

Microwave Assisted Efficient Synthesis of Flavone using ZnO Nanoparticles as Promoter under Solvent-Free Conditions

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A simple and highly efficient protocol for synthesis of flavones from 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones in presence of ZnO nanoparticles as a promoter in thermal as well as microwave irradiation under solvent-free conditions have been demonstrated. The catalyst is inexpensive, stable, can be easily recycled/reused for several cycles with consistent activity and observed almost same yield confirming the stability of the catalyst. It is believed that the present approach will become an alternative route for the conventional reactions. Because in this protocol, yield is quite high, short reaction time, simple work up, catalyst can be recycled as well as it is free of any hazardous by-products formation during workup.

Keywords: Flavone, Nanocrystalline ZnO, Heterogeneous, Green Synthesis, Solvent-free synthesis.

INTRODUCTION

Flavones are class of the flavonoids composing a 2-phenyl-1-benzopyran-4-one backbone structure, which is present in fruits and vegetables ubiquitously. We consume flavanoids in our daily diet by inadvertently which have a beneficial impact on our health [1]. The flavones exhibited various biological activities based on the position and nature of the various substituent on the flavone structure. The flavones show a broad spectrum of biological activities due to their unique capacity to modulate different enzyme systems [2].

The flavones are active against infectious and metabolic diseases such as antiestrogenic, antimicrobial [3], anti-inflammatory, antioxidant [4], antiallergic, antitumor, vascular and cytotoxic [5] activities. In many natural products, flavone structure is frequently found such as luteolin and kaempferol. Due to their fascinating structural features, they exhibit array of biological activities, especially, anti-inflammatory, antimicrobial, antitumor and cytotoxic [6-11].

A verity of methods are used for synthesis of different flavones, which broadly can be classified into two groups *viz.* chalcones and 1,3-diketones as intermediates synthesized from *o*-hydroxyacetophenone. Most of the recently used methods for the synthesis of flavones depends on 1,3-diketones which

is reported by Robinson and Venkataraman [12]. Several reported methods are available for synthesis of a flavone skeleton but one of the most commonly used methods are acid-catalyzed cyclization of various 1,3-diketone derived from 2-hydroxyacetophenones [13,14]. Various types of catalysts used for cyclization of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanedione. But most of the reported ways of synthesis of flavones suffer from considerable restrictions such as use of harsh reaction conditions, prolonged reaction time, low yields, toxic and expensive catalysts/reagents and solvents. In view of these restrictions, there is still a need for exploration of effortless, efficient, rapid, eco-compatible, and widely applicable routes for the synthesis of flavone owing to their immense synthetic and medicinal relevance. Also, due to the severe and burgeoning environmental regulations, organic chemists are call for the development of environmentally benevolent synthetic methodologies. Organic reactions under solvent-free conditions using microwave irradiation and conventional heating techniques has become a center of attraction for researchers over the years [15-17].

Recently, zinc oxide nanoparticles have received a significant attention because of its affordability, non-toxicity and has environmental advantages *i.e.* low corrosion, minimum completion time, easy transport, reuse of the catalyst, low waste and demolition of the catalyst [18]. Because of low coordi-

nation sites and higher surface area, ZnO nanoparticles are considered to be more reactive. As the size decreases, the surface area of catalyst increases immensely which is useful for the greater catalytic activity. Some researchers have synthesized flavones from chalcones by using ZnO nanoparticles [19-21].

Due to huge number of advantages correlated with this eco-friendly nature, it has been used as a powerful catalyst for various organic transformations [22,23]. Hence, in present work in green synthesis of flavones by various methods, here we report an efficient and eco-friendly catalytic application of zinc oxide nanoparticles for synthesis of flavone from cyclodehydration of various 1,3-propanedione in microwave or conventional heating under solvent free conditions.

