A Facile Synthesis of Xanthene-1,8(2*H*)-dione Derivatives by Using Tetrapropylammonium Bromide as Catalyst

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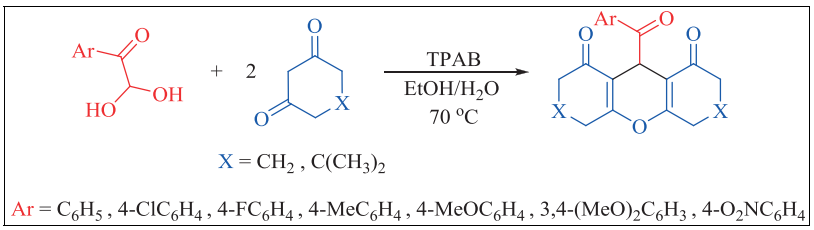

Several new derivatives of 9-aroyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione have been synthesized in yields varying from high to excellent by the condensation reaction of arylglyoxals with 1,3-diketones (cyclohexane-1,3-dione or dimedone) and TPAB as an inexpensive, recoverable, and non-toxic catalyst in the presence of ethanol/water under reflux conditions.

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INTRODUCTION

Among the fused organic heterocyclic compounds containing-oxygen atom, xanthenes and their derivatives are important because of their broad application in several areas such as catalysis, materials science, as dyes in laser technology, pH-sensitive fluorescent materials, and for their biological properties [1,2].

Such compounds have been intensively studied in medicinal chemistry because they exhibit a wide range of biological and pharmaceutical properties such as antibacterial [3,4], anti-cancer [5–8], anti-inflammatory [9], anti-fungal [10], anti-hypertensive [11], anti-malarial [12], anti-plasmodial [13,14], and anti-viral [15].

Several methods for the synthesis of xanthene derivatives appear in the literature [16], but the reported methods are limited by low yields, high cost, use of toxic solvents, high reaction temperatures, and the requirement of special apparatus.

Tetrapropylammonium bromide is an inexpensive and readily available phase transfer catalyst that has inherent properties of environmental compatibility, operational simplicity, being non-corrosive, and ease of reusability, that has made it a suitable material in the preparation of high silica zeolites of the ZSM type such as ZSM-5, and also has many applications in different catalytic processes [17,18].

In continuation of our interest in the development of highly expedient methods for the synthesis of various heterocyclic compounds with potential pharmaceutical and biological properties [19–25], herein we report a synthetic route for the synthesis of a new series of xanthene-1,8(2*H*)-dione derivatives via the condensation reaction of arylglyoxals **1** with 1,3-diketones **2**, such as cyclohexane-1,3-dione or dimedone, and TPAB in the presence of ethanol/water under reflux conditions, in high to excellent yields.

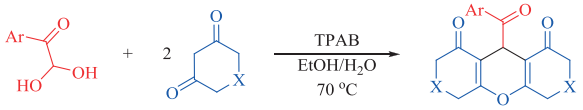
RESULTS AND DISCUSSION

In attempting to develop a simple and short reaction route to some novel substituted heterocyclic compounds under mild conditions, we found that the reactions of arylglyoxal monohydrates **1a**–**g** with 2 eq of 1,3-diketone [such as cyclohexane-1,3-dione (**2a**) or dimedone (**2b**)] as active methylene compounds in the presence of ethanol/water and TPAB under reflux conditions afforded the corresponding new 9-aroyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-diones **3a**–**n** in 70–98% yield (Scheme 1).

In the absence of catalyst, no product was observed at room temperature even after 24 h. Then, we evaluated the yield and rate of reaction by using several catalysts such as Alginate, Nano-Ag, SeO_2, *L*-proline, sulfanilic acid, *p*-TSA, and TPAB. The effects of solvent and temperature for these catalysts are summarized in Table 1.

The best result in terms of yield (98%) and reaction time (39 min) was obtained when the reaction was carried out using TPAB as a catalyst in H_2O/EtOH (1:3) (entry 11). In this procedure, TPAB plays a crucial role in accelerating the reaction, and its efficacy was examined in various solvents such as water, ethanol, acetone, and formic acid; H_2O/EtOH proved to be the best.

