Iranian Journal of Organic Chemistry Vol. 6, No. 3 (2014) 1315-1321

Copolymer p-toluenesulfonic acid: an efficient catalyst for synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives

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Received: June 2014; Revised: July 2014; Accepted: July 2014

Abstract: Copolymer p-toluenesulfonic acid (CPPTSA), is an efficient catalyst for the synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives via the condensation of various aldehyde, and dimedone with 2-naphthol. Copolymer p-toluenesulfonic acid is a novel heterogeneous strong acid catalyst. Furthermore, the catalyst possesses the advantages of the high thermal stability (200 °C) and low cost for the simple synthetic procedure. Simplicity of procedure, mild conditionhigh yields, easy workup and green process are some advantages of this protocol.

Keywords: Copolymer p-toluenesulfonic acid, Tetrahydrobenzo[*a*]xanthenes-11-one, Green process.

Introduction

A novel heterogeneous strong acid catalyst has been prepared through a simple procedure. The catalyst owns the advantages of high strength and density of the acid sites and high thermal and chemical stability. Furthermore, the low cost through simple procedure, low toxicity, stability in air, commercial availability, and ease of handling properties made the catalyst hold great potential for the replacement of the homogeneous catalysts for the green process. According to the literature, Copolymer p-toluenesulfonic acid was applied for some organic transformations such as esterification and acetalization [1], Preparation of fructone (ethyl 3,3-ethylendioxybutyrate) [2], synthesis of 2,3-dihydroquinazolin- 4(1*H*)-ones [3].

Benzoxanthene moiety in the structure of molecules causes important biological activities such as anti infalammatory [4], antiplasmodial [5], and photodynamic therapy [6] antibacterial activity [7, 8].

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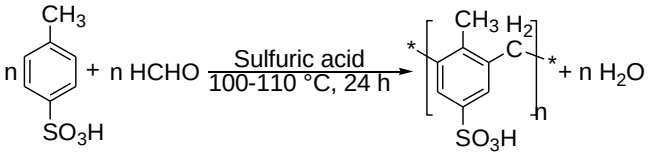
Tetrahydrobenzo[*a*]xanthenes-11-ones as benzoxanthene derivatives could be synthesized via one – pot condensation of 2-naphthol, aldehyde, and 1,3-diketone in the presence of an acidic catalyst. According to the literature, this protocol was catalyzed by indium(III)chloride [9], proline triflate [10], p-toluenesulfonic acid [11], Tetradecyl trimethylammonium bromide (TTAB) [12], strontium triflate [13], dodecatungstophosphoric acid [14], tetrabutyl ammonium fluoride [15], Silica supported sodium hydrogen sulfate [16], trityl chloride [17], Boron trifluoride diethyl etherate [18] Nano-silica supported titanium tetrachloride [19].

Results and discussion

Some of the advantages of insoluble polymeric catalysts are Ease of separation, Reuse of catalyst, Adaptability to continuous flow processes, Reduced toxicity and odour, Chemical differences (potential altered selectivity or activity), easy recovery from the

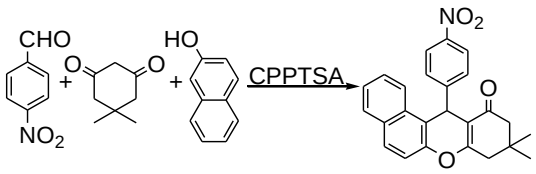
reaction system which prevents the release of toxic chemical into the environment. Here, we present a simple procedure for preparation of the novel heterogeneous acid catalyst. The novel catalyst was synthesized through the copolymerization of p-toluenesulfonic acid (PTSA) and paraformaldehyde in the catalyst amount of sulfuric acid (Scheme **1**).



Scheme 1: The synthetic route of the novel catalyst.

