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FULL PAPER

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Silica-supported Cu(II)–quinoline complex: Efficient and recyclable nanocatalyst for one-pot synthesis of benzimidazolquinoline derivatives and 2*H*-indazoles

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The synthesis, characterization and catalytic activity of a Cu(II) complex derived from 2-oxoquinoline-3-carbaldehyde Schiff base supported on amino-functionalized silica are reported. 3-(1*H*-Benzo[*d*]imidazol-2-yl)quinolines containing piperidine, morpholine and phenylpiperazine skeletons at the C-2 position were formed in good to excellent yields via the one-pot reaction of 2-chloroquinoline-3-carbaldehyde, benzene-1,2-diamines and secondary amines in the presence of the nanocatalyst under mild conditions. Moreover, the nanocatalyst was found to be recyclable for up to seven runs without significant loss of activity. Also, a series of 2*H*-indazoles were synthesized by the catalytic condensation of 2-bromobenzaldehyde, sodium azide and primary amines.

KEYWORDS

2*H*-indazoles, benzimidazole–quinoline molecules, nanocatalyst, one-pot reaction, quinoline-based catalyst

1 | INTRODUCTION

In the past decade, a great deal of attention has focused on copper-based nanocatalysts because of their high activity and selectivity in various organic reactions including multicomponent, cross-coupling and click reactions.[1–8] These Cu(II)-based catalysts are readily available, of low cost, stable in air and can be easily handled in comparison to other transition metal catalysts.[9] Frequently, copper complexes with suitable and stable ligands including bipyridine,[10] dabco,[11] triazole dendrimer,[12] triazine-based polyethyleneamine dendrimer[13] and amidoxime[14] have been supported on various solid supports to efficiently perform organic reactions. Schiff base[15,16] catalysts supported on various solid supports have also been applied for a range of organic reactions.

In this connection, silica solid supports are of the interest owing to their considerable properties including high surface area, non-toxicity, good recyclability, excellent stability (chemical and thermal) and changeable chemical functional groups.[17,18]

Over the past few decades, one-pot multicomponent reactions have been paid great attention by organic, combinatorial and medicinal chemists. From the perspective of green chemistry, construction of some bonds in one pot clearly is an intense challenge, providing rapid and efficient tools for transforming simpler starting materials into structurally much more complex molecules. Moreover, multicomponent reactions have various benefits over traditional multistep synthesis including flexibility, simplicity, good yields, short reaction durations, high atom economy, avoidance of expensive purification and lower costs.[3–6,19,20]

The synthesis and evaluation of hybrid molecules have been under continuing development because of their biological potential that includes anti-inflammatory, anticancer, anti-HIV, antidepressant and contraceptive activities. In this regard, there is an extensive potential

for synthesizing new hybrid scaffolds to be utilized as building blocks for the next generation of pharmaceuticals. Therefore, an investigation of the literature reveals various synthetic approaches for their formation.[21–23]

Benzimidazole-based compounds are a class of nitrogen-based benzo-fused heterocyclic products which possess several kinds of applications, particularly in coordination chemistry and catalysis. It has been shown that they play an important role in numerous pharmaceutical products with a wide range of biological activities including anticancer, antioxidant, antimicrobial, antihypertensive, anthelmintic, anti-inflammatory, and so on (Figure 1).[24–26] Benzimidazoles bearing quinolines are an excellent choice for producing many hybrid molecules with remarkable properties.[27–29] For the reasons mentioned above, it is of great interest for researchers to combine the quinoline and benzimidazole rings to produce new structural types of biologically or analytically active agents.

Indazole derivatives are an important class of N-heterocyclic compounds having a broad range of pharmaceutical activities (such as HIV protease inhibition,[30] antitumour,[31] antiplatelet,[32] anticancer[33] and antimicrobial[34] activities) and agricultural applications[35] and are used as electronically active materials.[36]

In the present paper, we report the synthesis of a Cu(II) complex derived from 2-oxoquinoline-3-carbaldehyde Schiff base supported on amino-functionalized silica (Cu@QCSSi) and its application in the one-pot synthesis of 3-(1*H*-benzo[*d*]imidazol-2-yl)quinolines containing piperidine, morpholine and phenylpiperazine skeletons at the C-2 position under mild conditions. Also, we report an efficient route to the preparation of 2*H*-indazoles using the reaction of 2-bromobenzaldehyde, sodium azide and amines using this heterogeneous nanocatalyst system.

