



Formation of benzoxanthenones and benzochromenones via cerium-impregnated-MCM-41 catalyzed, solvent-free, three-component reaction and their biological evaluation as anti-microbial agents

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ABSTRACT

We report here, three-component condensation reaction of naphthols, aldehydes and 1,3-dicarbonyl compounds catalyzed by Ce-MCM-41 under solvent-free conditions. Several advantages can be perceived using this eco-friendly protocol such as, a green and cost-effective procedure with excellent yield, shorter reaction time, simpler work-up, recovery and reusability of solid acid heterogeneous catalyst and tolerance towards a wide range of functional groups. We also report here the anti-microbial activities of the new compounds. Particularly, it was found that the new compounds have shown promising effect on Pseudomonas infections.

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1. Introduction

The central theme in the present day organic synthesis predominantly encompasses the carbon–carbon (C–C) and carbon–heteroatom (C–X) bond forming and bond breaking reactions. These reactions are often mediated by an efficient catalyst system. The development of simple, practical and eco-friendly processes usually involves the assistance of a new reagent or a new catalyst for improving the rate as well as yield of a reaction. Structural diversity and complexity can possibly be achieved by formulating reaction sequences that allow minimum number of steps for synthesizing compounds [1]. Enormous potential

of multicomponent procedures in organic synthesis has opened up new avenues and vistas for augmenting these aspects [2]. Hence, the need of the hour is to develop inorganic solid materials for facilitating simple product isolation, catalyst recovery, reuse and reduction of waste by-products [3]. Multicomponent reactions, over a period of time, have been utilized extensively for the preparation of diverse range of chemical libraries of heterocyclic compounds [4]. These methodologies have effectively demonstrated their versatility in synthesizing various important biologically active compounds. These include Hantzsch reaction [5], Biginelli reactions [6], Schopf's tropinone synthesis [7], Tietze's reaction [8], Ugi [9] and Mannich type reactions [10].

Xanthenes represent the most common structural motifs found in several natural products and synthetic bioactive compounds. Xanthenes, benzoxanthenes and benzochromenones form a distinct class of compounds having diverse applications in dyes [11], as fluorescent agents [12] and in laser technologies [13]. They also display a wide range of biological and therapeutic properties such as analgesic [14], anti-inflammatory [15], antibacterial [16], antiviral [17]

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and non-peptidic inhibitor properties etc. [18]. The predominant route adopted in this process involves an ortho-quinone methide [o-QM] intermediate and its interaction with carbon nucleophiles [19]. It has been reported that these intermediates mainly interact with various dienophiles via [4+2] cycloaddition reactions [20]. Xanthenes and benzoxanthenes are usually formed by an in situ trapping of the o-QM with carbon nucleophiles like phenols and naphthols.

During the past decade, the scope of three-component condensation of 2-naphthol, aldehyde and 1,3-dicarbonyl compounds has been explored by the use of a wide range of solid catalysts and inorganic salts. These predominantly include the inorganic compounds; namely, BF_3 , Et_2O [21], I_2 [22], $\text{HClO}_4\text{-SiO}_2$ [23], HClSO_3 [24] and inorganic salts such as InCl_3 [25], $\text{Zr}(\text{HSO}_4)_4$ [26], $\text{Sr}(\text{OTf})_2$ [27], Caro's acid-silica [28], tungstophosphoric acid [29], CAN [30] and Ce (IV) salts [31]. Some of the organic acids like PTSA [32], TBAF [33], sulfamic acid [34], cyanuric acid [35] and $\text{N,N}'$ -dibromo- $\text{N,N}'$ -1,2-ethanediy-bis(p-toluenesulfonamide) [36] have also been reported. Most of such solid acid catalyzed reactions often involve elongated reaction time, drastic reaction conditions and formation of non-desirable side products. The intrinsic reaction conditions preferably utilize strong acidic media, high reaction temperatures and stoichiometric ratios resulting in tedious work-up and purification processes. Thus, there is tremendous scope for the development of new greener synthetic protocols to assemble such frameworks.

The inherent properties of mesoporous materials such as, their tuneable pore size and acid-base sites have been utilized for widespread applications in catalysis [37]. MCM-41 [38] and SBA-15 [39] have demonstrated exceptional properties by virtue of their hexagonal pore array arrangement and narrow pore size distribution [40]. It was observed from the literature that the Ce(IV) derivatives have shown better catalytic activity among other catalysts such as FeCl_3 , SnCl_4 , ZnCl_2 and AlCl_3 are normally employed as single-electron oxidants [30]. The commercial availability, ease of handling and inexpensive ceric ammonium nitrate (CAN) in carbon-carbon and carbon-heteroatom bond forming reactions has recently attracted much attention [41]. The catalyst, Ce-MCM-41, has received considerable attention due to its low toxicity, cost effectiveness, air and water compatibility, ease of handling, good reactivity, experimental simplicity and remarkable ability to suppress side reactions in acid sensitive substrates [42]. Recently, we have explored the activity of Ce-MCM-41 catalyst towards the regioselective dual C-H bond activation under heterogeneous conditions [42b]. In furtherance of our studies, we report the use of cerium containing MCM-41 as a heterogeneous and reusable catalyst for the multicomponent one pot synthesis of benzoxanthenones.

