

An efficient strategy for oxidative aromatization of 1,3,5-trisubstituted pyrazolines to pyrazoles using Star-Cu(OAc)₂

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Abstract : A novel heterogeneous catalyst [Star-Cu(OAc)₂] was prepared by chemically immobilizing copper (II) acetate onto the surface of organically modified starch and its catalytic activity was evaluated for the oxidative aromatization of 1,3,5-trisubstituted pyrazolines to corresponding pyrazoles using molecular oxygen as oxidant. The catalyst was found to be quite active and selective under the selected reaction conditions and could be easily recovered by simple filtration. Moreover, the catalyst can be reused without significant loss of activity.

Keywords - Heterogeneous, Oxidative aromatization, Pyrazoles, Recyclability, Star-Cu(OAc)₂.

I. INTRODUCTION

The oxidative aromatization of 1,3,5-trisubstituted pyrazolines to pyrazoles is an important transformation in organic syntheses due to the immense biological activities[1-3] associated with pyrazoles. These were found to possess anti-inflammatory[4], antipyretic[5], gastric secretion stimulators[6], antidepressant[7], anti-rheumatoid arthritis[8], antibacterial[9], anticonvulsant[10], antitumor[11], antipsychotic[12], antimicrobial[13], antiviral[14], antifungal and antifilarial activities[15]. Due to their immense biological importance, pyrazoles have received considerable attention of chemists and therefore, a number of synthetic strategies have been developed for their synthesis[16-17]. The most common approach for the synthesis of substituted pyrazoles is the condensation of α,β -unsaturated carbonyl compounds with hydrazines to form 5-dihydro-1H-pyrazoles (pyrazolines) that need to be further oxidized to corresponding pyrazoles using a variety of oxidants such as Zr(NO₃)₄[18], Pd/C[19], Co(II) and oxygen[20], iodobenzene diacetate[21], MnO₂[22], potassium permanganate[23], NBS[24] carbon-activated oxygen[25] Pd/C/AcOH[26], Pb(OAc)₄[27], Ag(NO₃)₂[28], HgO[29], *N*-hydroxyphthalimide (NHPI)[30], I₂O₅/KBr[31], and Nitric oxide[32]. In addition to these, various other methods[33-37] are also available for the oxidative aromatization of 1,3,5-trisubstituted pyrazolines. However, many of the above reported methods suffer from disadvantages such as use of excess reagent, longer reaction times, higher temperatures, formation of side products, use of toxic solvents and difficulty in removing the oxidant from the reaction mixture at the end of the reaction. Such limitations necessitate further demand to develop other environmentally benign protocols for the oxidation of 1,3,5-trisubstituted pyrazolines.

Keeping in view the importance of pyrazoles in organic syntheses, an efficient and cost-effective procedure has been developed for the oxidative aromatization of 1,3,5-trisubstituted pyrazolines to corresponding pyrazoles using Star-Cu(OAc)₂ as a recyclable heterogeneous catalyst under mild reaction conditions using O₂ as oxidant.

RESULTS AND DISCUSSION

The preparation procedure for starch functionalized copper(II) acetate [Star-Cu(OAc)₂] is outlined in **Fig. 1**. It involves the chemical modification by grafting a suitable ligand structure onto the surface of expanded corn starch, which was then treated with copper(II) acetate to give the starch-functionalized copper(II) acetate. Star-Cu(OAc)₂ was further conditioned for 12 h by refluxing each in acetonitrile (2 × 2 h), ethanol (2 × 2 h) and toluene (2 × 2 h) so as to remove the physisorbed copper(II) acetate.

The characterization of Star-Cu(OAc)₂ was done by FTIR, TGA, AAS, XRD, SEM and TEM.

