

# Synthesis of New 3-Aryl-1-methylbenzo[f]quinolines

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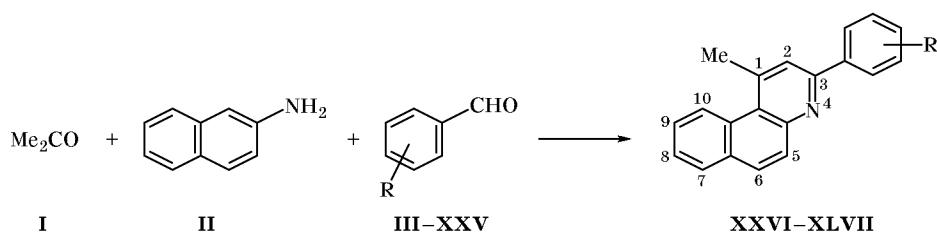
**Abstract**—Three-component condensation of 2-aminonaphthalene, acetone, and substituted benzaldehydes in alcoholic solution in the presence of concentrated hydrochloric acid gave 3-aryl-1-methylbenzo[f]quinolines. 1-Methyl-3-(nitrophenyl)benzo[f]quinolines were reduced to the corresponding amines which were converted into amides having a sulfonyl or chloroacetyl group in the aryl substituent.

Synthesis of compounds of the benzoquinoline series has been well documented [1–4]. They are formed as final products of heterocyclization of Schiff bases with various CH acids. Owing to their very poor solubility in most organic solvents, benzoquinoline derivatives are low reactive, and they cannot be used in the synthesis of more complex molecules. Among these compounds, methyl-substituted benzoquinolines occupy a specific place: they are starting materials in the synthesis of difficultly accessible and hence poorly studied styrylquinolines. Despite a limited number of known styryl derivatives, they have found application in photochemistry. The conjugated system including the quinoline ring and styryl group gives rise to photosensitizing properties, so that these compounds may be used as components of light-sensitive layer in photographic materials [5]. However, specific interest in styryl derivatives of quinoline is explained by antitumor [6] and immunoprotective properties [7] of some compounds of this series.

The goal of the present work was to develop a procedure for the synthesis of methyl-substituted aryl-benzo[f]quinolines with a view to extend the source of raw materials for the preparation of new styryl-quinoline derivatives. We previously succeeded in obtaining 3-aryl-1-methylbenzo[f]quinolines in 35–55% yield by condensation of 2-arylmethyleneamino-naphthalenes with acetone in the presence of amino-naphthalene hydrochloride. In the present work we synthesized such compounds by three-component condensation of acetone (**I**), 2-aminonaphthalene (**II**), and benzaldehyde (**III**) (or substituted benzaldehydes **IV–XXV**) on heating in boiling ethanol in the presence of concentrated hydrochloric acid (Scheme 1). The reaction was selective; no intermediate arylamino ketones (which are usually formed in reactions of Schiff bases with ketones [9]) were isolated.

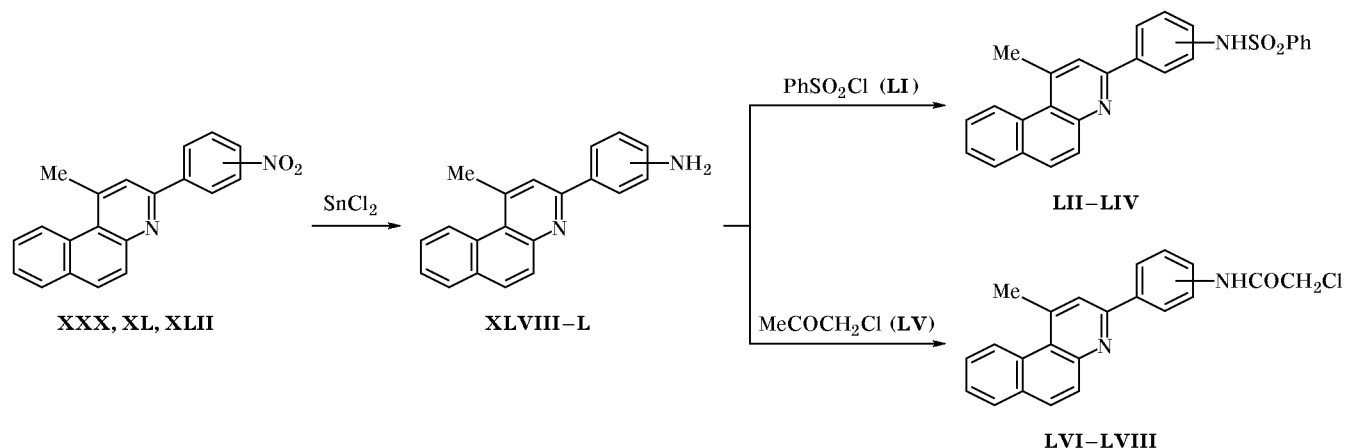
As previously [10, 11], the effect of substituent in the aldehyde on the yield of the final product was observed. Acceptor substituents in the *para* position

