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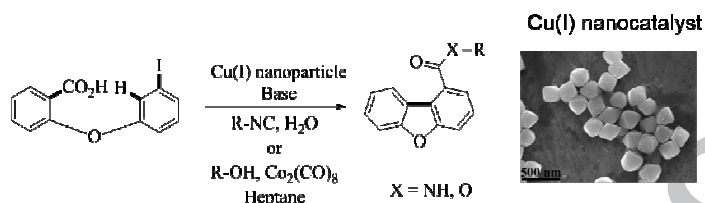


## Graphical Abstract

**Cubic nano-copper(I) oxides as reusable catalyst in consecutive decarboxylative C-H arylation and carbonylation: rapid synthesis of carbonyl dibenzofurans**

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## Cubic nano-copper(I) oxides as reusable catalyst in consecutive decarboxylative C-H arylation and carbonylation: rapid synthesis of carbonyl dibenzofurans

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### ABSTRACT

Consecutive chemo- and regio-selective decarboxylative C-H arylation, followed by carbonylative C-C coupling of aryl halide with isocyanide/alcohol was applied for the first time in one-step synthesis of carbonyl dibenzofurans with nanodomain cuprous oxide under aerobic condition. As a proof of concept, several novel dibenzofurans were synthesized from 2-(3-iodophenoxy) benzoic acid in good yield. The tandem protocol eliminates the use of excess catalysts, hazardous organic solvents, heavy metals like palladium or rhodium, ligands, oxidants or external additives. More importantly, the cubic Cu(I) nanocatalyst can be recovered and recycled for three consecutive reactions without any significant loss of catalytic activity or any change in its morphology. Use of water as solvent and reusable catalyst makes the reaction environment friendly.

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Transition metal catalyzed intramolecular C-C and C-N bond forming reactions via oxidative coupling of C-H bond and heteroatom functionality have emerged as a promising method for the synthesis of structurally diverse heterocycles.<sup>1</sup> In this regard, domino reactions, in which multiple chemical bonds can be constructed in one-pot, have evolved as highly atom-economic alternative to the classical coupling approaches using pre-functionalized substrates.<sup>2</sup> Incorporation of C-H functionalization into a domino reaction may be arguably ideal and is no doubt very challenging. Compared to Pd-catalyzed domino reactions involving C-H activation,<sup>3</sup> comparable approaches involving Cu-salts are underdeveloped.<sup>4</sup> Apart from atom economy and bond-forming efficiency, the prevalence of consecutive reactions may lead to structurally diverse scaffolds particularly important for medicinal chemistry research.

Although very few references<sup>5</sup> are available for the use of copper(I) oxide nanoparticles in organic synthesis including various C-C cross coupling reactions, the feasibility of using nanocatalyst in complicated reactions like domino decarboxylative C-H arylations and carbonylative C-C coupling still remains unexplored. Application of nano-copper

(I) oxide could be more promising compared to the corresponding bulk materials or expensive palladium systems due to its high reactivity, stability in aqueous medium, environmental compatibility, non-toxicity and more importantly its reusability. In addition, the regeneration of the catalyst by simple centrifugation makes the work up processes simpler.

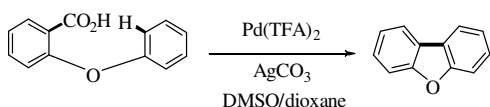
Dibenzofurans exist in a wide variety of biologically active compounds.<sup>6</sup> Methodologies leading to the edifice of this skeleton are primarily based on Pd- and/or Cu-catalyzed intramolecular O-arylation of 2-chlorobiphenyl alcohols, tandem decarboxylation/C-C coupling of 2-phenoxybenzoic acids (Scheme 1a), and consecutive C-H activation/C-O bond formation of 2-arylphenols or oxidative C-C cyclization of diphenylethers.<sup>7</sup> Strategy involving tandem decarboxylation/C-C coupling of ortho-aryloxybenzoic acids for the synthesis of dibenzofurans requires usage of higher amount of Ag-salts as oxidants or excess metals. Shen *et al.*<sup>8</sup> reported palladium-catalyzed decarboxylative cyclization involving 2-(2-bromophenoxy)benzoic acid where halides were used as second reaction site and as leaving functionality (Scheme 1b) using *N*-methyl-2-pyrrolidone (NMP, 0.2 M) as solvent. We

