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Nano titania-supported sulfonic acid catalyzed synthesis of α,α' -bis(substituted-benzylidene)cycloalkanones and of their xanthene derivatives under solvent-free conditions

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ABSTRACT

An efficient, rapid and green synthesis of α,α' -bis(substituted-benzylidene)cycloalkanones and their xanthene derivatives is reported under solvent-free conditions using nano titania-supported sulfonic acid (n-TSA) as a reusable catalyst. This method offers many advantages, such as environmental friendliness reaction conditions, simplicity, short reaction times, easy work-up, reusability of catalyst, and high yields of products. Eight new compounds are reported too.

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1. Introduction

Nowadays, for considering green chemistry aspects, chemists are concerned with minimizing the environmental pollution caused by traditional solvents and try to establish methodologies based on solvent-free conditions. The drive for the development of dry media reactions are ease of purification, high reaction rates, environmentally friendly conditions, less energy requirement and considering economic and environmental demands [1].

The employment of a reusable solid supported heterogeneous catalyst for the efficient synthesis of heterocyclic compounds remains a challenge to chemists. Reactions with reagents that are immobilized on inorganic solid supports show several advantages over the conventional

reactions in solution. Recently, the use of heterogeneous catalysts under solvent-free conditions has emerged as an eco-friendly alternative of great importance within organic synthesis [2–4].

As we have recently reported [5], nano titania-supported sulfonic acid (n-TSA) is a heterogeneous nano catalyst, which can be efficiently used for the promotion of the reactions that need the use of an acidic catalyst, because it acts as a Lewis and a Brønsted acid simultaneously. Simple work-up procedures, improved product yields, greater ease of purification, shorter reaction times, milder reaction conditions and recyclability of the catalyst are the main superiorities of n-TSA.

Xanthene–dibenzopyran—is a polyaromatic cyclic ether in which two benzene rings are fused to tetrahydropyran. Xanthene derivatives are very important heterocyclic compounds due to their broad spectrum of pharmacological and biological properties such as antibacterial, antidepressant, antimalarial, anti-inflammatory and antiviral activities [6]. Furthermore, they can be used

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as dyes, pH-sensitive fluorescent materials, in laser technologies and in photodynamic therapy [7–10]. Owing to their wide range of applications, their synthesis has gained a lot of attention in recent years.

The most common methodology for the synthesis of xanthenes derivatives is the condensation of cyclohexan-1,3-diones or β -naphthol with aliphatic and aromatic aldehydes in the presence of different catalysts and solvents [11–14], but there are only two reports on cyclocondensation reaction between α,α' -bis(substituted-benzylidene)cycloalkanones and 1,3-diketones in the literature that has been published in 2013 [15,16]. However, these few studies suffer from significant limitations like using toxic solvents, tedious work-up, long reaction times, poor yields, harsh conditions and difficult separation methods. Hence, a simple, rapid, efficient and green procedure is still strongly desired for this type of reaction.

In this paper, we describe a facile and efficient method for the synthesis of (*E*)-5-benzylidene-3,3-dimethyl-9-phenyl-2,3,4,5,6,7,8,9-octahydro-1*H*-xanthen-1-one derivatives by using α,β -unsaturated cycloalkanones as starting materials (Scheme 1). To the best of our knowledge there are no literature reports on solvent-free conditions for this type of reaction.

2. Results and discussion

As part of our continuing efforts for the development of efficient green methodologies [17–19] and n-TSA-catalyzed organic transformations [5], herein, we report a new and simple synthesis of (*E*)-5-benzylidene-3,3-dimethyl-9-phenyl-2,3,4,5,6,7,8,9-octahydro-1*H*-xanthen-1-one derivatives (5). As we have mentioned earlier, there are only two reports about their synthesis meaning that probably the reaction must be difficult. On the other hand, we have reported n-TSA as a very efficient new nano catalyst in our last work for a vast variety of organic syntheses. So we have decided to investigate it for this type of condensation.

As α,α' -Bis(substituted-benzylidene)cycloalkanones (3) are not commercially sourced, so, first of all we have reported a simple and rapid method for their synthesis. α,α' -Bis(substituted-benzylidene)cycloalkanones (3) are prepared by cross-Aldol condensation of aromatic aldehydes (2) with cyclic ketones (1). We have commenced our experiments by examining the model reaction of cyclohexanone and

Table 1

Optimum conditions for the synthesis of α,α' -bis(Substituted-benzylidene)cycloalkanones^a.

