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Nano-Silica Phosphoric Acid: An Efficient Catalyst for One-Pot Synthesis of Tetrahydrobenzo[*a*]xanthenes-11-one Under Solvent-Free or Sonication Conditions

A. Bamoniri[a,*] B. F. Mirjalili [b], S. Nazemian[a]

[a]*Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I. R. Iran*
[b]*Department of Chemistry, College of Science, Yazd University, Yazd, PO Box 89195-741, I. R. Iran*

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**Corresponding author:*
E-mail address:
bamoniri@kashanu.ac.ir
Phone: +98 361 5912384
Fax: +98 3615552930

Abstract

Two simple protocols for the synthesis of tetrahydrobenzo[*a*]xanthenes-11-ones using nano silica phosphoric acid are reported. Short reaction times, high yields, reusability of catalyst and easy workup are some advantages of these protocols.

1. Introduction

Multi-component reactions (MCRs) are special types of synthetically useful organic reactions in which three or more different starting materials react to a final product in an one pot procedure [1]. Such reactions are atom-efficient processes by incorporating the essential parts of the starting materials into the final product. Benzoxanthene moiety in the structure of molecules causes important biological activities such as anti infalammatory [2], antiplasmodial [3], and photodynamic therapy [4].

Tetrahydrobenzo[*a*]xanthenes-11-ones as benzoxanthene derivatives could be synthesized *via* one pot condensation of 2-naphthol, aldehyde, and 1, 3-diketone in the presence of an acidic catalyst. According to the literature, this protocol was catalyzed by indium(III)chloride [5], proline

triflate [6], *p*-toluenesulfonic acid [7], strontium triflate [8], dodecatungstophosphoric acid [9], tetrabutyl ammonium fluoride [10], and $NaHSO_4.SiO_2$ [11].

Silica phosphoric acid (SPA) [12] is an efficient and reusable catalyst. It was prepared by reaction of silica chloride [13] with dry phosphoric acid. It is noted that, silica chloride was prepared *via* reaction of silica gel and thionyl chloride. By using nano silica gel instead of silica gel, according to above pathway, nano silica phosphoric acid (nano-SPA) was prepared. The particle size of nano-SPA was measured by SEM phothography (figure1).

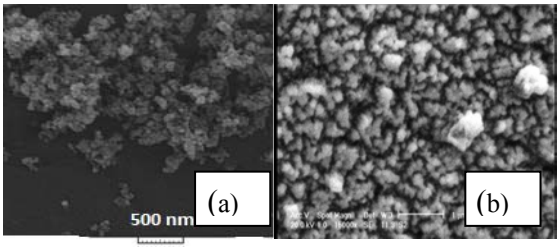
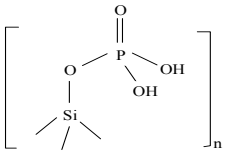


Fig. 1. The SEM photograph of a) nano silica-gel and b) nano-SPA.

The acidic capacity of nano-SPA is 10.32 $mmol.g^{-1}$ and was determined *via* titration of 0.2 g of catalyst with standard solution of NaOH.

The FT-IR (ATR) spectra of silica chloride, nano-SPA.and $H_3PO_4.SiO_2$ were shown in figure 2. In all ATR spectra, the Si-O-H and Si-O-Si stretching bonds are appeared in 900 until 1100 cm^{-1}. In silica chloride spectrum, the Si-Cl stretching bond is appeared in 700 cm^{-1}. In ATR spectra of nano-SPA and $H_3PO_4.SiO_2$, the P-O-H, P=O, P-O stretching bonds are appeared 910-1040, 1637 and 2400-2800 cm^{-1} respectively. According to above data, we suggested one structure for nano-SPA with PO_3H_2 on silica gel (scheme 1).



Scheme 1

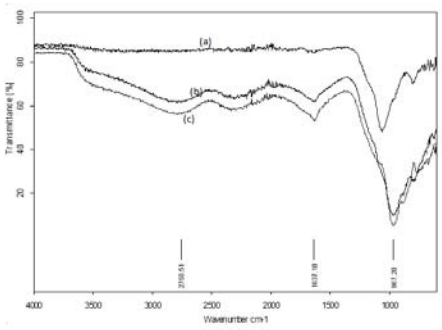


Fig. 2. ATR of a) silica chloride, b) nano-SPA and c) $H_3PO_4.SiO_2$

The X-ray diffraction (XRD) patterns of nano-SiO_2 and nano-SPA are shown in figure 3. Nano-SiO_2 XRD pattern has a strong peak in 2θ value of 21.8024° and FWHM equal to 0.1771 and nano-SPA XRD pattern has a strong broad peak in 21.718 and FWHM equal to 2.3616.

