ACTA CHEMICA IASI, **34_2**, 337-350 (2026)
DOI: 10.47743/achi-2026-2-0014

Article

NANOCATALYZED SYNTHESIS OF SOME BIGINELLI SCAFFOLDS

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Abstract: This research article describes the green and easy synthesis of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) and –thiones using an efficient multi-doped-Bi/Cr-ZnO-(g-C_3N_4) (multi-doping bismuth/Chromium zinc oxide graphitic carbon nitride) composite nanocatalyst via Biginelli reaction. The series of multi-subtituted DHPM derivatives were synthesised from aldehyde, ethyl acetoacetate and urea/thiourea under microwave irradiation (MWI) and conventional heating conditions. All of the synthesised compounds were characterised using spectroscopic techniques and melting points. The nanocatalyst showed greater efficiency under MWI than conventional conditions with shorter reaction times and excellent yields.

***Keywords*:** Nanocomposite; Green method; MWI; Biginelli reaction.

Introduction

Dihydropyrimidinones (DHPMs) were first prepared by Pietro Biginelli in 1893 through a one-pot, acid-catalyzed cyclocondensation of an

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aldehyde, a β-keto ester, and urea (or thiourea).[1] Over the past decade, nanomaterials have gained significant attention from researchers due to their unique nanoscale properties, including shape, size, surface characteristics, and internal structure. Various forms of nanocatalysts have been explored for the Biginelli reaction, such as nanoparticles (NPs), nanotubes (NTs), nanofibers, nanocages, nanowires, nanosheets, and nanopores.[2] According to the available literature, nanoscale catalysts–whether organic, inorganic, hybrid, or their nanocomposites–have been effectively utilized in multicomponent Biginelli synthesis.[3] Among these, magnetic nanoparticles (MNPs) have emerged as particularly advantageous due to their ease of magnetic recovery, simplifying the catalytic process.[4] Nanocatalysts have proven effective in the synthesis of substituted 3,4-dihydropyrimidin-2(1H)-ones (or thiones) (DHPMs).[5] A variety of polymer-based catalysts have been reported to enhance the Biginelli reaction, including heteropoly acids,[6] silica,[7] biocatalysts,[8] alumina,[9] clays and minerals, cyclodextrins, heteropolyanions, and organocatalysts.[2] Nanocatalysis, or polymer-supported catalysis, has emerged as a leading area of research in recent years, becoming one of the most exciting subfields in catalysis. Its primary goal is to accelerate beneficial chemical reactions by modifying the size, shape, or surface chemistry of nanomaterials, which exhibit outstanding and tunable chemical activity, specificity, and selectivity. Currently, there is a strong shift towards safer and more eco-friendly synthesis methods. Nanocatalyst systems play a crucial role in advancing green chemistry by facilitating organic transformations in an eco-conscious manner.[10,11]

Thus, this study reports the applicability of multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposites as catalyst for the synthesis of Biginelli scaffolds through one pot multicomponent approach. The nanocatalyst have been

effectively synthesize 3,4-dihydropyrimidin-2(1*H*)-one and -thione derivatives and marked its place to the Biginelli advancements.

Experimental

Materials

The chemical compounds used were all of the research grade; therefore, no further purification was needed. Fisher Scientific, India, supplied the $Zn(NO_3)_2 \cdot 6H_2O$ (97 %), $Bi(NO_3)_2 \cdot 5H_2O$, $Cr(NO_3)_2 \cdot 6H_2O$, and HNO_3. From Merck, India, we acquired $CS(NH_3)_2$ (99 %), $CO(NH_3)_2$, and PEG-200 (99.8 %).

All starting reagents and chemicals purchased from commercial sources viz., Loba Chemie Pvt. Ltd., Merck Specialities Pvt. Ltd. Silica gel 60 F254 plates were used to monitor reaction.

