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Microwave-Assisted Solvent-Free Synthesis of 2-Styrylquinolines in the Presence of Zinc Chloride

V. M. Li, T. N. Gavrishova, and M. F. Budyka

Institute of Chemical Physics Problems, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: leevit@icp.ac.ru

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Abstract—An efficient solvent-free procedure has been developed for the synthesis of (*E*)-2-styrylquinoline derivatives under microwave irradiation in the presence of zinc chloride. The developed procedure is advantageous due to shorter reaction time and simpler workup.

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Derivatives of 2-styrylquinoline (**I**) are used in the synthesis of compounds exhibiting various kinds of biological activity, including antifungal [1], antitumor [2], anti-inflammatory, and antiallergic [3], as well as of compounds acting as HIV-1 integrase [4] and lipoxygenase inhibitors [3] and leukotriene d4 antagonists [3]. In addition, they can be used as models for the design of molecular logic devices [5] and supramolecular systems [6].

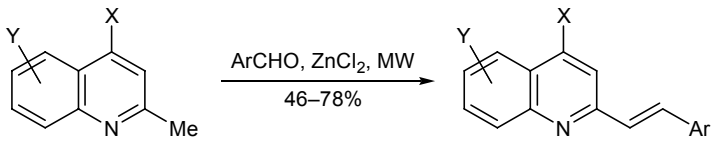
The most general procedure for the synthesis of 2-styrylquinolines is based on condensation of quinaldine with aromatic aldehydes, which is usually carried out in acetic anhydride [7, 8]. However, this traditional procedure involves prolonged heating of the reaction mixture, while the yields of targeted compounds are reduced as a result of tarring and formation of by-products.

In recent time, much interest is attracted by the synthesis of heterocyclic derivatives in a microwave oven under solvent-free conditions. This methodology makes it possible to shorten the reaction time, save energy, reduce expenses for chemicals and amount of wastes, and avoid laborious workup for isolation of the products [9].

The synthesis of 2-styrylquinolines under microwave irradiation has been reported in some publications. Li et al. [10] described the microwave-activated condensation of quinaldine with substituted benzaldehydes in acetic anhydride. However, acetic anhydride is a quite potent acylating agent capable of reacting with hydroxy and amino groups, so that subsequent hydrolysis of the corresponding acetates and acetamides was necessary. Musiol et al. [11, 12] reported on the synthesis of 2-styrylquinoline derivatives under microwave (MW) irradiation in the absence of solvent and catalyst, but this procedure was effective only in the case of 2-styrylquinolines containing carboxy or hydroxy groups in the quinoline fragment; therefore, it cannot be regarded as general method.

We previously synthesized a number of 4-styrylquinoline derivatives by condensation of 4-methylquinoline with substituted benzaldehydes under MW

Scheme 1.



I–XVIII

I–XV, X = Y = H; **I**, Ar = Ph; **II**, Ar = 4-$O_2NC_6H_4$; **III**, Ar = 4-$MeOCOC_6H_4$; **IV**, Ar = 4-IC_6H_4; **V**, Ar = 4-FC_6H_4; **VI**, Ar = 4-$EtOC_6H_4$; **VII**, Ar = 4-$Me_2NC_6H_4$; **VIII**, Ar = 4-HOC_6H_4; **IX**, Ar = 2-HOC_6H_4; **X**, Ar = 1-naphthyl; **XI**, Ar = 2-naphthyl; **XII**, Ar = 9-anthryl; **XIII**, Ar = pyridin-2-yl; **XIV**, Ar = pyridin-3-yl; **XV**, Ar = pyridin-4-yl; **XVI**, **XVII**, X = H, Y = 5,6-benzo; **XVI**, Ar = Ph; **XVII**, Ar = pyridin-2-yl; **XVIII**, X = Cl, Y = 6,7-benzo, Ar = Ph.

