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Lactic acid-catalyzed Eco-friendly Cyclization Reaction for the Synthesis of 4*H*-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes in EtOH/H_2O as an Efficient Green Reaction Medium

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Abstract

An environmentally friendly, green, and highly efficient process for the synthesis of biologically and pharmacologically 4H-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes is developed by condensing cyclic aromatic aldehydes, malononitrile, and dimedone or 4-hydroxycoumarin in the presence of lactic acid as an efficient and green catalyst. The corresponding products have been synthesized in 50–97% yield in middle condition reaction which confirmed the excellent catalytic activity of the lactic acid. Furthermore, this methodology shows unique advantages, such as operational simplicity, short reaction time, high yields, low cost, absence of any tedious workup or purification and avoidance of hazardous or toxic reagents/catalysts/solvents.

Keywords: Multi-component reactions (MCRs), 4*H*-benzo[*b*]pyran, 3,4-dihydropyrano[*c*]chromene, Lactic acid, Green chemistry.

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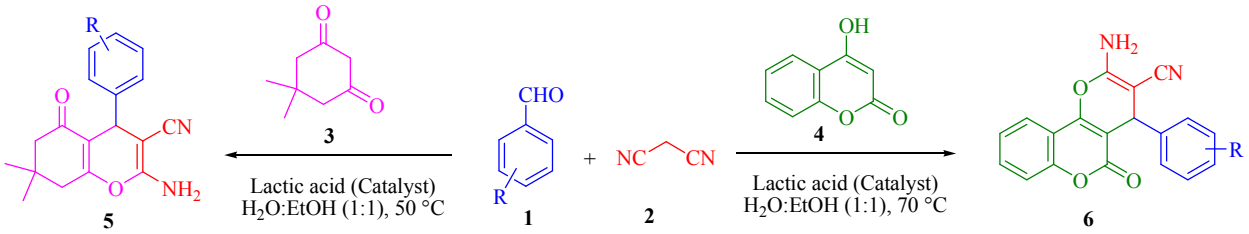
Introduction

Nowadays, interest in green chemistry [1-3] has developed, and a major challenge of organic chemists is the reduction of application of organic solvents and toxic reagents for facile, efficient, and nonpolluting synthetic procedures. In this area, the use of natural materials as a promising catalyst in organic reactions has received a considerable attention due to their green credentials [4, 5], and also the replacement of hazardous solvents with environmentally benign solvents [6-8] is one of the major focus areas of green chemistry. Organic solvents used in most of the synthetic organic chemistry evaporate into the atmosphere with destructive effects on the environment and ozone layer [9]. Thus, aqueous phase organic synthesis has attracted the attention of chemists as it overcomes the harmful effects associated with the organic solvents and is environmentally benign. The water, due to its strong hydrogen bonding ability, hydrophobic effects, and high polarity can be used as the medium and surfactants to build micelles and provide chemical yields and reaction times [10-12]. Also, the proper choice of atom economic methodologies with a minimum number of chemical steps and efficient strategies for product isolation and purification are part of the exploration towards the green chemistry for sustainability. In this context, multi-component reactions (MCRs) have attracted great attention as a very influential and efficient bond-forming strategy in the field of medicinal organic and combinatorial chemistry. High atom-economy, cost-effectively, energy-saving, lower reaction time and raw materials, structural complexity and environmentally benign synthesis of chemically and biologically important organic frameworks are one of the most advantageous features encountered in MCRs [13-15].

Functionalized oxygen-heterocycles are of interest due to their potential medicinal and biological activity. Polyfunctionalized pyran and chromene are oxygen-containing heterocycles that are common structural subunits in a variety of important biological effects such as antimicrobial, antifungal, anticancer, antioxidant, anti-tumor and anti-HIV [16-20].Moreover, the pyran moiety, including that of 2*H*-pyran and 4*H*-pyran which is present in a number of important pharmaceuticals and natural products such as alkaloids, carbohydrates, polyether antibiotics, iridoids and pheromones [21], they could be useful in the treatment of neurodegenerative diseases, including Parkinson's and Alzheimer's disease, Down's syndrome, and AIDS-associated dementia as well as for the treatment of schizophrenia [22]. Additionally, several properties such as optical brighteners, laser dyes, fluorescence markers, cosmetics, and potent biodegradable agrochemicals [23] are well known for decades.

