Clean Synthesis of 1,8-Dioxo-octahydroxanthene Derivatives Catalyzed by *p*-Dodecylbenezenesulfonic Acid in Aqueous Media

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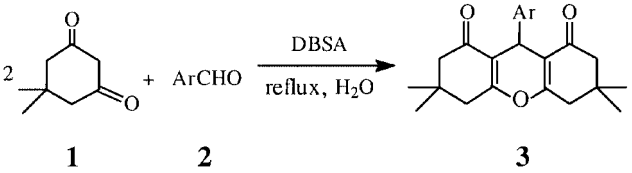
Abstract: An efficient and convenient approach to the synthesis of 3,3,6,6-tetramethyl-9-aryl-1,8-dioxo-octahydroxanthene derivatives using *p*-dodecylbenezenesulfonic acid (DBSA) as the catalyst (10 mol%) is described. This method provides several advantages such as being environmentally friendly, processing high yields and simple work-up procedure. In addition, water was chosen as a green solvent.

Key words: octahydroxanthene, *p*-dodecylbenezenesulfonic acid, clean synthesis, aqueous media

With the increasing environmental concerns and the regulatory constraints faced in the chemical and pharmaceutical industries, development of environmentally benign organic reactions has become a crucial and demanding research area in modern organic chemical research.[1] Therefore more and more chemists synthetic endeavors are devoted toward 'green synthesis' which means the reagent, solvent and catalyst are environmental friendly. In modern organic chemical research, Wender defined the 'ideal synthesis' as one in which the target components are produced in one step, in quantitative yield from readily available and inexpensive starting materials in resource-effective and environmentally acceptable process.[2] Multicomponent condensations represent a possible instrument to perform a near ideal synthesis because they possess one of the aforementioned qualities, namely the possibility of building-up complex molecules with maximum simplicity and brevity.

In 1980, Breslow discovered that the Diels–Alder reaction performed in water can be subject to huge rate accelerations.[3] This observation led to increased interest from synthetic organic chemists in organic reactions in water. Soon it was discovered that other organic reactions, like the Claisen rearrangement,[4] the aldol condensation,[5] and the benzoin condensation[6] exhibit rate enhancements in water. To date, many more organic transformations have been carried out in water.[7]

DBSA has been used in a number of organic reactions as a good catalyst. While DBSA as a good phase transfer catalyst is a new field, it can also been used in many organic reactions.[8] However, the use of DBSA as a catalyst in aqueous media for the synthesis of the 1,8-dioxo-octahydroxanthene and their derivatives has not been reported.[9,10] In this manuscript, we wish to report a general and highly efficient route for the synthesis of 1,8-dioxo-octahydroxanthene and their derivatives using an inexpensive and commercially available DBSA as catalyst. This is an efficient synthesis in aqueous media, which consistently gives the corresponding products in good to excellent yields (Scheme 1).



1 **2** **3**

Scheme 1

In a typical general experimental procedure, a solution of an aromatic aldehyde and 5,5-dimethyl-1,3-cyclohexanedione in water was heated under reflux in water in the presence of a catalytic amount of DBSA (10 mol%) for a period of time required to complete the reaction, resulting in the formation of 1,8-dioxo-octahydroxanthene, the reaction mixture was filtered off and washed with H_2O and the filtrate was recycled through reuse. The crude product was purified by recrystallization from ethanol to afford the pure product.[11]

To study the generality of this process, several examples illustrating this method for the synthesis of polyfunctionalized 1,8-dioxo-octahydroxanthene were studied. The results are summarized in Table 1. Varying the substituents on the aromatic ring did not detrimentally effect the yields. The cyclocondensation reaction proceeded smoothly under reflux in water to give the corresponding products **3** in high yields. Benzaldehyde and other aromatic aldehydes containing electron-withdrawing groups (such as nitro group, halide) or electron-donating groups (such as hydroxy group, alkoxyl group, dimethylamino group) were employed and reacted well to give the corresponding 1,8-dioxo-octahydroxanthene in good to excellent yields.

