N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium chloride as a highly efficient catalyst for synthesis of some nitrogen- and oxygen-containing heterocyclic compounds

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Abstract

In this research, a Brønsted acidic ionic liquid namely N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium chloride $\{[TMBSED][Cl]_2\}$ was employed as a highly efficient catalyst for the solvent-free production of some nitrogen- and oxygen-containing heterocyclic compounds including: (i) polyhydroquinolines (from arylaldehydes, dimedone, β-ketoesters and ammonium acetate), (ii) 3,4-dihydropyrimidin-2-(1H)-ones/thiones (from arylaldehydes, β-ketoesters and urea/thiourea), and (iii) 14-aryl-14H-dibenzo[a,j]xanthenes (from aromatic aldehydes and β-naphthol). In all cases, the heterocycles were obtained in high yields and in short reaction times.

Keywords: Brønsted acidic ionic liquid; polyhydroquinoline; 3,4-dihydropyrimidin-2-(1H)-one; 3,4-dihydropyrimidin-2-(1H)-thione; 14-aryl-14H-dibenzo[a,j]xanthene.

Introduction

In recent years, preparation of ionic liquids and their applications, as solvent as well as catalyst in synthetic chemistry, have fascinated the attention of chemists; because ionic liquids have many useful properties which consist of low vapor pressure, high thermal and chemical stability, non-flammability, good solvating ability, tunable polarity, and capability to catalyze numerous organic transformations (especially acidic ionic liquid catalysts) [1-7]. They have been also used in the other areas of chemical industries consisting of application as matrices for mass spectroscopy, as electrolyte in batteries, as plasticizers and as lubricant, and in separation as well as extraction [8,9].

Among the nitrogen-containing heterocycles, polyhydroquinolines display a broad spectrum of biological and pharmacological activities such as geroprotective, vasodilator, anti-atherosclerotic, bronchodilator, antidiabetic and hepatoprotective properties [10-12]. This class of heterocycles has been also used as drugs for treatment of cardiovascular and Alzheimer's diseases, and as neuroprotectants and chemosensitizers in tumor therapy [13-15]. In view of the high importance of polyhydroquinolines, several catalysts have been developed to synthesize

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these compounds by the reaction of arylaldehydes with dimedone, β-ketoesters and ammonium acetate; some of these catalysts contain Fe_3O_4 nanoparticles [16], ZnO [17], $LaCl_3.7H_2O$ [18], organocatalyst [19], $BiBr_3$ [20], Co_3O_4-CNT nanocomposites [21], 1,3-disulfonic acid imidazolium hydrogen sulfate [22], Fe_3O_4@B-MCM-41 [23], and sulfonic acid functionalized SBA-15 [24].

The another important class of *N*-heterocycles is 3,4-dihydropyrimidin-2-(1*H*)-ones (and -thiones). These compounds have various pharmacological activities, such as antibacterial, antitumor, antiviral and antihypertensive properties [25-28]. The condensation reaction of aldehydes with β-ketoesters and urea (or thiourea) is the best protocol for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones. Several catalysts have been utilized to achieve this reaction, such as TiO_2 [29], sulfonated carbon [30], silica gel supported *L*-pyrrolidine-2-carboxylic acid-4-hydrogen sulfate [31], eutectic mixture choline chloride-chloroacetic acid [32], urease [33], $H_5PW_{10}V_2O_{40}$/Pip-SBA-15 [34], silica coated $NiFe_2O_4$ nanoparticles [35], *N*,*N*-diethyl-*N*-sulfoethanaminium hydrogen sulfate [36], and imidazol-1-yl-acetic acid [37].

Oxygen-containing heterocyclic compounds are also of importance. Xanthene derivatives are an important class of *O*-heterocycles which have a variety of biological activities such as anti-inflammatory, antiviral and antibacterial properties [38-40]. Furthermore, these compounds have been used in laser technology and visualization of biomolecules [41-42]. The best method for the synthesis of 14-aryl-14*H*-dibnzo[*a,j*]xanthenes, as a class of xanthenes, is the condensation

reaction between aromatic aldehydes and β-naphthol. Some catalysts have been used to promote this transformation, e.g. Sc[N(SO2C8F17)2]3 [43], nano-TiO2 [44], silver functionalized on hydroxyapatite-core-shell magnetic γ-Fe2O3 [45], pyrazinium di(hydrogen sulfate) [46], Ph3CCl [47], [H-NMP][HSO4] [48], triethylamine-bonded sulfonic acid [49], 1-carboxymethyl-3-methylimidazolium bromide [50] and 1-butyl-3-methyl imidazolium phosphotungstate [51].

