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Diastereoselective Synthesis of Spiro Derivatives of 3-Substituted 2,3,4,4a,5,6-Hexahydro-1*H*-benzo[*c*]quinolizines

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Abstract—The cyclization via the mechanism of "*tert*-amino effect" of 2-(4-R-piperidino)benzaldehydes with cyclic active methylene components (Meldrum's acid, 1,3-cyclohexanedione, and N,N-disubstituted barbituric acids) proceeded stereoselectively giving spiro-joined 2,3,4,4a,5,6-hexahydro-1*H*-benzo[*c*]quinolizines with axially oriented hydrogen atoms in the positions *3* and *4a* of the benzo[c]quinolizine ring.

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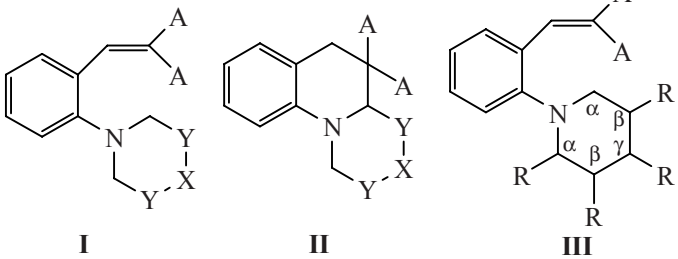
The cyclization reactions of *o*-vinyldialkylanilines **I** to form partially hydrogenized fused pyridines **II** are described in the literature like occurring via the mechanism of "*tert*-amino effect" [1–3]. The designation "*tert*-amino effect" was introduced in [4], and this approach was further developed for the creation of a C–C bond [5]. It was shown formerly that the cyclization of *o*-vinyldialkylanilines **III** containing a substituent at the α-carbon of the dialkylamino group proceeded with a high regio- and stereoselectivity [6, 7]. We described in a short communication [8] that at the introduction of substituents into the β-position with respect to the nitrogen of the cyclic amino group the selective cyclization of compound **III** was also possible.



I **II** **III**

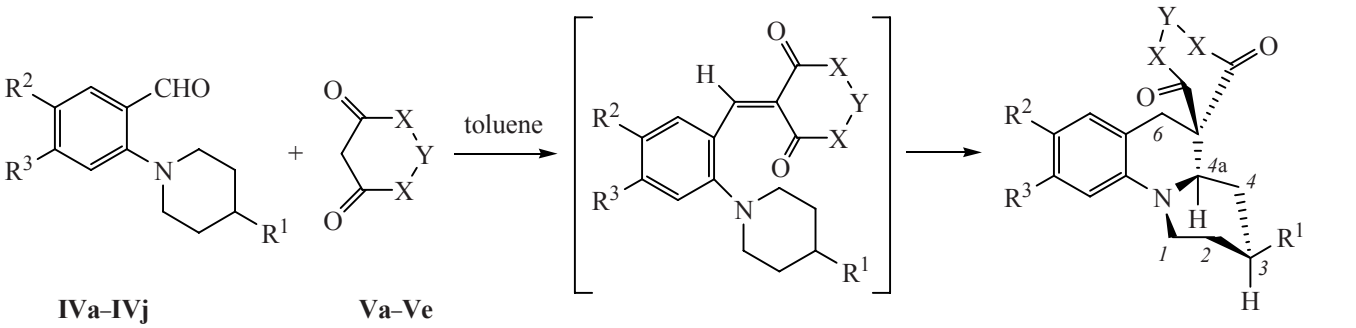
In this report we treat the case when the substituent is located in the γ-position with respect to the nitrogen of the dialkylamino group and descried the stereoselective synthesis of spiro-joined fused quinolines starting from 2-(4-R-piperidino)benzaldehydes **IVa–IVj**. Prior to our preliminary communication [9] no published data existed on a stereoselective cyclization by the mechanism of "*tert*-amino effect" at the use of 4-substituted piperidines [10–13].

The reactions of 2-(4-R-piperidino)benzaldehydes **IVa–IVj** with cyclic CH-active compounds **Va–Ve** at boiling in toluene led to the formation of products of a tandem process of the Knoevenagel reaction and cyclization via '*tert*-amino effect". The reactions proceeded stereoselectively affording exclusively isomers **VI–X** in 65–91% yields (Scheme 1).

In the ^{1}H NMR spectra of compounds **VI–X** in some cases was found the presence of the second isomer in an amount less than 2–3%, and we failed to separate it in a pure form. The structure and relative configuration of the asymmetric carbon atoms on the positions *4*a and *3* of spiro compounds **VI–X** were established by means of 2D correlation ^{1}H and ^{13}C NMR spectroscopy, and also by XRD analysis.

In the ^{1}H NMR spectra of spiro compounds **VI–X** the proton H^{4a} of the benzoquinolizine ring gave rise to a doublet of doublets in the region 3.4–4.1 ppm ($J_{4a,4a}$ 10–15, $J_{4a,4e}$ 1–4 Hz) revealing its axial position. The axial orientation of the proton H^3 of the ring is shown by the multiplicity of the signal of H^{4a} proton whose resonance appeared as a doublet of doublets ($J_{4a,4a}$ 10–15, $J_{4e,4a}$ 10–15, $J_{3,4a}$

Scheme 1.



IVa–IVj **Va–Ve**

VIa–VIe, VIg, VIi, VIIa–VIIe, VIIi, VIIj, VIIIa–VIIIi, IXa, IXd, IXg, IXh, Xa, Xb, Xd, Xf–Xi

IV, VI–X, R^1 = Me, R^2 = H, R^3 = H (**a**), Cl (**b**); R^1 = Ph: R^2 = H, R^3 = H (**c**), Cl (**d**), Br (**e**), F (**f**); R^2 = CF_3, R^3 = H (**g**); R^1 = CH_2Ph, R^2 = H, R^3 = H (**h**), Cl (**i**), Br (**j**); X = Y = CH_2 (**Va**, **VI**); X = CH_2, Y = CMe_2 (**Vb**, **VII**); X = O, Y = CMe_2 (**Vc**, **VIII**); X = NPh, Y = CO (**V**d, **IX**), X = NMe, Y = CO (**Ve**, **X**).

10–15 Hz) in the region 0.8–1.1 ppm. The multiplet of proton H^3 was observed in the region 1.68–1.89 ppm. In the two-dimensional. ^{1}H–^{1}H NMR correlation spectrum the interactions were observed between the atoms H^{4a}, H^3, and H^6 confirming their axial orientation (Fig. 1). Thus three axial protons H^{4a}, H^3, and H^6 are located in the reciprocal *cis*-position on the same side of the molecule.

The carbon atoms in the spiro ring are nonequivalent and have different chemical shifts in the ^{13}C NMR spectrum.

The final proof of the structure of compound **Xf** was obtained by XRD analysis (Fig. 2).

The diastereoselective reaction course may occur by spatial reasons. Evidently at the formation of the benzylidene the double bond is so turned that the equatorial proton at the α-carbon is approached to the double bond, and the substituent in the β-position of the piperidine fragment

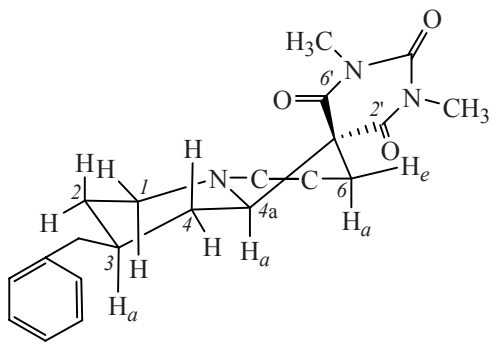


Fig. 1. Relative configuration of spiro compound **Xh**.

is located in the equatorial position due to the effect of the sterical hindrances caused by the presence of a bulky cyclic substituent at the double bond.

This effect is lacking in the reaction with the malonodinitrile [8]; presumably, in this case the cyclization occurs with a high energy barrier and therefore it is accompanied by the isomerization of the intermediate resulting in the formation of two isomers .

In reaction of piperidinobenzaldehydes **IVa, IVg**, and **IVh** with the malonodinitrile in boiling toluene formed benzylidenemalonodinitriles **XIa–XIc** (Scheme 2)**.** Their cyclization along the mechanism of "*tert*-amino effect" occurred at boiling in butanol and resulted in the formation of isomers mixture of benzo[*c*]quinolizines **XII** and **XIII**, 1:1.

In the ^{1}H NMR spectra of compounds obtained a double set of signals was observed demonstrating the formation of diastereomers. Isomers **XII** and **XIII** are distinguished by the axial and equatorial position of the H^3 atom.

Isomer **XIIIb** with the axial proton at the nodal atom C^{4a} and with the equatorial proton at C^3 is less soluble in ethanol, and we succeeded in its isolation by fractional crystallization in 25% yield.

Thus at the presence of a substituent in the γ-position with respect to the nitrogen atom of the cyclic amine the cyclization by the mechanism of "*tert*-amino effect" proceeded diastereoselectively in the case of *ortho*-vinylanilines obtained by the condensation of benzaldehydes with cyclic CH-active compounds.

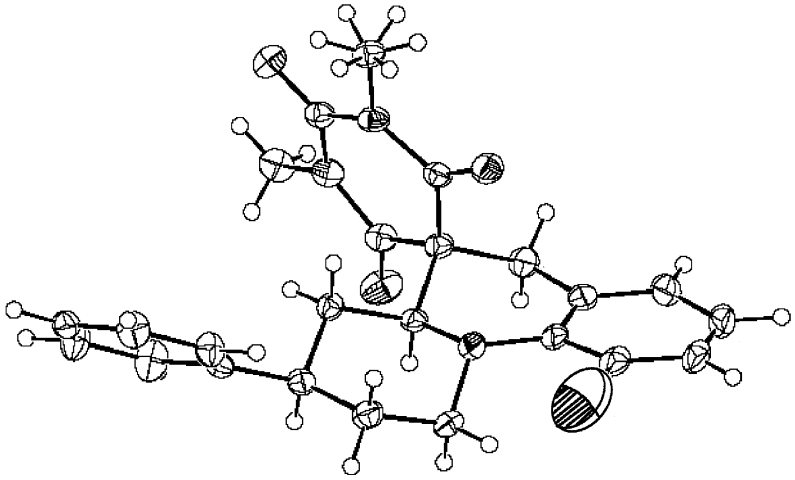


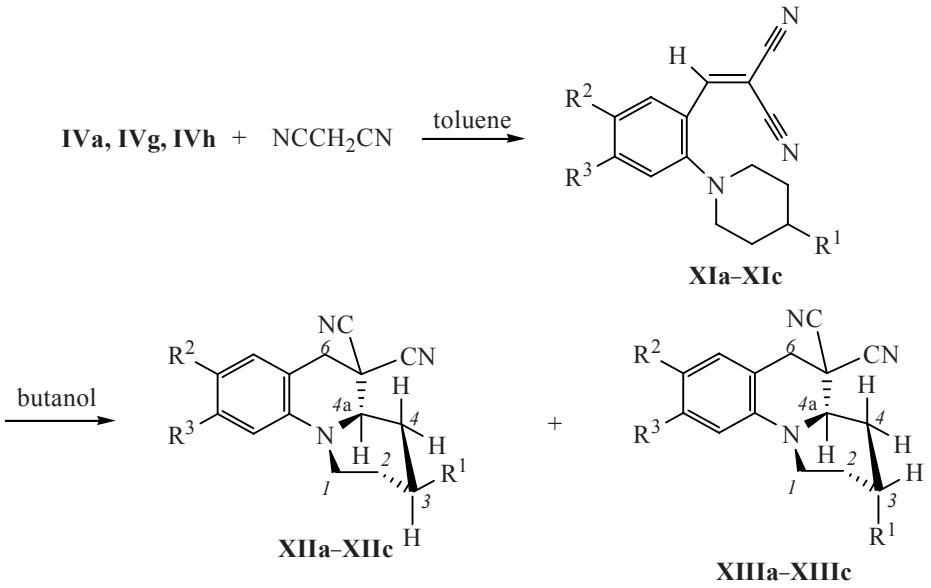
Fig. 2. Structure of compound **Xf** according to XRD data.

