

## Magnetically recoverable nano-crystalline NiFe<sub>2</sub>O<sub>4</sub> catalyzed green and sustainable synthesis of functionalized pyrano-pyrazol, pyrano-coumarin, and 4H-chromene derivatives

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Received 12 August 2023; received in revised form 24 September 2023; accepted 18 October 2023 (DOI: 10.30495/IJC.2023.1993771.2041)

### ABSTRACT

Synthesis of pyrano-pyrazol, pyrano-coumarin, and 4H-chromene derivatives has been achieved by the multicomponent reaction of substituted 1,3-diketo compounds, dialkyl acetylene dicarboxylates and alkyl nitrile derivatives in presence of nano-NiFe<sub>2</sub>O<sub>4</sub>. The nano-NiFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticle was prepared by a simple and effective method and characterized by using XRD, HRTEM images, IR, and VSM studies. The green, convenient, and mild protocol provided large access to desired products in almost quantitative yield. High catalytic activity, very low catalyst loading, and high recyclability are the attractive features of the developed protocol. All reactions were easily performed and preceded with high efficiency under very mild conditions avoiding time-consuming, costly catalysts, and tedious workup and purification of process.

**Keywords:** Nano-NiFe<sub>2</sub>O<sub>4</sub>, Multicomponent reaction, Pyrano-pyrazol, Pyrano-coumarin and 4H-chromene

### 1. Introduction

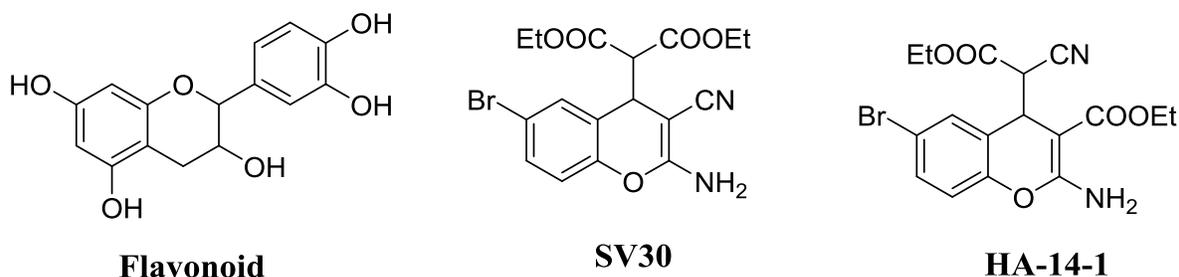
Pyrano-pyrazol derivatives are often part of various naturally occurring compounds with antihyperglycemic [1, 2], antidyslipidemic [3], cytotoxic [4], molluscicidal [5], anti-inflammatory [6], antifungal [7], anticancer [8], and antimalarial [9, 10] properties. These scaffolds have potential applications as cognitive enhancers in neurological diseases, including schizophrenia and myoclonus, as well as for the treatment of Alzheimer's disease [11-14]. The 4H-chromene derivatives are also applied as photoactive materials which can undergo photochemical ring contraction to cyclobutenes from the triplet state [15-17] and are important structural motifs found widely in natural products and pharmaceuticals such as coumarins [18], anthraquinones [19], flavonoids [20], heliannuols B, C, and D [21], ricchiocarpin A and ricchiocarpin B [22], lobatrienetriol [23], KW-3635 [24], oxepinamides C [25], janoxepin [26], bauhiniastatin A [27], SV30, HA-14-1 [28, 29] etc. (Fig. 1). Various natural products like calophyllolides,

calanolides, calanone etc. [30] contain pyrano-[3,2-c]coumarin skeletons. Many of them are broadly employed as biodegradable agrochemicals, cosmetics, and pigments [31].

Hence many synthetic chemists have been fascinated by the astonishing biological activity of these heterocyclic scaffolds and tried to develop an easy protocol for their synthesis. Before this work, few other methods have also been developed [32-35] but those have major limitations. In the multicomponent synthesis of these heterocyclic cores, harsh reaction conditions, longer reaction times, and expensive catalysts were applied. In the domain of multicomponent reactions, metal-anchored heterogeneous compounds have received immense attention in recent times in view of their benefits and improved efficacy due to their stable active sites and recyclability of the catalyst [36]. Functionalized magnetic nanomaterials have appeared as viable alternatives to conventional materials, as a readily available, robust, high-surface-area heterogeneous catalyst [37-39]. They offer the added benefit of being magnetically separable, thereby excluding the requirement of catalyst filtration after

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**Fig. 1.** 4H-chromenes with biological activities

completion of the reaction. There is an urgent need to develop less expensive and easily available, non-precious metal catalysts for this multicomponent reaction. Herein, an efficient and green magnetically recoverable nano crystalline  $\text{NiFe}_2\text{O}_4$  catalyzed methodology is demonstrated for the preparation of desired heterocyclic nucleus by combining the basic units in aqueous media.

## 2. Experimental

### 2.1. Preparation of Catalyst

An aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.4M) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9(\text{H}_2\text{O})$  (0.8M) was mixed with 10M aqueous solution of Triton-X. Then, the required amount of 25%  $\text{NH}_4\text{OH}$  was added slowly to the resulted solution with stirring until a green and transparent solution (pH 7.5) was obtained. The solution was boiled to evaporate the water in an oil bath under continuous stirring. The resultant powder was calcined at  $700^\circ\text{C}$  for 10 h with a heating rate of  $5^\circ\text{C}$  per minute to remove the organic molecules and to obtain spinel nano-NFO.