2. Experimental procedure

2.1. General. The materials were purchased from Merck company and were used without any additional purification. Products were characterized by FT-IR, ^{1}H-NMR and comparison of their physical properties with those reported in the literature. FT-IR (ATR) spectra were run on a Bruker, Eqinox 55 spectrometer.A Bruker (DRX-400 Avanes) NMR was used to record the ^{1}H NMR spectra. The SEM of nano particles determined with VEGA/TESCAN scanning electron microscope. A BANDELIN Sonopulse HD 3200 ultrasonic apparatus was used for sonication. The X-ray diffraction (XRD) patterns of materials were recorded by employing a Philips Xpert MPD

diffractometer equipped with a Cu Kα anode (λ = 1.54 A°) in the 2θ range from 5 to 80◦.

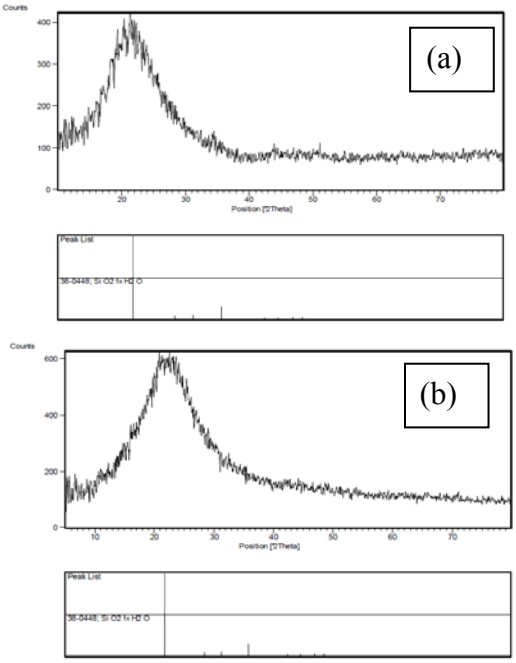


Fig. 3. : X-ray diffraction (XRD) pattern of a) nano SiO_2 and b) nano-SPA.

2.2. Typical procedures for the preparation of tetrahydrobenzo[a]xanthenes-11-one in the presence of nano-SPA. A mixture of 2-naphthol (1 mmol), aldehyde (1 mmol), 1, 3-diketone (1.2 mmol), and nano-SPA (0.02 g) was heated with stirring at 60 °C or sonicated in ethylacetate. The progress of the reaction was monitored by TLC. After completion of reaction, the product was dissolved in hot ethanol and filtered to recover the catalyst. The filtrate was concentrated to obtain the product. The crude product recrystallized from ethanol.

3. Results and discussion

In continuation of our investigation on application of solid acids in organic synthesis [14-20], we have used nano-SPA in tetrahydrobenzo[a]xanthenes-11-one multi-component reaction. Initially, we have studied the synthesis of 9, 9-dimethyl-12-(4-nitrophenyl)-8, 9, 10, 12-tetrahydrobenzo-[*a*]xanthen-11-one under various conditions (Table 1).

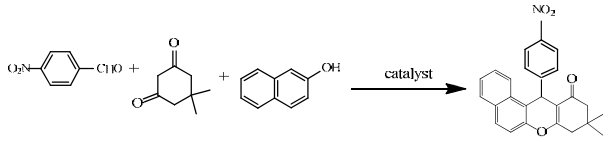


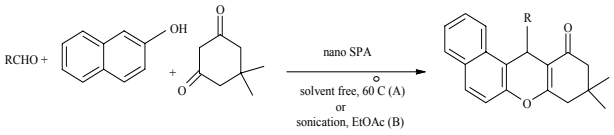
Table 1: Synthesis of 9, 9-dimethyl-12-(4-nitrophenyl)-8, 9, 10, 12-tetrahydrobenzo-[*a*]xanthen-11-one under various conditions.[a]

