

Immobilized Copper Complex on Biodegradable Cellulose: Catalytic Application for the Green Synthesis of 2H-indazolo[1,2-b]phthalazine Trione Derivatives and Synthesis of CuO Nanoparticles

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ABSTRACT: *An immobilized copper (II) complex on micro cellulose (Cell-DABCO-Cu) was synthesized and characterized by FT-IR, TGA, and SEM. The catalytic activity of Cell-DABCO-Cu was evaluated as a recoverable and green catalyst for the four-component synthesis of 2H-indazolo[1,2-b]phthalazine trione derivatives in solvent-free conditions. The notable advantages of this procedure include excellent yields, short experimental time, and easy preparation of the catalyst. The feature of this work is using of Cell-DABCO-Cu as a starting material to prepare single-phase CuO nanoparticles (CuO NPs) via a solid-state decomposition procedure. The CuO nanoparticles with an average size of 40 nm were obtained by the direct calcination of Cell-DABCO-Cu.*

KEYWORDS: *Cellulose; CuO nanoparticles; Copper complex; Multi-component reaction.*

INTRODUCTION

Health, sustainability, and environmental protection are important challenges in the modern world. In this regard, designing and developing hybrid materials have improved the quality of life and technology. Many composites have been synthesized by the combination of organic and inorganic compounds which attracted significant attention due to their application. By entering the polymer science to functional material–inorganic hybrids the new advantages were obtained by combining the properties of polymers with the inorganic components [1]. The biodegradable nature of materials that were obtained from bioresources makes them the ideal candidate for the development of green polymer micro composites in catalytic systems [2-5]. Using harmful solvents with micro

Composite in catalytic systems is a big problem and leads to the reduction of the applications of these important composites in different industries [6-8]. Therefore, performing the reactions in solvent-free conditions has attracted great attention in the recent past decades [6, 7, 9, 10].

The MultiComponent Reactions (MCRs) are powerful tools for the synthesis of complex organic compounds from readily available reagents. The major advantages of MCRs include lower costs, short experimental times, high atom economy, and energy savings from the avoidance of time-consuming and expensive purification processes [8, 11]. New ways for the synthesis of organic compounds containing heterocyclic frames have been considered due to the wide applicability of these compounds [12-14].

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Heterocycles containing phthalazine are considered in heterocyclic synthesis because of pharmacological and biological activities [15-17].

We recently reported the removal of pyrene and related aromatic hydrocarbons by several complexes-based catalyst systems and also friendly environmental reaction [18-20]. In continuing our work on the synthesis of heterocyclic compounds [21-23], a novel copper complex was fabricated on a micro-fibril cellulose template as a heterogeneous catalyst and used for the four-component synthesis of 2*H*-indazolo[1,2-*b*]phthalazine triones in solvent-free condition. After finishing the catalytic system, CuO NPs were obtained via solid-state thermal decomposition of Cell-DABCO-Cu at 800°C.

EXPERIMENTAL SECTION

Materials and Physical measurements

Chemicals were either prepared in our laboratory or purchased from Merck or Fluka chemical companies and were used without any further purification. IR spectra of compounds in the 4000–400 cm⁻¹ regions as KBr disks were recorded on a Thermo SCIENTIFIC model NICOLET iS10 spectrophotometer. SEM (Shimadzu 50, model s4160) analysis was performed for checking the morphology and topology of the products. Powder X-Ray Diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer or on a X'Pert Pro MPD diffractometer with Cu K α (λ = 0.154 nm) radiation. A Shimadzu thermogravimetric analyzer (TG-50, Japan) is the model of thermogravimetric analysis (TGA). ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 and 100 MHz, respectively) in DMSO-d₆, internal standard TMS. All reactions were monitored by thin-layer chromatography (TLC) on silica gel Polygram SILG/UV 254 plates (eluent EtOAc:hexane = 3:1). Melting points were determined on an Electrothermal-9100 apparatus and are uncorrected. Elemental analyzes were carried out using a Heraeus CHN-O-Rapid analyzer. Cellulose was purchased from Aldrich (microcrystalline, 20^mm).

Synthesis of Cell-DABCO-Cu

Synthesis of chloro-functionalized cellulose (Cell-Cl)

A mixture of 3-chloropropyltrimethoxysilane (1mL) and triethylamine (0.1 mL) was added to 1g cellulose in dry toluene (10 mL) and refluxed for 24 hours. Chloro functionalized cellulose was separated by centrifugation

at 3000 rpm for 15 min and washed with ethanol. The resulting product was dried under a vacuum.

Synthesis of DABCO supported on cellulose (Cell-DABCO)

A mixture of 0.5 g chloro functionalized cellulose and 1,4-diazabicyclo[2.2.2]octane (DABCO) (2 g) in dry acetone (40 mL) was stirred magnetically for 15min. After refluxing within 24 hours, the resulted DABCO supported on cellulose was separated by centrifugation at 3000 rpm for 15 min and washed with acetone to remove the excess DABCO.

The synthesis of the immobilized copper complex on DABCO supported on cellulose (Cell-DABCO-Cu)

To a solution of copper (II) acetate (0.5 g) in dry acetone (40 mL), 1g of DABCO-supported cellulose was added. After stirring for 36 hours, the final product was separated by centrifugation at 3000 rpm for 15 min and dried under a vacuum.

Synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-trione compounds

A mixture of hydrazinium hydrate **3** (1.2 mmol), phthalic anhydride **4** (1 mmol), dimedone **1** (1 mmol), aryl aldehyde **2a-n** (1 mmol), and Cell-BABCO-Cu (0.01 g) as a catalyst was stirred at 80°C under solvent-free conditions. The completion of the reaction is monitored by TLC. After satisfactory completion of the reaction, 5mL ethanol was added and the catalyst was removed by centrifugation and the solvent was evaporated. The crude product was recrystallized from ethanol/water. The desired pure products were characterized by a comparison of their physical data with those of known compounds.

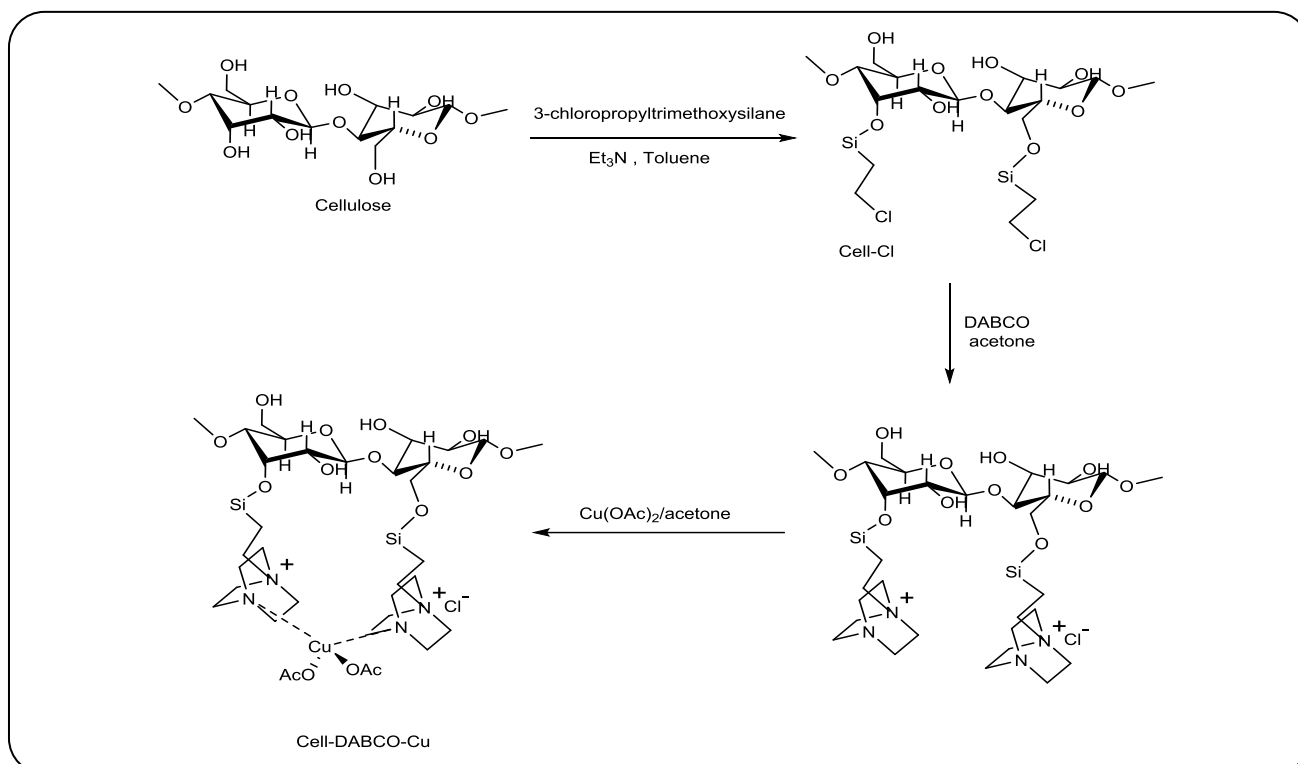
Synthesis of CuO nanoparticles

The Cell-DABCO-Cu micro-composite was heated at 2 °C/min up to 800 °C in a laboratory thermal furnace with a residence time of 5 h to produce the black powder.

RESULTS AND DISCUSSION

Synthesis and characterization of Cell-DABCO-Cu

Cellulose-supported DABCO (Cell-DABCO) was synthesized via the nucleophilic substitution of Cell-Si-Cl with DABCO in a S_N2 reaction as shown in Scheme 1. Then the resulting Cell-DABCO was coordinated with copper acetate to give the final catalyst Cell-DABCO-Cu complex.



Scheme 1: Synthesis of Cell-DABCO-Cu catalyst.

To approve the successful synthesis of Cell-BABCO-Cu composite, FT-IR analysis was carried out. The FT-IR spectra of cellulose, Cell-Cl, and Cell-DABCO-Cu are shown in Fig. 1. In the cellulose spectrum (Fig. 1a), the strong broad stretching at $3200\text{--}3600\text{cm}^{-1}$ corresponds to OH groups of cellulose, C-H stretching of methine and methylene groups are appeared in $2800\text{--}3000\text{cm}^{-1}$, and the alcoholic C-O and glycosidic bond vibrations are located around $1100\text{--}1150\text{cm}^{-1}$ [24, 25]. As seen in Cell-Cl spectra (Fig1b), the absorption peaks at 2910, 2930, and 1475 cm^{-1} are related to CH_2 of 3-chloropropyltrimethoxysilane and $1000\text{--}1100\text{cm}^{-1}$ Si-O in oxygen-silica tetrahedral, indicating that the cellulose was successfully functionalized by 3-chloropropyltrimethoxysilane [26]. The C-N⁺ stretching vibration of DABCO and also terminal COO of the catalyst are appeared in $1400\text{--}16120\text{cm}^{-1}$ (Fig 1C) [27]. The absorption peaks at $1400\text{--}1630\text{ cm}^{-1}$ are corresponding to the bridged C=O of the acetate group.

