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Magnetic nickel catalyst: Efficient and economical synthesis of aryl 2-oxazolines from aromatic nitriles and amino alcohols

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Abstract
This study represents a magnetically recoverable nickel-supported iron oxide (Ni/Fe_3O_4) catalyst as a breakthrough technique for the synthesis of aromatic 2-oxazolines. The Ni/Fe_3O_4 catalyst has outstanding flexibility and can efficiently convert several aromatic nitriles and amino-alcohols into the desired aryl-2-oxazoline outputs. The high level of catalytic activity resulting in competent conversion of the starting materials to the desired products is a remarkable feature of the catalytic platform we have developed. The use of an external magnetic field enhances the ease with which the catalyst can be separated from the reaction mixture, thereby speeding up the purification process and reducing the dependence on chemicals and energy that is typically associated with conventional separation techniques. This approach offers both ecological and practical benefits, making it ideal for possible larger-scale applications. Notably, our catalytic design is particularly noteworthy for its exceptional reusability. The Ni/Fe_3O_4 catalyst retains its catalytic activity over numerous cycles, ensuring consistent performance. In particular, there is no significant reduction in the catalytic efficiency of the catalyst after five consecutive recycling runs. This study presents a sustainable approach to aromatic 2-oxazoline synthesis, improves its economics through reduced catalyst consumption and confirms the durability and stability of Ni/Fe_3O_4 catalyst under given reaction conditions. The study utilises a magnetically recoverable Ni/Fe_3O_4 catalyst. This is an innovative and promising catalyst. Its potential as a valuable tool in the synthetic chemist's toolkit is highlighted by its broad substrate compatibility, enhanced catalytic efficiency, easy catalyst recovery and impressive recyclability.

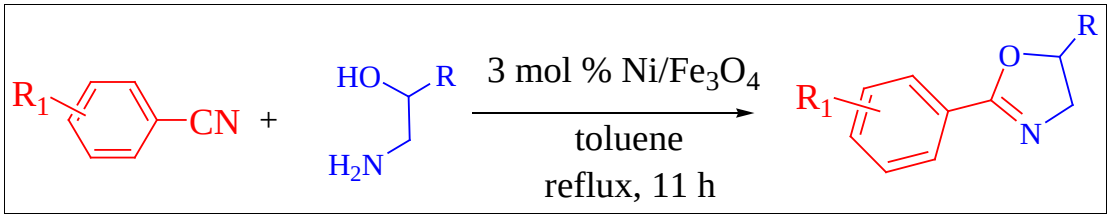
Keywords: Oxazolines, amino alcohols, aromatic nitriles, magnetically recoverable Ni/Fe_3O_4

1. Introduction
Synthesis of Nitrogen and Oxygen containing five-member heterocyclic compounds occupy a significant position in the chemical industry such as biological activity. Due to their wide range of applications, among them 2-oxazolines, (4, 5-dihydrooxazoles) exist in various natural products and biologically active compounds and as enzyme inhibitors [1]. A few of the natural products having oxazoline framework are *trans*, *trans*- ceratospongamide, westiellamide, acinetobactin, ascidiacyclamide, Bistratamide, agrobactin, [2]. These heterocyclic compounds show significant activity towards antidiabetic, antihypertensive, antidepressive, anticancer, anti HIV-1, antitumor and antialzheimer activities to name a few [3]. Optically active mono- and bis- oxazolines are used as chiral auxillaries and ligands in asymmetric synthesis [4]. Achiral oxazolines find their use as an important protecting group, and a valuable intermediate in organic synthesis [5].
Several methods have been reported for the synthesis of oxazolines by using carboxylic acids and amino alcohols [7]. Moreover, Natale and co-workers were developed an in-situe one-pot synthesis of 2-oxazolines from ester and amino alcohols in presence of $LnCl_3$/Zinc triflate [8]. Recently Bedekar and co-workers found that natural kaolinitic clay as an effective as catalyst for the conversion of aromatic and aliphatic nitriles with 1, 2-aminoalcohol to 2-oxazolines [9].
The requirement of coupled products in chemical industries leads to the development of different transition metal catalyst
The development of environmentally benign and efficient synthetic methods continues to be a central goal of current research in chemistry. In this regard, catalysis and organometallic chemistry are key techniques for achieving these objectives and for contributing to a “greener” chemistry in the future.

