



FORM-F

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Human Resource Development Group

(Extra Mural Research Division)

CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

PROFORMA FOR PREPARING FINAL TECHNICAL REPORT

(Five copies of the report must be submitted immediately after completion of the research scheme)

1. Title of the scheme

<i>Synthesis and characterization of task-specific ionic liquid systems for one pot synthesis of pyrimidine derivatives</i>	Scheme No.: 02(0282)/16/EMR-II dated on 6/12/2016 Date of Commencement: <u>06/03/2017</u> Date of termination : 06/03/2020
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2. Name and address of Principal Investigator

Dr. Ruli Borah Professor Department of Chemical Sciences, Tezpur University Napaam, Tezpur – 784 028, Assam, India, Tel : 03712-267173 (O); 237008 (R), Fax: 03712-267006, 237005 E-mail : ruli@tezu.ernet.in

3. Name of Sponsoring laboratory of CSIR (If applicable)

Nor applicable

4. Total grant sanctioned and expenditure during the entire tenure

	Amount Sanctioned (Rs.)	Expenditure (Rs.)
Staff	426353.00	397133.00
Contingency & overhead	642698.00	615342.00
Equipment	200000.00	199839.00
Total (A)	1269051.00	1212314.00
Interest earned (B)	4051.00	
Grand total =	1269051.00 + 4051.00 = 1273102.00 [(A)+ (B)]	
Money refund to CSIR through Demand Draft		60,788.00 Demand Draft No. 534619 dt. 23 July 2020

[5] Equipment (s) purchased out of CSIR

Name	Cost (Including 18% GST)
Vacuum Oven, NSW, Model No. NSW-251	Rs. 68930.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18 /2312 date : 28.08.2017
Rotamantle with magnetic stirrer (2L) (JSGW)	Rs.7350.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18 /2312 date : 28.08.2017
Refrigerator, Make: LG, Model : GL-B281BPZX	Rs.23,500.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18/2159 Dt. 16.08.2017

Distillation Unit (Single, Rankem , Avantor) cat. No. WS-SSTG-2	Rs.30,000.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18/2124 Dt. 22.08.2017
Clinical Centrifuge (REMI) Cat. No. C-854/8	Rs.7400.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18/2124 Dt. 22.08.2017
Hot Plate (JSGW) cat. No. 1199/2	Rs.5850.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18/2124 Dt. 22.08.2017
Magnetic Stirrer with hot plate (ABDOS) cat. no. E11231	Rs. 15000.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18/2124 Dt. 22.08.2017
Universal Oven (JSGW), cat.no. 1210/4	14910.00 Order Ref: TU/11-3 /Pur/Chem.Sc./2017-18/2124 Dt. 22.08.2017
Total	

6. Research fellows associated with scheme

Name& Designation	Date of Joining	Date of leaving
Miss Susmita Saikia, Senior Research Fellow	1-04-2017	30/04/2018
Miss Kabita Baruah, Senior Research Fellow	20-09-2018	31-12-2019*
*Kabita Baruah resigned from the project with effect from 1 st January 2020. The resignation letter is attached with this report.		

7. Name(s) of the fellow(s) who received Ph.D. by working in the scheme, along with the Title(s) of thesis:

Name of Fellow : Dr. Susmita Saikia

Title of the thesis:

Design and Implementation of Ionic Liquids Derived Catalysts in Organic Reactions

Year of Ph.D. degree awarded: 30.10.2019

8. List of research papers published/communicated, based on the research work done under the scheme (Name(s) of author(s), Title, Journal, Volume number, Year and Pages should be given for each paper published and a copy of each of them should be enclosed; reprints/copies of papers appearing after submission of FTR should also be sent to CSIR): Attached reprints of publications

- (1) Susmita Saikia and Ruli Borah, One-pot sequential synthesis of 2-amino-4, 6-aryl pyrimidines involving $-SO_3H$ functionalized piperazinium based dicationic ionic liquids as homogeneous catalysts, **ChemistrySelect**, **2019**, **4**, 8751-8756.
- (2) Pinky Gogoi, Kabita Boruah and Ruli Borah, Synthesis of triethylamine-bridged basic tricationic ionic liquids and evaluation of their catalytic efficiencies for preparation of arylidene or alkylidenemalononitrile, **ChemistrySelect**, **2018**, **3**, 9476-9483.
- (3) Arup Kumar Dutta, Kabita Boruah and Ruli Borah, Development of N,N-disulfo-1,1,3,3-tetramethylguanidinium chlorometallates as heterogeneous catalysts for one pot synthesis of 1,2-dihydro-1-aryl-3H-naphth[1, 2-e][1,3]oxazin-3-one derivatives, **Current Organocatalysis** (accepted, 2020)

9. Details of new apparatus or equipment designed or constructed during the investigation:

Not applicable in this project work

10. The likely impact of the completed work on the scientific/technological potential in the country (this may be attached as Enclosure-I):

The completed work has significant impact for development of functionalized ionic liquid based acidic/basic material with capacity to work as efficient recyclable catalysts for organic reactions under environmentally benign methodologies. Here we tried to utilize the prepared acidic/basic ionic liquid systems for one pot synthesis of pyrimidine derivatives in addition to other reactions such as Knoevenagel condensation and naphthoxazine derivatives. The prepared metal centered $-SO_3H$ functionalized halometallate ionic salts can be studied as heterogeneous Bronsted-Lewis acidic catalysts for industrially important reactions such as Friedel-Craft alkylation/acylation reactions, as catalytic equivalent of sulfuric acid in nitration reaction, transesterification etc .

11. Is the research work done of some industrial or agricultural importance and whether patent(s) should be taken? Yes/No; if yes, what action has been/should be taken:

Yes, the synthesized task-specific ionic liquids have significant potential to replace traditional non-recyclable acid /basic catalysts in industrial scale reaction for preparation of fine chemicals. Presently we are not patent these ionic liquid materials. It will require more study as recyclable catalysts with replacement of traditional Bronsted acids /bases in industrial scale reactions.

12. How has the research work complemented the work of CSIR Laboratory that sponsored your scheme?

The newly synthesized task-specific materials may fulfil some of the objectives of CSIR laboratory in material science for further study in industrial scale reaction. The ionic materials which are designed in this project are Bronsted acidic, Bronsted-Lewis acidic and basic in nature exist as viscous liquids or in solid form. The viscous form of ionic liquids with wide electrochemical window can be used as electrolyte in fuel cell and other electrochemical devices. They may be employed as media for metal ion extraction process, energy conversion process via biomass degradation, removal of sulfur from refinery feedstock etc. The metal containing solid ionic compounds can be evaluated as paramagnetic materials, semiconductor materials and sensing of toxic gases such as CO₂, SO₂, NH₃, H₂S. Similarly, the prepared pyrimidine derivatives can be examined as bioactive molecules.

13. Detailed account of the work carried out in terms of the objective(s) of the project and how for they have been achieved; results and discussion should be presented in the manner of a scientific paper/project report in about 5000 words; and this should be submitted as Enclosure-II to this report.

Attached as Enclosure -II

14. An abstract of research achievements in about 200-500 words, suitable for publication.

Attached as Enclosure -III

15. Mention here whether or not the unspent grant has been refunded to CSIR:

I have refunded the unspent grant Rs. 60,788.00 to CSIR with demand draft No. 534619 dated on 23/07/2020(Demand draft is attached with this report).

The rest sanctioned amount **Rs. 1212314.00** have been utilized in the project works out of the total released grant **Rs. 1273102.00** including earned bank interest Rs.4051 during the term of project duration 2016-2020. In support of that I have attached **five sets of the Final Utilization Certificate and Statement of Expenditure** of last grant for the financial year 2019-20 with this report.

Date: 28.07.2020



Signature of PI

Professor

(Dr. Ruli Borah)

Department of Chemical Science
Tezpur University
Tezpur - 784028

Note: Final Technical Report is expected to be self-contained complete report of the work done. Please do not leave any column unanswered.

Enclosure -II

13. Detailed account of the work done under the project :

Objectives

- (i) Synthesis of task-specific chiral/achiral ionic liquids based on imidazolium cations with achiral anions.
- (ii) Synthesis of task-specific chiral ionic liquids using chiral anions and achiral cations.
- (iii) Characterization of the synthesized task-specific ionic liquids with various analytical techniques.
- (iv) Synthesis of hybrid materials of task-specific ionic liquids in combination with solid supports (such as polymers, zeolite and layered material) and their characterizations.
- (v) Applications of these task-specific ILs / supported materials as reusable catalysts for the one pot multistep/multicomponent synthesis of pyrimidine derivatives.
- (vi) Asymmetric synthesis of 3,4-dihydropyrimidinone derivatives using chiral ionic liquids systems.
- (vii) Characterization of novel pyrimidine and optically pure Biginelli DHPMs derivatives by various analytical tools.
- (viii) Observation of novel heterocyclic compound as bioactive molecules.