Scheme 1.



**III, XXVI**, R = H; **IV, XXVII**, R = 4-F; **V, XXVIII**, R = 4-Cl; **VI, XXIX**, R = 4-Br; **VII, XXX**, R = 4-NO<sub>2</sub>; **VIII, XXXI**, R = 4-OH; **IX, XXXII**, R = 4-Me<sub>2</sub>N; **X, XXXIII**, R = 4-Et<sub>2</sub>N; **XI, XXXIV**, R = 4-Et; **XII, XXXV**, R = 4-MeO; **XIII, XXXVI**, R = EtO; **XIV, XXXVII**, R = 4-PrO; **XV, XXXVIII**, R = 4-MeS; **XVI, XXXIX**, R = 3-HO; **XVII, XL**, R = 3-O<sub>2</sub>N; **XVIII, XLI**, R = 3-PhO; **XIX, XLII**, R = 2-O<sub>2</sub>N; **XX, XLIII**, R = 2-Me; **XXI, XLIV**, R = 2,3-(MeO)<sub>2</sub>; **XXII, XLV**, R = 2,5-(MeO)<sub>2</sub>; **XXIII, XLVI**, R = 3-EtO-4-HO; **XXIV, XLVII**, R = 3-MeO-4-PhCH<sub>2</sub>O; **XXV**, R = 2-HO-4-Et<sub>2</sub>N.

Scheme 2.



**XLVIII**, 4-H<sub>2</sub>N; **XLIX**, 3-H<sub>2</sub>N; **L**, 2-H<sub>2</sub>N; **LII**, 4-PhSO<sub>2</sub>NH; **LIII**, 3-PhSO<sub>2</sub>NH; **LIV**, 2-PhSO<sub>2</sub>NH; **LVI**, 4-CICH<sub>2</sub>CONH; **LVII**, 3-CICH<sub>2</sub>CONH; **LVIII**, 2-CICH<sub>2</sub>CONH.

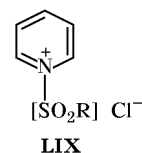
of the aromatic ring favor the reaction most strongly, and the yield of 3-aryl-1-methylbenzo[f]quinolines **XXVII-XXX** reaches 55–74%; the yields of 3-aryl-1-methylbenzo[f]quinolines from aldehydes having electron-donor substituents are considerably lower.

Presumably, substituents in the *ortho*-position of the aromatic ring in the aldehyde exert steric effect on the heterocyclization process. The yield of *o*-nitro derivative **XLII** is lower by 10% despite favorable electronic effect of the nitro group. The steric effect is more pronounced in the reaction with *o*-methylbenzaldehyde (**XX**). In this case, the yield of benzoquinoline **XLIII** decreases by 25%.

Aldehydes having two substituents require more severe conditions for the condensation to occur. The reactions with 4-benzyloxy-3-methoxybenzaldehyde (**XXIV**) and 2,3-dimethoxybenzaldehyde (**XXI**) took 7 h in the presence of increased amount of hydrochloric acid, and the yield of products **XLIV** and **XLVII** did not exceed 20%. In the reaction with 4-diethylamino-2-hydroxybenzaldehyde (**XXV**) no heterocyclization occurred. In this case, both steric and electronic factors are unfavorable.

