Fluorine-containing quinoline and quinoxaline styryl derivatives: synthesis and photophysical properties

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(*E*)-2-Styryl-substituted 6,7-difluoroquinolines and quinoxalines were synthesized by the condensation of the corresponding 2-methylbenzazines with aromatic aldehydes. Photoluminescence of the synthesized 6,7-difluoro-2-styrylbenzazines was studied.

Key words: styrylbenzazines, photoluminescence, 6,7-difluoroquinaldine, 6,7-difluoroquinoline-4-carboxylic acid.

Fluorescent styryl dyes and metallochelates are important electroluminescent organic materials.[1] The luminophore structure includes π-deficient heterocyclic fragments (quinoline, quinoxaline, and others), which opens prospects for the construction of materials of the electron-transporting layer.[2] Tris(8-hydroxyquinolinato)aluminum is an excellent electroluminescent and electron-transporting material.[3]

Interest in zinc complexes of 2-styryl-8-hydroxyquinoline has increased in the recent time, since they are recommended themselves as materials for monolayer organic light-emitting diodes.[4] The study of a correlation between the solvent polarity and the maximum of emission of 4-dimethylamino-2-(*E*)-styryl-(6-chloroquinoline) made it possible to recommend it as a biosensor.[5] Search for photoluminescent materials in the series of styrylbenzazines is topical, which is indicated by the study of the photophysical characteristics of 2-styryl derivatives of 3*H*-quinazolin-4-ones.[6] Since fluorinated poly(*p*-phenylenevinylene) exceeds polyphenylvinylene in electron conductivity,[7,8] the study of the photophysical characteristics of fluorine-containing styrylbenzazines seems promising.

We chose fluorine-containing styryl derivatives of such π-deficient heterocycles as quinoline and quinoxaline as objects of investigation, because the non-fluorinated analogs demonstrated considerable luminescence properties and the introduction of fluorine atoms can enhance the solubility in organic solvents, which is important for the production of electronic devices.

Several publications[9—11] are devoted to the search for optimal conditions of quinaldine condensation with aromatic aldehydes. Only one fluorine-containing styrylquinoline derivative, *viz.*, 3-[2-(6,7-difluoroquinolin-2-yl)-vinyl]benzaldehyde, was described as an intermediate for the preparation of leukotriene antagonist LTD_4.[12] The condensation of 6,7-difluoroquinaldine **2b** with benzaldehyde, *p*-nitrobenzaldehyde, and *p*-methoxybenzaldehyde on heating in glacial acetic acid in the presence of sodium acetate for 12 h afforded new (*E*)-2-(arylvinyl)-6,7-difluoroquinolines **3a—c** (Scheme 1). The ^{1}H NMR spectra of quinolines **3** are characterized by doublets of the fragment CH=CH in regions of 7.22—7.63 and 7.73—7.90 ppm with the spin-spin coupling constant (SSCC) 16.2—16.6 Hz, which indicates its (*E*)-configuration along with signals of protons of the difluoroquinoline fragment and aryl residue.

Polymer materials with the nonlinear optical properties were obtained from the 2-styryl derivatives of quinoline-4-carboxylic acid.[13] The fluorescence properties of push—pool systems based on 4-trifluoromethylquinoline were described.[14] The photoluminescence spectra of 2-styrylquinoline-4-carboxylic acids were not studied, and data on syntheses of the fluorinated analogs are lacking in the literature. In order to obtain 6,7-difluorine analogs of 2-styrylquinazolinones, we developed the synthetic approach to 6,7-difluoro-2-styrylquinolines **6a—c** (Scheme 2). The Pfitzinger reaction of isatin **4** with acetone in the presence of potassium hydroxide affords 6,7-difluoro-2-methylquinoline-4-carboxylic acid **5**, and the reaction conditions are analogous to those described for the non-fluorinated analog.[15] The condensation of **5** with aromatic aldehydes in acetic acid in the presence of sodium acetate on reflux for 7—12 h resulted in the formation of styryl

