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Brønsted acidic imidazolium salts containing perfluoroalkyl tails catalyzed one-pot synthesis of 1,8-dioxo-decahydroacridines in water

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ABSTRACT

One-pot three-component synthesis of 1,8-dioxo-9,10-diaryl-decahydroacridines in water was efficiently realized in the presence of the Brønsted acidic imidazolium salts containing perfluoroalkyl tails in good yields. The method provided several advantages such as low catalyst loading; recycle of the catalyst and simple work procedure.

1. Introduction

Because of the great potential of room temperature imidazolium salts as environmentally benign media for catalytic processes [1], much attention has currently been focused on the organic reactions catalyzed with or in imidazolium salts, and many organic reactions, especially in the reactions promoted with acid–base catalysts, were performed in imidazolium salts with high performances [2]. An attractive feature of imidazolium salts is that their solubility, depending on the choice of cations and anions, can be tuned readily so that they can phase separate from organic as well as aqueous media [3]. Recently, the synthesis of "task-specific" imidazolium salts with special functions according to the requirement of a specific reaction have become an attractive field [4,5]. Task-specific imidazolium salts are a unique subclass of imidazolium salts which possess a potential spectrum of utility extending far beyond that likely for more conventional IL. By virtue of the incorporated functional groups, these unique salts can act not only as solvents but also as catalysts and reagents in an array of synthetic, separations and electrochemical applications.

Meanwhile, it is obvious that water is the most inexpensive and environmentally benign solvent. In light of the advantages of water and imidazolium salts respectively, we envisioned combination of these two advantages together by developing a task-specific imidazolium salts as organocatalyst used in water as solvent. Herein, we have developed a new type of Brønsted acidic imidazolium salts containing perfluoroalkyl tails (**6a** and **6b**) as a Brønsted acid–surfactant combined catalyst for the synthesis of 1,8-dioxo-decahydroacridine derivatives in water (Scheme 1). 1,8-Dioxo-9,10-diaryl-decahydroacridines and their derivatives are polyfunctionalized 1,4-dihydropyridine derivatives. Reportedly, the conventional synthesis of 1,4-dihydropyridine derivatives was performed in organic solvent such as HOAc [6], CH_3CN [7] and DMF [8]. There is only one literature about synthesis of those compounds in water [9], but the substrate amine was specialized in *p*-toluidine. Our group had reported the synthesis of β-amino carbonyl compounds [10] and homoallylic alcohols and amines [11] in sole water as solvent. Consequently, there is scope for further research toward simple work procedure, low catalyst loading, and expand of substrate for the synthesis of 1,8-dioxo-decahydroacridine.

2. Results and discussion

2.1. Synthesis of compound 6

The synthesis of the Brønsted acidic imidazolium salts **6a** was outlined in Scheme 2. First, 3-perfluorooctyl-1-propanol **2** was synthesized according to Qing's method [12] from the corresponding perfluoroalkyl iodide $C_8F_{17}I$. Compound **2** was then treated with KI in the presence of P_2O_5 and 85% H_3PO_4 to afford 3-perfluorooctyl-1-iodopropane **3** as described in the literature [13]. The next step proceeded by the conjunction of compound **3** with imidazole in the presence of NaOH to provide compound **4a** in 73% yield. The zwitterionic-type compound **5a** was obtained by one step reaction of compound **4a** and 1,3-propanesultone in dried

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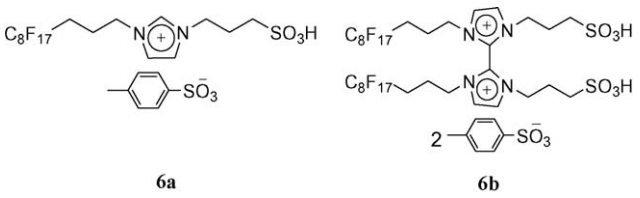


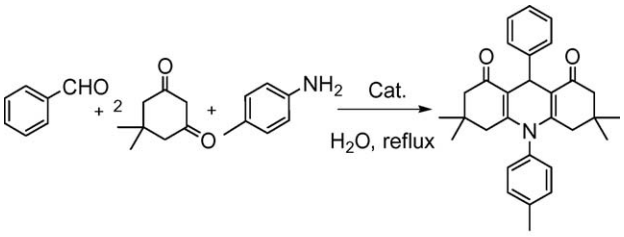
Scheme 1.

acetone. Finally, acidification of compound **5** with *p*-toluenesulfonic acid (PTSA) in refluxing ethanol gave the final product **6a**.

