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# Magnetically recoverable catalysts for the preparation of pyridine derivatives: an overview

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Magnetically recoverable nano-catalysts can be readily separated from the reaction medium using an external magnet. In recent years, chemistry researchers have employed them as catalysts in chemical reactions. The high surface area, simple preparation, and modification are among their major advantages. Pyridine derivatives are an important category of heterocyclic compounds, which show a wide range of excellent biological activities, including IKK- $\beta$  inhibitors, anti-microbial agents, A2A adenosine receptor antagonists, inhibitors of HIV-1 integrase, anti-tumor, anti-inflammatory, and anti-Parkinsonism. Recently, the catalytic activity of magnetic nanoparticles was investigated in multicomponent reactions in the synthesis of pyridine derivatives, which is discussed in this review.

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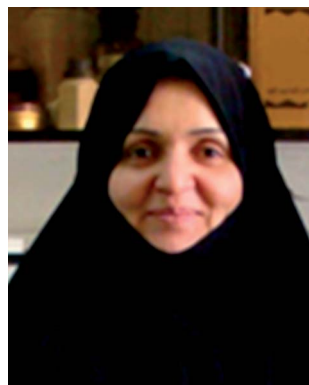
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## 1. Introduction

In recent decades, nanotechnology has attracted much attention in various fields.<sup>1,2</sup> One of the most influential families of nanomaterials is magnetic nanoparticles, which have been extensively employed in different sciences, including drug delivery,<sup>3</sup> illness recognition,<sup>4</sup> water desalination,<sup>5</sup> ambience scrubbing,<sup>6</sup> and chemical catalysis.<sup>7</sup> Recently, magnetic nano-catalysts have attracted the consideration of many researchers due to their high activity, selectivity, availability, large surface area, low toxicity, excellent reusability, and easy separation.<sup>8,9</sup>



Ghodsi Mohammadi Ziarani was born in Iran in 1964. She received her BSc degree in Chemistry from the Teacher Training University, Tehran, Iran, in 1987, her M.Sc. degree in Organic Chemistry from the Teacher Training University, Tehran, Iran, under the supervision of Professor Jafar Asgarin and Professor Mohammad Ali Bigdeli in 1991 and her PhD degree in asymmetric synthesis

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Prof. Ghodsi Mohammadi Ziarani, in 2019. She is currently a postdoctoral researcher in Organic Chemistry at Alzahra University under the supervision of Prof. Ghodsi Mohammadi Ziarani.

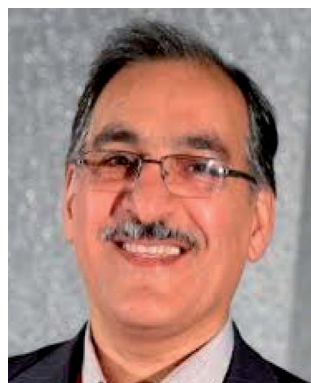


Magnetic nanoparticles (MNPs) have high surface-to-volume ratios, and can be functionalized with inorganic and organic compounds.<sup>10–15</sup> The magnetic nano-catalysts can be separated by external magnetic fields.<sup>16</sup> Fe<sub>3</sub>O<sub>4</sub> nanoparticles can be coated with organic and inorganic materials, including silica,<sup>17</sup> surfactants,<sup>18</sup> polymers,<sup>17,19</sup> cellulose,<sup>20</sup> carbon,<sup>21</sup> chitosan,<sup>22</sup> as well as prepared with a core-shell structure. The coating layer on magnetic nanoparticles can be prevented from aggregation or oxidation and their stability can be increased.

Heterocyclic compounds have high biological and pharmaceutical activities. Among them, pyridine derivatives are important heterocyclic compounds, which attracted the attention of scientists. Pharmaceutical molecules and natural products can be based on heterocyclic compounds such as pyridine derivatives,<sup>23</sup> which have biological activities, such as inhibitors of HIV-1 integrase, A2A adenosine receptor antagonists, IKK-β inhibitors, anti-microbial, anti-tumor, analgesic, anti-inflammatory, and antipyretic agents.<sup>24</sup> In continuation our research work,<sup>25–29</sup> this contribution will be aimed to discuss the synthesis of magnetic nano-catalysts as well as their applications in the synthesis of pyridine derivatives.



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*Alireza Badii was born in Iran in 1965. He received his BSc and MSc degrees in Chemistry and Inorganic Chemistry from the Teacher Training University (Kharazmi), Tehran, Iran, in 1988 and 1991, respectively, and his PhD degree in the synthesis and modification of nanoporous materials from Laval University, Quebec, Canada, in 2000. He is currently a full Professor in the Chemistry*

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## 2. The synthesis of pyridine derivatives by diverse magnetic catalysts

### 2.1. Basic magnetic catalyst

The core-shell structure of Fe<sub>3</sub>O<sub>4</sub>@KCC-1-*n*pr-NH<sub>2</sub> **6** as an effective basic magnetic catalyst was prepared and employed in the synthesis of tetrahydro di-pyrazolopyridines by Azizi, and his co-workers. Core-shell Fe<sub>3</sub>O<sub>4</sub>@KCC-1 **4** was prepared by adding cetyl trimethyl ammonium bromide (CTAB) **2** and tetraethylorthosilicate (TEOS) **3**. Then, Fe<sub>3</sub>O<sub>4</sub>@KCC-1 **4** was functionalized with 3-aminopropyl)triethoxysilane **5** to produce Fe<sub>3</sub>O<sub>4</sub>@KCC-1-*n*pr-NH<sub>2</sub> **6** with excellent basic properties. Details for the preparation of Fe<sub>3</sub>O<sub>4</sub>@KCC-1-*n*pr-NH<sub>2</sub> **6** are shown in Scheme 1. Various characterization techniques, including FT-IR, SEM, TEM, BET, and XRD, confirmed the structure of Fe<sub>3</sub>O<sub>4</sub>@KCC-1-*n*pr-NH<sub>2</sub> **6** as magnetic nano-catalyst.<sup>30</sup>

Fe<sub>3</sub>O<sub>4</sub>@KCC-1-*n*Pr-NH<sub>2</sub> **6** was employed in the tetra-component reaction of ethyl acetoacetate **7**, hydrazine hydrate **8**, ammonium acetate **10**, and various aromatic aldehydes **9** in ethanol under reflux condition for the synthesis of tetrahydrodipyrzolo pyridine **11** in excellent yields, short reaction times. According to obtained results, different substituents including electron-donating or electron-withdrawing groups on the aromatic ring, did not affect the product yields. All products were obtained in high purity and excellent yields. Also, the anticancer activity of tetrahydrodipyrzolo pyridine derivatives **11** was studied that some of these compounds showed good cytotoxic activity toward types of cancer cell (Scheme 2).<sup>30</sup>

Fe<sub>3</sub>O<sub>4</sub> MNPs **1** were also synthesized according to the literature,<sup>31</sup> and then coated by TEOS to yield Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs **4**,<sup>32</sup> which were modified by 3-aminopropyl-trimethoxysilane (APTS) **5** to provide Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-pr-NH<sub>2</sub> MNPs **6**, followed by mixing with a solution of *N,N*-dimethylaniline **12**, and formaldehyde **13** in DMF, and then refluxed for 24 h to provide poly *N,N*-dimethylaniline-formaldehyde supported on silica-coated Fe<sub>3</sub>O<sub>4</sub> MNPs (PDMAF-MNPs) **14** (Scheme 3).<sup>33</sup>

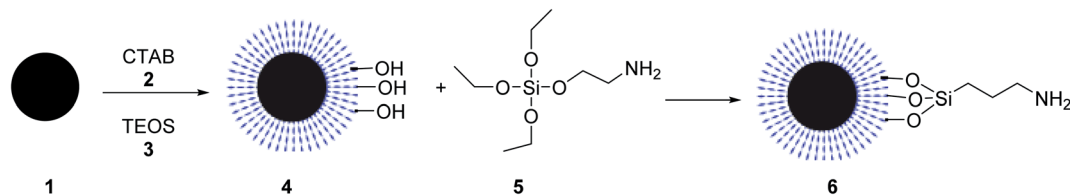
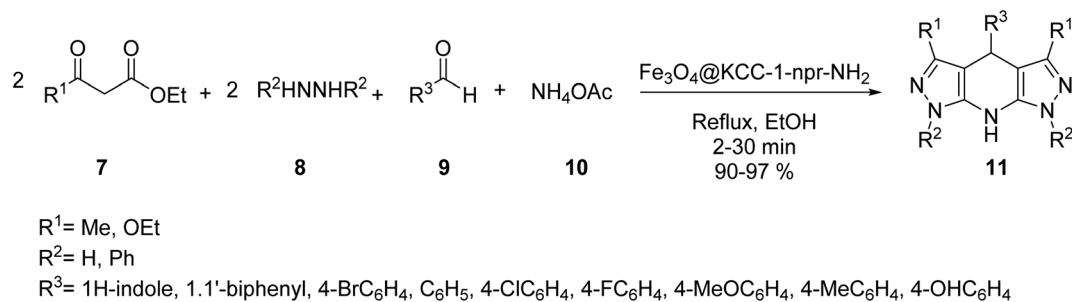
PDMAF-MNPs was investigated in the multicomponent reaction of aldehydes **9**, malononitrile **16**, ammonium acetate



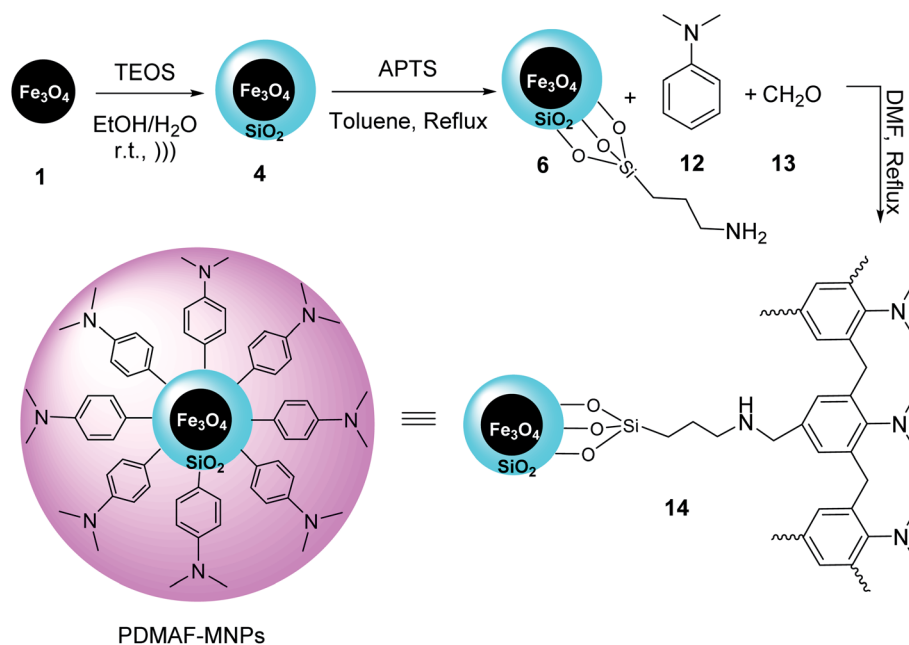
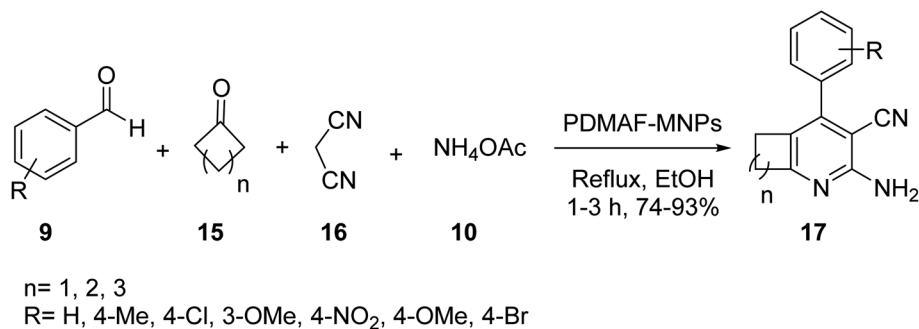
*Rafael Luque, Full Professor from Departamento de Quimica Organica at UCO, Spain as well as Director of the Scientific Center for Molecular Design and Synthesis of Innovative compounds for Medicine at RUDN University, Russia, Distinguished Chair Professor at Xi'an Jiaotong University and DSFP Fellow at King Saud University, Saudi Arabia is an internationally recognized*

