Chemistry of Heterocyclic Compounds, Vol. 47, No. 2, May, 2011 (Russian Original Vol. 47, No. 2, February, 2011)

SYNTHESIS AND PROPERTIES OF PHOTOSENSITIVE COMPOUNDS BASED ON BROMINE-CONTAINING 3-ACYL-2-FURYLCHROMONES*

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Methods have been developed for the synthesis of new photosensitive compounds based on the reaction of N,S,O-nucleophiles with 3-acyl-2-(5-bromofur-2-yl)chromones and 3-acyl-2-(5-bromomethylfur-2-yl)chromones. The relationship between the spectral properties and the structure of compounds has been shown.

Keywords: chromones, nucleophilic substitution, optical disks, absorption spectra, fluorescence spectra.

We showed previously that derivatives of 3-acetyl-2-furylchromones are promising components of recording media for providing a single two-photon record on multilayer optical disks of ultra-high information capacity [1, 2]. It is known that 3-acetyl-2-furylchromones in the initial form **A** do not possess fluorescence, but on irradiation with UV light undergo irreversible photochemical conversion with the formation of the fluorescing form **B** [1-4], which provides multiple fluorescent reading of optical information.

In the present work we have continued the study of the effect of structural factors on the photochemical properties of 3-acyl-2-furylchromones. In the previous investigation it was shown that the spectral characteristics of chromones depend to a significant extent on the substituents in the furan ring. The introduction of halogen atoms or a nitro group leads to a strong bathochromic shift of the absorption band of the initial form **A**, and also a shift of the absorption and fluorescence band of the photoproduct **B** [2]. It seemed expedient to study the effect of donor groups on the photochemical and fluorescent properties of chromones.

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* Dedicated to our dear colleague L. I. Belen'kii on the occasion of his famous jubilee.

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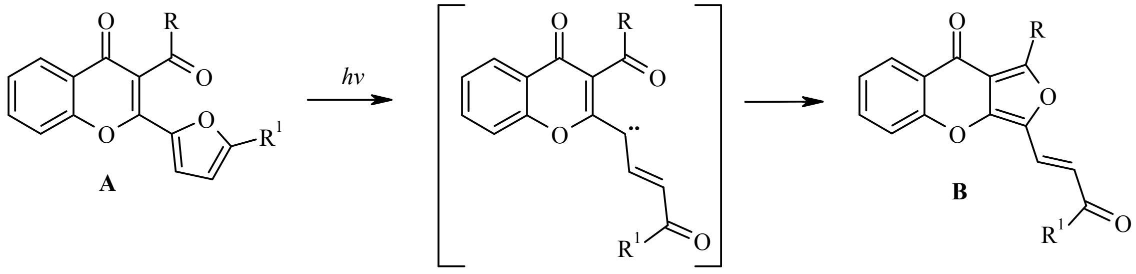
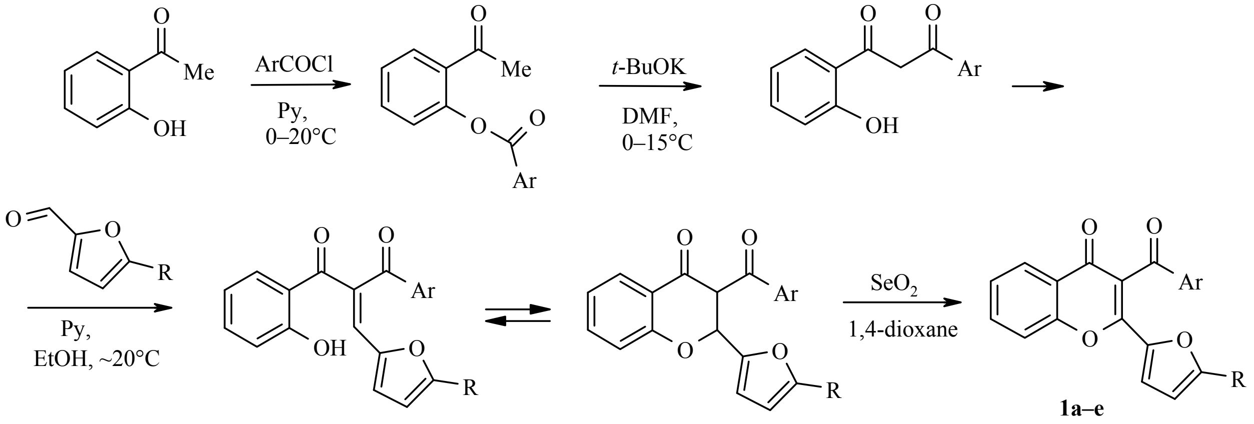
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 198-210, February, 2011. Original article submitted January 21, 2011.



Proceeding from the fact that the benzopyranone fragment possesses electron-withdrawing properties it might be proposed that under its influence atoms of halogen in the furan ring must possess enhanced reactivity under conditions of a nucleophilic substitution reaction, which also permits the introduction of various donor groups into the chromone system.

3-Acyl-2-furylchromones **1** containing a bromine atom at position 5 of the furan ring were synthesized from 2-hydroxyacetophenone under the conditions proposed by us in the previous work [2], according to the following scheme.

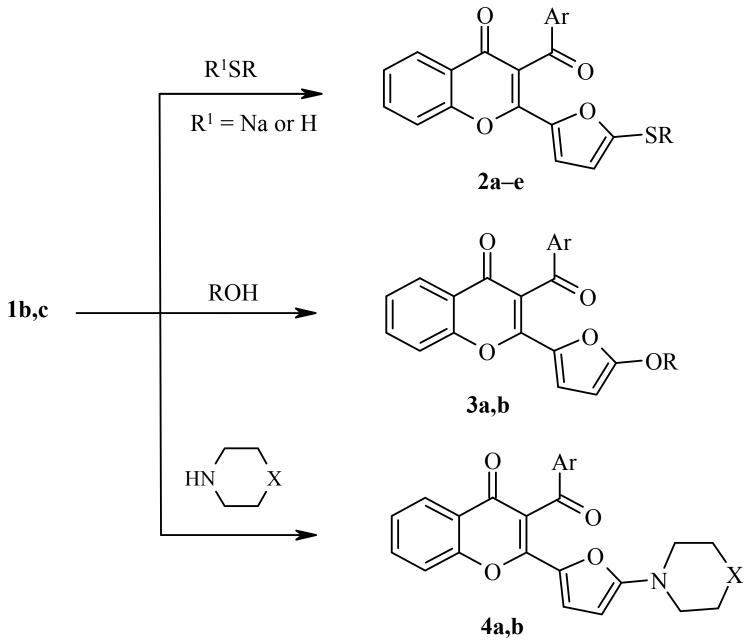


1 a Ar = Ph, R = Me; **b** Ar = Ph, R = Br; **c** Ar = thien-2-yl, R = Br; **d** Ar = Ph, R = H; **e** Ar = thien-2-yl, R = H

It turned out that on boiling in ethyl alcohol or on heating in DMF in the presence of K_2CO_3, or without it in several cases, a nucleophilic substitution reaction takes place smoothly. Compounds **2-4** obtained in these reactions are given in Table 1.

