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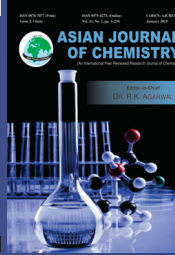
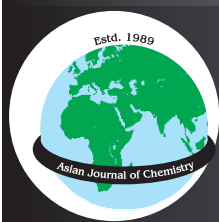
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Synthesis, Characterization and Antimicrobial Screening of Novel Hydrazone Ligand & Its Transition Metal Complexes

S.P. BHALE¹, A.R. YADAV¹, S.U. TEKALE¹, R.B. NAWALE², R.P. MARATHE², P.S. KENDREKAR³ and R.P. PAWAR^{1,*}

¹Department of Chemistry, Deogiri College, Aurangabad-431005, India

²Department of Chemistry, Government College of Pharmacy, Aurangabad-431005, India

³Department of Health Sciences, Central University of Technology, Bloemfontein 9033, Free State, South Africa

*Corresponding author: E-mail: rppawar@yahoo.com

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Different transition metal complexes were synthesized from novel 3-bromo-2-[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)ethylidene]hydrazide ligand (H₂L) and characterized by spectral techniques. The synthesized ligand was found to act mono as well as di deprotonated (OH, NH) manner and stoichiometry of the ligand to metal ions was confirmed to be 1:1 in case of complex using metal chloride salts, whereas 1:2 in case of metal(II) complexes using metal acetate(II) salt. Structures of metal complexes were confirmed by IR, ¹H NMR, TGA, XRD, elemental analysis and UV technique which revealed that Mn(II), Co(II), Ni(II), Cu(II) complexes were octahedral geometry and those of Cu(II), Zn(II) showed square planer and tetrahedral geometry around metal ion respectively. Furthermore H₂L and its metal complexes were screened for antimicrobial activity which showed that ligand enhanced its biological activity after coordination with metal ions. In particular, Cd(II) and Mn(II) complexes exhibited excellent antifungal activity.

Keywords: ONO donor ligand, Transition metal complexes, Antimicrobial.

INTRODUCTION

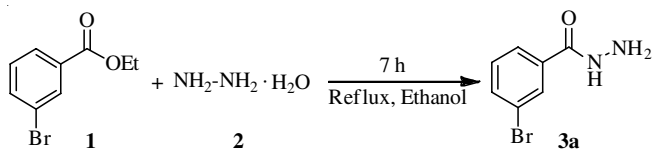
Coordination chemistry of substituted hydrazone ligands is well known since past few decades due to their structural flexibility, chelating abilities, diverse bonding modes towards transition metal ions and numerous biological applications [1-4]. The presence of azomethine group in Schiff's bases is known for antifungal [5], antibacterial [6], antitubercular [7], antitumor [8] and anticancer [9] properties. Oxygen containing heterocyclic compound like dehydroacetic acid (DHA) is well known chelating agent with excellent insecticidal and herbicidal activities [10,11]. The copper complex of hydrazone based ligand prepared by the condensation of dehydroacetic acid with 1,2-diaminopropane displays electro catalytic behaviour towards electro reduction of aryl and alkyl halides [12]. Transition metal complexes of hydrazone are reported for excellent catalytic activities in different chemical reactions such as polymerization of ethylene [13], epoxidation of olefins [14,15] and transamination of carboxamides with amines [16].

In continuation of our present work in the synthesis and biological evaluation of metal complexes [17-19]; in the present article we report synthesis of dehydroacetic acid (DHA) based tridentate 3-bromo-2-[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3yl)ethylidene]hydrazide (H₂L) ligand and its transition metal complexes. H₂L was synthesized by the condensation of dehydroacetic acid (DHA) and 3-bromobenzhydrazide. Synthesized ligand was characterized by different spectroscopic techniques. The synthesized ligand and its complexes were furthermore screened for antimicrobial activity.

EXPERIMENTAL

All the purchased chemicals were analytical grade and used without further purification. Solvents were purified and dried according to literature method [20]. Dehydroacetic acid (DHA) and ethyl-3-bromo benzoate were Alfa Aesar and Spectrochem made respectively. Metal salts were SD Fine made & used without further purification.

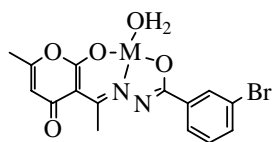
Synthesis of 3-bromobenzhydrazide (3a): A mixture of ethyl-3-bromobenzoate (**1**) (2 mmol) and hydrazine hydrate (**2**) (80 %) (3 mmol) was refluxed for 7 h. The progress of reaction was monitored by TLC using 20 % EtOAc:*n*-hexane. After completion of reaction; the reaction mixture was cooled, the precipitated solid was filtered off, recrystallized from ethanol and confirmed by ¹H NMR as the pure hydrazone (**3a**) (**Scheme-I**). Yield = 80 %, Colour-White, solid, m.p. 158 °C; ¹H NMR (200 MHz, DMSO-*d*₆) ppm 4.54 (br., s., 2 H, NH₂), 7.37 - 7.47 (dd, *J* = 8.5, 8 Hz, 1H), 7.67 - 7.86 (m, 2 H), 7.98 (dd, *J* = 1.83, 1.71 Hz, 1H), 9.89 (br., s., 1 H, NH).



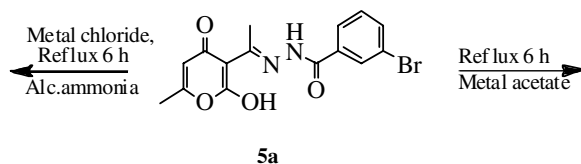
Scheme-I: Synthesis of 3-bromobenzhydrazide

Synthesis of 3-bromo-2-[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)ethylidene]-hydrazide (H₂L) (5a): 3-Bromobenzhydrazide (**3a**) (1 g; 0.004 mol) was added to a solution of dehydroacetic acid (DHA) (**4**) (0.785 g; 0.004 mol) in ethanol (15 mL) and the mixture was refluxed for 1.5 h. The pale yellow precipitate obtained was filtered off; washed with ethanol and recrystallized from ethanol as the pure ligand H₂L. Yield-85 %, Colour-White, m.p. 278 °C (**Scheme-II**).

