Synthesis and reactivity of 1-aryl-9*H*-thieno[3,4-*b*]chromon-9-ones†

Mikhail M. Krayushkin,[a] Konstantin S. Levchenko,[a] Vladimir N. Yarovenko,[a] Ludmila V. Christoforova,[a] Valery A. Barachevsky,[b] Yury A. Puankov,[b] Tatyana M. Valova,[b] Olga I. Kobeleva[b] and K. Lyssenko[c]

Received (in Victoria, Australia) 5th June 2009, Accepted 23rd July 2009
First published as an Advance Article on the web 2nd September 2009
DOI: 10.1039/b9nj00237e

Methods were developed for the synthesis of 1-aryl-9*H*-thieno[3,4-*b*]chromon-9-ones based on the reaction of bromo and dibromo derivatives of 2-methyl-4*H*-chromon-4-one with thioacetamide in DMF. The thienochromones were modified and their fluorescence properties were studied. Bis(thienochromones) were synthesized by the reaction of thienochromones with ketoaldehydes.

Introduction

The chromone fragment is involved in many natural compounds with a wide spectrum of biological activities. Many chromones have fluorescence properties and have found use as sensors for microscopy studies of proteins, micro-organelles, and cells.[1a–c] Chromones have been studied as antioxidants,[2] agents for wound[3] and ulcer healing,[4] immune stimulators,[5] and anti-HIV agents.[6] Heteroarylchromones (Fig. 1) are of great interest for the design of various drugs and fluorescent labels for biological substrates. Lupinalbin A (phytoestrogen),[7] lisetin (analog of lupinalbin A) isolated from plants of the *Leguminosae* family (**2**),[8] and pyralomicins, which were isolated from the microorganism *Microtetraspora spiralis* and have antitumor and antibacterial properties,[9] belong to natural heterocycle-annelated chromones. Synthetic hetaryl-chromones have found use as anti-ulcer drugs (Aphthasol) (**1**)[10] and drugs for the asthma treatment[11] and are considered as antiallergic agents.[12]

In the above-described pyrrole, thiophene or furan containing compounds, the five-membered heterocyclic moiety is generally fused to chromone forming [2,3-*b*] or [3,2-*b*] derivatives. [3,4-*b*]Chromone derivatives are scarce and their properties are unknown. The development of methods for the synthesis of this type of compounds and investigation of their physico-chemical properties present interesting problems.

Chromones fused to the thiophene ring (3) have been investigated as local anesthetics or central nervous system stimulators.[13] The synthesis of thieno[3,4-*b*]chromone by reaction of a 3-acyl-2-(bromomethyl)chromone with thio-acetamide was described for one example **11a**.[14]

In the present study, we synthesized a wide range of 3-acyl-2-methylchromones **7** according to the procedure developed earlier[15] (Scheme 1), studied the cyclization of their bromo derivatives, and showed that thieno[3,4-*b*]chromones thus prepared can be functionalized.

Earlier, it has been shown that monobromo derivative **9a** is formed by the addition of one equivalent of bromine to a hot (60–70 °C) solution of chromone **7a** in CCl_4. However, we found that, under these conditions, the reaction affords compound **9a** along with dibromo derivative **8a** as a by-product. It is known that the reactions of dibromo- and mono-bromomethyl moieties with nucleophiles can give the same products. Hence, we also examined the possibility of using dibromo derivatives **8a–c** in the step of cyclization to thienochromones.

Earlier, the cyclization of monobromo derivative **9a** was carried out with the use of an ethanolic solution of thioacetamide in the presence of a small excess of sodium acetate.[14] We showed that, in the presence of sodium acetate, the reaction giving rise to thienochromone **11a** is accompanied by side reactions both in ethanol and DMF. Compound **9a** reacts with sodium acetate under reflux in an ethanolic solution or under cooling in DMF, resulting in the replacement

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. E-mail: mkray@mail.ioc.ac.ru; Fax: +7 (495) 135 5328*
[b] *Photochemistry Center, Russian Academy of Sciences, 7a ul. Novatorov, 119421 Moscow, Russian Federation*
[c] *N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation*

† CCDC reference number 742366. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00237e

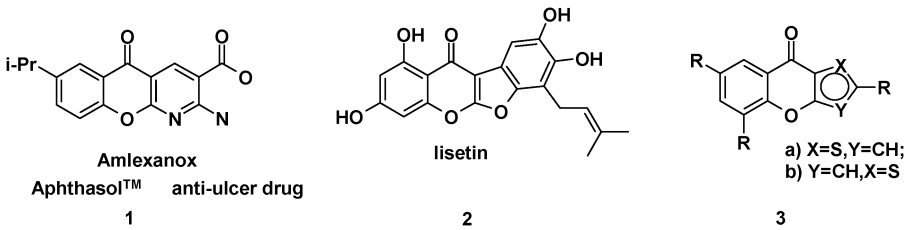
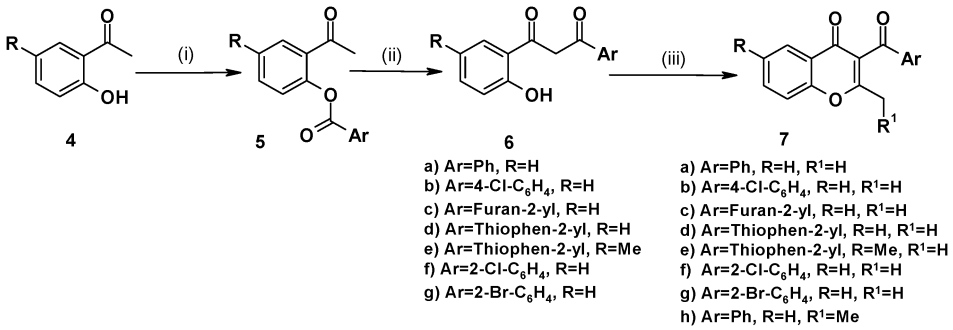
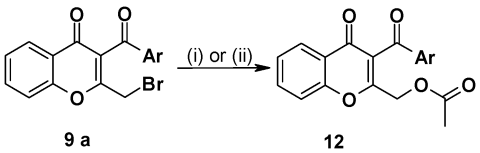


Fig. 1



Scheme 1 *Reagents and conditions*: (i) ArC(O)Cl, pyridine, r.t. 40–60 min; (ii) *t*-BuOK, DMF, 0 °C; (iii) $(RCO)_2O$, RCOONa, reflux, 30–60 min.



Scheme 2 *Reagents and conditions*: (i) AcONa, DMF, 0–40 °C; (ii) AcONa, EtOH, reflux.

of bromine with the acetate fragment to give compound **12** (Scheme 2). An increase in the temperature of the reaction mixture in DMF leads to resinification of the products.

We found that the cyclisation to the thienochromone proceeded easily in DMF without the addition of sodium acetate. Heating of monobromo derivatives **9a–h** in DMF at 60–80 °C in the presence of excess thioacetamide for 1 h affords thienochromones **11a–h** in 60–80% yields.

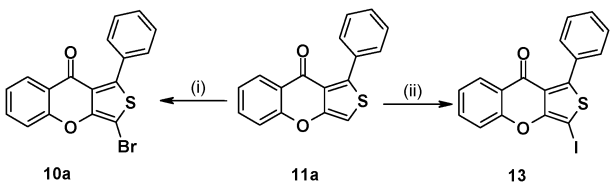
The reactions of chromones **7a**, **7b**, **7d** with a twofold excess of bromine in boiling CCl_4 were shown[14] to give only dibromo derivatives **8a**, **8b**, **8d** (Scheme 3). The reactions of these compounds with thioacetamide in DMF at 80–100 °C are accompanied by elimination of two bromine atoms to give the corresponding thienochromones **11a–h** also in good yields. It should be noted that the component **10** is not formed. Hence, a mixture of mono- and di-bromo derivatives can be used in the heterocyclization reactions with thioacetamide.

The possibility of modifying thienochromones was demonstrated with several examples.

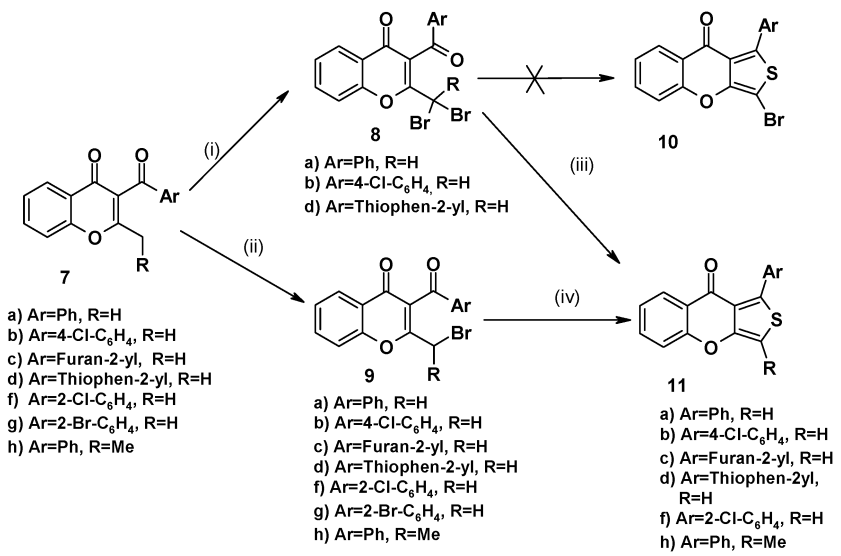
Halogen-containing biologically active chromones were described in the literature. In particular, pyrrolomycins containing the 2-chloropyrrolochromone system are antibiotics.[9] However, halogen derivatives of thienochromone are unknown.

The bromination of compound **11a** in dichloromethane at room temperature affords bromo derivative **10a**, whereas the reaction with iodine in dichloromethane in the presence of mercury oxide gives iodo derivative **13** (Scheme 4).

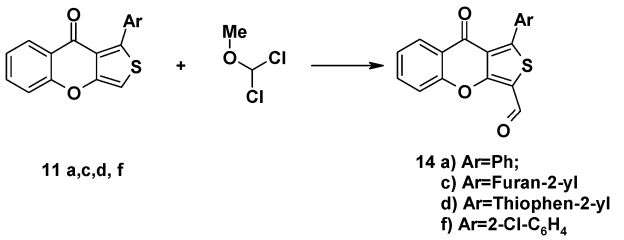
The aldehyde group is a convenient substituent for modifications of chromones. However, we failed to introduce



Scheme 4 *Reagents and conditions*: (i) Br_2, CH_2Cl_2, r.t., 1 h; (ii) HgO, I_2, benzene, 1 h.



