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$ZrOCl_2 \cdot 8H_2O$: a highly efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthene derivatives under solvent-free conditions

Hong-Yan Lü, Jian-Jiong Li and Zhan-Hui Zhang*

$ZrOCl_2 \cdot 8H_2O$ has been found to be an efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes from aldehydes and 5,5-dimethylcyclohexane-1,3-dione under solvent-free conditions.

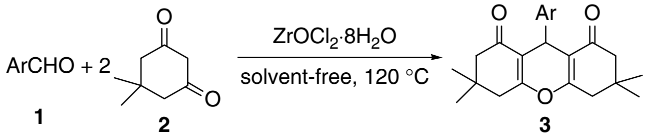
Keywords: xanthenes; aldehyde; zirconium oxide chloride; solvent-free conditions

Introduction

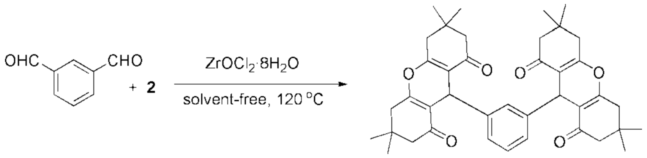
The development of new methods for the synthesis of xanthene derivatives is an important area of synthetic research because of the broad spectrum of their biological and pharmaceutical properties such as antibacterial, antiviral and anti-inflammatory activities as well as phototoxicity and antagonist activity.[1–3] Some xanthene derivatives are used in industry, such as florescent material for visualization of biomolecules,[4] in laser technologies due to their useful spectroscopic properties[5] and as dyes.[6] Xanthenedione derivatives are valuable synthons because of the inherent reactivity of the inbuilt pyran ring.[7] They are also found as core units in several natural products.[8]

Because of their wide range of pharmacological activity and industrial and synthetic applications, many methods for their preparation are reported in the literature. Of these methods, the acid-catalyzed condensation reaction of aldehydes with 5,5-dimethylcyclohexane-1,3-dione is one of most simple and straightforward approaches for the synthesis of 1,8-dioxo-octahydroxanthenes. A variety of reagents such as $InCl_3 \cdot 4H_2O$,[9] $BiCl_3$,[10] $NaHSO_4 \cdot SiO_2$,[11] *p*-dodecylbenzenesulfonic acid,[12] tetrabutylammonium hydrogen sulfate,[13] polyaniline-*p*-toluenesulfonate,[14] silica sulfuric,[15] Dowex-50W,[16] Amberlyst-15,[17] PPA-SiO_2,[18] $SbCl_3/SiO_2$ [19] and ethylene glycol[20] have been employed to accomplish this transformation. Although there are currently a number of methods available, they have one or more disadvantage, such as long reaction time, the use of expensive reagents, low yields of products in some cases, high catalyst loading, corrosive reagents, strongly acidic conditions and tedious workup procedures. Therefore, to avoid these limitations, the development of a new readily available catalyst with high catalytic activity, short reaction time and simple work-up for the preparation of 1,8-dioxo-octahydroxanthenes is highly desirable.

In recent years, zirconium compounds have been used as catalysts in organic synthesis because these compounds are relatively non-toxic, easy to handle, low-cost and possess good stability.[21–27] Among these, $ZrOCl_2 \cdot 8H_2O$ has gained special attention because this compound not only is commercially available and inexpensive, but also has high stability and water tolerance. Handling of $ZrOCl_2 \cdot 8H_2O$ is easier than that of moisture-sensitive $ZrCl_4$. $ZrOCl_2 \cdot 8H_2O$ has been reported to be an efficient catalyst for many important organic transformations.[28–35] In continuation of our previous work on the development of new synthetic methodologies,[36–43] we herein report the synthesis of 1,8-dioxo-octahydroxanthenes from aldehydes and 5,5-dimethylcyclohexane-1,3-dione in the presence of a catalytic amounts of $ZrOCl_2 \cdot 8H_2O$ (10 mol%) under solvent-free conditions (Scheme 1).



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



Scheme 2. Synthesis of bis(1,8-dioxo-octahdroxanthene).

Experimental

Melting points were determined on X-4 apparatus and are uncorrected. IR spectra were obtained using a Shimadzu FTIR-8900 spectrometer. ^1H NMR spectra were recorded with a Varain Mercury Plus 400 spectrometer using TMS as internal standard. Elemental analyses were performed on a Vario EL III CHNOS elemental analyzer.