TABLE 1. Products of Nucleophilic Substitution of 3-Acyl-2-(5-bromofur-2-yl)chromones

Nucleophile	Solvent	Base	Conditions	Compounds	R	Yield, %
PhSNa	EtOH	—	Boiling	**2a**	Ph	66
t-BuSH	EtOH	K_2CO_3	Boiling	**2b**	*t*-Bu	59
t-BuSH	EtOH	K_2CO_3	Boiling	**2c**	*t*-Bu	29
$HSCH_2CO_2Et$	EtOH	K_2CO_3	Boiling	**2d**	CH_2CO_2Et	30
$HS(CH_2)_2N(Et)_2$	EtOH	K_2CO_3	Boiling	**2e**	$(CH_2)_2NEt_2$	35
PhOH	DMF	K_2CO_3	50°C	**3a**	Ph	45
4-*t*-BuC_6H_4OH	DMF	K_2CO_3	50°C	**3b**	4-*t*-BuC_6H_4	35
Morpholine	EtOH	Morpholine	Boiling	**4a**	—	79
Piperidine	EtOH	Piperidine	Boiling	**4b**	—	72



2a,b,d,e, 3a,b, 4a,b Ar = Ph; **2c** Ar = thien-2-yl; **4 a** X = O, **b** X = CH_2

Typical photoinduced changes of absorption and fluorescence spectra for compounds of the type of **2-4** are given in Figs. 1-3 respectively.

It is seen in Fig. 1 that on sequential irradiation of a solution of chromone **2e** the intensity of the long-wave absorption band of the initial form **A** at 354 nm is reduced with the simultaneous appearance and increase of intensity of a long wave absorption band at 420 nm, explained by the formation of photoproduct **B**. The appearance of the absorption band of the photoproduct is accompanied by the appearance of photoinduced fluorescence with a maximum at 495 nm. On increasing the exposure to UV light its intensity grows.

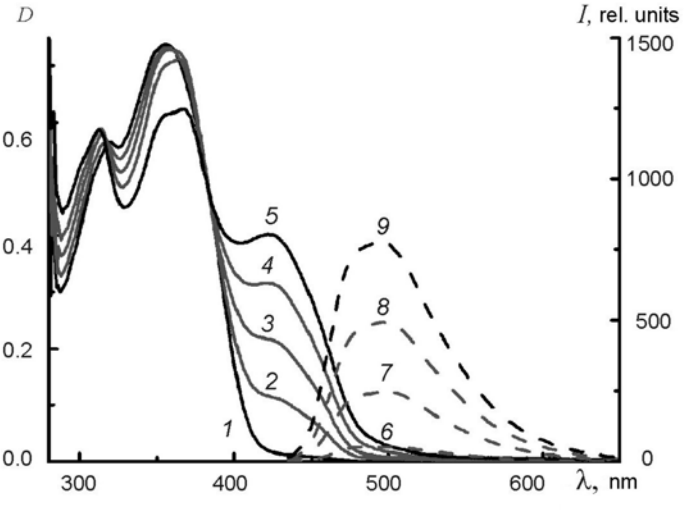


Fig. 1. Absorption (*1-5*) and fluorescence (*6-9*) spectra of a solution of compound **2e** in toluene before (*1*) and after (*2-9*) irradiation with UV light through a UFS-1 filter. Fluorescence spectra were measured on excitation with light of λ 425 nm (absorption band maximum of the photoproduct).

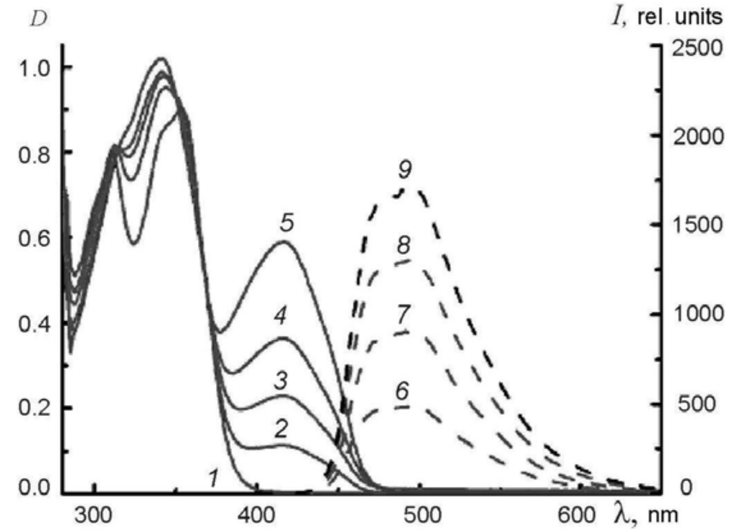


Fig. 2. Absorption (*1-5*) and fluorescence (*6-9*) spectra of a solution of compound **3a** in toluene before (*1*) and after (*2-9*) irradiation with UV light through a UFS-1 filter. The fluorescence spectra were measured on excitation with light of λ 415 nm (maximum of the absorption band of the photoproduct).

Analogous photoinduced spectral changes were observed for compound **3a** (Fig. 2).

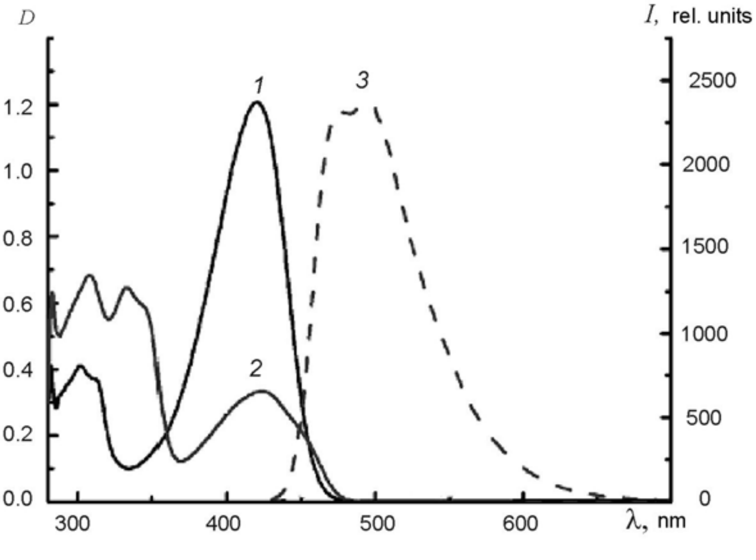


Fig. 3. Absorption (*1, 2*) and fluorescence (*3*) spectra of a solution of compound **4b** in toluene before (*1*) and after irradiation (*2, 3*). The fluorescence spectra were measured on excitation with light of λ 420 nm.