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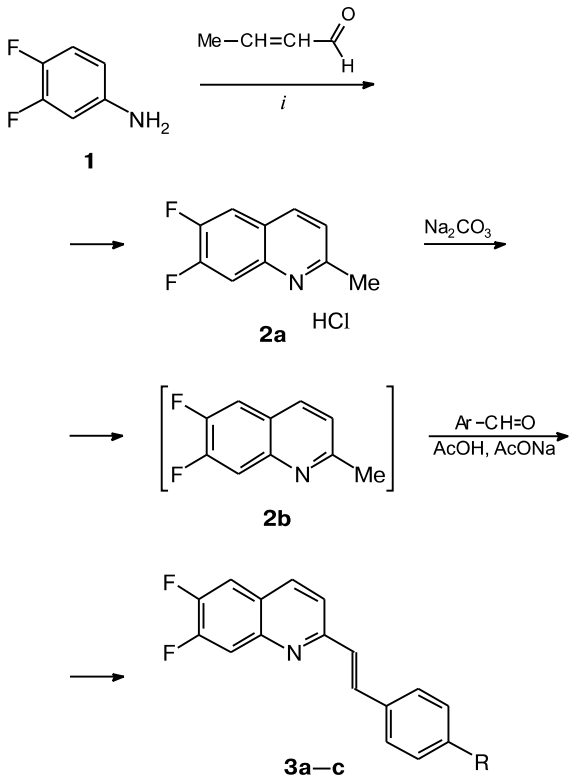
Scheme 1



i. Chloranil, butanol.

3: R = H (**a**), NO_2 (**b**), OMe (**c**)

derivatives **6a—c**; the reaction duration is maximum for the formation of methoxy derivative **6c** because of the lower reactivity of 4-methoxybenzaldehyde in the condensation reactions. The characteristic doublets of protons of the CH=CH fragment with the coupling constants ^3J = 16.2—16.3 Hz appear in the ^{1}H NMR spectrum at 7.30—7.71 and 7.79—7.96 ppm.

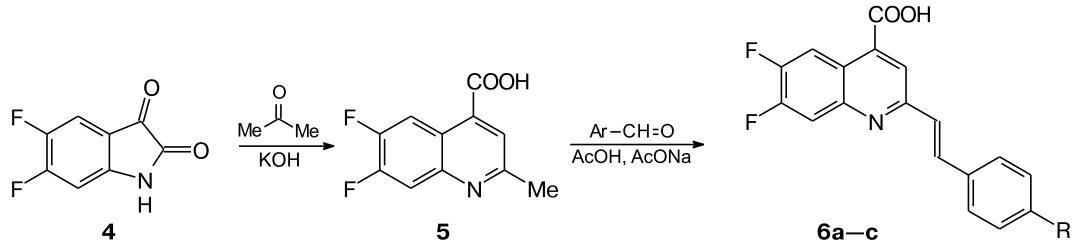
6,7-Difluoro-2-styrylquinoxalines **8** are other analogs of 6,7-difluoro-2-styrylquinolines containing the electron-withdrawing group in position 4. The synthesis of compounds **8** from 4,5-difluoro-*o*-phenylenediamine and isonitrosoacetone was described,[16] and we proposed to use pyruvic aldehyde for cyclocondensation. The synthesis of non-fluorinated analog **9c** and the photophysical behavior of (*E*)-2-styrylquinoxaline conformers were described.[17,18] The condensation of methylquinoxaline **8** with aromatic aldehydes on reflux in glacial MeCOOH in the presence of sodium acetate for 6—12 h gave new (*E*)-2-(arylvinyl)-6,7-difluoroquinoxalines **9a—c** (Scheme 3). The ^{1}H NMR spectra of quinoxalines **9** are characterized by doublets of the fragment CH=CH in regions of 7.31—7.76 and 7.92—8.10 ppm with the ^3J = 16.3—16.6 Hz along with signals of protons of the difluoroquinoxaline fragment and the aryl residue.

2-Thienylvinyl derivatives of 8-acetoxyquinoline were described as promising materials for π-conjugated oligomers applied in organic light-emitting diodes, being donor-acceptor conjugated systems suitable for film preparation.[19] The synthesis of 2-(2-thienyl)vinyl derivatives **10a—c** was achieved by reflux of **2b**, **5**, and **8** with thiophene-2-carbaldehyde and sodium acetate in acetic acid for 12—36 h in 26—55% yields (Scheme 4). Structures **10a—c** were confirmed by the ^{1}H NMR and mass spectral data.