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* *Correspondence to: Zhan-Hui Zhang, The College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang 050016, People's Republic of China. E-mail: zhanhui@126.com*

The College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050016, People's Republic of China

General Synthetic Procedure for Synthesis of 1,8-Dioxo-octahydroxanthenes

A mixture of aldehydes (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) and $ZrOCl_2 \cdot 8H_2O$ (0.1 mmol, 10 mol%) was ground and heated to 120 °C. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and dissolved in ethyl acetate (20 ml), then washed with water (20 ml). The organic layer was then dried over $MgSO_4$ and evaporated under vacuum. The crude product was purified by short column chromatography (ethyl acetate/hexane as eluent) to obtain pure product.

Analytical Data of New Compounds

*3,3,6,6-Tetramethyl-9-(3,4-dimethylphenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3d**)*

IR (KBr): 2870 ($-CH_3$), 1659 ($=C-C=O$), 1622 ($C=C$), 1456 ($-CH_3$), 1201 ($=C-O-C$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 0.99 (s, 6H), 1.09 (s, 6H), 2.13–2.18 (m, 8H), 2.22 (d, $J = 16.4$ Hz, 2H), 2.45 (s, 4H), 4.67 (s, 1H), 6.95(s, 2H), 7.08 (s, 1H); anal. calcd for $C_{25}H_{30}O_3$: C, 79.33; H, 7.99. Found: C, 79.51; H, 8.12.

*3,3,6,6-Tetramethyl-9-(2,3,4-trimethoxyphenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3j**)*

IR (KBr): 2957 ($-CH_3$), 1678 ($=C-C=O$), 1654 ($C=C$), 1466 ($-CH_3$), 1361 ($-CH_3$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 1.01 (s, 6H), 1.08 (s, 6H), 2.13 and 2.30 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.42 (s, 4H), 3.74 (s, 3H), 3.77 (s, 3H), 3.93 (s, 3H), 4.79 (s, 1H), 6.53 (d, $J = 8.4$ Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 1H); anal. calcd for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 70.71; H, 7.40.

*3,3,6,6-Tetramethyl-9-(4-phenoxyphenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3m**)*

IR (KBr): 2954 ($-CH_3$), 2870 ($-CH_3$), 1674 ($=C-C=O$), 1654 ($C=C$), 1591($C=C$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 0.96 (s, 6H), 1.09 (s, 6H), 2.18 and 2.24 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.42 (s, 4H), 4.74 (s, 1H), 6.73–6.76 (m, 1H), 6.87–7.06 (m, 5H), 7.17–7.18 (m, 2H), 7.27–7.29 (m, 1H); anal. calcd for $C_{29}H_{30}O_4$: C, 78.71; H, 6.83. Found: C, 78.62; H, 6.75.

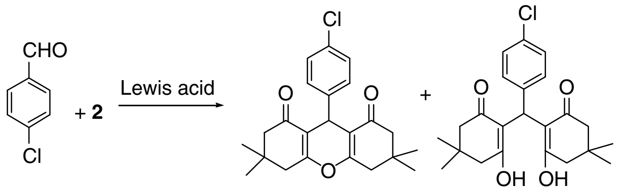
*3,3,6,6-Tetramethyl-9-(2-fluorophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3r**)*

IR (KBr): 2960 ($-CH_3$), 1681 ($=C-C=O$), 1662 ($C=C$), 1167 ($=C-O-C$), 1004 ($C-F$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 0.97 (s, 6H), 1.09 (s, 6H), 2.15 and 2.22 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.44 (s, 4H), 4.81 (s, 1H), 6.88 (t, $J = 8.4$ Hz, 1H), 7.02–7.12 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 1H); anal. calcd for $C_{23}H_{25}FO_3$: C, 74.98; H, 6.84. Found: C, 75.12; H, 6.68.

*3,3,6,6-Tetramethyl-9-(3,4-dichlorophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3x**)*

IR (KBr): 2962 ($-CH_3$), 1659 ($=C-C=O$), 1618 ($C=C$), 1465 ($-CH_3$), 1200 ($=C-O-C$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 1.00 (s, 6H), 1.10 (s, 6H), 2.17 and 2.24 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.47 (s, 4H), 4.68 (s, 1H), 7.18 (dd, $J = 8.0, 2.4$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 2.4$ Hz, 1H); anal. calcd for $C_{23}H_{24}Cl_2O_3$: C, 65.88; H, 5.77. Found: C, 65.67; H, 5.91.

