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Nano Copper(0)-Stabilized on Alumina: Efficient and Recyclable Heterogeneous Catalyst for Chemoselective Synthesis of 1,2-Disubstituted Benzimidazoles and Quinoxalines in Aqueous Medium

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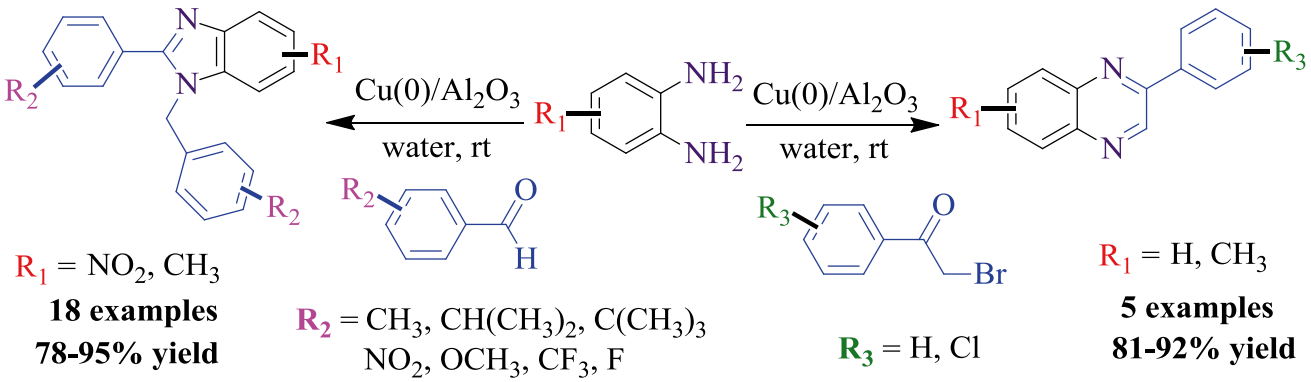
Abstract The present communication elicits the use of copper nanoparticles on aluminium oxide derived from Cu–Al hydrotalcite as a heterogeneous catalyst in the green and operationally simple approach for the synthesis of selective 1,2-disubstituted benzimidazoles and quinoxaline. Wide ranges of substituted *o*-phenylenediamines and aldehydes or α-bromo ketones were used to achieve the desired products using water as the reaction medium. The recoverability and reusability of the catalyst are the significant features in this eco-friendly green protocol.

Graphical Abstract A simple and efficient process for the synthesis of benzimidazoles and quinoxaline in presence of $Cu(0)/Al_2O_3$ catalyst at room temperature is described.



Keywords Benzimidazole · Quinoxaline · Heterogeneous catalysis · Copper nanoparticles on alumina · Recyclability · Aqueous medium

1 Introduction

Benzimidazole and quinoxaline are important *N*-heterocyclic units in pharmaceutical industry due to their broad biological functions such as antiviral, antiulcer, antihypertensive and anticancer activities [1–5]. Additionally, benzimidazole

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moieties frequently find applications in materials science, especially in organic light-emitting diodes and membranes for fuel cells [6, 7]. Similarly, quinoxalines are interesting class of compounds due to the presence of its core structure in many biocides [8], various biofunctional molecules [9] and pharmaceuticals [10].

In general, the synthesis of benzimidazoles moieties comprises the condensation of 1,2-phenylenediamines with aldehydes [11, 12] or carboxylic acid derivatives [13] in presence of strong acids such as polyphosphoric acid or mineral acids. Recently, transition-metal-catalyzed C–N cross-coupling reactions for the synthesis of benzimidazole derivatives have been reported [14–21]. Palladium- and copper-catalyzed aryl amination/condensation protocols have been utilized for the synthesis of 1,2-disubstituted benzimidazoles [22]. Brasche and Buchwald reported the copper catalyzed synthesis of benzimidazoles from amidines through C–H functionalization/C–N bond formation reaction [23]. Shi and co-workers have used the palladium catalyzed C–H activation reaction for the formation of benzimidazoles [24]. The CuI/*N,N′*-dimethylethylenediamine (DMEDA)-mediated regiospecific reaction of 1,2-dihaloarenes with N-substituted amidines or guanidines for the formation of benzimidazoles was reported by Deng and co-workers [25]. Later, You and co-workers have described the regio-specific synthesis of 1,2-disubstituted benzimidazoles [26].

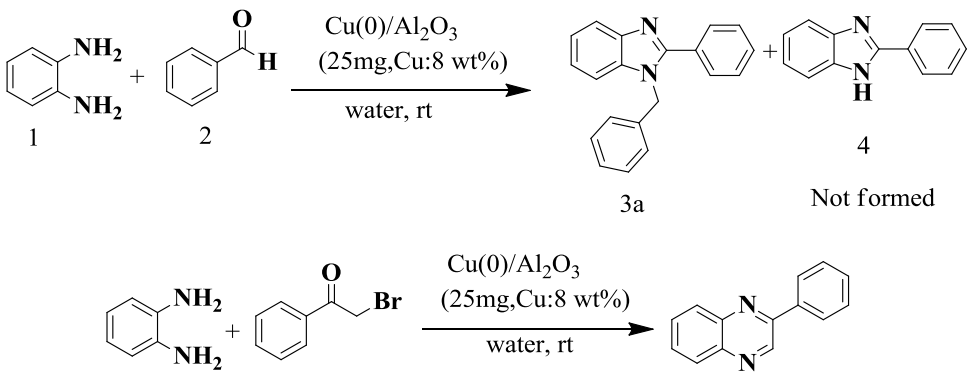
Other synthetic methodologies, such as reductive cyclization reaction of *o*-nitroaniline with aldehydes [27], rhodium catalyzed hydroformylation of *N*-alkenyl-1,2-diaminobenzenes [28], tandem carbonylation–cyclization reaction of *o*-phenylenediamines [29] and tandem dehydration–coupling reaction of 2-bromoaniline catalyzed by palladium have been reported [30]. However, the main limitation of these methodologies is the formation of both 2-substituted and 1,2-disubstituted benzimidazoles. The selective synthesis of 1,2-disubstituted benzimidazoles have been reported by very few research groups [31–34]. Among the methods reported, some of the processes suffer from long reaction times, use of toxic catalysts/solvent and a tedious work-up process.

Further, the synthesis of quinoxaline is generally accomplished by the oxidative cascade reactions of *o*-phenylenediamine with α-hydroxy ketones [35, 36], epoxides [37] and diols [38] in the presence of either noble metal or additional oxidants. Reaction of *o*-phenylenediamine with dicarbonyl compounds also produces quinoxaline as reported by Lindsley and co-workers [39]. Additionally, multicomponent reactions have recently been introduced for the formation of quinoxaline [40]. Progress has also been made in the synthesis of quinoxaline derivatives by using Brønsted acid [41], and molecular iodine [42, 43]. However, It is intriguing to note that rarely α-bromoketones have been used as reaction partners of *o*-phenylenediamine for the formation of quinoxalines [33, 44] and most of the reported methodologies suffer from serious draw backs such as use of stoichiometric amount of catalyst, long reaction time, use of toxic solvents, unsatisfactory yields and inability to recover and reuse the catalyst.

