

**ASCORBIC ACID AS A NATURAL GREEN, HIGHLY  
EFFICIENT AND ECONOMICAL CATALYST PROMOTED  
ONE-POT FACILE SYNTHESIS OF 12-ARYL-  
TETRAHYDROBENZO[ $\alpha$ ]XANTHENE-11-ONES, 1,8-DIOXO-  
OCTAHYDROXANTHENES AND 14-ARYL-14H-  
DIBENZO[A,J]XANTHENES UNDER SOLVENT-FREE  
CONDITIONS**

Farzaneh MOHAMADPOUR<sup>1\*</sup>

*A green, convenient and highly versatile procedure for the facile synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14H-dibenzo[ $\alpha$ ,j]xanthenes under solvent-free conditions is presented. This protocol is based on the use of ascorbic acid as a natural green and highly effective catalyst. A series of aromatic aldehydes afforded the various xanthenes derivatives in high to excellent yields during the relatively short reaction times. Furthermore, inexpensive and green catalyst, facile reaction profiles, solvent-free conditions, simple work-up procedure and one-pot synthesis are the noteworthy features of this economical green protocol.*

**Keywords:** Ascorbic acid, Solvent-free conditions, 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes, 14-aryl-14H-dibenzo[ $\alpha$ ,j]xanthenes

### 1. Introduction

Recently, the use of green catalysts has achieved considerable importance in green chemistry because of their applications as eco-friendly materials and green catalyst has become an important research area in synthetic chemistry. Also the principles of green chemistry have been introduced to reduce or eliminate of hazardous solvents. Due to considerable efforts from our group research have been focused on the development of multi-component reactions [1-4] at present of green catalyst [5-6].

In recent years, the use of ascorbic acid (Fig. 1) has received considerable attention in organic chemistry as a catalyst [7] because of its important advantages, such as green, natural, low-cost, high efficiently and also, it is well known that the ascorbic acid has many applications in the pharmacy and food.

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Because of the important antioxidant and metabolic functions of ascorbic acid it must therefore be incorporated as part of the human diet and is known as vitamin C. L-ascorbic acid in plants, the main source of vitamin C for humans, is also an essential compound for plants, with important roles as an antioxidant and as a modulator of plant development through hormone signaling [8].

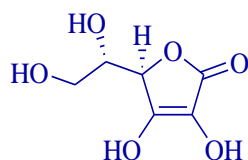


Fig. 1. Structure of ascorbic acid.

Synthesis of heterocyclic compounds has attracted great interests due to their wide applicability in life and nature. The compounds with xanthene derivatives ring systems are reported as antiplasmodial [9], antiviral [10], anti-inflammatory [11]. Besides, these heterocyclic molecules have been widely used as pH sensitive fluorescent materials for visualization of biomolecules [12, 13], laser technology [14, 15], luminescent dyes [16, 17] and sensitizers in photodynamic therapy [18, 19] (Fig. 2).

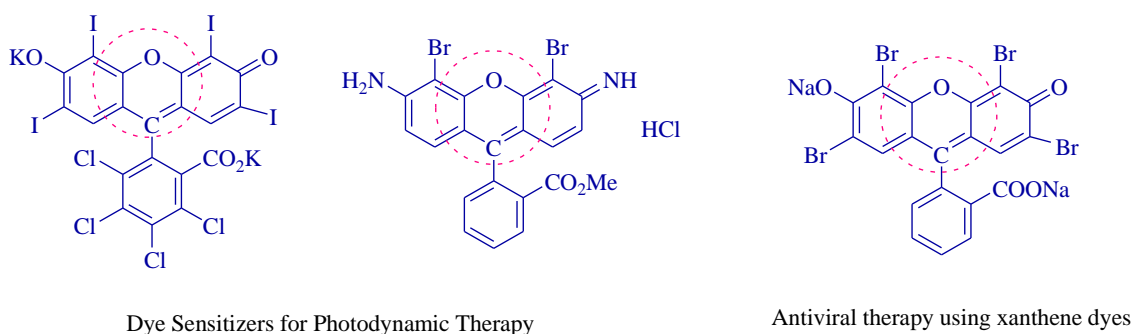


Fig. 2. Pharmaceutical active compounds with xanthene unit.

In recent decades, a number of methodologies for preparation of these compounds have been reported that is including various catalysts [20-37]. Some of these methodologies have limitations such as difficult work-up, toxic and expensive catalysts, low yields, use of strongly acidic conditions, long time reactions, high temperature. As part of our ongoing research program on the development of green methodologies, herein, we report a clean and facile one-pot synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[ $\alpha$ , $j$ ]xanthenes in the presence of catalytic amount of ascorbic acid under thermal and solvent-free conditions.