*leader and mentor in the areas of (nano)materials science and Green Chemistry/Sustainability (h-index = 83, >34 000 citations to own work, 2018, 2019 and 2020 Highly Cited Researcher-Clarivate Analytics).*



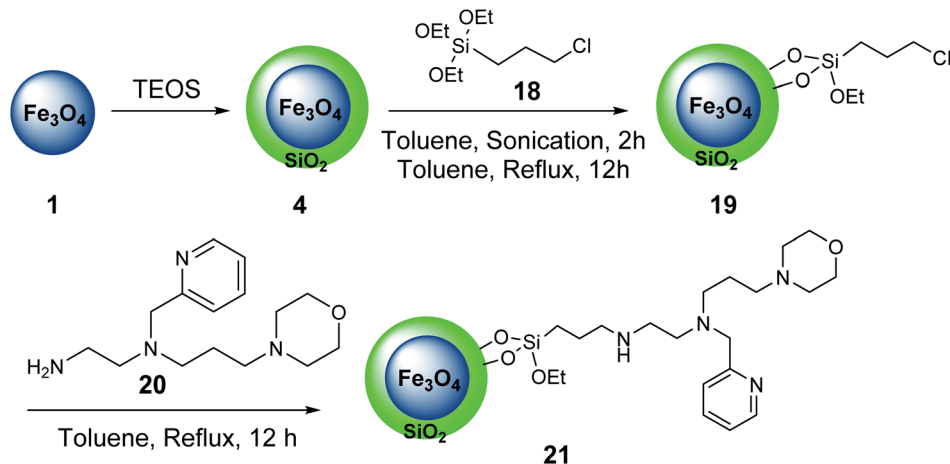
Scheme 1 Synthesis of  $\text{Fe}_3\text{O}_4@KCC-1-npr-NH_2$  6.

Scheme 2 Synthesis of tetrahydropyrazolopyridine 11.

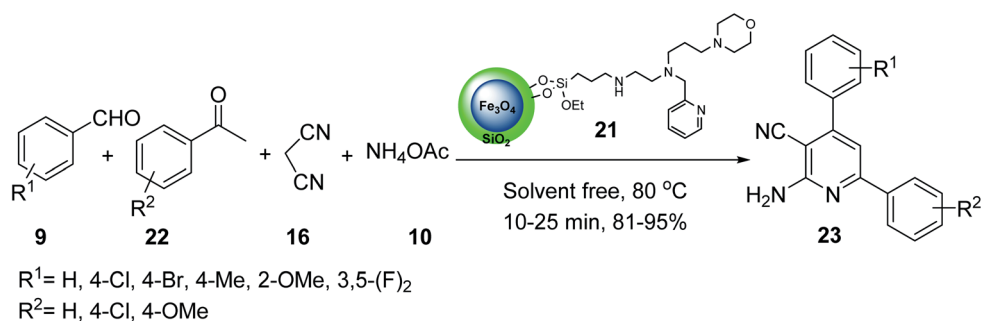
Scheme 3 Synthesis of poly *N,N*-dimethylaniline-formaldehyde supported on silica-coated  $\text{Fe}_3\text{O}_4$  MNPs (PDMAF-MNPs) 14.

Scheme 4 Synthesis of 2-amino-3-cyanopyridines 17.

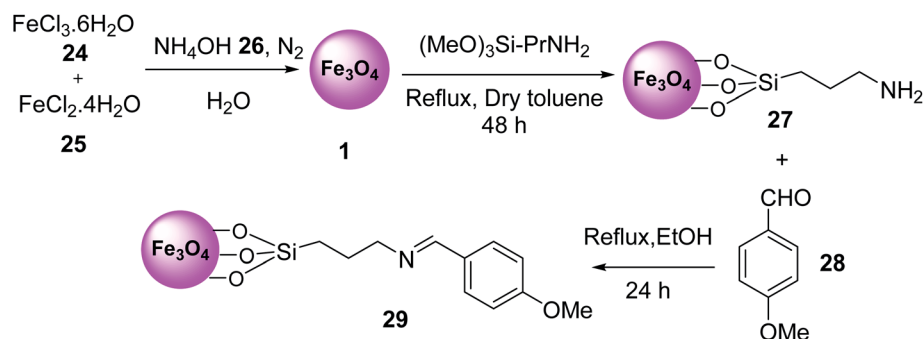




Scheme 5 Synthesis of magnetic nanoparticles with morpholine tags 21.



Scheme 6 Synthesis of 2-amino-4,6-diphenylnicotinonitriles 23.

Scheme 7 Synthesis of  $\text{Fe}_3\text{O}_4\text{-Si-(CH}_2\text{)}_3\text{-N=CH-Ph-OMe}$  MNPs 29.

10, and various ketones 15 under reflux condition in EtOH to obtain 2-amino-3-cyanopyridines 17 in high yields. It was demonstrated that the electron-donating groups results in low reaction yields and long reaction time (Scheme 4).<sup>33</sup>

In another example, iron oxide 1 was prepared and reacted with tetraethylorthosilicate (TEOS) 3 to provide  $\text{Fe}_3\text{O}_4\text{@SiO}_2$  4,<sup>34</sup> which was treated with 3-chloropropyltriethoxysilane 18 to give  $\text{Fe}_3\text{O}_4\text{@SiO}_2\text{-Pr-Cl}$  19, followed by the reaction with the ligand bearing morpholine tags 20 to obtain the nano-magnetic catalyst 21 (Scheme 5).<sup>35</sup>

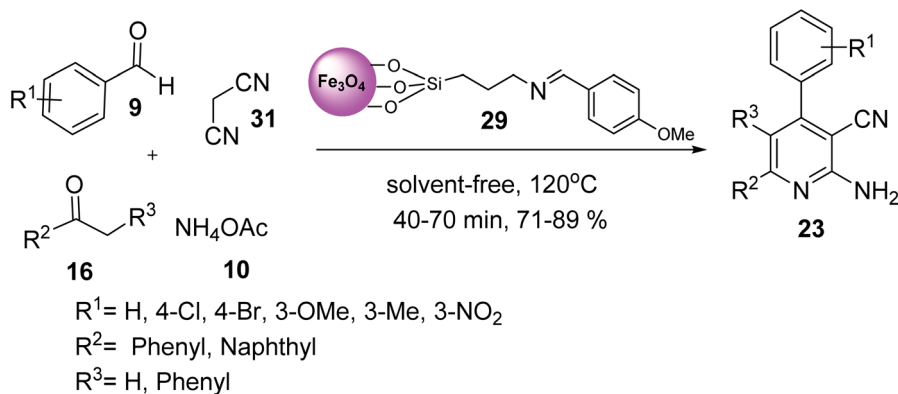
The nano-magnetic catalyst 21 was examined in the multi-component reaction of benzaldehydes 9, acetophenone derivatives 22, malononitrile 16, and ammonium acetate 10 under the

solvent-free condition in 80 °C for the preparation of 2-amino-4,6-diphenylnicotinonitriles 23 (Scheme 6).<sup>35</sup>

Nano-magnetic  $\text{Fe}_3\text{O}_4\text{-Si-(CH}_2\text{)}_3\text{-N=CH-Ph-OMe}$  MNPs 29 was prepared by the reaction of  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  24,  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  25, and  $\text{NH}_4\text{OH}$  26 in  $\text{H}_2\text{O}$  under  $\text{N}_2$  atmosphere to prepare  $\text{Fe}_3\text{O}_4$  MNPs 1, which was functionalized with aminopropyl silane 5 to provide  $\text{Fe}_3\text{O}_4\text{-Si-(CH}_2\text{)}_3\text{-NH}_2$  27, followed by modification with 4-methoxy benzaldehyde 28 under reflux conditions in ethanol for 24 h (Scheme 7).<sup>36</sup>

$\text{Fe}_3\text{O}_4\text{-Si-(CH}_2\text{)}_3\text{-N=CH-Ph-OMe}$  MNPs 29 was used in the synthesis of 2-amino-3-cyanopyridines 23 *via* the multi-component reaction of various aromatic aldehydes 9, 2-

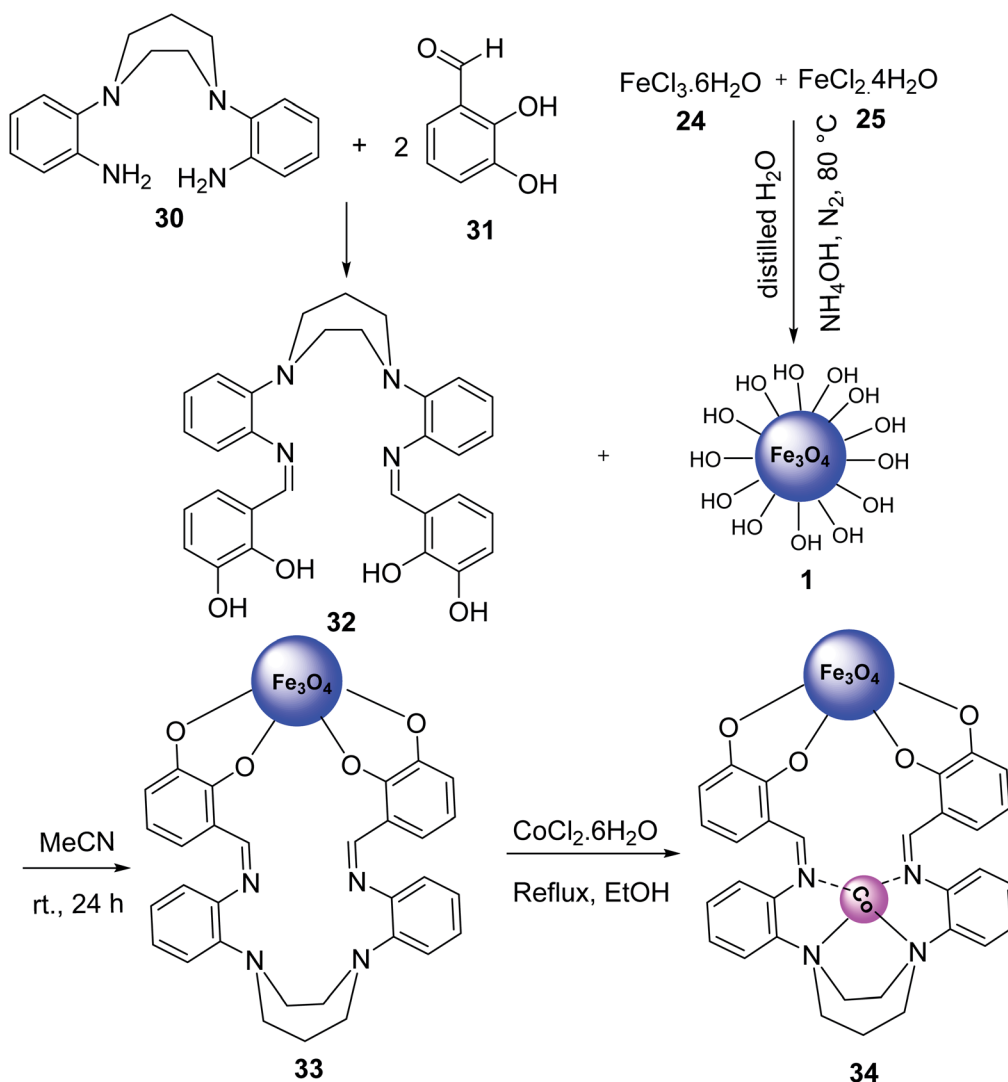


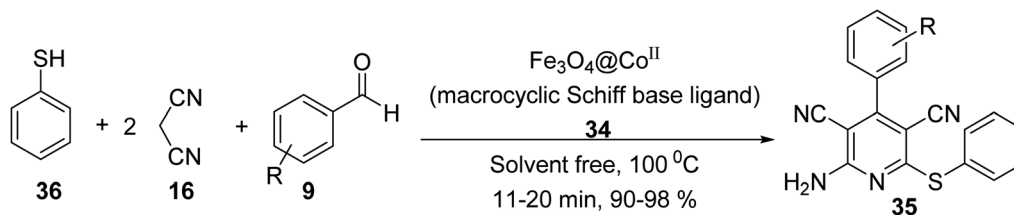
Scheme 8 Synthesis of 2-amino-3-cyanopyridines **23**.

