JOC The Journal of Organic Chemistry

Anatolian University Libraries Consortium a·n·k·o·s

Subscriber access provided by HACETTEPE UNIVERSITESI KUTUPHANESI

Article

Reaction of Push-pull Enaminoketones and in situ Generated ortho-Quinone Methides: Synthesis of 3-Acyl-4H-chromenes and 2-Acyl-1H-benzo[f]chromenes as Precursors for Hydroxybenzylated Heterocycles

Anton Vladimirovich Lukashenko, Vitaly Aleksandrovich Osyanin, Dmitry Vladimirovich Osipov, and Yuri N. Klimochkin

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b02716 • Publication Date (Web): 16 Jan 2017

Downloaded from http://pubs.acs.org on January 16, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Reaction of Push-pull Enaminoketones and *in situ* Generated *ortho*-Quinone Methides: Synthesis of 3-Acyl-4*H*-chromenes and 2-Acyl-1*H*-benzo[*f*]chromenes as Precursors for Hydroxybenzylated Heterocycles

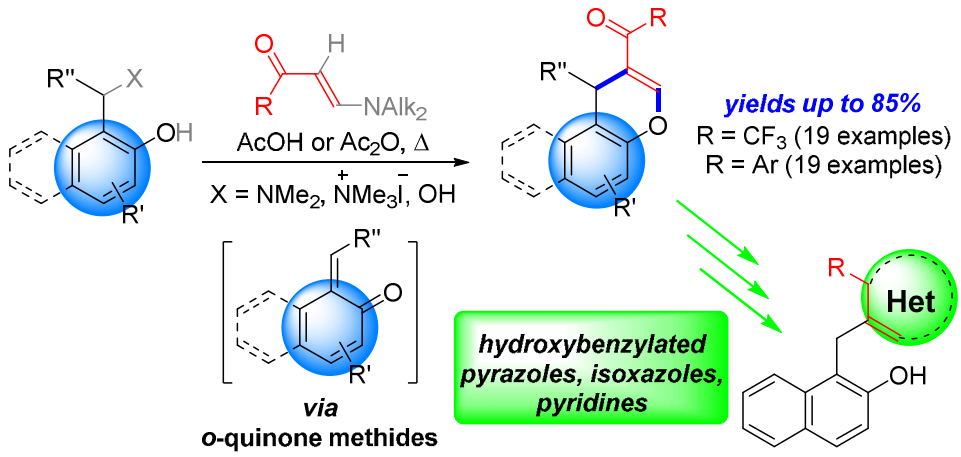
Anton V. Lukashenko,[a] Vitaly A. Osyanin,[*a,b]

Dmitry V. Osipov,[a] Yuri N. Klimochkin[a]

[a] *Department of Organic Chemistry, Chemical Technological Faculty, Samara State Technical University, 244 Molodogvardeyskaya St., Samara 443100, Russian Federation.*

[b] *Organic Chemistry Department, Faculty of Science, RUDN University, 6 Miklukho-Maklaya St., Moscow 117198, Russian Federation.*

Fax +7(846)3322122; E-mail: vosyanin@mail.ru



ABSTRACT: A simple and efficient method for the synthesis of 4*H*-chromenes and 1*H*-benzo[*f*]chromenes containing trifluoroacetyl or aroyl group in pyran ring from *o*-quinone methide precursors and push-pull enaminoketones has been developed. The chromenes are presumably formed through an initial oxa-Diels-Alder reaction followed by an elimination of amine. Possibility of further transformations of given chromenes to *o*-hydroxybenzylated pyrazoles, isoxazoles and pyridines has been demonstrated.

Key words *o*-quinone methide, push-pull olefin, Diels-Alder reaction, 4*H*-chromene, 1*H*-benzo[*f*]chromene, enaminoketone.

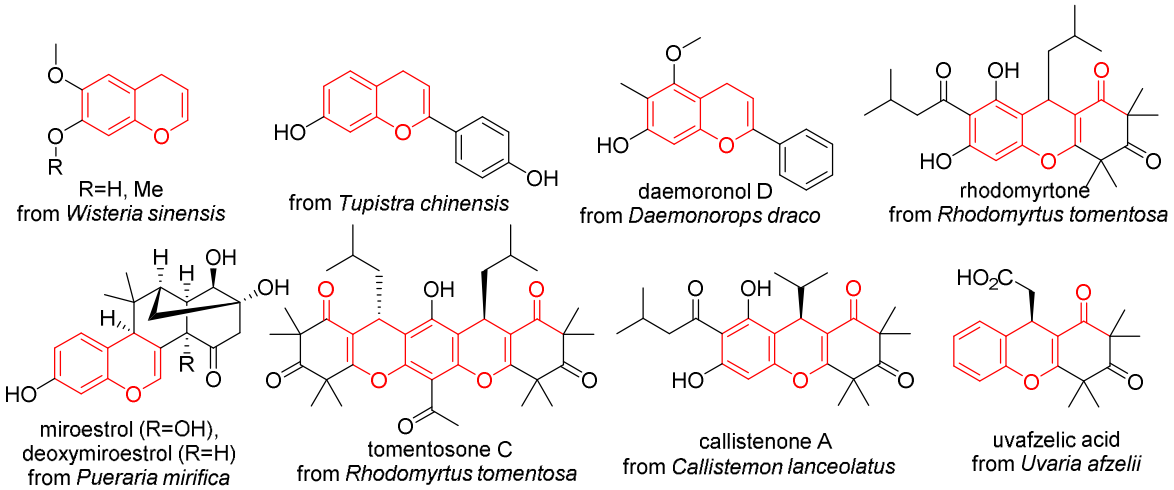
INTRODUCTION

Push-pull olefins, which are compounds containing electron-donating groups and electron-withdrawing groups at the opposite ends of a double bond, have attracted considerable attention due to their unusual physicochemical properties, such as high stability, easy *E*/*Z*-isomerization,

significant charge transfer, that make them suitable for both nucleophilic and electrophilic attack.[1] Such compounds are very useful building blocks and widely used in organic synthesis.[2] β-Enaminones that combine the ambident nucleophilicity of enamines with the ambident electrophilicity of enones fall into this push-pull category. The carbonyl group, conjugated to the enamine moiety, gives this high reactive system enough stability to be easily prepared, isolated and stored under atmospheric conditions at room temperature. Owing to this, they have found numerous applications on the field of the heterocyclic chemistry.[3] At the same time, their reactions as dienophiles with polarized dienes or heterodienes remain little known,[4] although push-pull nature of the double bond might make them potentially excellent partners in Diels-Alder reaction. We assumed that highly polarized *o*-quinone methides (*o*-QMs), which, similar to push-pull olefins, are ambiphilic reagents,[5] would react with such olefins through an addition-elimination mechanism to form 4*H*-chromene derivatives.

4*H*-Chromene skeleton constitutes a key structural element in many biologically active compounds, primarily anticancer agents.[6] In contrast to 2*H*-chromenes,[7] the 4*H*-chromenes as a class of natural products are rather unusual. Some examples of naturally occurring 4*H*-chromenes including chromenes bearing carbonyl group at C-3 position of the pyran ring are presented (Figure 1).[8] Among them there are phytoestrogens miroestrol and deoxymiroestrol,[8d] antibiotic rhodomyrtone,[8e,f] antimicrobial acylphloroglucinols callistenone A[8g] and tomentosone C,[8h] uvafzelic acid[8i] and others.

Figure 1. Selection of Natural Products Containing 4*H*-Chromene Rings



Comprehensive literature survey discloses that many efforts were made towards the synthesis of 3-acyl substituted 4*H*-chromenes. A number of methods for their preparation have been developed, such as coupling of benzylic alcohols with ketene dithioacetals,[9] cycloaddition of enamines to *o*-QM precursors,[4a,10] Michael addition of C-nucleophiles to 2-(1-tosylalkyl)phenols,[11] reactions of *o*-halogenobenzyl bromides or *o*-hydroxybenzyl alcohols with

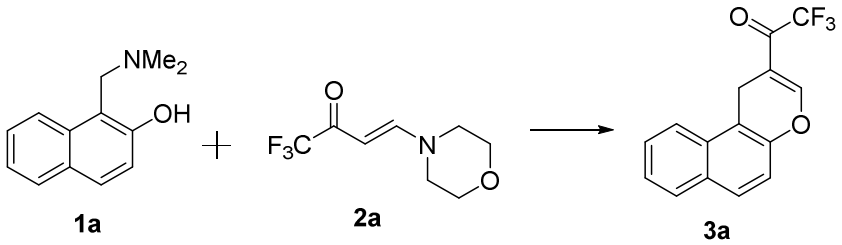
1,3-dicarbonyl compounds,[12] reaction of phenol and naphthol Mannich bases with aryl(ethynyl)ketones,[13] three-component condensation of 1,3-diketones, 2-naphthol and aromatic aldehydes,[14] Me_3SiI-promoted reaction of salicylic aldehydes with β-diketones[15] and aluminum triflate catalyzed acylation of bridge benzopyrans.[16] 4-Substituted 3-acetylchromenes were prepared from salicylic aldehydes or salicyl N-tosylimines and acetylenic ketones.[17] It should be noted that most of these methods involve the use of 1,3-dicarbonyl compounds or their synthetic equivalents, whereby the resulting acylchromenes have substituents at the 2- and/or 4-position of the pyran ring. This fact limits the range of possible further reactions involving them. At the same time, the presence of electron-withdrawing acyl substituent in the pyran fragment increases the reactivity of double bond C(2)=C(3) conjugated with a carbonyl group with regard to nucleophiles, and for this reason 3-acyl-4*H*-chromenes and 2-acyl-1*H*-benzo[*f*]chromenes are valuable substrates for the preparation of more complex heterocycles.

o-QMs are highly reactive intermediates and their utility for preparation of various fused pyran derivatives, common scaffolds in natural products, has recently gained considerable interest.[18] Since the *o*-QMs are inverse electron demand dienes, most of the dienophiles employed have been electron rich. Dienophiles such as ketene acetals, vinyl ethers and vinyl sulfides readily participate in the [4+2]-cycloaddition with *o*-QM.[19] However, the use of large excesses of 2π partners are often required for efficient cycloaddition.[20] The Diels-Alder reaction of *o*-OMs with olefins substituted with mildly electron-releasing (alkyl) or electron-accepting substituents does not occur readily.[21] Their reactions with push-pull olefins also remain little known.[4,22] In continuation of our interest in *o*-QM chemistry, we now report a novel route for the synthesis of electron deficient 3-acyl-4*H*-chromenes and 2-acyl-1*H*-benzo[*f*]chromenes from push-pull enaminoketones and *o*-QM precursors.

RESULTS AND DISCUSSION

We first investigated the reaction between the 2-naphthol Mannich base **1a** and 1,1,1-trifluro-4-morpholinobut-3-en-2-one **2a** in different solvents under reflux. The results showed that the reaction can be performed in acetic or propionic anhydride, or acetic acid, which afforded the highest yield. The reaction could also proceed in other solvents, such as DMF and *o*-xylene, but the yields of 1*H*-benzo[*f*]chromene **3a** were low. In 1,4-dioxane, acetonitrile and $BF_3 \cdot Et_2O$ the reaction did not proceed (Table 1). Attempts to improve the yield by increasing the reaction time were unsuccessful. We observed only starting materials in acetic acid at 80 ^oC after 3 h. Moreover, the reaction with equimolar amount of acetic acid or acetic anhydride in 1,4-dioxane or *o*-xylene under reflux led to formation of chromene **3a** with low yield. Thus, the choice of solvent for the preparation of **3a** is critical. The reaction was repeated on several different scales (up to 50 mmol), all with comparable yields using the optimal conditions.

Table 1. Effect of Solvent and Time on the Synthesis of 3a[a]



1a **2a** **3a**

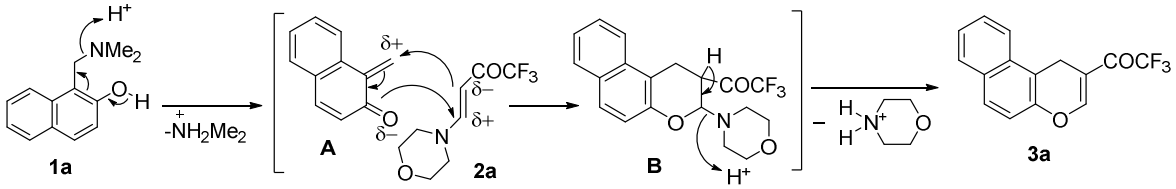
solvent	time, h	yield of **3a**, %
Ac_2O	3	56
AcOH	1	75
AcOH	2	76
AcOH	3	74
AcOH[b]	3	-
1,4-dioxane	5	-
1,4-dioxane (1 eq AcOH)	5	12
1,4-dioxane (1 eq Ac_2O)	3	19
$(EtCO)_2O$	0.5	55
$(EtCO)_2O$	1	56
DMF	3	15
o-xylene	5	17
o-xylene (1 eq AcOH)	3	17
$BF_3 \cdot Et_2O$	5	-
MeCN	10	-

[a]Reaction conditions: Mannich base **1a** (1 mmol) and enaminone **2a** (1 mmol) in solvent (5 mL) under reflux. [b]Reaction was performed at 80 °C.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 1. We suppose that the reaction proceeds via the *o*-QM intermediate **A**, which is formed by the thermal desamination of the Mannich base **1a**. Subsequent cycloaddition of the *o*-QMs with enaminone **2a** affords the unstable benzochroman cycloadduct **B** which is desaminated to give 1*H*-benzo[*f*]chromene derivative **3a**. The driving force of the cycloaddition is the resulting rearomatization of the benzene ring.[23] In this reaction the *o*-QM reacts as electron-deficient heterodiene. Its reaction with push-pull enamine proceeds regioselectively in a way that the carbon connected with morpholine fragment reacts with the *o*-QM oxygen, and the neighbouring

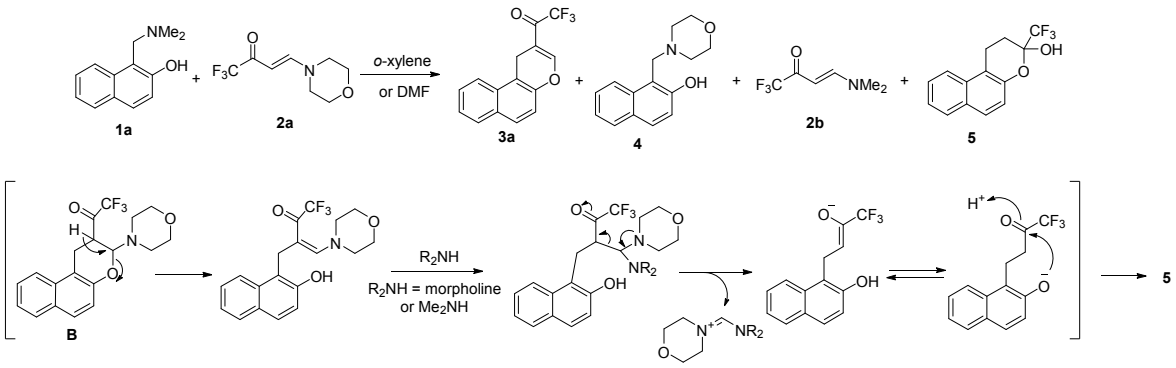
vinylic carbon with the methylene carbon of the *o*-QM. The regioselectivity can be readily explained by ionic resonance forms of the coreactants.