### 2.2. General procedure for the synthesis of dihydropyrano[2,3-c]pyrazole derivatives

A mixture of substituted hydrazines (1 mmol), ethyl acetoacetate (1 mmol) and  $\text{NiFe}_2\text{O}_4$  (5 mol %) was stirred for 15 minutes at room temperature. The resulting solid mixture was stirred with dialkyl acetylenedicarboxylates (1 mmol), malononitrile or ethyl cyanoacetate (1 mmol) in 5 ml water at  $60^\circ\text{C}$  for a required period of time (TLC). After completion of the reaction, water was removed under reduced pressure from the reaction mixture and was stirred with 5mL ethanol and the catalyst was recovered by applying an external magnet, leaving the clear reaction mixture. After removing the catalyst the solvent was evaporated under vacuum to give the crude product, which was purified by column chromatography.

### 2.3. General procedure for the synthesis of pyrano[3,2-c]coumarin and 4H-chromene derivatives

A mixture of dimedone or cyclohexane-1,3-dione or 4-hydroxycoumarin (1 mmol), dialkyl acetylenedicarboxylates (1 mmol) and malononitrile or ethyl cyanoacetate (1 mmol) and  $\text{NiFe}_2\text{O}_4$  (5 mol %) in 5 ml water was stirred at  $60^\circ\text{C}$  for a required period of time (TLC). After completion of the reaction, water was removed under reduced pressure from the reaction mixture and was stirred with 5mL ethanol and within a few seconds after stirring was stopped, catalyst was deposited on the magnetic bar and removed using an external magnet, leaving the clear reaction mixture. After removing the catalyst the solvent was evaporated under vacuum to give the crude product, which was purified by column chromatography.

### 2.4. General procedure for the synthesis of alkyl-1,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate derivatives:

A mixture of phenylhydrazine (1 mmol), dimethyl acetylenedicarboxylates (2 mmol), malononitrile (1 mmol), and  $\text{NiFe}_2\text{O}_4$  (5 mol%) was stirred in 5 ml water at  $60^\circ\text{C}$  for a required period of time (TLC). After completion of the reaction, water was removed under reduced pressure from the reaction mixture and was stirred with 5ml ethanol, and within a few seconds after stirring was stopped, the catalyst was deposited on the magnetic bar and removed using an external magnet, leaving the clear reaction mixture. After removing the catalyst the solvent was evaporated under vacuum to give the crude product, which was purified by column chromatography.

## 3. Results and Discussion

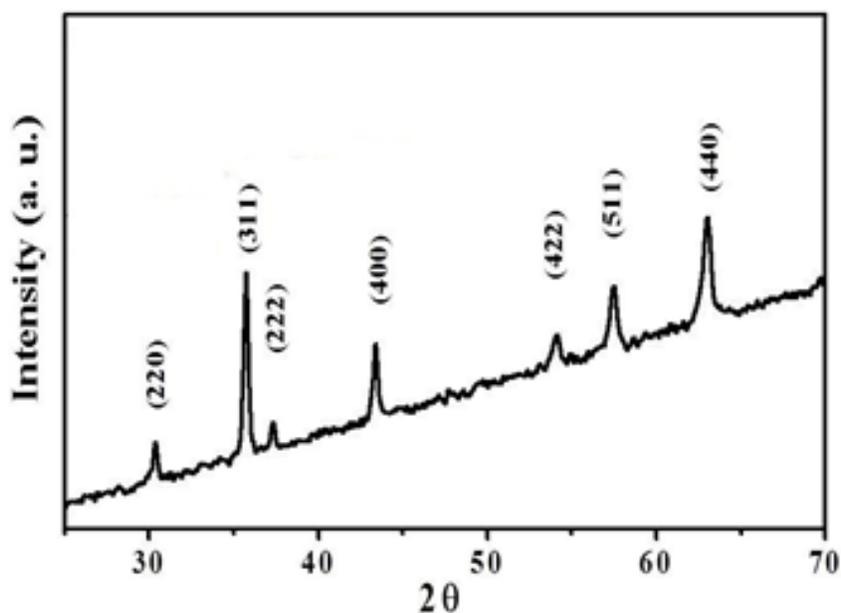
The crystalline phase of prepared [40-44]  $\text{NiFe}_2\text{O}_4$  nanoparticle (NFO nanoparticle) was identified at room temperature using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The XRD pattern of NFO nanoparticle [45, 46] shown in **Fig. 2** describes many strong and sharp peaks indicating face-centered cubic nickel ferrite phase with lattice constant  $a = 0.8335 \text{ nm}$ . All the characteristic peaks of NFO are clearly observed:  $30.29^\circ$  (220),  $35.7^\circ$  (311),  $37.31^\circ$  (222),  $43.36^\circ$  (400),  $53.80^\circ$  (422),  $57.36^\circ$  (511),

62.92° (440) and 74.64° (533) which corresponds to standard diffraction data of NFO (JCPDS No. 74-2081). The XRD pattern indicates the absence of any traces of iron oxide (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>), nickel oxide (NiO), and very high purity of NiFe<sub>2</sub>O<sub>4</sub> nanoparticle. The average sizes of the NFO nanoparticle calculated by the Debye–Scherrer formulae (equation 1) applying the (440) peak of the XRD pattern are 33 and 38 nm respectively.

