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PAPER

Syntheses of furo[3,4-*c*]coumarins and related furyl coumarin derivatives *via* intramolecular Wittig reactions†

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A new and general strategy for highly functional furo[3,4-*c*]coumarins and related furyl coumarin derivatives has been developed, which is based on an extraordinarily facile intramolecular Wittig reaction, starting from α,β-unsaturated ketones, tributylphosphine, and acyl chlorides. The phosphorus ylides were proposed to be the key intermediates for constructing the crucial furan ring, leading to a wide variety of substituted furyl coumarins in one step.

Introduction

Coumarin derivatives form a valuable group of compounds in nature, which belong to the flavonoid class of plant secondary metabolites and are well known to possess multiple biological activities. In recent years they have attracted strong scientific interest stemming from their broad spectrum of pharmacological activities, including antioxidant, antiinflammatory, antibacterial, and antiviral activities. Therefore, the coumarin unit can be found not only in many natural products but also in synthetic drug molecules.[1]

Similarly, as an important class of heterocyclic fused coumarin derivatives, furocoumarins also have attracted considerable attention due to their photochemical, photophysical and photobiological properties.[2] They are photosensitizers of plant origin and increase the sensitivity of biological objects to UVA radiation. These properties have rendered them useful in a variety of applications such as useful molecular probes, and skin and autoimmune disease drugs. Consequently, much effort has been directed towards the synthesis of this class of compounds.[3]

Among a large variety of furan fused coumarins (Fig. 1), one can easily imagine there are two major groups which differ in the position of fusion between the furan and coumarin unit. Compared to derivatives with a fused furan on the lactone ring, coumarins with a fused furan on the aromatic ring are broadly studied because of their abundance in nature. Furthermore, among the three possible structural isomers with furan fused on the lactone ring, only one report to the best of our knowledge is published for the syntheses of furo[3,4-*c*]coumarins.[4] In 2006, Brahmbhatt[4] and co-workers demonstrated that furo[3,4-*c*]coumarins could be synthesized by the demethylation–cyclization of 3-aryl-4-ethoxycarbonyl furans, which were prepared from β-methyl-β-nitrostyrenes through Nef reactions. However, their application has been limited due to difficulties in tolerating a broad range of functional groups, which is a result of high temperatures and harsh reaction conditions. In addition, the preparation of 3-aryl-4-ethoxycarbonyl furans from substituted benzaldehydes *via* β-methyl-β-nitrostyrenes is laborious and low yielding, even though the protocol is general and well-known. Therefore, the efficient synthesis of functionalized furo[3,4-*c*]coumarins for various pharmacological purposes is still a challenging endeavor.

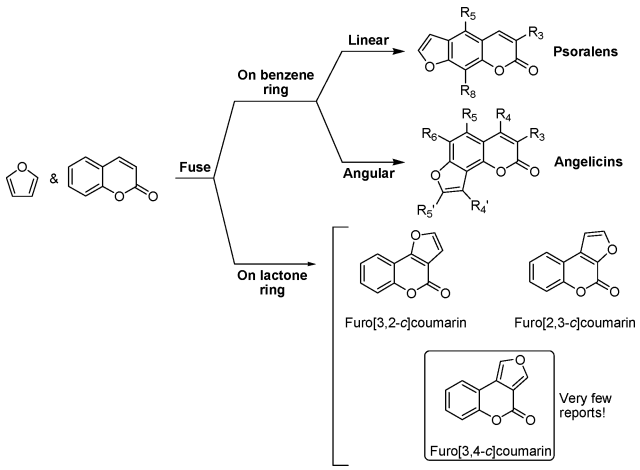

Fig. 1 Some representative furocoumarin core structures.

