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ORIGINAL PAPER

Preparation and application of highly efficient and reusable TBAPIL@Si$(CH_2)_3$@nano-silica-based nano-catalyst for preparation of benzoxanthene derivatives

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Abstract
Tetrabutylammonium prolinate ionic liquid (TBAPIL) was prepared, and mesoporous silica nanoparticles (NPs) were synthesized. Both of these were linked through propyltriethoxysilane to prepare a reusable catalyst TBAPIL@Si$(CH_2)_3$@silica NPs (TBAPILS). The formation of TBAPIL was checked through Fourier-transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) analysis. X-ray diffraction analysis confirmed the structure of silica NPs and linking of TBPAIL on it. Transmission electron microscopy proved the flourishing development of silica NPs. Scanning electron microscopy graphs exposed the altering in morphology of silica NPs and TBAPILS. FT-IR analysis also confirmed the formation of TBAPILS catalyst. Moreover, the effectiveness of the TBAPILS was also checked for the synthesis of various derivatives of tetrahydrobenzoxanthenes-11-ones. The formation and structure of obtained compounds were confirmed by FT-IR, elemental analysis, ^{1}HNMR and ^{13}C NMR spectral analysis. The catalyst TBAPILS was found to be used successfully up to five cycles without significant loss of activity.

Keywords Tetrabutylammonium prolinate ionic liquid · Mesoporous silica nanoparticles · Tetrahydrobenzoxanthene · TBAPILS · Transmission electron microscopy · Scanning electron microscopy · X-ray diffraction

Introduction

Nano-catalysis is a very exciting field which is originated from nanoscience. Nano-catalysts are gaining importance increasingly [1]. The main aim of the nano-catalysts is to control the chemical reactions through changing their size, morphology and composition of reaction center [2]. The overall approach opens various areas for designing of nano-catalysts having a distinct, selective and specific chemical activity. The nano-shape, size and a large surface area by volume ratio provide unique characteristics to nano-catalysts due to the structural and electronic changes which differentiate them from the original materials [3]. Nanoparticles (NPs) can replace conventional materials and serve as heterogeneous catalytic systems or as a material of support for different catalytic systems [4, 5]. Catalyst is a substance which speeds up the chemical reactions, enhances the product yield and shrinks the energy of activation, but a severe trouble with reactions in catalytic conditions is the parting of catalytic system from the ongoing reaction mixture so that it may be used again [6]. To defeat this trouble, a heterogeneous catalytic system may be used in synthetic organic chemistry. Currently, heterogeneous catalytic systems may be prepared by a variety of substances in a straightforward way [7]. Heterogeneous catalytic systems may capably be formed by modifying the support with NPs and combining these with catalytic system [8, 9]. Recently a range of methods have been reported for the synthesis of silica NPs with controlled size and chemical stability with a variety of applications in drug delivery [10]. Moreover, these silica-based catalysts have also been used to catalyze a range of chemical reactions [11, 12].

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Ionic liquids are salts having melting point lower than the boiling point of water. Ionic liquids have several alternative names such as designer solvents, molten salts and ionic fluids [13]. Ionic liquids are generally colorless liquids with moderately low viscosity. Ionic liquids are made up of two parts positive and negative ions, therefore there is wide scope to prepare them in large numbers and to fine-tune their properties according to the requirement. These advantages are unavailable for single constituent molecular solvents. In addition to all these properties, ionic liquids can be readily formed by using commercially accessible reagents [14]. Ionic liquids also have an important role in catalysis and synthesis [15]. Various methods for the preparation along with their applications in catalysis have been reported for tetrabutylammonium prolinate and other ionic liquids [16–18]. But most of these ionic liquids are associated with disadvantages like harsh conditions and non-reusability.

Tetrahydrobenzoxanthen-11-one and its derivatives are a chief class of bioactive compounds having activities like anti-inflammatory [19], free radical scavenging [20], mGlu1 receptor enhancing [21], antiplasmodial [22], antitumor [23], inhibitors of recombinant human calpain I [24], molecular probes in chemical biology [25], antibacterial [26, 27], antiproliferative [28], antineoplastic [29], drug development [30, 31], antileukemic [32] and insecticidal [33]. Due to special spectroscopic properties, these derivatives have also been used as pH-indicators [34], fluorescent materials in visualization of molecules [35] and as photodynamic therapy agents [36]. Various methods have been developed for the synthesis of tetrahydrobenzoxanthen-11-one using PMA/SiO_2 [37], ZnO [38], $InCl_3$/ionic liquid [39], *p*-dodecylbenzenesulfonic acid [40], iron oxide NPs [41], trichloroacetic acid [42], silica sulfuric acid [43], strontium triflate [44], PEG [45], bismuth nitrate [46], phenylboronic acid [47], molecular iodine [48], p-TSA [49] and other heterogeneous catalysts [50, 51]. Most of them have the limitations such as low yield, formation of mixture of products, long reaction time and harsh reaction conditions, so it is imperative to develop new and efficient methods with reduced reaction time and mild reaction conditions for the synthesis of derivatives of biologically active tetrahydrobenzoxanthen-11-one compounds. To the best of our knowledge, we are first to report the synthesis of tetrahydrobenzoxanthen-11-one in solvent-less condition by using TBAPILS nano-catalyst.

Experimental

Materials and methods

All reagents and chemicals were of L.R. grade and procured from Hi-media and Molychem and directly used with no additional purification. The glasswares used during the study were made of Borosil. IR spectra were taken on BRUCKER FT-IR spectrophotometer of BRUCKER. BRUCKER AVANCE II 400 MHz instrument was used for 1HNMR analysis with $CDCl_3$ solvent. Decibel digital melting point equipment was used for recording of melting points. The progress of reaction and compounds purity was checked by TLC on silica gel plates with hexane and ethyl acetate solvents and visualized through vapors of iodine and UV light. JSM-1011 transmission electron microscope was used for TEM analysis and JEOL (JSM-6610 LV) with a prime ray power of 5 kV apparatus was used to record SEM analysis. XRD analysis of powdered samples was recorded at room temperature (RT) over Rigaku-Geigerflex X-Ray diffractometer by using Cu-Ka radiation ($k = 0.154$ nm) in the series of 108–708 at 30 kV and 15 mA with step size 0.05 and step time of 19.2 s.

