

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Final Report of the work done on the Major Research Project

1. Project report No. **Final Project Report**
2. UGC Reference No. F. NO.40-96/2011 (SR) dated 5th July 2011
3. Period of report **1st July, 2011 - 31st December, 2014**
4. Title of research project **Development of Novel Supported Ionic Liquid Phase (SILP) Catalysts for Efficient Organic Transformations**
5. (a) Name of the Principal Investigator **Dr. Gajanan S. Rashinkar**
- (b) Department and University **Department of Chemistry,**
/ College where work has progressed **Shivaji University, Kolhapur-416004, M.S.**
6. Effective date of starting of the project **1st July 2011**
7. (a) **Total Grant approved** **Rs. 11,15,790/-**
- (b) **Expenditure incurred during the period of the report** **Rs. 10,54,888/-**
8. **Report of the work done: (Please attach a separate sheet)**
 - i) Brief objective of the project:- **Please see Appendix-I**
 - ii) Work done so far and results achieved and publications, if any, resulting from the work :- The work done so far has been included in **Appendix-II.**

The publications achieved from project till date are two.

(1) Synergistic catalysis by an aerogel supported ionic liquid phase (ASILP) in the synthesis of 1,5-benzodiazepines, Rajanikant Kurane, Jagannath Jadhav, Sharanabasappa Khanapure, Rajashri Salunkhe, Gajanan Rashinkar*, Green Chemistry, 2013, 15, 1849–1856.

(2) Ferrocene tagged functional polymer: A robust solid-phase reagent for O-demethylation. Rajanikant Kurane, Vipul Gaikwad, Jagannath Jadhav, Rajashri Salunkhe, Gajanan Rashinkar*, Tetrahedron Letters, 2012, 53, 6361–6366.

- iii) Has the progress been according to original plan of work and towards achieving the objective? if not, state reasons:- **YES**
- iv) Please indicate the difficulties, if any, experienced in implementing the project:- **NO**
- v) If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet:- **NA**
- vi) If the project has been completed, please enclose a summary of the findings of the study: **Two bound copies of the final report of work done** are provided along with this report.
- vii) Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any :-

During the tenure of the project, Mr. Rajanikant M. Kurane was appointed as a project fellow. He has registered for his Ph. D. degree at Shivaji University, Kolhapur. His laboratory work is over and he will submit his Ph. D. thesis in last week of May, 2015.

PRINCIPAL INVESTIGATOR

REGISTRAR

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002**

Utilization certificate from 1st July 2011 to 31st Dec. 2014

Certified that the total grant of **Rs 11,15,790/-** (Rupees Eleven lakhs fifteen thousand and seven hundred ninety only) has been sanctioned by University Grant Commission. Out of which total **Rs. 10,20,841/-** (Rupees Ten lakhs twenty thousand and eight hundred forty one only) [(**Rs. 4,72,800/-** as 1st installment and **Rs. 5,48,041/-** as 2nd installment)] was received as first installment and second installment as mentioned above in bracket from the University Grants Commission under the scheme of support for Major Research Project entitled, “**Development of Novel Supported Ionic Liquid Phase (SILP) Catalysts for Efficient Organic Transformations**” with a wide UGC letter No.- **F. No. 40-96/2011 (SR) dated 05th July, 2011**. The amount of **Rs. 10,54,888/-** (Rupees Ten lakhs fifty four thousand eight hundred and eighty eight only) has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission during the year 2011-14. The excess expenditure over the received amount is **Rs. 34,047/-** (Rs. Thirty four thousand forty seven only) which will be adjusted after receipt of next fund from University Grants Commission. Therefore UGC has requested to release funds of **Rs. 91,105/-** (Rupees Ninety one thousand one hundred five only) [Excess expenditure over the received amount but within sanctioned amount **Rs. 34,047/-** + Fellowship arrears **Rs. 57,058/-**] as early as possible.