Photoinduced spectral changes, different from those described above, were displayed by chromones of group **4** (Fig. 3). It is seen from the figure that the absorption bands of the initial form of chromone **A** and its photoproduct overlap considerably.

As is shown by the data of Table 2 the photochemical and fluorescence properties of the obtained chromones **2-4** differ strongly from the properties of the unsubstituted chromone **1d**. The absorption bands of the chromones in the initial state **A** were displaced bathochromically by 12-105 nm, the absorption and fluorescence bands of the photoinduced form **B** had a low displacement (Table 2).

TABLE 2. Spectrokinetic Characteristics* of the Photoconversions of Chromones

Compound	$\lambda_{\mathbf{A}\,\max}$, nm ($D_\mathbf{A}$)	$\lambda_{\mathbf{B}\,\max}$, nm ($D_\mathbf{B}$)	$\lambda_{\mathbf{B}\,\mathrm{fl}\,\max}$, nm	$\Delta\lambda = \lambda_{\mathbf{B}\,\mathrm{fl}\,\max} - \lambda_{\mathbf{B}\,\max}$, nm	$I_{\mathbf{B}\,\mathrm{fl}}$, rel. units
1d	315 (0.9)	415 (0.15)	495	80	260
2a	327 (1.0)	420 (0.39)	490	70	1000
2d	338 (0.8)	420 (0.19)	488	68	250
2e	354 (0.7)	420 (0.40)	495	75	770
3a	340 (1.0)	415 (0.60)	490	75	1700
3b	345 (0.8)	415 (0.45)	490	75	1650
4a	406 (1.2)	418 (0.36)	491	73	1840
4b	420 (1.2)	423 (0.33)	491	68	2350

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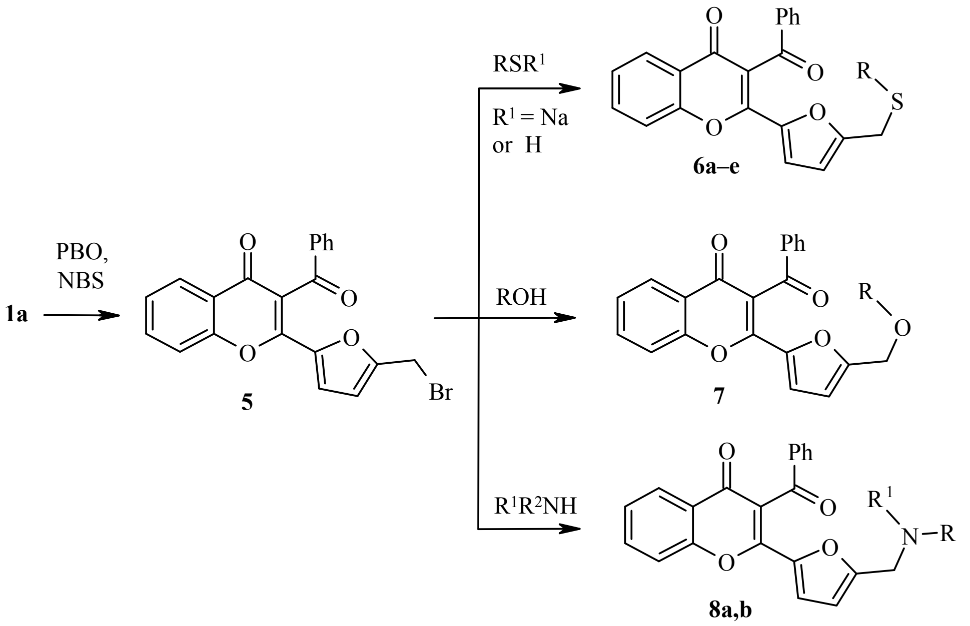
* $\lambda_{\mathbf{A}\,\max}$ and $\lambda_{\mathbf{B}\,\max}$ are wavelengths of absorption band maxima of initial and photoinduced forms of chromones respectively; $\lambda_{\mathbf{B}\,\mathrm{fl}\,\max}$ is the wavelength of the band maximum of fluorescence of photoinduced form of chromone; $D_\mathbf{A}$ is the photoinduced optical density at the absorption band maximum of the photoproduct; $I_{\mathbf{B}\,\mathrm{fl}}$ is the intensity of the fluorescence in the state of photo-equilibrium.



a R^1R^2NH = morpholine, **b** R^1R^2NH = 2-methylaniline

From chromone derivatives containing a bromomethyl group, we synthesized analogs of chromones **2-4** differing only in the methylene fragment between the furan ring and the amino, thio, or oxy group (compounds **6-8**). The given compounds were synthesized according to the scheme given above.

In the first stage 3-benzoyl-2-(5-bromomethylfur-2-yl)chromone **5** was formed from methyl derivative **1a** by boiling with NBS and catalytic amounts of dibenzoyl peroxide (PBO) in CCl_4. On interaction of compound **5** with nucleophiles in DMF substitution of the bromine atom occurs with the formation of thio, oxo, or amino derivatives of chromones **6**, **7**, **8** (Table 3).

TABLE 3. Products of Nucleophilic Substitution of 3-Acyl-2-(5-bromomethylfur-2-yl)chromone **5***

Nucleophile	Base	Conditions	Compound	R	R^1	Yield, %
PhSNa	—	~20°C	**6a**	Ph	—	75
t-BuSH	K_2CO_3	50°C	**6b**	*t*-Bu	—	80
BuSH	K_2CO_3	50°C	**6c**	Bu	—	47
$HSCH_2CO_2Et$	K_2CO_3	50°C	**6d**	CH_2CO_2Et	—	64
KSCN	—	Boiling	**6e**	CN	—	80
PhOH	K_2CO_3	50°C	**7**	Ph	—	20
Morpholine	Morhholine	~20°C	**8a**	$(CH_2)_2O(CH_2)_2$		60
2-Methylaniline	K_2CO_3	~20°C	**8b**	$2\text{-}MeC_6H_4$	H	70

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*Solvents: DMF (compounds **6a-d**, **7**, **8a**,**b**) and EtOH (compound **6e**).