Synthesis of mesoporous silica nanoparticles (NPs)

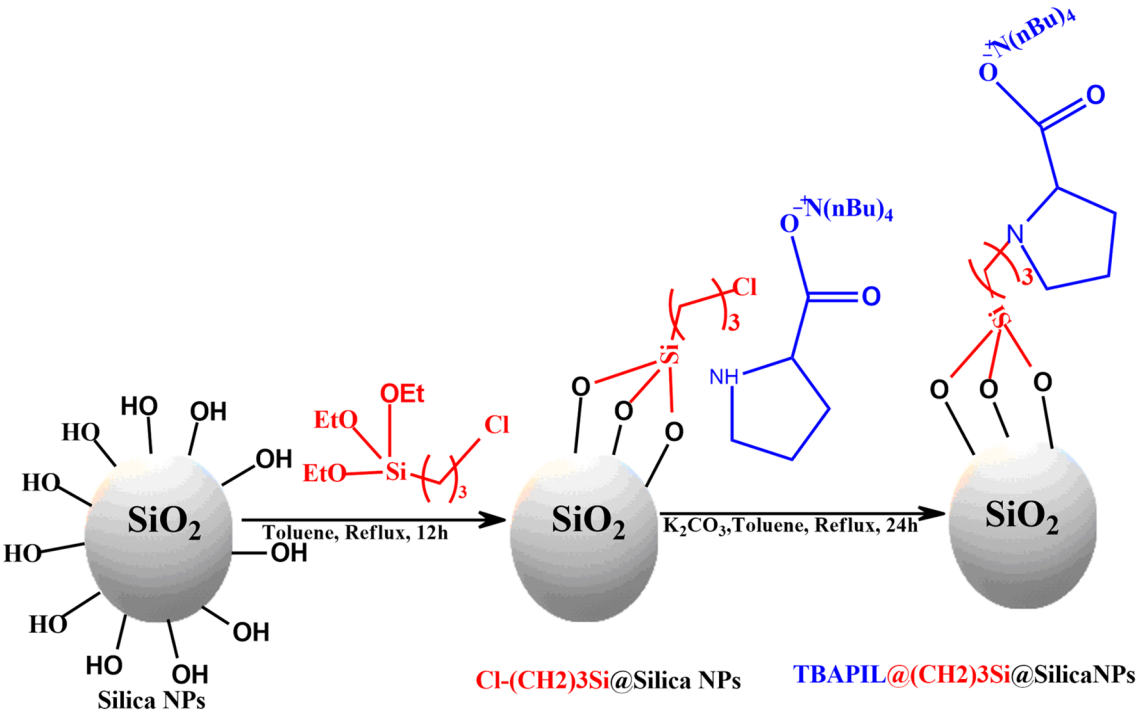
In a round-bottom flask, 100 mL methanol was placed. To it, 60 mL solution of ammonia (32%) and 1.98 mL water were mixed. The mixture was stirred up to 5–6 min and after that 10.40 g tetraethyl orthosilicate (TEOS) was added drop-wise. The solution was again stirred for 72 h at an ambient temperature [52, 53]. Then, it was centrifuged for 30 min, after which solvent was evaporated by rotavapor, washed with ethanol and particles obtained were put in oven at 250 °C for 1 h.

Synthesis of tetrabutylammonium prolinate ionic liquid (TBAPIL)

Tetrabutylammonium hydroxide [(TBA)(OH)] aqueous solution was prepared by modified literature method [54] from Tetrabutylammonium bromide (20 mmol) using anion exchange resin AMBERLITE IRA400 OH. The obtained [(TBA)(OH)] aqueous solution (10 mmol) was then added drop-wise with a slightly excess aqueous proline solution (10 mmol). This combination was stirred at RT for 12 h, then water was removed in vacuum and obtained residue was dissolved in CH_3CN (40 mL) and the solution was filtered to remove unreacted proline. Filtrate was dried over anhydrous Na_2SO_4 and solvent was removed in vacuum to give the desired TBAPIL as low viscous colorless oil [17].

Preparation of TBAP@Si$(CH_2)_3$@nano-silica (TBAPILS) catalyst

The supporting of the TBAPIL on propyl silane-grafted silica nanoparticles is shown in Scheme 1. Silica NPs (1 g) and 3-chloropropyltriethoxysilane (3 mmol) were added to 20 mL of dry toluene and then refluxed for 12 h. The resultant grafted SiO_2@Si$(CH_2)_3$Cl was filtered, washed



Scheme 1 Synthesis of [TBA][Pro] @Si(CH2)3@nano-silica catalyst

thrice with dry toluene and with dry diethyl ether and dried at 75 °C for 6 h in vacuum oven. Then, TBAPIL (10 mmol) was added to the round-bottom flask containing SiO2@Si$(CH_2)_3$Cl (1 mmol), K_2CO_3 (5 mmol) in 50 mL of dry toluene. The mixture was refluxed for 24 h. The resultant solid was then filtered, washed and dried to give TBAPILS. After the usual workup and washings, the material was dried at 75 °C for 5 h in a vacuum oven.

Synthesis of tetrahydrobenzoxanthen-11-one derivatives using TBAPILS catalyst

β-naphthol (10 mmol)/α-naphthol(10 mmol), cyclic 1,3 dicarbonyl compound (10 mmol) and benzaldehyde derivative (10 mmol) were mixed with TBAPILS (5 mol%). The mixture of was stirred vigorously at 80 °C (Scheme 2) and progress of reaction was observed using TLC (ethyl acetate: n-hexane:: 3:7 v/v). After completion of reaction, cold water was added to the reaction mixture to ease the precipitation of product. The solid obtained was dissolved in ethyl alcohol and filtered. The catalyst obtained as solid was washed three times with alcohol to remove any traces of product and then dried in vacuum oven at 70 °C to be used for next cycle. Solvent was distilled off from filtrate to get the solid product. The crude product was then recrystallized from dichloromethane to give pure product.