EXPERIMENTAL

All the chemical reactions were performed in corning glassware which is oven-dried. All chemicals and solvents were obtained from professional suppliers and used as such for further reactions. Thin-layer chromatography (TLC) was carried out on Merck silica gel plates, visualized with a UV lamp and stained in DNP solution and KMnO_4 . The standard methods are used for synthesis of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones and their purities were established before utilization by melting point. Melting points were determined by open capillary tubes in paraffin oil bath. ^1H and ^{13}C NMR spectra were obtained as solutions in CDCl_3 solvents. The standard ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Varian Mercury spectrometer in CDCl_3 solution. The tetramethylsilane was used as an internal standard. Perkin Elmer Model 1600 series FTIR instrument was used to record IR spectra. LC/MS (ES-API) instrument were used record Mass spectra. The QTOF Micromass Mass Spectrometer (electro spray ionization mode) was used for high-resolution mass spectra (HRMS). All the compounds synthesized in this article were previously reported. The spectroscopic and physical data is in matching with reported values.

Synthesis of flavones using ZnO nanoparticles

By conventional method: A mixture of substituted 1,3-propanedione (0.5 g, 2.08 mmol, 1.0 eq.) and ZnO nanoparticles (1.0 eq.) was warmed in an oil bath at 100°C for 30 min. After the finishing of reaction (TLC check), the product of reaction was allowed to cool at room temperature. To this reaction mixture 10 mL of water and 10 mL of ethyl acetate were added. Organic layer was isolated and the water layer was extracted in (2×10 mL) ethyl acetate. Mixed organic extract was dried over anhydrous sodium sulfate and concentrated in vacuum. Catalyst recycles by filtration of aqueous layer. The column chromatography is used for purification of crude product by using silica gel in hexane-ethylacetate solvent system to give the corresponding flavones (**4a-l**) in high yields.

Microwave method: A mixture of substituted 1,3-propanedione (0.5 g, 2.08 mmol, 1.0 eq.) and ZnO nanoparticles (1.0 eq.) was heated in a microwave oven for 15 min. Same procedure used for purification of flavones as mentioned in the conventional heating method.

2-Phenyl-chromen-4-one (4a): m.p. $96-98^\circ\text{C}$ [lit. 21]; IR (KBr, ν_{max} , cm^{-1}): 756, 1130, 1568, 1604, 1645; ^1H NMR

(300 MHz, CDCl_3): δ 6.81 (s, 1H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.46-7.56 (m, 4H), 7.65-7.70 (m, 1H), 7.88-7.91 (m, 2H), 8.21 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 107.3, 117.9, 123.7, 125.1, 125.5, 126.1, 128.9, 131.5, 131.6, 133.7, 156.1, 163.3, 178.3; LC-MS m/z : 223 (M+H) $^+$.

2-(4-Methoxyphenyl)chromen-4-one (4b): m.p. $157-158^\circ\text{C}$ [lit. 21]; IR (KBr, ν_{max} , cm^{-1}): 767, 1133, 1465, 1608, 1649; ^1H NMR (300 MHz, CDCl_3): δ 3.87 (s, 3H), 6.80 (s, 1H), 7.01 (m, 2H), 7.40 (t, $J = 7.2$ Hz), 7.68 (m, 1H), 7.53 (d, $J = 8.1$ Hz), 7.88 (d, 2H, $J = 7$ Hz), 8.21 (dd, $J = 8.2$ & 2.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.4, 105.9, 114.4, 117.9, 123.7, 123.9, 125.1, 125.6, 127.9, 133.6, 156.1, 162.4, 163.5, 178.5; LC-MS m/z : 253 (M+H) $^+$.

2-(4-Fluorophenyl)chromen-4-one (4c): m.p. $148-150^\circ\text{C}$ [lit. 21]; IR (KBr, ν_{max} , cm^{-1}): 755, 806, 869, 1134, 1234, 1467, 1574, 1608, 1663; ^1H NMR (300 MHz, CDCl_3): δ 6.79 (s, 1H), 7.23 (m, 2H), 7.47 (t, $J = 7.1$ Hz, 1H), 7.58 (d, $J = 7.1$ Hz, 1H), 7.72 (m, 1H), 7.94 (m, 2H), 8.24 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 107.1, 116.6, 117.0, 123.9, 125.5, 126.0, 127.1, 128.1, 134.2, 156.0, 161.2, 162.6, 178.1; LC-MS m/z : 241 (M+H) $^+$.

