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ORIGINAL ARTICLE

Sulfamic acid functionalized 3D-network nanoporous polymer based on calix[4]resorcinarene: a recyclable heterogeneous nanocatalyst for the efficient synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes under thermal neat conditions

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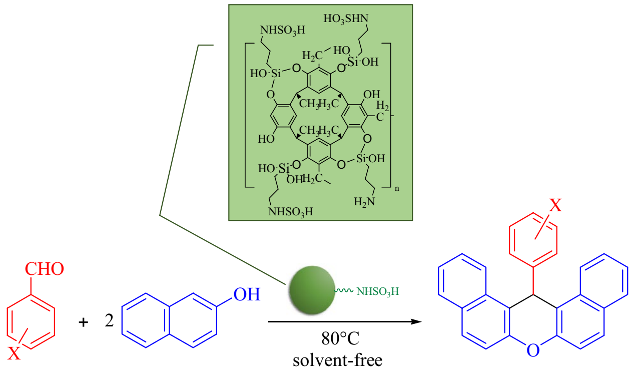
Abstract

The new synthesized sulfamic acid functionalized catalyst on the basis of calix[4]resorcinarene catalyzed successfully and efficiently the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives through a one-pot condensation reaction of β-naphthol with various aryl aldehydes under thermal solvent-free conditions. As the major advantages of the present method, solvent-free and mild acidic conditions, catalyst recyclability, easy purification of the products, high yields along with relatively less reaction times can be mentioned. IR spectroscopy, field emission scanning electron microscopy and transmission electron microscopy are some of the spectroscopic methods used to characterize the new synthesized solid support.

Graphical Abstract



Keywords Porous organic polymers · *N*-propyl sulfamic acid functionalized nanocatalyst · Heterogeneous catalysis · Multi-component reactions · 14-aryl-14H-dibenzo[a,j]xanthene

Introduction

In recent times developing the reaction conditions in synthesizing xanthenes and specifically benzoxanthenes has greatly attracted the attention of medicinal and organic chemists as these products could be employed extensively in pharmaceutical and material-based applications such as photodynamic therapies, dye and laser technologies and also in pH-sensitive fluorescent materials [1–6]. These compounds

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are also known for having antiviral, antibacterial and anti-inflammatory properties [7–11].

So far various procedures have been reported for the synthesis of these titled materials among which the condensation of β-naphthol with aryl aldehydes to produce 14-aryl-14H-dibenzo[a,j]xanthenes as one of the related products and simplest strategies has been focused widely during recent decades to optimize the reaction conditions [12–17]. One-pot multi-component reactions have been recently known as powerful alternatives to a large number of traditional strategies in organic chemistry due to their unique properties including simplicity resulted from products generation in a single step without need for intermediates isolation, environmentally friendly processes by elimination or reduction of the solvent amount and waste materials, diversity of products by varying the reacting components and so on [18–20].

The mentioned method in synthesizing 14-aryl-14H-dibenzo[a,j]xanthene derivatives can be promoted efficiently through applying acidic conditions [21–25]. Different homogeneous acidic catalysts such as H_2SO_4, HCl, $AlCl_3$, H_3PO_4 and so many others are commonly used in various organic reactions. However, most of the aforementioned acidic catalysts suffer from some disadvantages like being toxic, corrosive or volatile. Avoiding these problems homogeneous catalysts can be heterogenized by anchoring them onto the surface of solid supports including silica, alumina, zeolite, polymers etc. to develop eco-friendly solid acids which could be recovered and reused for the next catalytic cycles [26–28].

Over the past decades, among various heterogeneous matrices, porous organic polymers (POPs), have garnered considerable attention from the aspects of post-functionalization and chemical catalysis on account of having large surface area, well-defined pore size distribution, generally easy synthesis and functionalization, facile separation, high thermal and mechanical stability as well as low toxicity and price [29–32]. Mounting interest has been recently expressed for the surface functionalization of these solid supports to promote simplicity along with economic and environmental features of chemical reactions [33–35]. Surface functionalized porous organic polymers (POPs), as a novel category of functional materials have been widely utilized in nanotechnology and chemical catalysis during recent decades [36–38]. In this vein, integration of acidic functional groups like sulfamic acid (NH_2SO_3H, SA) moieties into the mentioned polymeric supports has been greatly explored to produce promising mild solid acids as efficient substituents for conventional acidic catalysts for being applied in various organic transformations [39–42].

Calix[4] resorcinarene as an expedient synthetic macrocycle has been concentrated interestingly over recent years due to its ability for being linked selectively with various substrates as well as being capable of undergoing polycondensation with formaldehyde to afford promising cross-linked porous organic polymers [43]. The achieved 3D-network polymer on the basis of calix[4] resorcinarene with its unique properties could be introduced as an ideal candidate to develop novel functionalized solid supports.