Table 1. Reaction of 2-methylquinoline with benzaldehyde in the presence of zinc chloride under microwave irradiation

Ratio quinaldine–PhCHO–$ZnCl_2$	Irradiation time, min	Yield of **I**, %
1:2:0.45	0	0
1:2:0.45	1	37
1:2:0.45	2	57
1:2:0.45	3	65
1:2:0.45	5	70
1:2:0.45	8	75
1:2:0.45	10	78
1:2:0.45	12	79
1:2:0.45	16	77
2:1:0.45	10	37
1:1:0.45	10	58
1:2:0.45	10	78
1:2:0	10	0
1:2:0.25	10	61
1:2:0.45	10	78
1:2:1	10	76

Table 2. Yields of 2-styrylquinoline derivatives **I**–**XVIII** in the condensation of 2-methylquinolines with aromatic aldehydes in the presence of zinc chloride under microwave irradiation

Compound no.	Time, min	Yield, %
I	12	63
II	5	78
III	10	67
IV	12	61
V	12	64
VI	12	62
VII	15	60
VIII	10	71
IX	10	66
X	10	62
XI	10	65
XII	14	46
XIII	10	65
XIV	11	66
XV	12	60
XVI	12	57
XVII	12	59
XVIII	10	64

irradiation in the presence of zinc chloride without a solvent [13]. In the present work we extended the same procedure to the synthesis of a large series of 2-styrylquinolines.

The reaction conditions were optimized by studying the condensation of 2-methylquinoline with benzaldehyde as model reaction. The kinetics of accumulation of the *E* isomer of 2-styrylquinoline (**I**) was examined by spectrophotometry, taking into account that the initial compounds (benzaldehyde and quinaldine) do not absorb in the region λ 330–380 nm and that compound **I** in ethanol is characterized by an absorption maximum at λ 340 nm (ε = 28900 l mol^{-1} cm^{-1}) [14]. Therefore, we were able to estimate the yield of **I** without isolating it from the reaction mixture. The effects of reaction (irradiation) time and initial reactant ratio (at a constant irradiation time) were studied (Table 1).

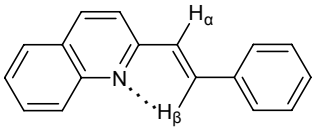
We found that the yield of **I** reaches 37% in 1 min after irradiation started; after irradiation for 10–12 min, the yield of **I** no longer changed. The yield of **I** increased in parallel with the amount of benzaldehyde. The optimal amount of the catalyst was 0.45 equiv. In subsequent preparative experiments the ratio quinaldine–benzaldehyde–zinc chloride was 1:2:0.45. Under these conditions we performed condensations of quinaldine with various aromatic and heterocyclic aldehydes. Apart from quinaldine, the condensations with its benzo-fused derivatives, 3-methylbenzo[*f*]quinoline and 4-chloro-2-methylbenzo[*g*]quinoline [15, 16], were carried out. The results are collected in Table 2.

It is seen that the synthesis of nitro derivative **II** required the shortest irradiation time and was characterized by the highest yield. This may be due to strong activating effect of electron-withdrawing nitro group. It should be noted that the proposed procedure was also efficient for compounds containing an electron-donating substituent in the aldehyde component (compounds **VI**–**IX**). The low yield of **XII** is likely to be related to difficulties in its separation from excess anthracene-9-carbaldehyde.

Comparison of the developed procedure utilizing MW irradiation (method *a*) with traditional condensation by heating in acetic anhydride (method *b*; Table 3) shows that the former ensures much higher yield of the target products in much shorter time (10–12 min against 14 h). Moreover, method *a* implies simpler isolation and purification procedures.

Regardless of the method of synthesis, all compounds **I**–**XVIII** had *E* configuration of the exocyclic

double bond, as followed from the presence in their ^{1}H NMR spectra of doublet signals due to olefinic protons at δ 7.21–8.63 ppm with a coupling constant of about 16 Hz. It is interesting that in all cases the H_β proton resonated in a weaker field as compared to H_α. Analogous pattern was observed previously for structurally related compounds in which the nitrogen atom occupied *ortho* position with respect to the ethenyl substituent due to formation of intramolecular hydrogen bond N···H_β [17, 18]. In the spectrum of pyridine derivative **XIII** having two nitrogen atoms in the *ortho* positions with respect to the ethenyl substituent, signals from both olefinic protons are displaced downfield, and their chemical shifts are very similar.



