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# Diethyldisulfoammonium chlorometallates as heterogeneous Brønsted–Lewis acidic catalysts for one-pot synthesis of 14-aryl-7-(N-phenyl)-14H-dibenzo[a,j]acridines

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Funding information CSIR-New Delhi, India, Grant/Award Number: 02(0067)/12/EMR-II A new series of Brønsted–Lewis acidic diethyldisulfoammonium chlorometallates, [DEDSA][FeCl<sub>4</sub>] and [DEDSA]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>], were synthesized as solid materials from the reaction of  $[(Et)_2N(SO_3H)_2][Cl]$  ionic liquid with transition metal chlorides (FeCl<sub>3</sub> and ZnCl<sub>2</sub>) at 80 °C in neat condition for 2 h. The chlorometallates were fully characterized using various spectroscopic and analytical techniques such as Fourier transform infrared, UV–visible and Raman spectroscopies, powder X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray and thermogravimetric analyses, Hammett acidity and elemental analyses. Their catalytic activity was studied as reusable heterogeneous catalysts for the three-component synthesis of novel 14-aryl-7-(*N*-phenyl)-14*H*-dibenzo[*a*,*j*]acridines under solvent-free conditions at 100 °C.

#### KEYWORDS

14-aryl-7-(*N*-phenyl)-14*H*-dibenzo[*a*,*j*]acridines, diethyldisulfoammonium chlorometallates, heterogeneous catalysis, multicomponent, recyclable catalyst

# **1 | INTRODUCTION**

Ionic liquids (ILs) incorporated with metal chlorides are commonly known chlorometallate ILs. as Chloroaluminates(III) were the first example of such type of Lewis acidic ILs that received growing attention in the field of catalysis.<sup>[1,2]</sup> However, their applications were limited due to their hygroscopic nature. The anionic composition determines the properties of chlorometallates which again depend on the types of metal chloride and the ratios of metal chloride to parent organic chloride.[3-5] The various developments of such ionic salts over the last two decades have recognized these chlorometallates/halometallates as functional materials with unique and useful properties including photophysical, magnetic, catalytic and semiconducting properties<sup>[6–8]</sup> among others. Some of them can be developed as air- and water-stable ionic salts by varying the type of cationic and anionic compositions and also the concentration of metal halides that directly relates to characteristic and individual properties. Gogoi et al. developed -SO<sub>3</sub>H-functionalized 1-methylimidazolium-based chlorometallates of Fe(III) and Zn(II) as Brønsted-Lewis acidic heterogeneous catalysts for the preparation of bis(indolyl)methane derivatives under mild conditions.<sup>[9]</sup> Saikia et al. also prepared 1,3disulfoimidazolium-based chlorometallates of Fe(III) and Zn (II) as bifunctionalized acidic materials for the Mannich-type reaction at ambient temperature in solution.<sup>[8]</sup> These chlorometallates bearing -SO<sub>3</sub>H group provide higher thermal and water stabilities as compared to their parent ILs. In the work reported herein, we aimed to synthesize bifunctionalized diethyldisulfoammonium chlorometallates, namely [(Et)2N  $(SO_3H)_2]_n[X]$ , where n = 1 and 2 for  $X = FeCl_4^-$  (IL-2) and  $Zn_2Cl_6^{2-}$ (IL-3), from the reaction of diethyldisulfoammonium chloride [(Et)<sub>2</sub>N(SO<sub>3</sub>H)<sub>2</sub>][Cl] (IL-1) with the respective transition metal chlorides (FeCl<sub>3</sub> and ZnCl<sub>2</sub>) at 80 °C under solvent-free conditions (Scheme 1).

