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Fluorinated 2-Benzoylcyclohexane-1,3-diones and Their Vinylogous Acyl Chlorides in the Reactions with Primary and Secondary Amines

T. S. Khlebnikova, V. G. Isakova, and F. A. Lakhvich

Institute of Bioorganic Chemistry, Belarus National Academy of Sciences,
ul. Akademika Kuprevicha 5/2, Minsk, 22014 Belarus
e-mail: khlebnicova@iboch.bas-net.by

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Abstract—The reaction of 5,5-dimethyl-2-[(3-fluoro- and 4-fluoro)benzoyl]cyclohexane-1,3-diones with primary and secondary amines affords their exocyclic enamine derivatives. Under similar conditions 5,5-dimethyl-2-(2-fluorobenzoyl)]cyclohexane-1,3-dione undergoes dehydrofluorination and intramolecular cyclization to give 3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthene-1,9-dione. The reaction of vinylogous substitution of the enol derivatives of the fluorinated 5,5-dimethyl-2-benzoylcyclohexane-1,3-diones (vinylogous acyl chlorides) with amines results in the formation of the endocyclic enaminoderivatives.

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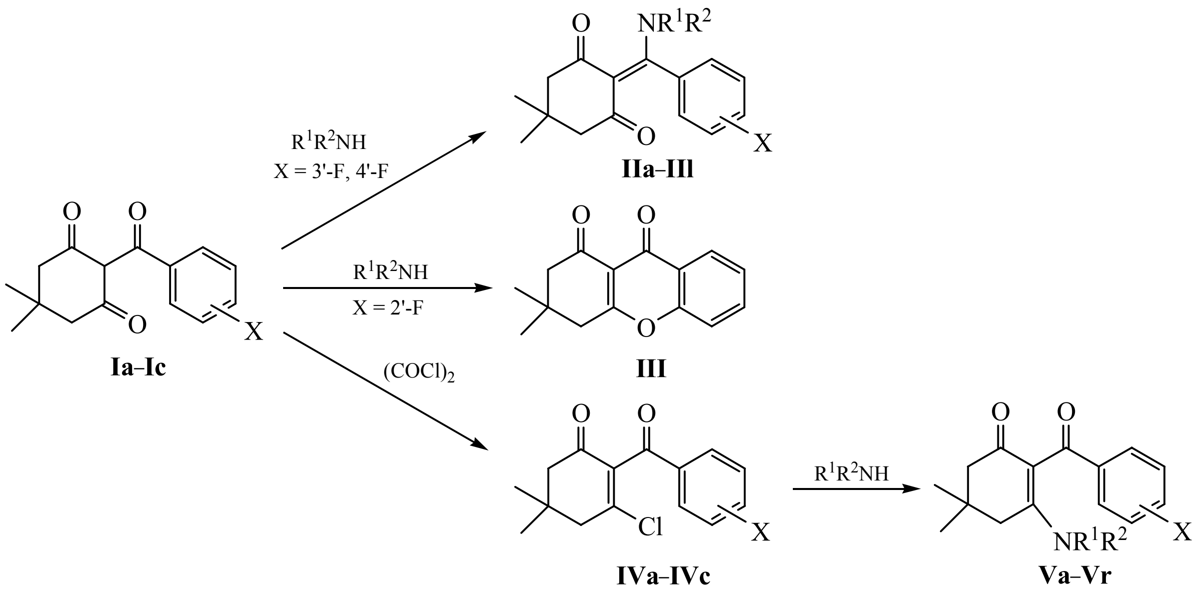
The enaminoderivatives of 2-acylcycloalkane-1,3-diones, depending on the structure of the cycle and the side chain, possess different types of biological activity, such as antibacterial, anti-inflammatory, antiaggregant, antiischemic [1–4] and other types of physiological activity; they are also known as effective and ecologically safe plant protection agents [5, 6]. Recently fluorine compounds found wide application in the production of drugs and pesticides [7–10]. The introduction of fluorine atoms in the structure of compounds substantially affects their physical and chemical properties, reactivity, and biological activity. The use of the readily available polycarbonyl “building blocks” seems to be most effective for the design of the fluorinated organic compounds.

The recently synthesized fluorinated 2-benzoylcyclohexane-1,3-diones [11] are promising polyfunctional block-synthons for preparation of various carbo- and heterocyclic structures containing fluorine atoms in the aromatic ring, including the compounds with high biological activity. The described chemical transformations of the fluorinated 2-benzoylcyclohexane-1,3-diones include their reactions as well as the reactions of methyl ethers of the enol forms with N,N-dinucleophiles with the formation of regioisomeric indazolones [12].

The goal of the present work was to synthesize new enaminoderivatives of 2-benzoylcyclohexane-1,3-diones having fluorine atoms in the molecule.

The fluorinated 2-benzoylcyclohexane-1,3-diones (**Ia**–**Ic**) existing in the enol form, as well as their nonfluorinated analogs [13, 14], are rather strong vinylogous acids, which may enter the reaction of condensation with N-nucleophiles, including primary and secondary amines. We have investigated the reactions of 5,5-dimethyl-2-benzoylcyclohexane-1,3-diones (**Ia**–**Ic**) having fluorine atoms in different positions of the aromatic ring, with primary (aniline, 4-fluoroaniline, benzylamine, 4-fluorobenzylamine) and secondary (pyrrolidine, piperidine) amines.

The reaction of condensation was performed by refluxing the equivalent amounts of the fluorinated 2-benzoylcyclohexane-1,3-diones (**Ib, Ic**) and primary (aniline, 4-fluoroaniline, benzylamine, 4-fluorobenzylamine) or secondary (pyrrolidine, piperidine) amines for 3 h in benzene. The amination at the carbonyl group of the side acyl chain took place and the corresponding exocyclic enaminoderivatives **IIa**–**IIl** were formed in 80–98% yield. It should be noted that in the case of 5,5-dimethyl-2-(2-fluorobenzoyl) cyclohexane-1,3-dione (**Ia**) we failed to obtain the corresponding enaminoderivatives, since under the



