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Cyclopropanation of *N*-Substituted 3-Aryl-2-cyanoprop-2-enamides and Derivatives of 5,5-Dimethyl-2-oxo-2,5-dihydrofuran-3-carboxylic Acid and 2-Oxochromene-3-carboxylic Acid with Bromine-Containing Zinc Enolates

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Abstract—Zinc enolates derived from 1-aryl-2,2-dibromoalkanones react with N-substituted 3-aryl-2-cyanoprop-2-enamides and 5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-carboxylic and 2-oxochromene-3-carboxylic acid derivatives to give, respectively, N-substituted 2-alkyl-3-aryl-2-aroyl-1-cyanocyclopropane-1-carboxamides, 6-(4-bromobenzoyl)-4,4,6-trimethyl-2-oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylic acid ethyl ester and morpholide, and 1-alkyl-1-aroyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acids as a single geometric isomer. Treatment of 1-alkyl-1-aroyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acids with carboxylic acid anhydrides leads to the formation of the corresponding 9c-alkyl-1-aryl-3,4-dioxo-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalen-1-yl carboxylates.

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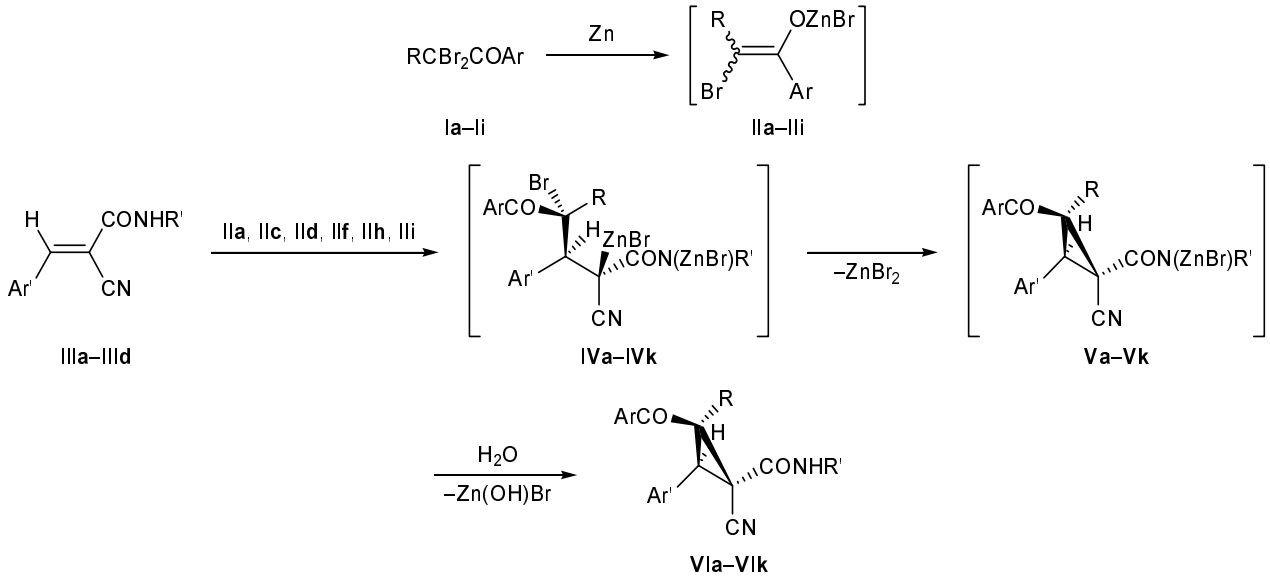
We previously showed that 1-aryl-2,2-dibromobutan-1-ones react with zinc and dialkyl 2-arylmethylidene- or 2-isobutylidenemalonates to give the corresponding cyclopropane derivatives having one aroyl and two ester moieties [1, 2]. With the goal of extending the synthetic potential of this reaction, in the present work we examined reactions of N-substituted 3-aryl-2-cyanoprop-2-enamides with bromine-containing zinc enolates derived from 1-aryl-2,2-dibromoalkanones.

Zinc enolates **IIa**, **IIc**, **IId**, **IIf**, **IIh**, and **IIi** preliminarily prepared from dibromo ketones **Ia**, **Ic**, **Id**, **If**, **Ih**, and **Ii**, respectively, and zinc add at the double bond of electrophilic substrates **IIIa**–**IIId** to give intermediates **IVa**–**IVk** which undergo intramolecular ring closure to cyclopropane derivatives **Va**–**Vk**. Hydrolysis of the latter gives N-substituted 2-alkyl-3-aryl-2-aroyl-1-cyanocyclopropane-1-carboxamides **VIa**–**VIk** (Scheme 1). The structure of compounds **VIa**–**VIk** was proved by the analytical data and IR and ^{1}H and ^{13}C NMR spectra. The IR spectra of **VIa**–**VIk** contain absorption bands due to stretching vibrations of the ketone and amide carbonyl groups (1665–1695 cm^{-1}) and NH bond (3325–3405 cm^{-1}). In the ^{1}H NMR spectra we observed signals from protons in the methyl group (δ 1.50–1.68 ppm, s, R = CH_3; δ 0.65–0.82 ppm, t, R = C_2H_5) and a singlet from the 3-H proton at δ 3.51–3.80 ppm. The presence of only one set of signals indicates formation of cyclopropane derivatives **VIa**–**VIk** as a single stereoisomer.

The steric configuration of compounds **VId** and **VIe** was determined by ^{1}H and ^{13}C NMR spectroscopy. Their ^{13}C NMR spectra were consistent with the assumed structure (see Experimental). The carbon signals were assigned on the basis of the HSQC and HMBC two-dimensional correlation spectra. The signals at δ_C 30.97, 40.73, and 46.23 ppm (**VId**) and at δ_C 30.50, 40.89, and 52.59 ppm (**VIe**) were assigned to the C^1, C^3, and C^2 nuclei, respectively; these signals are typical of cyclopropane fragment. The configuration of substituents at the cyclopropane fragment in *N*-cyclohexyl-3-(3-bromophenyl)-2-(4-chlorobenzoyl)-1-cyano-2-methylcyclopropan-1-carboxamide (**VId**) was proved by comparing the $^3J_{CH}$ vicinal coupling constants between 3-H and 2-CH_3 with analogous values found for cyclopropa[*c*]chromenes. We previ-

