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

INVESTIGATION OF ONE POT SYNTHESIS OF ACRIDINE DERIVATIVES USING GREENER APPROACH	Scheme No.: **02(0067)/12/EMR-II** dated on 16-05-2012 **Date of Commencement** : 22-08-2012 **Date of termination :** 29-02-2016

2. Name and address of Principal Investigator

Dr(Mrs) Ruli Borah,

Associate Professor

Department of Chemical Sciences

Tezpur University

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

Not applicable

4. Total grant sanctioned and expenditure during the entire tenure

	Amount Sanctioned(Rs)	Expenditure(Rs)
Staff	543613.00	543613.00
Contingency + overhead	519436.00	519436.00
Equipment	3,50,000.00	3,50,000.00
Total	1413049.00	1413049.00

5. Equipment(s) purchased out of CSIR grant

Name	Cost
1. Eyela rotary vacuum evaporator system M/S Tokyo Rikakikai Co.Ltd The procuring and installation of this instrument was completed in 2013-2014 financial year Order date: 20.11.2012	**JPY 5,14000** (C.I.F. Kolkata) plus 9% extra charges on CIF value to Tezpur University

6. Research fellows associated with scheme

Name	Designation	Date of Joining	Date of leaving
Mr Arup Kumar Dutta	JRF	24-08-2012	23-08-2014
	SRF	24-08-2014	29-02-2016

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 the fellow: **Mr Arup Kumar Dutta**

Title of the thesis: ***Development of catalytic one-pot synthetic strategies of acridine, xanthene and naphthoxazine derivatives using Bronsted-Lewis acidic systems***

He has **completed** **his Ph.D. thesis** and he is going to submit the **thesis within May-2016.**

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) A.K .Dutta, P.Sarma, C. Dutta, B.Sarma, R. Borah "Synthesis of anti-2,3-dihydro-1,2,3-trisubstituted-1H-naphth [1,2-e][1,3]oxazine derivatives via multicomponent approach" ***RSC. Adv.*, 2014**, *4*, 10912-10917.

(2) A.K.Dutta, P.Gogoi, R.Borah " Synthesis of dibenzoxanthene and acridine derivatives catalysed by 1.3-disulfonic acid imidazolium carboxylate ionic liquids" ***RSC. Adv.*** 4, **2014,** 41287-41291.

(3) P. Sarma, A.K.Dutta, P.Gogoi, B.Sarma and R. Borah " 3-Methyl-1-sulfoimidazolium ionic liquids as recyclable medium for efficient synthesis of quinoline derivatives by Friedlander annulation" ***Monatshefte für Chemie – Chemical Monthly,*** *146,* **2015**, 173-180.

(4) P.Gogoi, A.K.Dutta, P.Sarma, R. Borah "Development of Bronsted-Lewis acidic solid catalytic system of 3-methyl-1-sulfonic imidazolium transition metal chlorides for the preparation of bis(indolyl)methanes" ***Applied Catalysis A : General,*** 492,**2015,** 133-139.

(5) A K. Dutta , P. Gogoi, M. P. Saikia and R. Borah "Development of environmentally benign methods towards the synthesis of *anti*-2, 3-dihydro-1, 2, 3-trisubstituted-1*H*-naphth[1, 2-e][1, 3] oxazines using Brønsted acidic catalysts" ***Catalysis Letters, 2016***

(6) P. Sarma, S. Saikia and R. Borah "Studies on –SO_3H functionalized Brønsted acidic imidazolium ionic liquids (ILs) for one-pot two step synthesis of 2-styrylquinolines ***"Syn. Commun."*** (Revision submitted), May-**2016**.

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

Not applicable for 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 works has two potential areas for further uses in industry or in different fields. The synthesis of –SO_3H bearing acidic ionic liquid system has generated a new types of functionalized material with specific properties which have many potential in different fields. These functionalized materials can be applicable as surfactant, ligand in complex synthesis, chromatographic stationary phases, mobile phase additives or electroosmotic flow modifiers in high-performance liquid chromatography and capillary electrophoresis, stabilizer in nano-synthesis. They can also be employed in different industrial processes like membrane separation process, metal ion extraction process, removal of pollutants from refinery feedstocks, desulfurization of fuels, electrodepositions of metal etc. Depending on the nature of cations and anions, we can use these materials in the above mentioned fields. The simple one-pot preparation of *anti*-1,2,3-trisubstituted naphthoxazines can be evaluate for bioactivity tests with different substituents which may lead to potential uses as drug molecules. The fluorescent property of trisubstituted naphthoxazine can be used for different purpose.

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:

Definitely, the synthesized Bronsted-Lewis acidic ionic materials can be applicable as electrolyte, fluorescent materials and as greener designer solvent/ catalyst for organic synthesis. But, at present stage it is not possible to patent these ionic systems without carrying out complete study of other physicochemical properties such as viscosity, density, conductance, DSC and liquid crystal properties etc. We have planned to extent our investigation in those directions so that we can explore these functional materials in different fields.

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

In this project, we have developed two novel multicomponent syntheses of oxygen and nitrogen heterocycles within the framework of green chemistry principles using reusable acidic ionic liquid systems or reusable conventional Bronsted acids catalysts. The three heterocycles are *anti*-2,3-dihydro-

1,2,3-trisubstituted-1H-naphth[1,2-e][1,3]oxazines and tetrahydrobenzo[a]acridinones. These two classes of heterocycles have tremendous potential as bioactive molecules and as fluorescent material. Thus, the above works have complemented some of the basic objectives of CSIR Laboratory works. For detail biological studies, we can make collaboration in near future with CSIR laboratory.

With this grant, a new type of work under CSIR has been started in the field of ionic liquids. Till date I have prepared several novel Bronsted acidic or Bronsted-Lewis acidic chlorometallate ionic liquids based on imidazolium, tetramethyl guanidinium and phosphonium cations. Various analytical techniques were used for characterization of the ionic liquid systems. They can be applicable as surfactant, ligand in complex synthesis, chromatographic stationary phases, mobile phase additives or electroosmotic flow modifiers in high-performance liquid chromatography and capillary electrophoresis, etc,. Such type of ionic material has fulfilled some of the objective of the CSIR Laboratory in material sciences. I will try to extend these studies in those directions.

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 utilized the grants fully in my project works. 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 2015-2016 with this report.

R. Borah

Signature of PI

Date: 9/05/2016

(Dr Ruli Borah)

Associate Professor
Dept. of Chemical Sciences
Tezpur University
Estd- 1994
Napaam

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 of the project

* Development of acid catalyzed one pot synthetic strategies of acridine derivatives in solution and solvent-free medium.

* Investigation of one pot synthesis of acridine derivatives in tunable solvent systems for recycling of homogeneous acid catalysts.

* Synthesis and characterization of soluble polymer supported acid catalyst for the synthesis of acridine derivatives in greener solvent.

* Observation of novel acidine derivatives as bioactive molecules.

Work done

The objectives of the works had been completed in different steps during the course of investigation as included in ''**Results and discussion**'' section. The major works can be classified in two categories.

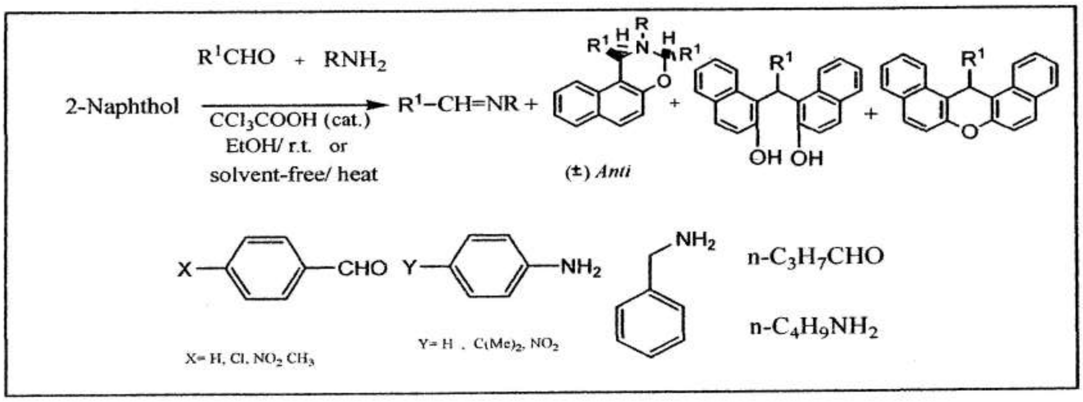
(a)The first one is development of one-pot catalytic strategies of acridines, xanthene and naphthoxazine derivatives with acidic catalytic systems.

(b) The second part represents the synthesis and characterization of task-specific ionic liquids as viscous liquid and solid material with various analytical tools such as ^{1}HNMR, ^{13}CNMR, FT-IR, Raman, SEM-EDX, TGA, Powder XRD, AAS, BET,, UV/Vis and elemental analysis. These ionic systems were examined as homogeneous or heterogeneous catalysts for the synthesis of above mentioned heterocycles via one-pot approach in environmentally benign condition. It includes the comparative studies of conventional acids with task-specific ionic liquid system for the preparation of naphthoxazine derivatives.

Results and discussions

In order to achieve the goal of the objectives, the work had been completed in the following manner.

[1] Initially, we tried to synthesize dibenzoacridine derivatives according to **Scheme-1** of the proposed plan of work via multicomponent approach using acetic acid derivatives (AcOH and CCl_3COOH) in organic solvent (dichloromethane) at room temperature or in neat condition at different temperature. Unexpectedly, we isolated*anti*-2,3-dihydro-1,2,3-trisubstituted- 1H-naphth [1,2-e][1,3]oxazine derivatives as single product from the model reaction in both conditions. The product was characterized by ^{1}HNMR, ^{13}CNMR, COSY, NOESY, HETCOR, DEPT, FT-IR and single crystal XRD as well as elemental analysis. This is the first acid catalyzed multicomponent diastereoselective preparation of *anti*-2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-e][1,3]oxazines in solvent-free method at 100 °C and aqueous ethanol at room temperature stirring within short period with excellent yields.Without catalyst the above synthesis required 6-7 days stirring in absolute ethanol at ambient temperature. One literatureprepared via two step method from the reaction preformed Schiff base with 2-naphthol in acetic acid for several hours. The isolation of product was also carried out by simple precipitation method from the solution of crude reaction mixture in absolute ethanol. Several conventional Brønsted /Lewis acids were examined as reusable catalysts for the synthesis. The use of acidic ionic liquid 1, 3-disulfoimidazolium trifluoroacetate[Dsim][CF_3COO] was also developed as the best efficient reusable **homogeneous catalyst** for the same synthesis in both methods with excellent yields of product. The same synthesis was again carried out successfully in solvent-free condition at 80°C and aqueous ethanol at mild condition in presence of triphenylsulfophosphonium chlorometallates as reusable **heterogeneous catalyst** up to eight consecutive cycles.



