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ORIGINAL ARTICLE

# Preparation of a new, green and recyclable catalyst, silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride, and a solvent- and metal-free protocol for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*] xanthene derivatives

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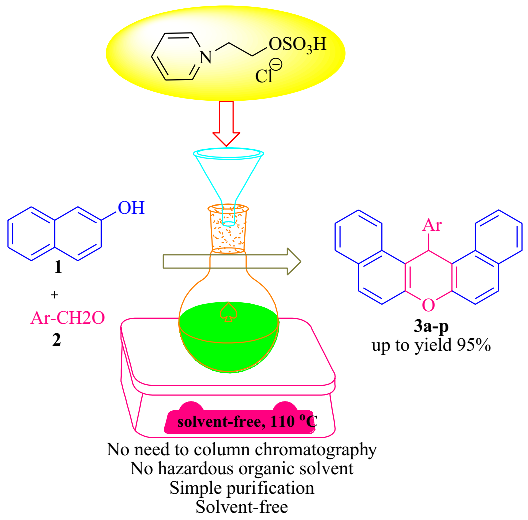
## Abstract

A cost-effective and convenient procedure for the synthesis of silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride $SiO_2$/[SEP]Cl as a recoverable heterogeneous and Brønsted acid catalyst is described, and was used for the one-pot synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes under solvent- and metal-free conditions at 110 °C in short reaction time with a yield of up to 95%. The present method offers several advantages such as simplicity in operation, ease of preparation and recycling of Brønsted acidic ionic liquid (BAIL), solvent-free reaction conditions, and no hazardous organic solvents are used in the entire procedure including workup and purification.

### Graphical abstract



**Keywords** 1-(2-Sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride · One-pot reaction · 14-Aryl-14*H*-dibenzo[*a,j*]xanthene · Solvent- and metal-free conditions · Brønsted acidic ionic liquid

## Introduction

Recently ionic liquids (ILs) are considered as dual reagents (catalysts and solvents) and a greener alternative for a range of various organic reactions, but the application of them as

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catalyst in the absence of solvent is vital and important in organic and inorganic chemistry [1]. As well as, ILs are an appropriate alternative instead of volatile and toxic organic solvents in the future due to high polarity, solubility with certain organic solvents and/or water, low vapor pressure, and excellent solubility in organic and inorganic materials [2]. On the other hand, ILs have been frequently used as solar cell, catalysts, biocatalysts, in nanomaterial synthesis, liquid–liquid separations, polymerization reactions, extraction, dissolution processes, electrochemistry and electrodeposition, and as supercapacitors [3–10].

Among organic compounds, the synthesis of xanthene and its derivatives has received specific attention among pharmacological activities and organic chemists due to having a wide range of biological and therapeutic properties such as antioxidant [11], cytotoxic [12], anti-proliferative [13], antifungal [14], anti-inflammatory, antiviral [15], and antibacterial properties [16]. Furthermore, xanthene and its derivatives would be used in laser technologies [17], as pH-sensitive fluorescent materials for visualization of biomolecules [18], sensitisers in dye-sensitized solar cells (DSSCs) [19], in photodynamic therapy [20], as hole-transporting materials in organic light-emitting devices (OLEDs) [21], and in the food industry as additives [22]. Xanthene and its derivatives are available in natural plants [23, 24]. For instance, examples of natural xanthenes are 3-isopropyl-9a-methyl-1,2,4a,9a-tetrahydroxanthene **A**, used as an antidote for all snake venoms, blumeaxanthene **B** and lumeaxanthene **C**, used to treat gynecological disorders (Scheme 1).

Different procedures have been employed for the preparation of xanthenes and benzoxanthenes [25–29]. In addition, one of the best, easiest, and cost-effective procedures for the synthesis of xanthene derivatives is condensation between aldehydes with 2-naphthols under different conditions in the presence of various Lewis and Brønsted acid catalysts such as $Fe_2(SO_4)_{3.7}H_2O$ [30], polyvinylpolypyrrolidone-bound boron trifluoride [31], pentafluorophenyl ammonium triflate [32], silica sulfuric acid [33], $\gamma$-$Fe_2O_3$–HAp–$Fe^{2+}$ NPs [34], $H_5PW_{10}V_2O_{40}$ [35], cellulose sulfuric acid [36], $Yb(OTf)_3$ [37], 2,6-Pyridinedicarboxylic acid [38], silica-supported [2-(sulfooxy)ethyl]sulfamic acid [39], Selectfluor™ [40], carbon-based solid acid [41], $I_2$ [42], ZnO NPs [43], *p*-toluenesulfonic acid/ionic liquid [44], trityl chloride [45], and polytungstozincate acid [46]. Although several of these procedures suffer from disadvantages such as the use of excess reagents/catalysts, tedious workup procedures, toxicity of the reagent, unsatisfactory yields, low yields of products, use of organic solvents, prolonged reaction time, use of the often expensive catalysts and non-recyclability, the focus on introducing efficient, economical, and solvent-free procedures with high activity, simple reaction workup, and reusability of the catalyst to overcome these problems is still in demand for the synthesis of xanthene derivatives.

