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Synthesis of Chiral Benzoacridinone Derivatives by Three-Component Condensation of [(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde with Naphthalen-1-amine and Cyclic β-Diketones

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Abstract—Three-component condensation of [(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde with naphthalen-1-amine and cyclic β-diketones gave 7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydro-7*H*-benzo[*c*]acridin-8-one derivatives possessing three or more asymmetric carbon atoms. Steric factors were found to be responsible for the predominant formation of the (7*R*)-isomers (*R*/*S* ≈ 7 : 5) and orientation of substituents in the cyclohexenone fragment. The same factors determined complete regioselectivity of the reaction with methyl 2,4-dioxocyclohexane-1-carboxylates as dicarbonyl component, which led to exclusive formation of methyl 8-oxobenzoacridine-11-carboxylates. In the reaction of [(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde with naphthalen-1-amine and barbituric acid as dicarbonyl component, the only product was that formed by two-component condensation of barbituric acid with bicyclic aldehyde.

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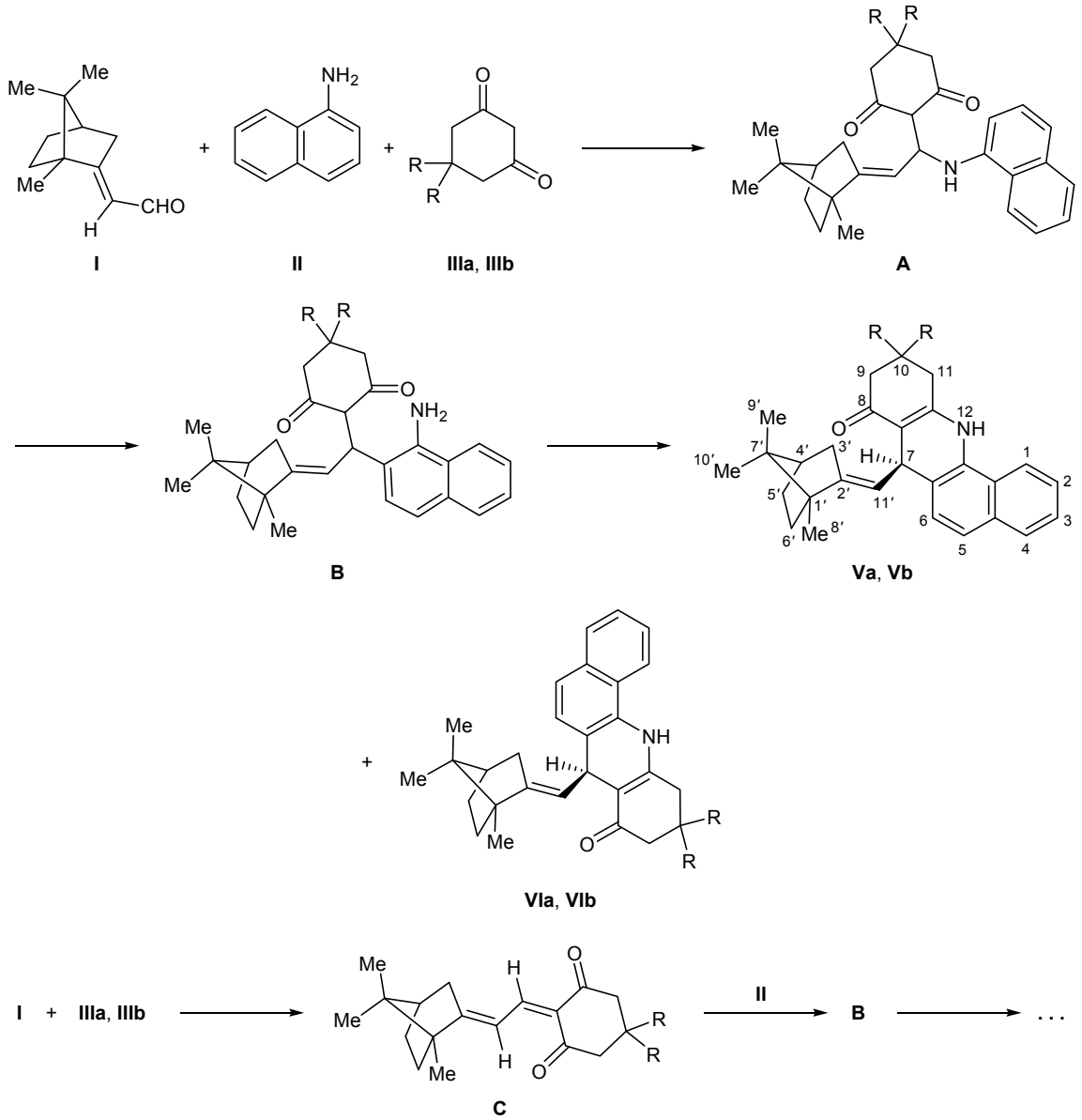
Three-component condensation of aromatic aldehydes with amines and cyclic β-diketones is widely used in the synthesis of benzo[*a*]acridine and 4,7-phenanthroline derivatives, as well as derivatives of other fused nitrogen-containing heterocycles [1–3]. Products of such condensations possess a variety of practically useful properties, in particular they exhibit a broad spectrum of biological activity [4–6]. Published data on cyclocondensations with participation of non-aromatic aldehydes are very few in number; reactions involving formaldehyde were mainly reported [7–9]. We were the first to demonstrate that [(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde (**I**) reacts with naphthalen-2-amine and cyclic β-diketones, following the cascade heterocyclization pattern with formation of chiral benzoacridinone derivatives, 12-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-ylidenemethyl]-8,9,10,12-tetrahydro-7*H*-benzo-[*a*]acridin-11-ones [10].

In the present work we examined three-component condensation of bicyclic aldehyde **I** with naphthalen-1-amine (**II**) and different cyclic β-diketones **III**. The reactions were carried out according to the standard procedure, by heating equimolar amounts of the reactants in boiling ethanol [11]. The products were precipitated from the reaction solution by adding excess diethyl ether. Repeated recrystallizations of stereoisomer mixtures from acetone, ethanol, and/or its mixtures with benzene gave samples enriched in each stereoisomer up to 80–85%.

The reaction with participation of naphthalen-1-amine (**II**) was characterized by the same regio- and stereoselectivity as in the condensation described by us previously [10]. The reactions of [(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde (**I**) with naphthalen-1-amine (**II**) and β-diketones having no asymmetric or enantiotopic carbon atoms [cyclohexane-1,3-dione (**IIIa**) and 5,5-dimethylcyclohexane-1,3-dione (**IIIb**, dimedone)] gave mixtures of the corresponding stereoisomeric fused heterocyclic compounds differing by configuration (*R* or *S*) of the asymmetric C^7 atom. In the condensations of **I** and **II**

Scheme 1.



with cyclohexane-1,3-dione and dimedone, the ratio of the (7*R*)- and (7*S*)-isomers **V** and **VI** ws the same as in the reaction with naphthalen-2-amine (~7 : 5) (Scheme 1).

The product structure was determined on the basis of their IR and ^{1}H and ^{13}C NMR spectra. In the IR spectra of **V** and **VI** absorption bands in the region 3200–3300 cm^{-1} were assigned to stretching vibrations of the N–H bond. One or two strong absorption bands belonging to vibrations of conjugated ketoenamine fragment (vinylogous amide) were observed at about 1590 cm^{-1}. All compounds obtained from naphthalen-2-amine displayed two bands in the same region, indicating different symmetry of vibrations of the corresponding fragment. The steric structure of benzoacridinones **V** and **VI** was determined by ^{1}H NMR spectroscopy. The NMR spectra were obtained from samples enriched in the corresponding stereoisomer up to 80% or more, using DMSO-d_6 as solvent, for the products are almost insoluble in other organic solvents. In many cases, the solvent signals (δ 2.50 and ~3 ppm) partially or completely overlapped signals from protons in the examined compounds, including the key signals, so that steric structure determination was con-

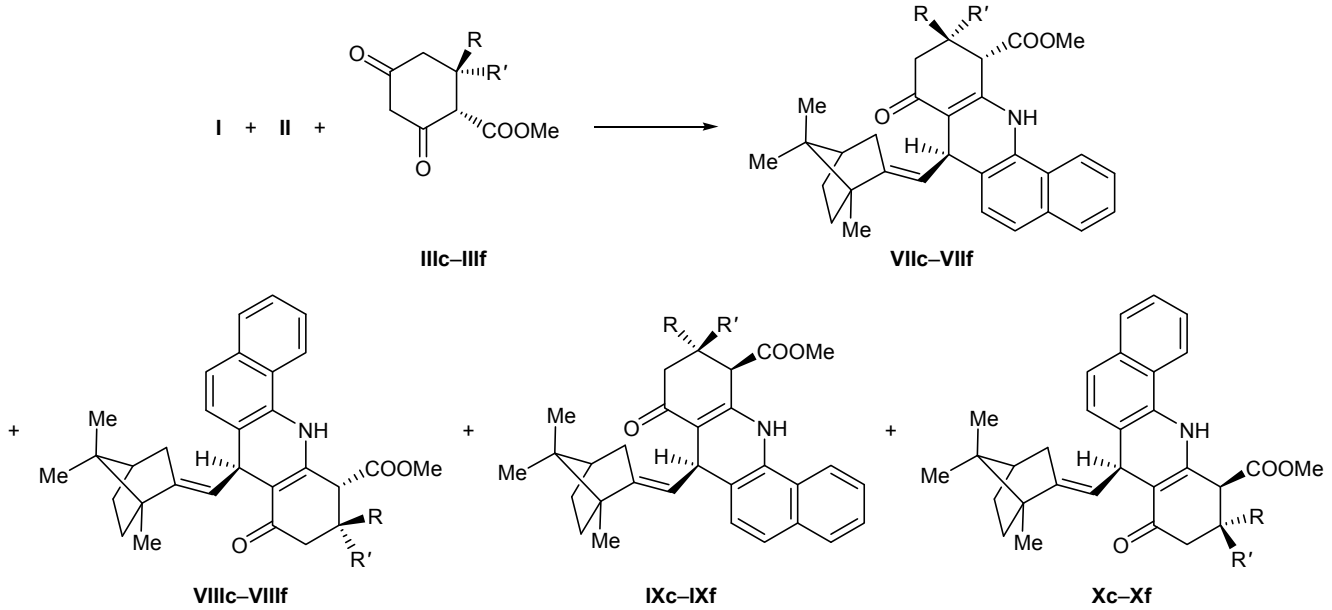
siderably complicated. To overcome this obstacle, a few drops of D_2O or CCl_4 were added to a solution in DMSO-d_6. As a result, some displacement of signals (downfield or upfield, respectively) from both solvent (δ 3 ppm) and dissolved compound occurred, and we were able to determine the multiplicity of overlapped signals. Signals were assigned taking into account their multiplicity; in some cases, double resonance techniques were used.

