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# Synthesis of novel benzimidazoles and benzothiazoles via furan-2-carboxaldehydes, *o*-phenylenediamines, and 2-aminothiophenol using Cu(II) Schiff-base@$SiO_2$ as a nanocatalyst

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2-(5-Substituted phenyl)furan-2-carboxaldehyde derivatives were prepared by using an efficient copper(II) complex of tetradentate Schiff-base ligand immobilized onto silica as a heterogeneous nanocatalyst [Cu(II) Schiff-base@-$SiO_2$] (5.0 mol%) using anilines, sodium nitrite, and furan-2-carboxaldehyde. Furthermore, attractive di-heteroaryl benzo-fused systems such as benzimidazole and benzothiazole derivatives were synthesized using this nanocatalyst (5.0 mol%) via the reaction of *o*-phenylenediamines and 2-aminothiophenol with 2-(5-substituted phenyl)furan-2-carboxaldehydes in EtOH. The catalyst was characterized by Fourier transform infrared (FT-IR), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), and inductively coupled plasma (ICP) techniques. The advantages of the present catalytic system are short reaction times, mild conditions, good to excellent yields, and low amount of nanocatalyst. Moreover, to the best of our knowledge, this is the first time of using the same catalyst in two steps including synthesis of 2-(5-substituted phenyl)furan-2-carboxaldehyde and benzimidazole or benzothiazole derivatives. In addition, the synthesized catalyst was recycled very well and reused several times without significant loss of its catalytic activity.

**KEYWORDS**
benzimidazole, benzothiazole, copper(II) complex, di-heteroaryl, heterogeneous nanocatalyst

## 1 | INTRODUCTION

Heterocycles are an important class of compounds because of their widespread appearance in drugs, natural products, and biologically active compounds.[1–9] Also, these compounds have reactive sites that allow for further functionalization.[10] Between various kinds of heterocyclic compounds, di-heterocycles benzo-fused systems including benzimidazole and benzothiazole derivatives are more attractive motifs found in a wide range of pharmaceuticals such as Nexium (esomeprazole) antiulcerant (1), PARP-1 inhibitor (2), zopolrestat (for the treatment of diabetes) (3), and aldose reductase inhibitor (4) (Figure 1).[11–14] Moreover, these compounds have unique properties. The basic core structures are used to produce drugs with different properties like anticancer, antimicrobial, anthelmintic, antiulcer, antiallergic, human glucagon receptor antagonistic, and anti-

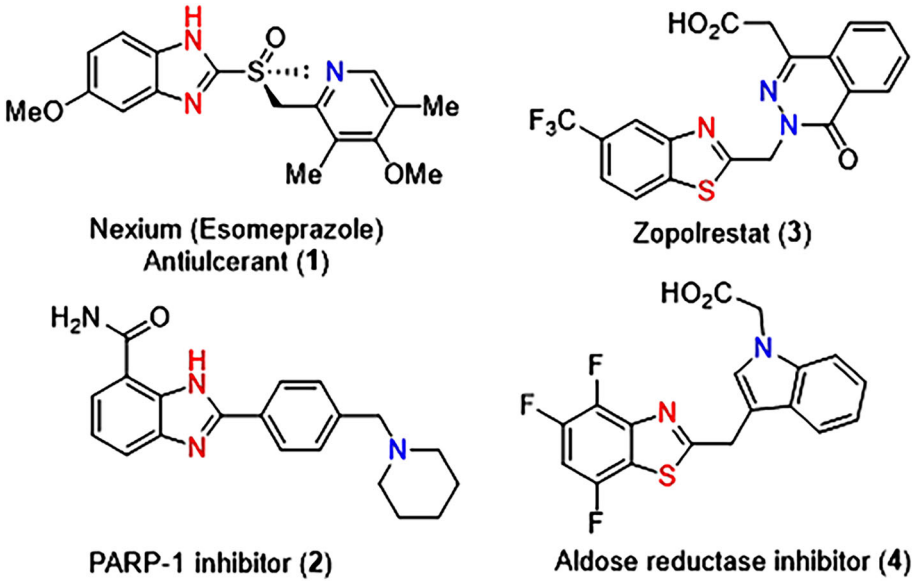



**FIGURE 1** Structures of bioactive substituted benzimidazoles and benzothiazoles

infectives.[15–21] Due to their wide range of applications, various different synthetic paths have been developed using catalytic systems.[22,23]

One of the most common methods for synthesizing benzimidazole and benzothiazole derivatives is through oxidative cyclization reaction between *o*-phenylenediamines and 2-aminothiophenol with benzaldehyde. In recent years, the syntheses of benzimidazoles and benzothiazoles were reported using a plethora of catalysts, such as metal–organic framework (MOF) MIL-101(Cr),[24] $NH_2$-MIL-125(Ti),[25] $MgCl_2$,[26] $Ce(NO_3)_3.6H_2O$,[27] copper metallovesicles (CuMVs),[28] Ni-MCM-41,[29] $Yb(OTf)_3$,[30] $H_2O_2/Fe(NO_3)_3$,[31] vanadium–salen nanoparticles supported on silica,[32] cobalt–salen complex supported on activated carbon,[33] copper nanoparticles on charcoal,[34] $Co^{2+}$ complex of [7-hydroxy-4-methyl-8-coumarinyl]glycine ([Co(MCG)$(H_2O)_3$]),[35] iron-doped multi-walled carbon nanotubes (Fe/MWCNTs),[36] chromium (III)–salen complex nanoparticles on $AlPO_4$,[37] $CoFe_2O_4$@$SiO_2$@PAF-IL,[38] and 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-$NO_2$]C$(NO_2)_3$.[39]

Nowadays, metal catalysts play a vital role in enhancing the life quality of human society and support the global economy. Copper catalysts have some interesting physical and chemical properties such as having a cheap and ubiquitous metal, which is one of the most abundant transition metals present in living systems.[40] Cu-based compounds have been used as catalysts for a wide range of organic transformations such as multicomponent reactions, reduction and oxidation reactions, cross-coupling, click chemistry, C–H functionalization, and oxidative coupling.[41–46] Also, there are various reports about metal complexes stabilized on inorganic supports for the preparation of heterocyclic compounds.[47–58]

Heterogeneous catalytic systems are of particular importance because they demonstrate excellent levels of stability, are easily separated from the reaction mixture by filtration, the catalysts can be reused several times, possess high catalytic activity through increased interaction with reactants, and have lots of application in heterocyclic chemistry and pharmaceutical industry.[59–70]

In continuation of our interest in exploring efficient and diverse copper catalysts for organic processes,[71–78] and as a result of our interest in the preparation of organic compounds,[79–82] in the present study, first, we synthesized and characterized copper(II) complex of tetradentate Schiff-base ligand immobilized onto silica as a heterogeneous nanocatalyst and applied it for the synthesis of 2-(5-substituted phenyl)furan-2-carboxaldehyde and di-heteroaryl molecules including 2-(5-substituted phenylfuran-2-yl)-1*H*-benzo[*d*]imidazole and benzothiazole derivatives from furan-2-carboxaldehyde, anilines, sodium nitrite, *o*-phenylenediamines, and 2-aminothiophenol in EtOH solvent.

