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One-pot synthesis of 3-(furan-2-yl)-4-hydroxy-2*H*-chromen-2-ones using K10 montmorillonite clay as heterogeneous catalyst

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ABSTRACT

A facile and efficient one-pot synthesis of 3-(furan-2-yl)-4-hydroxy-2*H*-chromen-2-ones was developed. The reaction of ethyl 3-(2-hydroxyphenyl)-3-oxopropanoates and 2,5-dimethoxy-2,5-dihydrofuran were performed in presence of K10 Montmorillonite Clay heterogeneous catalyst under the solvent-free condition at 80 °C for 1 h, and followed by further converted to 3-(furan-2-yl)-4-hydroxy-2*H*-chromen-2-ones *via* refluxing in the alkaline EtOH solution for 0.5 h. The demonstrate method not only avoided the usage of any expensive transition-metals, but also eliminated the tedious intermediate purification. Moreover, due to the wide functional group tolerance, it could be applied to various substrates and gave product in good to excellent yields.

1. Introduction

Coumarin was an important heterocyclic core structure, which was present in a large variety of natural plants, and constituted a member of significant organic compounds due to their wide applications. For example, various of biological and pharmaceutical properties have been reported for coumarin analogues, e.g. antimicrobial [1], anti-inflammatory [2], anticancer [3], antihypertensive [4], anti-HIV [5] and anticoagulants [6]. It has also been utilized as corrosion inhibitors [7] and urease-inhibitors [8]. Moreover, coumarin could be also found in fluorochrome [9], cosmetics and pigments [10]. The 3-aromatic substituted coumarin analogues exhibited various important potential biological activities as well, e.g. antileishmanial [11], antioxidant [12] properties, MAO inhibitors [13] and inhibit cell proliferation [14].

Although a number of methods for the preparation of 3-aryl substituted coumarin analogues were known in the last decade [15–18], only a few reports on the synthesis of 3-furan-4-hydroxycoumarins was disclosed. Palmisano and co-workers reported a [3 + 2] cycloaddition of 3-diazo-4-hydroxycoumarin and 2-methylfuran in the presence of $Rh_2(OAc)_4$ for the synthesis of furo [3,2-*c*]coumarin analogues **5** and **6**, along with the formation of 4-hydroxy-3-(5-methylfuran-2-yl)-2*H*-chromen-2-one **7** in 30% yields as a byproduct (Scheme 1) [19].

Later on, Zhu's group reported the synthesis of 3-arylcoumarin analogues **9** *via* Pd-catalyzed cross-coupling of aryl boronic acids with phenyliodonium zwitterion **8** in 80%–88% yields, which were obtained by the iodination of 4-hydroxycoumarin with iodobenzene diacetate (Scheme 2a) [20]. Recently, it was reported that Pd-catalyzed Sukuzi coupling of 3-chloro-4-alkoxy coumarins with heteroarylboronic acids in the presence of base and SPhos gave 3-(benzo)furyl/thiophenyl substituted 4-alkoxycoumarin analogues **10** in 64%–93% yields (Scheme 2b) [21]. The reported methods required both prolonged heating and expensive transition-metal catalysts, which were difficult to recycle and not environmental friendly.

Montmorillonite K10 clay has been known for its tunable Bronsted and Lewis acidities and used as an environmental friendly catalyst in synthetic organic chemistry [22–24]. The K10 clay offered several advantages compared with other catalysts, such as non-corrosive properties, non-toxic, low cost, ease of handling and mild reaction conditions [25–27]. Moreover, it could be easily separated and recycled, which made it an excellent heterogeneous