Recently, we have focused our efforts on the synthesis of mono dispersed and highly stable Cu(0) from copper–aluminium hydrotalcite [45–47]. One of the important characteristics of nano-Cu(0) on alumina is that it is prepared from single precursor, Cu–Al HT Brucite like structures and, upon reduction, Cu(II) gets selectively reduced to Cu(0) with high dispersion and stability. Herein, we report the activity of this nano-Cu(0) on alumina catalyst towards the synthesis of benzimidazole and quinoxaline derivatives (Scheme 1).

2 Results and Discussion

Copper–aluminum hydrotalcites [(Cu–Al HT) Cu:Al 3:1] was prepared by co-precipitation of Cu- and Al nitrates. The thermal reduction of copper aluminiumhydrotalcite to nano copper(0) on alumina catalyst in presence of hydrogen flow is performed according to the procedure reported earlier [45]. Copper:aluminium ratio (Cu:Al) in nano Cu(0)/Al_2O_3 catalysts was found to be 2.49:1 by inductively coupled plasma-atomic emission spectroscopy (ICPMS). The Cu content of Cu(0)/Al_2O_3 was obtained



Scheme 1 Synthesis of 1,2-disubstituted benzimidazole and quinoxaline by using nano copper supported alumina at room temperature in aqueous medium

8 wt% by atomic absorption analysis (AAS). The average particle size of $Cu(0)/Al_2O_3$ was estimated to be 8.0 nm which is well matched with transmission electron microscopy.

The XRD pattern was used to investigate both the crystal structure and the average crystalline size of Cu nano particles.

As shown in Fig. 1, the clear and strong peaks corresponding to (111), (200), and (220) indicate the formation of highly crystalline Cu nanoparticles [48].

There is no change in the crystal structure of Cu nano particles phases in both fresh and used form of catalysts (Fig. 1a, c). Transmission electron microscopic (TEM) studies of both fresh and used catalysts were carried out to understand the shape and size of the particles. Figure 2 a and b shows the TEM images of the fresh and the used catalyst after the fifth cycle. Interestingly it is observed that the shape and size of the particles remain unchanged. This supports that the morphology of the catalyst remains the same even after recycling.

The X-ray photoelectron spectroscopic (XPS) investigation of Cu–Al HT, Fig. 3a and fresh $Cu(0)/Al_2O_3$, Fig. 3b shows that there is a change in oxidation state of copper from +2 to 0. The XPS analysis of $Cu(0)/Al_2O_3$ and Cu–Al HT catalyst at the Cu 2p level shows $2p_{3/2}$ line at 932.3, and 934.7 eV and 952.2 and 954.6 eV for $2p_{1/2}$, which corresponds to Cu in 0 and +2 oxidation states, respectively.

2.1 Optimization Conditions

In the optimization study for the benzimidazole synthesis, various solvents such as dichloromethane, acetonitrile, acetone, methanol, toluene and DMF were tested to check their activity and selectivity (Table 1). Surprisingly, dichloromethane produced poor yield of the product (Table 1, entry 1), while acetonitrile gave good yields. However, increase in reaction temperature had no effect on the isolated yield of the product (Table 1, entries 2 and 3). Only moderate yields of the product was obtained at room temperature and in 60–110 °C with the other organic solvents used (Table 1,

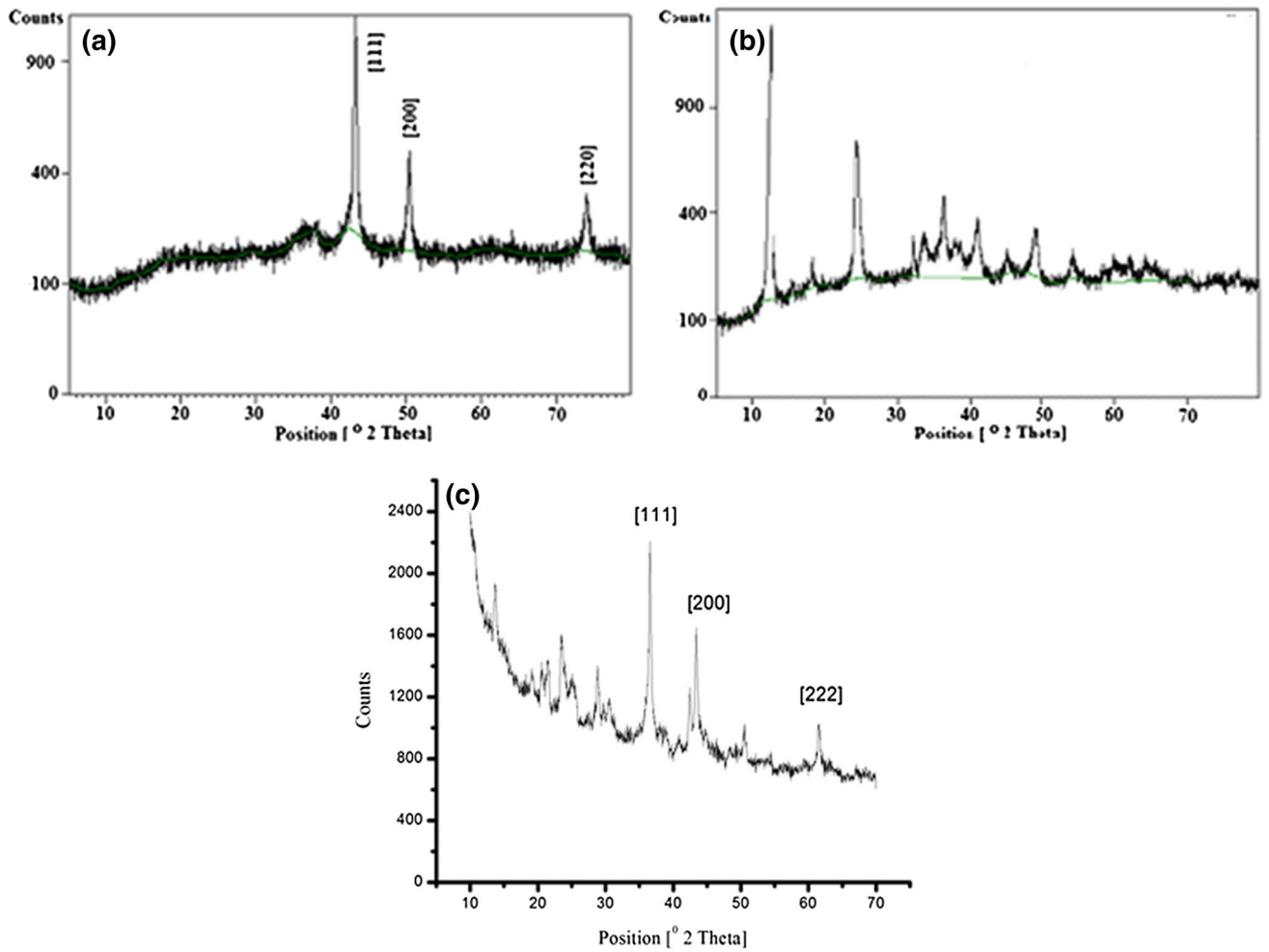


Fig. 1 XRD profiles of **a** fresh $Cu(0)/Al_2O_3$, **b** Cu(II)–Al HT and (**c**) used catalyst

