

FACILE AND EFFICIENT SYNTHESIS OF XANTHENE DERIVATIVES MEDIATED BY LANTHANUM(III) NITRATE HEXAHYDRATE UNDER SOLVENT FREE CONDITIONS

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Abstract: The present paper shows that lanthanum(III) nitrate hexahydrate can be used as mild and environment friendly homogeneous catalyst for an efficient one-pot multi-component synthesis of biologically active 1,8-dioxo-octahydroxanthene and 14*H*-dibenzo[*a,j*]xanthene derivatives. The solvent free condensation reaction of aromatic aldehydes and dimedone or β -naphthol was carried out at 70-80°C during 10-30 min. The obtained compounds were analysed by mass and NMR spectroscopic techniques. The advantages of this eco-friendly synthesis route are numerous, and include the use of an inexpensive catalyst, high to excellent yield, short reaction time and high catalytic activity that can make this method an interesting alternative to multi-step approaches.

Keywords: lanthanum(III) nitrate, xanthene derivative, dimedone, β -naphthol, solvent free condition.

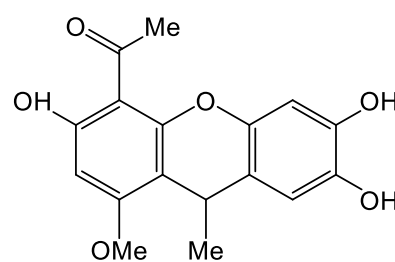
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Introduction

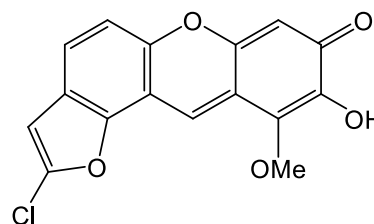
Recently, the synthesis of heterocyclic compounds such as xanthene and benzoxanthene derivatives has received great attention from researchers, because of their important pharmaceutical and biological properties such as anti-malarial [1], anti-inflammatory [2], photodynamic therapy [3]. Furthermore, xanthenes have been used as additives in the food industries [4,5], as dyes [6,7], as fluorescent materials [8], and in laser technologies [9]. In natural plants xanthenes are rare; the majority of them are synthesized or are present as microbial metabolites. To present date, xanthenes have been isolated only from plants of two families, *Fabaceae* and *Compositae*. Natural novel xanthenes, blumeaxanthene (A) and blumeaxanthene (B) have been isolated from *Blumea riparia* (Blume) DC (*Compositae* family), a Chinese medicinal herb traditionally used to treat gynecological disorders (Figure 1) [10].

Recently, several methods have been developed for the synthesis of xanthene derivatives using various catalysts, such as succinic acid [11], γ -Fe₂O₃ hydroxyapatite-Fe²⁺ nanoparticles [12], iron oxide nanoparticles (FeNP@SBA-15) [13], acetic acid [14], sulphamic acid [15,16], succinamide-*N*-sulphonic

acid [17], silica sulphuric acid [18], citric acid [19], lactic acid [20], tartaric acid [21], niobium pentachloride [22], *p*-toluenesulphonic acid [23,24], indium(III) chloride and metaphosphoric acid [25], silica functionalized propyl sulphonic acid [26], montmorillonite K₁₀ [27], iodine [28].



Blumeaxanthene (A)



Blumeaxanthene (B)

Figure 1. Examples of natural xanthene.

However, all of the synthetic protocols needed longer reaction time, high temperature, expensive and toxic catalyst, excess solvent and offered lower yields as compared to the present developed method; thus, the present work tries to overcome all these disadvantages with excellent yield.

In the past decades, lanthanum(III) nitrate based catalysts have attracted rising interests due to their versatility, and notable chemical and physical properties such high acidity, relevant stability, low toxicity, and easy to handle, low price and availability. The importance of lanthanum(III) nitrate as a homogeneous catalyst in biologically significant organic transformations has been highlighted in the literature [29-35]. Previously, lanthanum(III) nitrate was successfully used in the synthesis of 2-arylbenzothiazoles [36].