## 2 | EXPERIMENTAL SECTION

Melting points and infrared (IR) spectra were measured on an Electrothermal 9100 apparatus and a JASCO FT-IR-460 plus spectrometer, respectively. All reagents and solvents were purchased from Merck, Fluka, or Sigma-Aldrich. The $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) were obtained on Bruker DRX-400 Avance instruments with DMSO-$d_6$ and $CDCl_3$ as a solvent. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer using nickel-filtered Cu Kα radiation ($k = 1.5406$ A°). Field emission scanning electron micrograms (FESEM) were obtained

using a KYKY-EM3200 instrument. The inductively coupled plasma (ICP) analysis data were obtained using a Varian Vista-Pro analyzer.

## 2.1 | Synthesis of copper(II) Schiff-base complex

The Schiff-base *N*,*N*′-bis-(pyridin-2-ylmethylene)-ethane-1,2-diamine was prepared via reaction of pyridine-2-carbaldehyde with ethylenediamine in EtOH. Copper(II) Schiff-base complex was synthesized by *N*,*N*′-bis-(pyridin-2-ylmethylene)-ethane-1,2-diamine with $CuCl_2.2H_2O$ (1.0 mmol) in ethanol solvent (10.0 mL) at room temperature for 4 h. After completion of the reaction, the thick precipitate was filtered off and washed with ethanol (3 × 5 mL) and obtained dark green solid copper(II) Schiff-base complex.[83–87]

## 2.2 | Anchoring of copper(II) Schiff-base complex onto silica

3-Aminopropyl-functionalized silica gel (1.0 g) was added to copper(II) Schiff-base complexes (1.5 mmol) in ethanol solvent (10.0 mL) under stirring at room temperature for 24 h. The solid product was separated by centrifuging and washed three times with EtOH (3 × 5 mL). Finally, the solid product was dried at 60°C in a vacuum.

## 2.3 | General procedure for the synthesis of 5-phenylfuran-2-carbaldehydes, 2-(5-arylfuran-2-yl)-1*H*-benzo[*d*]imidazole, and 2-(5-arylfuran-2-yl) benzothiazole in the presence of cu(II) complex nanoparticles onto silica

4-Substituted aniline (7.0 mmol) was dissolved in a mixture of $H_2O$ (1.2 mL) and concentrated HCl (1.7 mL). The solution was cooled to 0°C and diazotized at 0–5°C with $NaNO_2$ (7.0 mmol) dissolved in $H_2O$ (1.3 mL). The solution was stirred for 15 min, filtered, and then, furan-2-carboxaldehyde (8.5 mmol) in $H_2O$ (2.5 mL) was added along with a solution of nanocatalyst Cu(II) Schiff-base@-$SiO_2$ (5.0 mol%) in $H_2O$ (1.3 mL) at a temperature of 10–15°C. The reaction mixture was slowly warmed up to 40°C and stirred at this temperature for 4 h. The precipitate was filtered and washed with water and an aqueous solution of $NaHCO_3$ (5.0%). The 5-phenylfuran-2-carbaldehydes and nanocatalyst were dried at room temperature. Next, a solution of *o*-phenylenediamines/2-aminothiophenol (1.0 mmol), 5-phenylfuran-2-carbaldehydes (1.0 mmol), and nanocatalyst in EtOH (5.0 mL) was stirred at 25°C or 78°C. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was centrifuged to separate the nanocatalyst. The organic layer was washed with deionized water (3 × 10 mL) and was evaporated in vacuum. The crude product was purified by silica gel column chromatography.

## 2.4 | Characterization data of synthesized compounds

### 2.4.1 | *N*,*N*′-bis-(pyridin-2-ylmethylene)-ethane-1,2-diamine (Schiff-base)

Isolated yield: 90%. Brown solid, mp: 66–67°C; IR (KBr): 1644 (C═N); $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) 4.06 (s, 4H), 7.30 (ddd, $J = 7.5$, 5.0, 2.5 Hz, 2H), 7.68–7.75 (m, 2H), 7.97 (d, $J = 7.5$ Hz, 2H), 8.41 (s, 2H), 8.61 (d, $J = 5.0$ Hz, 2H).

### 2.4.2 | 2-(5-(4-Chlorophenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole (**3a**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 81%. Dark brown solid, mp: 225–227°C; IR (KBr): 3440 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.21–7.26 (m, 2H), 7.25 (d, $J = 4.0$ Hz, 1H), 7.31 (d, $J = 4.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.59–7.62 (m, 2H), 7.96 (d, $J = 12.0$ Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 108.9, 112.4, 112.5, 122.3, 122.4, 125.5, 128.3, 128.9, 128.9, 132.5, 145.3, 152.9. Anal. Calcd for $C_{17}H_{11}ClN_2O$: C, 69.28; H, 3.76; N, 9.50; Found: C, 69.02; H, 3.54; N, 9.65.

### 2.4.3 | 2-(5-(4-Bromophenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole (**3b**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 81%. Dark brown solid, mp: 243–245°C; IR (KBr): 3438 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.21–7.24 (m, 2H), 7.26 (d, $J = 4.0$ Hz, 1H), 7.31 (d, $J = 4.0$ Hz, 1H), 7.59–7.64 (m, 2H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.89 (d, $J = 12.0$ Hz, 2H), 13.12 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 108.9, 111.3, 112.6, 118.7, 121.1, 121.9, 122.8, 125.8, 128.7, 131.8, 134.2, 143.2, 143.7, 145.1, 153.0. Anal. Calcd for $C_{17}H_{11}BrN_2O$: C, 60.20; H, 3.27; N, 8.26; Found: C, 60.05; H, 3.13; N, 8.34.

### 2.4.4 | 2-(5-(4-Methoxyphenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole (**3c**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 72%. Brown solid, mp: 262–263°C; IR (KBr): 3435 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 3.81 (s, 3H), 7.03–7.11 (m, 3H), 7.19–7.22 (m, 2H), 7.28 (d, $J = 4.0$ Hz, 1H), 7.59 (d, $J = 12.0$ Hz, 2H), 7.87 (d, $J = 12.0$ Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 55.7, 106.8, 113.2, 114.9, 122.6, 122.8, 126.0, 127.7, 144.5, 154.8, 159.7. Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65; Found: C, 74.19; H, 4.65; N, 9.79.

