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Salicylic Acid as a Bio-based and Natural Brønsted Acid Catalyst Promoted Green and Solvent-free Synthesis of Various Xanthene Derivatives

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1,8-Dioxo-octahydroxanthenes
14-Aryl-14*H*-dibenzo[α,j]xanthenes

ABSTRACT

In this research study, a green protocol for facile and eco-safe synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[α,j]xanthenes using salicylic acid as a bio-based and natural Brønsted acid catalyst in a one-pot, multi-component synthesis under solvent-free conditions is reported. The present methodology is an environmentally friendly approach for the synthesis of various xanthene derivatives. It also offers several merits including, good yields, short reaction times, efficient, eco-friendly, solvent-free conditions, and materials available.

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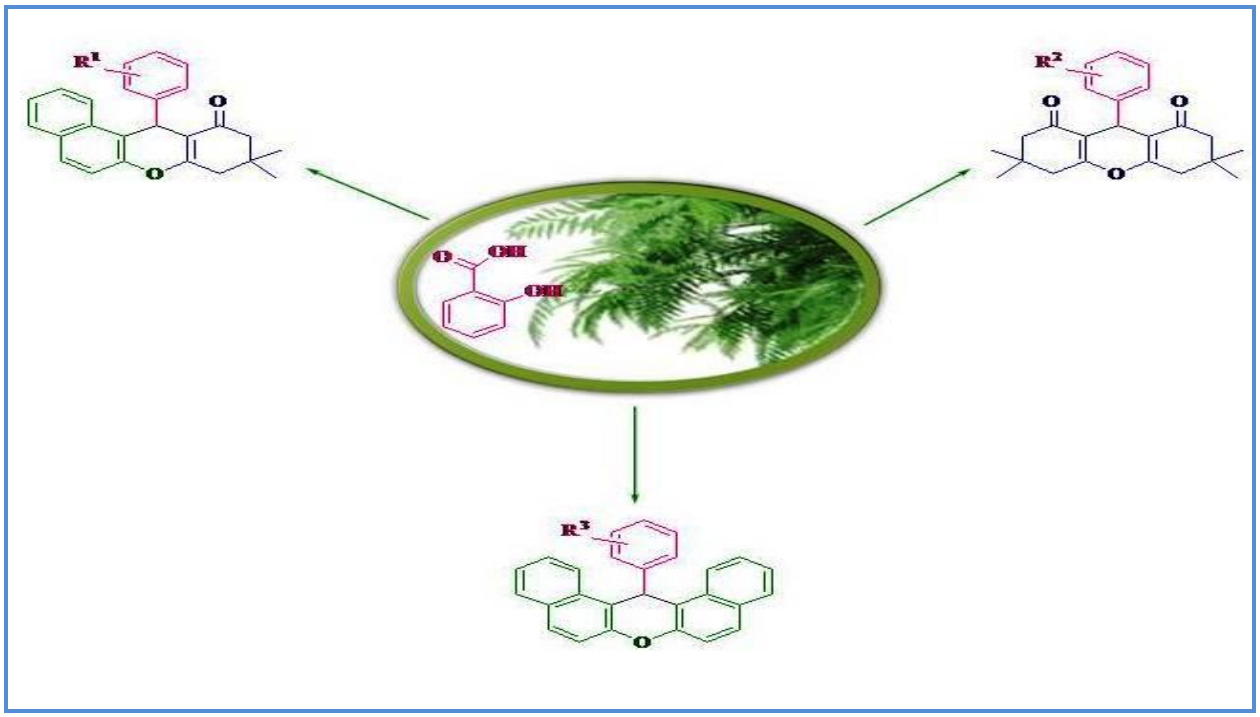
Graphical Abstract



Introduction

Over the last few decades, multi-component domino reactions (MCRs) [1-8] for the synthesis of fine chemicals have attracted considerable interest from both the environmental and eco-friendly points. Furthermore, mild, low-cost and one-pot operation is the notable advantages of these reactions.

In recent years, there has been much interest reported for the synthesis of xanthenes derivatives because of their specially pharmaceutical and biological activities. These compounds have been used as antiplasmodial [9], antiviral [10], and 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].