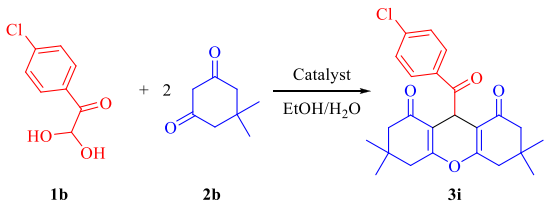
Scheme 1. The synthesis of compounds **3a**–**n**. [Color figure can be viewed at wileyonlinelibrary.com]



Ar = C_6H_5 , 4-ClC_6H_4 , 4-FC_6H_4 , 4-MeC_6H_4 , 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 4-$O_2NC_6H_4$

Table 1

Optimizing the reaction condition for the synthesis of compound **3i**.



Entry	Solvent	Catalyst (20 mol%)	Temperature (°C)	Time (h)	Yield (%)
1	H_2O	—	Reflux	24	—
2	H_2O	*p*-TSA	Reflux	24	10
3	EtOH/H_2O	—	Reflux	5	10
4	EtOH/H_2O	*p*-TSA	Reflux	2	15
5	EtOH/H_2O	Sulfanilic acid	Reflux	1	17
6	EtOH/H_2O	SeO_2	Reflux	1	—
7	EtOH/H_2O	Nano-Ag	Reflux	3	21
8	EtOH/H_2O	Alginate	RT-Reflux	3	27
9	EtOH/H_2O	*L*-proline	RT-Reflux	1	37
10	EtOH/H_2O	*L*-proline	40	3	45
11	EtOH/H_2O	**TPAB**	**70**	**39 min**	**98**
12	EtOH	TPAB	RT-Reflux	1.5	57
13	Acetone/H_2O	*L*-proline	RT-Reflux	2	53
14	HCO_2H/H_2O	*L*-proline	RT-Reflux	4	55

After optimizing the reaction conditions, the scope of this reaction was examined by using various electron rich and deficient arylglyoxals to obtain a new series of xanthene-1,8(2*H*)-dione derivatives **3a–n**. The structure of all products with their yields are shown in Figure 1.

The proposed mechanism for the formation of compounds **3a**–**n** is shown in Scheme 2. It involves the initial *Knoevenagel* condensation of arylglyoxal **1a–g** and one mole of 1,3-diketone (cyclohexane-1,3-dione or dimedone) to form the corresponding intermediate **4**, followed by *Michael* addition of another mole of 1,3-diketone to this intermediate, followed by ring closure to afford the compounds **3a**–**n**.

In the ^{1}H-NMR spectra of the all compounds **3a–n**, a sharp singlet in the regions δ = 5.26–5.48 ppm was attributed to the CH of the pyran ring. In the ^{13}C-NMR spectra of products **3a–n**, signals located around δ = 196.56–201.71 ppm were due to the carbonyl groups. In the FT-IR spectra, the characteristic absorption band at ν = 1660–1666 cm^{-1} could be assigned to the vibration of the carbonyl groups.

The recyclability of TPAB was also studied in the reaction for synthesis of **3i**. For this purpose, the recovered catalyst was recycled and reused up to four times without any significant loss of its catalytic performance.

The structures of products **3a–n** were confirmed by microanalysis and by their ^{1}H-NMR, ^{13}C-NMR, and FT-IR spectral data, and X-ray crystallography of **3a**. The crystal structure of **3a** and its crystal packing diagram is shown in Figure 2. A summary of the crystal data and experimental details of the data collections and structure refinements are listed in Table 2.