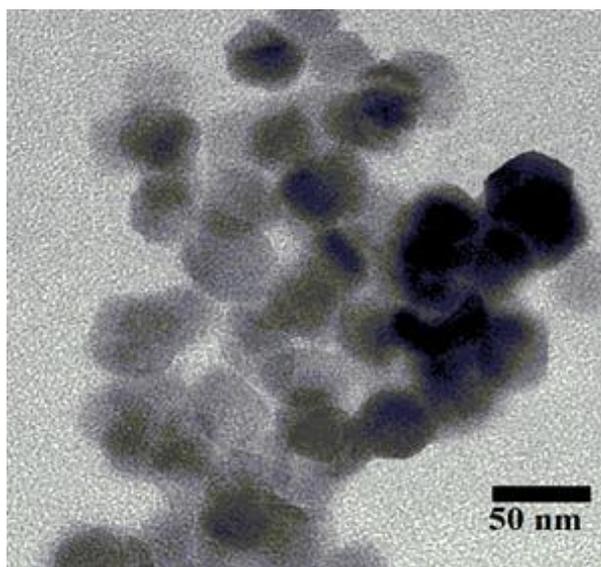
$$d = \frac{K \lambda}{\beta \cos \theta} \quad (1)$$

Where  $\beta$  represents the breadth of the diffraction line at its half intensity maximum;  $K$  is the so-called shape factor which with a value of about 0.9, and  $\lambda$  is the X-ray wavelength used in the XRD.

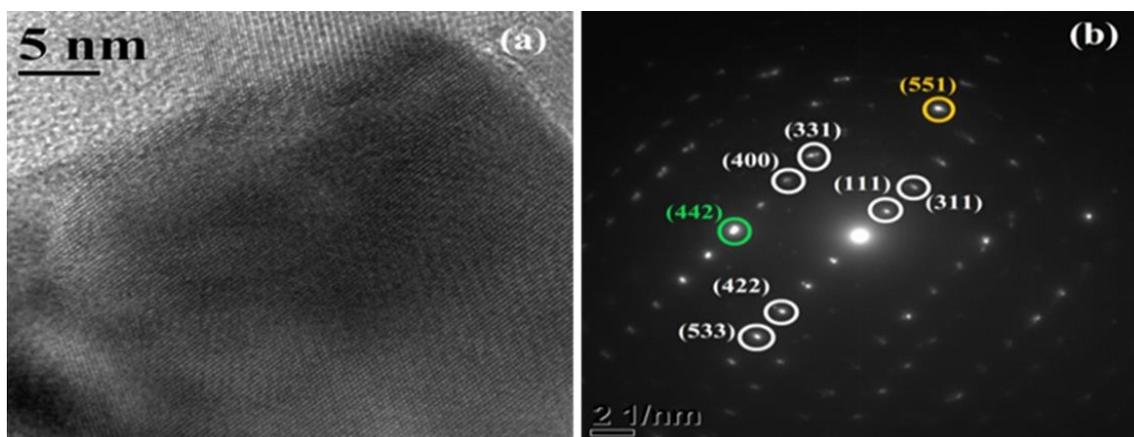
The size and morphology of the synthesized catalysts were determined by UHR-FEG-TEM. The UHR-FEG-TEM image depicts that the nano-catalyst has a nearly hexagonal morphology (**Fig. 3**). The average size was about  $33 \pm 5$  nm from the TEM micrograph measurements which is in good agreement with XRD data. **Fig. 4a** and **Fig. 4b** display the HRTEM image and corresponding SAED pattern of a single nanocrystal.



**Fig. 2:** XRD pattern of the synthesized NiFe<sub>2</sub>O<sub>4</sub> nanoparticle



**Fig. 3.** TEM image of hexagonal NiFe<sub>2</sub>O<sub>4</sub> nanoparticle



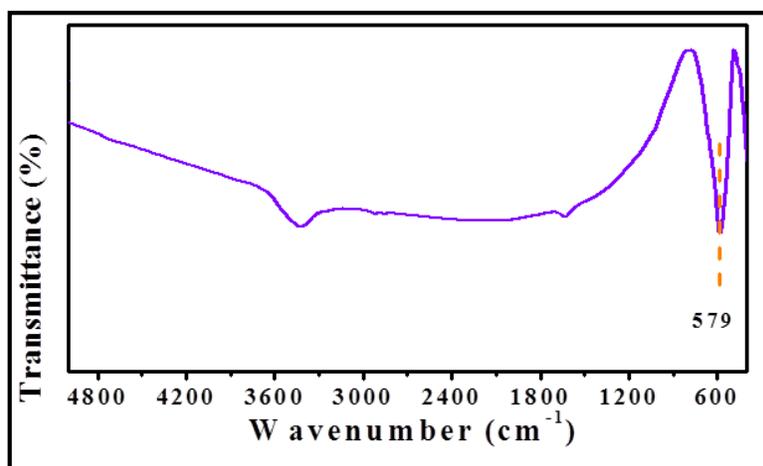
**Fig. 4.** (a) The HRTEM image and (b) corresponding SAED pattern of a single nanocrystal

The FT-IR spectrum of prepared  $\text{NiFe}_2\text{O}_4$  nano-crystals clearly demonstrates the presence of the peak ( $579\text{ cm}^{-1}$ ) for the metal-oxygen stretching vibration as shown in **Fig. 5**. The field dependence of magnetization of synthesized spinel nickel ferrite was measured using a vibrating sample magnetometer at 300 K with an applied field  $-17.5\text{ kOe} \leq H \leq 17.5\text{ kOe}$ .  $\text{NiFe}_2\text{O}_4$  prepared by hydrothermal method shows a ferromagnetic behavior as demonstrated in **Fig. 6**.

