



www.asianpubs.org

## Asian Journal of Organic & Medicinal Chemistry

Volume: 1                      Year: 2016  
Issue: 4                        Month: October-December  
pp: 101–105  
DOI: <https://doi.org/10.14233/ajomc.2016.AJOMC-P30>

Received: 6 November 2016  
Accepted: 25 November 2016  
Published: 17 January 2017

### Author affiliations:

<sup>1</sup>Department of Chemistry, Vivekanand Arts & S. D. Commerce and Science College, Aurangabad-431 001, India

<sup>2</sup>Department of Chemistry, Sant Ramdas. Arts, Commerce & Science College, Jalna-431 009, India

<sup>3</sup>Department of Chemistry, Shivaji University, Kolhapur-416 004, India

✉To whom correspondence to be addressed:

Fax: +91 2483 231313

E-mail: [profsantoshjadhav@gmail.com](mailto:profsantoshjadhav@gmail.com)

Available online at: <http://ajomc.asianpubs.org>

ARTICLE

### Catalyst Free in Aqueous Medium Olefination of 1-Methyl-4-hydroxyquinolinone under Microwave Irradiation Method

S.A. Jadhav<sup>1,✉</sup>, S.R. Vaidya<sup>1</sup>,  
R.K. Pardeshi<sup>2</sup> and Devanand B. Shinde<sup>3</sup>

#### ABSTRACT

3-Benzilidene quinolones have been synthesized by Knoevenagel condensation reactions starting from 1-methyl-4-hydroxyquinolinone with substituted aromatic aldehydes. Olefination of N-methyl 4-hydroxy quinolinone have been successfully carried out in aqueous medium under microwave irradiation method. An expeditious reaction was carried out under the microwave irradiation technique with good to excellent yield (92-98 %). The proposed method is environmentally benign, mild and simple protocol for the synthesis of chalcone of 4-hydroxy quinolondione (**3a-1**). The final products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, Mass and elemental analysis as spectral property.

#### KEYWORDS

Olefination, 4-Hydroxyquinolondione, Knoevenagel condensation reaction, Microwave irradiation.

#### INTRODUCTION

Quinolone derivatives constituent is an important class of nitrogen containing heterocycles with diverse useful bioactivity. They are widely used as a key intermediate preparation of some natural products and related structures. A broad number of fascinating pharmacological activities have been associated with 2-quinolinone derivatives. The quinolinone alkaloids isolated from the *Rutaceae* family of plants (Fig. 1) have been shown to exhibit a variety of biological properties corresponding compound exhibit similar properties such as antiviral, antifungal, antibacterial [1], hydroxyquinolinone and its arylidene analogues of hydroxyquinolinone, particularly at 3-position has excellent biological activity, Such as hepatoprotective effects in human [2]. On the basis of biological evaluation 4-hydroxyquinolinone and its analogues has wide spectrum of pharmacokinetic usability, it constituent an important area of research because of their use as antioxidant, antiangiogenic, brain antitumor *in vivo*, analgesic, dye-stuff, herbicides, orally active Antagonist and anti-inflammatory, antiallergenic, antitubercles and cardiovascular agent, herbicidal [3-7] and competitive inhibitor [8]. Keeping focus on green protocol, to our best of knowledge this is first report of synthesis of quinolone chalcone in aqueous media.