The crystallographic data for structure **3a** were deposited at the Cambridge Crystallographic Data Center (entry no. CCDC-1813573) and are available free of charge upon request to CCDC, 12 Union Road, Cambridge, UK (Fax: +44–1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

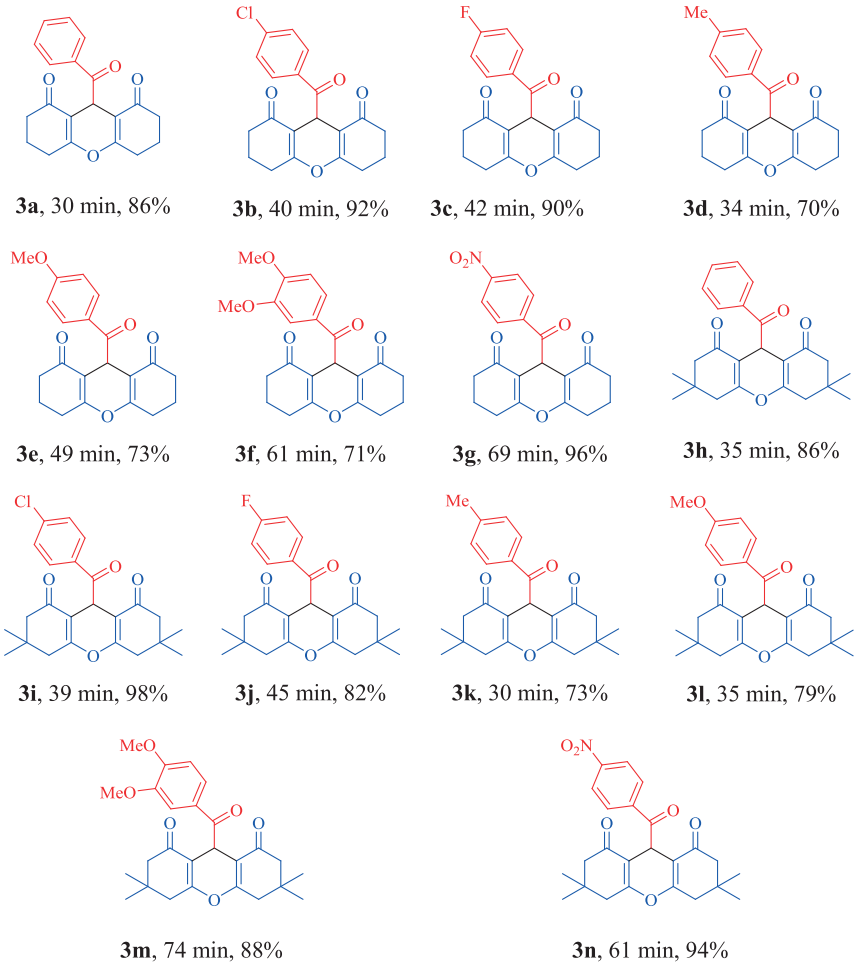


Figure 1. Structures of products synthesized. [Color figure can be viewed at wileyonlinelibrary.com]

EXPERIMENTAL

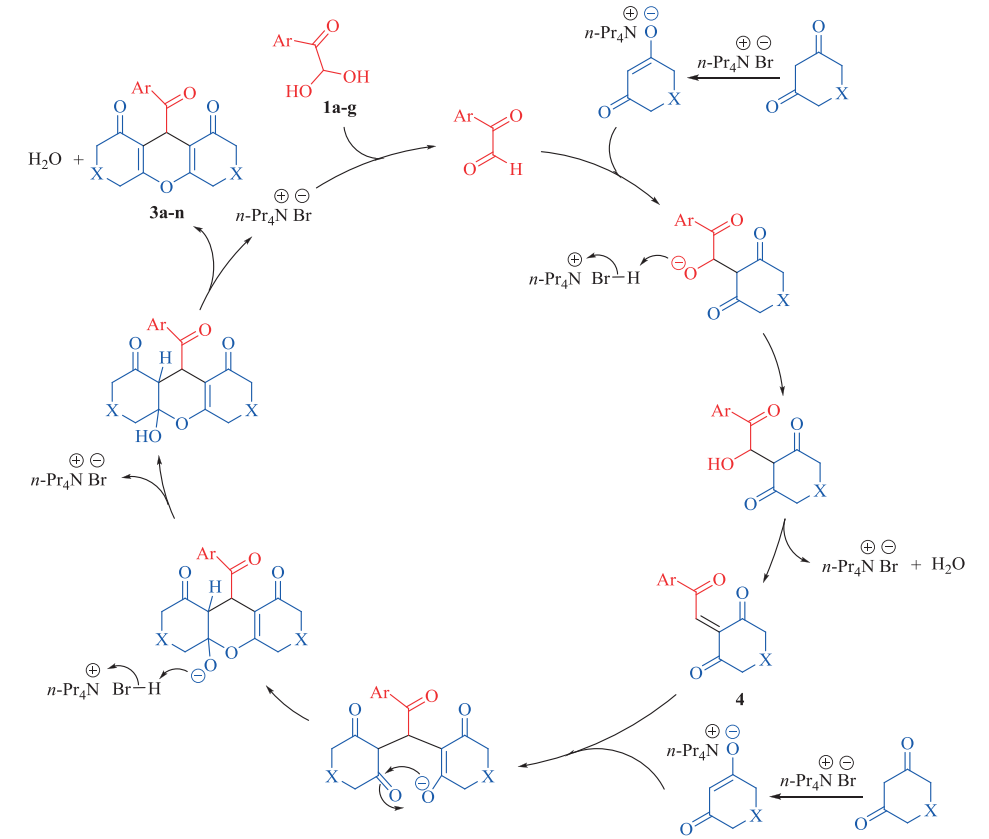
The chemicals used in this work were purchased from Acros Organics or from Merck and were used without purification. Melting points were determined on a digital melting point apparatus (Electrothermal, Cole-Parmer, Staffordshire, UK) and reported uncorrected. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with a Bruker spectrometer at 300 and 75 MHz, respectively (Bruker, Billerica, MA). The spectra were measured in $CDCl_3$ using TMS as the internal standard. Infrared spectra were recorded on a Thermo Nicolet (Nexus 670) FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA), using KBr disks. Elemental analyses were performed using a Leco Analyzer 932 (Leco Corp., St. Joseph, MI).