Entry	Catalyst (mmol)	Solvent	Temperature (°C)	Yield ^b (%)
1	0	–	90	4
2	n-TSA (0.03)	–	90	42
3	n-TSA (0.05)	–	90	54
4	n-TSA (0.10)	–	90	78
5	n-TSA (0.20)	–	90	93
6	n-TSA (0.30)	–	90	92
7	n-TSA (0.20)	–	Room temperature	Trace
8	n-TSA (0.20)	–	50	63
9	n-TSA (0.20)	–	70	82
10	n-TSA (0.20)	–	110	90
11	n-TSA (0.20)	EtOH	90	41
12	n-TSA (0.20)	H ₂ O	90	17
13	n-TSA (0.20)	PEG	90	36
14	n-TSA (0.20)	CH ₃ CN	90	12
15	Nano-TiO ₂ (0.20)	–	90	0
16	Bulk-TiO ₂ (0.20)	–	90	0
17	Bulk-TiO ₂ -SO ₃ H (0.20)	–	90	75

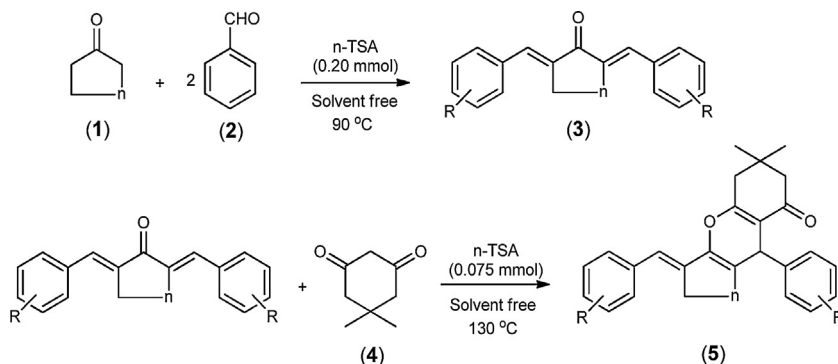
^a Reaction conditions: cyclohexanone (1 mmol), benzaldehyde (2 mmol), reaction time: 20 min.

^b Isolated yields.

benzaldehyde in the presence of n-TSA in various amounts of catalyst, temperatures and solvents. The results are summarized in Table 1.

As Table 1 shows, the trial reaction gives the best yield under solvent-free conditions and proceeds smoothly at 90 °C (oil bath) with a catalytic amount of n-TSA to afford the desired product, α,α' -bisbenzylidenecyclohexanone (3), in 20 min (Table 1, entry 5). With other selected temperatures and solvents (Table 1, entries 7–14), the reaction gave rather lower yields within comparable reaction times. It is notable that no product formed within a reasonable time in the absence of catalyst (Table 1, entry 1) and other titanium dioxide base such as unmodified nano TiO₂ and unmodified bulk TiO₂ (Table 1, entries 15, 16). On the other hand, bulk-modified TiO₂ provides lower yield in comparison to n-TSA as we expected (Table 1, entry 17) [5].

Using the optimized reaction conditions (Table 1, entry 5), we have explored the generality of this method with different aldehydes to prepare a series of benzylidenes (Table 2).

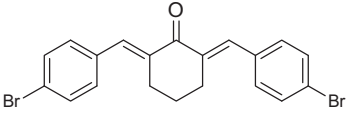
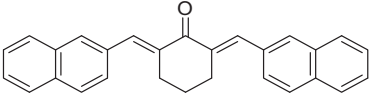
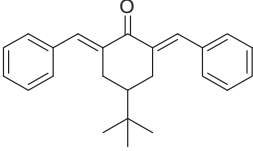
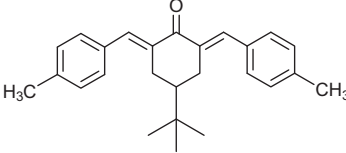
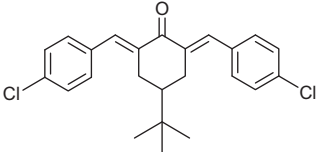
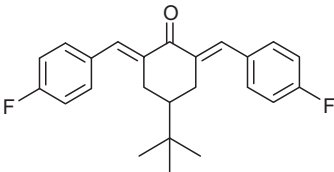
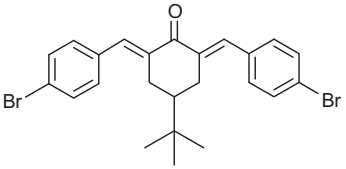


Scheme 1. Synthesis of xanthenes derivatives.