Table 1. Investigation of the amounts of catalyst and temperature effects on the reaction of 4-chlorobenzaldehyde and 5,5-dimethylcyclohexane-1,3-dione



1u **3u** **4**

Entry	Catalyst loading (mol%)	Temperature (°C)	Time (min)	Yield (%)[a]
1	No	25	8 h	–[b]
2	No	120	4 h	–[c]
3	10	60	90	75
4	10	80	90	85
5	5	120	90	85
6	10	120	40	95
7	15	120	40	95
8	20	120	40	93
9	10	120	40	95, 93, 92 94[d]

[a] Isolated yields. [b] Compound **4** was formed in 30% yield. [c] Compound **4** was formed in 91% yield and **3u** was not obtained. [d] The same catalyst was used for each of the four runs.

*9-(3-Bromo-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3z**)*

IR (KBr): 2956 ($-CH_3$), 1662 ($=C-C=O$), 1591 ($C=C$), 1471 ($-CH_2$), 1203 ($=C-O-C$), 574 ($C-Br$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 0.99 (s, 6H), 1.09 (s, 6H), 2.17 and 2.23 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.46 (s, 4H), 4.70 (s, 1H), 7.05–7.10 (m, 1H), 7.21–7.25 (m, 1H), 7.27–7.34 (m, 2H); anal. calcd for $C_{23}H_{25}BrO_3$: C, 64.34; H, 5.87. Found: C, 64.19; H, 5.98.

*3,3,6,6-Tetramethyl-9-(4-hydroxy-3-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3ae**)*

IR (KBr): 2958 ($-CH_3$), 1638 ($=C-C=O$), 1629 ($C=C$), 1537 ($-NO_2$), 1197 ($=C-O-C$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 1.01 (s, 6H), 1.11 (s, 6H), 2.17 and 2.25 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.49 (s, 4H), 4.70 (s, 1H), 7.03 (d, $J = 8.8$ Hz, 1H), 7.69 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.88 (d, $J = 2.0$ Hz, 1H), 10.45 (s, 1H); anal. calcd for $C_{23}H_{25}NO_6$: C, 67.14; H, 6.12; N, 3.40. Found: C, 67.00; H, 6.28, N, 3.38.

*3,3,6,6-Tetramethyl-9-(3-trifluoromethyl-phenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3ag**)*

IR (KBr): 2906 ($-CH_3$), 1676 ($=C-C=O$), 1620 ($C=C$), 1473 ($-CH_2$), 1002 ($C-F$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 0.98 (s, 6H), 1.11 (s, 6H), 2.16 and 2.24 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.48 (s, 4H), 4.79 (s, 1H), 7.34–7.40 (m, 3H), 7.61–7.63 (m, 1H); anal. calcd for $C_{24}H_{25}F_3O_3$: C, 68.89; H, 6.02. Found: C, 68.98; H, 5.90.

*3,3,6,6-Tetramethyl-9-(pyridine-3-yl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3ak**)*

IR (KBr): 2961 ($-CH_3$), 1676 ($=C-C=O$), 1622 ($C=C$), 1471($-CH_2$), 1195 ($=C-O-C$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ ppm: 0.99

Table 2. Synthesis of 1,8-dioxo-octahydroxanthene derivatives catalyzed by $ZrOCl_2{\bullet}8H_2O$