I, IV, X = 2'-F (**a**), 3'-F (**b**), 4'-F (**c**); **II, V**, R^1 = H: R^2 = C_6H_5, X = 3'-F (**a**); R^2 = C_6H_5, X = 4'-F (**b**); R^2 = 4-FC_6H_4, X = 3'-F, (**c**); R^2 = 4-FC_6H_4, X = 4'-F (**d**); R^2 = $C_6H_5CH_2$, X = 3'-F (**e**); R^2 = $C_6H_5CH_2$, X = 4'-F (**f**); R^2 = 4-$FC_6H_4CH_2$, X = 3'-F (**g**); R^2 = 4-$FC_6H_4CH_2$, X = 4'-F (**h**); R^1-R^2 = $(CH_2)_4$: X = 3'-F (**i**); X = 4'-F (**j**); R^1-R^2 = $(CH_2)_5$: X = 3'-F (**k**); X = 4'-F (**l**); **V**, R^1 = H: R^2 = C_6H_5, X = 2'-F (**m**); R^2 = 4-FC_6H_4, X = 2'-F (**n**); R^2 = $C_6H_5CH_2$, X = 2'-F (**o**); R^2 = 4-$FC_6H_4CH_2$, X = 2'-F (**p**); R^1-R^2 = $(CH_2)_4$, X = 2'-F (**q**); R^1-R^2 = $(CH_2)_5$, X = 2'-F (**r**).

reaction conditions the elimination of hydrogen fluoride and the intramolecular cyclization occurred with the formation of 3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthene-1,9-dione (**III**), identical to the one obtained earlier [15, 16] by trying to perform the O–C-isomerization of 3-benzoyloxy-2-cyclohexene-1-ones having the fluorine atom in the *ortho*-position of the benzene ring in the presence of aluminum chloride in dichloroethane or in the presence of KCN and triethylamine in methylene chloride in order to synthesize the corresponding fluorinated 2-benzoylcyclohexane-1,3-diones.

The reactions of the enol derivatives of 2-acylcyclohexane-1,3-diones (vinylogous acyl chlorides and methyl ethers) with N-nucleophiles are different from the reactions of β,β'-triketones: they do not react at the carbonyl group of the acyl moiety but rather enter the reaction of vinylogous nucleophilic substitution with the formation of the endocyclic products [13]. These enol derivatives possess an enhanced reactivity as compared with β,β'-triketones, therefore the substitution takes place at room temperature. We performed the reaction of chlorovinyldiketones **IVa–IVc** prepared by treatment of the fluorinated 2-benzoylcyclohexane-1,3-diones **Ia–Ic** with excess of oxalyl chloride at room temperature, with primary (aniline, 4-fluoroaniline, benzylamine, 4-fluorobenzylamine) and secondary (pyrrolidine, piperidine) amines. Compounds **IVa–IVc** were treated with two-fold excess of the amine for 2–3 h in anhydrous chloroform at room temperature (1 equivalent of amine bound the evolved hydrogen chloride). The reaction proceeds regioselectively with exclusive formation of the endocyclic enamino-derivatives of 2-(fluorobenzoyl)cyclohexane-1,3-diones (**Va–Vr**) in 78–90% yield.

The structure of all synthesized compounds was proved by the data of elemental analysis, IR and ^1H, ^{13}C, ^{19}F NMR spectroscopy (see the table). IR spectra of compounds **IIa–IIl** contain three characteristic absorption bands corresponding to the double bond in the region 1515–1560 cm^{-1} and conjugated carbonyl groups at 1575–1615, 1640–1670 cm^{-1}. In the ^1H NMR spectra the signal of the proton of NH group in enaminoderivatives **IIa–IId** and **IIe–IIh** linked by a strong intramolecular hydrogen bond with the carbonyl group resonates at δ 14.6–14.7 and 13.6 ppm, respectively. The signal of the carbon atom at the