### 2.4.5 | 2-(5-(2-Chlorophenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole (**3d**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 82%. Orange solid, mp: 251–253°C; IR (KBr): 3437 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.23–7.26 (m, 2H), 7.36–7.39 (m, 2H), 7.42 (dd, $J = 1.2$, 7.6 Hz, 1H), 7.53 (t, $J = 7.6$ Hz 1H), 7.59–7.64 (m, 3H), 7.42 (dd, $J = 1.6$, 8.0 Hz, 1H), 13.15 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 112.4, 113.2, 122.3, 122.4, 122.5, 127.5, 127.6, 128.1, 129.2, 129.4, 130.7, 143.1, 145.0, 150.1. Anal. Calcd for $C_{17}H_{11}ClN_2O$: C, 69.28; H, 3.76; N, 9.50; Found: C, 68.95; H, 3.47; N, 9.31.

### 2.4.6 | 2-(5-(3-Chlorophenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole (**3e**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 55% Dark brown solid, mp: 232–234°C; IR (KBr): 3412 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.23 (d, $J = 4.0$ Hz, 2H), 7.33 (q, $J = 4.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.53 (t, $J = 8.0$ Hz, 1H), 7.59–7.64 (m, 2H), 7.90 (d, $J = 8.0$ Hz, 1H), 8.05 (s, 1H), 13.16 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 109.6, 112.5, 122.3, 122.4, 123.3, 123.4, 127.7, 130.8, 131.4, 133.9, 143.2, 145.4, 152.4. Anal. Calcd for $C_{17}H_{11}ClN_2O$: C, 69.28; H, 3.76; N, 9.50; Found: C, 69.02; H, 3.49; N, 9.38.

### 2.4.7 | 2-(5-(4-chlorophenyl)furan-2-yl)-5-methyl-1*H*-benzo[*d*]imidazole (**3f**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 68%. Dark brown solid, mp: 215–217°C; IR (KBr): 3442 (NH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 2.41 (s, 3H), 6.69 (d, $J = 4.0$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 4.0$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.34 (s, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.4, 109.7, 114.4, 121.7, 122.3, 122.6, 125.4, 125.9, 126.8, 128.2, 132.0, 133.7, 147.6, 153.3, 154.3, 156.3. Anal. Calcd for $C_{18}H_{13}ClN_2O$: C, 70.02; H, 4.24; N, 9.07; Found: C, 69.68; H, 4.09; N, 8.81.

### 2.4.8 | 2-[5-(4-Bromophenyl)-2-furanyl]-5-methyl-1*H*-benzimidazole (**3g**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 57%. Pale brown solid, mp: 270–271°C; IR (KBr): 3455 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 2.38 (s, 3H), 6.95–7.01 (m, 1H), 7.19 (d, $J = 4.0$ Hz, 1H), 7.26 (s, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.81 (d, $J = 12.0$ Hz, 2H), 12.91 (s,1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 21.3, 108.9, 110.8, 111.0, 112.2, 112.3, 118.3, 118.4, 121.0, 123.4, 124.2, 125.7, 128.7, 131.8, 145.3, 152.8. Anal. Calcd for $C_{18}H_{13}BrN_2O$: C, 61.21; H, 3.71; N, 7.93; Found: C, 61.52; H, 3.40; N, 8.02.

### 2.4.9 | 2-(5-(4-Bromophenyl)furan-2-yl)-5-chloro-1*H*-benzo[*d*]imidazole (**3h**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 56%. Brown liquid, mp: 167–168°C; IR (KBr): 3451 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.23–7.26 (m, 1H), 7.28 (d, $J = 4.0$ Hz, 1H), 7.33 (d, $J = 4.0$ Hz, 1H), 7.56–7.68 (m, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H), 13.26 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 109.0, 110.9, 112.5, 113.2, 113.3, 118.0, 119.9, 121.3, 122.3, 122.8, 125.8, 128.6, 131.9, 144.6, 153.3. Anal. Calcd for $C_{17}H_{10}BrClN_2O$: C, 54.65; H, 2.70; N, 7.50; Found: C, 54.32; H, 2.50; N, 7.44.

### 2.4.10 | 5-Chloro-2-(5-(2-chlorophenyl) furan-2-yl)-1*H*-benzo[*d*]imidazole (**3i**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 80%. Dark orange solid, mp: 224–226°C; IR (KBr): 3432 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.25–7.70 (m, 8H), 8.19 (s, 1H), 13.32 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 112.9, 113.3, 116.0,

118.1, 120.0, 122.8, 126.8, 127.5, 127.5, 127.6, 128.2, 129.3, 129.5, 130.8, 131.2, 144.6, 150.5. Anal. Calcd for $C_{17}H_{10}Cl_2N_2O$: C, 62.03; H, 3.06; N, 8.51; Found: C, 62.22; H, 3.15; N, 8.74.

### 2.4.11 | 2-[5-(3-Chlorophenyl)-2-furanyl]-5-chlor-1*H*-benzimidazole (**3j**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 55%. Dark brown, mp: 231–233°C; IR (KBr): 3431 (NH); $^1$H NMR (400 MHz, $CDCl_3$): 6.68 (d, $J = 4.0$ Hz, 1H), 7.11–7.19 (m, 5H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.52 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 108.5, 112.9, 122.3, 123.2, 123.5, 124.0, 126.6, 127.9, 129.3, 130.0, 131.5, 134.7, 137.0, 144.8, 145.1, 153.6. Anal. Calcd for $C_{17}H_{10}Cl_2N_2O$: C, 62.03; H, 3.06; N, 8.51; Found: C, 61.86; H, 3.017; N, 8.46.

### 2.4.12 | 2-[5-(4-Chlorophenyl)-2-furanyl]-5-chlor-1*H*-benzimidazole (**3k**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 80%. Pale brown solid, mp: 210–212°C; IR (KBr): 3434 (NH); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.21–7.27 (m, 1H), 7.28 (d, $J = 4.0$ Hz, 1H), 7.34 (d, $J = 4.0$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.63–7.71 (m, 2H), 7.96 (d, $J = 8.0$ Hz, 2H), 13.28 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 109.0, 110.7, 113.2, 119.9, 122.5, 125.6, 128.3, 129.0, 132.7, 136.4, 144.6, 147.6, 153.2. Anal. Calcd for $C_{17}H_{10}Cl_2N_2O$: C, 62.03; H, 3.06; N, 8.51; Found: C, 61.73; H, 2.95; N, 8.59.