Scheme 1. Proposed Mechanism for the Synthesis of 3a



AcOH plays two roles in the reaction: activating the Mannich base to generate *o*-QM, and catalysing the elimination of morpholine from cycloadduct to give chromene. Besides, evolving morpholine and dimethylamine are converted into corresponding amides. Because the morpholine is sequestered, a potential side reaction, namely conjugated addition of morpholine to the *o*-QM intermediate to give Mannich base **4**, is prevented. In *o*-xylene and DMF, the reaction was very sluggish and complicated mixture of products, including the expected benzochromene **3a** as well as Mannich base **4**, enaminoketone **2b** and 3-(trifluoromethyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-ol **5** was obtained (Scheme 2). The proposed mechanism for the formation of chromenol **5** includes the following steps: retro-oxa-Michael reaction – opening of dihydropyran ring in the intermediate **B**, aza-Michael addition of secondary amines (morpholine or dimethylamine), a retro-Mannich reaction and intramolecular addition at the carbonyl group (hemiketalization). The product **2b** is a result of nucleophilic vinylic substitution (S_N Vin).[24]

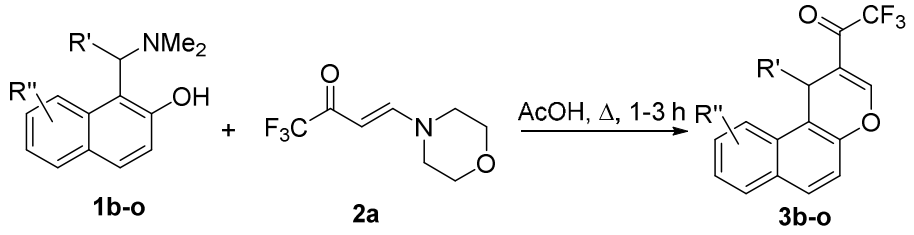
Scheme 2. Reaction of 1a and 2a in *o*-Xylene or DMF

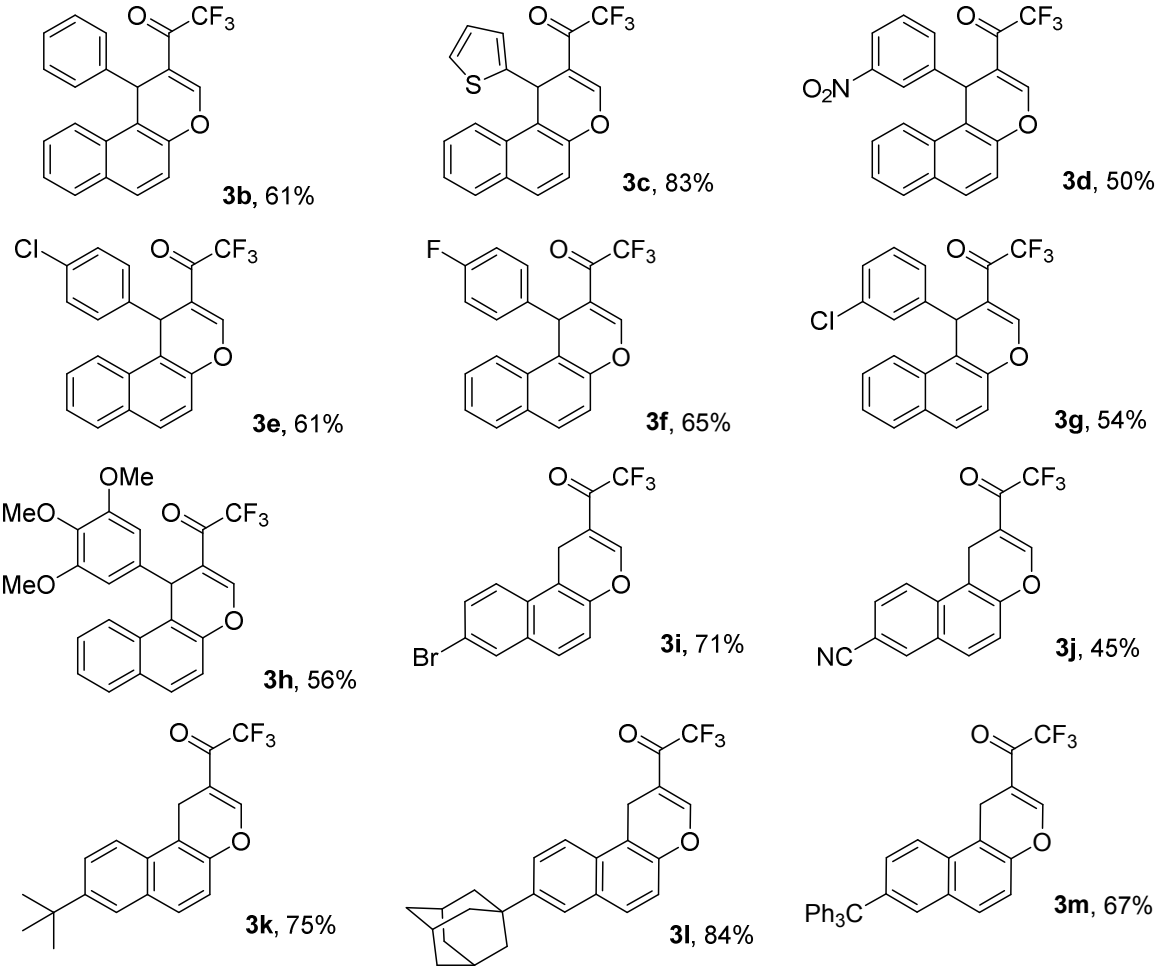


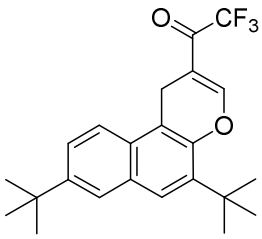
Under the optimized reaction conditions, the scope and generality of this reaction were then explored. A variety of electronically divergent *o*-QM precursors were examined, and the results are summarized in Table 2. The reactions were carried out until complete conversion of enaminone. Products can be easily purified from impurities by single recrystallization. The method turned out to be tolerant toward a broad range of functional groups. The reaction proceeded without any problems for a wide range of substrates bearing electron-donating (Alk, MeO) or electron-withdrawing (Hal, NO_2, CN) substituents on the aryl ring and naphthalene

fragment, providing the corresponding benzochromenes **3b**–**o** in moderate to good yields. The sterically hindered *tert*-butyl-substituted chromene **3n** was obtained in good yield, indicating that steric hindrance had no obvious influence on the efficiency of this method. This reaction was also extended to heterocyclic precursor **1o** of *o*-QM. From 5-((dimethylamino)methyl)-6-hydroxy-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-one **1o** and enaminone **2a** a novel heterocyclic system 7,9,10,11-tetrahydropyrano[3,2-*e*]pyrido[3,4-*b*]indol-8(1*H*)-one **3o** was prepared in 45% yield.

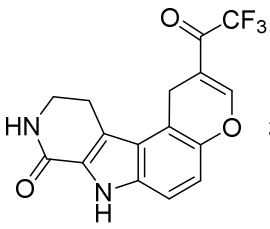
Table 2 Preparation of 2-Trifluoroacetyl-1*H*-benzo[*f*]chromenes 3b–o[a]







3n, 58%

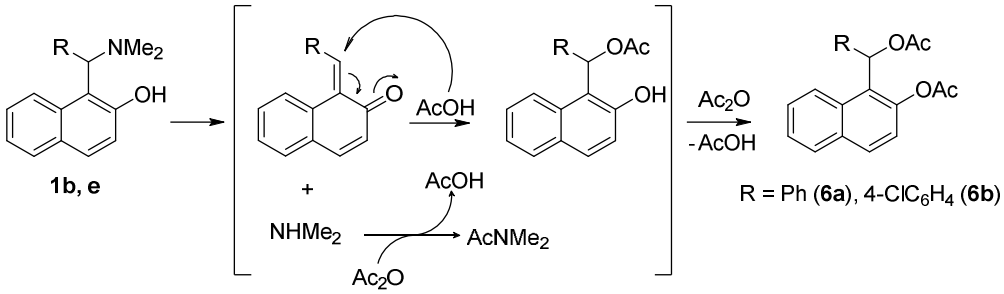


3o, 45%

[a]Reaction conditions: Mannich base **1b**–**o** (1.45 mmol) and enaminone **2a** (1.45 mmol) in acetic acid (5 mL) under reflux for 1 h (**3b,c,h**–**n**) or 3 h (**3d**–**g,o**).

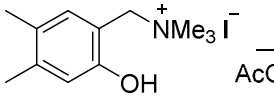
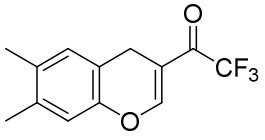
In the case of 1-unsubstituted Mannich bases the reaction can also be carried out in Ac_2O under reflux. At the same time, in the case of naphthol Mannich bases bearing aryl substituent at the 1-position using of acetic anhydride as a solvent afforded diacetates **6a** and **6b** as a result of addition of acetic acid to *o*-QM followed by *O*-acetylation of 2-naphthol hydroxyl group (Scheme 3).

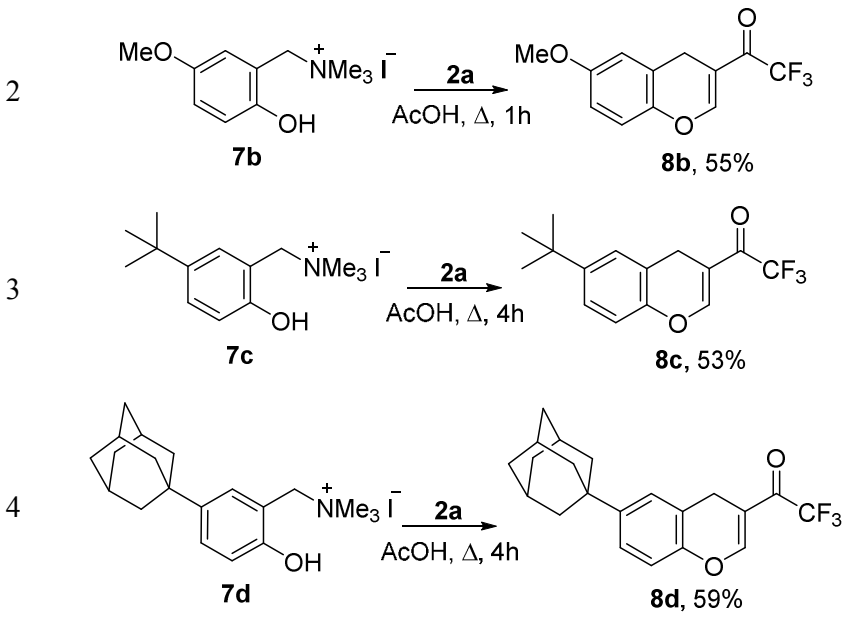
Scheme 3. Reaction of Mannich Bases 1b and 1e with Acetic Anhydride



Having successfully applied the 'Mannich route' to the synthesis based on the *o*-naphthoquinone methides, it was of interest to see if we might be successful in applying the synthesis to *o*-benzoquinone methides. Attempts to extend this reaction to the Mannich bases of simple phenols, however, failed to furnish the expected products. The reason for the failure may be due to the relatively greater thermal stability of the *o*-phenolic Mannich bases compared to that of the 2-naphthol derivatives and consequent difficulty in generating the *o*-QMs. Nevertheless, in the reaction with quaternary ammonium salts **7a**–**d** which are more reactive precursors of the *o*-QMs corresponding 4*H*-chromene derivatives **8a**–**d** were prepared in moderate to good yields (Table 3).

Table 3. Preparation of 3-Trifluoroacetyl-4*H*-chromenes 8a–d[a]

Entry	Quaternary ammonium salt **7**	Product **8**
1	 **7a**	 **8a**, 75%

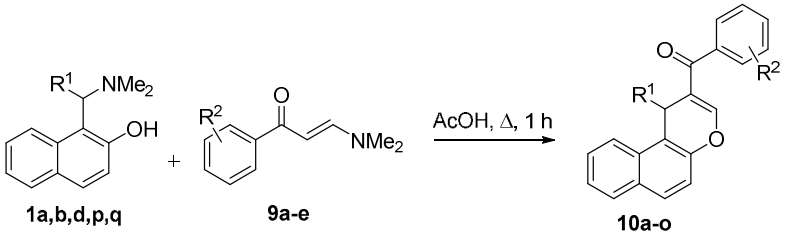


[a]Reaction conditions: quaternary ammonium salt **7a**–**d** (1.45 mmol) and enaminone **2a** (1.45 mmol) in acetic acid (5 mL) under reflux.

The new compounds **8** can be considered as useful trifluoromethyl-containing substrates for the synthesis of a variety of heterocyclic compounds with potential biological activity. Besides, introduction of such powerful electron-withdrawing group as trifluoroacetyl in the 2-position of the 1*H*-benzo[*f*]chromenes or in the 3-position of the 4*H*-chromenes increases their reactivity toward nucleophilic reagents and opens up a broad synthetic scope of these heterocyclic systems.[24]

In the next step, variation of the acyl groups was studied and a number of 2-aroyl-1*H*-benzo[*f*]chromenes **10a**–**o** was synthesized from aroylenamines **9a**–**e** and 2-naphthol Mannich bases using the optimal reaction conditions (Table 4). The electronic properties of the R^1 and R^2 substituents have little effect on the yield.

