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Sonochemical syntheses of xanthene derivatives using zeolite-supported transition metal catalysts in aqueous media

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Abstract An efficient green method for the syntheses of biologically active xanthene derivatives by use of zeolite-supported transition metal catalysts is described. A Fe-Cu/ZSM-5 heterogeneous catalyst has the highest activity in the one-pot syntheses with a wide range of aldehydes and cyclic 1,3-diketones, under ultrasonic irradiation in water at ambient temperatures. The three-component condensation in the presence of supported metal catalysts is operationally simple, requires no expensive or toxic reagents, and gives high yields in short reaction times.

Keywords Xanthenes · Fe-Cu/ZSM-5 · Ultrasonic irradiation · MCRs · Supported catalyst · Water

Introduction

In green chemistry, which covers all chemical processes that minimize the use and generation of substances injurious to human health [1], catalysis is a key area. The use of metal oxides supported on various inorganic solid supports has attracted wide attention [2]. Zeolites, such as Cu-modified HY, H-USY, H-Beta, mordenite, and ZSM-5 [4], have been used in the synthesis of specialty and fine chemicals because

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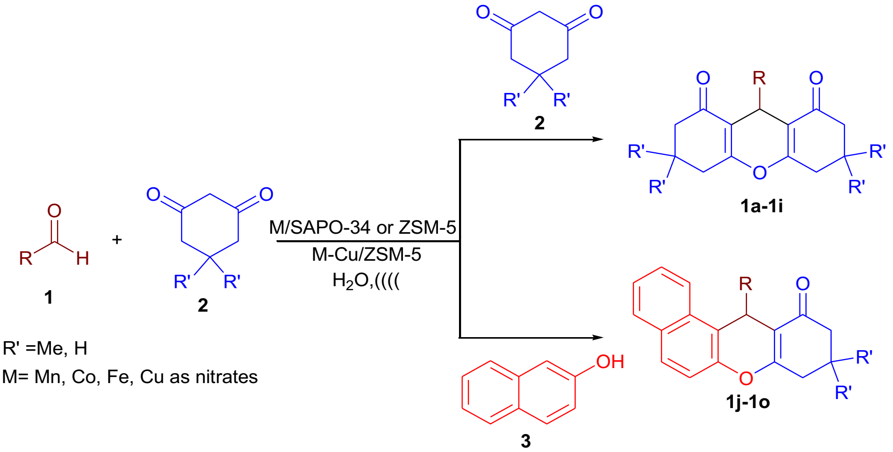
of their tunable acidity, the variety of their structures and pore dimensions, and their excellent thermal stability [3]. For the development of green syntheses, however, the catalysts must be effective in aqueous solution [1, 5–7]. Multicomponent coupling reactions (MCRs) with fewer steps, lower energy consumption, and less waste are particularly suitable for the synthesis of new biologically and pharmaceutically active compounds [3].

Derivatives of xanthenes and benzoxanthenes have been investigated because of their antiviral, antibacterial, anti-inflammatory, anticancer, and antitumor activities [8–11]. They are also used as pH-sensitive fluorescent materials for visualization of biomaterials, in laser technologies, and as luminescent dyes [12, 13]. These wide-ranging applications show that the development of synthetic procedures is important. Established reaction procedures [14–16] have been much improved by the use of ultrasonic radiation to achieve more efficient mixing and chemical selectivity, with lower reaction temperatures, better yields, and shorter reaction times. To the best of our knowledge, no reports are available on the synthesis of xanthenes and benzoxanthenes by use of zeolite-supported bimetallic nanostructures as catalysts. We describe here the use of sonochemistry in the one-pot syntheses of xanthene derivatives in the presence of heterogeneous M-Cu/ZSM-5 (M: Mn, Co and Fe) zeolite eco-friendly and inexpensive catalysts in aqueous solution.

Results and discussion

Because of the wide use of acidic zeolites in organic chemistry and our continuing interest in the use of various catalysts in multicomponent reactions (MCR) [3, 17–21], we wish to report the synthesis of xanthenes and benzoxanthenes by a one-pot three-component condensation of 2-naphthol or a series of cyclic 1,3-diketones with

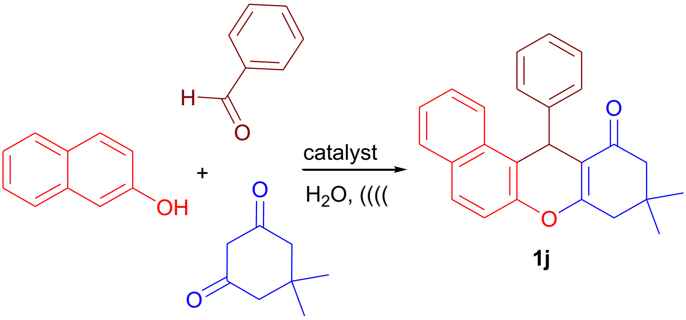


Scheme 1 Preparation of xanthene and benzoxanthene derivatives using zeolite-supported transition metal catalysts

a wide range of aldehydes in the presence of zeolite-supported transition metal catalysts as recyclable catalysts in water under ultrasonic irradiation at ambient temperature (Scheme 1).