Work done

The objective of the work has been done in different steps during investigation as discussed in "Results and Discussion" section. The major outcomes can be mentioned as below.

- (a) In the objective of proposal, we proposed to synthesize task-specific imidazolium chiral/achiral ionic liquids and their catalytic uses for one pot synthesis of pyrimidine derivatives. Initially we prepared achiral acidic imidazolium ionic liquids with different organic or inorganic anions. Then we characterized the prepared ionic liquids with various analytical techniques which included $^1\text{H NMR}$, $^{13}\text{C NMR}$, IR and elemental analysis. The catalytic efficiencies of these achiral ionic liquids were investigated for one pot synthesis of pyrimidine derivative followed by sequential conversion of Biginelli dihydropyrimidinone derivatives to 2-amino-pyrimidine derivatives
- (b) The same catalytic study was also extended with another new series of $-\text{SO}_3\text{H}$ functionalized dicationic ionic liquids based on N,N,N',N' -tetrasulfopiperazinium cation $[\text{TSPi}]^+$ and various anions $[\text{X}]^-$ ($\text{X}=\text{Cl}$, CF_3SO_3 , TsO) under solvent-free grinding method. The synthesized ionic liquids were characterized by $^1\text{H NMR}$, $^{13}\text{C NMR}$, FTIR, elemental analysis and thermogravimetric studies. Brønsted acidity of these ionic liquids is determined by Hammett plot using UV-Visible absorbance spectra. The most acidic $[\text{TSPi}][\text{CF}_3\text{SO}_3]_2$ catalyst

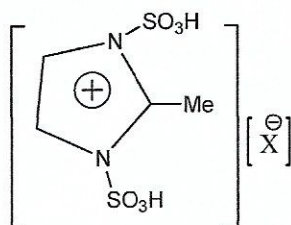
offers good to satisfactory yield within 15-25 min reaction time. Easy recyclability, simple and mild reaction conditions represent the advantages of this method.

- (c) Next step we tried to synthesize imidazolium chiral -SO₃H functionalized acidic ionic liquids containing chiral anions of amino acids. The reactions were not succeeded as per our expectations.
- (d) Four members of N,N-disulfo-1,1,3,3-tetramethylguanidinium chlorometallates [DSTMG]_n[X], where n= 1 or 2; X= FeCl₄⁻, Zn₂Cl₆²⁻, NiCl₄²⁻, MnCl₄²⁻ were synthesized as solid Brønsted-Lewis acidic compounds and studied the catalytic activity using the most acidic catalyst for three-component synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones.
- (e) To improve the thermal stability, hydrophobic nature and catalytic activity of the Bronsted-Lewis acidic halometallates [DSTMG]_n[FeCl₄], it was immobilized on Montmorillonite-K10 Clay with different loading percentage to get a stable heterogeneous catalyst with high surface area. The work is not yet completed.
- (f) Besides the proposed plan of works six new members of tricationic triethylamine bridged imidazolium/pyridinium based basic ionic ionic liquids were developed and their structures confirmed with ¹H NMR, ¹³C NMR, IR and elemental analysis. Their thermal stability, Bronsted basicity and hydrophilic properties were studied to identify the appropriate basic ionic liquid catalysts for preparation of arylidene or alkylidenemalononitrile derivatives.
- (g) The bioactivity study of novel pyrimidine derivative is under progress.

Results and Discussions

To achieve the goal of the objectives, the works have been performed in the following manner.

[1]The preparation of achiral imidazolium acidic ILs was done by preparing three members of 2-methyl 1,3-disulfoimidazolium based Bronsted acidic ionic liquids (BAILs) containing chloride and carboxylate anions of the following structures (Fig.1) which were confirmed by analyzing data of ¹H NMR, ¹³C NMR, FT-IR and elemental analysis.



X= Cl, CH₃COO⁻, CF₃COO⁻

Fig .1 : Structure of imidazolium based acidic ionic liquids

Spectral analysis of imidazolium ionic liquids

2-methyl-1,3-disulfoimidazolium chloride [MDSIM][Cl]: Yellow colored viscous oil; FT-IR (KBr) ν cm^{-1} : 1627, 1445, 1191, 1050, 873, 753, 580; ^1H NMR (DMSO- d_6 , 400 MHz) : δ 2.51(s, 3H), 7.46(s, 2H), 11.9(s, 1H), 13.9(s, 1H) ; ^{13}C (DMSO- d_6 , 100 MHz) : δ 11.5, 119.1 , 144.6. ; CHN analysis, Mol. Formula. $\text{C}_6\text{H}_{10}\text{ClN}_2\text{O}_6\text{S}_2$ (%) : cal. C 17.05, N 9.94 , H 3.58; Found C 17.11, N 9.97, H 3.56

2-methyl-1,3-disulfoimidazolium acetate [MDSIM][CH₃COO]: Brown viscous liquid; FT-IR (KBr) ν cm^{-1} : 1732, 1629, 1443, 1182, 1048 ,884, 756 , 585; ^1H NMR (DMSO- d_6 , 400MHz) : δ 1.85 (s, 3H), 2.46 (s, 3H), 7.34 (s,2H), 12.43 (s, 1H), 13.8(s, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz,) : δ 11.5, 119.1, 144.6 , 172.6.; CHN analysis, Mol. Formula. $\text{C}_6\text{H}_{13}\text{N}_2\text{O}_8\text{S}_2$ (%) : cal. C 23.60, N 9.18 , H 4.29; Found C 23.63, N 9.22, H 3.31.

2-methyl-1,3-disulfoimidazolium trifluoroacetate [MDSIM][CF₃COO]: Brown viscous liquid; FT-IR (KBr) ν cm^{-1} : 1748, 1627, 1445, 1198, 1054, 881, 756 , 585; ^1H NMR (DMSO- d_6 , 400 MHz) : δ 2.51(s, 3H), 7.41-7.48(m,2H), 12.9(s, 1H), 13.90(s, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz) : δ 11.5, 119.6, 144.9 , 159.5. CHN analysis, Mol. Formula $\text{C}_6\text{H}_{10}\text{F}_3\text{N}_2\text{O}_8\text{S}_2$ (%) : cal. C 20.06, N 7.80 , H 2.81; Found C 20.10, N 7.84, H 2.84.

Acidity study

The Brønsted acidity of the acidic ionic liquids was evaluated using the Hammett acidity functions H^0 (Equation 1, Table-1 and Fig.2) using an UV-visible spectrophotometer, with 4-nitroaniline as a basic indicator in ethanol. The Hammett function H^0 for each BAIL was calculated using Equation (1), by measuring the absorption differences $[\text{I}]/[\text{HI}]^+$.

$$\text{H}^0 = \text{pK}(\text{I})_{\text{aq.}} + \log([\text{I}]/[\text{HI}]^+) \quad \text{Equation (1)}$$

where $\text{pK}(\text{I})_{\text{aq.}}$ is the pK_a value of the basic indicator in aqueous solution. The order of acidity of these BAILs was found from the Hammett plot (Fig.2) in the decreasing order as follows: [MDSIM][CF₃COO] > [MDSIM][CH₃COO] > [MDSIM][Cl].

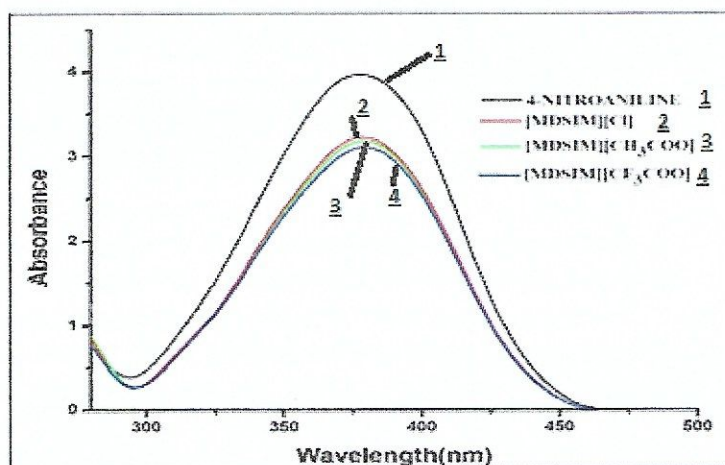


Fig.2 : Hammett plot of BAILs using basic indicator 4-nitroaniline

Table 1: Acidity of the BAILs from the Hammett plot

Entry	BAIL	Λ_{\max}	[I]%	[HI]%	H ^o
1	Blank	3.97	100	0	-
2	[MDSIM][Cl]	3.23	81.4	18.6	1.631
3	[MDSIM][CH ₃ COO]	3.19	80.4	19.6	1.603
4	[MDSIM][CF ₃ COO]	3.10	78.1	21.9	1.542

Thermal stability study

The thermogravimetric profiles of three BAILs were expressed in Fig.3 which showed maximum moisture content and less stability of the chloride anion paired IL.