Water is a desirable solvent for reasons of safety, environmental benign, availability and cost. Organic reactions under solvent free condition or in water as solvent are interest from both industrial and academic viewpoints. Meanwhile, the Copolymer p-toluenesulfonic acid is bench-top catalyst which is reusable, cheap, readily available, eco-friendly, versatile and efficient for promotion of many acid catalyzed organic reactions. These catalysts do not need special precautions for Preparation, handling or storage, and they can be stored at ambient temperature for months without losing their catalytic activity. In this work, we have investigated the application of Copolymer p-toluenesulfonic acid for synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives.

The reactions were carried out in stirring at 80 °C under solvent free conditions for 15 minutes or using water as solvent at 60 °C for 25 minutes (Scheme **2**).



Scheme 2: Standard model reaction.

Initialy, we have examined the synthesis of 9,9-Dimethyl-12-(4-nitro-phenyl)-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one using 4-Nitrobenzaldehyde (2 mmol, 0.31g), Dimedone (2 mmol, 0.30g), β-Naphthol (2 mmol, 0.29g) and CPPTSA as the catalyst under various conditions (Table **1**). We have found that the best conditions are using CPPTSA (0.30 g) under solvent-free conditions at 80 °C or aqueous condition at 60 °C for 25 minutes (Table **1**, entry 10, entry 14).

To examine the reusability of CPPTSA in solvent free condition, after each run, the product was dissolved to $CHCl_3$ and filtered. The catalyst residue was washed with acetone and reused. The obtained CPPTSA was washed with 5 ml H_2SO_4 (50%) and heated in an oven at 120°C for 30 min (Table **1**, entry 19). the catalysts recovered from the reaction could be reused without loss of activity.

To examine the reusability of CPPTSA in aqueous condition, after each run, the mixture was charged in to an isolating funnel and extracted with chloroform to isolate the product. The catalyst residue removed by filtration and was washed with acetone and reused. The obtained CPPTSA was washed with 5 ml H_2SO_4 (50%) and heated in an oven at 120°C for 30 min. (Table **1**, entry 20). the catalysts recovered from the reaction could be reused without loss of activity.

Next, the synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives were studied and summarized in Table **2**. In all cases, the three-component reaction proceeded smoothly to give the corresponding tetrahydrobenzo[*a*]xanthenes-11-one in moderate to good yields. In summary, we have described Copolymer p-toluenesulfonic acid (CPPTSA) is an efficient, eco-friendly catalyst for synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives under solvent-free or aqueous conditions. Most of the products are known and were characterized by FT-IR and ^{1}H-NMR and through comparison of their physical properties with those reported in the literature.

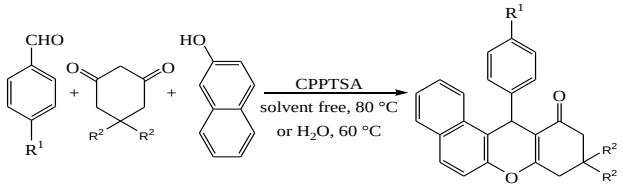
The applicability of the solvent free and aqueous condition method to a large scale process has been examined with 4-Nitrobenzaldehyde (20 mmol, 3.08g), Dimedone (20 mmol, 2.95g), β-Naphthol (20 mmol, 2.91g) which has given 9,9-dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo-[*a*]xanthen-11-one in 90% and 91% yield respectively.

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

Entry	Catalyst	Catal.(g):	Solvent	Condition	Time (min)	Yield (%)[b]
1	CPPTSA	0.3	Ethanol	r.t.	120	55
2	CPPTSA	0.3	n-Hexane	r.t.	120	32
3	CPPTSA	0.3	$CHCl_3$	r.t.	120	40
4	CPPTSA	0.3	CH_2Cl_2	r.t.	120	35
5	CPPTSA	0.3	Ethanol	Reflux	30	70
6	CPPTSA	0.3	n-Hexane	Reflux	30	74
7	CPPTSA	0.3	$CHCl_3$	Reflux	30	79
8	CPPTSA	0.3	CH_2Cl_2	Reflux	30	76
9	CPPTSA	0.3	Solvent-free	60 °C	45	71
10	CPPTSA	0.3	Solvent-free	80 °C	45	92
11	CPPTSA	0.3	Solvent-free	100 °C	45	93
12	CPPTSA	0.3	Water	r.t.	120	69
13	CPPTSA	0.3	Water	40 °C	25	78
14	CPPTSA	0.3	Water	60 °C	25	93
15	CPPTSA	0.3	Water	80 °C	25	95
16	CPPTSA	0.3	Water	Reflux	25	95
17	CPPTSA	0.2	Water	80 °C	25	76
18	CPPTSA	0.4	Water	80 °C	25	95
19	CPPTSA.2nd	0.3	Solvent-free	80 °C	45	92
20	CPPTSA.2nd	0.3	Water	60 °C	25	93