To design the synthetic protocol, an one pot four-component coupling reaction of substituted hydrazines (**I**), ethyl acetoacetate (**II**), dialkyl acetylene dicarboxylates (**III**), and malononitrile or ethyl cyanoacetate (**IV**) was assumed as a model reaction to get dihydropyrano[2,3-*c*]pyrazol core (**Scheme 1**).

Keeping in mind the greener aspects of the ongoing scheme, the search for a proper recoverable and reusable catalyst which can be used in water solvent was the initial goal. As a continuation of my previous research on nano-catalysts, various nano metal oxides like nano ZnO, nano  $\text{Al}_2\text{O}_3$ , nano  $\text{SiO}_2$ , nano CuO, nano  $\text{Fe}_2\text{O}_3$ ,

and nano NiO were tested for their activity on the model reaction of phenylhydrazines, ethyl acetoacetate, diethyl acetylenedicarboxylates and malononitrile (**Scheme 2**). **Table 1**, entry 1 showed that without catalyst the reaction fails to give any product even after 48 hours. With nano ZnO, nano  $\text{Al}_2\text{O}_3$ , nano  $\text{SiO}_2$ , and nano CuO, the yield of the reaction was not so satisfactory (**Table 1**, entries 2, 3, 4, 5). Entries 6 and 7 in **Table 1** clearly showed that nano  $\text{Fe}_2\text{O}_3$  and nano NiO were able to produce superior yield of the desired dihydropyrano[2,3-*c*]pyrazol derivative. Thus, a catalyst containing both  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  metal ions will probably provide a higher amount of product. Hence 5 mol%  $\text{NiFe}_2\text{O}_4$  magnetic nanoparticle was administered for the MCR and as expected, an excellent result was obtained at  $60\text{ }^\circ\text{C}$  in aqueous media (**Table 1**, entry 8). Several solvents were also screened to test their efficiency at  $60\text{ }^\circ\text{C}$  and the results are summarized in **Table 1** (entries 9, 10, and 11). It is noteworthy to mention that the polar solvents afforded better yield than nonpolar ones and the best result was obtained in an aqueous medium.



**Fig. 5.** FT-IR spectrum of prepared  $\text{NiFe}_2\text{O}_4$  nano-crystals

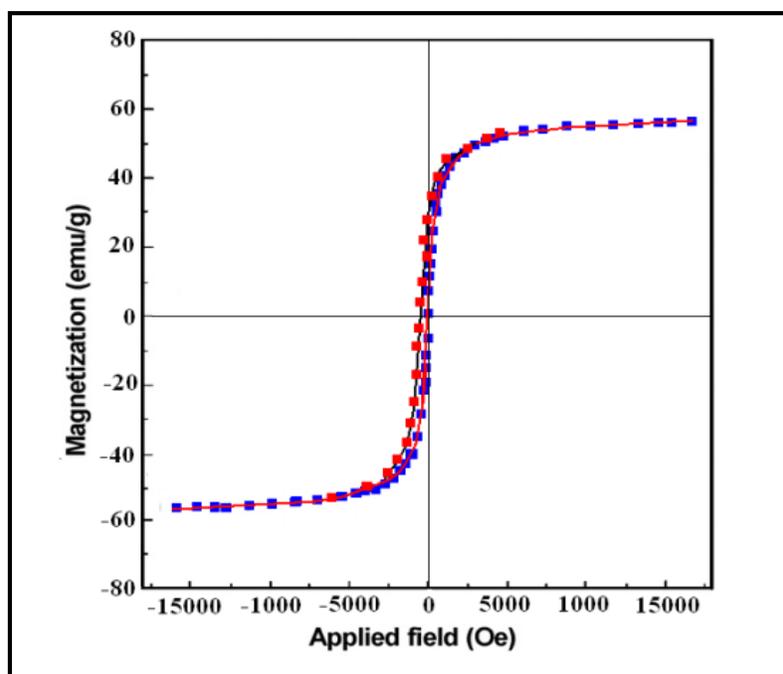
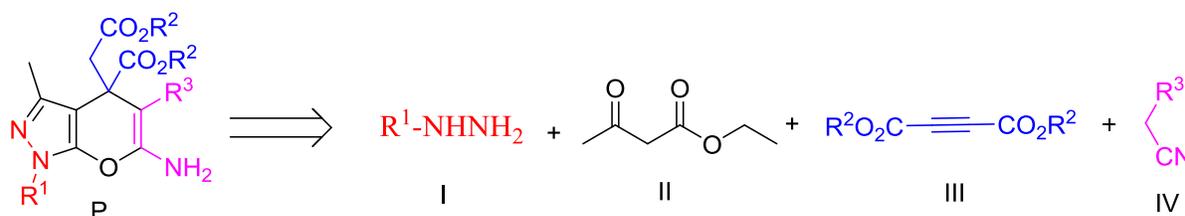
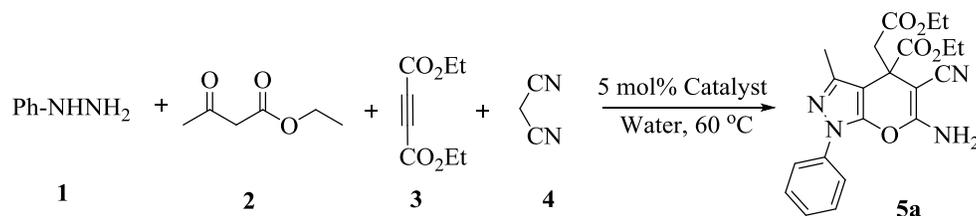