Green, efficient, readily, low-cost and non-toxic catalyst, high to excellent yields, short reaction times and eco-friendly that makes our protocol alternative in comparison to some of the earlier reported methods. Furthermore, one of the sources of environmental pollution is the usage of organic solvents under reflux conditions and the need for column chromatography to purify the products. In this present work, the products were obtained through simple filtering with no need for column chromatographic separation.

## 2. Experimental

### 2.1. General

Melting points of all compounds were determined using an Electro thermal 9100 apparatus. Also, nuclear magnetic resonance,  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX-400 Avance instrument with  $\text{CDCl}_3$  as solvents. In this article, all reagents and solvents were purchased from Merck, Fluka and Acros chemical companies and were used without further purification.

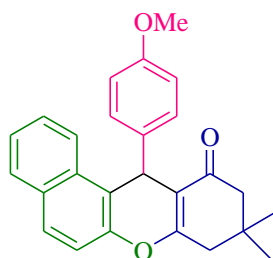
### 2.2. General procedure for preparation of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes

**Synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones (4):** A mixture of  $\beta$ -naphthol (**1**, 1.0 mmol), aromatic aldehyde derivatives (**2**, 1.0 mmol), dimedone (**3**, 1.0 mmol) and ascorbic acid (15 mol %) was heated at 70 °C for appropriate time. After completion of the reaction (by thin layer chromatography TLC) the mixture was cooled to r.t. and ethanol was added and the precipitated was separated with filtration and solid was recrystallized from ethanol to afford the pure products (**4a-l**).

**Synthesis of 1,8-dioxo-octahydroxanthenes (5):** A mixture of dimedone (**3**, 2.0 mmol), aromatic aldehyde derivatives (**2**, 1.0 mmol), and ascorbic acid (15 mol %) was heated at 70 °C for appropriate time. After completion of the reaction (by thin layer chromatography TLC) the mixture was cooled to r.t. and ethanol was added and the precipitated was separated with filtration and solid was recrystallized from ethanol to afford the pure products (**5a-l**).

**Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (6):** A mixture of  $\beta$ -naphthol (**1**, 2.0 mmol), aromatic aldehyde derivatives (**2**, 1.0 mmol) and ascorbic acid (15 mol %) was heated at 70 °C for appropriate time. After completion of the reaction (by thin layer chromatography TLC) the mixture was cooled to r.t. and ethanol was added and the precipitated was separated with filtration and solid was recrystallized from ethanol to afford the pure products (**6a-l**). The products have been characterized by melting points and  $^1\text{H}$  NMR spectroscopy. Spectra data of selected and known products are represented below:

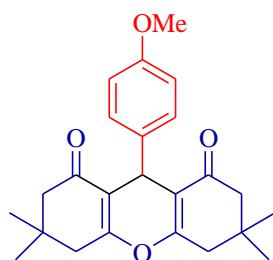
**9,9-dimethyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (4i):**



White solid; Yield: 87%; M.p. 200-202 °C.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 0.99 (3H, s,  $\text{CH}_3$ ), 1.12 (3H, s,  $\text{CH}_3$ ), 2.16-2.35 (2H, m,  $\text{CH}_2$ ), 2.58 (2H, s,  $\text{CH}_2$ ), 3.71 (3H, s,  $\text{OCH}_3$ ), 5.68 (1H, s,  $\text{CHAr}$ ), 6.72 (2H, d,  $J = 8.4$  Hz, ArH), 7.21-7.47 (5H, m, ArH), 7.85 (2H, t,  $J = 9.2$  Hz, ArH), 8.01 (1H, d,  $J = 8.4$  Hz, ArH).

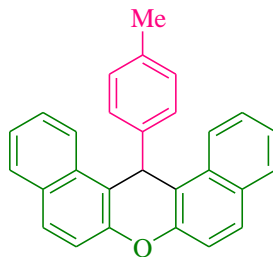
**3,3,6,6-tetramethyl-9-(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (5i):**



White solid; Yield: 91%; M.p. 241-243 °C.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 1.01 (6H, s,  $2\text{CH}_3$ ), 1.12 (6H, s,  $2\text{CH}_3$ ), 2.16-2.27 (4H, q,  $J = 8.2$  Hz,  $2\text{CH}_2$ ), 2.47 (4H, s,  $2\text{CH}_2$ ), 3.75 (3H, s,  $\text{OCH}_3$ ), 4.72 (1H, s, CH), 6.77 (2H, d,  $J = 8.8$  Hz, ArH), 7.22 (2H, d,  $J = 8.8$  Hz, ArH).