Data of photochemical investigations of the obtained compounds are given in Table 4.

The photoinduced spectral changes of compounds **6-8** were similar to those displayed for compounds **2** and **3**. Comparison of the spectral characteristics of compounds **2-4** and **6-8** showed that introduction of a nucleophile directly into the furan ring leads to a more substantial change in the position of the absorption band of the initial form **A** of compounds while retaining the position of absorption and fluorescence bands of the photoinduced form **B**. Amines showed the strongest influence. The introduction of morpholine and piperidine rings leads to the strongest displacement in comparison with the unsubstituted chromone **1d** from 315 to 406 and 420 nm, respectively (compounds **4a**,**b**), while amines removed by one methylene link gave only a small (5-10 nm) bathochromic shift (compounds **8a**,**b**). A similar parallel was also observed for the oxo and thio derivatives, however, the bathochromic displacement of absorption band maxima was significantly less (15-30 nm). It must be emphasized that, as shown by the comparative investigation of the fluorescent properties, the introduction of a nucleophile directly into the furan nucleus leads to a substantial improvement of the fluorescent properties of the photoproduct. In reality, for the series of compounds **6-8** the fluorescence intensity of the photoinduced form does not exceed 100 rel. units on average, while for compounds **2-4** this parameter is from 200 to 2350 rel. units.

The conjugation of electron-donor groups with the furan ring therefore makes it more inclined to photoinduced conversion, since all compounds of this type possess high photosensitivity, which is displayed in high values of photoinduced optical density and of fluorescence intensity. Distancing the heteroatoms from the furan nucleus by a methylene fragment leads to a reduction in the fluorescence intensity of the photoinduced form.

TABLE 4. Spectrokinetic Characteristics of Photoconversions of Chromones

Compound	$\lambda_{\mathbf{A}\,\max}$, nm ($D_\mathbf{A}$)	$\lambda_{\mathbf{B}\,\max}$, nm ($D_\mathbf{B}$)	$\lambda_{\mathbf{B}\,\mathrm{fl}\,\max}$, nm	$\Delta\lambda = \lambda_{\mathbf{B}\,\mathrm{fl}\,\max} - \lambda_{\mathbf{B}\,\max}$, nm	$I_{\mathbf{B}\,\mathrm{fl}}$, rel. units
6a	330 (1.4)	420 (0.15)	490	70	57
6b	330 (1.2)	420 (0.12)	495	75	60
6c	331 (1.0)	417 (0.13)	490	73	63
6d	329 (1.2)	417 (0.14)	490	73	61
6e	319 (1.3)	420 (0.23)	493	73	63
7	318 (0.9)	420 (0.20)	495	75	40
8a	320 (1.1)	415 (0.14)	490	75	118
8b	327 (1.2)	400 sh (0.50)	490	90	57

EXPERIMENTAL

The ^1H NMR spectra were recorded on Bruker AC 200 (200 MHz) and AM 300 (300 MHz) instruments in $CDCl_3$. ^{13}C NMR spectra were recorded on a Bruker AM300 (75 MHz) instrument in $CDCl_3$, internal standard was by the residual protons of the carbon atom of the solvent. Mass spectra were recorded on a Varian MAT CH-6 instrument by direct insertion of the sample into the radiation source, ionization energy was 70 eV and operating voltage 1.75 kV. Melting points were measured on a Boetius hot stage and are not corrected. The analysis of all reaction mixtures and checks on the purity of isolated compounds was by TLC on Merck Silica gel 60 F254 UV-254 plates.

Absorption–kinetic measurements (absorption spectra of initial compounds and photoproducts, kinetics of photocoloration processes, kinetics of photoinduced optical density) were recorded on a Varian Cary 50 spectrophotometer. Toluene (Aldrich) was used as solvent. Solution concentration = $2 \cdot 10^{-4}$ M. A quartz cuvette of thickness 0.2 cm was used for measurements. Irradiation was effected by light from a LC-4 Hamamatsu lamp through a UV light filter. The efficiency of photocoloring of compounds was assessed according to the maximum value of the photoinduced optical density at the maximum of the absorption band of the photoproduct. It was determined from the kinetic curve of the dependence of optical density on time of irradiation after establishment of the photostationary state.

Fluorescence spectra were obtained on a Varian Cary Eclipse spectrophotometer. The working concentration of compounds in toluene $c = 4 \cdot 10^{-5}$ M. A quartz cuvette of thickness 1 cm was used for measurements. Fluorescence spectra were measured after reaching maximum change of the photoinduced optical density at the maximum of the absorption band of the photoproduct on excitation by light of the same wavelength.

Compounds **1** were synthesized by the procedure developed previously in [2].

3-Benzoyl-2-(5-bromofur-2-yl)-4H-chromen-4-one (1b). Yield 1.09 g (70%); mp 209-210°C (ethanol). ^1H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.23 (1H, d, *J* = 7.7, H-5); 7.99 (2H, d, *J* = 7.7, H'-2); 7.75 (1H, t, *J* = 7.8, H-7); 7.55-7.60 (2H, m, H Ar); 7.43-7.48 (3H, m, H Ar); 7.02 (1H, d, *J* = 3.7, H-3 furan); 6.42 (1H, d, *J* = 3.7, H-4 furan). Mass spectrum, *m/z* (I_{rel}, %): 396 $[M]^+$ (5), 394 (9), 316 (95), 315 $[M-Br]^+$ (100). Found, %: C 60.69; H 2.73; Br 20.12. $C_{20}H_{11}BrO_4$. Calculated, %: C 60.78; H 2.81; Br 20.22.

2-(5-Bromofur-2-yl)-3-(thiophen-2-carbonyl)-4H-chromen-4-one (1c). Yield 0.95 g (69%); mp 178°C (ethanol). ^1H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.25 (1H, d, *J* = 7.9, H-5); 7.70-7.80 (2H, m, H Ar); 7.40-7.65 (3H, m, H Ar); 7.05-7.10 (2H, m, H Ar); 6.48 (1H, d, *J* = 3.6, H-4 furan). Mass spectrum, *m/z* (I_{rel}, %): 402 $[M]^+$ (8), 400 (8), 322 (90), 321 $[M-Br]^+$ (100). Found, %: C 53.80; H 2.21. $C_{18}H_9BrO_4S$. Calculated, %: C 53.88; H 2.26.