The most convenient for interpretation were the spectra of dimedone derivatives **Vb** and **VIb**, which contained the simplest set of signals. Due to strong steric shielding, the exocyclic double bond in (1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)acetaldehyde retains its *trans* configuration, as follows from the *trans*-allylic coupling between 3′-H and 11′-H ($^4J \approx$ 2 Hz). The vicinal coupling constants between protons on $C^{11'}$ (δ 4.61, 4.68 ppm) and C^7 (δ 4.85, 4.88 ppm) in both stereoisomers are equal to 10 Hz, indicating that their mutual arrangement approaches *antiperiplanar* configuration. Thus stereoisomeric compounds **V** and **VI** differ from each other by mutual orientation of the bornane and benzoacridinone fragments: the dimethylmethylene bridge in one isomer is oriented toward the cyclohexenone fragment, and in the other, toward the naphthalene fragment. Different shielding effects of these fragments on protons in the bornane moiety allowed us to unambiguously assign the steric structure of the isomeric products. In the ^{1}H NMR spectrum of the major isomer the *exo*-3′-H proton resonated as a double doublet of triplets (^2J = 16, $^3J_{exo\text{-}3',4'}$ = 3.5, $^4J_{exo\text{-}3',exo\text{-}5'} = {}^4J_{exo\text{-}3'\text{-},11'}$ = 1.5 Hz). The chemical shift of *exo*-3′-H is 2.86 ppm, indicating that this proton is spatially close to the carbonyl group; therefore, the major isomer has (7*R*)-configuration **Vb**. The *endo*-3′-H signal is located in the spectrum of **Vb** at δ 2.10 ppm (d, ^2J = 16 Hz). The corresponding signals of (7*S*)-stereoisomer **VIb** are characterized by the same multiplicities, and they appear at δ 2.53 (*exo*-3′-H) and 2.61 ppm (*endo*-3′-H). Change of the environment of $C^{3'}$ in **VIb** compared to **Vb** leads to upfield shift of the *exo*-3′-H signal (Δδ = –0.33 ppm) and downfield shift of the *endo*-3′-H signal (Δδ = +0.51 ppm). Analogous pattern was observed previously for structurally related benzo[*a*]acridinones [10]. We also noted that the benzoacridinone fragment considerably shields the bornane fragment, so that many signals from protons in the latter appear in anomalously strong field. Signals of the corresponding protons in **Vb** and **VIb** are also displaced upfield, but to a lesser extent than in the spectra of analogous benzo[*a*]acridinones. The chemical shifts of protons in the 1′-CH_3 and *syn*-7′-CH_3 methyl groups of **Vb** are 0.61 and 0.66 ppm, and the corresponding signals of the benzo[*a*]acridinone analog are located at δ 0.47 and 0.59 ppm, respectively. Obviously, weaker shielding effect of the benzo[*c*]acridinone system is related to remoteness of the naphthalene fragment from the bicycloheptane moiety. Signals of the 1′-CH_3 and *syn*-7′-CH_3 methyl groups in (7*S*)-isomer **VIb** appear at δ 0.64 and 0.69 ppm, respectively. The *endo*-protons on $C^{5'}$ and $C^{6'}$ resonate as double doublets of doublets at δ 1.11 and 1.05 ppm (^2J = 12.0, $^3J_{endo,endo}$ = 8.0, $^3J_{endo,exo}$ = 4.0 Hz) in the spectrum of **Vb** and at δ 1.09 and 1.07 ppm in the spectrum of **VIb** (the coupling constants are the same as for **Vb**). The positions and multiplicities of the other signals are very consistent with the assumed structures (see Experimental).

We previously found that methylene protons in the α-position with respect to the carbonyl group in the cyclohexenone ring of benzo[*a*]acridinones display a larger geminal coupling constant (^2J = 18 Hz), as compared to those on the carbon atom neighboring to the double C=C bond (^2J = 16 Hz). The chemical shifts of protons on C^8 and C^{10} depend on the substituents in both cyclohexenone ring and on C^{12}, and they may vary over a quite broad range. In the spectra of stereoisomeric compounds **Vb** and **VIb** methylene protons on C^9 (in the α-position with respect to the carbonyl group) resonate in a weaker field (δ ~2.60 and ~2.40 ppm, ^2J = 18.0 Hz) relative to the methylene protons on C^{11} (δ ~2.20 and ~2.00 ppm, ^2J = 16.0 Hz). These findings were used while determining the structure of more complex benzoacridinone derivatives (see below).

Dimedone derivatives **Vb** and **VIb** isolated from the isomer mixture had a satisfactory purity, and their amounts were sufficient to record their ^{13}C NMR spectra. The carbon signals were assigned on the basis of their positions and multiplicities, as well as by comparing the chemical shifts of analogous carbon nuclei in **Vb** and **VIb** with those in previously examined bornane and benzacridinone derivatives. As a rule, differences in the carbon chemical shifts of stereoisomers did not exceed 1 ppm. Furthermore, the chemical shicts of carbon atoms in the bornane fragment (except for $C^{2'}$) almost coincided with those typical of camphor. Presumably, shielding effect of the naphthalene ring in molecules **Vb** and **VIb** compensates deshielding produced by the enone carbonyl group.

Scheme 2.



R = R′ = Me (**c**); R′ = H, R = 2,4,6-$Me_3C_6H_2$ (**d**), 3,4-$(CH_3O)_2C_6H_3$ (**e**), 3,4-$CH_2O_2C_6H_3$ (**f**).

The mechanism of three-component cyclocondensation has been discussed repeatedly [12]. The most probable is intermediate formation of Mannich base **A** (Scheme 1) which may be transformed into next intermediate **B** via retro-hydride rearrangement. Intramolecular ring closure in **B** yields compound **V** and/or **VI**. Theoretically, intermediate **B** can also be generated by alkylation of naphthalene-1-amine with the crotonization product of aldehyde **I** and β-diketone **III**, diketodiene **C**. However, participation of the latter seems to be hardly probable, taking into account that considerable difference in spatial accessibilities of the α- and β-sides in intermediate **C** should give rise to higher stereoselectivity in the alkylation process, and the fraction of (7*R*) stereoisomer in the reaction mixture should be greater. Some prevalence of (7*R*)-isomers **V** in the reactions with cyclohexane-1,3-dione (**IIIa**) and dimedone (**IIIb**) is likely to be determined by moderate preference for the formation of intermediates **A** in which the bulky molecular fragments (bornane and naphthalene) appear maximally remote from each other.

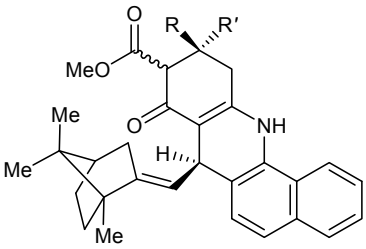
Stereochemical control was also observed in the reactions of aldehyde **I** with naphthalen-1-amine and methyl 2,4-dioxocyclohexane-1-carboxylates **IIIc**–**IIIf** having different substituents on C^5. For example, in the reaction with methyl 2,2-dimethyl-4,6-dioxocyclohexane-1-carboxylate (**IIIc**) we obtained a mixture of four stereoisomers **VIIa**–**Xc** whose fractions in the reaction mixture were 42, 33, 17, and 8%, respectively (Scheme 2).

The (7*R*)-configuration was assigned to isomeric compounds **VIIc** and **IXc**, taking into account the chemical shift of the *exo*-3′-H proton in the ^{1}H NMR spectra, δ 2.82 and 2.81 ppm, respectively. The downfield position of the *exo*-3′-H signal suggests that this proton is spatially close to the carbonyl group. The *endo*-3′-H signal appeared at δ 2.09 and 2.08 ppm, respectively. In the ^{1}H NMR spectra of (7*S*)-stereoisomers **VIIIc** and **Xc** the corresponding signals were observed at δ 2.59 and 2.58 ppm (*exo*-3′-H) and 2.63 and 2.62 ppm (*endo*-3′-H). The orientation of the methoxycarbonyl group in isomeric compounds **VII**–**X** was determined by analysis of chemical shifts of the proton on C^{11}. Compounds **VIIc** and **VIIIc** displayed signals from 11-H as singlets at δ 3.06 and 3.12 ppm, respectively, whereas the corresponding signals of **IXc** and **Xc** were located in a weaker field, at δ 3.34 and 3.35 ppm, respectively. These findings suggest shielding of 11-H by the bornane fragment in molecules **VIIc** and **VIIIc** and hence *trans* orientation of the substituents on C^7 and C^{11}.

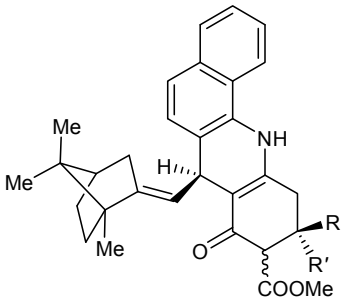
The results showed that the formation of (7*R*)-stereoisomers **VIIc** and **IXc** is preferred (42 + 17%) and that isomers **VIIc** and **VIIIc** with *trans* orientation of the bicyclic fragment and ester group also predominate (42 + 33%). The isomer ratio is determined by not only steric factors but also stoichiometry of the reaction.

Insofar as initial β-diketone **IIIc** is a racemate, the fraction of products with (*S*)-configuration of C^{11} (**VIIc** + **Xc**) should be equal to the fraction of products with (*R*)-configuration of the same center (**VIIIc** + **IXc**); this is actually the case.