The catalyst plays a crucial role in the success of the reaction in terms of the rate and the yields. For example, 4-chlorobenzoaldehyde reacted with 5,5-dimethyl-1,3-cyclohexane-dione in the presence of 1 mol% DBSA to give the product **3b** in modest yield (66%) at reflux in water after six hours of reaction time. Increasing the amount of

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Table 1 Synthesis of 1,8-Dioxo-octahydroxanthene Catalyzed by DBSA in Aqueous Media

Entry	Ar	Product	Yield (%)[a]	Mp (°C)	
				Found	Reported[9]
1	C_6H_5 **2a**	**3a**	89	202–204	204–205
2	4-ClC_6H_4 **2b**	**3b**	92	228–230	
3	3-ClC_6H_4 **2c**	**3c**	94	183–184	
4	2-ClC_6H_4 **2d**	**3d**	90	228–230	224–226
5	2,4-Cl_2-C_6H_3 **2e**	**3e**	91	253–254	
6	2-$NO_2C_6H_4$ **2f**	**3f**	92	247–249	246–248
7	3-$NO_2C_6H_4$ **2g**	**3g**	94	168–170	171.5–172.5
8	4-$NO_2C_6H_4$ **2h**	**3h**	94	226–228	222
9	4-HOC_6H_4 **2i**	**3i**	96	246–248	246
10	4-$CH_3OC_6H_4$ **2j**	**3j**	93	242–244	241–243
11	4-$Me_2NC_6H_4$ **2k**	**3k**	90	226–228	220–222
12	4-$CH_3C_6H_4$ **2l**	**3l**	93	217–218	
13	4-HO-3-$CH_3OC_6H_3$ **2m**	**3m**	91	226–228	
14	3,4-$OCH_2OC_6H_3$ **2n**	**3n**	92	224–226	
15	C_6H_5CH=CH **2o**	**3o**	90	175–177	

[a] Isolated yields.

the catalyst to 5 mol%, 10 mol%, and 15 mol% results in increasing the reaction yields to 85%, 92% and 92%, respectively. Use of just 10 mol% DBSA at reflux in water is sufficient to push the reaction forward. Higher amounts of the catalyst did not improve the results to a greater extent. The yields are, in general, very high regardless of the structural variations in aromatic aldehyde. The reaction was carried out in the absence of DBSA at reflux in water for 6 hours, we found that the product we obtained was not **3b**, but the intermediate **8b** in a yield of 40%. To find the optimum reaction time, the reaction was carried out in the presence of DBSA for 3, 6, or 9 hours, resulting in the isolation of **3b** in 72%, 92% and 93% yield respectively. Thus, 10 mol% DBSA and a reaction time of 6 hours were chosen, the catalyst could be reused 6–8 times for the synthesis of **3b** without significant loss of activity. The results were summarized in Table 2.

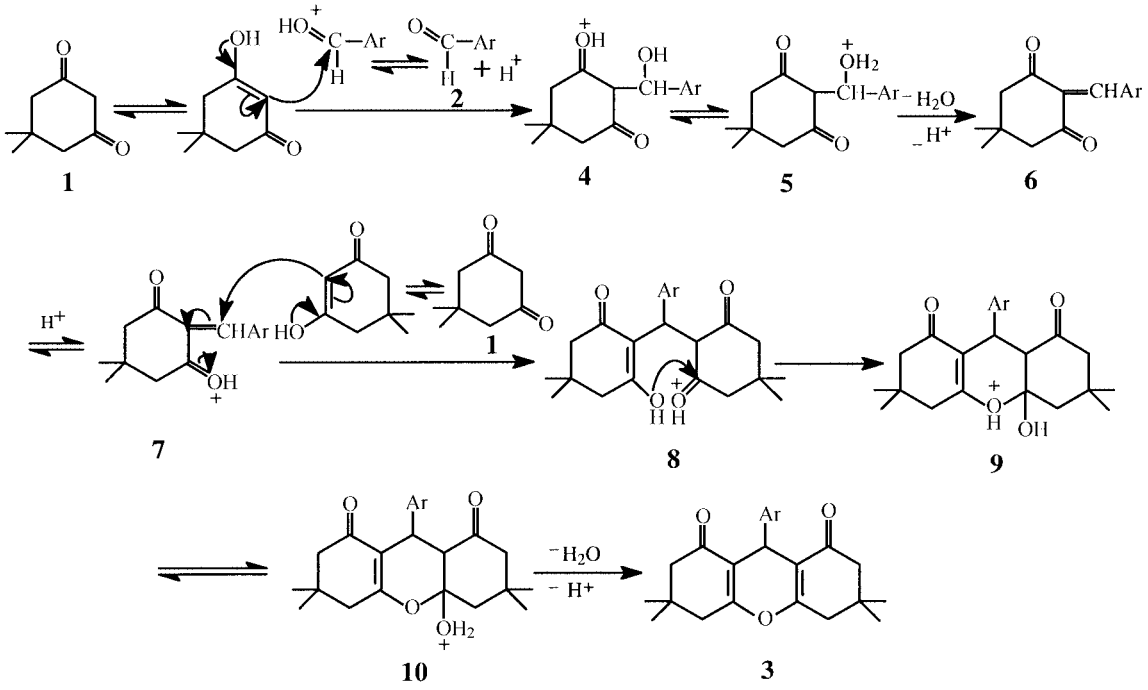
Table 2 Reuse of the Catalyst for Synthesis of **3b**