Ent.	Catalyst	Solvent	Condition	Time (h)/ Yield (%)[ref]
1	SPA (0.04)	Ethanol	r.t.	4/10
2	SPA (0.04)	n-Hexane	r.t.	4/40
3	SPA (0.04)	$CHCl_3$	r.t.	4/10
4	SPA (0.04)	CH_2Cl_2	r.t.	4/15
5	SPA (0.04)	Ethanol	Ref.	3/30
6	SPA (0.04)	n-Hexane	Ref.	3/74
7	SPA (0.04)	$CHCl_3$	Ref.	3/79
8	SPA (0.04)	CH_2Cl_2	Ref.	3/76
9	SPA (0.04)	$C_2H_4Cl_2$	Ref.	3/60
10	SPA (0.04)	-	60 ˚C	0.7/94
11	nano-SPA (0.02)	-	60˚C	0.7/98
12	nano-SPA (0.02),2nd run	-	60˚C	4.5/65
13	nano-SPA (0.02), 3rd run	-	60˚C	4.5/60
14	SPA	EtOAc	Ultra.	40/90
15	nano-SPA	EtOAc	Ultra,	0.5/88
16	nano-SPA	S.F.	M.W	0.3/77
17	$Sr(OTf)_2$ (10 mol%)	$C_2H_4Cl_2$	80 °C	5/85[8]
18	$InCl_3$ (30 mol%)	S.F.	120 °C	0.5/84[5]
19	P_2O_5 (50 mol%)	S.F.	120 °C	0.7/76[5]
20	*p*-TSA (0.1 mmol)	[bmim]BF_4	80 °C	3/90[7]
21	*p*-TSA (0.02 mmol)	S.F.	120 °C	0.8/88[7]
22	TBAF (10 mol%)	Water	Ref.	9/99[10]
23	$NaHSO_4.SiO_2$ (100 mg)	CH_2Cl_2	Ref.	4/87[11]
24	PWA (5 mol%)	S.F.	60 °C	1.2/86[9]
25	Prolinetriflate (10 mol%)	Water	Ref.	3/85[9]

is 1:1.2:1.

The best conditions were obtained by using 0.04 g of SPA for 1 mmol of each substrate under solvent-

free conditions at 60 °C (table 1, entry 10). We have repeated the above mentioned reaction with 0.01 g of nano-SPA and we found that the activity of nano-SPA was four times as much as SPA (Table 1, entry 11). To examine the reusability of nano-SPA in solvent free condition, after each run, the product was dissolved in $CHCl_3$ and filtered. Then, the catalyst residue was washed with acetone and reused. Treatment with acetone removes the tar from the catalyst surface more efficiently (table 1, entries 12 and 13). The catalyst was reusable although a gradual decline was observed in its activity. The ultrasonic assisted synthesis of the present reaction was studied by using SPA or nano-SPA in ethyl acetate under reflux conditions (Table 1, entries 14 and 15). It was found that under sonication conditions, the reaction time decreased to 25 minutes. 2-Naphthol, dimedone and various aldehydes were used as substrates for the synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives at 60 °C or sonication in ethyl acetate as a solvent (Scheme 2 and Table 2).



Scheme 2

According to the literature, two types of mechanism are reported for the formation of tetrahydrobenzo[*a*]xanthenes-11-one from the condensation of β-naphthol, aldehyde and 1, 3-diketone in the presence of an acidic catalyst. In the first one (a), initially, by the condensation of aldehyde and β-naphthol, ortho-quinone methide (*o*-QM) was formed as an intermediate. [5,7,8] In the second one (b), the intermediate was formed by the condensation of aldehyde and 1,3-diketone.[6]

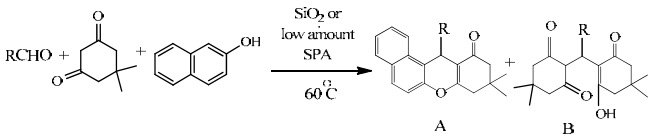
Table 2: Synthesis of tetrahydrobenzo[*a*] xanthenes-11-ones in the presence of nano-SPA

