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CuI nanoparticles mediated expeditious synthesis of 2-substituted benzimidazoles using molecular oxygen as oxidant

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A general and easy method for the synthesis of several 2-substituted benzimidazoles from cyclization of *o*-diaminobenzenes and various aldehydes using CuI nanoparticles as a heterogeneous catalyst is described. Short reaction times, easy and quick isolation of the products and excellent yields are the main advantages of this procedure. This CuI nanoparticles catalyst system was found to be air/O_2 stable and also used for large scale cyclization reaction with recoverable and reusable properties without loss of catalytic activity for upto six cycles.

Introduction

Nitrogen containing heterocyclic compounds are pivotal building blocks in natural products, pharmaceuticals and materials chemistry. In particular, benzimidazoles have been found to possess a broad spectrum of biological activities such as anti-bacterial,[1] anti-fungal,[2] anti-inflammatory,[3] anti-viral[4] and anti-cancer[5,6] activities. Owing to their significance, numerous methods have been reported for benzimidazole synthesis and the increasing demands for green and sustainable protocols have revived the focus on their synthesis in recent years.[7]

The traditional method for the synthesis of benzimidazoles involves the condensation of *o*-phenylenediamines with carboxylic acids and their derivatives in the presence of strong acids at high temperatures (~200 °C).[8,9] Various catalysts have been employed and use of microwave irradiation has also shortened the reaction time but the conditions remain harsh, hence hampering the synthetic applicability of these protocols.[7,10] Oxidative cyclization of Schiff-base derivatives from *o*-phenylenediamine and aldehydes also give the corresponding 2-substituted benzimidazoles which is a more acceptable route (Fig. 1). Use of different catalysts has improved this strategy for the generation of benzimidazoles, notable examples being H_2O_2-CAN,[11] oxone,[12] DDQ,[13] $PhI(OAc)_2$,[14] copper-triflate,[15] 4-Methoxy-TEMPO,[16] $Yb(OTf)_3$,[17] $In(OTf)_3$,[18] and $I_2/KI/K_2CO_3$[19] as oxidising agents at relatively mild conditions. Although most of these homogeneous reaction conditions are milder, they still suffer from some

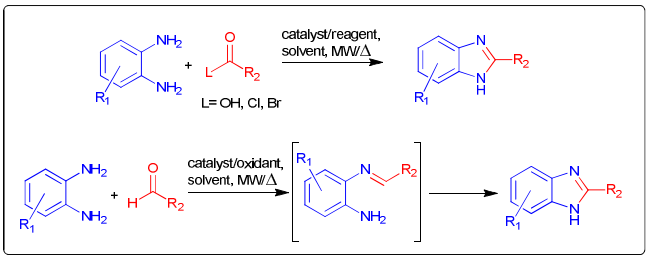

Fig.1 General routes for the synthesis of 2-substituted benzimidazoles

disadvantages like prolonged reaction times, high cost of the catalysts, formation of side products, difficulties in separation of the products and generation of highly hazardous metallic and organic wastes. The above mentioned limitations warrant the development of a green and recyclable, environmentally benign catalytic system for the synthesis of 2-substituted benzimidazoles preferably employing a greener oxidant.

In recent times, various heterogeneous catalysts, including highly active nano-catalysts have been developed for the synthesis of benzimidazoles *via* condensation of *o*-phenylenediamines with aromatic aldehydes. Examples include $CuFe_2O_4$-nanoparticles,[20] Mesoporous Titania-Iron(III) Oxide,[21] Pt-TiO_2,[22] SBA-15 supported Cobalt Nanocatalysts,[23] β-cyclodextrin,[24] $Fe_3O_4/SiO_2/(CH_2)_3N^+Me_3Br^-_3$ core-shell nanoparticles,[25] nano zinc oxide/nano-crystalline sulfated zirconia,[26] Fe_3O_4-SiO_2-$(NH_4)_6Mo_7O_{24}$ magnetic coreshell nanocomposite,[27] Cu(II)-nanosilica triazine dendrimer,[28] α-MoO_3 nanobelts,[29] CuO/Silica,[30] Co(III)-salen on activated carbon[31] etc. However, most of these methods use stoichiometric amounts of hazardous oxidants, employ expensive metal catalysts and generate toxic by-products which solicit the development of a greener protocol.