7-Methoxy-2-phenyl-chromen-4-one (4d): m.p. $109-110^\circ\text{C}$ [lit. 24]; IR (KBr, ν_{max} , cm^{-1}): 767, 908, 1163, 1450, 1606, 1626, 1647; ^1H NMR (300 MHz, CDCl_3): δ 3.91 (s, 3H), 6.77 (s, 1H), 6.95 (m, 2H), 7.51 (m, 3H), 7.88 (m, 2H), 8.11 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.8, 100.3, 107.3, 114.9, 117.6, 126.0, 126.9, 128.9, 131.4, 131.6, 157.8, 162.9, 164.1, 177.7; LC-MS m/z : 253 (M+H) $^+$.

7-Methoxy-2-(4-fluorophenyl)-chromen-4-one (4d): m.p. $172-173^\circ\text{C}$ [lit. 21]; IR (KBr, ν_{max} , cm^{-1}): 781, 841, 1022, 1294, 1456, 1514, 1608, 1660; ^1H NMR (300 MHz, CDCl_3): δ 3.84 (s, 3H), 6.41-6.48 (m, 2H), 6.64 (s, 1H), 7.15 (t, $J = 8.7$ Hz, 2H), 7.89 (m, 1H), 7.90 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.6, 101.3, 108.1, 110.1, 115.7, 116.1, 128.9, 128.9, 130.1, 163.4, 165.3, 165.9, 166.7, 174.8; LC-MS m/z : 271 (M+H) $^+$.

7-Methoxy-2-(4-methoxyphenyl)chromen-4-one (4f): m.p. $194-195^\circ\text{C}$ [lit. 24]; IR (KBr, ν_{max} , cm^{-1}): 862, 977, 1186, 1260, 1379, 1516, 1593, 1629; ^1H NMR (300 MHz, CDCl_3): δ 3.82 (s, 3H), 3.86 (s, 3H), 6.86 (m, 2H), 6.60 (s, 1H), 6.93 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.3, 55.7, 100.2, 105.9, 114.0, 114.2, 117.6, 126.7, 127.6, 157.7, 162.1, 162.8, 163.9, 177.6; LC-MS m/z : 283 (M+H) $^+$.

6-Methoxy-2-phenyl-chromen-4-one (4g): m.p. $160-161^\circ\text{C}$ [lit. 24]; IR (KBr, ν_{max} , cm^{-1}): 658, 846, 1030, 1255, 1361, 1488, 1618, 1641; ^1H NMR (300 MHz, CDCl_3): δ 3.89 (s, 3H), 6.79 (s, 1H), 7.28 (dd, $J = 6.6$ & $J = 3.5$ Hz, 1H), 7.46-7.50 (m, 4H), 7.57 (d, $J = 2.7$ Hz, 1H), 7.88-7.91 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.8, 104.7, 106.7, 119.4, 123.6, 124.4, 126.1, 128.8, 131.4, 131.7, 150.8, 156.9, 163.0, 178.2; LC-MS m/z : 253 (M+H) $^+$.

2-(4-Fluorophenyl)-6-methoxy-chromen-4-one (4h): m.p. $152-153^\circ\text{C}$ [lit. 24]; IR (KBr, ν_{max} , cm^{-1}): 719, 910, 1024, 1168, 1488, 1620, 1661, 1727; ^1H NMR (300 MHz, CDCl_3): δ 3.90 (s, 3H), 6.76 (s, 1H), 7.18-7.30 (m, 3H), 7.48 (d, $J = 9.3$ Hz, 1H), 7.58 (d, $J = 2.4$ Hz, 1H), 7.92 (d, $J = 9$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.9, 104.8, 116.1, 116.4, 119.4, 123.8, 124.4, 128.3, 128.4, 150.9, 157.0, 162.1, 166.3, 178.1; LC-MS

m/z : 271 (M+H)⁺; HRMS m/z [M+H]⁺: calcd for C₁₆H₁₁O₃F: 271.0692.

6-Methoxy-2-(4-methoxyphenyl)chromen-4-one (4i): m.p. 195-196 °C [lit. 24]; IR (KBr, ν_{\max} , cm⁻¹): 558, 817, 1014, 1196, 1268, 1454, 1584, 1607, 1647; ¹H NMR (300 MHz, CDCl₃): δ 3.88 (s, 3H), 3.90 (s, 3H), 6.73 (s, 1H), 7.01 (d, J = 9.0 Hz, 2H), 7.27 (m, 1H), 7.58 (d, J = 3.0 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 55.4, 55.9, 104.8, 105.4, 114.4, 119.3, 123.5, 124.1, 124.4, 127.8, 150.9, 156.8, 162.3, 163.1, 178.2; LC-MS m/z : 283 (M+H)⁺.

