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Application of silica-bonded imidazolium-sulfonic acid chloride (SBISAC) as a heterogeneous nanocatalyst for the domino condensation of arylaldehydes with 2-naphthol and dimedone

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ABSTRACT

In this work, a novel nanostructured silica-bonded ionic liquid namely silica-bonded imidazolium-sulfonic acid chloride (SBISAC) has been prepared, and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG), transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX) spectra. Then, SBISAC was utilized as an efficient and heterogeneous nanocatalyst for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]-xanthen-11-ones via the one-pot three-component condensation reaction of arylaldehydes with 2-naphthol and dimedone (5,5-dimethylcyclohexane-1,3-dione) under solvent-free conditions.

1. Introduction

Multi-component reactions (MCRs) play an important role in combinatorial chemistry because of the ability to prepare target compounds with greater efficiency and atomic economy by generating structural complexity from three or more reactants. Moreover, MCRs offer the advantages of simplicity and synthetic efficiency over conventional chemical reactions [1–3].

Xanthenes and benzoxanthenes are of importance as they have various biological activities. For example, these compounds have been frequently used as antibacterial [4], anti-inflammatory [5], and antiviral [6] agents, and as antagonists for inhibiting the action of zoxalamine [7]. Moreover, xanthene derivatives could be applied as dyes [8], and as pH sensitive fluorescent materials for visualization of biomolecular assemblies [9], and in laser technology [10]. The one-pot multi-component condensation reaction between arylaldehydes, 2-naphthol, and dimedone (5,5-dimethylcyclohexane-1,3-dione) has been used as the best procedure for synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]-xanthen-11-one derivatives. Several catalysts have been used to promote this reaction, including ceric ammonium nitrate [11], proline triflate [12], $NaHSO_4 \cdot SiO_2$ [13], strontium triflate [14], $Zr(HSO_4)_4$ [15], dodecatungstophosphoric acid [16], iodine [17], $InCl_3/P_2O_5$ [18], *p*-toluenesulfonic acid/ionic liquid [19], $RuCl_4$ [20], Brønsted acidic ionic liquid [21], [Pyridine–SO_3H]Cl [22], and tityl chloride [23]. Although several methods and catalysts for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]-xanthen-11-ones are known, considering the different application of these compounds, search for finding efficient catalysts and methods for their synthesis is still of significance.

We have recently introduced a new category of Brønsted acidic ionic liquids (ILs), namely sulfonic acid-functionalized imidazolium salts (SAFIS) [24–35], and applied them as catalysts or reagent for synthesis of bis(indolyl)methans [24], *N*-sulfonyl imines [25], nitro aromatic compounds [26,27], 1-amidoalkyl-2-naphthols [28], benzimidazoles [29], xanthenes [30], 1-carbamatoalkyl-2-naphthols [31], 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s [32], *t*-butyl aryl carbamates [33], 1,2,4,5-tetrasubstituted imidazoles [34], and *β*-acetamido ketones [35].

In continuation of our previous projects on the preparation and application of SAFIS in organic synthesis, we have prepared a heterogeneous member of these salts namely silica-bonded imidazolium-sulfonic acid chloride (SBISAC) (Fig. 1). This novel silica-supported ionic liquid was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray

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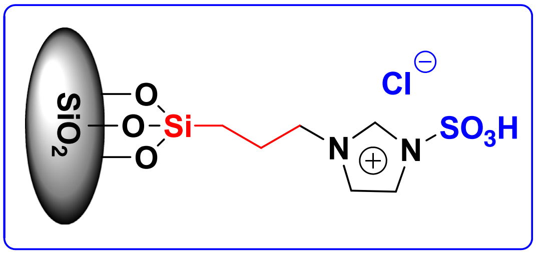


Fig. 1. The structure of silica-bonded imidazolium-sulfonic acid chloride (SBISAC).

diffraction (XRD), thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG), transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX) spectra, and applied as an efficient and heterogeneous nanocatalyst for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]-xanthen-11-ones by the one-pot three-component condensation of aromatic aldehydes with 2-naphthol and dimedone in the absence of solvent (Scheme 1).

2. Experimental

2.1. Materials

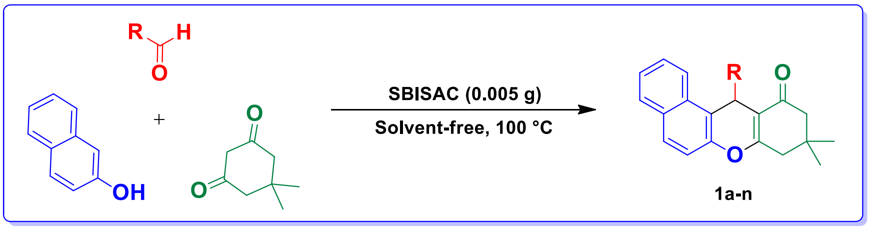
All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The ^{1}H NMR (500 or 300 MHz) and ^{13}C NMR (125 or 75 MHz) were recorded on a Bruker Avance DPX FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Thermal gravimetry (TG) and differential thermal gravimetric (DTG) were analyzed by a Perkin Elmer (Model: Pyris 1). TG/DTG analysis was achieved at range of 25 to 600 °C (temperature increase rate of 10 °C · min^{-1} under nitrogen atmosphere). Optical rotations were measured in spectral grade solvents using a Perkin–Elmer 341 polarimeter.