The presence of metal in the catalyst was confirmed by ICP-AES, and which amount of Cu in each gram of catalyst was determined $68\text{ }\mu\text{mol}$.

The thermal behavior of Cell-DABCO-Cu (Fig. 2) was studied by thermogravimetric analysis (TGA) (15 mg

of Cell-DABCO-Cu micro composite was used with temperature range $30\text{ }^\circ\text{C}$ to $900\text{ }^\circ\text{C}$, at 80 K/min heating rates. The inner atmosphere was maintained with a nitrogen purge flow rate 40 mL/min to protect the sample from oxidation). As shown in Fig. 2, the degradation of this biocatalyst occurred at $380\text{ }^\circ\text{C}$ which exhibits its high thermal stability. The organic component was decomposed completely at more than $800\text{ }^\circ\text{C}$. According to the TGA, $69.50\text{ }\mu\text{mol/g}$ of copper or copper complex was loaded.

SEM image was used to study the surface morphology of this novel biocatalyst (Fig. 3).

The Fibril shape of cellulose is observable before supporting the copper complex.

Synthesis of 2H-indazolo [2,1-b]phthalazine-triones

In this context, the novel synthesized bio-nano hybrid was employed in the four-component synthesis of 2H-indazolo[1,2-b]phthalazine triones **5a-n** in solvent-free conditions (Scheme 2).

To determine the best conditions, the reaction of benzaldehyde **2a** (1 mmol), hydrazine hydrate **3** (1.2 mmol), dimedone**1** (1 mmol) and phthalic anhydride **4** (1 mmol), in the presence of metal cellulose catalyst

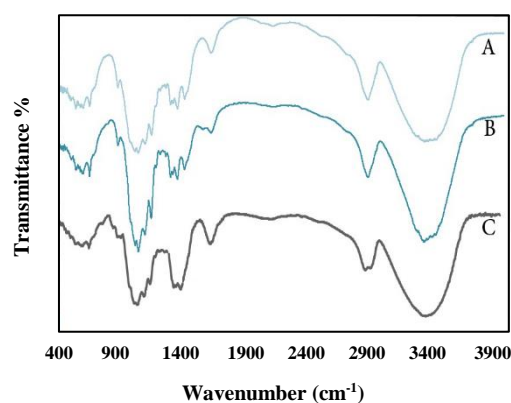


Fig. 1: FT-IR spectra of A) Cellulose, B) Cell-Cl, and C) Cell-DABCO-Cu.

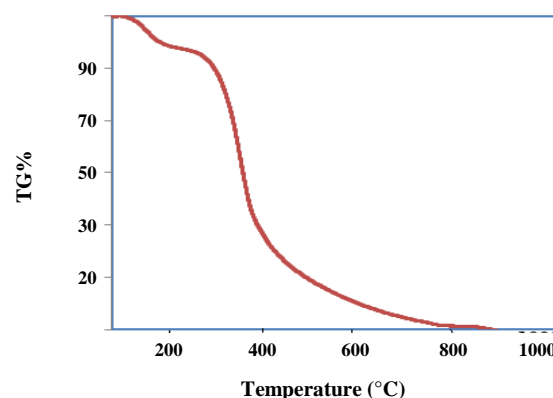


Fig. 2: Thermo gravimetric analysis of Cell-DABCO-Cu.

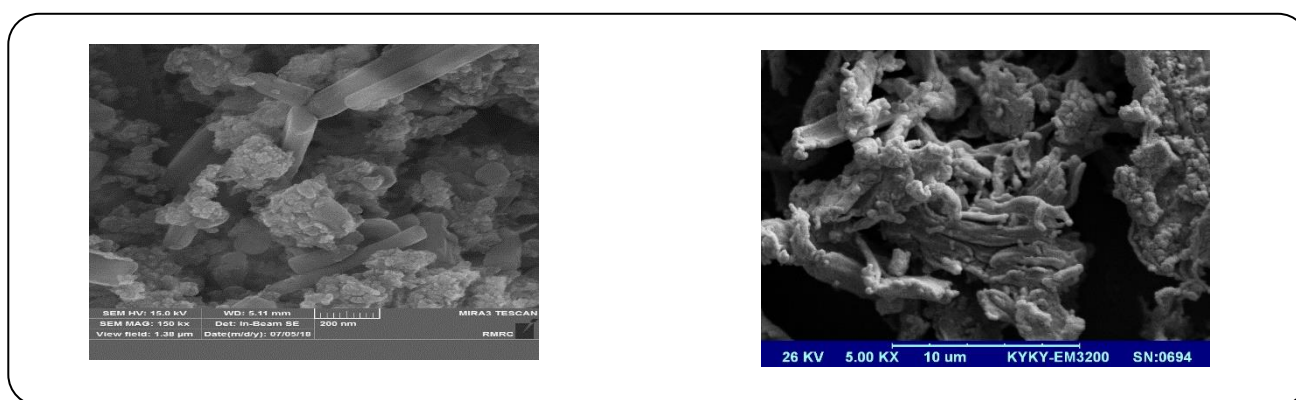
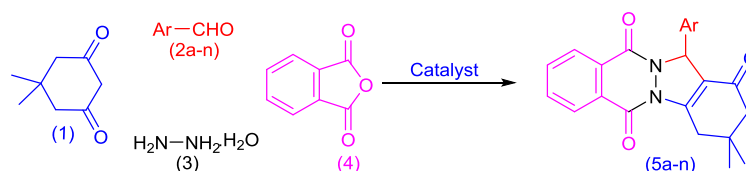


Fig. 3: SEM image of a) Cell-DABCO-Cu and b) cellulose.