The synthesis of double fluorotailed acidic imidazolium salts **6b** was more or less the same as **6a** (Scheme 3). 2,2′-Biimidazole is an intriguing biaryl molecule which is prepared from glyoxal and ammonium acetate according to the literature elsewhere [14]. Alkylation of 2,2′-biimidazole with 3-perfluorooctyl-1-iodopropane occurred at N-1 and N-1′ to form 1,1′-di(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-2,2′-biimidazole **4b** in modest yields. Then under the nucleophlic attack of **4b**, 1,3-propanesultone underwent ring-opening reaction to afford zwitterion **5b**. Then, acidification of compound **5b** with *p*-toluenesulfonic acid (PTSA) in refluxing ethanol gave the final product **6b**.

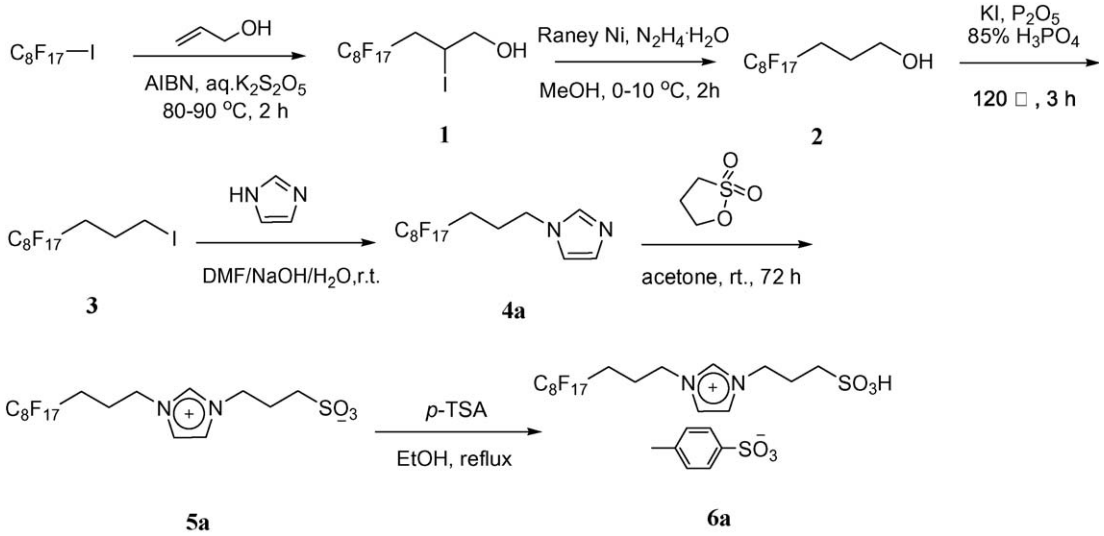
Washing **6a** and **6b** with toluene or diethyl ether results in no extraction of free PTSA (soluble in either liquid). This behavior was consistent with the donor acid being fully incorporated into the IL

Table 1
Screening of Brønsted acid catalyst for synthesis of **7a** in water.

