

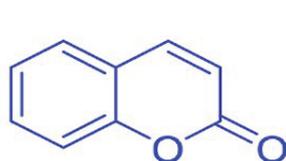


# Synthesis and Characterization of New Coumarin Substituted Chromone (8-Methyl-4-phenyl-2H,10H-pyrano[2,3-f] chromene-2,10-dione) Using Benzyl Acetoacetate and Studied their Fluorescence Properties

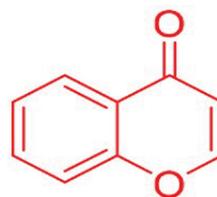
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## Abstract

In the present review developed a new method for synthesis coumarin substituted chromone, as they are an important building block in organic chemistry. Also, they are valuable synthetic intermediates in the preparation of new biological relevant heterocyclic system have been synthesized by using effective and efficient synthetic pathway. The synthesized compound has been characterized by FT-IR, <sup>1</sup>H-NMR, UV and Mass spectrometry for their structural elucidation. Further, we have studied their fluorescence properties.



Coumarin



Chromone

Graphical Abstract

**Keywords:** Resorcinol; Benzyl acetoacetate; Coumarin synthesis; Coumarin substituted chromone; Fluorescence properties

## Introduction

Chromones are benzoannulated  $\gamma$ -pyrone ring (4H-chromen-4-one, 4H-1-benzopyran-4-one) and coumarin ring system is 2H-1-benzopyran-2-one-4 Heterocycles that are widely distributed in nature. They have been used since ancient times in traditional medicine [1] and are well-known by their diversity of pharmacological properties, such as anti-allergic, anti-inflammatory, anti-diabetic, antitumor and antimicrobial [2-4].

Fluorescent compounds play an important role in solid state lighting, solar energy conversion and as biomarkers in the life sciences [5-10]. Fluorescent heterocyclic compounds are of immense interest as functional materials in the emitters of electroluminescence devices and in the molecular probes used for biochemical research, as well as in the traditional textile and polymer fields [11-13]. Heterocyclic fluorophores are useful materials in the search for new biologically active compounds and diagnostic methods [14]. Coumarin fluorescent probes or labels have extensive and diverse applications, as they exhibit extended spectral range and high emission quantum yields [15]. Coumarin-based fluorescent chemo dosimeter with salicylaldehyde functionality was used as a binding site for selective detection of cyanide anions over other anions in water at biological pH. Coumarin core moieties have wide biological application in particular for the imaging of living cells [16]. The coumarins have been promising candidates for the applications in molecular electronics and biological imaging [17].

In present research, we have developed new ecofriendly synthetic pathway for the synthesis of coumarin substituted chromone and

further studied of their fluorescence properties which can influence their optical application.

## Experimental

### Materials and instrumentation

Resorcinol (98%), acetic anhydride (99%) was procured from Sigma Aldrich and used as received. Benzyl acetoacetate (98%),  $AlCl_3$  were purchased from the (Loba chemie). TLC plates (silica gel 60 F 254) and Acetyl chloride (98%) was received from Merck chemicals. Acetone (98%) and  $H_2SO_4$  (98%) was provided by Fisher scientific chemicals Dimethylformamide was purchased from the SD Fine chemicals and NaOH was procured from Ranchem.

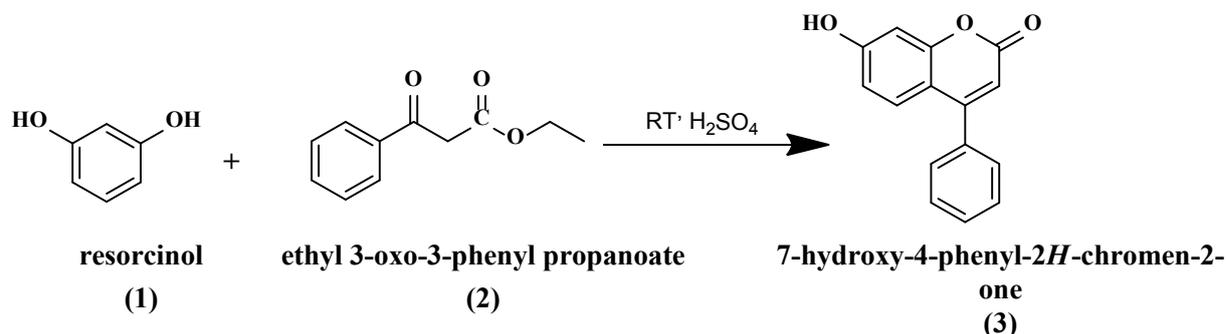
TLC plates have been used Merck silica gel 60 F254. Detection under UV light at 254 nm and 366 nm without dipping Reagent. The FT-IR analysis was conducted on Shimadzu (8400s, Japan)