Preparation of multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposite catalyst

The synthesis of multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposites catalyst was achieved using a previously reported method.[12] Initially, hydrothermal co-precipitation approach of ZnO NPs modified with Bi and Cr was achieved. Later making of g-C_3N_4 was accomplished using an earlier described method.[13] Then the doping of graphitic carbon nitride (g-C_3N_4) with nanoparticles (NPs) was performed using hydrothermal ultrasonication, resulted into the nanocomposites catalyst.[12]

Optimization of multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposite catalyst

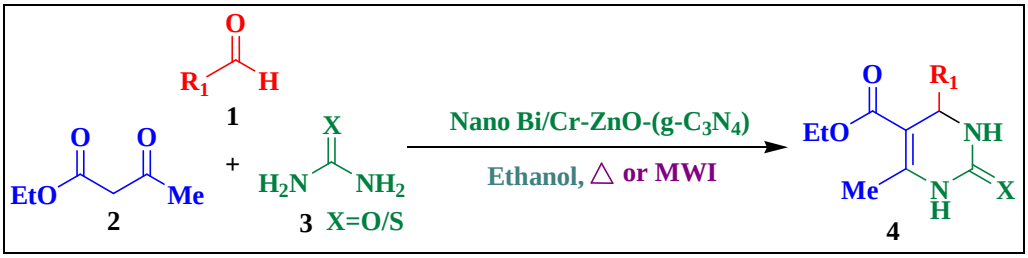
The optimized catalytic conditions demonstrated favourable outcomes regarding the yield and purity of the compounds under both reaction settings with a quantity of 0.1g, as outlined in Table 1. No notable difference in reaction time and yield was detected with catalyst amounts exceeding 0.1 g; thus, 0.1 g of multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nano-composites was utilized as a catalyst for the preparation of Biginelli

derivatives. The microwave approach found to be more effective than the traditional method, demonstrating significantly reduced reaction times and outstanding product yields (Table 1).

Table 1. Optimization of quantity of nano Bi/Cr-ZnO-(g-C_3N_4) for Biginelli reaction.

Entry	Catalyst, g	Conventional method		Microwave irradiation	
		Time, min	Yield, %	Time, min	Yield, %
1	0.025	120	79	13	85
2	0.050	90	83	10	89
3	0.075	70	88	8	93
4	**0.100**	**45**	**90**	**3**	**96**
5	0.125	45	90	3	96
6	0.150	45	90	3	96

Model Biginelli reaction was considered for optimization of nanocatalyst amount using benzaldehyde, ethyl acetoacetate and urea in ethanol.



Scheme 1. Multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposites catalyzed Biginelli reaction.

Conventional method for the synthesis of DHPMs using nanocomposite catalyst

A reaction flask containing mixture of aldehyde (**1**) (10 mmol), ethyl acetoacetate (**2**) (10 mmol), urea/thiourea (**3**) (12 mmol) and 0.1g multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposites catalyst was refluxed with 5 mL ethanol for the required time. Reaction progress was monitored using TLC. Upon completion, the warm mixture was filtered to recover the nanocatalyst. The ethanol was removed from the filtrate using a rotary

evaporator, and the crude product was recrystallized from ethanol to yield DHPMs and thiones in good to excellent yields.[12]

Microwave irradiation method for the synthesis DHPMs using nanocomposite catalyst

A reaction flask containing mixture of aldehyde (10 mmol), ethyl acetoacetate (10 mmol), urea/thiourea (12 mmol) in 5 mL ethanol was added with 0.1g multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposites catalyst subjected to microwave irradiation for the period of time mentioned in the table. The reaction mixture was irradiated at 1-minute intervals, and its progress was monitored by TLC. Upon completion of the reaction, the worked up was done as described in conventional method.

