IRANIAN JOURNAL OF CATALYSIS

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

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Received 6 June 2012; received in revised form 23 October 2012; accepted 28 October 2012

ABSTRACT

Brønsted acidic ionic liquid triethylamine-bonded sulfonic acid {[Et_3N-SO_3H]Cl} efficiently catalyzes the one-pot multi-component condensation of 2-naphthol with arylaldehydes and dimedone (5,5-dimethylcyclohexane-1,3-dione) under solvent-free conditions to afford 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones in high yields and relatively short reaction times.

***Keywords**: Brønsted acidic ionic liquid, Triethylamine-bonded sulfonic acid {[Et_3N-SO_3H]Cl}, 12-Aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one, 2-Naphthol, Arylaldehyde, Dimedone (5,5-dimethylcyclohexane-1,3-dione).*

1. Introduction

Xanthenes and benzoxanthenes are important class of heterocycles which possess multiple biological activities, such as antiviral [1], antibacterial [2], and anti-inflammatory [3] properties. They have been also used in photodynamic therapy [4]. Moreover, these compounds have been applied as dyes or fluorescent agents, in laser technologies [5] or visualization of biomolecules [6]. 12-Aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones are an interesting type of xanthenes derivatives which have been prepared by the one-pot multi-component condensation of 2-naphthol with arylaldehydes and dimedone (5,5-dimethylcyclohexane-1,3-dione) using some catalysts [7-15]. These reported procedures for the synthesis of these biologically important compounds are associated with disadvantages like inadequate yields, long reaction times, the use of toxic and expensive catalysts, the use of volatile organic solvents and poor compliance with the green chemistry protocols. These subjects prompted us to try development a new method for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones without the above drawbacks. Multi-component reactions have emerged as a valuable tool in the context of modern combinatorial synthesis. Moreover, one-pot multi-component condensation reactions due to their productivity, facile execution and simple reaction profile are one of the important strategies in multi-component reactions, which have expanded rapidly in organic chemistry [16-19].

One of the undeniable problems posed to the chemical industries is deal with the fact that all chemical plants rely widely on hazardous, volatile, flammable, difficult to recycle and expensive organic solvents. Organic solvents used in most of the synthetic processes in chemical industries evaporate into the atmosphere with nocuous effects on the environment and ozone layer [20]. One of the best ways to solve this problem, is application of solvent-free conditions in chemical reactions. Along this line, solvent-free technique has been applied as useful protocols in organic synthesis. Solvent-free reactions often lead to shorter reaction times, increased yields and easier workup, in addition to working well in green chemistry protocols, and enhancing the regio- and stereoselectivity of reactions [21-23].

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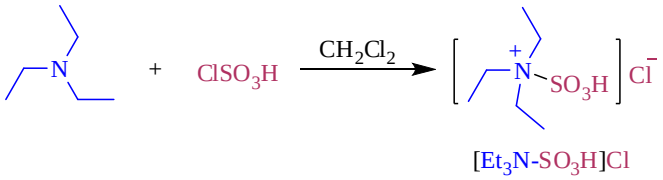


Scheme 1. The synthesis of $[Et_3N\text{-}SO_3H]Cl$.

Ionic liquids (ILs) have attracted more and more attentions as green reaction media and catalysts for organic transformations because of their unique properties such as negligible vapor pressures, electrochemical stability, low flammability, reasonable thermal stability, outstanding recyclability and reusability, excellent ionic conductivities, eco-friendly, and tunable hydrophobicity [20,24-26]. Among the different kinds of ILs, Brønsted acidic ones have designed to replace solid acids and traditional mineral liquid acids like sulfuric acid and hydrochloric acid to catalyze chemical transformations [27-31]. Triethylamine-bonded sulfonic acid {$[Et_3N\text{-}SO_3H]Cl$} is an interesting and inexpensive acidic ionic liquid which has been recently introduced as an efficient and homogeneous catalyst in organic synthesis (Scheme 1) [31].