2 | EXPERIMENTAL

2.1 | Instrumentation, analysis and starting materials

Chemical materials and solvents were purchased from Fluka, Sigma-Aldrich and Merck and used without further purification. Aminopropyl silica gel was also obtained from Fluka. NMR spectra were recorded in $CDCl_3$ or deuterated dimethylsulfoxide (DMSO-d_6) with a Bruker Avance DPX-250 (^{1}H NMR, 250 MHz; ^{13}C NMR, 62.9 MHz) spectrometer. Infrared (IR) spectra were obtained using a Shimadzu FT-IR 8300

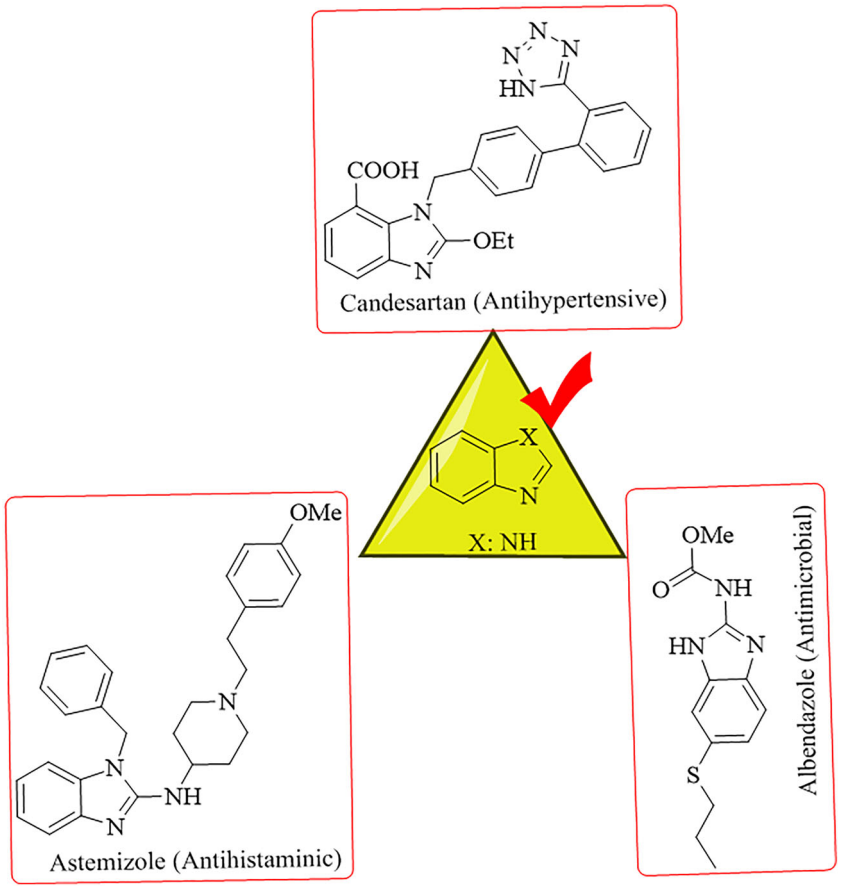


FIGURE 1 Biologically active benzo-fused heterocyclic compounds

spectrophotometer. Characterization and surface determination of the morphology of the nanocatalyst were performed with a MIRA3 TESCAN scanning electron microscopy (SEM) instrument, operating at 20.0 kV. Energy dispersive X-ray (EDX) analysis was done using a Sirius SD EDX analyser. Mass spectra were recorded at 70 or 20 eV with a Shimadzu GCMS-QP 1000 EX instrument. Using a Büchi-535 circulating oil melting point apparatus, melting points were obtained in open capillary tubes. Characterization of the catalyst was conducted using X-ray diffraction (XRD; D8 Advance, Bruker AXS). Thermogravimetric analysis (TGA) of the samples was carried out using a laboratory-made instrument. Inductively coupled

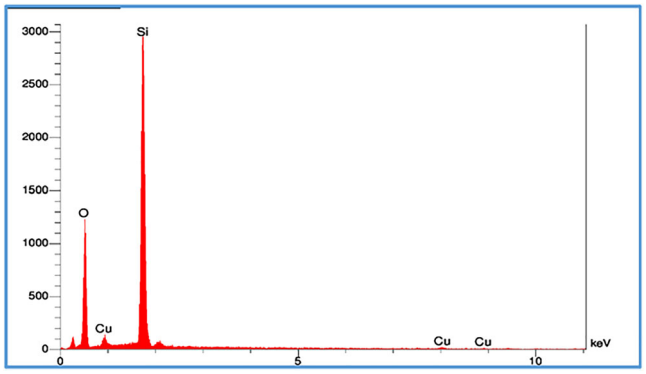
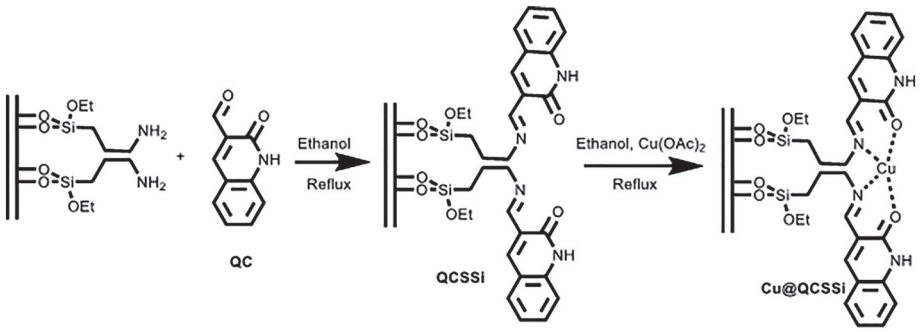


FIGURE 3 EDX analysis of Cu@QCSSi catalyst



SCHEME 1 Synthetic route for Cu@QCSSi catalyst.