EXPERIMENTAL

The reaction progress was monitored and the homogeneity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluents chloroform, chloroform–ethanol, 9:1, 15:1, 20:1, ethyl acetate–hexane, 1.5:2, 1:2. IR spectra were recorded on a spectrophotometer UR-20 from KBr pellets. NMR spectra were registered from solutions in DMSO-d_6 on spectrometers Bruker WM-250 (250 MHz for ^{1}H) and Bruker DRX-400 (400 for ^{1}H and 100 MHz for ^{13}C), internal reference TMS. Mass spectra were measured on mass spectrometers Varian MAT 311A and Finnigan MAT 8200 at the ionizing electrons energy 70 eV at the direct admission of the sample into the ion source. The solvents were purified and dried by standard procedures. Compound **IVc** was described in [8].

Aldehydes IV. To a solution of 10 mmol of 2-fluorobenzaldehyde in 8.0 ml of DMF was added 11 mmol of dialkylamine and 1.52 g (11 mmol) of K_2CO_3. The mixture was boiled on a glycerol bath at 150°C for 20 h. On

Scheme 2.



XI–XIII, $R^1 = CH_3$, $R^2 = R^3 = H$ (**a**); $R^1 = CH_2Ph$, $R^2 = R^3 = H$ (**b**); $R^1 = Ph$, $R^2 = CF_3$, $R^3 = H$ (**c**).

completion of the reaction (TLC monitoring) the reaction mixture was cooled to room temperature, diluted with 75 ml of water, the reaction product was extracted with ethyl acetate (3×60 ml). The combined extracts were washed with an ammonium chloride solution, dried with Na_2SO_4, and evaporated in a vacuum.

2-(4-Methylpiperidin-1-yl)benzaldehyde (IVa). Yield 1.62 g (80%), oily compound. ^{1}H NMR spectrum, δ, ppm: 1.01 d (3H, CH_3, *J* 5.8 Hz), 1.44 d.d.q.d (1H, CH, *J* 11.9, 10.2, 5.8, 3.3 Hz), 1.48–1.58 m (2H, 2CH), 1.76 br.d (2H, 2CH, *J* 11.9 Hz), 2.86 d.d (2H, 2NCH, *J* 11.6, 12.2 Hz), 3.21 br.d (2H, 2NCH, *J* 12.2 Hz), 7.05 d.d.d (1H_{Ar}, *J* 8.3, 7.3, 0.8 Hz), 7.12 d.d (1H_{Ar}, *J* 8.3, 0.8 Hz), 7.50 d.d.d (1H_{Ar}, *J* 7.3, 7.8, 1.5 Hz), 7.65 d.d (1H_{Ar}, *J* 7.8, 1.5 Hz) 10.18 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 203 (98) $[M]^+$. Found, %: C 76.87; H 8.50; N 6.95. $C_{13}H_{17}NO$. Calculated, %: C 76.81; H 8.43; N 6.89.

2-(4-Methylpiperidin-1-yl)-4-chlorobenzaldehyde (IVb). Yield 2.04 g (86%), mp 110–112°C. ^{1}H NMR spectrum, δ, ppm: 1.01 d (3H, CH_3, *J* 6.1 Hz), 2.77–2.93 m (2H, NCH), 3.21–3.27 m (2H, NCH), 3.21–3.27 m (5H, CH, $2CH_2$), 7.04 d (1H_{Ar}, *J* 8.2 Hz), 7.10 s (1H_{Ar}), 7.65 d (1H_{Ar}, *J* 8.2 Hz), 10.07 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 239 (30) $[M+2]^+$, 237 (78) $[M]^+$. Found, %: C 65.78; H 7.00; N 6.01. $C_{13}H_{16}ClNO$. Calculated, %: C 65.68; H 6.78; N 5.89.

2-(4-Phenylpiperidin-1-yl)-4-chlorobenzaldehyde (IVd). Yield 2.27 g (76%), mp 124–126°C. ^{1}H NMR spectrum, δ, ppm: 1.89–1.99 m (4H, $2CH_2$), 2.68 quintet (1H, CHPh, *J* 8.2 Hz), 2.97–3.09 m (2H, NCH_2), 3.34–3.41 m (2H, NCH_2), 7.07 d.d (1H_{Ar}, *J* 8.2, 1.1 Hz), 7.13–7.33 m (6H_{Ar}), 7.68 d (1H_{Ar}, *J* 8.3 Hz), 10.16 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 301 (30) $[M+2]^+$, 299 (78) $[M]^+$. Found, %: C 72.11; H 6.00; N 4.69. $C_{18}H_{18}ClNO$. Calculated, %: C 72.11; H 6.05; N 4.67.

4-Bromo-2-(4-phenylpiperidin-1-yl)benzaldehyde (IVe). Yield 3.03 g (88%), mp 105–108°C. ^{1}H NMR spectrum δ, ppm: 1.85–2.02 m (4H, $2CH_2$), 2.60–2.69 m (1H, CHPh), 2.99–3.11 m (2H, NCH_2), 3.39 d (2H, NCH_2, *J* 11.9 Hz), 7.15–7.33 m (7H_{Ar}), 7.60 d (1H_{Ar}, *J* 8.2 Hz), 10.17 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 346 (80) $[M+2]^+$, 344 (79) $[M]^+$. Found, %: C 62.99; H 5.35; N 4.09. $C_{18}H_{18}BrNO$. Calculated, %: C 62.80; H 5.27; N 4.07.

2-(4-Phenylpiperidin-1-yl)-4-fluorobenzaldehyde (IVf). Yield 2.69 g (95%), mp 76–78°C. ^{1}H NMR spectrum, δ, ppm: 1.62–1.69 m (3H, 3CH), 1.82–1.95 m (4H, $2CH_2$), 2.59–2.73 m (1H, CH), 3.21–3.45 m (4H, $2NCH_2$), 7.11–7.55 m (8H_{Ar}), 10.43 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 283 (100) $[M]^+$. Found, %: C 76.36; H 6.44; N 5.04. $C_{18}H_{18}FNO$. Calculated, %: C 76.30; H 6.40; N 4.94.

2-(4-Phenylpiperidin-1-yl)-5-trifluoromethylbenzaldehyde (IVg). Yield 89%, mp 122°C. Mass spectrum, *m/z* (I_{rel}, %): 347 (100) $[M]^+$. Found, %: C 69.36; H 5.90; N 4.14. $C_{20}H_{20}F_3NO$. Calculated, %: C 69.15; H 5.80; N 4.03.

2-(4-Benzylpiperidin-1-yl)benzaldehyde (IVh). Yield 2.29 g (82%), mp 70–72°C. ^{1}H NMR spectrum, δ, ppm: 1.42–1.49 m (2H, 2CH), 1.62–1.69 m (3H, 3CH), 2.59 d (2H, CH_2, *J* 6.6 Hz), 2.80 d.d (2H, 2NCH, *J* 11.6, 12.2 Hz), 3.21 br.d (2H, 2NCH, *J* 12.2 Hz), 7.09 t (1H, Ph, *J* 7.0 Hz), 7.16–7.22 m (4H, Ph+ArH), 7.28 d.d (2H, Ph, *J* 7.0, 7.0 Hz), 7.48 d.d.d (1H_{Ar}, *J* 6.0, 7.0, 1.7 Hz), 7.67 d.d (1H_{Ar}, *J* 6.0, 1.7 Hz), 10.16 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 279 (100) $[M]^+$. Found, %: C 81.67; H 7.59; N 5.04. $C_{19}H_{21}NO$. Calculated, %: C 81.68; H 7.58; N 5.01.

2-(4-Benzylpiperidin-1-yl)-4-chlorobenzaldehyde (IVi). Yield 90%, mp 65–67°C. ^{1}H NMR spectrum, δ, ppm: 1.38–1.49 m (2H, 2CH), 1.62–1.70 m (3H, 3CH), 2.57 d (2H, CH_2, *J* 6.4 Hz), 2.81 d.d (2H, 2NCH, *J* 11.6, 12.0 Hz), 3.23 br.d (2H, 2NCH, *J* 12.0 Hz), 7.06–7.42 m (7H, Ph + ArH), 7.66 d (1H_{Ar}, *J* 8.3 Hz), 10.06 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 315 (38) $[M+2]^+$, 313 (100) $[M]^+$. Found, %: C 72.77; H 5.50; Cl 11.54; N 4.54. $C_{19}H_{20}ClNO$. Calculated, %: C 72.72; H 6.42; Cl 11.30; N 4.46.

2-(4-Benzylpiperidin-1-yl)-4-bromobenzaldehyde (IVj). Yield 82%, mp 76°C. ^{1}H NMR spectrum, δ, ppm: 1.37–1.47 m (2H, 2CH), 1.62–1.70 m (3H, 3CH), 2.57 d (2H, CH_2, *J* 6.4 Hz), 2.81 d.d (2H, 2NCH, *J* 11.9, 12.0 Hz), 3.23 br.d (2H, 2NCH, *J* 12.0 Hz), 7.12–7.35 m (7H, Ph + ArH), 7.57 d (1H_{Ar}, *J* 8.3 Hz), 10.06 s (1H, CHO). Mass spectrum, *m/z* (I_{rel}, %): 359 (100) $[M+2]^+$, 357 (97) $[M]^+$. Found, %: C 63.76; H 5.65; N 4.04. $C_{19}H_{20}BrNO$. Calculated, %: C 63.70; H 5.63; N 3.91.

Spiro compounds VI–X. To a solution of 1 mmol of benzaldehyde **IV** in 10 ml of toluene was added 1 mmol of compound **Va–Ve.** The reaction mixture was boiled for 3–6 h (TLC monitoring). The reaction mixture was cooled to room temperature, the solvent was evaporated in a vacuum, the residue was ground with ethanol.

3-Methyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro-[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIa). Yield 0.19 g (65%), mp 217–220°C. ^{1}H NMR

spectrum, δ, ppm: 0.81 d (3H, CH_3, *J* 6.5 Hz), 0.82 d.d.d (1H, H^4, *J* 13.3, 11.3, 12.5 Hz), 1.08 br.d (1H, H^2, *J* 13.3 Hz), 1.10 br.d (1H, H^4, *J* 13.3 Hz), 1.38 br.d (1H, H^2, *J* 12.5 Hz), 1.50–1.55 m (1H, H$^{5'}$), 1.80–1.85 m (1H, H$^{5'}$), 2.09–2.20 m (1H, H^3), 2.32 br.d (1H, H$^{6'}$, *J* 17.0 Hz), 2.44 br.d (1H, H$^{4'}$, *J* 14.0 Hz), 2.67 br.d (1H, H$^{6'}$, *J* 17.0 Hz), 2.97 d.d.d (1H, H^1, *J* 15.0, 13.3, 2.8 Hz), 3.06 and 3.09 *AB* (2H, $ArCH_2$, *J* 17.4 Hz), 3.31 d.d.d (1H, H$^{4'}$, *J* 14.0, 14.4, 7.0 Hz), 3.98 br.d (1H, H^1, *J* 15.0 Hz), 4.27 br.d (1H, H^{4a}, *J* 11.3 Hz), 6.61 d.d ($1H_{Ar}$, *J* 7.9, 8.0 Hz), 6.70 d ($1H_{Ar}$, *J* 7.9 Hz), 6.94 d.d ($1H_{Ar}$, *J* 8.0, 7.0 Hz), 7.00 d ($1H_{Ar}$, *J* 7.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 297 (100) $[M]^+$. Found, %: C 76.87; H 7.99; N 4.84. $C_{19}H_{23}NO_2$. Calculated, %: C 76.74; H 7.80; N 4.71.