Ent.	R	Time (min) / Yield (%)		Mp (°C)
		A	B	
1	C_6H_5	40/88	25/85	151-153[5]
2	4-ClC_6H_4	40/98	25/88	178-180[5]
3	4-BrC_6H_4	45/90	30/87	181-183[9]
4	3- BrC_6H_4	40/80	30/80	175-176
5	4-$NO_2C_6H_4$	35/84	30/88	178-180[5]
6	3-$NO_2C_6H_4$	40/79	35/89	167-168[5]
7	4-$CH(CH_3)_3C_6H_4$	45/83	35/80	160-162
8	4-OHC_6H_4	50/87	40/89	151-150[9]
9	4-$OMeC_6H_4$	50/85	35/85	206-207[5]
10	2,3-OHC_6H_3	45/80	35/82	243-245

A: The molar ratio of aldehyde:dimedone:β-naphthol is 1:1.2:1was heated solvent-free.

B: The molar ratio of aldehyde:dimedone:β-naphthol is 1:1.2:1inethyl acetate was sonicated under power 100

Our investigation has shown that in a one-pot reaction between β-naphthol, 4-nitrobenzaldehyde and dimedone in the presence of SiO_2 or low-amount of SPA, the side product (B) could be form (scheme 3). Also, the same product was formed in a reaction of 4-nitrobenzaldehyde and dimedone in the absence of β-naphthol. According to the obtained data, our proposed mechanism is similar to (b) (Scheme 4).

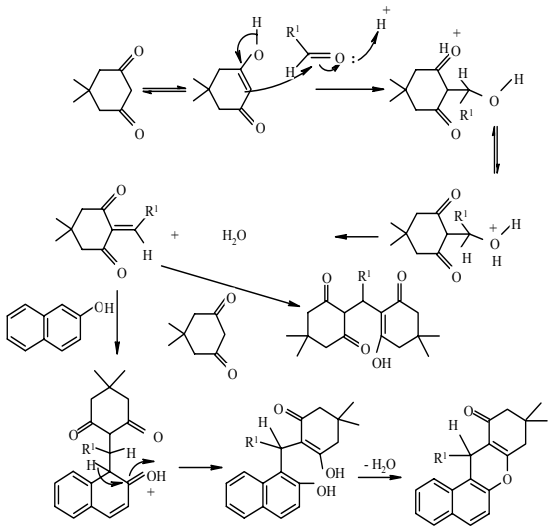


Scheme 3

Selected spectroscopic data:

12-phenyl- 9, 9-Dimethyl-8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one (table 2, entry1):

FT-IR (KBr): υ_{max}: 3053, 2957, 2891, 1649, 1620, 1596, 1469, 1452, 1372, 1241, 1226, 1184, 1032, 837, 747, 723, 697 cm^{-1}.



Scheme 4

^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, *J*=16 Hz, 1H, $COCH_2$), 2.32 (d, *J*=16.4 Hz, 1H, $COCH_2$), 2.58 (s, 2H), 5.71 (s, 1H), 7.06 (t, *J*=7.6, 1H), 7.18 (t, *J*=8, 2H), 7.32-7.46 (m, 5H), 7.77 (d, *J*=8.4 Hz, 1H), 7.79 (d, *J*=6.4 Hz, 1H), 8.00 (d, *J*=8.4Hz, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ= 27.59, 29.72, 32.69, 35.14, 41.85, 51.34, 114.71, 117.46, 118.14, 124.11, 125.31, 126.65, 127.42, 128.65, 128.80, 128.85, 129.25, 131.85, 131.93, 145.18, 148.19, 164.30, 197.29 ppm.

12-(4-Chlorophenyl)- 8, 9, 10, 12-tetrahydro benzo[a]xanthen-11-one (table 2, entry 2):

FT-IR (KBr): υ_{max}: 3063, 1645, 1622, 1593, 1488, 1458, 1226, 1189, 1089, 1014, 838, 818, 751 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94-2.10 (m, 2H), 2.35-2.50 (m, 2H), 2.63-2.78 (m, 2H), 5.72 (s, 1H), 7.15 (d, *J*=8 Hz, 2H), 7.28 (d, *J*=8.4 Hz, 2H), 7.34 (d, *J*=8.8 Hz, 1H), 7.39 (t, *J*=8 Hz, 1H), 7.44 (t, *J*=8 Hz, 1H), 7.78 (d, *J*=8.4 Hz, 1H), 7.80 (d, *J*=8.4 Hz, 1H), 7.89 (d, *J*=8 Hz, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ= 20.72, 28.16, 34.61, 37.46, 115.56, 117.44, 122.86, 123.93, 124.81, 125.47, 127.56, 128.94, 129.06, 129.56, 130.35, 131.97, 132.42, 144.02, 148.21, 166.17, 197.43 ppm.