Table 4. Preparation of 2-Aroyl-1*H*-benzo[*f*]chromenes 10a–o[a]



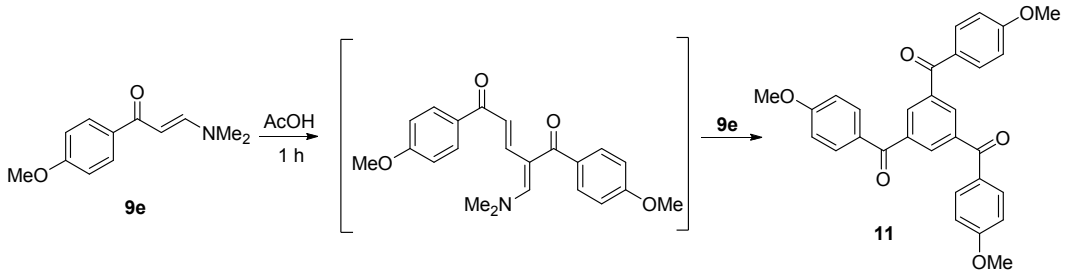
entry	Mannich base	R^1	enaminone	R^2	product	yield, %
1	**1a**	H	**9a**	H	**10a**	75
2	**1b**	Ph	**9a**	H	**10b**	80

3	**1d**	*m*-$NO_2C_6H_4$	**9a**	H	**10c**	64
4	**1p**	*p*-$MeOC_6H_4$	**9a**	H	**10d**	85
5	**1a**	H	**9b**	*o*-HO	**10e**	68
6	**1b**	Ph	**9c**	*p*-Me	**10f**	75
7	**1d**	*m*-$NO_2C_6H_4$	**9c**	*p*-Me	**10g**	60
8	**1p**	*p*-$MeOC_6H_4$	**9c**	*p*-Me	**10h**	70
9	**1a**	H	**9d**	*p*-Cl	**10i**	74
10	**1b**	Ph	**9d**	*p*-Cl	**10j**	73
11	**1d**	*m*-$NO_2C_6H_4$	**9d**	*p*-Cl	**10k**	65
12	**1p**	*p*-$MeOC_6H_4$	**9d**	*p*-Cl	**10l**	69
13	**1b**	Ph	**9e**	*p*-MeO	**10m**	68
14	**1p**	*p*-$MeOC_6H_4$	**9e**	*p*-MeO	**10n**	68
15	**1q**	1-benzyl-1*H*-imidazol-5-yl	**9a**	H	**10o**	85

[a]Reaction conditions: Mannich base **1** (1.45 mmol) and enaminone **9** (1.45 mmol) in acetic acid (5 mL) under reflux for 1 h.

Although aroylenamines are not stable under acidic reaction conditions and easily undergo trimerization to give 1,3,5-triaroylbenzenes,[25] we have observed such by-product **11** only in the case of enaminone **9e** (Scheme 4).

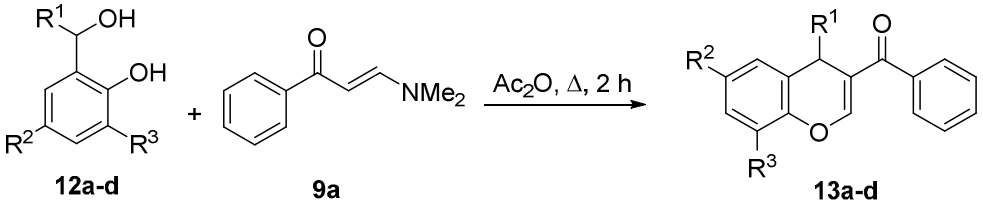
Scheme 4. AcOH-catalysed Trimerization of Enaminone 9e



The generation of *o*-QM *via* thermolytic extrusion of H_2O from salicylic alcohols is widely used for preparation of fused heterocycles. These reactions are often performed in refluxing DMF or under solvent-free conditions, at sufficiently high temperature to ensure the thermal decomposition of the *o*-QM precursors.[26] In our case, however, the reaction between salicylic alcohols and enaminone **9a** in refluxing DMF does not take place. At the same time, 3-benzoyl-4*H*-chromenes **13a**–**d** were obtained in 48–66% yields by heating salicylic alcohols **12a**–**d** and enaminone **9a** in acetic anhydride (Table 5). Reaction also takes place with equimolar amount of acetic anhydride in refluxing *o*-xylene with comparable yield. However, no product was

observed in the mixture of 1,4-dioxane and 1 equivalent of acetic anhydride. These facts can be explained by the transformation of *o*-hydroxybenzyl alcohols in acetates[27] which are more reactive precursors of *o*-QMs (Scheme 5), but refluxing temperature of 1,4-dioxane is not sufficient. The enhanced reactivity allows the reactions to proceed to completion without the need for an excess of dienophile, thus simplifying greatly the work-up procedure.

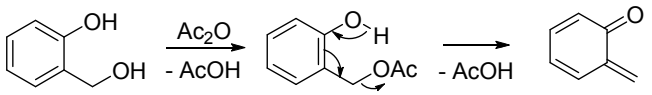
Table 5. Preparation of 3-Benzoyl-4*H*-chromenes 13a–d[a]



entry	2-hydroxybenzyl alcohol	R^1	R^2	R^3	product	yield, %
1	**12a**	Ph	H	H	**13a**	66 (67)[b]
2	**12b**	H	Me	1-Ad	**13b**	49
3	**12c**	H	H	OMe	**13c**	50
4	**12d**	H	1-Ad	Br	**13d**	48

[a]Reaction conditions: 2-hydroxybenzyl alcohol **12** (2 mmol) and enaminone **9a** (2 mmol) in acetic anhydride (4 mL) under reflux for 2 h. [b]Reaction was performed in *o*-xylene under reflux for 3 h with 1 eq of Ac_2O.

Scheme 5. Activation of Salicylic Alcohols in Acetic Anhydride

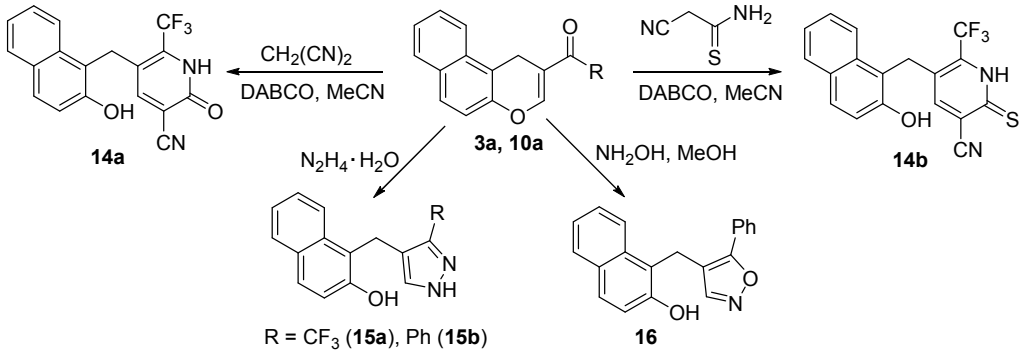


Structural assignment was based on elemental analyses and absence of an OH-band in the IR and of the phenolic proton signal in the ^{1}H NMR spectra of the chromene derivatives, respectively. In the IR spectra of compounds **3a**–**o** and **8a**–**d** there were strong absorption bands corresponding to the vibrations of the carbonyl group in the region of 1681–1708 cm^{-1} and pyran C=C double bond at 1627–1655 cm^{-1}. ^{13}C NMR spectra of compounds **3a**–**o** and **8a**–**d** showed the carbon atom of trifluoromethyl group and the adjacent carbonyl carbon atom as quartets at 116.4–116.8 ppm with $^1J_{C–F}$ = 288.9–290.0 Hz and at 178.5–179.6 ppm with $^2J_{C–F}$ = 34.3–35.6 Hz, respectively. The carbon atom of the carbonyl group of aroylchromenes **10** and **13** except the compound **10e** (δ = 180.2 ppm) resonated at 193.1–195.6 ppm. The signals for the atoms C-3 (1*H*-benzo[*f*]chromenes) and C-2 (4*H*-chromenes) in the ^{13}C NMR spectra are found at 150.8–156.6 ppm. In the ^{1}H NMR spectra, protons attached to these carbon atoms appeared in the

region of 7–8 ppm. The number of protons that were directly linked to ^{13}C atoms, inferred from DEPT spectra, was in accordance with the presented structures.

Having established a strategy for the synthesis of acylchromenes, the applicability of these structures was studied. The introduction of the electron-withdrawing group at the C2 position of the 1*H*-benzo[*f*]chromene system changes the reactivity of the pyran ring with respect to nucleophiles. The diversity of properties of these compounds comes from the fact that they are highly reactive push-pull olefins with a good leaving group at the β-carbon atom. The role of this group is played by the phenolate anion. On the other hand, they can be considered as masked α-hydroxybenzyl α-formylketones. Heterocyclic moieties such as pyridine, pyrazole and isoxazole based structures **14**–**16** were obtained treating the 1*H*-benzo[*f*]chromene **3a** and **10a** with the appropriate C- and N-nucleophiles (Scheme 6).

Scheme 6. Heterocyclic Compounds Obtained from 1*H*-benzo[*f*]chromenes 3a and 10a



CONCLUSION

We have developed a facile protocol for the synthesis of 2-acyl-1*H*-benzo[*f*]chromenes and 3-acyl-4*H*-chromenes based on cascade oxa-Diels-Alder and elimination reactions. Their synthesis by the suggested procedure does not require an excess of any reagents and the use of any catalysts. Besides, the advantages of this method include the use of available reagents, simple workup procedure, easy isolation, scalability and good functional group tolerance.

EXPERIMENTAL SECTION

Materials and Characterization. FTIR spectra were taken in KBr pellets. ^{1}H, ^{13}C, and DEPT NMR spectra were recorded using a 400 MHz NMR spectrometer in $CDCl_3$, DMSO-d_6, or CD_3CN solutions, relative to residual solvent signal. Chemical shifts and coupling constants were recorded in units of parts per million and hertz, respectively. The melting points were determined by capillary method and uncorrected. Elemental analysis was carried out on an automatic CHNS analyzer. The reaction progress was controlled by TLC on aluminum foil-backed silica gel plates, visualization under UV light and in iodine vapor, eluent CH_2Cl_2. Known

o-QM precursors,[22b,28] and enaminones **2a**,[29] **9a**–**e**[30] were prepared according to the literature procedures.

*1-[(Dimethylamino)methyl]-6-tritylnaphthalen-2-ol (**1m**).* Dimethylamine (3 mL of a 33% aqueous solution, 0.02 mol) and formaldehyde (1.5 mL of a 37% aqueous solution, 0.02 mol) were added to a solution of 6-tritylnaphthalen-2-ol (6.95 g, 0.018 mol) in isopropanol (50 mL) at 40 ºC. The reaction mixture was stored at room temperature for 1 day. The precipitate formed was filtered off, washed with ice-cold isopropanol. Yield: 78%, 6.22 g. Colorless solid, mp 216–218 °C. IR (KBr) υ_{max}: 2982, 2949, 2826, 2779, 1603, 1489, 1474, 1460, 1441, 1373, 1275, 1256, 1240, 1177, 995, 806, 758, 745, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.42 (s, 6H), 4.07 (s, 2H), 7.05 (d, J = 8.9 Hz, 1H), 7.17–7.27 (m, 20H), 7.53 (d, J = 8.7 Hz, 1H), 7.63–7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$,) δ: 44.8 ($2CH_3$), 57.8 (CH_2), 64.8 (C), 111.4 (C), 119.1 (CH), 120.1 (CH), 126.0 (3CH), 127.6 (6CH), 127.8 (C), 129.4 (CH), 129.8 (CH), 130.8 (C), 131.2 (CH), 131.3 (6CH), 140.9 (C), 146.8 (3C), 157.1 (C). Anal. Calcd (%) for $C_{32}H_{29}NO$: C, 86.65; H, 6.59; N, 3.16. Found (%): C, 86.54; H, 6.49; N, 3.27.

*3,6-Di-tert-butyl-1-[(dimethylamino)methyl]naphthalen-2-ol (**1n**).* Title compound was prepared similarly to compound **1m** from 3,6-di-*tert*-butylnaphthalen-2-ol (4.6 g, 0.018 mol) in isopropanol (50 mL) at room temperature. Yield: 80%, 4.51 g. Colorless solid, mp 187–189 °C. IR (KBr) υ_{max}: 2951, 2901, 2864, 1605, 1572, 1516, 1460, 1425, 1358, 1252, 1234, 1209, 1173, 1090, 997, 905, 839, 808 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.40 (s, 9H), 1.52 (s, 9H), 2.42 (s, 6H), 4.10 (s, 2H), 7.48 (dd, J = 8.9, J = 2.0 Hz, 1H), 7.66 (s, 1H), 7.69 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.8 ($3CH_3$), 31.4 ($3CH_3$), 34.5 (C), 35.3 (C), 44.3 ($2CH_3$), 57.4 (CH_2), 112.1 (C), 120.3 (CH), 124.0 (CH), 124.5 (CH), 125.5 (CH), 127.9 (C), 129.5 (C), 139.4 (C), 144.9 (C), 156.6 (C). Anal. Calcd (%) for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47. Found (%): C, 80.32; H, 10.05; N, 4.34.

*5-[(Dimethylamino)methyl]-6-hydroxy-2-naphthonitrile (**1j**).* Dimethylamine (3 ml of a 33% aqueous solution, 20 mmol) and formaldehyde (1.5 ml of a 37% aqueous solution, 20 mmol) were added to a solution of 6-hydroxy-2-naphthonitrile (3.04 g, 18 mmol) in isopropyl alcohol (10 ml) at 40 ºC. The reaction mixture was stored at room temperature for 1 day. The precipitate formed was filtered off, washed with ice-cold isopropanol. Yield 2.03 g (50%), brown solid, mp 137–139 °C. IR (KBr): 2955, 2924, 2853, 2220, 1614, 1589, 1578, 1466, 1400, 1381, 1369, 1303, 1277, 1242, 1157, 967, 813, 804. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.43 (s, 6 H, NMe_2), 4.14 (s, 2 H), 7.16 (d, J = 8.7 Hz, 1 H), 7.56 (d, J = 8.5 Hz, 1 H), 7.75–7.77 (m, 2 H), 8.13 (s, 1 H). Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.36; H, 6.22; N, 12.33. Found: C, 74.31; H, 6.24; N, 12.38.

General Experimental Procedure for the Synthesis of 1*H*-Benzo[*f*]chromenes 3a–o, 8a–p and 4*H*-Chromenes 6a–d, 10a–o. A solution of Mannich base **1a–o** or quaternary ammonium salt **7a–d** (1.45 mmol) and corresponding enaminone **2a, 9a–e** (1.45 mmol) in AcOH (5 mL) was heated under reflux as much as indicated in tables 2–4. The reaction mixture was cooled to room temperature and formed precipitate was collected. The crude product was purified by recrystallization. In cases there was no precipitation (compounds **3h** and **3i**), reaction mixture was concentrated under reduced pressure and residue was purified by column chromatography (silica gel, CCl_4).