As a continuation of the ongoing work, the aim set for the present study was to develop a new method for the synthesis of xanthene derivatives using inexpensive, eco-friendly and non-hazardous homogeneous lanthanum(III) nitrate (10 mol%) as catalyst under solvent-free conditions.

Experimental

Generalities

The β -naphthol, dimedone, aromatic aldehyde, *n*-hexane, ethyl acetate and lanthanum(III) nitrate hexahydrate were purchased from Merck, S.D. fine-Chem and Sigma-Aldrich.

Melting point values of all compounds were recorded using the Contemp Melting Point Apparatus MEPOAP121 by the open tube capillary method; uncorrected values are given and compared with those reported in literature and found to be identical.

The progress of the reaction and the purity of the compounds were monitored by *thin-layer chromatography* (TLC), using analytical silica gel plates (Merck 60 F₂₅₄).

The ¹H and ¹³C NMR spectra were registered on a Bruker Avance Spectrometer 500 and 125 MHz, respectively, in CDCl₃ solvent and with tetramethylsilane (TMS) as internal standard. Chemical shift values were recorded as parts per million (ppm) and the coupling constants (*J*) were expressed in Hertz (Hz).

Mass spectra were recorded on a Bruker IMPACT HD mass spectrometer, applying the electrospray ionization (ESI) method. Also, the structures of some products were confirmed by ¹H and ¹³C NMR and mass spectral data.

General procedure for the synthesis of 14H-dibenzo[*a,j*]xanthene derivatives (Table 2, entry 1-6)

The reaction mixture of one of aromatic aldehydes **1a-i** (1 mmol), β -naphthol (**2**) (2 mmol) and lanthanum(III) nitrate (10 mol%) was prepared and heated at 80°C for an appropriate time. After completion of the reaction, the mixture was washed with cold water and the solid was separated by filtration. The crude product was recrystallized with ethanol.

*14-(4-Hydroxyphenyl)-14H-dibenzo[*a,j*]xanthene (3b)*. ¹H NMR: δ 4.73 (1H, br. s., OH), 6.42 (1H, s, CH), 6.56 (2H, d, *J*= 8.8, Ar-H), 7.35-7.58 (8H, m, Ar-H), 7.76-7.82 (4H, m, Ar-H), 8.34 (2H, d, *J*= 8.4, Ar-H), ¹³C NMR: δ 37.0, 115.2, 117.4, 118.0, 122.6, 124.2, 126.7, 128.7, 128.8, 129.3, 131.0, 131.3, 137.4, 148.6, 153.8. MS: *m/z*= 375 (M+H).

*14-(4-Chlorophenyl)-14H-dibenzo[*a,j*]xanthene (3c)*. ¹H NMR: δ 6.45 (1H, s, CH), 7.07 (2H, d, *J*= 9.3, ArH), 7.39-7.83 (12H, m, ArH), 8.29 (2H, d, *J*=9.5, ArH). ¹³C NMR: δ 37.3, 116.7, 118.0, 122.4, 124.3, 126.9, 128.6, 128.9, 129.0, 129.4, 131.0, 131.2, 132.0, 143.4, 148.7. MS: *m/z*= 393 (M+H).

*14-(3-Nitrophenyl)-14H-dibenzo[*a,j*]xanthene (3e)*. ¹H NMR: δ 6.58 (1H, s, CH), 7.25-7.85 (13H, m, ArH), 8.28 (2H, d, *J*= 7.5, ArH), 8.40 (1H, s, ArH). ¹³C NMR: δ 37.7, 115.8, 118.1, 121.7, 122.0, 122.7, 124.5, 127.2, 129.0, 129.5, 131.0, 134.2, 146.9, 148.2, 148.8. MS: *m/z*= 404 (M+H).