The catalytic performances of these chlorometallates were examined for the three-component synthesis of novel



SCHEME 1 Preparation of diethyldisulfoammonium chlorometallates

14-aryl-7-(N-phenyl)-14H-dibenzo[a,j]acridine derivatives (1) from the reaction of an equimolar mixture of 2-naphthol, N-phenyl-2-naphthylamine and aromatic aldehyde under solvent-free conditions at 100 °C. The benzoacridine derivatives have a wide range of pharmacological activities such as antitumour, antiviral, antimicrobial, antimalarial, analgesic and anti-inflammatory activities. They are also used in material sciences as fluorescent dyes.<sup>[10-14]</sup> However, limited approaches have been made to date for the synthesis of dibenzoacridine derivatives. Dutta et al. in 2003 prepared a few N-alkyl derivatives of acridine, benzo[c]acridine and dibenzo[c,h]acridine in dry tetrahydrofuran at 0 °C through treatment of these basic units with phenyllithiumtetramethylethylenediamine and then quenching the reaction mixture in D<sub>2</sub>O or alkyl halide.<sup>[15]</sup> Later on, Benniston and Rewinska isolated 14-phenyl-7-*N*-phenyldibenzo[*a*,*i*]acridine as an unoptimized reaction intermediate in 22% vield by refluxing an equimolar mixture of 2-naphthol, N-phenyl-2naphthylamine and benzaldehyde in glacial acetic acid.[11] Tu and co-workers reported the synthesis of 14-aryl-7,14dihydrodibenzo[a,j]acridine derivatives via one-pot reaction of 2-naphthylamine and various aromatic aldehydes under microwave irradiation in the presence of thiosalicylic acid catalyst within a short reaction time.<sup>[10]</sup> Osyanin et al. also studied the same preparation from the reaction of Betti base with 2-naphthylamine in acetic acid for 6 h in argon atmosphere to get 20-50% yield of 14-aryl-7,14-dihydrodibenzo [a,j] acridines.<sup>[16]</sup>

## **2** | MATERIALS AND METHODS

#### 2.1 | General Remarks

All chemicals were of analytical grade and used without further purification. TLC was conducted on glass plates using Merck silica gel. NMR spectra were obtained with a JEOL 400 MHz spectrometer ( $\delta$  in ppm) in DMSO- $d_6$  and CDCl<sub>3</sub> solvents. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet Impact-410 spectrometer. The acidity of ionic salts was measured using a UV 2550 spectrophotometer as Hammett plot against 4-nitroaniline as indicator. The thermal stability of the three ILs was investigated with a Shimadzu TGA 50. A PerkinElmer 20 analyser was utilized for elemental analysis of all compounds. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6390LV SEM, equipped with an energydispersive X-ray (EDX) analyser. Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku Multiflex instrument using a nickel-filtered Cu Ka (0.15418 nm) radiation source and scintillation counter detector. A Horiba Lab RAMHR spectrometer containing a He-Ne laser was used to obtain the laser micro-Raman spectra of the bifunctional catalysts with an excitation wavelength of 514.5 nm. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of the chlorometallates was done using a PerkinElmer Optima 2100DV instrument. Melting points were recorded with a Buchi-560 apparatus. The spectral data of novel dibenzoacridine derivatives are included in the supporting information.

## 2.2 | Preparation of Diethyldisulfoammonium Chlorometallates IL-2 and IL-3

The preparation of IL-2 and IL-3 involved two-step reactions. The initial IL diethyldisulfoammonium chloride, [DEDSA] [Cl] (IL-1), was prepared by dropwise addition of ClSO<sub>3</sub>H (30 mmol) at 0 °C to a solution of Et<sub>2</sub>NH (15 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> in a two-necked 100 ml round-bottomed flask fitted with a vacuum system through water and alkali trap for removal of HCl gas. The mixture was stirred continuously at room temperature for another hour to produce IL-1 as a reddish liquid immiscible with CH<sub>2</sub>Cl<sub>2</sub>. Then the crude IL was washed three times with dry  $CH_2Cl_2$  (3 × 5 ml) and dried under vacuum to get analytically pure (98%) IL-1. In the next step, the transition metal chlorides were added to IL-1 in their respective mole fractions (0.5 for both FeCl<sub>3</sub> and ZnCl<sub>2</sub>) and heated at 80 °C for 2 h under nitrogen atmosphere to afford the corresponding chlorometallates IL-2 and IL-3 in the solid state in 96–97% yield after washing  $(3 \times 10 \text{ ml})$  with dry dichloromethane (DCM).