Scheme 3 *Reagents and conditions*: (i) Br_2 (2.2 equiv.), CCl_4, reflux, 1.5–2 h; (ii) Br_2 (1.1 equiv.), CCl_4, heating 60–70 °C, 30 min; (iii) $CH_3C(S)NH_2$ (2.2 equiv.), DMF, 80–100 °C, 60–90 min; (iv) $CH_3C(S)NH_2$ (1.5 equiv.), DMF, 70–80 °C, 40–60 min.



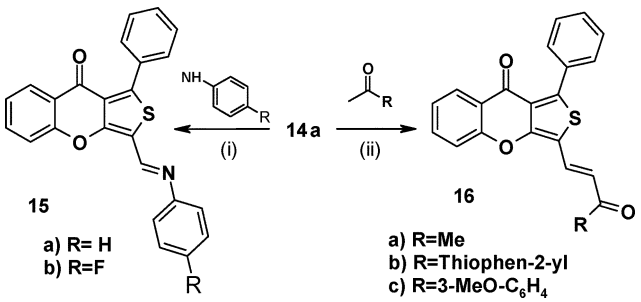
Scheme 5 *Reagents and conditions*: (i) tin(IV) chloride, 1,2-dichloroethane, ice/brine cooling, 1,5 h.

the aldehyde group at the free position of the thiophene ring in compounds **11a–f** with the use of lithium diisopropylamide and DMF or a mixture of phosphorus oxychloride and DMF. This is indicative of a substantial electron-withdrawing effect of the substituents on the thiophene ring in thienochromones. We succeeded in performing formylation of **11a–f** with dichloromethyl ether in the presence of $SnCl_4$ (Scheme 5).

The presence of the aldehyde group allows the further modification of the thienochromones, in particular, the synthesis of azomethines or unsaturated ketones (Scheme 6).

We examined the possibility of synthesizing compounds **19a–e**. The presence of two thienochromyl moieties in the molecules should enhance the fluorescence properties of the compounds. In addition, certain analogs, containing the 2,2-diarylethanone moiety (*e.g.* PD85639) have a local anesthetic effect due to selective sodium channel blockade in cells.[16]

Bis(thienochromones) **19a–e** were synthesized by the reaction of two equivalents of thiophene-containing derivatives **11a–f** with one equivalent of ketoaldehydes **17** in the presence of tin tetrachloride (Scheme 7). We failed to isolate intermediate **18**, which could be formed in the reaction. It should be noted that the formation of this type of compounds in the reactions with ketoaldehydes has not been documented earlier in the literature.



Scheme 6 *Reagents and conditions*: (i) EtOH, reflux; (ii) KOH (40% aq.), EtOH, r.t. (in case of **16a** an acetone–ethanol mixture (1 : 1) and ice cooling are used).

The structures of compounds **19a–e** were established by spectroscopy and elemental analysis. Bis(thienochromone) **19a** was studied by X-ray diffraction (Fig. 2).

According to X-ray diffraction data, the compound **19a** in the crystal exists in a keto-form with the C(43)–O(44) bond length being 1.224(3) Å and all covalent bonds formed by the C(22) atom (1.512(3)–1.547(3) Å) are close to ordinary C–C ones (Fig. 3). As the consequence, there is no conjugation between the heterocyclic moieties in **19a**. The C═O double bond is almost coplanar with one of the heterocycles, namely C(23)–S(35), with the value of the pseudo-torsion angle

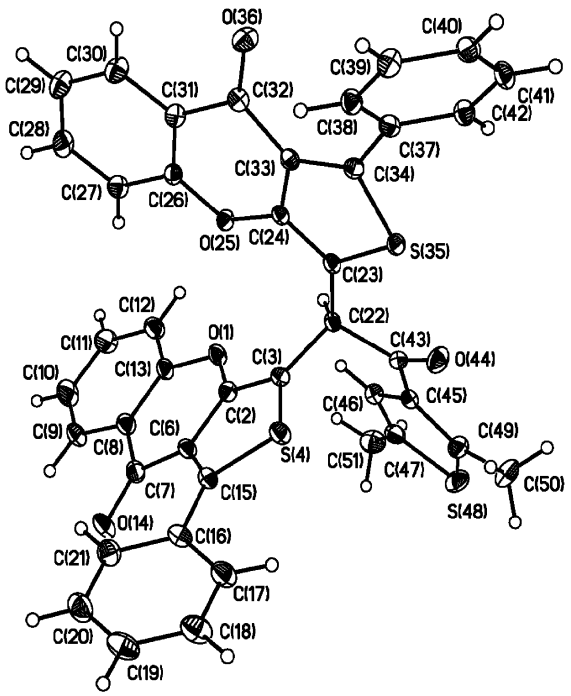
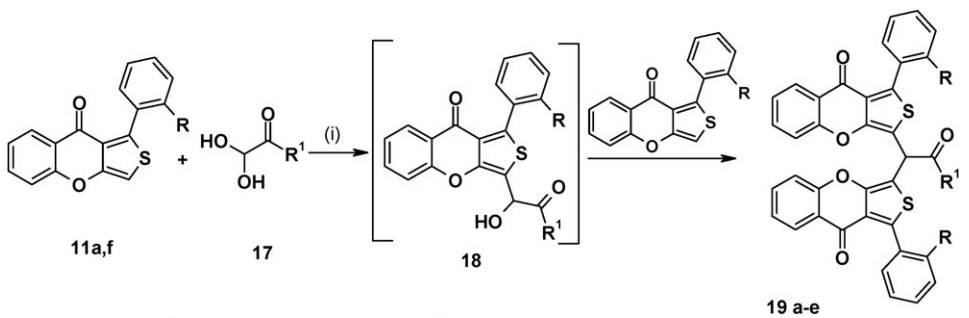


Fig. 2 The general view of **19a** with representation of atoms *via* thermal ellipsoids (p = 50%).



Scheme 7 *Reagents and conditions*: (i) tin(IV) chloride, CH_2Cl_2, r.t., 1 h.

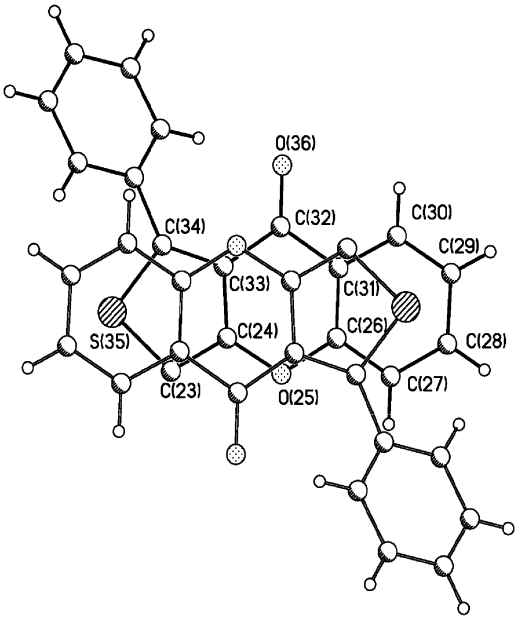


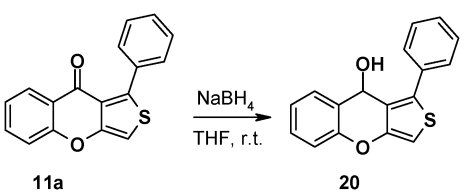
Fig. 3 The stacking interaction in crystal of **19a**.

S(35)C(23)C(43)O(44) equal to 12.7°. Such disposition of C═O bond leads to the formation of the shortened intramolecular contact O(44)···S(35); the corresponding interatomic distance is equal to 2.659(2) Å. Considering its directionality—the bond angle O(44)S(35)C(34) is 169.5(1)°—we can expect the presence of a charge transfer from the lone pair on oxygen to the antibonding C–S orbital. However, comparing the similar S(35)–C(34) and S(4)–C(15) bonds clearly shows that, despite the possible charge transfer, the former is shorter (1.717(2) *vs.* 1.728(2) Å). At the same time, we cannot exclude that this variation of S–C bond lengths is caused by crystal packing effects. Indeed, the C(23)–S(35) fragment in the crystal of **19a** participates in the formation of an intermolecular stacking interaction with its symmetry-related analogue (Fig. 3). This contact is rather strong with the smallest C···C distance of 3.396(2) Å and a pronounced overlap of π-systems.

To study the relationship between the thienochromone structure, on the one hand, and the biological activity and the fluorescence properties of the compounds, on the other hand, we reduced the carbonyl group in compound **11a** (Scheme 8).

Principal spectral/luminescent characteristics of the synthesized compounds are presented in Fig. 4–6 and Table 1.

These data were compared with the corresponding parameters of compound **11a**, whose spectral/luminescent characteristics are presented in Fig. 4 and Table 1.



11a **20**

Scheme 8

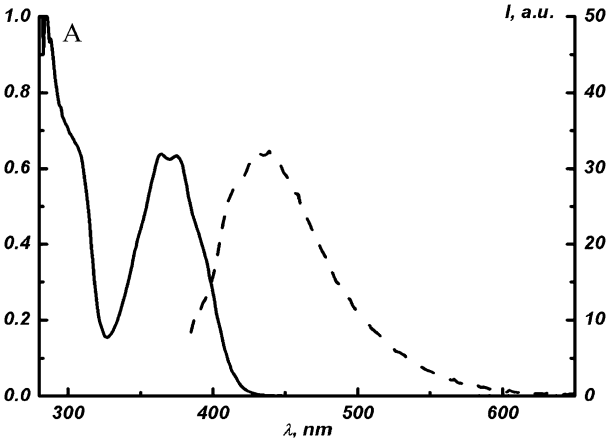


Fig. 4 Absorption spectra (1) and fluorescence spectra (2) of a solution of compound **11a** in toluene. The fluorescence excitation wavelength is 375 nm.

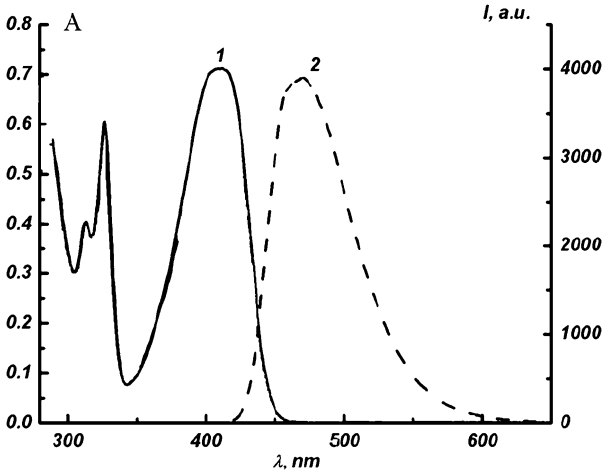


Fig. 5 Absorption spectra (1) and fluorescence spectra (2) of a solution of compound **11c** in toluene. The fluorescence excitation wavelength is 410 nm.