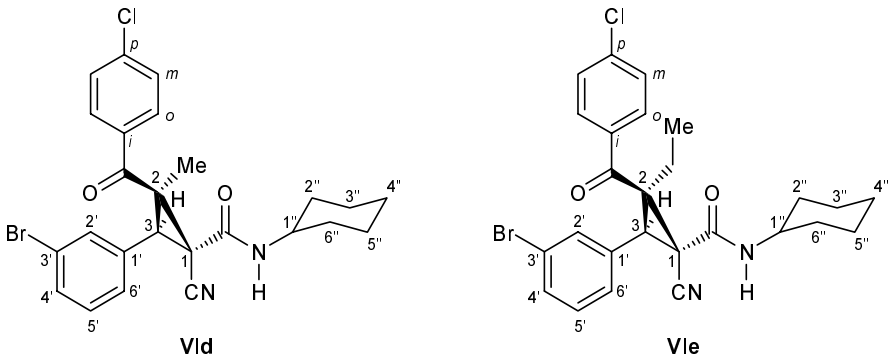
Scheme 1.



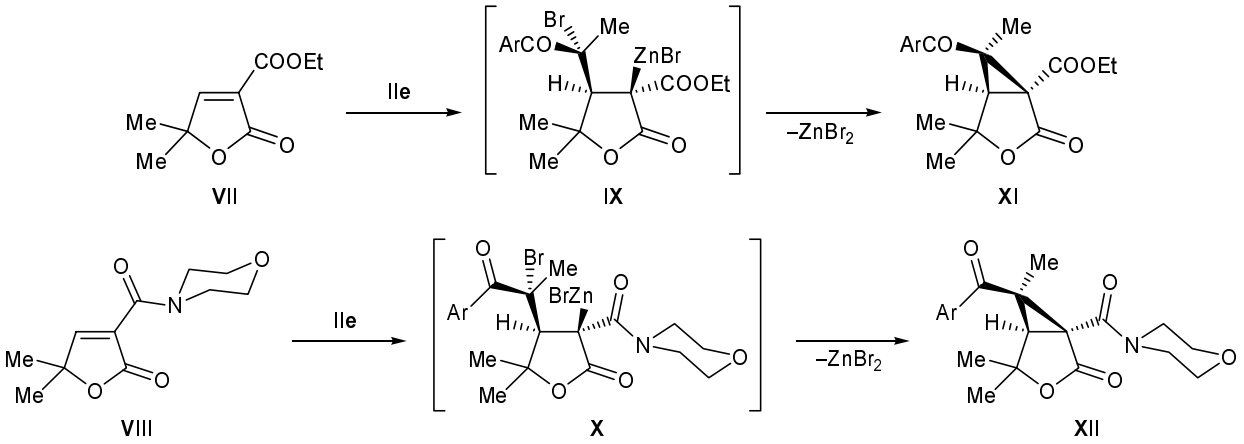
I, **II**, R = Me, Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-FC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**); R = Et, Ar = Ph (**f**), 4-MeC_6H_4 (**g**), 4-FC_6H_4 (**h**), 4-ClC_6H_4 (**i**); **III**, Ar' = Ph, R' = 3-MeC_6H_4 (**a**), $PhCH_2$ (**b**), 2-$MeOC_6H_4$ (**c**); Ar' = 3-BrC_6H_4, R' = C_6H_{11} (**d**); **IV**–**VI**, Ar' = Ph, R' = $PhCH_2$, Ar = 4-FC_6H_4, R = Me (**a**), Et (**b**); Ar' = 3-BrC_6H_4, R' = *cyclo*-C_6H_{11}, R = Me, Ar = Ph (**c**), 4-ClC_6H_4 (**d**); Ar' = 3-BrC_6H_4, R' = *cyclo*-C_6H_{11}, R = Et, Ar = 4-ClC_6H_4 (**e**); Ar' = Ph, R' = 3-MeC_6H_4, R = Me, Ar = Ph (**f**), 4-ClC_6H_4 (**g**); Ar' = Ph, R' = 3-MeC_6H_4, R = Et, Ar = Ph (**h**), 4-ClC_6H_4 (**i**); Ar' = Ph, R' = 2-$MeOC_6H_4$, R = Me, Ar = Ph (**j**), 4-ClC_6H_4 (**k**).

ously synthesized cyclopropanated chromenes with *E* and *Z* arrangement of the corresponding hydrogen atom and methyl group, and their configuration was established using NOE techniques, both two-dimensional (2D ROESY) and one-dimensional difference NOE experiments [3, 4]. The coupling constant $^3J_{CH}$ in 1-benzoyl-6-bromo-1-methyl-1a-morpholinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-one, in which the H atom and methyl group are located at the opposite sides of the cyclopropane ring (*E* isomer), was equal to 1.7 Hz, while *N*-benzyl-1-benzoyl-6-bromo-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxamide with *Z* arrangement of the corresponding moieties was characterized by a $^3J_{CH}$ value of 5.3 Hz. The coupling constant $^3J_{CH}$ measured for compound **VId** is 5.6 Hz, i.e., the 3-H atom and 2-methyl group in molecule **VId** are located at the same side of the cyclopropane ring (*Z* isomer). Likewise, similar coupling constants $^3J_{CH}$ between the same proton and amide carbonyl carbon atom suggest their *cis* orientation with respect to each other, as in cyclopropa[*c*]-chromenes.

Thus compound **VId** is a diastereoisomer in which the 3-H proton, 2-methyl group, and 1-carboxamide group reside at the same side of the cyclopropane ring. The 2-CH_2 carbon signal in the ^{13}C NMR spectrum of compound **VIe** appeared as a complex multiplet, and we failed to reliably determine the corresponding coupling constant $^3J_{CH}$. On the other hand, comparison of the chemical shifts of carbon atoms in **VIg** and **VId** indicated that these compounds have the same stereoconfiguration, for ^{13}C chemical shifts are known to be



Scheme 2.



Ar = 4-BrC_6H_4.