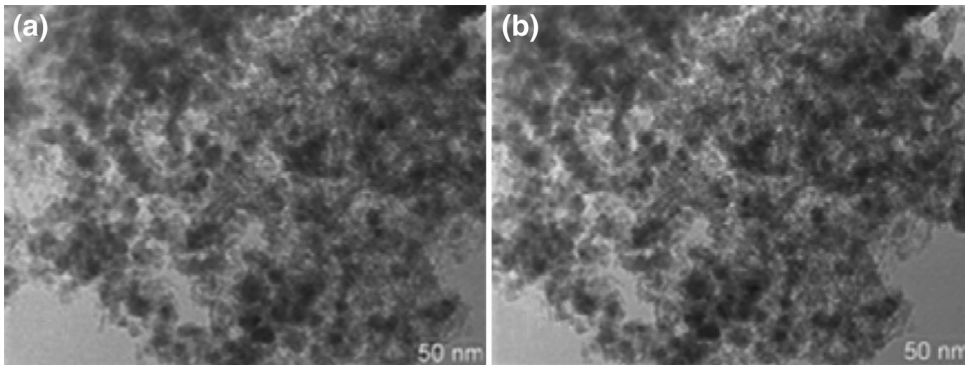


Fig. 2 TEM images of the $Cu(0)/Al_2O_3$: **a** fresh and **b** used catalyst

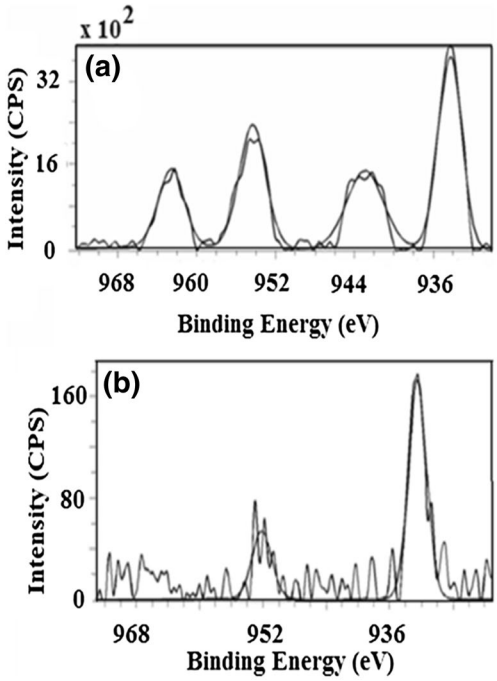


Fig. 3 **a** The XPS spectra of Cu(II)–Al HT and **b** fresh $Cu(0)/Al_2O_3$

entries 4–7). Importantly, $Cu(0)/Al_2O_3$ catalyst showed excellent yield and chemoselectivity by furnishing **3a** as the sole product in water at room temperature (Table 1, entry 8).

The model reaction was also optimized for catalyst concentration and reaction time (Table 1, entries 9–11). 8 wt% of nano $Cu(0)/Al_2O_3$ was sufficient for maximum product yields (Table 1, entry 8) while 4 wt% catalyst loading gave moderate yields of the product (Table 1, entry 9). Interestingly, an increment in catalyst concentration more than 8 wt% did not show effective increase in product yields (Table 1, entry 11).

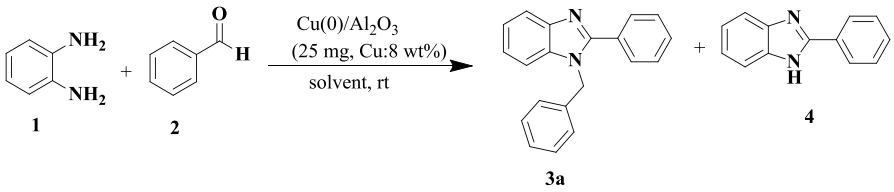
We also screened a variety of other copper catalysts such as commercially available CuO, Cu_2O, copper bronze, CuCl, $CuSO_4$ and Cu–Al HT with the model substrates and water as solvent (Table 2). The reaction proceeded even without the presence of any catalyst. However, nearly equal quantities of product **3a** and **4** were obtained (Table 2, entry 1). The $Cu(0)/Al_2O_3$ catalyst was found to be more active and selective than the other copper catalysts tested (Table 2, entries 2–8).

The excellent yield and chemoselectivity mediated by $Cu(0)/Al_2O_3$ catalyst in water inspired us to further investigate this transformation. Under the optimized reaction conditions, the scope of this reaction was extended by subjecting different diamines and aldehydes. The aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents reacted efficiently to produce the corresponding products in good to excellent yields.

Methyl, isopropyl and tertiary butyl groups on the aldehydes were well tolerated and the corresponding products were obtained in good yields (Table 3, products **3b–3d**). The aromatic mono-, di- and tri-sustituted benzaldehydes containing electron donating groups (4-methoxy, 2,3-dimethoxy and 3,4,5-trimethoxy benzaldehyde) produced good yields of the corresponding products (Table 3, products **3e**–**3h**). Furthermore, the reactivity of the substituent groups varies with their position on the aromatic ring of the aldehyde. Introduction of an electron-withdrawing group at the *para* and *meta*-position of benzaldehyde compared to *ortho*-position gave better product yields (Table 3, products **3i–3k**). This variation in product yields with position of the substituent group may be due to resonating, inductive or steric effects. Substituted benzaldehydes containing electron-withdrawing fluoro and trifluoromethyl group also furnished good yields of product (Table 3, products **3l** and **3m**) Interestingly, heteroaromatic aldehydes such as pyridine-2-aldehyde, pyridine-3-aldehyde and furfuraldehyde produced moderate to good yields of the products under similar reaction conditions (Table 3, products **3n-3r**).