FTIR

The FTIR of 3-aminopropyl starch displayed CH₂ stretching bands at 2925 and 2855 cm⁻¹ and aliphatic deformation bands at 1457 and 1404 cm⁻¹. The FTIR of chemically modified starch (imine) showed a sharp peak at 1650 cm⁻¹ due to C=N bond, which on complexation with Cu(OAc)₂ disappeared and appeared as a band at 1645 cm⁻¹. The lowering in frequency of the C=N peak is indicative of the formation of metal-ligand bond

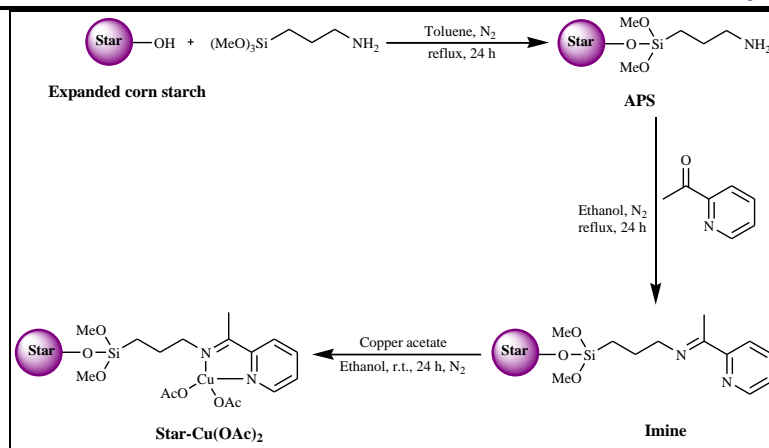


Fig. 1 Preparation of starch-functionalized copper(II) acetate [Star-Cu(OAc)₂]

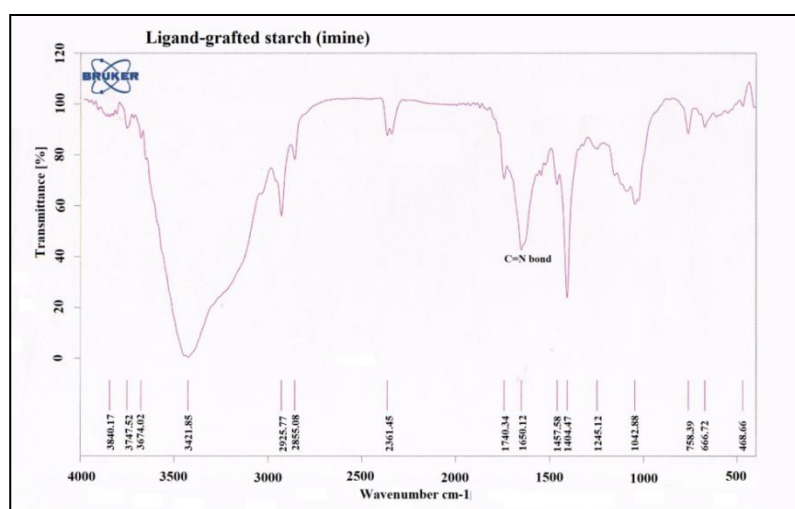


Fig. 2 FTIR of ligand-grafted starch (imine).

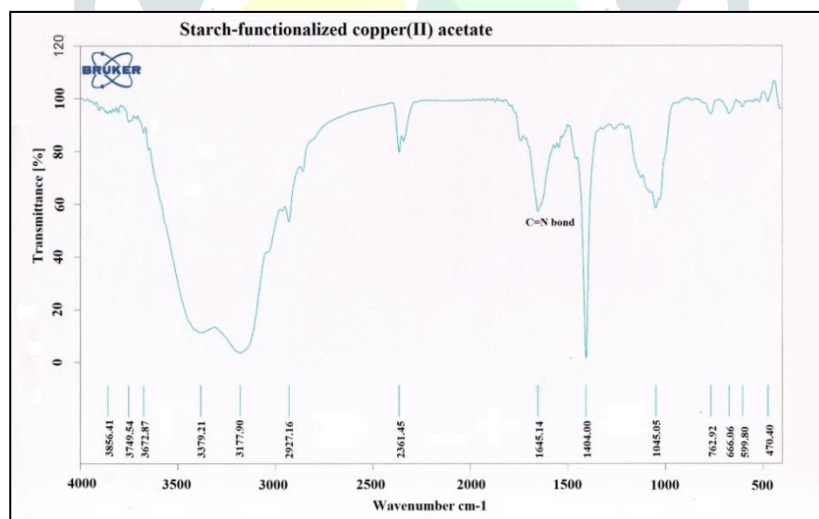


Fig. 3 FTIR of Star-Cu(OAc)₂.