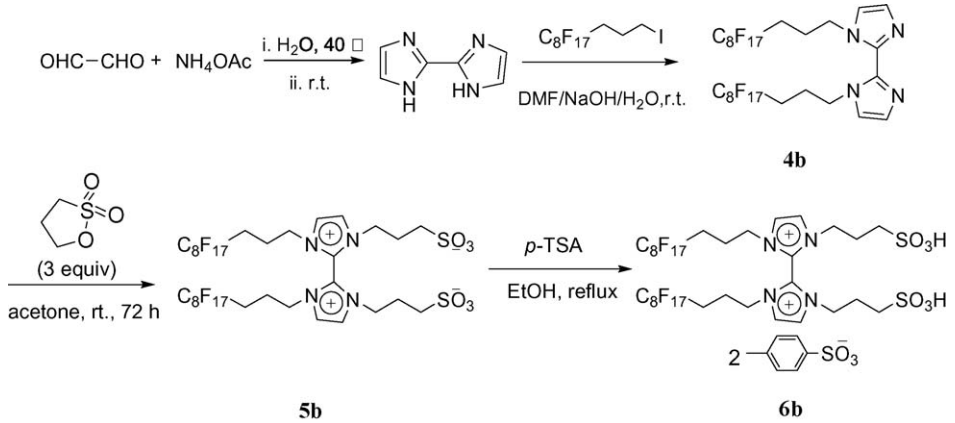


Entry	Cat.	Amount (mol%)	Time (h)	Yield (%)[a]
1	PTSA	2	6	18
2	SDS + PTSA	2 + 2	6	29
3	$C_{11}H_{23}COOH$	2	6	Trace
4	$C_7F_{15}COOH$	2	6	31
5	DBSA	2	6	41
6	**6a**	1	4	53
7	**6a**	2	4	71
8	**6b**	1	4	73
9	**6b**	1.5	4	86
10	**6b**	2	4	87
11	**6b**	1.5	4	84,81,82[b]

[a] Isolated yields.
[b] Catalytic system was reused for three times.

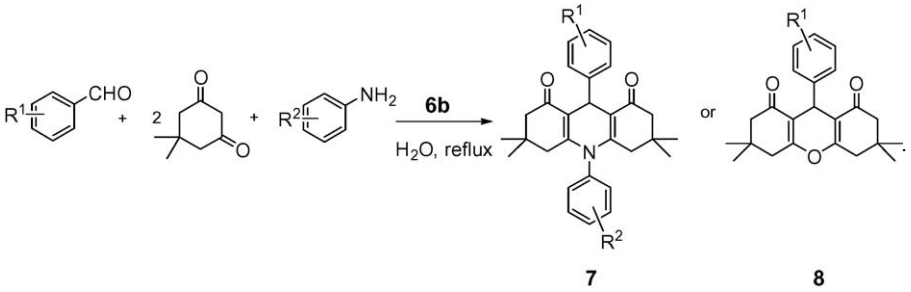


Scheme 2.



Scheme 3.

Table 2
Synthesis of different 1,8-dioxo-9,10-diaryl-decahydroacridines in the presence of **6b** in water[a]



Entry	R^1	R^2	Product	Yield (%)[b]	Mp (°C)	Lit. (°C)
1	H	4-CH_3	**7a**	86	260–262	262–263 [9]
2	4-CH_3	4-CH_3	**7b**	87	292–294	296–297 [15]
3	4-CH_3O	4-CH_3	**7c**	84	281–283	282–283 [9]
4	4-Cl	4-CH_3	**7d**	86	269–271	273–274 [9]
4	3-Cl	4-CH_3	**7e**	83	309–311	315–317 [9]
5	3-NO_2	4-CH_3	**7f**	91	283–284	285–286 [9]
6	3,4-Cl_2	4-CH_3	**7g**	81	250–252	251–253 [15]
7	H	4-CH_3O	**7h**	79	215–217	
8	4-CH_3	4-CH_3O	**7i**	87	238–241	
9	4-CH_3O	4-CH_3O	**7j**	90	210–211	
10	4-Cl	4-CH_3O	**7k**	85	251–252	
11	H	H	**8a**	85	203–205	208–209 [16]
12	H	4-Cl	**8a**	86	–	–
13	H	4-NO_2	**8a**	85	–	–

[a] All the reaction were carried out with 1.5 mol% of **6b** in water.
[b] Isolated yields.

