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# Recent advances in the application of magnetic bio-polymers as catalysts in multicomponent reactions

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Magnetic nanoparticles have attracted significant attention due to their high surface area and superparamagnetic properties. Bio-polymers composed of polysaccharides including alginate, cellulose, glucose, dextrin, chitosan, and starch can be immobilized on magnetic nanoparticles. Bio-polymers can be obtained from natural sources, such as plants, tunicates, algae, and bacteria. Bio-polymers obtained from natural sources have attracted attention due to their various properties including efficient functional groups, non-toxicity, low cost, availability, and biocompatibility. According to the targets of "green chemistry", the application of bio-polymers is effective in reducing pollution. Furthermore, they are excellent agents for the functionalization of magnetic nanoparticles to yield nanomagnetic bio-polymers, which can be applied as recoverable and eco-friendly catalysts in multicomponent reactions.

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## 1. Introduction

Among the various magnetic nanoparticles, nano magnetic iron oxide ( $\text{Fe}_3\text{O}_4$ ) is very important because of its low cost, easy synthesis, and high magnetic ability. Recently, magnetic nanoparticles have been extensively applied in various fields including drug delivery, sensing, water treatment, removal of heavy metals, and catalysis. However, they are unstable in alkaline and acidic media due to the easy oxidation of their surface area.<sup>1–8</sup> These drawbacks can be alleviated *via* the modification of  $\text{Fe}_3\text{O}_4$  nanoparticles with materials such as silanes,<sup>9,10</sup> activated carbon,<sup>11</sup> and biocompatible polymers.<sup>12,13</sup> Another class of magnetic nanoparticles is ferrite magnetic nanomaterials and hexaferrite (M-type). Ferrite magnetic nanomaterials and hexaferrite have various applications including high chemical strength materials, home appliances, supercapacitors, loudspeakers, electromagnetic wave absorption, and permanent magnets.<sup>14–18</sup> Overall, due to the properties of ferrite magnetic nanomaterials and hexaferrite (M-type), they

can be used for the adsorption of various metals ions, cationic and anionic dyes from wastewater.<sup>19–23</sup>

The design and synthesis of biocompatible magnetic nanoparticles are important subjects in green chemistry.<sup>24</sup> Bio-polymers including alginate, cellulose, glucose, dextrin, chitosan, and starch are known as polysaccharides, which are present in the carbohydrates in plants, animals, microbes, and algae (Fig. 1).<sup>24</sup> These bio-polymers have different properties such as biodegradable nature, biocompatibility, non-toxicity, availability, low cost, and heat resistance.<sup>25</sup> They are excellent agents for the functionalization of magnetic nanoparticles to yield nanomagnetic bio-polymers, promoting their longevity, hardness, and strength. These composites have many applications such as drug delivery,<sup>26–28</sup> chemotherapy,<sup>29,30</sup> magnetic resonance imaging (MRI) agents,<sup>31,32</sup> solar cells,<sup>33</sup> chemical sensors,<sup>34,35</sup> catalysts,<sup>36</sup> water treatment,<sup>37,38</sup> and biomedical sensors.<sup>39</sup>

In comparison to conventional catalysts, heterogeneous magnetic bio-polymers have various advantages such as non-toxicity, easy separation, and eco-friendly nature. According to the functional groups on the magnetic nanoparticles, the catalysts can be grouped in various categories including, Lewis and Brønsted acids and bases.<sup>40,41</sup> In continuation of our research,<sup>42–44</sup> in this review, the importance of nanomagnetic bio-polymers is studied in multicomponent reactions. Multicomponent reactions (MCRs) are essential tools in medicinal and organic chemistry, which have various advantages including simplicity, easy workup, availability, and reduced generation of waste. Hence, the design and application of MCRs for the synthesis of organic compounds are highly important.<sup>45–50</sup>

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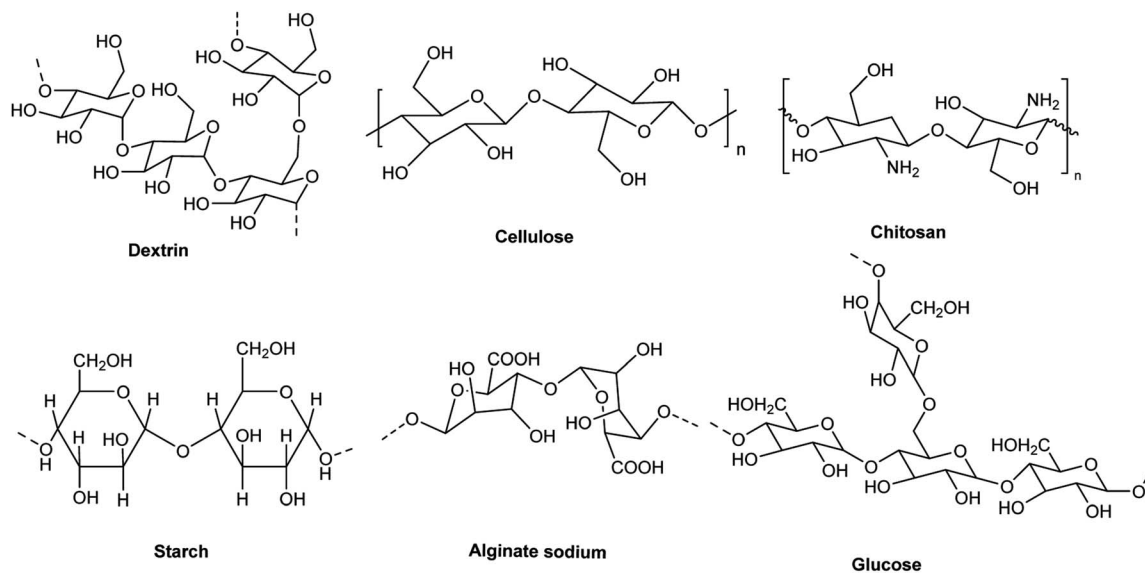


Fig. 1 Various bio-polymers.

## 2. Synthesis of various magnetic bio polymers

### 2.1. Magnetic bio-polymers based on cellulose

**2.1.1. Synthesis and application of  $\text{Fe}_3\text{O}_4$ /cellulose/Co-MOF nanocomposite.** Initially,  $\text{Fe}_3\text{O}_4$  nanoparticles **4** were modified with cellulose **5** using urea **6**/NaOH **7** to provide  $\text{Fe}_3\text{O}_4$ /cellulose **8**, which was reacted with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  **9**, terephthalic acid **10**, and imidazole (IM) **11** in DMF to form  $\text{Fe}_3\text{O}_4$ /cellulose/Co-MOF nanocomposite **12** (Scheme 1).<sup>51</sup>

$\text{Fe}_3\text{O}_4$ /cellulose/Co-MOF **12** has two sites including Lewis acidic sites ( $\text{Co}^{2+}$ ) and basic sites (IM), which were used in the Knoevenagel condensation reaction of aromatic aldehydes **13** with malononitrile **14** under solvent-free conditions (Scheme 2). This catalyst was reused five times without a decrease its catalytic activity.<sup>51</sup>

**2.1.2. Synthesis and application of  $\text{Fe}_3\text{O}_4$ @NCs/Sb(v).** Initially, raw cotton was converted to nano-cellulose (NCs) **5** in the presence of NaOH **7**, NaClO **16**, and  $\text{H}_2\text{SO}_4$  **17** at 80 °C. Then,  $\text{Fe}_3\text{O}_4$  was functionalized with nano-cellulose (NCs) **5**, providing  $\text{Fe}_3\text{O}_4$ @NCs **8**. In the next step,  $\text{SbCl}_5$  was mixed with the reaction mixture in chloroform to provide  $\text{Fe}_3\text{O}_4$ @NCs/Sb(v) **18** (Scheme 3).<sup>52</sup>

$\text{Fe}_3\text{O}_4$ @NCs/Sb(v) was used as a Lewis acid for the activation of carbonyl groups, which was investigated in the synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazoles **22** *via* the three-component reaction of aldehydes **19**, 2-aminobenzothiazole **20**, and ethyl-acetoacetate **21** under solvent-free conditions at 90 °C (Scheme 4). This catalyst was used five times without loss in its catalytic activity, which was compared with  $\text{Fe}_3\text{O}_4$  with 39% yield in 3 h.<sup>52</sup>

**2.1.3. Synthesis and application of  $\text{Fe}_3\text{O}_4$ @NFC@Co(II).**  $\text{Fe}_3\text{O}_4$  MNPs were synthesized *via* the reaction of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in the presence of  $\text{NH}_4\text{OH}$  solution at 80 °C under an  $\text{N}_2$  atmosphere. The  $\text{Fe}_3\text{O}_4$  nanoparticles were dispersed in  $\text{H}_2\text{O}$ , and then nanofiber cellulose (NFC) **24** was

added to the reaction mixture at room temperature to obtain  $\text{Fe}_3\text{O}_4$ @NFC **25** precipitate, which was reacted with an ethanolic solution of cobalt(II) acetate to form  $\text{Fe}_3\text{O}_4$ @NFC@Co(II) **26** (Scheme 5).<sup>53</sup>

Its catalytic activity was useful for the synthesis of 4*H*-pyrans *via* the multicomponent reaction of aldehydes, ethyl-acetoacetate, and malononitrile in  $\text{H}_2\text{O}$  (Scheme 6).<sup>53</sup>

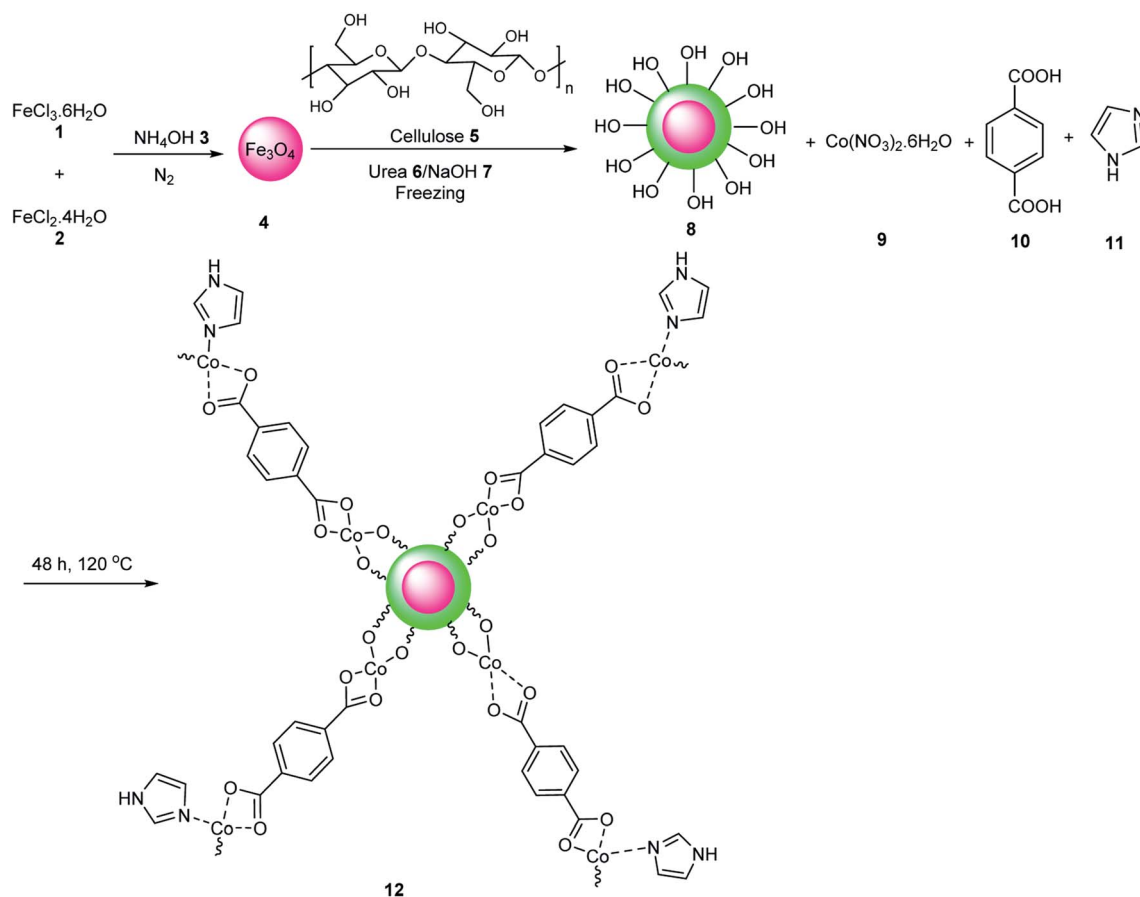
Also, the catalytic activity of **26** was tested for the synthesis of pyranopyrazole derivatives **29** *via* the four-component reaction of hydrazine hydrate **28**, ethyl acetoacetate **21**, benzaldehyde **19**, and malononitrile **14** in  $\text{H}_2\text{O}$  (Scheme 7). The metal ions on the catalyst surface act as Lewis acids, which were activated by the malononitrile and carbonyl groups. Also, the catalyst was used five times in the model reaction without a reduction in activity.<sup>53</sup>

**2.1.4. Synthesis and application of cellulose@pumice.** Initially, the microcrystalline cellulose was mixed with a solution of NaOH **7** and urea **6** in  $\text{H}_2\text{O}$ , and then was cooled in an ice bath at 8 °C to form a gel solution, which was mixed with pumice powder **32** and stirred for 24 h to obtain cellulose@pumice **33** (Scheme 8).<sup>54</sup>

Cellulose@pumice as an acidic catalyst activated carbonyl groups in the synthesis of 2,4,5-triarylimidazoles **36** through the reaction of benzaldehyde **19** and ammonium acetate **35** in EtOH under ultrasonic irradiation (Scheme 9). In the reusability test, this catalyst was used ten times without a reduction in activity.<sup>54</sup>

**2.1.5. The synthesis and application of ( $\text{Fe}_3\text{O}_4$ @NFC@NSalophCu)CO<sub>2</sub>H.** Nanofiber cellulose **37** was functionalized with  $\text{Fe}_3\text{O}_4$  *via* the sol-gel method to give  $\text{Fe}_3\text{O}_4$ @NFC nanoparticles **39**, which were functionalized with (3-aminopropyl)triethoxysilane (APTES) **40** to obtain  $\text{Fe}_3\text{O}_4$ @NFC@APTES **41**. The reaction of salicylaldehyde **42**, paraformaldehyde **43**, and HCl solution under reflux conditions provided 5-chloromethyl salicylaldehyde **44**, which was reacted with 3,5-diaminobenzoic acid **45** in  $\text{CH}_2\text{Cl}_2$  at room temperature to give the Schiff base 3,5-bis((*E*)-5-(chloromethyl)-2-





Scheme 1 Synthesis of  $\text{Fe}_3\text{O}_4$ /cellulose/Co-MOF nanocomposite 12.

hydroxybenzylidene)amino) benzoic acid ((5-Cl-Saloph) $\text{CO}_2\text{H}$ ) 46, followed by reaction with copper acetate in EtOH at room temperature to obtain complex [(5-Cl-Saloph) $\text{Cu(II)}$ ] $\text{CO}_2\text{H}$  47. Finally, the reaction of [(5-Cl-Saloph) $\text{Cu(II)}$ ] $\text{CO}_2\text{H}$  complex 47 and  $\text{Fe}_3\text{O}_4$ @NFC@APTES 41 at 70 °C for 24 h gave ( $\text{Fe}_3\text{O}_4$ @NFC@NSalophCu) $\text{CO}_2\text{H}$  48 (Scheme 10).<sup>55</sup>

( $\text{Fe}_3\text{O}_4$ @NFC@NSalophCu) $\text{CO}_2\text{H}$  48 was tested in the synthesis of 5-substituted-1H-tetrazole 51 *via* the multicomponent reaction of various aldehydes 19, hydroxylamine 49, and sodium azide 50 (Scheme 11), and also in the synthesis of 1-substituted-1H-tetrazoles 54 *via* the multicomponent reaction of aniline 52, triethyl orthoformate 53, and sodium azide 50 (Scheme 12). This catalyst was used in the click reaction four times without a decrease in its activity. In this catalyst, copper metal plays a vital role in the click reactions.<sup>55</sup>

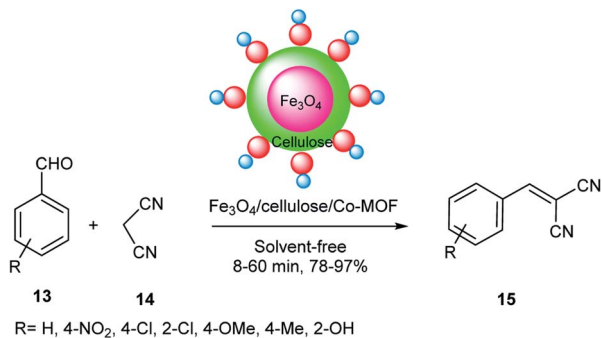
**2.1.6. Synthesis and application of  $\text{Fe}_3\text{O}_4$ @NFC@NNSM-Mn(III).**  $\text{Fe}_3\text{O}_4$  nanoparticles were functionalized with NFC nanospheres to prepare  $\text{Fe}_3\text{O}_4$ @NFC 39, which was dispersed in toluene, and then 3-chloropropyl-trimethoxy silane 55 was added to the reaction mixture under  $\text{N}_2$  gas and reflux conditions to obtain  $\text{Fe}_3\text{O}_4$ @NFC-Cl 56, followed by reaction with *o*-phenylenediamine 54 in  $\text{CH}_2\text{Cl}_2$  under reflux conditions to give  $\text{Fe}_3\text{O}_4$ @NFC@NN 57. Then, 5-(chloromethyl)-2-hydroxy benzaldehyde 58 was reacted with  $\text{Fe}_3\text{O}_4$ @NFC@NN 57 to form  $\text{Fe}_3\text{O}_4$ @NFC@NNS 59, which was complexed with

$\text{Mn(OAc)}_3 \cdot 2\text{H}_2\text{O}$  60 in EtOH to prepare  $\text{Fe}_3\text{O}_4$ @NFC@NNS-Mn 61, followed by reaction with melamine 62 in the presence of triethylamine in MeOH to generate  $\text{Fe}_3\text{O}_4$ @NFC@NNSM-Mn(III) 63 (Scheme 13).<sup>56</sup>

The activity of  $\text{Fe}_3\text{O}_4$ @NFC@NNSM-Mn(III) 63 was tested for the synthesis of xanthenes 65 *via* the pseudo-three-component reaction of aldehydes 19 and dimedone 64 in EtOH at 45 °C (Scheme 14). The manganese metal on the surface of  $\text{Fe}_3\text{O}_4$ @NFC@NNSM-Mn(III) acts as a Lewis acid to activate the carbonyl groups. This catalyst was used five times without a decrease in its activity.<sup>56</sup>

**2.1.7. Synthesis and application of  $\text{Fe}_3\text{O}_4$ @NFC@ONSM-Ni(II).** Initially,  $\text{Fe}_3\text{O}_4$ @NFC 39 was functionalized with 3-chloropropyl-trimethoxy silane 55 to obtain  $\text{Fe}_3\text{O}_4$ @NFC@CPTMS 56. Subsequently, 2-hydroxy 4-chloromethyl benzaldehyde 44 was prepared *via* the reaction of salicylaldehyde 42, paraformaldehyde 43, and HCl 37% in the presence of  $\text{H}_2\text{SO}_4$  as a catalyst at 70 °C for 20 h. In the next step, the Schiff base ligand was synthesized *via* the reaction of 2-aminophenol 66 and 5-chloromethylsalicylaldehyde 67 in dichloromethane at 40 °C for 3 h. Then,  $\text{Fe}_3\text{O}_4$ @NFC@ONS 68 was obtained through the reaction of 4-(chloromethyl)-2-(((2-hydroxyphenyl)imino)methyl) phenol 67 and  $\text{Fe}_3\text{O}_4$ @NFC@CPTMS 56 in the presence of triethylamine in acetonitrile under reflux conditions. In the next step,  $\text{Fe}_3\text{O}_4$ @NFC@ONS 68 was reacted with  $\text{Ni(OAc)}_2$





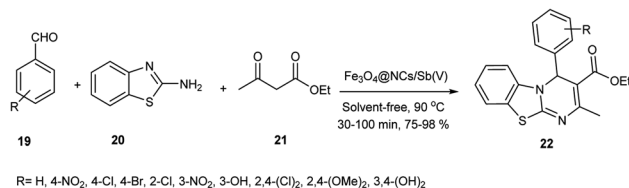
Scheme 2 Knoevenagel condensation in the presence of Fe<sub>3</sub>O<sub>4</sub>/cellulose/Co-MOF 12.

in EtOH at room temperature for 12 h to obtain Fe<sub>3</sub>O<sub>4</sub>@NFC@ONS-Ni(II) **69**. Finally, Fe<sub>3</sub>O<sub>4</sub>@NFC@ONSM-Ni(II) **70** was synthesized as a nanocatalyst *via* the reaction of Fe<sub>3</sub>O<sub>4</sub>@NFC@ONS-Ni(II) **69** and melamine **62** in the presence of triethylamine in the MeOH under reflux conditions and N<sub>2</sub> gas for 12 h (Scheme 15).<sup>57</sup>

This catalyst was used in the synthesis of polyhydroquinolines **72** through the Hantzsch reaction among benzaldehydes **19**, dimedone **64**, ethyl acetoacetate **21**, and ammonium acetate **71** (Scheme 16).<sup>57</sup>