Considering the high significance of ionic liquid-catalysts with Brønsted acidic property, and also extensive applications of polyhydroquinoline, 3,4-dihydropyrimidin-2-(1*H*)-one (-thione) and 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives, introducing a new Brønsted acidic ionic liquid-catalyst for the production of the aforesaid compounds is of importance.

In this research, Brønsted acidic ionic liquid N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium chloride {[TMBSED][Cl]$_2$} has been used as a highly effective catalyst to promote three significant kinds of organic reactions, including: (i) the synthesis of polyhydroquinolines by the reaction of arylaldehydes with dimedone, β-ketoesters and ammonium acetate, (ii) the preparation of 3,4-dihydropyrimidin-2-(1*H*)-ones (and -thiones) *via* the condensation of aldehydes with β-ketoesters and urea (or thiourea), and (iii) the production of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes from arylaldehydes and β-naphthol.

Experimental

All chemicals were purchased from Fluka or Merck 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 thin layer chromatography (TLC). The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^{1}H NMR (250, 300, 400 and 500 MHz) and ^{13}C NMR (62.5, 75, 100 and 125 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometers, δ in ppm. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model.

Procedure for the production of [TMBSED][Cl]₂

A solution of N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (5 mmol, 0.581 g) in dry CH₂Cl₂ (30 mL)

was added dropwise to a stirring solution of chlorosulfonic acid (10 mmol, 1.165 g) in dry CH₂Cl₂ (30 mL) over a period of 10 min, at 10 °C. After that, the reaction mixture was allowed to heat to room temperature (accompanied with stirring), and stirred for another 4 h. The solvent was evaporated under reduced pressure, and the liquid residue was triturated with dry petroleum ether (3×2 mL), and dried under powerful vacuum at 90 °C to give [TMBSED][Cl]₂ as a viscous pale yellow oil in 97% yield [5].
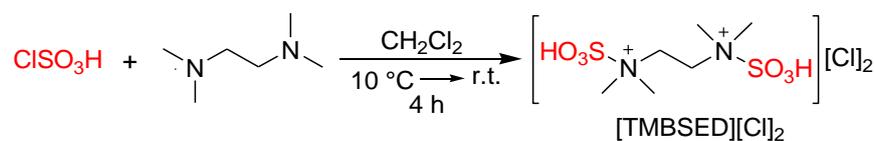
Scheme 1. The preparation of [TMBSED][Cl]₂

General procedure for the synthesis of polyhydroquinolines 1a-o

A mixture of compounds including arylaldehyde (1 mmol), dimedone (1 mmol, 0.140 g), β-ketoester (1 mmol), ammonium acetate (1.2 mmol, 0.093 g) and [TMBSED][Cl]₂ (0.025 mmol, 0.0088 g) was initially stirred magnetically at 40 °C, and after solidification of the reaction mixture, it was stirred by a small rod at the same temperature. The reaction progress was monitored by TLC; after completion, the reaction mixture was cooled to room temperature, and the resulting precipitate was recrystallized from EtOH (95%) to give the pure product. In few cases, the products were purified by short column chromatography on silica gel eluted *n*-hexane/ethyl acetate (4/1).

General procedure for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones 2a-o

A mixture of arylaldehyde (1 mmol), β-ketoester (1 mmol) and urea (1.2 mmol,

0.072 g) [or thiourea (1.2 mmol, 0.091 g)] and [TMBSED][Cl]₂ (0.05 mmol, 0.018 g) was firstly stirred magnetically at 70 ºC, and after solidification of the reaction mixture, it was stirred by a small rod at the same temperature. After the reaction was completed, as monitored by TLC, the reaction mixture was cooled to room temperature, and the resulting precipitate was recrystallized from EtOH (95%) to give the pure 3,4-dihydropyrimidin-2-(1*H*)-one (-thione).

General method for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes 3a-h

A mixture of arylaldehyde (1 mmol), β-naphthol (2 mmol, 0.289 g) and [TMBSED][Cl]₂ (0.15 mmol, 0.053 g) was initially stirred magnetically at 110 °C, and after solidification of the reaction mixture, it was stirred with a small rod at the same temperature. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled to room

temperature, and the resulting precipitate was recrystallized from EtOH (95%) to afford the pure 14-aryl-14*H*-dibenzo[*a,j*]xanthene.

Note: The "Supplementary Material" file consists of selected spectral data of the products.

