


 Cite this: *RSC Adv.*, 2021, **11**, 17456

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- β 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.

 Received 26th March 2021
 Accepted 26th April 2021

DOI: 10.1039/d1ra02418c

rsc.li/rsc-advances

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1. Introduction

In recent decades, nanotechnology has attracted much attention in various fields.^{1,2} One of the most influential families of nanomaterials is magnetic nanoparticles, which have been extensively employed in different sciences, including drug delivery,³ illness recognition,⁴ water desalination,⁵ ambience scrubbing,⁶ and chemical catalysis.⁷ 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.^{8,9}



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

(Biotransformation) from Laval University, Quebec, Canada under the supervision of Professor Chenevert, in 2000. She is a Full Professor of Organic Chemistry in the chemistry department of Alzahra University. Her research interests include organic synthesis, heterocyclic synthesis, asymmetric synthesis, natural product synthesis, synthetic methodology, and applications of nano-heterogeneous catalysts in multicomponent reactions.



Zohreh Kheilkordi was born in Ramsar/Mazandaran, Iran, in 1990. She received her BSc in Chemistry from Mazandaran University, Babolsar in 2012, and her M.Sc. in Organic Chemistry from Yazd University, under the supervision of Dr Mohammad Ali Amrollahi, in 2014. She received her PhD degree in organic chemistry from Alzahra University, Tehran, Iran, under the supervision of

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.^{10–15} The magnetic nano-catalysts can be separated by external magnetic fields.¹⁶ Fe₃O₄ nanoparticles can be coated with organic and inorganic materials, including silica,¹⁷ surfactants,¹⁸ polymers,^{17,19} cellulose,²⁰ carbon,²¹ chitosan,²² 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,²³ 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.²⁴ In continuation our research work,^{25–29} this contribution will be aimed to discuss the synthesis of magnetic nano-catalysts as well as their applications in the synthesis of pyridine derivatives.



Fatemeh Mohajer was born in Tehran, Iran, and she received her BSc in Applied Chemistry from Bu-Ali Sina University and M.Sc degree in Organic Chemistry from Azad University in Karaj. She is a PhD student under the supervision of Prof. Ghodsi Mohammadi Ziarani at Alzahra University in Tehran, Iran.



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

faculty of Tehran University. His research interests include nanoporous materials synthesis, modification of nanoporous materials, and application of organic-inorganic hybrid materials in various fields such as catalysis, adsorption, separation, and sensors.

2. The synthesis of pyridine derivatives by diverse magnetic catalysts

2.1. Basic magnetic catalyst

The core-shell structure of Fe₃O₄@KCC-1-*n*pr-NH₂ **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 Fe₃O₄@KCC-1 **4** was prepared by adding cetyl trimethyl ammonium bromide (CTAB) **2** and tetraethylorthosilicate (TEOS) **3**. Then, Fe₃O₄@KCC-1 **4** was functionalized with 3-aminopropyl)triethoxysilane **5** to produce Fe₃O₄@KCC-1-*n*pr-NH₂ **6** with excellent basic properties. Details for the preparation of Fe₃O₄@KCC-1-*n*pr-NH₂ **6** are shown in Scheme 1. Various characterization techniques, including FT-IR, SEM, TEM, BET, and XRD, confirmed the structure of Fe₃O₄@KCC-1-*n*pr-NH₂ **6** as magnetic nano-catalyst.³⁰

Fe₃O₄@KCC-1-*n*Pr-NH₂ **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).³⁰

Fe₃O₄ MNPs **1** were also synthesized according to the literature,³¹ and then coated by TEOS to yield Fe₃O₄@SiO₂ MNPs **4**,³² which were modified by 3-aminopropyl-trimethoxysilane (APTS) **5** to provide Fe₃O₄@SiO₂-pr-NH₂ 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 Fe₃O₄ MNPs (PDMAF-MNPs) **14** (Scheme 3).³³

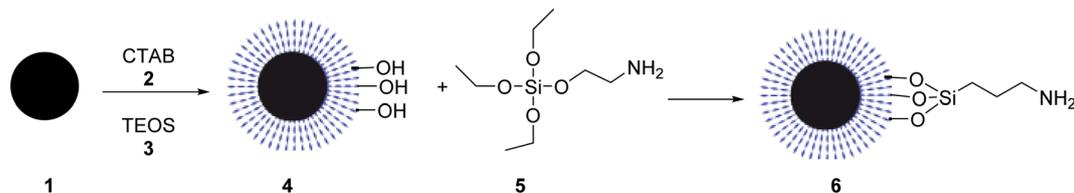
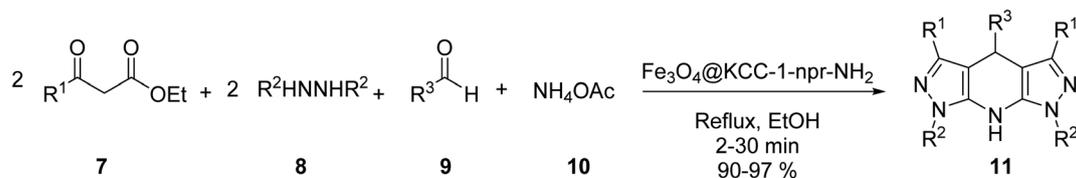
PDMAF-MNPs was investigated in the multicomponent reaction of aldehydes **9**, malononitrile **16**, ammonium acetate



Rafael Luque, Full Professor from Departamento de Química 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).



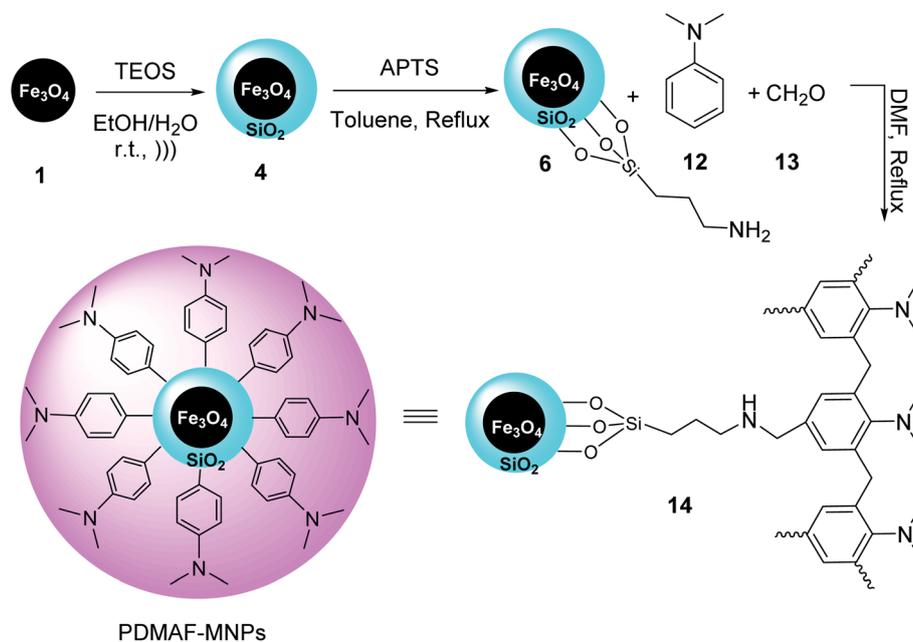
Scheme 1 Synthesis of $\text{Fe}_3\text{O}_4\text{@KCC-1-npr-NH}_2$ 6.

$\text{R}^1 = \text{Me, OEt}$

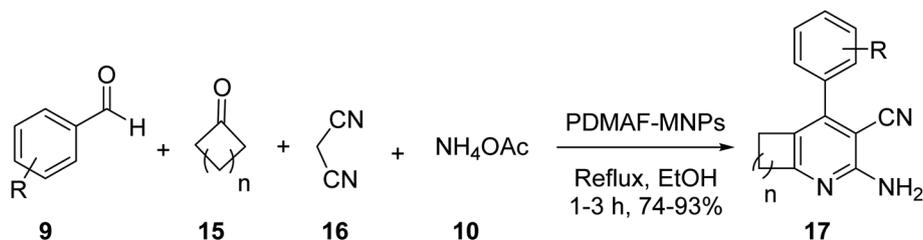
$\text{R}^2 = \text{H, Ph}$

$\text{R}^3 = 1\text{H-indole, 1,1'-biphenyl, 4-BrC}_6\text{H}_4, \text{C}_6\text{H}_5, 4\text{-ClC}_6\text{H}_4, 4\text{-FC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4, 4\text{-MeC}_6\text{H}_4, 4\text{-OHC}_6\text{H}_4$

Scheme 2 Synthesis of tetrahydropyrazolopyridine 11.



PDMAF-MNPs

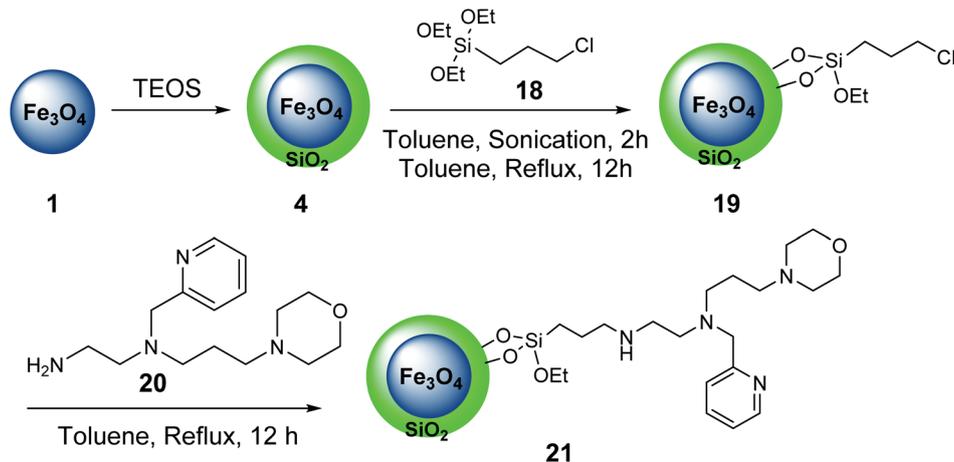
Scheme 3 Synthesis of poly *N,N*-dimethylaniline-formaldehyde supported on silica-coated Fe_3O_4 MNPs (PDMAF-MNPs) 14.