Results and discussion

TBAPILS catalyst

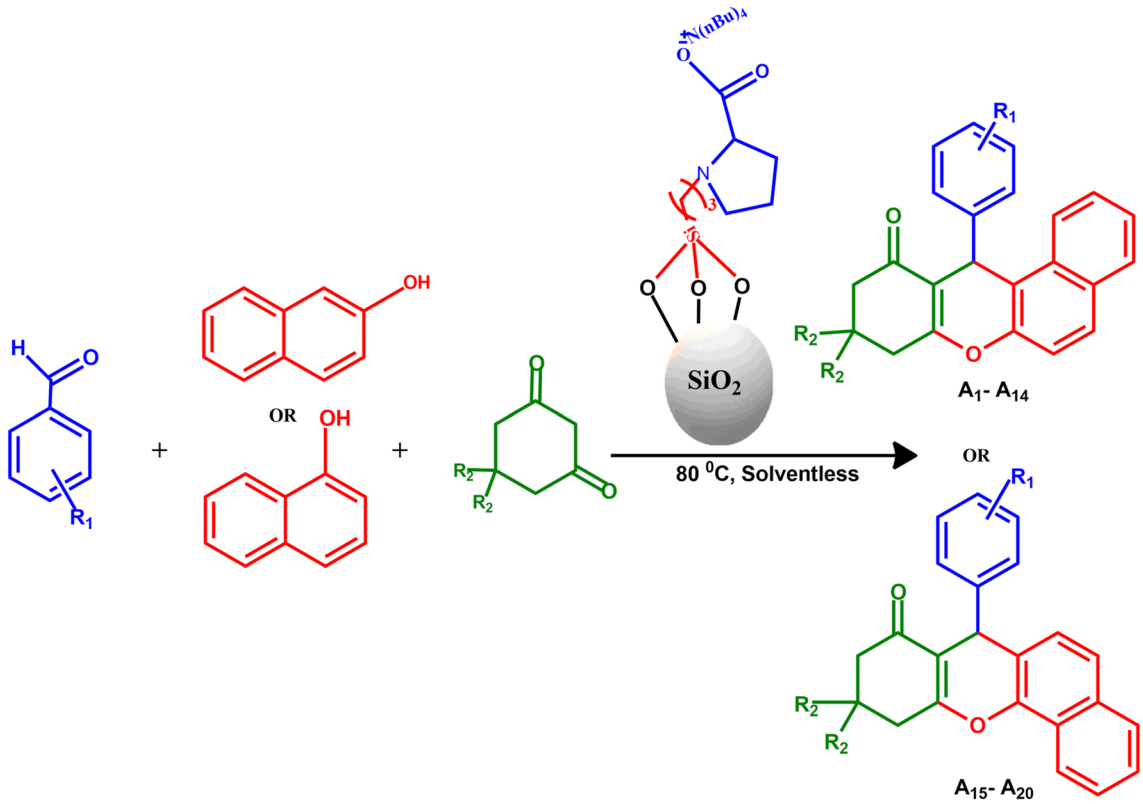
TEM analysis of Mesoporous Silica NPs

The size of silica NPs was characterized from TEM. The results are shown in Fig. 3a, b. The size of silica NPs was found to be 40–50 nm.

^{1}H NMR of TBAPIL 1H NMR ($CDCl_3$, 400 MHz): δppm 3.28 (t, 2H), 3.26 (t, 1H), 2.33 (t, 2H), 1.93(s, 1H), 1.62 (m, 2H), 1.58 (m, 2H), 1.56 (m, 2H), 1.37 (m, 2H), 0.91(t, 3H) (Fig. 1).

FT-IR analysis

The functional groups of the prepared TBAPILS catalyst and its precursors were characterized by FT-IR technique, as shown in Fig. 2. In mesoporous nano-silica, two characteristic bands by the side of 963 cm^{-1} and 783 cm^{-1} are for Si–O–Si symmetric and asymmetric stretching, and at 3562 cm^{-1} due to surface Si–OH stretching. Two bands at 459 and 1633 cm^{-1} are due to Si–O–Si and Si–OH bending, respectively (Fig. 2a). The characteristic bands of



Scheme 2 Synthesis of Tetrahydrobenzoxanthen-11-one derivatives

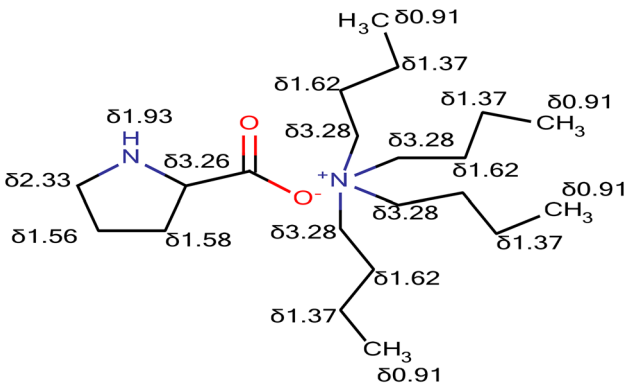


Fig. 1 Structure of tetrabutylammonium prolinate ionic liquid

chloropropylsilane-coated silica appearing at 1057, 1237 and 2965 cm^{-1} are due to the Si–O–Si stretching, C–H bending and stretching, respectively (Fig. 2b). The characteristic bands at 1359, 1625, 3524, 2938 cm^{-1} are due to –C–OH, –C = O, –NH and –C–H stretching. The bands by the side of 1455 and 735 $cm^{-1}$are due to the –C–H and –C = O bending (Fig. 2c). The presence of groups in TBAPILS catalyst such as Si–O–Si, –C = O, –C–H is confirmed by bands at 461, 791, 1121, 1241, 1681, 2986 and 3600 cm^{-1} (Figs. 2d, 3).

SEM analysis silica NPs and TBAPILS catalyst

The surface morphology of silica NPs and TBAPILS catalyst was characterized by SEM. Silica nanoparticles demonstrate a porous morphology (Fig. 4a). TBAPILS grafted on silica nanoparticles fill the pores in the surface thereby making a different topological arrangement which gives rise to changed morphology (Fig. 4b). Perusal of Fig. 4a, b clearly indicates the difference in surface morphology of silica NPs and TBAPILS (Fig. 4a, b).

XRD analysis

The XRD pattern of silica NPs clearly conforms to the amorphous nature of it with the broad peak (2θ) at 23.70. The XRD results are in well agreement with the reported facts JCPDS card number (00-049-1711) [55]. The change in intensity in TBAPILS (Fig. 5b) in comparison with silica NPs (Fig. 5a) clearly indicates the linking of TBAPIL on surface of silica NPs. These XRD results are supported by the SEM results whereby changed morphology is observed after grafting on the silica NPs.

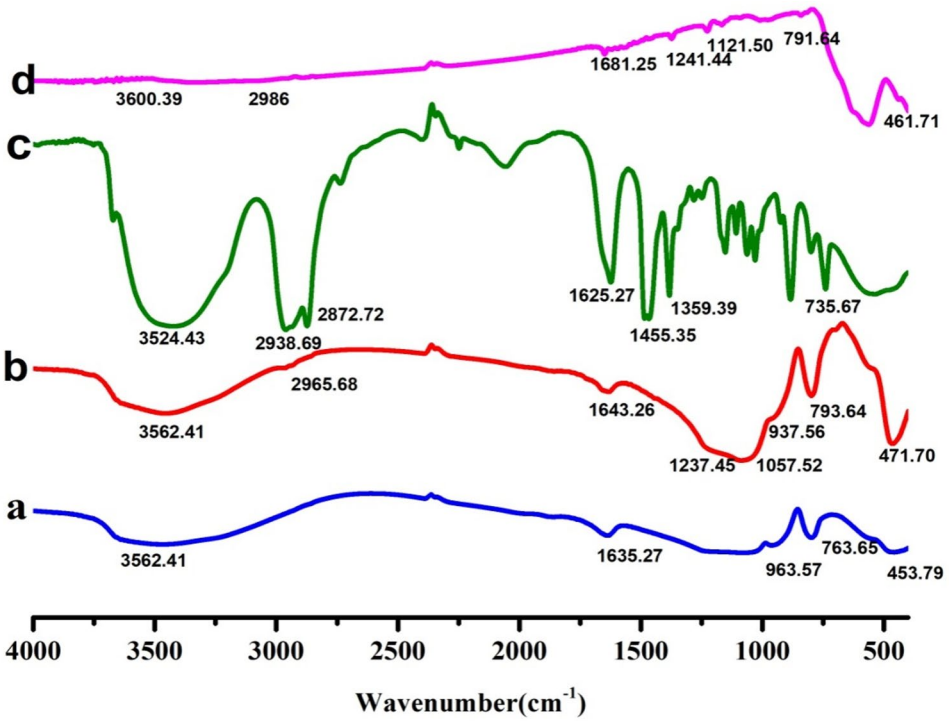


Fig. 2 FT-IR of **a** SiO_2 NPs, **b** $Si(CH_2)_3@SiO_2$, **c** TBAPIL and **d** TBAPILS catalyst