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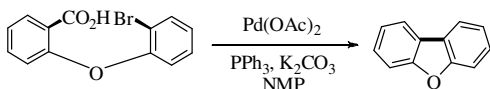
‡ These authors contributed equally to this work

used 2-(3-iodophenoxy)benzoic acid which made both C-H and C-I available for decarboxylative cyclization (Scheme 1c). With this compound, competitive reaction like intermolecular decarboxylative C-C coupling at iodide site is theoretically possible.<sup>8</sup> Also, transition metal (like palladium) catalyzed carbonylation of aromatic halides with various nucleophiles, often leads to amides or esters.<sup>9</sup> We, therefore, checked the feasibility of the one-pot synthesis of carbonyldibenzofuran in presence of nano sized cuprous oxide (Scheme 1c) under sonication. Synthesis of amidodibenzofurans was executed in

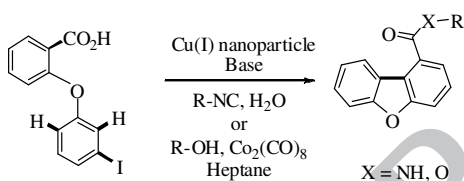
a) Palladium catalyzed decarboxylative C-H arylation



b) Palladium catalyzed decarboxylative C-Br arylation



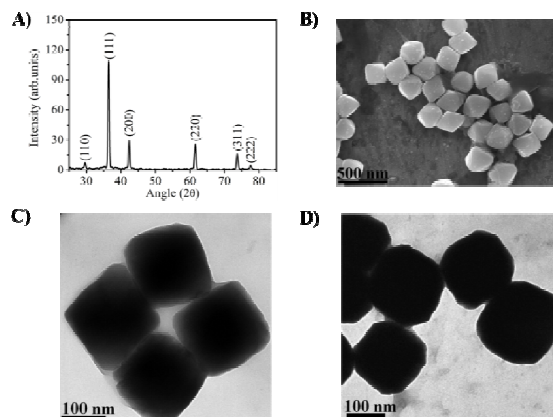
c) This work: Reusable nano copper(I) mediated regioselective decarboxylative C-H arylation, C-I carbonylation



**Scheme 1.** Tandem decarboxylation/C-C coupling for the synthesis of dibenzofurans from 2-aryloxybenzoic acids.

aqueous environment, whereas, for the ester, 'green organic solvent',<sup>10</sup> heptane was used. Ultrasonication provided enhancement of the reaction rate compared to the conventional procedures by dispersing insoluble ingredients in the medium. We applied isocyanide or  $\text{Co}_2(\text{CO})_8$  as the carbonyl source in our domino strategy. Consecutive chemo- and regio-selective decarboxylative C-H arylation, and carbonylative C-C coupling of aryl halides lead to carbonyldibenzofurans only. Here, intramolecular C-C coupling through C-H arylation was found to be more favored in comparison to the decarboxylative C-iodo arylation or intermolecular decarboxylative C-C coupling at iodide site. C-iodo bond underwent C-C coupling with organic isocyanides or alkoxycarbonylation with various alcohols in chemoselective manner. For carbonylation of the aryl halides, no externally added CO gas was required. Use of CO at high pressure is, however, never recommended for practical applications. Nano sized cubic cuprous oxide was used as reusable catalyst under aerobic condition. No additional oxidants or organic solvents were needed. Also, application of air as oxidant and recyclable catalyst is attractive from economic and environmental concerns. It is worth mentioning that, previously known methods generally required the involvement of intricate combination of ligands, heavy metal catalyst, and organic solvents as reaction media with various additives.