$n = 1, 2, 3$

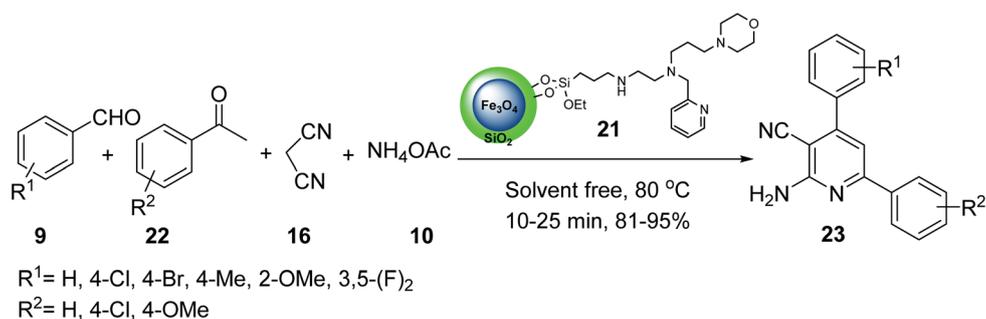
$\text{R} = \text{H, 4-Me, 4-Cl, 3-OMe, 4-NO}_2, 4\text{-OMe, 4-Br}$

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

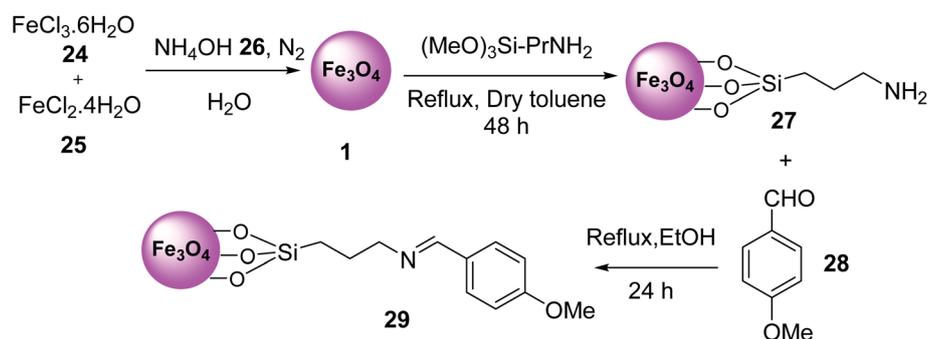




Scheme 5 Synthesis of magnetic nanoparticles with morpholine tags 21.



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

Scheme 7 Synthesis of $\text{Fe}_3\text{O}_4\text{-Si}-(\text{CH}_2)_3\text{-N}=\text{CH}-\text{Ph}-\text{OMe}$ 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).³³

In another example, iron oxide 1 was prepared and reacted with tetraethylorthosilicate (TEOS) 3 to provide $\text{Fe}_3\text{O}_4@\text{SiO}_2$ 4,³⁴ 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).³⁵

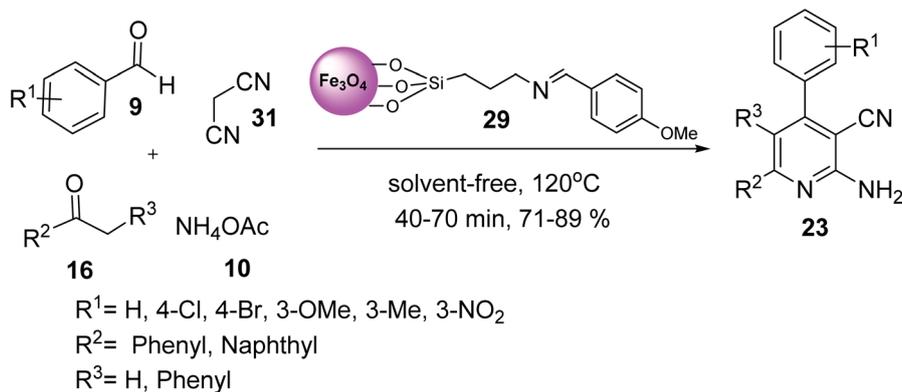
The nano-magnetic catalyst 21 was examined in the multi-component reaction of benzaldehydes 9, acetophenone derivatives 22, malononitrile 16, and ammonium acetate 10 under the

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

Nano-magnetic $\text{Fe}_3\text{O}_4\text{-Si}-(\text{CH}_2)_3\text{-N}=\text{CH}-\text{Ph}-\text{OMe}$ 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 NH_4OH 26 in H_2O under N_2 atmosphere to prepare Fe_3O_4 MNPs 1, which was functionalized with aminopropyl silane 5 to provide $\text{Fe}_3\text{O}_4\text{-Si}-(\text{CH}_2)_3\text{-NH}_2$ 27, followed by modification with 4-methoxy benzaldehyde 28 under reflux conditions in ethanol for 24 h (Scheme 7).³⁶

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

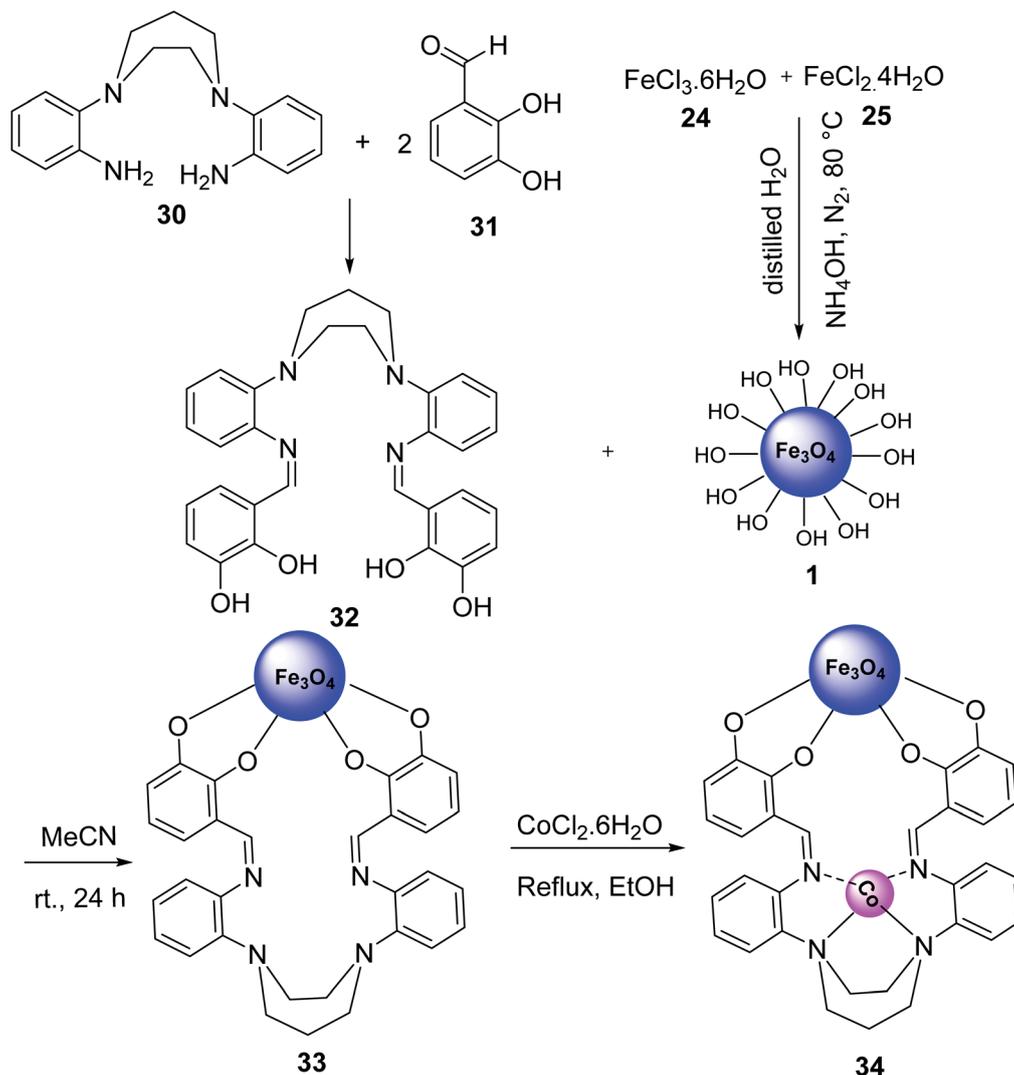


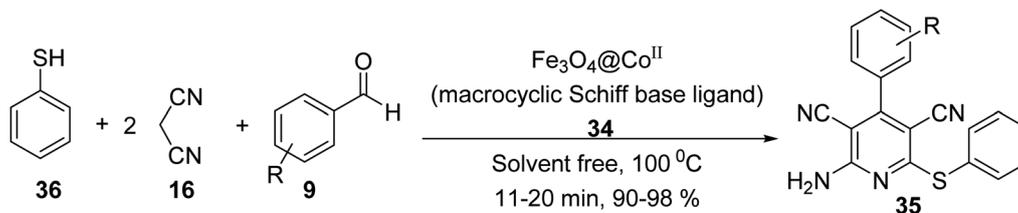
Scheme 8 Synthesis of 2-amino-3-cyanopyridines **23**.

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).³⁶

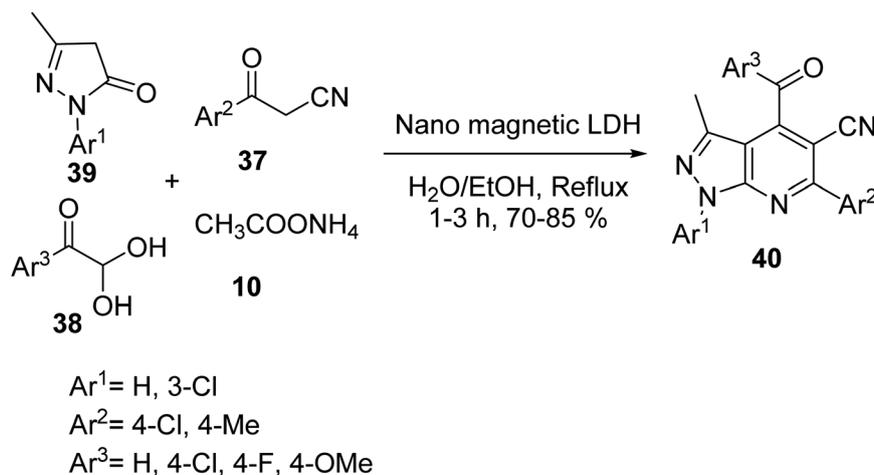
2.2. Acidic magnetic catalysts

$\text{Fe}_3\text{O}_4@\text{Co}^{\text{II}}$ (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 $\text{Fe}_3\text{O}_4@\text{Co}^{\text{II}}$ (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.