In recent decades, a number of methodologies for preparation of these compounds have been reported that include various catalysts Fe_3O_4@SiO_2–SO_3H [20], $NaHSO_4$·SiO_2 [21], NO_2–Fe(III)Pc/C [22], sulfamic acid [23], DSIMHS [24], ceric ammonium nitrate [25], trityl chloride [26], silica sulfuric acid [27], strontium triflate [28], [cmmim][BF_4] [29], zinc oxide nanoparticle [30], [Hbim]BF_4 [31], $Mg(BF_4)_2$ doped in [BMIm][BF_4] [32], sulfonic acid-functionalized phthalimide [33], SiO_2-Pr-SO_3H [34], nano-alumina sulfuric acid [35], [H-NMP][HSO_4] [36], sulfonated diatomite [37], and ascorbic acid [38].

Some of these methodologies have limitations such as difficult work-up, toxic and expensive catalysts, low yields, use of strongly acidic conditions and long time reactions.

Salicylic acid (SA) is a phenolic phytohormone and is found in plants (white willow (*Salix alba*) is a natural source of salicylic acid) (Figure 1) with roles in plant growth and development, photosynthesis, transpiration, ion uptake and transport [39, 40].

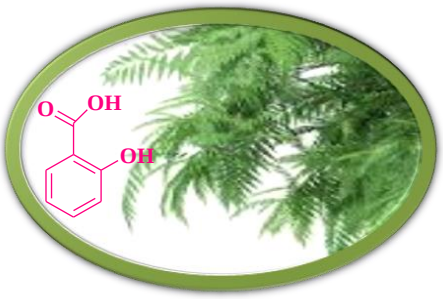


Figure 1. Structure of salicylic acid

As part of our ongoing research program on the development of green methodologies, we report a green and facile one-pot synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*α,j*]xanthenes in the presence of catalytic amount of salicylic acid under thermal and solvent-free conditions. Green, bio-based, efficient, readily and low-cost catalyst, good yields, short reaction times and eco-friendly make our protocol alternative in comparison to some of the earlier reported methods.

Experimental

General

Melting points of all compounds were determined using an electro thermal 9100 apparatus. Also, nuclear magnetic resonance, ^{1}H NMR spectra were recorded on a Bruker DRX-400 avance instruments with $CDCl_3$ as solvents. In this work, all the reagents and solvents were purchased from the Merck, Fluka and Acros chemical companies and were used without further purification.

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

Synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones (4)

A mixture of *β*-naphthol (**1**, 1.0 mmol), aromatic aldehyde derivatives (**2**, 1.0 mmol), dimedone (**3**, 1.0 mmol) and salicylic acid (20 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-k**).

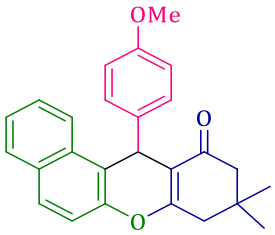
Synthesis of 1,8-dioxo-octahydroxanthenes (5): A mixture of dimedone (**3**, 2.0 mmol), aromatic aldehyde derivatives (**2**, 1.0 mmol), and salicylic acid (10 mol%) was heated at 70 °C for appropriate time. After completion of the reaction (by thin layer chromatography TLC) the mixture was cooled to 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-j**).

Synthesis of 14-aryl-14*H*-dibenzo[*α,j*]xanthenes (6)

A mixture of *β*-naphthol (**1**, 2.0 mmol), aromatic aldehyde derivatives (**2**, 1.0 mmol) and salicylic acid (20 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-k**). The products have been characterized by melting points and ^{1}H NMR spectroscopy. Spectra data of selected and known products are represented below.

Selected spectral data

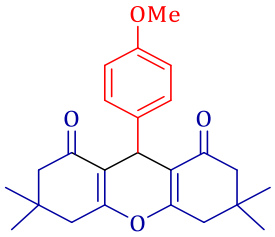
9,9-dimethyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4h)



White solid; yield: 82%; m.p. 201-203 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 0.99 (3H, s, CH_3), 1.12 (3H, s, CH_3), 2.16-2.35 (2H, m, CH_2), 2.58 (2H, s, CH_2), 3.71 (3H, s, OCH_3), 5.68 (1H, s, 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).