Scheme-1

Spectral data and single crystal structure of one trisubstituted naphthoxazine derivative

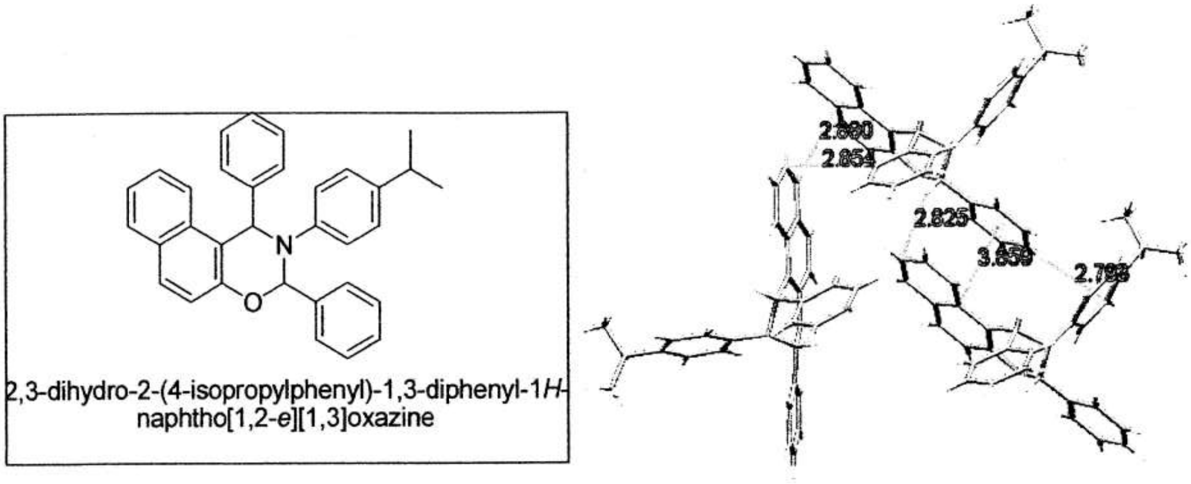
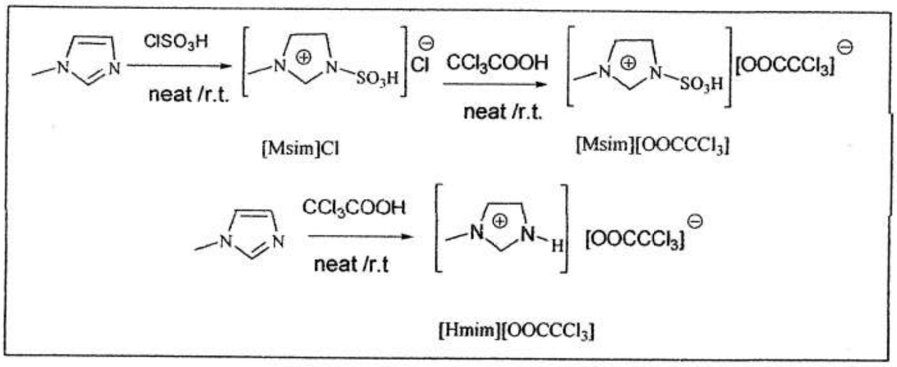


Fig. 1 : Chemical structure andCrystal structure

2,3-Dihydro-2-(4-isopropylphenyl)-1,3-diphenyl-1H-naphth[1,2-e][1,3]oxazine: White solid; M.p.: 171-173 ^{0}C; FT-IR (KBr) cm^{-1}: 3026,2953,21507, 2379,1606,1507,1451,1397, 1336,1222,954, 813, 704.; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.08(s, 6H), 2.68(m, 1H) 6.04(d, *J*=5.1 Hz,1H), 6.21(d, *J*=5.1,1H), 6.87(m, 2H), 7.08(m,2H), 7.20-7.38(m, 10H), 7.45-7.48(m, 2H), 7.54(m, 2H), 7.78-7.82(m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 23.8, 23.9, 30.9, 33.2, 65.2, 84.5, 113.6, 119.2, 123.2, 123,4, 125.2, 126.4, 126.6, 126.6, 127.5, 127.9, 128.4, 128.5, 129.3, 129.4, 137.5, 143, 144, 144.8 , 153.1; CHN analysis (%) : $C_{33}H_{29}NO$ Cal. C 87.03, H 6.37, N 3.08 ; Found C 87.12, H 6.41, N 3.11.

[2]The synthesis of novel Bronsted acidic ILs [Msim][OOCCCl$_3$] and [Hmim][OOCCCl$_3$] and [Dsim][OTs] were observed from the reaction of trichloroacetic acid with [Msim]Cl ionic liquid and 1-methylimidazole respectively at room temperature stirring (**Scheme -2).**



Scheme-2

These new ionic liquids were characterized by ^{1}HNMR, ^{13}CNMR, FI-IR, TGA and elemental analysis. The acidity was measured on Uv-visible spectrophotometer by plotting Hammett plot(**Fig-2**) and compared with the basic ionic liquid [Msim]Cl. The relative acidity of the three ILs was observed according to their decreasing order as follows: [Msim][OOCCCl$_3$]>[Msim]Cl>[Hmim][OOCCCl$_3$].The more acidic ILs were utilized for the one pot synthesis of quinoline derivatives as single product via the Friedländer annulation. (**Scheme-3**).

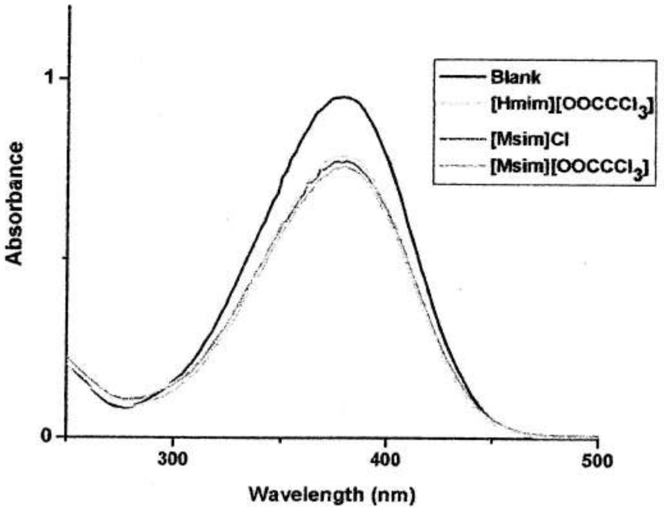
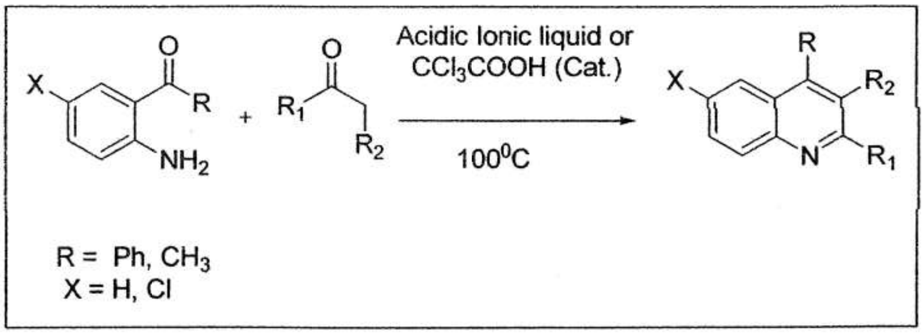


Fig. 2. Absorption spectra of 4-nitroaniline for various acidic ILs in ethanol



Scheme-3: Ionic liquid mediatedFriedländer annulation

Structure of some quinoline derivatives using cyclic ketones:

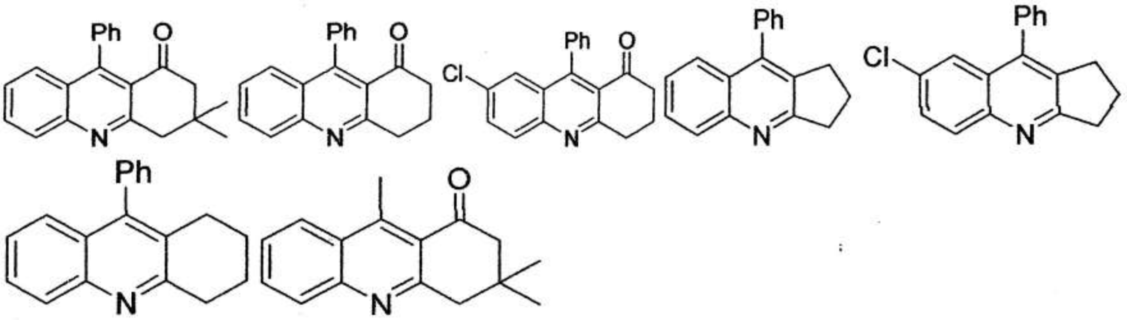
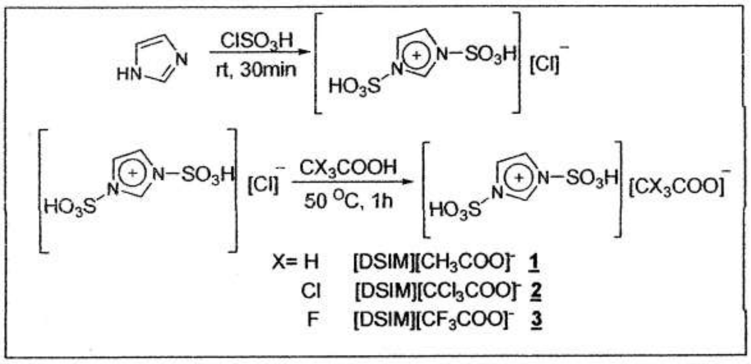


Fig.3 : Structure of quinoline derivatives

[3]New members of 1,3-disulfonic acid imidazolium carboxylate ionic liquids [DSIM][X] (where X= [CH$_3$COO]$^-$, [CCl$_3$COO]$^-$, [CF$_3$COO]$^-$) were prepared(**Scheme-4**) and characterized by ^{1}H NMR,^{13}C NMR, FT-IR, TGA,UV-vis and elemental analysis. The more acidic ILs [DISM][CCl$_3$COO] and [DSIM][CF$_3$COO] were efficiently utilized as recyclable catalyst for the preparation of 1,8-dioxo-decahydroacridine derivatives(**Scheme-5**) and 14*H*-dibenzo[*a,j*]xanthene(**Scheme-6**) and in short time under solvent-free condition at 80-100 °C with excellent yields. The above two ILs could be effectively utilized as catalysts for the synthesis of 1, 8-dioxo-decahydroacridine in water at the same temperature.