3-Methyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIb). Yield 0.26 g (78%), mp 121–123°C. ^{1}H NMR spectrum, δ, ppm: 0.89 d.d.d (1H, H^4, *J* 11.2, 12.9, 11.6 Hz), 0.95 d (3H, CH_3, *J* 6.1 Hz), 1.16 d.d.d.d.d (1H, H^2, *J* 10.3, 12.8, 11.9, 3.5, 1.8 Hz), 1.45–1.85 m (9H, 9CH), 2.84 d.d.d (1H, H^1, *J* 10.3, 12.8, 2.3 Hz), 3.26 and 3.27 *AB* (2H, $ArCH_2$, *J* 14.2 Hz), 3.44 d.d (1H, H^{4a}, *J* 12.9, 2.4 Hz), 4.01 br.d (1H, H^1, *J* 12.8 Hz), 6.62 d.d ($1H_{Ar}$, *J* 2.7, 8.2 Hz), 6.85 d ($1H_{Ar}$, *J* 2.7 Hz), 6.93 d ($1H_{Ar}$, *J* 8.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 333 (25) $[M+2]^+$, 331 (68) $[M]^+$. Found, %: C 68.67; H 6.65; N 4.29. $C_{19}H_{22}ClNO_2$. Calculated, %: C 68.77; H 6.68; N 4.22.

3-Phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro-[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIc). Yield 0.24 g (68%), mp 228–230°C. ^{1}H NMR spectrum, δ, ppm: 0.89 d.d.d (1H, H^4, *J* 12.2, 14.4, 12.9 Hz), 1.26 d.d.d.d (1H, H^2, *J* 10.3, 11.7, 11.2, 1.8 Hz), 1.44–1.60 m (3H, H^2, H^4, H$^{5'}$), 2.08–2.18 m (1H, H$^{5'}$), 2.33 br.d (1H, H$^{6'}$, *J* 14.2 Hz), 2.46 br.d (1H, H$^{4'}$, *J* 16.8 Hz), 2.69 br.d (1H, H$^{6'}$, *J* 14.2 Hz), 3.08 d (1H, H^6, *J* 14.6 Hz), 3.14 d.d.d (1H, H^1, *J* 14.4, 11.2, 5.0 Hz), 3.14 d (1H, H^6, *J* 14.6 Hz), 3.24 d.d.d.d (1H, H^3, *J* 11.7, 14.1, 2.9, 3.8 Hz), 3.38 d.d.d (1H, H$^{4'}$, *J* 12.2, 16.8, 4.8 Hz), 4.15 br.d (1H, H^1, *J* 14.4 Hz), 4.55 br.d (1H, H^{4a}, *J* 12.2 Hz), 6.56 d.d ($1H_{Ar}$, *J* 7.4, 7.4 Hz), 6.87 d ($1H_{Ar}$, *J* 8.2 Hz), 7.00 d ($1H_{Ar}$, *J* 7.4 Hz), 7.05 d ($2H_{Ph}$, *J* 7.2 Hz), 7.08 d.d ($1H_{Ar}$, *J* 7.4, 8.2 Hz), 7.14 d.d ($1H_{Ph}$, *J* 7.6, 7.2 Hz), 7.23 d.d ($2H_{Ph}$, *J* 7.2, 7.6 Hz). Mass spectrum, *m/z* (I_{rel}, %): 359 (100) $[M]^+$. Found, %: C 80.14; H 7.15; N 3.79. $C_{24}H_{25}NO_2$. Calculated, %: C 80.19; H 7.01; N 3.90.

3-Phenyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VId). Yield 0.34 g (86%), mp 182–185°C. ^{1}H NMR spectrum, δ, ppm: 1.23 d.d.d (1H, H^4, *J* 12.0, 12.4, 11.9 Hz), 1.25–1.29 m (1H, CH), 1.45–1.64 m (3H, 3CH), 2.11–2.19 m (1H, CH), 2.35 br.d (1H, CH, *J* 13.6 Hz), 2.42 br.d (1H, CH, *J* 14.2 Hz), 2.69 br.d (1H, CH, *J* 13.6 Hz), 3.02–3.40 m (7H, 7CH), 4.08 br.d (1H, H^{4a}, *J* 14.4 Hz), 4.50 br.d (1H, H^1, *J* 10.1 Hz), 6.63 d.d ($1H_{Ar}$, *J* 8.0, 1.6 Hz), 6.78 d ($1H_{Ar}$, *J* 1.6 Hz), 6.97–7.21 m (6H, Ph, ArH). Mass spectrum, *m/z* (I_{rel}, %): 395 $[M+2]^+$ (36), 393 $[M]^+$ (100). Found, %: C 73.21; H 6.07; N 3.66. $C_{24}H_{24}ClNO_2$. Calculated, %: C 73.18; H 6.14; N 3.56.

9-Bromo-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIe). Yield 0.38 g (86%), mp 191–193°C. ^{1}H NMR spectrum, δ, ppm: 1.22–1.29 m (2H, 2CH), 1.45–1.64 m (3H, 3CH), 2.11–2.19 m (1H, CH), 2.35 br.d (1H, CH, *J* 13.7 Hz), 2.44 br.d (1H, CH, *J* 14.2 Hz), 2.66 d (1H, CH, *J* 17.4 Hz), 3.00–3.40 m (5H, 5CH), 4.08 br.d (1H, H^{4a}, *J* 14.4 Hz), 4.50 br.d (1H, H^1, *J* 9.4 Hz), 6.77 d.d ($1H_{Ar}$, *J* 8.0, 1.5 Hz), 6.91 d ($1H_{Ar}$, *J* 1.5 Hz), 6.98 d ($1H_{Ar}$, *J* 8.0 Hz), 7.02–7.23 m ($5H_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 440 (99) $[M+2]^+$, 438 (100) $[M]^+$. Found, %: C 65.87; H 5.57; N 3.25. $C_{24}H_{24}BrNO_2$. Calculated, %: C 65.76; H 5.52; N 3.20.

8-Trifluoromethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIg). Yield 0.24 g (67%), mp 214°C. ^{1}H NMR spectrum, δ, ppm: 1.19–1.69 m (6H, CH), 2.13–2.21 m (1H, CH), 2.42 br.d (1H, CH, *J* 14.0 Hz), 2.75 d (1H, CH, *J* 17.1 Hz), 3.00–3.20 m (3H, 3CH), 3.26–3.40 m (2H, 2CH), 4.20 br.d (1H, H^{4a}, *J* 14.0 Hz), 4.57 br.d (1H, H^1, *J* 10.3 Hz), 6.93 d ($1H_{Ar}$, *J* 8.6 Hz), 7.00–7.33 m (7H, Ph, ArH). Mass spectrum, *m/z* (I_{rel}, %): 427 (100) $[M]^+$. Found, %: C 70.29; H 6.00; N 3.26. $C_{25}H_{24}F_3NO_2$. Calculated, %: C 70.25; H 5.66; N 3.28.

3-Benzyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIi). Yield 0.36 g (89%), mp 176°C. ^{1}H NMR spectrum, δ, ppm: 0.90 d.d.d (1H, H^4, *J* 11.9, 12.5, 11.3 Hz), 1.01–1.18 m (1H, H$^{5'}$), 1.23 br.d (1H, H^2, *J* 12.8), 1.35 br.d (1H, H^4, *J* 11.9 Hz), 1.52 br.d (1H, H^2, *J* 12.8 Hz), 2.00–2.20 m (2H, H^3, H$^{5'}$), 2.26 d.d.d, (1H, CH_2, *J* 8.9, 10.1, 13.3 Hz), 2.31 d.d.d (1H, CH_2, *J* 14.0, 14.1, 7.0 Hz), 2.38 br.d (1H, H$^{4'}$, *J* 14.1 Hz), 2.44–2.56 m (2H, H^1, H$^{6'}$), 2.67 d (1H, H$^{6'}$, *J* 13.1 Hz), 2.98 and 3.02 *AB* (2H, $ArCH_2$, *J* 14.7 Hz), 3.26 br.d (1H, H$^{4'}$, *J* 14.1 Hz), 3.63 br.d (1H, H^{4a}, *J* 14.3 Hz), 4.29 br.d (1H,

H^{1}, *J* 11.3 Hz), 6.62 d.d (1H$_{Ar}$, *J* 1.9, 7.9 Hz), 6.69 d (1H$_{Ar}$, *J* 1.9 Hz), 7.01 d (1H$_{Ar}$, *J* 7.9 Hz), 7.02–7.25 m (5H$_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 409 (40) $[M + 2]^+$, 407 (100) $[M]^+$. Found, %: C 73.63; H 6.49; N 3.53. $C_{25}H_{26}ClNO_2$. Calculated, %: C 73.61; H 6.42; N 3.43.

3,5',5'-Trimethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIIa). Yield 0.23 g (71%), mp 147–150°C. ^{1}H NMR spectrum, δ, ppm: 0.71 c (3H, CH_3), 0.80 d (3H, CH_3, *J* 6.4 Hz), 0.82 d.d.d (1H, H^{4}, *J* 12.3, 11.0, 11.9 Hz), 1.00–1.20 m (2H, H^{2}, H^{4}), 1.23 s (3H, CH_3), 1.38 br.d (1H, H^{2}, *J* 15.3 Hz), 1.83–1.93 m (1H, H^{3}), 2.09 d.d (1H, H$^{6'}$, *J* 17.0, 2.3 Hz), 2.23 d.d (1H, H$^{4'}$, *J* 13.4, 2.3 Hz), 2.59 d (1H, H$^{6'}$, *J* 17.0 Hz), 3.12 d.d.d (1H, H^{1}, *J* 11.2, 12.3, 3.5 Hz), 3.08 and 3.12 *AB* (2H, $ArCH_2$, *J* 16.4 Hz), 3.40 d (1H, H$^{4'}$, *J* 13.4 Hz), 3.97 br.d (1H, H^{1}, *J* 13.3 Hz), 4.29 d (1H, H^{4a}, *J* 11.0 Hz), 6.61 d.d (1H$_{Ar}$, *J* 7.9, 8.2 Hz), 6.70 d (1H$_{Ar}$, *J* 7.9 Hz), 6.94 d.d (1H$_{Ar}$, *J* 8.2, 7.0 Hz), 7.00 d (1H$_{Ar}$, *J* 7.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 325 (100) $[M]^+$. Found, %: C 77.57; H 8.39; N 4.55. $C_{21}H_{27}NO_2$. Calculated, %: C 77.50; H 8.36; N 4.30.