Thermogravimetric analysis (TGA)

The stability of Star-Cu(OAc)₂ was determined by thermal analysis (TGA). TGA curve of Star-Cu(OAc)₂ showed an initial weight loss upto 100 °C which was due to loss the of residual solvent and water and then from 275 to 332 °C, which was due to the loss of organic functionality. Thus, the catalyst is stable up to 275 °C and it is safe to carry out the reaction at room temperature or 80-100 °C.

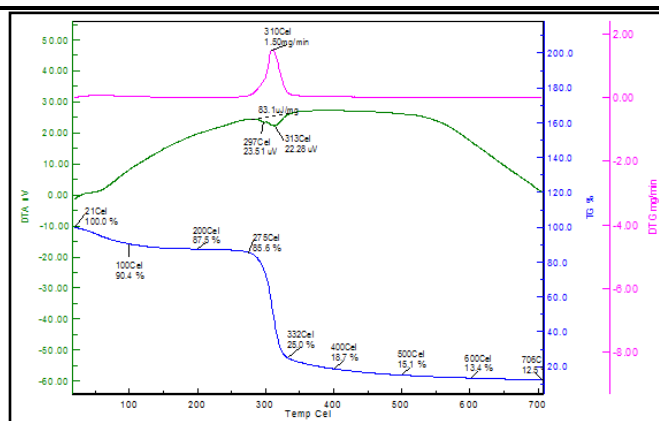


Fig. 4 TGA of Star-Cu(OAc)₂.

Atomic Absorption Spectrophotometric Analysis (AAS)

The amount of the copper loaded onto the surface of starch in Star-Cu(OAc)₂ was determined by AAS analysis. The catalyst was stirred in dil. HNO₃ and the solution was subjected to AAS analysis. Star-Cu(OAc)₂ was found to contain 0.009540 g of Cu per gram of the catalyst.

X-Ray Diffractometry (XRD)

The powdered X-ray diffraction patterns of Star-Cu(OAc)₂ showed the peaks in the pattern which were indexed on the basis of crystallographic data for the known structure of starch (Fig. 5). Three additional reflection patterns were obtained corresponding to $2\theta = 30.5^\circ$ (27.75), 35.6° (68.22) and 38.6° (97.37) which corresponds to Cu(OAc)₂.

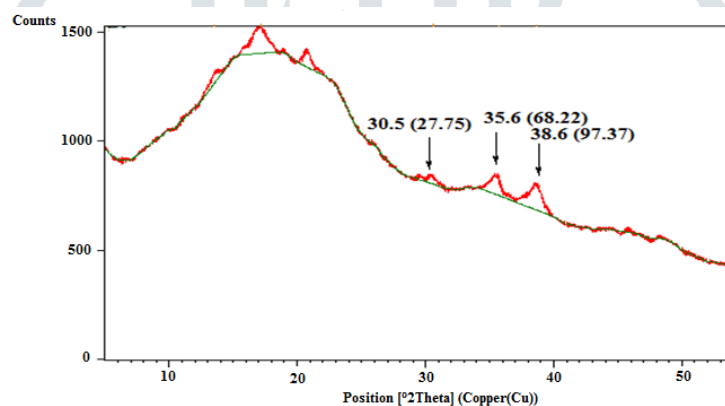


Fig. 5 XRD of Star-Cu(OAc)₂.

Scanning Electron Microscopy (SEM)

The microstructure and morphology of Star-Cu(OAc)₂ was studied using Scanning Electron Microscopy (SEM, Fig. 6). SEM image indicated that the complex has been successfully anchored onto the surface of starch and catalyst was found to be a homogeneous powder with porous structure