The common methods have been reported for the synthesis of 4H-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes in the presence of catalysts such as MNPs-$PhSO_3H$ [24], Nano-SiO_2 [25], DBU [26], MCM-41-NH_2 [27], starch solution [28], and $NiFe_2O_4$ Nanoparticles [29].

Considering the importance of biologically active pyran and chromene templates, an efficient and environmentally benign approach was developed for the synthesis of 4*H*-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes *via* one-pot three-component condensation of aromatic aldehydes, malononitrile, and dimedone or 4-hydroxycoumarin in the presence of lactic acid as a readily available, non-toxic and highly efficient catalyst in H_2O/EtOH as an inexpensive and non-toxic medium (Scheme 1).



Scheme 1. Lactic acid-catalyzedsynthesis of 4*H*-benzo[*b*]pyrans (**5**) and 3,4dihydropyrano[*c*]chromenes (**6**) in H_2O/EtOH.

Experimental

General

Experimental Melting points were measured on an Electrothermal 9100 apparatus. Infrared (IR) spectra were recorded on a JASCO FT-IR 460 plus spectrometer. 1H nuclear magnetic resonance (NMR) spectra were obtained with a Bruker DRX-400 Advance spectrometer with using deuterated dimethylsulfoxide (DMSO) and acetone as solvents. All reagents and solvents were provided from chemical producer Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland) and used without further purification. Thin-layer chromatography (TLC) was performed on silicagel Polygram SILG/UV 254 plates.

General procedure for the synthesis of 4H-benzo[b]pyran and 3,4-dihydropyrano[c]chromene derivatives

A mixture of aromatic aldehydes **1** (1.0 mmol), malononitrile **2** (1.0 mmol) and dimedone **3** (1.0 mmol) or 4-hydroxycoumarin **4** (1.0 mmol) in the presence of 20 mol % of lactic acid in H_2O/EtOH (1:1, v/v) (10 mL) was stirred in around bottomed flask at 50 or 70 °C in a preheated oil bath for the appropriate time (Table 2 and 5). After completion of the reaction which was monitored by TLC using ethyl acetate-petroleum (1:3) as the eluent. Finally, the precipitate was filtered out, washed with water, and purified by recrystallization from ethanol to give the pure corresponding product **5**/**6**.

Selected spectra for four Known products are given below

2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-chromene-3-carbonitrile ***(4a)***

M.p. 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.07 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 2.26 (dd, 2H, *J*= 22 Hz,*J*= 16.4 Hz), 2.49 (s, 2H, CH_2), 4.44 (s, 1H, CH), 4.55 (s, 2H, NH_2), 7.21-7.34 (m, 5H).

2-amino-5,6,7,8-tetrahydro-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile ***(4b)***

IR (KBr, cm^{-1}): 3395 (NH_2), 3324 (NH_2), 2963 (C-$H_{aliphatic}$), 2192 (CN), 1250 (CO),^{1}H NMR (300 MHz, DMSO-d_6): *δ* 0.98 (s, 3H, CH_3) , 1.06 (s, 3H, CH_3), 2.13 (d, 1H, *J*= 16.2 Hz), 2.29 (d, 1H, *J*= 15.9 Hz), 2.52 (s, 2H, CH_2), 4.39 (s, 1H,CH), 7.21 (s, 2H, NH_2), 7.48 (dd, 2H, Ar, *J*=7.0 Hz, *J*= 1.5 Hz), 8.19 (dd, 2H, Ar, *J*= 7.0 Hz, *J*= 1.8 Hz).

2-amino-5,6,7,8-tetrahydro-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-4H-chromene-3- carbonitrile ***(4c)***

IR (KBr, cm^{-1}): 3380 (NH_2), 3285 (NH_2), 2958 (C-$H_{aliphatic}$), 2188 (CN), 1248 (CO), ^{1}H NMR (300 MHz, DMSO-d_6): *δ* 0.97(s, 3H, CH_3) , 1.05 (s, 3H, CH_3), 2.13 (d, 1H, *J*= 16.0 Hz), 2.27 (d, 1H, *J*= 16.0 Hz), 2.53 (s, 2H, CH_2), 4.24 (s, 1H, CH), 7.10 (s, 2H, NH_2), 7.21 (d, 2H, Ar, *J*= 8.1 Hz), 7.37 (d, 2H, Ar, *J*= 5.4 Hz).

