Sulfonic acid functionalized CoFe$_2$O$_4$ magnetic nanocatalyst for the synthesis of benzimidazoles and benzothiazoles

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A simple and efficient method for the synthesis of substituted benzimidazole and benzothiazole using sulfonic acid functionalized cobalt ferrite magnetic nanocatalyst has been developed. The synthesis is achieved via condensation of o-phenylenediamine or 2-amino thiophenol and aldehydes in ethanol at room temperature. The catalyst can be easily recovered using an external magnet and reused for at least seven catalytic cycles without significant loss of catalytic activity.

Keywords: Cobalt ferrite, magnetic nanoparticles, heterogeneous catalyst, benzimidazoles, benzothiazoles

The five-member aromatic heterocyclic rings bearing C=N bond resembles the basic structural unit of most pharmaceutical and natural compounds which includes benzimidazoles, benzothiazoles and benzoaxazole$^{1-3}$. These heterocycles represent a kind of privileged substructure, which has potential to establish strong interaction with different proteins and enzymes$^4$. Thus these compounds find wide application as polymers, enzyme inhibitors, building blocks in natural products, drugs and dyes$^{5,6}$. They possess a wide variety of biological properties such as antiulcer, antiviral, antihypertensive, antifungal, anticancer and antihistaminic activities$^{7-14}$. Omeprazole (antiulcer), telmisartan (antihypertensive), astemizole (antihistaminic), albendazole (anthelmintic), lansoprazole, rabeprazole, bendazol, and bendamustine are some of the commercially available benzimidazole-based drugs that find application in different therapeutic areas$^{15}$. Extensive use of these heterocycles makes an important challenging area for research for the development of various synthetic methodologies that are economical and environment friendly.

The traditional synthetic method involves the condensation of substituted o-phenylenediamine or 2-aminothiophenol with aldehydes$^{16,18}$. Various reports have been found using orthoesters$^{19,20}$, carboxylic acid$^{21-23}$, alcohols$^{24}$ or acid chlorides$^{25}$ instead of aldehydes. Although various catalysts including metal based heterogeneous catalysts have been reported on synthesis of these two heterocycles, but most reports suffer from some disadvantages like longer reaction times, high temperature, formation of side products, use of expensive and hazardous catalyst, leaching problem, heavy metal toxicity, etc. These limitations of the synthetic methods compel the researchers towards the search for some better catalysts and methodologies that are environmentally benign in terms of being metal free, reusable, more selective and requiring milder reaction conditions for synthesis of benzimidazoles and benzothiazoles.

In recent times, several catalysts and reagents such as Na$_2$S$_2$O$_7$, FeCl$_3$, 6H$_2$O$^{27}$, Zn-proline$^{28}$, ZrCl$_4$, Phl(OAc)$_2$$_{30}$, CoCl$_2$, 6H$_2$O$^{31}$, MgCl$_2$, 6H$_2$O$^{32}$, sodium perborate$^{33}$, Sc(OTf)$_3$, In(OTf)$_3$, Cu(OTf)$_2$, TiCl$_4$, OTf$^{35,36}$, sulfamic acid$^{38}$, nano In$_2$O$_3$, iron(III)sulfate-silica$^{39}$, MnFe$_2$O$_4$, cetyltrimethylammonium bromide$^{42}$, trichloroisocyanuric acid$^{43}$, HClO$_4$/PANI$^{44}$, Bakers’ yeast$^{45}$, SDS$^{46}$, glucose oxidase–peroxidase$^{47}$, Dowex 50W$^{48}$, Montmorillonite K-10$^{49}$, silica sulfuric acid$^{50}$, VOSO$_4$, CuI nanoparticles$^{6}$, etc. have been reported for the synthesis of the heterocycles. Recently, we have reported the synthesis of both benzimidazoles and benzothiazoles by using sulfonic acid functionalized activated carbon as catalyst$^{51}$. In the last few years, magnetic nano particle derived materials were used as efficient catalysts for various organic transformations$^{52}$. In the present work, we intend to report the synthesis of the heterocycles using cobalt ferrite magnetic nanocatalyst. Magnetic nanocatalysts are gaining popularity among the scientific
community because of their efficiency and the ease of recovery and reuse via a simple magnetic decantation. However, to the best of our knowledge, there is no report in the literature on the use of cobalt ferrite magnetic nano catalyst for the synthesis of benzimidazoles and benzothiazoles. In continuation of our work on the use of magnetic nanocatalysts we report herein an efficient method for the synthesis of benzimidazoles and benzothiazoles at ambient temperature from substituted o-phenylenediamine and 2-aminothiophenol in presence of sulfonic acid functionalized-cobalt ferrite (CoFe$_2$O$_4$@SiO$_2$–SO$_3$H) nanoparticles (Figure 1) without using any additives.