*14-(3,4-Dimethoxy phenyl)-14H-dibenzo[*a,j*]xanthene (3f)*. ¹H NMR: δ 3.68 (3H, s, OCH₃), 3.72 (3H, s, OCH₃), 6.44 (1H, s, CH), 6.65 (1H, d, *J*= 8.3, ArH), 6.91(1H, d, *J*= 1.7, ArH), 7.11-7.13 (1H, dd, *J*= 8.3, 1.8, ArH), 7.39-7.58 (6H, m, ArH), 7.77-7.83 (4H, m, ArH), 8.40 (2H, d, *J*= 8.4, ArH). ¹³C NMR: δ 37.4, 55.7, 110.7, 111.6, 117.4, 117.9, 120.3, 122.7, 124.2, 126.7, 128.7, 128.8, 131.1, 131.4, 137.6, 147.5, 148.7, 149.0. MS: *m/z*= 419 (M+H).

General procedure for the synthesis of 1,8-dioxo-octahydroxanthene derivatives (Table 2, entry 7-12)

The reaction mixture of one of aromatic aldehydes **1a-i** (1 mmol), dimedone (**4**) (2 mmol) and lanthanum(III) nitrate (10 mol%) was heated at 80°C for an appropriate time. After completion of the reaction, the mixture was washed with cold water and the solid was separated by filtration. The crude product was recrystallized with ethanol.

9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene (5b). ¹H NMR: δ 0.99 (6H, s, 2CH₃),

1.09 (6H, s, 2CH₃), 2.18(4H, d, *J*= 18.2, 2CH₂), 2.45 (4H, d, *J*= 16.2, 2CH₂), 3.73 (3H, s, OCH₃), 4.69 (1H, s, CH), 6.76 (2H, d, *J*= 8.8, Ar-H), 7.20 (2H, d, *J*= 8.8, Ar-H). ¹³C NMR: δ 27.3, 29.2, 30.9, 32.2, 40.8, 50.7, 55.1, 113.4, 115.8, 129.3, 136.5, 157.9, 162.0, 196.5. MS: *m/z*= 381 (M+H).

9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene

(**5d**). ¹H NMR: δ 0.99 (6H, s, 2CH₃), 1.12 (6H, s, 2CH₃), 2.15-2.27 (4H, d, *J*= 18.2, 2CH₂), 2.49 (4H, d, *J*= 16.2, 2CH₂), 4.82 (1H, s, CH), 7.48 (2H, d, *J*= 8.6, ArH), 8.08 (2H, d, *J*= 8.8, Ar-H). ¹³C NMR: δ 27.2, 29.2, 32.2, 32.3, 40.8, 50.6, 114.5, 123.4, 129.3, 146.4, 151.5, 162.9, 196.2. MS: *m/z*= 396 (M+H).

9-(2,4-dichlorophenyl)-1,8-dioxo-octahydroxanthene

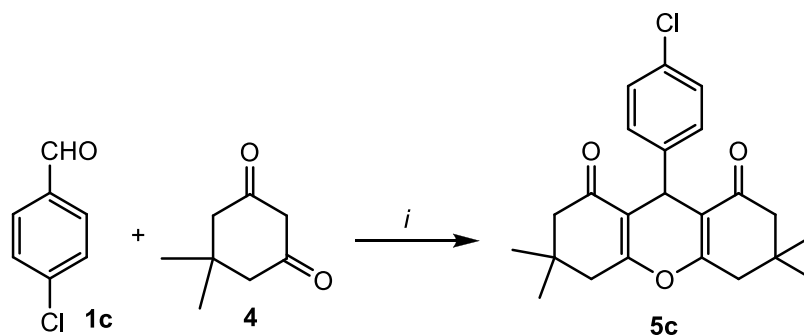
(**5e**). ¹H NMR: δ 1.01 (6H, s, 2CH₃), 1.10 (6H, s, 2CH₃), 2.17 (2H, d, *J*= 18.2, CH₂), 2.24 (2H, d, *J*= 18.2, CH₂), 2.44 (2H, d, *J*= 16.2, CH₂), 2.48 (2H, d, *J*= 16.2, CH₂), 4.94 (1H, s, CH), 7.13-7.15 (1H, d, *J*= 1.8, ArH), 7.24 (1H, dd, *J*= 8.3,1.8, Ar-H), 7.38 (1H, d, *J*= 8.3, ArH). ¹³C NMR: δ 27.3, 29.2, 32.0, 40.7, 50.6, 113.3, 126.7, 129.8, 132.7, 133.7, 134.0, 138.6, 163.2, 196.5. MS: *m/z*= 419 (M+H).