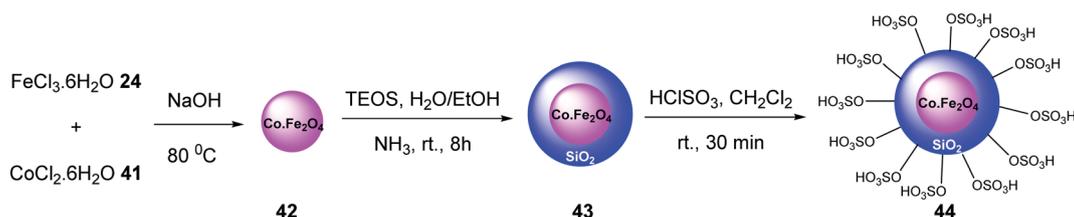
reaction of 2,2'-(1,4-diazepane-1,4-diyl)-di-aniline **30** and 2,3-dihydroxybenzaldehyde **31** in ethanol under reflux for 24 hours. Then, a mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ **24**, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ **25**, and NH_4OH **26** was stirred in H_2O under N_2 gas at 100 °C to give Fe_3O_4 **1**, which was treated with macrocyclic Schiff base ligand (**iii**) **32** to give Fe_3O_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 Fe_3O_4 @macrocyclic Schiff base ligand **34** (Scheme 9).³⁷

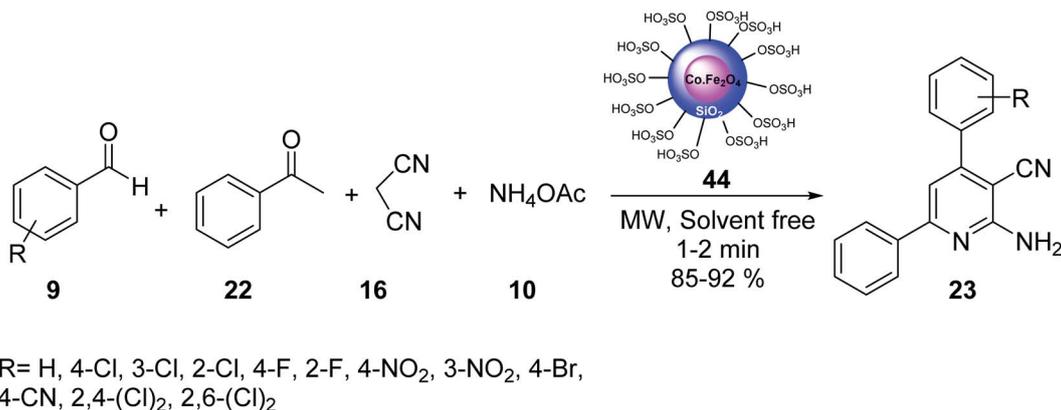
Fe_3O_4 @macrocyclic Schiff base ligand **34** was employed in the synthesis of 2-amino-4-aryl-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile derivatives **35** *via* three-component reaction of aldehyde derivatives **9**, malononitrile **16**, thiophenol **36** under solvent-free conditions (Scheme 10). The catalytic activity of Fe_3O_4 @ Co^{II} (macrocyclic Schiff base ligand) **34** was separately compared to that of Fe_3O_4 , macrocyclic Schiff base ligand, Fe_3O_4 @macrocyclic Schiff base ligand **33**. It was demonstrated that Fe_3O_4 @ Co^{II} **34** showed the best results.³⁷

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/ H_2O (1 : 1) under the reflux conditions (Scheme 11). In addition, pyrazolo[3,4-*b*] pyridines **40** have biological and pharmacological activity.³⁸

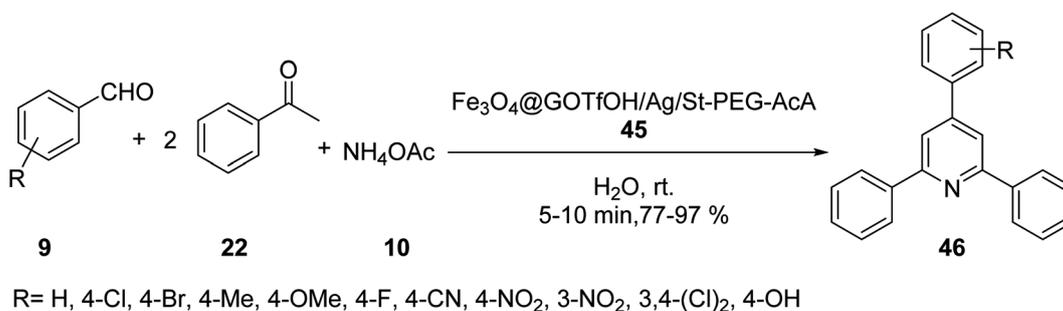
CoFe_2O_4 @ SiO_2 - SO_3H **44** was synthesized as a reusable nano-catalyst by Hosseinzadeh *et al.* Initially, CoFe_2O_4 magnetic nanoparticles **42** were prepared according to previous works.³⁹ Then, it was modified with tetraethylorthosilicate to provide CoFe_2O_4 @ SiO_2 **43**,⁴⁰ which was dispersed in dry CH_2Cl_2 , and ClSO_3H to give CoFe_2O_4 @ SiO_2 - SO_3H **44** (Scheme 12).⁴¹

CoFe_2O_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 CoFe_2O_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.

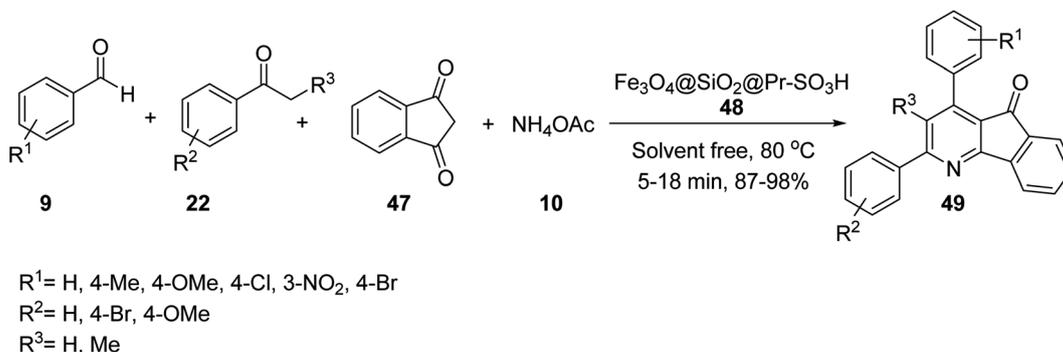
irradiation to provide 2-amino-4,6-diarylnicotinonitrile derivatives 23 in good yields (Scheme 13).⁴¹

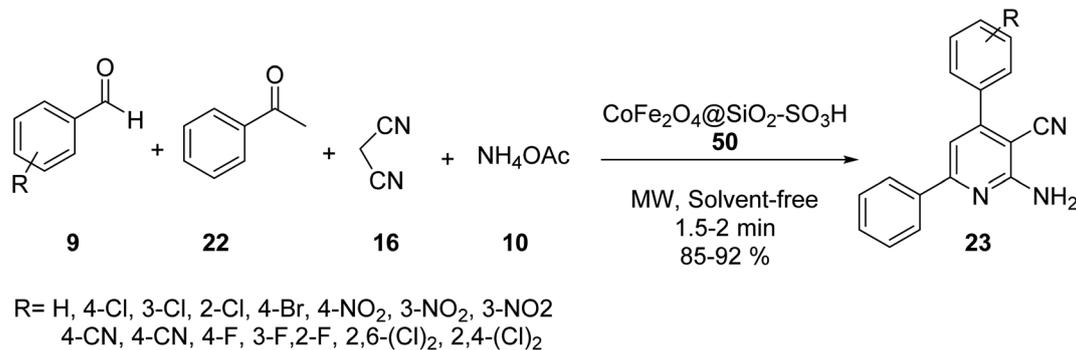
Forouzandehdel and co-workers synthesized a novel, recyclable nano-catalyst Fe₃O₄@GO_{TfOH}/Ag/St-PEG-AcA 45, which was employed in the synthesis of 2,4,6-tri-arylpyridine derivatives 46 by the reaction of aldehyde derivatives 9, acetophenone 22, and ammonium acetate 10 in H₂O at room temperature (Scheme 14).⁴²

Fe₃O₄@SiO₂@Pr-SO₃H 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).⁴³

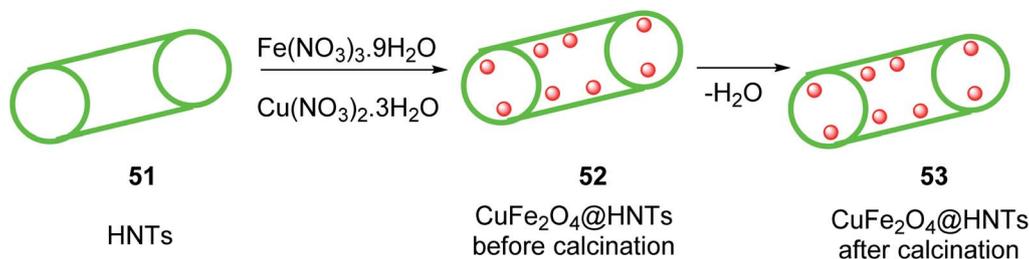
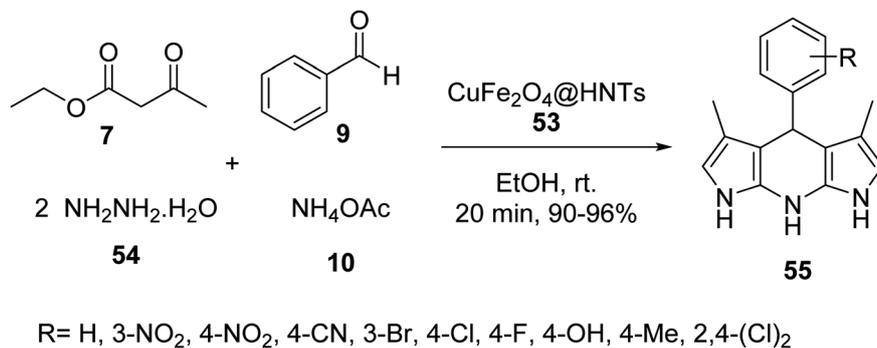
Hosseinzadeh and *et al.* synthesized 2,6-diaryl-substituted pyridine derivatives 23 *via tetra* component reaction of aldehyde derivatives 9, acetophenone 22, malononitrile 16, and ammonium acetate 10 in the presence of CoFe₂O₄@SiO₂-SO₃H 50 under microwave irradiation and solvent-free conditions (Scheme 16).⁴⁴