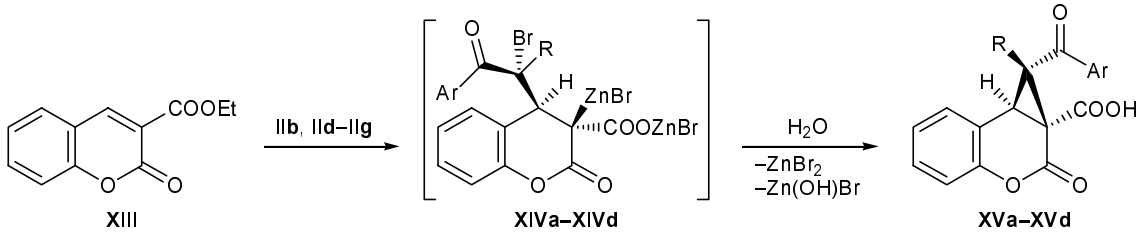
highly sensitive to steric factor. On the basis of the similarity of ^{1}H NMR spectral patterns of compounds **VId** and **VIe**, on the one hand, and cyclopropane derivatives **VIa**–**VIc** and **VIf**–**VIk**, on the other, the latter were assigned the same configuration.

We previously studied reactions of ethyl 5,5-dimethyl-2,5-dihydro-2-oxofuran-3-carboxylate with bromine-containing zinc enolates derived from 1-aryl-2,2-dibromoalkanones and obtained the corresponding cyclopropanation products, ethyl 6-aroyl-6-ethyl-4,4-dimethyl-2-oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylates as a single stereoisomer [5]. However, their structure, specifically the configuration of substituents on C^6, remained unclear. To elucidate this problem, in the present work we synthesized 6-(4-brombenzoyl)-4,4,6-trimethyl-2-oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylic acid ethyl ester **XI** and morpholide **XII**. For this purpose, compounds **VII** and **VIII** were treated with zinc enolate **IIe** in diethyl ether–ethyl acetate. Attack by the organozinc reagent on the C^4 atom in **VII** or **VIII** gave adduct **IX** or **X**, and spontaneous cyclization of the latter resulted in the formation of bicyclic product **XI** or **XII**, respectively (Scheme 2). Compound **XI** showed in the IR spectrum absorption bands typical of aroyl, ester, and lactone carbonyl groups (1680, 1720, and 1770 cm^{-1}, respectively), and the IR spectrum of morpholide **XII** contained absorption bands due to aroyl and amide carbonyl groups (1665 cm^{-1}) and lactone carbonyl (1750 cm^{-1}). Signals from protons of the methyl group on C^6 and 5-H appeared in the ^{1}H NMR spectra at δ 1.59 and 2.59 ppm for ethyl ester **XI** and at δ 1.44 and 2.80 ppm for morpholide **XII**, respectively.

The ^{13}C NMR spectra of **XI** and **XII** (see Experimental) were fully consistent with the assumed structures. The ^{13}C signals were assigned using HSQC and HMBC two-dimensional correlation techniques. The cyclopropane fragment in molecules **XI** and **XII** is characterized by resonance signals at δ_C 42.61, 42.84, 44.76 (**XI**) and 42.91, 43.61, 46.91 ppm (**XII**). The steric configuration of compounds **XI** and **XII** was determined as described above for **VId** and **VIe**. The coupling constants $^3J_{CH}$ are 5.2 (**XI**) and 5.4 Hz (**XII**), indicating that the 5-H atom and 6-CH_3 group are located at the same side of the cyclopropane ring plane.

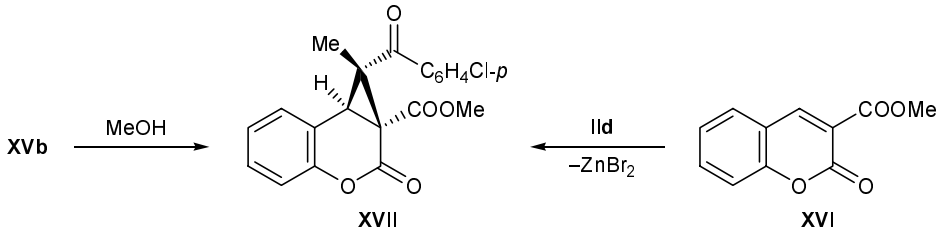
Zinc enolates **IIb**, **IId**–**IIg** obtained from dibromo ketones **Ib** and **Id**–**Ig**, respectively, were brought into reaction with 2-oxochromene-3-carboxylic acid **XIII**

Scheme 3.



R = Me, Ar = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**); R = Et, Ar = Ph (**d**), 4-MeC_6H_4 (**e**).

Scheme 4.

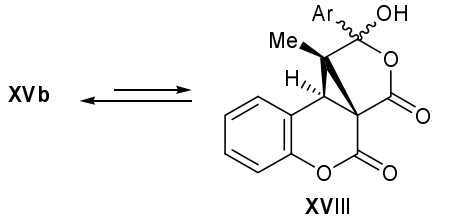


(Scheme 3). The reaction involved 2 equiv of zinc enolate **II** which added in succession at the carboxy group and C^4 of molecule **XIII** to give intermediates **XIVa**–**XIVe**. The subsequent intramolecular nucleophilic substitution of the bromine atom may occur by the action of both carboxylate oxygen atom and C^3 of the heteroring. The latter pathway turned out to be preferred, and the products isolated after hydrolysis were 1-alkyl-1-aryl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acids **XVa**–**XVe**. In the IR spectra of compounds **XVa**, **XVb**, **XVd**, and **XVe** we observed absorption bands belonging to stretching vibrations of the aroyl, acid, and lactone carbonyl groups (1660–1715 and 1740–1745 cm^{-1}) and O–H bond (3150–3180 cm^{-1}). The 7b-H proton gave a signal at δ 3.52–3.82 ppm in the ^1H NMR spectra.

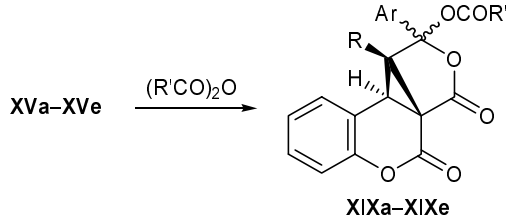
Double recrystallization of acids **XVa**, **XVd**, and **XVe** from methanol resulted in their partial or complete (compound **XVb**) esterification; for example, from acid **XVb** we obtained methyl 1-(4-chlorophenyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]-chromene-1a-carboxylate (**XVII**). The structure of ester **XVII** was proved by independent synthesis via cyclopropanation of methyl 2-oxochromene-3-carboxylate (**XVI**) with zinc enolate **IId** (Scheme 4). According to our previous data, analogous reactions give exclusively stereoisomers with *Z* configuration of the aroyl group and substituent on C^{1a} [3], and the chemical shifts of the methyl protons range from δ 1.12 to 1.40 ppm. In the ^1H NMR spectra of compounds **XVa** and **XVb**, the 1-CH_3 signal appeared at δ 1.10–1.27 ppm; therefore, we concluded that the examined reaction is strictly stereoselective and that the products are stereoisomers with *Z* configuration of the carboxy and aroyl groups. This configuration is favorable for intramolecular cyclization via nucleophilic addition of the acid hydroxy group at the aroyl carbonyl group to produce hydroxy lactone. For example, 1-(4-chlorophenyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]-chromene-1a-carboxylic acid (**XVb**) could be converted into cyclic isomer **XVIII**.

