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ARTICLE

# Multicomponent reactions (MCRs) for the facile access of coumarin fused dihydroquinolines and quinolines: Synthesis and photophysical studies

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A simple and straightforward method for the easy access of coumarin fused dihydroquinolines (**4**) has been developed using bismuth triflate catalyzed microwave (MW) assisted multicomponent reactions of 4-hydroxycoumarin, aldehydes and aromatic amines in water. Under solvent free and conventional heating conditions, the same combination provided the corresponding coumarin fused quinolines (**5**). An alternative and rapid method for the conversion of (**4**) to (**5**) using N-bromosuccinamide with very good yields is also reported. The single-crystal X-ray crystallographic analysis for one of the product (**4q**) has revealed that the products are regioselective and the reactions undergo via 1,2-addition followed by 6π-electrocyclization instead of Skraup-Doebner-von Miller type reaction. Substituted quinoline carboxylic acid derivatives (**7**) were synthesized selectively from (**4**) by ring opening of coumarin moiety followed by aromatization using NaOH/DMSO under reflux conditions. Considering the presence of polycyclic conjugated structure of synthesized **4** and **5** with coumarin moiety, their preliminary photophysical studies were carried out and promising quantum yields were observed along with maximum quantum yield ($\varnothing_f$ = 0.65) for **4j**.



## Introduction

Multicomponent reactions (MCRs) have become a very popular and powerful strategy in modern organic synthesis for the easy access of complex organic molecules especially heterocycles in single step.[1] The fused polycyclic heterocycles are important class of organic molecules because of their widespread applications as pharmaceutical candidates, optical materials and sensors.[2] Coumarin moiety is abundant in various natural as well as synthetic products having applications in medicinal chemistry as well as in optoelectronics.[3] Coumarin fused polycyclic heterocycles posses very interesting properties and therefore development of new methods for the easy access of these molecules have lot of scope in recent times. E.g. recently, Yang et al. have reported synthesis of coumarin/pyrrole-fused heterocycles with their photochemical and redox switching properties.[4] Likewise, coumarin/phenanthridine fused heterocycles exhibit interesting photochemical and thermochromic properties.[5] Red fluorescent dyes based on coumarin fused rhodamines were synthesized recently and used for bioimaging in vitro.[6] Similarly, synthesis and interesting photophysical studies on a series of non-symmetrical coumarin-fused BODIPY has also been reported in the literature.[7] Coumarin fused dihydroquinolines have also been reported as antitumor agents.[8] Considering the widespread applications of coumarin fused heterocycles and in continuation of our work on multicomponent reactions for the easy access of diverse functionalized[9] or polycyclic heterocycles,[10] we were interested in developing a general and versatile method for the synthesis of coumarin fused dihydroquinoline (CFDQ) and quinoline (CFQ) derivatives from the readily available starting materials and to study the photophysical properties of the synthesized molecules (Figure 1).

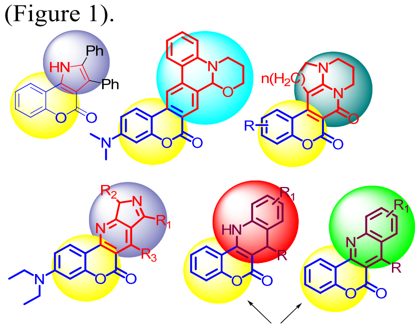
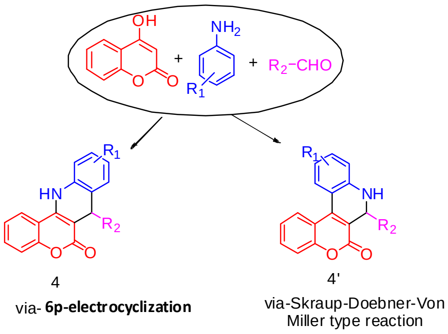



**Figure 1** Structural correlation of known coumarin fused polycyclic molecules with our target molecules.

4-Hydroxycoumarin is one of the widely explored and readily available substrate in organic synthesis.[11] It is also one of the very important building block for the construction of coumarin fused polycyclic molecules. Very recently we have developed a few MCRs involving 4-hydroxycoumarin for the preparation of diverse heterocycles.[12] In continuation of our work on exploration of various readily available substrates in MCRs, we were interested in exploring 4-hydroxycoumarin along with aromatic amines as a 1,3-binucleophile to form a CFDQ moiety by reacting with aldehydes. From the literature it is evident that aromatic amines acting as 1,3-binucleophile in multicomponent reactions is still limited and only few methods are known.[13] Thus, there is lot of scope to explore this reactivity pattern of aromatic amines in MCRs. Initially, we presumed that the combination of 4-hydroxycoumarin, aldehydes and aromatic amines will provide either **4** or **4'** as shown in scheme 1.