3,5',5'-Trimethyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIIb). Yield 0.29 g (82%), mp 190–192°C. ^{1}H NMR spectrum, δ, ppm: 0.77 s (3H, CH_3), 0.82 d (3H, CH_3, *J* 6.4 Hz), 0.79–0.82 m (1H, H^{2}), 1.00–1.20 m (2H, H^{2}, H^{4}), 1.23 s (3H, CH_3), 1.43 br.d (1H, H^{4}, *J* 13.1 Hz), 1.80–1.99 m (1H, H^{3}), 2.10 d.d (1H, H$^{6'}$, *J* 14.1, 2.5 Hz), 2.25 d.d (1H, H$^{4'}$, *J* 15.4, 2.5 Hz), 2.58 d (1H, H$^{6'}$, *J* 14.1 Hz), 3.12 d.d (1H, H^{4}, *J* 11.2, 12.9, 2.3 Hz), 3.04 and 3.11 *AB* (2H, $ArCH_2$, *J* 17.4 Hz), 3.39 d (1H, H$^{4'}$, *J* 15.4 Hz), 3.93 br.d (1H, H^{4a}, *J* 14.3 Hz), 4.28 br.d (1H, H^{1}, *J* 11.2 Hz), 6.59 d.d (1H$_{Ar}$, *J* 1.5, 8.0 Hz), 6.68 d (1H$_{Ar}$, *J* 1.5 Hz) 6.99 d (1H$_{Ar}$, *J* 8.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 361 (35) $[M + 2]^+$, 359 (100) $[M]^+$. Found, %: C 70.07; H 7.32; N 3.99. $C_{21}H_{26}ClNO_2$. Calculated, %: C 70.08; H 7.28; N 3.89.

5',5'-Dimethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIIc). Yield 0.26 g (68%), mp 228–230°C. ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, CH_3), 1.23 s (3H, Me), 1.18–12.3 m (2H, 2CH), 1.47–1.59 m (2H, 2CH), 2.14 d.d (1H, CH, *J* 13.8, 2.1 Hz), 2.27 d.d (1H, CH, *J* 13.8, 2.1 Hz), 2.64 d (1H, H$^{4'}$, *J* 16.9 Hz), 3.11 d (1H, H^{6}, *J* 13.3 Hz), 3.11–3.32 m (3H, 3CH), 3.48 d (1H, H^{6}, *J* 13.3 Hz), 4.13 d (1H, H^{4a}, *J* 14.5 Hz), 4.59 d.d (1H, H^{1}, *J* 12.2, 3.1 Hz), 6.66 d.d.d (1H$_{Ar}$, *J* 7.3, 7.4, 1.0 Hz), 6.86 d (1H$_{Ar}$, *J* 7.9 Hz), 7.00 d.d.d (1H$_{Ar}$, *J* 7.9, 7.2, 1.3 Hz), 7.05–7.10 m (2H$_{Ar}$), 7.07 d (1H$_{Ar}$, *J* 7.6 Hz), 7.16 t.t (1H$_{Ph}$, *J* 7.6, 1.3 Hz), 7.23 d.d (2H$_{Ph}$, *J* 7.6, 7.6 Hz). ^{13}C NMR spectrum, δ, ppm: 23.56 (Me), 26.18 (Me), 27.91 (C^{5}), 29.46 (C^{4}), 30.69 (C^{6}), 31.14 (C^{3}), 42.11 (C$^{5'}$), 48.09 (C$^{6'}$), 49.09 (C$^{4'}$), 50.83 (C^{5}), 60.09 (C^{1}), 67.32 (C^{4a}), 113.22 (Ar), 117.66 (Ar), 122.32 (Ar), 125.37 (Ar), 126.15 (Ar), 126.45 (Ar), 128.37 (Ar), 129.32 (Ar), 141.67 (Ar), 145.22 (Ar), 205.01 (CO), 205.99 (CO). Mass spectrum, *m/z* (I_{rel}, %): 387 (100) $[M]^+$. Found, %: N 3.47. $C_{26}H_{29}NO_2$. Calculated, %: N 3.61.

5',5'-Dimethyl-3-phenyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIId). Yield 0.3 g (71%), mp 256–259°C. ^{1}H NMR spectrum, δ, ppm: 0.72 s (3H, CH_3), 1.15–1.25 m (2H, H^{2}, H^{4}), 1.24 c (3H, CH_3), 1.50–1.70 m (2H, H^{2}, H^{4}), 2.15 d (1H, H$^{6'}$, *J* 17.1 Hz), 2.25 d (1H, H$^{3'}$, *J* 13.6 Hz), 2.61 d (1H, H$^{6'}$, *J* 17.1 Hz), 3.02–3.25 m (4H, 4CH), 3.28 d (1H, H$^{3'}$, *J* 13.6 Hz), 4.05 d (1H, H^{4a}, *J* 14.0 Hz), 4.52 br.d (1H, H^{1}, *J* 9.1 Hz), 6.63 d (1H$_{Ar}$, *J* 8.0 Hz), 6.78 s (1H$_{Ar}$), 6.91–7.28 m (6H, Ph, ArH). Mass spectrum, *m/z* (I_{rel}, %): 423 (36) $[M + 2]^+$, 421 (100) $[M]^+$. Found, %: C 74.11; H 6.88; N 3.33. $C_{26}H_{28}ClNO_2$. Calculated, %: C 74.01; H 6.69; N 3.32.

9-Bromo-5',5'-dimethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIIe). Yield 0.32 g (69%), mp 252–254°C. ^{1}H NMR spectrum, δ, ppm: 0.71 s (3H, CH_3), 1.15–1.25 m (2H, 2CH), 1.24 s (3H, CH_3), 1.50–1.65 m (2H, 2CH), 2.13 d (1H, H$^{6'}$, *J* 13.8 Hz), 2.23 d (1H, H$^{3'}$, *J* 13.1 Hz), 2.58 and 3.12 *AB* (2H, $ArCH_2$, *J* 17.7 Hz), 3.12 d.d.d (1H, H^{1}, *J* 12.1, 9.3, 1.9 Hz), 3.25 d (1H, H$^{6'}$, *J* 13.8 Hz), 3.29 d.d.d.d (1H, H^{3}, *J* 12.2, 12.0, 3.0, 4.9 Hz), 3.45 d (1H, H$^{3'}$, *J* 13.1 Hz), 4.08 d (1H, H^{4a}, *J* 14.3 Hz), 4.53 d (1H, H^{1}, *J* 9.3 Hz), 6.77 d (1H$_{Ar}$, *J* 7.9 Hz), 6.90 c (1H$_{Ar}$), 6.98 d (1H$_{Ar}$, *J* 7.9 Hz), 7.00–7.22 m (5H$_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 468 (89) $[M + 2]^+$, 466 (88) $[M]^+$. Found, %: C 67.05; H 6.08; N 3.22. $C_{26}H_{28}BrNO_2$. Calculated, %: C 66.95; H 6.05; N 3.00.

9-Benzyl-5',5'-dimethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIIh). Yield 0.36 g (89%), mp 154–156°C. ^{1}H NMR spectrum, δ, ppm: 0.65 C (3H, CH_3), 0.82 d.d.d (1H, H^{4}, *J* 11.8, 14.2, 12.3 Hz), 1.03 d.d.d.d (1H, H^{2}, *J* 14.2, 13.4, 10.1, 2.3 Hz), 1.11 br.d (1H, H^{2}, *J* 13.4 Hz), 1.19 s (3H, CH_3), 1.23 br.d (1H, H^{4}, *J* 14.2 Hz), 2.06–2.14 m (1H, H^{3}), 2.08 d (1H, H$^{3'}$, *J* 17.3 Hz), 2.23 d.d (1H, CH_2Ph, *J* 13.1, 8.1 Hz), 2.28 d (1H, H$^{6'}$, *J* 16.9 Hz), 2.42 d.d (1H, CH_2Ph, *J* 13.1, 6.3 Hz), 2.60 d (1H, H$^{6'}$,

J 16.9 Hz), 3.02 d.d.d (1H, H^{1}, *J* 11.3, 10.9, 1.8 Hz), 3.05 d (1H, H$^{3'}$, *J* 17.3 Hz), 3.16 and 3.41 *AB* (2H, $ArCH_2$, *J* 13.4 Hz), 3.98 br.d (1H, H^{4a}, *J* 14.1 Hz), 4.40 br.d (1H, H^{1}, *J* 11.3 Hz), 6.65 d.d.d (1H_{Ar}, *J* 7.4, 8.0, 1.1 Hz), 6.77 d (1H_{Ar}, *J* 8.0 Hz), 6.97 d.d.d (1H_{Ar}, *J* 7.4, 8.0, 1.1 Hz), 7.06 br.d (1H_{Ar}, *J* 7.4 Hz), 7.10 d (2H_{Ph}, *J* 7.1 Hz), 7.16 t (1H_{Ph}, *J* 7.5 Hz), 7.25 d.d (2H_{Ph}, *J* 7.1, 7.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 401 (100) $[M]^+$. Found, %: C 80.77; H 7.81; N 3.52. $C_{27}H_{31}NO_2$. Calculated, %: C 80.76; H 7.78; N 3.49.

9-Benzyl-5',5'-dimethyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIIi). Yield 0.34 g (78%), mp 221–233°C. ^{1}H NMR spectrum, δ, ppm: 0.88 d.d.d (1H, H^{4}, *J* 11.6, 12.2, 11.6 Hz), 0.71 s (3H, CH_3), 1.22 s (3H, CH_3), 1.11 d.d.d.d (1H, H^{2}, *J* 11.0, 13.4, 10.9, 1.8 Hz), 1.15 br.d (1H, H^{2}, *J* 13.4 Hz), 1.35 br.d (1H, H^{4}, *J* 12.8 Hz), 2.10 d (1H, H$^{3'}$, *J* 11.7 Hz), 2.08–2.14 m (1H, H^{3}), 2.24 d (1H, H$^{6'}$, *J* 17.1 Hz), 2.28 d.d (1H, CH_2Ph, *J* 15.9, 7.4 Hz), 2.47 d.d (1H, CH_2Ph, *J* 6.0, 15.9 Hz), 2.60 d (1H, H$^{6'}$, *J* 17.1 Hz), 3.03 d.d.d (1H, H^{1}, *J* 11.0, 10.9, 1.8 Hz), 3.05 d (H, H^{6}, *J* 13.7 Hz), 3.11 d (H, H$^{3'}$, *J* 11.7 Hz), 3.35 d (H, H^{6}, *J* 13.7 Hz), 3.63 br.d (1H, H^{4a}, *J* 14.0 Hz), 4.15 br.d (1H, H^{1}, *J* 11.0 Hz), 6.61 d.d (1H_{Ar}, *J* 1.5, 8.0 Hz), 6.68 d (1H_{Ar}, *J* 1.5 Hz), 7.01 d (1H_{Ar}, *J* 8.0 Hz), 7.03–7.26 m (5H_{Ph}). Mass spectrum, *m/z* (I_{rel}, %): 437 (36) $[M + 2]^+$, 435 (100) $[M]^+$. Found, %: C 74.44; H 6.99; N 3.30. $C_{27}H_{30}ClNO_2$. Calculated, %: C 74.38; H 6.94; N 3.21.

