 (*HS*V-1), *Cytomegalo* virus (*CM*V), and *Vericella-Zoster* virus (*VZ*V). Compound **2** (referred to as B-220) and its congeners are believed to act *via* inhibition of the decapsidation process of the virus [12].

In the present study, we wish to report on the synthesis of indolo[2,3-*b*]quinoxalines condensed



1 (*R* = *R′* = H)
2 (*R* = $CH_2CH_2NMe_2$; *R′* = *Me*)

Fig. 1 6*H*-Indolo[2,3-*b*]quinoxaline (**1**), and its antiviral derivative **2**

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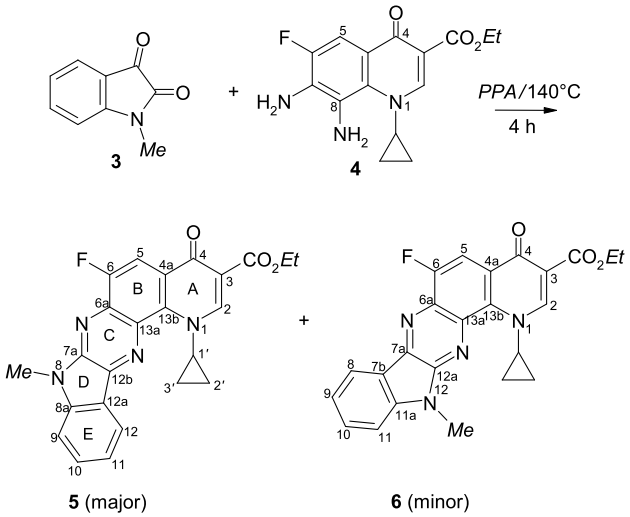
with 4-pyridone-3-carboxylate, exemplified by **5**/**6** and **9**/**10** as depicted in Schemes 1 and 2. These hybrid pentacyclic heterocycles might have potential bioactivity arising from the combination of bioactive entities of which the 4-pyridone moiety (ring A in **5**, **6**, **9**, and **10**) forms an integral part of the fluoroquinolone antibacterial agents, *e.g.*, ciprofloxacine [14].

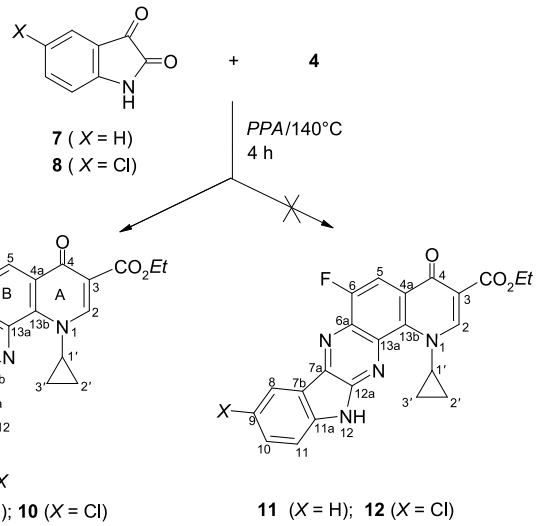
Results and discussion

Synthesis

Herein, the cyclocondensation reaction of ethyl 7,8-diamino-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate (**4**) with 1-methylisatin (**3**), induced by polyphosphoric acid (*PPA*), is investigated. This process involves two consecutive condensations between the *unsym*-diamine **4** and the *unsym*-dione **3**, and is likely to produce two isomeric products (**5**, **6**), depending on which amino group of **4** initiates the reaction *via* nucleophilic addition at the keto group in **3** (Scheme 1). As would be expected, initial addition of the more nucleophilic amino group (residing at C-8) occurs onto the more electrophilic carbon-3 of the keto group with consequent formation of ethyl 1-cyclopropyl-6-fluoro-8-methyl-4-oxo-4,8-dihydro-1*H*-indolo[2,3-*b*]pyrido[2,3-*f*]quinoxaline-3-carboxylate (**5**) as the major regioselective product in 58% yield. Conversely, initiation of the reaction by the less nucleophilic amino group (appended at C-7) takes place to a much lesser extent