IR and ^{1}H, ^{13}C, ^{19}F NMR spectra of compounds **IIa–IIl** and **Va–Vr**

Comp. no.	IR, ν, cm^{-1}	^{1}H NMR, δ, ppm (*J*, Hz)	^{13}C NMR, δ, ppm (J_{C-F}, Hz)	^{19}F NMR, δ, ppm
IIa	1670, 1615, 1560	1.11 s (6H, 2CH$_3$), 2.34 s (2H, CH$_2$), 2.58 s (2H, CH$_2$), 6.80 m (3H, H$_{arom}$), 6.89 m (1H, H$_{arom}$), 7.00 m (1H, H$_{arom}$), 7.13 m (3H, H$_{arom}$), 7.24 m (1H, H$_{arom}$), 14.71 br.s (1H, NH)	28.4, 30.4, 52.4, 53.2, 108.3, 115.1 d (*J* 23), 116.0 d (*J* 21), 123.5 d (*J* 2), 125.2, 126.8, 128.9, 130.0 d (*J* 8), 136.0 d (*J* 8), 136.8, 162.5 d (*J* 247), 167.6, 195.3, 200.5	–112.49 m
IIb	1670, 1615, 1560	1.12 s (6H, 2CH$_3$), 2.34 s (2H, CH$_2$), 2.57 s (2H, CH$_2$), 6.77 m (2H, H$_{arom}$), 6.97 m (2H, H$_{arom}$), 7.09 m (3H, H$_{arom}$), 7.15 m (2H, H$_{arom}$), 14.68 br.s (1H, NH)	28.4, 30.3, 52.4, 53.4, 108.5, 115.6 d (*J* 22), 125.3, 126.6, 128.9, 129.9 d (*J* 8), 137.0, 162.9 d (*J* 250), 168.3, 195.5, 200.5	–111.32 m
IIc	1660, 1590, 1555	1.11 s (6H, 2CH$_3$), 2.33 s (2H, CH$_2$), 2.58 s (2H, CH$_2$), 6.79 m (2H, H$_{arom}$), 6.85 m (3H, H$_{arom}$), 7.01 m (1H, H$_{arom}$), 7.26 m (1H, H$_{arom}$), 14.66 br.s (1H, NH)	28.4, 30.4, 52.4, 53.2, 108.3, 115.0 d (*J* 23), 115.9 d (*J* 23), 116.1 d (*J* 21), 123.5 d (*J* 2), 127.0 (*J* 9), 130.1 d (*J* 8), 132.9 d (*J* 2), 135.8 d (*J* 8), 160.9 d (*J* 248), 162.6 d (*J* 248), 167.9, 195.2, 200.7	–114.45 m, –112.23 m
IId	1660, 1620, 1555	1.11 s (6H, 2CH$_3$), 2.33 s (2H, CH$_2$), 2.57 s (2H, CH$_2$), 6.75 m (2H, H$_{arom}$), 6.85 m (2H, H$_{arom}$), 6.98 m (2H, H$_{arom}$), 7.07 m (2H, H$_{arom}$), 14.64 br.s (1H, NH)	28.4, 30.3, 52.4, 53.3, 108.5, 115.6 d (*J* 22), 115.9 d (*J* 23), 127.0 d (*J* 9), 129.7, 129.8 d (*J* 8), 133.0 d (*J* 3), 160.8 d (*J* 248), 162.9 d (*J* 250), 169.5, 195.4, 200.5	–114.62 m, –111.05 m
IIe	1660, 1570	1.06 s (6H, 2CH$_3$), 2.25 s (2H, CH$_2$), 2.49 s (2H, CH$_2$), 4.24 d (2H, CH$_2$, *J* 6.0), 6.85 m (1H, H$_{arom}$), 6.92 m (1H, H$_{arom}$), 7.13 m (3H, H$_{arom}$), 7.32 m (3H, H$_{arom}$), 7.42 m (1H, H$_{arom}$), 13.58 br.s (1H, NH)	28.4, 30.3, 48.3, 52.3, 52.9, 107.5, 113.5 d (*J* 23), 115.9 d (*J* 21), 121.8, 127.2, 128.1, 129.0, 130.6 d (*J* 8), 136.0, 136.4 d (*J* 8), 162.8 d (*J* 248), 170.3, 194.9, 200.1	–111.76 m
IIf	1650, 1590, 1560	1.05 s (6H, 2CH$_3$), 2.25 s (2H, CH$_2$), 2.48 s (2H, CH$_2$), 4.25 d (2H, CH$_2$, *J* 6.0), 7.11 m (6H, H$_{arom}$), 7.30 m (3H, H$_{arom}$), 13.59 br.s (1H, NH)	28.4, 30.3, 48.2, 52.3, 52.9, 107.8, 115.9 d (*J* 22), 127.1, 128.0 d (*J* 7), 128.1, 129.0, 130.3 d (*J* 3), 136.1, 162.8 d (*J* 249), 171.2, 195.2, 199.9	–111.84 m
IIg	1660, 1575, 1525	1.06 s (6H, 2CH$_3$), 2.25 s (2H, CH$_2$), 2.48 s (2H, CH$_2$), 4.21 d (2H, CH$_2$, *J* 5.9), 6.84 d (1H, H$_{arom}$, *J* 8.7), 6.90 d (1H, H$_{arom}$, *J* 7.6), 7.02 m (2H, H$_{arom}$), 7.09 m (2H, H$_{arom}$), 7.14 m (1H, H$_{arom}$), 7.42 m (1H, H$_{arom}$), 13.55 br.s (1H, NH)	28.4, 30.3, 47.6, 52.3, 52.9, 107.6, 113.5 d (*J* 23), 116.0 d (*J* 22), 121.7 (*J* 2), 128.3, 129.0 d (*J* 8), 130.6 d (*J* 8), 131.8 d (*J* 3), 136.3 d (*J* 8), 162.4 d (*J* 247), 162.9 d (*J* 248), 170.2, 194.9, 200.2	–113.96 m, –111.62 m
IIh	1655, 1585, 1560	1.06 s (6H, 2CH$_3$), 2.25 s (2H, CH$_2$), 2.48 s (2H, CH$_2$), 4.24 d (2H, CH$_2$, *J* 6.0), 7.01 m (2H, H$_{arom}$), 7.10 m (6H, H$_{arom}$), 13.56 br.s (1H, NH)	28.4, 30.3, 47.5, 52.3, 52.9, 107.9, 116.0 d (*J* 22), 128.1 d (*J* 8), 129.0 d (*J* 8), 130.2 d (*J* 4), 131.9 d (*J* 3), 162.4 d (*J* 247), 162.9 d (*J* 249), 171.2, 195.2, 200.1	–114.15 m, –111.84 m
IIi	1650, 1595, 1525	1.07 s (6H, 2CH$_3$), 2.02 quint (2H, CH$_2$, *J* 6.8), 2.08 quint (2H, CH$_2$, *J* 6.8), 2.28 s (4H, CH$_2$), 3.63 t (2H, CH$_2$, *J* 6.8), 3.80 t (2H, CH$_2$, *J* 6.8), 7.11 m (2H, H$_{arom}$), 7.16 m (1H, H$_{arom}$), 7.37 m (1H, H$_{arom}$)	24.9, 25.1, 28.5, 30.9, 52.1, 53.8, 55.6, 111.4, 115.4 d (*J* 23), 117.2 d (*J* 21), 123.9 (*J* 2), 130.0 d (*J* 8), 139.1 d (*J* 7), 162.4 d (*J* 248), 173.0, 192.9	–112.32 m
IIj	1650, 1600, 1515	1.07 s (6H, 2CH$_3$), 2.02 quint (2H, CH$_2$, *J* 6.6), 2.08 quint (2H, CH$_2$, *J* 6.6), 2.28 s (4H, CH$_2$), 3.65 t (2H, CH$_2$, *J* 6.6), 3.81 t (2H, CH$_2$, *J* 6.6), 7.09 m (2H, H$_{arom}$), 7.40 m (2H, H$_{arom}$)	25.0, 25.1, 28.5, 30.9, 52.1, 53.9, 55.3, 111.6, 115.6 d (*J* 22), 130.5 d (*J* 9), 133.3 (*J* 3), 163.6 d (*J* 252), 173.6, 192.8	–109.47 m
IIk	1650, 1595, 1535	1.08 s (6H, 2CH$_3$), 1.82 m (6H, 3CH$_2$), 2.30 s (4H, CH$_2$), 3.50 m (2H, CH$_2$), 3.64 m (2H, CH$_2$), 7.09 m (1H, H$_{arom}$), 7.17 m (2H, H$_{arom}$), 7.38 m (1H, H$_{arom}$)	23.5, 27.0, 27.5, 28.6, 30.8, 52.2, 52.9, 57.3, 111.7, 116.1 d (*J* 23), 117.9 d (*J* 21), 124.8 (*J* 1), 130.1 d (*J* 8), 138.8 d (*J* 8), 162.5 d (*J* 248), 174.9, 193.3	–112.24 m

