

Synthesis, DFT Calculations and Catalytic Activity in the Biginelli Reaction of Two Hydrazone Cu(II) Complexes

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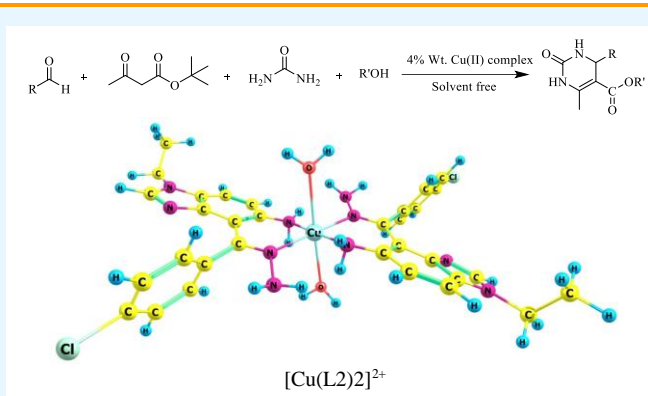
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Abstract: In this work, two Cu(II) complexes containing 5-amino-1-R-1H-benzimidazol-4-yl(4-chloro)phenylmethanone hydrazones ligands were synthesized and their spectral characterization, DFT calculations, and catalytic activity were reported. New heterocyclic hydrazone ligands were prepared by the reaction of *o*-amino-ketones with hydrazine hydrate in high yield. Structural assignments of new compounds were based on their microanalytical and spectral data and formula $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2](\text{SO}_4)$ was suggested for complexes. Moreover, to gain a further insight into the geometry of synthesized complexes, the DFT calculations were carried out at the B3LYP/6-311+G(d,p) level of theory. The catalytic activity of Cu(II) complexes as heterogeneous catalysts were also investigated in the synthesis of biologically active compound 3,4-dihydropyrimidin-2(1H)-one C5 ester, *via* classical Biginelli reaction followed by *trans*-esterification reaction. The results confirmed that the current method formed the products at the lower reaction time and high yields, which might as a result of the enhanced reactivity of the reactants on the surface sites of Cu(II) complexes.

Keywords: Cu(II) complex, Amino-benzimidazol-hydrazone ligand, DFT, Biginelli reaction, Catalyst stability



1. INTRODUCTION

Biginelli reaction is one of the most important multicomponent reactions which suggests a simple approach to make an *N*-heterocyclic moiety such as 3,4-dihydropyridine-2(1H)-ones (DHPMs). These compounds have showed important pharmacological properties such as the integral backbones of several calcium channel blockers,¹ antihypertensive agents,² treatment of Alzheimer's disease,³ alpha-1a-antagonists,⁴ and neuropeptide Y (NPY) antagonists.⁵ The increasing attention in the synthesis of DHPMs *via* Biginelli reaction has demanded the development of new catalysts for the reason that traditional Biginelli reaction regularly suffers from insensitive reaction conditions, usage of harmful and non-volatile solvents, low yield, low selectivity, requirement of high temperature, extended reaction time etc.⁶⁻⁹ Therefore, the discovery of milder and practical routes for the synthesis of dihydropyrimidin-2(1H)-ones by the Biginelli reaction continues to attract the attention of researchers. On the other hand, Cu(II) complexes are employed as catalyst in many reactions such as oxidation-reduction,¹⁰ polymerization,¹¹ cycloaddition¹² and enantioselective alkylation reactions.¹³ Furthermore,

hydrazones compounds are ligands under very intensive study in modern coordination and supramolecular chemistry.¹⁴⁻¹⁷ These ligand systems tend to form binuclear complexes with exchange couplings between the metal ions. Such complexes allow relatively easy variation in the electron-donating centers, central ions, and exogenous bridging groups and hence can serve as convenient models for investigation of the main factors that determine the character and strength of exchange couplings between paramagnetic centers; both antiferromagnetic and ferromagnetic exchange is possible.¹⁸⁻²²

In the light of the findings, two Cu(II) complexes derived from 5-amino-1-R-1H-benzimidazol-4-yl(4-chloro)phenylmethanone hydrazones ligands were obtained and then identified by both spectroscopic and analytical methods. Density functional theory (DFT) studies were also used to gain the optimized structures and their related parameters. In addition, the catalytic activity of Cu(II) complexes was examined, as new heterogeneous catalysts under thermal and solvent-free conditions, on Biginelli/Transesterification multicomponent reactions for the preparation of 3,4-dihydropyrimidin-2(1H)-one C5

ester derivatives.

