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Preparation of Fluorine-containing Exo- and Endocyclic Enamine Derivatives of 2-Acylcyclopentane-1,3-diones

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Abstract—The interaction of aromatic amines (4-fluorinebenzylamine, 3-trifluoromethylbenzylamine, 4-fluoroaniline, or 3,4-difluoroaniline) with either 2-acylcyclopentane-1,3-diones (fluorine-substituted or fluorine-free) or their enol derivatives (chlorovinyldiketones) has led to fluorine-containing exo- or endocyclic enamine derivatives of 2-acylcyclopentane-1,3-diones.

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Organofluorine compounds are attractive due to numerous applications in pharmaceutics, agricultural chemistry, and material science [1−5]. The recently emerging trend is incorporation of fluorine atoms into natural as well as synthetic biologically active compounds in order to enhance their lipophilicity and biological accessibility [6, 7]. Triacylmethane fragment is found in many natural compounds produced by various plants, microbes, insects, and in their synthetic derivatives; such compounds are used as drugs and modern plant protectants [8−11]. The presence of β-tricarbonyl moiety leads to high reactivity of 2-acylcyclopentane-1,3-diones (both natural and synthetic) and thus opens vast possibilities towards their chemical transformation into physiologically active compounds of various classes [12−14]. Enamine derivatives of 2-acylcyclopentane-1,3-diones, depending on the cycle and the side chain structure, reveal antibacterial, herbicide, antiinflammatory, antiaggregatory, anti-ischemic, and gastroprotective activity [15−19].

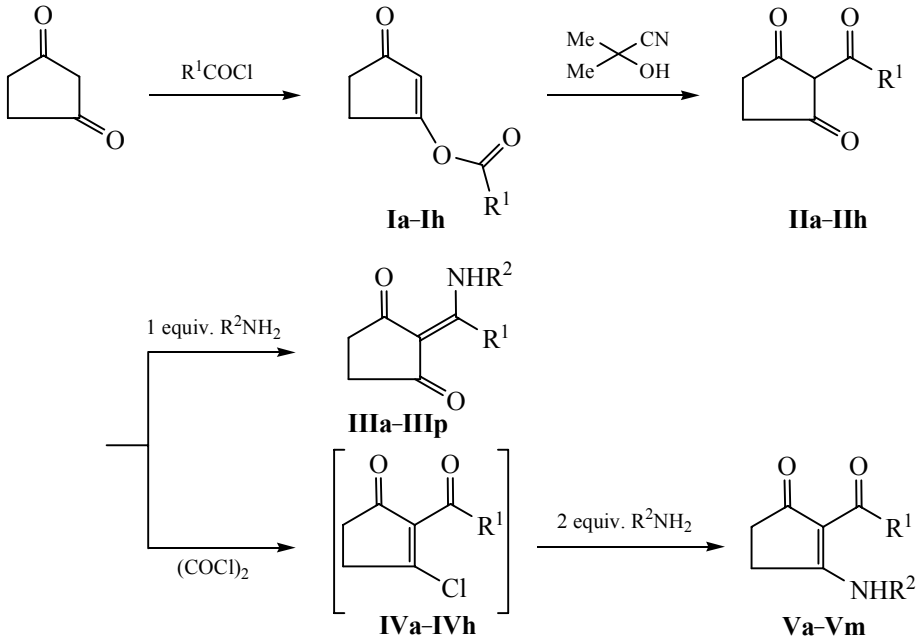
This work aimed at preparation of new fluorine-containing exo- and endocyclic enamine derivatives of 2-acylcyclopentane-1,3-diones.

The most common and efficient method of preparation of fluorine-free cyclopentane-type β-triketones is O–C-isomerization of cyclopentane-1,3-dione enol acylates under the action of anhydrous aluminum chloride [20] or acetone cyanohydrin [21]; β-triketones containing perfluoroalkanoyl groups can be prepared by acylation of cyclopentane-1,3-dione with perfluorocarboxylic acids in the presence of imidazole in chloroform [22].

O–C-Isomerization of enol acylates **Ia**–**Ih** in the presence of triethylamine with acetone cyanohydrin as catalyst gave the corresponding 2-acylcyclopentane-1,3-diones **IIa**–**IIh** containing various acyl side groups (acetyl, propanoyl, cyclopropanoyl, furanoyl, benzoyl, fluorobenzoyl, or fluorophenylacetyl) in 61–89% yields (Scheme 1). With anhydrous aluminum chloride as catalyst the target products were obtained in a lower yield due to sensitivity of the catalyst to moisture and the necessity to work up the products in strongly acid medium; in some cases the mixture of products was obtained inseparable by chromatography. Enol acylates **Ia**–**Ih** were prepared following a known procedure [20], via O-acylation of cyclopentane-1,3-dione with the corresponding acyl chlorides in chloroform in the presence of pyridine.

Cyclopentane-type β-triketones existing in the enol form could participate in various chemical transformations involving different active sites of the molecule, including exo- and endocyclic carbonyls. The interaction of fluorinated 2-acylcyclopentane-1,3-diones (as well as their fluorine-free analogs) with fluorine-substituted compounds led to the fluorine-

Scheme 1.



I, **II**, **IV**, R^1 = Me (**a**), Et (**b**), cyclopropyl (**c**), furan-2-yl (**d**), Ph (e), 2-FC_6H_4 (**f**), 3-FC_6H_4 (**g**); 4-$FC_6H_4CH_2$ (**h**); **III**, R^1 = Me: R^2 = 4-FC_6H_4 (**a**), 4-$FC_6H_4CH_2$ (**b**); R^1 = Et: R^2 = 4-FC_6H_4 (**c**), 4-$FC_6H_4CH_2$ (**d**); R^1 = cyclopropyl: R^2 = 4-FC_6H_4 (**e**), 4-$FC_6H_4CH_2$ (**f**); R^1 = furan-2-yl: R^2 = 4-FC_6H_4 (**g**), 4-$FC_6H_4CH_2$ (**h**); R^1 = Ph: R^2 = 4-FC_6H_4 (**i**), 4-$FC_6H_4CH_2$ (**j**); R^1 = 2-FC_6H_4, R^2 = 4-$FC_6H_4CH_2$ (**k**); R^1 = 3-FC_6H_4: R^2 = 4-FC_6H_4 (**l**), 4-$FC_6H_4CH_2$ (**m**); R^1 = 4-$FC_6H_4CH_2$: R^2 = 4-FC_6H_4 (**n**), 4-$FC_6H_4CH_2$ (**o**), 3-$CF_3C_6H_4CH_2$ (**p**); **V**, R^1 = Me, R^2 = 4-FC_6H_4 (**a**); R^1 = Et, R^2 = 4-FC_6H_4 (**b**); R^1 = cyclopropyl: R^2 = 4-FC_6H_4 (**c**), 4-$FC_6H_4CH_2$ (**d**); R^1 = furan-2-yl: R^2 = 4-FC_6H_4 (**e**), 4-$FC_6H_4CH_2$ (**f**); R^1 = Ph: R^2 = 4-FC_6H_4 (**g**), 4-$FC_6H_4CH_2$ (**h**); R^1 = 3-FC_6H_4, R^2 = 4-$FC_6H_4CH_2$ (**i**); R^1 = 4-$FC_6H_4CH_2$: R^2 = 4-FC_6H_4 (**j**), 4-$FC_6H_4CH_2$ (**k**), 3,4-$F_2C_6H_3$ (**l**), 3-$CF_3C_6H_4CH_2$ (**m**).