3-Benzyl-9-bromo-5',5'-dimethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,2'-cyclohexane]-1',3'-dione (VIIj). Yield 0.35 g (72%), mp 161–164°C. ^{1}H NMR spectrum, δ, ppm: 0.71 s (3H, CH_3), 0.90 d.d (1H, H^{4}, *J* 12.1, 10.2 Hz), 1.21 s (3H, CH_3), 1.09 d.d.d.d (1H, H^{2}, *J* 12.9, 11.2, 13.4, 2.4 Hz), 1.20 br.d (1H, H^{2}, *J* 13.4 Hz), 1.34 br.d (1H, H^{4}, *J* 12.9 Hz), 2.00–2.12 m (1H, H^{3}), 2.10 d (1H, H$^{3'}$, *J* 13.4 Hz), 2.23 d (1H, H$^{6'}$, *J* 12.8 Hz), 2.26 d.d (1H, CH_2Ph, *J* 14.1, 6.8 Hz), 2.49 d.d (1H, CH_2Ph, *J* 14.1, 5.4 Hz), 2.55 d (1H, H$^{6'}$, *J* 12.8 Hz), 3.02 d.d.d (1H, H^{1}, *J* 11.5, 10.9, 1.9 Hz), 3.04 d (1H, H^{6}, *J* 17.7 Hz), 3.08 d (1H, H^{6}, *J* 17.7 Hz), 3.34 d (1H, H$^{3'}$, *J* 13.4 Hz), 3.90 d.d (1H, H^{4a}, *J* 14.8, 2.8 Hz), 4.28 d (1H, H^{1}, *J* 11.5 Hz), 6.75 d (1H_{Ar}, *J* 8.0 Hz), 6.82 s (1H_{Ar}), 6.96 d (1H_{Ar}, *J* 8.0 Hz), 7.00–7.29 m (5H_{Ph}). Mass spectrum, *m/z* (I_{rel}, %): 482 (99) $[M + 2]^+$, 480 (100) $[M]^+$. Found, %: C 67.57; H 6.28; N 2.21. $C_{27}H_{30}BrNO_2$. Calculated, %: C 67.50; H 6.29; N 2.92.

3,2',2'-Trimethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIIa). Yield 0.17 γ (72%), mp 108–110°C. ^{1}H NMR spectrum, δ, ppm: 0.93 d.d.d (1H, H^{4}, *J* 11.9, 11.6, 12.0 Hz), 0.95 d (3H, CH_3, *J* 6.1 Hz), 1.18 d.d.d.d (1H, H^{2}, *J* 13.4, 12.6, 13.0, 3.8 Hz), 1.56 br.d (1H, H^{4}, *J* 11.6 Hz), 1.70 br.d (1H, H^{2}, *J* 13.4 Hz), 1.70–1.80 m (1H, H^{3}), 1.77 s (6H, $2CH_3$), 2.78 d.d.d (1H, H^{1}, *J* 12.6, 13.2, 2.8 Hz), 3.22 and 3.27 *AB* (2H, $ArCH_2$, *J* 17.1 Hz), 3.39 d.d (1H, H^{4a}, *J* 11.9, 2.4 Hz), 4.05 br.d (1H, H^{1}, *J* 13.2 Hz), 6.63 d.d (1H_{Ar}, *J* 6.3, 8.4 Hz), 6.85 d (1H_{Ar}, *J* 8.4 Hz), 6.94 d (1H_{Ar}, *J* 7.3 Hz) 7.03 d.d (1H_{Ar}, *J* 6.3, 7.3 Hz). Mass spectrum, *m/z* (I_{rel}, %): 329 (70) $[M]^+$. Found, %: C 69.22; H 7.15; N 4.32. $C_{19}H_{23}NO_4$. Calculated, %: C 69.28; H 7.04; N 4.25.

3,2',2'-Trimethyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIIb). Yield 0.30 g (83%), mp 208–210°C. ^{1}H NMR spectrum, δ, ppm: 0.94 d.d.d.d (1H, H^{4}, *J* 12.8, 12.6, 11.6 Hz), 0.95 d (3H, CH_3, *J* 6.1 Hz), 1.16 d.d.d (1H, H^{2}, *J* 12.6, 10.1, 3.4 Hz), 1.50–1.80 m (3H, H^{2}, H^{3}, H^{4}), 1.77 s (6H, $2CH_3$), 2.83 d.d.d (1H, H^{1}, *J* 11.0, 10.1, 2.7 Hz), 3.25 and 3.22 *AB* (2H, $ArCH_2$, *J* 17.3 Hz), 3.43 d.d (1H, H^{4a}, *J* 11.6, 2.2 Hz), 4.00 br.d (1H, H^{1}, *J* 11.0 Hz), 6.61 d.d (1H_{Ar}, *J* 1.6, *J* 7.9 Hz), 6.85 d (1H_{Ar}, *J* 1.6 Hz), 6.94 d (1H_{Ar}, *J* 7.9 Hz). Mass spectrum, *m/z* (I_{rel}, %): 365 (30) $[M + 2]^+$, 363 (98) $[M]^+$. Found, %: C 62.78; H 6.22; N 3.89. $C_{19}H_{22}ClNO_4$. Calculated, %: C 62.72; H 6.09; N 3.85.

2',2'-Dimethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIIc). Yield 0.31 g (80%), mp 237–240°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 d.d.d (1H, H^{2}, *J* 12.8, 12.8, 12.8 Hz), 1.36 d.d.d (1H, H^{2}, *J* 12.8, 12.8, 4.6 Hz), 1.75 s (3H, CH_3), 1.76 s (3H, CH_3), 1.72–1.78 m (1H, H^{4}), 2.50 d.d (1H, H^{3}, *J* 13.7, 7.8 Hz), 2.60 d.d (1H, H^{4}, *J* 13.7, 6.0 Hz), 2.72 d.d.d (1H, H^{1}, *J* 12.8, 12.8, 2.6 Hz), 3.11 d (1H, H^{6}, *J* 16.4 Hz), 3.43 d.d (1H, H^{4a}, *J* 11.8, 2.4 Hz), 3.52 d (1H, H^{6}, *J* 16.4 Hz), 4.10 d.d.d (1H, H^{1}, *J* 12.8, 4.6, 2.6 Hz), 6.74 d.d.d (1H_{Ar}, *J* 7.4, 7.4, 1.0 Hz), 6.93 d (1H_{Ar}, *J* 8.3 Hz), 6.97 d (1H_{Ar}, *J* 7.3 Hz), 7.09–7.12 m (2H_{Ar}), 7.15 d.d.d (1H_{Ar}, *J* 8.2, 6.9, 1.3 Hz), 7.19 t.t (1H_{Ph}, *J* 7.4, 1.9 Hz), 7.27 d.d (2H_{Ph}, *J* 7.4, 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 28.20 (Me), 30.28 (Me), 30.62 (C^{2}), 34.56 (C^{4}), 34.72 (C^{6}), 37.63 (C^{3}), 43.00 (C^{5}), 48.27 (C^{1}), 52.21 (OCO), 61.24 (C^{4a}), 113.52 (Ar), 118.49 (Ar), 119.50 (Ar), 126.23 (Ar), 127.67 (Ar), 128.37 (Ar), 128.71 (Ar), 129.06 (Ar), 139.46 (Ar), 144.60 (Ar), 164.78 (CO),

169.28 (CO). Mass spectrum, *m/z* (I_{rel}, %): 391 (78) $[M]^+$. Found, %: N 3.55. $C_{24}H_{25}NO_4$. Calculated, %: N 3.58.

2',2'-Dimethyl-3-phenyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIId). Yield 0.30 g (71%), mp 189–191°C. ^{1}H NMR spectrum, δ, ppm: 1.44 d.d.d (1H, H^4, *J* 11.8, 13.2, 12.2 Hz), 1.60–1.80 m (2H, H^2, H^4), 1.73 s (3H, CH_3), 1.76 s (3H, CH_3), 1.90 br.d (1H, H^2, *J* 12.2 Hz), 2.82 d.d.d.d (1H, H^3, *J* 12.2, 11.8, 2.8, 3.0 Hz), 3.02 d.d.d (1H, H^1, *J* 12.2, 11.3, 3.0 Hz), 3.27 and 3.28 *AB* (2H, $ArCH_2$, *J* 17.0 Hz), 3.63 d.d (1H, H^{4a}, *J* 11.3, 2.5 Hz), 4.15 br.d (1H, H^1, *J* 13.2 Hz), 6.65 d.d ($1H_{Ar}$, *J* 1.8, 8.0 Hz), 6.91 d ($1H_{Ar}$, *J* 1.8 Hz), 6.96 d ($1H_{Ar}$, *J* 8.0 Hz), 7.12–7.29 m ($5H_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 427 (38) $[M+2]^+$, 425 (100) $[M]^+$. Found, %: C 67.85; H 5.44; N 3.33. $C_{24}H_{24}ClNO_4$. Calculated, %: C 67.68; H 5.68; N 3.29.

9-Bromo-2',2'-dimethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIIe). Yield 0.30 g (84%), mp 183–186°C. ^{1}H NMR spectrum, δ, ppm: 1.41 d.d.d (1H, H^4, *J* 13.2, 11.9, 12.2 Hz), 1.60–1.71 m (2H, H^2, H^4), 1.88 br.d (1H, H^2, *J* 12.5 Hz), 1.74 s (3H, CH_3), 1.77 s (3H, CH_3), 2.85 d.d.d.d (1H, H^3, *J* 12.2, 11.6, 3.3, 3.0 Hz), 2.99 d.d.d (1H, H^1, *J* 12.8, 11.3, 3.0 Hz), 3.28 and 3.25 *AB* (2H, $ArCH_2$, *J* 17.2 Hz), 3.63 d.d (1H, H^1, *J* 11.2, 2.1 Hz), 4.15 br.d (1H, H^1, *J* 12.8 Hz), 6.78 d.d ($1H_{Ar}$, *J* 7.9, 1.2 Hz), 6.92 d ($1H_{Ar}$, *J* 7.9 Hz), 7.00 d ($1H_{Ar}$, *J* 1.2 Hz), 7.12–7.30 m ($5H_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 472 (98) $[M+2]^+$, 470 (100) $[M]^+$. Found, %: C 61.51; H 5.41; N 3.11. $C_{24}H_{24}BrNO_4$. Calculated, %: C 61.29; H 5.14; N 2.98.

2',2'-Dimethyl-3-phenyl-9-fluoro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIIf). Yield 0.36 g (88%), mp 142–145°C. ^{1}H NMR spectrum, δ, ppm: 1.54 d.d.d (1H, H^4, *J* 11.0, 12.8, 11.6 Hz), 1.60–1.80 m (2H, H^2, H^4), 1.69 s (3H, CH_3), 1.78 s (3H, CH_3), 1.88 d.d.d.d (1H, H^2, *J* 11.6, 4.0, 3.4, 4.0 Hz), 2.84 d.d.d.d (1H, H^3, *J* 11.6, 11.0, 4.0, 5.8 Hz), 3.00 d.d.d (1H, H^1, *J* 13.6, 12.8, 6.3 Hz), 3.27 and 3.42 *AB* (2H, $ArCH_2$, *J* 15.8 Hz), 3.69 d.d (1H, H^{4a}, *J* 11.0, 1.9 Hz), 4.36 d.d.d (1H, H^1, *J* 12.8, 3.4, 3.8 Hz), 6.66 d.d.d ($1H_{Ar}$, *J* 4.8, 7.3, 7.0 Hz), 6.91 d ($1H_{Ar}$, *J* 7.3 Hz), 6.86 d.d.d ($1H_{Ar}$, *J* 7.0, 14.3, 1.2 Hz), 7.12–7.30 m ($5H_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 409 (100) $[M]^+$. Found, %: C 70.44; H 5.98; N 3.33. $C_{24}H_{24}FNO_4$. Calculated, %: C 70.40; H 5.91; N 3.42.