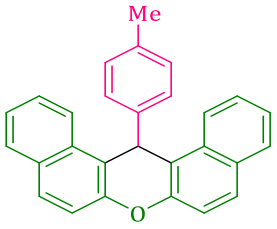
3,3,6,6-tetramethyl-9-(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (5d)



White solid; yield: 84%; m.p. 240-242 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (6H, s, $2CH_3$), 1.12 (6H, s, $2CH_3$), 2.16-2.27 (4H, q, *J*= 8.2 Hz, $2CH_2$), 2.47 (4H, s, $2CH_2$), 3.75 (3H, s, OCH_3), 4.72 (1H, s, CH), 6.77 (2H, d, *J*= 8.8Hz, ArH), 7.22 (2H, d, *J*= 8.8 Hz, ArH).

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

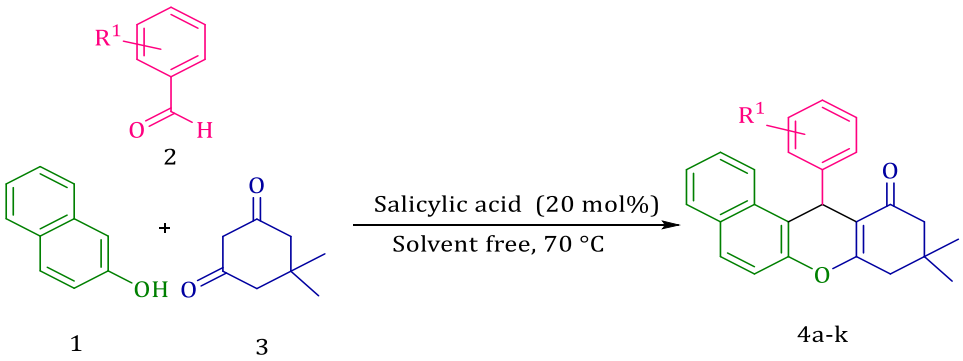


White solid; yield: 88%; m.p. 226-227 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 2.18 (3H, s, 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).

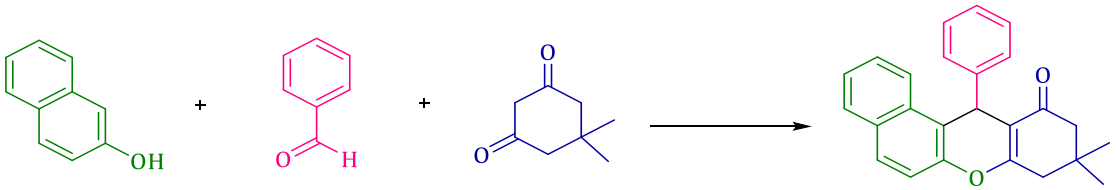
Results and discussion

Initial study was performed by treatment of the *β*-naphthol (**1**), benzaldehyde (**2**) and dimedone (**3**) under solvent-free conditions in the presence of salicylic acid. Best results were obtained with molar ratio 1:1:1 for synthesis of 12-(phenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*α*]xanthenes-11-one at 70 °C in the presence of 20 mol% of catalyst (Table1, entry 5). To demonstrate the generality of this method we investigated the scope of this reaction. The results are summarized in Table 2 (Scheme 1). As seen in Table 2, this method is equally effective for both electron-donating and electron-withdrawing aldehyde derivatives. This reaction is also economical, and free from side reactions. In addition, green, bio-based and inexpensive catalyst, simplicity of operation with no necessity of chromatographic purification steps is another advantage of this environmentally friendly procedure.



Scheme 1. Synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones

Table 1. Optimization of the reaction condition for the synthesis of **4a**[a]



Entry	Salicylic acid (mol %)	Temperature (°C)	Time (min)	Isolated yields (%)
1	Catalyst free	70	180	trace
2	5	70	50	37
3	10	70	30	54
4	15	70	15	69
5	20	70	10	88
6	20	rt	180	trace
7	20	40	75	29
8	20	50	45	48
9	20	60	20	71
10	20	80	10	88
11	25	70	10	87

