## **Supporting Information**

# Cu/Cu<sub>x</sub>O<sub>y</sub> NPs Architectured COF: A Recyclable Catalyst for Oxazolidinedione Synthesis via Atmospheric Cyclizative CO<sub>2</sub> Utilization

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#### **Materials and Equipments**

The starting agent *1,3,5*–triformylphloroglucinol (Tp) was synthesized in the lab following the previous literature.<sup>1</sup> Carboethoxymethylidenetriphenyl-phosphorane was bought from Sigma-Aldrich. All commercially available reagents and solvents were employed without further purification. All the commercially available materials were purchased from Sigma-Aldrich, Fisher Scientific, TCI chemicals and Avra Chemicals depending upon their accessibility. <sup>1</sup>H and <sup>13</sup>C NMR spectra were conducted on Bruker DPX-300/500 NMR spectrometer. NMR spectra were recorded at 298 K.

A D8 Advance SWAX diffractometer from Bruker-AXS utilizing a constant current (40 mA) and voltage (40 kV) was used to obtain the powder XRD pattern of the Cu/Cu<sub>x</sub>O<sub>y</sub>NPs embedded COF catalyst. The XRD machine was calibrated with silicon sample utilizing Ni-filtered Cu K $\alpha$  radiation ( $\lambda$ =0.15406 nm). Quantachrome Autosorb-iQ (USA) surface area analyser was used for N<sub>2</sub> adsorption/desorption analysis at 77 K. The sample was activated at 403 K for 12 h under high vacuum before the adsorption of gas. Pore size distribution was obtained by using NLDFT method employing the carbon/cylindrical pore model as reference. For the analysis of HR TEM, 10 mg of COF-BD(OH)<sub>2</sub> or Cu@COF-BD(OH)<sub>2</sub> was dispersed into absolute EtOH under the application of sonication for 5 min, followed by the sample coating on a carbon coated Cu-grid and dried in air. JEOL JEM 6700 field emission-scanning electron microscope (FE SEM) was employed to analyze particle size and morphology of COF-BD(OH)<sub>2</sub> or Cu@COF-BD(OH)<sub>2</sub>. UV-visible diffuse reflectance spectroscopy (UV 2401PC) and FT-IR (Nicolet MAGNA-FT IR 750 spectrometer Series II) were used to understand the framework and coordination. A TA Instruments

thermal analyser (TA-SDT Q-600) was used for the differential thermal analysis (DTA) and thermogravimetric (TGA) of the parent COF or Cu/Cu<sub>x</sub>O<sub>y</sub> NPs embedded COF with a temperature (ramped at 10°C/min) under continuous air flow. A CHNOS elemental analyser (Vario EL III) was used to determine the contents of C, N and H in COF-BD(OH)<sub>2</sub> or Cu@COF-BD(OH)<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the desired products were kept on a Bruker DPX-300/500 NMR spectrometer.

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#### Section S1: Experimental section

#### **S1.1. Synthesis procedure**

#### S1.1.1. Synthesis of COF-BD(OH)<sub>2</sub>

Synthesis of 1,3,5-Triformylphloroglucinol were conducted following the previously published method.<sup>1</sup> Usually, trifluoroacetic acid (90 mL) was poured into 15.098 g (108 mmol) of hexamethylenetetramine and 6.014 g (49 mmol) of dried phloroglucinol under the application of inert condition (i.e. N<sub>2</sub> atmosphere). The mixture was then warmed to a particular temperature (100 °C) for a definite time (2.5 h). Approximately, 3 M HCl (150 mL) was poured and the mixture was then warmed to a certain temperature (100 °C) for a definite time period (1 h). After bringing it to normal temperature around 25°C, the resultant mixture was then allowed to completely filter through Celite, subjected to properly extract with a definite quantity of dichloromethane (350 mL), allowed to dry over magnesium sulphate as a commonly used drying agent, and allowed to filter (Scheme 1). Performance of solvent evaporation of the resulting mixture with the help of rotavap device provided one gram of a solid powder featuring off-white colour.

A definite quantity of TFP (1,3,5-triformylphloroglucinol, 0.2 mmol) and a certain amount of BD(OH)<sub>2</sub> or DHBD (3,3'-dihydroxybenzidine, 0.2 mmol) were poured into a pyrex tube and subjected to dissolve in a certain quantity of o-Dichlorobenzene (10 ml) and 5 ml Butanol solution. A tiny amount of acetic acid (1 ml) was poured into this resulting solution and was allowed to continuously stir. Additionally, this special pyrex tube was flash frozen employing liquid N<sub>2</sub> (LN<sub>2</sub>) and sealed properly. The solution in the closed system was warmed to a certain temperature (120°C) for a definite time period (3 days). After bringing it to normal temperature around 25°C, the reddish brown colored solid was allowed to filter and subjected to properly wash with THF, DMF, EtOH. The solid powder was then subjected to dry at a certain temperature range (80°C) for a definite time period (4 h).<sup>2</sup> The desired product featuring crystalline nature was cleaned properly employing Soxhlet extractor (Scheme 1). 89% yield of the desired product,. Observed CHN is H = 5.69; C = 82.45; N = 8.31.

#### S1.1.2. Synthesis of Cu@COF-BD(OH)<sub>2</sub>

A certain amount of COF (100 mg) was allowed to suspend in a definite quantity of THF (15 ml) and subjected to sonicate for a particular time period (30 mins), a tiny amount of CuCl<sub>2</sub> (60 mg) dissolved in a small amount of water (4 ml) was poured into this resulting dispersion (Scheme 1). The resultant contents were then subjected to stir at normal temperature around 25°C for 24 hrs, followed by the extraction employing filtration technique. The resulting solid was cleaned with H<sub>2</sub>O and methanolic solvent. It was then allowed to dry at a particular temperature (120°C) under the application of vacuum condition. This resultant solid was subjected to resuspend in a mixture of H<sub>2</sub>O and methanolic solvent (5:2) and the solution was warmed to a certain temperature (80°C). At 80°C, the reduction of copper featuring higher oxidation state ( $Cu^{2+}$ ) was conducted by pouring 1M ascorbic acid (5 ml) into H<sub>2</sub>O solvent. The resulting contents were subjected to continuously stir for a particular time period (20 hrs). At the end of the method, the resulting precipitate was then separated by conducting filtration and subjected to wash with excess quantities of H<sub>2</sub>O, EtOH, THF solvent and allowed to dry under the application of vacuum condition. Observed CHN is C = 69.71; H =5.65; N = 7.92. We were not able to track the loading of copper featuring higher oxidation state (Cu<sup>2+</sup>) or copper NPs (Cu<sup>0</sup>) as a function of colour variation owing to the reddish brown colored COF. In the absence of ascorbic acid, the parent COF can reduce Cu<sup>2+</sup> leading to copper (I) and not copper nanoparticles.

Characterization of the parent COF-BD(OH)<sub>2</sub> and resultant Cu@COF-BD(OH)<sub>2</sub> is performed by analyzing thermogravimetry (TG), N<sub>2</sub> adsorption–desorption analysis, Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, transmission electron microscopy (TEM), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

#### S1.1.3. Production of bromocarbethoxymethylenetriphenylphosphorane.<sup>3,4a</sup>



Carboethoxymethylidenetriphenyl-phosphorane (13.9 g, 40 mmol) was allowed to dissolve in DCM (80 mL) and the resultant mixture was then allowed to bring it to a definite temperature (5°C) with the help of ice-water bath. The as-prepared solution of bromine (6.4g, 40 mmol) in DCM (30 mL) was steadily poured under dropwise conditions, and the batch was subjected to stir overnight. The organic part was then cleaned with H<sub>2</sub>O (30 mL), and then twice with a solution of NaHCO<sub>3</sub> (50 mL) until HBr was neutralized. The DCM part was allowed to dry over easily obtainable Na<sub>2</sub>SO<sub>4</sub> and concentrated under the application of vacuum condition. The residue was then recrystallized from acetone/n-hexane (2:1) (30 mL). The crystals were allowed dry the application of vacuum condition to under to provide bromocarbethoxymethylenetriphenylphosphorane as a yellow solid, yield 76% (12.6 g).

S1.1.4. Production of 2-bromo-3-alkylacrylic acids (1a-1g).<sup>3,4a</sup>



A mixture of bromocarbethoxymethylenetriphenylphosphorane (8.5 g, 20 mmol) and aldehyde (20 mmol) was poured into a two-neck round bottom flask with a magnetic stirrer under the application of nitrogen atmosphere. The resulting solution was warmed to a definite temperature (100 °C) to generate a homogeneous melt and the ensuing mixture was kept at 100 °C for 8 h. After cooling it to room temperature, the resultant mixture was subjected to column chromatography on silica gel to achieve ethyl 2-bromo-3-ethylacrylate; Ethyl 2-bromo-3-alkylacrylate (10 mmol) was allowed to dissolve in DCM/CH<sub>3</sub>OH (9:1) (100 mL), and the resulting mixture was allowed to bring to 0°C in ice-water bath. NaOH (20 mmol, 8.0 g) was added, and the solution was subjected to stir for a definite time (12 h) at ambient temperature (25°C). The solvents were eliminated under the application of vacuum condition,

the residue was diluted with  $H_2O$ , and extraction of the aqueous solution was conducted with diethyl ether in order to eliminate the remaining ester. The aqueous part was allowed to cool, acidified to pH 2-3 with dilute HCl, and properly extracted with Et<sub>2</sub>O. The combined organic layer was allowed to dry over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was then eliminated to provide 2-bromo-3-phenylacrylic acid (**1a-1g**) with Z-form (100%). **1a**: 71%, **1b**: 86%, **1c**: 79%, **1d**: 68%, **1e**: 84%, **1f**: 62%, **1g**: 84% yield.