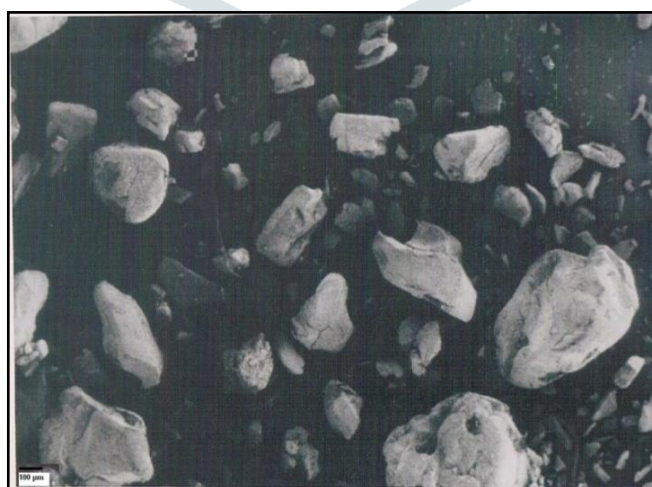


Fig. 6 SEM micrograph of Star-Cu(OAc)₂.

Transmission Electron Microscopy (TEM)

The TEM images (Fig. 7) shows the distribution of copper onto the surface of starch. From the image, it is clear that no bulk aggregation of the metal occurred indicating that copper is evenly distributed onto the surface of support material. In the TEM images, the copper nanoparticles are shown as dark spots of average diameter 7.8 nm.

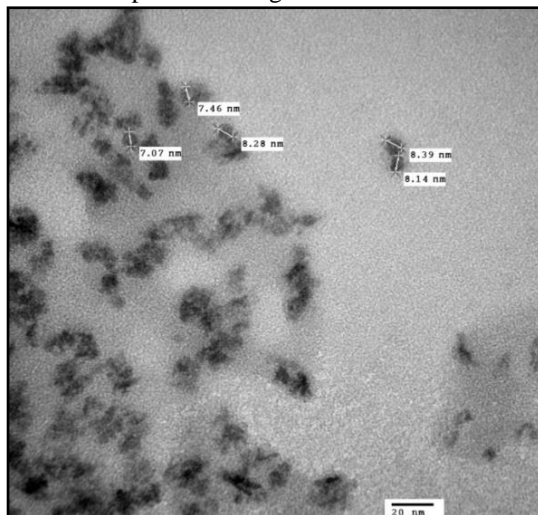


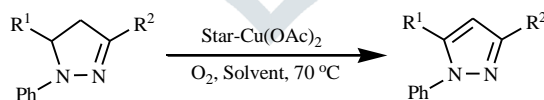
Fig. 7 TEM micrographs of Star-Cu(OAc)₂.

OPTIMIZATION OF THE REACTION CONDITIONS

Pyrazolines were oxidatively converted to pyrazoles by stirring in acetonitrile using molecular oxygen as oxidant and Star-Cu(OAc)₂ as catalyst at 70 °C.

To optimize the reaction conditions, 1,3,5-triphenylpyrazoline was selected as the test substrate and the reaction was carried out using various solvents like acetonitrile, DMF, methylene chloride, toluene and ethanol (Table 1) at different temperatures. When the reaction was carried out for 20 h in methylene chloride, the corresponding pyrazole was obtained in 40% yield, while in DMF, the same reaction under similar conditions gave product with 60% yield and in toluene, 70% yield of the corresponding pyrazole was obtained. In ethanol, the yield of the corresponding pyrazole increased to 80% under similar conditions, while in acetonitrile, the reaction got completed in 12 h with 92% isolated yield. The results are shown in Table 1, which indicated that acetonitrile was the excellent reaction medium in terms of reaction time and selectivity. The reaction conditions were further screened to select the optimum reaction temperature. It was found that when the reaction was carried out at room temperature, the reaction didn't go to completion even after 20 h and also by increasing catalyst amount to 12 mol%. However, increasing the reaction temperature to 70 °C, enhanced the rate of reaction and pyrazole was obtained in 92% isolated in 12 h. Hence, 70 °C was selected as the optimum reaction temperature. The reaction conditions were further investigated for absence and presence of oxidant. It was found that when the reaction was carried out without using any oxidant under N₂ atmosphere so as to avoid the interference of O₂ from air, only 25% conversion was observed upto 20 h, whereas the same reaction in the presence of O₂ under similar conditions dramatically enhanced the rate of reaction completing it in 12 h. Thus O₂ has been selected as the green oxidant. The optimum conditions selected are: 1,3,5-trisubstitutedpyrazoline (1 mmol), Star-Cu(OAc)₂ (0.2 g, 3 mol% Cu), acetonitrile (5 mL), 70 °C as the reaction temperature and O₂ as the oxidant.