2-amino-5,6,7,8-tetrahydro-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile ***(4i)***

M.p. 202-204 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.10 (d,1H, *J*= 16.0 Hz), 2.25 (d, 1H, *J* = 16.0), 3.37 (d, 2H, *J*= 7.0 Hz), 3.72 (s, 3H, OCH_3), 4.13 (s, 1H, CH), 6.85 (d, 2H, Ar, *J*= 8.7 Hz), 6.98 (br, NH_2), 7.06 (d, 2H, Ar, *J*= 8.4 Hz).

2-amino-5,6,7,8-tetrahydro-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile ***(4f)***

M.p. 268-270 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 3H, CH_3) , 1.12 (s, 3H, CH_3), 2.25 (dd, 2H *J*= 16.0 Hz, *J*= 20.0 Hz), 2.46 (dd, 2H, *J*= 16.0 Hz, *J*= 20.0 Hz) , 4.35 (s, 1H, CH), 4.61(s, 2H, NH_2), 6.05 (s, 1H, OH), 6.67-7.28 (m, 4H, Ar).

2-Amino-4,5-dihydro-4-(4-chlorophenyl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile ***(6b)***

IR(KBr, cm^{-1}): 3369 (NH_2), 3334 (NH_2), 2195 (CN), 1346 (CO),^{1}H NMR (300 MHz, DMSO-d_6): *δ* 4.51 (s, 1H, CH), 7.31-7.93 (m, 10H, Ar, NH_2).

*2-Amino-4,5-dihydro-4-(3-nitrophenyl)-5-oxopyrano[3,2-c]chromene-3-carbonitrile (**6d**)*

M.p. 261-263 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.75 (s, 1H, CH), 7.48-8.16 (m, 9H, Ar, NH_2).

Results and Discussion

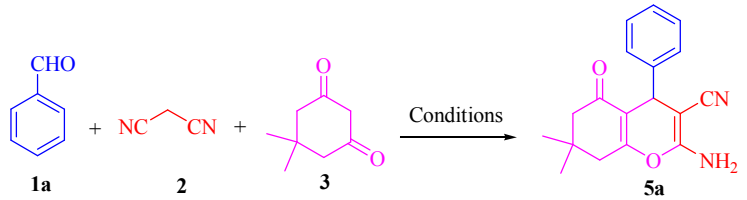
Considering the importance of biologically active pyran and chromene templates, an efficient and environmentally benign approach was developed for the synthesis of 4*H*-benzo[*b*]pyran derivatives (**5a-o**)by one-pot, three-component condensation reaction between aromatic aldehydes, malononitrile, and dimedonethrough condensation-Knoevenagel-Michael-annulation sequences in the absence of any hazardous or toxic catalysts and organic solvents.

In order to investigate the standard operating conditions for the synthesis of 4*H*-benzo[*b*]pyrans, the reaction between benzaldehydes **1a** (1.0 mmol), malononitrile **2** (1.0 mmol) and dimedone **3** (1.0 mmol) was chosen as a model reaction. Initially, the effect of different solvents was investigated on the model reaction using various solvents such as EtOH, H_2O, EtOH/H_2O (1:1), and any other organic solvents weren't investigated because of the green chemistry concept. Higher yields and shorter reaction times were obtained when the reaction was carried out in EtOH/H_2O (1:1), due to its strong hydrogen bonding ability, hydrophobic effects and high polarity (Table 1, entry 2). Then, the use of different amounts of catalysts at different temperatures was investigated. The best result was obtained with 20 mol% of lactic acid at 50 °C (Table 1, entry 14).

To explore the scope of the reaction further, the present study was extended by various aromatic aldehydes under optimized conditions.

All of the products have efficiently synthesized in excellent yields at short reaction times without the formation of any side products and the corresponding results are presented in Table 2. All the reactions were completed in 5-90 minutes and the formation of the target structures was carried out in high yields by lactic acid as an expedient catalyst (20 mol %) in EtOH/H_2O (1:1) as an eco-friendly medium. The reaction benzaldehydes with electron-withdrawing groups reacted rapidly and gave higher yields, while substitutions of electron-rich groups on the benzene ring required longer reaction times and got lower yields.

Table 1. Effect of the catalyst amount, solvent, and temperature on the model reaction.