To check the above assumption, we performed reactions of compounds **XVa**–**XVe** with carboxylic acid anhydrides; we hoped that the reaction will occur just with the hydroxy lactone isomer of **XVa**–**XVe**. In fact, by heating compounds **XVa**–**XVe** with acetic and propionic anhydrides we obtained 9c-alkyl-1-aryl-3,4-dioxo-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalen-1-yl acetates and propionates **XIXa**–**XIXe** (Scheme 5). The IR spectra of compounds **XIXa**–**XIXe** contained absorption bands at 1750 and 1805 cm^{-1} due to lactone carbonyl groups in the six- and five-membered rings and ester carbonyl. The 9b-H signal appeared in the ^1H NMR spectra at δ 2.80–3.00 ppm.

Scheme 5.



Ar = 4-ClC_6H_4.



R = R' = Me, Ar = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**); R = Me, R' = Et, Ar = 4-ClC_6H_4 (**d**); R = Et, R' = Me, Ar = 4-ClC_6H_4 (**e**).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra were measured from solutions in $CDCl_3$ (**VIa**, **VIb**, **VId**, **VIe**, **XVa**, **XVII**, **XIXb**,

XIXd, **XIXe**) or $CDCl_3$–DMSO-d_6 (**VIf**, **VIi**, **XVb**, **XIXa**, **XIXc**) on a Tesla BS-576A instrument (100 MHz, HMDS) and from solutions in DMSO-d_6 (**VIc**–**VIe**, **VIg**, **VIh**, **VIj**, **VIk**, **XVd**, **XVe**) on a Bruker DRX-500 spectrometer (500 MHz, TMS). The ^{13}C NMR spectra of compounds **VId**, **VIe**, **XI**, and **XII** and their 1D and 2D NMR spectra were obtained from solutions in $CDCl_3$ on a Bruker DRX-400 spectrometer (400 and 100 MHz for ^1H and ^{13}C, respectively).

N-Substituted 2-alkyl-3-aryl-2-aroyl-1-cyanocyclopropane-1-carboxamides Va–Vk (*general procedure***).** A solution of 0.025 mol of 1-aryl-2,2-dibromoalkanone **I** in 3 ml of ethyl acetate was added to a mixture of 4 g of zinc prepared as fine turnings, 8 ml of diethyl ether, and 5 ml of ethyl acetate. The mixture was heated to initiate the reaction which then occurred spontaneously. When the reaction was complete, the mixture was heated for 10 min under reflux, cooled, and separated from zinc by decanting. N-Substituted 3-aryl-2-cyanoprop-2-enamide, 0.01 mol, was added, the mixture was heated for 30 min, cooled, treated with a solution of acetic acid, and extracted with diethyl ether, the extract was dried over Na_2SO_4, the solvent was distilled off, and the residue was recrystallized from methanol.

***N*-Benzyl-1-cyano-2-(4-fluorobenzoyl)-2-methyl-3-phenylcyclopropane-1-carboxamide (VIa).** Yield 66%, mp 159–160°C. IR spectrum, ν, cm^{-1}: 1680, 3390. ^1H NMR spectrum, δ, ppm: 1.50 s (3H, CH_3), 3.54 s (1H, CH), 4.38 d (2H, C**H**$_2$Ph, J = 7.1 Hz), 6.80–7.80 m (14H, H_{arom}), 9.07 m (1H, NH). Found, %: C 75.59; H 5.08; N 6.69. $C_{26}H_{21}FN_2O_2$. Calculated, %: C 75.71; H 5.13; N 6.79.

***N*-Benzyl-1-cyano-2-ethyl-2-(4-fluorobenzoyl)-3-phenylcyclopropane-1-carboxamide (VIb).** Yield 63%, mp 179–180°C. IR spectrum, ν, cm^{-1}: 1680, 3395. ^1H NMR spectrum, δ, ppm: 0.65 t (3H, C**H**$_3$CH$_2$, J = 7.4 Hz), 1.89 q (2H, CH$_3$C**H**$_2$, J = 7.4 Hz), 3.58 s (1H, CH), 4.33 d (2H, C**H**$_2$Ph, J = 7.1 Hz), 6.75–7.80 m (14H, H_{arom}), 9.06 m (1H, NH). Found, %: C 75.96; H 5.35; N 6.45. $C_{27}H_{23}FN_2O_2$. Calculated, %: C 76.04; H 5.44; N 6.57.

2-Benzoyl-3-(3-bromophenyl)-1-cyano-*N*-cyclohexyl-2-methylcyclopropane-1-carboxamide (VIc). Yield 68%, mp 197–198°C. IR spectrum, ν, cm^{-1}: 1690, 3405. ^1H NMR spectrum, δ, ppm: 1.54 s (3H, CH_3), 1.10–1.80 m (10H, C_6H_{11}), 3.59 s (1H, CH), 3.66 m (1H, C_6H_{11}), 7.17–7.60 m and 7.87 d (9H, H_{arom}), 8.56 m (1H, NH). Found, %: C 64.44; H 5.33; N 5.93. $C_{25}H_{25}BrN_2O_2$. Calculated, %: C 64.52; H 5.41; N 6.02.