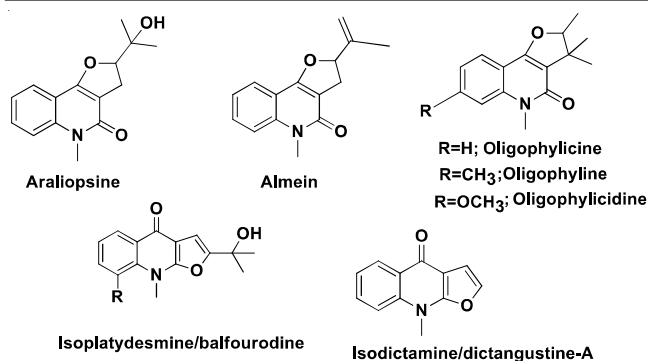


Fig. 1. Naturally occurring alkaloid derivatives

Previous workers reported the synthesis of hydroxy-quinolinone and its derivatives by non-green methods using catalyst, reagent and organic solvent [2,9], diethylamine in benzene and in dioxane and triethylamine in benzene [10,11]. However, all of these methods have been some disadvantages, such as an environmentally hazardous, cost effective, toxic, water sensitive reagent and catalyst, unacceptable yields and difficult product separation. To overcome all these drawbacks and the reaction performed in water [12-14], it is a unique solvent due to being readily available, inexpensive, non-toxic, safer and environmentally benign. It enhanced reaction rates, higher yields of pure products and easier workup and selectivity of many organic reactions in addition to green solvent under the microwave irradiation method compared to thermal reactions [15]. A novel green protocol performs reaction in water under microwave irradiation [16]. The concept of sustainable chemistry was introduced in the early 1990s. P.T. Anastas defines 'Green Chemistry', as a chemistry able to promote innovative chemical technologies that reduced or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products with the twelve principles in the green chemistry [17] (Fig. 2). The green chemistry has gradually become recognized as both culture and methodology for achieving sustainability [18]. In our earlier research work an environmentally benign for the searching of some nitrogen and sulfur containing heterocyclic compound [19-23]. Thus, we developed new eco-friendly, catalyst free and more convenient route for the synthesis of 1-methyl-4-hydroxyquinolinones.

## EXPERIMENTAL

All the compounds used in synthesis were of analytical grade, alum is easily available naturally occurring catalyst. The melting points of the compounds were determined in open head capillary and are uncorrected. Chemical shifts are given in parts per million ( $\delta$ -scale) and the coupling constants are given in hertz. Silica gel-G plates (Merck) were used for thin layer chromatography analysis with a mixture of (ethyl acetate-*n*-hexane) as eluent. The IR spectra of the compounds were recorded in the region of 4000-400  $\text{cm}^{-1}$  by using KBr pallet on FT-IR Perkin spectrophotometer.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra were recorded on a DRX-300 Bruker FT-NMR spectrophotometer in  $\text{DMSO-}d_6$  as a solvent. Satisfactory elemental analysis was obtained on a Perkin Elmer CHN analyzer.

**Synthesis of 1-methyl, 3-benzylidene, quinolin-2,4-dione (3a-l):** Mixture of 1-methyl-4-hydroxyquinolinone (1

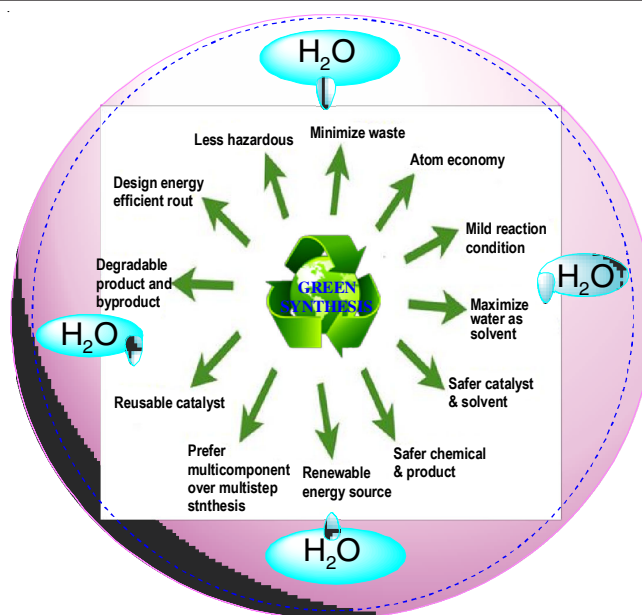


Fig. 2. Green synthesis; twelve principles with casing of aqueous mediated

mmol) and substituted aryl aldehydes (1.1 mmol) in 15 mL solution (water 10 mL and ethanol 5 mL) were irradiated on microwave oven program at 100 °C and 350 watt for the appropriate time of reaction (Table-2), progress of reaction was monitored by TLC (ethyl acetate-*n*-hexane). After completion of reaction, hot water-ethanol (1:1) was added, filtered and recrystallized from appropriate solvent.