Scheme 1

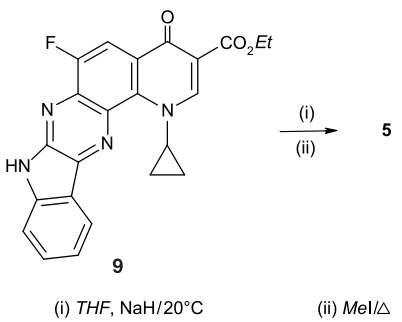


Scheme 2

to form ethyl 1-cyclopropyl-6-fluoro-12-methyl-4-oxo-4,12-dihydro-1*H*-indolo[3,2-*b*]pyrido[2,3-*f*]quinoxaline-3-carboxylate (**6**) in about 2% yield. The isomeric products (**5**, **6**) were seperated from the reaction mixture on preparative silica gel TLC plates.

Under similar reaction conditions, cyclocondensation of **4** with 1*H*-isatins **7** and **8** proceeded in a regiospecific manner and gave the corresponding indolo[2,3-*b*]quinoxaline-3-carboxylates **9** and **10** as the sole products, whilst the respective isomeric indolo[3,2-*b*]quinoxaline-3-carboxylates **11** and **12** were not detected (Scheme 2).

The structure of **9** (and by inference **10**) is unequivocally established *via* methylation of its indolic NH group; the resulting *N*-methylated product was shown to be identical (IR and NMR data) with an authentic sample of **5** (accessible from *N*-methylisatin and **4**/Scheme 1) the structure of which is confirmed by X-ray data (*vide infra*).



Scheme 3

Spectroscopic data

The IR, MS, NMR spectral data and microanalyses for the new compounds **5**, **6**, **9**, and **10** are in accordance with the assigned structures; details are given in the experimental part. Thus, the mass spectra display the correct molecular ion peaks for which the measured high resolution (HRMS) data are in good agreement with the calculated values. DEPT and 2D (COSY, HMQC, HMBC) experiments showed correlations that helped in the ^{1}H- and ^{13}C-signal assignments to the different carbons and the attached/neighboring hydrogens in compounds **5**, **6**, **9**, and **10**. In the ^{13}C-NMR spectrum of **5**, carbon-7a resonates as a doublet centered at 144.5 ppm due to spin–spin coupling with the fluorine atom ($^{4}J_{C-F} = 1.5$ Hz), while the more distant carbon-12b appears as a singlet at $\delta = 137.1$ ppm. Long-range correlations are observed between H-12 and each of C-12b and C-8a, as well as between the N(8)–CH_3 protons and the C-7a doublet. These ^{1}H-^{13}C correlations are compatible with the assigned structure for **5** which is further confirmed by X-ray crystallography (*vide infra*). On the other hand, the HMBC experiment for **6** shows that the N(12)-CH_3 protons are strongly correlated with the C-12a singlet at 143.2 ppm (as well as with the C-11a signal at 145.4 ppm), while the C-7a doublet at 139.5 ($^{4}J_{C-F} = 1.7$ Hz) is correlated with H-8. These three-bond correlations are in conformity with the suggested structure for **6**.

Corresponding long-range correlations are also observed in the HMBC experiments for **9** and **10**. Thus, H-12 is correlated with each of C-8a, C-12b, and C-10, H-10 with C-8a, while H-9 is correlated with C-12a and C-11.

X-Ray structure

An X-ray crystal structure determination was performed to confirm the structure of **5**. A summary of data collection and refinement parameters is given in Table 1. The molecular structure of **5**, based on crystallographic data, is displayed in Fig. 2, while Fig. 3 shows a packing diagram for **5**. The molecule adopts an almost planar configuration with the cyclopropyl ring in a likewise expected conformation. The intermolecular interactions of pairwise grouped molecules around inversion centers in the solid state are dominated by C–H···O weak hydrogen bonds between the *syn*-cyclopropyl H-atoms and the carbonyl groups, with distances of 2.51 and 2.49 Å, respectively for H24A···O1 and H23B···O2, and C–H···O bond angles of 138.3 and 160.6° as displayed in Fig. 4.

