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JOURNAL FULL TITLE: Journal of Biomedical Research & Environmental Sciences
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JOURNAL OF BIOMEDICAL RESEARCH & ENVIRONMENTAL SCIENCES
ISSN: 2766-2276
SUBJECT AREA(S): ORGANIC CHEMISTRY | MATERIAL SCIENCE
DOI: 10.37871

RESEARCH ARTICLE

Preparation and Characterization of 3-Amino-1H-1,2,4-Triazole Grafted on the Surface of Silica Nanoparticles Support (SNP_s-AT) for the Synthesis of Pyrano[2,3-c]Pyrazole Derivatives as the Novel, Effective, and Reclaimable Catalyst

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Abstract

The main objective of the current research, 3-amino-1H-1,2,4-triazole immobilized on 3-chloropropyl joined SiO2 nanoparticles as a recyclable, environment-friendly, and novel heterogeneous base catalyst. It was characterized by fourier transform infrared, X-ray diffraction patterns, field emission scanning electron microscopes, and energy-dispersive X-ray spectroscopy. This new material as a green and efficient catalyst was used for the synthesis of pyrano [2,3-c]pyrazoles derivatives through the reaction of aromatic aldehydes, malononitrile, and 3-methyl-1-phenyl-2-pyrazoline-5-one. The reactions did in solvent-free conditions at 60°C and the related pyran derivatives prepared in excellent yields. Also, this catalyst could be used several times without decreasing the activity.

Introduction

About 1.5% of the Gross National Product (GNP) in the world is related to catalyst technology and plays a significant role in economic advancement and the promotion of the chemical industry [1]. On the other hand, in today's modern world, the inclination to use tinier and more efficient systems in the field of nanoscience and technology by researchers causes them to synthesize smaller materials with improved properties. The application of nanomaterials as heterogeneous catalysts has attracted a lot of consideration due to their economic, environmental, and structural specifications [2], and as the forerunner of green chemistry plays an important role in achieving selectivity, excellent activity, desired flexibility, chemical and thermal stabilization [3]. In recent research, attempts to the synthesis of supported nanocatalysts on various substrates such as charcoal, alumina, magnetic nanoparticles, silica, and polymers, as green materials have obtained great attention [4]. SiO_2 nanomaterials have unique and adjustable physiochemical properties with a high surface

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DOI: 10.37871/jbres2184

Submitted: 13 September 2025

Accepted: 17 September 2025

Published: 19 September 2025

Keywords

- Nano-silica
- 3-Amino-1H-1,2,4-Triazole
- Pyrano [2,3-C]Pyrazole
- Reusable catalysts
- Solvent-free condition

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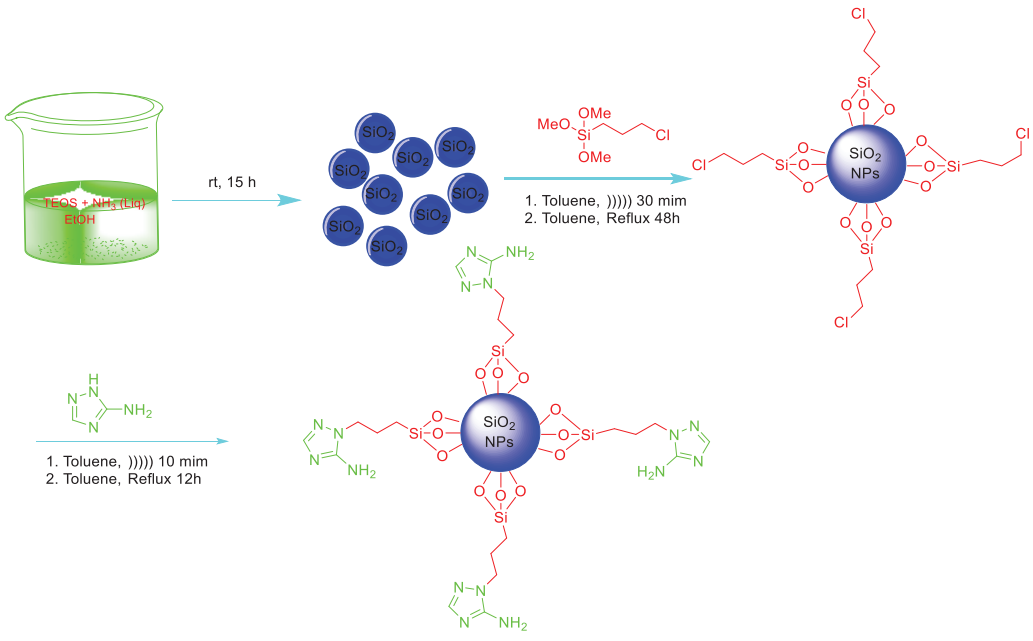
How to cite this article: Pourkazemi A, Karami B, Farahi M. Preparation and Characterization of 3-Amino- 1H-1,2,4-Triazole Grafted on the Surface of Silica Nanoparticles Support (SNPs-AT) for the Synthesis of Pyrano[2,3-c]Pyrazole Derivatives as the Novel, Effective, and Reclaimable Catalyst. J Biomed Res Environ Sci. 2025 Sept 19; 6(9): 1290-1301. doi: 10.37871/jbres2184, Article ID: JBRES2184, Available at: https://www.jelsciences.com/articles/jbres2184.pdf

