

# One-pot Synthesis of 1*H*-benzo[f]chromen-2-yl (phenyl)methanone Derivatives in the Presence of Copper Triflate as Catalyst Using Ultrasonic Irradiation

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## Authors' contributions

This work was carried out in collaboration between all authors. Author TYZ performed the experiments. Authors ZT and KT planned the study, managed the literature searches and wrote the manuscript. All authors read and approved the final manuscript.

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## ABSTRACT

A rapid, efficient and environment-friendly protocol for the synthesis of naphthopyranes has been developed by one-pot condensation of 2-naphthol, various aromatic aldehydes and benzoylacetone or 1,3-diphenyl-1,3-propanedione in the presence of Cu(OTf)<sub>2</sub> as catalyst under ultrasonic irradiation. The present approach offers the advantages of clean reaction, simple methodology, short reaction time, high yield and economic availability of the catalyst.

**Keywords:** Copper(II)triflate; naphthopyran; one-pot reaction; ultrasound.

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## 1. INTRODUCTION

Naphthopyranes or benzochromenes are important biologically active oxygenated heterocyclic compounds, which possess antiviral [1], antibacterial [2], antimicrobial [3], anti-proliferative [4], antitumor [5], anti-HIV [6], and antileishmanial [7] activity. The various substituted benzochromene derivatives can be mentioned for molecular modeling as potential drugs for treatment of Alzheimer's disease [8]. Furthermore, naphthopyranes are photochromic compounds [9,10]. Therefore, a number of methods have been reported for the synthesis of naphthopyran derivatives in the literature [11-17]. However, some of these methods are not environment-friendly due to long reaction times. Thus improvements in these syntheses have been sought continuously. As a result, in the synthesis of various new naphthopyran derivatives the development of more rapid, eco-friendly and efficient method is preferred.

One-pot reaction (multi-component method) has been becoming one of the most important aspects in Organic Chemistry. One-pot synthesis is carrying out successive chemical reactions in just one reactor. One-pot offers a significant advantages over single linear step synthesis such as simple work-up, less time, less energy and less raw-material consuming. Since one-pot method avoids a lengthy separation process and purification of the intermediate chemical compounds, it would save time and resources while increasing chemical yield. Concisely, multi-component reactions provide both economic and environmental advantages [16,18-22].

Lewis acid catalysis is one of the most powerful tools in modern organic synthesis; it has to be generally carried out under strictly anhydrous conditions because of its water-labile nature. Recently, metal triflates (trifluoromethanesulfonate), a new type of Lewis acids, have been widely used in organic synthesis as catalyst due to their high stability, water tolerance, and recoverability from water [23]. This process is efficiently promoted by the copper(II)triflate [Cu(OTf)<sub>2</sub>].

The significance of environmental friendly chemical processes is becoming more and more prevalent due to increasing pollution rates during the last decades. Ultrasonic-assisted organic synthesis (UAOS) as a green synthetic approach is an efficient method that is widely used in the acceleration of many organic reactions. This

approach enhances reaction rates and helps the formation of purer products in high yields. The manipulation of this process is easier; it helps the conservation of energy and waste minimization in comparison to traditional methods. Thus, ultrasound method has become so popular and received substantial interest. However, the use of ultrasound method in heterocyclic systems needs some further investigation due to a few applications found in literature on the synthesis of naphthopyran derivatives [13,24]. Therefore, developing a general, more efficient and eco-friendly method for the synthesis of hydrobenzo[f]chromen-2-yl phenyl methanone is being considered in order to deploy the application of ultrasound method in the synthesis of heterocyclic compounds.

In this work, naphthopyran derivatives were obtained by one-pot reaction of 2-naphthol, aromatic aldehydes and acyclic 1,3-dicarbonyl compound in the presences of Cu(OTf)<sub>2</sub> as a catalyst in dichloroethane assisted with ultrasound irradiation method. In comparison with other routes, the one that employs one-pot reaction of 2-naphthol, 1,3-dicarbonyl compounds and aromatic aldehydes under various conditions has been chosen as the most efficient.