In this work, we report a new method for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones by the one-pot multi-component condensation of 2-naphthol with arylaldehydes and dimedone using $[Et_3N\text{-}SO_3H]Cl$ as an efficient, homogeneous and regenerable catalyst under solvent-free conditions at 120 °C (Scheme 2).

It is noteworthy the ionic liquid catalyst used in this protocol, is inexpensive and non-corrosive, and has different unique properties such as environmental compatibility, ready availability of the starting materials for the catalyst synthesis, operational simplicity and easy regenerability as well as reusability. The other advantages of the work are generality, efficiency, simple work-up procedure and purification, short reaction times, clean production of the products, low cost and finally good agreement with the green chemistry protocols. Considering the above-mentioned drawbacks accompanied with the reported methods for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones, and also the advantages of our method, we can state that the presented method has solved most of the drawbacks of the reported protocols.

2. Experimental

2.1. General

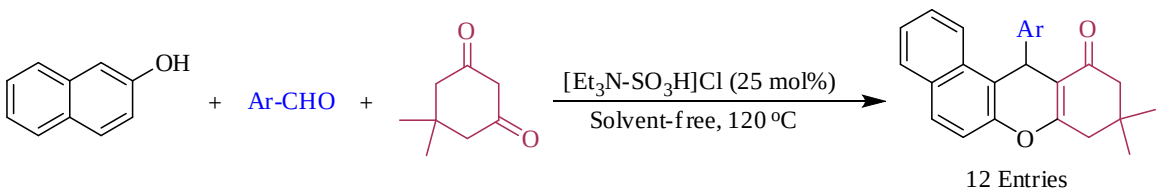
All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The ^1H NMR (300 or 500 MHz) and ^{13}C NMR (75 or 125 mhz) were run on Bruker Avance DPX, FT-NMR spectrometers (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

2.2. Procedure for the preparation of ionic liquid [Et3N-SO3H]Cl

A solution of triethylamine (0.50 g, 5 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a stirring solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry CH_2Cl_2 (40 mL) over a period of 10 min at 10 °C. Afterward, the reaction mixture was allowed to heat to room temperature (accompanied with stirring), and stirred for another 4 h. The solvent was evaporated, and the liquid residue was triturated with t-butylmethyl ether (3×10 mL) and dried under powerful vacuum at 90 °C to give $[Et_3N\text{-}SO_3H]Cl$ as a viscous pale yellow oil in 93% yield [31]; pK_a = 1.29. IR (Nujol): 624 (S-O), 1217 (S=O), 1307 (N-S), 3200-3500 (OH).

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

To a mixture of 2-naphthol (0.144 g, 1 mmol), arylaldehyde (1 mmol) and dimedone (0.140 g, 1 mmol) in a test tube, was added $[Et_3N\text{-}SO_3H]Cl$ (0.055 g, 0.25 mmol).



Scheme 2. The synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives.

The resulting mixture was firstly stirred magnetically, and after solidification of the reaction mixture with a small rod at 120 ºC. After completion of the reaction, the mixture was cooled to room temperature, H_2O (3 mL) was added to it, stirred for 3 min and filtered. The solid residue was recrystallized from aqueous ethanol (90 %) to give the pure product.

The selected spectral data

9,9-Dimethyl-12-phenyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 1). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ: 0.84 (s, 3H), 1.02 (s, 3H), 2.09 (d, *J* = 16.2 Hz, 1H), 2.30 (d, *J* = 16.2 Hz, 1H), 2.60 (Distorted AB System, 2H), 5.54 (s, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.36-7.48 (m, 3H), 7.89 (d, *J* = 8.5 Hz 2H), 8.01 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ: 26.6, 29.2, 32.3, 34.5, 40.7, 50.5, 113.6, 117.6, 117.7, 123.7, 125.4, 126.6, 127.6, 128.5, 128.6, 129.0, 129.5, 131.0, 131.5, 145.3, 147.6, 164.3, 196.2.