Table 2
 Synthesis of α,α' -bis(Substituted-benzylidene)cycloalkanone derivatives^a.

Entry	3	Time (min)	Yield ^b (%)	Melting point (°C)	
				Found	Reported [17,20,21]
1		25	90	187–190	188–189
2		30	93	240–242	242–243
3		15	95	153–156	154–156
4		18	98	225–228	228–229
5		20	96	205–208	204–205
6		15	90	254–257	252–257
7		20	93	118–121	116–117
8		25	91	160–163	161–163
9		30	90	165–168	164–165
10		20	95	100–103	102–104
11		18	98	148–150	147–148
12		17	95	154–157	156–158

Table 2 (Continued)

Entry	3	Time (min)	Yield ^b (%)	Melting point (°C)	
				Found	Reported [17,20,21]
13		15	90	161–164	163–164
14		20	92	197–200	199–202
15		25	92	137–140	137–138
16		30	94	156–159	156–157
17		20	98	175–178	177–178
18		20	97 ^c	174–177	Not reported
19		15	90 ^c	185–189	Not reported

^a Reaction conditions: cycloalkanone (1 mmol), aldehyde (2 mmol), n-TSA (0.20 mmol), solvent-free, temp. 90 °C.

^b Isolated yields.

^c New compounds.

In all these cases, the corresponding products were obtained in excellent yields. The results (Table 2) indicated that substrates (2) bearing both electron-donating groups and electron-withdrawing groups can be involved in this reaction to afford the desired products (3) with high yields.

After this preliminary success, our study was followed by the synthesis of the xanthenes (5) and the reaction of α,α' -bisbenzylidenecyclohexanone (3) and dimedone (4) in the presence of n-TSA was chosen as a model reaction to determine the optimum conditions.

Initially, we performed the scope of the catalyst in order to find the required catalyst load. The results are listed in Table 3.

Table 3
Optimum amount of catalyst on the synthesis of xanthenes^a.

Entry	Catalyst (mmol)	Time (h)	Yield ^b (%)
1	0	3	20
2	0.045	3:30	60
3	0.060	3:45	70
4	0.075	2	80
5	0.090	2:45	75

^a Reaction conditions: α,α' -bisbenzylidenecyclohexanone (1 mmol), dimedone (1 mmol), temperature 110 °C, solvent-free.

^b Isolated yields.

Table 4
TiO₂-based catalyzed synthesis of xanthenes^a.

Entry	Catalyst (0.075 mmol)	Time (h)	Yield ^b (%)
1	Nano-TiO ₂	2	0
2	Bulk-TiO ₂	2	0
3	Bulk-TiO ₂ -SO ₃ H	2	70
4	Nano-TiO ₂ -SO ₃ H	2	80

^a Reaction conditions: α,α' -bisbenzylidenecyclohexanone (1 mmol), dimedone (1 mmol), temperature 110 °C, solvent-free.

^b Isolated yields.

Table 5
Optimization of temperature in the synthesis of xanthenes^a.

Entry	Temperature (°C)	Time (h)	Yield ^b (%)
1	Room temperature	2	Trace
2	70	2	20
3	90	2	35
4	110	2	80
5	130	2	90

^a Reaction conditions: α,α' -bisbenzylidenecyclohexanone (1 mmol), dimedone (1 mmol), n-TSA (0.075 mmol), solvent-free.

^b Isolated yields.

As indicated in Table 3, the best yield was obtained in presence of 0.075 mmol of catalyst (Table 3, entry 4). In order to evaluate the effect of the catalyst particle size and acidity on the catalytic activity, the results were compared with those obtained using unmodified nano TiO₂, unmodified bulk TiO₂ and bulk-modified TiO₂. The results are shown in Table 4.

No activity was observed in the presence of nano TiO₂ and unmodified bulk TiO₂ (Table 4, entries 1–2). Bulk-modified TiO₂ was found to be effective but the yield of desired product was not satisfactory in comparison to modified nano TiO₂ (Table 4, entries 3, 4).

In the next step the effect of temperatures were examined over the reaction.

As indicated in Table 5, temperatures under 90 °C did not provide remarkable yields (Table 5, entries 1–3). It was observed that fast reaction occurred when raising the temperature from 90 °C to 110 °C (Table 5, entries 3,4) and the yield of product increased significantly. The best yield was obtained at 130 °C, which was considered as the optimum temperature (Table 5, entry 5).