6-Fluoro-2-phenyl-chromen-4-one (4j): m.p. 128-129 °C [lit. 21]; IR (KBr, ν_{\max} , cm⁻¹): 767, 835, 1176, 1359, 1570, 1624, 1660; ¹H NMR (300 MHz, CDCl₃): δ 6.82 (s, 1H), 7.39-7.46 (m, 1H), 7.50-7.61 (m, 4H), 7.85-7.93 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 106.7, 110.7, 120.2, 121.7, 122.0, 126.2, 129.0, 131.3, 131.7, 152.3, 161.1, 163.1, 177.5; LC-MS m/z : 241 (M+H)⁺.

6-Bromo-2-phenyl-4H-chromen-4-one (4k): m.p. 176 °C; IR (KBr, ν_{\max} , cm⁻¹): 756, 1130, 1568, 1604, 1645; ¹H NMR (300 MHz, CDCl₃): δ 7.12 (s, 1H), 7.63 (m, 3H), 7.83 (d, J = 3.2 Hz, 1H), 8.11 (dd, J = 10.8 & 2.4 Hz, 1H), 8.13 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 107.4, 118.3, 121.7, 125.3, 126.9, 127.3, 129.6, 131.3, 132.5, 137.3, 155.1, 163.4, 176.3; HRMS m/z [M+H]⁺: calcd for C₁₅H₉O₂Br: 300.9864, found: 300.9867.

6-Chloro-2-phenyl-chromen-4-one (4l): m.p. 183-184 °C [lit. 24]; IR (KBr, ν_{\max} , cm⁻¹): 682, 908, 1132, 1307, 1438, 1457, 1567, 1601, 1651; ¹H NMR (300 MHz, CDCl₃): δ 6.82 (s, 1H), 7.50-7.56 (m, 4H), 7.60-7.65 (m, 1H), 7.88-7.90 (m, 2H), 8.17 (d, J = 2.3 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 107.3, 119.7, 124.7, 125.1, 126.3, 129.1, 131.1, 131.2, 131.8, 133.0, 154.4, 163.7, 177.1; LC-MS m/z : 257 (M+H)⁺.

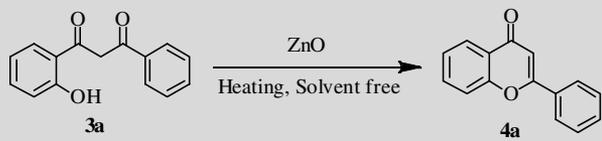
RESULTS AND DISCUSSION

Optimization of reaction conditions: To study the catalytic activity in synthesis of flavones from 1-(2-hydroxyphenyl)-3-aryl-1,3-propanedione (**3a**) was chosen as a representation reaction. For this, we first examined the synthesis of 2-phenyl-4H-chromen-4-one (**4a**) in the presence of 0.1 equivalent of ZnO nanoparticles (0.208 mmol, 0.012 g). While performing conventional heating even after 60 min, the desired product **4a** was produced in a low yield (entry 1, Table-1). Using 0.2 (0.442 mmol, 0.034 g) and 0.4 (0.832 mmol, 0.068 g) equivalents of ZnO nanoparticles gives the desired amount of product in moderate yields (entries 2 and 3, Table-1), while using 0.6 (0.10 g, 1.25 mmol) and 0.8 (0.166 mmol, 0.14 g) equivalents of ZnO nanoparticles, there was insignificant raise in the yield of the desired product (entry 4 and 5, Table-1).

Finally, it was observed that 1.0 (0.16 g, 2.08 mmol) equivalent of ZnO nanoparticles was the most suitable amount of catalyst for achieving the desired product (Table-1, entry 6). By applying the same approach under microwave heating, it was also observed that the time taken for completion of this reaction was now reduced to half of the time taken by conventional heating (entry 1- 6, Table-1).