9,9-Dimethyl-12-(*m*-tolyl)-9,10-dihydro-8*H*-benzo[*a*] xanthen-11(12*H*)-one (Table 3, entry 2). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.87 (s, 3H), 1.06 (s, 3H), 2.14 (d, *J* = 16.0 Hz, 1H), 2.32 (d, *J* = 16.0 Hz, 1H), 2.62 (Distorted AB System, 2H), 3.36 (s, 3H), 5.59 (s, 1H), 7.12 (t, *J*= 7.8, 1H), 7.23-7.25 (m, 2H), 7.41-7.50 (m, 4H), 7.90 (t, *J* = 7.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 1H).

9,9-Dimethyl-12-(4-methoxyphenyl)-9,10-dihydro-8*H*-benzo [*a*]xanthen-11(12*H*)-one (Table 3, entry 3). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ: 0.87 (s, 3H), 1.05 (s, 3H), 2.13 (d, *J* = 15.4 Hz, 1H), 2.34 (d, *J* = 16.1 Hz, 1H), 2.72 (Distorted AB System, 2H), 3.58 (s, 3H), 5.86 (s, 1H), 7.11-7.32 (m, 3H), 7.34-7.52 (m, 4H), 7.90 (s, 2H), 8.03 (s, 1H).

9,9-Dimethyl-12-(3-chlorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 4). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.88 (s, 3H), 1.03 (s, 3H), 2.11 (d, *J* = 12.8 Hz, 1H), 2.32 (d, *J* = 16.1 Hz, 1H), 2.61 (Distorted AB System, 2H), 5.60 (s, 1H), 7.11 (s, 1H), 7.19 (d, *J* = 4.4 Hz, 2H), 7.36 (s, 1H), 7.40-7.50 (m, 3H), 7.89-8.01 (m, 2H), 8.02 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 27.0, 29.6, 32.7, 34.7, 41.0, 50.9, 113.5, 117.3, 118.0, 124.0, 125.9, 127.2, 127.6, 128.2, 128.8, 129.4, 130.3, 130.9, 131.3, 131.9, 133.5, 148.0, 148.1, 165.0, 196.7.

9,9-Dimethyl-12-(4-chlorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 5). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.86 (s, 3H), 1.04 (s, 3H), 2.12 (d, *J* = 16.1 Hz, 1H), 2.32 (d, *J* = 16.1 Hz, 1H), 2.56 (d, *J* = 17.3 Hz, 1H), 2.66 (d, *J* = 17.4 Hz, 1H), 5.58 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.41-7.49 (m, 3H), 7.89-7.92 (m, 2H), 7.99 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 27.0, 29.6, 32.7, 32.4, 41.0, 50.9, 113.6, 117.5, 118.0, 124.0, 125.9, 128.1, 128.9, 129.4, 130.2, 130.8, 131.3, 131.6, 131.9, 144.6, 148.0, 164.8, 196.7.

9,9-Dimethyl-12-(2,3-dichlorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 6). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.88 (s, 3H), 1.06 (s, 3H), 2.10 (d, *J* = 16.0 Hz, 1H), 2.32 (d, *J* = 16.0 Hz, 1H), 2.57 (d, *J* = 17.3 Hz, 1H), 2.69 (d, *J* = 17.3 Hz, 1H), 5.86 (s, 1H), 7.16-7.22 (m, 1), 7.27 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.41-7.43 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.91 (t, *J* = 6.6 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 26.7, 29.2, 32.3, 33.6, 50.5, 55.3, 113.6, 113.8, 115.0, 117.6, 118.0, 123.7, 125.4, 127.5, 128.9, 129.4, 129.5, 131.0, 131.5, 137.5, 147.5, 157.8, 163.1, 164.0, 196.4. MS (*m/z*): 424 (M^+ + 1), 423 (M^+).