area to volume ratio, excellent chemical, thermal, and mechanical stability. Hence, They have high potential chemical reactivity [5]. Former articles have authenticated that substituted pyrano[2,3-c] pyrazoles are an appealing category of heterocyclic compounds due to biological and medicinal activities [6]. In specific, their advantages have resulted in fungicidal, anticancer, antibacterial, antitumor, antiplatelet, and antioxidant of these compounds [7]. So far, there have been many reports for the synthesis of the pyrano[2,3-c]pyrazole. The common method is condensation reaction of aryl aldehydes, malononitrile, and 3-methyl-1-phenyl-2-pyrazoline-5-one in the presence of various catalysts including HDBAC, HTMAB, MDOs, D and L-Proline, [Dsim]AlC_{l4}, silicotungstic acid, isonicotinic acid, gamma-Alumina. Each of the above methods has its own merits, while most of these techniques suffer from disadvantages such as long reaction times, low product yields, use of excess amounts of catalyst, application of hazardous solvents, and toxic effluents [8,9].

Results and Discussion

In continuation of research on developing supported catalysts done by Karami group, several green catalysts were reported such as STA [4], SSC [10] Fe_3O_4@TiO_2@$(CH_2)_3OWO_3H$ [6], Fe_3O_4@SiO_2@$(CH_2)_3OMoO_3H$ [11], MCM-41-HWO_4 [12], phthalhydrazide-MCM-41 [13]. Herein, we have reported a new heterogeneous nanocatalyst using Azoles because other researcher groups have used them in the synthesis of catalysts, too [14,15]. Accordingly, we grafted 3-amino-1H-1,2,4-triazole (3-AT) on 3-chloropropyl, which is coated on silica nanoparticles, and used in the multi-component reactions in organic chemistry. The SiO_2 NPs were initially synthesized through the sol-gel process. Then, SiO_2@$(CH_2)_3Cl$ was formed via the reaction of SiO_2 NPs with 3-chloropropyl tri methoxy silane according to the previous report [13]. Finally, as expected, in the reaction of SiO_2@$(CH_2)_3Cl$ with 3-amino-1H-1,2,4-triazole (3-AT), the chloride group was replaced by (3-AT), to obtain nano-catalyst SiO_2@$(CH_2)_3$-(3-AT) (SNP_s-AT) (Scheme 1). Chemical analysis of SiO_2@$(CH_2)_3$(3-AT) bases catalyst was determined using fourier transform infrared (FT-IR), X-ray diffraction patterns (XRD), field emission scanning electron microscopes (FE-SEM), and energy-dispersive X-ray spectroscopy (EDS).

To prove the produced catalyst, FT-IR spectra of the synthesized particles (SiO_2, SiO_2@$(CH_2)_3Cl$ and SNP_s-AT) are from wavelength 400 to 4000 cm^{-1}, shown in figure 1. FT-IR spectra of SiO_2 (Figure 1a) illustrate the absorption bands at the region 809, 1103 cm^{-1} assigned to Si–O–Si stretching symmetric and Si–O–Si stretching asymmetric, respectively. The bending vibrations Si–O–Si appear at 462 cm^{-1} [16]. FT-IR spectra of the SiO_2@ $(CH_2)_3Cl$ structure (Figure 1b) in comparison with that of SiO_2 (Figure 1a)



Scheme 1 Preparation of SNPs-AT.

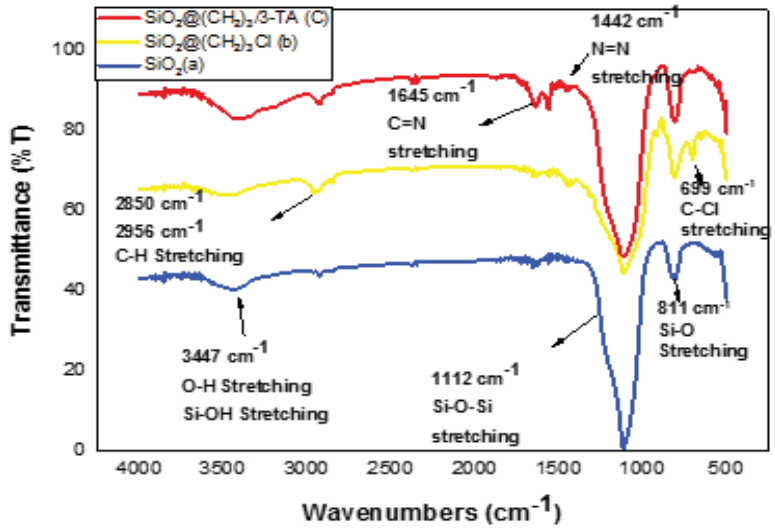


Figure 1 The FT-IR spectrum of SiO2 (a), SiO2@(CH2)3Cl (b), SNPs-AT (c).

confirm that the CH_2 of the alkyl chains is in the 2854 cm^{-1} for symmetric CH_2 and 2923 cm^{-1} for asymmetric stretching peaks [17]. Compare with FT-IR spectra of figure 1b, SiO_2 @ $(CH_2)_3$ (3-AT), shown in figure 1c, has been formed. Moreover, two peaks that appear at 1442 cm^{-1} and 1645 $cm^{-1}$are related to N = N and C = N stretching vibration bands of the (3-AT) material immobilized on the surface catalyst [15,18].