Halloysite nanotubes CuFe₂O₄@HNTs 53 was synthesized by the reaction of Halloysite nanotubes HNTs 51 was added to Fe(NO₃)₃·9H₂O and 0.14 g (0.58 mmol) of Cu(NO₃)₂·3H₂O 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 CuFe₂O₄@HNTs 52, which was separated by an external

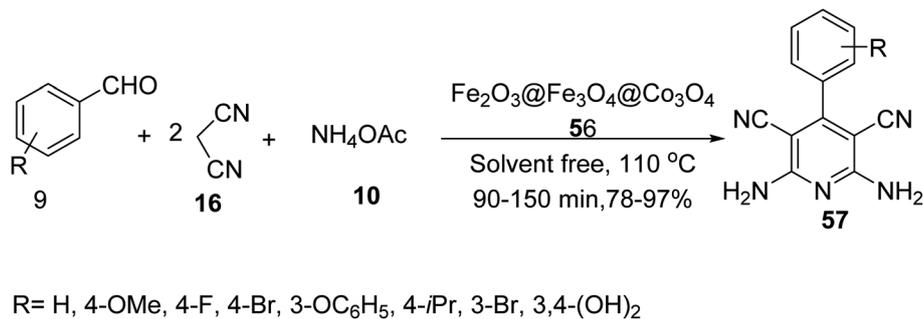
Scheme 15 Synthesis of indeno[1,2-*b*]pyridines 49.



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

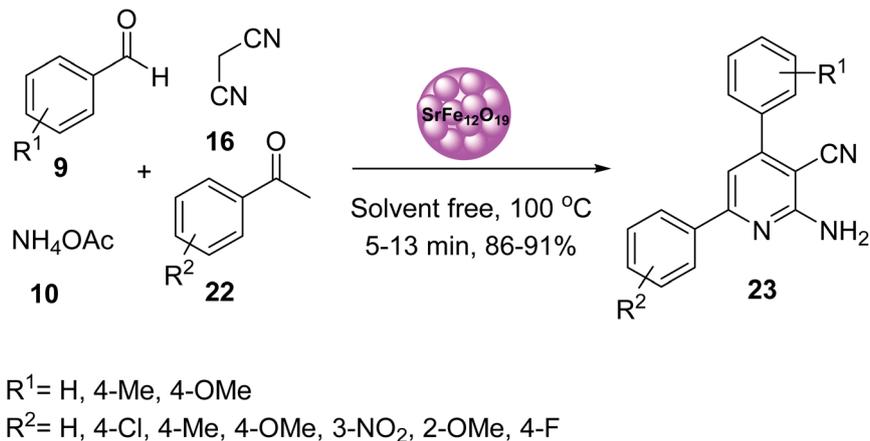
Scheme 17 Synthesis of CuFe₂O₄@HNTs 53.

Scheme 18 Synthesis of pyrazolopyridine derivatives 55.

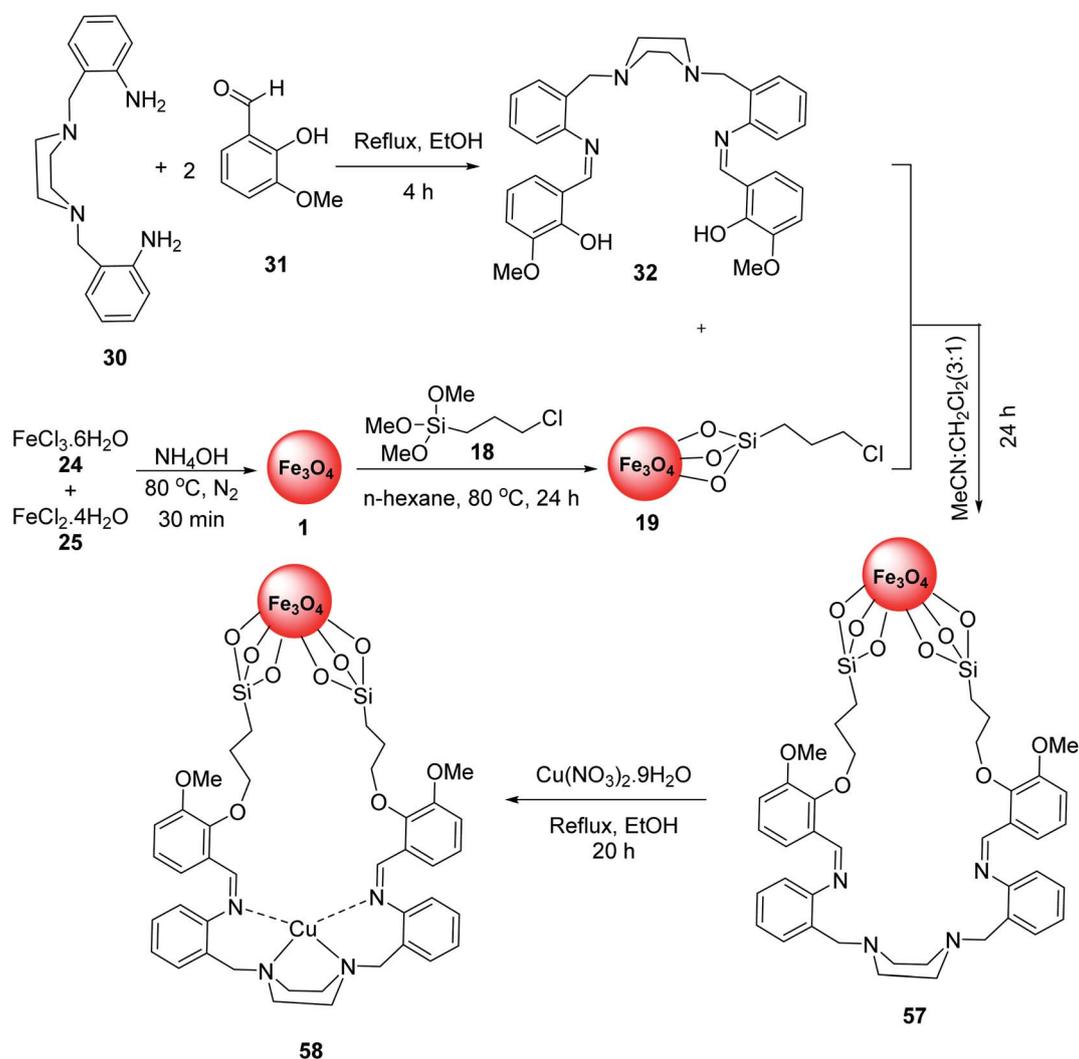


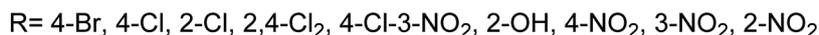
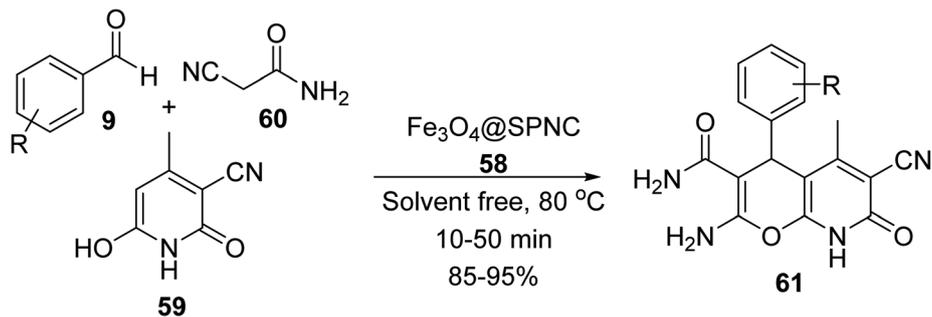
Scheme 19 The synthesis of polysubstituted pyridines 57.





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

Scheme 21 Synthesis of Fe_3O_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 CuFe₂O₄@HNTs 53 (Scheme 17).⁴⁵

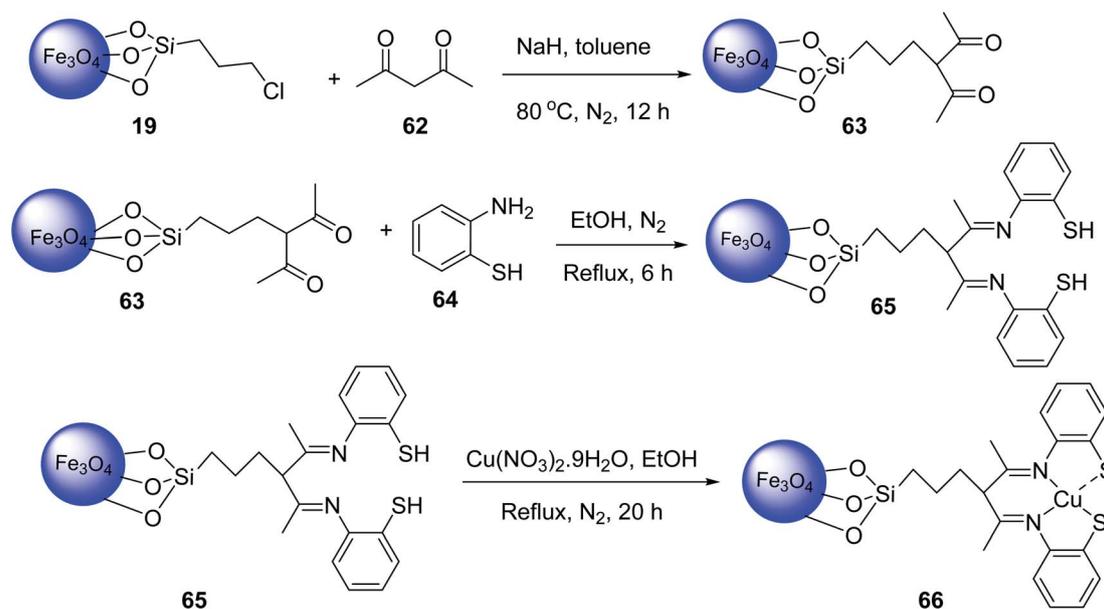
The catalytic activity of CuFe₂O₄@HNTs 53 was tested in the synthesis of pyrazolopyridine derivatives 55 *via* the multicomponent reaction of ethyl acetoacetate 7, hydrazine hydrate 54, benzaldehyde 9, and ammonium acetate 10 in EtOH at room temperature for 20 min (Scheme 18).⁴⁵