**(Z)-3-Benzylidene-1-methylquinoline-2,4-(1H,3H)-dione (3a):** Yield: 98 %; m.p. 188-190 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 3.43 (s, 3H,  $\text{CH}_3\text{-N}$ ); 8.61 (s, 1H,  $\text{CH=C-Ar}$ ); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 7.60 (dd, 2H, Ar-H); 7.41 (dd, 2H, Ar-H); 7.30 (dd, 1H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  ppm: 162.8, 131.1, 176.2, 131.2, 124.8, 128.9, 134.2, 115.8, 140.4, 150.1, 131.8, 128.1, 128.2, 127.8, 128.5, 128, 30.1; MS ( $m/z$ , %): 264.29 [ $\text{M}^+$ ], Elem. anal. (%): C = 77.55, H = 4.98, N = 5.32, O = 12.15.

**(Z)-3-(2-Chlorobenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3b):** Yield: 94 %; m.p. 196-198 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 3.43 (s, 3H,  $\text{CH}_3\text{-N}$ ); 8.61 (s, 1H,  $\text{CH=C-Ar}$ ); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 7.41 (d, 1H, Ar-H), 7.34 (d, 1H, Ar-H), 7.37 (dd, 1H, Ar-H), 7.29 (dd, 1H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  ppm: 164.2, 130.1, 177.2, 131.7, 125.8, 130.1, 134.2, 115.6, 140.4, 30.3, 150.1, 133.2, 133.8, 129.7, 129.8, 126.3, 127.6; MS ( $m/z$ , %): 298.74 [ $\text{M}^+$ ]; Elem. anal. (%): C = 68.58, H = 4.06, N = 4.70, O = 10.75, Cl = 11.91.

**(Z)-3-(3-Chlorobenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3c):** Yield: 94 %; m.p. 223-225 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 3.43 (s, 3H,  $\text{CH}_3\text{-N}$ ); 8.61 (s, 1H,  $\text{CH=C-Ar}$ ); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 7.31 (s, 1H, Ar-H), 7.39 (d, 1H, Ar-H), 7.32 (dd, 1H, Ar-H), 7.44 (d, 1H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  ppm: 164.2, 130.2, 177.5, 133.1, 125.8, 129.7, 133.9, 116.2, 140.1, 30.3, 149.7, 135.9, 126.5, 134.2, 128.1, 130.3, 126.7; MS ( $m/z$ , %): 298.74 [ $\text{M}^+$ ]; Elem. anal. (%): C = 68.58, H = 4.06, N = 4.70, O = 10.75, Cl = 11.91.

**(Z)-3-(4-Chlorobenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3d):** Yield: 95 %; m.p. 228-230 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 3.43 (s, 3H, CH<sub>3</sub>-N); 8.61 (s, 1H, CH=C-Ar); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H), 7.69 (d, 2H, Ar-H), 7.44 (d, 2H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.1, 130.7, 177.4, 132.2, 126.1, 129.7, 134.5, 116.1, 140.1, 30.4, 150.1, 131.2, 134.7, 128.6, 133.7, 128.7, 134.6; MS (*m/z* %): 298.74 [M<sup>+</sup>], Elem. anal. (%): C = 68.58, H = 4.06, N = 4.70, O = 10.75, Cl = 11.91.

**(Z)-1-Methyl-3-(2-nitrobenzylidene)quinoline-2,4-(1H,3H)-dione (3e):** Yield: 98 %; m.p. 210-212 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 3.43 (s, 3H, CH<sub>3</sub>-N); 8.91 (s, 1H, CH=C-Ar); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 8.19 (d, 1H, Ar-H), 8.01 (d, 1H, Ar-H), 7.78 (dd, 1H, Ar-H), 7.89 (dd, 1H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.1, 130.8, 177.3, 132.2, 125.6, 129.2, 134.2, 116.3, 140.1, 30.2, 150.1, 130.2, 148.1, 123.3, 128.9, 134.3, 130.3; MS (*m/z* %): 309.29 [M<sup>+</sup>]; Elem. anal. (%): C = 66.23, H = 3.92, N = 9.09, O = 20.76.