2',2'-Dimethyl-8-trifluoromethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]-quinolizine-5,5'-dioxane]-4',6'-dione (VIIIg). Yield 0.25 g (85%), mp 218–220°C. ^{1}H NMR spectrum, δ, ppm: 1.42 d.d.d (1H, H^4, *J* 12.2, 13.1, 11.5 Hz), 1.60–1.80 m (2H, H^2, H^4), 1.75 s (3H, CH_3), 1.79 s (3H, CH_3), 1.90 br.d (1H, H^2, *J* 11.9 Hz), 2.89 d.d.d.d (1H, H^3, *J* 11.9, 12.2, 2.8, 3.1 Hz), 3.08 d.d.d (1H, H^1, *J* 13.1, 10.4, 2.4 Hz), 3.32 and 3.42 *AB* (2H, $ArCH_2$, *J* 16.8 Hz), 3.73 d.d (1H, H^{4a}, *J* 11.5, 2.2 Hz), 4.28 br.d (1H, H^1, *J* 13.1 Hz), 7.04 d ($1H_{Ar}$, *J* 8.5 Hz), 7.12–7.35 m (7H, Ph, ArH). Mass spectrum, *m/z* (I_{rel}, %): 459 (100) $[M]^+$. Found, %: C 65.48; H 5.25; N 3.03. $C_{25}H_{24}F_3NO_4$. Calculated, %: C 65.35; H 5.27; N 3.05.

9-Benzyl-2',2'-dimethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIIh). Yield 0.36 g (88%), mp 155–157°C. ^{1}H NMR spectrum, δ, ppm: 0.95 d.d.d (1H, H^4, *J* 11.5, 14.9, 12.1 Hz), 1.17 d.d.d.d (1H, H^2, *J* 15.2, 14.9, 9.9, 1.9 Hz), 1.52 br.d (1H, H^2, *J* 15.2 Hz), 1.56 br.d (1H, H^4, *J* 14.9 Hz), 1.74 s (6H, $2CH_3$), 1.69–1.84 m (1H, H^3), 2.42–2.50 m (2H, CH_2Ph), 2.71 d.d.d (1H, H^1, *J* 13.0, 14.9, 2.1 Hz), 3.24 and 3.28 *AB* (2H, $ArCH_2$, *J* 17.1 Hz), 3.37 d.d (1H, H^{4a}, *J* 11.5, 2.3 Hz), 4.05 br.d (1H, H^1, *J* 14.9 Hz), 6.65 d.d.d ($1H_{Ar}$, *J* 8.5, 7.9, 1.7 Hz), 6.91 d.d ($1H_{Ar}$, *J* 6.9, 1.4 Hz), 6.98 d.d ($1H_{Ar}$, *J* 7.9, 1.4 Hz), 7.04 d.d.d ($1H_{Ar}$, *J* 6.9, 8.5, 1.7 Hz), 7.16 d ($2H_{Ph}$, *J* 7.0 Hz), 7.18 t ($1H_{Ph}$, *J* 7.4 Hz), 7.27 d.d ($2H_{Ph}$, *J* 7.0, 7.4 Hz). Mass spectrum, *m/z* (I_{rel}, %): 405 (100) $[M]^+$. Found, %: C 74.08; H 6.92; N 3.49. $C_{25}H_{27}NO_4$. Calculated, %: C 74.05; H 6.71; N 3.45.

9-Benzyl-2',2'-dimethyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-dioxane]-4',6'-dione (VIIIi). Yield 77%, mp 175–177°C. ^{1}H NMR spectrum, δ, ppm: 0.97 d.d.d (1H, H^4, *J* 11.6, 14.8, 11.9 Hz), 1.23 d.d.d.d (1H, H^2, *J* 11.9, 13.4, 15.2, 7.2 Hz), 1.58 br.d (1H, H^2, *J* 15.2 Hz), 1.70 br.d (1H, H^4, *J* 14.8 Hz), 1.74–1.86 m (1H, H^3), 1.74 s (6H, $2CH_3$), 2.52 d.d (2H, CH_2Ph, *J* 13.1, 6.6 Hz), 2.56 d.d (1H, CH_2Ph, *J* 13.1, 7.2 Hz), 2.76 d.d.d (1H, H^1, *J* 13.4, 12.9, 2.3 Hz), 3.20 and 3.22 *AB* (2H, $ArCH_2$, *J* 17.2 Hz), 3.39 d.d (1H, H^{4a}, *J* 11.6, 2.4 Hz), 3.98 br.d (1H, H^1, *J* 13.4 Hz), 6.61 d.d ($1H_{Ar}$, *J* 8.2, 1.8 Hz), 6.93 d ($1H_{Ar}$, *J* 8.2 Hz), 6.82 d ($1H_{Ar}$, *J* 1.8 Hz), 7.11 d ($2H_{Ph}$, *J* 7.3 Hz), 7.15 t ($1H_{Ph}$, *J* 6.7 Hz), 7.24 d.d ($2H_{Ph}$, *J* 6.7, 7.3 Hz). Mass spectrum, *m/z* (I_{rel}, %): 441 (39) $[M+2]^+$, 439 (100) $[M]^+$. Found, %: C 68.29; H 5.99; N 3.30. $C_{25}H_{26}ClNO_4$. Calculated, %: C 68.25; H 5.96; N 3.18.

3-Methyl-1',3''-diphenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-

dione (IXa). Yield 0.35 g (76%), mp 238–240°C. ^{1}H NMR spectrum, δ, ppm: 0.86 d (3H, CH_3, *J* 6.8 Hz), 1.04 d.d.d (1H, H^4, *J* 12.8, 1.3, 12.9 Hz), 1.26 br.d (1H, H^2, *J* 12.8 Hz), 1.45–1.53 m (2H, H^2, H^4), 1.92–2.01 m (1H, H^3), 3.13 d.d.d (1H, H^1, *J* 11.3, 12.5, 2.3 Hz), 3.05 and 3.45 *AB* (2H, $ArCH_2$, *J* 17.1 Hz), 4.11 br.d (1H, H^{4a}, *J* 10.8 Hz), 4.15 br.d (1H, H^1, *J* 11.3 Hz), 6.62 d.d (1H_{Ar}, *J* 7.4, 8.3 Hz), 6.79 d (1H_{Ar}, *J* 8.3 Hz), 6.98 d.d (1H_{Ar}, *J* 7.3, 7.4 Hz), 7.03 d (1H_{Ar}, *J* 7.3 Hz), 7.23–7.51 m (10H, 2 Ph). Mass spectrum, *m/z* (I_{rel}, %): 465 (100) [*M*]$^+$. Found, %: C 74.95; H 5.87; N 9.18. $C_{29}H_{27}N_3O_3$. Calculated, %: C 74.82; H 5.85; N 9.03.

1',3,3''-Triphenyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (IXd). Yield 0.5 g (91%), mp 172–174°C. ^{1}H NMR spectrum, δ, ppm: 1.47 d.d.d (1H, H^2, *J* 12.5, 9.8, 12.8 Hz), 1.62–1.75 m (3H, 3CH), 3.00 and 3.02 *AB* (2H, $ArCH_2$, *J* 18.9 Hz), 3.20–3.30 m (2H, 2CH), 4.20 br.d (1H, H^{4a}, *J* 14.0 Hz), 4.48 br.d (1H, H^1, *J* 10.1 Hz), 6.64 d.d (1H_{Ar}, *J* 8.2, 1.8 Hz), 6.86 d (1H_{Ar}, *J* 1.8 Hz), 7.04 d (1H_{Ar}, *J* 8.2 Hz), 7.00–7.50 m (15H, 3Ph). Mass spectrum, *m/z* (I_{rel}, %): 563 (20) [*M* + 2]$^+$, 561 (65) [*M*]$^+$. Found, %: C 72.58; H 6.48; N 7.48. $C_{34}H_{28}ClN_3O_3$. Calculated, %: C 72.66; H 5.02; N 7.48.

1',3,3''-Triphenyl-8-trifluoromethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (IXg). Yield 0.49 g (82%), mp 262°C. ^{1}H NMR spectrum, δ, ppm: 1.48 d.d.d (1H, H^4, *J* 12.5, 11.6, 13.7 Hz), 1.62–1.75 m (3H, 3CH), 3.31 d.d.d.d (1H, H^3, *J* 12.5, 11.6, 4.5, 2.9 Hz), 3.44 d.d.d (1H, H^1, *J* 10.7, 11.6, 4.8 Hz), 3.58 and 3.12 *AB* (2H, $ArCH_2$, *J* 17.4 Hz), 4.31 br.d (1H, H^{4a}, *J* 13.7 Hz), 4.57 br.d (1H, H^1, *J* 10.7 Hz), 7.00 d (1H_{Ar}, *J* 8.8 Hz), 7.08–7.50 m (17H, 3Ph, ArH). Mass spectrum, *m/z* (I_{rel}, %): 595 (100) [*M*]$^+$. Found, %: C 70.58; H 4.77; N 7.04. $C_{35}H_{28}F_3N_3O_3$. Calculated, %: C 70.58; H 4.74; N 7.05.

3-Benzyl-1',3''-diphenyl-2,3,4,4a,5,6-hexahydro-6*1*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (IXh). Yield 0.47 g (86%), mp 232–234°C. ^{1}H NMR spectrum, δ, ppm: 0.97 d.d.d (1H, H^4, *J* 11.7, 12.4, 10.9 Hz), 1.24 d.d.d.d (1H, H^2, *J* 11.4, 13.5, 10.1, 2.8 Hz), 1.45 br.d (1H, H^2, *J* 13.2 Hz), 1.53 br.d (1H, H^4, *J* 12.5 Hz), 2.20–2.30 m (1H, H^3), 2.33 d.d (1H, CH_2Ph, *J* 9.2, 12.9 Hz), 2.62 d.d (1H, CH_2Ph, *J* 5.1, 12.9 Hz), 3.16 d.d.d (1H, H^1, *J* 14.8, 12.8, 2.8 Hz), 3.02 and 3.40 *AB* (2H, $ArCH_2$, *J* 17.3 Hz), 4.10 br.d (1H, H^{4a}, *J* 10.9 Hz), 4.12 br.d (1H, H^1, *J* 14.8 Hz), 6.64 d.d.d (1H_{Ar}, *J* 6.7, 7.8, 0.7 Hz), 6.87 br.d (1H_{Ar}, *J* 8.1 Hz), 6.98–7.08 m (4H_{Ph}), 7.12–7.47 m (13H, Ph, ArH). Mass spectrum, *m/z* (I_{rel}, %): 541 (87) [*M*]$^+$. Found, %: C 77.68; H 5.79; N 7.88. $C_{35}H_{31}N_3O_3$. Calculated, %: C 77.61; H 5.77; N 7.76.

1',3,3'-Trimethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (Xa). Yield 0.25 g (74%), mp 178–180°C. ^{1}H NMR spectrum, δ, ppm: 0.84 d (3H, CH_3, *J* 6.4 Hz), 1.08 d.d.d (1H, H^4, *J* 13.1, 11.3, 12.6 Hz), 1.11 d.d.d.d (1H, H^2, *J* 11.5, 12.8, 10.8, 3.2, 1.8 Hz), 1.32 br.d (1H, H^4, *J* 12.6 Hz), 1.52 br.d (1H, H^2, *J* 12.8 Hz), 1.59–1.68 m (1H, H^3), 2.88 d.d.d (1H, H^1, *J* 11.3, 13.1, 1.8 Hz), 3.16 s (3H, CH_3), 3.17 s (3H, CH_3), 3.01 and 3.28 *AB* (2H, $ArCH_2$, *J* 1.1 Hz), 3.44 d.d (1H, H^{4a}, *J* 11.3, 1.1), 4.01 d.d.d (1H, H^1, *J* 13.1, 3.2, 1.8 Hz), 6.60 d.d (1H_{Ar}, *J* 6.8, 8.0 Hz), 6.77 d (1H_{Ar}, *J* 8.0 Hz), 6.95 d (1H_{Ar}, *J* 6.1 Hz), 6.98 d.d (1H_{Ar}, *J* 6.4, 6.1 Hz). Mass spectrum, *m/z* (I_{rel}, %): 341 (100) [*M*]$^+$. Found, %: C 66.84; H 6.72; N 12.33. $C_{19}H_{23}N_3O_3$. Calculated, %: C 66.84; H 6.79; N 12.31.