Also, Bagherzade *et al.* applied this catalyst in the synthesis of 1,4-dihydropyridine **72** *via* the multicomponent reaction of aldehydes **19**, ethyl acetoacetate **21**, and ammonium acetate **71** (Scheme 17). The carbonyl groups in the multi-component reaction were activated in the presence of nickel metal on the surface of Fe<sub>3</sub>O<sub>4</sub>@NFC@ONSM-Ni(II) as a Lewis acid. Also, this catalyst was tested 6 times without loss in its activity.<sup>57</sup>

**2.1.8. Synthesis and application of cell-LA-TEA<sup>+</sup>/Fe<sub>3</sub>O<sub>4</sub>.** Initially, cellulose **5** was reacted with tosyl chloride **74** in the



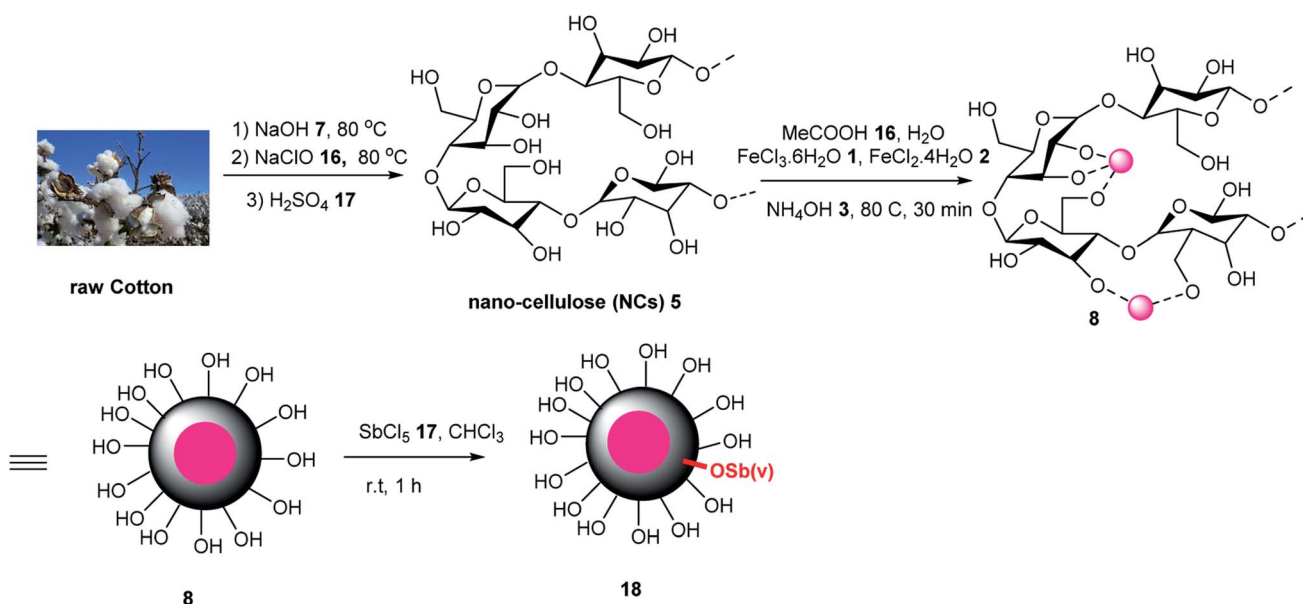
Scheme 4 Synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazole derivatives **22**.

presence of Et<sub>3</sub>N to form cell-tosyl **75**, which was reacted with lactic acid **76** to produce cell-LA **77**, followed by reaction with triethanolamine **78** to prepare cell-LA-TEA<sup>+</sup> **79**. Finally, cell-LA-TEA<sup>+</sup> **79** was magnetized *via* the reaction of FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, and ammonium solution in aqueous media to form cell-LA-TEA<sup>+</sup>/Fe<sub>3</sub>O<sub>4</sub> **80** (Scheme 18).<sup>58</sup>

Cell-LA-TEA<sup>+</sup>/Fe<sub>3</sub>O<sub>4</sub> was used as a catalyst for the regioselective synthesis of pyrazolo quinolones **82** *via* the three-component reaction of dimedone **64**, 5-amino pyrazolone **81**, and aromatic aldehydes **19** in EtOH/H<sub>2</sub>O under ultrasonic irradiation (Scheme 19). The catalyst was used with high stability in 7 cycles without loss in its activity.<sup>58</sup>

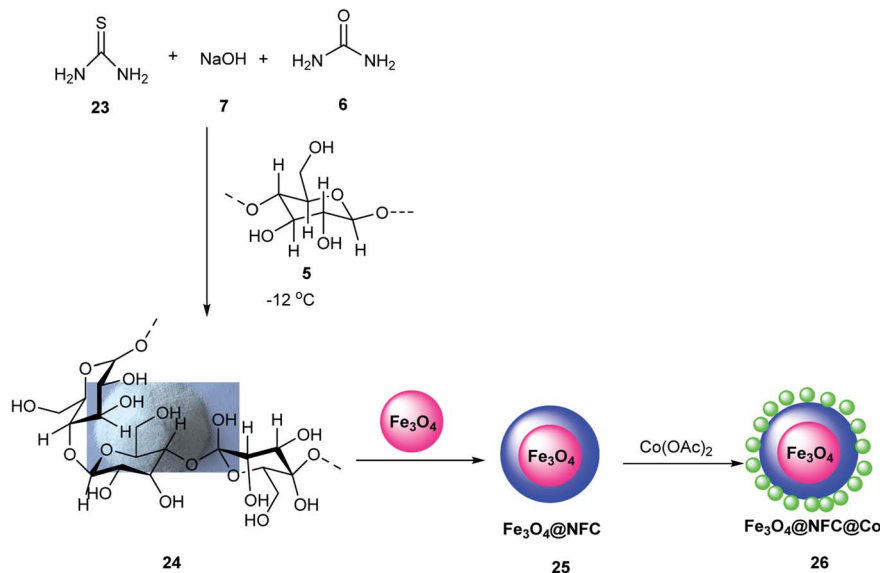
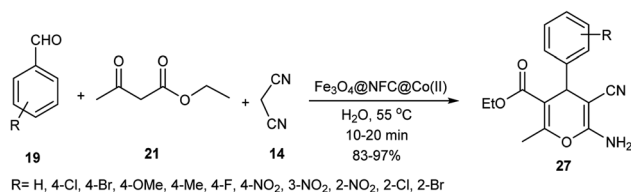
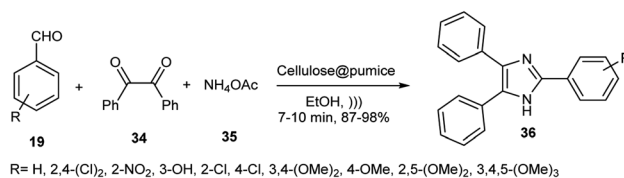
**2.1.9. Synthesis and application of Fe<sub>3</sub>O<sub>4</sub>@nano-cellulose-OPO<sub>3</sub>H.** Initially, nano-cellulose **5** was prepared from cotton. Then, Fe<sub>3</sub>O<sub>4</sub>@nano-cellulose (Fe<sub>3</sub>O<sub>4</sub>@NCS) **8** was obtained through the reaction of nano-cellulose solution in acetic acid with FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, and ammonium hydroxide at 80 °C. Finally, Fe<sub>3</sub>O<sub>4</sub>@NCS were immobilized with P<sub>4</sub>O<sub>10</sub> at room temperature under grinding conditions to produce Fe<sub>3</sub>O<sub>4</sub>@NCS-PA **83** (Scheme 20).<sup>59</sup>

2,3-Dihydroquinazolin-4(1*H*)-ones **85** were prepared *via* the condensation reaction of 2-aminobenzamide **84** and aldehydes **19** in the presence of Fe<sub>3</sub>O<sub>4</sub>@NCS-PA **83** as a Brønsted acid in H<sub>2</sub>O: EtOH under reflux conditions (Scheme 21). The main

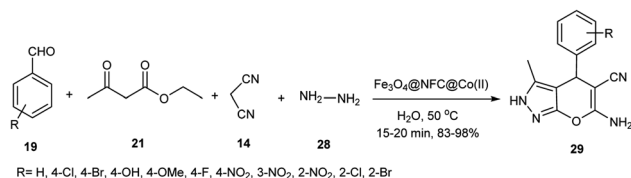


Scheme 3 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@NCS/Sb(v).



Scheme 5 Synthesis of  $\text{Fe}_3\text{O}_4@\text{NFC}@\text{Co(II)}$  26.Scheme 6 Synthesis of 4H-pyran 27 in the presence of  $\text{Fe}_3\text{O}_4@\text{NFC}@\text{Co(II)}$ .

Scheme 9 Synthesis of 2,4,5-triarylimidazole derivatives 36.

Scheme 7 Synthesis of pyranopyrazole derivatives 29 using  $\text{Fe}_3\text{O}_4@\text{NFC}@\text{Co(II)}$ .

advantages of this method are its excellent yields, simple workup, and eco-friendly catalyst. This reaction was accomplished in  $\text{H}_2\text{O}:\text{EtOH}$  under reflux conditions in the presence of  $\text{Fe}_3\text{O}_4$  with 60% yield; however,  $\text{Fe}_3\text{O}_4@\text{NCS-PA}$  performed better than  $\text{Fe}_3\text{O}_4$  in this reaction.<sup>59</sup>

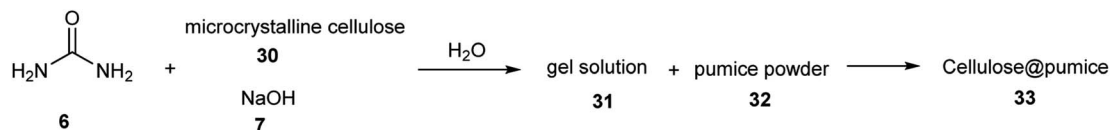
**2.1.10. Synthesis and application of  $\text{Fe}_3\text{O}_4@\text{NCS}/\text{Cu(II)}$ .**  $\text{Fe}_3\text{O}_4$  was functionalized with nano-cellulose 5 to obtain

$\text{Fe}_3\text{O}_4@\text{NCS}$  8, which was added to NaOH solution to give  $\text{Fe}_3\text{O}_4@\text{NCS}$  8, followed by reaction with  $\text{CuCl}_2$  to provide  $\text{Fe}_3\text{O}_4@\text{NCS}/\text{Cu(II)}$  86 (Scheme 22).<sup>60</sup>

$\text{Fe}_3\text{O}_4@\text{NCS}/\text{Cu(II)}$  as a Lewis acid activated the carbonyl groups of the starting materials by copper metal in the synthesis of indenopyrido[2,3-*d*]pyrimidines 89 through the three-component reaction of 6-amino-2-(methylthio)pyrimidin-4(3*H*)-one 88, 1,3-indanedione 87 and aldehydes 19 in EtOH (Scheme 23). The activity of the catalyst was preserved after four runs.<sup>60</sup>

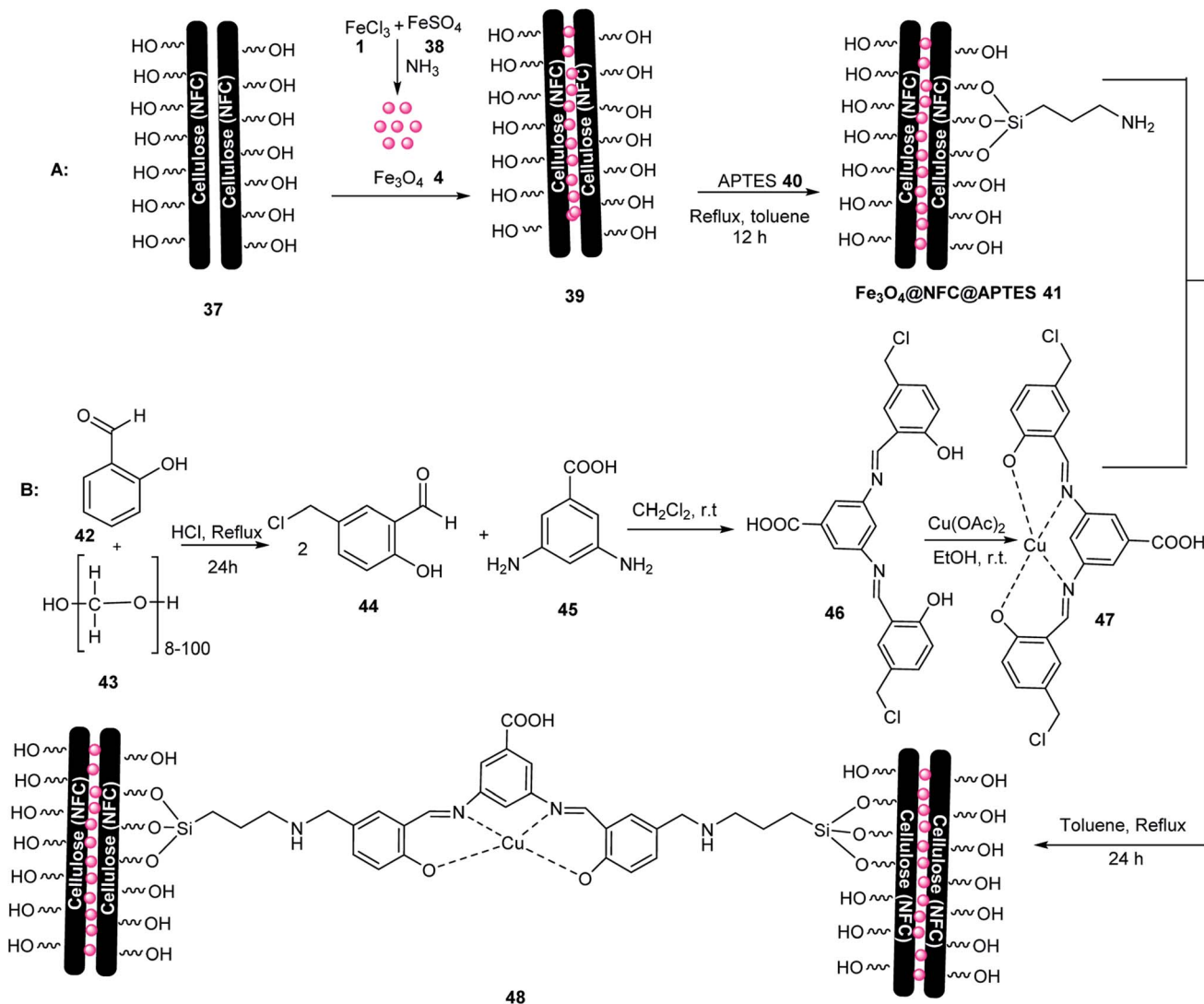
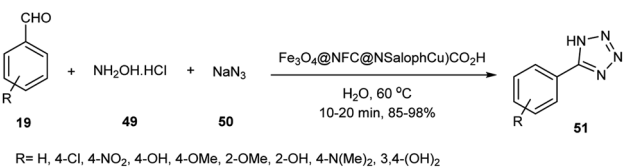
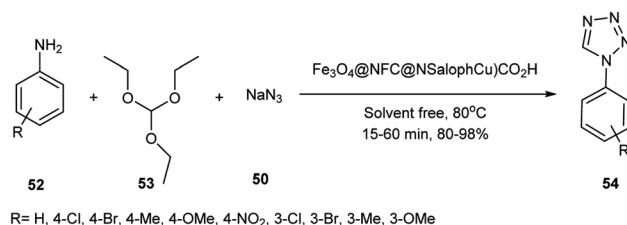
**2.1.11. Synthesis and application of  $\text{Fe}_3\text{O}_4@\text{nano-cellulose}/\text{Cu(II)}$ .** The reaction of nano-cellulose 5,  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ , and  $\text{NH}_4\text{OH}$  at 80 °C gave  $\text{Fe}_3\text{O}_4@\text{nano-cellulose}$  8, which was reacted with  $\text{CuCl}_2$  using sodium hydroxide at room temperature to obtain  $\text{Fe}_3\text{O}_4@\text{nano-cellulose}/\text{Cu(II)}$  90 (Scheme 24).<sup>61</sup>

$\text{Cu(II)}$  in  $\text{Fe}_3\text{O}_4@\text{nanocellulose}/\text{Cu(II)}$ , as a Lewis acid, activated the carbonyl groups in the three-component reaction of



Scheme 8 Synthesis of cellulose@pumice 33.



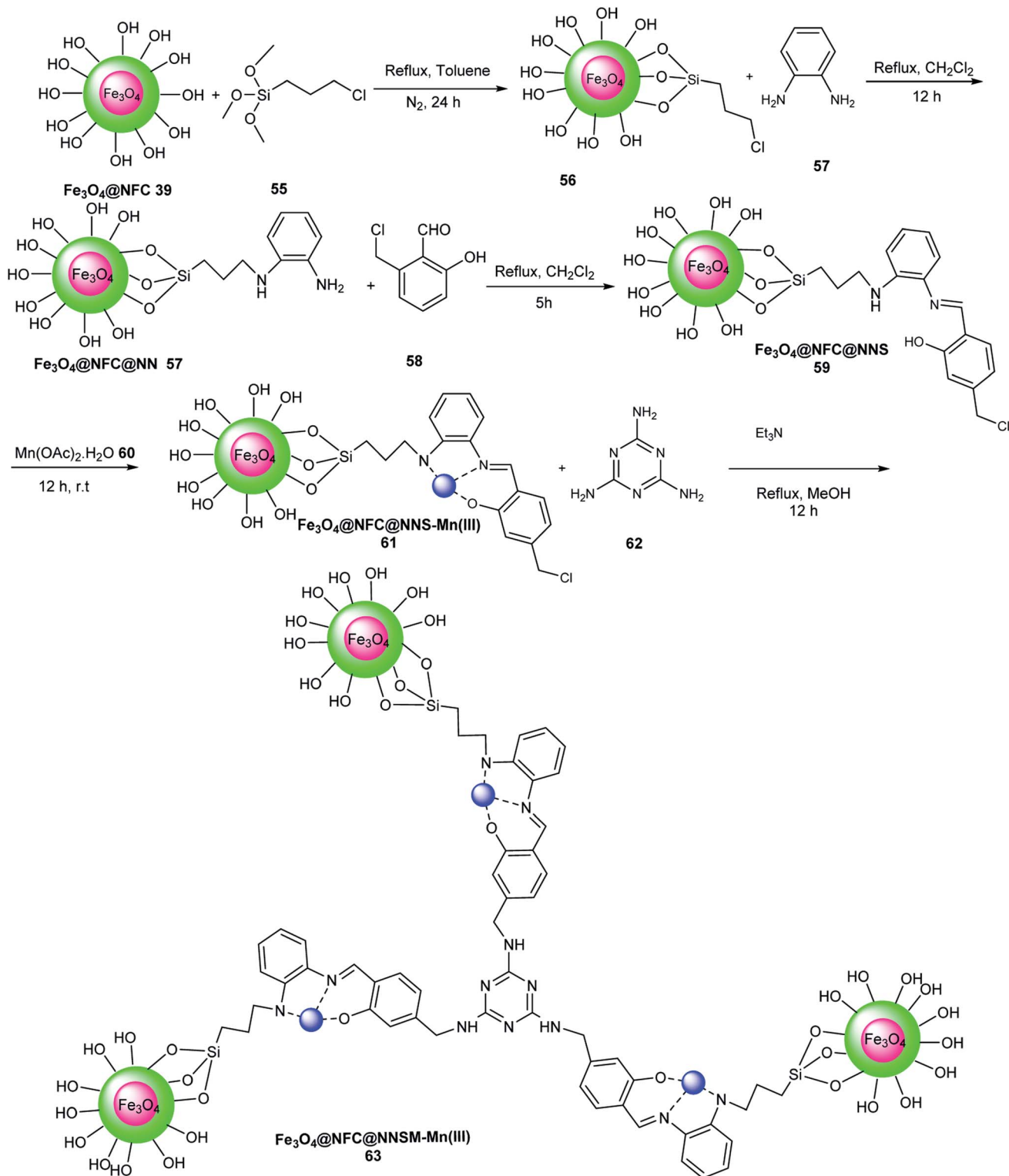
Scheme 10 Synthesis of  $(\text{Fe}_3\text{O}_4@\text{NFC}@\text{NSalophCu})\text{CO}_2\text{H}$ .Scheme 11 Synthesis of 5-substituted-1*H*-tetrazole **47** using  $(\text{Fe}_3\text{O}_4@\text{NFC}@\text{NSalophCu})\text{CO}_2\text{H}$ .Scheme 12 Synthesis of 1-substituted-1*H*-tetrazoles using  $(\text{Fe}_3\text{O}_4@\text{NFC}@\text{NSalophCu})\text{CO}_2\text{H}$ .

aromatic aldehydes **19**, 2-aminobenzothiazole **20**, and ethyl acetoacetate **21** for the synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazoles **22** (Scheme 25). The catalytic activity of  $\text{Fe}_3\text{O}_4@\text{nano-cellulose}/\text{Cu}(\text{II})$  was preserved after four runs. The yield of this reaction in the presence of  $\text{Fe}_3\text{O}_4$  as a catalyst after 3 h was reported to be about 37%. Therefore,  $\text{Fe}_3\text{O}_4@\text{nano-cellulose}/\text{Cu}(\text{II})$  is more active than  $\text{Fe}_3\text{O}_4$ .<sup>61</sup>

