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An efficient one-pot solvent-free synthesis and photophysical properties of 9-aryl/alkyl-octahydroxanthene-1,8-diones

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ABSTRACT

A facile and efficient protocol for the synthesis of 9-aryl/alkyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-diones has been developed by one-pot reaction of dimedone with aldehydes in the presence of $InCl_3$ or P_2O_5 under solvent-free conditions. The optical behaviors of the xanthenediones have been investigated by UV–vis and fluorescence spectroscopy. The present approach offers the advantages of simple methodology, clean and mild reaction, high atom-economy, short reaction time, low environmental impact, wide substrate scope, high yield, and excellent purity.

1. Introduction

There are a number of environmental implications of the use of a large volume of organic solvents since they are utilized in larger quantities than the solutes they carry, and are wasted into the environment through evaporation and leakage. Because of the increasing concern for the harmful effects of organic solvents on the environment and human body, organic reactions that are operated without conventional organic solvents have aroused attention of organic chemists. Many organic reactions have been reported to proceed efficiently under solvent-free conditions and sometimes show enhanced selectivity[1] also. Therefore, more and more chemist's synthetic endeavors are devoted toward nature friendly synthesis[2a] to reduce drastic prerequisites for reactions. Among the proposed solutions, solvent-free conditions hold a leading position. So, it is now often claimed that 'the best solvent is no solvent'.[2b]

Xanthenes are important classes of organic compounds of a large number of naturally occurring as well as synthetic derivatives, and occupy a prominent position in medicinal chemistry.[3] They are important biologically active heterocyclic compounds possessing antiviral,[4] anti-inflammatory,[5] and antibacterial[6] activities. These are being utilized as antagonists for paralyzing action of zoxazolamine[7] and in photodynamic therapy.[8] Furthermore, these compounds can be used as dyes,[9] in laser technologies,[10] and as pH sensitive fluorescent materials for visualization of biomolecules.[11] In particular, xanthenediones constitute a key structural motif in a number of natural products,[12] and have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring.[13] Synthesis of xanthenediones is a continuing hot topic because these moieties are privileged pharmacophores as well as valuable reactive intermediates for both synthetic and medicinal chemists.

Several elegant strategies for the synthesis of xanthenediones involving different types of catalysts have been reported.[1j,14–20] The above methods show varying degrees of successes as well as limitations, such as prolonged reaction times, low yields, use of toxic and costly reagents/catalysts, harsh reaction conditions, and complex work-up procedures. Keeping in view the disadvantages associated with reported protocols as well as increasing importance of xanthenediones in pharmaceutical and industrial chemistry, there still remains a high demand for the development of more general, efficient, and eco-friendly protocol to assemble such scaffolds. Indium trichloride has emerged as a highly efficient and effective potential Lewis acid catalyst imparting high regio- and chemo-selectivity in various chemical transformations,[21] due to its low toxicity, air and water compatibility, operational simplicity, and remarkable ability to suppress side reactions in acid sensitive substrates. A literature survey shows that P_2O_5 is a mild and

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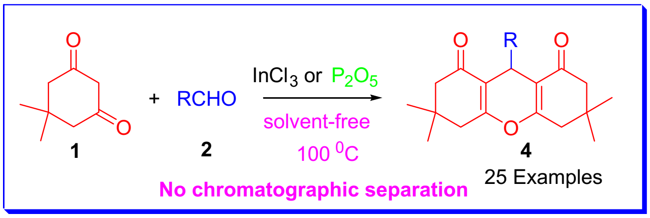
selective catalyst, easy to handle and readily biodegradable, and has been utilized widely in various organic transformations,[22] and given many advantages in several organic synthesis.[23]

2. Results and discussion

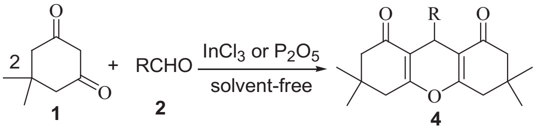
Our literature survey at this stage revealed that there are no reports on the use of $InCl_3$ or P_2O_5 as catalyst in the synthesis of octahydroxanthene-1,8-diones under solvent-free conditions. Our main strategy in this work is to develop a solvent-free organic reaction enhancement methodology, which is extremely fast and cleaner than conventional reactions, and lead to higher atom economy. In continuation of our interest in the area of clean synthesis under solvent-free conditions using $InCl_3$ or P_2O_5 as efficient and effective catalysts for the development of useful synthetic methodology[24] herein, we report a simple, efficient, and one-pot reaction of dimedone and aldehydes using $InCl_3$ or P_2O_5 at 100 °C for the preparation of 9-aryl/alkyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-diones in high yields (Scheme 1).



Scheme 1. $InCl_3$ and P_2O_5 promoted synthesis of 9-substituted tetramethyloctahydroxanthene-1,8-diones.