With this background in mind, in the way of creating new and applicable catalytic supports [44–49], herein it is tried to explore the addition of SO_3H acidic groups to the previously reported amine functionalized polymer based on calix[4] resorcinarene [45]. To the best of our knowledge this is the first report of sulfamic acid functionalized polymeric network on the basis of calix[4] resorcinarene as a solid acid catalyst that was utilized to promote an efficient, eco-friendly and convenient method for the preparation of 14-aryl-14H-dibenzo[a,j]xanthenes by the condensation reaction of aromatic aldehydes with β-naphthol.

Experimental

Materials and methods

All the chemicals were purchased from Merck, Fluka and Aldrich companies and used as received. The progress of the reactions were monitored by TLC and the reported yields referred to isolated products after recrystallization. The obtained products were characterized by comparison of their physical and spectral data with those of authentic samples. Melting points were measured using Thermo Scientific 9200 melting point apparatus. The synthesized nanostructure morphology was investigated by a Zeiss—EM10C transmission electron microscope (TEM) on an accelerating voltage of 80 kV. Scanning electron microscopy (SEM) was performed using a MIRA3 TESCAN model of field emission scanning electron microscope (FE-SEM). FT-IR measurements were recorded using KBr pellets on a Bomen MB:102 infrared spectrophotometer. Elemental analysis for C, H, N and S were performed using a Thermo Finnigan Flash EA 1112 CHNS-Analyzer. Thermal stability of the synthesized catalyst was investigated using a NETZSCH STA 409 PC/PG apparatus under a nitrogen atmosphere with the scanning rate of heating about 1 L h^{-1}.

Synthesis of calix[4] resorcinarene 1

Calix[4] resorcinarene was synthesized according to the previously reported procedure [50].

Synthesis of the 3D-network polymer based on calix[4] resorcinarene 2

In a round-bottomed flask 42 mmol of formaldehyde was added to 14 mmol of the prepared calix[4] resorcinarene and the mixture was dissolved in 40 cm^3 NaOH solution (10%) at room temperature. In the following, the mixture was heated to 90 °C and remained at this temperature for 20 h. After the mentioned time completion the resultant gel was washed thoroughly with cold water to remove the excess alkali. Then the gel was kept at 100 °C for 1 h and finally it became acidic via treatment with 0.1 M HCl solution. The solid product was dried at 100 °C for 10 h [43].

Synthesis of amine-functionalized polymer 3

1.0 g of polymer 2 and 0.4 g 3-(triethoxysilyl)propylamine (18 mmol) were stirred vigorously under reflux condition in 10 cm^3 1:1 solution of H_2O/EtOH for 20 h. In the next step, the solid product was separated through filtration and washed consecutively with hot toluene. The amine-functionalized polymer 3 as the intended product was collected after being dried at 100 °C for 10 h [45].

Synthesis of the new *N*-propyl sulfamic acid functionalized catalyst 4

In an ice bath 5 cm^3 chlorosulfonic acid (75.2 mmol) was added drop by drop to 5 g of the previously obtained NH_2-functionalized polymer 3 in $CHCl_3$ (20 cm^3) over 2 h. After the addition was completed, the mixture was stirred for another 3 more hours to remove all HCl from the reaction medium. At the end, the solid product was filtered off, washed with ethanol (30 cm^3) and dried at room temperature overnight.

Determination of the amount of sulfamic acid functionalities grafted onto the polymer 2

The amount of sulfamic acid functionalities grafted onto the prepared polymeric network 2 was determined using elemental analysis which revealed 1.55 mmol S per gram of dry polymer.

In addition, the acidic capacity of the polymeric solid acid was determined via pH analysis. For this purpose, 50 mg of the synthesized catalyst was added to an aqueous solution of NaCl (1 M, 25 cm^3) with primary pH equal to 6.01. The mixture was stirred at room temperature for 2 h. At the end of this time, as the consequence of an ion exchange between sufamic acid protons and sodium ions, pH value reached 2.49 which is equal to a loading of 1.62 mmol H^+ per gram of the solid catalyst that is relatively in good compatibility with the achieved quantity through elemental analysis [51].

General procedure for the one-pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes

A mixture of β-naphthol (0.29 g, 2 mmol), aromatic aldehydes (1 mmol), and 0.09 mmol catalyst (0.06 g) was added to a round-bottomed flask. The reaction mixture was placed in an oil bath at 80 °C and stirred for the appropriate time (TLC). Upon the reaction completion, hot ethanol was added to the mixture, it was stirred for 3 min and then the catalyst was recovered through filtration. The solid residue was recrystallized from hot ethanol to give pure products in high yields.