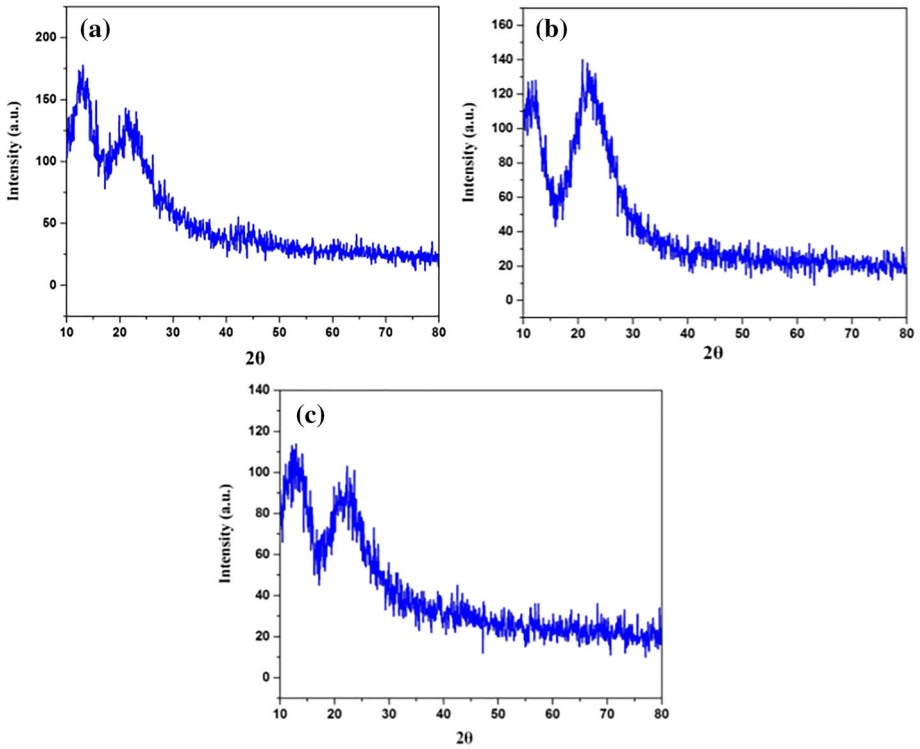


FIGURE 2 XRD patterns: (a) amino-functionalized silica; (b) QCSSi; (c) Cu@QCSSi

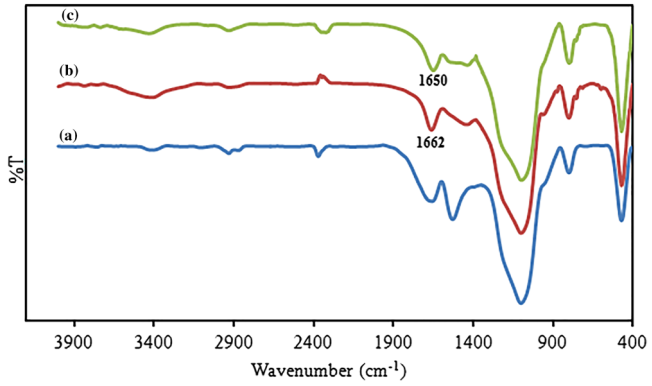


FIGURE 4 IR spectra: (a) amino-functionalized silica; (b) QCSSi; (c) Cu@QCSSi

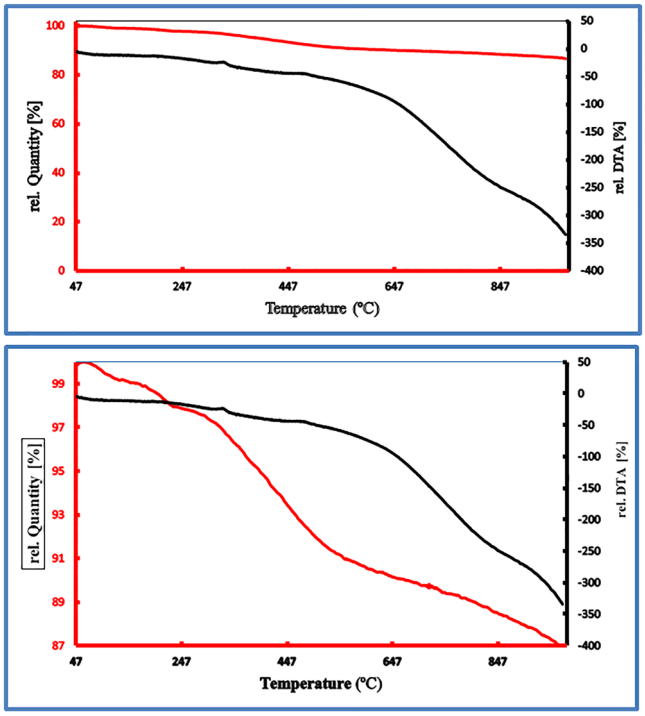


FIGURE 5 TGA and DTA curves for Cu@QCSSi

plasma (ICP) analysis data were obtained using a Varian Vista-Pro analyser. The determination of purity of substrates and reaction monitoring were conducted using TLC with silica gel PolyGram SILG/UV 254 plates. Column chromatography was performed with glass columns on short columns of silica gel 60 (70–230 mesh).