In continuation of our efforts towards the development of novel catalysts for important synthetic transformations,[32-42] herein we report CuI nanoparticles (CuI-np) catalysed synthesis of 2-aryl/alkyl- benzimidazoles using molecular oxygen as the

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oxidant. The CuI-nps were prepared as described previously[41] and characterized by XRD, XPS, TEM and EDX. It was then evaluated for its catalytic activity for the synthesis of 2-substituted benzimidazoles by using *o*-phenylediamines and various aromatic aldehydes as starting materials using air/oxygen as a green oxidant under ambient conditions. The prepared CuI nps were found to be stable under the employed reaction conditions and were easily recovered and recycled upto five times without showing any appreciable loss in yield.

Results and discussion

In an effort to devise a heterogeneous catalyst for the benzimidazole synthesis, initially we screened various catalysts and solvents for the model coupling between *o*-phenylediamine and benzaldehyde to yield 2-phenyl-1*H*-benzimidazole, including ferrites, TiO_2, CuI and CuI nps (Table 1). The CuI nps were prepared by the 'sodium citrate assisted hydrothermal method' as previously reported.[41] The TEM images and EDX spectrum for the prepared catalyst is shown in Fig.1. As shown in table 1, in the case of ferrites, the yields were increased by doping the ferrite nanoparticles with copper and cobalt metals (entries **5-7**, Table 1). Among the various catalysts screened, the prepared CuI nps gave the best yield of the corresponding benzimidazole when acetonitrile was used as the solvent (entry **8**, Table 1). Even though water gave moderate yield at room temperature, unfortunately there was no further increase in the yield even at reflux temperature of water. On the other hand, we found acetonitrile as a solvent of choice with no base or additional heat required to give the desired cyclized product in excellent yield at room temperature maintaining the selectivity. Subsequently, we performed the reaction with an O_2-filled balloon and found a remarkable increase in yield with the shortening of reaction time (entry **13**, Table 1). Control experiments without catalyst (entry **14**, Table 1) and without O_2 (using degassed solvent and Argon atmosphere; entry **15**, Table 1) were performed which ascertained the necessity of the CuI np catalyst and molecular oxygen as the oxidant for this reaction under the ambient conditions.

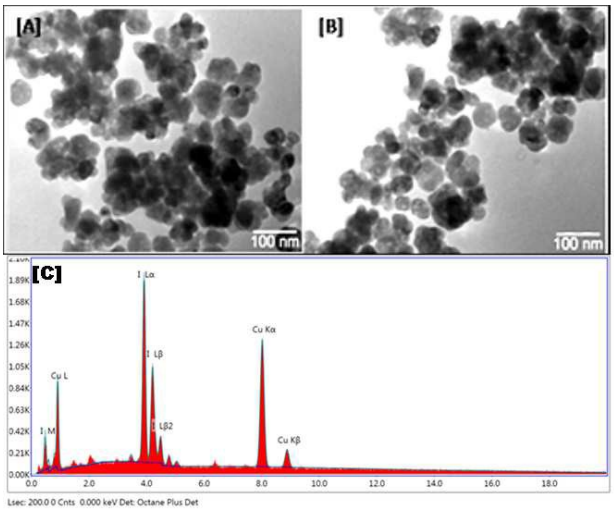
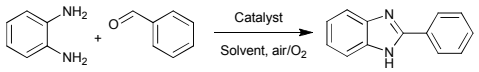


Fig.2 TEM images of A) fresh and B) re-used CuI nps; C) EDX spectrum for synthesised CuI nps.