### 2.4.13 | 2-(5-(2-Chlorophenyl)furan-2-yl)-5-methyl-1*H*-benzo[*d*]imidazole (**3l**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 79%.brown oil, mp: 240–241°C; IR (KBr): 3440 (NH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 2.64 (s, 3H), 6.66 (t, $J = 8.0$ Hz, 1H), 6.98 (t, $J = 8.0$ Hz, 1H), 7.11 (d, $J = 4.0$ Hz, 1H), 7.14 (s, 1H), 7.23 (t, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 4.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H) 12.15 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 17.6, 112.6, 113.2, 123.3, 123.8, 125.7, 126.5, 127.6, 127.9, 128.4, 130.0, 130.5, 138.5, 138.7, 143.9, 144.5, 151.5. Anal. Calcd for $C_{18}H_{13}ClN_2O$: C, 70.02; H, 4.24; N, 9.07; Found: C, 70.21; H, 4.17; N, 9.14.

### 2.4.14 | 2-[5-(4-Chlorophenyl)-2-furanyl]-benzothiazole (**3m**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 85%. Pale brown solid, mp: 182–183°C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.35 (d, $J = 4.0$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 4.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 12.0$ Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 1H), 8.17 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 109.7, 114.5, 122.3, 122.6, 125.5, 125.8, 126.5, 127.9, 129.3, 134.3, 147.5, 155.6, 156.3. Anal. Calcd for $C_{17}H_{10}ClNOS$: C, 65.49; H, 3.23; N, 4.49; Found: C, 65.31; H, 3.11; N, 4.34.

### 2.4.15 | 2-(5-(4-Bromophenyl)furan-2-yl) benzo[*d*]thiazole (**3n**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 80%. Dark orange solid, mp: 189–190°C; IR (KBr): $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.36 (d, $J = 4.0$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 4.0$ Hz, 1H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 109.7, 114.4, 121.7, 122.3, 122.6, 125.4, 125.9, 126.8, 128.2, 132.0, 133.7, 147.6, 153.3, 154.3, 156.3. Anal. Calcd for $C_{17}H_{10}BrNOS$: C, 57.32; H, 2.83; N, 3.93; Found: C, 57.41; H, 2.98; N, 4.05.

### 2.4.16 | 2-(5-(2-Chlorophenyl)furan-2-yl) benzo[*d*]thiazole (**3o**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield: 77%. Pale brown solid, mp: 208–210°C; H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.39 (d, $J = 4.0$ Hz, 1H), 7.46–7.50 (m, 2H), 7.53–7.56 (m, 2H), 7.58–7.60 (m, 1H), 7.64 (dd, $J = 0.8$, 7.6 Hz, 1H), 7.98 (dd, $J = 1.6$, 8.0 Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 8.17 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 113.7, 113.8, 122.4, 122.7, 125.5, 126.8, 127.3, 127.8, 128.4, 129.6, 130.0, 130.9, 133.8, 147.5, 151.6, 153.3, 156.2. Anal. Calcd for $C_{17}H_{10}BrNOS$: C, 65.49; H, 3.23; N, 4.49; Found: C, 65.31; H, 3.12; N, 4.57.

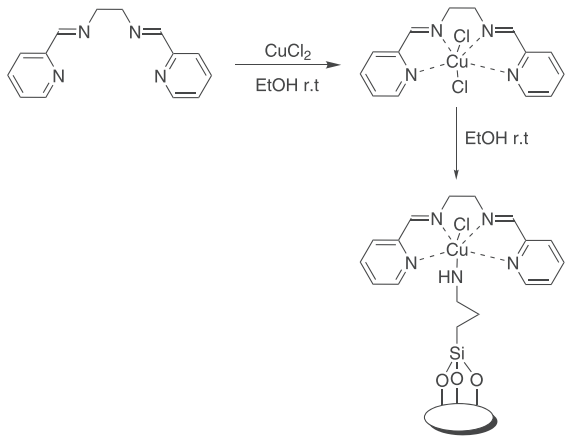
### 2.4.17 | 2-(5-(3-Chlorophenyl)furan-2-yl) benzo[*d*]thiazole (**3p**)

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether. Isolated yield:

72%. Pale brown solid, mp: 204–206°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 6.80 (d, $J = 3.6$ Hz, 1H), 7.22–7.25 (m, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.42–7.46 (m, 1H), 7.59–7.62 (m, 1H), 7.72 (t, $J = 1.6$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 108.8, 113.4, 119.1, 121.6, 122.4, 123.1, 123.9, 124.3, 125.2, 126.5, 128.3, 128.8, 130.1, 131.3, 134.9, 153.8, 154.5. Anal. Calcd for $C_{17}H_{10}ClNOS$: C, 65.49; H, 3.23; N, 4.49; Found: C, 65.31; H, 3.15; N, 4.42.

## 3 | RESULTS AND DISCUSSION

Copper(II) complex of tetradentate Schiff-base ligand immobilized onto silica [Cu(II) Schiff-base@$SiO_2$] was produced by adding 3-aminopropyl-functionalized silica gel to copper(II) Schiff-base complex in EtOH solvent at room temperature for 24 h.[75] Copper(II) Schiff-base complex was prepared via the reaction of *N*,*N*′-bis-(pyridin-2-ylmethylene)-ethane-1,2-diamine in the presence of $CuCl_2.2H_2O$ and EtOH at room temperature (Scheme 1).[83–87] The catalyst was characterized by FT-IR, FESEM, energy-dispersive X-ray spectroscopy (EDX), XRD, and ICP.




**SCHEME 1** Copper(II) complex of tetradentate Schiff-base ligand immobilized onto silica [Cu(II) Schiff-base@$SiO_2$]

Figure 2 shows the Fourier transform infrared (FT-IR) spectra of Schiff-base, Cu(II) Schiff-base complex, and Cu(II) Schiff-base@$SiO_2$. The observed peaks at 1644 $cm^{-1}$ represent the stretching band of imine (C═N) nitrogen groups of Schiff-base (Figure 2a).[85] The shift of the (C═N) stretching band to around 1604 $cm^{-1}$ suggests the coordination of ligand to the copper ion (Figure 2b).[85] The appearance of a peak in ~471 $cm^{-1}$ is related to the formation of Cu–N during the immobilization of the Cu(II) Schiff-base@$SiO_2$ (Figure 2c).[85] The peaks at 797 and 1103 $cm^{-1}$ are related to the symmetric and asymmetric stretching vibration of Si–O groups.[75]

Figure 3a shows the morphology of the nanoparticles of copper(II) complex onto silica substrate in spherical features. A little aggregation may be due to the hydrogen bonds from the site of NH connected to the propyl group. Figure 3b with a higher magnification shows a rough and porous structure suggesting the improvement of the surface area resulting in high catalytic activity. Figure 3b also shows the nanoparticles size is in the range of 15–20 nm approximately. This feature could improve catalytic activity, as well.