## 2. EXPERIMENTAL

### 2.1 General Information

Sonication was performed in an Intersonik ultrasound cleaner (model: MIN4) with a frequency of 25 kHz, an US output power of 100 W, a heating 200 W. The temperature of the water bath was controlled by a controlled automatic constant temperature cooling circulatory system. TLC was carried out on silica gel 60 F<sub>254</sub> pre-coated plates and visualized with "Camag UV light" (254/366 nm). Column chromatography was performed on silica gel 60 (70–230 mesh). FTIR spectra were recorded on a Philips PU 9714 ATR spectrophotometer using "Perkin-Elmer Spectrum One" program. <sup>1</sup>H NMR (500MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a "Inova 500" and "Bruker 500" spectrometers using TMS as an internal standard in CDCl<sub>3</sub> or DMSO. Mass Spectra were obtained using "Agilent 6890 N GC System-5973 MSD" instrument. CHN analyses were performed on "Thermo Finnigan Flash Ea 1112 Series". Melting points were determined with Gallenkamp melting point apparatus and were uncorrected. All

chemical reagents were purchased from Merck, Fluka, Aldrich and were used without purification.

## 2.2 General Procedure for Synthesis of Hydrobenzo[f]chromen-2-yl Phenyl Methanone

Copper triflate (0.1 mmol) in 1,2-dichloroethane (2 mL) was added to a mixture of  $\beta$ -naphthol (1.0 mmol), aromatic aldehyde (1.0 mmol), and acyclic 1,3-dicarbonyl compound (1.0 mmol). The reaction mixture was stirred at 80°C for a given time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, mixture was diluted by 10 mL of ethyl acetate and water (8:2). Organic phase was separated and aqueous phase extracted with 10 mL ethyl acetate three times. The collected organic phase was dried over  $MgSO_4$  and the solvent was evaporated, and the crude product was purified by column chromatography on silica gel with dichloromethane: n-hexane as eluents.

## 2.3 Ultrasound-assisted Synthesis of Hydrobenzo[f]chromen-2-yl Phenyl Methanone

$Cu(OTf)_2$  (0.1 mmol) in 1,2-dichloroethane (2 mL) was added to a mixture of  $\beta$ -naphthol (1.0 mmol), aromatic aldehyde (1.0 mmol), and acyclic 1,3-dicarbonyl compounds (1.0 mmol). The reaction mixture was sonicated at 50°C in an ultrasound cleaner bath according to the given times in Table 1. The maximum energy area in the ultrasound cleaner is the center of the bath, so the flask was suspended there. The progress of the reaction was monitored by TLC and then stopped by the addition of water. The product was extracted with 10 mL of EtOAc three times. The organic layer was dried over  $MgSO_4$  and evaporated, and the crude product was purified

by column chromatography (n-hexane/dichloromethane) to obtain pure products (**5a-d**, **6a-d**).

### 2.3.1 (1-(3,5-dichlorophenyl)-3-methyl-1H-benzof[chromen-2-yl] phenyl methanone (5a)

White solid, m.p.249-50°C; FTIR (near)  $\nu_{max/cm^{-1}}$ : 3058, 2921, 1671, 1619, 1592, 1514, 1468, 1403, 1220, 995, 807, 735;  $^1H$  NMR (500MHz,  $CDCl_3$ ):  $\delta$  (ppm) 1.51 (s, 3H), 5.80 (s,1H), 6.89-6.93 (d,  $J=8.79$  Hz, 2H), 7.22-7.31 (m, 2H), 7.42-7.51 (m, 4H), 7.59-7.63 (m,3H), 7.79-7.87 (3H, m, Ar-H);  $^{13}C$  NMR (100MHz,  $CDCl_3$ ):  $\delta$  (ppm)17.61, 35.87, 112.37, 114.17, 116.23, 122.00, 123.73, 126.22, 127.04, 127.52, 127.68, 128.02, 128.18, 128.34, 130.09, 130.11, 130.85, 131.48, 131.88, 131.96, 137.30, 139.89, 147.90, 150.18, 195.81; Anal. Calcd. for  $C_{27}H_{18}Cl_2O_2$  C: 72.82; H: 4.07. Found C: 72.77; H: 4.28;  $M^+$  (m/z) = 445.