Table 1. Effect of solvent on Star-Cu(OAc)₂ catalyzed oxidative aromatization of 1,3,5-trisubstituted pyrazolines to corresponding pyrazoles in ethanol at 70 °C using O₂ as an oxidant^a

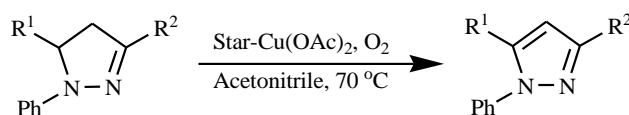


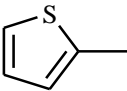
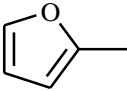
Entry	Solvent	Time (h)	Yield (%)
1	Methylene chloride	20	40 ^b
2	DMF	20	60 ^b
3	Toluene	20	70 ^b
4	Ethanol	20	80 ^c
5	Acetonitrile	12	92 ^c

^aReaction conditions: 1,3,5-Triphenylpyrazoline (0.298 g, 1 mmol), Star-Cu(OAc)₂ (0.2 g, 3 mol% Cu), solvent (5 mL) and 70 °C was the reaction temperature under oxygen atmosphere.

^bColumn chromatographic yields.

^cIsolated yields.

Table 2. Star-Cu(OAc)₂ catalyzed oxidative aromatization of 1,3,5-trisubstituted pyrazolines in ethanol at 70 °C using O₂ as an oxidant^a

Entry	R ¹	R ²	Time (h)	Yield (%) ^b	m.p./Lit. m.p. (°C)
1	C ₆ H ₅	C ₆ H ₅	12	92	140-141/141-142[18]
2	4-OMeC ₆ H ₄	C ₆ H ₅	12	92	80-81/79-80[18]
3	4-ClC ₆ H ₄	C ₆ H ₅	13	92	113-114/114-115[18]
4	4-NO ₂ C ₆ H ₄	C ₆ H ₅	14	90	141-142/142-144[18]
5	4-MeC ₆ H ₄	C ₆ H ₅	14	90	115-116/116-117[38]
6	4-BrC ₆ H ₄	C ₆ H ₅	12	90	132-134/134-135[18]
7	2,4-Cl ₂ C ₆ H ₃	C ₆ H ₅	12	89	75-76/75.9-76.5[38]
8	C ₆ H ₅	4-ClC ₆ H ₄	13	88	136-138/137-140[38]
9	C ₆ H ₅	4-BrC ₆ H ₄	13	85	155-156/156-157[38]
10	4-ClC ₆ H ₄	4-CH ₃ C ₆ H ₄	15	90	109-110/109.5-110.4[38]
11		4-ClC ₆ H ₄	18	90	132-134/134-135[18]
12		4-CH ₃ C ₆ H ₄	17	85	96-97/96-98[18]

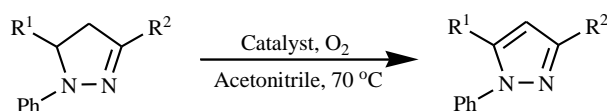
^aReaction conditions: 1,3,5-Trisubstituted pyrazoline (1 mmol), Star-Cu(OAc)₂ (0.2 g, 3 mol% Co), acetonitrile (5 mL) and 70 °C as the reaction temperature using oxygen as an oxidant.

^bIsolated yield.

All the reactions were carried out under similar conditions. With optimized conditions in hand, we next turned our attention to examine the scope of the reaction and the results are presented in **Table 2**.

Various substituted pyrazolines were tested to establish its generality and efficiency, and all reactions proceeded smoothly under similar conditions. The experimental results showed that the substituent (electron-withdrawing groups or electron-releasing groups) has not much affect on the reaction time and yields of the products. The present reaction conditions tolerated several functionalities such as halogen, nitro, methoxy and ether groups.