**14-(4-methylphenyl)-7,14-dihydro-dibenzo[a,j]xanthenes (6e):**

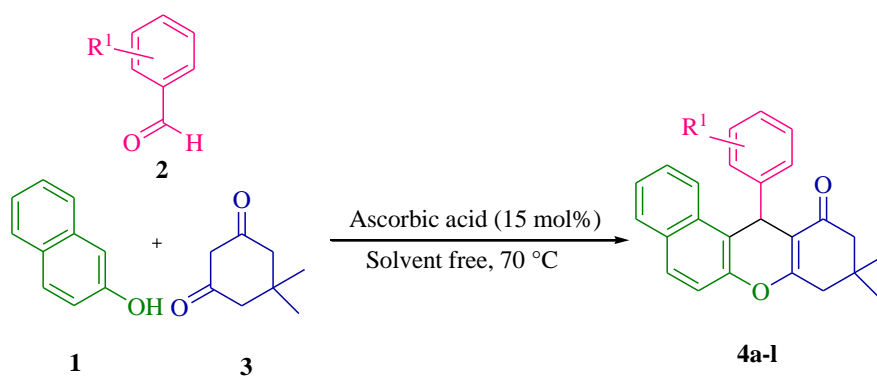


White solid; Yield: 90%; M.p. 227-229 °C.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 2.18 (3H, s,  $\text{CH}_3$ ), 6.47 (1H, s, CH), 6.81(1H, d,  $J=7.6$  Hz, ArH), 6.81(1H, t,  $J=7.6$  Hz, ArH), 7.40-7.85 (12H, m, ArH), 8.42 (2H,d,  $J= 8.8$  Hz, ArH).

### 3. Result and discussions

Initial study was performed by treatment of  $\beta$ -naphthol (**1**), benzaldehyde (**2**) and dimedone (**3**) under solvent-free conditions in the presence of ascorbic acid. Best results were obtained with molar ratio 1:1:1 for synthesis of 12-(phenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[ $\alpha$ ]xanthenes-11-one at 70 °C in the presence of 15 mol % of catalyst (Table1, entry 4). To demonstrate the generality of this method, we next investigated the scope of this reaction, and the results are summarized in Table 2 (Scheme 1). As shown in Table 2, this method is equally effective for both electron-donating and electron-withdrawing aldehydes derivatives. This reaction is economical, and free from side reactions. Also, green, inexpensive and non-toxic catalyst and the simplicity of operation, with no necessity of chromatographic purification steps, are other advantages of this environmental friendly procedure.



**Scheme1.** Synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones.

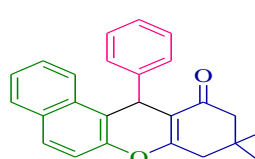
Optimization of the reaction condition for the synthesis of <b>4a</b> <sup>a</sup>				
Entry	Ascorbic acid (mol %)	Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	70	360	trace
2	5	70	35	56
3	10	70	20	78

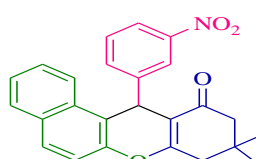
<b>4</b>	<b>15</b>	<b>70</b>	<b>15</b>	<b>92</b>
5	15	rt	360	trace
6	15	40	40	58
7	15	60	25	75
8	15	80	15	93
9	20	70	15	92

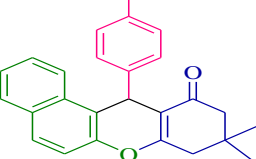
<sup>a</sup> Reaction conditions:  $\beta$ -naphthol (1.0 mmol); benzaldehyde (1.0 mmol); dimedone (1.0 mmol) and ascorbic acid was heated under various temperatures for the appropriate time.

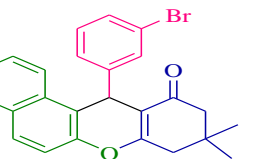
Table 2

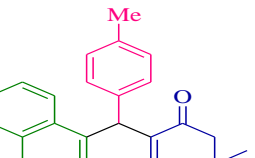
**Ascorbic acid catalyzed synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones**