### 2.3.2 (1-(4-chlorophenyl)-3-methyl-1H-benzof[chromen-2-yl] phenyl methanone (5b)

White solid, m.p.281-82°C; FTIR (near)  $\nu_{max/cm^{-1}}$ : 3067, 2919, 1644, 1592, 1486, 1228, 1083, 807, 741;  $^1H$  NMR (500MHz,  $CDCl_3$ ):  $\delta$  (ppm) 1.47 (s, 3H), 5.68 (s,1H), 7.07-7.11(d  $J= 9.20$  Hz, 2H), 7.39-7.48 (m, 5H), 7.54-7.60 (m, 3H), 7.73-7.85 (m, 4H), 8.28-8.31 (d,  $J = 8.59$  Hz,1 H);  $^{13}C$  NMR (100MHz,  $CDCl_3$ ):  $\delta$  (ppm) 21.05, 37.34, 116.71, 117.99, 122.37, 123.37, 124.34, 124.69, 126.65, 126.88, 127.35, 128.35, 128.49, 128.61, 128.88, 128.96, 128.99, 129.06, 129.46, 131.01, 131.21, 132.05, 143.43, 148.65, 182.02; Anal. Calcd. for  $C_{27}H_{19}ClO_2$  C: 78.92; H: 4.66. Found C: 78.89; H: 4.72;  $M^+$  (m/z) = 410.

Table 1. Synthesis of hydrobenzo[f]chromen-2-yl phenyl one in the presence of  $Cu(OTf)_2$

| Entry | R   | Product | Conventional method |                        | Ultrasound method |                        |
|-------|---|---------|---------------------|------------------------|-------------------|------------------------|
|       |   |         | Time (h)            | Yield (%) <sup>a</sup> | Time (h)          | Yield (%) <sup>a</sup> |
| 1     | 3,5-(Cl <sub>2</sub> ) C <sub>6</sub> H <sub>3</sub>  | 5a      | 5                   | 87                     | 1                 | 93                     |
| 2     | p-(Cl) C <sub>6</sub> H <sub>4</sub>                  | 5b      | 5                   | 89                     | 0.5               | 94                     |
| 3     | p-(NO <sub>2</sub> ) C <sub>6</sub> H <sub>4</sub>    | 5c      | 5                   | 74                     | 1                 | 83                     |
| 4     | p-(Br) C <sub>6</sub> H <sub>4</sub>                  | 5d      | 5                   | 79                     | 0.5               | 87                     |
| 5     | C <sub>6</sub> H <sub>5</sub>                         | 6a      | 5                   | 73                     | 2                 | 82                     |
| 6     | p-(Cl) C <sub>6</sub> H <sub>4</sub>                  | 6b      | 5                   | 76                     | 2                 | 85                     |
| 7     | p-(CH <sub>3</sub> ) C <sub>6</sub> H <sub>4</sub>    | 6c      | 5                   | 75                     | 2                 | 83                     |
| 8     | 3,5-(OCH <sub>3</sub> ) C <sub>6</sub> H <sub>3</sub> | 6d      | 5                   | 81                     | 2                 | 87                     |