Initially, a blank reaction using 4-nitrobenzaldehyde and dimedone (mole rate 1:2) at 100 °C without $InCl_3$ or P_2O_5 was performed in order to establish the real effectiveness of the catalyst. We did not found the trace amount of desired product even after 12 h of heating. We then focused on optimizing the catalyst and its percentage loading. In order to evaluate the most appropriate catalyst loading, a model reaction using 4-nitrobenzaldehyde and dimedone (mole rate 1:2) was carried out using 5 mol %, 10 mol %, 15 mol %, and 20 mol % of $InCl_3$, and 10 mol %, 15 mol %, 20 mol %, and 25 mol % of P_2O_5 separately at different temperatures under solvent-free conditions (Table 1). It was found that 15 mol % of $InCl_3$ and 20 mol % of P_2O_5 showed maximum yield in minimum time at 100 °C (Table 1, entry 13). A further increasing of catalyst loading did not affect the yield (Table 1, entry 14). Herein, the reaction temperature was crucial in terms of the reaction rate and product yield. The above model reaction was carried out at different temperatures (60, 70, 80, and 100 °C) with 15 mol % of $InCl_3$ and 20 mol % of P_2O_5 loading separately. It was found that the desired compound **4b** was obtained in excellent yield at 100 °C (Table 1, entries 10–13). Further increase of the temperature (120 °C) neither increased the yield nor shortened the reaction time. The time taken for complete conversion (monitored by TLC) and the isolated yields at different temperatures are recorded in Table 1 for both the catalysts.

Table 1
Optimization of the catalyst on model reaction[a]



Entry	Temp (°C)	Method A ($InCl_3$) time/loading (%)/yield[b] (%)	Method B (P_2O_5) time/loading (%)/yield[b] (%)
1	100	12 h/no catalyst/0	12 h/no catalyst/0
2	60	2.0 h/5/87	2.5 h/10/90
3	70	1.5 h/5/90	2 h/10/88
4	80	80 min/5/92	1.5 h/10/89
5	100	70 min/5/94	80 min/10/92
6	60	1.5 h/10/88	1.75 h/15/87
7	70	75 min/10/87	1.5 h/15/85
8	80	60 min/10/91	70 min/15/90
9	100	40 min/10/93	45 min/15/92
10	60	75 min/15/82	85 min/20/82
11	70	60 min/15/90	65 min/20/84
12	80	30 min/15/92	40 min/20/91
13	100	15 min/15/98	20 min/20/96
14	100	20 min/20/98	23 min/25/96

[a] Reaction of 4-nitrobenzaldehyde (1 mmol) and dimedone (2 mmol) under solvent-free condition.

[b] Isolated pure yields.

With the optimized condition in hand, to explore the scope and generality of the reaction, we extended our study with other structurally varied aromatic, heteroaromatic, and aliphatic aldehydes to prepare a series of 9-aryl/heteroaryl/alkyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-diones (Table 2, entries 1–25). This protocol tolerates well aromatic aldehydes containing both electron-donating and electron-withdrawing substituents. The electronic effects and the nature of the substituents on the aldehydes show some obvious effects in terms of yields and reaction times. The aromatic aldehydes with electron-withdrawing groups as substrates reacted very well at faster rate and the reaction time is shorter compared with aromatic aldehydes with electron-donating groups. Though *meta*- and *para*-substituted aromatic aldehydes gave almost equally good results. However, *ortho*-substituted aromatic aldehydes turned out to be reluctant to undergo smooth reaction probably because of steric hindrance. Thus, longer reaction time is required for *ortho*-substituted aromatic aldehydes to get the corresponding products in high yields (Table 2, entries 3, 8, 12, and 17–22).

Table 2
Synthesis of tetramethyloctahydroxanthene-1,8-diones (**4a–y**)

Entry	R	Product	Time (min) $InCl_3/P_2O_5$	Yield[a] (%) $InCl_3/P_2O_5$
1	C_6H_5	**4a**	36/40	83/80
2	*p*-$NO_2 \cdot C_6H_4$	**4b**	15/20	98/96
3	*o*-$NO_2 \cdot C_6H_4$	**4c**	42/45	78/75
4	*m*-$NO_2 \cdot C_6H_4$	**4d**	27/32	87/82
5	*p*-$Me \cdot C_6H_4$	**4e**	35/40	85/81
6	*p*-$Cl \cdot C_6H_4$	**4f**	45/48	83/79
7	*m*-$Cl \cdot C_6H_4$	**4g**	35/40	90/88
8	*o*-$Cl \cdot C_6H_4$	**4h**	60/63	80/76
9	*p*-$Br \cdot C_6H_4$	**4i**	55/58	82/79
10	*p*-$F \cdot C_6H_4$	**4j**	32/36	88/85
11	*p*-$OMe \cdot C_6H_4$	**4k**	42/47	83/81
12	*o*-$OMe \cdot C_6H_4$	**4l**	55/60	79/78
13	4-$Me_2N \cdot C_6H_4$	**4m**	50/55	74/72
14	2,4-$Cl_2 \cdot C_6H_3$	**4n**	35/40	82/79
15	*p*-$OH \cdot C_6H_4$	**4o**	45/48	90/88
16	*m*-$OH \cdot C_6H_4$	**4p**	55/60	87/86
17	*o*-$OH \cdot C_6H_4$	**4q**	65/70	80/78
18	5-Br–2-$OH \cdot C_6H_3$	**4r**	60/65	83/80
19	5-NO_2–2-$OH \cdot C_6H_3$	**4s**	65/70	90/87
20	2-$OH \cdot C_{10}H_6$	**4t**	70/74	77/73
21	2-OH–3-$OEt \cdot C_6H_3$	**4u**	55/60	87/81
22	2-OH–3-$OMe \cdot C_6H_3$	**4v**	50/55	78/76
23	2-C_4H_3S	**4w**	25/30	70/68
24	$(CH_3)_2CH$	**4x**	65/70	60/58
25	$C_6H_5CH{=}CH$	**4y**	55/60	58/56

[a] Yields of isolated pure products.