Thus there is systematic interest in robust and cost-efficient synthetic methods. During the past centuries, transition metal-catalyzed combination reactions of aryl alcohols through all types of nucleophiles have emerged as the most significant tool for the manufacture of 2-Oxazolines.

Heterogeneous catalysis is particularly attractive as it allows the production and ready separation of large quantities of products with the use of a small amount of catalyst. Magnetic nanoparticles are a class of nano-structured materials of current interest, due largely to their advanced technological and medical applications, envisioned or realized [10]. Among the various magnetic nanoparticles under investigation, Fe_3O_4 nanoparticles are arguably the most extensively studied [11] and recently emerged as promising supports for the immobilization metal nanoparticles. Fe_3O_4-supported metal catalysts can be separated from the reaction medium by an external permanent magnet. Ni/Fe_3O_4 was prepared according to the literature [14] and the amount of nickel in the catalyst was determined with an inductively coupled plasma, atomic emission spectroscopy (ICP-AES) instrument and the weight percentage of Ni in the catalyst was found to be 8.3%.

In the present work, we report our investigations on the application of Fe3O4-supported Ni(0) nanoparticles (Ni/Fe_3O_4) [13] for the synthesis of practical and atom-economic aromatic 2-oxazolines from the reaction of aromatic nitriles and 2-amino alcohols (Scheme 1).

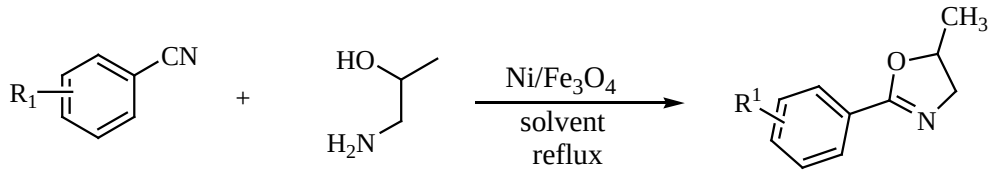


Scheme 1

2. Results and Discussion

In our initial studies, various solvents were investigated using benzonitrile and 1-aminopropan-2-ol as model substrates to know solvent effect on the synthesis of oxazolines (Table 1). The reaction conditions were optimized and the best conditions were found to be 1.5 mol % of Ni/Fe_3O_4 and toluene as the solvent as shown in Table 1, entry 1. By virtue of these optimized conditions, the reaction afforded the desired product an 83 % yield. Subsequently, the reaction condition was optimized by employing different solvents, wherein various polar and non-polar solvents were examined and it was found that all of them had a negative influence on the reaction to different degrees (Table 1, entries 2 - 8).

Table 1: Optimization of reaction conditions for the synthesis of oxazolinies.[a]



Entry	Solvent	Time (h)	Yield (%)[b]
1	Toluene	11	83
2	Benzene	13	62
3	CH_2Cl_2	13	23
6	DMF	24	0
7	DMSO	24	0
8	1,4 dioxane	24	40
9	CH_3CN	24	20
10	CH_3NO_2	12	45

[a] Reaction conditions: benzonitrile (1 mmol), 1-aminopropan-2-ol (1.2 mmol), Ni/Fe_3O_4 (1.5 mol %) and solvent (3 mL) at their reflux temperature.

The general applicability of this reaction was evaluated with diverse nitriles and amino alcohols. In case of 1-amino-propan-2-ol as the amino-alcohol variant, it was observed that the reaction yielded better results for electron releasing substrates (Table 2, entries 1-5). When 2-aminobutan-1-ol was taken the substrate, electron withdrawing nitriles yielded better results than electron releasing one (Table 2, entries 6-10). Overall the yields are better compared to 1-amino-propan-2-ol. When the reaction was carried out with a hetero-aromatic aldehyde, pyridine-3-aldehyde and the yield was moderate (Table 2, entry 10).