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Comp. no.	IR, ν, cm^{-1}	^{1}H NMR, δ, ppm (*J*, Hz)	^{13}C NMR, δ, ppm ($J_{C–F}$, Hz)	^{19}F NMR, δ, ppm
IIl	1640, 1595, 1540	1.08 s (6H, $2CH_3$), 1.83 m (6H, $3CH_2$), 2.29 s (4H, CH_2), 3.53 m (2H, CH_2), 3.65 m (2H, CH_2), 7.10 m (2H, H_{arom}), 7.39 m (2H, H_{arom})	23.5, 26.9, 27.5, 28.6, 30.8, 52.1, 52.8, 57.0, 111.7, 115.8 d (*J* 22), 131.3 d (*J* 9), 132.6 (*J* 3), 164.3 d (*J* 252), 175.5, 193.2	–108.52 m
Va	1650, 1620, 1570	1.09 s (6H, $2CH_3$), 2.33 s (2H, CH_2), 2.53 s (2H, CH_2), 7.10 m (1H, H_{arom}), 7.20 m (4H, H_{arom}), 7.35 m (2H, H_{arom}), 7.46 m (2H, H_{arom}), 13.01 br.s (1H, NH)	28.2, 31.8, 41.5, 51.6, 108.2, 114.3 d (*J* 23), 116.9 d (*J* 21), 123.0 d (*J* 2), 126.0, 127.8, 129.2 d (*J* 8), 129.7, 136.7, 144.8 d (*J* 7), 162.2 d (*J* 246), 170.1, 194.3, 196.5	–113.93 m
Vb	1645, 1600, 1560	1.09 s (6H, $2CH_3$), 2.34 s (2H, CH_2), 2.53 s (2H, CH_2), 7.04 m (2H, H_{arom}), 7.20 m (2H, H_{arom}), 7.37 m (1H, H_{arom}), 7.45 m (2H, H_{arom}), 7.52 m (2H, H_{arom}), 12.90 br.s (1H, NH)	28.2, 31.8, 41.5, 51.7, 108.3, 114.7 d (*J* 22), 126.0, 127.7, 129.7, 130.0 d (*J* 9), 136.8, 138.5 d (*J* 2), 164.1 d (*J* 250), 169.7, 194.4, 196.5	–110.13 m
Vc	1660, 1580, 1520	1.08 s (6H, $2CH_3$), 2.32 s (2H, CH_2), 2.48 s (2H, CH_2), 7.09 m (1H, H_{arom}), 7.18 m (6H, H_{arom}), 7.32 m (1H, H_{arom}), 12.88 br.s (1H, NH)	28.2, 31.8, 41.4, 51.5, 108.3, 114.3 d (*J* 23), 116.7 d (*J* 23), 117.0 d (*J* 21), 123.1 d (*J* 2), 128.0 d (*J* 9), 129.3 d (*J* 8), 132.7 d (*J* 2), 144.7 d (*J* 7), 161.8 d (*J* 249), 162.3 d (*J* 246), 170.4, 194.3, 196.5	–113.91 m, –113.30 m
Vd	1645, 1610, 1580, 1520	1.09 s (6H, $2CH_3$), 2.33 s (2H, CH_2), 2.47 s (2H, CH_2), 7.04 m (2H, H_{arom}), 7.16 m (4H, H_{arom}), 7.51 m (2H, H_{arom}), 12.78 br.s (1H, NH)	28.2, 31.8, 41.4, 51.6, 108.4, 114.7 d (*J* 22), 116.7 d (*J* 23), 128.0 d (*J* 9), 130.1 d (*J* 9), 132.8 d (*J* 2), 138.3 d (*J* 3), 161.7 d (*J* 249), 164.1 d (*J* 250), 169.9, 194.3, 196.5	–113.41 m, –109.90 m
Ve	1650, 1580	1.11 s (6H, $2CH_3$), 2.27 s (2H, CH_2), 2.55 s (2H, CH_2), 4.60 d (2H, CH_2, *J* 5.9), 7.08 m (2H, H_{arom}), 7.18 m (1H, H_{arom}), 7.31 m (4H, H_{arom}), 7.40 m (2H, H_{arom}), 11.90 br.s (1H, NH)	28.4, 31.1, 40.2, 47.4, 51.0, 107.7, 114.2 d (*J* 23), 116.6 d (*J* 21), 122.9 d (*J* 1), 126.9, 128.2, 129.1, 129.2, 135.8, 145.1 d (*J* 7), 162.2 d (*J* 246), 171.6, 193.7, 196.1	–114.07 m
Vf	1630, 1600, 1575, 1505	1.12 s (6H, $2CH_3$), 2.28 s (2H, CH_2), 2.54 s (2H, CH_2), 4.59 d (2H, CH_2, *J* 5.9), 7.32 m (5H, H_{arom}), 7.43 m (4H, H_{arom}), 11.80 br.s (1H, NH)	28.5, 31.1 40.2, 47.4, 51.1, 107.7, 114.6 d (*J* 22), 126.9, 128.2, 129.2, 129.9 d (*J* 9), 135.9, 138.8 d (*J* 2), 163.9 d (*J* 250), 171.3, 193.8, 196.2	–110.56 m
Vg	1650, 1585, 1525	1.12 s (6H, $2CH_3$), 2.28 (2H, CH_2), 2.54 s (2H, CH_2), 4.57 d (2H, CH_2, *J* 5.8), 7.08 m (4H, H_{arom}), 7.17 m (1H, H_{arom}), 7.29 m (3H, H_{arom}), 11.87 br.s (1H, NH)	28.5, 31.2, 40.3, 46.7, 51.0, 107.8, 114.2 d (*J* 23), 116.2 d (*J* 22), 116.7 d (*J* 21), 122.9, 131.6 d (*J* 7), 128.8 d (*J* 8), 129.2 d (*J* 7), 145.0 d (*J* 7), 162.2 d (*J* 246), 162.5 d (*J* 248), 171.4, 193.7, 196.3	–114.04 m, –113.78 m
Vh	1630, 1600, 1570, 1515	1.12 s (6H, $2CH_3$), 2.28 s (2H, CH_2), 2.53 s (2H, CH_2), 4.56 d (2H, CH_2, *J* 5.8), 7.01 m (2H, H_{arom}), 7.09 m (2H, H_{arom}), 7.27 m (2H, H_{arom}), 7.45 m (2H, H_{arom}), 11.76 br.s (1H, NH)	28.5, 31.1, 40.3, 46.7, 51.1, 107.8, 114.6 d (*J* 22), 116.2 d (*J* 22), 128.8 d (*J* 8), 129.9 d (*J* 9), 131.7 d (*J* 3), 138.7 d (*J* 2), 162.5 d (*J* 247), 164.0 d (*J* 250), 171.1, 193.8, 196.3	–110.42 m, –113.83 m
Vi	1650, 1615, 1530	1.14 s (6H, $2CH_3$), 1.88 m (4H, $2CH_2$), 2.26 s (2H, CH_2), 2.55 s (2H, CH_2), 3.21 m (4H, $2CH_2$), 7.14 m (1H, H_{arom}), 7.35 m (1H, H_{arom}), 7.52 m (1H, H_{arom}), 7.62 m (1H, H_{arom})	25.3, 28.6, 31.5, 44.1, 50.7, 60.7, 110.6, 115.6 d (*J* 22), 118.5 d (*J* 22), 125.0, 129.6 d (*J* 8), 142.5 d (*J* 6), 162.7 d (*J* 246), 163.2, 194.7, 196.5	–108.20 m
Vj	1665, 1600, 1540	1.14 s (6H, $2CH_3$), 1.90 m (4H, $2CH_2$), 2.26 s (2H, CH_2), 2.54 s (2H, CH_2), 4.40 m (4H, $2CH_2$), 7.05 m (2H, H_{arom}), 7.86 m (2H, H_{arom})	25.2, 28.6, 29.7, 31.6, 44.1, 50.7, 110.7, 115.1 d (*J* 22), 131.8 d (*J* 9), 136.5, 163.0, 165.0 d (*J* 252), 194.6, 196.3	–108.20 m

