Chinese Journal of Catalysis 34 (2013) 2245–2254

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Article

Silica-bonded *N*-propylpiperazine sodium *n*-propionate as recyclable catalyst for synthesis of 4*H*-pyran derivatives

Khodabakhsh Niknam [a,*], Nassim Borazjani [a], Reza Rashidian [a], Abbas Jamali [b]

[a] *Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Iran*
[b] *Presian Gulf Reaserch and Studies Center, Persian Gulf University, Bushehr 75169, Iran*

ARTICLE INFO

Article history:
Received 30 June 2013
Accepted 21 August 2013
Published 20 December 2013

Keywords:
Silica-bonded *n*-propylpiperazine sodium *n*-propionate
Heterogeneous solid base catalyst
Aldehyde
4*H*-Pyran derivative
Malononitrile

ABSTRACT

Silica-bonded *N*-propylpiperazine sodium *n*-propionate (SBPPSP) was found to act as an efficient solid base for the preparation of a series of 4*H*-benzo[b]pyran derivatives. SBPPSP was used as a recyclable heterogeneous solid base catalyst for the synthesis of 3,4-dihydropyrano[c]chromenes, 2-amino-4*H*-pyrans, 1,4-dihydropyrano[2,3-c]pyrazoles, and 2-amino-4*H*-benzo[e]-chromenes via the condensation reaction of dimedone, ethyl acetoacetate, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, and α-naphthol, respectively, with aromatic aldehydes and malononitrile in refluxing aqueous ethanol. The heterogeneous solid base showed similar efficiency when reused in consecutive reactions.

1. Introduction

The development of environmentally benign, efficient, and economical methods for the synthesis of biologically interesting compounds remains a significant challenge in synthetic chemistry. Multi-component reactions have become very popular in the discovery of biologically active novel compounds because of simple experimentation, atom economy, and high yields of the products [1].

2-Amino-4*H*-pyran derivatives represent an important class of compounds. They are often used in cosmetics, pigments, and as potentially biodegradable agrochemicals [2,3]. Polyfunctionalized 4*H*-pyrans also constitute a structural unit of many natural products [4,5] and biologically interesting compounds that possess various pharmacological activities [6], such as antiallergic [2], antitumor [7], and antibacterial properties [8–10]. 4*H*-Pyran derivatives are also potential calcium channel antagonists [11] and are structurally similar to biologically active 1,4-dihydropyridines.

Base-catalyzed condensation and addition reactions are important in the industrial production of drugs, fragrances, and chemical intermediates [12–17]. In addition, solid base catalysts are also used particularly for asymmetric organic syntheses [18,19], other organic syntheses [20–23], and characterization of active centers [24]. The potential uses of microporous and mesoporous base catalysts in fine chemical production are very promising [25]. These heterogeneous catalysts are known to suppress side reactions, which include self-condensation and oligomerization, resulting in better selectivity and product yield. This approach also avoids the complex neutralization and separation steps needed to recover the homogeneous base catalysts from the reaction mixture. Heterogeneous catalysts hold advantages over conventional homogeneous catalysts because they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation, thereby making the process more economically viable. Recently, we

* Corresponding author. Tel: +98-771-4541494; Fax: +98-771-4545188; E-mail: niknam@pgu.ac.ir, khniknam@gmail.com
DOI: 10.1016/S1872-2067(12)60693-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 12, December 2013

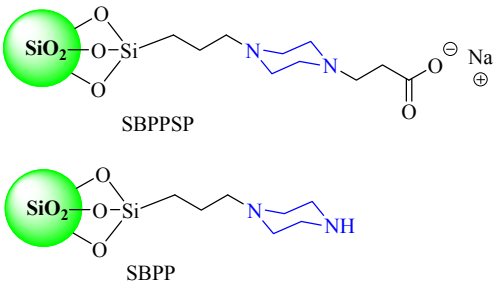


Fig. 1. Proposed structure for SBPPSP and SBPP.

prepared silica-bonded *N*-propylpiperazine sodium *n*-propionate (SBPPSP) as a solid base catalyst for the synthesis of 3,4-dihydropyrano[c]chromenes [26] (Fig. 1). In addition, silica-bonded *N*-propylpiperazine (SBPP) and SBPPSP were used as support to immobilized of Pd nanoparticles for catalyzing C–C bond formation in Heck, Suzuki, and Sonogashira couplings, and in cyanation reactions [27–29]. We report here the application of SBPPSP as a heterogeneous and recyclable solid base catalyst for the preparation of a series of 4*H*-benzo[b]pyran derivatives (Scheme 1).

