Chapter 4

Evaluation of N, N-disulfo-1, 1, 3, 3-tetramethylguanidinium carboxylate ionic liquids as reusable homogeneous catalysts for multicomponent synthesis of tetrahydrobenzo[a]xanthenone and tetrahydrobenzo[a]acridinone derivatives

4.1. Introduction

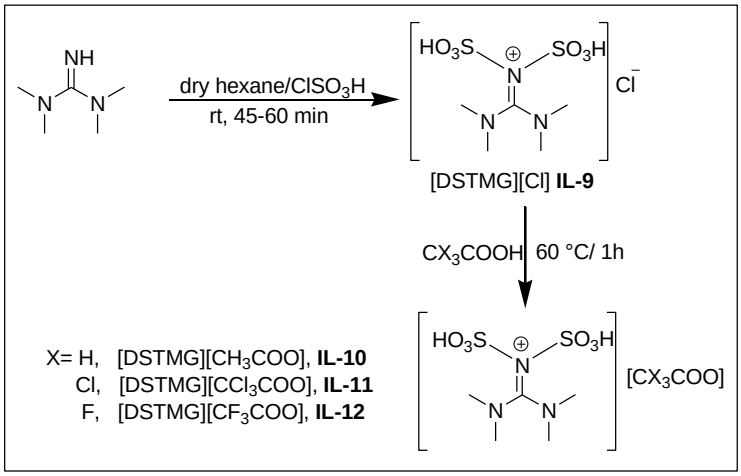
The work in this chapter has focused on the synthesis and characterization of three new members of 1, 1, 3, 3-tetramethylguanidinium (TMG) based carboxylate ionic liquids bearing $–SO_3H$ group in the cation [DSTMG][CX_3COO] where X= H, Cl, F using NMR, FT-IR, UV-visible and thermogravimetric analysis (**Scheme-4.1**). A large number of Brønsted acidic ionic liquids (ILs) bearing $–SO_3H$ have been observed in the review section (**Chapter-1, section 1.3**) using either imidazolium or N-heterocycle as carbocation in combination with organic or inorganic anions. However examples were found in literature for the synthesis of TMG-based sulfonic acid functionalized ionic liquids. TMG is a strong organic base with pKa value of 15.2 in aqueous solution which generates stable-acyclic guanidine cation by protonation of basic imino nitrogen (= NH) [1-3]. The unusual thermodynamic stability of guanidine cation is attributed for resonance stabilization via delocalization of positive charge over two amino nitrogen, Y-aromaticity and solvation of the protonated form [3]. Therefore, there is a scope to generate new disulfonic functionalized TMG-based carboxylate ILs [DSTMG][CX_3COO] as reusable acid catalysts for the multicomponent synthesis of tetrahydrobenzo[a]xanthenones and tetrahydrobenzo[a]acridinones under environmentally benign conditions. The acidity of such IL depends on the strength of ionic interaction between N, N-disulfo-tetramethylguanidinium cation and carboxylate anion which can easily be monitored from Hammett acidity study [4]. The literature review in the first chapter revealed the lack of use of reusable ionic liquid or acidic catalyst for the different multicomponent (MC) synthesis of tetrahydrobenzo[a]acridinone derivatives including the three component reactions of 2-naphthylamine, dimedone and aromatic aldehyde [5-6]. Till date, no reports are available for the four component synthesis of this nitrogen containing heterocycle. In our study we have synthesized the above heterocycle from the reaction of 2-naphthol, dimedone, aromatic aldehydes and ammonium chloride in presence of acid catalyst.

At the same time, several groups efficiently utilized neutral or acidic ionic liquids as catalyst or medium for the MC synthesis of tetrahydrobenzo[a]xanthenone derivatives in solvent-free thermal energy or microwave irradiation during shorter to longer reaction time [7-9] .Under thermal condition, some of those ILs mediated methods needed high temperature (100-120°C) to produce better results [9-10].

4.2. Results and Discussion

4.2.1. Preparation and characterization of ILs

We have synthesized the three acidic N, N-disulfo-tetramethylguanidinium carboxylate ILs such as [DSTMG][CH_3COO] (**IL-10**), [DSTMG][CCl_3COO] **(IL-11**) and [DSTMG][CF_3COO] (**IL-12**) from the reaction of N, N-disulfotetramethylguanidinium chloride [DSTMG][Cl] (**IL-9**) with equivalent amount of carboxylic acid (AcOH, CCl_3COOH and CF_3COOH) at 60 °C in hexane for 45-60 min stirring (**Scheme-4.1**). All these ILs were characterized using different spectroscopic and analytical tools which are discussed below.



Scheme-4.1: Synthetic route of TMG-based –SO_3H functionalized ILs

4.2.1.1. Spectral analysis

Fig.4.1 expressed the various characteristic absorption peaks for –SO_3H groups, and stable-guanidinium cation in the IR region within 600-2000 cm^{-1} for the four synthesized ILs. The symmetric and antisymmetric S-O stretching frequencies were observed at 1141-1161 cm^{-1} and 1027-1038 cm^{-1} of –SO_3H groups. The peak at 860-871 cm^{-1} represented the stretching vibration of N-S bond. The strong absorption peak around 1608-1613 cm^{-1} confirmed the attachment of carboxylate anion with N, N-disulfo-tetramethylguanidinium cation. Furthermore, the band at 1560-1568 cm^{-1} can be assigned for the -C= N- stretching vibration of guanidinium cation. The smaller peak at 1409-1413 cm^{-1} may be attributed for C-H bending and rocking vibration. The absence of two -NH_2 stretching vibrations at 3474 cm^{-1} and 3398 cm^{-1} eliminated the formation of tetramethylguanidinium chlorosulfonate IL as reported by Reddi *et al* and Kala *et al* [11-12].

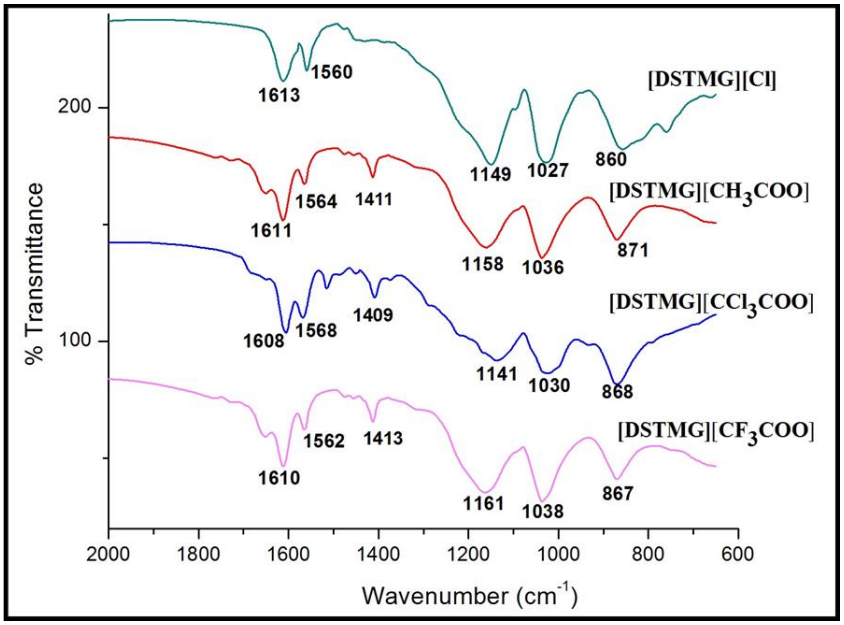


Fig.4.1: FT-IR spectra of three ionic liquids

The typical ^{1}H NMR and ^{13}C NMR spectra of **IL-12** was displayed the **Fig.4.2**. The single peak around 12-12.4 ppm for two proton in ^{1}H NMR spectra of the three ILs in DMSO-d_6 confirmed the attachment of two -SO_3H groups in the imino (=NH) nitrogen of tetramethylguanidinium cation **(Fig.4.2b)**. The twelve protons of two –NMe_2 groups appeared as singlet in the region 3-3.2 ppm. The presence of characteristic C= O signal at 155-170 ppm in ^{13}C NMR spectra fully supported the existence of carboxylate anions in each ionic liquid **(Fig.4.2c)**. The four N-methyl carbons appeared at 38.8 ppm which is also agreements with the literature data [11]. Interestingly, the same spectra displayed two peaks in the aromatic region around 134.7 ppm and 119.9 ppm in contrast to reported value of C= N carbon at 161.0 ppm by Kim *et al* [12]. These two peaks can be easily attributed for two types of chemical environment of C= N carbon present in the resonating structures of N, N-disulfo tetramethylguanidinium cations as shown in **Fig.4.2a**. Further evidences were observed from the elemental analysis data of the three ILs.