**Results and Discussion**

**Synthesis of CoFe$_2$O$_4$@SiO$_2$–SO$_3$H (CF-SA) catalyst**

The catalyst was synthesized by following the previously reported procedure (Scheme 1). We have also utilized sulfonic acid functionalized CoFe$_2$O$_4$ (CF) magnetic nanoparticles as catalyst for the synthesis of $\alpha,\alpha'$-dibromoketones from alkynes. Initially, cobalt ferrite magnetic core was synthesized by following the method reported by us. Chlorosulfonic acid was used as a source for sulfonic acid group, which was structurally over the surface of cobalt ferrite-silica composite. The resulted MNPs were subjected to repetitive washing with ethanol and water using centrifugation technique (5000 rpm) to remove the excess of unreacted acid group. Finally, the magnetic composite was separated with the help of an external magnet and dried in an oven (100°C) to get a brown powder of CoFe$_2$O$_4$@SiO$_2$–SO$_3$H (designated as CF-SA).

**Characterization of CoFe$_2$O$_4$@SiO$_2$–SO$_3$H (CF-SA)**

The sulfonic acid functionalized - cobalt ferrite were prepared by following reported procedure and characterized by XRD, SEM, TEM, VSM and EDX analysis. In addition to above mentioned characterization techniques, BET surface area analysis and Boehm titration were performed to determine the total surface acidity of the synthesized catalyst.

The surface area of the cobalt ferrite magnetic nanomaterial was determined by nitrogen adsorption desorption method. The BET isotherm of the material is shown in Figure 2. Isotherms were found to be of type II according to IUPAC classification. A comparison of surface area of the precursor cobalt ferrite and CoFe$_2$O$_4$@SiO$_2$–SO$_3$H (Table 1) indicates that surface functionalization led to lowering of surface area of the material. The decrease in surface area was found to be 81.2 m$^2$/g.

![Figure 1 — CoFe$_2$O$_4$@SiO$_2$–SO$_3$H nanoparticle](image1.png)

![Figure 2 — N$_2$ adsorption desorption isotherm of the CoFe$_2$O$_4$@SiO$_2$–SO$_3$H MNPs](image2.png)

![Scheme 1](image3.png)
area may be due to functionalization of the surface of the precursor ferrite material. Figure 3 represents the SEM image of the synthesized catalyst.

The surface acidity of the catalyst was determined by using Boehm titration method\textsuperscript{44}. For this, a specific amount of the catalyst (0.15 g) was treated with 0.05 N solution of NaOH (30 mL) for 24 h under sealed condition. Thereafter, the mixture was filtered and the filtrate (10 mL) was titrated against 0.05 N HCl. This experiment indicated that the parent cobalt ferrite had 0.59 mmol/g of surface acidic groups, which increased up to 1.62 mmol/g after surface modification with sulfonic acid groups.