3-Benzoyl-2-[5-(phenylthio)fur-2-yl]-4H-chromen-4-one (2a). A mixture of compound **1b** (0.395 g, 1 mmol) and sodium phenothiolate (0.139 g, 1.05 mmol) was boiled in ethanol. After the end of the reaction (check by TLC) the solvent was evaporated in vacuum, the residue dissolved in methylene chloride, and the solution was filtered through a layer of silica gel. After evaporation in vacuum the residue was recrystallized from ethanol. Yield 0.28 g (66%); mp 178-180°C. ^1H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.22 (1H, d, *J* = 8.1, H-5); 7.92 (2H, d, *J* = 7.7, H'-2); 7.74 (1H, t, *J* = 7.9, H-7); 7.36-7.56 (5H, m, H Ar); 7.02-7.21 (6H, m, H Ar); 6.65 (1H, d, *J* = 3.7, H-4 furan). ^{13}C NMR spectrum (75 MHz), δ, ppm: 193.61; 176.18, 155.78, 141.71, 136.60, 136.11, 135.87, 134.45, 134.23, 133.93, 131.92, 129.74, 129.62, 129.52, 129.44, 129.17, 129.02, 127.68, 126.10, 125.74, 123.29, 117.97. Mass spectrum, *m/z* (I_{rel}, %): 317 $[M-SPh]^+$ (9), 316 (36), 315 (100), 314 (5), 287 (5), 277 (2), 267 (3), 259 (4), 231 (9), 202 (9), 182 (18), 110 (57). Found, %: C 73.50; H 3.69; $C_{26}H_{16}O_4S$. Calculated, %: C 73.57; H 3.80.

Reaction of Bromo Derivatives of Furylchromones with Alkanethiols (General Method). A mixture of compound **1b** or **1c** (1 mmol) with *t*-BuSH or thioglycolic acid ethyl ester (1.05 mmol) was boiled in ethanol in the presence of K_2CO_3. After completion of the reaction (check by TLC) the solvent was removed in vacuum. The residue was dissolved in methylene chloride and the solution was processed by filtering through silica gel. After evaporating in vacuum the residue was recrystallized from ethanol.

3-Benzoyl-2-[5-(*tert*-butylthio)fur-2-yl]-4H-chromen-4-one (2b). Yield 0.24 g; (59%); mp 105-106°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.21 (1H, *J* = 6.9, H-5); 8.02 (2H, d, *J* = 6.7, H'-2); 7.76 (1H, t, *J* = 7.6, H-7); 7.34-7.65 (5H, m, H Ar); 7.17 (1H, d, *J* = 3.4, H-3 furan); 6.65 (1H, d, *J* = 3.5, H-4 furan); 1.13 (9H, s, $C(C\underline{H}_3)_3$) ^{13}C NMR spectrum (75 MHz), δ, ppm: 192.20; 176.27; 155.63; 151.89; 150.70; 148.05; 137.18; 134.41; 133.72; 129.57; 128.73; 126.11; 125.62; 123.60; 121.91; 119.55; 117.98; 116.82; 48.88, 30.93. Mass spectrum (EI), *m/z* (I_{rel}, %): 404 $[M]^+$ (5), 374 (1), 350 (18), 349 (13), 348 (80), 330 (5), 319 (4), 317 (7), 316 (65), 315 [M-S(*t*-Bu)]$^+$ (100), 306 (3), 294 (2), 288 (10), 287 (7), 275 (6), 271 (13), 270 (26). Found, %: C 71.35; H 5.06. $C_{24}H_{20}O_4S$. Calculated, %: C 71.27; H 4.98.

2-[5-(*tert*-Butylthio)fur-2-yl]-3-(thiophen-2-ylcarbonyl)-4H-chromen-4-one (2c). Yield 0.119 g (29%); mp 133-135°C. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.23 (1H, d, *J* = 8.1, H-5); 7.78-7.62 (5H, m, H Ar); 7.19 (1H, d, *J* = 3.3, H thiophene); 7.07 (1H, *J* = 4.4, H thiophene); 6.67 (1H, d, *J* = 3.7, H-4 furan); 1.22 (9H, s, $C(CH_3)_3$). Mass spectrum, *m/z* (I_{rel}, %): 411 $[M]^+$ (2), 410 (8), 355 (2), 354 (8), 353 (8), 341 (2), 323 (6), 322 (31), 321 (84) [M-S(*t*-Bu)]$^+$ (84), 301 (2), 293 (2), 278 (2), 272 (13), 271 (17), 270 (100). Found, %: C 64.43; H 4.47. $C_{22}H_{18}O_4S_2$. Calculated, %: C 64.37; H 4.42.

Ethyl Ester of 2-[5-(3-Benzoyl-4-oxo-4H-chromen-2-yl)fur-2-ylthio]acetic Acid (2d). Yield 0.130 g (30%); mp 138-139°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.22 (1H, d, *J* = 6.6, H-5); 8.04 (2H, d, *J* = 7.1, H'-2); 7.76 (1H, t, *J* = 7.1, H-7); 7.63-7.42 (5H, m, H Ar); 7.14 (1H, d, *J* = 3.5, H-3 furan; 6.56 (1H, d, *J* = 3.4, H-4 furan); 4.12 (2H, q, *J* = 7.1, $C\underline{H}_2CH_3$); 3.17 (2H, s, $C\underline{H}_2COOEt$); 1.23 (3H, t, *J* = 7.2, CH_3). Found, %: C 66.29; H 4.14. $C_{24}H_{18}O_6S$. Calculated, %: C 66.35; H 4.18.

3-Benzoyl-2-{5-[2-(diethylamino)ethylthio]fur-2-yl}-4H-chromen-4-one (2e). Yield 0.156 g (35%); mp 111-113°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.22 (1H, dd, *J* = 7.9, *J* = 1.6, H-5); 8.03 (2H, d d, *J* = 7.1, J = 1.6, H'-2); 7.75 (1H, dt, *J* = 7.3, *J* = 1.7, H-7); 7.37-7.62 (5H, m, H Ar); 7.14 (1H, d, *J* = 3.5, H-3 furan); 6.45 (1H, d, *J* = 3.6, H-4 furan); 2.62-2.69 (2H, m, SCH_2); 2.41-2.53 (6H, m, $C\underline{H}_2N(C\underline{H}_2Me)_2$); 0.93 (6H, t, *J* = 7.1 $N(CH_2C\underline{H}_3)_2$). ^{13}C NMR spectrum (75 MHz), δ, ppm: 192.59; 176.17; 155.60; 153.76; 150.84; 146.43; 137.17; 134.34; 133.74; 129.41; 128.81; 126.09; 125.57; 123.59; 117.91; 117.45; 115.21; 51.91; 46.90, 32.55; 11.88. Found, %: C 69.74; H 5.62. $C_{26}H_{25}NO_4S$. Calculated, %: C 69.78; H 5.63.

