Organic & Biomolecular Chemistry

PAPER

Cite this: Org. Biomol. Chem., 2015, 13, 729

Synthesis of functionalized 2-salicyloylfurans, furo[3,2-*b*]chromen-9-ones and 2-benzoyl-8*H*-thieno[2,3-*b*]indoles by one-pot cyclizations of 3-halochromones with β-ketoamides and 1,3-dihydroindole-2-thiones†

Iryna Savych,[a] Tim Gläsel,[a] Alexander Villinger,[a] Vyacheslav Ya. Sosnovskikh,[b] Viktor O. Iaroshenko*[a,c,d] and Peter Langer*[a,e]

Received 13th August 2014,
Accepted 30th October 2014

DOI: 10.1039/c4ob01730g

www.rsc.org/obc

Functionalized 2-salicyloylfurans and 2-benzoyl-8*H*-thieno[2,3-*b*]indoles were prepared under mild conditions by reaction of 3-halochromones with β-ketoamides and 1,3-dihydroindole-2-thiones, correspondently. The subsequent oxidative cyclization of the products resulted in formation of the corresponding furo[3,2-*b*]chromen-9-ones. These molecules could also be directly prepared from 3-halochromones using a one-pot protocol. The cyclization reactions reported herein are mechanistically surprising as they proceed *via* the oxygen and not *via* the (more nucleophilic) nitrogen atom of the β-ketoamide.

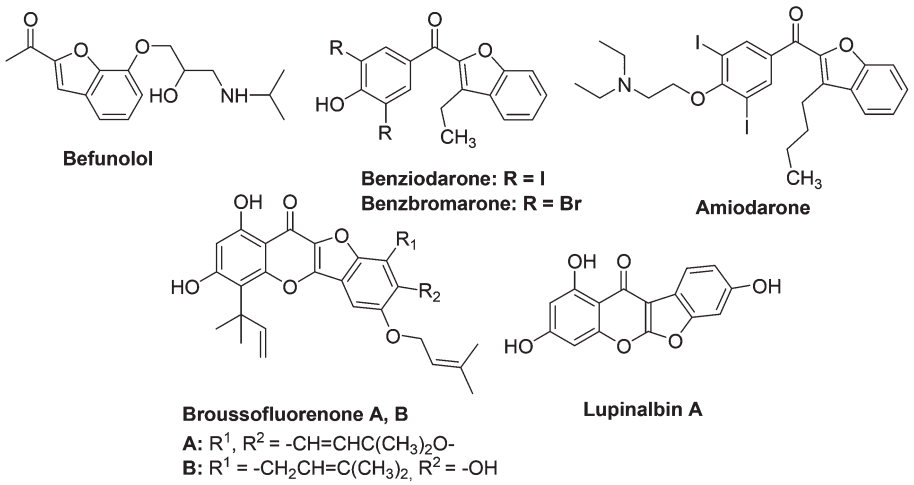
Introduction

An important method for the development of new pharmacologically relevant scaffolds in drug discovery is based on the diversity oriented synthesis of heterocycles related to natural products.[1,2] A great number of molecules containing the furan and thiophene ring display a wide range of biological activity and find applications as pharmaceuticals.[3,4] Furan derivatives are present in a variety of natural and synthetic molecules which exhibit important biological activities.[5–8] Structures of some important bioactive benzofuranes, 2-benzoylfuranes and furochromones are depicted in Scheme 1. For example, befunolol exhibits antiglaucoma activity,[4] the 2-benzoylfuran benziodarone has been reported to possess vasodilation activity.[9] Benzbromarone is a uricosuric agent and non-competitive inhibitor of xanthine oxidase used in the treatment of gout.[10] Amiodarone is an antiarrhythmic agent used for various types of cardiac dysarhythmias. All these compounds are clinically used nowadays. Phytoestrogen Lupinalbin A, a furochromone, represents a selective estrogen receptor modulator.[11] Broussofluorenones A, B show potent α-glucosidase and anticholinesterase inhibition.[12,13]

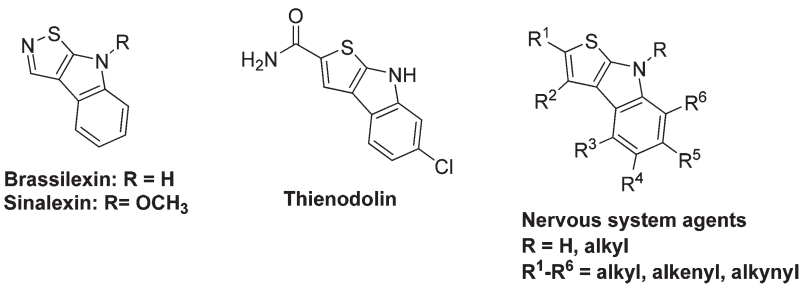
The indole ring system is one of the most important privileged scaffold in medicinal chemistry.[4] Heterocycle-fused thiophene systems,[14–16] such as thienoindoles, have attracted a considerable attention, due to their presence in natural products, such as thienodolin,[17,18] in phytoalexines, such as brassilexin[19–23] and sinalexin,[19,24] and also in synthetic molecules, which exhibit antifungal activity,[17,21] anticancer activity.[25,26] In addition, they act in the nervous system and are used in the treatment of epilepsy and different neurological diseases, as senile dementia, Parkinson's disease, pain and others[27] (Scheme 2). On the other hand, thienoindoles are also used in organic electronics as novel electroluminescence materials for designing light-emitting devices[28,29] and as novel conducting polymers.[30,31] A number of approaches reported in the literature for the synthesis of thieno[2,3-*b*]indole derivatives,[32–37] including Pd-catalysed methods of synthesis.[38–40] However, most of these methods suffer from some drawbacks and are limited in scope and generality. Therefore more flexible and efficient general methods for the preparation of thieno[2,3-*b*]indole derivatives are still desirable.

Chromones are an important class of oxygenated heterocyclic compounds which represent important building blocks in organic chemistry. In addition, they are very attractive

[a]Institut für Chemie, Universität Rostock, Albert Einstein Str. 3a, 18059 Rostock, Germany. E-mail: iva108@googlemail.com, peter.langer@uni-rostock.de
[b]Department of Chemistry, Ural Federal University, 51 Lenina Ave., 620083 Ekaterinburg, Russia
[c]National Taras Shevchenko University, 62 Volodymyrska Str., 01033 Kyiv, Ukraine
[d]Department of Chemistry (MC 111), University Illinois at Chicago, 845 West Taylor Street, RM 4500, Chicago, Illinois 60607, USA
[e]Leibniz Institut für Katalyse, Albert Einstein Str., 18059 Rostock, Germany
†Electronic supplementary information (ESI) available. CCDC 982675–982677. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob01730g



Scheme 1 Pharmacologically relevant 2-benzoylfurans and furochromones.



Scheme 2 Pharmacologically relevant thieno-fused heterocycles.

targets in their own right because of their biological activities and occurrence in natural products.[41,42] 3-Halochromones, containing an α,β-unsaturated carbonyl moiety and a halide as a potential leaving group,[43] and are highly functionalized molecules which have been used for the synthesis of various heterocycles.[44–47] Reactions of 3-substituted chromones usually proceed by initial 1,4-addition.[48–54] Reported transformations of 3-halochromones include the synthesis of 3-substituted chromones,[43,47,55,56] 2,3-methanochromanones,[56] 2-substituted chromones,[57] and benzofuranone derivatives.[47,48]

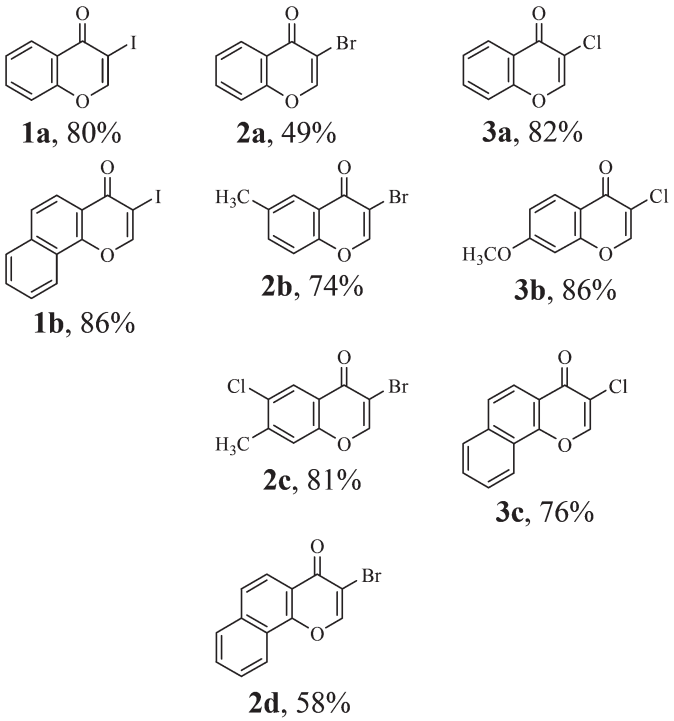
In contrast to simple substitution reactions, cyclization reactions of 3-halochromones with dinucleophiles have only scarcely been reported to date.[47] The reaction of 3-bromochromone with 1,3-diketones and β-ketoesters has been previously reported.[47,58] The reaction of 3-iodochromone with mercaptoazoles and also with 2-mercaptobenzimidazoles has already been reported.[16] In the same time, other powerful 1,3-dinucleophiles, such as 1,3-dihydroindole-2-thiones, were explored in various cyclization reactions under the action of diverse bielectrophiles in our[59,60] and other scientific groups.[61–67] The reaction of α-halocarbonyl compounds with 1,3-dihydroindole-2-thione derivatives is also known.[34] All these facts have inspirited us to study the reactions of 3-halochromones with 1,3-dinucleophiles, which were not studied before, such as β-ketoamides and 1,3-dihydroindole-2-thiones. Herein, we report, to the best of our knowledge, a new and convenient one-pot synthesis of 2-salicyloylfurans, containing a 2-aminofuran substructure, furo[3,2-*b*]chromen-9-ones and 2-{8*H*-thieno[2,3-*b*]indole-2-carbonyl}phenols by cyclization reactions of 3-halochromones with β-ketoamides and 1,3-dihydroindole-2-thiones, correspondently. These products, which are not readily available by other methods, are structurally related to clinically relevant drugs and natural products. The cyclization reactions of 3-halochromones with β-ketoamides reported herein are mechanistically interesting as they proceed *via* the oxygen and not *via* the (more nucleophilic) nitrogen atom of the β-ketoamide.

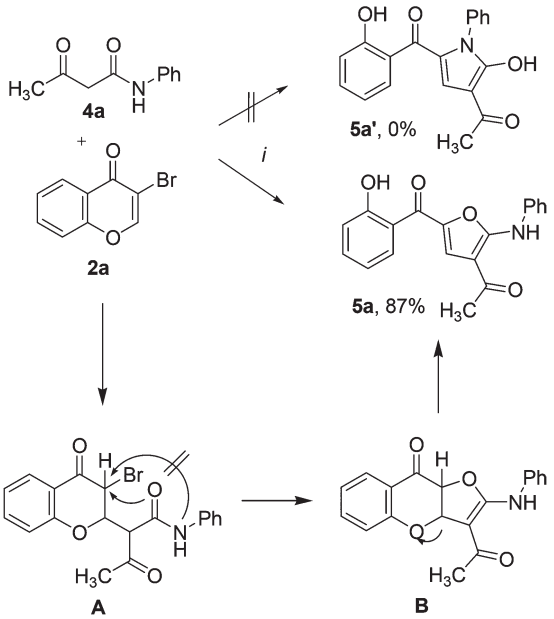
Results and discussion

Our starting point was the synthesis of a series of 3-halochromones, including 3-iodochromones **1a,b**, 3-bromochromones **2a–d**, and 3-chlorochromones **3a–c** (Table 1). The products were prepared by transformation of 2-hydroxyacetophenones to 3-dimethylamino-1-(2-hydroxyaryl)prop-2-en-1-ones. The desired 3-iodo-, 3-bromo-, and 3-chlorochromones were subsequently prepared by halogenation using iodine, bromine, and iodine monochloride, respectively.[47,68–75] Although all these syntheses are known, the synthesis of 3-iodochromones

Table 1 3-Halochromones **1–3** used in this study (yields refer to isolated yields of product in the halogenation step)

3-Halochromones





Scheme 3 Formation of 2-salicyloylfuran **5a**. *Reaction conditions*: (i) DBU (1.3 equiv.), 1,4-dioxane, 20 °C.

was optimized by using iodine (2 equiv.) in the presence of pyridine (2.1 equiv.) in chloroform. All 3-halogenated chromones were purified by recrystallization (system heptane/isopropanol) or, in the case of **2a** and **2d**, by silica gel chromatography. The chromatography was necessary in order to remove a dibrominated site-product.

The reaction of 3-bromochromone (**2a**) with equimolar amounts of β-ketoamide **4a**, in the presence of DBU (1.3 equiv.),[76] resulted in the formation of 2-salicyloylfuran **5a** in 87% yield (Scheme 3, Table 2). The reaction was carried out in 1,4-dioxane at room temperature. The formation of **5a** can be explained by 1,4-addition of the β-ketoamide at position 2 of the 3-halochromone to give intermediate **A**. Subsequent attack of the amide oxygen atom to the carbon atom attached to the bromide atom resulted in the formation of intermediate **B** which underwent cleavage of the carbon–oxygen bond to give **5a**. Employment of 3-chlorochromone (**3a**) instead of **2a** resulted in a slight decrease of the yield of **5a** (Table 3). The use of 3-iodochromone (**1a**) instead of **2a** resulted in a dramatic decrease of the yield.

The preparative scope was next studied. The cyclization of 3-halochromones **1–3** with β-ketoamides **4a–f** afforded 2-salicyloylfurans **5a–x** in good to excellent yields (46–99%) (Table 2). In most cases, the products could be isolated by simple filtration of the precipitate or by recrystallization from the solvent system heptane/isopropanol, or by column chromatography using silica gel. The progress of the reaction was monitored by TLC. The influence of the leaving group of the 3-halochromone on the yield was studied in case of the synthesis of products **5a**, **5q** and **5u**. The reaction of β-ketoamide **4a** with 3-chlorochromone (**3a**), 3-bromochromone (**2a**), and 3-iodochromone (**1a**) revealed that the yields strongly depend on the type of halogen atom located at position 3 of the chromone (Table 3). It was found that 3-chlorochromone (**3a**) gave the best yields of products **5q** and **5u**. However, for some other products (other than **5a,q,u**) the yields were slightly better in case of employment of 3-bromochromone (**2a**). In addition, the type of leaving group had an influence on the reaction time (3–4 h for 3-chlorochromones **3**, 10–12 h in case of 3-iodochromones **1** and 3-bromochromones **2**). The structure of **5e** was independently confirmed by X-ray crystal structure analysis (Fig. 1).

In general, all cyclizations proceeded regioselectively *via* the amide oxygen atom of intermediate **A** and afforded 2-salicyloylfurans **5a–x**. In contrast, cyclization *via* the amide nitrogen atom and formation of isomeric 2-benzoylpyrrols, such as product **5a′** (Scheme 3), was not observed. However, in some reactions of 3-bromo and 3-chlorochromones the formation of a small amount of by-product was observed in TLC. In case of the synthesis of **5o**, the by-product could be isolated and structurally elucidated. The product turned out to be 2-benzoylfuran **6** formed by cyclization *via* the ketone instead of the amide oxygen atom. The structure of **6** was independently confirmed by X-ray crystal structure analysis (Fig. 2).

Our next goal was to transform 2-benzoylfuran **5m** to furo[3,2-*b*]chromen-9-one **7a** (Scheme 4, Table 4). We have studied the use of various oxidizing agents, such as iodine,[45] *o*-chloranil and DDQ.[11] In addition, we investigated the employment of various bases, including DBU and potassium carbonate, and

Table 2 Synthesis of compounds **5** (yields refer to isolated products)

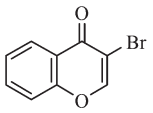
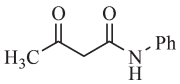
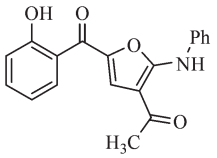
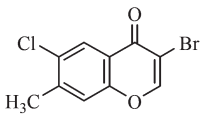
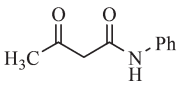
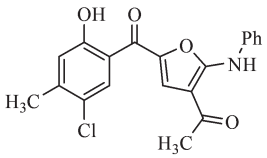
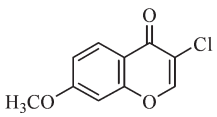
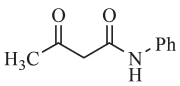
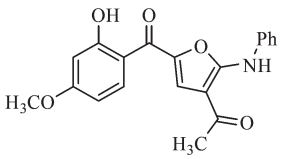
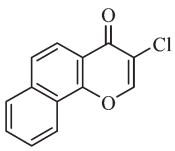
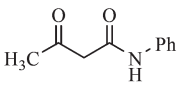
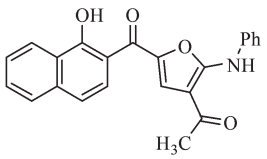
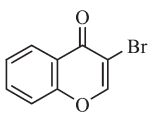
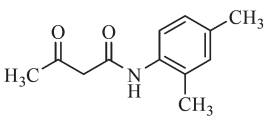
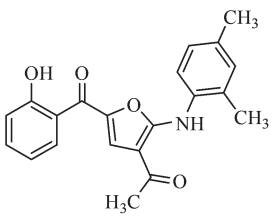
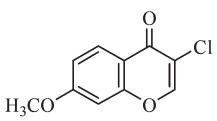
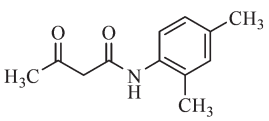
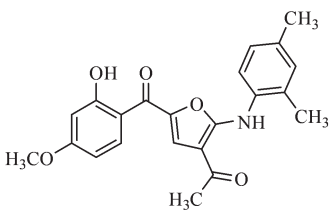
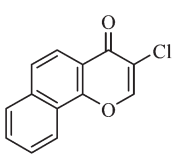
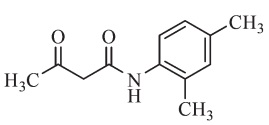
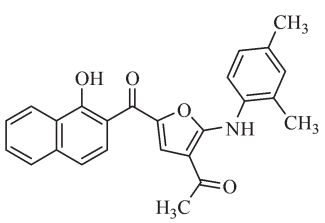
3-Halochromone	β-Ketoamide	Product
 **2a**	 **4a**	 **5a**, 87%
 **2c**	 **4a**	 **5b**, 99%
 **3b**	 **4a**	 **5c**, 98%
 **3c**	 **4a**	 **5d**, 53%
 **2a**	 **4b**	 **5e**, 93%
 **3b**	 **4b**	 **5f**, 69%
 **3c**	 **4b**	 **5g**, 76%