**(Z)-1-Methyl-3-(3-nitrobenzylidene)quinoline-2,4-(1H,3H)-dione (3f):** Yield: 92 %; m.p. 198-200 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 3.43 (s, 3H, CH<sub>3</sub>-N); 8.61 (s, 1H, CH=C-Ar); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 8.21 (s, 1H, Ar-H), 8.12 (d, 1H, Ar-H), 7.62 (dd, 1H, Ar-H), 7.93 (d, 1H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.2, 130.7, 177, 133.1, 125.2, 129.8, 134.6, 116.3, 140.3, 30.3, 150.1, 131.9, 125.7, 148.1, 123.3, 128.9, 124.1; MS (*m/z* %): 309.29 [M<sup>+</sup>]; Elem. anal. (%): C = 66.23, H = 3.92, N = 9.09, O = 20.76.

**(Z)-1-Methyl-3-(4-nitrobenzylidene)quinoline-2,4-(1H,3H)-dione (3g):** Yield: 96 %; m.p. 233-235 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 3.43 (s, 3H, CH<sub>3</sub>-N); 8.61 (s, 1H, CH=C-Ar); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H), 8.17 (d, 2H, Ar-H), 8.04 (d, 2H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.2, 130.7, 177.2, 133.2, 125.6, 129.8, 134.6, 116.3, 40.3, 30.1, 149.9, 139.2, 132.2, 123.7, 147.2, 123.7, 133.1; MS (*m/z* %): 309.29 [M<sup>+</sup>]; Elem. anal. (%): C = 66.23, H = 3.92, N = 9.09, O = 20.76.

**(Z)-3-(3-Hydroxybenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3h):** Yield: 92 %; m.p. 179-181 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 3.43 (s, 3H, CH<sub>3</sub>-N); 8.61 (s, 1H, CH=C-Ar); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 6.70 (s, 1H, Ar-H), 6.86 (d, 1H, Ar-H), 5.34 (s, 1H, Ar-OH), 7.17 (d, 1H, Ar-H), 7.54 (dd, 1H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.3, 130.7, 177.6, 133.1, 126.1, 129.3, 134.7, 116.4, 140.9, 30.2, 149.3, 136.3, 112.5, 159.2, 115.1, 129.9, 121.3; MS (*m/z* %): 280.29 [M<sup>+</sup>]; Elem. anal. (%): C = 73.11, H = 4.69, N = 5.02, O = 17.19.

**(Z)-3-(4-Hydroxybenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3i):** Yield: 92 %; m.p. 202-204 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 3.43 (s, 3H, CH<sub>3</sub>-N); 8.61 (s, 1H, CH=C-Ar); 5.34 (s, 1H, Ar-OH); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H), 6.67 (d, 2H, Ar-H), 7.57 (d, 2H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.3, 130.7, 177.2, 133.2, 126.3, 129.7, 134.7, 116.3, 140.6, 30.1, 150.1, 125.8, 130.3, 116.2, 158.3, 116.2, 130.2; MS (*m/z* %): 280.29 [M<sup>+</sup>], Elem. anal. (%): C = 73.11, H = 4.69, N = 5.02, O = 17.19.