Table 2: Synthesis of aromatic 2-oxazolines from different benzonitriles and amino alcohols[a]

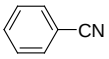
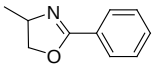
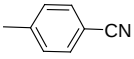
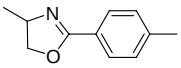
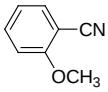
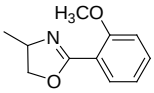
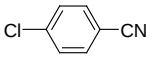
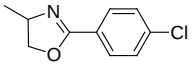
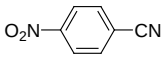
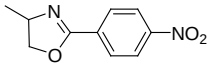
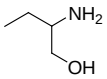
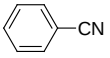
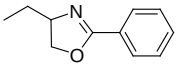
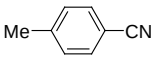
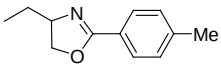
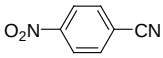
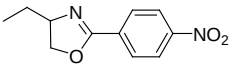
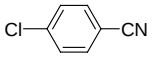
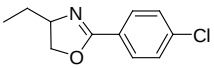
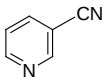
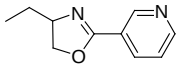
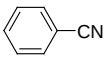
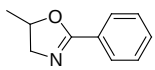
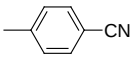
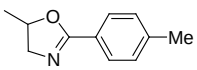
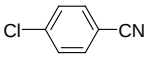
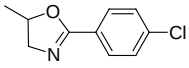
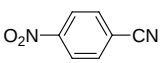
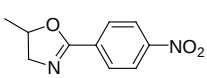
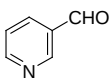
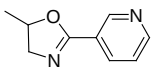
Entry	Amino alcohol	Arylnitrile	Product	Yield(%)
1				75
2				70
3				76
4				53
5				57
6				81
7				61
8				72
9				82
10				58

Table 2: (Continued)

Entry	Amino alcohol	Arylnitrile / Aldehyde	Product	Yield(%)
11				57
12				95
13				73
14				78
15				65

[a] Reaction conditions: benzonitrile (1 mmol), amino alcohol (1.2 mmol), Ni/Fe_3O_4 (1.5 mol %) and toluene (3 mL) at 100 ^oC for 11 h.With 2-aminopropan-1-ol, electron-withdrawing groups gave better yield compared to electron donating substrate. (Table 2, entry 11-15).

To check the recyclability of the catalyst, as can be seen in (Fig 1), the reaction was performed with benzonitrile and amino alcohol. The catalyst was separated from the reaction mixture by applying external magnetic field and reused without significant loss of catalytic activity.

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are very important factors. To clarify this issue, we established a set of experiments using the recycled catalyst for the Synthesis of phenyl-2-oxazoline (Fig. 1). The reactions were carried out under similar conditions in toluene. After the completion of the first reaction to afford the corresponding oxazole in 75 % yield, the catalyst was recovered magnetically, washed with ethyl acetate and then ether and finally dried at 60° C for 30 min. A new reaction was then performed with fresh solvent and reactants under the same conditions. To our satisfaction, nano-ferrite-supported Ni catalyst could be used at least five times without any change in activity. Metal leaching was studied by ICP-AES analysis of the catalyst before and after the reaction. The Ni concentration was found to be 8.25% before the reaction and 8.20 % after the reaction, which confirmed negligible Ni leaching. Also, no Ni-metal was detected in the final hydrogenated product. In fact, to date there is no 100% leach-proof metal catalyst; hence, the most important criterion in choosing the catalyst is metal recovery. It would be preferable to use a more accessible, lower-cost Ni-catalyst, provided that the process works at high turnover numbers and turnover frequencies and that the catalyst leaves no remnants of metal in the end product since metal contamination is highly regulated by the pharmaceutical industry. All the above conditions are well satisfied by our recyclable nano-ferrite-supported Ni catalyst.

