

Copper Ferrite super magnetic nano-catalysed synthesis of 6-Amino-3-methyl-4-(substituted-phenyl)-2, 4- dihydro-pyrano-[2, 3-c] pyrazole-5-carbonitrile

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Manuscript Details

Available online on <http://www.irjse.in>
ISSN: 2322-0015

Editor: Dr. Arvind Chavhan

Cite this article as:

Suryavanshi AW. Copper Ferrite super magnetic nano-catalysed synthesis of 6-Amino-3-methyl-4-(substituted-phenyl)-2, 4- dihydro-pyrano-[2, 3-c] pyrazole-5-carbonitrile, *Int. Res. Journal of Science & Engineering*, 2018; Special Issue A5: 123-126.

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ABSTRACT

A series of 6-Amino-3-methyl-4-(3-substituted-phenyl)-2,4 dihydro-pyrano-[2,3-c] pyrazole-5-carbonitrile synthesized via one pot, four component reaction of ethylacetoacetate, phenyl hydrazine hydrate, aromatic aldehydes and malononitrile in the presence of catalytic amount of Cu-Fe₂O₄ in ethanol. The key advantages of his process are high yields, shorter reaction time, easy to workup, purification of product by non-chromatographic method and the reusability of the catalyst.

Key words: ethanol, reusability of the catalyst, purification of product by non-chromatographic method.

INTRODUCTION

An increasing interest is now a day's devoted to the high activity and selectivity of nanocatalysts which allow developing greener and waste-minimized. In addition, nanoparticles are suitable catalyst for processes carried out in neoteric ecofriendly solvents. For these reasons, green chemistry can play a prominent role in guiding the development of nanotechnology to provide the maximum benefit of these products for society and the environment.

Over the several past decades, catalysts and catalytic reactions have attracted considerable attention with the finding meaningful applications in the pharmaceutical and fine chemical industries. The nanocatalysts are highly selective, reactive and stable; thereby it supersedes the conventional catalyst.

Environment-friendly and comparatively inexpensive copper-based nanoparticles have been extensively explored as highly selective catalyst in heterocyclic compounds synthesis. Due to the effective activity of magnetically separable copper based nanoparticles, several organic transformations are carried out with these particles and reported earlier in the literature. Copper ferrite is prepared from CuO and α -Fe₂O₃ by a ceramic processing technique, which comprises several steps, such as powder homogenization, densification and finally prolonged high temperature heat treatment in several steps. It is however, difficult to prepare nanoparticles from sintered materials produced in this manner, which requires ball milling of synthesized ferrites for many hours.

Pyranopyrazole derivatives are very interesting class of nitrogen class of nitrogen and oxygen containing heterocyclic compounds because of their wide range of pharmacological importance and significant role in biochemical process [1-9]. Multicomponent reactions MCRs occupy an interesting position in organic synthesis because of their atom economy, simple procedures and convergent characters [10-22].

Recently the redox condensation reaction, in the synthesizing nitrogen containing heterocyclic compounds have attracted much importance because their efficient, direct and atom economical approach. Some of the direct redox condensation reactions are carried out using the external reducing and oxidizing reagents, noble metals and ligands. We report the synthesis of pyranopyrazole derivatives by using ethylacetoacetate, phenyl hydrazine hydrate, aromatic aldehydes and malononitrile in the presence of catalytic amount of Cu-Fe₂O₄ in ethanol.

METHODOLOGY

All the chemicals are purchased from commercial sources and liquid aromatic aldehydes, malononitriles and ethyl acetate are purified before use. Melting points of the products were recorded by using melting point apparatus and they were compared with literature values. ¹H NMR spectral data were performed on the Bruker-Avance 400 MHz in CDCl₃. The chemical shift values were reported on the δ -scale in part per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. IR spectra were recorded in KBr disks with a Bruker α -FTIR spectrometer. The flask containing the reaction mixture was located on the stirring machine.

Catalyst preparation:

The spinel nano-copper ferrite has been synthesized by citrate sol-gel precursor method as reported earlier.

General procedure for the synthesis of 6-Amino-3-methyl-4-(substituted-phenyl)-2,4-dihydro-pyrano-[2,3-c] pyrazole-5-carbonitrile.

In 50 ml round bottom flask phenyl hydrazine hydrate (10 mmol), ethyl acetoacetate (10 mmol), substituted benzaldehyde (10 mmol), malononitrile and catalytic amount of Cu-Fe₂O₄ were taken. The reaction mixture was stirred for 60-70 min. at room temperature. The completion of reaction were checked by TLC. The precipitate formed by the addition ice cold water was filtered, washed with water, dried and recrystallised from methanol.