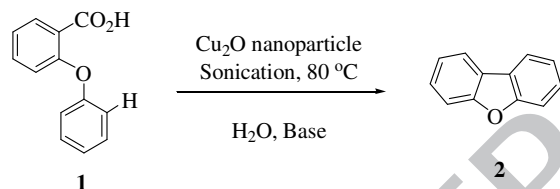
We synthesized cuprous oxide nanoparticles by reduction of cupric chloride dihydrate using fructose as reducing and capping agent in water. The cubic Cu(I) nanoparticles had an average edge length of  $180 \pm 20$  nm and were fully characterized using TEM, XRD, IR etc. Peaks at  $627 \text{ cm}^{-1}$  in FT-IR (Figure S1) can be assigned as Cu(I)-O stretching frequency and the absence of any peak around  $512 \text{ cm}^{-1}$  ensures nonexistence of traces of Cu(II)-O as contaminant in the synthesized particles.<sup>11</sup> The shape of the particles was established by Scanning and Transmission Electron Microscopy. The powdered X-ray Diffraction (XRD) pattern (Figure 1A) indicates the typical reflection patterns of cuprite (JCPDS no. 77-0199).<sup>12</sup>  $2\theta$  values in the XRD plot at  $29.4^\circ$ ,  $36.37^\circ$ ,  $42.29^\circ$ ,  $61.40^\circ$ ,  $73.64^\circ$  and  $77.46^\circ$  were ascribed as the crystal plane of 110, 111, 200, 220, 311 and 222 respectively.  $d$  spacing values of the planes were calculated as 3.14, 2.59, 2.29, 1.75, 1.61, 1.58 Å respectively. The SEM and TEM images (Figure 1B and 1C) fully confirmed the regular cubic shape of the synthesized nanoparticles.



**Figure 1.** A) Powder XRD pattern; B) SEM and C) TEM image of cuprous oxide nanoparticles before reaction; D) TEM image of cuprous oxide nanoparticles after 3 times use.

Before proceeding to the one-pot sequence, attempt was made to customize the reaction parameters for the decarboxylated C-H arylation (Scheme 2) in aqueous medium. Initially we chose both compounds **1** and **3** for this purpose. With compound **1**, use of bulk copper (I) salts like CuI, Cu<sub>2</sub>O or [(<sup>i</sup>Pr)<sub>2</sub>Cu]PF<sub>6</sub> did not produce the product **2**, in the presence of various inorganic or organic bases like Et<sub>3</sub>N, DBU, <sup>i</sup>Pr<sub>2</sub>EtN, Cs<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> or KOH and even after prolonged heating (24 h) at 80 °C. Application of various additives like Piv<sub>2</sub>O, Ag<sub>2</sub>CO<sub>3</sub> also failed to promote the reaction. We next applied Cu<sub>2</sub>O nano-catalyst in the reaction and it was found that under similar conditions the reaction proceeded well with compound **1** in considerable yield, without the requirement of any external additives (Table 1, entry 14-16). These reactions were completed within 2 h. The effect of different bases was also explored successively. We found both organic and inorganic bases gave comparable yield when employed in 5.0 mole equivalent.

On the contrary, compound **3** when subjected to the above reactions, produced a complex array of products (without any major spot) as visualized by TLC (Table 1, entry 17-19). It was not possible to separate them by column chromatography (data not included). This happened because of the involvement of iodide in various intermolecular coupling such as, self coupling and in conjunction with single or double C-H activation. Therefore, the data obtained using compound **1** was subsequently used for designing the one-pot reaction in aqueous medium.



**Scheme 2.** Decarboxylative C-H arylation.

Next the methodology was applied in the tandem sequence (Scheme 3). 2-(3-Iodophenoxy)benzoic acid (**3**) was used for this study and the results are shown in Figure 2. Aryl isocyanides, e.g., phenyl isocyanide, *p*-toluidine isocyanide, *p*-methoxy and

**Table 1.** Optimization of reaction conditions.

Entry <sup>a</sup>	Catalyst	Base	Additives	Yield (%) <sup>b</sup>
1	CuI	<sup>i</sup> Pr <sub>2</sub> EtN	-	0
2	CuI	-	AgCO <sub>3</sub>	0
3	CuI	<sup>i</sup> Pr <sub>2</sub> EtN	AgCO <sub>3</sub>	0
4	CuI	<sup>i</sup> Pr <sub>2</sub> EtN	Piv <sub>2</sub> O	0
5	CuI	<sup>i</sup> Pr <sub>2</sub> EtN	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
6	CuI	-	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
7	Cu <sub>2</sub> O	-	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
8	Cu <sub>2</sub> O	<sup>i</sup> Pr <sub>2</sub> EtN	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
9	[( <sup>i</sup> Pr) <sub>2</sub> Cu]PF <sub>6</sub>	<sup>i</sup> Pr <sub>2</sub> EtN	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
10	Cu <sub>2</sub> O	DBU	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
11	Cu <sub>2</sub> O	Et <sub>3</sub> N	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
12	Cu <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0