2.2 | General procedure for synthesis of benzimidazolquinoline hybrid derivatives from 2-chloroquinoline-3-carbaldehyde, secondary amine derivatives and *o*-phenylenediamines

A mixture of 2-chloroquinoline-3-carbaldehyde (**1**; 1.0 mmol) and secondary amine (**2**; (1.0 mmol) was stirred under solvent-free conditions at 120°C for 12 h.

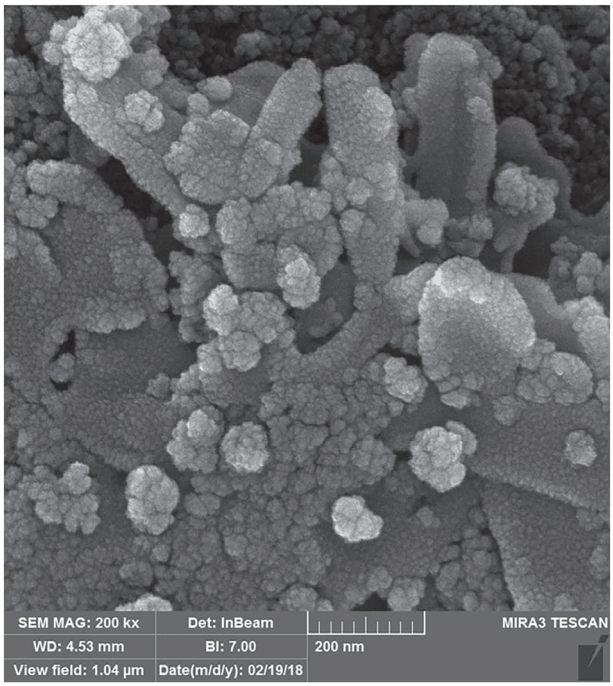


FIGURE 7 SEM image of QCSSi

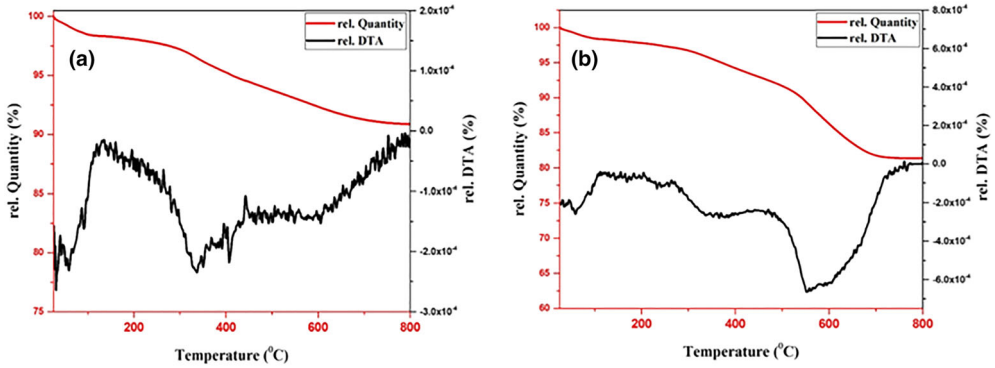


FIGURE 6 TGA and DTA curves: (a) amino-functionalized silica; (b) QCSSi

After forming the intermediate, o-phenylenediamine (**3**), the nanocatalyst (5.0 mol%) and 10.0 ml of ethanol were added to the mixture and stirred at 50°C to form the desired product. After completion of the reaction, the whole reaction mixture was centrifuged for 20 min to separate the nanocatalyst. The recovered nanocatalyst was

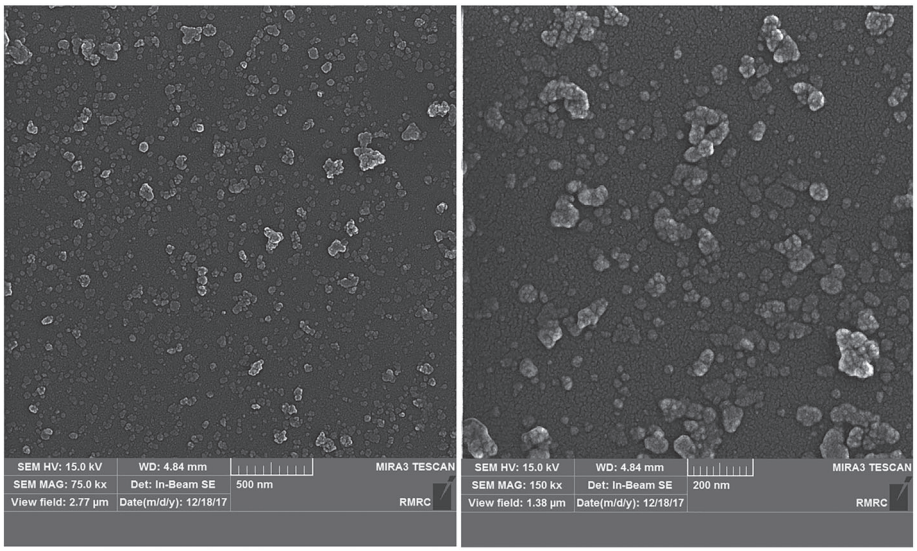
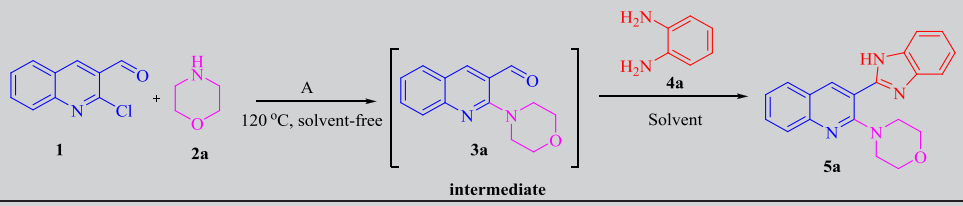