2-Styryl derivatives **3—10** are characterized by the long-wavelength absorption band at 348—376 nm in the electronic spectra (Table 1). The introduction of a strong electron-withdrawing (R = NO_2) or electron-releasing group (R = OMe) into the *p*-position of the aryl fragment results in the bathochromic shift of the long-wavelength absorption band by 8—11 nm.

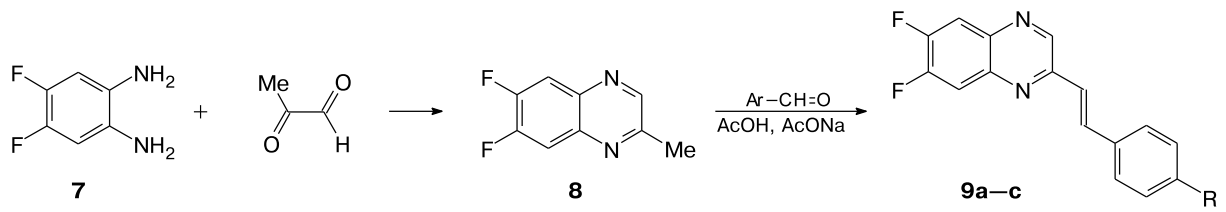
The synthesized styrylquinolines and styrylquinoxalines exhibit photoluminescence in an acetonitrile solution with the emission maximum at 399—569 nm (see Table 1). The elongation of the conjugation chain due to the variation of substituent R shifts the emission band to a longer-wavelength region and results in the transition from blue to green or yellow-orange fluorescence regardless of the electronic character of the introduced group. However, the value of shift for the nitrophenyl derivatives (**3b**, **6b**, **9b**) is higher than that for the methoxy derivatives (**3c**, **6c**, **9c**). The nitro derivative of the quinoxaline series **9b** has the maximum Stokes shift (200 nm, see Table 1).

Scheme 2



6: R = H (**a**), NO_2 (**b**), OMe (**c**)

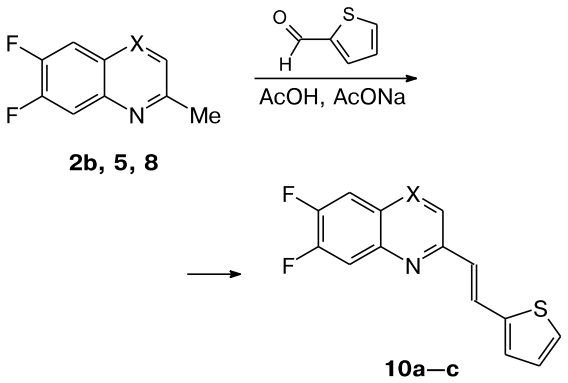
Scheme 3



7 **8** **9a—c**

9: R = H (**a**), NO_2 (**b**), OMe (**c**)

Scheme 4



2b, 5, 8 **10a—c**

10: X = CH (**a**), C—COOH (**b**), N (**c**)

At the same time, the photoluminescence intensity of the methoxy derivatives is considerably higher than that of the phenyl and nitrophenyl derivatives, the highest value of quantum yield was obtained for compound **9c** (0.186, see Table 1). The replacement of the phenyl fragment by thiophene (compounds **10a—c**) results in the red shift in the emission spectra with a decrease in the fluorescence intensity.

The quantum yields of compounds **3—10** (Table 1) lie in the same ranges as those for similar in structure 3-styryl derivatives of quinoxanin-2-ones (0.04—0.09, and a high value of 0.18—0.20 was obtained only for the compound containing the dimethylamino group).[20] As a whole, rather low luminescence intensity of the styryl derivatives of heterocycles in solutions is related to the occurrence of (*E*)-(*Z*)-isomerization.[21,22] In films or in the solid state the quantum yield can increase by several orders of magnitude.

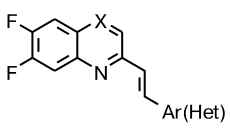
The results of this study suggests that the properties can be tuned by the variation of the styryldiazine structure. Styrylquinolines and styrylquinoxalines containing the nitro or methoxy group in the styryl fragment are promising for the further deepened study of the photophysical properties in various aggregation states.

Experimental

^{1}H NMR spectra in DMSO-d_6 were recorded on a Bruker DRX-400 spectrometer with a working frequency of 400.13 MHz, and chemical shifts were measured relative to $SiMe_4$.