Table 1 Summary of the crystal data and structure refinement parameters for **5**

Empirical formula	$C_{24}H_{19}FN_4O_3$
Formula weight	430.43 Da
Temperature/K	203(2)
Wavelength /Å	0.71073
Crystal system	monoclinic
Space group	*I* 2/*a*
Unit cell dimensions	
a/Å	20.4734(12)
b/Å	9.0443(5)
c/Å	21.3106(19)
β/°	99.828(2)
Volume /Å^3	3888.1(5)
Z	8
Calculated density/g cm^{-3}	1.471
Absorption coefficient/mm^{-1}	0.106
F (000)	1792
Theta range for data collection/°	1.94–32.17
Completeness to theta = 32.17°	97.8%
Index range	$-26 \le h \le 30$; $-13 \le k \le 12$; $-31 \le l \le 25$
Reflections collected	45127
Independent reflections	6709 ($R_{int} = 0.0295$)
Weight scheme	calcd $w = 1/[\sigma^2 (F_0)^2 + (0.0707P)^2 + 1.1917P]$ where $P = [(F_0)^2 + 2(F_c)^2]/3$
Data/restraints/parameters	5145/0/290
Goodness-of-fit on F^2	1.042
Final *R* indices [$I > 2\sigma$ (*I*)]	$R_1 = 0.0465$, $wR_2 = 0.1211$
R indices (all data)	$R_1 = 0.0641$, $wR_2 = 0.1324$
Largest difference peak/e · Å^{-3}	0.386
Largest difference hole/e · Å^{-3}	−0.276

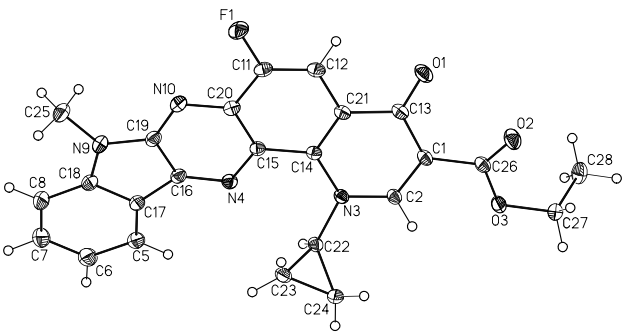


Fig. 2 An ORTEP plot of the molecular structure of **5** showing the arbitrary crystallographic numbering scheme, being different from the IUPAC numbering adopted in Scheme 2. Displacement ellipsoids are drawn at the 50% probability level, while H atoms are shown as spheres of arbitrary radii

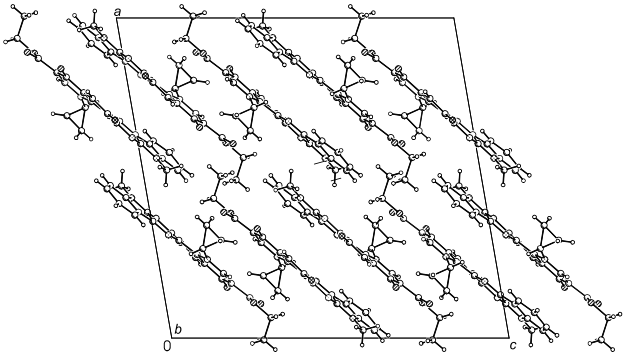


Fig. 3 Packing diagram for **5** in the unit cell ($z = 8$)/viewed along the *c*-axis