*1-(1H-Benzo[f]chromen-2-yl)-2,2,2-trifluoroethan-1-one (**3a**).* Yield: 76%, 305 mg. Colorless solid, mp 112–114 °C (ethanol). IR (KBr) υ_{max}: 1682, 1643, 1616, 1593, 1512, 1462, 1358, 1265, 1238, 1211, 1184, 1146, 922, 814 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 3.73 (s, 2H), 7.29 (d, J = 8.9 Hz, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.3 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 8.22 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 19.4 (CH_2), 110.6 (C), 112.5 (C), 116.8 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 117.3 (CH), 123.4 (CH), 126.1 (CH), 128.0 (CH), 128.9 (CH), 129.5 (CH), 131.4 (C), 131.5 (C), 146.1 (C), 157.4 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.1 (q, $^2J_{C–F}$ = 34.3 Hz, C). Anal. Calcd (%) for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26. Found (%): C, 64.88; H, 3.29.

*2,2,2-Trifluoro-1-(1-phenyl-1H-benzo[f]chromen-2-yl)ethan-1-one (**3b**).* Yield: 61%, 315 mg. Colorless solid, mp 139–141°C (ethanol). IR (KBr) υ_{max}: 3033, 2885, 1681, 1640, 1590, 1242, 1211, 1145, 824 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 5.64 (s, 1 H), 7.06 (tt, J = 7.3, J = 1.4 Hz, 1H), 7.19 (t, J = 7.6 Hz, 2H), 7.30–7.33 (m, 2H), 7.40–7.51 (m, 3H), 7.90 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 8.42 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 35.3 (CH), 115.5 (C), 116.62 (C), 116.63 (q, $^1J_{C–F}$ = 289.9 Hz, CF_3), 117.4 (CH), 123.9 (CH), 126.0 (CH), 127.4 (CH), 127.9 (CH), 128.8 (2CH), 129.0 (2CH), 129.2 (CH), 130.2 (CH), 130.7 (C), 132.1 (C), 144.2 (C), 146.7 (C), 157.1 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 178.2 (q, $^2J_{C–F}$ = 34.3 Hz, C). Anal. Calcd (%) for $C_{21}H_{13}F_3O_2$: C, 71.19; H, 3.70. Found (%): C, 71.03; H, 3.62.

*2,2,2-Trifluoro-1-[1-(thiophen-2-yl)-1H-benzo[f]chromen-2-yl]ethan-1-one (**3c**).* Yield: 83%, 435 mg. Light-yellow solid, mp 141–142 °C (ethanol). IR (KBr) υ_{max}: 3062, 2916, 1685, 1643, 1589, 1238, 1211, 1138, 810 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 6.01 (s, 1H), 6.80 (dd, J = 5.0, J = 3.7 Hz, 1H), 6.90 (d, J = 3.0 Hz, 1H), 7.24 (dd, J = 5.0, J = 0.9 Hz, 1H), 7.46–7.57 (m, 3H), 7.94 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 9.2 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 8.45 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 30.0 (CH), 115.1 (C), 116.3 (C), 116.7 (q, $^1J_{C–F}$ = 289.9 Hz, CF_3), 117.4 (CH), 123.7 (CH), 125.9 (CH), 126.2 (CH), 126.4 (CH), 127.2 (CH), 128.1 (CH), 129.2 (CH), 130.5 (CH), 130.7 (C), 132.1 (C), 146.7 (C), 147.6 (C), 157.5 (q, $^4J_{C–F}$ = 5.7

Hz, CH), 178.2 (q, $^{2}J_{C–F}$ = 34.3 Hz, C). Anal. Calcd (%) for $C_{19}H_{11}F_3O_2S$: C, 63.33; H, 3.08; S, 8.90. Found (%): C, 63.45; H, 2.94; S, 8.78.

2,2,2-Trifluoro-1-[1-(3-nitrophenyl)-1H-benzo[f]chromen-2-yl]ethan-1-one ***(3d)****.* Yield: 50%, 290 mg. Light-yellow solid, mp 150–152 °C (ethanol). IR (KBr) υ_{max}: 3086, 2924, 1693, 1639, 1589, 1531, 1354, 1242, 1207, 1138, 821 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.82 (s, 1H), 7.39–7.51 (m, 4H), 7.77 (d, J = 7.8 Hz, 1H), 7.82–7.88 (m, 3H), 7.99 (ddd, J = 8.2, J = 2.3, J = 0.9 Hz, 1H), 8.08 (s, 1H), 8.13 (t, J = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.5 (CH), 114.6 (C), 114.8 (C), 116.4 (q, $^{1}J_{C–F}$ = 288.9 Hz, CF_3), 117.0 (CH), 122.4 (CH), 123.0 (CH), 123.5 (CH), 125.9 (CH), 127.9 (CH), 129.0 (CH), 129.5 (CH), 130.48 (C), 130.55 (CH), 132.2 (C), 134.8 (CH), 145.3 (C), 147.0 (C), 148.6 (C), 156.0 (q, $^{4}J_{C–F}$ = 5.7 Hz, CH), 178.7 (q, $^{2}J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{21}H_{12}F_3NO_4$: C, 63.16; H, 3.03; N, 3.51. Found (%): C, 63.27; H, 2.96; N, 3.42.

1-[1-(4-Chlorophenyl)-1H-benzo[f]chromen-2-yl]-2,2,2-trifluoroethan-1-one ***(3e)****.* Yield: 61%, 345 mg. Colorless solid, mp 144–146 °C (ethanol). IR (KBr) υ_{max}: 3025, 2883, 1683, 1640, 1592, 1241, 1211, 1145, 819 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.68 (s, 1 H), 7.18 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.9 Hz, 1H), 7.41–7.49 (m, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.5 Hz, 1H), 8.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.1 (CH), 115.3 (C), 115.7 (C), 116.5 (q, $^{1}J_{C–F}$ = 288.9 Hz, CF_3), 116.8 (CH), 123.4 (CH), 125.7 (CH), 127.6 (CH), 128.8 (3CH), 129.9 (CH), 130.0 (2CH), 130.8 (C), 132.1 (C), 132.9 (C), 141.9 (C), 146.9 (C), 155.5 (q, $^{4}J_{C–F}$ = 5.7 Hz, CH), 178.7 (q, $^{2}J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{21}H_{12}ClF_3O_2$: C, 64.88; H, 3.11. Found (%): C, 64.95; H, 3.06.

2,2,2-Trifluoro-1-[1-(4-fluorophenyl)-1H-benzo[f]chromen-2-yl]ethan-1-one ***(3f)****.* Yield: 65%, 350 mg. Colorless solid, mp 208–210 °C (isopropanol). IR (KBr) υ_{max}: 3059, 1685, 1641, 1589, 1504, 1244, 1213, 1157, 1132, 927, 813, 742, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.69 (s, 1 H), 6.89 (t, J = 8.7 Hz, 2H), 7.28–7.33 (m, 2H), 7.37 (d, J = 9.2 Hz, 1H), 7.40–7.49 (m, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.2 Hz, 1H), 8.01 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.9 (CH), 115.5 (d, $^{2}J_{C–F}$ = 21.0 Hz, 2CH), 115.6 (C), 116.0 (C), 116.5 (q, $^{1}J_{C–F}$ = 289.8 Hz, CF_3), 116.8 (CH), 123.4 (CH), 125.7 (CH), 127.6 (CH), 128.8 (CH), 129.8 (CH), 130.2 (d, $^{3}J_{C–F}$ = 7.6 Hz, 2CH), 130.8 (C), 132.1 (C), 139.2 (C), 146.9 (C), 155.4 (q, $^{4}J_{C–F}$ = 5.7 Hz, CH), 161.7 (d, $^{1}J_{C–F}$ = 244.1 Hz, C–F), 178.7 (q, $^{2}J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{21}H_{12}F_4O_2$: C, 67.75; H, 3.25. Found (%): C, 67.80; H, 3.20.

1-(1-[3-Chlorophenyl)-1H-benzo[f]chromen-2-yl]-2,2,2-trifluoroethan-1-one ***(3g)****.* Yield: 54%, 305 mg. Colorless solid, mp 143–145 °C (isopropanol). IR (KBr) υ_{max}: 3067, 2924, 1686, 1639, 1589, 1466, 1242, 1207, 1165, 1142, 934, 848, 814 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.68 (s, 1 H), 7.09 (d, J = 8.0 Hz, 1H), 7.16 (td, J = 7.3, J = 2.0 Hz, 1H), 7.25–7.29 (m, 2H), 7.38

(dd, J = 8.9, J = 2.0 Hz, 1H), 7.42–7.51 (m, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 8.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.3 (CH), 115.1 (C), 115.5 (C), 116.5 (q, $^1J_{C–F}$ = 289.9 Hz, CF_3), 116.9 (CH), 123.3 (CH), 125.7 (CH), 127.0 (CH), 127.5 (CH), 127.7 (CH), 128.7 (CH), 128.8 (CH), 129.8 (CH), 130.0 (CH), 130.8 (C), 132.1 (C), 134.6 (C), 145.2 (C), 147.0 (C), 155.6 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 178.6 (q, $^2J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{21}H_{12}ClF_3O_2$: C, 64.88; H, 3.11. Found (%): C, 64.74; H, 3.03.

*2,2,2-Trifluoro-1-[1-(3,4,5-trimethoxyphenyl)-1H-benzo[f]chromen-2-yl]ethan-1-one (**3h**).* Yield: 56%, 360 mg. Colorless solid, mp 157–159 °C (isopropanol). IR (KBr) υ_{max}: 3064, 2997, 2938, 2837, 1692, 1644, 1616, 1591, 1504, 1464, 1240, 1201, 1169, 1126, 999, 929, 819 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.74 (s, 9H), 5.65 (s, 1H), 6.51 (s, 2H), 7.37 (d, J = 8.9 Hz, 1H), 7.42–7.51 (m, 2H), 7.79–7.85 (m, 2H), 7.96 (d, J = 8.2 Hz, 1H), 8.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.6 (CH), 56.2 (2CH_3), 60.8 (CH_3), 105.8 (2CH), 115.6 (C), 116.1 (C), 116.5 (q, $^1J_{C–F}$ = 289.4 Hz, CF_3), 116.7 (CH), 123.6 (CH), 125.7 (CH), 127.5 (CH), 128.7 (CH), 129.7 (CH), 131.1 (C), 132.1 (C), 137.0 (C), 139.0 (C), 147.0 (C), 153.2 (2C), 155.4 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 178.8 (q, $^2J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{24}H_{19}F_3O_5$: C, 64.86; H, 4.31. Found (%): C, 64.99; H, 4.22.

*1-(8-Bromo-1H-benzo[f]chromen-2-yl)-2,2,2-trifluoroethan-1-one (**3i**).* Yield: 71%, 367 mg. Colorless solid, mp 173–174 °C (ethanol). IR (KBr) υ_{max}: 3117, 3082, 2905, 1690, 1647, 1612, 1585, 1501, 1354, 1238, 1203, 1172, 1130, 1076, 968, 922, 864, 806, 729 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.77 (s, 2H), 7.21 (d, J = 8.9 Hz, 1H), 7.63 (d, J = 8.7 Hz, 1H), 7.65–7.70 (m, 2H), 7.92 (s, 1H), 7.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.5 (CH_2), 110.3 (C), 112.5 (C), 116.6 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 118.1 (CH), 119.8 (C), 124.6 (CH), 128.1 (CH), 130.2 (C), 130.5 (CH), 130.8 (CH), 132.4 (C), 146.3 (C), 156.2 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.5 (q, $^2J_{C–F}$ = 35.6 Hz, C). Anal. Calcd (%) for $C_{15}H_8BrF_3O_2$: C, 50.45; H, 2.26. Found (%): C, 50.30; H, 2.16.

*2-(2,2,2-Trifluoroacetyl)-1H-benzo[f]chromene-8-carbonitrile (**3j**).* Yield: 45%, 198 mg. Colorless solid, mp 210–213 °C (isopropanol). IR (KBr) υ_{max}: 3113, 2224, 1684, 1641, 1595, 1585, 1468, 1394, 1240, 1209, 1190, 1132, 891, 814, 735 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.87 (s, 2H), 7.34 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.95 (s, 1H), 7.96 (d, J = 8.9 Hz, 1H), 8.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.6 (CH_2), 109.4 (C), 110.5 (C), 112.76 (C), 112.82 (C), 116.8 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 119.0 (CH), 124.3 (CH), 128.2 (CH), 129.6 (CH), 130.4 (C), 133.4 (C), 134.3 (CH), 148.4 (C), 155.9 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.4 (q, $^2J_{C–F}$ = 35.6 Hz, C). Anal. Calcd (%) for $C_{16}H_8F_3NO_2$: C, 63.37; H, 2.66; N, 4.62. Found (%): C, 63.49; H, 2.60; N, 4.51.

*1-[8-(tert-Butyl)-1H-benzo[f]chromen-2-yl]-2,2,2-trifluoroethan-1-one (**3k**).* Yield: 75%, 365 mg. Colorless solid, mp 120–121 °C (ethanol). IR (KBr) υ_{max}: 3078, 2963, 2874, 1689, 1647,

1601, 1585, 1470, 1396, 1308, 1269, 1219, 1200, 1169, 1134, 906, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.43 (s, 9H), 3.83 (s, 2H), 7.18 (d, J = 8.9 Hz, 1H), 7.70–7.73 (m, 2H), 7.78 (s, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.5 (CH_2), 31.3 ($3CH_3$), 34.9 (C), 110.4 (C), 111.9 (C), 116.7 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 116.7 (CH), 122.7 (CH), 123.7 (CH), 126.3 (CH), 128.9 (CH), 129.7 (C), 131.4 (C), 145.8 (C), 148.6 (C), 156.5 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.6 (q, $^2J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{19}H_{17}F_3O_2$: C, 68.26; H, 5.13. Found (%): C, 68.31; H, 5.06.