The heterocyclization could also give rise to regioisomeric 9-methoxycarbonyl derivatives **XI** and **XII**.



XI



XII

The position of the ester moiety in the cyclohexenone ring of compounds **VIIc**–**Xc** was determined taking into account that the ^{1}H NMR spectra of all four stereoisomers contained a couple of doublets from protons on C^9 with a geminal coupling constant ^2J of 18 Hz. The chemical shifts of these protons are very consistent with the position of the methoxycarbonyl group on C^{11}. In the spectra of analogous compounds **Vb** and **VIb** having no ester group, the corresponding signals appear at δ 2.60 and 2.42 ppm. Among these, the upfield signal is likely to belong to the proton oriented *cis* with respect to the bornylidenemethyl substituent, so that this proton is shielded by the latter. In the spectrum of compound **VIIc** signals from protons on C^9 are observed at δ 2.40 and 2.88 ppm. Obviously, the signal from *trans*-9-H is displaced downfield (Δδ = ~0.3 ppm) as a result of 1,3-nonvalence interaction with the polar ester group. The position of the *cis*-9-H signal almost does not change, for steric environments of that proton in compounds **Vb** and **VIIc** are similar. The same chemical shift ratio is typical of the second *trans* isomer, compound **VIIIc**.

cis-Isomer **IXc** displayed in the ^{1}H NMR spectrum signals from protons on 9-H at δ 2.70 and 2.60 ppm. It is obvious that in this case the downfield signal belongs to the proton oriented *cis* with respect to the 11-methoxycarbonyl group due to deshielding by the latter (Δδ ≈ 0.3 ppm). In contrast, the chemical shift of *trans*-9-H (δ 2.60 ppm) is the same as in analog **Vb**. The chemical shifts of protons in the second *cis* isomer (**Xc**) are very similar to those of compound **IXc**.

The formation of benzoacridinone-11-carboxylates corresponds to the cyclization of intermediate **C** at the less sterically accessible carbonyl group (shielded by the ester group) in the β-diketone fragment. Nevertheless, no 9-substituted regioisomers were detected in the reaction mixture. Obviously, the formation of a conformer with spatially close bornane fragment and ester group involves strong steric hindrances, so that the reaction is strictly regioselective.

Heterocyclizations with racemic methyl 6-aryl-2,4-dioxocyclohexane-1-carboxylates **IIId**–**IIIf** with *trans* arrangement of the ester and aryl substituents also afforded four stereoisomers **VII**–**X** whose weight fractions in the reaction mixture were ~26, 18, 32, and 24%, respectively. As previously, the structure of stereoisomers was determined on the basis of chemical shifts of key protons at $C^{3'}$, C^{11}, and C^{10}. The (7*R*) or (7*S*) configuration was assigned taking into account the chemical shifts of 3′-H in the bornane fragment. Compounds **IXd**–**IXf** and **Xd**–**Xf** which displayed the 10-H signal in a stronger field (δ ~4.0 ppm) were assigned the structure of stereoisomers with *trans* orientation of the aryl substituent on C^{10} with respect to the bornane fragment. The corresponding proton in *cis* isomers **VIId**–**VIIf** and **VIIId**–**VIIIf** is not shielded by the alicyclic fragment, and it appears at ~4.3 ppm. The 11-H proton in compounds **IXd**–**IXf** and **Xd**–**Xf** resonates in a weaker field (δ ~3.6 ppm), as compared to isomers **VIId**–**VIIf** and **VIIId**–**VIIIf** with *trans*-oriented methoxycarbonyl group (δ ~3.3 ppm).

As follows from the isomer ratio, the reactions with methyl 6-aryl-2,4-dioxocyclohexane-1-carboxylates also result in preferential formation of (7*R*)-stereoisomers (58% of **VII** + **IX** in the reaction mixture). The fractions of the *trans* and *cis* isomers differ less significantly than in the case of methyl 2,2-dimethyl-4,6-dioxocyclohexane-1-carboxylate derivatives. This is related to steric structure of the initial β-diketones. Insofar as the aryl and methoxycarbonyl substituents in β-diketones **IIId**–**IIIf** are oriented *trans* with respect to each other, the methoxycarbonyl group in the benzoacridinone isomer with *trans*-oriented aryl substituent should inevitably be oriented *cis* and vice versa. As

a result, the stereoselectivity with respect to the C^{10} and C^{11} chiral centers is low, and stereoisomers with *trans* orientation of the aryl substituent slightly prevail in the reaction mixture.

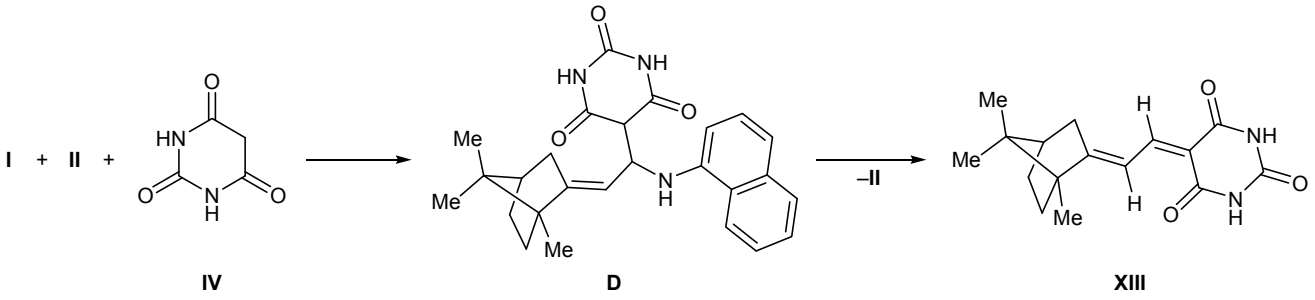
In the ^{1}H NMR spectra of all stereoisomeric 10-aryl-11-methoxycarbonyl derivatives **VII–X** the multiplicity of signals from protons on C^{11} and C^{10} corresponds to their axial (or pseudoaxial) orientation (see Experimental). Obviously, the formation of axial–pseudoaxial conformer is unfavorable for steric reasons (repulsion of the bornane fragment from one of the substituents on C^{10} or C^{11}).

Thus three-component condensation of (1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)acetaldehyde (**I**) with naphthalen-1-amine (**II**) and cyclic β-diketones ensured successful synthesis of 7-(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl)-7,8,9,10,11,12-hexahydrobenzo[*c*]acridin-8-one derivatives having various substituents in the cyclohexenone fragment. The cyclization was completely regioselective and moderately stereoselective due to different stabilities of different conformers of the aminodiketone intermediate whose formation precedes the cyclization. It should be noted that the condensation studied in the present work afforded stereoisomeric products at absolutely the same ratio as in analogous condensation with naphthalen-2-amine, which was reported previously. Presumably, steric control in these reactions arises at the stage of formation of aminodiketone intermediate **A** due to difference in spatial accessibilities of the α- and β-sides of the Schiff base generated from bicyclic aldehyde **I** and aromatic amine in the initial stage.

We also tried to obtain a fused heterocyclic compound possessing three nitrogen atoms via three-component condensation of (1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)acetaldehyde (**I**) with naphthalen-1-amine (**II**) and barbituric acid (**IV**). Unexpectedly, we isolated 5-[2-(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)ethylidene]hexahydropyrimidine-2,4,6-trione (**XIII**) which is the product of two-component condensation of aldehyde **I** with CH acid **IV** (Scheme 3). We made an attempt to modify the synthetic procedure with a view to avoid formation of compound **XIII**. For this purpose, a solution of aldehyde **I** and naphthalen-1-amine (**II**) in alcohol was heated to obtain the corresponding Schiff base (GLC), the solution was cooled, barbituric acid (**IV**) was added, and the mixture was heated again. Nevertheless, after some time compound **XIII** separated from the solution instead of expected fused heterocyclic derivatives. The only by-product detected in the reaction mixture was the corresponding Schiff base. The observed reaction pattern may be rationalized as follows. Unlike intermediates **A** described above, the carbonyl groups in intermediate **D** generated by addition of barbituric acid at the double C=N bond in the Schiff base are amide-like rather than ketone and are less reactive in condensation processes. On the other hand, deamination of Mannich base **D** with formation of compound **XIII** occurs fairly readily and is irreversible due to poor solubility of the deamination product in ethanol.

The structure of 5-[2-(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)ethylidene]hexahydropyrimidine-2,4,6-trione (**XIII**) was determined on the basis of its IR and ^{1}H and ^{13}C NMR spectra. The IR spectrum of **XIII** contained absorption bands at 3410 and 3150 cm^{-1}, typical of stretching vibrations of NH groups, a band at 3050 cm^{-1} due to stretching vibrations of olefinic C–H bonds, and bands at 2950 and 2865 cm^{-1} belonging to vibrations of aliphatic C–H bonds. Bands at 1655 and 1565 cm^{-1} were assigned to vibrations of the barbituric acid fragments (amide I and amide II), and stretching vibrations of conjugated C=C bonds gave rise to absorption at 1610 cm^{-1}. In the ^{1}H NMR spectrum of **XIII** we observed singlets from methyl protons in the bornane fragment at δ 0.69, 0.91, and 1.00 ppm together with signals from other protons in the bicyclic skeleton. The geminal coupling constant

Scheme 3.



for *exo*-3′-H (δ 2.78 ppm, d.d.t) and *endo*-3′-H (δ 2.32 ppm, d.d) is 18 Hz, indicating that these protons are neighboring to conjugated double bond system. The NH protons resonated at δ 11.10 and 11.20 ppm. The $C^{2'}$=$C^{11'}$–C^{7}=C^{5} diene fragment was assigned *s-trans* configuration on the basis of the vicinal coupling constant for protons on $C^{11'}$ (δ 7.40 ppm, d.t) and C^{7} (δ 7.97 ppm, d), which was equal to 10 Hz. The ^{13}C NMR data were also very consistent with the assumed structure. The ^{13}C NMR spectrum of **XIII** contained signals from carbon atoms in the bicyclic fragment, two singlets and two doublets from double-bonded carbon atoms, and signals typical of amide and urea carbonyl carbon atoms (see Experimental).