containing products, potentially bioactive agents. In view of that, in this work the 2-acylcyclopentane-1,3-diones **IIa**–**IIh** were introduced into the reactions with primary amines fluorinated at their aromatic substituents. In particular, exocyclic enaminodiketones **IIIa**–**IIIp** were prepared by condensation of triketones **IIa**–**IIh** with fluoroaromatic amines (4-fluoroaniline, 3,4-difluoroaniline, 4-fluorobenzylamine, or 3-trifluoromethylbenzylamine) upon boiling the equimolar amounts of the reagents in benzene for 4 h (4-fluorobenzylamine or 3-trifluoromethyl-benzylamine) or for 30 h (4-fluoroaniline or 3,4-difluoroaniline). The reactions proceeded with high regioselectivity at carbonyl of the side acyl chain to give the corresponding enamine derivatives **IIIa**–**IIIp** with yields of 50–83%. It is known that, in contrast to cyclic β-triketones, their enol derivatives (chlorovinyldiketones and enol esters) react with amines via vinyl substitution to give the endocyclic enaminodiketones [12]. Therefore, in order to change the site of the nucleophilic attack, cyclopentane-type triketones **IIa**–**IIh** were converted into chlorovinyldiketones **IVa**–**IVh** by treatment with oxalyl chloride. Being unstable, the chlorovinyldiketones were introduced without isolation into the reaction with double amount of the above-listed aromatic amines. The amination was performed at room temperature in chloroform for 2 h, the target endocyclic enamine derivatives **Va**–**Vm** were isolated by column chromatography in yields of 54–78%. Parent chlorovinyldiketones **IVb**–**IVh** were prepared by treating the corresponding triketones with 10-fold excess of oxalyl chloride at room temperature during 10–30 min; compound **IVa** was obtained by refluxing triketone **IIa** in anhydrous chloroform with 5-fold excess of oxalyl chloride during 2.5 h followed by removal of the excess of oxalyl chloride and chloroform.

Structures of the prepared products were confirmed by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectroscopy (see table). IR spectra of compounds **IIIa**–**IIIp** contained three characteristic absorption bands assigned to the double bond (1560–1600 cm^{-1}) and to two conjugated endocyclic carbonyl bonds (1610–1640 and 1660–1690 cm^{-1}). In the ^{1}H