Table 2 *(Contd.)*

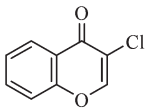
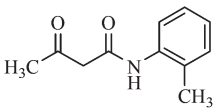
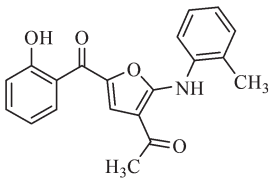
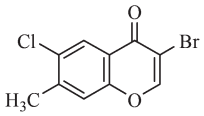
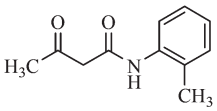
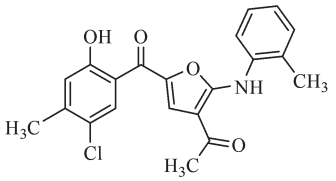
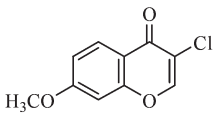
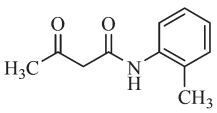
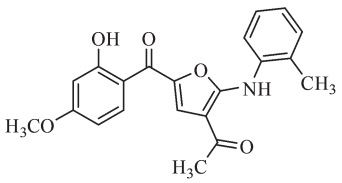
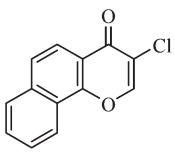
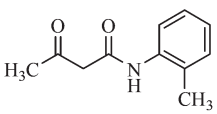
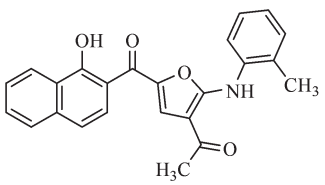
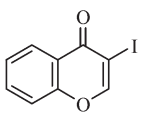
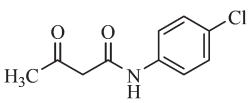
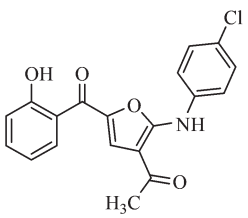
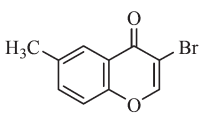
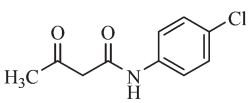
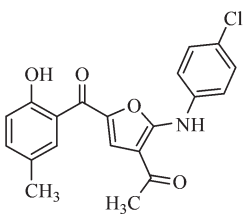
3-Halochromone	β-Ketoamide	Product
 **3a**	 **4c**	 **5h**, 85%
 **2c**	 **4c**	 **5i**, 99%
 **3b**	 **4c**	 **5j**, 98%
 **3c**	 **4c**	 **5k**, 93%
 **1a**	 **4d**	 **5l**, 46%
 **2b**	 **4d**	 **5m**, 99%

Table 2 *(Contd.)*

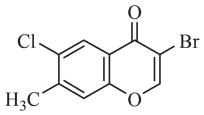
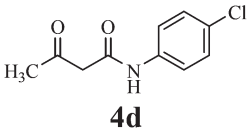
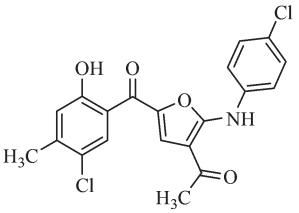
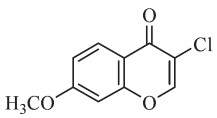
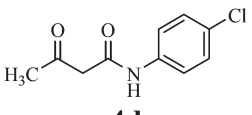
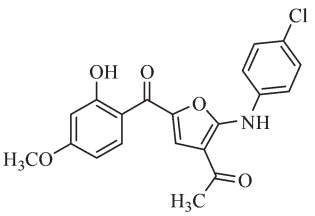
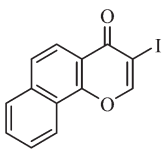
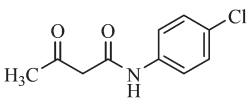
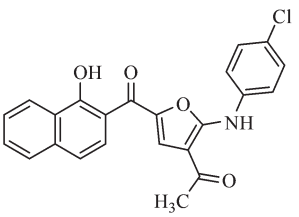
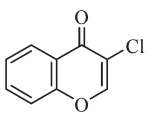
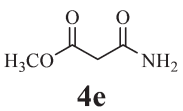
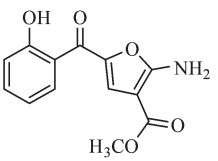
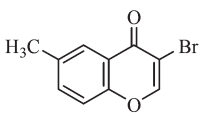
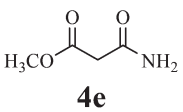
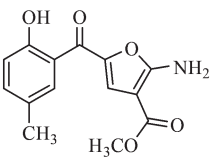
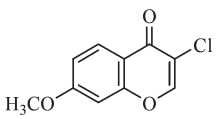
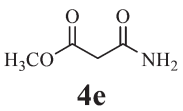
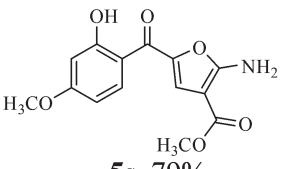
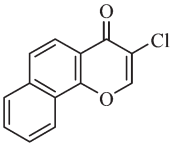
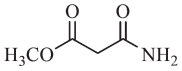
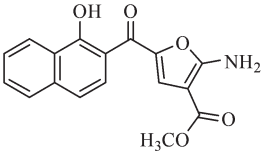
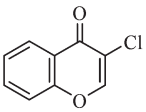
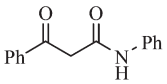
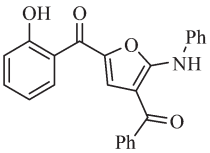
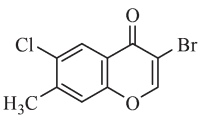
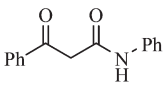
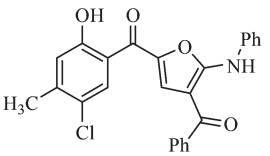
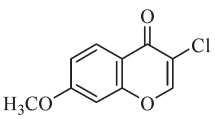
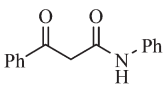
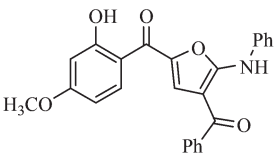
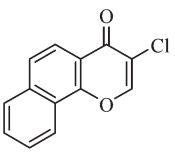
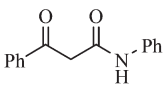
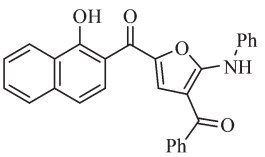
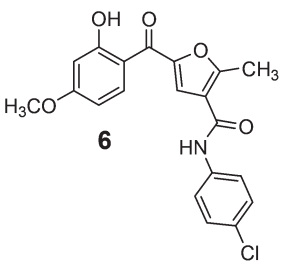
3-Halochromone	β-Ketoamide	Product
 **2c**	 **4d**	 **5n**, 98%
 **2b**	 **4d**	 **5o**, 47% [a]
 **1b**	 **4d**	 **5p**, 56%
 **3a**	 **4e**	 **5q**, 98%
 **2b**	 **4e**	 **5r**, 90%
 **3b**	 **4e**	 **5s**, 79%

Table 2 *(Contd.)*

3-Halochromone	β-Ketoamide	Product
 **3c**	 **4e**	 **5t**, 88%
 **3a**	 **4f**	 **5u**, 81%
 **2c**	 **4f**	 **5v**, 72%
 **3b**	 **4f**	 **5w**, 69%
 **3c**	 **4f**	 **5x**, 70%

[a] Besides, compound **6** was isolated in 7% yield (structure see below).


6

of various solvents, such as dichloromethane (DCM), acetonitrile (MeCN) and dimethyl formamide (DMF). The best yield of **7a** (up to 32%) was obtained using iodine (2 equiv.) and DBU (3 equiv.) in MeCN. The rather low yield can be explained by the instability of the product and decomposition.

The application of a one-pot protocol for the direct preparation of furo[3,2-*b*]chromen-9-one from 3-halochromones was next studied. The reaction of **2a** with **4a** in the presence of 1.3 equiv. of DBU in 1,4-dioxane and subsequent oxidative cyclization by addition of iodine afforded product **7b** in 37% yield.

Table 3 Optimization of the yield by variation of the leaving group of the 3-halochromones

Chromone	β-Ketoamide	X	Product	Yield[a] (%)
1a	**4a**	I	**5a**	53
2a	**4a**	Br		87
3a	**4a**	Cl		83
1a	**4e**	I	**5q**	49
2a	**4e**	Br		79
3a	**4e**	Cl		98
1a	**4f**	I	**5u**	45
2a	**4f**	Br		63
3a	**4f**	Cl		81

[a] Isolated yields.

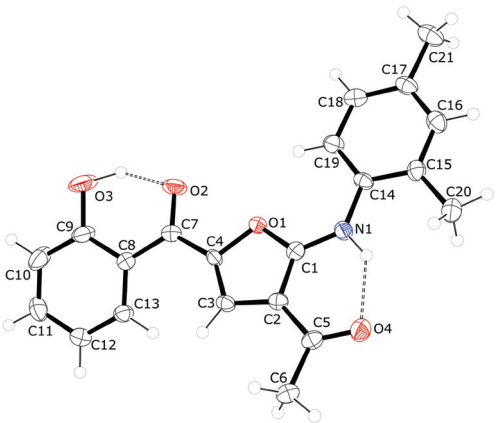


Fig. 1 ORTEP plot of compound **5e** shown with ellipsoids at the 50% level.

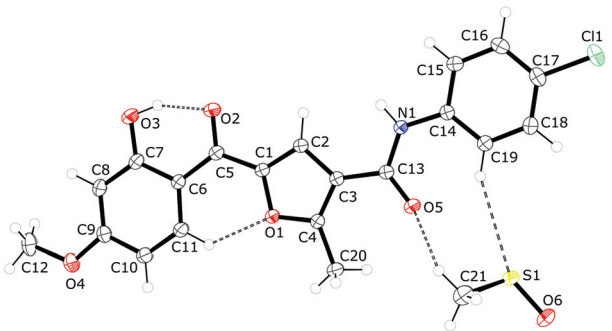
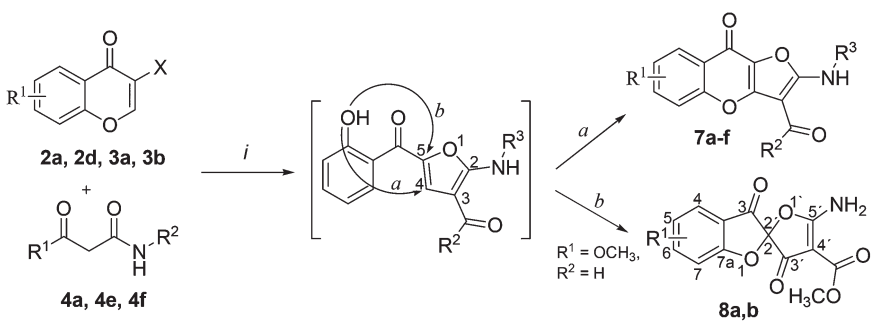


Fig. 2 ORTEP plot of compound **6** shown with ellipsoids at the 50% level.

The progress of the reaction was monitored by TLC (completion of the starting material). Interestingly, the yield was higher than in the stepwise process and comparison of the yields show that the main loss in yield takes place in the second step of the reaction. With regard to the yield and operational simplicity, the one-pot process is clearly advantageous with regard to the stepwise synthesis. Therefore, the preparative scope of our methodology was studied using the one-pot protocol. For this purpose we used 3-bromo- and 3-chlorochromones as they proved to give better yields than 3-iodochromones (*vide supra*). The reaction of 3-halochromones **2a**, **2d**, **3a** and **3b** with β-ketoamide **4a** afforded furo[3,2-*b*]chromen-9-ones **7a–f**, albeit, in moderate or low yields. The lowest yield was obtained for product **7d** derived from chromone **2d**, presumably due to steric hindrance. We have also studied the use of metal catalysts, such as $Cu(OAc)_2$ in the presence of $Zn(OTf)_2$.[77] However, no products could be isolated using these reagents. The structure of **7e** was independently confirmed by X-ray crystal structure analysis (Fig. 3).

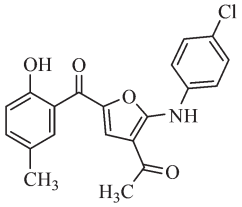
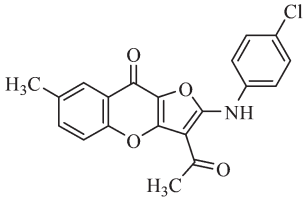
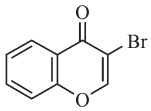
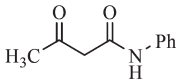
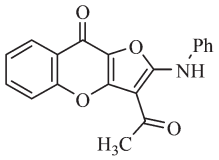
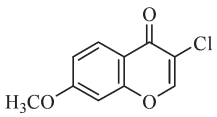
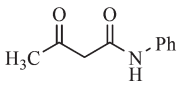
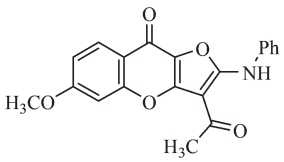
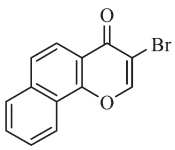
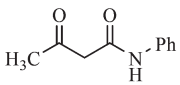
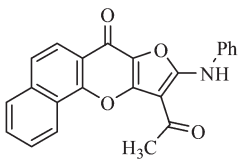
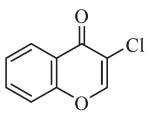
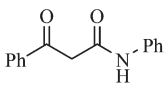
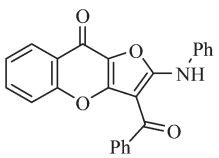
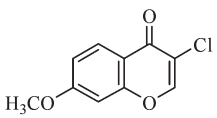
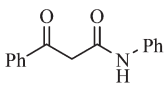
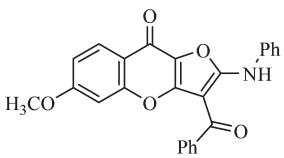
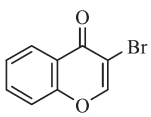
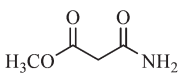
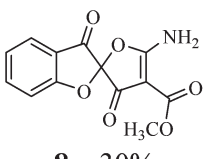
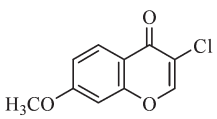
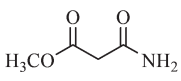
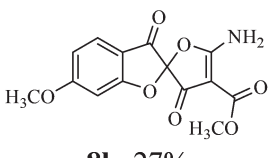
It is necessary to be noted, that in the case of the reaction of 3-halochromones with methyl 2-carbamoylacetate (**4e**) the unexpected spiro-compounds **8** were formed. This can be explained by nucleophilic attack of the phenolic OH-group of the formed 2-salicyloylfuran to the 5-position (instead of 4-position) of the activated double bond using iodine followed by further additional oxidation at 4-position. The structure of products **8** were confirmed by NMR-spectra and mass-spectroscopy. Typical signals for carbon atoms C-3, C3′, C-4′, C-7a and for the carbonyl carbon of the carboxylate group (δ = 163–192 ppm) were observed in the low yield region of the ^{13}C NMR spectra, in contrast to compounds **7**, where there was only one signal observed for the carbonyl group (δ = 185–190 ppm). An X-ray crystal structure analysis of derivative **8b** suggested the spirocyclic structure of compounds **8a,b**, which are also in accordance with 2D NMR experiments. However, due to the relatively low quality of the obtained crystal data, the X-ray structure cannot be published.

Our last goal in this investigation was to study reaction of 3-halochromones **1–3** with 1,3-dihydroindole-2-thiones **8** (Scheme 5, Table 5), which are electron rich heterocycles and a powerful 1,3-dinucleophiles. For the carrying out the reaction we decided to try different bases, such as DBU and potassium carbonate, in different solvents, such as 1,4-dioxane and DMF.



Scheme 4 Synthesis of compounds **7** and **8**. *Reaction conditions*: (i) (1) DBU (1.3 equiv.), 1,4-dioxane, 20 °C; (2) I_2 (2 equiv.), DBU (3 equiv.), MeCN or DMF.

Table 4 Synthesis of products 7 and 8 (yields refer to isolated products)

Starting materials		Product
 **5m**		 **7a**, 32%
 **2a**	 **4a**	 **7b**, 37%
 **3b**	 **4a**	 **7c**, 28%
 **2d**	 **4a**	 **7d**, 14%
 **3a**	 **4f**	 **7e**, 42%
 **3b**	 **4f**	 **7f**, 21%
 **2a**	 **4e**	 **8a**, 30%
 **3b**	 **4e**	 **8b**, 27%

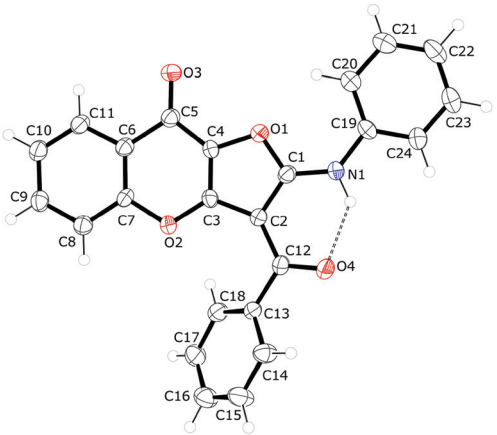
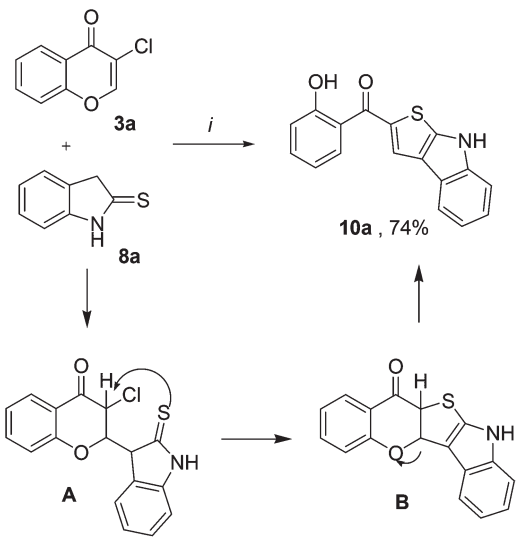


Fig. 3 ORTEP plot of compound **7e** shown with ellipsoids at the 50% level.