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Scheme 1: Synthesis of 7-Hydroxy-4-phenyl-2H-chromen-2-one.

instrument using the ATR technique and the spectrum was obtained in the wavelength range of 4000-600 cm<sup>-1</sup>. BRUKER AVANCE II 400 the spectra were calibrated according to the solvent signals: 7.26 ppm for CDCl<sub>3</sub>, 2.50 ppm for DMSO-d<sub>6</sub>. Peak characterization: s=singlet, d=doublet, t=triplet, dd=double of doublets, td=triplet of doublets, dt=doublet of triplets, q=quartet, m=multiplet. Instrument Cary 60, instrument version 2.00, X mode Nanometer, Y mode Abs, UV-Vis scan rate (nm/min) 24000.00, Ave. Time (sec) 0.0125, Beam Mode-Dual Beam. GC 689 N/MSD 5973 (Agilent) or Finnigan MAT 95-XP (Thermo Electron).

#### Procedure for the synthesis of 8-methyl-4-phenyl-2H,10H-pyrano-[2,3-f]-chromene-2,10-dione (6)

**Synthesis of 7-Hydroxy-4-phenyl-2H-chromen-2-one (Pechmann condensation):** A 100 ml Erlenmeyer conical flask equipped over magnetic stirrer was charge with resorcinol (2 gm) containing Benzyl acetoacetate 2.36 (gm) is added concentrated H<sub>2</sub>SO<sub>4</sub> (4 ml) below 10°C with constant stirring. Afterward, the reaction was continuing over the period of 0 to 5 hours in anhydrous condition. The progress of the reaction was monitored by TLC. On completion of the reaction, the reaction mass was poured over crushed ice resulted in the formation of yellow amorphous solid. The formed solid was filtered, washed with water, dried and crystallized from ethanol. The yield of product was found to be 94%. Melting point 215°C (Scheme 1).

Spectral data of synthesized compounds 7-hydroxy-4-phenyl-2H-chromen-2-one (3): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm): 6.07 (1H s, -C(=O)O-R, Gem), 6.10 (1H s, Benzene), 7.14 (1H s, benzene), 7.21 (1H d, benzene -C=C), 7.31(1H s, benzene), 7.36 (1H d, benzene -C=C). Mass-spectral analysis: Calculated-[C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>]<sup>+</sup>-261.22; Found-[C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>]<sup>+</sup>-261.05, 254.11, 249.09, 245.07. IR (Vmax, KBr, cm<sup>-1</sup>): 3738 (m) O-H stretch free, 3116 (m) Aromatic C-H stretch, 2804 (s) Alkane C-H stretch, 1693 (s) Aromatic conj. C=O stretch, 1496 (m), 1608 (s) Aromatic C=C stretch, 1257(s) Aromatic C-O stretch (Intensity-s (strong), m (medium), w (weak)).

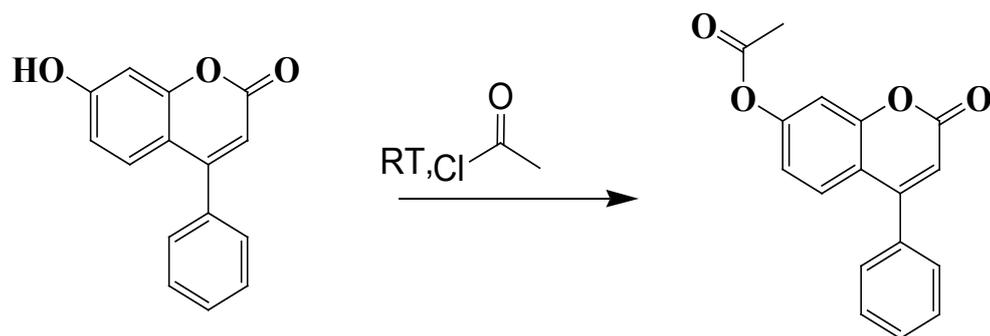
**Synthesis of 2-oxo-4-phenyl-2H-chromen-7-yl acetate (Acetylation):** In a 100 ml round bottom flask equipped with magnetic stirrer was charge 7-hydroxy-4-methyl-2-H-chromen-2-one (1gm), NaOH (1 gm) and acetyl chloride (1.5 gm). The reaction mass stirred gently over the time of 3 hours at room temperature, the progress of the reaction was monitored by TLC. On completion of the reaction, the reaction mass was poured over crushed ice resulted in the formation of brown amorphous solid. The formed solid was filtered, washed with water, dried and crystallized from ethanol. The yield of product was found to be 88%. Melting point-135°C (Scheme 2).