Reaction of Bromo Derivatives of Furylchromones with Phenols (General Method). A mixture of compound **1b** (1 mmol), phenol or 4-*tert*-butylphenol (2.1 mmol) was heated (~70°C) in DMF solution in the presence of K_2CO_3. After completion of the reaction (check by TLC) the mixture was poured into water, extracted with methylene chloride, the extract was washed with a small amount of ice water, and filtered through silica gel. After evaporation in vacuum the residue was recrystallized from ethanol.

3-Benzoyl-2-(5-phenoxyfur-2-yl)-4H-chromen-4-one (3a). Yield 0.184 g (45%); mp 146-147°C. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.20 (1H, d, *J* = 7.8, H-5); 7.87 (2H, d, *J* = 7.8, H'-2); 7.73 (1H, t, *J* = 7.8, H-7); 7.27-7.58 (7H, m, H Ar); 7.11-7.18 (2H, m, H Ar + H-3 furan); 6.92 (2H, d, *J* = 8.0, H'' Ar); 5.60 (1H, d, *J* = 3.4, H-3 furan). ^{13}C NMR spectrum (75 MHz), δ, ppm: 192.75, 176.00, 160.49, 155.60, 155.09, 151.04, 137.10, 136.79, 134.18, 133.54, 129.92, 129.35, 128.79, 128.66, 126.09, 125.46, 125.14, 123.57, 118.63, 118.11, 117.99, 117.84. Mass spectrum, *m/z* (I_{rel}, %): 408 $[M]^+$ (6), 363 (2), 317 (2), 316 (14), 315 [M-OPh]$^+$ (100), 288 (3), 275 (2). Found, %: C 76.40; H 3.89. $C_{26}H_{16}O_5$. Calculated, %: C 76.46; H 3.95.

3-Benzoyl-2-[5-(4-*tert*-butylphenoxy)fur-2-yl]-4H-chromen-4-one (3b). Yield 0.162 g (35%); mp 168-169°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz); 8.21 (1H, d, *J* = 7.9, H-5); 7.90 (2H, d, *J* = 7.6, H'-2); 7.73 (1H, t, *J* = 7.5, H-7); 7.30-7.56 (7H, m, H Ar); 7.11 (1H, d, *J* = 3.4, H-3 furan); 6.86 (2H, d, *J* = 8.5, H'' Ar); 5.55 (1H, d, *J* = 3.4, H-4 furan); 1.33 (9H, s, $C(CH_3)_3$). Mass spectrum, *m/z* (I_{rel}, %): 464 $[M]^+$ (2), 407 (1), 388 (1), 360 (2), 338 (2), 317 (11), 316 (15), 315 [M-OPh(*t*-Bu)]$^+$ (100), 302 (2), 275 (4), 259 (4). Found, %: C 77.49; H 5.31. $C_{30}H_{24}O_5$. Calculated, %: C 77.57; H 5.21.

Reaction of Bromo Derivatives of Furylchromones with Amines (General Method). A mixture of compound **1b** (1 mmol) and morpholine or piperidine (2.1 mmol) was boiled in ethanol. After completion of the reaction (check by TLC) the solvent was evaporated in vacuum. The residue was dissolved in methylene chloride, washed with water, dried, and filtered through silica gel. After evaporation in vacuum the residue was recrystallized from ethanol.

3-Benzoyl-2-(5-morpholinofur-2-yl)-4H-chromen-4-one (4a). Yield 0.316 g (79%); mp 260-261°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.18 (1H, d, *J* = 7.7, H-5); 8.03 (2H, d, *J* = 7.3, H'-2); 7.68 (1H, t, *J* = 7.7, H-7); 7.56 (1H, t, *J* = 7.2, H'-4); 7.36-7.48 (4H, m, H Ar); 7.24 (1H, d, *J* = 3.8, H-3 furan); 5.26 (1H, d, *J* = 3.7, H-4 furan); 3.56-3.59 (4H, m, $N(CH_2C\underline{H_2})_2O$); 2.88-2.92 (4H, m, $N(C\underline{H_2}CH_2)_2O$). Mass spectrum, *m/z* (I_{rel}, %): 329 $[M-(CH_2)_2O]^+$ (2), 316 (2), 315 [M-morpholine]$^+$ (40), 293 (2), 282 (2), 257 (3), 242 (3), 231 (5), 87 [morpholine] (100). Found, %: C 71.75; H 4.71. $C_{24}H_{19}NO_5$. Calculated, %: C 71.81; H 4.77.

3-Benzoyl-2-[5-(piperidino)fur-2-yl]-4H-chromen-4-one (4b). Yield 0.287 g (72%); mp 212-213°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.17 (1H, d, *J* = 7.8, H-5); 8.06 (2H, d, *J* = 7.6, H'-2); 7.33-7.70 (6H, m, H Ar); 7.25 (1H, d, *J* = 3.4, H-3 furan); 5.20 (1H, d, *J* = 3.8, H-4 furan); 2.91-2.96 (4H, m, $N(C\underline{H_2}CH_2)_2CH_2$); 1.41-1.46 (6H, m, $N(CH_2C\underline{H_2})_2C\underline{H_2}$). Mass spectrum, *m/z* (I_{rel}, %): 400 (20), 399 [M]$^+$ (64), 368 (3), 342 (4), 318 (5), 317 (10), 316 (25), 315 [M-piperidine]$^+$ (100), 289 (8), 288 (36).

3-Benzoyl-2-[5-(bromomethyl)fur-2-yl]-4H-chromen-4-one (5). A mixture of compound **1a** (0.330 g, 1 mmol), NBS (0.187 g, 1.05 mmol), and a catalytic amount of dibenzoyl peroxide in carbon tetrachloride was boiled for 2 h (check by TLC). After completion of the reaction the solution was diluted with petroleum ether (1:1) and filtered through a layer of silica gel. The solution obtained was evaporated in vacuum and the residue was recrystallized from an acetone–petroleum ether mixture (1:1). Yield 0.31 g (85%); mp 185-186°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.23 (1H, dd, *J* = 7.9, *J* = 1.5, H-5); 8.02 (2H, d, *J* = 7.5, H'-2); 7.75 (1H, dt, *J* = 5.0, *J* = 1.7, H-7); 7.55-7.60 (2H, m, H Ar); 7.43-7.48 (3H, m, H Ar); 7.07 (1H, d, *J* = 3.5, H-3 furan); 6.46 (1H, d, *J* = 3.5, H-4 furan); 4.22 (2H, s, CH_2Br). ^{13}C NMR spectrum (75 MHz), δ, ppm: 192.49; 176.18; 155.63; 154.71; 150.70; 145.55; 137.04; 134.48; 133.81; 129.55; 129.33; 128.85; 126.12; 125.69; 123.57; 119.66; 118.02; 116.62; 112.01; 21.54. Mass spectrum, *m/z* (I_{rel}, %): 410 [M]$^+$ (8), 409 (5), 408 (7), 373 (4), 343 (9), 330 (26), 329 [M-Br]$^+$ (100), 315 $[M-CH_2Br]^+$ (31), 303 (18), 302 (13), 301 (59), 283 (6), 273 (6). Found, %: C 61.61; H 3.18. $C_{21}H_{13}BrO_4$. Calculated, %: C 61.63; H 3.20.