Maleki and co-workers also synthesized Fe₃O₄@Fe₃-O₄@Co₃O₄ 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).⁴⁶

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

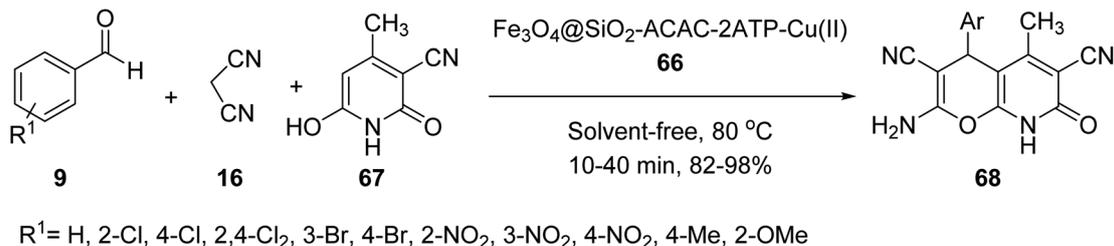
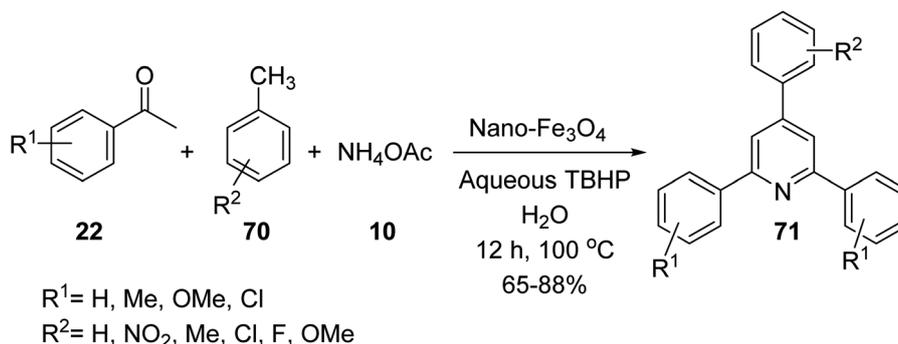
ammonium acetate 10, in the presence of SrFe₁₂O₁₉ as magnetic catalyst under solvent-free conditions at 100 °C. The spectrophotometric properties of 2-amino-4,6-diphenylnicotinonitrile 23 as organo-ligand and several metal ions such as Ag⁺, Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Hg²⁺, Mn²⁺, Ni²⁺, Pb²⁺, and Zn²⁺ in CH₃CN 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 Hg²⁺ (Scheme 20).⁴⁷

Fe₃O₄-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 FeCl₃·6H₂O 24, FeCl₂·4H₂O 25 and NH₄OH in H₂O under N₂ atmosphere provided Fe₃O₄ MNPs 1, which were functionalized by 3-chloropropyl(trimethoxy)silane (CPTMS) 18 to give Fe₃O₄@Si-PrCl 19. The reaction of compound 32 with Fe₃O₄@Si-PrCl 19 gave the



Scheme 23 Synthesis of Fe₃O₄@SiO₂-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 Fe_3O_4 -supported Schiff-base copper(II) complex **58** (Scheme 21).⁴⁸

Fe_3O_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).⁴⁸

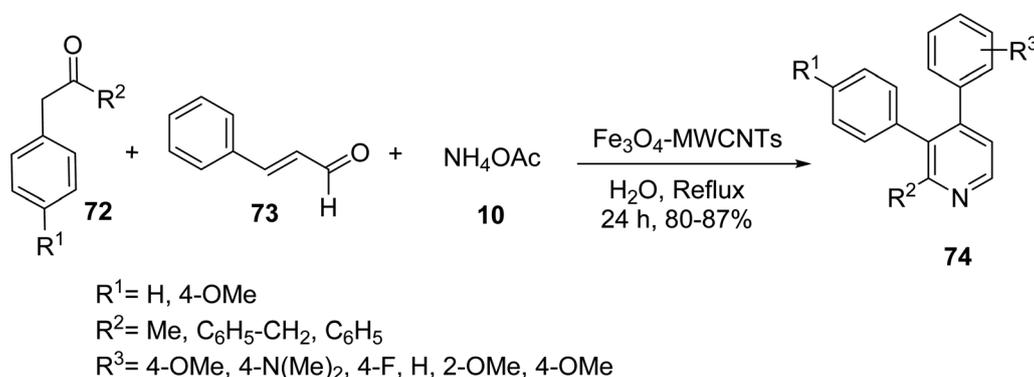
Similar Cu complexes on magnetic nanomaterials were also synthesized from Fe_3O_4 @CPTMS MNPs **19** (ref. 49 and ⁵⁰) according to the literature. The reaction of Fe_3O_4 @CPTMS MNPs **19**, acetylacetone **62** and sodium hydride in toluene at 80 °C under nitrogen atmosphere gave Fe_3O_4 @SiO₂-*n*-Pr-acac MNPs **63**, which was reacted with 2-aminobenzenethiol **64** in EtOH under reflux condition and nitrogen atmosphere to provide Fe_3O_4 @SiO₂-acac-2ATP **65**, followed by reacting with

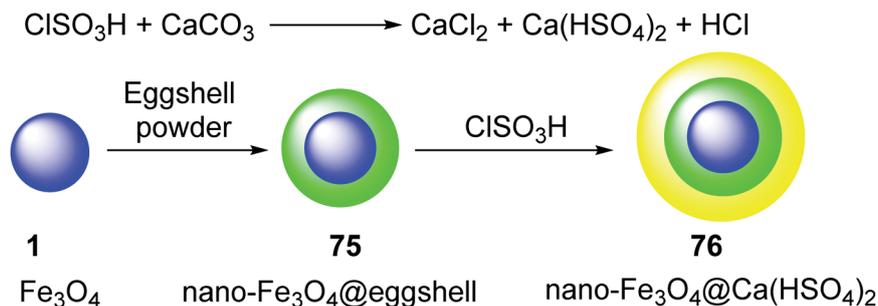
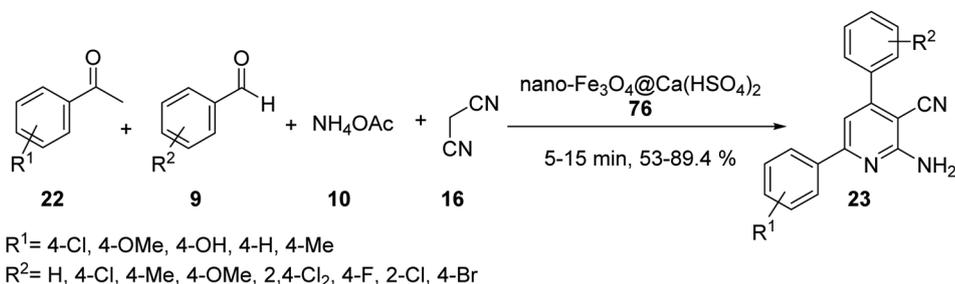
$\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ in ethanol under reflux and nitrogen gas for 12 h to obtain Fe_3O_4 @SiO₂-acac-2ATP-Cu(II) **66** (Scheme 23).⁵¹

Fe_3O_4 @SiO₂-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).⁵¹

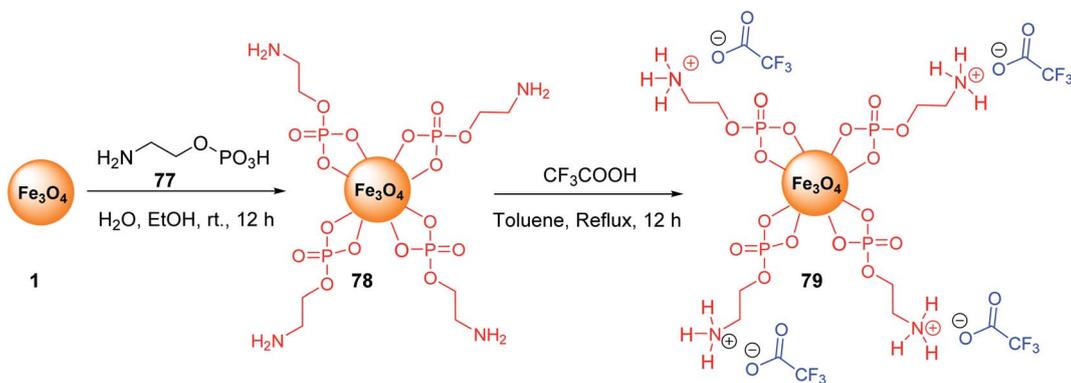
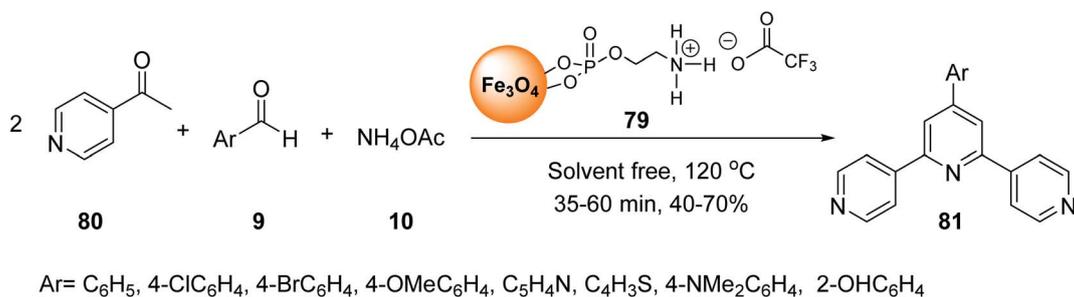
Gajaganti and his co-workers utilised nano- Fe_3O_4 as a catalyst in the synthesis of 2,4,6-*tri*-arylpyridines **71** via a three-component reaction of acetophenone derivatives **22**, methyl arenes **70**, and ammonium acetate **10** (Scheme 25).⁵²