3. Conclusion

It can be concluded that a simple and straightforward method for the synthesis of oxazoline from benzonitrile and an amino alcohol using magnetically recoverable Ni/Fe3O4 as the catalyst has been described. The reaction was carried out under milder conditions and no other side products were obtained. The new catalytic reactions presented in this letter could be a meaningful addition to the existing methods.

4. Experimental Section

4.1 General

All chemicals were purchased from Sigma-Aldrich and S.D Fine Chemicals, Pvt. Ltd. India and used as received. ACME silica gel (100–200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-precoated silica gel 60-F_{254} plates. All the other chemicals and solvents were obtained from commercial sources and purified using standard methods. The IR spectra of all compounds were recorded on a Perkin-Elmer, Spectrum GX FTIR spectrometer. The IR values are reported in reciprocal centimeters (cm^{-1}). The ^1H, ^{13}C NMR spectra were recorded on a Varian- 400 MHz, Bruker-Avance 300 MHz Spectrometer. Chemical shifts (δ) are reported in ppm, using TMS (δ =0) as an internal standard in $CDCl_3$. ESI mass spectra were recorded on a Finnigan LCQ Advantagemax spectrometer.

4.2 Typical experimental procedure

To a solution of benzonitrile (1 mmol), amino alcohol (1.2 mmol) in toluene (3 ml), Ni/Fe3O4 (1.5 mol %) was added. The reaction mixture was stirred at 100 ^oC and monitored by TLC. After completion of the reaction, the reaction mixture was quenched with $NaHCO_3$ solution. The aqueous layer was extracted with ethyl acetate (3 x 20 mL), and the combined organics were dried over anhydrous Na_2SO_4, concentrated in vacuum and purified by column chromatography on silica gel to afford the pure product. All products were characterized by IR, ^1H NMR, ^{13}C NMR and mass spectroscopic techniques.

Spectroscopic data for the representative compounds:

4.2.1 4-methyl-2-phenyl-4, 5-dihydrooxazole (Table 2, Entry 1): ^1H NMR δ(300 MHz, $CDCl_3$) 7.90 (d, *J* = 7.5 Hz, Ar, 2H), 7.33 – 7.44 (m, Ar, 3H), 4.47 (t, *J* = 9.0 Hz, 7.5 Hz, 1H), 4.30- 4.40 (m, 1H), 3.91 (t, J = 7.5 Hz, 7.5 Hz, 1H), 1.34 (d, J = 6.8 -CH_3, 3H). GC-MS m/z 161.1 (M^+ peak), 146.0, 131.0, 103.0,77.0.

4.2.2 4-methyl-2-p-tolyl-4, 5-dihydrooxazole (Table 2, Entry 2): ^1H NMR δ(300 MHz, $CDCl_3$) 7.81 (d, *J* = 7.9 Hz,Ar, 2H), 7.20 (d, *J* = 7.9 Hz, Ar, 2H), 4.51 (t, *J* = 9.0 Hz, 8.1 Hz, 1H), 4.31- 4.43 (m, 1H), 3.94 (t, J = 7.5 Hz, 7.7 Hz, 1H), 2.42(s, -CH_3, 3H), 1.38 (d, J = 6.6 -CH_3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.8, 149.3, 135.6, 124.9, 123.1, 74.2, 62.0, 29.6, 21.3. GC-MS m/z 175.1 (M^+ peak), 160.0, 132.1, 105.0, 91.0, 65.0.