General procedure for the synthesis of 9-aroyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione 3a–n. A mixture of arylglyoxal monohydrate (1 mmol), cyclohexane-1,3-dione or dimedone (2 mmol), and TPAB (20 mol%) in absolute ethanol and water (3:1) (5 mL) was refluxed for an appropriate time (30–74 min) as monitored by TLC (CH_2Cl_2:n-hexane:MeOH / 20:10:1 as eluents, R_f = 0.78–0.93). After completion of the reaction, half of the solvent was evaporated, and the precipitate was filtered, washed with cold water, and recrystallized from ethanol to afford the pure products **3a**–**n** in 70–98%.

9-Benzoyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3a). Orange crystals; yield 86%; mp 213–215°C [lit. [26], mp 210–212°C]. ^{1}H-NMR δ (ppm): 8.30 (d, *J* = 7.2 Hz, 2H, Ar H), 7.56 (t, *J* = 6.9 Hz, 1H, Ar H), 7.48 (t, *J* = 7.2 Hz, 2H, Ar H), 5.44 (s, 1H, CH), 2.71 (t, *J* = 6.6 Hz, 1H), 2.65 (t, *J* = 6.6 Hz, 1H), 2.59 (t, *J* = 6.6 Hz, 1H), 2.53 (t, *J* = 6.6 Hz, 1H), 2.44–2.28 (m, 4H, 2 × CH_2), 2.09–1.99 (m, 4H, 2 × CH_2). ^{13}C-NMR δ (ppm): 20.11, 27.19, 34.23, 36.42, 114.32, 128.14, 129.42, 132.93, 137.02, 165.87, 196.83, 201.71. FT-IR ν_{max}: 3441, 3057, 2953, 2893, 1663, 1435, 1351, 1180, 1128, 967, 736, 676 cm^{-1}.

9-(4-Chlorobenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3b). White crystals; yield 92%; mp 210–212°C. ^{1}H-NMR δ (ppm): 8.23 (dd, *J* = 8.4 Hz, 2H, Ar

Scheme 2. Proposed mechanism for the synthesis of xanthene-1,8(2*H*)-diones **3a–n**. [Color figure can be viewed at wileyonlinelibrary.com]