Similar Fe_3O_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).⁵³

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

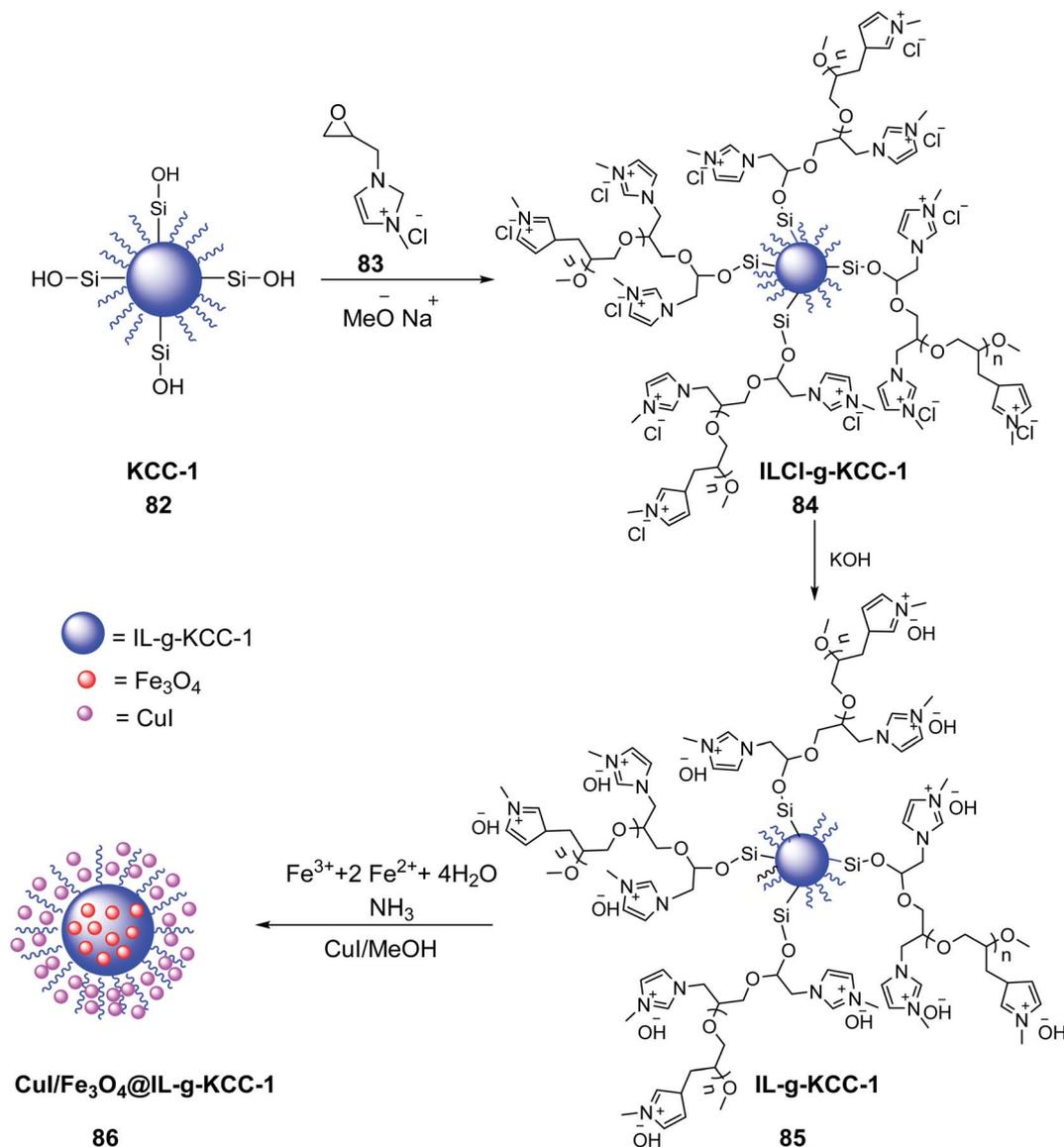
Scheme 27 Synthesis of $\text{Fe}_3\text{O}_4\text{@Ca}(\text{HSO}_4)_2$ 76.

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/Fe₃O₄ NPs@Biimidazole IL-KCC-1 86.

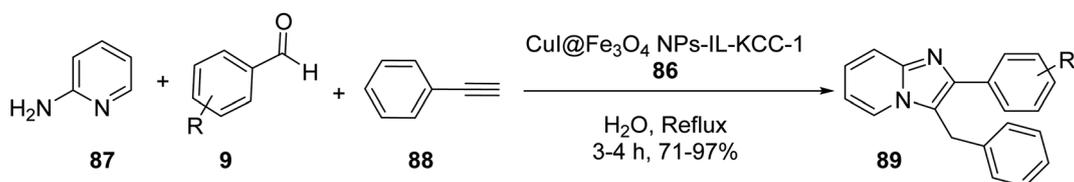
The eggshell powder was coated on the surface of magnetic nano-Fe₃O₄ **1**, to give nano-Fe₃O₄@eggshell **75**, which was treated with ClSO₃H to yield nano-magnetic acid catalyst Fe₃O₄@Ca(HSO₄)₂ **76**. In this process, CaCO₃ from the eggshell was converted to Ca(HSO₄)₂ through reaction with ClSO₃H (Scheme 27).⁵⁴

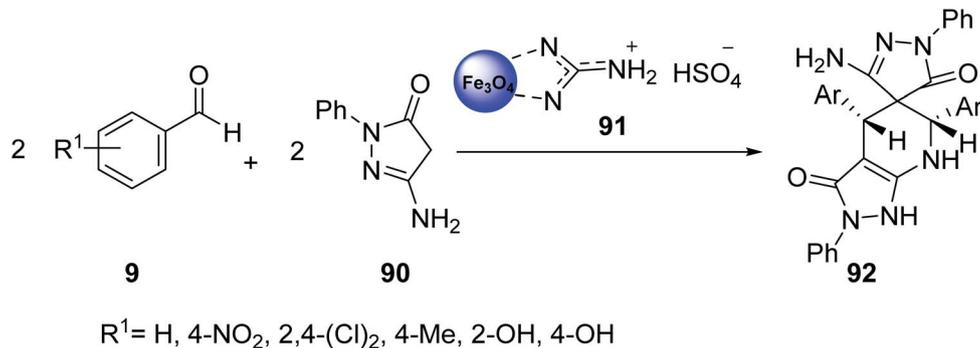
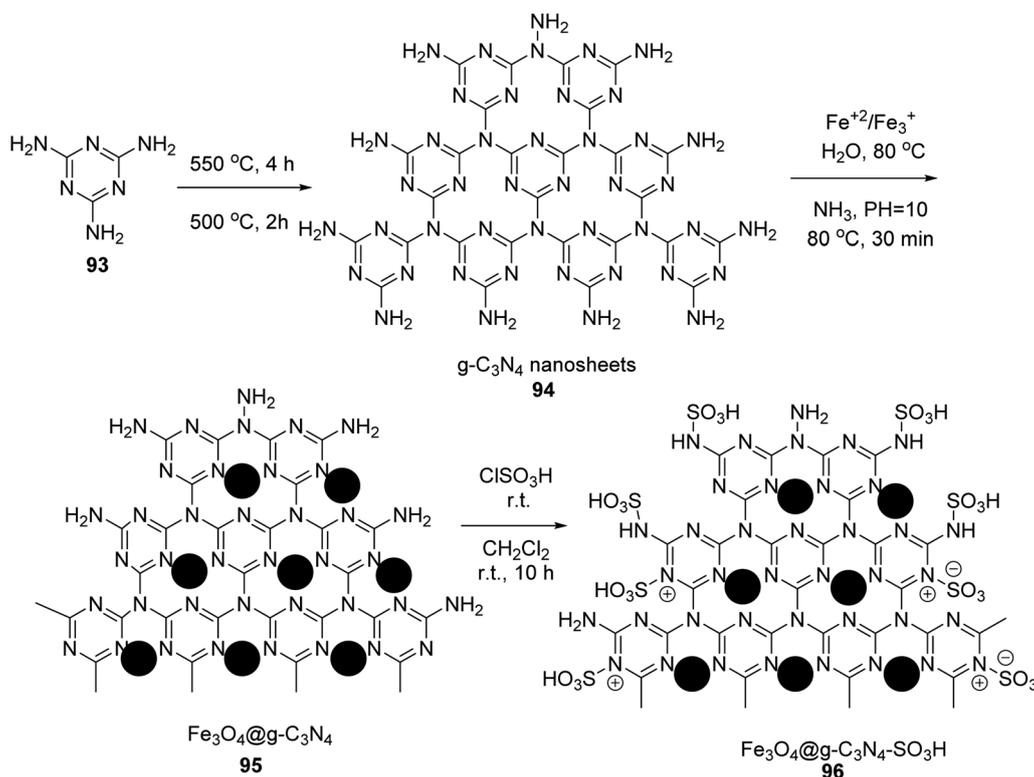
Nano-Fe₃O₄@Ca(HSO₄)₂ **76** was subsequently utilised in the synthesis of 2-amino-3-cyanopyridines **23** via four-component reaction of different benzaldehydes **9**, acetophenone **22**,

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

2.3. Ionic liquid-based magnetic nanomaterials

Fe₃O₄@O₂PO₂(CH₂)₂NH₂ MNPs **78** was prepared according to the reported method.^{34,55} After dispersion in the ultrasonic bath, it was reacted with CF₃CO₂H to prepare Fe₃O₄@O₂PO₂(CH₂)₂-NH₃ CF₃CO₂ **79** (Scheme 29).⁵⁶