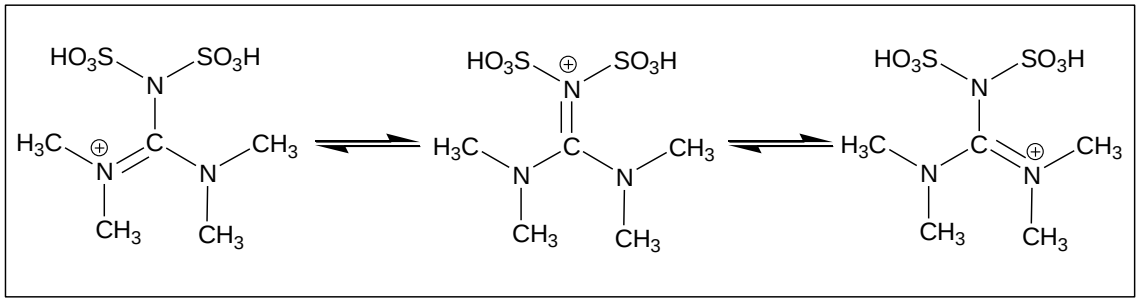


Fig.4.2a: Resonating structure of N, N-disulfotetramethylguanidinium cation

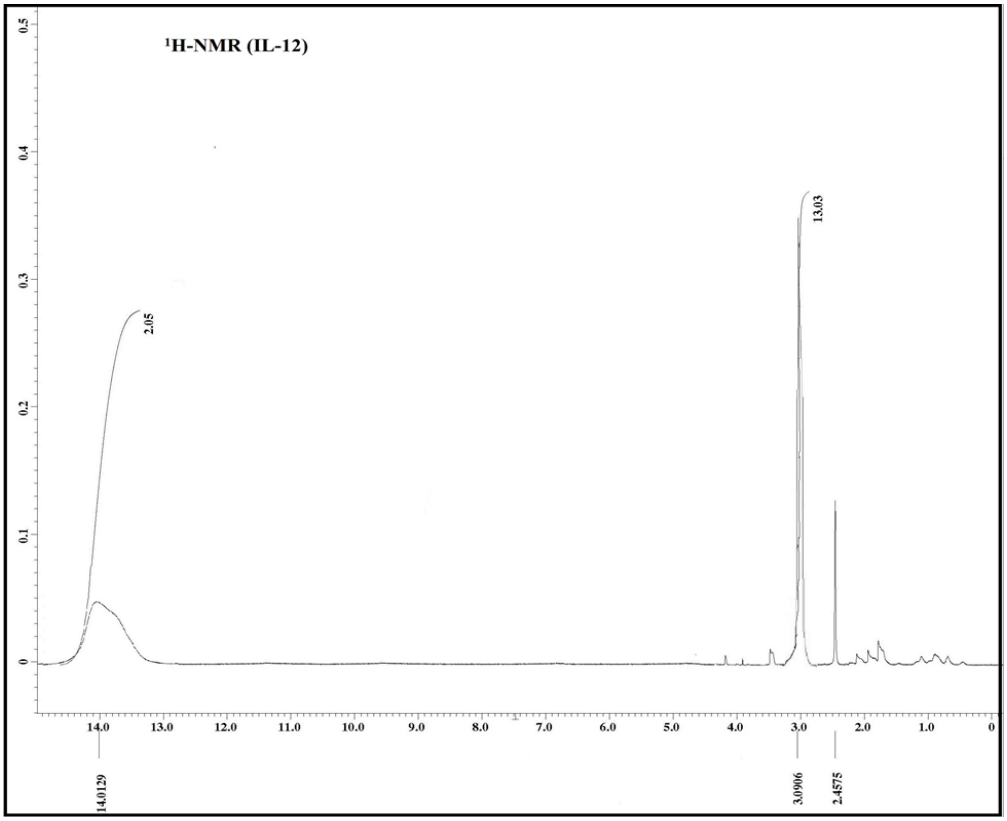


Fig.4.2b: ^{1}H NMR spectrum of **IL-12**

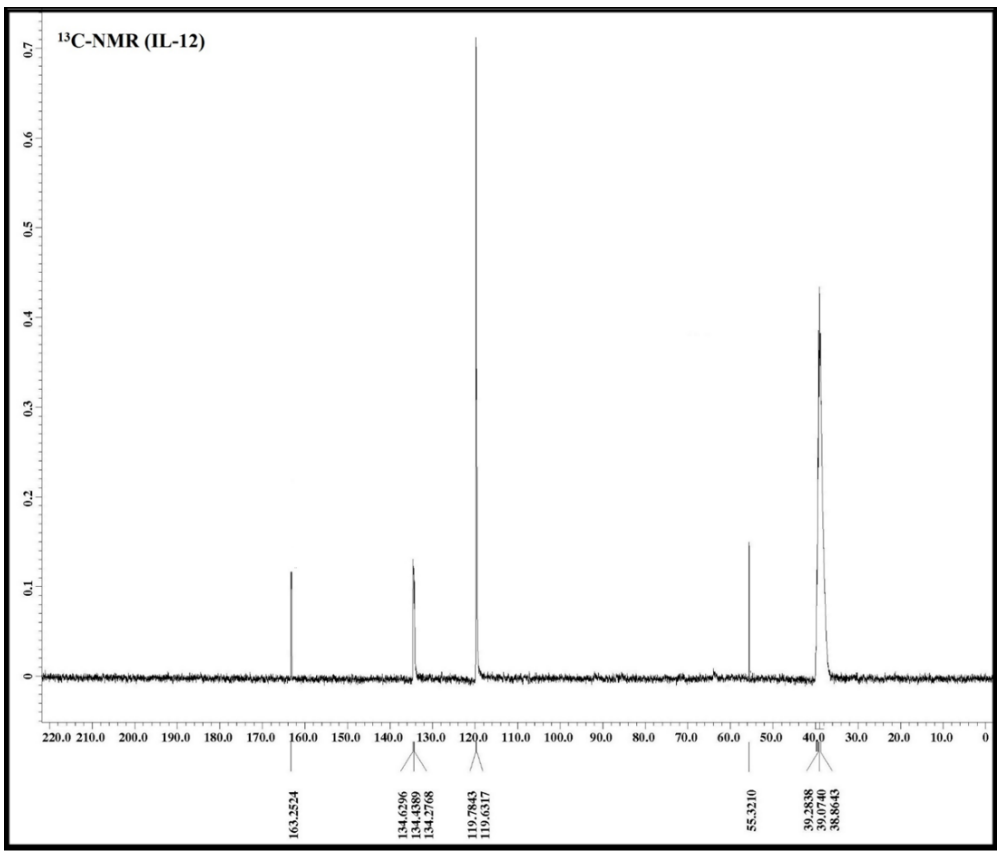


Fig.4.2c: ^{13}C NMR spectrum of **IL-12**

4.2.1.2. Thermogravimetric analysis (TGA)

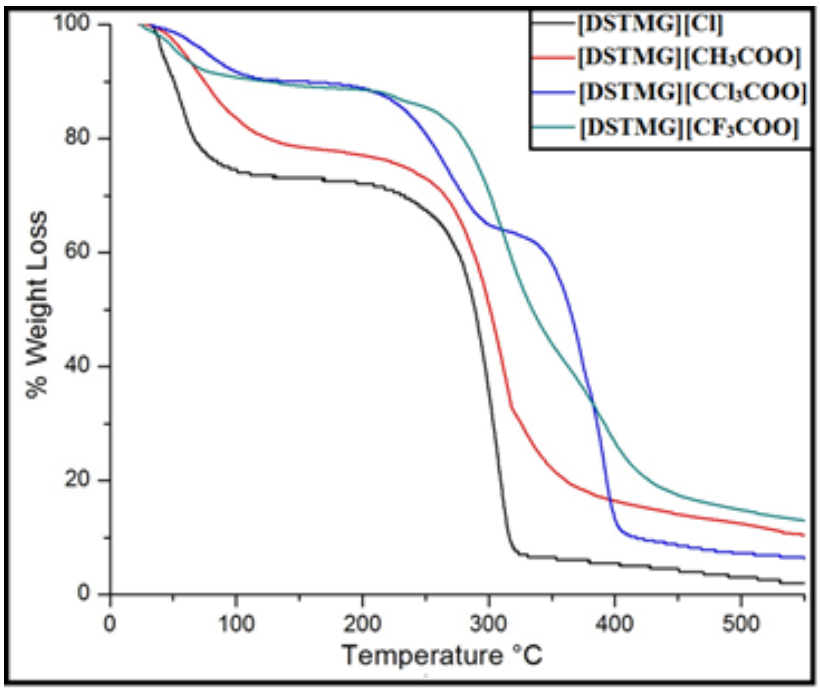


Fig.4.3: TGA curves of ILs

The TGA patterns of four ILs displays in **Fig. 4.3.** Initial 5-15 % weight loss around 95-100 °C of the three carboxylate ILs can be attributed for absorbed moisture. The TGA curve of parent IL [DSTMG][Cl] expresses higher amount of moisture content (approx. 25 %). Then the major weight loss started from 270-300 °C that indicates greater stability of TMG-based $–SO_3H$ functionalized ILs which is generally higher than the common reaction temperature of organic synthesis. The curve for [DSTMG][CF_3COO] (**IL-12)** shows thermal stability up to 300 °C. The stability of these ILs can be expressed in the decreasing order: [DSTMG][CF_3COO] (**IL-12)**> [DSTMG][CCl_3COO] (**IL-11)>** [DSTMG][CH_3COO] (**IL-10)>** [DSTMG][Cl] (**IL-9**).

4.2.1.3. UV visible Hammett acidity study

The acidity order of the new ILs was measured on UV-visible spectrophotometer for the Hammett plot (**Fig.4.4**) by following the same method in **Chapter-2.** The calculated values of Hammett function (H^o) were tabulated in **Table-4.1** which reflected the decreasing order of acidities against increasing values of H^o as **IL-12**> **IL-11**> **IL-10> IL-9**. The acidity order clearly demonstrated the presence of strong ionic interaction between more electronegative carboxylate anion and thermodynamically stable-guanidinium cation

for the highest acidic ionic liquid [DSTMG][CF_3COO] (**IL-12)** which was again supported by the thermal stability in TGA analysis (**Fig.4.3**).

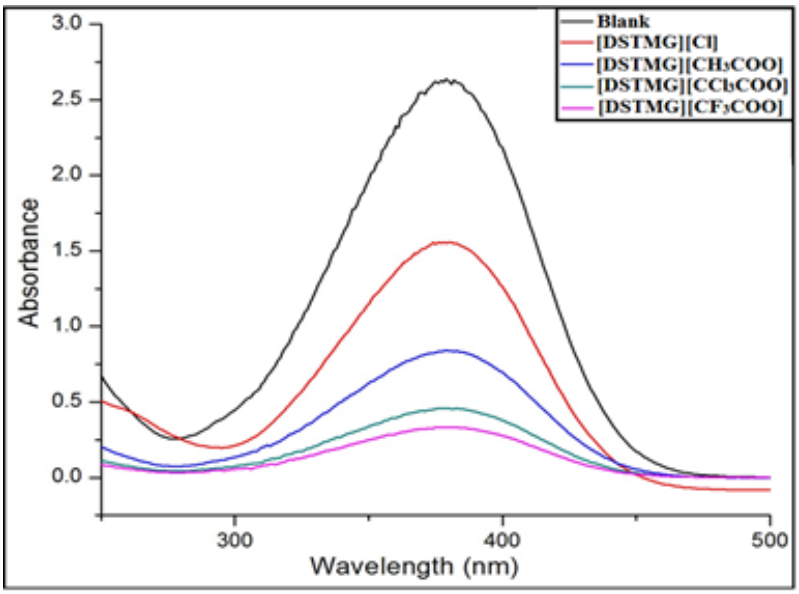


Fig.4.4: Hammett acidity measurement of Ionic liquid

Table-4.1: Hammett function (H°) values for ionic liquids