IR, ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of compounds **IIIa**–**IIIp** and **Va**–**Vm**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)	^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz)	^{19}F NMR spectrum, δ_F, ppm
IIIa	1685, 1630, 1610, 1580	2.52–2.55 m (2H, $CH_{2cyclopent}$), 2.53 m (3H, CH_3), 2.59–2.62 m (2H, $CH_{2cyclopent}$), 7.16–7.18 m (4H, H_{arom}), 13.31 br.s (1H, NH)	16.0, 32.9, 34.5, 107.5, 116.7 d (*J* 23), 127.5 d (*J* 9), 131.6 (*J* 2), 162.0 d (*J* 249), 169.6, 202.8, 206.6	−112.7
IIIb	1675, 1620, 1605, 1580	2.46–2.53 m (4H, $2CH_{2cyclopent}$), 2.62 s (3H, CH_3), 4.59 d (2H, CH_2, *J* 6.0), 7.07–7.10 m (2H, H_{arom}), 7.23–7.26 m (2H, H_{arom}), 12.20 br.s (1H, NH)	14.3, 32.7, 34.2, 46.1, 107.0, 116.3 d (*J* 22), 128.9 d (*J* 8), 130.8 d (*J* 2) 162.6 d (*J* 248), 170.8, 202.8, 206.5	−113.6
IIIc	1680, 1620, 1605, 1570	1.13 t (3H, CH_3, *J* 7.4), 2.47–2.51 m (2H, $CH_{2cyclopent}$), 2.56–2.58 m (2H, $CH_{2cyclopent}$), 2.85 q (2H, CH_2, *J* 7.4), 7.13–7.18 m (4H, H_{arom}), 13.26 br.s (1H, NH)	12.5, 21.5, 33.0, 34.2, 106.2, 116.7 d (*J* 23), 127.8 d (*J* 8), 131.5 d (*J* 2), 162.1 d (*J* 249), 175.2, 201.9, 207.3	−112.6
IIId	1670, 1610, 1595, 1570	1.20 t (3H, CH_3, *J* 7.6), 2.46–2.48 m (2H, $CH_{2cyclopent}$), 2.51–2.54 m (2H, $CH_{2cyclopent}$), 3.07 q (2H, CH_2, *J* 7.6), 4.62 d (CH_2, CH_2, *J* 6.1), 7.07–7.10 m (2H, H_{arom}), 7.25–7.28 m (2H, H_{arom}), 12.19 br.s (1H, NH)	11.6, 20.7, 32.8, 34.1, 45.6, 105.8, 116.3 d (*J* 22), 129.0 d (*J* 8), 131.1 d (*J* 2), 162.7 d (*J* 247), 175.4, 201.9, 207.1	−113.6
IIIe	1660, 1605, 1575	0.55–0.58 m (2H, $CH_{2cycloprop}$), 1.07–1.11 m (2H, $CH_{2cycloprop}$), 2.25–2.31 m (1H, $CH_{cycloprop}$), 2.56 s (4H, $2CH_{2cyclopent}$), 7.11–7.14 m (2H, H_{arom}), 7.21–7.24 m (2H, H_{arom}), 13.63 br.s (1H, NH)	11.2, 12.9, 33.6, 109.1, 116.3 d (*J* 23), 126.6 d (*J* 8), 132.9 d (*J* 2), 151.5 d (*J* 248), 171.7, 201.3	−113.6
IIIf	1680, 1605, 1575	0.88–0.91 m (2H, $CH_{2cycloprop}$), 1.26–1.30 m (2H, $CH_{2cycloprop}$), 1.91–1.97 m (1H, $CH_{cycloprop}$), 2.49 s (4H, $2CH_{2cyclopent}$), 4.79 d (2H, CH_2, *J* 6.0), 7.06–7.10 m (2H, H_{arom}), 7.25–7.28 m (2H, H_{arom}), 12.41 br.s (1H, NH)	9.3, 11.2, 33.5, 47.5, 107.9, 116.2 d (*J* 22), 128.9 d (*J* 8), 131.4 d (*J* 3), 162.5 d (*J* 247), 173.3, 203.8	−113.8
IIIg	1680, 1610, 1580, 1570, 1555	2.57–2.66 m (4H, $2CH_{2cyclopent}$), 6.55–6.56 m (1H, $H_{furanоил}$), 6.83–6.85 m (2H, H_{arom}), 6.97–7.00 m (2H, H_{arom}), 7.37 d (1H, H_{furan}, *J* 1.0), 7.42 d (1H, H_{furan}, *J* 3.3), 13.50 br.s (1H, NH)	33.1, 34.1, 105.8, 112.3, 116.0 d (*J* 23), 121.8, 125.5 d (*J* 8), 134.6 d (*J* 2),141.6, 145.6, 152.8, 161.0 d (*J* 248), 200.0, 207.5	−114.7
IIIh	1665, 1610, 1580, 1570, 1555	2.53 s (4H, $2CH_{2cyclopent}$), 4.70 d (2H, CH_2, *J* 5.9), 6.63–6.64 m (1H, H_{furan}), 7.04–7.07 m (2H, H_{arom}), 7.24–7.27 m (2H, H_{arom}), 7.42 d (1H, H_{furan}, *J* 3.3), 7.68 d (1H, H_{furan}, *J* 1.0), 12.50 br.s (1H, NH)	33.3, 49.3, 105.3, 112.2, 116.0 d (*J* 22), 121.5, 129.2 d (*J* 8), 131.8 d (*J* 2), 141.9, 145.8, 155.8, 162.5 d (*J* 247), 203.0	−113.9
IIIi	1690, 1630, 1600, 1560	2.49–2.51 m (2H, $CH_{2cyclopent}$), 2.67–2.69 m (2H, $CH_{2cyclopent}$), 6.78–6.81 m (2H, H_{arom}), 6.85–6.89 m (2H, H_{arom}), 7.22–7.23 m (2H, H_{arom}), 7.35–7.38 m (2H, H_{arom}), 7.42–7.45 m (1H, H_{arom}), 13.55 br.s (1H, NH)	33.1, 34.2, 106.7, 116.1 d (*J* 22), 126.4 d (*J* 8), 128.4, 128.6, 129.3, 130.6, 132.7 d (*J* 2), 160.1 d (*J* 249), 166.3, 200.3, 207.6	−114.2
IIIj	1685, 1620, 1560, 1550	2.40–2.43 m (2H, $CH_{2cyclopent}$), 2.57–2.60 m (2H, $CH_{2cyclopent}$), 4.36 d (2H, CH_2, *J* 6.3), 7.01–7.05 m (2H, H_{arom}), 7.10–7.13 m (2H, H_{arom}), 7.23–7.24 m (2H, H_{arom}), 7.48–7.54 m (3H, H_{arom}), 12.27 br.s (1H, NH)	32.0, 34.0, 47.3, 106.5, 116.0 d (*J* 22), 127.1, 128.6, 129.0 d (*J* 8), 129.8, 130.4, 131.6 d (*J* 3), 162.5 d (*J* 248), 169.2, 200.4, 207.2	−113.8
IIIk	1690, 1630, 1560	2.41–2.44 m (2H, $CH_{2cyclopent}$), 2.57–2.60 m (2H, $CH_{2cyclopent}$), 4.32 d.d (1H, CH_2, *J* 15.2, 6.4), 4.42 d.d (1H, CH_2, *J* 15.2, 6.0), 7.01–7.04 m (2H, H_{arom}), 7.12–7.14 m (2H, H_{arom}), 7.17−7.29 m (3H, H_{arom}), 7.51–7.55 m (1H, H_{arom}), 12.20 br.s (1H, NH)	33.1, 34.1, 47.7, 106.9, 116.2 d (*J* 22), 116.3 d (*J* 21), 117.9 d (*J* 16), 124.7 d (*J* 3), 129.2 d (*J* 1), 129.4 d (*J* 8), 131.2 d (*J* 3), 132.7 d (*J* 8), 158.8 d (*J* 249), 162.7 d (*J* 248), 163.4, 200.3, 207.0	−113.6, −113.9
IIIl	1685, 1640, 1585, 1565	2.50–2.53 m (2H, $CH_{2cyclopent}$), 2.67–2.70 m (2H, $CH_{2cyclopent}$), 6.81–6.84 m (2H, H_{arom}), 6.89−6.96 m (3H, H_{arom}), 6.99–7.01 m (1H, H_{arom}), 7.11–7.15 m (1H, H_{arom}), 7.31–7.36 m (2H, H_{arom}), 13.51 s (1H, NH)	33.2, 34.3, 106.8, 116.1 d (*J* 23), 116.4 d (*J* 23), 117.8 d (*J* 21), 124.5 d (*J* 2), 126.6 (*J* 8), 130.4 (*J* 8), 131.4 d (*J* 8), 132.5 (*J* 2), 161.2 d (*J* 249), 162.5 d (*J* 248), 164.7, 200.4, 207.7	−111.6, −113.7

Table (Contd.)