Spectral data of synthesized compounds 2-oxo-4-phenyl-2H-chromen-7-yl acetate (4): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm): 2.1 (-CH<sub>3</sub>-(-C=O)-O), 6.08 (1H, s -C(=O) O-R, Gem), 7.3 (1H d, benzene -C=C), 7.5 (1H d, benzene -C=C), 7.29 (1H s, benzene), 7.31 (1H s, benzene). Mass-spectral analysis: Calculated-[C<sub>17</sub>H<sub>13</sub>O<sub>4</sub>]<sup>+</sup>- 281.08; Found-[C<sub>17</sub>H<sub>13</sub>O<sub>4</sub>]<sup>+</sup>-280.16, 280.16, 279.72. IR (Vmax, KBr, cm<sup>-1</sup>) 3113 (m) Aromatic C-H stretch, 2804(s), 2935 (w) Alkane C-H stretch, 1689 (s), 1797 (w) Aromatic conj. C=O stretch, 1253 (s) Aromatic C-C stretch, 1118 (w),1252 (s) C-O stretch.

**Synthesis of 8-acetyl-7-hydroxy-4-phenyl-2H-chromen-2-one (Fries rearrangement):** 100 ml round bottom flask equipped with a reflux condenser with 4-methyl-2-oxo-2H-chromon-7-yl acetate (1 gm), in a catalyst AlCl<sub>3</sub> (1 gm), reflux for 2 hours in an oil bath and maintained the temperature 135 to 145°C then add 1% HCl for 12 hours. The progress of the reaction was monitored by TLC at room temperature. On completion of the reaction, the reaction mass was poured over crushed ice resulted in the formation of black crystalline solid. The formed solid dried and crystallized from ethanol. The yield of product was found to be 86%. Melting point-210°C (Scheme 3).

Spectral data of synthesized compounds 8-acetyl-7-hydroxy-4-phenyl-2H-chromen-2-one (5): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm): 2.9 (3H S-CH<sub>3</sub>), 6.10(1H S-C(=O) O-R, Gem), 7.3 (1H s, benzene), 7.3 (1H s, benzene), 7.5 (1H d, benzene -C=C), 7.5 (1H d, benzene -C=C), 9.5 (1H s, Phenolic -OH). Mass-spectral analysis: Calculated-[C<sub>17</sub>H<sub>13</sub>O<sub>4</sub>]<sup>+</sup>- 281.08; Found-[C<sub>17</sub>H<sub>13</sub>O<sub>4</sub>]<sup>+</sup>-281.92, 280.92. IR (Vmax, KBr, cm<sup>-1</sup>) 3106 (w) Aromatic C-H stretch, 2808 (m) 2931w Alkane C-H stretch, 1693 (s) C=O, 1793 (s) Aromatic conj. C=O stretch, 1608 (s) Aromatic C=C stretch, 1257 (s) Aromatic C-O stretch.

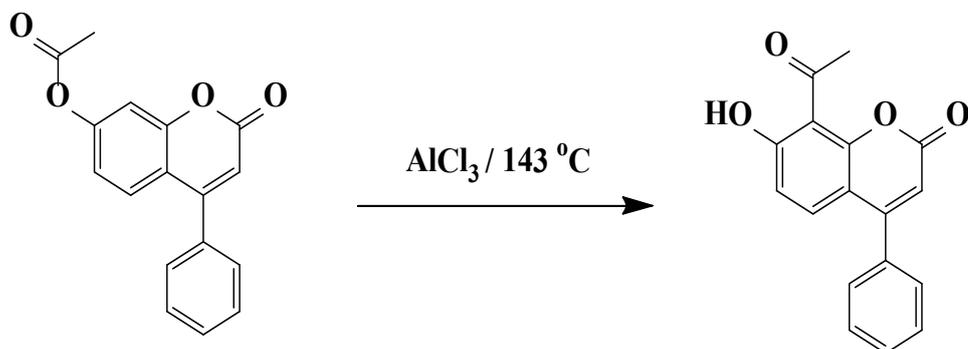
**Synthesis of 8-methyl-4-phenyl-2H,10H-pyrano[2,3-f]chromene-2,10-dione:** In 100 ml round bottom flask place over magnetic stirrer, charge 8-acetyl-7-hydroxy-4-methyl-2H-chromen-2-one (1 gm) in NaOEt (1 gm), acetyl chloride (1.5 ml), dry acetone (10 ml). Add 40% 7 ml aqueous KOH in the reaction mixture, reaction mixture gently started stirring for 12 hours at room temperature and the progress of the reaction was monitored by TLC. Upon completion of reaction, the reaction mass was poured over crushed ice resulted in the formation of brown amorphous solid, dried and crystallized from ethanol. The yield of product was found to be 75%. Melting point 180°C and molecular weight 304.30 (Schemes 4 and 5). The complete schematic representation of the synthesis of 8-methyl-4-phenyl-2H, 10-H-pyrano [2,3-f]chromene-2,10-dione is given below in Scheme 1.