Scheme 5 Formation of 2-{8*H*-thieno[2,3-*b*]indole-2-carbonyl}phenol **10a**. *Reaction conditions*: (i) K_2CO_3 (4 equiv.), DMF, 20 °C.

The reaction of 3-chlorochromone (**3a**) with equimolar amount of 3*H*-indole-2-thione **8a**, in the presence of DBU (1.3 equiv.) in 1,4-dioxane (Method A), resulted in the formation of 2-{8*H*-thieno[2,3-*b*]indole-2-carbonyl}phenol **10a** in up to 57% yield and in the presence of K_2CO_3 (4 equiv.) in DMF (Method B) in up to 74% (Scheme 5, Table 5). In both methods reactions were carried out at the room temperature. The progress of the reaction was monitored by TLC (completion of the starting material, the reaction times were about 3–4 hours), the products were isolated by column chromatography using silica gel. In the case of reactions with DBU, which is a strong base, we saw more side-products on the TLC and the yields of obtained products (35–60%) were lower, than by using less strong base as a K_2CO_3 (56–78%), see Table 5. The use of 3-iodochromone **1a** instead of 3-chlorochromone **3a** by the method B resulted in a dramatic decrease of the yield up to 30% (Table 5). It shows, that the yields strongly depend on the type of halogen atom located at position 3 of the chromone (*vide supra*). For the further study of preparative scope we used mainly 3-chlorochromones **3** as the most active 3-halochromones.

The plausible mechanism of formation of **10a** can be explained by 1,4-addition of the 1,3-dihydroindole-2-thiones **8a** at position 2 of the 3-halochromone to give intermediate **A**. Subsequent attack of the sulfur atom to the carbon attached to the chlorine resulted in the formation of intermediate **B** which underwent cleavage of the carbon-sulfur bond to give **10a** (Scheme 5). The structure of **10i** was independently confirmed by X-ray crystal structure analysis (Fig. 4). We have also tried to carry out oxidative cyclization of obtained 2-benzoyl-8*H*-thieno[2,3-*b*]indoles **10** using iodine, unfortunately, it was unsuccessful, and we did not see any product on the TLC, only the starting materials.

Conclusion

In conclusion, we have developed an efficient and convenient method for the synthesis of functionalized 2-salicyloylfurans and 2-benzoyl-8*H*-thieno[2,3-*b*]indoles by the reaction of 3-halochromones with β-ketoamides and 1,3-dihydroindole-2-thiones, correspondently. The oxidative cyclization of the obtained 2-salicyloylfurans afforded furo[3,2-*b*]thromen-9-ones. These products could also be directly prepared from 3-halochromones in a one-pot reaction. The formation of the 2-salicyloylfurans proceeds by a new type of cyclization reaction which includes an initial conjugate addition, regioselective cyclization and cleavage of the chromone moiety. The regioselectivity of cyclization is surprising, since the oxygen and not the more nucleophilic nitrogen atom is involved. The products are of pharmacological relevance, as their core fragment occurs in natural products and clinically used drugs.

Experimental section

General information

NMR spectra were recorded on a Brucker AV 300 instruments. IR spectra were recorded on a Perkin Elmer FT IR 1600 spectrometer (ATR). Mass spectra were obtained on a Hewlett Packard HPGC/MS 5890/5972 instrument (EI, 70 eV) by GC inlet or on a MX-1321 instrument (EI, 70 eV) by direct inlet. Column chromatography was performed on silica gel (63–200 mesh, Merck), silica gel Merck $60F_{254}$ plates were used for TLC. All solvents were purified and dried by standard methods. The starting 3-iodochromones **1**,[73–75] 3-bromochromones **2** [70,71] and 3-chlorochromones **3** [69] were prepared according to described procedures by transformation of 2-hydroxyacetophenones to 3-dimethylamino-1-(2-hydroxyaryl)prop-2-en-1-ones and then their halogenation using iodine, bromine and iodine monochloride, respectively.[47,68] 1,3-Dihydroindole-2-thiones **8**

Table 5 Synthesis of compounds **10** (yields refer to isolated products)

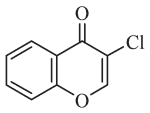
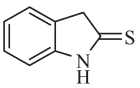
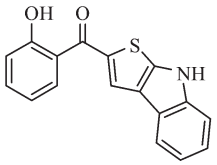
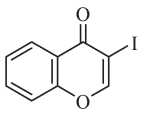
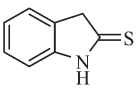
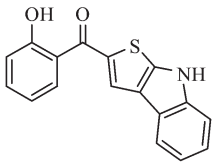
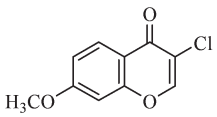
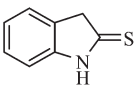
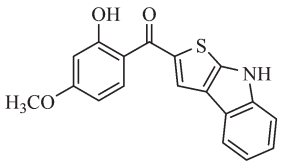
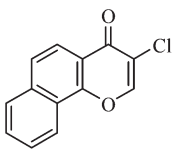
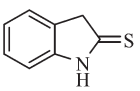
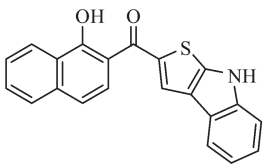
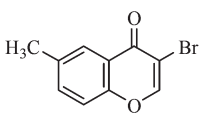
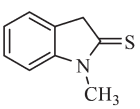
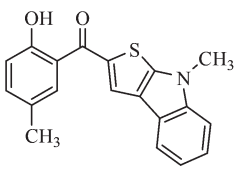
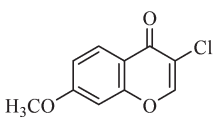
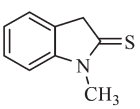
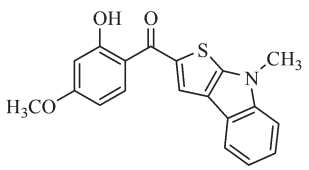
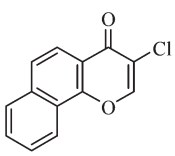
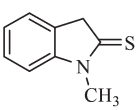
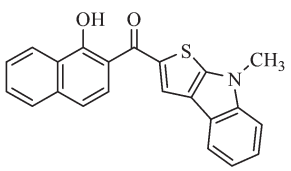
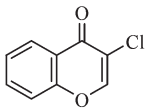
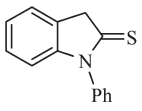
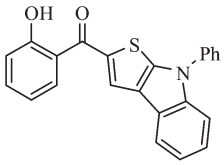
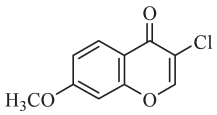
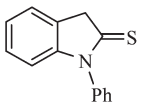
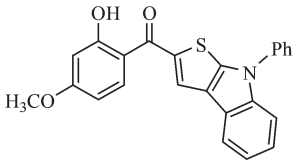
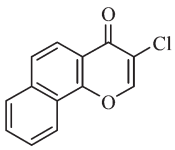
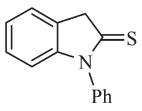
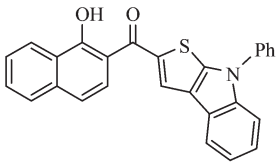
3-Halochromone	3*H*-Indole-2-thione	Product
 **3a**	 **8a**	 **10a**, 57%[a], 74%[b]
 **1a**	 **8a**	 **10a**, 30%[b]
 **3b**	 **8a**	 **10b**, 56%[b]
 **3c**	 **8a**	 **10c**, 78%[b]
 **2b**	 **8b**	 **10d**, 43%[a]
 **3b**	 **8b**	 **10e**, 46%[a]
 **3c**	 **8b**	 **10f**, 55%[a]

Table 5 *(Contd.)*

3-Halochromone	3*H*-Indole-2-thione	Product
 **3a**	 **8c**	 **10g**, 60%[a]
 **3b**	 **8c**	 **10h**, 35%[a]
 **3c**	 **8c**	 **10i**, 58%[a]

[a] Reaction conditions (Method A): DBU (1.3 equiv.), 1,4-dioxane, 20 °C. [b] Reaction conditions (Method B): K_2CO_3 (4 equiv.), DMF, 20 °C.

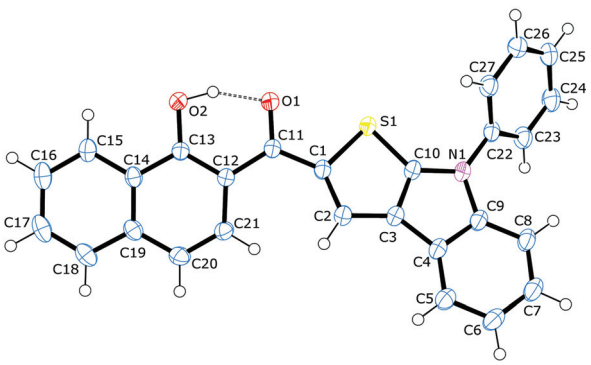


Fig. 4 ORTEP plot of compound **10i** shown with ellipsoids at the 50% level.

were synthesized from corresponding commercial available oxindoles.[19]

General procedure for the synthesis of compounds 5a–x

To a stirred reaction mixture of the corresponding 3-halochromone (1.0 mmol) and β-ketoamide (1.1 mmol) in dioxane (6–7 mL), DBU (1.3 mmol) was slowly added by syringe at room temperature. Stirring was continued until the chromone was consumed (approximately 3–4 h for 3-chlorochromones **3** and 10–12 h in case of 3-iodochromones **1** and 3-bromochromones **2**, TLC control). The solvent was distilled off under reduced pressure, and the resulting residue was washed with a diluted aqueous solution of HCl. The formed precipitate was filtered off. In some cases, it was necessary to purify the obtained product by washing with a mixture of isopropanol and heptane (1 : 10) or by chromatography (silica gel, heptane–ethyl acetate).

Procedure for the synthesis of 7a

To a solution of 2-benzoylfuran **5m** (1.0 mmol) in dichloromethane (10 mL) was added I_2 (2.0 mmol) in solid form. Subsequently, DBU (3.0 mmol) was slowly added by syringe and the mixture was stirred vigorously at room temperature. The progress of the reaction was monitored by TLC. When the starting 2-benzoylfuran **5m** was consumed, an aqueous solution of $K_2S_2O_3$ (2 mmol) and K_2CO_3 (2.0 mmol) was added and the solution was extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers were concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, heptane–ethylacetate = 3 : 1).

General procedures for the synthesis of compounds 7b–h

To a stirred mixture of 3-halochromone **2** or **3** (1.0 mmol) and β-ketoamide **4** (1.1 mmol) in dioxane (6–7 mL) DBU (1.3 mmol) was added slowly by syringe at room temperature. Stirring was continued until the chromone was completely consumed (TLC control). Dichloromethane (10 mL), solid I_2 (2.0 mmol) and DBU (3.0 mmol) were added and the mixture was stirred vigorously for 2–3 hours at room temperature. The progress of the reactions was monitored by TLC. An aqueous solution of $K_2S_2O_3$ (2 mmol) and K_2CO_3 (2.0 mmol) was added and the solution was extracted with $CHCl_3$ (3 × 15 ml). The

combined organic layers were concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, heptane–ethylacetate = 3 : 1). In the case of the reaction of 3-bromochromone **2d**, the second step of the reaction was carried out in refluxing DMF instead of dichloromethane.

General procedures for the synthesis of compounds 10

Method A. To a stirred reaction mixture of the corresponding 3-halochromone (1.0 mmol) and 3*H*-indole-2-thione (1.1 mmol) in 1,4-dioxane (12 mL), DBU (1.3 mmol) was slowly added by syringe at room temperature. Stirring was continued until the starting 3-halochromone was consumed (TLC control). The solvent was distilled off under reduced pressure, the resulting residue was purified by column chromatography (silica gel, heptane–ethyl acetate).

Method B. To a stirred reaction mixture of the corresponding 3-halochromone (1.0 mmol) and 3*H*-indole-2-thione (1.1 mmol) in DMF (12 mL), K_2CO_3 (4 mmol) was slowly added by syringe at room temperature. Stirring was continued until the chromone was consumed (TLC control). The solvent was distilled off under reduced pressure, the resulting residue was purified by column chromatography (silica gel, heptane–ethyl acetate).

1-{5-[(2-Hydroxyphenyl)carbonyl]-2-(phenylamino)furan-3-yl}ethan-1-one (5a). Yield 87%, yellow solid, mp: 141–143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H, CH_3), 6.87 (t, ^3J = 7.6 Hz, 1H, H_{Ar}), 6.98 (t, ^3J = 8.0 Hz, 1H, H_{Ar}), 7.12 (t, ^3J = 7.3 Hz, 1H, H_{Ar}), 7.33–7.47 (m, 5H, H_{Ar}), 7.55 (s, 1H, H_{Ar}), 7.98 (dd, ^1J = 1.4 Hz, ^3J = 8.0 Hz, 1H, H_{Ar}), 10.15 (s, 1H, NH or OH), 11.81 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 27.1, 103.5, 118.6, 118.8, 118.9, 2 × 119.3, 123.0, 124.9, 2 × 129.7, 130.1, 135.5, 136.3, 141.7, 159.7, 162.6, 182.4, 193.4; MS (GC, 70 eV) *m*/*z* (%) 321 ([M]$^+$, 51), 201 (24), 172 (32), 130 (35), 121 (18), 93 (100), 77 (26), 65 (15), 43 (19); HRMS (EI): calcd for $C_{19}H_{15}NO_4$ ([M]$^+$) 321.09956, found 321.09941; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3250 (w), 2922 (w), 2852 (w), 2732 (w), 1651 (m), 1616 (s), 1600 (m), 1575 (m), 1532 (s), 1472 (s), 1436 (m), 1417 (m), 1354 (w), 1323 (m), 1302 (m), 1288 (m), 1235 (m), 1222 (m), 1205 (s), 1181 (s), 1150 (s), 1110 (m), 1064 (w), 1034 (w), 1018 (w), 966 (m), 954 (m), 896 (m), 870 (w), 852 (m), 823 (m), 791 (w), 776 (w), 752 (s), 726 (s), 701 (s), 686 (m), 656 (s), 633 (s), 613 (m), 600 (m), 582 (s), 567 (m), 550 (m).

1-{5-[(5-Chloro-2-hydroxy-4-methylphenyl)carbonyl]-2-(phenylamino)furan-3-yl}ethan-1-one (5b). Yield 99%, orange solid, mp: 187–188 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.32 (s, 3H, CH_3), 2.40 (s, 3H, $COCH_3$), 6.96 (s, 1H, H_{Ar}), 7.18 (t, ^3J = 7.4 Hz, 1H, H_{Ar}), 7.39–7.44 (m, 2H, H_{Ar}), 7.56–7.59 (m, 3H, H_{Ar}), 7.84 (s, 1H, H_{Ar}), 10.23 (s, 1H, NH or OH), 10.77 (s, 1H, NH or OH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.7, 27.1, 103.5, 117.4, 2 × 119.2, 120.5, 123.2, 124.3, 125.0, 2 × 129.8, 129.9, 136.1, 142.1, 144.8, 159.5, 161.5, 180.5, 193.5; MS (GC, 70 eV) *m*/*z* (%): 369 ([M]$^+$, 45), 201 (51), 172 (29), 169 (18), 130 (38), 93 (100), 77 (52), 69 (10), 51 (13), 43 (21); HRMS (EI): calcd for $C_{20}ClH_{16}NO_4$ ([M]$^+$) 369.07624, found 369.07613; IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3239 (w), 3203 (w), 3140 (w), 3054 (w), 2952 (w), 2916 (w), 1722 (w), 1713 (w), 1641 (s), 1621 (m), 1601 (m), 1580 (m), 1514 (s), 1478 (s), 1458 (m), 1444 (m), 1384 (w), 1374 (m), 1343 (s), 1320 (m), 1230 (s), 1200 (s), 1166 (s), 1113 (m), 1021 (w), 950 (m), 879 (w), 858 (w), 837 (s), 815 (m), 744 (m), 728 (s), 689 (m), 648 (s), 610 (m), 597 (m), 531 (s).

1-{5-[(2-Hydroxy-4-methoxyphenyl)carbonyl]-2-(phenylamino)furan-3-yl}ethan-1-one (5c). Yield 98%, yellow solid, mp: 169–171 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 4.44–6.47 (m, 2H, H_{Ar}), 7.17 (t, ^3J = 7.5 Hz, 1H, H_{Ar}), 7.40 (t, ^3J = 8.4 Hz, 2H, H_{Ar}), 7.47–7.49 (m, 2H, H_{Ar}), 7.56 (s, 1H, H_{Ar}), 8.01 (d, ^3J = 8.7 Hz, 1H, H_{Ar}), 10.15 (s, 1H, NH or OH), 12.73 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 27.1, 55.6, 101.2, 103.2, 107.7, 112.4, 119.3, 120.3, 121.7, 124.8, 129.1, 129.6, 131.8, 136.4, 141.9, 159.3, 165.7, 166.1, 181.2, 193.4; MS (GC, 70 eV) *m*/*z* (%): 351 ([M]$^+$, 57), 259 (23), 258 (100), 243 (43), 217 (33), 216 (12), 201 (18), 188 (13), 172 (26), 161 (10), 151 (45), 130 (45), 128 (10), 108 (11), 93 (84), 77 (37), 69 (14), 51 (10), 43 (20); HRMS (EI): calcd for $C_{20}H_{17}NO_5$ ([M]$^+$) 351.11012, found 351.10989; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3152 (w), 3056 (w), 1681 (m), 1641 (w), 1621 (m), 1592 (s), 1524 (w), 1510 (w), 1486 (w), 1466 (m), 1435 (m), 1411 (m), 1383 (m), 1357 (m), 1296 (m), 1278 (m), 1223 (m), 1206 (s), 1196 (m), 1178 (m), 1153 (m), 1138 (m), 1089 (m), 1031 (w), 1010 (w), 989 (w), 941 (w), 925 (w), 890 (w), 976 (w), 811 (m), 773 (m), 728 (s), 697 (m), 680 (s), 638 (s), 606 (m), 580 (m), 565 (s), 549 (m).