acetylnaphthalene **31**, or deoxybenzoin **31**, malononitrile **16**, and ammonium acetate **10** under solvent-free conditions at 120 °C for 40–70 min in good to high yield in short times (Scheme 8).<sup>36</sup>

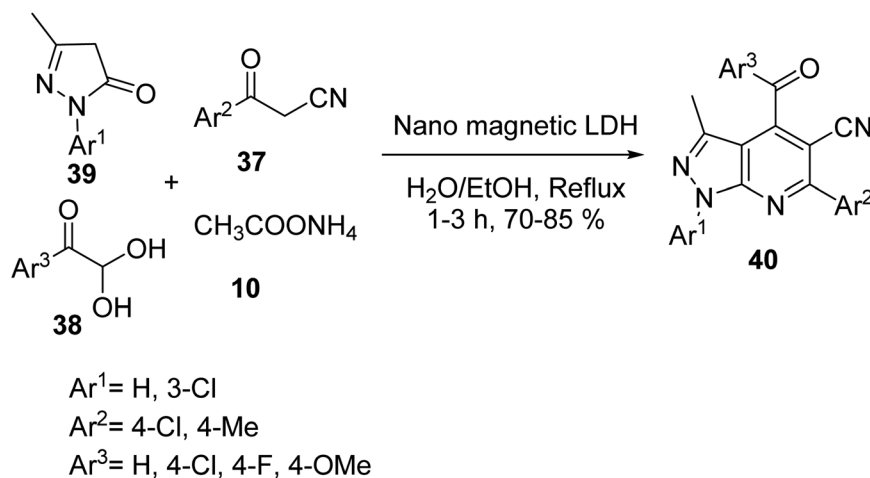
## 2.2. Acidic magnetic catalysts

$\text{Fe}_3\text{O}_4@Co^{II}$  (macrocyclic Schiff base ligand) **34** was synthesized as an efficient and recoverable catalyst for the synthesis of thiopyridine. Macrocyclic Schiff base ligand **32** was obtained *via*

Scheme 9 Synthesis of  $\text{Fe}_3\text{O}_4@Co^{II}$  (macrocyclic Schiff base ligand) **34**.



Scheme 10 Synthesis of 2-amino-4-aryl-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile derivatives 35.

Scheme 11 Synthesis of pyrazolo[3,4-*b*] pyridines 40.

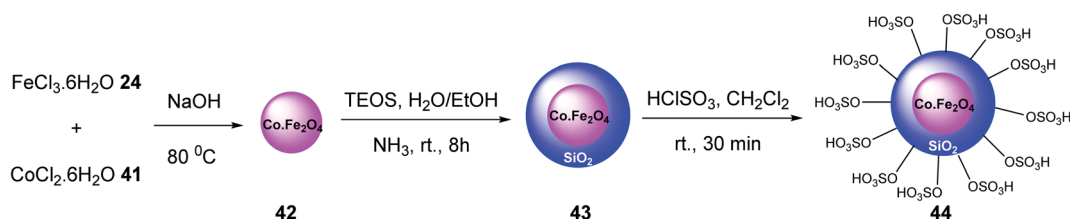
reaction of 2,2'-(1,4-diazepane-1,4-diyl)-di-aniline **30** and 2,3-dihydroxybenzaldehyde **31** in ethanol under reflux for 24 hours. Then, a mixture of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  **24**,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  **25**, and  $\text{NH}_4\text{OH}$  **26** was stirred in  $\text{H}_2\text{O}$  under  $\text{N}_2$  gas at 100 °C to give  $\text{Fe}_3\text{O}_4$  **1**, which was treated with macrocyclic Schiff base ligand (**iii**) **32** to give  $\text{Fe}_3\text{O}_4$ -supported macrocyclic Schiff base ligand (**iii**) **33**, followed by the reaction with  $\text{Co}(\text{Cl})_2 \cdot 6\text{H}_2\text{O}$  EtOH under reflux for 24 hours to obtain  $\text{Fe}_3\text{O}_4$ @macrocyclic Schiff base ligand **34** (Scheme 9).<sup>37</sup>

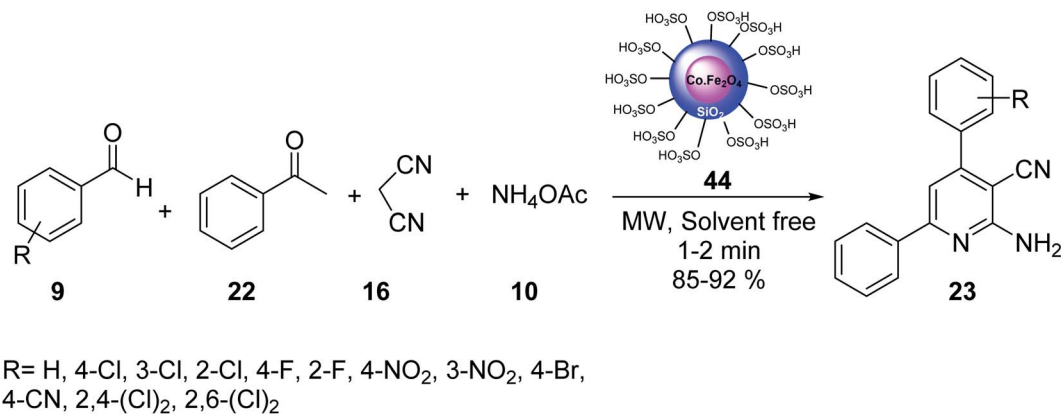
$\text{Fe}_3\text{O}_4$ @macrocyclic Schiff base ligand **34** was employed in the synthesis of 2-amino-4-aryl-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile derivatives **35** *via* three-component reaction of aldehyde derivatives **9**, malononitrile **16**, thiophenol **36** under solvent-free conditions (Scheme 10). The catalytic activity of  $\text{Fe}_3\text{O}_4$ @ $\text{Co}^{\text{II}}$  (macrocyclic Schiff base ligand) **34** was separately compared to that of  $\text{Fe}_3\text{O}_4$ , macrocyclic Schiff base ligand,  $\text{Fe}_3\text{O}_4$ @macrocyclic Schiff base ligand **33**. It was demonstrated that  $\text{Fe}_3\text{O}_4$ @ $\text{Co}^{\text{II}}$  **34** showed the best results.<sup>37</sup>

4-Aroyl-3-methyl-1,6-diaryl-1*H*-pyrazolo[3,4-*b*] pyridine-5-carbonitrile derivatives **40** were synthesized *via* one-pot, the four-component reaction of 1-aryl-3-methyl-1*H*-pyrazol-5-(4*H*) one **39**, 3-aryl-3-oxopropanenitriles **37**, arylglyoxals **38**, and ammonium acetate **10** in the presence of metal oxide silica based-metal bifunctional LDH (layered double hydroxide) as a magnetic nano-catalyst in EtOH/ $\text{H}_2\text{O}$  (1 : 1) under the reflux conditions (Scheme 11). In addition, pyrazolo[3,4-*b*] pyridines **40** have biological and pharmacological activity.<sup>38</sup>

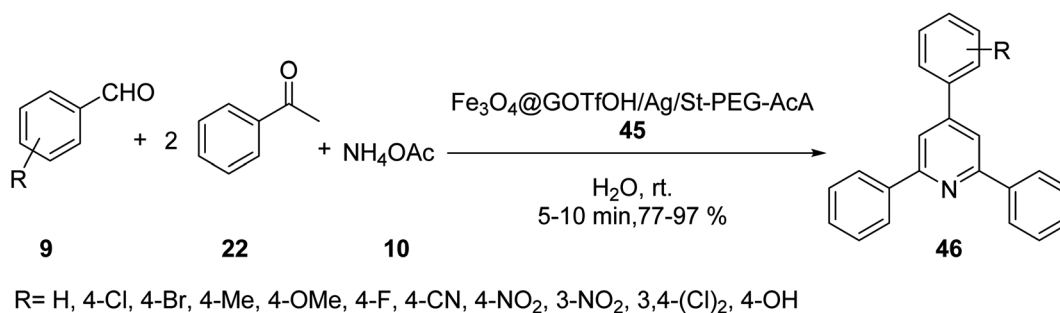
$\text{CoFe}_2\text{O}_4$ @ $\text{SiO}_2$ - $\text{SO}_3\text{H}$  **44** was synthesized as a reusable nano-catalyst by Hosseinzadeh *et al.* Initially,  $\text{CoFe}_2\text{O}_4$  magnetic nanoparticles **42** were prepared according to previous works.<sup>39</sup> Then, it was modified with tetraethylorthosilicate to provide  $\text{CoFe}_2\text{O}_4$ @ $\text{SiO}_2$  **43**,<sup>40</sup> which was dispersed in dry  $\text{CH}_2\text{Cl}_2$ , and  $\text{ClSO}_3\text{H}$  to give  $\text{CoFe}_2\text{O}_4$ @ $\text{SiO}_2$ - $\text{SO}_3\text{H}$  **44** (Scheme 12).<sup>41</sup>

$\text{CoFe}_2\text{O}_4$ @Silica MNPs **44** was used in the multicomponent reaction of aldehydes **9**, acetophenone **22**, malononitrile **16**, and ammonium acetate **10** in solvent-free conditions under MW

Scheme 12 Synthesis of  $\text{CoFe}_2\text{O}_4$ @Silica MNPs **44**.



Scheme 13 Synthesis of 2-amino-4,6-diarylnicotinonitrile derivatives 23.



Scheme 14 Synthesis of 2,4,6-triarylpyridine derivatives 46.

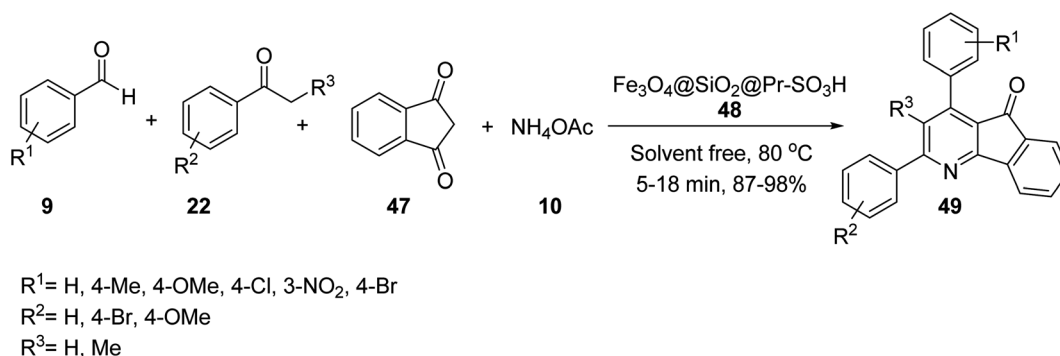
irradiation to provide 2-amino-4,6-diarylnicotinonitrile derivatives 23 in good yields (Scheme 13).<sup>41</sup>

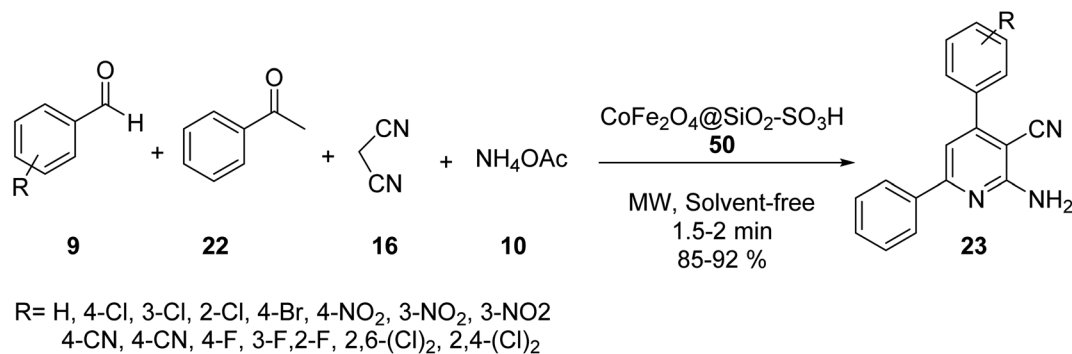
Forouzandehdel and co-workers synthesized a novel, recyclable nano-catalyst Fe<sub>3</sub>O<sub>4</sub>@GO<sub>TfOH</sub>/Ag/St-PEG-AcA 45, which was employed in the synthesis of 2,4,6-tri-arylpyridine derivatives 46 by the reaction of aldehyde derivatives 9, acetophenone 22, and ammonium acetate 10 in H<sub>2</sub>O at room temperature (Scheme 14).<sup>42</sup>