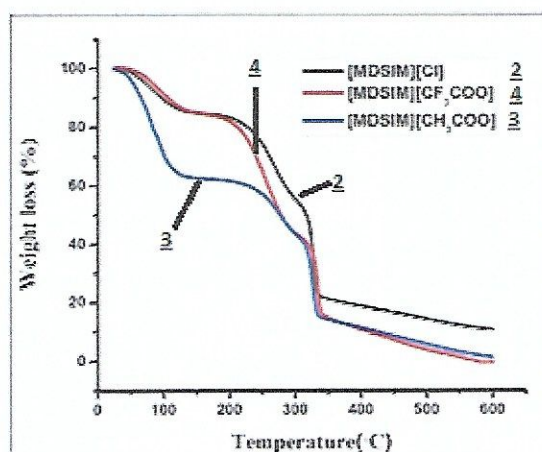
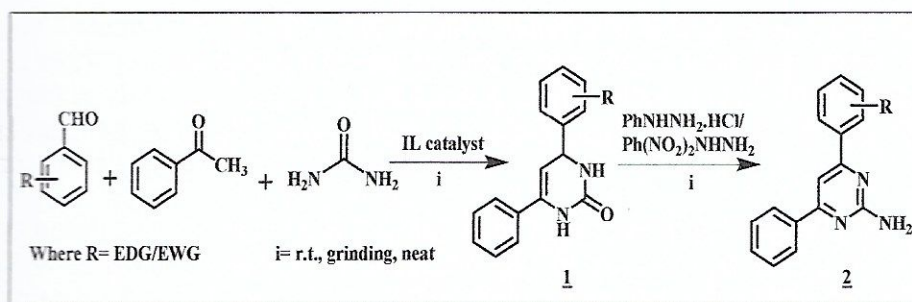


Fig.3: TGA curve of the BAILs

Catalytic study

By knowing the Hammett acidity and thermal stability of the three BAILs we utilized [MDSIM][CF₃COO] as efficient homogeneous catalyst for the three-component Biginelli reaction of aromatic aldehyde, acetophenone and urea in solvent-free grinding method. The crude 3, 4-dihydropyrimidinone derivative was then subjected for sequential conversion to 2-amino-pyrimidine derivatives (**Scheme-1**) at the same procedure after addition of equimolar amount of 2, 4-dinitrophenyl hydrazine for the specific reaction time under thermal treatment with various substituted aldehydes.



Scheme 1: Ionic liquid catalyzed synthesis of pyrimidin-2-amine

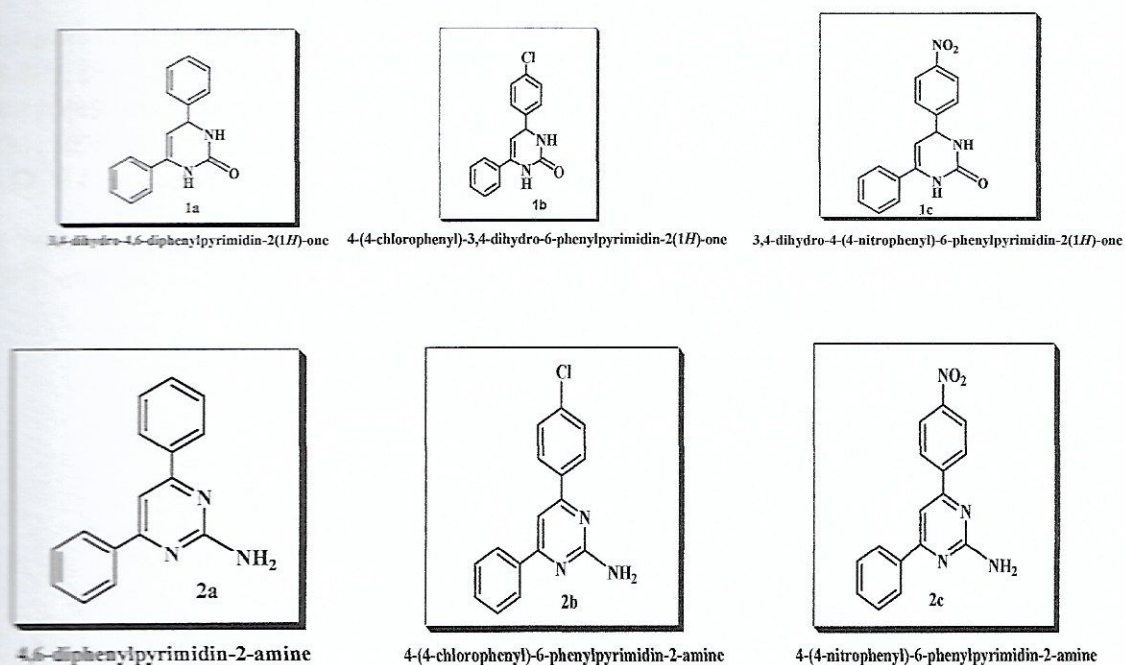


Fig.4 Structures of pyrimidine derivatives

1a : Color: white, melting point: 247°C ; ^1H NMR(DMSO- d_6 , 400MHz): δ 7.93 (s, 1H), 7.29-7.23(m, 5H), 7.14-7.06 (m, 5H), 6.15 (brs, 1H), 5.60(brs, 1H), 4.23(s, 1H); ^{13}C NMR(DMSO- d_6 , 100MHz): δ 157.8, 154.8, 141.8, 133.8, 129.2, 129.6, 128.4, 127.8, 127.4, 127.1, 54.4; IR (KBr) cm^{-1} :3237,3093, 3058, 1674, 1350, 755; CHN analysis, Mol. Formula $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$ (%) : cal. C 76.78, N 11.19, H 5.64; Found C 76.83, N 11.22, H 5.65.

1b:Color:- white, melting point:-, **4c**, ^1H NMR (DMSO- d_6 , 400MHz): δ 7.36-7.30 (m, 2H), 7.13 (s, 3H), 6.96 (s, 4H), 6.73 (brs, 1H), 5.65 (brs, 1H), 4.19 (s, 1H); ^{13}C NMR (DMSO- d_6 , 100MHz): δ 154.6, 142.4, 140.7, 131.9, 129.0, 128.4, 127.9, 127.2 and 53.9; IR (KBr) cm^{-1} : 3237, 3073, 1666, 1343, 820, 763; CHN analysis, Mol. Formula $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}$ (%) : cal. C 67.49, N 9.84, H 4.60; Found C 67.54, N 9.87, H 4.58.

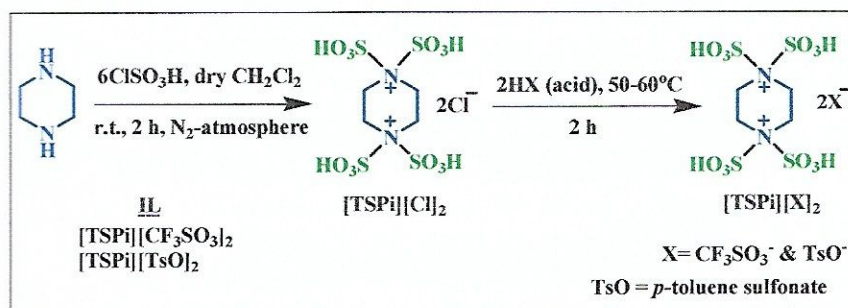
1c Color: , melting point: 206°C ^1H NMR(DMSO- d_6 , 400MHz): δ 8.19-8.12(m, 3H), 7.54-7.45 (m, 3H), 7.26-7.18 (m, 2H), 6.96-6.88 (m, 1H), 6.27-6.14(m, 1H), 5.72(s, 2H), 4.30-4.27(m, 1H); ^{13}C NMR(DMSO- d_6 , 100MHz): δ 157.8, 156.1, 151.0, 147.1, 130.8,127.8, 123.8, 59.3; IR (KBr) cm^{-1} : 3294, 3073, 1670, 1243, 1516, 1350, 856; CHN analysis, Mol. Formula $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_3$ (%) : cal. C 65.08, N 14.23, H 4.44; Found C 65.12, N 14.26, H 4.47.