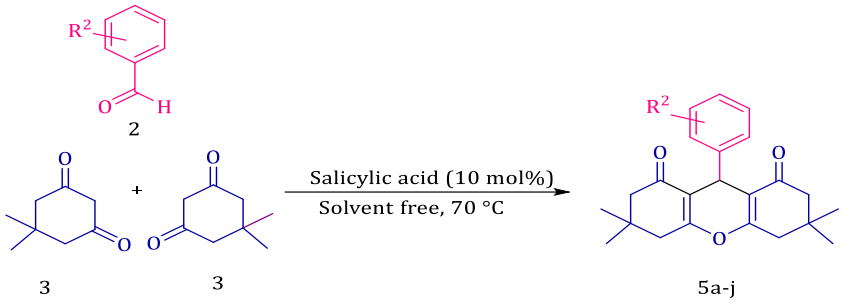
[a] Reaction conditions: *β*-naphthol (1.0 mmol); benzaldehyde (1.0 mmol); dimedone (1.0 mmol) and salicylic acid was heated under various temperatures for the appropriate time

Table 2. Salicylic acid catalyzed synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones

Entry	R^1	Product	Time (min)	Isolated yields (%)	M.p. °C	M.p. °C
1	C_6H_5	**4a**	10	88	150-152	148-150 [24]
2	4-Br-C_6H_4	**4b**	25	76	185-187	184-186 [24]
3	4-F-C_6H_4	**4c**	10	90	183-185	184-185 [20]
4	4-Cl-C_6H_4	**4d**	25	79	174-176	176-178 [24]
5	3-Br-C_6H_4	**4e**	25	75	161-163	161-164 [26]
6	4-OH-C_6H_4	**4f**	30	81	220-222	222-223 [24]
7	3-O_2N-C_6H_4	**4g**	10	89	167-169	167-169 [20]
8	4-OMe-C_6H_4	**4h**	15	82	201-203	202-204 [24]
9	3-Me-C_6H_4	**4i**	10	88	180-181	178-180 [23]
10	4-O_2N-C_6H_4	**4j**	10	86	177-179	175-178 [26]
11	4-Me-C_6H_4	**4k**	15	84	169-171	171-173 [24]

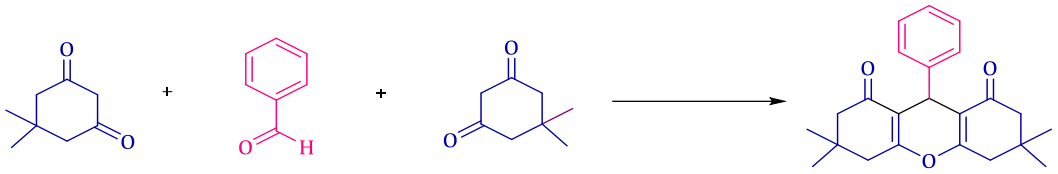
After the successful synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones, we turned our attention toward the synthesis of 1,8-dioxo-octahydroxanthenes. We found that, salicylic acid can efficiently catalyze between aromatic aldehyde derivatives (**2**, 1.0 mmol) and dimedone (**3**, 2.0 mmol) to give 1,8-dioxo-octahydroxanthenes. At first, the condensation of benzaldehyde (1.0 mmol) and dimedone (2.0 mmol) was examined in the presence of different amounts of salicylic 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 10 mol% of the catalyst at 70 °C (Table 3, entry 3). 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 demonstrated in Table 4, reactions of various aromatic aldehydes with dimedone proceeded efficiently and the desired products were obtained in good yields and in short reaction times.



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

Table 3. Optimization of the reaction condition for the synthesis of **5a**[a]



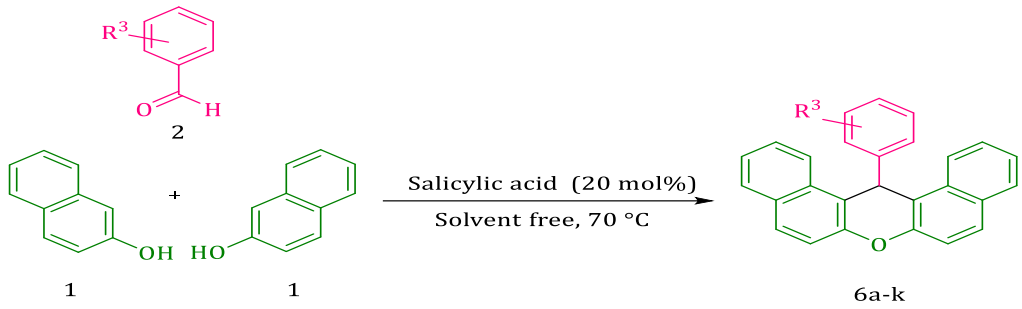
Entry	Salicylic acid (mol %)	Temperature (°C)	Time (min)	Isolated yields (%)
1	Catalyst free	70	180	trace
2	5	70	20	68
3	10	70	10	90
4	10	rt	180	trace
5	10	40	55	37
6	10	50	35	56
7	10	60	20	72
8	10	80	10	90
9	15	70	10	91