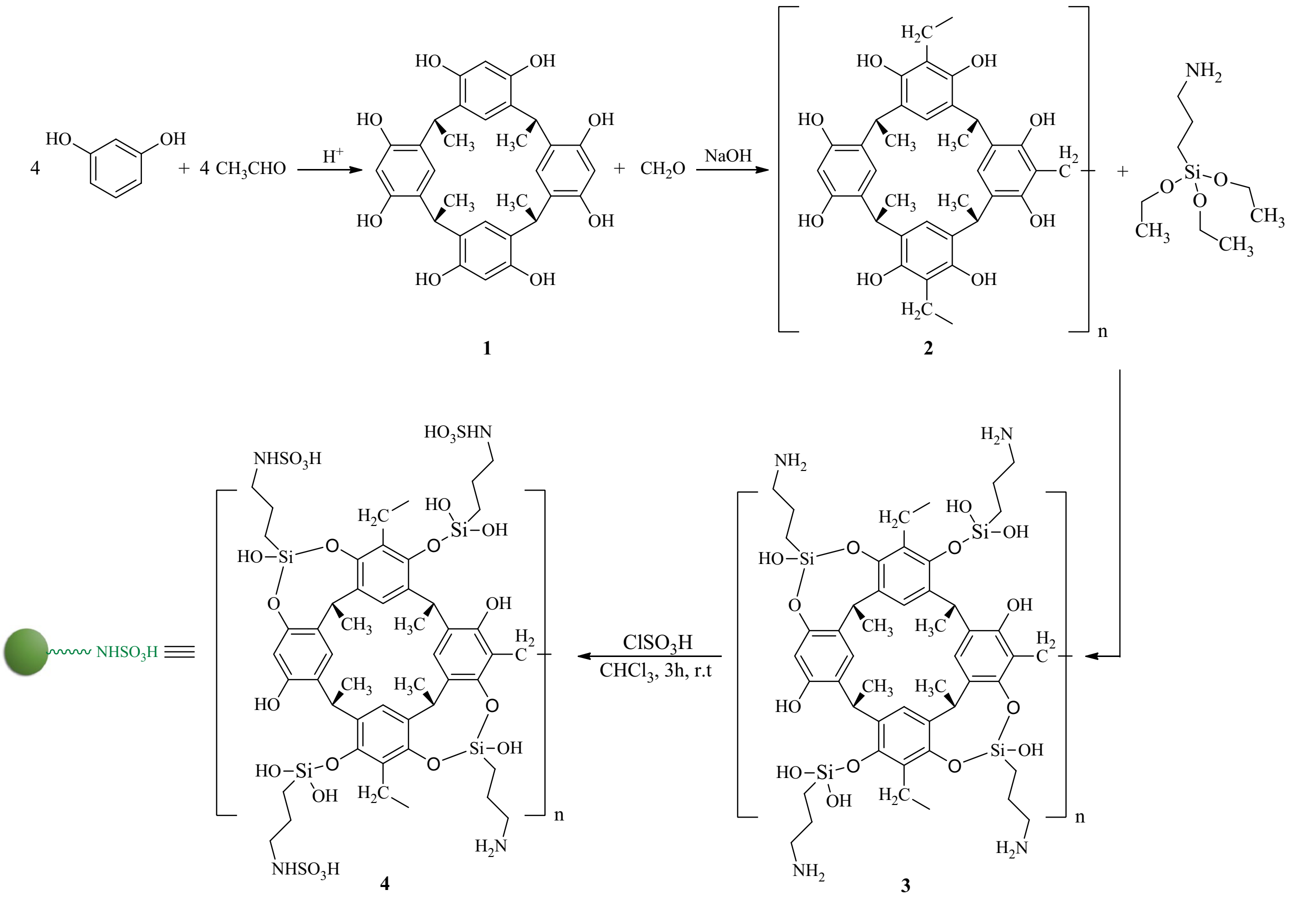
Recycling of the *N*-propyl sulfamic acid functionalized catalyst 4

As it was mentioned, at the end of the reaction, the catalyst was recovered from the reaction mixture via simple filtration and washed several times with dichloromethane (5 cm^3), n-hexane (5 cm^3) and ethanol (5 cm^3). Then the catalyst was dried for being used again in the following cycle.