1a **2** **3** **5a**

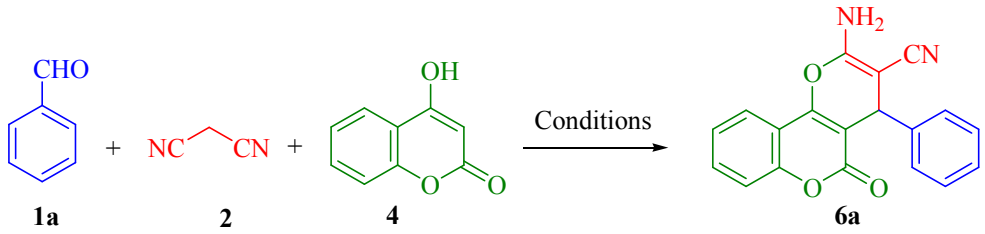
Entry	Solvent	Catalyst (mol %)	Temperature (°C)	Time (min)	Isolated Yield (%)
1	Solvent-free	20	60	60	47
2	H_2O:EtOH (1:1)	20	60	25	85
3	EtOH	20	60	45	69
4	H_2O	20	60	50	83
5	H_2O:EtOH (1:1)	No catalyst	60	60	84
7	H_2O:EtOH (1:1)	10	60	35	74
8	H_2O:EtOH (1:1)	20	60	25	85
9	H_2O:EtOH (1:1)	25	60	25	82
10	H_2O:EtOH (1:1)	30	60	15	86
11	H_2O:EtOH (1:1)	35	60	15	90
12	H_2O:EtOH (1:1)	40	60	25	76
13	H_2O:EtOH (1:1)	20	30	60	70
14	H_2O:EtOH (1:1)	20	50	25	97
15	H_2O:EtOH (1:1)	20	70	20	85
16	H_2O:EtOH (1:1)	20	80	15	84
17	H_2O:EtOH (1:1)	20	90	15	82
18	H_2O:EtOH (1:1)	20	100	10	87
19	H_2O:EtOH (1:1)	20	110	10	79

Table 2. Synthesis of 4*H*-benzo[*b*]pyrans by reaction of aromatic aldehyde, malononitrile and dimedonein the presence of lactic acid (**20%**) in water/ethanol (**1:1**) at **50 °C**.

Entry	R_1	Product	Time (min)	Isolated Yield (%)	M.p (°C)	M.p (°C) [Lit.]Ref.
1	H	**4a**	25	97	228-230	229-231 [18]
2	4-NO_2	**4b**	10	88	174-176	177-178 [19]
3	4-Cl	**4c**	15	79	204-207	207-209 [20]
4	5-Br-2-OH	**4d**	5	56	189-190	190–193 [21]
5	3-NO_2	**4e**	20	82	204-206	209-211 [19]
6	4-OH	**4f**	90	51	264-267	269-270 [22]
7	3-OH	**4g**	70	74	223-225	222-224 [23]
8	2-Cl	**4h**	10	75	211-213	210-212 [28]
9	4-OMe	**4i**	35	79	200-202	201-203[29]
10	2-NO_2	**4j**	5	92	216-219	220-223[30]
11	2,4- di Cl	**4k**	5	97	113-115	115-117[21]
12	4-Me	**4l**	55	45	215-217	214-216 [18]
13	2,4- di OMe-2-OH	**4m**	55	99	168-170	169-171[29]

14	3-OMe	**4n**	15	70	191-193	190-192 [21]
15	4-di-Me(NH_3)$_2$	**4o**	20	91	213-215	211-214[21]

In the next step, in order to prepare 3,4dihydropyrano[*c*]chromene derivatives in a more efficient way, and to minimize the reaction time and the required amount of catalyst, the three-component reaction between benzaldehydes **1a** (1.0 mmol), malononitrile 2 (1.0 mmol) and 4-hydroxycoumarin 4 (1.0 mmol) was selected as a model system (Scheme 2). In order to optimize the reaction conditions, the model reaction was performed at a wide series of conditions. At first, the model reaction was studied using different solvents. The best condition was found in EtOH/H_2O (1:1) (Table 3, entry 2). Then, the amount of catalyst and temperature were also changed. After the broad screening, we found that the best yields and time profiles were obtained with 20 mol % of lactic acid in EtOH/H_2O (1:1) at 70 °C, which the corresponding 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile **6a** was generated in 97% yield within 5 minutes proceed efficiently (Table 4, entry11).



Scheme 2. The model reaction for optimizing conditions for the synthesis of 3,4-dihydropyrano[*c*]chromenes

Table 3. Optimization of solvent in 60 °C.