1',3,3''-Trimethyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (Xa). Yield 0.27 g (72%), mp 188–190°C. ^{1}H NMR spectrum, δ, ppm: 0.82 d.d.d (1H, H^4, *J* 12.8, 12.8, 12.9 Hz), 0.87 d (3H, CH_3, *J* 6.4 Hz), 1.14 d.d.d (1H, H^2, *J* 12.8, 12.8, 3.0 Hz), 1.35 br.d (1H, H^4, *J* 12.8 Hz), 1.56 br.d (1H, H^2, *J* 13.4 Hz), 1.63–1.69 m (1H, H^3), 2.87 d.d.d (1H, H^1, *J* 12.8, 13.4, 1.8 Hz), 3.17 c (6H, 2CH_3), 3.25 and 2.98 *AB* (2H, $ArCH_2$, *J* 16.7 Hz), 3.47 d.d (1H, H^{4a}, *J* 11.6, 1.5 Hz), 3.98 br.d (1H, H^1, *J* 12.8 Hz), 6.60 d.d (1H_{Ar}, *J* 1.8, 8.2 Hz), 6.76 d (1H_{Ar}, *J* 1.8 Hz), 6.92 d (1H_{Ar}, *J* 8.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 377 (38) [*M* + 2]$^+$, 375 (100) [*M*]$^+$. Found, %: C 60.84; H 6.02; N 11.09. $C_{19}H_{22}ClN_3O_3$. Calculated, %: C 60.72; H 5.90; N 11.18.

1',3''-Dimethyl-3-phenyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (Xd). Yield 0.34 g (77%), mp 204–206°C. ^{1}H NMR spectrum, δ, ppm: 1.28 d.d.d (1H, H^2, *J* 12.8, 12.0, 11.8 Hz), 1.52 br.d (1H, H^2, *J* 12.5 Hz), 1.58–1.79 m (2H, 2CH), 2.80–3.00 m (1H, CH), 3.16 s (6H, 2CH_3), 3.10–3.20 m (1H, CH), 2.98 and 3.31 *AB* (2H, $ArCH_2$, *J* 17.0 Hz), 3.72 br.d (1H, H^{4a}, *J* 9.8 Hz), 4.12 br.d (1H, H^1, *J* 13.7 Hz), 6.62 d.d (1H_{Ar}, *J* 6.7, 1.6 Hz), 6.84 d (1H_{Ar}, *J* 1.6 Hz), 6.97 d (1H_{Ar}, *J* 6.7 Hz), 7.06–7.25 m (5H_{Ph}). Mass spectrum, *m/z* (I_{rel}, %): 439 (30) [*M* + 2]$^+$, 437 (87) [*M*]$^+$. Found, %: C 65.55; H 5.80; N 9.69. $C_{24}H_{24}ClN_3O_3$. Calculated, %: C 65.83; H 5.52; N 9.60.

1',3''-Dimethyl-3-phenyl-9-fluoro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (Xf). Yield 0.39 g (89%), mp 187–189°C. ^{1}H NMR spectrum, δ, ppm: 1.47 d.d.d (1H, H^2, *J* 11.6, 12.5, 11.8 Hz), 1.62 br.d (1H, H^2, *J* 14.0 Hz), 1.70–1.82 m (2H, H^2, H^4), 2.80–3.00 m (1H, H^1), 3.12 s (3H, CH_3), 3.21 s (3H, CH_3), 3.10–3.20 m (1H, H^3), 3.23 and 3.08 *AB* (2H, $ArCH_2$, *J* 16.9 Hz), 3.69 d.d (1H, H^{4a}, *J* 11.0, 1.9 Hz), 4.36 d.d.d (1H, H^1, *J* 12.8, 3.4, 3.8 Hz), 6.61 d.d ($1H_{Ar}$, *J* 4.8, 7.2 Hz), 6.82 d.d ($1H_{Ar}$, *J* 7.2, 1.8 Hz), 6.87 d.d.d ($1H_{Ar}$, *J* 7.2, 14.3, 1.8 Hz), 7.09–7.32 m ($5H_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 439 (30) $[M + 2]^+$, 437 (87) $[M]^+$. Found, %: C 65.55; H 5.80; N 9.69. $C_{24}H_{24}ClN_3O_3$. Calculated, %: C 65.83; H 5.52; N 9.60.

1',3''-Dimethyl-8-trifluoromethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (Xg). Yield 0.38 g (80%), mp 224–226°C. ^{1}H NMR spectrum, δ, ppm: 1.28 d.d.d (1H, H^4, *J* 12.5, 10.7, 11.8 Hz), 1.52 br.d (1H, H^2, *J* 12.5 Hz), 1.64 br.d (H, H^4, *J* 13.7 Hz), 1.65 br.d (H, H^2, *J* 11.6 Hz), 2.92 d.d.d.d (1H, H^3, *J* 11.6, 10.7, 4.2, 3.2 Hz), 3.16 s (3H, CH_3), 3.17 s (3H, CH_3), 3.10–3.20 m (1H, H^1), 3.05 and 3.32 *AB* (2H, $ArCH_2$, *J* 17.1 Hz), 3.82 br.d (1H, H^{4a}, *J* 10.0 Hz), 4.25 br.d (1H, H^1, *J* 13.7 Hz), 6.98 d ($1H_{Ar}$, *J* 8.5 Hz), 7.06–7.32 m (7H, Ph, ArH). Mass spectrum, *m/z* (I_{rel}, %): 471 (100) $[M]^+$. Found, %: C 63.77; H 5.18; N 9.09. $C_{25}H_{24}F_3N_3O_3$. Calculated, %: C 63.69; H 5.13; N 8.91.

3-Benzyl-1',3''-dimethyl-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (Xh). Yield 0.38 g (91%), mp 220–222°C. ^{1}H NMR spectrum, δ, ppm: 0.95 d.d.d (1H, H^4, *J* 11.7, 14.4, 11.4 Hz), 1.09 d.d.d.d (1H, H^2, *J* 11.4, 13.2, 13.6, 4.1 Hz), 1.35 br.d (1H, H^2, *J* 13.0 Hz), 1.39 br.d (1H, H^4, *J* 14.4 Hz), 1.75–1.88 m (1H, H^3), 2.36 d.d (1H, CH_2Ph, *J* 7.9, 13.4 Hz), 2.46 d.d (1H, CH_2Ph, *J* 7.6, 13.4 Hz), 2.72 d.d.d (1H, H^1, *J* 13.1, 13.6, 2.8 Hz), 3.08 s (3H, CH_3), 3.10 s (3H, CH_3), 3.05 and 3.26 *AB* (2H, $ArCH_2$, *J* 17.2 Hz), 3.42 d.d (1H, H^{4a}, *J* 11.7, 1.6 Hz), 4.00 d.d.d (1H, H^1, *J* 13.1, 4.1, 2.8 Hz), 6.65 d.d.d ($1H_{Ar}$, *J* 6.5, 7.4, 1.7 Hz), 6.84 d.d ($1H_{Ar}$, *J* 8.1, 1.4 Hz), 7.00 d.d ($1H_{Ar}$, *J* 7.4, 1.4 Hz), 7.01 d.d.d ($1H_{Ar}$, *J* 6.5, 8.1, 1.7 Hz), 7.10 d.d ($2H_{Ph}$, *J* 7.0, 8.2 Hz), 7.17 t ($1H_{Ph}$, *J* 7.6 Hz), 7.26 d.d.d ($2H_{Ph}$, *J* 7.0, 8.2, 7.6 Hz). Mass spectrum, *m/z* (I_{rel}, %): 417 (100) $[M]^+$. Found, %: C 71.97; H 6.52; N 10.04. $C_{25}H_{27}N_3O_3$. Calculated, %: C 71.92; H 6.52; N 10.06.

3-Benzyl-1',3''-dimethyl-9-chloro-2,3,4,4a,5,6-hexahydro-1*H*-spiro[benzo[*c*]quinolizine-5,5'-pyrimidine]-4',6'-dione (Xi). Yield 0.35 g (78%), mp 151–154°C. ^{1}H NMR spectrum, δ, ppm: 0.89 d.d (1H, H^4, *J* 11.5, 12.9 Hz), 1.15 d.d.d.d (1H, H^2, *J* 12.6, 12.5, 9.9, 1.8 Hz), 1.45 br.d (1H, H^4, *J* 12.9 Hz), 1.50 br.d (1H, H^2, *J* 12.6 Hz), 1.68–1.89 m (1H, H^3), 2.33 d.d (1H, CH_2Ph, *J* 13.4, 7.9 Hz), 2.52 d.d (1H, CH_2Ph, *J* 13.4, 7.9 Hz), 2.77 d.d.d (1H, H^1, *J* 12.9, 12.7, 1.8 Hz), 3.13 s (3H, CH_3), 3.13 s (3H, CH_3), 3.08 and 3.21 *AB* (2H, $ArCH_2$, *J* 17.0 Hz), 3.41 d.d (1H, H^{4a}, *J* 11.5, 1.8 Hz), 3.95 br.d (1H, H^1, *J* 12.5 Hz), 6.60 d.d ($1H_{Ar}$, *J* 7.9, 1.6 Hz), 6.75 d ($1H_{Ar}$, *J* 1.6 Hz), 6.93 d ($1H_{Ar}$, *J* 7.9 Hz) 7.03–7.26 m ($5H_{Ph}$). Mass spectrum, *m/z* (I_{rel}, %): 453 (41) $[M + 2]^+$, 451 (97) $[M]^+$. Found, %: C 66.52; H 5.80; N 9.45. $C_{25}H_{26}ClN_3O_3$. Calculated, %: C 66.44; H 5.80; N 9.30.

2-[2-(4-R-Piperidino)benzylidene]malononitriles XIa–XIc. To a solution of 1 mmol of benzaldehyde **IVa**, **IVg**, and **IVh** in 10 ml of toluene was added 1 mmol of malononitrile, and the mixture was boiled for 3–6 h (TLC monitoring). The reaction mixture was cooled to room temperature, the solvent was evaporated in a vacuum, the residue was ground with ethanol.

2-[2-(4-Methylpiperidino)benzylidene]-malononitrile (XIa). Yield 0.22 g (88%), mp 105–108°C. ^{1}H NMR spectrum, δ, ppm: 1.90–2.09 m (4H, $2CH_2$), 2.60–2.70 m (1H, CH), 2.94–3.05 m (2H, 2NCH), 3.20–3.25 m (2H, 2NCH), 7.03 d.d ($1H_{Ar}$, *J* 7.9, 1.4 Hz), 7.14 d ($1H_{Ar}$, *J* 8.4 Hz), 7.58 d.d.d ($1H_{Ar}$, *J* 8.4, 8.1, 1.4 Hz), 7.94 d.d ($1H_{Ar}$, *J* 8.1, 7.9), 8.12 s (1H, CH=). Mass spectrum, *m/z* (I_{rel}, %): 251 (100) $[M]^+$. Found, %: C 76.47; H 6.85; N 16.40. $C_{16}H_{17}N_3$. Calculated, %: C 76.46; H 6.82; N 16.72.