2. RESULTS AND DISCUSSION

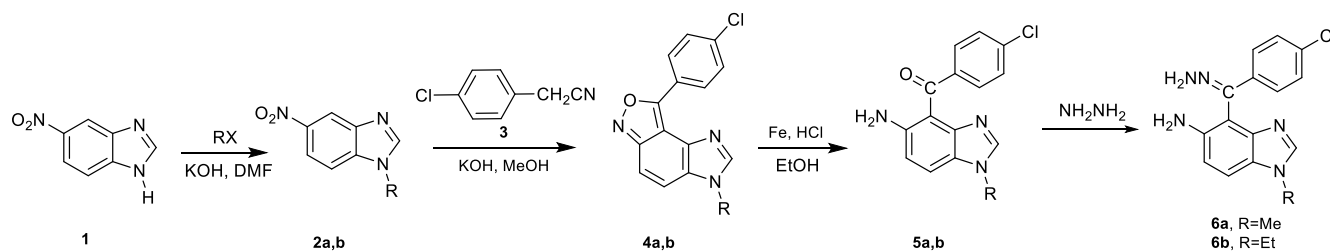
Synthesis and structure of the new ligands **6a,b** and complexes **7a,b**

To prepare the desired complexes **7a,b**, the precursors were obtained according to the published methods.²³⁻²⁵ 1-Alkyl-5-nitro-1H-benzimidazoles (**2a,b**) were prepared by reaction of 5-nitro-1H-benzimidazole (**1**) with methyl iodide and ethyl bromide in DMF and KOH.²³ The reaction of compounds **2a,b** with (4-chlorophenyl)acetonitrile **3** led to the formation of 6H-isoxazolo[4,3-*e*]benzimidazoles (**4a,b**) in methanol solution.²⁴ The reduction reaction of compounds **4a,b** by Fe/HCl in EtOH resulted in the formation of the heterocyclic *o*-amino-ketones **5a,b** in high yields.²⁵ When the latter compounds were reacted with hydrazine hydrate in EtOH, new ligands **6a,b** were obtained (Scheme 1).

Structures of ligands **6a,b** were confirmed by NMR, IR, mass spectra, and elemental analyses. For example, in the ¹H NMR spectrum of compound **6b** the ethyl group protons were observed at δ 1.38 (t, $J = 7.5$ Hz, 3H, CH₃) and 4.34 (q, $J = 7.5$ Hz, 2H, NCH₂). Furthermore, NH₂ group of protons can be seen at δ 6.21 and 7.74 ppm. Four doublet signals at δ 6.81 (d, $J = 8.9$ Hz, 1H, Ar H), 7.35 (d, $J = 8.9$ Hz, 1H, Ar H), 7.89 (d, $J = 8.1$ Hz, 2H, Ar H), and 8.62 (d, $J = 8.1$ Hz, 2H, Ar H); and a singlet signal at δ 8.09 ppm were also appeared for seven protons of aromatic rings. Moreover, 14 different carbon atoms were observed in the ¹³C NMR spectrum of compound **6b**. In

the FT-IR spectrum of compound **6b**, a broad signal at 3355 and 3288 cm⁻¹ is attributed to two NH₂ groups. Moreover, the results of mass spectroscopy and elemental analysis are in accordance with the structure of ligand **6b**. Finally, two new complexes **7a,b** were obtained from the coordination of ligands **6a,b** and Cu(II) cation in aqueous methanolic solution in high yields. The stoichiometry of Cu(II) complexes **7a,b** (ML₂) was obtained by Job's method.²⁶ Job's curve of equimolar solutions for Cu(II) complex **7a** in aqueous methanolic solution can be found in Supplementary Data (Figures S1). Based on the results of the mass spectroscopy and elemental analysis data, formula [Cu(L)₂(H₂O)₂](SO₄) can be suggested for complexes **7a,b**. Also, density functional theory (DFT) calculations were used to get more comprehensive data in geometrical and structural parameters of Cu(II) complexes **7a,b**. As described in Figure 1, two L ligand as well as two aqua ligands are coordinated to Cu²⁺ metal ion. In the structure of complex **7b**, the L species coordinates to Cu²⁺ ion through the nitrogen atoms of amine and imine groups as a bidentate ligand.