Mass spectra were recorded on a MicrOTOF-Q II mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an electrospray ionization source, a six-port valve, and a kd

Table 1. Data on the absorption and photoluminescence spectra of styrylbenzazines **3**, **6**, **9**, and **10**



3, **6**, **9**, **10**

Compound	X	Ar (Het)	λ^{abs}	λ^{fl}_{max}*	Stokes shift/nm	Quantum yield
			nm			
3a	CH	Ph	348, 335	399	51	0.0100
3b	CH	4-$NO_2C_6H_4$	356	483	127	0.0003
3c	CH	4-$OMeC_6H_4$	356	451	95	0.0240
6a	C—COOH	Ph	352, 340	430	78	0.0590
6b	C—COOH	4-$NO_2C_6H_4$	359	495	136	0.0002
6c	C—COOH	4-$OMeC_6H_4$	360	484	124	0.0860
9a	N	Ph	365, 353	425	60	0.0500
9b	N	4-$NO_2C_6H_4$	369	569	200	0.0002
9c	N	4-$OMeC_6H_4$	376	493	117	0.1860
10a	CH	2-thienyl	360	439	79	0.0040
10b	C—COOH	2-thienyl	363	476	113	0.0180
10c	N	2-thienyl	378	479	101	0.0160

* Excitation in the region of the long-wavelength absorption band.

Scientific device of direct injection (flow rate 180 μL h^{-1}). The mass spectrometer was controlled by the micrOTOFcontrol 2.3 patch 1 and HyStar 3.2 program software (Bruker Daltonics). The nominal resolution of the instrument was 17 500. The mass spectrometer worked in the positive ionization mode in the mass range m/z = 50—800 Da. The voltage on the capillary of the ionization source was 4500 V, and the voltage potential at the outlet from the glass capillary was 166 V. The pressure of the spraying gas was 0.8 bar, and the flow rate of the drying gas was 4 L min^{-1}. The temperature of the gas heater was 250 °C. The averaging was 3, and the value of summation was 5000, which corresponds to one spectrum per 1 s. The time of ion transit was 70 μs, and the radio frequency of the hexafield was 100 Vpp. The external calibration of the instrument was carried out by six points before each detection. The peaks of lithium formate clusters were used as reference points upon the introduction into the instrument of a LiOH solution (10 mmol L^{-1}) in a propan-2-ol—0.2% aqueous solution of formic acid (1 : 1 vol/vol) mixture.

Absorption spectra were recorded using a Shimadzu UV-2401PC spectrophotometer (Japan) in an acetonitrile solution. Luminescence spectra were measured on a Cary Eclipse spectrofluorimeter (Varian, USA) in an acetonitrile solution with a concentration of ~$5 \cdot 10^{-6}$ mol L^{-1}. The relative quantum yield was determined by a known procedure[23] using quinine bisulfate as a standard (φ = 0.546). Melting points were determined on a Stuart SMP3 instrument. The reaction course was monitored using thin layer chromatography on silica gel.

6,7-Difluoro-2-methylquinoline (**2a**), difluoroisatin **4**, and diamine **7** were synthesized by known procedures (see Refs 12, 24, and 25).

(*E*)-6,7-Difluoro-2-[2-(4-nitrophenyl)vinyl]quinoline (3b). A 2 *M* solution of Na_2CO_3 (10 mL) was added to a suspension of 6,7-difluoro-2-methylquinoline hydrochloride **2a** (0.3 g, 2.1 mmol) in water (10 mL), the mixture was stirred for 5 min, and the colorless precipitate of base **2b** that formed was filtered off and dried. Then methylquinoxaline **2b** was dissolved in glacial acetic acid (20 mL), sodium acetate (0.1 g) and *p*-nitrobenzaldehyde (0.5 g, 3.3 mmol) were added, and the reaction mixture was refluxed for 12 h. After cooling the solution was concentrated by evaporation to dryness and washed with water and then with ethanol. The yield was 0.4 g (45%), m.p. 200—202 °C. ^{1}H NMR (DMSO-d_6), δ: 7.63 (d, 1 H, CH=, ^3J = 16.2 Hz); 7.82 (dd, 1 H, H(5) or H(8), ^3J = 11.6 Hz, ^4J = 7.9 Hz); 7.85 (d, 1 H, H(3), ^3J = 8.5 Hz); 7.89 (dd, 1 H, H(8) or H(5), ^3J = 11.4 Hz, ^4J = 9.3 Hz); 7.90 (d, 1 H, CH=, ^3J = 16.2 Hz); 7.94 and 8.25 (both d, 2 H each, H(2′), H(3′), H(5′), H(6′), ^3J = 8.6 Hz); 8.34 (d, 1 H, H(4), ^3J = 8.5 Hz). MS, m/z (I_{rel} (%)): 313 $[M + H]^+$ (100%). Found (%): C, 65.35; H, 3.19; N, 9.02. $C_{17}H_{10}F_2N_2O_2$. Calculated (%): C, 65.39; H, 3.23; N, 8.97.