Initially, the catalysts with various transition metals (Mn, Fe, Co, and Cu) deposited on ZSM-5 or silicoaluminophosphate-34 (SAPO-34) supports were prepared by the homogeneous deposition precipitation (HDP) method [29], and tested for the synthesis of xanthene derivatives. In order to optimize the reaction parameters, the catalytic influence of different transition metals supported on the zeolites, the weight loadings of metal (wt%), the acidity of supports, the amounts of catalysts, and different reaction media were investigated for the cyclo-condensation reaction of 5,5-dimethylcyclohexane-1,3-dione (dimedone), 2-naphthol and benzaldehyde as a model reaction for the preparation of 9,10-dihydro-9,9-dimethyl-12-phenyl-8*H*-benzo[a]xanthene-11(12*H*)-one (**1j**). It has been reported that the

Table 1 Optimization of the reaction conditions



Entry	Catalyst	Time (min)	Yield (%)[a]
1	Mn/SAPO-34	45	21
2	Co/SAPO-34	45	35
3	Fe/SAPO-34	45	48
4	Cu/SAPO-34	45	52
5	Mn/ZSM-5	45	25
6	Co/ZSM-5	45	39
7	Fe/ZSM-5	45	55
8	Cu/ZSM-5	45	58
9	Mn-Cu/ZSM-5	10	52
10	Co-Cu/ZSM-5	10	75
11	Fe-Cu/ZSM-5	7	94
12	H-SAPO-34	1 h	31
13	H-ZSM-5	1 h	35

Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), 2-naphthol (1 mmol), and (5 wt% from monometallic catalyst) and (3 wt% from bimetallic catalyst) in water under ultrasonic irradiation at ambient temperature at 40 % power of the processor

[a] Yields refer to isolated products

activity of catalysts with a loading of 10 wt% is lower than that with a loading of 5 mol%. The decrease is attributed to metal agglomeration leading to inactive metal particles. Zeolite H-ZSM-5 with 5 wt% Cu loading gave **1j** in 58 % yield under ultrasonic irradiation in water. Cu-ZSM-5 showed higher activity than the Cu-SAPO-34 perhaps because the ZSM-5 acidity is greater than that of SAPO-34. The nature of the transition metal in the zeolite-supported catalysts has more influence than the support on catalyst activity.

The incorporation of other transition metals into Cu/ZSM-5 to give a series of M-Cu/ZSM-5 (M: Mn, Co, and Fe) bimetallic oxide nano-catalysts has been studied. Incorporation of Fe into Cu/ZSM-5 increased the product yield to 94 % and reduced the reaction time (7 min) with decreased catalyst loading (3 wt%) (Table 1, entry 11). Ultrasound irradiation provides well mixing and acoustic cavitations appear to facilitate the bringing together of the reactants on the catalyst surface [14, 15]. We studied the effect of various solvents under ultrasound irradiation and also solvent-free conditions on a model reaction with Fe-Cu/ZSM-5 catalyst. As can be seen from Table 2, the polar solvents and solvent-free conditions afforded better yield than the non-polar ones and the best result was obtained in aqueous medium.

To show the applicability of this method, the preparation of derivatives (**1a**–**1o**) with variety of aromatic aldehydes bearing both electron-withdrawing and electron-donating groups was investigated under the same experimental conditions and the corresponding products were obtained in high yields without the formation of detectable side products (Table 3). Some of the xanthene derivatives are known compounds and their identity was confirmed by IR, NMR, elemental analyses, and melting points [8, 27, 28].

On 4*H*-pyran-4-one (4-pyrone) derivatives are widely distributed in a variety of bio-active compounds [22–26]. We have therefore designed a synthetic strategy for molecules bearing both xanthene and pyrone fragments. The three-component reaction of 5-(benzyloxy)-4-oxo-4*H*-pyran-2-carbaldehyde, with a cyclic 1,3-diketone **2** and 2-naphthol **3** in the presence of Cu-Fe/ZSM-5 in water under ultrasonic irradiation gave the expected xanthene derivatives (**1h**, **1i**, and **1l**) in high yields.