Entry	1	2	3	4	5	6	7
Yield (%)	93	90	91	90	89	90	88

We have also examined other solvents. As a model reaction, the reaction of 4-chlorobenzaldehyde with 5,5-dimethyl-1,3-cyclohexanedione catalyzed by DBSA (10 mol%), various solvents including water, ethanol, trichloromethane and cyclohexane was investigated resulting in the product being isolated in 92%, 86%, 72% and 56% yields respectively. Thus water is obviously the best choice for these reactions.

Finally to test other catalysts the reaction of 4-chlorobenzaldehyde and 5,5-dimethyl-1,3-cyclohexanedione in the presence of an acid catalyst in water was selected as a model reaction. Among the catalysts tested, DBSA was found to be the most efficient catalyst. The catalysts we tested TsOH, TsOH + SDS (SDS: sodium dodecyl sulfate), DBSA and lauric acid gave 13%, 86%, 92% and 26% yields, respectively. DBSA formed a white turbid reaction mixture, while TsOH formed two immiscible layers. This indicates that the long alkyl chain of DBSA is necessary for the formation of the colloidal dispersion that is assumed to lead to efficient catalysis. A combination of TsOH and SDS, which formed colloidal dispersion in the presence of the substrates, afforded the adduct in a modest yield (86%), confirming the importance of the long alkyl chain. A carboxylic acid having a long alkyl chain, lauric acid, was much less effective (26%) than DBSA, suggesting that the strong acidity of DBSA is essential for the catalysis.

We propose the possible following mechanism to account for the reaction. One molecule of 5,5-dimethyl-1,3-cyclohexanedione (**1**) was firstly condensed with an aromatic aldehyde **2** to afford **7**. The step (**1** + **2** → **4** → **5** → **6** → **7**) can be regarded as a fast Knoevenagel addition. Then the active methylene of another molecule of 5,5-dimethyl-



Scheme 2

1,3-cyclohexanedione (**1**) reacted with **7** via conjugate addition reaction to give the intermediate **8**. Then the intermediate **8** cyclized by nucleophilic attack of the OH group on the carbonyl (C=O) moiety and gave the intermediate **9**. Finally, the expected products **3** resulted from elimination of water (**9** → **10** → **3**) (Scheme 2). In this process, DBSA is not only a protonic acid but also an emulsifying agent, which catalyzes this reaction and forms the stable colloidal particles in the presence of the substrates in water and this colloid formation plays an important role in acceleration of the reactions.

In conclusion, we have described a general and highly efficient procedure for the preparation of polyfunctionalized 1,8-dioxo-octahydroxanthene catalyzed by DBSA, in refluxing water. In addition, it is possible to apply the tenets of green chemistry to the generation of interesting products using aqueous media methods that are less expensive and less toxic than those with organic solvents. Moreover, the procedure offers several advantages including high yields, operational simplicity, cleaner reactions and minimal environmental impact, which makes it a useful and attractive process for the synthesis of these compounds.