Scheme 2: Four component synthesis of 2H-indazolo[1,2-b]phthalazine trione derivatives (5a-n).

was performed in different solvents, different amounts of catalyst, and various temperatures. The results are collected in table 1, (entries 1–11). The best yield and reaction time were obtained in the case of solvent-free and 0.01 g of catalyst and 80°C.

By using the optimized reaction conditions, the possibility and efficiency of this procedure were discovered by the synthesis of 2H-indazolo[1,2-b]phthalazine trione derivatives **5a-n** with a different aromatic aldehyde in the presence of Cell-DABCO-Cu as an efficient and green catalyst. Interestingly, the aromatic aldehydes with both

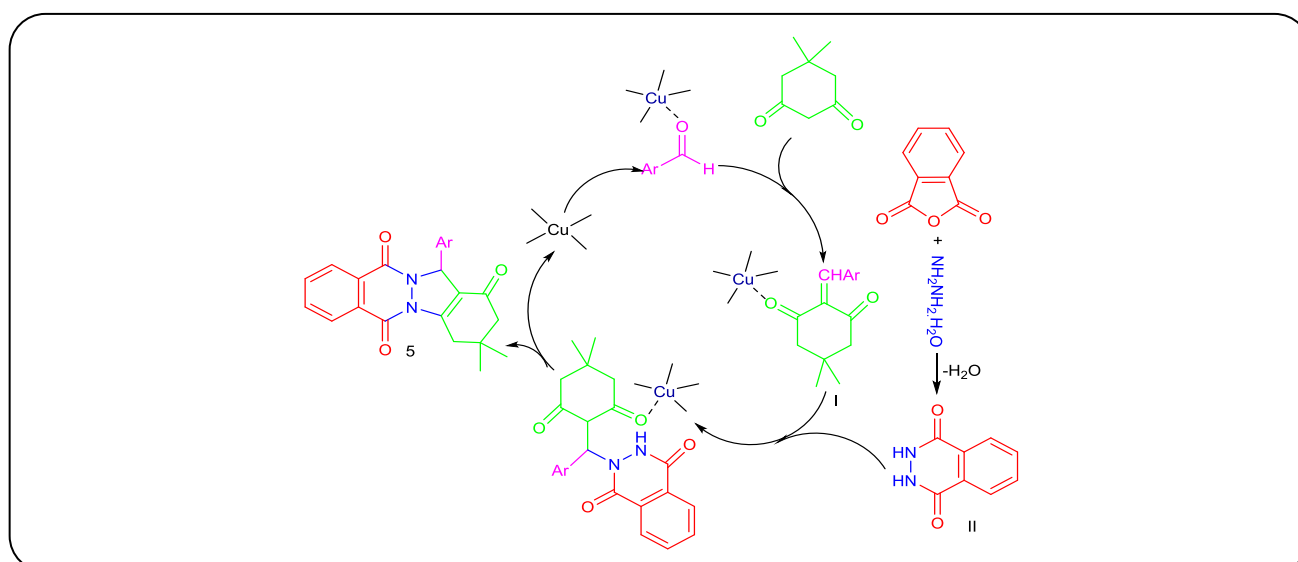
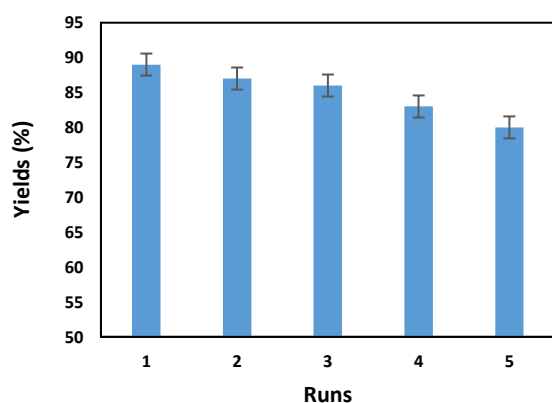
electron-donating and withdrawing groups participated well in this reaction and provided the corresponding products in good to excellent yields (Table2). The obtained products were characterized by spectral data IR, ¹H NMR, and ¹³C NMR and have been recognized by comparison of the spectral data and melting point with those obtained in authentic samples.

The suggested mechanism for the synthesis of the desired products in the presence of a metal cellulose catalyst is shown in Scheme 3. By the Knoevenagel condensation of aryl aldehydes with dimedone in the presence of Cell-DABCO-Cu

Table 1: Optimization of the reaction conditions.