**(Z)-3-(3-Methoxybenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3j):** Yield: 96 %; m.p. 245-247 °C; 3.43 (s, 3H, CH<sub>3</sub>-N); δ 8.61(s, 1H, CH=C-Ar); δ 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 6.70 (s, 1H, Ar-H), 6.86 (d, 1H, Ar-H), 2.34 (s, 1H, Ar-CH<sub>3</sub>), 7.17 (d, 1H, Ar-H), 7.54 (dd, 1H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.8, 131.3, 177.2, 131.1, 124.7, 128.8, 134.1 (C7), 115.5 (C8), 140.1 (C9), 30.2 (C10), 149.9 (C11), 137.3, 114.1, 161.2, 114.3, 129.7, 121.6, 56.1; MS (*m/z* %): 294.32 [M<sup>+</sup>]; Elem. anal. (%): C = 73.71, H = 5.15, N = 4.78, O = 16.36.

**(Z)-3-(4-Methoxybenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3k):** Yield: 98 %; m.p. 257-259 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 3.43 (s, 3H, CH<sub>3</sub>-N); 8.61 (s, 1H, CH=C-Ar); 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H), 3.84 (s, 3H, Ar-H), 6.97 (d, 2H, Ar-H), 8.23 (d, 2H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.3, 130.9, 177.2, 131.2, 124.6, 128.7, 134.4 (C7), 115.6 (C8), 140.7 (C9), 30.1, 150.1, 125.7, 130.7, 115.3, 160.1, 114.5, 131.1, 56.2; MS (*m/z* %): 294.32 [M<sup>+</sup>]; Elem. anal. (%): C = 73.70, H = 5.14, N = 4.78, O = 16.36.

**(Z)-3-(3-Bromobenzylidene)-1-methylquinoline-2,4-(1H,3H)-dione (3l):** Yield: 95 %; m.p. 241-243 °C; 3.43 (s, 3H, CH<sub>3</sub>-N); δ 8.61 (s, 1H, CH=C-Ar); δ 8.01 (d, 1H, Ar-H); 7.86 (d, 1H, Ar-H); 7.71 (dd, 1H, Ar-H); 7.29 (dd, 1H, Ar-H); 6.70 (s, 1H, Ar-H), 6.86 (d, 1H, Ar-H), 7.17 (d, 1H, Ar-H), 7.54 (dd, 1H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ ppm: 164.6, 131.2, 176.4, 131.5, 124.9, 128.8, 134.3, 115.6, 140.7, 30.3, 150.2, 137.8, 130.1, 122.9, 130.8, 127.1, 128.3; MS (*m/z* %): 343.19 [M<sup>+</sup>]; Elem. anal. (%): C = 59.67, H = 3.53, N = 4.09, O = 9.35, Br = 23.35.

## RESULTS AND DISCUSSION

Initially, we screened various catalysts and solvent and solvent free condition for the set of reaction starting from 1-methyl-4-hydroxy quinolinone (1 mmol), substituted aryl aldehydes (1.1 mmol), solvent (15 mL) and 15 mol % of catalyst. The different solvents were examined such as H<sub>2</sub>O, EtOH and solvent free with catalyst as Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, boric acid, oxalic acid, KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (alum) and catalyst free condition under the conventional and microwave irradiation method (Table-1). We observed that an excellent yield was obtained in water under the catalyst free under microwave irradiation method (Table-1 entry 2).

An excellent yield of product in aqueous medium under the microwave irradiation technique (Table-1, entry 2), due to the role of water act as acid catalyst and the reaction more imitate using more energetic condition as microwave irradiation technique. If we tried catalyst such as Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, boric acid, oxalic acid, KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, here better yield was obtained in alum, water under the same reaction condition (Table-1, entry 7). Whereas under the solvent free condition the poor yield was obtained (Table-1, entry 8). The reaction performed in different time interval (Table-1, entry 1-9). If we increase the time of reaction more than three minutes there is no significant effect was observed on the yield of product (Table-1, entry 2). Thus we decided that all the examples were tested reasonably good to excellent yield in water and catalyst