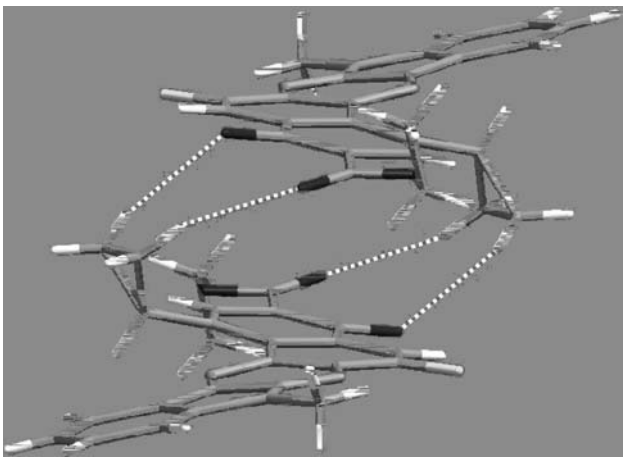


Fig. 4 Centrosymmetric pairwise arranged molecules for **5** in the crystal, linked *via* C–H···O bonds

In conclusion, *PPA*-catalyzed cyclocondensation reaction of isatins with ethyl 7,8-diamino-1-cyclopropyl-6-fluoro-4-oxoquinoline-3-carboxylate proceeds in high degree of regioselectivity such that the respective indolo[2,3-*b*]pyrido[2,3-*f*]quinoxalines (**5**, **9**, and **10**/Schemes 1 and 2) are formed as the main products. The structures of these novel pentacyclic heterocycles are evidenced from their spectral data and confirmed by X-ray crystal structure determination for the N(6)-methylated derivative **5** (Fig. 2).

Experimental

2,4-Dichloro-5-fluoro-3-nitrobenzoic acid, ethyl 3-(dimethylamino)acrylate, cyclopropylamine, isatin, 5-chloroisatin, and 1-methylisatin were purchased from Acros. Melting points were determined on a Gallenkamp electrothermal melting-temperature apparatus. IR spectra were recorded as KBr discs on a Nicolet Impact-400 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-300 instrument. Chemical shifts are expressed in ppm with reference to *TMS* as internal standard. High resolution mass spectra (HRMS) were measured in positive ion mode by electrospray (ESI) on an APEX-Qe 94 instrument. The samples were dissolved in acetonitrile, diluted in spray solution (methanol/water, 1/1, $v/v + 0.1\%$ formic acid) and infused using a syringe pump with a flow of 2 mm^3/min. External calibration was conducted using arginine cluster in a mass range $m/z = 175$–871. Elemental analyses (C, H, N, Cl) were preformed at the Microanalytical Laboratory of the Hashemite University, Zarqa-Jordan, and the results were found to be in good agreement ($\pm 0.4\%$) with the calculated values. Ethyl 7,8-diamino-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate (**4**) was prepared by reduction of ethyl 7-azido-1-cyclopropyl-6-fluoro-8-nitro-4-oxo-1,4-dihydroquinoline-3-carboxylate [15] using $SnCl_2$ and conc HCl at room temp according to a literature procedure [1].

Ethyl 1-cyclopropyl-6-fluoro-8-methyl-4-oxo-4,8-dihydro-1H-indolo[2,3-b]pyrido[2,3-f] quinoxaline-3-carboxylate (**5**, $C_{24}H_{19}FN_4O_3$)