Entry	Solvent	catalyst (g)	Temp (°C)	Time (min)	Yield ^a (%)
1	CH ₂ Cl ₂	0.01	Reflux	120	15
2	THF	0.01	r.t.*	110	12
3	THF	0.02	reflux	120	17
4	H ₂ O	0.01	r.t	54	23
5	H ₂ O	0.01	80°C	10	61
6	EtOH	0.01	r.t	53	48
7	EtOH	0.01	reflux	11	69
8	None	None	80 °C	120	trace
9	None	0.008	80 °C	15	85
10	None	0.01	80 °C	10	89
11	None	0.015	80 °C	10	90

^aExperimental conditions: benzaldehyde **2a** (1 mmol), hydrazine hydrate **3** (1.2 mmol), dimedone **1** (1 mmol), phthalic anhydride **4** (1 mmol), catalyst and solvent (5 mL). *Room temperature.

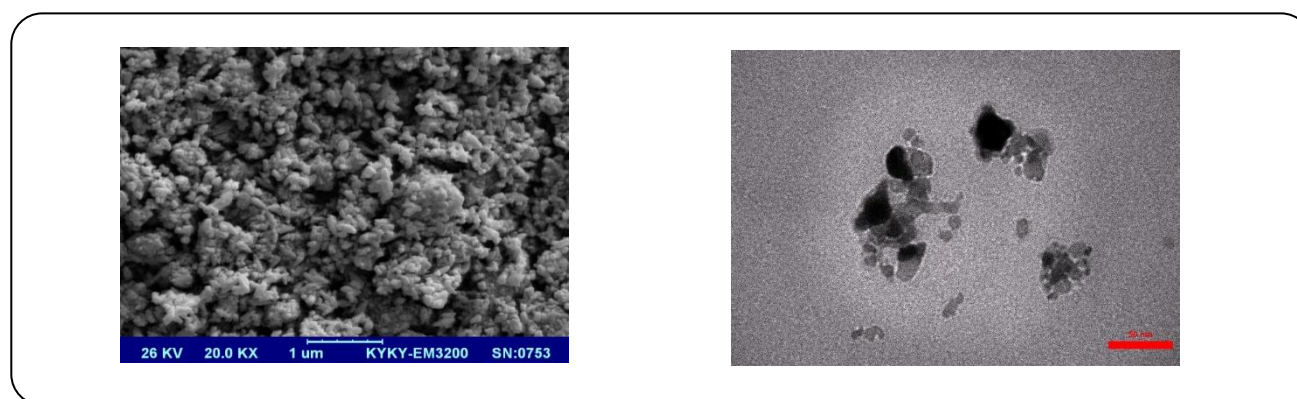
**Scheme 3: The proposed reaction mechanism for the desired reaction.****Fig. 4: The reuse test of Cell-DABCO-Cu catalyst.**

as an acidic catalyst, intermediate (**I**) was prepared. The condensation of hydrazinemonohydrate with phthalic anhydride afforded phthalhydrazide (**II**) by dehydration. In the next step, 1,4-conjugate addition of the phthalhydrazide (**II**) to intermediate (**I**) followed by cyclization provides the corresponding product (**5a-n**). (Scheme 3)

The recycling of the catalyst was investigated by checking the model reaction in the presence of 0.01 g Cell-DABCO-Cu (Fig. 4). After completion of the reaction, the catalyst was separated from the reaction mixture by centrifuge and washed with ethanol three times. It was shown that the catalyst could be reusable for five cycles without any considerable loss of its activity.

Table 3: Comparison the result of Cell-DABCO-Cu catalyst with other reported catalysts for the synthesis of compound 5a.

Entry	Catalyst (mol%)	Reaction condition	Time (min)	Yield (%) [Ref]
1	p-TSA (30mol%)	[bmim]Br/ 100°C	180	94[35]
2	Et ₃ N (20mol%)	EtOH/50°C/ultrasound	60	90[36]
3	[Bmim]OH (20mol%)	MW,100W/45°C	4	96[37]
4	Cell-DABCO-Cu	Solvent free/ 80°C	8	89 (Present work)

**Fig. 5: a) SEM and b) TEM images of the CuO NPs.**

Finally, in order to show the efficiency of the proposed method, Cell-DABCO-Cu catalyst was compared with other catalysts reported earlier for the synthesis of 3,4-Dihydro-3,3-dimethyl-13-phenyl-2*H*-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione **5a**. As demonstrated in Table 3, the use of, this catalyst lead to an improved protocol in terms of compatibility with the environment, reaction time, and yield when compared with another catalyst.

Synthesis and characterization of CuO

By using the Cell-DABCO-Cu as a starting material the single-phase CuO nanoparticles (CuO NPs) were prepared *via* a solid-state decomposition procedure. Morphology, shape, and size of CuO NPs were studied by SEM and TEM images (Fig 5). As shown in Fig 5a, b the diameter of Cu(II) was revealed 50 nm. It is notable that the size of CuO NPs in this study is smaller than the other reported studies (250-480nm).[38, 39] Therefore, the biodegradable Cell-DABCO-Cu can be used as an alternative precursor to produce nano-size copper oxide.

Fig. 6 presents the XRD pattern of CuO NPs with the sharp peaks centered on 2θ values of 32.11, 35.76°, and 38.96°, corresponding to (110), (002), and (111) planes of this nanomaterial, respectively. Minor peaks at 48.86,

53.35, 58.39, 61.93, 66.96, and 67.99 ° can be indexed to reflection from (202), (020), (202), (113), (311), and (113). Hence the crystallographic structure of CuO nanocrystal is monoclinic bravais lattic with space group C2/c and unit cell lattice parameters a=4.684, b= 3.424, and c= 5.129. The average crystallite size of CuO NPs has obtained 30 nm by using the debye–scherrer formula.