Entry	IL	λ_{max}	[I]%	[IH]%	H^o
1	Blank	2.638	100.0	0	-
2	[DSTMG]Cl	1.554	58.91	41.09	1.14
3	[DSTMG][CH_3COO]	0.841	31.88	68.12	0.66
4	[DSTMG][CCl_3COO]	0.457	17.32	82.68	0.31
5	[DSTMG][CF_3COO]	0.332	12.59	87.41	0.15

4.2.2. Catalytic activity study

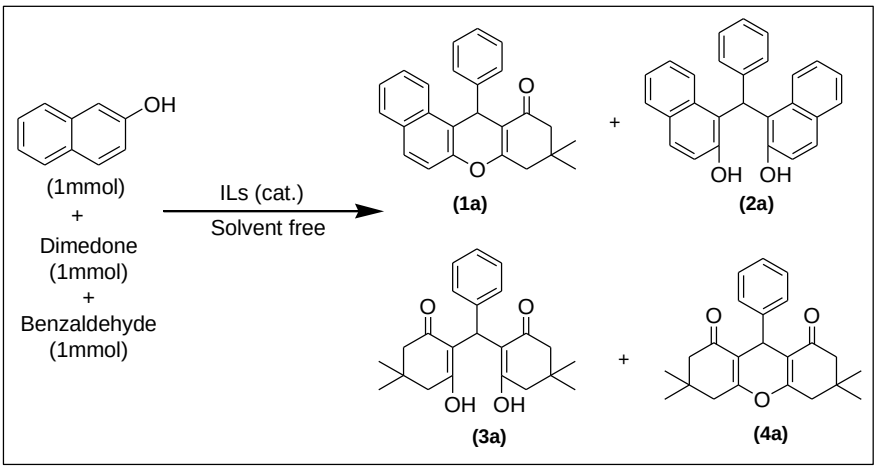
The catalytic activity of the three carboxylate ILs was investigated for the MC one-pot preparation of tetrahydrobenzo[a]xanthenones and tetrahydrobenzo[a]acridinones in solution and neat condition at different temperature.

4.2.2.1. Optimization of reaction conditions

Initially, the amount of four ILs were optimized as acidic catalysts for the multicomponent synthesis of tetrahydrobenzo[a]xanthenone **(1a)** and tetrahydrobenzo[a]acridinone (**5a**)

according to the reaction schemes as shown in **Table-4.2** and **Table-4.3** with 20 mol% of IL at different temperatures without any solvent (table-4.2 and table-4.3, entries 1-4). With these conditions, the three component reaction produced excellent yield of (**1a)** (90-94 %) at 75 °C with more acidic **IL-11** and **IL-12** during 10-12 min reaction as compared to weaker acidic **IL-9** and **IL-10** (table-4.2, entries 1-4). The same multicomponent reaction generated side products from parallel reactions at 75 °C with **IL-9** and **IL-10** (table-4.2, entries 1-2) which were identified as mixture of aryldi-(2-hydroxy-1-naphthyl)methane **(2a)** and 1, 8-dioxodecahydroxanthenone (**4a**). The similar results were also observed for the **IL-11** and **IL-12** at room temperature reactions within one hour (table-4.2, entries 3, 4). The amount of catalyst was optimized as 5 mol% for the two efficient catalysts **IL-11** and **IL-12** by comparing their results with 10 mol % at 75 °C (table-4.2, entries 5-6) which required only 10-12 min to form 90-94 % of expected product. By increasing the reaction temperature to 85°C, we didn't find any appreciable change in the reaction rate using 5 mol % of the two ILs (table-4.2, entries 7-8).