Fig. 6. Field dependence magnetization of the as-prepared nano nickel ferrites



Scheme 1. Retrosynthetic analysis of dihydropyrano[2,3-c] pyrazol scaffold



Scheme 2. Synthesis of dihydropyrano[2,3-c]pyrazol derivative

Table 1. Optimization of reaction conditions for the synthesis<sup>a</sup> of dihydropyrano[2,3-c] pyrazol derivative 5a

Entry	Catalyst	Solvent	Time (h)	Yield <sup>b</sup> %
1	-	Water	48	0
2	Nano ZnO	Water	10	15
3	Nano Al <sub>2</sub> O <sub>3</sub>	Water	10	15
4	Nano SiO <sub>2</sub>	Water	8	20
5	Nano CuO	Water	8	35
6	Nano Fe <sub>2</sub> O <sub>3</sub>	Water	4	65
7	Nano NiO	Water	4	45
8	Nano NiFe <sub>2</sub> O <sub>4</sub>	Water	1	95
9	Nano NiFe <sub>2</sub> O <sub>4</sub>	Toluene	3	48
10	Nano NiFe <sub>2</sub> O <sub>4</sub>	Dichloromethane	3	76
11	Nano NiFe <sub>2</sub> O <sub>4</sub>	Ethanol	2	88

<sup>a</sup> All reactions were carried out with 1 mmol of each reactant in 5 ml solvent and 5 mol % of specified catalyst at 60 °C

<sup>b</sup> Yield of isolated products

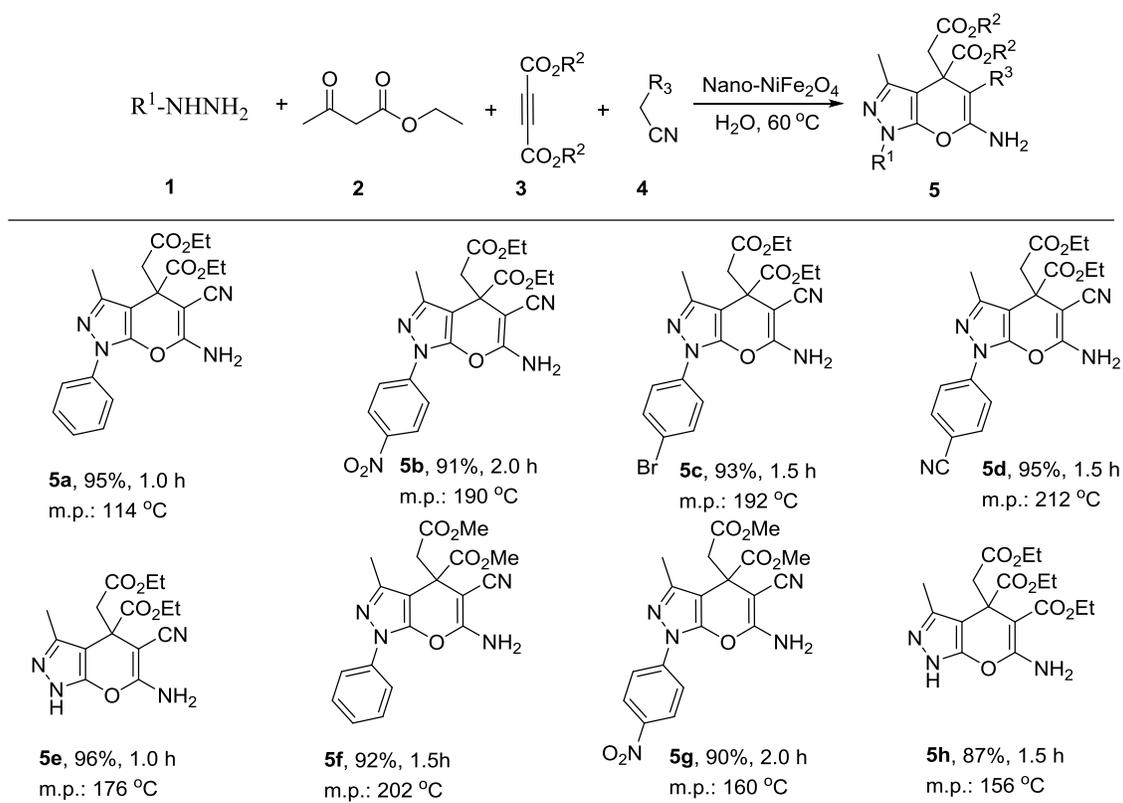
With this standardized protocol, a wide variety of dihydropyrano[2,3-*c*] pyrazol derivatives were synthesized using differently substituted starting materials (**Table 2**). This developed methodology was applied for the reaction of various hydrazine derivatives with diverse electronic environments. As demonstrated in **Table 2**, the nano-crystalline NiFe<sub>2</sub>O<sub>4</sub> catalyzed tandem four-component synthesis provided dihydropyrano[2,3-*c*]pyrazol derivatives in almost quantitative yield.