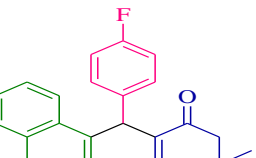
  
**4a**

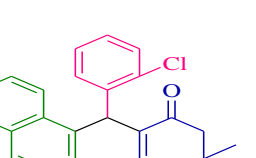
  
**4b**

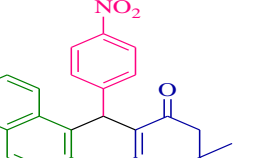
  
**4c**

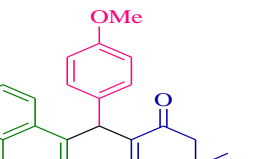
  
**4d**

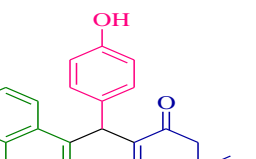
  
**4e**

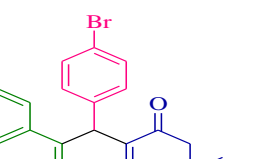
  
**4f**

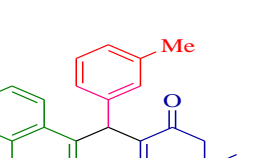
  
**4g**

  
**4h**

  
**4i**

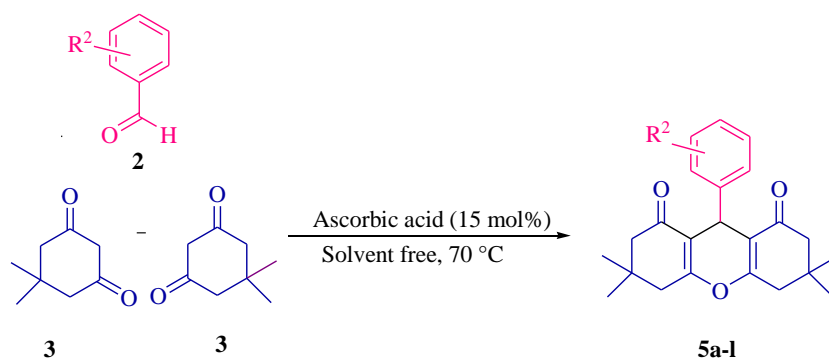
  
**4j**

  
**4k**

  
**4l**

Entry	R <sup>1</sup>	Product	Time (min)	Isolated Yields (%)	M.p. °C	M.p. °C
1	C <sub>6</sub> H <sub>5</sub>	<b>4a</b>	15	92	147-149	148-150 <sup>24</sup>
2	3-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	<b>4b</b>	15	93	165-167	167-169 <sup>20</sup>
3	4- Cl-C <sub>6</sub> H <sub>4</sub>	<b>4c</b>	20	86	177-179	176-178 <sup>24</sup>
4	3-Br- C <sub>6</sub> H <sub>4</sub>	<b>4d</b>	25	84	162-164	161-164 <sup>26</sup>
5	4-Me- C <sub>6</sub> H <sub>4</sub>	<b>4e</b>	15	89	171-173	171-173 <sup>24</sup>
6	4-F- C <sub>6</sub> H <sub>4</sub>	<b>4f</b>	10	94	182-184	184-185 <sup>20</sup>
7	2- Cl-C <sub>6</sub> H <sub>4</sub>	<b>4g</b>	20	87	178-180	179-180 <sup>27</sup>
8	4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	<b>4h</b>	15	91	176-178	175-178 <sup>26</sup>
9	4-OMe- C <sub>6</sub> H <sub>4</sub>	<b>4i</b>	20	87	200-202	202-204 <sup>24</sup>
10	4-OH- C <sub>6</sub> H <sub>4</sub>	<b>4j</b>	25	83	223-225	222-223 <sup>24</sup>
11	4-Br- C <sub>6</sub> H <sub>4</sub>	<b>4k</b>	25	82	183-185	184-186 <sup>24</sup>
12	3-Me- C <sub>6</sub> H <sub>4</sub>	<b>4l</b>	15	92	179-181	178-180 <sup>23</sup>

After the successful synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones, we turned our attention toward the synthesis of 1,8-dioxo-octahydroxanthenes. Herein, we found that ascorbic acid can efficiently catalyze between aromatic aldehyde derivatives (**2**, 1.0 mmol) and dimedone (**3**, 2.0 mmol) to give 1,8-dioxo-octahydroxanthenes. At first, the condensation of benzaldehyde (2.0 mmol) and dimedone (1.0 mmol) was examined in the presence of different amounts of ascorbic acid at range of rt-80 °C under solvent-free conditions in order to optimize the reaction conditions with respect to amount of the catalyst and temperature (Table 3). As Table 3 indicates, reasonable results were obtained when the reaction was performed using 15 mol % of the catalyst at 70°C (Table 3, entry 4). To assess the generality and scope of the methodology, the reaction was examined with aromatic aldehyde derivatives (**2**, 1.0 mmol) and dimedone (**3**, 2.0 mmol) (Scheme 2). As it is shown in Table 4, reactions of various aromatic aldehydes with dimedone proceeded efficiently and the desired products were obtained in high to excellent yields and in short reaction times.



Scheme 2. Synthesis of 1,8-dioxo-octahydroxanthenes.