Results and discussion

Lanthanum(III) nitrate hexahydrate reagent was explored for the synthesis of 1,8-dioxo-octahydroxanthene and 14*H*-dibenzo[*a,j*]xanthene derivatives as an efficient catalyst. The solvent

free condensation reaction of aromatic aldehydes **1a-i** and dimedone (**4**) or β-naphthol (**2**) was carried out at 80°C. Initially, for reaction conditions optimization, the condensation reaction of dimedone (**4**) (2 mmol) and *p*-chlorobenzaldehyde (**1c**) (1 mmol) at 70-80°C under solvent-free condition was used as a model reaction (Scheme 1). When the reaction of *p*-chlorobenzaldehyde (**1c**) (1 mmol) was carried out with dimedone (**4**) (2 mmol) at 70°C in absence of lanthanum(III) nitrate catalyst, no significant amount of product formed (Table 1, entry 1). This means that the involvement of catalyst is necessary for the initiation of the reaction. By increasing the amount of catalyst used from 2 to 10 mol%, the yield gradually increased from 45 to 95% (Table 1, entries 2-6). The obtained results show that the best yield for the synthesis of compound **5c** were observed when using 10 mol% of the catalyst, the reaction completes in 10 min with a yield of 95% at 80°C (Table 1, entry 6).

Increasing the concentration from 10 to 20 mol% of lanthanum(III) nitrate, at 80°C, does not result in any noticeable changes in the reaction time or yields (Table 1, entries 7-9). Moreover, when the reaction temperature was increased, no improvement in the yield of the product was observed (Table 1, entries 5-7).



Reagent and conditions: *i*) lanthanum(III) nitrate, solvent free, 80°C, 10 min, 95%.

Scheme 1. Synthesis of 9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene (**5c**).

Table 1

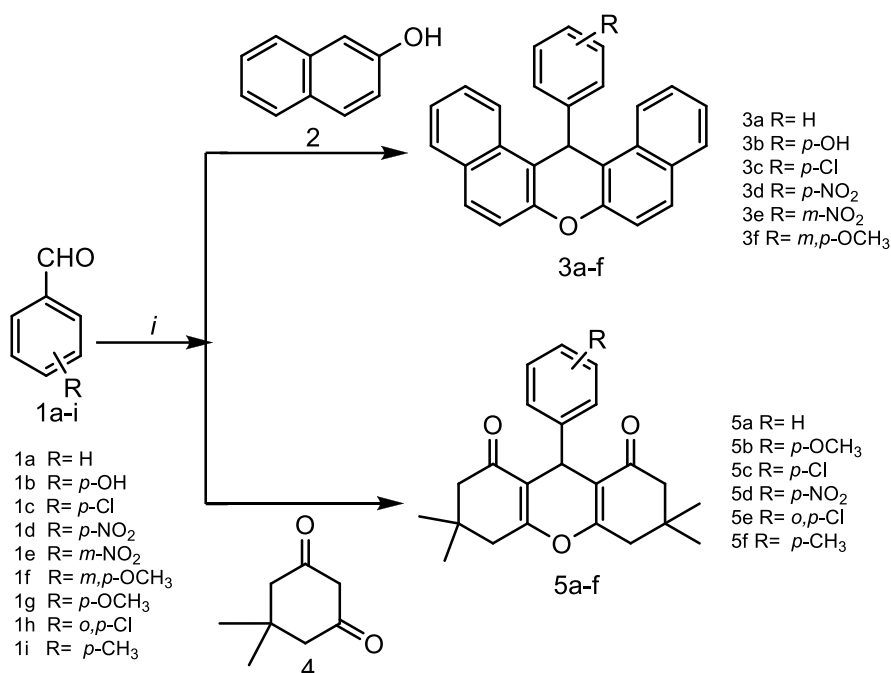
The optimization of reaction conditions^a for synthesis of **5c**.