A stirred suspension of 0.61 g **4** (2 mmol) and 0.32 g 1-methylisatin (**3**) (2 mmol) in 30 g polyphosphoric acid (*PPA*) was heated at 140°C for 4 h. After cooling to room temp, the reaction mixture was poured with stirring onto crushed ice and extracted with 3×30 cm^3 CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure, and the resulting two isomeric yellow products (**5** + **6**) were separated on silica gel TLC plates using *Ac*O*Et*/$CHCl_3$ (1/4, *v*/*v*) as the developing solvent mixture, and recrystallized from chloroform/isopropyl ether. Yield of **5**: 0.5 g (58%); mp > 300°C (darkens at 240°C). IR: $\bar{\nu} = 3068$, 2978, 2925, 2849, 1724, 1644, 1610, 1580, 1524, 1468, 1395, 1301, 1263, 1197, 1120, 1087, 1033 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$, 1.29 (2m, H$_2$-2′ + H$_2$-3′), 1.44 (t, J = 7.1 Hz, C*H*$_3$CH$_2$O–), 3.97 (s, N(8)–CH$_3$), 4.43 (q, J = 7.1 Hz, –OC*H*$_2$CH$_3$), 4.84 (m, H-1′), 7.41 (dd, $J = 7.5$, 7.6 Hz, H-11), 7.50 (d, $J = 8$ Hz, H-9), 7.74 (dd, $J = 7.5$, 8 Hz, H-10), 8.23 (d, $J = 7.6$ Hz, H-12), 8.37 (d, $^3J_{H-F}$ = 10.8 Hz, H-5), 8.78 (s, H-2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.2$ (C-2′ + C-3′), 14.5 (*C*H$_3$CH$_2$O–), 27.8 (N(8)–CH$_3$), 42.9 (C-1′), 61.1 (–O*C*H$_2$*Me*), 109.1 (d, $^2J_{C-F}$ = 21.3 Hz, C-5), 110.0 (C-9), 112.1 (C-3), 119.1 (C-12a), 121.9 (C-11), 122.2 (C-12), 126.5 (d, $^3J_{C-F} = 7.1$ Hz, C-4a), 131.8 (C-10), 132.1 (d, $^3J_{C-F} = 1.7$ Hz, C-13a), 134.3 (d, $^2J_{C-F}$ = 14 Hz, C-6a), 135.5 (d, $^4J_{C-F} = 2.3$ Hz, C-13b), 137.1 (C-12b), 144.5 (d, $^4J_{C-F} = 1.5$ Hz, C-7a), 145.1 (C-8a), 150.1 (C-2), 154.4 (d, $^1J_{C-F} = 255$ Hz, C-6), 165.6 (*C*O$_2$*Et*), 172.7 (d, $^4J_{C-F} = 2$ Hz, C-4) ppm; HRMS(ESI): m/z calcd. for $C_{24}H_{20}FN_4O_3^+$ $[M + H]^+$ 431.15194, found 431.15152.

Ethyl 1-cyclopropyl-6-fluoro-12-methyl-4-oxo-4,12-dihydro-1H-indolo[3,2-b]pyrido [2,3-f]quinoxaline-3-carboxylate (**6**, $C_{24}H_{19}FN_4O_3$)

This compound is obtained as a minor product in the preparation of **5** (*vide supra*). Yield: 0.02 g (2.4%); mp > 300°C. IR: $\bar{\nu} = 3081$, 3007, 2980, 2910, 2882, 1723, 1617, 1585, 1530, 1466, 1395, 1297, 1255, 1166, 1124, 1082 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.98$, 1.27 (2m, H$_2$-2′ + H$_2$-3′), 1.44

(t, $J = 7.1$ Hz, C*H*$_3$CH$_2$O–), 3.96 (s, N(12)–CH$_3$), 4.44 (q, $J = 7.1$ Hz, –OC*H*$_2$CH$_3$), 4.93 (m, H-1′), 7.45 (dd, $J = 7.7$, 7.8 Hz, H-9), 7.52 (d, $J = 8$ Hz, H-11), 7.78 (dd, $J = 7.7$, 8 Hz, H-10), 8.33 (d, $^3J_{H-F} = 10.8$ Hz, H-5), 8.55 (d, $J =$ 7.8 Hz, H-8), 8.85 (s, H-2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.4$ (C-2′ + C-3′), 14.5 (*C*H$_3$CH$_2$O–), 29.8 (N(12)–CH$_3$), 42.6 (C-1′), 61.2 (–OC*H*$_2$*Me*), 106.4 (d, $^2J_{C-F} = 21.8$ Hz, C-5), 109.6 (C-11), 112.0 (C-3), 118.8 (C-7b), 121.9 (C-9), 123.6 (C-8), 129.1 (d, $^3J_{C-F} = 7.6$ Hz, C-4a), 132.3 (C-10), 134.2 (d, $^2J_{C-F} = 12.4$ Hz, C-6a), 134.3 (d, $^4J_{C-F} = 1.8$ Hz, C-13b), 137.3(C-13a),139.5 (d, $^4J_{C-F} = 1.7$ Hz, C-7a), 143.2 (C-12a), 145.4 (C-11a), 150.1 (C-2), 155.4 (d, $^1J_{C-F} = 256$ Hz, C-6), 165.7 (*C*O$_2$*Et*), 172.8 (d, $^4J_{C-F} = 2.2$ Hz, C-4) ppm; HRMS (ESI): m/z calcd. for $C_{24}H_{20}FN_4O_3^+$ $[M+H]^+$ 431.15194, found 431.15128.