The proposed mechanism of the $Cu(0)/Al_2O_3$ catalyzed synthesis of 1,2-disubstituted benzimidazoles, may tentatively be visualized to occur via the formation of an *N*,N′-dibenzylidene-*o*-phenylenediamine. The aldehyde firstly reacted with diamine to form the intermediate 1 (Scheme2). Then in the presence of electrophilic catalyst, the intramolecular 1,3-hydride migration was induced to produce the 1,2-disubstituted benzimidazole. This kind of mechanism has

Table 1 Screening of reaction parameters



Entry	Solvent	Temp (°C)	Time (h)	Yield (%)	
				3a	**4**
1	DCM	Rt	1.0	40	35
2	Acetonitrile	Rt	2.0	85	–
3	Acetonitrile	60	2.0	85	–
4	Acetone	70	2.5	50	35
5	Methanol	60	1.0	65	15
6	Toluene	100	1.5	78	05
7	DMF	110	2.5	70	10
8	**Water**	**Rt**	**1.0**	**96**	–
9	Water	Rt	1.0	62[a]	–
10	Water	Rt	0.5	78[b]	–
11	Water	Rt	1.0	89[c]	–

Reaction conditions: 1,2-phenylenediamine (1 mmol), benzaldehyde (2 mmol), 25 mg $Cu(0)/Al_2O_3$ (8 wt% of Cu), solvent (2 mL), room temperature

The bold row shows copper(0) on alumina catalyst activity more prominantly

[a]12.5 mg catalyst (4 wt% Cu)

[b]25 mg catalyst (8 wt% Cu) in 0.5 h

[c]50 mg catalyst (16 wt% Cu)

Table 2 Screening of different catalysts

Entry	Catalyst	Time (h)	Yield (%)	
			3a	**4**
1	None	1.0	45	39
2	Cu–Al HT	1	80	
3	**$Cu(0)/Al_2O_3$**	**1.0**	**96**	–
4	CuCl	1.0	84	–
5	CuO	1.0	82	10
6	Cu–Bronze	1.0	75	22
7	Cu_2O	2.0	65	18
8	$CuSO_4$	2.0	–	–

Reaction conditions: 1,2-phenylenediamine (1 mmol), benzaldehyde (2 mmol), copper catalyst (8 wt% of Cu), water (2 mL), room temperature

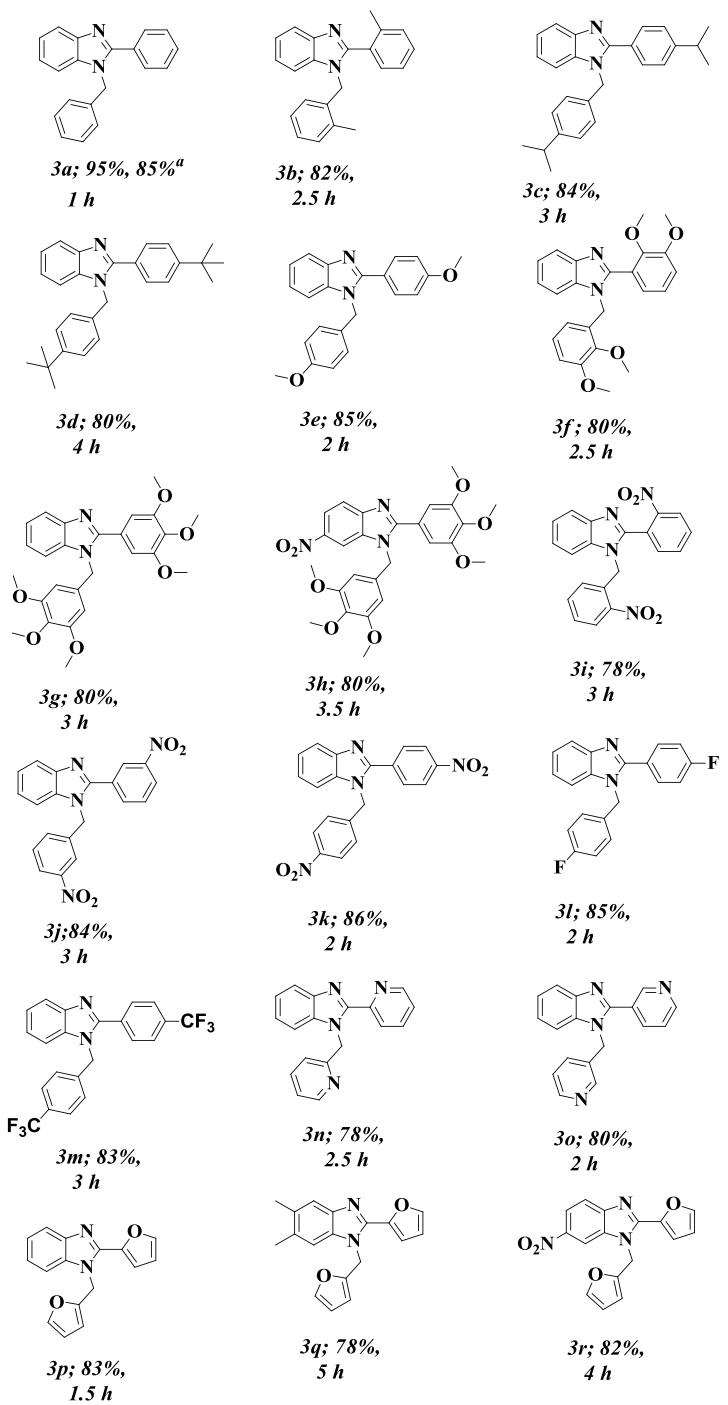
The bold row shows copper(0) on alumina catalyst activity more prominantly

been previously proposed in literature [12, 49] while Yuanjiang Pan and co-workers where the first ones to validate it with isotope labelling reaction using benzaldehyde-d_1 [33].

Encouraged by the high catalytic activity of $Cu(0)/Al_2O_3$ in the reaction of *o*-phenylenediamines with aldehydes, we thought that functional ketones may also react with *o*-phenylenediamine to give functional heterocyclic compounds. As illustrated in Table 4, the catalyst, $Cu(0)/Al_2O_3$ (Cu 8 wt%, 25 mg, 2.69 mol%) and water as solvent at room temperature with a variety of α-bromoketones and *o*-phenylenediamines proved to be efficient catalytic protocol to produce functionalized quinoxalines. The minimal effect of the substituent groups on the course of the reaction was observed when both substituted ketones as well as amines were used (Table 4, entries 4b–4e).