1-{5-[(1-Hydroxynaphthalen-2-yl)carbonyl]-2-(phenylamino)-furan-3-yl}ethan-1-one (5d). Yield 53%, orange solid, mp 206–208 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.45 (s, 3H, CH_3), 7.21 (t, ^3J = 7.3 Hz, 1H, H_{Ar}), 7.38–7.48 (m, 3H, H_{Ar}), 7.55–7.63 (m, 3H, H_{Ar}), 7.69 (t, ^3J = 7.0 Hz, 1H, H_{Ar}), 7.91 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 8.04 (d, ^3J = 8.9 Hz, 1H, H_{Ar}), 8.12 (s, 1H, H_{Ar}), 8.33 (t, ^3J = 8.2 Hz, 1H, H_{Ar}), 10.27 (s, 1H, NH or OH), 13.9 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 27.3, 104.0, 112.4, 118.4, 2 × 120.5, 123.4, 124.5, 124.8, 2 × 125.1, 126.1, 127.5, 2 × 129.3, 129.9, 136.2, 136.6, 140.6, 158.9, 160.9, 181.0, 193.0; MS (EI, 70 eV) *m*/*z* (%): 371 ([M]$^+$, 41), 278 (21), 263 (13), 237 (15), 201 (100), 186 (10), 171 (18), 130 (17), 93 (53), 77 (11), 69 (12), 43 (9); HRMS (ESI): calcd for $C_{23}H_{18}NO_4$ ([M + H]$^+$) 372.12303, found 372.12341, calcd for $C_{23}H_{17}NO_4Na$ ([M + Na]$^+$) 394.10498, found 394.10503; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3235 (w), 3065 (w), 2921 (w), 2851 (w), 1641 (w), 1621 (m), 1602 (w), 1574 (m), 1520 (s), 1482 (w), 1455 (m), 1409 (m), 1382 (m), 1350 (m), 1322 (m), 1263 (m), 1243 (s), 1202 (s), 1156 (m), 1145 (m), 1128 (s), 1096 (m), 1062 (w), 1023 (m), 1000 (w), 955 (m), 922 (w), 906 (w), 880 (w), 857 (m), 809 (w), 790 (s), 749 (s), 718 (s), 691 (s), 650 (s), 628 (m), 612 (m), 596 (w), 572 (m), 529 (s).

1-{2-[(2,4-Dimethylphenyl)amino]-5-[(2-hydroxyphenyl)carbonyl]furan-3-yl}ethan-1-one (5e). Yield 93%, orange solid, mp: 141–143 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.25 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.86–6.98 (m, 2H, H_{Ar}), 7.07–7.11 (m, 2H, H_{Ar}), 7.42 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, H_{Ar}), 7.54–7.60 (m, 2H, H_{Ar}), 7.75 (s, 1H, H_{Ar}), 10.15 (s, 1H, NH or OH), 10.70 (s, 1H, NH or OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 17.3, 20.4, 27.0, 103.1, 116.9, 118.9, 120.6, 123.1, 123.9, 127.3, 128.6, 129.7, 131.3, 132.4, 133.1, 134.4,

141.5, 157.6, 159.7, 180.5, 193.3; MS (GC, 70 eV) *m*/*z* (%): 349 ([M]$^+$, 61), 229 (18), 200 (19), 121 (100), 105 (12), 77 (12), 65 (12), 43 (10); HRMS (EI): calcd for $C_{21}H_{19}NO_4$ ([M]$^+$) 349.13086, found 349.13057; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3097 (w), 3042 (w), 3012 (w), 2959 (w), 2919 (w), 2853 (w), 2731 (w), 1650 (m), 1606 (m), 1565 (m), 1526 (s), 1481 (s), 1435 (m), 1392 (w), 1376 (w), 1349 (m), 1293 (m), 1285 (m), 1264 (w), 1231 (s), 1205 (ss), 1177 (m), 1152 (s), 1134 (m), 1116 (m), 1034 (m), 1018 (m), 956 (m), 932 (m), 889 (m), 866 (w), 842 (s), 805 (s), 796 (s), 775 (m), 754 (s), 726 (s), 696 (s), 672 (s), 625 (s), 583 (s), 547 (s).

1-{2-[(2,4-Dimethylphenyl)amino]-5-[(2-hydroxy-4-methoxyphenyl)carbonyl]furan-3-yl}ethan-1-one (5f). Yield 69%, brawn solid, mp: 137–139 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.42–6.47 (m, 2H, H_{Ar}), 7.08–7.10 (m, 2H, H_{Ar}), 7.60 (s, 1H, H_{Ar}), 7.69 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 8.02 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 10.16 (s, 1H, NH or OH), 12.84 (s, 1H, NH or OH); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 17.7, 20.8, 26.9, 55.5, 101.1, 103.2, 107.7, 112.4, 119.6, 121.9, 127.7, 127.8, 131.7, 131.9, 132.4, 134.8, 141.8, 160.0, 165.6, 166.2, 181.1, 193.3; MS (GC, 70 eV) *m*/*z* (%): 379 ([M]$^+$, 22), 217 (20), 151 (20), 121 (100); HRMS (EI): calcd for $C_{22}H_{21}NO_5$ ([M]$^+$) 379.14142, found 379.14136; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3012 (w), 2971 (w), 2920 (w), 2850 (w), 1725 (w), 1710 (w), 1689 (w), 1642 (m), 1607 (m), 1572 (m), 1530 (s), 1502 (m), 1484 (m), 1469 (m), 1442 (m), 1412 (w), 1369 (m), 1355 (m), 1329 (w), 1294 (w), 1243 (s), 1207 (s), 1184 (m), 1162 (w), 1129 (s), 1021 (w), 950 (m), 932 (w), 877 (w), 867 (w), 851 (w), 829 (m), 800 (m), 757 (w), 729 (m), 691 (m), 632 (s), 614 (w), 585 (m), 551 (w).

1-{2-[(2,4-Dimethylphenyl)amino]-5-[(1-hydroxynaphthalen-2-yl)carbonyl]furan-3-yl}ethan-1-one (5g). Yield 76%, yellow solid, mp 161–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 7.10 (s, 1H, H_{Ar}), 7.15 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 7.28 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 7.54 (dt, ^3J = 6.9 Hz, ^1J = 0.9 Hz, 1H, H_{Ar}), 7.63 (dt, ^3J = 8.1 Hz, ^1J = 1.2 Hz, 1H, H_{Ar}), 7.70 (s, 1H, H_{Ar}), 7.76–7.80 (m, 2H, H_{Ar}), 8.06 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 8.48 (d, ^3J = 8.3 Hz, 1H, H_{Ar}), 10.20 (s, 1H, NH or OH), 14.12 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.8, 20.9, 27.0, 103.5, 112.0, 118.2, 119.6, 122.7, 124.4, 124.7, 125.5, 125.9, 127.3, 127.7, 127.8, 130.0, 131.7, 132.4, 134.8, 136.8, 141.9, 160.1, 163.6, 182.0, 193.4; MS (EI, 70 eV) *m*/*z* (%): 399 ([M]$^+$, 52), 237 (16), 230 (12), 229 (93), 200 (10), 171 (12), 121 (100); HRMS (EI): calcd for $C_{25}H_{21}NO_4$ ([M]$^+$) 399.14651, found 399.14623; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3118 (w), 3051 (w), 3015 (w), 2972 (w), 2922 (w), 2860 (w), 1642 (m), 1626 (m), 1611 (w), 1601 (w), 1568 (m), 1528 (s), 1503 (m), 1482 (w), 1461 (s), 1420 (m), 1376 (m), 1354 (m), 1328 (w), 1271 (w), 1244 (s), 1205 (s), 1150 (m), 1130 (m), 1117 (m), 1098 (m), 1061 (w), 1025 (w), 999 (w), 958 (m), 931 (w), 920 (w), 874 (m), 802 (m), 787 (s), 754 (s), 732 (m), 716 (m), 660 (w), 631 (s), 587 (w), 572 (m), 551 (w).

1-{5-[(2-Hydroxyphenyl)carbonyl]-2-[(2-methylphenyl)amino]-furan-3-yl}ethan-1-one (5h). Yield 85%, yellow solid, mp 109–111 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.31 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 6.89–6.99 (m, 2H, H_{Ar}), 7.14 (td, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 1H, H_{Ar}), 7.27–7.34 (m, 2H, H_{Ar}), 7.42 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_{Ar}), 7.59 (dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_{Ar}), 7.72 (d, ^3J = 8.00 Hz, 1H, H_{Ar}), 7.78 (s, 1H, H_{Ar}), 10.23 (s, 1H, NH or OH), 10.66 (s, 1H, NH or OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 17.3, 27.0, 103.2, 116.9, 118.9, 120.3, 123.2, 123.6, 125.0, 127.0, 128.5, 129.6, 130.8, 133.1, 135.0, 141.7, 157.5, 159.5, 180.6, 193.5; MS (GC, 70 eV) *m*/*z* (%): 335 ([M]$^+$, 62), 215 (18), 186 (28), 144 (17), 121 (18), 107 (100), 91 (31), 65 (27), 43 (14); HRMS (EI): calcd for $C_{20}H_{17}NO_4$ ([M]$^+$) 335.11521, found 335.11497; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3145 (w), 2969 (w), 2734 (w), 1641 (s), 1615 (m), 1594 (s), 1577 (m), 1538 (s), 1481 (s), 1440 (m), 1403 (m), 1379 (w), 1348 (m), 1324 (m), 1295 (s), 1237 (s), 1216 (s), 1187 (m), 1151 (s), 1112 (m), 1033 (w), 996 (w), 968 (m), 957 (m), 899 (w), 862 (m), 824 (m), 794 (w), 781 (w), 752 (s), 734 (s), 699 (s), 678 (m), 653 (s), 631 (s), 591 (m), 573 (m), 558 (w).

1-{5-[(5-Chloro-2-hydroxy-4-methylphenyl)carbonyl]-2-[(2-methylphenyl)amino]furan-3-yl}ethan-1-one (5i). Yield 99%, yellow solid, mp 166–167 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.31 (s, 6H, 2 × CH_3), 2.40 (s, 3H, CH_3), 6.94 (s, 1H, H_{Ar}), 7.14 (t, ^3J = 6.7 Hz, 1H, H_{Ar}), 7.31 (m, 2H, H_{Ar}), 7.58 (s, 1H, H_{Ar}), 7.70 (d, ^3J = 7.6 Hz, 1H, H_{Ar}), 7.84 (s, 1H, H_{Ar}), 10.24 (s, 1H, NH or OH), 10.84 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 17.3, 19.9, 27.1, 103.3, 119.3, 120.5, 122.5, 123.0, 124.1, 125.2, 127.0, 128.7, 129.2, 130.9, 134.9, 140.7, 141.7, 156.2, 159.6, 178.7, 193.5; MS (GC, 70 eV) *m*/*z* (%): 383 ([M]$^+$, 33), 215 (29), 186 (18), 169 (12), 144 (12), 107 (100), 91 (27), 77 (13), 65 (11), 43 (13); HRMS (ESI): calcd for $C_{21}ClH_{19}NO_4$ ([M + H]$^+$) 384.09971, found 384.09934, calcd for $C_{21}{}^{37}ClH_{19}NO_4$ ([M + H]$^+$) 386.09763, found 386.09792; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3140 (w), 3113 (w), 3027 (w), 2918 (w), 2858 (w), 1641 (s), 1621 (m), 1597 (m), 1574 (m), 1531 (s), 1505 (m), 1479 (m), 1464 (m), 1415 (w), 1372 (m), 1344 (m), 1323 (m), 1307 (m), 1247 (s), 1227 (s), 1178 (m), 1168 (m), 1112 (m), 1049 (w), 1021 (w), 1001 (w), 958 (m), 947 (m), 870 (w), 847 (m), 807 (m), 778 (w), 743 (w), 690 (m), 647 (m), 622 (m), 599 (m), 555 (w), 536 (m).

1-{5-[(2-Hydroxy-4-methoxyphenyl)carbonyl]-2-[(2-methylphenyl)amino]furan-3-yl}ethan-1-one (5j). Yield 98%, yellow solid, mp: 156–158; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.32 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 6.48–6.51 (m, 2H, H_{Ar}), 7.14 (t, ^3J = 8.1 Hz, 1H, H_{Ar}), 7.31 (t, ^3J = 7.5 Hz, 2H, H_{Ar}), 7.71 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 7.85 (d, ^3J = 8.7 Hz, 1H, H_{Ar}), 7.98 (s, 1H, H_{Ar}), 10.22 (s, 1H, NH or OH), 12.11 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 17.6, 27.3, 55.8, 101.5, 103.4, 107.0, 113.6, 121.0, 123.8, 125.4, 127.2, 129.1, 131.0, 132.2, 135.2, 141.0, 160.0, 163.4, 164.7, 180.3, 193.6; MS (GC, 70 eV) *m*/*z* (%): 365 ([M]$^+$, 32), 258 (18), 217 (19), 186 (11), 151 (25), 144 (12), 107 (100), 91 (25), 65 (13), 43 (12); HRMS (ESI): calcd for $C_{21}H_{20}NO_5$ ([M + H]$^+$) 366.13360, found 366.13368, calcd for $C_{21}H_{19}NaNO_5$ ([M + Na]$^+$) 388.11554, found 388.11563; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3100 (w), 3031 (w), 3014 (w), 2985 (w), 2951 (w), 2917 (w), 2894 (w), 2849 (w), 1639 (s), 1617 (m), 1592 (s), 1574 (s), 1556 (w), 1528 (s), 1503 (s), 1475 (m), 1462 (s), 1430 (m), 1397 (w), 1359 (s), 1322 (m), 1307 (w), 1296 (w), 1254 (s), 1229 (s), 1202 (s), 1183 (m), 1172 (s), 1140 (s), 1128 (s), 1107 (s), 1062 (w), 1048 (w), 1024 (s), 960

(m), 948 (m), 878 (w), 851 (m), 835 (s), 809 (w), 799 (m), 780 (w), 744 (s), 729 (s), 686 (s), 647 (m), 631 (s), 599 (m), 555 (m), 526 (m).

1-{5-[(1-Hydroxynaphthalen-2-yl)carbonyl]-2-[(2-methylphenyl)amino]furan-3-yl}ethan-1-one (5k). Yield 93%, yellow solid, mp: 166–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 7.14 (t, ^3J = 7.5 Hz, 1H, H_{Ar}), 7.26–7.30 (m, 2H, H_{Ar}), 7.35 (t, ^3J = 7.5 Hz, 1H, H_{Ar}), 7.50–7.56 (m, 1H, H_{Ar}), 7.60–7.65 (m, 1H, H_{Ar}), 7.69 (s, 1H, H_{Ar}), 7.74 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 7.92 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 8.03 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 8.46 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 10.31 (s, 1H, NH or OH), 14.12 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.6, 26.8, 103.4, 111.7, 118.0, 119.1, 122.3, 124.1, 124.4, 124.7, 125.2, 125.7, 127.1, 127.1, 127.3, 129.8, 130.8, 134.8, 136.6, 141.8, 159.6, 163.4, 182.1, 193.3; MS (EI, 70 eV) *m*/*z* (%): 385 ([M]$^+$, 53), 237 (15), 216 (11), 215 (96), 186 (12), 171 (17), 170 (11), 152 (39), 151 (40), 144 (11), 137 (14), 123 (18), 115 (12), 107 (100), 98 (12), 96 (17), 91 (16), 69 (15), 43 (10), 41 (10); HRMS (EI): calcd for $C_{24}H_{19}NO_4$ ([M]$^+$) 385.13086, found 385.13065; IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3122 (w), 3067 (w), 2915 (w), 2859 (w), 1643 (s), 1619 (m), 1594 (m), 1573 (m), 1524 (s), 1459 (s), 1415 (m), 1375 (m), 1356 (m), 1328 (w), 1294 (w), 1265 (m), 1243 (s), 1229 (s), 1209 (m), 1194 (m), 1177 (w), 1148 (m), 1129 (m), 1111 (m), 1096 (w), 1050 (w), 1023 (w), 998 (w), 958 (m), 911 (m), 867 (m), 809 (w), 797 (m), 790 (m), 775 (m), 755 (s), 732 (s), 721 (s), 694 (w), 660 (w), 644 (s), 626 (m), 572 (m), 544 (m).

1-{2-[(4-Chlorophenyl)amino]-5-[(2-hydroxyphenyl)carbonyl]-furan-3-yl}ethan-1-one (5l). Yield 46%, braun solid, mp 175–177 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.39 (s, 3H, CH_3), 6.91–7.00 (m, 2H, H_{Ar}), 7.42–7.45 (m, 3H, H_{Ar}), 7.58–7.60 (m, 3H, H_{Ar}), 7.77 (s, 1H, H_{Ar}), 10.24 (s, 1H, NH or OH), 10.64 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 27.3, 103.8, 116.9, 118.9, 2 × 121.7, 123.2, 123.4, 128.2, 2 × 129.0, 129.7, 133.2, 135.8, 141.8, 157.4, 158.2, 180.7, 192.9; MS (GC, 70 eV) *m*/*z* (%): 355 ([M]$^+$, 44), 235 (24), 206 (22), 187 (26), 164 (35), 127 (100), 111 (13), 65 (18), 43 (30); HRMS (ESI): calcd for $C_{19}ClH_{15}NO_4$ ([M + H]$^+$) 356.06841, found 356.06842, calcd for $C_{19}{}^{37}ClH_{15}NO_4$ ([M + H]$^+$) 358.06621, found 358.06626; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3237 (w), 3196 (w), 3154 (w), 3099 (w), 3054 (w), 1643 (w), 1615 (m), 1587 (w), 1574 (m), 1557 (w), 1526 (s), 1505 (m), 1479 (s), 1435 (m), 1417 (m), 1385 (w), 1337 (m), 1295 (m), 1282 (m), 1241 (m), 1229 (m), 1203 (m), 1181 (m), 1155 (s), 1093 (m), 1062 (w), 1034 (w), 1014 (w), 958 (m), 891 (m), 864 (w), 852 (w), 836 (m), 808 (s), 755 (s), 725 (s), 697 (s), 671 (s), 633 (m), 617 (s), 592 (m), 567 (s), 529 (s).

