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ORIGINAL ARTICLE

# A Simple And Ecofrindly Synthesis Of Coumarins

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**Abstract:**

*A simple and convenient method for the synthesis of coumarins catalysed by K2CO3 in aqueous media is described.*

***KEYWARDS:***

*K2CO3, Coumarins, Water mediated reaction.*

## INTRODUCTION

The development of heterogeneous catalysts for fine chemical synthesis has become a major area of research. The potential advantages of these materials over homogeneous system (simplified recovery and reusability, the potential for incorporation in continuous reactors and micro reactors) could lead to novel environmentally benign chemical procedures for use academia and industry1. application of solid acids in organic transformations has on important role, because they have many advantages such as facile handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal2-6. Coumarin derivatives are natural products widely distributed in the plant kingdom and their main applications are as fragrance, pharmaceuticals, and agrochemicals7. synthesis of coumarins has been carried out by the Pechmann rection8-10, i.e. by condensation of phenol with β-keto-ester in acidic media. A large number of reagents have been used for this reaction, e. g . H2SO4 8-10, HClO411, P2O5 12, and chloroaluminate ionic liquid13. However, these reagents are required in excess and their corrosive nature makes them difficult to handle, and formation of several side products is a problem. Several other acid catalysts, including Lewis acid, are known to affect this condensation14. However, moisture sensitivity of the majority of Lewis acids to the water produced in the Pechmann reactions renders them unsuitable for use in large-scale applications. Other methods have utilized ionic liquids13-17 and microwave irradiation 18, but these methods also generate strongly acidic by- products and /or they utilize highly expensive and non-recyclable reagents. Recently , a number of heterogeneous catalysts such as Nafion- H19, Zeolote H-BETA, Amberlyst 15 20 , montmorillonite clay 21, silica sulfuric acid22, alum23, water-tolerant sulfonic

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acid nanoreactor4 Scandium (III) triflate24 and ultrasound irradiation25 have been employed in the Pechmann condensation. However, these methods required prolonged reaction time and exotic reaction condensation. Thus, the development of a new method for the synthesis of coumarins derivatives would be highly desirable. In 1980, Breslow discovered that the Diels- Alder reaction performed in water could be subjected to huge rate. Acceleration 26, thus observations leads to increased interest from synthetic organic chemists in organic reactions in water or aqueous media. To date, many more organic transformations have been carried out in water or aqueous media27-29. In recent years, K2CO3 as a catalyst has gained special attention as a catalyst in organic synthesis because many advantages such as excellent solubility in water, non- toxic, uncomplicated handling, inexpensiveness, eco-friendly nature, readily available and high reactivity. Recently, several synthetically useful organic transformations using K2CO3 as a catalyst have been reported in the literature30.

## EXPERIMENTAL

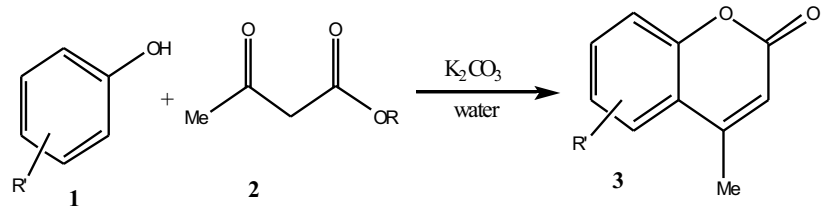
### General procedure synthesis of coumarins 3 a-e

To a mixture of phenolic substrate (1 mmol) and β-keto-ester (1.5 mmol), K2CO3 was (20 mol %) added and water (5 mL) was added and stirred at room temperature for about 1 h. the progress of the reaction was followed by TLC. After completion of the reaction, warm (ethanol 10 mL) was added and filtered and warm ethanol (2 x 10 mL) in order to separate catalyst. Ethanol was evaporated under reduced pressure and crude product was recrystallized from EtOH.