**Catalytic activity of CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–SO\textsubscript{3}H catalyst for the synthesis of benzimidazoles and benzothiazoles**

Initial experiments on the study of the catalytic activity of CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–SO\textsubscript{3}H material was carried out for the synthesis of benzimidazoles by treating 4-methylbenzaldehyde (1 mmol) with o-phenylenediamine (1.1 mmol) in presence of the catalyst CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–SO\textsubscript{3}H. Results are presented in Table II. When the reaction was carried out in presence of 10 wt % of CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–SO\textsubscript{3}H in ethanol, the yield obtained was 95% within 45 min of reaction time. Effect of different solvents for the synthesis of imidazole derivatives was studied for further evaluation. The reaction was carried out using solvents such as ethanol, methanol, water and acetonitrile. In the absence of catalyst, the reaction did not produce good yield even after a long duration, but a sharp increase in yield was observed within a short period of time after the addition of catalyst. Reaction in aqueous medium also produced an impressive yield of 81%. The reactivity profile for the reaction was found to be best both in ethanol and acetonitrile. Considering the environmental issues and reactivity profile, ethanol was chosen as the most suitable solvent for this reaction. The reaction was also studied with varying catalyst concentrations. When the reaction was carried out by using 5 wt% of catalyst, the yield of the reaction was found to decline to 80%. Control experiments were also performed with cobalt ferrite and cobalt ferrite-silica composite for about 5 h at RT which produced unsatisfactory yield. These factors ascertain the need of the CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–

![Figure 3 — SEM image of CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–SO\textsubscript{3}H MNPs](image)

**Table I — Surface area of different materials**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{BET}) (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe\textsubscript{2}O\textsubscript{4} MNPs (CF)</td>
<td>82.8</td>
</tr>
<tr>
<td>CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–SO\textsubscript{3}H MNPs (CF-SA)</td>
<td>71.2</td>
</tr>
</tbody>
</table>

**Table II — Optimization of the reaction conditions for benzimidazole synthesis**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (wt %)</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Yield (%) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF-SA (10)</td>
<td>Ethanol</td>
<td>45</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>CF-SA (10)</td>
<td>Methanol</td>
<td>45</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>CF-SA (10)</td>
<td>(\text{H}_2\text{O})</td>
<td>45</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>CF-SA (10)</td>
<td>Acetonitrile</td>
<td>45</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>No Catalyst</td>
<td>Ethanol</td>
<td>300</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>CF-SA (5)</td>
<td>Ethanol</td>
<td>45</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>CF (10)</td>
<td>Ethanol</td>
<td>300</td>
<td>17</td>
</tr>
<tr>
<td>8</td>
<td>CoFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2} (10)</td>
<td>Ethanol</td>
<td>300</td>
<td>20</td>
</tr>
</tbody>
</table>

Reaction conditions: 4-methylbenzaldehyde (1 mmol), o-phenylenediamine (1.1 mmol), ethanol (3 mL), RT, \(^a\) Isolated yield after column chromatography.
SO$_3$H catalyst for the reaction under ambient reaction conditions. After determining the most suitable reaction condition, the method was further extended for various substituted aldehyds. The results are shown in Table III. Aldehydes with both electron withdrawing and electro donating substituent were used successfully for synthesis of corresponding imidazole derivatives.