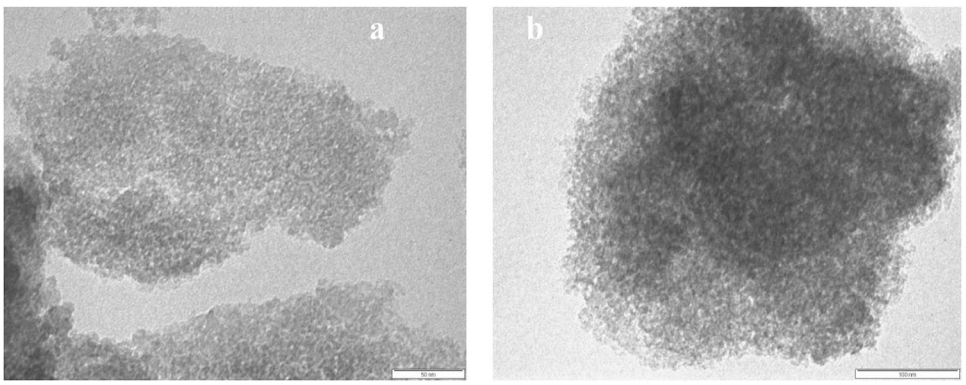


Fig. 3 TEM images of silica NPs: **a** low magnification and **b** high magnification

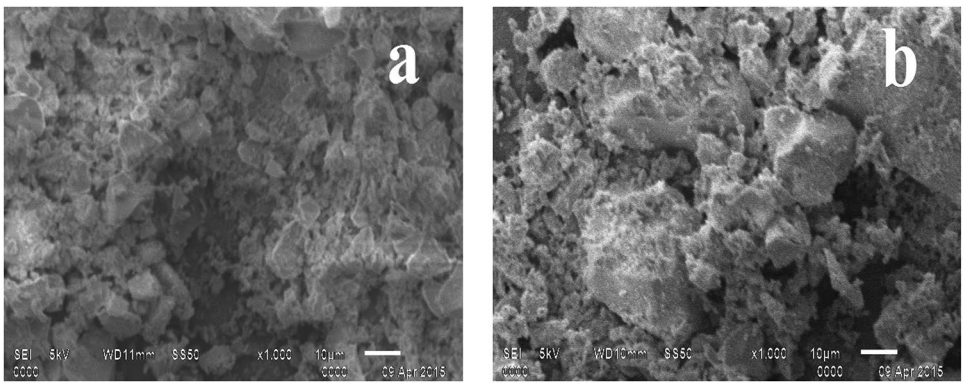


Fig. 4 **a** SEM of silica NPs and **b** SEM of TBAPILS catalyst

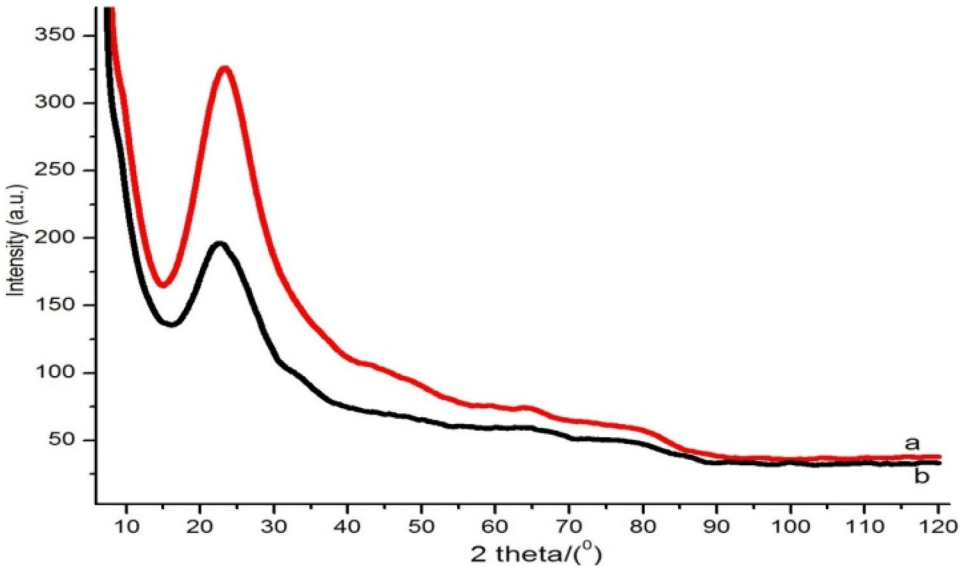
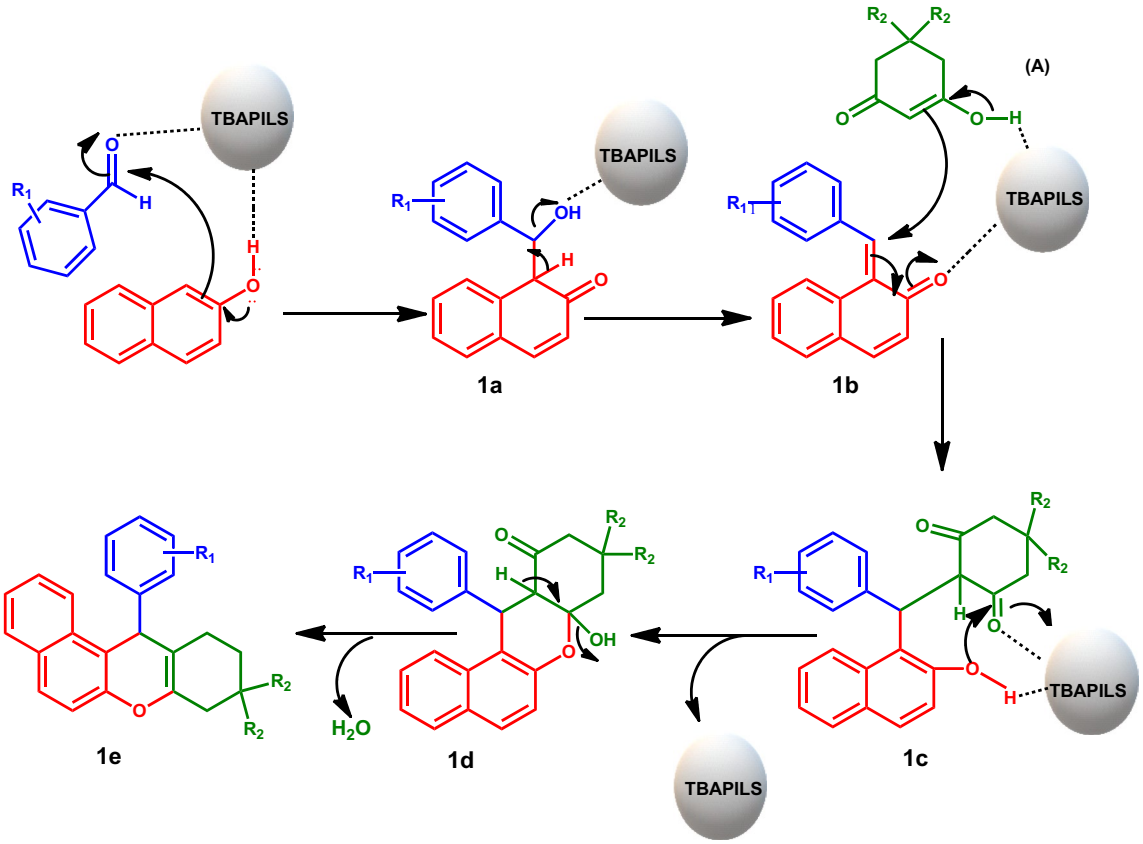