## **2.3** | General Method for Preparation of 14-Aryl-7-(*N*-phenyl)-14*H*-dibenzo[*a*,*j*]acridine Derivatives (1)

In a 50 ml round-bottomed flask, a mixture of 2-naphthol (1 mmol), aldehyde (1 mmol) and N-phenyl-2-naphthylamine (1 mmol) was heated at 100 °C in the presence of 10 mol% of [DEDSA][FeCl<sub>4</sub>] or [DEDSA]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] as catalyst under solvent-free conditions. The course of the reaction was monitored by TLC using ethyl acetate-hexane (1:3) as solvent system. To the reaction flask, 3 ml of dry DCM was added to dissolve the crude organic product after completion of the reaction. The solution of DCM was filtered for separation of solid residue of catalyst on the filter paper. Then the catalyst was washed with dry DCM  $(2 \times 3 \text{ ml})$  and dried in a vacuum oven at 80 °C for the next cycle of the reaction. The DCM solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then evaporated in a rotary evaporator to isolate the crude dibenzoacridine as a solid mixture. The crude product was again precipitated from absolute ethanol which provided analytically pure product.

# **3 | RESULTS AND DISCUSSION**

## 3.1 | Characterization of IL Materials

The three ammonium-based acidic IL systems were characterized using various spectroscopic and analytical techniques and then subjected to UV–visible acidity study and thermogravimetric analysis (TGA).

# 3.1.1 | FT-IR analysis

The FT-IR spectra of the three IL systems displayed characteristic bands of  $-SO_3H$  group as shown in Figure 1. For example, the strong symmetric and antisymmetric stretching vibrations of S-O bond are observed at 1147–1166 and



FIGURE 1 FT-IR spectra of disulfonic ammonium IL systems

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1044–1052 cm<sup>-1</sup>, respectively. The strong stretching vibration band at 869–879 cm<sup>-1</sup> can be attributed to N-S bond which confirms the attachments of -SO<sub>3</sub>H groups with the ammonium nitrogen. Two small peaks at around 1362– 1385 and 1408–1427 cm<sup>-1</sup> can be assigned to C-H bending and rocking vibrations of methyl groups. The -OH broad band is observed at 3380–3420 cm<sup>-1</sup>.

## 3.1.2 | NMR analysis

The <sup>1</sup>H NMR spectrum of **IL-1** shows one two-proton singlet at 11.3 ppm for two -SO<sub>3</sub>H groups. The same spectrum also indicates the presence of two ethyl groups with a triplet at 1.41 ppm for six -Me protons and a multiplet at around 2.82–2.92 ppm for four -CH<sub>2</sub>- protons. Similarly, the <sup>13</sup>C NMR spectrum of this IL shows signals of -CH<sub>3</sub> carbon at 16.7 ppm and -CH<sub>2</sub>- carbon at 54 ppm. The low solubility of the two chlorometallates in DMSO-*d*<sub>6</sub> restricted their NMR studies. Both spectra are included in the supporting information.

## 3.1.3 | Spectral data of chlorometallates

## [DEDSA][Cl] (IL-1)

Light reddish liquid. FT-IR (KBr, cm<sup>-1</sup>): 3410, 1411, 1370, 1147, 1044, 871. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 1.41 (t, 6H, J = 7.32 Hz), 2.82–2.92 (m, 4H), 11.30 (s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 16.7, 54.0. CHN analysis: calculated for C<sub>4</sub>H<sub>12</sub>ClNO<sub>6</sub>S<sub>2</sub> (%): C, 17.81; H, 4.48; N, 5.19; found (%): C. 17.96; H, 4.62; N, 5.33.