**Table III — Substrate scope for synthesis of benzimidazoles**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = H, R$_1$ = H (1a, 45 min, 91%)</td>
<td>R = OCH$_3$, R$_1$ = H (1p, 45 min, 92%)</td>
<td>CoFe$_2$O$_4$/SiO$_2$/SO$_3$H (10 wt%), Ethanol (3 mL), rt</td>
</tr>
<tr>
<td>R = CH$_3$, R$_1$ = H (1b, 45 min, 95%)</td>
<td>R = OH, R$_1$ = H (1q, 60 min, 85%)</td>
<td></td>
</tr>
<tr>
<td>R = OCH$_3$, R$_1$ = H (1c, 45 min, 93%)</td>
<td>R = OCH$_3$, R$_1$ = OCH$_3$ (1r, 50 min, 91%)</td>
<td></td>
</tr>
<tr>
<td>R = Cl, R$_1$ = H (1d, 60 min, 85%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = F, R$_1$ = H (1e, 50 min, 89%)</td>
<td>R = F, R$_1$ = H (1f, 60 min, 82%)</td>
<td></td>
</tr>
<tr>
<td>R = Br, R$_1$ = H (1f, 60 min, 82%)</td>
<td>R = NO$_2$, R$_1$ = H (1g, 45 min, 85%)</td>
<td></td>
</tr>
<tr>
<td>R = NO$_2$, R$_1$ = H (1g, 45 min, 85%)</td>
<td>R = NO$_2$, R$_1$ = H (1h, 60 min, 83%)</td>
<td></td>
</tr>
<tr>
<td>R = F, R$_1$ = H (1h, 60 min, 83%)</td>
<td>R = OCH$_3$, R$_1$ = H (1i, 45 min, 91%)</td>
<td></td>
</tr>
<tr>
<td>R = Cl, R$_1$ = OCH$_3$ (1j, 60 min, 80%)</td>
<td>R = NO$_2$, R$_1$ = H (1j, 60 min, 80%)</td>
<td></td>
</tr>
<tr>
<td>R = Cl, R$_1$ = OCH$_3$ (1j, 60 min, 80%)</td>
<td>R = NO$_2$, R$_1$ = H (1j, 60 min, 80%)</td>
<td></td>
</tr>
<tr>
<td>(1k, 65 min, 72%)</td>
<td>(1k, 65 min, 72%)</td>
<td></td>
</tr>
<tr>
<td>R = H, R$_1$ = Cl (1l, 60 min, 87%)</td>
<td>R = H, R$_1$ = Cl (1l, 60 min, 87%)</td>
<td></td>
</tr>
<tr>
<td>R = Br, R$_1$ = Cl (1m, 60 min, 93%)</td>
<td>R = CH$_3$, R$_1$ = Cl (1n, 45 min, 95%)</td>
<td></td>
</tr>
<tr>
<td>R = CH$_3$, R$_1$ = Cl (1n, 45 min, 95%)</td>
<td>R = OCH$_3$, R$_1$ = CH$_3$ (1o, 45 min, 88%)</td>
<td></td>
</tr>
<tr>
<td>R = OCH$_3$, R$_1$ = Cl (1o, 45 min, 88%)</td>
<td>R = H, R$_1$ = Cl (1o, 60 min, 91%)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reaction condition: aldehyde (1 mmol), o-phenylenediamine, substituted o-phenylenediamine (1.1 mmol), catalyst 10 wt%, $^b$Isolated yield after chromatographic purification
in excellent yield. Other aldehydes such as 9-anthracene carboxaldehyde, 2-naphthaldehyde and cinnamaldehyde were also found to react with excellent yield under this catalytic condition. However, in case of aliphatic aldehyde such as n-octanal, the reaction yield was found to be slightly lower.

After getting success in synthesizing benzimidazoles derivatives, we have extended the same process for the synthesis of benzothiazoles. The reaction was carried out under the same optimized condition as in the case of benzimidazoles by treating 2-aminothiophenol with various aldehydes in presence of 10 wt % of catalyst in ethanol at RT. Results are summarized in Table IV. It can be seen from the table that various benzothiazoles could be produced under the influence of CoFe₂O₄@SiO₂–SO₃H as catalyst. Excellent yield of the product was obtained irrespective of the nature of aldehyde and 2-aminothiophenol. However, slightly lower yield was obtained in case of aliphatic aldehyde.

From Table III and Table IV, it can clearly be observed that CoFe₂O₄@SiO₂–SO₃H is a very efficient catalyst for synthesis of both the heterocycles. The increase in acid capacity has a vital role for the enhanced catalytic activity of the surface modified cobalt ferrite in comparison to the cobalt ferrite itself.

Catalyst reusability
After the reaction, the catalyst was separated from the reaction mixture using an external magnet, washed with ethyl acetate and ethanol and then dried in an oven at 100°C for 1 h. The recovered catalyst was further used for the cyclization reaction between 4-methyl benzaldehyde and o-phenylenediamine to check the catalytic activity. The catalyst could be reused for at least seven cycles without significant change of it's activity (Figure 4).

Experimental Section
All the chemicals used were purchased from Himedia Chemicals (India) and Sigma-Aldrich.