Table-4.2: Optimization of reaction condition for the synthesis of tetrahydrobenzo[a]xanthenone **(1a)**

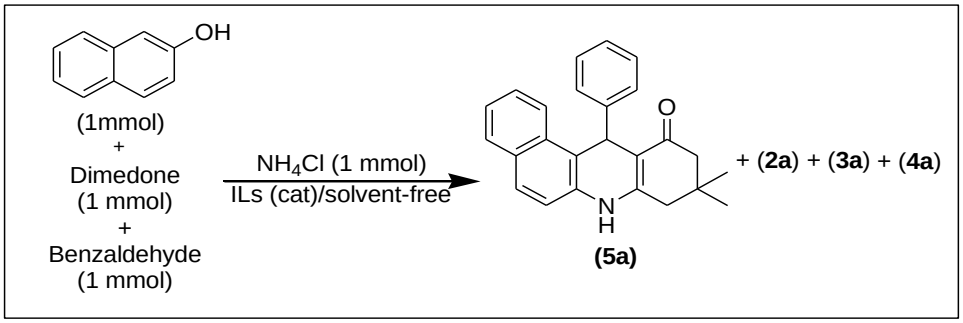


Entry	Ionic liquids	Mol%	Temp (°C)	Time (min)	% of yield [a, b]			
					(1a)	**(2a)**	**(3a)**	**(4a)**
1	**IL-9**	20	75	40	60	7	-	10
2	**IL-10**	20	75	25	70	-	-	15
3	**IL-11**	20	rt/75	1h/12	-/90	35/-	43/-	-
4	**IL-12**	20	rt/75	1h/10	-/94	40/-	45/-	-

5	**IL-11**	10/5	75	12/12	91/90	-	-	-
6	**IL-12**	10/5	75	10/10	94/93	-	-	-
7	**IL-11**	5	85	12	92	-	-	-
8	**IL-12**	5	85	10	94	-	-	-

[a] Isolated yield; [b] All the side products were characterized by comparing their melting points and NMR spectra with reported data [13-15]

Table-4.3: Optimization of reaction condition for the synthesis of tetrahydrobenzo[a]acridinones (**5a)**



Entry	Ionic liquids	Mol%	Temp (°C)	Time (min)	% of yield [a, b]			
					(5a)	**(2a)**	**(3a)**	**(4a)**
1	**IL-9**	20	85	50	55	12	-	13
2	**IL-10**	20	85	30	65	15	-	10
3	**IL-11**	20	rt /85	1h/15	-/89	30/-	46/-	-
4	**IL-12**	20	rt /85	1h/12	-/92	37/-	43/-	-
5	**IL-11**	10/5	85	15	89/88	-	-	-
6	**IL-12**	10/5	85	12	92/90	-	-	-
7	**IL-11**	5	95	15	91	-	-	-
8	**IL-12**	5	95	12	93	-	-	-

[a] Isolated yield; [b] All the side products were characterized by comparing their melting points and NMR spectra with reported data [13-15]

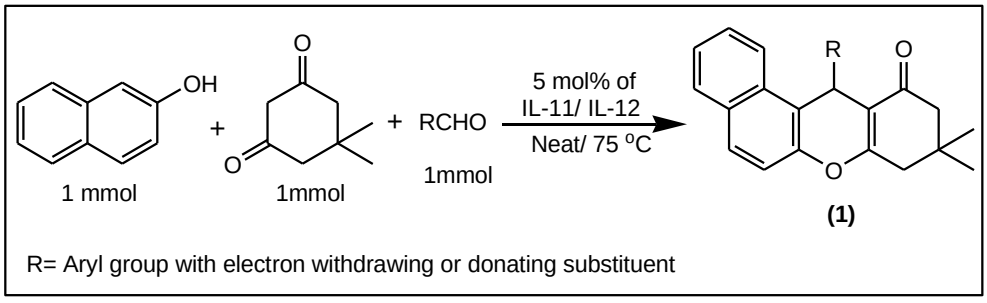
Similarly, the four component reactions of tetrahydrobenzo[a]acridinone (**5a)** produced 89-92 % of expected product at 85 °C with 20 mol% of **IL-11** and **IL-12** within short time (table-4.3, entries 3-4). For the weaker acidic ILs, the model reaction produced small amounts of aryldi-(2-hydroxy-1-naphthyl)methane (**2a**) and 1,8-dioxodecahydro-

xanthenone **(4a)** as side products along with acridinone derivative **(5a)** (table-4.3, entries 1-2). On the other hand we isolated a mixture of aryldi-(2-hydroxy-1-naphthyl) methane (**2a**) and aryl-di-(3-hydroxy-5,5-dimethyl-2-cycloxenone) (**3a**) from the room temperature reaction in presence of 20 mol% of either **IL-11** or **IL-12** for 1 hour (table-4.3, entries 3-4).

It was observed that the use of 5 mol% of **IL-11** and **IL-12** was sufficient for the selective formation of 88-90 % of product (**5a)** at 85 °C (table-4.3, entries 5-6). Similarly the reaction rate didn't change much when the temperature was raised to 95 °C under optimized condition (table-4.3, entries 7-8).

These optimization studies revealed the existence of parallel reactions for the multicomponent synthesis of tetrahydrobenzo[a]xanthenone **(1a**) and tetrahydrobenzo[a]acridinone (**5a**) derivatives at different temperature junction. The above study was also extended for the model compounds (**1a**) and (**5a**) EtOH, CH_2Cl_2, CH_3CN and $CHCl_3$ separately at room temperature stirring for one hour using 5 mol% of **IL-11** and **IL-12.** These investigations didn't show any selective formation of the desired products in solutions. They formed only a mixture of side products that has already observed in the **Table-4.2** and **Table-4.3** (entries 1-2 and 3-4).

Table-4.4: Substrate scope study for the synthesis of tetrahydrobenzo[a]xanthenone (**1**) derivatives

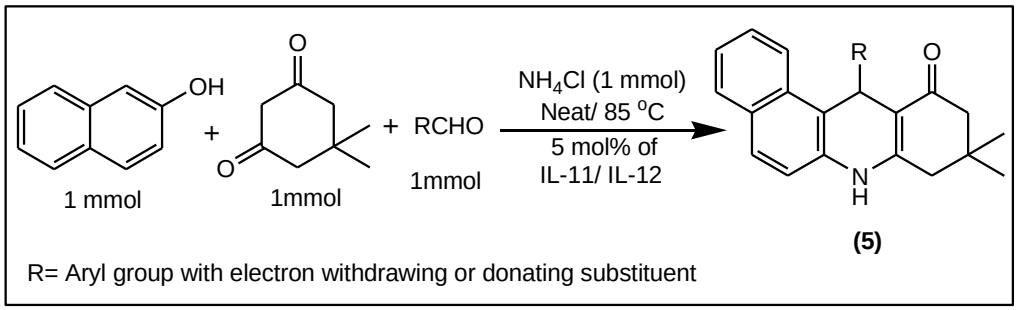


Entry	Aldehyde	Time (min)		% of Yield[a, b] **(1)**	
		IL-11	**IL-12**	**IL-11**	**IL-12**
1	Benzaldehyde	12	10	90 **(1a)**	94 **(1a)**

2	4-Nitrobenzaldehyde	15	12	88 **(1b)**	90 **(1b)**
3	4-Chlorobenzaldehyde	14	12	90 **(1c)**	92 **(1c)**
4	4-Anisaldehyde	13	10	93 **(1d)**	95 **(1d)**
5	4-Tolualdehyde	12	10	92 **(1e)**	95 **(1e)**
6	2-Naphthaldehyde	14	11	89 **(1f)**	92 **(1f)**

[a] Isolated yield; [b] Reactions were performed at 75 °C using 5 mol % of **IL-11** or **IL-12**