1-{2-[(4-Chlorophenyl)amino]-5-[(2-hydroxy-5-methylphenyl)-carbonyl]furan-3-yl}ethan-1-one (5m). Yield 99%, yellow solid, mp 188–190 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.24 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 6.88 (d, ^3J = 8.3 Hz, 1H, H_{Ar}), 7.22 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 7.40–7.43 (m, 3H, H_{Ar}), 7.57–7.59 (m, 2H, H_{Ar}), 7.78 (s, 1H, H_{Ar}), 10.24 (s, 1H, NH or OH), 10.61 (s, 1H, NH or OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 19.9, 27.3, 103.7, 116.8, 2 × 121.8, 123.3, 127.6, 128.2, 2 × 129.0, 129.6, 134.1, 135.8, 141.9, 155.6, 155.7, 158.2, 180.8, 192.9; MS (GC, 70 eV) *m*/*z* (%): 369 ([M]$^+$, 58), 242 (13), 237 (20), 235 (57), 227 (10), 206 (23), 201 (27), 166 (14), 164 (45), 135 (48), 127 (100), 111 (21), 107 (11), 77 (38), 75 (15), 69 (16), 53 (11), 43 (47); HRMS (EI): calcd for $C_{20}ClH_{16}NO_4$ ([M]$^+$) 369.07624, found 369.07589, calcd for $C_{20}{}^{37}ClH_{16}NO_4$ ([M]$^+$) 371.07329, found 371.07380; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3233 (w), 3190 (w), 2917 (w), 2859 (w), 2710 (w), 1643 (w), 1608 (m), 1567 (m), 1520 (s), 1478 (s), 1418 (m), 1384 (m), 1341 (s), 1324 (s), 1291 (m), 1284 (m), 1253 (m), 1244 (m), 1230 (s), 1213 (s), 1201 (s), 1161 (s), 1107 (m), 1092 (s), 1061 (m), 1027 (w), 1011 (m), 978 (w), 961 (m), 913 (w), 889 (w), 870 (w), 800 (s), 762 (m), 738 (s), 697 (m), 679 (s), 635 (m), 619 (s), 588 (m), 573 (m), 549 (m).

1-{5-[(5-Chloro-2-hydroxy-4-methylphenyl)carbonyl]-2-[(4-chlorophenyl)amino]furan-3-yl}ethan-1-one (5n). Yield 98%, yellow solid, mp: 214–216 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.32 (s, 3H, CH_3), 2.40 (s, 3H, $COCH_3$), 6.96 (s, 1H, H_{Ar}), 7.43–7.48 (m, 2H, H_{Ar}), 7.57–7.61 (m, 3H, H_{Ar}), 7.83 (s, 1H, H_{Ar}), 10.27 (s, 1H, NH or OH), 10.78 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 19.9, 27.3, 103.9, 119.2, 2 × 122.0, 122.7, 123.01, 123.9, 128.4, 2 × 129.1, 129.2, 135.7, 140.7, 141.8, 156.1, 158.4, 178.8, 192.9; MS (GC, 70 eV) *m*/*z* (%): 403 ([M]$^+$, 42), 237 (25), 236 (10), 235 (74), 206 (30), 169 (26), 166 (12), 164 (32), 129 (32), 127 (100), 111 (14), 77 (20), 75 (11), 69 (12), 43 (30); HRMS (ESI): calcd for $C_{20}Cl_2H_{16}NO_4$ ([M + H]$^+$) 404.04509, found 404.04507, calcd for $C_{20}{}^{37}Cl_2H_{16}NO_4$ ([M + H]$^+$) 406.04256, found 406.0426; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3242 (w), 3196 (w), 3109 (w), 2979 (w), 2919 (w), 2855 (w), 1641 (m), 1621 (m), 1573 (m), 1525 (s), 1494 (s), 1373 (m), 1340 (s), 1310 (m), 1247 (s), 1202 (s), 1167 (s), 1118 (m), 1092 (m), 1061 (w), 1011 (m), 968 (w), 947 (m), 880 (w), 842 (m), 803 (m), 742 (m), 690 (m), 634 (w), 618 (m), 592 (m), 546 (m).

1-{2-[(4-Chlorophenyl)amino]-5-[(2-hydroxy-4-methoxyphenyl)carbonyl]furan-3-yl}ethan-1-one (5o). Yield 47%, yellow solid, mp: 187–189 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.43 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.52–6.56 (m, 2H, H_{Ar}), 7.46 (d, ^3J = 8.7 Hz, 2H, H_{Ar}), 7.59 (d, ^3J = 9.0 Hz, 2H, H_{Ar}), 7.87 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 7.95 (s, 1H, H_{Ar}), 10.25 (s, 1H, NH or OH), 12.08 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 27.5, 55.8, 101.5, 104.0, 107.0, 113.6, 2 × 122.1, 123.6, 128.5, 2 × 129.3, 132.2, 136.0, 141.1, 158.3, 163.3, 164.8, 180.4, 193.1; MS (GC, 70 eV) *m*/*z* (%): 385 ([M]$^+$, 37), 258 (100), 243 (40), 235 (12), 217 (46), 206 (15), 188 (12), 166 (11), 164 (35), 151 (53), 129 (23), 127 (63), 111 (16), 75 (10), 69 (17), 43 (29); HRMS (ESI): calcd for $C_{20}ClH_{17}NO_5$ ([M + H]$^+$) 386.07898, found 386.07883, calcd for $C_{20}{}^{37}ClH_{17}NO_5$ ([M + H]$^+$) 388.07688, found 388.07679; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3231 (w), 3119 (w), 3008 (w), 2916 (w), 2849 (w), 1643 (m), 1618 (m), 1573 (m), 1525 (s), 1500 (s), 1438 (m), 1418 (w), 1374 (m), 1351 (m), 1320 (w), 1296 (w), 1245 (s), 1205 (s), 1183 (m), 1136 (s), 1110 (m), 1091 (m), 1061 (w), 1027 (w), 1021 (w), 1013 (w), 952 (s), 881 (w), 834 (s), 806 (m), 757 (w), 722 (m), 706 (w), 694 (w), 694 (m), 675 (w), 638 (m), 619 (m), 593 (w), 562 (s), 528 (w).

1-{2-[(4-Chlorophenyl)amino]-5-[(1-hydroxynaphthalen-2-yl)-carbonyl]furan-3-yl}ethan-1-one (5p). Yield 56%, yellow solid, mp 230–232 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3H, CH_3), 7.27–7.40 (m, 3H, H_{Ar}), 7.45–7.48 (m, 2H, H_{Ar}), 7.53 (t, ^3J = 7.7 Hz, 1H, H_{Ar}), 7.61–7.64 (m, 2H, H_{Ar}), 7.77 (d, ^3J = 8.0 Hz,

1H, H_{Ar}), 7.98 (d, ^3J = 8.8 Hz, 1H, H_{Ar}), 8.46 (d, ^3J = 8.3 Hz, 1H, H_{Ar}), 10.19 (s, 1H, NH or OH), 13.92 (s, 1H, NH or OH); ^{13}C NMR (62.3 MHz, $CDCl_3$): δ = 27.1, 103.6, 111.9, 118.3, 2 × 120.4, 122.3, 124.3, 124.4, 125.4, 126.0, 127.3, 2 × 129.7, 129.9, 130.2, 135.0, 136.9, 142.1, 159.1, 163.5, 182.2, 193.6; MS (EI, 70 eV) *m*/*z* (%): 405 ([M]$^+$, 32), 278 (28), 263 (14), 235 (100), 171 (42), 164 (21), 127 (47), 115 (17), 110 (15), 43 (11); HRMS (ESI): calcd for $C_{23}H_{16}ClNO_4$ ([M − H]$^-$) 404.06951, found 404.07002, calcd for $C_{23}H_{16}{}^{37}ClNO_4$ ([M − H]$^-$) 406.06755, found 406.06784; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3240 (w), 3119 (w), 3049 (w), 2961 (w), 2923 (w), 2853 (w), 1731 (w), 1651 (m), 1620 (m), 1575 (m), 1537 (s), 1494 (m), 1464 (m), 1422 (m), 1385 (m), 1349 (m), 1317 (w), 1271 (m), 1253 (s), 1209 (m), 1181 (w), 1150 (m), 1094 (m), 1062 (w), 1027 (w), 1016 (w), 1004 (m), 962 (m), 925 (w), 863 (m), 803 (s), 787 (m), 751 (m), 723 (m), 712 (m), 691 (w), 650 (w), 637 (m), 619 (m), 571 (m), 547 (m).

Methyl 2-amino-5-[(2-hydroxyphenyl)carbonyl]furan-3-carboxylate (5q). Yield 98%, yellow solid, mp 142–144 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.70 (s, 3H, OCH_3), 6.87–6.95 (m, 2H, H_{Ar}), 7.18 (s, 1H, H_{Ar}), 7.38 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_{Ar}), 7.53 (dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1H, H_{Ar}), 8.09 (s, 2H, NH_2), 10.59 (s, 1H, OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 50.9, 91.2, 116.8, 118.9, 123.4, 125.2, 129.5, 132.8, 140.7, 157.2, 163.2, 164.6, 179.7; MS (GC, 70 eV) *m*/*z* (%): 261 ([M]$^+$, 33), 244 (100), 213 (20), 184 (10), 158 (21), 141 (23), 121 (42), 109 (28), 93 (11), 65 (22), 52 (19), 39 (11); HRMS (EI): calcd for $C_{13}H_{11}NO_5$ ([M]$^+$) 261.06317, found 261.06323; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3370 (w), 3307 (w), 3244 (w), 3174 (w), 1699 (m), 1668 (m), 1628 (w), 1568 (m), 1557 (m), 1537 (s), 1470 (m), 1427 (w), 1372 (m), 1315 (m), 1287 (m), 1247 (s), 1223 (s), 1182 (m), 1150 (s), 1115 (m), 1093 (m), 1041 (m), 962 (w), 947 (w), 893 (m), 876 (w), 865 (w), 821 (w), 806 (m), 777 (m), 738 (s), 708 (m), 695 (m), 668 (m), 627 (s), 580 (m).

Methyl 2-amino-5-[(2-hydroxy-5-methylphenyl)carbonyl]furan-3-carboxylate (5r). Yield 90%, yellow solid, mp 111–113 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.24 (s, 3H, CH_3), 3.70 (s, 3H, OCH_3), 6.82 (d, ^3J = 8.3 Hz, 1H, H_{Ar}), 7.17–7.19 (m, 2H, H_{Ar}), 7.32 (s, 1H, H_{Ar}), 8.08 (s, 2H, NH_2), 10.38 (s, 1H, OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 20.0, 50.9, 91.1, 116.7, 123.1, 125.1, 127.6, 129.4, 133.4, 140.7, 155.0, 163.3, 164.6, 179.9; MS (GC, 70 eV) *m*/*z* (%): 275 ([M]$^+$, 38), 258 (100), 230 (17), 227 (18), 172 (15), 141 (40), 135 (64), 109 (36), 107 (13), 77 (31), 52 (23); HRMS (EI): calcd for $C_{14}H_{13}NO_5$ ([M]$^+$) 275.07882, found 275.07859; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3418 (w), 3368 (w), 3307 (w), 3242 (w), 3152 (w), 2952 (w), 2922 (w), 2860 (w), 1699 (m), 1682 (w), 1674 (w), 1668 (w), 1651 (w), 1627 (m), 1615 (m), 1574 (s), 1568 (s), 1557 (s), 1538 (s), 1531 (s), 1526 (s), 1520 (s), 1480 (s), 1428 (m), 1408 (w), 1371 (w), 1345 (w), 1307 (w), 1285 (s), 1245 (m), 1226 (s), 1165 (s), 1141 (s), 1125 (s), 1090 (m), 1044 (m), 953 (w), 919 (w), 868 (w), 851 (w), 820 (m), 810 (m), 774 (s), 734 (m), 709 (m), 697 (m), 678 (s), 574 (m), 534 (s).

Methyl 2-amino-5-[(2-hydroxy-4-methoxyphenyl)carbonyl]furan-3-carboxylate (5s). Yield 79%, braun solid, mp: 116–118 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ = 3.72 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.47–6.53 (m, 2H, H_{Ar}), 7.42 (s, 1H, H_{Ar}), 7.87 (d, ^3J = 8.6 Hz, 1H, H_{Ar}), 8.08 (s, 2H, NH_2), 12.25 (s, 1H, OH); ^{13}C NMR (62.3 MHz, DMSO-d_6): δ = 50.9, 55.5, 91.4, 101.3, 106.8, 113.4, 124.6, 131.9, 140.0, 163.2, 163.3, 164.3, 164.4, 179.6; MS (GC, 70 eV) *m*/*z* (%): 291 ([M]$^+$, 30), 274 (100), 259 (11), 246 (26), 243 (24), 231 (18), 188 (12), 151 (46), 109 (13), 108 (10), 52 (13); HRMS (EI): calcd for $C_{14}H_{13}NO_6$ ([M]$^+$) 291.07374, found 291.07358; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3365 (w), 3308 (w), 3234 (w), 3171 (w), 2949 (w), 2843 (w), 2207 (w), 1697 (w), 1672 (w), 1613 (m), 1566 (m), 1529 (s), 1503 (m), 1468 (m), 1453 (w), 1432 (m), 1373 (w), 1328 (w), 1314 (w), 1293 (w), 1251 (s), 1230 (s), 1209 (s), 1185 (s), 1160 (s), 1121 (s), 1097 (s), 1050 (m), 1022 (m), 969 (w), 884 (w), 870 (w), 819 (m), 807 (m), 778 (m), 756 (w), 738 (m), 706 (m), 693 (m), 665 (w), 642 (w), 618 (s), 580 (s), 558 (s).

Methyl 2-amino-5-[(1-hydroxynaphthalen-2-yl)carbonyl]-furan-3-carboxylate (5t). Yield 88%, yellow solid, mp: 192–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OCH_3), 6.32 (s, 2H, NH_2), 7.26 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 7.49–7.54 (m, 1H, H_{Ar}), 7.56 (s, 1H, H_{Ar}), 7.58–7.63 (m, 1H, H_{Ar}), 7.74 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 7.86 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 8.43 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 13.78 (s, 1H, OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.7, 93.6, 112.1, 118.5, 2 × 124.5, 124.8, 125.6, 126.1, 127.5, 130.1, 137.0, 141.3, 163.1, 164.0, 164.7, 182.5; MS (EI, 70 eV) *m*/*z* (%): 311 ([M]$^+$, 59), 295 (21), 294 (100), 266 (15), 263 (23), 197 (25), 196 (24), 171 (59), 170 (45), 142 (10), 141 (88), 115 (24), 114 (29), 109 (52); HRMS (EI): calcd for $C_{17}H_{13}NO_5$ ([M]$^+$) 311.07882, found 311.07879; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3435 (w), 3422 (w), 3310 (w), 3258 (w), 3151 (w), 3055 (w), 2948 (w), 1693 (m), 1623 (m), 1600 (w), 1564 (m), 1536 (m), 1479 (w), 1454 (s), 1427 (m), 1413 (m), 1385 (w), 1317 (w), 1268 (s), 1251 (s), 1210 (m), 1163 (s), 1148 (s), 1105 (m), 1023 (m), 978 (w), 914 (w), 871 (w), 837 (w), 805 (w), 792 (s), 761 (s), 737 (s), 716 (m), 660 (w), 638 (w), 602 (m), 549 (m), 526 (m).

2-{[4-Benzoyl-5-(phenylamino)furan-2-yl]carbonyl}phenol (5u). Yield 81%, yellow solid, mp: 170–172 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.88–6.98 (m, 2H, H_{Ar}), 7.21 (t, ^3J = 7.4 Hz, 1H, H_{Ar}), 7.37–7.47 (m, 4H, H_{Ar}), 7.53–7.66 (m, 6H, H_{Ar}), 7.79–7.81 (m, 2H, H_{Ar}), 10.54 (s, 1H, NH or OH), 10.65 (s, 1H, NH or OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 101.8, 116.8, 119.0, 2 × 120.4, 123.2, 123.6, 124.7, 2 × 128.0, 2 × 128.8, 129.3, 2 × 129.7, 132.0, 133.1, 136.6, 138.4, 142.1, 157.0, 160.6, 180.6, 188.2; MS (EI, 70 eV) *m*/*z* (%): 383 ([M]$^+$, 44), 291 (13), 263 (18), 234 (14), 171 (9), 121 (10), 105 (100), 93 (99), 91 (18), 77 (78), 66 (11), 51 (11); HRMS (EI): calcd for $C_{24}H_{17}NO_4$ ([M]$^+$) 383.11521, found 383.11551; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 1635 (s), 1599 (m), 1587 (m), 1578 (m), 1566 (s), 1542 (s), 1499 (m), 1481 (m), 1470 (m), 1445 (m), 1394 (m), 1351 (w), 1336 (w), 1325 (w), 1299 (m), 1289 (m), 1265 (m), 1245 (s), 1218 (m), 1203 (m), 1178 (m), 1147 (s), 1137 (m), 1103 (w), 1031 (w), 1000 (w), 972 (m), 937 (m), 923 (w), 890 (m), 870 (w), 846 (w), 822 (w), 799 (w), 786 (m), 761 (m), 739 (s), 710 (m), 690 (s), 657 (s), 616 (m), 601 (m), 575 (m), 565 (m), 530 (m).

2-{[4-Benzoyl-5-(phenylamino)furan-2-yl]carbonyl}-4-chloro-5-methylphenol (5v). Yield 72%, yellow solid, mp: 200–202 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 3H, CH_3), 6.92 (s, 1H,

H_{Ar}), 7.21–7.26 (m, 1H, H_{Ar}), 7.47–7.56 (m, 7H, H_{Ar}), 7.82–7.84 (m, 3H, H_{Ar}), 8.24 (s, 1H, H_{Ar}), 10.75 (s, 1H, NH or OH), 12.17 (s, 1H, NH or OH); ^{13}C NMR (62.3 MHz, $CDCl_3$): δ = 20.7, 102.3, 117.4, 2 × 119.5, 120.5, 124.2, 124.3, 125.1, 125.2, 2 × 128.2, 2 × 128.8, 2 × 130.0, 132.2, 136.1, 138.5, 142.4, 144.9, 161.3, 161.6, 180.8, 189.7; MS (GC, 70 eV) *m*/*z* (%): 431 ($[M]^+$, 52), 263 (51), 234 (17), 169 (21), 105 (100), 93 (82), 77 (80), 53 (14), 51 (14); HRMS (ESI): calcd for $C_{25}ClH_{19}NO_4$ ($[M + H]^+$) 432.09971, found 432.09984, calcd for $C_{25}{}^{37}ClH_{19}NO_4$ ($[M + H]^+$) 434.09789, found 434.09821; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3234 (w), 3062 (w), 2991 (w), 2949 (w), 2916 (w), 1628 (m), 1594 (w), 1579 (w), 1525 (s), 1495 (m), 1485 (m), 1471 (m), 1455 (w), 1443 (m), 1385 (w), 1369 (w), 1331 (m), 1315 (m), 1312 (m), 1248 (m), 1228 (m), 1200 (w), 1170 (s), 1123 (m), 1114 (m), 1078 (w), 1031 (w), 1014 (w), 1001 (w), 960 (w), 936 (w), 924 (w), 909 (m), 880 (w), 871 (w), 864 (w), 841 (w), 811 (w), 797 (m), 788 (m), 751 (m), 740 (m), 733 (s), 714 (m), 692 (s), 681 (s), 665 (m), 652 (s), 637 (s), 609 (m), 596 (s), 578 (m), 546 (s), 528 (s).