2a: Color:- Bright Orange, melting point:- 240.4°C, **5a**, $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ 11.62 (s, 1H), 8.84 (s, 1H), 8.66 (s, 1H), 8.35-8.32(m, 1H), 8.05-8.02(m, 1H), 7.76 (s, 2H), 7.44(m, 5H); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ 149.9, 145.0, 137.4, 134.0, 131.0, 130.2, 129.6, 127.6, 123.4, 117.3, 86.6; IR (KBr) cm^{-1} : 3445, 3093, 1616, 1594, 1350, 763; CHN analysis, Mol. Formula $\text{C}_{16}\text{H}_{13}\text{N}_3$ (%) : cal. C 77.71, N 16.99, H 5.30; Found C 77.74, N 17.10, H 5.33.

2b: Color:- light pink, melting point:-119.7°C, **5c**, $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ 7.63 (s, 1H), 7.59 (d, $J=8.0\text{Hz}$, 2H), 7.34 (d, $J=8.0\text{Hz}$, 2H), 7.29-7.25 (m, 2H), 7.11 (d, $J=8.0\text{Hz}$, 2H), 6.86-6.89 (m, 1H); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ 144.4, 135.7, 133.1, 129.2, 128.8, 127.2, 120.3, 112.8; IR (KBr) cm^{-1} : 3445, 3051, 1609, 1566, 1365, 827, 748; CHN analysis, Mol. Formula $\text{C}_{16}\text{H}_{12}\text{Cl N}_3$ (%) : cal. C 68.21, N 14.91, H 4.29; Found C 68.24, N 14.88, H 4.33.

2c: Color:- Orange, melting point:-158.3°C, **5b**, $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ 10.85 (s, 1H), 8.19 (d, $J=8.0\text{Hz}$, 2H), 8.0 (s, 1H), 7.85 (d, $J=8.0\text{Hz}$, 2H), 7.23-7.22 (m, 2H), 7.12-7.10 (m, 2H), 6.91-6.77 (m, 1H); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ 146.6, 144.9, 143.2, 134.1, 129.8, 126.6, 124.6, 120.4, 113.1; IR (KBr) cm^{-1} : 3438, 3079, 1610, 1573, 1530, 1336, 755; CHN analysis, Mol. Formula $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2$ (%) : cal. C 65.75, N 19.17, H 4.14; Found C 65.78, N 19.20, H 4.18.

[2] Three $-\text{SO}_3\text{H}$ functionalized dicationic ionic liquids (DIL) of N,N,N',N'-tetrasulfopiperazinium cation [TSPi] $^{2+}$ with three anions namely $[\text{X}]^- = \text{Cl}, \text{CF}_3\text{SO}_3, \text{TsO}$ were synthesized (Scheme 2).



Scheme 2. Synthesis of $[\text{TSPi}][\text{X}]_2$ ($\text{X} = \text{Cl}, \text{CF}_3\text{SO}_3 \text{ \& \ } \text{TsO}$)

Spectral data of $[\text{TSPi}][\text{X}]_2$ ($\text{X} = \text{Cl}, \text{CF}_3\text{SO}_3 \text{ \& \ } \text{TsO}$) :

N, N, N', N'-tetrasulfopiperazinium chloride $[\text{TSPi}][\text{Cl}]_2$: Brown viscous liquid, FTIR (KBr) cm^{-1} : 3429, 2923, 2851, 1629, 1463, 1167, 1043, 870, 725, 581; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ 13.48 (s, 4H), 3.75 (s, 8H); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ 52.4; CHN analysis $\text{C}_4\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_{12}\text{S}_4$: Calcd. C, 10.02; H, 2.52; N, 5.84; Found: C, 9.92; H, 2.77; N, 5.86.

N, N, N', N'-tetrasulfopiperazinium triflate $[\text{TSPi}][\text{CF}_3\text{SO}_3]_2$: Brown viscous liquid, FTIR (KBr) cm^{-1} : 3429, 2923, 2851, 1629, 1463, 1167, 1043, 870, 725, 639, 581; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ 13.50 (s, 4H), 3.79 (s, 8H); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ 87.4, 100.1; CHN analysis $\text{C}_6\text{H}_{12}\text{F}_6\text{N}_2\text{O}_{18}\text{S}_6$: Calcd. C, 10.20; H, 1.71; N, 3.96; Found: C, 10.32; H, 1.77; N, 3.86.

N, N, N', N'-tetrasulfopiperazinium p-toluene sulfonate $[\text{TSPi}][\text{TsO}]_2$: Brown viscous liquid, FTIR (KBr) cm^{-1} : 3429, 2923, 2851, 1629, 1463, 1167, 1043, 870, 725, 581; $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ 2.17 (s, 3H), 2.24 (s, 3H), 3.26 (s, 8H), 7.07 (s, 4H), 7.45 (s, 4H), 12.82 (s, 4H); $^{13}\text{C NMR}$ (DMSO- d_6 , 100 MHz): δ

143.9, 139.4, 129.1, 126.0, 87.3, 21.2; CHN analysis $C_{18}H_{26}N_2O_{18}S_6$: Calcd. C, 28.80; H, 3.49; N, 3.73; Found: C, 28.92; H, 3.57; N, 3.76.

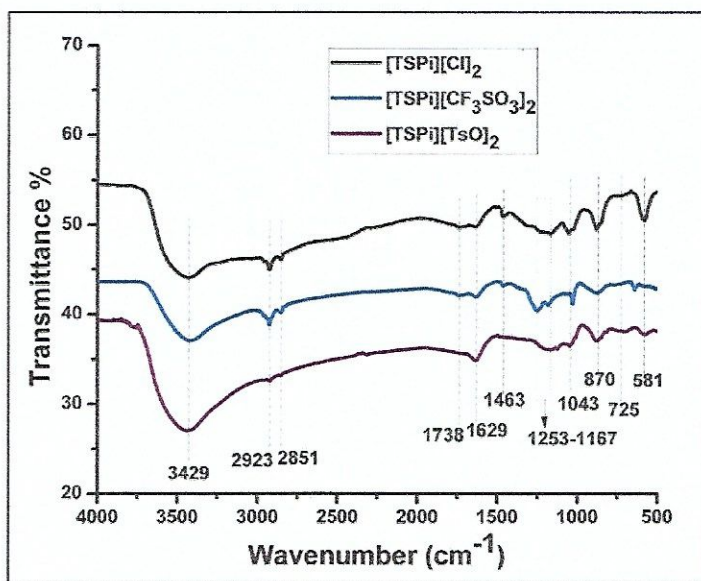


Fig.5 FT-IR spectra of $[TSPi][X]_2$ ($X = Cl, CF_3SO_3, TsO$)

Assignments of all IR peaks of the ionic liquids in Fig.5 are summarized in Table 2. Typical vibrations of $-SO_3H$ groups were observed in finger-print region of the IR spectra.

Table 2 :FT-IR band assignments of piperazinium ionic liquids

Bands (cm^{-1})	Assignment
581	S-O bending
725	Out-of-plane ring C-H bending
870	N-S stretch
1043	S-O antisymmetric stretch
1167-1253	S-O symmetric stretch
1463	Out of phase C-H bending of methyl group
1629	Aromatic C=C stretch
2851 & 2923	C-H stretch (CH_2)
3429	O-H stretch of $-SO_3H$ group

The representative ^1H NMR and ^{13}C NMR spectra of $[\text{TSPi}][\text{TsO}]_2$ are expressed in Fig. 6a and 6b.