Compounds **3a,c** were synthesized similarly. To isolate compound **3c**, after the reaction mixture was evaporated, water (10 mL) was added to the residue, the product was extracted with methylene chloride, and the precipitate formed after the partial evaporation of the extragent was filtered off and washed with hexane.

(*E*)-6,7-Difluoro-2-styrylquinoline (3a). The yield was 0.2 g (36%), m.p. 140—142 °C. ^{1}H (DMSO-d_6), δ: 7.32 (m, 1 H, Ph); 7.37 (d, 1 H, CH=, ^3J = 16.6 Hz); 7.40 (m, 2 H, Ph); 7.67 (m, 2 H, Ph); 7.77 (d, 1 H, H(3), ^3J = 8.6 Hz); 7.78 (d, 1 H, CH=, ^3J = 16.6 Hz); 7.83 and 7.86 (both m, 2 H each, H(5), H(8)); 8.28 (d, 1 H, H(4), ^3J = 8.6 Hz). MS, m/z (I_{rel} (%)): 268 $[M + H]^+$ (100%). Found (%): C, 76.35; H, 4.11; N, 5.26. $C_{17}H_{11}F_2N$. Calculated (%): C, 76.40; H, 4.15; N, 5.24.

(*E*)-6,7-Difluoro-2-[2-(4-methoxyphenyl)vinyl]quinoline (3c). The yield was 31%, m.p. 160—162 °C. ^{1}H NMR (DMSO-d_6), δ: 3.83 (s, 3 H, OCH_3); 6.94 (d, 2 H, H(3′), H(5′), ^3J = 8.7 Hz); 7.22 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.61 (d, 2 H, H(2′), H(6′), ^3J = 8.7 Hz); 7.73 (d, 1 H, CH=, ^3J = 16.2 Hz); 7.74 (d, 1 H, H(3), ^3J = 8.6 Hz); 7.77 (dd, 1 H, H(5) or H(8), ^3J = 11.7 Hz, ^4J = 7.9 Hz); 7.83 (dd, 1 H, H(8) or H(5), ^3J = 10.7 Hz, ^4J = 8.9 Hz); 8.24 (d, 1 H, H(4), ^3J = 8.6 Hz). MS, m/z (I_{rel} (%)): 298 $[M + H]^+$ (100%). Found (%): C, 72.69; H, 4.38; N, 4.75. $C_{18}H_{13}F_2NO$. Calculated (%): C, 72.72; H, 4.41; N, 4.71.

6,7-Difluoro-2-methylquinoline-4-carboxylic acid (5). A solution of potassium hydroxide (5.5 g, 98 mmol) in water (11 mL) was added to difluoroisatin **4** (2.25 g, 12.3 mmol). The mixture was stirred for 5 min at 25 °C, after which the mixture turned green and became viscous. Acetone (18 mL, 24.5 mmol) was added to the contents of the flask, and the flask was heated for 6 h at 90 °C. After the reaction mixture was cooled down, neutralization was carried out to pH 5—6 by the addition of 10% hydrochloric acid, and the precipitate that formed was filtered off. The yield was 2.3 g (79%), m.p. 228—230 °C. ^{1}H NMR (DMSO-d_6), δ: 2.72 (s, 3 H, CH_3); 7.82 (dd, 1 H, H(8) or H(5), ^3J = 11.4 Hz, ^4J = 8.1 Hz); 7.90 (s, 1 H, H(3)); 8.71 (dd, 1 H, H(5) or H(8), ^3J = 12.8 Hz, ^4J = 9.1 Hz); 13.7 (br.s, 1 H, COOH). MS, m/z (I_{rel} (%)): 224 $[M + H]^+$ (100%). Found (%): C, 59.24; H, 3.19; N, 6.24. $C_{11}H_7F_2NO_2$. Calculated (%): C, 59.20; H, 3.16; N, 6.28.