PRINCIPAL INVESTIGATOR

REGISTRAR

STATUTARY AUDITOR

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 002**

STATEMENT OF EXPENDITURE IN RESPECT OF MAJOR RESEARCH PROJECT

1. Name of Principal Investigator: **Dr. G. S. Rashinkar**
2. Name of Institution : **Department of Chemistry,
Shivaji University,
Kolhapur-416004 (MS)**
3. UGC approval no. and date: **F. No. 40-96/2011 (SR) dated 05/07/2011**
4. Title of the Research Project: **“Development of Novel Supported Ionic Liquid Phase
(SILP) Catalysts for Efficient Organic Transformations”**
5. Effective date of starting the project: **1st July 2011**
6. Budget head: **D.1.P.174**
7. (A) Period of Expenditure: **From 01.07.2011 to 31.03.2015**

(B) Details of Expenditure:

Sr. No.	Item	Amount Sanctioned	Expenditure Incurred 2011-2012	Expenditure Incurred 2012-2013	Expenditure Incurred 2013-2015	Total Expenditure
i.	Books & Journals	----	-----	-----	-----	-----
ii.	Equipment	95,000/-	94,952/-	94,952/-
iii.	Contingency	75,000/-	12,999/-	18,284/-	43,716/-	74,999/-
iv.	Field Work/Travel (Give details in the proforma at Annexure-VII).	20,000/- + 10,000/- (Additional Grant)	810/-	19,003/-	6568/-	26,381/-
v.	Hiring Services	50,000/-	NIL	28,675/-	21,300/-	49,975/-
vi.	Chemicals / Glassware/ consumables	2,00,000/-	60,614/-	73,238/-	65,998/-	1,99,850/-
vii.	Salary of project fellow	5,03,742/- + 1,00,748/- (HRA 20%)	68,671/-	2,01600/-	2,77,161/-	5,47,432/-
viii.	Overhead	61,300/-	20,433/-	20,433/-	20,433/-	61,299/-
	Any other items	NA	NA	NA	NA	NA
	TOTAL	11,15,790/-	2,58,479/-	3,61,233/-	4,35,176/-	10,54,888/-

Total Amount Sanctioned	Grant Received till date	Total Expenditure	Grant to be Received
11,15,790/-	10,20,841/-	10,54,888/-	91,105/-

(c) Staff Date of Appointment: Mr. Rajanikant Kurane as Project Fellow on 16th Aug. 2011

Sr No	Expenditure Incurred for	Amount Approved	Expenditure Incurred (2011-2012)	Expenditure Incurred (2012-2013)	Expenditure Incurred (2013-2015)	Total
i.	Honorarium to PI	NA	NA	NA	NA	NA
ii.	Project Fellow consolidated salary @ Rs.14000/- + HRA p.m. for initial 2 years. And@16000/- + HRA p.m. for third year.	5,03,742/- + 1,00,748/- (HRA 20%)/-	68,671/-	2,01600/-	2,77,161/-	5,47,432/-

[The 20% HRA is considered for a "Kolhapur" city from 1st August, 2009 to onwards.]

1. It is certified that the appointment has been made in accordance with the terms and conditions laid down by the Commission.
2. It as a result of checks or audit objective, some irregularly is noticed, later date, action will be taken to refund, adjust or regularize the objected amounts.
3. Payment @ revised rates shall be made with arrears on the availability of additional funds.
4. It is certified that the total grant of **Rs 11,15,790/-** (Rupees Eleven lakhs fifteen thousand and seven hundred ninety only) has been sanctioned by University Grant Commission. Out of which total Rs. **10,20,841/-** (Rupees Ten lakhs twenty thousand and eight hundred forty one only) [(**Rs. 4,72,800/-** as **1st installment** and **Rs. 5,48,041/-** as **2nd installment**)] was received as first installment and second installment as mentioned above in bracket from the University Grants Commission under the scheme of support for Major Research Project entitled, “**Development of Novel Supported Ionic Liquid Phase (SILP) Catalysts for Efficient Organic Transformations**” with a wide UGC letter No.- **F. No. 40-96/2011 (SR) dated 05th July, 2011**. The amount of **Rs. 10,54,888/-** (Rupees Ten lakhs fifty four thousand eight hundred and eighty eight only) has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission in 2011-14 financial years. The excess expenditure over the received amount is **Rs. 34,047/-** (Rs. Thirty four thousand forty seven only) which will be adjusted after receipt of next fund from University Grants Commission. Therefore UGC has requested to release funds of **Rs. 91,105/-** (Rupees Ninety one thousand one hundred five only) [Excess expenditure over the received amount but within sanctioned amount **Rs. 34,047/-** + Fellowship arrears **Rs. 57,058/-**] as early as possible.