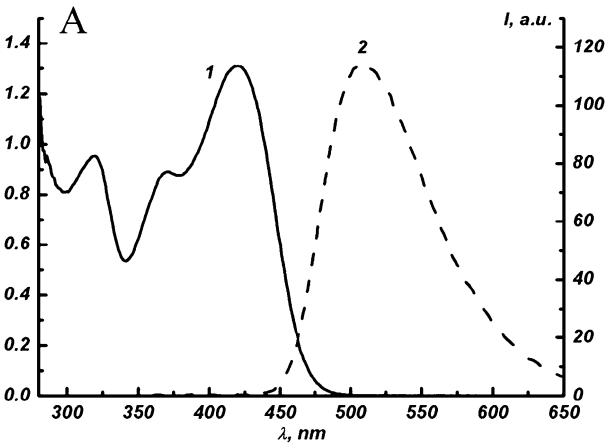


Fig. 6 Absorption spectra (1) and fluorescence spectra (2) of a solution of compound **16b** in toluene. The fluorescence excitation wavelength is 420 nm.

Table 1 Spectral/luminescent characteristics of the synthesized compounds[a]

Structure	λ_{abs}^{max}/nm (D^{ini})	$10^{-4}\varepsilon$/l cm^{-1} M^{-1}	λ_{flu}^{max}/nm	I_{flu}/a.u.
10	380 (0.28)	0.70	470	40
11a	370 (0.62)	1.55	435	30
11b	324 (0.24)	0.60		
	406 (0.32)	0.80	485	605
11c	311 (0.40)	1.00		
	326 (0.60)	1.50	470	3915
	410 (0.71)	1.78		
11d	375 (0.21)	0.52	460	30
11h	383 (0.36)	0.90	472	245
13	380 (0.55)	1.38	473	100
14a	320 (0.29)	0.72	458	5
	380 (0.37)	0.92		
16a	315 (0.61)	1.52	505	120
	339 (0.43)	1.08		
	405 (0.46)	1.15		
16c	320 (0.54)	1.35	510	60
	367 (0.56)	1.40		
	415 (0.80)	2.00		
16b	318 (0.95)	2.38	510	100
	360 (0.89)	2.22		
	420 (1.30)	3.25		
20	304 (0.32)	0.80	370	225

[a] λ_{abs}^{max} and λ_{flu}^{max} are the wavelengths of the absorption and fluorescence maxima, respectively, D^{ini} is the absorbance at the absorption maxima, ε is the molar extinction coefficient, and I_{flu} is the relative fluorescence intensity.

As can be seen from Fig. 4, compound **11a** is characterized by an intense structured absorption band with a maximum at 370 nm. The excitation of compound **11a** at the absorption maximum of this compound causes the fluorescence with the maximum intensity at 435 nm.

The disruption of the conjugation due to reduction of the carbonyl group to an alcohol group (compound **20**) leads to a strong hypsochromic shift (by 65 nm) of the absorption and fluorescence maxima (to 304 and 370 nm, respectively). However, this is accompanied by an increase in the fluorescence intensity.

The introduction of the thienyl (compound **11b**) or furyl (compound **11c**) substituent instead of the phenyl group causes substantial bathochromic shifts of both the absorption and fluorescence bands, which is accompanied by a sharp increase in the fluorescence intensity, particularly for compound **11c** containing the furan substituent. Apparently, this is attributed to the stronger electron-donating ability of these substituents compared to the phenyl-substituted compound. The absorption spectra of these compounds show short-wavelength absorption bands apparently assigned to the nature of these groups (Fig. 5).

An analogous strong bathochromic shift is observed for the fluorescence band of compound **11a** after the introduction of the weak electron-donating methyl group into the thiophene moiety (compound **11d**), which is accompanied by a decrease in the fluorescence intensity.

In the presence of electron-withdrawing substituents either in the phenyl (compound **11d**) or thiophene (compounds **9a** and **13**) moieties, weak fluorescence is observed; the fluorescence intensity of these compounds is comparable with that of unsubstituted compound **11a** (Table 1). This is accompanied by a slight bathochromic shift of the fluorescence maximum and an increase in the fluorescence intensity with increasing electron-withdrawing ability of the substituents.

The introduction of the formyl group (compound **14a**) leads to a sharp decrease in the fluorescence intensity even compared to compound **11a**, which is accompanied by a bathochromic shift of the fluorescence band.

The replacement of the formyl group by the ethylenic ketone (compound **16a**), ethylenic ketophenol (compound **16c**), or ethylenic ketothiophene (compound **16b**) group causes bathochromic shifts of the absorption and fluorescence maxima in accordance with an increase in the number of conjugated bonds. However, the fluorescence intensity of these compounds is lower than that of compounds **11b**, **11c** and **11e**, which may be associated with a partial photoexcitation energy loss for the *cis–trans* isomerization of these substituents and, consequently, with a decrease in the fluorescence efficiency. These compounds, like compound **11c**, are characterized by the complex absorption spectrum in the UV region (Fig. 6).

A comparative analysis of the spectral/luminescent characteristics of the newly synthesized compounds shows that the positions of the absorption and fluorescence bands, as well as the fluorescence intensity, substantially depend on the nature of the substituents in the thiophene moiety. The compounds containing the thienyl or furyl substituent in the thiophene moiety of chromones have the best fluorescence properties. The structure–property relationships revealed in the present study suggest possibilities for a further improvement of the spectral/luminescent characteristics of this class of compounds by the directed synthesis.

Experimental

General procedures

^{1}H NMR spectra were recorded on Bruker AM-300, Bruker AC-200 (200 MHz) and WM-250 (250 MHz) instruments in DMSO-d_6 or $CDCl_3$. Mass spectra were obtained on a Varian MAT CH-6 instrument using a direct inlet system; the ionization energy was 70 eV; the acceleration voltage was 1.75 kV. The melting points were measured on a Boetius hot-stage apparatus and are uncorrected. The reaction mixtures were analyzed and the purity of all products was checked by TLC on Merck Silica gel 60 F254 UV-254 plates. Compounds **17** were prepared from corresponding acetyl derivatives according to literature methods.[17]

Spectral/luminescent study of synthesized compounds were carried out in toluene (Aldrich) solutions at 25 °C. A Cary 50 bio. Spectrophotometer (Varian) was used to measure the absorption spectra; the concentration of compounds in solution was $C = 2 \times 10^{-4}$ mol dm^{-3}. Absorption spectra were measured in quartz cuvettes with thickness 0.2 cm.

Fluorescence spectra were taken using quartz cuvettes (thickness 1 cm) on a Cary Eclipse spectrofluorimeter (Varian). The working concentrations of compounds in solution was $C = 4 \times 10^{-5}$ mol dm^{-3}.

General procedure for acylation of 2′-hydroxyacetophenones (5)

Freshly distilled anhydrous pyridine (5 ml) was added to 2′-hydroxyacetophenone or 2′-hydroxy-5′-methylacetophenone

(25 mmol) under cooling with iced water. Then aromatic acid chloride (30 mmol) was added dropwise at <25 °C. The mixture was allowed to stand for 40–60 min at room temperature and then poured into a cold 3% hydrochloric acid solution. The precipitate that formed was filtered off, dried, and recrystallized from ethanol.

2-Acetylphenyl benzoate (5a). Yield 90%, mp = 87–88 °C (EtOH) (lit. 87–88 °C[18]). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J = 7.5 Hz, $2H_{Ar}$), 7.87 (d, J = 7.8, Hz, $1H_{Ar}$), 7.72–7.50 (m, $4H_{Ar}$), 7.39 (t, J = 7.5, $1H_{Ar}$), 7.25 (d, J = 7.7 Hz, $1H_{Ar}$), 2.57 (s, $3H_{Me}$). Anal. Calc. for $C_{15}H_{12}O_3$: C 74.99; H 5.03. Found: C 75.16; H 4.98%.

2-Acetylphenyl 4-chlorobenzoate (5b). Yield 90%, mp = 93–94 °C (EtOH) (lit 92–93 °C[19]). ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 8.4 Hz, $2H_{Ar}$), 7.88 (d, J = 7.7 Hz, $1H_{Ar}$), 7.22–7.65 (m, $5H_{Ar}$), 2.55 (s, $3H_{Me}$). MS m/z 274, 183, 142, 141, 140, 139, 121, 113, 111. Anal. Calc. for $C_{15}H_{11}ClO_3$: C 65.59; H 4.04; Cl 12.91. Found: C 65.47; H 3.38; Cl 12.80%.

2-Acetylphenyl furan-2-carboxylate (5c). Yield 80%, mp = 90–92 °C (EtOH) (lit. 92 °C[20]). ^{1}H NMR ($CDCl_3$) δ 7.87 (d, J = 7.7 Hz, $1H_{Ar}$), 7.7 (s, 1H), 7.58 (t, J = 7.62 Hz, $1H_{Ar}$), 7.25–7.45 (m, $3H_{Ar}$), 6.63 (dd, J = 3.2, 1.4 Hz, $1H_{Ar}$), 2.58 (s, $3H_{Me}$). Anal. Calc. for $C_{13}H_{10}O_4$: C 67.82; H 4.38. Found: C 67.69; H 4.30%.

2-Acetylphenyl thiophene-2-carboxylate (5d). Yield 86%, mp = 113–114 °C (EtOH) (lit. 112–114 °C[21]). ^{1}H NMR ($CDCl_3$) δ 8.05 (d, J = 3.3 Hz, $1H_{Ar}$), 7.87 (dd, J = 7.7, 1.3 Hz, $1H_{Ar}$), 7.70 (d, J = 4.5 Hz, $1H_{Ar}$), 7.60 (dt, J = 7.7, 1.5 Hz, $1H_{Ar}$), 7.38 (t, J = 7.4 Hz, $1H_{Ar}$), 7.17–7.20 (m, $2H_{Ar}$), 2.59 (s, $3H_{Me}$). Anal. Calc. for $C_{13}H_{10}O_3S$: C 63.40; H 4.09; S 13.02. Found: C 63.50; H 3.98; S 13.13%.

2-Acetyl-4-methylphenyl thiophene-2-carboxylate (5e). Yield 84%, mp = 90–91 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 8.0 (d, J = 3.6 Hz, $1H_{Ar}$), 7.63–7.71 (m, $2H_{Ar}$), 7.37 (d, J = 8.2 Hz, $1H_{Ar}$), 7.1–7.2 (m, $2H_{Ar}$), 2.55 (s, $3H_{Me}$), 2.42 (s, $3H_{Me}$). Anal. Calc. for $C_{14}H_{12}O_3S$: C 64.60; H 4.65; S 12.32. Found: C, 64.50; H, 4.58; S, 12.45%.