Recently, we have reported an efficient and convenient synthetic route to highly substituted furans[5] *via* an intramolecular Wittig reaction.[6] During the course of this research, we have found that enones can serve as strong acceptors of phosphines and can be smoothly converted into furans by using phosphorus ylides as intermediates. On the basis of these findings, we reasoned that the readily available enones, with the coumarin core structure, might also undergo a similar one-step reaction through ylide intermediates to give furo[3,4-*c*]coumarins (Fig. 2A). Our retrosynthetic

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of substrates **1**, **3**, **4**, **5**, **6**, **7**, and **8**; and X-ray crystallographic data (CCDC numbers: 805741 (**3cag**) and 833192 (**6p**)). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06571h

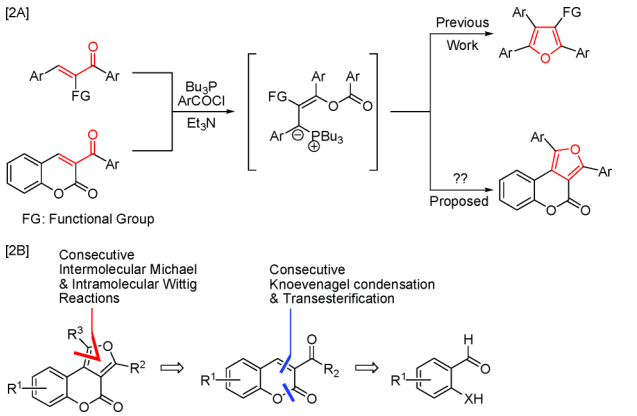


Fig. 2 Proposed new reaction pattern and retrosynthetic analysis.

analysis of furo[3,4-*c*]coumarins has led to a strategy involving just two consecutive reactions; an intramolecular Wittig reaction from the phosphorus ylides, which should be obtained by a Michael reaction from Bu_3P and the readily available enones (Fig. 2B).

In continuation of our previous work, aiming at the synthesis of different highly functionalized furans, we are now focused on furocoumarins with novel structures which have not been thoroughly investigated before. Therefore, we would like to report an efficient and mild approach for the synthesis of furo[3,4-*c*]coumarin derivatives. In addition, other than fused furocoumarins, several types of derivatives with furan moieties outside the coumarin core are prepared for investigating the chemoselective, regioselective, and photoluminescence properties. It is envisaged that the compounds containing both these moieties in a single molecule may show enhanced biological and optical properties.

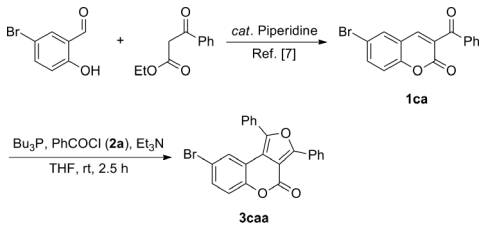
Results and discussion

With the above-mentioned hypotheses in mind, 3-benzoyl-6-bromocoumarin (**1ca**) was proposed as a test substrate and prepared according to the literature.[7] We began our study by examining the reaction of **1ca** and benzoyl chloride (**2a**) under different reaction conditions (Table 1).

Initially, the Michael acceptor **1ca**, Bu_3P (1.1 equiv.), **2a** (2 equiv.), and Et_3N (2.2 equiv.) reacted smoothly in anhydrous THF at room temperature for 2.5 h, providing the desired furo[3,4-*c*]coumarin **3caa** in 69% NMR yield (Table 1, entry 1). Encouraged by this important result, different amounts of each reagent were screened under the same conditions (Table 1). Finally, we were pleased to find that using Bu_3P (1.5 equiv.), **2a** (2 equiv.), and Et_3N (2.2 equiv.) were the best conditions, giving **3caa** in 71% isolated yield (Table 1, entry 3).

With the optimal conditions in hand, we turned our attention to the reaction scope of this transformation by changing the enone **1**. In order to investigate the syntheses of different furo[3,4-*c*]coumarins and to explore the effects of different substitutent groups (Table 2). Various electron-withdrawing and electron-donating R^1 and R^2 substituents of enone **1** were all well-tolerated when reacting with benzoyl chloride (**2a**). In general, electron-withdrawing R^1 substituents at the 6-position of enone **1** were uniformly of great benefit with regard to both the time required for the reaction and the yield produced (Table 2, entries 2–5 *vs.* 1), but it had little impact on the yield while electron-withdrawing R^1

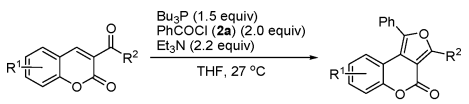
Table 1 Optimization of the reaction conditions for the formation of **3caa** from **1ca** *via* the intramolecular Wittig reaction[a]



Entry	Bu_3P (equiv.)	PhCOCl (**2a**) (equiv.)	Et_3N (equiv.)	Yield of **3caa** (%)[b]
1	1.1	2	2.2	69
2	1.3	2	2.2	68
3	1.5	2	2.2	79 (71)[c]
4	1.5	1.5	1.7	68
5	1.5	1.1	1.3	45

[a] Reactions were carried out with **1ca** (1 mmol) in THF (5 mL) under nitrogen at rt. [b] NMR yields with triphenylmethane as the internal standard. [c] Yield of isolated product.