<sup>a</sup>Yields after column chromatography

**2.3.3 (1-(4-nitrophenyl)-3-methyl-1H-benzof[chromen-2-yl) phenyl methanone (5c)**

Yellow solid, m.p. 317.5-18.5°C; FTIR (near)  $\nu_{\max/\text{cm}^{-1}}$ : 3064, 2927, 1642, 1590, 1507, 1399, 1302, 1236, 1106, 825, 740;  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.47 (s, 3H), 5.48 (s, 1H), 7.41-7.48 (m, 3H), 7.50-7.52 (d,  $J = 8.90$  Hz, 2 H), 7.58-7.62 (m, 3H), 7.67-7.71 (d,  $J = 8.80$  Hz, 2H), 7.82-7.88 (m, 3H), 7.98-8.02 (d,  $J = 8.80$  Hz, 2H);  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 19.80, 38.04, 111.78, 114.72, 116.72, 117.04, 120.98, 122.83, 123.25, 123.77, 126.16, 127.35, 127.88, 128.04, 128.52, 128.56, 130.02, 130.04, 130.22, 132.41, 145.26, 146.68, 147.74, 148.57, 150.95, 152.34, 189.71; Anal. Calcd. for  $\text{C}_{27}\text{H}_{19}\text{NO}_4$  C: 76.95; H: 4.54; N:3.32. Found C: 76.92; H: 4.58; N: 3.30;  $\text{M}^+$  (m/z) = 421.

**2.3.4 (1-(4-bromophenyl)-3-methyl-1H-benzof[chromen-2-yl) phenyl methanone (5d)**

White solid, m.p. 186°C; FTIR (near)  $\nu_{\max/\text{cm}^{-1}}$ : 3067, 2968, 1646, 1591, 1482, 1399, 1288, 1008, 824, 739;  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.83 (s, 3H), 5.75 (s, 1H), 7.03-7.08 (d,  $J=8.45$  Hz, 2H), 7.24-7.28 (m, 2H), 7.29-7.32 (d,  $J=8.91$  Hz, 1H), 7.35-7.42 (m, 3H), 7.47-7.58 (m, 4H), 7.71-7.84 (m, 3H);  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 19.39, 39.95, 111.78, 114.65, 115.16, 117.18, 120.49, 123.83, 123.32, 124.70, 127.02, 128.56, 128.68, 128.77, 129.23, 129.55, 131.05, 131.27, 131.80, 132.65, 139.56, 143.88, 148.28, 152.95, 197.90; Anal. Calcd. for  $\text{C}_{27}\text{H}_{19}\text{BrO}_2$  C: 71.22; H: 4.21. Found C: 71.18; H: 4.25;  $\text{M}^+$  (m/z) = 455.

**2.3.5 (1,3-diphenyl-1H-benzof[chromen-2-yl) phenyl methanone (6a)**

White solid, m.p. 191°C; FTIR (near)  $\nu_{\max/\text{cm}^{-1}}$ : 3055, 2874, 1664, 1596, 1445, 1330, 1224, 813, 728;  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 5.82 (1H, s, CH), 6.90-6.97 (m, 2H), 6.99-7.10 (m, 4H), 7.12-7.15 (m, 4H), 7.28-7.33 (m, 4H), 7.33-7.39 (m, 5H), 7.73-7.75 (d,  $j = 8.3$  Hz, 1H), 7.84-7.88 (d,  $j = 8.30$ Hz, 1H);  $^{13}\text{C NMR}$ ; (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 40.32, 114.40, 115.34, 116.33, 122.52, 123.64, 125.64, 125.94, 126.15, 126.62, 126.85, 127.05, 127.45, 127.61, 127.66, 127.97, 128.05, 128.18, 128.63, 130.17, 130.37, 130.72, 131.43, 132.79, 137.58, 143.53, 147.71, 153.25, 196.99; Anal. Calcd. for  $\text{C}_{32}\text{H}_{22}\text{O}_2$  C: 87.65; H: 5.06. Found C:87.71; H: 5.10;  $\text{M}^+$  (m/z) = 438.