EDS is an analytical technique used for the elemental or chemical characterization of a sample. According to figure 2, it shows the presence of elements Si,O,C, and N in the SNP_s-AT that agrees with our predictions. Also, the successful bonding of the 3-AT groups is fully confirmed by the presence of nitrogen.

XRD is one of the most significant, non-destructive instruments used to study the structure, composition, and quality control. The presence of amorphous SiO_2

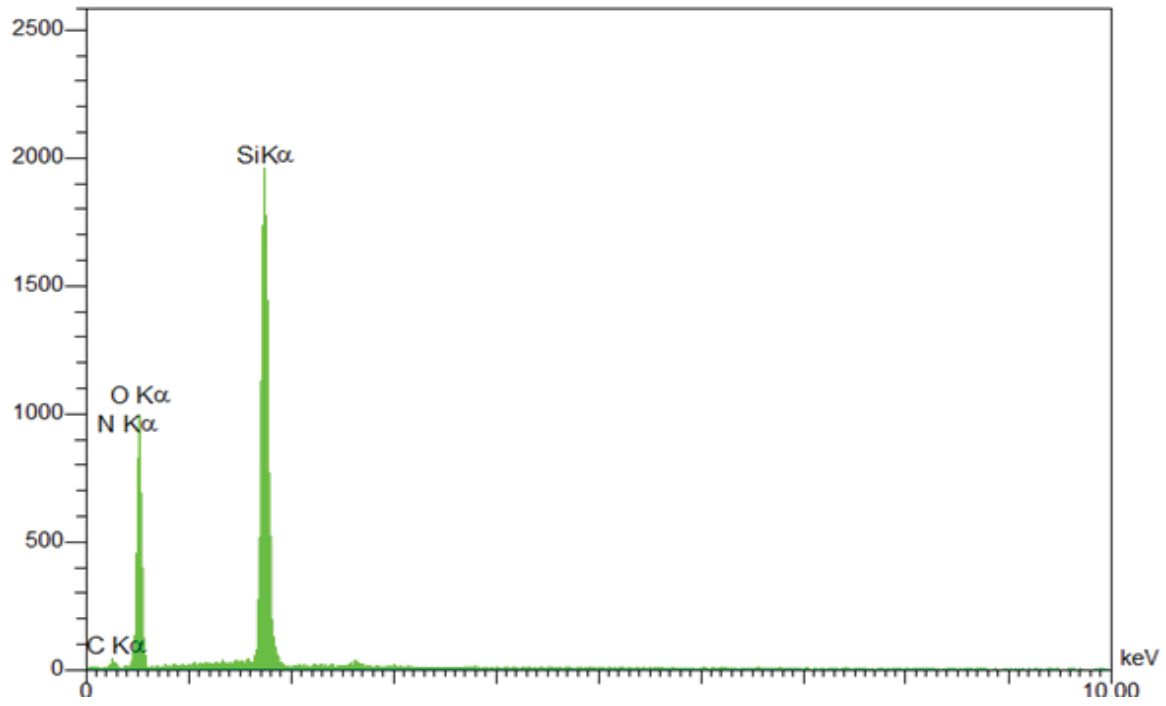


Figure 2 EDX spectrum a of SNPs-AT.

structure with a wide scattering centered in the range of ($20^{\circ} < 2\theta < 32^{\circ}$) was observed in figure 3a. The XRD pattern in figure 3b displays the nanoparticles SNP_s-AT and in comparison with figure 3a, the existance of nitrogen in the structure confirmed the formation of SNP_s-AT [19].

FE-SEM images show the morphology and size of the novel catalyst SNP_s-AT. The result proves that the nanoparticles are spherical with average diameters of 37.96-64.91 nm (Figure 4). All this evidence demonstrates that the novel nanocatalyst SNP_s-AT was produced successfully. Continuing this research, we have tested the catalytic activity through one-pot, the multicomponent reaction for the synthesis of pyrano[2,3-c] pyrazoles derivatives (4a-r). In this work, the one-pot reaction was performed between a mixture of 3-methyl-1-phenyl-2-pyrazoline -5-one (1) (1mmol, 0.174 g), malononitrile (2) (1.25 mmol, 0.08 g) and aromatic aldehydes (3a-r) (1 mmol, 0.14 g) and $SiO_2@(CH_2)_3$ (3-AT) as catalyst under different conditions (Scheme 2). As a replacement of toxic organic solvents, solvent-free reactions were shown to be an impressive technique in chemist organic. frequently, solvent-free conditions lead to a significant decrease in reaction times, increased production, and regioselectivity, and stereoselectivity of reactions [20,21].

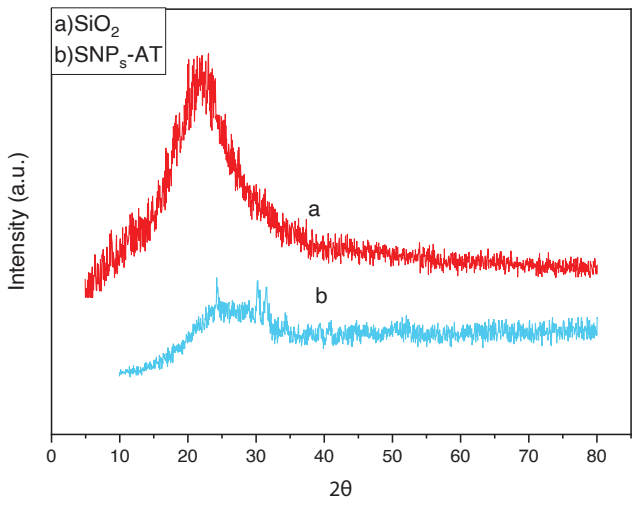


Figure 3 XRD patterns of SiO2 (a), SNPs-AT (b).