Table 6
Optimization of solvent in the synthesis of xanthenes^a.

Entry	Solvent	Time (h)	Yield ^b (%)
1	CH ₂ Cl ₂	4	30
2	CH ₃ CN	4	50
4	H ₂ O	4	0
5	PhCH ₃	4	70
6	PEG-400	4	20
7	–	2	90

^a Reaction conditions: α,α' -bisbenzylidenecyclohexanone (1 mmol), dimedone (1 mmol), n-TSA (0.075 mmol), temperature 130 °C.

^b Isolated yields.

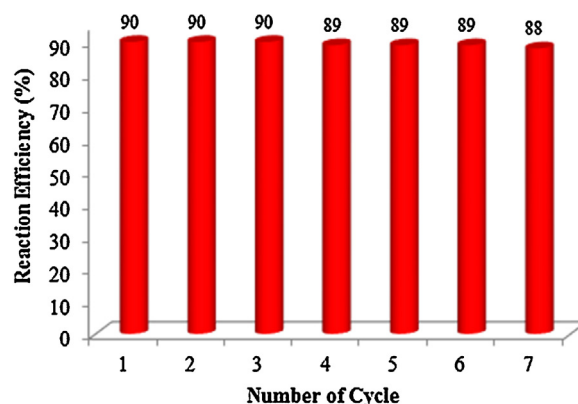


Fig. 1. Reusability of n-TSA for the synthesis of octahydroxanthenes. Reaction conditions: α,α' -bisbenzylidenecyclohexanones (1 mmol), dimedone (1 mmol), n-TSA (0.075 mmol), reaction time: 2 h at 130 °C in solvent-free conditions.

We also investigated different solvents for the model reaction (Table 6).

The results of Table 6 indicate that neither polar nor non-polar solvents are suitable for this reaction (Table 6, entries 1–6) and the best yield was obtained under solvent-free conditions (Table 6, entry 7).

We then investigated the reaction scope of this catalytic system and its tolerance of functional groups in the case of other α,α' -bis(substituted-benzylidene)cycloalkanes under the optimized reaction conditions. The results are shown in Table 7.

As indicated in Table 7, the reaction works easily for a vast range of benzylidenes with electron-donating and

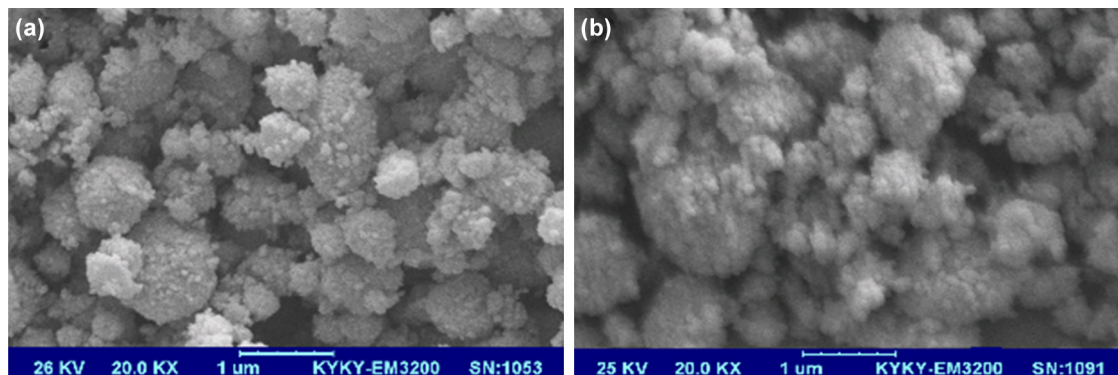


Fig. 2. SEM images of n-TSA before use (a) and after having reused it seven times (b).

Table 7
 Synthesis of xantheno derivatives under optimized reaction conditions^a.