[a] Reaction conditions: dimedone (2.0 mmol); benzaldehyde (1.0 mmol) and salicylic acid was heated under various temperatures for the appropriate time

Table 4. Salicylic acidcatalyzed synthesis of 1,8-dioxo-octahydroxanthenes

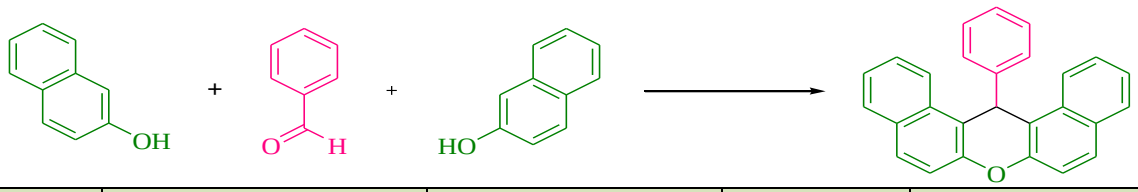
Entry	R^2	Product	Time (min)	Isolated yields (%)	M.p. °C	M.p. °C
1	C_6H_5	**5a**	10	90	205-207	206-208 [24]
2	4-F-C_6H_4	**5b**	10	92	193-195	193-195 [24]
3	3-O_2N-C_6H_4	**5c**	15	87	172-174	171-172 [20]
4	4-OMe-C_6H_4	**5d**	20	84	240-242	241-243 [20]
5	3,4-$(OMe)_2$- C_6H_3	**5e**	25	81	174-176	174-176 [29]
6	4-OH-C_6H_4	**5f**	30	78	245-247	246-248 [29]
7	4-Me-C_6H_4	**5g**	10	89	218-220	216-218 [29]
8	4-Br-C_6H_4	**5h**	30	76	241-243	239-241 [20]
9	4-Cl-C_6H_4	**5i**	25	82	236-238	235-238 [20]
10	4-O_2N-C_6H_4	**5j**	15	85	220-222	222-224 [29]

In continuation of our work on developing the simple and environmentally friendly synthesis of various xanthene derivatives using salicylic acid as a green and bio-based catalyst, we synthesized the 14-aryl-14*H*-dibenzo[*α,j*]xanthenesby using a one-pot multi-component domino reaction *via β*-naphthol (**1**, 2.0 mmol) and aromatic aldehyde derivatives (**2**, 1.0 mmol) at the presence of salicylic acid as a catalyst with good yields and short reaction times (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 20 mol% of catalyst at 70 °C was utilized (Table 5, entry 5). Longer reaction times were required when lower amounts of salicylic acid and temperatures 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 salicylic acid in the reaction mixture (Table 5, entry 1).



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

Table 5. Optimization of the reaction condition for the synthesis of **6a**[a]