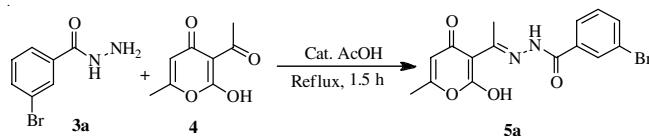
Spectral data of ligand (H₂L): IR (KBr, ν_{\max} , cm⁻¹): 3134.33 (NH), 1662.64 (pyranone C=O), 1600 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ ppm 2.13 (s, 3H, CH₃), 2.63 (s, 3H, N=C-CH₃), 5.89 (s, 1H, ring proton), 7.50-7.54 (dd, *J* =



6e, f.
M= Cu (II), Zn (II).



Scheme-III: Synthesis of metal complexes (**6a-g**)



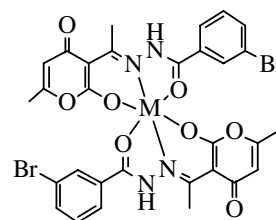
Scheme-II: Synthesis of ligand (H₂L)

10,7.5 Hz, 1H, Ar-H), 7.86-7.92 (m, 2H, Ar-H), 8.08-8.09 (dd, *J* = 1.8, 1.5 Hz, 1H, Ar-H), 11.73 (br., s, 1H, CONH), 16.00 (br., s, 1H, enolic OH of DHA); ¹³C NMR (500 MHz, DMSO-*d*₆): δ ppm-17.07 (s, azomethine- CH₃), 19.30 (s, DHA-CH₃), 94.93 (quat, DHA), 105.91 (s, DHA), 121.80 (quat, Ar), 127.08 (s, Ar), 130.45 (s, Ar), 133.68 (quat, Ar), 135.21 (s, Ar) 162.32 (quat, azomethine), 163.34 (quat, C=O), 171.28 (quat, DHA), 182.00 (quat, 2C, DHA enolic); LC-MS: *m/z* (%) 365.0 (M+H), 367 (M+2).

General procedure for the synthesis of metal complexes (6a-g): Methanolic solution of corresponding metal salt (chloride or acetate) was added to the methanolic solution of ligand (H₂L). A slightly basic pH of the mixture for 1:1 ratio of metal to ligand was maintained by adding alcoholic ammonia and the contents were refluxed for 6 h. The reaction was confirmed to be complete after the disappearance of starting materials on TLC. The products were filtered off, washed with hot methanol thrice (**Scheme-III**). The physical and analytical data of synthe-sized compounds is mentioned in Table-1.

RESULTS AND DISCUSSION

Infrared spectra: The band at 3514 cm⁻¹ in infrared spectrum of free ligand for -OH stretching of pyranone ring



6a, b, c, d, g.
M= Mn (II), Co (II), Ni (II), Cu (II), Cd (II).

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE SYNTHESIZED COMPOUNDS

Compd. No.	Compound	m.f. (F.W.)	m.p. (°C)	Colour	Elemental analysis (%): Found (Calcd.)			
					C	H	N	M
5a	Ligand (H ₂ L)	C ₁₅ H ₁₃ N ₂ O ₄ Br (364.00)	278	White	49.20 (49.33)	3.63 (3.59)	7.77 (7.67)	-
6a	[Mn(HL) ₂]	C ₃₀ H ₂₄ N ₄ O ₈ Br ₂ Mn (780.93)	> 300	Light yellow	46.12 (46.00)	3.04 (3.09)	7.26 (7.15)	7.08 (7.01)
6b	[Co(HL) ₂]	C ₃₀ H ₂₄ N ₄ O ₈ Br ₂ Co (385.00)	> 300	Brown	45.84 (45.77)	3.30 (3.07)	7.03 (7.12)	7.36 (7.49)
6c	[Ni (HL) ₂]	C ₃₀ H ₂₄ N ₄ O ₈ Br ₂ Ni (384.00)	> 300	Orange	45.84 (45.78)	3.13 (3.07)	7.26 (7.12)	7.35 (7.46)
6d	[Cu(HL) ₂]	C ₃₀ H ₂₄ N ₄ O ₈ Br ₂ Cu (788.92)	> 300	Greenish	45.46 (45.50)	3.23 (3.05)	7.15 (7.08)	8.01 (8.02)
6e	[Cu(L)(H ₂ O)]	C ₁₅ H ₁₃ N ₂ O ₅ BrCu (442.93)	> 300	Blue	40.62 (40.51)	2.77 (2.95)	6.28 (6.30)	14.35 (14.29)
6f	[Zn(L)(H ₂ O)]	C ₁₅ H ₁₃ N ₂ O ₅ BrZn (443.92)	> 300	Yellow	40.53 (40.34)	2.82 (2.93)	6.36 (6.27)	14.60 (14.64)
6g	[Cd(HL) ₂]	C ₃₀ H ₂₄ N ₄ O ₈ Br ₂ Cd (839.89)	> 300	Cream yellow	42.95 (42.86)	2.79 (2.88)	6.78 (6.66)	13.25 (13.37)

disappearing in all metal complexes clearly indicates the participation of pyranone oxygen in coordination with the metal ions by deprotonation [21]. The strong band for azomethine group at 1595 cm^{-1} in ligand was shifted to lower side in the IR spectrum of all metal complexes, indicating the coordination of azomethine nitrogen to metal ion. In free ligand band at 1662 cm^{-1} arises due to C=O stretch of pyranone ring in all metal complexes which indicates its non-participation in coordination. Spectral data suggests that the ligand has coordinated through azomethine nitrogen, amide carbonyl oxygen and oxygen of pyranone ring by deprotonation in all metal complexes, but in 2:1 ratio of ligand to metal the amide C=O coordinated without deprotonation.

The band for O-H stretch at 3514 cm^{-1} in free ligand disappears in $[\text{Zn}(\text{L})(\text{H}_2\text{O})]$. An additional band appearing at 3522 cm^{-1} is due to coordination of water molecule to metal ion. Azomethine nitrogen band at 1595 cm^{-1} was shifted to lower region at 1573 cm^{-1} indicating the coordination of azomethine nitrogen to metal ion. The absence of band at 3134 cm^{-1} for amide N-H stretch in complex indicates the coordination of amide oxygen through enolate by deprotonation. Thus, from IR data the ligand acts as monobasic for $[\text{Mn}(\text{HL})_2]$, $[\text{Co}(\text{HL})_2]$, $[\text{Cu}(\text{HL})_2]$, $[\text{Ni}(\text{HL})_2]$ complexes and dibasic for $[\text{Zn}(\text{L})(\text{H}_2\text{O})]$, $[\text{Cu}(\text{L})(\text{H}_2\text{O})]$ complexes.