FIGURE 8 SEM images of Cu@QCSSi

TABLE 1 Effect of various conditions for synthesis of 4-(3-(1*H*-benzo[*d*]imidazol-2-yl)quinolin-2-yl)morpholine from 2-chloroquinoline-3-carbaldehyde (**1**), morpholine (**2a**) and benzene-1,2-diamine (**4a**)[a]



Entry	Catalyst (mol%)	Temp. (°C)	Solvent	Time (h)	Yield (%)[b]
1	—	50	Ethanol	3	<10
2	**5**	50	**Ethanol**	**2**	**90**
3	3	50	Ethanol	2	87
4	1	50	Ethanol	2	83
5	5	50	Methanol	2	95
6	5	50	Acetonitrile	2	27
7	5	50	Dioxane	2	30
8	5	50	Water	5	24
9	5	50	Dimethylformamide	5	7
10	5	r.t.	Ethanol	5	48
11	5	70	Ethanol	2	96
12	Nano-silica (0.05 g)	50	Ethanol	3	<10
13	Copper acetate (5 mol%)	50	Ethanol	3	80
14	Nano-silica (0.05 g) and copper acetate (5 mol%)	50	Ethanol	3	81
15	QCSSi (0.05 g)	50	Ethanol	3	<10

[a]Reaction conditions: (a) 2-chloroquinoline-3-carbaldehyde (**1**; 1.0 mmol), secondary amine (**2a**; 1.0 mmol), 120°C, 12 h, then (b) *o*-diamine (**4a**; 1.0 mmol), various amounts of Cu@QCSSi catalyst, solvent (10 ml), various temperatures.

[b]Isolated yield.

washed with ethanol and water, vacuum dried and stored for subsequent reaction runs. Evaporation of the solvent gave the crude product, which was purified by column chromatography over silica gel employing *n*-hexane–ethyl acetate (5:1) as eluent.

2.3 | General procedure for preparation of 2*H*-indazoles from 2-bromobenzaldehyde, sodium azide and amines

To a mixture of 2-bromobenzaldehyde (1.0 mmol), amine (1.1 mmol) and sodium azide (2.0 mmol) in DMSO (1.0 ml) was added the nanocatalyst (5.0 mol%) and the mixture was stirred at 120°C. After completion of the reaction, the reaction mixture was cooled to room temperature; the mixture was poured into EtOAc (20.0 ml). The reaction mixture was centrifuged for 20 min to separate the nanocatalyst. Then, the organic layer was washed with deionized water (3 × 20.0 ml), dried ($CaCl_2$) and evaporated *in vacuo* to affoed the crude product, which was purified by silica gel column chromatography employing *n*-hexane–EtOAc (10:1) as eluent.

3 | RESULTS AND DISCUSSION

Cu@QCSSi was synthesized in three steps. In the first step, 2-oxo-1,2-dihydroquinoline-3-carbaldehyde (QC; 0.1 mmol) was grafted on amino-functionalized silica (0.1 g) in ethanol solvent at reflux condition for 3 h. In the second step, 2-oxoquinoline-3-carbaldehyde Schiff base supported on amino-functionalized silica (QCSSi) was centrifuged, washed with ethanol and then dried under vacuum. In the third step, copper acetate (0.05 mmol) and QCSSi were stirred in ethanol at reflux condition for 12 h. Finally, Cu@QCSSi was centrifuged, washed with ethanol and then dried under vacuum (Scheme 1).