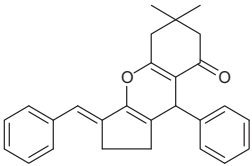
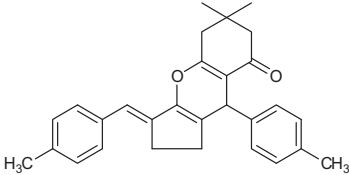
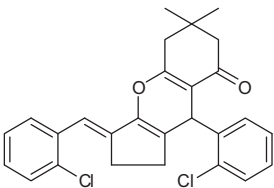
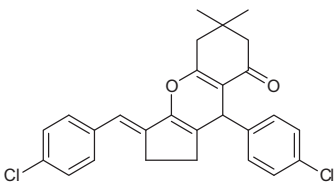
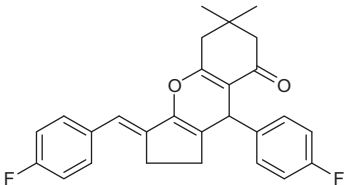
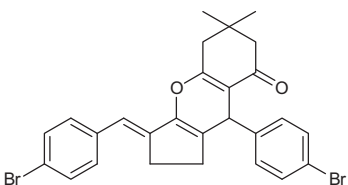
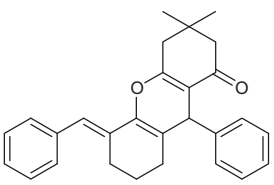
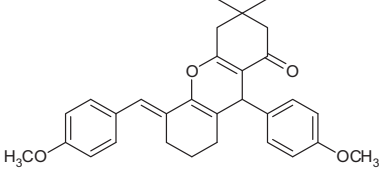
Entry	5	Time (h:min)	Yield ^b (%)	Melting point (°C)	
				Found	Reported [15,16]
1		1:50	92	206–208	204–206
2		2:10	60	228–231	230–232
3		2	93	239–242	235–237
4		2:10	90	233–236	233–234
5		2:35	80	196–199	198–199
6		2:25	94	249–252	250–252
7		2	90	165–168	166–168
8		1:45	82	157–160	158–160

Table 7 (Continued)

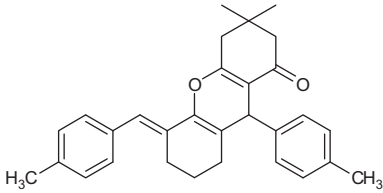
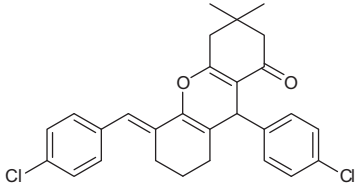
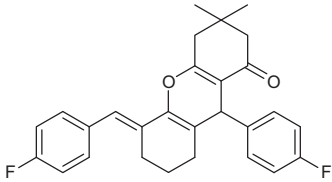
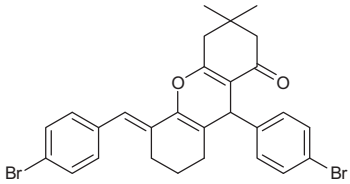
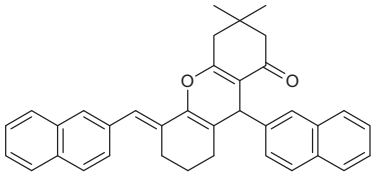
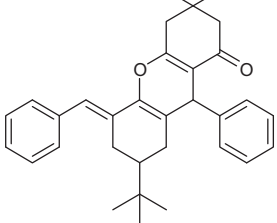
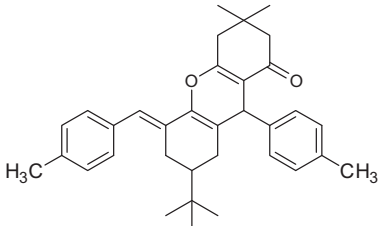
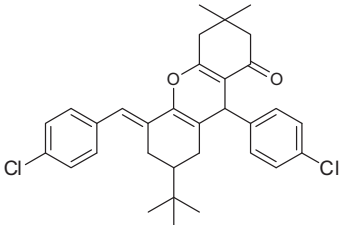
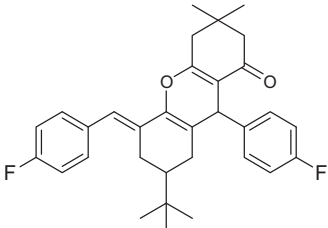
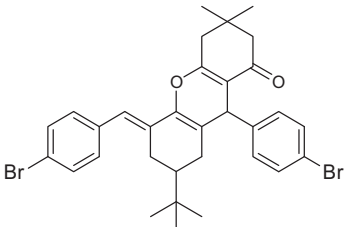
Entry	5	Time (h:min)	Yield ^b (%)	Melting point (°C)	
				Found	Reported [15,16]
9		1:50	87	166–169	165–167
10		1:35	90	157–160	156–159
11		1:55	85	150–153	149–152
12		1:55	95	165–168	165–167
13		2:30	90 ^c	208–210	Not reported
14		1:55	85 ^c	173–176	Not reported
15		2:05	92 ^c	207–212	Not reported

Table 7 (Continued)

Entry	5	Time (h:min)	Yield ^b (%)	Melting point (°C)	
				Found	Reported [15,16]
16		1:40	98 ^c	249–253	Not reported
17		1:45	91 ^c	228–233	Not reported
18		1:50	94 ^c	250–254	Not reported

^a Reaction conditions: α,α' -bis(substituted-benzylidene)cycloalkanonones (1 mmol), dimedone (1 mmol), n-TSA (0.075 mmol), temperature 130 °C, solvent-free.