Nitro-substituted compounds **XXX**, **XL**, and **XLII** were converted into amides **LII-LVIII** (Scheme 2). We tried to reduce 1-methyl-3-(nitrophenyl)benzo[f]quinolines **XXX**, **XL**, and **XLII** in several ways: with iron in hydrochloric and acetic acid, with zinc or magnesium in acetic acid, and with sodium dithionite. However, these reducing agents turned out to be low efficient. Acceptable results were obtained using tin(II) chloride in concentrated hydrochloric acid on heating for 1 h. Phenylsulfonylamino derivatives **LII-**

**LIV** were synthesized by condensation of 3-(aminophenyl)-1-methylbenzo[f]quinolines **XLVIII-L** with benzenesulfonyl chloride (**LI**) in pyridine at 90–100°C. Presumably, in this reaction pyridine acts not only as solvent but also as catalyst; it reacts with chloride **LI** to form pyridinium salt **LIX** [12]:



Amides **LVI-LVIII** were prepared by reaction of 3-(aminophenyl)-1-methylbenzo[f]quinolines **XLVIII-L** with chloroacetone (**LV**) in hexane in the presence of boron trifluoride-ether complex.

The structure of the products was confirmed by the IR, NMR, UV, and mass spectra (GC-MS). Their melting points, yields, and analytical data are given in Table 1. The IR spectra of compounds **XXVI-L**, **LII-LIV**, and **LVI-LVIII** contain a clearly defined band in the region corresponding to out-of-plane bending vibrations of aromatic C–H bonds (840–820 cm<sup>-1</sup>), which arises from the two adjacent C–H bonds at C<sup>5</sup> and C<sup>6</sup> of the quinoline ring [13]. The bands at 695–690 and 770–760 cm<sup>-1</sup> correspond to bending vibrations of C–H bonds in the benzene ring. Compound **XXVII** shows in the IR spectrum a strong band at 1150 cm<sup>-1</sup>, which belongs to stretching vibrations of the C–F bond; compounds **XXVIII** and **LVI-LVIII** are characterized by C–Cl absorption at 850–845 cm<sup>-1</sup>; the C–Br bond in **XXIX** gives rise to absorption band at 569 cm<sup>-1</sup>. Strong bands in the

**Table 1.** Yields, melting points, and elemental analyses of 3-aryl-1-methylbenzo[*f*]quinolines **XXVI–XLVII** and their derivatives **XLVIII–L**, **LII–LIV**, and **LVI–LVIII**