Scheme-4. Synthesis of 1,3disulfonic acid imidazolium carboxylate

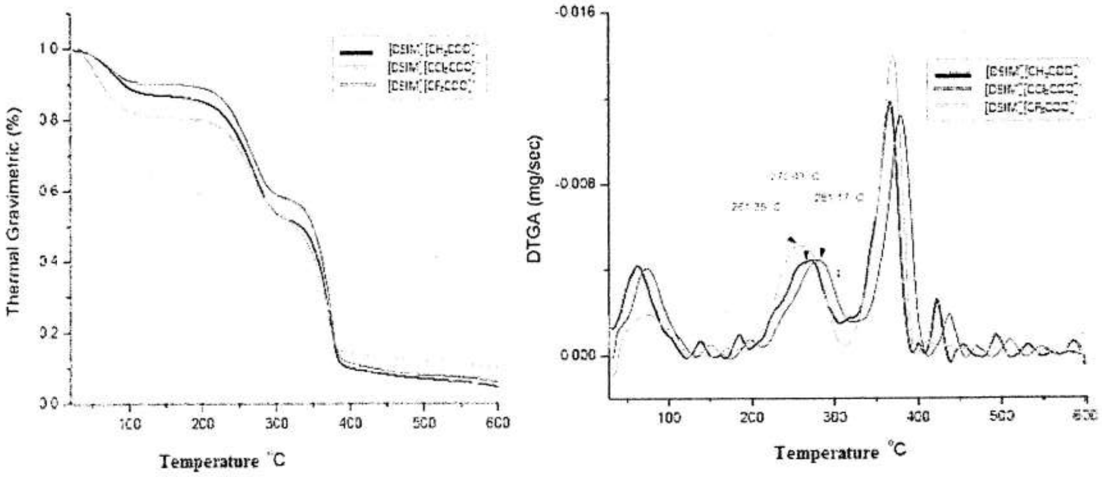
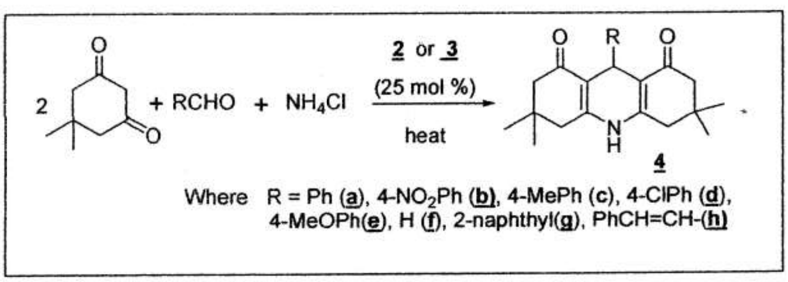
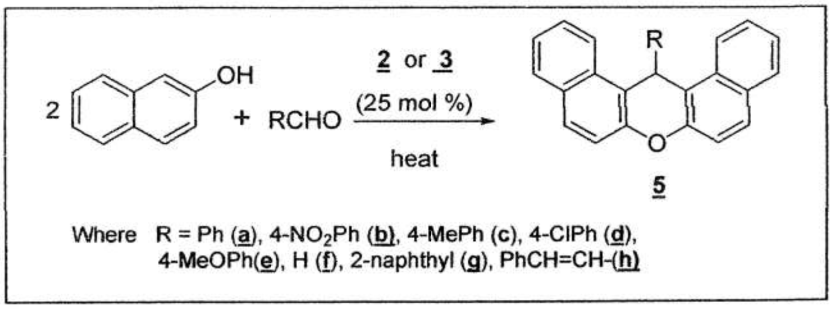


Fig.4. The TG/DTG diagrams of ILs



Scheme-5 Synthesis of 1,8-dioxo-decahydroacridines using ionic liquids **2** and **3** as catalysts



Scheme-6 Synthesis of dibenzoxanthene derivatives 5 using ionic liquids 2and 3 as catalysts

The reusability of the ionic liquids 2 and 3 were expressed by using bar diagram **(Fig 5.)** for three consecutive runs for the synthesis of 1, 8-dioxo-decahydroacridine **4a** and dibenzoxanthene**5a** under the optimized reaction conditions in solvent-free medium.

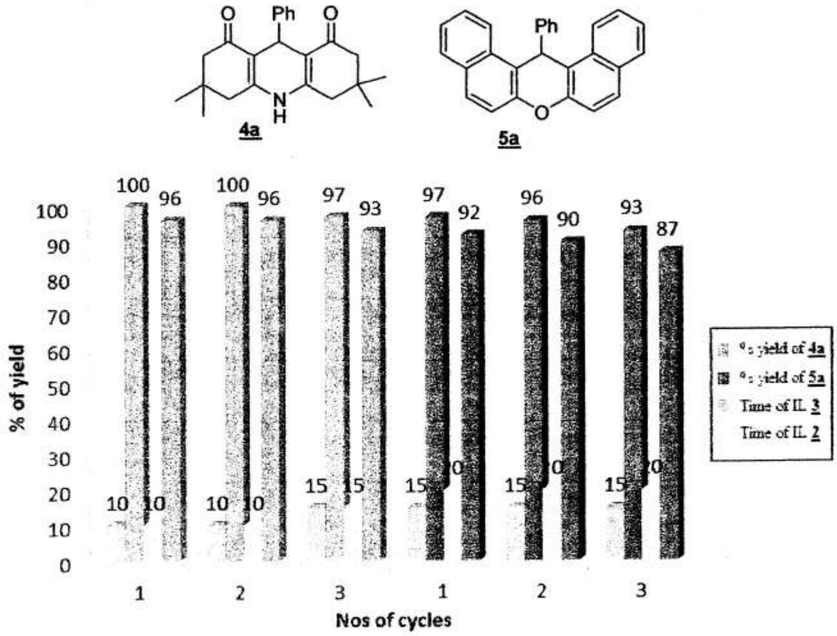
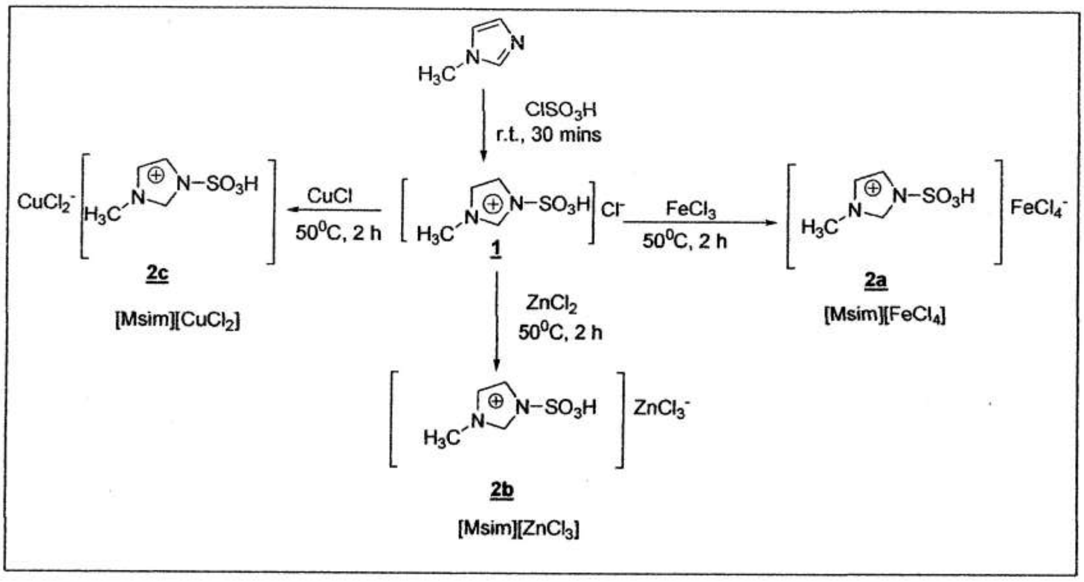


Fig. 5: Recycling of the ILs during the synthesis of **4a** and **5a**

[4] Three new heterogeneous catalysts of 3-methyl-1-sulfonic acid imidazolium transition metal chlorides [Msim][X] (where X= $[FeCl_4]^-$, $[ZnCl_3]^-$, $[CuCl_2]^-$) were synthesized containing(**Scheme-7**) both Lewis and Brönsted acidic sites. These solid acids were fully characterized by various analytical tools such as FT-IR, Raman, ^{1}HNMR, ^{13}CNMR, SEM-EDX, TGA, Powder XRD, AAS, BET, UV/Vis and elemental analysis. All of them were efficiently utilized as reusable catalysts (5-10 mol %) for the selective synthesis of *bis*(indolyl)methane derivatives (**Scheme-8**) in ethylacetate at room temperature within short time with excellent yields.