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Pr-SO<sub>3</sub>H 48 was employed as heterogeneous acidic catalyst in the multicomponent reaction of 1,3-indandione 47, aromatic aldehydes 9, acetophenone or propiophenone 22, and ammonium acetate 10 under solvent-free conditions at 80 °C to obtain indeno[1,2-*b*]pyridines 49 (Scheme 15).<sup>43</sup>

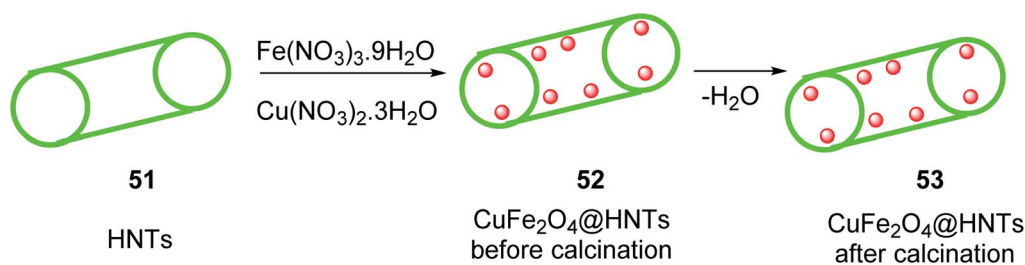
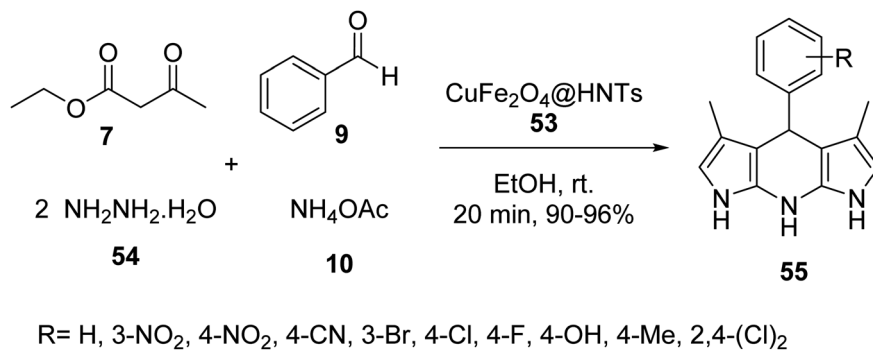
Hosseinzadeh and *et al.* synthesized 2,6-diaryl-substituted pyridine derivatives 23 *via tetra* component reaction of aldehyde derivatives 9, acetophenone 22, malononitrile 16, and ammonium acetate 10 in the presence of CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H 50 under microwave irradiation and solvent-free conditions (Scheme 16).<sup>44</sup>

Halloysite nanotubes CuFe<sub>2</sub>O<sub>4</sub>@HNTs 53 was synthesized by the reaction of Halloysite nanotubes HNTs 51 was added to Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.14 g (0.58 mmol) of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in distilled water and stirred at room temperature for 1 h, and then the solution of NaOH was added dropwise to it for 10 min at 25 °C, followed by stirring for 2 h at 90 °C to give CuFe<sub>2</sub>O<sub>4</sub>@HNTs 52, which was separated by an external

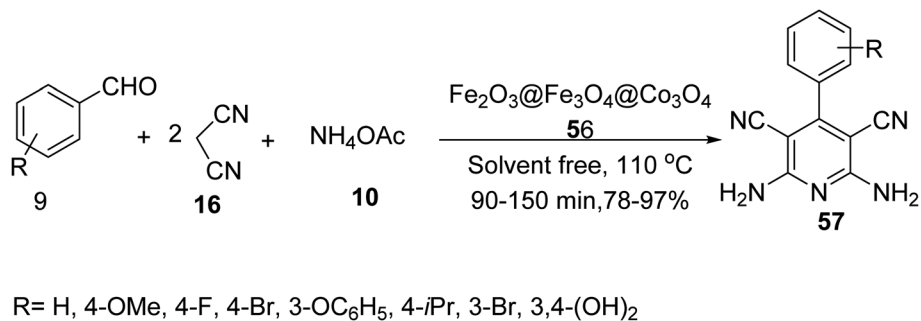
Scheme 15 Synthesis of indeno[1,2-*b*]pyridines 49.



Scheme 16 Synthesis of 2,6-diaryl-substituted pyridine derivatives 23.

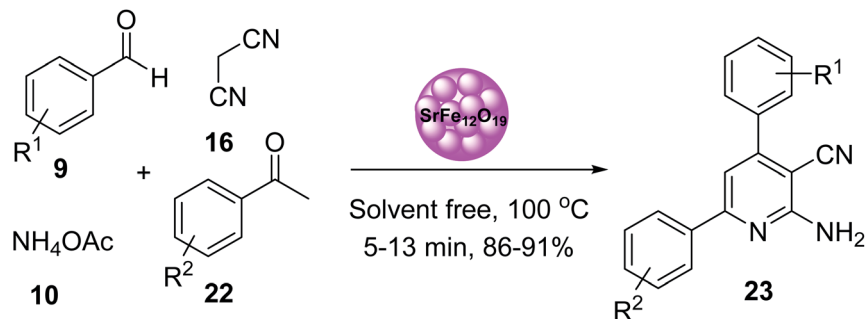
Scheme 17 Synthesis of CuFe<sub>2</sub>O<sub>4</sub>@HNTs 53.

Scheme 18 Synthesis of pyrazolopyridine derivatives 55.



Scheme 19 The synthesis of polysubstituted pyridines 57.

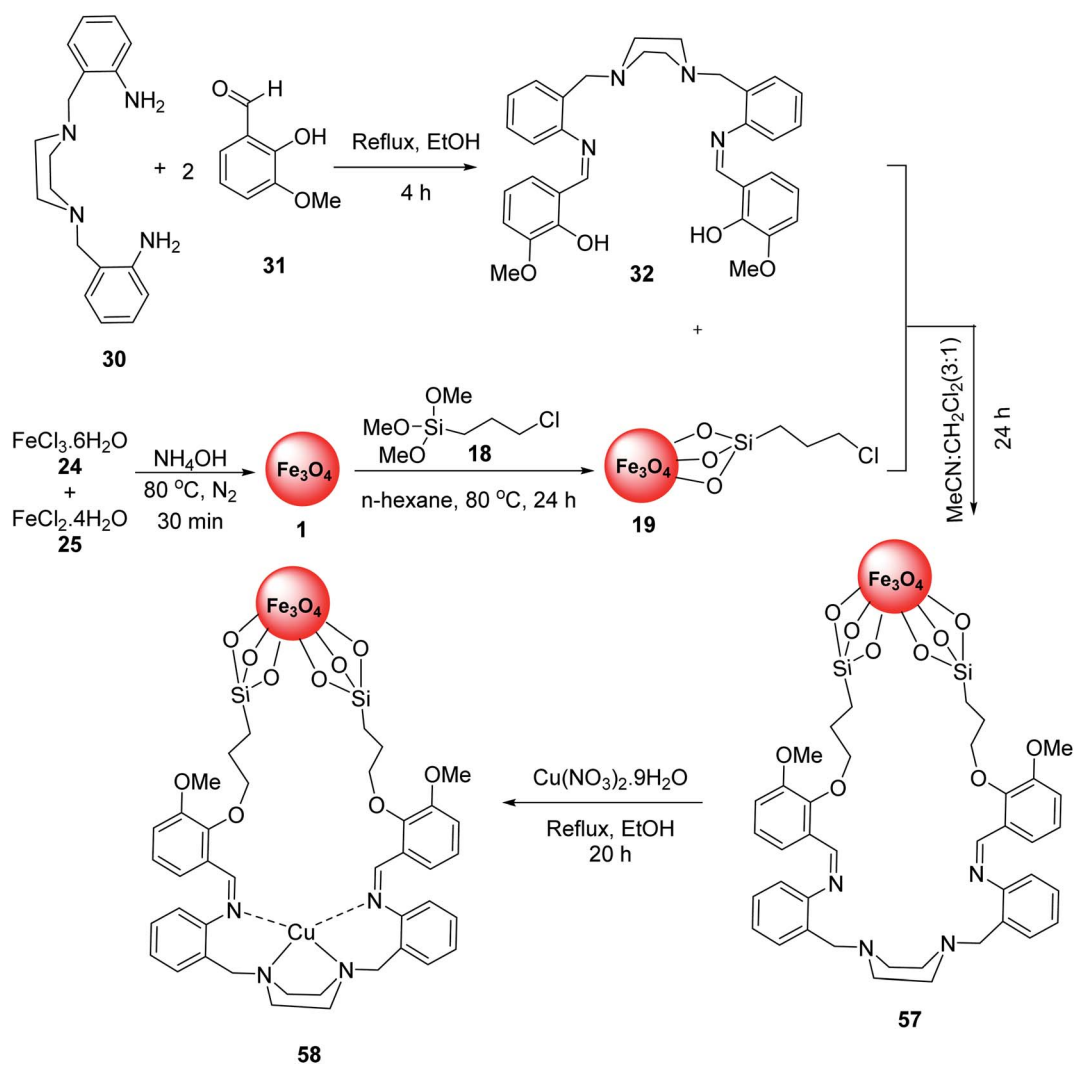




$\text{R}^1 = \text{H}, 4\text{-Me}, 4\text{-OMe}$

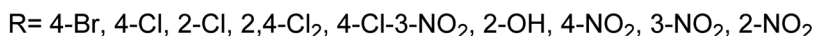
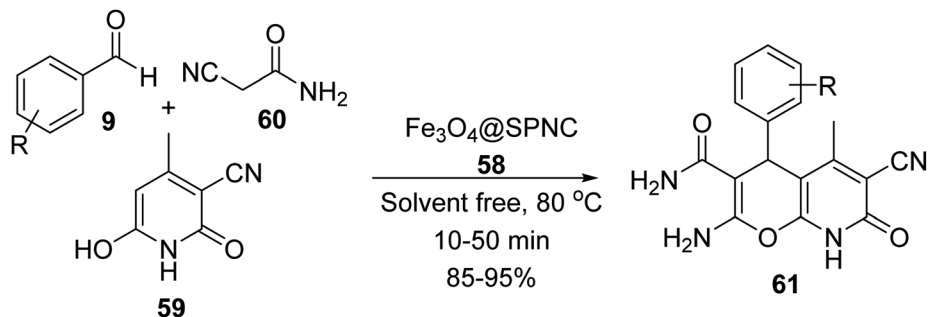
$\text{R}^2 = \text{H}, 4\text{-Cl}, 4\text{-Me}, 4\text{-OMe}, 3\text{-NO}_2, 2\text{-OMe}, 4\text{-F}$

Scheme 20 Synthesis of 2-amino-3-cyanopyridine **23**.



Scheme 21 Synthesis of  $\text{Fe}_3\text{O}_4$ -supported Schiff-base copper(II) complex **58**.