The recyclability study of recovered catalyst $Cu(0)/Al_2O_3$ in the quinoxaline synthesis was also performed. Figure 4 presents the results of recycling of the catalyst using 1,2-phenylenediamine and α-bromoketone as the model substrate. $Cu(0)/Al_2O_3$ catalyst shows nearly consistent activity up to five reaction cycles. After each cycle, the $Cu(0)/Al_2O_3$ catalyst was recovered by simple centrifugation, washed with water and diethyl ether, oven-dried and used directly for the next cycle without any further purifications. Only a slight loss of catalytic activity was observed. Moreover, the leaching of the copper metal after each cycle was determined by AAS and was found to be negligible. Interestingly, the recovered catalyst's

Table 3 Investigation of substrate scope

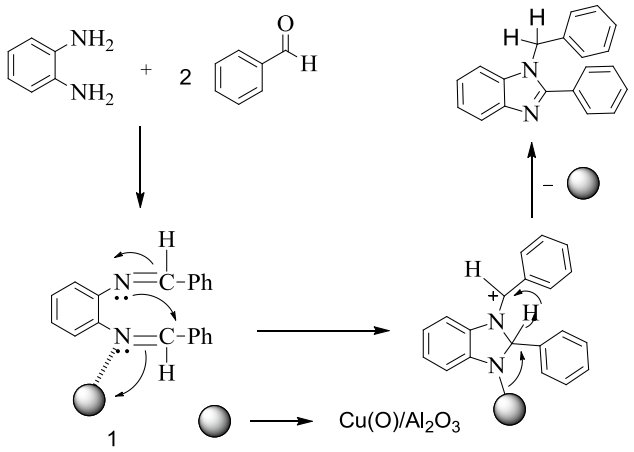


Reaction conditions: Diamine (1 mmol), aldehyde (2 mmol), 25 mg Cu(0)/Al_2O_3, water (2 mL), room temperature

[a]after 3rd cycle

diminished catalytic activity could be regenerated using thermal reduction in presence of hydrogen flow (Fig. 4 cycle 6).

We envisaged a plausible reaction mechanism of the formation of quinoxaline derivatives from o-phenylenediamine and phenacyl bromide (Scheme 3). Initially the electrophilic catalyst activates the phenacyl bromide making it susceptible



Scheme 2 Plausible mechanism of 1,2-disubstituted benzimidazole synthesis

for a nucleophilic attack by the amino group of phenylenediamine to afford the intermediate (1) intermediate 1 then cyclises to form the intermediate (2) the charged water group in intermediate 3 is expelled out by the nucleophilic attack from the adjacent amino group which results in the formation of intermediate 4 which readily undergoes aromatization under air oxidation to afford 2-phenylquinoxaline as the final product.

3 Conclusion

In summary, a practical and green catalytic synthetic method has been developed for the facile synthesis of 1,2-disubstituted benzimidazoles and quinoxalines with excellent yields. The broad ranges of functional heterocyclic compounds have been synthesized in water in the presence of copper nanoparticles stabilised on alumina without using any additional surfactant or oxidant. The catalyst can be used for five cycles with almost consistent activity.

4 Experimental Section

4.1 General Experimental Procedure for the Synthesis of 1,2-Disubstituted Benzimidazoles in Water

A 10 mL Schlenk flask was charged with aldehyde (2 mmol), 1,2-diamine (1 mmol), $Cu(0)/Al_2O_3$ catalyst (Cu 8 wt%, 25 mg) in water (2 mL). The reaction mixture was stirred at room temperature under vigorous stirring for appropriate time. After the completion of the reaction, as

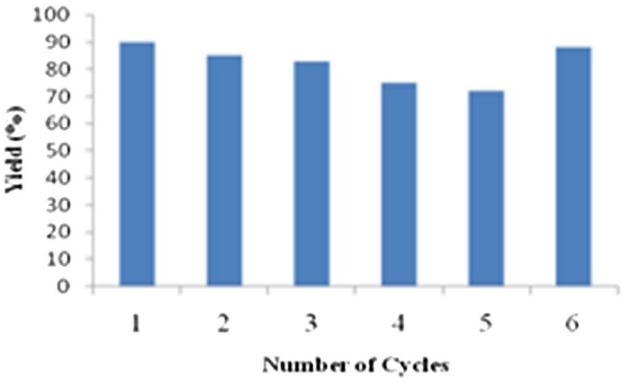
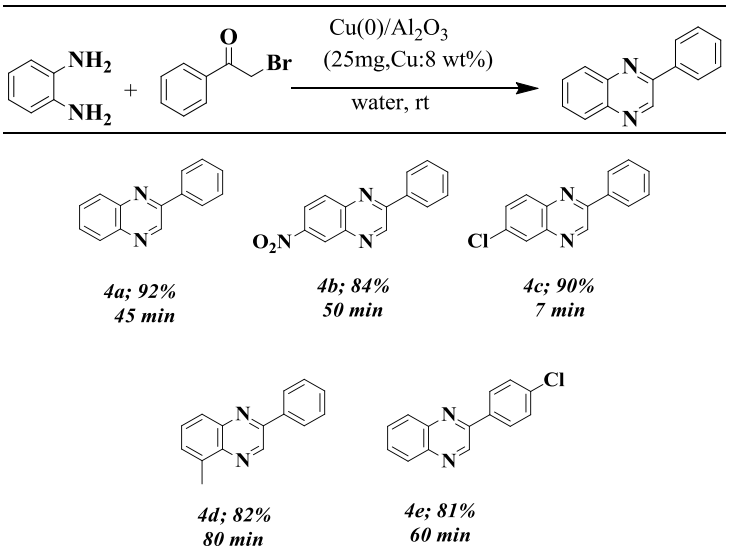
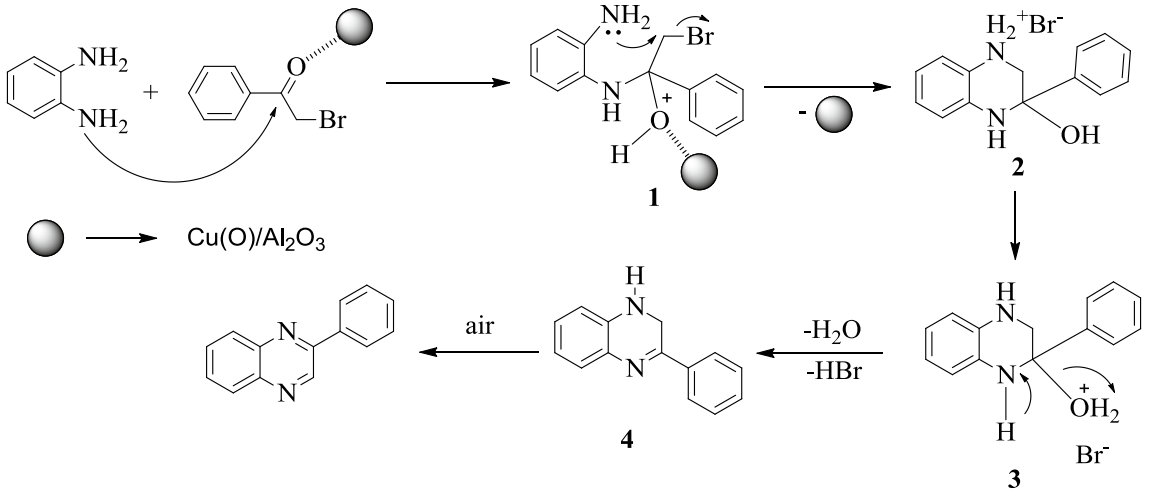