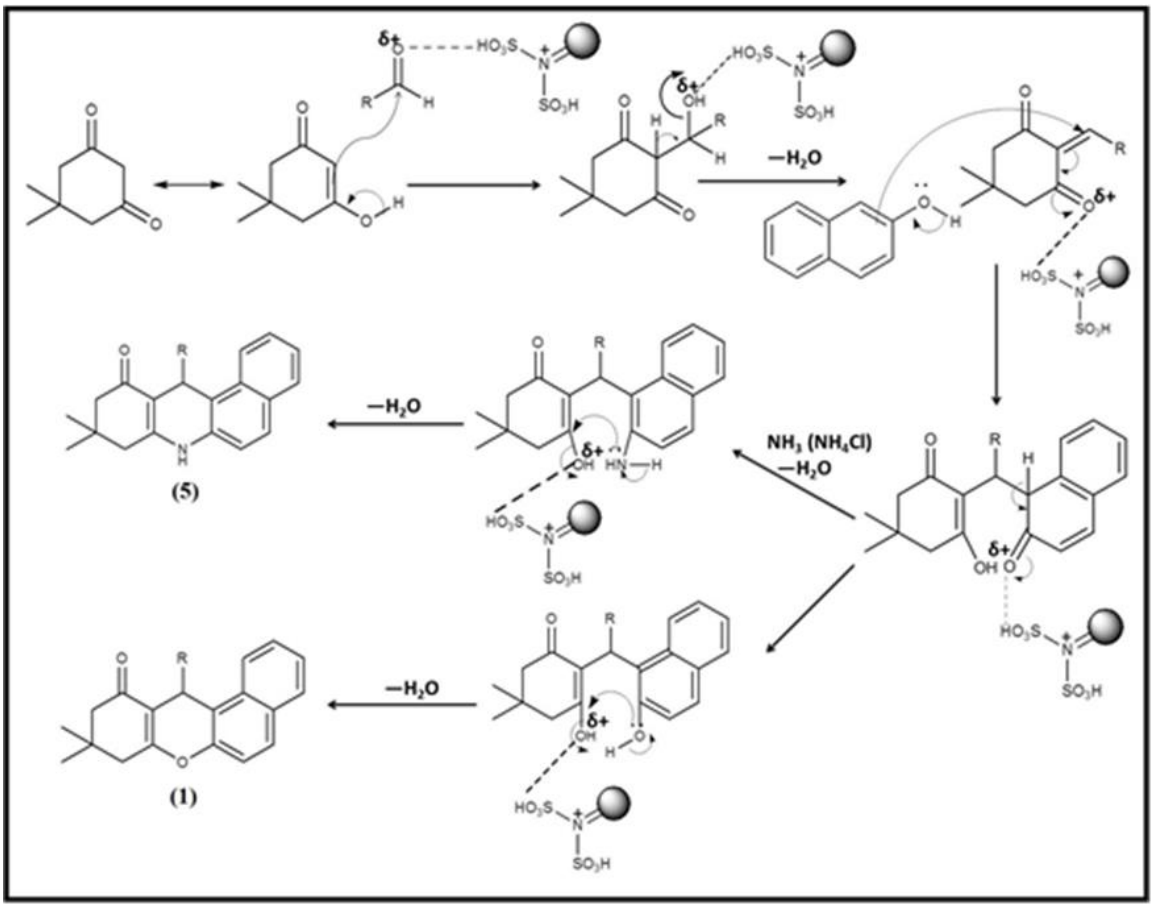
Table-4.5: Substrate scope study for the synthesis of tetrahydrobenzo[a]acridinone (**5**) derivatives



Entry	Aldehyde	Time (min)		% of Yield[a, b] **(5)**	
		IL-11	**IL-12**	**IL-11**	**IL-12**
1	Benzaldehyde	15	12	88 **(5a)**	90 **(5a)**
2	4-Nitrobenzaldehyde	18	14	85 **(5b)**	88 **(5b)**
3	4-Chlorobenzaldehyde	16	12	87 **(5c)**	90 **(5c)**
4	4-Anisaldehyde	13	10	91 **(5d)**	94 **(5d)**
5	4-Tolualdehyde	14	12	90 **(5e)**	94 **(5e)**
6	2-Naphthaldehyde	16	14	87 **(5f)**	90 **(5f)**

[a] Isolated yield; [b] Reactions were carried out using 5 mol % of **IL-11** or **IL-12** at 85 °C

4.2.2.2. Substrate scope study and plausible mechanism



Scheme-4.2: Plausible mechanism of tetrahydrobenzo[a]xanthenone and tetrahydrobenzo[a]acridinone derivatives

The optimized conditions were successfully utilized for the generation of different derivatives of xanthenones and acridinones with variety of substituted aromatic aldehyde using **IL-11** and **IL-12** as catalysts. All those results were included in **Table-4.4** and **Table-4.5**. Aliphatic aldehydes gave complex mixtures of products under optimized condition. The product formation was not affected by the nature of electron withdrawing or donating group bearing aromatic aldehydes (table-4.4 and table-4.5, entries 1-6).

The plausible mechanisms of these MC reactions can be proposed through activation of aldehyde by acidic IL followed by nucleophilic attack of dimedone molecule and then subsequent steps according to the reaction **Scheme-4.2**.

4.2.2.3. Reusability test of ionic liquids

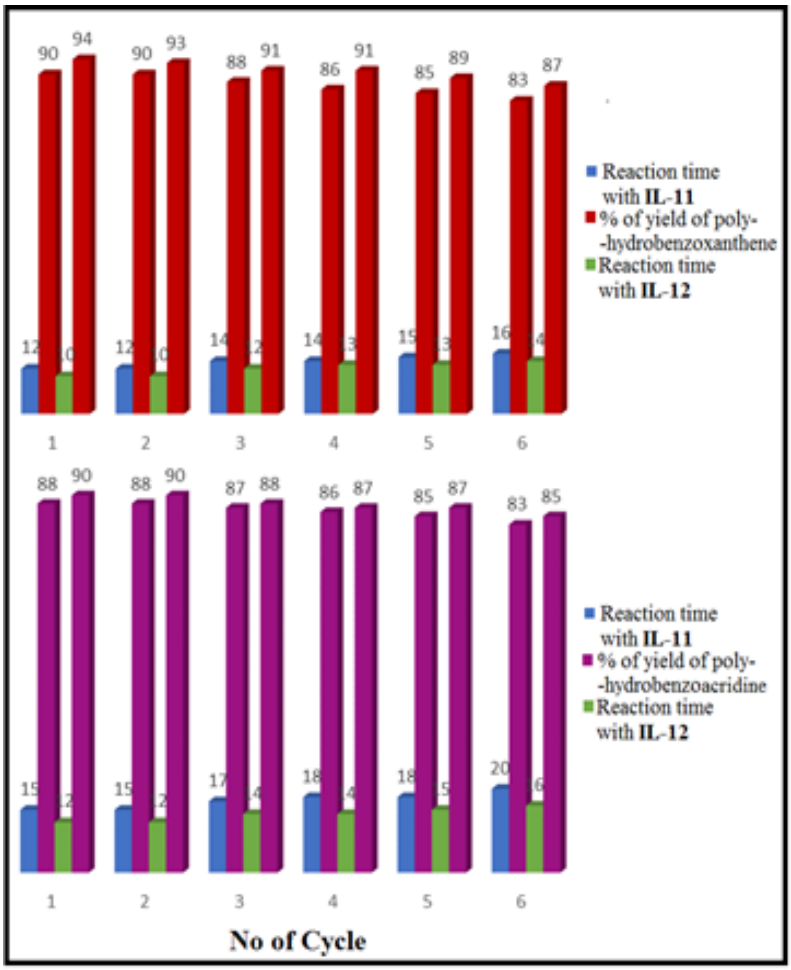


Fig.4.5 : Recycling of **IL-11** and **IL-12**

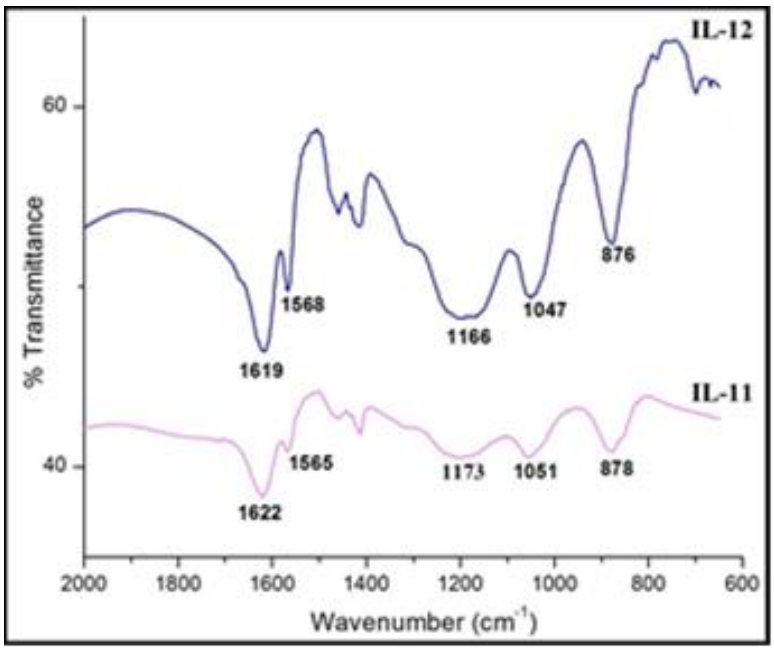


Fig.4.6: FT-IR spectra of reused catalysts after 6th cycle

The reusability study of **IL-11** and **IL-12** was conducted for the model compound of tetrahydrobenzo[a]xanthenones **(1a**) and acridinone derivatives **(5a)** in 5 mmol scale. **Fig.4.5** expressed higher catalytic efficiency of the two ILs up to six consecutive cycles with a slight increase in reaction time. The identical FT-IR spectra of reused spectra after 6^{th} run (**Fig.4.6**) and the fresh spectra (**Fig.4.1)** evidenced the retention of catalytic activity of **IL-11** and **IL-12.**