Comp. no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)	^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz)	^{19}F NMR spectrum, δ_F, ppm
IIIm	1690, 1630, 1560	2.41–2.44 m (2H, $CH_{2cyclopent}$), 2.57–2.60 m (2H, $CH_{2cyclopent}$), 4.34 d (2H, CH_2, *J* 6.3), 6.93–6.95 m (1H, H_{arom}), 7.00−7.06 m (3H, H_{arom}), 7.09–7.12 m (2H, H_{arom}), 7.20–7.24 m (1H, H_{arom}), 7.45–7.49 m (1H, H_{arom}), 12.22 br.s (1H, NH)	33.1, 34.1, 47.5, 106.5, 114.7 d (*J* 24), 116.3 d (*J* 22), 117.6 d (*J* 21), 122.9 d (*J* 2), 129.1 d (*J* 8), 130.9 d (*J* 8), 131.4 d (*J* 3), 131.8 d (*J* 8), 162.7 d (*J* 247), 162.8 d (*J* 249), 167.8, 200.5, 207.3	−111.1, −113.5
IIIn	1685, 1620, 1555	2.57–2.60 m (2H, $CH_{2cyclopent}$), 2.64–2.66 m (2H, $CH_{2cyclopent}$), 4.37 s (2H, CH_2), 6.84–6.90 m (4H, H_{arom}), 6.97–7.00 m (2H, H_{arom}), 7.05–7.08 m (2H, H_{arom}), 13.32 br.s (1H, NH)	31.9, 32.9, 34.4, 107.1, 115.5 d (*J* 21), 116.5 d (*J* 23), 128.1 d (*J* 9), 130.0 d (*J* 8), 131.0 d (*J* 2), 131.4 d (*J* 2), 161.8 d (*J* 246), 162.3 d (*J* 250), 170.3, 202.2, 207.4	−112.1, −115.7
IIIo	1685, 1620, 1555	2.52–2.58 m (4H, $2CH_{2cyclopent}$), 4.50 d (2H, CH_2, *J* 6.0), 4.53 s (2H, CH_2), 6.99−7.05 m (4H, H_{arom}), 7.08–7.10 m (2H, H_{arom}), 7.16–7.19 m (2H, H_{arom}), 12.23 br.s (1H, NH)	31.5, 32.7, 34.3, 46.3, 106.8, 116.0 d (*J* 22), 116.2 d (*J* 22), 129.0 d (*J* 8), 129.9 d (*J* 8), 130.2 d (*J* 2), 130.6 d (*J* 2), 161.9 d (*J* 246), 162.6 d (*J* 248), 170.5, 202.3, 207.0	−113.4, −115.3
IIIp	1680, 1620, 1570	2.54–2.61 m (4H, $CH_{2cyclopent}$), 4.54 s (2H, CH_2), 4.59 d (2H, CH_2, *J* 6.2), 6.97–7.00 m (2H, H_{arom}), 7.14–7.17 m (2H, H_{arom}), 7.27–7.32 m (2H, H_{arom}), 7.45–7.48 m (1H, H_{arom}), 7.57–7.58 m (1H, H_{arom}), 12.31 br.s (1H, NH)	31.5, 32.7, 34.3, 46.4, 107.0, 116.1 d (*J* 22), 123.6 q (*J* 273), 124.0 q (*J* 2), 125.3 q (*J* 3), 129.8, 129.9 d (*J* 8), 130.0, 130.3, 131.5 q (*J* 33), 135.9, 161.9 d (*J* 247), 170.7, 202.4, 207.2	−63.0 (CF_3), −115.2
Va	1675, 1615, 1580	2.44–2.47 m (2H, $CH_{2cyclopent}$), 2.56 s (3H, CH_3), 2.70–2.72 m (2H, $CH_{2cyclopent}$), 7.12–7.17 m (2H, H_{arom}), 7.21–7.24 m (2H, H_{arom}), 11.94 br.s (1H, NH)	25.3, 29.0, 33.8, 112.0, 116.8 d (*J* 23), 126.4 d (*J* 9), 133.0 d (*J* 2), 161.5 d (*J* 248), 180.5, 198.1, 200.2	−113.8
Vb	1680, 1615, 1585	1.13 t (3H, CH_3, *J* 7.3), 2.44–2.46 m (2H, $CH_{2cyclopent}$), 2.71–2.73 m (2H, $CH_{2cyclopent}$), 3.01 q (2H, CH_2, *J* 7.3), 7.11–7.15 m (2H, H_{arom}), 7.21–7.24 m (2H, H_{arom}), 12.01 br.s (1H, NH)	7.9, 25.3, 33.7, 34.2, 111.4, 116.7 d (*J* 23), 126.1 d (*J* 8), 133.1 d (*J* 2), 161.4 d (*J* 248), 180.5, 200.0, 201.3	−114.0
Vc	1665, 1605, 1565	0.97–0.99 m (2H, $CH_{2cycloprop}$), 1.12–1.14 m (2H, $CH_{2cycloprop}$), 2.48–2.51 m (2H, $CH_{2cyclopent}$), 2.70–2.73 m (2H, $CH_{2cyclopent}$), 3.48–3.53 m (1H, $CH_{cycloprop}$), 7.10–7.12 m (2H, H_{arom}), 7.20–7.22 m (2H, H_{arom}), 12.13 br.s (1H, NH)	11.7, 17.3, 25.0, 33.9, 111.7, 116.6 d (*J* 23), 126.1 d (*J* 9), 133.1 d (*J* 2), 161.3 d (*J* 248), 180.1, 200.2, 200.4	−114.0
Vd	1670, 1600, 1585	0.90–0.94 m (2H, $CH_{2cycloprop}$), 1.05–1.07 m (2H, $CH_{2cycloprop}$), 2.48–2.51 m (2H, $CH_{2cyclopent}$), 2.68–2.71 m (2H, $CH_{2cyclopent}$), 3.43–3.48 m (1H, $CH_{cycloprop}$), 4.52 d (2H, CH_2, *J* 6.2), 7.05–7.09 m (2H, H_{arom}), 7.23–7.26 m (2H, H_{arom}), 10.74 br.s (1H, NH)	11.3, 17.1, 24.0, 33.8, 47.1, 111.1, 116.0 d (*J* 22), 128.9 d (*J* 8), 131.6 d (*J* 2), 162.5 d (*J* 247), 181.4, 199.7, 200.2	−113.8
Ve	1670, 1605, 1565	2.51–2.53 m (2H, $CH_{2cyclopent}$), 2.76–2.78 m (2H, $CH_{2cyclopent}$), 6.57–6.58 m (1H, H_{furan}), 7.13–7.17 m (2H, H_{arom}), 7.25–7.28 m (2H, H_{arom}), 7.65–7.66 m (1H, H_{furan}), 8.25 d (1H, H_{furan}, *J* 3.6), 12.41 br.s (1H, NH)	25.5, 33.6, 110.5, 112.1, 116.7 d (*J* 23), 121.0, 126.5 d (*J* 9), 133.0 d (*J* 2), 146.6, 151.8, 161.5 d (*J* 248), 177.8, 182.5, 197.6	−113.6
Vf	1685, 1610, 1575	2.51–2.54 m (2H, $CH_{2cyclopent}$), 2.76–2.79 m (2H, $CH_{2cyclopent}$), 4.59 d (2H, CH_2, *J* 6.2), 6.53–6.55 m (1H, H_{furan}), 7.06–7.10 m (2H, H_{arom}), 7.27–7.30 m (2H, H_{arom}), 7.61–7.62 m (1H, H_{furan}), 8.26 d (1H, H_{furan}, *J* 3.6), 11.18 br.s (1H, NH)	24.6, 33.6, 47.4, 110.0, 112.1, 116.3 d (*J* 22), 120.6, 129.0 d (*J* 22), 131.6 d (*J* 3), 146.5, 151.9, 162.7 d (*J* 247), 177.7, 187.8, 197.7	−113.7
Vg	1675, 1610, 1575	2.48–2.51 m (2H, $CH_{2cyclopent}$), 2.77–2.79 m (2H, $CH_{2cyclopent}$), 7.14–7.17 m (2H, H_{arom}), 7.26–7.29 m (2H, H_{arom}), 7.41–7.44 m (2H, H_{arom}), 7.49–7.52 m (1H, H_{arom}), 7.72–7.74 m (2H, H_{arom}), 12.06 br.s (1H, NH)	25.4, 33.7, 111.0, 116.8 d (*J* 23), 126.4 d (*J* 9), 127.6, 128.9, 131.7, 133.0 d (*J* 2), 138.8, 161.5 d (*J* 248), 182.0, 193.7, 198.2	−113.6

Table (Contd.)