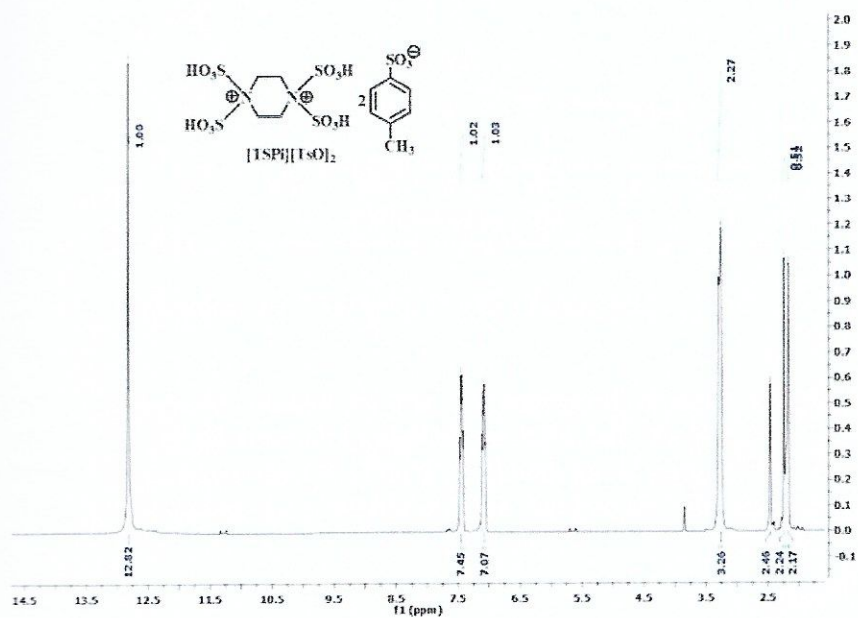


Fig. 6a. ^1H NMR of $[\text{TSPi}][\text{TsO}]_2$

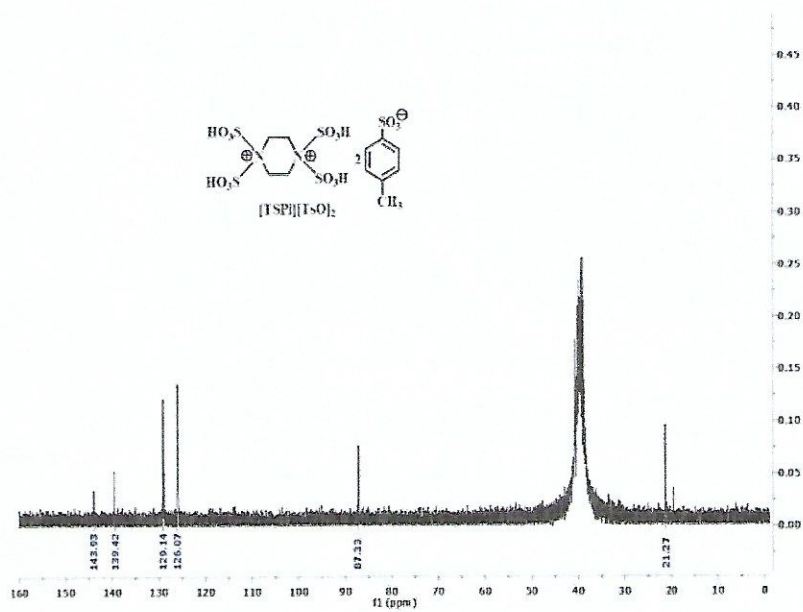


Fig. 6b. ^{13}C NMR of $[\text{TSPi}][\text{TsO}]_2$

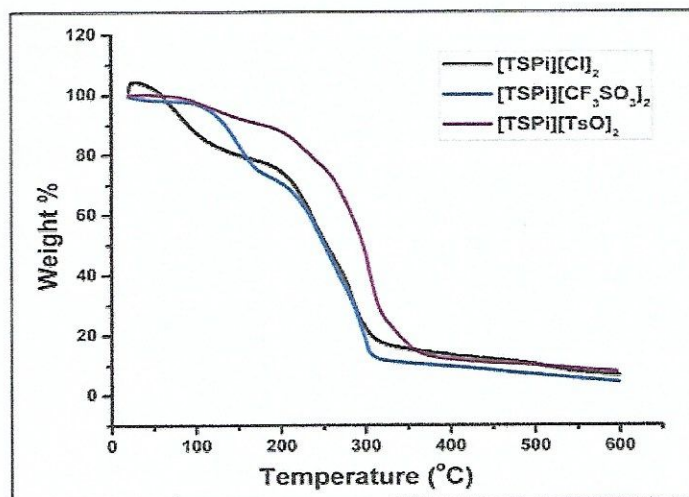


Fig.7.TGA graph of $[TSPi][X]_2$ ($X = Cl, CF_3SO_3, TsO$)

Fig.7 corresponding to thermal analysis of the ILs expressed absence of physisorbed water in $[TSPi][CF_3SO_3]_2$ and $[TSPi][TsO]_2$ in contrast to approximate 13% loss of moisture for $[TSPi][Cl]_2$ below 100 °C. This study showed greater stability of the $[TSPi][TsO]_2$ ionic liquid up to 200 °C than the triflate based ionic liquid which can be attributed for presence of more number of resonating structures of *p*-toluene sulfonate anion.

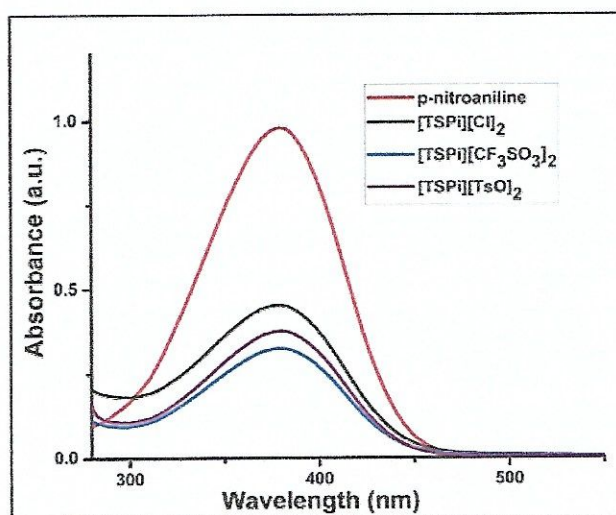


Fig.8 Hammett plot of dicationic ionic liquids in ethanol

The Brønsted acidities of three dicationic ILs were measured from Hammett acidity function using UV-Visible Hammett plots according to the reported experimental procedure (Fig.8). The decreasing acidity order of the ILs was obtained as : $[TSPi][CF_3SO_3]_2 > [TSPi][TsO]_2 > [TSPi][Cl]_2$ in accordance with the Hammett acidity function. The most acidic catalyst $[TSPi][CF_3SO_3]_2$ was used as recyclable catalyst for the same one-pot preparation (Table-3) of 2-amino-4, 6-diaryl pyrimidines involving Biginelli-like

reaction (Scheme 1) followed by condensation-aromatization reaction with phenylhydrazine under solvent-free grinding method.

Table 3: Substrate scope study for the synthesis of **2a** using 2.5 mol% of [TSPi][CF₃SO₃]₂ under solvent-free grinding condition

Entry	R	Product	Time (min) ^c	Yield (%) ^d
1	H ^a	2a	16	89
2	4-OCH ₃ ^b	2b	25	82
3	2-OH ^a	2c	18	82
4	2, 4-dichloro ^a	2d	15	88
5	4-OH ^b	2e	20	85
6	4-CH ₃ ^a	2f	16	88
7	4-NO ₂ ^a	2g	15	85
8	3, 4, 5-trimethoxy ^a	2h	20	84
9	4-Cl ^a	2i	15	90
10	2-Naphthaldehyde ^b	2j	20	80

^a Reaction was carried out using phenylhydrazine hydrochloride; ^b Reaction was carried out using 2, 4-dinitrophenyl hydrazine; ^c Reaction time was given as total reaction time including both steps; ^d Isolated yield.

This work was published in **ChemistrySelect**, 2019, 4, 8751-8756

(3) For preparation of chiral ionic liquids, we performed the reaction of 1,3-disulfo-2-methyl /ethyl imidazolium chloride ionic liquid with selected amino acids. But the chiral ionic liquids were not produced as per our expectations.

(4) A new type of chlorometallates of sulfonic acid functionalized guanidinium cation with composition [DSTMG]_n[X], where X= FeCl₄⁻/Zn₂Cl₆²⁻/ NiCl₄²⁻/ MnCl₄²⁻ and n= 1 or 2 were developed after treatment of ionic liquid N, N-disulfo-1,1,3,3-tetramethylguanidinium chloride [DSTMG][Cl] with the respective metal chlorides in different mole fractions at 75 °C. They were isolated as solid acids with varied thermal stability (150-250 °C) and physisorbed water (0-20%) as observed from the thermogravimetric study. From them, the most Brønsted acidic Fe(III) salt was employed as efficient recyclable heterogeneous catalyst for the one-pot synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones in neat condition

