Nano-$TiCl_4/SiO_2$: An Efficient and Reusable Catalyst for the Synthesis of Tetrahydrobenzo[*a*]xanthenes-11-ones

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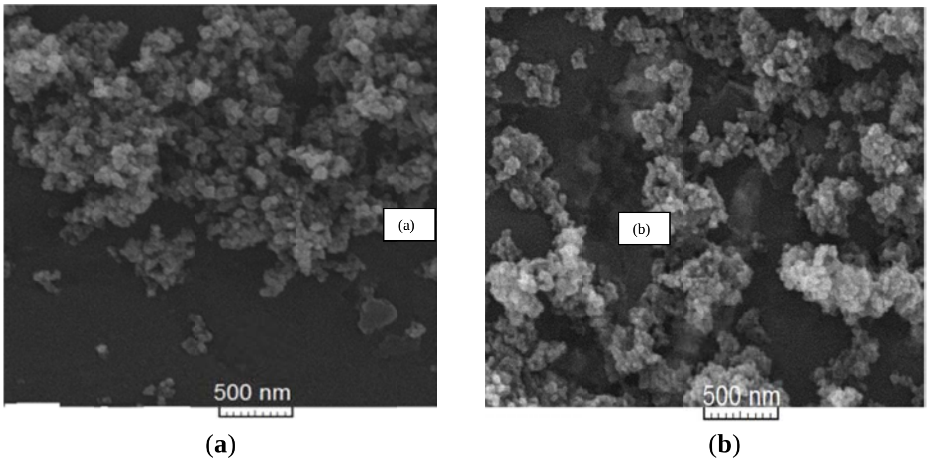
Abstract: Tetrahydrobenzo[*a*]xanthen-11-ones have been synthesized using 50% nano-$TiCl_4/SiO_2$ as a reusable, inexpensive, and efficient Lewis acid catalyst. Short reaction times, high yields, scale up, and easy work-up are the advantages of this protocol.

Keywords: Heterogeneous catalyst, multi component reaction, Nano-$TiCl_4/SiO_2$, one-pot reactions, Tetrahydrobenzo [*a*]xanthen-11-one, solvent free condition.

INTRODUCTION

Titanium tetrachloride as a powerful Lewis acid is a liquid which is highly volatile, corrosive and difficult to handle. It hydrolyses to produce HCl in the presence of moisture. Silica-supported $TiCl_4$ is a mild solid Lewis acid that promotes acidic catalyzed organic reactions. This catalyst does not need special precautions for preparation, handling, or storage. It can be stored at an ambient temperature for months without losing its catalytic activity. This catalyst was previously applied for the production of polymers [1].

Nano silica supported titanium chloride (nano-$TiCl_4/SiO_2$) as an efficient acidic catalyst was prepared *via* a reaction of nano SiO_2 with $TiCl_4$. The dimensions of nanoparticles were observed with SEM. The particle sizes of the commercial silica gel and synthesized nano-$TiCl_4/SiO_2$ were about 16-24 nm and 37-41 nm (Fig. **1**), respectively.



(**a**) (**b**)

Fig. (1). SEM photograph of (**a**) nano-SiO_2 and (**b**) nano-$TiCl_4/SiO_2$.

Tetrahydrobenzo[*a*]xanthen-11-ones have important biological and pharmaceutical activities such as anti-bacterial [2] and anti-inflammatory ones [3]. Previously, these products were catalyzed by indium(III)chloride [4], proline triflate [5] *p*-toluene sulfonic acid [6] strontium triflate [7], tetrabutyl ammonium fluoride [8], $NaHSO_4/SiO_2$ [9] and HBF_4/SiO_2 [10]. Many of these protocols have high product yields and easy work-up but they have some disadvantages such as difficult preparation and high price of catalyst. In this work, we wish to report the application of nano-$TiCl_4/SiO_2$ as catalyst for the synthesis of tetrahydrobenzo[*a*]xanthen-11-ones under solvent free condition. Nano-$TiCl_4/SiO_2$ has some advantages such as easy preparation procedure and low cost.