(*E*)-6,7-Difluoro-2-styrylquinoline-4-carboxylic acid (6a). Anhydrous sodium acetate (0.1 g) and benzaldehyde (0.4 mL, 3.8 mmol) were added to a solution of quinolinecarboxylic acid **5** (0.2 g, 0.89 mmol) in glacial acetic acid (5 mL). The reaction mixture was refluxed for 7 h, and the precipitate that formed after cooling was filtered off and washed with ethanol. The yield was 0.2 g (72%), m.p. 268—270 °C. ^{1}H NMR (DMSO-d_6), δ: 7.33 (m, 1 H, Ph); 7.41 (m, 2 H, Ph); 7.43 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.68 (m, 2 H, Ph); 7.83 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.88 (dd, 1 H, H(8) or H(5), ^3J = 11.3 Hz, ^4J = 8.1 Hz); 8.28 (s, 1 H, H(3)); 8.72 (dd, 1 H, H(5) or H(8), ^3J = 12.8 Hz, ^4J = = 9.1 Hz); 13.0—14.0 (br.s, 1 H, COOH). MS, m/z (I_{rel} (%)): 312 $[M + H]^+$ (100%). Found (%): C, 69.50; H, 3.61; N, 4.46. $C_{18}H_{11}F_2NO_2$. Calculated (%): C, 69.45; H, 3.56; N, 4.50.

Quinoline derivatives **6b,c** were synthesized similarly. For the synthesis of **6c**, the duration of the reaction was elongated to 12 h and recrystallization from ethanol was used.

(*E*)-6,7-Difluoro-2-[2-(4-nitrophenyl)vinyl]quinoline-4-carboxylic acid (6b). The yield was 78%, m.p. 276—278 °C. ^{1}H NMR, δ: 7.71 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.91 (dd, 1 H, H(8) or H(5), ^3J = 11.2 Hz, ^4J = 8.2 Hz); 7.96 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.97 and 8.25 (both d, 2 H each, H(2′), H(3′), H(5′), H(6′), ^3J = 8.8 Hz); 8.35 (s, 1 H, H(3)); 8.75 (dd, 1 H, H(5) or H(8), ^3J = 12.7 Hz, ^4J = 9.1 Hz); 13.5—14.5 (br.s, 1 H, COOH). MS, m/z (I_{rel} (%)): 357 $[M + H]^+$ (100%). Found (%): C, 60.70; H, 2.85; N, 7.82. $C_{18}H_{10}F_2N_2O_4$. Calculated (%): C, 60.68; H, 2.83; N, 7.86.

(*E*)-6,7-Difluoro-2-[2-(4-methoxyphenyl)vinyl]quinoline-4-carboxylic acid (6c). The yield was 49%, m.p. 278—280 °C. ^{1}H NMR (DMSO-d_6), δ: 6.95 (d, 2 H, H(3′), H(5′), ^3J = 8.6 Hz); 7.30 (d, 1 H, CH=, ^3J = 16.2 Hz); 7.64 (d, 2 H, H(2′), H(6′), ^3J = 8.6 Hz); 7.79 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.86 (dd, 1 H, H(8) or H(5), ^3J = 11.3 Hz, ^4J = 8.2 Hz); 8.25 (s, 1 H, H(3));

8.71 (dd, 1 H, H(5) or H(8), ^3J = 12.6 Hz, ^4J = 9.2 Hz); 13.0—14.0 (br.s, 1 H, COOH). MS, m/z (I_{rel} (%)): 342 $[M + H]^+$ (100%). Found (%): C, 66.91; H, 3.86; N, 4.05. $C_{19}H_{13}F_2NO_3$. Calculated (%): C, 66.86; H, 3.84; N, 4.10.