4.3. Conclusion

In this study, we developed a new series of strong Brønsted acidic N, N di-sulfonic tetramethyl guanidinium carboxylate ionic liquids and characterized them with various analytical tool. The high thermal stability and acidity of [DSTMG][CX_3COO] ILs revealed a strong ionic interaction between carboxylate anion and guanidinium cation. They were employed as efficient reusable homogeneous catalysts for the multicomponent synthesis of tetrahydrobenzo[a]xanthenone and tetrahydrobenzo[a]acridinone derivatives in solvent-free medium at 75-85 °C with excellent yields in less time. Furthermore, we have introduced the first ever IL catalyzed and also four component method for the synthesis of tetrahydrobenzo[a]acridinone derivatives.

4.4. Experimental Section

4.4.1. General information

All synthesized products were characterized with ^{1}HNMR, ^{13}CNMR, FT-IR and elemental analysis data using the instruments described in the experimental section of **Chapter-2**. The melting point of known tetrahydrobenzo[a]xanthenones **(1)** and acridinone derivatives **(5)** were compared with the literature values [6-7].

4.4.2. Experimental procedures

4.4.2.1. Preparation of N, N-disulfotetramethyl guanidinium carboxylate ionic liquids [DSTMG][CX_3COO] where X= H, Cl, F

The parent ionic liquid [DSTMG][Cl] was prepared by drop wise addition of $ClSO_3H$ (10 mmol) to a solution of TMG (5 mmol) in dry hexane at 0 °C in a two necked 50 mL round bottomed flask fitted with a vacuum system through water and alkali trap for removal of HCl gas. The mixture was stirred continuously for one hour at room temperature to get [DSTMG][Cl] as pale yellow liquid immiscible with hexane. To the crude IL solution, 5

mmol of carboxylic acid (CH_3COOH, CCl_3COOH, CF_3COOH) was added slowly with vigorous stirring and heated up to 60 °C for 1h to complete the elimination of HCl gas. Then the mixture was diluted with 10 ml of dry hexane. The hexane layer was decanted and again washed the crude IL with dry hexane (3 x 5 mL). Finally the ionic liquid residue was dried under vacuum to get 96-98% yields of [DSTMG][CX_3COO] as yellow/reddish colored viscous liquids.

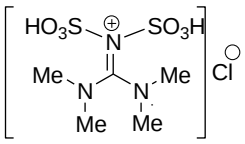
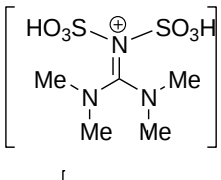
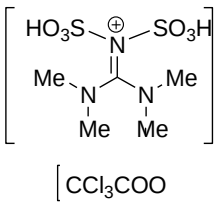
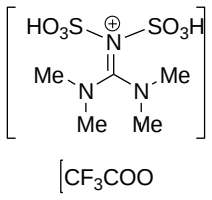
4.4.2.2. General procedure for the synthesis of tetrahydrobenzo[a]xanthenone derivatives (1)

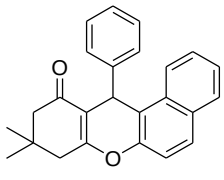
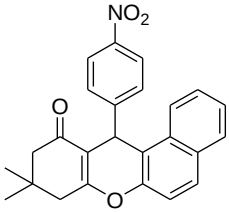
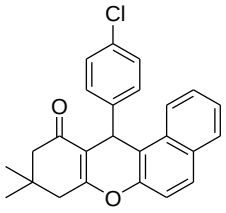
In a 50 mL round bottomed flask, a three component mixture of 2-naphthol (1 mmol), aromatic aldehyde (1mmol) and dimedone (1 mmol) was treated with 5 mol % of **IL-11** or **IL-12** at 75 °C under solvent-free condition for the specified time. After completion of the reaction as observed from TLC technique the product mixture was extracted from the IL catalyst using dry dichloromethane (3 x 3 mL) as IL immiscible solvent. The isolation of crude product involved with decantation and evaporation of the CH_2Cl_2 layer under reduced pressure. The IL catalyst was recycled for next run after washing several times with more dichloromethane solvent. The crude product, thus isolated was subjected to further purification by recrystallization in 15% aqueous ethanol to get analytically pure product.

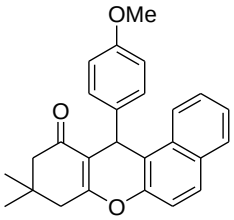
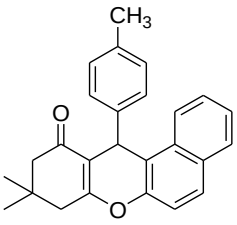
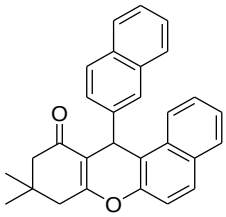
4.4.2.3. General procedure for the synthesis of tetrahydrobenzo[a]acridinone derivatives (5)

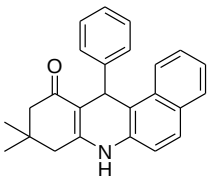
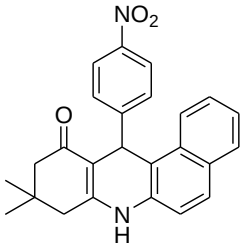
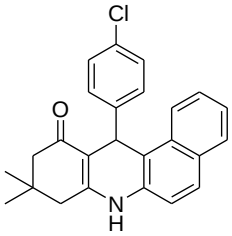
A four component mixture of dimedone (1 mmol), 2-naphthol (1mmol), aromatic aldehydes (1 mmol) and NH_4Cl (1 mmol) was treated with 5 mol% of **IL-11** or **IL-12** in a 50 mL round bottomed flask at 85 °C in neat condition. After completion of the reaction as monitored by TLC technique, the crude mixture was extracted from the ionic liquid phases using dry dichloromethane (3 x 3 mL) as immiscible solvent. Decantation of organic layer separated the product mixture from the viscous IL catalyst remain in the reaction vessel. This IL was reactivated for next cycle after washing with CH_2Cl_2 solvent. Removal of CH_2Cl_2 solvent from the organic solution yielded tetrahydrobenzoacridinone derivative as solid residue. Recrystallization of the crude product from 15% aqueous ethanol gave analytically pure product.

