

# A Comparative Study of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> Nanoparticles as Reusable Heterogeneous Catalysts in the Synthesis of Tetrahydrobenzo[*a*]xanthene-11-ones<sup>1</sup>

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Received August 2, 2016

**Abstract** — Catalytic effect of three nanosized metal oxides TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the one-pot synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by three-component reaction of β-naphthol with aromatic aldehydes and dimedone has been studied. Various reaction conditions were tested in the presence of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The results demonstrated that nano Fe<sub>3</sub>O<sub>4</sub> was the more efficient heterogeneous catalyst than Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. The reaction completed within shorter period of time under solvent-free conditions with higher yield. The catalysts used were recyclable.

**Keywords:** metal oxide nanoparticles, tetrahydrobenzo[*a*]xanthene, solvent-free synthesis

**DOI:** 10.1134/S1070363216120495

## INTRODUCTION

The problems associated with most homogeneous catalysts, such as their environmental issues and difficult recovery initiated development of alternative procedures based on heterogeneous catalysis [1–6]. Highly developed surface of nanoparticles [7, 8] supports their efficient accessibility to a big number of active centers thus promoting activity of such catalysts. Though various metal oxide nanoparticles have been synthesized and tested as catalysts in organic transformations [9–12], no reports on application of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> catalysts for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones have been presented. These compounds are synthesized via the one-pot three-component reaction of β-naphthol with an aldehyde and dimedone initiated by various catalysts [13–28].

Here we present the results of our study of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles as heterogeneous catalysts in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones (Scheme 1) as the development of our earlier research of reusable catalysts in the synthesis of organic compounds [29–31].

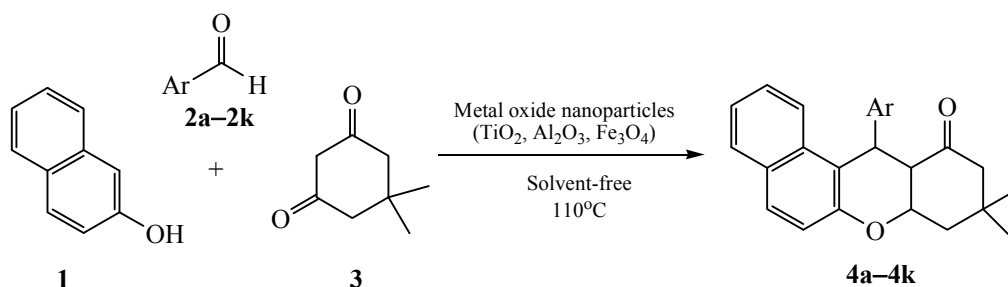
The reaction of β-naphthol **1** (1 mmol) with 4-chlorobenzaldehyde **2f** (1 mmol) and dimedone **3**

(1 mmol) for the synthesis of compound **4f** was selected as the test process optimized with different nano metal oxide catalysts and various parameters like catalyst amount, effect of solvent and influence of temperature. According to the optimization experiments (Table 1) all nano metal oxide catalysts involved demonstrated good catalytic effects in the model reaction. Nanoparticles of Fe<sub>3</sub>O<sub>4</sub> promoted the reaction more efficiently than the others, leading to higher yields of **4f**. The optimal amount of the catalyst was determined to be 20 mol % (Table 1, entry 16) under solvent-free conditions. The higher amount of the catalyst had no significant effect on the yield and reaction time. For all catalysts tested, the best result was achieved under solvent-free conditions. It was determined that yield of the process increased at elevated temperature and at 110°C the product **4f** was obtained with very high yield. To substantiate the important role of the catalyst, the reaction was carried out at 110°C in the absence of the catalyst under solvent-free conditions (Table 1, entry 1). As a result, only low yield of the product was achieved, indicating importance of the catalyst in the reaction.

Thereafter, applicability of the method was evaluated for the synthesis of other tetrahydrobenzo[*a*]xanthene-11-ones using a wide range of substituted aromatic aldehydes (Table 2). According to the accumulated data the substituents in the aromatic ring

<sup>1</sup> The text was submitted by the authors in English.