**2.1.12. Synthesis and application of  $\text{Fe}_3\text{O}_4@\text{NFC-ImSalophCu}(\text{II})$ .** Initially, imidazole **11** was treated with 3-

chloropropyl-trimethoxy silane **55** in toluene to produce imidazole-propyl-trimethoxy silane **91**, which was immobilized on  $\text{Fe}_3\text{O}_4@\text{NFC}$  **39** using  $\text{Et}_3\text{N}$  as a catalyst in dry toluene to give  $\text{Fe}_3\text{O}_4@\text{NFC-Im}$  **92**. The reaction of salicylaldehyde **42** and paraformaldehyde **43** in the presence of  $\text{HCl}/\text{H}_2\text{SO}_4$  gave 5-(chloromethyl)-2-hydroxybenzaldehyde **44**, which was reacted with 1,2-phenylenediamine **93** in dichloromethane under reflux



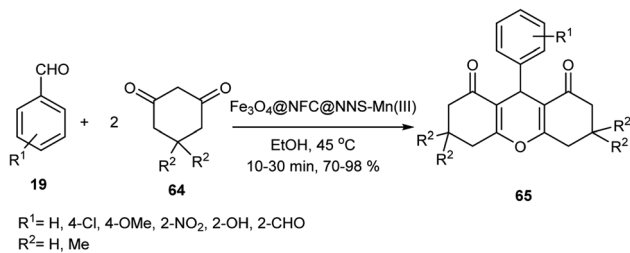
Scheme 13 Synthesis of  $\text{Fe}_3\text{O}_4@NFC@NNSM-\text{Mn(III)}$ .

conditions to produce *N,N*-bis(5-chloromethylsalicylidene)-1,2-phenylenediamine **94**, followed by reaction with  $\text{Cu}(\text{OAc})_2$  in EtOH at room temperature to prepare 5-Cl-Salophen-Cu(II) **95**. Finally,  $\text{Fe}_3\text{O}_4@NFC-\text{ImSalophCu(II)}$  **96** was synthesized *via* the

reaction of  $\text{Fe}_3\text{O}_4@NFC-\text{Im}$  **92** and 5-Cl-Salophen-Cu(II) **95** in toluene under reflux conditions (Scheme 26).<sup>62</sup>

The copper of  $\text{Fe}_3\text{O}_4@NFC-\text{ImSalophCu}$  **96** was applied in the click reaction of phenacyl bromides **97**, sodium azide **90**,





Scheme 14 Synthesis of xanthenes derivatives **65** in the presence of  $\text{Fe}_3\text{O}_4@\text{NFC}@\text{NNSM}-\text{Mn}(\text{III})$ .

and alkynes **98** in  $\text{H}_2\text{O}$  to synthesize 1,2,3-triazoles **99** (Scheme 27). The reusability of this catalyst was tested in the click reaction four times without loss in its activity.<sup>62</sup>

**2.1.13. Synthesis and application of  $\text{Fe}_3\text{O}_4@\text{walnut shell}/\text{Cu}(\text{II})$ .** Nanomagnetic  $\text{Fe}_3\text{O}_4@\text{walnut shell}/\text{Cu}(\text{II})$  was prepared by Mirjalili's research group. Nanomagnetic  $\text{Fe}_3\text{O}_4@\text{walnut shell}/\text{Cu}(\text{II})$  **100** was prepared *via* the reaction of dried powdered walnut shell with NaOH, hypochlorite solution, and sulfuric acid aqueous to afford a nano walnut shell, followed by reaction with  $\text{CH}_3\text{COOH}$ ,  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  **1**,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}_2$ , and  $\text{NH}_4\text{OH}$  to generate nanomagnetic  $\text{Fe}_3\text{O}_4@\text{walnut shell}$  **8**, which was modified by  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{NaOH}$  to produce nanomagnetic  $\text{Fe}_3\text{O}_4@\text{walnut shell}/\text{Cu}(\text{II})$  **100** (Scheme 28).<sup>63</sup>

Its catalytic activity was explored using 2-aryl/alkyl-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazines **102** or **104** or **106** *via* the *pseudo*-three-component reaction of  $\beta$ -naphthol **101** or  $\alpha$ -naphthol **103** or phenol derivatives **105**, formaldehyde **52**, and various amines **43** (Scheme 29). The catalytic activity of nano- $\text{Fe}_3\text{O}_4@\text{walnut shell}/\text{Cu}$  did not decrease after five-times use. The copper metal on the nano- $\text{Fe}_3\text{O}_4@\text{walnut shell}/\text{Cu}(\text{II})$  increased the reaction rate *via* interaction with the carbonyl group of the starting materials.<sup>63</sup>

## 2.2. Magnetic bio-polymers based on dextrin

**2.2.1. Synthesis and application of magnetic dextrin nanocomposite.** Dextrin **107** is a water-soluble polysaccharide obtained *via* the hydrolysis of starch and glycogen. Magnetic dextrin nanocomposite **108** was prepared *via* the addition of dextrin **107** to a solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and ammonium hydroxide at  $90^\circ\text{C}$  under an  $\text{N}_2$  atmosphere *via* the co-precipitation method (Scheme 30).<sup>64</sup>

The magnetic dextrin was tested as a catalyst in the synthesis of polyhydroquinolines *via* four-component reactions of aromatic aldehydes **19**, ethyl acetoacetate **21**, dimedone **61**, ammonium acetate **71** in EtOH under reflux conditions (Scheme 31). The yield of the products did not decrease after five runs. This reaction was performed in the presence of dextrin in ethanol in 28% yield, and thus magnetic dextrin is better than dextrin to catalyze this reaction.<sup>64</sup>

**2.2.2. Synthesis and application of magnetized dextrin.** Magnetized dextrin **72** was obtained *via* the reaction of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , dextrin **71**, and  $\text{NH}_4\text{OH}$  in  $\text{H}_2\text{O}$  at  $90^\circ\text{C}$  under a nitrogen atmosphere (Scheme 32).<sup>65</sup>

Maleki *et al.* studied the catalytic activity of magnetized dextrin **29** for the synthesis of dihydropyrano[2,3-*c*]pyrazoles **29** through the reaction of hydrazine hydrate **28**, ethyl acetoacetate **21**, aromatic aldehydes **19**, and malononitrile **14** under reflux conditions in EtOH (Scheme 33). This catalyst was used for five runs without a decrease in its catalytic activity.<sup>65</sup>

**2.2.3. Synthesis and application of FND-Ti(IV).**  $\text{Fe}_3\text{O}_4@\text{nano-dextrin}$  **108** was prepared through the reaction of nano-dextrin **107**,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and ammonia solution in  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$ .  $\text{Fe}_3\text{O}_4@\text{nano-dextrin}$  **108** was coated with  $\text{TiCl}_4$  in  $\text{CH}_2\text{Cl}_2$  to prepare FND-Ti(IV) **109** (Scheme 34).<sup>66</sup>

Its catalytic activity as a Lewis acid was investigated in the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones **85** *via* the condensation reaction of 2-aminobenzamide **84** and aldehydes **19** under mild conditions (Scheme 35). This catalyst was used five times without loss in its catalytic activity.<sup>66</sup>

## 2.3. Magnetic bio-polymers based on starch

**2.3.1. Synthesis and application of magnetic  $\text{Ag}/\text{Fe}_3\text{O}_4@\text{starch}$  nanocatalyst.** To aqueous starch solution **110**, citric acid **111** and sodium hypophosphite **112** were added and refluxed to give the precipitate crude product, which was crushed and dried to give cross-linked starch **113**, followed by dissolving in  $\text{H}_2\text{O}$  to produce gelatinized starch **114**. The obtained gelatinized starch was reacted with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  at room temperature, and then mixed with  $\text{NH}_3$  dropwise to give the  $\text{Fe}_3\text{O}_4@\text{starch}$  nanocatalyst, which was treated with  $\text{AgNO}_3$  (aq) to generate the magnetic  $\text{Ag}/\text{Fe}_3\text{O}_4@\text{starch}$  **115** nanocatalyst (Scheme 36).<sup>67</sup>

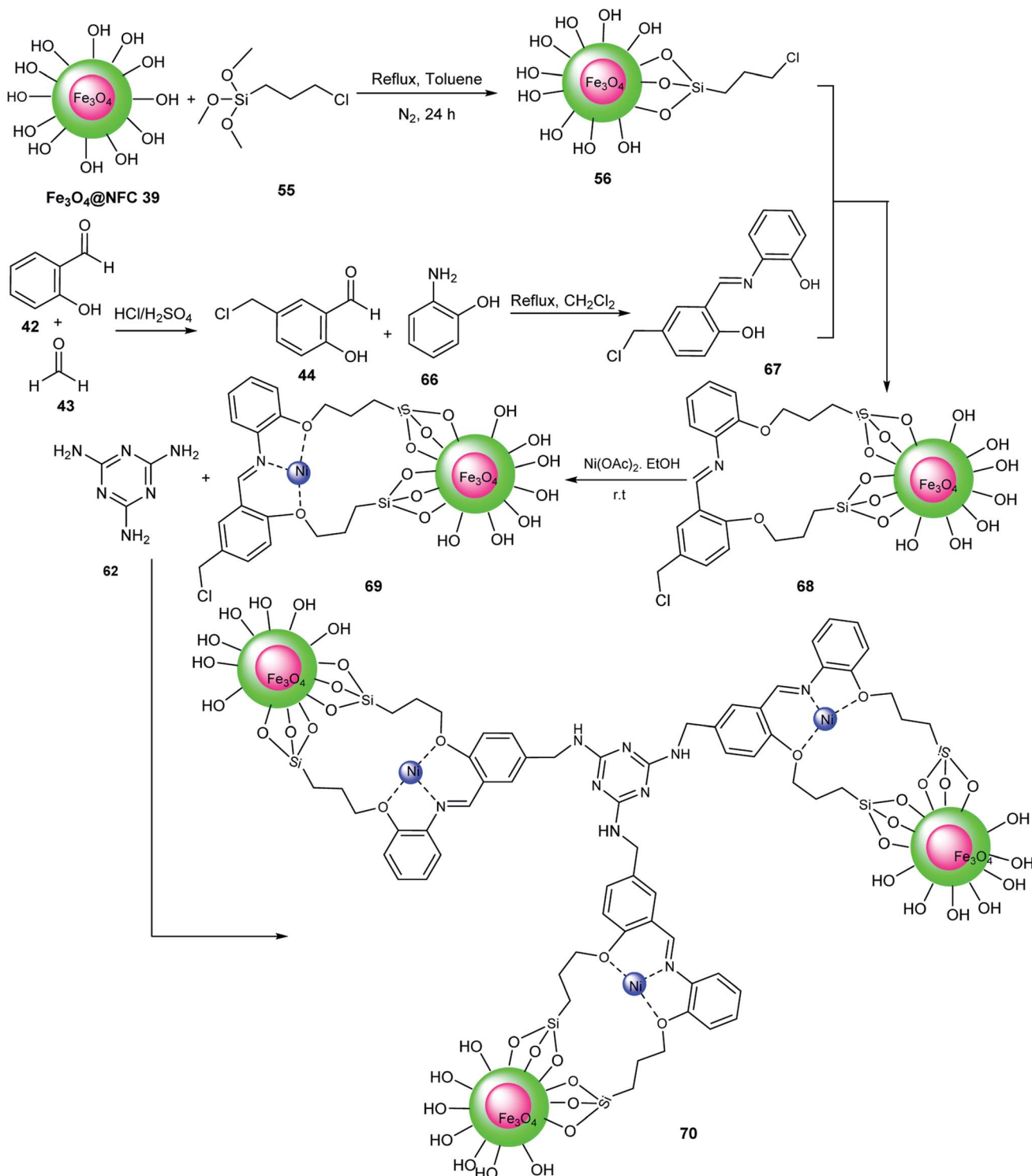
The catalytic activity of  $\text{Ag}/\text{Fe}_3\text{O}_4@\text{starch}$  as Lewis acid **115** was evaluated in the one-pot reaction of benzaldehydes **19**, malononitrile **14**, and dimedone **64** in EtOH for the synthesis of 4*H*-pyran **116** (Scheme 37). Also, the magnetic nanocatalyst was reused five times with no loss in its activities.<sup>67</sup>

**2.3.2. Synthesis and application of magnetic  $\text{CuFe}_2\text{O}_4@\text{starch}$ .** To obtain  $\text{CuFe}_2\text{O}_4@\text{starch}$  **122**,  $\text{Cu}(\text{NO}_3)_2$  **117** was reacted with  $\text{Fe}(\text{NO}_3)_3$  **118** using sodium hydroxide in  $\text{H}_2\text{O}$  to give  $\text{CuFe}_2\text{O}_4$  nanoparticles **121**, followed by reaction with starch to obtain  $\text{CuFe}_2\text{O}_4@\text{starch}$  **122**. Its catalytic activity was tested in the synthesis of 4*H*-chromene **125** or **126** *via* the three-component reaction of various aldehydes **19**, malononitrile **14**, 2-hydroxy-1,4-naphthoquinone **123**, or 4-hydroxycoumarin **124** (Scheme 38).<sup>68</sup>

In another attempt, 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyrans **27** or **116** were synthesized *via* the reaction of aldehydes **19**, malononitrile **14**, and enolizable C-H-activated acidic compounds, including dimedone **64** and ethyl acetoacetate **21**, in the presence of  $\text{CuFe}_2\text{O}_4@\text{starch}$  **122** as a Lewis acid in EtOH. The reaction rate for aldehydes with electron-withdrawing groups was faster than that with electron-donating groups (Scheme 39 and 40), respectively. This catalyst was used in six runs without a decrease in its activity.<sup>68</sup>

**2.3.3. Synthesis and application of magnetic starch/SPION@ $\text{SO}_3\text{H}$ .** Superparamagnetic iron oxide nanoparticles (SPION) **127** were synthesized *via* the reaction of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and ammonia in aqueous media. Then, SPION **127** was coated with



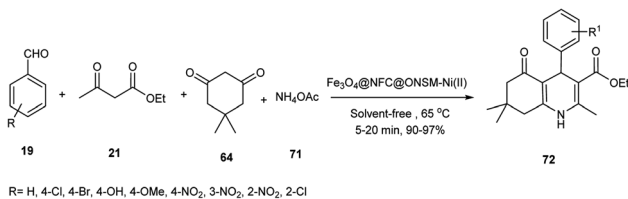
Scheme 15 Synthesis of  $\text{Fe}_3\text{O}_4@NFC@ONSM-Ni(II)$ .

tetraethyl orthosilicate (TEOS) to give  $\text{SPION}@SiO_2$  128, which was reacted with starch 110 to give magnetic starch, followed by reaction with allyltrimethoxysilane 130 to prepare allyl-functionalized magnetic starch 131. Finally, starch/ $\text{SPION}@SO_3H$  133 was synthesized *via* the polymerization of

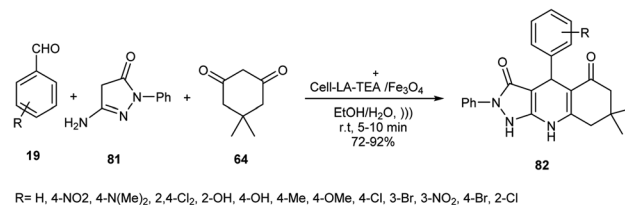
allyl-functionalized magnetic starch 131 and 4-styrenesulfonic acid 132 (Scheme 41).<sup>69</sup>

Starch/ $\text{SPION}@SO_3H$  133 as a Brønsted acid ( $\text{SO}_3\text{H}$ ) activated the carbonyl groups in the multicomponent reaction of 4-hydroxycoumarin 124, benzaldehydes 19, dimedone 64, and

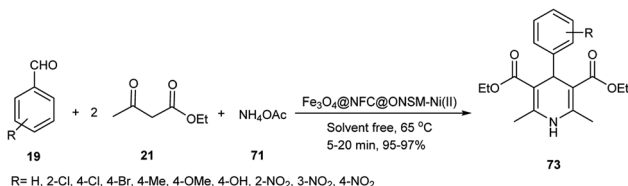




**Scheme 16** Synthesis of polyhydroquinolines **72** in the presence of  $\text{Fe}_3\text{O}_4\text{@NFC@ONSM-Ni(II)}$ .



**Scheme 19** Synthesis of pyrazolo quinolones **82** in the presence of  $\text{Cell-LA-TEA}^+/\text{Fe}_3\text{O}_4$ .



**Scheme 17** Synthesis of 1,4-dihydropyridine **73** in the presence of  $\text{Fe}_3\text{O}_4\text{@NFC@ONSM-Ni(II)}$ .

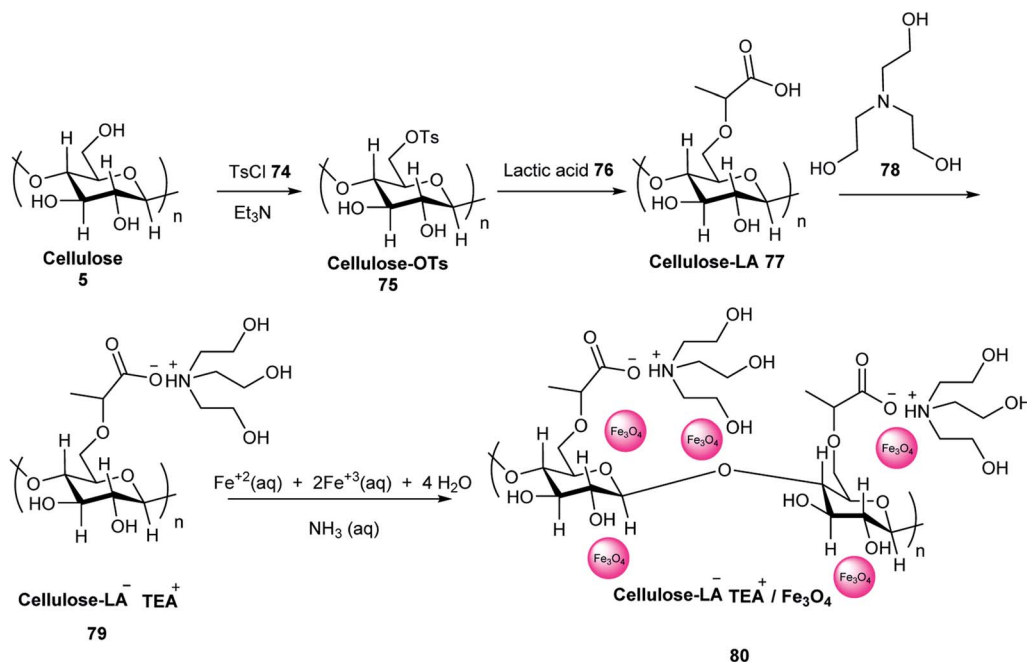
ammonium acetate **71** in the synthesis of chromeno[4,3-*b*]quinoline-6,8(9*H*)-dione derivatives **134** (Scheme 42). This catalyst was applied ten times without any loss in its activity.<sup>69</sup>

**2.3.4. Synthesis and application of magnetic  $\text{Fe}_3\text{O}_4\text{@GOTfOH/Ag/St-PEG-AcA}$ .** Initially, through the Hummers' method, graphite **135** was treated with  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$ , and  $\text{H}_2\text{O}$  to give GO **136**, which was treated with  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ , and ammonium solution at 80 °C to achieve  $\text{Fe}_3\text{O}_4\text{@GO}$  **137**, followed by reaction with trifluoro methanesulfonic acid in  $\text{CH}_2\text{CH}_2$  to give  $\text{Fe}_3\text{O}_4\text{@GOTfOH}$  **138**. In the next step, starch **139** was dissolved in water at 80 °C. Subsequently, *N,N*-

methylene acrylene acrylamide (MBA) **140** was dissolved in water. Then, the above-mentioned two mixtures were mixed to obtain a homogeneous viscous mixture. Then, a certain amount of acrylic acid **141** and PEG-poly **142** was added to the reaction mixture. Then, ammonium persulfate (APS) **143** solution was added to the reaction mixture until a hydrogel was obtained. The above-mentioned homogeneous solution, AgNP **144** colloidal solution and  $\text{Fe}_3\text{O}_4\text{@GOTfOH}$  **138** were mixed to obtain  $\text{Fe}_3\text{O}_4\text{@GOTfOH/Ag/St-PEG-AcA}$  **146** (Scheme 43).<sup>70</sup>

