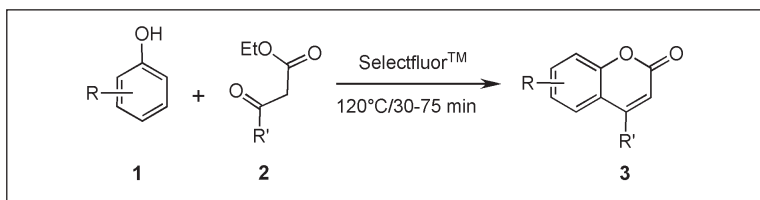


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Selectfluor<sup>TM</sup> is used as an alternative catalyst to conventional catalysts for the synthesis of substituted coumarins *via* Pechmann condensation of phenols with β-ketoesters under solvent-free conditions at 120 °C. This method of synthesis is simple, cost-effective, requires short reaction time, solvent-free and gives good yields.

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## Introduction.

Coumarins and chromones occupy a special place in the realm of natural and synthetic organic chemistry. This group of compounds display a wide range of applications [1,2] as fragrances, pharmaceuticals, additives to food and cosmetics, agrochemicals, optical brightening agents, fluorescent brighteners [3] and also possess biological activities like antihelminthic, hypnotic, insecticidal and anticoagulant [4] properties. Coumarins also act as intermediates for the synthesis of fluorocoumarins, chromenes, coumarones and 2-acyl resorcinols [5]. The Pechmann reaction is a common method for the synthesis of coumarins [6] that involves the condensation of phenols and β-ketoesters in the presence of acidic catalysts. In addition to this reaction, several routes have been reported for the synthesis of coumarins including Knoevenagel [7], Reformatsky [8] and Wittig [9] reactions. However, the Pechmann reaction is a most commonly used and important method for the synthesis of coumarins. Several types of acidic reagents, such as sulphuric acid, hydrochloric acid, polyphosphoric acid, trifluoroacetic acid, solid superacid [ZrO<sub>2</sub>/SO<sub>4</sub><sup>-2</sup> (or) TiO<sub>2</sub>/SO<sub>4</sub><sup>-2</sup>], ZnCl<sub>2</sub>, POCl<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub> have been used for this condensation [10]. Recently, cation exchange resins [11] and solid acid catalysts [12] have been used for the synthesis of coumarins. The Pechmann condensation reaction has also been attempted using microwave irradiation [13] and ionic liquids [14]. However, in the current

context of environmental impact, these methods are not attractive as it requires catalyst in excess, for example sulphuric acid in 10-12 equivalents [15], trifluoroacetic acid in 3-4 equivalents [10b] and P<sub>2</sub>O<sub>5</sub> is required in 5 fold excess [16]. Further, such reactions required long reaction time and in some cases gave lower yields. Consequently it is necessary to develop more effective, non-stoichiometric alternative catalyst for the synthesis of coumarins. However, there were no reports for the synthesis of coumarins using selectfluor<sup>TM</sup> as a catalyst. Recently selectfluor<sup>TM</sup> has been introduced commercially as an electrophilic fluorinating agent. Selectfluor<sup>TM</sup> is a low-cost readily available acidic material and recently it has been employed as an efficient Lewis acid catalyst for the one-pot allylation reactions of imines, hydrolysis of acetals, dithia acetals and tetrahydropyranyl ethers and for the synthesis of β-hydroxy thiocyanates [17]. Herein, we report the use of selectfluor<sup>TM</sup> as a new and efficient catalyst for the synthesis of substituted coumarins *via* Pechmann condensation of phenols and β-ketoesters under solvent-free conditions at 120 °C.

## Results and Discussion.

The Pechmann condensation of resorcinol with ethylacetoacetate was selected as an example to test the feasibility of selectfluor<sup>TM</sup> used as a catalyst. To optimize the molar stoichiometry of selectfluor<sup>TM</sup> and

Scheme I

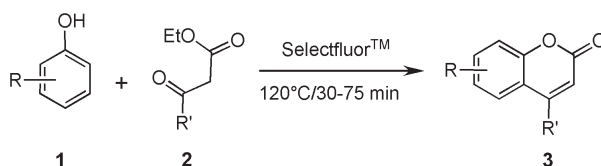


Table 1  
 Synthesis of Substituted Coumarins from Phenols and  $\beta$ -Ketoesters Catalyzed by Selectfluor<sup>TM</sup><sup>a</sup>