TABLE-1  
SCREENING OF VARIOUS SOLVENTS AND CATALYSTS FOR THE SYNTHESIS OF COMPOUND **3a**

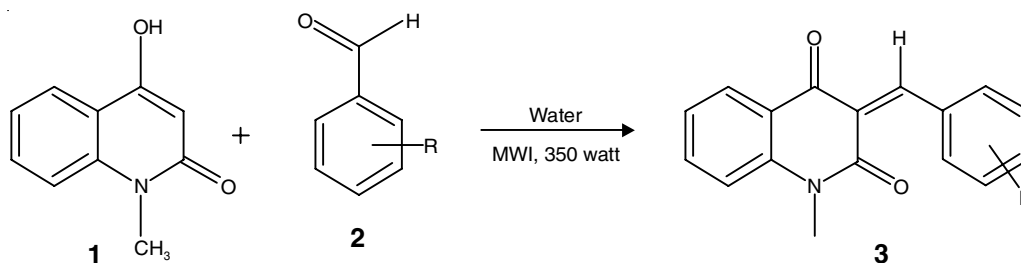
Entry	Catalyst	Solvent	Time (min) / Yield (%) <sup>b</sup>				
			Conventional method		Microwave method		
1	Without	Without	40/00	60/00	02/00	04/00	06/00
2	Without	H <sub>2</sub> O	40/82	60/86	01/38	03/90	04/98
3	Na <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	40/20	60/35	01/20	03/48	04/48
4	MgSO <sub>4</sub>	H <sub>2</sub> O	40/40	60/48	01/25	03/53	04/53
5	Boric acid	H <sub>2</sub> O	40/50	60/58	01/28	03/67	04/67
6	Oxalic acid	H <sub>2</sub> O	40/43	60/53	01/30	03/68	04/68
7	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	H <sub>2</sub> O	40/72	60/80	01/32	03/82	04/89
8	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	Without	40/43	60/49	01/20	03/58	04/58
9	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH	40/56	60/62	01/34	03/78	04/78

<sup>a</sup>Reaction condition: **1** (1 mmol, 175.18 g); **2** (1.1 mmol); solvent 15 mL and catalyst (15 mol %); <sup>b</sup>Isolated yield.

TABLE-2  
SYNTHESIS OF 1-METHYL, 3-BENZYLIDINE, QUINOLIN-2,4-DIONE DERIVATIVES IN WATER

Entry	Compound ( <b>3a-l</b> )	Substituent (R)	m.f.	Yield (%) / Time (min)	m.p. (°C)
1	<b>3a</b>	H	C <sub>17</sub> H <sub>13</sub> NO <sub>2</sub>	98/04	188-190
2	<b>3b</b>	2-Cl	C <sub>17</sub> H <sub>12</sub> NO <sub>2</sub> Cl	94/04	196-198
3	<b>3c</b>	3-Cl	C <sub>17</sub> H <sub>12</sub> NO <sub>2</sub> Cl	94/04	223-225
4	<b>3d</b>	4-Cl	C <sub>17</sub> H <sub>12</sub> NO <sub>2</sub> Cl	95/04	228-230
5	<b>3e</b>	2-NO <sub>2</sub>	C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	98/04	210-212
6	<b>3f</b>	3-NO <sub>2</sub>	C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	92/04	198-200
7	<b>3g</b>	4-NO <sub>2</sub>	C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	96/04	233-235
8	<b>3h</b>	3-OH	C <sub>17</sub> H <sub>13</sub> NO <sub>3</sub>	92/04	179-181
9	<b>3i</b>	4-OH	C <sub>17</sub> H <sub>13</sub> NO <sub>3</sub>	92/04	202-204
10	<b>3j</b>	3-OMe	C <sub>18</sub> H <sub>15</sub> NO <sub>3</sub>	96/04	245-247
11	<b>3k</b>	4-OMe	C <sub>18</sub> H <sub>15</sub> NO <sub>3</sub>	98/04	257-259
12	<b>3l</b>	3-Br	C <sub>17</sub> H <sub>12</sub> NO <sub>2</sub> Br	95/04	241-243

<sup>a</sup>Reaction condition: **1** (1 mmol, 175.18 g); **2** (1.1 mmol); solvent 15 mL and catalyst (15 mol %); <sup>b</sup>Isolated yield.