2-Acetylphenyl 2-chlorobenzoate (5f). Yield 88%, mp = 63–65 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 8.19 (d, J = 6.9 Hz, $1H_{Ar}$), 7.88 (d, J = 7.8 Hz, $1H_{Ar}$), 7.30–7.65 (m, $6H_{Ar}$), 2.58 (s, $3H_{Me}$). Anal. Calc. for $C_{15}H_{11}ClO_3$: C 65.59; H 4.04; Cl 12.91. Found: C 65.45; H 3.93; Cl 12.99%.

2-Acetylphenyl 2-brombenzoate (5g). Yield 70%, mp = 72–74 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 8.18 (d, J = 7.3 Hz, $1H_{Ar}$), 7.88 (d, J = 7.7 Hz, $1H_{Ar}$), 7.75 (d, J = 7.6 Hz, $1H_{Ar}$), 7.62 (t, J = 7.7 Hz, $1H_{Ar}$), 7.25–7.35 (m, $4H_{Ar}$), 2.59 (s, $3H_{Me}$). Anal. Calc. for $C_{15}H_{11}BrO_3$: C 56.45; H 3.47; Br 25.04. Found: C 56.38; H 3.58; Br 24.90%.

General procedure for the preparation of propane-1,3-dione derivatives (6)

A solution of *o*-acyloxyacetophenone (**5**) (0.0125 mol) in DMF (20 ml) was added to a solution of *t*-BuOK (2.8 g, 0.025 mol) under argon at 0 °C during 10 min. The mixture was kept for 1 h and then poured into an ice-cooled 3% hydrochloric acid solution. The product that precipitated was filtered off, dried in air, and recrystallized from ethanol.

1-(2-Hydroxyphenyl)-3-phenylpropane-1,3-dione (6a). Yield 83%, mp = 121–122 °C (EtOH) (lit. 122 °C[22]) ^{1}H NMR ($CDCl_3$) δ 15.55 (s, $1H_{OH}$), 12.10 (s, $1H_{OH}$), 7.95 (d, J = 6.6 Hz, $2H_{Ar}$), 7.80 (d, J = 7.9 Hz, $1H_{Ar}$), 7.40–7.70 (m, $4H_{Ar}$), 6.80–7.10 (m, $3H_{Ar}$). Anal. Calc. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.85; H, 4.96%.

1-(2-Hydroxyphenyl)-3-(4-chlorophenyl)propane-1,3-dione (6b). Yield 66%, mp = 125–127 °C (EtOH) (lit. 122–124 °C[19]). ^{1}H NMR ($CDCl_3$) δ 15.52 (s, $1H_{OH}$), 12.00 (s, $1H_{OH}$) 7.88 (d, J = 9.3 Hz, $2H_{Ar}$), 7.78 (d, J = 9.2 Hz, $1H_{Ar}$) 7.5 (m, $3H_{Ar}$), 6.69–7.05 (m, $2H_{Ar}$), 6.81 (s, 1H). Anal. Calc. for $C_{15}H_{11}ClO_3$: C 65.59; H 4.04; Cl 12.91. Found: C, 65.45; H, 3.99; Cl, 12.80%.

1-(2-Hydroxyphenyl)-3-(furan-2-yl)propane-1,3-dione (6c). Yield 70%, mp = 85–87 °C (EtOH) (lit. 88 °C[23]). ^{1}H NMR ($CDCl_3$) δ 15.12 (s, $1H_{OH}$), 12.11 (s, $1H_{OH}$), 7.80 (d, J = 8.1 Hz, $1H_{Ar}$), 7.65 (s, $1H_{Ar}$), 7.50 (t, J = 7.8 Hz, $1H_{Ar}$), 7.19 (d, J = 3.5 Hz, $1H_{Ar}$), 6.89–7.02 (m, $2H_{Ar}$), 6.6.79 (s, 1H), 6.61 (m, $1H_{Ar}$). Anal. Calc. for $C_{13}H_{10}O_4$: C 67.82; H 4.38. Found: C, 67.68; H 4.31%.

1-(2-Hydroxyphenyl)-3-(thiophen-2-yl)propane-1,3-dione (6d). Yield 67%, mp = 90–92 °C (EtOH) (lit. 86–87 °C[14]). ^{1}H NMR ($CDCl_3$) δ 11.30 (s, $1H_{OH}$), 11.00 (s, $1H_{OH}$), 7.80–8.10 (m, $3H_{Ar}$), 7.40–7.60 (m, $1H_{Ar}$), 7.25–7.35 (m, $1H_{Ar}$), 6.90–7.00 (m, $2H_{Ar}$), 4.80 (s, 1H). Anal. Calc. for $C_{13}H_{10}O_3S$: C, 63.40; H, 4.09; S, 13.02. Found: C, 63.50; H, 4.02; S, 13.13%.

1-(2-Hydroxy-5-methylphenyl)-3-(thiophen-2-yl)propane-1,3-dione (6e). Yield 57.5%, mp 84–86 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 15.75 (s, $1H_{OH}$), 11.70 (s, $1H_{OH}$), 7.50–7.80 (m, $3H_{Ar}$), 6.70–7.35 (m, $3H_{Ar}$), 4.45 (s, 1H), 2.36 (s, $3H_{Me}$). Anal. Calc. for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65; S, 12.32. Found: C 64.45; H 4.57; S 12.47%.

1-(2-Hydroxyphenyl)-3-(2-chlorophenyl)propane-1,3-dione (6f). Yield 78%, mp = 92 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 14.8 (s, $1H_{OH}$), 12.02 (s, $1H_{OH}$), 7.66–7.74 (m, $2H_{Ar}$), 7.34–7.52 (m, $4H_{Ar}$), 6.88–7.04 (m, $2H_{Ar}$), 6.80 (s, 1H). Anal. Calc. for $C_{15}H_{11}ClO_3$: C 65.59; H 4.04; Cl 12.91. Found: C 65.72; H 4.20; Cl 13.02%.

1-(2-Hydroxyphenyl)-3-(2-bromphenyl)propane-1,3-dione (6g). Yield 86%, mp = 85–88 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 15.19 (s, $1H_{OH}$), 12.04 (s, $1H_{OH}$), 7.30–7.73 (m, $6H_{Ar}$), 6.88–7.04 (m, $2H_{Ar}$), 6.72 (s, 1H). Anal. Calc. for, $C_{15}H_{11}BrO_3$: C 56.45; H 3.47; Br 25.04. Found: C 56.38; H 3.56; Br 24.95%.

General procedure for the preparation of 3-acyl-2-alkyl-4*H*-chromen-4-ones (7)

AcONa/C_2H_5COONa (6.5 mmol) was added to diketone (6.5 mmol) in 10 ml of acetic anhydride/propionic anhydride. The reaction solution was refluxed for 30–60 min (TLC monitoring). After completion of the reaction, the solution

was poured into water. The solid compound was filtered off and recrystallized from EtOH.

3-Benzoyl-2-methyl-4*H*-chromen-4-one (7a). Yield 90%, mp = 115–117 °C (EtOH) (lit. 117 °C[19]). ^{1}H NMR ($CDCl_3$), δ 8.20 (d, J = 7.8 Hz, 1H$_{Ar}$), 7.92 (d, J = 6.9, 2H$_{Ar}$), 7.70 (t, J = 7.6 Hz, 1H$_{Ar}$), 7.60 (d, J = 7.3 Hz, 1H$_{Ar}$), 7.40–7.51 (m, 4H$_{Ar}$), 2.4 (s, 3H$_{Me}$). Anal. Calc. for $C_{17}H_{12}O_3$: C 77.26; H 4.58. Found: C 77.12; H 4.50%.

3-(4-Chlorobenzoyl)-2-methyl-4*H*-chromen-4-one (7b). Yield 79%, mp = 126 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.18 (d, J = 7.8 Hz, 1H), 8.85 (d, J = 8.4 Hz, 2H), 7.72 (t, J = 7.8 Hz, 1H), 7.40–7.52 (m, 4H), 2.41 (s, 3H). Anal. Calc. for $C_{17}H_{11}ClO_3$: C 68.35; H 3.71; Cl 11.87. Found: C 68.27; H 3.60; Cl 11.83%.

3-(Furancarbonyl)-2-methyl-4*H*-chromen-4-one (7c)

Yield 78.5%, mp = 146–148 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.18 (d, J = 7.9 Hz, 1H$_{Ar}$), 7.60–7.72 (m, 2H$_{Ar}$), 7.43 (t, J = 7.0 Hz, 2H$_{Ar}$), 7.20 (d, J = 3.5 Hz, 1H$_{Ar}$), 6.55 (t, J = 1.7 Hz, 1H$_{Ar}$), 2.40 (s, 3H$_{Me}$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 180.6 (C=O), 175.5 (C=O), 166.0, 155.9, 153.0, 147.5, 134.1, 126.0, 125.6, 123.6, 122.6, 120.1, 117.9, 112.7, 19.0 (CH_3). Anal. Calc. for $C_{15}H_{10}O_4$: C 70.86; H 3.96. Found: C 70.80; H 4.03%.

2-Methyl-3-(thiophene-2-carbonyl)-4*H*-chromen-4-one (7d). Yield 75%, mp = 116–118 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.20 (d, J = 7.9 Hz, 1H$_{Ar}$), 7.71 (t, J = 6.5 Hz, 2H$_{Ar}$).7.62 (d, J = 3.2 Hz, 1H$_{Ar}$), 7.39–7.50 (m, 2H$_{Ar}$), 7.12 (t, J = 4.2 Hz, 1H$_{Ar}$), 2.42 (s, 3H$_{Me}$). Anal. Calc. for $C_{15}H_{10}O_3S$: C 66.65; H 3.73; S 11.86. Found: C 66.58; H 3.84; S 11.75%.

2,6-Dimethyl-3-(thiophene-2-carbonyl)-4*H*-chromen-4-one (7e). Yield 60%, mp = 123–125 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.0 (s, 1H$_{Ar}$), 7.71 (d, J = 4.9 Hz, 1H$_{Ar}$), 7.62 (d, J = 3.8 Hz, 1H$_{Ar}$), 7.50 (d, J = 9.5, 1H$_{Ar}$), 7.37 (d, J = 8.6 Hz, 1H$_{Ar}$), 7.11 (t, J = 4.3 Hz, 1H$_{Ar}$), 2.47 (s, 3H$_{Me}$), 2.40 (s, 3H$_{Me}$). Anal. Calc. for $C_{16}H_{12}O_3S$: C 67.59; H 4.25; S 11.28. Found: C 67.48; H 4.40; S 11.15%.