Table 1 Optimization of the reaction conditions for benzimidazole synthesis [a]

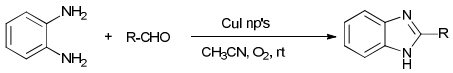


Entry	Catalyst	Solvent	Time (h)	Yield[b] (%)
1	CuI salt	CH_3CN	6	25
2	CuI salt	EtOH	6	16
3	TiO_2	CH_3CN	6	38
4	Fe_3O_4	CH_3CN	6	27
5	$CuFe_2O_4$	CH_3CN	6	54
6	$CoFe_2O_4$	CH_3CN	6	65
7	$CoFe_2O_4$	CH_3CN	12	82
8	CuI np	CH_3CN	3	92
9	CuI np	MeOH	3	40
10	CuI np	Toluene	6	30
11	CuI np	H_2O	6	50, 66[c]
12	CuI np	Ethylene glycol	6	25
13	CuI np	CH_3CN	1	97[d]
14	-	CH_3CN	12	15[d]
15	CuI np	CH_3CN (degassed)	6	18[e]

[a] Reaction conditions: *o*-phenylenediamine (1.0 mmol), benzaldehyde (1.1 mmol), catalyst (10 mol%) and solvent (2 mL) were stirred at rt; [b] Isolated yields. [c] at reflux conditions; [d] under O_2-balloon; [e] under inert (Ar) atmosphere.

To test the general scope and versatility of this procedure for the synthesis of a variety of 2-substituted benzimidazoles, we examined a number of aldehydes (Table 2) and different *o*-substituted diamines (Table 3). We were pleased to find that the optimized set of conditions afforded moderate to excellent

Table 2 Cyclization of *o*-phenylenediamine with substituted aldehydes using CuI nanoparticles as catalyst [a]



Entry	R	Time (h)	Yield* (%)	m.p. (°C)	Ref.
2a	C_3H_7	2	55	148-150	[43]
2b	C_5H_{11}	1.5	76	158-160	[44]
2c	C_6H_5-CH=CH	1	88	196-198	[43]
2d	C_6H_5	1	97[b]	291-293	[45]
2e	2-ClC_6H_4	1	90	233-235	[46]
2f	4-ClC_6H_4	1	95	264-266	[44]
2g	2,6-ClC_6H_3	2	78	275-276	[47]
2h	2-MeC_6H_4	1.5	84	221-223	[44]
2i	4-MeC_6H_4	1.5	89	277-279	[44]
2j	2,6-MeC_6H_3	2	72	295-297	[48]
2k	4-$MeOC_6H_4$	2	82	222-224	[44]
2l	4-$NO_2C_6H_4$	1	95	259-261	[44]
2m	2-$NO_2C_6H_4$	2	83	264-266	[49]
2n	Thiolyl	2	88	340-341	[44]
2o	Cyclohexyl	4	nr	-	

[a]Reaction conditions: O-phenylenediamine (1.0 mmol), aldehyde (1.1 mmol), catalyst (10 mol%), CH_3CN (2 mL) were stirred at rt; [b] kept at 10mmol scale; nr: No reaction; * Isolated yield

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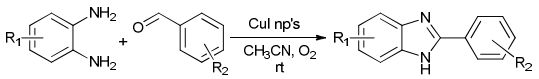
Table 3 Cyclization of substituted *O*-phenylenediamine with benzaldehyde using CuI nanoparticles as catalyst [a]



Entry	R^1	R^2	Time (h)	Yield * (%)	m.p. (^{o}C)	Ref.
3a	4-Me	H	1	91	244-246	[43]
3b	4,5-Me	H	1	95	235-237	[50]
3c	4-NO_2	H	2	65	154-156	[43]
3d	4,5-Cl	H	1	76	224-226	[51]
3e	4-Me	4-OMe	1	87	168-170	[43]
3f	4,5-Me	4-OMe	1	92	195-197	[52]
3g	4,5-Cl	2-OMe	2	67	197-199	-
3h	4-NO_2	4-n-Bu	2	72	185-186	-
3i	4,5-Cl	4-Me	2	80	236-238	-

[a] Reaction conditions: *o*-phenylenediamine (1.0 mmol), aldehyde (1.1 mmol), catalyst (10 mol%), CH_3CN (2 mL), reactions stirred at rt; * isolated yields.