#### S1.1.5. Typical synthetic procedure for 3aa\*-3be\*

Cu@COF-BD(OH)<sub>2</sub> composite catalyst (40 mg) was added to a mixture of amine (1.2 mmol), 2-bromo-3-phenylacrylic acid (1 mmol) and DMF solvent (6 mL) in a Schlenk flask. The inside of the reaction vessel was purged with carbon dioxide (0.1 MPa) by a balloon two times. The resulting solution was then subjected to stir at ambient temperature (25°C-80°C) for a definite time (10-96 h). Aqueous solution of NaHCO<sub>3</sub> was poured to reaction mixture and the aqueous part was then separated with funnel employing CHCl<sub>3</sub>. The combined organic layer was allowed to dry over Na<sub>2</sub>SO<sub>4</sub>, concentrated under low pressure. The pure desired oxazolidinedione was obtained without any additional decontamination.



COF-BD(OH)<sub>2</sub>



# Cu@COF-BD(OH)<sub>2</sub>

Photographic images of the parent COF and Cu@COF-BD(OH)<sub>2</sub> composite catalyst. S1.1.6. Synthesis of Cu<sub>2</sub>O NPs<sup>4b</sup>

The generation of cuprous oxide nanoparticles (Cu<sub>2</sub>O NPs) was accomplished through reduction of copper acetate by hydrazine hydrate at room temperature under constant stirring in air. In a typical method, copper acetate monohydrate (0.25 mmol) was taken in a 50 mL beaker and was dissolved in 20 mL water. Then hydrazine hydrate of 20  $\mu$ L was introduced into the beaker under constant stirring. The stirring was continued for about 0.5 h. Then the solution of the resultant reddish Cu<sub>2</sub>O NPs suspension was centrifuged at around 6000 rpm, and followed by washing with water several times and finally absolute ethanol to afford red precipitate. Finally, it was dried in vacuum for 2 h to furnish the red powder of  $Cu_2O$  NPs. The product was confirmed from XRD (Figure S32). Then the as-prepared  $Cu_2O$  NPs was used as catalyst for the aforementioned  $CO_2$ -incorporated cyclization reaction.

#### S1.1.7. Synthesis of Cu NPs (i.e. Cu<sup>0</sup>)<sup>4b</sup>

The synthesis of copper nanoparticles (Cu NPs) was also conducted through the reduction of copper acetate using hydrazine hydrate under closed condition at room temperature. In a typical synthetic procedure, copper acetate monohydrate (0.25 mmol) was placed in a 15 mL vial and dissolved in water (4.8 mL). Subsequent to that hydrazine hydrate (200 µL) was introduced to the reaction mixture drop wise and gently shacked. The whole reaction mixture was kept standing under closed condition at room temperature for 12 h. Cu NPs with fine reddish-brown color deposited onto the inner surface and bottom of the vial. The solvent was carefully decanted. Then 2 mL water was added and sonicated for few seconds (approximately 10 seconds) carefully and the solution of fine reddish brown color was centrifuged, washed with water several times and absolute alcohol, and finally dried in vacuum affording a fine reddish brown powder of Cu NPs. The product was confirmed from XRD (Figure S33). After that, the as-obtained Cu NPs was used as catalyst for the aforementioned CO<sub>2</sub>-incorporated cyclization reaction.

#### S1.1.8. Synthesis of CuO NPs<sup>4c</sup>

A simple wet method was used for the synthesis of CuO NPs. The aqueous solution of precursor salt of copper (copper acetate monohydrate) was preheated and stirred continuously. Followed by the dropwise addition of sodium hydroxide and allowed this reaction for 3 h under continuous stirring. After completion of the reaction, NPs were isolated via centrifugation at 10,000 rpm for 10 min and washed thrice with distilled water. Pellets were dried in a hot air oven at 60 °C overnight and calcined at 450 °C. The product was confirmed

from XRD (Figure S34). After that, the as-obtained CuO NPs was used as catalyst for the aforementioned CO<sub>2</sub>-incorporated cyclization reaction.



#### Section S2: Results and discussion

Scheme S1. Schematic illustration of the cyclizative CO<sub>2</sub>-incorporated reaction.



**Scheme S2.** Generation of oxazolidinediones facilitated with a potential Cu/Cu<sub>x</sub>O<sub>y</sub> NPs embedded COF under benign conditions.



Scheme S3. Generation of the desired oxazolidinedione through  $CO_2$ -incorporated cyclizative multi component reaction of bromoacrylic acid with aromatic amines.

To establish our present hypothesis, 2-bromo-3-phenylacrylic acid **1b** and aniline  $2b^*$  are employed as model substrates for the sustainable synthesis of oxazolidinedione ( $3bb^*$ ) in the presence of catalytic COF-NPs composite under atmospheric CO<sub>2</sub> (0.1 MPa) (Table S1). We next tested the influences of several parameters on the advancement of the CO<sub>2</sub>-incorporated cyclization reaction including catalytic systems, amount of the investigated catalyst, reaction temperatures, solvents, bases and reaction times (Table S1). Some

investigated metal catalytic systems were primarily employed for the CO<sub>2</sub>-incorporated cyclization reaction of **1b** as a model substrate in the solvent (DMF) at a definite temperature under 0.1 MPa of CO<sub>2</sub> (Table S1). Control investigation confirmed that no reaction proceeded in the absence of the metal salts or any other catalytic systems (entry 20, Table S1). Obviously, Palladium salt has poor impact on its performance for the generation of oxazolidinediones (entries 3 and 8, Table S1). Of note, several copper catalytic systems were employed under mild condition at a certain temperature of 60 °C in DMF as an optimal solvent (Table S1, entries 1, 7 and 9-15). For effective comparison, a series of known metal catalytic systems (such as zinc, silver, nickel and cobalt salts) were also employed for this title CO<sub>2</sub> capture cyclization reaction, which commonly displayed inferior performance for the generation of the high-value oxazolidinediones at a definite temperature of 60 °C in the optimal solvent (DMF) (Table S1, entries 2, 4, 5 and 6). As described in Table S1, the optimal solvent (DMF), and catalytic Cu/Cu<sub>x</sub>O<sub>y</sub> NPs decorated COF displayed the enhanced performance with a decent yield of 96% at a certain temperature of 60 °C in Cs<sub>2</sub>CO<sub>3</sub> as an alkali (Table S1, entry 16). The desired oxazolidinediones were confirmed by NMR.

Inspired by this attractive outcome, we tested the effect of several solvents with a potential  $Cu/Cu_xO_y$  NPs loaded COF as an optimal catalytic system. Evidently, the use of investigated DMF have highest impact on the yields of several oxazolidinediones even under alkali-free condition (Table S1, entry 22) and it displayed the best performance, affording the corresponding product in satisfactory conversion. A series of alkalis such as NaOC(CH<sub>3</sub>)<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, 1,8-Diazabicycloundec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO) and triazabicyclodecene (TBD) were employed for this title CO<sub>2</sub> fixation, which obviously displayed inferior performances for the generation of the high-value oxazolidinediones (Table S1, entries 8 and 12-15). The better result observed indicates that  $Cs_2CO_3$  as an alkali is crucial for this CO<sub>2</sub>-incorporated reaction. Although, organic base DBU has good impact on

the advancement of this  $CO_2$ -incorporated cyclization. Conducting this activated  $CO_2$  triggered cyclization reaction under alkali-free condition results in excellent yield of the corresponding oxazolidinedione. Excitedly, this  $CO_2$ -incorporated reaction was easily facilitated by dioxane, toluene, DMSO solvent (Table S1, entries 18, 19 and 21) and it was already mentioned that DMF was optimal for the title cyclization. The use of  $Cu/Cu_xO_y$  NPs embedded COF as a potential catalytic system at an ambient temperature of 25°C provided an excellent yield (Table S1, entry 22). Failure of the next effort to employ the parent COF as a catalytic system for this activated  $CO_2$  triggered cyclization suggests the importance of copper species (Table S1, entry 23). This cyclization reaction is extremely straightforward with comparatively better yield. The initial outcome is very attractive because no extra ligand was necessary to facilitate the process in the presence of this potential catalytic system.