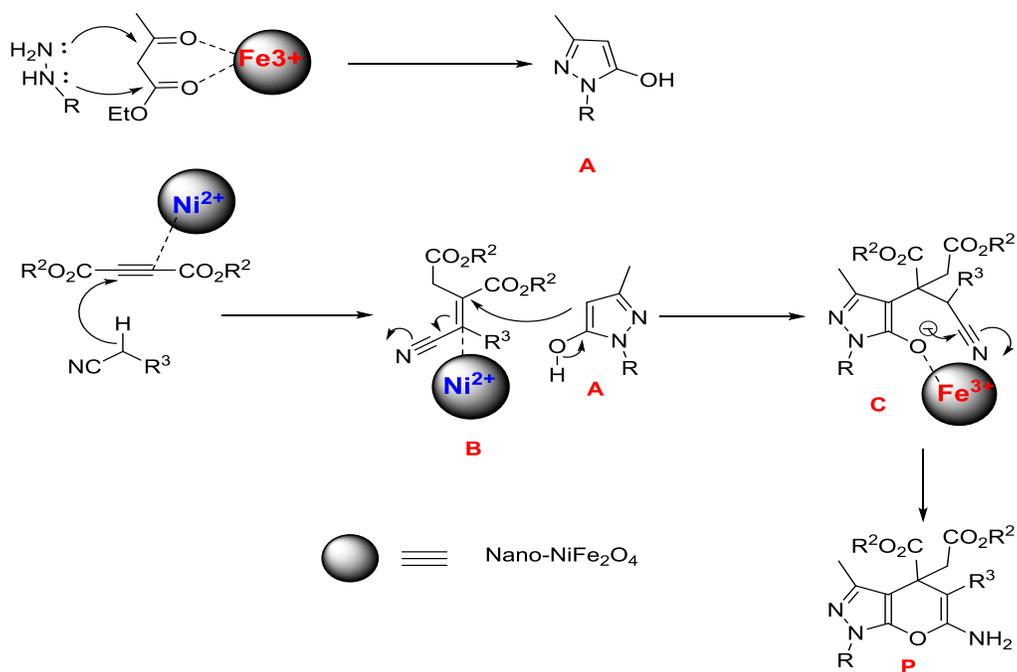
On the basis of experimental data and literature survey, the product formation may be rationalized by the initial generation of pyrazolone intermediate (A) through Lewis acidic Fe<sup>3+</sup> (active catalyst of nano-NiFe<sub>2</sub>O<sub>4</sub>)-promoted reaction of phenylhydrazine and ethyl acetoacetate (**Scheme 3**). Subsequently, Ni<sup>2+</sup> (active catalyst of nano-NiFe<sub>2</sub>O<sub>4</sub>) catalyze the Michael addition reaction between dialkyl acetylenedicarboxylate and alkyl nitrile derivatives to form the intermediate B. Next, the  $\pi$  electron cloud of intermediate B is polarized by Ni<sup>2+</sup> and its  $\beta$  position is attacked by the pyrazolone intermediate (A) to produce enolate type intermediate C.

Finally, upon intramolecular electrophilic cyclization of C in the presence of Lewis acidic Fe<sup>3+</sup> produces the desired pyran rings. Both the metal ions (Ni<sup>2+</sup> and Fe<sup>3+</sup>) in nano-NiFe<sub>2</sub>O<sub>4</sub> are necessary for the very high activity. However, the catalyst screening study (**Table 1**) indicates that Fe<sup>3+</sup> has a greater influence in this reaction. The strong Lewis acidic Fe<sup>3+</sup> efficiently catalyzed condensation and intramolecular cyclization step.

The four-component reaction passes through the formation of pyrazolone intermediate which can be viewed as an active methylene compound. Hence scope of this methodology was further extended by using other active methylene compounds like dimedone, cyclohexane-1,3-dione and 4-hydroxycoumarin in place of pyrazolone intermediate. In this case, the protocol turned out to be a three-component synthesis of multi-functionalized pyrano[3,2-*c*]coumarin and 4*H*-chromene derivatives with excellent yield (**Table 3**).

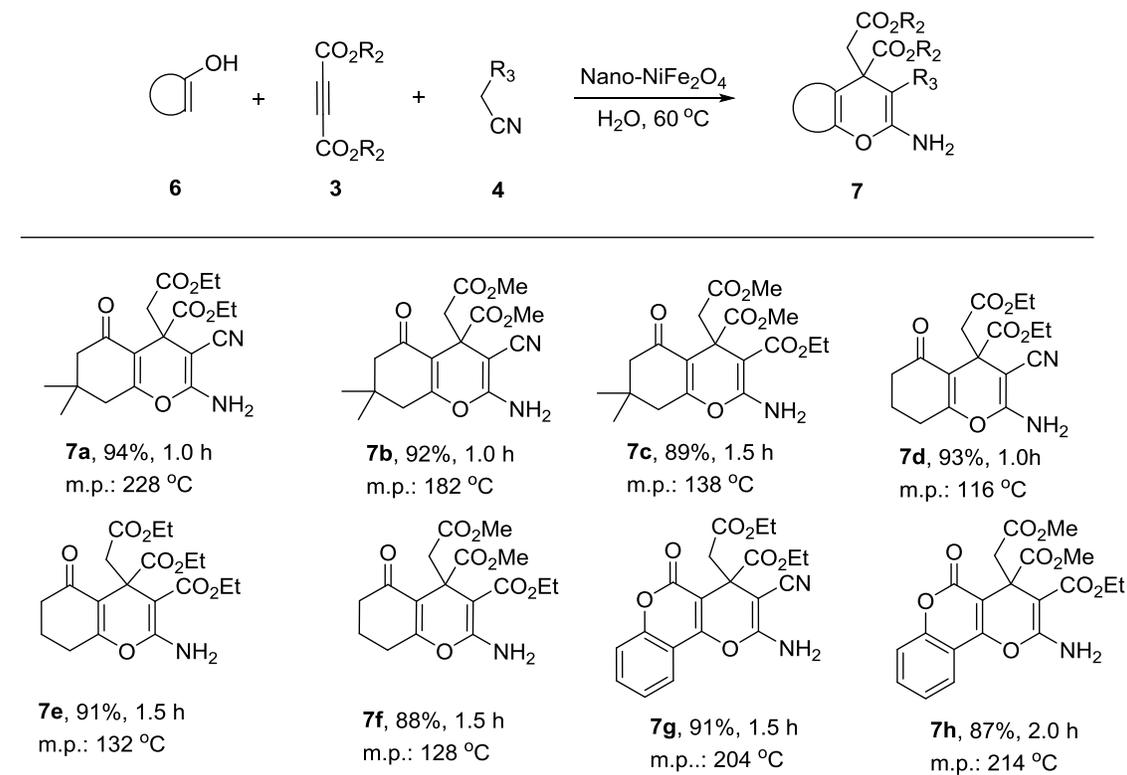
**Table 2.** Four component synthesis of 3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole derivatives