2. Experimental

2.1. General

Chemicals were purchased from Fluka, Merck, and Aldrich. All products were characterized by comparison of their infrared (IR), ^{1}H nuclear magnetic resonance (NMR), and ^{13}C NMR spectroscopic data and their melting points (mp) with the reported values [24–66]. SBPP was prepared according to previously reported procedures [26,30].

2.2. Catalyst preparation

2.2.1. Preparation of silica-bonded propylpiperazine methyl N-propionate (SBPPMP)

To a magnetically stirred mixture of 3-piperazine-*N*-propylsilica (25 g) in methanol (50 mL), methyl acrylate (25 mL) was added and heated at 40–50 °C for 48 h under N_2. The mixture was filtered and washed with methanol (2 × 50 mL) and dried for 8 h under vacuum to afford SBPPMP as a white powder (26.6 g). Elemental analysis: C 13.47%, H 2.28%, and N 2.18%.

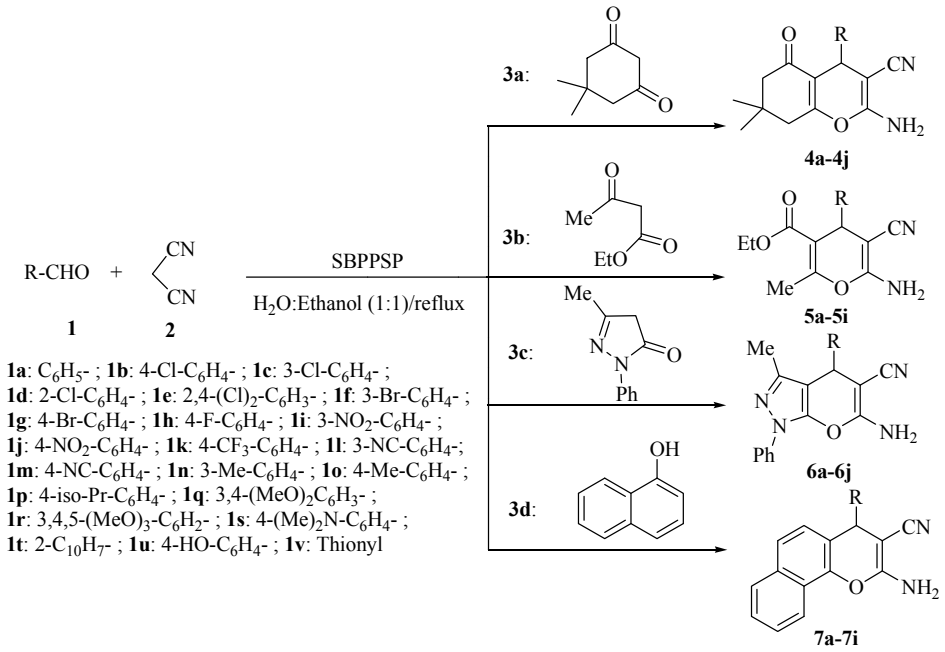
2.2.2. Preparation of SBPPSP

A magnetically stirred mixture of SBPPMP (26.6 g) was treated with HCl (0.5 mol/L, 50 mL). The mixture was filtered and dried overnight under vacuum [26]. Subsequently, the mixture was treated with saturated $NaHCO_3$ solution (50 mL) for 2 h. Then the mixture was filtered and dried overnight under vacuum to afford SBPPSP as a white powder (26.7 g). Elemental analysis: C 13.72%, H 2.30%, and N 2.78% [26].

The pH of the prepared SBPPSP was determined using a pH-ISE conductivity titration controller (Denver Instrument Model 270). The pH was 10.82 for 0.1 g of the solid base at 25 °C [26].

2.3. General procedure for synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromenes

To a mixture of aromatic aldehyde (1 mmol), malonitrile (1 mmol), and dimedone (1 mmol) in 3 mL of aqueous ethanol (1:1), SBPPSP catalyst (0.05 g, 4.3 mol%) was added, and the mixture was refluxed for an appropriate time. After completion of the reaction, as indicated by thin-layer chromatography (TLC), ethanol (10 mL) was added, and the reaction mixture was filtered. The residue was washed with warm ethanol (3 × 5 mL) to separate the heterogeneous catalyst. After cooling, the crude product was precipitated and then purified by recrystal-



Scheme 1. Synthesis of 4*H*-pyran derivatives in the presence of SBPPSP.