Compound no.	Yield, %	mp, °C	Found, %			Formula	Calculated		
			C	H	N (Hlg)		C	H	N (Hlg)
<b>XXVI</b>	52	155–156 <sup>a</sup>	89.20	5.59	5.21	C <sub>20</sub> H <sub>15</sub> N	89.21	5.58	5.21
<b>XXVII</b>	68	130	–	–	4.87 (6.58)	C <sub>20</sub> H <sub>14</sub> FN	83.62	4.88	4.88 (6.62)
<b>XXVIII</b>	70	182	79.19	4.62	4.63 (11.50)	C <sub>20</sub> H <sub>14</sub> ClN	79.18	4.61	4.61 (11.66)
<b>XXIX</b>	74	177–178 <sup>a</sup>	68.98	4.00	4.01 (22.91)	C <sub>20</sub> H <sub>14</sub> BrN	68.98	4.02	4.02 (22.98)
<b>XXX</b>	55	193–194 <sup>a</sup>	76.44	4.43	8.94	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	76.43	4.46	8.92
<b>XXXI</b>	40	243 <sup>a</sup>	84.20	5.25	4.90	C <sub>20</sub> H <sub>15</sub> NO	84.21	5.26	4.91
<b>XXXII</b>	6	240	84.63	6.40	8.98	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub>	84.62	6.41	8.97
<b>XXXIII</b>	9	138	84.71	7.06	8.23	C <sub>24</sub> H <sub>24</sub> N <sub>2</sub>	84.70	7.06	8.24
<b>XXXIV</b>	29	263–264	88.84	6.36	4.70	C <sub>22</sub> H <sub>19</sub> N	88.88	6.40	4.72
<b>XXXV</b>	44	124–125 <sup>a</sup>	84.26	5.67	4.69	C <sub>21</sub> H <sub>17</sub> NO	84.28	5.68	4.68
<b>XXXVI</b>	40	205–206	84.35	6.06	4.49	C <sub>22</sub> H <sub>19</sub> NO	84.35	6.07	4.47
<b>XXXVII</b>	38	338–339	84.38	6.43	4.27	C <sub>23</sub> H <sub>21</sub> NO	84.40	6.42	4.28
<b>XXXVIII</b>	42	199	80.01	5.42	4.43	C <sub>21</sub> H <sub>17</sub> NS	80.00	5.40	4.44
<b>XXXIX</b>	18	217	84.20	5.24	4.87	C <sub>20</sub> H <sub>15</sub> NO	84.21	5.26	4.91
<b>XL</b>	26	186 <sup>a</sup>	76.41	4.45	8.93	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	76.43	4.46	8.92
<b>XLI</b>	25	170	86.43	5.24	3.89	C <sub>26</sub> H <sub>19</sub> NO	86.43	5.26	3.88
<b>XLII</b>	45	188	76.41	4.47	8.90	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	76.43	4.46	8.92
<b>XLIII</b>	28	164	89.03	6.01	4.96	C <sub>21</sub> H <sub>17</sub> N	89.04	6.00	4.96
<b>XLIV</b>	20	305	80.01	6.05	4.22	C <sub>22</sub> H <sub>20</sub> NO <sub>2</sub>	80.00	6.06	4.24
<b>XLV</b>	18	227	80.02	6.04	4.23	C <sub>22</sub> H <sub>20</sub> NO <sub>2</sub>	80.00	6.06	4.24
<b>XLVI</b>	17	269–270	79.97	6.04	4.26	C <sub>22</sub> H <sub>20</sub> NO <sub>2</sub>	80.00	6.06	4.24
<b>XLVII</b>	15	154	82.73	5.90	3.46	C <sub>28</sub> H <sub>24</sub> NO <sub>2</sub>	82.75	5.91	3.45
<b>XLVIII</b>	54	270	84.50	5.64	9.86	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub>	84.51	5.63	9.86
<b>XLIX</b>	52	263	84.47	5.62	9.87	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub>	84.51	5.63	9.86
<b>L</b>	50	267	84.49	5.58	9.84	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub>	84.51	5.63	9.86
<b>LII</b>	47	241	73.54	4.70	6.57	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S	73.58	4.72	6.60
<b>LIII</b>	49	235	73.56	4.74	6.58	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S	73.58	4.72	6.60
<b>LIV</b>	50	243	73.59	4.67	6.62	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S	73.58	4.72	6.60
<b>LVI</b>	42	210	73.38	4.69	7.74 (9.70)	C <sub>22</sub> H <sub>17</sub> ClN <sub>2</sub> O	73.33	4.73	7.77 (9.72)
<b>LVII</b>	37	198	73.29	4.75	7.80 (9.74)	C <sub>22</sub> H <sub>17</sub> ClNO <sub>2</sub>	73.33	4.73	7.77 (9.72)
<b>LVIII</b>	30	218–219	73.35	4.69	7.79 (9.74)	C <sub>22</sub> H <sub>17</sub> ClNO <sub>2</sub>	73.33	4.73	7.77 (9.72)

<sup>a</sup> The melting points correspond to those reported in [4].

region 2860–2840 cm<sup>-1</sup> arise from stretching vibrations of C–H bonds in the methoxy groups of compounds **XXXV**, **XLIV**, **XLV**, and **XLVII**. The IR spectra of **XLVIII–L** are characterized by the presence of two N–H stretching vibration bands at 3430–3410 and 3550–3530 cm<sup>-1</sup>, N–H bending vibration bands at 1630–1625 cm<sup>-1</sup>, and C–N stretching vibration bands at 1310–1300 cm<sup>-1</sup>, which correspond to the primary amino group.

Compounds **LII–IV** show in the IR spectra absorption bands at 1350–1340 and 1170–1160 cm<sup>-1</sup> due to asymmetric and symmetric vibrations of the S=O

group. A strong carbonyl absorption band is observed in the spectra of compounds **LVI–LVIII** in the region 1650–1640 cm<sup>-1</sup>.