Fig. 7 was shown the FT-IR of CuO nanoparticles. The peak at 536 cm⁻¹ is assigned to CuO stretching vibration [40]. On the other hand, the absence of stretching vibration of functional groups of the Cell-DABCO-Cu well confirmed the presence of CuO as a sole product.

CONCLUSIONS

In summary, a novel heterogeneous biocatalyst was synthesized, characterized, and developed successfully as a highly efficient and greener approach for the one-pot, four-component synthesis of 2*H*-indazolo[1,2-*b*]phthalazine trione derivatives **5a-n**. The merits of the presented methodology are efficiency, generality, high the excellent yield of the products, short reaction time, simplicity, no elevated temperature, ease of product isolation, cleaner reaction profile, avoidance of any hazardous solvents or catalysts, and acceptance with the green chemistry agreements. Furthermore, the catalyst could be reused

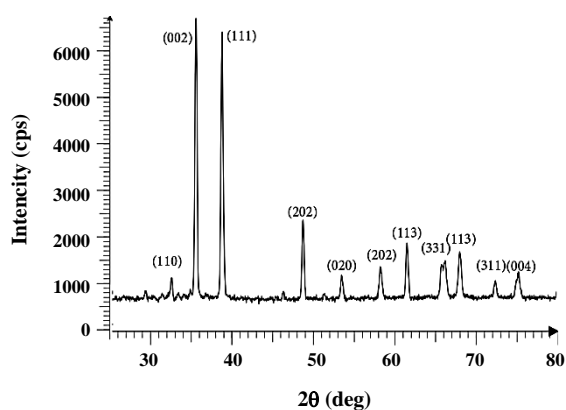


Fig. 6: The XRD pattern of CuO NPs.

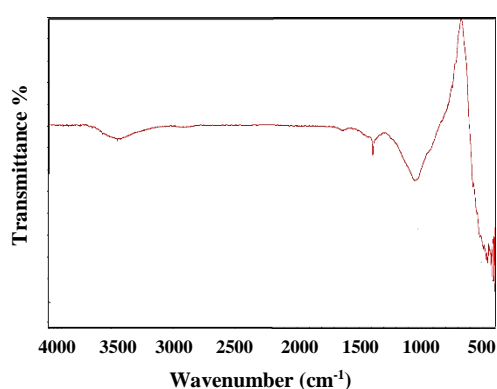


Fig. 7: FT-IR spectrum of the CuO nanoparticles.

easily without noticeable loss of its activity which is the standpoint of this green procedure for the synthesis of 2*H*-indazolo[1,2-*b*]phthalazine triones. After finishing the catalytic activities of this biodegradable catalyst, single-phase CuO nanoparticles were obtained *via* a solid-state decomposition procedure which makes it proper for the industrial goals.

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REFERENCES

[1] Kim C.S., Randow C., Sano T., "Hybrid and Hierarchical Composite Materials." Springer, (2015).
Research Article

- [2] Yoon K., Hsiao B.S., Chu B., Functional Nanofibers for Environmental Applications., *J. Mater. Chem.*, **18(44)**:5326-5334 (2008).
- [3] Bang H., Watanabe K., Nakashima R., Kai W., Song K.H., Lee J.S., Gopiraman M., Kim I.S., A Highly Hydrophilic Water-Insoluble Nanofiber Composite as an Efficient and Easily-Handleable Adsorbent for the Rapid Adsorption of Cesium from Radioactive Wastewater., *RSC Adv.*, **4(103)**: 59571-59578 (2014).
- [4] Chauhan P., Yan N., Nanocrystalline Cellulose Grafted Phthalocyanine: A Heterogeneous Catalyst for Selective Aerobic Oxidation of Alcohols and Alkyl arenes At Room Temperature in a Green Solvent., *RSC Adv.*, **5(47)**: 37517-37520 (2015).
- [5] Shaabani A., Keshipour S., Hamidzad M., Shaabani S., Cobalt(II) Phthalocyanine Covalently Anchored to Cellulose as a Recoverable and Efficient Catalyst for the Aerobic Oxidation of Alkyl Arenes and Alcohols., *J. Mol. Catal. A: Chem.*, **395**: 494-499 (2014).
- [6] Costa A.M.S., Mano J.F., Solvent-Free Strategy Yields Size and Shape-Uniform Capsules., *J. Am. Chem. Soc.*, **139(3)**: 1057-1060 (2017).
- [7] Wang X., Wu G., Wang F., Liu H., Jin T., Solvent-Free Selective Oxidation of Toluene with O₂ Catalysed by Anion Modified Mesoporous Mixed Oxides with High Thermal Stability, *Catal. Commun.*, **98**: 107-111 (2017).
- [8] Li M., Kong W., Wen L.R., Liu F.H., Facile Isocyanide-Based One-Pot Three-Component Regioselective Synthesis of Highly Substituted Pyridin-2(1*H*)-One Derivative at Ambient Temperature., *Tetrahedron*, **68(24)**: 4838-4845 (2012).
- [9] Poursattar Marjani A., Khalafy J., Eslamipour P., Ahmadi Sabegh M., Synthesis of a New Series of 4*H*-benzo[*h*]chromenes by a Multicomponent Reaction under Solvent-Free Microwave Conditions, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **38(4)**: 51-57 (2019).
- [10] Arab-Salmanabadi S., Microwave-Assisted Synthesis of Novel Functionalized Ketenimines and Azadienes via a Solvent-Free Reaction of Isatoic Anhydride, Alkyl-Isocyanides and Dialkyl Acetylenedicarboxylates, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **38(6)**: 205-211 (2019).