**2.3.6 (1-(4-chlorophenyl)-3-phenyl-1H-benzof[chromen-2-yl) phenyl methanone (6b)**

White solid, m.p. 208°C; FTIR (near)  $\nu_{\max/\text{cm}^{-1}}$ : 3055, 2958, 1649, 1590, 1486, 1270, 1222, 1073, 729;  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 5.80 (s,1H), 6.98-7.04 (m, 2H), 7.08-7.18 (m, 5H), 7.29-7.35 (d,  $J = 8.45$  Hz, 2H), 7.37-7.51 (m, 7H), 7.81-7.85 (d,  $J = 8.75$  Hz, 2H), 7.87-7.91 (d,  $J = 8.35$  Hz, 2H);  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 40.52, 114.70, 116.09, 117.33, 123.25, 124.84, 127.11, 127.16, 127.75, 127.92, 128.22, 128.60, 128.68, 128.78, 129.05, 129.23, 129.45, 129.90, 130.94, 131.41, 131.85, 132.37, 132.46, 133.60, 135.51, 138.49, 143.22, 148.63, 155.43, 185.76; Anal. Calcd. for  $\text{C}_{32}\text{H}_{21}\text{ClO}_2$  C: 81.26; H: 4.48. Found C: 81.32; H: 4.42;  $\text{M}^+$  (m/z) = 472.

**2.3.7 (1-(4-methylphenyl)-3-phenyl-1H-benzof[chromen-2-yl) phenyl methanone (6c)**

White solid, m.p: 171.5°C, FTIR (near)  $\nu_{\max/\text{cm}^{-1}}$ : 3022, 2940, 1631, 1589, 1508, 1343, 1222, 903, 803;  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 2.11 (3H, s, CH), 5.81 (1H, s, CH), 6.89-6.95 (m, 5H), 7.02-7.11 (m, 4H), 7.15-7.20 (m, 2H), 7.29-7.38 (m, 5H), 7.71-7.74 (m, 4H);  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 19.97, 39.86, 114.51, 115.66, 116.33, 122.48, 123.61, 125.91, 126.15, 126.63, 26.83, 126.91, 127.44, 127.66, 127.84,128.11, 128.23, 128.31, 128.61, 130.17, 130.37, 130.68, 132.84, 135.11, 137.62, 140.67, 147.61, 153.42, 196.92; Anal. Calcd. for  $\text{C}_{33}\text{H}_{24}\text{O}_2$  C: 87.58; H: 5.35. Found C: 87.32; H: 5.27;  $\text{M}^+$  (m/z) = 452.

**2.3.8 (1-(3,5-dimethoxyphenyl)-3-phenyl-1H-benzof[chromen-2-yl) phenyl methanone (6d)**

White solid, m.p: 213°C; FTIR (near)  $\nu_{\max/\text{cm}^{-1}}$ : 3058, 2928, 1702, 1592, 1516, 1334, 1202, 811;  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 3.71 (s, 3H), 3.77 (s, 3H), 5.78 (s, 1H), 6.92-6.98 (m, 4H), 7.01-7.18 (m, 5H), 7.29-7.39 (m, 5H), 7.72-7.75 (m, 3H), 7.86-7.91 (d,  $J = 8.30$  Hz,2H);  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 40.50, 54.18, 97.26, 114.20, 114.85, 116.35, 122.51, 123.64, 125.93, 126.15, 126.67, 126.85, 127.44, 128.03, 128.09, 128.56, 130.29, 130.33, 130.80, 132.81, 137.55, 145.75, 147.80, 152.86, 159.80, 197.04; Anal. Calcd. for  $\text{C}_{34}\text{H}_{26}\text{O}_4$  C: 81.91; H: 5.26. Found C: 81.82; H: 4.98;  $\text{M}^+$  (m/z) = 498.