Scheme 7: Synthesis of 3-methyl-1-sulfonic acid imidazolium metal chlorides

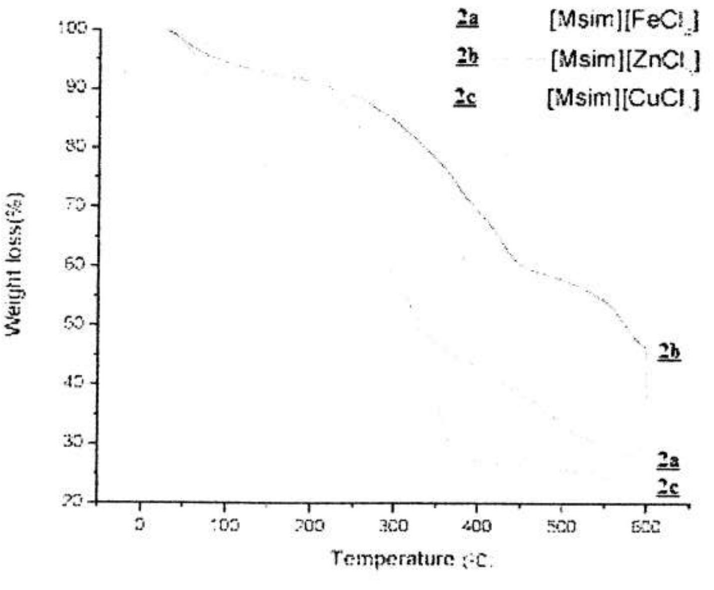


Fig. 6: TGA patterns of 3-methyl-1-sulfonic acid imidazolium metal chlorides

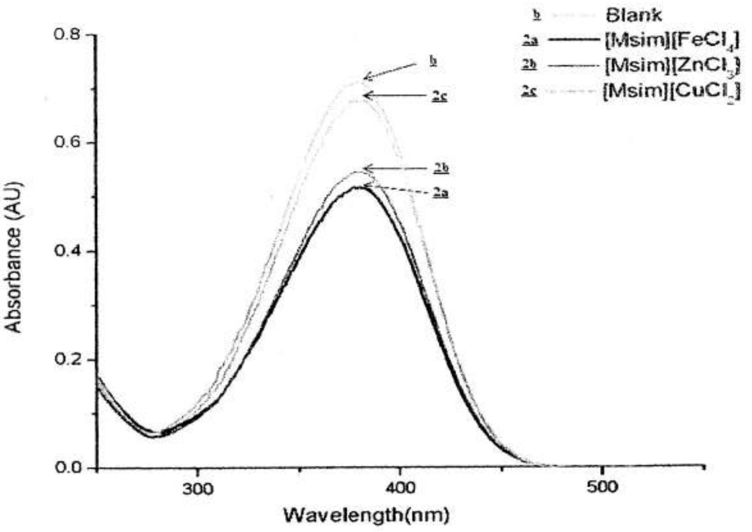
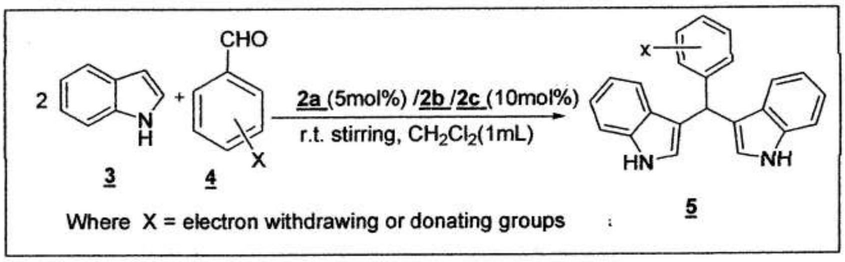


Fig. 7: Hammett plot of the three solid acids



Scheme-8 Synthesis of *bis*(indolyl)methane derivatives 5 using the solid acid catalysts

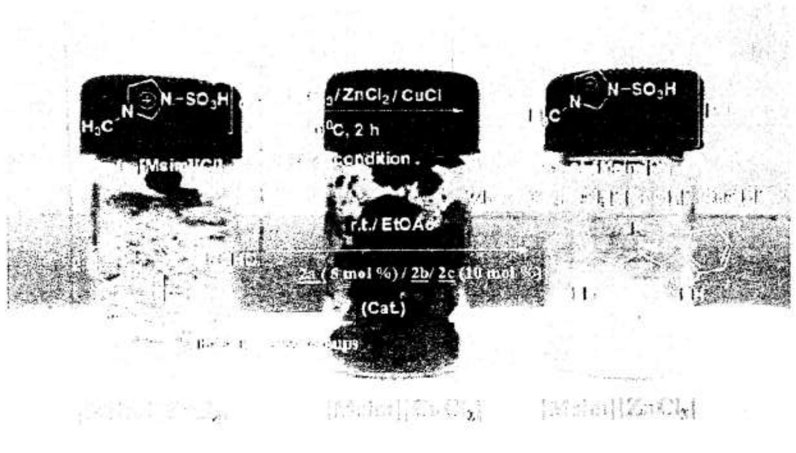
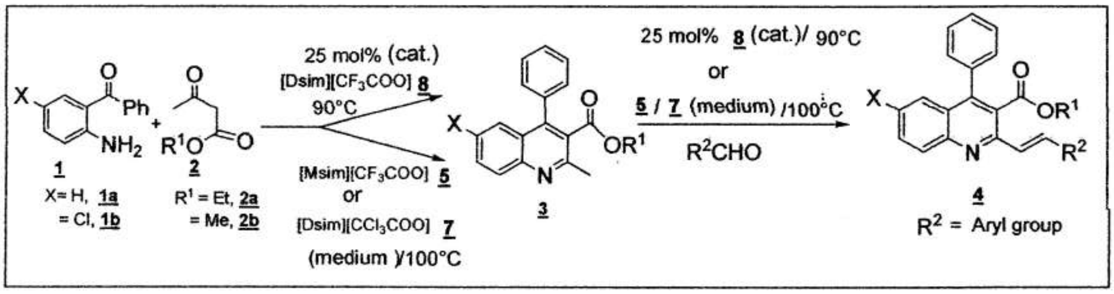


Fig.8 Physical appearance of the three solid acids

[5] Four task-specific $-SO_3H$ functionalized imidazolium ionic liquids were investigated for the Brønsted acidities by Hammett functions. After knowing their thermal stabilities, the catalytic activity was observed for the preparation of 2-styrylquinolines by following a consecutive Friedländer and Knoevenagel reactions (Scheme-) in solvent-free thermal energy. The acidity order ([Dsim][OOCCF$_3$]>[Dsim][OTs]>[Dsim][OOCCl$_3$]> [Msim][OOCCF$_3$]) of three ILs was consistent with their activity order observed in the acid-catalyzed synthesis of 2-styrylquinolines under solvent-free condition at 90° C except [Dsim][OTs]. The TGA curve of ([Dsim][OTs]) expressed 40 % decomposition at 57.5°C. The reason may be the weaker strength of ionic bond between imidazolium cation and tosylate anion in ([Dsim][OTs]) with increasing temperature and thus, the –OTs group can easily eliminate as strong leaving group from the IL by abstraction of proton from $-SO_3H$ group.The best catalytic activity showed by 25 mol% of [Dsim][OOCCF$_3$] IL. The less acidic ILs required 50 mol% to give good yields of 2-styrylquinolines under the optimized conditions.



Scheme-9: Preparation of 2-styrylquinoline derivatives 4

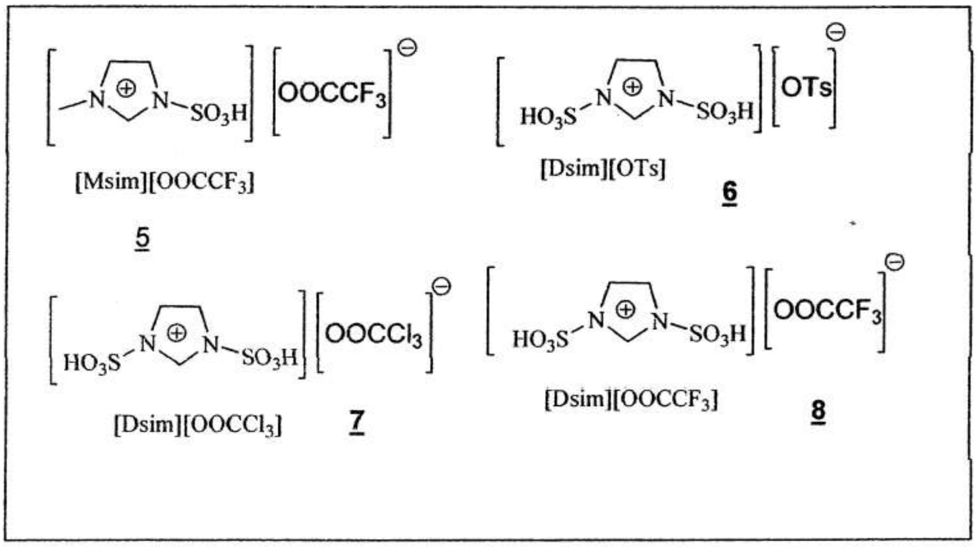


Fig.9 Structure of four sulfoimidazoliumBronsted acidic ionic liquids

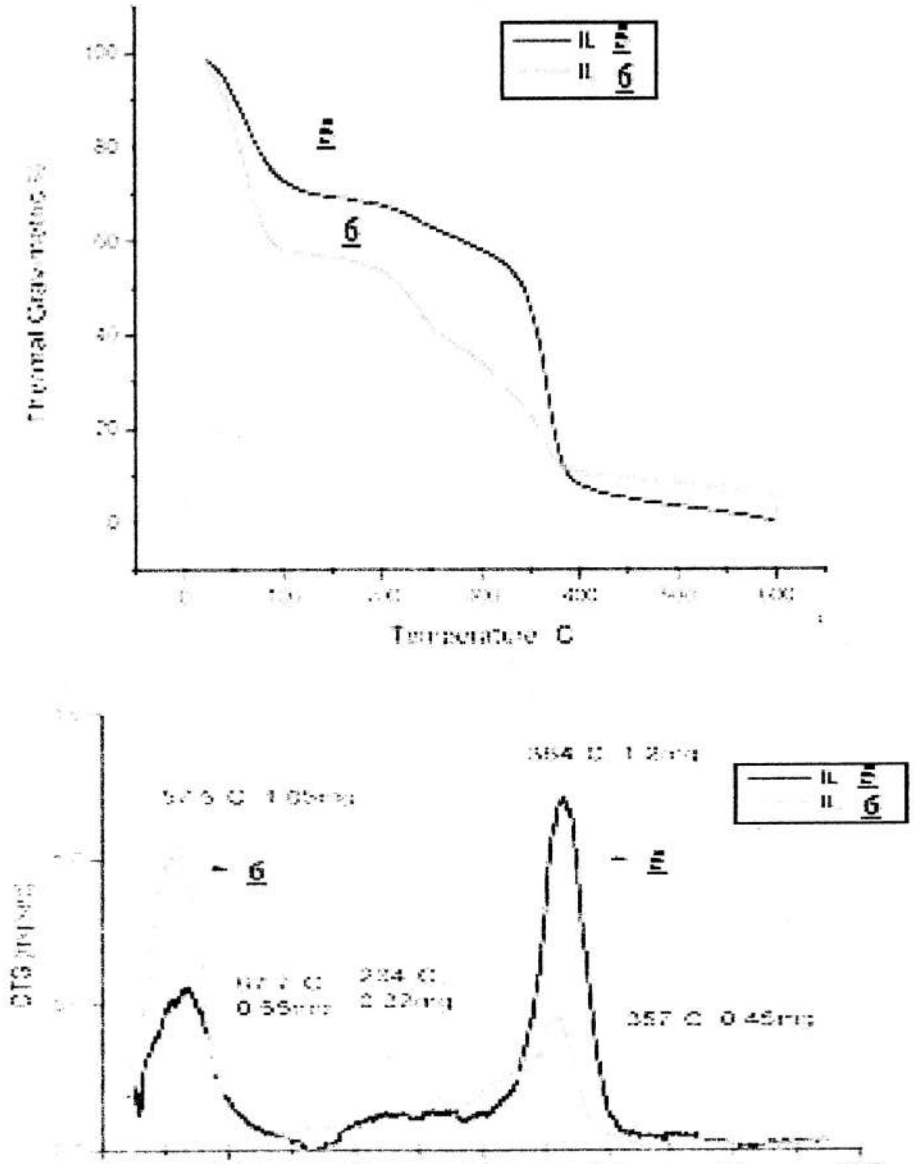
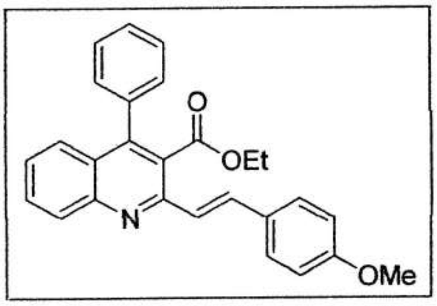