The mass spectra of benzoquinolines **XXVI–L** and their derivatives **LII–LIV** and **LVI–LVIII** indicate that these compounds are unstable under electron impact. The most abundant ion (100%) is [M–2]<sup>+</sup>; also, [M–1]<sup>+</sup> (40–46%), [M–2–CH<sub>3</sub>]<sup>+</sup> (25–30%), M<sup>+</sup> (20–25%), [M–R]<sup>+</sup> (20–25%), and R<sup>+</sup> (30–35%) ion peaks are observed. Compounds **LII–LIV** show in the mass spectra peaks with m/z 268 (55–60%), which correspond to the [M–NHSO<sub>2</sub>Ph]<sup>+</sup> ion.

**Table 2.**  $^1\text{H}$  NMR spectra of 3-aryl-1-methylbenzo[f]quinolines **XXVI–XLVII** and their derivatives **XLVIII–L**, **LII–LIV**, and **LVI–LVIII** (2–5% solutions in  $\text{DMSO-}d_6$ )

Compound no.	Chemical shifts $\delta$ , ppm ( <i>J</i> , Hz)	
	Me, s	PhR
<b>XXVI</b>	3.10	7.20–7.45 m, 7.50–7.70 m, 7.90–8.10 m, 8.20–8.40 m, 8.50–8.70 m, 8.90 d (7.0)
<b>XXVII</b>	3.20	7.30–7.50 m, 7.60–7.80 m, 8.00–8.20 m, 8.25–8.40, 8.70 d (7.6)
<b>XXVIII</b>	3.20	7.50–7.80 m, 7.90–8.10 m, 8.40 d (7.5), 8.90 d (7.0)
<b>XXIX</b>	3.20	7.10 d (7.0), 7.30 d (7.8), 7.80 d (8.2), 8.10–8.30 m, 8.90 d (8.0)
<b>XXX</b>	3.25	7.40–7.60 m, 8.00 d (7.4), 8.10–8.20 m, 8.30 s, 8.40 d (7.6), 8.60 d (7.0), 8.90 d (8.0)
<b>XXXI</b>	3.15	6.90 d (8.2), 7.50–7.70 m, 7.90 d (7.2), 8.10 d (7.8), 8.90 d (8.0), 9.40 s (1H, OH)
<b>XXXII</b>	3.10	3.18 s (6H, 2CH <sub>3</sub> ), 6.80 d (7.9), 6.95 d (8.0), 7.00 d (8.4), 7.30 d (7.0), 7.40–7.50 m, 7.90–8.10 m, 8.90 d (7.6)
<b>XXXIII</b>	3.15	1.20 t (6H, 2CH <sub>2</sub> CH <sub>3</sub> ), 2.50 q (4H, 2CH <sub>2</sub> CH <sub>3</sub> ), 6.80 d (7.0), 7.60–7.80 m, 7.90–8.20 m, 8.90 d (7.0)
<b>XXXIV</b>	3.10	1.20 t (3H, CH <sub>2</sub> CH <sub>3</sub> ), 2.60 q (2H, CH <sub>2</sub> CH <sub>3</sub> ), 7.20–7.40 m, 7.60–7.70 m, 7.80–8.20 m, 8.90 d (7.0)
<b>XXXV</b>	3.32	3.90 s (3H, OCH <sub>3</sub> ), 7.20 d (8.0), 7.82 q, 8.16 d (7.3), 8.20 d (7.5), 8.30–8.36 m, 9.00 d (7.0)
<b>XXXVI</b>	3.25	1.50 t (3H, OCH <sub>2</sub> CH <sub>3</sub> ), 4.70 q (2H, OCH <sub>2</sub> CH <sub>3</sub> ), 6.70–6.90 m, 7.10 d (7.0), 7.80–8.10 m, 8.90 d (7.0)
<b>XXXVII</b>	3.15	0.80 t (3H, OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.50 q (2H, OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 3.50 t (2H, OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 6.60–6.90 m, 7.00 d (7.0), 7.90–8.10 m, 8.95 d (7.0)