NMR analysis: Two signals observed at 16.00 and 11.73 δ ppm correspond to enolic OH and amide NH respectively in the ^1H NMR spectrum of the free ligand. These signals were disappeared in ^1H NMR spectrum of $[\text{Zn}(\text{L})(\text{H}_2\text{O})]$ complex indicating the coordination of these two sites *via* deprotonation. The aromatic protons in the range of 7.902-8.092 δ ppm resonating as multiplet in ^1H NMR spectrum of non-coordinated ligand have shifted slightly to downfield in the range 8.05-8.16 δ ppm of metal complex. Two CH_3 protons were observed as singlets at 2.136 and 2.632 δ ppm in free ligand have moved to 2.06 and 2.55 δ ppm respectively after formation of the complex [22].

In ^{13}C NMR spectrum of free ligand signals observed at 182.00 and 17.07 ppm corresponds to 2C (quat.) (DHA) and azomethine(s) CH_3 respectively were shifted to 178.86 and 19.19 δ ppm in the spectrum of $[\text{Zn}(\text{L})(\text{H}_2\text{O})]$ complex, indicating the coordination of ligand-OH *via* deprotonation. The azomethine carbon has moved to downfield in the spectrum of complex indicating the participation of azomethine nitrogen in complexation with metal ion. The two aromatic quartets for carbons observed at 121.80 and 133.68 δ ppm in the ligand were shifted to downfield at 121.44 and 132.21 δ ppm, which also confirms the coordination of amide NH *via* deprotonation.

Thermal analysis: Thermal study of metal complexes gives an idea about the presence or absence of lattice or coordinated held solvent molecules and is useful to confirm their composition and thermal stability. The thermal analysis was performed under nitrogen atmosphere in the temperature range of 25-800 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}$ per min.

The thermogram of $[\text{Zn}(\text{L})(\text{H}_2\text{O})]$ gives two peaks as shown in Fig. 1. At about 260 $^\circ\text{C}$, most of the organic material along with water has been evaporated. Whereas at 450 $^\circ\text{C}$, the metal was converted to its oxide which is not decomposed upon heating upto 600 $^\circ\text{C}$.

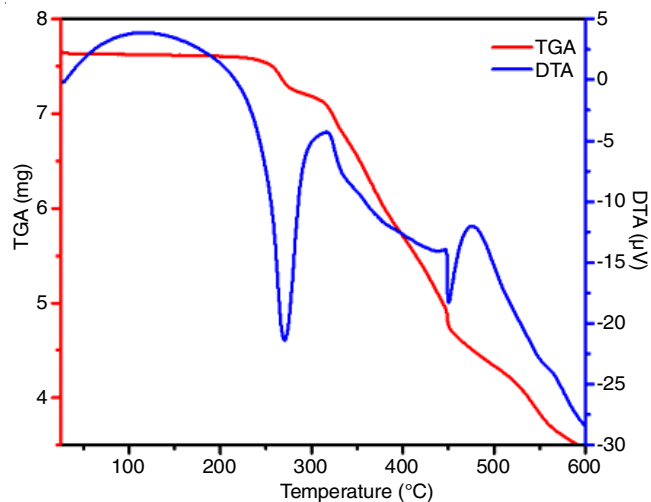


Fig. 1. TGA-DTA analysis of $[\text{Zn}(\text{L})(\text{H}_2\text{O})]$

Electronic spectra: Electronic spectra of the synthesized transition metal complexes were recorded in DMSO solvent at room temperature. The complexes exhibited two bands in the range 349-375 nm which were assigned for charge transfer spectra observed after complex formation [23]. This indicated the coordination of azomethine nitrogen to metal ions and another band in the range of 280-290 nm corresponding to the $\pi \rightarrow \pi^*$ transition (Fig. 2).

Antimicrobial study: Antimicrobial activity of the synthesized compounds was evaluated against one bacterial *Streptococcus aureus* and two fungal species *Aspergillums niger* and *Alternaria alternata* using petri plate method at 250 ppm concentration in DMSO solvent and compared with the standard antibiotics - streptomycin and carbendazim respectively. The petri plate (stains) containing 30 mL nutrient agar and potato dextrose agar (PDA) medium for bacteria and fungi were incubated for 20-24 h and 24-48 h respectively at 37 $^\circ\text{C}$ and the zones of inhibition were measured in terms of mm. The results were compared with the standard antibiotics. The metal complexes showed more inhibitory effects than the non-coordinated ligand against used species under identical condition.

From Table-2, antibacterial activity of ligand and the synthesized metal complexes was found to be less against *Streptococcus aureus* as compared with the standard drug streptomycin. However Cd(II) and Mn(II) complexes exhibited excellent activity against *Alternaria alternata* than the standard drug carbendazim. The remaining compounds showed lesser activity. On the other hand; Cd (II) complex exhibited excellent activity against *Aspergillums niger* even more than the standard drug carbendazim.

Conclusion

In conclusion, a new 3-bromo-2-[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)ethylidene] hydrazide ligand and its transition metal complexes were synthesized and characterized. Antimicrobial activity of the synthesized compounds revealed that the Cd(II) complex shows excellent activity against fungal species and Mn(II) complex shows moderate to good activity against *A. niger* and *Alternaria alternata*, respectively. However, antibacterial activity of all the screened compounds was found to be less in comparison with the standard.