Entry	Catalyst (mol%)	Temperature (°C)	Time (min)	Yield ^b (%)
1	-	70	60	No reaction
2	2	70	40	45
3	5	70	30	75
4	7	70	20	85
5	10	70	15	94
6	10	80	10	95
7	10	90	10	95
8	15	80	10	95
9	20	80	10	94

^aReaction conditions: *p*-chlorobenzaldehyde (**1c**) (1 mmol), dimedone (**4**) (2 mmol), lanthanum(III) nitrate (10 mol%) under solvent-free conditions. ^bIsolated yield.

Based on the optimized reaction conditions, the scope of this cyclization reaction was explored. The reaction of β -naphthol (**2**) or dimedone (**4**) with various aldehydes bearing electron-withdrawing and electron-donating group was carried out in the presence of lanthanum(III) nitrate under solvent-free reaction condition (Scheme 2). Aromatic aldehydes bearing both electron-withdrawing substituents and electron donating substituents showed better activity. All results are summarized in Table 2.

In order to find out the efficiency and greenness of the method, obtained results for the synthesis of xanthene derivative **3a** were compared with the pre-eminent data from the literature as shown in Table 3. It was noted that many of the formerly reported methodologies experience from one or more disadvantages such as necessity of excess amount of catalyst, high temperature, prolonged reaction time, use of volatile and toxic organic solvents. The present method helps avoiding the disadvantages within the formerly reported methodologies.



Reagent and conditions: *i*) lanthanum(III) nitrate, solvent free, 70-80°C, 10-30 min.

Scheme 2. General procedure for the synthesis of xanthene derivatives (5).

Table 2

Synthesis of xanthenes derivatives catalysed by lanthanum(III) nitrate.

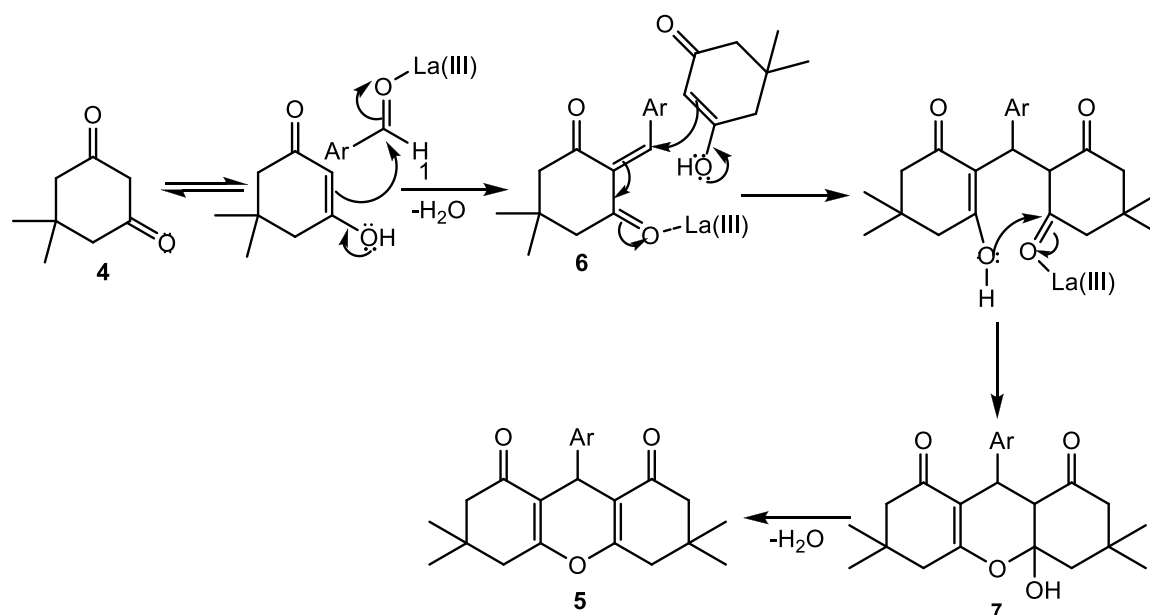
Entry	Aromatic aldehyde	Compound	Product	Time (min)	Yield ^b (%)	Melting point values (°C)	
						Found	Reported [Ref.]
1	C ₆ H ₅	2	3a	25	92	181-182	180-183 [14]
2	<i>p</i> -OH-C ₆ H ₄	2	3b	30	88	138-140	136-139 [21]
3	<i>p</i> -Cl-C ₆ H ₄	2	3c	20	94	287-290	286-289 [14]
4	<i>p</i> -NO ₂ -C ₆ H ₄	2	3d	20	94	307-309	306-308 [13]
5	<i>m</i> -NO ₂ -C ₆ H ₄	2	3e	22	92	212-213	211-213 [13]
6	<i>m, p</i> -OCH ₃ -C ₆ H ₃	2	3f	22	85	170-172	-
7	C ₆ H ₅	4	5a	10	94	202-204	203-206 [14]
8	<i>p</i> -OCH ₃ -C ₆ H ₄	4	5b	12	94	247-249	249-251 [14]
9	<i>p</i> -Cl-C ₆ H ₄	4	5c	10	95	230-232	231-233 [14]
10	<i>p</i> -NO ₂ -C ₆ H ₄	4	5d	10	95	228-230	229-231 [14]
11	<i>o, p</i> -Cl-C ₆ H ₃	4	5e	14	88	255-257	254-256 [14]
12	<i>p</i> -CH ₃ -C ₆ H ₄	4	5f	10	92	215-216	216-218 [15]