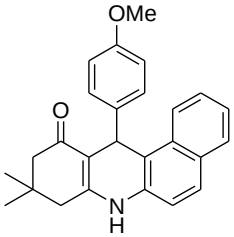
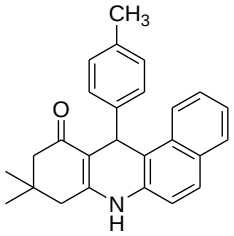
4.4.3. Spectral data of ionic liquids, tetrahydrobenzo[a]xanthenone derivatives (1) and tetrahydrobenzo[a]acridinone derivatives (5)

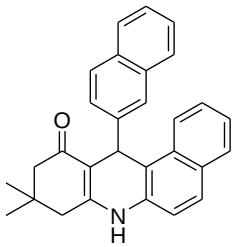
Product	Spectral data
	**N,N-Disulfo-tetramethylguanidiniumchloride (IL-9)**: Pale yellow viscous liquid; FT-IR: 3301, 1630, 1560, 1149, 1027, 860 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6): δ 3.01 (s, 12H), 14.2 (s, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 39.1, 119.8, 134.7; CHN analysis: Calculated for $C_7H_{17}N_3O_8S_2$ (%): Cal. C 25.07, H 5.11, N 12.53; Found C 25.02, H 5.16, N 12.5.
	**N,N-Disulfo-tetramethylguanidiniumacetate (IL-10):** Reddish viscous liquid, FT-IR: 3313, 1611, 1564, 1411, 1158, 1036, 871 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6): δ 1.91(s, 3H), 2.96 (s, 12H), 14.18 (s, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 15.5, 39.1, 119.7, 134.7, 151.71; CHN analysis: Calculated for $C_7H_{17}N_3O_8S_2$ (%): Cal. C 25.07, H 5.11, N 12.53; Found C 25.02, H 5.16, N 12.5.
	**N,N-Disulfo-tetramethylguanidinium-trichloroacetate (IL-11):** Pale yellow liquid, FT-IR: 3299, 1608, 1568, 1409, 1141, 1030, 868 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6): δ 3.02 (s, 12H), 14.14 (s, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 39.4, 62.4, 119.7, 134.6, 158.5; CHN analysis: Calculated for $C_7H_{14}N_3O_8S_2Cl_3$ (%): Cal. C 19.16, H 3.22, N 9.58; Found C 19.15, H 3.25, N 9.55.
	**N,N-Disulfo-tetramethylguanidinium-trifluoroacetate (IL-12):** Light reddish liquid, FT-IR: 3321, 1610, 1562, 1413, 1161, 1038, 868 cm^{-1}; ^1H NMR (400MHz, DMSO-d_6): δ 3.09 (s, 12H), 14.01 (s, 2H); ^{13}C NMR (100MHz, DMSO-d_6): δ 38.8, 55.3, 119.8, 134.6, 163.3; CHN analysis: Calculated for $C_7H_{14}N_3O_8S_2F_3$ (%): Cal. C 21.59, H 3.62, N 10.79; Found C 21.55, H 3.68, N 10.77.
	9,10-Dihydro-9,9-dimethyl-12-phenyl-8*H*-benzo[a]xanthen-11 (12*H*)-one (1a) (table-4.4, entry 1): White amorphous solid; m.p. 152-154 °C; FT-IR (KBr): 3088, 2946, 2844, 1641, 1506, 1420, 1328, 1216, 1124, 1009, 817, 737 cm^{-1}; ^1H NMR (400MHz,

	$CDCl_3$): δ 1.04 (s, 6H), 2.27 (s, 4H), 6.58 (s, 1H), 7.42(t, 1H, *J* = 8.2 Hz), 7.50 (d, 1H, *J* = 8.7 Hz), 7.58 (t, 1H, *J* = 6.9 Hz), 7.67 (d, 1H, *J* = 9.2 Hz), 7.80-7.85 (m, , 3H), 7.98 (d, 2H, *J* = 9.2Hz), 8.28 (d, 2H, *J* = 8.2Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$): 27.2, 29.3, 32.3, 34.7, 41.4, 50.9, 117.1, 123.7, 126.3, 127.0, 128.3, 128.4, 128.5, 128.9, 144.8, 147.8, 163.9. 196.9; CHN analysis: Calculated for $C_{25}H_{22}O_2$ (%): C 84.72, H 6.26, Found C 84.70, H 6.30.
	**9,10-Dihydro-9,9-dimethyl-12-(4-nitrophenyl)-8*H*-benzo[a] xanthen-11(12*H*)-one (1b) (table-4.4, entry 2):** Yellow solid; m.p. 180-183 °C; FT-IR (KBr): 3068, 2966, 2219, 1649, 1511, 1418, 1344, 1223, 1144, 1024, 848, 740 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.04 (s, 6H), 2.28 (s, 4H), 6.46 (s, 1H), 6.97 (t, 1H, *J* = 7.32 Hz), 7.13 (t, 1H, *J* = 7.32 Hz), 7.39 (t, 1H, *J* = 6.9 Hz), 7.48 (d, 1H, *J* = 8.7 Hz), 7.51-7.58 (m, 3H), 7.76-7.82 (m, 2H), 8.39 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 27.2, 29.6, 31.9, 38.1, 46.1, 113.5, 117.5, 118.1, 122.8, 124.3, 126.9, 128.3, 128.5, 128.8, 128.9, 131.0, 131.5, 145.1, 148.8 189.7; CHN analysis: Calculated for $C_{25}H_{21}O_4N$ (%): C 75.17, H 5.30, N 3.51; Found C 75.17, H 5.33, N 3.50.
	**12-(4-Chlorophenyl)-9,10-dihydro-9,9-dimethyl-8*H*-benzo[a] xanthen-11(12*H*)-one (1c) (table-4.4, entry 3)**: White solid; m.p. 188-190 °C; FT-IR (KBr): 3040, 2961, 1644, 1501, 1408, 1244, 1131, 1018, 866, 751 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.04 (s, 6H), 2.27 (s, 4H), 6.45 (s, 1H), 7.09(d, 1H, *J* = 8.7 Hz), 7.39-7.47 (m, 4H), 7.56 (t, 1H, *J* = 7.32Hz), 7.77-7.83 (m, 3H), 8.29 (d, 1H, *J* = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 27.1, 29.6, 31.9, 37.4, 46.1, 113.6, 117.5, 118.1, 122.5, 124.4, 127.0, 128.7, 128.9, 129.2, 129.6, 131.5, 131.7, 132.0, 143.5, 148.7, 189.7 CHN analysis: Calculated for $C_{25}H_{21}ClO_2$ (%): C 77.21, H 5.44, Found C 77.18, H 5.48.

	**9,10-Dihydro-12-(4-methoxyphenyl)-9,9-dimethyl-8*H*-benzo [a]xanthen-11(12*H*)-one (1d) (table-4.4, entry 4):** Brown solid; m.p. 208-210 °C; FT-IR (KBr): 3052, 2956, 1631, 1498, 1389, 1240, 1154, 1021, 767 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.06 (s, 6H), 2.28 (s, 4H), 3.59 (s, 3H), 6.42 (s, 1H), 6.65(d, 2H, *J* = 8.2 Hz), 7.37-7.42 (m, 2H), 7.46 (d, 1H, *J* = 8.7 Hz), 7.56 (t, 1H, *J* = 7.32 Hz), 7.77 (d, 1H, *J* = 8.7 Hz), 7.81(d, 1H, *J* = 7.8 Hz), 8.35 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 27.1, 29.6, 31.9, 37.2, 46.1, 51.1, 55.1, 113.6, 113.9, 118.1, 122.8, 124.3, 126.8, 128.8, 129.2, 131.1, 137.5, 148.7, 157.9, 189.7; CHN analysis: Calculated for $C_{26}H_{24}O_3$ (%): C 81.22, H 6.29, Found C 81.18, H 6.34.
	**9,10-Dihydro-9,9-dimethyl-12-p-tolyl-8*H*-benzo[a]xanthen-11 (12*H*)-one (1e) (table-4.4, entry 5):** Yellow solid, m.p. 218-182°C; FT-IR (KBr): 3060, 2958, 1646, 1501, 1404, 1220, 1108, 1016, 808, 729 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.04 (s, 6H), 2.11 (s, 3H), 2.28 (s, 4H), 6.45 (s, 1H), 6.94 (d, 1H, *J* = 7.8Hz), 7.38-7.41 (m, 3H), 7.47 (d, 1H, *J* = 8.7 Hz), 7.55 (t, 1H, *J* = 8.3 Hz), 7.77-7.81(m, 3H), 8.37 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 20.9, 27.2, 29.6, 31.9, 37.8, 46.1, 113.6, 117.5, 118.1, 122.8, 124.3, 126.8, 128.2, 128.8, 128.9, 129.2, 131.1, 131.5, 135.9, 142.2, 148.7, 189.7; CHN analysis: Calculated for $C_{26}H_{24}O_2$ (%): C 84.75, H 6.57, Found C 84.72, H 6.61.
	**9,10-Dihydro-9,9-dimethyl-12-(naphthalen-2-yl)-8*H*-benzo[a] xanthen-11(12*H*)-one (1f) (table-4.4, entry 6):** White solid; m.p. 288-291 °C; FT-IR (KBr): 3049, 2951, 2820, 1626, 1509, 1399, 1241, 1131, 1018, 832, 751 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.04 (s, 6H), 2.29 (s, 4H), 6.65 (s, 1H), 7.29 (t, 1H, *J* = 7.3 Hz), 7.35-7.38 (m, 2H), 7.49-7.59 (m, 4H), 7.45-7.80 (m, 3H), 8.05 (s, 1H), 8.49 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 27.2, 29.6, 31.9, 38.4, 46.1, 113.6, 117.5, 118.1, 122.8, 124.3, 126.6, 126.9, 127.9, 128.9, 129.1, 131.5, 131.7, 132.0, 133.1,