6,7-Difluoro-2-methylquinoxaline (8). A 35% aqueous solution of methylglyoxal (pyruvic aldehyde) (1.07 g, 5.2 mmol) was added to a solution of 2-amino-4,5-difluoroaniline (0.75 g, 5.2 mmol). The reaction mixture was stored for 1.5 h at 80 °C. The precipitate of quinoxaline formed after cooling was filtered off. The yield was 0.8 g (85%). According to the melting point and spectral characteristics, the product is identical to that described earlier.[16]

(*E*)-6,7-Difluoro-2-[2-(4-nitrophenyl)vinyl]quinoxaline (9b). Anhydrous sodium acetate (0.15 g) and *p*-nitrobenzaldehyde (0.6 g, 4 mmol) were added to a solution of 6,7-difluoro-2-methylquinoxaline **8** (0.3 g, 1.65 mmol) in glacial acetic acid (20 mL). The reaction mixture was refluxed for 6 h and after cooling concentrated to 0.5 volume. The precipitate that formed was filtered off, washed with water (50 mL) and then with ethanol (15 mL) (to separate aldehyde excess), and recrystallized from ethanol. The yield was 0.23 g (45%), m.p. 210—212 °C. ^{1}H NMR (DMSO-d_6), δ: 7.76 (d, 1 H, CH=, ^3J = 16.4 Hz); 7.95 (dd, 1 H, H(5) or H(8), ^3J = 10.9 Hz, ^4J = 8.4 Hz); 7.98 (dd, 1 H, H(8) or H(5), ^3J = 11.2 Hz, ^4J = 7.6 Hz); 8.00 and 8.28 (both d, 2 H each, H(2′), H(3′), H(5′), H(6′), ^3J = 8.8 Hz); 8.10 (d, 1 H, CH=, ^3J = 16.4 Hz); 9.25 (s, 1 H, H(3)). MS, m/z (I_{rel} (%)): 314 $[M + H]^+$ (100%). Found (%): C, 61.30; H, 2.86; N, 13.44. $C_{16}H_9F_2N_3O_2$. Calculated (%): C, 61.35; H, 2.90; N, 13.41.

Compounds **9a,c** were synthesized similarly, and the reaction duration was 12 h. To isolate compound **9c**, after evaporation of the reaction mixture, water (10 mL) was added to the residue, and the product was extracted with methylene chloride. The precipitate that formed after the partial evaporation of the extragent was filtered off and washed with hexane.

(*E*)-6,7-Difluoro-2-styrylquinoxaline (9a). The yield was 29%, m.p. 153—155 °C. ^{1}H (DMSO-d_6), δ: 7.36 (m, 1 H, Ph); 7.43 (m, 2 H, Ph); 7.47 (d, 1 H, CH=, ^3J = 16.6 Hz); 7.70 (m, 2 H, Ph); 7.90 (dd, 1 H, H(5) or H(8), ^3J = 11.0 Hz, ^4J = 8.5 Hz); 7.94 (dd, 1 H, H(8) or H(5), ^3J = 10.5 Hz, ^4J = 8.0 Hz); 7.97 (d, 1 H, CH=, ^3J = 16.6 Hz); 9.19 (s, 1 H, H(3)). MS, m/z (I_{rel} (%)): 269 $[M + H]^+$ (100%). Found (%): C, 71.68; H, 3.80; N, 10.39. $C_{16}H_{10}F_2N_2$. Calculated (%): C, 71.64; H, 3.76; N, 10.44.

(*E*)-6,7-Difluoro-2-[2-(4-methoxyphenyl)vinyl]quinoxaline (9c). The yield was 25%, m.p. 238—240 °C. ^{1}H (DMSO-d_6), δ: 3.83 (s, 3 H, OMe), 6.96 (d, 2 H, H(3′), H(5′), ^3J = 8.3 Hz); 7.31 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.65 (d, 2 H, H(2′), H(6′), ^3J = 8.3 Hz); 7.92 (d, 1 H, CH=, ^3J = 16.3 Hz); 7.87 (m, 2 H, H(5), H(8)); 9.13 (s, 1 H, H(3)). MS, m/z (I_{rel} (%)): 299 $[M + H]^+$ (100%). Found (%): C, 68.50; H, 4.09; N, 9.35. $C_{17}H_{12}F_2N_2O$. Calculated (%): C, 68.45; H, 4.05; N, 9.39.