In order to further investigate the scope of this reaction with aliphatic (isobutyraldehyde), heteroaromatic (thiophene-2-aldehyde), and α,β-unsaturated aldehyde (cinnamaldehyde) the reactions of dimedone were examined and found to produce the products in somewhat lower yields than those with aromatic aldehydes (Table 2, entries 23–25). However, furfuraldehyde under this protocol gave very poor yield of the expected product, which might be attributed toward the decomposition/polymerization of furfuraldehyde under the reaction condition. Also, acyclic ketone, such as 2,4-dioxopentane when treated with benzaldehyde/*p*-anisaldehyde failed to give the expected products under this protocol. The products were easily isolated in almost pure state simply by aqueous washing and extraction with ethyl acetate. The octahydroxanthene-1,8-diones, thus isolated were homogeneous on TLC and pure enough ($\geq$97% by ^{1}H NMR) for all practical purposes.

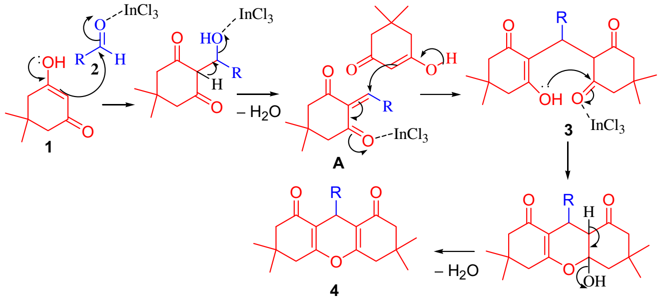
Finally, in order to show the accessibility of the present work we compared this method with the reported results in the literature (Table 3), which showed that $InCl_3$ and P_2O_5 are the most efficient catalysts with respect to the reaction time and temperature and exhibited broad applicability in terms of yields. The reason for the efficiency of the current procedure might be due to an enhanced second-order reaction rate resulting from ultimately high concentrations of reactants in the absence of solvent.

Table 3
Comparison of the efficiency of $InCl_3$ and P_2O_5 with reported catalysts for the synthesis of octahydroxanthene-1,8-diones

Entry	Catalyst	Temp (°C)	Time	Yield (%)	Ref.
1	*p*-DBSA	100	6–8 h	89–92	14a
2	CH_3SO_3H	120	1–1.5 h	90–95	14b
3	*p*-TSA	80	1–2.5 h	87–96	14c
4	TiO_2/SO_4^{2-}	rt	48 h	88–92	1j
5	Fe^{3+}-montmorillonite	100	6 h	84–94	15a
6	$InCl_3 \cdot 4H_2O$ in IL	80	4–10 h	83–95	15c
7	([Hmim]TFA)	80	3–4 h	82–93	15d
8	[TMPSA]-HSO_4/IL	100	1–2 h	88–95	15e
9	$NaHSO_4 \cdot SiO_2$ or Silica chloride	100	1213 h	88–94	16a
10	PPA/SiO_2	140	1012 h	54–82	16b
11	PMA/SiO_2	90	46 h	88–96	16c
12	Amberlyst-15	125	0.52 h	80–94	17a
13	SiO_2/H_2SO_4	80	12.5 h	88–97	17b
14	TBAHS	110	3–3.5 h	88–94	17c
15	Dowex-50W	100	2–4 h	78–91	17d
16	$SbCl_3/SiO_2$	120	1–1.5 h	85–93	18
17	TCT	120	1 h	88–95	19a
18	TMSCl	100	8–10 h	72–84	19b
19	$BiCl_3$	80	2–4 h	75–90	20
20	$InCl_3$ (5 mol %)	100	1.5–2.5 h	84–90	—
21	$InCl_3$ (10 mol %)	100	1.0–1.5 h	80–93	—
22	$InCl_3$ (15 mol %)	100	15–60 min	89–98	—
23	P_2O_5 (10 mol %)	100	1.5–2.0 h	84–92	—
24	P_2O_5 (15 mol %)	100	45–95 min	82–93	—
25	P_2O_5 (20 mol %)	100	20–70 min	88–97	—