PRINCIPAL INVESTIGATOR

REGISTRAR

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG, NEW DELHI - 110 002

STATEMENT OF EXPENDITURE INCURRED ON TRAVEL/FIELD WORK

Name of the Principal Investigator: **Dr. G. S. Rashinkar**

Title of the research project: **"Development of Novel Supported Ionic Liquid Phase (SILP) Catalysts for Efficient Organic Transformations"**

Name of Person	Purpose of Journey	Duration of Journey	Mode of Journey	Expenditure Incurred in Rs.
Prof. P. D. Lokhande	Subject expert for selection of project fellow	08-08-2011 to 09-08-2011	Bus	810/-
Dr. G. S. Rashinakar	Visit to Savitribai Phule Pune University, Pune.	19-05-2012 to 21-05-2012	Private hired car	5390/-
Mr. R. M. Kurane	Visit to Savitribai Phule Pune University, Pune for analysis of samples.	03-07-2012	Bus	693/-
Dr. G. S. Rashinakar	Mid -Term presentation of the project (New Delhi)		Travel (by plane) Taxi, etc	12,920/-
Dr. G. S. Rashinkar	Visit to Solapur University, Solapur	21-12-2014	Private hired car	3568/-
Mr. R. M Kurane	Visit to Savitribai Phule University, Pune for analysis of samples	25-2-2014	Travel	1000/-
Mr. R.M. Kurane	Visit to Indian Institute of Science (IISc) Bangalore for analysis of samples	28-12-2014 to 30-12-2014	Travel	2000/-
			Total:-	26,381/-

PRINCIPAL INVESTIGATOR

REGISTRAR



**PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING
THE FINAL REPORT OF THE WORK DONE ON THE PROJECT**

- 1] Title of the Project : Development of Novel Supported Ionic Liquid Phase (SILP) Catalysts for Efficient Organic Transformations
- 2] Name and address of the principal investigator : Dr. G. S. Rashinkar
- 3] Name and address of the institution : Shivaji University,
Kolhapur-416004 (MS)
- 4] UGC approval no and date : F. NO.40-96/2011 (SR) dated 5th
July 2011
- 5] Date of implementation : 1st July 2011
- 6] Tenure of the project : 3 & 1/2 years
- 7] Total grant allocated : Rs. 11,15,790/-
- 8] Total grant received : Rs. 10,20,841/-
- 9] Final expenditure : Rs. 10,54,888/-
- 10] Title of the project : Development of Novel Supported Ionic Liquid Phase (SILP) Catalysts for Efficient Organic Transformations
- 11] Objective of the project:
The prime objective of the project was the development of novel SILP catalysts for achieving efficient and economical organic transformations. The project aimed toward the environmentally benign synthesis through the development of a series of novel SILP catalysts for the reactions leading to synthetically important products (**The details are listed in Appendix I**).
- 12] Whether objectives were achieved: **Yes**
For details **Please refer Appendix II**
- 13] Achievements from the project: **Please see Appendix-II**
- 14] Summary of the findings: **Please see Appendix-II**
- 15] Contribution to the society: **Please see Appendix III**

16] Whether any Ph.D. Enrolled /produced Out of the project:

During the tenure of the project, Mr. Rajanikant M. Kurane was appointed as a project fellow. He has registered for his Ph. D. degree at Shivaji University, Kolhapur. His laboratory work is over and he will submit his Ph. D. thesis in may-2015.

17] No. of publications out of the project:

(1) Synergistic catalysis by an aerogel supported ionic liquid phase (ASILP) in the synthesis of 1,5-benzodiazepines, Rajanikant Kurane, Jagannath Jadhav, Sharanabasappa Khanapure, Rajashri Salunkhe, Gajanan Rashinkar*, **Green Chemistry**, 2013, 15, 1849–1856.