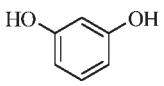
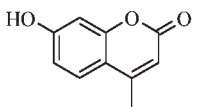
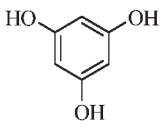
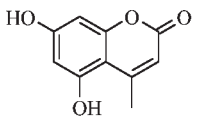
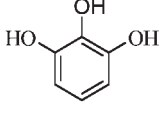
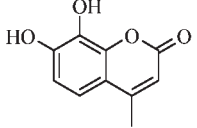
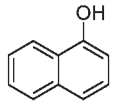
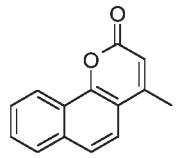
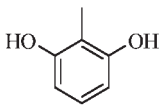
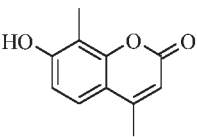
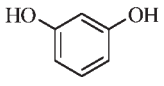
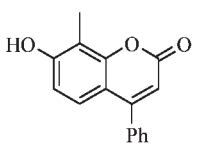
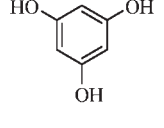
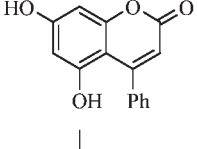
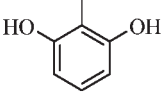
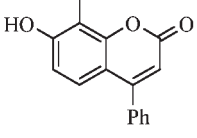
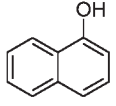
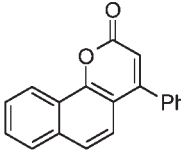
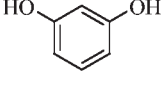
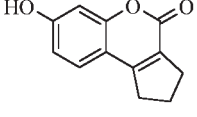
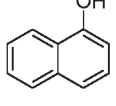
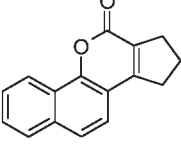
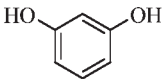
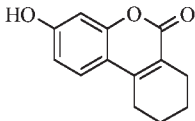
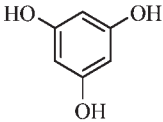
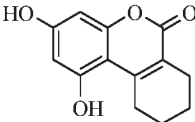
| Entry | Phenol (1)                                                                          | $\beta$ -Ketoester (2)      | Product (3)                                                                          | Time (min) | Yield (%) <sup>b</sup> |
|-------|-------------------------------------------------------------------------------------|-----------------------------|--------------------------------------------------------------------------------------|------------|------------------------|
| 1     |    | Ethyl acetoacetate          |    | 30         | 95                     |
| 2     |    | Ethyl acetoacetate          |    | 45         | 91                     |
| 3     |    | Ethyl acetoacetate          |    | 45         | 90                     |
| 4     |    | Ethyl acetoacetate          |    | 60         | 88                     |
| 5     |    | Ethyl acetoacetate          |   | 45         | 92                     |
| 6     |  | Ethyl benzoylacetate        |  | 30         | 93                     |
| 7     |  | Ethyl benzoylacetate        |  | 45         | 85                     |
| 8     |  | Ethyl benzoylacetate        |  | 45         | 89                     |
| 9     |  | Ethyl benzoylacetate        |  | 60         | 85                     |
| 10    |  | 2-carbethoxy cyclopentanone |  | 75         | 90                     |
| 11    |  | 2-carbethoxy cyclopentanone |  | 60         | 85                     |

Table 1 (continued)

| Entry | Phenol (1)                                                                        | $\beta$ -Ketoester (2)     | Product (3)                                                                        | Time (min) | Yield (%) <sup>b</sup> |
|-------|-----------------------------------------------------------------------------------|----------------------------|------------------------------------------------------------------------------------|------------|------------------------|
| 12    |  | 2-carbethoxy cyclohexanone |  | 60         | 90                     |
| 13    |  | 2-carbethoxy cyclohexanone |  | 60         | 93                     |

<sup>a</sup>Phenol: 10 mmol;  $\beta$ -ketoester: 10 mmol; selectfluor<sup>TM</sup>: 5 mmol; 120 °C; solvent-free conditions; <sup>b</sup>Isolated and unoptimized yields.

temperature, we carried out several experiments at various temperatures under solvent-free conditions. The best result was obtained with 0.5:1:1 molar ratio of selectfluor<sup>TM</sup>, resorcinol and ethylacetoacetate respectively at 120 °C.

In conclusion, we have demonstrated a simple, cost-effective and efficient alternative method for the preparation of substituted coumarins *via* Pechmann condensation using selectfluor<sup>TM</sup> as catalyst. Prominent among the advantages of this method are operational simplicity, good yields in short reaction times, solvent-free conditions, and easy workup procedure employed.

#### EXPERIMENTAL

##### General Procedure.

To the weighed quantity of phenol (10 mmol) and  $\beta$ -ketoester (10 mmol), the selectfluor<sup>TM</sup> (5 mmol) was added and the reaction mixture was stirred at 120 °C. After completion of the reaction at the desired time as indicated in Table, the reaction mixture was poured into cold water and the resultant product was collected by filtration. The products were further purified by column chromatography. All the compounds are well known and in agreement with spectral and physical data.

##### Acknowledgement.

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