4.2.3 4-methyl-2-p-tolyl-4,5-dihydrooxazole (Table 2, Entry 3): ^1H NMR δ(300 MHz,$CDCl_3$) 7.95 (d, *J* = 8.1 Hz, Ar, 1H), 7.30-7.50 (m, Ar, 1H), 6.97-7.04 (m, Ar, 1H), 5.90 (t, *J* = 9.0 Hz, 8.1 Hz, 1H), 5.60-5.80 (m, 1H), 5.15 (t, *J* = 9.0 Hz, 8.1 Hz, 1H), 3.95 (s, -CH_3, 3H), 2.27 (d, *J* = 5.3, -CH_3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.4, 141.4, 128.8, 128.0, 124.9, 71.8, 67.7, 28.5, 21.4. GC-MS m/z 190.1 (M^+ peak), 189.0, 160.0, 118.0, 91.0, 77.0, 63.0.

4.2.4 2-(4-chlorophenyl)-4-methyl-4, 5-dihydrooxazole (Table 2, Entry 4): ^1H NMR δ(300 MHz, $CDCl_3$) 7.81 (d, *J* = 8.8 Hz, Ar, 2H), 7.32 (d, *J* = 8.1 Hz, Ar, 2H), 4.45 (t, *J* = 8.1 Hz, 1H), 4.26- 4.35 (m, 1H), 3.88 (t, J = 7.3 Hz,8.1 Hz, 1H), 2.42(s, -CH_3, 3H), 1.38 (d, *J* = 6.6 -CH_3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.6, 137.4, 129.5, 128.6, 126.3, 74.2, 62.0, 21.4. GC-MS m/z 195.0 (M^+ peak), 180.0, 125.0, 111.0, 75.0.

4.2.5 4-methyl-2-(4-nitrophenyl)-4, 5-dihydrooxazole (Table 2, Entry 5):

^1H NMR δ(300 MHz, $CDCl_3$) 8.21 (d, *J* = 8.8 Hz, Ar, 2H), 8.10 (d, *J* = 8.1 Hz, Ar, 2H), 4.53 (t, *J* = 8.1 Hz, 1H), 4.31-4.37 (m, 1H), 3.94 (t, *J* = 7.8 Hz, 1H), 1.42 (d, *J* = 6.7, -CH_3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.6, 137.4, 129.5, 128.6, 126.3, 74.2, 62.0, 21.4. GC-MS m/z 206.0 (M^+ peak), 190.9, 176.0, 163.0, 130.0, 117.0, 103.0, 76.0.

4.2.6 4-ethyl-2-phenyl-4, 5-dihydrooxazole (Table 2, Entry 6): ^1H NMR δ(300 MHz, $CDCl_3$) 7.82 (d, *J* = 8.1 Hz, Ar, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, Ar, 2H), 4.50 (t, *J* = 7.9 Hz, 1H), 4.27- 4.48 (m, 1H), 4.03 (t, *J* = 7.9 Hz, 1H), 1.62 – 1.91 (m, 2H), 1.0 (t, *J* = 7.4 Hz, 3H). GC-MS m/z 175.0 (M^+ peak), 146.0, 118.0, 91.0, 77.0.

4.2.7 4-ethyl-2-p-tolyl-4, 5-dihydrooxazole (Table 2, Entry 7): ^{1}H NMR δ(300 MHz, $CDCl_3$) 7.82 (d, *J* = 8.1 Hz, Ar, 2H), 7.20 (d, *J* = 7.9 Hz, Ar, 2H), 4.46 (t, *J* = 7.9 Hz, 1H), 4.17-4.43 (m, 1H), 4.02 (t, *J* = 7.9 Hz, 1H), 2.42 (s, -CH_3, 3H), 1.57 – 1.82 (m, 2H), 1.3 (t, *J* = 7.4 Hz, 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.4, 137.1, 134.1, 131.7, 130.2, 120.6, 111.8, 56.1, 11.6. GC-MS m/z 189.1 (M^+ peak), 160.0, 105.1, 91.0, 65.0.

4.2.8 4-ethyl-2-(4-nitrophenyl)-4,5-dihydrooxazole (Table 2, Entry 8): ^{1}H NMR δ(300 MHz, $CDCl_3$) 8.28 (d, *J* = 8.8 Hz, Ar, 2H), 8.12 (d, *J* = 8.8 Hz, Ar, 2H), 4.54 (t, *J* = 8.1 Hz, 1H), 4.24- 4.34 (m, 1H), 4.10 (t, J = 7.9 Hz, 1H), 1.61 – 1.86 (m, 2H), 1.06 (d, *J* = 7.4 Hz, 3H). GC-MS m/z 220 (M^+ peak), 191.0, 163.0, 146.0, 117.0, 90.0, 76.0.