Fig. 5 **a** XRD of silica NPs and **b** XRD of TBAPILS catalyst



Scheme 3 Plausible mechanism for the synthesis of tetrahydrobenzoxanthene-11-one derivatives

Mechanism

A plausible mechanism has been proposed for the preparation of tetrahydrobenzoxanthen-11-one derivatives using TBAPILS catalyst (Scheme 3). The cation is attached to the oxygen of the carbonyl group of aldehyde which increases the electrophilicity of carbonyl group and anion activates the nucleophile b-naphthol, consequent upon this nucleophilic attack of β-naphthol at carbonyl carbon is facilitated and ortho-quinone methide intermediates (1a) is formed.

After removal of a water molecule, 1b is formed. With the removal of a water molecule, the catalyst TBAPILS which is attached to oxygen of carbonyl group of aldehyde is detached and now it interacts with active methylene group containing compound **(A)** via oxygen and makes it more reactive while anion interacts with enolic –OH of bicarbonyl. Due to combined effect of these activations, Michael addition is facilitated. Ring closure step, next to Michael addition step, is also facilitated by the catalyst. Here also, electrophilicity of carbonyl carbon of bicarbonyl is increased due to its interaction with cation and interaction of anion with –OH group of naphthol moiety assists in removal of hydrogen thus facilitating ring closure. After ring closure, dehydration takes place and final product (1e) is obtained (Scheme 3). The mechanism proposed is the modification to the mechanism reported in the literature [47, 51] in which interaction of anion and combined effect of cation and anion are not discussed. In our view, it is simultaneous interaction of cation as well as anion of the catalyst with substrates in each step that makes the catalyst more active. Comparison of the activity of catalyst with those of tetrabutylammonium bromide and proline supports this view (Table 3).

Optimization of reaction conditions

A model reaction of β-naphthol, benzaldehyde and cyclic 1,3 dicarbonyl was carried out using TBAPILS under solvent less condition to optimize temperature. No yield was obtained at RT even up to 10 h stirring. After this, the reaction was tried at different temperatures from 40 to 100 °C with a difference of 10 °C. As a result of rising temperature, the yield increased and the reaction time decreased. After 80 °C, no rise in yield was observed. Time also remained constant. So, 80 °C was taken as the optimum temperature for the reaction.

Scope of substrate

Derivatives of substituted tetrahydrobenzoxanthen-11-one were produced by the reaction between substituted α/β-naphthol, benzaldehyde derivative and cyclic 1, 3 dicarbonyl. The substituted group, % yield, M.P. and reaction time are displayed in Table 1. To inspect the scope of substrate, a range of benzaldehyde derivative was used. All the products were obtained in good to excellent yield. The reaction was completed within 15 to 180 min. The reaction was viable for electron-withdrawing as well as for electron-donating groups substituted on the benzene ring of benzaldehyde. The reaction could be carried out well for both α-naphthol and β-naphthol which clearly establishes broad substrate scope of the reaction catalyzed by TBAPIS (Table 1). Turn over number (TON) and turn over frequency (TOF) values of catalyst for all the products have been calculated and are presented in Table 1. TON values were obtained in the range

Table 1 Substituted tetrahydrobenzoxanthen-11-one derivatives

Code	$-R_1$	$-R_2$	Yield (%)[a]	TON	TOF (min^{-1})	M.P. (°C)	M.P. (°C) Ref	Time (min)
A_1	–H	$-CH_3$	92	184	3	150–152	151–153 [57]	60
A_2	3-NO_2	$-CH_3$	88	176	2	170–172	168–170 [47]	90
A_3	4-Cl	$-CH_3$	84	168	6	175–177	176–179 [42]	30
A_4	4-$NH(CH_3)_2$	$-CH_3$	80	160	11	210–215	218–220 [58]	15
A_5	3-OH	$-CH_3$	82	164	5	225–227	240–241 [57]	30
A_6	3,4- $(OCH_3)_2$	$-CH_3$	88	176	2	165–168		90
A_7	2,4-$(Cl)_2$	$-CH_3$	85	170	8	173–175	175–178 [59]	20
A_8	4-OH,3-OCH_3	$-CH_3$	80	160	5	196–198	213–215 [57]	30
A_9	2-OH,3-OCH_3	$-CH_3$	80	160	4	215–217	213–215 [59]	40
A_{10}	4-F	$-CH_3$	88	176	3	180–182	184–185 [47]	60
A_{11}	–H	–H	90	180	1	190–192	202–203 [58]	180
A_{12}	3-NO_2	–H	72	144	1	210–215	230–232 [60]	120
A_{13}	4-Cl	–H	80	160	2	208–210	204–206 [58]	90
A_{14}	–H	$-CH_3$	82	164	5	160–162	155–157 [58]	30
A_{15}	3-NO_2	$-CH_3$	81	162	11	170–172	167–170 [61]	15
A_{16}	4-Cl	$-CH_3$	82	164	11	215–218	185–187 [61]	15
A_{17}	–H	–H	84	168	3	156–158	173–175 [58]	60
A_{18}	3-NO_2	–H	86	192	2	178–180	167–170	90
A_{19}	4-Cl	–H	85	190	2	170–172	175–177 [58]	120

[a]Isolated yield

[b]Reaction conditions: β-naphthol (10 mmol)/α-naphthol(10 mmol), benzaldehyde derivative (10 mmol) and cyclic 1,3 dicarbonyl (10 mmol) in the absence of solvent with TBAPILS (5 mol%) at 80 °C

144–192. The values clearly indicate that catalyst is quite stable. The TOF values calculated per minute were obtained in the range 1–11 indicating variable efficiency of the catalyst for different reactants.

