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New One-Step Procedure for the Synthesis of 6*H*-Chromeno[4,3-*b*]quinolines and 8a,9,14,14a-Tetrahydro-8*H*-benzo[5,6]chromeno[4,3-*b*]quinolines

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Abstract—Schiff bases generated *in situ* from substituted anilines and 2-allyloxybenzaldehyde underwent acid-catalyzed intramolecular Diels–Alder reaction followed by dehydrogenation to give 6*H*-chromeno[4,3-*b*]-quinolines. Under analogous conditions, derivatives of 2-allyloxynaphthalene-1-carbaldehyde were converted into 8a,9,14,14a-tetrahydro-8*H*-benzo[5,6]chromeno[4,3-*b*]quinolines. Possible dehydrogenation mechanisms are discussed.

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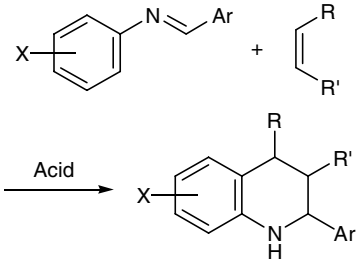
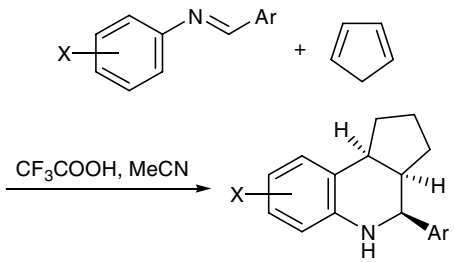
Multicomponent cascade transformations directly leading to target compounds are the most efficient methods for the synthesis of complex structures. Such synthetic schemes are highly convergent; in addition, an advantage of these procedures is that they may formally be regarded as one-step, which compensates for moderate or even relatively poor yields. Among a large number of known transformations of this sort, a specific place is occupied by reactions of Schiff bases with alkenes, which lead to 1,2,3,4-tetrahydroquinoline derivatives [1] (Scheme 1).

Scheme 1.



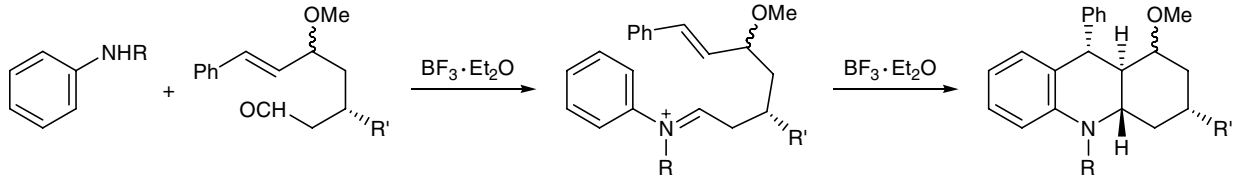
These reactions are catalyzed by Lewis or protic acids; Schiff bases may be generated *in situ*; nucleophilic and/or strained alkenes, e.g., vinyl ethers (or, less frequently, styrenes), may be used as substrates [1]. Reactions of cyclopentadiene in combination with benzaldehydes under catalysis by trifluoroacetic acid in acetonitrile are very popular; in these cases, the process is regio- and stereoselective [2] (Scheme 2). A known and obvious disadvantage of the above scheme is low positional selectivity in reactions with *meta*-substituted anilines.

Scheme 2.



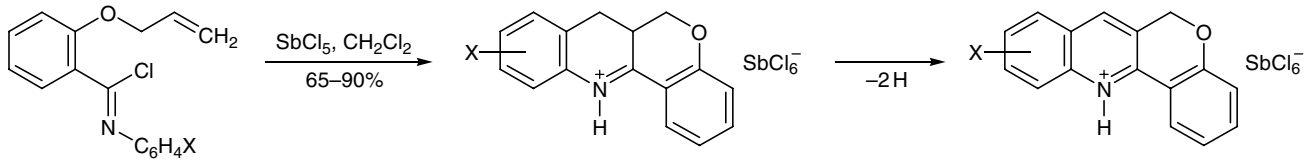
There are reasons to believe that such cyclocondensations involve the reverse Diels–Alder reaction (where alkene acts as dienophile) as the key stage [3]. This mechanism requires definite electronic properties of both alkenes and substituents in Schiff bases. Obviously, electron-withdrawing substituents should favor the process, unless the formation of Schiff bases is hampered by low nucleophilicity of the aniline (as in reactions with 2,4-dinitroaniline and related compounds). Numerous 1,2,3,4-tetrahydroquinoline derivatives were synthesized in such a way [1, 4, 5]; however, only two examples of intramolecular reaction of Schiff bases with alkenes were reported despite obvious prospects in applying such approach to the synthesis of more complex fused systems. The first attempt to effect intramolecular condensation of Schiff

Scheme 3.