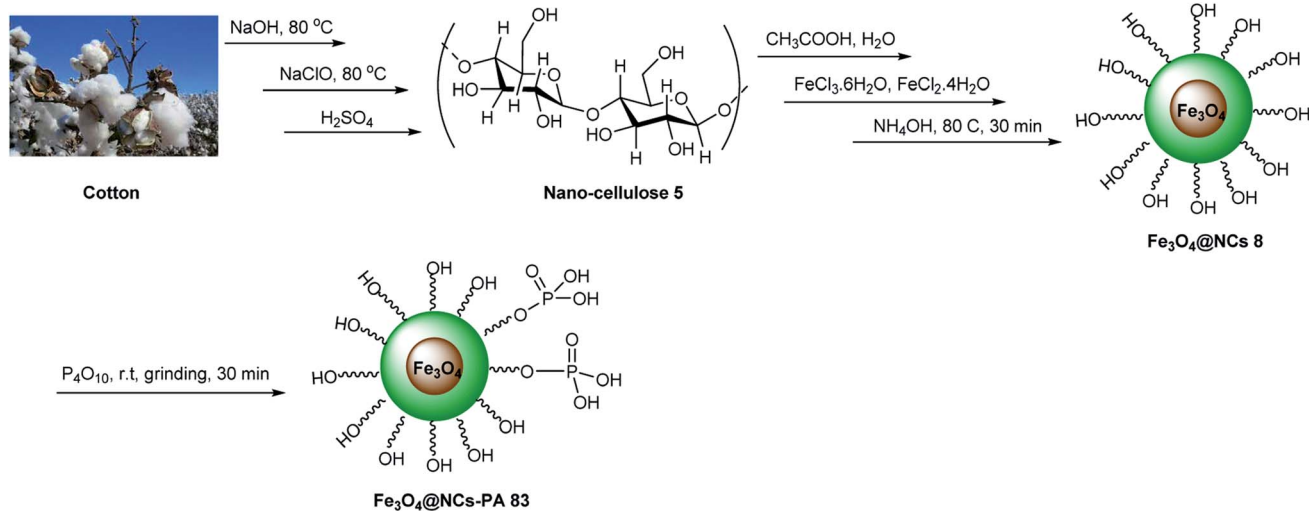
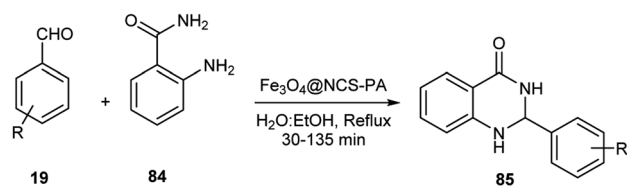
The catalytic activity of  $\text{Fe}_3\text{O}_4\text{@GOTfOH/Ag/St-PEG-AcA}$  **146** was examined in the synthesis of 2,4,6-triarylpyridines **137** through the pseudo-three-component reaction of aryl aldehydes **19**, acetophenone **147** and ammonium acetate **71** (Scheme 44). According to the catalyst structure, the carbonyl groups were activated *via* interaction with the Brønsted acid site and Lewis acid of  $\text{Fe}^{3+}$ . Also, the catalytic activity of **146** did not decrease after 10 runs.<sup>70</sup>

**2.3.5. Synthesis and application of magnetic  $\gamma\text{-Fe}_2\text{O}_3\text{@starch-}n\text{-butyl SO}_3\text{H}$ .**  $\text{Fe}_3\text{O}_4$  nanoparticles **4** were synthesized *via* the reaction of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  **2** and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  **1** and  $\text{NH}_4\text{OH}$  solution in  $\text{H}_2\text{O}$  an under argon atmosphere at room

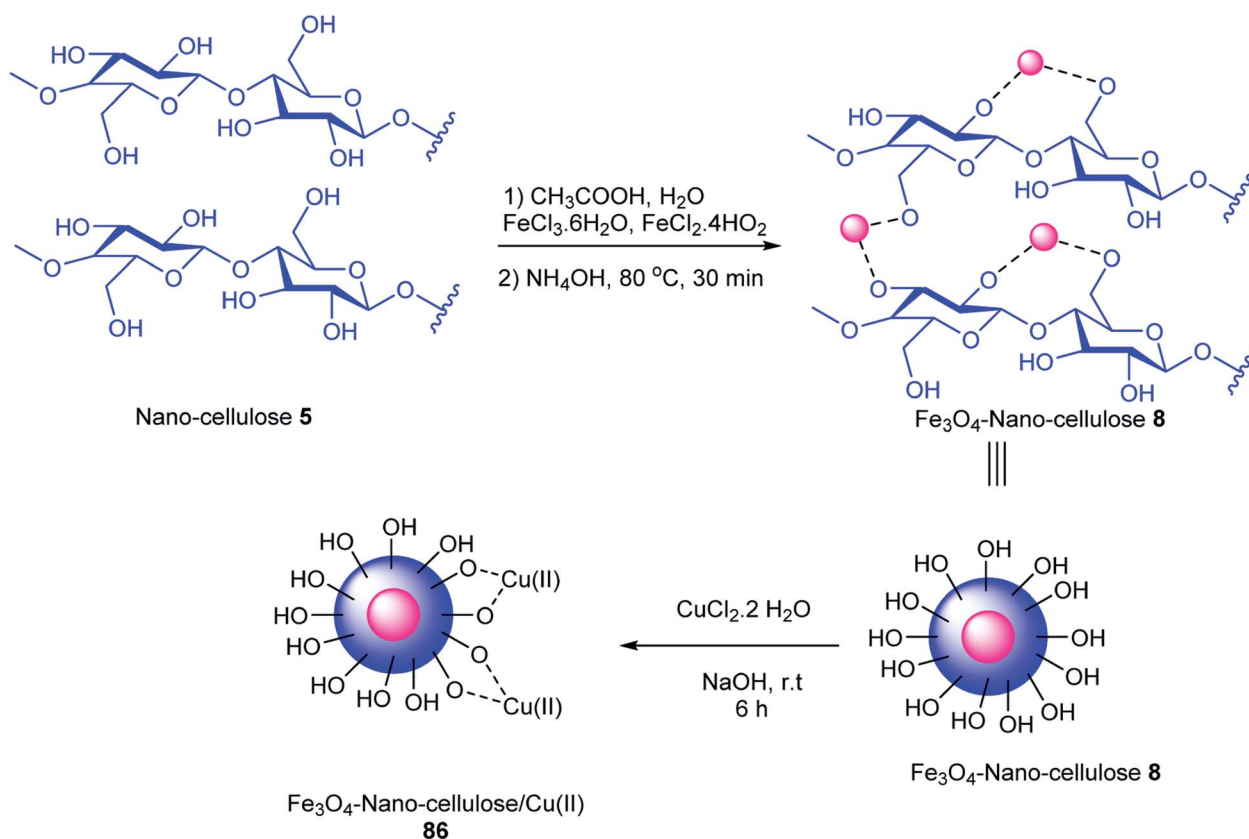


**Scheme 18** Synthesis of  $\text{Cell-LA-TEA}^+/\text{Fe}_3\text{O}_4$ .



Scheme 20 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@NCS-PA.R = H, 4-NO<sub>2</sub>, 3-NO<sub>2</sub>, 2-NO<sub>2</sub>, 4-OH, 2-Cl, 4-Cl, 2,4-(Cl)<sub>2</sub>, 2,4-(OMe)<sub>2</sub>, 4-N(Me)<sub>2</sub>

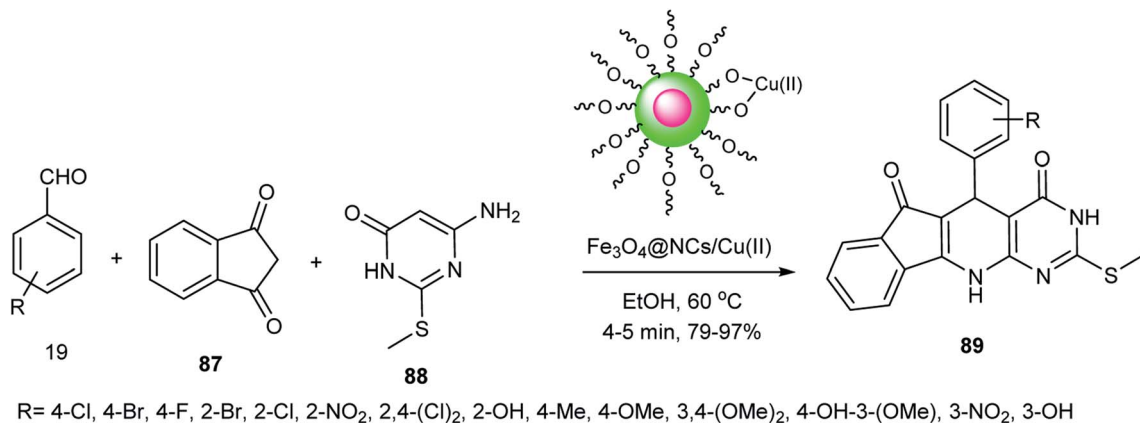
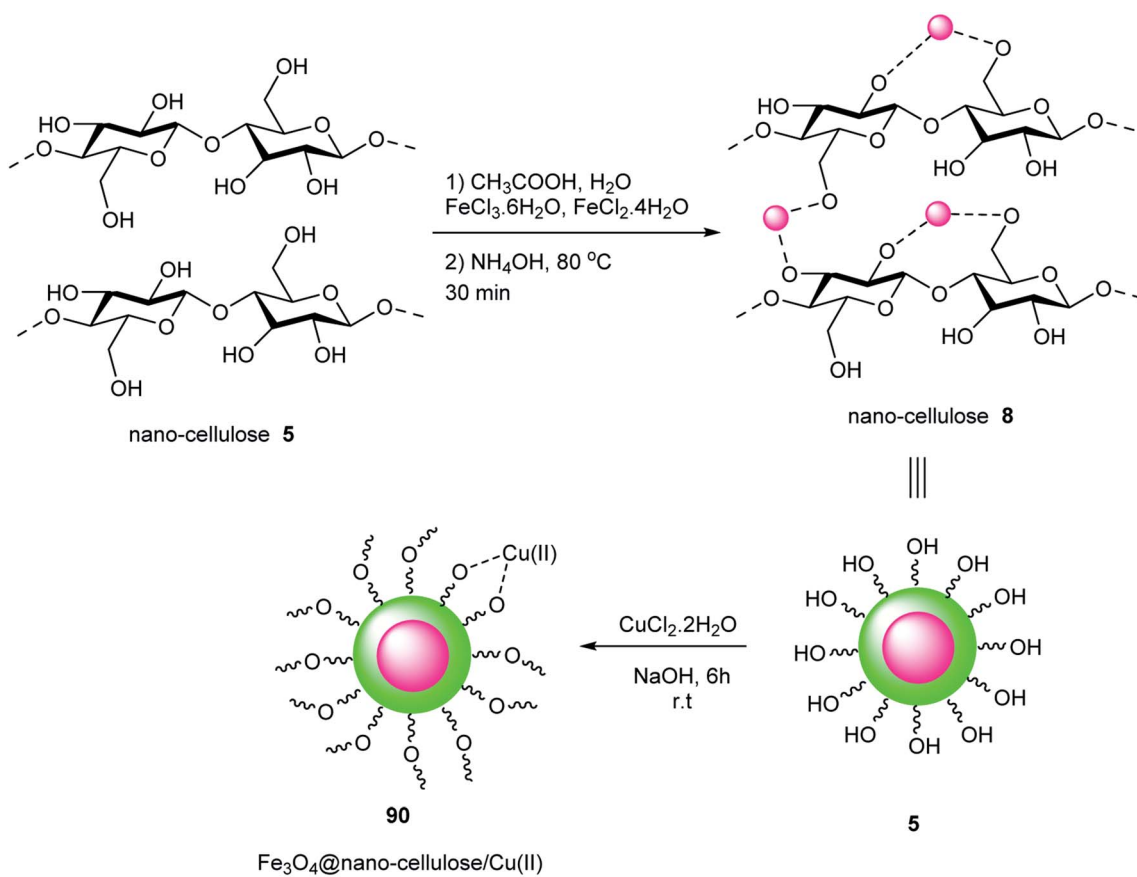
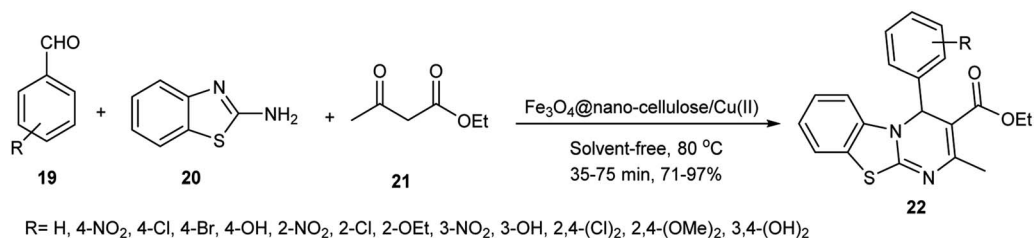
Scheme 21 Synthesis of 2,3-dihydroquinazolin-4(1H)-ones.

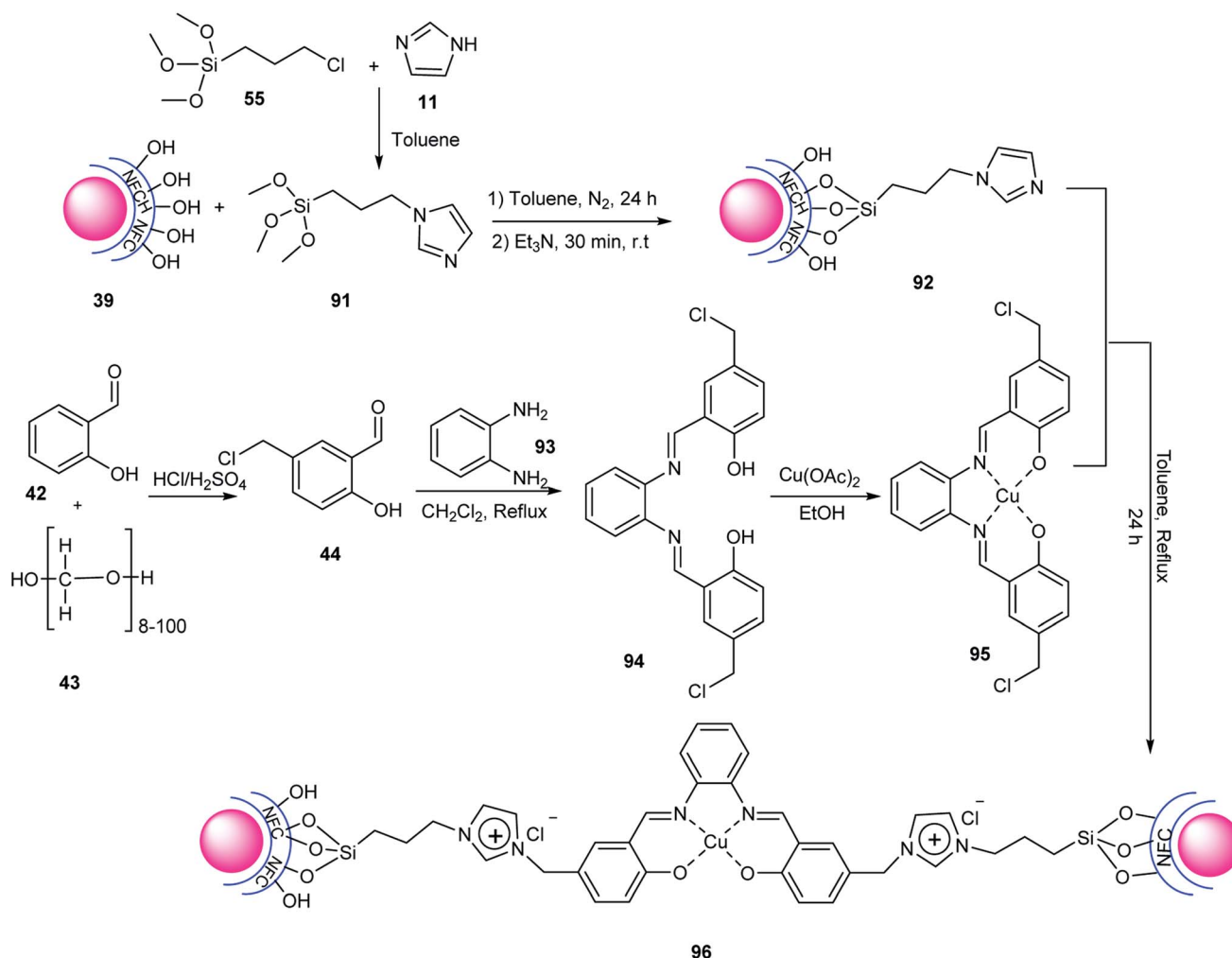
Scheme 22 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@NCS/Cu(II) 86.

temperature. Then,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was synthesized using Fe<sub>3</sub>O<sub>4</sub> at 250 °C. In the next step,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was coated with starch at room temperature to obtain  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@starch 150, followed by reaction with 1,4-butane sultone 151 in dry toluene under reflux conditions to produce  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@starch-*n*-butylSO<sub>3</sub>H 152 nanoparticles (Scheme 45).<sup>71</sup>

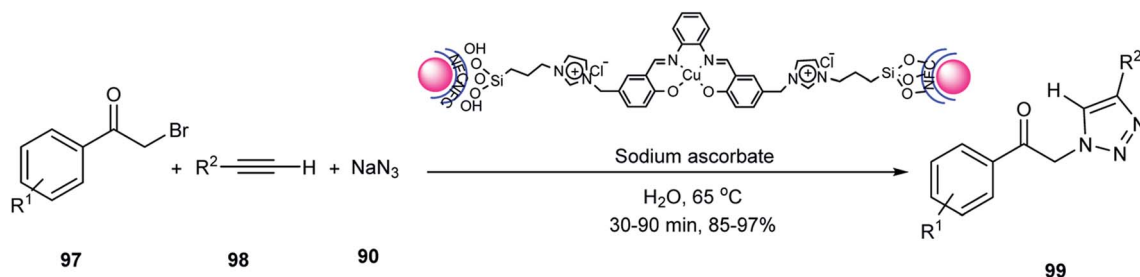
$\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@starch-*n*-butylSO<sub>3</sub>H 152 as Brønsted acid activated the carbonyl groups in the multicomponent reactions of



Scheme 23 Synthesis of indenopyrido [2,3-*d*] pyrimidines in the presence of Fe<sub>3</sub>O<sub>4</sub>@NCs/Cu(II).Scheme 24 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@nano-cellulose/Cu(II).Scheme 25 Synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazole derivatives 22 using Fe<sub>3</sub>O<sub>4</sub>@nano-cellulose/Cu(II).



Scheme 26 Synthesis of 4H-pyrimido[2,1-*b*]benzothiazole derivatives using  $\text{Fe}_3\text{O}_4@\text{NFC-ImSalophCu(II)}$  **96**.



Scheme 27 Synthesis of 1,2,3-triazoles **99** using  $\text{Fe}_3\text{O}_4@\text{NFC-ImSalophCu}$ .

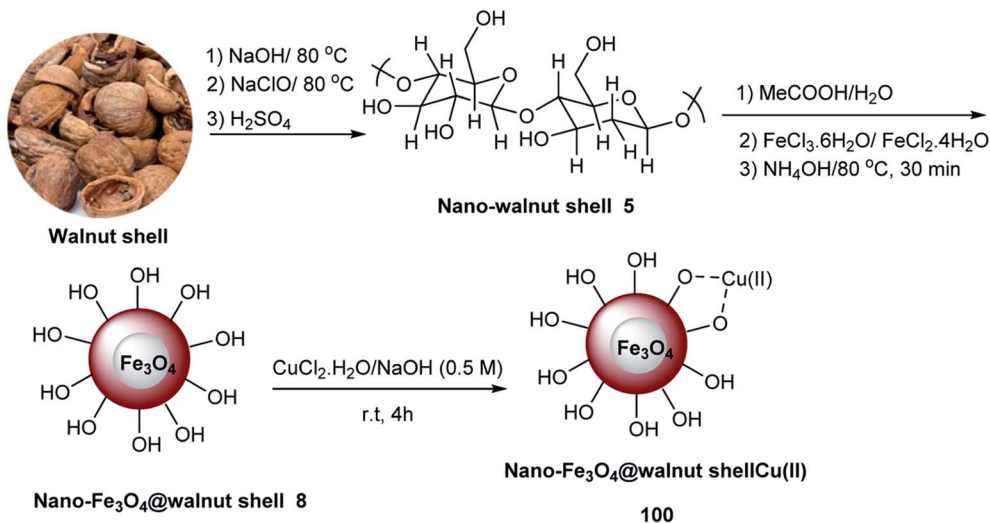
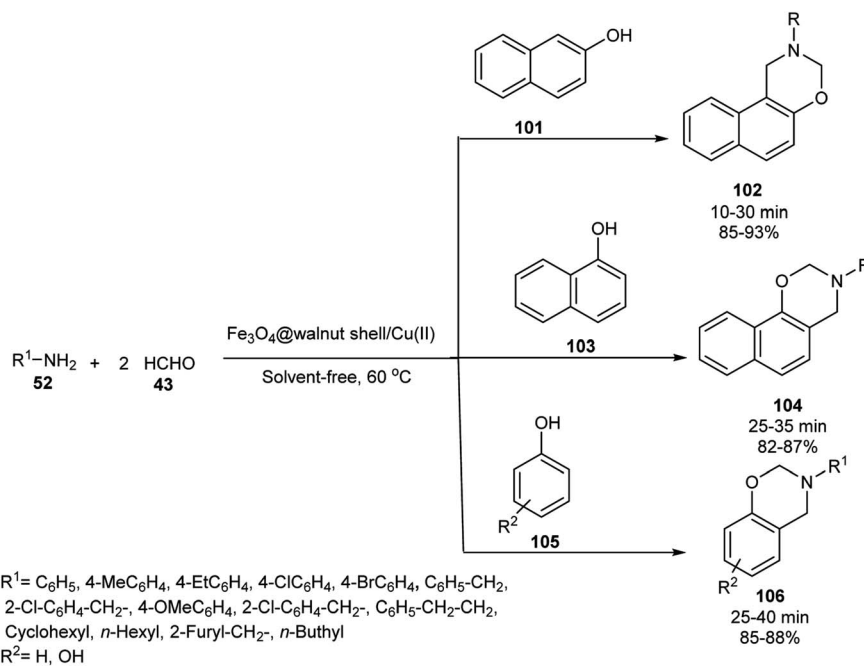
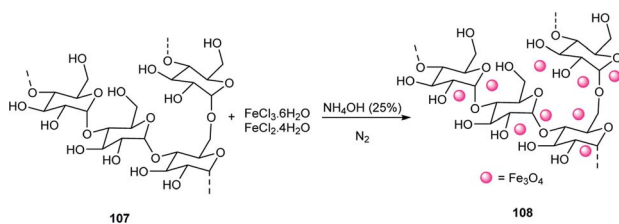
aldehydes **19**, dimedone **64**, and 2-aminobenzimidazole **153** or phthalhydrazide **154** to synthesize tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-ones **155** or 2*H*-indazolo[2,1-*b*]phthalazine-trione **156** (Scheme 46). This catalyst was used seven times without loss in any of its activities.<sup>71</sup>