Another interesting feature, a considerable downfield shift of the H_β signal, was observed for 1-naphthyl and 9-anthryl derivatives **X** and **XII** but not for 2-naphthyl derivative **XI** (Table 4). 1,2-Diarylethenes with different aryl substituents exist as a set of *s*-conformers due to restricted rotation of the aryl groups about quasisingle carbon–carbon bonds in the ethene bridge [19]. In those conformers of **X** where the *ortho*-fused benzene ring is oriented toward the H_β proton the latter appears strongly deshielded, and its signal shifts downfield. The H_β proton in 9-anthryl derivative **XII** is deshielded by either one or another *ortho*-fused benzene ring, regardless of the orientation of the anthracene fragment; therefore, the H_β signal in the spectrum of **XII** is located most downfield.

To conclude, we have developed a convenient, cost-effective, and ecologically safe procedure for the synthesis of (*E*)-2-styrylquinoline derivatives under microwave irradiation in the absence of a solvent.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker Avance III, Bruker DRX-500, and Bruker DRX-200 spectrometers at 500 and 200 MHz using $CDCl_3$, DMSO-d_6, or CCl_4 as solvent and tetramethylsilane as internal reference. The IR spectra were measured in KBr on a Perkin Elmer Spectrum BX-2 spectrometer with Fourier transform. The mass spectra were obtained on an ESI O-TOF MS custom-made high-resolution time-of-flight mass spectrometer [20] and on a Q-TOF QSTAR MDS Sciex high-resolution tandem mass spectrometer. The melting points were measured on a Kofler hot stage by heating at a rate of 4 deg/min. The elemental compositions were determined on an Elementar Vario Micro Cube analyzer. Microwave-assisted reactions were carried out in a DAEWOO-KOR-4115SA household microwave oven (600 W, 2450 MHz).

Table 3. Yields of compounds **IV**–**VI**, **X**, and **XI** under microwave irradiation ($ZnCl_2$, method *a*) and under traditional conditions (Ac_2O, method *b*)

Compound no.	Reaction time, h		Yield, %	
	method *a*	method *b*	method *a*	method *b*
IV	0.20	14	61	54
V	0.20	14	64	57
VI	0.20	14	62	46
X	0.17	14	62	50
XI	0.17	14	65	53

Typical procedure for the synthesis of 2-styrylquinoline derivatives. *a*. *Under microwave irradiation.* A glass test tube was charged with 1.0 mmol of quinaldine, 2.0 mmol of aromatic aldehyde, and 0.45 mmol of zinc chloride. The test tube was placed into a 100-ml beaker containing 15–20 ml of water and subjected to MW irradiation at a power of 600 W in 2 to 4 4–5-min periods with 30-s intervals (overall irradiation time 5–14 min). The progress of the reaction was monitored by TLC using acetone–hexane (1:5) as eluent. The mixture was cooled and treated with a 5% solution of potassium hydroxide. In the synthesis of hydroxy derivatives **VIII** and **IX**, the mixture was treated with aqueous ethanol, and in the synthesis of **XIV** and **XV**, with a hot concentrated alkali solution. The solid or oily material thus formed was separated by decanting and washed with a small amount of hexane or hexane–methylene chloride, and

Table 4. Chemical shifts of the CH=CH protons in the ^{1}H NMR spectra of 2-styrylquinoline derivatives $HtCH_\alpha=CH_\beta Ar$

Compound no.	H_α	H_β
I	7.41	7.68
X	7.47	8.52
XI	7.53	7.86
XII	7.29	8.63
XIII	7.86, 7.90	

the solid product thus obtained was recrystallized from appropriate solvent.

b. *Condensation in acetic anhydride*. A mixture of 1 mmol of quinaldine and 2 mmol of aromatic aldehyde in 5 ml of acetic anhydride was heated for 14 h under reflux. The mixture was cooled, treated with an aqueous solution of sodium carbonate, and the dark solid or oily material was subjected to chromatography on silica gel (Silpearl) or recrystallization from appropriate solvent.