Results and discussion

At the outset, the catalytic performance of [TMBSED][Cl]$_2$ was tested for the production of polyhydroquinolines from arylaldehydes, dimedone, β-ketoesters and ammonium acetate. To screen the optimal reaction conditions for this synthesis, the condensation between benzaldehyde, dimedone, methyl acetoacetate and ammonium acetate was chosen as a model reaction (Scheme 2), and studied in the presence of different amounts of [TMBSED][Cl]$_2$ at range of 25-50 °C under solvent-free conditions. The satisfactory results were obtained when the reaction was performed using 2.5 mol% of the catalyst at 40 °C (yield = 90%, and time = 5 min).
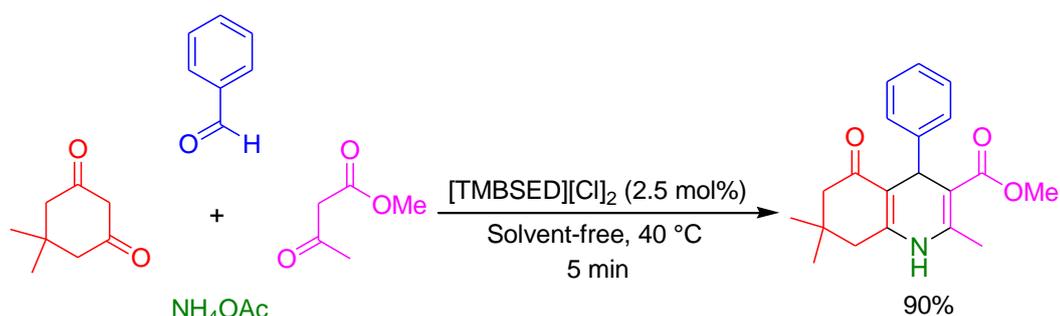
Scheme 2. The synthesis of polyhydroquinolines using [TMBSED][Cl]$_2$

The scope and efficacy of the catalyst, under the optimized conditions, were explored by the reaction between a variety of aromatic aldehydes, β-ketoesters, dimedone and ammonium acetate. The results are summarized in Table 1. As it can be seen in this Table, electron-deficient and electron-rich arylaldehydes worked well, leading to high yields of the desired polyhydroquinolines in short reaction times. The electronic effect seemed to have a slight influence on the reaction, since all substituents on the different positions of the aromatic ring gave high yields of the corresponding products in short times.

Table 1. The synthesis of polyhydroquinolines using [TMBSED][Cl]$_2$

Product	Ar	R	Time (min)	Yield^a (%)	M.p. °C (Lit.)
1a	C$_6$H$_5$	Et	6	90	204-206 (203-204) [16]
1b	3-NO$_2$-C$_6$H$_4$	Et	14	90	177-179 (175-176) [16]
1c	4-NO$_2$-C$_6$H$_4$	Et	10	93	245-247 (245-247) [21]
1d	2-Cl-C$_6$H$_4$	Et	9	90	207-209 (210-211) [21]
1e	3-Br-C$_6$H$_4$	Et	7	95	234-236 (235-237) [16]
1f	4-Br-C$_6$H$_4$	Et	5	93	254-256 (255-256) [22]
1g	3,4-di-OMe-C$_6$H$_3$	Et	7	96	205-206 (207-209) [24]
1h	4-OMe-C$_6$H$_4$	Et	9	95	257-259 (258-259) [21]
1i	4-Me-C$_6$H$_4$	Et	7	97	258-260 (256-258) [22]
1j	4-OH-C$_6$H$_4$	Et	9	97	232-234 (234-236) [22]
1k	4-NMe$_2$-C$_6$H$_4$	Et	15	88	259-261 (262-263) [19]
1l	C$_6$H$_5$	Me	5	90	(261-263) (260-262) [22]
1m	4-Cl-C$_6$H$_4$	Me	3	97	(221-222) (220-221) [16]
1n	3-Br-C$_6$H$_4$	Me	5	91	(224-226) (221-223) [22]
1o	4-OMe-C$_6$H$_4$	Me	5	90	(256-257) (257-259) [22]