**7-hydroxy-4-phenyl-2H-chromen-2-one**  
(3)

**2-oxo-4-phenyl-2H-chromen-7-yl acetate**  
(4)

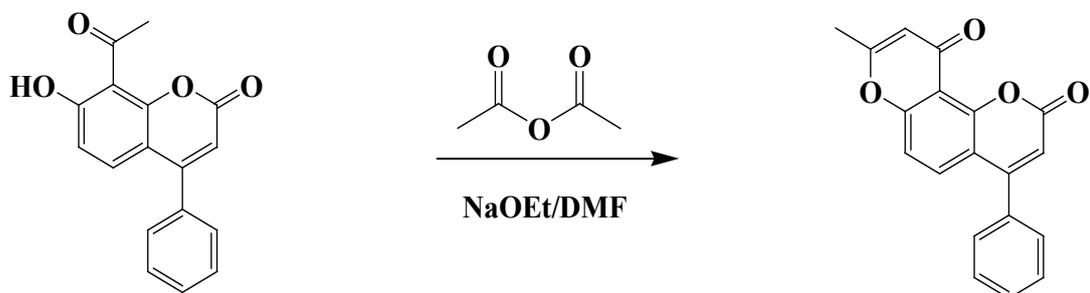
Scheme 2: Synthesis of 2-oxo-4-phenyl-2H-chromen-7-yl acetate.



**2-oxo-4-phenyl-2H-chromen-7-yl acetate**  
(4)

**8-acetyl-7-hydroxy-4-phenyl-2H-chromen-2-one**  
(5)

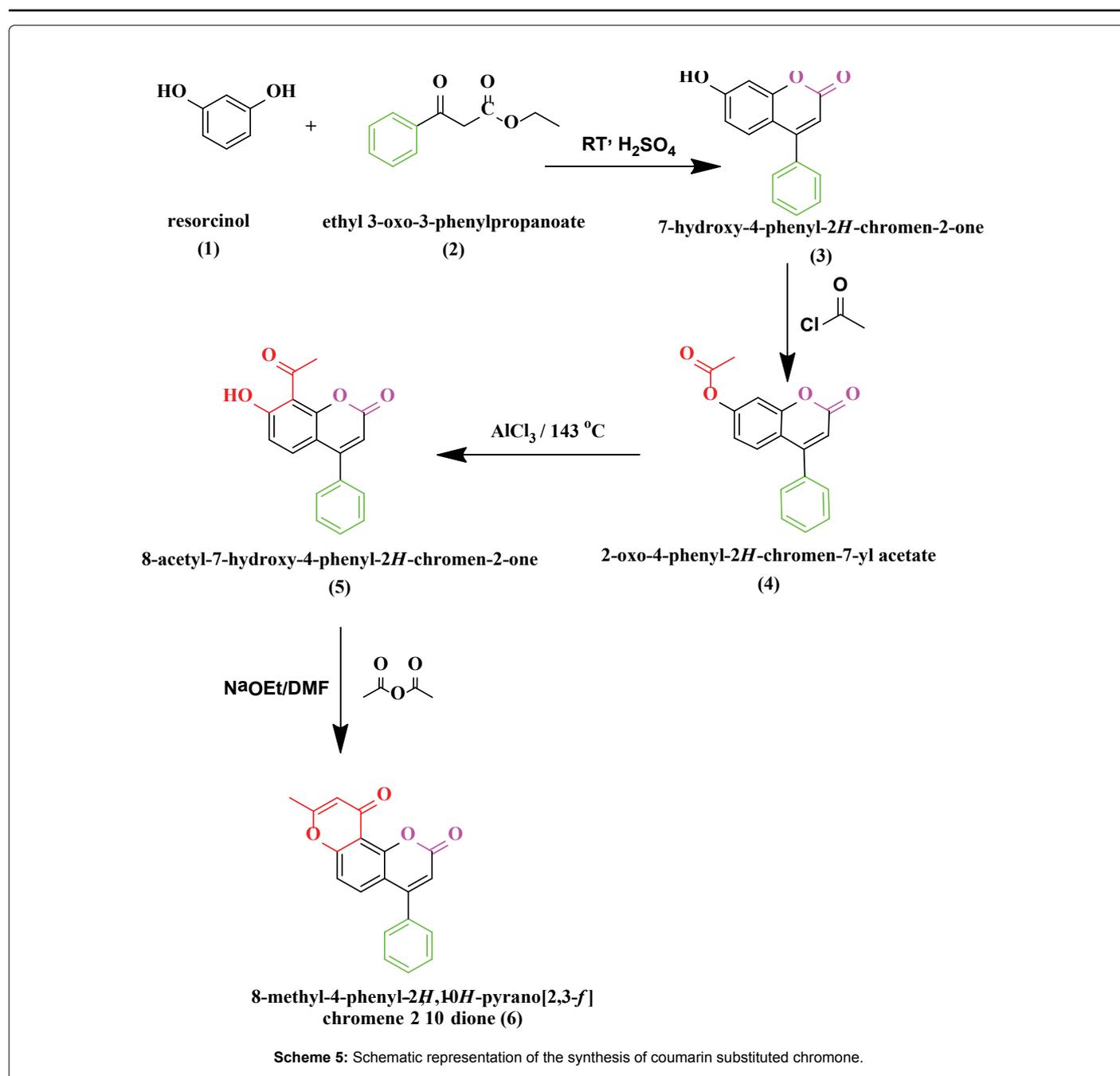
Scheme 3: Synthesis of 8-acetyl-7-hydroxy-4-phenyl-2H-chromen-2-one.