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).⁵⁷

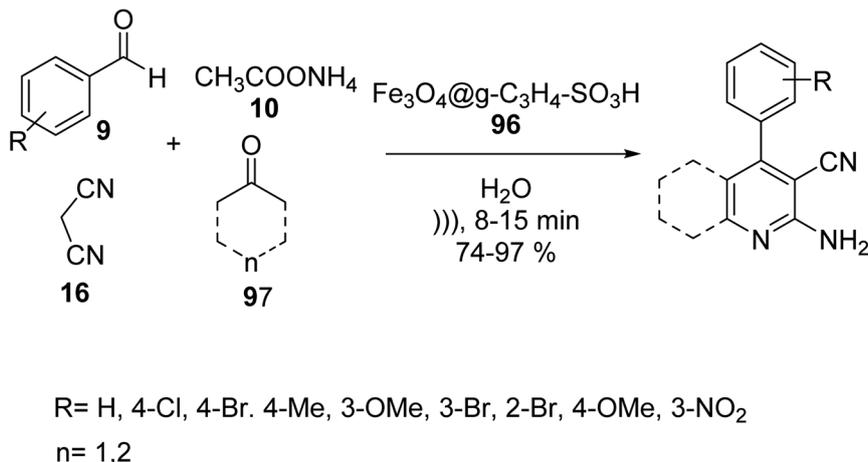
$\text{CuI/Fe}_3\text{O}_4$ NPs@Biimidazole IL-KCC-1 **86** was prepared by Azizi *et al.* in 2020. Firstly, 1-methyl-3-(oxiran-2-ylmethyl)-1*H*-imidazol-3-ium chloride **83** and sodium methoxide were added to the prepared KCC-1 **82** in dimethylformamide (DMF), and stirred for 60 min under a nitrogen 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**.⁵⁸ 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. Fe_3O_4 NPs were subsequently doped on

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

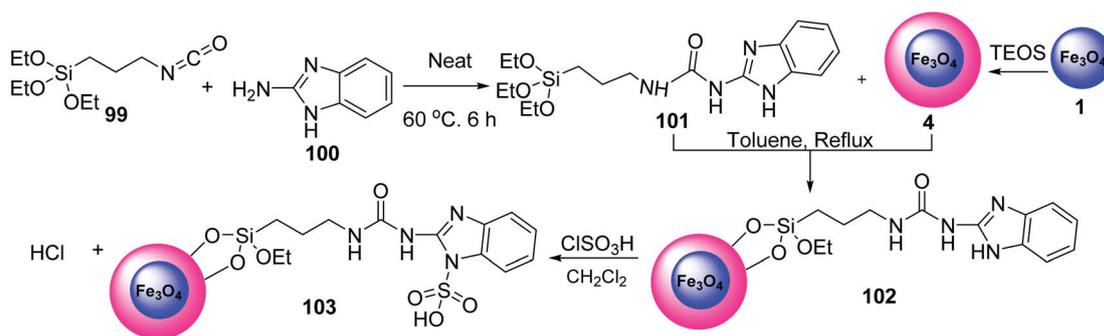
$\text{CuI/Fe}_3\text{O}_4$ NPs@IL-KCC-1 **86** was investigated in the three-component reaction of 2-aminopyridine **87**, aldehydes **9**, phenylacetylene **88**, and CTAB in H_2O under reflux condition to obtain imidazo[1,2-*a*]pyridines **89** in high yields (Scheme 32).⁵⁹

Shojaei *et al.* was studied the catalytic activity of guanidinium hydrogen sulfate on Fe_3O_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).⁶⁰





Scheme 35 Synthesis of pyridine derivatives 98.

Scheme 36 Synthesis of $\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n\text{-(CH}_2)_3\text{-urea-benzimidazole sulfonic acid 103}$.

2.4. Bifunctional magnetic catalysts

In 2019, Edrisi *et al.* synthesized $g\text{-C}_3\text{N}_4$ **94** according to the reported method.⁶¹ $g\text{-C}_3\text{N}_4$ **94** was functionalized with Fe_3O_4 nanoparticles⁶² to give $\text{Fe}_3\text{O}_4@g\text{-C}_3\text{N}_4$ **95**. Finally, $\text{Fe}_3\text{O}_4@g\text{-C}_3\text{N}_4\text{-SO}_3\text{H}$ **96** was washed with methanol and ethyl acetate and afterward dried under vacuum at 60°C (Scheme 34).⁶³

$\text{Fe}_3\text{O}_4@g\text{-C}_3\text{N}_4\text{-SO}_3\text{H}$ **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_2O under ultrasonic irradiation (Scheme 35).⁶³

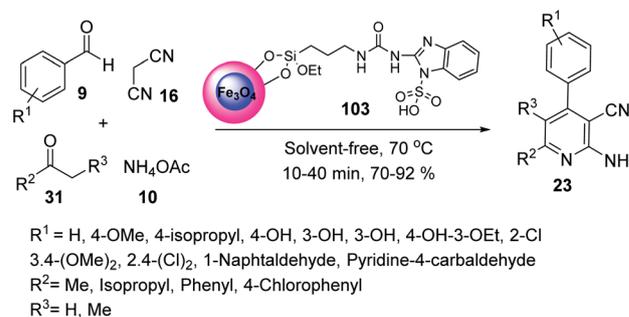
Torabi and *et al.* prepared Ligand **101** *via* the reaction of 1H-benzo[d]imidazol-2-amine **100** and compound **99** under solvent-free conditions. Fe_3O_4 was then functionalized with tetraethyl orthosilicate (TEOS) in toluene under reflux conditions to give $\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n$ **4**, which was reacted with ligand **101** to yield $\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n\text{-(CH}_2)_3\text{-urea-benzimidazole}$ **102**, followed by the reaction with chlorosulfuric acid in dichloromethane to obtain $\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n\text{-(CH}_2)_3\text{-urea-benzimidazole sulfonic acid}$ **103** (Scheme 36).⁶⁴

$\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n\text{-(CH}_2)_3\text{-urea-benzimidazole sulfonic acid}$ **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).⁶⁴

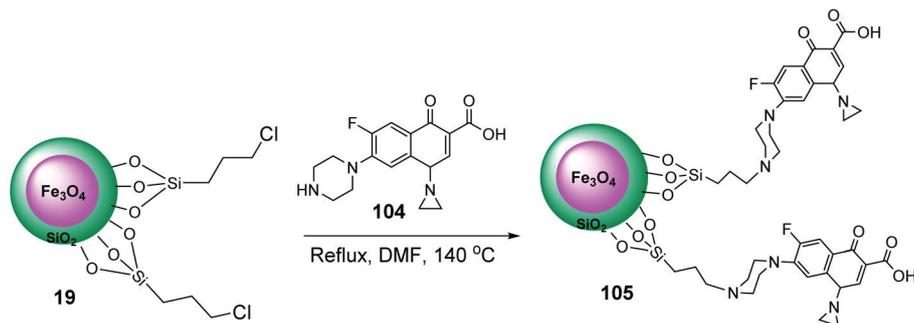
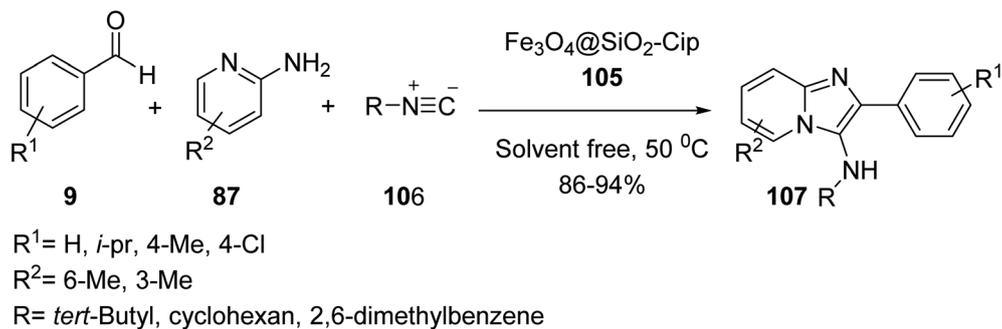
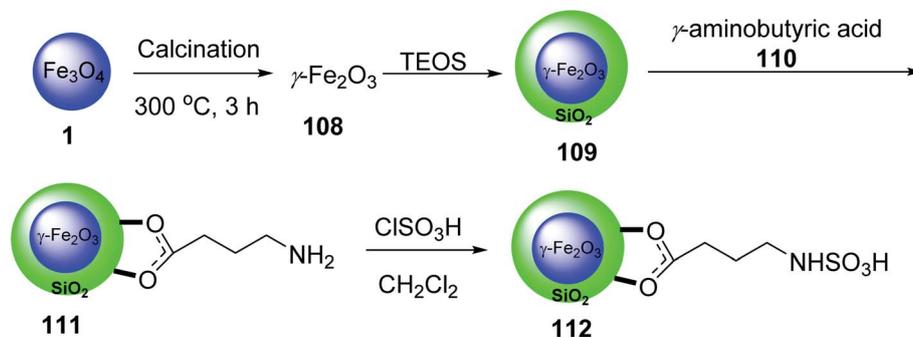
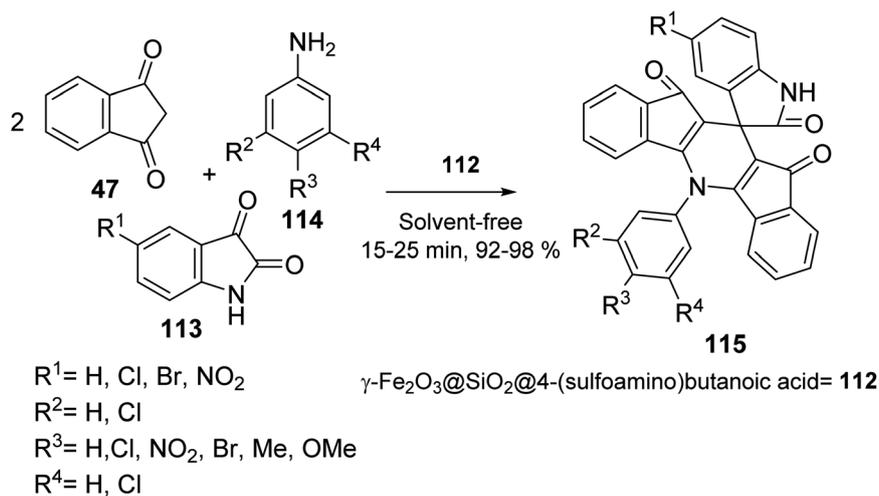
Initially, according to previous works,⁶⁵ $\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n\text{-Pr-Cl}$ **19** was prepared and dispersed in dry DMF, and then reacted with ciprofloxacin **104** to give $\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n\text{-Pr-ciprofloxacin}$ **105** (Scheme 38).⁶⁶