## Scheme 1.



Ar = C<sub>6</sub>H<sub>5</sub> (**a**), 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> (**b**), 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> (**c**), 4-MeC<sub>6</sub>H<sub>4</sub> (**d**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**e**), 4-ClC<sub>6</sub>H<sub>4</sub> (**f**), 2-ClC<sub>6</sub>H<sub>4</sub> (**g**), 4-BrC<sub>6</sub>H<sub>4</sub> (**h**), 3-BrC<sub>6</sub>H<sub>4</sub> (**i**), 4-FC<sub>6</sub>H<sub>4</sub> (**j**), 2-thienyl (**k**).

of aldehydes or use of heteroaromatic aldehydes had no significant effect on time of the reaction and yield of the products. Under the same conditions, however, no reaction occurred when aliphatic aldehydes were used. Fe<sub>3</sub>O<sub>4</sub> nanoparticles proved to be the better

catalyst than nanosized TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in terms of yield and reaction time.

All three catalysts tested could be used at least five times without significant reduction in their activity

**Table 1.** Synthesis of compound **4f** in the presence of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> nanoparticles as catalysts under various reaction conditions<sup>a</sup>

Entry	Nanometal oxide	Catalyst, mol %	Solvent	T, °C	Time, min	Yield <sup>b</sup> , %
1	–	–	–	110	120	12
2	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	4	–	90	55/60/55	45/41/47
3	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	4	–	100	55/55/50	49/42/50
4	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	4	–	110	50/50/45	52/44/57
5	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	8	–	90	50/50/45	52/47/53
6	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	8	–	100	45/50/40	58/51/61
7	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	8	–	110	40/40/37	61/52/68
8	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	12	–	90	40/45/35	61/55/66
9	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	12	–	100	40/40/35	65/58/69
10	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	12	–	110	35/35/30	69/62/77
11	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	16	–	90	30/35/30	68/65/75
12	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	16	–	100	30/33/28	71/68/77
13	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	16	–	110	27/30/25	78/71/85
14	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	–	90	27/30/23	80/76/84
15	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	–	100	25/30/23	82/79/87
16	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	–	110	25/27/18	85/81/94
17	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	25	–	90	30/30/25	80/77/82
18	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	25	–	100	30/30/25	81/80/87
19	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	25	–	110	25/30/20	84/82/94
20	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	–	130	30/30/25	83/82/93
21	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	EtOH	Reflux	120/120/90	70/66/75
22	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	MeOH	Reflux	120/120/90	58/57/66
23	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	120/120/90	33/31/34
24	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	CH <sub>3</sub> CN	Reflux	120/120/90	41/41/52
25	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20	CH <sub>3</sub> CO <sub>2</sub> Et	Reflux	120/120/90	50/47/55

<sup>a</sup> Reaction conditions: β-naphthol **1** (1 mmol), 4-chlorobenzaldehyde **2f** (1 mmol) and dimedone **3** (1 mmol). <sup>b</sup> Isolated yields.

**Table 2.** Synthesis data for tetrahydrobenzo[*a*]xanthene-11-ones **4a–4k** catalyzed by metal oxides nanoparticles<sup>a</sup>

Comp. no.	Ar	Catalyst	Time, min	Yield <sup>b</sup> , %	mp, °C	
					found	calculated
<b>4a</b>	C <sub>6</sub> H <sub>5</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	25/30/17	90/80/92	151–152	149–151 [16]
<b>4b</b>	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	27/27/18	86/81/91	166–168	168–172 [16]
<b>4c</b>	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	17/20/8	87/84/95	180–181	178–181 [16]
<b>4d</b>	4-MeC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20/25/16	88/83/92	176–178	175–176 [16]
<b>4e</b>	4-MeOC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20/25/13	89/85/95	205–207	207–208 [20]
<b>4f</b>	4-ClC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	25/27/18	85/81/94	190–192	188–189 [20]
<b>4g</b>	2-ClC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	25/30/20	87/82/90	178–180	179–181 [22]
<b>4h</b>	4-BrC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	18/23/14	91/85/93	185–187	187–189 [23]
<b>4i</b>	3-BrC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20/23/17	85/80/90	166–168	170–171 [23]
<b>4j</b>	4-FC <sub>6</sub> H <sub>4</sub>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	20/25/16	90/83/93	186–188	185–186 [23]
<b>4k</b>	2-Thienyl	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	25/25/14	92/86/97	181–183	177–179 [23]

<sup>a</sup> Reaction conditions: β-naphthol **1** (1 mmol), an aromatic aldehyde **2a–2k** (1 mmol), dimedone **3** (1 mmol), nano metal oxide (20 mol %), 110°C, solvent-free. <sup>b</sup> Isolated yields.