The catalyst composition was surveyed by EDX analysis. The obtained result is shown in Figure 4. The result

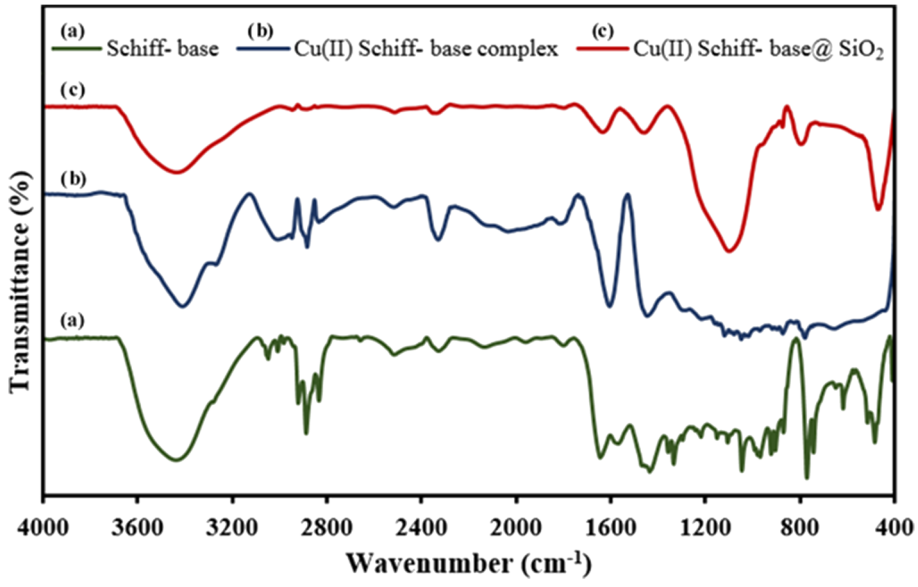



**FIGURE 2** Fourier transform infrared (FT-IR) spectra of Schiff-base (a), Cu(II) Schiff-base complex (b), and Cu(II) Schiff-base@$SiO_2$ (c)

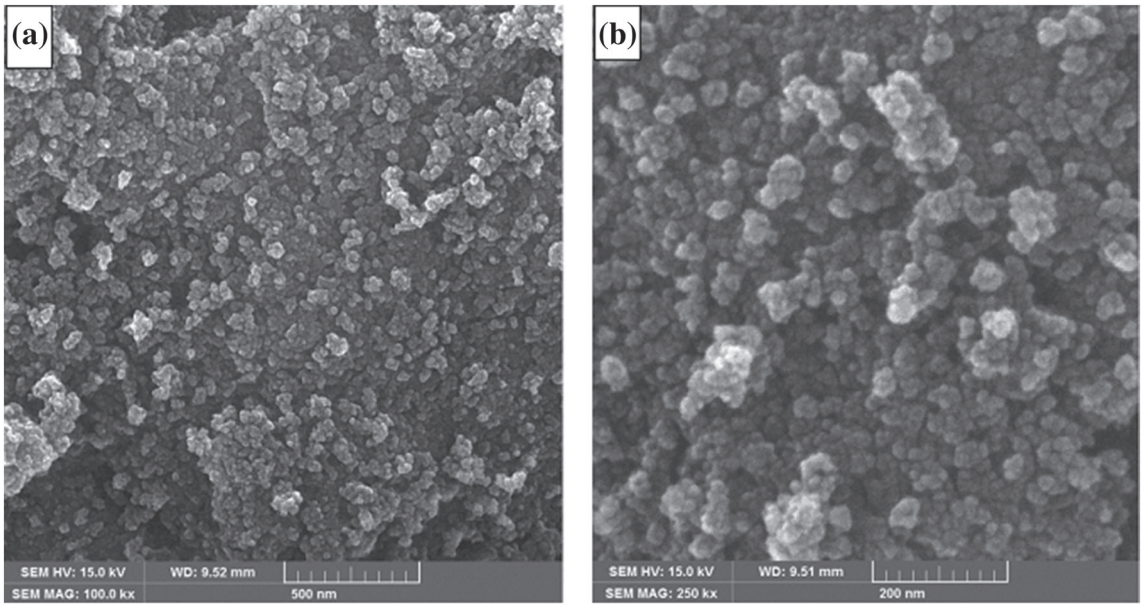



**FIGURE 3** Field emission scanning electron microscope (FESEM) images of Cu(II) Schiff-base@$SiO_2$

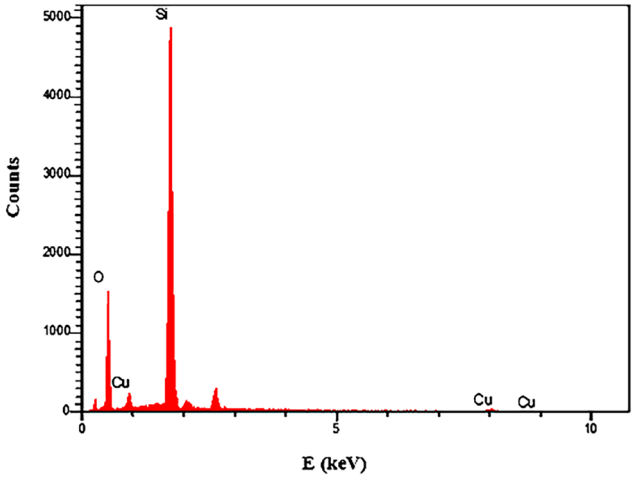



**FIGURE 4** Energy-dispersive X-ray spectroscopy (EDX) of Cu(II) Schiff-base@$SiO_2$

confirms the presence of Cu, Si, O, and N elements in the synthesized sample composition.

Figure 5 shows the XRD pattern of Cu(II) Schiff-base@$SiO_2$. As shown in the Figure 5, the pattern includes the indexed peaks attributed to the different phases of (111), (110), (200), (222), and (400) planes of Cu from the Cu(II) Schiff-base@$SiO_2$.[78,88]

Also, the content of copper in the Cu(II) Schiff-base@$SiO_2$ was determined by ICP analysis. Based on the ICP results, the quantity of copper nanoparticles was evaluated to be 3.37 wt%.