We have also investigated the effect of other supports on this CO<sub>2</sub>-incorporated cyclization (Table S1). We have loaded Cu/Cu<sub>x</sub>O<sub>y</sub> NPs over TpBD-Me<sub>2</sub> (covalent organic framework) according to the literature.<sup>4d</sup> When Cu/Cu<sub>x</sub>O<sub>y</sub>@COF was used as a potential catalytic system for this CO<sub>2</sub>-incorporated cyclization, it displayed lower catalytic activity due to poor surface area compared to Cu@COF-BD(OH)<sub>2</sub> (Table S1, entry 32). The BET surface area for the synthesized material (Cu/Cu<sub>x</sub>O<sub>y</sub>@COF) is 131.31 m<sup>2</sup>g<sup>-1</sup> (Fig. S37). This synthesiszed Cu/Cu<sub>x</sub>O<sub>y</sub>@COF was confirmed from XRD (Fig. S35). It is noteworthy that metal nanoparticles decorated on solid supports featuring excellent surface areas display excellent catalytic performances for the synthesis of oxazolidinedione through CO<sub>2</sub>-incorporated cyclizative multicomponent reaction. Different synthetic techniques are adopted to synthesize copper/copper oxide nanoparticles (Cu NPs, CuO NPs and Cu<sub>2</sub>O NPs). Cu<sub>2</sub>O NPs, Cu NPs and CuO NPs were confirmed from XRD (Fig. S32, S33 and S34, respectively). When Cu<sub>2</sub>O NPs, CuO NPs and Cu NPs were used as catalyst for this atmospheric cyclizative CO<sub>2</sub> capture, no reaction took place in the absence of base (Table S1, Entries 27, 29 and 31,

respectively). Cu<sub>2</sub>O NPs, CuO NPs and Cu NPs were slightly active in the presence of Cs<sub>2</sub>CO<sub>3</sub>, but the yields were lower compared to the yields of Cu/Cu<sub>x</sub>O<sub>y</sub> NPs decorated COFs (Cu@COF-BD(OH)<sub>2</sub> and Cu/Cu<sub>x</sub>O<sub>y</sub>@COF) (Table S1, Entries 26, 28 and 30, respectively). In the absence of Cu/Cu<sub>x</sub>O<sub>y</sub> NPs, COF-BD(OH)<sub>2</sub> and TpBD-Me<sub>2</sub> were unable to afford the desired product (Table S1, entries 23 and 33, respectively).

**Table S1.** Optimization of reaction conditions for the generation of the desired oxazolidinedione through  $CO_2$ -incorporated cyclizative multicomponent reaction of bromoacrylic acid with aromatic amine.<sup>a</sup>



Entry	Catalyst	Alkali	Solvent	time	Cat.	Temp	Yield <sup>b</sup>
				(h)	Amount	(°C)	
					(mg)		
1	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	5	60	32
2	$Zn(OAc)_2$	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	5	60	0
3	$Pd(OAc)_2$	$Cs_2CO_3$	DMF	12	5	60	0
4	AgOAc	DBU	DMF	12	5	60	12
5	Ni(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	12	5	60	0
6	Co(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	24	5	60	0
7	CuCl <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	5	60	29
8	PdCl <sub>2</sub>	DBU	DMF	10	5	60	0
9	CuCl	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	5	60	16

10	CuBr	$Cs_2CO_3$	DMF	10	5	60	36
11	CuI	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	5	60	51
12	CuI	DABCO	DMF	10	5	60	36
13	CuI	TBD	DMF	10	5	60	50
14	CuI	Na <sub>2</sub> CO <sub>3</sub>	DMF	12	5	60	22
15	CuI	NaOC(CH <sub>3</sub> ) <sub>3</sub>	DMF	12	5	60	0
16	Cu@COF-	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	40	60	96
	BD(OH) <sub>2</sub>						
17	Cu@COF-	$Cs_2CO_3$	DMF	10	40	25	96
	BD(OH) <sub>2</sub>						
18	Cu@COF-	$Cs_2CO_3$	DMSO	10	40	25	82
	BD(OH) <sub>2</sub>						
19	Cu@COF-	$Cs_2CO_3$	Toluene	8	40	25	52
	BD(OH) <sub>2</sub>						
20	Without catalyst	Cs <sub>2</sub> CO <sub>3</sub>	DMF	24	40	60	0
21	Cu@COF-	Cs <sub>2</sub> CO <sub>3</sub>	Dioxane	10	40	25	69
	BD(OH) <sub>2</sub>						
22	Cu@COF-	none	DMF	10	40	25	96
	BD(OH) <sub>2</sub>						
23	COF-BD(OH) <sub>2</sub>	none	DMF	10	40	25	0
24	Cu@COF-	none	DMF	10	30	25	83
	BD(OH) <sub>2</sub>						
25	Cu@COF-	none	DMF	10	50	25	96
	BD(OH) <sub>2</sub>						
26	Cu <sub>2</sub> O NPs	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	5	25	37
27	Cu <sub>2</sub> O NPs	none	DMF	10	5	25	Trace
28	CuO NPs	Cs <sub>2</sub> CO <sub>3</sub>	DMF	10	5	25	31
29	CuO NPs	none	DMF	10	5	25	Trace

30	Cu NPs	$Cs_2CO_3$	DMF	10	5	25	12
31	Cu NPs	none	DMF	10	5	25	Trace
32	Cu/Cu <sub>x</sub> O <sub>y</sub> @COF	none	DMF	10	40	25	71
	[COF=TpBD-Me <sub>2</sub> ]						
33	TpBD-Me <sub>2</sub>	none	DMF	10	40	25	0

**aReaction conditions:** 2-bromo-3-phenylacrylic acid **1b** (1 mmol), aniline **2b**<sup>\*</sup> (1.2 mmol), catalyst, CO<sub>2</sub> (0.1 MPa), solvents (6 ml). <sup>b</sup> Isolated yield.

#### The individual role of Cu, CuO and Cu<sub>2</sub>O species:

The activity of Cu<sub>2</sub>O NPs was almost similar to that of CuO NPs whereas Cu<sub>2</sub>O exhibited slightly higher activity compared to CuO NPs in the presence of Cs<sub>2</sub>CO<sub>3</sub> (Table S1, Entries 26 and 28). The activity of Cu NPs was lower when compared to CuO (Table S1, Entries 28 and 30). Thus, in this case, also Cu<sub>2</sub>O and CuO are the preferred sites for the catalytic reaction. Moreover, the catalytic activities of  $Cu(a)COF-BD(OH)_2$  and Cu/Cu<sub>x</sub>O<sub>v</sub>@COF were much higher than copper/copper oxide nanoparticles (Cu NPs, CuO NPs and Cu<sub>2</sub>O NPs) (Table S1). This clearly confirms the individual role of Cu, CuO and Cu<sub>2</sub>O species of the nanocomposite which seems to proceed via the similar pathways as discussed above in the case of this title reaction. It may be noted that the activity of CuO was slightly lower than Cu<sub>2</sub>O under identical reaction condition. These results clearly demonstrate that the combination of Cu, CuO and Cu<sub>2</sub>O species in Cu@COF-BD(OH)<sub>2</sub> was ideal for the aforementioned reaction. Though the independent activity of Cu, CuO and Cu<sub>2</sub>O are low, but when they are present as nanocomposite in the highly dispersed state on COFs, its activity is significantly improved. This is also consistent with the higher surface area of Cu@COF- $BD(OH)_2$  when compared to Cu/Cu<sub>x</sub>O<sub>y</sub>@COF. The synthesized materials (Cu@COF-BD(OH)<sub>2</sub> and Cu/Cu<sub>x</sub>O<sub>v</sub>@COF) exhibited higher activities compared to Cu, CuO and Cu<sub>2</sub>O species, which shows that the dispersion of Cu/Cu<sub>x</sub>O<sub>y</sub> NPs on the as-prepared COFs also favoured the title reaction. Intriguingly, the reaction described above is mostly catalyzed by CuO and Cu<sub>2</sub>O sites present in Cu@COF-BD(OH)<sub>2</sub>, therefore it is also important to show the application of Cu@COF-BD(OH)<sub>2</sub> which mostly consists of CuO sites.

#### The role of covalent organic framework (COF):

The synthesized catalyst, namely, Cu@COF-BD(OH)<sub>2</sub>, was used as a potential porous adsorbent for CO<sub>2</sub> capture.<sup>4e</sup> Although the CO<sub>2</sub>-incorporated cyclizative solid multicomponent reaction occurs even in the absence of alkali, indicating that this COF can provide an alkaline environment. These are extremely vital roles played by the pore environment. The pore walls are decorated with strategically positioned phenolic groups. The high chemical/thermal stability of the parent COF and its strong interactions with different Cu ions featuring different oxidation states render the catalytic system to be highly recyclable. The micropores of the parent COF benefit not only to retain the moisture stability, but also to maintain the performance of CO<sub>2</sub> capture in the presence of atmospheric moisture. Several pores of the obtained COF can be utilized to stabilize nanoparticles (NPs) as dispersions, and give exceptional NP access. Embedding several substrate binding sites in this parent laboratory-fabricated COF can produce host-guest synergy, thereby leading to intriguing catalytic performance. In this work, Cu/Cu<sub>x</sub>O<sub>y</sub> NPs (8-16 nm) are decorated on this functionalized COF, which is constructed by linking a triamine and a trialdehyde via the formation of Schiff bonds.





<sup>a</sup>All the reactions were monitored by TLC. <sup>b</sup>All yields correspond to isolated products.

The substrate scope of  $CO_2$ -incorporated cyclizative multicomponent reaction of some derivatized bromoacrylic acids with several amines was also investigated under the optimal conditions and the outcomes obtained are presented in Table 1. Several amine derivatives and different as-prepared 2-bromo-3-alkylacrylic acids were employed to synthesize different

derivatized products under the application of the optimal conditions: 40 mg of Cu@COF-BD(OH)<sub>2</sub> catalyst, 10 h, 25°C, 6 ml DMF solvent.