Results and discussion

Growing interest in applying heterogeneous catalysis for developing useful and green synthetic methodologies in chemical transformations, prompted us to report an efficient, convenient and practical procedure for synthesizing a series of benzoxanthene derivatives using the new developed sulfamic acid functionalized nanocatalyst on the basis of calix[4] resorcinarene as an eco-friendly solid acid catalyst with high catalytic activity under thermal neat conditions. Scheme 1 represents the synthetic strategy for the mentioned catalyst preparation. In the first step, the reaction of resorcinol and acetaldehyde resulted in calix[4] resorcinarene 1 production which in the following step, under polycondensation with formaldehyde created the polymeric network 2 [43, 50]. Formation of compounds 1 and 2 was confirmed through a series of spectroscopic analysis (see ESI) [44]. In the following, amine functionalized polymer 3 was produced as the result of the reaction between compound 2 and 3-aminopropyltriethoxysilane (APTES). Compound 3 formation was also confirmed spectroscopically (see ESI). Ultimately, the reaction of amino groups with chlorosulfonic acid led to the sulfamic acid functionalized polymeric network on the basis of calix[4] resorcinarene 4 (Scheme 1). Elemental analysis revealed the S content to be 4.728% which is indicative of a loading equal to 1.55 mmol H^+ per gram of the dry polymer.

As shown in Fig. 1, the Fourier transform infrared (FT-IR) spectrum of the new synthesized catalyst 4 is consisted of peaks at 685, 1035 and 747 cm^{-1} attributed to the N–S



Scheme 1 Synthesis of calix[4] resorcinarene 1, 3D-network polymer 2, amine-functionalized polymer 3 and *N*-propyl sulfamic acid functionalized polymeric catalyst 4

stretching, Si–O–Si symmetric and asymmetric stretching respectively. The presence of anchored APTES moieties to the surface of the polymer is confirmed by bands at 1108 and 1035 cm^{-1} assigned to the Si–O stretching vibrations. Revealed bands at 2965 and 2887 are representative of the C–H stretching vibrations of the anchored propyl groups. The broad band at 3100–3600 cm^{-1} is attributed to the N–H stretching vibration and also the unfunctionalized phenolic hydroxyl groups of polymer 2. The reaction of compound 3 with chlorosulfonic acid resulted in sulfamic acid functionalities production and the presence of sulfonyl moieties is proved by appeared peaks at nearly 1217 cm^{-1} in the FT-IR spectra.

To investigate the morphology of the synthesized nanoporous catalytic system 4, SEM and TEM techniques were applied. As illustrated in Figs. 2 and 3, SEM and TEM images show an amorphous network with nearly spherical pores in the range of mesoporous systems (Figs. 2, 3).

The thermal stability of the prepared catalyst was checked by TGA under N_2 atmosphere. A mass loss of about 3% up to 172 °C is due to the removal of water and residual

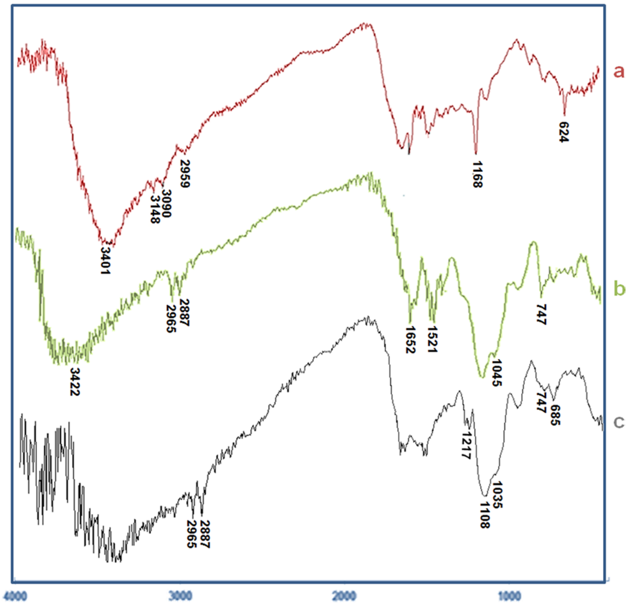


Fig. 1 The comparative FT-IR spectra for **a** polymeric network 2, **b** amine functionalized polymer 3, **c** catalyst 4