Due to complexation or low percentage of Cu(II) in the catalyst, the signals relating to Cu(II) were not detected well by XRD (Figure 2).[37] With the purpose of

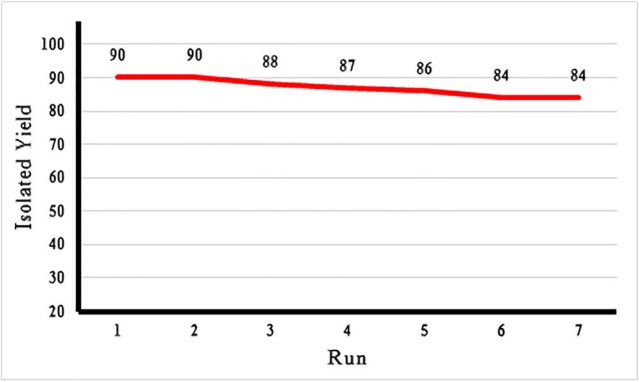
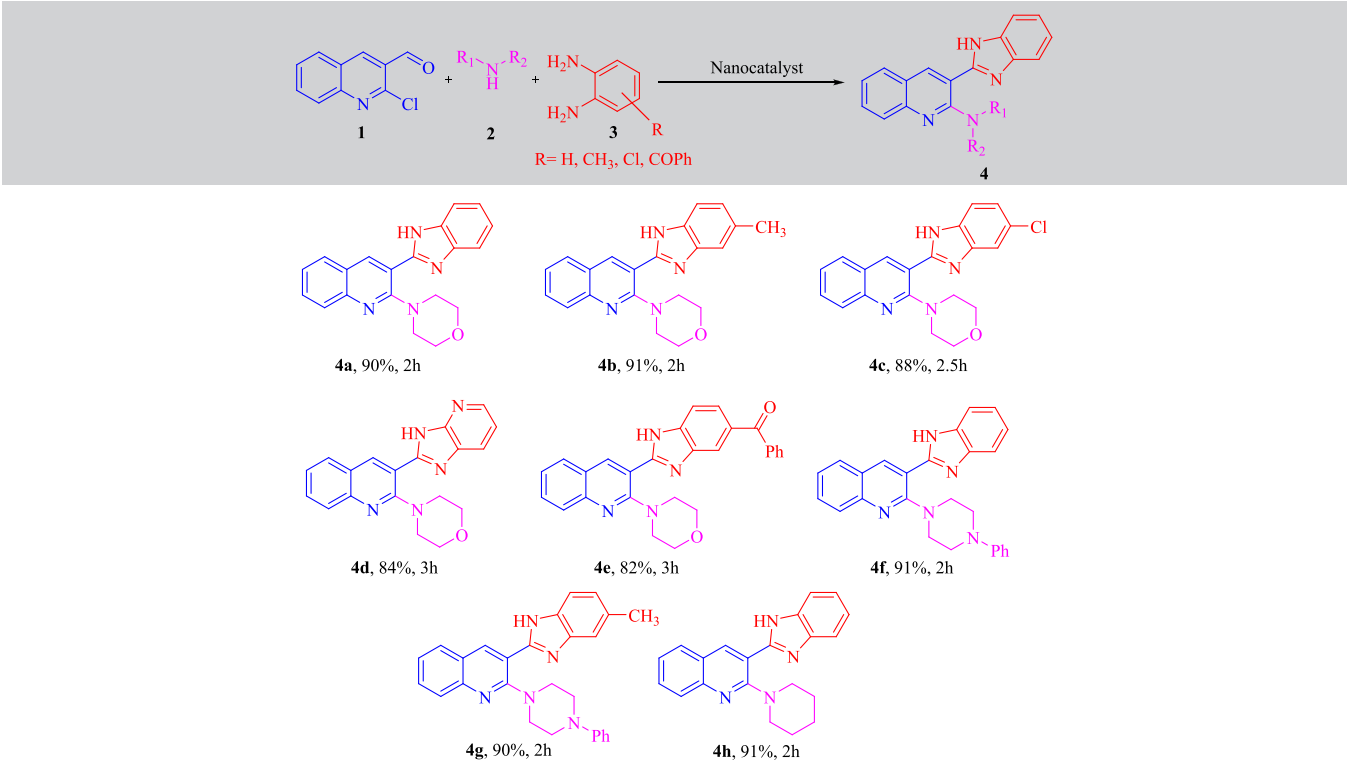


FIGURE 9 Recyclability of Cu@QCSSi catalyst in the synthesis of **4**

TABLE 2 Synthesis of quinoline–secondary amine–benzimidazole hybrids



evaluating the Cu content, the Cu@QCSSi catalyst was subjected to ICP analysis. The Cu content was determined to be 5.57% (w/w). As shown in Figure 3, the presence of copper was also proved from the EDX analysis of the Cu@QCSSi catalyst.

As shown in Figure 4, the ν(C═N) stretching band of imine nitrogens in the IR spectrum of QCSSi shifted to lower wavenumber in the spectrum of Cu@QCSSi, confirming production of the catalyst. The thermal stability of the Cu@QCSSi catalyst was investigated using TGA and differential thermal analysis (DTA) curves (Figure 5). The TGA showed three different mass loss stages. The first stage of weight loss, at around of 120°C, is related to water, organic solvents and absorbed moisture on the surface of the Cu@QCSSi catalyst. The second and third decomposition steps occurred in the ranges 120–230 and 230–530°C, respectively, which could be ascribed to the decomposition of copper complex. The silica was decomposed above 530°C. The TGA result indicated that the thermal stability of the Cu@QCSSi catalyst is considerable in comparison to that of previously reported Shift base catalysts.[38–44] On raising the temperature to 300°C, only 2.65% of catalyst was decomposed. The TGA curves of amino-functionalized silica and QCSSi are illustrated in Figure 6. The SEM images for QCSSi and the Cu@QCSSi catalyst are shown in Figures 7 and 8, displaying nanoparticles with average sizes of less than 100 nm.