2-{[4-Benzoyl-5-(phenylamino)furan-2-yl]carbonyl}-5-methoxyphenol (5w). Yield 69%, yellow solid, mp: 181–183 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OCH_3), 6.42–6.49 (m, 2H, H_{Ar}), 7.17–7.24 (m, 1H, H_{Ar}), 7.42–7.60 (m, 7H, H_{Ar}), 7.66 (s, 1H, H_{Ar}), 7.79–7.83 (m, 2H, H_{Ar}), 8.01 (d, ^3J = 8.8 Hz, 1H, H_{Ar}), 10.67 (s, 1H, NH or OH), 12.74 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.6, 101.2, 102.0, 107.7, 112.4, 2 × 119.5, 122.7, 124.9, 2 × 128.1, 2 × 128.7, 2 × 129.7, 131.9, 132.0, 136.4, 138.7, 142.2, 161.2, 165.8, 166.2, 181.4, 189.6; MS (EI, 70 eV) *m*/*z* (%): 413 ($[M]^+$, 38), 321 (24), 320 (100), 151 (14), 105 (98), 93 (32), 78 (13), 77 (23), 71 (11), 69 (16), 63 (13), 57 (18), 55 (11), 44 (18), 43 (11); HRMS (EI): calcd for $C_{25}H_{19}NO_5$ ($[M]^+$) 413.12577, found 413.12575; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3266 (w), 3152 (w), 3106 (w), 3055 (w), 3014 (w), 2975 (w), 2917 (w), 2847 (w), 1626 (s), 1601 (m), 1579 (m), 1566 (m), 1526 (s), 1500 (s), 1494 (s), 1469 (m), 1450 (m), 1415 (w), 1362 (m), 1347 (m), 1301 (w), 1249 (s), 1198 (m), 1185 (s), 1167 (m), 1140 (s), 1127 (s), 1081 (m), 1025 (m), 1002 (w), 983 (w), 959 (w), 949 (w), 930 (m), 908 (w), 873 (w), 827 (s), 802 (m), 739 (s), 692 (s), 670 (s), 650 (s), 628 (m), 614 (m), 595 (m), 560 (s), 526 (m).

2-{[4-Benzoyl-5-(phenylamino)furan-2-yl]carbonyl}naphthalen-1-ol (5x). Yield 70%, orange solid, mp 165–167 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.26 (t, ^3J = 7.4 Hz, 1H, H_{Ar}), 7.38 (d, ^3J = 8.9 Hz, 1H, H_{Ar}), 7.49 (t, ^3J = 7.9 Hz, 2H, H_{Ar}), 7.55–7.65 (m, 4H, H_{Ar}), 7.65–7.71 (m, 3H, H_{Ar}), 7.75 (s, 1H, H_{Ar}), 7.85–7.91 (m, 3H, H_{Ar}), 7.99 (d, ^3J = 8.9 Hz, 1H, H_{Ar}), 8.32 (d, ^3J = 8.3 Hz, 1H, H_{Ar}), 10.73 (s, 1H, NH or OH), 13.65 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 102.3, 112.6, 118.4, 2 × 120.9, 123.4, 124.5, 124.7, 125.0, 125.1, 126.1, 127.5, 2 × 128.2, 2 × 128.8, 2 × 129.3, 129.9, 132.1, 136.2, 136.5, 138.3, 141.1, 160.7, 160.8, 181.2, 188.1; MS (EI, 70 eV) *m*/*z* (%): 433 ($[M]^+$, 33), 340 (39), 263 (100), 171 (11), 105 (74), 93 (35), 77 (20); HRMS (ESI): calcd for $C_{28}H_{20}NO_4$ ($[M + H]^+$) 434.13868, found 434.13892, calcd for $C_{28}H_{19}NaNO_4$ ($[M + Na]^+$) 456.12063, found 456.12034; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3275 (w), 3054 (w), 2921 (w), 2851 (w), 1653 (w), 1626 (w), 1597 (w), 1577 (w), 1565 (w), 1524 (s), 1462 (s), 1444 (m), 1410 (m), 1381 (m), 1348 (m), 1337 (m), 1320 (m), 1253 (s), 1206 (m), 1177 (m), 1150 (m), 1125 (m), 1098 (m), 1078 (m), 1026 (m), 995 (m), 941 (m), 930 (m), 917 (m), 891 (m), 867 (m), 851 (m), 809 (m), 787 (m), 752 (s), 738 (s), 721 (s), 689 (s), 667 (s), 648 (s), 625 (s), 599 (s), 581 (m), 569 (s), 549 (s).

***N*-(4-Chlorophenyl)-5-[(1-hydroxynaphthalen-2-yl)carbonyl]-2-methylfuran-3-carboxamide (6).** Yield 7%, pale yellow solid, mp: 214–216 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.71 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.56 (d, ^1J = 2.4 Hz, 1H, H_{Ar}), 6.61 (dd, ^3J = 8.9 Hz, ^1J = 2.5 Hz, 1H, H_{Ar}), 7.40 (dt, ^3J = 8.9 Hz, ^1J = 2.5 Hz, 2H, H_{Ar}), 7.76 (dd, ^3J = 8.9 Hz, ^1J = 2.5 Hz, 2H, H_{Ar}), 8.00–8.04 (m, 2H, H_{Ar}), 10.07 (s, 1H, NH or OH), 11.96 (s, 1H, NH or OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 14.0, 55.7, 101.3, 107.2, 113.7, 118.3, 119.7, 2 × 121.8, 127.4, 2 × 128.5, 132.6, 137.6, 148.5, 160.6, 162.4, 163.5, 165.1, 181.9; MS (GC, 70 eV) *m*/*z* (%): 385 ($[M]^+$, 36), 260 (15), 259 (100), 258 (87), 243 (15), 217 (24), 151 (47), 129 (15), 127 (42), 109 (99), 108 (10), 43 (14); HRMS (ESI): calcd for $C_{20}ClH_{17}NO_5$ ($[M + H]^+$) 386.07898, found 386.07870, calcd for $C_{20}{}^{37}CH_{17}NO_5$ ($[M + H]^+$) 388.07688, found 388.07690; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3325 (w), 3016 (w), 2923 (w), 2851 (w), 1734 (w), 1713 (w), 1650 (w), 1626 (m), 1606 (m), 1594 (m), 1575 (m), 1531 (m), 1515 (s), 1495 (m), 1454 (w), 1441 (w), 1403 (w), 1371 (s), 1342 (s), 1314 (m), 1294 (w), 1271 (m), 1255 (s), 1223 (m), 1213 (m), 1196 (s), 1177 (m), 1157 (w), 1136 (s), 1093 (w), 1082 (m), 1024 (w), 1016 (m), 999 (m), 962 (s), 894 (w), 874 (m), 853 (m), 835 (s), 815 (s), 760 (m), 735 (w), 711 (w), 698 (m), 685 (m), 656 (m), 634 (w), 623 (s), 611 (m), 596 (w), 534 (m).

3-Acetyl-2-[(4-chlorophenyl)amino]-7-methyl-9*H*-furo[3,2-*b*]-chromen-9-one (7a). Yield 32%, white solid, mp 228–230 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 7.36–7.39 (m, 2H, H_{Ar}), 7.46–7.52 (m, 4H, H_{Ar}), 8.16 (s, 1H, H_{Ar}), 10.61 (s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.9, 28.7, 117.4, 2 × 121.0, 123.7, 124.8, 125.9, 128.8, 2 × 129.8, 130.5, 133.6, 134.3, 135.2, 152.7, 153.5, 159.6, 162.5, 191.9; MS (GC, 70 eV) *m*/*z* (%): 367 ($[M]^+$, 100), 366 (28), 325 (16), 296 (18), 242 (44), 160 (12), 111 (14), 43 (13); HRMS (ESI): calcd for $C_{20}ClH_{15}NO_4$ ($[M + H]^+$) 368.06841, found 368.06838, calcd for $C_{20}{}^{37}ClH_{15}NO_4$ ($[M + H]^+$) 370.06627, found 370.06631, calcd for $C_{20}ClH_{14}NaNO_4$ ($[M + Na]^+$) 390.05036, found 390.05035, calcd for $C_{20}{}^{37}ClH_{14}NaNO_4$ ($[M + Na]^+$) 392.04822, found 392.04803; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3045 (w), 2923 (w), 2853 (w), 1734 (w), 1709 (w), 1659 (m), 1631 (s), 1615 (s), 1594 (s), 1573 (m), 1562 (s), 1502 (s), 1479 (s), 1435 (s), 1382 (m), 1347 (w), 1313 (w), 1290 (w), 1275 (w), 1251 (m), 1235 (m), 1198 (m), 1145 (w), 1115 (m), 1095 (m), 1060 (w), 1044 (w), 1011 (m), 959 (s), 931 (w), 894 (w), 851 (w), 828 (s), 814 (s), 794 (w), 770 (m), 759 (m), 736 (m), 710 (w), 693 (w), 673 (m), 653 (w), 631 (m), 614 (m), 548 (m).

3-Acetyl-2-(phenylamino)-9*H*-furo[3,2-*b*]chromen-9-one (7b). Yield 37%, white solid, mp 258–260 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.68 (s, 3H, CH_3), 7.21 (t, ^3J = 7.4 Hz, 1H, H_{Ar}), 7.40–7.48 (m, 3H, H_{Ar}), 7.55–7.58 (m, 3H, H_{Ar}), 7.66 (td, ^3J = 7.7 Hz, ^1J = 1.6 Hz, 1H, H_{Ar}), 8.40 (dd, ^3J = 7.9 Hz, ^1J = 1.6 Hz, 1H, H_{Ar}), 10.62 (s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.7, 93.4, 117.6, 2 × 119.9, 125.1, 125.2, 125.3, 126.4, 128.6, 2 × 129.7, 132.4, 135.6, 152.9, 155.2, 160.0, 162.2,

191.8; MS (GC, 70 eV) *m*/*z* (%): 319 ([M]$^+$, 100), 318 (37), 277 (20), 248 (20), 228 (27), 146 (11), 77 (31), 76 (9), 43 (13); HRMS (EI): calcd for $C_{19}H_{13}NO_4$ ([M]$^+$) 319.08391, found 319.08370; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3151 (w), 3049 (w), 3014 (w), 1660 (m), 1637 (s), 1620 (s), 1596 (s), 1581 (s), 1555 (s), 1510 (s), 1459 (s), 1426 (s), 1384 (m), 1360 (m), 1326 (m), 1313 (w), 1275 (w), 1251 (m), 1205 (w), 1187 (m), 1143 (m), 1102 (m), 1082 (w), 1062 (w), 1025 (w), 999 (w), 958 (s), 898 (m), 866 (w), 845 (w), 831 (w), 802 (w), 783 (w), 745 (s), 733 (s), 704 (m), 687 (s), 656 (s), 639 (w), 624 (s), 611 (m), 593 (m), 563 (w), 538 (w).

3-Acetyl-6-methoxy-2-(phenylamino)-9*H*-furo[3,2-*b*]chromen-9-one (7c). Yield 28%, white solid, mp 259–261 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.63 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 7.09 (dd, ^3J = 8.8 Hz, ^2J = 2.4 Hz, 1H, H_{Ar}), 7.22–7.29 (m, 2H, H_{Ar}), 7.43–7.58 (m, 4H, H_{Ar}), 8.09 (d, ^3J = 8.8 Hz, 1H, H_{Ar}), 10.41 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 27.9, 55.6, 92.9, 101.1, 113.0, 117.7, 2 × 120.5, 124.7, 126.0, 127.2, 2 × 128.8, 135.4, 151.8, 156.1, 158.8, 160.6, 162.6, 190.0; MS (GC, 70 eV) *m*/*z* (%): 349 ([M]$^+$, 100), 307 (15), 292 (16), 278 (20), 258 (27), 77 (24), 43 (11); HRMS (EI): calcd for $C_{20}H_{15}NO_5$ ([M]$^+$) 349.09447, found 349.09448; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3223 (w), 3065 (w), 3044 (w), 3013 (w), 2990 (w), 2948 (w), 2840 (w), 1660 (w), 1652 (w), 1616 (s), 1602 (s), 1592 (s), 1579 (s), 1553 (m), 1495 (m), 1458 (m), 1441 (s), 1378 (w), 1359 (w), 1346 (w), 1323 (w), 1271 (m), 1244 (s), 1201 (w), 1151 (w), 1133 (w), 1095 (s), 1059 (w), 1023 (m), 953 (s), 903 (w), 877 (w), 856 (m), 826 (w), 801 (w), 761 (m), 747 (s), 737 (s), 714 (m), 688 (s), 649 (m), 621 (m), 610 (s), 589 (s).

15-Acetyl-14-(phenylamino)-13,17-dioxatetracyclo-[8.7.0.0$^{2.7}$.0$^{12.16}$]heptadeca-1(10),2(7),3,5,8,12(16),14-heptan-11-one (7d). Yield 14%, pale yellow solid, mp 292–294 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.82 (s, 3H, CH_3), 7.28 (d, ^3J = 7.25 Hz, 1H, H_{Ar}), 7.46–7.53 (m, 2H, H_{Ar}), 7.58–7.62 (m, 2H, H_{Ar}), 7.78–7.83 (m, 2H, H_{Ar}), 7.96 (d, ^3J = 8.7 Hz, 1H, H_{Ar}), 8.09–8.12 (m, 1H, H_{Ar}), 8.20 (d, ^3J = 8.7 Hz, 1H, H_{Ar}), 8.55–8.58 (m, 1H, H_{Ar}), 10.44 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 27.9, 92.8, 119.9, 2 × 120.4, 120.5, 120.9, 121.6, 124.2, 124.6, 126.9, 127.3, 127.8, 128.1, 2 × 128.6, 134.3, 135.3, 157.9, 158.9, 160.5, 162.9, 189.6; MS (GC, 70 eV) *m*/*z* (%): 369 ([M]$^+$, 100), 327 (12), 298 (17), 278 (27), 196 (11), 171 (11), 77 (23), 43 (11); HRMS (EI): calcd for $C_{23}H_{15}NO_4$ ([M]$^+$) 369.09956, found 369.09932; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3246 (w), 3205 (w), 3169 (w), 3060 (w), 1665 (m), 1648 (s), 1635 (s), 1619 (s), 1595 (s), 1577 (s), 1556 (m), 1510 (s), 1501 (s), 1459 (m), 1438 (s), 1426 (s), 1378 (m), 1340 (m), 1324 (w), 1267 (w), 1242 (m), 1223 (m), 1188 (w), 1177 (w), 1145 (w), 1110 (w), 1093 (w), 1076 (w), 1060 (w), 1027 (w), 986 (w), 960 (m), 941 (w), 900 (w), 875 (w), 869 (w), 843 (w), 826 (m), 780 (w), 786 (w), 765 (m), 756 (s), 741 (m), 734 (m), 710 (w), 686 (m), 672 (m), 649 (w), 631 (m), 619 (w), 606 (m), 598 (w), 579 (w), 566 (m), 532 (w).

3-Benzoyl-2-(phenylamino)-9*H*-furo[3,2-*b*]chromen-9-one (7e). Yield 42%, white solid, mp 223–225 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ = 7.22–7.32 (m, 2H, H_{Ar}), 7.43–7.53 (m, 3H, H_{Ar}), 7.57–7.73 (m, 6H, H_{Ar}), 7.88–7.92 (m, 2H, H_{Ar}), 8.19 (dd, ^3J = 7.9 Hz, ^1J = 1.6 Hz, 1H, H_{Ar}), 10.79 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 92.1, 117.0, 2 × 120.9, 124.3, 124.4, 124.8, 125.0, 2 × 127.4, 127.5, 2 × 127.6, 2 × 128.8, 121.5, 132.1, 135.4, 138.2, 151.2, 154.1, 160.6, 160.8, 186.9; MS (GC, 70 eV) *m*/*z* (%): 381 ([M]$^+$, 100), 352 (21), 248 (20), 105 (63), 77 (51), 51 (9); HRMS (ESI): calcd for $C_{24}H_{16}NO_4$ ([M + H]$^+$) 382.10738, found 382.10739; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 1660 (m), 1633 (m), 1610 (m), 1591 (m), 1579 (m), 1555 (s), 1497 (m), 1469 (w), 1457 (m), 1421 (s), 1348 (m), 1336 (m), 1323 (m), 1310 (m), 1275 (w), 1263 (s), 1206 (m), 1186 (m), 1162 (m), 1145 (w), 1104 (m), 1079 (w), 1027 (w), 1001 (w), 987 (m), 960 (w), 934 (w), 911 (m), 897 (s), 873 (w), 843 (w), 823 (w), 800 (w), 784 (m), 744 (s), 691 (s), 684 (s), 665 (s), 657 (s), 637 (m), 614 (m), 592 (s), 570 (w), 536 (w), 531 (w).