^b Isolated yields.

^c New compounds.

electron-withdrawing groups. This result justified once more the efficiency of n-TSA.

The reusability of the catalyst was checked by recovering n-TSA and reusing it for seven consecutive reactions; a yield of 88–90% was obtained. This indicates that n-TSA does not lose its activity and can be recyclable (Fig. 1).

The characterization by scanning electron microscopy of the nano-TiO₂-SO₃H before use and after it has been reused seven times showed the same particle size (Fig. 2).

3. Conclusion

In summary, an efficient and rapid route for the synthesis of α,α' -bis(substituted-benzylidene)cycloalkanonones and their xanthene derivatives is reported under green conditions. Operational simplicity, neat conditions, short reaction time, simple work-up without column chromatographic purification, reusability of the catalyst, tolerance of various functional groups and high yields of products are the advantages of this protocol.

4. Experimental

Chemicals were purchased from the Merck chemical companies. Thin-Layer Chromatography (TLC) on commercial

plates of silica gel 60 F254 was used to monitor the progress of reactions. The products were characterized by FT-IR spectra, ¹H NMR, ¹³C NMR and X-ray. FT-IR spectra were recorded on Shimadzu FT-IR 8400 instrument. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 300 MHz and 75 MHz spectrometers, respectively, using CDCl₃-d as a solvent. The chemical shifts are expressed in parts per million (ppm) and tetramethylsilane (TMS) was used as an internal reference. Melting points were recorded on a THERMO SCIENTIFIC 9100 apparatus.

4.1. General procedure for the synthesis of catalyst (n-TSA)

Chlorosulfonic acid (1 mL, 15 mmol) was added dropwise to a suspension of powdered nano TiO₂ (4 g) in dry CH₂Cl₂ (20 mL) over a period of 30 min while the mixture was stirred slowly in an ice bath. The mixture was stirred for 30 min at room temperature until HCl evolution was seized. Then, the CH₂Cl₂ was removed under reduced pressure and the solid powder was washed with ethanol (10 mL) and dried at 70 °C. n-TSA was obtained as a white solid powder [5].

The number of millimoles of H⁺ per gram of catalyst was also evaluated. For this purpose, the surface acidic protons of nano-TiO₂-SO₃H (100 mg) were ion-exchanged with a saturated solution of NaCl (10 mL) by sonication. This

process was repeated twice more, yielding 30 mL of proton-exchanged brine solution. Therefore, to determine the loading of acid sites on the synthesized catalyst the obtained solution was titrated by an NaOH (0.1 M) solution in the presence of phenol red indicator solution or a pH meter. The amounts of acidic protons found to be 4.5 mmol/g of n-TSA. This finding means the effective density of the acid sites.

The catalyst was already characterized by FT-IR spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and the acid strength of n-TSA was determined by the Hammett indicator method too [5].

4.2. General procedure for the synthesis of α,α' -bis(substituted-benzylidene)cycloalkanones (3)

A mixture of cycloalkanone (1 mmol), aromatic aldehyde (2 mmol) and 0.20 mmol (0.032 g) n-TSA was stirred at 90 °C under solvent-free conditions for an appropriate time. After completion of the reaction (monitored by TLC), the reaction mixture was cooled, eluted with hot ethanol (5 mL) and was centrifuged to filter the catalyst. The title compounds were obtained in their yellowish crystalline forms by recrystallization of ethanol solution.