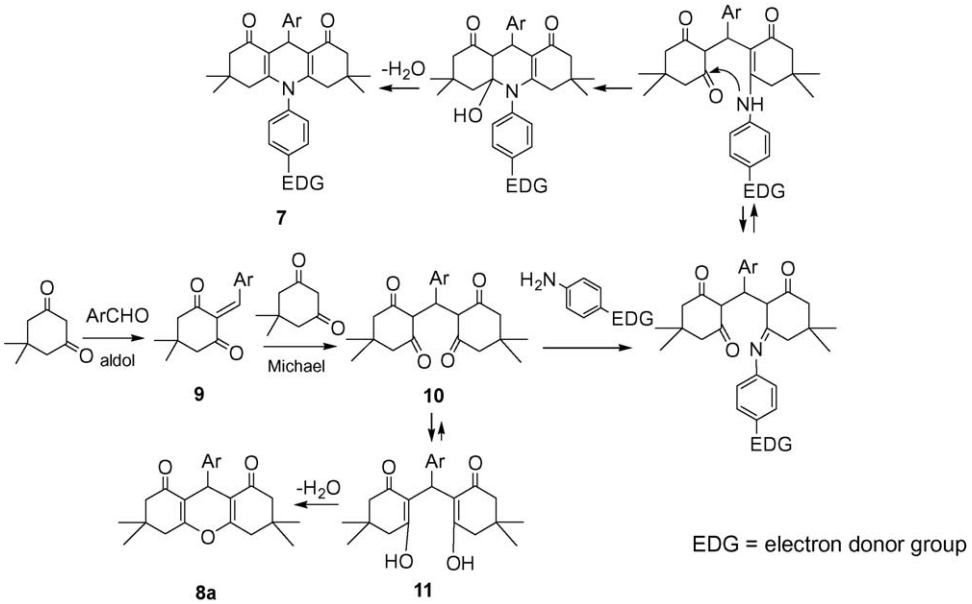
structure, rather than remaining simply mixtures of added strong acid with dissolved zwitterions, in which case some retention of premixing characteristics.

The Brønsted acidic imidazolium salts containing perfluoroalkyl tails **6a** and **6b** are stable in atmosphere with weak absorption of moisture. Both of them show good solubility in water. As a matter of fact, fluorous compounds **6a** and **6b** have potential use as surfactant, antimicrobial or Brønsted acidic catalyst which must be much more superior than their hydroalkyled counterparts. Here we first investigated their catalytic activities for three-component synthesis of 1,8-dioxo-decahydroacridine derivatives in water.

2.2. Synthesis of 1,8-dioxo-decahydroacridine derivatives

In a typical general experimental procedure, a solution of an aromatic aldehyde, 5,5-di- methyl-1,3-cyclohexanedione and *p*-toluidine in water was heated under refluxing water in the presence of various Brønsted acid for a certain period of time required to complete the reaction. The results were summarized in Table 1.

It was found that with only 1 mol% of **6a**, the reaction finished within 4 h and afforded modest yield which was even higher than that of *p*-dodecylbenzenesulfonic acid (DBSA), a Brønsted acid–surfactant combined catalyst. Owned two sulfonic acid groups,



Scheme 4.

compound **6b** was two more times effective than **6a**. With only 1.5 mol% amounts, **6b** provided as high as 86% yield. Further study showed that use of just 1.5 mol% of **6b** was sufficient to provided satisfied yield in 4 h. An increase in the amount of catalyst did not improve the result to any great extent. After the reaction was completed, the product would congregate to form a hard lump. Then, the separation of the product could simply be carried out by decanting the supernatant liquid which could be recycled. Thus, the catalyst could be reused for several times for the synthesis of **7a** without significant loss of activity.