3-Benzoyl-6-methoxy-2-(phenylamino)-9*H*-furo[3,2-*b*]-chromen-9-one (7f). Yield 21%, pale yellow solid, mp 249–251 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ = 3.87 (s, 3H, OCH_3), 6.65 (d, ^1J = 2.3 Hz, 1H, H_{Ar}), 7.06 (dd, ^3J = 8.9 Hz, ^1J = 2.3 Hz, 1H, H_{Ar}), 7.28 (t, ^3J = 7.3 Hz, 1H, H_{Ar}), 7.46–7.52 (m, 2H, H_{Ar}), 7.58–7.63 (m, 4H, H_{Ar}), 7.68 (d, ^3J = 7.1 Hz, 1H, H_{Ar}), 7.88–7.91 (m, 2H, H_{Ar}), 8.09 (d, ^3J = 8.8 Hz, 1H, H_{Ar}), 10.72 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 55.3, 92.1, 100.8, 112.5, 117.8, 2 × 120.6, 124.7, 126.0, 2 × 127.3, 127.4, 2 × 127.5, 2 × 128.7, 131.3, 135.4, 138.1, 150.7, 155.6, 160.2, 160.8, 162.4, 186.8; MS (GC, 70 eV) *m*/*z* (%): 411 ([M]$^+$, 100), 410 (50), 382 (21), 278 (28), 105 (75), 77 (56), 51 (7); HRMS (ESI): calcd for $C_{25}H_{18}NO_5$ ([M + H]$^+$) 412.11795, found 412.11770, calcd for $C_{25}H_{17}NaNO_5$ ([M + Na]$^+$) 434.09989, found 434.09988; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3046 (w), 3004 (w), 2922 (w), 2852 (w), 1660 (m), 1631 (s), 1618 (s), 1592 (s), 1577 (m), 1568 (m), 1553 (s), 1506 (m), 1494 (m), 1455 (m), 1435 (m), 1418 (m), 1381 (m), 1368 (m), 1347 (w), 1334 (w), 1317 (w), 1278 (m), 1267 (m), 1245 (m), 1212 (m), 1197 (w), 1187 (w), 1165 (m), 1153 (w), 1143 (w), 1110 (s), 1099 (m), 1045 (w), 1028 (m), 988 (m), 941 (w), 905 (m), 889 (w), 870 (m), 843 (s), 821 (m), 811 (w), 791 (m), 748 (s), 738 (s), 715 (m), 696 (s), 680 (s), 667 (s), 637 (m), 625 (m), 614 (w), 590 (m), 579 (m), 547 (w).

Methyl 5′-amino-3,3′-dioxo-3*H*,3′*H*-spiro[1-benzofuran-2,2′-furan]-4′-carboxylate (8a). Yield 30%, white solid, mp 292–294 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.69 (s, 3H, OCH_3), 7.33 (t, ^3J = 7.5 Hz, 1H, H_{Ar}), 7.46 (d, ^3J = 8.3 Hz, 1H, H_{Ar}), 7.89 (d, ^3J = 7.6 Hz, 1H, H_{Ar}), 7.91 (td, ^3J = 7.8 Hz, ^1J = 1.2 Hz, 1H, H_{Ar}), 9.11 (s, 1H, NH), 10.15 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 50.7, 84.4, 101.7, 113.5, 118.0, 124.4, 125.3, 140.7, 162.6, 171.4, 178.0, 180.8, 192.1; MS (EI, 70 eV) *m*/*z* (%): 275 ([M]$^+$, 23), 151 (15), 150 (100), 121 (11), 105 (25), 68 (12), 44 (18); HRMS (ESI): calcd for $C_{13}H_{10}NO_6$ ([M + H]$^+$) 276.05026, found 276.05037; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3451 (w), 3101 (w), 3028 (w), 2962 (w), 1743 (m), 1729 (m), 1671 (m), 1640 (s), 1616 (s), 1492 (s), 1477 (s), 1460 (s), 1362 (w), 1323 (m), 1304 (m), 1237 (m), 1231 (m), 1202 (m), 1170 (m), 1153 (m), 1107 (w), 1012 (s), 1007 (s), 902 (w), 866 (m), 812 (w), 799 (m), 785 (m), 759 (s), 727 (m), 712 (w), 692 (m), 631 (s), 569 (w).

Methyl 5′-amino-6-methoxy-3,3′-dioxo-3*H*,3′*H*-spiro[1-benzofuran-2,2′-furan]-4′-carboxylate (8b). Yield 27%, white solid, mp 294–296 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.69 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.86 (dd, ^3J = 8.7 Hz, ^1J = 2.0 Hz, 1H, H_{Ar}), 7.02 (d, ^1J = 1.9 Hz, 1H, H_{Ar}), 7.67 (d, ^3J = 8.7 Hz, 1H,

H_{Ar}), 9.06 (s, 1H, NH), 10.10 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 50.7, 56.8, 84.4, 97.3, 102.7, 110.8, 113.4, 126.4, 162.7, 169.6, 174.1, 178.0, 181.0, 189.0; MS (EI, 70 eV) *m*/*z* (%): 305 ([M]$^+$, 27), 181 (14), 180 (100), 165 (11), 151 (15), 135 (27), 78 (15), 68 (13), 63 (19), 59 (13), 44 (28); HRMS (ESI): calcd for $C_{14}H_{11}NO_7$ ([M + H]$^+$) 306.06083 found 306.06078, calcd for $C_{14}H_{10}NaNO_7$ ([M + Na]$^+$) 328.04277 found 328.04291; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3381 (w), 3084 (w), 3024 (w), 2964 (w), 2844 (w), 1724 (m), 1689 (m), 1644 (s), 1626 (s), 1590 (m), 1501 (s), 1460 (w), 1454 (w), 1445 (m), 1424 (w), 1348 (m), 1297 (m), 1282 (m), 1265 (m), 1218 (w), 1188 (w), 1182 (w), 1158 (m), 1139 (s), 1120 (s), 1050 (m), 1023 (m), 1009 (s), 959 (w), 930 (w), 867 (w), 840 (w), 827 (w), 797 (m), 775 (w), 766 (m), 755 (w), 730 (w), 661 (m), 634 (s), 555 (w).

2-{8*H*-Thieno[2,3-*b*]indole-2-carbonyl}phenol (10a). Yield 57% (Method A), 74% (Method B), orange solid, mp 212–213 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.94–7.02 (m, 2H, H_{Ar}), 7.14 (td, ^1J = 1.0 MHz, ^3J = 7.5 MHz, 1H, H_{Ar}), 7.27 (td, ^1J = 1.2 MHz, ^3J = 7.6 MHz, 1H, H_{Ar}), 7.41 (td, ^1J = 1.7 MHz, ^3J = 7.8 MHz, 1H, H_{Ar}), 7.50–7.53 (m, 2H, H_{Ar}), 7.90 (d, ^3J = 7.6 MHz, 1H, H_{Ar}), 7.98 (s, 1H, H_{Ar}), 10.21 (s, 1H, NH or OH), 12.09 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 112.0, 116.7, 118.9, 119.8, 120.2, 121.9, 123.5, 125.1, 125.4, 128.6, 129.4, 132.0, 135.7, 142.5, 148.1, 155.9, 188.3; MS (GC, 70 eV) *m*/*z* (%): 293 ([M]$^+$, 42), 261 (20), 260 (100), 174 (14), 173 (93), 172 (29), 128 (16), 65 (14); HRMS (EI): calcd for $C_{17}H_{11}NO_2S$ ([M]$^+$) 293.05050, found 293.05043; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3256 (w), 3079 (w), 3055 (w), 1651 (w), 1623 (w), 1583 (w), 1544 (w), 1504 (m), 1484 (w), 1470 (s), 1446 (m), 1400 (s), 1333 (m), 1312 (w), 1299 (m), 1233 (s), 1215 (s), 1154 (m), 1131 (m), 1115 (m), 1099 (w), 1085 (m), 1035 (w), 1014 (w), 979 (w), 947 (w), 924 (w), 892 (w), 880 (w), 866 (m), 825 (m), 775 (m), 752 (s), 729 (s), 715 (m), 694 (s), 662 (s), 628 (m), 600 (s), 590 (m), 566 (m), 552 (m), 544 (m).

5-Methoxy-2-{8*H*-thieno[2,3-*b*]indole-2-carbonyl}phenol (10b). Yield 56%, yellow solid, mp 228–229 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.84 (s, 3H, OCH_3), 6.56–6.62 (m, 2H, H_{Ar}), 7.17 (t, ^3J = 7.4 MHz, 1H, H_{Ar}), 7.28 (td, ^1J = 0.9 MHz, ^3J = 7.6 MHz, 1H, H_{Ar}), 7.53 (d, ^3J = 8.1 MHz, 1H, H_{Ar}), 7.84 (d, ^3J = 8.7 MHz, 1H, H_{Ar}), 7.93 (d, ^3J = 7.7 MHz, 1H, H_{Ar}), 8.23 (s, 1H, H_{Ar}), 11.65 (s, 2H, OH, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 55.5, 101.5, 106.4, 112.1, 115.4, 119.9, 120.3, 122.0, 123.5, 125.5, 128.1, 132.3, 134.9, 142.6, 147.9, 161.3, 163.9, 187.8; MS (EI, 70 eV) *m*/*z* (%): 323 ([M]$^+$, 21), 291 (17), 290 (100), 173 (34); HRMS (ESI): calcd for $C_{19}H_{13}NO_3S$ ([M + H]$^+$) 324.06889, found 324.06883; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3246 (w), 3079 (w), 3059 (w), 3004 (w), 2982 (w), 2952 (w), 2904 (w), 2835 (w), 2719 (w), 2635 (w), 1633 (m), 1581 (m), 1550 (w), 1504 (s), 1473 (m), 1446 (m), 1396 (m), 1372 (m), 1346 (m), 1314 (w), 1278 (m), 1266 (s), 1237 (s), 1214 (s), 1194 (m), 1156 (m), 1145 (m), 1130 (w), 1101 (m), 1086 (m), 1029 (m), 1015 (w), 966 (w), 922 (w), 866 (w), 842 (m), 823 (w), 801 (w), 784 (m), 767 (m), 748 (w), 729 (s), 708 (w), 692 (s), 640 (w), 617 (m), 591 (s), 562 (w), 542 (w).

2-{8*H*-Thieno[2,3-*b*]indole-2-carbonyl}naphthalen-1-ol (10c). Yield 78%, dark yellow solid, mp 283–284 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.19 (t, ^3J = 7.4 MHz, 1H, H_{Ar}), 7.30 (t, ^3J = 7.4 MHz, 1H, H_{Ar}), 7.53–7.64 (m, 3H, H_{Ar}), 7.71 (t, ^3J = 7.4 MHz, 1H, H_{Ar}), 7.97 (d, ^3J = 7.8 MHz, 2H, H_{Ar}), 8.08 (d, ^3J = 8.8 MHz, 1H, H_{Ar}), 8.36 (d, ^3J = 8.3 MHz, 1H, H_{Ar}), 8.46 (s, 1H, H_{Ar}), 12.19 (s, 1H, NH or OH), 13.03 (s, 1H, NH or OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 112.2, 114.2, 118.6, 120.1, 120.4, 122.0, 123.4, 123.8, 124.7, 126.0, 2 × 126.1, 127.6, 129.1, 129.5, 134.4, 136.0, 142.7, 148.6, 158.9, 188.9; MS (EI, 70 eV) *m*/*z* (%): 343 ([M]$^+$, 37), 311 (10), 310 (49), 174 (22), 173 (100), 172 (21), 155 (10); HRMS (ESI): calcd for $C_{21}H_{14}NO_2S$ ([M + H]$^+$) 344.07398, found 344.07393; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3247 (w), 3077 (w), 3056 (w), 1629 (w), 1600 (w), 1574 (m), 1554 (m), 1502 (m), 1476 (w), 1456 (m), 1445 (m), 1424 (w), 1399 (s), 1333 (m), 1312 (m), 1274 (m), 1257 (w), 1235 (s), 1209 (m), 1190 (m), 1156 (m), 1129 (m), 1089 (m), 1025 (w), 1014 (w), 986 (w), 956 (m), 931 (w), 918 (w), 911 (w), 879 (w), 866 (w), 847 (w), 825 (w), 796 (s), 765 (m), 753 (s), 746 (s), 733 (s), 704 (m), 684 (m), 658 (m), 638 (m), 615 (m), 596 (m), 582 (s), 573 (s), 548 (m), 527 (m).

4-Methyl-2-{8-methyl-8*H*-thieno[2,3-*b*]indole-2-carbonyl}-phenol (10d). Yield 43%, yellow solid, mp 142–143 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.29 (s, 3H, CH_3), 3.92 (s, 3H, NCH_3), 6.90 (d, ^3J = 8.2 MHz, 1H, H_{Ar}), 7.18–7.23 (m, 2H, H_{Ar}), 7.29 (d, ^1J = 1.8 MHz, 1H, H_{Ar}), 7.35 (td, ^1J = 1.2 MHz, ^3J = 7.7 MHz, 1H, H_{Ar}), 7.60 (d, ^3J = 8.2 MHz, 1H, H_{Ar}), 7.94 (d, ^3J = 7.7 MHz, 1H, H_{Ar}), 8.02 (s, 1H, H_{Ar}), 9.93 (s, 1H, OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 20.0, 32.3, 110.3, 116.6, 120.0, 120.5, 121.9, 123.4, 123.6, 125.1, 127.6, 128.9, 129.4, 132.6, 135.8, 142.9, 150.4, 153.7, 188.1; MS (GC, 70 eV) *m*/*z* (%): 321 ([M]$^+$, 32), 288 (45), 187 (100), 172 (18), 115 (12), 77 (17); HRMS (EI): calcd for $C_{19}H_{15}NO_2S$ ([M]$^+$) 321.08180, found 321.08162; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3046 (w), 2917 (w), 1621 (w), 1575 (w), 1553 (m), 1506 (m), 1495 (m), 1480 (s), 1461 (s), 1429 (m), 1422 (m), 1399 (s), 1385 (s), 1347 (m), 1315 (s), 1287 (m), 1267 (s), 1241 (s), 1211 (s), 1194 (s), 1130 (s), 1089 (m), 1052 (m), 1015 (m), 930 (m), 906 (w), 882 (w), 868 (w), 847 (w), 821 (s), 789 (s), 781 (s), 746 (s), 696 (m), 685 (m), 673 (m), 625 (s), 598 (m), 571 (w), 543 (m), 541 (m).

5-Methoxy-2-{8-methyl-8*H*-thieno[2,3-*b*]indole-2-carbonyl}-phenol (10e). Yield 46%, yellow solid, mp 158–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 6.44–6.48 (m, 2H, H_{Ar}), 7.14–7.19 (m, 1H, H_{Ar}), 7.26–7.28 (m, 2H, H_{Ar}), 7.73 (d, ^3J = 7.7 Hz, 1H, Ar), 7.86–7.89 (m, 2H, H_{Ar}), 12.25 (s, 1H, OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 32.4, 55.5, 101.3, 107.2, 109.4, 113.3, 119.8, 120.7, 122.3, 123.5, 124.2, 127.0, 132.7, 134.7, 143.0, 150.7, 164.8, 165.2, 188.7; MS (GC, 70 eV) *m*/*z* (%): 337 ([M]$^+$, 27), 304 (100), 187 (64), 172 (12), 155 (14); HRMS (ESI): calcd for $C_{19}H_{16}NO_3S$ ([M + H]$^+$) 338.08450, found 338.08450, calcd for $C_{19}H_{15}NaNO_3S$ ([M + Na]$^+$) 360.06650, found 360.06620; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2971 (w), 2930 (w), 2848 (w), 1612 (m), 1573 (m), 1552 (w), 1491 (s), 1454 (s), 1441 (m), 1397 (m), 1364 (s), 1330 (s), 1317 (s), 1297 (m), 1250 (s), 1206 (s), 1172 (m), 1163 (s), 1139 (s), 1126 (s), 1089 (s), 1052 (s), 1023 (s), 1015 (s), 963 (s), 894 (m), 850 (s), 822 (m), 808 (s), 757 (s), 747 (s), 735 (s), 708 (s), 694 (s), 671 (m), 644 (m), 637 (s), 594 (s), 546 (s).

2-{8-Methyl-8*H*-thieno[2,3-*b*]indole-2-carbonyl}naphthalen-1-ol (10f). Yield 55%, yellow solid, mp 180–181 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.93 (s, 3H, NCH_3), 7.24 (td, ^1J = 0.9 MHz, ^3J = 7.5 MHz, 1H, H_{Ar}), 7.37 (td, ^1J = 1.2 MHz, ^3J = 7.7 MHz, 1H, H_{Ar}), 7.53 (d, ^3J = 8.8 MHz, 1H, H_{Ar}), 7.58–7.63 (m, 2H, H_{Ar}), 7.71 (td, ^1J = 1.3 MHz, ^3J = 7.5 MHz, 1H, H_{Ar}), 7.95–8.01 (m, 2H, H_{Ar}), 8.06 (d, ^3J = 8.8 MHz, 1H, H_{Ar}), 8.36 (d, ^3J = 8.3 MHz, 1H, H_{Ar}), 8.47 (s, 1H, H_{Ar}), 13.01 (s, 1H, OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 32.5, 110.5, 114.1, 118.6, 120.2, 120.7, 121.9, 123.4, 123.7, 124.5, 124.7, 125.7, 126.1, 127.6, 129.4, 129.5, 134.4, 136.0, 143.1, 150.8, 158.9, 188.6; MS (EI, 70 eV) *m*/*z* (%): 357 ([M]$^+$, 30), 324 (21), 187 (100), 172 (11); HRMS (ESI): calcd for $C_{22}H_{16}NO_2S$ ([M + H]$^+$) 358.08963, found 358.08948, calcd for $C_{22}H_{15}NaNO_2S$ ([M + Na]$^+$) 380.07157, found 380.07118; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3047 (w), 2935 (w), 1658 (w), 1642 (w), 1628 (m), 1599 (w), 1574 (m), 1556 (w), 1536 (w), 1508 (m), 1493 (m), 1454 (s), 1425 (m), 1415 (m), 1398 (s), 1380 (s), 1343 (m), 1317 (m), 1277 (m), 1264 (s), 1253 (s), 1210 (m), 1197 (m), 1155 (m), 1139 (m), 1129 (m), 1116 (m), 1091 (m), 1052 (m), 1024 (m), 1017 (m), 953 (m), 919 (w), 883 (m), 865 (m), 843 (m), 820 (m), 804 (m), 791 (m), 772 (s), 756 (m), 733 (s), 717 (s), 704 (m), 686 (m), 658 (m), 637 (m), 605 (m), 586 (s), 572 (m), 546 (m), 532 (m).