**Scheme 1** Possible regioisomers from the reaction of 4-hydroxycoumarin, aldehydes and aromatic amines

## Results and discussion

### Synthesis of CFDQ (**4**) and CFQ (**5**) :

For the preliminary investigation, reaction of 4-hydroxycoumarin, 4-bromobenzaldehyde and 4-methylaniline was chosen as model reaction. Interestingly, in absence of any catalyst and water as reaction medium, even after 24h of stirring at room temperature, we did not observe any desired three component product. Under the reflux and catalyst free conditions, the same combination provided 87% of biscoumarin **6** within 24h from the condensation of two molecules of 4-hydroxycoumarin with the aldehyde. Interestingly, use of L-proline (10 mol%) in the model reaction provided desired CFDQ (**4j**) 25% along with the 70% biscoumarin (**6a**) (Table 1, entry 3). Both the isolated compounds **4j** and **6a** were characterized by, IR, $^1$H and $^{13}$C NMR as well as elemental analysis. The presence of one singlet at 5.21 ppm and a broad singlet at 9.73 ppm indicates the presence of a benzylic proton (CH) and a NH proton respectively. In $^{13}$C NMR the benzylic carbon appeared at 40.7 ppm. The possibility of formation of **4'** type product as shown in scheme 1, was ruled out due to the absence of doublet for benzylic proton and the lower than the expected $^{13}$C NMR value of benzylic carbon. Next, we turned our attention to explore various catalysts to achieve the optimum yield for **4j** by minimizing the formation of unwanted biscoumarin. In case of imidazole as well as acetic acid as catalyst (Table 1, entries 4 and 5) the yield for **4j** was not satisfactory as like L-proline. So we focused our attention to use other acidic catalysts such as protic acid HCl and $CF_3COOH$ and also Lewis acids such as $InCl_3$ and metal triflates (Metal = Cu, Ag, Yt, Sc and Bi) were screened and the results are summarized in Table 1 (entries: 6-13). From the Table 1, we realized that among all the screened catalysts $Bi(OTf)_3$ provided the maximum yield in water under reflux conditions. Next, various solvents were screened in presence of $Bi(OTf)_3$ as catalyst at reflux temperature. To our surprise we observed that the reaction predominantly gives unwanted biscoumarin **6a** along with traces of **4j** and **5j** in organic solvents such as acetonitrile, ethanol, tetrahydrofuran and toluene (Table 1, entries 14-17).

From this study, we realized water as the best solvent for this MCR. It is noteworthy to mention that, when the same reaction was performed under the influence of Microwave irradiation at 130 °C in water and $Bi(OTf)_3$ as catalyst, within 15 minutes the desired CFDQ **4j** was observed in good yields (Table 1, entry 18). The variation in catalyst loading was also checked to see the impact on yields and time. In case of 5 mol% catalyst loading and MW irradiation at 130 °C for 15 minutes 70% of the desired product along with considerable amount of biscoumarin a side product (Table 1, entry 19) was isolated. By increasing the catalyst loading up to 15 mol% keeping other parameters same, no significant change in yield was observed. From the optimization studies we have observed that, reaction temperatures, type of solvent and catalyst are very much important for the success of this type of MCRs. Interestingly, the same set of substrates under solvent free and MW conditions at 140 °C in the presence of 10 mol% $Bi(OTf)_3$ provided biscoumarin **6a** in 87% yield along with trace amount for **4j** and **5j.** To our surprise, the same reaction under neat and conventional heating conditions at 140 °C provided coumarin fused quinoline (CFQ) **5c** in 90% yield along with traces amount of **4j** and **6a** (Table 1, entry-23).

With the optimized conditions in hand, we turned our attention to investigate the scope and general applicability of this methodology by carrying out the synthesis of CFDQ, a tetracyclic heterocycles using different aldehydes and aromatic amines (Table 2). We found that a series of substituted aromatic aldehydes tethered with either electron-withdrawing or electron-donating groups produced CFDQ derivatives in good to excellent yields (Table 2, entries 2-4, 8-9, 12 and 16-17). Heteroaromatic aldehyde such as thiophene-2-carbaldehyde (Table 2, entry 13) also underwent this multicomponent reaction smoothly to provide the corresponding CFDQ in good yield. Aliphatic aldehyde such as formaldehyde was also tested and was found to be suitable in this multicomponent reaction to obtain the desired product (Table 2, entry 15). Similarly, the variability of aromatic amines were also tested under the same reaction conditions. All the synthesized compounds were fully characterized using IR, $^1$H and $^{13}$C NMR and elemental analysis. The structures of these CFDQs were further confirmed by recording the single crystal XRD of one the product (**4q**) as shown in Figure 2.