[a] 4-Nitrobenzaldehyde (2 mmol), Dimedone (2 mmol), β-Naphthol (2 mmol).
[b] Isolated yields

Table 2: synthesis of tetrahydrobenzo-[*a*]xanthen-11-one in the presence of CPPTSA.



Entry	R^1	R^2	Yeild (%)[a]	Yeild (%)[b]	m.p.(°C) found	m.p.(°C) reported[lit]
1	3- BrC_6H_4	Me	88	88	181-183	185-187[15]
2	4-$CH(CH_3)_3C_6H_4$	Me	85	95	161-162	160-162[17]
3	2,3-OHC_6H_3	Me	89	98	243-244	243-245[17]
4	C_6H_5	Me	96	91	151-153	151-153[7]
5	4-ClC_6H_4	Me	97	95	178-180	178-179[15]
6	4-BrC_6H_4	Me	93	88	181-183	187-189[10]
7	4-$NO_2C_6H_4$	Me	92	95	178-180	178-180[7]
8	3-$NO_2C_6H_4$	Me	88	96	167-168	167-170[15]
9	4-OHC_6H_4	Me	94	91	222-223	222-224[10]
10	4-$OMeC_6H_4$	Me	97	94	206-207	205-207[10]
11	C_6H_5	H	96	91	186-187	188-189[16]
12	4-ClC_6H_4	H	97	95	202-204	197-199[16]
13	4-$NO_2C_6H_4$	H	92	95	236-238	234-235[12]
14	4-MeC_6H_4	H	97	94	207-208	205-208[12]

[a]Aldehyde (2 mmol), 1,3-diketone (2 mmol), CPPTSA (0.30 g) under solvent-free conditions at 80 °C for 45 min.
[b]Aldehyde (2 mmol), 1,3-diketone (2 mmol), CPPTSA (0.30 g) under aqueous condition at 60 °C for 25 min.

Conclusion

We have demonstrated simple methods for the synthesis of tetrahydrobenzo-[*a*]xanthen-11-one using Copolymer p-toluenesulfonic acid (CPPTSA) 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.

Experimental

The materials were purchased from Sigma–Aldrich and Merck 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 spectra were run on a Bruker, Eqinox 55 spectrometer. A Bruker (DRX-500 Avanes) NMR was used to record the ^{1}H NMR spectra.

Preparation of Copolymer p-toluenesulfonic acid (CPPTSA):

The catalyst was synthesized through the polymerization of p-toluenesulfonic acid (PTSA) and paraformaldehyde catalyzed by sulfuric acid (Scheme **1**). In the typical procedure: The mixture of p-Toluenesulfonic acid monohydrate (19.02 g), paraformaldehyde (3.00 g) and sulfuric acid (1.00 mL) was heated in a three necked round bottomed flask equipped with a magnetic stirrer, a thermometer and a funnel. The reaction mixture was kept in the range of 100–110 °C for 24 h to form black solid. The solid was washed with hot H_2SO_4 (50%) (≥80 °C) and filtrated until no $SO4^{2-}$ was detected in the filtrate. The obtained solid was heated in an oven at 150°C for 3 hours.