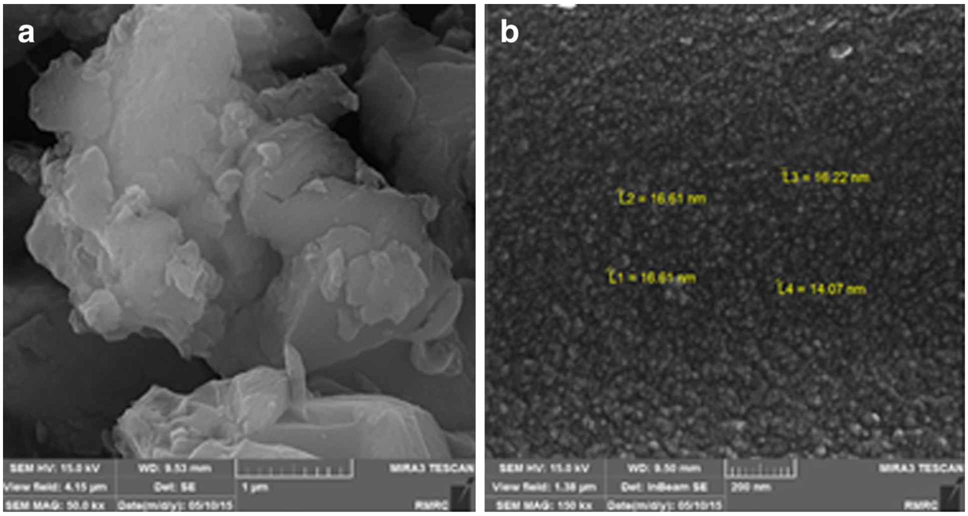


Fig. 2 SEM images of *N*-propyl sulfamic acid functionalized polymeric catalyst 4. **a** low magnification and **b** high magnification

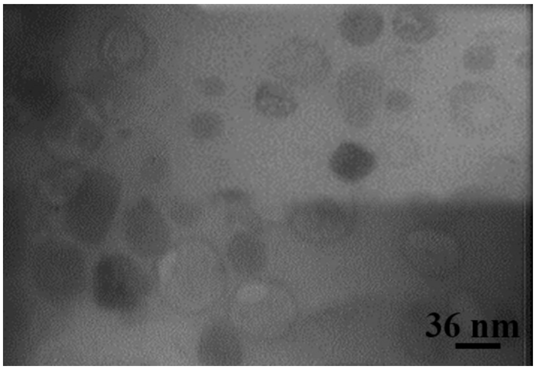


Fig. 3 TEM image of *N*-propyl sulfamic acid functionalized polymeric catalyst 4

amounts of solvents trapped inside the pores during the synthesis procedure. The second mass loss of about 62% which occurs in the temperature range of nearly 172–796 °C is mainly pertained to the cleavage of the grafted linkers and organic moieties. The retained mass of about 34% which is attributed to the remained polymeric architecture is stable up to 800 °C. All the achieved via TGA methodology shows the high stability of the synthesized structure (Fig. 4).

To study the catalytic efficiency of the synthesized catalyst 4 in the condensation reaction of aldehydes with β-naphthol into the corresponding xanthenes, the reaction of 1 mmol benzaldehyde with 2 mmol β-naphthol under solvent-free conditions was chosen as the model reaction (Scheme 2). We started to investigate this condensation

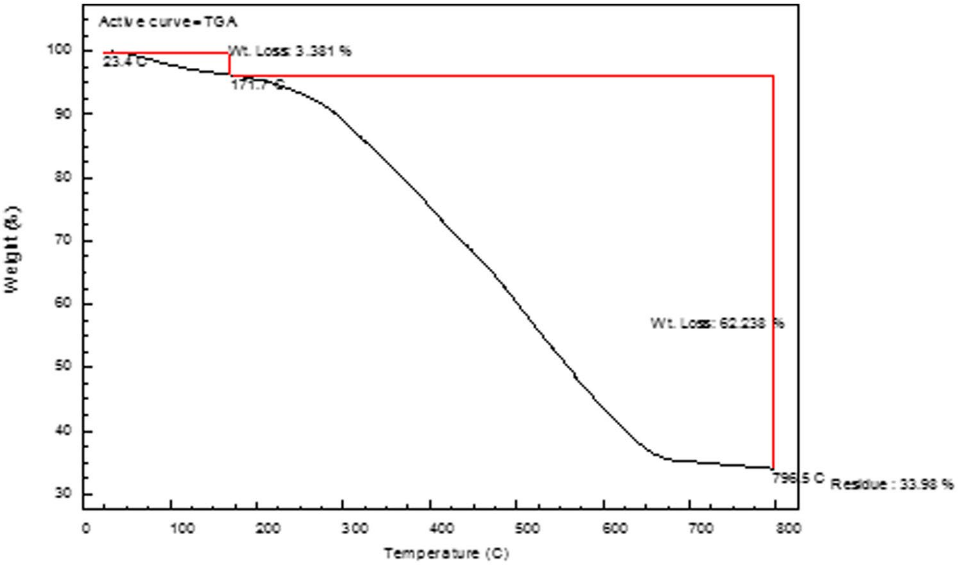
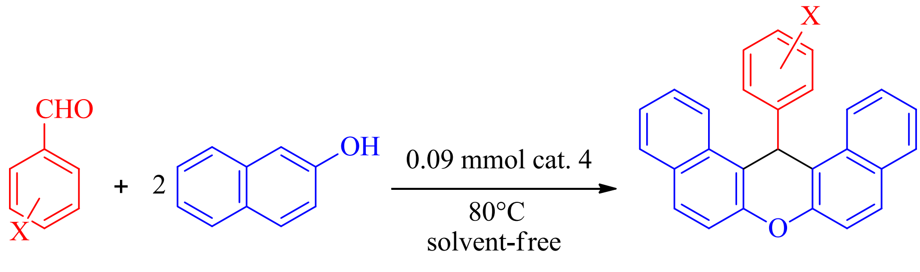