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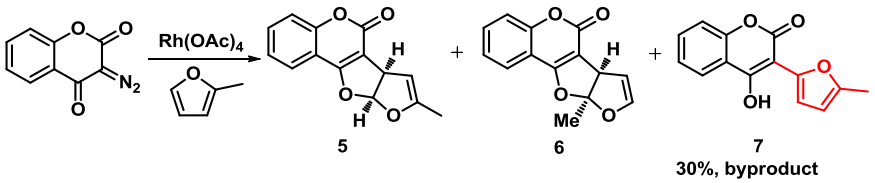
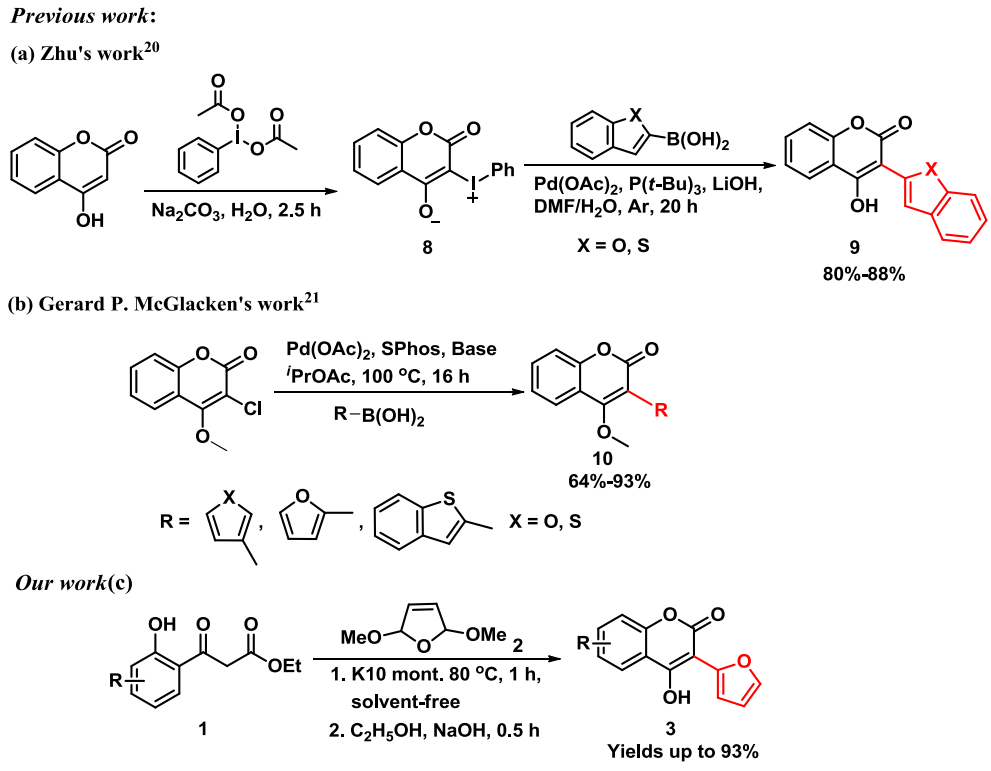


Scheme 1. Preparation of 4-hydroxy-3-(5-methylfuran-2-yl)-2*H*-chromen-2-one (**7**).



Scheme 2. Synthesis of 3-heterocyclicaryl-4-hydroxy-2*H*-chromen-2-ones.

green catalyst [28–30].

Herein, we would like to report a facile and efficient K10 Montmorillonite Clay heterogeneously catalyzed two-step one-pot synthesis of 3-(furan-2-yl)-4-hydroxy-2*H*-chromen-2-ones **3** from ethyl 3-(2-hydroxyphenyl)-3-oxopropanoates **1** and 2,5-dimethoxy-2,5-dihydrofuran (DHDMF, **2**) (Scheme 2c).

2. Results and discussion

On the basis of literature report [31,32], refluxing ethyl 3-(2-hydroxyphenyl)-3-oxopropanoate **1a** [33] with DHDMF in the presence of K10 montmorillonite Clay in anhydrous dichloromethane (DCM) for 2 h, ethyl 2-(furan-2-yl)-3-(2-hydroxyphenyl)-3-oxopropanoate **4a** was given in 12% yield (Table 1, Entry 1). Replacement of DCM with hexane, the reaction was heated at a higher temperature (70 °C), which led to the formation of **4a** in 25% yields (Entry 2). It was interesting to find out that the yield of **4a** was significantly improved when reaction was carried out under solvent-free condition (86%, Entry 3). In order to further optimized the reaction conditions, various ratios of **1a**: DHDMF: K10 were carefully screened (Entries 4–7). The result showed that **4a** was obtained as high as 96% yields with 1.5 equiv. of **2** (Entry 4), while the yield was not significantly affected by the continued increased loading of **2** (Entry 5). Reducing or increasing the loading of K10 led to the lower yield of **4a** (Entries 6–7). Taking into account for the economic and environmental factors, further temperature optimization was performed with the ratio listed in Entry 4. Slight adjusting the reaction temperature did not improved the yield of **4a** as well (Entries 8–9). The K10 montmorillonite was recycled and it's reaction activity showed a gradual decrease. The yields of five recycles were 85%, 82%, 75%, 70% and 64%, respectively.

The cyclization of **4a** was initially performed in the mixture of hydrochloric acid ethanol solution for refluxing 0.5 h, which gave corresponding cyclization product 3-furan-4-hydroxycoumarin **3a** in 22% yields (Table 2, Entry 1). It has been found out that different acids slightly affected the yield of **3a**. Product **3a** was obtained in higher yield in the presence of CF_3COOH (Entry 2), while only trace amount of **3a** was detected in the presence of *p*-$CH_3C_6H_4SO_3H$ (Entry 3). Surprisingly, the addition of a base significantly increased the yield of **3a** compared with an acid (85%, Entry 4). Further investigation on the loading of base revealed that 2 equiv. of NaOH gave product **3a** in best yield (92%, Entries 4–6). In the end, the optimal conditions for the generation of **3a** was Entry 5.

To further simplify the methodology and operation, we attempted to perform the coupling and cyclization under the optimized conditions without isolation and purification of **4a**