As shown in Scheme 2, 5-(benzyloxy)-4-oxo-4*H*-pyran-2-carbaldehyde was obtained from commercially available Kojic acid [5-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one] by benzylation of the phenolic OH [26], followed by oxidation of

Table 2 Synthesis of 9,10-dihydro-9,9-dimethyl-12-phenyl-8*H*-benzo[a]xanthen-11(12*H*)-one (**1j**) using (3 wt%) Fe-Cu/ZSM-5 bimetallic catalyst

Entry	Conditions	Time (min)	Yield (%)[a]
1	Ethanol	20	50
2	Methanol	20	52
3	Acetonitrile	20	48
4	Ethanol/water	20	70
5	Water	7	94
6	CH_2Cl_2	50	20
7	Solvent-free (120 °C)	10	84

[a] Yields refer to isolated product

Table 3 Synthesis of xanthene and benzoxanthene derivatives catalyzed by Cu-Fe/ZSM-5 nanocatalyst

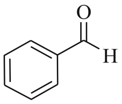
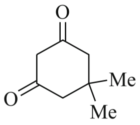
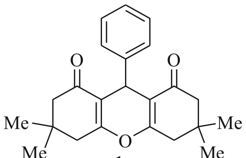
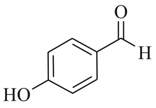
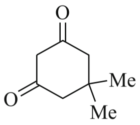
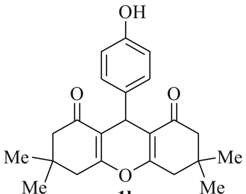
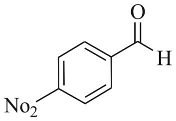
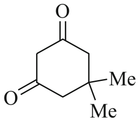
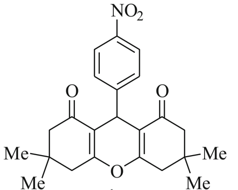
Entry	**1** (aldehyde)	**2** and/or **3**	Product	Time (min)	Yield (%)[a]	M.P. (lit. m.p.) (°C)
a			 **1a**	7	92	200–202 (199–200 [8])
b			 **1b**	9	90	245–247 (246–248 [28])
c			 **1c**	5	95	223–224 (222–224 [27])

Table 3 continued

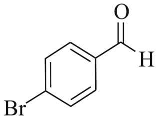
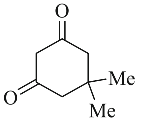
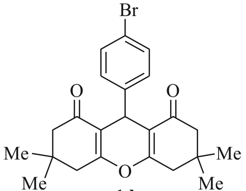
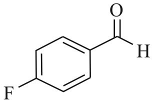
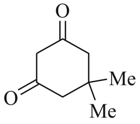
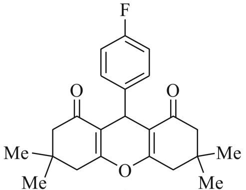
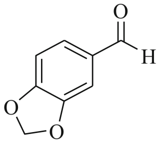
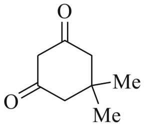
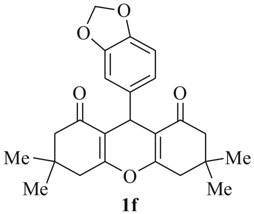
Entry	**1** (aldehyde)	**2** and/or **3**	Product	Time (min)	Yield (%)[a]	M.P. (lit. m.p.) (°C)
d			 **1d**	6	92	235–237 (234–236 [27])
e			 **1e**	6	93	224–226 (225–227 [8])
f			 **1f**	7	94	220–222

Table 3 continued

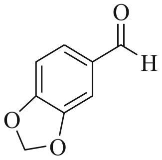
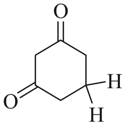
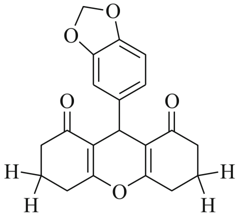
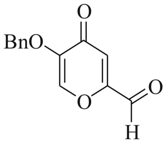
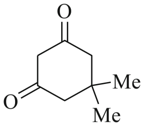
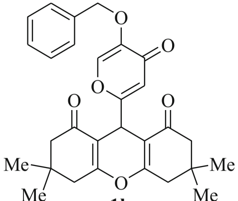
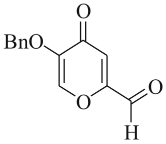
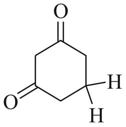
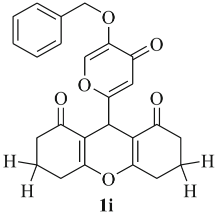
Entry	**1** (aldehyde)	**2** and/or **3**	Product	Time (min)	Yield (%)[a]	M.P. (lit. m.p.) (°C)
g			 **1g**	7	95	243–245
h			 **1h**	5	95	190–192
i			 **1i**	5	96	188–190

