



Polystyrene-supported ionic liquid copper complex: A reusable catalyst for one-pot three-component click reaction



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ABSTRACT

Copper(II) complex of 1,2-bis(4-pyridylthio)ethane immobilized on polystyrene was used as a highly stable, active, reusable and green catalyst for click synthesis of 1,2,3-triazoles via one-pot three-component reaction of organic halides, sodium azide and alkynes. The catalyst was characterized by FT-IR spectroscopy, thermogravimetric analysis, elemental analysis, field emission scanning electron microscopy, energy dispersive X-ray, transmission electron microscopy and elemental analysis. High selectivity, broad diversity of organic halides or α -bromoketones and alkyl/aryl terminal alkynes, and excellent yields of the products were obtained using 0.2 mol% of catalyst. This catalytic system also showed excellent activity in the synthesis of bis-1,4-disubstituted 1,2,3-triazoles. Moreover, the catalyst could be recycled and reused for seven cycles without any decrease in its catalytic activity.

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1. Introduction

The use of transition metal complexes as catalyst has rapidly increased in recent years because of their ability to catalyze a wide range of chemical transformations [1]. Among them, Cu(II) complexes have long been found as effective catalysts in a variety of organic synthesis [2]. Due to their low cost, high activity and selectivity, these complexes have also found numerous industrial such as dehydrogenation of alcohols [3], methanol synthesis [4], production of hydrogen in fuel cells [5].

In last decade, the copper complexes have attracted much attention in click chemistry. Click chemistry, first introduced by the groups of Meldal [6] and Sharpless [7], describes a new concept for conducting organic reactions. Based upon the premise, organic synthesis should take advantages such as being modular, stereospecific, high-yielding and involving simple and green protocols [8]. Preparation of 1,2,3-triazoles by copper-catalysed alkyne-azide cycloaddition (CuAAC) has emerged as a prominent “Click” chemistry [9–11]. 1,2,3-Triazoles have received considerable attention in synthetic organic chemistry due to their numerous biological and

pharmaceutical activities such as anti-HIV [12–14], antibacterial [15–17], and antiallergic [18] properties.

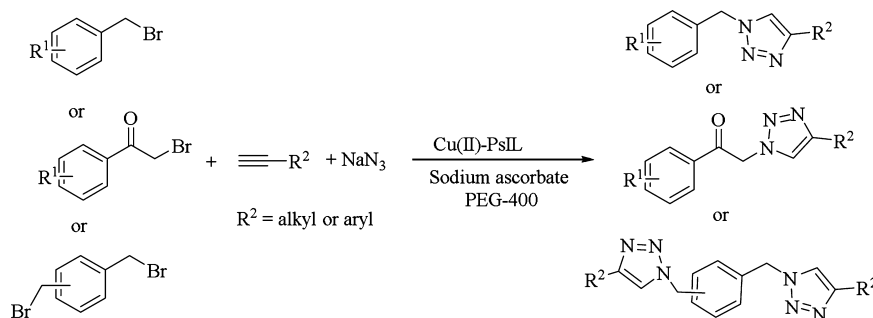
The typical procedure for synthesis of 1,2,3-triazoles is Huisgen [3+2] cycloaddition of organic azides and terminal alkynes in the presence of copper catalysts [19]. However, the early Huisgen cycloaddition process required a strong electron-withdrawing substituent on either azide or alkyne and high temperature for a prolonged period of time, and often afforded a mixture of 1,4- and 1,5-disubstituted isomers. [20,21] During the past decades, alternative copper-catalysed processes have represented a significant advance in regioselective synthesis of 1,2,3-triazoles [22–25]. In the first report of this reaction, the active Cu(I) species (CuI, CuBr) were directly formed from Cu(I) salts in the presence of ligands [26]. Because of the instability of Cu(I) salts, Cu(I) was prepared *in situ* via reduction of different Cu(II) salts (CuCl₂, CuBr₂ or CuSO₄) [27–30] with ascorbate or by comproportionation of Cu(0) nano size clusters and Cu(II) [31,32]. Nevertheless, the preparation of copper immobilized on supports such silica [33], Zeolite [34] and magnetic nanoparticles have become increasingly more profitable from easy recovery and economical viewpoints [35].

However, long reaction times, high temperature, formation of homocoupling products of alkynes (Glaser coupling) and the use of large amounts of copper are the limitations and drawbacks of many of the previously reported methods [36,37]. Therefore, the development of a reusable, eco-friendly and more convenient catalyst for the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles is still in demand.

Abbreviations: Ps, Polystyrene; PsIL, Polystyrene supported ionic liquid; Cu(II)-PsIL, Polystyrene supported ionic liquid copper complex.

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Scheme 1. Click reaction catalysed by Cu(II)-PsIL.

Accordingly, various procedures for the preparation of 1,4-disubstituted 1,2,3-triazoles through the *in situ* generation of organic azides have been developed. [38,39] But, only a few reports are available dealing with the synthesis of *bis*-1,4-disubstituted 1,2,3-triazoles [40].