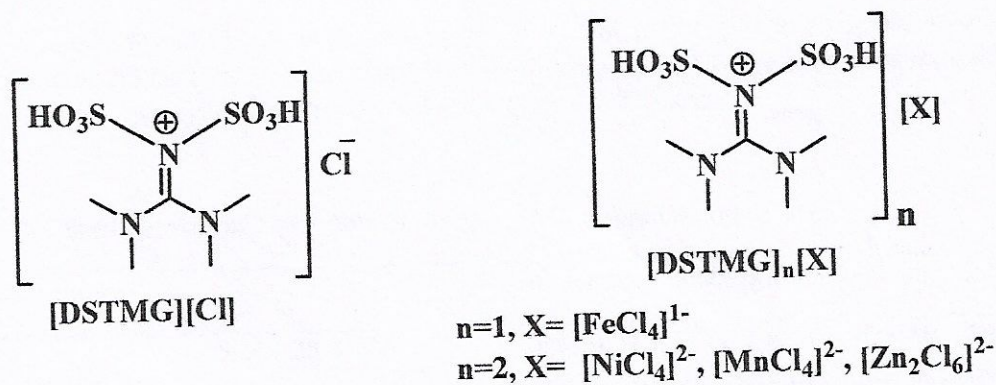
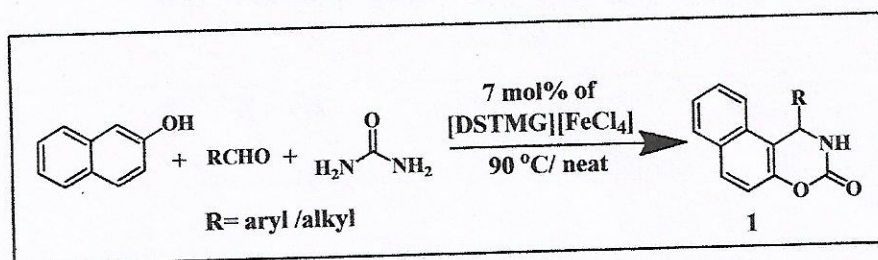


Fig. 9: Structure of TMG-based chlorometallates



Scheme 3: Synthesis of 1, 2-dihydro-1-aryl-3H-naphth[1,2-e] [1,3] oxazin-3-one derivatives

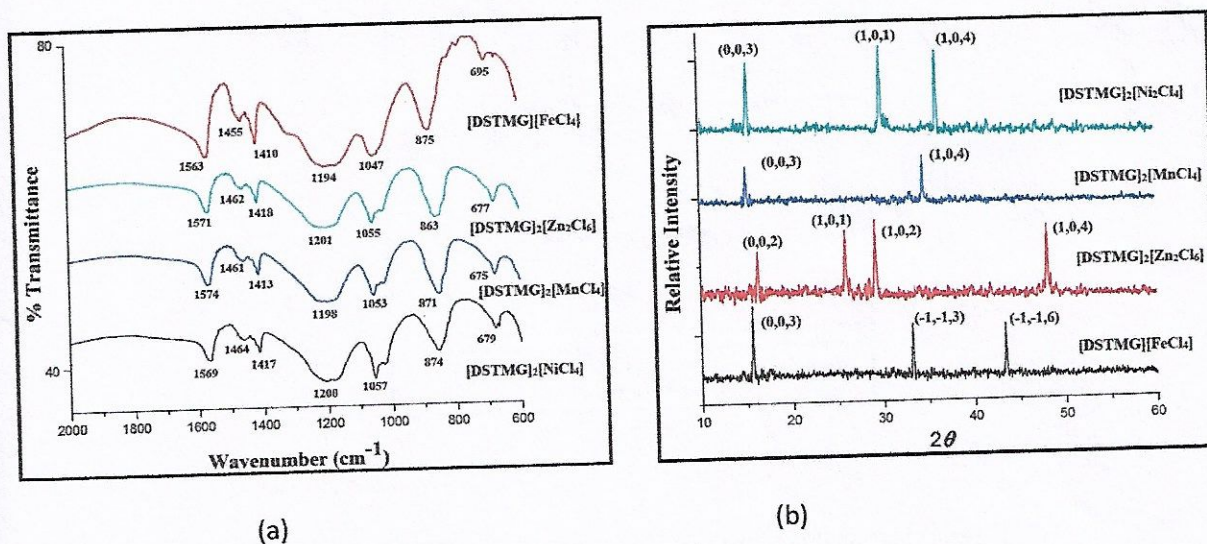


Fig. 10 (a) FT-IR and (b) PXRD analysis of TMG-based chlorometallates

The various typical IR peaks of the tetramethyl guanidinium cation and sulfonic acid group can be expressed in $600-2000\text{ cm}^{-1}$ region in Fig.10(a). The three strong to medium intensity bands around $1194-1201\text{ cm}^{-1}$, $1047-1057\text{ cm}^{-1}$ and $675-695\text{ cm}^{-1}$ corresponding to S-O symmetric stretch, anti-symmetric stretch, and bending vibrations of $-SO_3H$ group. Powder XRD-analyses of the four chlorometallates were taken to investigate the existence of metal chloride as complex anionic forms

within these salts in Fig.10(b). The diffraction peaks of each of the ionic salts are analyzed in support of the corresponding JCPDS card number of PXRD data in Table 4 . This study expressed crystalline nature of the ionic salts by displaying sharp peaks in the respective XRD pattern.

Table 4: JCPDS card number of PXRD data of the four TMG-based halometallates

JCPDS Card Number	$2\theta^\circ$	Reflection Planes	Ionic salts
71-2032	15.3°, 30.3°, 36.3	(0,0,3), (1,0,1), (1,0,4)	[DSTMG] ₂ [NiCl ₄]
76-0235	15.1°, 34.5°	(0,0,3), (1,0,4)	[DSTMG] ₂ [MnCl ₄]
74-0517.	16.5°, 25.5°, 29.4°, 48.8°	(0,0,2), (1,0,1), (1,0,2), (1,1,4)	[DSTMG] ₂ [Zn ₂ Cl ₆]
77-0998	16°, 33.3°, 43.1°	to (0,0,3), (-1,-1, 3), (-1,-1,6)	[DSTMG][FeCl ₄]

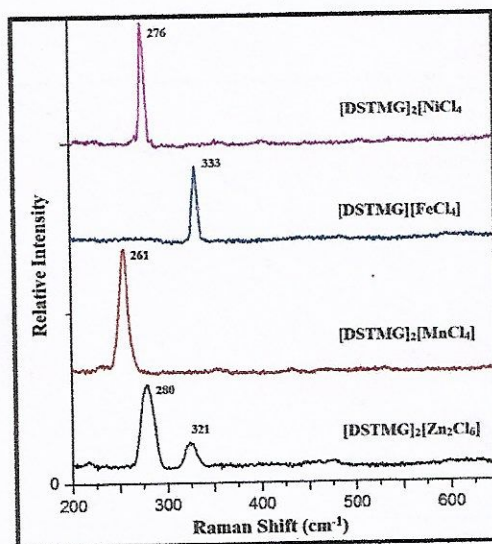


Fig.11 : Raman spectra of TMG-based chlorometallates

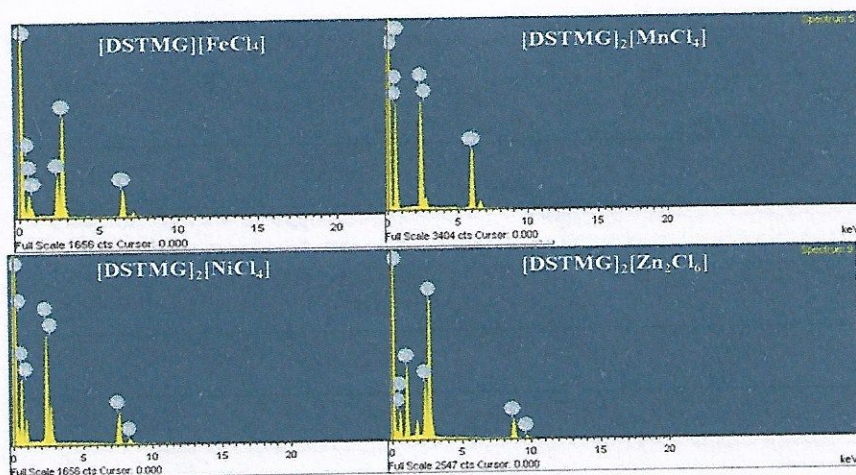


Fig.12: EDX images of TMG-based chlorometallates

Raman spectra of the ionic salts in Fig.11 detected characteristics peaks of complex metal halide anions against their literature data. Fig.12 distinctly evidenced the presence of key elements in TMG-based chlorometallate salts in their respective energy dispersive X-ray (EDX) images