(85/81/94, 84/80/94, 84/79/93, 83/79/92, and 81/78/91% yields for Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nano catalysts in first to fifth use, respectively). In case of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, easy magnetic separation makes this catalyst attractive in view of green chemistry and catalysis science.

Applicability and efficiency of the studied catalysts were compared with some of the reported methods of synthesis of tetrahydrobenzo[*a*]xanthene-11-ones (Table 3). The current procedure that involved nano Fe<sub>3</sub>O<sub>4</sub> as the catalyst gave high yields of the products in shorter reaction time than the other methods. Magnetic recyclability of Fe<sub>3</sub>O<sub>4</sub> nanoparticles makes it superior over other reported methods.

## EXPERIMENTAL

Nanosized TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles were purchased from Tecnan Spanish company. All other chemicals were purchased from Merck and Aldrich and used without purification. Melting points were measured on a Stuart SMP3 melting point apparatus. IR spectra were recorded on a Tensor 27 Bruker spectrophotometer in KBr disks. <sup>1</sup>H NMR spectra were measured in CDCl<sub>3</sub> on a Bruker 400 spectrometer.

**General procedure for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones **4a–4k** catalyzed by nanosized metal oxides.** A mixture of β-

naphthol **1** (1 mmol), an aromatic aldehyde **2a–2k** (1 mmol), dimedone **3** (1 mmol), and a nanosized metal oxide (20 mol %) was heated in an oil bath at 110°C. The reaction was monitored by TLC. Upon completion of the process, the reaction mixture was cooled down to room temperature and hot ethanol was added. This resulted in precipitation of the catalyst, which was filtered off (TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> nanoparticles) or separated using an external magnet (Fe<sub>3</sub>O<sub>4</sub> nanoparticles). The product was recrystallized from ethanol to give compounds **4a–4k**. The separated catalyst was washed with hot ethanol, dried at 60°C under vacuum for 1 h and reused in the similar experiments. All products were identified by comparison of their melting points with those of authentic samples. The structures of some products were confirmed by their IR and <sup>1</sup>H NMR spectral data.

**9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (4a).** <sup>1</sup>H NMR spectrum, δ, ppm: 0.99 s (3H, CH<sub>3</sub>), 1.15 s (3H, CH<sub>3</sub>), 2.31 AB<sub>q</sub> (Δν = 27.6 Hz, J<sub>AB</sub> = 16.4 Hz, 2H, CH<sub>2</sub>), 2.61 s (2H, CH<sub>2</sub>), 5.74 s (1H, CH), 7.09 t.t (J = 7.6, 2.0 Hz, 1H, H<sub>arom</sub>), 7.20 t (J = 7.6 Hz, 2H, H<sub>arom</sub>), 7.35–7.50 m (5H, H<sub>arom</sub>), 7.80 d (J = 8.8 Hz, 2H, H<sub>arom</sub>), 8.02 d (J = 8.4 Hz, 1H, H<sub>arom</sub>). IR spectrum, ν<sub>max</sub>, cm<sup>-1</sup>: 2962, 1595, 1492, 1447, 1374, 1299, 1250, 1166, 870.

**9,9-Dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (4b).** <sup>1</sup>H NMR

**Table 3.** Efficiency of various catalysts in synthesis of tetrahydrobenzo[*a*]xanthene-11-ones

Catalyst	Conditions			Time, min	Yield, %	References
	solvent	<i>T</i> , °C	other			
PEG-400	–	120	–	330–450	79–90	13
HY zeolite	–	80	–	60–240	70–95	14
I <sub>2</sub>	AcOH	reflux	–	150–180	70–89	15
SO <sub>3</sub> H-functionalized ionic liquids	–	120	–	55–95	75–95	16
Guanidine hydrochloride	–	80	–	25–60	88–93	17
Rice husk	–	90	–	30–60	93–98	18
ρ-TSA	–	120	–	35–45	80–92	19
Cyanuric chloride	–	80	–	30–70	84–93	20
HClO <sub>4</sub> /SiO <sub>2</sub>	–	80	–	48–90	86–95	21
CAN	CH <sub>2</sub> Cl <sub>2</sub> /EtOH	26	Ultrasound	120–144	82–87	22
Ce(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	–	120	–	8–30	85–97	23
NaHSO <sub>4</sub> –SiO <sub>2</sub>	ClCH <sub>2</sub> CH <sub>2</sub> Cl	reflux	–	280–420	69–89	24
InCl <sub>3</sub>	–	120	–	30–75	63–88	25
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	–	60	–	40–90	81–94	26
Sulfamic acid	–	120	–	115–136	79–84	27
Sr(OTf) <sub>2</sub>	ClCH <sub>2</sub> CH <sub>2</sub> Cl	80	–	300–420	70–88	28
TiO <sub>2</sub> Nanoparticles	–	110	–	17–25	85–92	This work
Al <sub>2</sub> O <sub>3</sub> Nanoparticles	–	110	–	23–30	80–86	This work
Fe <sub>3</sub> O <sub>4</sub> Nanoparticles	–	110	–	8–20	90–97	This work