Table 3 continued

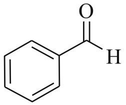
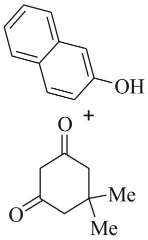
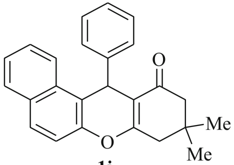
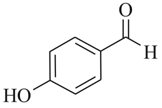
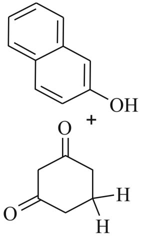
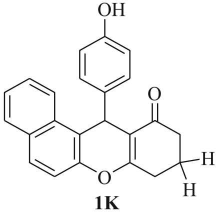
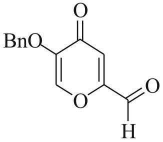
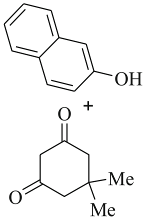
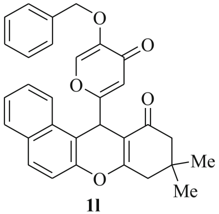
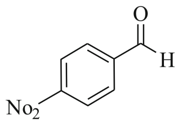
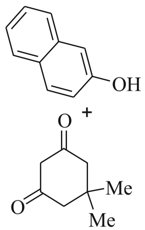
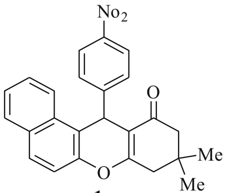
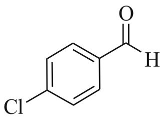
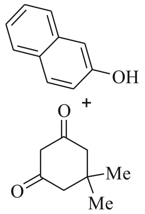
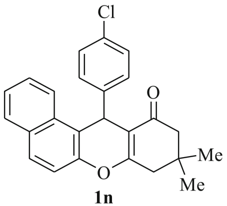
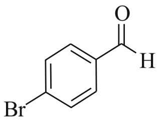
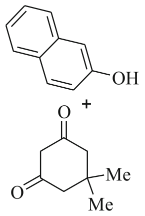
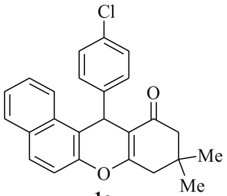
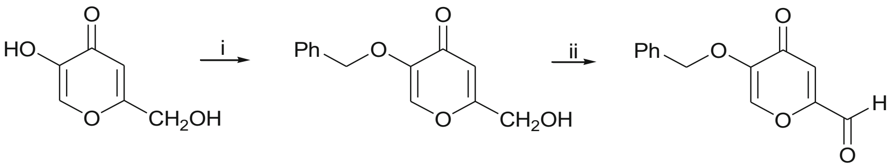
Entry	**1** (aldehyde)	**2** and/or **3**	Product	Time (min)	Yield (%)^a	M.P. (lit. m.p.) (°C)
j			 **1j**	7	94	151–153 (152–154 [8])
k			 **1K**	9	94	271–273 (270–271 [30])
l			 **1l**	5	94	196–198

Table 3 continued

Entry	**1** (aldehyde)	**2** and/or **3**	Product	Time (min)	Yield (%)^a	M.P. (lit. m.p.) (°C)
m			 **1m**	5	95	176–178 (175–177 [31])
n			 **1n**	6	94	181–183 (180–182 [30])
o			 **1o**	6	94	184–185 (186–188 [32])

[a] Yields refer to isolated products



Scheme 2 (*i*) $PhCH_2Br$ (1eq), NaOH (1eq), $MeOH/H_2O$: 10/1, 60 °C, 4 h. (*ii*) IBX, $DMSO/H_2O$: 90/10, 80 °C, 2 h

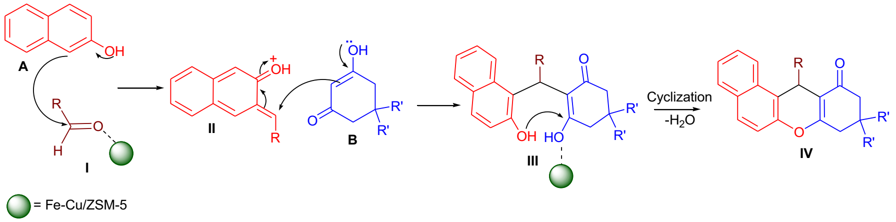
the hydroxymethyl group with 2-iodobenzoic acid (IBX) in $DMSO:H_2O$ (90:10) [17].