4.3. Spectral data of new compounds

4.3.1. 2,6-bis(4-fluorobenzylidene)-4-(tert-butyl)cyclohexanone

Yellow crystal; m.p. = 174–177 °C; IR (KBr) (cm^{-1}) ν_{max} : 2956, 2869, 1664, 1602, 1508, 1155; ^1H NMR (300 MHz, CDCl_3) 0.95 (s, 9H), 1.47 (tt, $J = 12.7 \text{ Hz}/2.8 \text{ Hz}$, 1H), 2.41 (m, 2H), 3.11 (dd, $J = 15.6 \text{ Hz}/2.3 \text{ Hz}$, 2H), 7.73 (s, 2H), 7.08–7.47 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.23, 29.37, 32.49, 44.32, 115.45, 115.73, 132.02, 132.06, 132.11, 132.22, 135.65, 135.68, 135.78, 160.94, 164.26, 190.22 (Table 2, entry 18).

4.3.2. 2,6-bis(4-bromobenzylidene)-4-(tert-butyl)cyclohexanone

Yellow crystal; m.p. = 161–164 °C; IR (KBr) (cm^{-1}) ν_{max} : 2958, 2867, 1662, 1604, 1487, 1074; ^1H NMR (300 MHz, CDCl_3) 0.94 (s, 9H), 1.47 (tt, $J = 12.8 \text{ Hz}/3.2 \text{ Hz}$, 1H), 2.40 (m, 2H), 3.09 (dd, $J = 15.5 \text{ Hz}/2.3 \text{ Hz}$, 2H), 7.68 (s, 2H), 7.30–7.56 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.22, 29.42, 32.51, 44.26, 122.89, 131.71, 134.73, 135.76, 136.48, 190.06 (Table 2, entry 19).

4.4. General procedure for the synthesis of xanthenes (5)

A mixture of α,α' -bis(substituted-benzylidene)cycloalkanones (1 mmol), dimedone (1 mmol) and 0.075 mmol (0.012 g) n-TSA was added in a test tube and heated in an oil bath at 130 °C under solvent-free condition for an appropriate time. After completion of the reaction (monitored by TLC), the reaction mixture was cooled, eluted with hot ethanol (5 mL) and was centrifuged to filter the catalyst. The products were obtained in white powder by recrystallization of ethanol solution.

4.5. Spectral data of new compounds

4.5.1. (E)-3,3-dimethyl-9-(naphthalen-2-yl)-5-(naphthalen-2-ylmethylene)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

White powder; m.p. = 208–210 °C; IR (KBr) (cm^{-1}) ν_{max} : 3421, 3051, 2941, 1622, 1660, 1220, 748; ^1H NMR (300 MHz, CDCl_3) 1.04 (s, 3H), 1.15 (s, 3H), 1.65 (m, 2H), 2.17 (m, 4H), 2.66 (m, 3H), 2.86 (m, 1H), 4.42 (s, 1H), 7.16 (s, 1H), 7.39–7.84 (m, 14H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 22.46, 27.31, 27.42, 27.75, 29.39, 32.18, 40.53, 41.39, 50.82, 112.42, 118.30, 122.20, 125.40, 125.83, 126.17, 126.54, 127.02, 127.53, 127.60, 127.92, 128.01, 128.08, 130.67, 132.12, 132.49, 133.27, 133.40, 134.90, 141.47, 142.01, 164.13, 197.22 (Table 7, entry 13).

4.5.2. (E)-5-benzylidene-7-(tert-butyl)-3,3-dimethyl-9-phenyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

White powder; m.p. = 173–176 °C; IR (KBr) (cm^{-1}) ν_{max} : 3024, 2956, 1660, 1627, 1380, 1340, 1224, 769; ^1H NMR (300 MHz, CDCl_3) 0.78 (s, 9H), 1.00 (s, 3H), 1.10 (s, 3H), 1.25 (m, 1H), 1.96 (m, 2H), 2.18 (m, 3H), 2.52 (m, 2H), 3.03 (dd, $J = 14.70 \text{ Hz}/2.76 \text{ Hz}$, 1H), 4.23 (s, 1H), 6.93 (s, 1H), 7.15–7.40 (m, 10H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.14, 27.23, 27.33, 27.91, 28.22, 29.33, 32.15, 32.18, 39.69, 41.36, 43.86, 50.82, 112.65, 118.39, 121.80, 126.46, 126.50, 128.19, 128.42, 129.21, 130.95, 137.43, 142.18, 143.97, 164.30, 197.19 (Table 7, entry 14).