spectrum,  $\delta$ , ppm: 0.98 s (3H, CH<sub>3</sub>), 1.16 s (3H, CH<sub>3</sub>), 2.31 AB<sub>q</sub> ( $\Delta\nu = 35.2$  Hz,  $J_{AB} = 16.4$  Hz, 2H, CH<sub>2</sub>), 2.64 s (2H, CH<sub>2</sub>), 5.84 s (1H, CH), 7.38–7.50 m (4H, H<sub>arom</sub>), 7.82–7.92 m (4H, H<sub>arom</sub>), 7.96 d.d ( $J = 8.0$ , 1.2 Hz, 1H, H<sub>arom</sub>), 8.14 s (1H, H<sub>arom</sub>). IR spectrum,  $\nu_{\max}$ , cm<sup>-1</sup>: 3089, 2961, 2870, 1597, 1527, 1378, 1342, 1251, 1044, 894.

**9,9-Dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (4c).** <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.98 s (3H, CH<sub>3</sub>), 1.17 s (3H, CH<sub>3</sub>), 2.32 AB<sub>q</sub> ( $\Delta\nu = 36.4$  Hz,  $J_{AB} = 16.4$  Hz, 2H, CH<sub>2</sub>), 2.63 AB<sub>q</sub> ( $\Delta\nu = 20.0$  Hz,  $J_{AB} = 18.0$  Hz, 2H, CH<sub>2</sub>), 5.85 s (1H, CH), 7.38–7.50 m, (3H, H<sub>arom</sub>), 7.55 d ( $J = 8.4$  Hz, 2H, H<sub>arom</sub>), 7.84–7.88 m (3H, H<sub>arom</sub>), 8.07 d ( $J = 8.4$  Hz, 2H, H<sub>arom</sub>). IR spectrum,  $\nu_{\max}$ , cm<sup>-1</sup>: 3074, 2956, 1646, 1619, 1595, 1516, 1376, 1345, 1223, 1183, 850.

**12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (4f).** <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.99 s (3H, CH<sub>3</sub>), 1.15 s (3H, CH<sub>3</sub>), 2.31 AB<sub>q</sub> ( $\Delta\nu = 28.8$  Hz,  $J_{AB} = 16.4$  Hz, 2H, CH<sub>2</sub>), 2.60 s (2H, CH<sub>2</sub>), 5.72 s (1H, CH), 7.16 d ( $J = 8.0$  Hz, 2H, H<sub>arom</sub>), 7.28–7.50 m (5H, H<sub>arom</sub>), 7.82 t ( $J = 8.0$  Hz, 2H, H<sub>arom</sub>), 7.93 d ( $J = 8.0$  Hz, 1H, H<sub>arom</sub>). IR spectrum,  $\nu_{\max}$ , cm<sup>-1</sup>: 3079, 2953, 2870, 1650, 1597, 1488, 1371, 1225, 1184, 1166, 1017, 835, 812, 753.

**12-(2-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (4g).** <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.03 s (3H, CH<sub>3</sub>), 1.17 s (3H, CH<sub>3</sub>), 2.30 AB<sub>q</sub> ( $\Delta\nu = 36.6$  Hz,  $J_{AB} = 16.0$  Hz, 2H, CH<sub>2</sub>), 2.64 s (2H, CH<sub>2</sub>), 6.03 s (1H, CH), 7.00–7.12 m (2H, H<sub>arom</sub>), 7.28–7.38 m (3H, H<sub>arom</sub>), 7.41 t ( $J = 7.2$  Hz, 1H, H<sub>arom</sub>), 7.51 t ( $J = 7.6$  Hz, 1H, H<sub>arom</sub>), 7.79 t ( $J = 8.4$  Hz, 2H, H<sub>arom</sub>), 8.26 d ( $J = 8.8$  Hz, 1H, H<sub>arom</sub>). IR

spectrum,  $\nu_{\max}$ , cm<sup>-1</sup>: 3059, 2946, 1651, 1619, 1597, 1471, 1370, 1226, 1143, 1100, 812, 743.