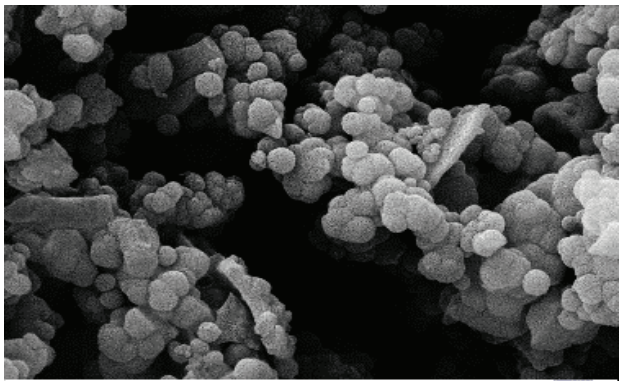


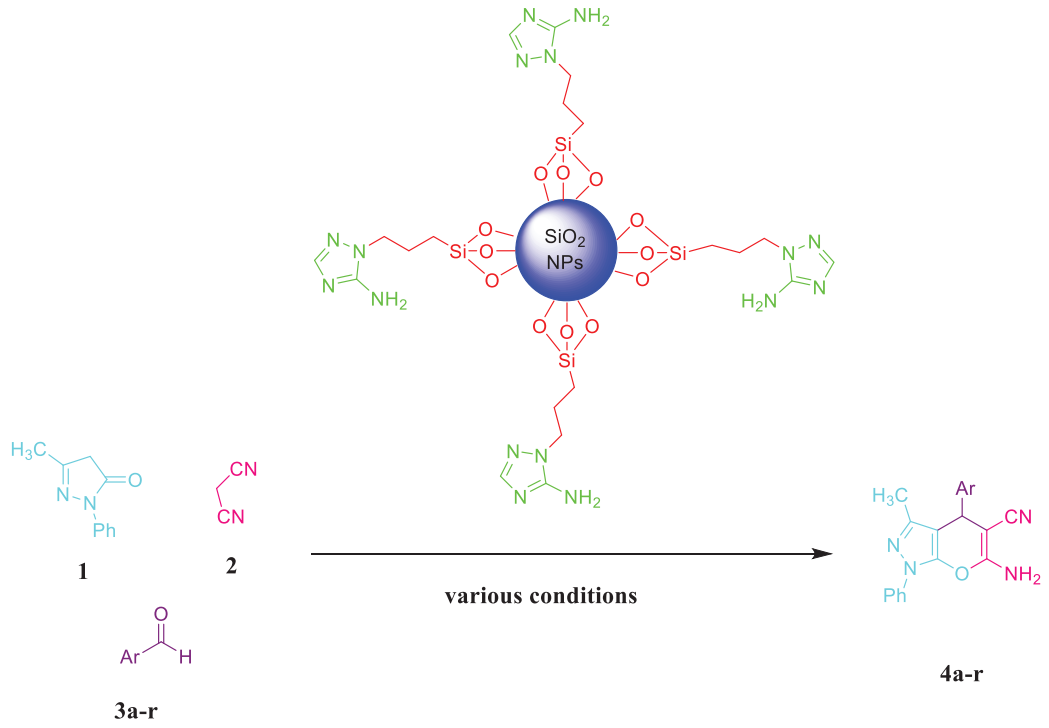
Figure 4 Fe-SEM image of SNPs-AT.

At first, the optimized conditions for the model reaction should be obtained. The model reaction in the absence of catalyst checked out but the favorable product was not created even after a long time reaction. The model reaction was performed by various amounts of SNP_s-AT at the range of 25-70°C. Results are shown in table 1. According to table 1, the products were produced efficiently utilizing 0.003g of the catalyst (Table 1). Also, maximized product yield obtained at 60°C (Table 1). To investigate the solvent effect, the model reaction was performed using 0.003g nanocatalyst SNP_s-AT in solvent-free conditions and several polar and nonpolar solvents including water, ethanol, carbon tetrachloride, tetrahydrofuran, and acetonitrile conditions (Table 1). Using the solvents couldn't increase the yields of the product, while under solvent-free conditions, product yield was in the range of 85-95 percentage (Table 1). In this way, the optimized conditions are shown in entry 11 of table 1, for pyrano[2,3-c] pyrazoles derivatives which have been synthesized by SNP_s-AT catalyst in solvent-free condition at 60°C. Under these conditions, the modal reaction was studied in an extensive range of aromatic aldehydes containing both electron-donating and electron-withdrawing groups completely. Acceptable efficiency of the products was obtained by both aromatic aldehydes groups in the short reaction times showed in table 2. According to (Scheme 3), a possible mechanism for the synthesis of product 4 is brought in the following steps. the first step includes the Knoevenagel condensation between aryl aldehyde (3a-o) and malononitrile (2) using a base catalyst. Then, Michael's addition occurred between intermediate (6) and 2-benzylidene malononitrile (5). Finally, cyclization and tautomerization of intermediates (7) and (8) give the expected product (4) (**Scheme 3,4**).