Table 1 shows selected structural parameters of complex **7b**. For comparison, reported structural parameters for the free L ligand **6b** are reported in Table 1. The calculated dihedral angles prove that the four coordinating atoms of two ligands as well as Cu²⁺ metal ion are in a same plane (Table 1). The O23 and O61 atoms of two H₂O ligands occupy two other positions of the octahedral complex. These structural calculated parameters are consistent with the reported data to analogous structures.²⁷



Scheme 1. Synthesis of the new ligands **6a,b**

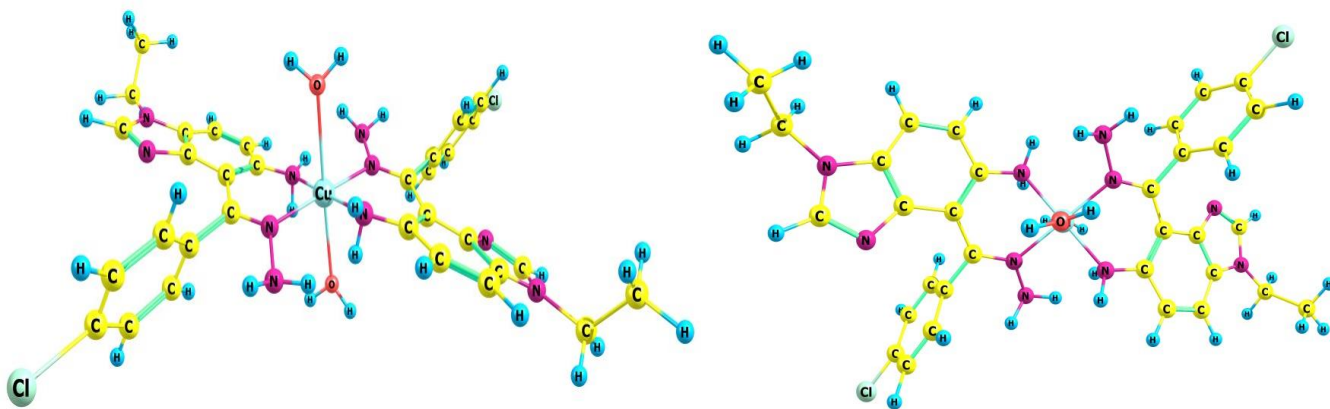


Figure 1. Optimized geometry of [Cu(L)₂]²⁺ **7b** in two views.

Table 1. a,b) Important structural parameters of complex **7b** together with free L ligand **6b**

a)					
Bond length (pm)	L	[CuL ₂ (H ₂ O) ₂]	Dihedral angle (°)	L	[CuL ₂ (H ₂ O) ₂]
C22-C1	145.3	144.6	C24-C22-C1-C2	-30.5	-22.4
C1-C6	141.7	142.0	Cu-O23-C22-C1	-	22.8
C6-N35	136.6	138.9	O23-N35-O61-N73	-	2.3
N35-H36	102.6	101.2	O23-N35-O61-Cu	-	-2.0
Cu-N35	-	219.2	O81-Cu-N73-C43	-	-91.4
C22-C24	148.2	147.5	C1-C2-C7-N8	-177.8	-178.6
C1-C2	146.8	147.5	C2-C7-N8-N9	0.03	0.06
C7-N8	133.2	133.8	C7-N8-N9-C12	178.5	178.9
N8-N9	136.9	136.6	N8-N9-C12-C15	99.3	99.8
b)					
Angle (°)	L	[CuL ₂ (H ₂ O) ₂]			
C1-C6-N35	121.7	121.9			
C6-N35-H36	132.6	133.4			
O23-Cu-O61	-	178.3			
Cu-N35-C6	-	123.6			
C1-C2-C7	133.5	134.4			
C7-N8-N9	106.1	106.6			
N8-N9-C12	121.3	121.6			

Catalytic activity of Cu(II) complexes **7a,b**

Complexes **7a,b** can be considered as Lewis acid to activate the carbonyl groups in starting material. To evaluate the activity of Cu(II) complexes **7a,b** in the synthesis of DHPMs as catalyst, a reaction of four-component containing 4-methoxybenzaldehyde (**8b**), tert-butyl- β -ketoester (**9**), urea (**10**) and propargyl alcohol (**11b**) (Scheme 2) was selected as a type of reaction to make optimum conditions such as the molar ratio of the catalyst, temperature, and solvents. Also, in order to select the appropriate solvent and temperature, the catalytic activity of Cu(II) complex **7a** was examined in solvents toluene, ethanol, water, and solvent free conditions. Based on the obtained results, the highest yield of the desired product and maximum performance of Cu(II) complex **7a** was obtained once the reaction was carried out in solvent-free conditions at 110 °C.