**12-(3-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4i).** <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.01 s (3H, CH<sub>3</sub>), 1.15 s (3H, CH<sub>3</sub>), 2.32 AB<sub>q</sub> ( $\Delta\nu = 22.6$  Hz,  $J_{AB} = 16.0$  Hz, 2H, CH<sub>2</sub>), 2.61 AB<sub>q</sub> ( $\Delta\nu = 20.6$  Hz,  $J_{AB} = 17.6$  Hz, 2H, CH<sub>2</sub>), 5.71 s (1H, CH), 7.08 t ( $J = 8.0$  Hz, 1H, H<sub>arom</sub>), 7.20–7.25 m (1H, H<sub>arom</sub>), 7.35–7.52 m (5H, H<sub>arom</sub>), 7.80–7.85 m (2H, H<sub>arom</sub>), 7.95 d ( $J = 8.4$  Hz, 1H, H<sub>arom</sub>). IR spectrum,  $\nu_{\max}$ , cm<sup>-1</sup>: 2955, 1650, 1594, 1471, 1375, 1220, 1167, 875, 807.

**12-(4-Fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4j).** <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.99 s (3H, CH<sub>3</sub>), 1.15 s (3H, CH<sub>3</sub>), 2.31 AB<sub>q</sub> ( $\Delta\nu = 28.4$  Hz,  $J_{AB} = 16.0$  Hz, 2H, CH<sub>2</sub>), 2.60 s (2H, CH<sub>2</sub>), 5.72 s (1H, CH), 6.88 t ( $J = 8.8$  Hz, 2H, H<sub>arom</sub>), 7.28–7.50 m (5H, H<sub>arom</sub>), 7.82 t ( $J = 8.8$  Hz, 2H, H<sub>arom</sub>), 7.95 d ( $J = 8.0$  Hz, 1H, H<sub>arom</sub>). IR spectrum,  $\nu_{\max}$ , cm<sup>-1</sup>: 2956, 1650, 1595, 1507, 1466, 1375, 1227, 1185, 1143, 840, 815, 745.

**9,9-Dimethyl-12-(thiophen-2-yl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4k).** <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.99 s (3H, CH<sub>3</sub>), 1.09 s (3H, CH<sub>3</sub>), 2.23 d ( $J = 16.0$  Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.40 d ( $J = 16.0$  Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.65 AB<sub>q</sub> ( $\Delta\nu = 43.0$  Hz,  $J_{AB} = 16.4$  Hz, 2H, CH<sub>2</sub>), 5.94 s (1H, CH), 6.79 d.d ( $J = 5.2, 3.6$  Hz, 1H, H<sub>arom</sub>), 6.85 d ( $J = 2.8$  Hz, 1H, H<sub>arom</sub>), 7.22 dd ( $J = 5.0, 1.2$  Hz, 1H, H<sub>arom</sub>), 7.44–7.51 m (2H, H<sub>arom</sub>), 7.57 t ( $J = 8.8$  Hz, 1H, H<sub>arom</sub>), 7.96 d ( $J = 8.8$  Hz, 2H, H<sub>arom</sub>), 8.11 d ( $J = 8.4$  Hz, 1H, H<sub>arom</sub>). IR spectrum,  $\nu_{\max}$ , cm<sup>-1</sup>: 3052, 2962, 1651, 1594, 1376, 1358, 1223, 1177, 1147, 840, 700.

## CONCLUSIONS

Catalytic activity of three commercially available nanosized metal oxides including TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> was compared in the one-pot synthesis of tetrahydrobenzo[a]xanthen-11-ones by three-component reaction of  $\beta$ -naphthol with aromatic aldehydes and dimedone. The reaction proceeded under solvent-free conditions at 110°C giving high yields of the products in short reaction time. Among three tested nanocatalysts, Fe<sub>3</sub>O<sub>4</sub> nanoparticles proved to be the most efficient catalyst. The catalysts could be used at least five times without substantial reduction in their catalytic activity.

## ACKNOWLEDGMENTS

This work was supported by Islamic Azad University, Mashhad Branch, as a research project.

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