<b>XXXVIII</b>	3.20	2.00 s (3H, SCH <sub>3</sub> ), 7.10 d (8.0), 7.80 q, 8.20 d (7.0), 8.30–8.45 m, 9.00 d (7.0)
<b>XXXIX</b>	3.18	6.70 d (7.3), 6.90 d (7.5), 7.40 t, 7.60–7.80 m, 8.00–8.20 m, 8.90 d (7.0), 9.70 s (1H, OH)
<b>XL</b>	3.25	7.60–7.70 m, 7.75 t, 7.87–8.02 m, 8.10 s, 8.26 d (7.0), 8.65 d (7.0), 8.82 d (7.0), 9.2 s
<b>XLI</b>	3.20	7.00–7.20 m, 7.30–7.60 m, 7.70–7.90 m, 8.00–8.20 m, 8.90 d (7.2)
<b>XLII</b>	3.30	7.30–7.50 m, 8.00 d (7.0), 8.20–8.40 m, 8.60 d (7.0), 8.90 d (8.0)
<b>XLIII</b>	3.30	2.90 s (3H, OCH <sub>3</sub> ), 7.70 d (7.2), 7.75–7.90 m, 8.00 q, 8.94 d (7.0)
<b>XLIV</b>	3.10	3.90 s (3H, OCH <sub>3</sub> ), 4.10 s (3H, OCH <sub>3</sub> ), 7.10–7.20 m, 7.40–7.50 m, 7.60–7.80 m, 7.90–8.10 m, 8.80 d (7.1)
<b>XLV</b>	3.40	3.90 s (3H, OCH <sub>3</sub> ), 4.03 s (3H, OCH <sub>3</sub> ), 7.05 q, 7.60 d (7.4), 7.80 t, 8.10 d (7.0), 8.20 d (6.5), 8.90 d (7.0), 9.60 d (8.0)
<b>XLVI</b>	3.40	1.49 t (3H, OCH <sub>2</sub> CH <sub>3</sub> ), 4.30 q (2H, OCH <sub>2</sub> CH <sub>3</sub> ), 7.00 d (7.0), 7.70–7.90 m, 8.00 s, 8.10 d (7.2), 8.30 d (7.0), 8.60 d (7.8), 8.90 d (7.6)
<b>XLVII</b>	3.19	3.90 s (3H, OCH <sub>3</sub> ), 5.20 s (2H, OCH <sub>2</sub> ), 6.80–7.20, 7.30–7.60 m, 7.80–7.90 m, 8.00–8.20 m, 8.80 d (7.0)
<b>XLVIII</b>	3.15	5.50 s (2H, NH <sub>2</sub> ), 6.70 d (8.3), 7.60–7.80 m, 7.90–8.20 m, 8.80 d (8.2)
<b>XLIX</b>	3.15	5.45 s (2H, NH <sub>2</sub> ), 6.60 d (8.0), 7.50–7.80 m, 8.00–8.20 m, 8.60 d (8.0)
<b>L</b>	3.10	5.50 s (2H, NH <sub>2</sub> ), 6.70 d (8.0), 7.40–7.60 m, 7.80–8.00 m, 8.50 d (8.0)
<b>LII</b>	3.30	6.50 d (8.0), 7.00 s, 7.50–7.70 m, 7.90–8.10 m, 8.20–8.40 m, 8.70 d (7.8)
<b>LIII</b>	3.30	6.60 d (8.0), 7.10 s, 7.40–7.60 m, 7.80–8.00 m, 8.30–8.50 m, 8.60 d (7.6)
<b>LIV</b>	3.35	6.60 d (8.0), 7.00 s, 7.50–7.70 m, 7.90–8.20 m, 8.30–8.50 m, 8.80 d (7.5)
<b>LVI</b>	3.30	4.25 d (2H, CH <sub>2</sub> Cl), 6.40 d (7.8), 7.10–7.30 m, 7.80–8.10 m, 8.30–8.45 m, 8.60 d (7.5)
<b>LVII</b>	3.25	4.20 d (2H, CH <sub>2</sub> Cl), 6.30 d (7.6), 7.00–7.30 m, 7.80–8.10 m, 8.30–8.40 m, 8.70 d (7.6)
<b>LVIII</b>	3.20	4.20 d (2H, CH <sub>2</sub> Cl), 6.35 d (7.6), 7.10–7.40 m, 7.90–8.30 m, 8.40–8.60 m, 8.80 d (7.5)