Results and discussion

The characterization of synthesized multi-doped Bi/Cr-ZnO-(g-C_3N_4) composite nanocatalyst was performed by advanced spectrochemical techniques to determine the surface properties and morphology of the nanocomposites. XRD data provided the details of phase composition and the crystal size of the catalyst. The morphological nature and the size of crystals were also studied using TEM. The constitution of the material and its porosity was detected by EDS (Energy-dispersive X-ray spectroscopy) analysis paired with SEM (scanning electron microscopy) analysis.[12] The multi-doped Bi/Cr-ZnO-(g-C_3N_4) composite nanocatalyst showed good surface characteristics and morphology that enable it to play a role as a catalyst for the synthesis of different heterocyclic compounds.

The multi-doped Bi/Cr-ZnO-(g-C_3N_4) composite nanocatalyst was subsequently utilized to produce DHPM and -thione derivatives by using substituted aromatic aldehydes, ethyl acetoacetate, and urea or thiourea. To assess the catalytic effectiveness of the multi-doped Bi/Cr-ZnO-(g-C_3N_4) composite nanocatalyst, DHPM and -thione derivatives were synthesized under both microwave irradiation and traditional refluxing methods. In both conditions, the mild acid charcoal catalyst demonstrated effectiveness;

however, under microwave conditions, its performance was significantly better (yielding 80 – 96 %) compared to the conventional method (yielding 76-92 %) (Table 2).

Table 2. Multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposites catalyzed synthesis of Biginelli derivatives under conventional as well as microwave irradiation conditions.

Entry	Product *	R_1	X	Conventional		Microwave irradiation		Melting point, °C	
				Time, min	Yield, %	Time, min	Yield, %	Observed	Reported
1.	**4a**	C_6H_5-	O	45	92	3	96	200-202	200-202[14]
2.	**4b**	4-OCH_3-C_6H_4	O	130	76	8	82	196-198	196-198[14]
3.	**4c**	4-OH-C_6H_4-	O	60	79	5	86	228-230	228-230[14]
4.	**4d**	4-NO_2- C_6H_4-	O	50	89	3	94	212-214	210-212[15]
5.	**4e**	n-Propyl	O	80	91	5	93	180-182	180-182[16]
6	**4f**	C_6H_5-	S	60	86	4	94	204-206	205-207[17]
7.	**4g**	4-OCH_3-C_6H_4-	S	140	76	8	80	154-156	154-156[17]
8.	**4h**	2-OH- C_6H_4-	S	130	80	6	87	206-208	206-208[18]
9.	4i	4-Cl- C_6H_4-	S	60	83	5	89	180-182	180-182[15]
10.	4j	n-Propyl	S	90	89	5	90	150-152	148-152[17]

*Multi-doped-Bi/Cr-ZnO-(g-C_3N_4) nanocomposites was employed as a catalyst for the synthesis of different Biginelli derivatives.

The aldehydes with electron-donating and electron- withdrawing groups reacted effectively using both traditional and microwave methods.

The assessment of a Nano Bi/Cr-ZnO-(g-C_3N_4) catalyst for the Biginelli multicomponent cyclo-condensation was particularly significant.

Table 3 presents a summary of microwave-assisted techniques for synthesizing DHPMs and -thiones. The range of literature methods included catalysts in various amounts and exhibited different reaction times, resulting in a diverse range of yields for DHPMs. Several of the approaches required a greater quantity of catalyst (10 – 25 mL), and in certain instances, the yields were favourable (82 – 93 %) but necessitated longer reaction times (240 – 480 min). Various catalysts, including those supported on clays, acidic alumina, nano-silica, as well as heteropolyacids and nanopolymers, were compared. The reusability of recovered nano Bi/Cr-ZnO-(g-C_3N_4) catalyst for four cycles was performed and showed promising results up to fourth cycle.