Comp. no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)	^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz)	^{19}F NMR spectrum, δ_F, ppm
Vh	1685, 1610, 1575	2.49–2.52 m (2H, $CH_{2cyclopent}$), 2.77–2.80 m (2H, $CH_{2cyclopent}$), 4.61 d (2H, CH_2, *J* 6.3), 7.08–7.11 m (2H, H_{arom}), 7.28–7.31 m (2H, H_{arom}), 7.38–7.41 m (2H, H_{arom}), 7.46–7.49 m (1H, H_{arom}), 7.67–7.69 m (2H, H_{arom}), 10.77 br.s (1H, NH)	24.4, 33.5, 47.2, 110.3, 116.2 d (*J* 22), 127.5, 128.8, 129.0 d (*J* 8), 131.4, 131.5 d (*J* 2), 138.9, 162.6 d (*J* 248), 183.1, 193.3, 198.0	−113.7
Vi	1685, 1610, 1600, 1585, 1565	2.49–2.52 m (2H, $CH_{2cyclopent}$), 2.78–2.81 m (2H, $CH_{2cyclopent}$), 4.61 d (2H, CH_2, *J* 6.2), 7.08–7.12 m (2H, H_{arom}), 7.14–7.18 m (1H, H_{arom}), 7.28–7.31 m (2H, H_{arom}), 7.33–7.37 m (2H, H_{arom}), 7.46–7.47 m (1H, H_{arom}), 10.72 br.s (1H, NH)	24.5, 33.6, 47.4, 110.2, 115.8 d (*J* 23), 116.4 d (*J* 22), 118.3 d (*J* 21), 124.6, 129.1 d (*J* 8), 129.2, 131.4 d (*J* 2), 141.1 d (*J* 6), 162.2 d (*J* 246), 162.7 d (*J* 248), 183.3, 191.8, 198.0	−113.5, −114.1
Vj	1675, 1620, 1575	2.48–2.50 m (2H, $CH_{2cyclopent}$), 2.71–2.72 m (2H, $CH_{2cyclopent}$), 4.31 c (2H, CH_2), 6.99–7.02 m (2H, H_{arom}), 7.10–7.14 m (2H, H_{arom}), 7.18–7.20 m (2H, H_{arom}), 7.28–7.31 m (2H, H_{arom}), 11.95 br.s (1H, NH)	25.3, 33.8, 45.6, 110.9, 115.1 d (*J* 21), 116.7 d (*J* 23), 126.1 d (*J* 9), 131.1 d (*J* 2), 131.4 d (*J* 8), 132.8 d (*J* 2), 161.5 d (*J* 248), 161.8 d (*J* 244), 181.2, 197.2, 199.9	−113.6, −116.9
Vk	1670, 1620, 1580	2.48–2.51 m (2H, $CH_{2cyclopent}$), 2.71–2.73 m (2H, $CH_{2cyclopent}$), 4.25 s (2H, CH_2), 4.50 d (2H, CH_2, *J* 6.2), 6.95–6.99 m (2H, H_{arom}), 7.04–7.07 m (2H, H_{arom}), 7.21–7.26 m (4H, H_{arom}), 10.58 br.s (1H, NH)	24.3, 33.6, 45.5, 47.3, 110.6, 110.3, 115.1 d (*J* 21), 116.2 d (*J* 22), 129.1 d (*J* 8), 131.2 d (*J* 2), 131.4 d (*J* 8), 161.7 d (*J* 244), 162.6 d (*J* 248), 182.2, 196.7, 199.9	−113.5, −117.2
Vl	1670, 1620, 1575	2.50–2.52 m (2H, $CH_{2cyclopent}$), 2.76–2.78 m (2H, $CH_{2cyclopent}$), 4.30 c (2H, CH_2), 6.95−7.01 m (3H, H_{arom}), 7.06–7.10 m (1H, H_{arom}), 7.20−7.29 m (3H, H_{arom}), 12.02 br.s (1H, NH)	25.4, 33.8, 45.6, 111.3, 113.7 d (*J* 19), 115.2 d (*J* 22), 118.4 d (*J* 18), 120.4 d.d (*J* 5, 4), 130.9 d (*J* 2), 131.4 d (*J* 8), 133.2 d.d (*J* 7, 3), 149.3 d.d (*J* 251, 12), 150.4 d.d (*J* 252, 14), 161.8 d (*J* 245), 180.7, 197.5, 199.7	−116.8, −133.6, −137.8
Vm	1675, 1620, 1580	2.50–2.52 m (2H, $CH_{2cyclopent}$), 2.71–2.74 m (2H, $CH_{2cyclopent}$), 4.26 s (2H, CH_2), 4.60 d (2H, CH_2, *J* 6.3), 6.96–7.00 m (2H, H_{arom}), 7.23–7.26 m (2H, H_{arom}), 7.45–7.46 m (1H, H_{arom}), 7.50–7.53 m (2H, H_{arom}), 7.60–7.62 m (1H, H_{arom}), 10.58 br.s (1H, NH)	24.3, 33.6, 45.5, 47.5, 110.6, 115.1 d (*J* 21), 123.7 d (*J* 273), 124.1 q (*J* 3), 125.4 q (*J* 3), 129.9, 130.5, 131.3 d (*J* 2), 131.4 d (*J* 8), 131.7 d (*J* 33), 136.6, 161.8 d (*J* 244), 182.4, 196.9, 199.5	−63.0 (CF_3), −117.1

NMR spectra of enamine derivatives **IIIa**–**IIIp**, the signal of N–H group (strongly bound to the cycle carbonyl via the hydrogen bond) was observed as broadened singlet at δ 12.20–13.63 ppm. The signal of carbon adjacent to nitrogen was found at δ 166.3–175.4 ppm in ^{13}C NMR spectra of exocyclic enaminodiketones **IIIa**–**IIIp**. IR spectra of the endocyclic enaminodiketones **Va**–**Vm** contained three characteristic absorption bands as well, at 1565–1585, 1605–1620, and 1670–1685 cm^{-1}, assigned to the double bond and to conjugated carbonyl bonds of the side groups and of the cycle, respectively. In ^1H NMR spectra of enaminodiketones **Va**–**Vm**, the signal of N–H proton bound to the exocyclic carbonyl via the intramolecular bond was observed as broadened singlet at δ 10.58–12.41 ppm, that is, it was shifted upfield as compared with the spectra of the isomeric products **IIIa**–**IIIp**. In the ^{13}C NMR spectra of the endocyclic products **Va**–**Vm**, the signal of carbon adjacent to nitrogen was observed at δ 177.7–183.3 ppm, that is, it was shifted downfield as compared with spectra of the isomeric exocyclic products **IIIa**–**IIIp**.

EXPERIMENTAL

^1H, ^{19}F, and ^{13}C NMR spectra were registered with the AVANCE 500 (Bruker–Biospin) spectrometer at 500.13 (^1H), 470.59 (^{19}F), and 125.77 (^{13}C) MHz using the 5 mm probe (QNP) with Z-gradient. The spectra were recorded at 293 K in $CDCl_3$. TMS was used as the internal reference (^1H and ^{13}C NMR), α,α,α-trifluorotoluene with δ_F −63 ppm was used as the external reference (^{19}F NMR). IR spectra were recorded using the Bomem Michelson 100 instrument (KBr pellets in the case of solid products and thin film in the case of oily products). Melting points were determined with the Boetius instrument. Elemental analysis was performed with the Eurovector EA3000 CHNS-O analyzer. The reaction course and the

products purity were monitored by TLC (Silufol UV-254 plates, ethyl acetate – hexane). Column chromatography was performed on silica gel (70−230 mesh) eluting with ethyl acetate – hexane mixture. IR, ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectral data of compounds **IIIa**–**IIIp** and **Va**–**Vm** are collected in the table.

3-Acyloxy-2-cyclopenten-1-ones (Ia–Ig) were prepared following the procedure in [20]. 3-Acetoxy-2-cyclopenten-1-one (**Ia**) [20], 3-propyonyloxy-2-cyclopenten-1-one (**Ib**) [13], 3-cyclopropanecarbonyloxy-2-cyclopenten-1-one (**Ic**) [23], and 3-benzoyloxy-2-cyclopenten-1-one (**Ie**) [13] were identical to the reference samples.