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Protégé-460 spectrometer with Fourier transform. The NMR spectra were measured on a Bruker Avance instrument (500 MHz for ^{1}H) from solutions in DMSO-d_6 using tetramethylsilane as internal reference. The progress of reactions and the purity of products were monitored by GLC on a Chrom-5 chromatograph equipped with a glass column, 2000×2 mm, which was packed with Chromaton N-AW-DMCS (0.16–0.20 mm) impregnated with Apiezon L.

[(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde (**I**) was synthesized according to the procedure described in [10]. Methyl 2-aryl-4,6-dioxocyclohexane-1-carboxylates **IIId**–**IIIf** were synthesized as described in [13] from dimethyl malonate and the corresponding β-arylvinyl methyl ketones (condensation products of equimolar amounts of acetone and aromatic aldehydes). Methyl 2,2-dimethyl-4,6-dioxocyclohexane-1-carboxylate (**IIIc**) was synthesized in a similar way from dimethyl malonate and 4-methylpent-3-en-2-one.

Typical procedure for three-component condensation of [(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde (I) with naphthalen-1-amine and cyclic β-diketones. The reactions were carried out following the procedure described in [12]. A mixture of equimolar amounts (2 mmol) of aldehyde **I**, amine **II**, and β-diketone **III** in 10 ml of ethanol was heated under reflux in the absence of any catalyst until the reaction was complete (3–4 h, GLC). The mixture was evaporated to ~1/4 of the initial volume, and the products were precipitated by adding excess diethyl ether. The crystalline solid was filtered off and recrystallized. Recrystallization from ethanol gave a substance enriched in the major (7*R*)-isomer (or isomers). The mother liquor was evaporated, and the residue enriched in (7*S*)-isomers was recrystallized from anhydrous acetone. By repeated dissolution–recrystallization procedures we obtained samples containing 80% and more of the corresponding isomer. Stereoisomers at C^{11} and/or C^{10} were separated by crystallization from ethanol–benzene or acetone as described previously in [10]. The spectra were recorded from samples containing no less than 80% of the main component.

Compounds **Va** and **VIa** were isolated in an overall yield of 57%. By five recrystallizations from ethanol we obtained a sample containing ~86% of (7*R*)-isomer **Va**. The product isolated from the mother liquor was recrystallized six times from acetone to obtain a sample containing ~82% of (7*S*)-isomer **VIa**.

(7*R*)-7-[(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]-hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridin-8-one (Va). IR spectrum, ν, cm^{-1}: 3415, 3250 (NH); 3050, 3010 (C–H_{arom}); 2925, 2870, 2855 (C–H_{aliph}); 1585, 1570 (NH–C=C–C=O); 1525, 1505 (C=C_{arom}); 1190 (C–N–C); 780 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.69 s (3H, 1′-CH_3), 0.70 s (3H, *syn*-7′-CH_3), 0.84 s (3H, *anti*-7′-CH_3), 0.99 d.d.d (1H, *endo*-6′-H, ^{2}J = 12, $^{3}J_{endo,endo}$ = 8, $^{3}J_{endo,exo}$ = 4 Hz), 1.19 d.d.d (1H, *endo*-5′-H, ^{2}J = 12, $^{3}J_{endo,endo}$ = 8, $^{3}J_{endo,exo}$ = 4 Hz), 1.51 d.t (1H, *exo*-6′-H, ^{2}J = $^{3}J_{exo,exo}$ = 12, $^{3}J_{endo,exo}$ = 4 Hz), 1.75 t.t.d (1H, *exo*-5′-H, ^{2}J = $^{3}J_{exo,exo}$ = 12, $^{3}J_{endo,exo}$ = $^{3}J_{exo\text{-}5',4'}$ = 4, $^{W}J_{exo\text{-}5',exo\text{-}3'}$ = 1.5 Hz), 1.78 t (1H, 4′-H, $^{3}J_{4',exo\text{-}5'}$ = $^{3}J_{4',exo\text{-}3'}$ = 4 Hz), 1.81 m (2H, 10-H), 1.96 d.d.d (1H, 11-H_{ax}, ^{2}J = 16, $^{3}J_{ax,ax}$ = 9, $^{3}J_{ax,eq}$ = 5 Hz), 2.11 d.t (1H, 11-H_{eq}, ^{2}J = 16, $^{3}J_{eq,ax}$ = $^{3}J_{eq,eq}$ = 5 Hz), 2.17 br.d (1H, *endo*-3′-H, ^{2}J = 16, $^{4}J_{3',11'}$ = 2 Hz), 2.39 d.d.d (1H, 9-H_{ax}, ^{2}J = 18, $^{3}J_{ax,ax}$ = 9, $^{3}J_{ax,eq}$ = 5 Hz), 2.53 d.t (1H, 9-H_{eq}, ^{2}J = 18, $^{3}J_{eq,ax}$ = $^{3}J_{eq,eq}$ = 5 Hz), 2.95 d.d.t (1H, *exo*-3′-H, ^{2}J = 16, $^{3}J_{exo\text{-}3',4'}$ = 4, $^{W}J_{exo\text{-}3',exo\text{-}5'}$ = $^{4}J_{3',11'}$ = 1.5 Hz), 4.60 d.t (1H, 11′-H, ^{3}J = 10, $^{4}J_{3',11'}$ = 1.5 Hz), 4.96 d (1H, 7-H, ^{3}J = 10 Hz), 7.19 d (1H, 4-H, ^{3}J = 8.5 Hz), 7.48 t (1H, 3-H, ^{3}J = 8.5 Hz), 7.50 d (1H, 5-H, ^{3}J = 7 Hz), 7.56 t (1H, 2-H, ^{3}J = 8.5 Hz), 7.84 d (1H, 6-H, ^{3}J = 7 Hz), 8.38 d (1H, 1-H, ^{3}J = 8.5 Hz), 9.08 s (1H, NH).

(7*S*)-7-[(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]-hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridin-11-one (VIa). IR spectrum, ν, cm^{-1}: 3420, 3245 (NH); 3050, 3010 (C–H_{arom}); 2930, 2870, 2850 (C–H_{aliph}); 1590, 1570 (HN–C=C–C=O); 1525, 1505 (C=C_{arom}); 1190 (C–N–C); 780 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.69 s (3H, 1′-CH_3), 0.71 s (3H, *syn*-7′-CH_3), 0.83 s (3H, *anti*-7′-CH_3), 1.07 d.d.d

(1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.17 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.49 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.67 m (2H, 10-H), 1.74 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 3.5, $^WJ_{exo\text{-}5',exo\text{-}3'}$ 1.5 Hz), 1.78 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 3.5 Hz), 1.99 d.d.d (1H, 11-H$_{ax}$, ^2J = 16, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 5 Hz), 2.11 d.t (1H, 11-H$_{eq}$, ^2J = 16, $^3J_{eq,ax}$ = $^3J_{eq,eq}$ = 5 Hz), 2.40 d.d.d (1H, 9-H$_{ax}$, ^2J = 18, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 5 Hz), 2.50 d.d.t (1H, *exo*-3′-H, ^2J = 16, $^3J_{exo\text{-}3',4'}$ = 3.5, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 1.5 Hz), 2.53 d.t (1H, 9-H$_{eq}$, ^2J = 18, $^3J_{eq,ax}$ = $^3J_{eq,eq}$ = 5 Hz), 2.56 d.d (1H, *endo*-3′-H, ^2J = 16, $^4J_{3',11'}$ = 1.5 Hz), 4.62 d.t (1H, 11′-H, ^3J = 10, 2 $^4J_{3',11'}$ = 1.5 Hz), 4.94 d (1H, 7-H, ^3J = 10 Hz), 7.12 d (1H, 4-H, ^3J = 8.5 Hz), 7.47 t (1H, 3-H, ^3J = 8.5 Hz), 7.48 t (1H, 5-H, ^3J = 7 Hz), 7.58 t (1H, 2-H, ^3J = 8.5 Hz), 7.83 d (1H, 6-H, ^3J = 7 Hz), 8.38 d.d (1H, 1-H, ^3J = 8.5 Hz), 9.06 s (1H, NH).

Compounds **Vb** and **VIb** were isolated in an overall yield of 64%. Samples containing ~83% of the (7*R*)-isomer and ~81% of the (7*S*)-isomer were obtained as described above for **Va** and **VIa**.

(7*R*)-10,10-Dimethyl-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridin-8-one (Vb). IR spectrum, ν, cm^{-1}: 3440, 3310, 3190 (NH); 3060 (C–H$_{arom}$); 2950, 2920, 2865 (C–H$_{aliph}$); 1590 (HN–C=C–C=O); 1520, 1495 (C=C$_{arom}$); 1145 (C–N–C); 775 (δC–H$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 0.61 s (3H, 1′-CH$_3$), 0.66 s (3H, *syn*-7′-CH$_3$), 0.80 s (3H, *anti*-7′-CH$_3$), 1.02 s and 1.04 s (3H each, 10-CH$_3$), 1.05 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.11 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.51 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.71 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.75 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.05 d (1H, 11-H$_{ax}$, ^2J = 16 Hz), 2.10 d.d (1H, *endo*-3′-H, ^2J = 16, $^4J_{3',11'}$ = 2 Hz), 2.18 d (1H, 11-H$_{eq}$, ^2J = 16 Hz), 2.43 d (1H, 9-H$_{ax}$, ^2J = 18 Hz), 2.60 d (1H, 9-H$_{eq}$, ^2J = 18 Hz), 2.86 d.d.t (1H, *exo*-3′-H, ^2J = 16, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 4.61 d.t (1H, 11′-H, ^3J = 10, 2 $^4J_{3',11'}$ = 2 Hz), 4.88 d (1H, 7-H, ^3J = 10 Hz), 7.18 d (1H, 4-H, ^3J = 8.5 Hz), 7.47 t (1H, 3-H, ^3J = 8.5 Hz), 7.48 d (1H, 5-H, ^3J = 7 Hz), 7.54 t (1H, 2-H, ^3J = 8.5 Hz), 7.82 d (1H, 6-H, ^3J = 7 Hz), 8.38 d (1H, 1-H, ^3J = 8.5 Hz), 9.05 s (1H, NH). ^{13}C NMR spectrum, δ$_C$, ppm: 12.8 q (1′-CH$_3$), 18.8 q (*syn*-7′-CH$_3$), 19.5 q (*anti*-7′-CH$_3$), 26.0 q (10-CH$_3$), 27.7 t (C$^{5'}$), 29.3 q (10-CH$_3$), 32.0 t (C$^{6'}$), 34.2 s (C^{10}), 34.4 t (C$^{3'}$), 34.6 t (C^{11}), 40.3 t (C^9), 44.0 d (C$^{4'}$), 46.9 s (C$^{7'}$), 50.1 s (C$^{1'}$), 106.7 s (C$^{2'}$); 120.4 d, 121.0 d, 121.2 d, 125.4 d, 125.6 d, 127.6 d, 128.1 d (C^1, C^2, C^3, C^4, C^5, C^6, C$^{11'}$); 130.9 s (C^{7a}), 132.3 s (C^{6a}), 145.7 s (C^{12b}), 151.0 (C^{11a}), 193.4 s (C^8).