In a possible mechanism (Scheme 3), the carbonyl group of the aromatic aldehyde is initially activated by the Fe-Cu/ZSM-5 catalyst to give the intermediate **I**. This is then attacked by β-naphthol (**A**) to afford **II** as a Michael acceptor. Michael addition of dimedone (**B**) with intermediate **II** gives intermediate **III**. Finally by elimination of H_2O from **III**, the tetrahydrobenzoxanthene derivative **IV** is produced.

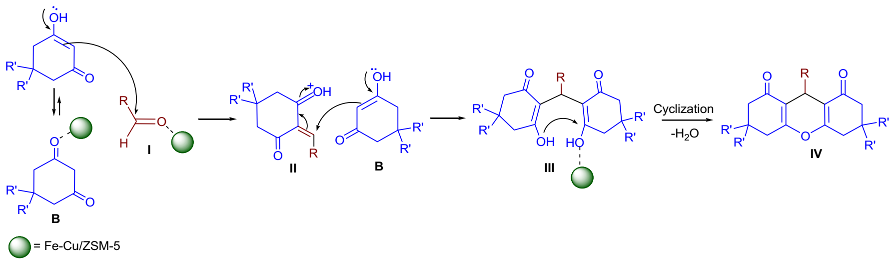
The synthesis of 1,8-dioxooctahydroxanthene derivatives (Scheme 4) could proceed similarly. The activated carbonyl group of the aromatic aldehyde (**I**) is attacked by the cyclic 1,3-diketone (**B**). Then Michael addition of the cyclic 1,3-diketone (**B**) gives **III** and elimination of H_2O gives **IV** [33, 34].

Conclusions

The zeolite H-ZSM-5, impregnated with Cu(II) and Fe(III) by treatment with metal nitrates, has been used as an efficient supported catalyst for an improved one-pot synthesis of tetrahydrobenzoxanthene and 1,8-dioxooctahydroxanthene derivatives in water under ultrasound irradiation. The simple procedures, combined with easy recovery and reuse of this catalyst, make this method economically and environmentally benign. Xanthene derivatives possessing pyrone moieties were prepared under the same experimental conditions and the corresponding products were obtained in high yields.



Scheme 3 Possible mechanism for the synthesis of tetrahydrobenzoxanthene



Scheme 4 Possible mechanism for the synthesis of 1,8-dioxooctahydroxanthene derivatives

Experimental

Materials and technique

Chemicals were either prepared in our laboratory or purchased from Merck, Fluka, and Aldrich. Commercial products were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and with $CDCl_3$ as solvent. The FTIR spectra were recorded on a Bruker Tensor 270 spectrometer. The reactions were carried out by used of an ultrasonic processor probe (SONOPULS Ultrasonic homogenizers). The elemental analyses were carried out with an Elementar Vario EL III instrument. The abbreviations used for NMR signals are: s = singlet, d = doublet, t = triplet and m = multiplet. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Synthesis of nanocatalysts

The catalysts were prepared as indicated by Niaei et al. [29]. The characterization of Fe-Cu/ZSM-5 catalyst is described in supporting information.

*General procedure for preparation of 1,8-dioxo-octahydroxanthene derivatives (**1a**–**1o**)*

In a typical experiment, various aromatic aldehyde (1 mmol), cyclic 1,3-diketone (2 mmol) and 3 wt% of Fe-Cu/ZSM-5 in 2 ml water was introduced in a 20-ml heavy-walled, pear-shaped, two-necked flask with nonstandard tapered outer joint. The flask was attached to a 12-mm-tip diameter probe and the reaction mixture was sonicated at ambient temperature at 40 % power of the processor. After completion of the reaction (monitored by TLC, within 5–10 min), the solid product was filtered, washed with water, dried, and recrystallized from ethanol. The zeolite-supported transition metal catalysts was washed three times with water and ethanol and dried under vacuum before reuse.