(Contd.)

Comp. no.	IR, ν, cm^{-1}	^{1}H NMR, δ, ppm (*J*, Hz)	^{13}C NMR, δ, ppm (J_{C-F}, Hz)	^{19}F NMR, δ, ppm
Vk	1660, 1610, 1540	1.18 s (6H, 2CH$_3$), 1.60 m (6H, 3CH$_2$), 2.27 s (2H, CH$_2$), 2.47 s (2H, CH$_2$), 3.17 m (4H, CH$_2$), 7.16 m (1H, H$_{arom}$), 7.37 m (1H, H$_{arom}$), 7.50 m (1H, H$_{arom}$), 7.58 m (1H, H$_{arom}$)	23.7, 26.1, 28.8, 44.0, 50.2, 51.8, 60.7, 111.1, 115.4 d (*J* 22), 118.9 d (*J* 22), 124.8 d (*J* 1), 129.8 d (*J* 8), 141.9 d (*J* 6), 162.8 d (*J* 246), 166.8, 194.6, 196.8	–113.38 m
Vl	1655, 1605, 1540	1.18 s (6H, 2CH$_3$), 1.59 m (6H, 3CH$_2$), 2.27 s (2H, CH$_2$), 2.46 s (2H, CH$_2$), 3.17 m (4H, CH$_2$), 7.07 m (2H, H$_{arom}$), 7.84 m (2H, H$_{arom}$)	23.7, 26.2, 28.9, 32.4, 44.0, 50.2, 51.7, 111.4, 115.3 d (*J* 22), 131.6 d (*J* 9), 135.9, 164.2 d (*J* 253), 166.5, 194.6, 196.6	–107.53 m
Vm	1645, 1580	1.06 s (6H, 2CH$_3$), 2.31 s (2H, CH$_2$), 2.52 s (2H, CH$_2$), 7.00 m (1H, H$_{arom}$), 7.21 m (3H, H$_{arom}$), 7.38 m (3H, H$_{arom}$), 7.47 m (2H, H$_{arom}$), 13.57 br.s (1H, NH)	28.1, 31.5, 41.5, 51.4, 109.6, 115.0 d (*J* 22), 124.1 d (*J* 2), 126.1, 127.8, 128.6 d (*J* 3), 129.7, 130.8 d (*J* 8), 131.9 d (*J* 16), 136.8, 158.7 d (*J* 247), 170.0, 192.4, 194.3	–115.91 m
Vn	1645, 1610, 1570, 1510	1.06 s (6H, 2CH$_3$), 2.31 s (2H, CH$_2$), 2.46 s (2H, CH$_2$), 7.00 m (1H, H$_{arom}$), 7.18 m (5H, H$_{arom}$), 7.38 m (2H, H$_{arom}$), 13.45 br.s (1H, NH)	28.1, 31.5, 41.5, 51.3, 109.8, 115.0 d (*J* 22), 116.7 d (*J* 23), 124.1 d (*J* 2), 128.0 d (*J* 8), 128.6 d (*J* 3), 130.9 d (*J* 8), 131.7 d (*J* 16), 132.7 d (*J* 2), 158.7 d (*J* 247), 161.8 d (*J* 249), 170.2, 192.5, 194.3	–115.82 m, –113.31 m
Vo	1640, 1575	1.09 s (6H, 2CH$_3$), 2.27 s (2H, CH$_2$), 2.54 s (2H, CH$_2$), 4.62 d (2H, CH$_2$, *J* 5.8), 6.98 m (1H, H$_{arom}$), 7.16 m (1H, H$_{arom}$), 7.34 m (5H, H$_{arom}$), 7.41 m (2H, H$_{arom}$), 12.42 br.s (1H, NH)	28.3, 31.0, 40.3, 47.4, 50.8, 109.2, 115.0 d (*J* 22), 124.0, 127.0, 128.2, 128.5 d (*J* 3), 129.2, 130.6 d (*J* 8), 132.1 d (*J* 16), 135.8, 158.6 d (*J* 247), 171.5, 192.0, 193.9	–116.19 m
Vp	1640, 1580, 1520	1.09 s (6H, 2CH$_3$), 2.27 s (2H, CH$_2$), 2.53 s (2H, CH$_2$), 4.59 d (2H, CH$_2$, *J* 5.8), 6.97 m (1H, H$_{arom}$), 7.10 m (2H, H$_{arom}$), 7.16 m (1H, H$_{arom.}$), 7.30 m (2H, H$_{arom.}$), 7.34 m (2H, H$_{arom.}$), 12.39 br.s (1H, NH)	28.4, 31.0, 40.3, 46.7, 50.9, 109.3, 115.0 d (*J* 22), 116.2 d (*J* 22), 124.0 d (*J* 2), 128.5 d (*J* 3), 128.8 d (*J* 8), 130.7 d (*J* 8), 131.6 d (*J* 3), 132.0 d (*J* 16), 158.6 d (*J* 247), 162.5 d (*J* 247), 171.3, 192.1, 193.9	–113.86 m, –116.18 m
Vq	1660, 1615, 1525	1.10 s (6H, 2CH$_3$), 1.95 s (4H, 2CH$_2$), 2.23 s (2H, CH$_2$), 2.56 s (2H, CH$_2$), 3.30 m (4H, 2CH$_2$), 6.98 m (1H, H$_{arom}$), 7.19 m (1H, H$_{arom}$), 7.38 m (1H, H$_{arom}$), 7.69 m (1H, H$_{arom}$)	25.3, 28.5, 29.7, 30.9, 44.5, 51.0, 113.6, 115.5 d (*J* 23), 124.1 d (*J* 2), 130.1, 130.6 d (*J* 12), 132.2 d (*J* 9), 160.5 d (*J* 251), 164.2, 190.5, 194.3	–114.81 m
Vr	1640, 1605, 1510	1.14 s (6H, 2CH$_3$), 1.68 m (6H, 3CH$_2$), 2.24 s (2H, CH$_2$), 2.47 s (2H, CH$_2$), 3.26 m (4H, CH$_2$), 6.99 m (1H, H$_{arom}$), 7.20 m (1H, H$_{arom}$), 7.41 m (1H, H$_{arom}$), 7.67 m (1H, H$_{arom}$)	23.7, 26.4, 28.8, 32.1, 44.4, 50.4, 52.5, 113.7, 115.5 d (*J* 23), 124.2 d (*J* 2), 130.1, 130.2 d (*J* 13), 132.4 d (*J* 9), 160.5 d (*J* 251), 168.2, 191.6, 194.5	–115.49 m