2.2. General procedure for the preparation of silica-bonded imidazolium-sulfonic acid chloride (SBISAC)

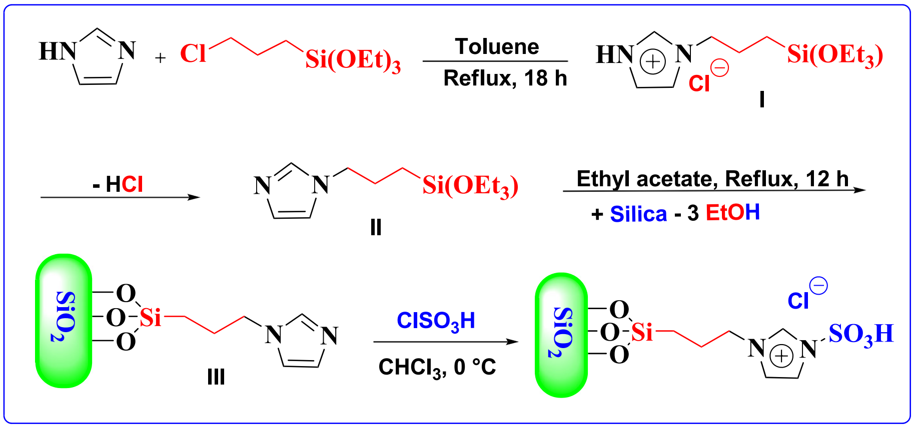
A mixture of imidazole (0.34 g, 5 mmol), (3-chloropropyl) triethoxysilane (1.125 g, 5 mmol) and toluene (15 mL) in a 50 mL round-bottomed flask connected to a reflux condenser, was stirred for 18 h under reflux conditions. In the next step, the obtained white precipitate was separated by filtration, and reacted with silica (0.30 g, 5 mmol) in refluxed ethyl acetate (15 mL) for 12 h to give a solid after removing the ethyl acetate. Then, a solution of chlorosulfuric acid (5 mmol) in chloroform (10 mL) was added dropwise to the resulted solid at 0 °C (ice-water bath), and stirred for 2 h. The chloroform was removed, and the residue was triturated with chloroform (3 × 10 mL), and dried under powerful vacuum at 90 °C to give SBISAC as a white precipitate in 95% yield (Scheme 2).

2.3. General procedure for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones ***1a-n***

A mixture of 2-naphthol (0.144 g, 1 mmol), dimedone (0.140 g, 1 mmol), arylaldehyde (1 mmol) and SBISAC (0.005 g) in a 10 mL round-bottomed flask connected to a reflux condenser, was stirred in an oil-bath at 100 °C. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, and extracted by warm EtOAc (20 mL) to separate the catalyst (the product is soluble in warm EtOAc; however, SBISAC isn't soluble in this solvent). EtOAc was removed, and the crude product was recrystallized from aqueous ethanol (90%) to afford the pure racemic product which



Scheme 1. The reaction of 2-naphthol with aldehydes and dimedone catalyzed by silica-bonded imidazolium-sulfonic acid chloride (SBISAC).



Scheme 2. The synthesis of silica-bonded imidazolium-sulfonic acid chloride (SBISAC).

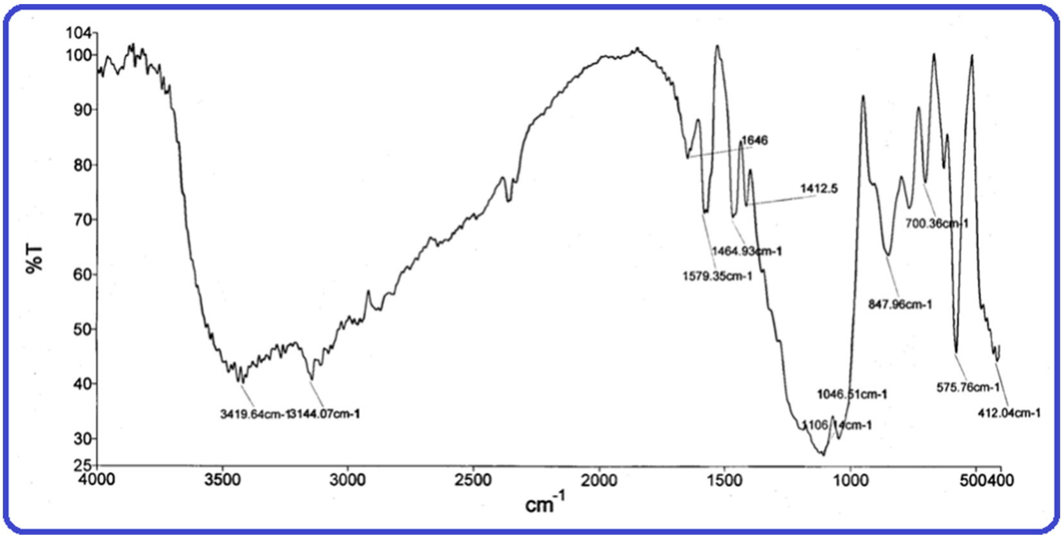


Fig. 2. The IR spectrum of SBISAC.

required no further purification. The recovered catalyst was washed with EtOAc (2 × 20 mL), dried and reused for the next run. The catalyst was reused for four times without any significant changes in the yield and the reaction time.

3. Results and discussion

3.1. The preparation of SBISAC

According to the previous works on the synthesis of silica-bonded imidazolium compounds [36–39], initially, imidazole was reacted with (3-chloropropyl) trimethoxysilane under reflux conditions to afford **I**, which transformed to **II** as s white precipitate by releasing of one molecule of HCl. In the next step, **II** was reacted with silica in refluxed ethyl acetate to give **III**. Finally, by the reaction of **III** with chlorosulfuric, silica-bonded imidazolium-sulfonic acid chloride (SBISAC) was synthesized (Scheme 2).

3.2. Characterization of SBISAC

The structure of the silica-bonded imidazolium-sulfonic acid chloride was characterized by IR, XRD, TG, DTG, EDX, SEM, and TEM analysis.

The IR spectrum of the catalyst showed a broad peak at 2500–3600 cm^{-1} related to O–H stretching of the SO_3H group. Also, the two peaks observed at 1046 cm^{-1} and 1106 cm^{-1} correspond to vibrational modes of $N\text{–}SO_2$ and $O\text{–}SO_2$ bonds (Fig. 2).