Loading of TBAPILS catalyst

To optimize the amount of catalyst, model reaction of β-naphthol (10 mmol), benzaldehyde derivative (10 mmol) and cyclic 1,3 dicarbonyl (10 mmol) was tried in the presence of various amounts of catalyst such as 1, 2, 3, 4, 5, 6 and 7 mol%, there is an increase in yield and decrease in time with increase in the amount of catalyst up to 5 mol% (Fig. 6). No further significant increase in yield was observed in by further increasing the catalyst amount (Table 2). The results showed that 5 mol% of the catalyst and 80 °C temperature was the best combination to afford product A_1 in excellent yield.

Table 2 Optimization of the amount of TBAPILS catalyst for the formation of A_1

Entry	Catalyst (mol %)	Time (min)	Yield (%)[a]
1	1	240	40
2	2	220	50
3	3	180	65
4	4	120	80
5	5	60	92
6	6	60	92
7	7	60	92

[a]Isolated yield

Table 3 Optimal conditions for the synthesis of A_1 catalyzed by TBAPILS

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]
1	–	–	80	10	–
2	–	Ethanol	RT	10	–
3	–	Ethanol	80	10	–
4	–	Water	RT	10	–
5	–	Water	80	10	–
6	Silica NPs	–	RT	10	–
7	Silica NPs	–	80	10	–
8	SiO_2@$Si(CH_2)_3Cl$	–	RT	10	–
9	SiO_2@$Si(CH_2)_3Cl$	–	80	10	–
10	TBABr	–	RT	10	–
11	TBABr	–	80	5	30
12	Proline	–	RT	10	–
13	Proline	–	80	4	20
14	TBAPIL	–	80	1	92
15	TBAPILS	–	80	1	92

[a]Isolated yield

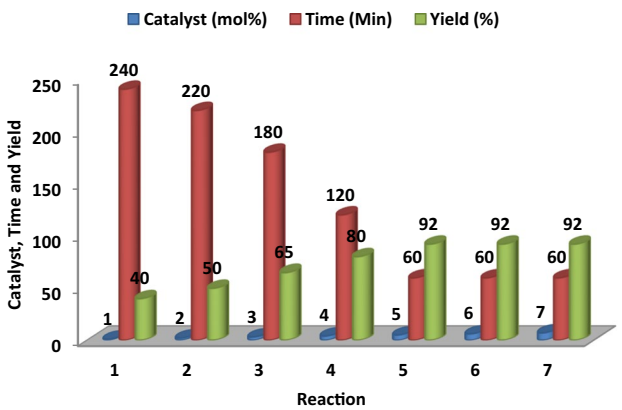


Fig. 6 Recycling study of TBAPIL up to five cycles for the synthesis of A_1

Structure and catalytic ability relationship of TBAPILS catalyst

Perusal of structure of the catalyst TBAPILS reveals that it is a bifunctional ionic liquid organocatalyst. It contains cation (tetrabutylammonium) and an effective anion which also contains base (–N). These features make it excellent and task specific for this reaction. These features are lacking in tetrabutylammonium bromide and proline. Though tetrabutylammonium bromide contains same cation, it does not have an effective anion or a base. Proline contains both acidic as well as basic group but it lacks effective cation. This is supported by experimental observations (Table 3). The catalyst prepared by us has activity much higher than tetrabutylammonium bromide and proline. The interaction of the catalyst with substrates at different stages of reaction is explained to understand its structure activity relationship. Cation of the catalyst is effective in catalyzing the reaction of benzaldehyde and b-naphthol by interacting with the carbonyl group of benzaldehyde via oxygen while its base/anion interacts with the nucleophile (b-naphthol) via hydrogen of –OH group of naphthol. Then, in the reaction between the intermediate formed thus and dicarbonyl compound, cation interacts in the same way with the carbonyl group of the intermediate and anion/ base interacts with the dicarbonyl facilitating Michael addition. Finally, in the cyclization step, carbonyl group of bicarbonyl moiety and OH group of b-naphthol moiety interact with cation and base/ anion, respectively. Thus, in every step, catalyst functions as acid as well as a base. Jimenez et al. [56] have explained these interactions of bifunctional organocatalyst containing thiourea moiety working as Lewis acid and amine working as

base on the basis of electron density topological analysis using quantum chemical technology.

Hot filtration test

To confirm the heterogeneity of TBAPILS catalyst and in order to prove that tetrabutylammonium ionic liquid was not leaching out from the TBAPILS catalyst, the hot filtration test was performed with the model reaction of β-naphthol, benzaldehyde derivative and cyclic 1,3 dicarbonyl under optimized reaction conditions. After 30 min which is half of the reaction time, the catalyst was filtered off and 45% yield was obtained and filtrate was allowed to react further but no significant amount of product was obtained. These results show that immobilized ionic liquid is not leached out from the coated silica NPs and the TBAPILS catalyst is heterogeneous in nature.

Recycling studies of TBAPILS catalyst

After completion of reaction, the catalyst was filtered off the reaction mixture, washed, dried and used for the next cycle in the synthesis of A_1. The process was repeated constantly up to seven cycles and observed not a major reduction in yield until fifth cycle. In sixth and seven cycles, the yield decreased significantly (Fig. 7). By these results, we can say that catalyst successfully may be used up to five cycles without significant loss of activity.

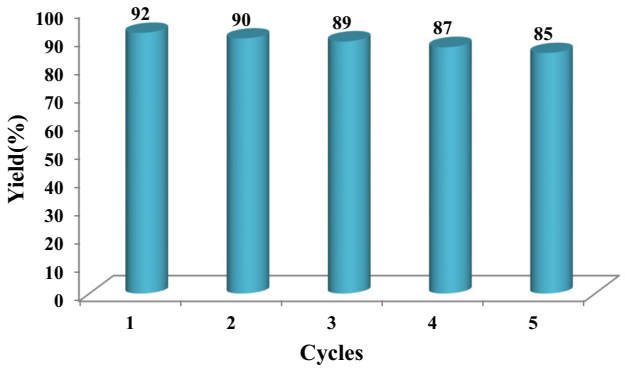


Fig. 7 Optimization of the amount of TBAPILS catalyst for the formation of A_1

Comparison of the efficiency of TBAPILS catalyst with other reported catalysts

To prove the superiority of TBAPILS catalyst (Table 4), we compared our results with some of those catalysts reported in the literature for compound A_1. The results clearly indicate the superiority of the catalyst developed by us. Moreover, solvent less condition makes the reaction economic.