fluorine atom in the ^{13}C NMR spectrum of exocyclic enaminodiketones **IIa–IIl** appears at δ 162.4–162.9 ppm ($^1J_{C-F}$ 247–250 Hz).

The IR spectra of endocyclic enaminodiketones **Va–Vr** also contain three characteristic absorption bands at 1505–1570, 1570–1620, and 1630–1665 cm^{-1}, corresponding to the double bond, conjugated carbonyl groups of the side chain, and the cycle. The signals of the protons of the NH group linked by the intramolecular hydrogen bond with the carbonyl group, in the ^{1}H NMR spectra of enaminodiketones **Va–Vd, Vm, Vn** and **Ve–Vh, Vo, Vp** appear upfield from the signals of the regioisomers **IIa–IIl**, at δ 12.8–13.6 and 11.8–12.4 ppm, respectively. It should be noted that the signal of the carbon atom at the fluorine atom in the ^{13}C NMR spectrum of compounds **Va–Vr** is characterized by rather large range of chemical shifts and the spin-spin coupling constants: δ 158.6–165.0 ppm ($^1J_{C-F}$ 246–253 Hz).

EXPERIMENTAL

NMR spectra were registered on a Bruker Avance-500 spectrometer in $CDCl_3$ using TMS as an internal reference for ^{1}H (500 MHz) and ^{13}C (125 MHz) and CCl_3F for ^{19}F (470 MHz). IR spectra were recorded on a UR-20 instrument in KBr. Melting points were determined on a Boetius apparatus. IR and ^{1}H, ^{13}C, ^{19}F NMR spectra of compounds **IIa–IIl** and **Va–Vr** are given in the table. Fluorinated 2-benzoylcyclohexane-1,3-diones **Ia–Ic** were prepared according to [11]. The reactions were followed and the purity of the products controlled by thin layer chromatography on Silufol UV–254 plates with ether as eluent. Preparative TLC was performed on silica 60 HF_{254} plates (Aldrich).

Condensation of 2-(fluorobenzoyl)cyclohexane-1,3-diones Ia–Ic with amines. To the solution of 1 mmol of β,β'-triketone **Ia–Ic** in anhydrous benzene (40 ml) 1 mmol of amine was added. The reaction mixture was refluxed with separation of water for 3 h. After removal of benzene on a rotary evaporator, from the starting compounds **Ib, Ic**, enaminodiketones **IIa–IIl** were isolated by preparative TLC on silica (ether–hexane 2:1) as colorless crystals, and from compound **Ia** xanthene **III** was obtained. IR, ^{1}H, ^{13}C, ^{19}F NMR spectra of compounds **IIa–IIl** are given in the table.

5,5-Dimethyl-2-[phenylamino(3-fluorophenyl)-methylene]cyclohexane-1,3-dione (IIa). Yield 90%, mp 112–115°C. Found, %: C 74.87; H 6.03; N 4.21. $C_{21}H_{20}FNO_2$. Calculated, %: C 74.76; H 5.97; N 4.15.

5,5-Dimethyl-2-[phenylamino(4-fluorophenyl)-methylene]cyclohexane-1,3-dione (IIb). Yield 85%, mp 151–154°C. Found, %: C 74.82; H 6.02; N 4.22. $C_{21}H_{20}FNO_2$. Calculated, %: C 74.76; H 5.97; N 4.15.

5,5-Dimethyl-2-[(3-fluorophenyl)(4-fluorophenyl-amino)methylene]cyclohexane-1,3-dione (IIc). Yield 90%, mp 99–103°C. Found, %: C 70.90; H 5.36; N 3.90. $C_{21}H_{19}F_2NO_2$. Calculated, %: C 70.97; H 5.39; N 3.94.

5,5-Dimethyl-2-[(4-fluorophenyl)(4-fluorophenyl-amino)methylene]cyclohexane-1,3-dione (IId). Yield 87%, mp 150–153°C. Found, %: C 70.89; H 5.42; N 3.97. $C_{21}H_{19}F_2NO_2$. Calculated, %: C 70.97; H 5.39; N 3.94.

2-[Benzylamino(3-fluorophenyl)methylene]-5,5-dimethylcyclohexane-1,3-dione (IIe). Yield 97%, mp 79–82°C. Found, %: C 75.12; H 6.35; N 4.01. $C_{22}H_{22}FNO_2$. Calculated, %: C 75.19; H 6.31; N 3.99.

2-[Benzylamino(4-fluorophenyl)methylene]-5,5-dimethylcyclohexane-1,3-dione (IIe). Yield 90%, mp 155–158°C. Found, %: C 75.09; H 6.34; N 3.92. $C_{22}H_{22}FNO_2$. Calculated, %: C 75.19; H 6.31; N 3.99.

5,5-Dimethyl-2-[(4-fluorobenzylamino)(3-fluorophenyl)methylene]cyclohexane-1,3-dione (IIg). Yield 89%, mp 134–137°C. Found, %: C 71.61; H 5.77; N 3.85. $C_{22}H_{21}F_2NO_2$. Calculated, %: C 71.53; H 5.73; N 3.79.

5,5-Dimethyl-2-[(4-fluorobenzylamino)(4-fluorophenyl)methylene]cyclohexane-1,3-dione (IIh). Yield 82%, mp 117–120°C. Found, %: C 71.48; H 5.70; N 3.74. $C_{22}H_{21}F_2NO_2$. Calculated, %: C 71.53; H 5.73; N 3.79.