Experimental

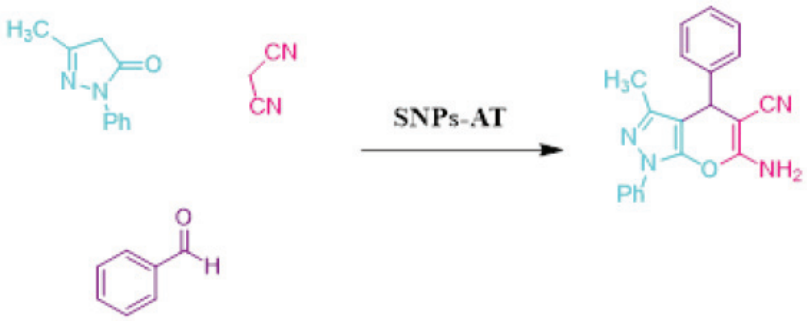
Materials and methods

Tetraethyl Orthosilicate (TEOS), 3-Chloropropyl Tri Methoxy silane (CPTMO), 3-Amino-1H-1,2,4-



Scheme 2 Novel SNPs-AT as catalysts for the synthesis of pyrano [2,3-C] pyrazoles.

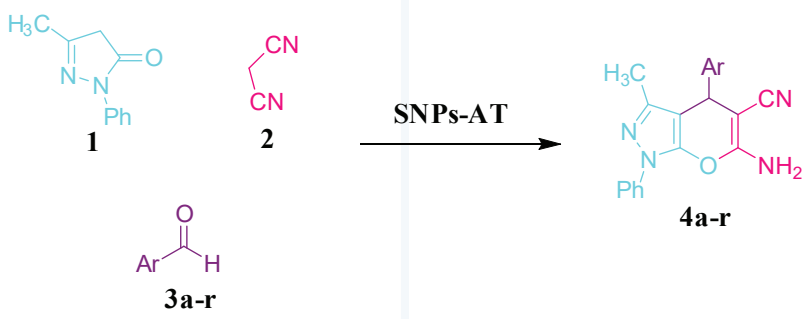
Table 1: Optimization of the model reaction for the synthesis of pyranopyrazoles 4a-r [a].

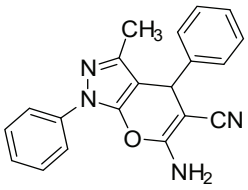
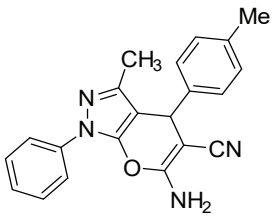
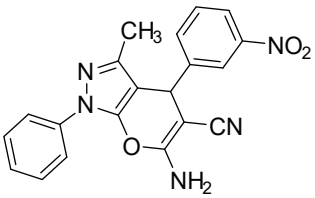
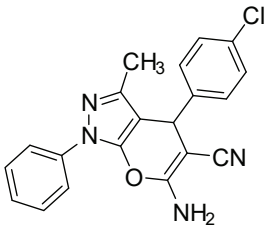
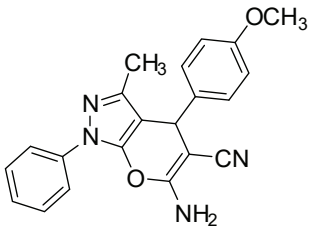
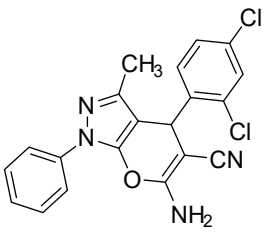


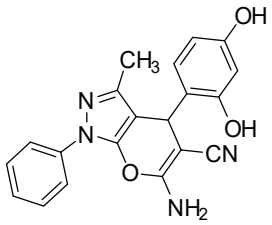
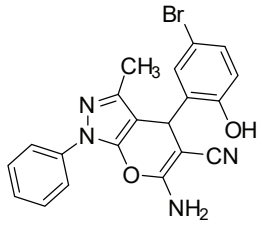
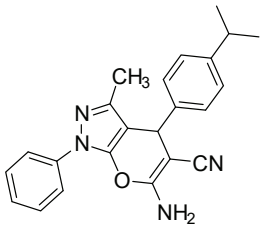
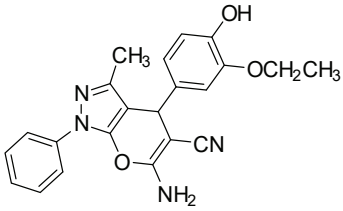
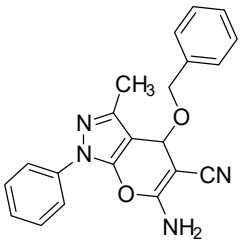
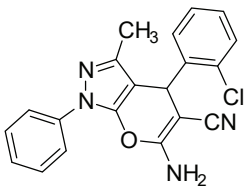
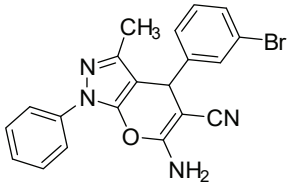
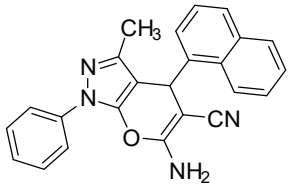
Entry	Catalyst (g)	Solvent	Time (min)	Temp (°C)	Yield (%) [b]
1	No Catalyst	No solvent	240	25	No product
2	0.005	EtOH	120	Reflux	85
3	0.005	H_2O	120	Reflux	70
4	0.005	THF	120	Reflux	55
5	0.005	CCl_4	120	Reflux	48
6	0.005	CH_3CN	120	Reflux	40
7	0.005	Solvent-free	60	25	40
8	0.005	Solvent-free	60	60	95
9	0.005	Solvent-free	60	70	95
10	0.004	Solvent-free	30	60	93
11	0.003	Solvent-free	30	60	90
12	0.003	Solvent-free	30	70	93
13	0.002	Solvent-free	60	60	75