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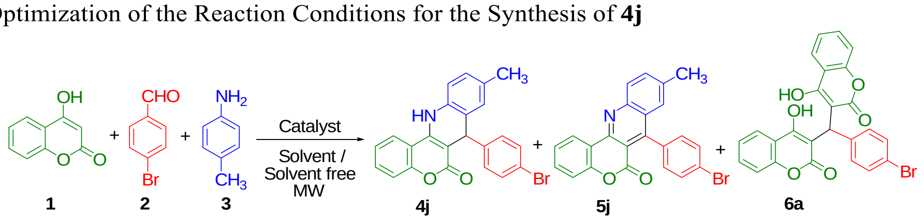
**Table 1** Optimization of the Reaction Conditions for the Synthesis of **4j**



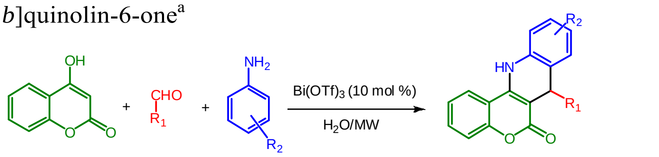

| Entry | catalyst (10 mol %) | reaction conditions | yield[a] (%) **4j** | yield[a] (%) **5j** | yield[a] (%) **6a** |
|---|---|---|---|---|---|
| 1. | ---- | $H_2O$, rt, 24 h | nil | nil | 81 |
| 2. | ---- | $H_2O$, reflux, 24 h | Traces | Traces | 87 |
| 3. | L-proline | $H_2O$, reflux, 24 h | 25 | Traces | 70 |
| 4. | Imidazole | $H_2O$, reflux, 24 h | 30 | Traces | 60 |
| 5. | $CH_3COOH$ | $H_2O$, reflux, 24 h | 30 | Traces | 60 |
| 6 | HCl | $H_2O$, reflux, 24 h | 10 | Traces | 85 |
| 7 | $CF_3COOH$ | $H_2O$, reflux, 24 h | Traces | Traces | 95 |
| 8 | $InCl_3$ | $H_2O$, reflux, 24 h | 15 | Traces | 74 |
| 9 | $Cu(OTf)_3$ | $H_2O$, reflux, 24 h | 20 | Traces | 75 |
| 10 | $Ag(OTf)_3$ | $H_2O$, reflux, 24 h | 15 | Traces | 78 |
| 11 | $Yt(OTf)_3$ | $H_2O$, reflux, 24 h | 58 | Traces | 20 |
| 12 | $Sc(OTf)_3$ | $H_2O$, reflux, 24 h | 55 | Traces | 30 |
| 13 | $Bi(OTf)_3$ | $H_2O$, reflux, 24 h | 65 | Traces | 30 |
| 14 | $Bi(OTf)_3$ | $CH_3CN$, reflux, 24 h | Traces | Traces | 95 |
| 15 | $Bi(OTf)_3$ | EtOH, reflux, 24 h | Traces | Traces | 97 |
| 16 | $Bi(OTf)_3$ | THF, reflux, 24 h | Traces | Traces | 90 |
| 17 | $Bi(OTf)_3$ | Toluene, reflux, 24 h | Traces | Traces | 82 |
| **18** | **$Bi(OTf)_3$** | **$H_2O$, MW, 130 °C, 15 min** | **86** | **Traces** | **Traces** |
| 19 | $Bi(OTf)_3$ ( 5 mol %) | $H_2O$, MW, 130 °C, 15 min | 70 | Traces | 20 |
| 20 | $Bi(OTf)_3$ ( 15 mol %) | $H_2O$, MW, 130 °C, 15 min | 87 | Traces | Traces |
| 21 | $Bi(OTf)_3$ | $H_2O$, MW, 100 °C, 15 min | 78 | Traces | 15 |
| 22 | $Bi(OTf)_3$ | Neat, MW, 140 °C, 15 min | Traces | Traces | 87 |
| **23** | **$Bi(OTf)_3$** | **Neat, 140 °C, 2 h** | **Traces** | **90** | **Traces** |

*Reaction conditions*: 4-Hydroxycoumarin (0.5 mmol), aldehyde (0.5 mmol), aromatic amine (0.5 mmol), catalyst (10 mol%) and solvent. [a]yields of isolated product w.r.t '**1**'.

After the successful demonstration of the generality and applicability of this method for the synthesis of a wide range of CFDQs (**4a-4s**), next we wanted to prepare some CFQ so that we can study the photophysical properties of both the CFDQ and the CFQ derivatives and compare their relative quantum yields. Using the procedure of Table 1 (entry 23) the reaction of aromatic amines with 4-hydroxycoumarin and aldehydes in the presence of $Bi(OTf)_3$ under neat conditions at 140 °C provided the corresponding aromatized CFQ as the major product. Some of the corresponding CFQ derivatives (**5e**, **5h**, **5j**, **5l**, **5m**, **5n** and **5q**) were synthesized using this method under neat conditions and the results are summarized in Table 3 (Method A). Although this method is an effective method for the direct synthesis of CFQ derivatives, we realized that the long reaction time (2-4 hours) and the tedious purification process may be avoided if we synthesize the fused CFDQ by our MW-$H_2O$ method in presence of $Bi(OTf)_3$ and then convert to the corresponding quinoline using a rapid and clean method. Thus an alternate and time effective method was looked for and initially **4j** was chosen to find a suitable condition for conversion to the corresponding **5j**. In this direction a wide range of reagents such as $HNO_3$, $KMnO_4$, $H_2O_2$, CAN, BDMS and NBS in stoichimetric amount (1 equiv.) were screened in different solvents. When **4j** was refluxed with $HNO_3$ in water for 10h, only trace amount of the **5j** was formed. Similarly, $KMnO_4$ and $H_2O_2$ gave only 20% and 10% respectively for the same reaction time in water at reflux conditions. Interestingly, when CAN was employed in acetonitrile at room temperature 86% of the desired product **5j** was formed. The best result was obtained with 1.0 eqv. NBS in THF at room temperature and 99% yield was isolated within 2 min. NBS with other solvents such as, DCM and DMSO was also tested and the isolated yields were 96% and 98% respectively with long reaction time. Hence, the best optimized condition to obtain **5j** from **4j** was NBS/THF at room temperature. Using this optimized condition other CFQs were prepared and the results are summarized in Table 3 (Method B).