X-ray diffraction analysis (XRD) pattern of SBISAC was studied in a domain of 0–90° (Fig. 3). As shown in Fig. 3, the XRD pattern exhibited diffraction lines of a high crystalline nature at about $2\theta \approx 9.6°$, 12.1°, 19.5°, 20.2°, 22.8° and 81.7°.

Thermal gravimetric analysis (TGA) of SBISAC was also investigated. The corresponding diagrams are depicted in Fig. 4. The thermogravimetry (TG) and differential thermal gravimetric (DTG) of the catalyst showed weight losses in one step (after 325 °C).

Energy-dispersive X-ray spectroscopy (EDX) of the catalyst (Fig. 5) showed the presence of the expected elements in its structure, i.e. carbon, oxygen, nitrogen, sulfur, chlorine and silicon.

In another investigation, the scanning electron microscope (SEM) micrographs of the catalyst showed that the particles have not completely agglomerated. Moreover, particles of the catalyst were observed in nanosize (Fig. 6).

The nanostructure of silica-bonded imidazolium-sulfonic acid chloride was confirmed by TEM (Fig. 7). The TEM micrograph clearly proved that the particles were in nanosize.

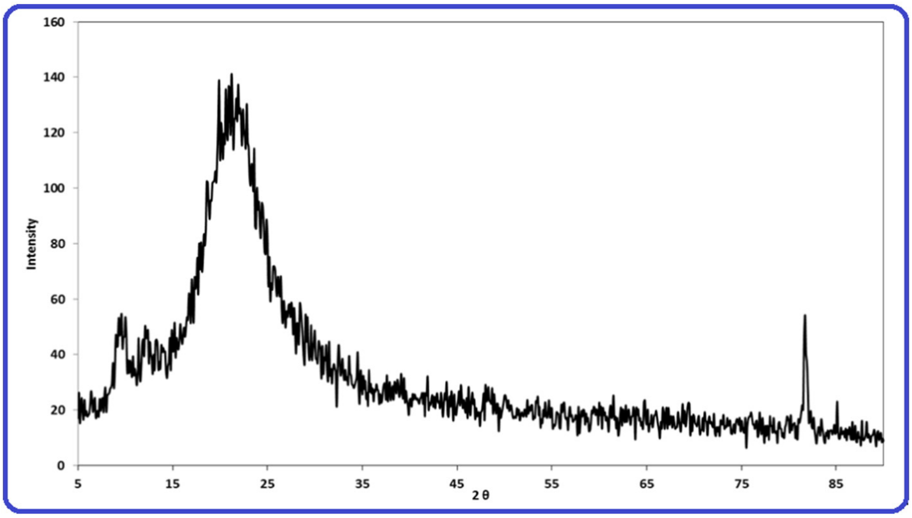


Fig. 3. The XRD diagram of SBISAC.

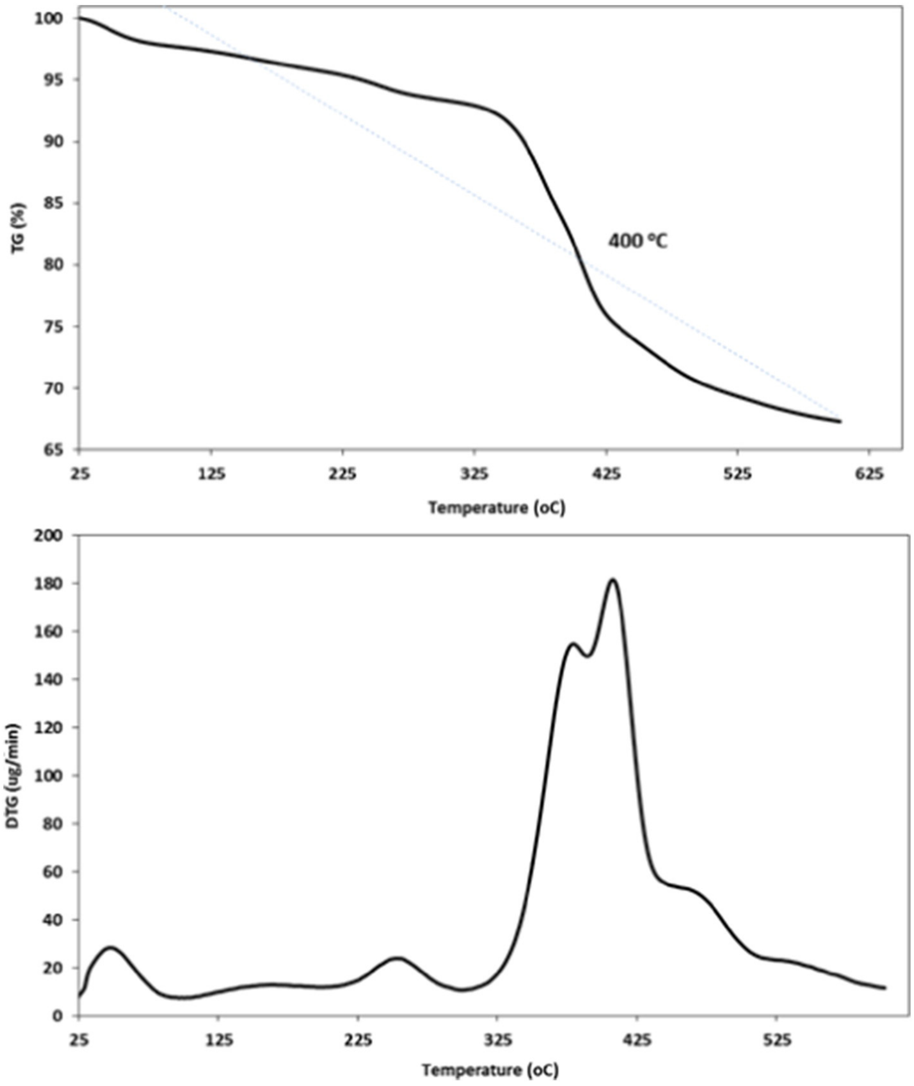


Fig. 4. The TG/DTG diagrams of the catalyst.