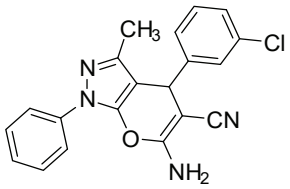
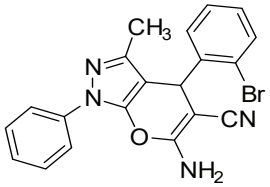
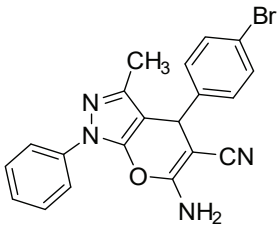
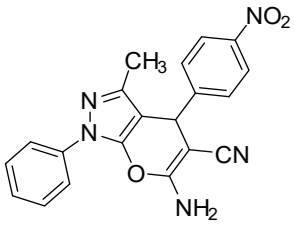
[a]benzaldehyde 1 mmol, 3-methyl-1-phenyl-2-pyrazoline-5-one 1 mmol, malononitrile 1.25 mmol
[b]Isolated yield.

Table 2: Synthesis of pyrano [2,3-c] pyrazoles derivatives 4a-r using SNP_s-AT[a].



Entry	Product	Time (min)	Yield (%)[b]	Mp. (˚C) [lit]
4a		15	97	172-173 (171-173) [22]
4b		25	86	175-177 (176-177) [22]
4c		20	88	190-192 (190-192) [22]
4d		20	90	171-173 (172-174) [23]
4e		25	90	174-175 (174-175) [23]
4f		30	92	186-188 (185-186) [23]

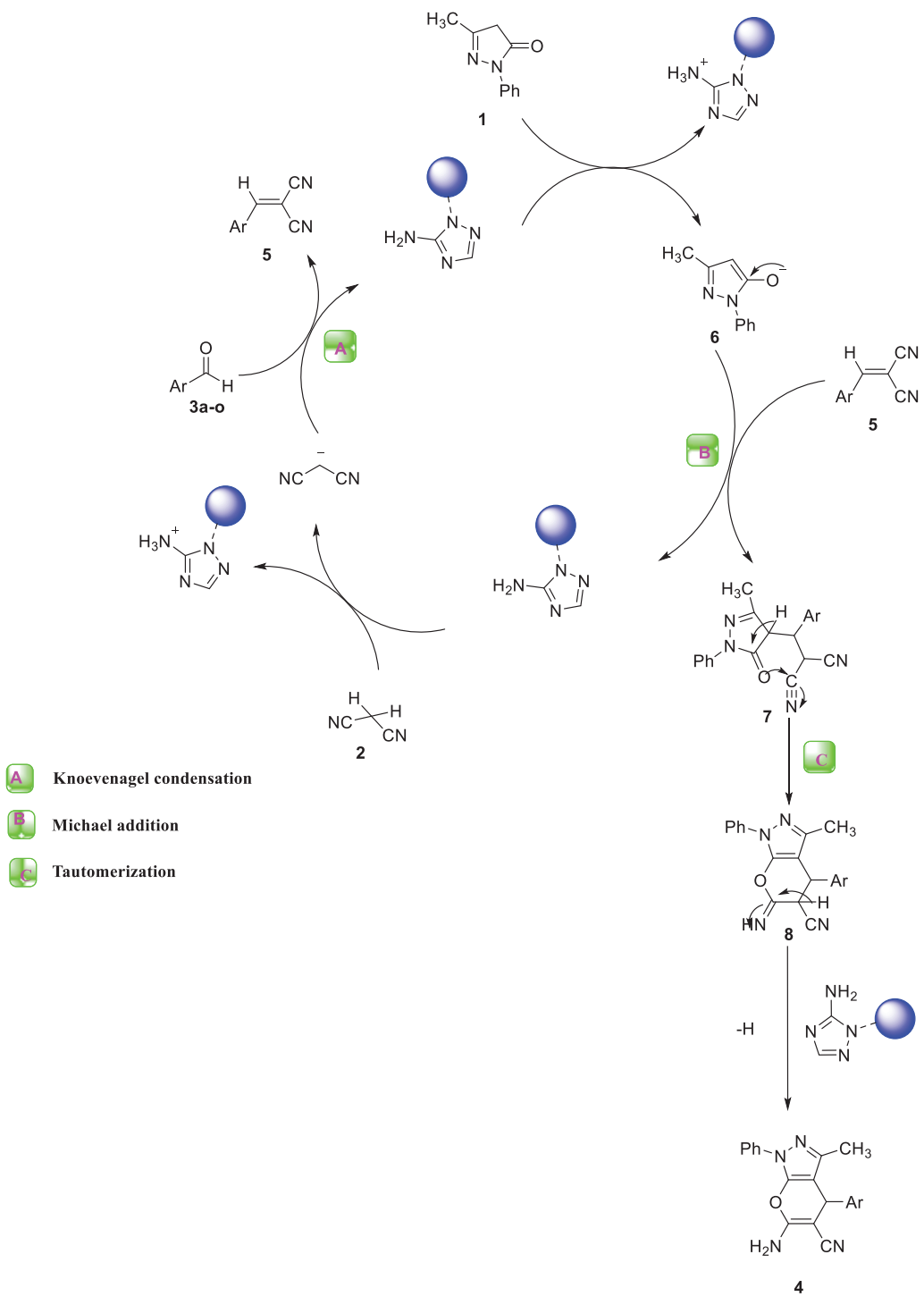
4g		40	80	322-325 (320-322) [6]
4h		50	90	316-318 (314-315) [6]
4i		35	88	169-170 (169-170) [23]
4j		30	80	169-171 (169-171) [23]
4k		25	89	160-162 (160-161) [23]
4l		35	80	144-146 (144-146) [23]
4m		30	80	159-161 (159-160) [24]
4n		30	92	159-160 (159-160) [25]