3-(3-Bromophenyl)-2-(4-chlorobenzoyl)-1-cyano-*N*-cyclohexyl-2-methylcyclopropane-1-carboxamide (VId). Yield 71%, mp 213–214°C. IR spectrum, ν, cm^{-1}: 1665, 3375. ^1H NMR spectrum, δ, ppm: 500 MHz, DMSO-d_6: 1.52 s (3H, CH_3); 1.05–1.80 m (10H, C_6H_{11}); 3.58 s (1H, CH); 3.66 m (1H, C_6H_{11}); 7.20 m, 7.41 m, 7.53 m, and 7.89 d (8H, 4-ClC_6H_4, 3-BrC_6H_4); 8.60 m (1H, NH); 400 MHz, $CDCl_3$: 1.67 s (3H, CH_3), 1.18–2.00 m (10H, C_6H_{11}), 3.62 s (1H, 3-H), 3.84 m (1H, 1''-H), 6.56 d (1H, NH, J = 7.7 Hz), 6.95 d.t (1H, 6'-H, J = 7.9, 1.5 Hz), 7.30–7.34 m (3H, *m*-H, 4'-H), 7.46 t (1H, 2'-H, J = 1.8 Hz), 7.72 d (2H, *o*-H, J = 8.6 Hz); 100 MHz, $CDCl_3$: 1.58 s (3H, CH_3), 1.15–1.95 m (10H, C_6H_{11}), 3.51 s (1H, CH), 3.72 m (1H, C_6H_{11}), 6.42 d (1H, NH), 6.75–7.30 m and 7.55 d (8H, 4-ClC_6H_4, 3-BrC_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 18.40 q.d (CH_3, $^1J_{CH}$ = 131.2, $^3J_{CH}$ = 5.6 Hz), 24.71 t.m ($C^{3''}$, $^1J_{CH}$ = 131.5 Hz), 24.75 t.m ($C^{5''}$, $^1J_{CH}$ = 131.5 Hz), 25.31 t.m ($C^{4''}$, $^1J_{CH}$ = 126.0), 30.97 d.q (C^1, $^3J_{CH}$ = $^2J_{CH}$ = 4.0 Hz), 32.56 d.d.m ($C^{6''}$, $^1J_{CH}$ = 132.7, 128.0 Hz), 33.01 d.d.m ($C^{2''}$, $^1J_{CH}$ = 134.1, 130.0 Hz), 40.73 d.q (C^3, $^1J_{CH}$ = 163.7, $^3J_{CH}$ = 4.6 Hz), 46.23 q.d (C^2, $^2J_{C,Me}$ = 4.6, $^2J_{C,3\text{-}H}$ = 2.7 Hz), 50.20 d.m ($C^{1''}$, $^1J_{CH}$ = 143.2 Hz), 116.41 d (C≡N, $^3J_{CH}$ = 3.7 Hz), 122.52 d.t ($C^{3'}$, J = 8.1, 4.2 Hz), 125.78 d.d.t ($C^{6'}$, J = 160.3, 7.3, 6.6 Hz), 129.12 d.d (C^m, J_{CH} = 168.1, 5.1 Hz), 129.90 d ($C^{5'}$, $^1J_{CH}$ = 163.4 Hz), 130.83 d.d (C^o, J_{CH} = 163.0, 6.7 Hz), 131.22 d.d.d.d ($C^{4'}$, J_{CH} = 167.4, 7.5, 5.3, 2.1 Hz), 131.82 t (C^i, $^3J_{CH}$ = 7.4 Hz), 132.50 d.d.t ($C^{2'}$, J_{CH} = 164.4, 6.1, 5.6 Hz), 134.23 d.m ($C^{1'}$, J_{CH} = 8.0 Hz), 140.56 t.t (C^p, J_{CH} = 10.8, 3.3 Hz), 160.92 t.d (NCO, J_{CH} = 4.2, 2.5 Hz), 193.03 m (CO). Found, %: C 59.98; H 4.79; N 5.49. $C_{25}H_{24}ClBrN_2O_2$. Calculated, %: C 60.08; H 4.84; N 5.60.

3-(3-Bromophenyl)-2-(4-chlorobenzoyl)-1-cyano-*N*-cyclohexyl-2-ethylcyclopropane-1-carboxamide (VIe). Yield 64%, mp 199–200°C. IR spectrum, ν, cm^{-1}: 1690, 3400. ^1H NMR spectrum, δ, ppm: 500 MHz, DMSO-d_6: 0.82 t (3H, CH_3, J = 7.4 Hz); 1.05–1.87 m (10H, C_6H_{11}, 1H, C**H**$_2$CH$_3$); 1.99 m (1H, C**H**$_2$CH$_3$); 3.64 s (1H, CH); 3.66 m (1H, C_6H_{11}); 7.20 m, 7.41 m, 7.51 m, and 7.93 d (8H, 4-ClC_6H_4, 3-BrC_6H_4); 8.14 m (1H, NH); 400 MHz, $CDCl_3$: 0.83 t (3H, CH_3, J = 7.4 Hz), 1.19–2.48 m (5H), 1.67 m (1H), 1.80 m (2H), 1.99 d (2H, C**H**$_2$C$_6$H$_{11}$), 2.21 q (2H, C**H**$_2$CH$_3$, J = 7.4 Hz), 3.70 s (1H, 3-H), 3.87 m (1H, 1''-H), 6.63 d (1H, NH, J = 7.9 Hz), 6.98 d.t (1H, 6'-H, J = 7.9, 1.7 Hz), 7.03 t (1H, 5'-H, J = 7.9 Hz), 7.30–7.34 m (3H, *m*-H, 4'-H), 7.51 t (1H, 2'-H, J = 1.7 Hz),

7.74 d (2H, *o*-H, J = 8.7 Hz); 100 MHz, $CDCl_3$: 0.74 t (3H, CH_3, J = 7.4 Hz), 1.10–2.15 m (10H, C_6H_{11}, 2H, C**H**$_2$CH$_3$), 3.59 s (1H, CH), 3.75 m (1H, C_6H_{11}), 6.48 d (1H, NH, J = 7.9 Hz), 6.80–7.34 m and 7.56 d (8H, 4-ClC_6H_4, 3-BrC_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 10.68 q.t (CH_3, $^1J_{CH}$ = 126.7, $^2J_{CH}$ = 4.3 Hz), 24.73 t.m ($C^{3''}$,$C^{5''}$, $^1J_{CH}$ = 129.5 Hz), 25.32 t.m ($C^{4''}$, $^1J_{CH}$ = 125 Hz), 25.48 t.m (2-CH_2, $^1J_{CH}$ = 131.2 Hz), 30.50 d.t (C^1, J_{CH} = 5.6, 2.9 Hz), 32.55 t.m ($C^{6''}$, $^1J_{CH}$ = 130 Hz), 32.67 t.m ($C^{2''}$, $^1J_{CH}$ = 130 Hz), 40.89 d.m (C^3, $^1J_{CH}$ = 163.7 Hz), 50.12 d.m ($C^{1''}$, $^1J_{CH}$ = 143.5 Hz), 52.59 m (C^2), 116.76 d (C≡N, $^3J_{CH}$ = 4.0 Hz), 122.56 d.d.d ($C^{3'}$, J_{CH} = 11.0, 4.5, 3.1 Hz), 125.75 d.d.t ($C^{6'}$, J_{CH} = 160.4, 6.9, 6.6 Hz), 129.09 d.d (C^m, J_{CH} = 167.9, 5.2 Hz), 129.96 d ($C^{5'}$, $^1J_{CH}$ = 163.4 Hz), 130.78 d.d (C^o, J_{CH} = 163.2, 6.9 Hz), 131.26 d.d.d.d ($C^{4'}$, J_{CH} = 167.7, 7.1, 5.1, 1.9 Hz), 132.12 t (C^i, $^3J_{CH}$ = 7.4 Hz), 132.61 d.q ($C^{2'}$, J_{CH} = 164.5, 6.0 Hz), 134.32 d.q ($C^{1'}$, J_{CH} = 8.5, 1.3 Hz), 140.48 t.t (C^p, J_{CH} = 10.7, 3.3 Hz), 161.10 t.d (NCO, J_{CH} = 4.4, 2.4 Hz), 192.42 m (CO). Found, %: C 60.71; H 5.03; N 5.32. $C_{26}H_{26}ClBrN_2O_2$. Calculated, %: C 60.77; H 5.10; N 5.45.