12-(4-Bromophenyl)- 9, 9-dimethyl- 8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one (table 2, entry 3):

FT-IR (KBr): υ_{max}: 2966, 2876, 1640, 1622, 1593, 1484, 1372, 1274, 1220, 1174, 1071, 1010, 837, 811, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, *J*=16.4 Hz, 1H, $COCH_2$), 2.32 (d, *J*=16 Hz, 1H, $COCH_2$), 2.58 (s, 2H), 5.67 (s,1H), 7.22 (d, *J*=7.2 Hz, 2H), 7.29 (d, *J*=7.2 Hz, 2H), 7.33 (d, *J*=9.2 Hz, 1H), 7.40 (t, *J*=7.6 Hz, 1H), 7.45 (t, *J*=7.6 Hz, 1H), 7.78 (d, *J*=7.2 Hz, 1H), 7.80 (d, *J*=6.8 Hz, 1H), 7.91 (d, *J*=8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ= 27.59, 29.72, 32.68, 34.70, 41.83, 51.29, 114.18, 117.41, 117.46, 120.54, 123.88, 125.46, 127.56, 128.92, 129.54, 130.62, 131.64, 131.77, 131.95, 144.19, 148.17, 164.49, 197.27 ppm**.**

12-(3-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (table 2, entry 4):

FT-IR (ATR, neat): υ_{max}: 2958, 2891, 1646, 1622, 1594, 1470, 1432, 1370, 1282, 1218, 1175, 1076, 1024, 805, 879, 775, 692, 744.^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (s, 3H), 1.13 (s, 3H), 2.26 (d, *J*=16.4 Hz, 1H), 2.32 (d, *J*=16 Hz, 1H), 2.59 (s,

2H), 5.68 (s,1H), 7.06 (t, *J*=8 Hz, 1H), 7.20 (d, *J*=8.4 Hz, 1H), 7.34 (d, *J*=8.4 Hz, 2H), 7.39-7.42 (m, 2H), 7.47 (t, *J*=8 Hz, 1H), 7.79 (d, *J*=5.2 Hz, 1H), 7.81 (d, *J*=6.4 Hz, 1H), 7.92 (d, *J*=8.4 Hz, 1H) ppm.

12-(4-Nitrophenyl)- 9, 9-dimethyl- 8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one (table 2, entry 5).

FT-IR (KBr): υ_{max}: 2956, 1643, 1622, 1594, 1477, 1513, 1477, 1376, 1342, 1244, 1221, 1183, 1031, 850, 830, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ= 0.95 (s, 3H), 1.14 (s, 3H), 2.25 (d, *J*=16.4 Hz, 1H, $COCH_2$), 2.34 (d, *J*=16 Hz, 1H, $COCH_2$), 2.61 (s, 2H), 5.82 (s,1H), 7.36 (d, *J*= 9.2, 1H), 7.39-7.47 (m, 2H), 7.52 (d, *J*=8.8 Hz, 2H), 7.81-7.85 (m, 3H), 8.05 (d, *J*=8.4 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ= 27.50, 29.72, 32.69, 35.30, 41.85, 51.21, 113.42, 116.47, 117.52, 123.54, 124.05, 125.67, 127.81, 129.09, 129.79, 130.06, 131.46, 132.01, 146.78, 148.22, 152.29, 165.05, 197.14.ppm.