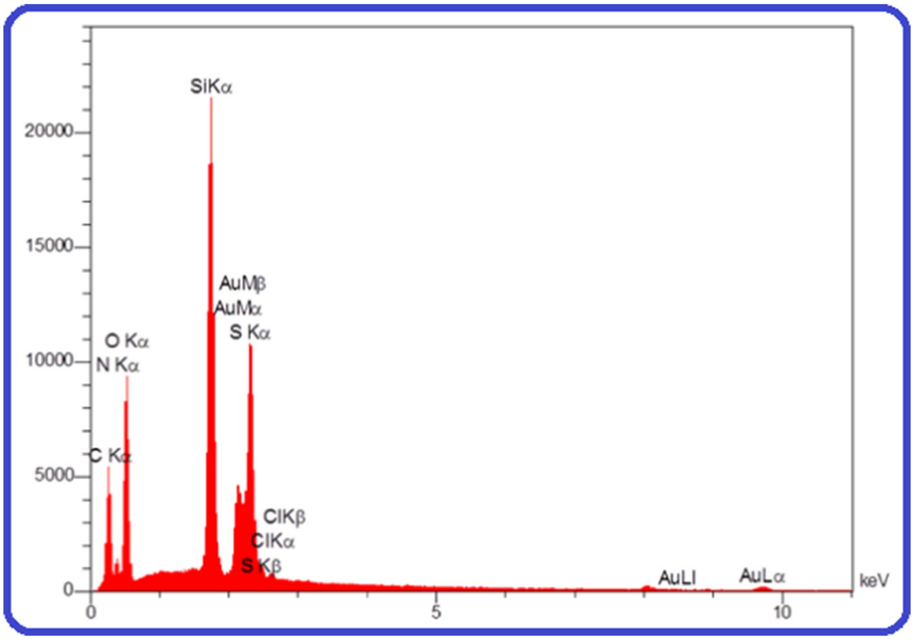


Fig. 5. The energy-dispersive X-ray spectroscopy (EDX) of SBISAC.

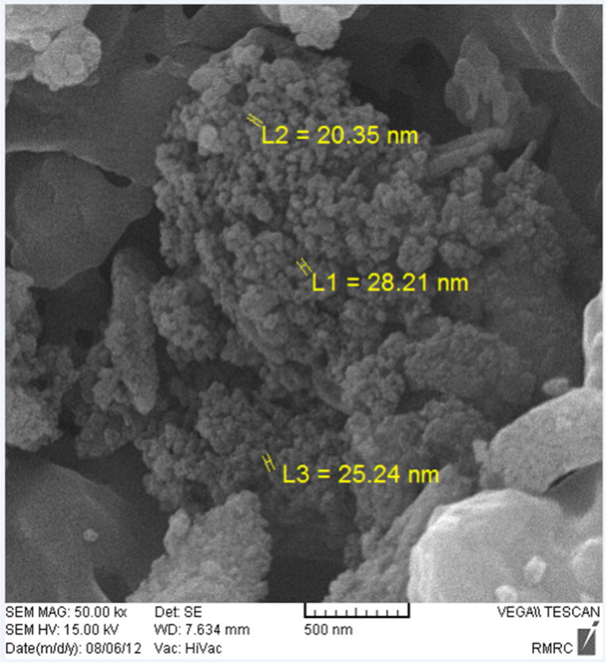


Fig. 6. The SEM micrographs of SBISAC.

3.3. Optimization the reaction condition

After full characterization of SBISAC, its catalytic activity was examined on the reaction of arylaldehydes with β-naphthol and dimedone to provide 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]-xanthen-11-ones (Scheme 1). For this purpose, as a model reaction, the condensation of β-naphthol (1 mmol) with dimedone (1 mmol) and 4-chlorobenzaldehyde (1 mmol) was tested using different amounts of SBISAC at range of 70–110 °C in the absence of solvent (Table 1). As it is shown in Table 1, 5 mg of the catalyst was sufficient to promote the reaction efficiently at 100 °C, and give the product in excellent yield and in short reaction time (Table 1, entry 2).

To compare the efficiency of solution conditions versus the solvent-free procedure, the reaction between β-naphthol (1 mmol), dimedone (1 mmol) and 4-chlorobenzaldehyde (1 mmol) using SBISAC (5 mg) was checked in some solvents (2 mL) under reflux conditions. The results are summarized in Table 2. As this Table indicates, low yields of the product were obtained in solution conditions even after elongated reaction times.

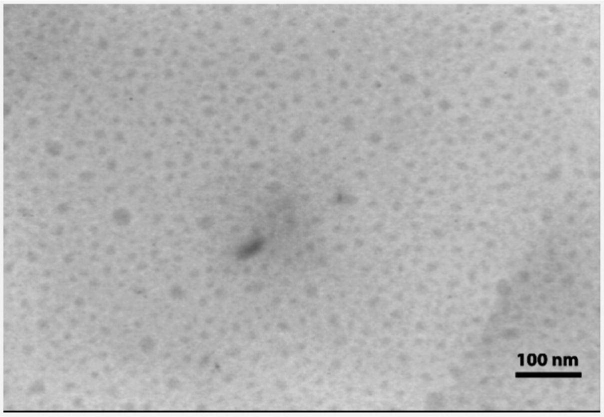


Fig. 7. The transmission electron micrographs (TEM) of SBISAC.

Table 1
Effect of the catalyst amount and temperature on the reaction between β-naphthol (1 mmol) with dimedone (1 mmol) and 4-chlorobenzaldehyde (1 mmol).

Entry	Catalyst	Catalyst amount (g)	Temp.(°C)	Time (min)	Yield[a] (%)
1	SBISAC	0.002	100	28	81
2	SBISAC	0.005	100	12	94
3	SBISAC	0.01	100	12	94
4	SBISAC	0.005	110	12	94
5	SBISAC	0.005	70	65	–

[a] Isolated yield.