4o		25	85	158-159 (157-159) [26]
4p		30	82	166-168 (166-167) [26]
4q		30	89	183-185 (183-184) [23]
4r		20	94	193-195 (194-196) [23]

[a]Reaction conditions: 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol), arylaldehyde (1 mmol), malononitrile (1.25 mmol), and SNP_s-AT (0.003 g), solvent-free, 60˚C.
[b]Isolated yields.

Scheme 3

Triazole (3-AT), and another chemical material in this research were buying from Fluka and Merck chemical companies in high-level purity. The reaction progress was controlled by utilizing Thin Layer Chromatography (TLC) (silica-gel SIL G/UV254 plates, n-Hexane/ EtOAc: 2/1). Melting points were determined by a KRUSS model measuring device. ^{1}H NMR spectra were recorded with a Bruker 400 Ultrashield and ^{13}C NMR spectra were recorded at 100 MHz, with DMSO-d_6 as the solvent and TMS as the internal standard. Fourier Transform Infrared (FT-IR) spectra were taken with a JASCO FT-IR/680 plus spectrometer, using KBr pills. Energy Dispersive Spectroscopy (EDS) was recorded exploitation TESCAN Vega model instrument. Energy Dispersive X-Ray (XRD) spectroscopy was performed using a Bruker AXS (D_8 Advance) model instrument, with Cu-Ka radiation (λ =



Scheme 4 Novel SNP_s-AT as catalysts for the synthesis of pyrano [2,3-C] Pyrazoles.

0.15418 nm). The measurement in 2θ ranging from 10° to 80° at the rate of 0.05° min^{-1} was done. Field Emission Scanning Electron Microscopy determination for the particle size and morphology of the samples through a MIRA3TESCAN-XMU FE-SEM instrument under an acceleration voltage of 26 kV was observed.

A general manner for preparation of SiO_2 nanoparticle: The SiO_2 nanoparticles applied in this process are prepared using the sol-gel method. These nanoparticles were made by mixing TEOS (6.2 ml) with ethanol (100 ml) as the solvent and ammonium hydroxide (6.5 ml) as a catalyst to create alkaline conditions under magnetic stirring for 15 h at room temperature. The mixture was filtered by Centrifuge (4000 rpm, 30 min), washed three times with ethanol

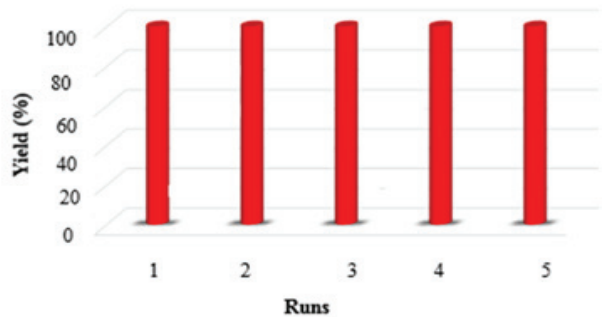


Figure 5 Reuse of the catalyst in the synthesis of pyrano [2,3-c] pyrazole derivatives.

solution and water, and then white powder dried at 60˚C for 12 h in the vacuum [27].

Method for the synthesis of 3-chloropropyl-SiO_2 NPs: (1g) SiO_2 nanoparticles were dispersed in dried toluene (60 mL) by ultrasonic for 15 min. Then, in the reflux method, 3-chloropropyl tri methoxy silane (2 ml) was added dropwise into a round bottom flask under moderate stirring and argon atmosphere for 24 h. Finally, the mixture was cooled to room temperature, separated by Centrifugation (4000 rpm, 10 min), and washed with water and ethanol several times. The 3-chloropropyl-SiO_2 NPs were dried at 80˚C for 6 h in the vacuum [13].

Synthesis of 3-amino 1H-1,2,4-triazole (3-AT) -3-chloropropyl- SiO_2 NPs: 3-Amino-1H-1,2,4-Triazole (3-AT) (0.42 g, 5 mmol) in the presence of K_2CO_3 (0.69 g, 5 mmol) was added into a suspension of SiO_2@$(CH_2)_3Cl$ powder (1.0 g) and dry toluene (30 mL) under stirring and refluxed at 110˚C for 12 h. After completion of the reaction, the mixture was filtered and the obtained powder washed several times with ethanol and water, then the solid powder was dried at 100˚C in the Vacuum for 24 h.