12-(3-Nitrophenyl)- 9, 9-dimethyl- 8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one, (table 2, entry 6):

FT-IR (KBr): υ_{max}: 2969, 2891, 1645, 1622, 1594, 1465, 1536, 1477, 1371, 1355, 1249, 1218, 1174, 1024, 830, 806, 779, 689, 741 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ= 0.96 (s, 3H), 1.14 (s, 3H), 2.25 (d, *J*=16.4 Hz, 1H, $COCH_2$), 2.34 (d, *J*=16 Hz, 1H, $COCH_2$), 2.62 (s, 2H), 5.82 (s,1H), 7.36-7.48 (m, 4H), 7.81-7.84 (m, 3H), 7.78 (d, *J*=8.4 Hz, 1H), 7.94 (d, *J*=8 Hz, 1H), 8.12 (s, 1H) ppm.

12-(4-Isopropylphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (table 2, entry 7):

FT-IR (ATR, neat): υ_{max}: 2960, 2873, 1649, 1622, 1596, 1469, 1370, 1241, 1227, 1145, 1016, 833, 818, 745.^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (s, 3H), 1.12 (s, 3H), 1.13 (d, *J*=6.8, 6H), 2.26 (d, *J*=16 Hz, 1H), 2.31 (d, *J*=16.4 Hz, 1H), 2.58 (s, 2H), 2.76 (m,1H), 5.68 (s,1H), 7.01 (d, *J*=8 Hz, 2H), 7.24 (d, *J*=8.4 Hz, 2H), 7.32 (d, *J*=8.8 Hz, 1H), 7.38 (t, *J*=8.4 Hz, 1H), 7.43 (t, *J*=8.4 Hz, 1H), 7.76 (d, *J*=8.8 Hz, 1H), 7.78 (d, *J*=8.8 Hz, 1H), 8.04 (d, *J*=8.4 Hz, 1H) ppm.

12-(4-Hydroxyphenyl)- 9, 9-dimethyl- 8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-onele 2, (table 2, entry 8):

FT-IR (KBr): υ_{max}: 3610, 3141-3440, 3029, 2952, 2891, 1649, 1615, 1595, 1510, 1466, 1371, 1234, 1227, 1174, 1014, 837, 818, 747 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ= 0.99 (s, 3H), 1.14 (s, 3H), 2.31 (d, *J*=16.4 Hz, 1H, $COCH_2$), 2.35 (d, *J*=16 Hz, 1H, $COCH_2$), 2.48(s,1H), 2.59 (s, 2H), 5.65 (s,1H), 6.62 (d, *J*=8.5 Hz, 2H), 7.19 (d, *J*=8.6 Hz, 2H), 7.39 (d, *J*=6.8 Hz, 1H), 7.45 (t, *J*=8.4 Hz, 1H), 7.47 (t, *J*=8.4 Hz, 1H), 7.78 (d, *J*=8.8 Hz, 1H), 7.80 (d, *J*=6.9 Hz, 1H), 8.0 (d, *J*=8.4 Hz, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ= 27.56, 27.76, 29.64, 32.77, 34.31, 41.84, 51.28, 114.90, 115.67, 117.42, 118.28, 124.17, 125.34, 127.39, 128.80, 129.18, 129.95, 131.79, 131.96, 137.18, 148.01, 154.67, 164.82 ppm.

12-(4-Methoxyphenyl)- 9, 9-dimethyl- 8, 9, 10, 12-tetrahydrobenzo[a]xanthen-11-one, (table 2, entry 9):

FT-IR (KBr): υ_{max}: 2957, 2898, 1644, 1611, 1594, 1509, 1460, 1371, 1245, 1249, 1223, 1164, 1027, 1025, 833, 812, 747 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ= 0.98 (s, 3H), 1.12 (s, 3H), 2.25 (d, *J*=16 Hz, 1H, $COCH_2$), 2.32 (d, *J*=16.4 Hz, 1H, $COCH_2$), 2.57 (s, 2H), 3.69 (s,3H), 5.66 (s,1H), 6.71 (d, *J*=8.4 Hz, 2H), 7.20-7.27 (m, 2H), 7.32 (d, *J*=8.8 Hz, 1H), 7.38 (t, *J*=8 Hz, 1H), 7.44 (t, *J*=8 Hz, 1H), 7.76 (d, *J*=9.2 Hz,

1H), 7.78 (d, *J*=9.2 Hz, 1H), 7.99 (d, *J*=8.4 Hz, 1H) ppm.