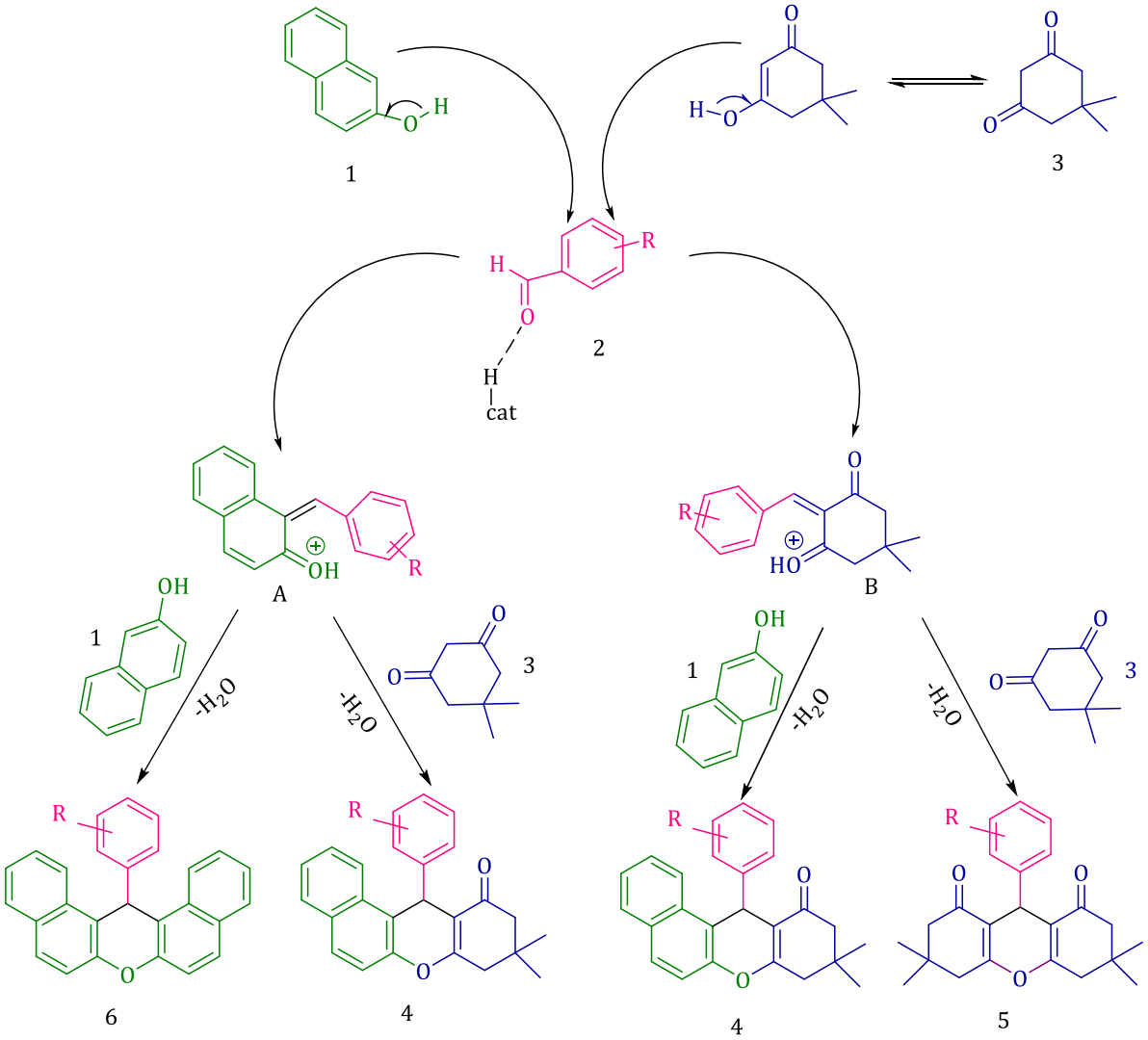


Entry	Salicylic acid (mol %)	Temperature (°C)	Time (min)	Isolated yields (%)
1	Catalyst free	70	180	trace
2	5	70	60	34
3	10	70	45	52
4	15	70	25	70
5	20	70	15	85
6	20	rt	180	Trace
7	20	40	60	32
8	20	50	40	47
9	20	60	25	64
10	20	80	15	84
11	25	70	15	87

[a] Reaction conditions: *β*-naphthol (2.0 mmol); benzaldehyde (1.0 mmol) and salicylic acid was heated under various temperatures for the appropriate time

Table 6. Salicylic acid catalyzed synthesis of 14-aryl-14*H*-dibenzo[*α,j*]xanthenes

Entry	R^3	Product	Time (min)	Isolated yields (%)	M.p. °C	M.p. °C
1	C_6H_5	**6a**	15	85	182-184	183-184 [37]
2	4-Br-C_6H_4	**6b**	35	74	295-297	297-298 [24]
3	2-Cl-C_6H_4	**6c**	25	81	213-215	212-213 [37]
4	3-O_2N-C_6H_4	**6d**	15	85	210-212	212-213 [36]
5	4-O_2N-C_6H_4	**6e**	15	82	307-309	308-309 [36]
6	4-Me-C_6H_4	**6f**	20	88	226-227	227-228 [24]
7	3-Me-C_6H_4	**6g**	15	86	198-200	197-198 [36]
8	4-OH-C_6H_4	**6h**	35	76	137-139	138-140 [36]
9	4-F-C_6H_4	**6i**	15	89	238-240	240-242 [30]
10	4-Cl-C_6H_4	**6j**	30	78	290-292	289-290 [37]
11	4-OMe-C_6H_4	**6k**	20	83	205-207	204-205 [24]