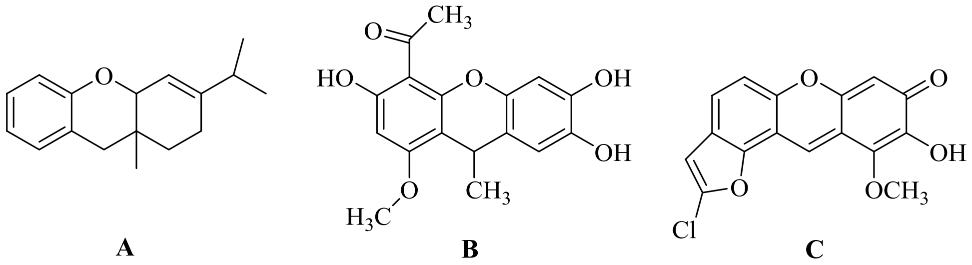
It is necessary to introduce milder, simple reaction workup, solvent- and metal-free, faster, reusability of the catalyst, and generally a greener approach accompanied with higher yields for the synthesis of xanthene derivatives. Therefore, and according to the above-mentioned notes, it seems that silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride $SiO_2$/[SEP]Cl as a catalyst can be an appropriate in the synthesis of these organic compounds.

In this research, we wish to report a rapid and cost-effective procedure for the synthesis of silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride $SiO_2$/[SEP]Cl as a new, highly efficient, and Brønsted acid catalyst for the preparation of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene **3a–p** derivatives under solvent-, metal-free and thermal conditions (Scheme 2).

## Experimental

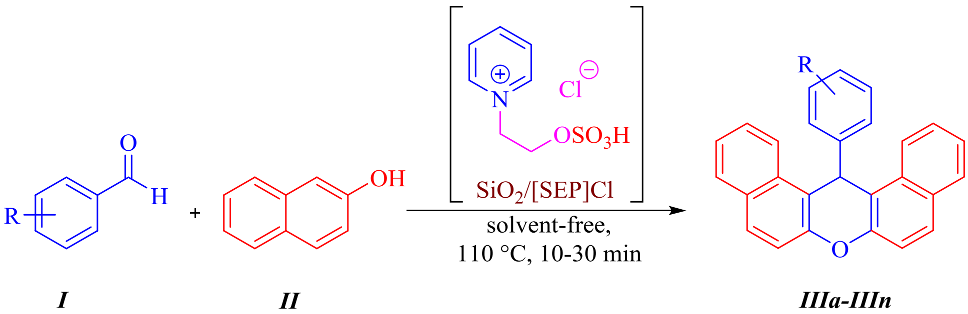
### General

All of the reagents used in the current study were purchased from Merck, Aldrich, and Fluka and used without further purification. All the products are known compounds and were characterized by comparing the IR (KBr), $^1$H NMR, and $^{13}$C NMR spectroscopic data and their melting point to the literature values. Nuclear magnetic resonance ($^1$H NMR and $^{13}$C NMR) was recorded in $CDCl_3$ solvent on a Bruker DRX-300 and -400 spectrometer using tetramethylsilane (TMS) as an internal reference. IR spectra were recorded on a Frontier FT-IR (PerkinElmer) spectrometer using a KBr disk. The purities of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/



**Scheme 1** Examples of natural xanthenes

**Scheme 2** One-pot synthesis of xanthene derivatives in the presence of BAIL under solvent-free conditions



UV 254 plates. Melting points (MP) were determined on a Thermo Scientific 9300 melting point apparatus.

## Preparation of silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride SiO$_2$/[SEP]Cl

In this study, silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride SiO$_2$/[SEP]Cl as a BAIL catalyst was prepared according to the literature procedure (Fig. 1) [47]. Spectral data of 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride are as follows: viscous brown oil: IR (KBr): OH (3200–3600 cm$^{-1}$), C=N (1658 cm$^{-1}$), C=C (1426 cm$^{-1}$), S=O (1232 cm$^{-1}$), and S–O (614 cm$^{-1}$). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.13–3.16 (t, $J = 5.6$ Hz, 2H), 3.93–3.970 (t, $J = 8$ Hz, 2H), 8.10–8.17 (t, $J = 12$ Hz, 2H), 8.61 (s, 1H), 8.92–8.99 (t, $J = 6.4$ Hz, 2H), 9.00–9.42 (d, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): 60.7, 61.8, 128.2, 142.2, 146.0.