Fig.10. TGA and DTGA analysis of the ionic liquids **5** and**6**

Spectral data and single crystal structure of selected 2-styryl quinoline derivatives

Ethyl 2-(4-methoxystyryl)-4-phenylquinoline-3-carboxylate:



Yellow solid, Mp.126.7-129°C, FT-IR (KBr) cm^{-1} : 3320,2975,2375,1716,1557,1429,1385,1282,1220,1165,1057,825,758,698;^{1}HNMR(400MHz, $CDCl_3$) δ ppm : 0.97(t, *J*= 7.4Hz, 3H), 3.8 (s, 3H), 4.11 (q, *J*= 7.3Hz, 2H), 6.93(d, *J*= 8.7 Hz, 2H), 7.25-7.30 (m,2H), 7.36-7.40(m, 2H), 7.45-7.50 (m, 3H),7.54- 7.59 (m, 3H) , 7.76(m, 1H),8.07(d, *J*= 15.6 Hz, 1H),8.18(d, *J*= 8.4 Hz, 1H);^{13}CNMR(100MHz, $CDCl_3$)δ ppm: 168.4,160.4,157.6,151.4,147.9,136.0,133.0,130.6,129.7,129.6,129.2,128.6,128.3,126.6,122.0, 114.3,61.6,55.4,13.8;CHN analysis (%) : $C_{27}H_{23}NO_3$, Cal. C 79.20, H 5.66, N 3.42; Found C 79.18, H 5.68, N 3.40.

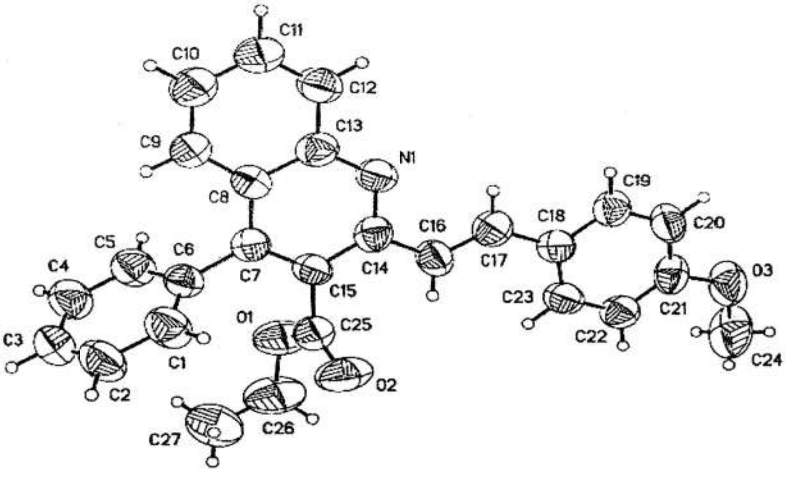
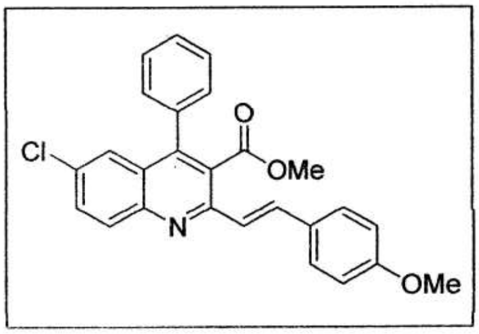


Fig. 11 Single crystal structure of ethyl 2-(4-methoxystyryl)-4-phenylquinoline-3-carboxylate. The displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii

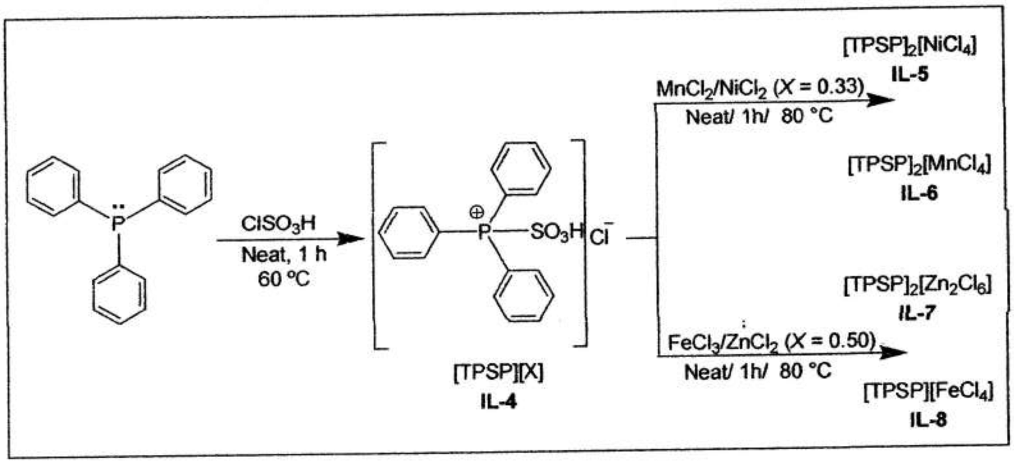
(E)-methyl-2-(4-methoxystyryl)-6-chloro-4-phenyl-quinoline-3-carboxylate :



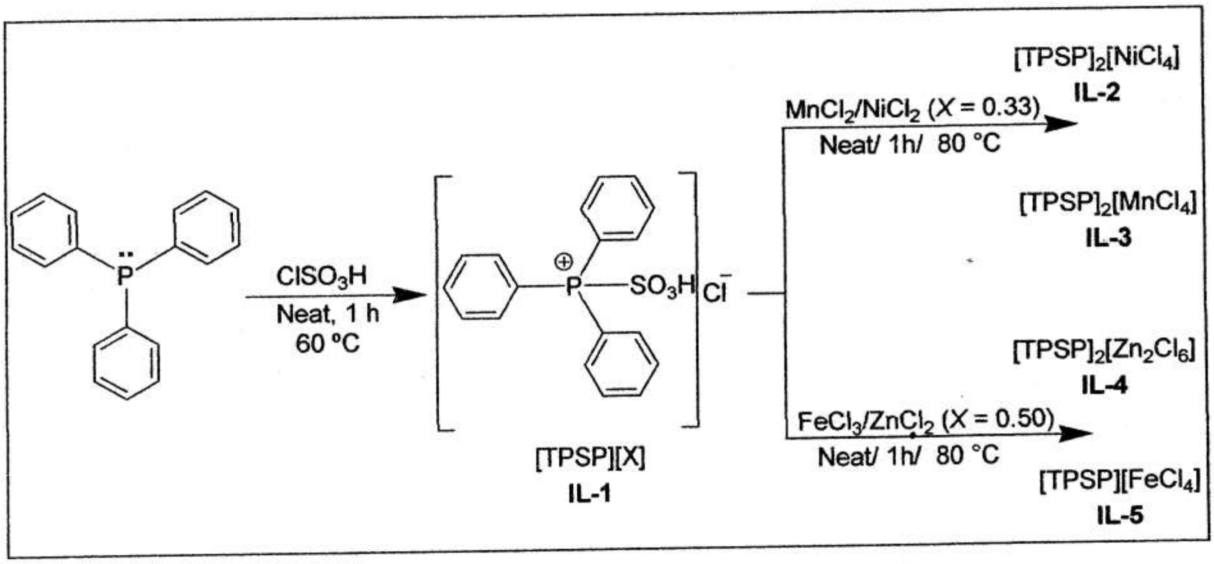
Yellow solid, Mp. 146.3-146.9° C, FT-IR (KBr)cm^{-1}:3431, 3059, 2946, 2838, 2379, 1730, 1565, 1509, 1476, 1437, 1391, 1313, 1223, 1159, 1073, 882, 831, 765, 704; ^{1}HNMR(400MHz, $CDCl_3$) δ ppm : 3.60(s, 3H), 3.85(s,3H), 6.92(d, J= 8.7Hz,2H),7.11(d, J= 15.6 Hz, 1H), 7.36-7.38(m, 2H), 7.51-7.53(m, 4H),7.57(d, J= 8.7 Hz, 2H),7.66(dd, J = 9.2, 2.3Hz ,1H), 8.08-8.14(m, 2H);^{13}CNMR(100MHz, $CdCl_3$) δ ppm: 168.6, 160.6, 151.6, 132.5, 131.7, 129.3, 129.2, 128.6, 127.5, 125.4, 114.3, 55.5, 52.5; CHN analysis (%) : $C_{26}H_{20}ClNO_3$, Cal. C 72.64, H 4.69, N 3.26; Found C 72.60, H 4.73, N 3.22.

[6] Four new $-SO_3H$ functionalized triphenylsulfophosphonium chlorometallates [TPSP]$_n$[X], were prepared from the reaction of triphenylsulfophosphonium chloride [TPSP][Cl] with $FeCl_3$ ([TPSP][$FeCl_4$]), $ZnCl_2$ ([TPSP]$_2$[Zn_2Cl_6]), $NiCl_2$ ([TPSP]$_2$[$NiCl_4$])

and $MnCl_4$ ([TPSP]$_2$[$MnCl_4$]) as solid material and characterized via NMR, FT-IR, Raman, TGA, powder XRD, UV-visible, SEM-EDX, ICP and CHN elemental analyses. Their catalytic activities were evaluated as task specific acidic heterogeneous catalysts for diastereoselective synthesis of *anti*-2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-e][1,3]oxazines in 50 % aqueous EtOH at room temperature and under neat condition at 80 °C. The best catalysts were also reused for eight consecutive cycles for the model reaction. In addition fluorescence property of the naphthoxazine derivatives were also studied and emission wereobserved in the region of 370-440 nm with fluorescence emission maxima around λ_{emi}= 420-430 nm. Melting points, NMR, FT-IR, and elemental analysis was used to characterise the synthesized trisubstitutednapthoxazines.