1-[8-(Adamantan-1-yl)-1H-benzo[f]chromen-2-yl]-2,2,2-trifluoroethan-1-one ***(3l)****.* Yield: 83%, 500 mg. Colorless solid, mp 150–152 °C (isopropanol). IR (KBr) υ_{max}: 3059, 2904, 2851, 1686, 1647, 1593, 1219, 1173, 1138, 906, 802 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.78–1.85 (m, 6H), 1.98–2.02 (m, 6H), 2.15 (br s, 3H), 3.84 (s, 2H), 7.18 (d, J = 8.9 Hz, 1H), 7.69–7.73 (m, 3H), 7.82 (d, J = 8.7 Hz, 1H), 7.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.6 (CH_2), 29.0 (3CH), 36.4 (C), 36.9 ($3CH_2$), 43.2 ($3CH_2$), 110.4 (C), 111.9 (C), 116.7 (CH), 116.8 (q, $^1J_{C–F}$ = 290.0 Hz, CF_3), 122.7 (CH), 123.7 (CH), 125.8 (CH), 129.1 (CH), 129.9 (C), 131.5 (C), 145.8 (C), 148.9 (C), 156.7 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.7 (q, $^2J_{C–F}$ = 35.0 Hz, C). Anal. Calcd (%) for $C_{25}H_{23}F_3O_2$: C, 72.80; H, 5.62. Found (%): C, 72.67; H, 5.57.

2,2,2-Trifluoro-1-(8-trityl-1H-benzo[f]chromen-2-yl)ethan-1-one ***(3m)****.* Yield: 67%, 505 mg. Yellow solid, mp 118–121 °C (isopropanol). IR (KBr) υ_{max}: 1688, 1645, 1595, 1585, 1491, 1470, 1441, 1240, 1190, 1171, 1138, 922, 847, 824, 752, 741, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.81 (s, 2H), 7.16 (d, J = 8.7 Hz, 1H), 7.20–7.31 (m, 15H), 7.39 (dd, J = 8.9, J = 2.0 Hz, 1H), 7.61 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.5 (CH_2), 65.0 (C), 110.4 (C), 112.1 (C), 116.7 (q, $^1J_{C–F}$ = 289.9 Hz, CF_3), 116.8 (CH), 121.8 (CH), 126.2 (3CH), 127.8 (6CH), 128.9 (CH), 129.4 (CH), 129.9 (C), 130.9 (C), 131.3 (6CH), 132.4 (CH), 144.5 (C), 146.4 (4C), 156.5 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.5 (q, $^2J_{C–F}$ = 35.0 Hz, C). Anal. Calcd (%) for $C_{34}H_{23}F_3O_2$: C, 78.45; H, 4.45. Found (%): C, 78.33; H, 4.36.

1-(5,8-Di-tert-butyl-1H-benzo[f]chromen-2-yl)-2,2,2-trifluoroethan-1-one ***(3n)****.* Yield: 58%, 330 mg. Colorless solid, mp 144–146 °C (ethanol). IR (KBr) υ_{max}: 2957, 2912, 2872, 1708, 1659, 1584, 1572, 1558, 1258, 1200, 1175, 1148, 1138, 916, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.42 (s, 9H), 1.50 (s, 9H), 3.87 (s, 2H), 7.66 (d, J = 9.0 Hz, 1H), 7.69 (s, 1H), 7.76 (s, 1H), 7.78 (d, J = 9.1 Hz, 1H), 8.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.7 (CH_2), 30.3 ($3CH_3$), 31.3 ($3CH_3$), 34.9 (C), 35.3 (C), 110.2 (C), 112.4 (C), 116.7 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 122.3 (CH), 123.7 (CH), 125.5 (CH), 125.6 (CH), 128.4 (C), 130.9 (C), 137.7 (C), 145.6 (C), 148.6 (C), 155.5 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.5 (q, $^2J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{23}H_{25}F_3O_2$: C, 70.75; H, 6.45. Found (%): C, 70.70; H, 6.48.

2-(2,2,2-Trifluoroacetyl)-7,9,10,11-tetrahydropyrano[3,2-e]pyrido[3,4-b]indol-8(1H)-one ***(3o)***. Yield: 45%, 220 mg. Colorless solid, mp 295–297 °C (isopropanol). IR (KBr) υ_{max}: 3418, 3179, 3028, 2966, 2866, 1682, 1655, 1632, 1605, 1500, 1427, 1342, 1203, 1169, 1142, 910, 779 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 3.09 (t, J = 6.8 Hz, 2H), 3.47 (td, J = 6.8, J = 2.5 Hz, 2H), 3.82 (s, 2H), 6.95 (d, J = 8.9 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 7.62 (s, 1H), 8.12 (s, 1H), 11.8 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.0 (CH_2), 22.3 (CH_2), 41.5 (CH_2), 109.3 (C), 111.5 (C), 112.8 (CH), 114.6 (CH), 116.8 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 119.0 (C), 123.3 (C), 129.3 (C), 135.0 (C), 142.2 (C), 158.1 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 161.9 (C=O), 178.9 (q, $^2J_{C–F}$ = 34.3 Hz, C). Anal. Calcd (%) for $C_{16}H_{11}F_3N_2O_3$: C, 57.15; H, 3.30; N, 8.33. Found (%): C, 57.23; H, 3.40; N, 8.22.

1-(6,7-Dimethyl-4H-chromen-3-yl)-2,2,2-trifluoroethan-1-one ***(8a)***. Yield: 75%, 280 mg. Colorless solid, mp 119–121 °C (ethanol). IR (KBr) υ_{max}: 2924, 1689, 1635, 1577, 1508, 1354, 1219, 1184, 1138, 894 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.20 (s, 3H), 2.21 (s, 3H), 3.50 (s, 2H), 6.79 (s, 1H), 6.90 (s, 1H), 7.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.2 (CH_3), 19.6 (CH_3), 21.2 (CH_2), 110.3 (C), 115.9 (C), 116.6 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 117.6 (CH), 130.4 (CH), 134.3 (C), 136.9 (C), 146.9 (C), 157.1 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.4 (q, $^2J_{C–F}$ = 35.1 Hz, C). Anal. Calcd (%) for $C_{13}H_{11}F_3O_2$: C, 60.94; H, 4.33. Found (%): C, 60.82; H, 4.30.

2,2,2-Trifluoro-1-(6-methoxy-4H-chromen-3-yl)ethan-1-one ***(8b)***. Yield: 54%, 205 mg. Colorless solid, mp 134–136 °C (ethanol). IR (KBr) υ_{max}: 2918, 1689, 1630, 1582, 1510, 1219, 1182, 1140, 799 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.56 (s, 2H), 3.78 (s, 3H), 6.64 (d, J = 2.3 Hz, 1H), 6.73 (dd, J = 8.9, J = 2.3 Hz, 1H), 6.95 (d, J = 8.9 Hz, 1H), 7.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.0 (CH_2), 55.7 (CH_3), 109.4 (C), 113.8 (CH), 114.0 (CH), 116.6 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 117.9 (CH), 120.0 (C), 143.0 (C), 157.0 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 157.2 (C), 179.2 (q, $^2J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{12}H_9F_3O_3$: C, 55.82; H, 3.51. Found (%): C, 55.94; H, 3.41.

1-(6-tert-Butyl-4H-chromen-3-yl)-2,2,2-trifluoroethanone ***(8c)***. Yield: 53%, 220 mg. Colorless solid, mp 112–114 °C (methanol). IR (KBr) υ_{max}: 3118, 3032, 2957, 2906, 2868, 1687, 1633, 1587, 1498, 1274, 1240, 1197, 1186, 1163, 1132, 943, 879, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.30 (s, 9H), 3.58 (s, 2H), 6.94 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 2.3 Hz, 1H), 7.22 (dd, J = 8.7, J = 2.3 Hz, 1H), 7.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9 (CH_2), 31.4 ($3CH_3$), 34.5 (C), 110.3 (C), 116.4 (CH), 116.6 (q, $^1J_{C–F}$ = 288.9 Hz, CF_3), 118.3 (C), 125.3 (CH), 126.5 (CH), 146.9 (C), 149.1 (C), 157.0 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.3 (q, $^2J_{C–F}$ = 35.3 Hz, C). Anal. Calcd (%) for $C_{15}H_{15}F_3O_2$: C, 63.38; H, 5.32. Found (%): C, 63.41; H, 5.38.

1-[(6-Adamantan-1-yl)-4H-chromen-3-yl]-2,2,2-trifluoroethan-1-one ***(8d)***. Yield: 59%, 310 mg. Colorless solid, mp 142–144 °C (methanol). IR (KBr) υ_{max}: 3109, 3066, 3043, 2935,

2881, 2846, 1689, 1631, 1585, 1496, 1261, 1120, 1130, 937, 887, 806, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.71–1.80 (m, 6H), 1.86–1.88 (m, 6H), 2.09 (br s, 3H), 3.58 (s, 2H), 6.96 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 2.3 Hz, 1H), 7.20 (dd, J = 8.5, J = 2.3 Hz, 1H), 7.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9 (CH_2), 29.0 (3CH), 36.1 (C), 36.8 ($3CH_2$), 43.3 ($3CH_2$), 110.3 (C), 116.5 (CH), 116.7 (q, $^1J_{C–F}$ = 289.8 Hz, CF_3), 118.4 (C), 125.0 (CH), 126.2 (CH), 146.9 (C), 149.4 (C), 157.1 (q, $^4J_{C–F}$ = 5.7 Hz, CH), 179.4 (q, $^2J_{C–F}$ = 34.8 Hz, C). Anal. Calcd (%) for $C_{21}H_{21}F_3O_2$: C, 69.60; H, 5.84. Found (%): C, 69.50; H, 5.78.

*(1H-Benzo[f]chromen-2-yl)(phenyl)methanone (**10a**).* Yield: 75%, 310 mg. Colorless solid, mp 158–160 °C (ethanol). IR (KBr) υ_{max}: 1655, 1628, 1593, 1512, 1466, 1439, 1389, 1323, 1281, 1223, 1180, 972, 910, 849, 814, 716 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.01 (s, 2H), 7.17 (d, J = 8.7 Hz, 1H), 7.45–7.57 (m, 5H), 7.61 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 7.1 Hz, 2H), 7.72 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6 (CH_2), 112.9 (C), 115.2 (C), 117.1 (CH), 123.1 (CH), 125.2 (CH), 127.2 (CH), 128.4 (CH), 128.5 (2CH), 128.6 (CH), 128.9 (2CH), 131.1 (C), 131.5 (CH), 132.1 (C), 138.8 (C), 146.8 (C), 155.2 (CH), 195.7 (C). Anal. Calcd (%) for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found (%): C, 84.07; H, 4.85.

*Phenyl(1-phenyl-1H-benzo[f]chromen-2-yl)methanone (**10b**).* Yield: 80%, 420 mg. Colorless solid, mp 209–211 °C (ethanol). IR (KBr) υ_{max}: 1639, 1593, 1454, 1381, 1319, 1231, 1192, 991, 849, 833, 814, 729, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.02 (s, 1H), 7.08 (t, J = 7.3 Hz, 1H), 7.20 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.9 Hz, 1H), 7.37–7.44 (m, 7H), 7.49 (t, J = 7.4 Hz, 1H), 7.54 (d, J = 7.3 Hz, 2H), 7.76–7.80 (m, 2H), 7.99 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.5 (CH), 116.5 (C), 117.1 (CH), 120.6 (C), 123.8 (CH), 125.0 (CH), 126.6 (CH), 127.1 (CH), 128.4 (2CH), 128.5 (3CH), 128.6 (2CH), 128.9 (2CH), 129.2 (CH), 131.6 (C), 131.70 (CH), 131.74 (C), 138.8 (C), 144.8 (C), 148.7 (C), 152.6 (CH), 194.9 (C). Anal. Calcd (%) for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found (%): C, 86.02; H, 4.89

*[1-(3-Nitrophenyl)-1H-benzo[f]chromen-2-yl](phenyl)methanone (**10c**).* Yield: 64%, 380 mg. Light-yellow solid, mp 175–177 °C (ethanol). IR (KBr) υ_{max}: 1636, 1593, 1531, 1350, 1319, 1277, 1227, 1180, 1080, 988, 922, 849, 810, 729, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.12 (s, 1H), 7.36–7.54 (m, 9H), 7.57 (s, 1H), 7.82–7.89 (m, 4H), 7.96 (d, J = 8.0 Hz, 1H), 8.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.4 (CH), 115.0 (C), 117.3 (CH), 119.3 (C), 122.0 (CH), 123.2 (CH), 123.4 (CH), 125.4 (CH), 127.5 (CH), 128.6 (2CH), 128.8 (2CH), 128.9 (CH), 129.4 (CH), 130.0 (CH), 131.1 (C), 131.88 (C), 131.93 (CH), 134.9 (CH), 138.3 (C), 146.8 (C), 147.8 (C), 148.7 (C), 153.8 (CH), 194.4 (C). Anal. Calcd (%) for $C_{26}H_{17}NO_4$: C, 76.65; H, 4.21; N, 3.44. Found (%): C, 76.81; H, 4.15; N, 3.32.

[1-(4-Methoxyphenyl)-1H-benzo[f]chromen-2-yl](phenyl)methanone (***10d***). Yield: 85%, 485 mg. Colorless solid, mp 212–214 °C (ethanol). IR (KBr) υ_{max}: 1639, 1593, 1508, 1462, 1381, 1319, 1312, 1257, 1227, 1177, 1037, 833, 810, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.69 (s, 3H), 5.97 (s, 1H), 6.73 (d, J = 8.7 Hz, 2H), 7.28–7.32 (m, 3H), 7.36–7.51 (m, 6H), 7.54–7.56 (m, 2H), 7.75–7.80 (m, 2H), 7.99 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.7 (CH), 55.2 (CH_3), 113.9 (2CH), 116.7 (C), 117.1 (CH), 120.7 (C), 123.9 (CH), 125.0 (CH), 127.1 (CH), 128.4 (2CH), 128.5 (CH), 128.9 (2CH), 129.1 (CH), 129.5 (2CH), 131.6 (C), 131.7 (CH), 131.8 (C), 137.3 (C), 138.8 (C), 147.7 (C), 152.4 (CH), 158.1 (C), 195.0 (C). Anal. Calcd (%) for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14. Found (%): C, 82.52; H, 5.19.

(1H-Benzo[f]chromen-2-yl)(2-hydroxyphenyl)methanone (***10e***). Yield: 68%, 297 mg. Colorless solid, mp 163–165 °C (ethanol). IR (KBr) υ_{max}: 3300–2600, 1628, 1601, 1570, 1466, 1443, 1400, 1354, 1308, 1265, 1231, 1142, 991, 822, 760, 687 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.19 (s, 2H), 7.27 (d, J = 9.2 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.53 (ddd, J = 8.3, J = 6.9, J = 1.2 Hz, 1H), 7.64–7.69 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 8.23 (dd, J = 8.0, J = 1.4 Hz, 1H), 8.38 (s, 1H), 10.15 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.2 (CH_2), 116.5 (C), 118.1 (CH), 121.0 (CH), 121.6 (CH), 122.9 (CH), 123.0 (C), 123.5 (C), 125.6 (CH), 126.1 (CH), 126.6 (CH), 129.1 (CH), 129.3 (CH), 129.6 (C), 133.1 (C), 134.4 (CH), 153.5 (C), 154.2 (CH), 156.6 (C), 180.2 (C). Anal. Calcd (%) for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found (%): C, 79.30; H, 4.56.