3-(Furane-2-carbonyloxy)-2-cyclopenten-1-one (Id). Yield 63%, colorless crystalline solid, mp 108–110°C. IR spectrum, ν, cm^{-1}: 1770, 1710, 1685, 1600. ^{1}H NMR spectrum, δ, ppm: 2.51–2.53 m (2H, $CH_{2,cyclopent}$), 2.89–2.91 m (2H, $CH_{2,cyclopent}$), 6.37 s (1H, H_{vinyl}), 6.63 d.d (1H, H_{furan}, *J* 1.7, 3.5 Hz), 7.41 d (1H, H_{furan}, *J* 3.4 Hz), 6.73 d (1H, H_{furan}, *J* 0.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8, 33.4, 112.6, 116.7, 121.2, 142.6, 148.4, 153.7, 179.3, 206.5.

3-(2-Fluorobenzoyloxy)-2-cyclopenten-1-one (If). Yield 72%, colorless crystalline solid, mp 112–114°C. IR spectrum, ν, cm^{-1}: 1765, 1710, 1680, 1600. ^{1}H NMR spectrum, δ, ppm: 2.52–2.54 m (2H, $CH_{2,cyclopent}$), 2.90–2.92 m (2H, $CH_{2,cyclopent}$), 6.40 s (1H, H_{vinyl}), 7.21–7.25 m (1H, H_{arom}), 7.27–7.32 m (1H, H_{arom}), 7.63–7.68 m (1H, H_{arom}), 8.02–8.05 m (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 28.9, 33.6, 116.8 d (*J* 9 Hz), 117.2, 117.6 d (*J* 22 Hz), 124.5 d (*J* 3 Hz), 132.7, 136.4 d (*J* 9 Hz), 159.7 d (*J* 4 Hz), 162.6 d (*J* 263 Hz), 179.6, 206.7. ^{19}F NMR spectrum, δ_F: −107.5 ppm.

3-(3-Fluorobenzoyloxy)-2-cyclopenten-1-one (Ig). Yield 70%, colorless crystalline solid, mp 98–101°C. IR spectrum, ν, cm^{-1}: 1750, 1705, 1680, 1600. ^{1}H NMR spectrum, δ, ppm: 2.53–2.56 m (2H, $CH_{2,cyclopent}$), 2.91–2.94 m (2H, $CH_{2,cyclopent}$), 6.40 s (1H, H_{vinyl}), 7.36–7.40 m (1H, H_{arom}), 7.50–7.54 m (1H, H_{arom}), 7.80–7.82 m (1H, H_{arom}), 7.93–7.95 m (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 28.8, 33.5, 117.1, 117.3, 121.7 d (*J* 21 Hz), 126.2 d (*J* 2 Hz), 130.2 d (*J* 7 Hz), 130.6 d (*J* 8 Hz), 161.1 d (*J* 2 Hz), 162.6 d (*J* 248 Hz), 179.4, 206.5. ^{19}F NMR spectrum, δ_F: −111.4 ppm.

3-(4-Fluorophenylacetoxy)-2-cyclopenten-1-one (Ih). Yield 80%, colorless crystalline solid, mp 58–62°C. IR spectrum, ν, cm^{-1}: 1790, 1715, 1680, 1600. ^{1}H NMR spectrum, δ, ppm: 2.45–2.47 m (2H, $CH_{2,cyclopent}$), 2.74–2.77 m (2H, $CH_{2,cyclopent}$), 3.82 s (2H, CH_2), 6.24 s (1H, H_{vinyl}), 7.04–7.08 m (2H, H_{arom}), 7.26–7.29 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 28.7, 33.3, 40.6, 115.8 d (*J* 22 Hz), 116.7, 127.8, 131.0 d (*J* 8 Hz), 162.4 d (*J* 247 Hz), 167, 179.7, 206.9. ^{19}F NMR spectrum, δ_F: −114.7 ppm.

2-Acylcyclopentane-1,3-diones (IIa–IIh). A mixture of 4 mmol (0.4 g, 0.55 mL) of triethylamine and 0.2 mL of acetone cyanohydrin was added to the solution of 2 mmol of enol acylates **Ia**–**Ih** in 8 mL of anhydrous acetonitrile. The reaction mixture was stirred for 16 h at room temperature, treated with 30 mL of 3% HCl, and extracted with chloroform (3 × 10 mL); the organic part was washed with water (2 × 10 mL) and dried over $MgSO_4$. After removal of the solvent under a reduced pressure compounds **IIa**–**IIh** were obtained in 61–89% yield.

2-Acetylcyclopentane-1,3-dione (IIa). Yield 72%, colorless crystalline solid, mp 72–75°C. The spectral features coincided with the literature data [24].

2-Propyonylcyclopentane-1,3-dione (IIb). Yield 61%, colorless crystalline solid, mp 75–77°C. The spectral features coincided with the literature data [13].

2-(Cyclopropanecarbonyl)cyclopentane-1,3-dione (IIc). Yield 76%, colorless crystalline solid, mp 46–49°C. IR spectrum, ν, cm^{-1}: 1705, 1620, 1585. ^{1}H NMR spectrum, δ, ppm: 1.17–1.20 m (2H, $CH_{2,cycloprop}$), 1.31–1.34 m (2H, $CH_{2,cycloprop}$), 2.54–2.57 m (2H, $CH_{2,cyclopent}$), 2.73–2.75 m (2H, $CH_{2,cyclopent}$), 3.15–3.20 m (1H, $CH_{cycloprop}$). ^{13}C NMR spectrum, δ_C, ppm: 13.7, 16.5, 28.5, 33.9, 114.1, 200.6, 201.3, 204.3. Found, %: C 65.01; H 6.10. $C_9H_{10}O_3$. Calculated, %: C 65.05; H 6.07.

2-(Furan-2-carbonyl)cyclopentane-1,3-dione (IId). Yield 81%, colorless crystalline solid, mp 115–118°C. IR spectrum, ν, cm^{-1}: 1690, 1620, 1580. ^{1}H NMR spectrum, δ, ppm: 2.60–2.62 m (2H, $CH_{2,cyclopent}$), 2.83–2.85 m (2H, $CH_{2,cyclopent}$), 6.66 d.d (1H, H_{furan}, *J* 1.6, 3.8 Hz), 6.78 d (1H, H_{furan}, *J* 0.8 Hz), 8.82 d (1H, H_{furan}, *J* 3.8 Hz), 16.71 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 29.3, 33.5, 111.8, 113.4, 126.0, 148.9, 149.2, 176.6, 198.1, 207.9. Found, %: C 62.47; H 4.24. $C_{10}H_8O_4$. Calculated, %: C 62.50; H 4.20.

2-Benzoylcyclopentane-1,3-dione (IIe). Yield 82%, colorless crystalline solid, mp 45–47°C. The spectral features coincided with the literature data [13].