Table 3. Comparison of microwave assisted protocols for Biginelli reaction

Entry	Catalyst utilized (amount)	Solvent, mL	Time, min	Yield, %
1	$FeCl_3$/Si-MCM-41 (0.03 g/ 20 wt %)[18]	-	3	89
2	3D printed α-Al_2O_3 (0.350 g) [19]	-	10	95
3	nanosized $Ni0._{45}Zn_{0.55}Fe_2O_4$ (0.03 g)[20]	-	10	67
4	$FeCl_3$/Nanopore Silica (0.05 g)[21]	-	15	75
5	ZrO_2-pillared clay (0.25 g)[22]	-	5	94
6	PEG-SO_3H[23]	-	6	91
7	Polystyrene sulphonic acid [PSSA] (20 % solution)[24]	Water	20	89
8	$[PyPS]_3PW_{12}O_{40}$ (0.314 g)[25]	-	5	95
9	**Nano Bi/Cr-ZnO-(g-C_3N_4) (0.1 g)**	**EtOH (5)**	**3**	**96**

*Various catalyst systems are evaluated under microwave irradiation conditions for the substrate R_1 = C_6H_5- and X = O and ethyl acetoacetate.

Conclusions

The catalytic efficacy of multi-doped Bi/Cr-ZnO-(g-C_3N_4) composite nanocatalyst has been evaluated successfully for the

multicomponent reaction via Biginelli reaction. The nanocatalysts have proven to be more efficient by yielding good economy in shorter reaction times under microwave irradiation conditions. The catalyst has also been found effective for diverse category of substrates such as differently substituted aromatic aldehydes and aliphatic aldehyde. We have synthesized DHPM's and their -thione derivatives by using urea and thiourea respectively, the multi-doped Bi/Cr-ZnO-(g-C_3N_4) composite nanocatalyst showed good results in both the cases.

Funding: Authors declare that no funding is utilized from any sources.

Acknowledgments

The authors gratefully acknowledge the Principal and the Head of the Department of Chemistry at Poojya Sane Guruji Vidya Prasarak Mandal's SIP Arts, GBP Science, and STKV Sangh Commerce College in Shahada, India for their support in providing research and library facilities. The authors also extend their appreciation to the Central Instrumentation Facility at Savitribai Phule Pune University, Pune for granting access to the characterization facility.

Characterization Data

*5-(Ethoxycarbony)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (**4a**).* IR (KBr, cm^{-1}): 3480, 3247, 2980, 1728, 1705, 1646, 1466, 1222, 1090. ^{1}H NMR (400 MHz, δ, ppm) (DMSO-d_6): δ 9.17 (s, 1H), 7.75 – 7.69 (m, 1H), 7.37 – 7.27 (m, 2H), 7.24 (ddt, *J* = 6.9, 3.3, 1.5 Hz, 3H), 5.15 (d, *J* = 3.4 Hz, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 2.09 (s, 2H), 1.10 (t, *J* = 7.1 Hz, 3H). MS (m/z): 261 (M+1)

*5-(Ethoxycarbonyl)-4-(4-methoxyphenyl)-6-methyl-3,4 dihydropyrimidin- 2(1H)-one (**4b**).* IR (KBr, cm^{-1}): 3479, 3413, 3246, 2928, 1724, 1705, 1651, 1513, 1224, 1220. ^{1}H NMR (400 MHz, δ, ppm) (DMSO-d_6): δ 9.13 (s, 1H), 8.25 – 8.17 (m, 2H), 7.91(dd, *J* = 3.5, 2.0 Hz, 1H), 7.54

– 7.47 (m, 2H), 5.27 (d, *J* = 3.3 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

*5-Ethoxycarbonyl-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (**4c**).* IR (KBr, cm^{-1}): 3520, 3362, 2991, 1737, 1705, 1652, 1566, 1250. ^{1}H NMR (400 MHz, δ, ppm) (DMSO-d_6): δ 9.33 (s, 1H), 9.08 (d, *J* = 2.2 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.07 – 6.99 (m, 3H), 6.83 (s, 1H), 6.73 – 6.65 (m, 3H), 5.05 (d, *J* = 3.3 Hz, 2H), 3.98 (q, *J* = 7.1 Hz, 3H), 2.23 (s, 5H), 2.09 (s, 1H), 1.10 (t, *J* = 7.1 Hz, 5H), 1.06 (s, 1H).