To find optimum conditions of the amount of the catalyst for the preparation of DHPMs, reaction of 4-methoxybenzaldehyde (**8b**), tert-butyl- β -ketoester (**9**), urea (**10**) and propargyl alcohol (**11b**) in the presence of Cu(II) complex **7a** in solvent-free conditions at 110 °C was carried out with varying amounts of the catalyst (1.0-6.0 Wt.% to aldehyde) and unchanging the reaction time to 2 h. Figure 2 reveals that using 4.0 Wt.% to aldehyde for catalyst (%) is sufficient for achieving the best yield. The observed increase in the percentage conversion with increasing in amount of catalyst (%) can be due to the availability of more active site on the catalyst surface during the reaction circumstance of four component Biginelli reaction followed by transesterification process. However, further increase in the catalyst amount (%) over 4.0 % might have resulted in the increase in viscosity of the system which in turn reduces the interaction

between the catalyst and reaction medium. According to obtained optimal considered conditions, some 3,4-dihydropyrimidin-2(1*H*)-one C5 esters were obtained and the results were reported in Table 2. An additional important quality of this procedure is continued existence of a variety of functional groups, such as nitro, alkoxy, and halides under reaction circumstances. In all these cases, the reactions were clean and the products were obtained with simple work-up in excellent to outstanding yields. Cu(II) complex **7b** was also utilized as a novel catalyst in the synthesis of 3,4-dihydropyrimidin-2(1*H*)-one C5 ester derivatives and the same results was obtained. Moreover, blank catalytic experiments were carried out using the ligands L1, L2 and CuSO₄·5H₂O. The results of the experiments showed that products obtained at the lower reaction time and high yields compared to Cu(II) complexes **7a,b** (ligands L1 and L2 had no effect on increasing the reaction efficiency and reducing the reaction time).

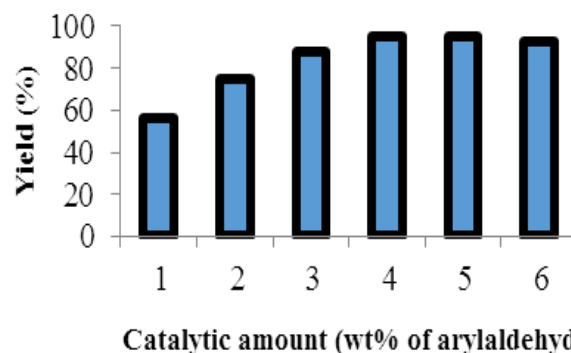
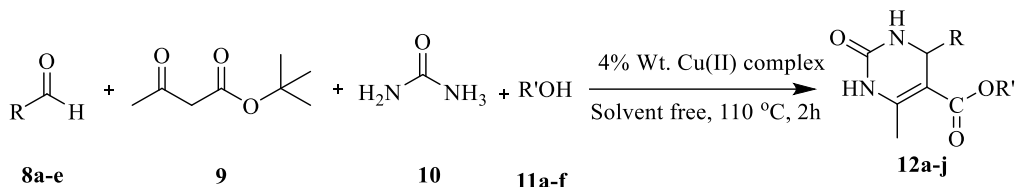


Figure 2. Effect of catalyst amount (%) for the solvent-free synthesis of DHPMs (**8a-e** (1.0 mmol), **9** (1.0 mmol), **10** (1.2 mmol) and **11a-f** (1.5 mmol) at 110 °C).