Optimization of the reaction condition for the synthesis of 5a <sup>a</sup>				
Entry	Ascorbic acid (mol %)	Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	70	360	trace
2	5	70	25	62
3	10	70	15	81
<b>4</b>	<b>15</b>	<b>70</b>	<b>10</b>	<b>94</b>
5	15	rt	360	trace
6	15	40	30	64
7	15	60	15	78

8	15	80	10	94
9	20	70	10	95

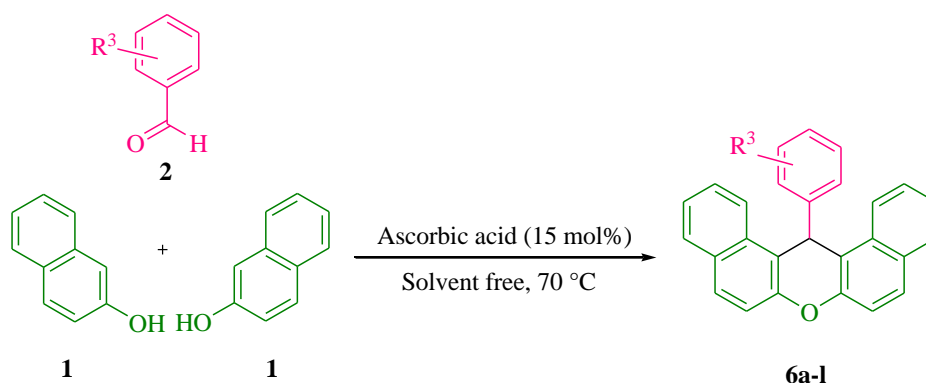
<sup>a</sup> Reaction conditions: dimedone (2.0 mmol); benzaldehyde (1.0 mmol) and ascorbic acid was heated under various temperatures for the appropriate time.

Ascorbic acid catalyzed synthesis of 1,8-dioxo-octahydroxanthenes							Table 4
Entry	R <sup>2</sup>	Product	Time (min)	Isolated Yields (%)	M.p. °C	M.p. °C	
1	C <sub>6</sub> H <sub>5</sub>	<b>5a</b>	10	94	206-208	206-208 <sup>24</sup>	
2	3-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	<b>5b</b>	10	91	170-172	171-172 <sup>20</sup>	
3	4- Cl-C <sub>6</sub> H <sub>4</sub>	<b>5c</b>	15	88	235-237	235-238 <sup>20</sup>	
4	3-Br- C <sub>6</sub> H <sub>4</sub>	<b>5d</b>	15	87	194-196	192-194 <sup>29</sup>	
5	4-Me- C <sub>6</sub> H <sub>4</sub>	<b>5e</b>	10	92	217-219	216-218 <sup>29</sup>	
6	4-F- C <sub>6</sub> H <sub>4</sub>	<b>5f</b>	10	95	192-194	193-195 <sup>24</sup>	
7	2- Cl-C <sub>6</sub> H <sub>4</sub>	<b>5g</b>	15	89	224-226	224-227 <sup>20</sup>	
8	4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	<b>5h</b>	10	94	221-223	222-224 <sup>29</sup>	
9	4-OMe- C <sub>6</sub> H <sub>4</sub>	<b>5i</b>	10	91	241-243	241-243 <sup>20</sup>	
10	4-OH- C <sub>6</sub> H <sub>4</sub>	<b>5j</b>	15	86	246-249	246-248 <sup>29</sup>	
11	4-Br- C <sub>6</sub> H <sub>4</sub>	<b>5k</b>	15	85	238-240	239-241 <sup>20</sup>	
12	3,4-(OMe) <sub>2</sub> - C <sub>6</sub> H <sub>3</sub>	<b>5l</b>	15	89	173-175	174-176 <sup>29</sup>	

In continuation of our work on the development of simple and environmental friendly synthesis of xanthene derivatives using ascorbic acid as a green catalyst synthesis of 14-aryl-14*H*-dibenzo[*α*,*j*]xanthenes by using of a one-pot multi-component domino reaction via  $\beta$ -naphthol (**1**, 2.0 mmol) and aromatic aldehydes



derivatives (**2**, 1.0 mmol) in the presence of ascorbic acid as a green catalyst at ambient temperature with high to excellent yields and short reaction times under solvent-free conditions (Table 6) (Scheme 3). As shown in Table 5, the reactions occurred excellently under solvent-free conditions. The experimental results indicate that the most effective conversion occurred when a 15 mol% of catalyst was used (Table 5, entry 4). Longer reaction times were required when lower amounts of ascorbic acid were employed. It is important to note that trace amount of 3, 4, 6, 7 - tetrahydro-3, 3, 6, 6 - tetramethyl - 9 - phenyl - 2*H* - xanthene-1, 8 (5*H*, 9*H*) - dione were afforded when the reactions were performed in the absence of ascorbic acid in the reaction mixture (Table 5, entry 1).