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References

(1) Anastas, P.; Williamson, T. *Green Chemistry, Frontiers in Benign Chemical Synthesis and Procedures*; Oxford Science Publications: Oxford, **1998**.
(2) Wender, P. A.; Handy, S. L.; Wright, D. L. *Chem. Ind. (London)* **1997**, 765.
(3) (a) Rideout, D. C.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 7817. (b) Breslow, R.; Maitra, U.; Rideout, D. *Tetrahedron Lett.* **1983**, *24*, 1901. (c) Eggelte, T. A.; de Koning, H.; Huisman, H. O. *Tetrahedron* **1973**, *29*, 2491.
(4) (a) Gajewski, J. J.; Jurayj, J.; Kimbrough, D. R.; Grande, M. E.; Ganem, B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 1170. (b) Brandes, E.; Grieco, P. A.; Gajewski, J. J. *J. Org. Chem.* **1989**, *54*, 515. (c) Grieco, P. A.; Brandes, E. B.; McCann, S.; Clark, J. D. *J. Org. Chem.* **1989**, *54*, 5849. (d) Severance, D. L.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1992**, *114*, 10966. (e) Gao, J. *J. Am. Chem. Soc.* **1994**, *116*, 1563. (f) Gajewski, J. J.; Brichford, N. L. *J. Am. Chem. Soc.* **1994**, *116*, 3165.
(5) (a) Lubineau, A. *J. Org. Chem.* **1986**, *51*, 2143. (b) Lubineau, A.; Meyer, E. *Tetrahedron* **1988**, *44*, 6065.
(6) (a) Kool, E. T.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 1596. (b) Breslow, R. *Acc. Chem. Res.* **1991**, *24*, 159.
(7) (a) Li, C. J. *Chem. Rev.* **1993**, *93*, 2023. (b) Grieco, P. A. *Organic Synthesis in Water*; Blacky: London, **1998**. (c) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; Wiley: New York, **1997**. (d) Jin, T. S.; Xiao, J. C.; Wang, S. J.; Li, T. S.; Song, X. R. *Synlett* **2003**, 2001.
(8) Manabe, K.; Mori, Y.; Kobayashi, S. *Tetrahedron* **2001**, *57*, 2537.
(9) Horning, E. C.; Horing, M. G. *J. Org. Chem.* **1946**, *11*, 95.
(10) Shi, D. Q.; Lu, Z. S.; Gao, Y.; Feng, Y. J.; Zhou, L. H.; Dai, G. Y. *Chinese J. Org. Chem.* **1998**, *18*, 82.
(11) **General Procedure for the Preparation of 1,8-Dioxo-octahydroxanthene:** A mixture of an aromatic aldehyde (1.0 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2.0 mmol) and DBSA (10 mol%) in H_2O (20 mL) was stirred at refluxing for 6 h. The progress of the reaction was monitored

by thin layer chromatograph. After completion of the reactions, the mixture was cooled to r.t. and solid was filtered off and washed with H_2O (40 mL) and the crude products isolated. The crude products were purified by recrystallization by EtOH (95%). Data of the compounds are shown below:

Compound 3a, 3,3,6,6-Tetramethyl-9-benzene-1, 8-dioxo-octahydroxanthene. Mp 202–204 °C (from EtOH). IR (KBr): ν_{max} = 3030, 2980, 1685, 1670, 1470, 1360, 1200, 1170, 1140, 1005, 740, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 098 (s, 6 H, 2 × CH_3), 1.12 (s, 6 H, 2 × CH_3), 2.20 (dd, 4 H, *J* = 1.6 Hz, *J* = 2.4 Hz, 2 × CH_2, H-4, H-5), 2.45 (s, 4 H, 2 × CH_2, H-2, H-7), 4.66 (s, 1 H, H-9), 7.21 (m, 5 H, Ar-H). Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.47. Found: C, 78.95; H, 7.42.

Compound 3b, 3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene. Mp 228–230 °C (from EtOH). IR (KBr): ν_{max} = 3025, 2980, 1680, 1660, 1620, 1490, 1480, 1360, 1200, 1170, 1140, 1090, 1010, 1000, 850, 840 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.98 (s, 6 H, 2 × CH_3), 1.10 (s, 6 H, 2 × CH_3), 2.23 (dd, 4 H, *J* = 1.6 Hz, *J* = 3.6 Hz, 2 × CH_2, H-4, H-5), 2.50 (s, 4 H, 2 × CH_2, H-2, H-7), 4.64 (s, 1 H, H-9), 7.26–7.43 (m, 4 H, ArH). Anal. Calcd for $C_{23}H_{25}ClO_3$: C, 71.77; H, 6.54. Found: C, 71.89; H, 6.45.