After optimizing the reaction conditions, the catalytic system was applied to synthesize structurally diverse 1,8-dioxo-9,10-diaryl-decahydroacridine derivatives. The results were summarized in Table 2 which showed that aromatic amines substituted with electron-donating group gave expected molecules **7**, while the ones substituted with electron-withdrawing group or none gave compound **8**. The reason may be that aromatic amines substituted with electron-withdrawing group or none did not have enough nucleophilicity so the reaction stopped at Michael adduct stage and the adducts are quite readily cyclized to afford octahydroxanthones **8a** (Scheme 4). The effect of electron and the nature of substituents on the ring of aromatic aldehydes did not show expected strong effects in terms of yields under these reaction conditions. Benzaldehyde and other aromatic aldehydes were employed and they were found to react well to give the corresponding 1,8-dioxo-9,10-diaryl-decahydroacridine in good yields.

3. Conclusions

In summary, a novel type of Brønsted acidic imidazolium salts containing perfluoroalkyl tails was prepared. With little loading, the acidic imidazolium salts served as a highly effective catalyst for three-component one-pot synthesis of 1,8-dioxo-9,10-diaryl-decahydroacridines in water in good to excellent yields. The mother liquid containing catalyst could be easily recycled and reused without obvious loss of activities. Further studies of other use for compound **6a** and **6b** are in progress.

4. Experimental

4.1. Methods and apparatus

Melting points were determined on a Kofler hot plate. ^{1}H NMR spectra were recorded on a BRUKER AM 400 (400 MHz) using TMS as internal standard. ^{19}F NMR spectra were recorded on a BRUKER WP-500SY (376 MHz) spectrometer and were taken with $CFCl_3$ as internal standard. Coupling constants (J) are given in Hz. Elemental analysis was carried out by using a Perkin-Elmer 2400 CHNS analyzer. All solvents were distilled and dried according to the standard procedures. All the chemicals were of reagent grade and were used without further purification.

4.2. Synthesis of the Brønsted acidic IL 6

4.2.1. 1-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-1H-imidazole (4a)

In a 25 ml flask imidazole (3.4 mmol, 0.23 g), 6 ml DMF and 0.5 ml of 40% aqueous NaOH were stirred for 1 h. The mixture turned brown after which 3-perfluorooctyl-1-iodopropane **3** (3.7 mmol, 2.20 g) dissolved in DMF (3 ml) was added slowly. The mixture was stirred overnight at room temperature. The reaction crude was poured into H_2O (30 ml), extracted with chloroform (3 × 20 ml). The combined organic layer was washed with H_2O (3 × 20 ml), dried by Na_2SO_4. After evaporating the solvent, the residue was chromatographed on silica gel. Elution with CH_2Cl_2/CH_3OH (25:1) afforded the pure product (1.31 g, 73%).

White solid; Mp: 48–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04–2.14 (m, 4H), 4.06 (t, J = 6.6 Hz, 2H), 6.92 (s, 1H), 7.10 (s, 1H), 7.48 (s, 1H); MS (EI) m/z 528 (M^+). Anal. Calcd for $C_{14}H_9F_{17}N_2$: C, 31.83; H, 1.72; N, 5.30. Found: C, 31.78; H, 1.78; N, 5.24.

4.2.2. Single fluorotailed zwitterionic compound (5a)

Compound **4** (1.12 g, 2.1 mmol) was dissolved in acetone (4 ml), and then 1,3-propane sultone (0.26 g, 2.1 mmol) was added to the solution. The solution was stirred under dry nitrogen at room temperature for 72 h. The insoluble zwitterion was separated by filtration. It was further recrystallized from ethanol to give the pure product (0.71 g, 51%).

White solid; Mp 240–241 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 2.12–2.21 (m, 2H), 2.24–2.43 (m, 4H), 2.84 (t, J = 7.0 Hz, 2H), 3.47 (t, J = 7.8 Hz, 2H), 4.36 (t, J = 7.2 Hz, 2H), 7.72 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 1.6 Hz, 1H), 9.07 (s, 1H). MS (FAB) m/z: 651 [M+H]. Anal. Calcd for $C_{17}H_{15}F_{17}N_2O_3S$: C, 31.40; H, 2.32; N, 4.31. Found: C, 31.49; H, 2.38; N, 4.40.