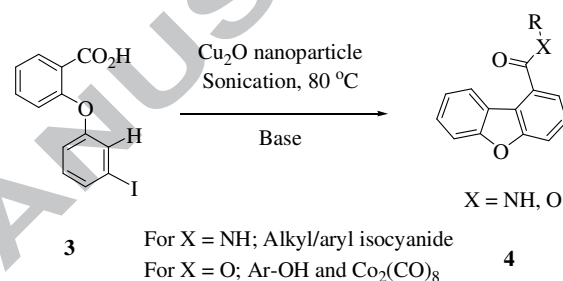
13	Cu <sub>2</sub> O	Cs <sub>2</sub> CO <sub>3</sub>	AgCO <sub>3</sub> / Piv <sub>2</sub> O	0
14	Nano-Cu <sub>2</sub> O	<sup>i</sup> Pr <sub>2</sub> EtN	-	76
15	Nano-Cu <sub>2</sub> O	Et <sub>3</sub> N	-	73
16	Nano-Cu <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	-	80
17 <sup>c</sup>	Nano-Cu <sub>2</sub> O	<sup>i</sup> Pr <sub>2</sub> EtN	-	Multiple spots <sup>d</sup>
18 <sup>c</sup>	Nano-Cu <sub>2</sub> O	Et <sub>3</sub> N	-	Multiple spots <sup>d</sup>
19 <sup>c</sup>	Nano-Cu <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	-	Multiple spots <sup>d</sup>

<sup>a</sup> Reactions were performed in water (10 mL) using **1** (1 equiv.), nano-Cu<sub>2</sub>O (20 mol %), base (5 equiv.) under sonication (80 °C) for 2 h and aerobic condition.

<sup>b</sup> Recovered yield.

<sup>c</sup> Reaction performed with compound **3** using similar experimental conditions.

<sup>d</sup> No product could not be isolated in pure form.

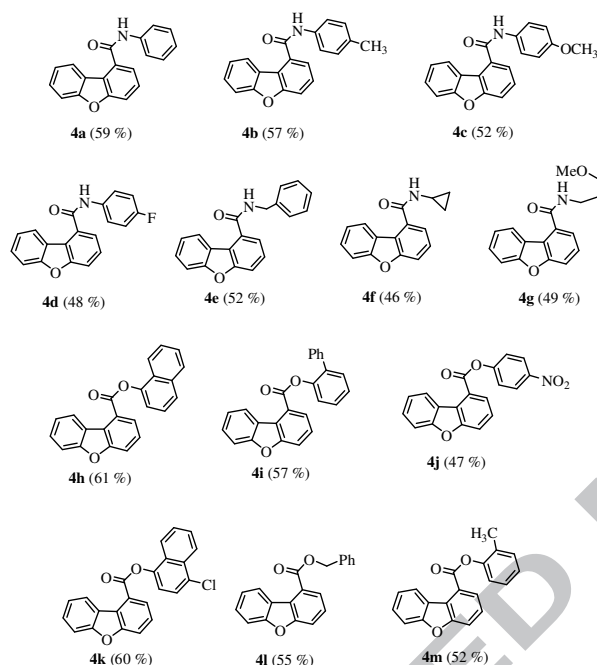


**Scheme 3.** Decarboxylative C-H arylation-carbonylative C-C functionalization in tandem.

*p*-fluoro-isocyanide produced desired amido-dibenzofurans, **4a**, **4b**, **4c** and **4d** in 59, 57, 52 and 48 % respectively. Use of aliphatic isocyanides did not affect the yield of the product. The cyclopropyl amido derivative **4f** and **4g** were formed respectively in 46% and 49% yield when cyclopropyl isocyanide was used as carbon source. Activated aliphatic isocyanide like benzyl isocyanide also reacted under similar condition to provide **4e** in 52% yield. For the synthesis of ester, similar protocol was applied with Co<sub>2</sub>(CO)<sub>8</sub>. Baburajan *et al.*<sup>13</sup> used the same cobalt-complex as CO source for the Pd-catalyzed alkoxy carbonylation of aryl halides. However, the scope of the reaction was not investigated using copper salts. Using copper nano-catalyst and various aromatic alcohols, desired dibenzofuran derivatives (**4h-4m**) were obtained in good yield using our one-pot cascade strategy.  $\alpha$ -Naphthol gave the maximum yield (**4h**) of 61%. The presence of bulky phenyl at the ortho-position did not affect the tandem reaction, and 57% of **4i** was obtained when [1,1'-biphenyl]-2-ol was used as alcohol source. However, the presence of strong electron withdrawing group at *p*-position decreased the yield of the corresponding ester **4j** (47%). Halogens such as chloride were also found to be compatible with the process to afford the corresponding dibenzofurans **4k** in good yield. Substrates having an activated hydroxyl like benzyl alcohol reacted smoothly to afford **4l** in 55%. It is worth to mention that similar reaction can be carried out with bulk copper salt (Cu<sub>2</sub>O/CuI) in polar organic solvents like DMF. Compound **4b** was formed in comparable yield (60%, data not shown) from compound **3** under similar reaction conditions. However, the