Interaction of Compound 5 with Thiol Salts (General Method). A mixture of compound **5** (0.409 g, 1 mmol) and sodium thiophenolate or KSCN (1.05 mmol) was heated in ethanol (60-70°C). After completion of the reaction (check by TLC) the solvent was evaporated in vacuum. The residue was dissolved in methylene chloride and filtered through a layer of silica gel. After evaporation in vacuum the residue was recrystallized from ethanol.

3-Benzoyl-2-[5-(phenylthiomethyl)fur-2-yl]-4H-chromen-4-one (6a). Yield 0.332 g (75%); mp 114-115°C. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.23 (1H, d, *J* = 7.8, H-5); 8.02 (2H, d, *J* = 7.6, H'-2); 7.73 (1H, t, *J* = 7.8, H-7); 7.42-7.59 (5H, m, H Ar); 7.14-7.30 (5H, m, H Ar); 7.00 (1H, d, *J* = 3.5, H-3 furan); 6.17 (1H, d, *J* = 3.5, H-4 furan); 3.84 (2H, s, CH_2Ph). Mass spectrum, *m/z* (I_{rel}, %): 438 [M]$^+$ (4), 348 (2), 330 (33), 329 (38), 316 (3), 315 $[M-CH_2Ph]^+$ (100), 303 (5), 302 (10), 301 (38), 285 (7). Found, %: C 73.87; H 4.10. $C_{27}H_{18}O_4S$. Calculated, %: C 73.96; H 4.14.

3-Benzoyl-2-[5-(thiocyanatomethyl)fur-2-yl]-4H-chromen-2-one (6e). Yield 0.309 g (80%); mp 180-181°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.23 (1H, d, *J* = 7.8, H-5); 8.00 (2H, d, *J* = 7.3, H'-2); 7.77 (1H, t, *J* = 7.6, H-7); 7.43-7.63 (5H, m, H Ar); 7.13 (1H, d, *J* = 3.2, H-3 furan); 6.56 (1H, d, *J* = 3.2, H-4 furan); 3.94 (2H, s, CH_2SCN). Mass spectrum, *m/z* (I_{rel}, %): 387 [M]$^+$ (4), 343 (2), 340 (5), 332 (10), 331 (26), 330 (68), 329 (100), 321 (6), 316 (32), 315 $[M-CH_2SCN]^+$ (82), 302 (26), 301 (28), 288 (5), 286 (8), 273 (6). Found, %: C 73.77; H 4.00. $C_{22}H_{13}NO_4S$. Calculated, %: C 68.21; H 3.38.

Reaction of Compound 5 with Thiols (General Method). A mixture of compound **5** (0.409 g, 1 mmol) with BuSH, *t*-BuSH, or thioglycolic acid ethyl ester (1.05 mmol) was stirred in DMF with gentle heating (<50°C) in the presence of K_2CO_3. After completion of the reaction (check by TLC) the mixture was poured into water. The precipitated solid was filtered off, washed with water, dissolved in methylene chloride, the solution was dried, and filtered through silica gel. After evaporation in vacuum the residue was recrystallized from ethanol.

3-Benzoyl-2-[5-(*tert*-butylthiomethyl)fur-2-yl]-4H-chromen-4-one (6b). Yield 0.334 g (80%); mp 130-132°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.22 (1H, d, *J* = 7.3, H-5); 8.02 (2H, d, *J* = 7.3, H'-2); 7.74 (1H, t, *J* = 7.3, H-7); 7.41-7.60 (5H, m, H Ar); 7.09 (1H, d, *J* = 3.4, H-3 furan); 6.35 (1H, d, *J* = 3.4 H-4 furan); 3.51 (2H, s, CH_2SCMe_3); 1.16 [9H, s, $SC(CH_3)_3$]. Mass spectrum, *m/z* (I_{rel}, %): 419 $[M]^+$ (2), 418 (6), 343 (2), 330 (2), 329 (9), 317 (5), 316 (75), 315 $[M-CH_2SCHMe_3]^+$ (100), 301 (11), 287 (4). Found, %: C 71.71; H 5.23. $C_{25}H_{22}O_4S$. Calculated, %: C 71.75; H 5.30.

3-Benzoyl-2-[5-(butylthiomethyl)fur-2-yl]-4H-chromen-4-one (6c). Yield 0.196 g (47%); mp 85-86°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.22 (1H, d, *J* = 7.7, H-5); 8.00 (2H, d, *J* = 7.5, H'-2); 7.74 (1H, t, *J* = 7.6, H-7); 7.42-7.58 (5H, m, H Ar); 7.10 (1H, d, *J* = 2.9, H-3 furan); 6.32 (1H, d, *J* = 2.8, H-4 furan); 3.45 (2H, s, $C\underline{H}_2SC_4H_{10}$); 2.30 (2H, t, *J* = 6.7, $SC\underline{H}_2(CH_2)_2Me$); 1.29-1.42 (4H, m, $SCH_2(C\underline{H}_2)_2Me$); 0.88 (3H, t, *J* = 6.8, $SCH_2(CH_2)_2C\underline{H}_3$). Mass spectrum, *m/z* (I_{rel}, %): 418 $[M]^+$ (14), 361 (3), 347 (2),331 (15), 330 (68), 316 (23), 315 $[M-CH_2SBu]^+$ (100), 302 (8), 301 (27). Found, %: C 71.70; H 5.25. $C_{25}H_{22}O_4S$. Calculated, %: C 71.75; H 5.30.