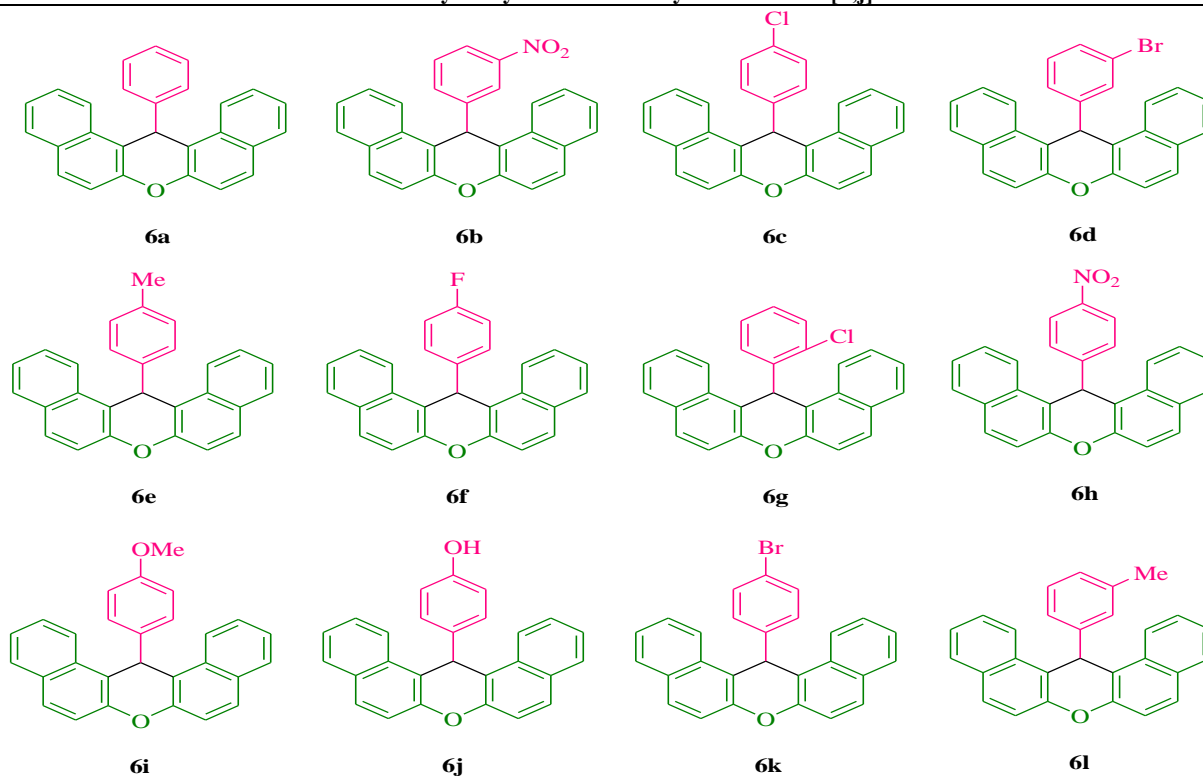


Scheme 3. Synthesis of 14-aryl-14*H*-dibenzo[ $\alpha$ , $j$ ]xanthenes.

Optimization of the reaction condition for the synthesis of <b>6a</b> <sup>a</sup>				
Entry	Ascorbic acid (mol %)	Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	70	360	trace
2	5	70	25	58
3	10	70	20	76
<b>4</b>	<b>15</b>	<b>70</b>	<b>10</b>	<b>91</b>
5	15	rt	360	Trace
6	15	40	35	61
7	15	60	15	75
8	15	80	10	91
9	20	70	10	92

<sup>a</sup> Reaction conditions:  $\beta$ -naphthol (2.0 mmol); benzaldehyde (1.0 mmol) and ascorbic acid was heated under various temperatures for the appropriate time.