	142.4, 148.8, 189.7; CHN analysis: Calculated for $C_{29}H_{24}O_2$ (%): C 86.11, H 5.98, Found C 86.10, H 6.01
	**9,10-Dihydro-9,9-dimethyl-12-phenyl-benzo[a]acridin-11(7*H*,8*H*,12*H*)-one (5a) (table-4.5, entry 1):** White amorphous solid; m.p. 313-15 °C; FT-IR (KBr): 3260, 2944, 1587, 1457, 1381, 1255, 1140, 1014, 822, 758, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 6H), 2.27 (s, 4H), 6.46 (s, 1H), 6.97 (t, 1H, *J* = 7.3 Hz), 7.13 (t, 1H, *J* = 7.8 Hz), 7.38 (t, 1H, *J* = 7.8 Hz), 7.48 (d, 1H, *J* = 9.1Hz), 7.51-7.56 (m, 4H), 7.75-7.81 (m, 2H), 8.37 (d, 1H, *J* = 8.7); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1, 27.2, 29.6, 31.9, 38.1, 46.1, 114.0, 117.5, 118.1, 122.8, 124.3, 126.9, 128.3, 128.5, 128.8, 128.9, 131.5, 132.0, 145.1, 148.8 189.7; CHN analysis: Calculated for $C_{25}H_{23}NO$ (%): C 84.95, H 6.56, N 3.96; Found C 84.93, H 6.57, N 3.95.
	**9,10-Dihydro-9,9-dimethyl-12-(4-nitrophenyl)benzo[a] acridin-11(7*H*,8*H*,12*H*)-one (5b) (table-4.5, entry 2):** Yellow amorphous solid; m.p. 246-49 °C; FT-IR (KBr): 3303, 2962, 1569, 1495, 1377, 1257, 1050, 866, 769, 664 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 6H), 2.27 (s, 4H), 6.59 (s, 1H), 7.42 (t, 1H, *J* = 6.9 Hz), 7.49 (d, 1H, *J* = 9.2 Hz), 7.58 (s, 1H, *J* = 6.9 Hz), 7.65 (d, 1H , *J* = 8.7 Hz), 7.80-7.84 (m, 2H), 7.98 (d, 2H, *J* = 8.7Hz), 8.26 (d, 2H, *J* = 8.7Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 27.1, 29.3, 32.3, 34.9, 41.4, 50.8, 87.2, 117.1, 123.1, 123.7, 125.3, 127.4, 128.7, 129.4, 129.7, 146.4, 147.8, 151.9, 164.7, 196.8; CHN analysis: Calculated for $C_{25}H_{22}N_2O_3$ (%): C 75.36, H 5.57, N 7.03; Found C 75.33, H 5.60, N 7.04
	**12-(4-Chlorophenyl)-9,10-dihydro-9,9-dimethylbenzo[a] acridin-11(7*H*,8*H*,12*H*)-one (5c) (table-4.5, entry 3):** Brown amorphous solid; m.p. 348-350 °C; FT-IR (KBr): 3324, 2966, 1620, 1560, 1388, 1240, 1156, 1022, 808, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 6H), 2.27 (s, 4H), 6.44 (s, 1H), 7.07 (d, 1H, *J* = 8.7 Hz), 7.38-7.47 (m, 4H), 7.56 (t, 1H, *J* = 6.9 Hz), 7.77-

	7.83 (m, 3H), 8.30 (d, 1H, *J* = 8.7Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 27.1, 29.6, 37.4, 46.1, 113.9, 117.2, 118.1, 122.5, 124.4, 126.9, 128.7, 128.9, 129.2, 129.6, 131.7, 132.0, 143.5, 148.7 189.7; CHN analysis: Calculated for $C_{25}H_{22}ClNO$ (%): C 77.41, H 5.72, N 3.61; Found C 77.37, H 5.77, N 3.58
	**9,10-Dihydro-12-(4-methoxyphenyl)-9,9-dimethylbenzo[a] acridin-11(7*H*,8*H*,12*H*)-one (5d) (table-4.5, entry 4):** White amorphous solid; m.p. 295-300 °C; FT-IR (KBr): 3344, 2961, 1595, 1491, 1386, 1240, 1155, 1040, 817, 759, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 6H), 2.28 (s, 4H), 3.58 (s, 3H), 6.42 (s, 1H), 6.65 (d, 1H, *J* = 8.7 Hz), 7.36-7.42 (m, 3H), 7.46 (d, 1H, *J* = 9.2Hz), 7.56 (t, 1H, *J* = 6.9 Hz), 7.75-7.81 (m, 3H), 8.34 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 27.2, 29.6, 31.9, 37.2, 46.1, 55.1, 113.6, 113.9 118.1, 122.8, 124.3, 126.8, 128.8, 128.9, 129.2, 131.0, 131.1, 137.2, 148.7, 157.9, 189.7; CHN analysis: Calculated for $C_{26}H_{25}NO_2$ (%): C 81.43, H 6.57, N 3.66; Found C 81.40, H 6.61, N 3.66
	**9,10-Dihydro-9,9-dimethyl-12-p-tolylbenzo[a]acridin-11(7*H*,8*H*,12*H*)-one (5e) (table-4.5, entry 5):** White amorphous solid; m.p. 295-300 °C; FT-IR (KBr): 3303, 2954, 1605, 1478, 1390, 1262, 1145, 1011, 785, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (s, 6H), 2.10 (s, 3H), 2.28 (s, 4H), 6.43 (s, 1H), 6.94 (d, 1H, *J* = 7.8 Hz), 7.35-7.40(m, 2H), 7.47 (d, 1H, *J* = 8.7 Hz), 7.57 (t, 2H, *J* = 8.3Hz), 7.74-7.80 (m, 3H), 8.36 (d, 1H, *J* = 8.7Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 20.9, 27.2, 29.6, 31.9, 37.7, 46.1, 113.6, 117.5 118.1, 122.8, 124.3, 126.8, 128.2, 128.8, 128.9, 129.2, 131.1, 131.5, 136.0, 142.2, 148.7, 189.7; CHN analysis: Calculated for $C_{26}H_{25}NO$ (%): C 84.98, H 6.86, N 3.81; Found C 85.01, H 6.88, N 3.84
	9,10-Dihydro-9,9-dimethyl-12-(naphthalen-2-yl)benzo[a] acridin-11(7*H*,8*H*,12*H*)-one (5f) (table-4.5, entry 6): Yellow amorphous solid; m.p. 353-357 °C; FT-IR (KBr): 3334, 2993, 1610, 1498, 1404, 1366, 1224, 1104, 808, 746, 678 cm^{-1}; ^{1}H NMR

	(400 MHz, $CDCl_3$): δ 1.05 (s, 6H), 2.28 (s, 4H), 6.64 (s, 1H), 7.28 (t, 1H, *J* = 8.2 Hz), 7.32-7.37(m, 2H) , 7.49-7.58 (m, 4H), 7.74-7.79 (m, 3H), 8.03 (s, 1H), 8.46 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 27.2, 29.6, 31.9, 38.4, 46.1, 113.6, 117.5, 118.1, 122.8, 124.3, 126.6, 126.8, 128.9, 129.1, 131.1, 131.8, 132.0, 134.0, 142.4, 148.8, 189.7; CHN analysis: Calculated for $C_{29}H_{25}NO$ (%): C 86.32, H 6.24, N 3.47; Found C 86.34, H 6.30, N 3.45

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