## 2.4. Magnetic bio-polymers based on alginate

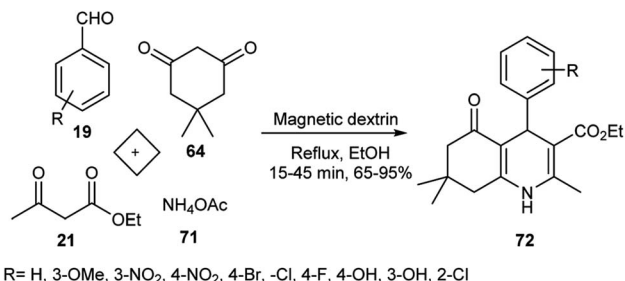
### 2.4.1. Synthesis and application of $\text{Fe}_3\text{O}_4@\text{Alg@CPTMS@Arg}$ . Alginate **157** was immobilized on $\text{Fe}_3\text{O}_4$ **4** via

the co-precipitation method. Initially,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  **1**,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  **2**, and sodium alginate **157** were dissolved in  $\text{H}_2\text{O}$  under a nitrogen atmosphere. Then, an ammonia solution was added to this mixture to give  $\text{Fe}_3\text{O}_4@\text{Alg}$  nanoparticles **158**, which were functionalized with 3-chloropropyltrimethoxysilane **55** to prepare  $\text{Fe}_3\text{O}_4@\text{Alg@CPTMS}$  **159**, followed by reaction with *L*-arginin **160** using trimethylamine in EtOH for 48 h to give  $\text{Fe}_3\text{O}_4@\text{Alg@CPTMS@Arg}$  **161** (Scheme 47).<sup>72</sup>



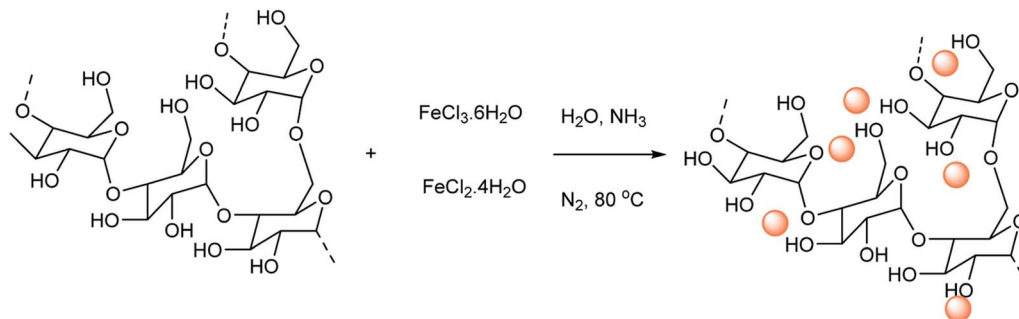
Scheme 28 Synthesis of nano-Fe<sub>3</sub>O<sub>4</sub>@walnut shell/Cu.Scheme 29 Synthesis of 2-aryl/alkyl-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazines 102 or 104 or 106 using nano-Fe<sub>3</sub>O<sub>4</sub>@walnut shell/Cu(II).

Scheme 30 Synthesis of magnetic dextrin.

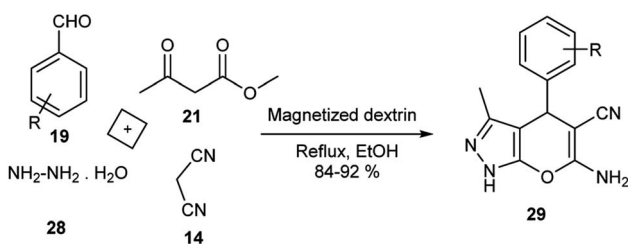


Scheme 31 Synthesis of polyhydroquinolines 72 in the presence of magnetic dextrin.





Scheme 32 Synthesis of magnetized dextrin.

R = 4-Me, 3-NO<sub>2</sub>, 4-OMe, 3-OMeScheme 33 Synthesis of dihydropyrano[2,3-c]pyrazoles **29** using magnetized dextrin.

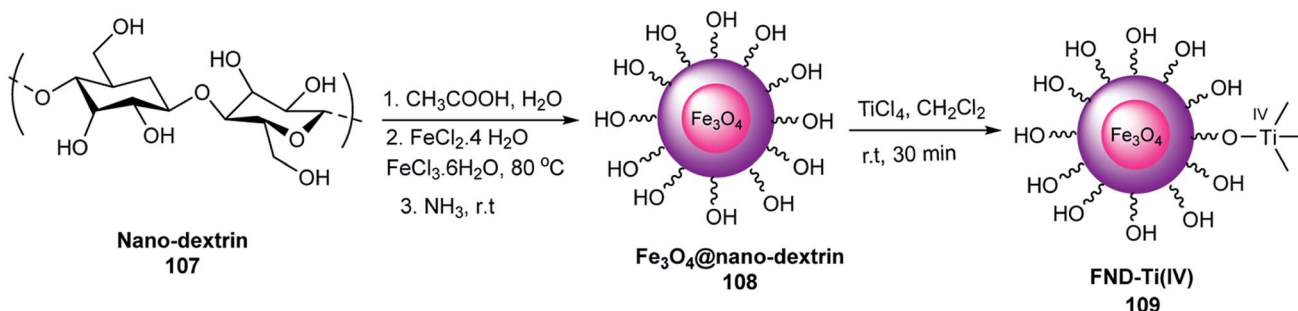
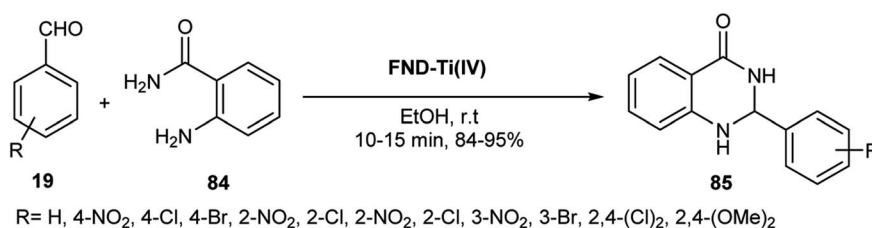
Subsequently, Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS@Arg, which has two acidic and basic functional sites, activated the carbonyl groups in the synthesis of 2,4,5-triarylimidazoles through the reaction of ammonium acetate, aldehydes, and benzil in EtOH under reflux conditions (Scheme 48). The recyclability of the catalyst

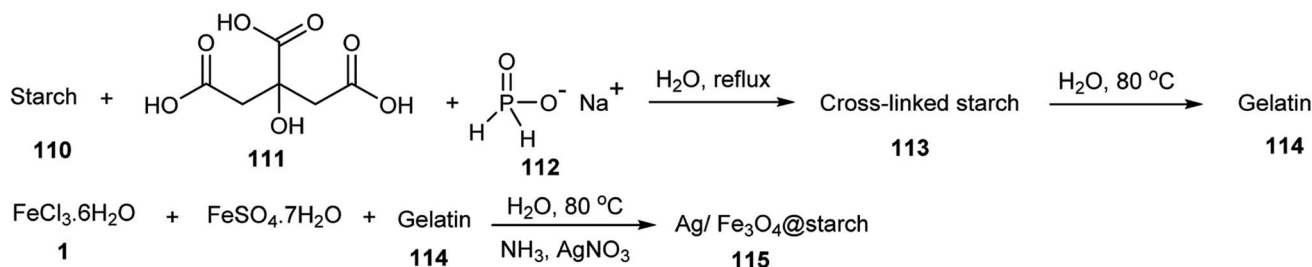
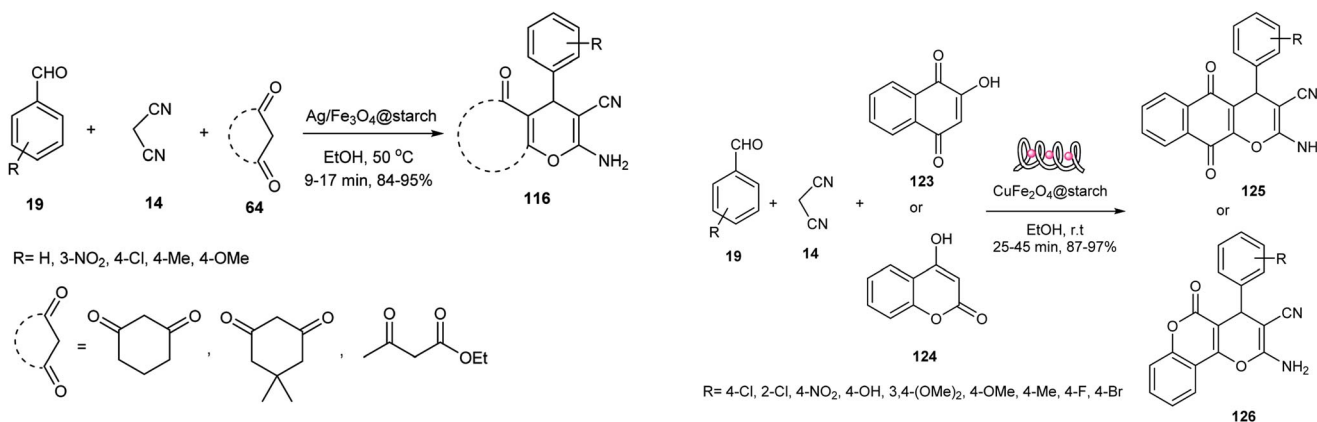
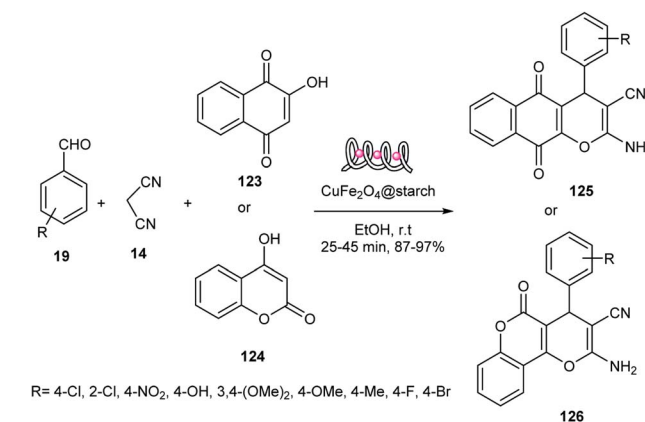
was tested 7 times using the model reaction without loss in any of its activities. When Fe<sub>3</sub>O<sub>4</sub> was used as the catalyst, the yield of this reaction was about 65%.<sup>72</sup>

**2.4.2. Synthesis and application of Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS@Arg.** The reaction of Fe<sub>3</sub>O<sub>4</sub>@Alg **165** and 3-chloropropyltrimethoxysilane (CPTMS) **55** in toluene under reflux conditions and nitrogen atmosphere gave Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS **166**, which was reacted with arginine **167** in the presence of trimethylamine in dry toluene to provide Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS@Arg nanocomposites **168** (Scheme 49).<sup>73</sup>

The activity of Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS@Arg was tested as a catalyst in the synthesis of 2,4,5-triarylimidazoles **36** via the reaction of ammonium acetate **71**, aldehyde derivatives **19**, and benzil **34** in EtOH (Scheme 50). Its catalytic activity did not decrease after seven uses. It has two functional groups including a Lewis base (NH<sub>2</sub>) and Brønsted acidic (COOH), which catalyzed the synthesis of 2,4,5-triarylimidazoles.<sup>73</sup>

**2.4.3. Synthesis and application of Fe<sub>3</sub>O<sub>4</sub>@FU.** Fe<sub>3</sub>O<sub>4</sub>@FU **170** was prepared via the reaction of fucoidan powder **169**,

Scheme 34 Synthesis of FND-Ti(IV) **109**.R = H, 4-NO<sub>2</sub>, 4-Cl, 4-Br, 2-NO<sub>2</sub>, 2-Cl, 2-NO<sub>2</sub>, 2-Cl, 3-NO<sub>2</sub>, 3-Br, 2,4-(Cl)<sub>2</sub>, 2,4-(OMe)<sub>2</sub>Scheme 35 Synthesis of 2,3-dihydroquinazolin-4(1H)-ones **85** using Fe<sub>3</sub>O<sub>4</sub>@nano-dextrin/Ti(IV).

Scheme 36 Synthesis of Ag/Fe<sub>3</sub>O<sub>4</sub>@starch 115.Scheme 37 Synthesis of 4H-pyran 116 in the presence of Ag/Fe<sub>3</sub>O<sub>4</sub>@starch.Scheme 39 Synthesis of 4H-chromenes using CuFe<sub>2</sub>O<sub>4</sub>@starch.

FeCl<sub>2</sub>·4H<sub>2</sub>O 2, and FeCl<sub>3</sub>·6H<sub>2</sub>O 1 in aqueous ammonia solution (25%) in distilled water under a nitrogen atmosphere at 80 °C (Scheme 51).<sup>74</sup>

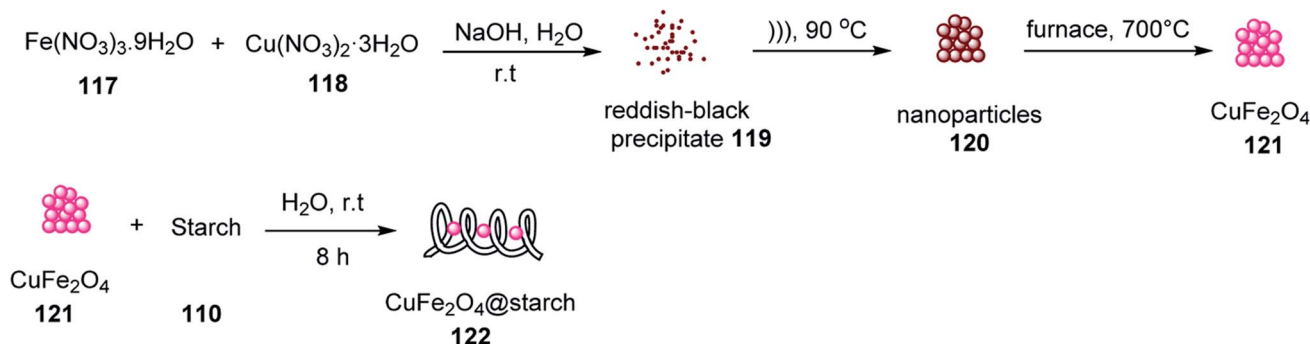
The activity of Fe<sub>3</sub>O<sub>4</sub>@FU was evaluated as a catalyst in the synthesis of *tri*- and *tetra*-substituted imidazoles 36 or 171 *via* three- and four-component reactions of benzil 34, aldehydes 19, NH<sub>4</sub>OAc 71, and amine 52 under reflux conditions in EtOH (Scheme 52), respectively. The catalyst was used six times in the model reaction without loss in any of its activities. This reaction was accomplished in ethanol under reflux conditions in the presence of Fe<sub>3</sub>O<sub>4</sub> as a catalyst after 40 min with 55% yield. The carbonyl groups were activated *via* hydrogen bonding with Fe<sub>3</sub>O<sub>4</sub>@FU as a catalyst.<sup>74</sup>

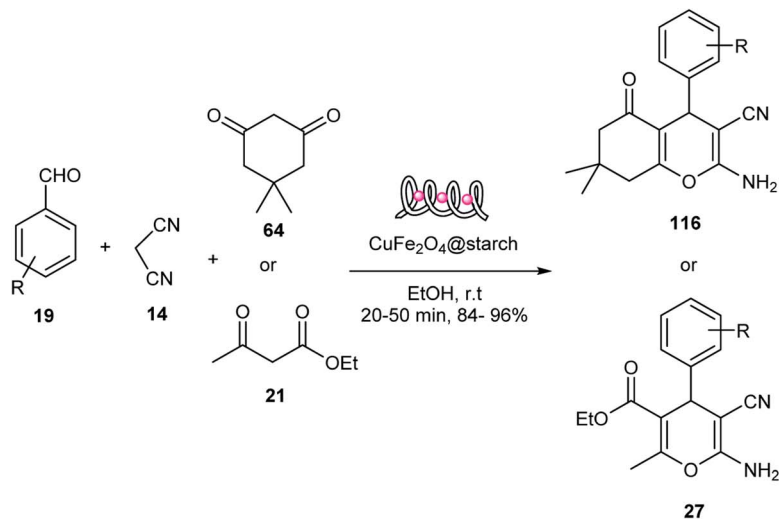
## 2.5. Magnetic bio-polymers based on glucose

### 2.5.1. Synthesis and application of Fe<sub>3</sub>O<sub>4</sub>@C@ONa.

Initially, FeCl<sub>3</sub>·6H<sub>2</sub>O solution, CO(NH<sub>2</sub>)<sub>2</sub>, and glucose were added to ethylene glycol 172 to produce a black powder of carbon-coated magnetic nanoparticles (CCMNPs: Fe<sub>3</sub>O<sub>4</sub>@C) 173, followed by reaction with NaOH solution to obtain basic carbon-coated magnetic nanoparticles (BCCMNPs: Fe<sub>3</sub>O<sub>4</sub>@C@ONa) 174 (Scheme 53).<sup>75</sup>

Subsequently, the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>@C@ONa was tested for the synthesis of 4H-chromene derivatives 174 *via* the reaction of salicylaldehyde 42, dimedone 64, and β-naphthol 101 in water at 60 °C (Scheme 54). Also, the catalyst was used five times in the model reaction without loss in any of its

Scheme 38 Synthesis of CuFe<sub>2</sub>O<sub>4</sub>@starch.



Scheme 40 Synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-benzo[b]pyrans **116** or **27**.