Table IV — Substrate scope for synthesis of benzothiazoles

<table>
<thead>
<tr>
<th>R</th>
<th>R₁</th>
<th>Reaction condition: aldehyde (1 mmol), o-amino thiophenol (1.1 mmol), catalyst 10 wt%, Isolated yield after chromatographic purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>(2a, 45 min, 92%)</td>
</tr>
<tr>
<td>CH₃</td>
<td>H</td>
<td>(2b, 45 min, 95%)</td>
</tr>
<tr>
<td>OCH₃</td>
<td>H</td>
<td>(2c, 45 min, 95%)</td>
</tr>
<tr>
<td>F</td>
<td>H</td>
<td>(2d, 40 min, 90%)</td>
</tr>
<tr>
<td>Br</td>
<td>H</td>
<td>(2e, 60 min, 85%)</td>
</tr>
<tr>
<td>OCH₃</td>
<td>H</td>
<td>(2f, 60 min, 88%)</td>
</tr>
<tr>
<td>R</td>
<td>R₁</td>
<td>(2g, 45 min, 92%)</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>(2h, 60 min, 82%)</td>
</tr>
<tr>
<td>N</td>
<td>N₂</td>
<td>(2i, 60 min, 84%)</td>
</tr>
<tr>
<td>N</td>
<td>O₂</td>
<td>(2j, 60 min, 78%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2k, 60 min, 85%)</td>
</tr>
</tbody>
</table>
230-400 mesh silica purchased from Merck and SRL chemicals were used for column chromatography. X-ray powder diffraction (XRD) patterns were recorded using Bruker D-8 Advance X-ray diffractometer. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu, IR affinity-1 spectrophotometer in presence of aqueous ammonia. TEOS was used as tetraethyl orthosilicate (TEOS) in presence of aqueous silica source to form a shell to protect and stabilize CoFeO$_4$ MNP's. Thereafter 0.1 mL of chlorosulfonic acid was added drop-wise to the dispersed composite (CoFeO$_4$@SiO$_2$ in dimethoxyethane) under ice cooled condition to yield the desired CoFeO$_4$@SiO$_2$–SO$_3$H composite having sulfonic acid surface functionality.

**General procedure for the synthesis of benzimidazole**

A mixture of aliphatic and aromatic aldehyde (1 mmol), o-phenylenediamine (1.1 mmol), catalyst CoFeO$_4$@SiO$_2$–SO$_3$H (10 wt%) in ethanol was stirred at RT for specified period as indicated in Table III. After completion of reaction as indicated by the TLC, the catalyst was separated by using an external magnet and the reaction mixture was concentrated under vacuum. The crude residue was purified by using column chromatography using silica gel (230-400 mesh) using a combination of ethyl acetate and petroleum ether as eluent.

**2-Phenyl-1H-benzimidazole, 1a:** m.p.287-290°C (lit. 290-291°C). $^1$H NMR (300 MHz, CDCl$_3$+DMSO-$_d_6$): $\delta$ 7.20-7.23 (m, 2H), 7.43 (d, $J = 6.3$ Hz, 2H), 7.62-7.65 (m, 2H), 8.19 (t, $J = 5.7$ Hz, 2H).

**2-p-Tolyl-1H-benzimidazole, 1b:** m.p.261-264°C (lit. 262-265°C). $^1$H NMR (300 MHz, CDCl$_3$+DMSO-$_d_6$): $\delta$ 2.33 (s, 3H), 7.18-7.23 (m, 4H), 7.59-7.62 (m, 2H), 8.05 (d, $J = 8.1$ Hz, 2H).

**2-(4-Methoxyphenyl)-1H-benzimidazole, 1c:** m.p.224-226°C (lit. 225-226°C). $^1$H NMR (300 MHz, CDCl$_3$+DMSO-$_d_6$): $\delta$ 3.76 (s, 3H), 6.90 (d, $J = 8.7$ Hz, 2H), 7.13-7.16 (m, 2H), 7.53-7.56 (m, 2H), 8.09 (d, $J = 8.7$ Hz, 2H).

**2-(4-Chlorophenyl)-1H-benzimidazole, 1d:** m.p.286-288°C (lit. 288-290°C). $^1$H NMR (300 MHz, CDCl$_3$+DMSO-$_d_6$): $\delta$ 7.22 (s, 2H), 7.62 (d, $J = 7.8$ Hz, 4H), 8.17 (d, $J = 7.5$ Hz, 2H).