^{a}Isolated yield

The proposed mechanism for the production of polyhydroquinolines is shown in Scheme 3. The mechanism is supported by the literature [16,22].
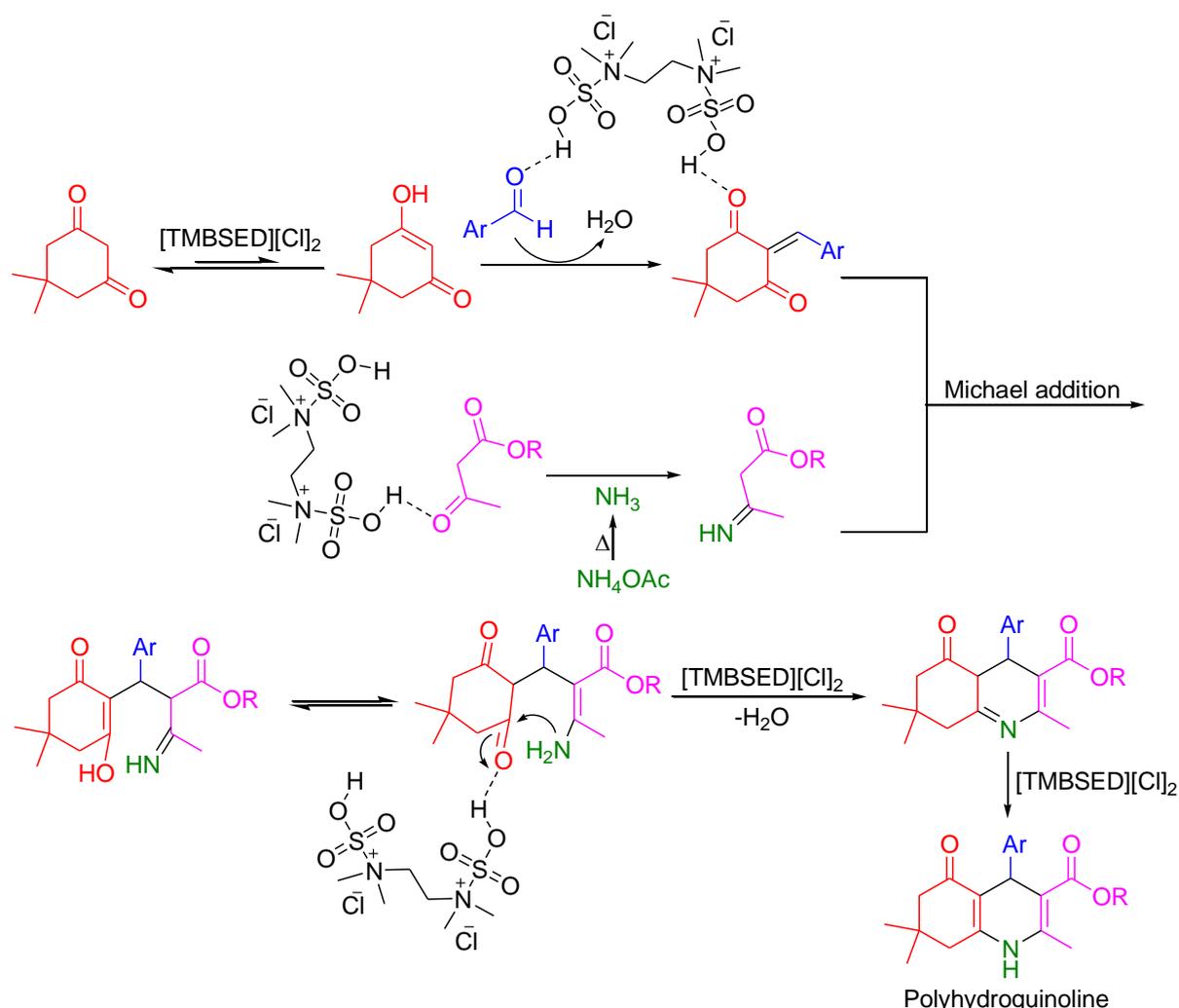
Scheme 3. The proposed mechanism for the preparation of polyhydroquinolines

The preparation of 3,4-dihydropyrimidin-2-(1*H*)-ones (and -thiones) was also tested using the ionic liquid as catalyst. For this purpose, as a model, the reaction of 3-nitrobenzaldehyde with ethyl acetoacetate and urea was checked using various molar ratios of [TMBSED][Cl]$_2$ at range of 50-80 °C (Scheme 4). Higher yield and shorter reaction time were observed when the reaction was carried out in the presence of 5 mol% of the catalyst at 70 °C (yield = 98%, and time = 12 min).
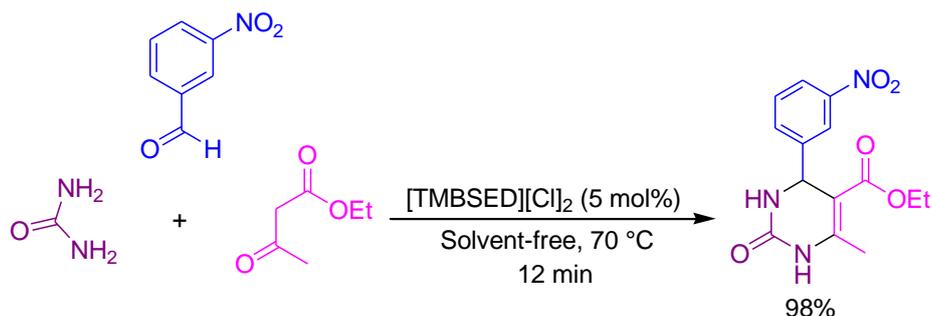

Scheme 4. The synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones catalyzed by [TMBSED][Cl]$_2$

After optimization of the reaction conditions, the efficiency and generality of [TMBSED][Cl]$_2$ to catalyze the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones (and thiones) were assessed by the reaction of arylaldehydes (having different substituents on various positions) with β-ketoesters (ethyl and methyl acetoacetate) and urea (or thiourea); the results are displayed in Table 2. As this Table indicates, both electron-deficient and electron-rich aromatic aldehydes afforded the corresponding products in high yields within short reaction times. The catalyst was also efficient when thiourea was used instead of urea.