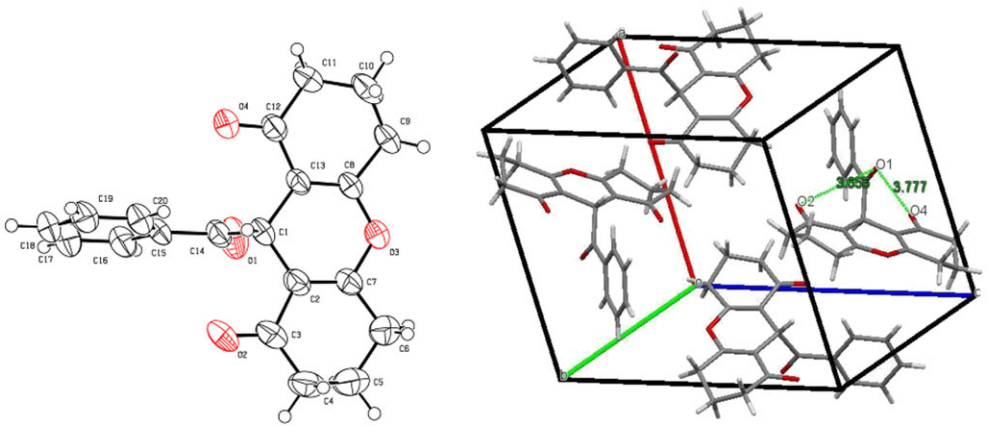


Figure 2. Crystal structure and crystal packing diagram of **3a**. [Color figure can be viewed at wileyonlinelibrary.com]

H), 7.46 (d, J = 8.4 Hz, 2H, Ar H), 5.34 (s, 1H, CH), 2.72 (t, J = 5.7 Hz, 1H, CH), 2.68 (t, J = 6.6 Hz, 1H, CH), 2.55 (t, J = 6.6 Hz, 1H, CH), 2.50 (t, J = 5.7 Hz, 1H, CH), 2.43–2.28 (m, 4H, 2 × CH_2), 2.11–2.02 (m, 4H, 2 × CH_2). ^{13}C-NMR δ (ppm): 20.11, 27.16, 34.40, 36.38, 114.23, 128.42, 130.76, 135.58, 139.23, 165.88, 196.86, 200.66. FT-IR ν_{max}: 3432, 3065, 2950, 2894, 1664, 1587, 1353, 1182, 1133, 972, 850, 771, 531 cm^{-1}. *Anal*. Calcd for $C_{20}H_{17}ClO_4$: C, 67.33; H, 4.80. Found: C, 67.42; H, 4.68%.

9-(4-Fluorobenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3c). White crystals; yield 90%; mp 214–216°C. ^{1}H-NMR δ (ppm): 8.32 (d, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 2H, Ar H), 7.15 (t, J = 8.7 Hz, 2H, Ar H), 5.38 (s, 1H, CH), 2.72 (t, J = 8.7 Hz, 1H, CH), 2.66 (t, J = 8.4 Hz, 1H, CH), 2.61 (t, J = 6.9 Hz, 1H, CH), 2.54

Table 2

Crystal data and structure refinement for **3a**.

Empirical formula	$C_{20}H_{18}O_4$
Formula weight (g mol^{-1})	322.34
Crystal size (mm^3)	0.46 × 0.23 × 0.10
Crystal shape, color	Broken, Orange
Temperature (K)	296 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a, *b*, *c* (Å)	11.299 (7), 9.134 (6), 15.454 (9)
α, γ	90
β (°)	91.495 (8)
V (Å^3)	1594.3 (17)
Z	4
Density (Mg/m^3)	1.343
Absorption coefficient μ (mm^{-1})	0.093
Maximum and minimum transmission	0.9907 and 0.9584
θ range for data collection (°)	2.21–25.78
Index ranges	$-13 \leq \leq h \leq 13$, $-11 \leq k \leq 11$, $-18 \leq l \leq 18$
Reflections collected	11795
Independent reflections (R_{int})	3036 (0.0475)
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.028
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0662$, $wR_2 = 0.1841$
R indices (all data)	$R_1 = 0.1031$, $wR_2 = 0.2178$
Largest difference in peak and hole (e Å^{-3})	0.584 and −0.244

(t, *J* = 6.6 Hz, 1H, CH), 2.44–2.28 (m, 4H, 2 × CH_2), 2.09–2.00 (m, 4H, 2 × CH_2). ^{13}C-NMR δ (ppm): 20.11, 27.17, 34.52, 36.40, 114.41, 114.21, 115.01, 133.09, 133.54, 165.90, 167.46, 196.86, 200.13. FT-IR ν_{max}: 3433, 3072, 2956, 2894, 1663, 1590, 1353, 1207, 1182, 1132, 967, 850, 532 cm^{-1}. *Anal*. Calcd for $C_{20}H_{17}FO_4$: C, 70.58; H, 5.03. Found: C, 70.67; H, 4.90%.