In what continues, we synthesized 5-phenylfuran-2-carbaldehyde derivatives[89] via reaction of aniline derivatives with sodium nitrite, HCl, furan-2-carbaldehyde in the presence of 5.0 mol% Cu(II) Schiff-base@$SiO_2$ as nanocatalyst (Scheme 2). After completion

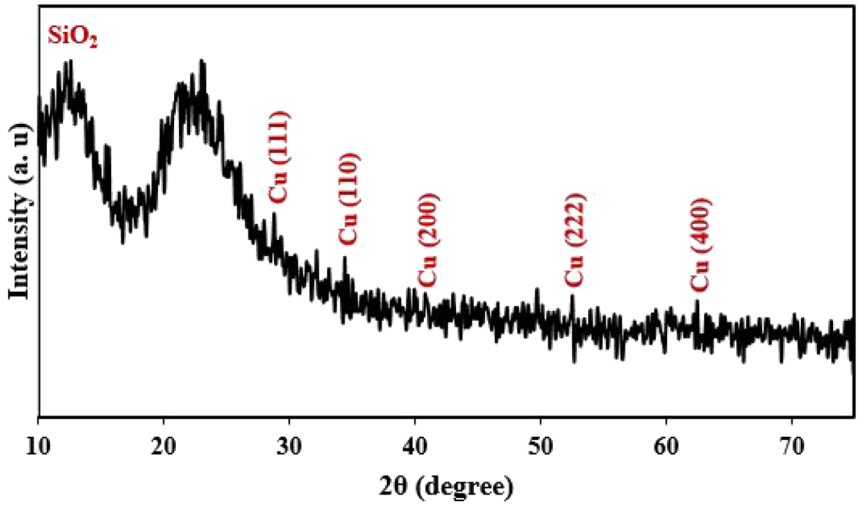
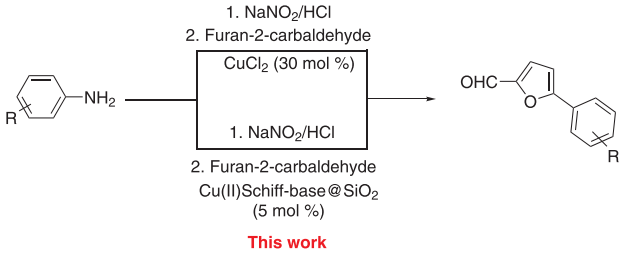



**FIGURE 5** X-ray diffraction (XRD) patterns of Cu(II) Schiff-base@silica as a nanocatalyst




**SCHEME 2** Synthesis of 5-phenylfuran-2-carbaldehyde derivatives

of the reaction, the thick precipitate was filtered off and washed with water and an aqueous solution of $NaHCO_3$ (5%) and water. The 5-phenylfuran-2-carbaldehyde and Cu(II) Schiff-base@$SiO_2$ were dried at room temperature.

After synthesis of 5-phenylfuran-2-carbaldehyde and characterization of the Cu(II) Schiff-base@$SiO_2$ as nanocatalyst, its catalytic ability was studied in the synthesis of benzimidazole and benzothiazole derivatives. To find out the suitable condition for the reaction, a series of experiments for different parameters such as solvent and temperature were performed with the standard reaction of *o*-phenylenediamine **1a** (1.0 mmol) and 5-(4-chlorophenyl)furan-2-carbaldehyde **2a** (1.0 mmol) for the synthesis of 2-(5-(4-chlorophenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole **3a** (Table 1). At first, the reaction was tested in the absence of catalyst, and no product was obtained under the catalyst-free conditions (Table 1, Entry 1). Also, when the reaction was screened in the presence of Cu(II) Schiff-base@$SiO_2$ (5.0 mol%) under solvent-free conditions, only 25% product was obtained after 12 h (Table 1, Entry 2). In the following, we examined the effect of various solvents such as EtOH, DMSO, DMF, $CH_3CN$, EtOAc, and DCM on the model reaction, and the best yield was achieved in EtOH at 25°C (Table 1, Entries 3–8). So, 5 mol% Cu(II) Schiff-base@$SiO_2$ in EtOH solvent was found to be the optimal condition to push the reaction forward (Table 1, Entry 3). Moreover, the reaction was also tested at reflux using the catalyst, and it was found that the temperature has a reverse effect on the yield of model reaction (Table 1, Entry 9). Eventually, Schiff-base-Cu(II) was applied as a catalyst, and lower yield of desired product (88%) was obtained (Table 1, Entry 10). The solubility of Schiff-base-Cu(II) in ethanol makes the catalyst separation and recycling process difficult. This observation proves the role necessity of heterogeneous nano-Cu(II) Schiff-base@$SiO_2$ for this reaction.

After optimization of the reaction conditions, a series of new 2-(5-substituted phenylfuran-2-yl)-1*H*-benzo[*d*]imidazole and benzothiazole derivatives were synthesized via the reaction of heterocyclic aromatic aldehydes with *o*-phenylenediamines/or 2-aminothiophenol in the presence of 5 mol% Cu(II) Schiff-base@$SiO_2$ as a heterogeneous nanocatalyst, and the desired products were

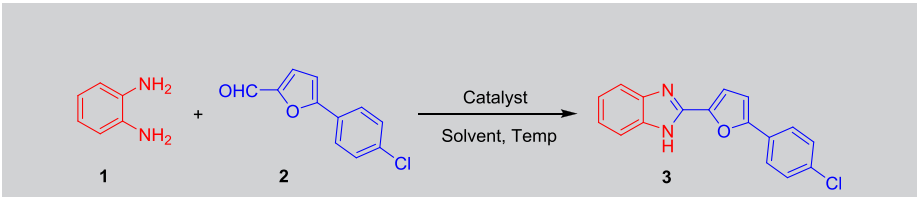



**TABLE 1** Optimization of the reaction conditions for synthesis of 2-(5-(4-chlorophenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole[a,b]

| Entry | Catalyst/mol% | Solvent | Temp. | Time (h) | Yield[a] % |
|---|---|---|---|---|---|
| 1 | - | EtOH | 25°C | 12 | Trace |
| 2 | Schiff-base-Cu(II)@$SiO_2$/5 | - | 25°C | 12 | 25 |
| **3** | **Cu(II)Schiff-base@$SiO_2$/5** | **EtOH** | **25°C** | **2** | **90** |
| 4 | Schiff-base-Cu(II)@$SiO_2$/5 | DMSO | 25°C | 5 | 60 |
| 5 | Schiff-base-Cu(II)@$SiO_2$/5 | DMF | 25°C | 5 | 72 |
| 6 | Schiff-base-Cu(II)@$SiO_2$/5 | $CH_3CN$ | 25°C | 6 | 65 |
| 7 | Schiff-base-Cu(II)@$SiO_2$/5 | EtOAc | 25°C | 6 | 51 |
| 8 | Schiff-base-Cu(II)@$SiO_2$/5 | DCM | 25°C | 8 | 44 |
| 9 | Schiff-base-Cu(II)@$SiO_2$/5 | EtOH | Reflux | 2 | 75 |
| 10 | Schiff-base-Cu(II)/5 | EtOH | 25°C | 2 | 88 |

*Note:* The best optimization condition is bold.