RESULTS AND DISCUSSION

For the identification of the structure of nano-$TiCl_4/SiO_2$, we studied IR spectra of SiO_2, nano-$TiCl_4/SiO_2$, and $TiCl_4$

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(Fig. **2**). In all of the spectra, very broad OH stretching bands are observed with a strong intermolecular hydrogen bonding. In FT-IR spectra of nano-TiCl$_4$/SiO$_2$ and SiO$_2$, the absorption bands for Si-OH and Si-O-Si appears in ~700 cm^{-1} and ~1100 cm^{-1}, respectively. The absorption band of Ti-Cl appear in 1600 cm^{-1} in TiCl$_4$ spectrum. In the FT-IR spectrum of nano-TiCl$_4$/SiO$_2$, the O-Ti-Cl, Si-OH and Si-O-Si absorption bands are observed in 900, 700 and 1100 cm^{-1} respectively [11,12]. We have suggested the following structure for nano-TiCl$_4$/SiO$_2$ (Scheme **1**).

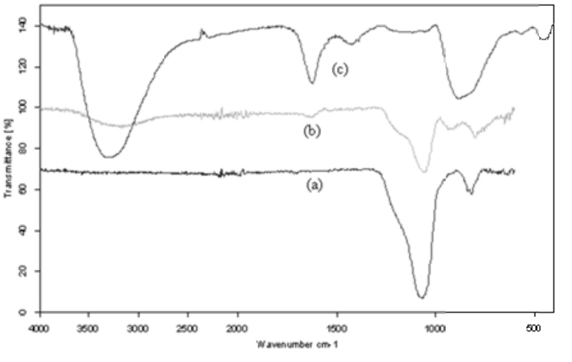
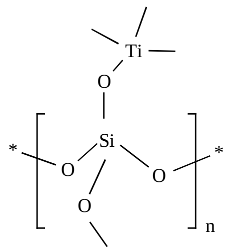


Fig. (2). FT-IR spectrum of: (**a**) SiO$_2$, (**b**) nano-TiCl$_4$/SiO$_2$, and (**c**) TiCl$_4$.



Scheme 1. Suggested structure for nano-TiCl$_4$/SiO$_2$.

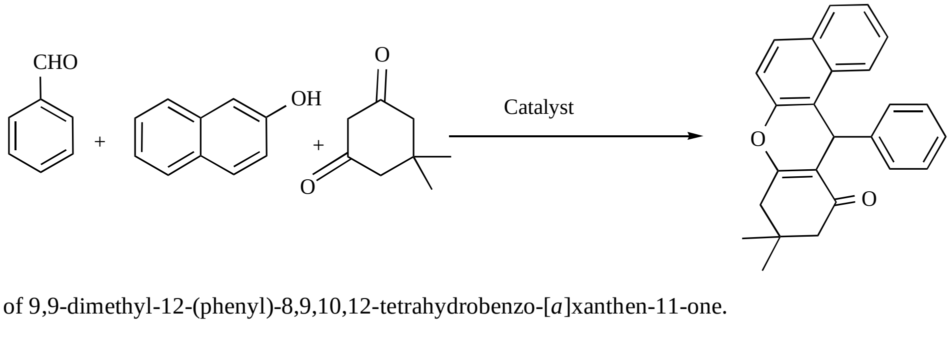
Because the nano-TiCl$_4$/SiO$_2$ produces HCl in water, we have determined the concentration of the acidic aqueous solution by titration. We have found that 0.1 g of catalyst produced a 0.0064 M aqueous solution. For the determination of the loading amount of Ti on 0.1 g of nano-TiCl$_4$/SiO$_2$, we have extracted Ti from the catalyst using EDTA solution (0.004 M) at pH of 4. The standard solutions of titanium (IV) were prepared by dissolving a proper amount of TiCl$_4$ in acetone. Determination of the extracted Ti was carried out by an atomic absorption spectrometer with a hollow cathode lamp at a wavelength of 346 nm using C_2H_2/N_2O flame. The calibration equation for titanium was found as A=0.012C-0.1895 (R^2=0.9998). In this equation, A and C are the absorbance and concentration (mg L^{-1}) of titanium, respectively. The calculated loading amount of Ti in catalyst is 7mg g^{-1}.

In continuation of our investigation on application of solid acids in organic synthesis [13-15], we wish to apply the nano-TiCl$_4$/SiO$_2$ for the synthesis of tetrahydrobenzo [*a*]xanthenes-11-one derivatives under various conditions.

The reaction of benzaldehyde (1 mmol), dimedone (1.2 mmol) with 2-naphthol (1 mmol) was examined to optimize the reaction condition (Scheme **2**). Reaction in different conditions in the presence of TiCl$_4$/SiO$_2$ revealed that the best condition for all the reactions was a solvent-free one at 90°C (entry 21, Table **1**).