Next, to explore the diversity of the process and to achieve different functionalized quinolines from the same starting materials, we attempted to open the cyclic ester of the coumarin moiety both from the CFDQ (**4**) and CFQ (**5**) to achieve the corresponding quinoline scaffolds (**7**) bearing carboxylic acid at the 3-position in the quinoline ring. From the literature we realized that quinoline-3-carboxylates or quinoline-3-carboxamide are promising drug candidates and act as sweet flavor modifiers.[14]

**Table 2** Synthesis of 7-phenyl-7,12-dihydro-6*H*-chromeno[4,3-*b*]quinolin-6-one[a]

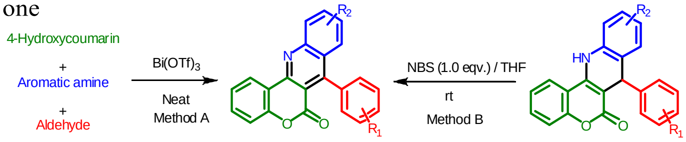



1 2 3 4

| Entry | $R_1$ | $R_2$ | product | time (min) | yield[b] (%) |
|---|---|---|---|---|---|
| 1 | $C_6H_5$- | H | **4a** | 12 | 82 |
| 2 | 4-OMe-$C_6H_4$- | H | **4b** | 10 | 89 |
| 3 | 4-CN- $C_6H_4$- | H | **4c** | 15 | 87 |
| 4 | 4-Br- $C_6H_4$- | H | **4d** | 15 | 90 |
| 5 | $C_6H_5$- | 4-OMe- | **4e** | 10 | 87 |
| 6 | 4-CN- $C_6H_4$- | 4-OMe- | **4f** | 15 | 88 |
| 7 | 4-Br- $C_6H_4$- | 4-OMe- | **4g** | 16 | 89 |
| 8 | 3-OMe-$C_6H_4$- | 4-OMe- | **4h** | 16 | 88 |
| 9 | 3-$NO_2$-$C_6H_4$- | 4-OMe- | **4i** | 16 | 92 |
| 10 | 4-Br- $C_6H_4$- | 4-Me- | **4j** | 12 | 92 |
| 11 | 3-$NO_2$-$C_6H_4$- | 4-Me- | **4k** | 10 | 89 |
| 12 | 2,4-Cl- $C_6H_3$- | 4-Me- | **4l** | 18 | 93 |
| 13 | 2-Thiophene | 4-Me- | **4m** | 10 | 93 |
| 14 | $C_6H_5$- | 4-Br- | **4n** | 15 | 90 |
| 15 | H | 4-Br- | **4o** | 10 | 94 |
| 16 | 4-Cl-$C_6H_4$- | 3-Br-- | **4p** | 14 | 89 |
| 17 | 4-Me-$C_6H_4$- | 3,4-OMe | **4q** | 5 | 92 |
| 18 | $C_6H_5$- | 3,4-(-O($CH_2$)$_2$-O)- | **4r** | 8 | 90 |
| 19 | 4-Br-$C_6H_4$- | 4(piperidin-1-yl)- | **4s** | 10 | 91 |
| 20 | $C_6H_5$- | 4-$NO_2$- | **4t** | 20 | 0 |

[a]Reaction conditions: 4-Hydroxycoumarin (0.5 mmol), aldehyde (0.5 mmol), aromatic amine (0.5 mmol), $Bi(OTf)_3$ (0.05 mmol) and $H_2O$ (1 ml) were heated in MW at 130 °C. [b]Isolated yields.