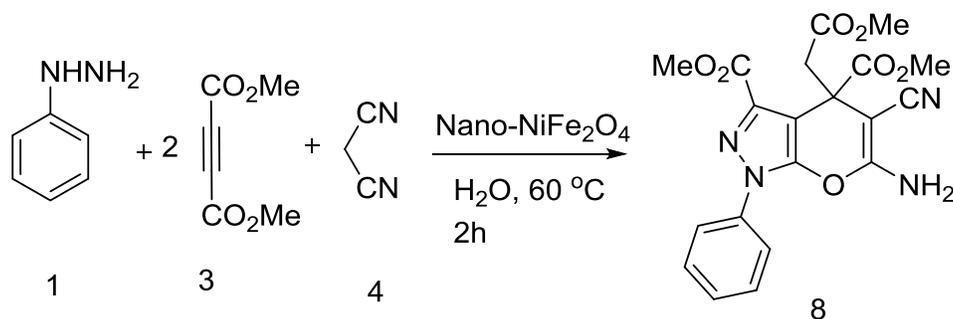
**Scheme 3.** The proposed mechanisms for the formation of the products

**Table 3.** Synthesis of pyrano[3,2-*c*]coumarin and 4*H*-chromene derivatives



Interestingly, in the presence of nano NiFe<sub>2</sub>O<sub>4</sub>, the reaction of phenyl hydrazine, two equivalent dimethyl acetylenedicarboxylates, and malononitrile provided

new dihydropyrano[2,3-*c*]pyrazol **8** in 45 % yield (**Scheme 4**).



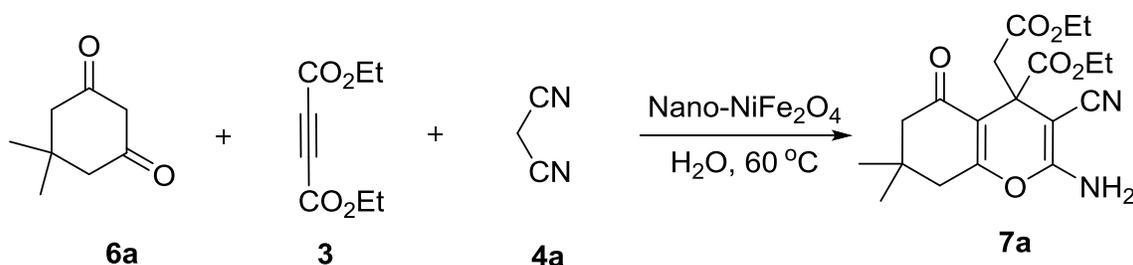
**Scheme 4:** Synthesis of alkyl-1,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

A heterogeneous catalyst is more attractive towards chemists when it is easily recovered and re-used. The reusability study of the nano-NiFe<sub>2</sub>O<sub>4</sub> catalyst was performed for the synthesis of **7a** (Scheme 5).

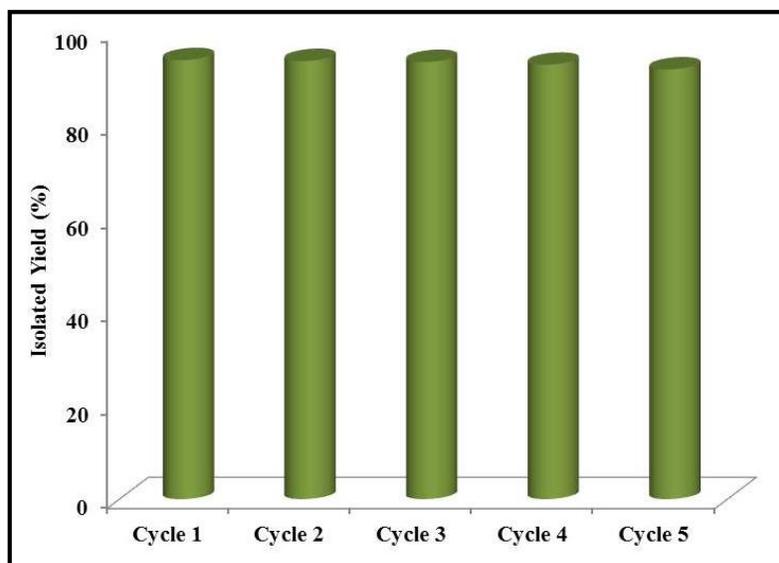
The recycling of the catalyst was achieved by magnetic separation followed by washing with ethanol and finally drying before reuse. No significant loss of catalyst

performance was observed after five rounds of use of catalyst due to insignificant catalyst leaching (Fig. 7).