(1-Phenyl-1H-benzo[f]chromen-2-yl)(p-tolyl)methanone (***10f***). Yield: 75%, 410 mg. Colorless solid, mp 205–206 °C (ethanol). IR (KBr) υ_{max}: 1639, 1601, 1508, 1454, 1416, 1377, 1304, 1254, 1227, 1177, 1026, 988, 837, 810, 760, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 6.02 (s, 1H), 7.08 (tt, J = 7.3, J = 1.2 Hz, 1H), 7.17–7.21 (m, 4H), 7.31 (d, J = 8.9 Hz, 1H), 7.36–7.48 (m, 7H), 7.76–7.80 (m, 2H), 7.98 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6 (CH_3), 36.6 (CH), 116.4 (C), 117.1 (CH), 120.5 (C), 123.9 (CH), 125.0 (CH), 126.6 (CH), 127.1 (CH), 128.48 (2CH), 128.50 (CH), 128.6 (2CH), 129.1 (4CH), 129.2 (CH), 131.6 (C), 131.7 (C), 136.0 (C), 142.4 (C), 144.8 (C), 147.8 (C), 152.0 (CH), 194.7 (C). Anal. Calcd (%) for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36. Found (%): C, 86.25; H, 5.32.

[1-(3-Nitrophenyl)-1H-benzo[f]chromen-2-yl](p-tolyl)methanone (***10g***). Yield: 60%, 365 mg. Light-yellow solid, mp 188–190 °C (ethanol). IR (KBr) υ_{max}: 1636, 1593, 1528, 1462, 1350, 1315, 1227, 1180, 991, 922, 853, 826, 810, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 6.11 (s, 1H), 7.21 (d, J = 7.3 Hz, 2H),7.35–7.46 (m, 6H), 7.56 (s, 1H), 7.81–7.88 (m, 4H), 7.96 (d, J = 8.0 Hz, 1H), 8.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6 (CH_3), 36.5 (CH), 115.0 (C), 117.3 (CH), 119.2 (C), 121.9 (CH), 123.3 (CH), 123.4 (CH), 125.3 (CH), 127.5 (CH), 128.8 (CH), 129.0 (2CH), 129.2 (2CH), 129.4 (CH), 130.0 (CH), 131.1 (C), 131.8 (C), 134.9

(CH), 135.6 (C), 142.7 (C), 146.9 (C), 147.8 (C), 148.6 (C), 153.2 (CH), 194.2 (C). Anal. Calcd (%) for $C_{27}H_{19}NO_4$: C, 76.95; H, 4.54; N, 3.32. Found (%): C, 76.82; H, 4.62; N, 3.25.

[1-(4-Methoxyphenyl)-1H-benzo[f]chromen-2-yl](p-tolyl)methanone ***(10h)***. Yield: 70%, 410 mg. Colorless solid, mp 210–212 °C (ethanol). IR (KBr) υ_{max}: 1639, 1609, 1589, 1508, 1462, 1439, 1400, 1373, 1315, 1227, 1184, 1107, 1026, 988, 922, 829, 810, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 3.68 (s, 3H), 5.97 (s, 1H), 6.72 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.4 Hz, 2H), 7.26–7.51 (m, 8H), 7.74–7.80 (m, 2H), 7.98 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6 (CH_3), 35.8 (CH), 55.2 (CH_3), 113.9 (2CH), 116.7 (C), 117.1 (CH), 120.6 (C), 123.9 (CH), 125.0 (CH), 127.1 (CH), 128.5 (CH), 129.07 (3CH), 129.10 (2CH), 129.4 (2CH), 131.6 (C), 131.7 (C), 136.1 (C), 137.3 (C), 142.4 (C), 147.8 (C), 151.8 (CH), 158.1 (C), 194.8 (C). Anal. Calcd (%) for $C_{28}H_{22}O_3$: C, 82.74; H, 5.46. Found (%): C, 82.70; H, 5.36.

(1H-Benzo[f]chromen-2-yl)(4-chlorophenyl)methanone ***(10i)***. Yield: 74%, 340 mg. Colorless solid, mp 210–212 °C (ethanol) (lit. mp 198–199 °C).[13] IR (KBr) υ_{max}: 1632, 1593, 1520, 1466, 1319, 1281, 1231, 1180, 1088, 972, 833, 810, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.01 (s, 2H), 7.18 (d, J = 8.9 Hz, 1H), 7.45–7.52 (m, 4H), 7.60–7.66 (m, 3H), 7.74 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5 (CH_2), 112.8 (C), 115.2 (C), 117.1 (CH), 123.1 (CH), 125.3 (CH), 127.2 (CH), 128.4 (CH), 128.6 (CH), 128.8 (2CH), 130.3 (2CH), 131.1 (C), 132.1 (C), 137.0 (C), 137.9 (C), 146.8 (C), 155.1 (CH), 194.3 (C). Anal. Calcd (%) for $C_{20}H_{13}ClO_2$: C, 74.89; H, 4.08. Found (%): C, 74.99; H, 4.01.

(4-Chlorophenyl)(1-phenyl-1H-benzo[f]chromen-2-yl)methanone ***(10j)***. Yield: 73%, 420 mg. Colorless solid, mp 163–165 °C (ethanol). IR (KBr) υ_{max}: 3028, 2916, 1643, 1593, 1311, 1222, 1188, 837 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.00 (s, 1H), 7.09 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 8.9 Hz, 1H), 7.36–7.45 (m, 7H), 7.49 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.9 Hz, 1H), 7.79 (d, J = 7.1 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.6 (CH), 116.3 (C), 117.1 (CH), 120.5 (C), 123.8 (CH), 125.1 (CH), 126.7 (CH), 127.2 (CH), 128.5 (2CH), 128.56 (CH), 128.65 (2CH), 128.8 (2CH), 129.3 (CH), 130.3 (2CH), 131.5 (C), 131.8 (C), 137.0 (C), 138.1 (C), 144.7 (C), 147.7 (C), 152.5 (CH), 193.6 (C). Anal. Calcd (%) for $C_{26}H_{17}ClO_2$: C, 78.69; H, 4.32. Found (%): C, 78.79; H, 4.24.

(4-Chlorophenyl)[1-(3-nitrophenyl)-1H-benzo[f]chromen-2-yl]methanone ***(10k)***. Yield: 65%, 415 mg. Light-yellow solid, mp 237–239 °C (ethanol). IR (KBr) υ_{max}: 1632, 1589, 1524, 1396, 1346, 1315, 1227, 1192, 1088, 991, 822, 806, 760, 741, 683 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.08 (s, 1H), 7.36–7.49 (m, 8H), 7.54 (s, 1H), 7.81–7.87 (m, 4H), 7.96 (ddd, J = 8.2, J = 2.0, J = 0.9 Hz, 1H), 8.15 (t, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.4 (CH), 114.9 (C), 117.2 (CH), 119.2 (C), 122.0 (CH), 123.2 (CH), 123.3 (CH), 125.4 (CH), 127.6 (CH), 128.9

(3CH), 129.4 (CH), 130.1 (CH), 130.2 (2CH), 131.0 (C), 131.9 (C), 134.8 (CH), 136.6 (C), 138.3 (C), 146.7 (C), 147.7 (C), 148.6 (C), 153.7 (CH), 193.1 (C). Anal. Calcd (%) for $C_{26}H_{16}ClNO_4$: C, 70.67; H, 3.65; N, 3.17. Found (%): C, 70.52; H, 3.71; N, 3.06.

(4-Chlorophenyl)[1-(4-methoxyphenyl)-1H-benzo[f]chromen-2-yl]methanone ***(10l)***. Yield: 69%, 425 mg. Colorless solid, mp 156–158 °C (ethanol). IR (KBr) υ_{max}: 1639, 1589, 1508, 1462, 1439, 1396, 1315, 1227, 1184, 1096, 1026, 988, 922, 825, 806, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.68 (s, 3H), 5.94 (s, 1H), 6.73 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.9 Hz, 1H), 7.35–7.46 (m, 5H), 7.49 (d, J = 8.2 Hz, 2H), 7.75–7.80 (m, 2H), 7.97 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.7 (CH), 55.2 (CH_3), 114.0 (2CH), 116.6 (C), 117.1 (CH), 120.6 (C), 123.8 (CH), 125.1 (CH), 127.2 (CH), 128.6 (CH), 128.7 (2CH), 129.2 (CH), 129.4 (2CH), 130.3 (2CH), 131.5 (C), 131.8 (C), 137.1 (2C), 138.0 (C), 147.6 (C), 152.3 (CH), 158.2 (C), 193.8 (C). Anal. Calcd (%) for $C_{27}H_{19}ClO_3$: C, 75.97; H, 4.49. Found (%): C, 76.12; H, 4.40.

(4-Methoxyphenyl)(1-phenyl-1H-benzo[f]chromen-2-yl)methanone ***(10m)***. Yield: 68%, 385 mg. Colorless solid, mp 175–177 °C (ethanol). IR (KBr) υ_{max}: 1639, 1601, 1512, 1458, 1319, 1304, 1258, 1227, 1177, 1026, 837 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 6.03 (s, 1H), 6.88 (d, J = 8.7 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 7.19 (t, J = 7.6 Hz, 2H), 7.31–7.44 (m, 6H), 7.57 (d, J = 8.7 Hz, 2H), 7.76–7.80 (m, 2H), 7.97 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.9 (CH), 55.5 (CH_3), 113.7 (2CH), 116.4 (C), 117.1 (CH), 120.4 (C), 123.9 (CH), 125.0 (CH), 126.6 (CH), 127.1 (CH), 128.4 (2CH), 128.5 (CH), 128.6 (2CH), 129.2 (CH), 131.2 (2CH), 131.3 (C), 131.6 (C), 131.7 (C), 144.9 (C), 147.9 (C), 151.0 (CH), 162.7 (C), 193.8 (C). Anal. Calcd (%) for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14. Found (%): C, 82.55; H, 5.12.

(4-Methoxyphenyl)[1-(4-methoxyphenyl)-1H-benzo[f]chromen-2-yl]methanone ***(10n)***. Yield: 68%, 415 mg. Colorless solid, mp 173–175 °C (ethanol). IR (KBr) υ_{max}: 1639, 1601, 1508, 1462, 1319, 1265, 1227, 1180, 1107, 1026, 988, 918, 841, 825, 810, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.68 (s, 3H), 3.83 (s, 3H), 5.97 (s, 1H), 6.71 (d, J = 7.3 Hz, 2H), 6.88 (d, J = 7.4 Hz, 2H), 7.25–7.31 (m, 3H), 7.35–7.45 (m, 3H), 7.58 (d, J = 7.4 Hz, 2H), 7.74–7.79 (m, 2H), 7.96 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.0 (CH), 55.2 (CH_3), 55.5 (CH_3), 113.7 (2CH), 113.9 (2CH), 116.6 (C), 117.1 (CH), 120.5 (C), 123.9 (CH), 124.9 (CH), 127.0 (CH), 128.5 (CH), 129.0 (CH), 129.4 (2CH), 131.2 (2CH), 131.3 (C), 131.6 (C), 131.7 (C), 137.3 (C), 147.8 (C), 150.8 (CH), 158.1 (C), 162.7 (C), 193.9 (C). Anal. Calcd (%) for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found (%): C, 79.72; H, 5.18.

[1-(1-Benzyl-1H-imidazol-5-yl)-1H-benzo[f]chromen-2-yl](phenyl)methanone ***(10o)***. Yield: 85%, 545 mg. Colorless solid, mp 228–229 °C (isopropanol). IR (KBr) υ_{max}: 3117, 3086, 3059, 3024, 2966, 2908, 2854, 1647, 1627, 1593, 1492, 1323, 1300, 1276, 1222, 1180, 991, 925,

848, 817, 729, 678 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.32 (d, J = 15.8 Hz, 1H), 5.71 (d, J = 15.8 Hz, 1H), 5.96 (s, 1H), 6.68 (s, 1H), 6.99 (d, J = 8.5 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 8.7 Hz, 1H), 7.30–7.34 (m, 3H), 7.40–7.47 (m, 6H), 7.53–7.56 (m, 4H), 7.72 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.4 (CH), 49.3 (CH_2), 114.3 (C), 117.0 (CH), 119.0 (C), 122.9 (CH), 125.2 (CH), 127.4 (CH), 127.9 (2CH), 128.5 (CH), 128.6 (CH), 128.66 (2CH), 128.73 (CH), 129.0 (2CH), 129.3 (2CH), 129.8 (CH), 130.9 (C), 131.7 (C), 132.2 (CH), 135.6 (C), 136.1 (C), 137.6 (CH), 138.2 (C), 147.9 (C), 154.6 (CH), 195.1 (C). Anal. Calcd (%) for $C_{30}H_{22}N_2O_2$: C, 81.43; H, 5.01; N, 6.33. Found (%): C, 81.48; H, 4.89; N, 6.20.

General Experimental Procedure for the Synthesis of 3-Benzoyl-4*H*-chromenes 13a–d. To a solution of 2-hydroxybenzyl alcohol (2 mmol) **12a–d** in Ac_2O (4 mL) enaminone **9a** (2 mmol) was added. The mixture was heated for 2h under reflux, cooled to room temperature. The precipitate was filtered off, washed with H_2O. The crude product was purified by recrystallization from ethanol.

*Phenyl(4-phenyl-4H-chromen-3-yl)methanone (**13a**).* Yield: 66%, 410 mg. Colorless solid, mp 196–197 °C. IR (KBr) υ_{max}: 3097, 3024, 3003, 1633, 1600, 1575, 1487, 1450, 1386, 1321, 1292, 1224, 1178, 1155, 1101, 958, 920, 785, 752, 727, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.34 (s, 1H), 7.02–7.07 (m, 2H), 7.10–7.20 (m, 3H), 7.25 (t, J = 7.7 Hz, 2H), 7.31–7.34 (m, 2H), 7.40 (t, J = 7.9 Hz, 2H), 7.46 (s, 1H), 7.49 (tt, J = 8.7, J = 1.3 Hz, 1H), 7.56–7.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.3 (CH), 116.7 (CH), 119.5 (C), 124.4 (C), 125.3 (CH), 126.8 (CH), 128.0 (CH), 128.3 (2CH), 128.4 (2CH), 128.7 (2CH), 128.9 (2CH), 130.5 (CH), 131.7 (CH), 138.7 (C), 145.7 (C), 149.2 (C), 153.5 (CH), 194.7 (C). Anal. Calcd (%) for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found (%): C, 84.47; H, 5.10.