3-(2-Chlorobenzoyl)-2-methyl-4*H*-chromen-4-one (7f). Yield 94%, mp = 157–159 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.12 (d, J = 7.9 Hz, 1H$_{Ar}$), 7.66–7.73 (m, 2H$_{Ar}$), 7.40–7.49 (m, 5H$_{Ar}$), 2.61 (s, 3H$_{Me}$). Anal. Calc. for $C_{17}H_{11}ClO_3$: C 68.35; H 3.71; Cl 11.87. Found: C 68.28; H 3.82; Cl 11.94%.

3-(2-Brombenzoyl)-2-methyl-4*H*-chromen-4-one (7g). Yield 80%, mp = 156–158 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.12 (d, J = 7.9 Hz, 1H$_{Ar}$), 7.58–7.73 (m, 3H$_{Ar}$), 7.33–7.49 (m, 4H$_{Ar}$), 2.63 (s, 3H$_{Me}$). Anal. Calc. for $C_{17}H_{11}BrO_3$: C 59.50; H 3.23; Br 23.28. Found: C 59.38; H 3.41; Br 23.20%.

3-Benzoyl-2-ethyl-4*H*-chromen-4-one (7h). Yield 60%, mp = 63–65 °C (EtOH) (lit. 64–65 °C[24]). ^{1}H NMR ($CDCl_3$), δ 8.19 (dd, J = 8.0, 1.5 Hz, 1H$_{Ar}$), 7.94 (d, J = 8.5 Hz, 2H$_{Ar}$), 7.72 (t, J = 8.6 Hz, 1H$_{Ar}$), 7.60 (t, J = 7.3 Hz, 1H$_{Ar}$), 7.41–7.53 (m, 4H$_{Ar}$), 2.65 (q, J = 7.5 Hz, 2H$_{CH}$), 1.32 (t, J = 7.5 Hz, 3H$_{Me}$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 193.9, 176.2, 169.3, 156.2, 137.3, 134.1, 133.9, 129.5, 128.8, 126.1, 125.5, 123.6, 122.5, 118.0, 26.4, 11.8. Anal. Calc. for $C_{18}H_{14}O_3$: C 77.68; H 5.07. Found: C 77.55; H 5.15%.

General procedure for the preparation of 3-acyl-2,2-dibromomethyl-4*H*-chromen-4-one (8)

A solution of bromine (7.5 mmol) in 5 ml of CCl_4 was added portionwise to methylchromone **7** (3.4 mmol) in 20 ml of hot CCl_4. The solution was refluxed for 1.5–2 h (TLC monitoring). After completion of the reaction, the solution was concentrated. The solid compound was washed or recrystallized from EtOH.

2,2-Dibromomethyl-3-benzoyl-4*H*-chromen-4-one (8a). Yield 85%, mp = 157 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.20 (d, J = 9.2 Hz, 1H$_{Ar}$), 7.79–7.92 (m, 3H$_{Ar}$); 7.61–7.73 (m, 2H$_{Ar}$), 7.47–7.53 (m, 3H$_{Ar}$), 6.5 (s, 1H$_{CH}$). MS (EI 70 eV) m/z (relative intensity): 424(2), 422(3), 420(2), 346(1), 345(3), 343(76), 342(75), 241(11), 314(1), 277(3), 267(3), 265(16), 264(16), 263(100), 262(23), 250(4), 249(32), 236(22), 235(67), 234(35), 233(59). Anal. Calc. for $C_{17}H_{10}Br_2O_3$: C 48.38; H 2.39; Br 37.86. Found: C 48.23; H 2.43; Br 37.80%.

2,2-Dibromomethyl-3-(4-chlorobenzoyl)-4*H*-chromen-4-one (8b). Yield 89%, mp = 196–197 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.19 (d, J = 8.0 Hz, 1H$_{Ar}$), 7.69–7.88 (m, 4H$_{Ar}$), 7.43–7.55 (m, 3H$_{Ar}$), 6.5 (s, 1H$_{CH}$). MS (EI 70 eV) m/z (relative intensity): 457(5), 456(11), 455(7), 380(1), 379(31), 377(77), 376(67), 342(14), 340(31), 298(31), 297(7), 296(100), 283(26), 271(24), 270(41), 269(57), 262(66). Anal. Calc. for $C_{17}H_9Br_2ClO_3$: C 44.73; H 1.99; Br 35.01; Cl 7.77. Found: C 44.61; H 2.10; Br 34.97; Cl 7.65%.

2,2-Dibromomethyl-3-(thiophene-2-carbonyl)-4*H*-chromen-4-one (8d). Yield 55%, mp = 153–155 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.22 (d, J = 7.8, 1H$_{Ar}$), 7.47–7.87 (m, 5H$_{Ar}$), 7.16 (d, J = 3.7 Hz, 1H$_{Ar}$), 6.5 (s, 1H$_{CH}$). MS (EI 70 eV) m/z (relative intensity): 430(12), 428(16), 427(5), 426(10), 350(4), 349(26), 348(43), 347(30), 349(41), 302(5), 280(6), 270(15), 269(100), 268(96), 266(17). Anal. Calc. for $C_{15}H_8Br_2O_3S$: C 42.09; H 1.88; Br 37.33; S 7.49. Found: C 41.98; H 2.00; Br 37.07; S 7.44%.

General procedure for the preparation of 3-acyl-2-bromoalkyl-4*H*-chromen-4-one (9)

Bromine (0.84 mmol) was added portionwise to alkylchromone **7** (0.76 mmol) in 5 ml of hot CCl_4. The solution was stirred for 30 min at 60–70 °C (TLC monitoring). After completion of the reaction, the solution was concentrated. The solid compound was washed with or recrystallized from EtOH. The resulting ethanol solution contains a small amount of dibromide **8** that can be isolated by column chromatography.

2-Bromomethyl-3-benzoyl-4*H*-chromen-4-one (9a). Yield 80%, mp = 152–153 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.18 (d, J = 7.7 Hz, 1H$_{Ar}$), 7.91 (d, J = 7.62 Hz, 2H$_{Ar}$), 7.77 (t, J = 7.7 Hz, 1H$_{Ar}$), 7.46–7.68 (m, 5H$_{Ar}$), 4.34 (s, 2H$_{CH}$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 193.2 (C=O), 176.3 (C=O), 162.1, 156.0, 137.3, 135.1, 134.0, 129.8, 129.2, 126.5, 126.4, 123.9, 118.6, 25.2. MS (EI 70 eV) m/z (relative intensity): 343(2), 315(6), 313(4), 297(1), 278(2), 265(12), 264(43), 263(100),

262(4). Anal. Calc. for $C_{17}H_{11}BrO_3$: C 59.50; H 3.23; Br 23.28. Found: C 59.62; H 3.35; Br 23.20%.

2-Bromomethyl-3-(4-chlorobenzoyl)-4*H*-chromen-4-one (9b). Yield 94%, mp = 177–179 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.19 (d, J = 8.1 Hz, 1H_{Ar}), 7.75–7.89 (m, 3H_{Ar}), 7.60–7.44 (m, 4H), 4.36 (s, 2H_{CH}). MS (EI 70 eV) m/z (relative intensity): 380(13), 378(17), 377(5), 376(9), 342(3), 300(9), 299(40), 298(22), 297(100), 284(3), 283(6), 272(2), 271(32), 269(52), 267(6), 262(27). Anal. Calc. for $C_{17}H_{10}BrClO_3$: C 54.07; H 2.67; Br 21.16; Cl 9.39. Found: C 54.13; H 2.55; Br 21.07; Cl 9.33%.

2-Bromomethyl-(3-furan-2-carbonyl)-4*H*-chromen-4-one (9c). Yield 65%, mp = 182–183 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.22 (d, J = 8.0 Hz, 1H_{Ar}), 7.76 (t, J = 7.7 Hz, 1H_{Ar}), 7.67 (s, 1H_{Ar}), 7.55 (d, J = 8.5 Hz, 1H_{Ar}), 7.47 (t, J = 7.6 Hz, 1H_{Ar}), 7.29 (s, 1H_{Ar}), 6.6 (s, 1H_{Ar}), 4.37 (s, 2H_{CH}). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 179.1 (C=O), 175.6 (C=O), 162.2, 155.9, 152.7, 148.0, 134.8, 126.2, 126.1, 123.66, 120.93, 118.23, 112.92. MS (EI 70 eV) m/z (relative intensity): 334(2), 332(2), 280(1), 265(2), 255(3), 254(16), 253(100), 252(59), 237(2), 236(5), 228(2), 227(15), 226(94), 225(34), 224(20), 223(6). Anal. Calc. for $C_{15}H_9BrO_4$: C 54.08; H 2.72; Br 23.99. Found: C 53.97; H 2.60; Br 23.87%.

2-Bromomethyl-3-(thiophene-2-carbonyl)-4*H*-chromen-4-one (9d). Yield 69%, mp = 158–160 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.21 (d, J = 7.8 Hz, 1H_{Ar}), 7.87–7.54 (m, 5H_{Ar}), 7.13-7.14 (m, 1H_{Ar}), 4.34 (s, 2H_{CH}). MS (EI 70 eV) m/z (relative intensity): 351(2), 350(15), 349(4), 348(15), 347(4), 270(26), 269(80), 242(13), 241(46), 240(33), 239(36), 225(17), 213(9), 209(26), 187(21), 184(38), 175(7), 163(7), 151(13), 148(17), 139(46), 135, 121(100). Anal. Calc. for $C_{15}H_9BrO_3S$: C 51.59; H 2.60; Br 22.88; S 9.18. Found: C 51.48; H 2.52; Br 23.03; S 9.24%.

2-Bromomethyl-3-(2-chlorobenzoyl)-4*H*-chromen-4-one (9f). Yield 94%, mp = 128–130 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.05 (d, J = 7.9 Hz, 1H_{Ar}), 7.60–7.70 (m, 2H_{Ar}), 7.47 (d, J = 8.4 Hz, 1H_{Ar}), 7.30–7.40 (m, 4H_{Ar}), 4.52 (s, 2H_{CH}). MS (EI 70 eV) m/z (relative intensity): 378(1), 376(1), 343(8), 341(8), 296(3), 265(4), 264(41), 263(100), 262(34), 261(7). Anal. Calc. for $C_{17}H_{10}BrClO_3$: C 54.07; H 2.67; Br 21.16; Cl 9.39. Found: C 54.18; H 2.80; Br 21.03; Cl 9.23%.

2-Bromomethyl-3-(2-brombenzoyl)-4*H*-chromen-4-one (9g). Yield 82%, mp = 155–156 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.12 (d, J = 7.7 Hz, 1H_{Ar}), 7.78–7.43 (m, 7H_{Ar}), 4.61 (s, 2H_{CH}), MS (EI 70 eV) m/z (relative intensity): 344(2), 342(2), 265(5), 264(58), 263(100), 262(51), 249(23), 236(27), 235(52), 234(12), 205(6), 191(2), 189(6), 187(34). Anal. Calc. for $C_{17}H_{10}Br_2O_3$: C 48.38; H 2.39; Br 37.86. Found: C 48.29 H 2.45 Br 37.80%.