## [DEDSA][FeCl<sub>4</sub>] (IL-2)

Light yellow solid; 97% yield; m.p. 117 °C. FT-IR (KBr, cm<sup>-1</sup>): 3397, 1427, 1385, 1161, 1049, 869. CHN analysis: calculated for  $C_4H_{12}Cl_4FeNO_6S_2$  (%): C, 5.95; H, 2.00; N, 3.47; found (%): C, 5.91; H, 2.06; N, 3.52.

## $[DEDSA]_2[Zn_2Cl_6]$ (IL-3)

Off-white solid; 96% yield; m.p. 122 °C. FT-IR (KBr, cm<sup>-1</sup>): 3380, 1408, 1362, 1166, 1052, 879. CHN analysis: calculated for  $C_8H_{24}Cl_6Zn_2N_2O_{12}S_4$  (%): C, 6.36; H, 2.13; N, 3.71; found (%): C. 6.44; H, 2.22; N, 3.78.

## 3.1.4 | Surface morphology

SEM images identify unique types of surface morphology for the two chlorometallates as shown in Figure 2. The image of the Fe salt has a distribution of some rod-like structures with non-uniform aggregation of small or medium size particles. The surface of the Zn salt appears as a highly viscous material distributed as plain surfaces with various size holes without any aggregations. 4 of 9 WILEY-Organometallic



FIGURE 2 SEM images of (a)  $[DEDSA][FeCl_4]$  and (b)  $[DEDSA]_2$   $[Zn_2Cl_6]$ 

## 3.1.5 | EDX analysis

EDX analysis confirms the presence of corresponding constituent elements of the chlorometallates on their surfaces, as shown in Figure 3.

### 3.1.6 | Powder XRD analysis

Powder XRD patterns exhibit several peaks with sharp intensity for the chlorometallate ILs [DEDSA][FeCl<sub>4</sub>] and [DEDSA]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] as shown in Figure 4. The peaks at  $2\theta$ = 15.1°, 33.0°, 33.5° and 42.5° for the Fe salt match well the planes (0,0,12), (1,1,-12), (0,0,26) and (0,0,-24) of JCPDS-770999. Likewise, for the Zn salt, the observed  $2\theta$ values at 16.2°, 25.3°, 29.2° and 48.1° can be assigned to the planes (0,0,2), (1,0,1), (1,0,2) and (1,1,4) from literature data (JCPDS-704517). All these data confirm the existence of metal chlorides in the ionic solid chlorometallates.

#### 3.1.7 | Raman analysis

In the Raman spectrum of  $[DEDSA][FeCl_4]$  (Figure 5), a sharp peak at 332 cm<sup>-1</sup> confirms the presence of  $FeCl_4^-$  in



**FIGURE 3** EDX analysis of (a)  $[DEDSA][FeCl_4]$  and (b)  $[DEDSA]_2$   $[Zn_2Cl_6]$ 

the chlorometallate.<sup>[17,18]</sup> Similarly the spectrum of the Zn salt exhibits characteristic peaks of dimeric  $Zn_2Cl_6^{2-}$  anion at 257 and 315 cm<sup>-1</sup> in agreement with literature values.<sup>[19,20]</sup>



FIGURE 4 Powder XRD patterns of  $[DEDSA][FeCl_4]$  and  $[DEDSA]_2[Zn_2Cl_6]$ 



FIGURE 5 Raman spectra of  $[DEDSA][FeCl_4]$  and  $[DEDSA]_2$  $[Zn_2Cl_6]$ 

## 3.1.8 | Hammett plot for acidity study

The Brønsted acidity of the two chlorometallates and parent IL was determined from the Hammett plots (Figure 6) obtained using a UV–visible spectrophotometer with 4-nitroaniline as indicator.<sup>[21]</sup> A typical procedure involved the equimolar mixing of 4-nitroaniline ( $pK_a = 0.99$ ) and IL in ethanol. The relative acidity of the ILs can be obtained by determining the values of  $H^{\circ}$  (Table 1).using equation 1. The absorbance of the basic indicator [I] was determined in IL solution which decreases with increasing acidity of IL. The protonated form [HI]<sup>+</sup> of the indicator never appeared because of low molar absorptivity. The Hammett function  $H^{\circ}$  for each IL was calculated using equation 1 by measuring the absorption differences [I]/[IH]<sup>+</sup>:



FIGURE 6 Hammett plots of three diethyldisulfoammonium-based ionic salts

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TABLE 1 Values of Hammett function for the three ILs

Entry	IL	A <sub>max</sub>	[I] (%)	[IH] (%)	$H^{\circ}$
1	Blank	2.63	100.0	0	—
2	[DEDSA]Cl	1.00	38.02	61.98	0.78
3	[DEDSA] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ]	0.86	32.70	67.30	0.68
4	[DEDSA][FeCl4]	0.74	28.14	71.86	0.58

$$H^{\circ} = pK(I)aq + \log[I]/[IH]^{+}$$
(1)

where pK(I) aq is the  $pK_a$  value of the basic indicator in aqueous solution. From this experiment the Brønsted acidity of the ILs decrease in the order [DEDSA][FeCl<sub>4</sub>] > [DEDSA]<sub>2</sub>



FIGURE 7 TGA curves of three diethyldisulfoammonium-based ionic salts



FIGURE 8 Electronic spectra of chlorometallates

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#### TABLE 2 ICP analyses for metal content of the disulfoammonium chlorometallates

		Mol. weight	Atomic weight of		Amount of metal (mg l <sup>-1</sup> )	
Entry	Sample	(g mol <sup>-1</sup> )	metal (g mol <sup>-1</sup> )	Exp.	Calcd	Spent catalyst (after sixth cycle)
1	[DEDSA][FeCl <sub>4</sub> ]	403.88	55.85	1.38	1.43	1.01
2	[DEDSA] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ]	755.94	130.76	1.73	1.76	1.17

#### TABLE 3 Optimization of reaction conditions



Entry	Catalyst	Catalyst amount (mol%)	Temp. (°C)	Time (min)	<b>Yield of</b> $1a (\%)^a$
1	[DEDSA][FeCl <sub>4</sub> ]	15	110	45	84
2	[DEDSA][FeCl <sub>4</sub> ]	15	100	45	84
3	[DEDSA][FeCl <sub>4</sub> ]	15	90	50	81
4	[DEDSA][FeCl <sub>4</sub> ]	10	100	45	84
5	[DEDSA][FeCl <sub>4</sub> ]	8	100	55	77
6	[DEDSA] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ]	15	110	50	81
7	[DEDSA] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ]	15	100	50	81
8	[DEDSA] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ]	15	90	60	75
9	[DEDSA] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ]	10	100	50	81
10	[DEDSA] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ]	8	100	65	70

<sup>a</sup>Isolated yield.

#### TABLE 4 Synthesis of acridine derivatives 1 using IL-2 and IL-3 as catalysts<sup>a</sup>



81 (1f)

44 (**2a**)

38 (2b)

55

60

50

80 (1f)

41 (**2a**)

35 (**2b**)

50

60

50

<sup>a</sup>Reactions were performed at 100 °C under neat condition using IL-2 and IL-3.

2-Naphthyl

*n*-Butanal

Paraformaldehyde

<sup>b</sup>Isolated yield.

Entry 1

2

3

4

5

6

7

8

 $[Zn_2Cl_6] > [DEDSA][Cl]$ , which is also supported by  $H^\circ$  values calculated for these ILs (Table 1).

#### 3.1.9 | Thermogravimetric analysis

TGA was used to determine the thermal stability of the chlorometallates as well as the parent IL as shown in Figure 7. The TGA curve of [DEDSA][Cl] shows an approximately 20% weight loss for elimination of adsorbed moisture around 100 °C which is reduced to 5–8% for the two chlorometallates and thus represents the less hygroscopic nature of the Fe- and Zn-containing ionic salts. For the Zn salt, a weight loss of around 20% is observed in the temperature range 140–300 °C which can be attributed to elimination of -SO<sub>3</sub>H groups. Similarly the second decomposition of the Fe salt starts at around 300 °C which indicates its higher thermal stability than both [DEDSA][Cl] and [DEDSA]\_2 [Zn<sub>2</sub>Cl<sub>6</sub>].