2-[(*E*)-2-Phenylethenyl]quinoline (I). Light yellow crystals, mp 99–100°C (from hexane) [21]. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.30–7.35 m (1H, C_6H_5), 7.37–7.44 m (3H, C_6H_5, =CH–), 7.47–7.52 m (1H, Ht), 7.61–7.73 m (5H, C_6H_5, –CH=, Ht), 7.77 d (1H, Ht, *J* = 8.1 Hz), 8.08 d (1H, Ht, *J* = 8.7 Hz), 8.11 d (1H, Ht, *J* = 8.6 Hz).

2-[(*E*)-2-(4-Nitrophenyl)ethenyl]quinoline (II). Yellow crystals, mp 165–167°C (from EtOH–$CHCl_3$); published data [21]: mp 169°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.50–7.58 m (2H, Ht, =CH–), 7.67 d (1H, Ht, *J* = 8.5 Hz), 7.71–7.85 m (5H, *m*-H, –CH=, Ht), 8.10 d (1H, Ht, *J* = 8.4 Hz), 8.19 d (1H, Ht, *J* = 8.5 Hz), 8.26 d (2H, *o*-H, *J* = 8.7 Hz).

Methyl 4-[(*E*)-2-(quinolin-2-yl)ethenyl]benzoate (III). White crystals, mp 133–135°C (from hexane); published data [22]: mp 135–136°C. ^{1}H NMR spectrum (200 MHz, CCl_4), δ, ppm: 2.25 s (3H, CH_3), 7.04 d (2H, *m*-H, *J* = 8.5 Hz), 7.21 d (1H, =CH–, *J* = 16.1 Hz), 7.37 t (1H, Ht, = *J* 7.4 Hz), 7.48 d (1H, Ht, *J* = 8.5 Hz), 7.52–7.72 m (5H, Ht, *o*-H, –CH=), 7.92–8.04 m (2H, Ht).

2-[(*E*)-2-(4-Iodophenyl)ethenyl]quinoline (IV). *a*. White crystals, mp 158–159°C (from hexane). IR spectrum: δ 969 cm^{-1} (*trans*-CH=CH). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.36–7.44 m (3H, *o*-H, =CH–), 7.52 t (1H, Ht, *J* = 7.5 Hz), 7.63 d (1H, –CH=, *J* = 16.6 Hz), 7.66 d (1H, Ht, *J* = 8.7 Hz), 7.70–7.77 m (3H, *m*-H, Ht), 7.80 d (1H, Ht, *J* = 8.0 Hz), 8.08 d (1H, Ht, = *J* 8.4 Hz), 8.15 d (1H, Ht, *J* = 8.6 Hz). Mass spectrum: *m*/*z* 358.011 $[M + H]^+$. Found, %: C 56.86; H 3.22; N 3.58. $C_{17}H_{12}IN$. Calculated, %: C 57.16; H 3.39; N 3.92. *M* 357.001.

b. The precipitate obtained after decomposition of the reaction mixture was washed with aqueous acetone and recrystallized from hexane. Yield 54%.

2-[(*E*)-2-(4-Fluorophenyl)ethenyl]quinoline (V). *a*. White crystals, mp 118–120°C (from hexane). IR spectrum, ν, cm^{-1}: 1219 (C–F), 967 (δ*trans*-CH=CH). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.14 t (2H, *o*-H, *J* = 8.6 Hz), 7.36 d (1H, =CH–, *J* = 16.3 Hz), 7.55 t (1H, Ht, *J* = 7.4 Hz), 7.63–7.78 m (5H, *m*-H, –CH=, Ht), 7.83 d (1H, Ht, *J* = 8.1 Hz), 8.12 d (1H, Ht, *J* = 8.4 Hz), 8.18 d (1H, Ht, *J* = 8.5 Hz). Mass spectrum: *m*/*z* 250.084 $[M + H]^+$. Found, %: C 81.78; H 4.88; N 5.56. $C_{17}H_{12}NF$. Calculated, %: C 81.91; H 4.85; N 5.62. *M* 249.095.

b. Yield 57% after purification by column chromatography (heptane–methylene chloride, 1 : 1).