## General procedure for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes

A mixture of 2-naphthol (1 mmol), various aldehydes (1 mmol) and SiO$_2$/[SEP]Cl (20 mol%) in a 10-mL round-bottomed flask connected to a reflux condenser was stirred in an oil bath at 110 °C. Completion of the reaction was indicated by TLC (monitored by TLC, ethylacetate:*n*-hexane 1:3). After completion, the solvent was removed under reduced pressure and the crude product was recrystallized with ethanol to afford the pure product in 81–95% yield. All the products were known compounds and characterized by comparing the melting point, $^1$H NMR and $^{13}$C NMR spectra with those reported in the literature.

## 14-(4-Bromophenyl)-14*H*-dibenzo[*a,j*]xanthenes (Table 4, entry 3e)

$^1$HNMR (300 MHz, CDCl$_3$): $\delta$ 5.34 (1H, s, CH), 6.16–6.48 (10H, m, Ar–H), 6.68–6.75 (4H, m, Ar–H), 7.19–7.22 (2H, m, J = 7.8, Ar–H). $^{13}$CNMR (75 MHz, CDCl$_3$): $\delta$ 37.46, 116.65, 118.01, 120.21, 122.39, 124.37, 126.92, 128.91, 129.11, 129.88, 131.04, 131.24, 131.58, 143.98, 148.67.

## 4-(4-Methoxyphenyl)-14*H*-dibenzo[*a,j*]xanthenes (Table 4, entry 3 g)

$^1$H NMR (300 MHz, CDCl$_3$): 2.49 (3H, s, OMe), 5.36 (1H, s, CH), 5.59–5.61 (2H, d, $J = 8.66$ Hz, Ar–H), 6.32–6.45 (6H, m, Ar–H), 6.49–6.55 (2H, m, Ar–H), 6.69–6.76 (4H, m, Ar–H), 7.31–7.33 (2H, d, J = 8.48, Ar–H); $^{13}$C NMR (75 MHz, CDCl$_3$): 37.17, 55.05, 113.89, 117.58, 118.06, 122.77, 124.28, 126.81, 128.80, 128.87, 129.23, 131.13, 131.47, 137.45, 148.69, 157.89.

## 14-(2-Chlorophenyl)-14*H*-dibenzo[*a,j*]xanthenes (Table 4, entry 3 l)

$^1$HNMR (300 MHz, CDCl$_3$): $\delta$ 5.69 (1H, s, CH), 5.81–5.82 (2H, d, Ar–H), 6.27–6.40 (5H, m, Ar–H), 6.50 (2H, d, Ar–H), 6.55–6.67 (4H, m, Ar–H), 7.63–7.66 (2H, J = 8.5, d, Ar–H). $^{13}$CNMR (75 MHz, CDCl$_3$): $\delta$ 34.63, 118.02, 118.11,

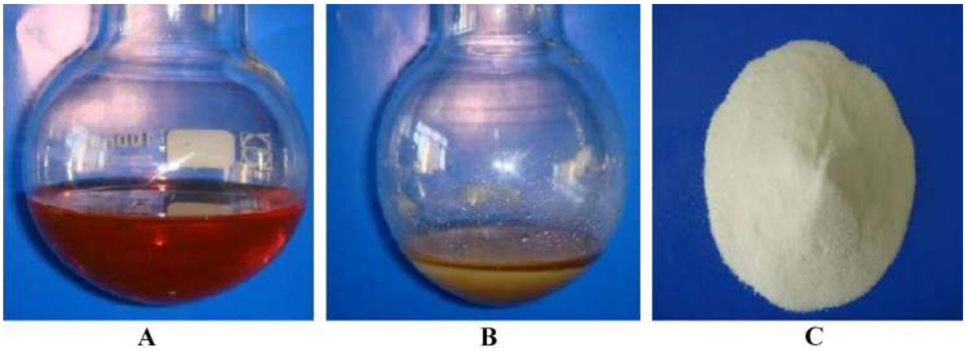


**Fig. 1** Pictures of reaction between pyridine and 2-chloroethanol (**a**), 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride (**b**), and silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride (**c**)

123.46, 124.44, 126.93, 127.87–127.94, 128.66, 129.08, 129.60, 130.13, 130.89, 131.76, 131.81, 143.57, 148.95.

## Results and discussion

For this work, BAIL **C** as a green and reusable catalyst was prepared by condensation reaction between pyridine and 2-chloroethanol that led to ionic liquid **B**, following which chlorosulfonic acid was added dropwise and slowly to ionic liquid **B** for 45–60 min at 0 °C, which afforded BAIL **C** (Scheme 3) [47].