We have repeated the above-mentioned reaction with 50% nano-TiCl$_4$/SiO$_2$ and found that the 0.05 g of it is necessary for 1 mmol of substrate (entry 23, Table **1**). To examine the reusability of nano-TiCl$_4$/SiO$_2$ in a solvent-free condition, after each run, the product was dissolved to CHCl$_3$ and filtered. The catalyst residue was washed with acetone and reused. Treatment with acetone removes the tar from the catalyst surface more efficiently (Table **1**, entries 24 and 25). The catalyst was reusable although a gradual decline was observed in its activity. All of the products were known and characterized by FT-IR, ^{1}H-NMR, and the physical properties of those reported in the literature. According to the best obtained condition, we have applied 2-Naphthol, dimedone or 1,3-cyclohexadione and various aldehydes were used as substrates for the synthesis of tetrahydrobenzo [*a*]xanthenes-11-one derivatives at 90 °C (Table **2**, Scheme **3**).

According to the literature, two types of mechanisms 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-QMs) was formed as an intermediate [4, 6, 7]. In the second one (b), an intermediate was formed by the condensation of aldehyde and 1, 3-diketone [5]. Our investigation has shown that in a one-pot reaction between β -naphthol, 4-nitrobenzaldehyde and dimedone in the presence of low-amount TiCl$_4$/SiO$_2$, the side product (6) could be formed (Scheme **4**). Also, the same

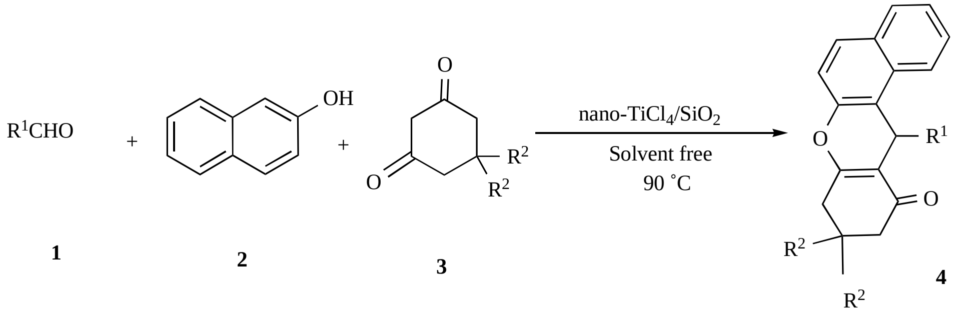


Scheme 2. Synthesis of 9,9-dimethyl-12-(phenyl)-8,9,10,12-tetrahydrobenzo-[*a*]xanthen-11-one.

Table 1. Synthesis of 9,9-dimethyl-12-(phenyl)-8,9,10,12-tetrahydrobenzo-[*a*]xanthen-11-one under Various Conditions[a]