2-[(*E*)-2-(4-Ethoxyphenyl)ethenyl]quinoline (VI). *a*. Light yellow crystals, mp 135–137°C (from hexane); published data [7]: mp 137.5–138°C. ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm: 1.35 t (3H, CH_3, *J* = 7.0 Hz), 4.08 q (2H, OCH_2, *J* = 7.0 Hz), 6.98 d (2H, *o*-H, *J* = 8.4 Hz), 7.33 d (1H, =CH–, *J* = 16.5 Hz), 7.53 t (1H, Ht, *J* = 7.6 Hz), 7.67 d (2H, *m*-H, *J* = 8.4 Hz), 7.74 t (1H, Ht, *J* = 7.6 Hz), 7.78 d (1H, –CH=, *J* = 16.5 Hz), 7.83 d (1H, Ht, *J* = 8.6 Hz), 7.93 d (1H, Ht, *J* = 8.0 Hz), 7.97 d (1H, Ht, *J* = 8.4 Hz), 8.32 d (1H, Ht, *J* = 8.5 Hz).

b. Yield 46% after purification by column chromatography (methylene chloride), followed by recrystallization from heptane.

***N*,*N*-Dimethyl-4-[(*E*)-2-(quinolin-2-yl)ethenyl]-aniline (VII).** Yellow crystals, mp 185–187°C (from EtOH); published data [23]: mp 184–185°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 3.07 s (6H, NMe_2), 6.78 d (2H, *o*-H, *J* = 8.8 Hz), 7.26 d (1H, =CH–, *J* = 16.2 Hz), 7.49 t (1H, Ht, *J* = 7.5 Hz), 7.59 d (2H, *m*-H, *J* = 8.8 Hz), 7.65 d (1H, –CH=, *J* = 16.2 Hz), 7.68–7.74 m (2H, Ht), 7.79 d (1H, Ht, *J* = 8.0 Hz), 8.08 d (1H, Ht, *J* = 8.5 Hz), 8.11 d (1H, Ht, *J* = 8.6 Hz).

4-[(*E*)-2-(Quinolin-2-yl)ethenyl]phenol (VIII). Light yellow crystals, mp 270°C (from *i*-PrOH); published data [3]: mp 268–270°C. ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm: 6.77 d (2H, *o*-H, *J* = 8.4 Hz), 7.19 d (1H, =CH–, *J* = 16.2 Hz), 7.47–7.54 m (3H, *m*-H, Ht), 7.66–7.73 m (2H, –CH=, Ht), 7.78 d (1H, Ht, *J* = 8.6 Hz), 7.88 d (1H, Ht, *J* = 8.0 Hz), 7.92 d (1H, Ht, *J* = 8.4 Hz), 8.26 d (1H, Ht, *J* = 8.6 Hz), 10.25 br.s (1H, OH).

2-[(*E*)-2-(Quinolin-2-yl)ethenyl]phenol (IX). Light yellow crystals, mp 210–212°C (from *i*-PrOH); published data [23]: mp 212°C. ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm: 6.85 t (1H, C_6H_4, *J* = 7.4 Hz), 6.91 d (1H, C_6H_4, *J* = 7.8 Hz), 7.16 t (1H, C_6H_4, *J* = 7.5 Hz), 7.46 d (1H, =CH–, *J* = 16.4 Hz),

7.53 t (1H, C_6H_4, J = 7.5 Hz), 7.68 d (1H, Ht, J = 7.6 Hz), 7.72 t (1H, Ht, J = 7.6 Hz), 7.78 d (1H, Ht, J = 8.6 Hz), 7.92 d (1H, Ht, J = 7.9 Hz), 7.97 d (1H, Ht, J = 8.3 Hz), 8.03 d (1H, –CH=, J = 16.4 Hz), 8.31 d (1H, Ht, J = 8.6 Hz), 9.99 s (1H, OH).