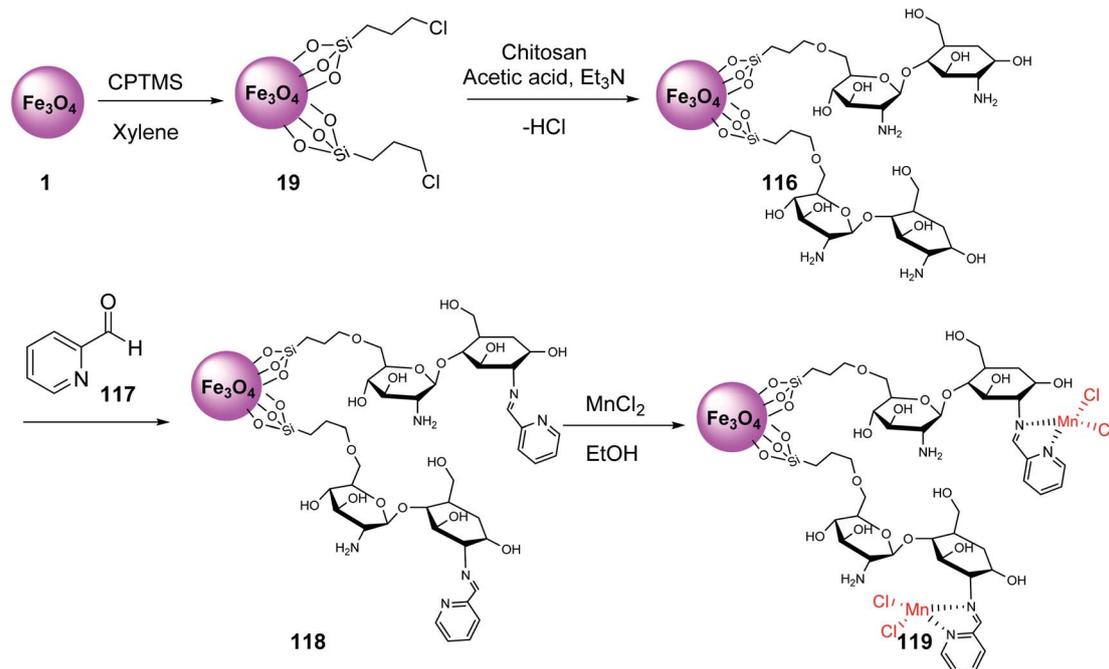
$\text{Fe}_3\text{O}_4@(\text{SiO}_2)_n\text{-Pr-Cip}$ **105** was then investigated in the synthesis of imidazo[1,2-*a*]pyridines **107** through the three-component reaction of various benzaldehyde **9**, 2-amino-pyridine **87**, and cyclohexyl isocyanide **106** (Scheme 39).⁶⁶



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



Scheme 38 Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Pr}$ -ciprofloxacin **105**.Scheme 39 Synthesis of the imidazo[1,2-a]pyridines **107**.Scheme 40 $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$ γ -aminobutyric acid- SO_3H **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 Fe_2O_3 nanoparticles **1** according to a previously reported method.⁶⁷ Calcination of Fe_2O_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 γ -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 $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$ γ -aminobutyric acid- SO_3H **112** (Scheme 40).⁶⁸

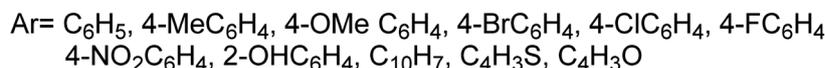
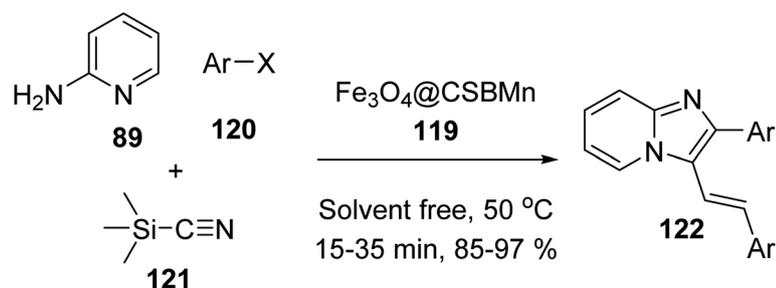
$\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$ @4-(sulfoamino)butanoic acid- SO_3H **112** was utilized in the synthesis of 5-(aryl)-5*H*-spiro[diindenol[1,2-*b*:2',1'-*e*]pyridine-11,30-indoline]-2',10,12-trione derivatives **115** through the pseudo four-component reaction of 1,3-indandione **47**, isatins **113** with various aromatic amines **114** (Scheme 41).⁶⁸

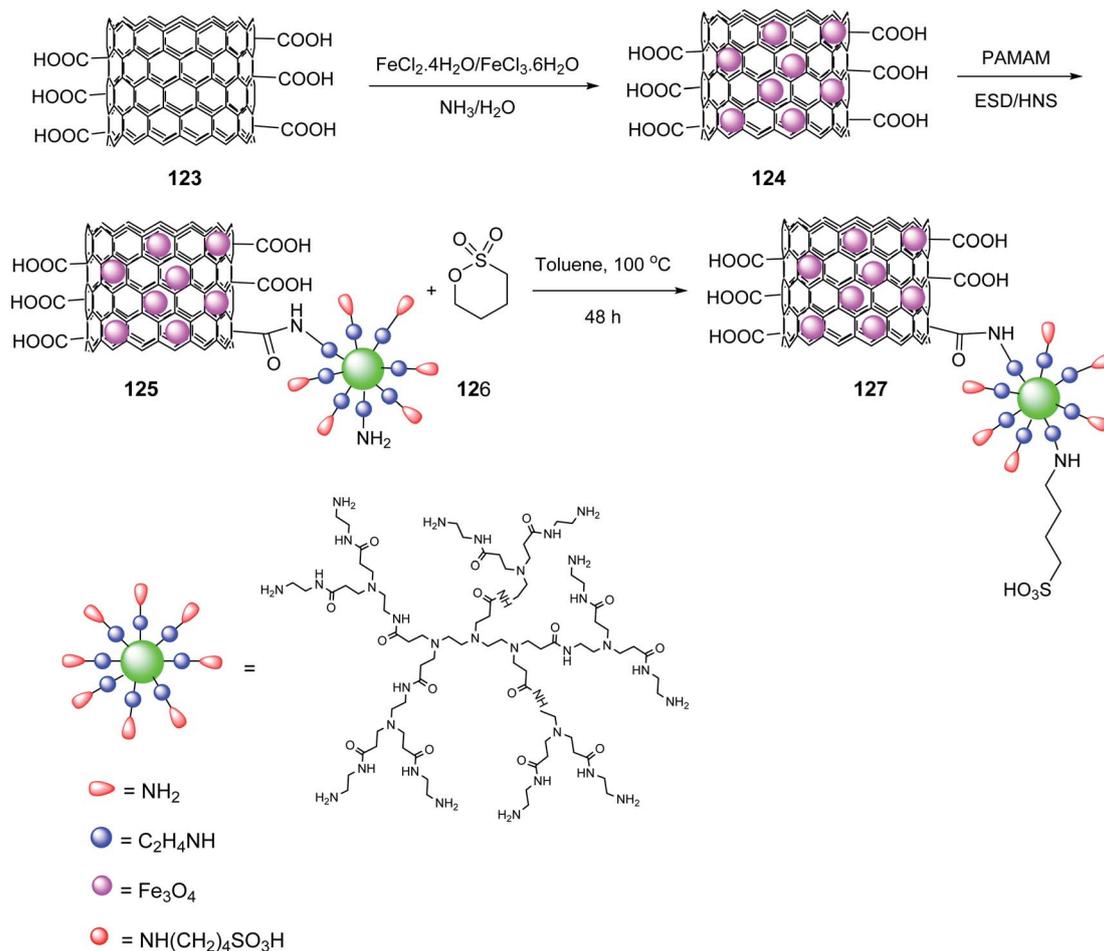
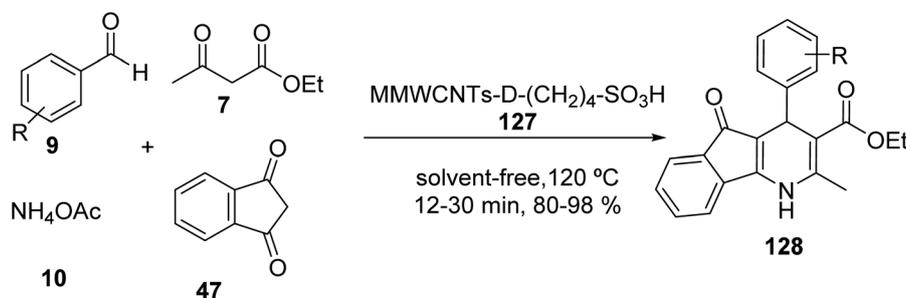
$\text{Fe}_3\text{O}_4\text{@Si-Pr-Cl}$ **19** was reacted with chitosan and acetic acid solutions to provide chitosan-coated MNPs **116**, which were

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).^{69,70}

$\text{Fe}_3\text{O}_4\text{@CSBMn}$ **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.⁷⁰

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-(CH₂)₄-SO₃H 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-NH₂ 125 followed by reaction with 1,4-butanediol 126 to yield MMWCNTs-D-(CH₂)₄-SO₃H 127 (Scheme 44).⁷²

MMWCNTs-D-(CH₂)₄-SO₃H 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).⁷²

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

We are grateful for the Research Council support of Alzahra University. R. Luque gratefully acknowledges MINECO for funding under project PID2019-109953GB-I00. This paper has been supported by RUDN University Strategic Academic Leadership Program (R. Luque).

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