Fig. 4 Recyclability of the catalyst in the quinoxaline reaction

Table 4 Substrate scope for the synthesis of quinoxalines derivatives



Reaction conditions: 1,2-phenylenediamine (1 mmol), α-bromoketone (1 mmol), copper catalyst (8 wt% of Cu), water (2 mL), room temperature



Scheme 3 Plausible mechanism of quinoaline synthesis

monitored by TLC, 5 mL of ethyl acetate was added in the reaction mixture. The catalyst was separated by simple centrifugation and the reaction mixture was treated with brine (10 mL). The organic layer was separated and the aqueous layer was back extracted with ethyl acetate (3 × 5 mL). The combined ethyl acetate extract was dried with anhydrous Na_2SO_4 (50 g) and was concentrated under reduced pressure. The pure product was isolated by flash column chromatography on silica gel using ethyl acetate/hexane (10%) as an eluent.

*4.1.1 1-Benzyl-2-phenyl-1H-benzo[d]imidazole (**3a**) [49]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, 1H), 7.71–7.65 (m, 2H), 7.48–7.40 (m, 3H), 7.36–7.25 (m, 4H), 7.22 (q, 2H), 7.09 (d, 2H), 5.44 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 143.2, 136.4, 136.1, 130.0, 129.3, 129.2, 128.7, 127.8, 126.0, 123.0, 122.7, 120.0, 48.4. ESI-MS $[M+H]^+$: m/z = 285; HRMS (ESI orbitrap): calc. for $C_{20}H_{16}N_2$ $[M+H]^+$: 285.1386, found: 285.1386.

*4.1.2 1-(2-Methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole (**3b**) [32]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.38–7.26 (m, 3H), 7.24–7.16 (m, 2H), 7.16–7.10 (m, 2H), 7.05–6.99 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 5.18 (s, 2H), 2.23 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 143.1, 138.3, 134.9, 134.0, 130.4 25.7, 130.3, 129.8, 127.5, 126.3, 126.0, 125.6, 122.8, 122.3, 120.0, 110.5, 45.7, 19.8, 19.0. ESI-MS $[M+H]^+$: m/z = 313; HRMS (ESI orbitrap): calc. for $C_{22}H_{20}N_2$ $[M+H]^+$: 313.16993, found: 313.16824.

*4.1.3 1-(4-Isopropylbenzyl)-2-(4-isopropylphenyl)-1H-benzo[d] imidazole (**3c**) [50]*

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.32–7.26 (m, 3H), 7.22–7.14 (m, 4H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.42 (s, 2H), 2.99–2.83 (m, 2H), 1.27 (s, 3H), 1.26 (s, 3H), 1.23 (d, J = 3.8 Hz, 3H), 1.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 150.9, 148.4, 143.2, 136.1, 133.8, 129.3, 127.5, 127.1, 126.8, 125.9, 122.8, 122.5, 119.8, 110.6, 48.2, 34.1, 33.7, 23.9. ESI-MS $[M+H]^+$: m/z = 369; HRMS (ESI orbitrap): calc. for $C_{26}H_{28}N_2$ $[M+H]^+$: 369.23064 found: **369.23064**.

*4.1.4 1-(4-(Tert-butyl)benzyl)-2-(4-(tert-butyl) phenyl)-1H-benzo[d]imidazole (**3d**) [51]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.32–7.27 (m, 1H), 7.21 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.44 (s, 2H), 1.34 (s, 8H), 1.30 (s, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 153.2, 150.7, 143.1, 136.0, 133.4, 129, 127.0, 126.0, 126.0, 122.8, 122.7, 119.8, 110.6, 48.2, 34.8, 34.5, 31.3; ESI-MS $[M+H]^+$: m/z = 397; HRMS (ESI orbitrap): calc. for $C_{28}H_{32}N_2$ $[M+H]^+$: 397.2638, found: 397.2637.

*4.1.5 1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (**3e**) [29]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.29 (ddd, *J* = 7.3, 5.3, 2.6 Hz, 1H), 7.21 (dd, *J* = 6.1, 3.1 Hz, 2H), 7.03 (d,

$J = 8.7$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 5.38 (s, 2H), 3.85 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 159.1, 154.1, 143.1, 136.1, 130.7, 128.5, 127.2, 122.7, 122.5, 119.7, 114.33, 114.0, 110.4, 55.3, 47.9 ; ESI-MS $[M + H+]^+$: m/z = 345; HRMS (ESI orbitrap): calc. for $C_{22}H_{20}N_2O_2$ $[M + H]^+$: 345.1597, found: 345.1611.

*4.1.6 1-(2,3-Dimethoxybenzyl)-2-(2,3-dimethoxyphenyl)-1 H-benzo[d]imidazole (**3f**)*

Yellow solid (MP: 86–90 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 7.8$ Hz, 2H), 7.30–7.23 (m, 5H), 7.22–7.17 (m, 2H), 7.16–7.13 (m, 4H), 7.07–7.02 (m, 2H), 6.82 (t, $J = 7.9$ Hz, 2H), 6.76 (dd, $J = 8.2$, 1.3 Hz, 2H), 6.28 (dd, $J = 7.6$, 1.3 Hz, 2H), 5.34 (s, 4H), 3.91 (s, 6H), 3.82 (s, 6H), 3.65 (t, $J = 5.7$ Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 152.5, 151.7, 147.5, 146.4, 143.2, 135.3, 130.0, 125.4, 124.5, 124.1, 123.8, 122.6, 122.0, 119.8, 114.0, 111.7, 110.9, 61.4, 60.4, 55.9, 55.72, 43.4; ESI-MS $[M + H]^+$: m/z = 405; HRMS (ESI orbitrap): calc. for $C_{24}H_{24}N_2O_4$ $[M + H]^+$: 405.1808, found: 405.1809.

*4.1.7 1-(3,4,5-Trimethoxybenzyl)-2-(3,4,5-trimethoxypheny l)-1H-benzo[d]imidazole (**3g**) [49]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.84 (m, 1H), 7.37–7.34 (m, 1H), 7.34–7.28 (m, 2H), 6.92 (s, 2H), 6.36 (s, 2H), 5.40 (s, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 3.72 (d, J = 1.2 Hz, 6H), 3.71 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 154.0, 153.3, 142.8, 139.4, 137.4, 136.4, 132.5, 125.1, 123.2, 122.8, 119.9, 110.0, 106.3, 102.7, 60.89, 56.2, 56.0, 48.5; ESI-MS $[M + H]^+$: m/z = 465; HRMS (ESI orbitrap): calc. for $C_{26}H_{28}N_2O_6$ $[M + H]^+$: 465.2020, found: 465.2033, calc. for $C_{26}H_{28}N_2O_6$ $[M + Na]^+$: 487.1839, found: 487.1852.