Table 2
Effect of various solvents on the reaction of β-naphthol (1 mmol) with dimedone (1 mmol) and 4-chlorobenzaldehyde (1 mmol), in the presence of SBISAC (5 mg).

Entry[a]	Solvent	Time (min)	Yield[b] (%)
1	$CHCl_3$	30	40
2	EtOAc	30	33
3	EtOH	30	40
4	CH_2Cl_2	30	30
5	H_2O	30	45

[a] All reactions were carried out under reflux condition.
[b] Isolated yield.

3.4. Using the optimal conditions for the reaction

To assess the efficiency and the scope of SBISAC in the preparation of tetrahydrobenzo[*a*]xanthene-11-ones, various aromatic aldehydes (including aldehydes possessing electron-releasing substituents, electron-withdrawing substituents and halogens on their aromatic ring) were reacted with β-naphthol and dimedone in the optimal reaction conditions to produce the desired products in high yields and in short reaction times. The results are displayed in Table 3.

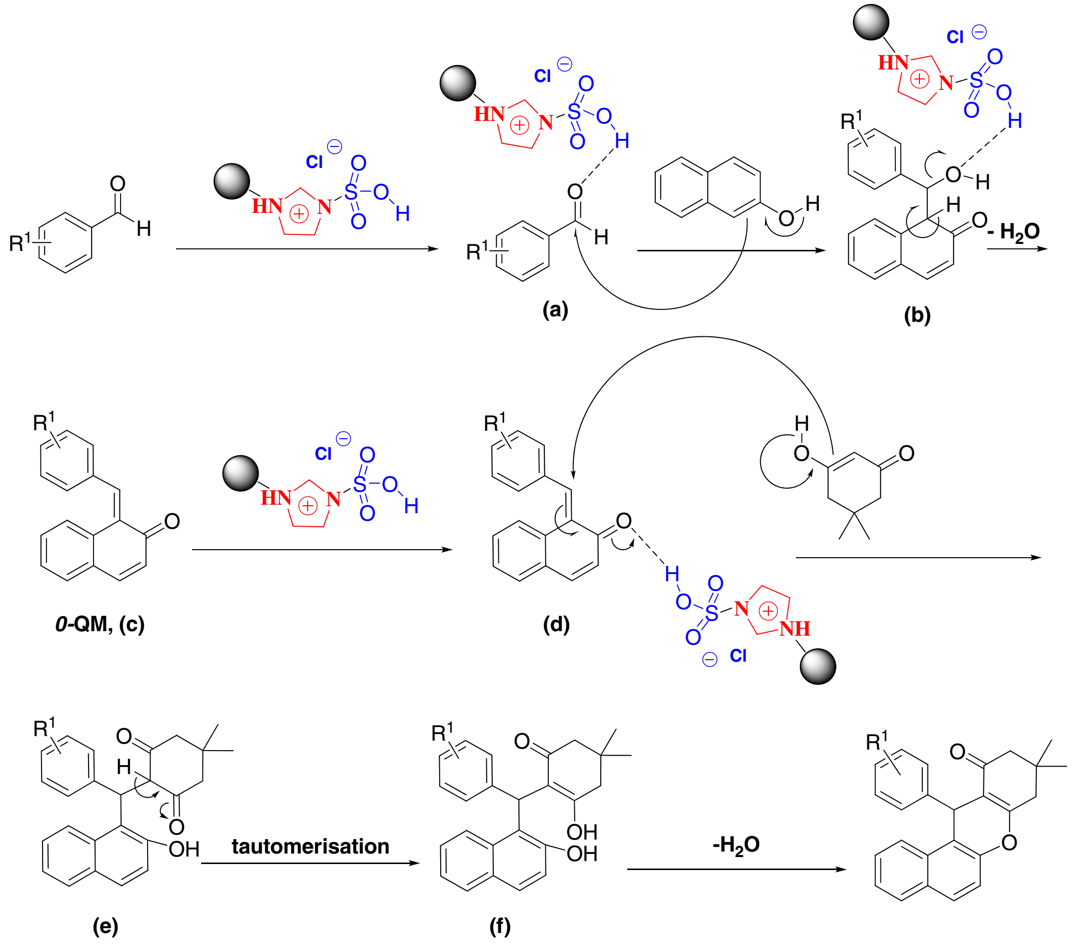
In a proposed mechanism which is supported by the literature [30] (Scheme 3), at first, aromatic aldehyde is activated by acidic group of SBISAC to produce **a**. Then, β-naphthol attacks to the activated carbonyl group of aldehyde to afford intermediate **b**. Then, by removing one molecule of H_2O from **b**, orthoquinone methide [(*o*-QM, **c**)] is prepared. SBISAC again activates intermediate **c** to give **d** as a Michael acceptor. Afterward, Michael addition of dimedone to intermediate **d** affords **e**. Intermediate **e** converts to **f** after tautomerisation. At last, tetrahydrobenzo[*a*]xanthene-11-one produces by removing one molecule of H_2O from **f**.

In another investigation, recyclability of SBISAC was investigated. For this purpose, the reaction of β-naphthol (1 mmol) with dimedone

Table 3
The solvent-free synthesis of tetrahydrobenzo[*a*]xanthene-11-ones using silica-bonded imidazolium-sulfonic acid chloride (SBISAC).