Scheme-I: Synthesis of 3-arylidine, N-methyl quinolon-2,4-dione (**3**)

free condition under the microwave irradiation technique (Table-2) yield 92-98 %. The electron donating substituent reacts well under the reaction condition, un-substituted arylaldehyde do reacts and gives good yield as compare to electron withdrawing substituted group (Table 2). Finally, the structures of the products were substantiated by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectrometry and elemental analysis.

## Conclusion

We have demonstrated that totally eco-friendly method for the synthesis of 1-methyl-3-benzylidene quinolin-2, 4-dione derivatives. The results illustrated that considerable potential of an in aqueous medium synthesis, thus method has the advantages of straightforward workup, avoided hazardous catalyst and solvent and to avoid chromatographic separation method, to obtained pure products, and further studies are progress in our laboratory to expand the synthetic utility of an eco-friendly catalyst or catalyst and solvent free condition.

## REFERENCES

- S.-L. Zhang, Z.-S. Huang, Y.-M. Li, A.S.C. Chan and L.-Q. Gu, *Tetrahedron*, **64**, 4403 (2008); <https://doi.org/10.1016/j.tet.2008.02.052>.
- B. Refouvet, C. Guyon, Y. Jacquot, C. Girard, H. Fein, F. Bévalot, J.-F. Robert, B. Heyd, G. Manton, L. Richert and A. Xicluna, *Eur. J. Med. Chem.*, **39**, 931 (2004); <https://doi.org/10.1016/j.ejmech.2004.07.006>.
- K. Arya and M. Agarwal, *Bioorg. Med. Chem. Lett.*, **17**, 86 (2007); <https://doi.org/10.1016/j.bmcl.2006.09.082>.
- A. van Oeveren, M. Motamedi, E. Martinborough, S. Zhao, Y. Shen, S. West, W. Chang, A. Kallel, K.B. Marschke, F.J. López, A. Negro-Vilar and L. Zhi, *Bioorg. Med. Chem. Lett.*, **17**, 1527 (2007); <https://doi.org/10.1016/j.bmcl.2007.01.001>.
- R. Kumabe and A. Nishino, *Tetrahedron Lett.*, **45**, 703 (2004); <https://doi.org/10.1016/j.tetlet.2003.11.054>.
- S. Chimichi, M. Bocalini, M.M.M. Hassan, G. Viola, F. Dall'Acqua and M. Curini, *Tetrahedron*, **62**, 90 (2006); <https://doi.org/10.1016/j.tet.2005.09.135>.