**Table 3** Synthesis of 7-phenyl-6*H*-chromeno[4,3-*b*]quinolin-6-one




5 4

| entry | substrate | product | Method A time (h) | Method A yield[a] (%) | Method B time (min) | Method B yield[a] (%) |
|---|---|---|---|---|---|---|
| 1 | **4e** | **5e** | 3 | 86 | 2 | 98 |
| 2 | **4h** | **5h** | 3.5 | 88 | 2 | 99 |
| 3 | **4j** | **5j** | 4 | 85 | 2 | 99 |
| 4 | **4l** | **5l** | 2 | 90 | 2 | 99 |
| 5 | **4m** | **5m** | 3 | 88 | 5 | 97 |
| 6 | **4n** | **5n** | 2 | 90 | 1.5 | 99 |
| 7 | **4q** | **5q** | 3 | 87 | 3 | 98 |

[a]Isolated yields, Method A (neat reaction): 4-hydroxycoumarin (1.0 mmol), aldehyde (1.0 mmol), aromatic amine (1.0 mmol) and $Bi(OTf)_3$ (0.1mmol), at 140 °C heating; Method B: CFDQs (1.0 mmol), NBS (1.0 mmol) in THF (5ml) at room temperature.

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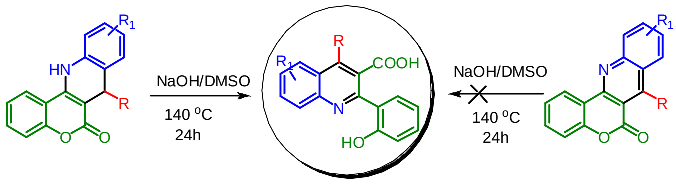
Considering the importance of these types of functionalized quinolines, initially we took **4h** for the conversion to the corresponding **7h** by ring opening of coumarin moiety followed by aromatization**.** Using NaOH in DMSO at 140 °C we observed the best result for this conversion. Similarly, **7q** was also synthesized from **4q** using same strategy in good yields. It is noteworthy to mention that when similar strategy for the conversion of product **5** to **7** were tried the reaction failed (Scheme 2). This may be due to thermodynamically less stable, flexible ring which leads to facile cleavage of the coumarin ring in case of **4**. We believe that in this method initially ring opening of the coumarin followed by oxidation of dihydroquinoline moiety takes place to form the desired compounds.




4 7 5

**7h** : R = 3-OMe-$C_6H_4$-, $R_1$= 4-OMe- ; yield: 54%
**7q** : R = 4-Me-$C_6H_4$-, $R_1$= 3,4-OMe- ; yield : 60%

**Scheme 2** Selective synthesis of 3-quinolinecarboxylic acid derivatives from **4**.

## Mechanism

The proposed mechanism for the formation of CFDQ (**4)** has been described in Scheme 3a. We believe initially, aromatic amine **3** condense with aldehyde **2** to form a Schiff base **A**, to which 4-hydroxycoumarin undergoes nucleophilic addition to form an unstable intermediate **B**. The side product **6** forms when another equivalent of 4-hydroxycoumarin reacts with the intermediate **C**. The formation of **6** minimizes when the rate of reaction of aromatic amine is faster than the nucleophilic addition of 4-hydroxycoumarin to the intermediate **C**. The aromatic amine can undergo either 1, 2- or 1,4-addition to **C**. In case of 1,4-addition obeying Skraup-Doebner-von Miller process[15] the expected product is **4'.** However, from the the X-ray crystal structure of one of the CFDQ (**4q**) (Figure 2) we have realized that the observed product **4q** possibly formed by a 1,2-addition of aromatic amine with the intermediate **C** instead of aza-Michael addition followed by 6 π–electrocyclization and isomerisation to yield product (**4**). We are not sure whether in this MCR, $Bi(OTf)_3$ in water medium acting as a source of *in situ* triflic acid or as Lewis acid. In the literature most of the methods have assumed that in water medium $Bi(OTf)_3$ acts as a