[a]General conditions: *o*-phenylendiamine (1.0 mmol), 5-(4-chlorophenyl)furan-2-carbaldehyde (1.0 mmol), solvent (5.0 mL), air.

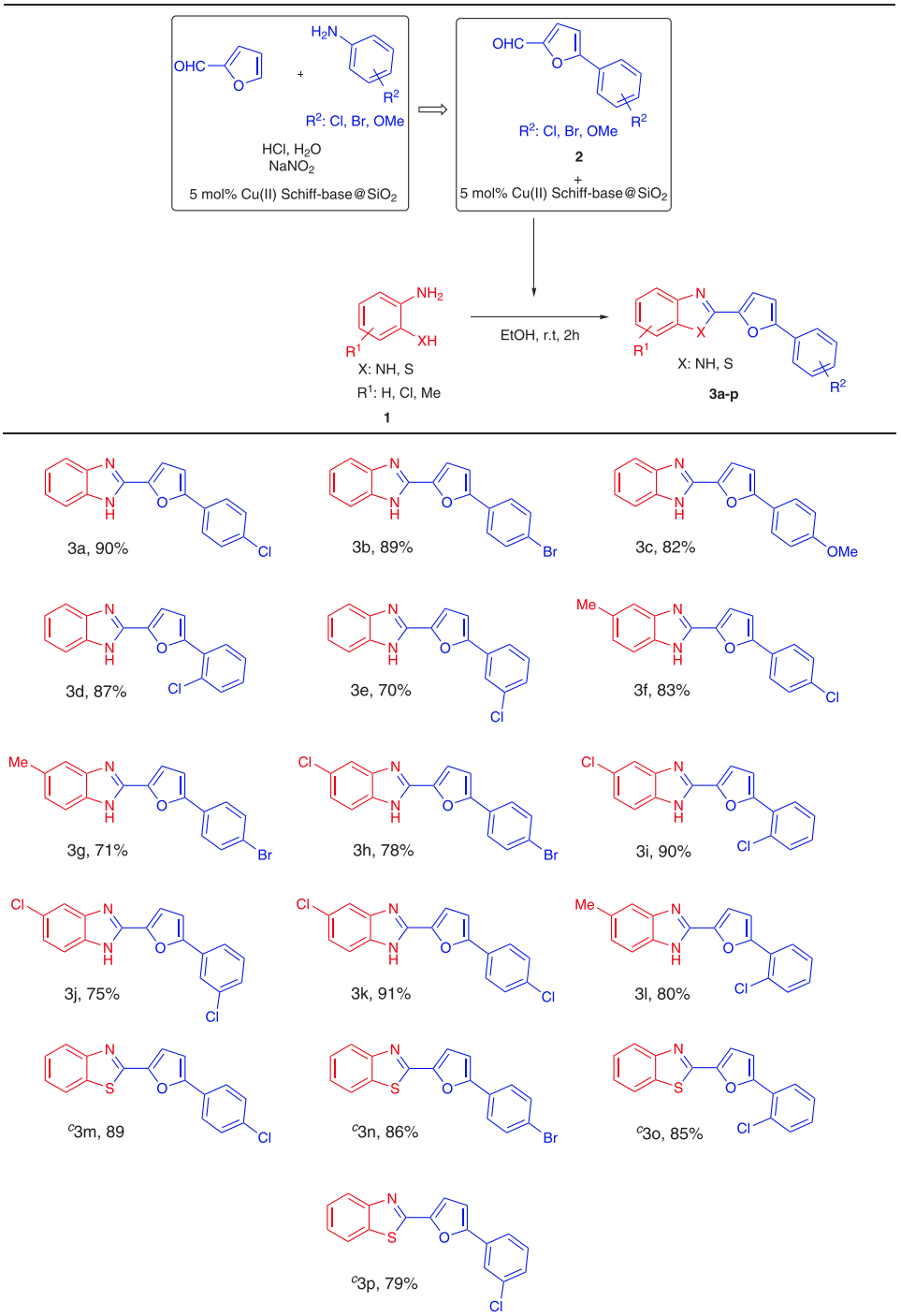
[b]Isolated yield.

obtained in good to excellent yields. The structures of the new synthesized organic compounds were confirmed by FT-IR, $^{1}$H NMR, $^{13}$C NMR, and elemental analysis (Scheme 3, **3a–p**).

As shown in Scheme 3, heterocyclic aromatic aldehydes containing different groups such as Cl, Br, and OMe reacted with *o*-phenylenediamine and afforded the desired benzimidazole derivatives in good to excellent yields (Scheme 3, **3a–e**).

Also, *o*-phenylenediamines, including Cl and Me groups, participated in the reaction with different heterocyclic aromatic aldehydes to achieve corresponding products in good yields at room temperature (Scheme 3, **3f–l**).

To further highlight the usefulness of this protocol, 2-aminothiophenol reacted with heterocyclic aromatic aldehydes and led to the synthesis of benzothiazole derivatives with good yields (Scheme 3, **3m–p**).




**SCHEME 3** Synthesis of benzimidazole and benzothiazole derivatives.[a,b] [a]General conditions: **1** (1.0 mmol), **2** (1.0 mmol), Cu(II) Schiff-base@$SiO_2$ (5 mol%), EtOH (5.0 mL), air, r.t. [b]Isolated yield. [c]78°C

[a]General conditions: **1** (1.0 mmol), **2** (1.0 mmol), Cu(II) Schiff-base@$SiO_2$ (5 mol%), EtOH (5.0 mL), air, r.t. [b]Isolated yield. [c]78 °C.

Herein, according to the literature,[24,33,38,39] a plausible mechanism for the synthesis of benzimidazole in the presence of Cu(II) Schiff-base@$SiO_2$ is demonstrated in Scheme 4. First, 5-(4-chlorophenyl)furan-2-carbaldehyde (**I**) was activated using Cu(II) Schiff-base@$SiO_2$. Next, *o*-phenylenediamine (**II**) attacks to the carbonyl group, which after the elimination of $H_2O$ leads to the formation of Schiff-base (**III**). Subsequently, intermediate (**IV**) is generated via intramolecular cyclization. Finally, product (**V**) is produced through the oxidative dehydrogenation of intermediate (**IV**) in the presence of air and Cu(II) Schiff-base@$SiO_2$ (Scheme 4).