Scheme 2. Synthesis of various 3,4-dihydropyrimidin-2(1H)-one C5 esters using Cu(II) complex **7a** via Biginelli/Transesterification multicomponent reactions in 1:1:1.2:1.5 ratio

Table 2. Synthesis of some DHPMs in the presence of Cu(II) complex **7a** as catalyst under solvent-free condition at 110 °C and 2 h^a

Entry	Aldehyde/R	Alcohol/R'	Product	Yield (%) ^b	M.p °C/Lit ^c [29]
1			12a	92	169-171 (168-170)
2			12b	89	159-161 (158-160)
3			12c	93	175-177 (174-176)
4			12d	86	180-182 (180-182)
5			12e	83	157-159 (156-158)
6			12f	95	193-195 (194-196)
7			12g	92	168-170 (168-170)
8			12h	94	153-155 (152-154)
9			12i	91	201-203 (200-202)
10			12j	87	177-179 (178-180)

^aReaction conditions: **8a-e** (1.0 mmol), **9** (1.0 mmol), **10** (1.2 mmol) and **11a-f** (1.5 mmol) at 110 °C. ^bIsolated yield. ^cThe products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by the procedure given in the references.

The stability of two Cu(II) complexes **7a,b** in solution was also assessed. This is quite simple as UV-Vis spectroscopy will allow to monitor this over a long period. The UV-Vis spectroscopy of Cu(II) complexes **7a,b** in MeOH solution (10^{-5} M) was recorded and added to Supporting Material as Figure S2. The λ_{abs} 435 nm was observed for Cu(II) complexes in pure solution, catalytic solutions, and after recovery which confirmed the stability

of complexes **7a,b** in solution (10^{-5} M).

Comparing the efficiency of the present method with the previous methods²⁸⁻³² confirmed that the presented method has numerous advantages, which include operational simplicity, short reaction time and acceptable yields, does not need any chromatographic separation and broad spectrum of substrate extent are the input features of this protocol. For example, Cu-Schiff base complex

over SBA-15 found to be efficient catalyst for the synthesis of DHMPs [32]. In the same model reaction, yield of the **12f** found to be 87% (10 mg of catalyst) compared to the yield of the **12f** in presented method (95%).

3. EXPERIMENTAL

Equipment and materials

Percentage of the Cu(II) was measured by a 2-2000 Hitachi atomic absorption spectrophotometer model. Thermo Finnigan Flash EA microanalyzer was used to Elemental analysis. The mass spectrum was obtained by a Varian Mat, CH-7 at 70 eV and the mass spectrum of ESI was measured by a ZQ Waters Micromass spectrometer. The FT-IR spectra were also recorded on KBr pellets by a Tensor 27 spectrometer and only remarkable transmission were reported. The ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were obtained using a Bruker Avance DRX-300 spectrometer. Chemical shifts were listed in ppm downfield from TMS as internal standard; coupling constants were given as *J* value in Hz. The melting points of compounds were determined using an Electrothermal type-9100 melting-point device. All solvents in this work were dried in accordance with the standard procedures. Compounds **2a,b**²³, **4a,b**²⁴ and **5a,b**²⁵ were synthesized according to the published methods and other compounds were commercially available.

Computational methods

The density functional theory (DFT) calculations were carried out by Gaussian 03 software package.³³ The B3LYP hybrid functional³⁴ and the 6-31+G(d,p) basis set were used, except for the Cu atom, where the LANL2DZ basis set³⁵ was computed. The complex was fully optimized which has no imaginary frequency in the frequency calculation. Sum of the electronic energies and the zero-point corrections (E+ZPE) were considered in calculation of the electronic energies, which were obtained from the frequency calculations. The Polarizable-Continuum Model (PCM)³⁶ was employed to consider the solvent effects.