Table 2. The solventless preparation of 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones using [TMBSED][Cl]$_2$
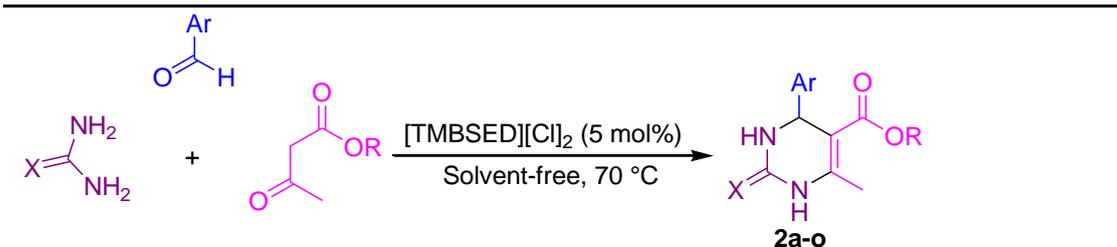

Product	Ar	R	X	Time (min)	Yield[a] (%)	Mp °C (Lit.)	
2a	C$_6$H$_5$	Et	O	15	98	205-207	(205-207)
2b	3-O$_2$NC$_6$H$_4$	Et	O	12	98	226-228	(222-224)
2c	4-O$_2$NC$_6$H$_4$	Et	O	10	95	210-212	(208-210)
2d	4-ClC$_6$H$_4$	Et	O	4	95	213-215	(215-217)
2e	3-BrC$_6$H$_4$	Et	O	20	96	189-191	(192-194)
2f	4-HOC$_6$H$_4$	Et	O	22	98	234-236	(234-236)
2g	4-MeC$_6$H$_4$	Et	O	40	95	214-216	(211-213)
2h	4-MeOC$_6$H$_4$	Et	O	60	92	202-204	(200-202)
2i	4-Me$_2$NC$_6$H$_4$	Et	O	60	95	255-257	(253-254)
2j	4-O$_2$NC$_6$H$_4$	Me	O	10	98	234-236	(232-234)
2k	4-ClC$_6$H$_4$	Me	O	10	95	205-208	(205-208)
2l	4-HOC$_6$H$_4$	Me	O	20	96	246-248	(247-249)
2m	3-O$_2$NC$_6$H$_4$	Et	S	60	90	205-207	(206-208)
2n	4-ClC$_6$H$_4$	Et	S	45	92	190-192	(192-193)
2o	3,4,5-(CH$_3$O)$_3$C$_6$H$_4$	Et	S	35	92	201-203	(200-202)