7. J. Jampilek, R. Musiol, M. Pesko, K. Kralova, M. Vejsova, J. Carroll, A. Coffey, J. Finster, D. Tabak, H. Niedbala, V. Kozik, J. Polanski, J. Csollei and J. Dohnal, *Molecules*, **14**, 1145 (2009); <https://doi.org/10.3390/molecules14031145>.
8. Y. Wu, Z. Chen, Y. Liu, L. Yu, L. Zhou, S. Yang and L. Lai, *Bioorg. Med. Chem.*, **19**, 3361 (2011); <https://doi.org/10.1016/j.bmc.2011.04.039>.
9. D. Villemain, M. Benabdallah, N. Choukchou-Braham and M.B. Mostefa-Kara, *Synth. Commun.*, **40**, 3109 (2010); <https://doi.org/10.1080/00397911003797916>.
10. J.H. Ye, K.Q. Ling Y. Zhang, N. Li and J.-H. Xu, *J. Chem. Soc. Perkin Trans. 1*, 2017 (1999); <https://doi.org/10.1039/A902728I>.
11. (a) V. Nair and S. Kumar, *Synlett*, 1143 (1996); <https://doi.org/10.1055/s-1996-5699>.  
(b) V. Nair, K.V. Radhakrishnan, A.G. Nair and M.M. Bhadbhade, *Tetrahedron Lett.*, **37**, 5623 (1996); [https://doi.org/10.1016/0040-4039\(96\)01172-0](https://doi.org/10.1016/0040-4039(96)01172-0).
12. (a) S.A. Jadhav, M.G. Shioorkar, O.S. Chavan, A.P. Sarkate, D.B. Shinde and R.K. Pardeshi, *Eur. J. Chem.*, **6**, 410 (2015); <https://doi.org/10.5155/eurjchem.6.4.410-416.1312>.  
(b) U.M. Lindstrom, *Organic Reactions in Water: Principles, Strategies and Applications*, Blackwell, Oxford (2007).
13. (a) C.J. Li, *Chem. Rev.*, **93**, 2023 (1993); <https://doi.org/10.1021/cr00022a004>.  
(b) C.J. Li, *Chem. Rev.*, **105**, 3095 (2005); <https://doi.org/10.1021/cr030009u>.
14. A. Chanda and V.V. Fokin, *Chem. Rev.*, **109**, 725 (2009); <https://doi.org/10.1021/cr800448q>.
15. (a) J.D. Moseley and C.O. Kappe, *Green Chem.*, **13**, 794 (2011); <https://doi.org/10.1039/c0gc00823k>.  
(b) P. Lidström, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, **57**, 9225 (2001); [https://doi.org/10.1016/S0040-4020\(01\)00906-1](https://doi.org/10.1016/S0040-4020(01)00906-1).  
(c) A. de la Hoz, Á. Díaz-Ortiz and A. Moreno, *Chem. Soc. Rev.*, **34**, 164 (2005); <https://doi.org/10.1039/B411438H>.  
(d) C.O. Kappe, *Chem. Soc. Rev.*, **37**, 1127 (2008); <https://doi.org/10.1039/b803001b>.
16. (a) Y. Sarrafi, M. Sadatshahabi, K. Alimohammadi and M. Tajbakhsh, *Green Chem.*, **13**, 2851 (2011); <https://doi.org/10.1039/c1gc15625j>.  
(b) J.D. Moseley and C.O. Kappe, *Green Chem.*, **13**, 794 (2011); <https://doi.org/10.1039/c0gc00823k>.  
(c) F. Ke, Y. Qu, Z. Jiang, Z. Li, D. Wu and X. Zhou, *Org. Lett.*, **13**, 454 (2011); <https://doi.org/10.1021/ol102784c>.  
(d) S. De, S. Dutta and B. Saha, *Green Chem.*, **13**, 2859 (2011); <https://doi.org/10.1039/c1gc15550d>.  
(e) X. Zhang, D. Ye, H. Sun, D. Guo, J. Wang, H. Huang, X. Zhang, H. Jiang and H. Liu, *Green Chem.*, **11**, 1881 (2009); <https://doi.org/10.1039/b916124b>.
17. P.T. Anastas and J.C. Warner, *Green Chemistry: Theory and Practice* Oxford University Press: New York, p. 30 (1998).
18. J.H. Clark, *Green Chem.*, **8**, 17 (2006); <https://doi.org/10.1039/B516637N>.
19. S.A. Jadhav, M.G. Shioorkar, O.S.M.A. Baseer and R.K. Pardeshi, *Elixir Org. Chem. Int. J.*, **90**, 37490 (2016).
20. S.A. Jadhav and R.K. Mazahar, *Heterocycl. Lett.*, **2**, 195 (2016).
21. S.A. Jadhav, M.G. Shioorkar, O.S. Chavan, A.P. Sarkate, D.B. Shinde and R.K. Pardeshi, *Eur. J. Chem.*, **6**, 410 (2015); <https://doi.org/10.5155/eurjchem.6.4.410-416.1312>.
22. S.A. Jadhav and R.K. Mazahar Farooqui, *Elixir Org. Chem. Int. J.*, **92**, 38824 (2016).
23. S.A. Jadhav, A.V. Raut, M. Farooqui, D.B. Shinde, A.P. Sarkate and R.K. Pardeshi, *Asian J. Org. Med. Chem.*, **1**, 91 (2016); <https://doi.org/10.14233/ajomc.2016.AJOMC-P28>.