- [11] Gao H., Sun J., Yan C.G., [Synthesis of Functionalized 2-Pyrrolidinones via Domino Reactions of Arylamines, Ethyl Glyoxylate and Acetylenedicarboxylates.](#), *Tetrahedron*, **69(2)**: 589-594 (2013).
- [12] Kotov A.D., Prokaznikov M.A., Antonova E.A., Rusakov A.I., [Synthesis of Nitrogen-Containing Heterocycles from Nitroarenes \(Minireview\).](#), *Chem. Heterocycl. Comp.*, **50**: 647-657 (2014).
- [13] Nakhaei A., Davoodnia A., Yadegarian S., [An Efficient Green Approach for the Synthesis of Fluoroquinolones Using Nano Zirconia Sulfuric Acid as Highly Efficient Recyclable Catalyst in two Forms of Water.](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **37(3)**: 33-42 (2018).
- [14] Nakhaei A., Ramezani S., [Synthesis, Characterization, and Theoretical Studies of the New Antibacterial Zn\(II\) Complexes from New Fluorescent Schiff Bases Prepared by imidazo\[4',5':3,4\]benzo\[1,2-c\]isoxazole.](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **38(4)**: 79-90 (2019).
- [15] Al- Assar F., Zelenin K.N., Lesiovskaya E.E., Bezhan I.P., Chakchir B.A., [Synthesis and Pharmacological Activity of 1-Hydroxy-, 1-Amino-, and 1-Hydrazino-Substituted 2,3-Dihydro-1H-pyrazolo\[1,2-a\]pyridazine-5,8-diones and 2,3-Dihydro-1H-pyrazolo\[1,2-b\]phthalazine-5,10-diones.](#), *Pharm. Chem. J.*, **36(11)**: 598-603 (2002).
- [16] Jain R.P., Vederas J.C., [Structural Variations in Keto-Glutamines for Improved Inhibition Against Hepatitis A Virus 3C Proteinase.](#), *Bioorg. Med. Chem. Lett.*, **14(5)**: 3655-3658 (2004).
- [17] Carling R.W., Moore K.W., Street L.J., Wild D., Isted C., Leeson P.D., Thomas S., O'Connor D., McKernan R.M., Quirk K., Cook S.M., Atack J.R., Wafford K.A., Thompson S.A., Dawson G.R., Ferris P., Castro J.L., [3-phenyl-6-\(2-pyridyl\)methoxy-1,2,4-triazolo\[3,4-a\]phthalazines and Analogues: High-Affinity Gamma-Aminobutyric Acid-A Benzodiazepine Receptor Ligands with Alpha 2, Alpha 3, and Alpha 5-Subtype Binding Selectivity over Alpha 1.](#), *J. Med. Chem.*, **47(7)**: 1807-1822 (2004).
- [18] Lopez-Moreno A., Clemente-Tejeda D., Calbo J., Naeimi A., Bermejo F.A., Orti E., Perez E.M., [Biomimetic Oxidation of Pyrene and Related Aromatic Hydrocarbons. Unexpected Electron Accepting Abilities of Pyrenequinones.](#), *Chem. Commun. (Camb)*, **50(66)**: 9372-9375 (2014).
- [19] Aguiló J., Naeimi A., Bofill R., Mueller-Bunz H., Llobet A., Escriche L., Sala X., Albrecht M., [Dinuclear Ruthenium Complexes Containing a New Ditopic Phthalazin-bis\(triazole\) Ligand that Promotes Metal-Metal Interactions.](#), *New J. Chem.*, **38(5)**: 1980-1987 (2014).
- [20] Naeimi A., Saeednia S., Yoosefian M., Rudbari H.A., Nardo V.M., [A Novel Dinuclear Schiff Base Copper Complex as an Efficient and Cost Effective Catalyst for Oxidation of Alcohol: Synthesis, Crystal Structure and Theoretical Studies.](#), *J. Chem. Sci.*, **127**: 1321-1328 (2015).
- [21] Honarmand M., Naeimi A., Zahedifar M., [Nanoammonium Salt: A Novel and Recyclable Organocatalyst for One-Pot Three-Component Synthesis of 2-Amino-3-Cyano-4H-Pyran Derivatives.](#), *J. Iran. Chem. Soc.*, **14**: 1875-1888 (2017).
- [22] Zahedifar M., Mohammadi P., Sheibani H., [Synthesis and Characterization of Novel Magnetic Nanoparticles Supported Imidazole Ion as an Efficient Catalytic System for the Three-Component Reaction of Arylaldehydes, Malononitrile and \$\alpha\$ -hydroxy or \$\alpha\$ -Amino Active Methylene Compounds.](#), *Lett. Org. Chem.*, **14(5)**: 315-323 (2017).
- [23] Zahedifar, M., Shojaei, R., Sheibani, H. [Convenient Regioselective Reaction in Presence of H3PW12O40: Synthesis and Characterization of Pyrazolo\[3,4-b\]quinoline-3,5-diones.](#), *Res. Chem. Intermed.*, **44(2)**: 873-882 (2017).
- [24] Reddy B.V.S., Majumder N., Prabhakar Rao T., Sridhar B., [A Novel Sugar Based Intramolecular Ugi 3CC for the N-alkyl-3-oxo-4-aryl-octahydrofuro\[2,3-f\]\[1,4\]oxazepine-5-carboxamides.](#), *Tetrahedron Lett.*, **53(18)**: 2273-2276 (2012).
- [25] Guibal E., [Heterogeneous Catalysis on Chitosan-Based Materials: A Review.](#), *Prog. Polym. Sci.*, **30(1)**: 71-109 (2005).
- [26] Sobhani, S., Pakdin-Parizi, Z. [Palladium-DABCO complex supported on \$\gamma\$ -Fe₂O₃ magnetic nanoparticles: A new catalyst for CC bond formation via Mizoroki-Heck cross-coupling reaction.](#), *Appl. Catal. A: Gen.* **479**: 112-120 (2014).
- [27] Sobhani S., Falatouni Z.M., Asadi S., Honarmand M., [Palladium-Schiff Base Complex Immobilized Covalently on Magnetic Nanoparticles as an Efficient and Recyclable Catalyst for Heck and Suzuki Cross-Coupling Reactions.](#), *Catal. Lett.*, **146(1)**: 255-268 (2015).