### 3. RESULTS AND DISCUSSION

The condensation of  $\beta$ -naphthol, 1,3-diones (benzoylacetone or 1,3-diphenyl-1,3-propanedione) with substituted benzaldehydes was carried out in 1,2-dichloroethane for 5h in reflux conditions in presence of  $\text{Cu}(\text{OTf})_2$  at the commencement phase of our research. The mixture was stirred at  $80^\circ\text{C}$ . The synthesis of naphthopyran compounds were compared with the conventional heating ones in order to show the effect of using ultrasonic irradiation method in these reactions. The experimental results show that the reaction times are reducing when ultrasound method was used. The ultrasound-assisted reaction was carried out at  $50^\circ\text{C}$  and took shorter time than the conventional methods.

Benzoylacetone and 1,3-diphenyl-1,3-propanedione were also tried out as 1,3-dicarbonylacyclic compounds. The reactions proceeded steadily to afford series of 1-aryl-3-phenyl-1H-benzo[f]chromen-2-yl phenyl methanones (5a-d) and 1-aryl-3-phenyl-1H-benzo[f]chromen-2-yl phenyl methanones (6a-d) under similar conditions. Aromatic aldehydes substituted with either electron-donating or electron-withdrawing group underwent the reaction smoothly and gave the products in moderate yields in all cases. However, the yields of **5a-d** series were slightly lower than the yields of **6a-d** the series.

As part of this green concept, "ultrasound" has become so popular and received substantial

interest. Then, in the second step; we investigated the condensation reaction of  $\beta$ -naphthol, aldehydes and acyclic-1,3-diones using  $\text{Cu}(\text{OTf})_2$  catalyst with ultrasonic irradiation in 1,2-dichloroethane and the results are listed in Table 1. Copper(II) trifluoromethane sulphonate) has been received as an inexpensive, water tolerant and potentially useful metal triflate.

This study report is a rapid procedure for the preparation of naphthopyrans by using  $\text{Cu}(\text{OTf})_2$  as a green catalyst under ultrasound irradiation. To the best of our knowledge, only a few reported on the synthesis of hydrobenzo[f]chromen-2-yl phenyl)one derivatives, and no reports are available using ultrasound. The structures of the obtained new compounds have been clarified by spectroscopic methods (FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, EA and GC/MS) after the purification processes.

A tentative mechanism for the formation of of hydrobenzo[f]chromen-2-yl phenyl methanone derivatives is proposed in Fig. 2. By following the literature [12,15], we suppose that the reaction might have proceeded via ortho-quinone methides intermediate, which was formed by the nucleophilic addition of 2-naphthol to aldehydes catalyzed by  $\text{Cu}(\text{OTf})_2$ . Subsequent substitution of the oxygen atom, coordinated by  $\text{Cu}(\text{OTf})_2$  with acyclic 1,3-dicarbonyl compounds. After one molecule of water eliminated, the new products **5** and **6** were obtained.