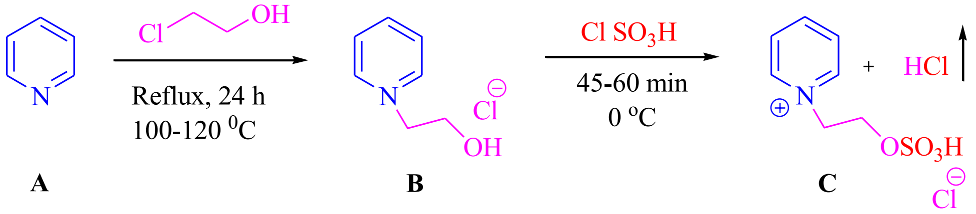
The structure of 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride [SEP]Cl was characterized on the basis of its IR (KBr), $^{1}$H and $^{13}$C NMR data, which were presented in the "Experimental" section. The characterization of BAIL **C** in comparison to compounds **A** and **B** was further conducted by FT-IR spectrum (Fig. 2). As it can be seen from Fig. 2, the broad peak is at around 3200–3600 cm$^{-1}$ which is related to the OH group. On the other hand, the spectra show that the broad peak is at around 1658 cm$^{-1}$ for C=N and 1426 cm$^{-1}$ for C=C, which imply both are related to pyridine ring, and the strong peak at 1232 cm$^{-1}$ is related to the stretching vibration of S=O bond.

$^{1}$H and $^{13}$C NMR spectra of the BAIL **C** are presented in Figs. 3 and 4. The important peaks of $^{1}$H NMR spectrum of BAIL **C** were related to the acidic hydrogen ($SO_3H$) which was observed in 8.61 ppm. The $^{13}$C NMR spectrum of the BAIL **C** exhibited five signals in agreement with the proposed structure.

The activity of the new BAIL **C** as a reusable and green catalyst was tested using a one-pot condensation reaction of various aromatic aldehydes (1 mmol) with 2-naphthol (2 mmol) under solvent-free conditions for the preparation of biologically active 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene derivatives (Scheme 2).

For this purpose, to optimize the reaction conditions for the synthesis of compound **3a**, the condensation reaction of benzaldehyde (1 mmol) and 2-naphthol (2 mmol) was chosen using different amounts of BAIL as a heterogeneous and Brønsted acid catalyst under solvent-free conditions at room temperature (Table 1). As it can be seen in Table 1, when reaction was carried out in the absence of the catalyst, after 120 min the reaction was without yield (Table 1, entry 1). The best results were achieved when 20 mol% of the BAIL was appropriate to promote the reaction efficiently and give the product in excellent yield and in short reaction time (Table 1, entry 6). Additionally, it is worth noting that