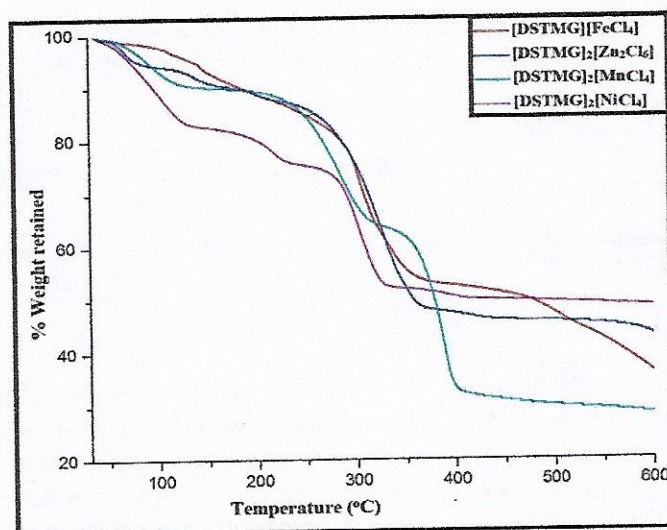


Fig.13:TGA plots of TMG-based chlorometallates

TGA profile (Fig.13) displayed no loss of physisorbed water for the Fe(III) salt at 100 °C in contrast to 20 % highest weight loss by the Ni(II) salt. From the Hammett plots the acidity order of the ionic salts are found to be: $[DSTMG][FeCl_4] > [DSTMG]_2[Zn_2Cl_6] > [DSTMG]_2[MnCl_4] > [DSTMG]_2[NiCl_4]$. After that the Fe(III) salt was employed in catalytic study for the reaction Scheme-3.

This work is accepted for publication in "Current Organocatalysis".

(4) To improve the catalytic efficiency and thermal stability of the Brønsted-Lewis acidic halometallates $[\text{DSTMG}]_n[\text{FeCl}_4]$, it was immobilized on Montmorillonite Clay with different loading percentage to get a stable heterogeneous catalyst with high surface area. The work is not yet completed.

(5) Two series of triethylamine based tricationic basic imidazolium/pyridinium ionic liquids were synthesized and their structures are included in Fig. 7.

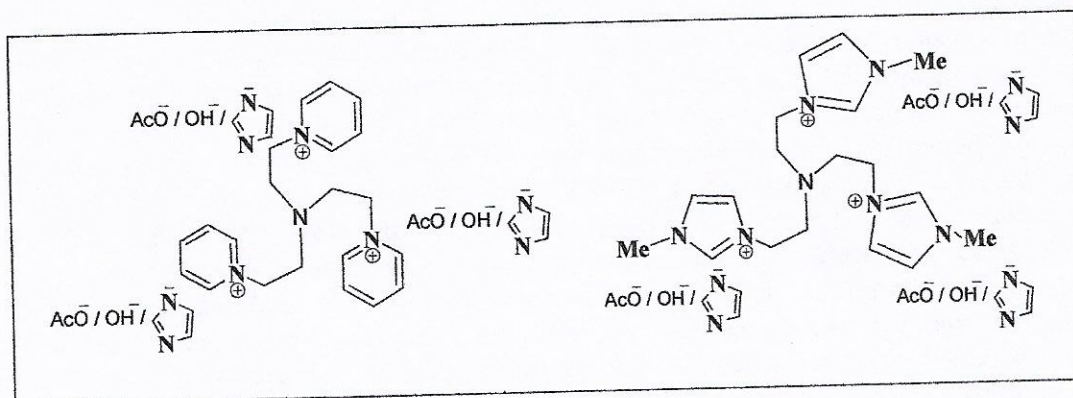


Fig. 14 : Triethylamine based tricationic basic ionic liquids

After characterization they were subjected as reusable homogeneous basic catalyst for preparation of arylidene or alkylidenemalononitrile derivatives via Knoevenagel condensation reaction at room temperature.

This was published in *Chemistry Select*, 2018, 3, 9476-9483.

(6) Biological study of pyrimidine derivatives is in progress and not yet completed.

Conclusions

Several task-specific ionic liquid systems consisting of mono/dicationic imidazolium/piperazinium Brønsted acidic ionic liquids, monocationic Brønsted-Lewis acidic halometallates and tricationic basic ionic liquids were developed and characterized with various analytical techniques. The prepared Brønsted acidic ionic liquids showed excellent catalytic activities for one-pot two step synthesis of pyrimidine derivatives under solvent-free grinding method at atmospheric temperature within short time without isolation of intermediate formed in the 1st step of reaction. The most Brønsted-Lewis acidic halometallates was used as reusable heterogeneous catalyst for one-pot synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones in neat condition. Finally, the tricationic basic ionic liquids was tested as efficient recyclable liquid bases for preparation of arylidene or alkylidenemalononitrile derivatives via Knoevenagel condensation reaction at room temperature. Till date, we have published two papers and one more paper is accepted for publication. Two more papers are in the process of writing stage. The initially joined Senior Research Fellow **Susmita Saikia** received her Ph.D. degree in 2019 and the other Senior Research Fellow **Kabita Baruah** is going to submit her thesis within December 2020.

Enclosures -III

14. Abstract of the project work

The major achievement of this project can be summarized as development of task-specific ionic liquid systems consisting of mono/dicationic imidazolium/piperazinium Brønsted acidic ionic liquids, monocationic tetramethyl guanidinium(TMG) based Brønsted-Lewis acidic halometallates and triethylamine based tricationic basic imidazolium/pyridinium ionic liquids with investigation of their thermal stability, UV-Vis Brønsted acidity/ Brønsted basicity studies and hydrophilic properties. In addition, the semiconductor properties of TMG- based halometallates were analyzed using Tauc-plot from their electronic spectra. The structures of the ionic liquid systems were determined using proton and ^{13}C NMR, FT-IR, Raman, PXRD, electronic spectra, SEM-EDX and elemental analysis. Except the solid acidic TMG-based four halometallates, the prepared sulfonic acid functionalized imidazolium/piperazinium ionic liquids were isolated as viscous liquids with varied thermal stability and hygroscopic properties as observed from their thermogravimetric analysis. The most Brønsted acidic imidazolium/piperazinium ionic liquids were employed as reusable catalyst for one-pot two step synthesis of 2-amino-4, 6-diaryl pyrimidines involving Biginelli-like reaction of acetophenone, aromatic aldehydes and urea followed by condensation-aromatization reaction with phenylhydrazine under solvent-free grinding method using the same amount of catalyst with excellent yields. The Brønsted-Lewis acidic halometallates was investigated as reusable heterogeneous catalyst for one-pot synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones in neat condition. The triethylamine based tricationic imidazolium/pyridinium Brønsted basic ionic liquids were observed as efficient safer recyclable liquid bases for preparation of arylidene or alkylidenemalononitrile derivatives via Knoevenagel condensation reaction at room temperature. Two papers published and one paper is accepted for publication. Two more papers are in the process of writing stage. The initially joined Senior Research Fellow **Susmita Saikia** received her Ph.D. degree in 2019 and the other Senior Research Fellow **Kabita Baruah** is going to submit her thesis within December 2020.

Date: 7/09/2020

To,

The Head, Human Resource Development Group
Council of Scientific and Industrial Research (CSIR)
CSIR Complex, Pusa
New Delhi-110012

Through: Head of the Institute

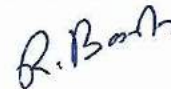
Subject: Submission of **Final Utilization Certificate, Consolidated Statement of Accounts (2019-20) and Final Technical Report** for the CSIR project sanction No. 02(0282)/16/EMR-II dated 6/12/2016

Sir,

Please find herewith the documents of *Final Utilization Certificate (Form-L, five copies), Consolidated Statement of Accounts (Five copies), Final Technical Report (Form-F, 5 copies)* for the research project entitled "*Synthesis and characterization of task-specific ionic liquid systems for one pot synthesis of pyrimidine derivatives*", against the sanctioned letter no. 02(0282)/16/EMR-II dated 6/12/2016 which is terminated on 06/03/2020 after completion of three years as per your requirement for closing the account. The unutilized amount Rs. **60,788.00** at the end of the financial year 2019-20 has been surrendered to EMR, HRDG (CSIR) through Demand draft No. 534619 dated 23/07/2020 enclosed herewith for your information. Kindly acknowledge the same through mail.

Thanking You,

You're faithfully



Signature of the Principal Investigator

Dr. Ruli Borah

List of enclosure

- [1] UC and Statement of accounts
- [2] Demand draft No. 534619 dated 23/07/2020 of Rs. **60,788.00** for surrender amount
- [2] Approved claim bill by CSIR 2019-20 and resignation letter of SRF from project
- [3] Final Technical report
- [4] Print copy of published papers.