4.2.3. Single fluorotailed Brønsted acidic imidazolium salts (6a)

In a 25 ml flask equimolar quantities of PTSA hydrate and the zwitterion **5** was dissolved in 10 ml ethanol, the mixture was heated to reflux for 2 h and then cooled to room temperature. The solvent was removed in reduced pressure, and the residue was washed repeatedly with toluene and ether to remove nonionic residues, and dried in vacuum. The product was formed quantitatively with high purity.

White solid; Mp: 127–129 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 2.08 (m, 4H), 2.14 (m, 2H), 2.32 (s, 3H), 2.50 (t, J = 7.0 Hz, 2H), 2.71 (t, J = 7.8 Hz, 2H), 4.12 (t, J = 7.2 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.36 (s, 1H), 7.56 (s, 1H), 7.65 (d, J = 8.8 Hz, 2H), 8.92 (s, 1H); ^{19}F NMR (376 MHz, CD_3OD): δ = −80.74 (t, J = 7.5 Hz, 3F), −114.22 (t, J = 15.0 Hz, 2F), −121.89 (m, 6F), −122.70 (s, 2F), −123.41 (s, 2F), −126.08 (s, 2F); ESI-MS: 651.06 [cation]$^+$. Anal. Calcd for $C_{24}H_{23}F_{17}N_2O_6S_2$: C, 35.04; H, 2.82; N, 3.41. Found: C, 35.11; H, 2.76; N, 3.48.

4.2.4. 1,1′-di(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-2,2′-biimidazole (4b)

Following the general procedure for N-alkylation described for compound **4a**, two equivalents of **3** was used, and the crude product was purified by chromatography (CH_2Cl_2/CH_3OH, 20:1) to afford **4b** (56%).

White solid; Mp: 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06–2.14 (m, 8H), 4.65 (t, J = 6.4 Hz, 4H), 6.99 (s, 2H), 7.12 (s, 2H); MS (FAB) m/z: 1055 [M+H]$^+$. Anal. Calcd for $C_{28}H_{16}F_{34}N_4$: C, 31.89; H, 1.53; N, 5.31. Found: C, 31.81; H, 1.62; N, 5.27.

4.2.5. Double fluorotailed zwitterionic compound (5b)

Following the general procedure described for compound **5a**, three equivalents of 1,3-propanesultone were used to give **5b** as a white solid (53%).

White solid; Mp: 281–283 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 2.12–2.21 (m, 4H), 2.24–2.43 (m, 8H), 2.84 (t, J = 7.0 Hz, 4H), 3.47 (t, J = 7.8 Hz, 4H), 4.36 (t, J = 7.2 Hz, 4H), 7.47 (d, J = 2.0 Hz, 2H), 7.58 (d, J = 1.6 Hz, 2H); MS (FAB) m/z: 1299 [M+H]. Anal. Calcd for $C_{34}H_{28}F_{34}N_4O_6S_2$: C, 31.44; H, 2.17; N, 4.31. Found: C, 31.51; H, 2.09; N, 4.36.

4.2.6. Double fluorotailed Brønsted acidic imidazolium salts (6b)

Following the general procedure described for compound **6a**, two equivalents of PTSA were used to give **6b** in quantitative yield.

