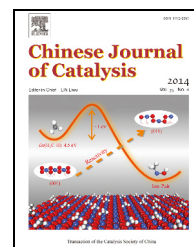


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Article

A facile, green, one-pot synthesis of amidoalkyl naphthols under solvent-free conditions catalyzed by a carbon-based solid acid

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ABSTRACT

An efficient, environmentally friendly procedure for the synthesis of amidoalkyl naphthols through the one-pot, three-component reaction of β -naphthol, aryl aldehydes, and acetamide in the presence of a carbon-based solid acid under thermal solvent-free conditions is described. The beneficial features of this new synthetic approach include short reaction time, high yields, clean reaction profiles, and a simple work-up procedure. Furthermore, the catalyst can be readily recycled and reused four times without obvious significant loss of activity. The structure of the catalyst was confirmed by Fourier transform infrared spectroscopy, N_2 adsorption/desorption analysis, and X-ray diffraction.

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1. Introduction

The increasing focus on environmental protection over the last few decades has led both academic and industrial researchers to develop chemical processes which maximize yield and minimum cost while using non-toxic reagents, solvents and catalysts or solvent-free conditions [1,2]. One of the tools used to attain both economic and environmental goals is the multi-component reaction (MCR) strategy. MCRs have attracted much interest and are highly regarded in modern organic synthesis and medicinal chemistry because they are one-pot processes that bring together three or more components and show high atom economy and high selectivity [3–5]. MCRs have been widely used in the convergent synthesis of complex and important organic molecules from simple and readily available starting materials, and have emerged as powerful tools for drug discovery [6,7]. The development of new MCRs and improvement of known MCRs are therefore areas of considerable current interest. One such reaction is the synthesis of amidoalkyl

naphthols. These compounds are generally synthesized via the three-component reaction of an aldehyde, an amide, and β -naphthol in the presence of various catalysts, such as iodine [8,9], $K_5CoW_{12}O_{40} \cdot 3H_2O$ [10], sulfamic acid [11], thiamine hydrochloride [12], $Yb(OTf)_3$ in $[bmim][BF_4]$ [13], molybdophosphoric acid [14], copper *p*-toluenesulfonate [15], silica supported methanesulfonic acid [16], $Fe(HSO_4)_3$ [17], $HClO_4 \cdot SiO_2$ [18], nano-sulfated zirconia [19], montmorillonite K10 [20], and $Al(H_2PO_4)_3$ [21]. Although some of these methods have convenient protocols with good to high yields, the majority suffer from at least one of the following disadvantages: unsatisfactory yields, the use of toxic halogenated solvents or catalysts, long reaction time, or the use of expensive catalysts. To avoid these limitations and to improve the reaction conditions available for the synthesis of amidoalkyl naphthols, the exploration of novel methodologies using new heterogeneous and reusable catalysts is still ongoing.

The development of heterogeneous catalysts and the analysis of their effects on specific transformations in chemical syn-

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thesis have become a major area of research. The potential advantages of these materials over homogeneous systems, in terms of their simplified recovery and reusability, could potentially allow for the development of environmentally benign chemical procedures in both academic and industrial settings. Catalysts of this type have the potential to make the processes to which they are applied cleaner, safer, higher-yielding, and relatively inexpensive [22–25]. The toxicity and volatile nature of many organic solvents have posed a serious threat to the environment and thus the design of solvent-free catalytic reactions has received significant attention in the area of green synthesis. In addition, reactions performed in the absence of a solvent typically require shorter reaction time and simpler work-up procedures [26,27].

During the course of our recent studies directed towards the development of practical and environmentally friendly procedures for the synthesis of organic compounds using reusable catalysts [28–37], we investigated the application of a carbon-based solid acid (CBSA). This material is easily prepared by heating naphthalene and concentrated sulfuric acid [38] and represents a potential catalyst for a series of organic transformations. This reusable heterogeneous catalyst performed well and showed a high level of catalytic activity in the Mannich [39] and Biginelli [40] reactions, as well as in the synthesis of tetrasubstituted imidazoles [41]. These findings prompted us to investigate the catalytic activity of this material in the synthesis of amidoalkyl naphthols (Scheme 1).

2. Experimental

2.1. Preparation of CBSA catalyst

Naphthalene (20 g) was heated in concentrated sulfuric acid (> 96%, 200 ml) at 250 °C under a flow of N₂. After heating for 15 h, excess sulfuric acid was removed from the dark brown tar by vacuum distillation at 250 °C for 5 h, resulting in a black solid. The dry solid was subsequently ground to powder and was washed repeatedly in boiling water until impurities such as sulfate ions were no longer detected in the wash water. The density of SO₃H groups in the product was determined by acid-base potentiometric titration with NaOH (0.01 mol/L) and the concentration of SO₃H groups attached to the polycyclic aromatic carbon product was found to be 2.81 mmol/g. The resulting black powder was insoluble in common solvents such as water, methanol, ethanol, benzene, and hexane even at their boiling temperatures [38].