purpose of the present study is to develop novel green reaction methodology with water as solvent.

Having shown that the reaction proceeds with generality, the possible mechanism of the reaction was explored (Figure 3). It is expected that initially oxidative addition of Cu(I) into **I** forms intermediate **II**, which is then readily converted into intermediate **III** due to the liberation of iodide and the formation of Cu(III)-O bond in the presence of base. The chemoselectivity may be attributed from the formation of the cyclic intermediate **III**, where the Cu(III) is coordinated with both the aryl ring and the oxygen of the carboxylic acid simultaneously and thus preventing intermolecular C-C coupling at the iodide site.



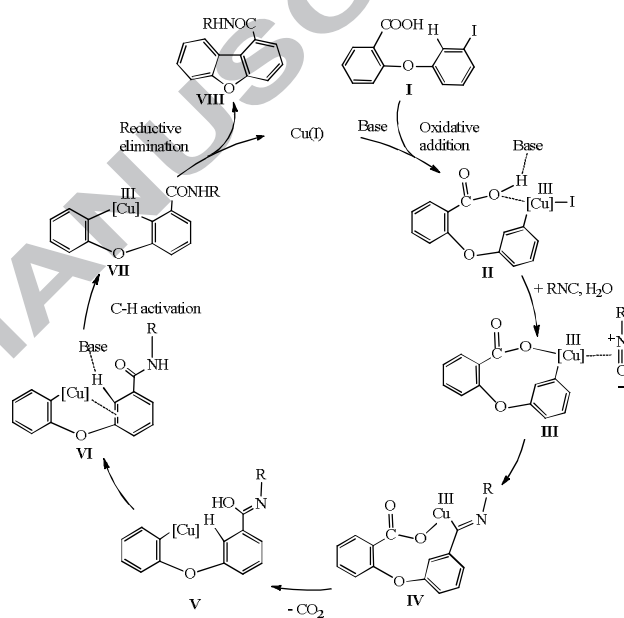
**Figure 2.** Synthesized dibenzofurans via decarboxylative C-H arylation and carbonylative C-C functionalization.

Cu(III) in the cyclic intermediate **III**, may easily form coordinate bond with the  $\pi$ -electrons of linear isocyanide and migratory insertion of isocyanide happens to generate intermediate **IV**. Decarboxylation of **IV** may lead to the formation of intermediate **V**. In the presence of  $\text{H}_2\text{O}$ , this unstable intermediate **V** isomerized to amide **VI**. The arylcopper intermediate **VI** thus formed readily participates in intramolecular C-H activation to yield the intermediate **VII**, from which C-C bond forming reductive elimination affords the substituted dibenzofuran product **VIII** with the regeneration of Cu(I) to be used for the next cycle.

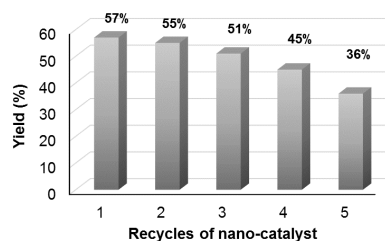
The reusability of the nano particles (NPs) towards the synthesis of dibenzofuran derivative **4a** was investigated next and the results are appended in Figure 4. The nano-catalyst was recovered (~95%) by centrifugation after each reaction and was washed with ethanol repeatedly to avoid any contamination. It is evident that, the catalytic activity did not affect much up to three consecutive cycles, however, significant loss in the catalytic property was noticed afterwards. The unchanged morphology of the nanocatalyst was confirmed by TEM-analysis (Figure 1D) up to 3<sup>rd</sup> recycles. The oxidation state and unchanged morphology of the nanoparticles (after reaction) was further confirmed by

FTIR and powder XRD pattern of the nanoparticle and are depicted in Figure S1 and Figure S2 respectively (supplementary information).