Fig. 4 TGA profile of the synthesized catalyst **4**

Scheme 2 Synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes



(5) **(6)** **(7)**

Table 1 Optimization of the reaction conditions for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives under solvent free conditions

Entry	Catalyst amount (mmol)	Temp (°C)	Time (min)	Yield (%)
1	0.09	120	15	95
2	0.09	80	15	92
3	0.09	60	45	88
4	0.09	r.t	180	Negligible
5	0.07	80	30	88
6	0.05	80	70	75
7	0.1	80	15	90
8	–	120	180	Negligible

by testing different parameters including catalyst amount, reaction time and temperature in the mentioned reaction. In an initial experiment, 1 mmol of benzaldehyde (5) was reacted with 2 mmol of β-naphthol (6) for 3 h at 120 °C in the absence of solvent and catalyst. However, trace amounts of 14-phenyl-14H-dibenzo[a,j]xanthene was obtained (entry 8, Table 1). In the following, the reaction was explored in the presence of various amounts catalyst 4 and temperatures. As seen in Table 1, under the same amount of catalyst (9 mol%), the best results (92%, 15 min) were gained when the model reaction was carried out under solvent-free conditions and at 80 °C (entry 2, Table 1).

Successful reaction optimization with promising results encouraged us to generalize the scope of this procedure. For this purpose, optimized conditions were exerted for a number of structurally diverse aldehydes under condensation with β-naphthol and for aryl aldehydes with both electron-donating and also electron-withdrawing substituents the corresponding 14-aryl-14H-dibenzo[a,j]xanthenes were obtained in high yields (entries 1–9, Table 2). It is noteworthy to mention that aliphatic aldehydes were intact during this condensation reaction (entries 10 and 11, Table 2). It seems that owing to the fact that the present catalytic system is a polymeric matrix consisted of monomers with aromatic phenyl sections, the mentioned reaction proceeds well in the presence of aromatic aldehydes and not the aliphatic ones. In fact, the occurred π–π stacking interactions between theses phenolic walls and aromatic aldehydes and the more stable achieved aromatic products has led to facilitate the H-transfer mechanism and therefore to accelerate the product creation. Additionally, investigating the reaction mixture closely revealed that aliphatic aldehydes were more quickly evaporated or sublimated out of the reaction mixture. So the reaction did not proceed well in proper contact of substrates and good yields did not achieve.

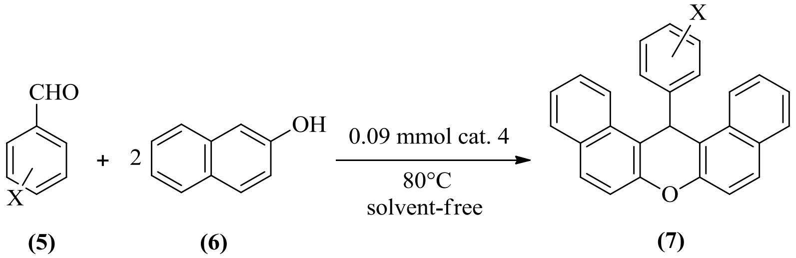
The suggested mechanism for the catalytic operation of catalyst 4 in this condensation reaction is designated in scheme 3. As seen, initially activation of the aryl aldehyde carbonyl group with the acidic catalyst 4 facilitates nucleophilic attack of β-naphthol (6) to the aldehyde (5) and formation of the corresponding carbocation (A). In the following, the reaction of intermediate (A) with the second mol of β-naphthol results in creating arylmethanebisnaphthol (B) which finally undergoes dehydration to give the desired product (7) (Scheme 3).

After the reaction completion, the product was recrystallized from hot ethanol while the solid catalyst was separated from the reaction mixture via filtration, washed, dried and its activity after recycling was examined in the next runs under the determined optimized conditions. It was found that no appreciable loss in the catalyst activity was observed up to five cycles (Table 3).

Various catalysts have been reported in the literature for the reaction of aryl aldehydes with β-naphthol. A comparison between some of these catalysts activity and the present work catalyst is listed in Table 4. It is clearly showed that the presented methodology in this paper is superior to the most of the previously reported methods in terms of catalyst amount, reaction time or product yield.