Table 2 Preparation of highly functionalized furocoumarins **3** from benzoyl chloride (**2a**) and **1**[a]



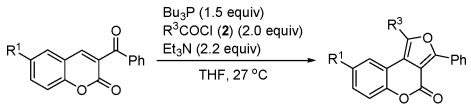
Entry	**1** R^1	R^2		Time (h)	Yield of **3** (%)[b]
1	H	C_6H_5	**1aa**	24	**3aaa**, 38(63)[c]
2	6-Cl	C_6H_5	**1ba**	4	**3baa**, 66
3	6-Br	C_6H_5	**1ca**	2.5	**3caa**, 71
4	6-NO_2	C_6H_5	**1da**	1.5	**3daa**, 89
5	6,8-Cl_2	C_6H_5	**1ea**	3	**3eaa**, 69
6	6-Br	3-$NO_2C_6H_4$	**1cb**	8	**3cba**, 73
7	6-Br	4-$NO_2C_6H_4$	**1cc**	6	**3cca**, 86
8	6-Br	4-$MeOC_6H_4$	**1cd**	24	**3cda**, 24(76)[c]
9	6-Br	CH_3	**1ce**	2	**3cea**, 55

[a] Reactions were carried out with **1** (0.5 mmol) in THF (2.5 mL) under nitrogen at 27 °C. [b] Yields of isolated products. [c] Recovered yields.

substituents were at the 8-position (Table 2, entry 2 *vs.* 5). Similarly, the reaction proceeded acceptably when electron-withdrawing and -donating groups were used at the R^2 position (Table 2, entries 6–8). The presence of electron-withdrawing or -donating groups on the R^2 substituents also followed the general trend mentioned above which was generated by R^1. Remarkably, substituents at R^1 can have a larger influence on the yield and reaction time than those at R^2 (Table 2, entries 3–4 *vs.* 7). Not only an aromatic substituent but also an aliphatic substituent was introduced as R^2, and it was compatible with this transformation (Table 2, entry 9).

To thoroughly investigate the generality of this transformation, many other acid chlorides **2** were tested and the results are summarized in Table 3. To our delight, a wide variety of multi-substituted furo[3,4-*c*]coumarins were constructed in medium to good yields without difficulty. Similarly, higher yields and shorter reaction times were facilitated by electron-withdrawing R^3

Table 3 Preparation of highly functionalized furocoumarins **3ca** and **3da** from **1ca** and **1da** with different acid chlorides **2**[a]



Entry	R^1 (**1**)	R^3 (**2**)	Time (h)	Yield of **3** (%)[b]
1	Br	C_6H_5 (**2a**)	2.5	**3caa**, 71
2	Br	2-ClC_6H_4 (**2b**)	3	**3cab**, 77
3	Br	3-ClC_6H_4 (**2c**)	5	**3cac**, 93
4	Br	4-ClC_6H_4 (**2d**)	30 min	**3cad**, 95
5	Br	2-BrC_6H_4 (**2e**)	4	**3cae**, 57
6	Br	4-$NO_2C_6H_4$ (**2f**)	10 min	**3caf**, 86
7	Br	4-$MeOC_6H_4$ (**2g**)	24	**3cag**, 64
8	Br	Cyclohexyl (**2h**)	1	**3cah**, 65
9	NO_2	C_6H_5 (**2a**)	1.5	**3daa**, 89
10	NO_2	4-ClC_6H_4 (**2d**)	30 min	**3dad**, 91
11	NO_2	4-$MeOC_6H_4$ (**2g**)	24	**3dag**, 62

[a] Reactions were carried out with **1ca** or **1da** (0.5 mmol) in THF (2.5 mL) under nitrogen at 27 °C. [b] Yields of isolated products.