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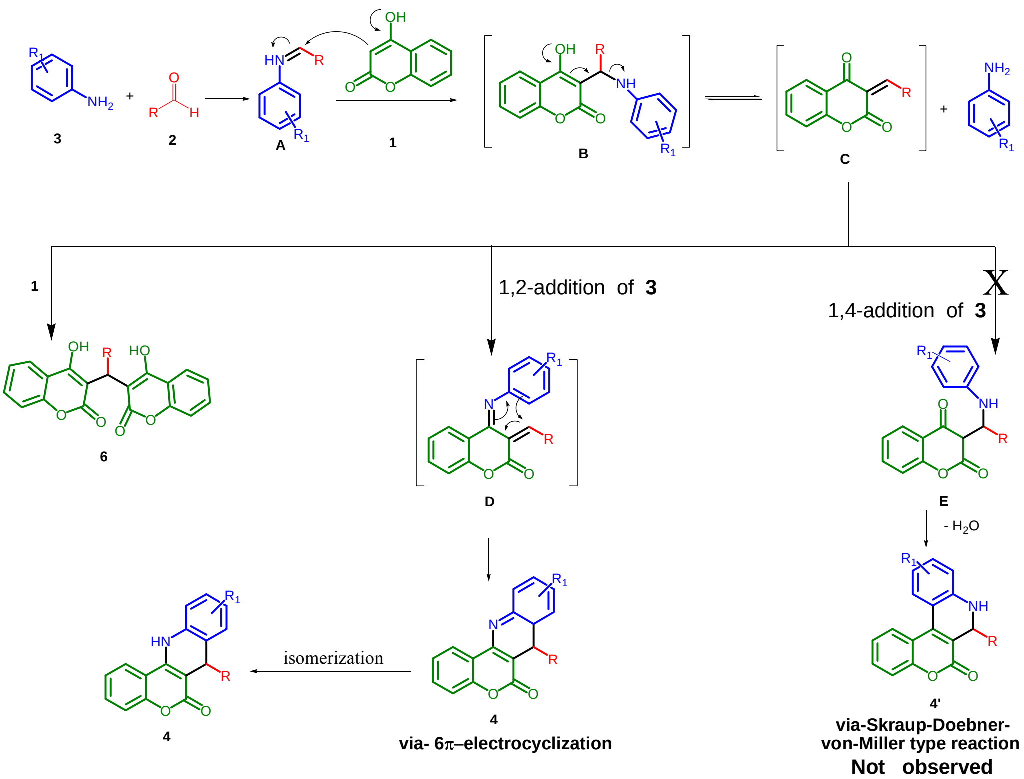
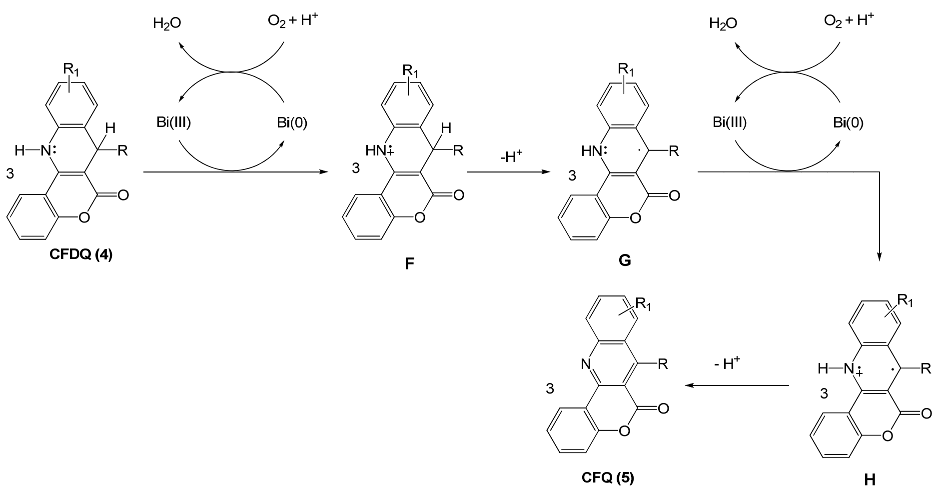
source of triflic acid which actually catalyzes various reactions.[16] It is also reported that $(BiOTf)_3$ can be stabilized in water and acts as Lewis acid in the presence of basic ligand.[17] Thus we believe that both the Bi(III) ion and triflic acid may be helping at a time in this case for the formation of **A**, **B**, **C** and **D** intermediates. In case of neat and conventional heating conditions, the observed major product is CFQ (5) which may be explained *via* the formation of **4** and followed by free-radical mechanism involving Bi(III)/Bi(0) as shown in scheme 3b. To know the role of bismuth in this reaction, compound **4e** was heated at 140 °C without adding any oxidant under open air. Even after 6 hours we did not observe any conversion from **4e** to **5e**.Thus the possibility of aerial oxidation can be ruled out.



**Scheme 3a** Proposed mechanism for the formation of CFDQ (**4**)



**Scheme 3b** Plausible mechanism for the formation of CFQ (**5**) from CFDQ (**4**) using Method-A: one-pot neat condition in presence of $Bi(OTf)_3$.

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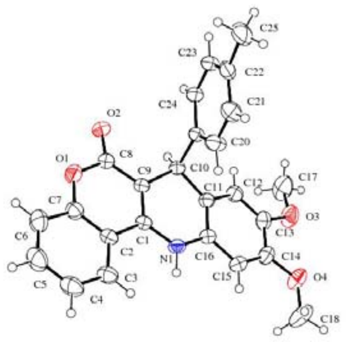

**Figure 2** ORTEP plot of compound **4q** (CCDC 997125)**.**

Next, Compound **4e** was heated at 140 °C in the presence of 10 mol% $Bi(OTf)_3$ under solvent-free conditions and within 2 hours, the corresponding **5e** was obtained in 30% yield. The less conversion as compared to one pot three component method may be due to inhomogeneous mixing of the catalyst under solvent free conditions. From the literature it is understood that Bi(III) compounds can be used for various oxidative reactions including aromatization reactions.[18] Thus we also presume that the conversion of **4** to **5** takes place via a radical mechanism involving Bi(III)/Bi(0).

**Photophysical Properties**

In recent time, search for organic molecules with high quantum yield has been the subject of intense study owing to their demands for organic light-emitting diodes (OLED), biological markers, functional organic devices and sensors, organic rectifiers as well as in dyes.[19] Fluorophores embedded with donor-acceptor that connected to a rigid π-system believes to prevent non-radiative decay.[20] CFDQs (**4**) bearing an electron withdrawing group at 3-position possess such structural features. Considering these features we were interested to see the optical behaviour of the synthesized CFDQs containing D-π-A (Donar-π system-Acceptor) push pull system.