**Scheme 3** The synthesis of 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride [SEP]Cl



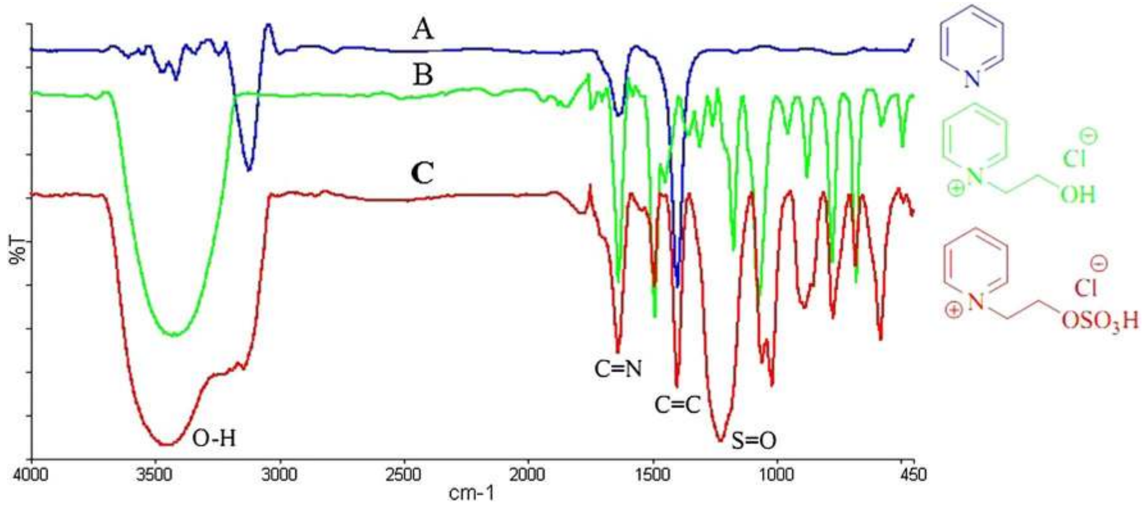
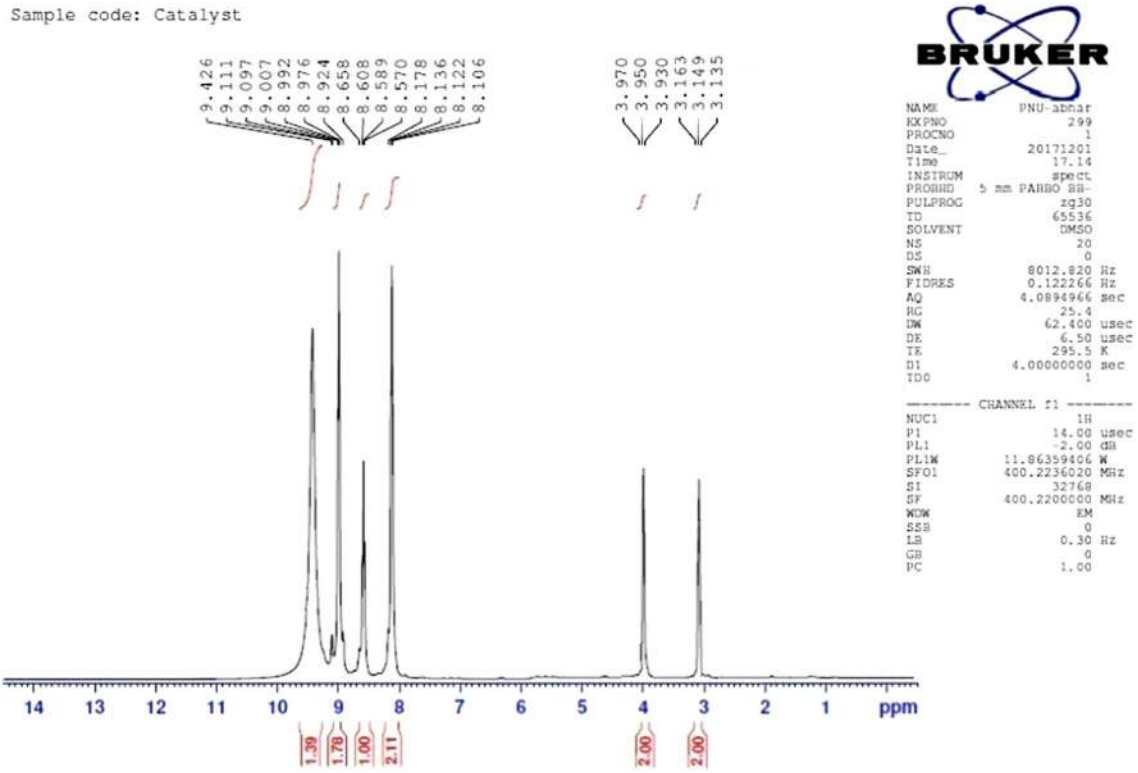


**Fig. 2** Comparison of IR spectrum of compounds **A** and **B** with BAIL **C**



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EXPNO             299
PROCNO              1
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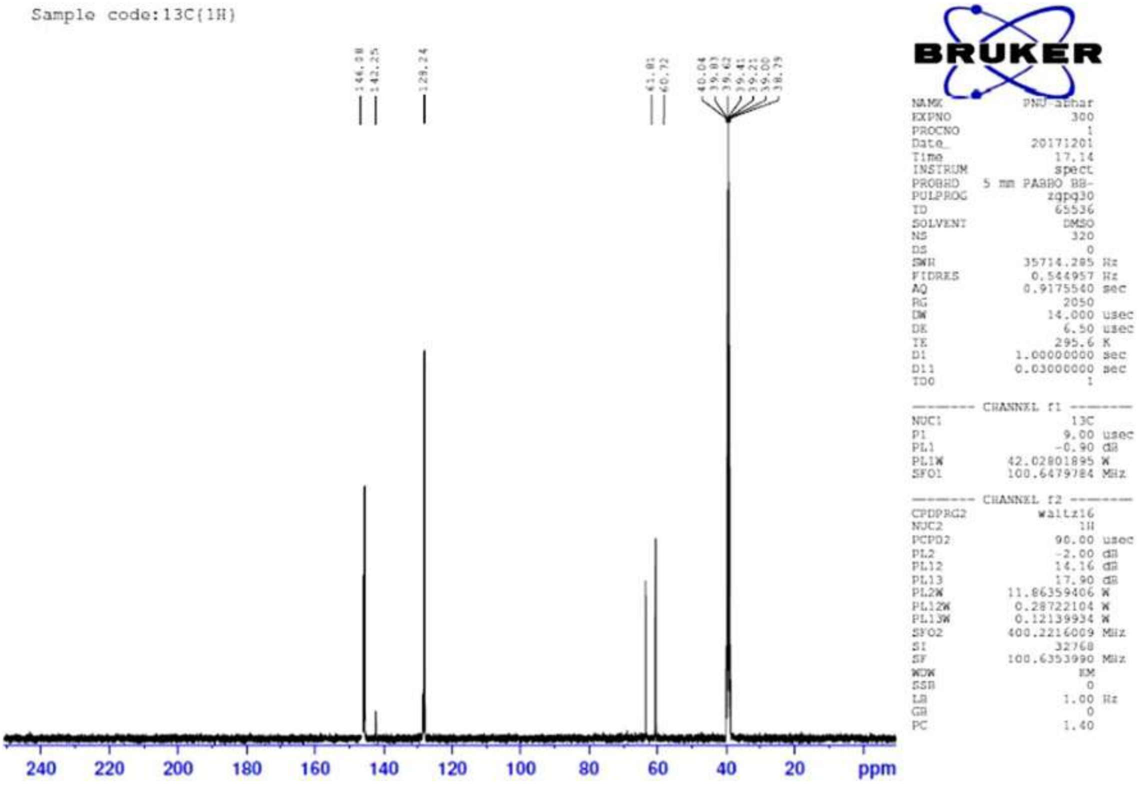
Time            17.14
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          DMSO
NS                 20
DS                  0
SWH          8012.820 Hz
FIDRES       0.122266 Hz
AQ          4.0894966 sec
RG               25.4
DW             62.400 usec
DE               6.50 usec
TE              295.5 K
D1         4.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              14.00 usec
PL1             -2.00 dB
PL1W      11.86359406 W
SFO1      400.2236020 MHz
SI              32768
SF        400.2200000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