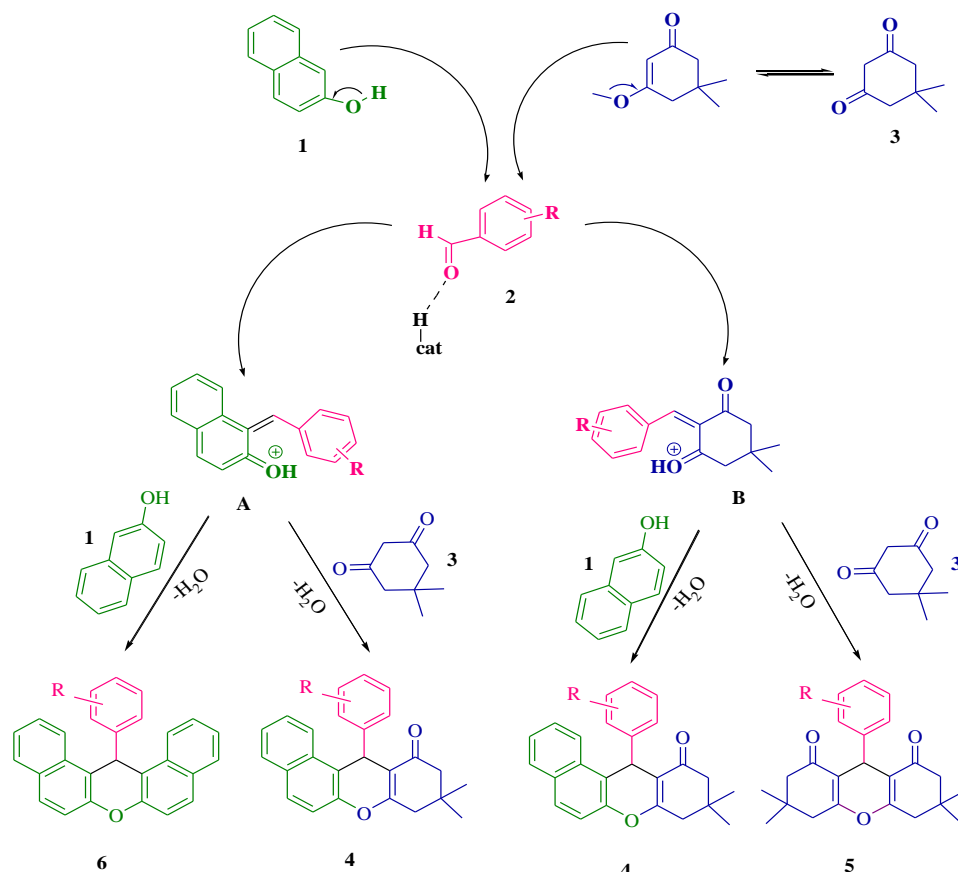
Table 6

Ascorbic acid catalyzed synthesis of 14-aryl-14*H*-dibenzo[ $\alpha$ , $j$ ]xanthenes

Entry	R <sup>3</sup>	Product	Time (min)	Isolated Yields (%)	M.p. °C	M.p. °C
1	C <sub>6</sub> H <sub>5</sub>	<b>6a</b>	10	91	183-185	183-184 <sup>37</sup>
2	3-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	<b>6b</b>	10	89	211-213	212-213 <sup>36</sup>
3	4-Cl-C <sub>6</sub> H <sub>4</sub>	<b>6c</b>	20	80	287-289	289-290 <sup>37</sup>
4	3-Br-C <sub>6</sub> H <sub>4</sub>	<b>6d</b>	20	84	192-194	191-193 <sup>20</sup>
5	4-Me-C <sub>6</sub> H <sub>4</sub>	<b>6e</b>	10	90	227-229	227-228 <sup>24</sup>
6	4-F-C <sub>6</sub> H <sub>4</sub>	<b>6f</b>	10	91	239-241	240-242 <sup>30</sup>
7	2-Cl-C <sub>6</sub> H <sub>4</sub>	<b>6g</b>	15	87	210-212	212-213 <sup>37</sup>
8	4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	<b>6h</b>	10	88	306-308	308-309 <sup>36</sup>
9	4-OMe-C <sub>6</sub> H <sub>4</sub>	<b>6i</b>	10	89	201-203	204-205 <sup>24</sup>
10	4-OH-C <sub>6</sub> H <sub>4</sub>	<b>6j</b>	25	83	136-138	138-140 <sup>36</sup>
11	4-Br-C <sub>6</sub> H <sub>4</sub>	<b>6k</b>	20	82	298-300	297-298 <sup>24</sup>
12	3-Me-C <sub>6</sub> H <sub>4</sub>	<b>6l</b>	10	93	196-198	197-198 <sup>36</sup>

And proposed mechanistic route for the synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones (**4**), 1,8-dioxo-octahydroxanthenes (**5**) and 14-aryl-14*H*-dibenzo[ $\alpha$ , $j$ ]xanthenes (**6**) in the presence of ascorbic acid are shown in scheme 4. On the basis of this mechanism, ascorbic acid donated the proton to the oxygen atom of the aldehyde and activates it. Then, nucleophilic  $\beta$ -naphthol (**1**) or dimedone (**3**) attacks the carbonyl group of the activated aldehyde and by removing H<sub>2</sub>O, the knoevenagel products (**A** or **B**) is generated. The following

addition of these intermediates to **1** or **3**, gives the acyclic adduct intermediate, which undergoes an intramolecular cyclization with the participation of two hydroxyl groups to afford the xanthene derivatives (Scheme 4).