The spectral data of some of the selected products

*3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione (**1a**)*

White powder; yield 92 %; M.P. = 200–202 °C; FTIR (KBr, cm^{-1}): 3031 (Ar–H), 2957 (C–H), 1661 (C=O), 1626 (C=C), 1362, 1199, 1163 (C–O), 968, 699. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.98 (s, 6H, $2CH_3$), 1.09 (s, 6H, $2CH_3$), 2.16 (d, J = 16.2 Hz, 2H, $2CH_2$), 2.23 (d, J = 16.3 Hz, 2H, $2CH_2$), 2.46 (s, 4H, $2CH_2$), 4.74 (s, 1H, CH), 7.09 (t, J = 7.3 Hz, 1H, Ar–H), 7.21 (t, J = 7.6 Hz, 2H, Ar–H), 7.28 (d, J = 6.8 Hz, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.27, 28.23, 30.77, 31.15, 39.80, 49.68, 114.60, 125.31, 126.99, 127.32, 143.03, 161.22, 195.38. Anal. Calc. for $C_{23}H_{26}O_3$: C 78.83, H 7.48 %. Found: C 78.69, H 7.24 %.

*3,4,6,7-Tetrahydro-9-(4-hydroxyphenyl)-3,3,6,6-tetramethyl-2H-xanthene-1,8(5H,9H)-dione (**1b**)*

White powder; yield 90 %; M.P. = 245–247 °C; FTIR (KBr, cm^{-1}): 3412 (O–H), 3022 (Ar–H), 2960 (C–H), 1653 (C=O), 1615 (C=C), 1365, 1197, 1137 (C–O), 931, 698. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.99 (s, 6H, $2CH_3$), 1.09 (s, 6H, $2CH_3$), 2.17 (d, J = 16.3 Hz, 2H, $2CH_2$), 2.23 (d, J = 16.3 Hz, 2H, $2CH_2$), 2.45 (s, 4H, $2CH_2$), 4.67 (s, 1H, CH), 6.20 (s, 1H, OH, exchanged with D_2O), 6.57 (d, J = 8.4 Hz, 2H, Ar–H), 7.08 (d, J = 8.4 Hz, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.35, 28.15, 29.92, 31.24, 39.81, 49.71, 114.19, 114.82, 128.33, 134.65, 153.57, 161.37, 196.19. Anal. Calc. for $C_{23}H_{26}O_4$: C 75.38, H 7.15 %. Found: C 75.47, H 7.10 %.

*3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(4-nitrophenyl)-2H-xanthene-1,8(5H,9H)-dione (**1c**)*

White powder; yield 95 %; M.P. = 222–224 °C; FTIR (KBr, cm^{-1}): 3081 (Ar–H), 2962 (C–H), 1666 (C=O), 1615, 1519, 1467 (C=C), 1352, 1200, 1165, 1138 (C–O), 911, 699. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.92 (s, 6H, $2CH_3$), 1.05 (s, 6H, $2CH_3$), 2.10 (d, J = 16.3 Hz, 2H, $2CH_2$), 2.19 (d, J = 16.3 Hz, 2H, $2CH_2$), 2.43 (s, 4H, $2CH_2$), 4.76 (s, 1H, CH), 7.41 (d, J = 8.6 Hz, 2H, Ar–H), 8.03 (d, J = 8.6 Hz, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.21, 28.22, 31.21, 31.31, 39.77, 49.53, 113.47, 122.41, 128.32, 145.40, 150.49, 161.92, 195.29. Anal. Calc. for $C_{23}H_{25}NO_5$: C 69.86, H 6.37, N 3.54 %. Found: C 69.71, H 6.24, N 3.65 %.

*9-(4-Bromophenyl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2H-xanthene-1,8(5H,9H)-dione (**1d**)*

White powder; yield 92 %; M.P. = 235–236 °C; FTIR (KBr, cm^{-1}): 3042 (Ar–H), 2957 (C–H), 1661 (C=O), 1618, 1486, 1468 (C=C), 1362, 1198, 1162, 1140 (C–O), 942, 696. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.98 (s, 6H, $2CH_3$), 1.10 (s, 6H, $2CH_3$), 2.15 (d, J = 16.3 Hz, 2H, $2CH_2$), 2.23 (d, J = 16.3 Hz, 2H, $2CH_2$), 2.46 (s, 4H, $2CH_2$), 4.69 (s, 1H, CH), 7.17 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.33 (d, $J = 8.4$ Hz, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.25, 28.26, 28.67, 30.52, 31.18, 39.79, 49.63, 114.14, 119.21, 129.15, 130.12, 142.18, 161.43, 195.37. Anal. Calc. for $C_{23}H_{25}BrO_3$: C 64.34, H 5.87 %. Found: C 64.51, H 5.69 %.