Entry	R	Time (min)/yield[a] (%)	M.p. °C (Lit.)
1a	C_6H_5	10/93	140–152 (151–153) [18]
1b	$3\text{-}ClC_6H_4$	10/94	174–176 (175–178) [23]
1c	$4\text{-}ClC_6H_4$	7/94	177–179 (180–182) [18]
1d	$2,3\text{-}Cl_2C_6H_3$	10/95	221–224 (223–225) [23]
1e	$2,4\text{-}Cl_2C_6H_3$	11/96	180–183 (181–182) [16]
1f	$2\text{-}BrC_6H_4$	17/85	169–171 (–) [19]
1g	$3\text{-}BrC_6H_4$	12/90	160–162 (–) [19]
1h	$4\text{-}BrC_6H_4$	11/91	186–187 (186–187) [17]
1i	$3\text{-}NO_2C_6H_4$	8/93	166–169 (168–170) [18]
1j	$4\text{-}NO_2C_6H_4$	10/93	176–179 (178–180) [18]
1k	$3\text{-}OHC_6H_4$	15/91	238–239 (240–241) [18]
1l	$2\text{-}MeC_6H_4$	25/85	166–168 (161–164) [23]
1m	$3\text{-}MeC_6H_4$	27/83	181–183 (178–180) [23]
1n	$4\text{-}OMeC_6H_4$	25/84	202–204 (204–205) [18]

[a] Isolated yield.



Scheme 3. The plausible mechanism for the condensation reaction of β-naphthol with aldehydes and dimedone catalyzed by the SBISAC.

(1 mmol) and 4-chlorobenzaldehyde (1 mmol), was performed in the presence of SBISAC (5 mg) at 100 °C. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, extracted with warm EtOAc to separate the catalyst (the product is soluble in warm EtOAc; however, SBISAC isn't soluble in this solvent). EtOAc was removed, and the recovered catalyst was washed with EtOAc, dried and reused for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones according to the mentioned procedure. The catalyst was reused for four times without any significant changes in the yields and the reaction times (Fig. 8).

To compare the efficiency of our catalyst with the reported catalysts for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones, we have tabulated the results of these catalysts to perform the reaction of β-naphthol with dimedone and 4-chlorobenzaldehyde, in Table 4. As Table 4 indicates, SBISAC has remarkably improved the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones; the reaction times were shorter, and the yields were higher when our catalyst was utilized.

To recognize the scalability of our method, we examined some reactions in larger scale (15 mmol of each reactants). The respective results are summarized in Table 5. As shown in Table 5, the reactions were

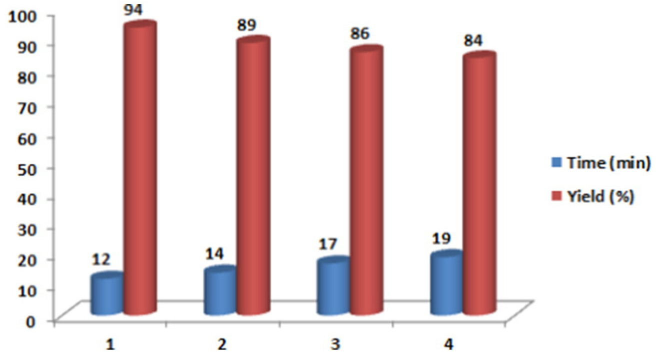


Fig. 8. The condensation of β-naphthol (1 mmol) with dimedone (1 mmol) and 4-chlorobenzaldehyde (1 mmol) in the presence of the recycled SBISAC.

Table 4
Comparison of the results of the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones catalyzed by our new catalyst with those obtained by the recently reported catalysts.[a].

Reaction condition	Catalyst loading	Time (min)	Yield[b] (%)	Ref.
TrCl, solvent-free, 110 °C	7 mol%	45	90	[23]
[Dsim]Cl, solvent-free, 110 °C	10 mol%	10	88	[30]
Py$(HSO_4)_2$, solvent-free, 110 °C	10 mol%	30	87	[40]
[Et_3N–SO_3H]Cl, solvent-free, 120 °C	25 mol%	40	89	[41]
CA–SiO_2, solvent-free, 60 °C	0.1 g	30	90	[42]
pTSA, [bmim]BF_4, 80 °C	10 mol%	120	85	[19]
pTSA, solvent-free, 120 °C	2 mol%	35	86	[19]
PWA, solvent-free, 60 °C	5 mol%	60	92	[16]
$InCl_3$, solvent-free, 120 °C	30 mol%	30	80	[18]
P_2O_5, solvent-free, 120 °C	20 mol%	40	76	[18]
SBISAC, solvent-free, 100 °C	0.005 g	7	94	–[c]

[a] The reactions were carried out by the condensation of β-naphthol with dimedone and 4-chlorobenzaldehyde.
[b] Isolated yield.
[c] Our work.

Table 5
The scalability of the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]-xanthen-11-ones by the reaction of 2-naphthol (15 mmol) with arylaldehydes (15 mmol) and dimedone (15 mmol) using SBISAC (0.075 g) at 100 °C.

Entry	R	Time (min)/yield[a] (%)
1a	C_6H_5	25/89
1c	$4\text{-}ClC_6H_4$	7/92
1i	$3\text{-}NO_2C_6H_4$	15/90
1m	$3\text{-}MeC_6H_4$	35/82

[a] Isolated yield.

successfully performed at the larger scale without significant loss of the yields.

The mentioned xanthene derivatives which produce in achiral media were racemic. To confirm this subject, optical activity of the compounds were measured by polarimeter. This study clearly confirmed the racemization of the xanthene derivatives in our protocol.

4. Conclusions

In conclusion, we have synthesized a novel nanostructured silica-supported ionic liquid namely silica-bonded imidazolium-sulfonic acid chloride (SBISAC), and successfully used as catalyst for the one-pot three-component condensation of arylaldehydes with 2-naphthol and dimedone. The novel catalyst was fully characterized by several techniques including Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG), transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX).