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

Proposed mechanistic route for the synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones (**4**), 1,8-dioxo-octahydroxanthenes (**5**) and 14-aryl-14*H*-dibenzo[*α,j*]xanthenes (**6**) at the presence of the salicylic acid are illustrated in Scheme 4. On the basis of this mechanism, salicylic acid donated the proton to the oxygen atom of the aldehyde and activates it. Then, nucleophilic *β*-naphthol (**1**) or dimedone (**3**) attacks the carbonyl group of the activated aldehyde and by removing H_2O, 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 various xanthene derivatives (Scheme 4).

Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-one (**4**), 1,8-dioxo-octahydroxanthenes (**5**) and 14-aryl-14*H*-dibenzo[*α,j*]xanthenes (**6**) are shown in Tables 7-9. This study reveals that salicylic acid has shown its extraordinary potential to be an alternative green, bio-based, inexpensive, highly efficient, readily and versatilecatalyst for eco-safe, one-pot and solvent-free synthesis of these heterocyclic compounds, in addition to good yields and short reaction times are the notable advantages this present methodology.

Table 7. Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones[a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Fe_3O_4@SiO_2-SO_3H	Solvent-free, 110 °C	30 min/95	[20]
2	$NaHSO_4/SiO_2$	CH_2Cl_2, Reflux	300 min/91	[21]
3	NO_2–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	$Sr(OTf)_2$	1,2-Dichloroethane, 80 °C	300 min/85	[28]
7	Salicylic acid	Solvent-free, 70 °C	10 min/88	This work

[a] Based on the three-component reaction of *β*-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[a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Fe_3O_4@SiO_2-SO_3H	Solvent-free, 110 °C	4 min/94	[20]
2	DSIMHS	Solvent-free, 55 °C	4 min/95	[24]
3	[cmmim][BF_4]	Microwave irradiation	2 min/92	[29]
4	[Hbim]BF_4	Microwave irradiation	45 min/85	[31]
5	[BMim][BF_4]	Mg (BF_4)$_2$, 80 °C	30 min/97	[32]
6	Salicylic acid	Solvent-free, 70 °C	10 min/90	This work

[a] 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-14*H*-dibenzo[*α,j*]xanthenes[a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Fe_3O_4@SiO_2-SO_3H	Solvent-free, 110 °C	30 min/94	[20]
2	DSIMHS	Solvent-free, 90 °C	3 min/94	[24]
3	[BMim][BF_4]	Mg (BF_4)$_2$, 80 °C	15 min/95	[32]
4	SFP	Solvent-free, 90 °C	30 min/98	[33]
5	SiO_2-Pr-SO_3H	Solvent-free, 125 °C	20 min/98	[34]
6	[H-NMP][HSO_4]	Solvent-free, 110 °C	12 min/94	[36]
7	Diatomite-SO_3H	Solvent-free, 90 °C	10 min/93	[37]
8	Salicylic acid	Solvent-free, 70 °C	15 min/85	This work

[a] Based on the three-component reaction of *β*-naphthol (2.0 mmol) and benzaldehyde (1.0 mmol)

Conclusion

In this work, expedient and convenient protocol were developed for the synthesis of 12-aryl-tetrahydrobenzo[*α*]xanthene-11-ones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*α,j*]xanthenes using the salicylic acid as a green and bio-based catalyst under solvent-free conditions. This protocol provided economic and highly efficient method for the synthesis of these biologically active compounds. Use of the inexpensive and easy handling of the salicylic acid as a green and bio-based catalyst, good yields, high catalytic efficiency, simple experimental, straightforward work-up with no column chromatographic separation, economic availability of the catalyst and environmentally benign nature procedure are the notable advantages of this one-pot and facile protocol. Also, the solvent-free conditions and time-saving aspects of the reaction suggest that this method presents real alternatives over the conventional reaction protocols.

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Conflict of Interest

We have no conflicts of interest to disclose.

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