3-Benzoyl-2-(1-bromoethyl)-4*H*-chromen-4-one (9h). Yield 75%, mp = 105–106 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.19 (d, J = 7.9 Hz, 1H_{Ar}), 7.93 (d, J = 7.6 Hz, 2H_{Ar}), 7.78 (t, J = 7.8 Hz, 1H_{Ar}), 7.60–7.67 (m, 2H_{Ar}). 7.45–7.55 (m, 3H_{Ar}), 5.00 (q, J = 13.6, 6.8 Hz, 1H_{CH}), 2.05 (d, J = 6.8 Hz, 3H_{Me}). MS (EI 70 eV) m/z (relative intensity): 358(4), 356(4), 284(2), 279(6), 278(14), 277(100), 276(53), 275(44), 263(13), 262(13), 250(6), 249(57), 248(4), 247(35), 235(2), 234(13). Anal. Calc. for $C_{18}H_{13}BrO_3$: C 60.53; H 3.67; Br 22.37. Found: C 60.43; H 3.56; Br 22.48%.

Procedure for the preparation of 5-bromo-1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one (10)

Thienochromone **11** (1 mmol) was dissolved in 5 ml of dichloromethane. Then Br_2 (1.1 mmol) was added portion-wise. The solution was stirred at room temperature for 1 h (TLC monitoring). The solvent was evaporated, and the residue was washed with hot ethanol.

Yield 87%, mp = 184–186 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.22 (d, J = 7.9 Hz, 1H_{Ar}), 7.67–7.74 (m, 3H_{Ar}), 7.46–7.49 (m, 4H_{Ar}), 7.32–7.36 (m, 1H_{Ar}). MS (EI 70 eV) m/z (relative intensity): 359(21), 358(98), 357(21), 356(100), 355(39), 279(9), 278(33), 277(19), 276(32), 249(5), 248(3), 221(4), 220(7), 219(3), 189(3), 179(5), 176(31), 158(6), 157(57). Anal. Calc. for $C_{17}H_9BrO_2S$: C 57.16; H 2.54; Br 22.37; S 8.98. Found: C 57.04; H 2.39; Br 22.24; S 8.93%.

General procedure for the preparation of 1-aryl-9*H*-thieno[3,4-*b*]-chromen-9-ones (11)

Thioacetamide (144 mg, 1.92 mmol) or (211 mg, 2.81 mmol) was added to 1.3 mmol of monobromo (**9**) or dibromomethyl-chromone (**8**), respectively in 5 ml of DMF. The reaction mixture was heated at 70–80 °C for 40–60 min (TLC monitoring) in the case of **9** and 80–100 °C for 60–90 min in the case of **8** (TLC monitoring), cooled to room temperature, and diluted with water. The solid product was filtered off, dried, dissolved in CH_2Cl_2/petroleum ether (1:1), and filtered through silica gel. After evaporation of the solvent, the sample was dried in air. The analytical sample was obtained by recrystallization of the compound from boiling ethanol.

1-Phenyl-9*H*-thieno[3,4-*b*]chromen-9-one (11a). Yield 86% (from **9**), 74% (from **8**), mp = 159–160 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.25 (d, J = 7.9 Hz, 1H_{Ar}), 7.65–7.77 (m, 3H_{Ar}), 7.29–7.48 (m, 5H_{Ar}), 7.02 (s, 1H_{Ar}). MS (EI 70 eV) m/z (relative intensity): 280(5), 279(19), 278(82), 277(100), 261(2), 249(1), 248(2), 233(2), 221(6), 220(2), 205(3), 195(1), 189(6), 176(8), 171(4). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 175.1 (C=O), 156.7, 153.4, 149.3, 135.3, 133.4, 130.3, 129.6, 128.5, 127.7, 123.7, 121.9, 121.5, 117.7, 102.9. Anal. Calc. for $C_{17}H_{10}O_2S$: C 73.36; H 3.62; S 11.52. Found: C 73.43; H 3.67; S 11.43%.

1-(4-Chlorophenyl)-9*H*-thieno[3,4-*b*]chromen-9-one (11b). Yield 75% (from **9**), 70% (from **8**), mp = 205 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.25 (d, J = 7.8 Hz, 1H_{Ar}), 7.70 (d, J = 8.1 Hz, 3H_{Ar}), 7.31–7.47 (m, 4H_{Ar}), 7.07 (s, 1H_{Ar}). MS (EI 70 eV) m/z (relative intensity): 315(2), 314(42), 313(36), 312(100), 311(58), 306(2), 302(1), 300(3), 295(1), 280(1), 279(4). Anal. Calc. for $C_{17}H_9ClO_2S$: C 65.28; H 2.90; Cl 11.33; S 10.25. Found: C 65.15; H 3.01; Cl 11.22; S 10.19%.

1-Furyl-9*H*-thieno[3,4-*b*]chromen-9-one (11c). Yield 75% (from **9**), mp = 138–140 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.30 (d, J = 7.9 Hz, 1H_{Ar}), 8.13 (d, J = 3.5 Hz, 1H_{Ar}), 7.67 (t, J = 7.7 Hz, 1H_{Ar}), 7.51 (s, 1H_{Ar}), 7.29–7.36 (m, 2H_{Ar}), 6.91 (s, 1H_{Ar}), 6.60 (dd, J = 3.1, 1.4 Hz, 1H_{Ar}). ^{13}C NMR ($CDCl_3$,

75 MHz), δ 174.7, 156.1, 153.0, 148.5, 143.4, 134.9, 127.3, 123.5, 121.6, 117.3, 113.86, 113.0, 100.8. MS (EI 70 eV) *m*/*z* (relative intensity): 270 (38), 269(41), 268(100), 267(30), 251(2), 242(6), 241(24), 240(57), 239(59), 214(8), 213(7), 212(65), 211(96). Anal. Calc. for $C_{15}H_8O_3S$, C 67.15; H 3.01; S 11.95. Found: C 67.23; H 3.10; S 11.82%.

1-Thienyl-9*H*-thieno[3,4-*b*]chromen-9-one (11d). Yield 85% (from **9**), 55% (from **8**), mp = 137–138 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.29 (d, *J* = 7.9 Hz, $1H_{Ar}$), 7.87 (d, *J* = 3.5 Hz, $1H_{Ar}$), 7.87 (t, *J* = 7.6 Hz, $1H_{Ar}$), 7.47 (d, *J* = 5.1 Hz, $1H_{Ar}$), 7.24–7.37 (m, $2H_{Ar}$), 7.14 (t, *J* = 4.4 Hz, $1H_{Ar}$), 6.92 (s, $1H_{Ar}$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 174.9, 156.2, 152.9, 141.9, 135.0, 134.7, 129.8, 128.7, 127.7, 127.4, 123.5, 121.5, 120.7, 117.3, 101.3. MS (EI 70 eV) *m*/*z* (relative intensity): 287(2), 286(15), 285(6), 284(100), 283(33). Anal. Calc. for $C_{15}H_8O_2S_2$: C 63.36; H 2.84; S 22.55. Found: C 63.46; H 2.99; S 22.45%.

1-(2-Chlorophenyl)-9*H*-thieno[3,4-*b*]chromen-9-one (11f). Yield 75% (from **9**), mp = 155–156 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.20 (d, *J* = 7.8 Hz, $1H_{Ar}$), 7.68 (t, *J* = 7.4 Hz, $1H_{Ar}$), 7.29–7.64 (m, 6H), 7.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 174.5, 156.7, 152.3, 143.4, 135.1, 134.8, 132.3, 132.1, 130.5, 129.7, 127.3, 126.5, 123.8, 123.5, 121.5, 117.6. MS (EI 70 eV) *m*/*z* (relative intensity): 312(2), 311(1), 280(2), 279(14), 278(20), 277(100), 276(4), 269(1), 264(3), 263(26). Anal. Calc. for $C_{17}H_9ClO_2S$: C 65.28; H 2.90; Cl 11.33; S 10.25. Found: C 65.15; H 3.01; Cl 11.40; S 10.15%.

3-Methyl-1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one (11h). Yield 55% (from **9**), mp = 142–143 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.25 (d, *J* = 7.8 Hz, $1H_{Ar}$), 7.64–7.75 (m, $3H_{Ar}$), 7.39–7.46 (m, $4H_{Ar}$), 7.25–7.30 (m, $1H_{Ar}$), 2.61 (s, $3H_{Me}$). MS (EI 70 eV) *m*/*z* (relative intensity): 294(8), 293(30), 292(87), 291(100), 277(2). Anal. Calc. for $C_{18}H_{12}O_2S$: C 73.95; H 4.14; S 10.97. Found: C 73.81; H 4.02; S 11.04%.

Procedure for the preparation of (3-aryl-4-oxo-4*H*-chromen-2-yl)-methyl acetate (12)

A solution of bromochromone **9a** (343 mg, 1 mmol) in 6 ml of DMF was added to AcONa (106.6 mg, 1.3 mmol). After stirring at 0 °C for 4 h, the temperature of the solution was raised to 30–40 °C. After completion of the reaction (TLC monitoring), the solution was poured into cold water and extracted three times with CH_2Cl_2 or AcOEt. The combined extracts were washed with brine and dried with Na_2SO_4. Petroleum ether (1 volume in the case of the CH_2Cl_2 solvent and 3 volumes in the case the AcOEt solvent) was added to the reaction solution. After filtration through silica gel and evaporation of the solvent, the solid compound was washed with cold ethanol, and a white acylated product was obtained.

(3-Benzoyl-4-oxo-4*H*-chromen-2-yl)methyl acetate (12)

Yield 65%, mp = 168 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.21 (d, *J* = 7.9 Hz, $1H_{Ar}$), 7.92 (d, *J* = 7.5 Hz, $2H_{Ar}$), 7.75 (t, *J* = 7.4 Hz, $1H_{Ar}$), 7.44–7.63 (m, $5H_{Ar}$), 5.07 (s, $2H_{CH}$), 1.85 (s, $3H_{Me}$). MS (EI 70 eV) *m*/*z* (relative intensity): 324(3), 322(11), 321(2), 293(9), 281(2), 280(31), 279(50), 264(6), 263(31), 262(100), 252(5), 251(7), 250(6), 249(18), 236(2), 235(13), 234(38). Anal. Calc. for $C_{19}H_{14}O_5$: C 70.80; H 4.38. Found: C 70.71; H 4.33%.

Procedure for the preparation of 3-iodo-1-phenyl-9*H*-thieno[3,4-*b*]-chromen-9-one (13)

Thienochromone **11a** (278 mg, 1 mmol) was dissolved in 3 ml of benzene. Then HgO (217 mg, 1 mmol) and I_2 (258 mg, 1 mmol) were successively added portionwise. The solution was stirred at room temperature for 1 h (TLC monitoring). The solvent was evaporated. The residue was washed with hot ethanol.