5,5-Dimethyl-2-[(pyrrolidin-1-yl)(3-fluorophenyl)-methylene]cyclohexane-1,3-dione (IIi). Yield 98%, mp 139–143°C. Found, %: C 72.43; H 7.06; N 4.48. $C_{19}H_{22}FNO_2$. Calculated, %: C 72.36; H 7.03; N 4.44.

5,5-Dimethyl-2-[(pyrrolidin-1-yl)(4-fluorophenyl)-methylene]cyclohexane-1,3-dione (IIj). Yield 95%, mp 160–163°C. Found, %: C 72.41; H 7.07; N 4.49. $C_{19}H_{22}FNO_2$. Calculated, %: C 72.36; H 7.03; N 4.44.

5,5-Dimethyl-2-[(piperidin-1-yl)(3-fluorophenyl)-methylene]cyclohexane-1,3-dione (IIk). Yield 98%, mp 165–167°C. Found, %: C 72.84; H 7.30; N 4.21. $C_{20}H_{24}FNO_2$. Calculated, %: C 72.92; H 7.34; N 4.25.

5,5-Dimethyl-2-[(piperidin-1-yl)(4-fluorophenyl)-methylene]cyclohexane-1,3-dione (IIl). Yield 80%, mp 176–179°C. Found, %: C 72.99; H 7.38; N 4.30. $C_{20}H_{24}FNO_2$. Calculated, %: C 72.92; H 7.34; N 4.25.

3,3-Dimethyl-2,3,4,9-tetrahydro-1*H*-xanthene-1,9-dione (III). Yield 90%, mp 128–130°C. IR spectrum, ν, cm^{-1}: 1710, 1620. ^{1}H NMR spectrum, δ, ppm: 1.18 s (6H, $2CH_3$), 2.48 s (2H, CH_2), 2.88 s (2H, CH_2), 7.41 m (2H, H_{arom}), 7.67 m (1H, H_{arom}), 8.24 m (1H, H_{arom}). ^{13}C NMR spectrum, δ, ppm: 28.2, 31.8, 43.1, 52.4, 115.9, 117.7, 125.1, 125.9, 126.8, 133.9, 154.9, 173.6, 176.7, 194.0. Found, %: C 74.43; H 5.87. $C_{15}H_{14}O_3$. Calculated, %: C 74.36; H 5.82.

Synthesis of chlorovinyldiketones. To 1 mmol of 2-(fluorobenzoyl)cyclohexane-1,3-dione **Ia–Ic** 10 mmol of oxalyl chloride was added. The reaction mixture was kept for 5 h at room temperature, excess oxalyl chloride was removed under a reduced pressure, the residue dissolved in 15 ml of chloroform, washed with saturated solution of $NaHCO_3$ (2×5 ml), water (2×5 ml), dried over magnesium sulfate. After removal of chloroform on a rotary evaporator the vinylogous acyl chlorides **IVa–IVc** were obtained as colorless crystalline compounds.

5,5-Dimethyl-2-(2-fluorobenzoyl)-3-chloro-2-cyclohexene-1-one (IVa). Yield 95%, mp 53–57°C. IR spectrum, ν, cm^{-1}: 1690, 1635, 1620. ^1H NMR spectrum, δ, ppm: 1.18 s (6H, $2CH_3$), 2.41 s (2H, CH_2), 2.70 s (2H, CH_2), 7.07 m (1H, H_{arom}), 7.25 m (1H, H_{arom}), 7.55 m (1H, H_{arom}), 7.98 m (1H, H_{arom}). ^{13}C NMR spectrum, δ, ppm: 28.1, 33.5, 48.1, 50.6, 116.6 d (*J* 23 Hz), 124.7 d (*J* 3 Hz), 130.9, 135.8 d (*J* 9 Hz), 139.3, 151.6 d (*J* 3 Hz), 162.3 d (*J* 257 Hz), 188.7, 194.4. ^{19}F NMR, δ, ppm: –111.93 m (1F).

5,5-Dimethyl-2-(3-fluorobenzoyl)-3-chloro-2-cyclohexene-1-one (IVb). Yield 98%, mp 67–70°C. IR spectrum, ν, cm^{-1}: 1700, 1635, 1595. ^1H NMR spectrum, δ, ppm: 1.23 s (6H, $2CH_3$), 2.45 s (2H, CH_2), 2.76 s (2H, CH_2), 7.30 m (1H, H_{arom}), 7.46 m (1H, H_{arom}), 7.54 m (1H, H_{arom}), 7.60 m (1H, H_{arom}). ^{13}C NMR, δ, ppm: 28.3, 33.8, 48.8, 50.6, 115.6 d (*J* 23 Hz), 121.1 d (*J* 22 Hz), 125.0, 130.6 d (*J* 8 Hz), 137.1, 137.8 d (*J* 6 Hz), 153.4, 163.0 d (*J* 249 Hz), 191.5, 194.5. ^{19}F NMR, δ, ppm: –111.82 m.

5,5-Dimethyl-2-(4-fluorobenzoyl)-3-chloro-2-cyclohexen-1-one (IVc). Yield 97%, mp 86–89°C. IR spectrum, ν, cm^{-1}: 1690, 1630, 1605. ^1H NMR spectrum, δ, ppm: 1.22 s (6H, $2CH_3$), 2.44 s (2H, CH_2), 2.76 s (2H, CH_2), 7.15 m (2H, H_{arom}), 7.87 m (2H, H_{arom}). ^{13}C NMR spectrum, δ, ppm: 28.3, 33.8, 48.17, 50.6, 116.1 d (*J* 22 Hz), 131.9 d (*J* 10 Hz), 132.2, 137.2, 153.1, 166.3 d (*J* 256 Hz), 191.1, 194.6. ^{19}F NMR, δ, ppm: –103.48 m.

Reaction of vinylogous substitution in chlorovinyldiketones (IVa-IVc) with amines. To the solution of 1 mmol of chlorovinyldiketone **IIIa–IIIc** in 15 ml of chloroform 2 mmol of amine was added. The reaction mixture was stirred for 2–3 h (TLC control) at room temperature, washed with water (2×5 ml), dried over magnesium sulfate, solvent removed under reduced pressure, the residue was crystallized from the mixture ether-hexane. Endocyclic enaminodiketones **Va–Vr** were obtained as colorless crystals in 78–90% yield. IR, ^1H, ^{13}C, ^{19}F NMR spectra of compounds **Va–Vr** are given in the table.