Compound 3c, 3,3,6,6-Tetramethyl-9-(3-chlorophenyl)-1,8-dioxo-octahydroxanthene. Mp 183–184 °C (from EtOH). IR (KBr): ν_{max} = 3030, 2980, 1685, 1660, 1620, 1490, 1475, 1365, 1200, 1170, 1135, 1095, 1000, 850, 840 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.02 (s, 6 H, 2 × CH_3), 1.12 (s, 6 H, 2 × CH_3), 2.30 (dd, 4 H, *J* = 1.6 Hz, *J* = 3.6 Hz, 2 × CH_2, H-4, H-5), 2.49 (s, 4 H, 4 × CH_2, H-2, H-7), 4.74 (s, 1 H, H-9), 7.11–7.25 (m, 4 H, ArH). Anal. Calcd for $C_{23}H_{25}ClO_3$: C, 71.77; H, 6.54. Found: C, 71.92; H, 6.41.

Compound 3d, 3,3,6,6-Tetramethyl-9-(2-chlorophenyl)-1,8-dioxo-octahydroxanthene. Mp 228–230 °C (from EtOH). IR (KBr): ν_{max} = 3030, 2980, 1680, 1665, 1620, 1495, 1470, 1360, 1200, 1170, 1140, 1100, 1000, 850, 840 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.98 (s, 6 H, 2 × CH_3), 1.10 (s, 6 H, 2 × CH_3), 2.06 (dd, 4 H, *J* = 1.6 Hz, *J* = 3.0 Hz, 2 × CH_2, H-4, H-5), 2.49 (s, 4 H, 2 × CH_2, H-2, H-7), 4.64 (s, 1 H, H-9), 7.26–7.35 (m, 4 H, ArH). Anal. Calcd for $C_{23}H_{25}ClO_3$: C, 71.77; H, 6.54. Found: C, 71.88; H, 6.35.

Compound 3e, 3,3,6,6-Tetramethyl-9-(2,4-dichlorophenyl)-1,8-dioxo-octahydroxanthene. Mp 253–254 °C (from EtOH). IR (KBr): ν_{max} = 3035, 2980, 1685, 1660, 1633, 1490, 1480, 1410, 1360, 1210, 1195, 1155, 1100, 1000, 850, 770 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.03 (s, 6 H, 2 × CH_3), 1.12 (s, 6 H, 2 × CH_3), 2.21 (dd, 4 H, *J* = 1.6 Hz, *J* = 3.2 Hz, 2 × CH_2, H-4, H-5), 2.46 (s, 4 H, 2 × CH_2, H-2, H-7), 4.96 (s, 1 H, H-9), 7.18 (s, 1 H, ArH), 7.39 (d, 2 H, *J* = 8.4 Hz, ArH). Anal. Calcd for $C_{23}H_{24}Cl_2O_3$: C, 65.87; H, 5.73. Found: C, 65.96; H, 5.59.

Compound 3f, 3,3,6,6-Tetramethyl-9-(2-nitrophenyl)-1,8-dioxo-octahydroxanthene. Mp 247–249 °C (from EtOH). IR (KBr): ν_{max} = 3035, 2980, 1685, 1673, 1620, 1533, 1360, 1211, 1173, 1152, 1010, 860, 800, 780, 745, 703 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.99 (s, 6 H, 2 × CH_3), 1.12 (s, 6 H, 2 × CH_3), 2.16 (dd, 4 H, *J* = 1.6 Hz, *J* = 3.6 Hz, 2 × CH_2, H-4, H-5), 2.41 (s, 4 H, 2 × CH_2, H-2, H-7), 5.61 (s, 1 H, H-9), 7.36–7.45 (m, 4 H, ArH). Anal. Calcd for $C_{23}H_{25}NO_5$: C, 69.85; H, 6.37; N, 3.54. Found: C, 69.93; H, 6.54; N, 3.36.

Compound 3g, 3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-1,8-dioxo-octahydroxanthene. Mp 168–170 °C (from EtOH). IR (KBr): ν_{max} = 3030, 2980, 1680, 1675, 1625, 1535, 1365, 1335, 1210, 11750, 1145, 1006, 830, 765, 730, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.02 (s, 6 H, 2 × CH_3), 1.13 (s, 6 H, 2 × CH_3), 2.22 (dd, 4 H, *J* = 1.6 Hz, *J* = 3.6 Hz, 2 × CH_2, H-4, H-5), 2.53 (s, 4 H, 2 × CH_2, H-2, H-7), 4.85 (s, 1 H, H-9), 7.43 (s, 1 H, ArH), 7.88–7.95 (m, 3 H, ArH). Anal. Calcd for $C_{23}H_{25}NO_5$: C, 69.85; H, 6.37; N, 3.54. Found: C, 69.90; H, 6.50; N, 3.42.