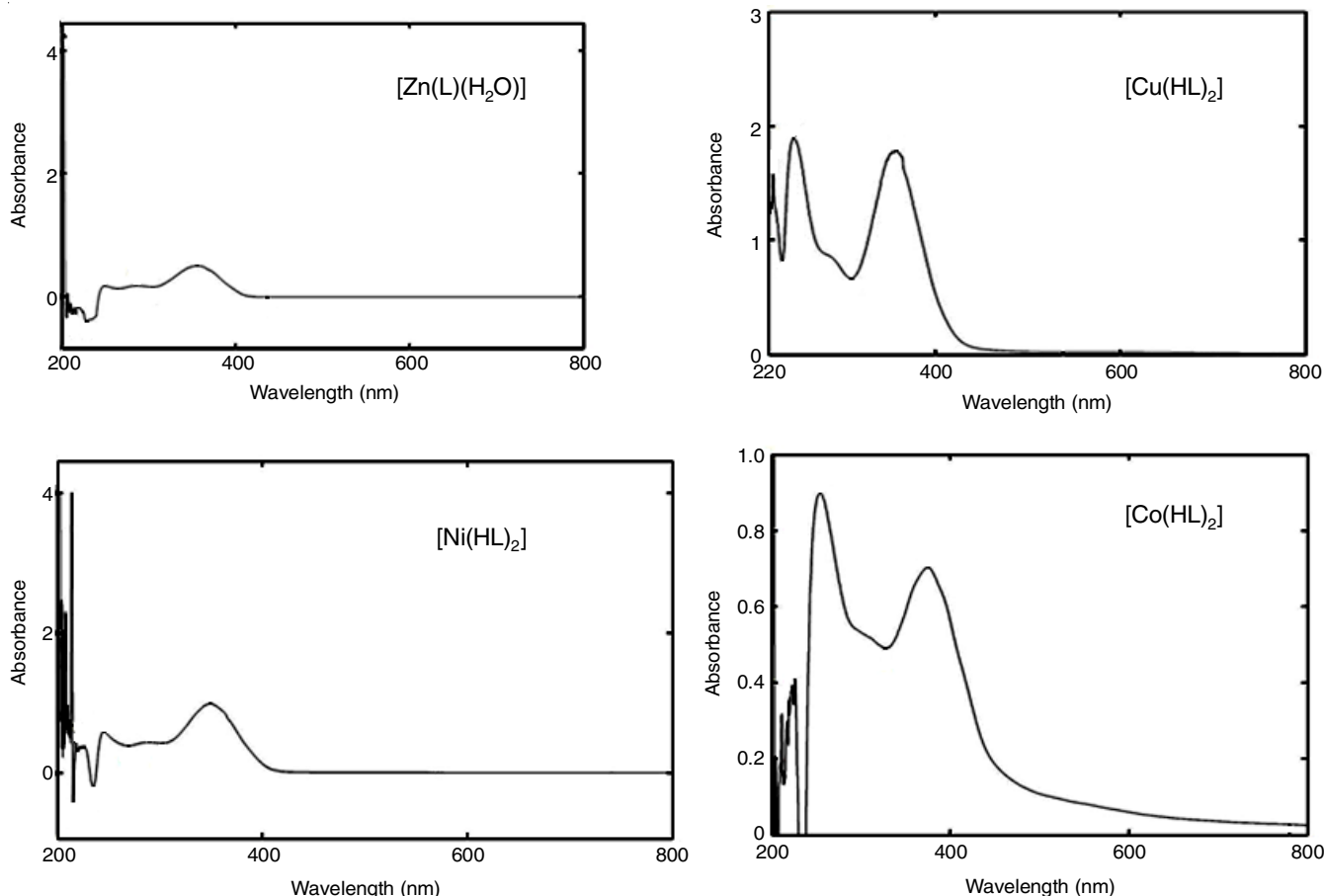


Fig. 2. Electronic spectra of the synthesized metal complexes

TABLE-2
ANTIMICROBIAL ACTIVITY OF THE SYNTHESIZED
LIGANDS AND ITS TRANSITION METAL COMPLEXES

Compd. No.	Compound	Mean zone of inhibition diameter in mm		
		Antifungal screening		Antibacterial screening
		<i>A. niger</i>	<i>A. alternata</i>	<i>S. aureus</i>
5a	Ligand (H ₂ L)	15	5	15
6a	[Mn(HL) ₂]	22	35	15
6b	[Co(HL) ₂]	20	27	17
6c	[Ni(HL) ₂]	15	5	11
6d	[Cu(HL) ₂]	5	20	12
6e	[Cu(L)(H ₂ O)]	20	35	12
6f	[Zn(L)(H ₂ O)]	20	22	20
6g	[Cd(HL) ₂]	30	40	12
	Standard (Carbendazim)	24	26	–
	Standard (Streptomycin)	–	–	40

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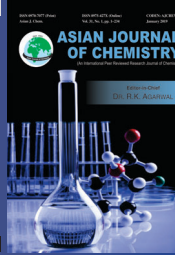
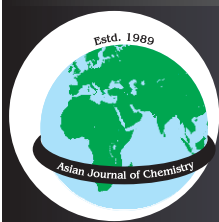
CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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Microwave Assisted One Pot Synthesis of 3,4-Dihydropyrano[c]chromene Derivatives using [Emim]OH Ionic Liquid as Novel Catalyst

D.S. BHAGAT^{1,*}, S.G. PANDE¹, M.V. KATARIYA², R.P. PAWAR² and P.S. KENDREKAR³

¹Department of Forensic Chemistry, Government Institute of Forensic Science, Aurangabad-431001, India

²Department of Chemistry, Deogiri College, Station Road, Aurangabad-431005, India

³Department of Health Sciences, Central University of Technology, Bloemfontein 9300, Free State, South Africa

*Corresponding author: Tel/Fax: +91 240 2400219; E-mail: dsbhagat999@gmail.com

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One-pot efficient protocol to the synthesis of 2-amino-5-oxo-4,5-dihydropyrano(3,2-*c*)chromene-3-carbonitrile derivatives *via* condensation of various aryl aldehydes, dicyanomethane and 4-hydroxycoumarin in presence of Emim hydroxide as an excellent homogeneous liquid catalyst. The key advantages of this methodology are mild reaction conditions, novel catalyst, short reaction time, eco-friendly, easy work-up procedure and high yield of isolation of derivatives.

Keywords: Microwave assisted, [Emim]OH, Homogeneous catalyst, Green approach, 3,4-Dihydropyrano[c]chromene.