(7*S*)-10,10-Dimethyl-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridin-8-one (VIb). IR spectrum, ν, cm^{-1}: 3440, 3305, 3200 (NH); 3060 (C–H$_{arom}$); 2955, 2930, 2865 (C–H$_{aliph}$); 1590 (HN–C=C–C=O); 1515, 1495 (C=C$_{arom}$); 1145 (C–N–C); 775 (δC–H$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 0.64 s (3H, 1′-CH$_3$), 0.69 s (3H, *syn*-7′-CH$_3$), 0.81 s (3H, *anti*-7′-CH$_3$), 1.05 s and 1.07 s (3H each, 10-CH$_3$), 1.07 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.09 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.51 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.69 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.76 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.08 d (1H, 11-H$_{ax}$, ^2J = 16 Hz), 2.18 d (1H, 11-H$_{eq}$, ^2J = 16 Hz), 2.42 d (1H, 9-H$_{ax}$, ^2J = 18 Hz), 2.53 d.d.t (1H, *exo*-3′-H, ^2J = 16, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 2.60 d (1H, 9-H$_{eq}$, ^2J = 18 Hz), 2.61 d.d (1H, *endo*-3′-H, ^2J = 16, $^4J_{3',11'}$ = 2 Hz), 4.68 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.85 d (1H, 7-H, ^3J = 10 Hz), 7.10 d (1H, 4-H, ^3J = 8.5 Hz), 7.46 t (1H, 3-H, ^3J = 8.5 Hz), 7.46 d (1H, 5-H, ^3J = 7 Hz), 7.56 t (1H, 2-H, ^3J = 8.5 Hz), 7.81 d (1H, 6-H, ^3J = 7 Hz), 8.38 d (1H, 1-H, ^3J = 8.5 Hz), 9.04 s (1H, NH). ^{13}C NMR spectrum, δ$_C$, ppm: 12.7 q (1′-CH$_3$), 18.7 q (*syn*-7′-CH$_3$), 20.8 q (*anti*-7′-CH$_3$), 27.7 t (C$^{5'}$), 27.9 q (10-CH$_3$), 29.1 q (10-CH$_3$), 32.1 t (C$^{6'}$), 34.4 s (C^{10}), 34.5 t (C$^{3'}$), 35.1 t (C^{11}), 40.4 t (C^9), 44.0 d (C$^{4'}$), 47.2 s (C$^{7'}$), 50.2 s (C$^{1'}$), 106.3 s (C$^{2'}$); 120.0 d, 120.9 d, 121.1 d, 122.0 d, 126.4 d, 127.5 d, 128.2 d (C^1, C^2, C^3, C^4, C^5, C^6, C$^{11'}$); 130.7 s (C^{7a}), 132.2 s (C^{6a}), 145.9 s (C^{12b}), 151.3 (C^{11a}), 193.3 s (C^8).

Compounds **VIIc**, **VIIIc**, **IXc**, and **Xc** were obtained in an overall yield of 59%.

Methyl (7*R*,11*S*)-10,10-dimethyl-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (VIIc). IR spectrum, ν, cm^{-1}: 3310, 3205 (NH); 3060 (C–H$_{arom}$); 2950, 2930, 2870 (C–H$_{aliph}$); 1735 (C=O, ester); 1585, 1570 (HN–C=C–C=O); 1535, 1495 (C=C$_{arom}$); 1250, 1190 (C–O–C); 1150 (C–N–C); 805, 785 (δC–H$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 0.59 s (3H, 1′-CH$_3$), 0.64 s (3H, *syn*-7′-CH$_3$), 0.78 s (3H, *anti*-7′-CH$_3$), 0.98 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.03 s

and 1.10 s (3H each, 10-CH_3), 1.12 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.48 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.68 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.70 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.09 d.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.40 d (1H, *cis*-9-H,* ^2J = 18 Hz), 2.82 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 2.88 d (1H, *trans*-9-H,* ^2J = 18 Hz), 3.06 s (1H, 11-H), 3.58 s (3H, OCH_3), 4.61 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.89 d (1H, 7-H, ^3J = 10 Hz), 7.19 d (1H, 4-H, ^3J = 8.5 Hz), 7.47 t (1H, 3-H, ^3J = 8.5 Hz), 7.49 d (1H, 5-H, ^3J = 7 Hz), 7.56 t (1H, 2-H, ^3J = 8.5 Hz), 7.88 d (1H, 6-H, ^3J = 7 Hz), 8.39 d (1H, 1-H, ^3J = 8.5 Hz), 9.25 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.4 q (1′-CH_3), 19.4 q (*syn*-7′-CH_3), 19.9 q (*anti*-7′-CH_3), 24.9 q (10-CH_3), 28.2 t ($C^{5'}$), 28.7 q (10-CH_3), 34.5 s (C^{10}), 34.9 t ($C^{6'}$), 35.5 t ($C^{3'}$), 41.2 t (C^9) 44.6 d ($C^{4'}$), 47.5 s ($C^{7'}$), 50.8 s ($C^{1'}$), 52.4 d (C^{11}), 63.5 q (OCH_3), 106.2 s ($C^{2'}$); 121.5 d, 123.2 d, 124.8 d, 126.3 d, 127.1 d, 127.6 d, 128.7 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$); 133.0 s (C^{7a}), 134.6 s (C^{6a}), 146.9 s (C^{12b}), 152.8 (C^{11a}), 170.8 s (COO), 190.2 s (C^{11}).

Methyl (7*S*,11*R*)-10,10-dimethyl-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (VIIIc). IR spectrum, ν, cm^{-1}: 3320, 3210 (NH); 3060 (C–H_{arom}); 2950, 2930, 2870 (C–H_{aliph}); 1735 (C=O, ester); 1585, 1570 (HN–C=C–C=O); 1525, 1495 (C=C_{arom}); 1250, 1190 (C–O–C); 1150 (C–N–C); 805, 785 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.61 s (3H, 1′-CH_3), 0.67 s (3H, *syn*-7′-CH_3), 0.79 s (3H, *anti*-7′-CH_3), 1.06 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.08 s and 1.10 s (3H each, 10-CH_3), 1.11 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.51 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.66 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.72 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.40 d (1H, *cis*-9-H, ^2J = 18 Hz), 2.56 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 2.60 d.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.87 d (1H, *trans*-9-H, ^2J = 18 Hz), 3.12 s (1H, 11-H), 3.54 s (3H, OCH_3), 4.65 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.87 d (1H, 7-H, ^3J = 10 Hz), 7.10 d (1H, 4-H, ^3J = 8.5 Hz), 7.45 t (1H, 3-H, ^3J = 8.5 Hz), 7.47 d (1H, 5-H, ^3J = 7 Hz), 7.59 t (1H, 2-H, ^3J = 8.5 Hz), 7.86 d (1H, 6-H, ^3J = 7 Hz), 8.39 d (1H, 1-H, ^3J = 8.5 Hz), 9.27 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.3 q (1′-CH_3), 19.3 q (*syn*-7′-CH_3), 20.1 q (*anti*-7′-CH_3), 26.7 q (10-CH_3), 28.0 q (10-CH_3), 28.2 t ($C^{5'}$), 34.4 s (C^{10}), 34.5 t ($C^{6'}$), 34.9 t ($C^{3'}$), 41.2 t (C^9) 44.6 d ($C^{4'}$), 47.9 s ($C^{7'}$), 50.8 s ($C^{1'}$), 52.0 d (C^{11}), 63.3 q (OCH_3), 106.0 s ($C^{2'}$); 120.6 d, 123.6 d, 126.0 d, 126.3 d, 127.0 d, 128.0 d, 128.9 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$), 131.0 s (C^{7a}), 134.8 s (C^{6a}), 147.1 s (C^{12b}), 153.1 (C^{11a}), 170.5 s (COO), 188.7 s (C^8).

Methyl (7*R*,11*R*)-10,10-dimethyl-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (IXc). IR spectrum, ν, cm^{-1}: 3310, 3200 (NH); 3060 (C–H_{arom}); 2950, 2930, 2870 (C–H_{aliph}); 1735 (C=O, ester); 1585, 1570 (HN–C=C–C=O); 1530, 1495 (C=C_{arom}); 1250, 1190 (C–O–C); 1150 (C–N–C); 810, 785 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.59 s (3H, 1′-CH_3), 0.64 s (3H, *syn*-7′-CH_3), 0.78 s (3H, *anti*-7′-CH_3), 0.98 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.04 s and 1.11 s (3H each, 10-CH_3), 1.12 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.48 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.68 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.70 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.08 d.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.60 d (1H, *cis*-9-H, ^2J = 18 Hz), 2.81 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 2.71 d (1H, *trans*-9-H, ^2J = 18 Hz), 3.34 s (1H, 11-H), 3.56 s (3H, OCH_3), 4.61 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.89 d (1H, 7-H, ^3J = 10 Hz), 7.19 d (1H, 4-H, ^3J = 8.5 Hz), 7.48 t (1H, 3-H, ^3J = 8.5 Hz), 7.50 d (1H, 5-H, ^3J = 7 Hz), 7.56 t (1H, 2-H, ^3J = 8.5 Hz), 7.89 d (1H, 6-H, ^3J = 7 Hz), 8.39 d (1H, 1-H, ^3J = 8.5 Hz), 9.23 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.4 q (1′-CH_3), 19.4 q (*syn*-7′-CH_3), 19.9 q (*anti*-7′-CH_3), 24.9 q (10-CH_3), 28.2 t ($C^{5'}$), 28.3 q (10-CH_3), 34.5 s (C^{10}), 34.7 t ($C^{6'}$), 35.5 t ($C^{3'}$), 41.1 t (C^9) 44.6 d ($C^{4'}$), 47.5 s ($C^{7'}$), 50.8 s ($C^{1'}$), 52.4d (C^{11}), 63.5 q (OCH_3), 106.2 s ($C^{2'}$); 120.1 d, 121.5 d, 123.6 d, 124.8 d, 126.3 d, 127.9 d, 128.7 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$); 132.9 s (C^{7a}), 134.6 s (C^{6a}), 146.8 s (C^{12b}), 152.8 (C^{11a}), 170.8 s (COO), 190.2 s (C^8).