Compound **3a**: mp: 186-188 oC; (Lit. 22 mp. 187-188 oC) 1H NMR (500 MHz, CDCl3- DMSO-d6, δ ppm): 2.29 (s , 3H), 5.96 (s, 1H), 6.71-6.74 (m, 2H), 7.34 (d, 1H , J=8.4 Hz), 9.74 (s, 1H). 13C NMR (125 MHz, CDCl3-DMSO-d6, δ ppm): 19.00, 103.01, 111.20, 112.93, 113.54, 126.03, 153.41, 155.61, 161.65, 162.02

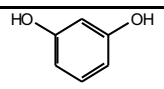
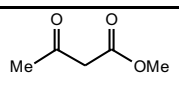
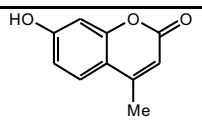
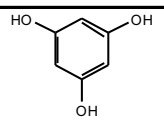
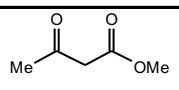
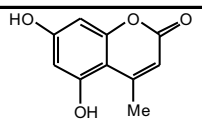
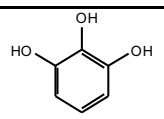
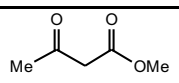
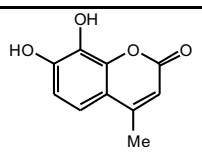
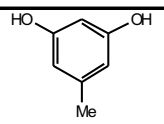
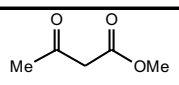
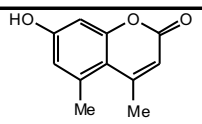
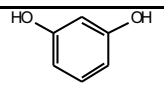
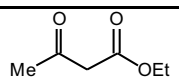
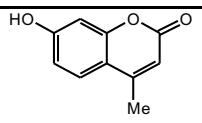
Compound **3b:** mp: 284-288 oC; (Lit. 22 mp. 285-287 oC) 1H NMR (500 MHz, CDCl3- DMSO-d6, δ ppm): 2.44 (s, 3H), 5.67 (d, 1H, J= 1.1 Hz), 6.17 (d, 1H, J= 2.3 Hz), 6.19 (d, 1H, J= 2.3 Hz), 9.48 (s, 1H), 9.59 (s, 1H). 13C NMR (125 MHz, CDCl3-DMSO-d6, δ ppm): 24.32, 95.64, 99.97, 103.37, 109.53, 156.14, 157.13, 158.29, 161.42, 162.17

## RESULT AND DISCUSSION




**SCHEME 1**

**TABLE 1. SYNTHESIS OF COUMARINS (3A-E)**

| Entry | Phenol | β-ketoester | Product 3 | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|
| **1** |  |  |  | 15 | 89 |
| **2** |  |  |  | 15 | 87 |
| **3** |  |  |  | 15 | 89 |
| **4** |  |  |  | 12 | 84 |
| **5** |  |  |  | 15 | 89 |

[a]Isolated yield.

We herein disclose a simple and convenient method for the efficient synthesis of coumarins in water catalyzed by K2CO3 (Scheme 1). In order to study the scope and limitations of the reaction, various bases, including sodium acetate, potassium acetate, ammonium acetate, basic alumina, potassium carbonate, and sodium carbonate and different solvent synthesis were investigated. The potassium carbonate (K2CO3) in water. Optimal result was obtained using 20 mol% of K2C03.

The experiment was conducted with phenolic substrate 1 and β − keto −ester 2 in the presence of catalytic amount of K2CO3 (20 mol%) in water . the reaction proceeded spontaneously at ambient temperature and was completed within 1 h. The isolated of product was straight forward as the solid precipitated on completion of the reaction. The precipitated on completion of the reaction. The precipitated solid was filtered, dried and washed with 20 % ethyl acetate in petroleum ether to offered coumarins 3.
The result provided the incentive for further study of reactions with various other phenolic, substrate 1 and corresponding coumarins.

## CONCLUSION

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