This new reported sulfamic acid functionalized catalyst 4 plays a crucial role in accelerating the reaction of aromatic aldehydes with β-naphthol in producing 14-aryl-14H-dibenzo[a,j]xanthenes. In fact, the catalyst pores act as kinds of nanoreactors in which the reaction takes place. The catalyst nanoporous structure provides a proper medium for the reagents in high concentration which results in products in short times and high yields. Totally this protocol can be introduced as one of the most efficient procedures

Table 2 Conversion of various aldehydes (**5**) and β-naphthol (**6**) into the corresponding 14-aryl-14H-dibenzo[a,j]xanthenes (**7**) in the presence of catalyst **4** under solvent-free conditions



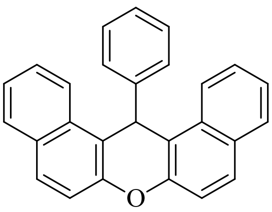
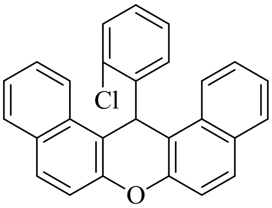
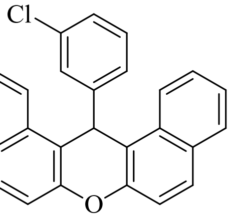
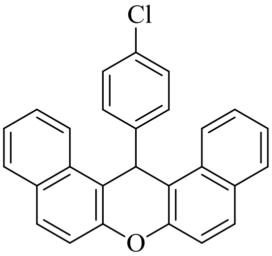
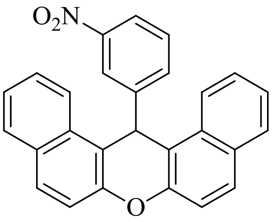
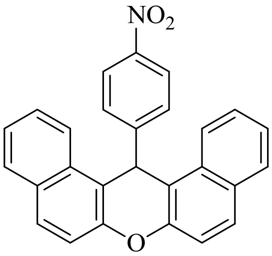
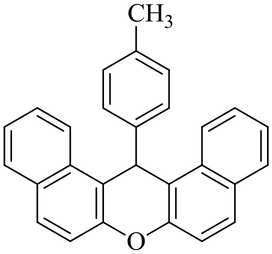
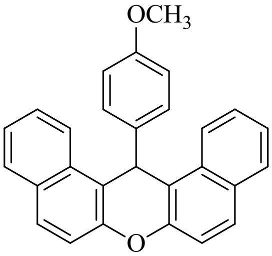
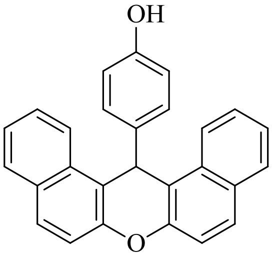
Entry	Aldehyde (5)	Product (7)	Yield (%)[a]	Time (min)	mp (°C)	References
1	C_6H_5CHO		92	15	185–187	[52]
2	$2\text{-}ClC_6H_4CHO$		94	15	213–215	[52]
3	$3\text{-}ClC_6H_4CHO$		92	15	208–210	[53]
4	$4\text{-}ClC_6H_4CHO$		95	10	288–290	[52]
5	$3\text{-}NO_2C_6H_4CHO$		95	5	210–212	[54]