Seven kinds of bromoacrylic acids with phenyl (1b), *p*-methoxyphenyl (1a), *p*-tolyl (1c), *m*-tolyl (1d), *p*-chlorophenyl (1e), 3,5-dimethylphenyl (1f) and 4-hydroxyphenyl (1g) parts were initially generated by conducting multistep processes (See Supporting Information for additional information). The as-obtained bromoacrylic acid derivatives were allowed to react with aromatic and aliphatic amine derivatives under identical conditions.

#### **Density Functional Theory Calculations**

To further explore mechanism about the activity in catalytic system, Density Functional Theory (DFT) calculations have been utilized to provide the pathways of this CO<sub>2</sub>-incorporated multicomponent reaction. To study and understand the present work from molecular level, the computation has been performed through GAUSSIAN 09.<sup>5,6</sup> Since the results obtained from XRD and XPS confirmed the presence of Cu atmosphere Cu (0), Cu (I) and Cu (II), hence DFT calculations have been performed with COF-NPs composite as active catalytic system presented in Fig. S1 and Cu@COF-BD(OH)<sub>2</sub> part is used for DFT calculation in straightforward manner which make convenient to calculate all intermediates and transition states. From the computation, the stabilization of Cu species on COF-BD(OH)<sub>2</sub> framework has been confirmed. The individual role of catalyst has been studied. All ground state geometries have been optimized without any symmetry constraints. The transition state has been optimized with one imaginary frequency along with the desired bond breaking or making. All calculations have been carried out using B3LYP functional<sup>7,8</sup> and LanL2DZ basis because it was confirmed<sup>9</sup> that for the transition metal this combination yields proper geometries and electronic properties.



Figure S1. Stabilization of  $Cu_2O$  (a) and CuO (b) on the parent COF (i). Optimized structures of several intermediates and transition states (iii). Distances are given in Å.

Activation energies ( $E_a$ ) are calculated as the difference in the energy between the transition ( $E^{TS}$ ) and initial states ( $E_{IS}$ ),

### $E_a = E^{TS} - E_{IS}$

Whereas, the reaction energy  $(E_r)$  is calculated using the difference in the energy between the final  $(E_{FS})$  and initial state  $(E_{IS})$  of the reaction.

$$\mathbf{E}_{\mathbf{r}} = \mathbf{E}_{\mathbf{FS}} - \mathbf{E}_{\mathbf{IS}}$$

A series of aromatic amine derivatives as well as bromoacrylic acids can be converted in excellent yields to the value-added oxazolidinediones. Related experiments and DFT calculations are employed to explore the mechanistic study on copper-facilitated CO2 capture reaction.



**Figure S2.** Catalytic mechanism for oxazolidinedione production via CO<sub>2</sub>-incorporated multicomponent reaction with their optimized structures of intermediates and transition states, and energy profile diagram for different transition states and intermediates for the generation of oxazolidinediones.

Figure S2 displays hypothetical catalytic mechanism of the title reaction. Initially, the activated CO<sub>2</sub> was allowed to react with the amine to generate a conjugate base of the corresponding carbamic acid (a significant intermediate) named structure (I).<sup>10</sup> Of note, the as-obtained bromoacrylic acid interacts with a Cu/Cu<sub>x</sub>O<sub>y</sub> NPs anchored on COF and generates structure (II) under alkali-free condition. Excitedly, Cu/Cu<sub>x</sub>O<sub>y</sub>-NPs-bromoacrylic acid complex structures (II) undergo oxidative addition of intramolecular nature, followed by the formation of a complex with the intermediate (I) to produce an important Cu complex structure (III), and the reductive elimination of Cu complex structure (III) affords the significant intermediate (IV). The amino group present in IV attacks the electropositive carbon of the carbonyl group in an intramolecular manner provides the corresponding oxazolidinedione, freeing the COF-NPs composite. Ultimately, in this hypothetical catalytic mechanism, the desired oxazolidinedione contains the notorious carbon dioxide that is introduced into a heterocyclic system. The above mechanism has conceptually been shown in Fig. S2 with their optimized structures.

From DFT study, it is found that Cu@COF-BD(OH)<sub>2</sub> activates the bromoacrylic acid for the reaction and also stabilizes the adduct to form the intermediate and plays a vital role in the cyclization to generate the product (Fig. S1 and S2).

Encouraged by previously reported works,<sup>11,12</sup> we investigated DFT calculations which were employed to explore the reason underlying superior catalytic performance. From DFT study, it is found that  $Cu@COF-BD(OH)_2$  activates the bromoacrylic acid for the reaction and also stabilizes the adduct to form the intermediate and plays a vital role in the cyclization reaction to generate the product. The stabilization of different Cu ions featuring different oxidation states by the COF has been studied. For this investigation, only a portion of the COF has been selected for the simplicity of computation. Absorption energy of Cu ion featuring an oxidation state of +1 is about -31.37 kcal/mol. Absorption energy of Cu ion featuring an oxidation state of +2 is -38.12 kcal/mol. It has been observed that  $Cu^{2+}$  is stabilized by the carbonyl group existing in the structure of COF while Cu<sup>1+</sup> is stabilized by Vander Waals force of interaction (Figure S1(i)). To understand the mechanistic pathway of the reaction along with the role of catalyst, a plausible mechanism for oxazolidinedione production via CO<sub>2</sub>-incorporated multicomponent reaction in presence of catalyst Cu@COF-BD(OH)<sub>2</sub> has been displayed in Figure S2, which was further confirmed from DFT calculations. In step-I, coordination of CO<sub>2</sub> to Cu@COF-BD(OH)<sub>2</sub> helps to push back the Cu-O bond pair towards oxygen which assists the formation of N-C bond to form the intermediate (I) of this reaction. The energy profile diagram for this reaction has been demonstrated in Fig. S2 (see the main manuscript). Of note, the copper nanocluster binds strongly on the as-prepared COF, with the adsorption energy found to be -0.97 eV. The bromoacrylic acid combines with the Cu species in bridging mode as shown in Figure S1, with the Cu-O bond distance is calculated to be 2.0 Å. The activation energy for complexation of R<sup>1</sup>NHCOO<sup>-</sup> by Cu/Cu<sub>x</sub>O<sub>y</sub>-NPs-bromoacrylic acid composite system is calculated to be 1.16 eV (Figure S2: Int1 $\rightarrow$  TS1 2). In the transition state (Figure S2: TS1 2), the C-Br bond is elongated from 1.9 Å in the initial state (Figure S2: Int1) to 3.7Å in the transition state (Figure S2: TS1 2). Activation barrier for the ring formation is found to be 1.88 eV, Figure S2 (Int3  $\rightarrow$  TS3 4). The C-N bond distance at the transition state is found to be 2.3 Å (Figure S2: TS3 4), which is shorter than the C-N distance of 3.3 Å in the initial state. Additionally, the C-O bond (1.5 Å) in the initial state (Figure S2: Int3) is elongated to 2.2 Å in the transition state (Figure S2: TS3 4). In the transition state (Figure S2: TS3\_4), the N-H bond is elongated from 1.0 Å in the initial state (Figure S2: Int3) to 1.4 Å in the transition state (Figure S2: TS3 4). The overall reaction energy for the entire reaction cycle (Figure S2) is determined to be exothermic by -1.09 eV. The entire structure of the as-prepared COF has not been displayed here for the adsorption and transition state geometries for clarity.

#### Recyclability of Cu@COF-BD(OH)<sub>2</sub> composite catalyst

To examine the reusability of Cu@COF-BD(OH)<sub>2</sub>, the CO<sub>2</sub>-incoporated multicomponent cyclization reaction was conducted employing a catalytic quantity of Cu@COF-BD(OH)<sub>2</sub> under sustainable conditions. After the process was terminated, 10 mL of water was poured into the resulting solution, which was allowed to isolate by centrifugation technique and the process was repeated employing 5 ml of acetone as a washing solvent. The used solvent (propanone) was safely stored and this catalytic system was recovered after elimination of propanone with the help of a device named rotavap. The isolated catalyst was allowed to use for next catalytic run without any additional decontamination. The outcomes presented in Figure S3 suggest that COF-NPs composite could be reused and recycled over six times without any noticeable reduction of catalytic performance. To get hidden information about heterogeneous nature of Cu@COF-BD(OH)<sub>2</sub>, we have conducted ICP-AES experiment of the resultant filtrate and recovered Cu@COF-BD(OH)<sub>2</sub>. We did not detect any noticeable copper trace in the filtrate and resultant Cu@COF-BD(OH)<sub>2</sub> catalyst retains almost the same copper loading as that of fresh catalyst ( $\approx 6.80$  wt%). All these observations undoubtedly revealed the heterogeneous nature of Cu@COF-BD(OH)<sub>2</sub>. The AAS observation corroborates well with the ICP-AES observation because only negligible amounts of leached Cu (≈6 ppm) were detected in the resultant solution collected by hot filtration experiment. These outcomes obtained certainly indicated that the as-obtained Cu@COF-BD(OH)<sub>2</sub> catalytic system is a heterogeneous in nature. This suggests that this COF-NPs composite is true a zero-leaching catalytic system of heterogeneous nature.