2-[(*E*)-2-(1-Naphthyl)ethenyl]quinoline (X). *a*. Light yellow crystals, mp 102–103°C (from hexane–CH_2Cl_2); published data [24]: mp 101°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.47 d (1H, =CH–, J = 16.0 Hz), 7.49–7.55 m (3H, H_{arom}), 7.56–7.60 m (1H, H_{arom}), 7.69–7.74 m (2H, H_{arom}), 7.79 d (1H, H_{arom}, J = 8.1 Hz), 7.86 d (1H, Ht, J = 8.2 Hz), 7.90 t (2H, Ht, J = 7.3 Hz), 8.13 d (1H, Ht, J = 8.4 Hz), 8.15 d (1H, Ht, J = 8.6 Hz), 8.34 d (1H, Ht, J = 8.5 Hz), 8.52 d (1H, –CH=, J = 16.0 Hz).

b. Yield 50% after purification by column chromatography (acetone–heptane, 1:5), followed by recrystallization from heptane–diethyl ether.

2-[(*E*)-2-(2-Naphthyl)ethenyl]quinoline (XI). *a*. Light yellow crystals, mp 163–164°C (from hexane–acetone). IR spectrum: δ 963 cm^{-1} (*trans*-CH=CH). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.45–7.52 m (3H, Naphth, Ht),7.53 d (1H, =CH–, J = 16.3 Hz), 7.69–7.74 m (2H, Naphth), 7.80 d (1H, Ht, J = 8.3 Hz), 7.82–7.89 m (5H, –CH=, Naphth, Ht), 8.00 s (1H, Naphth), 8.09 d (1H, Ht, J = 8.3 Hz), 8.15 d (1H, Ht, J = 8.5 Hz). Mass spectrum: m/z 282.127 $[M + H]^+$. Found, %: C 89.49; H 5.28; N 4.90. $C_{21}H_{15}N$. Calculated, %: C 89.65; H 5.37; N 4.98. M 281.120.

b. Yield 53% after purification by column chromatography (acetone–heptane, 1:5), followed by recrystallization from petroleum ether–chloroform.

2-[(*E*)-2-(9-Anthryl)ethenyl]quinoline (XII). Dark yellow crystals, mp 174–176°C (from petroleum ether); published data [25]: mp 170–172°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.29 d (1H, =CH–, J = 16.4 Hz), 7.47–7.52 m (4H, H_{arom}), 7.53–7.57 m (1H, Ht), 7.73–7.77 m (1H, Ht), 7.80 d (1H, Ht, J = 8.5 Hz), 7.85 d (1H, Ht, J = 8.2 Hz), 8.01–8.06 m (2H, H_{arom}), 8.16 d (1H, Ht, J = 8.4 Hz), 8.23 d (1H, Ht, J = 8.5 Hz), 8.41–8.47 m (3H, H_{arom}), 8.63 d (1H, –CH=, J = 16.4 Hz).

2-[(*E*)-2-(Pyridin-2-yl)ethenyl]quinoline (XIII). *a*. Yield 65%, light yellow crystals, mp 94–96°C (from hexane); published data [26]: mp 94–95°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.20–7.24 m (1H, Py), 7.53 t (1H, Ht, J = 7.5 Hz), 7.61 d (1H, Ht, J = 7.8 Hz), 7.68–7.75 m (3H, Py, Ht), 7.80 d (1H, Ht, J = 8.1 Hz), 7.86 d (1H, =CH–, J = 16.0 Hz), 7.90 d (1H, –CH=, J = 16.0 Hz), 8.15–8.21 m (2H, Ht), 8.65 d (1H, Py, J = 4.8 Hz).