A literature review has revealed the importance of benzimidazoles, quinolines and secondary amines for finding new bioactive hybrids.[45] A series of this type of hybrid molecule have been proved to have anti-inflammatory, antiasthmatic and antihypertensive properties. Advantages including simplicity, greater efficiency and atom economy with the generation of complex 'drug-like' N-heterocyclic products in a one-vessel transformation prompted us to investigate a one-pot and three component synthesis of quinoline–amine–benzimidazole molecules (**5**) from the reaction of a pre-mixture of 2-chloroquinoline-3-carbaldehyde (**1**) and secondary amine derivatives (**2**) with *o*-phenylenediamines (**4**).

At the outset of this investigation, we decided to test the three-component reaction of **1**, morpholine (**2a**) and *o*-phenylenediamine (**4a**) using the Cu@QCSSi catalyst as a new nanocatalyst. The reaction was screened as a model considering various parameters. Initially, **1** and **2a** were reacted under solvent-free conditions at 120°C for 12 h to form intermediate **3a**. After cooling the reaction, we investigated the effect of various factors such as different amounts of Cu@QCSSi catalyst, solvent (10 ml; ethanol, methanol, acetonitrile, dioxane, water and dimethylformamide) and temperature on the yield of the reaction of **3a** and **4a**. We used amino-functionalized silica, copper acetate, a mixture of amino-functionalized silica and copper acetate, and QCSSi as catalyst in the reaction, as well. The best result was obtained when this

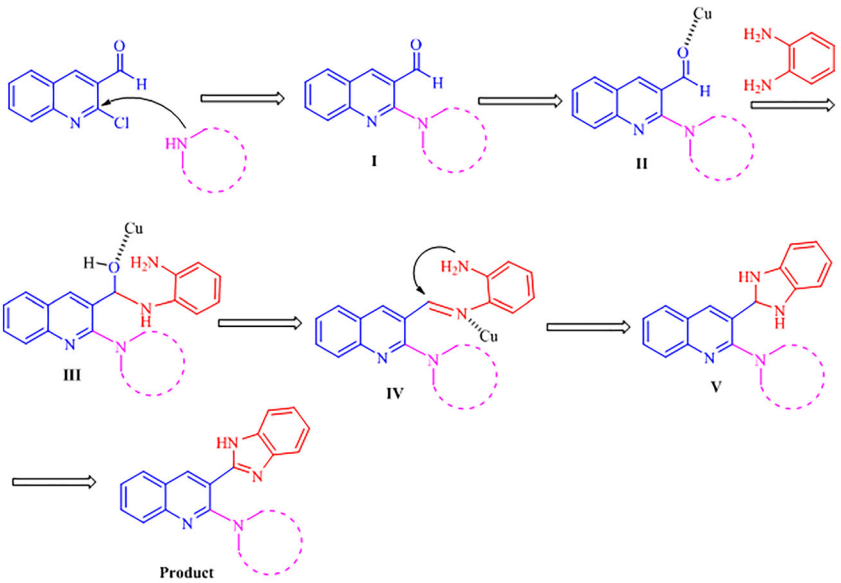
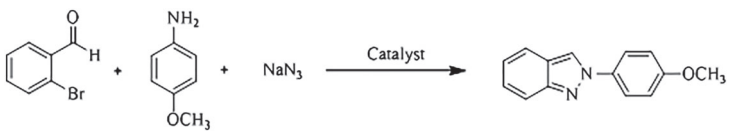


FIGURE 10 Proposed mechanism



SCHEME 2 Model reaction for the synthesis of 2-(4-methoxyphenyl)-2*H*-indazole

reaction was performed in ethanol at 50°C using 5.0 mol% of Cu@QCSSi catalyst (Table 1).

After optimization of the reaction conditions, the catalytic activity of the Cu@QCSSi catalyst was investigated using various *o*-phenylenediamine derivatives (**4**) bearing CH_3, Cl and COPh substituents, **1** and **2**. In all cases, the reaction proceeded well to afford quinoline–secondary amine–benzimidazole hybrids (Table 2).

The reusability of the Cu@QCSSi catalyst was investigated for the one-pot synthesis of 3-(1*H*-benzo[*d*]imidazol-2-yl)quinolines containing secondary amine skeleton at the C-2 position in the presence of the catalyst (5.0 mol%), **1**, **2a** and **4a**. The Cu@QCSSi catalyst was centrifuged from the reaction mixture, washed with ethanol (10 ml) and dried in air. The catalyst was then applied for the next run. The catalyst was successfully recycled in seven consecutive runs and showed appreciable conversions in each run (Figure 9). The nanocatalyst after seven runs was separated and the copper content in the heterogeneous catalyst was determined using ICP analysis; ICP results showed 89.2% recovery for this anchoring procedure.

To test the heterogeneous nature of the catalyst, the hot filtration technique was used. The catalyst was stirred in ethanol under reflux for 6 h. The catalyst was separated from the hot solvent using centrifugation. The reaction was performed using this solvent under optimized conditions. But, corresponding benzimidazolquinoline product was not observed after 6 h.