Compound 3h, 3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene. Mp 226–228 °C (from EtOH). IR (KBr): ν_{max} = 3030, 2980, 1665, 1650, 1623, 1530, 1360, 1340, 1200, 1070, 1042, 1005, 875, 833 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.00 (s, 6 H, 2 × CH_3), 1.12 (s, 6 H, 2 × CH_3), 2.16 (dd, 4 H, *J* = 1.6 Hz, *J* = 3.6 Hz, 2 × CH_2, H-4, H-5), 2.41 (s, 4 H, 2 × CH_2, H-2, H-7), 4.46 (s, 1 H, H-9), 7.50–7.63 (m, 2 H, ArH), 8.06–8.16 (m, 2 H, ArH). Anal. Calcd for $C_{23}H_{25}NO_5$: C, 69.85; H, 6.37; N, 3.54. Found: C, 69.89; H, 6.46; N, 3.40.

Compound 3i, 3,3,6,6-Tetramethyl-9-(4-hydroxyphenyl)-1,8-dioxo-octahydroxanthene. Mp 246–248 °C (from EtOH). IR (KBr): ν_{max} = 3360, 3025, 2980, 1795, 1725, 1700, 1633, 1613, 1525, 1390, 1375, 1260, 1233, 1200, 1196, 850, 843 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.99 (s, 6 H, 2 × CH_3), 1.10 (s, 6 H, 2 × CH_3), 2.13 (dd, 4 H, *J* = 1.6 Hz, *J* = 4.0 Hz, 2 × CH_2, H-4, H-5), 2.47 (s, 4 H, 2 × CH_2, H-2, H-7), 4.62 (s, 1 H, H-9), 6.77 (d, 2 H, *J* = 8.0 Hz, ArH), 6.98 (d, 2 H, *J* = 8.0, ArH). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.26; H, 7.09.

Compound 3j, 3,3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene. Mp 242–244 °C (from EtOH). IR (KBr): ν_{max} = 3025, 2980, 1685, 1660, 1620, 1513, 1450, 1375, 1360, 1260, 1235, 1170, 1142, 1032, 1003, 840 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.01 (s, 6 H, 2 × CH_3), 1.09 (s, 6 H, 2 × CH_3), 2.20 (dd, 4 H, *J* = 1.6 Hz, *J* = 2.0 Hz, 2 × CH_2, H-4, H-5), 2.46 (s, 4 H, 2 × CH_2, H-2, H-7), 3.73 (s, 3 H, CH_3O), 4.70 (s, 1 H, H-9), 6.67–7.28 (m, 4 H, ArH). Anal. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.41. Found: C, 75.85; H, 7.31.

Compound 3k, 3,3,6,6-Tetramethyl-9-(4-dimethylaminophenyl)-1,8-dioxo-octahydroxanthene. Mp 226-228 °C (from EtOH). IR (KBr): ν_{max} = 3035, 2980, 2195, 1687, 1665, 1580, 1500, 1454, 1400, 1234, 1195, 1040, 811, 743 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.02 (s, 6 H, 2 × CH_3), 1.11 (s, 6 H, 2 × CH_3), 2.21 (dd, 4 H, *J* = 1.6 Hz, *J* = 2.4 Hz, 2 × CH_2, H-4, H-5), 2.46 (s, 4 H, 2 × CH_2, H-2, H-7), 2.88 [s, 6 H, -N(CH_3)$_2$], 4.67 (s, 1 H, H-9), 6.62 (s, 2 H, ArH), 7.15 (s, 2 H, ArH). Anal. Calcd for $C_{25}H_{31}NO_3$: C, 76.34; H, 7.89; N, 3.56. Found: C, 76.48; H, 7.86; N, 3.43.

Compound 3l, 3,3,6,6-Tetramethyl-9-(4-methylphenyl)-1,8-dioxo-octahydroxanthene. Mp 217–218 °C (from EtOH). IR (KBr): ν_{max} = 3035, 2980, 1685, 1665, 1633, 1515, 1470, 1365, 1200, 1165, 1140, 790, 775cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.03 (s, 6 H, 2 × CH_3), 1.12 (s, 6 H, 2 × CH_3), 2.07 (dd, 4 H, *J* = 1.6 Hz, *J* = 2.4 Hz, 2 × CH_2, H-4, H-5), 2.40 (s, 4 H, 2 × CH_2, H-2, H-7), 2.43 (s, 3 H, CH_3Ar), 4.69 (s, 1 H, H-9), 6.80–7.28 (m, 4 H, ArH). Anal. Calcd for $C_{24}H_{28}O_3$: C, 79.08; H, 7.74. Found: C, 79.25; H, 7.59.