yields in the condensation of *o*-phenylenediamine with aliphatic, aromatic and hetero-aromatic aldehydes as shown in table 2. In case of aliphatic aldehydes, hexanal gave good yield than butanal (entries **2a** and **2b**, Table 2). We also observed that cinnamaldehyde, an α,β-unsaturated aldehyde, also gave the corresponding benzimidazole in excellent yield (entry **2c**, Table 2). For aryl aldehydes, those with electron-withdrawing substituents gave better yields when compared to those having electron-donating groups (entries **2e-g** and **2l-m** vs **2h-k**, Table 2). *Para*-substituted benzaldehydes resulted in higher yields than the *ortho*-substituted ones and the low yields can be explained due to steric hindrance caused at the *ortho* position (entry **2e** vs **2f** and **2h** vs **2i**, Table 2). For di-*ortho*-substitutions, the effect was even more pronounced (**2g** and **2j**, Table 2). Heteroaryl aldehyde (entry **2n**, Table 2) also gave the acceptable yield, whereas no product was obtained when alicyclic aldehyde was used (entry **2o**, Table 2). 2-Phenylbenzimidazole (**2d**) was also synthesised at a 10 mmol scale, in excellent yield.

In the case of synthesis of benzimidazoles from different substituted *o*-phenylenediamines and aldehydes, it was observed that *o*-phenylenediamines with electron-donating substituents at *para* position yielded benzimidazoles with increasing yields (entries **3a-b** vs **3c-d**, Table 3). The yields were lower with the combination of electron-withdrawing diamines and benzaldehydes containing electron-donating groups (entries **3g-i**, Table 3).

Having checked the generality of this protocol for the synthesis of variety of benzimidazoles, next we studied the recyclability of the CuI nps. CuI nanoparticles were easily separated from the reaction mixture by centrifugation. The recovered catalyst was washed with acetone and then dried at 65 ^{o}C. It was then used for the next cycle and consistent catalytic activity was observed (see Fig. 3 and Table 2, entry **2d**: 1st cycle 97 %; 6th cycle 93 %). TEM image (Fig. 1B) showed no changes in the morphology of the recycled catalyst. Both the used and fresh CuI np catalysts were also

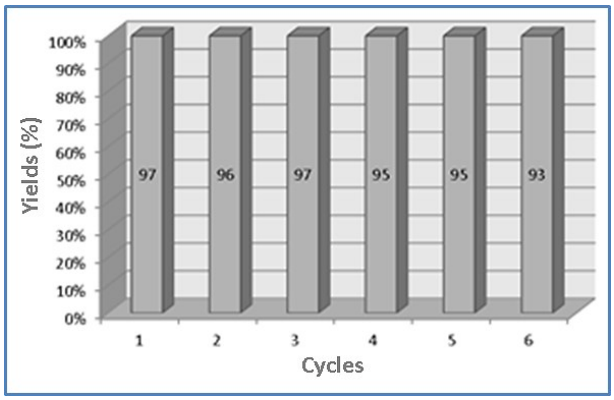


Fig. 3 Recyclability of CuI nps for synthesis of 2d

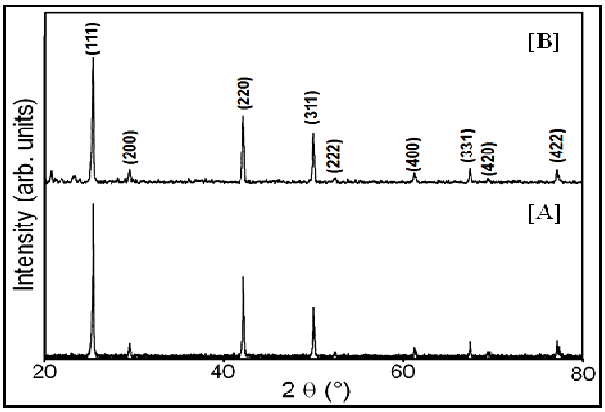


Fig. 4 XRD spectra of A) fresh CuI nps and B) CuI nps after sixth cycle.

characterized by XRD. According to the diffraction data card (JCPDS, 06-0246); all of the peaks can be perfectly indexed to CuI in peak position as shown in Fig. 4.