General procedure for the synthesis of ligands **6a,b**

Hydrazine hydrate (0.8 g, 16 mmol) was added dropwise over 15 min to a stirring solution of compounds **5a,b** (10 mmol) in EtOH (100 mL). The resulting mixture was refluxed and after 2 h poured into water. Then the mixture was filtrated. After washing the precipitate with water, and air-drying, compound **6a,b** was obtained. The product was purified by crystallization in ethanol to provide yellow needle crystals of **6a,b**. 4-((4-Chlorophenyl)(hydrazono)methyl)-1-methyl-1H-benzo[d]imidazol-5-amine (**6a**, L1) mp.: 209-211 °C; Yield: 79%, IR (ν, cm⁻¹): 3349, 3283 (NH₂). ¹H NMR (DMSO-*d*₆, δ, ppm): 4.17 (s, 3H, NCH₃), 6.39 (br s, 2H, NH₂), 6.83 (d, *J* = 8.9 Hz, 1H, Ar H), 7.38 (d, *J* = 8.9 Hz, 1H, Ar H), 7.81 (br s, 2H, NNH₂), 7.85 (d, *J* = 8.1 Hz, 2H, Ar H), 8.10 (s, 1H, Ar H), 8.59 (d, *J* = 8.1 Hz, 2H, Ar H); ¹³C NMR (DMSO-*d*₆, δ, ppm): 38.1, 111.2, 116.4, 117.2, 123.0, 123.7, 127.6, 129.1, 130.7, 134.5, 136.1, 142.7, 158.3. MS (m/z) 299 (M⁺). Anal. Calcd. For C₁₅H₁₄ClN₅ (299.8%): C, 60.10; H, 4.71; N, 23.36. Found (%): C, 59.89; H, 4.68; N, 23.49.

4-((4-Chlorophenyl)(hydrazono)methyl)-1-ethyl-1H-benzo[d]imidazol-5-amine (**6b**, L2) mp.: 195-197 °C; Yield: 74%, IR (ν, cm⁻¹): 3355, 3288 (NH₂). ¹H NMR (DMSO-*d*₆, δ, ppm): 1.38 (t, *J* = 7.5 Hz, 3H, CH₃), 4.34 (q, *J* = 7.5 Hz, 2H, NCH₂), 6.21 (br s, 2H, NH₂), 6.81 (d, *J* = 8.9 Hz, 1H, Ar H), 7.35 (d, *J* = 8.9 Hz, 1H, Ar H), 7.74 (br s, 2H, NNH₂), 7.89 (d, *J* = 8.1 Hz, 2H, Ar H), 8.09 (s, 1H, Ar H), 8.62 (d, *J* = 8.1 Hz, 2H, Ar H); ¹³C NMR (DMSO-*d*₆, δ, ppm): 17.2, 44.5, 111.3, 116.2, 116.9, 122.8, 123.8, 127.2, 129.3, 130.3, 134.7, 136.5, 142.7, 159.2. MS (m/z) 313 (M⁺). Anal. Calcd. for C₁₆H₁₆ClN₅ (313.8%): C, 61.24; H, 5.14; N, 22.32. Found (%): C, 60.91; H, 5.11; N, 22.47.

General procedure for the synthesis of the complexes **7a,b**

Copper(II) sulfate pentahydrate (0.5 g, 1 mmol) was added to the **6a,b** ligand solutions (2 mmol) in aqueous methanolic solution (MeOH: H₂O, 10:90, 20 mL). The reaction continued for another 4 hs at rt. When the solution was concentrated at reduced pressure, the precipitate was filtered, washed with water, cold EtOH, and then air-dried to give new complexes **7a,b**. More purification was obtained when precipitates were crystallized in EtOH. [Cu(L1)₂(H₂O)₂](SO₄) (**7a**): m.p. > 300 °C (decomp). IR (ν, cm⁻¹): 3491 (OH), 3371, 3259 (NH₂). ESI-MS (+) m/z (%): 663 [Cu(L1)₂]²⁺. Anal. Calcd. for C₃₀H₃₂Cl₂CuN₁₀O₆S (795.2%): C, 45.31; H, 4.06; N, 17.62; Cu, 7.99. Found (%): C, 45.08; H, 4.04; N, 17.86; Cu, 8.09.

[Cu(L2)₂(H₂O)₂](SO₄) (**7b**): mp > 300 °C (decomp). IR (ν, cm⁻¹): 3487 (OH), 3373, 3259 (NH₂). ESI-MS (+) m/z (%): 691 [Cu(L1)₂]²⁺. Anal. Calcd. for C₃₂H₃₆Cl₂CuN₁₀O₆S (823.2%): C, 46.69; H, 4.41; N, 17.01; Cu, 7.72. Found (%): C, 46.42; H, 4.38; N, 17.31; Cu, 7.79.