*4.1.8 6-Nitro-1-(3,4,5-trimethoxybenzyl)-2-(3,4,5-trimetho xyphenyl)-1H-benzo[d]imidazole (**3h**)*

Orange Solid (MP: 144–148 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33–8.26 (m, 2H), 7.92 (d, $J = 9.0$ Hz, 1H), 6.96 (s, 2H), 6.32 (s, 2H), 5.47 (d, $J = 17.1$ Hz, 2H), 3.91 (s, 3H), 3.83 (s, 3H), 3.74 (s, 6H), 3.73 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 154.1, 153.6, 147.4, 143.8, 140.4, 137.9, 135.8, 131.2, 123.8, 120.0, 118.9, 106.9, 106.5, 102.8, 60.9, 56.3, 56.0, 48.9. ESI-MS $[M + H]^+$: m/z = 510; HRMS (ESI orbitrap): calc. for $C_{26}H_{27}N_3O_8$ $[M + H]^+$: 310.08223, found: 310.08375.

*4.1.9 1-(2-Nitrobenzyl)-2-(2-nitrophenyl)-1H-benzo[d] imidazole (**3i**) [49]*

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (ddd, $J = 13.0$, 7.2, 2.6 Hz, 2H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.74–7.60 (m, 2H), 7.56–7.42 (m, 3H), 7.39–7.33 (m, 1H), 7.33–7.27 (m, 1H), 7.15 (d, $J = 7.9$ Hz, 1H), 6.95 (d, $J = 7.1$ Hz, 1H), 5.69 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 149.0, 147.0, 143.0, 134.8, 134.3, 133.1, 132.1, 131.5, 128.9, 128.4, 125.5, 125.27, 123.9, 123.2, 110.2, 45.7. ESI-MS $[M + H]^+$: m/z = 375; HRMS (ESI orbitrap): calc. for $C_{20}H_{14}N_4O_4$ $[M + H]^+$: 375.10878, found: 375.10951.

*4.1.10 1-(3-Nitrobenzyl)-2-(3-nitrophenyl)-1H-benzo[d] imidazole (**3j**) [33]*

Pale yellow solid; ^{1}H NMR(300 MHz, $CDCl_3$ + DMSO) δ 8.52 (d, $J = 1.9$ Hz, 1H), 8.39–8.32 (m, 1H), 8.19 (d, $J = 8.1$ Hz, 1H), 8.11–8.00 (m, 2H), 7.89 (d, $J = 6.8$ Hz, 1H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.58 (t, $J = 7.9$ Hz, 1H), 7.45–7.29 (m, 4H), 5.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 151.0, 148.4, 142.8, 138.0, 135.8, 134.8, 131.8, 131.4, 130.3, 130.0, 124.6, 124.1, 124.0, 123.5, 123.2, 121.0, 120.4, 110.2, 47.6; ESI-MS $[M + H]^+$: m/z = 375; HRMS (ESI orbitrap): calc. for $C_{20}H_{14}N_4O_4$ $[M + H]^+$: 375.10878, found: 375.10954.

*4.1.11 1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1H-benzo[d] imidazole (**3k**) [49]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, $J = 8.9$ Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 7.93 (d, $J = 7.9$ Hz, 1H), 7.85 (d, $J = 8.8$ Hz, 2H), 7.44–7.38 (m, 1H), 7.38–7.32 (m, 1H), 7.27 (d, $J = 9.3$ Hz, 3H), 7.21 (d, $J = 7.9$ Hz, 1H), 5.58 (s, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 148.5, 147.9, 143.1, 142.8, 135.7, 130.0, 126.7, 124.6, 124.1, 123.8, 120.8, 110.2, 48.0; ESI-MS $[M + H]^+$: m/z = 375; HRMS (ESI orbitrap): calc. for $C_{20}H_{14}N_4O_4$ $[M + H]^+$: 375.10878, found: 375.10947.

*4.1.12 1-(4-Fluorobenzyl)-2-(4-fluorophenyl)-1H-benzo[d] imidazole (**3l**) [33]*

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, $J = 7.9$ Hz, 1H), 7.64 (dd, $J = 7.9$, 5.4 Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.26 (t, $J = 7.4$ Hz, 1H), 7.21 (d, $J = 7.9$ Hz, 1H), 7.14 (t, $J = 8.4$ Hz, 2H), 7.02 (dd, $J = 15.7$, 7.2 Hz, 4H), 5.39 (s, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 143.1, 140.0, 135.9, 133.3, 131.8, 130.6, 129.5, 126.2, 125.9, 125.1, 123.9, 123.3, 122.4, 120.5, 110.3, 48.0; ESI-MS $[M + H]+$: m/z = 321; HRMS (ESI orbitrap): calc. for $C_{20}H_{14}F_2N_2$ $[M + H]^+$: 321.1197, found: 320.1198.

*4.1.13 1-(4-(Trifluoromethyl)benzyl)-2-(4-(trifluoromethyl) phenyl)-1H-benzo[d]imidazole (**3m**) [52]*

Red solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.40–7.35 (m, 1H), 7.33–7.28 (m, 1H), 7.21 (t, J = 7.1 Hz, 3H), 5.51 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 143.17, 140.0, 135.9. 133.3, 129.5, 126.2, 125.8, 123.9, 123.3, 120.5, 110.3, 48.06. ESI-MS $[M+H]^+$: m/z = 421; HRMS (ESI orbitrap): calc. for $C_{22}H_{14}F_6N_2$ $[M+H]^+$: 286.1133, found: 286.1128.

*4.1.14 2-(Pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-benz o[d]imidazole (**3n**) [49]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (tdd, J = 2.6, 1.7, 0.8 Hz, 2H), 8.49 (d, J = 8.1 Hz, 1H), 7.89–7.86 (m, 1H), 7.84 (dd, J = 7.9, 1.8 Hz, 1H), 7.49 (td, J = 7.8, 1.8 Hz, 1H), 7.38 (dd, J = 7.2, 0.9 Hz, 1H), 7.35–7.29 (m, 2H), 7.29–7.25 (m, 2H), 7.15 (dd, J = 6.7, 5.0 Hz, 1H), 6.91 (d, J = 7.9 Hz, 1H), 6.30 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 149.8, 149.1, 148.7, 137.2, 124.6, 123.9, 123.1, 122.3, 120.0, 110.8, 51.1. ESI-MS $[M+H]^+$: m/z = 286; HRMS (ESI orbitrap): calc. for $C_{18}H_{14}N_4$ $[M+H]^+$: 287.12912 found: 287.12764.