Figure 4 — Reusability of the catalyst
2-(4-Fluorophenyl)-1H-benzimidazole, 1e: m.p.248-252°C (lit. 251°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 7.08 (t, J = 8.7 Hz, 2H), 7.18-7.21 (m, 2H), 7.57-7.60 (m, 2H), 8.14-8.19 (m, 2H).

2-(4-Bromophenyl)-1H-benzimidazole, 1f: m.p. 257-258°C (lit. 251°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 7.20-7.25 (m, 1H), 7.30-7.36 (m, 3H), 7.45 (t, J = 7.5 Hz, 1H), 7.52 (s, 1H), 7.86 (s, 1H), 8.26 (t, J = 7.8 Hz, 2H), 8.37 (d, J = 8.7 Hz, 2H).

2-(2-Fluorophenyl)-1H-benzimidazole, 1h: m.p. 225°C (lit. 232-235°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 7.20-7.25 (m, 1H), 7.30-7.36 (m, 3H), 7.45 (t, J = 7.5 Hz, 1H), 7.52 (s, 1H), 7.86 (s, 1H), 8.52 (t, J = 7.5 Hz, 1H), 10.02 (s, 1H).

2-(2-Methoxyphenyl)-1H-benzimidazole, 1i: m.p. 163-165°C (lit. 157-158°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 3.99 (s, 3H), 6.97-7.06 (m, 2H), 7.16-7.19 (m, 2H), 7.36 (t, J = 8.7 Hz, 1H), 7.60-7.64 (m, 2H).

2-(3-Nitrophenyl)-1H-benzimidazole, 1j: m.p. 196-199°C (lit. 203-205°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 7.38-7.24 (m, 2H), 7.65 (t, J = 7.8 Hz, 3H), 8.24 (d, J = 7.8 Hz, 1H), 8.63 (d, J = 7.5 Hz, 1H), 9.09 (s, 1H).

2-Heptyl-1H-benzimidazole, 1k: m.p. 134-138°C (lit. 138-140°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 0.80-0.87 (m, 3H), 1.21-1.35 (m, 8H), 1.82-1.89 (m, 2H), 2.99 (t, J = 8.1 Hz, 2H), 6.16 (s, 1H), 7.23-7.27 (m, 2H), 7.60 (s, 2H).

5,6-Dichloro-2-phenyl-1H-benz[d]imidazole, 1l: m.p. 214-215°C. 1H NMR (300 MHz, CDCl3, DMSO-d6): δ 7.51-7.60 (m, 3H), 7.75 (s, 1H), 7.92 (d, J = 7.5 Hz, 1H), 8.13-8.16 (m, 2H), 13.28 (s, 1H).

5,6-Dichloro-4-p-tolyl-1H-benz[d]imidazole, 1n: m.p. 220-221°C (lit. 223-225°C). 1H NMR (300 MHz, DMSO-d6): δ 7.36 (d, J = 8.7 Hz, 2H), 7.81 (s, 2H), 8.03 (d, J = 6 Hz, 2H), 13.19 (s, 1H).

5,6-Dichloro-2-(4-methoxyphenyl)-1H-benz[d]imidazole, 1o: m.p. 216-217°C (lit. 218-220°C). 1H NMR (300 MHz, DMSO-d6): δ 3.82 (s, 3H), 7.09 (d, J = 9 Hz, 2H), 7.69 (s, 1H), 7.85 (s, 1H), 8.08 (d, J = 9.3 Hz, 2H), 13.09 (s, 1H).

2-(3,4-Dimethoxyphenyl)-1H-benzimidazole, 1p: m.p. 186-188°C (lit. 180-181°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 3.86 (s, 6H), 6.87 (d, J = 8.4 Hz, 1H), 7.16-7.20 (m, 2H), 7.56-7.59 (m, 2H), 7.71 (d, J = 8.1 Hz, 1H), 7.79 (s, 1H).

4-(1H-Benzimidazol-2-yl) benzene-1,2-diol, 1q: m.p. 255-257°C (lit. 258°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 6.69 (d, J = 8.4 Hz, 1H), 6.90-6.93 (m, 2H), 7.30-7.33 (m, 3H), 7.46 (s, 1H).