4.2.9 2-(4-chlorophenyl)-4-ethyl-4, 5-dihydrooxazole (Table 2, Entry 9): ^{1}H NMR δ(300 MHz, $CDCl_3$) 7.80 (d, *J* = 8.6 Hz, Ar, 2H), 7.32 (d, *J* = 8.6 Hz, Ar, 2H), 4.46 (t, *J* = 8.1 Hz, 1H), 4.21- 4.30 (m, 1H), 3.96 (t, *J* = 7.9 Hz, 1H), 1.72 – 1.80 (m, 2H), 1.04 (d, *J* = 7.7 Hz, 7.6 Hz, 3H). GC-MS m/z 209.1 (M^+ peak), 182.0,179.9, 125.0, 111.0, 75.0.

4.2.10 4-ethyl-2-(pyridine-3-yl)-4, 5-dihydrooxazole (Table 2, Entry 10): ^{1}H NMR δ(300 MHz, $CDCl_3$) 9.02(s, Ar, 1H), 8.58 (d, *J* = 8.1 Hz, Ar, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.27 (m, Ar, 1H), 4.37 (t, *J* = 8.1 Hz, 1H), 4.17- 4.43 (m, 1H), 4.09 – 4.20 (m, 1H), 3.93 – 3.99 (m, 1H), 1.48 – 1.71 (m, 2H), 0.91 -0.96 (m, 3H) [13]. C NMR (75 MHz, $CDCl_3$): 161.4, 151.8, 149.4, 135.5, 123.9, 123.1, 72.3, 67.9, 28.5, 9.9.GC-MS m/z 176.1 (M^+ peak), 147.0, 119.0, 92.0, 78.0.

4.2.11 5-methyl-2-p-tolyl-4, 5-dihydrooxazole (**Table 2, Entry 11):** ^{1}H NMR δ(300 MHz, $CDCl_3$) 7.80 (d, *J* = 7.9 Hz, Ar, 2H), 7.18 (d, *J* = 7.9 Hz, Ar, 2H), 4.77 – 4.87 (m, 1H), 4.11 (dd, *J* = 9.3 Hz,9.2 Hz, 1H), 3.57 (dd, *J* = 7.4 Hz, 7.2 Hz), 2.4 (s, -CH_3, 3H), 1.43 (d, *J* = 6.0Hz, -CH_3, 3H). GC-MS m/z 175.1 (M^+ peak), 130.9, 91.0, 65.0.

4.2.12 5-methyl-2-(4-nitrophenyl)-4, 5-dihydrooxazole (Table 2, Entry 12): ^{1}H NMR δ(300 MHz, $CDCl_3$) 8.29 (d, *J* = 9.1 Hz, Ar, 2H), 8.12 (d, J = 8.9 Hz, Ar, 2H), 4.86 – 4.98 (m, 1H), 4.21 (dd, *J* = 9.4 Hz, 9.2 Hz, 1H), 3.67 (dd, *J* = 7.5 Hz, 7.5 Hz), 1.50 (d, J = 6.2Hz, -CH_3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.0, 133.8, 129.0, 123.4, 61.8, 31.8, 29.6, 20.9. GC-MS m/z 206.1 (M^+ peak), 162.0, 117.1, 116.0, 89.0, 76.0.

4.2.13 2-(4-chlorophenyl)-5-methyl-4, 5-dihydrooxazole (**Table 2, Entry 13):** ^{1}H NMR δ(300 MHz, $CDCl_3$) 7.86 (d, *J* = 8.5 Hz, Ar, 2H), 7.37 (d, *J* = 8.5 Hz, Ar, 2H), 4.77 – 4.89 (m, 1H), 4.12 (dd, *J* = 9.4 Hz, 9.4 Hz, 1H), 3.58 (dd, *J* = 7.3 Hz, 7.5 Hz), 1.43 (d, *J* =6.2Hz, -CH_3, 3H). GC-MS m/z 195.0, 153.0, 150.9, 111.0, 89.0, 75.0.