12-(2, 3-Dihydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (table 2, entry 10):

FT-IR (ATR, neat): υ_{max}: 3511, 3130-3400, 2960, 2880, 1626, 1611, 1592, 1474, 1469, 1377, 1228, 1179, 1030, 838, 758.^{1}H NMR (400 MHz, $CDCl_3$, DMSO): δ = 1.02 (s, 3H), 1.18 (s, 3H), 2.39 (d, *J*=16.6 Hz, 1H), 2.46 (d, *J*=16.6 Hz, 1H), 2.63 (s, 2H), 5.78 (s,1H),6.10 (s,1H), 6.13 (dd, *J*=8, 1.4 Hz, 1H), 6.56 (t, *J*=7.9 Hz, 1H), 6.71 (dd, *J*=7.9, 1.4 Hz, 1H),7.36 (d, *J*=8.9 Hz, 1H), 7.41 (td, *J*=6.8, 1.3 Hz, 1H), 7.46 (td, *J*=6.8, 1.3 Hz, 1H), 7.67 (d, *J*=8.2 Hz, 1H), 7.82 (d, *J*=8.8 Hz, 2H), 9.51 (s, 1H) ppm.

4. Conclusion

We have demonstrated simple methods for the synthesis of tetrahydrobenzo[*a*]xanthen-11-one using nano-SPA as eco-friendly and efficient catalyst. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of these protocols.

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References

[1] A. Domling. I. Ugi. Angew. Chem. Int. Ed., 39 (2000) 3168-3210

[2] J. P. Poupelin, G. Saint-Ruf, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, R. Lacroix. Eur. J. Med. Chem., 13 (1978) 67-71.

[3] F. Zelefack, D. Guilet, N. Fabre, C. Bayet, S. Chevalley, S. Ngouela, B. N. Lenta, A. Valentin, E. Tsamo, M. G. Dijoux-Franca, J. Nat. Prod., 72 (2009) 954-957.

[4] R. M. Ion, D. Frackowiak, A. Planner, K. Wiktorowicz. Acta Biochim. Pol., 45 (1998) 833-845.

[5] G. C. Nandi, S. Samai, R. Kumar, M. S. Singh. Tetrahedron, 65 (2009) 7129-7134.

[6] J. Li, L. Lu, W. Su, Tetrahedron Lett. 51 (2010) 2434-2437.

[7] J. M. Khurana, D. Magoo, Tetrahedron Lett. 50 (2009) 4777-4780.

[8] J. Li, W .Tang, L. Lu, W. Su, Tetrahedron Lett. 49 (2008) 7117-7120.

[9] H. J. Wang, X. Q. Ren, Y. Y. Zhang and Z. H. Zhang J. Braz.Chem. Soc., 20 (2009) 1939-1943.

[10] S. Gao, C. H. Tsai and C. F. Yao, Synlett, 6 (2009) 949-954.

[11] B. Das, K. Laxminarayana, M. Krishnaiah; Y. Srinivas Synlett, 20 (2007) 3107-3112. 1414

[12] M. A. Zolfigol, F. Shirini, K. Zamani, E. Ghofrani, S. Ebrahimi, Phosphorus, Sul- fur Silicon Relat. Elem. 179 (2004) 2177-2182.

[13] A. Shaabani, A. Rahmati, E. Farhangi, Z. Badri, Catal.Commun., 8 (2007) 1149-1152.

[14] B. F. Mirjalili, A. Bamoniri, L. Zamani, Scientia Iranica. 2012, in press.

[15] B. F. Mirjalili, A. Bamoniri, A. Akbari, Tetrahedron Lett. 49 (2008) 6454-6456.

[16] B. F. Mirjalili, A. Bamoniri, A. Akbari, N.. Taghavinia, J. Iran. Chem. Soc. 8 (2011) S129-S134.

[17] B. F. Mirjalili, A. Bamoniri, A. Akbari, J. Iran. Chem. Soc. 8 (2011)S135-S140.

[18] B.F. Mirjalili, A. Bamoniri, A. Akbari, Chin. Chem. Lett. 22 (2011) 45-48.

[19] B. Sadeghi, B. F. Mirjalili, M. M. Hashemi, Tetrahedron Lett. 49 (2008) 2575-2577.

[20] B. F. Mirjalili, A. Bamoniri, S. Nazemian, J Nanostruct., (2012), inpress.