XPS survey scan of CuI nanoparticles showed the presence of copper, Cu 2p (at 933.37 eV), and iodine, I 3d (at 620 eV). The XPS high resolution narrow scans of Cu 2p for the fresh and used CuI nanoparticles are shown in Fig. 5 A and B. The observed Cu 2p binding energy peaks could be deconvoluted into two peaks, 933.379, 954.721 and 933.395, 953.059 eV for the fresh and used CuI nanoparticles, which are characteristic of $2p_{3/2}$ and $2p_{1/2}$ core levels. These observed binding energy

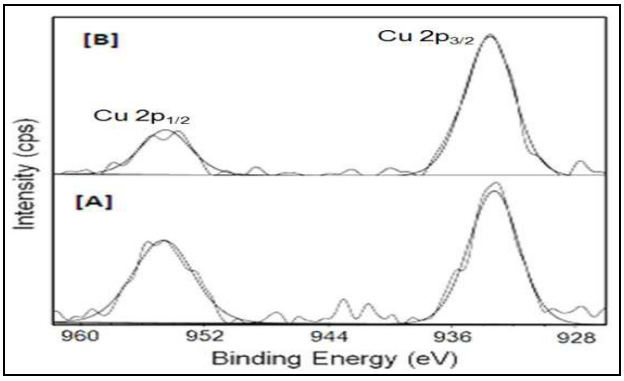


Fig. 5 XPS high resolution narrow scan of Cu 2p for CuI nanoparticles [A] fresh and [B] used (after 6th cycle).

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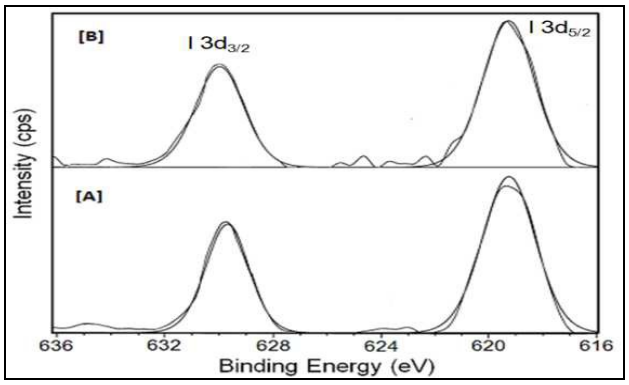

Fig. 6 XPS high resolution narrow scan of I 3d for CuI nanoparticles [A] fresh and [B] used (after 6th cycle)

peaks can be attributed to the Cu in +1 oxidation state. Similarly, the observed peak of I 3d peak at 620 eV could be deconvoluted into two peaks 3d5/2 and 3d3/2 at 619.313,629.724 and 619.808, 630.017 eV for the fresh and used CuI nanoparticles, respectively as shown in Fig. 6.

Next, to confirm the heterogeneity of the CuI nanoparticles, a reaction between *o*-phenylenediamine and benzaldehyde was terminated after a small conversion (20 min, 30% conversion), the catalyst was filtered-off and the reaction was continued with the filtrate for next 2 h. Almost no change in the conversion of *o*-phenylenediamine was observed. These studies and the non-activity in the absence of CuI nanoparticles in cyclization of *o*-phenylenediamine and benzaldehyde clearly prove that the reaction occurs heterogeneously.

Table 4 compares the catalytic activity of the prepared CuI nps with other recently reported heterogeneous nanocatalysts for the synthesis of 2-substituted benzimidazole (**2d** or **2f**). It can be clearly observed that while most of the catalysts require higher temperatures to exhibit their catalytic activity, the present CuI nps were active at ambient temperature. Two catalysts (entries 7 and 8, Table-4) yield the desired benzimidazole in less time, but require the use of hazardous oxidants, while in our case environmentally benign molecular oxygen is used as the oxidant. Furthermore, the use of molecular oxygen as the oxidant leads to a higher atom economy (84.35%) for the synthesis of benzimidazole (**2d**) than with the use of hydrogen peroxide or tert-butyl peroxide which render lower atom economies to the reaction having the values of 78.23% and 63.81%, respectively (calculations of atom economies can be found in the ESI). This further elucidates the 'greenness' of this protocol.

Table 4: Comparison of CuI nps with reported nano-catalysts for the synthesis of 2-phenyl benzimidazole (**2d**).