Scheme-10: Synthesis of triphenylsulfophosphonium chlorometallates



Scheme-10: Synthesis of triphenylsulfophosphonium chlorometallates

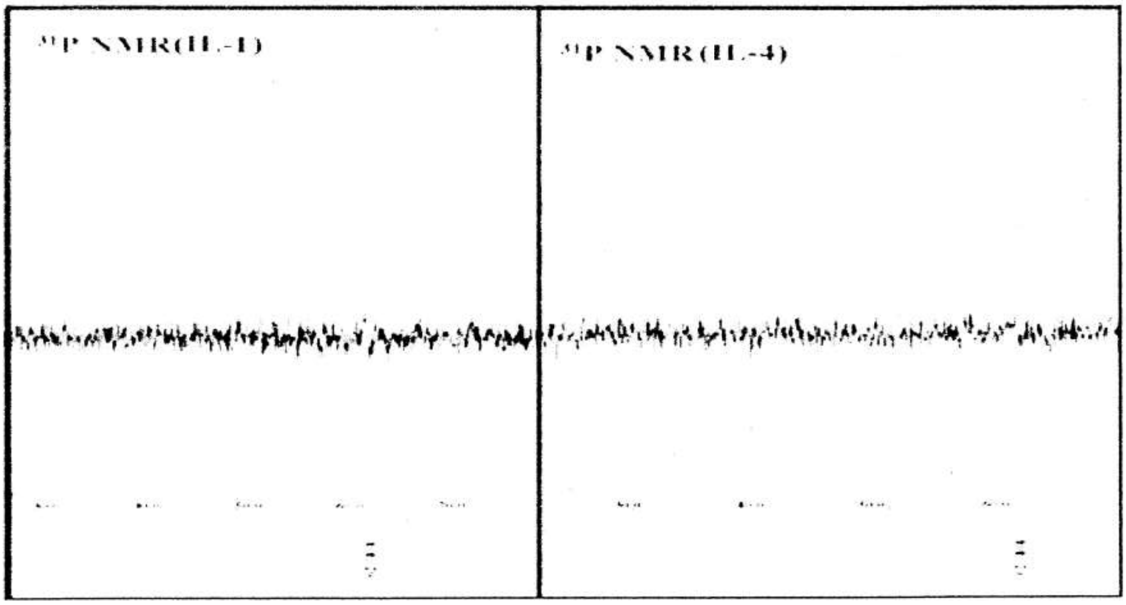


Fig.12: ^{31}P NMR spectrum of IL-1 and IL-4

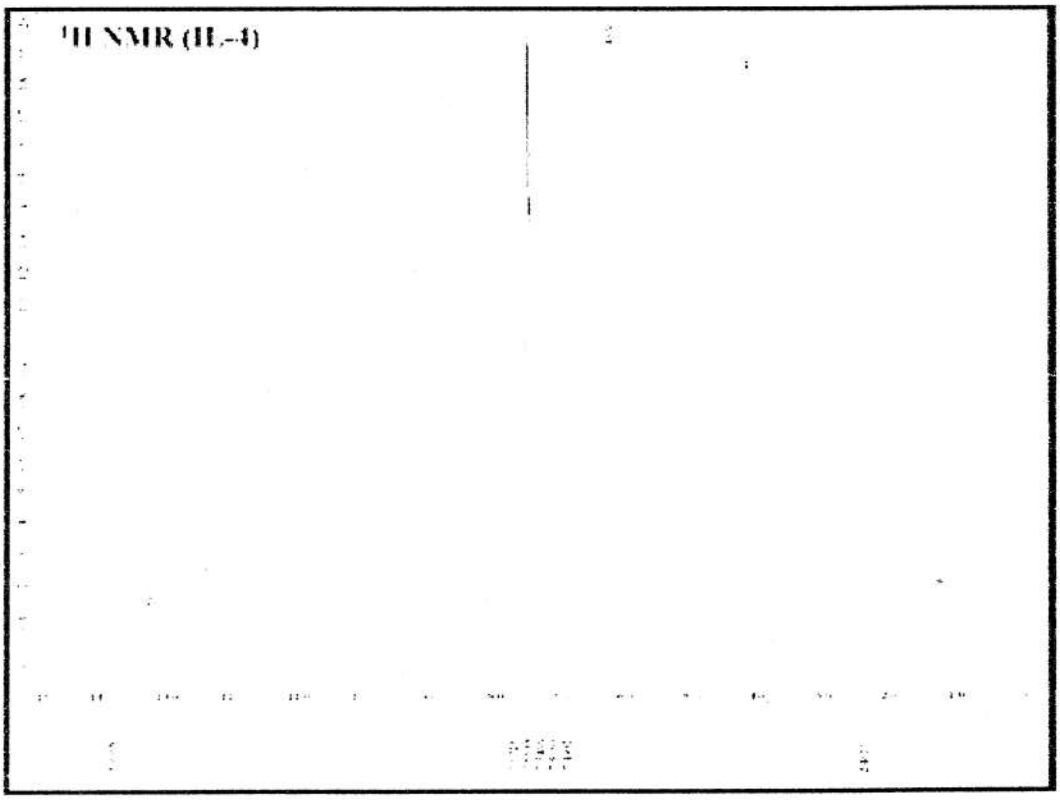


Fig.13: ^{1}H NMR of **IL- 1**

Characterisation data for synthesized triphenylsulfophosphonium IL:

[TPSP][Cl] **(IL-1):** Light reddish semi-solid,98% yields**;** FT-IR (KBr): 3444, 1622, 1177, 1044, 870, 586 cm^{-1}; ^{1}H NMR (400MHz, DMSO-d6): δ 7.49-7.7.57 (m, 15H), 13.9 (broad, 1H); CHN analysis of $C_{18}H_{16}O_3PSCl$ (%):Cal. C 57.07, H 4.26; Found C 57.22, H 4.32

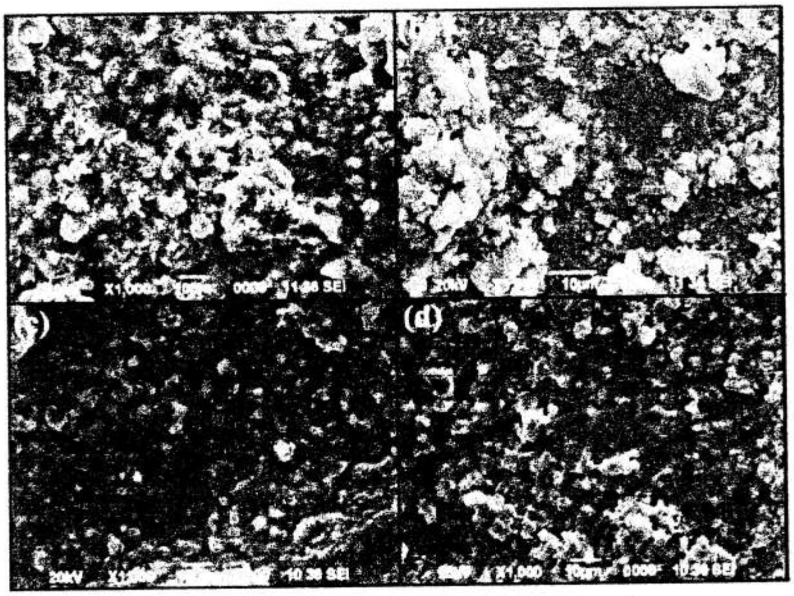


Fig.14: SEM images of (a) [TPSP][FeCl$_4$];(b)[TPSP]$_2$[MnCl$_4$]; (c) [TPSP]$_2$[Zn$_2$Cl$_6$]; (d) [TPSP]$_2$[NiCl$_4$]