In ^{1}H NMR spectra of compounds **4**, the four methyl groups form two sets of axial and equatorial methyl groups, hence appear differently giving rise to two singlets each with six hydrogens at around 0.99 ppm and at 1.12 ppm, respectively. Due to the possibility of free rotation and conformational considerations, the four methyl groups are not becoming equivalent and appear as two singlets at different chemical shifts in all the compounds showing axial and equatorial positions. The two methylene protons in the four positions are not equivalent due to adjacent substituents and ring conformation. They are located as axial and equatorial therefore, are non-equivalent and give rise to two doublets in the region 2.13–2.28 ppm (J=14.0 Hz). The proton at the bridge between the two dimedone rings appears normally in the region 4.6–4.8 ppm, and is not much affected by its neighboring substituents except in compounds **4t** and **4w**, in which it appears at somewhat lower fields at 5.25 ppm and 5.14 ppm, respectively. In ^{13}C NMR the two dimedone portion's carbon atoms were symmetrical and give rise to one signal for each set of carbons. The carbon at the bridge between the two dimedone rings appears around 40.1 ppm. The carbonyl carbons appear in the expected region around 195.3–200.9 ppm.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2. One molecule of dimedone **1** was firstly condensed with an aromatic aldehyde **2** to afford intermediate **A**, which can be regarded as a fast Knoevenagel addition. Then the active methylene of the second molecule of dimedone reacted with intermediate **A** via conjugate Michael addition to generate the intermediate **3**, which undergoes intramolecular cyclodehydration to give the octahydroxanthene-1,8-diones (**4**). P_2O_5 is not only a catalyst but also acts as a water scavenger, which plays an important role in acceleration of the reaction.



Scheme 2. Mechanism for the formation of octahydroxanthene-1,8-diones.

3. Photophysical properties

The hydroxanthenes or xanthenedione derivatives are supposed to exhibit optical behavior because of extended conjugation with inbuilt pyran ring. Therefore, we further extended our study to understand the optical behavior of synthesized hydroxanthene derivatives containing variable chromophores and auxochromes at different positions. In general, the UV–vis absorption spectra of some of the derivatives containing either electron-donating group like $-OH$, $-OCH_3$, and $-N(CH_3)_2$ or electron-withdrawing groups like $-NO_2$, $-Cl$, $-Br$, etc. have been recorded in different solvents, such as cyclohexane (Fig. 2), acetonitrile (Fig. 4), methanol (Fig. 6), and THF (Fig. 8) and their absorption bands are given in Table 4. In acetonitrile and tetrahydrofuran UV–vis absorption spectra appeared around 254–314 nm range and in polar protic solvent, such as MeOH, absorption bands appeared around 270–275 nm range. Comparatively in non-polar solvent like cyclohexane, xanthene derivatives containing $-NO_2$, $-Cl$, and $-OH$ substituents at *ortho-* and *para*-positions exhibited relatively higher absorption than the *meta*-substituted derivatives. However, in case of polar aprotic and protic solvents no such consistent effects of substituents were observed.

Similarly, the fluorescence behaviors of all the xanthene derivatives were investigated in different non-polar, polar-aprotic and polar-protic solvents (Table 4). In a non-polar aprotic solvent, such as cyclohexane (Fig. 1) relatively high fluorescence intensity at around 360 nm (Stokes shift 3539.79–6425.77 cm^{-1}) was observed. In acetonitrile (Fig. 3) upon excitation at the respective wavelengths, high energy band was observed at around 275–283 nm range. However, in the case of derivatives **4c**, **4h**, and **4y**, a broad low energy band was observed at around 333–345 nm range due to the presence of electron-withdrawing group at *ortho*-position, which extended conjugation in the skeleton of the xanthenes. However, in polar-protic solvent, such as methanol (Fig. 5) nitro-substituted derivative has shown a low energy band at around 365 nm due to interaction of substituents with xanthenedione ring. In case of THF (Fig. 7) beside high energy emission bands, a significant low intensity emission bands at around 402 and 423 nm were observed in the case of derivative **4t** that contains a naphthalene ring at position 9 of the xanthenedione skeleton. The observed low energy band may be attributed due to the formation of non-structured excimer fluorescence (Fig. 9), since upon increasing the concentration of probe the intensity of excimer fluorescence rises. The above behavior shows their potential application as new fluorescent probes or luminescence material.

Table 4

UV–vis and fluorescence data of all the derivatives of xanthene-1,8-dione (**4**)