*4.1.15 3-(Pyridin-3-yl)-1-(pyridin-3-ylmethyl)-1H-benz o[d]imidazole (**3o**) [32]*

Yellow gummy liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.72 (t, J = 12.7 Hz, 1H), 8.60 (dd, J = 25.7, 10.1 Hz, 1H), 8.47 (s, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.43 (dd, J = 7.7, 4.9 Hz, 1H), 7.40–7.33 (m, 1H), 7.30 (t, J = 6.2 Hz, 2H), 7.28–7.22 (m, 2H), 5.50 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 149.5, 147.8, 143.2, 136.7, 135.7, 133.6, 131.5, 126.3, 123.9, 123.8, 123.3, 120.4, 110.2, 46.16; ESI-MS $[M+H]^+$: m/z = 286; HRMS (ESI orbitrap): calc. for $C_{18}H_{14}N_4[M+H]^+$: 286.1291, found: 286.1292.

*4.1.16 2-(Furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzo[d] imidazole (**3p**) [49]*

Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.74 (m, 1H), 7.62 (d, J = 19.4 Hz, 1H), 7.49 (dd, J = 5.9, 2.9 Hz, 1H), 7.35–7.27 (m, 3H), 7.22 (d, J = 3.3 Hz, 1H), 6.63–6.59 (m, 1H), 6.31–6.20 (m, 2H), 5.64 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 145.4, 143.9, 142.9, 142.6, 135.5, 123.2, 122.9, 119.8, 112.9, 112.1, 110.5, 110.0, 108.3, 41.7; ESI-MS $[M+H]^+$: m/z = 265; HRMS (ESI orbitrap): calc. for $C_{16}H_{12}N_2O_2[M+H]^+$: 265.0971, found: 265.0979.

*4.1.17 2-(Furan-2-yl)-1-(furan-2-ylmethyl)-5, 6-dimethyl-1H-benzo[d]imidazole (**3q**) [53]*

Brown Solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 31.2 Hz, 2H), 7.33 (s, 1H), 7.24 (d, J = 11.4 Hz, 1H), 7.14 (s, 1H), 6.58 (s, 1H), 6.23 (d, J = 30.9 Hz, 2H), 5.57 (s, 2H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 145.6, 143.6, 143.2, 142.5, 141.6, 134.0, 132.5, 131.8, 119.8, 112.2, 111.9, 110.5, 110.1, 108.1, 41.6, 20.7, 20.3. ESI-MS $[M+H]^+$: m/z = 293; HRMS (ESI orbitrap): calc. for $C_{18}H_{16}N_2O_2$ $[M+H]^+$: 293.12845, found: 293.12657.

*4.1.18 2-(Furan-2-yl)-1-(furan-2-ylmethyl)-6-nitro-1H-benzo[d]imidazole (**3r**)*

Brown solid; (MP: 146–150 °C) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 2.0 Hz, 1H), 8.23 (dd, J = 8.9, 2.1 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 1.1 Hz, 1H), 7.39 (d, J = 3.5 Hz, 1H), 7.36 (t, J = 3.1 Hz, 1H), 6.69 (dd, J = 3.5, 1.7 Hz, 1H), 6.37 (d, J = 3.1 Hz, 1H), 6.33 (dd, J = 3.1, 1.8 Hz, 1H), 5.76 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 145.1, 143.2, 119.6, 119.0, 115.2, 112.6, 110.7, 109.2, 107.1, 42.1; ESI-MS $[M+H]^+$: m/z = 310; HRMS (ESI orbitrap): calc. for $C_{16}H_{11}N_3O_4$ $[M+H]^+$: 310.0837, found: 310.0822.

4.2 General Experimental Procedure for the Synthesis of Quinoxalines from Substituted 1, 2-Diamines and α-Bromo Ketones

A 10 mL Schlenk flask was charged with diamines (1 mmol), α-bromoketone (1 mmol), $Cu(0)/Al_2O_3$ catalyst (Cu 8 wt%, 25 mg) in water (2 mL). The reaction mixture was stirred at room temperature for appropriate time. After the completion of the reaction, as monitored by TLC, 5 mL of diethyl ether was added and the catalyst was separated by simple centrifugation. The reaction mixture was treated with brine (10 mL) and the organic layer was separated. The aqueous layer was back extracted with diethyl ether (3 × 5 mL). The combined organic extract was dried with anhydrous Na_2SO_4 (50 g) and was concentrated under reduced pressure. The pure product was isolated by flash column chromatography on silica gel using ethyl acetate/hexane (10%) as an eluent.

*4.2.1 2-Phenylquinoxaline (**4a**) [51]*

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.23–8.18 (m, 2H), 8.18–8.10 (m, 2H), 7.82–7.72 (m, 2H), 7.61–7.50 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.90 (s), 143.40 (s), 142.35 (s), 141.63 (s), 136.83 (s), 130.27 (d,

$J = 9.7$ Hz), 129.62 (d, $J = 9.8$ Hz), 129.19 (s), 127.59 (s). ESI-MS $[M+H]^+$: m/z = 207.

4.2.2 6-Nitro-2-phenylquinoxaline (**4b**) [53]

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 9.03 (d, $J = 2.4$ Hz, 1H), 8.56 (dd, $J = 9.2$, 2.4 Hz, 1H), 8.33–8.23 (m, 3H), 7.66–7.56 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 147.4, 145.5, 144.9, 140.3, 135.6, 131.4, 131.2, 129.4, 127.9, 125.6, 123.8.ESI-MS $[M+H]^+$: m/z = 252.

4.2.3 6-Chloro-2-phenylquinoxaline (**4c**) [54]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.25–8.13 (m, 3H), 8.05 (d, $J = 8.9$ Hz, 1H), 7.68 (dd, $J = 17.2$, 10.1 Hz, 1H), 7.62–7.50 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 142.8, 142.2, 141.6, 136.6, 135.2, 130.5, 129.8, 129.5, 129.1, 128.8. ESI-MS $[M+H]^+$: m/z = 241.

4.2.4 5-Methyl-2-phenylquinoxaline (**4d**) [55]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.16 (t, $J = 14.6$ Hz, 2H), 8.10–7.82 (m, 2H), 7.66–7.45 (m, 4H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 140.1, 137.0, 132.6, 131.8, 130.0, 129.1, 127.4, 21.8. ESI-MS $[M+H]^+$: m/z = 221.

4.2.5 2-(4-Chlorophenyl)quinoxaline (**4e**) [51]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.20–8.10 (m, 4H), 7.84–7.72 (m, 2H), 7.55 (d, $J = 8.6$ Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 142.8, 142.2, 141.6, 136.6, 135.2, 130.5, 129.8, 129.5, 129.1, 128.8. ESI-MS $[M+H]^+$: m/z = 241.

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