**Figure S3.** Recyclability chart of Cu@COF-BD(OH)<sub>2</sub> catalytic system, constructed utilizing the generation of 3bb<sup>\*</sup> under the optimal conditions (a), A significant comparison of the XPS spectra of as-obtained Cu@COF-BD(OH)<sub>2</sub> composite catalyst with the post-catalysis Cu@COF-BD(OH)<sub>2</sub> material, i.e.  $6^{th}$  run (b) and FE-SEM pictures of reused Cu@COF-BD(OH)<sub>2</sub> composite catalyst at several magnifications (c).

#### Section S3: Domain size of the crystallites of the as-prepared COF and Cu@COF-

#### **BD(OH)**<sub>2</sub>

The powder X-ray pattern with <100> diffraction peak has been employed for the distinction of crystallinity of the as-synthesized COF and COF-NPs composite (Table S3). The effective comparison has been conducted following the intensity count. If we consider, e.g., COF-BD(OH)<sub>2</sub>, it exhibits PXRD intensity count (<100> plane) of 4923 (intensity, a.u.). The count undoubtedly displays that the COF-NPs composite has superior crystallinity.

Materials	Peak Intensity (a.u.) <sup>a</sup>
COF-BD(OH) <sub>2</sub>	4923
Cu@COF-BD(OH) <sub>2</sub>	5048

Table S3. PXRD peak intensity count (<100> plane) of all the as-synthesized COF

<sup>a</sup>The COF has intensity count of more than 4000 (<100> plane) has been addressed herein.

The outcome has been further authenticated with Scherrer's equation by obtaining the Evaluation has been conducted considering the Gaussian fitting of the first peak possessing higher intensity (<100> facet). The measurement demonstrates that the crystallites size of the as-obtained COF could vary when Cu/Cu<sub>x</sub>O<sub>y</sub> NPs were decorated over the surface of the parent COF (Table S4).

The Scherrer's equation can be presented as:

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

where:

 $\tau$  is the size of the ordered (crystalline) domains;

K is a dimensionless shape factor, with a value close to unity. The shape factor varies with the actual shape of the crystallite. Herein we have considered the shape factor as unity for the ease of calculation.

 $\lambda$  is the X-ray wavelength which has the value 1.5418 Å;

 $\beta$  is the line broadening at half of the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians.

### $\beta exp^2 - \beta ins^2 = \beta^2$

β ins and β exp are the line broadening of the standard sample and COF samples respectively. θ is the Bragg angle (in degrees).

#### Table S4. Domain sizes of the crystallites.

Materials	COF crystallite size (Å)
COF-BD(OH) <sub>2</sub>	132.5
Cu@COF-BD(OH) <sub>2</sub>	143.0

#### Section S4: Physico-chemical properties of the as-prepared COF and Cu@COF-

### **BD(OH)**<sub>2</sub>

Table S5. Wall thicknesses of the as-obtained COF and Cu@COF-BD(OH)<sub>2</sub>

Materials	d <sub>100</sub> (nm)	a <sub>100</sub> (nm)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	PD <sub>NLDFT</sub> (nm)	PV (cm <sup>3</sup> g <sup>-1</sup> )	WT (nm)
COF-BD(OH) <sub>2</sub>	2.66	3.071	252.52	1.8	0.209	1.271
Cu@COF-BD(OH) <sub>2</sub>	2.64	3.048	192.31	1.8	0.201	1.248

 $d_{100}$  is the d(100) spacing.

 $a_{100}$  (unit cell parameter) = 2  $d_{100}/\sqrt{3}$ .

 $S_{BET}$  = Surface area measured from BET.

 $PD_{NLDFT}$  is average pore diameter employing NLDFT technique.

PV is the total pore volume.

WT (wall thickness) =  $a_{100}$  - PD<sub>NLDFT</sub>

### Section S5: Molecular modelling, indexing and unit cell parameters of 2D hexagonal

#### structure of COF-BD(OH)2

The experimental small angle PXRD has been correlated with the theoretical PXRD pattern

using REFLEX software.

Symmetry Hexagonal

Lattice parameters a=b=30.5, c=23,  $\alpha$ = $\beta$ =90°,  $\gamma$ =120°

Wavelength (Å) 1.54056

Range of data collection  $0.4 \le 2\theta \le 10$ 

Table S6. d-spacing of 2D hexagonal structure of COF-BD(OH)<sub>2</sub>.

h	k	l	θ	20	D
1	0	0	1.65851	3.31701	26.652

We have conducted the energy minimization for the hexagonal structure of COF-BD(OH)<sub>2</sub> employing chem.3D ultra 12.0 software. The resultant structure provides pore width of 2.512 nm and wall thickness 0.433 nm. Thus the summation of wall thickness and pore size is 2.95 nm and it matches closely with the unit cell parameter 3.07 nm (obtained from PXRD). Observed from the HR-TEM pictures (Figure S11c and S11d), thick pore wall (1.4 nm) can be seen which is of almost equal to the width with the pores (1.8 nm). A proposed justification for this is that the stacking between the 2D sheets may not be absolutely of eclipsed arrangement (AA type), and 1,3,5-triformylphloroglucinol (TFP) and DHBD (3,3'-dihydroxybenzidine) moiety of one layer-sheet is not located accurately above that of another adjacent layer, which enhances the wall thickness (WT) and reduces the pore width of the gross structure (as noticed from the HR-TEM pictures). d-spacing (<100> facet) is the spacing between the 100 planes, which includes the wall thickness, whereas the pore size obtained from HR-TEM and N<sub>2</sub> sorption analysis does not include the wall thickness. Due to thick pore wall (1.4 nm) of COF-BD(OH)<sub>2</sub> the d<sub>100</sub> and pore size is differing. The energy minimized single layer structure and the proposed multi-layer stacking is presented below.



**Figure S4.** Molecular modeling of single sheet of 2D hexagonal framework of COF-

 $BD(OH)_2$  and space filling representation of the parent COF.



**Figure S5.** Multiple stacking planes of 2D hexagonal framework of COF-BD(OH)<sub>2</sub> (not perfectly AA type).

#### Section S6: PXRD and N<sub>2</sub> adsorption-desorption analysis

The PXRD pattern of the as-prepared COF-BD(OH)<sub>2</sub> completely agreed with the PXRD pattern of the composite catalyst based on the stacked arrangement. The evaluated *d* spacing (d) is 2.66 nm according to the Bragg's equation (for 100 reflection plane,  $n\lambda=2d_{100}\sin\theta$ , where  $\lambda=0.15406$  nm and n=1 for first order of diffraction). The physico-chemical properties of the parent COF and Cu@COF-BD(OH)<sub>2</sub> are presented in Table S5. As noticed from PXRD pattern of Cu@COF-BD(OH)<sub>2</sub>, one hump-shaped visible band caused by the (001) facet, situated at a diffraction angle of ~27.3°, and appearance of this mentioned weak band suggests a special interaction coming from  $\pi$ - $\pi$  stacking among the aromatic rings present in the ordered layered-sheet COF-NPs composite.



Figure S6. Powder X-ray diffraction pattern of COF-BD(OH)<sub>2</sub>.



Figure S7. Powder X-ray diffraction pattern of Cu@COF-BD(OH)<sub>2</sub>.

#### **Calculation of d-Spacing**

The value of d (the interplanar spacing between the atoms) is calculated using Bragg's Law.

#### Bragg's Law: $2d\sin\theta = n \lambda$

**Debye-Scherrer equation:** 

$$_{\mathbf{D}} = \frac{k\lambda}{\beta cos \square}$$

Where, 'k' (shape factor) is equal to 0.9, ' $\lambda$ ' is wavelength of X-Ray (0.15418 nm), ' $\beta$ ' is full width at half maximum (FWHM), ' $\Theta$ ' is diffraction angle and 'D' is the particle diameter size.

The particle sizes (crystallite size) of Cu NPs were calculated to be within the range of 14 to 17 nm determined from the Scherrer's equation (Table S7). Employing Debye-Scherrer formula, the determined crystallite sizes are found to be 25.03 nm and 24.69 nm for the (002) facet (CuO) and (111) facet (CuO), respectively. The TEM results are in good accordance with the calculated values obtained from the Scherrer's equation. Employing Debye-Scherrer equation, the crystallite sizes of Cu<sub>2</sub>O are determined to be in the range of 18.5 $\pm$ 1.5 nm (Table S8).

20 of the intense peak (deg)	Hkl	θ of the intense peak (deg)	FWHM of intense peak (deg)	Size of the particle (D) nm	d-spacing nm
43.64	(111)	21.82	0.5449	16.41	0.21
50.80	(200)	25.40	0.6389	14.38	0.18
74.42	(220)	37.21	0.6529	15.97	0.13

Table S7: The grain size of Cu NPs

Table S8: The grain size of Cu2O

20 of the intense peak (deg)	Hkl	θ of the intense peak (deg)	FWHM of intense peak (deg)	Size of the particle (D) nm	d-spacing nm
36.43	(111)	18.21	0.4420	19.77	0.25

61.44 (220)	30.72	0.5431	17.78	0.15
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As presented in Figure S8, The N<sub>2</sub> desorption/adsorption isotherm of the as-prepared microporous  $\pi$ -bonded, stacked COF-BD(OH)<sub>2</sub> displays usually the copious features of type I with few additional natures of type IV pattern. Adsorption of copious amount of N<sub>2</sub> in the domain of low pressure (0-0.1 bar) illustrates the existence of numerous micropores in COF-BD(OH)<sub>2</sub>. The surface area measured from BET experiment (Brunauer-Emmett-Teller) and observed pore volume of the parent COF are 252.52 m<sup>2</sup>g<sup>-1</sup> and 0.209 ccg<sup>-1</sup>, respectively.