Spectral data of some representative compounds:-

6-Amino-3-methyl-4-phenyl)-2,4-dihydro-pyrano-[2,3-c] pyrazole-5-carbonitrile.

IR (KBr): 3365, 3240, 2180, 1612, 1440 cm.⁻¹

¹H NMR (CDCl₃) δ ppm: 1.75 (s, 1H), 4.80 (s, 1H), 6.90 (s, 2H), 7.10-7.40 (m, 5H), 12.30 (s, 1H).

6-Amino-3-methyl-4-(4-Chloro-phenyl)-2,4-dihydro-pyrano-[2,3-c] pyrazole-5-carbonitrile.

IR (KBr): 3335, 3235, 2180, 1620, 1430 cm.⁻¹

¹H NMR (CDCl₃) δ ppm: 1.70 (s, 1H), 4.70 (s, 1H), 6.70 (s, 2H), 7.10 (dd, 2H), 7.40 (dd, 2H), 12.30 (s, 1H).

RESULTS AND DISCUSSIONS

Table 1: Shows time, yields and m.p. of the target molecule.

Entry	Aldehydes	Time in min.	Yield %	m.p. 0C
1a	Ar-CHO	65	82	227
2a	p-Cl-Ar-CHO	60	88	232
3a	o-Cl-Ar-CHO	62	90	245
4a	p-NO ₂ -Ar-CHO	75	72	250
5a	p-OH-Ar-CHO	65	90	222
6a	m-NO ₂ -Ar-CHO	80	70	214

Multicomponent one pot synthesis of these 6-Amino-3-methyl-4-(substituted-phenyl)-2, 4- dihydro-pyrano-[2, 3-c] pyrazole-5-carbonitrile carried out by several method. In addition the synthesis of these heterocyclic compounds was carried out by different catalyst. All these process generate waste containing catalyst. Thus design of reusable catalytic reaction has received tremendous attention in recent time in the area of green synthesis.

In extension to our work here we report an efficient method for the synthesis of 6-Amino-3-methyl-4-(substituted-phenyl)-2,4-dihydro-pyrano-[2,3-c] pyrazole-5-carbonitrile by cyclo condensation of aromatic aldehydes, malanonitriles, ethyl acetoacetate and phenyl hydrazine hydrate in the presence of copper nano-ferrite. The structure of the compound was confirmed by IR and ¹HNMR spectral data. The absence of ester carbonyl group and presence of -NH₂ group at 3365 cm⁻¹ and other spectral data shows condensed product of target molecule.

This process was demonstrated by taking wide range of substituted aromatic aldehydes to synthesize the corresponding product in good yield. Aromatic aldehydes bearing electron releasing group leads some better results than electron withdrawing group.

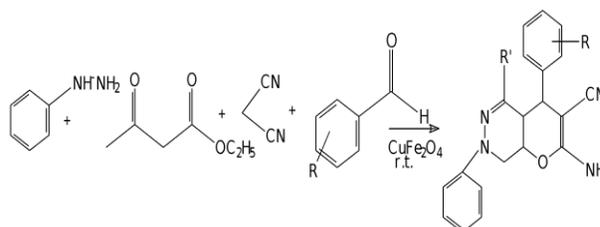
Recycling of the catalyst:-

Catalyst reusability is major concern in heterogeneous catalyst. The recovery and reusability of the catalyst was investigated in this reaction with benzaldehyde.

Catalyst recycling was achieved by fixing the catalyst magnetically at the bottom of flask with a strong magnet, after which the solution was taken off with a pipette and concentrated in rotary evaporator then the solid was washed with twice with chloroform. The fresh substrate dissolved in the same solvent was introduced into the flask, allowing the reaction to proceed for the next run. The catalyst was consecutively reused five times without any noticeable loss of its catalytic activity. These catalysts are highly magnetic and their saturation magnetization values are much higher than other reported magnetic catalyst. Therefore, they could be easily and almost completely separated by an external magnet which is of a great advantage for a heterogeneous catalyst.

CONCLUSION

In conclusion, we have reported an efficient, convenient and environmentally benign one pot greener synthesis of substituted organopyrazole derivatives using nano copper ferrite reusable catalyst. The notable features offered by this methodology are mild reaction condition, simple procedure, cleaner reaction and good yields of the product.



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