9-(4-Methylbenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3d). White crystals; yield 70%; mp 189–191°C. ^{1}H-NMR δ (ppm): 8.21 (d, *J* = 8.1 Hz, 2H, Ar H), 7.28 (d, *J* = 6.9 Hz, 2H, Ar H), 5.45 (s, 1H, CH), 2.51–2.74 (m, 4H, 2 × CH_2), 2.42 (s, 3H, CH_3), 2.09–2.00 (m, 4H, 2 × CH_2), 2.36–2.28 (m, 4H, 2 × CH_2). ^{13}C-NMR ($CDCl_3$) δ (ppm): 20.85, 28.40, 32.89, 37.76, 43.75, 113.75, 119.74, 128.91, 133.65, 136.45, 163.37, 195.05, 196.64. FT-IR ν_{max}: 3426, 2903, 2855, 1664, 1580, 1499, 1420, 1368, 1254, 1160, 1016, 755. *Anal*. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.75; H, 5.82%.

9-(4-Methoxybenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3e). White crystals; yield 73%; mp 204–205°C. ^{1}H-NMR δ (ppm): 8.30 (d, *J* = 8.7 Hz, 2H, Ar H), 6.96 (d, *J* = 8.7 Hz, 2H, Ar H), 5.42 (s, 1H, CH), 3.86 (s, 3H, OCH_3), 2.70 (t, *J* = 5.7 Hz, 1H, CH), 2.64 (t, *J* = 5.7 Hz, 1H, CH), 2.56 (t, *J* = 6.9 Hz, 1H, CH), 2.51 (t, *J* = 6.6 Hz, 1H, CH), 2.42–2.26 (m, 4H, 2 × CH_2), 2.06–1.97 (m, 4H, 2 × CH_2). ^{13}C-NMR δ (ppm): 20.11, 27.19, 33.77, 36.47, 55.42, 113.38, 114.23, 129.78, 131.94, 163.53, 165.92, 196.84, 199.68. FT-IR ν_{max}: 3303, 3065, 2955, 1661, 1606, 1509, 1444, 1356, 1315, 1178, 1125, 1022, 961, 850, 783, 729, 681, 607 cm^{-1}. *Anal*. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.64; H, 5.66%.

9-(3,4-Dimethoxybenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3f). Yellow crystals; yield 71%; mp 183–185°C. ^{1}H NMR δ (ppm): 8.20 (d, *J* = 8.7 Hz, 1H, Ar H), 7.72 (s, 1H, Ar H), 6.99 (d, *J* = 7.8 Hz, 1H, Ar H), 5.48 (s, 1H, CH), 3.97 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 2.74–2.54 (m, 4H, 2 × CH_2), 2.40–2.34 (m, 4H, 2 × CH_2), 2.07–2.02 (m, 4H, 2 × CH_2). ^{13}C-NMR δ (ppm): 20.11, 27.23, 33.76, 36.51, 55.84, 55.96, 110.11, 111.59, 114.24, 125.09, 129.79, 148.53, 153.43, 165.93, 196.59, 199.53. FT-IR ν_{max}: 3434, 3085, 2951, 2367, 1666, 1592, 1456, 1361, 1261, 1164, 953, 773, 638 cm^{-1}. *Anal*. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 69.00; H, 5.93%.