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References

[1] J. Zhu, H. Bienayme (Eds.), Multicomponent Reactions, Wiley, Weinheim, 2005.
[2] E. Ruijter, R. Scheffelaar, R.V.A. Orru, Multicomponent reaction design in the quest for molecular complexity and diversity, Angew. Chem. Int. Ed. 50 (2011) 6234–6246.
[3] (a) A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, F. Abi, A. Zare, H. Kaveh, V. Khakyzadeh, M. Kazem-Rostami, A. Parhami, H. Torabi-Monfared, Discovery of an in situ carbocationic system using trityl chloride as a homogeneous organocatalyst for the solvent-free condensation of β-naphthol with aldehydes and amides/thioamides/alkyl carbamates in neutral media, Tetrahedron 69 (2013) 212–218;
(b) A.R. Moosavi-Zare, M.A. Zolfigol, S. Farahmand, A. Zare, A.R. Pourali, R. Ayazi-Nasrabadi, Synthesis of 2,4,6-triarylpyridines using $ZrOCl_2$ under solvent-free conditions, Synlett 25 (2014) 193–196.
[4] Hideo, T.; Teruomi, J., (Sankyo Co.) Jpn. Patent 56005480, 1981.
[5] J.P. Poupelin, G. Saint-Ruf, O. Foussard-Blanpin, G. Marcisse, G. Uchida-Ernouf, R. Lacroix, Synthese et proprietes anti inflammatoires de derives du bis (hydroxy 2 naphtyl 1) methane. I. Derives monosubstitues|[synthesis and antiinflammatory properties of bis (2 hydroxy 1 naphthyl) methane derivatives], Eur. J. Med. Chem. 13 (1978) 67–71.
[6] R.W. Lambert, J.A. Martin, J.H. Merrett, K.E.B. Parkes, G.J. Thomas, PCT Int. Appl. (1997) WO9706178.
[7] G.B.D. Rao, M.P. Kaushik, A.K. Halve, An efficient synthesis of naphtha[1,2-e]oxazinone and 14-substituted-14H-dibenzo[a, j]xanthene derivatives promoted by zinc oxide nanoparticle under thermal and solvent-free conditions, Tetrahedron Lett. 53 (2012) 2741–2744.
[8] F. Shirini, N.G. Khaligh, Succinimide-N-sulfonic acid: an efficient catalyst for the synthesis of xanthene derivatives under solvent-free conditions, Dyes Pigments 95 (2012) 789–794.
[9] C.G. Knight, T. Stephens, Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. Studies in phospholipid vesicles, Biochem. J. 258 (1989) 683–687.
[10] P.V. Shinde, A.H. Kategaonkar, B.B. Shingate, M.S. Shingare, Surfactant catalyzed convenient and greener synthesis of tetrahydrobenzo[a]xanthene-11-ones at ambient temperature, Beilstein J. Org. Chem. 7 (2011) 53–58.
[11] A. Kumar, S. Sharma, R.A. Maurya, J. Sarkar, Diversity oriented synthesis of benzoxanthene and benzochromene libraries via one-pot, three-component reactions and their anti-proliferative activity, J. Comb. Chem. 12 (2010) 20–24.
[12] J. Li, L. Lu, W. Su, A new strategy for the synthesis of benzoxanthenes catalyzed by proline triflate in water, Tetrahedron Lett. 51 (2010) 2434–2437.
[13] B. Das, K. Laxminarayana, M. Krishnaiah, Y. Srinivas, An efficient and convenient protocol for the synthesis of novel 12-aryl- or 12-alkyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivatives, Synlett (2007) 3107–3112.
[14] J. Li, W. Tang, L. Lu, W. Su, Strontium triflate catalyzed one-pot condensation of β-naphthol, aldehydes and cyclic 1,3-dicarbonyl compounds, Tetrahedron Lett. 49 (2008) 7117–7120.
[15] N. Foroughifar, A. Mobinikhaledi, H. Moghanian, A catalytic and green procedure for synthesis of 12-Aryl- or 12-alkyl-8,9,10,12-tetrahydrobenzo[α]xanthen-11-one derivatives under solvent-free conditions, Int. J. Green Nanotechnol. Phys. Chem. 1 (2009) 57–63.
[16] H.-J. Wang, X.-Q. Ren, Y.-Y. Zhang, Z.-H. Zhang, Synthesis 12-aryl or 12-alkyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivatives catalyzed by dodecatungstophosphoric acid, J. Braz. Chem. Soc. 20 (2009) 1939–1943.
[17] R.-Z. Wang, L.-F. Zhang, Z.-S. Cui, Iodine-catalyzed synthesis of 12-aryl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one derivatives via multicomponent reaction, Synth. Commun. 39 (2009) 2101–2107.
[18] G.C. Nandi, S. Samai, R. Kumar, M.S. Singh, An efficient one-pot synthesis of tetrahydrobenzo[a]xanthene-11-one and diazabenzo[a]anthracene-9,11-dione derivatives under solvent free condition, Tetrahedron 65 (2009) 7129–7134.
[19] J.M. Khurana, D. Magoo, pTSA-catalyzed one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a] xanthen-11-ones in ionic liquid and neat conditions, Tetrahedron Lett. 50 (2009) 4777–4780.
[20] K. Tabatabaeian, A. Khorshidi, M. Mamaghani, A. Dadashi, M.K. Jalali, One-pot synthesis of tetrahydrobenzo[a]xanthen-11-one derivatives catalyzed by ruthenium chloride hydrate as a homogeneous catalyst, Can. J. Chem. 89 (2011) 623–627.
[21] M. Zakeri, M.M. Heravi, M. Saeedi, N. Karimi, H.A. Oskooie, N. Tavakoli-Hoseini, One-pot green procedure for synthesis of tetrahydrobenzo[a]xanthene-11-one catalyzed by Brønsted ionic liquids under solvent-free conditions, Chin. J. Chem. 29 (2011) 1441–1445.
[22] A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, Preparation, characterization and application of ionic liquid sulfonic acid functionalized pyridinium chloride as an efficient catalyst for the solvent free synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones, J. Mol. Liq. 186 (2013) 63–69.
[23] A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, A. Zare, M. Khojasteh, Z. Asgari, V. Khakyzadeh, A. Khalafi-Nezhad, Organocatalyst trityl chloride efficiently promoted the solvent-free synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones by in situ formation of carbocationic system in neutral media, Catal. Commun. 20 (2012) 54–57.
[24] M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, Ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride as a novel and highly efficient catalyst for the very rapid synthesis of bis(indolyl)methanes under solvent-free conditions, Org. Prep. Proced. Int. 42 (2010) 95–102.
[25] M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, 3-methyl-1-sulfonic acid imidazolium chloride as a new, efficient and recyclable catalyst and solvent for the preparation of n-sulfonyl imines at room temperature, J. Iran. Chem. Soc. 7 (2010) 646–651.
[26] A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, A. Zare, An efficient method for the nitration of phenols with $NaNO_2$ in the presence of 3-methyl-1-sulfonic acid imidazolium chloride, Sci. Iran. Trans. C Chem. Chem. Eng. 17 (2010) 31–36.
[27] M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, H.G. Kruger, Z. Asgari, V. Khakyzadeh, M. Kazem-Rostami, Design of ionic liquid 3-methyl-1-sulfonic acid imidazolium nitrate as reagent for the nitration of aromatic compounds by in situ generation of NO_2 in acidic media, J. Org. Chem. 77 (2012) 3640–3645.
[28] M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, V. Khakyzadeh, Rapid synthesis of 1-amidoalkyl-2-naphthols over sulfonic acid functionalized imidazolium salts, Appl. Catal. A Gen. 400 (2011) 70–81.
[29] A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, A. Zare, E. Ghaemi, V. Khakyzadeh, Z. Asgari, A. Hasaninejad, Sulfonic acid functionalized imidazolium salts/$FeCl_3$ as novel and highly efficient catalytic systems for the synthesis of benzimidazoles at room temperature, Sci. Iran. Trans. C Chem. Chem. Eng. 18 (2011) 1365–1371.
[30] M.A. Zolfigol, V. Khakyzadeh, A.R. Moosavi-Zare, A. Zare, S.B. Azimi, Z. Asgari, A. Hasaninejad, Preparation of various xanthene derivatives over sulfonic acid functionalized imidazolium salts (SAFIS) as novel, highly efficient and reusable catalysts, C. R. Chim. 15 (2012) 719–736.
[31] A. Zare, T. Yousofi, A.R. Moosavi-Zare, Ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate: a novel and highly efficient catalyst for the preparation of 1-carbamatoalkyl-2-naphthols and 1-amidoalkyl-2-naphthols, RSC Adv. 2 (2012) 7988–7991.
[32] A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, Z. Asgari, M. Shekouhy, A. Zare, A. Hasaninejad, Preparation of 4,49-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s over 1,3-disulfonic acid imidazolium tetrachloroaluminate as a novel catalyst, RSC Adv. 2 (2012) 8010–8013.
[33] M.A. Zolfigol, V. Khakyzadeh, A.R. Moosavi-Zare, G. Chehardoli, F. Derakhshan-Panah, A. Zare, O. Khaledian, Novel ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate {[Dsim]HSO_4} efficiently catalyzed N-boc protection of amines, Sci. Iran. Trans. C Chem. Chem. Eng. 19 (2012) 1584–1590.
[34] M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, Z. Asgari, V. Khakyzadeh, A. Hasaninejad, Design of ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate as a dual-catalyst for the one-pot multi-component synthesis of 1,2,4,5-tetrasubstituted imidazoles, J. Ind. Eng. Chem. 19 (2013) 721–726.