Compound 3m, 3,3,6,6-Tetramethyl-9-(4-hydroxy-3-methoxyphenyl)-1,8-dioxo-octahydrox-anthene. Mp 226–228 °C (from EtOH). IR (KBr): ν_{max} = 3443, 3030, 2985, 2195, 1687, 1660, 1580, 1500, 1454, 1400, 1234, 1195, 1040, 811, 743 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.02 (s, 6 H, 2 × CH_3), 1.12 (s, 6 H, 2 × CH_3), 2.24 (d, 4 H, *J* = 3.6 Hz, 2 × CH_2, H-4, H-5), 2.47 (s, 4 H, 2 × CH_2, H-2, H-7), 3.91 (s, 3 H, OCH_3), 4.68 (s, 1 H, H-9), 5.49 (s, 1 H, OH), 6.60 (s, 1 H, ArH), 6.74 (s, 1 H, ArH), 7.03 (s, 1 H, ArH). Anal. Calcd for $C_{24}H_{28}O_5$: C, 77.84; H, 7.57. Found: C, 77.98; H, 7.43.

Compound 3n, 3,3,6,6-Tetramethyl-9-(3,4-dioxymethylenephenyl)-1,8-dioxo-octahydrox-anthene. Mp 224–226 °C (from EtOH). IR (KBr): ν_{max} = 3030, 2980,

1725, 1680, 1560, 1510, 1495, 1445, 1383, 1360, 1320, 1275, 1230, 1045, 945, 920, 890, 812, 790 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.00 (s, 6 H, 2 × CH_3), 1.13 (s, 6 H, 2 × CH_3), 2.16 (dd, 4 H, *J* = 1.6 Hz, *J* = 2.8 Hz, 2 × CH_2, H-4, H-5), 2.41 (s, 4 H, 2 × CH_2, H-2, 7), 4.58 (s, 1 H, H-9), 5.90 (s, 2 H, OCH_2O), 6.75–6.86 (m, 3 H, ArH). Anal. Calcd for $C_{24}H_{26}O_5$: C, 73.07; H, 6.64. Found: C, 73.16; H, 6.68.

Compound 3o, 3,3,6,6-Tetramethyl-9-(2-phenylethylene)-1,8-dioxo-octahydroxanthene. Mp 175–177 °C (from EtOH). IR (KBr): ν_{max} = 3035, 2980, 1710, 1670, 1600, 1580, 1500, 1454, 1400, 1375, 1310, 1264, 1210, 1040, 970, 740, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.14 (s, 12 H, 4 × CH_3), 2.32 (s, 4 H, 4 × CH_2), 2.46 (s, 4 H, 4 × CH_2), 4.42 (s, 1 H, H-9), 6.25–6.33 (m, 2 H, -CH=CH-), 7.18–7.28 (m, 5 H, ArH). Anal. Calcd for $C_{25}H_{28}O_3$: C, 79.79; H, 7.45. Found: C, 79.91; H, 7.30.

Compound 8b, 2,2′-(4-Chlorophenyl)methylene-bis(3-hydroxy-5,5-dimethyl-2-cyclohexene- 1-one). Mp 141–143 °C (from EtOH), 140–142 °C(reported).[10] IR (KBr): ν_{max} = 3443, 3000~2500, 2980, 2922, 1635, 1490, 1480, 1380, 1290, 1230, 1140, 1090, 1000, 745 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.06 (s, 6 H, 2 × CH_3), 1.17 (s, 6 H, 2 × CH_3), 2.21 (d, 4 H, *J* = 2.8 Hz, 2 × CH_2), 2.53 (s, 4 H, 4 × CH_2), 5.62 (s, 1 H, CH), 7.09–7.40 (m, 4 H, ArH), 9.63 (br, s, 1 H, OH, enol), 11.88 (br, s, 1 H, OH, enol). Anal. Calcd for $C_{23}H_{27}ClO_4$: C, 68.59; H, 6.75. Found: C, 68.66; H, 6.53.