Reference	Yield (%)	Time (h)	Condition	Solvent	Catalyst(g)	Entry
-	10	4	r.t.	Ethanol	$TiCl_4/SiO_2$ (0.2)	1
-	40	4	r.t.	n-Hexane	$TiCl_4/SiO_2$ (0.2)	2
-	10	4	r.t.	$CHCl_3$	$TiCl_4/SiO_2$ (0.2)	3
-	15	4	r.t.	CH_2Cl_2	$TiCl_4/SiO_2$ (0.2)	4
-	15	4	r.t	$ClCH_2CH_2Cl$	$TiCl_4/SiO_2$ (0.2)	5
-	30	3	Reflux	Ethanol	$TiCl_4/SiO_2$ (0.2)	6
-	60	3	Reflux	n-Hexane	$TiCl_4/SiO_2$ (0.2)	7
-	65	3	Reflux	$CHCl_3$	$TiCl_4/SiO_2$ (0.2)	8
-	69	3	Reflux	CH_2Cl_2	$TiCl_4/SiO_2$ (0.2)	9
-	60	3	Reflux	$ClCH_2CH_2Cl$	$TiCl_4/SiO_2$ (0.2)	10
-	75	3	90 ˚C	Solvent-free	$TiCl_4/SiO_2$ (0.2)	11
-	70	1	90˚C	Solvent-free	30%$TiCl_4/SiO_2$ (0.2)	16
-	85	1	90˚C	Solvent-free	50% $TiCl_4/SiO_2$ (0.2)	17
-	85	1	90˚C	Solvent-free	60% $TiCl_4/SiO_2$ (0.2)	18
-	84	1	90˚C	Solvent-free	50% $TiCl_4/SiO_2$ (0.15)	19
-	84	1	90˚C	Solvent-free	50% $TiCl_4/SiO_2$ (0.125)	20
-	84	1	90˚C	Solvent-free	50% $TiCl_4/SiO_2$ (0.1)	21
-	95	0.5	90˚C	Solvent-free	50%Nano-$TiCl_4/SiO_2$ (0.075)	22
-	94	0.5	90˚C	Solvent-free	50%Nano-$TiCl_4/SiO_2$ (0.05)	23
-	84	0.8	100 °C	Solvent-free	50% nano-$TiCl_4/SiO_2$ (0.05), 2nd run	24
-	76	1	120 °C	Solvent-free	50% nano-$TiCl_4/SiO_2$ (0.05), 3rd run	25
[4]	84	30min	120 °C	Solvent-free	$InCl_3$	26
[7]	85	5	80 °C	$ClCH_2CH_2Cl$	$Sr(OTf)_2$	27
[5]	85	3	Reflux	Water	proline triflate	28
[9]	87	4	Reflux	CH_2Cl_2	$NaHSO_4/SiO_2$	29
[8]	99	9	Reflux	Water	TBAF	30
[10]	92	1	80˚C	Solvent-free	HBF_4/SiO_2	31

[a] The molar ratio of aldehyde:dimedone:β-naphthol is 1:1.2:1.



Scheme 3. Synthesis of tetrahydrobenzo[*a*]xanthen-11-one in the presence of nano-$TiCl_4/SiO_2$ at 90 °C under solvent-free condition.

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).

CONCLUSION

We have demonstrated simple methods for the synthesis of tetrahydrobenzo-[*a*]xanthen-11-one with using 50% nano-$TiCl_4/SiO_2$ 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 this protocol.

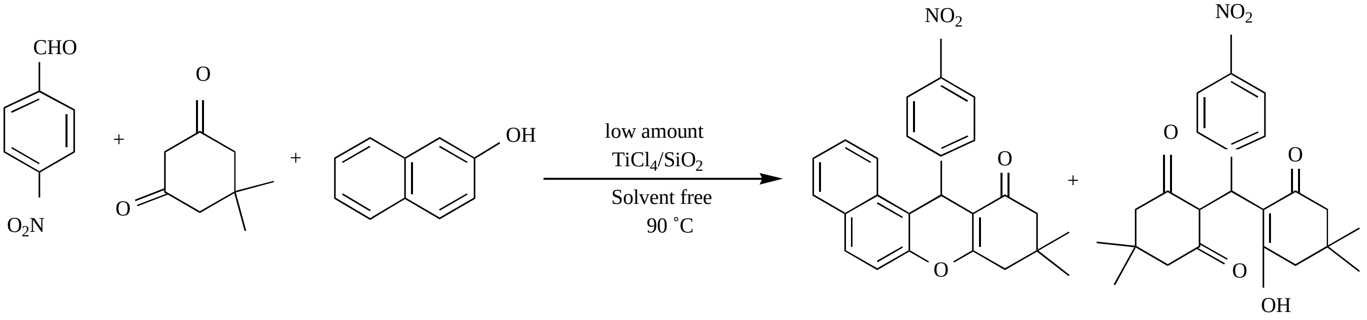
EXPERIMENTAL SECTION

The chemicals were used without any additional purification. The products were characterized by FT-IR, ^{1}H-NMR, and a 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-400

Table 2. Synthesis of Tetrahydrobenzo[*a*]xanthen-11-one in the Presence of 50% Nano-$TiCl_4/SiO_2$ at 90 °C

Reference	Mp (°C)		Yeild[b] (%)	R^2	R^1	Entry
	Reported	Found				
[4]	151-153	151-153	88	Me	C_6H_5	1
[4]	186-187	184-185	87	Me	4-Br–C_6H_4	2
[6]	150-151	150-151	86	Me	4-OH–C_6H_4	3
[5]	180-182	183-184	96	Me	4-Cl–C_6H_4	4
[7]	183-185	181-182	87	Me	4-O_2N–C_6H_4	5
[4]	204-205	206-207	84	Me	4-MeO–C_6H_4	6
[3]	160-162	160-161	84	Me	4-$CH(CH_3)_3C_6H_4$	7
[9]	175-176	174-176	77	Me	3-Br-C_6H_4	8
[3]	168-170	167-168	70	Me	3-$NO_2C_6H_4$	9
[6]	188-189	186-187	82	H	C_6H_5	10
[3]	205-206	200-204	84	H	4-ClC_6H_4	11
[4]	205-206	205-208	79	H	4-MeC_6H_4	12