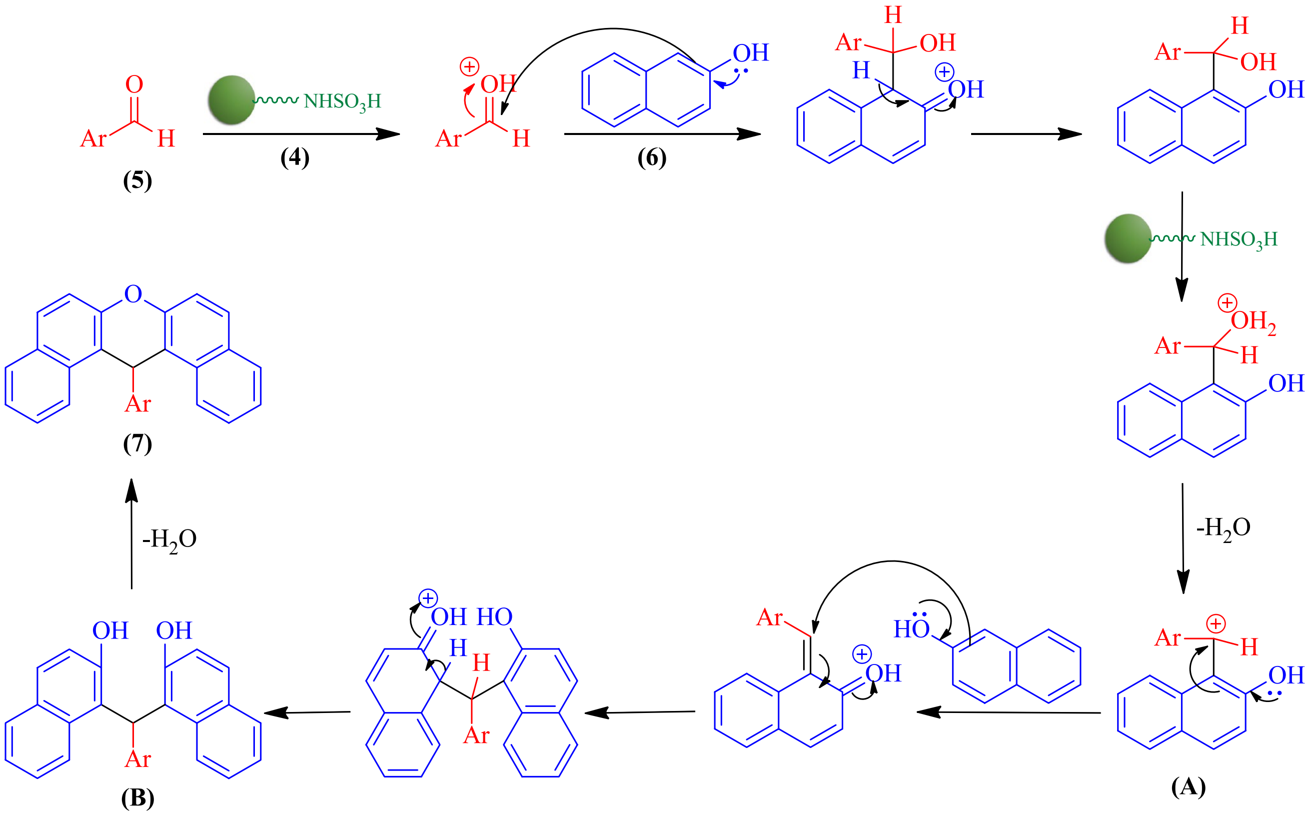
Table 2 (continued)

Entry	Aldehyde (5)	Product (7)	Yield (%)[a]	Time (min)	mp (°C)	References
6	4-$NO_2C_6H_4CHO$		98	5	310–312	[54]
7	4-$CH_3C_6H_4CHO$		90	20	227–229	[52]
8	4-$CH_3OC_6H_4CHO$		88	25	202–204	[52]
9	4-OHC_6H_4CHO		88	20	138–140	[52]
10	C_4H_9CHO	–	–	–	–	–
11	$C_6H_{13}CHO$	–	–	–	–	–

Reaction conditions β-naphthol (2 mmol), aromatic aldehydes (1 mmol), catalyst 4 (0.09 mmol) catalyst, 80 °C, solvent-ftree

[a]Isolated yields

in synthesizing 14-aryl-14H-dibenzo[a,j]xanthenes by providing considerable advantages such as easy reaction work up and products purification, catalyst recyclability, mild reaction conditions and gaining high yields in short times along with avoiding many problems associated with solvent use such as safety, cost, pollution and handling.



Scheme 3 Plausible mechanism for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes catalyzed by catalyst 4

Table 3 Recyclability of catalyst 4

Run	Time (min)	Yield (%)[a]
1	15	92
2	15	92
3	15	90
4	15	90
5	15	90

Reaction conditions β-naphthol (2 mmol), aromatic aldehydes (1 mmol), catalyst 4 (0.09 mmol) catalyst, 80 °C, solvent-ftree

[a]Isolated yields

Conclusion

In summary, a novel and highly efficient methodology for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives has been developed in the presence of our newly synthesized solid acid catalyst through condensation reaction of aryl aldehydes with β-naphthol. The most attractive features of this protocol are simple procedure and reaction handling, easy work up, short reaction times, high yields and catalyst reusability. This method avoids the use of expensive reagents and catalyst, toxic solvents together with time and cost consuming chromatographic separation.

Table 4 Comparisons of some other reported procedures with the present method for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes

Entry	Reaction conditions	Catalyst loadings (mol%/g)	Time (min)	Yield (%)	References
1	Sulfamic acid/solvent-free/125 °C	10	480	93	[54]
2	$NbCl_5$/dichloromethane/N_2/a. t	25	2880	95	[55]
3	SESA/solvent-free/130 °C	15	45	94	[56]
4	$NaHSO_4$/solvent-free/90 °C	10	40	88	[57]
5	PSA/solvent-free/110 °C	5	35	93	[52]
6	PVPP-BF_3/solvent-free/120 °C	0.05 g	90	94	[58]
7	Catalyst 4/solvent-free/80 °C	9	15	92	Present work

SESA silica supported [2-(sulfooxy)ethyl]sulfamic acid, *PSA* phosphosulfonic acid, *PVPP-BF_3* polyvinylpolypyrrolidone-supported boron trifluoride

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