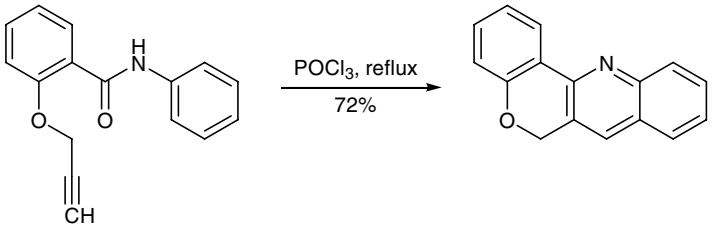


R = H, Me; R' = $(MeOCO)_2CH$, $(EtOCO)_2CH$, PhS.

Scheme 4.



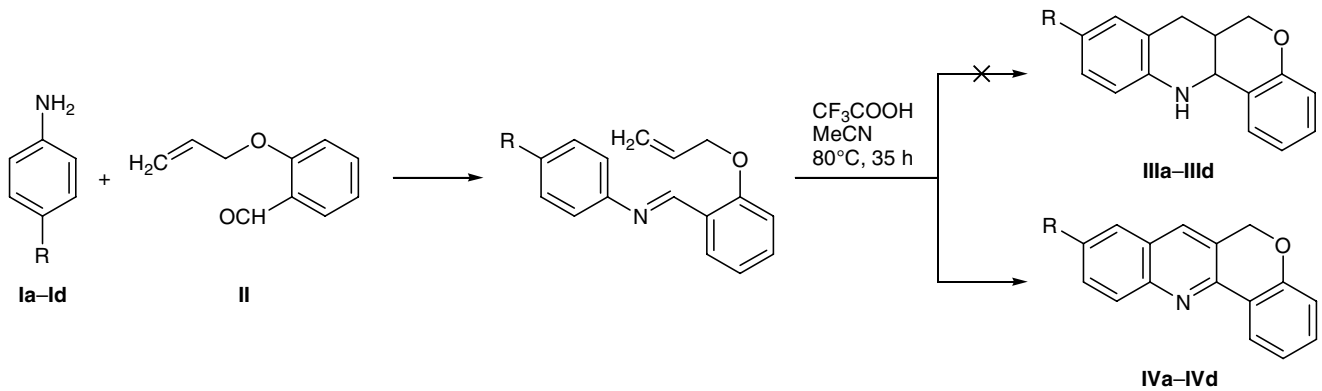
X = H, 4-Cl, 4-Me.



base having a vinyl ether fragment (genarated *in situ*) was unsuccessful [6]. A few later successful attempts are illustrated by Schemes 3 [7] and 4 [8, 9].

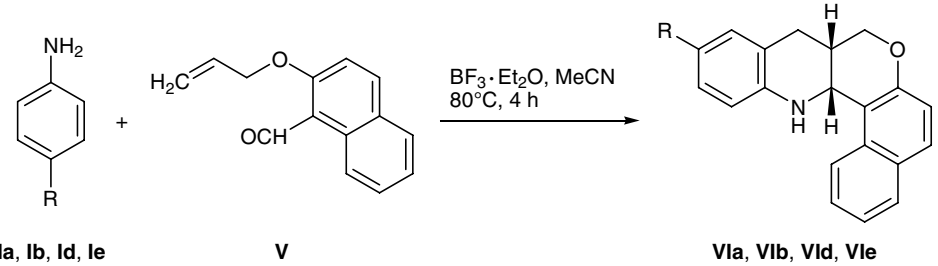
Therefore, we believed it to be reasonable to examine the possibility for synthesizing 6a,7,12,12a-tetrahydro-6*H*-chromeno[4,3-*b*]quinolines from Schiff bases generated *in situ* from the corresponding substituted anilines **Ia**–**Id** and 2-allyloxybenzaldehyde (**II**); the initial compounds are readily accessible, and their structures may be varied over a wide range. We found that the intramolecular cyclization of intermediate Schiff bases occurs at a low rate under fairly severe conditions and that the products were not expected 6a,7,12,12a-tetrahydro-6*H*-chromeno[4,3-*b*]-quinolines **IIIa**–**IIId** but their dehydrogenated derivatives **IVa**–**IVd** (Scheme 5). By reactions of anilines **Ia**, **Ib**, **Id**, and **Ie** with 2-allyloxynaphthalene-1-carbaldehyde (**V**) we obtained 8a,9,14,14a-tetrahydro-8*H*-benzo[5,6]chromeno[4,3-*b*]quinolines **VIa**, **VIb**, **VId**, and **VIe** (Scheme 6). In the reactions catalyzed by CF_3COOH and CH_3SO_3H, the yields of **VIa** were 41 and 40%, respectively; when the reaction with **Ib** was carried out in boiling DMF (reaction time 4 h), the yield of **VIb** was 44%.