Compound (**4**) R=	λ_{max}^{abs} (nm)				λ_{max}^{em} (nm)				ϵ (M^{-1} cm^{-1})				$\Delta\bar{\nu}$ (cm^{-1})				φ_f[a]			
	c-C_6H_{12}	THF	CH_3CN	CH_3OH	c-C_6H_{12}	THF	CH_3CN	CH_3OH	c-C_6H_{12}	THF	CH_3CN	CH_3OH	c-C_6H_{12}	THF	CH_3CN	CH_3OH	c-C_6H_{12}	THF	CH_3CN	CH_3OH
C_6H_5 (**4a**)	307	302	294	274	360	331	345	304	7400	17,000	5300	84,000	4795.51	2901.10	5028.09	3601.61	0.90	0.19	0.095	0.01
p-$NO_2\cdot C_6H_4$ (**4b**)	291	296	281	275	330	314	330	312	40,600	11,100	16,000	44,500	4061.23	1936.65	5284.16	4312.35	0.018	0.168	0.04	0.37
o-$NO_2\cdot C_6H_4$ (**4c**)	ND	302	253	274	ND	331	343	312	ND	7800	11,300	18,900	ND	2901.10	10371.17	4445.06	ND	0.052	0.186	0.145
m-$NO_2\cdot C_6H_4$ (**4d**)	ND	298	268	275	ND	312	ND	313	ND	7200	13,200	54,100	ND	1505.76	ND	4414.75	ND	0.135	ND	0.033
p-$Cl\cdot C_6H_4$ (**4f**)	307	302	294	281	359	331	345	305	9400	2100	5700	11,700	4718.13	2901.10	5028.09	2800.30	0.896	0.19	0.089	0.09
m-$Cl\cdot C_6H_4$ (**4g**)	295	301	293	274	364	330	344	304	14,200	2100	9500	5800	6425.77	2919.56	5059.92	3601.61	0.009	0.19	0.064	0.20
o-$Cl\cdot C_6H_4$ (**4h**)	305	277	ND	276	359	309	ND	304	9900	8300	ND	7500	4931.73	3738.62	ND	3337.1	0.876	0.114	ND	0.16
p-$Br\cdot C_6H_4$(**4i**)	285	277	294	274	344	310	347	303	22,600	16,200	5000	14,300	6017.95	3843.01	5195.16	3493.05	0.216	0.055	0.095	0.08
p-$F\cdot C_6H_4$ (**4j**)	295	302	294	274	356	332	345	304	7200	2300	5700	9600	5808.41	2992.10	5028.09	3601.61	0.91	0.16	0.086	0.103
p-$OMe\cdot C_6H_4$ (**4k**)	310	298	285	275	361	326	328	304	8300	3400	9500	22,000	4557.23	2882.20	4599.91	3468.89	0.952	0.16	0.072	0.047
4-$Me_2N\cdot C_6H_4$ (**4m**)	306	301	296	275	359	330	347	307	18,500	9000	14,300	51,200	4824.58	2919.56	4965.33	3790.34	0.431	0.069	0.431	0.017
2,4-$Cl_2\cdot C_6H_3$ (**4n**)	310	304	296	274	361	334	344	304	9300	14,000	5700	13,700	4557.23	4954.61	4714.06	3601.61	0.967	0.26	0.084	0.077
p-$OH\cdot C_6H_4$ (**4o**)	313	314	272	274	352	345	352	305	28,300	7400	44,200	34,100	3539.79	2861.62	8355.61	3709.46	0.019	0.043	0.014	0.034
m-$OH\cdot C_6H_4$ (**4p**)	295	299	286	276	359	328	331	305	22,100	4500	8500	14,700	6043.15	2957.01	4753.55	3444.99	0.215	0.12	0.078	0.073
o-$OH\cdot C_6H_4$ (**4q**)	305	313	247	272	360	348	283	304	28,600	2700	6200	24,400	5009.10	3213.24	5150.14	3869.96	0.254	0.23	0.234	0.044
5-Br–2-$OH\cdot C_6H_3$(**4r**)	313	ND	ND	272	361	ND	ND	306	8800	ND	ND	17,600	4248.05	ND	ND	4084.96	0.89	ND	ND	0.056
2-$OH\cdot C_{10}H_6$ (**4t**)	316	316	269	277	366	405, 427	359	313	7500	14,100	17,400	28,300	4323.16	8335.54	9319.56	4152.00	0.89	0.06	0.03	0.08
2-OH–3-$OEt\cdot C_6H_3$ (**4u**)	311	304	257	268	361	333	283	304	15,200	8300	19,500	19,300	4453.50	2864.70	3574.81	4418.69	0.55	0.05	0.121	0.053
2-OH–3-$OMe\cdot C_6H_3$ (**4v**)	314	276	262	268	363	310	283	306	13,200	1100	18,300	20,700	4298.92	3973.81	2832.24	4633.69	0.63	0.77	0.139	0.056
2-C_4H_3S (**4w**)	299	300	285	282	358	329	329	306	14,700	1100	7600	10,900	5511.85	2938.19	4692.58	2781.25	0.47	0.415	0.075	0.094
$(CH_3)_2CH$ (**4x**)	316	302	290	ND	361	331	344	ND	2400	400	5900	ND	3944.73	2901.10	5412.99	ND	0.94	0.92	0.122	ND
$C_6H_5CH{=}CH$ (**4y**)	315	300	231	ND	364	329	343	ND	3900	2600	26,400	ND	4273.50	2938.19	14135.52	ND	0.91	0.056	0.056	ND

φ_f=Quantum yield.
λ_{max}^{abs}=Absorbance maxima.
λ_{max}^{em}=Fluorescence maxima.
ϵ=Molar absorptivity.
$\Delta\bar{\nu}$=Stoke's shift.

[a] Quantum yield was calculated with respect to naphthalene in CH_3CN.

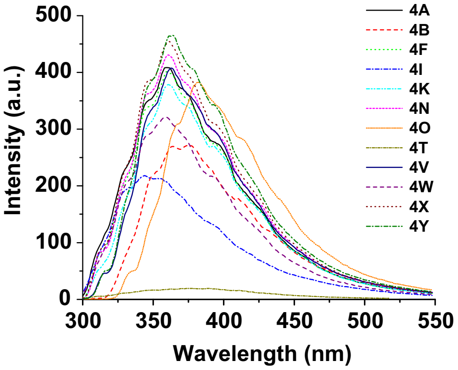


Fig. 1. Fluorescence spectra of some selected xanthenediones in cyclohexane solution (10^{-5} M) were collected using their corresponding λ_{max}^{abs}.