*[8-(Adamantan-1-yl)-6-methyl-4H-chromen-3-yl](phenyl)methanone (**13b**).* Yield: 41%, 315 mg. Colorless solid, mp 140–142 °C. IR (KBr) υ_{max}: 2911, 2897, 2878, 2849, 1628, 1593, 1449, 1391, 1323, 1292, 1209, 1179, 1103, 866, 849, 725, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.74 (br s, 6H), 2.05 (br s, 9H), 2.29 (s, 3H), 3.69 (s, 2H), 6.85 (s, 1H), 6.91 (s, 1 H), 7.42 (s, 1H), 7.44–7.55 (m, 3H), 7.61–7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2 (CH_3), 23.0 (CH_2), 29.1 (3CH), 36.9 (C), 37.0 ($3CH_2$), 41.0 ($3CH_2$), 115.1 (C), 120.2 (C), 126.3 (CH), 128.1 (CH), 128.5 (2CH), 128.7 (2CH), 131.3 (CH), 134.0 (C), 137.8 (C), 139.0 (C), 146.7 (C), 155.1 (CH), 195.5 (C). Anal. Calcd (%) for $C_{27}H_{28}O_2$: C, 84.34; H, 7.34. Found (%): C, 84.21; H, 7.37.

*(8-Methoxy-4H-chromen-3-yl)(phenyl)methanone (**13c**).* Yield: 50%, 265 mg. Colorless solid, mp 191–193 °C. IR (KBr) υ_{max}: 1643, 1612, 1578, 1477, 1439, 1396, 1315, 1273, 1215, 1084, 856, 767, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.73 (s, 2H), 3.88 (s, 3H), 6.78 (d, J =

8.0 Hz, 2H), 7.04 (t, *J* = 8.0 Hz, 1H), 7.41–7.45 (m, 3H), 7.50–7.54 (m, 1H), 7.62 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.7 (CH_2), 56.1 (CH_3), 110.3 (CH), 115.0 (C), 121.2 (C), 121.4 (CH), 124.8 (CH), 128.4 (2CH), 128.9 (2CH), 131.6 (CH), 138.5 (C), 139.3 (C), 147.9 (C), 155.2 (CH), 195.3 (C). Anal. Calcd (%) for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found (%): C, 76.79; H, 5.28.

[6-(Adamantan-1-yl)-8-bromo-4H-chromen-3-yl](phenyl)methanone ***(13d)****.* Yield: 25%, 225 mg. Colorless solid, mp 143–145 °C. IR (KBr) υ_{max}: 2901, 2847, 1628, 1568, 1468, 1447, 1325, 1288, 1219, 1169, 889, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.71–1.80 (m, 6H), 1.85–1.87 (m, 6H), 2.09–2.11 (m, 3H), 3.75 (s, 2H), 7.09 (d, *J* = 2.3 Hz, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.40–7.46 (m, 3H), 7.50–7.55 (m, 1H), 7.61–7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.5 (CH_2), 28.9 (3CH), 36.1 (C), 36.7 ($3CH_2$), 43.2 ($3CH_2$), 110.6 (C), 115.5 (C), 121.3 (C), 125.6 (CH), 128.5 (2CH), 128.6 (CH), 128.8 (2CH), 131.7 (CH), 138.4 (C), 144.5 (C), 149.4 (C), 155.2 (CH), 195.1 (C). Anal. Calcd (%) for $C_{26}H_{25}BrO_2$: C, 69.49; H, 5.61. Found (%): C, 69.56; H, 5.56.

Synthesis of Chromene 13a in mixture of *o*-Xylene and acetic anhydride. To a solution of 2-(hydroxy(phenyl)methyl)phenol (2 mmol) **12a** and in enaminone **9a** (2 mmol) in *o*-xylene (4 ml) acetic anhydride (2 mmol) was added. The mixture was heated for 3h under reflux, cooled to room temperature. The precipitate was filtered off, washed with H_2O. The crude product was purified by recrystallization from ethanol. Yield of **13a** – 67%, 417 mg.

Synthesis of 1*H*-Benzo[*f*]chromene 3a in *o*-Xylene. A mixture of 1-[(dimethylamino)methyl]naphthalen-2-ol **1a** (500 mg, 2.5 mmol) and enaminone **2a** (520 mg, 2.5 mmol) in *o*-xylene (5 mL) was heated at reflux temperature for 5 h. The solvent was removed by evaporation under reduced pressure and the residue was separated by column chromatography (silica gel, $CHCl_3$). 2,3-Dihydro-1*H*-benzo[*f*]chromen-3-ol **5** (15%, 100 mg), 1,1,1-trifluoro-4-morpholinobut-3-en-2-one **2a** (25%, 130 mg), 4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one **2b** (36%, 150 mg), 1*H*-benzo[*f*]chromene **3a** (17%, 120 mg) and Mannich base **4** (49%, 300 mg) were isolated. Products **5**,[31] **2b**[32] and **4**[33] were identical in melting point and spectral characteristics to literature data.

Reaction of Mannich Bases 1b and 1e with Enaminone 2a in Ac_2O. When Ac_2O was used instead of AcOH as a solvent, only diacetates **6a** and **6b** were isolated under the conditions previously indicated. After refluxing for 3 h, excess of Ac_2O was evaporated under reduced pressure and diacetates **6a** and **6b** were purified by column chromatography (silica gel, CCl_4).

1-[Acetoxy(phenyl)methyl]naphthalen-2-yl acetate ***(6a)****.* Yield: 76%, 370 mg. Colorless solid, mp 103–105 °C. Product was identical in spectral characteristics to a sample prepared previously.[34]

*1-[Acetoxy(4-chlorophenyl)methyl]naphthalen-2-yl acetate (**6b**).* Yield: 80%, 430 mg. Yellow solid, mp 149–150 °C (ethanol). IR (KBr) υ_{max}: 1747, 1489, 1362, 1223, 1204, 1169, 1088, 1065, 1011, 964, 810, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.14 (s, 3H), 2.35 (s, 3H), 7.15 (d, J = 8.5 Hz, 2H), 7.24–7.27 (m, 3H), 7.37–7.45 (m, 2H), 7.76 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.0 (CH_3), 21.1 (CH_3), 69.0 (CH), 122.0 (CH), 124.9 (C), 125.6 (CH), 125.7 (CH), 126.9 (CH), 127.1 (2CH), 128.7 (2CH), 128.8 (CH), 130.9 (CH), 131.7 (C), 132.6 (C), 133.3 (C), 138.2 (C), 147.7 (C), 169.8 (C=O), 170.2 (C). Anal. Calcd (%) for $C_{21}H_{17}ClO_4$: C, 68.39; H, 4.65. Found (%): C, 68.28; H, 4.53.

*5-[(2-Hydroxynaphthalen-1-yl)methyl]-2-oxo-6-(trifluoromethyl)-1,2-dihydropyridine-3-carbonitrile (**14a**).* A solution of chromene **3a** (200 mg, 0.72 mmol), malononitrile (50 mg, 0.76 mmol) and DABCO (85 mg, 0.76 mmol) in acetonitrile (5 mL) was heated at reflux temperature for 7 h. The reaction mixture was stored at –20 ºC for 12 h and formed precipitate collected. The crude product was purified by recrystallization from ethanol. Yield: 69%, 0.17 g. Yellow solid, mp 217–218 ºC. IR (KBr) υ_{max}: 3476, 3383, 3175, 2218, 1701, 1601, 1582, 1470, 1369, 1346, 1292, 1234, 1188, 1142, 1015, 810 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 4.24 (s, 2H), 7.26 (d, J = 8.9 Hz, 1H), 7.51–7.55 (m, 1H), 7.63–7.69 (m, 2H), 7.86–7.95 (m, 4H), 8.05 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 23.9 (CH_2), 109.9 (C), 111.3 (C), 112.4 (C), 116.8 (C), 117.0 (CH), 120.1 (q, $^1J_{C–F}$ = 274.6 Hz, CF_3), 123.0 (CH), 126.2 (CH), 128.3 (CH), 129.1 (CH), 129.8 (CH), 131.1 (C), 131.4 (C), 142.4 (q, $^2J_{C–F}$ = 34.3 Hz, $\underline{C}CF_3$), 143.8 (CH), 145.7 (C), 162.0 (C). Anal. Calcd (%) for $C_{18}H_{11}F_3N_2O_2$: C, 62.79; H, 3.22; N, 8.14. Found (%): C, 62.69; H, 3.18; N, 8.09.

*5-[(2-Hydroxynaphthalen-1-yl)methyl]-2-thioxo-6-(trifluoromethyl)-1,2-dihydropyridine-3-carbonitrile (**14b**).* A solution of chromene **3a** (300 mg, 1.1 mmol), cyanothioacetamide (120 mg, 1.2 mmol) and DABCO (130 mg, 1.2 mmol) in acetonitrile (5 mL) was heated at reflux temperature for 3 h. The reaction mixture was cooled to room temperature and formed precipitate was collected. The thiolate salt of DBU was suspended in isopropanol (4 mL), neutralized with conc. HCl until pH 4 and then poured into water (6 mL). The precipitate that formed was filtered off, washed with water and recrystallized from benzene. Yield: 63%, 250 mg. Yellow solid, mp 218–219 °C. IR (KBr) υ_{max}: 3500–3000, 2234, 1628, 1582, 1514, 1439, 1422, 1379, 1358, 1329, 1308, 1296, 1271, 1209, 1182, 1105, 1092, 1065, 991, 860, 816, 748. ^1H NMR (400 MHz, DMSO-d_6) δ: 4.45 (s, 2H), 7.26–7.30 (m, 2H), 7.37 (t, J = 8.2 Hz, 1H), 7.40 (s, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.80–7.84 (m, 2H), 10.05 (s, 1H). The NH proton signal does not appear, probably due to a fast exchange with deuterium. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 25.4 (CH_2), 112.0 (C), 113.7 (C), 114.5 (C), 118.9 (CH), 121.8 (q, $^1J_{C–F}$ = 275.5 Hz, CF_3), 122.3

(CH), 123.3 (CH), 127.4 (CH), 129.1 (C), 129.2 (CH), 130.0 (CH), 133.6 (C), 135.6 (C), 144.1 (CH), 147.4 (q, $^{2}J_{C–F}$ = 33.4 Hz, CF_3), 154.2 (C), 155.8 (C). Anal. Calcd (%) for $C_{18}H_{11}F_3N_2OS$: C, 60.00; H, 3.08; N, 7.77; S, 8.90. Found (%): C, 60.13; H, 2.96; N, 7.68; S, 8.79.

1-[(3-(Trifluoromethyl)-1H-pyrazol-4-yl)methyl]naphthalen-2-ol ***(15a)****.* A solution of chromene **3a** (300 mg, 1.1 mmol) in hydrazine hydrate (5 mL) was heated at reflux temperature for 1 h. The solvent was removed by evaporation under reduced pressure and the residue was recrystallized from methanol. Yield: 75%, 235 mg. Colorless solid, mp 221–223 °C. IR (KBr) υ_{max}: 3343, 3300–3100, 1630, 1584, 1506, 1462, 1437, 1379, 1354, 1341, 1312, 1292, 1275, 1244, 1182, 1146, 1117, 1078, 1045, 993, 957, 812, 754 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.17 (s, 2H), 6.86 (s, 1H), 7.20–7.25 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 9.73 (s, 1H), 13.16 (br s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 19.0 (CH_2), 116.9 (C), 118.7 (CH), 119.1 (C), 122.9 (CH), 123.0 (CH), 123.3 (q, $^{1}J_{C–F}$ = 271.7 Hz, CF_3), 126.9 (CH), 128.6 (CH), 128.8 (C), 128.9 (CH), 129.9 (CH), 133.5 (C), 138.4 (q, $^{2}J_{C–F}$ = 35.3 Hz, $\underline{C}CF_3$), 153.1 (C). Anal. Calcd (%) for $C_{15}H_{11}F_3N_2O$: C, 61.65; H, 3.79; N, 9.59. Found (%): C, 61.54; H, 3.77; N, 9.47.

1-[(3-Phenyl-1H-pyrazol-4-yl)methyl]naphthalen-2-ol ***(15b)****.* Title compound was prepared similarly to compound **15a** from chromene **10a.** Yield: 76%, 250 mg. Colorless solid, mp 208–209 °C (ethanol). IR (KBr) υ_{max}: 3389, 3200–2800, 1678, 1624, 1576, 1504, 1472, 1437, 1412, 1354, 1302, 1275, 1248, 1103, 978, 947, 812, 739, 694, 665 cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN) δ: 2.23 (br. s, single averaged peak with residual water, NH, OH), 4.30 (s, 2 H), 6.75 (s, 1H), 7.16 (d, J = 9.0 Hz, 1H), 7.22–7.31 (m, 2H), 7.38–7.42 (m, 1H), 7.47–7.52 (m, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.75–7.79 (m, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ: 20.3 (CH_2), 117.8 (C), 118.0 (CH), 118.6 (C), 122.8 (CH), 123.2 (CH), 126.3 (CH), 127.69 (CH), 127.73 (2CH), 128.0 (CH), 128.4 (CH), 128.7 (2CH), 129.1 (C), 132.6 (CH), 133.2 (C), 133.4 (C), 145.4 (C), 151.8 (C). Anal. Calcd (%) for $C_{20}H_{16}N_2O$: C, 79.98; H, 5.37; N, 9.33. Found (%): C, 80.08; H, 5.27; N, 9.24.

1-[(5-Phenylisoxazol-4-yl)methyl]naphthalen-2-ol ***(16)****.* An 1 M solution of hydroxylamine in methanol (3 mL) was added to a suspension of chromene **10a** (250 mg, 0.87 mmol) in methanol (5 mL) and the mixture was heated at reflux temperature for 1 h. The solvent was removed by evaporation under reduced pressure and the residue was recrystallized from ethanol. Yield: 80%, 210 mg. Colorless solid, mp 171–173 °C. IR (KBr) υ_{max}: 3500–3000, 1628, 1605, 1578, 1514, 1441, 1389, 1354, 1277, 1254, 1159, 1109, 1067, 995, 897, 812, 770, 746, 691. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.18 (s, 2H), 7.20–7.25 (m, 2H), 7.30–7.35 (m, 1H), 7.53–7.59 (m, 3H), 7.63 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.82–7.85 (m, 2H), 7.89 (s, 1H), 9.81 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 19.0 (CH_2), 116.7 (C),

118.6 (C), 118.7 (CH), 122.9 (CH), 123.1 (CH), 127.0 (CH), 128.77 (2CH, C), 128.81 (CH), 128.9 (CH), 129.6 (2CH, C), 130.3 (CH), 133.3 (C), 153.0 (C), 158.1 (CH), 161.3 (C). Anal. Calcd (%) for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found (%): C, 79.87; H, 4.97; N, 4.57.