9-(4-Nitrobenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3g). Orange crystals; yield 96%; mp 218–220°C. ^{1}H-NMR δ (ppm): 8.39 (d, *J* = 8.4 Hz, 2H, Ar H), 8.31 (d, *J* = 8.4 Hz, 2H, Ar H), 5.26 (s, 1H, CH), 2.71–2.59 (m, 4H, 2 × CH_2), 2.43–2.34 (m, 4H, 2 × CH_2), 2.11–2.03 (m, 4H, 2 × CH_2). ^{13}C-NMR δ (ppm): 20.08, 27.09, 35.04, 36.23, 114.28, 122.32, 124.38, 130.82, 142.55, 166.01, 197.10, 201.02. FT-IR ν_{max}: 3434, 3101, 2950, 2889, 1660, 1525, 1349, 1181, 1131, 972, 852, 740, 690, 532 cm^{-1}. *Anal*. Calcd for $C_{20}H_{17}NO_6$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.43; H, 4.52; N, 3.75%.

9-Benzoyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3h). Yellow crystals; yield 86%; mp 217–218°C [lit. [27], mp 219–220°C]. ^{1}H-NMR δ (ppm): 8.28 (d, *J* = 8.1 Hz, 2H, Ar H), 7.56 (t, *J* = 6.9 Hz, 1H, Ar H), 7.48 (t, *J* = 6.6 Hz, 2H, Ar H), 5.42 (s, 1H, CH), 2.49 (s, 4H, 2 × CH_2), 2.24 (s, 4H, 2 × CH_2), 1.13 (s, 6H, 2 × CH_3), 1.08 (s, 6H, 2 × CH_3). ^{13}C-NMR δ (ppm): 27.40, 29.00, 32.27, 40.97, 50.39, 113.13, 128.06, 129.29, 132.76, 137.29, 164.32, 196.61, 200.35. FT-IR ν_{max}: 3427, 3079, 2954, 1666, 1453, 1360, 1300, 1202, 1148, 995, 760, 677, 574 cm^{-1}.

9-(4-Chlorobenzoyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3i). White crystals; yield 98%; mp 199–201°C [lit. [27], mp 198–200°C]. ^{1}H-NMR δ (ppm): 8.21 (d, *J* = 8.4 Hz, 2H, Ar H), 7.45 (d, *J* = 8.7 Hz, 2H, Ar H), 5.32 (s, 1H, CH), 2.48 (s, 4H, 2 × CH_2), 2.24 (s, 4H, 2 × CH_2), 1.13 (s, 6H, 2 × CH_3), 1.08 (s, 6H, 2 × CH_3). ^{13}C-NMR δ (ppm): 27.38, 28.95, 32.28, 40.91, 50.34, 113.01, 128.34, 130.70, 135.83, 139.05, 164.40, 196.72, 200.38. FT-IR ν_{max}: 2963, 2935, 2874, 1666, 1571, 1588, 1357, 1289, 1204, 1168, 1093, 988, 799 cm^{-1}.

9-(4-Fluorobenzoyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3j). White crystals; yield 82%; mp 178–180°C. ^{1}H-NMR δ (ppm): 8.31 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 2H, Ar H), 7.15 (t, *J* = 8.4 Hz,

2H, Ar H), 5.35 (s, 1H, CH), 2.49 (s, 4H, 2 × CH_2), 2.24 (s, 4H, 2 × CH_2), 1.12 (s, 6H, 2 × CH_3), 1.08 (s, 6H, 2 × CH_3). ^{13}C-NMR δ (ppm): 27.55, 29.03, 32.33, 40.91, 50.36, 113.01, 115.90, 131.17, 132.95, 146.24, 164.45, 196.89, 199.96. FT-IR ν_{max}: 3424, 3066, 2959, 2876, 2332, 1665, 1598, 1507, 1359, 1207, 1161, 811, 581 cm^{-1}. *Anal*. Calcd for $C_{24}H_{25}FO_4$: C, 72.71; H, 6.36. Found: C, 72.60; H, 6.41%.