^aReaction conditions: aromatic aldehyde (1 mmol), β -naphthol (**2**) or dimedone (**4**) (2 mmol), lanthanum(III) nitrate (10 mol%) under solvent free conditions.

^bIsolated yield.

Table 3

Comparison of the efficiency of various catalysts used in the synthesis of 3a.				
Entry	Catalysts	Conditions/T (°C)	Time (h)	Yield % [Ref.]
1	Sulphamic acid	Solvent free/125	8	93 [15]
2	Silica sulphuric acid	Solvent free/80	0.75	89 [18]
3	Niobium pentachloride	DCM/ ambient temperature	48	90 [22]
4	Montmorillonite K10	Solvent free/120	3	75 [27]
5	Lanthanum(III) nitrate hexahydrate	Solvent free/80	0.41	92 [Present work]



Scheme 3. Proposed mechanism for the synthesis of xanthenes 5.

A plausible mechanism for the synthesis of xanthenes derivatives was proposed in Scheme 3. Due to the strong oxophilicity, lanthanum(III) nitrate appears to play a more efficient catalytic role. Initially, the carbonyl group of the aromatic aldehyde coordinates with lanthanum ion and facilitates the nucleophilic attack. Then, the carbon atom of the carbonyl group of aldehydes is attacked by the nucleophilic dimedone (**4**) to form Knoevenagel product **6**. Next, the subsequent addition of **6** with **4** gives the acyclic adduct intermediates, followed by intramolecular cyclization with the participation of two hydroxyl groups to give the xanthenes derivative **5**.

Conclusions

An efficient and green protocol for the synthesis of xanthenes derivatives was developed. The advantage of this method is the use of a one-pot multi-component reaction catalyzed by 10 mol% lanthanum(III) nitrate hexahydrate. Due to the strong oxophilicity, lanthanum(III) nitrate appears to play a more efficient catalytic role in the synthesis of xanthenes derivatives.

The obtained compounds were confirmed by mass and NMR spectroscopic techniques. The merit of the present synthesis protocol is the use of non-toxic catalyst, eco-friendliness, shorter reaction time, excellent yield and high catalytic activity which can make the proposed method an interesting alternative to multi-step approaches.

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