**Scheme 4.** Proposed mechanistic route for the synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-one (**4**), 1,8-dioxo-octahydroxanthenes (**5**) and 14-aryl-14*H*-dibenzo[ $\alpha$ , $\beta$ ]xanthenes (**6**).

Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-one (**4**), 1,8-dioxo-octahydroxanthenes (**5**) and 14-aryl-14*H*-dibenzo[ $\alpha$ , $\beta$ ]xanthenes (**6**) are shown in Table 7, 8, 9.

Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones <sup>a</sup>				
Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H	Solvent-free, 110 °C	30 min/95	[20]
2	NaHSO <sub>4</sub> /SiO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> , Reflux	300 min/91	[21]
3	NO <sub>2</sub> -FePc/C	EtOH, Reflux	30 min/91%	[22]

4	DSIMHS	Solvent-free, 55 °C	20 min/93	[24]
5	CAN	Microwave irradiation, 120 °C	120 min/85	[25]
6	Sr(OTf) <sub>2</sub>	1,2-Dichloroethane, 80 °C	300 min/85	[28]
7	Ascorbic acid	Solvent-free, 70 °C	15 min/92	This work

<sup>a</sup> Based on the three-component reaction of  $\beta$ -naphthol (1.0 mmol); benzaldehyde (1.0 mmol) and dimedone (1.0 mmol).

Table 8				
Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 1,8-dioxo-octahydroxanthenes <sup>a</sup>				
Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H	Solvent-free, 110 °C	4 min/94	[20]
2	DSIMHS	Solvent-free, 55 °C	4 min/95	[24]
3	[cmmim][BF <sub>4</sub> ]	Microwave irradiation	2 min/92	[29]
4	[Hbim]BF <sub>4</sub>	Microwave irradiation	45 min/85	[31]
5	[BMim][BF <sub>4</sub> ]	Mg(BF <sub>4</sub> ) <sub>2</sub> , 80 °C	30 min/97	[32]
6	Ascorbic acid	Solvent-free, 70 °C	10 min/94	This work

<sup>a</sup> Based on the three-component reaction of dimedone (2.0 mmol) and benzaldehyde (1.0 mmol).

Table 9				
Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 14-aryl-14H-dibenzo[ $\alpha$ ,j]xanthenes <sup>a</sup>				
Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H	Solvent-free, 110 °C	30 min/94	[20]
2	DSIMHS	Solvent-free, 90 °C	3 min/94	[24]
3	[BMim][BF <sub>4</sub> ]	Mg(BF <sub>4</sub> ) <sub>2</sub> , 80 °C	15 min/95	[32]
4	SFP	Solvent-free, 90 °C	30 min/98	[33]
5	SiO <sub>2</sub> -Pr-SO <sub>3</sub> H	Solvent-free, 125 °C	20 min/98	[34]
6	[H-NMP][HSO <sub>4</sub> ]	Solvent-free, 110 °C	12 min/94	[36]
7	Diatomite-SO <sub>3</sub> H	Solvent-free, 90 °C	10 min/93	[37]
8	Ascorbic acid	Solvent-free, 70 °C	10 min/91	This work

<sup>a</sup> Based on the three-component reaction of  $\beta$ -naphthol (2.0 mmol) and benzaldehyde (1.0 mmol).

This study reveals that ascorbic acid has shown its extraordinary potential to be an alternative green, inexpensive, highly efficient, readily and versatile catalyst for eco-safe, one-pot and solvent-free synthesis of these heterocyclic compounds, in addition to high to excellent yields and short reaction times are the notable advantages this present methodology.

#### 4. Conclusions

In conclusion, a green, simple and efficient procedure has been developed using ascorbic acid as natural green catalyst for clean and facile synthesis of 12-aryl-tetrahydrobenzo[ $\alpha$ ]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14H-dibenzo[ $\alpha$ ,j]xanthenes under solvent-free reaction conditions. Use of safe, green, easily handled and low-cost ascorbic acid, operational simplicity, high

to excellent yields, solvent-free conditions with economic benefits and one-pot are among the other added advantages that make this approach an attractive alternative for the synthesis of target heterocycles.

### Acknowledgments

We gratefully acknowledge financial support from the Research council of the Young Researchers and Elite Club of Islamic Azad University of Shiraz.

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