Professor
Department of Chemical Sciences
Tezpur University
Tezpur - 784028



FORM-L
UTILISATION CERTIFICATE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Human Resource Development Group
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

CSIR-HRDG Scheme No. 02(02820/16/EMR-II dated 6/12/2016

S. No.	Particulars	Letter No. /Bank Transaction ID Nos. & Date	Amount (Rs.)
1	Grants received from CSIR during the year 2019-20	<u>Bank Transaction ID Nos.</u> <u>NEFT*SYNB0009100*P1911291100950</u> <u>5*NPLdated29/11/2020</u> (approved date of Claim bill form by CSIR for the financial year 2019-20 is 31/10/2019)*	2,90,353.00
2	Unspent balance of previous year 2018-19	-	92777.00
3	Interest earned/accrued on CSIR grant	--	2600.00
Total			3,85,730.00
*Approved Claim Bill Form by CSIR (2019-20 year) is attached with this Utilization Certificate.			

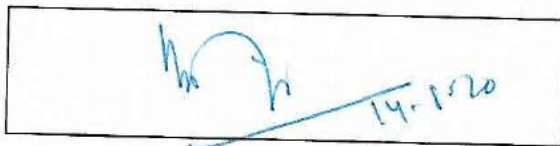
1. Certified that out of **Rs. 2,90,353.00** (Rupees *Two lakh ninety thousand three hundred fifty three only*) of grant-in-aid released by Extramural Research (EMR) Division of HRDG (CSIR) vide Letter No/Bank Transaction ID Nos. NEFT*SYNB0009100*P19112911009505*NPLdated 29/11/2020 as given in the margin during the year 2019-20 and **Rs. 2600.00** earned/accrued as interest from bank on grants released by CSIR and **Rs. 92777.00** on account of unspent balance of the previous year, a sum of **Rs. 324942.00** has been utilized for the purpose for which it was sanctioned and that the balance of **Rs. 60,788.00** remaining unutilized at the end of the year has been surrendered to EMR, HRDG (CSIR) through Demand Draft No. 534619 dated 23/07/2020 enclosed herewith.

2. Certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned have been duly fulfilled/are being fulfilled and that I have exercised the following checks to see that the

money was actually utilized for the purpose for which it was sanctioned. The detail expenditure incurred during the year is shown in the enclosed "Statement of Accounts (Receipt & Payment)".

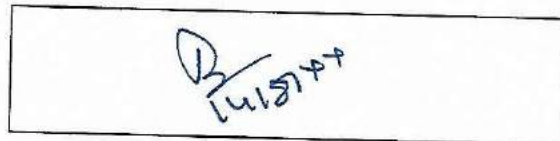
(Kinds of checks exercised)

1. Vouchers and Statement of Accounts
2. Grant-in-Aid
3. Expenditure Register
4. Bank statements for accrual interest
5. Surrender amount of Rs. 60788.00 to CSIR with Demand Draft No. 534619 dt. 23/07/2020



Signature of Finance Officer, Tezpur University
Finance Officer
Tezpur University

Date&Seal



Countersigned by Registrar, Tezpur University
Registrar
Tezpur University

Date & Seal

The Utilization certificate and statement should be signed by Head of the Finance & Accounts and countersigned by Registrar/Dean/Director of the University/Institute.

Consolidated Statement of Accounts

(From the date of 1-04-2019 to till 31st March, 2020)

Title of the Research Scheme:

Synthesis and characterization of task-specific ionic liquid systems for one pot synthesis of pyrimidine derivatives

Name of the Principal Investigator: Dr. Ruli Borah

Date of Commencement: 6-03-2017

Date of Termination: 6-03-2020

Receipts(Particulars of grants received)

Payments(Particulars of grants spent)

Period(ending 31 st)	Check No.	Date:	Contingency(Rs)	Stipend (Rs)	Interest	Overhead Grant(Rs)	Unspent balance From 1918-19 year (Rs)	Total(Rs)	Stipend (Rs) (Period 1/04/2019 to 31/12/2019*)	Contingency(Rs)	Overhead	Equipment Grant(Rs)	HRA+ MA	Total(Rs)	Balance(Rs)
01-04-2019 to 31-03-2020	Received through RBI-Electronic Funds Transfer	Dated 29 Nov 2019	2,00,000*-	90353 /-	2600/-	15130/-	92,777 /-	3,85,730/-	126000/-*	198942/-	Nil	Nil	-	324942/-	60,788/-
		Rs/- 2,90,353.00													

*Kabita Boruah resigned from the project as Senior Research Fellow with effect from 1 January 2020.

(Registrar)

Tezpur University
Registrar
Tezpur University

(Finance Officer)

Tezpur University
Finance Officer
Tezpur University

(Principal Investigator)

Dr. Ruli Borah

Professor
Department of Chemical Sciences
Tezpur University
Tezpur - 784028

INDU-velop Avenue 021

Alc Payee

TEZPUR UNIVERSITY
CODE No. 14250
Tel No. 03712-267265

मांगद्राफ्ट
DEMAND DRAFT

Key: NIJDEY
Sr. No: 428707

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मागे जानेपर EMR, HRDG(CSIR) *****

या उनके आदेश पर

ON DEMAND PAY

OR ORDER

Sixty Thousand Seven Hundred and Eighty Eight Only

रुपये RUPEES

अदा करें ₹ 60785.00

IOI 000471531619
Name of Applicant

Key: NIJDEY Sr. No: 428707
TEZPUR UNIVERSITY R & D

AMOUNT BELOW 60785(6/5)

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प्राधिकृत हस्ताक्षर

शाखा प्रबंधक
BRANCH MANAGER

कंप्यूटर द्वारा मुद्रित होने पर ही वैध
VALID ONLY IF COMPUTER PRINTED

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VALID FOR 3 MONTHS ONLY

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INSTRUMENTS FOR ₹ 1,50,000- & ABOVE ARE NOT VALID UNLESS SIGNED BY TWO OFFICERS

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**FORM-1
CLAIM BILL FORM**

To:

The Head (HRDCG)
Council of Scientific & Industrial Research
CSIR COMPLEX, PUSHA
NEW DELHI-110012

Roll No. CSIR TU/DP/CHEM/01
CSIR Sanction No. 02(0282)/16/EMR-II dated on 6/12/2016
% of Scheme as full

Synthesis and characterization of task-specific ionic liquid systems for one pot synthesis of pyrimidine derivatives

PARTICULARS	AMOUNT OF GRANT(Rs)						REMARK
	Staff ^a	Cont.	Equip.	Over.	HRA	Total	
Amount Sanctioned for Financial Year 1.04.2015 to 31.03.2019	1,68,000	2,00,000	nil	25919	--	3,93,919	
Amount claimed for period from 1.04.2019 to 31.03.2020	1,68,000	2,00,000	nil	41,049 15,130		4,09,049 3,83,130	*T am we do the in ye 20
Carry over Balance from the grant of last Year	64867	540	--	25919*	--	91,326 145112	
Net amount claimed	1,03,133	1,99,460	nil	15130 (10,789)	(-1451)	3,17,723 2,90,353	

- 1) Certified that the amount claimed in this bill will be utilized for the purpose for which it has been sanctioned and the audited statement of expenditure will be furnished as per requirement. We agree and abide by the Terms and Conditioned that the excess expenditure, if any, incurred will be met from institution's funds and not from CSIR funds.
- 2) Certified that the persons for whom HRA has been claimed have not been provided any accommodation and HRA claim is as per rules of this Institute. The rate of HRA may be indicated against the name of Fellow for whom HRA has been claimed.

R. Borah
(Registrar, Tezpur University)
Registrar
Tezpur University

R. Borah
Dr. (Mrs) Ruli Borah

(Project Investigator)

Professor
Dept. of Chemical
Tezpur University
Esttd-1994
Nagarn

④ Interest earned

To.

Principal Investigator

Memo no. DoRD/Chem.Sc./RB/20-303/344-A

Tezpur University

Dated: 01/01/2020

Subject: Approval for resignation from SRF in CSRI project with memo no. DoRD/Chem.Sc./RB/20-303/344-A

Madam,

With reference to the subject cited above, I would like to inform you that I am resigning from the SRF position for the project entitled "Synthesis and characterization of task-specific ionic liquid systems for one pot synthesis of pyrimidine derivatives" as instructed vide the memo no. DoRD/Chem.Sc./RB/20-303/344-A with effect from 01-01-2020 on personal reason. I will be grateful if you kindly approve my resignation from the fellowship.

Thanking you in anticipation.

Yours Sincerely

Kabita Boruah

(Kabita Boruah)

Department of Chemical Sciences

Enrollment No. CHP16108

Accepted
R. Boruah
1/01/2020

Professor
Department of Chemical Sciences
Tezpur University
Tezpur - 784028