2-[2-(4-Benzylpiperidino)benzylidene]-malononitrile (XIb). Yield 0.12 g (90%), mp 105–107°C. ^{1}H NMR spectrum, δ, ppm: 1.48–1.78 m (2H, 2CH), 1.82–2.94 m (3H, 3CH), 2.61 d (2H, CH_2Ph, *J* 6.4 Hz), 2.79 d.d (2H, 2NCH, *J* 11.3, 11.9 Hz), 3.09 br.d (2H, 2NCH, *J* 11.9 Hz), 7.10–7.18 m (7H, Ph, ArH), 7.54 d.d ($1H_{Ar}$, *J* 7.9, 7.6 Hz), 7.94 d ($1H_{Ar}$, *J* 7.3 Hz), 8.14 s (1H, CH=). Mass spectrum, *m/z* (I_{rel}, %): 327 (100) $[M]^+$. Found, %: C 80.75; H 6.47; N 12.88. $C_{22}H_{21}N_3$. Calculated, %: C 80.70; H 6.46; N 12.83.

2-[2-(4-Phenylpiperidino)-5-trifluoromethylbenzylidene]malononitrile (XIc). Yield 0.34 g (89%), mp 111–112°C. ^{1}H NMR spectrum, δ, ppm: 1.90–2.08 m (4H, $2CH_2$), 2.69–2.75 m (1H, CH), 2.97–3.16 m (2H, 2NCH), 3.33–3.42 m (2H, 2NCH), 7.10–7.30 m

($5H_{Ar}$), 7.35 d ($1H_{Ar}$, *J* 8.8 Hz), 7.79 d.d ($1H_{Ar}$, *J* 8.8, 2.2 Hz), 8.16 br.s ($1H_{Ar}$), 8.25 s (1H, CH=). Mass spectrum, *m/z* (I_{rel}, %): 381 (100) $[M]^+$. Found, %: C 69.25; H 4.75; N 11.32. $C_{22}H_{18}F_3N_3$. Calculated, %: C 69.28; H 4.76; N 11.02.

Quinolizinedicarbonitriles XIIa–XIIc, XIIIa–XIIIc. A solution of 2 mmol of compound **XI** in 20 ml of butanol was boiled for 2–10 h (TLC monitoring). The reaction mixture was cooled to room temperature, the solvent was evaporated in a vacuum, the residue was ground with ethanol.

(3*S,4a*R**)-3-Methyl-2,3,4,4a,5,6-hexahydro-1*H*-benzo[*c*]quinolizine-5,5-dicarbonitrile (XIIa).** Yield 0.12 g (44%), mp 106–108°C. ^{1}H NMR spectrum, δ, ppm: 1.05 d (3H, CH_3, *J* 6.3 Hz), 1.27 d.d.d (1H, H^4, *J* 11.3, 12.1, 12.5 Hz), 1.74–2.00 m (2H, H^4, H^2), 2.12 br.d (1H, H^2, *J* 12.2 Hz), 2.22–2.29 m (1H, H^3), 2.77 d.d.d (1H, H^1, *J* 13.1, 12.5, 2.5 Hz), 3.47 and 3.61 *AB* (2H, $ArCH_2$, *J* 15.5 Hz), 3.78 d.d (1H, H^{4a}, *J* 11.3, 4.0 Hz), 4.03 d.d.d (1H, H^1, *J* 13.1, 5.1, 2.6 Hz), 6.74 d.d ($1H_{Ar}$, *J* 8.6, 9.2 Hz), 6.95 d ($1H_{Ar}$, *J* 8.2 Hz), 7.07 d ($1H_{Ar}$, *J* 9.2 Hz), 7.14 d.d ($1H_{Ar}$, *J* 8.2, 8.6 Hz). Mass spectrum, *m/z* (I_{rel}, %): 251 (100) $[M]^+$. Found, %: C 76.54; H 6.85; N 16.78. $C_{16}H_{17}N_3$. Calculated, %: C 76.46; H 6.82; N 16.72.

(3*R,4a*R**)-3-Methyl-2,3,4,4a,5,6-hexahydro-1*H*-benzo[*c*]quinolizine-5,5-dicarbonitrile (XIIIa)**. Yield 0.20 g (40%), mp 107–109°C. ^{1}H NMR spectrum, δ, ppm: 1.13 d (3H, CH_3, *J* 7.0 Hz), 1.62 br.d (1H, H^2, *J* 14.2 Hz), 1.89 d.d.d (1H, H^4, *J* 14.2, 12.5, 3.0 Hz), 1.94–2.05 m (2H, H^4, H^2), 2.22–2.29 m (1H, H^3), 3.02 d.d.d (1H, H^1, *J* 13.6, 12.5, 3.1 Hz), 3.70 and 3.52 *AB* (2H, $ArCH_2$, *J* 15.8 Hz), 3.77 d.d.d (1H, H^1, *J* 11.6, 5.5, 4.2 Hz), 3.80 d.d (1H, H^{4a}, *J* 10.5, 2.8 Hz), 6.74 d.d ($1H_{Ar}$, *J* 8.6, 9.2 Hz), 6.95 d ($1H_{Ar}$, *J* 8.2 Hz), 7.07 d ($1H_{Ar}$, *J* 9.2 Hz), 7.14 d.d ($1H_{Ar}$, *J* 8.2, 8.6 Hz). Mass spectrum, *m/z* (I_{rel}, %): 251 (100) $[M]^+$. Found, %: C 76.49; H 6.95; N 16.89. $C_{16}H_{17}N_3$. Calculated, %: C 76.46; H 6.82; N 16.72.

(3*S,4a*R**)-3-Benzyl-2,3,4,4a,5,6-hexahydro-1*H*-benzo[*c*]quinolizine-5,5-dicarbonitrile (XIIb)**. Yield 0.21 g (32%), mp 112–113°C. ^{1}H, δ, ppm: 1.66 br.d (1H, H^4, *J* 13.1 Hz), 1.78 d.d.d (1H, H^4, *J* 14.9, 2.7, 2.1 Hz), 1.88 d.d.d.d (1H, H^2, *J* 14.9, 15.0, 10.0, 4.3 Hz), 2.03 br.d (1H, H^2, *J* 13.7 Hz), 2.20–2.40 m (1H, H^3), 2.69 d.d (1H, CH_2Ph, *J* 7.2, 11.1 Hz), 2.81 d.d (1H, CH_2Ph, *J* 6.1, 11.1 Hz), 3.12 d.d.d (1H, H^1, *J* 11.6, 12.2, 2.7 Hz), 3.68 and 3.49 *AB* (2H, $ArCH_2$, *J* 16.2 Hz), 3.80 d.d.d (1H, H^1, *J* 12.2, 3.0, 4.3 Hz), 3.97 d.d (1H, H^{4a}, *J* 13.9, 2.7 Hz), 6.73 d.d ($1H_{Ar}$, *J* 7.5, 7.5 Hz), 6.75 d.d ($1H_{Ar}$, *J* 6.9, 7.5 Hz), 6.98 d ($1H_{Ar}$, *J* 7.5 Hz), 7.09 d ($1H_{Ar}$, *J* 6.9 Hz), 7.19 d ($2H_{Ph}$, *J* 7.1 Hz), 7.22 t ($1H_{Ph}$, *J* 7.3 Hz), 7.30 d.d ($2H_{Ph}$, *J* 7.1, 7.3 Hz). Mass spectrum, *m/z* (I_{rel}, %): 327 (100) $[M]^+$. Found, %: C 80.88; H 6.49; N 12.93. $C_{22}H_{21}N_3$. Calculated, %: C 80.70; H 6.46; N 12.83.

(3*R,4a*R**)-3-Benzyl-2,3,4,4a,5,6-hexahydro-1*H*-benzo[*c*]quinolizine-5,5-dicarbonitrile (XIIIb)**. Yield 0.21 g (38%), mp 107–109°C. ^{1}H NMR spectrum, δ, ppm: 1.20–1.30 m (2H, H^2, H^4), 1.88 br.d (1H, H^4, *J* 13.5 Hz), 1.80–1.90 m (1H, H^3), 2.17 d.d (1H, H^2, *J* 12.1, 1.6 Hz), 2.55 d.d (1H, CH_2Ph, *J* 7.5, 13.3 Hz), 2.69 d.d (1H, CH_2Ph, *J* 6.5, 13.3 Hz), 2.73 d.d.d (1H, C^1, *J* 11.3, 10.1, 2.5 Hz), 3.53 d.d (1H, H^{4a}, *J* 12.7, 2.5 Hz), 3.47 and 3.58 *AB* (2H, $ArCH_2$, *J* 16.1 Hz), 4.02 d.d.d (1H, H^1, *J* 11.3, 2.3, 2.8 Hz), 6.73 d.d ($1H_{Ar}$, *J* 7.0, 7.1 Hz), 6.92 d ($1H_{Ar}$, *J* 7.1 Hz), 7.00 d ($1H_{Ar}$, *J* 7.6 Hz), 7.13 d.d ($1H_{Ar}$, *J* 7.6, 7.0 Hz), 7.19 d ($2H_{Ph}$, *J* 8.2 Hz), 7.23 t ($1H_{Ph}$, *J* 7.2 Hz), 7.28 d.d ($2H_{Ph}$, *J* 8.2, 7.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 327 (100) $[M]^+$. Found, %: C 80.88; H 6.49; N 12.93. $C_{22}H_{21}N_3$. Calculated, %: C 80.98; H 6.49; N 13.08.

(3*S,4a*R**)-8-Trifluoromethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-benzo[*c*]quinolizine-5,5-dicarbonitrile (XIIc).** Yield 0.30 g (39%), mp 109°C. ^{1}H NMR spectrum, δ, ppm: 2.21–2.35 m (2H, 2CH), 2.52–2.62 m (2H, 2CH), 3.19 d.d.d.d (H, CHPh, *J* 5.8, 4.5, 2.5, 1.2 Hz), 3.37 d.d.d (1H, H^1, *J* 6.3, 12.5, 10.5 Hz), 3.63 and 3.73 *AB* (2H, $ArCH_2$, *J* 16.5 Hz), 3.84 d.d (1H, H^1, *J* 12.3, 2.0 Hz), 4.08 d.d (1H, H^{4a}, *J* 11.3, 3.6 Hz) 7.10–7.42 m ($7H_{Ar}$), 7.03 d ($1H_{Ar}$, *J* 8.8 Hz). Mass spectrum, *m/z* (I_{rel}, %): 381 (100) $[M]^+$. Found, %: C 69.33; H 4.65; N 11.11. $C_{22}H_{18}F_3N_3$. Calculated, %: C 69.28; H 4.76; N 11.02.

(3*R,4a*R**)-8-Trifluoromethyl-3-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-benzo[*c*]quinolizine-5,5-dicarbonitrile (XIIIc).** Yield 0.30 g (39%), mp 105–106°C. ^{1}H NMR spectrum, δ, ppm: 2.21–2.35 m (2H, 2CH), 2.52–2.62 m (2H, 2CH), 3.00 d (1H, CHPh, *J* 10.8, 14.3 Hz), 3.38 d.d.d.d (1H, H^1, *J* 10.8, 12.2, 3.2, 1.8 Hz), 3.68 and 3.84 *AB* (2H, $ArCH_2$, *J* 12.3 Hz), 3.95 d.d (1H, H^{4a}, *J* 10.8, 2.0 Hz), 4.28 br.d (1H, H^1, *J* 12.8 Hz), 7.03 d ($1H_{Ar}$, *J* 8.8 Hz), 7.10–7.42 m ($7H_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 381 (100) $[M]^+$. Found, %: C 69.25; H 4.75; N 11.32. $C_{22}H_{18}F_3N_3$. Calculated, %: C 69.28; H 4.76; N 11.02.

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