**8-acetyl-7-hydroxy-4-phenyl-2H-chromen-2-one**  
(5)

**8-methyl-4-phenyl-2H,10H-pyrano[2,3-f]  
chromene-2,10-dione (6)**

Scheme 4: Synthesis of 8-methyl-4-phenyl-2H,10H-pyrano[2,3-f]chromene-2,10-dione.



## Results and Discussion

In this work, we report the synthesis of coumarin substituted chromone and investigated their influence on fluorescence properties.

All the products were characterized by IR, <sup>1</sup>H NMR and MS analysis. FTIR spectral characterization of compound (6) show absorption bond correspond the 1739 cm<sup>-1</sup> for ν(C=O) stretching of coumarin moiety. The most prominent bond due to (-C-O-C) aromatic stretch occurs at range 1134(s), 1215(s) cm<sup>-1</sup>. It is generally occurring at 1000-1300 cm<sup>-1</sup>. The characteristics absorption peak at 1604 cm<sup>-1</sup> assign to ν(C=C) aromatic stretch. and 3074 (m) aromatic -CH stretch. <sup>1</sup>H NMR spectra of compound (6) in CDCl<sub>3</sub> showed chemical shifts for CH<sub>3</sub> protons in the range of δ 2.28 ppm for alkyl groups. For protons associated with the heterocyclic ring chemical shifts are observed in the range of 6.03 (s, 1H)-CH adj to CH<sub>3</sub>, 6.69(s 1H-CH adj to benzene) ppm and

7.03(1H d, benzene), 7.21 (1H, d, benzene). Mass-spectra of compound (6) Calculated-[C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>]<sup>+</sup>- 242.22; Found-[C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>]<sup>+</sup>-241.05, 219.07, 177.05. UV spectra of compound (6) reveals that synthesized compound a wider transparency range extending into entire visible and absorbance takes place in the UV range 223 nm to 301 nm and the cut off wavelength (X cm-off) within the range between 329 to 223 nm in benzyl acetoacetate with λ-max was found to be 301 nm. This absorbance maximum is to be assigned to π→π\*, n→π\* transition and may be attributed to the excitation in the aromatic ring and C=O group.

From all above observation, spectral properties and analytical data was confirmed the structure as coumarin substitute chromone. The result obtained in the present study shows that this information would give rise to design of better molecule with good yields, developed of new synthetic green strategies and efficient is desirable for the synthesis of coumarin substituted chromone.