substituents of the acid chlorides **2** (Table 3, entries 2–4 and 6 *vs.* 7), and both aromatic and aliphatic R^3 substituents could be used for this transformation (Table 3, entry 8). In addition, three points were noteworthy: [1] steric effects were observed when substituents were introduced at the *ortho*-position of R^3; for example, **2b** (R^3 = 2-ClC_6H_4) reacted with **1ca** to give **3cab** (77%) in a lower yield than the **3cad** (95%) produced from **2d** (R^3 = 4-ClC_6H_4) (Table 3, entry 2 *vs.* 4), [2] EWG substituents at R^3 had a greater impact on the yield and reaction time than at R^2 (Table 3, entry 6 *vs.* Table 2, entry 7), and [3] not only 6-Br, but also 6-NO_2 can be introduced at R^1, and both of them had high reactivities with acid chlorides in similar reaction patterns and behavior (Table 3, entries 9–11).

The inspiring results obtained so far prompted us to study further the synthetic application associated with the introduction and construction of more functionalities on the coumarin core structures. It would be unquestionably desirable to extend our method to conjugated carbonyl compounds in addition to enones. For this purpose, five compounds as depicted in Fig. 3 were prepared and tested in a reaction with Bu_3P and benzoyl chloride (**2a**) under typical conditions. However, no product could be observed in the reactions and these five starting substrates were almost completely recovered, even though the structures of the first two thiocoumarin derivatives (Fig. 3A–B) were very similar to our previous substrates. From these results, it seemed that the enone functionality was crucial to this transformation while the conjugated lactone group also played an important role in the reaction.

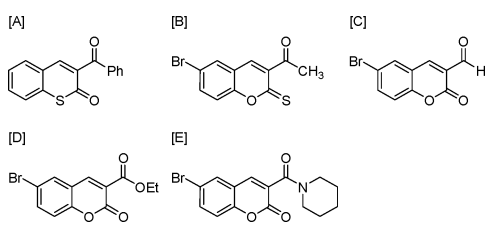


Fig. 3 The five conjugated carbonyl compounds tested for the transformation.

As mentioned before, owing to their attractive applications in material science[8] and diverse pharmacological properties, coumarins have recently received intense interest. On the other hand, chalcones form another important class of natural compounds, which display interesting biological activities including anti-inflammatory, antioxidant, antimalarial, antibacterial and anticancer. In the recent design of new materials or drugs, research suggests that the development of hybrid compounds through the combination of different chromophores or pharmacophores may lead to molecules with interesting profiles. Based on our previous reports, chalcones can be easily transformed to highly substituted furans by our protocol.[5] Therefore, we were especially interested in molecules with these two moieties together, both for investigating their reactivities in our method and for examining the photophysical properties of the generated furans.

Inspired by these proposals, we have designed and prepared a series of novel compounds that have both coumarin and chalcone entities together (Fig. 4) and have reacted them with Bu_3P and benzoyl chloride (**2a**) (Table 4 and Schemes 1–2).

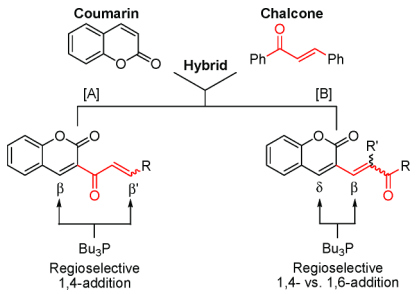
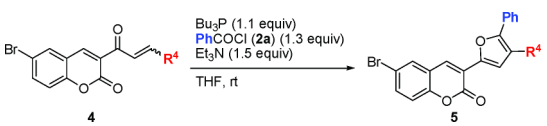


Fig. 4 Novel hybrid molecules through the combination of coumarin and chalcone.