Ionic liquids are able to dissolve and stabilize copper salts for regioselective click reaction [41]. But they have some disadvantages such as difficulties in reusability of catalyst and product isolation, which make them economically and environmentally unfavorable. Thus, the ionic liquid supported species can solve this serious drawback [42].

Polystyrene as a solid support has gained substantial popularity, due to its low cost, ready availability, chemical inertness, and facile functionalization [43].

These results in combination with our efforts on the development of efficient copper catalysts for organic transformations [44–46], prompted us to report a green, convenient and regioselective method for synthesis of mono- and *bis*-1,4-disubstituted 1,2,3-triazoles in the presence of Cu(II) immobilized on polystyrene supported ionic liquid as a reusable catalyst (Scheme 1).

2. Experimental

2.1. General remarks

The chemicals were purchased from Fluka and Merck chemical companies. FT-IR spectra were recorded on a JASCO 6300D spectrophotometer. ^1H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer using CDCl_3 as solvent. Elemental analysis was performed on a LECO CHNS-932 analyzer. Thermogravimetric analysis (TGA) was carried out on a Mettler TG50 instrument under air flow at a uniform heating rate of $10^\circ\text{C min}^{-1}$ in the range 30–600°C. The scanning electron micrographs were taken on a Hitachi S-4700 field emission-scanning electron microscope (FE-SEM). The transmission electron microscopy (TEM) was carried out on a Philips CM10 transmission electron microscope operating at 100 kV. The copper content of the catalyst was determined by a Jarrell-Ash 1100 ICP analysis. The CV measurements were carried out on Autolab Potentiostat/Galvanostat 101 instrument controlled by Nova 1.8 Software (Eco Chemie, Utrecht, the Netherlands).

2.2. Synthesis of 1,2-bis(4-pyridylthio)ethane, (1)

A mixture of 4-bromopyridinium chloride (5.1 mmol, 1 g), 1,2-ethanedithiol (0.3 mL, 3.5 mmol) and sodium hydroxide (7.7 mmol, 0.3 g) in 10 mL of DMF was stirred at 80°C for 24 h. The reaction progress was monitored by TLC (eluent diethyl ether/ methanol, 2:1). The mixture was diluted with water and EtOAc. The aqueous layer was extracted, and evaporated under reduced pressure. Then,

residue was purified by recrystallization from ethanol to afford the pure product.

2.3. Immobilization of 1,2-bis(4-pyridylthio)ethane on polystyrene, (2)

In a round-bottomed flask equipped with a condenser and a magnetic stirrer bar, a mixture of chloromethylated polystyrene (1), (1 g) and 1,2-bis(pyridylthio) ethane, (0.1 g, 0.4 mmol) in DMF (10 mL) was stirred at 80°C for 24 h. Then, the reaction mixture was filtered and the resulting solid washed with ethanol (2×20 mL) and dried in a vacuum oven at 50°C.

2.4. Synthesis of polystyrene supported ionic liquid (PsIL), (3)

To a slurry of polystyrene-bound 1,2-bis(4-pyridylthio)ethane (2) (1 g) in toluene (10 mL) was added methyl iodide (5 mL) and stirred at room temperature for 6 h. Then, the mixture was filtered; the precipitate was washed with ethanol (2×20 mL) and dried in a vacuum oven at 50°C.

2.5. Immobilization of Cu(II) triflate on PsIL, (Cu(II)-PsIL), (4)

A mixture of $\text{Cu}(\text{OTf})_2$ (15 mg) and PsIL, (3), (1 g) in ethanol (10 mL) was refluxed for 24 h. The reaction mixture was filtered; the solid material was washed with ethanol (2×20 mL) and then dried in a vacuum oven at 40°C to afford the Cu-PsIL catalyst.

2.6. Electrochemical studies

The cyclic voltammograms (CVs) were recorded at 25°C using a three-electrode assembly including, an Ag/AgCl (3 M KCl) reference electrode, a large area Pt plate as the counter electrode (70 times larger than that of the working electrode), and the modified glassy carbon electrode (GCE) disk as the working. Toward the study of electrochemical behavior of Cu(II)-PsIL, the catalyst was casted on the GCE surface. CVs were recorded in acetate buffer electrolyte ($\text{pH} = 5$) at a potential scan rate of 10 mV s^{-1} .

2.7. General procedure for synthesis of 1,2,3-triazoles by the reaction of benzyl bromides, alkynes and sodium azide

A mixture of Cu(II)-PsIL (0.2 mol%, 10 mg) and sodium ascorbate (5 mg) in PEG-400 (2 mL) was allowed to stirrer for 2 min and then, benzyl bromide (1 mmol), sodium azide (1.2 mmol) and alkyl/phenyl acetylene were added to mixture. The reaction mixture was stirred at 65°C and its progress was monitored by TLC (eluent diethyl ether/ethyl acetate, 2:1). After completion of the reaction, water and ethyl acetate were added; the catalyst was separated by filtration and washed with acetone and water, and dried under vacuum. The organic layer was separated and dried

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