The FT-IR spectra (Fig. 8) and X-ray diffraction (XRD) patterns (Fig. 9) indicated that the crystal structure of the nano-NiFe<sub>2</sub>O<sub>4</sub> was unharmed after the fifth runs, which not only enlightened the excellent reusability but



**Scheme 5.** Model reaction for recyclability study



**Fig. 7.** Recyclability study of nano-NiFe<sub>2</sub>O<sub>4</sub> catalyst

also reconfirmed the high chemical stability of this catalyst. The nano  $\text{NiFe}_2\text{O}_4$  showed greater catalytic performance and recyclability in the multicomponent reaction between cyclic-1,3-diketone, diethyl acetylenedicarboxylate, and malononitrile compared to

the previously reported catalyst system (**Table 4**). Very low catalyst loading of nano  $\text{NiFe}_2\text{O}_4$  demonstrates very high activity in this reaction. The catalyst displayed excellent recyclability compared to other reported catalyst systems.

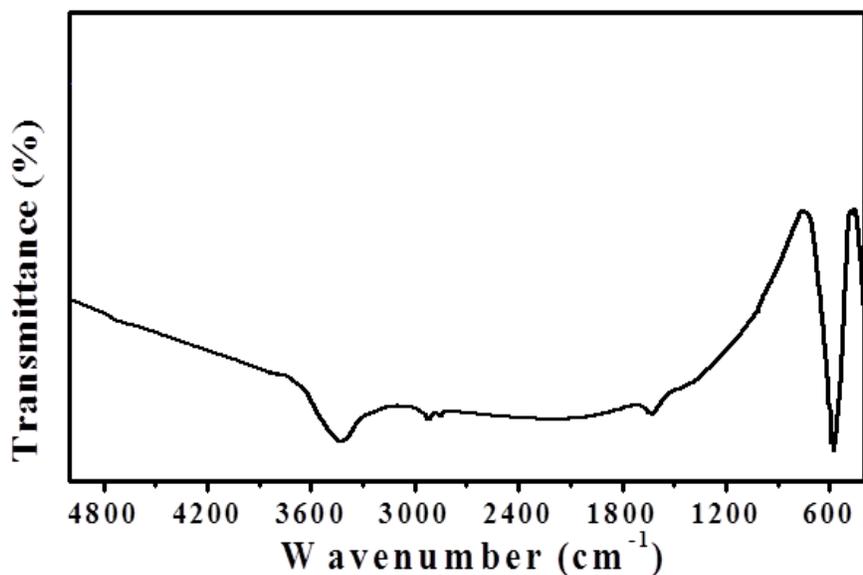


Fig. 8. FT-IR spectra of nano- $\text{NiFe}_2\text{O}_4$  after 5th catalytic cycle

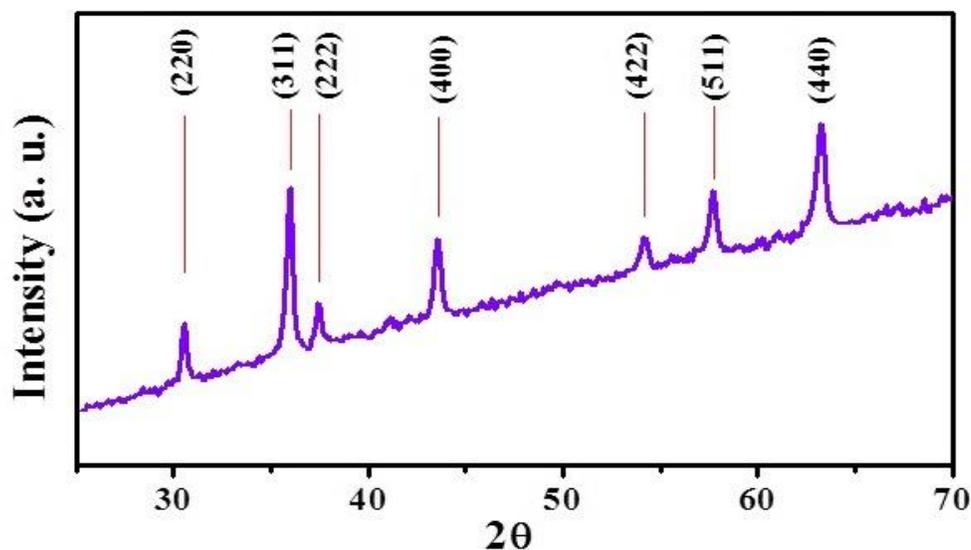


Fig. 9. XRD) pattern of nano- $\text{NiFe}_2\text{O}_4$  after the 5th catalytic cycle

**Table 4.** Comparative study of the efficiency of catalysts

Catalyst	Catalyst loading (mol%)	Time	Reusability	Yield (%)	References
$\text{CH}_3\text{NH}_2$	30	30 min	No Reusability	81	24a
$\text{Na}_2\text{CO}_3$	20	2.5 h	No Reusability	81	24b
nano- $\text{NiFe}_2\text{O}_4$	5	1 h	Recycled five cycles	93	This work

#### 4. Conclusions

Overall, a sustainable green efficient protocol for the synthesis of dihydropyrano[2,3-*c*]pyrazol, pyrano[3,2-*c*]coumarin, and 4*H*-chromene scaffolds from easily accessible reactants by one-pot four- and three-component reaction has been achieved. The problem of removal of conventional catalysts can also be solved by using magnetically separable nano NiFe<sub>2</sub>O<sub>4</sub>. The catalyst is highly stable in aqueous media at 60 °C and a very small change of activity was observed after the fifth cycle of use of the catalyst. Hope this methodology will extend the scope of synthesis of this wide spectrum of novel compounds.

#### Acknowledgements

I gratefully acknowledge the financial support from Gobardanga Hindu College.

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