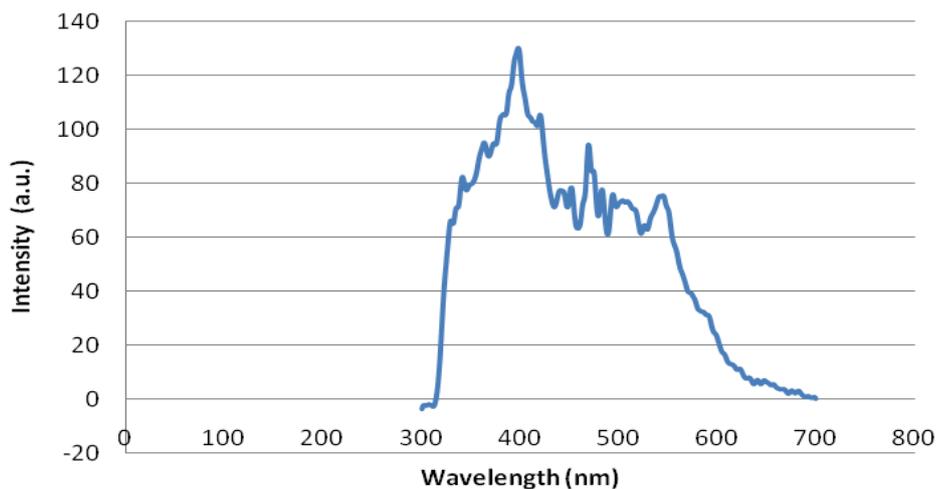


Figure 1: Fluorescence emission of compound.

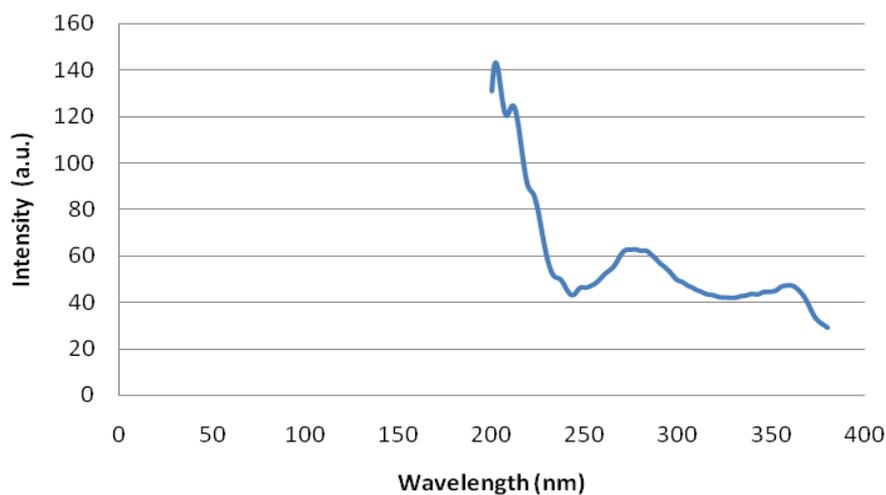


Figure 2: The excitation spectrum of compounds.