INTRODUCTION

The important feature of Green Chemistry is removal of harmful solvents or use of greener solvents such as to replace hazardous solvents with comparatively mild solvents like alcohol, surfactant and ionic liquids in chemical processes. Ethyl alcohol is the naturally benign, clean, economical solvent. Today major universal problem is pollution, so the most interesting challenge in organic synthesis for scientist community is to design easy and eco-friendly methodology such as multi-component reactions (MCRs). The MCRs has been attracting attention of numerous chemists because it is a powerful technique for synthesis of derivatives with biological activity and pharmaceutical properties [1]. To develop clean, easy and eco-friendly method for the synthesis of organic moiety with significant biological activity is the further most important objective in synthetic organic chemistry and is also helpful in research area of green or sustainable chemistry [2].

The natural products are rich source of active ingredients having wide range of medicinal application. The chromene is important heterocyclic compound showing great application in medicinal drug discovery. The chromene is a heterocyclic ring system containing 2*H*-chromen-2-one ring fused to pyran ring. Chromene forms the basic framework which is widely

found in natural products like tocopherols, flavonoids, vitamin E, warfarin, chalcone and luteic acid. Chromene derivatives are structural moiety commonly found in most of the alkaloids with manifesting diverse biological activities [3,4]. The dihydropyrano[c]chromenes derivatives has fascinated attention of an important class of heterocyclic chemistry having useful pharmacological and biological activity such as analgesic [5], anti-HIV [6], anticancer [7], antituberculosis agents [8], anticoagulant [9], antibacterial [10], anti-Alzheimer [11], antimalarial [5], antimicrobials [8], antifungal [12], molluscicidal [13], acetyl cholinesterase inhibitor [14] and anti-inflammatory [15]. The derivatives of dihydropyrano[2,3-*c*]chromene can also be employed as cosmetic pigment and utilized as potential biodegradable agrochemical [16].

The synthesis of various 3,4-dihydropyrano[c]chromene derivatives have been reported using catalysts such as K₂CO₃ [17], tetrabutylammonium bromide (TBAB) [18], *s*-proline [19], nano Al₂O₃ [20], cesium carbonate [21], thiourea dioxide [22], [DBU][Ac] [23], nano-structured ZnO [24], LSMO [25], HEAA [26], SuSa [27], [Bmim]HSO₄ [28], Amberlite A21 [29], Ru(II) [30], Mo132 [31], ammonium acetate [32], DBU [33], piperidine [34], NaBr [35], ([DMAP-PEG1000-DIL][BF₄]) [36] and ionic liquid [37].

EXPERIMENTAL

The solvents, starting material and catalyst were purchased from S.D. Fine Chemicals, Spectrochem and Sigma Aldrich with high purity and used without further purification. All the materials were of commercial grade. Melting points of synthesized derivatives were found out using open capillaries by visual melting point instrument. The FT-IR spectra recorded using KBr on Perkin-Elmer FT-IR spectrometer 65. The ^1H NMR spectras were recorded on Bruker Advance spectrometer a 400 MHz in CDCl_3 as a solvent at 295 K and chemical shift record in δ (ppm) using TMS (tetramethylsilane) as an internal standard. The reactions progresses was monitored by TLC. The experiments under microwave irradiation were carried out in 700 W and 2450 MHz frequency model made by RAGA's Scientific Microwave Synthesis System Pvt. Ltd., Pune, India.

General Procedure for the synthesis of 2-amino-5-oxo-4,5-dihydro-4H-pyrano[3,2-c]chromene-3-carbonitriles (3a-p)

Conventional method: A mixture of aryl aldehyde (1.0 mmol), 4-hydroxycoumarin (1.0 mmol), malononitrile (1.1 mmol) and [Emim]OH (0.5 mL) in 50 mL round bottom flask with 5 mL ethyl alcohol as solvent, was refluxed at 50-60 °C for 40-55 min. The reaction progress was observed using TLC in *n*-hexane:ethyl acetate (70: 30 v/v) solvent system. After completion of reaction, the reaction mixture was poured on ice-cold water, stirred and filtered. The obtained residue was purified by crystallization from aqueous ethyl alcohol (**Scheme-I**).

Non-conventional (microwave assisted) method: The mixture of aryl aldehyde (1.0 mmol), 4-hydroxycoumarin (1.0 mmol), malononitrile (1.1 mmol) and [Emim]OH (0.5 mL). The reaction mixture was refluxed in microwave oven at 700 W for 2-4 min. The reaction progress was observed using thin layer chromatography in *n*-hexane:ethyl acetate (70:30 v/v) solvent system. As soon as reaction is completed the reaction mixture was poured on ice cold water, stirred and filtered. The obtained residue was purified by crystallization from aqueous ethyl alcohol (**Scheme-I**).

Spectral data

2-Amino-4,5-dihydro-4-phenyl-4,5-oxopyrano[3,2-c]-chromene-3-carbonitrile (3a): Light yellow colour, m.p. 256-

258 °C; FT-IR (KBr, ν_{max} , cm^{-1}): 3350, 3250, 2955, 2180, 1690, 1570, 1080. ^1H NMR (CDCl_3 , 400 MHz): δ 4.5 (s, 1H), 7.1-7.4 (m, 5H), 7.6-7.8 (m, 4H), 8.6 (s, 2H). Elemental analysis of $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_3$ calcd. (found) (%):C, 72.15 (72.10); H, 3.82 (3.82); N, 8.86 (8.85).

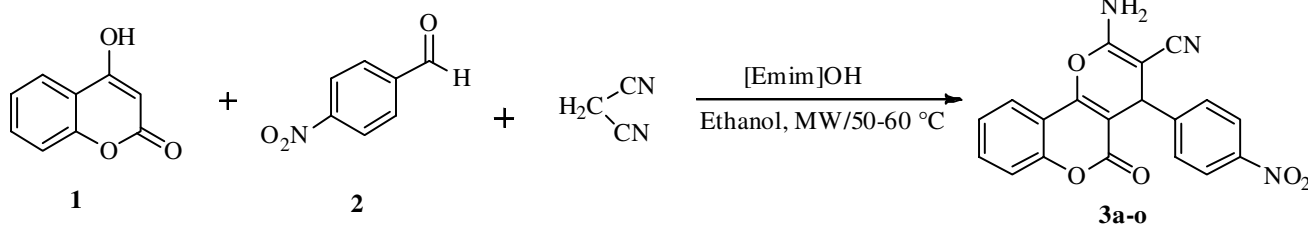
2-Amino-4,5-dihydro-4-(3-nitrophenyl)-5-oxopyrano-[3,2-c]chromene-3-carbonitrile (3c): Yellow colour solid; yield 92 %; melting point 257-258 °C; Recrystallized in ethanol; FT-IR (KBr, ν_{max} , cm^{-1}): 1045, 1088, 1378, 1527, 1664, 1706, 1717, 2199, 2978, 3349, 3367 (broad); ^1H NMR (CDCl_3): δ 5.5 (s, 1H), 7.2 (dd, 1H) 7.4-7.6 (m, 5H), 7.6 (s, 2H), 7.9 (dd, 1H), 8.0 (dd, 1H); MS m/z 384 ($\text{M}^+ + 23$).