2.2. General procedure for the synthesis of amidoalkyl

naphthols **4a–4j**

A mixture of β-naphthol **1** (2 mmol), an aromatic aldehyde **2a–2j** (2 mmol), acetamide **3** (2 mmol), and CBSA (0.07 g) was heated in an oil bath at 130 °C for 2–20 min while monitoring the reaction process by TLC. Upon completion of the transformation, the reaction mixture was cooled to room temperature and hot ethanol was added. This resulted in the precipitation of the catalyst, which was collected by filtration. The product was collected from the filtrate after cooling to room temperature and subsequently recrystallized from ethanol to give compounds **4a–4j** (Scheme 1). The melting points of the products were determined using a Stuart SMP3 melting point apparatus. The Fourier transform infrared (FT-IR) spectra of the products were obtained in the form of KBr disks with a Tensor 27 Bruker spectrophotometer while ¹H NMR (500 MHz) spectra were acquired on a Bruker 500 spectrometer, with the following results.

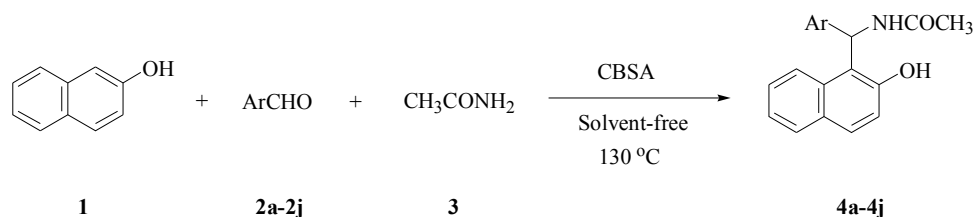
N-[(2-Hydroxynaphthalen-1-yl)(phenyl)methyl]acetamide (**4a**). ¹H NMR (500 MHz, DMSO-d₆): δ 1.95 (s, 3H), 7.05–7.25 (m, 8H), 7.32 (t, 1H, *J* = 7.2 Hz), 7.73 (d, 1H, *J* = 8.8 Hz), 7.77 (d, 1H, *J* = 7.9 Hz), 7.81 (br., 1H), 8.40 (d, 1H, *J* = 8.3 Hz), 9.95 (s, 1H); FT-IR (KBr, cm⁻¹): ν 3408, 3245, 3064, 1639, 1517, 1438, 1370, 1338, 1275, 810, 745.

N-[(4-Bromophenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (**4b**). ¹H NMR (500 MHz, DMSO-d₆): δ 1.97 (s, 3H), 7.04 (s, 1H), 7.10 (d, 2H, *J* = 8.3 Hz), 7.19 (d, 1H, *J* = 8.8 Hz), 7.24 (t, 1H, *J* = 7.4 Hz), 7.37 (t, 1H, *J* = 7.2 Hz), 7.43 (d, 2H, *J* = 8.5 Hz), 7.74 (d, 1H, *J* = 8.8 Hz), 7.79 (d, 2H, *J* = 7.8 Hz), 8.55 (br., 1H), 10.44 (br., 1H); FT-IR (KBr, cm⁻¹): ν 3387, 3064, 2973, 1638, 1516, 1487, 1438, 1370, 1329, 1277, 1072, 1010, 816, 745.

N-[(2-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (**4c**). ¹H NMR (500 MHz, DMSO-d₆): δ 1.88 (s, 3H), 7.03 (d, 1H, *J* = 8.0 Hz), 7.08 (d, 1H, *J* = 8.8 Hz), 7.17–7.32 (m, 4H), 7.36 (t, 1H, *J* = 7.2 Hz), 7.52 (d, 1H, *J* = 7.6 Hz), 7.70 (d, 1H, *J* = 8.8 Hz), 7.75 (d, 1H, *J* = 7.8 Hz), 7.94 (d, 1H, *J* = 8.6 Hz), 8.51 (d, 1H, *J* = 8.0 Hz), 9.75 (s, 1H); FT-IR (KBr, cm⁻¹): ν 3428, 3062, 1650, 1515, 1471, 1438, 1371, 1328, 1269, 809, 753.

N-[(4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (**4d**). ¹H NMR (500 MHz, DMSO-d₆): δ 1.99 (s, 3H), 7.10 (d, 1H, *J* = 8.2 Hz), 7.16 (d, 2H, *J* = 8.3 Hz), 7.22 (d, 1H, *J* = 8.8 Hz), 7.25–7.35 (m, 3H), 7.38 (t, 1H, *J* = 7.3 Hz), 7.78 (d, 1H, *J* = 8.8 Hz), 7.81 (a doublet overlapped with a broad signal, 2H, *J* = 7.5 Hz), 8.46 (d, 1H, *J* = 8.2 Hz), 10.03 (s, 1H); FT-IR (KBr, cm⁻¹): ν 3392, 3053, 2966, 1638, 1515, 1439, 1374, 1332, 1279, 1244, 1092, 820, 748.

N-[(2,4-Dichlorophenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (**4e**). ¹H NMR (500 MHz, DMSO-d₆): δ 1.89 (s, 3H),



Scheme 1. CBSA-catalyzed synthesis of amidoalkyl naphthols.

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