Ethyl 1-cyclopropyl-6-fluoro-4-oxo-4,8-dihydro-1H-indolo-[2,3-b]pyrido[2,3-f]quinoxaline-3-carboxylate
(**9**, $C_{23}H_{17}FN_4O_3$)
A stirred suspension of 0.61 g **4** (2 mmol) and 0.30 g isatin (**7**) (2 mmol) in 30 g *PPA* was heated at 140°C for 4 h. After cooling to room temp, the reaction mixture was poured with stirring onto crushed ice, the resulting brown precipitate was collected, triturated with methanol, and recrystallized from methanol/chloroform. Yield: 0.5 g (58%); mp > 300°C. IR: $\bar{\nu} = 3415$, 3235, 2926, 2860, 1727, 1691, 1617, 1528, 1467, 1394, 1325, 1299, 1116 cm^{-1}; ^{1}H NMR (300 MHz, *DMSO*-d$_6$): $\delta = 0.94$, 1.25 (2m, H$_2$-2′ + H$_2$-3′), 1.29 (t, $J = 7.1$ Hz, C*H*$_3$CH$_2$–), 4.25 (q, $J = 7.1$ Hz, –C*H*$_2$CH$_3$), 4.91 (m, H-1′), 7.41 (dd, $J = 7.5$, 7.7 Hz, H-11), 7.63 (d, $J = 7.9$ Hz, H-9), 7.75 (dd, $J = 7.5$, 7.9 Hz, H-10), 8.12 (d, $^3J_{H-F} = 10.9$ Hz, H-5), 8.43 (d, $J =$ 7.7 Hz, H-12), 8.73 (s, H-2), 12.54 (s, N–H) ppm; ^{13}C NMR (75 MHz, *DMSO*-d$_6$): $\delta = 11.3$ (C-2′ + C-3′), 14.8 (–*C*H$_3$CH$_2$), 43.5 (C-1′), 60.5 (–*C*H$_2$*Me*), 108.0 (d, $^2J_{C-F} = 20.7$ Hz, C-5), 112.0 (C-3), 113.0 (C-9), 119.5 (C-12a), 122.0 (C-11), 123.2 (C-12), 125.7 (d, $^3J_{C-F} = 6.5$ Hz, C-4a), 132.4 (C-10), 132.7 (d, $^4J_{C-F} = 1.8$ Hz, C-13a), 134.2 (d, $^2J_{C-F} = 14.2$ Hz, C-6a), 136.2 (d, $^4J_{C-F} = 2.5$ Hz, C-13b), 137.8 (C-12b), 144.7 (C-8a), 145.4 (C-7a), 150.4 (C-2), 154.2 (d, $^1J_{C-F} = 252$ Hz, C-6), 164.8 (*C*O$_2$*Et*), 171.8 (d, $^4J_{C-F} = 2.2$ Hz, C-4) ppm; HRMS (ESI): m/z calcd. for $C_{23}H_{18}FN_4O_3^+$ $[M+H]^+$ 417.13629, found 417.13571; m/z calcd. for $C_{23}H_{17}FN_4O_3Na^+$ $[M+Na]^+$ 439.11824, found 439.11761.