(*E*)-6,7-Difluoro-2-(2-thienyl)vinylquinoline (10a). Anhydrous sodium acetate (0.1 g) and thiophene-2-carbaldehyde (0.6 mL, 6.4 mmol) were added to quinoline **2b** (0.3 g, 2.1 mmol) in glacial acetic acid (15 mL). The reaction mixture was refluxed for 12 h, cooled down, and evaporated. The residue was washed with water (20 mL) and ethanol (5 mL) and recrystallized from ethanol. The yield was 27%, m.p. 125—127 °C. ^{1}H NMR (DMSO-d_6), δ: 7.08 (dd, 1 H, H(4′), ^3J = 5.0 Hz, ^3J = 3.4 Hz), 7.09 (d, 1 H, CH=, ^3J = 16.0 Hz); 7.33 (d, 1 H, H(5′), ^3J = 3.4 Hz); 7.45 (d, 1 H, H(3′), ^3J = 5.0 Hz); 7.73 (d, 1 H, H(3), ^3J = 8.6 Hz); 7.77 (dd, 1 H, H(5) or H(8), ^3J = 11.6 Hz, ^4J = 7.9 Hz); 7.84 (dd, 1 H, H(8) or H(5), ^3J = 10.8 Hz, ^4J = 8.9 Hz); 7.96 (d, 1 H, CH=, ^3J = 16.0 Hz); 8.26 (d, 1 H, H(4), ^3J = 8.6 Hz). MS, m/z (I_{rel} (%)): 274 $[M + H]^+$ (100%). Found (%): C, 65.88; H, 3.27; N, 5.14. $C_{15}H_9F_2NS$. Calculated (%): C 65.92; H 3.32; N 5.12.

Compounds **10b,c** were synthesized similarly. To obtain **10c**, the reaction duration was elongated to 36 h.

(*E*)-6,7-Difluoro-2-(2-thienyl)vinylquinoline-4-carboxylic acid (10b). The yield was 51%, m.p. 240—242 °C. ^{1}H NMR (DMSO-d_6), δ: 7.09 (dd, 1 H, H(4′), ^3J = 4.9 Hz, ^3J = 3.3 Hz); 7.15 (d, 1 H, CH=, ^3J = 16.0 Hz); 7.37 (d, 1 H, H(5′), ^3J = 3.3 Hz); 7.47 (d, 1 H, H(3′), ^3J = 4.9 Hz); 7.85 (dd, 1 H, H(8) or H(5), ^3J = 11.2 Hz, ^4J = 8.2 Hz); 8.02 (d, 1 H, CH=, ^3J = 16.0 Hz); 8.23 (s, 1 H, H(3)); 8.72 (dd, 1 H, H(5) or H(8), ^3J = 12.7 Hz, ^4J = 9.6 Hz); 13.0—14.0 (br.s, 1 H, COOH). MS, m/z (I_{rel} (%)): 318 $[M + H]^+$ (100%). Found (%): C, 60.60; H, 2.91; N, 4.38. $C_{16}H_9F_2NO_2S$. Calculated (%): C, 60.56; H, 2.86; N, 4.41.

(*E*)-6,7-Difluoro-2-(2-thienyl)vinylquinoxaline (10c). The yield was 55%, m.p. 139—141 °C. ^{1}H NMR (DMSO-d_6), δ: 7.12 (dd, 1 H, H(4′), ^3J = 5.0 Hz, ^3J = 3.6 Hz); 7.18 (d, 1 H, CH=, ^3J = 16.0 Hz); 7.42 (d, 1 H, H(5′), ^3J = 3.6 Hz); 7.54 (d, 1 H, H(3′), ^3J = 5.0 Hz); 7.87 (dd, 1 H, H(8) or H(5), ^3J = 11.0 Hz, ^4J = 8.4 Hz); 7.93 (dd, 1 H, H(5) or H(8), ^3J = 10.8 Hz, ^4J = 8.4 Hz); 8.15 (d, 1 H, CH=, ^3J = 16.0 Hz); 9.14 (s, 1 H, H(3)). MS, m/z (I_{rel} (%)): 275 $[M + H]^+$ (100%). Found (%): C, 61.27; H, 2.90; N, 10.24. $C_{14}H_8F_2N_2S$. Calculated (%): C, 61.31; H, 2.94; N, 10.21.

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