2-(1H-Pyrrol-2-yl)-1H-benzimidazole, 1r: m.p. 275-277°C (lit. 273-275°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 6.11 (t, J = 5.4 Hz, 1H), 6.87 (s, 1H), 6.93 (d, J = 3 Hz, 1H), 7.04-7.08 (m, 2H), 7.36-7.40 (m, 2H), 11.59 (s, 1H).

2-(Anthracen-9-yl)-1H-benzimidazole, 1s: m.p. 255°C (lit. 261-263°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 7.33-7.44 (m, 6H), 7.61 (d, J = 7.8 Hz, 2H), 7.72-7.75 (m, 2H), 7.98 (d, J = 8.4 Hz, 2H), 8.52 (s, 1H).

2-(Naphthalen-1-yl)-1H-benzimidazole, 1t: m.p. 205-207°C (lit. 212-215°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 7.08-7.10 (m, 2H), 7.35 (s, 2H), 7.52 (s, 2H), 7.68 (d, J = 4.2 Hz, 1H), 7.76 (d, J = 8.1 Hz, 2H), 8.15 (d, J = 8.4 Hz, 1H), 8.58 (s, 1H).

2-(Furan-2-yl)-1H-benzimidazole, 1u: m.p. 284-285°C (lit. 278-283°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 6.44-6.46 (m, 1H), 7.10-7.13 (m, 2H), 7.26 (t, J = 3.3 Hz, 1H), 7.46-7.50 (m, 3H).

2-Stryryl-1H-benzimidazole, 1v: m.p. 200-204°C (lit. 200-202°C). 1H NMR (300 MHz, CDCl3+DMSO-d6): δ 7.04-7.06 (m, 3H), 7.11-7.18 (m, 3H), 7.33-7.40 (m, 4H), 7.57 (d, J = 16.8 Hz, 1H).

6-Methyl-2-phenyl-1H-benz[d]imidazole, 1w: m.p. 244-245°C (lit. 246°C). 1H NMR (300 MHz, CDCl3): δ 2.34 (s, 3H), 7.96 (d, J = 8.4 Hz, 1H), 7.09 (s, 1H), 7.25-7.26 (m, 1H), 7.39-7.60 (m, 3H), 7.99-8.02 (m, 2H), 8.28 (d, J = 7.8 Hz, 1H).

6-Methyl-2-p-tolyl-1H-benz[d]imidazole, 1x: m.p. 104-105°C (lit. 101-103°C). 1H NMR (300 MHz, CDCl3): δ 2.27 (s, 3H), 2.39 (s, 3H), 7.07-7.00 (m, 3H), 7.33 (s, 1H), 7.46 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 7.8 Hz, 2H).

2-(4-Methoxyphenyl)-6-methyl-1H-benz[d]imidazole, 1y: m.p. 165-166°C (lit. 168-170°C). 1H NMR (300 MHz, DMSO-d6): δ 2.39 (s, 3H),
3.81 (s, 3H), 6.97 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 9 Hz, 1H), 7.32-7.43 (m, 2H), 8.07 (d, J = 8.7 Hz, 2H), 12.60 (s, 1H).

5-Chloro-2-phenyl-1H-benzo[d]imidazole, 1z: m.p.216-218°C (lit. 212-214°C). 1H NMR (300 MHz, CDCl3): δ 6.91-6.95 (m, 1H), 7.23-7.29 (m, 5H), 7.90-7.94 (m, 2H), 12.32 (s, 1H).

General procedure for the synthesis of benzimidazole
A mixture of aliphatic and aromatic aldehyde (1 mmol), 2-amino thiophenol (1.1 mmol), catalyst CF-SA (10 wt %) in ethanol was stirred under RT for specified period as indicated in Table IV. After completion of reaction, as indicated by TLC, the catalyst was separated by using an external magnet. The crude residue was purified by using column chromatography using silica gel (230-400 mesh) using a combination of ethyl acetate and petroleum ether as eluent. The catalytic effect on the yield.