(2) Ferrocene tagged functional polymer: A robust solid-phase reagent for O-demethylation. Rajanikant Kurane, Vipul Gaikwad, Jagannath Jadhav, Rajashri Salunkhe, Gajanan Rashinkar*, **Tetrahedron Letters**, 2012, 53, 6361–6366.

Principal Investigator

Registrar

Objectives of the Project

The project work aims towards the development of novel SILP catalysts for achieving efficient and economical organic transformations. The project will promote the environmentally benign synthesis through the development of a series of SILP catalysts for the reactions leading to synthetically important products. The objectives of the proposed work are:

- To synthesize novel SILP catalysts by both covalent bonding of ionic liquid fragments to the support and by physisorption via van der Waals and dipole forces.
- To study the fundamental properties such as micro polarities of SILP catalysts.
- To make use of the synthesized SILP catalysts for promoting organic transformations such as oxidation reactions, olefin metathesis reactions and important organic reactions.
- To investigate the compatibility of molecules like silica nanoparticles, cucurbiturils as supports for the synthesis of SILP catalysts.
- To employ green chemistry principles in some reactions using SILP catalysts.

Work done so far

Title of the Project: “Development of Novel Supported Ionic Liquid Phase (SILP) Catalysts for Efficient Organic Transformations” (F. NO. 40-96/2011 (SR) dated 5 July 2011)

Duration: 01-07-2011 to 31-12-2014

Summary of work done:

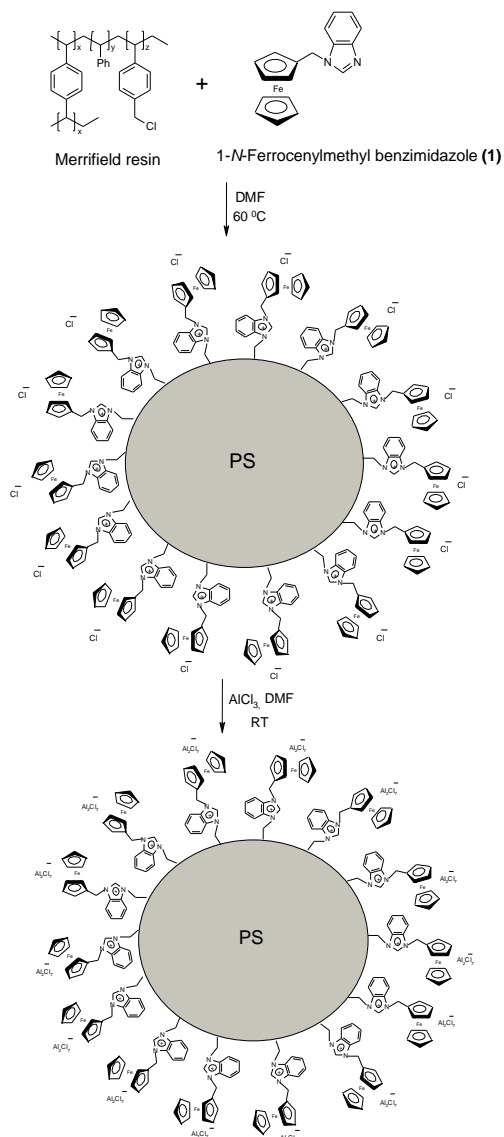
Initially we have done extensive referencing on supported ionic liquid phase (SILP) catalysis and important organic transformations. Eight schemes as per the proposed work in the project have been carried out during the tenure 01-07-2011 to 31-12-2014. The details regarding these schemes are given below.

1st Scheme:

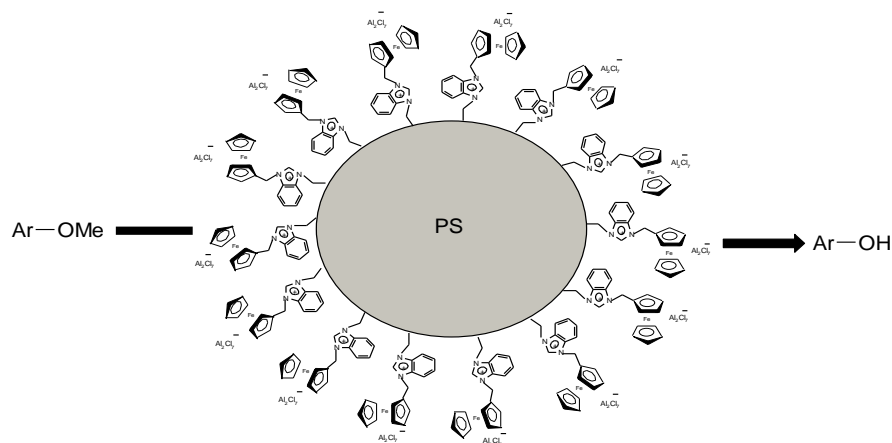
The protection of functional groups and their regeneration is an important area of research in organic synthesis. In this context, O-demethylation constitutes an important method in the light of its importance for protection of hydroxyl groups from phenols and its involvement in the manufacture of number of pharmaceuticals, drugs, and other fine chemicals.^[1] It is a nearly ubiquitous process in the synthesis of multifunctional heterocyclic compounds where aryl methyl ethers are used as protected phenols.^[2] The methoxy unit, being stable to a vast array of reaction conditions, is particularly well utilized for protection of phenols. However, it is this fact that makes O-demethylation difficult under normal milder conditions.^[3] A variety of reagents have been developed for O-demethylation.^[4-17] However, despite of numerous and significant methods to perform this transformation, a mild protocol for O-demethylation using highly robust heterogeneous catalyst still represents a considerable synthetic challenge.

According to our research project objective, we have synthesized ferrocene tagged SILP catalyst containing chloroaluminate anion (Scheme 1). The SILP catalyst was synthesized by quaternization of ferrocenylmethylbenzimidazole with Merrifield resin followed by anion metathesis reaction with AlCl_3 . The loading of aluminum was determined by EDAX spectroscopy. The synthesized catalyst was characterized by FT-IR and FT-Raman spectroscopy. The thermal stability of catalyst was studied using Thermo gravimetric analysis (TGA) while the morphology was assessed by scanning electron microscopy (SEM). The synthesized SILP catalyst served as excellent reagent for the solid phase O-demethylation of aromatic methyl ethers (Scheme 2). The SILP catalyst when employed as a solid phase reagent for effecting O-demethylation of aryl methyl ethers showed TON in the

range of 7373-8930 and TOF in the range of 279-494 h⁻¹. Additionally, SILP catalyst could be reused at least five times without noticeably decrease in the catalytic activity.



Scheme 1: Synthesis of SILP catalyst acronymed as [FemMerBen]Al₂Cl₇



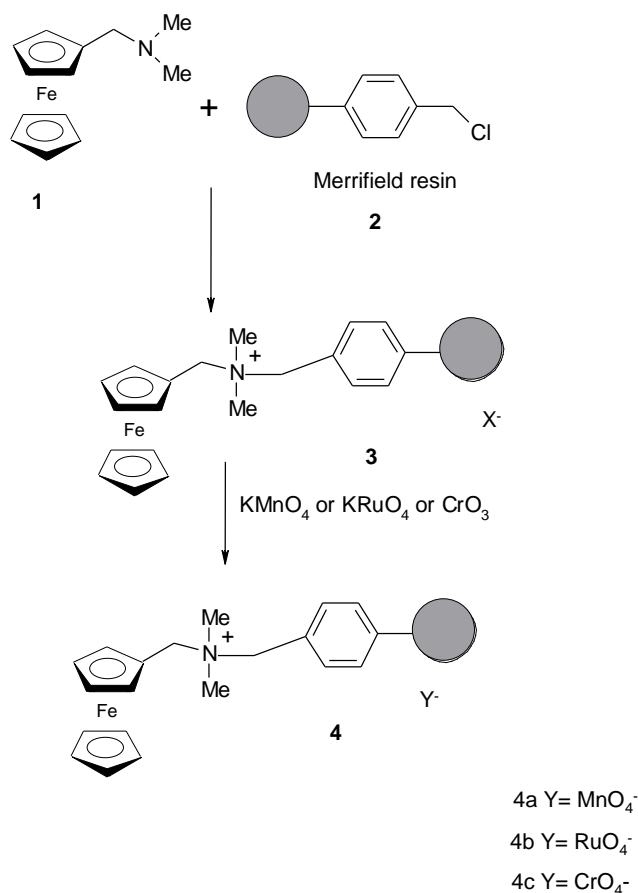
Scheme 2: O-demethylations using [FemMerBen]Al₂Cl₇

The work carried out under this scheme is published in *Tetrahedron Letters*, Volume 53, Issue 47, Pages 6361-6366.