We further investigated the role of Star-Cu(OAc)₂ for the oxidative aromatization of 1,3,5-trisubstituted pyrazolines. For this, we have carried out the model test reaction with Cu(OAc)₂, 3-aminopropyl starch (APS), ligand grafted starch (imine) and in the absence of Star-Cu(OAc)₂ under the similar conditions as applied for Star-Cu(OAc)₂. The results are summarized in **Table 3**. The results reported in **Table 3** showed that Star-Cu(OAc)₂ is the actual catalyst of the reaction with its fast conversion rate and yield of the product.

Table 3. Effect of the catalyst on the Star-Cu(OAc)₂ catalyzed oxidative aromatization of 1,3,5-trisubstituted pyrazolines in ethanol at 70 °C using O₂ as an oxidant^a

Entry	Catalyst	Time (h)	Yield (%)
1	No catalyst	20	Traces
2	APS	20	30 ^b
3	Imine	20	30 ^b
4	Cu(OAc) ₂	20	55 ^b
5	Star-Cu(OAc) ₂	12	92 ^c

^aReaction conditions: 1,3,5-Triphenylpyrazoline (0.298 g, 1 mmol), Star-Cu(OAc)₂ (0.2 g, 3 mol% Cu), APS (0.2 g), or imine (0.2 g), Cu(OAc)₂ (0.0054 g, 3 mol% Cu), acetonitrile (5 mL) and 70 °C as the reaction temperature using oxygen as an oxidant.

^bColumn chromatography yields.

^cIsolated yield.

The recyclability of the catalyst was studied for 5 consecutive runs in case of entry **1** (Table 2) under the selected conditions. The results are shown in Fig. 8, which indicated that there is a significant change in the activity of the catalyst due to the leaching of metal during the oxidation process. Leaching of copper (3%) has been indicated by AAS analysis of the supernatant.

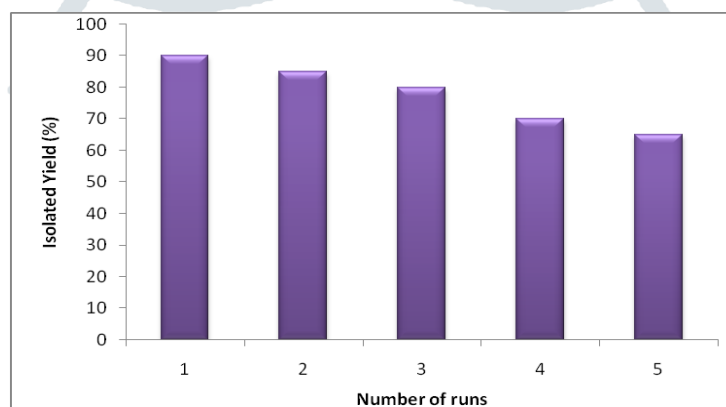


Fig.8 Recyclability of Star-Cu(OAc)₂. Reaction conditions: 1,3,5-Triphenylpyrazoline (0.298 g, 1 mmol), Star-Cu(OAc)₂ (0.2 g, 3 mol% Co), acetonitrile (5 mL) and 70 °C as the reaction temperature using O₂ as an oxidant.

EXPERIMENTAL

MATERIALS

The chemicals used were purchased from Aldrich chemical company and Merck. The products were characterized by their spectral data and comparison of their physical data with those of known samples. The ¹H NMR data were recorded in CDCl₃ or CDCl₃+DMSO-*d*₆ on Bruker DPX 200 (200 MHz) spectrometer using TMS as an internal standard. The IR spectra were recorded using KBr disc on Perkin-Elmer FTIR spectrophotometer. Mass spectral data were recorded on Esquire 3000 (ESI). Thermal analysis was carried out on DTG-60 Shimadzu make thermal analyzer with heating rate of 10 C/min. SEM was recorded using Jeol make T-300 Scanning Electron Microscope and Transmission Electron Microscope (TEM) on H7500 Hitachi. The amount of Palladium in HAP-Pd (0) was determined on double beam Atomic Absorption Spectrophotometer (AAS), GBC 932 AB manufactured in Australia. The catalyst was stirred in dil. HCl for 10 h and then subjected to AAS analysis.