S. No	Catalyst[a]/solvent/oxidant	*T* (°C)	Time (h)	Yield (%)	Ref.
1.	$CuFe_2O_4$-nps (20 mol%), Toluene, O_2	110	24	89[b]	[19]
2.	Mesoporous TiO_2-Fe_2O_3 (20 mg), H_2O, O_2	40	3	97	[20]
3.	Pt-TiO_2 (1 mol%), mesitylene	165	1	78	[21]
4.	Co/SBA-15 (0.4 mol%), EtOH	60	4	98	[22]
5.	$Fe_3O_4/SiO_2/(CH_2)_3N^+Me_3Br^-_3$ nps (7 mg)	80	0.3	92	[24]
6.	Nano-ZnO (10 mol%), EtOH	80	1.67	88	[25]
7.	Fe_3O_4-SiO_2-$(NH_4)_6Mo_7O_{24}$ nanocomposite (220 mg), EtOH, H_2O_2	rt	0.5	90	[26]
8.	α-MoO3 nanobelts (2 mol%), t-BuOOH	50	0.5	93	[28]
9.	CuO np/Silica (10 mol%), MeOH	rt	4	93	[29]
10.	CuI nps, acetonitrile, O_2	rt	1	97	This work

[a]catalyst loading per 1mmol reaction scale; [b] for 2f.

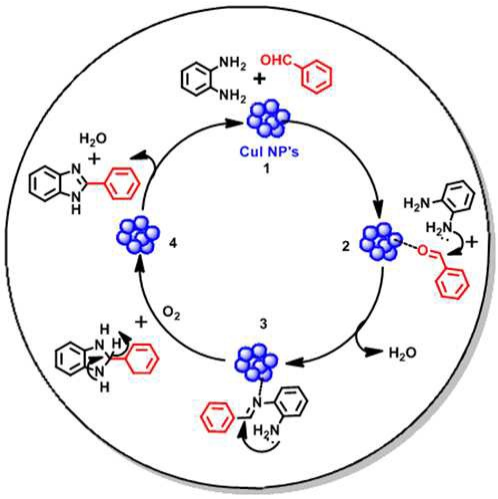

Fig. 7 Plausible reaction mechanism for CuI nps catalysed condensation of benzaldeyde with *o*-phenylenediamine.

A plausible mechanism for the CuI nps catalysed formation of 2-substituted benzimidazoles *via* the condensation of benzaldehyde with *o*-phenylenediamine is proposed (Fig. 7). The reaction generally proceeds via condensation mechanism, which involves the formation of Schiff's base and followed by oxidative cyclization. CuI has been recognized as a Lewis acid catalyst for important organic reactions.[53,54] So, in this catalytic process, the Cu(I) may be acting as a Lewis acid, forming a complex with the benzaldehyde and increasing the electrophilicity of its carbonyl group thereby facilitating imine formation with one of the amino group of the diamine. The other amino group (*ortho*) then proceeds with a nucleophilic attack on the imine and subsequent oxidative aromatization by dioxygen leads to the formation of the desired 2-substituted benzimidazole through removal of a water molecule.

Conclusions

In conclusion, we report nanostructured Copper Iodide as a simple and highly efficient catalytic system for the oxidative cyclization of various *o*-phenylenediamines with substituted benzaldehydes/aldehydes at room temperature to generate 2-substituted benzimidazoles. CuI nps were found to be stable under the employed reaction conditions and well-

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characterized by various spectroscopic analyses. The developed catalytic system was also employed at large scale cyclization reaction with recoverable and reusable properties without loss of catalytic activity for several cycles in the synthesis of benzimidazoles. The developed protocol is environmentally benign, does not involve the use of any toxic oxidants and devoid of generation of any toxic/hazardous by-products.

Experimental

All reagents were purchased from commercial sources and were used as such. The reaction progress was monitored using pre-coated TLC plates (E. Merck Kieselgel 60 F_{254}) and spots were visualised under UV light and also by exposing TLC plates to iodine vapour. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL Spectrospin spectrometer at 400 MHz and 100 MHz, respectively, using TMS as an internal standard. Melting points were recorded in open capillary tubes on an ERS automated melting point apparatus and are uncorrected. Mass spectra were recorded on an Agilent Accurate Mass Q-TOF MS system or micromass LCT Mass Spectrometer/Data system. IR spectra were recorded using Bruker FT-IR in the range of 4000–400 cm^{-1} and only characteristic frequencies are expressed. CuI nanoparticles were synthesized as reported previously.[40]