White solid; Mp: 157–159 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 2.11–2.23 (m, 4H), 2.26–2.43 (m, 8H), 2.35 (s, 6H), 2.84 (t, J = 7.0 Hz, 4H), 3.47 (t, J = 7.8 Hz, 4H), 4.36 (t, J = 7.2 Hz, 4H), 7.32 (s,

4H), 7.57 (d, J = 2.0 Hz, 2H), 7.66 (s, 4H), 7.74 (d, J = 1.6 Hz, 2H); ^{19}F NMR (376 MHz, CD_3OD): δ = −81.46 (t, J = 7.5 Hz, 6F), −113.52 (t, J = 15.0 Hz, 4F), −122.30 (m, 4F), −122.41 (m, 8F), −123.25 (s, 4F), −123.96 (s, 4F), −126.64 (s, 4F); ESI-MS: 650.43 [cation]$^{2+}$. Anal. Calcd for $C_{48}H_{44}F_{34}N_4O_{12}S_4$: C, 35.09; H, 2.70; N, 3.41. Found: C, 35.13; H, 2.76; N, 3.38.

4.3. General procedure for the preparation of 7

A mixture of an aromatic aldehyde (1.0 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2.0 mmol), an aromatic amine (1.0 mmol) and compound **6b** (1.5 mol%) in water (8 ml) was stirred at reflux for 4 h. After completion of the reactions, the mixture was cooled to r.t. and solid was filtered off and washed with H_2O (40 ml) and the crude products were obtained. The crude products were purified by recrystallization from EtOH. The mother solution containing of the catalyst could be reused again.

The spectral (^{1}H NMR and MS) and analytical data of all the compounds are given below. Among which **7h–k** were unknown compounds.

*3,3,6,6-Tetramethyl-1,8-dioxo-9-benzene-10-(4-methylphenyl)-decahydroacridine (**7a**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 6H), 0.95 (s, 6H), 1.89 (d, J = 16.0 Hz, 2H), 2.05–2.21 (m, 6H), 2.50 (s, 3H), 5.34 (s, 1H), 7.11 (d, J = 6.4 Hz, 2H), 7.18–7.26 (m, 5H), 7.36 (d, J = 6.4 Hz, 2H); MS (EI) m/z 439 (M^+).

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-methylphenyl)-10-(4-methylphenyl)-decahydroacridine (**7b**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (s, 6H), 0.95 (s, 6H), 1.83 (d, J = 17.4 Hz, 2H), 2.05–2.21 (m, 6H), 2.49 (s, 3H), 2.61 (s, 3H), 5.23 (s, 1H), 6.82 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 8.4 Hz, 4H); MS (EI) m/z 453 (M^+).

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-methoxyphenyl)-10-(4-methylphenyl)-decahydroacridine (**7c**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (s, 6 H), 0.94 (s, 6H), 1.83 (d, J = 18.0 Hz, 2H), 2.04–2.21 (m, 6H), 2.48 (s, 3H), 3.75 (s, 3H), 5.21 (s, 1H), 6.79 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 4.8 Hz, 4H); MS (EI) m/z 469 (M^+).

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-chlorophenyl)-10-(4-methylphenyl)-decahydroacridine (**7d**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (s, 6H), 0.94 (s, 6H), 1.83 (d, J = 17.4 Hz, 2H), 2.05–2.21 (m, 6H), 2.49 (s, 3H), 5.23 (s, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 8.4 Hz, 4H); MS (EI) m/z 473 (M^+).

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(3-chlorophenyl)-10-(4-methylphenyl)-decahydroacridine (**7e**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (s, 6H), 0.92 (s, 6H), 1.84 (d, J = 16.8 Hz, 2H), 2.08–2.24 (m, 6H), 2.48 (s, 3H), 5.36 (s, 1H), 7.12 (s, 1H), 7.18 (d, J = 7.6 Hz, 2H), 7.22–7.30 (m, 3H), 7.36 (d, J = 6.4 Hz, 2H); MS (EI) m/z 473 (M^+).

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(3-nitrophenyl)-10-(4-methylphenyl)-decahydroacridine (**7f**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (s, 6H), 0.95 (s, 6H), 1.89 (d, J = 16.2 Hz, 2H), 2.04–2.21 (m, 6H), 2.53 (s, 3H), 5.40 (s, 1H), 7.12 (d, J = 6.4 Hz, 2H), 7.23–7.32 (m, 4H), 7.34 (d, J = 6.4 Hz, 2H); MS (EI) m/z 484 (M^+).