2-Phenylbenzothiazole, 2a: m.p.112-115°C (lit. 111-112°C). 1H NMR (300 MHz, CDCl3): δ 6.69 (d, J = 8.4 Hz, 1H), 6.90-6.93 (m, 2H), 7.30-7.33 (m, 3H), 7.46 (s, 1H).

2-p-Tolybenzothiazole, 2b: m.p.82-86°C (lit. 81-83°C). 1H NMR (300 MHz, CDCl3): δ 2.43 (s, 3H), 7.30-7.41 (m, 3H), 7.50 (t, J = 7.8 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.99 (d, J = 7.8 Hz, 2H), 8.07 (d, J = 8.4 Hz, 1H).

2-(4-Methoxyphenyl) benzothiazole, 2c: m.p.125°C (lit. 120-121°C). 1H NMR (300 MHz, CDCl3): δ 3.90 (s, 3H), 7.02 (d, J = 9 Hz, 2H), 7.38 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.7 Hz, 3H).

2-(4-Fluorophenyl) benzothiazole, 2d: m.p.100°C (lit. 100-102°C). 1H NMR (300 MHz, CDCl3): δ 7.20 (t, J = 8.7 Hz, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 8.07-8.13 (m, 3H).

2-(4-Bromophenyl) benzothiazole, 2e: m.p.100°C (lit. 101-102°C). 1H NMR (300 MHz, CDCl3): δ 7.42 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.90-7.98 (m, 3H), 8.08 (d, J = 8.1 Hz, 1H).

2-(2-Fluorophenyl) benzothiazole, 2f: m.p.91-93°C (lit. 95-98°C). 1H NMR (300 MHz, CDCl3): δ 7.23-7.37 (m, 2H), 7.42-7.58 (m, 3H), 7.96 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.50 (t, J = 8.1 Hz, 1H).

2-(2-Methoxyphenyl) benzothiazole, 2g: m.p.108°C (lit. 110-112°C). 1H NMR (300 MHz, CDCl3): δ 4.08 (s, 3H), 7.07-7.18 (m, 2H), 7.37-7.42 (m, 1H), 7.45-7.53 (m, 2H), 7.94 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 8.56 (d, J = 9.6 Hz, 1H).

2-(2,4-Dichlorophenyl) benzothiazole, 2h: m.p.148°C (lit. 151-152°C). 1H NMR (300 MHz, CDCl3): δ 7.40-7.48 (m, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.97 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H).

2-(3-Nitrophenyl) benzothiazole, 2i: m.p.190°C (lit. 194-197°C). 1H NMR (300 MHz, CDCl3): δ 7.46 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 8.1 Hz, 1H), 7.70 (t, J = 8.1 Hz, 1H), 7.96 (d, J = 7.5 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 9.3 Hz, 1H), 8.43 (d, J = 7.5 Hz, 1H), 8.95 (s, 1H).

2-Heptyl-1H-benzothiazole, 2j: 1H NMR (300 MHz, CDCl3): δ 0.88 (t, J = 6.6 Hz, 3H), 1.29-1.48 (m, 8H), 1.82-1.92 (m, 2H), 3.11 (t, J = 9 Hz, 2H), 3.34 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H).

2-(Naphthalen-1-yl) benzothiazole, 2k: m.p.126-128°C (lit. 128-130°C). 1H NMR (300 MHz, CDCl3): δ 7.42 (t, J = 7.5 Hz, 1H), 7.50-7.58 (m, 3H), 7.88-8.00 (m, 4H), 8.13 (d, J = 8.1 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 8.58 (s, 1H).

Conclusion
In conclusion, we have developed an efficient, simple and green method for the synthesis of benzimidazoles and benzothiazoles derivatives using sulfonic acid functionalized cobalt ferrite nanoparticles (CoFe2O4@SiO2–SO3H). The catalytic approach was utilized for a wide range of cyclization reaction with reusable potential without significant effect on the yield. The mild reaction conditions, cost effective, shorter reaction times, non toxic, wide functional group tolerance, high yields make this method suitable for the synthesis of substituted benzimidazoles and benzothiazoles.

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References