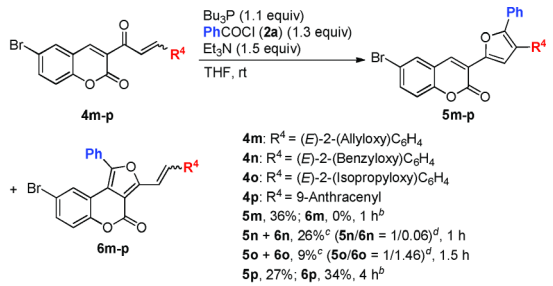
With this proposal in mind, we firstly focused on the Michael additions of 3-aryl-1-(3-coumarinyl)propen-1-ones **4** (of the type shown in Fig. 4A) which were synthesized by the reaction of 3-acetyl-6-bromocoumarin **1ce** and various substituted aromatic

Table 4 Preparation of highly functionalized 6-bromo-3-(2-furyl)-coumarins **5** from benzoyl chloride (**2a**) and various coumarin–chalcone hybrids **4** based on the idea in Fig. 4A[a]



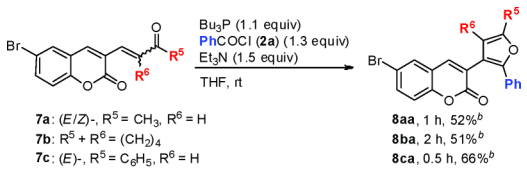
Entry	R^4 (**4**)	Time (h)	Yield of **5** (%)[b]
1	C_6H_5 (**4a**)	1.5	**5a**, 81
2	4-BrC_6H_4 (**4b**)	1	**5b**, 83
3	(*Z*)-2-$MeOC_6H_4$ (**4c**)	2	**5c**, 70
4	(*Z*)-4-$MeOC_6H_4$ (**4d**)	4	**5d**, 68
5	Piperonyl (**4e**)	3	**5e**, 71
6	4-$MeSC_6H_4$ (**4f**)	30 min	**5f**, 75
7	(*E*)-2-MeC_6H_4 (**4g**)	1	**5g**, 24
8	4-MeC_6H_4 (**4h**)	2	**5h**, 87
9	2-Furyl (**4i**)	30 min	**5i**, 74
10	(*E*)-2-Thiophenyl (**4j**)	30 min	**5j**, 86
11	(*Z*)-3-Pyridinyl (**4k**)	30 min	**5k**, 51
12	2-Naphthyl (**4l**)	30 min	**5l**, 65

[a] Reactions were carried out with **4** (0.2 mmol) in THF (1 mL) under nitrogen at rt. [b] Yields of isolated products.



[a]Reactions were carried out with **4** (0.2 mmol) in THF (1 mL) under nitrogen at rt. [b]Yields of isolated products. [c]Total isolated yield of two regioisomers. [d]NMR ratio between two regioisomers in the isolated product.

Scheme 1 Regioselective preparation of highly functionalized furyl coumarin derivatives **5** and/or **6** from benzoyl chloride (**2a**) and various coumarin–chalcone hybrids **4m–q**.[a]



[a]Reactions were carried out with **7** (0.5 mmol) in THF (2.5 mL) under nitrogen at rt. [b]Yields of isolated products.

Scheme 2 Preparation of highly functionalized 6-bromo-3-(3-furyl)-coumarins **8** from benzoyl chloride (**2a**) and various coumarin–chalcone hybrids **7** based on the idea in Fig. 4B.[a]

aldehydes in the presence of piperidine in ethanol under reflux (Table 4).

Based on our previous reports[5] and the present work, the Michael addition of Bu_3P with **4** could in principle lead to the following results, (1) addition at the β-position or (2) addition at β′-position. However, the addition selectively took place at the β′-carbon of the coumarinyl chalcone to give **5** as the sole product even though the β-carbon possessed an electron-withdrawing activating group (coumarinyl lactone) and the β′-carbon had electron-donating deactivating substituents (Table 4, entries 3–5 and 7–8). This surprising and striking regioselectivity suggested that the coumarinyl lactone was too weak an activating group to govern the selective addition of Bu_3P. Therefore, the steric effect played a key role in the determination of the regiochemistry of the Michael addition, and Bu_3P selectively attacked the less hindered chalcony *β′*-carbon. As a result, a variety of polysubstituted 3-(2-furyl)-coumarins **5** were constructed in medium to high yields in similar reaction patterns and behavior to those in Tables 2–3. Thus, better yields and faster reaction rates were promoted by electron-withdrawing R^4 substituents of the coumarinyl chalcones **4**, and *vice versa* (Table 4, entries 1–2 and 10 *vs.* others).[9]