Entry	Solvent	Time (min)	Isolated Yield (%)
1	Solvent Free	15	72
2	H_2O:EtOH (1:1)	5	83
3	EtOH	45	53
4	H_2O	50	53

Table 4. Effect of the catalyst amount and temperature on the model reaction.

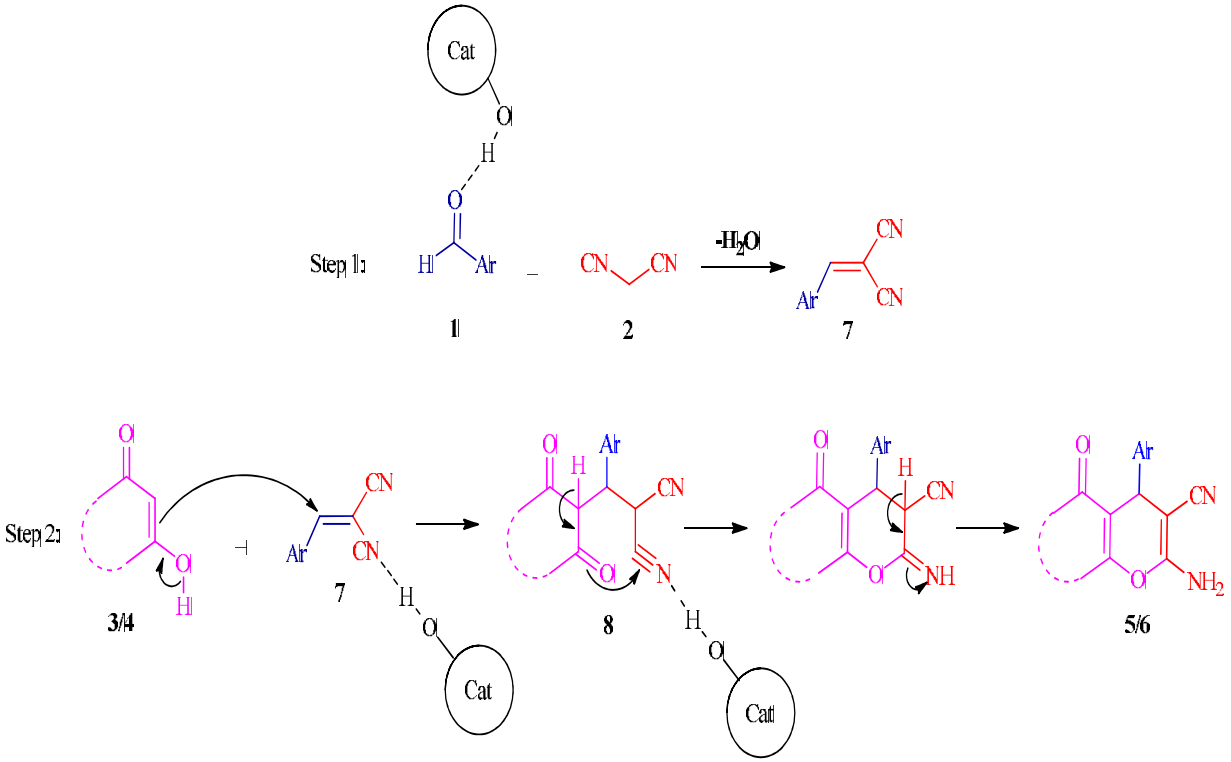
Entry	Catalyst (% mol)	Time (min)	Temperature (°C)	Isolated Yield (%)
1	No catalyst	35	60	Trace
2	10	15	60	54
3	20	5	60	83
4	25	10	60	72
5	30	20	60	69
7	35	15	60	70
8	40	10	60	67
9	20	20	35	51
10	20	5	50	72
11	**20**	**5**	**70**	**97**
12	20	5	80	68
13	20	10	90	61

In order to display the scope and efficiency of this novel protocol, the various aromatic aldehydes were explored for the synthesis of a wide variety of 3,4-dihydropyrano[*c*]chromenes **6a-p**. The results are summarized in Table 5.

Table 5. Synthesis of 3,4-dihydropyrano[*c*]chromene derivatives by reaction of aromatic aldehyde, malononitrile, and 4-hydroxycoumarin in the presence of lactic acid(20 mol %) in water/ethanol (1:1) at 70 °C.