[a]Isolated yield

The proposed mechanism for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones, which supported by the literature [30], is shown in Scheme 5.
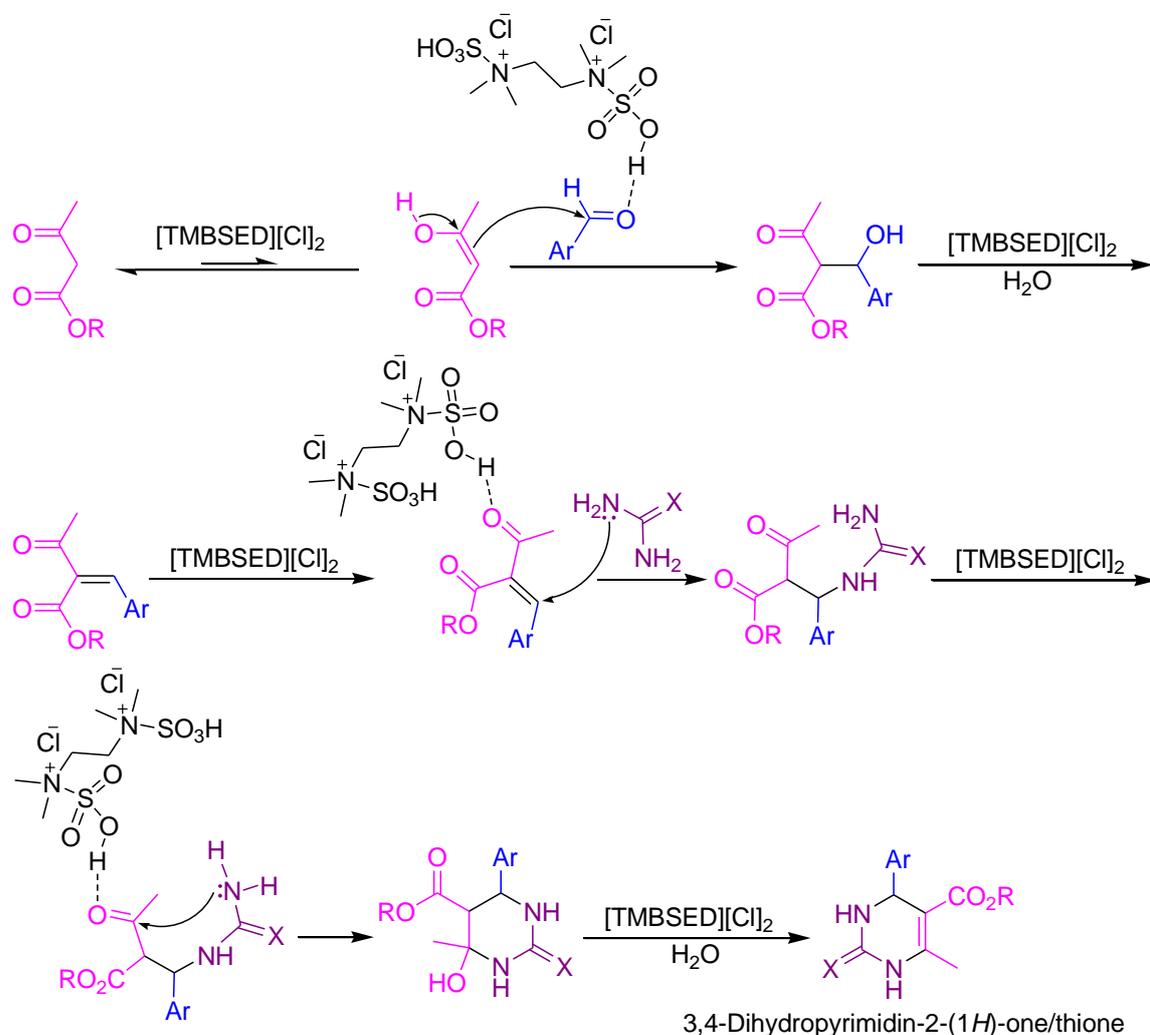
Scheme 5. The proposed mechanism for the preparation of 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones

The third reaction checked using [TMBSED][Cl]₂ as catalyst was the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes. Thus, the condensation of 3-nitrobenzaldehyde with β-naphthol was selected as a model reaction (Scheme 6), and its behavior was observed in the presence of different mol% of the ionic liquid at 90-115 °C. The best results were obtained when 15 mol% of the catalyst was utilized at 110 °C (yield = 98%, and time = 40 min).
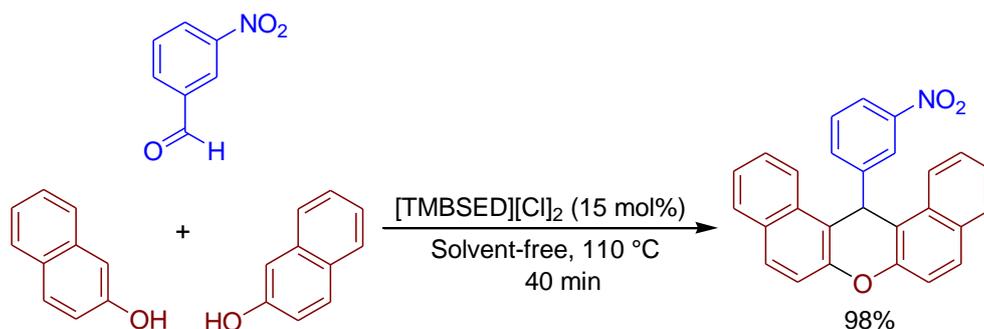
Scheme 6. The production of 14-aryl-14*H*-dibenzo[*a,j*]xanthene catalyzed by [TMBSED][Cl]$_2$

In order to show the efficiency and scope of the catalyst for the 14-aryl-14*H*-dibenzo[*a,j*]xanthenes synthesis, various electron-deficient and electron-rich arylaldehydes were reacted with β-naphtol using 15 mol% of [TMBSED][Cl]$_2$ at 110 °C; the corresponding results are shown in Table 3. As the Table indicates, all reactions were achieved efficiently, and afforded the corresponding 14-aryl-14*H*-dibnzo[*a,j*] xanthenes in excellent yields, and in relatively short reaction times.

Table 3. The reaction of arylaldehydes with 2-naphthol using [TMBSED][Cl]$_2$ leading to 14-aryl-14*H*-dibenzo[*a,j*]xanthenes.