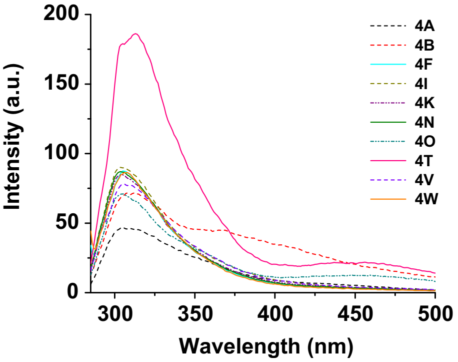


Fig. 5. Fluorescence spectra of some selected xanthenediones in methanol solution (10^{-5} M) were collected using their corresponding λ_{max}^{abs}.

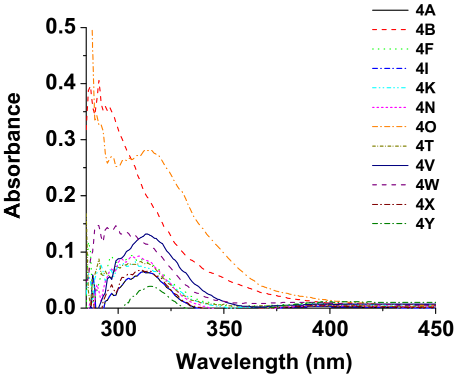


Fig. 2. UV–vis spectra of xanthenedione derivatives in cyclohexane solution (10^{-5} M).

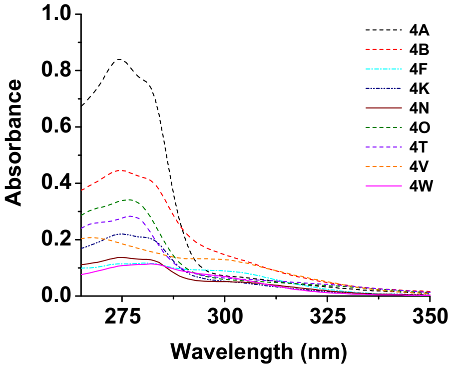


Fig. 6. UV–vis spectra of xanthenedione derivatives in methanol solution (10^{-5} M).

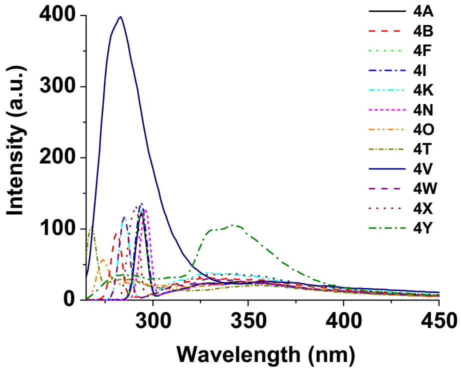


Fig. 3. Fluorescence spectra of some selected xanthendiones in CH_3CN solution (10^{-5} M) were collected using their corresponding λ_{max}^{abs}.

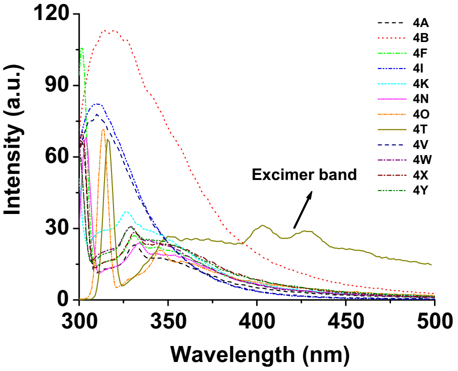


Fig. 7. Fluorescence spectra of some selected xanthenediones in THF solution (10^{-5} M) were collected using their corresponding λ_{max}^{abs}.

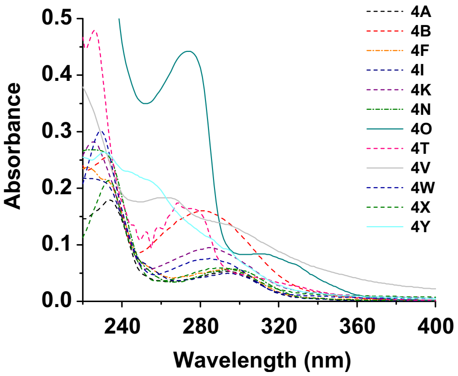


Fig. 4. UV–vis spectra of xanthendione derivatives in acetonitrile solution (10^{-5} M) were collected using there corresponding λ_{max}^{abs}.

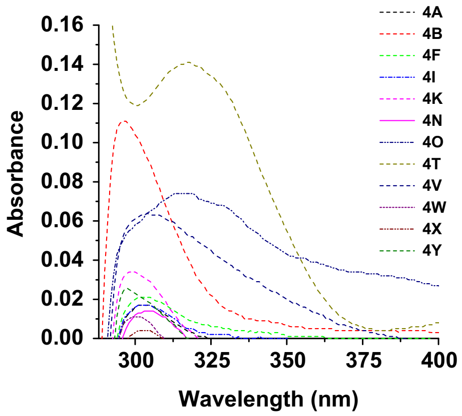


Fig. 8. UV–vis spectra of xanthenedione derivatives in THF solution (10^{-5} M).