Scheme 22 Synthesis of pyrano[2,3-*b*]pyridine-3-carboxamide derivatives 61.

magnet, and washed four times with distilled water, dried for 4 h, and calcinated at 500 °C for 5 h to yield extra pure CuFe<sub>2</sub>O<sub>4</sub>@HNTs 53 (Scheme 17).<sup>45</sup>

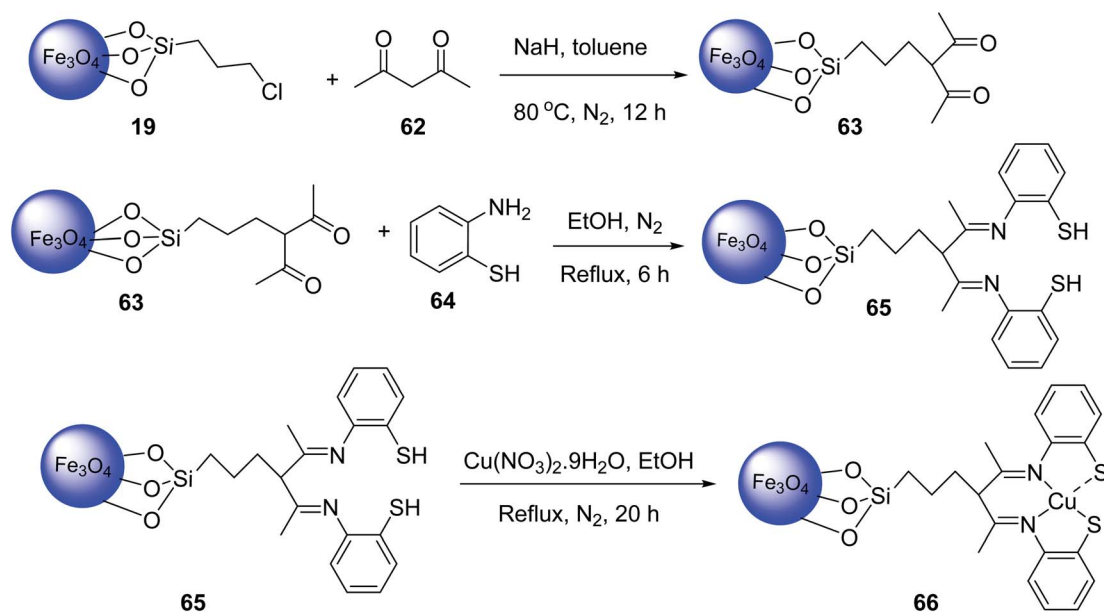
The catalytic activity of CuFe<sub>2</sub>O<sub>4</sub>@HNTs 53 was tested in the synthesis of pyrazolopyridine derivatives 55 *via* the multicomponent reaction of ethyl acetoacetate 7, hydrazine hydrate 54, benzaldehyde 9, and ammonium acetate 10 in EtOH at room temperature for 20 min (Scheme 18).<sup>45</sup>

Maleki and co-workers also synthesized Fe<sub>2</sub>O<sub>3</sub>@Fe<sub>3</sub>-O<sub>4</sub>@Co<sub>3</sub>O<sub>4</sub> 56 as catalyst to provide polysubstituted pyridines 57 through the pseudo-four-component reaction of aldehyde derivatives 9, malononitrile 16, and ammonium acetate 10 under solvent-free conditions at 110 °C (Scheme 19).<sup>46</sup>

In 2019, Mohammadi and co-workers also prepared 2-amino-3-cyanopyridine 23 *via* multicomponent reaction of aromatic aldehydes 9, acetophenone derivatives 22, malononitrile 16, and

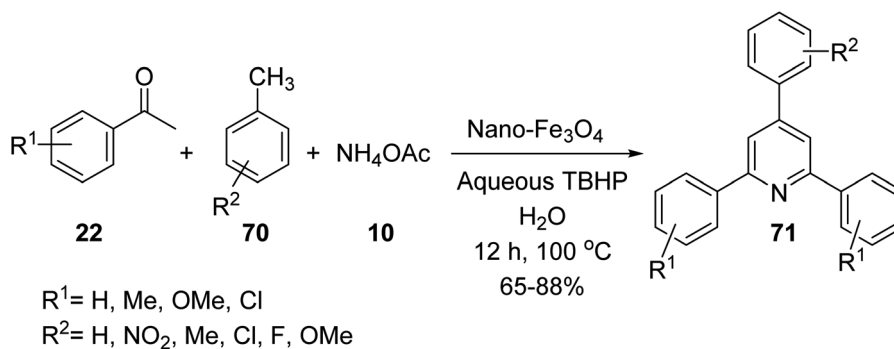
ammonium acetate 10, in the presence of SrFe<sub>12</sub>O<sub>19</sub> as magnetic catalyst under solvent-free conditions at 100 °C. The spectrophotometric properties of 2-amino-4,6-diphenylnicotinonitrile 23 as organo-ligand and several metal ions such as Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> in CH<sub>3</sub>CN solution at 25 °C was also investigated. According to the results, 2-amino-4,6-diphenylnicotinonitrile 23 exhibited a good complexation as organo-ligand with Hg<sup>2+</sup> (Scheme 20).<sup>47</sup>

Fe<sub>3</sub>O<sub>4</sub>-supported Schiff-base copper(II) complexes 58 were reported by Mahmoudi-GomYek *et al.* Ligand 32 was synthesized *via* the reaction of 2,2'-[piperazine-1,4-diylbis-(methylene)]dianiline 30 and 2-hydroxy-3-methoxy benzaldehyde 31. The reaction of FeCl<sub>3</sub>·6H<sub>2</sub>O 24, FeCl<sub>2</sub>·4H<sub>2</sub>O 25 and NH<sub>4</sub>OH in H<sub>2</sub>O under N<sub>2</sub> atmosphere provided Fe<sub>3</sub>O<sub>4</sub> MNPs 1, which were functionalized by 3-chloropropyl(trimethoxy)silane (CPTMS) 18 to give Fe<sub>3</sub>O<sub>4</sub>@Si-PrCl 19. The reaction of compound 32 with Fe<sub>3</sub>O<sub>4</sub>@Si-PrCl 19 gave the



Scheme 23 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-acac-2ATP-Cu(II) MNPs 66.



Scheme 24 Synthesis of 4*H*-pyrano[2,3-*b*]pyridine-3,6-dicarbonitrile derivatives **68**.Scheme 25 Synthesis of 2,4,6-*tri*-arylpyridines **71**.

compound **57**, which reacted with  $\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  to yield  $\text{Fe}_3\text{O}_4$ -supported Schiff-base copper(II) complex **58** (Scheme 21).<sup>48</sup>

$\text{Fe}_3\text{O}_4$ @SPNC **58** was used as catalyst in the synthesis of pyrano[2,3-*b*]pyridine-3-carboxamide derivatives **61** via the three-component reaction of aldehydes **9**, 2-isocyanoacetamide **59**, and 3-cyano-6-hydroxy-4-methyl-pyridin-2(1*H*)-one **60** under solvent-free conditions at 80 °C (Scheme 22).<sup>48</sup>

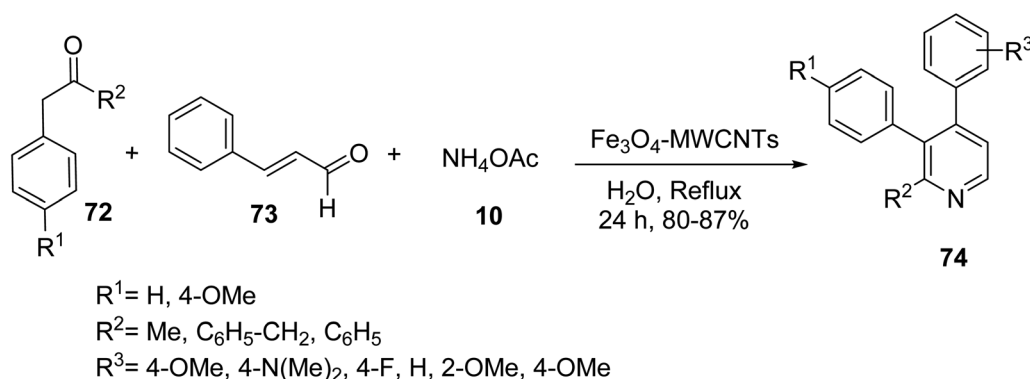
Similar Cu complexes on magnetic nanomaterials were also synthesized from  $\text{Fe}_3\text{O}_4$ @CPTMS MNPs **19** (ref. 49 and <sup>50</sup>) according to the literature. The reaction of  $\text{Fe}_3\text{O}_4$ @CPTMS MNPs **19**, acetylacetone **62** and sodium hydride in toluene at 80 °C under nitrogen atmosphere gave  $\text{Fe}_3\text{O}_4$ @SiO<sub>2</sub>-*n*-Pr-acac MNPs **63**, which was reacted with 2-aminobenzenethiol **64** in EtOH under reflux condition and nitrogen atmosphere to provide  $\text{Fe}_3\text{O}_4$ @SiO<sub>2</sub>-acac-2ATP **65**, followed by reacting with

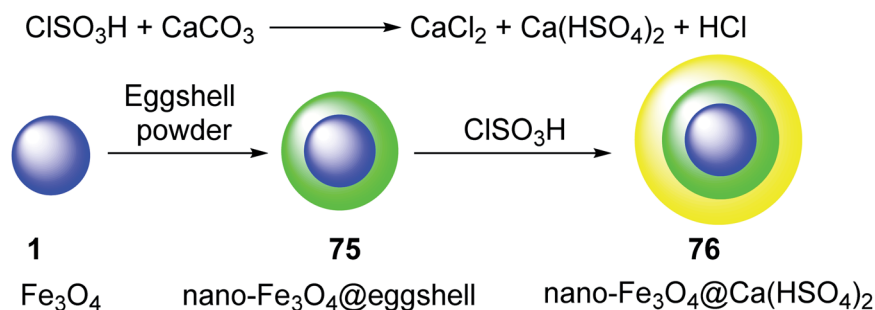
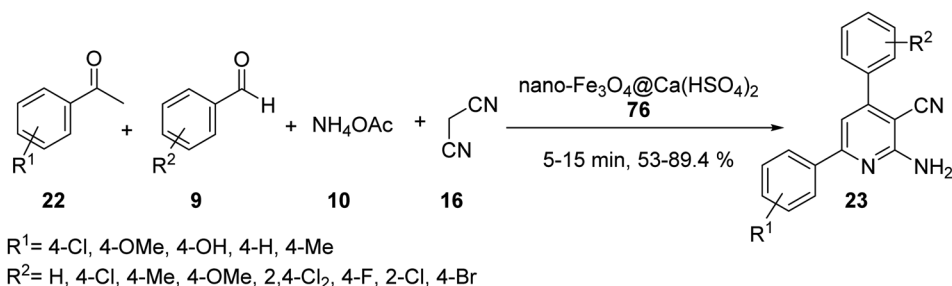
$\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  in ethanol under reflux and nitrogen gas for 12 h to obtain  $\text{Fe}_3\text{O}_4$ @SiO<sub>2</sub>-acac-2ATP-Cu(II) **66** (Scheme 23).<sup>51</sup>

$\text{Fe}_3\text{O}_4$ @SiO<sub>2</sub>-acac-2ATP-Cu(II) MNPs **66** was then employed as catalyst in the three-component reaction of aldehydes **9**, malononitrile **16**, and 3-cyano-6-hydroxy-4-methyl pyridine-2(1*H*)-one **67** under solvent-free conditions at 80 °C for the synthesis of 4*H*-pyrano[2,3-*b*]pyridine-3,6-dicarbonitrile derivatives **68** by Azarifar and co-workers (Scheme 24).<sup>51</sup>

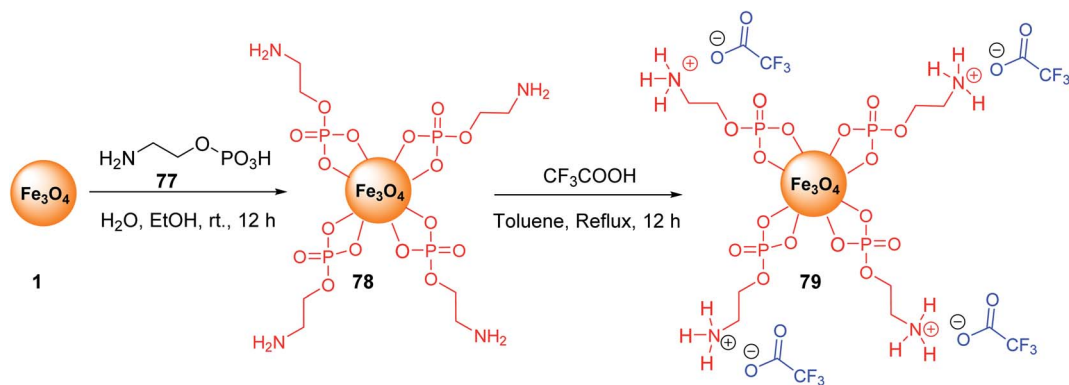
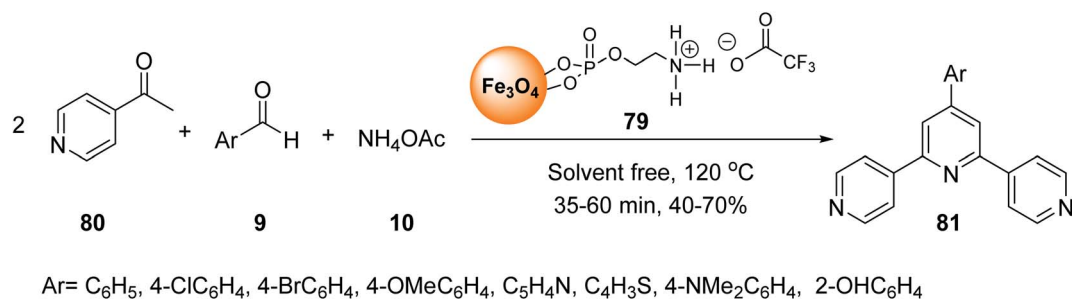
Gajaganti and his co-workers utilised nano- $\text{Fe}_3\text{O}_4$  as a catalyst in the synthesis of 2,4,6-*tri*-arylpyridines **71** via a three-component reaction of acetophenone derivatives **22**, methyl arenes **70**, and ammonium acetate **10** (Scheme 25).<sup>52</sup>

Similar  $\text{Fe}_3\text{O}_4$  multi-walled carbon nanotubes (MWCNTs) were prepared and employed as catalyst in the three-component reaction of ketones **72**, different cinnamaldehyde **73**, and ammonium acetate **10** to synthesize the functionalized pyridines **74** (Scheme 26).<sup>53</sup>

Scheme 26 Synthesis of functionalized pyridines **74**.