Scheme 5.



R = O_2N (**a**, 15%), HOCO (**b**, 9%), EtOCO (**c**, 13%), Me (**d**, 10%).

Scheme 6.



Ia, **Ib**, **Id**, **Ie** **V** **VIa**, **VIb**, **VId**, **VIe**

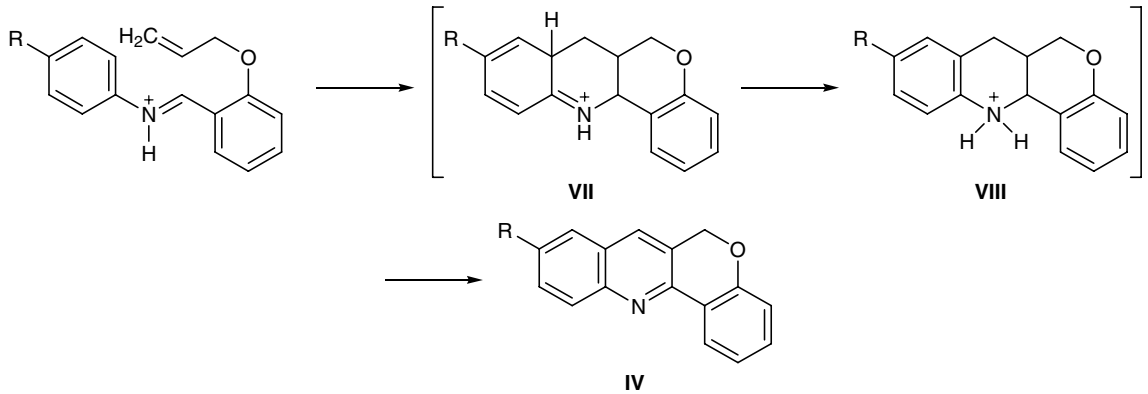
R = O_2N (**a**, 60%), HOCO (**b**, 89%), Me (**d**, 57%), Cl (**e**, 51%).

Thus, unlike aldehyde **II**, the cyclization of naphthalenecarbaldehyde derivatives was not accompanied by dehydrogenation. Moreover, compounds **VIa**, **VIb**, **VId**, and **VIe** were formed as a single diastereoisomer, and their ^{1}H NMR spectra were similar. The coupling constant between protons on C^{8a} and C^{14a} (J = 3.6 Hz) in compound **VIa** was determined from the two-dimensional ^{1}H–^{1}H COSY spectrum; its value indicates *cis* junction of the pyran and piperidine rings. An analogous structure was assigned to compounds **VIb**, **VId**, and **VIe**, taking into account similarity of their spectral parameters.