3,3,6,6-Tetramethyl-9-(4-methylbenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3k). White crystals; yield: 73%; mp 207–209°C [lit. [27], mp 210–212°C]. ^{1}H NMR δ (ppm): 8.18 (d, *J* = 8.1 Hz, 2H, Ar H), 7.27 (d, *J* = 8.1 Hz, 2H, Ar H), 5.41 (s, 1H, CH), 2.49 (s, 4H, 2 × CH_2), 2.41 (s, 3H, CH_3), 2.23 (s, 4H, 2 × CH_2), 1.11 (s, 6H, 2 × CH_3), 1.07 (s, 6H, 2 × CH_3). ^{13}C-NMR δ (ppm): 21.65, 27.39, 29.02, 32.27, 40.97, 50.43, 113.13, 128.82, 129.51, 134.65, 143.51, 164.29, 196.56, 200.75. FT-IR ν_{max}: 3433, 2953, 1665, 1590, 1514, 1359, 1262, 1198, 1151, 1019, 891, 751, 640, 575 cm^{-1}.

9-(4-Methoxybenzoyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3l). Yellow crystals; yield 79%; mp 152–154°C [lit. [27], mp 154–155°C]. ^{1}H NMR δ (ppm): 8.29 (d, *J* = 7.2 Hz, 2H, Ar H), 6.97 (d, *J* = 7.2 Hz, 2H, Ar H), 5.40 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 2.49 (s, 4H, 2 × CH_2), 2.21 (s, 4H, 2 × CH_2), 1.11 (s, 6H, 2 × CH_3), 1.07 (s, 6H, 2 × CH_3). ^{13}C-NMR δ (ppm): 28.63, 32.32, 33.14, 34.12, 40.92, 50.41, 113.03, 129.99, 130.80, 131.91, 132.75, 164.40, 196.78, 199.40. FT-IR ν_{max}: 3433, 2954, 1664, 1598, 1463, 1375, 1173, 1019, 808, 562 cm^{-1}.

9-(3,4-Dimethoxybenzoyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3m). White crystals; yield 88%; mp 116–118°C. ^{1}H NMR δ (ppm): 8.17 (d, *J* = 8.1 Hz, 1H, Ar H), 7.69 (s, 1H, Ar H), 6.99 (d, *J* = 8.7 Hz, 1H, Ar H), 5.43 (s, 1H, CH), 3.97 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 2.49 (s, 4H, 2 × CH_2), 2.24 (s, 4H, 2 × CH_2), 1.13 (s, 6H, 2 × CH_3), 1.09 (s, 6H, 2 × CH_3). ^{13}C-NMR δ (ppm): 27.87, 28.63, 32.33, 33.12, 40.99, 50.47, 50.90, 110.58, 113.03, 125.86, 129.92, 148.41, 153.27, 158.69, 164.49, 196.79, 199.35. FT-IR ν_{max}: 3433, 2953, 1665, 1514, 1359, 1262, 1152, 891, 751, 640, 575 cm^{-1}. *Anal*. Calcd for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 71.38; H, 6.74%.

3,3,6,6-Tetramethyl-9-(4-nitrobenzoyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3n). Orange crystals; yield 94%; mp 160–162°C. ^{1}H NMR δ (ppm): 8.38 (d, *J* = 8.7 Hz, 2H, Ar H), 8.31 (d, *J* = 8.7 Hz, 2H, Ar H), 5.26 (s, 1H, CH), 2.50 (s, 4H, 2 × CH_2), 2.24 (s, 2H, CH_2), 2.23 (s, 2H, CH_2), 1.13 (s, 6H, 2 × CH_3), 1.08 (s, 6H, 2 × CH_3). ^{13}C-NMR δ (ppm): 27.47, 28.83, 32.35, 40.85, 50.19, 113.06, 123.26, 129.90, 142.68, 149.84, 164.52, 196.99, 200.86. FT-IR ν_{max}: 3439, 3094, 2956, 2878, 1662, 1521, 1465, 1352, 1199, 1158, 1000, 850, 753 cm^{-1}. *Anal*. Calcd for $C_{24}H_{25}NO_6$: C, 68.07; H, 5.95; N, 3.31. Found: C, 67.96; H, 6.07; N, 3.24%.

CONCLUSIONS

In conclusion, an easy and efficient synthetic protocol for the synthesis of xanthene-1,8(2*H*)-dione derivatives has been described, by using a one-pot reaction of arylglyoxals with 1,3-diketones in the presence of TPAB as a catalyst. The method used has several advantages including reusability of the catalyst, short reaction times, high yield of the products, mild conditions, and easy workup. These products may have great potential pharmaceutical and biological applications.

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