*5-(Ethoxycarbonyl)-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (**4d**).* IR (KBr, cm^{-1}): 3343, 3107, 2981, 1704, 1651, 1520, 1347, 1213. ^{1}H NMR (400 MHz, δ, ppm) (DMSO-d_6): δ 9.37 (s, 1H), 8.25 – 8.17 (m, 2H), 7.91(dd, *J* = 3.5, 2.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 5.27 (d, *J* = 3.3 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

*5-(Ethoxycarbonyl)-4-(n-propyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one (**4e**).* IR (KBr, cm^{-1}): 3237, 3015, 1735, 1712, 1666, 1599, 1287. ^{1}H NMR (400 MHz, δ, ppm) ($CDCl_3$): δ 8.04 (s, 1H), 5.85 (s, 1H), 4.33 (dt, *J* = 7.6, 3.5 Hz, 1H), 4.28 – 4.12 (m, 2H), 2.30 (s, 3H), 2.19 (s, 2H), 1.67 – 1.39 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 4H), 0.93 (t, *J* = 7.1 Hz, 3H).

*5-Ethoxycarbonyl-4-(phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione (**4f**).* IR (KBr, cm^{-1}): 3380, 3186, 2986, 1720, 1703, 1660, 1586, 1270. ^{1}H NMR (400 MHz, δ, ppm) (DMSO-d_6): δ 9.81 (s, 1H), 9.65 (s, 1H), 7.37 – 7.21 (m, 5H), 5.17 (d, *J* = 3.4 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.10 (s, 3H). MS (m/z): 277 (M+1).

*5-Ethoxycarbonyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione (**4g**).* IR (KBr, cm^{-1}): 3463, 3192, 2889, 1737, 1708, 1653, 1573, 1243. ^{1}H NMR (400 MHz, δ, ppm) (DMSO-d_6): δ 9.9 (s, 1H), 9.60 (s, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H),

5.11 (d, *J* = 3.4 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 2.28 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H).

5-Ethoxycarbonyl-6-methyl-4-(2-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione ***(4h)***. IR (KBr, cm^{-1}): 3487, 3290, 2857, 1750, 1698, 1634, 1534, 1232. ^{1}H NMR (400 MHz, δ, ppm) (DMSO-d_6): δ 1.07 (t, *J* = 7.6 Hz, 3H), 2.4 (s, 3H), 4.1 (q, *J* = 7.6 Hz, 2H), 5.68 (s, 1H), 6.91-7.15 (m, 4H), 7.72 (s, 1H), 9.65 (s, 1H), 9.95 (s, 1H). MS (m/z): 293 (M+1).

5-(Ethoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione ***(4i)***. IR (KBr, cm^{-1}): 3410, 3269, 2897, 1755, 1631, 1575, 1365, 1268. ^{1}H NMR (400 MHz, δ, ppm) ($CDCl_3$): δ 7.52 (d, *J* = 8.7 Hz, 1H), 6.92 – 6.81 (m, 2H), 6.16 (q, *J* = 1.3 Hz, 1H), 4.14 (t, *J* = 5.9 Hz, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.42 (d, *J* = 1.2 Hz, 3H), 2.17–2.06 (m, 2H).

5-Ethoxycarbonyl-4-(n-propyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione ***(4j)***. IR (KBr, cm^{-1}): 3337, 3019, 1745, 1705, 1651, 1520, 1320. ^{1}H NMR (400 MHz, δ, ppm) ($CDCl_3$): δ 8.41 (s, 1H), 7.94 (s, 1H), 4.37 (dt, *J* = 7.7, 3.7 Hz, 1H), 4.28 – 4.09 (m, 2H), 2.32 (s, 3H), 2.18 (s, 1H), 1.69 – 1.55 (m, 1H), 1.55 – 1.43 (m, 1H), 1.46 (s, 1H), 1.47 – 1.30 (m, 1H), 1.30 (s, 1H), 1.28 (d, *J* = 7.1 Hz, 2H), 0.92 (t, *J* = 7.0 Hz, 3H).

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