2-(2-Fluorobenzoyl)cyclopentane-1,3-dione (IIf). Yield 85%, yellow oily substance. IR spectrum, ν, cm^{-1}: 1700, 1630, 1580. ^1H NMR spectrum, δ, ppm: 2.55–2.58 m (2H, $CH_{2,cyclopent}$), 2.82–2.85 m (2H, $CH_{2,cyclopent}$), 7.12–7.15 m (1H, H_{arom}), 7.22–7.27 m (1H, H_{arom}), 7.51–7.54 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 28.3 br.s, 33.4 br.s, 115.1, 116.1 d (*J* 22 Hz), 117.2 d (*J* 22 Hz), 124.1 d (*J* 2 Hz), 130.0, 134.2 d (*J* 9 Hz), 160.6 d (*J* 254 Hz), 190.4, 197.7 br.s, 204.4 br.s. ^{19}F NMR spectrum, δ_F −111.8 ppm. Found, %: C 65.43; H 4.10. $C_{12}H_9FO_3$. Calculated, %: C 65.45; H 4.12.

2-(3-Fluorobenzoyl)cyclopentane-1,3-dione (IIg). Yield 89%, yellow oily substance. IR spectrum, ν, cm^{-1}: 1700, 1630, 1580. ^1H NMR spectrum, δ, ppm: 2.63–2.85 m (4H, $CH_{2,cyclopent}$), 7.27–7.34 m (1H, H_{arom}), 7.44–7.48 m (1H, H_{arom}), 7.76–7.79 m (1H, H_{arom}), 7.87–7.91 m (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 28.9 br.s, 33.5 br.s, 113.5, 116.8 d (*J* 24 Hz), 120.9 d (*J* 21 Hz), 125.9 d (*J* 2 Hz), 129.8 d (*J* 8 Hz), 136.8 d (*J* 4 Hz), 162.4 d (*J* 247 Hz), 191.7, 198.2 br.s, 207.1 br.s. ^{19}F NMR spectrum, δ_F: −112.6 ppm. Found, %: C 65.42; H 4.15. $C_{12}H_9FO_3$. Calculated, %: C 65.45; H 4.12.

2-(4-Fluorophenylacetyl)cyclopentane-1,3-dione (IIh). Yield 86%, yellow oily substance. IR spectrum, ν, cm^{-1}: 1705, 1635, 1590. ^1H NMR spectrum, δ, ppm: 2.53–2.55 m (2H, $CH_{2,cyclopent}$), 2.73–2.76 m (2H, $CH_{2,cyclopent}$), 4.20 s (2H, CH_2), 6.99–7.05 m (2H, H_{arom}), 7.23–7.30 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 28.1, 33.6, 43.8, 114.0, 115.4 d (*J* 21 Hz), 129.2 d (*J* 2 Hz), 131.4 d (*J* 8 Hz), 162.1 d (*J* 246 Hz), 198.8, 199.8, 204.2. ^{19}F NMR spectrum, δ_F: −115.8 ppm. Found, %: C 66.63; H 4.77. $C_{13}H_{11}FO_3$. Calculated, %: C 66.66; H 4.73.

Exocyclic enaminodiketones (IIIa–IIIp). 1 mmol of the amine (4-fluoroaniline, 3,4-difluoroaniline, 4-fluorobenzylamine, or 3-trifluoromethylbenzylamine) was added to the solution of 1 mmol of the triketone (**IIa**–**IIh**) in benzene. The reaction mixture was refluxed with the Dean-Stark trap (4 h in the cases of 4-fluorobenzylamine and 3-trifluoromethylbenzylamine, 30 h in the cases of 4-fluoroaniline and 3,4-difluoroaniline). After removal of the solvent under a reduced pressure compounds **IIIa**–**IIIp** were isolated as colorless crystalline solids (yield of 50–83%) by column chromatography.

2-[1-(4-Fluorophenylamino)ethylidene]cyclopentane-1,3-dione (IIIa). Yield 75%, mp 122–124°C. Found, %: C 66.98; H 5.15; N 6.04. $C_{13}H_{12}FNO_2$. Calculated, %: C 66.94; H 5.19; N 6.01.

2-[1-(4-Fluorobenzylamino)ethylidene]cyclopentane-1,3-dione (IIIb). Yield 78%, mp 94–96°C. Found, %: C 68.03; H 5.70; N 5.70. $C_{14}H_{14}FNO_2$. Calculated, %: C 68.00; H 5.71; N 5.66.

2-[1-(4-Fluorophenylamino)propylidene]cyclopentane-1,3-dione (IIIc). Yield 83%, mp 135–137°C. Found, %: C 67.98; H 5.71; N 5.65. $C_{14}H_{14}FNO_2$. Calculated, %: C 68.00; H 5.71; N 5.66.

2-[1-(4-Fluorobenzylamino)propylidene]cyclopentane-1,3-dione (IIId). Yield 69%, mp 94–96°C. Found, %: C 68.93; H 6.20; N 5.40. $C_{15}H_{16}FNO_2$. Calculated, %: C 68.95; H 6.17; N 5.36.

2-[Cyclopropyl-(4-fluorophenylamino)methylene]-cyclopentane-1,3-dione (IIIe). Yield 55%, mp 79–82°C. Found, %: C 69.45; H 5.42; N 5.37. $C_{15}H_{14}FNO_2$. Calculated, %: C 69.49; H 5.44; N 5.40.

2-[Cyclopropyl-(4-fluorobenzylamino)methylene]cyclopentane-1,3-dione (IIIf). Yield 79%, mp 82–83°C. Found, %: C 70.34; H 5.94; N 5.16. $C_{16}H_{16}FNO_2$. Calculated, %: C 70.31; H 5.90; N 5.12.

2-[(4-Fluorophenylamino)(furan-2-yl)methylene]-cyclopentane-1,3-dione (IIIg). Yield 54%, mp 128–130°C. Found, %: C 67.36; H 4.25; N 4.88. $C_{16}H_{12}FNO_3$. Calculated, %: C 67.36; H 4.24; N 4.91.

2-[(4-Fluorobenzylamino)(furan-2-yl)methylene]-cyclopentane-1,3-dione (IIIh). Yield ход 51%, mp 123–126°C. Found, %: C 68.19; H 4.74; N 4.62. $C_{17}H_{14}FNO_3$. Calculated, %: C 68.22; H 4.71; N 4.68.

2-[Phenyl-(4-fluorophenylamino)methylene]cyclopentane-1,3-dione (IIIi). Yield 57%, mp 162–164°C. Found, %: C 73.24; H 4.74; N 4.70. $C_{18}H_{14}FNO_2$. Calculated, %: C 73.21; H 4.78; N 4.74.

2-[Phenyl-(4-fluorobenzylamino)methylene]cyclopentane-1,3-dione (IIIj). Yield 52%, mp 155–156°C. Found, %: C 73.81; H 5.24; N 4.51. $C_{19}H_{16}FNO_2$. Calculated, %: C 73.77; H 5.21; N 4.53.