As the last study, the catalyst reusability was investigated for the synthesis of product **3a** under optimized conditions. After the completion of the reaction, Cu(II) Schiff-base@$SiO_2$ was separated by centrifuging from the reaction mixture and washed with EtOH (3 mL, three times), dried, and utilized directly in the next cycle. The study showed that the Cu(II) Schiff-base@$SiO_2$ catalyst could be recovered 10 times, and a slight loss of catalytic activity was observed for each reaction (Figure 6). It is noteworthy that the catalyst recovery was performed after its application in two steps of the reaction, including synthesis of 5-phenylfuran-

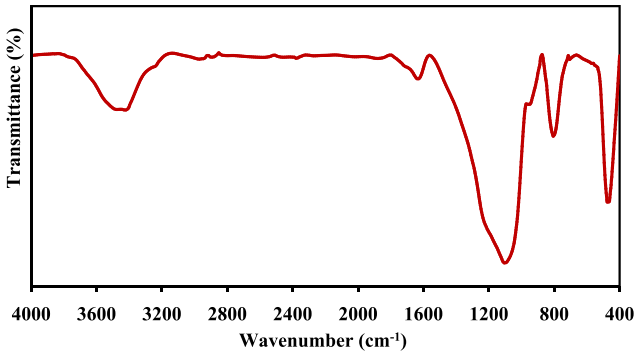
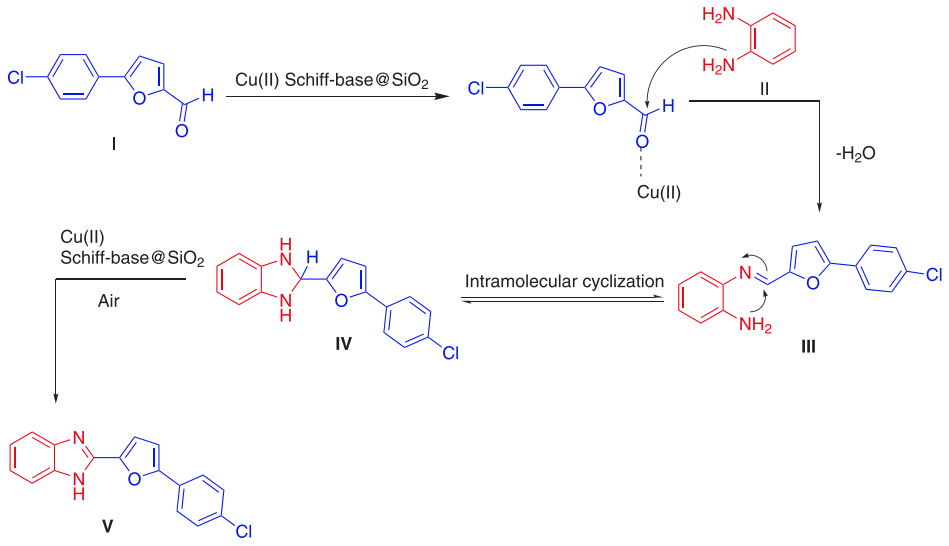



**FIGURE 7** Infrared (IR) spectrum for the Cu(II) Schiff-base@$SiO_2$ after the 10 cycles




**SCHEME 4** A plausible mechanism for the synthesis of 2-(5-(4-chlorophenyl)furan-2-yl)-1*H*-benzo[*d*]imidazole in the presence of Cu(II) Schiff-base@$SiO_2$

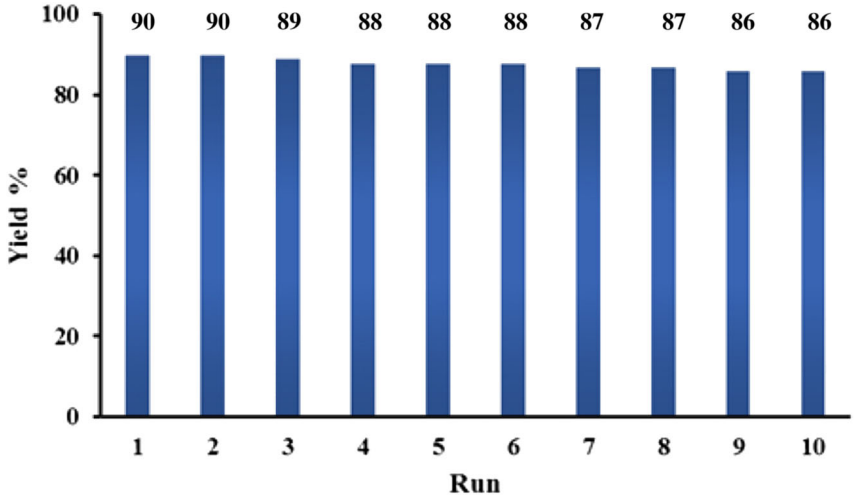



**FIGURE 6** Reusability of Cu(II) Schiff-base@$SiO_2$ for the synthesis of product **3a**

2-carbaldehydes, benzimidazole, and benzothiazole derivatives. Figure 6 shows the high activity of the catalyst after 10 runs. Additionally, the IR spectrum for the Cu(II) Schiff-base@$SiO_2$ after the 10 cycles are displayed in Figure 7. Therefore, after 10 times of recovery, the catalyst is stable and shows high activity.

## 4 | CONCLUSION

In summary, copper(II) complex of tetradentate Schiff-base ligand immobilized onto silica [Cu(II) Schiff-base@-$SiO_2$] has been successfully synthesized and characterized by the several techniques such as FT-IR, FE-SEM, EDX, XRD, and ICP. Cu(II) Schiff-base@$SiO_2$ was used as an efficient catalyst for a two-step reaction including synthesis of 5-phenylfuran-2-carbaldehydes and di-heteroaryl molecules including benzimidazole and benzothiazole derivatives via reaction of anilines, sodium nitrite, furan-2-carboxaldehyde, *o*-phenylenediamines, and 2-aminothiophenol. The significant advantages of this protocol include short reaction times, mild conditions, good to excellent yields, and low amount of nanocatalyst. Also, to the best of our knowledge, this is the first time of using the same catalyst in two steps including synthesis of 2-(5-substituted phenyl)furan-2-carboxaldehyde and benzimidazole or benzothiazole derivatives. In addition, this synthesized catalyst was recycled very well and reused several times after use in two steps of the reaction without significant loss of its catalytic activity.

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### AUTHOR CONTRIBUTIONS

**Hashem Sharghi:** Conceptualization; supervision. **Elahe Mashhadi:** Conceptualization; formal analysis; investigation. **Mahdi Aberi:** Conceptualization. **Jasem Aboonajmi:** Conceptualization.

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