In conclusion, we have demonstrated that the nano copper (I) oxide catalyzed decarboxylative intramolecular C-H arylation and carbonylative C-C coupling of 2-(3-iodophenoxy)benzoic acid with isocyanide/alcohol can generate a library of dibenzofuran derivatives.<sup>14</sup> The reaction parameters allow the reaction to take place with high chemo- and regio-selectivity. Use of 2-(3-iodophenoxy)benzoic acid made both C-H and C-I available for intra- as well as intermolecular C-C cross-coupling. The intramolecular C-C coupling through C-H arylation was found to be more favoured in comparison to decarboxylative C-iodo arylation at the iodide site. C-iodo bond underwent chemoselective C-C coupling with organic isocyanides or underwent alkoxyarylation with various



**Figure 3.** Plausible catalytic cycle for the formation of substituted dibenzofuran.



**Figure 4.** Reusability of the nano-catalyst towards the synthesis of **4a**.

alcohols in chemoselective manner. The protocol did not require use of heavy metals like palladium or rhodium, hazardous organic solvents, ligands, oxidants or external additives. More importantly, the cubic nanocatalyst can be recovered and recycled for three consecutive reactions without any significant loss of reactivity or any change in its morphology. Reaction methodology provides considerable functional group tolerance which may provide synthetic flexibility for further functional group interconversion. Further

applications of this strategy in organic synthesis are currently under investigation in our laboratory.

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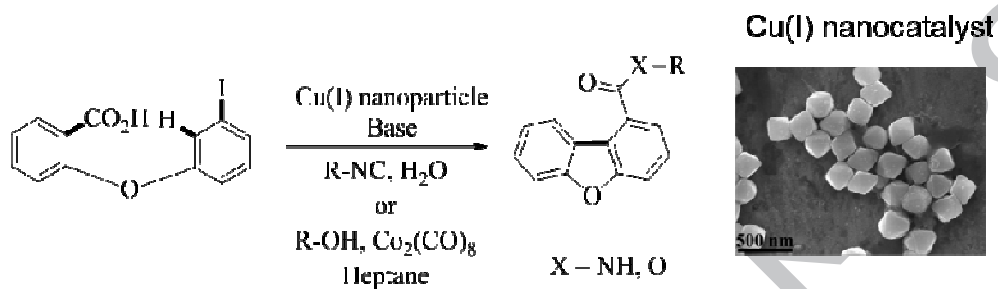
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- General procedure for the synthesis of benzofuran-1-carboxamide (4a-g) and dibenzofuran-1-carboxylate (4h-m)*: In an open round-bottomed flask containing water (25 mL), 2-(3-iodophenoxy)benzoic acid (**1**, 1.0 equiv.) and isocyanide (**2**, 1.2 equiv.), Cu<sub>2</sub>O-NPs (20

mol%) and K<sub>2</sub>CO<sub>3</sub> (5.0 equiv.) were added and stirred vigorously under sonication for 2 h at 80 °C. After that, ethyl acetate (50 mL) was added into the reaction mixture and thoroughly vortexed. It was then centrifuged to separate the nanoparticles, aqueous and ethyl acetate layers and were collected separately. The aqueous layer was re-extracted with ethyl acetate once. The combined ethyl acetate layer containing the product was concentrated and purified by column chromatography (Hexane/EtOAc) to give pure products (**4a-g**). The nanoparticles were washed with EtOAc-ethanol (1:1 x 3) and dried under vacuum before re-use. For the synthesis of dibenzofuran-1-carboxylate similar procedure was followed but the reaction was executed in commercial heptane with Co<sub>2</sub>(CO)<sub>8</sub> (0.5 equiv.) and Cu<sub>2</sub>O-NPs (40 mol%) under non-aerobic condition.

**Graphical Abstract:**

**Cubic nano-copper(I) oxides as reusable catalyst in consecutive decarboxylative C-H arylation and carbonylation: rapid synthesis of carbonyl dibenzofurans**

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### Highlights

1. The unique one-step synthesis of carbonyl dibenzofurans was developed
2. It involves decarboxylative C-H arylation and carbonylative C-C coupling
3. The reaction is highly chemo- and regio-selective and environ friendly
4. Reusable nanodomain cuprous oxide was used as catalyst under aerobic condition
5. Several derivatives were synthesized which showed high functional group tolerance

15.