2-{8-Phenyl-8*H*-thieno[2,3-*b*]indole-2-carbonyl}phenol (10g). Yield 60%, orange solid, mp 156–157 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.98 (td, ^1J = 0.9 MHz, ^3J = 7.4 MHz, 1H, H_{Ar}), 7.02 (dd, ^1J = 0.7 MHz, ^3J = 8.3 MHz, 1H, H_{Ar}), 7.29 (td, ^1J = 0.9 MHz, ^3J = 7.4 MHz, 1H, H_{Ar}), 7.36 (td, ^1J = 1.4 MHz, ^3J = 7.7 MHz, 1H, H_{Ar}), 7.43 (td, ^1J = 1.7 MHz, ^3J = 7.7 MHz, 1H, H_{Ar}), 7.51 (dd, ^1J = 1.7 MHz, ^3J = 7.7 MHz, 1H, H_{Ar}), 7.56 (d, ^3J = 7.7 MHz, 2H, H_{Ar}), 7.71 (t, ^3J = 7.7 MHz, 2H, H_{Ar}), 7.78–7.81 (m, 2H, H_{Ar}), 8.05 (dd, ^1J = 0.9 MHz, ^3J = 7.4 MHz, 1H, H_{Ar}), 8.12 (s, 1H, H_{Ar}), 10.19 (s, 1H, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 110.9, 116.7, 118.9, 120.5, 121.7, 122.7, 2 × 123.8, 124.3, 125.3, 125.5, 128.1, 128.7, 129.4, 2 × 130.6, 132.2, 135.9, 137.2, 141.7, 148.8, 155.8, 188.4; MS (GC, 70 eV) *m*/*z* (%): 370 ([M]$^+$, 14), 369 (57), 352 (17), 337 (20), 336 (81), 250 (20), 249 (100), 248 (12), 247 (15), 204 (19), 65 (10); HRMS (ESI): calcd for $C_{23}H_{16}NO_2S$ ([M + H]$^+$) 370.08963, found 370.08972; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 2921 (w), 2852 (w), 1615 (w), 1579 (m), 1557 (w), 1515 (w), 1500 (m), 1482 (m), 1467 (s), 1452 (m), 1443 (m), 1399 (s), 1373 (m), 1335 (m), 1325 (m), 1299 (m), 1275 (m), 1249 (m), 1210 (s), 1183 (m), 1150 (s), 1130 (m), 1099 (m), 1081 (m), 1035 (w), 1024 (w), 985 (w), 968 (w), 951 (w), 929 (w), 916 (w), 895 (m), 877 (w), 870 (w), 852 (w), 845 (w), 811 (w), 781 (m), 767 (s), 755 (s), 747 (s), 737 (s), 726 (s), 695 (s), 662 (s), 638 (m), 626 (m), 612 (m), 597 (s), 566 (w), 535 (m).

5-Methoxy-2-{8-phenyl-8*H*-thieno[2,3-*b*]indole-2-carbonyl}-phenol (10h). Yield 35%, orange solid, mp 149–150 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ = 3.84 (s, 3H, OCH_3), 6.58–6.63 (m, 2H, H_{Ar}), 7.28–7.40 (m, 2H, H_{Ar}), 7.52–7.59 (m, 2H, H_{Ar}), 7.68–7.85 (m, 5H, H_{Ar}), 8.07 (d, ^3J = 7.2 MHz, 1H, H_{Ar}), 8.35 (s, 1H, H_{Ar}), 11.33 (s, 1H, OH); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 55.5, 101.6, 106.5, 110.8, 110.9, 115.4, 120.5, 121.7, 122.7, 2 × 123.7, 124.3, 125.7, 128.1, 2 × 130.5, 132.2, 135.1, 137.3, 141.7, 148.4, 161.1, 164.0, 187.7; MS (GC, 70 eV) *m*/*z* (%): 399 ([M]$^+$, 31), 367 (26), 366 (100), 250 (13), 249 (69), 204 (11), 186 (13); HRMS (ESI): calcd for $C_{24}H_{18}NO_3S$ ([M + H]$^+$) 400.10019, found 400.10018; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3083 (w), 3054 (w), 3011 (w), 2952 (w), 2921 (w), 2852 (w), 2705 (w), 2659 (w), 1741 (w), 1621 (w), 1595 (w), 1568 (m), 1551 (w), 1515 (w), 1500 (m), 1467 (m), 1452 (m), 1445 (m), 1403 (s), 1384 (m), 1366 (s), 1335 (m), 1324 (m), 1300 (w), 1280 (w), 1253 (s), 1231 (s), 1216 (s), 1204 (s), 1188 (s), 1159 (m), 1144 (m), 1130 (s), 1102 (m), 1082 (s), 1044 (m), 1019 (s), 962 (m), 953 (m), 917 (w), 885 (w), 828 (s), 799 (s), 765 (m), 758 (m), 737 (s), 710 (s), 695 (s), 665 (m), 643 (m), 631 (m), 612 (m), 592 (s), 574 (s).

2-{8-Phenyl-8*H*-thieno[2,3-*b*]indole-2-carbonyl}naphthalen-1-ol (10i). Yield 58%, orange solid, mp 163–164 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.30–7.41 (m, 2H, H_{Ar}), 7.53–7.64 (m, 4H, H_{Ar}), 7.69–7.74 (m, 3H, H_{Ar}), 7.80 (d, ^3J = 7.5 MHz, 2H, H_{Ar}), 7.97 (d, ^3J = 8.1 MHz, 1H, H_{Ar}), 8.05–8.12 (m, 2H, H_{Ar}), 8.36 (d, ^3J = 8.3 MHz, 1H, H_{Ar}), 8.56 (s, 1H, H_{Ar}), 12.87 (s, 1H, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 110.9, 114.2, 118.8, 120.6, 121.8, 122.6, 123.4, 2 × 123.7, 124.5, 124.7, 125.8, 126.1, 126.2, 127.6, 128.2, 129.1, 129.6, 2 × 130.5, 134.6, 136.1, 137.2, 141.8, 149.0, 158.9, 188.9; MS (EI, 70 eV) *m*/*z* (%): 419 ([M]$^+$, 36), 386 (16), 384 (12), 250 (25), 249 (100); HRMS (ESI): calcd for $C_{27}H_{18}NO_2S$ ([M + H]$^+$) 420.10528, found 420.10519, calcd for $C_{27}H_{17}NaNO_2S$ ([M + Na]$^+$) 442, 08722, found 442, 08734; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 2953 (w), 2922 (w), 2852 (w), 1623 (w), 1593 (w), 1557 (w), 1514 (w), 1496 (m), 1446 (s), 1416 (m), 1399 (s), 1373 (m), 1339 (m), 1317 (m), 1296 (m), 1262 (m), 1250 (s), 1214 (s), 1186 (m), 1159 (m), 1149 (m), 1137 (m), 1095 (m), 1088 (m), 1075 (m), 1023 (m), 960 (m), 938 (w), 917 (m), 908 (m), 871 (w), 848 (m), 834 (m), 810 (m), 792 (m), 763 (s), 748 (s), 738 (s), 724 (s), 693 (s), 669 (m), 657 (m), 643 (m), 627 (m), 613 (m), 596 (w), 583 (s), 574 (s), 530 (m).

Acknowledgements

Financial support by the State of Mecklenburg-Vorpommern (scholarship for I. S.) and by the BMBF (REMEDIS project, grant no. 03IS2081A) is gratefully acknowledged.

Notes and references

1 S. Wetzel, R. S. Bon, K. Kumar and H. Waldmann, *Angew. Chem., Int. Ed.*, 2011, **50**, 10800–10826.
2 A. Dömling, W. Wang and K. Wang, *Chem. Rev.*, 2012, **112**, 3083–3135.
3 J. B. Press, Biologically Active Thiophene Derivatives Revisited: 1983–1988, in *Chemistry of Heterocyclic Compounds*, John Wiley & Sons, 2008, vol. 44, pp. 397–502.
4 M. E. Welsch, S. A. Snyder and B. R. Stockwell, *Curr. Opin. Chem. Biol.*, 2010, **14**, 347–361.
5 E. Lukevits and L. Demicheva, *Chem. Heterocycl. Compd.*, 1993, **29**, 243–267.

6 Y. Yang, T. Zhang, L. Xiao, L. Yang and R. Chen, *Fitoterapia*, 2010, **81**, 614–616.
7 C. P. Huttrer and E. Dale, *Chem. Rev.*, 1951, **48**, 543–579.
8 G. G. Kuiper, J. G. Lemmen, B. Carlsson, J. C. Corton, S. H. Safe, P. T. van der Saag, B. van der Burg and J. A. Gustafsson, *Endocrinology*, 1998, **139**, 4252–4263.
9 M. Pizzichini, M. F. Aleo, R. Marcolongo and E. Marinello, *Quad. Sclavo Diagn. Clin. Lab.*, 1982, **18**, 203–208.
10 D. S. Sinclair and I. H. Fox, *J. Rheol.*, 1975, **2**, 437–445.
11 C. P. Miller, M. D. Collini and H. A. Harris, *Bioorg. Med. Chem. Lett.*, 2003, **13**, 2399–2403.
12 H. W. Ryu, B. W. Lee, M. J. Curtis-Long, S. Jung, Y. B. Ryu, W. S. Lee and K. H. Park, *J. Agric. Food Chem.*, 2009, **58**, 202–208.
13 H. W. Ryu, M. J. Curtis-Long, S. Jung, I. Y. Jeong, D. S. Kim, K. Y. Kang and K. H. Park, *Food Chem.*, 2012, **132**, 1244–1250.
14 P. R. Kumar, S. Raju, P. S. Goud, M. Sailaja, M. R. Sarma, G. O. Reddy, M. P. Kumar, V. V. R. M. K. Reddy, T. Suresh and P. Hedge, *Bioorg. Med. Chem.*, 2004, **12**, 1221–1230.
15 J. M. Ontoria, J. I. M. Hernando, S. Malancona, B. Attenni, I. Stansfield, I. Conte, C. Ercolani, J. Habermann, S. Ponzi, M. D. Filippo, U. Koch, M. Rowley and F. Narjes, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 4026–4030.
16 S.-M. Yu, Z.-J. Cheng and S.-C. Kuo, *Br. J. Pharmacol.*, 1995, **114**, 1227–1235.
17 H. Z. Boeini, *Helv. Chim. Acta*, 2009, **92**, 1268–1272.
18 K. Kanbe, M. Okamura, S. Hattori, H. Naganawa, M. Hamada, Y. Okami and T. Takeuchi, *Biosci., Biotechnol., Biochem.*, 1993, **57**, 632–635.
19 M. S. C. Pedras and M. Jha, *J. Org. Chem.*, 2005, **70**, 1828–1834.
20 M. Devys, M. Barbier, I. Loiselet, T. Rouxel, A. Sarniguet, A. Kollmann and J.-F. Bousquet, *Tetrahedron Lett.*, 1988, **29**, 6447–6448.
21 M. S. C. Pedras and M. Suchy, *Bioorg. Med. Chem.*, 2006, **14**, 714–723.
22 M. S. C. Pedras and M. Suchy, *Org. Biomol. Chem.*, 2005, **3**, 2002–2007.
23 M. S. C. Pedras, R. S. Gadagi, M. Jha and V. K. Sarma-Mamillapalle, *Phytochemistry*, 2007, **68**, 1572–1578.
24 M. Soledade, C. Pedras and K. C. Smith, *Phytochemistry*, 1997, **46**, 833–837.
25 I. Beria, M. Caruso, V. Lupi, P. Orsini and M. Salsa, *WO* 2013149946 A1, 2013.
26 P. Jakobsen, A. Kanstrup, P. Faarup, P. H. Olesen and J. M. Lundbech, *US* 5783575 A, 1998.
27 P. Jakobsen, A. Kanstrup, P. Faarup and P. H. Olesen, *US* 5536721 A, 1996.
28 T. Qi, W. Qiu, Y. Liu, H. Zhang, X. Gao, Y. Liu, K. Lu, C. Du, G. Yu and D. Zhu, *J. Org. Chem.*, 2008, **73**, 4638–4643.
29 B. H. Sohn and H. Lim, *US* 20050181233 A1, 2005.
30 M. Mezlova, J. J. Aaron, J. Svoboda, A. Adenier, F. Maurel and K. Chane-Ching, *J. Electroanal. Chem.*, 2005, **581**, 93–103.
31 J.-F. Chang, B. Sun, D. W. Breiby, M. M. Nielsen, T. I. Solling, M. Giles, I. MacCulloch and H. Sirringhaus, *Chem. Mater.*, 2004, **16**, 4772–4776.
32 R. Engqvist, A. Javaid and J. Bergman, *Eur. J. Org. Chem.*, 2004, 2589–2592.
33 P. H. Olesen, J. B. Hansen and M. Engelstoft, *J. Heterocycl. Chem.*, 1995, **32**, 1641–1642.
34 F. M. Moghaddam, H. Saeidian, Z. Mirjafary, S. Taheri and S. Kheirjou, *Synlett*, 2009, 1047–1050.
35 H. Gao, Q.-L. Xu, M. Yousufuddin, D. H. Ess and L. Kurti, *Angew. Chem., Int. Ed.*, 2014, **53**, 2701–2705.
36 P. P. Singh, A. K. Yadav, H. Ila and H. Junjappa, *Eur. J. Org. Chem.*, 2011, 4001–4007.
37 A. V. Butin, F. A. Tsiunchik, V. T. Abaev and V. E. Zavodnik, *Synlett*, 2008, 1145–1148.
38 J. H. Smitrovich and I. W. Davies, *Org. Lett.*, 2004, **6**, 533–535.
39 K. C. Majumdar and S. Alam, *J. Chem. Res.*, 2006, **5**, 289–292.
40 P. Appukkuttan, E. Van der Eycken and W. Dehaen, *Synlett*, 2005, 127–133.
41 D. A. Horton, G. T. Bourne and M. L. Smythe, *Chem. Rev.*, 2003, **103**, 893–930.
42 S. T. Saengchantara and T. W. Wallace, *Nat. Prod. Rep.*, 1986, **3**, 465–475.
43 A. Y. Rulev, *Russ. Chem. Rev.*, 1998, **67**, 279–293.
44 T. W. Wallace, *Tetrahedron Lett.*, 1984, **25**, 4299–4302.
45 Y. Sugita and I. Yokoe, *Heterocycles*, 2000, **53**, 2191–2199.
46 S. T. Saengchantara and T. W. Wallace, *Tetrahedron*, 1990, **46**, 3029–3036.
47 V. Y. Sosnovskikh, *Russ. Chem. Rev.*, 2003, **72**, 489–516.
48 C. K. Ghosh and A. Patra, *J. Heterocycl. Chem.*, 2008, **45**, 1529–1547.
49 R. Gasparová and M. Lácova, *Molecules*, 2005, **10**, 937–960.
50 G. Sabitha, *Aldrichimica Acta*, 1996, **29**, 13–23.
51 H. Chen, F. Xie, J. Gong and Y. Hu, *J. Org. Chem.*, 2011, **76**, 8495–8500.
52 C. K. Ghosh, *Heterocycles*, 2004, **63**, 2875–2898.
53 C. K. Ghosh, *J. Heterocycl. Chem.*, 1983, **20**, 1437–1445.
54 L. Zhao, F. Xie, G. Cheng and Y. Hu, *Angew. Chem., Int. Ed.*, 2009, **48**, 6520–6523.
55 Y. Sugita, T. Iwaki, M. Okamoto and I. Yokoe, *Heterocycles*, 2001, **55**, 881–888.
56 Y. Sugita, K. Kawai and I. Yokoe, *Heterocycles*, 2000, **53**, 657–664.
57 Y. Sugita and I. Yokoe, *Heterocycles*, 1996, **43**, 2503–2511.
58 R. B. Gammill, *J. Org. Chem.*, 1979, **44**, 3988–3990.
59 M. Kiamehr, F. M. Moghaddam, V. Semeniuchenko, A. Villinger, P. Langer and V. O. Iaroshenko, *Tetrahedron Lett.*, 2013, **54**, 5018–5021.
60 M. Kiamehr, F. M. Moghaddam, P. V. Gormay, V. Semeniuchenko, A. Villinger, P. Langer and V. O. Iaroshenko, *Tetrahedron*, 2012, **68**, 9685–9693.
61 M. Kiamehr and F. M. Moghaddam, *Tetrahedron Lett.*, 2009, **50**, 6723–6727.

62 F. M. Moghaddam, Z. Mirjafary, H. Saeidian, S. Taheri, M. Doulabi and M. Kiamehr, *Tetrahedron*, 2010, **66**, 134–138.
63 K. C. Majumdar, A. Taher and K. Ray, *Tetrahedron Lett.*, 2009, **50**, 3889–3891.
64 K. C. Majumdar, A. Taher and S. Ponra, *Tetrahedron Lett.*, 2010, **51**, 147–150.
65 F. M. Moghaddam, S. Taheri, Z. Mirjafary and H. Saeidian, *Synlett*, 2010, 123–127.
66 L. K. Ransborg, L. Albrecht, C. F. Weise, J. R. Bak and K. A. Jorgensen, *Org. Lett.*, 2012, **14**, 724–727.
67 K. C. Majumdar, S. Ponra and R. K. Nandi, *Tetrahedron Lett.*, 2012, **53**, 1732–1737.
68 R. B. Gammill, *Synthesis*, 1979, 901–902.
69 I. Yokoe, K. Maruyama, Y. Sugita, T. Harashida and Y. Shirataki, *Chem. Pharm. Bull.*, 1994, **42**, 1697–1699.
70 S. G. Davies, B. E. Mobbs and C. J. Goodwin, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2597–2604.
71 A. E. Nibbs, A.-L. Baize, R. M. Herter and K. A. Scheidt, *Org. Lett.*, 2009, **11**, 4010–4013.
72 T. Patonay, A. Vasas, A. Kiss-Szikszai, A. M. S. Silva and J. A. S. Cavaleiro, *Aust. J. Chem.*, 2010, **63**, 1582–1593.
73 C. R. Eisnor, R. A. Gossage and P. N. Yadav, *Tetrahedron*, 2006, **62**, 3395–3401.
74 D. A. Vasselin, A. D. Westwell, C. S. Matthews, T. D. Bradshaw and M. F. G. Stevens, *J. Med. Chem.*, 2006, **49**, 3973–3981.
75 G. Li, Z.-T. Zhang, L.-Y. Dai, Y.-L. Du and D. Xue, *Helv. Chim. Acta*, 2012, **95**, 989–997.
76 M. A. Terzidis, C. A. Tsoleridis, J. Stephanidou-Stephanatou, A. Terzis, C. P. Raptopoulou and V. Psycharis, *Tetrahedron*, 2008, **64**, 11611–11617.
77 Y. Moon, Y. Kim, H. Hong and S. Hong, *Chem. Commun.*, 2013, **49**, 8323–8325.