Entry	Aldehydes	Product	Time (min)	Yield (%)[a]	m.p. (°C)	
					Found	Reported
1	PhCHO	**3a**	50	93	202–203	200–202[10]
2	4-MeC_6H_4CHO	**3b**	50	92	215–216	210–212[9]
3	3-MeC_6H_4CHO	**3c**	50	93	206–208	205–207[44]
4	3,4-$Me_2C_6H_3CHO$	**3d**	50	90	205–207	
5	4-$Me_2CHC_6H_4CHO$	**3e**	50	93	171–172	172–173[44]
6	3-$MeOC_6H_4CHO$	**3f**	55	92	162–165	161–162[10]
7	4-$MeOC_6H_4CHO$	**3g**	55	92	242–243	241–243[9]
8	3,4-$(MeO)_2C_6H_3CHO$	**3h**	55	94	175–176	170–172[20]
9	3,4,5-$(OMe)_3C_6H_2CHO$	**3i**	45	95	205–208	205–208[18]
10	2,3,4-$(OMe)_3C_6H_2CHO$	**3j**	70	88	204–207	
11	3,4-$(OCH_2O)C_6H_3CHO$	**3k**	50	93	224–225	224–226[12]
12	3-MeO-4-OHC_6H_3CHO	**3l**	50	93	225–227	226–228[12]
13	3-OPh-C_6H_3CHO	**3m**	50	92	191–193	
14	3-OHC_6H_4CHO	**3n**	50	92	213–215	215–218[18]
15	4-OHC_6H_4CHO	**3o**	50	91	247–248	245–250[18]
16	4-$Me_2NC_6H_4CHO$	**3p**	50	91	225–226	222–225[18]
17	4-FC_6H_4CHO	**3q**	45	94	226–227	224–226[9]
18	2-FC_6H_4CHO	**3r**	60	92	210–212	
19	2-ClC_6H_4CHO	**3s**	70	87	226–227	225–227[9]
20	3-ClC_6H_4CHO	**3t**	45	94	183–185	185–187[18]
21	4-ClC_6H_4CHO	**3u**	40	95	226–228	228–230[10]
22	2,4-$Cl_2C_6H_3CHO$	**3v**	70	88	248–251	253–254[10]
23	2,6-$Cl_2C_6H_3CHO$	**3w**	45	91	318–320	320[45]
24	3,4-$Cl_2C_6H_3CHO$	**3x**	40	92	238–239	
25	2-BrC_6H_4CHO	**3y**	80	85	226–229	226–228[9]
26	3-BrC_6H_4CHO	**3z**	55	96	172–175	
27	4-BrC_6H_4CHO	**3aa**	45	94	238–239	238–239[10]
28	2-$NO_2C_6H_4CHO$	**3ab**	70	86	260–262	258–262[18]
29	3-$NO_2C_6H_4CHO$	**3ac**	45	92	165–166	168–170[12]
30	4-$NO_2C_6H_4CHO$	**3ad**	45	94	222–224	222–224[9]
31	3-NO_2-4-OH-C_6H_3CHO	**3ae**	50	90	231–233	
32	4-CNC_6H_4CHO	**3af**	40	93	217–218	218–218[19]
33	3-$F_3CC_6H_4CHO$	**3ag**	40	95	192–194	
34	PhCH=CHCHO	**3ah**	50	90	173–174	175–177[12]
35	2-Thiophene-carbaldehyde	**3ai**	50	91	164–165	163–164[2]
36	2-Pyridine-carbaldehyde	**3aj**	60	90	190–191	188–190[13]
37	3-Pyridine-carbaldehyde	**3ak**	70	88	188–190	
38	4-Pyridine-carbaldehyde	**3al**	45	85	212–214	
39	3-$CHOC_6H_4CHO$	**3am**	80	75	238–240	236–238[13]

[a] Yields refer to isolated products.

(s, 6H), 1.10 (s, 6H), 2.17 and 2.30 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.48 (s, 4H), 4.73 (s, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.79 (t, $J = 6.4$ Hz, 1H), 8.35–8.42 (m, 2H); anal. calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99. Found: C, 75.02; H, 7.28, N, 3.87.

*3,3,6,6-Tetramethyl-9-(pyridine-4-yl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3al**)*

IR (KBr): 2956 ($-CH_3$), 1681($=C-C=O$), 1591 ($C=C$), 1385 ($-CH_3$), 1199 ($=C-O-C$) cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ 0.98 (s, 6H), 1.11 (s, 6H), 2.17 and 2.25 (AB system, $J = 16.0$ Hz, 2H, CH_aCH_bCO), 2.49 (s, 4H), 4.75 (s, 1H), 7.32 (d, $J = 5.6$ Hz, 2H), 7.47 (d, $J = 5.6$ Hz, 2H); anal. calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99. Found: C, 75.06; H, 7.02, N, 4.18.

Results and Discussion

First, we examined the reaction 4-chlorobenzaldehyde (**1u**) and 5,5-dimethylcyclohexane-1,3-dione (**2**) in the presence of 10 mol% of $ZrOCl_2{\bullet}8H_2O$ at 120 °C under solvent-free conditions. The reaction proceeded rapidly to afford the corresponding 1,8-dioxo-octahydroxanthene in high yield. In addition, it was found that at high temperatures, $ZrOCl_2 \cdot 8H_2O$ shows good catalytic activity; a 95% yield of **3u** was obtained at 120 °C. However at 80 °C a lower yield was obtained even after longer reaction times. With further optimization of the reaction conditions, we found that a lower catalyst loading gave decreased yields (Table 1, entry 5). Increasing the catalyst loading did not significantly affect the yield (Table 1, entries 7 and 8). The reaction was also examined in the absence of the catalyst. The obtained