General procedure for the synthesis of tetrahydrobenzo[a]xanthenes-11-one derivatives under solvent-free conditions:

A mixture of 2-naphthol (2 mmol), aldehyde (2 mmol), 1,3-diketone (2 mmol), Copolymer p-toluenesulfonic acid (CPPTSA) (0.30g), was heated at 80 °C in an oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was washed with chloroform and filtered to recover the catalyst. The chloroform layer was evaporated carefully and the obtained solid was crystallized in ethanol: water (80:20) to afford the pure tetrahydrobenzo[*a*]xanthenes-11-one derivatives in good to excellent yields.

General procedure for the synthesis of tetrahydrobenzo[a]xanthenes-11-one derivatives under aqueous condition:

A mixture of 2-naphthol (2 mmol), aldehyde (2 mmol), 1,3-diketone (2 mmol), Copolymer p-toluenesulfonic acid (CPPTSA) (0.30g), and 5 ml of water was heated at 60 °C in a water bath. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was charged in to an isolating funnel and extracted with chloroform to isolate the product. The chloroform layer was evaporated carefully and the obtained solid was crystallized in ethanol : water (80:20) to afford the pure tetrahydrobenzo[*a*]xanthenes-11-one derivatives in good to excellent yields. The aqueous layer containing CPPTSA and the catalyst was reused for another reaction.

9,9-dimethyl-12-(3-bromophenyl)-8,9,10,12-tetrahydrobenzo-[a]xanthen-11-one (Entry 1):

FT-IR (KBr): 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.

9,9-dimethyl-12-(4-isopropylphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 2):

FT-IR (KBr): υ_{max}: 2960, 2873, 1649, 1622, 1596, 1469, 1370, 1241, 1227, 1145, 1016, 833, 818, 745.^{1}H 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.

9,9-dimethyl-12-(2,3-dihydroxyphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 3):

FT-IR (KBr): υ_{max}: 3511, 3130-3400, 2960, 2880, 1626, 1611, 1592, 1474, 1469, 1377, 1228, 1179, 1030, 838, 758.^{1}H NMR (500 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.

9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 4):

FT-IR (KBr): υ_{max}: 3053, 2957, 2891, 1649, 1620, 1596, 1469, 1452, 1372, 1241, 1226,1184, 1032, 837, 747, 723, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, *J*=16 Hz, 1H), 2.32 (d, *J*=16.4 Hz, 1H), 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.

9,9-dimethyl-12-(4-chlorophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 5):

FT-IR (KBr): υ_{max}: 2957, 2884, 1644, 1622, 1596, 1487, 1469, 1372, 1234, 1221, 1141, 1088, 1013, 845, 838, 750. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, *J*=16.4 Hz, 1H), 2.32 (d, *J*=16 Hz, 1H), 2.58 (s, 2H), 5.69 (s,1H), 7.14 (d, *J*=8.4 Hz, 2H), 7.28 (d, *J*=8.4 Hz, 2H), 7.33 (d, *J*=8.8 Hz, 1H), 7.40 (td, *J*=6.8, 1.2 Hz, 1H), 7.45 (td, *J*=6.8, 1.2 Hz, 1H), 7.78 (d, *J*=8.8 Hz, 1H), 7.8 (d, *J*=5.6 Hz, 1H), 7.91 (d, *J*=8.4 Hz, 1H) ppm.

9,9-dimethyl-12-(4-bromophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 6):

FT-IR (KBr): υ_{max}: 2966, 2876, 1640, 1622, 1593, 1484, 1372, 1274, 1220, 1174, 1071, 1010, 837, 811, 756. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, *J*=16.4 Hz, 1H), 2.32 (d, *J*=16 Hz, 1H), 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.

9,9-Dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 7):

FT-IR (KBr): υ_{max}: 2956, 1643, 1622, 1594, 1477, 1513, 1477, 1376, 1342, 1244, 1221, 1183, 1031, 850, 830, 751. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 3H), 1.14 (s, 3H), 2.25 (d, *J*=16.4 Hz, 1H), 2.34 (d, *J*=16 Hz, 1H), 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.