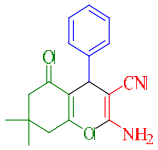
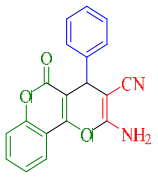
Entry	R_1	Product	Time (min)	Isolated Yield (%)	M.p (°C)	M.p (°C) [Lit.]
1	H	**6a**	5	97	249-252	254-256 [31]
2	4-Cl	**6b**	10	90	259-261	262-264 [31]
3	4-OMe	**6c**	25	73	240-242	242-244 [31]
4	3-NO_2	**6d**	15	89	261-1263	263-265 [32]
5	2-Cl	**6e**	10	69	262-265	266-268 [31]
6	3-Br	**6f**	20	21	275-277	274-276 [32]
7	4-NO_2	**6g**	5	98	253-255	259-261 [31]
8	4-Me	**6h**	5	97	246-248	249-251 [31]
9	2-NO_2	**6j**	10	89	257-259	258-259 [31]
10	3,4,5TriOMe	**6k**	5	66	265-267	269–271 [31]
11	2-OH-3OMe	**6l**	10	29	232-235	231-233 [33]
12	4-OH	**6m**	60	51	257-259	261-263 [31]
13	2,4-diCl	**6n**	5	86	253-255	257-259 [34]
14	4-di-Me(NH_3)	**6o**	15	80	254-256	261–264 [35]
15	2,4-diOMe	**6p**	10	80	229-232	233-237 [34]

Structural assignments of the desired pure products **5a-o** and **6a-p** have been made the basis of their physical data (melting points, IR, and ^{1}H NMR). A detailed reaction mechanism for the synthesis of 4*H*-benzo[*b*]pyran and 3,4-dihydropyrano[*c*]chromene derivatives **5/6** was reported using lactic acid, which act as a solid acid catalyst according to the literature [24,25]. As can see in Scheme 3, in this mechanism, lactic acid is an efficient catalyst to form the olefin **7** (2-benzylidene malononitrile), which readily prepares *in situ* from Knoevenagel condensation of aromatic aldehyde **1** with malononitrile **2**. Finally, the Michael addition of dimedone **3** or 4-hydroxycoumarin **4** with olefin **7** in the presence of lactic acid gives intermediate **8**, which then makes the inner molecular ring to be formed after a tautomeric proton shift to produce the corresponding product **5/6**.



Scheme 3. Proposed mechanism for the synthesis of 4*H*-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes.

Table 6 Comparison of the efficiency of various catalysts with Lactic acid in the studied reactions.

Entry	Product	Catalyst	Amount	Condition	Time (min)	Yield (%)	[Ref.]
1		MNPs–$PhSO_3H$	(0.01 g)	H_2O:EtOH (1:1), 100 °C	10	91	[24]
		Nano-SiO_2	(20 mol%)	H_2O, 70 °C	8	94	[25]
		MCM-41-NH_2	(10 mol%)	H_2O, 70 °C	30	69	[27]
		$NiFe_2O_4$ NPs	(20 mol%)	H_2O:EtOH (1:1), 40 °C	40	91	[29]
		Lactic acid	(20 mol%)	H_2O:EtOH (1:1), 50 °C	25	97	[This work]
2		MNPs–$PhSO_3H$	(0.01 g)	H_2O:EtOH (1:1), 70 °C	10	87	[24]
		Nano-SiO_2	(20 mol%)	H_2O, 70 °C	25	93	[25]
		DBU	(10 mol%)	H_2O, reflux	7	92	[26]
		$NiFe_2O_4$ NPs	(20 mol%)	H_2O:EtOH (1:1), 40 °C	45	88	[29]
		Lactic acid	(20 mol%)	H_2O:EtOH (1:1), 70 °C	5	97	[This work]

The obtained results in the synthesis of 4H-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes were compared to most of what reported in the literature (Table 6). In order to this purpose, the derivatives **6a** and **4a** were selected. The results show that lactic acid has good catalytic activity in the synthesis of 4H-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes.

Conclusion

To conclude, we have introduced a well-organized, eco-friendly, and simple procedure for the efficient synthesis of 4*H*-benzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes in high to excellent yields via a one-pot three-component reaction by using lactic acid as a mild, effective, non-toxic and inexpensive solid acid catalyst in H_2O/EtOH without the addition of organic co-solvent. The promising points for the presented methodology are environmental acceptability, economic viability, easy work-up, short reaction time, high atom economy, and finally compliance with the green chemistry protocols. Meanwhile, our work is expected to show interesting pharmacology activities and may act as potential drug candidates, since pyran and chromene motifs have a vast range of biological activities.

Acknowledgements

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