General procedure for the preparation starch-functionalized Cu(OAc)₂

Preparation of 3-aminopropyl starch (APS)

Corn starch (15 g) was taken in a round bottom flask (500 mL) containing double distilled water (300 mL) and stirred at 110 °C for 24 h. After this time, the vessel was cooled to room temperature and the contents were transferred to conical flask (500 mL) and kept in a refrigerator overnight. After this time, the water was decanted off and ethanol was added, and again kept in a refrigerator overnight. On the next day, ethanol was decanted off and acetone was added, and was again kept in a refrigerator for overnight. After this time, the starch was filtered and dried in an oven at 80 °C for 10 h. The starch so obtained was expanded starch with more surface area. To a mixture of expanded starch (10 g) and 3-aminopropyl(trimethoxy) silane (1.79 g, 10 mmol), dry toluene (150 mL) was added in a round bottom flask and the reaction mixture was stirred under nitrogen atmosphere at 110 °C for 24 h. The 3-aminopropyl starch (APS) was filtered, washed with toluene (200 mL) and ethanol (100 mL), and dried in a hot air oven at 80 °C for 5 h. The yield of the 3-aminopropyl starch (APS) obtained was 9.5 g.

Preparation of ligand-grafted starch (imine)

To a mixture of 3-aminopropyl starch (8 g) and 2-acetylpyridine (0.968 g, 8 mmol) in a round bottom flask (250 mL), ethanol (150 mL) was added and the reaction mixture was refluxed under nitrogen for 24 h. After this time, the reaction mixture was

cooled, filtered and the solid was washed with excess ethanol (150 mL) to remove the unreacted 2-acetylpyridine. Finally, it was dried at 80 °C in an oven for 5 h. The yield of ligand-grafted starch obtained was 7.5 g.

Preparation of starch-functionalized Cu(OAc)₂ [Star-Cu(OAc)₂]

Star-Cu(OAc)₂ was prepared by stirring a mixture of ligand-grafted starch (imine, 4 g) and Cu(OAc)₂ (0.920 g, 1.3 mmol/gm) in ethanol (60 mL) at room temperature under nitrogen atmosphere for 18 h. The solid was filtered off at pump and washed with acetone till washings were colourless. It was dried in an oven at 80 °C for 5 h and then conditioned for a total of 12 h (2 × 2 h each refluxing in acetonitrile, ethanol and toluene). The conditioned catalyst was dried under vacuum for 5 h before use. The yield of the Star-Cu(OAc)₂ was 3.5 g.

General procedure for the Star-Cu(OAc)₂ catalyzed oxidative aromatization of 1,3,5-trisubstituted pyrazolines to corresponding pyrazoles using molecular oxygen

To a mixture of 1,3,5-trisubstituted pyrazoline (1 mmol) and Star-Cu(OAc)₂ (0.2 g, 3 mol% Cu) in a round-bottom flask (25 mL), acetonitrile (5 mL) was added and the reaction mixture was stirred at 70 °C under oxygen atmosphere using balloon filled oxygen for an appropriate time (Table 2). After completion of the reaction (monitored by TLC), the reaction mixture was filtered while hot and the residue was washed with hot acetonitrile (2 × 5 mL). After removal of solvent under reduced pressure, the product was obtained either by crystallization or column chromatography. The catalyst was recovered from the residue after washing with methylene chloride (3 × 10 mL) followed by distilled water (200 mL) and then CH₂Cl₂ (3 × 10 mL) and acetonitrile (3 × 10 mL) and dried at 110 °C for 2 h. It was used further for carrying out the reaction (Fig. 8).

The structures of the products were confirmed by IR, ¹H NMR, ¹³C NMR, mass spectral data and comparison with authentic samples available commercially or prepared according to the literature methods.

CONCLUSION

In conclusion, an efficient one-pot procedure for the synthesis of pyrazoles has been reported via aromatization of 1,3,5-trisubstituted pyrazolines using Star-Cu(OAc)₂ in acetonitrile at 70 °C in the presence of molecular oxygen as oxidant. Simple work-up procedure, recyclability of the catalyst, use of cheap and green oxidant, shorter reaction times and high yields of the products are the advantages of the present procedure.

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