Most probably, dehydrogenated products **IVa**–**IVd** are formed as a result of oxidation of the primary Diels–Alder adduct, iminocyclohexadiene **VII**, or its isoaromatization product, protonated tetrahydroquinoline **VIII** (Scheme 7). However, our attempts to raise the yield by adding nitrobenzene as oxidant to the system (as in the Skraup synthesis of quinolines), bubbling oxygen through the reaction mixture, or carrying out the reaction in the presence of 10% Pd/C were unsuccessful. Either two other iminocyclohexadiene **VII** molecules or two molecules of the Schiff base could act as hydrogen acceptor (oxidant). In the two cases, the theoretical yield of compounds **IVa**–**IVd** should not exceed 33%. Hydrogen donor may be either iminocyclohexadiene **VII** or its isoaromatization product **VIII**. We tried to detect possible intermediates by analysis of the ^{1}H NMR spectra of the reaction mixture using acetonitrile-d_3 as solvent. Taking into account that the preparative yield of compound **IVa** was 11%, at least 22% of the reduction product (containing aliphatic fragments) should be formed, i.e., the relative intensity of signals from protons in these compounds should be sufficient to identify them. However, we observed no signals in the δ region 0.5–3.0 ppm, typical of aliphatic protons. Therefore, iminocyclohexadiene **VII** is not hydrogen acceptor in the process under study. On the other hand, no definite conclusion concerning hydrogen donor may be drawn on the basis of the absence of aliphatic proton signals, for either intermediate, **VII** or **VIII**, can be consumed at a much higher rate than the rate of its formation. The above findings suggest that the most probable hydrogen acceptor is Schiff base.

By carrying out the reaction in a hermetically closed ampule at 150°C (oil bath) for 4 h we succeeded in raising the yield of compounds **VIa** and **VIb** to 26 and 19%, respectively, but the yield of **IVc** and **IVd** did not change. The formation of unoxidized products **VI** in the reaction with aldehyde **V** may be rationalized in terms of hindered approach of the

Scheme 7.



VII **VIII** **IV**

reaction centers of two Schiff base molecules acting as hydrogen acceptors to intermediates like **VI** or **VIII** for steric reasons.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C). The chemical shifts were measured relative to the solvent signals ($CHCl_3$, δ 7.26 ppm; DMSO-d_5, δ 2.49 ppm; $CDCl_3$, δ_C 77.0 ppm; DMSO-d_6, δ_C 39.7 ppm). The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 mass spectrometer. The elemental compositions were determined on a Hewlett–Packard 185B automatic CHN-analyzer. Analytical TLC was performed on Silufol UV-254 plates.

2-Allyloxybenzaldehyde (II). A mixture of 13.4 g (0.11 mol) of salicylaldehyde, 12.1 g (0.1 mol) of allyl bromide, 18.0 g (0.13 mol) of anhydrous K_2CO_3, and 0.5 g of potassium iodide in 50 ml of DMF was stirred for 2 h at 60–70°C. The mixture was cooled, poured into 500 ml of cold water, and extracted with hexane–diethyl ether (1:1, 3×100 ml). The extracts were combined, washed with 5% aqueous potassium hydroxide and water, dried over K_2CO_3, and evaporated, and the residue was distilled under reduced pressure. Yield 12.9 g (80%), bp 90–95°C (1 mm); published data [10]: bp 130°C (10 mm).

9-Nitro-6*H*-chromeno[4,3-*b*]quinoline (IVa). A mixture of 2.00 g (12.4 mmol) of 2-allyloxybenzaldehyde (**II**), 1.62 g (11.8 mmol) of *p*-nitroaniline (**Ia**), and 1.55 g (13.6 mmol) of trifluoroacetic acid in 15 ml of acetonitrile was heated for 4 h at 150°C (oil bath) in a hermetically closed ampule. The mixture was evaporated on a rotary evaporator, the residue was dissolved in 50 ml of methylene chloride, the solution was washed with a saturated solution of $NaHCO_3$ (2×40 ml) and evaporated, and the residue was recrystallized from propan-2-ol. Yield 0.90 g (26%), mp 235–237°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.14 s (2H), 7.06 d (1H, *J* = 6.0 Hz), 7.21 t (1H, *J* = 7.7 Hz), 7.46 t (1H, *J* = 7.7 Hz), 8.04 s (1H), 8.23 d (1H, *J* = 9.3 Hz), 8.48 d.t (1H, *J* = 8.5, 2.3 Hz), 8.74 d (1H, *J* = 2.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 68.0; 117.5, 122.3, 122.7, 123.0, 124.0, 126.0, 126.2, 127.1, 130.9, 132.3, 133.2, 145.0, 150.4, 152.4, 157.9. Mass spectrum, *m*/*z* (I_{rel}, %): 278 (36) M^+, 231 (33), 203 (39), 176 (30), 101 (43), 88 (91), 75 (82), 63 (100), 51 (63), 39 (70). Found, %: C 67.80; H 3.59; N 9.74. $C_{16}H_{10}N_2O_3$. Calculated, %: C 68.09; H 3.55; N 9.93. *M* 278.27.