2-Amino-4,5-dihydro-4-(4-methoxyphenyl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile (3d): Light yellow color, m.p. 243-244 °C. FT-IR (KBr, ν_{max} , cm^{-1}): 3185, 2960, 2270, 1670, 1510, 1060. ^1H NMR (CDCl_3 , 400 MHz): δ 3.2 (s, 3H), 4.6 (s, 1H), 7.1-7.4 (m, 4H), 7.5-7.8 (m, 4H), 8.2 (s, 2H). Elemental analysis of $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_4$ calcd. (found) (%):C, 69.36 (69.36); H, 4.07 (4.08); N, 8.09 (8.10).

2-Amino-4,5-dihydro-4-(4-bromophenyl)-5-oxopyrano-[3,2-c]chromene-3-carbonitrile (3e): Light yellow colour solid; yield 90 %, m.p. 248-250 °C; recrystallized in ethanol; FT-IR (KBr, ν_{max} , cm^{-1}): 1088, 1374, 1485, 1601, 1673, 1707, 2190, 2973, 3308, 3349 (broad). ^1H NMR (CDCl_3 , 400 MHz): δ 4.6(s, 1H), 7.3 (dd, 1H) 7.4-7.5 (m, 3H), 7.6 (dd, 2H), 7.7 (dd, 1H), 7.9 (dd, 1H), 8.1 (s, 2H); MS m/z 395 ($\text{M}^+ + 1$). Elemental analysis of $\text{C}_{19}\text{H}_{11}\text{N}_2\text{O}_3\text{Br}$ calcd. (found) (%):C, 57.74 (57.75); H, 2.81 (2.80); N, 7.09 (7.10).

2-Amino-4,5-dihydro-4-(4-chlorophenyl)-5-oxopyrano-[3,2-c]chromene-3-carbonitrile (3f): Light yellow color, mp 256-258 °C; FT-IR (KBr, ν_{max} , cm^{-1}): 3120, 3270, 2945, 2250, 1710, 1610, 1060. ^1H NMR (CDCl_3 , 400 MHz): δ 4.6 (s, 1H), 7.2-7.4 (m, 4H), 7.3-7.5 (m, 4H), 8.7 (s, 2H). Elemental analysis of $\text{C}_{19}\text{H}_{11}\text{N}_2\text{O}_3\text{Cl}$ calcd. (found) (%):C, 65.06 (65.10); H, 3.16 (3.20); N, 7.99 (7.90); O, 13.68 (13.70).

2-Amino-4,5-dihydro-4-(4-fluorophenyl)-5-oxopyrano-[3,2-c]chromene-3-carbonitrile (3g): Light yellow colour, m.p. 261-63 °C; FT-IR (KBr, ν_{max} , cm^{-1}): 3150, 3280, 2955, 2250, 1720, 1620, 1070. ^1H NMR (CDCl_3 , 400 MHz): δ 4.7 (s, 1H), 7.3-7.5 (m, 4H), 7.4-7.5 (m, 4H), 8.8 (s, 2H). Elemental



Scheme-I: Synthetic path of 3,4-Dihydro-4-phenyl-4,5-oxopyrano[3,2-c]chromene derivatives

TABLE-1
COMPARISON OF REACTION CONDITION

Entry	Catalyst	Time (min)	Condition	Yield (%)	Ref.
1	Nano Al_2O_3	300	90 °C, Reflux	85	[20]
2	Cesium carbonate	45	Visible light	95	[21]
3	Water, thiourea	40	Reflux, 70 °C	90-95	[22]
4	[DBU][Ac]	6-30	Grading	90	[23]
5	Nano-structured ZnO	150	Reflux	78-91	[24]
6	[Emim]OH	10-20	Reflux, 50 °C	90-96	Present work

TABLE-2
 SCREENING OF CATALYST CONCENTRATION AND SOLVENTS

Entry	Catalyst concentration (mL)	Solvent	Condition	Time (min)	Yield (%)
1		DCM	Reflux	60	Trace
2		Chloroform	Reflux	60	Trace
3		Acetonitrile	Reflux	60	Trace
4		DMF	Reflux	60	Trace
5		Ethanol	Reflux	60	25
6	0.5	–	Reflux	60	60
7	0.5	–	50 °C	60	65
8	0.5	–	60 °C	60	70
9	0.5	–	70 °C	60	72
10	0.5	–	90 °C	60	78
11	0.5	DCM	Reflux	60	45
12	0.5	Chloroform	Reflux	60	60
13	0.5	Acetonitrile	Reflux	60	55
14	0.5	DMF	Reflux	60	40
15	0.5	Ethyl alcohol	Reflux	60	61
16	0.1	Ethyl alcohol	Reflux	60	35
17	0.2	Ethyl alcohol	Reflux	60	50
18	0.3	Ethyl alcohol	Reflux	60	65
19	0.4	Ethyl alcohol	Reflux	60	78
20	0.5	Ethyl alcohol	Reflux	60	81
21	0.5	Ethyl alcohol	Reflux	60	75
22	0.5	Ethyl alcohol	30-40 °C	60	85
23	0.5	Ethyl alcohol	50-60 °C	40	96
24	0.5	Ethyl alcohol	MW	3	95

analysis of $C_{19}H_{11}N_2O_3F$ calcd. (found) (%):C, 68.26 (68.24); H, 3.32 (3.30); N, 8.38 (8.40).