^{1}HNMR, ^{13}CNMR and elemental analysis of tetrahydrobenzoxanthen-11-one derivatives

A_1-9,9-dimethyl-12-phenyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one Anal. Calcd. For $C_{25}H_{22}O_2$: C, 84.74; H,6.21; N, Nil; O,9.03 Found: C, 82.58; H, 5.96; N, Nil; O,10.28% ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.10 (d,1H,–Ar), 7.74–7.80 (m,2H, –Ar), 7.43–7.31 (m, 5H, –Ar),7.21–7.14(m, 2H, –Ar), 7.06 (m, 1H, –Ar), 5.71 (s,1H, –CH), 2.57 (s, 2H, $–CH_2$), 2.26(m, 2H, $–CH_2$), 1.11 (s, 3H, $–CH_3$), 0.96 (m, 3H, $–CH_3$); ^{13}CNMR ($CDCl_3$,100 MHz,δppm): 197.10, 164.06, 147.81, 144.82, 131.57, 128.93, 128.52, 127.10, 126.33, 124.99, 123.76, 117.78, 117.13, 50.94, 41.48, 34.78, 32.36, 29.40, 27.24.

A_2-9,9-dimethyl-12-(3-nitrophenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.10 (m, 1H, –Ar), 7.92–7.94 (dd, 1H, –Ar), 7.84 (d, 1H, –Ar),7.82–7.79(m, 3H, –Ar), 7.45–7.35 (m, 4H, –Ar), 5.81 (s, 1H, –CH), 2.61 (s, 2H, $–CH_2$), 2.26 (m, 2H, $–CH_2$), 1.13 (s, 3H, $–CH_3$), 0.98 (m, 3H, $–CH_3$).

A_3-9,9-dimethyl-12-(4-chlorophenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one 1H NMR ($CDCl_3$, 400 MHz): δppm 7.91 (d,1H, –Ar), 7.80–7.76 (m,2H, –Ar), 7.44–7.38 (m, 2H, –Ar),7.33–7.26 (m, 2H, –Ar), 7.17–7.11 (m, 2H, –Ar), 6.99 (s,1H, –Ar), 5.68 (s,1H, –CH), 2.52 (s, 2H, $–CH_2$), 2.29 (m, 2H, $–CH_2$), 1.10 (s, 3H, $–CH_3$), 0.96 (s, 3H, $–CH_3$).

Table 4 Comparison of the efficiency of TBAPILS catalyst with other reported catalyst in the synthesis of A_1

Entry	Catalyst	Condition	Time (h)	Yield (%)[a]	References
1	$Sr(OTf)_2$	$ClCH_2CH_2Cl$ 80 °C	5	85	[44]
2	Phenylboronic acid	EtOH	4	79	[47]
3	–	PEG 120 °C	6.5	87	[45]
4	Proline triflate	H_2O/Reflux	3	85	[62]
5	PWA	60 °C	1.17	86	[63]
6	TBAPILS	Solvent less	1	92	Our work

[a]Isolated yield

A_4-9,9-dimethyl-12-(N,N-dimethylphenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 7.92 (d,1H, –Ar), 7.80–7.70 (m,2H, –Ar), 7.43–7.30 (m, 5H, –Ar),7.17–6.99 (m, 2H, –Ar), 5.67 (s,1H, –CH), 2.97 (s, 6H, $–CH_3$), 2.57 (s, 2H, $–CH_2$), 2.27 (s, 2H, $–CH_2$), 1.14 (s, 3H, $–CH_3$), 0.97 (s, 3H, $–CH_3$).

A_5-9,9-dimethyl-12-(3-hydroxyphenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.19 (d,1H, –Ar), 7.96–7.90 (m, 2H, –Ar), 7.72–7.78 (m, 1H, –Ar),7.47–7.36 (m, 1H, –Ar), 7.29–7.24 (m, 5H, –Ar), 5.96 (s, 1H, –OH), 5.66 (s, 1H, –CH), 2.59 (s, 2H, $–CH_2$), 2.26 (m, 2H, $–CH_2$), 1.10 (s, 3H, $–CH_3$), 0.96 (s, 3H, $–CH_3$); ^{13}CNMR($CDCl_3$,100 MHz,δppm): 194.26, 161.98, 155.51, 145.67, 144.54, 129.47, 127.27, 126.81, 125.30, 123.22, 121.66, 117.44, 115.84, 115.50, 113.71, 111.85, 48.80, 38.23, 32.52, 30.35, 27.39, 25.04.

A_6-9,9-dimethyl-12-(3,4-dimethoxyphenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.00 (d, 1H, –Ar), 7.79–7.70 (m, 2H, –Ar), 7.43–7.37 (m, 2H, –Ar),7.30 (d, 1H, –Ar), 6.96 (d, 2H, –Ar), 6.76–6.74 (dd, 1H, –Ar), 6.41 (s, 1H, –Ar), 5.66 (s, 1H, –CH), 3.79 (s, 3H,$–OCH_3$), 3.74 (s, 3H, $–OCH_3$), 2.56 (s, 2H, $–CH_2$), 2.29 (m, 2H, $–CH_2$), 1.11 (s, 3H, $–CH_3$), 0.97 (s, 3H, $–CH_3$).

A_8-9,9-dimethyl-12-(4-hydroxy,3-methoxyphenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.00 (d, 1H, –Ar), 7.79–7.74 (m, 2H, –Ar), 7.62 (dd, 1H, –Ar),7.43–7.37 (m, 3H, –Ar), 6.69–6.60 (m, 2H, –Ar), 5.65 (s, 1H, –CH), 5.51 (s, 1H, –OH),3.79 (s, 3H, $–OCH_3$), 2.55 (s, 2H, $–CH_2$), 2.05 (s, 2H, $–CH_2$), 1.11 (s, 3H, $–CH_3$), 0.97 (s, 3H, $–CH_3$).

A_9-9,9-dimethyl-12-(2-hydroxy,3-methoxyphenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 7.83–7.73 (m, 3H, –Ar), 7.41–7.26 (m, 3H, –Ar),6.62–6.55 (m, 2H, –Ar), 6.32–6.30 (m, 1H, –Ar), 5.82 (s, 1H, –CH),5.29 (s, 1H, –OH), 3.85 (s, 3H, $–OCH_3$), 2.62 (s, 2H, $–CH_2$), 2.36 (m, 2H, $–CH_2$), 1.13 (s, 3H, $–CH_3$), 0.99 (s, 3H, $–CH_3$).

A_{10}-9,9-dimethyl-12-(4-fluorophenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 7.93–7.91 (d, 1H, $J=8$ Hz, –Ar), 7.79–7.76 (m, 2H, –Ar),7.44–7.38 (m, 2H, –Ar),7.31–7.26 (m, 2H, –Ar), 6.89–6.82 (m, 2H, –Ar), 5.69 (s, 1H, –CH), 3.85(s, 3H, $–OCH_3$), 2.56 (s, 2H, $–CH_2$), 2.22–2.33(m, 2H, $–CH_2$), 1.12(s, 3H, $–CH_3$), 0.96(s, 3H, $–CH_3$).