According to the literature, herein we report a possible mechanism for this one-pot synthesis of benzimidazolquinoline derivatives catalysed by Cu@QCSSi. Initially, **I** is produced through a nucleophilic attack of secondary amine to 2-chloroquinoline-3-carbaldehyde. In the next step, amino-functionalized silica-supported Cu(II)–quinoline complex activates the aldehyde carbonyl group. The attack of $-NH_2$ to the aldehyde carbonyl group produces a Schiff base intermediate (**IV**). In continuation, ring closure takes place by the nucleophilic attack of the NH_2 group. Finally, oxidation process can convert the intermediate **V** to corresponding product (Figure 10).[3]

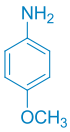
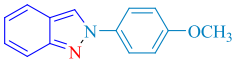
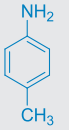
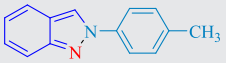
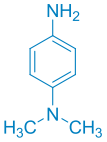
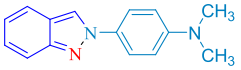
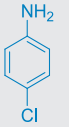
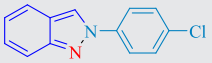
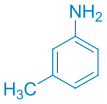
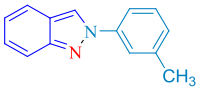
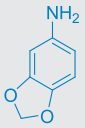
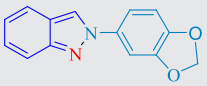
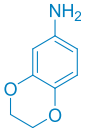
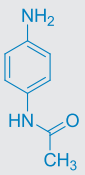
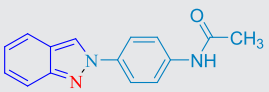
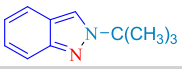
Also, we used the catalytic system for the preparation of 2*H*-indazoles from 2-bromobenzaldehyde, sodium

TABLE 3 Reaction of 2-bromobenzaldehyde (1.0 mmol), p-anisidine (1.1 mmol) and sodium azide (2.0 mmol) under various reaction conditions

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]
1	—	DMSO	120	24	—
2	10	DMSO	RT	24	—
3	3	DMSO	120	12	72
4	5	DMSO	120	12	87
5	10	DMSO	120	12	87
6	5	Toluene	Reflux	12	1
7	5	DMF	120	12	63
8	5	MeOH	Reflux	12	—
9	5	EtOH	Reflux	12	—
10	5	H_2O	Reflux	12	—

[a]Isolated yield.

TABLE 4 Synthesis of 2*H*-indazoles with Cu@QCSSi (5.0 mol%) as catalyst at 120°C

Entry	Amine	Product	Yield (%)[a]	Ref.
1			87	[46]
2			83	[46]
3			84	[46]
4			87	[46]
5			81	[46]
6			85	[46]
7			82	
8			80	31a
9	H_2N - $C(CH_3)_3$		67	31a

[a]Isolated yield.

azide and amines as starting materials using the heterogeneous nanocatalyst. Herein, we examined the synthesis of 2-(4-methoxyphenyl)-2*H*-indazole using 2-bromobenzaldehyde (1.0 mmol), *p*-anisidine (1.1 mmol) and sodium azide (2.0 mmol) in DMSO (1.0 ml) in the presence of 5.0 mol% catalyst at 120°C (Scheme 2). The progress of the reaction was monitored by TLC. The product (2-(4-methoxyphenyl)-2*H*-indazole) could be isolated in good yield after 12 h.

During our optimization studies, the effect of temperature, solvent and amount of catalyst for this three-component reaction was investigated. We found that the temperature, solvent and amount of catalyst play a significant role in terms of the isolated yield and the reaction rate. Among various conditions used, the best result was obtained using 5.0 mol% of catalyst in DMSO as a solvent at 120°C (Table 3).

In the next step, we studied the scope of the reaction with various anilines for the synthesis of 2*H*-indazoles under the optimized conditions (Table 4). The presented protocol has the ability to tolerate other functional groups, such as methyl, methoxy and halogen, on the anilines. The results are presented in Table 4. Also, aliphatic amines such as *tert*-butylamine are applicable for the synthesis of 2*H*-indazoles using the presented procedure (Table 4, entry 8).

4 | CONCLUSIONS

In summary, a simple, cost-effective and environmentally clean catalytic system containing a Cu(II) complex derived from 2-oxoquinoline-3-carbaldehyde Schiff base supported on amino-functionalized silica was successfully developed. The utility of the supported Cu(II) complex for catalysing the one-pot synthesis of 3-(1*H*-benzo[*d*]imidazol-2-yl) quinolines containing piperidine, morpholine and phenylpiperazine skeletons at the C-2 position under mild reaction conditions was proved. The catalyst was recycled and reused for seven consecutive runs without significant loss of catalytic activity. Also, we have developed a one-pot three-component reaction for the synthesis of 2*H*-indazoles using the catalyst from 2-bromobenzaldehyde, primary amines and sodium azide.

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SUPPORTING INFORMATION

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