Catalytic activity: synthesis of 3,4-dihydropyrimidin-2(1H)-one C5 ester derivatives via biginelli reaction via transesterification reaction

A mixture of tert-butyl acetoacetate **9** (1.0 mmol) and alcohol **11a-f** (1.5 mmol) were stirred for 30 min at 110 °C. The arylaldehyde **8a-e** (1.0 mmol), urea **10** (1.2 mmol) and catalytic amount (4.0 wt% of arylaldehyde) of Cu(II) complexes **7a,b** were added to the above mixture at room temperature. The precursors were mixed together and allowed to mechanical stirring for 2 h at 110 °C (oil bath) till the reaction was completed. After completion of the reaction, as indicated by TLC, it was cooled to room temperature and then ethyl acetate (50 ml) was added to the reaction mixture. The catalyst was collected by filtration and product was dried. The solution was evaporated until pure product was obtained. More purification was achieved by crystallization from EtOH and H₂O to afford 3,4-dihydropyrimidin-2(1H)-one C5 ester derivatives in high yield 83-95%. The structure of the products was characterized by physical and spectroscopic data.

2-(Dimethylamino)ethyl-6-methyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12a**). mp.: 169-171 °C [Lit mp. 168-170 °C]²². ¹H NMR (300 MHz, CDCl₃): δ 2.20 (s, 6H), 2.31 (s, 3H), 2.32 (s, 3H), 2.42-2.44 (t, *J* = 5.8 Hz, 2H), 4.12-4.13 (t, *J* = 5.8 Hz, 2H), 5.37 (s, 1H), 5.61 (s, 1H), 7.11-7.14 (d, *J* = 7.8 Hz, 2H), 7.20-7.22 (d, *J* = 7.8 Hz, 2H), 7.84 (s, 1H).

Prop-2-yn-1-yl-6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12d**). mp.: 182-184 °C [Lit mp. 180-182 °C]²². ¹H NMR (300 MHz, CDCl₃): δ 2.24 (s, 3H),

3.41-3.43 (t, 1H), 4.66 (s, 2H), 5.31-5.33 (d, 1H), 7.47-7.49 (d, $J = 8.8$ Hz, 2H), 7.89 (s, 1H), 8.21-8.23 (d, $J = 8.7$ Hz, 2H), 9.51 (s, 1H).

Isopentyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12g**). mp.: 168-170 °C [Lit mp. 168-170 °C]²². ¹H NMR (300MHz, CDCl₃): δ 0.73-0.79 (d, 6H), 1.30-1.34 (m, 2H), 1.37-1.42 (m, 1H), 2.17 (s, 3H), 3.75 (s, 3H), 3.90-4.00 (m, 2H), 5.05-5.06 (d, 1H), 6.87-6.89 (d, $J = 8.0$ Hz, 2H), 7.10-7.12 (d, $J = 8.0$ Hz, 2H), 7.58 (s, 1H), 9.09 (s, 1H).

4-Methoxybenzyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**12j**). mp.: 177-179 °C [Lit mp. 178-180 °C]²². ¹H NMR (300 MHz, CDCl₃): δ 2.19 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 4.96-4.97 (d, 2H), 5.11-5.13 (d, 1H), 6.78-6.82 (m, 4H), 7.11-7.17 (m, 4H), 7.62 (s, 1H), 9.06 (s, 1H).

4. CONCLUSIONS

Two new Cu(II) complexes were obtained from coordination of Cu(II) cation with 5-amino-1-*R*-1*H*-benzimidazol-4-yl(4-chloro)phenylmethanone hydrazones ligands in aqueous methanolic solution in high yields. The stoichiometry of Cu(II) complexes was obtained by Job's method as ML₂. Based on the results of the mass spectroscopy and elemental analysis data, formula [Cu(L)₂(H₂O)₂](SO₄) was suggested for Cu(II) complexes.

The optimized geometries and structural parameters of Cu(II) complexes were also studied by DFT calculations at the B3LYP/6-311+G(d,p) level of theory. In the structure of the complexes, the L species coordinates to Cu²⁺ ion through the nitrogen atoms of the amine and imine groups as a bidentate ligand. Catalytic activity of the Cu(II) complexes was also investigated on the synthesis of 3,4-dihydropyrimidin-2(1*H*)-one C5 ester derivatives under thermal and solvent-free methods. According to the findings, the remarkable advantages of this protocol are the straightforward operation, mild reaction conditions, no toxic solvents, and ease of the work-up procedure. The stability of Cu(II) complexes in solution was also confirmed by UV-Vis spectroscopy method. Moreover, investigation of the catalytic activity of the complexes as heterogeneous catalysts in other organic reactions is in progress and can be published elsewhere.

CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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