The distribution of pore size of the as-obtained COF-BD(OH)<sub>2</sub> determined with the help of NLDFT method (nonlocal density functional theory) employing  $N_2$  at a definite temperature (77 K) confirmed the existence of supermicropores possessing pore dimension (*ca.* 1.89 nm).



**Figure S8.** The N<sub>2</sub> desorption/adsorption isotherm of COF-BD(OH)<sub>2</sub> and the depiction of distribution of pore size by conducting NLDFT method.

#### Section S7: FE-SEM and UHR-TEM analysis

Observed from the pictures of FE-SEM, the micromorphology of reused Cu@COF-BD(OH)<sub>2</sub> displayed that this COF-NPs composite was an irregular rod that is somewhat curled (coral-like microscopic arrangement).



Figure S9. FE-SEM pictures of  $Cu@COF-BD(OH)_2$  composite catalyst at several magnifications.



Figure S10. The FE-SEM images of reused Cu@COF-BD(OH)<sub>2</sub> after 6<sup>th</sup> run.

To detect the phase of COF-BD(OH)<sub>2</sub>, transmission electron microscopy (TEM) pictures were recorded. As described in Figure S11, the HR-TEM pictures of COF-BD(OH)<sub>2</sub> display numerous micropores distributed irregularly throughout the total specimen of the system. As presented in Fig. S11(a–d), the TEM images of COF-BD(OH)<sub>2</sub> suggested a structural morphology of interlinked twisted wires. An experiment was conducted to detect

the internal morphology of COF-BD(OH)<sub>2</sub>, which illustrates the exact morphological similarity between this as-obtained COF and the layered-sheet arrangement. Figure S11(a-e) are TEM pictures of COF-BD(OH)<sub>2</sub> after conducting ultrasonic stripping treatment. Noticed from Figure S11d, it can be detected that the stacked layer sheets of this parent laboratory-fabricated COF are constructed due to deposition of several sheets in a layer-by-layer arrangement, fabricated through the arrangement of exfoliated sheets.

Observed from TEM pictures of Cu@COF-BD(OH)<sub>2</sub>, the spacing of the distinct lattice fringes observed is ascribed to copper NPs and copper oxide featuring lower oxidation state (Cu<sup>+</sup>). The observed spacing (d=0.212 nm) is ascribed to the (111) facet of the cubic metallic copper and it exactly matches the ICSD-4349326. Additionally, the calculated spacing (d) is about 0.236 nm, which is attributed to the (111) facet of the synthesized Cu<sub>2</sub>O NPs present in COF-NPs composite (standard ICSD 063281). So, the copper NPs have no amorphous character. The distribution of particle size observed from HRTEM pictures exhibits the Cu NPs featuring significant size range of the nanosized particles in between 8-16 nm (Figures S12). Such moderate-sized copper NPs are complicated to synthesize even in the presence of some additives such as stabilizers or capping agents.<sup>13</sup>



**Figure S11.** The UHR-TEM pictures of the assembled  $\text{COF-BD}(\text{OH})_2$  sheets at different scales (a) 100 nm, (b) 20 nm, (c) 20 nm, (d) 10 nm, (e) 2 nm and (f) SAED pattern of this fabricated stacked COF.



**Figure S12.** The UHR-TEM pictures of Cu@COF-BD(OH)<sub>2</sub> material displaying the distinct lattice fringes owing to the existence of different copper species at different scales (a) 100 nm, (b) 50 nm, (c) 20 nm, (d) 10 nm, (e) 20 nm, (f) 2 nm, (g) 5 nm and (h) SAED pattern of Cu@COF-BD(OH)<sub>2</sub>. The inset describes the distribution of particle size determined from TEM image.

COF-BD(OH)<sub>2</sub> displayed layered-sheet arrangement observed by TEM, which is in agreement with the SEM images. The PXRD pattern of the parent COF agrees well with the HR-TEM images. As described in Fig. 1 and 2, TEM and SEM images display that the structural morphology of the Cu@COF-BD(OH)<sub>2</sub> composite catalyst shows the same

morphology of COF-BD(OH)<sub>2</sub>. EDAX experiments illustrated the existence of O, N and C as displayed in Fig. S13 and S14. EDX also suggested the loading of copper in the COF–NPs composite to be at 6.4 wt%, which is in agreement with the copper loading (6.8 wt%) measured from the ICP experiment.

Figure S11f and S12h illustrate SAED patterns of COF-BD(OH)<sub>2</sub> and Cu@COF-BD(OH)<sub>2</sub> materials, respectively. Observed from the TEM pictures of the Cu/Cu<sub>x</sub>O<sub>y</sub> NPs embedded COF, the homogeneous dispersion of Cu/Cu<sub>x</sub>O<sub>y</sub> NPs (clearly visible dark dots) onto the fabricated COF sheets are detected. These observed SAED patterns agreed with the XRD observation.



#### Section S8: Electron images and EDAX patterns

**Figure S13.** Electron image of COF-BD(OH)<sub>2</sub> (a) and the EDAX pattern of COF-BD(OH)<sub>2</sub> (b).





Spectrum processing : No peaks omitted

Processing option : All elements analyzed Number of iterations = 5 (Normalised)

Elem... Weight% Atomic%

C K	50.79	59.06
N K	19.12	19.04
O K	23.70	20.53
Cu K	6.39	1.37
Totals	100.00	

**Figure S14.** Electron image of Cu@COF-BD(OH)<sub>2</sub> (a) and the EDAX pattern of Cu@COF-BD(OH)<sub>2</sub> (b).



**Figure S15.** Electron image of reused  $Cu@COF-BD(OH)_2$  (a) and the EDAX pattern of reused  $Cu@COF-BD(OH)_2$  (b) after six runs.



Section S9: PXRD patterns of the parent COF

Figure S16. Small angle powder X-ray diffraction pattern of COF-BD(OH)<sub>2</sub>.

#### Section S10: DRS-UV-visible absorption spectra

The UV-Visible reflectance diffuse spectra of Cu@COF-BD(OH)<sub>2</sub> and COF-BD(OH)<sub>2</sub> are established in Figure S17 and S19 using BaSO<sub>4</sub> disk as a reflecting white diffusive material. As seen from these images, the peaks of the as-prepared COF and Cu/Cu<sub>x</sub>O<sub>y</sub> NPs decorated COF in the region of UV-Vis wavelength suggested  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  transitions owing to existence of aromatic rings.



Figure S17.The DRS-UV-visible absorption spectrum of Cu@COF-BD(OH)<sub>2</sub>.



**Figure S18.** The DRS-UV-visible absorption spectrum of reused Cu@COF-BD(OH)<sub>2</sub> after six runs.



Figure S19. The DRS-UV-visible absorption spectrum of COF-BD(OH)<sub>2</sub>.



Figure S20. The DRS-UV-visible absorption spectrum of COF-BD(OH)<sub>2</sub> (boiled in water).

#### Section S11: FTIR spectra and thermal gravimetric analysis

Observed from the FT-IR spectra of COF-BD(OH)<sub>2</sub> and Cu@COF-BD(OH)<sub>2</sub>, we can detect that the unique absorption bands located at ~3400 and ~2970 cm<sup>-1</sup> could be attributed to the vibrations of N-H, C-H bonds as described in Fig. S21. Additionally, the characteristic bands located at ~3300 cm<sup>-1</sup> (-NH<sub>2</sub>) and ~2900 cm<sup>-1</sup> (-CHO) vanished after conducting the condensation process. On the other hand, the generation of two significant absorption bands centered at 1281 and 1598 cm<sup>-1</sup> corresponds to the vibrations of C=C-NH and C=C in parent COF-BD(OH)<sub>2</sub>.<sup>14,15</sup>



Figure S21. FT-IR spectra of COF-BD(OH)<sub>2</sub> and Cu@COF-BD(OH)<sub>2</sub>.



Figure S22. FT IR spectrum of reused Cu@COF-BD(OH)<sub>2</sub> after 6th run.



Figure S23. FT IR spectrum of COF-BD(OH)<sub>2</sub> (boiled in water).







Figure S25. TGA image of Cu@COF-BD(OH)<sub>2</sub>.

#### Section S12: X-ray photoelectron spectroscopy (XPS)

The prominent characterizations of the parent COF and Cu/Cu<sub>x</sub>O<sub>y</sub> NPs embedded COF have been conducted by XPS (X-ray photoelectron spectroscopy) as described in Figure S26, 3(ag). The C 1s spectrum (Figure S26b) of COF-BD(OH)<sub>2</sub> has three distinct bands which are ascribed to the carbon atoms of C=O (289.2 eV), C-N and C-O (286.1 eV) and C-C, C=C or C-H (284.5 eV), respectively.<sup>16,17</sup> Consequently, the band with binding energy of 284.5 eV corresponds to the carbon atom of C=C bonds within COF-BD(OH)<sub>2</sub>. The prominent N1s signal (Figure S26c) of COF-BD(OH)<sub>2</sub> has single band located at 400.04 eV, which is ascribed to the N atoms within several enamine units (-HN-C=C).