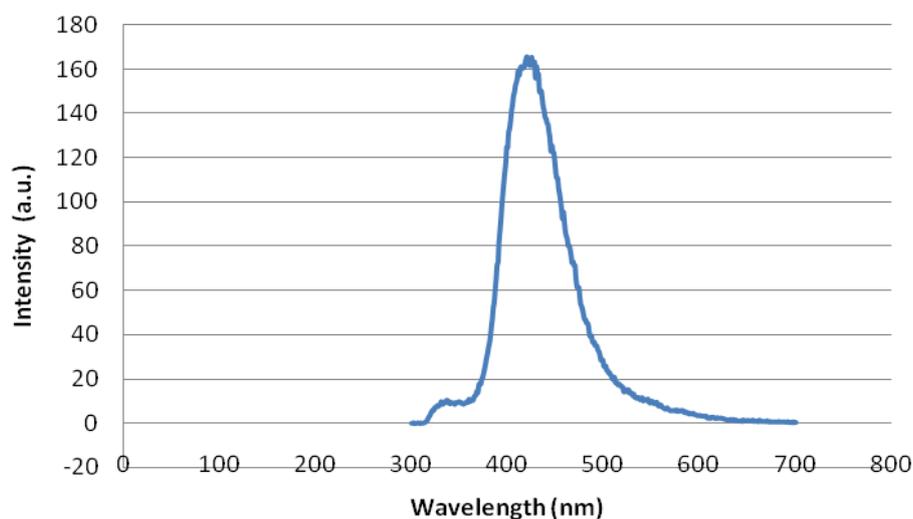
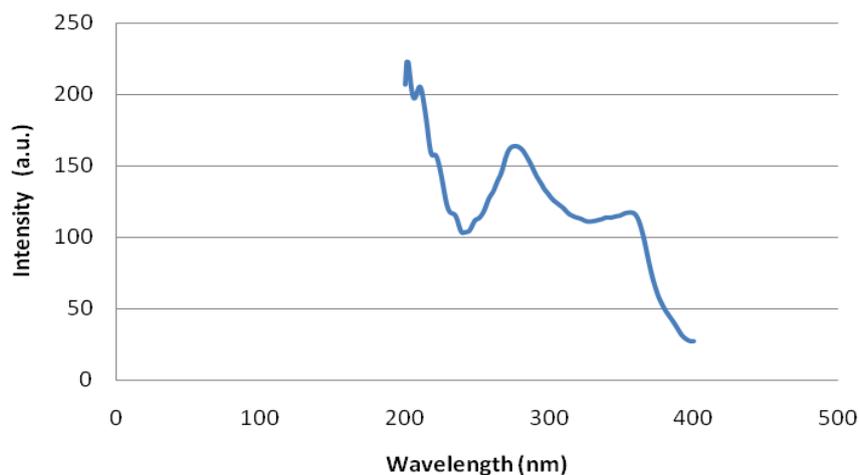
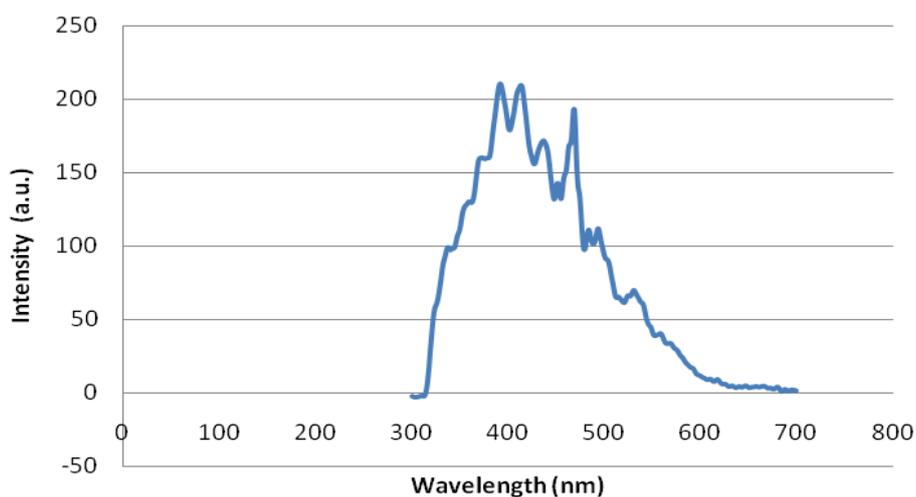


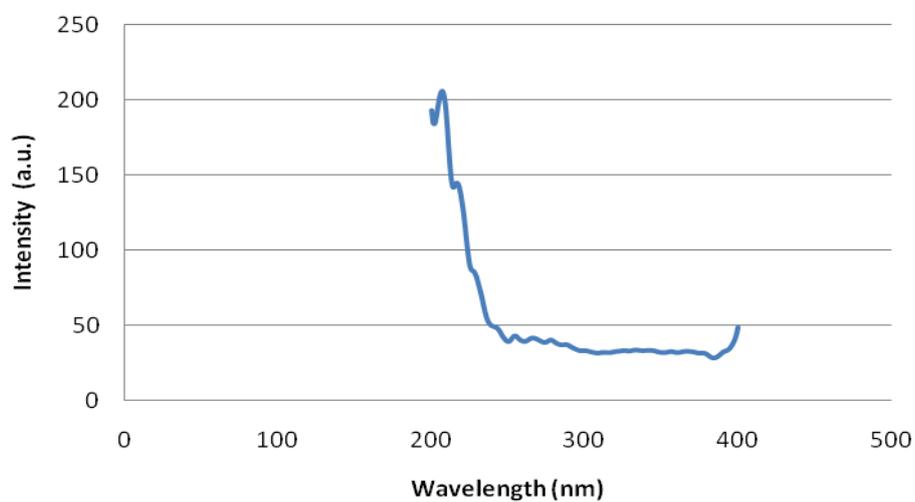
Figure 3: Fluorescence emission of compound.