- [28] Ghorbani-Vaghei R., Karimi-Nami R., Toghraei-Semiroimi Z., Amiri M., Ghavidel M., One-pot synthesis of Aliphatic and Aromatic 2H-indazolo[2,1-b]phthalazine-triones Catalyzed by N-Halosulfonamides under Solvent-Free Conditions, *Tetrahedron*, **67(10)**: 1930-1937 (2011).
- [29] Varghese A., Nizam A., Kulkarni R., George L., Solvent-Free Synthesis of 2H-indazolo[2,1-b]Phthalazine-Triones Promoted by Cavitation Phenomenon Using Iodine as Catalyst., *Eur. J. Chem.*, **4(2)**:132-137 (2013).
- [30] Khurana J.M., Magoo D., pTSA-catalyzed one-pot Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones in Ionic Liquid and Neat Conditions., *Tetrahedron Lett.*, **50(33)**: 4777-4780 (2009).
- [31] Mombani Godajdar B., Reza Kiasat A., Mahmoodi Hashemi M., One-Pot Synthesis of 2H-Indazolo[2,1-b]phthalazinetrione Catalyzed by Magnetic Room Temperature Dicationic Ionic Liquid under Solvent-Free Conditions., *Heterocycles*, **87**: 559-570 (2013).
- [32] Atashkar B., Rostami A., Gholami H., Tahmasbi B., Magnetic Nanoparticles Fe₃O₄-Supported Guanidine as an Efficient Nanocatalyst for the Synthesis of 2H-indazolo[2,1-b]phthalazine-triones under Solvent-Free Conditions., *Res. Chem. Intermed.*, **41**: 3675-3681 (2013).
- [33] Shaterian H.R., Hosseinian A., Ghashang M., Reusable Silica Supported Poly Phosphoric Acid Catalyzed Three Component Synthesis of 2H-indazolo[2,1-b]phthalazine-trione Derivatives., *ARKIVOC*, **ii**:59-67 (2009).
- [34] Mazaahir K., Ritika C., Anwar J., Efficient CAN Catalyzed Synthesis of 1H-indazolo[1,2-b]phthalazine-1,6,11-triones: An Eco-friendly Protocol., *Chinese Sci. Bull.*, **57**: 2273-2279 (2012).
- [35] Ghahremanzadeh R., Shakibaei G.I., Bazgir A., An Efficient One-Pot Synthesis of 1H-Pyrazolo[1,2-b]phthalazine-5,10-dione Derivatives., *Synlett.*, **2008(08)**: 1129-1132 (2008).
- [36] Nabid M.R., Rezaei S.J.T., Ghahremanzadeh R., Bazgir A., Ultrasound-Assisted One-Pot, Three-Component Synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones., *Ultrason. Sonochem.*, **17(1)**: 159-161 (2010).
- [37] Raghuvanshi, D.S., Singh, K.N. A highly Efficient Green Synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione Derivatives and Their Photophysical Studies., *Tetrahedron Lett.*, **52(43)**: 5702-5705 (2011).
- [38] Benbow E.M., Dalal N.S., Latturmer S.E., Crystal Growth and Magnetic Behavior of R₆T_{13-x}Al_xMy Phases (R= La, Nd; T= Mn, Fe; M= Main Group) Grown from Lanthanide-Rich Eutectic Fluxes, *J. Solid State Chem.*, **182(11)**: 3055-3062 (2009).
- [39] Saeednia S., Iranmanesh P., Rudbari H.A., Saeednia L., Sonochemical Synthesis of a New Nano-Scale 1D Copper Organic Coordination Polymer; Thermal and Spectroscopic Characterizations, *J. Macromol. Sci. A.*, **53(4)**: 227-236 (2016).
- [40] Taghavi F.S., Ramazani, A. Green Synthesis and Characterization of Copper Oxide Nanoparticles Using Coffee Powder Extract., *J. Nanostruct.*, **6(2)**: 167-171 (2016).