9,9-Dimethyl-12-(2,4-dichlorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 7). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.89 (s, 3H), 1.05 (s, 3H), 2.09 (d, *J* = 16.0 Hz, 1H), 2.31 (d, *J* = 16.0 Hz, 1H), 2.65 (d, *J* = 16.8 Hz, 1H), 2.67 (d, *J* = 17.3 Hz, 1H), 5.77 (s, 1H), 7.22-7.28 (m, 2H), 7.37-7.42 (m, 3H), 7.47-7.50 (m, 1H), 7.88-7.91 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 27.0, 29.5, 32.5, 32.6, 41.1, 51.0, 118.0, 123.7, 125.9, 127.5, 128.1, 128.3, 129.6, 129.7, 130.5, 131.6, 131.8, 132.5, 133.7, 140.7, 148.2, 165.1, 196.5.

9,9-Dimethyl-12-(2-bromorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 8). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.89 (s, 3H), 1.06 (s, 3H), 2.09 (d, *J* = 16 Hz, 1H), 2.32 (d, *J* = 16 Hz, 3H), 2.57

Table 1. Effect of the catalyst amount and temperature on the reaction of 2-naphthol with 4-nitrobenzaldehyde and dimedone in the absence of solvent.

Entry	Catalyst amount (mol%)	Temperature (°C)	Time (min)	Yield[a] (%)
1	-	120	120	Trace
2	20	120	30	87
3	25	120	30	94
4	30	120	30	85
5	25	110	30	80
6	25	130	25	84

[a]Isolated yield.

Table 2. The solvent-free reaction between 2-naphthol, arylaldehydes and dimedone catalyzed by $[Et_3N\text{-}SO_3H]Cl$ at 120 °C leading to 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones.

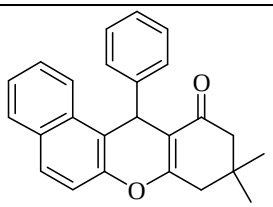
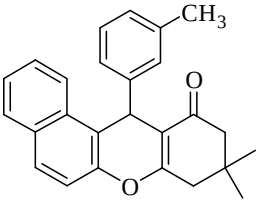
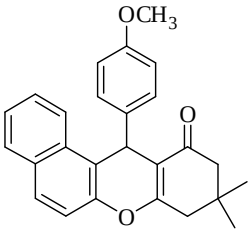
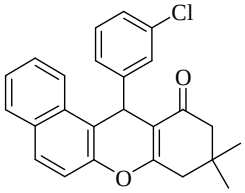
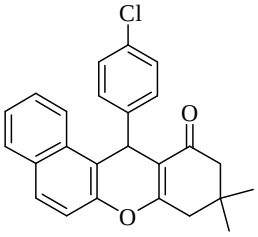
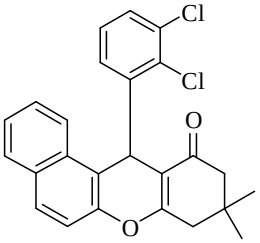
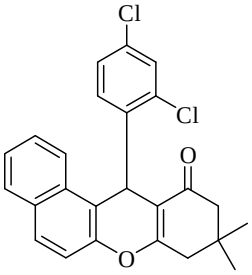
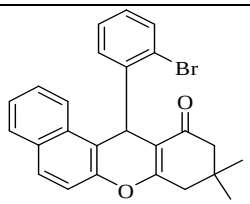
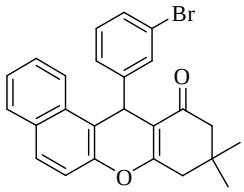
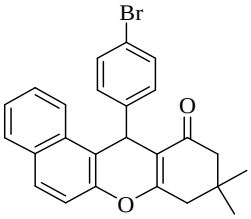
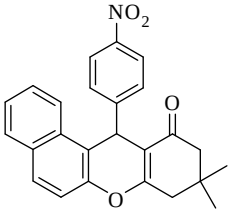
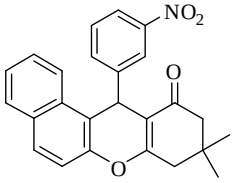
Entry	Product	Time (min)	Yield[a] (%)	m.p. °C (Lit.)
1		60	88	148-150 (151-153) [8]
2		45	91	178-180 (178-180) [32]
3		30	78	199-201 (204-205) [8]
4		45	81	175-178 (-) [10]
5		40	89	181-183 (185-187) [14]
6		50	90	223-225
7		50	87	183-185 (181-182) [11]