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(3,4-dichlorophenyl)-10-(4-methylphenyl)-decahydroacridine (**7g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (s, 6H), 0.92 (s, 6H), 1.89 (d, J = 16.0 Hz, 2H), 2.06–2.24 (m, 6H), 2.54 (s, 3H), 5.38 (s, 1H), 6.89–6.93 (m, 2H), 7.18 (d, J = 7.6 Hz, 2H), 7.24 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H); MS (EI) m/z 507 (M^+).

*3,3,6,6-Tetramethyl-1,8-dioxo-9-benzene-10-(4-methoxyphenyl)-decahydroacridine (**7h**).* IR (KBr): 3062, 2960, 2875, 1665, 1588, 1490, 1395, 1126 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (s, 6H), 0.95 (s, 6H), 1.85 (d, J = 18.4 Hz, 2H), 2.05–2.21 (m, 6H), 3.92 (s, 3H), 5.27 (s, 1H), 7.04 (d, J = 7.8 Hz, 2H), 7.11 (t, J = 7.6 Hz, 3H), 7.25 (m, 2H), 7.42 (d, J = 7.2 Hz, 2H); MS (EI) m/z 455 (M^+). Anal. Calcd for $C_{30}H_{33}NO_3$: C, 79.09; H, 7.30; N, 3.07. Found: C, 79.15; H, 7.28; N, 2.91.

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-methylphenyl)-10-(4-methoxyphenyl)-decahydroacridine (**7i**).* IR (KBr): 3058, 2983, 2930, 2895, 1653, 1582, 1485, 1378, 1170, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 6H), 0.95 (s, 6H), 1.83 (d, J = 18.0 Hz, 2H), 2.04–2.21 (m, 6H), 2.43 (s, 3H), 3.92 (s, 3H), 5.21 (s, 1H), 6.79 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 4.8 Hz, 4H); MS (EI) m/z 469 (M^+). Anal. Calcd for $C_{31}H_{35}NO_3$: C, 79.28; H, 7.51; N, 2.98. Found: C, 79.33; H, 7.47; N, 2.87.

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-methoxyphenyl)-10-(4-methoxyphenyl)-decahydroacridine (**7j**).* IR (KBr): 3077, 2980, 2926, 2865, 1645, 1582, 1474, 1387, 1152, 1135 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (s, 6H), 0.96 (s, 6H), 1.86 (d, J = 18.0 Hz, 2H), 2.04–2.22 (m, 6H), 3.75 (s, 3H), 3.92 (s, 3H), 5.21 (s, 1H), 6.78 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 6.8 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H); MS (EI) m/z 485 (M^+). Anal. Calcd for $C_{30}H_{32}ClNO_2$: C, 76.67; H, 7.26; N, 2.88. Found: C, 76.74; H, 7.37; N, 2.79.

*3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-chlorophenyl)-10-(4-methoxyphenyl)-decahydroacridine (**7k**).* IR (KBr): 3024, 2973, 2925, 2885, 1640, 1578, 1535, 1460, 1305, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 6H), 0.97 (s, 6H), 1.86 (d, J = 17.4 Hz, 2H), 2.06–2.23 (m, 6H), 3.93 (s, 3H), 5.25 (s, 1H), 7.05 (d, J = 7.8 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.25 (m, 2H), 7.42 (d, J = 7.2 Hz, 2H); MS (EI) m/z 489 (M^+). Anal. Calcd for $C_{30}H_{32}ClNO_3$: C, 73.53; H, 6.58; N, 2.86. Found: C, 73.46; H, 6.71; N, 2.88.

*3,3,6,6-Tetramethyl-1,8-dioxo-9-benzene-octahydroxanthene (**8a**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 6H), 1.23 (s, 6H), 2.30–2.48 (m, 8H), 5.54 (s, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.25–7.28 (m, 2H); MS (EI) m/z 350 (M^+). Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.74; H, 7.59.

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