# A highly active polymeric magnetic nanocatalyst for the preparation of 3-carboxycoumarins derivatives under mild conditions

**Ali Maleki,* Parisa Ravaghi, Morteza Aghaie and Hamed Movahed**

*Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 1684613114, Iran; * E-mail: maleki@iust.ac.ir*

**Abstract:**

In this work, an efficient method for the synthesis of 3-carboxycoumarins was reported via Knoevenagel condensation. The reaction of Meldrum's acid with substituted salicylaldehyde in the presence of polymeric magnetic nanocatalyst. This protocol has many advantages such as short reaction time, high yield, and easy isolation of the synthesized catalyst.

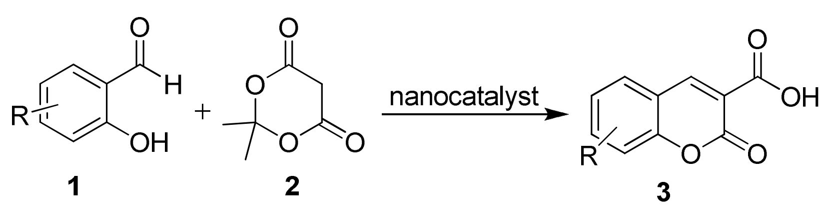
**Keywords:** Nanocatalyst, green chemistry, coumarin, salicylaldehyde, Knoevenagel condensation.

## 1. Introduction

Coumarins are a group of main natural compounds. Coumarin containing compounds demonstrate broad biological activity with, for example, antioxidant, anticoagulant, antifungal, anthelmintic, cytotoxic or hypnotic properties[1–3]. coumarins have a wide variety application in industry such as perfumery, soap and cosmetic industries, and also have been applied in agrochemicals, insecticides and pesticides[4]. Among coumarin derivatives, 3-carboxycoumarins are a dominant target for study in this field as the carboxyl group allows new functionalities to be easily prepared by introducing units of biological interest to enhance the chemical activity of the compound, for example, units of cephalosporin, triazole, thiadiazine, thiadiazole, penicillin, and isourea. They are also used as photosensitizers, photoinitiators and triplet sensitizers[5,6].

Catalytic reactions often reduce energy requirements and decrease separations due to increased selectivity; they may permit the use of renewable feedstocks or minimize the quantities of reagents needed. Catalysis often permits the use of less toxic reagents, as in the case of oxidations using hydrogen peroxide in place of traditional heavy metal catalysts. The field of nanocatalysis (which involves a substance or material with catalytic properties that possesses at least one nanoscale dimension, either externally or in terms of internal structures) is undergoing an explosive development. Nanocatalysis can help design catalysts with excellent activity, greater selectivity, and high stability. These characteristics can easily be achieved by tailoring the size, shape, morphology, composition, electronic structure, and thermal and chemical stability of the particular nanomaterial[7].

Different methods have been described for the preparation of 3-carboxycoumarins, but, there is no report on green methodology, yet. Therefore, we wish to report a developed green protocol for the synthesis of substituted 3-carboxycoumarins from salicylaldehyde and Meldrum's acid using polymeric magnetic nanocatalyst as a catalyst in ethanol at room temperature.




**Scheme 1.** Synthesis of substituted coumarins.

## 2. Experimental

### General

All the solvents, chemicals and reagents were purchased from Merck, Fluka and Aldrich. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellet.

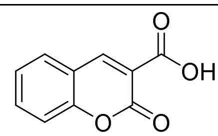
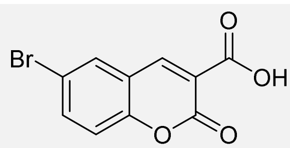
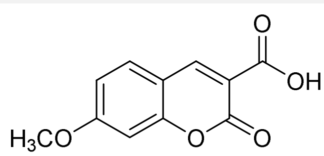
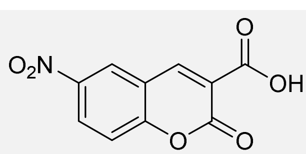
### General procedure for the synthesis of 3-carboxycoumarins

A mixture of the salicylaldehyde (1 mmol), and Meldrum's acid ( 1 mmol) in the presence of polymeric magnetic nanocatalyst and the reaction mixture was stirred magnetically for 120 min at room temperature until the reaction was completed. The progress of the reaction was monitored by thin layer chromatography (TLC) (ethyl acetate/*n*-hexane, 1/3). After the completion of the reaction the catalyst separated by using an external magnet. The precipitated solid was then collected and recrystallized from ethanol to obtain the pure product.

## 3. Results and discussion

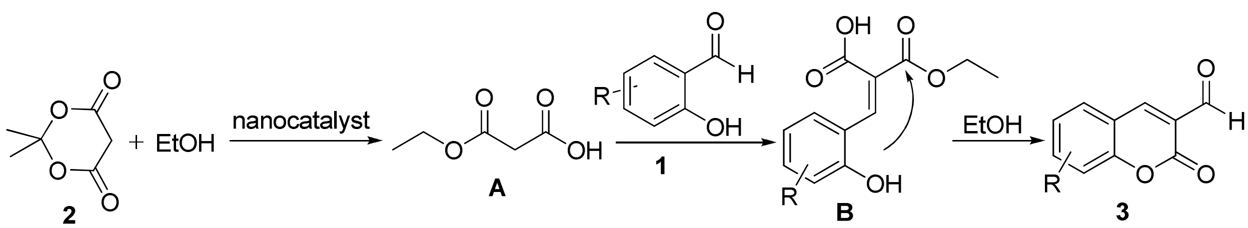
In this work, coumarin derivatives were synthesized by the reaction of salicylaldehyde and Meldrum's acid via polymeric magnetic nanocatalyst. The results are reported in Table 1. The work up procedure of the product was easy as the nanocatalyst can be separated simply by an external magnet. So, this process provides attractive advantages like operational simplicity and environmentally benign nature.

**Table 1.** Synthesis of 3-carboxy coumarins by using nanocatalyst at room temperature.

| Entry | R | Product | Time (min) | Yield (%)[a] | Mp (°C) | |
|---|---|---|---|---|---|---|
| | | | | | Observed | Reported |
| 1 | salicylaldehyde |  **3a** | 120 | 94 | 189-190 | 191-192[8] |
| 2 | 5-bromo salicylaldehyde |  **3b** | 120 | 90 | 196-197 | 195-196 [9] |
| 3 | 4-methoxy salicylaldehyde |  **3c** | 120 | 91 | 191-192 | 192-194 [9] |
| 4 | 5-nitro salicylaldehde |  **3d** | 140 | 92 | 230-232 | 234-235[9] |

[a] Isolated yield

At first, Meldrum's acid reacted with ethanol to give **A** in presence polymeric magnetic nanocatalyst. Then, a Knoevenagel condensation reaction was carried out between **A** and salicylaldehyde to result intermediate **B**. It was followed by a cycloaddition and the rearrangement reactions to form **3**.




**Scheme 2.** Proposed mechanism for the synthesis of 3-carboxy coumarins.

## 4. Conclusions

In summary, polymeric magnetic nanocatalyst is an environmentally friendly and recyclable catalyst which demonstrated to be an applicable catalyst for the synthesis of 3-carboxycoumarins derivatives. This efficient synthesis of 3-carboxycoumarin was carried out from simple and easily accessible precursors including Meldrum's acid and substituted benzaldehydes at room temperature.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