Regeneration of ZnO nanoparticles: The ZnO nanoparticles catalyst reused and recovered by filtration of reaction mixture. It was used for subsequent experiments (up to five times) under the same reaction conditions. It was also observed that

TABLE-1
EFFECT USE OF DIFFERENT AMOUNT OF CATALYST ON THE SYNTHESIS OF FLAVONES^a



Entry	Catalyst	Heating in oil bath		Heating in microwave	
		Time (min)	Yield (%)	Time (min)	Yield (%)
1	0.1 eq.	60	20	60	22
2	0.2 eq.	30	32	15	38
3	0.4 eq.	30	44	15	48
4	0.6 eq.	30	66	15	70
5	0.8 eq.	30	74	15	78
6	1.0 eq.	30	80	15	88

^aReagent: 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione (0.5 g)

yields of the product remained comparable to subsequent experiments (Fig. 1). Thus, it is finally inferred that the reusability and recyclability of the catalyst remain constant without significant loss of activity.

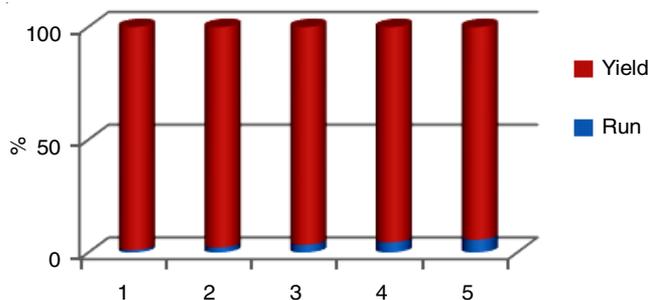


Fig. 1. Recyclability of ZnO nano catalyst

Next, to explore the diversity of this methodology, various 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones were tested under the above reaction condition. Results showed that cyclization of various 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones proceeded smoothly to completion within a short reaction time to give the corresponding flavones in good to excellent yields under both heating conditions (entry 1-10, Table-2).

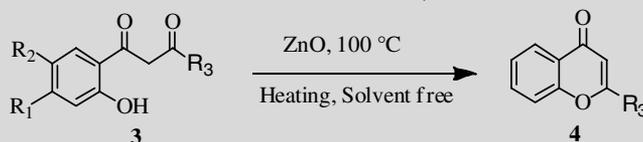
Conclusion

In summary, a simple, rapid and environmentally benign protocol is developed in which ZnO nanoparticles as an effective promoter for synthesis of various flavones under solvent free-conditions. Microwave assisted reactions are appeared to be slightly more energy efficient as it requires less time for completion as compared to the traditionally heated reaction. This protocol is more straight-forward because of mild reaction conditions, economically viable and eco-friendly, thus providing a very efficient alternative to traditional processes.

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TABLE-2
ZnO NANOPARTICLE PROMOTED SYNTHESIS OF FLAVONES FROM 1-(2-HYDROXYPHENYL)-3-ARYL-1,3-PROPANEDIONE^a



Entry	Compd.	R ₁	R ₂	R ₃	Conventional heating ^b		Microwave heating ^c	
					Yield ^d (%)		Yield ^d (%)	
1	4a	H	H	Ph	80		88	
2	4b	H	H	4-MeOC ₆ H ₄	81		87	
3	4c	H	H	4-FC ₆ H ₄	78		88	
4	4d	OMe	H	Ph	79		86	
5	4e	OMe	H	4-FC ₆ H ₄	80		88	
6	4f	OMe	H	4-MeOC ₆ H ₄	80		87	
7	4g	H	OMe	Ph	81		88	
8	4h	H	OMe	4-FC ₆ H ₄	80		86	
9	4i	H	OMe	4-MeOC ₆ H ₄	81		89	
10	4j	H	F	Ph	78		86	
11	4k	H	Br	Ph	79		85	
12	4l	H	Cl	Ph	80		87	

^aReagents: (1) (0.5 g.) various 1, 3-propanediones (**3a-3m**, 1.0 eq.), (2) ZnO nanoparticle (1.0 eq.). ^b30 min in conventional heating. ^c15 min in microwave. ^dIsolated yields.

CONFLICT OF INTEREST

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

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