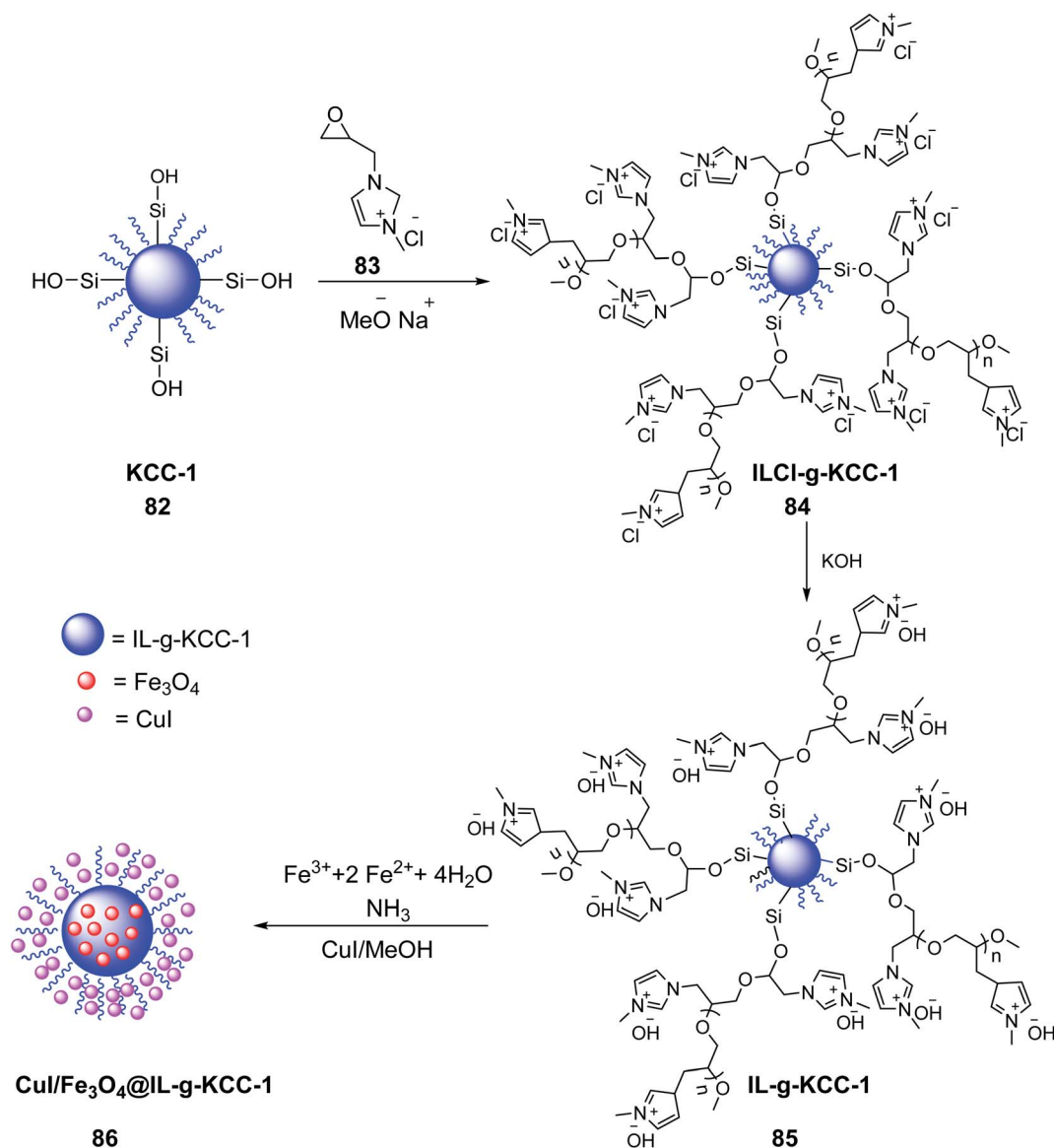
Scheme 27 Synthesis of  $\text{Fe}_3\text{O}_4\text{@Ca}(\text{HSO}_4)_2$  76.

Scheme 28 Synthesis of 2-amino-3-cyanopyridines 23.

Scheme 29 Synthesis of  $\text{Fe}_3\text{O}_4\text{@O}_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$  79.

Scheme 30 Synthesis of terpyridines 81.



Scheme 31 Synthesis of CuI/Fe<sub>3</sub>O<sub>4</sub> NPs@Biimidazole IL-KCC-1 86.

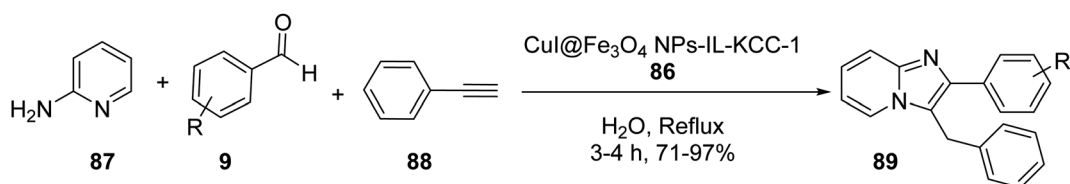
The eggshell powder was coated on the surface of magnetic nano-Fe<sub>3</sub>O<sub>4</sub> **1**, to give nano-Fe<sub>3</sub>O<sub>4</sub>@eggshell **75**, which was treated with ClSO<sub>3</sub>H to yield nano-magnetic acid catalyst Fe<sub>3</sub>O<sub>4</sub>@-Ca(HSO<sub>4</sub>)<sub>2</sub> **76**. In this process, CaCO<sub>3</sub> from the eggshell was converted to Ca(HSO<sub>4</sub>)<sub>2</sub> through reaction with ClSO<sub>3</sub>H (Scheme 27).<sup>54</sup>

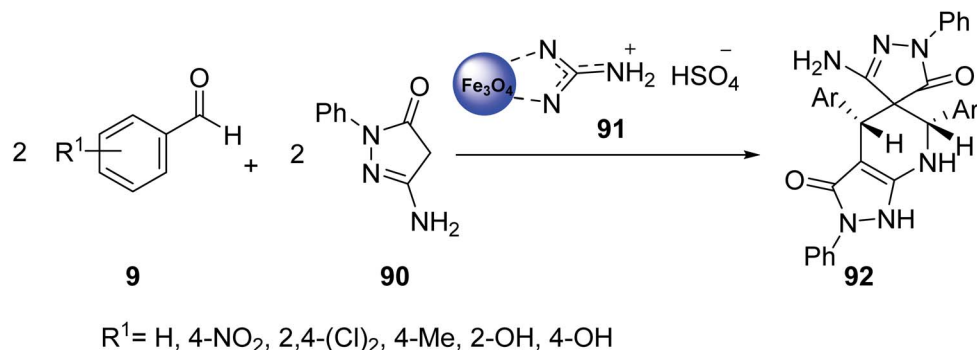
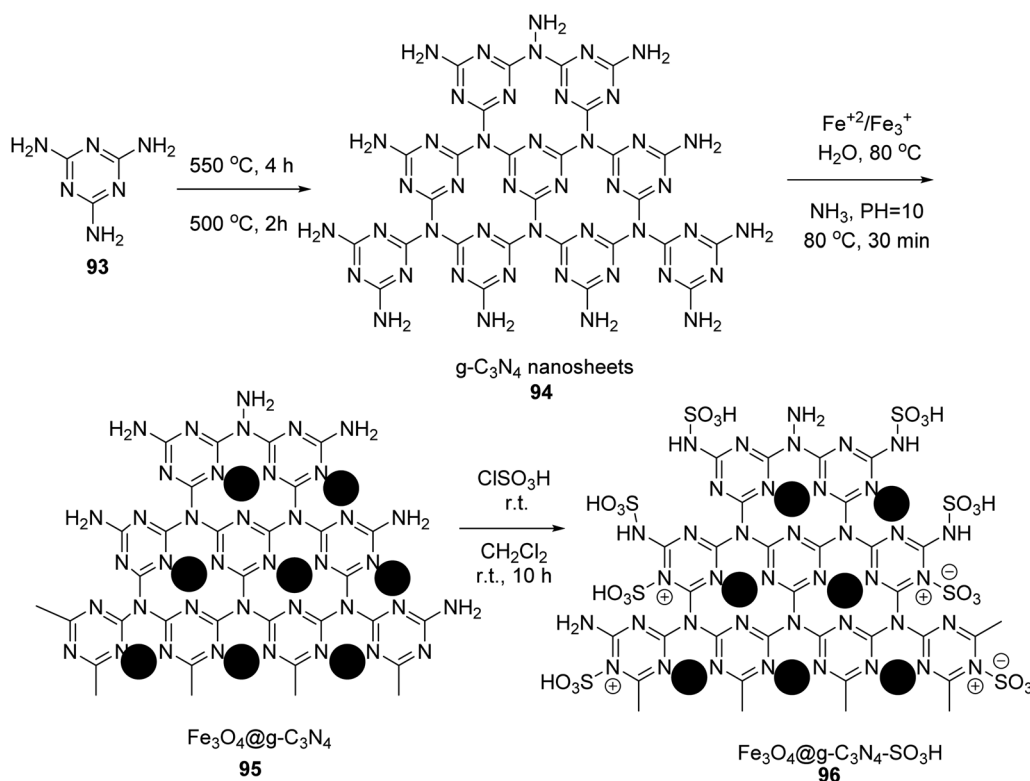
Nano-Fe<sub>3</sub>O<sub>4</sub>@Ca(HSO<sub>4</sub>)<sub>2</sub> **76** was subsequently utilised in the synthesis of 2-amino-3-cyanopyridines **23** via four-component reaction of different benzaldehydes **9**, acetophenone **22**,

ammonium acetate **10**, and malononitrile **16** under solvent-free conditions at 90 °C for 5–15 min (Scheme 28).<sup>54</sup>

### 2.3. Ionic liquid-based magnetic nanomaterials

Fe<sub>3</sub>O<sub>4</sub>@O<sub>2</sub>PO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> MNPs **78** was prepared according to the reported method.<sup>34,55</sup> After dispersion in the ultrasonic bath, it was reacted with CF<sub>3</sub>CO<sub>2</sub>H to prepare Fe<sub>3</sub>O<sub>4</sub>@O<sub>2</sub>PO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>-NH<sub>3</sub> CF<sub>3</sub>CO<sub>2</sub> **79** (Scheme 29).<sup>56</sup>

Scheme 32 Synthesis of imidazo[1,2-a]pyridines **89**.

Scheme 33 Synthesis of spiro [pyrazole-pyrazolo[3,4-*b*]pyridine]-dione derivatives **92**.Scheme 34 Synthesis of  $\text{Fe}_3\text{O}_4\text{@g-C}_3\text{N}_4\text{-SO}_3\text{H}$  **96**.