5,5-Dimethyl-3-(phenylamino)-2-(3-fluorobenzoyl)-2-cyclohexen-1-one (Va). Yield 79%, mp 106–109°C. Found, %: C 74.83; H 6.01; N 4.20. $C_{21}H_{20}NO_2F$. Calculated, %: C 74.76; H 5.97; N 4.15.

5,5-Dimethyl-3-(phenylamino)-2-(4-fluorobenzoyl)-2-cyclohexen-1-one (Vb). Yield 78%, mp 171–174°C. Found, %: C 74.70; H 6.94; N 4.11. $C_{21}H_{20}NO_2F$. Calculated, %: C 74.76; H 5.97; N 4.15.

5,5-Dimethyl-2-(3-fluorobenzoyl)-3-(4-fluorophenylamino)-2-cyclohexen-1-one (Vc). Yield 77%, mp 106–109°C. Found, %: C 71.05; H 5.43; N 3.99. $C_{21}H_{19}NO_2F_2$. Calculated, %: C 70.97; H 5.39; N 3.94.

5,5-Dimethyl-2-(4-fluorobenzoyl)-3-(4-fluorophenylamino)-2-cyclohexen-1-one (Vd). Yield 73%, mp 136–139°C. Found, %: C 70.90; H 5.34; N 3.91. $C_{21}H_{19}NO_2F_2$. Calculated, %: C 70.97; H 5.39; N 3.94.

3-(Benzylamino)-5,5-dimethyl-2-(3-fluorobenzoyl)-2-cyclohexen-1-one (Ve). Yield 65%, mp 162–164°C. Found, %: C 75.11; H 6.27; N 3.96. $C_{22}H_{22}NO_2F$. Calculated, %: C 75.19; H 6.31; N 3.99.

3-(Benzylamino)-5,5-dimethyl-2-(4-fluorobenzoyl)-2-cyclohexen-1-one (Vf). Yield 67%, mp 155–158°C. Found, %: C 75.10; H 6.26; N 3.94. $C_{22}H_{22}NO_2F$. Calculated, %: C 75.19; H 6.31; N 3.99.

5,5-Dimethyl-3-(4-fluorobenzylamino)-2-(3-fluorobenzoyl)-2-cyclohexen-1-one (Vg). Yield 75%, mp 188–191°C. Found, %: C 71.61; H 5.77; N 3.82. $C_{22}H_{21}NO_2F_2$. Calculated, %: C 71.53; H 5.73; N 3.79.

5,5-Dimethyl-3-(4-fluorobenzylamino)-2-(4-fluorobenzoyl)-2-cyclohexen-1-one (Vh). Yield 75%, mp 117–120°C. Found, %: C 71.62; H 5.78; N 3.84. $C_{22}H_{21}NO_2F_2$. Calculated, %: C 71.53; H 5.73; N 3.79.

5,5-Dimethyl-3-(pyrrolidin-1-yl)-2-(3-fluorobenzoyl)-2-cyclohexen-1-one (Vi). Yield 90%, mp 184–187°C. Found, %: C 72.29; H 7.00; N 4.41. $C_{19}H_{22}NO_2F$. Calculated, %: C 72.36; H 7.03; N 4.44.

5,5-Dimethyl-3-(pyrrolidin-1-yl)-2-(4-fluorobenzoyl)-2-cyclohexen-1-one (Vj). Yield 88%, mp 175–177°C. Found, %: C 72.43; H 7.07; N 4.49. $C_{19}H_{22}NO_2F$. Calculated, %: C 72.36; H 7.03; N 4.44.

5,5-Dimethyl-3-(piperidin-1-yl)-2-(3-fluorobenzoyl)-2-cyclohexen-1-one (Vk). Yield 88%, mp 155–158°C. Found, %: C 72.84; H 7.30; N 4.21. $C_{20}H_{24}NO_2F$. Calculated, %: C 72.92; H 7.34; N 4.25.

5,5-Dimethyl-3-(piperidin-1-yl)-2-(4-fluorobenzoyl)-2-cyclohexen-1-one (Vl). Yield 87%, mp 139–141°C.

Found, %: C 72.99; H 7.38; N 4.30. $C_{20}H_{24}NO_2F$. Calculated, %: C 72.92; H 7.34; N 4.25.

5,5-Dimethyl-3-(phenylamino)-2-(2-fluorobenzoyl)-2-cyclohexen-1-one (Vm). Yield 75%, mp 119–122°C. Found, %: C 74.68; H 5.93; N 4.10. $C_{21}H_{20}NO_2F$. Calculated, %: C 74.76; H 5.97; N 4.15.

5,5-Dimethyl-2-(2-fluorobenzoyl)-3-(4-fluorophenylamino)-2-cyclohexen-1-one (Vn). Yield 73%, mp 127–129°C. Found, %: C 70.88; H 5.36; N 3.91. $C_{21}H_{19}NO_2F_2$. Calculated, %: C 70.97; H 5.39; N 3.94.

5,5-Dimethyl-3-(benzylamino)-2-(2-fluorobenzoyl)-2-cyclohexen-1-one (Vo). Yield 74%, mp 148–151°C. Found, %: C 75.28; H 6.36; N 4.04. $C_{22}H_{22}NO_2F$. Calculated, %: C 75.19; H 6.31; N 3.99.

5,5-Dimethyl-2-(2-fluorobenzoyl)-3-(4-fluorobenzylamino)-2-cyclohexen-1-one (Vp). Yield 72%, mp 140–143°C. Found, %: C 71.44; H 5.70; N 3.76. $C_{22}H_{21}NO_2F_2$. Calculated, %: C 71.53; H 5.73; N 3.79.

5,5-Dimethyl-3-(pyrrolidin-1-yl)-2-(2-fluorobenzoyl)-2-cyclohexen-1-one (Vq). Yield 70%, mp 156–157°C. Found, %: C 72.30; H 6.99; N 4.40. $C_{19}H_{22}NO_2F$. Calculated, %: C 72.36; H 7.03; N 4.44.

5,5-Dimethyl-3-(piperidin-1-yl)-2-(2-fluorobenzoyl)-2-cyclohexen-1-one (Vr). Yield 73%, mp 123–125°C. Found, %: C 73.01; H 7.39; N 4.31. $C_{20}H_{24}NO_2F$. Calculated, %: C 72.92; H 7.34; N 4.25.

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