**Figure 4:** The excitation spectrum of compound.



**Figure 5:** Fluorescence emission of compound.



**Figure 6:** Excitation spectrum of compound.

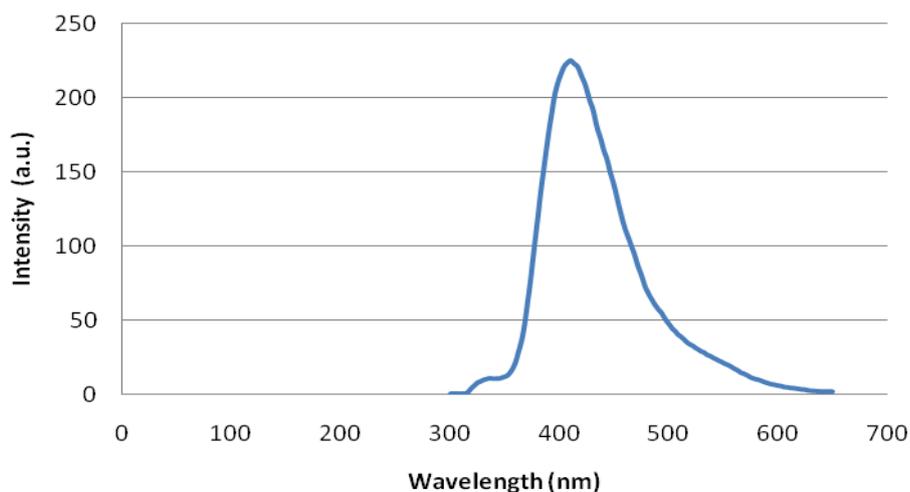


Figure 7: Fluorescence emission of compound.

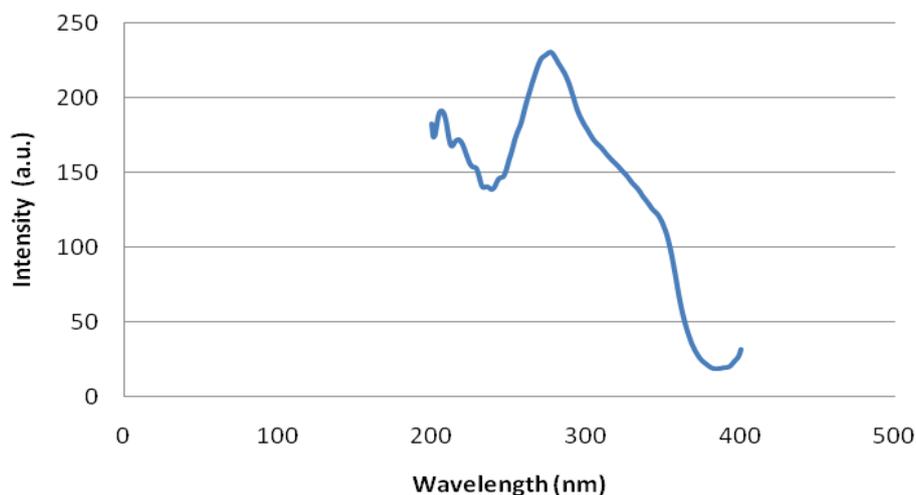


Figure 8: Excitation spectrum of compound.

### Fluorescence properties of coumarin substituted chromone

In this work, we present simple new fluorescent coumarin substituted chromone synthesis and we utilized the unique advantages of simple coumarin substituted chromone as a fluorescent compound, the approach of the synthesis these fluorescent compounds are demonstrated in Scheme 1. The studies of fluorescence were performed in ethanol at a concentration of  $1.0 \times 10^{-5}$  and studied Excitation spectra, emission spectra and stoke shifts (nm) of all compounds (Figures 1-8), were determined via comparison method [18,19]. Fluorescence spectra were obtained at their respective maximum excitation wavelength in Coumarin substituted chromone an electron-donating group was known to exhibit strong fluorescence.

Fluorescence emission and excitation spectra of synthesized compound 3 to 6 (Figures 1-8).

The electron donating substituent group exhibited longer emission wavelength ranging from 398 to 425 nm and longer excitation ranging from 202 to 276, where benzocoumarin part served as a strong donor to constitute a strong push-pull system to exhibit high fluorescent intensities [20,21]. The synthesized compounds, 2-oxo-4-phenyl-2H-

chromen-7-yl acetate is a show highest excitation and highest emission, 8-acetyl-7-hydroxy-4-phenyl-2H-chromen-2-one is highest stock shift Due to substituted highest electron donating group, 8-methyl-4-phenyl-2H,10H-pyrano[2,3-f]chromene-2,10-dione is lowest stock shift due to less electron donating group [22].

### Conclusion

In this paper we have successfully synthesized the coumarin substitute chromone and well characterized by the  $^1\text{H}$  NMR, FT-IR and Mass spectroscopic analysis and the result obtained in the present study shows that this information would give rise to design of better molecule with good yields, developed of new synthetic green strategies. Further we have checked its fluorescence properties. It has been conclude that compounds 3 to 6 show fluorescent in ethanol with high emission, excitation and show high activity. This work is useful for the synthesis of same type of compound and also useful in the fluorescence studies.

### Acknowledgments

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