6*H*-Chromeno[4,3-*b*]quinoline-9-carboxylic acid (IVb) was synthesized in a similar way from 2.00 g (12.4 mmol) of 2-allyloxybenzaldehyde (**II**) and 1.3 g (11.8 mmol) of *p*-aminobenzoic acid (**Ib**) in the presence of 1.6 g (13.6 mmol) of CF_3COOH. Yield 0.60 g (19%), mp 259–261°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.41 s (2H), 6.98 d (1H, *J* = 7.7 Hz), 7.13 d.t (1H, *J* = 7.7, 1.0 Hz), 7.39 d.t (1H, *J* = 8.5, 1.5 Hz), 8.04 d (1H, *J* = 8.5 Hz), 8.19 d.d (1H, *J* = 10.0, 2.3 Hz), 8.24 s (1H), 8.41 d.d (1H, *J* = 9.3, 1.6 Hz), 8.54 d (1H, *J* = 1.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 67.5, 117.4, 122.3, 122.4, 125.4, 125.9, 126.6, 128.2, 129.0 (2C), 130.5, 132.7, 132.9, 149.2, 150.1, 157.4, 166.9. Mass spectrum, *m*/*z* (I_{rel}, %): 278 (70) $[M + 1]^+$, 276 (100), 232 (24), 203 (16), 176 (8), 102 (7), 88 (9), 75 (10), 63 (13), 45 (20), 39 (12). Found, %: C 82.53; H 5.40; N 5.72. $C_{17}H_{11}NO_3$. Calculated, %: C 82.59; H 5.26; N 5.67. *M* 277.28.

Ethyl 6*H*-chromeno[4,3-*b*]quinoline-9-carboxylate (IVc). A mixture of 2.00 g (12.4 mmol) of 2-allyloxybenzaldehyde (**II**), 2.05 g (12.4 mmol) of ethyl *p*-aminobenzoate (**Ic**), and 1.6 g (13.6 mmol) of trifluoroacetic acid in 15 ml of acetonitrile was heated for 35 h under reflux. The precipitate was filtered off, washed in succession with propan-2-ol and diethyl ether, and dried in air. Yield 0.50 g (13%), mp 172–174°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.48 t (3H, *J* = 7.3 Hz), 4.47 q (2H, *J* = 7.3 Hz), 5.39 s (2H), 7.05 d (1H, *J* = 8.0 Hz), 7.19 t (1H, *J* = 7.6 Hz), 7.43 d.t (1H, *J* = 8.0, 1.4 Hz), 7.96 s (1H), 8.16 d (1H, *J* = 8.7 Hz), 8.30 d.d (1H, *J* = 8.7, 1.5 Hz), 8.50 d.d (1H, *J* = 7.3, 1.4 Hz), 8.54 d (1H, *J* = 2.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.2, 61.1, 68.0, 117.3, 122.4, 122.6, 125.6, 125.7, 126.5, 127.7, 128.9, 129.3, 130.2, 131.8, 132.3, 150.0, 150.8, 157.5, 166.0. Mass spectrum, *m*/*z* (I_{rel}, %): 305 (100) M^+, 304 (69), 276 (48), 260 (32), 233 (33), 203 (22), 130 (45), 116 (34), 102 (20), 88 (28), 63 (16). Found, %: C 73.70; H 4.06; N 4.96. $C_{19}H_{15}NO_3$. Calculated, %: C 73.65; H 3.97; N 5.05. *M* 305.34.

9-Methyl-6*H*-chromeno[4,3-*b*]quinoline (IVd) was synthesized in a similar way from 2.00 g (12.4 mmol) of 2-allyloxybenzaldehyde (**II**) and 1.3 g (12.1 mmol) of *p*-toluidine (**Id**) in the presence of 1.6 g (13.6 mmol) of CF_3COOH. Yield 0.3 g (10%), mp 120–122°C [11]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.55 s (3H), 5.35 s (2H), 7.04 d (1H, *J* = 8.7 Hz), 7.18 t (1H, *J* = 7.3 Hz), 7.21 d.t (1H, *J* = 7.3, 1.5 Hz), 7.54 d.d (2H, *J* = 7.3, 1.5 Hz), 8.04 d (1H, *J* = 9.4), 8.49 d.d (1H, *J* = 8.0, 1.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.4, 68.3, 117.1, 122.3, 123.3,

125.0, 125.2, 126.2, 127.5, 129.0, 130.1, 131.4, 131.6, 136.0, 146.8, 148.0, 151.7. Mass spectrum, *m*/*z* (I_{rel}, %): 247 (76) M^+, 246 (100), 232 (12), 217 (11), 203 (8), 124 (17), 118 (10), 96 (13), 77 (4), 63 (7), 39 (8). Found, %: C 74.62; H 4.97; N 4.52. $C_{17}H_{13}NO$. Calculated, %: C 74.75; H 4.92; N 4.59. *M* 247.30.