The general procedure for the synthesis of pyranopyrazole derivatives using SiO_2@ $(CH_2)_3$-(3-AT)(SNP_s-AT) as nanocatalyst: Aryl aldehydes (1 mmol), 3-methyl-1-phenyl-2-pyrazoline-5-one (1mmol), and malononitrile (1.25 mmol) in the presence (0.003 g) of **SNP_s-AT** catalyst were combined under solvent-free conditions and heated at 60˚C in an oil bath. The reaction completion was followed using TLC (n-hexane: ethyl acetate, 2:1). At the end of the reaction, the mixture was cooled to room temperature, then hot ethyl acetate (5 mL) was added, and the catalyst was collected by Centrifuge instrument. Extra purification and recrystallization were obtained by adding hot ethanol. Several selected spectral data of compounds (4c-4h) are given below.

6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4c): Mp. 190–192˚C, White crystals. IR spectrum, ῡ, cm^{-1}:3454, 3359 (NH_2), 2923 (CH arom.), 2854 (CH, CH_3), 2190 (CN), 1653, 1594 (C=N), 1446, 1351, 1267, 1184, 1069 (C-O, CN).

6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4d): Mp. 171–173˚C, White crystals. IR spectrum, ῡ, cm^{-1}:3454, 3330 (NH_2), 3068 (CH arom.), 2883 (CH, CH_3), 2195 (CN), 1655, 1594 (C=N), 1455, 1396, 1285, 1177, 1069 (C-O, CN), 692 (C-Cl).

6-amino-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4e): Mp. 174–175˚C, White crystals. IR spectrum, ῡ, cm^{-1}: 3392, 3321 (NH_2), 3023 (CH arom.), 2883 (CH, CH_3), 2197 (CN), 1658, 1590 (C=N), 1455, 1392, 1250, 1173, 1128 (C-O, CN).

6-amino-4-(2,4-dichlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4f): Mp. 186-188˚C, White crystals. IR spectrum, ῡ, cm^{-1}: 3457, 3324 (NH_2), 3023 (CH arom.), 2883 (CH, CH_3), 2191 (CN), 1660, 1595 (C=N), 1469, 1394, 1267, 1167, 1126 (C-O, CN), 756 (C-Cl).

6-amino-4-(2,4-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4g): Mp. 320–322˚C, White crystals. IR spectrum, ῡ, cm^{-1}:3424, 3309, 3183 (OH, NH_2), 2923 (CH arom.), 2854 (CH, CH_3), 2211 (CN), 1590, 1511 (C=N), 1400, 1351, 1255, 1189, 1045 (C-O, CN), 842, 800.^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.68 s (1H, OH), 7.92 s (1H, OH), 7.76 s (2H), 7.52–7.75 m (2H), 7.25–7.27 m (2H), 6.89 s (2H, NH_2), 6.45 d (J = 4 Hz, 2H), 6.32 s (1H), 5.53 s (1H, CH), 1.82 s (3H, ring CH_3). ^{13}C NMR spectrum, δ, ppm: 166.6, 162.2, 161.9, 159.7, 155.8, 153.6, 138.2, 126.3, 123.1, 117.1, 114.3, 108.8, 107.1, 103.8, 101.3, 75.7, 42.1, 26.1. Anal. Calcd. for $C_{20}H_{16}N_4O_3$: C, 66.66;H, 4.48;N, 15.55. Found: C, 66.58; H, 4.53; N, 15.60.

6-amino-4-(5-bromo-2-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c] pyrazole-5 carbonitrile (4h): Mp. 314-315°C, Yellow crystals, IR spectrum, ῡ, cm^{-1}: 3455, 3347, 3212 (OH, NH_2), 2935 (CH arom.), 2210 (CN), 1646, 1608, 1554 (C=N), 1477, 1388, 1280 (CN), 1222, 1087 (C-O), 802, 470 (C-Br). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm:

8.71 s (1H, OH), 7.71 d (J=4 Hz, 2H), 7.52 t (J=4 Hz, 2H), 7.36 s (1H), 7.27-7.30 m (2H), 6.83–6.93 m (2H, NH_2), 6.61 d (J= 4 Hz,1H), 5.46 s (1H, CH), 2.04 s (3H, CH_3). ^{13}C NMR spectrum, δ, ppm: 162.9, 162.3, 158.2, 158.1, 151.6, 140.9, 137.2, 127.6, 121.3, 118.3, 118.0, 118.0, 117.2, 116.7, 97.6, 75.2, 47.5, 23.8. Anal. Calcd. for $C_{20}H_{15}BrN_4O_2$: C, 56.75; H, 3.57; N, 13.24. Found: C, 56.70; H, 3.51; N, 13.29.

Conclusion

In this study, SNP_s-AT as a novel, eco-friendly and efficient nanocatalyst was synthesized. The characterization and catalytic activity were done by FT-IR, EDS, XRD, Fe-SEM analysis. SNP_s-AT has used for the synthesis of pyrano[2,3-c] pyrazoles derivatives. This procedure has unique advantages including excellent yields, reusability of the catalyst, short reaction times, simple protocol, that cause the present methodology will be effective.

Acknowledgment

We gratitude to thank the research council of the Yasouj University of Iran for the financial support of this project.

Conflict of Interests

The authors declare no conflict of interests.

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