Table 2. *(Continued)*

8		50	85	169-171 (-) [10]
9		35	80	159-162 (-) [10]
10		45	83	184-186 (186-188) [14]
11		30	94	176-178 (178-180) [8]
12		60	85	169-171 (168-170) [8]

[a]Isolated yield.

(d, *J* = 17.4 Hz, 1H), 2.70 (d, *J* = 17.3 Hz, 1H), 5.76 (s, 1H), 6.97-7.00 (m, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.22 (s, 1H), 7.41-7.43 (m, 2H), 7.47-7.51 (m, 2H), 7.89-7.92 (m, 2H), 8.20 (d, *J* = 16 Hz, 1H).

9,9-Dimethyl-12-(3-bromorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 9). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.88 (s, 3H), 1.05 (s, 3H), 2.13 (d, *J* = 16.1 Hz, 1H), 2.31 (d, *J* = 16.1 Hz, 1H), 2.62 (Distorted AB System, 2H), 5.52 (s, 1H), 6.85 (d, *J* = 6.2 Hz, 1H), 7.03-7.07 (m, 2H), 7.11 (s, 1H), 7.40-7.50 (m, 3H), 7.89 (d, *J* = 8.7 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 27.0, 29.6, 32.7, 34.9, 41.1, 51.3, 114.1, 118.0, 118.2, 124.1, 125.8, 126.2, 127.7, 127.9, 128.8, 129.3, 129.5, 129.8, 131.5, 131.9, 137.9, 145.7, 148.0, 164.9, 196.7.

9,9-Dimethyl-12-(4-bromorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 10). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.86 (s, 3H), 1.04 (s, 3H), 2.12 (d, *J* = 16.0 Hz, 1H), 2.32 (d, *J* = 16.0 Hz, 1H), 2.61 (Distorted AB System, 2H), 5.56 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.40-7.49 (m, 3H), 7.90 (t, *J* = 5.0 Hz 2H), 7.98 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 27.1, 29.6, 32.7, 34.5, 41.0, 50.9, 113.5, 117.4, 118.0, 120.1, 124.0, 125.9, 128.1, 129.4, 130.2, 131.2, 131.3, 131.91, 131.96, 145.0, 148.0, 164.8, 196.7.

9,9-Dimethyl-12-(4-nitrophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 11). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ: 0.82 (s, 3H), 1.02 (s, 3H), 2.11 (d, *J* = 15.9 Hz, 1H), 2.32 (d, *J* = 16.2 Hz, 1H), 2.63 (Distorted AB System, 2H), 5.75 (s, 1H), 7.38-7.48 (m, 4H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.88-7.94 (m, 3H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ: 26.6, 29.1, 32.4, 34.4, 40.8, 50.4, 112.8, 116.4, 117.6, 121.9, 123.0, 123.6, 125.6, 127.9, 129.1, 130.2, 130.8, 131.5, 135.3, 147.3, 147.7, 148.0, 164.8, 196.4.

9,9-Dimethyl-12-(3-nitrophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (Table 3, entry 12). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 0.84 (s, 3H), 1.04 (s, 3H),

Table 3. The reaction of 2-naphthol with 4-nitrobenzaldehyde and dimedone using $[Et_3N\text{-}SO_3H]Cl$, NEt_3, $ClSO_3H$ and $[Et_3N\text{-}H]Cl$ under solvent-free conditions at 120 °C.