*9-(Benzo[d] [1, 3] dioxol-5-yl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2H-xanthene-1,8(5H,9H)-dione (**1f**)*

White powder; yield 94 %; M.P. = 220–222 °C; FTIR (KBr, cm^{-1}): 3052 (Ar–H), 2959 (C–H), 1665 (C=O), 1619, 1483, 1436 (C=C), 1364, 1198, 1165, 1144 (C–O), 930, 690. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.00 (s, 6H, $2CH_3$), 1.09 (s, 6H, $2CH_3$), 2.17 (d, $J = 16.3$ Hz, 4H, $2CH_2$), 2.23 (d, $J = 16.3$ Hz, 4H, $2CH_2$), 2.45 (s, 4H, $2CH_2$), 4.66 (s, 1H, CH), 5.87 (s, 2H, O–CH_2–O), 6.65 (d, $J = 8.0$ Hz, 1H, Ar–H), 6.73 (d, $J = 8.4$ Hz, 1H, Ar–H), 6.80 (s, 1H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.39, 28.20, 28.68, 30.41, 31.17, 39.79, 49.71, 99.73, 106.84, 108.07, 114.62, 120.49, 137.24, 144.90, 146.26, 161.16, 195.54. Anal. Calc. for $C_{24}H_{26}O_5$: C 73.08, H 6.64 %. Found: C 73.23, H 6.72 %.

*9-(Benzo[d][1,3]dioxol-5-yl)-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione (**1g**)*

White powder; yield 95 %; M.P. = 243–245 °C; FTIR (KBr, cm^{-1}): 3055 (Ar–H), 2956 (C–H), 1655 (C=O), 1619, 1500, 1481, 1439 (C=C), 1360, 1200, 1177, 1133 (C–O), 925, 634. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.91–2.08 (m, 4H, $2CH_2$), 2.31–2.38 (m, 4H, $2CH_2$), 2.55–2.63 (m, 4H, $2CH_2$), 4.72 (s, 1H, CH), 5.87 (s, 2H, O–CH_2–O), 6.65 (d, $J = 8.5$, 1H, Ar–H), 6.78–6.79 (m, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 19.25, 26.10, 30.22, 35.94, 99.75, 106.87, 107.94, 115.89, 120.62, 137.45, 144.95, 146.29, 162.78, 195.61. Anal. Calc. for $C_{20}H_{18}O_5$: C 70.99, H 5.36 %. Found: C 70.74, H 5.51 %.

*9-(5-(Benzyloxy)-4-oxo-4H-pyran-2-yl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2H-xanthene-1,8(5H,9H)-dione (**1h**)*

White powder; yield 95 %; M.P. = 190–192 °C; FTIR (KBr, cm^{-1}): 3099 (Ar–H), 2963 (C–H), 1660 (C=O), 1640 (C=O pyrone), 1581, 1498, 1456 (C=C), 1390, 1360, 1201, 1167, 1137 (C–O), 928, 699. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.03 (s, 6H, $2CH_3$), 1.11 (s, 6H, $2CH_3$), 2.27 (s, 4H, $2CH_2$), 2.44 (s, 4H, $2CH_2$), 4.56 (s, 1H, CH), 4.99 (s, 2H, O–CH_2), 6.28 (s, 1H, H-3 pyrone), 7.30–7.38 (m, 5H, Ar–H), 7.51 (s, 1H, H-6 pyrone). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.43, 28.03, 30.02, 31.17, 39.83, 49.50, 70.76, 110.66, 113.07, 126.75, 127.28, 127.62, 139.60, 162.89, 195.12. Anal. Calc. for $C_{29}H_{30}O_6$: C 73.40, H 6.37 %. Found: C 73.61, H 6.23 %.

*9-(5-(Benzyloxy)-4-oxo-4H-pyran-2-yl)-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione (**1i**)*

White powder; yield 96 %; M.P. = 188–190 °C; FTIR (KBr, cm^{-1}): 3032 (Ar–H), 2922 (C–H), 1657 (C=O), 1637 (C=O pyrone), 1580, 1498, 1455 (C=C), 1358, 1360, 1206, 1178, 1128 (C–O), 989, 696. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.03–2.04 (m, 4H, $2CH_2$), 2.32–2.46 (m, 4H, $2CH_2$), 2.52–2.65 (m, 4H, $2CH_2$), 4.62 (s, 1H, CH), 4.98 (s, 2H, O–CH_2), 6.25 (s, 1H, H-3 pyrone), 7.29–7.36 (m, 5H, Ar–H), 7.50 (s, 1H, H-6 pyrone). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 18.96, 26.10, 29.83, 35.59, 70.65, 111.72, 113.00, 126.56, 127.21, 127.59, 134.83, 139.65, 164.54, 167.75, 173.78, 195.07. Anal. Calc. for $C_{25}H_{22}O_6$: C 71.76, H 5.30 %. Found: C 71.88, H 5.19 %.