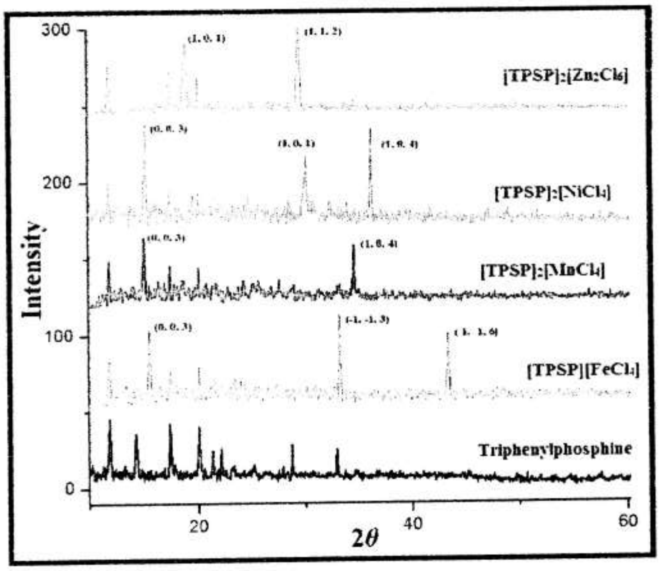


Fig.15: Powder XRD pattern of the four catalysts and PPh$_3$

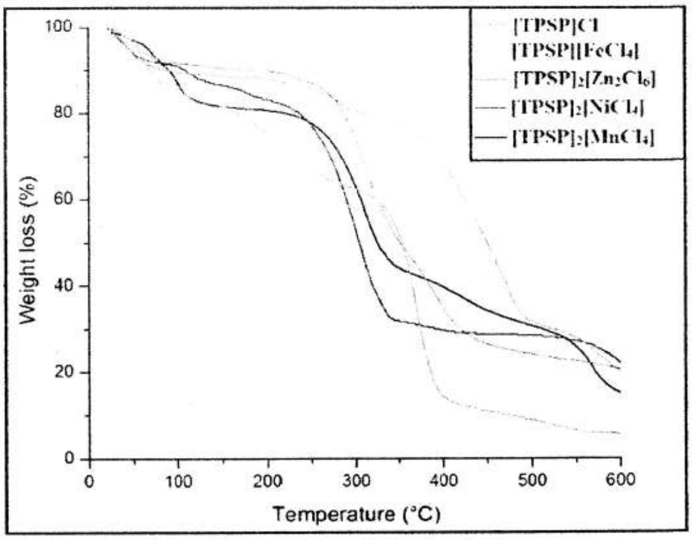


Fig.16: TGA analysis of chlorometallatessalts

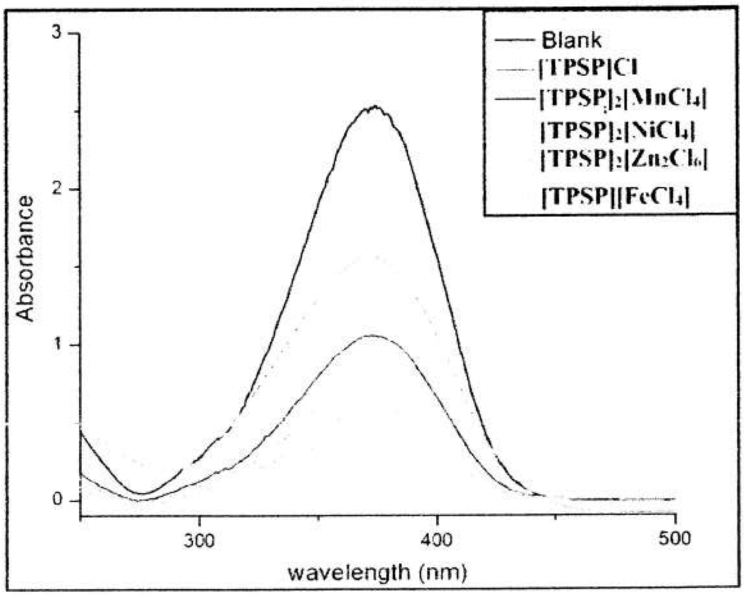
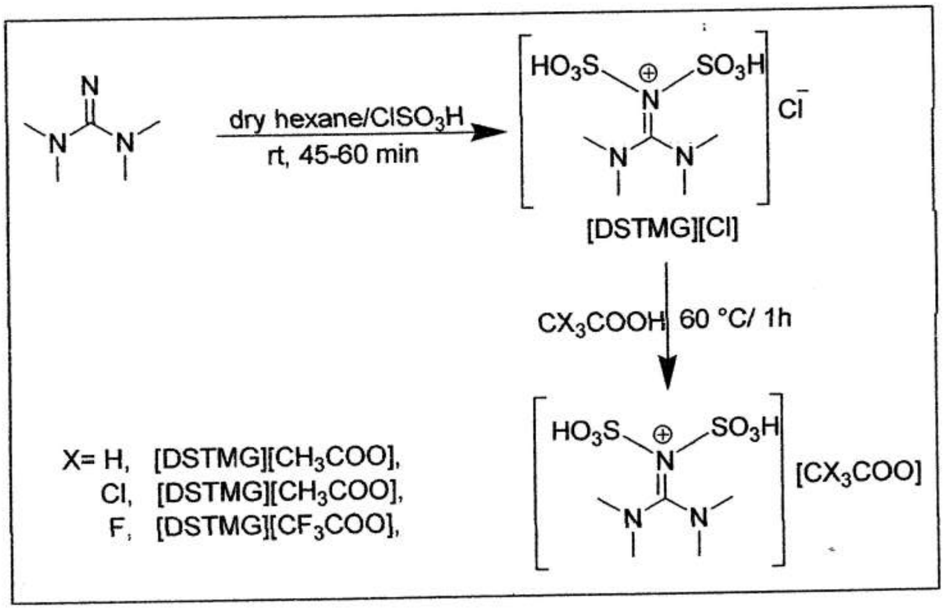


Fig.17: Hammett plot of phosphonium salts

From this experiment the Brønsted acidity order of the five acidic catalysts are:- [TPSP][$FeCl_4$] > [TPSP]$_2$[Zn_2Cl_6] > [TPSP]$_2$[$NiCl_4$] > [TPSP]$_2$[$MnCl_4$]> [TPSP][Cl] .

[7]A new series of task specific Brønsted acidic Ionic liquid N, N-disulfo-tetramethylguanidinium carboxylate [DSTMG][CX$_3$COO], (where X= H, Cl, F) was developed from the reaction between N, N-disulfo-tetramethylguanidinium chloride and corresponding acetic acid derivatives in 1:1 molar ratio at 60 °C for 1 hour **(Scheme-11)**. These ILs were characterized via NMR, FT-IR, TGA, UV-visible and CHN elemental analyses. The most acidic ILs [DSTMG][CCl$_3$COO] and [DSTMG][CF$_3$COO] were successfully utilized as reusable heterogeneous catalysts for the multicomponent synthesis of tetrahydrobenzo[a]acridinone and tetrahydrobenzo[a]xanthenone derivative **(Fig.2)**. Both the catalyst produced excellent yield of the two heterocycle within short time under solvent free condition at 75-85 °C. The reusability tests of the catalyst were also studied and found reusable for six consecutive run. Moreover this is for the first time that tetrahydrobenzo[a]acridinone was synthesized via four component reaction in presence of ionic liquid catalyst.



Scheme-11: Synthesis N, N-disulfo-1, 1, 3, 3-tetramethylguanidinium carboxylate ionic liquids

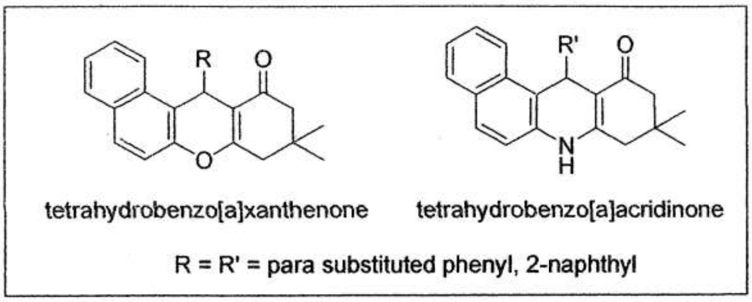


Fig.18: Structure of tetrahydrobenzo[a]xanthenone and tetrahydrobenzo[a]acridinone derivatives

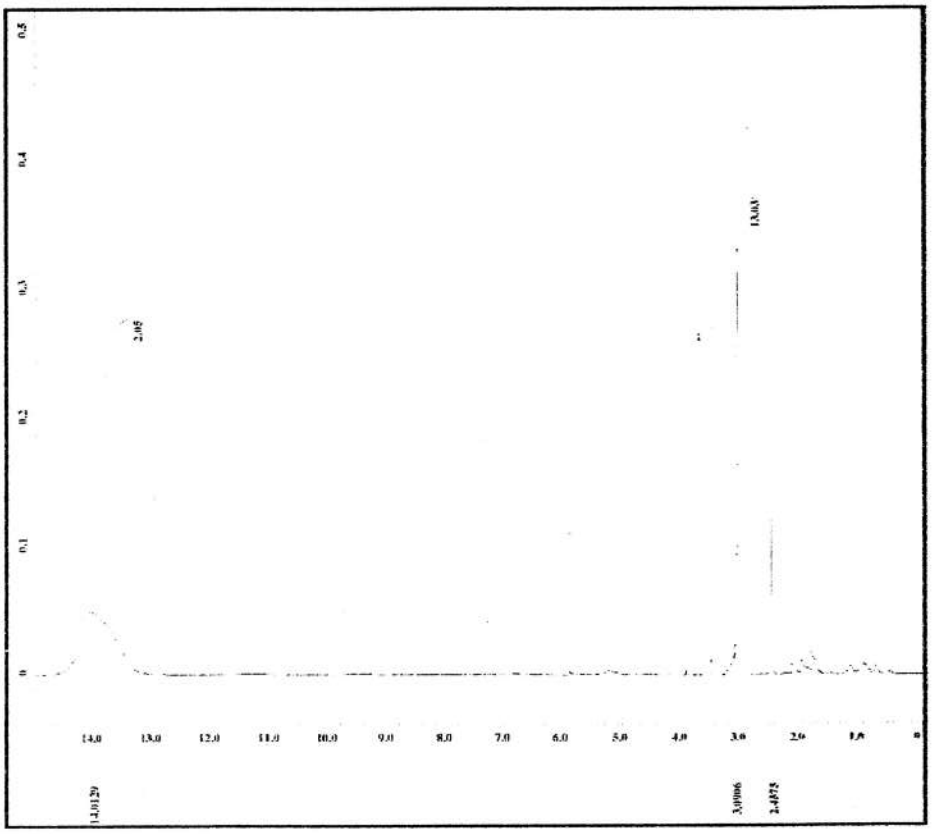


Fig.19: ^{1}H-NMR spectrum of [DSTMG][CF_3COO]

The stability of these ILs can be expressed in the decreasing order: [DSTMG][CF_3COO] > [DSTMG][CCl_3COO] > [DSTMG][CH_3COO] > [DSTMG][Cl] .