Initially, UV-Vis and fluorescence behaviour of compound **4j** was investigated at room temperature in different polar protic and aprotic solvents such as DMSO, THF, DCM, $CH_3CN$, MeOH and $CHCl_3$ (Figures **3a** and **3b**, for details: see Supporting Information) w.r.t. quinine sulphate dihydrate[21], interestingly we observed very good quantum yield ($Ø_f$ = 0.65) in DMSO. Because of solubility problem we could not study the UV-Vis and fluorescent property of **4j** in nonpolar solvents. Similar to **4j**, we have also screened the UV-Vis and fluorescence properties of the other synthesized CFDQs and the results are summarized in Table 4 (see Supporting Information). From these graphs for **4j**, we have found that UV-Vis and fluorescence spectra appeared around 345-357 nm and 422-441 nm respectively in different solvents. The emission band for **4j** appears at 422 nm in $CHCl_3$ solvent. On the other hand a large red-shift, low energy band was observed both in MeOH and dipolar aprotic DMSO solvents at 440 nm and 441 nm respectively. Similarly, from Figure 3a, the absorption band for **4j** was observed at 357 nm for DMSO and a large blue shift was observed at 345 nm in $CHCl_3$.

From the Table 4 (see Supporting Information) we have observed that the quantum yields of other compounds were in the range of $Ø_f$ = 0.00-0.59. Quantum yield above 50 % was observed for **4b**, **4c**, **4d**, **4g** and **4l** as 0.56 in MeOH, 0.58 in DMSO, 0.59 in THF, 0.56 in THF and 0.55 in DMSO respectively.

It is interesting to note that, the CFDQs polycyclic heterocycle fluorophores (4) becomes less fluorescent and in most cases non-fluorescent when converted to their corresponding CFQs analogues (5) (see Supporting Information, Table 4, **5e-5q)**. A representative picture of **4j** and **5j** in DMSO under the influence of UV at 366 nm is

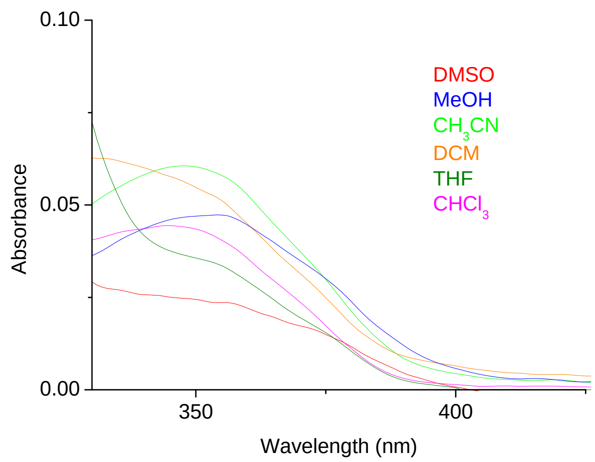


**Figure 3a** UV-Vis spectra of compound **4j** in different solvents ($10^{-5}$ M; 25 °C)

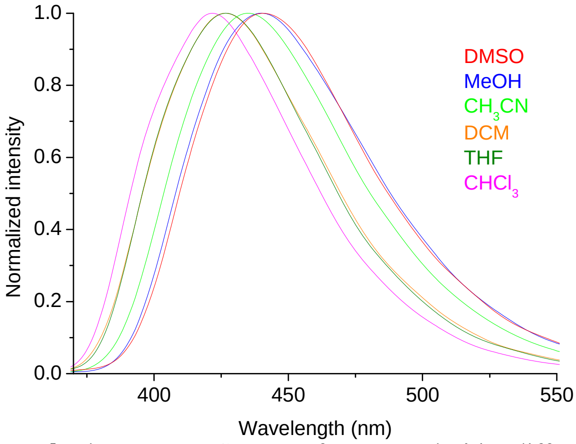


**Figure 3b** Fluorescence Spectra of compound **4j** in different solvents [$10^{-5}$M; 25 °C; slit = 1/1]

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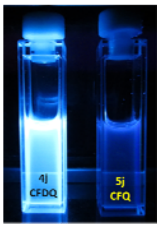


**Figure 4** CFDQ (**4j**) and CFQ (**5j**) in DMSO[$10^{-5}$M] at UV 366 nm.

shown in the Figure 4. This clearly indicates that the fluorescence intensity shrink in case of aromatized CFQs. Form the table 4, we also observed that both a highest stoke's shift of about 10094 in $CHCl_3$ and a lowest stoke's shift of about 2300 in THF was observed for **4s.**

The absorption maxima, emission maxima and fluorescence quantum yield depends on various factors such as structure of the molecule, nature of the solvent, probe-probe interaction, probe-solvent interaction, temperature, pH and concentration etc.[22] In this investigation we have observed that fluorescence quantum yield of these types of coumarin fused polycyclic heterocycles are dependent on the types of the substituent groups as well as solvent medium used. Considering the above behaviours, we believe that these coumarin fused polycyclic heterocycles may find some potential application as a new fluorescent probes or luminescence material.