A_{11}-12-phenyl-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 7.97–7.95 (d, 1H, $J=7.96$ Hz, –Ar), 7.79–7.75 (m, 2H, –Ar),7.42–7.32 (m, 5H, –Ar),7.19–7.15 (m, 2H, –Ar),7.08–7.06 (m, 1H, –Ar),5.74 (s, 1H, –CH), 2.73–2.71 (m, 2H, $–CH_2$), 2.37–2.44 (s, 2H, $–CH_2$), 2.01–2.04 (m, 2H, $–CH_2$); ^{13}C NMR($CDCl_3$,100 MHz,δppm): 197.26, 165.76, 147.78, 145.08, 131.51, 128.89, 128.42, 127.04, 126.32, 124.93, 123.71, 117.72, 117.01, 115.55, 37.08, 34.67, 27.75, 20.26.

A_{12}-12-(3-nitrophenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.07 (m,1H, –Ar), 7.93–7.91 (m, 1H, –Ar),7.81–7.78 (m, 4H, –Ar),7.40–7.34 (m, 2H, –Ar),5.82 (s, 1H, –CH), 2.75–2.71(m, 2H, $–CH_2$), 2.39–2.43 (s, 2H, $–CH_2$), 2.05–2.06(m, 2H, $–CH_2$).

A_{13}-12-(4-chlorophenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 7.86 (d, 1H, $J=6.4$ Hz, –Ar), 7.80–7.76 (m, 2H, –Ar),7.44–7.38 (m, 2H, –Ar),7.31 (d, 1H, $J=6.4$ Hz, –Ar), 7.26–7.24 (s, 2H, –Ar),7.15–7.11 (m, 2H, –Ar), 5.71(s, 1H, –CH), 2.73–2.67(m, 2H, $–CH_2$), 2.45–2.38 (s, 2H, $–CH_2$), 2.08–1.97 (m, 2H, $–CH_2$); ^{13}CNMR($CDCl_3$,100 MHz,δppm): 197.26, 165.91, 147.72, 143.56, 132.20, 131.51, 131.18, 129.92, 129.15, 128.52, 127.14, 125.05, 123.48, 117.01, 115.07, 109.46, 36.99, 34.19, 31.32, 27.72, 20.25.

A_{14} 10,10-dimethyl-7-phenyl-10,11-dihydro-7*H*-benzo[c]xanthen-8(*9H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.34 (d,1H, –Ar), 8.12 (d, 1H, $J=8.72$ Hz, –Ar),7.88 (d, 2H, –Ar),7.78 (d,2H, –Ar), 7.61–7.43 (m, 3H, –Ar),7.29–7.12 (m, 4H, –Ar), 5.14 (s,1H, –CH), 2.64–2.76 (m, 2H, $–CH_2$), 2.30 (d, 2H, $–CH_2$), 1.54 (m, 3H, $–CH_3$), 1.08(s, 3H, $–CH_3$).

A_{15}- 10,10-dimethyl-7-(3-nitrophenyl)-10,11-dihydro-7*H*-benzo[c]xanthen-8(*9H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.29 (d, 1H, $J=8$ Hz, –Ar), 8.00–7.95 (m, 2H, –Ar),7.78–7.50 (m, 4H, –Ar),7.44–7.36 (m, 3H, –Ar), 5.24 (s, 1H, –CH), 2.67–2.80 (m, 2H, $–CH_2$), 2.04 (s, 2H, $–CH_2$), 1.26 (m, 3H, $–CH_3$), 0.98 (s, 3H, $–CH_3$).

A_{16}- 10,10-dimethyl-7-(4-Chlorophenyl)-10,11-dihydro-7*H*-benzo[c]xanthen-8(*9H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.27 (m,2H, –Ar), 7.80–7.71 (m, 2H, –Ar),7.47–7.39 (m, 3H, –Ar),7.26–7.18 (m,3H, –Ar), 5.48 (s,1H, –CH), 2.75–2.61 (m, 2H, $–CH_2$), 2.04 (s, 2H, $–CH_2$), 1.20 (m, 3H, $–CH_3$), 1.08(s, 3H, $–CH_3$).

A_{17}-10,11-dihydro-7-phenyl-7*H*-benzo[c]xanthen-8(9*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 7.28 (d, 1H, –Ar), 7.27–7.26 (m, 2H, –Ar), 7.25–7.16 (d, 3H, $J=8$ Hz, –Ar), 7.11–7.09 (m, 5H, –Ar), 5.47 (s, 1H, –CH), 2.80 (m, 2H, $–CH_2$), 2.60 (m, 2H, $–CH_2$), 2.02 (m, 2H, $–CH_2$).

A_{18}-10,11-dihydro-7-(3-nitrophenyl-7*H*-benzo[c]xanthen-8(9*H*)-one ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.16 (d, 1H, $J=8.2$ Hz, –Ar), 8.03–7.97 (m, 4H, –Ar), 7.85–7.76 (m, 2H, –Ar), 7.49 (d, 1H, $J=8$ Hz, –Ar), 7.42–7.38 (m, 3H, –Ar), 4.88 (s, 1H, –CH), 2.68 (m, 2H, $–CH_2$), 2.36 (m, 2H, $–CH_2$), 2.06 (m, 2H, $–CH_2$).

A_{19}-10,11-dihydro-7-(4-chlorophenyl-7*H*-benzo[c]xanthen-8(9*H*)-one. ^{1}H NMR ($CDCl_3$, 400 MHz): δppm 8.30 (d, 1H, $J=8.2$ Hz, –Ar), 8.83–7.77 (m, 2H, –Ar), 7.57–7.38 (m, 4H, –Ar), 7.49 (d, 1H, $J=8$ Hz, –Ar), 7.26–7.10 (m, 3H, –Ar), 4.76 (s, 1H, –CH), 2.62 (m, 2H, $–CH_2$), 2.35–2.32 (m, 2H, $–CH_2$), 2.03–2.00 (m, 2H, $–CH_2$).

Conclusion

Tetrabutylammonium prolinate ionic liquid (TBAPIL) was grafted on silica NPs through propyltriethoxysilane linkage to afford supported catalyst TBAP@$Si(CH_2)_3$@nano-silica (TBAPILS). SEM results revealed the successful grafting of TBAPIL on silica NPs by indicating morphological changes. The TEM micrographs confirmed formation of silica NPs of the size of 40–50 nm and well matched with the values obtained for silica NPs from XRD measurements using JCPDS card number. The preparation of the catalyst was also confirmed by FT-IR analysis. The prepared catalyst TBAP-ILS was successfully and efficiently used for the synthesis of tetrahydrobenzoxanthene-11-one derivatives in solvent less condition in short reaction time and with easy workup. The catalyst could be used up to five cycles without significant loss of activity. The key advantages of the process are cost effectiveness, high efficiency and easy workup.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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