## 3.1.10 | Electronic spectra

Solid-state UV spectral analysis was employed in support to determine the composition of anionic species of the two chlorometallates **IL-2** and **IL-3** as shown in Figure 8. It is observed that for the Fe salt the transition for ligand-to-metal charge transfer in the range 270–380 nm is merged with a broad peak around 250–450 nm. There is also another weak d–d transition at 567 nm for FeCl<sub>4</sub><sup>-</sup> anion.<sup>[22,23]</sup> Similarly the two absorption peaks at around 226 and 340 nm for the Zn salt can be assigned as inter-ligand charge transfer transitions of two tetrahedral ZnCl<sub>4</sub><sup>-</sup> which are present in the Zn<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> anion via two bridging Cl ligands.<sup>[24]</sup> The determination of anionic component of the chlorometallate ILs through solid-state UV spectral analysis provides good support to the Raman study.

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## 3.1.11 | Elemental analysis

The quantity of C, H and N present in [DEDSA][Cl] and the two chlorometallate salts was determined using a CHN elemental analyser after heating the samples in a vacuum oven at 80 °C for 1 h, the data for which are included in Section 3.1.3. The metal contents in the two diethyldisulfoammonium transition metal chlorides were measured using ICP elemental analysis with 10 ppm solution of each solid ionic salt in aqua regia. The results as presented in Table 2 are very close to the calculated values which confirms the actual combination of metal chlorides with [DEDSA][Cl] for the formation of ionic salts **IL-2** and **IL-3**.

## 3.1.12 | Leaching test

The possibility of leaching [DEDSA][FeCl<sub>4</sub>] and [DEDSA]<sub>2</sub> [Zn<sub>2</sub>Cl<sub>6</sub>] was studied by stirring 100 mg of chlorometallate salts in 5 ml of four different solvents, namely EtOH, CH<sub>3</sub>CN, DCM and water at room temperature for 3 h. The pH of the filtrates was found as neutral, except that for water. The pH of the water filtrate was observed as 5, and thus indicated slight solubility of ionic salts in water within the stirring period. The TGA profiles of these chlorometallates also show 5-8% of weight loss for physisorbed water below 100 °C (Figure 7). The above studies were also performed in ethanol and DCM for 1 h without change of the pH value of 7 for each solvent. However, the catalytic recycling studies showed lowering of catalytic activities after the third run by taking 10-15 min additional time to give better results up to the sixth cycle. This can be attributed to the breakup of some chlorometallate salts in the presence of moisture because of repeated washing and reactivation in atmospheric conditions under thermal treatment up to the sixth cycle.



**SCHEME 2** Plausible mechanism of synthesis of dibenzoacridines

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## 3.2 | Catalytic Activity

#### 3.2.1 | Optimization of reaction conditions

The catalytic activity of  $[DEDSA][FeCl_4]$  and  $[DEDSA]_2$  $[Zn_2Cl_6]$  chlorometallates was explored for the three-component synthesis of derivatives 1 according to the reaction scheme included in Tables 3 and 4 starting from a mixture of 2-naphthol, aromatic aldehyde and *N*-2-naphthylamine under solvent-free conditions.

In order to optimize the reaction conditions, the reaction of 2-naphthol, benzaldehyde and N-phenyl-2-naphthylamine was investigated with 15 mol% of [DEDSA][FeCl<sub>4</sub>] and [DEDSA] <sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] salts at three different temperatures (90, 100 and 110 °C) under solvent-free conditions for 45-60 min reaction time (Table 3, entries 1-3 and 6-8). Of these three temperatures, we obtained the best results at 100 °C as 81–84% of product (1a) was formed within 45-50 min (Table 3, entries 2 and 7) while at 90 °C there was a small decrease in reaction rate (Table 3, entries 3 and 8). The model reaction produced aryldi(2hydroxy-1-naphthyl)methane as single product at room temperature in ethanol for 2 h where we collected N-phenyl-2naphthylamine as unreacted substrate. The amount of both catalysts was optimized as 10 mol% after investigating the model reaction with 8 and 10 mol% at 100 °C without any solvent (Table 3, entries 4, 5, 9 and 10).