Furthermore, the interesting results mentioned above inspired us to investigate the origin of the steric effects and regioselectivity. First of all, we examined the Michael addition of Bu_3P with **4**, which possessed different sterically sized alkoxy substituents at the *ortho*-position of the chalcony 3-benzene ring. (Scheme 1, **4m–p**). As expected, due to the steric hindrance coming from R^4, the products contained two regioisomers **5** and **6** when R^4 became bulkier so that the addition of Bu_3P towards **4** took place less selectively (Scheme 1, **4m** *vs.* **4n–p**). It could be assumed that the R^4 substituent served as a blocking group for β′-addition, but a small R^4 had little effect on the regiocontrol of the Michael addition of Bu_3P (Scheme 1, **4n–p** *vs.* Table 4 entries 1–12).

The scope of the work was further extended to 3-(3-coumarinyl)propen-1-ones **7**[10] (the type shown in Fig. 4B) as the conjugated acceptor with Bu_3P. To study which position was predominately chosen by the Bu_3P-conjugate addition, the coumarin–chalcone hybrids **7** were treated with Bu_3P, **2a** and triethylamine under similar conditions, the reactions gave 3-(3-furyl)-coumarins **8** as the only regioselective isomer in medium yields without any γ-addition (Scheme 2). In addition, it was worth mentioning that such highly functional 3-(3-furyl)-coumarins **8** were conveniently generated for the first time within only one step compared to methods in the literature.[11]

The preceding results showed that the intermolecular Bu_3P addition of conjugated enones with coumarin and chalcone moieties generally led to attack at the β′-carbon of Fig. 4A and β-carbon of Fig. 4B systems, respectively, with excellent regioselectivity.

Conclusions

In summary, we have developed a mild and efficient protocol for the syntheses of furo[3,4-*c*]coumarins and related furyl coumarin derivatives from readily available substrates. This set of conditions nicely compliments our previous work, and provides facile access to highly functionalized furo[3,4-*c*]coumarins which are not easily synthesized *via* known methods. Ease of operation, mild reaction conditions, possibilities for the large scale synthesis, and a wide functional-group tolerance are several merits of this highly efficient protocol. Most of the compounds reported in the present work are novel, and therefore further investigations by our group to extend the scope of this reaction, as well as biological evaluation of these compounds, are currently underway.

Experimental

Representative preparation of furo[3,4-*c*]coumarin: 3caa

In a dry, nitrogen-flushed Schlenk flask equipped with a septum and a magnetic stirrer bar, compound **1ca** (164.6 mg, 0.50 mmol) was dissolved in dry THF (2.5 mL) and stirred. After 5 min of stirring, tributylphosphine (187.3 μL, 0.75 mmol), benzoyl chloride (**2a**) (116.1 μL, 1.0 mmol), and Et_3N (152.9 μL, 1.1 mmol) were successively added. The resulting solution was stirred at 27 °C until the reaction was complete (monitoring by NMR). After completion (2.5 h), the solvent was removed *in vacuo*, and the crude product was purified by flash chromatography (silica gel; hexane/ethyl acetate, 10 : 1) to yield the desired product **3caa** (147.5 mg, 71%) as a white solid. M.p. 259.5–259.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.39 (d, J = 7.3 Hz, 2 H), 8.00 (d, J = 2.0 Hz, 1 H), 7.78 (d, J = 7.0 Hz, 2 H), 7.65–7.41 (m, 7H), 7.19 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.0, 157.2, 150.3, 147.5, 132.2, 130.5, 130.1, 129.7, 129.1, 128.6, 128.2, 128.1, 125.7, 119.3, 116.9, 116.8, 116.2, 107.5; IR (KBr): ν^{-1} = 1742 (s), 1266 (s), 1178 (s), 570 (w) cm^{-1}; MS (20 eV, EI): *m*/*z* (%): 418 (M + 2, 100), 416 (M$^+$, 87); HRMS (MALDI) for ($C_{23}H_{13}{}^{79}BrO_3$ + H)$^+$: 417.0126, found: 417.0137.

Acknowledgements

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9 Besides, we were interested not only in preparing heteroaromatic derivatives but also especially in the photophysical properties of these highly functional furyl cumarins **5**. Therefore, based on the present works, UV-vis absorption and fluorescence spectra of some selected coumarin derivatives were measured and given in **Figure SI-1-2** in the supporting information†.

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