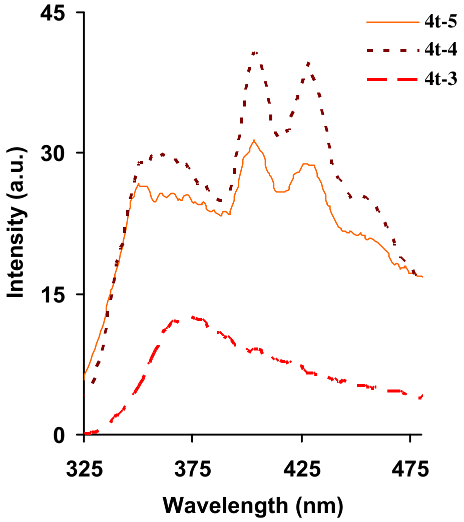


Fig. 9. Excimer fluorescence spectra of xanthenedione derivative **4t** in THF of 10^{-3} M, 10^{-4} M and 10^{-5} M solution.

4. Conclusion

In conclusion we have developed a convenient and atom-efficient protocol for the synthesis of 3,3,6,6-tetramethyl-9-aryl/heteroaryl/alkyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-diones. The remarkable catalytic activity of $InCl_3$ and P_2O_5 are superior to the reported other catalytic methods with respect to reduced reaction times. The pure products were obtained simply by aqueous washing and extraction with ethyl acetate. The higher yields, mild reaction condition, easy isolation and purification, and economic availability of the catalyst make the eco-friendly procedure an attractive alternative to the existing methods for the synthesis of octahydroxanthene-1,8-diones. Furthermore, the screening for optical properties showed that some products may have a good future as new luminescence materials or fluorescence probes.

5. Experimental section

5.1. General

All reagents were commercial and purchased from Merck, Aldrich and Fluka, and were used as received. All ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL 300 FT NMR spectrometer. Chemical shifts are given as δ value with reference to tetramethylsilane (TMS) as the internal standard. The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. The UV–vis absorption spectra were recorded on Shimadzu 1700 spectrophotometer using a quartz cuvette of 1 cm path length. Mass spectra were recorded at 70 eV ionizing voltage on a JEOL-D300 MS instrument. The C, H, and N analyses were performed with an Exeter Analytical Inc. ‘Model CE-400 CHN Analyzer’. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F_{254}) using UV light (254 nm/365 nm) for visualization. The fluorescence spectra were recorded at. Cary Eclipse fluorescence spectrophotometer. Melting points were determined with Büchi B-540 melting point apparatus and are uncorrected.

5.2. General procedure for the synthesis of 9-substituted-tetramethyloctahydroxanthene-1,8-diones (4)

To a nicely ground mixture of dimedone (2 mmol) and aldehyde (1 mmol), $InCl_3$ (15 mol %) or P_2O_5 (20 mol %) was added and the reaction mixture was heated at 100 °C for the appropriate period of time (Table 2). After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, water (25 mL) was added and extracted with ethyl acetate (3×20 mL). The combined organic extract was washed with water (2×15 mL), brine (1×25 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum to give the desired product, which was recrystallized from ethanol to afford the pure product. All products were characterized by elemental and spectral studies, and comparison of their physical and spectral data with those of reported ones. The spectral data of some representative and new octahydroxanthene-1,8-diones are given below.

*5.2.1. 9-Phenyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4a**).* White solid. Mp 204–205 °C. IR (KBr): 2954, 1664, 1364, 1199 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27–7.09 (m, 5H, ArH), 4.74 (s, 1H, CH), 2.46 (s, 4H, $2CH_2$), 2.19 (q, J=16.5 Hz, 4H, $2CH_2$), 1.10 (s, 6H, $2CH_3$), 0.98 (s, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.2, 162.3, 143.8, 128.4, 127.6, 115.2, 50.6, 40.7, 32.0, 31.6, 29.3, 27.2. EIMS (m/z): 350 (M^+). Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.47. Found: C, 78.96; H, 7.40.

*5.2.2. 9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4b**).* White solid. Mp 223–224 °C. IR (KBr): 2958, 1670, 1650, 1520, 1362, 1206, 870 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J=8.0 Hz, 2H, ArH), 7.46 (d, J=8.0 Hz, 2H, ArH), 4.82 (s, 1H, CH), 2.49 (s, 4H, $2CH_2$), 2.21 (q, J=16.2 Hz, 4H, $2CH_2$), 1.12 (s, 6H, $2CH_3$), 0.99 (s, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 162.9, 151.3, 146.6, 129.4, 123.5, 114.5, 50.5, 40.8, 32.3, 32.1, 29.6, 29.2, 27.2. EIMS (m/z): 395 (M^+). Anal. Calcd for $C_{23}H_{25}NO_5$: C, 69.85; H, 6.37; N, 3.54. Found: C, 69.96; H 6.49; N, 3.43.