Methyl (7*S*,11*S*)-10,10-dimethyl-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (Xc). IR spectrum, ν, cm^{-1}: 3320, 3210 (NH); 3060 (C–H_{arom}); 2950, 2930, 2870 (C–H_{aliph}); 1735 (C=O, ester); 1585, 1570 (HN–C=C–C=O);

* Hereinafter, relative to the 11-$COOCH_3$ group.

1525, 1495 (C=C_{arom}); 1250, 1190 (C–O–C); 1150 (C–N–C); 805, 785 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.61 s (3H, 1′-CH_3), 0.67 s (3H, *syn*-7′-CH_3), 0.79 s (3H, *anti*-7′-CH_3), 1.05 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.08 s and 1.11 s (3H each, 10-CH_3), 1.10 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.51 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.67 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.71 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.55 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 2.59 m (2H, *endo*-3′-H, *cis*-9-H), 2.72 d (1H, *trans*-9-H, ^2J = 18 Hz), 3.35 s (1H, 11-H), 3.59 s (3H, OCH_3), 4.66 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.87 d (1H, 7-H, ^3J = 10 Hz), 7.09 d (1H, 4-H, ^3J = 8.5 Hz), 7.44 t (1H, 3-H, ^3J = 8.5 Hz), 7.47 d (1H, 5-H, ^3J = 7 Hz), 7.60 t (1H, 2-H, ^3J = 8.5 Hz), 7.86 d (1H, 6-H, ^3J = 7 Hz), 8.38 d (1H, 1-H, ^3J = 8.5 Hz), 9.26 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.3 q (1′-CH_3), 19.3 q (*syn*-7′-CH_3), 20.1 q (*anti*-7′-CH_3), 26.6 q (10-CH_3), 28.0 q (10-CH_3), 28.2 t ($C^{5'}$), 34.4 s (C^{10}), 34.5 t ($C^{6'}$), 35.8 t ($C^{3'}$), 41.2 t (C^9), 44.6 d ($C^{4'}$), 47.9 s ($C^{7'}$), 50.8 s ($C^{1'}$), 52.0 d (C^{11}), 63.3 q (OCH_3), 106.0 s ($C^{2'}$); 120.7 d, 123.5 d, 126.1 d, 126.2 d, 127.1 d, 127.9 d, 128.7 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$); 130.8 s (C^{7a}), 134.8 s (C^{6a}), 147.1 s (C^{12b}), 153.1 (C^{11a}), 170.5 s (COO), 188.6 s (C^8).

Compounds **VIId**, **VIIId**, **IXd**, and **Xd** were obtained in an overall yield of 57%.

Methyl (7*R*,10*R*,11*S*)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-10-(2,4,6-trimethylphenyl)-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (VIId). IR spectrum, ν, cm^{-1}: 3300 (NH); 3050 (C–H_{arom}); 2955, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1590, 1570 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1250, 1180 (C–O–C); 1155 (C–N–C); 800, 780 (C–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.67 s (3H, 1′-CH_3), 0.72 s (3H, *syn*-7′-CH_3), 0.83 s (3H, *anti*-7′-CH_3), 0.97 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.15 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.53 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.73 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{5'\text{-}exo,4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.78 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.17 d.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.34 s (3H) and 2.47 s (6H) (CH_3), 2.52 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 2.93 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 3.33 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.25 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.37 s (3H, OCH_3), 4.27 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.75 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.94 d (1H, 7-H, ^3J = 10 Hz), 6.80 s (2H, H_{arom}), 7.20 d (1H, 4-H, ^3J = 8.5 Hz), 7.49 t (1H, 3-H, ^3J = 8.5 Hz), 7.54 d (1H, 5-H, ^3J = 7 Hz), 7.60 t (1H, 2-H, ^3J = 8.5 Hz), 7.90 d (1H, 6-H, ^3J = 7 Hz), 8.33 d (1H, 1-H, ^3J = 8.5 Hz), 9.32 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.1 q (1′-CH_3), 18.9 q (*syn*-7′-CH_3), 20.9 q (2CH_3), 21.5 q (*anti*-7′-CH_3), 22.4 q (CH_3), 30.8 t ($C^{5'}$), 35.2 t ($C^{6'}$), 38.1 t ($C^{3'}$), 41.2 t (C^9), 44.6 d ($C^{4'}$), 47.7 s ($C^{7'}$), 50.6 s ($C^{1'}$), 51.8 d (C^{10}), 56.6 d (C^{11}), 63.9 q (OCH_3), 106.7 s ($C^{2'}$), 110.1 s ($C^{1''}$), 121.0 s and 121.5 s ($C^{2''}$, $C^{4''}$, $C^{6''}$); 123.7 d, 124.8 d, 126.4 d, 127.1 d, 127.2 d, 128.9 d, 129.6 d, 130.0 d, 131.9 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$, $C^{3''}$, $C^{5''}$); 134.6 s (C^{7a}), 136.1 s (C^{6a}), 149.1 s (C^{12b}), 153.5 (C^{11a}), 171.5 s (COO), 191.3 s (C^8).

Methyl (7*S*,10*S*,11*R*)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-10-(2,4,6-trimethylphenyl)-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (VIIId). IR spectrum, ν, cm^{-1}: 3290 (NH); 3055 (C–H_{arom}); 2955, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1590, 1570 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1250, 1185 (C–O–C); 1150 (C–N–C); 800, 780 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, 1′-CH_3), 0.69 s (3H, *syn*-7′-CH_3), 0.82 s (3H, *anti*-7′-CH_3), 0.95 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.09 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.54 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.74 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{\text{exo-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.79 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.26 s (3H) and 2.42 s (6H) (CH_3), 2.55 m (2H, *endo*-3′-H + *exo*-3′-H), 2.63 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 3.21 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.23 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.35 s (3H, OCH_3), 4.28 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.69 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.96 d (1H, 7-H, ^3J = 10 Hz), 6.83 s (2H, H_{arom}), 7.12 d (1H, 4-H, ^3J = 8.5 Hz), 7.47 t (1H, 3-H, ^3J = 8.5 Hz), 7.51 d (1H, 5-H, ^3J = 7 Hz), 7.63 t (1H, 2-H, ^3J = 8.5 Hz), 7.88 d (1H, 6-H, ^3J = 7 Hz), 8.33 d (1H, 1-H, ^3J = 8.5 Hz), 9.32 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.3 q (1′-CH_3), 19.4 q (*syn*-7′-CH_3), 20.3 q (*anti*-7′-CH_3), 20.9 q (2CH_3), 22.4 q (CH_3), 30.5 t ($C^{5'}$), 35.4 t ($C^{6'}$), 38.3 t ($C^{3'}$), 40.8 t (C^9), 44.6 d ($C^{4'}$), 47.9 s ($C^{7'}$), 50.7 s ($C^{1'}$), 51.9 d (C^{10}), 56.7 d (C^{11}), 63.9 q (OCH_3), 106.6 s ($C^{2'}$), 110.3 s ($C^{1''}$), 121.0 s and 121.6 s ($C^{2''}$, $C^{4''}$, $C^{6''}$); 123.7 d, 124.8 d, 126.2 d, 127.1 d, 127.2 d, 127.6 d, 129.8 d, 130.0 d, 131.7 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$,

$C^{3''}$, $C^{5''}$); 134.0 s (C^{7a}), 136.5 s (C^{6a}), 149.0 s (C^{12b}), 153.7 (C^{11a}), 165.5 s (CO), 191.4 s (C^{11}).

Methyl (7*R*,10*S*,11*R*)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-10-(2,4,6-trimethylphenyl)-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (IXd). IR spectrum, ν, cm^{-1}: 3310 (NH); 3050 (C–H_{arom}); 2955, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1585, 1570 (HN–C=C–C=O); 1525, 1495 (C=C_{arom}); 1250, 1185 (C–O–C); 1155 (C–N–C); 800, 780 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.65 s (3H, 1′-CH_3), 0.70 s (3H, *syn*-7′-CH_3), 0.83 s (3H, *anti*-7′-CH_3), 0.99 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.20 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.53 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.72 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.78 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.18 d.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.32 s (3H) and 2.48 s (6H) (CH_3), 2.68 d.d (1H, 9-H_{ax}, ^2J = 18 Hz, $^3J_{ax,ax}$ = 9 Hz), 2.91 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 3.16 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.35 s (3H, OCH_3), 3.72 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 4.02 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.75 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 5.00 d (1H, 7-H, ^3J = 10 Hz), 6.80 s (2H, H_{arom}), 7.11 d (1H, 4-H, ^3J = 8.5 Hz), 7.50 t (1H, 3-H, ^3J = 8.5 Hz), 7.53 d (1H, 5-H, ^3J = 7 Hz), 7.61 t (1H, 2-H, ^3J = 8.5 Hz), 7.83 d (1H, 6-H, ^3J = 7 Hz), 8.33 d (1H, 1-H, ^3J = 8.5 Hz), 9.22 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.1 q (1′-CH_3), 18.9 q (*syn*-7′-CH_3), 20.9 q (2CH_3), 21.6 q (*anti*-7′-CH_3), 22.4 q (CH_3), 30.7 t ($C^{5'}$), 35.0 t ($C^{6'}$), 38.4 t ($C^{3'}$), 41.4 t (C^9), 44.7 d ($C^{4'}$), 47.7 s ($C^{7'}$), 50.6 s ($C^{1'}$), 51.8 d (C^{10}), 56.6 d (C^{11}), 63.9 q (OCH_3), 106.7 s ($C^{2'}$), 110.3 s ($C^{1''}$), 121.0 s and 121.6 s ($C^{2''}$, $C^{4''}$, $C^{6''}$); 123.7 d, 124.8 d, 126.2 d, 127.1 d, 127.2 d, 128.7 d, 129.5 d, 129.9 d, 131.8 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$; $C^{3''}$, $C^{5''}$); 134.8 s (C^{7a}), 136.5 s (C^{6a}), 149.0 s (C^{12b}), 153.7 (C^{11a}), 171.3 s (COO), 191.3 s (C^8).