Product	Ar	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
3a	C$_6$H$_5$	50	83	187-189 (185-187) [47]
3b	2-O$_2$NC$_6$H$_4$	50	96	211-213 (212-214) [49]
3c	3-O$_2$NC$_6$H$_4$	40	98	213-215 (215-217) [49]
3d	2-ClC$_6$H$_4$	40	86	208-210 (209-211) [49]
3e	4-ClC$_6$H$_4$	50	87	287-289 (284-286) [49]
3f	3-BrC$_6$H$_4$	60	85	184-186 (186-188) [49]
3g	4-MeOC$_6$H$_4$	60	86	197-199 (200-202) [47]
3h	4-MeC$_6$H$_4$	60	88	228-230 (227-229) [44]

[a]Isolated yield

The proposed mechanism for the production of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, which supported by the literature [45,47], is shown in Scheme 7.
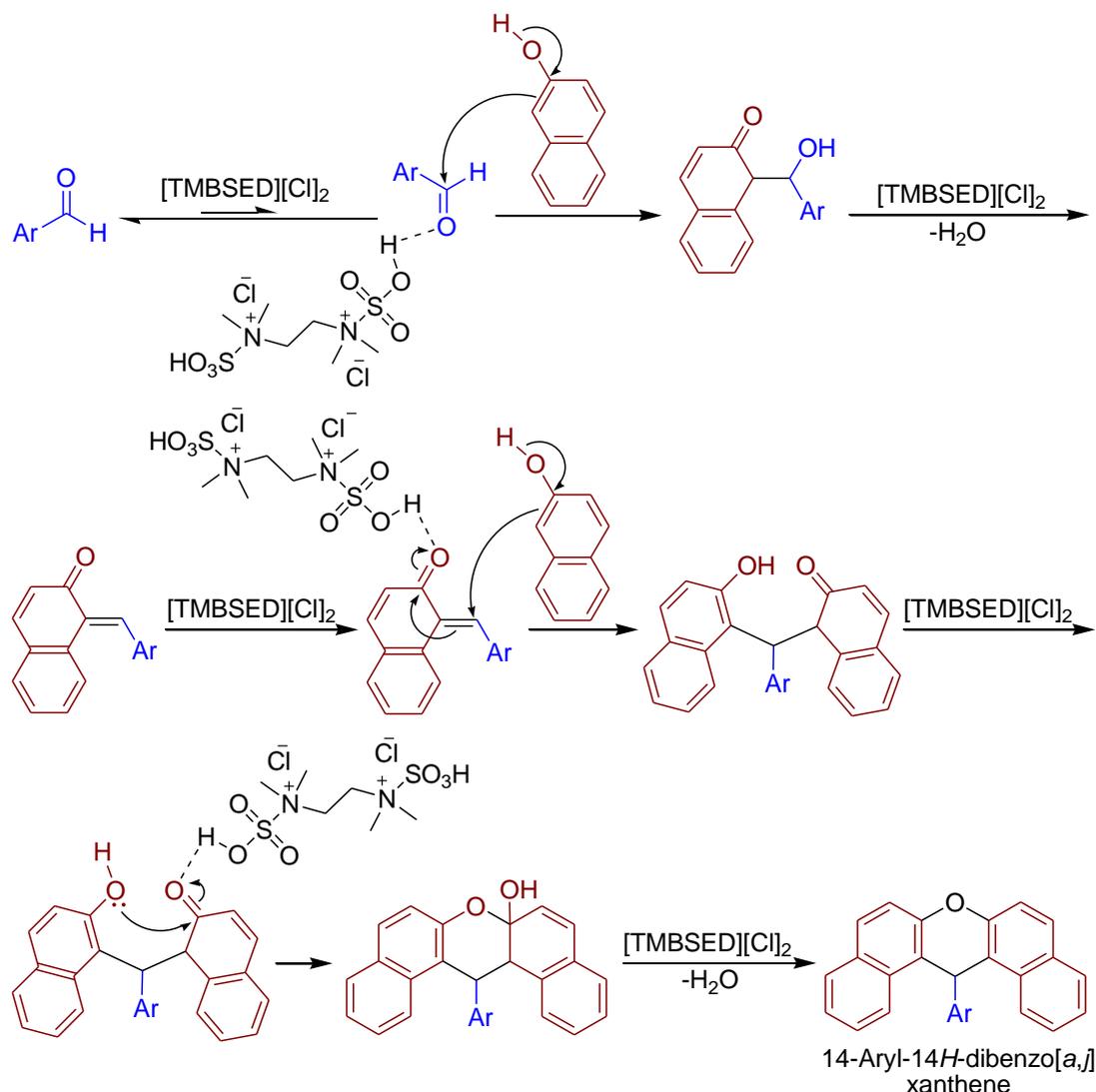
Scheme 7. The proposed mechanism for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes

Considering the above results, [TMBSED][Cl]$_2$ was highly efficient and general catalyst for the synthesis of polyhydroquinolines, 3,4-dihydropyrimidin-2-(1*H*)-ones, 3,4-dihydropyrimidin-2-(1*H*)-thiones and 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes.