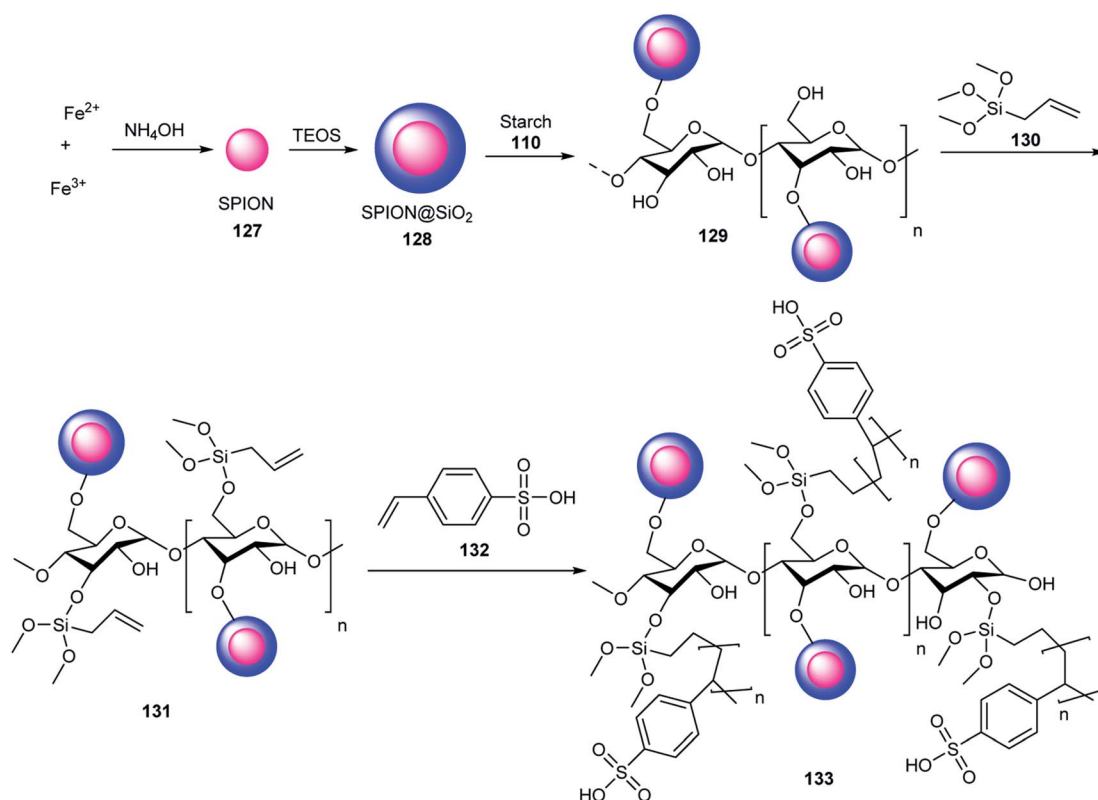
activities. This catalyst has two functional groups, including Fe<sup>3+</sup> as a Lewis acid and oxygen group as a Lewis base, which increased the reaction rate.<sup>75</sup>

## 2.6. Magnetic bio-polymers based on chitosan

**2.6.1. Synthesis and application of CSSNH@Arg.** Chitosan-silica sulfate nanohybrid (CSSNH@Arg) **178** was synthesized *via*

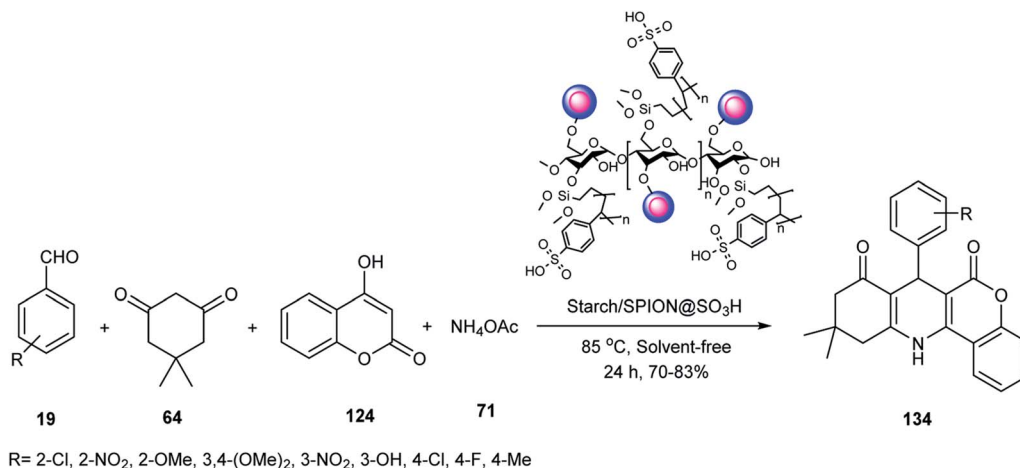
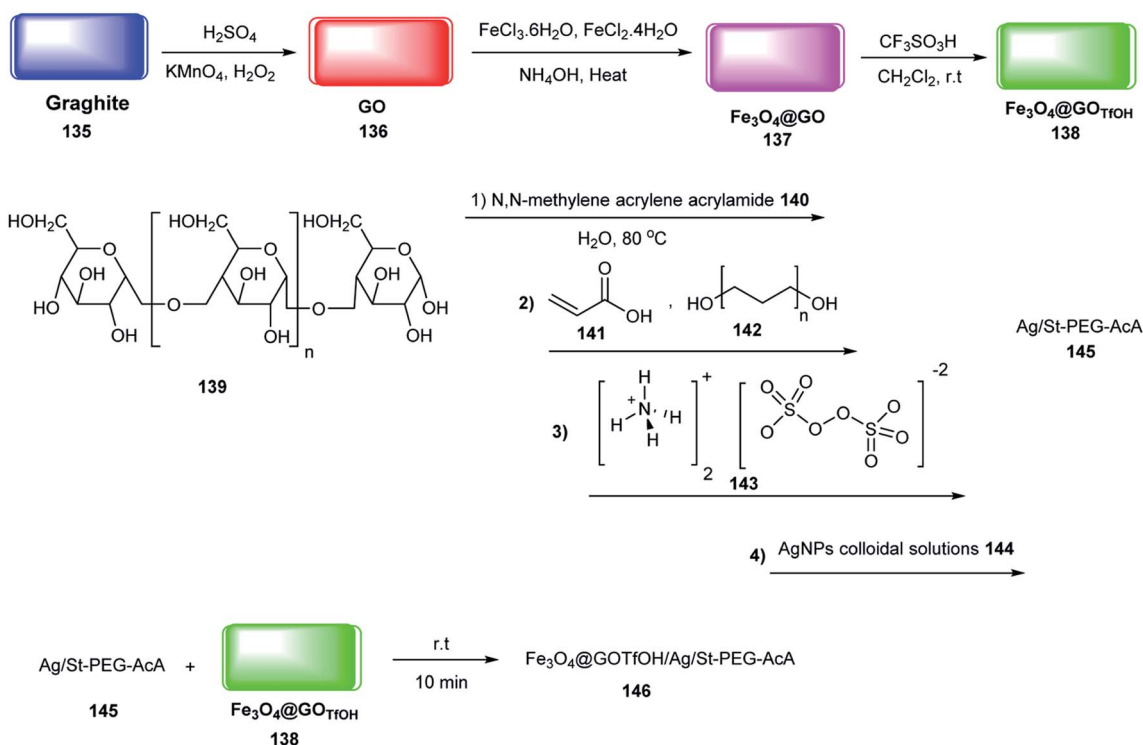
the reaction of chitosan **176** and silica sulfuric acid (SSA) **177** under ultrasonic irradiation (Scheme 55).<sup>76</sup>

A green method for the synthesis of 3,4-dihydropyrimidine-2(1H)-one/thione derivatives **179** was described by Behrouz and co-workers *via* the Biginelli reaction of (thio)urea **23** or urea **6**, methyl acetoacetate **21**, and aldehydes **19** using CSSNH@Arg **178** under solvent-free conditions (Scheme 56).



Scheme 41 Synthesis of starch/SPION@SO<sub>3</sub>H.

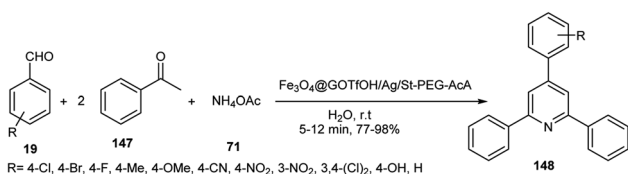


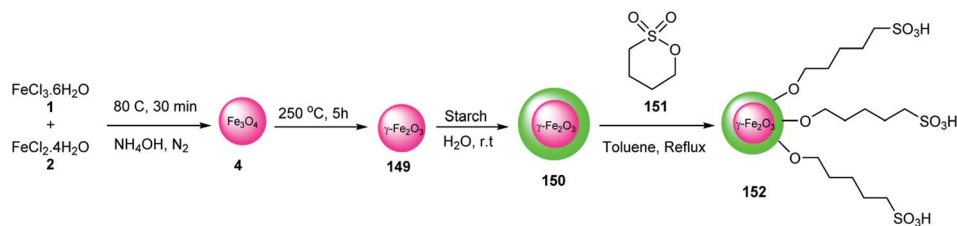
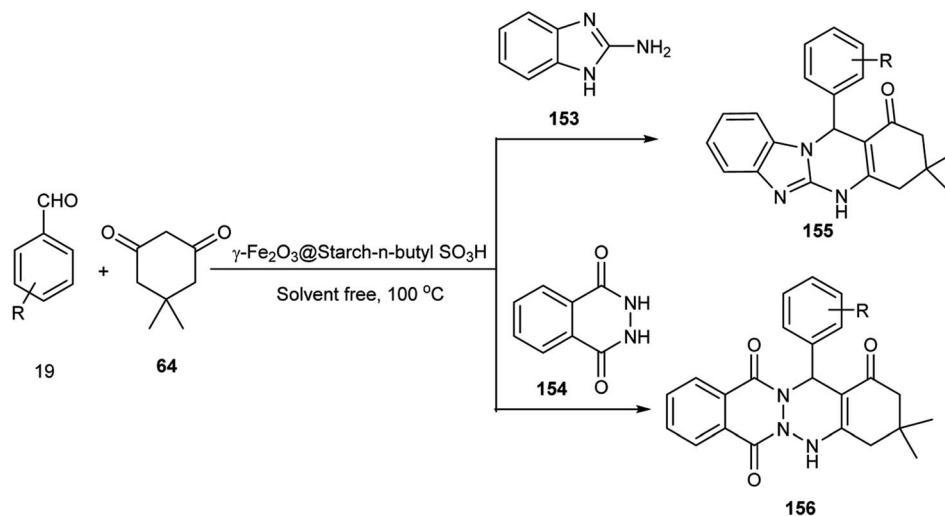
Scheme 42 Synthesis of chromeno[4,3-b]quinoline-6,8(9H)-diones in the presence of Starch/SPION@SO<sub>3</sub>H.Scheme 43 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@GOTfOH/Ag/St-PEG-AcA 146.

According to the reusability test, this catalyst was used five times without a decrease in any of its activities. The various functional groups including hydroxyl and amine on the

CSSNH@Arg can activate the carbonyl groups *via* hydrogen bonding.<sup>76</sup>

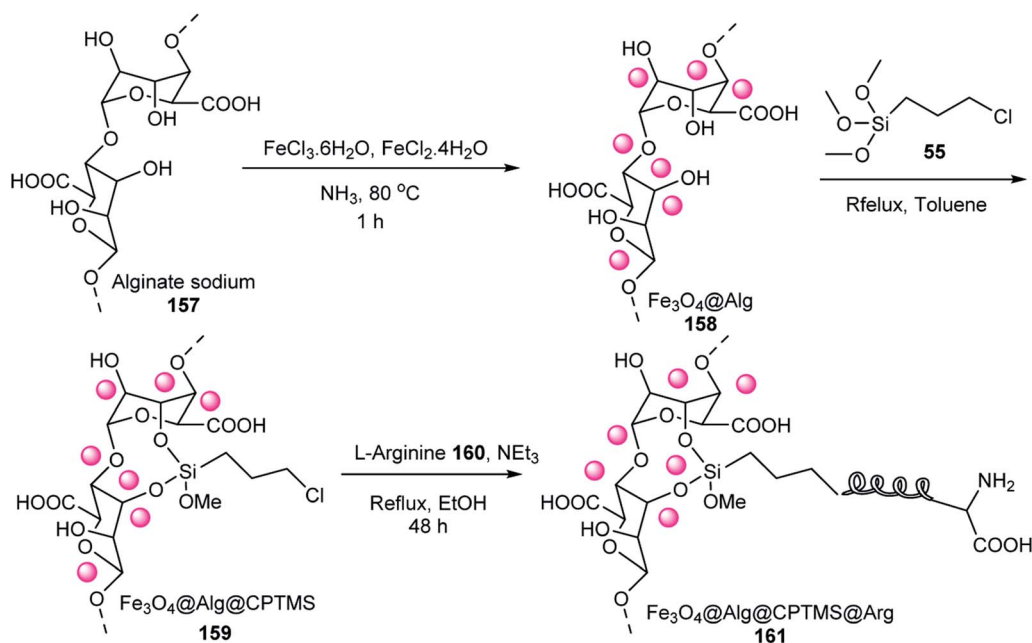
**2.6.2. Synthesis and application of Fe<sub>3</sub>O<sub>4</sub>@C-SO<sub>3</sub>H.** Initially, starch was mixed with sulfuric acid, and then the reaction mixture was transferred to an autoclave for 24 h at 180 °C, resulting in the formation of a solid black product (C-SO<sub>3</sub>H). The magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles, carbon-based solid acid (C-SO<sub>3</sub>H) 180, and H<sub>2</sub>O were placed in an oil bath at 100 °C to remove H<sub>2</sub>O, and then the reaction mixture was poured into a Teflon-sealed autoclave and heated at 180 °C for 6 h to achieve Fe<sub>3</sub>O<sub>4</sub>@C-SO<sub>3</sub>H 181 (Scheme 57).<sup>77</sup>

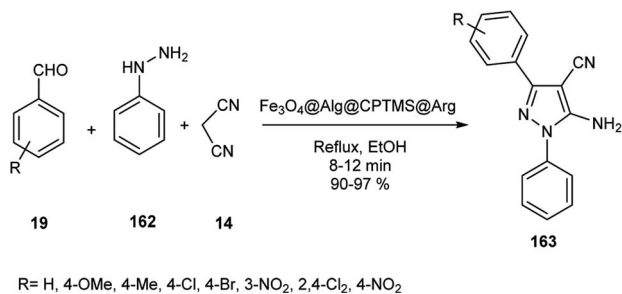
Scheme 44 Synthesis of 2,4,6-triarylpyridine derivatives 148 using Fe<sub>3</sub>O<sub>4</sub>@GOTfOH/Ag/St-PEG-AcA.

Scheme 45 Synthesis of  $\gamma\text{-Fe}_2\text{O}_3\text{@starch-}n\text{-butyl SO}_3\text{H}$ .Scheme 46 Synthesis of tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-ones **155** or 2*H*-indazolo[2,1-*b*]phthalazine-triones **156** using  $\gamma\text{-Fe}_2\text{O}_3\text{@starch-}n\text{-butyl SO}_3\text{H}$ .

CSSNH was applied as a Brønsted acid catalyst in the synthesis of 2-amino-3-cyano-4*H*-pyrans **126** and 2-amino-4*H*-chromenes **116** or **182** *via* the three-component reactions of malononitrile **14**,

benzaldehyde **19**, and  $\beta$ -naphthol **101** or dimedone **64** or 4-hydroxycoumarin **124**, respectively (Scheme 58). This catalyst was used four times without any loss in its activity.<sup>77</sup>

Scheme 47 Synthesis of  $\text{Fe}_3\text{O}_4\text{@Alg@CPTMS@Arg}$  **161**.



Scheme 48 Synthesis of 2,4,5-triarylimidazoles **163** using Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS@Arg.

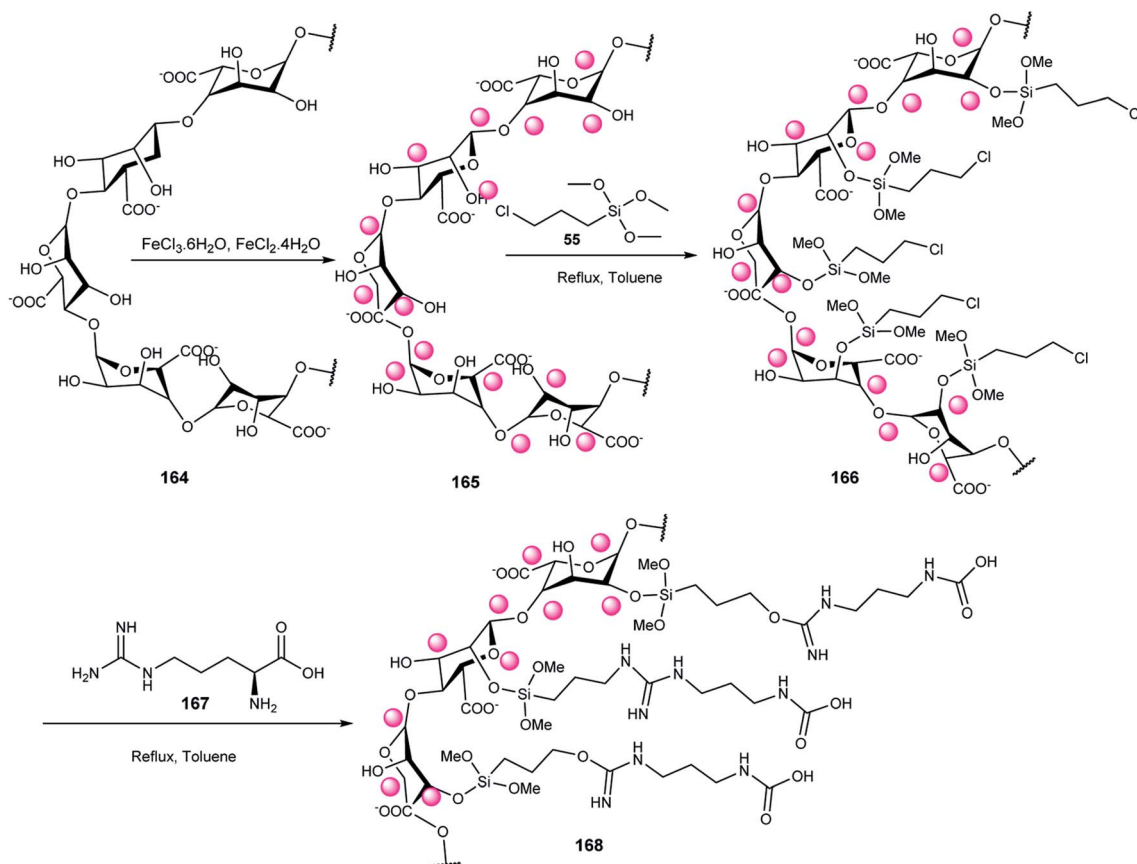
**2.6.3. Synthesis and application of magnetic chitosan-terephthaloyl-creatine bio-nanocomposite.** The reaction of terephthaloyl chloride **183** and creatine powders **184** in CH<sub>2</sub>Cl<sub>2</sub> under reflux conditions provided creatine-terephthaloyl chloride ligand **185**, which was added to chitosan **176** powder in a hydrochloric acid solution, and then refluxed to give chitosan-terephthaloyl-creatine bio-nanocomposite **186**, followed by immobilization on Fe<sub>3</sub>O<sub>4</sub> to provide magnetic chitosan-terephthaloyl-creatine bio-nanocomposite **187** (Scheme 59).<sup>78</sup>

Its catalytic activity was tested in the synthesis of polyhydroquinolines **72** *via* the reaction of aldehydes **19**, dimedone **67**, ammonium acetate **71**, and ethyl acetoacetate or methyl acetoacetate **21** in EtOH (Scheme 60). In another attempt, it was

used in the synthesis of 1,4-dihydropyridines **73** *via* the pseudo-three-component reaction of aldehydes **19**, methyl acetoacetate **21**, and ammonium acetate **71** (Scheme 61). The acidic site of the catalyst activated the carbonyl groups of the primary compounds. The activity of this catalyst did not decrease after use eight times.<sup>78</sup>

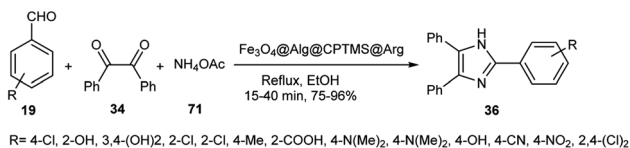
**2.6.4. Synthesis and application of magnetic cyanoguanidine-modified chitosan (MCGC).** Firstly, chitosan **176** was obtained *via* the deacetylation of chitin **74**, and then it was modified by treatment with cyanoguanidine **188** in HCl solution to produce cyanoguanidine-modified chitosan (CGC) **189**, which was immobilized on Fe<sub>3</sub>O<sub>4</sub> nanoparticles to afford magnetic cyanoguanidine-modified chitosan (MCGC) **190** (Scheme 62). Its catalytic activity was investigated in the synthesis of benzimidazoloquinazolines **155** *via* the reaction of aldehydes **19**, 2-aminobenzimidazole **153**, and dimedone **64** in EtOH under reflux conditions. The sonochemical method afforded better yields in shorter reaction times than the conventional method (Scheme 63).<sup>79</sup>

1,4-Dihydropyridines **73** were synthesized *via* the Hantzsch reaction of ethyl acetoacetate **35**, aromatic aldehydes **19**, and ammonium acetate **71** under ultrasonic irradiation in the presence of MCGC **190** as a catalyst, which activated the carbonyl groups *via* hydrogen bonding. Also, the yield of the reaction did not decrease after eight times usage of the catalyst (Scheme 64).<sup>79</sup>



Scheme 49 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS@Arg.

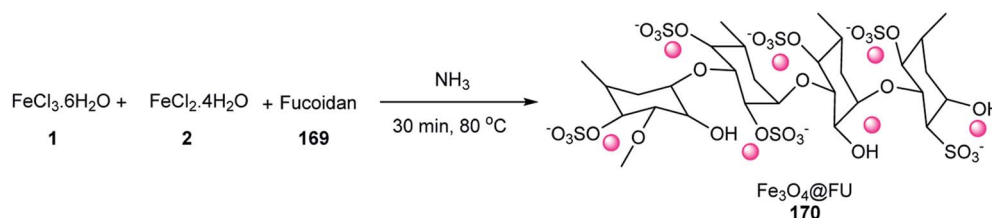




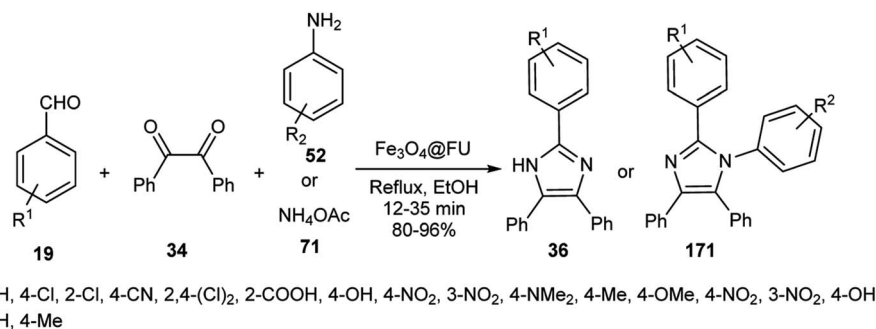
Scheme 50 Synthesis of 2,4,5-triarylimidazoles derivatives in the presence of Fe<sub>3</sub>O<sub>4</sub>@Alg@CPTMS.

