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Preparation and characterization of silica-supported magnetic nanocatalyst and application in the synthesis of 2-amino-4*H*-chromene-4-carboxylate and 2-amino-5*H*-pyrano[3,2-c]chromene-4-carboxylate derivatives

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Abstract: An efficient, one-pot multicomponent procedure for preparation of 2-amino-3-cyano-4*H*-chromene-4-carboxylate and 2-amino-3-cyano-5*H*-pyrano[3,2-*c*]chromene-4-carboxylate using amine-functionalized silica-coated magnetic nanoparticles as a facile prepared, easily recoverable and heterogeneous nanocatalyst was investigated. The catalyst was characterized successfully by Fourier transforms infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses. No significant decrease in catalytic activity is another major point of this reusable nanocatalyst.

Keywords: Nanocatalyst, MCRs, Fe_3O_4, SiO_2, Chromene.

Introduction

Benzopyrans or chromenes are one of the most important privileged medicinal pharmacophore classes which appear as an abundant structural component in natural compounds and generated great attention, because of their interesting biological activities. They are heterocyclic ring systems consisting of a benzene ring fused to a pyran ring. It is well known that certain natural and synthetic chromene derivatives possess important biological activities such as antitumor, antivascular, antimicrobial, antioxidant, TNF-α inhibitor, antifungal, anticoagulant, antispasmolytic, estrogenic, antiviral, anti-helminthic, anticancer, anti-HIV, antitubercular, anti-inflammatory, herbicidal, analgesic and anticonvulsant activity [1]. Most of the methods reported for the synthesis of these valuable compounds suffer from one or more drawbacks such as harsh reaction conditions, low yields, long reaction times or expensive catalysts [2,3].

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 [4].

In continuation of our research on the introduction of new recoverable nanocatalysts in organic synthesis [5,6], in this work, we report convenient and facile multicomponent, one-pot synthesis of 2-amino-4*H*-chromene-4-carboxylate and 2-amino-5*H*-pyrano[3,2-*c*]chromene-4-carboxylate derivatives **4** via the condensation of 1,3-dicarbonyl compounds or 4-hydroxy coumarine **1**, dimethyl acetylenedicarboxylate (DMAD) or diethyl acetylenedicarboxylate **2** and malononitrile **3** in the presence of amine-functionalized silica-coated magnetic core-shell nanostructure as an efficient, eco-friendly, superparamagnetic and heterogeneous catalyst (Table 1).

Experimental

General

All solvents, chemicals and reagents were purchased from Merck and Aldrich chemical companies. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

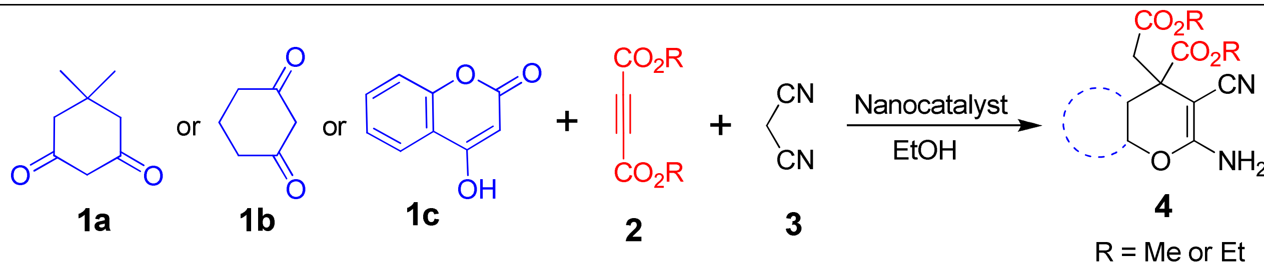
Synthesis of chromene derivatives

A reaction mixture of a 1,3-dicarbonyl compounds or 4-hydroxycoumarine **1** (1 mmol), dimethyl acetylenedicarboxylate (DMAD) or diethyl acetylenedicarboxylate **2** (1 mmol) and malononitrile **3** (1 mmol), were added to EtOH (5 mL) including nanocatalyst; and stirred at 60 °C for the appropriate time. After completion of the reaction (TLC monitoring), the catalyst was separated easily by an external magnet and reused as such for the next experiments.

Results and discussion

In this work, we have prepared different chromene derivatives by catalytic amount of the amine-functionalized silica-coated magnetic nanocatalyst. The results are collected in Table 1. The workup procedure of the product was easy as the nanocatalyst can be separated simply by an external magnet. So, this process offers convenient preparation of chromene derivatives in presence of the environmentally friendly and reusable magnetic nanocatalyst.

Table 1. One-pot synthesis of chromene derivatives by using amine-functionalized magnetic nanocatalyst.



Product	1,3-Dicarbonyl compound	R	Mp (°C)	
			Observed	Reported
4a	**1a**	Me	182-184	180-182 [7]
4b	**1a**	Et	231-233	229-232 [8]
4c	**1b**	Me	136-137	136-138 [7]
4d	**1b**	Et	118-121	118-120 [9]
4e	**1c**	Me	204-207	205-207 [10]
4f	**1c**	Et	208-210	208-210 [10]

Conclusions

In summary, we have simply prepared an amine-functionalized silica-coated magnetic nanostructure and developed a simple, green and extremely efficient protocol for the synthesis of chromene derivatives in presence of the mentioned environmentally friendly and reusable magnetic nanocatalyst.

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