Entry	Catalyst	Time (min)	Yield[a] (%)
1	-	120	Trace
2	$[Et_3N\text{-}SO_3H]Cl$	30	94
3[b]	NEt_3	120	Trace
4	$ClSO_3H$	70	54
5	$[Et_3N\text{-}H]Cl$	90	36

[a]Isolated yield.
[b]Because of the low boiling point of NEt_3, this reaction was carried out at 85 °C.

2.13 (d, *J* = 16.0 Hz, 1H), 2.33 (d, *J* = 16.1 Hz, 1H), 2.64 (Distorted AB System, 2H), 5.77 (s, 1H), 7.40-7.49 (m, 4H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.89-7.95 (m, 3H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.17 (t, *J* = 1.8 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ: 27.0, 29.5, 32.7, 34.8, 41.7, 50.8, 113.2, 116.7, 117.0 118.0, 122.3, 123.4, 124.0, 126.0, 128.3, 129.5, 130.6, 131.2, 132.0, 135.6, 147.7, 148.1, 148.4, 165.2, 196.8.

3. Results and Discussion

Initially, the condensation of 2-naphthol with 4-nitrobenz aldehyde and dimedone was selected as a model reaction, and effect of the catalyst amount and temperature on it was studied under solvent-free conditions. The results are summarized in Table 1. As it can be seen in Table 1, the best yield and the reaction time were observed when 25 mol% of $[Et_3N\text{-}SO_3H]Cl$ was applied as catalyst at 120 °C. Increment the reaction temperature or the catalyst amount didn't improve the yield.

In order to assess the efficiency and the generality of the catalyst, 2-naphthol was reacted with different aromatic aldehydes (including benzaldehyde and aryl aldehydes bearing electron-donating substituents, halogens and electron-withdrawing substituents) and dimedone under the optimal reaction conditions. The results are displayed in Table 2. As Table 2 indicates, all reactions proceeded effectively and afforded the corresponding xanthene derivatives in high yield and in relatively short reaction times. Thus, $[Et_3N\text{-}SO_3H]Cl$ was highly efficient and general for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivatives.

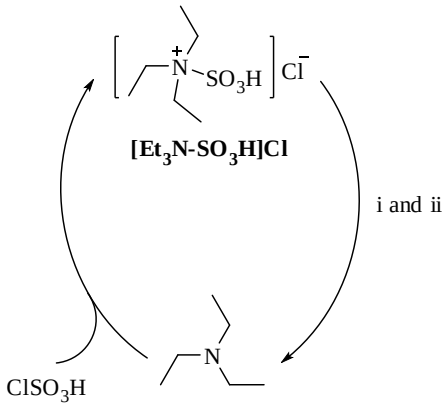
In another study, to prove the critical role of the catalyst to promote the reaction, the condensation between 2-naphthol 4-nitrobenzaldehyde and dimedone was examined in the presence of 25 mol% of the starting materials used for the preparation of the catalyst (i.e. NEt_3 and $ClSO_3H$) as well as the possible product formed by the reaction of NEt_3 with $ClSO_3H$ {this possible product is $[Et_3N\text{-}H][ClSO_3]$; however, there wasn't this compound in the Chemical Companies catalogs. Moreover, the acidic hydrogen of the cation of $[Et_3N\text{-}H][ClSO_3]$ can catalyze the reaction, not its anion. Thus, we used $[Et_3N\text{-}H]Cl$ instead of it} at 120 °C under solvent-free conditions; the respective results are summarized in Table 3. As it is shown in Table 3, $[Et_3N\text{-}SO_3H]Cl$ catalyzed the reaction in excellent yield and in short reaction time; NEt_3 gave trace yield of the product in long reaction time; and $ClSO_3H$ as well as $[Et_3N\text{-}H]Cl$ afforded moderate yields of the product in relatively long reaction times. Thus, triethylamine-bonded sulfonic acid had an essential role to promote the reaction.