**Figure S26.** XPS spectra of COF-BD(OH)<sub>2</sub> material consisting of elements C 1s (b), N 1s (c), O 1s (d) and the typical XPS survey scan (a).

The outcomes are completely related to the structures of the ultimate material after tautomerism (imine-enamine) in the production process of the parent COF. Furthermore, the O 1s narrow scan was illustrated in Figure S26d. The bands situated at binding energies of 533.05 eV and 531.5 eV are ascribed to the O atoms of C-O and C=O bonds, respectively, which are in agreement with the frameworks of the as-prepared COF.<sup>16,17</sup> A hump-shaped band located at 535.8 eV is ascribed to the oxygen atoms within H<sub>2</sub>O molecules.<sup>18</sup> All the outcomes from data collection, associated with elemental observation (CHN analysis), undoubtedly demonstrate the construction of the fabricated COF sheets with the expected structural morphology.

As described in Fig. 3c, the significant Cu LMM peak that appeared at 570.4 eV is ascribed to the copper species featuring lower oxidation state (Cu<sub>2</sub>O) in addition to the Auger parameters of the copper  $2p_{3/2}$ . Additionally, O 1s, N 1s and C 1s narrow scan (Fig. 3) demonstrate the structural morphology of the Cu/Cu<sub>x</sub>O<sub>y</sub> NPs anchored COF. The C 1s core level peak by conducting peak deconvolution displayed that bands with binding energies of 289.2, 286.02 and 284.5 eV for Cu@COF-BD(OH)<sub>2</sub> are ascribed to the carbon atoms of C=O, C–O/C–N and C–C, C=C and C–H, respectively. The N 1s signal illustrates a band with a binding energy of 399.9 eV corresponding to the enamine nitrogen atoms (Fig. 3d). The band located at 400.8 eV corresponds to the existence of poor Cu–N attachment due to an interaction between copper species and enamine nitrogen atoms.





**Figure S27.** XPS survey scan measurement on reused Cu@COF-BD(OH)<sub>2</sub> (a), the XPS spectrum of reused Cu@COF-BD(OH)<sub>2</sub> illustrating the bands corresponding to metallic copper NPs and copper oxide NPs featuring different oxidation states (Cu<sup>1+</sup>and Cu<sup>2+</sup>) (b), C 1s narrow scan (c), N 1s narrow scan (d) and O 1s narrow scan measurement (e) on reused Cu@COF-BD(OH)<sub>2</sub> composite catalyst after 6<sup>th</sup> run.

A typical XPS spectrum of copper nanoparticle was measured and the spectrum of Cu  $2p_{3/2}$  is depicted in Fig. S28. The deconvolution of Cu  $2p_{3/2}$  was performed to determine the contents of Cu<sub>2</sub>O, CuO and Cu NPs in the catalyst. The Cu  $2p_{3/2}$  spectrum shows that the Cu<sup>2+</sup> peak lies at 934.86 eV, with two shake-up satellites at higher binding energy (BE 939.28 and 944.43 eV). The Cu<sup>1+</sup> peak appeared at 932.63 eV was attributed to Cu<sub>2</sub>O. Furthermore, two unique satellite peaks located at 964 and 944 eV are ascribed to the copper species featuring a higher oxidation state. The prominent shake-up satellite arrangements and a strong Cu  $2p_{3/2}$ peak were subjected to deconvolution into four distinct bands, as presented in Fig. 3g. Two clearly visible peaks located at 932.6 and 934.8 eV could be attributed to Cu(I) from Cu<sub>2</sub>O NPs and Cu(II) from CuO phases, respectively. The XPS results indicate that the sample is composed of Cu NPs, CuO and Cu<sub>2</sub>O. 92.32 % of CuO and 7.68 % of Cu<sub>2</sub>O were found in Cu@COF-BD(OH)<sub>2</sub>. Cu NPs and Cu<sub>2</sub>O cannot be resolved by this deconvolution because their binding energies are very close and are different by only 0.1 eV. One can distinguish them from the position of their LMM-2 auger transition in XPS spectra which are 568.08 eV and 570.40 eV for Cu and Cu<sub>2</sub>O, respectively. The Cu metal and Cu<sub>2</sub>O are best distinguished from the x-ray-excited Cu LMM Auger spectra.

Two overlapping peaks at 568.08 eV and 570.40 eV in the XAES spectra were related to Cu<sup>0</sup> and Cu<sup>+</sup>, respectively, and the deconvolution results of these peaks were used to calculate the molar ratios of copper species ( $X_{Cu^+} = Cu^+/(Cu^0 + Cu^+)$ ). As listed in Table S10, the  $X_{Cu^+}$  of Cu@COF-BD(OH)<sub>2</sub> was 77.75%, which was much higher than  $X_{Cu(0)}$  (22.25%) of Cu@COF-BD(OH)<sub>2</sub>.



Figure S28 Typical deconvolution of Cu 2p<sub>3/2</sub> of Cu@COF-BD(OH)<sub>2</sub>.

Table S9	. The results	of decon	volution	of XPS	Cu 2p <sub>3/2</sub> peaks
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Binding	Cu phase	Width	Area	Height	Percentage
energy					(%)
(eV)					
932.63	Cu <sub>2</sub> O	1.3237	12617	7605.3	7.68
934.86	CuO	1.8199	97629	42803	59.45
939.28	CuO	1.8157	12761	5607.5	7.78
944.43	CuO	3.0515	41210	10775	25.09



Figure S29. Cu LMM spectra of Cu@COF-BD(OH)<sub>2</sub>.

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Table S10.	I he molar	ratios c	of surface	copper	species
				F F -	

Binding energy (eV)	Cu phase	Width	Area	Height	X <sub>Cu</sub> ª/%
570.40	Cu <sub>2</sub> O (Cu <sup>+</sup> )	2.5002	97402	31083	77.75
568.08	Cu (Cu <sup>0</sup> )	1.7403	27870	12778	22.25

<sup>a</sup> Molar ratio of Cu species determined by the deconvolution of Cu LMM XAES spectra.



Section S13: The characterization of the recovered catalyst

Figure S30. The UHR-TEM pictures of the reused  $Cu@COF-BD(OH)_2$  sheets at different scales (a) 50 nm, (b) 10 nm, (c) 10 nm and (d) SAED pattern of this reused  $Cu@COF-BD(OH)_2$  after 6<sup>th</sup> run.



Figure S31. XRD pattern of reused Cu@COF-BD(OH)<sub>2</sub> after 6<sup>th</sup> run.

Section S14: XRD patterns of Cu<sub>2</sub>O, Cu NPs and CuO



Figure S32. XRD pattern of Cu<sub>2</sub>O NPs.



Figure S33. XRD pattern of Cu NPs.



Figure S34. XRD pattern of CuO NPs

Section S15: Powder X-ray diffraction pattern and N<sub>2</sub> desorption/adsorption isotherm

### of Cu/Cu<sub>x</sub>O<sub>y</sub>@COF



Figure S35. Powder X-ray diffraction pattern of Cu/Cu<sub>x</sub>O<sub>y</sub>@COF.



Figure S36. Space filling representation of the parent COF (TpBD-Me<sub>2</sub>).



Figure S37. The N<sub>2</sub> desorption/adsorption isotherm of  $Cu/Cu_xO_y@COF$  and the depiction of distribution of pore size by conducting NLDFT method.

#### Section S16: Leaching test and kinetic curves

Furthermore, the advancement of this reaction with the solution after hot filtration at around 55% yield essentially stopped, undoubtedly demonstrating that the reaction likely occurred on the surface of heterogeneous material, as displayed in Figure S38.



**Figure S38.** Leaching test revealing no contribution from homogeneous catalysis of the active species leaching into the resultant solution.

#### Kinetic curves (conversion vs. time) for oxazolidinedione synthesis

We have studied the conversion rates for CO<sub>2</sub>-incorporated cyclizative multicomponent reaction with time in presence of Cu@COF-BD(OH)<sub>2</sub> catalyst and from the obtained data, the kinetic curves (Figure S39) have been drawn. The conversion rates of different recycling runs for this CO<sub>2</sub>-incorporated cyclizative multicomponent reaction have been studied and compared (Figure S40). This figure suggested that there were minimal decrease in the conversion rates after six recycling runs, suggesting the Cu@COF-BD(OH)<sub>2</sub> catalyst is reusable with almost similar activity for this cyclizative multicomponent reaction.



Figure S39. Kinetic curve for oxazolidinedione synthesis (CO<sub>2</sub>-incorporated cyclizative



multicomponent reaction of 1b with 2b\*).

**Figure S40.** Comparison of conversion rates of different recycling runs for oxazolidinedione synthesis (CO<sub>2</sub>-incorporated cyclizative multicomponent reaction of 1b with 2b\*).