2-[(4-Fluorobenzylamino)(2-fluorophenyl)methylene]cyclopentane-1,3-dione (IIIk). Yield 58%, mp 145–148°C. Found, %: C 69.76; H 4.64; N 4.30. $C_{19}H_{15}F_2NO_2$. Calculated, %: C 69.72; H 4.62; N 4.28.

2-[(3-Fluorophenyl)(4-fluorophenylamino)methylene]cyclopentane-1,3-dione (IIIl). Yield 50%, mp 151–154°C. Found, %: C 68.96; H 4.16; N 4.45. $C_{18}H_{13}F_2NO_2$. Calculated, %: C 69.01; H 4.18; N 4.47.

2-[(4-Fluorobenzylamino)-(3-fluorophenyl)methylene]cyclopentane-1,3-dione (IIIm). Yield 54%, mp 136–139°C. Found, %: C 69.69; H 4.66; N 4.25. $C_{19}H_{15}F_2NO_2$. Calculated, %: C 69.72; H 4.62; N 4.28.

2-[2-(4-Fluorophenyl)-1-(4-fluorophenylamino)-ethylidene]cyclopentane-1,3-dione (IIIn). Yield 55%, mp 144–147°C. Found, %: C 69.68; H 4.60; N 4.31. $C_{19}H_{15}F_2NO_2$. Calculated, %: C 69.72; H 4.62; N 4.28.

2-[1-(4-Fluorobenzylamino)-2-(4-fluorophenyl)-ethylidene]cyclopentane-1,3-dione (IIIo). Yield 53%, mp 114–117°C. Found, %: C 70.30; H 5.00; N 4.11. $C_{20}H_{17}F_2NO_2$. Calculated, %: C 70.37; H 5.02; N 4.10.

2-[2-(4-Fluorophenyl)-1-(3-trifluoromethylbenzylamino)ethylidene]cyclopentane-1,3-dione (IIIp). Yield 50%, mp 57–60°C. Found, %: C 64.41; H 3.50; N 3.55. $C_{21}H_{17}F_4NO_2$. Calculated, %: C 64.45; H 3.48; N 3.58.

Endocyclic enaminodiketones (Va–Vm). Oxalyl chloride (10 mmol) was added to 1 mmol of triketone **IIb**–**IIh**, and the reaction mixture was stirred for 10–30 min at room temperature. (In the case of **IIa**: 1 mmol of **IIa** was dissolved in 30 mL of anhydrous chloroform, then 5 mmol of oxalyl chloride was added, and the reaction mixture was refluxed for 2.5 h). The excess of oxalyl chloride and the solvent were removed under a reduced pressure. The residue was dissolved in 20 mL of chloroform; 2 mmol of the amine (4-fluoroaniline, 3,4-difluoroaniline, 4-fluorobenzylamine, or 3-trifluoromethylbenzylamine) was added, and the mixture was stirred for 2 h at room temperature. After removal of the solvent under a reduced pressure compounds **Va**–**Vm** were isolated as colorless crystalline solids (yield of 54–78%) by column chromatography.

2-Acetyl-3-(4-fluorophenylamino)-2-cyclopenten-1-one (Va). Yield 64%, mp 136–139°C. Found, %: C 66.98; H 5.22; N 6.05. $C_{13}H_{12}FNO_2$. Calculated, %: C 66.94; H 5.19; N 6.01.

2-Propionyl-3-(4-fluorophenylamino)-2-cyclopenten-1-one (Vb). Yield 71%, mp 145–147°C. Found, %: C 67.96; H 5.73; N 5.63. $C_{14}H_{14}FNO_2$. Calculated, %: C 68.00; H 5.71; N 5.66.

3-(4-Fluorophenylamino)-2-(cyclopropanecarbonyl)-2-cyclopenten-1-one (Vc). Yield 70%, mp 165–166°C. Found, %: C 69.46; H 5.47; N 5.43. $C_{15}H_{14}FNO_2$. Calculated, %: C 69.49; H 5.44; N 5.40.

3-(4-Fluorobenzylamino)-2-(cyclopropanecarbonyl)-2-cyclopenten-1-one (Vd). Yield 78%, mp 129–132°C. Found, %: C 70.28; H 5.87; N 5.13. $C_{15}H_{14}FNO_2$. Calculated, %: C 70.31; H 5.90; N 5.12.

3-(4-Fluorophenylamino)-2-(furan-2-carbonyl)-2-cyclopenten-1-one (Ve). Yield 67%, mp 167–168°C. Found, %: C 67.31; H 4.27; N 4.93. $C_{16}H_{12}FNO_3$. Calculated, %: C 67.36; H 4.24; N 4.91.

3-(4-Fluorobenzylamino)-2-(furan-2-carbonyl)-2-cyclopenten-1-one (Vf). Yield 58%, mp 119–121°C. Found, %: C 68.18; H 4.71; N 4.68. $C_{17}H_{14}FNO_3$. Calculated, %: C 68.22; H 4.71; N 4.68.

2-Benzoyl-3-(4-fluorophenylamino)-2-cyclopenten-1-one (Vg). Yield 61%, mp 140–143°C. Found, %: C 73.16; H 4.75; N 4.70. $C_{18}H_{14}FNO_2$. Calculated, %: C 73.21; H 4.78; N 4.74.

2-Benzoyl-3-(4-fluorobenzylamino)-2-cyclopenten-1-one (Vh). Yield 54%, mp 129–131°C. Found, %: C 73.81; H 5.24; N 4.51. $C_{19}H_{16}FNO_2$. Calculated, %: C 73.77; H 5.21; N 4.53.

3-(4-Fluorobenzylamino)-2-(3-fluorobenzoyl)-2-cyclopenten-1-one (Vi). Yield 67%, mp 97–100°C. Found, %: C 69.77; H 4.64; N 4.30. $C_{19}H_{15}F_2NO_2$. Calculated, %: C 69.72; H 4.62; N 4.28.

3-(4-Fluorophenylamino)-2-(4-fluorophenylacetyl)-2-cyclopenten-1-one (Vj). Yield 55%, mp 106–109°C. Found, %: C 69.65; H 4.60; N 4.30. $C_{19}H_{15}F_2NO_2$. Calculated, %: C 69.72; H 4.62; N 4.28.

3-(4-Fluorobenzylamino)-2-(4-fluorophenylacetyl)-2-cyclopenten-1-one (Vk). Yield 63%, mp 87–89°C. Found, %: C 70.31; H 5.04; N 4.14. $C_{20}H_{17}F_2NO_2$. Calculated, %: C 70.37; H 5.02; N 4.10.

3-(3,4-Difluorophenylamino)-2-(4-fluorophenylacetyl)-2-cyclopenten-1-one (Vl). Yield 64%, mp 109–111°C. Found, %: C 66.04; H 4.13; N 4.10. $C_{19}H_{14}F_3NO_2$. Calculated, %: C 66.09; H 4.09; N 4.06.

3-(3-Trifluoromethylbenzylamino)-2-(4-fluorophenylacetyl)-2-cyclopenten-1-one (Vm). Yield 55%, mp 81–83°C. Found, %: C 64.49; H 4.38; N 3.56. $C_{21}H_{17}F_4NO_2$. Calculated, %: C 64.45; H 4.38; N 3.58.

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