2-Allyloxynaphthalene-1-carbaldehyde (V) was synthesized as described above for aldehyde **II**. Yield 80%, mp 77–78°C (from hexane) [12].

11-Nitro-8a,9,14,14a-tetrahydro-8*H*-benzo[5,6]-chromeno[4,3-*b*]quinoline (VIa). A mixture of 0.65 g (4.72 mmol) of *p*-nitroaniline (**Ia**), 1.00 g (4.72 mmol) of aldehyde **V**, and 0.73 g (5.17 mmol) of $BF_3 \cdot Et_2O$ in 15 ml of acetonitrile was heated for 35 h under reflux. The mixture was evaporated on a rotary evaporator, the residue was dissolved in 30 ml of methylene chloride, the solution was washed with a saturated solution of $NaHCO_3$ and water and evaporated, and the residue was recrystallized from propan-2-ol. mp 235–237°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.7 m (1H), 2.86 d.d (1H, *J* = 17.1, 1.5 Hz), 3.38 d.d (1H, *J* = 16.7, 5.8 Hz), 3.95 t (1H, *J* = 12.0 Hz), 4.21 d.d (1H, *J* = 10.9, 3.6 Hz), 4.93 s (1H), 5.12 d (1H, *J* = 3.6 Hz), 6.36 d (1H, *J* = 6.5 Hz), 7.13 d (1H, *J* = 8.7 Hz), 7.43 t (1H, *J* = 7.6 Hz), 7.6 d.t (1H, *J* = 7.6, 1.5 Hz), 7.78 d (1H, *J* = 8.7 Hz), 7.86 d (1H, *J* = 8.0 Hz), 7.93 d.d (1H, *J* = 8.7, 2.2 Hz), 8.00 d (1H, *J* = 8.0 Hz), 8.01 s (1H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.2, 27.3, 44.0, 64.5, 112.6, 114.1, 116.4, 118.8, 122.5, 123.7, 124.2, 125.8, 127.3, 128.6, 128.8, 130.1, 132.6, 135.8, 149.1, 151.33. Mass spectrum, *m*/*z* (I_{rel}, %): 332 (51) M^+, 302 (24), 285 (20), 186 (22), 182 (46), 181 (100), 175 (25), 152 (26), 148 (30), 147 (31). Found, %: C 72.96; H 4.87; N 7.96. $C_{17}H_{13}NO$. Calculated, %: C 72.29; H 4.82; N 8.43. *M* 332.36.

8a,9,14,14a-Tetrahydro-8*H*-benzo[5,6]chromeno-[4,3-*b*]quinoline-11-carboxylic acid (VIb). A mixture of 0.65 g (4.72 mmol) of *p*-aminobenzoic acid (**Ib**), 1.00 g (4.72 mmol) of aldehyde **V**, and 0.73 g (5.17 mmol) of $BF_3 \cdot Et_2O$ in 15 ml of acetonitrile was heated for 35 h under reflux. The mixture was evaporated on a rotary evaporator, the residue was dissolved in 50 ml of 5% aqueous sodium hydroxide, the solution was filtered, the filtrate was carefully acidified until a solid material no longer separated, and the precipitate was filtered off and washed on a filter with water. mp 280–282°C (from propan-2-ol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.55 m (1H), 2.78 d (1H, *J* = 18.0 Hz), 3.32 d.d (1H, *J* = 15.0, 6.0 Hz), 3.96 t (1H, *J* = 12.0 Hz), 4.17 d.d (1H, *J* = 9.0, 3.0 Hz), 5.01 d (1H, *J* = 2.9 Hz), 6.56 s (1H), 6.58 d (1H, *J* = 8.7 Hz), 7.05 d (1H, *J* = 9.5 Hz), 7.36 t (1H, *J* = 8.0 Hz), 7.47 d.d (1H, *J* = 8.7, 1.4 Hz), 7.52–7.58 m (2H), 7.74 d (1H, *J* = 9.6 Hz), 7.80 d (1H, *J* = 6.0 Hz), 8.07 d (1H, *J* = 8.0 Hz), 11.5 br.s (1H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 28.6, 28.7, 44.7, 65.6, 113.3, 115.6, 115.8, 118.2, 119.4, 123.1, 123.8, 127.5, 128.9, 129.3, 129.8, 130.1, 131.8, 133.4, 146.9, 151.9, 168.3. Mass spectrum, *m*/*z* (I_{rel}, %): 331 (48) M^+, 330 (23), 187 (12), 182 (20), 181 (100), 174 (23), 166 (15), 152 (15), 115 (21), 77 (11). Found, %: C 76.11; H 5.18; N 4.23. $C_{21}H_{17}NO_3$. Calculated, %: C 76.14; H 5.21; N 4.23. *M* 331.37.