Table 3. Effect of different Lewis acids on the reaction of 4-chlorobenzaldehyde and 5,5-dimethylcyclohexane-1,3-dione[a]

Entry	Catalyst	Conversion (%)	Yield(%)[b]
1	$ZrOCl_2{\cdot}8H_2O$	100	95
2	$ZrO(NO_3)_2{\cdot}2H_2O$	95	88
3	$ZrSO_4{\cdot}4H_2O$	90	86
4	$ZrCl_4$	90	55
5	$ZrO(OC_2H_5)_4$	80	5
6	$InBr_3$	90	82
7	$In(OTf)_3$	70	75
8	$Co(NO_3)_2{\cdot}6H_2O$	60	41
9	$LiClO_4$	80	43
10	$LaCl_3{\cdot}7H_2O$	80	32
11	LaF_3	80	0
12	$La(NO_3)_3{\cdot}6H_2O$	90	60
13	$SrSO_4$	80	0
14	$Mn(OAc)_3{\cdot}4H_2O$	80	0
15	$Cu(NO_3)_2{\cdot}3H_2O$	50	0
16	$FeCl_3$	52	0
17	$SnCl_4{\cdot}5H_2O$	48	0
18	CAN	90	53
19	$CdCl_2$	90	5
20	$Ce(SO_4)_2{\cdot}(NH_4)SO_4{\cdot}4H_2O$	90	58

[a] The reaction was carried out using 10 mol% of catalyst at 120 °C.
[b] Isolated yields.

results showed that only the non-cyclodehydrated intermediate 9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-exahydro-1*H*-xanthene-1,8(2*H*)-dione (**4**) was formed (Table 1, entries 1 and 2). The recovery and reusability of $ZrOCl_2 \cdot 8H_2O$ were investigated. After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was filtered, washed with chloroform and dried at 100 °C for 1 h before being used with fresh 4-chlorobenzaldehyde (**1u**) and cyclohexanedione (**2**). As indicated in Table 1 (entry 9), no considerable loss of efficiency concerning reaction time and yield was observed after four runs.

Next, various aromatic aldehydes were tested under these optimized reactions and the results are listed in Table 2. This catalyst worked excellently for aromatic aldehydes bearing electron-donating or electron-withdrawing substituents. For examples, yields of product ranged from 88 to 95% (Table 2, entries 2–16) for electron-rich substrates such as 4-methoxyaldehyde, piperonyl aldehydes, vanillin and 3-phenoxybenzaldehyde. For the sterically hindered 2,3,4-trimethoxybenzaldehyde, 2-bromobenzaldehyde and 2-nitrobenzaldehyde, a prolonged reaction time was required to furnish products in 88, 85 and 86% yields (Table 2, entries 10, 25 and 28). The system also worked well for α,β-unsaturated aldehydes to afford the product in 90% yield (Table 2, entry 34). The acid-sensitive heterocyclic aldehydes such as thiophene-2-carbaldehyde, pyridine-2-carbaldehyde, pyridine-3-carbaldehyde and pyridine-4-carbaldehyde (Table 2, entries 35–38) were also tested and the corresponding xanthene derivatives were obtained in high yields. We also scaled up the reaction of 4-chlorobenzaldehyde (**1j**) by 10-fold without any significant decrease in the product yield (94% yield).

The efficacy of various Lewis acids was tested for this conversion, and the results are shown in Table 3. Among these catalysts, $ZrOCl_2 \cdot 8H_2O$ was found to be superior in terms of yield and reaction rates.

Furthermore, this reaction was further explored for the synthesis of bis(1,8-dioxo-octahydroxanthene) by the reaction of *m*-phthalaldehyde (**1am**) and 4 equiv. of 5,5-dimethylcyclohexane-1,3-dione (**2**) under similar conditions in good yields (Scheme 2).

Conclusion

In conclusion, $ZrOCl_2 \cdot 8H_2O$ has been employed for the first time as a novel and efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes by the reaction of aldehydes with 5,5-dimethylcyclohexane-1,3-dione. This method is applicable to a wide range of aldehydes, including aromatic, α,β-unsaturated and heterocyclic substrates. The salient features of this protocol are mild reaction conditions, high yields of products, cheapness and easy availability of the reagent, low catalyst loading and short reaction times.

Acknowledgment

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