2. Experimental

2.1. Instrumentation

The thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates using ethyl acetate and hexane as eluting agents. Thin layer chromatography plates were visualized by exposure to UV-light/iodine and/or by immersion in an acidic staining solution of phosphomolybdic acid followed by heating on a hot plate. Purification of products was carried out by column chromatography using silica gel and a mixture of ethyl acetate and hexane as eluting agent. All the products were characterized by mass, ^1H and ^{13}C NMR spectroscopy. The NMR spectra of samples were acquired on a Varian Unity Inova 500 MHz, Inova 400 MHz and Bruker Avance 300 MHz spectrometer using TMS as an internal standard in CDCl_3 and DMSO. Mass spectra were acquired on a Thermo LCQ fleet ion trap mass spectrometer. High resolution mass

spectra were acquired on a Q STAR XL Hybrid LC/MS/MS system, Applied Biosystems, USA. FT-IR data were acquired on a Thermo Nicolet Nexus 670 FT-IR spectrometer with DTGS KBr detector. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode apparatus using the Mg $\text{K}\alpha$ anode. X-ray powder diffraction data was collected on a Siemens/D-5000 diffractometer using Cu $\text{K}\alpha$ radiation. Pore size distribution measurements were performed on Auto sorb-1 instrument (Quanta chrome, USA) using by nitrogen physisorption. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscopy (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. Diffuse reflectance UV/vis spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV-vis spectrometer in the range 200–800 nm with a scan speed 400 nm/min.

2.2. Synthesis of catalyst (Ce-MCM-41)

The pure MCM-41 was prepared by direct hydrothermal method described in the previously reported procedures [43] and was activated by heating in oven prior to use. The cerium-loaded mesoporous material MCM-41, designated by Ce-MCM-41, was prepared by a wet impregnation method using aqueous solution of ceric ammonium nitrate [44]. To 10 mL of an aqueous solution of ceric ammonium nitrate (0.12 g, 0.02 M), the MCM-41 (calcined) support (0.21 g) was added and stirred vigorously for 24 h at room temperature. The pale yellow solid, obtained after evaporation of the solvent, was dried overnight at 100 °C and then again calcined at 500 °C in air for 5 h to obtain Ce-MCM-41 with (0.247 g) 75% yield. The EDX analysis result showed the presence of cerium, oxygen and silicon at 14.97 wt%, 55.18 wt% and 29.85 wt%, respectively, which indicates the formation of ceric ion functionalized MCM-41. All the characterization studies were carried out with 15 wt% Ce-MCM-41.

2.3. General procedure for the synthesis of benzoxanthenone

In a 25 mL round-bottom flask, aldehyde (1 mmol), naphthol (1 mmol), 1,3 diketone (1 mmol) and Ce-MCM-41 (1.7 mol %) were taken. The reaction mixture was stirred at 80 °C under solvent-free conditions for 30–50 min. The reaction was monitored by TLC and on completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dissolve all organic components and filtered to remove catalyst. The filtrate was concentrated and purified by silica gel column chromatography.

3. Results and discussion

In the present work, we demonstrate Ce-MCM-41 as an inexpensive, highly efficient, heterogeneous and reusable solid acid catalyst for the preparation of aryl benzoxanthenone derivatives under mild reaction conditions. In recent years, solvent-free reactions have been explored extensively [45]. This convention offers several advantages such as higher yield, shorter reaction time, simpler work-up, recovery, reusability of catalyst and tolerance towards a wide range of functional groups with no side products. In continuation of our work on the applications of heterogeneous catalysts for organic reactions [42b], we intend to utilize Ce-MCM-41 as a promising candidate to perform the condensation of naphthols, aldehydes with 1,3-dicarbonyls (Scheme 1).

The improved ability of Ce-MCM-41 in the catalytic one pot multicomponent reaction is attributed to the inherent high surface area of the mesoporous catalyst that offers enough space for organic substrates to interact with active acidic sites present on the solid surface inside the ordered mesopore [37]. In addition, compared with pure MCM-41, a decrease in BET surface area, pore volume and

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