Yield 82%, mp = 176–178 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.22 (dd, *J* = 7.9, 1.6 Hz, $1H_{Ar}$), 7.66–7.75 (m, $3H_{Ar}$), 7.44–7.51 (m, $4H_{Ar}$), 7.26–7.38 (m, $1H_{Ar}$). MS (EI 70 eV) *m*/*z* (relative intensity): 405(21), 404(100), 402(4), 280(1), 279(4), 278(17), 277(30), 276(15), 254(1), 234(5), 233(16), 232(2), 221(10), 220(2), 219(6). Anal. Calc. for $C_{17}H_9IO_2S$: C 50.51; H 2.24; I 31.39; S 7.93. Found: C 50.63; H 2.32; I 31.47; S 7.79%.

General procedure for the preparation of 1-aryl-9*H*-thieno[3,4-*b*]-chromen-9-one-3-carbaldehyde (14)

$MeOCHCl_2$ (0.11 ml, 1.2 mmol) was added with stirring and ice/brine cooling to compounds **11a,c,d,f** (1 mmol) and $SnCl_4$ (390 mg, 1.5 mmol) in dry 1,2-dichloroethane (10 ml). After completion of the reaction (TLC monitoring), the solution was poured into water. The organic layer was separated, washed with water, dried, and filtered through silica gel with CH_2Cl_2 as the solvent. Evaporation of the solvent and washing with cold EtOH gave **14a,c,d,f**.

9-Oxo-1-phenyl-9*H*-thieno[3,4-*b*]chromene-3-carbaldehyde (14a). Yield 83%, mp = 186–187 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 10.39 (s, $1H_{CH}$), 8.28 (d, *J* = 7.8 Hz, $1H_{Ar}$), 7.74–7.81 (m, $3H_{Ar}$), 7.38–7.55 (m, $5H_{Ar}$). MS (EI 70 eV) *m*/*z* (relative intensity): 308(9), 307(13), 306(100), 305(95), 304(2), 294(1), 283(2), 278(4), 277(39), 276(2), 261(2), 251(2), 249(6), 245(2), 235(1), 234(4), 233(20). Anal. Calc. for $C_{18}H_{10}O_3S$: C 70.57; H 3.29; S 10.47. Found: C 70.68; H 3.36; S 10.34%.

1-Furan-2-yl-9-oxo-9*H*-thieno[3,4-*b*]chromene-3-carbaldehyde-one (14c). Yield 35% mp = 195–197 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 10.34 (s, $1H_{CH}$), 8.47 (d, *J* = 3.7 Hz, $1H_{Ar}$), 8.33 (d, *J* = 7.9 Hz, $1H_{Ar}$), 7.76 (t, *J* = 7.1 Hz, $1H_{Ar}$), 7.63 (s, $1H_{Ar}$), 7.40–7.50 (m, $2H_{Ar}$), 6.68 (dd, *J* = 3.5, 1.5 Hz, $1H_{Ar}$). MS (EI 70 eV) *m*/*z* (relative intensity): 298(7), 296(76), 295(100), 294(36), 268(10), 267(8), 239(11), 238(25), 211(8), 210(36). Anal. Calc. for $C_{16}H_8O_4S$: C 64.86; H 2.72; S 10.82. Found: C 64.93; H 2.84; S 10.75%.

9-Oxo-1-thiophen-2-yl-9*H*-thieno[3,4-*b*]chromene-3-carbaldehyde (14d). Yield 48% mp = 189–191 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 10.31 (s, $1H_{CH}$), 8.30 (d, *J* = 7.4 Hz, $1H_{Ar}$), 8.13 (d, *J* = 3.7 Hz, $1H_{Ar}$), 7.75 (t, *J* = 7.8 Hz, $1H_{Ar}$), 7.63 (d, *J* = 5.0 Hz, $1H_{Ar}$) 7.31–7.49 (m, $2H_{Ar}$), 7.19 (t, *J* = 4.9 Hz, $1H_{Ar}$). MS (EI 70 eV) *m*/*z* (relative intensity): 314(15), 313(11), 312(100), 311(28), 310(8), 284(21), 238(21), 255(3), 240(3), 239(24). Anal. Calc. for $C_{16}H_8O_3S_2$: C 61.52; H 2.58; S 20.53. Found: C 61.57; H 2.50; S 20.47%.

1-(2-Chlorophenyl)-9-oxo-9*H*-thieno[3,4-*b*]chromene-3-carbaldehyde (14f). Yield 55%, mp = 172–174 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 10.41 (s, $1H_{CH}$), 8.23 (d, J = 7.5 Hz, $1H_{Ar}$), 7.77 (t, J = 7.7 Hz, $1H_{Ar}$), 7.36–7.60 (m, $6H_{Ar}$). MS (EI 70 eV) m/z (relative intensity): 340(2), 308(6), 307(16), 306(73), 305(100), 279(3), 278(15), 277(82). Anal. Calc. for $C_{18}H_9ClO_3S$: C 63.44; H 2.66; Cl 10.40; S 9.41. Found: C 63.56; H 2.74; Cl 10.48; S 9.30%.

General procedure for the preparation of azomethines (15)

Amine (1 mmol) was added to aryl-5-carbonyl-9*H*-thieno[3,4-*b*]-chromen-9-one **14a** (306 mg, 1 mmol) in 5 ml of ethanol. The solution was refluxed and then cooled. The solid compound was filtered off and recrystallized from ethanol.

1-Phenyl-3-((phenylimino)methyl)-9*H*-thieno[3,4-*b*]chromen-9-one (15a). Yield 80%, mp = 185–186 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.99 (s, $1H_{CH}$); 8.27 (d, J = 7.6 Hz, $1H_{Ar}$), 7.70–7.82 (m, $3H_{Ar}$), 7.30–7.51 (m, $10H_{Ar}$). MS (EI 70 eV) m/z (relative intensity): 383(1), 382(29), 381(100), 380(6), 307(6), 306(14), 305(24), 279(1), 278(3), 277(10), 265(1), 264(5), 323(24). Anal. Calc. for $C_{24}H_{15}NO_2S$,%: C 75.57; H 3.96; N 3.67; S 8.41. Found: C 75.45; H 4.04; N 3.77; S 8.30%.

3-{[(4-Fluorophenyl)imino]methyl}-1-phenyl-9*H*-thieno[3,4-*b*]-chromen-9-one (15b). Yield 92%, mp = 220–222 °C (EtOH). ^{1}H NMR (2003 MHz, $CDCl_3$), δ 8.96 (s, $1H_{CH}$), 8.27 (d, J = 7.5, $1H_{Ar}$), 7.82–7.68 (m, $3H_{Ar}$), 7.40–7.21 (m, $7H_{Ar}$), 7.16–7.08 (m, $2H_{Ar}$). MS (EI 70 eV) m/z (relative intensity): 400(14), 399(100), 398(11), 397(2), 306(6), 305(2), 301(4), 292(1), 285(5), 284(9), 283(23). Anal. Calc. for $C_{24}H_{14}FNO_2S$: C 72.17; H 3.53; F 4.76; N 3.51; S 8.03. Found: C 72.03; H 3.65; F 4.66; N 3.61; S 8.00%.

General procedure for the preparation of 3-[3-oxo-3-(aryl)prop-1-en-1-yl]-1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one (16)

A 40% aqueous KOH solution (0.14 ml) was added to aldehyde **14** (1 mmol) in 10 ml of ethanol and the corresponding ketone (1 mmol) (in the case of acetone, an ice-cooled 1 : 1 mixture of ethanol and acetone (10 ml) was used as the solvent). The reaction mixture was stirred for 1 h (TLC monitoring) and diluted with water. The solid compound was filtered off, washed with water, and recrystallized from ethanol.

3-[3-Oxobut-1-en-1-yl]-1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one (16a). Yield 60%, mp = 189–190 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.26 (d, J = 8.1 Hz, $1H_{Ar}$), 8.01 (d, J = 15.9 Hz, $1H_{CH}$), 7.71–7.78 (m, $3H_{Ar}$), 7.33–7.52 (m. $5H_{Ar}$). 6.66 (d, J = 15.9 Hz, $1H_{CH}$), 2.44 (s, $3H_{Me}$). MS (EI 70 eV) m/z (relative intensity): 348(3), 347(22), 346(36), 333(3), 332(5), 331(61), 306(11), 305(19), 304(18), 303(100), 291(6), 284(3), 281(7), 278(3), 277(8). Anal. Calc. for $C_{21}H_{14}O_3S$: C 72.81; H 4.07; S 9.26. Found: C 72.79; H 4.13; S 9.34%.

3-[3-(3-Methoxyphenyl)-3-oxoprop-1-en-1-yl]-1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one (16b). Yield 85%, mp = 201–202 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.31 (d, J = 15.5 Hz, $1H_{CH}$), 8.25 (d, J = 8.9 Hz, $1H_{Ar}$), 7.31–7.82 (m, $12H_{Ar+CH}$), 7.16 (d, J = 8.1 Hz, $1H_{Ar}$), 3.91 (s, $3H_{Me}$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 181.3 (C=O), 174.2 (C=O), 155.8, 153.8, 151.1, 145.6, 135.5, 133.9, 132.2, 131.7, 131.6, 131.2, 130.2, 130.0, 129.9, 128.5, 128.4, 128.2, 127.4, 124.3, 121.7, 119.7, 117.9, 117.7. MS (EI 70 eV) m/z (relative intensity): 439(13), 438(99), 409(1), 381(2), 354(1), 332(3), 305(1), 304(15), 303(100), 288(1), 279(1), 278(6), 277(5), 276(1). Anal. Calc. for $C_{27}H_{18}O_4S$: C 73.96; H 4.14; S 7.31. Found: C 74.03; H 4.28; S 7.23%.

3-[-3-Oxo-3-(2-thienyl)prop-1-en-1-yl]-1-phenyl-9*H*-thieno-[3,4-*b*]chromen-9-one (16c). Yield 74%, mp = 208–212 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.31 (d, J = 15.3 Hz, $1H_{CH}$), 8.25 (d, J = 6.5 Hz, $1H_{Ar}$), 7.70–7.90 (m, $5H_{Ar}$), 7.40–7.52 (m, $4H_{Ar}$), 7.20–7.36 (m, $3H_{Ar+CH}$). MS (EI 70 eV) m/z (relative intensity): 441(1), 440(2), 439(7), 438(32), 411(1), 410(3), 409(7), 333(4), 332(4), 331(8), 306(3), 305(15), 304(23), 303(100), 280(2), 279(4), 278(27), 277(13). Anal. Calc. for $C_{24}H_{14}O_3S_2$: C 69.54; H 3.40; S 15.47. Found: C 69.43; H 3.51; S 15.54%.