*General procedure for preparation of tetrahydrobenzoxanthene derivatives (**1j–1o**)*

In a typical experiment, various aromatic aldehyde (1 mmol), cyclic 1,3-diketone (1 mmol), β-naphtol (1 mmol) and 3 wt% of Fe-Cu/ZSM-5 in 2 ml of water was introduced in a 20-ml, heavy-walled, pear-shaped, two-necked flask with nonstandard tapered outer joint. The flask was attached to a 12-mm tip diameter probe and the reaction mixture was sonicated at ambient temperature at 40 % power of the processor. After completion of the reaction (monitored by TLC, within 5–10 min), the solid product was filtered washed with water, dried, and recrystallized from ethanol. The zeolite-supported transition metal catalysts was washed three times with water and ethanol and dried under vacuum before reuse.

The spectral data of products

*9,10-Dihydro-9,9-dimethyl-12-phenyl-8H-benzo[a]xanthen-11(12H)-one (**1j**)*

White powder; yield 94 %; M.P. = 150–152 °C; FTIR (KBr, cm^{-1}): 3053 (Ar–H), 2956 (C–H), 1650 (C=O), 1619, 1595, 1515, 1489, 1451 (C=C), 1374, 1142, 1117 (C–O), 975, 698. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.96 (s, 3H, $1CH_3$), 1.12 (s, 3H, $1CH_3$), 2.24 (d, J = 16.3 Hz, 1H, CH_2), 2.26 (d, J = 16.3 Hz, 1H, CH_2), 2.57 (s, 2H, $2CH_2$), 5.71 (s, 1H, CH), 7.05 (t, J = 7.3 Hz, 1H, Ar–H), 7.17 (t, J = 7.3 Hz, 2H, Ar–H), 7.32–7.45 (m, 5H, Ar–H), 7.77 (t, J = 7.5 Hz, 2H, Ar–H), 8.00 (d, J = 8.4 Hz, 1H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.15, 28.27, 28.69, 31.25, 33.67, 40.39, 49.88, 116.02, 116.67, 122.66, 123.86, 125.20, 125.97, 127.20, 127.40, 127.79, 130.37, 130.46, 143.71, 146.71, 162.86. Anal. Calc. for $C_{25}H_{22}O_2$: C 84.72, H 6.26 %. Found: C 84.91, H 6.13 %.

*12-(5-(Benzyloxy)-4-oxo-4H-pyran-2-yl)-9,10-dihydro-9,9-dimethyl-8H-benzo[a]xanthen-11(12H)-one (**1l**)*

White powder; yield 94 %; M.P. = 196–198 °C; FTIR (KBr, cm^{-1}): 3071 (Ar–H), 2927 (C–H), 1656 (C=O), 1639 (C=O pyrone), 1621, 1593, 1517, 1497, 1453 (C=C), 1369, 1142, 1114 (C–O), 979, 691. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ

1.12 (s, 3H, 1CH_3), 1.19 (s, 3H, 1CH_3), 2.40 (s, 2H, CH_2), 2.62 (d, $J = 18.0$ Hz, 1H, CH_2), 2.68 (d, $J = 18.0$ Hz, 1H, CH_2), 4.96 (d, $J = 12.4$ Hz, 1H, O–CH_2), 5.00 (d, $J = 12.4$ Hz, 1H, O–CH_2), 5.65 (s, 1H, CH), 6.41 (s, 1H, H-3 pyrone), 7.30–7.34 (m, 6H, Ar–H), 7.45 (s, 1H, H-6 pyrone), 7.52 (t, $J = 7.4$ Hz, 1H, Ar–H), 7.60 (t, $J = 7.4$ Hz, 1H, Ar–H), 7.86 (d, $J = 8.8$ Hz, 1H, Ar–H), 7.88 (d, $J = 8.8$ Hz, 1H, Ar–H), 8.03 (d, $J = 8.4$ Hz, 1H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 26.32, 28.21, 28.68, 31.24, 32.45, 49.63, 70.69, 108.48, 111.81, 113.54, 116.12, 121.67, 124.44, 126.68, 127.27, 127.59, 127.71, 128.97, 130.12, 130.38, 134.67, 139.93, 145.84, 147.03, 165.24, 167.06, 173.66, 195.29. Anal. Calc. for $C_{31}H_{26}O_5$: C 77.81, H 5.48 %. Found: C 77.62, H 5.55 %.

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