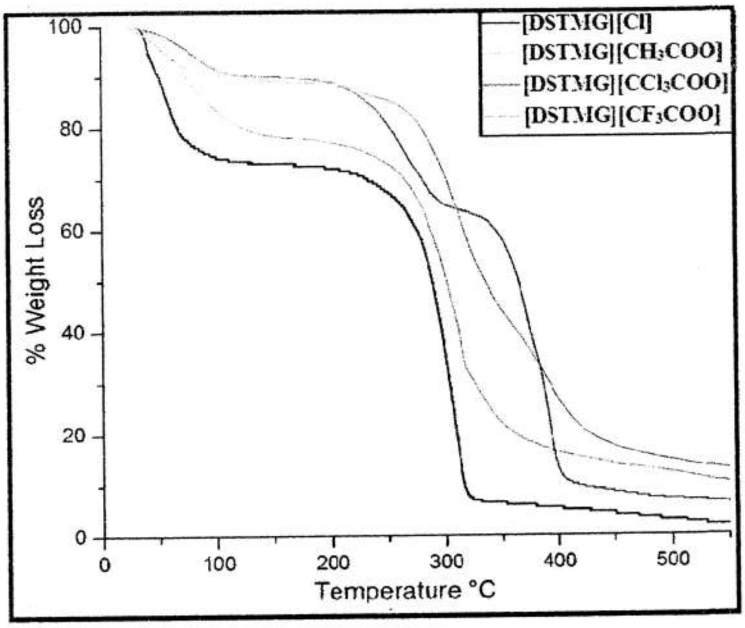
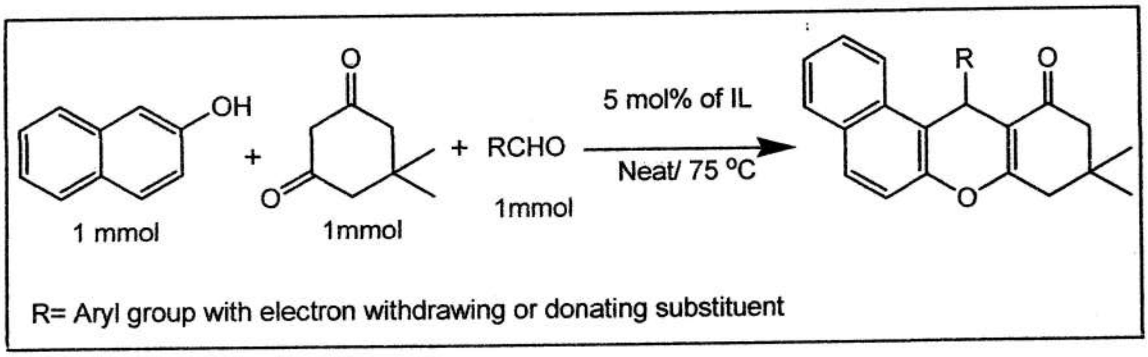
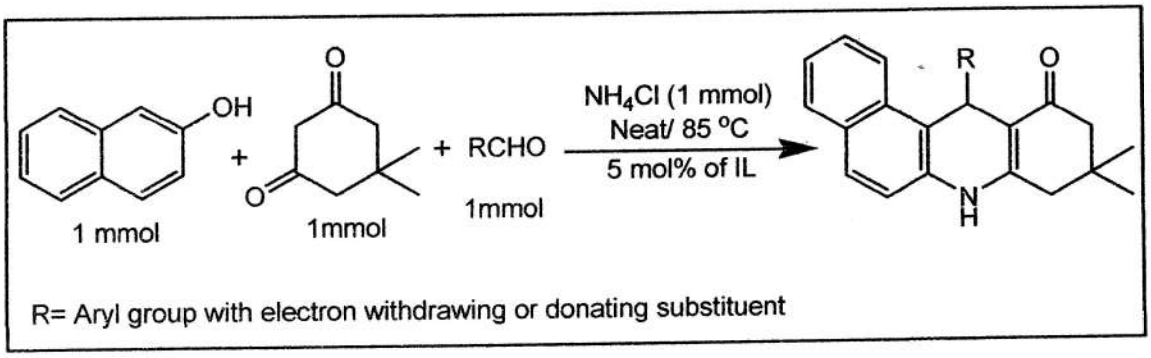


Fig.20: TGA curves of ILs



Scheme-13 : Synthesis of tetrahydrobenzo[a]xanthene derivatives



Scheme-14: Synthesis of tetrahydrobenzo[a]acridinederivatives

[8] We also tried to observe the bioactivity test of synthesized 1, 2, 3-trisubstituted oxazine derivatives. But due to solubility problem in suitable solvent, we did not proceed further. But we observed the fluorescent properties of ten derivatives and they have good fluorescent emission spectra.

Conclusions

The outcome of this project works has started a new opening in the field of – SO_3H functionalized ionic liquid materials which have tremendous potential in electrochemistry, catalysis and material sciences. Similarly, the novel hetrocycles as well as their synthetic route also has simplified the preparation of complex molecules of fused naptho[1,3-]oxazine, xanthene and acridine derivatives. They can be designed for asymmetric synthesis in near future. **Till date we published five papers and one paper is submitted for revision. Three more papers are** in the process of submitting stage in good quality journal. The research scholar **Mr Arup Kumar Dutta** is going to submit his **Ph.D**. thesis within **15 May of 2016.**

Enclosure-III

14. Abstract of the project work

The major achievement of this project can be summarized as development of novel Brønsted/ Brønsted-Lewis acidic ionic liquid systems and explored their catalytic activity for one-pot synthetic strategies of 1,2,3-trisubstituted naphthoxazine, acridine, quinoline, bis(indolyl)methane and xanthene derivatives under environmentally benign approach. Several $-SO_3H$ functionalized imidazolium, tetramethylguanidinium and phosphonium based Brønsted acidic / Brønsted-Lewis acidic ILs were synthesized and characterized with various analytical techniques such as ^{1}HNMR, ^{13}CNMR, FT-IR , TGA , SEM-EDX, Powder XRD, Raman, solid UV , ICP-OES, Hammett acidity , atomic absorption and elemental analysis. Some of them were isolated as viscous liquid and utilized as reusable homogeneous catalyst for the one-pot synthesis of 14*H*-dibenzo[a,*j*]xanthene , 1,8-dioxo-decahydroacridine and *anti*-2, 3-dihydro-1, 2, 3-trisubstituted-1*H*-naphth [1, 2-e][1,3]oxazine under neat or in greener reaction media like water, ethanol and aqueous ethanol at different temperatures. The solid Brønsted-Lewis acidic material was employed as heterogeneous catalyst for the preparation of complex derivatives of tetrahydrobenzo[a]xanthene and tetrahydrobenzo[a] acridine via three-component and four component reactions respectively in neat condition or in greener medium. Some examples of Brønsted /Brønsted-Lewis acidic IL systems are 1,3-disulfonic acid imidazolium carboxylate [DSIM][CX_3COO] (where X = H, Cl, F) ; N-disulfo-tetramethylguanidinium carboxylate [DSTMG][CX_3COO], (where X= H, Cl, F) ; 3-methyl-1-sulfonic acid imidazolium transition metal chlorides [Msim][X] (where X= $[FeCl_4]^-$, $[ZnCl_3]^-$, $[CuCl_2]^-$) ; triphenylsulfophosphonium chlorometallates $[TPSP]_n[X]$ (or $[PPh_3SO_3H]_x[X]$), where n = 1 or 2; X = $FeCl_4^-$, $Zn_2Cl_6^{2-}$, $NiCl_4^{2-}$, $MnCl_4^{2-}$.

A major achievements in heterocyclic chemistry is the first acid catalyzed three-component diastereoselective preparation of *anti*-2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-e][1,3]oxazines in solvent-free method at 80-100 °C and aqueous ethanol at room temperature stirring within less time. Several conventional Brønsted/Lewis acids were examined as reusable catalysts for the synthesis. The use of acidic ionic liquid 1, 3-disulfoimidazolium trifluoroacetate[Dsim][CF_3COO] was developed as the best efficient reusable homogeneous catalyst for the same synthesis in both methods with excellent yields of product. The same synthesis was also performed in solvent-free condition at 80°C and aqueous ethanol at mild condition in presence of triphenylsulfophosphonium chlorometallates as reusable heterogeneous catalyst up to eight consecutive cycles.

Another development of multicompoenent reaction is the IL catalyzed four-component novel reaction for the preparation of tetrahydrobenzo[a]acridinone derivatives starting from 2-naphthol, aromatic aldehydes, dimedone and NH_4Cl under solvent-free thermal method with excellent yields for short time reaction. The same reaction in absence of ammonium chloride gave tetrahydrobenzo[a]xanthenone derivatives.

The catalytic performances of 1,3-disulfonic acid imidazolium carboxylate [DSIM][CX_3COO] (where X = H, Cl, F) were tested with the preparation of 14*H*-dibenzo[a,*j*]xanthene and 1,8-dioxo-decahydroacridine derivatives under solvent-free thermal treatment. The same amount of IL catalyst was also sufficient to conduct the reaction in water with excellent yields which expressed the stability of IL catalyst in water.

The acidic IL [DSIM][CF_3COO] was employed for the two-step one-pot synthesis of 2-styryl quinoline derivatives via Friendlander annulation followed by Knoevenagel condensation reaction in solvent-free method at 90 °C.

The preparation of *bis*(indolyl)methane derivatives was observed in solution at room temperature stirring within short period using only 5-10 mol % of reusable 3-methyl-1-sulfonic acid imidazolium transition metal chlorides [Msim][X] as heterogeneous catalysts.

Finally the fluorescence properties of *anti*-2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-e][1,3]oxazines were studied and emission wereobserved in the region of 370-440 nm with fluorescence emission maxima around λ_{emi}= 420-430 nm.

Some of the above outcomes were reported as five published papers in ***RSC Advances***, ***Applied Catalysis A: General,Catalysis Letters***, ***Monatshefte für Chemie*** during 2014-2016. Three more papers are communicated for publications.

Date: 28/03/2016

UTILIZATION CERTIFICATE

Certified that the expenditure claimed under the different heads of research project entitled **"INVESTIGATION OF ONE POT SYNTHESIS OF ACRIDINE DERIVATIVES USING GREENER APPROACH"**, sanctioned letter no. 02(0067)/12/EMR-II dated on 16-05-2012, has actually been incurred and utilized properly during the period of 1-04-2015 to 31-03-2016, for which the payment was claimed and further that the grant has been exclusively utilized for the purpose for which it was sanctioned.

Dr (Mrs) Ruli Borah
R. Borah 28/03/2016
Signature of
Principal Investigator
With stamp

Associate Professor
Dept. of Chemical Sciences
Tezpur University
Estd. 1994
Napam

11/4/16
Finance Officer
With stamp
Finance Officer
Tezpur University

ANNEXURE-II

Consolidated Statement of Accounts

(For the financial year 1-04-2015 to till 31st March, 2016)

Title of the Research Scheme: ***INVESTIGATION OF ONE POT SYNTHESIS OF ACRIDINE DERIVATIVES USING GREENER APPROACH***
Name of the Principal Investigator: Dr (Mrs) Ruli Borah
Date of Commencement: 22-08-2012
Date of Termination: 29-02-2016 against the sanction letter no. 02(0067)/12/EMR-II dated on 11/06/2015

	Grant Receipts	Opening Balance(Particulars of unspent grants)						Total Amount	Payments(Particulars of grants spent)							
Period(ending 31st March)	Check No. Date: Amount	Contingency(Rs)	Stipend (Rs)	Scientist Allowance(for Emeritus Scientist Scheme Only)	Equipment Grant(Rs)	HRA+ MA	Total(Rs)	Grand total (Rs)	Stipend Period (1st April - 2015 to 29-02-2016)	Contingency(Rs)	Scientist Allowance(for Emeritus Scientist)	Equipment Grant(Rs)	HRA+ MA	Overhead	Total(Rs)	Balance(Rs)
1-04-2015 to 31-03-2016	Received through RBI-Electronic Funds Transfer Record date **30/10/2015** **Rs/- 292326 (A)**	2352#	Nil	Nil	Nil	--	2352 (B)	294678 (A + B)	154000 *	133192	Nil			7486	294678	Nil

Dr B Das
(Registrar)
Registrar
Tezpur University

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(Finance Officer)
Finance Officer
Tezpur University

R. Borah
Dr (Mrs) Ruli Borah 28/03/2016
(PI)
Associate Professor
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Estd. 1994
Napam

* As SRF @ **14,000/ pm.**
\# Unspent amount of the financial year 2014-2015.