## Conclusions

In conclusion, the present work describes an efficient one-pot multicomponent strategy for the synthesis of coumarin fused dihydroquinolines (**4**) from the reaction of 4-hydroxycoumarin, aldehydes and aromatic amines using an environmentally benign readily available bismuthtriflate as a catalyst in water medium under microwave irradiation. The same combination under solvent-free and conventional heating conditions provides coumarin fused quininolines (**5**) in one pot. Alternatively, coumarin fused quinolines **5** have also been synthesized using N-bromosuccinamide as an oxidizing agent at room temperature. We also have developed a new route for the synthesis of substituted 3-quinolinecarboxylic acid derivatives in a two step process by hydrolysis of the coumarin ring followed by simultaneous aerobic oxidation of **4**. The fluorescence property studies of the synthesized coumarin fused tetracyclic heterocycles in different solvents shows that some of the fused dihydroquinolines (**4**) are highly fluorescent with good quantum yields that may become a promising fluorescent probe. A comparative study on fluorescent property for some of the **4** with its analogues showed that **4** are more fluorescent than the corresponding **5**.



## Experimental

### Methods and materials

All reagents were used without further purification and procured from the commercial sources. Microwave irradiation was carried out with Initiator 2.5 Microwave Synthesizers from Biotage, Uppsala, Sweden. Shimadzu FTIR spectrophotometer was used for recording IR spectra. 1H NMR and 13C NMR spectra were recorded on a Jeol 500, Varian 400 and Bruker 300/400/500 MHz spectrometers in CDCl3 and DMSO-d6 using TMS as internal reference. Elemental analyses were carried out in a Perkin Elmer 2400 automatic CHN analyzer or Elementer Vario EL III. X-ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. All compounds were characterized by their melting points, 1H NMR and 13C NMR spectra and elemental analysis. The UV-Vis absorption spectra were recorded on Shimadzu UV-Vis spectrophotometer UV-2550 and fluorescence spectra was recorded at Horiba Jobin Yuon fluoromax-4 spectrofluorometer.

### General procedure for the synthesis of CFDQ (4).

A mixture of aldehyde (0.5 mmol), aromatic amine (0.5 mmol), 4-hydroxycoumarin (0.5 mmol) and $Bi(OTf)_3$ (0.05 mmol) in water (1.0 ml) was taken in a sealed 0.5-2.0 ml vial containing a Teflon coated magnetic stirring bar and was irradiated at 130 °C for an appropriate time mentioned in the table 2, using a microwave reactor. The resulting mixture was cool down to 50 °C by air flow. The water was decanted and 1-2 ml glacial acetic acid was added to the reaction mixture and stirred for 5 min to obtain the precipitate. The solid precipitate was filtered under suction and dried. The obtained solid was found pure enough for further characterization.

### General procedure for the synthesis of CFQ (5).

Method-A (one-pot neat condition)

A mixture of aldehyde (1.0 mmol), aromatic amine (1.0 mmol), 4-hydroxycoumarin (1.0 mmol) and $Bi(OTf)_3$ (0.1

mmol) was taken in a 10 ml round bottom flask fitted with a reflux condenser in an open air and was heated at 140 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, reaction mixture was cooled down to room temperature. To this mixture 1-2 ml glacial acetic acid was added and stirred to obtain the precipitate. The solid precipitate was filtered and washed with methanol under suction and dried. The crude product was dissolved in 20 ml dichloromethane and aqueous workup was carried out using 0.05N NaOH solution to remove the by-product biscoumarin. Finally the compounds were purified by recrystallization from acetonitrile.

Method-B (NBS oxidation)

The already prepared compound **4** (1.0 mmol) was taken in a 25 ml round bottom flask in 5 ml THF. NBS (1.0 mmol) was added to this solution and stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated and then methanol (5.0 ml) was added and refluxed for 30 min. The solid product was collected by simple filtration and washed with methanol and dried. The obtained solid was found pure enough for further characterization.

**General procedure for the synthesis of 7h and 7q.**

A mixture of **4h** or **4q** (1.0 mmol), NaOH (1.0 mmol) and DMSO (5.0 ml) was taken in a 25 ml round bottom flask fitted with a reflux condenser. The reaction mixture was heated to 140 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was gradually cooled to room temperature. To this solution water (30 ml) was added and stirred. The suspended solid was filtered off. The pH of the clear mother liquor was adjusted to neutral by adding HCl solution. The precipitated solid obtained at neutral pH was filtered off under suction and washed with water (5.0 ml x 2) and then dried. The crude product was purified by column chromatography on silica gel using ethylacetate/petroleum ether as eluent to afford the desired product.

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## Notes and references

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