*5.2.3. 9-(4-Methylphenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4e**).* White solid. Mp 213–215 °C. IR (KBr): 3030, 2980, 1685, 1660, 1620, 1490, 1365, 1200, 1135, 1000, 850, 840 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (d, J=8.0 Hz, 2H, ArH), 7.01 (d, J=8.0 Hz, 2H, ArH), 4.70 (s, 1H, CH), 2.45 (s, 4H, $2CH_2$), 2.23 (s, 3H, CH_3), 2.19 (q, J=16.3 Hz, 4H, $2CH_2$), 1.09 (s, 6H, $2CH_3$), 0.99 (s, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 162.1, 141.1, 135.7, 128.7, 128.1, 115.7, 50.7, 40.8, 32.1, 31.3, 29.2, 27.3, 20.9. EIMS (m/z): 364 (M^+). Anal. Calcd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 79.16; H 7.49.

*5.2.4. 9-(4-Hydroxyphenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4o**).* White solid. Mp 249–251 °C. IR (KBr): 3324, 2959, 1652, 1617, 1363 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (d, J=8.4 Hz, 2H, ArH), 6.60 (d, J=8.4 Hz, 2H, ArH), 5.72 (s, 1H, OH, D_2O exchangeable), 4.67 (s, 1H, CH), 2.45 (s, 4H, $2CH_2$), 2.20 (q, J=16.2 Hz, 4H, $2CH_2$), 1.09 (s, 6H, $2CH_3$), 0.99 (s, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 162.5, 140.7, 135.5, 128.2, 128.0, 115.2, 50.6, 40.1, 32.4, 31.2, 29.1, 27.2. EIMS (m/z): 366 (M^+). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.16; H 7.29.

*5.2.5. 9-(2-Hydroxynaphthyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4t**).* White solid. Mp 232–233 °C. IR (KBr): 3324, 2959, 1687, 1652, 1617, 1490, 1363, 1200, 1135, 1012, 854 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.65 (s, 1H, OH, D_2O exchangeable), 7.77–7.33 (m, 6H, ArH), 5.25 (s, 1H, CH), 2.60 (q, J=18.0 Hz, 2H, CH_2), 2.38 (s, 4H, $2CH_2$), 1.87 (q, J=16.8 Hz, 2H, CH_2), 1.15 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 0.70 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.9, 196.8, 170.2, 168.9, 148.7, 131.1, 130.8, 128.4, 128.3, 126.6, 124.5, 122.7, 117.5, 116.4, 116.0, 110.9, 50.6, 43.1, 41.2, 32.3, 30.5, 29.8, 26.9, 26.3, 25.2, 21.0, 14.1. EIMS (m/z): 416 (M^+). Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.74; H, 6.62.

*5.2.6. 9-(2-Hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4v**).* White solid. Mp 197–199 °C. IR (KBr): 3336, 2963, 1656, 1627, 1369 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.41 (s, 1H, OH, D_2O exchangeable), 6.96–6.91

(m, 1H, ArH), 6.75 (d, J=8.1 Hz, 1H, ArH), 6.58 (d, J=7.5 Hz, 1H, ArH), 4.65 (s, 1H, CH), 3.88 (s, 3H, OCH_3), 2.61 (q, J=17.4 Hz, 2H, CH_2), 2.36 (s, 2H, CH_2), 2.32 (s, 2H, CH_2), 1.96 (q, J=4.2 Hz, 2H, CH_2), 1.02 (s, 6H, $2CH_3$), 0.99 (s, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.3, 162.9, 140.4, 135.7, 128.3, 128.1, 114.9, 55.1, 50.2, 41.1, 32.6, 31.6, 29.3, 27.1. EIMS (m/z): 396 (M^+). Anal. Calcd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12. Found: C, 72.74; H, 7.69.

*5.2.7. 9-(2-Thienyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4w**).* White solid, Mp 161–162 °C. IR (KBr): 2956, 2895, 1658, 1622, 1496, 1199 cm^{-1}. ^1H NMR (300 MHz, $CDC1_3$): δ 7.01 (d, J=4.8 Hz, 1H, ArH), 6.96 (d, J=3.3 Hz, 1H, ArH), 6.83–6.81 (m, 1H, ArH), 5.14 (s, 1H, CH), 2.45 (s, 4H, $2CH_2$), 2.26 (s, 4H, $2CH_2$), 1.11 (s, 6H, $2CH_3$), 1.05 (s, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 162.6, 148.0, 126.6, 125.2, 123.3, 115.2, 50.7, 40.8, 32.0, 29.2, 27.3, 26.3. EIMS (m/z): 356 (M^+). Anal Calcd for $C_{21}H_{24}O_3S$: C, 70.78; H, 6.74. Found: C, 70.68; H, 6.63.

*5.2.8. 9-Isopropyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (**4x**).* White solid. Mp 146–147 °C. IR (KBr): 2950, 1690, 1645, 1612, 1460, 1370, 1210, 1145, 1022, 844 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (d, J=3.0 Hz, 1H, CH) 2.41–2.27 (m, 8H, $4CH_2$), 1.84–1.79 (m, 1H, CH), 1.13 (s, 6H, $2CH_3$), 1.11 (s, 6H, $2CH_3$), 0.75 (d, J=6.9 Hz, 6H, $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.9, 160.1, 113.5, 51.4, 44.1, 31.50, 30.2, 26.9, 25.6, 21.1, 15.8. EIMS (m/z): 316 (M^+). Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.74; H, 8.72.

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