2-Benzoyl-1-cyano-2-methyl-*N*-(3-methylphenyl)-3-phenylcyclopropane-1-carboxamide (VIf). Yield 67%, mp 200–201°C. IR spectrum, ν, cm^{-1}: 1690, 3325. ^1H NMR spectrum, δ, ppm: 1.59 s (3H, CH_3), 2.24 s (3H, CH_3), 3.61 s (1H, CH), 6.80–7.68 m (14H, H_{arom}), 10.22 s (1H, NH). Found, %: C 79.06; H 5.53; N 6.94. $C_{26}H_{22}N_2O_2$. Calculated, %: C 79.17; H 5.62; N 7.10.

2-(4-Chlorobenzoyl)-1-cyano-2-methyl-*N*-(3-methylphenyl)-3-phenylcyclopropane-1-carboxamide (VIg). Yield 72%, mp 222–223°C. IR spectrum, ν, cm^{-1}: 1675, 3330. ^1H NMR spectrum, δ, ppm: 1.59 s (3H, CH_3), 2.30 s (3H, CH_3), 3.71 s (1H, CH), 6.98–7.86 m (13H, H_{arom}), 10.71 s (1H, NH). Found, %: C 72.75; H 4.87; N 6.39. $C_{26}H_{22}ClN_2O_2$. Calculated, %: C 72.81; H 4.93; N 6.53.

2-Benzoyl-1-cyano-2-ethyl-*N*-(3-methylphenyl)-3-phenylcyclopropane-1-carboxamide (VIh). Yield 61%, mp 227–228°C. IR spectrum, ν, cm^{-1}: 1685, 3330. ^1H NMR spectrum, δ, ppm: 0.82 t (3H, CH_3, J = 7.4 Hz), 1.79 m and 2.18 m (2H, CH_2), 3.80 s (1H, CH), 6.98–7.88 m (14H, H_{arom}), 10.72 s (1H, NH). Found, %: C 79.27; H 5.88; N 6.70. $C_{27}H_{24}N_2O_2$. Calculated, %: C 79.39; H 5.92; N 6.86

2-(4-Chlorobenzoyl)-1-cyano-2-ethyl-*N*-(3-methylphenyl)-3-phenylcyclopropane-1-carboxamide (VIi). Yield 58%, mp 252–253°C. IR spectrum, ν, cm^{-1}: 1685, 3330. ^1H NMR spectrum, δ, ppm: 0.81 t (3H, CH_3, J = 7.4 Hz), 1.95 m (2H, CH_2), 3.66 s (1H, CH), 6.80–7.69 m (13H, H_{arom}), 10.32 s (1H, NH). Found, %: C 73.10; H 5.17; N 6.21. $C_{27}H_{23}ClN_2O_2$. Calculated, %: C 73.21; H 5.23; N 6.32

2-Benzoyl-1-cyano-*N*-(2-methoxyphenyl)-2-methyl-3-phenylcyclopropane-1-carboxamide (VIj). Yield 42%, mp 177–179°C. IR spectrum, ν, cm^{-1}: 1680, 3395. ^1H NMR spectrum, δ, ppm: 1.67 s (3H, CH_3), 3.75 s (1H, CH), 3.86 s (3H, OCH_3), 6.98–7.87 m (14H, H_{arom}), 9.79 s (1H, NH). Found, %: C 76.01; H 5.32; N 6.69. $C_{26}H_{22}N_2O_3$. Calculated, %: C 76.08; H 5.40; N 6.82.

2-(4-Chlorobenzoyl)-1-cyano-*N*-(2-methoxyphenyl)-2-methyl-3-phenylcyclopropane-1-carboxamide (VIk). Yield 38%, mp 173–174°C. IR spectrum, ν, cm^{-1}: 1695, 3395. ^1H NMR spectrum, δ, ppm: 1.66 s (3H, CH_3), 3.74 s (1H, CH), 3.84 s (3H, OCH_3), 6.98–7.88 m (13H, H_{arom}), 9.82 s (1H, NH). Found, %: C 70.08; H 4.70; N 6.18. $C_{26}H_{21}ClN_2O_3$. Calculated, %: C 70.19; H 4.76; N 6.30.

6-(4-Bromobenzoyl)-4,4,6-trimethyl-2-oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylic acid ethyl ester and morpholide XI and XII (*general procedure*). A solution of 0.013 mol of 2,2-dibromo-1-(4-bromophenyl)propan-1-one in 3 ml of ethyl acetate was added to a mixture of 3 g of zinc prepared as fine turnings, 8 ml of diethyl ether, and 5 ml of ethyl acetate. The mixture was heated to initiate the reaction which then occurred spontaneously. When the reaction was complete, the mixture was heated for 10 min under reflux, cooled, and separated from zinc by decanting. 5,5-Dimethyl-2-oxo-2,5-dihydrofuran-3-carboxylic acid ethyl ester or morpholide, 0.01 mol, was added, the mixture was heated for 30 min, cooled, treated with a solution of acetic acid, and extracted with diethyl ether, the extract was dried over Na_2SO_4, the solvent was distilled off, and the residue was recrystallized from methanol.