$\text{Fe}_3\text{O}_4\text{@O}_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+ \text{CF}_3\text{CO}_2^-$  **79** was employed in the multicomponent reaction between various acetyl pyridines **80**, aryl aldehydes **9**, and ammonium acetate **10** under solvent-free reaction conditions at 120 °C to synthesize terpyridines **81** (Scheme 30).<sup>57</sup>

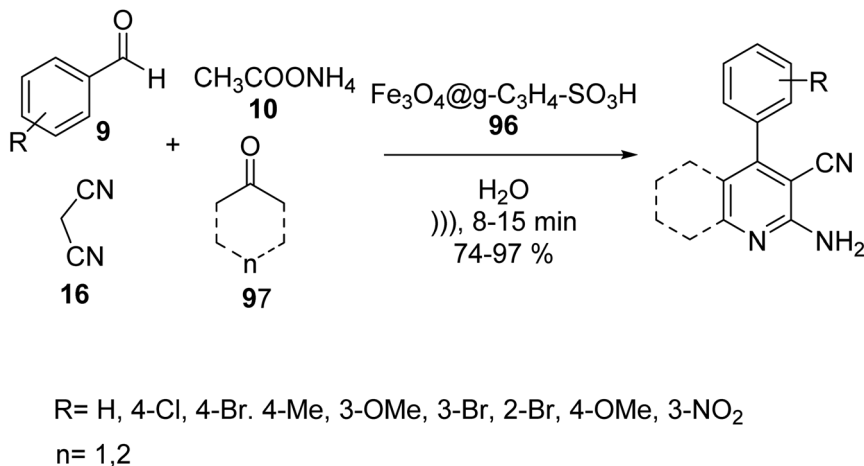
$\text{CuI/Fe}_3\text{O}_4$  NPs@Biimidazole IL-KCC-1 **86** was prepared by Azizi *et al.* in 2020. Firstly, 1-methyl-3-(oxiran-2-ylmethyl)-1*H*-imidazol-3-ium chloride **83** and sodium methoxide were added to the prepared KCC-1 **82** in dimethylformamide (DMF), and stirred for 60 min under a nitrogen atmosphere at 60 °C. Methanol and DMF were subsequently evaporated under vacuum to obtain 1-methyl-3-(oxiran-2-yl-methyl)-1*H*-imidazolium chloride (ILCl-*g*-KCC-1) **84**.<sup>58</sup> Then, solid potassium hydroxide was added to ILCl-*g*-KCC-1 **84** to yield IL-KCC-1 **85** by replacing chloride ions with hydroxide ions.  $\text{Fe}_3\text{O}_4$  NPs were subsequently doped on

the substrate of IL-KCC-1 **84** and treated with  $\text{CuI/MeOH}$  to obtain  $\text{CuI/Fe}_3\text{O}_4$  NPs@Biimidazole IL-KCC-1 **86** (Scheme 31).

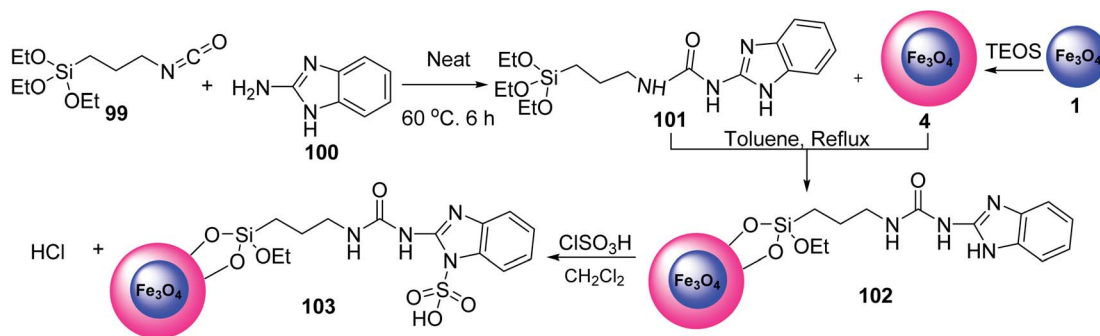
$\text{CuI/Fe}_3\text{O}_4$  NPs@IL-KCC-1 **86** was investigated in the three-component reaction of 2-aminopyridine **87**, aldehydes **9**, phenylacetylene **88**, and CTAB in  $\text{H}_2\text{O}$  under reflux condition to obtain imidazo[1,2-*a*]pyridines **89** in high yields (Scheme 32).<sup>59</sup>

Shojaei *et al.* was studied the catalytic activity of guanidinium hydrogen sulfate on  $\text{Fe}_3\text{O}_4$  nanoparticles **91** in the pseudo-four-component reactions of aryl aldehydes **9** with 3-amino-1-phenyl-2-pyrazolin-5-one **90** to give spiro[pyrazole-pyrazolo[3,4-*b*]pyridine]-dione derivatives **92** under mild conditions (Scheme 33).<sup>60</sup>





Scheme 35 Synthesis of pyridine derivatives 98.

Scheme 36 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@(CH<sub>2</sub>)<sub>3</sub>-urea-benzimidazole sulfonic acid 103.

#### 2.4. Bifunctional magnetic catalysts

In 2019, Edrisi *et al.* synthesized g-C<sub>3</sub>N<sub>4</sub> **94** according to the reported method.<sup>61</sup> g-C<sub>3</sub>N<sub>4</sub> **94** was functionalized with Fe<sub>3</sub>O<sub>4</sub> nanoparticles<sup>62</sup> to give Fe<sub>3</sub>O<sub>4</sub>@g-C<sub>3</sub>N<sub>4</sub> **95**. Finally, Fe<sub>3</sub>O<sub>4</sub>@g-C<sub>3</sub>N<sub>4</sub>-SO<sub>3</sub>H **96** was washed with methanol and ethyl acetate and afterward dried under vacuum at 60 °C (Scheme 34).<sup>63</sup>

Fe<sub>3</sub>O<sub>4</sub>@g-C<sub>3</sub>N<sub>4</sub>-SO<sub>3</sub>H **96** was then utilized in the synthesis of pyridine derivatives **98** *via* the one-pot multicomponent reaction of different aldehydes **9**, various ketones **97**, ammonium acetate **10**, and malononitrile **16** in H<sub>2</sub>O under ultrasonic irradiation (Scheme 35).<sup>63</sup>

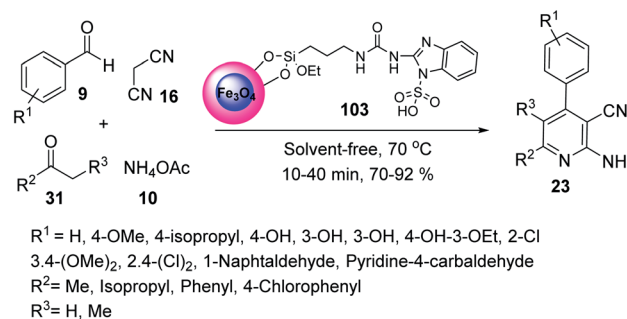
Torabi and *et al.* prepared Ligand **101** *via* the reaction of 1H-benzo[d]imidazol-2-amine **100** and compound **99** under solvent-free conditions. Fe<sub>3</sub>O<sub>4</sub> was then functionalized with tetraethyl orthosilicate (TEOS) in toluene under reflux conditions to give Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> **4**, which was reacted with ligand **101** to yield Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@(CH<sub>2</sub>)<sub>3</sub>-urea-benzimidazole **102**, followed by the reaction with chlorosulfuric acid in dichloromethane to obtain Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@(CH<sub>2</sub>)<sub>3</sub>-urea-benzimidazole sulfonic acid **103** (Scheme 36).<sup>64</sup>

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@(CH<sub>2</sub>)<sub>3</sub>-urea-benzimidazole sulfonic acid **103** was employed in the synthesis of 2-amino-3-cyano pyridines **23** through the multicomponent reaction of benzaldehyde **9**,

malononitrile **16**, methyl isopropyl ketone **31**, and ammonium acetate **10** under solvent-free conditions at 70 °C (Scheme 37).<sup>64</sup>

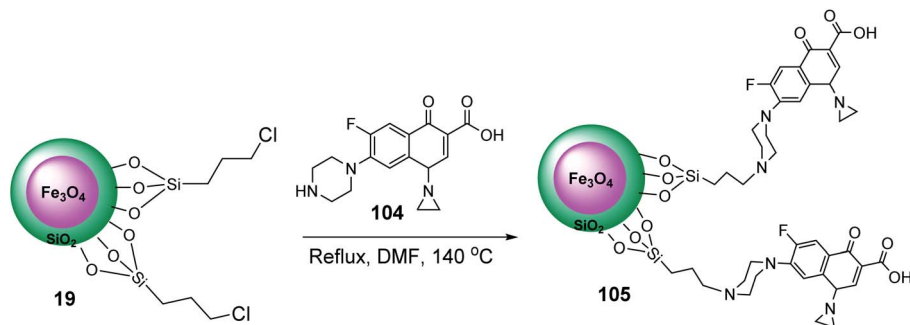
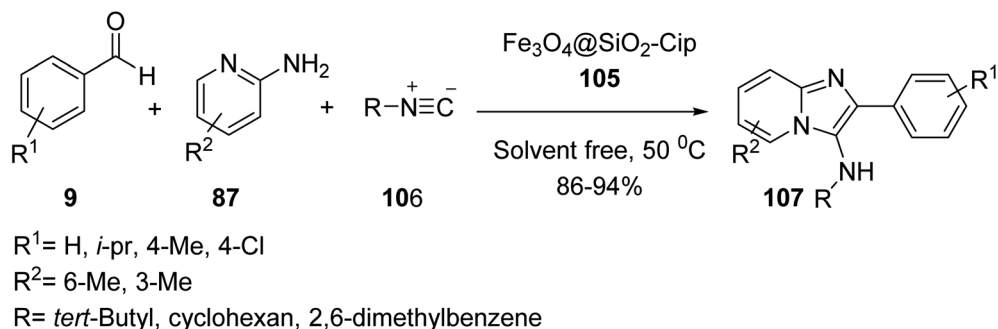
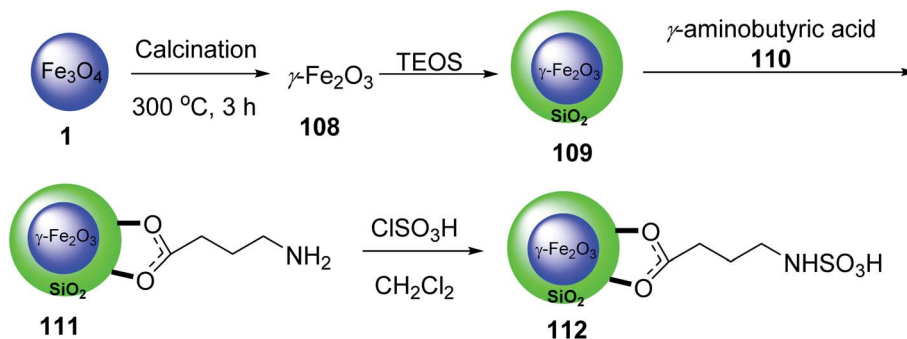
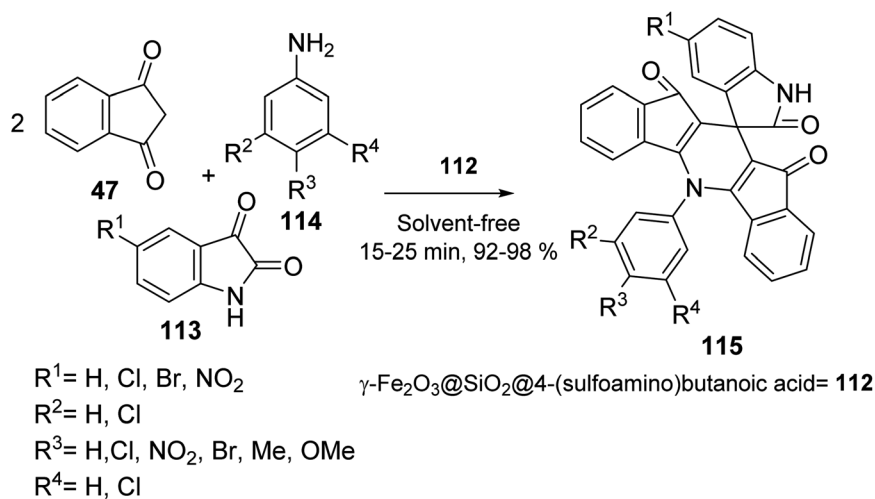
Initially, according to previous works,<sup>65</sup> Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Pr-Cl **19** was prepared and dispersed in dry DMF, and then reacted with ciprofloxacin **104** to give Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Pr-ciprofloxacin **105** (Scheme 38).<sup>66</sup>