[35] A. Zare, T. Hekmat-Zadeh, S. Mirzaei-Monfared, M. Merajoddin, H. Torabi-Monfared, M.A. Zolfigol, A.R. Moosavi-Zare, E. Rostami, M. Mokhlesi, F. Derakhshan-Panah, S. Porbahi, S. Balandeh, Ionic liquid 3-methyl-1-sulphonic acid imidazolium chloride {[Msim]Cl}: a highly efficient, mild and green catalyst for the synthesis of β-acetamido ketones, S. Afr. J. Chem. 65 (2012) 63–68.

[36] M. Nouri-sefat, D. Saberi, K. Niknam, Preparation of silica-based ionic liquid an efficient and recyclable catalyst for one-pot synthesis of α-aminonitriles, Catal. Lett. 141 (2011) 1713–1720.

[37] M. Baghernejad, K. Niknam, Synthesis of 4,4′-(arylmethylene)bis(1H-pyrazol-5-ols) using silica-bonded ionic liquid as recyclable catalyst, Int. J. Chem. 4 (2012) 52–60.

[38] K. Niknam, A. Piran, Silica-grafted ionic liquids as recyclable catalysts for the synthesis of 3,4-dihydropyrano[c]chromenes and pyra-no[2,3-c]pyrazoles, Green Sustain. Chem. 3 (2013) 1–8.

[39] A. Chrobok, S. Baj, W. Pudlo, A. Jarzebski, Supported hydrogensulfate ionic liquid catalysis in Baeyer–Villiger reaction, Appl. Catal. A Gen. 366 (2009) 22–28.

[40] A. Zare, R. Khanivar, M. Hatami, M. Mokhlesi, M.A. Zolfigol, A.R. Moosavi-Zare, A. Hasaninejad, A. Khazaei, V. Khakyzadeh, Efficient synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones using ionic liquid pyrazinium di(hydrogen sulfate) {Py$(HSO_4)_2$} as a novel, green and homogeneous catalyst, J. Mex. Chem. Soc. 56 (2012) 389–394.

[41] A. Zare, R. Khanivar, M. Merajoddin, M. Kazem Rostami, M.M. Ahmad Zadeh, A.R. Moosavi-Zare, A. Hasaninejad, Triethylamine bonded sulfonic acid {[Et_3N–SO_3H]Cl} as an efficient and homogeneous catalyst for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones, Iran. J. Catal. 2 (2012) 107–114.

[42] N. Karimi, H.A. Oskooie, M.M. Heravi, L. Tahershamsi, Caro's acid–silica gel-catalyzed one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a] xanthen-11-ones, Synth. Commun. 41 (2011) 307–312.