The electron absorption spectra of compounds **XXVI–L**, **LII–LIV**, and **LIV–LVIII** appear in the ultraviolet region, and the positions of absorption maxima therein are similar to those in the spectra of naphthalene compounds [14]. The absorption curve

has two long-wave absorption maxima which are displaced to longer wavelength relative to the corresponding bands of benzo[f]quinoline. Obviously, this is the result of extension of the conjugated bond system due to addition of the aryl fragment. Introduc-

tion of donor substituents into the *para* position of the benzene ring (compounds **XXXI–XXXVII**) leads to a red shift of the absorption maximum. Acceptor substituents in the *para* position of the benzene ring (compounds **XXVII–XXX**) induce a blue shift of the absorption maximum [15].

Table 2 contains the  $^1\text{H}$  NMR spectral parameters of compounds **XXVI–XLVII**, **LII–LIV**, and **LVI–LVIII**. All these characteristically show a singlet at 3.10–3.40 ppm from the methyl group on  $\text{C}^1$  and a doublet at  $\delta$  8.80–9.10 from 5-H. These data support the structure of 3-aryl-1-methylbenzo[f]quinolines, specifically the position of the methyl group on the  $\text{C}^1$  atom [16].

### EXPERIMENTAL

The IR spectra were recorded on a Protege-460 (Nicolet) spectrometer. The  $^1\text{H}$  NMR spectra were obtained on Bruker DRX 500 (500 MHz) and Tesla BS-567A (100 MHz) spectrometers. The chemical shifts were measured relative to TMS as internal reference. The mass spectra were run on a Finnigan MAT Inco 50 instrument (electron impact, 70 eV). The UV spectra were measured on a Specord UV-Vis spectrophotometer in ethanol ( $c = 1 \times 10^{-4}$  M).

**3-Aryl-1-methylbenzo[f]quinolines XXVI–XLVII.** A solution of 0.58 g (0.01 mol) of acetone (**I**), 0.01 mol of benzaldehyde **III–XXV**, 1.43 g (0.01 mol) of 2-aminonaphthalene (**II**), and 3–7 drops of concentrated hydrochloric acid in 20–30 ml of ethanol was refluxed for 1–7 h. The mixture was cooled, and the precipitate was filtered off, treated with aqueous ammonia (for neutralization), and recrystallized from ethanol–benzene (2:1).

**3-(Aminophenyl)-1-methylbenzo[f]quinolines XLVIII–L.** A solution of 3 g (0.015 mol) of  $\text{SnCl}_2$  in 3 ml of concentrated hydrochloric acid was added to a mixture of 1 g (0.03 mol) of 1-methyl-3-(nitrophenyl)benzo[f]quinoline **XXX**, **XL**, or **XLII** and 10 ml of isopropyl alcohol. The mixture was heated for 1 h on a water bath, cooled, and treated with a 40% solution of sodium hydroxide with addition of ice. The product was filtered off, washed with water until neutral washings, and recrystallized from toluene.

**1-Methyl-3-(phenylsulfonylamino)phenyl)benzo[f]quinolines LII–LIV.** Benzenesulfonyl chloride (**LI**), 0.5 g (0.003 mol), was added to a solution of 1 g (0.003 mol) of 3-(aminophenyl)-1-methylbenzo[f]quinoline **XLVIII–L** in 5 ml of freshly distilled pyridine, and the mixture was heated for 2 h on a boiling water bath. The mixture was cooled and

poured into 50 ml of water. The oily product separated and solidified on cooling. It was filtered off and recrystallized thrice from alcohol–toluene (1:3).

**3-(Chloroacetylaminophenyl)-1-methylbenzo[f]quinolines LVI–LVIII.** Boron trifluoride–ether complex, 5 ml, and chloroacetone (**LV**), 4.6 g (0.05 mol), were added to a solution of 1 g (0.03 mol) of 3-(aminophenyl)-1-methylbenzo[f]quinoline **XLVIII–L** in 20 ml of dioxane, and the mixture was heated for 30–40 min on a boiling water bath. The solvent was distilled off, and the crystals were treated with aqueous ammonia and recrystallized from alcohol–toluene (1:3).

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