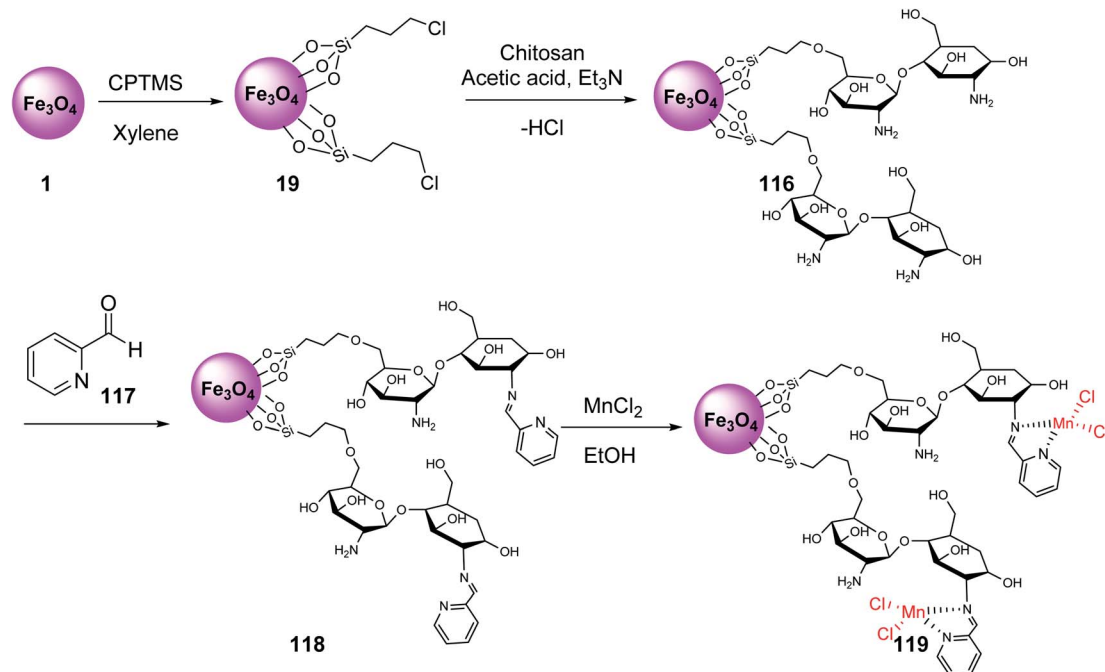
Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Pr-Cip **105** was then investigated in the synthesis of imidazo[1,2-*a*]pyridines **107** through the three-component reaction of various benzaldehyde **9**, 2-amino-pyridine **87**, and cyclohexyl isocyanide **106** (Scheme 39).<sup>66</sup>



Scheme 37 Synthesis of 2-amino-3-cyano pyridines 23.



Scheme 38 Synthesis of  $\text{Fe}_3\text{O}_4@SiO_2@Pr$ -ciprofloxacin **105**.Scheme 39 Synthesis of the imidazo[1,2-a]pyridines **107**.Scheme 40  $\gamma\text{-Fe}_2\text{O}_3@SiO_2$   $\gamma$ -aminobutyric acid- $\text{SO}_3\text{H}$  **112**.Scheme 41 Synthesis of 5-(aryl)-5H-spiro[diindeno[1,2-b:2',1'-e]pyridine-11,30-indoline]-2',10,12-trione derivatives **115**.

Scheme 42 Synthesis of  $\text{Fe}_3\text{O}_4\text{@CSBMn}$  119.

Mohammadi *et al.* synthesized  $\text{Fe}_2\text{O}_3$  nanoparticles **1** according to a previously reported method.<sup>67</sup> Calcination of  $\text{Fe}_2\text{O}_3$  provided  $\gamma\text{-Fe}_2\text{O}_3$  **108**, which was converted to  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$  MNPs **109** by the reaction with tetraethyl orthosilicate (TEOS) **3**, followed by the functionalization with  $\gamma$ -aminobutyric acid **110** to yield  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$ -aminobutyric acid nanoparticles **111**. Then, it was dispersed in chloroform and reacted with chlorosulfonic acid to provide  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$   $\gamma$ -aminobutyric acid- $\text{SO}_3\text{H}$  **112** (Scheme 40).<sup>68</sup>

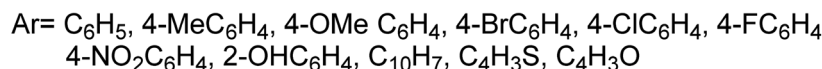
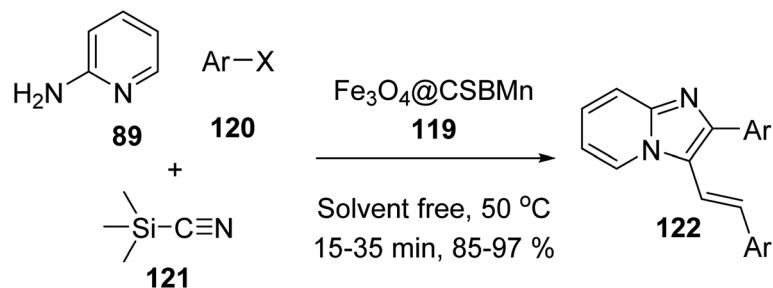
$\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{@4-(sulfoamino)butanoic acid-}\text{SO}_3\text{H}$  **112** was utilized in the synthesis of 5-(aryl)-5*H*-spiro[diindenol[1,2-*b*:2',1'-*e*]pyridine-11,30-indoline]-2',10,12-trione derivatives **115** through the pseudo four-component reaction of 1,3-indandione **47**, isatins **113** with various aromatic amines **114** (Scheme 41).<sup>68</sup>

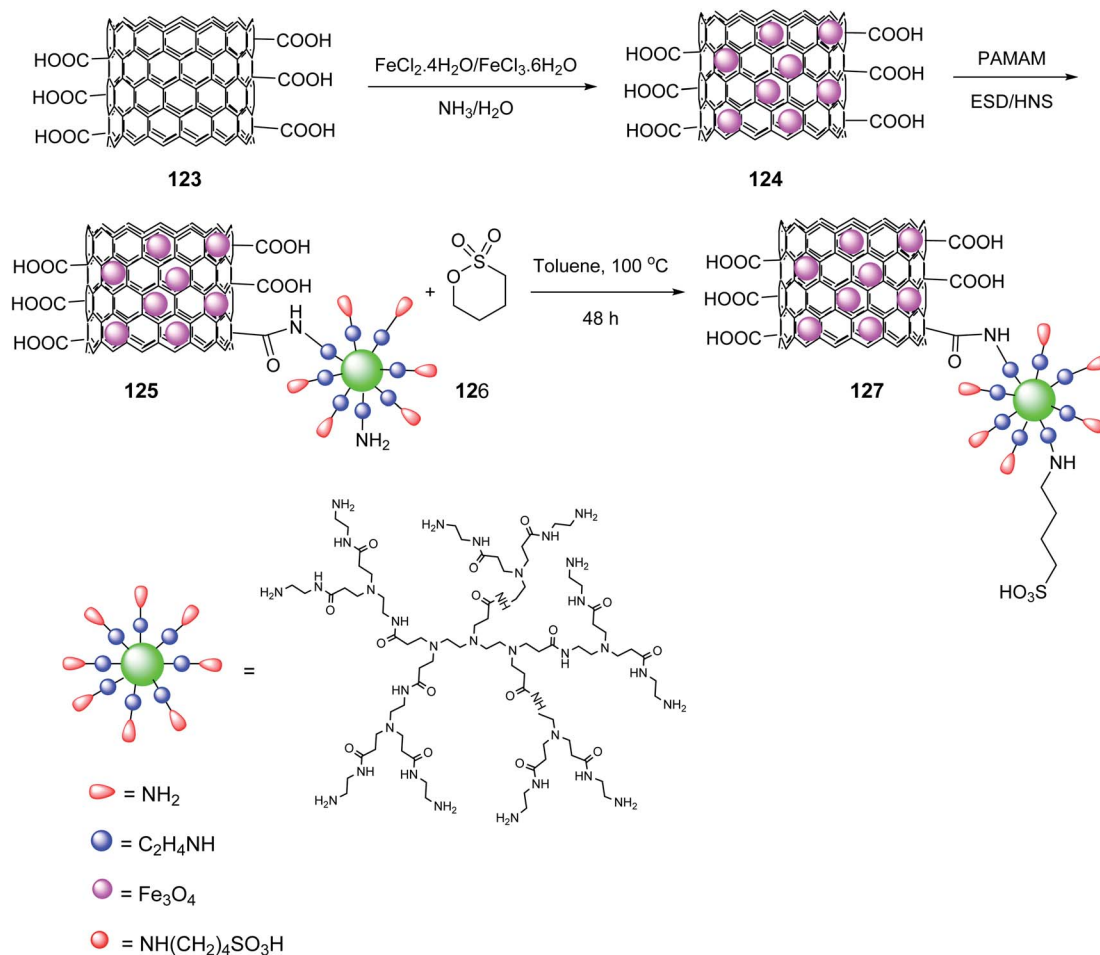
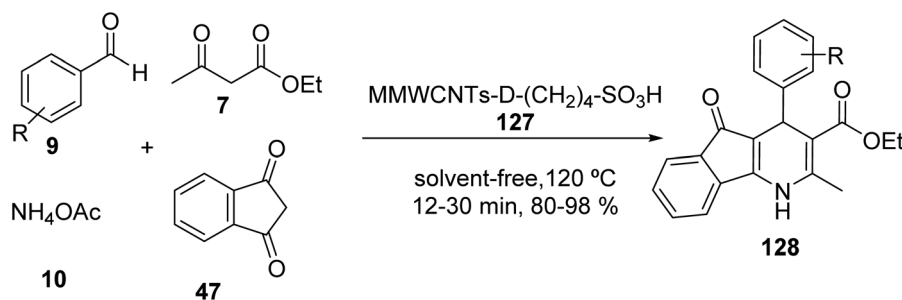
$\text{Fe}_3\text{O}_4\text{@Si-Pr-Cl}$  **19** was reacted with chitosan and acetic acid solutions to provide chitosan-coated MNPs **116**, which were

modified with 2-formylpyridine **117** to give compound **118**, followed by the reaction with manganese chloride to provide manganese Schiff-base complex  $\text{Fe}_3\text{O}_4\text{@CSBMn}$  **119** (Scheme 42).<sup>69,70</sup>

$\text{Fe}_3\text{O}_4\text{@CSBMn}$  **119** was employed in the synthesis of 3-iminoaryl-imidazo[1,2-*a*]pyridine (IAIP) derivatives **122** through the three-component reaction of aryl halide derivatives **120**, trimethylsilyl cyanide **121**, and 2-aminopyridine **89** (Scheme 43). According to the results, the aldehydes with an electron-withdrawing group provided higher yields in comparison with electron-donating groups.<sup>70</sup>

Multi-walled carbon nanotubes systems MWCNTs-COOH **123** (ref. 71) were synthesized according to the literature. A mixture of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was added to MWCNTs-COOH **123** in distilled water and stirred at 50 °C to give the magnetic multi-walled carbon nanotubes (MMWCNTs) **124**,

Scheme 43 Synthesis of 3-iminoaryl-imidazo[1,2-*a*]pyridine (IAIP) derivatives **122**.

Scheme 44 Synthesis of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H 127.Scheme 45 Synthesis of dihydro-1*H*-indeno[1,2-*b*] Pyridines 128.

which were subsequently reacted with 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC·HCl) and *N*-hydroxysuccinimide (NHS) to obtain MMWCNTs-D-NH<sub>2</sub> 125 followed by reaction with 1,4-butanediol 126 to yield MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H 127 (Scheme 44).<sup>72</sup>

MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H 127 was employed in the synthesis of dihydro-1*H*-Indeno[1,2-*b*] Pyridines 128 by the reaction of various aldehydes 9, 1,3-indandione 47, ethyl acetoacetate 7, and ammonium acetate 10 (Scheme 45).<sup>72</sup>

### 3. Conclusions

Due to the high importance of magnetic nano-catalysts, featuring non-toxic nature, high surface area, simple preparation, easy surface modification, and simple separation, such systems have relevant applications in organic synthesis and catalysis. In this contribution, the synthesis methods of magnetic nano-catalysts have been disclosed in view of their applications in the synthesis of pyridine derivatives. According to most studies, these catalysts have excellent activities to target



products, also featuring high reusability with the possibility to be recycled several times without reducing their catalytic activities.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

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