4.2.14 5-methyl-2-phenyl-4, 5-dihydrooxazole (Table 2, Entry 14): ^{1}H NMR δ(300 MHz, $CDCl_3$) 7.86 (d, *J* = 8.5 Hz, Ar, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, Ar, 2H), 4.70 – 4.85 (m, 1H), 4.05 (dd, *J* = 9.3 Hz, 9.3 Hz, 1H), 3.52 (dd, *J* = 7.4 Hz, 7.4 Hz), 1.37 (d, *J* =6.1Hz, -CH_3, 3H). GC-MS m/z 161.0, 117.0, 90.0, 77.0, 51.0.

4.2.15 5-methyl-2-(pyridin-3-yl)-4, 5-dihydrooxazole (**Table 2, Entry 15):** ^{1}H NMR δ(300 MHz, $CDCl_3$) 9.1 (s, Ar, 1H), 8.69 (s, Ar, 1H), 8.27 (d, *J* = 8.1 Hz, Ar, 1H), 7.32 (d, *J* = 8.1, Ar, 1H), 4.90 – 4.72 (m, 1H), 4.11 (dd, *J* = 9.4 Hz, 7.4 Hz, 1H), 3.58 (dd, *J* = 7.5 Hz, 9.5 Hz), 1.39 (d, *J* =6.3Hz, -CH_3, 3H). ^{13} C NMR (75 MHz, $CDCl_3$): 151.8, 149.3, 135.6, 124.9, 123.1, 74.2, 62.0, 29.6, 21.3. GC-MS m/z 162.0, 117.9, 91.0, 78.0, 51.0.

5. Synthesis of Catalyst: In 90 ml of distilled water, a mixture of $Ni(AcO)_2$ - $4H_2O$ and $FeCl_2$ - $4H_2O$ was dissolved. Gradual addition of NH_4OH until the solution reached a pH of 11.5 resulted in the formation and precipitation of nanoparticles and the formation of a dark brown solid. These solids were recovered by filtration, rinsed several times with distilled water and ethanol, and dried under vacuum. Different Fe:Ni ratios were used to adjust the nickel content (x) of the nanoparticles, giving spinels with x values of 1:9, 1:16 and 1:25. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to quantify the iron and nickel content in the synthesised samples.

5.1 Fe_3O_4 Supported Nanoparticles

A solution comprising a 1 M $FeCl_3$ solution and a 2 M $FeCl_2$ solution was prepared by combining them in 100 ml of distilled water. The resulting solution underwent stirring, followed by the addition of a 1 M NH_4OH solution. This led to the precipitation of nanoparticles, forming a solid material with a black appearance. The solid was separated through filtration and underwent repeated rinsing using distilled water. The chemical composition analysis of the samples was carried out using Induced Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using an MPX Varian instrument, as well as Fourier Transform Infrared spectroscopy (FTIR) using an Avatar Nicolet instrument. The structural characteristics of the synthesized nanoparticles were determined through X-ray diffraction using a Siemens D-5000 instrument with Cu K radiation.

Moreover, the morphological features of the nanoparticles were assessed through Transmission Electron Microscopy (TEM) using a JEOL JEM2000-FX instrument operating at 200 kV. Thermal analysis was performed employing Thermogravimetric Analysis (TA instrument HI-RES 2960) and Differential Scanning Calorimetry (TA instruments DSC Q-100). X-ray Absorption Near Edge Structure Spectroscopy (XANES) was conducted on both the Ni and Fe K-edges, utilizing the BM25 Beamline (CGR-Spline) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

The magnetic properties of the nanoparticles were studied using a SQUID magnetometer (Quantum design MPSXL7) for magnetic characterization.

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