#### Section S17: NMR Spectra of Oxazolidinediones

<sup>1</sup>H NMR data of isolated pureoxazolidinedionederivatives:

S17. 1. (Z)-5-(4-Methoxybenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione



Yield: 96%; color: pale yellowish white; mp = 198-200 °C; <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>)  $\delta$  3.83-3.89 (s, 6H, -OCH<sub>3</sub>), 6.91 (s, 1H), 6.98-7.03 (m, 4H), 7.40-7.45 (m, 2H), 7.74-7.79 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.3, 55.4, 114.2, 114.7, 114.8, 123.3, 123.4, 126.8, 133.0, 136.7, 151.5, 159.6, 161.58, 161.59.

S17.2. (Z)-5-(4-Methoxybenzylidene)-3-phenyloxazolidine-2,4-dione



Yield 85%; color: pale yellow; mp = 164-166°C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  3.88 (s, 3H, - OCH<sub>3</sub>), 6.91 (s, 1H), 6.99-7.05 (m, 2H), 7.53-7.62 (m, 5H), 7.82-7.88 (d, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.3, 114.3, 114.7, 123.5, 125.5, 128.8, 129.5, 130.9, 133.1, 135.6, 151.2, 161.2, 161.7.

S17.3. (Z)-5-Benzylidene-3-(4-methoxyphenyl)oxazolidine-2,4-dione



Yield: 88%; color: white; mp = 194-195 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.88 (s, 3H), 6.92 (s, 1H), 6.99-7.02 (m, 2H), 7.41-7.48 (m, 5H), 7.72-7.78 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.6, 113.5, 114.6, 123.1, 127.2, 129.1, 130.5, 130.7, 130.8, 131.1, 137.5, 151.1, 159.9, 161.2.



Yield: 96%; color: pale yellowish white; mp = 184-186°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.92 (s, 1H), 7.25-7.70 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  114.3, 125.3, 129.0, 129.1, 129.3, 130.8, 131.2, 137.1, 150.8, 161.2.

S17.5. (Z)-3-(4-Nitrophenyl)-5-(4-methylbenzylidene)oxazolidine-2,4-dione



Yield 68%; color: pale yellow; mp = 205-207 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.42 (s, 3H), 6.90 (s, 1H), 7.00-7.03 (d, 2H), 7.41-7.45 (m, 2H), 7.58-7.62 (m, 2H), 7.78-7.82 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.6, 55.5, 114.2, 114.7, 123.2, 126.9, 127.9, 129.8, 131.2, 136.6, 141.3, 151.3, 159.8, 161.5.

S17.6. (Z)-3-(4-Methoxyphenyl)-5-(3-methylbenzylidene)oxazolidine-2,4-dione



Yield 81%; color: pale yellow; mp = 205-206 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.42 (s, 3H, -CH<sub>3</sub>), 3.89 (s, 3H, -OCH<sub>3</sub>), 6.91 (s, 1H), 7.01-7.03 (m, 2H), 7.44-7.47 (m, 2H), 7.52-7.54 (m, 2H), 7.78-7.84 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.5, 55.5, 114.1, 114.6, 123.1, 126.8, 127.8, 129.8, 131.3, 136.6, 141.2, 151.3, 159.8, 161.4.



Yield: 90%; color: pale yellowish white; mp = 204-206 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.81 (s, 3H, -OCH<sub>3</sub>), 6.91 (s, 1H), 7.01-7.03 (d, 2H), 7.40-7.44 (m, 2H), 7.59-7.62 (m, 2H), 7.79-7.83 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 60.5, 115.1, 119.4, 128.5, 133.1, 133.2, 134.3, 134.5, 134.5, 135.3, 137.5, 139.7, 143.8, 156.2, 164.5, 166.8. *S17.8. (Z)-5-(4-Chlorobenzylidene)-3-p-tolyloxazolidine-2,4-dione* 



Yield: 93%; color: white; mp = 188-190°C; <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>)  $\delta$  2.42 (s, 3H), 6.92 (s, 1H), 7.26-7.35 (m, 2H), 7.39-7.49 (m, 4H), 7.75-7.83 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  21.1, 112.6, 125.2, 127.8, 129.3, 129.4, 130.1, 132.3,136.8, 137.4, 139.3, 150.9, 161.1;

S17.9. (Z)-3-(3-Chlorophenyl)-5-(3,5-dimethylbenzylidene)oxazolidine-2,4-dione



Yield: 36%; color: pale yellowish white; mp = 198-199 °C; <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>)  $\delta$  2.39 (s, 3H), 6.93 (s, 1H), 6.98-7.05 (m, 2H), 7.42-7.49 (m, 2H), 7.51-7.57 (m, 1H), 7.61-7.69 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  21.3, 112.7, 125.2, 127.7, 129.2,129.3, 130.1, 132.3,136.7, 137.5, 139.2, 150.8, 161.1.

S17.10. (Z)-5-(4-hydroxybenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione



Yield: 81%; color: pale yellowish white; mp = 201-204 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.86 (s, 3H), 6.89 (s, 1H), 7.02-7.09 (m, 2H), 7.38-7.41 (m, 2H), 7.42-7.49 (m, 2H), 7.72-7.80 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.5, 113.5, 114.5, 123.2, 127.1, 129.1, 130.4, 130.8, 130.9,131.1, 137.5, 151.0, 159.8, 161.3.

S17.11. (Z)-3-(4-chlorophenyl)-5-(4-methoxybenzylidene)oxazolidine-2,4-dione



Yield: 76%; color: pale yellow; mp = 188-190 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.91 (s, 3H, -OCH<sub>3</sub>), 6.91 (s, 1H), 7.05 (d, 2H), 7.51-7.56 (m, 4H), 7.80 (d, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 55.3, 114.7, 114.9, 123.3, 126.5, 129.5, 133.3, 134.6, 135.2, 150.7, 160.9, 161.6. *S17.12. (Z)-5-Benzylidene-3-p-tolyloxazolidine-2,4-dione* 



Yield: 79%; color: pale yellowish white; mp = 176-179°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.45 (s, 3H), 6.93 (s, 1H), 7.24-7.52 (m, 7H), 7.84 (d, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  21.1, 114.2, 125.2, 127.9, 129.1, 130.0, 130.6, 130.7, 131.2, 137.2, 139.2, 151.1, 161.2.

#### (Z)-5-(4-Methoxybenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione (aa\*)

### <sup>1</sup>H NMR spectra:



### (Z)-5-(4-Methoxybenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione (aa\*)



### (Z)-5-(4-Methoxybenzylidene)-3-phenyloxazolidine-2,4-dione(ab\*)

### <sup>1</sup>H NMR spectra:



(Z)-5-(4-Methoxybenzylidene)-3-phenyloxazolidine-2,4-dione (ab\*)



### (Z)-5-Benzylidene-3-(4-methoxyphenyl)oxazolidine-2,4-dione (ba\*)

### <sup>1</sup>H NMR spectra:



(Z)-5-Benzylidene-3-(4-methoxyphenyl)oxazolidine-2,4-dione (ba\*)



### (Z)-5-Benzylidene-3-phenyloxazolidine-2,4-dione (bb\*)

<sup>1</sup>H NMR spectra:



### (Z)-5-Benzylidene-3-phenyloxazolidine-2,4-dione (bb\*)



### (Z)-3-(4-Nitrophenyl)-5-(4-methylbenzylidene)oxazolidine-2,4-dione(cc\*)

### <sup>1</sup>H NMR spectra:



(Z)-3-(4-Nitrophenyl)-5-(4-methylbenzylidene)oxazolidine-2,4-dione (cc\*)



### (Z)-3-(4-Methoxyphenyl)-5-(3-methylbenzylidene)oxazolidine-2,4-dione (da\*)

### <sup>1</sup>H NMR spectra:



# (Z)-3-(4-Methoxyphenyl)-5-(3-methylbenzylidene)oxazolidine-2,4-dione (da\*)



### (Z)-5-(4-Chlorobenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione (ea\*)

### <sup>1</sup>H NMR spectra:



(Z)-5-(4-Chlorobenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione (ea\*)



### (Z)-5-(4-Chlorobenzylidene)-3-p-tolyloxazolidine-2,4-dione (ee\*)

### <sup>1</sup>H NMR spectra:



### (Z)-5-(4-Chlorobenzylidene)-3-p-tolyloxazolidine-2,4-dione (ee\*)



### (Z)-3-(3-Chlorophenyl)-5-(3,5-dimethylbenzylidene)oxazolidine-2,4-dione (ff\*)

#### <sup>1</sup>H NMR spectra:



#### (Z)-3-(3-Chlorophenyl)-5-(3,5-dimethylbenzylidene)oxazolidine-2,4-dione (ff\*)





# (Z)-5-(4-hydroxybenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione (ga\*)

### <sup>1</sup>H NMR spectra:



### (Z)-5-(4-hydroxybenzylidene)-3-(4-methoxyphenyl)oxazolidine-2,4-dione (ga\*)



### (Z)-3-(4-chlorophenyl)-5-(4-methoxybenzylidene)oxazolidine-2,4-dione (3ag\*)

### <sup>1</sup>H NMR spectra:





### (Z)-5-Benzylidene-3-p-tolyloxazolidine-2,4-dione (3be\*)

### <sup>1</sup>H NMR spectra:





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