2-Amino-4,5-dihydro-4-(3-chlorophenyl)-5-oxopyrano-[3,2-c]chromene-3-carbonitrile (3h): Light yellow colour, m.p. 245-247 °C; FT-IR (KBr, ν_{max} , cm^{-1}): 3150, 3240, 2951, 2253, 1690, 1580, 1070. 1H NMR ($CDCl_3$, 400 MHz): δ 4.4 (s, 1H), 7.1-7.2 (m, 4H), 7.1-7.3 (m, 4H), 8.5 (s, 2H). Elemental analysis of $C_{19}H_{11}N_2O_3Cl$ calcd. (found) (%):C, 65.06 (65.10); H, 3.20 (3.30); N, 7.99 (7.95).

2-Amino-4,5-dihydro-4-(p-tolyl)-5-oxopyrano[3,2-c]-chromene-3-carbonitrile (3i): Light yellow colour, m.p. 280-282 °C; FT-IR (KBr, ν_{max} , cm^{-1}): 3113, 3230, 2935, 2235, 1680, 1560, 1050. 1H NMR ($CDCl_3$, 400 MHz): δ 4.2 (s, 1H), 6.9-7.1 (m, 4H), 6.4-6.6 (m, 4H), 8.1 (s, 2H). Elemental analysis

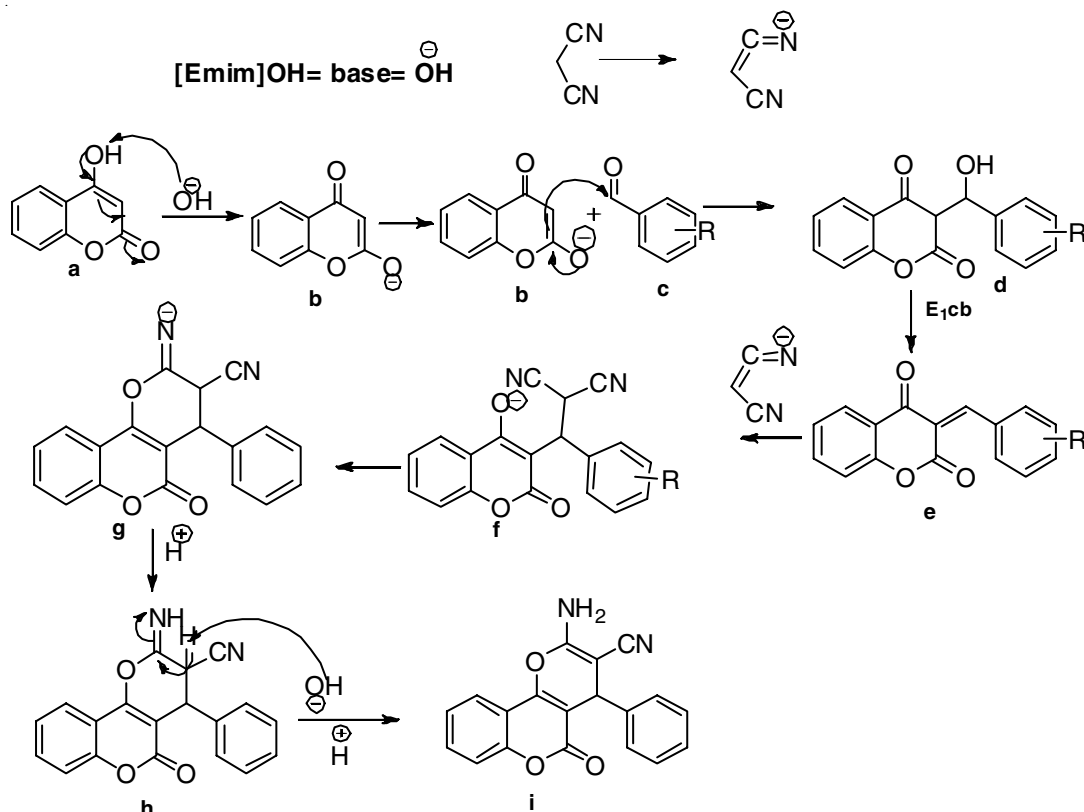
of $C_{20}H_{14}N_2O_3$ calcd. (found) (%):C, 72.72 (72.70); H, 4.27 (4.30); N, 8.48 (8.50).

2-Amino-4,5-dihydro-4-(4-hydroxyphenyl)-5-oxopyrano-[3,2-c]chromene-3-carbonitrile (3j): Light yellow color, mp 263-265 °C. FT-IR (KBr, ν_{max} , cm^{-1}): 3163, 3260, 2965, 2250, 1690, 1540, 1070. 1H NMR ($CDCl_3$, 400 MHz): δ 4.2 (s, 1H), 5.2 (s, 1H), 6.8-6.9 (m, 4H), 6.3-6.5 (m, 4H), 8.2 (s, 2H). Elemental analysis of $C_{20}H_{14}N_2O_4$ calcd. (found) (%):C, 68.67 (68.70); H, 3.64 (3.62); N, 8.43 (8.42).

2-Amino-4,5-dihydro-4-(2,4-dichlorophenyl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile (3k): Light yellow colour, m.p. 260-262 °C. FT-IR (KBr, ν_{max} , cm^{-1}): 3140, 3270, 2965, 2273, 1710, 1590, 1060. 1H NMR ($CDCl_3$, 400 MHz): δ 4.7 (s, 1H), 7.2-7.3 (m, 4H), 7.5-7.6 (m, 3H), 8.5 (s, 2H). Elem-

 TABLE-3
 [Emim]OH CATALYSED SYNTHESIS OF VARIOUS DIHYDROPYRANO[2,3-c]CHROMENE DERIVATIVES

Entry	Aldehyde	Time (min)		Yield (%)		m.p. (°C)	
		Conventional method	Microwave method	Conventional method	Microwave method	Found	Reported
3a	Benzaldehyde	55	3.0	92	90	256-258	255-257 [27,35]
3b	4-Nitrobenzaldehyde	40	3.0	96	95	245-247	257-262 [27,35]
3c	3-Nitrobenzaldehyde	40	2.5	92	92	257-258	260-264 [27,35]
3d	4-Methoxybenzaldehyde	55	3.0	90	88	243-244	241-243 [35,36]
3e	4-Bromobenzaldehyde	50	3.0	91	90	248-250	225-227 [27,36]
3f	4-Chlorobenzaldehyde	40	3.0	89	90	256-258	265-267 [35,36]
3g	4-Fluorobenzaldehyde	40	2.5	93	92	261-63	277-284 [35,36]
3h	3-Chlorobenzaldehyde	45	3.0	92	90	245-247	243-244 [37]
3i	4-Methylbenzaldehyde	50	3.5	90	86	280-282	262-265 [35,36]
3j	4-Hydroxybenzaldehyde	50	4.0	89	88	263-265	262-265 [35,36]
3k	2,4-Dichlorobenzaldehyde	55	3.0	90	89	260-262	258-266 [35]
3l	2-Methylbenzaldehyde	45	4.0	88	89	262-264	262-265 [35]
3m	2-Chlorobenzaldehyde	50	3.0	85	86	263-264	263-264 [37]
3n	Furan-2-carbaldehyde	45	3.0	88	90	223-224	223-224 [27]
3o	4-(Dimethylamino)benzaldehyde	50	4.0	85	88	225-226	225-226 [36]