Methyl (7*S*,10*R*,11*S*)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-10-(2,4,6-trimethylphenyl)-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (Xd). IR spectrum, ν, cm^{-1}: 3290 (NH); 3055 (C–H_{arom}); 2955, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1590, 1575 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1250, 1185 (C–O–C); 1150 (C–N–C); 800, 780 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.67 s (3H, 1′-CH_3), 0.71 s (3H, *syn*-7′-CH_3), 0.81 s (3H, *anti*-7′-CH_3), 0.97 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.16 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.54 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.73 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.79 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.30 s (3H) and 2.43 s (6H) (CH_3), 2.56 m (2H, *endo*-3′-H, *exo*-3′-H), 2.61 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 3.22 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.35 s (3H, OCH_3), 3.67 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 4.03 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.69 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 5.04 d (1H, 7-H, ^3J = 10 Hz), 6.83 s (2H, H_{arom}), 7.12 d (1H, 4-H, ^3J = 8.5 Hz), 7.48 t (1H, 3-H, ^3J = 8.5 Hz), 7.52 d (1H, 5-H, ^3J = 7 Hz), 7.61 t (1H, 2-H, ^3J = 8.5 Hz), 7.86 d (1H, 6-H, ^3J = 7 Hz), 8.33 d (1H, 1-H, ^3J = 8.5 Hz), 9.30 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.3 q (1′-CH_3), 19.3 q (*syn*-7′-CH_3), 20.1 q (*anti*-7′-CH_3), 20.9 q (2CH_3), 22.4 q (CH_3), 30.2 t ($C^{5'}$), 35.3 t ($C^{6'}$), 38.4 t ($C^{3'}$), 40.9 t (C^9), 44.6 d ($C^{4'}$), 47.9 s ($C^{7'}$), 50.7 s ($C^{1'}$), 51.9 d (C^{10}), 56.9 d (C^{11}), 63.9 q (OCH_3), 106.6 s ($C^{2'}$), 110.1 s ($C^{1''}$), 121.2 s and 121.5 s ($C^{2''}$, $C^{4''}$, $C^{6''}$); 123.8 d, 124.8 d, 126.0 d, 127.1 d, 127.2 d, 127.7 d, 129.8 d, 130.0 d, 131.6 d (C^1, C^2, C^3, C^4, C^5, C^6, $C^{11'}$, $C^{3''}$, $C^{5''}$); 133.9 s (C^{7a}), 136.6 s (C^{6a}), 149.1 s (C^{12b}), 153.7 (C^{11a}), 167.2 s (COO), 191.3 s (C^8).

Compounds **VIIe**, **VIIIe**, **IXe**, and **Xe** were obtained in an overall yield of 59%.

Methyl (7*R*,10*R*,11*S*)-10-(3,4-dimethoxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]-acridine-11-carboxylate (VIIe). IR spectrum, ν, cm^{-1}: 3375, 3210 (NH); 3060 (C–H_{arom}); 2950, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1590 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1265, 1250 (C–O–C); 1155 (C–N–C); 810, 770 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.69 s (3H, 1′-CH_3), 0.77 s (3H, *syn*-7′-CH_3), 0.81 s (3H, *anti*-7′-CH_3), 1.04 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.19 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $J_{endo,exo}$ = 4 Hz), 1.45 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.68 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.75 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.17 d.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.71 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 2.93 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 3.10 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.24 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.38 s (3H, $COOCH_3$), 3.70 s and 3.73 s (3H each, CH_3O), 4.26 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.62 d.t (1H, 11′-H, ^3J = 10, 2 $^4J_{3',11'}$ = 2 Hz), 4.83 d (1H, 7-H, ^3J = 10 Hz), 6.82 d (2H, H_{arom}),

6.89 s (1H, H_{arom}), 7.18 d (1H, 4-H, ^3J = 8.5 Hz), 7.47 t (1H, 3-H, ^3J = 8.5 Hz), 7.49 d (1H, 5-H, ^3J = 7 Hz), 7.58 t (1H, 2-H, ^3J = 8.5 Hz), 7.89 d (1H, 6-H, ^3J = 7 Hz), 8.36 d (1H, 1-H, ^3J = 8.5 Hz), 9.18 s (1H, NH).

Methyl (7*S*,10*S*,11*R*)-10-(3,4-dimethoxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]-acridine-11-carboxylate (VIIIe). IR spectrum, ν, cm^{-1}: 3375, 3200 (NH); 3060 (C–H_{arom}); 2950, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1590 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1265, 1250 (C–O–C); 1150 (C–N–C); 810, 770 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.63 s (3H, 1′-CH_3), 0.68 s (3H, *syn*-7′-CH_3), 0.82 s (3H, *anti*-7′-CH_3), 1.06 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.15 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.50 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.70 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.76 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.64 m (2H, *endo*-3′-H, *exo*-3′-H), 2.86 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 3.32 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.25 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.42 s (3H, $COOCH_3$), 3.67 s and 3.71 s (3H each, CH_3O), 4.28 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.68 d.t (1H, 11′-H, ^3J = 9.6, 2 $^4J_{3',11'}$ = 2 Hz), 4.85 d (1H, 7-H, ^3J = 9.6 Hz), 6.82 d (2H, H_{arom}), 6.89 s (1H, H_{arom}), 7.13 d (1H, 4-H, ^3J = 8.5 Hz), 7.46 t (1H, 3-H, ^3J = 8.5 Hz), 7.48 d (1H, 5-H, ^3J = 7 Hz), 7.58 t (1H, 2-H, ^3J = 8.5 Hz), 7.87 d (1H, 6-H, ^3J = 7 Hz), 8.39 d (1H, 1-H, ^3J = 8.5 Hz), 9.26 s (1H, NH).

Methyl (7*R*,10*S*,11*R*)-10-(3,4-dimethoxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]-acridine-11-carboxylate (IXe). IR spectrum, ν, cm^{-1}: 3375, 3210 (NH); 3060 (C–H_{arom}); 2950, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1590 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1265, 1250 (C–O–C); 1155 (C–N–C); 810, 770 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.65 s (3H, 1′-CH_3), 0.76 s (3H, *syn*-7′-CH_3), 0.81 s (3H, *anti*-7′-CH_3), 1.05 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.20 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.50 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.61 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.75 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.18 br.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.85 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 2.96 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'}$ = $^4J_{3',11'}$ = 2 Hz), 3.30 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.44 s (3H, $COOCH_3$), 3.65 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.70 s and 3.72 s (3H each, CH_3O), 3.99 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.69 d.t (1H, 11′-H, ^3J = 9.6, $^4J_{3',11'}$ = 2 Hz), 4.87 d (1H, 7-H, ^3J = 9.6 Hz), 6.82 d (2H, H_{arom}), 6.89 s (1H, H_{arom}), 7.18 d (1H, 4-H, ^3J = 8.5 Hz), 7.48 t (1H, 3-H, ^3J = 8.5 Hz), 7.50 d (1H, 5-H, ^3J = 7 Hz), 7.55 t (1H, 2-H, ^3J = 8.5 Hz), 7.88 d (1H, 6-H, ^3J = 7 Hz), 8.39 d (1H, 1-H, ^3J = 8.5 Hz), 9.22 s (1H, NH).

Methyl (7*S*,10*R*,11*S*)-10-(3,4-dimethoxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]-acridine-11-carboxylate (Xe). IR spectrum, ν, cm^{-1}: 3375, 3190 (NH); 3060 (C–H_{arom}); 2950, 2930, 2870 (C–H_{aliph}); 1740 (C=O, ester); 1590 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1265, 1250 (C–O–C); 1150 (C–N–C); 810, 770 (C–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.61 s (3H, 1′-CH_3), 0.66 s (3H, *syn*-7′-CH_3), 0.82 s (3H, *anti*-7′-CH_3), 1.04 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.14 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.48 d.t (1H, *exo*-6′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.71 t.t.d (1H, *exo*-5′-H, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.77 t (1H, 4′-H, $^3J_{4',exo\text{-}5'}$ = $^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.62 m (2H, *endo*-3′-H, *exo*-3′-H), 2.88 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 3.32 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.40 s (3H, $COOCH_3$), 3.58 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.71 s and 3.73 s (3H each, CH_3O), 3.99 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.66 d.t (1H, 11′-H, ^3J = 9.6, $^4J_{3',11'}$ = 2 Hz), 4.86 d (1H, 7-H, ^3J = 9.6 Hz), 6.82 d (2H, H_{arom}), 6.89 s (1H, H_{arom}), 7.11 d (1H, 4-H, ^3J = 8.5 Hz), 7.46 t (1H, 3-H, ^3J = 8.5 Hz), 7.48 d (1H, 5-H, ^3J = 7 Hz), 7.59 t (1H, 2-H, ^3J = 8.5 Hz), 7.86 d (1H, 6-H, ^3J = 7 Hz), 8.39 d (1H, 1-H, ^3J = 8.5 Hz), 9.31 s (1H, NH).

Compounds **VIIf**, **VIIIf**, **IXf**, and **Xf** were obtained in an overall yield of 47%.

