Supporting information

Synthesis of 4,8-dihydro-1H-pyrazolo[3,4-e][1,4]thiazepin -7(6H)-one derivatives by solid acid-catalyzed multi-component reaction in water

Furen Zhang,* Chunmei Li and Chenze Qi*

School of Chemistry and Chemical Engineering, Zhejiang Key Laboratory of Alternative Technologies for Fine Chemicals Process, Shaoxing University, Shaoxing, Zhejiang Province 312000, China. Email: frzhang@usx.edu.cn (F. R. Zhang) qichenze@usx.edu.cn (C. Z. Qi)

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Materials and Methods. All commercially available chemicals were used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm\(^{-1}\). NMR-data were recorded on Bruker Avance 400 Spectrometer. \(^1\)H- and \(^13\)C-spectra were referenced to the residue solvent signals in the deuterated solvent. \(^1\)H NMR spectra were recorded on a 400 MHz instrument. Chemical shifts (\(\delta\)) are given in ppm relative to TMS as the internal reference, with coupling constants (\(J\)) in Hz. \(^13\)C NMR spectra were recorded at 100 MHz. Chemical shift were reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. HRMS (ESI) was measured with a Bruker Daltonics APEXII instrument.

Preparation and characterization of the solid acid (C-SO\(_3\)H) catalyst

Fig. 1. The preparation of the carbon functionalized material

According to literature method,\(^1\) the polyvinyl alcohol (5.0 g), hydroxyethylsulfuric acid (3.5 g) and deionized water (50 mL) was mixed in Teflon-lined stainless steel autoclaves, which was heated at 180 °C for 4 h. Then, the resulting mixture were filtered, washed with water and methanol, and dried in a vacuum oven at 100 °C for 4 h. The goal product was obtained as black solid with 50% yield according to polyvinyl alcohol (Fig. 1).

The acidity of the sulfonated carbonaceous materials was 2.4 mmol/g by neutralization titration. According to XPS analysis, the S content of 7.6% indicated almost all the S existed in the forms of sulfonic acid groups and the O content was as high as 24% indicated that many oxygen-containing groups besides the carbonyl acid groups were exist. The BET surface of the solid acid was 146 m\(^2\)/g. The 1040 and 1195 cm\(^{-1}\) absorbability of IR spectra indicated the existence of the sulfuric acid groups. FT-IR spectra showed that the sulfonated carbonaceous materials contains resident functionalities such as hydroxyl (3500 cm\(^{-1}\)), carboxylate (1704 cm\(^{-1}\)), C=C groups (1604
cm$^{-1}$) and C-O groups (1204 cm$^{-1}$).

**General procedure for synthesis of 4,8-dihydro-1$H$-pyrazolo [3,4-e][1,4]thiazepin-7(6$H$)-one derivatives (4)**

3-Methyl-1$H$-pyrazol-5-amine (1, 1.0 mmol) was added to a 10-mL reaction vial in water (3.0 mL), to the resulting solution were sequentially added aldehydes (2, 1.0 mmol), thioglycollic acid (3, 1.0 mmol), and C-SO$_3$H (10 mg). The mixture was stirred at the indicated temperature until TLC showed that the conversion of the substrates was complete about 5-6 h. Then, the mixture was cooled to room temperature and the solid was filtered. The result solid was resolved in hot ethanol, filtered, and the mother liquor was concentrated and recrystallized to give goal products (4).

**General procedure for synthesis of 2-(((2,4-diamino-6-oxo-1,6-dihydropyrimidin-5-yl)(p-tolyl)methyl)thio)acetic acid (5)**

2,6-Diaminopyrimidin-4(3$H$)-one (1c, 1.0 mmol) was added to a 10-mL reaction vial in water (3.0 mL), to the resulting solution were sequentially added 4-methylbenzaldehyde (2o, 1.0 mmol), thioglycollic acid (3, 1.0 mmol), and C-SO$_3$H (10 mg). The mixture was stirred at the indicated temperature until TLC showed that the conversion of the substrates was complete about 6 h. Then, the mixture was cooled to room temperature and the solid was filtered. The result solid was resolved in hot ethanol, filtered, and the mother liquor was concentrated and recrystallized to give product (5).

**General procedure for synthesis of ethyl 2-(((5-amino-3-methyl-1-phenyl-1$H$-pyrazol-4-yl)(aryl)methyl)thio)acetate (7)**

3-Methyl-1-phenyl-1$H$-pyrazol-5-amine (1a, 1.0 mmol) was added to a 10-mL reaction vial in water (3.0 mL), to the resulting solution were sequentially added aromatic aldehydes (2, 1.0 mmol), thioglycollic acid (3, 1.0 mmol), ethanol (6, 3.0 mmol), and C-SO$_3$H (10 mg). The mixture was stirred at the indicated temperature until TLC showed that the conversion of the substrates was complete about 6 h. Then, the mixture was cooled to room temperature and the solid was filtered. The result solid was resolved in hot ethanol, filtered, and the mother liquor was concentrated. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (ethyl acetate/petroleum ether = 1:20–1:4) to provide desired product (7).

**References**
$^1$H and $^{13}$C NMR Spectra