**Fig. 3** $^{1}$H NMR spectrum of [SEP]Cl



```
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EXPNO             300
PROCNO              1
Date_        20171201
Time            17.14
INSTRUM         spect
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PULPROG        zgpg30
TD              65536
SOLVENT          DMSO
NS                320
DS                  0
SWH         35714.285 Hz
FIDRES       0.544957 Hz
AQ          0.9175540 sec
RG               2050
DW             14.000 usec
DE               6.50 usec
TE              295.6 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1               9.00 usec
PL1             -0.90 dB
PL1W      42.02801895 W
SFO1      100.6479784 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2               1H
PCPD2           90.00 usec
PL2             -2.00 dB
PL12            14.16 dB
PL13            17.90 dB
PL2W      11.86359406 W
PL12W      0.28722104 W
PL13W      0.12139934 W
SFO2      400.2216009 MHz
SI              32768
SF        100.6353990 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

**Fig. 4** $^{13}$C NMR spectrum of [SEP]Cl

**Table 1** Result of the amount of the catalyst in the synthesis of compound **3a** under solvent-free conditions

| Entry | Catalyst loading (%) | Reaction time (min) | Yield (%)[a] |
|---|---|---|---|
| 1 | None | 120 | – |
| 2 | 1 | 100 | 35 |
| 3 | 5 | 90 | 54 |
| 4 | 10 | 90 | 75 |
| 5 | 15 | 45 | 80 |
| 6 | 20 | 20 | 85 |
| 7 | 25 | 20 | 85 |

[a] Yield of isolated products

**Table 3** Optimization of various solvents in the synthesis of compound **3a** on the model reaction under reflux condition

| Entry | Solvent (5 ml) | Reflux conditions (°C) | Reaction time (min) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | EtOH | 78.3 | 60 | 44 |
| 2 | MeOH | 65 | 60 | 40 |
| 3 | $CHCl_3$ | 61.2 | 60 | 51 |
| 4 | $CH_2Cl_2$ | 39.6 | 60 | 45 |
| 5 | EtOAc | 77.1 | 60 | 30 |

[a] Yield of isolated products

when a higher percentage of loading of the BAIL was used, the yields did not improve (Table 2, entry 6).

To optimize the temperatures, the condensation of benzaldehyde (1 mmol) and 2-naphthol (2 mmol) in the presence of 20 mol% of BAIL was checked, and the results are tabulated in Table 2. As it can be seen in Table 2, temperature increase was appropriate for the synthesis of compound **3a**. Therefore, the model reaction in solvent-free conditions at 110 °C leads to the highest yield (94%) and shortest reaction time (15 min) compared to the other temperatures.

In the next study, to compare the efficiency of solvent-free conditions versus solvent conditions, the condensation reaction between benzaldehyde (1 mmol) and 2-naphthol (2 mmol) using BAIL (20 mol%) was tested in various solvents such as ethanol, methanol, chloroform, dichloromethane, and ethyl acetate under reflux conditions, and the results are summarized in Table 3. As it can be seen in Table 3, low yields of the product and longer reaction time rather than solvent-free conditions were obtained. Hence, performing the reaction under solvent-free conditions and in the presence of 20 mol% of BAIL at 110 °C was determined as the optimal condition.

To assess the efficiency and the scope of BAIL for the synthesis of biologically active 14-aryl-14*H*-dibenzo[*a*,*j*] xanthene derivatives, a variety of aromatic aldehydes (containing electron-withdrawing, electron-donating groups, and halogens on their aromatic ring) were reacted with 2-naphthol in the optimal reaction conditions to produce the desired products **3a–p** in excellent yields and in short reaction time (Table 4). As it can be seen in Table 4, in all cases, aromatic aldehydes **3a–p** containing both electron-donating and electron-withdrawing groups (–$NO_2$, –Me, –OMe, –Br, –Cl, –OH, –$NR_2$) reacted with 2-naphthol under solvent-free conditions at 110 °C for an appropriate time (10–30 min) and good to excellent yields (81–95%) to generate 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene derivatives.

**Table 2** Optimization of temperature in the synthesis of compound **3a** under solvent-free conditions

| Entry | Temperature (°C) | Reaction time (min) | Yield (%)[a] |
|---|---|---|---|
| 1 | 60 | 55 | 81 |
| 2 | 80 | 40 | 87 |
| 3 | 100 | 30 | 94 |
| 4 | 110 | 15 | 94 |
| 5 | 120 | 20 | 94 |

[a] Yield of isolated products

The recovery and reusability of the catalyst is a very important factor in industry and green chemistry, and also one of the advantages of heterogeneous catalyst. It is also worth noting that silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride $SiO_2$/[SEP]Cl as a catalyst can be recovered at the end of the reaction and can be used six times without losing its activity (Fig. 5). The yields of 4-(4-nitrophenyl)-14H-dibenzo[*a*,*j*]xanthenes **3i** obtained after 15 min include 95, 93, 93, 91, 91 and 88%, respectively.