Finally, to put the results obtained with [TMBSED][Cl]$_2$ as catalyst for the synthesis of polyhydroquinolines, 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones

and 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes into a better perspective, we compared the results and the reaction conditions of our catalyst with those of some reported catalysts. The results are summarized in Tables 4-6. The Tables clearly demonstrate [TMBSED][Cl]$_2$ to be superior in terms of one or more of these factors: yield, temperature, reaction media and time.

Table 4. Comparison of the results and reaction conditions of [TMBSED][Cl]$_2$ for the preparation of polyhydroquinolines with the reported catalysts.

Catalyst	Conditions	Time range	Yield range	Ref.
[TMBSED][Cl]$_2$	Solvent-free, 40 ℃	3-15	88-97	This work
Fe$_3$O$_4$ nanoparticles	Solvent-free, 60 ℃	5-28	85-96	[16]
ZnO	EtOH, 80 ℃	60	81-94	[17]
LaCl$_3$.7H$_2$O	EtOH, r.t.	60	30-210	[18]
L-Proline	Solvent-free, r.t.	30	93-96	[19]
BiBr$_3$	EtOH, r.t.	90-180	79-93	[20]
Co$_3$O$_4$-CNT nanocomposites	EtOH, reflux	30-45	88-98	[21]
[Dsim][HSO$_4$]^a	Solvent-free, 50 ℃	25-40	88-96	[22]
Fe$_3$O$_4$@B-MCM-41	EtOH, reflux	15-130	75-92	[23]
SO$_3$H-functionalized SBA-15	Solvent-free, 80 ℃	10-18	75-90	[24]

^{a}1,3-Disulfonic acid imidazolium hydrogen sulfate

Table 5. Comparison of the results and reaction conditions of [TMBSED][Cl]$_2$ for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones/thiones with the reported catalysts.

Catalyst	Conditions	Time range	Yield range	Ref.
[TMBSED][Cl]$_2$	Solvent-free, 70 ℃	4-60	90-98	This work
TiO$_2$	Solvent-free, 70 ℃	20-60	82-98	[29]
Sulfonated carbon	Solvent-free, 140 ℃	15-30	82-92	[30]
Silica supported *L*-pyrrolidine-2-carboxylic acid-4-hydrogen sulfate	EtOH, reflux	360	50-98	[31]
Catalyst-free	Choline chloride-chloroacetic acid, 70 H$_2$O, 70 ℃	5-75	70-95	[32]
Urease		150-210	85-97	[33]
H$_5$PW$_{10}$V$_2$O$_{40}$/Pip-SBA-15	Solvent-free, 100 ℃	33-225	46-98	[34]
Silica coated NiFe$_2$O$_4$ nanoparticles	EtOH, reflux	15-30	90-95	[35]
N,N-Diethyl-*N*-sulfoethanaminium hydrogen sulfate	Solvent-free, 70 ℃	15-100	86-98	[36]
Imidazol-1-yl-acetic acid	Solvent-free, 100 ℃	30-40	88-94	[37]

Table 6. Comparison of the results and reaction conditions of [TMBSED][Cl]$_2$ for the production of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes with the reported catalysts

Catalyst	Conditions	Time range	Yield range (%)	Ref.
[TMBSED][Cl]$_2$	Solvent-free, 110 ℃	40-60	83-98	This work
Sc[N(SO$_2$C$_8$F$_{17}$)$_2$]$_3$	Perfluorodecalin, 110 ℃	120-360	85-95	[43]
Ph$_3$CCl	Solvent-free, 120 ℃	60-130	83-96	[47]
[H-NMP][HSO$_4$]	Solvent-free, 110 ℃	8-20	80-96	[48]
Triethylamine-bonded sulfonic acid	Solvent-free, 120 ℃	15-40	92-97	[49]
1-Carboxymethyl-3-methylimidazolium bromide	Solvent-free, 115 ℃	15-30	83-95	[50]
1-Butyl-3-methyl imidazolium phosphotungstate	Solvent-free, 120 ℃	60-300	81-97	[51]

Conclusion

In summary, we have introduced acidic ionic liquid [TMBSED][Cl]$_2$ as a new and attractive catalyst for the production of polyhydroquinolines, 3,4-dihydropyrimidin-2-(1*H*)-ones (-thiones) and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes. The salient features of using [TMBSED][Cl]$_2$ in the reactions include effectiveness, generality, simple preparation of the catalyst from inexpensive and easy available reactants, achieving the reactions under solvent-free conditions, synthesis of the products with high yields in short reaction times and need to milder conditions compared with many reported methods for the preparation of the aforesaid organic compounds.

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