# 3.2.2 | Substrate scope and plausible mechanism

From the results discussed above, 10 mol% of chlorometallate salt at 100 °C were considered as the optimized conditions for generation of complex molecules of dibenzoacridine derivatives through variation of substituted aromatic aldehydes and also aliphatic aldehydes. These results are summarized in Table 4. Aromatic aldehydes bearing electron-donating or electron-withdrawing group produced very good amounts of dibenzoacridine in reasonable reaction time using the two catalysts without any side products (Table 4, entries 1-6). The overall catalytic activities of  $[DEDSA]_2[Zn_2Cl_6]$  and  $[DEDSA][FeCl_4]$ salts were observed to be equivalent for the three-component one-pot synthesis of derivatives 1 under optimized conditions. The reactions of aliphatic aldehydes, namely *n*-butanal and paragenerated 14-alkyl-14H-dibenzo[a,j]xanformaldehyde, thenes (2a, 2b) as products of incomplete reactions without formation of any dibenzoacridine derivatives (Table 4, entries 7 and 8). These types of dibenzoxanthene derivatives can be expected from favourable parallel reactions of 2-naphthol and aliphatic aldehydes in the presence of acidic chlorometallates under solvent-free conditions at 100 °C.<sup>[25]</sup>

The plausible mechanism of dibenzoacridine synthesis can be explained via activation of aldehyde through hydrogen

bonding with acidic IL followed by nucleophilic attack of 2naphthol and then subsequent steps according to Scheme 2.

## 3.2.3 | Reusability of catalysts

The reusability of the two heterogeneous catalysts was examined for the model reaction at 5 mmol scale under the optimized conditions in solvent-free medium up to six cycles.



**FIGURE 9** (a) Reusability of chlorometallate catalysts. (b) Powder XRD characterization of reused catalysts after sixth cycle. (c) FT-IR analysis of reused catalysts after sixth cycle

After each run, the catalyst was recovered from the reaction mixture as solid residue by simple filtration using DCM. Then it was dried in a vacuum oven at 80 °C and reused for the next run. These catalysts lost their activities slowly after the third cycle as reaction time was increased to produce a good amount of dibenzoacridine (1a) as shown in Figure 9 (a). These changes were evidenced from powder XRD analysis (Figure 9b) and ICP-OES determination of metal contents for the reused catalysts after the sixth run (Table 2). The FT-IR spectra of used Zn and Fe catalysts (Figure 9c) also revealed one additional peak each at 1621 and 1629 cm<sup>-1</sup>, respectively, ascribed to bending vibration of adsorbed water with slight change in the position of peaks in the fingerprint region as compared to the FT-IR spectra of fresh catalysts (Figure 1).<sup>[26]</sup>

## 4 | CONCLUSIONS

In summary, we have developed two  $-SO_3H$  groupfunctionalized diethyldisulfoammonium chlorometallate ILs, **IL-2** and **IL-3**, as solid acidic materials. Their compositions and properties were characterized using various spectroscopic and analytical techniques such as FT-IR, UV–visible and Raman spectroscopies, powder XRD, SEM-EDX, ICP-OES, TGA and CHN analysis. The acidity and thermal stability of [DEDSA][FeCl<sub>4</sub>] and [DEDSA]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] salts also supported their uses as efficient heterogeneous acidic catalysts for the three-component synthesis of 14-aryl-7-(*N*-phenyl)-14*H*-dibenzo[ $a_{ij}$ ]acridine derivatives for six consecutive cycles under optimized reaction conditions.

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#### SUPPORTING INFORMATION

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