**2.6.5. Synthesis and application of magnetic MnFe<sub>2</sub>O<sub>4</sub>-CS-Bu-SO<sub>3</sub>H.** Manganese ferrite nanoparticles were synthesized *via* the co-precipitation of Fe(III) **1** and Mn(II) **189** in the presence of NaOH solution at 97 °C to give MnFe<sub>2</sub>O<sub>4</sub> **191**, which was immobilized on chitosan **176** and 4-butane sultone **151** to prepare MnFe<sub>2</sub>O<sub>4</sub>-CS-Bu-SO<sub>3</sub>H **192** (Scheme 65).<sup>80</sup>

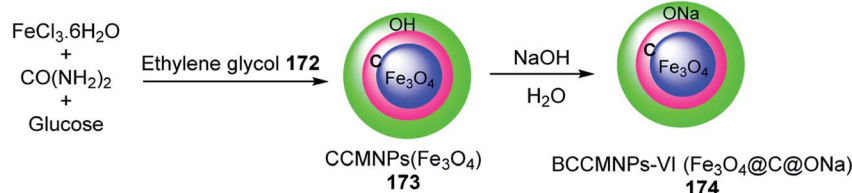
The catalyst activity of MnFe<sub>2</sub>O<sub>4</sub>-CS-Bu-SO<sub>3</sub>H was investigated in the synthesis of *spiro*[acenaphthylene-1,9'-acridine]



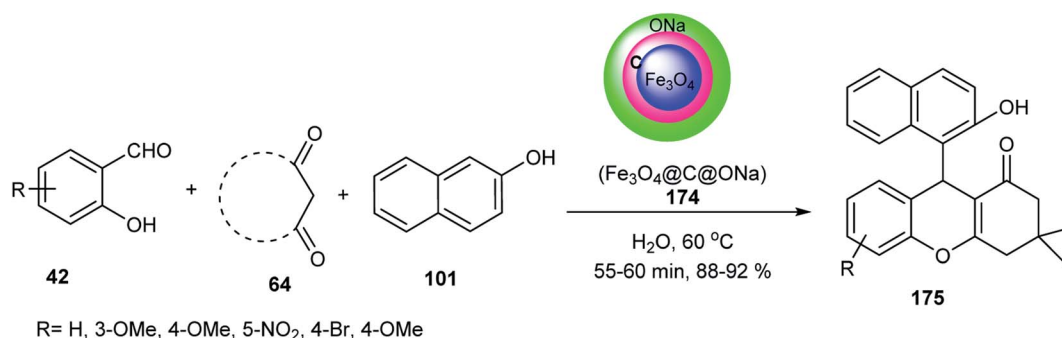
Scheme 51 Synthesis of magnetic Fe<sub>3</sub>O<sub>4</sub>@FU **170**.



Scheme 52 Synthesis of imidazole derivatives.

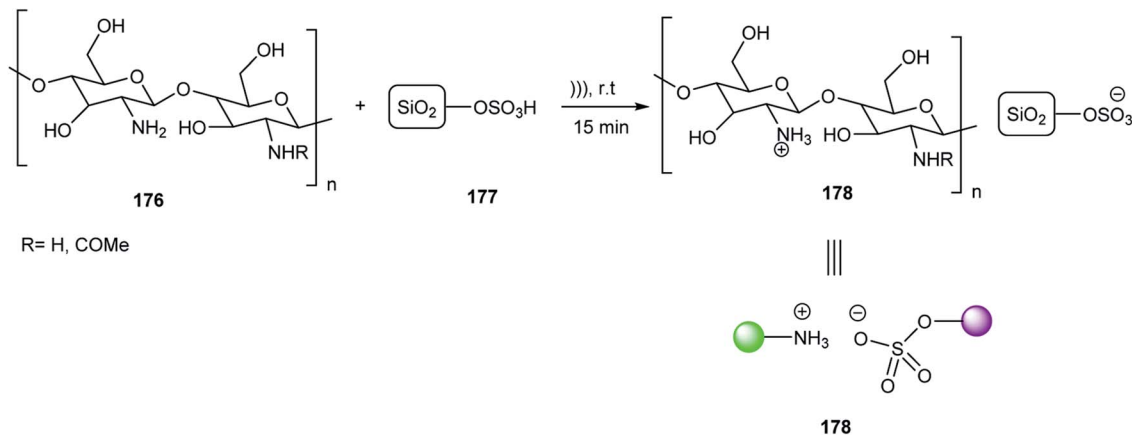


Scheme 53 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@C@ONa.

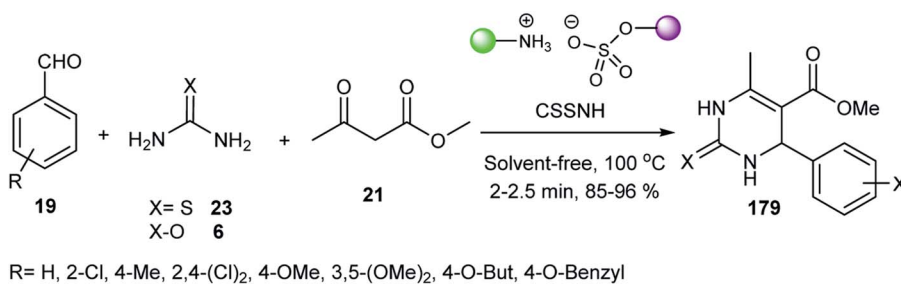


Scheme 54 Synthesis of 4H-chromene derivatives using Fe<sub>3</sub>O<sub>4</sub>@C@ONa **174**.





Scheme 55 Synthesis of CSSNH@Arg 178.



Scheme 56 Synthesis of 3,4-dihydropyrimidine-2(1H)-(thio)ones using of CSSNH@Arg 178.

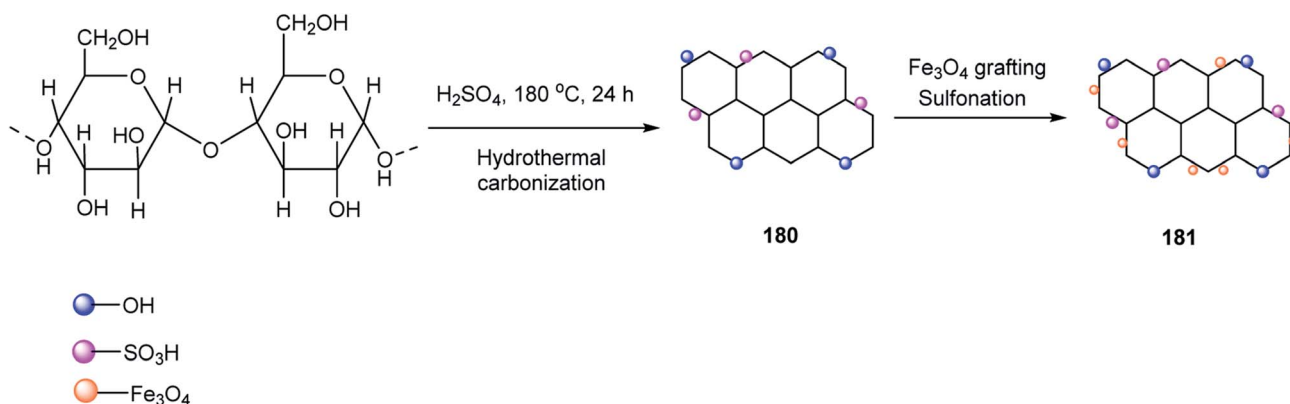
triones **194** *via* the multicomponent reaction of dimedone **64**, aldehydes **19**, and acenaphthoquinone **193** under ultrasonic irradiation in H<sub>2</sub>O (Scheme 66). Also, MnFe<sub>2</sub>O<sub>4</sub>-CS-Bu-SO<sub>3</sub>H as a Brønsted acid increased the reaction rate *via* hydrogen bonding with the carbonyl group. According to the reusability test, this catalyst was used five times without any loss in its activity.<sup>80</sup>

**2.6.6. Synthesis and application of magnetic Cu-MCS.** Fe<sub>3</sub>O<sub>4</sub> NPs **4** were reacted with carboxymethylated chitosan to obtain magnetic chitosan MCS **195**, which was reacted with

CuCl<sub>2</sub>·2H<sub>2</sub>O in H<sub>2</sub>O to generate Cu NPs@Fe<sub>3</sub>O<sub>4</sub>-chitosan (Cu-MCS) **196** (Scheme 67).

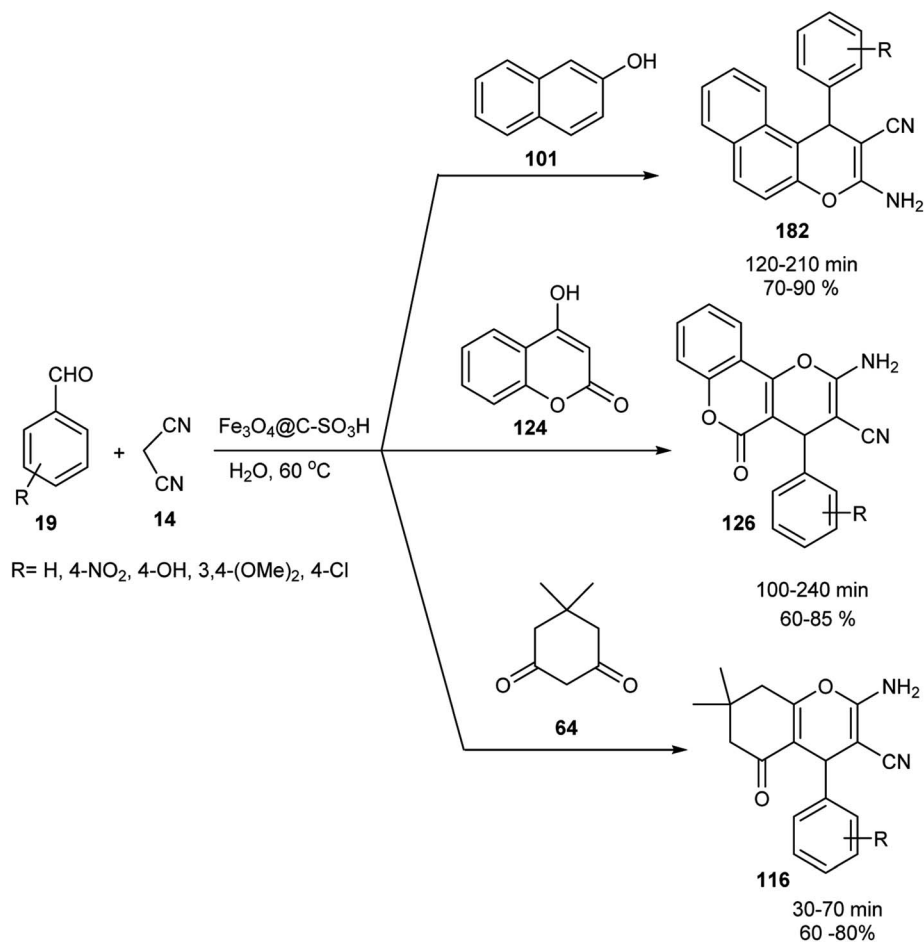
The catalytic activity of Cu-MCS was verified in the synthesis of various tetrazoles **198** or **199** *via* the reaction of cyanamides **197** and NaN<sub>3</sub> **50** in H<sub>2</sub>O under reflux conditions (Scheme 68). This catalyst could be used five times without loss in its activity.<sup>81</sup>

**2.6.7. Synthesis and application of magnetic Ch-Fe<sub>3</sub>O<sub>4</sub> NCs.** Chitosan was dissolved in an acetic acid solution, and then FeCl<sub>3</sub>·6H<sub>2</sub>O **1** and FeCl<sub>2</sub>·4H<sub>2</sub>O **2** were added to the reaction mixture for 6 h at 80 °C under an N<sub>2</sub> atmosphere. Then, NH<sub>4</sub>OH

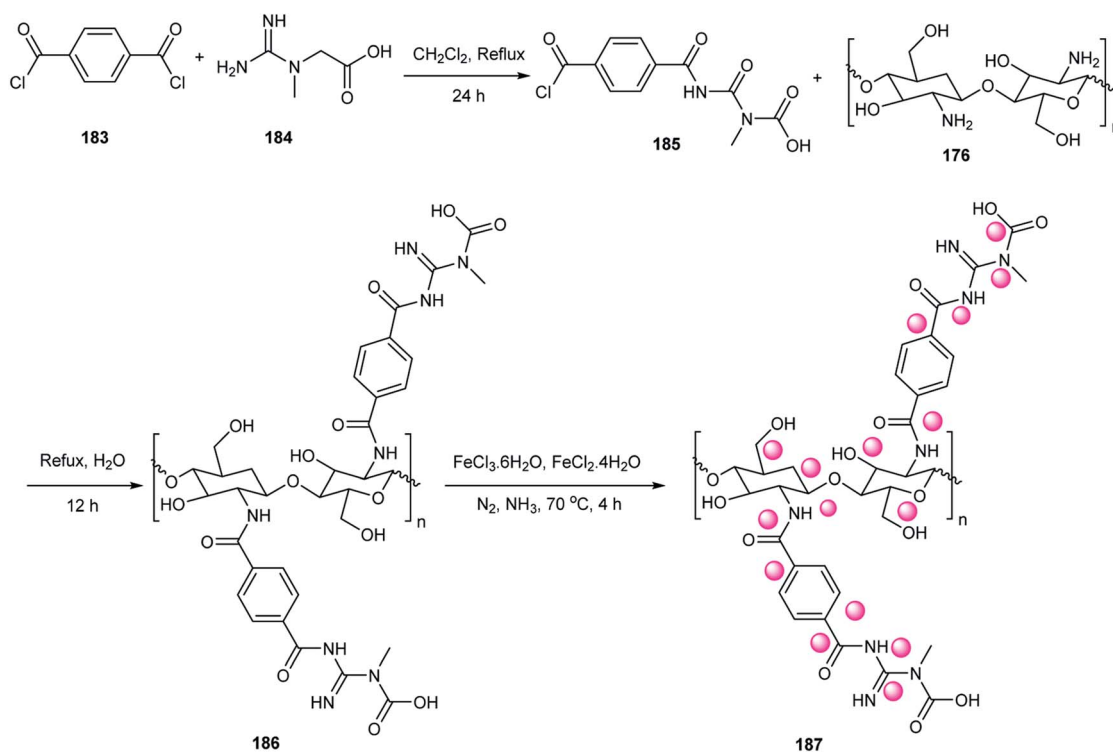


Scheme 57 Synthesis of 3,4-dihydropyrimidine-2(1H)-(thio)ones in the presence of CSSNH 178.



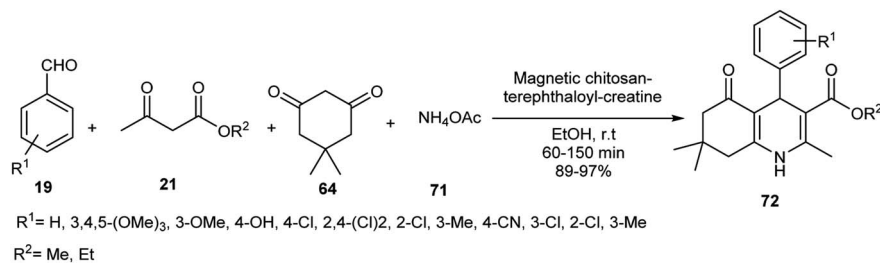


Scheme 58 Synthesis of 2-amino-4H-chromenes **116** and 2-amino-3-cyano-4H-pyrans **126** in the presence of  $\text{Fe}_3\text{O}_4\text{@C-SO}_3\text{H}$ .

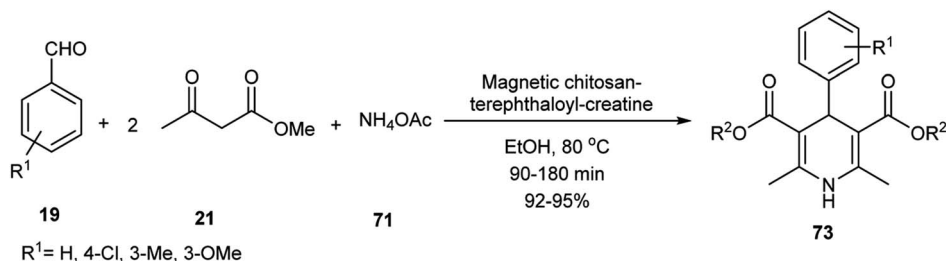


Scheme 59 Synthesis of magnetic chitosan-terephthaloyl-creatine bio-nanocomposite.





Scheme 60 Synthesis of polyhydroquinoline derivatives 72.



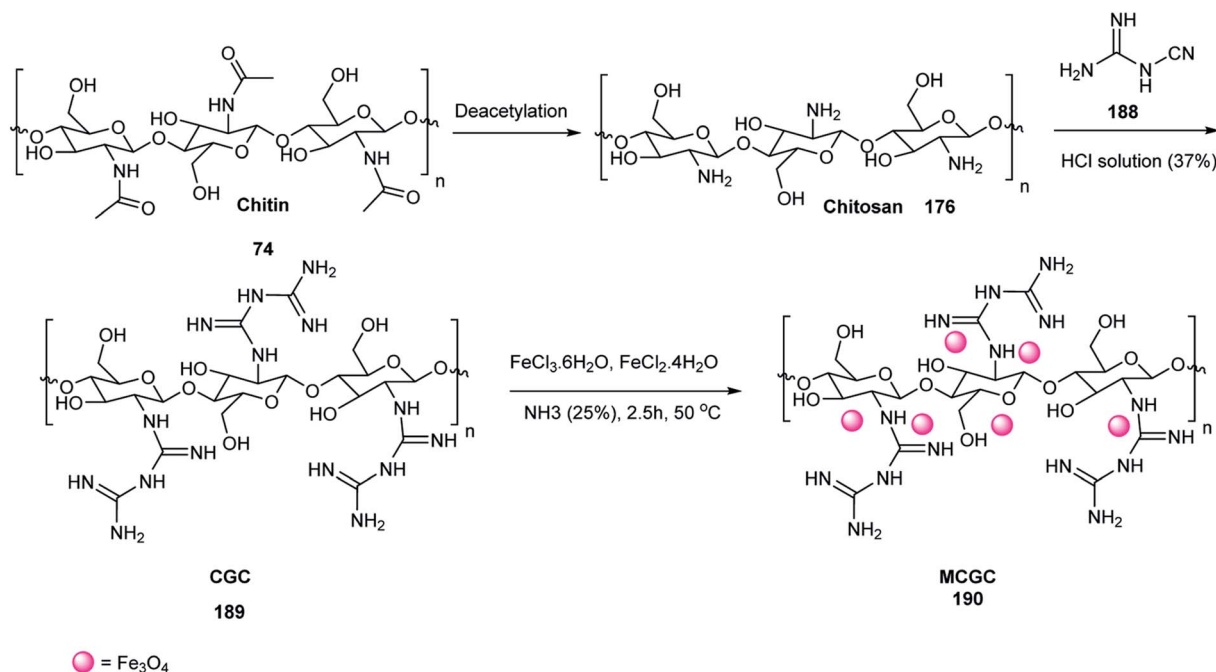
Scheme 61 Synthesis of 1,4-dihydropyridine derivatives 73 in the presence of terephthaloyl-creatine bio-nanocomposite.

was added to the reaction mixture to obtain Ch-Fe<sub>3</sub>O<sub>4</sub> NCs **200**. Finally, the chitosan magnetic nanocomposite of Ch-rhomboclase NCs **201** was synthesized *via* the reaction of Ch-Fe<sub>3</sub>O<sub>4</sub> NCs **200** with chlorosulfonic acid at room temperature under N<sub>2</sub> gas (Scheme 69).<sup>82</sup>

The condensation reaction of benzaldehyde **19**, ethyl acetoacetate **35** or dimedone **64**, and ammonium acetate **71** gave 1,4-dihydropyridine derivatives **73** or **202** in the presence of Ch-

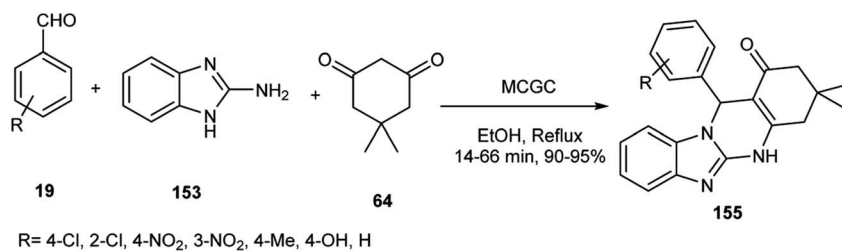
rhomboclase NCs **201** under solvent-free conditions at 80 °C (Scheme 70). In the Hantzsch reaction, this acidic catalyst activated carbonyl groups *via* hydrogen bonding. Also, according to the reusability test, the catalyst was used seven times without any decrease in its activity.<sup>82</sup>

**2.6.8. Synthesis and application of magnetic Fe<sub>3</sub>O<sub>4</sub>/CS/COF/Cu.** After the preparation of an FeCl<sub>3</sub>·6H<sub>2</sub>O solution in ethylene glycol at room temperature, chitosan, sodium acetate,

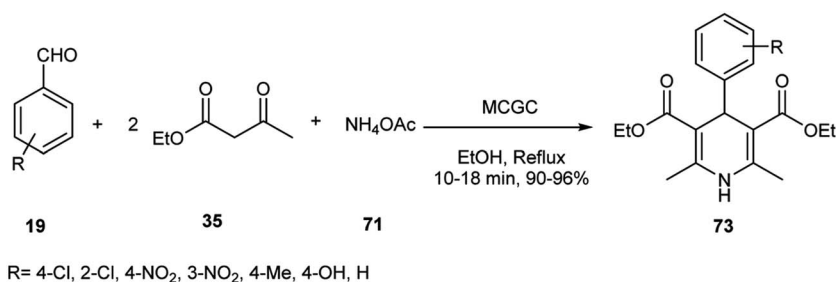


Scheme 62 Synthesis of magnetic cyanoguanidine-modified chitosan (MCGC).