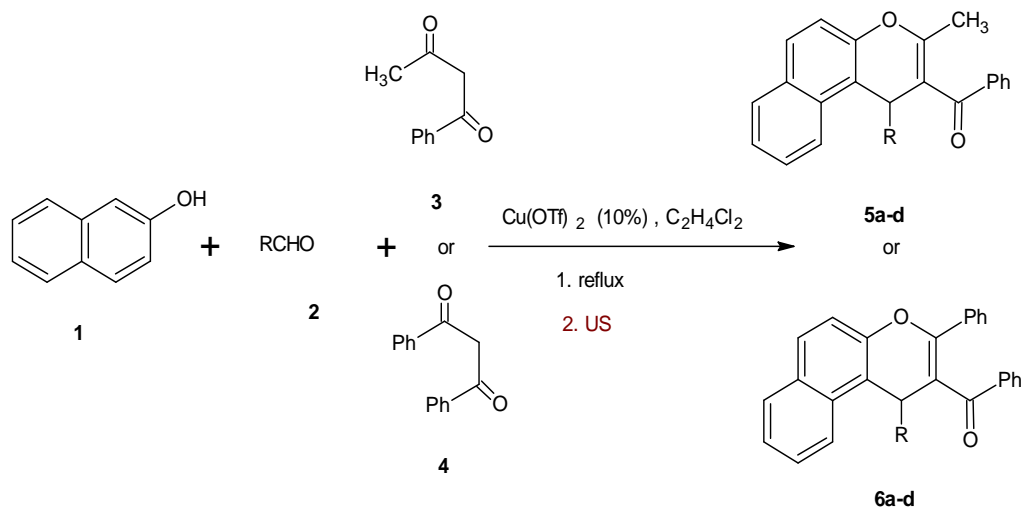
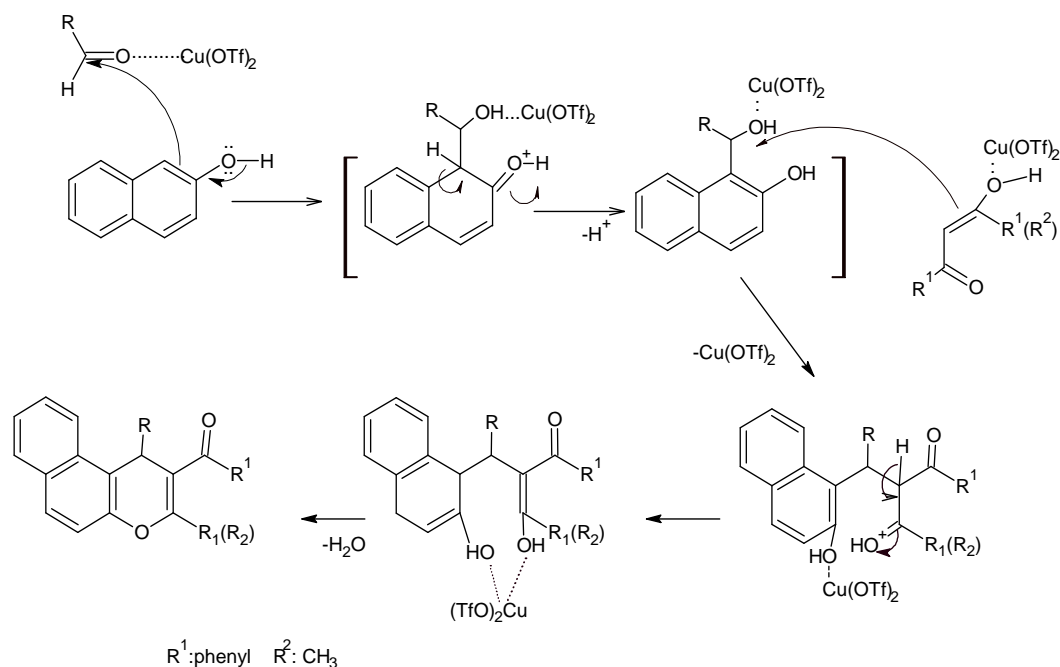


Fig. 1.  $\text{Cu}(\text{OTf})_2$  catalyzed condensation of  $\beta$ -naphthol, aromatic aldehydes, 1,3- dicarbonyl compounds



**Fig. 2. A tentative mechanism for the formation of hydrobenzo[f]chromen-2-yl phenyl methanone derivatives**

#### 4. CONCLUSION

We have demonstrated an efficient and simple one-pot method for the synthesis of 1H-benzo[f]chromen-2-yl)-one derivatives via cyclocondensation reaction of 2-naphthol, aromatic aldehydes, and 1,3-dicarbonyl compounds catalyzed by Cu(OTf)<sub>2</sub> in dichloroethane. This is the first report of one-pot synthesis of 1H-benzo[f]chromen-2-yl)(phenyl)one compounds catalyzed by copper(II) triflate under ultrasonic irradiation. The process has several advantages such as easy workup, fast reaction rates, mild reaction conditions, and good yields.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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