General procedure for the synthesis of 2-substituted benzimidazoles

A mixture of *o*-phenylenediamine (1 mmol) and aldehyde (1.1 mmol) was well stirred with CuI nps (10 mol%) and acetonitrile (2 mL) at room temperature for appropriate time. At the end of the reaction, as observed by TLC, the reaction mixture was then diluted with 2-3 mL of EtOAc, and centrifuged to remove the catalyst, and the catalyst was further washed with 5-10 mL of EtOAc to make it free from organic matter. To this reaction mixture, EtOAc (25 mL) was added and washed with water and then with brine. The organic phase was separated, dried over sodium sulfate and concentrated under vacuum to get the crude products. The crude products were purified by silica gel column chromatography using Hexane:EtOAc (80:20) as eluent.

Spectral data for representative compounds

2-(2,6-dichlorophenyl)-1H-benzo[d]imidazole (2g):
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.87 (brs, 1H), 7.72-7.51 (m, 5H), 7.30-7.17 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 146.72, 143.21, 135.08, 134.09, 132.40, 130.61, 128.36, 122.79, 121.60, 119.30, 111.61; anal. calcd for $C_{13}H_8Cl_2N_2$: C, 59.34; H, 3.06; N, 10.65, found: C, 59.52; H, 3.14; N, 10.55.

2-(thiophen-2-yl)-1H-benzo[d]imidazole (2n):
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.95 (s, 1H), 7.82 (d, *J* = 3.05 Hz, 1H), 7.71 (d, *J* = 5.34 Hz, 1H), 7.63-7.44 (m, 2H), 7.24-7.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.04, 143.66, 134.67, 133.73, 128.75, 128.28, 126.68, 122.39, 121.73, 118.59, 110.99., anal. calcd for $C_{11}H_8N_2S$: C, 65.97; H, 4.03; N, 13.99, found: C, 66.08; H, 4.09; N, 13.94.

5,6-dichloro-2-(2-methoxyphenyl)-1H-benzo[d]imidazole (3g):
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.29 (s, 1H), 8.32-8.27 (m, 1H), 7.90 (s, 1H), 7.78 (s, 1H), 7.50 (t, *J* = 8.39 Hz, 1H), 7.24 (d, *J* =8.39 Hz, 1H), 7.11 (t, *J* =7.63 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 156.94, 151.48, 142.40, 134.28, 132.05, 129.88, 124.14, 124.10, 121.00, 119.53, 117.13, 113.22, 112.25, 55.90; ESI-HRMS (m/z) calcd for $C_{14}H_{10}Cl_2N_2O$: 293.0243 $(MH)^+$; found: 293.0241 $(MH)^+$.

2-(4-butylphenyl)-6-nitro-1H-benzo[d]imidazole (3h):
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.52 (s, 1H), 8.60-8.27 (m, 1H), 8.11 (d, *J* = 7.63 Hz, 3H), 7.86-7.59 (m, 1H), 7.41 (d, *J* = 7.63 2H), 2.65 (t, *J* = 7.63 Hz, 2H), 1.63-1.54 (m, 2H), 1.37-1.27 (m, 2H), 0.90 (t, *J* = 7.63 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.78, 142.60, 129.06, 126.97, 126.53, 117.98, 34.72, 32.83, 21.79, 13.78. ESI-HRMS (m/z) calcd for $C_{17}H_{18}N_3O_2$: 296.1394 $(MH)^+$; found: 296.1373 $(MH)^+$.

5,6-dichloro-2-(p-tolyl)-1H-benzo[d]imidazole (3i):
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.16 (s, 1H), 8.04 (d, *J* = 8.39 Hz, 2H), 7.89 (s, 1H), 7.71 (s, 1H), 7.35 (d, *J* = 7.63 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.97, 140.43, 129.63, 126.68, 126.51, 124.25, 21.01; ESI-HRMS (m/z) calcd for $C_{14}H_{11}Cl_2N_2$: 277.0294 $(MH)^+$; found: 277.0300 $(MH)^+$.

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CuI nanoparticles mediated expeditious synthesis of 2-substituted benzimidazoles using molecular oxygen as oxidant

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2-substituted benzimidazoles from *o*-diaminobenzenes and aldehydes using CuI nanoparticles as a heterogeneous nano-catalyst and O_2 as an oxidant were synthesised in excellent yields.