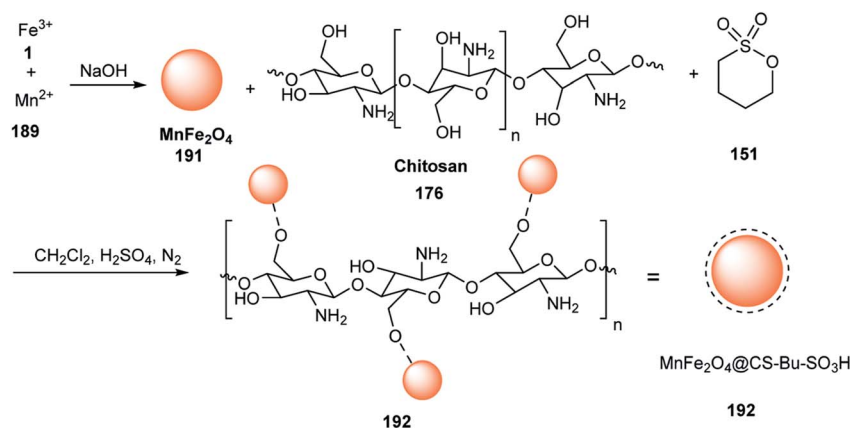
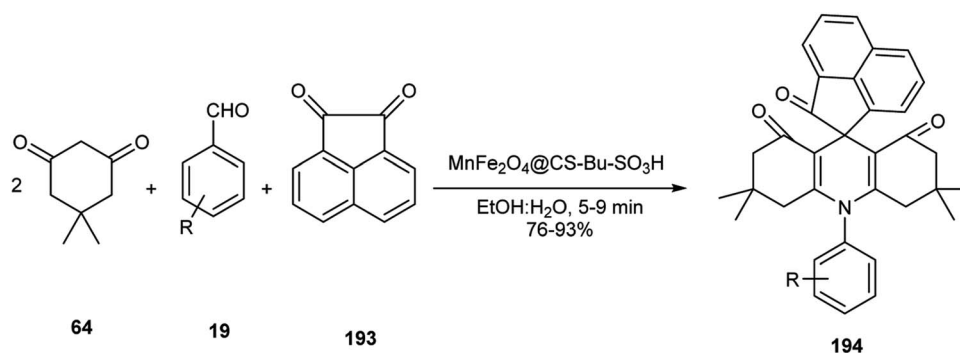


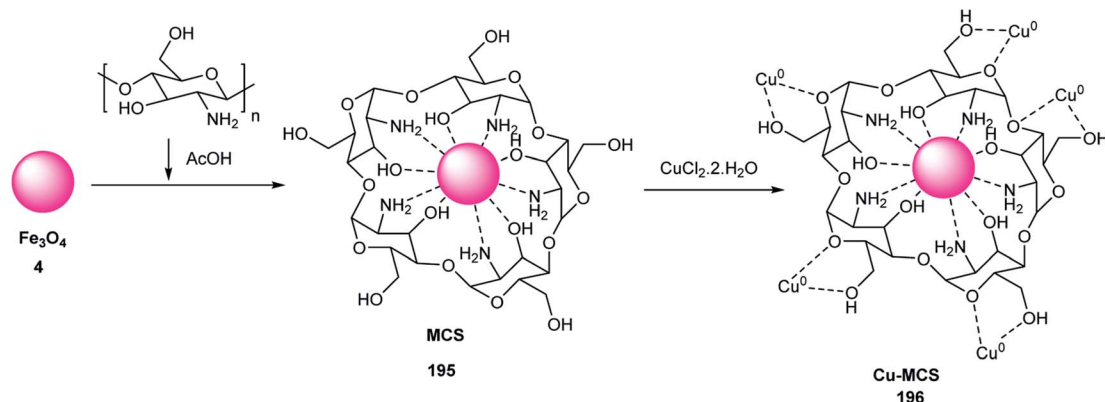


Scheme 63 Synthesis of benzimidazoquinazoline derivatives.

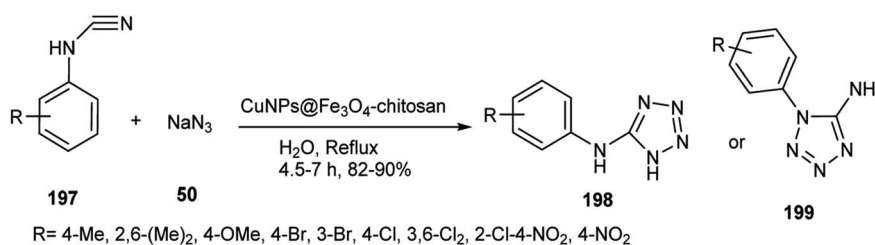


Scheme 64 Synthesis of 1,4-dihydropyridines.

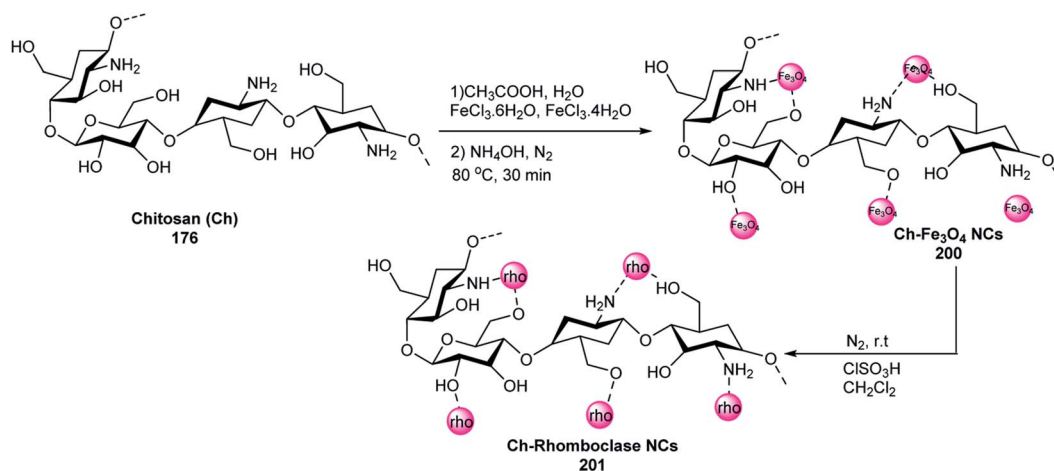
Scheme 65 Synthesis of MnFe<sub>2</sub>O<sub>4</sub>-CS-Bu-SO<sub>3</sub>H 192.Scheme 66 Synthesis of spiro[acenaphthylene-1,9'-acridine] triones 194 in the presence of MnFe<sub>2</sub>O<sub>4</sub>@CS-Bu-SO<sub>3</sub>H NPs.



Scheme 67 Synthesis of Cu-MCS.



Scheme 68 Synthesis of various tetrazoles 198 or 199 using Cu-MCS.



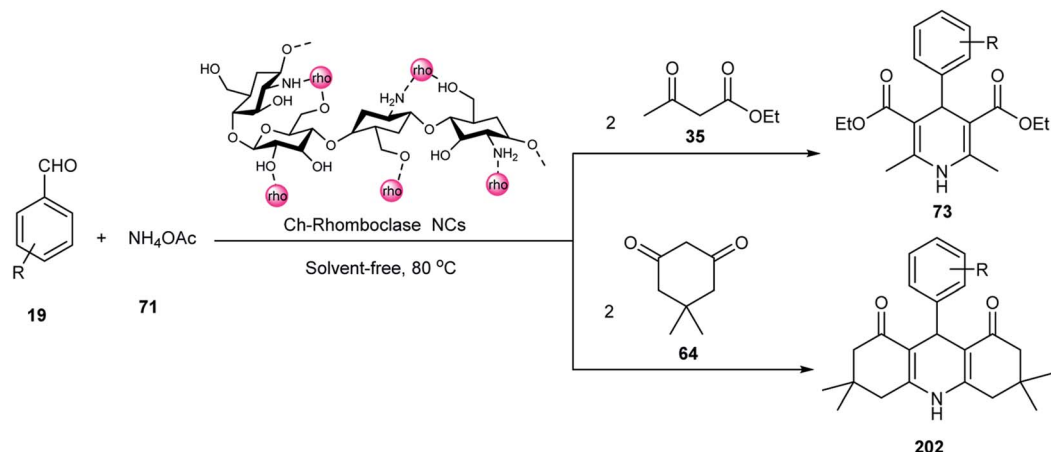
Scheme 69 Synthesis of Ch-rhomboclase NCs 201.

and ethylenediamine were added to it. Then, this mixture was placed in a Teflon-lined autoclave and heated at 200 °C for 8 h to obtain Fe<sub>3</sub>O<sub>4</sub>/CS 205, which was dispersed in DMSO under ultrasound irradiation to give CS-coated Fe<sub>3</sub>O<sub>4</sub>, followed by mixing with melamine 63 and terephthalaldehyde 203. The obtained mixture was transferred in a Teflon-lined autoclave at 180 °C for 12 h to obtain Fe<sub>3</sub>O<sub>4</sub>/CS/COF 206, which was reacted with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in EtOH under reflux conditions and

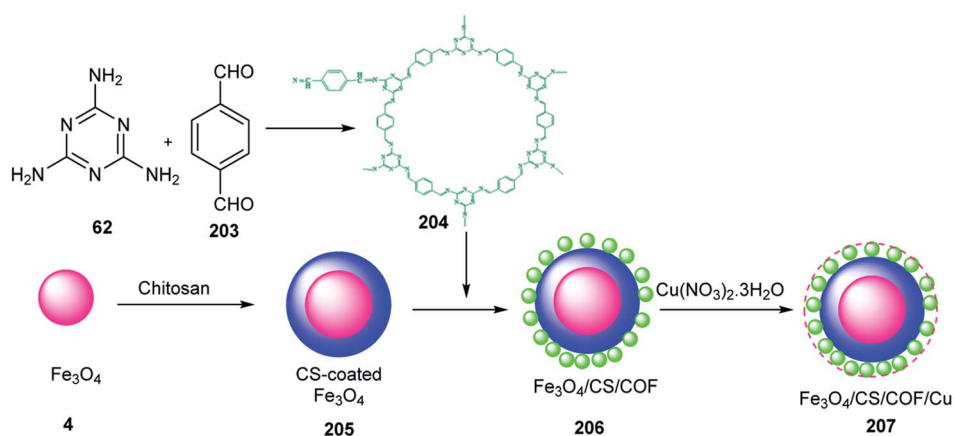
argon atmosphere for 24 h to generate Fe<sub>3</sub>O<sub>4</sub>/CS/COF/Cu 207 (Scheme 71).<sup>83</sup>

The catalytic activity of Fe<sub>3</sub>O<sub>4</sub>/CS/COF/Cu 207 was tested in the synthesis of polyhydroquinolines 72 *via* the Hantzsch reaction of aldehydes 19, dimedone 64, ammonium acetate 71, and ethyl acetoacetate 35 (Scheme 72). Fe<sub>3</sub>O<sub>4</sub>/CS/COF/Cu with two sites including a Lewis acid (Cu<sup>2+</sup>) and Lewis base (imine) catalyzed the Hantzsch reaction, which was used five times without a decrease in its activity.<sup>83</sup>





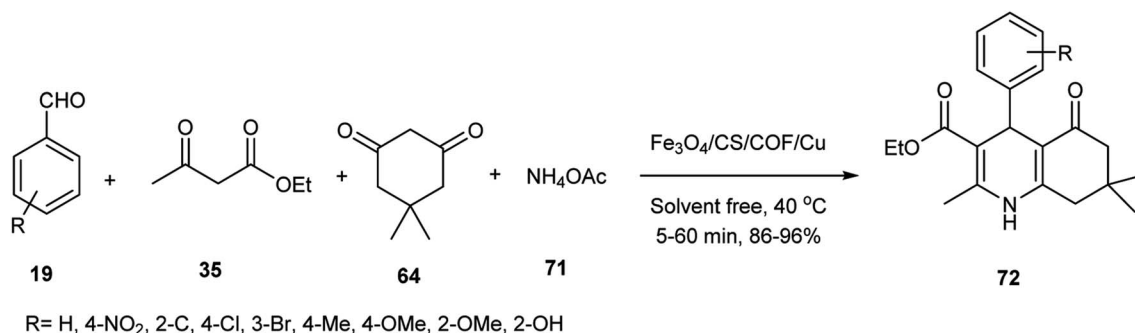
Scheme 70 Synthesis of 1,4-dihydropyridine derivatives 73 or 202.

Scheme 71 Synthesis of the  $\text{Fe}_3\text{O}_4/\text{CS}/\text{COF}/\text{Cu}$ .

## 2.7. Synthesis and application of magnetic $\text{ZnS}/\text{CuFe}_2\text{O}_4/\text{agar}$

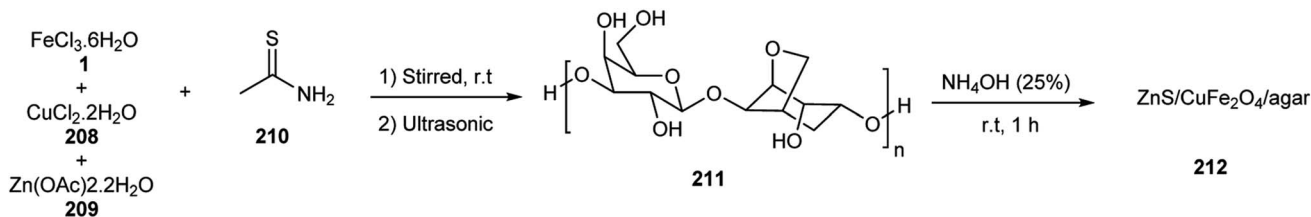
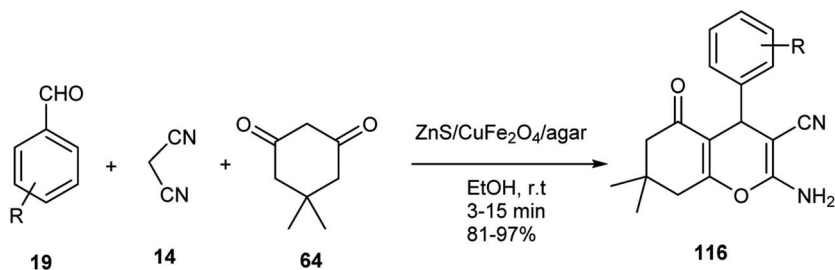
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  1,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  208,  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  209, and thioacetamide were dissolved in distilled  $\text{H}_2\text{O}$ . Then, agar 211 and ammonia solution were added to the reaction mixture to obtain  $\text{ZnS}/\text{CuFe}_2\text{O}_4/\text{agar}$  212 (Scheme 73).<sup>84</sup>

The catalytic activity of  $\text{ZnS}/\text{CuFe}_2\text{O}_4/\text{agar}$  212 was examined in the reaction of dimedone 64, malononitrile 14, and aldehydes 19 to synthesize 2-amino-tetrahydro-4H-chromene-3-carbonitriles 116 (Scheme 74). The carbonyl groups were activated in the presence of  $\text{ZnS}/\text{CuFe}_2\text{O}_4$  via interaction with the hydroxyl groups of agar and Zn metal as a Lewis acid. The catalyst was reused five times with no reduction in its activity.<sup>84</sup>

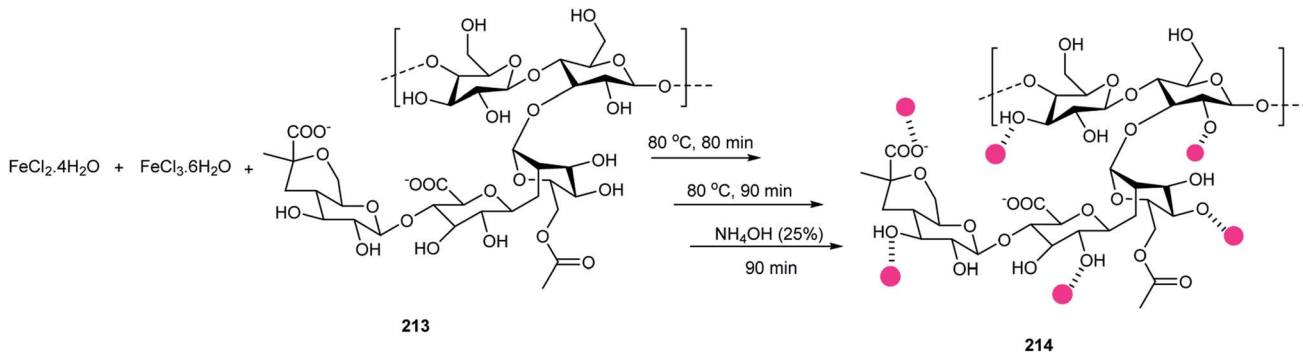
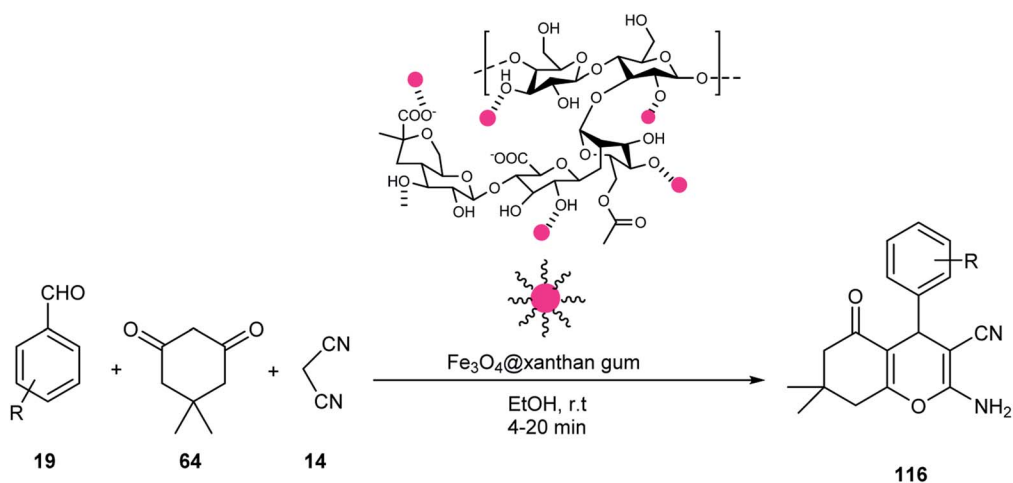


Scheme 72 Synthesis of polyhydroquinoline derivatives via Hantzsch reaction.



Scheme 73 Synthesis of ZnS/CuFe<sub>2</sub>O<sub>4</sub>/agar **212**.

R = 4-NO<sub>2</sub>, 3-NO<sub>2</sub>, 2-Cl, 3-Cl, 4-Cl, 3-Me, 4-Me, 4-CH(Me)<sub>2</sub>, 2-OMe, 3-OMe, 4-OMe, 3,4,5-(OMe)<sub>3</sub>, 3-OH, 4-OH, 2,4-Cl<sub>2</sub>

Scheme 74 Synthesis of 2-amino-tetrahydro-4*H*-chromene-3-carbonitrile derivatives.Scheme 75 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@xanthan gum **214**.

R = 2-Cl, 4-Cl, 2,4-Cl<sub>2</sub>, 2,6-Cl<sub>2</sub>, 2-Br, 4-CN, 3-Me

Scheme 76 Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives **116** using Fe<sub>3</sub>O<sub>4</sub>@xanthan gum.

## 2.8. Synthesis and application of magnetic Fe<sub>3</sub>O<sub>4</sub>@xanthan gum

NH<sub>4</sub>OH solution was added to a mixture of the FeCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O (1 : 2), and an aqueous suspension of xanthan gum 213 to give Fe<sub>3</sub>O<sub>4</sub>@xanthan gum 214 (Scheme 75).<sup>85</sup>

Fe<sub>3</sub>O<sub>4</sub>@xanthan gum was applied in the synthesis of 2-amino-3-cyano-4H-pyran derivatives 116 via the reaction of aldehydes 19, dimedone 64, and malononitrile 14 in EtOH (Scheme 76). The model reaction was performed about nine times and the yields did not decrease. This reaction was accomplished in the presence of Fe<sub>3</sub>O<sub>4</sub> after 45 min in 30% yield. It was shown that Fe<sub>3</sub>O<sub>4</sub>@xanthan gum activated the carbonyl groups via hydrogen bonding, which was more effective than Fe<sub>3</sub>O<sub>4</sub>.<sup>85</sup>

## 3. Conclusion

Many bio-polymers can be obtained from natural sources. According to the importance of green chemistry in organic reactions, in this review, the application of bio-polymers as a catalyst in multicomponent reactions was grouped and summarized. Herein, we highlighted the immobilization of magnetic nanoparticles with bio-polymers. Due to the excellent properties of magnetic nano-catalysts, including their non-toxic nature, high surface area, simple preparation, easy surface modification, and simple separation, these systems have been applied as catalysts in multicomponent reactions. Various organic compounds such as bio-polymers were used for the modification of magnetic nanoparticles. Bio-polymers have various advantages such as biodegradable, biocompatible, and heat-resistant nature. Therefore, herein, their synthesis and catalytic activities in multicomponent reactions were studied. We believe that this article will guide researchers in the design and synthesis of various compounds according to green chemistry. Magnetic nanocomposites have many applications in various fields including, drug delivery, solar cells, chemical sensors, water treatment, biomedical sensors, and catalysts. The importance of these topics could be discussed as a review article in the future.

## Conflicts of interest

There are no conflicts to declare.

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