The advantages of BAIL were compared (solvent, catalyst loading, time, yield, and temperature) with some other catalysts for the synthesis of compound **3a** from the reaction between benzaldehyde with 2-naphthol, and the results are represented in Table 5. In 2012, Rao et al. (Table 5, entry 3) reported the preparation of 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes using ZnO NPs; in this procedure, the yield of products are low (80%) and reaction time is long (60 min). On the other hand, this procedure needs high temperature (150 °C) to complete the reaction. In 2008, Khaksar et al. (Table 5, entry 5) reported a highly efficient method for the synthesis of 14-aryl(alkyl)-14*H*-dibenzo[*a*,*j*]xanthenes using pentafluorophenyl ammonium triflate (PFPAT); this method relies on the use of toxic solvent like toluene, and requires very long reaction time (4.5 h). In addition, one of the other problems is that the catalyst used in this method is non-recyclable. Recently, Kumara et al. in 2006 reported the use of Selectfluor™ (Table 5, entry 7) as a catalyst for the preparation of 14-aryl(alkyl)-14*H*-dibenzo[*a*,*j*]xanthene derivatives in which the reaction completion time

**Table 4** The solvent-free synthesis of biologically active 14-aryl-14H-dibenzo[*a*,*j*]xanthene derivatives using silica supported 1-(2-sulfooxy)ethyl)1H-pyridine-1-ium-chloride

| Entry | Aldehydes | Time (min)[a] | Yield (%)[b] | M.p. °C (Lit) | |
|---|---|---|---|---|---|
| | | | | Found | Reported |
| **3a** | $C_6H_5$ | 15 | 94 | 188–190 | 191–193 [34] |
| **3b** | $2\text{-}NO_2C_6H_4$ | 30 | 84 | 308–310 | 309–311 [34] |
| **3c** | $3\text{-}NO_2C_6H_4$ | 30 | 89 | 211–213 | 210–212 [34] |
| **3d** | $3\text{-}OCH_3C_6H_4$ | 12 | 90 | 261–263 | 260–262 [34] |
| **3e** | $4\text{-}BrC_6H_4$ | 25 | 94 | 295–296 | 294–295 [34] |
| **3f** | $4\text{-}CH_3C_6H_4$ | 20 | 88 | 225–227 | 226–228 [34] |
| **3g** | $4\text{-}OCH_3C_6H_4$ | 15 | 85 | 201–203 | 203–205 [34] |
| **3h** | $4\text{-}ClC_6H_4$ | 10 | 93 | 282–284 | 285–287 [34] |
| **3i** | $4\text{-}NO_2C_6H_4$ | 20 | 95 | 309–311 | 310–312 [34] |
| **3j** | $3\text{-}OHC_6H_4$ | 25 | 84 | 171–173 | 169–171 [34] |
| **3k** | $4\text{-}OHC_6H_4$ | 22 | 87 | 140–141 | 1387–139 [34] |
| **3l** | $2\text{-}ClC_6H_4$ | 17 | 85 | 221 | 219–220 [34] |
| **3m** | $2,4\text{-}ClC_6H_3$ | 13 | 95 | 86–88 | 87–89 [34] |
| **3n** | $4\text{-}C_6H_5C_6H_4$ | 30 | 81 | 279–281 | 281–283 [34] |
| **3o** | $2,3\text{-}ClC_6H_3$ | 15 | 94 | 220–222 | 221–224 [48] |
| **3p** | $4\text{-}N,N\text{-}(CH_3)_2C_6H_4$ | 30 | 90 | 222–224 | 224–226 [49] |

[a] Reactions were run till the completion as indicated by TLC

[b] Yield of isolated products

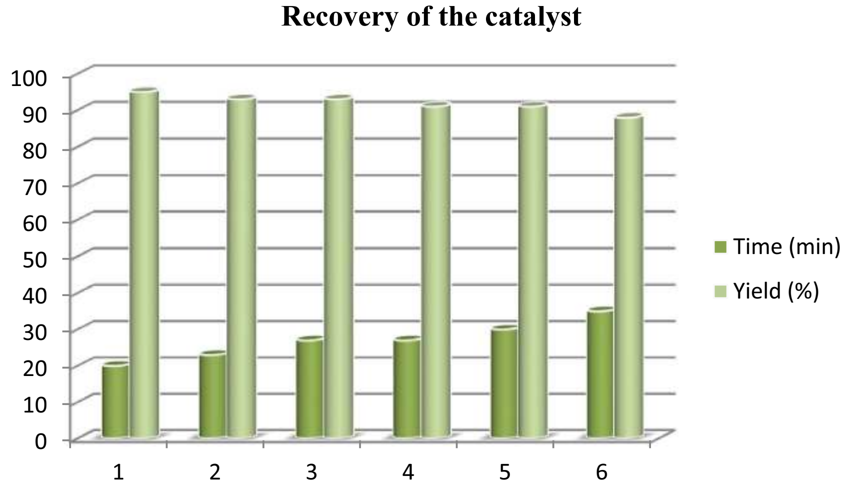

**Fig. 5** Recyclability of the $SiO_2$/[SEP]Cl for the synthesis of compound **3i** after 15 min

was very long and tedious (8 h), and also requires high temperature (125 °C). Wang et al. in 2009 reported the use of iodine (Table 5, entry 9) as a catalyst for the synthesis of 14-aryl(alkyl)-14*H*-dibenzo[*a*,*j*]xanthene derivatives under neat conditions; one of the main problems of this method is the use of iodine, which is toxic and biodegradable, and the reaction time is long. As it can be seen in Table 5, the reaction in the presence of BAIL was simpler, solvent free, economical, eco-friendly, the catalyst used was recyclable, and the reaction time was shorter. On the whole, it seems that this catalytic system can be an appropriate alternative method for the synthesis.

## Conclusion

In summary, silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride $SiO_2$/[SEP]Cl as a new and recoverable heterogeneous catalyst was employed for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene derivatives by the one-pot condensation reaction of various aldehydes with 2-naphthol under thermal and solvent-free conditions. This methodology offers very attractive features such as economic viability of catalyst, short reaction time, high yield of products, operational simplicity, easier workup

**Table 5** Comparison of various catalysts used for the synthesis of compound **3a**

| Entry | Reaction condition | Time (h) | Yield (%)[a] | Refs. |
|---|---|---|---|---|
| 1 | Silica sulfuric acid (0.05 g)/solvent free/125 °C | 20[b] | 90 | [33] |
| 2 | $Yb(OTf)_3$/[BPy]$BF_4$ (0.01 mmol)/110 °C | 7 | 89 | [37] |
| 3 | ZnO NPs (0.3 mmol)/solvent free/150 °C | 60[b] | 80 | [43] |
| 4 | PVPP-$BF_3$/solvent free (0.05 g)/120 °C | 1.5 | 94 | [31] |
| 5 | PFPAT (10 mol%)/toluene/25–30 °C | 4.5 | 90 | [32] |
| 6 | $H_5PW_{10}V_2O_{40}$ (0.5 mol%)/solvent-free/100 °C | 1 | 67 | [35] |
| 7 | Selectfluor™ (0.1 m mol)/neat conditions/125 °C | 8 | 93 | [40] |
| 8 | Polytungstozincate acid (0.05 g)/solvent free/80 °C | 1 | 81 | [46] |
| 9 | Iodine (0.1 mmol)/neat conditions/90 °C | 2.5 | 90 | [42] |
| 10 | $SiO_2$/[SEP]Cl (20 mol%)/solvent free/110 °C | 15[b] | 94 | – |

[a] Yield of isolated products

[b] In minute

procedure, ease of recovering and reusing of the catalyst, and higher turn-over frequency of the catalyst in comparison to previously reported catalysts.

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