9,9-Dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 8):

FT-IR (KBr): υ_{max}: 2969, 2891, 1645, 1622, 1594, 1465, 1536, 1477, 1371, 1355, 1249, 1218, 1174, 1024, 830, 806, 779, 689, 741. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (s, 3H), 1.14 (s, 3H), 2.25 (d, *J*=16.4 Hz, 1H), 2.34 (d, *J*=16 Hz, 1H), 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.

9,9-dimethyl-12-(4-hydroxyphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 9):

FT-IR (KBr): υ_{max}: 3610, 3141-3440, 3029, 2952, 2891, 1649, 1615, 1595, 1510, 1466, 1371, 1234, 1227, 1174, 1014, 837, 818, 747. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (s, 3H), 1.14 (s, 3H), 2.31 (d, *J*=16.4 Hz, 1H), 2.35 (d, *J*=16 Hz, 1H), 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.

9,9-dimethyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 10):

FT-IR (KBr): υ_{max}: 2957, 2898, 1644, 1611, 1594, 1509, 1460, 1371, 1245, 1249, 1223, 1164, 1027, 1025, 833, 812, 747. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 3H), 1.12 (s, 3H), 2.25 (d, *J*=16 Hz, 1H), 2.32 (d, *J*=16.4 Hz, 1H), 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-phenyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Entry 11):

FT-IR (KBr): υ_{max}: 3059, 2930, 1644, 1616, 1593, 1511, 1453, 1249, 1227,1189, 1032, 830, 757, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94-2.06 (m, 2H), 2.35-2.49 (m, 2H), 2.63-2.73 (m, 2H), 5.75 (s, 1H), 7.07 (t, *J*=7.6 Hz, 1H), 7.18 (t, *J*=7.6 Hz, 2H), 7.34 (d, *J*=8.4 Hz, 2H), 7.39-7.45 (m, 3H), 7.77 (d, *J*=7.2 Hz, 1H), 7.79 (d, *J*=6.8 Hz, 1H), 7.90 (d, *J*=8.4 Hz, 1H) ppm.

12-(4-Chlorophenyl)-8,9,10,12-tetrahydrobenzo[a] xanthen-11-one (Entry 12):

FT-IR (KBr): υ_{max}: 3063, 1645, 1622, 1593, 1488, 1458, 1226, 1189, 1089, 1014, 838, 818, 751. ^{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.

12-(4-Nitrophenyl)-8,9,10,12-tetrahydrobenzo[a] xanthen-11-one (Entry 13):

FT-IR (KBr): υ_{max}: 2891, 1651, 1630, 1592, 1492, 1514, 1458, 1340, 1253, 1237, 1187, 1036, 851, 827, 742. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.92-1.99 (m, 1H), 2.05-2.10 (m, 1H), 2.39-2.46 (m, 2H),2.67-2.77 (m, 2H), 5.82 (s, 1H), 7.35 (d, *J*=9 Hz, 1H), 7.37-7.44 (m, 2H), 7.49 (d, *J*=8.8 Hz, 2H), 7.78-7.81 (m, 3H), 8.01 (d, *J*=8.8 Hz, 2H) ppm

12-(4-Methylphenyl)-8,9,10,12-tetrahydrobenzo[a] xanthen-11-one (Entry 14):

FT-IR (KBr): υ_{max}: 2947, 1647, 1622, 1596, 1509, 1406, 1372, 1253, 1224,1188, 1032, 838, 808, 742. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99-2.06 (m, 2H), 2.22 (s, 3H), 2.38-2.46 (m, 2H), 2.67-2.74 (m, 2H), 5.72 (s, 1H), 6.99 (d, *J*=8 Hz, 2H), 7.23 (d, *J*=8 Hz, 2H), 7.34 (d, *J*=8.8 Hz, 1H), 7.35-7.50 (m, 2H), 7.76 (d, *J*=7.2 Hz, 1H), 7.78 (d, *J*=8.8 Hz, 1H), 7.98 (d, *J*=8.4 Hz, 1H) ppm.

Acknowledgement

The support for this study by the Research Council of University of Jiroft and Yazd University is gratefully acknowledged.

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