Methyl (7*R*,10*R*,11*S*)-10-(3,4-methylenedioxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (VIIf). IR spectrum, ν, cm^{-1}: 3300 (NH); 3060, 3020 (C–H_{arom}); 2950, 2920, 2870 (C–H_{aliph}); 1730 (C=O, ester); 1595 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1250, 1225 (C–O–C), 1160 (C–N–C); 810 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.69 s (3H, 1′-CH_3), 0.72 s (3H, *syn*-7′-CH_3), 0.85 s (3H, *anti*-7′-CH_3), 1.06 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.19 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8,

$^3J_{endo,exo}$ = 4 Hz), 1.52 d.t (1H, *exo*-6′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.73 t.t.d (1H, *exo*-5′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.77 t (1H, 4′-H, $^3J_{4',exo\text{-}5'} = {}^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.17 d.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.71 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 2.94 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'} = {}^4J_{3',11'}$ = 2 Hz), 3.09 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.33d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.38 s (3H, OCH_3), 4.28 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.64 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.91 d (1H, 7-H, ^3J = 10 Hz), 6.02 s (2H, OCH_2O), 6.82 d (2H, H_{arom}), 6.88 s (1H, H_{arom}), 7.18 d (1H, 4-H, ^3J = 8.5 Hz), 7.47 t (1H, 3-H, ^3J = 8.5 Hz), 7.49 d (1H, 5-H, ^3J = 7 Hz), 7.56 t (1H, 2-H, ^3J = 8.5 Hz), 7.87 d (1H, 6-H, ^3J = 7 Hz), 8.36 d (1H, 1-H, ^3J = 8.5 Hz), 9.19 s (1H, NH).

Methyl (7*S*,10*S*,11*R*)-10-(3,4-methylenedioxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (VIIIf). IR spectrum, ν, cm^{-1}: 3300 (NH); 3060, 3020 (C–H_{arom}); 2950, 2920, 2870 (C–H_{aliph}); 1730 (C=O, ester); 1595 (HN–C=C–C=O); 1520, 1490 (C=C_{arom}); 1250, 1220 (C–O–C); 1160 (C–N–C); 810 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, 1′-CH_3), 0.70 s (3H, *syn*-7′-CH_3), 0.85 s (3H, *anti*-7′-CH_3), 1.06 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.18 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.50 d.t (1H, *exo*-6′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.71 t.t.d (1H, *exo*-5′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.78 t (1H, 4′-H, $^3J_{4',exo\text{-}5'} = {}^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.67 m (2H, *endo*-3′-H, *exo*-3′-H), 2.84 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 3.31 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.33 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.43 s (3H, OCH_3), 4.29 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.70 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.91 d (1H, 7-H, ^3J = 10 Hz), 6.02 s (2H, OCH_2O), 6.81 d (2H, H_{arom}), 6.87 s (1H, H_{arom}), 7.12 d (1H, 4-H, ^3J = 8.5 Hz), 7.46 t (1H, 3-H, ^3J = 8.5 Hz), 7.48 d (1H, 5-H, ^3J = 7 Hz), 7.55 t (1H, 2-H, ^3J = 8.5 Hz), 7.86 d (1H, 6-H, ^3J = 7 Hz), 8.37 d (1H, 1-H, ^3J = 8.5 Hz), 9.21 s (1H, NH).

Methyl (7*R*,10*S*,11*R*)-10-(3,4-methylenedioxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (IXf). IR spectrum, ν, cm^{-1}: 3300 (NH); 3060, 3020 (C–H_{arom}); 2950, 2920, 2870 (C–H_{aliph}); 1730 (C=O, ester); 1595 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1250, 1225 (C–O–C); 1160 (C–N–C); 810 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.67 s (3H, 1′-CH_3), 0.72 s (3H, *syn*-7′-CH_3), 0.84 s (3H, *anti*-7′-CH_3), 1.05 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.21 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.53 d.t (1H, *exo*-6′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.69 t.t.d (1H, *exo*-5′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.78 t (1H, 4′-H, $^3J_{4',exo\text{-}5'} = {}^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.18 br.d (1H, *endo*-3′-H, ^2J = 16.4, $^4J_{3',11'}$ = 2 Hz), 2.82 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 2.96 d.d.t (1H, *exo*-3′-H, ^2J = 16.4, $^3J_{exo\text{-}3',4'}$ = 4, $^WJ_{exo\text{-}3',exo\text{-}5'} = {}^4J_{3',11'}$ = 2 Hz), 3.28 d.d (1H, 9-H_{ex}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.46 s (3H, OCH_3), 3.63 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.92 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9 Hz, $^3J_{ax,eq}$ = 4 Hz), 4.64 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.90 d (1H, 7-H, ^3J = 9.6 Hz), 6.02 s (2H, OCH_2O), 6.81 d (2H, H_{arom}), 6.87 s (1H, H_{arom}), 7.18 d (1H, 4-H, ^3J = 8.5 Hz), 7.47 t (1H, 3-H, ^3J = 8.5 Hz), 7.51 d (1H, 5-H, ^3J = 7 Hz), 7.56 t (1H, 2-H, ^3J = 8.5 Hz), 7.86 d (1H, 6-H, ^3J = 7 Hz), 8.37 d (1H, 1-H, ^3J = 8.5 Hz), 9.12 s (1H, NH).

Methyl (7*S*,10*R*,11*S*)-10-(3,4-methylenedioxyphenyl)-8-oxo-7-[(1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenemethyl]-7,8,9,10,11,12-hexahydrobenzo[*c*]acridine-11-carboxylate (Xf). IR spectrum, ν, cm^{-1}: 3300 (NH); 3060, 3020 (C–H_{arom}); 2950, 2920, 2870 (C–H_{aliph}); 1730 (C=O, ester); 1595 (HN–C=C–C=O); 1520, 1495 (C=C_{arom}); 1250, 1225 (C–O–C); 1160 (C–N–C); 810 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, 1′-CH_3), 0.72 s (3H, *syn*-7′-CH_3), 0.86 s (3H, *anti*-7′-CH_3), 1.06 d.d.d (1H, *endo*-6′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.21 d.d.d (1H, *endo*-5′-H, ^2J = 12, $^3J_{endo,endo}$ = 8, $^3J_{endo,exo}$ = 4 Hz), 1.49 d.t (1H, *exo*-6′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.68 t.t.d (1H, *exo*-5′-H, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{exo\text{-}5',4'}$ = 4, $^WJ_{exo\text{-}5',exo\text{-}3'}$ = 2 Hz), 1.77 t (1H, 4′-H, $^3J_{4',exo\text{-}5'} = {}^3J_{4',exo\text{-}3'}$ = 4 Hz), 2.64 m (2H, *endo*-3′-H, *exo*-3′-H), 2.85 d.d (1H, 9-H_{ax}, ^2J = 18, $^3J_{ax,ax}$ = 9 Hz), 3.30 d.d (1H, 9-H_{eq}, ^2J = 18, $^3J_{ax,eq}$ = 4 Hz), 3.46 s (3H, OCH_3), 3.58 d (1H, 11-H_{ax}, $^3J_{ax,ax}$ = 9 Hz), 3.93 t.d (1H, 10-H_{ax}, $^3J_{ax,ax}$ = 9, $^3J_{ax,eq}$ = 4 Hz), 4.70 d.t (1H, 11′-H, ^3J = 10, $^4J_{3',11'}$ = 2 Hz), 4.90 d (1H, 7-H, ^3J = 10 Hz), 6.02 s (2H, OCH_2O), 6.81 m (2H, H_{arom}), 6.86 s (1H, H_{arom}), 7.11 d (1H, 4-H, ^3J = 8.5 Hz), 7.45 t (1H, 3-H, ^3J = 8.5 Hz), 7.48 d (1H, 5-H, ^3J = 7 Hz), 7.57 t (1H, 2-H, ^3J = 8.5 Hz), 7.86 d (1H, 6-H, ^3J = 7 Hz), 8.37 d (1H, 1-H, ^3J = 8.5 Hz), 9.21 s (1H, NH).

5-{2-[(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene]ethylidene}hexahydropyrimidine-2,4,6-

trione (XIII) was obtained by heating equimolar amounts of (2 mmol) of (1,7,7-trimethylbicyclo[2.2.1]-hept-2-ylidene)acetaldehyde (**I**), naphthalen-1-amine (**II**), and barbituric acid (**IV**) in boiling ethanol. The precipitate was filtered off and washed with ethanol. The product contained almost no impurities. Yield 0.47 g (82%). The same compound was formed when Schiff base prepared from naphthalen-1-amine (**II**) and aldehyde **I** was heated with barbituric acid (**IV**) in ethanol. Yield 0.46 g (80%), mp 302–303°C. IR spectrum, ν, cm^{-1}: 3410, 3150 (N–H); 3050 (=C–H); 2950, 2865 ($C–H_{aliph}$); 1655 (C=O, amide I); 1610 (C=C, conjugated); 1565 (δNH, amide II). ^1H NMR spectrum, δ, ppm: 0.69 s (3H, 1′-CH_3), 0.91 s (3H, *syn*-7′-CH_3), 1.00 s (3H, *anti*-7′-CH_3), 1.21 m (2H, *endo*-5′-H, *endo*-6′-H), 1.76 m (2H, *exo*-5′-H, *exo*-6′-H), 1.92 t (1H, 4′-H, $^3J_{4',3'} = {}^3J_{4',5'} = 3.5$ Hz), 2.32 d.d (1H, *endo*-3′-H, $^2J = 18$, $^4J_{3',11'} = 1.6$ Hz), 2.78 d.d.t (1H, *exo*-3′-H, $^2J = 18$, $^3J_{4',3'} = 3.5$, $^4J_{3',5'} = {}^4J_{3',11'} = 1.6$ Hz), 7.40 d.t (1H, 11′-H, $^3J_{7,11'} = 10$, $^4J_{3',11'} = 1.6$ Hz), 7.97 d (1H, 7-H, $^3J_{7,11'} = 10$ Hz), 11.10 s and 11.20 s (1H each, NH). ^{13}C NMR spectrum, δ_C, ppm: 12.8 q (1′-CH_3), 19.2 q (*syn*-7′-CH_3), 20.0 q (*anti*-7′-CH_3), 27.3 t ($C^{5'}$), 34.6 t ($C^{6'}$), 35.9 t ($C^{3'}$), 44.2 d ($C^{4'}$), 48.8 s ($C^{7'}$), 55.1 s ($C^{1'}$), 113.2 s ($C^{2'}$), 115.3 d ($C^{11'}$), 151.0 d (C^7), 151.1 s (C^5), 163.7 s and 164.1 s (C^4, C^6), 183.1 s (C^2).

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