Scheme-II: Mechanism of 3,4-dihydropyrano[c]chromene derivatives

ental analysis of $C_{19}H_{10}N_2O_3Cl_2$ calcd. (found) (%):C, 59.24 (59.30); H, 2.62 (2.63); N, 7.27 (7.30).

2-Amino-4,5-dihydro-4-(2-methoxyphenyl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile (3l): Light yellow color, mp 280-282 °C. FT-IR (KBr, ν_{max} , cm^{-1}): 3113, 3230, 2935, 2235, 1680, 1560, 1050. 1H NMR ($CDCl_3$, 400 MHz): δ 4.2 (s, 1H), 6.9-7.1 (m, 4H), 6.4-6.6 (m, 4H), 8.1 (s, 2H). Elemental analysis of $C_{20}H_{14}N_2O_4$ calcd. (found) (%):C, 69.36 (69.30); H, 4.07 (4.10); N, 8.09 (8.10).

2-Amino-4,5-dihydro-4-(2-chlorophenyl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile (3m): Light yellow colour, m.p. 263-264 °C. FT-IR (KBr, ν_{max} , cm^{-1}): 3140, 3250, 2951, 2253, 1710, 1570, 1055. 1H NMR ($CDCl_3$, 400 MHz): δ 4.4 (s, 1H), 7.1-7.2 (m, 4H), 7.1-7.3 (m, 4H), 8.5 (s, 2H). Elemental analysis of $C_{19}H_{11}N_2O_3Cl$ calcd. (found) (%):C, 65.06 (69.30); H, 3.16 (3.15); N, 7.99 (7.95).

2-Amino-4,5-dihydro-4-(furan-2-yl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile (3n): Light yellow colour, m.p. 223-224 °C. FT-IR (KBr, ν_{max} , cm^{-1}): 3163, 3260, 2965, 2250, 1690, 1540, 1070. 1H NMR ($CDCl_3$, 400 MHz): δ 4.2 (s, 1H), 6.8-6.9 (m, 4H), 6.3-6.5 (m, 4H), 8.2 (s, 2H). Elemental analysis of $C_{17}H_{10}N_2O_4$ calcd. (found) (%):C, 66.67 (66.70); H, 3.29 (3.25); N, 9.15 (9.25).

2-Amino-4,5-dihydro-4-(4-(dimethylamino)phenyl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile (3o): Light yellow colour, m.p. 225-226 °C. FT-IR (KBr, ν_{max} , cm^{-1}): 3213, 3210, 2915, 2243, 1690, 1550, 1040. 1H NMR ($CDCl_3$, 400 MHz): δ 3.2 (s, 6H), 4.4 (s, 1H), 6.8-6.9 (m, 4H), 6.3-6.5 (m, 4H), 8.2 (s, 2H). Elemental analysis of $C_{21}H_{17}N_3O_3$ calcd. (found) (%):C, 70.18 (70.10); H, 4.77 (4.75); N, 11.69 (11.70); O, 13.36 (13.40).

RESULTS AND DISCUSSION

To set reaction conditions during continuation of present research work to develop new method, for synthesis of 2-amino-5-oxo-4,5-dihydropyrano(3,2-c)chromene-3-carbonitrile derivatives, we followed Multi-component reactions approach.

The reaction conditions were checked under various conditions as illustrated in Tables 1 and 2. The reaction tested in different solvents, such as chloroform, DCM, acetonitrile, DMF and ethyl alcohol gave poor yield in absence of catalyst (entry 1 to 5, Table-2) and we found that in presence of catalyst in solvent-free conditions and 0.5 mL [Emim]OH catalyst after refluxing at various temperature resulted into moderate yield *i.e.* upto 60 to 78 % (entry 6 to 10, Table-2). Further reaction conditions were checked using 0.5 mL of [Emim]OH and different solvents such as DCM, chloroform, acetonitrile, DMF, ethanol and found to give 45, 60, 55, 40, 61 % yield, respectively (entry 11 to 15, Table-2). To confirm catalyst concentration, reactions were performed at various catalyst concentration using ethyl alcohol as solvent from 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M which resulted into 35, 50, 65, 78, 81 % yield, respectively (entry 16 to 20, Table-2).

In order to set temperature condition, temperature was increased from room temperature to 60 °C and with increase in temperature the yield of products was increased from 81 to 96 % (entry 21 to 23, Table-2). All the reactions were monitored by thin layer chromatography. Similarly, to check the efficiency and practicality of proposed protocol, we used different aromatic aldehydes and the results are illustrated in Table-3. The reaction takes place with satisfied yield under microwave conditions in presence of polar solvents ethyl alcohol, DMF, water, aceto-

nitrile and methanol. It was observed that ethanol medium is the best reaction medium among the polar solvents used in demonstration and reaction proceeded very smoothly which gave the desired product with excellent yield within short reaction time (entry 24, Table-2). The aryl aldehydes which possess electron withdrawing substituent gave high yield as compared to aromatic aldehydes bearing electron donating substituent as illustrated in Table-3.

Reaction mechanism: In this reaction, [Emim]OH acts as the base, malononitrile and 4-hydroxycoumarin undergo enolization from a to b. The b on cross aldol condensation with c gave intermediate d. The intermediate d on E₁cB elimination gives intermediate e. The intermediate e with malononitrile on Michael addition gives intermediate f, which on cyclization gives intermediate g and after protonation forms intermediate h. Finally h on rearrangement converted into dihydropyrano[2,3-c]-chromene (**Scheme-II**).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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