[a] The ratio of 2-naphthol(mole): aldehydes (mole):dimedone (mole): nano-$TiCl_4/SiO_2$ (g) is 1:1:1.2:0.05.
[b] Isolated yield.



5 **6**

Scheme 4. Reaction between β-naphthol, 4-nitrobenzaldehyde and dimedone in the presence of low-amount $TiCl_4/SiO_2$.

Avanes) NMR was used to record the ^1H NMR spectra. The absorption of titanium solutions was determined by an atomic absorption spectrometer, AVONA AA300. Also the SEM of nano particles was determined with a VEGA/TESCAN scanning electron microscope.

Preparation of 50% Nano-$TiCl_4/SiO_2$ and 50% $TiCl_4/SiO_2$

0.5 g (0.29 mL) of $TiCl_4$ was added drop wise to a mixture of 0.5 g of silica gel or nano silica gel and 5 mL of chloroform. The mixture was stirred for one hour at room temperature. The resulted suspension was filtered. The obtained solid was washed with chloroform and dried at room temperature.

General Procedure for the Synthesis of Tetrahydrobenzo [*a*]xanthen-11-one

A mixture of 2-naphthol (1 mmol), aldehyde (1 mmol), dimedone (1.2 mmol) and 50% nano-$TiCl_4/SiO_2$ (0.05 g) was heated at 90 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was charged in to isolating funnel and extracted with chloroform to isolation of 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.

Selected Spectroscopic Data

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

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

^1H 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-bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Table 2, entry2)

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-(4-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-onele 2, (Table 2, entry 3)

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

^{1}H 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-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Table 2, entry 4)

FT-IR (KBr): υ_{max}: 2957, 2884, 1644, 1622, 1596, 1487, 1469, 1372, 1234, 1221, 1141,1088, 1013, 845, 838, 750cm^{-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), 5.69 (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).

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}.

^{1}H 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.

12-(4-methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one, (Table 2, entry 6)

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

^{1}H 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-(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, 745cm^{-1}.^{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.

12-(3-bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one, (Table 2, entry 8)

FT-IR (ATR, neat): υ_{max}: 2958, 2891, 1646, 1622, 1594, 1470, 1432, 1370, 1282, 1218, 1175, 1076, 1024, 805, 879, 775, 692, 744cm^{-1}.^{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-(3-nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo [a]xanthen-11-one, (Table 2, entry 9)

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.

^{1}H 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-phenyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Table 2, entry 10)

FT-IR (KBr): υ_{max}: 3059, 2930, 1644, 1616, 1593, 1511, 1453, 1249, 1227, 1189, 1032, 830, 757, 701cm^{-1}.

^{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.

^{13}C NMR (125 MHz, CDCl$_3$): δ = 20.71, 28.17, 35.10, 37.50, 116.01, 117.43, 118.16, 123.12, 124.14, 125.34, 126.71, 127.44, 128.73, 128.83, 128.95, 129.29, 131.85, 145.52, 148.24, 166.03, 197.46 ppm.

12-(4-Chlorophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Table 2, entry 11)

FT-IR (KBr): υ_{max}: 3063, 1645, 1622, 1593, 1488, 1458, 1226, 1189, 1089, 1014, 838, 818, 751cm^{-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, CDCl3): 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-Methylphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (Table 2, entry 12)

FT-IR (KBr): υ_{max}: 2947, 1647, 1622,, 1596, 1509, 1406, 1372, 1253, 1224, 1188, 1032, 838, 808, 742cm^{-1}.^{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.^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.74, 21.47, 28.17, 34.70, 37.53, 116.17, 117.44, 118.35, 123.17, 124.17, 125.32, 127.43, 128.83, 129.20, 129.47, 131.89, 131.96, 136.19, 142.69, 148.21, 165.94, 197.50 ppm.

CONFLICT OF INTEREST

Declared none.

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ABBREVIATIONS

TBAF = tetrabutyl ammonium fluoride

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