4.5.3. (E)-7-(tert-butyl)-3,3-dimethyl-5-(4-methylbenzylidene)-9-(p-tolyl)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

White powder; m.p. = 207–212 °C; IR (KBr) (cm^{-1}) ν_{max} : 3020, 2952, 1662, 1629, 1379, 1365, 1110, 833; ^1H NMR (300 MHz, CDCl_3) 0.78 (s, 9H), 1.00 (s, 3H), 1.10 (s, 3H), 1.25 (m, 1H), 1.99 (m, 2H), 2.20 (m, 3H), 2.26 (s, 3H), 2.37 (s, 3H), 2.53 (m, 2H), 3.04 (d, $J = 6.3 \text{ Hz}$, 1H), 4.18 (s, 1H), 6.89 (s, 1H), 7.04–7.26 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 21.08, 21.21, 27.18, 27.27, 27.38, 27.47, 27.86, 28.24, 29.33, 32.15, 32.21, 39.24, 40.56, 41.37, 43.76, 50.85, 112.78, 117.80, 118.16, 121.58, 127.96, 128.26, 128.87, 128.92, 129.01, 129.14, 130.34, 130.59, 134.56, 135.81, 135.91, 136.20, 141.01, 141.14, 163.74, 164.24, 197.23 (Table 7, entry 15).

4.5.4. (E)-7-(tert-butyl)-5-(4-chlorobenzylidene)-9-(4-chlorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

White powder; m.p. = 249–253 °C; IR (KBr) (cm^{-1}) ν_{max} : 2960, 1662, 1627, 1379, 1089; ^1H NMR (300 MHz, CDCl_3) 0.77 (s, 9H), 0.98 (s, 3H), 1.10 (s, 3H), 1.25 (m, 1H), 1.98 (m, 2H), 2.20 (m, 3H), 2.53 (m, 2H), 2.96 (dd, $J = 14.65 \text{ Hz}/2.78 \text{ Hz}$, 1H), 4.21 (s, 1H), 6.86 (s, 1H), 7.23–7.35 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.12, 27.20, 27.28, 27.91, 28.14, 29.30, 32.16, 32.18, 39.16, 41.32, 43.88, 50.75, 112.33, 118.19, 120.94, 128.40, 128.51, 129.48, 129.77, 130.43, 131.35, 132.18, 132.30, 135.75, 142.27, 142.44, 163.81, 164.33, 197.11 (Table 7, entry 16).

4.5.5. (E)-7-(tert-butyl)-5-(4-fluorobenzylidene)-9-(4-fluorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

White powder; m.p. = 228–233 °C; IR (KBr) (cm^{-1}) ν_{max} : 2958, 1652, 1600, 1380, 1222, 1157; ^1H NMR

(300 MHz, CDCl₃) 0.77 (s, 9H), 0.99 (s, 3H), 1.11 (s, 3H), 1.24 (m, 1H), 1.95 (m, 2H), 2.18 (m, 3H), 2.52 (m, 2H), 2.96 (dd, *J* = 14.63 Hz/2.83 Hz, 1H), 4.22 (s, 1H), 6.88 (s, 1H), 6.91–7.30 (m, 8H, ArH); ¹³C NMR (75 MHz, CDCl₃): δ 27.10, 27.27, 27.86, 28.12, 29.29, 32.16, 38.94, 41.33, 43.95, 50.78, 112.55, 114.84, 115.02, 115.13, 115.31, 118.09, 120.93, 129.80, 129.90, 130.67, 130.70, 130.77, 133.32, 133.37, 139.67, 139.71, 142.20, 159.81, 159.89, 163.08, 164.22, 197.17 (Table 7, entry 17).

4.5.6. (E)-7-(tert-butyl)-5-(4-bromobenzylidene)-9-(4-bromophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

White powder; m.p. = 250–254 °C; IR (KBr) (cm⁻¹) ν_{max}: 3056, 2866, 1658, 1625, 1380, 1064; ¹H NMR (300 MHz, CDCl₃) 0.79 (s, 9H), 0.98 (s, 3H), 1.12 (s, 3H), 1.26 (m, 1H), 2.03 (m, 2H), 2.18 (m, 3H), 2.53 (m, 2H), 2.80 (m, 1H), 4.20 (s, 1H), 6.95 (s, 1H), 7.16–7.35 (m, 8H, ArH); ¹³C NMR (75 MHz, CDCl₃): δ 26.60, 27.05, 28.04, 30.40, 32.31, 33.04, 39.59, 41.93, 43.93, 50.77, 113.57, 118.04, 121.13, 128.32, 128.43, 129.72, 130.48, 130.53, 132.27, 132.37, 135.67, 141.93, 142.60, 165.75, 197.33 (Table 7, entry 18).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2014.11.003>.

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