Ethyl 6-(4-bromobenzoyl)-4,4,6-trimethyl-2-oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylate (XI). Yield 73%, mp 160–161°C. IR spectrum, ν, cm^{-1}: 1680, 1720, 1770. ^1H NMR spectrum, δ, ppm: 1.39 t (3H, C**H**$_3$CH$_2$, J = 7.1 Hz), 1.44 s (3H, 4-CH_3), 1.51 s (3H, 4-CH_3), 1.59 s (3H, 6-CH_3), 2.59 s (1H, CH), 4.38 q (2H, CH_3C**H**$_2$, J = 7.1 Hz), 7.64 d and 7.98 d (4H, BrC_6H_4, J = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.20 q.t (CH_2C**H**$_3$, J = 127.4, 2.6 Hz), 20.15 q.d (6-CH_3, J = 130.9, 5.2 Hz), 22.21 q.q (4-CH_3, J = 128.1, 3.8 Hz), 31.07 q.q.d (4-CH_3, J = 127.8, 4.2, 2.3 Hz), 42.61 d.q (C^1 or C^6, J = 3.7 Hz), 42.84 q (C^6

or C^1, J = 4.8 Hz), 44.76 d.m (C^5, J = 168.2 Hz), 62.49 t.q (CH_2CH_3, J = 148.5, 4.4 Hz), 82.40 m (C^4), 129.47 t.t (C^p, J = 10.9, 3.1 Hz), 131.11 d.d (C^o, J = 163.9, 6.9 Hz), 132.01 d.d (C^m, J = 168.4, 5.4 Hz), 133.12 t (C^i, J = 7.4 Hz), 164.60 t.d (COO, J = 3.4 Hz), 168.09 d (C^2, J = 4.0 Hz), 194.32 m (CO). Found, %: C 54.56; H 4.74. $C_{18}H_{19}BrO_5$. Calculated, %: C 54.70; H 4.85.

6-(4-Bromobenzoyl)-1-morpholinocarbonyl-4,4,6-trimethyl-3-oxabicyclo[3.1.0]hexan-2-one (XII). Yield 64%, mp 237–238°C. IR spectrum, ν, cm^{-1}: 1665, 1750. ^1H NMR spectrum, δ, ppm: 1.19 s (3H, 4-CH_3), 1.44 s (3H, 6-CH_3), 1.57 s (3H, 4-CH_3), 2.80 s (1H, 5-H), 3.38–4.39 m (8H, NCH_2CH_2O), 7.68 d and 7.89 d (4H, BrC_6H_4, J = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.85 q.d (6-CH_3, J = 130.1, 5.4 Hz), 24.88 q.q (4-CH_3, J = 127.7, 3.8 Hz), 30.60 q.q.d (4-CH_3, J = 127.9, 3.8, 3.6 Hz), 42.91 m (C^1 or C^6), 42.91 t (NCH_2, J = 139.6 Hz), 43.61 q (C^6 or C^1, J = 4.5 Hz), 46.91 d.q.q (C^5, J = 169.8, 4.2 Hz), 46.96 t (NCH_2, J = 140.6 Hz), 66.60 t and 67.55 t (OCH_2, J = 144 Hz), 81.89 q.q.d (C^4, J = 4.4 Hz), 129.46 t.t (C^p, J = 10.9, 3.1 Hz), 131.31 d.d.d (C^o, J = 164.4, 7.1, 4.4 Hz), 132.16 d.d.d (C^m, J = 166.6, 8.0, 3.4 Hz), 133.42 t (C^i, J = 7.4 Hz), 161.82 d.t (NCO, J = 2.8 Hz), 169.46 d (C^2, J = 3.7 Hz), 194.59 m (CO). Found, %: C 54.94; H 4.96; N 3.05. $C_{20}H_{22}BrNO_5$. Calculated, %: C 55.06; H 5.08; N 3.21.

1-Alkyl-1-aryl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acids XVa–XVe (*general procedure*). A solution of 0.025 mol of 1-aryl-2,2-dibromoalkanone **Ib** or **Id**–**Ig** in 10 ml of ethyl acetate was added dropwise under stirring to a mixture of 5 g of zinc prepared as fine turnings, 10 ml of diethyl ether, and 10 ml of ethyl acetate. The mixture was heated to initiate the reaction which then occurred spontaneously. When the reaction was complete, the mixture was heated for 15 min on a water bath, cooled, and separated from zinc by decanting into another flask. Compound **XIII**, 0.01 mol, was then added, the mixture was heated for 30 min under reflux, cooled, treated with 5% hydrochloric acid, and extracted with diethyl ether, the extract was dried over Na_2SO_4, the solvent was distilled off, and the residue was recrystallized from benzene–hexane.

1-Methyl-2-oxo-1-(*p*-tolyl)-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acid (XVa). Yield 60%, mp 205–207°C. IR spectrum, ν, cm^{-1}: 1660, 1715, 1740, 3170. ^1H NMR spectrum, δ, ppm: 1.27 s (3H, CH_3), 2.32 s (3H, $CH_3C_6H_4$), 3.82 s (1H, CH), 6.85–7.80 m (8H, C_6H_4, $CH_3C_6H_4$), 10.85 br.s (1H, OH). Found, %: C 71.30; H 4.71. $C_{20}H_{16}O_5$. Calculated, %: C 71.42; H 4.80.

1-(4-Chlorophenyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acid (XVb). Yield 52%, mp 218–220°C. IR spectrum, ν, cm^{-1}: 1670–1700, 1740, 3150. ^1H NMR spectrum, δ, ppm: 1.11 s (3H, CH_3), 3.52 s (1H, CH), 6.85–7.85 m (8H, C_6H_4, 4-ClC_6H_4), 13.10 br.s (1H, OH). Found, %: C 63.91; H 3.61. $C_{19}H_{13}ClO_5$. Calculated, %: C 63.97; H 3.67.

1-(4-Bromophenyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acid (XVc) was brought into reaction with acetic anhydride without preliminary purification.

1-Ethyl-2-oxo-1-phenyl-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acid (XVd). Yield 55%, mp 193–195°C. IR spectrum, ν, cm^{-1}: 1670–1700, 1745, 3180. ^1H NMR spectrum, δ, ppm: 0.46 t (3H, CH_3CH_2, J = 7 Hz), 1.06 m and 1.98 m (2H, CH_3CH_2, J = 7 Hz), 3.62 s (1H, CH), 7.15–8.00 m (9H, C_6H_4, C_6H_5), 13.45 br.s (1H, OH). Found, %: C 71.48; H 4.82. $C_{20}H_{16}O_5$. Calculated, %: C 71.42; H 4.80.