General procedure for the preparation of 3,3′-(2-aryl-2-oxoethane-1,1-diyl)-bis(1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one) (19)

Tin(IV) tetrachloride (260 mg, 1 mmol) was added to a mixture of **11** (1 mmol) and ketoaldehyde (17) (0.5 mmol) in dry CH_2Cl_2 (5 ml) at room temperature. The solution was stirred for 1 h and poured into water. The organic layer was dried with Na_2SO_4, filtered through silica gel, and concentrated. The residue was washed with ethanol and petroleum ether.

3,3′-(2-Phenyl-2-oxoethane-1,1-diyl)-bis(1-phenyl-9*H*-thieno-[3,4-*b*]chromen-9-one) (19a). Yield 75%, mp = 242 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.33 (d, J = 7.2 Hz, $2H_{Ar}$), 8.25 (d, J = 7.9 Hz, $2H_{Ar}$), 7.32–7.74 (m, $20H_{Ar+CH}$). Anal. Calc. for $C_{42}H_{24}O_5S_2$: C 74.98; H 3.60; S 9.53. Found: C 74.84; H 3.75; S 9.42%.

3,3′-(2-(4-Methylphenyl)-2-oxoethane-1,1-diyl)-bis(1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one) (19b). Yield 87%, mp = 218–220 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.23 (d, J = 8.0 Hz, $4H_{Ar}$), 7.66–7.70 (m, $6H_{Ar}$), 7.31–7.48 (m, $13H_{Ar+CH}$), 2.43 ($3H_{Me}$). Anal. Calc. for: C 75.20; H 3.82; S 9.34. Found: C 75.30; H 3.72; S 9.43%.

3,3′-(2-(3-Methoxyphenyl)-2-oxoethane-1,1-diyl)-bis(1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one) (19c). Yield 78%, mp = 248–250 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.25 (d, J = 7.9 Hz, $2H_{Ar}$), 7.97 (d, J = 7.8 Hz, $1H_{Ar}$), 7.67–7.81 (m, $6H_{Ar}$), 7.18–7.51 (m, $14H_{Ar+CH}$), 3.87 (s, $3H_{Me}$). Anal. Calc. for $C_{43}H_{26}O_6S_2$: C 73.49; H 3.73; S 9.12. Found: C 73.49; H 3.73; S 9.12%.

3,3′-(2-(2.5-Dimethylthiophen-3-yl)-2-oxoethane-1,1-diyl)-bis-(1-phenyl-9*H*-thieno[3,4-*b*]chromen-9-one) (19d). Yield 80%, mp = 236–237 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.26 (d, J = 7.9 Hz, $2H_{Ar}$), 7.66–7.78 (m, $6H_{Ar}$), 7.31–7.48 (m, $11H_{Ar+CH}$), 7.10 (s, $1H_{Ar}$), 2.80 (s, $3H_{Me}$), 2.45 (s, $3H_{Me}$). Anal. Calc. for $C_{42}H_{26}O_5S_3$: C, 71.37; H, 3.71; S, 13.61. Found: C 71.25; H 3.84; S, 13.54%.

Bis(1-(2-chlorophenyl)-3,3′-(2-(3-methoxyphenyl)-2-oxoethane-1,1-diyl)-9*H*-thieno[3,4-*b*]chromen-9-one) (19e). Yield 65%, mp = 216–217 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 8.20 (d, J = 6.9 Hz, $2H_{Ar}$), 7.99 (d, J = 7.6 Hz, $1H_{Ar}$), 7.82 (s, $1H_{Ar}$), 7.71 (t, J = 7.2 Hz, $1H_{Ar}$), 7.20–7.54 (m, $16H_{Ar+CH}$), 3.88 (s, $3H_{Me}$). Anal. Calc. for $C_{43}H_{24}Cl_2O_6S_2$: C 66.93; H 3.13; Cl 9.19; S 8.31. Found: C 66.81; H 3.03; Cl 9.04; S 8.40%.

Procedure for the preparation of (20)

Sodium tetrahydroborate (42 mg, 1.1 mmol) was added to thienochromone (**11a**) (278 mg, 1 mmol.) in THF. After completion of the reaction, the solvent was evaporated and the residue was recrystallized from ethanol.

Yield 79%, mp = 153 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ 7.85 (d, J = 7.6 Hz, $2H_{Ar}$), 7.11–7.53 (m, $7H_{Ar}$), 6.76 (s, $1H_{Ar}$), 5.88 (d, J = 7.6 Hz, $1H_{CH}$), 2.13 (d, J = 7.5 Hz, $1H_{OH}$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ 151.7, 149.4, 141.5, 133.9, 130.4, 130.0, 129.1, 128.6, 128.4, 123.4, 122.7, 117.0, 101.3, 62.3. MS (EI 70 eV) m/z (relative intensity): 281(5), 280(38), 279(23), 278(13), 265(16), 264(30), 263(90), 262(4), 236(2), 235(6), 219(2), 218(5), 205(6), 204(100), 203(55), 202(53), 201(32), 193(7), 192(40), 191(13), 190(45), 189(21), 188(51). Anal. Calc. for $C_{17}H_{12}O_2S$: C 72.83; H 4.31; S 11.44. Found: C 72.91; H 4.41; S 11.32%.

Crystallographic data. Crystals of **19a** ($C_{49.50}H_{41.50}O_5S_3$, M_r = 809.99) are triclinic, space group $P\bar{1}$, at 100 K: a = 12.116(2), b = 12.633(3), c = 14.074(3) Å, α = 75.424(7), β = 88.977(6), γ = 73.821(7)°, V = 1999.2(8) Å^3, Z = 2 (Z' = 1), D_c = 1.350 g cm^{-3}, μ(Mo-Kα) = 2.35 cm^{-1}, F(000) = 853. Intensities of 14629 reflections were measured with a Smart APEX II CCD diffractometer [λ(Mo-Kα) = 0.71072 Å, ω-scans, $2\theta < 55°$] and 9103 independent reflections [R_{int} = 0.0284] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic/isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. Analysis of the Fourier density synthesis revealed that **19a** crystallizes with a solvate molecule, which is the superposition of *n*-alkanes (crystals were obtained from the petroleum ether). Upon the refinement of the solvate molecule, its atoms C(7S), C(8s), C(9s) and C(10s) disordered around the center of symmetry were refined with occupancies equal to 0.5, 0.5, 0.25 and 0.25, respectively. Due to the complicated disordering scheme the hydrogens for C(8S)–C(10S) atoms were not added. The refinement converged to $wR2$ = 0.1531 and GOF = 0.929 for all independent reflections ($R1$ = 0.0511 was calculated against F for 6580 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0.

References

1 (*a*) A. S. Klymchenko, T. Ozturk, V. G. Pivovarenko and A. P. Demchenkoa, *Tetrahedron Lett*., 2001, **42**, 7967–7970; (*b*) A. S. Klymchenko and A. P. Demchenko, *J. Am. Chem. Soc*., 2002, **124**, 12372–12379; (*c*) A. S. Klymchenko, V. G. Pivovarenko, T. Ozturkd and A. P. Demchenkoc, *New J. Chem*., 2003, **27**, 1336–1343.
2 S. V. Jovanovic, S. Steenken, M. Tosic, B. Marjanovic and M. G. Simic, *J. Am. Chem. Soc*., 1994, **116**, 4846–4851.
3 D. Grindlay and T. Reynolds, *J. Ethnopharmacol*., 1986, **16**, 117–151.
4 T. Hirata and T. Suga, *Bull. Chem. Soc. Jpn*., 1978, **51**, 842–849.
5 D. Womble and J. H. Helderman, *Int. J. Immunopharmacol*., 1988, **10**, 967–973.
6 D. Yu, A. Brossi, N. Kilgore, C. Wild, G. Alloway and K. H. Lee, *Bioorg. Med. Chem. Lett*., 2003, **13**(9), 1575–1576.
7 C. P. Miller, M. D. Collinia and H. A. Harris, *Bioorg. Med. Chem. Lett*., 2003, **13**, 2399–2403.
8 C. P. Falshaw and W. D. Ollis, *Chem. Commun. (London)*, 1966, 305–306.
9 T. R. Kelly and R. L. Moiseyeva, *J. Org. Chem*., 1998, **63**, 3147–3150.
10 J. S. Bell, *Clin. Drug Invest*, 2005, **25**, 555–566.
11 D. R. Buckle, D. J. Outred, C. J. M. Rockell, H. Smith and B. A. Spicer, *J. Med. Chem*., 1983, **26**(2), 251–254.
12 J. W. H. Watthey and M. Desai, *J. Org. Chem*., 1982, **47**, 1755–1759.
13 A. S. Sarenko, L. S. Éfros and I. Ya. Kvitko, *Pharm. Chem. J*., 1970, **4**, 488–491.
14 C. K. Ghosh and S. K. Karak, *Indian J. Chem., Sect. B*, 2004, **43**, 2401–2404.
15 D. S. Clarke, C. D. Gabbutt, J. D. Hepworth and B. M. Heron, *Tetrahedron Lett*., 2005, **46**, 5515–5519.
16 I. Roufos, S. J. Hays, D. J. Dooley, R. D. Schwarz, G. W. Campbell and A. W. Probert, *J. Med. Chem*., 1994, **37**, 268–274.
17 (*a*) S. N. Ivanov, B. V. Lichitskii, A. A. Dudinov, A. Yu. Martykin and M. M. Krayushkin, *Chem. Heterocycl. Compd*., 2001, **37**, 85–90; (*b*) S. P. Mushran, L. Pandey and S. Kameshwar, *Monatsh. Chem*., 1980, **111**, 1135–1142; (*c*) P. Satya, G. Mukta, G. Rajive and L. Andre, *Synthesis*, 2002, 175–178.
18 T. S. Wheeler, *Org. Synth*., 1963, **Coll. vol. IV**, 478–481.
19 W. Baker, J. B. Harborne and W. D. Ollis, *J. Chem. Soc*., 1952, 1294–1301.
20 W. D. Ollis, *J. Chem. Soc*., 1952, 3826–3830.
21 P. F. Devitt, A. Timoney and M. A. Vickars, *J. Org. Chem*., 1961, **26**, 4941–4944.
22 N. Akira, A. Hiroyuki, M. Kazushige and M. Takahiro, *Synthesis*, 1992, **9**, 839–841.
23 A. Corvaisier, *Bull. Soc. Chim. Fr*., 1962, 528–535.
24 A. K. Ganguly, S. Kaur, P. K. Mahata, D. Biswas, B. N. Pramanik and T. M. Chan, *Tetrahedron Lett*., 2005, **46**, 4119–4122.