2-[(*E*)-2-(Pyridin-3-yl)ethenyl]quinoline (XIV). Light yellow crystals, mp 95°C (from hexane); published data [26]: mp 95–96°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.32–7.36 m (1H, Py), 7.46 d (1H, =CH–, J = 16.3 Hz), 7.52 t (1H, Ht, J = 7.4 Hz), 7.65–7.75 m (3H, –CH=, Ht), 7.80 d (1H, Ht, J = 8.1 Hz), 7.97 d (1H, Py, J = 7.8 Hz), 8.09 d (1H, Ht, J = 8.7 Hz), 8.16 d (1H, Ht, J = 8.5 Hz), 8.55 d (1H, Py, J = 4.7 Hz), 8.84 s (1H, Py).

2-[(*E*)-2-(Pyridin-4-yl)ethenyl]quinoline (XV). Light yellow crystals, mp 123–125°C (from hexane); published data [26]: mp 125–126°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.48 d (2H, Py, J = 6.0 Hz), 7.51–7.59 m (2H, =CH–, Ht), 7.63 d (1H, –CH=, J = 16.3 Hz), 7.67 d (1H, Ht, J = 8.5 Hz), 7.73 t (1H, Ht, J = 7.7 Hz), 7.81 d (1H, Ht, J = 8.2 Hz), 8.09 d (1H, Ht, J = 8.2 Hz), 8.18 d (1H, Ht, J = 8.5 Hz), 8.63 d (2H, Py, J = 6.0 Hz).

3-[(*E*)-2-Phenylethenyl]benzo[*f*]quinoline (XVI). Light yellow crystals, mp 176–177°C (from EtOH); published data [27]: mp 173–174°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.33 t (1H, Ph, J = 7.3 Hz), 7.38–7.46 m (3H, =CH–, Ph), 7.61–7.71 m (4H, Ph, Ht), 7.76 d (1H, –CH=, J = 16.3 Hz), 7.78 d (1H, Ht, J = 8.6 Hz), 7.92 d (1H, Ht, J = 7.6 Hz), 7.97–8.00 m (2H, Ht), 8.59 d (1H, Ht, J = 8.1 Hz), 8.90 d (1H, Ht, J = 8.6 Hz).

3-[(*E*)-2-(Pyridin-2-yl)ethenyl]benzo[*f*]quinoline (XVII). Light brown crystals, mp 149°C (from aqueous acetone). IR spectrum: δ 974 cm^{-1} (*trans*-CH=CH). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.22–7.26 m (1H, Py), 7.61 d (1H, Py, J = 7.8 Hz), 7.66 t (1H, Py, J = 7.7 Hz), 7.69–7.77 m (2H, Ht), 7.84 d (1H, Ht, J = 8.6 Hz), 7.90–7.97 m (3H, Ht), 8.00–8.08 m (2H, CH=CH), 8.62 d (1H, Ht, J = 8.3 Hz), 8.69 d (1H, Py, J = 4.9 Hz), 8.97 d (1H, Ht, J = 8.6 Hz). Found, %: C 84.83; H 5.02; N 9.85. $C_{20}H_{14}N_2$. Calculated, %: C 85.08; H 5.00; N 9.92.

4-Chloro-2-[(*E*)-2-phenylethenyl]benzo[*g*]quinoline (XVIII). Light yellow crystals, mp 143–144°C (from acetone). IR spectrum: δ 972 cm^{-1} (*trans*-CH=CH). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.35–7.47 m (4H, Ph, =CH–), 7.55–7.59 m (2H, Ht), 7.68 d (2H, Ph, J = 7.3 Hz), 7.70 d (1H, –CH=, J = 16.3 Hz), 7.81 s (1H, Ht), 8.06–8.12 m (2H, Ht), 8.67 s (1H, Ht), 8.75 s (1H, Ht). Mass spectrum: m/z 316.088/318.083 $[M + H]^+$. Found, %: C 79.68;

H 4.51; N 4.38. $C_{21}H_{14}ClN$. Calculated, %: C 79.87; H 4.47; N 4.44. *M* 315.081/317.079.

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