1-Ethyl-2-oxo-1-(*p*-tolyl)-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylic acid (XVe). Yield 56%, mp 234–236°C. IR spectrum, ν, cm^{-1}: 1670–1700, 1740, 3170. ^1H NMR spectrum, δ, ppm: 0.46 t (3H, CH_3CH_2, J = 7 Hz), 1.05 m and 1.95 m (2H, CH_3CH_2, J = 7 Hz), 2.39 s (3H, 4-$CH_3C_6H_4$), 3.61 s (1H, CH), 7.15–7.86 m (8H, C_6H_4, 4-$CH_3C_6H_4$), 13.35 br.s (1H, OH). Found, %: C 72.09; H 5.25. $C_{21}H_{18}O_5$. Calculated, %: C 71.99; H 5.18.

Methyl 1-(4-chlorophenyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromene-1a-carboxylate (XVII). *a.* A solution of 0.015 mol of 2,2-dibromo-1-(4-chlorophenyl)propan-1-one in 10 ml of ethyl acetate was added dropwise under stirring to a mixture of 5 g of zinc prepared as fine turnings, 10 ml of diethyl ether, and 10 ml of ethyl acetate. The mixture was heated to initiate the reaction which then occurred spontaneously. When the reaction was complete, the mixture was heated for 15 min on a water bath, cooled, and separated from zinc by decanting into another flask. Compound **XVI**, 0.01 mol, was then added, the mixture was heated for 30 min under reflux, cooled, treated with 5% hydrochloric acid, and extracted with diethyl ether, the extract was dried over Na_2SO_4, the solvent was distilled off, and the residue was recrystallized from benzene–hexane. Yield 82%.

b. Acid **XVb** was heated for 1 h in boiling methanol. The solution was cooled to –5°C, and compound

XVII was filtered off and dried under reduced pressure. Yield 61%, mp 216–218°C. IR spectrum, ν, cm^{-1}: 1690, 1735, 1770. ^1H NMR spectrum, δ, ppm: 1.17 s (3H, CH_3), 2.49 s (3H, OCH_3), 3.60 s (1H, CH), 6.90–7.93 m (8H, C_6H_4, ClC_6H_4). Found, %: C 64.91; H 4.15. $C_{20}H_{16}O_5$. Calculated, %: C 64.79; H 4.08.

1-Aryl-9c-methyl-3,4-dioxo-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalen-1-yl acetates and propionate XIXa–XIXe (*general procedure***).** Compound **XVa**–**XVe**, 0.005 mol, was added to 5 ml of acetic or propionic anhydride, and the mixture was heated for 1 h. Excess anhydride was distilled off under reduced pressure, and the residue was recrystallized from toluene.

9c-Methyl-3,4-dioxo-1-(*p*-tolyl)-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalen-1-yl acetate (XIXa). Yield 50%, mp 221–223°C. IR spectrum, ν, cm^{-1}: 1750, 1805. ^1H NMR spectrum, δ, ppm: 1.18 s (3H, CH_3), 2.08 s (3H, $OCOCH_3$), 2.30 s (3H, 4-C**H**$_3C_6H_4$), 3.00 s (1H, CH), 6.80–7.30 m (8H, C_6H_4, 4-CH_3C_6**H**$_4$). Found, %: C 69.72; H 4.73. $C_{22}H_{18}O_6$. Calculated, %: C 69.84; H 4.80.

1-(4-Chlorophenyl)-9c-methyl-3,4-dioxo-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]-naphthalen-1-yl acetate (XIXb). Yield 47%, mp 223–224°C. IR spectrum, ν, cm^{-1}: 1750, 1805. ^1H NMR spectrum, δ, ppm: 1.22 s (3H, CH_3), 2.09 s (3H, $OCOCH_3$), 2.80 s (1H, CH), 6.80–7.30 m (8H, C_6H_4, 4-ClC_6H_4). Found, %: C 63.30; H 3.86. $C_{21}H_{15}ClO_6$. Calculated, %: C 63.25; H 3.80.

1-(4-Bromophenyl)-9c-methyl-3,4-dioxo-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]-naphthalen-1-yl acetate (XIXc). Yield 58%, mp 240–242°C. IR spectrum, ν, cm^{-1}: 1750, 1805. ^1H NMR spectrum, δ, ppm: 1.20 s (3H, CH_3), 2.10 s (3H, $OCOCH_3$), 3.06 s (1H, CH), 6.80–7.40 m (8H, C_6H_4, 4-BrC_6H_4). Found, %: C 57.01; H 3.48. $C_{21}H_{15}BrO_6$. Calculated, %: C 56.90; H 3.41.

1-(4-Chlorophenyl)-9c-methyl-3,4-dioxo-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]-naphthalen-1-yl propionate (XIXd). Yield 52%, mp 240–241°C. IR spectrum, ν, cm^{-1}: 1750, 1805. ^1H NMR spectrum, δ, ppm: 1.10 t (3H, C**H**$_3CH_2CO$, J = 7 Hz), 1.20 s (3H, CH_3), 2.35 q (2H, CH_3C**H**$_2CO$, J = 7 Hz), 2.80 s (1H, CH), 6.75–7.30 m (8H, C_6H_4, 4-ClC_6H_4). Found, %: C 63.50; H 4.07. $C_{22}H_{17}ClO_6$. Calculated, %: C 64.01; H 4.15.

1-(4-Chlorophenyl)-9c-ethyl-3,4-dioxo-9b,9c-dihydro-2,5-dioxacyclopenta[2,3]cyclopropa[1,2-*a*]-naphthalen-1-yl acetate (XIXe). Yield 64%, mp 189–191°C. IR spectrum, ν, cm^{-1}: 1750, 1805. ^1H NMR spectrum, δ, ppm: 0.80 t (3H, CH_3, J = 7 Hz), 1.65 q (2H, CH_3C**H**$_2$, J = 7 Hz), 2.10 s (3H, $OCOCH_3$), 2.95 s (1H, CH), 6.75–7.30 m (8H, C_6H_4, 4-ClC_6H_4). Found, %: C 64.10; H 3.89. $C_{22}H_{17}ClO_6$. Calculated, %: C 64.01; H 4.15.

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