Ethyl 11-chloro-1-cyclopropyl-6-fluoro-4-oxo-4,8-dihydro-1H-indolo[2,3-b]pyrido [2,3-f]quinoxaline-3-carboxylate
(**10**, $C_{23}H_{16}ClFN_4O_3$)
This compound was prepared from 0.61 g **4** (2 mmol) and 0.36 g 5-chloroisatin (**8**) (2 mmol) by following the procedure and experimental conditions described above for **9**. Yield: 0.48 g (53%); mp > 300°C (darkens at 280°C). IR: $\bar{\nu} = 3300$, 3183, 3101, 2976, 1724, 1684, 1612, 1524, 1467, 1429, 1376, 1329, 1273, 1251, 1181, 1083 cm^{-1}; ^{1}H NMR (300 MHz, *DMF*-d$_7$): $\delta = 1.08$, 1.40 (2m, H$_2$-2′ + H$_2$-3′), 1.35 (t, $J =$ 7.1 Hz, C*H*$_3$CH$_2$–), 4.33 (q, $J = 7.1$ Hz, –C*H*$_2$CH$_3$), 5.15 (m, H-1′), 7.78 (dd, $J = 8.7$, 0.8 Hz, H-9), 7.82 (dd, $J = 8.7$, 1.9 Hz, H-10), 8.26 (d, $^3J_{H-F} = 11.0$ Hz, H-5), 8.62 (dd, $J =$ 1.9, 0.8 Hz, H-12), 8.87 (s, H-2), 12.61 (br s, N–H) ppm; ^{13}C NMR (75 MHz, *DMF*-d$_7$): $\delta = 10.9$ (C-2′ + C-3′), 14.2 (–*C*H$_3$CH$_2$), 43.3 (C-1′), 60.4 (–*C*H$_2$*Me*), 108.3 (d, $^2J_{C-F} =$ 21.0 Hz, C-5), 112.9 (C-3), 114.5 (C-9), 121.2 (C-12a), 122.5 (C-12), 126.2 (d, $^3J_{C-F} = 6.5$ Hz, C-4a), 126.8 (C-11), 132.0 (d, $^3J_{C-F} = 1.6$, C-13a), 131.9 (C-10), 134.7 (d, $^2J_{C-F} =$ 15.2 Hz, C-6a), 136.5 (C-13b), 136.9 (C-12b), 143.4 (C-8a), 145.8 (C-7a), 150.3 (C-2), 154.4 (d, $^1J_{C-F} = 253$ Hz, C-6), 164.7 (*C*O$_2$*Et*), 171.9 (d, $^4J_{C-F} = 2.0$ Hz, C-4) ppm; HRMS (ESI): m/z calcd. for $C_{22}H_{17}ClFN_4O_3^+$ $[M+H]^+$ 451.09732, found 451.09685.

*Transformation of **9** into **5***
Sodium hydride 0.12 g (60% dispersion in mineral oil, 3 mmol) was added portionwise to a stirred solution of 0.83 g **9** (2 mmol) in 10 cm^3 dry *DMF* at room temp. To this resulting orange-colored solution was added 0.85 g iodomethane (6 mmol); the reaction mixture, which quickly acquired yellow coloration, was stirred for additional 15–20 min, and finally diluted with 70 cm^3 cold water. The precipitated yellow solid was collected under suction, washed with 2×10 cm^3 water, air-dried, and recrystallized from CH_2Cl_2/*n*-hexane. The IR and NMR spectral data of this product were found to be identical with those of **5** given above. Yield: 0.55 g (64%); mp > 300°C (darkens at 240°C).

*Collection of X-ray diffraction data and structure analysis of **5***
Yellow block crystals were grown by allowing a clear solution of **5** in $CHCl_3$ in an open vessel to stand at room temp for 3–4 days. Crystal data collection was made with a Siemens SMART CCD diffractometer (Mo-Kα-radiation, graphite monochromator) operating in the omega scan mode (0.3°). The data were reduced with the Siemens-Bruker program suite XSCANS [16] and the structure was solved by the direct method using SHELXTL PLUS programs [17]. All non-hydrogen atoms were refined anisotropically by full-matrix, least squares procedure based on F_2 using all unique data. Hydrogen atoms were placed in calculated positions and treated as riding groups, with the 1.2 fold (1.5 fold for methyl groups) isotropic displacement parameters of the equivalent U_{ij} of the corresponding carbon atom.

Crystallographic data for the structural analysis of **5** have been deposited with the Cambridge Crystallographic Data Center under the depository No. CSD 671311. Copies of information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: (deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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