ACKNOWLEDGMENT

This work was supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.21.0008) and by the Russian Foundation for Basic Research (grant 16-33-00773 mol_a).

Supporting Information

Copies of ^{1}H, ^{13}C NMR and DEPT spectra for all new synthesized compounds.

This material is available free of charge via the Internet at http://pubs.acs.org.

ORCID

Dmitry V. Osipov: 0000-0001-9217-0792

Notes

The authors declare no competing financial interest.

REFERENCES

(1) (a) Kleinpeter, E. *J. Serb. Chem. Soc*. **2006**, *71*, 1-17. (b) Lloyd, D.; McNab, H. *Angew. Chem. Int. Ed.* **1976**, *15*, 459-468. (c)

(2) (a) Stanovnik, B.; Svete, J. *Chem. Rev*. **2004**, *104*, 2433-2480. (b) Pan, L.; Bi, X.; Liu, Q. *Chem. Soc. Rev*. **2013**, *42*, 1251-1286. (c) Zhang, L.; Dong, J.; Xu, X.; Liu, Q. *Chem. Rev*. **2016**, *116*, 287-322. (d) Druzhinin, S. V.; Balenkova, E. S.; Nenaidenko, V. G. *Tetrahedron* **2007**, *63*, 7753-7808. (e) Nenaidenko, V. G.; Sanin, A. V.; Balenkova, E. S. *Russ. Chem. Rev*. **1999**, *68*, 437-458. (f) Rajappa, S. *Tetrahedron* **1999**, *55*, 7065-7114.

(3) (a) Greenhill, J. V. *Chem. Soc. Rev*. **1977**, *6*, 277-294. (b) Elassar, A. A.; El-Khair, A. A. *Tetrahedron* **2003**, *59*, 8463-8480. (c) Shawali, A. S. *ARKIVOC* **2012** (i), 383-431. (d) Lue, P.; Greenhill, J. V. *Adv. Heterocycl. Chem*. **1996**, *67*, 207-343. (e) Dar'in, D. V.; Lobanov, P. S. *Russ. Chem. Rev*. **2015**, *84*, 601-633.

(4) (a) René, L. *Synthesis* **1989**, 69-70. (b) Zhu, S.; Jin, G.; Peng, W.; Huang, Q. *Tetrahedron* **2003**, *59*, 2899-2905. (c) Gottschalk, F.-J.; Weyerstahl, P. *Chem. Ber*. **1980**, *113*, 555-565. (d) Osyanin, V. A.; Ivleva, E. A.; Klimochkin, Y. N. *Synth. Commun*. **2012**, *42*, 1832-1847. (e) Kumbaraci, V.; Ergunes, D.; Midilli, M.; Begen, S.; Talinli, N. *J. Heterocycl. Chem*. **2009**, *46*, 226-230. (f) Mohamed, N. R.; El-Saidi, M. M. T.; Ali, Y. M.; Elnagdi, M. H. *Bioorg. Med. Chem*. **2007**, *15*, 6227-6235.

(5) (a) Samarakoon, T. B.; Hur, M. Y.; Kurtz, R. D.; Hanson, P. R. *Org. Lett*. **2010**, *12*, 2182-2185. (b) Osyanin, V. A.; Osipov, D. V.; Demidov, M. R.; Klimochkin, Yu. N. *J. Org. Chem*. **2014**, *79*, 1192-1198.

(6) (a) Costa, M.; Dias, T.; Brito, A.; Proença, F. *Eur. J. Med. Chem.* **2016**, *123*, 487-507. (b) Patil, S. A.; Patil, R.; Preffer, L. M.; Miller, D. D. *Future Med. Chem*. **2013**, *5*, 1647-1660. (c) Parthiban, A.; Muthukumaran, J.; Priya, A. M.; Jayachandran, S.; Krishna, R.; Rao, H. S. P. *Med. Chem. Res*. **2014**, *23*, 642-659.

(7) (a) Pratap, R.; Ram, V. J. *Chem. Rev*. **2014**, *114*, 10476-10526. (b) Majumdar, N.; Paul, N. D.; Mandal, S.; de Bruin, B.; Wulff, W. D. *ACS Catal*. **2015**, *5*, 2329-2366.

(8) (a) Joulain, D.; Tabacchi, R. *Phytochemistry* **1994**, *37*, 1769-1770. (b) Pan, W.-B.; Wei, L.-M.; Wei, L.-L.; Wu, Y.-C. *Chem. Pharm. Bull*. **2006**, *54*, 954-958. (c) Nakashima, K.-I.; Abe, N.; Kamiya, F.; Ito, T.; Oyama, M.; Iinuma, M. *Helv. Chim. Acta* **2009**, *92*, 1999-2008. (d) Chansakaow, S.; Ishikawa, T.; Seki, H.; Sekine, K. (née Yoshizawa); Okada, M.; Chaichantipyuth, C. *J. Nat. Prod*. **2000**, *63*, 173-175. (e) Limsuwan, S.; Trip, E. N.; Kouwen, T. R. H. M.; Piersma, S.; Hiranrat, A.; Mahabusarakam, W.; Voravuthikunchai, S. P.; van Dijl J. M.; Kayser, O. *Phytomedicine* **2009**, *16*, 645-651. (f) Leejae, S.; Yingyongnarongkul, B.; Suksamrarn, A.; Voravuthikunchai, S. P. *Chin. Chem. Lett*. **2012**, *23*, 1011-1014. (g) Rattanaburi, S.; Mahabusarakam, W.; Phongpaichit, S.; Carroll, A. R. *Tetrahedron* **2013**, *69*, 6070-6075. (h) Liu, H.-X.; Tan, H.-B.; Qiu, S.-X. *J. Asian Nat. Prod. Res*. **2016**, *18*, 535-541. (i) Hufford, C. D.; Oguntimein, B. O.; Baker, J. K. *J. Org. Chem*. **1981**, *46*, 3073-3078.

(9) Liang, D.; Wang, M.; Bekturhun, B.; Xiong, B.; Liu, Q. *Adv. Synth. Catal.* **2010**, *352*, 1593-1599.

(10) Jones, R. M.; Selenski, C.; Pettus, T. R. R. *J. Org. Chem*. **2002**, *67*, 6911-6915.

(11) Wu, B.; Gao, X.; Yan, Z.; Huang, W.-X.; Zhou, Y.-G. *Tetrahedron Lett.* **2015**, *56*, 4334-4338.

(12) (a) Zhang, X. Y.; Fang, L. L.; Liu, N.; Wu, H. Y.; Fan, X. S. *Chin. Chem. Lett.* **2012**, *23*, 1129-1132. (b) Funabiki, K.; Komeda, T.; Kubota, Y.; Matsui, M. *Tetrahedron*, **2009**, *65*, 7457-7463. (c) Bunce, R. A.; Rogers, D.; Nago, T.; Bryant, S. A. *J. Heterocycl. Chem*. **2008**, 45, 547-550. (d) Aoyama, T.; Yamamoto, T.; Miyota, S.; Hayakawa, M.; Takido, T.; Kodomari, M. *Synlett* **2014**, 25, 1571-1576. (e) El-Sepelgy, O.; Haseloff, S.; Alamsetti, S. K.; Schneider, C. *Angew. Chem. Int. Ed*. **2014**, *53*, 7923-7927. (f) Reddy, C. R.; Vijaykumar, J.; Grée, R. *Synthesis* **2010**, 3715-3723. (g) Fan, J.; Wang, Z. *Chem. Commun*. **2008**, 5381-5383.

(13) Balasubramanian, K. K.; Selvaraj, S. *Tetrahedron Lett*. **1980**, *21*, 851-852.

(14) (a) Akondi, A. M.; Kantam, M. L.; Trivedi, R.; Sreedhar, B.; Buddana, S. K.; Prakasham, R. S.; Bhargava, S. *J. Mol. Catal. A: Chem*. **2014**, *386*, 49-60. (b) Sandaroos, R.; Damavandi, S. *Res. Chem. Intermed*. **2013**, *39*, 4167-4174.

(15) Wang, F.; Qu, M.; Chen, F.; Li, L.; Shi, M. *Chem. Commun*. **2012**, *48*, 437-439.

(16) Simelane, S. B.; Kinfe, H. H.; Muller, A.; Williams, D. B. G. *Org. Lett*. **2014**, *16*, 4543-4545.

(17) (a) Singh, S. N.; Bopanni, R.; Jayaprakash, S.; Reddy, K. V.; Ashfaq, M. A.; Kumar, K. S.; Pal, M. *RSC Adv*. **2014**, *4*, 24870-24873. (b) Shi, Y.-L.; Shi, M. *Chem. Eur. J*. **2006**, *12*, 3374-3378.

(18) (a) Jaworski, A. A.; Scheidt, K. A. *J. Org. Chem*. **2016**, *81*, 10145-10153. (b) Van De Water, R. W.; Pettus, T. R. R. *Tetrahedron* **2002**, *58*, 5367-5405. (c) Ferreira, S. B.; da Silva, F. C.; Pinto, A. C.; Gonzaga, D. T. G.; Ferreira, V. F. *J. Heterocycl. Chem*. **2009**, *46*, 1080-1097. (d) Osipov, D. V.; Osyanin, V. A.; Klimochkin, Yu. N. *Russ. Chem. Rev.* in press. (e) Zhang, Y.-C.; Zhu, Q.-N.; Yang, X.; Zhou, L.-J.; Shi, F. *J. Org. Chem.* **2016**, *81*, 1681-1688. (f) Saha, S.; Schneider, C. *Chem. Eur. J.* **2015**, *21*, 2348-2352. (g) Tsui, G. C.; Liu, L.; List, B. *Angew. Che. Int. Ed.* **2015**, *54*, 7703-7706. (h) Wang, J.; Sun, J. *Synthesis* **2015**, *47*, 3629-3644.

(19) Arduini, A; Bosi, A; Pochini, A.; Ungaro, R. *Tetrahedron* **1985**, *41*, 3095-3103.

(20) (a) Jones, R. M.; Selenski, C.; Pettus, T. R. R. *J. Org. Chem*. **2002**, *67*, 6911-6915. (b) Barrero, A. F.; Quílez del Moral, J. F.; Mar Herrador, M.; Arteaga, P.; Cortés, M.; Benites, J.; Rosellón. *Tetrahedron* **2006**, *62*, 6012-6017.

(21) (a) Wojciechowski, K.; Dolatowska, K. *Tetrahedron* **2005**, *61*, 8419-8422. (b) Chauhan, M. S.; Dean, F. M.; Matkin, D.; Robinson, M. L. *J. Chem. Soc., Perkin Trans. 1* **1973**, 120-125. (c) Chen, W.; Park, S. K.; Yu, W.; Xiong, A.; Sanders, B. G.; Kline, K. *Eur. J. Med. Chem.* **2012**, *58*, 72-83. (d) Wang, H.; Wang, Y.; Han, K.-L.; Peng, X.-J. *J. Org. Chem*. **2005**, *70*, 4910-4917. (e) Batsomboon, P.; Phakhodee, W.; Ruchirawat, S.; Ploypradith, P. *J. Org. Chem*. **2009**, *74*, 4009-4012.

(22) (a) Osyanin, V. A.; Lukashenko, A. V.; Osipov, D. V.; Klimochkin, Yu. N. *Chem. Heterocycl. Compd*. **2015**, *50*, 1528-1533. (b) Lukashenko, A. V.; Osyanin, V. A.; Osipov, D. V.; Klimochkin, Yu. N. *Chem. Heterocycl. Compd*. **2016**, *52*, 711-715.

(23) Wang, H.; Wang, Y.; Han, K.-L.; Peng, X.-J. *J. Org. Chem*. **2005**, *70*, 4910-4917.

(24) (a) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309-349. (b) Fernández, I.; Bickelhaupt, F. M.; Uggerud, E. *J. Org. Chem*. **2013**, *78*, 8574-8584.

(25) (a) Al-Saleh, B.; Abdelkhalik, M. M.; Eltoukhy, A. M.; Elnagdi, M. H. *J. Heterocycl. Chem*. **2002**, *39*, 1035-1038. (b) Wan, J.-P.; Lin, Y.; Hu, K.; Liu, Y. *RSC Adv*. **2014**, *4*, 20499-20505.

(26) (a) Osyanin, V. A.; Osipov, D. V.; Klimochkin, Yu. N. *Chem. Heterocycl. Compd*. **2010**, *46*, 377-378. (b) Osyanin, V. A.; Osipov, D. V.; Pavlov, S. A.; Klimochkin, Yu. N. *Chem. Heterocycl. Compd*. **2014**, *50*, 1195-1198. (c) Sidorina, N. E.; Osyanin, V. A. *Chem. Heterocycl. Compd*. **2007**, *43*, 1065-1071.

(27) Bray, C. D. *Org. Biomol. Chem*. **2008**, *6*, 2815-2819.

(28) (a) Osipov, D. V.; Osyanin, V. A.; Klimochkin, Yu. N. *Russ. J. Org. Chem*. **2013**, *49*, 398-402. (b) Bladé-Font, A.; Rocabayera, T. *J. Chem. Soc., Perkin Trans. 1* **1982**, 841-848. (c) Brode, W. R.; Littman, J. B. *J. Am. Chem. Soc*. **1931**, *53*, 1531-1532.

(29) Vdovenko, S. I.; Gerus, I. I.; Gorbunova, M. G. *J. Fluorine Chem.* **1997**, *82*, 167-169.

(30) Lienhard, U.; Fahrni, H.-P.; Neuenschwander, M. *Helv. Chim. Acta* **1978**, *61*, 1609-1621.

(31) Osyanin, V. A.; Popova, Yu. V.; Sakhnenko, D. V.; Osipov, D. V.; Klimochkin, Yu. N. *Chem. Heterocycl. Compd.* **2016**, *52*, 559-563.

(32) Baraznenok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **1998**, *54*, 119-128.

(33) Ganesan, S. S.; Rajendran, N.; Sundarakumar, S. I.; Ganesan, A.; Pemiah, B. *Synthesis* **2013**, *45*, 1564-1568.

(34) Smith, J. G.; Chu, N. G. *J. Org. Chem*. **1981**, *46*, 4083-4085.