11-Methyl-8a,9,14,14a-tetrahydro-8*H*-benzo-[5,6]chromeno[4,3-*b*]quinoline (VId) was synthesized as described above for compound **VIa**. mp 143–145°C (from hexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.17 s (3H), 2.45 m (1H), 2.63 d (1H, *J* = 16.7 Hz), 3.27 d.d (1H, *J* = 16.7, 6.5 Hz), 4.02–4.14 m (2H), 4.89 d (1H, *J* = 2.9 Hz), 5.29 s (1H), 6.42 d (1H, *J* = 8.0 Hz), 6.66 d (1H, *J* = 8.0 Hz), 6.71 s (1H), 7.04 d (1H, *J* = 9.5 Hz), 7.33 t (1H, *J* = 7.3 Hz), 7.52 t (1H, *J* = 7.6 Hz), 7.71 d (1H, *J* = 8.7 Hz), 7.78 d (1H, *J* = 8.0 Hz), 8.06 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.5, 28.0, 28.9, 44.2, 65.3, 114.0, 115.8, 116.7, 118.8, 122.5, 123.1, 124.5, 126.8, 127.5, 128.3, 128.8, 129.2, 129.5, 132.8, 140.0, 151.4. Mass spectrum, *m*/*z* (I_{rel}, %): 301 (99) M^+, 303 (23), 300 (51), 194 (31), 182 (23), 181 (100), 158 (23), 150 (25), 144 (40), 120 (24). Found, %: C 83.86; H 6.37; N 4.65. $C_{21}H_{19}NO$. Calculated, %: C 83.76; H 6.46; N 4.60. *M* 301.39.

11-Chloro-8a,9,14,14a-tetrahydro-8*H*-benzo-[5,6]chromeno[4,3-*b*]quinoline (VIe) was synthesized in a similar way. mp 180–182°C (from propan-2-ol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.45 m (1H), 2.69 d (1H, *J* = 16.9 Hz), 3.29 d.d (1H, *J* = 17.1, 6.5 Hz), 4.01 d.d (1H, *J* = 12.0, 10.2 Hz), 4.14 d.d (1H, *J* = 10.9, 3.6 Hz), 4.91 d (1H, *J* = 2.9 Hz), 5.93 s (1H), 6.57 d (1H, *J* = 8.7 Hz), 6.82 d.d (1H, *J* = 8.7, 2.2 Hz), 6.91 d (1H, *J* = 1.5 Hz), 7.06 d (1H, *J* = 8.7 Hz), 7.35 t (1H, *J* = 7.6), 7.54 t (1H, *J* = 7.6 Hz), 7.73 d (1H, *J* = 8.7 Hz), 7.8 d (1H, *J* = 8.0 Hz), 8.06 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 28.4, 28.9, 45.0, 65.8, 115.0, 115.2, 119.3, 119.5, 121.7, 121.9, 124.0, 127.6, 127.7, 129.3, 129.4, 130.3, 132.8, 140.5, 152.0. Mass spectrum, *m*/*z* (I_{rel}, %): 323 (18) M^+ (^{37}Cl), 321 (52) M^+ (^{35}Cl), 322 (16), 320 (22), 182 (20), 181 (100), 165 (21), 164 (20), 152 (21), 127 (14). Found, %: C 74.64; H 5.02; N 4.35. $C_{20}H_{16}ClNO$. Calculated, %: C 74.65; H 5.09; N 4.20. *M* 321.81.

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