Ethyl Ester of 2-{[5-(3-Benzoyl-4-oxo-4H-chromen-2-yl)fur-2-yl]methyl-thio}acetic Acid (6d). Yield 0.287 g (64%); mp 123-125°C. ^{1}H NMR spectrum (200 MHz), δ, ppm (*J*, Hz): 8.22 (1H, d, *J* = 8.1, H-5); 8.01 (2H, d, *J* = 7.3, H'-2); 7.75 (1H, t, *J* = 7.9, H-7); 7.41-7.58 (5H, m, H Ar); 7.09 (1H, d, *J* = 3.7, H-3 furan); 6.36 (1H, d, *J* = 3.7, H-4 furan); 4.17 (2H, q, *J* = 7.2, $C\underline{H}_2Me$); 3.64 (2H, s, $C\underline{H}_2SCH_2COOEt$); 2.94 (2H, s, $CH_2SC\underline{H}_2COOEt$); 1.28 (3H, t, *J* = 7.2, $OCH_2C\underline{H}_3$). Mass spectrum, *m/z* (I_{rel}, %): 451 (5), 449 $[M]^+$ (8), 435 (5), 416 (2), 403 (6), 385 (2), 373 (1), 362 (13), 361 (100), 343 (2), 333 (6), 331 (10), 330 (31), 329 (46), 316 (81), 315 $[M-CH_2SCH_2COOEt]^+$ (99), 302 (10), 301 (39). Found, %: C 66.91; H 4.39. $C_{25}H_{20}O_6S$. Calculated, %: C 66.95; H 4.49.

3-Benzoyl-2-[5-(phenoxymethyl)fur-2-yl]-4H-chromen-4-one (7). Bromo derivative **5** (0.409 g, 1 mmol) was added to a mixture of K_2CO_3 (1 mmol) and phenol (1.05 mmol) in DMF and stirred at 50°C. After completion of the reaction (check by TLC) the mixture was poured into water. The precipitated solid was filtered off, washed with water, dissolved in methylene chloride, the solution dried, and filtered through silica gel. After evaporation in vacuum the residue was recrystallized from ethanol. Yield of compound **7** was 84 mg (20%); mp 136-138°C. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.24 (1H, d, *J* = 7.9, H-5); 7.99 (2H, d, *J* = 7.8, H'-2); 7.75 (1H, t, *J* = 7.9, H-7); 7.40-7.58 (5H, m, H Ar); 7.22-7.25 (2H, m, H Ar); 7.10 (1H, d, *J* = 3.1, H-3 furan); 6.97 (1H, t, *J* = 7.8, H Ar); 6.76 (2H, d, *J* = 8.1, H Ar); 6.49 (1H, d, *J* = 3.4, H-4 furan); 4.82 (2H, s, $C\underline{H}_2OPh$). Mass spectrum, *m/z* (I_{rel}, %): 422 $[M]^+$ (2), 374 (1), 347 (1), 331 (7), 329 (100), 317 (2), 316 (8), 315 $[M-CH_2OPh]^+$ (14), 303 (1), 301 (27), 286 (4), 285 (8), 274 (4), 273 (11). Found, %: C 76.70; H 4.21. $C_{27}H_{18}O_5$. Calculated, %: C 76.77; H 4.29.

Reaction of Compound 5 with Amines (General Method). Bromo derivative **5** (1 mmol) was added to a mixture of K_2CO_3 (1 mmol), and aminotoluene (1.05 mmol) or morpholine or *o*-toluidine (2.05 mmol) in DMF and the mixture was stirred at room temperature. After completion of the reaction (check by TLC) the mixture was poured into water. The precipitated solid was filtered off, washed with water, dissolved in methylene chloride, the solution dried, and filtered through silica gel. After evaporation in vacuum the solid was recrystallized from ethanol.

3-Benzoyl-2-[5-(morpholinomethyl)fur-2-yl]-4H-chromen-4-one (8a). Yield 0.249 g (60%); mp 176-178°C. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.21 (1H, d, *J* = 7.8, H-5); 8.02 (2H, d, *J* = 7.3, H'-2); 7.74 (1H, t, *J* = 7.1, H-7); 7.54-7.59 (2H, m, H Ar); 7.42-7.47 (3H, m, H Ar); 7.13-7.15 (1H, d, *J* = 3.5, H-3 furan); 6.36 (1H, d, *J* = 3.7, H-4 furan); 3.51-3.54 (4H, m, $N(CH_2C\underline{H}_2)_2O$); 3.36 (2H, s, CH_2N); 2.15-2.17 (4H m, $N(C\underline{H}_2CH_2)_2O$). Mass spectrum, *m/z* (I_{rel}, %): 397 $[M-O]^+$ (2), 343 (1), 332 (4), 330 (19), 329 (100), 315 $[M-CH_2N(CH_2CH_2)_2O]^+$ (2), 314 (18), 301 (5), 293 (4), 285 (3), 273 (6), 271 (5), 261 (4), 86 (7). Found, %: C 72.19; H 5.00. $C_{25}H_{21}NO_5$. Calculated, %: C 72.28; H 5.10.

3-Benzoyl-2-{5-[(*o*-tolylamino)methyl]fur-2-yl}-4H-chromen-4-one (8b). Yield 0.3 g (70%); mp 91-93°C. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.23 (1H, dd, *J* = 8.0, *J* = 1.4, H-5); 8.00 (2H, d, *J* = 7.2, H'-2); 7.74 (1H, dt, *J* = 7.8, *J* = 1.6, H-7); 7.39-7.59 (5H, m, H Ar); 7.00-7.09 (3H, m, H Ar); 6.68 (1H, t, *J* = 7.4, H Ar); 6.33-6.41 (2H, m, H Ar); 4.18 (2H, s, CH_2); 2.08 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 436 $[M]^+$ (9), 435 (53), 434 (3), 417 (2), 407 (2), 331 (5), 330 (39), 329 (61), 328 (53), 317 (16), 315 $[M-CH_2NPhMe]^+$ (100). Found, %: C 77.15; H 4.78. $C_{28}H_{21}NO_4S$. Calculated, %: C 77.23; H 4.86.

The work was carried out with the support of the Russian Fund for Fundamental Investigations (Grant 10-03-00250-a).

REFERENCES

1. V. A. Barachevsky, Y. P. Strokach, Y. A. Puankov, O. I. Kobeleva, T. M. Valova, K. S. Levchenko, V. N. Yarovenko, and M. M. Krayushkin, *ARKIVOC*, ix, 70 (2009).
2. M. M. Krayushkin, K. S. Levchenko, V. N. Yarovenko, I. V. Zavarzin, V. A. Barachevsky, Y. A. Puankov, T. M. Valova, and O. I. Kobeleva, *ARKIVOC*, ix, 269 (2009).
3. K. R. Huffman, C. E. Kuhn, and A. Zweig, *J. Am. Chem. Soc.*, **92**, 599 (1970).
4. R. T. Cummings, J. P. Dizio, and G. A. Krafft, *Tetrahedron Lett.*, **29**, 69 (1988).