To compare the efficiency of our method with the previously reported methods for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]-xanthen-11-one derivatives, we have tabulated the reaction results of these methods for the condensation of dimedone with benzaldehyde and β-naphthol in Table 4.

The data reported in Table 4 accompanied with the valuable advantages of our protocol relative to the reported protocols (which mentioned in the introduction) shows merit of our method in comparison with the literature methods. To raise the method worth, recyclability and reusability of the catalyst was studied. For this purpose, the reaction between 2-naphthol, 4-nitrobenzaldehyde and dimedone using $[Et_3N\text{-}SO_3H]Cl$ was carried out several times, and the reaction mixtures were combined. Afterward, H_2O was added to the combined reaction mixtures, stirred for 3 min, and filtered (the catalyst is soluble in H_2O; however, the reaction mixture is not soluble in H_2O). The solvent of the filtrate (containing the catalyst) was evaporated, and the liquid residue was triturated with t-butylmethyl ether (3 times) and dried under powerful vacuum at 90 °C; in this case, viscous pale yellow oil was obtained [31]. To confirm that the viscous oil is pure recycled $[Et_3N\text{-}SO_3H]Cl$, we run ^1H NMR spectrum of it. The spectrum showed that the recovered catalyst is not pure; we thought that few amount of $[Et_3N\text{-}SO_3H]Cl$ hydrolyzes by H_2O to give $[Et_3NH]Cl$ and H_2SO_4 [31]. Thus, we decided to regenerate the catalyst.

Table 4. Comparison of the results of the reaction of dimedone with benzaldehyde and β-naphthol using our method with those obtained by the reported methods.

Catalyst	Time (min)	Yield (%)	Ref.
$[Et_3N\text{-}SO_3H]Cl$	60	88	Our method
Proline triflate	300	79	7
$InCl_3$	30	84	8
P_2O_5	40	76	8
$Sr(OTf)_2$ in $Cl(CH_2)_2Cl$	300	85	9
PTSA/$[bmim]BF_4$	180	90	10
Dodecatungstophosphoric acid	70	86	11
$HClO_4/SiO_2$	72	89	12



i) The synthesis of the xanthenes

ii) Addition of NaOH solution

Scheme 3. The regenerate and reuse cycle of the catalyst.

For this purpose, after the addition of H_2O to the combined reaction mixtures, stirring and filtration, the filtrate (containing the catalyst) was basified by NaOH solution; in these conditions, $[Et_3N\text{-}SO_3H]Cl$ was converted to Et_3N and Na_2SO_4. Then, the solution was extracted with CH_2Cl_2 (for transferring NEt_3 to organic phase), washed with H_2O and dried over Na_2SO_4. The recovered NEt_3 in CH_2Cl_2 was reacted with chlorosulfonic acid according to the reported procedure to give $[Et_3N\text{-}SO_3H]Cl$ [31]. The catalytic activity of the reproduced catalyst was as same as the first one. The regenerate and reuse cycle of $[Et_3N\text{-}SO_3H]Cl$ is summarized in Scheme 3.

4. Conclusion

In conclusion, we have introduced a new catalyst for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones as biologically interesting compounds *via* the one-pot condensation of 2-naphthol with aromatic aldehydes and dimedone. $[Et_3N\text{-}SO_3H]Cl$ is an inexpensive catalyst with unique properties like environmental compatibility, operational simplicity, non-corrosive and easy for regenerability and reusability. Moreover, its starting materials are ready available. The advantages of the presented methodology are generality, efficiency, simple work-up procedure and purification, short reaction times, clean production of the products, low cost and finally good agreement with the green chemistry protocols.

Acknowledgements

The authors are respectfully acknowledged from Research Councils of the Payame Noor University for the provided financial supports of this work.

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