IInd Scheme:

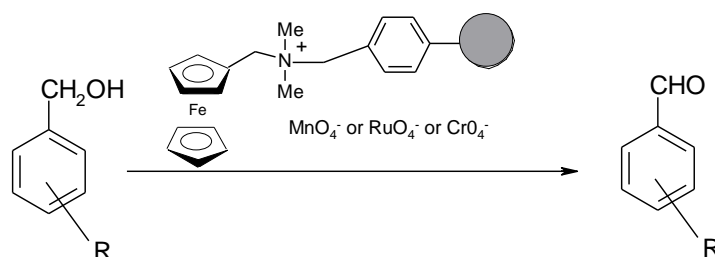
Oxidation of alcohols has been the focus of much research, especially the search for suitable catalysts that use more environmentally friendly oxidants than the typical organic peroxides or amine oxides.^[18] Catalytic systems, both homogeneous and heterogeneous, based on copper, ruthenium, palladium, rhodium, cobalt, and manganese, have been reported to oxidize various alcohols into the corresponding carbonyl compound using molecular oxygen as an oxidant.^[19] Over the years, large number of reagents have been developed to show higher selectivity and functional group tolerance, thus permitting the preparation of target molecules with ever increasing levels of structural complexity.

As per the objectives of our project we have synthesized SILP catalyst having ability to carry out oxidation. The SILP catalyst was synthesized by quaternization of dimethylaminomethyl ferrocene (1) with Merrifield resin (2) (Scheme 3).



Scheme 3

The resultant onium salt (3) was treated with KMnO_4 , CrO_3 and KRuO_4 to form desired SILP catalyst containing MnO_4^- , CrO_4^- and RuO_4^- (4a-c). The synthesized catalysts were characterized by FT-IR, FT-Raman and EDAX spectroscopy. The synthesized SILP catalysts were employed for the oxidation of structurally diverse primary alcohols (Scheme 4). In all the investigated cases, the corresponding aldehydes were obtained in excellent yields without over oxidation into corresponding carboxylic acids.



Scheme 4

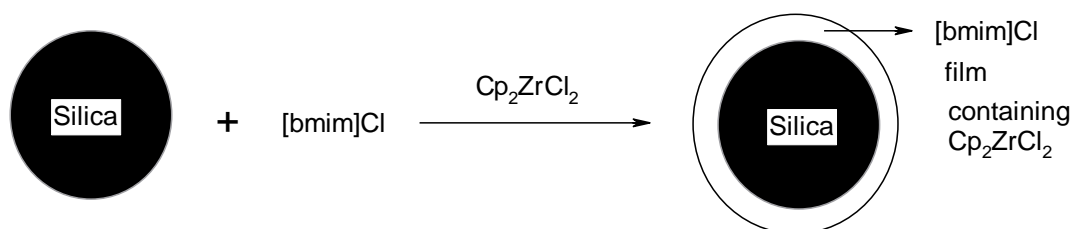
The manuscript is communicated to the Journal of Applied Organometallic Chemistry.

IIIrd Scheme:

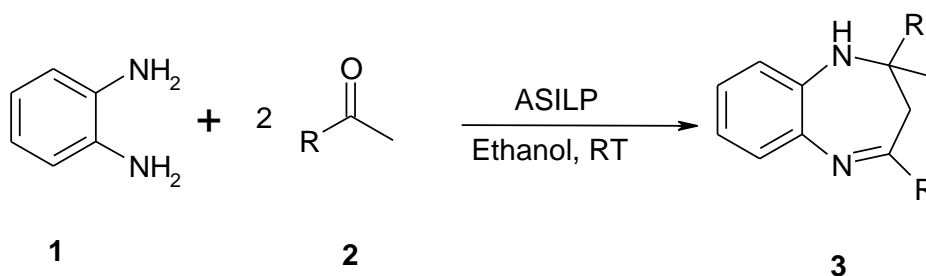
1,5-Benzodiazepines are arguably one of the most important class of azaheterocycles that are extensively used as anticonvulsant, antianxiety, antitumor, psychosis, hypnotic, antipyretic and anti-inflammatory agents.^[20] They are key intermediates in the synthesis of triazoles as well as oxadiazoles.^[21] Moreover, many of its derivatives are used as dyes for acrylic fibres.^[22] The widespread utility of 1,5-benzodiazepines has stimulated development of numerous methodologies for their synthesis. The condensation reaction between *o*-phenylenediamine (OPD) with α,β -unsaturated carbonyl compounds, β -haloketones, β -aminoketones or ketones has been extensively used for their synthesis. Although large number of catalytic systems have been developed for synthesis of 1,5-benzodiazepines using aforementioned routes,^[23] there is a still scope for improvement especially towards developing an efficient protocol using highly robust catalyst.

In the present work, we have carried out the synthesis of 1,5-benzodiazepines from OPD and ketones using aerogel supported ionic liquid phase (ASILP) catalyst. In a typical procedure for the preparation of catalyst, a mixture of powdered aerogel, ionic liquid (1-butyl-3-methyl-imidazolium chloride [Bmim]Cl) and catalyst (Cp_2ZrCl_2) was stirred in ethanol at ambient temperature for 24h (Scheme 5). The confinement of [Bmim]Cl and Cp_2ZrCl_2 in aerogel matrix was confirmed by FTIR spectroscopy, XRD and EDAX spectroscopy. The generality of the protocol was evaluated by the reactions of several

diversified ketones with OPD under optimized reaction conditions (Scheme 6). The synthesized aerogel supported ionic liquid phase catalyst was successfully employed in the synthesis of medicinally relevant 1,5-benzodiazepines. The simple procedure combined with ease of recovery and reuse of the catalyst make this method economic, generous and a waste-free chemical process for the synthesis of bioactive 1,5-benzodiazepines.



Scheme 5



Scheme 6

The work carried out under this scheme has been published in *Green Chemistry*, 2013, 15, 1849–1856.

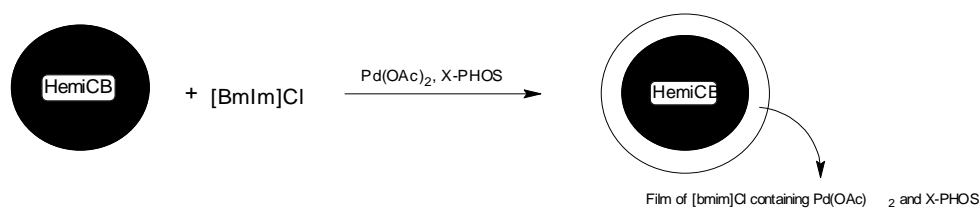
IVth Scheme:

Alkyl aryl ethers are common structural motifs that occur in a wide range of natural products, pharmaceuticals, agrochemicals and organic materials.^[24] They are important solvents and synthetic building blocks for the production of fragrances, cosmetics, pharmaceuticals, and dyestuffs. Apart from anti-inflammatory agents such as Nabumetone and Naproxen and the sandalwood fragrance trans-3-isocamphyl-cyclohexanol, alkyl aryl ethers are used as UV absorbers in skin protection products. Further, growth in this market is expected in the future as a result of the depletion of the ozone layer and the increased awareness on the part of customers of the damage caused by the sun's rays.^[25] Consequently

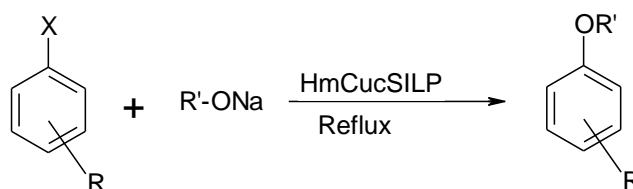
there has been a considerable amount of research into their synthesis. A variety of reagents have been developed for synthesis of alkyl aryl ethers.^[26] However, despite of numerous and significant methods, a mild protocol for synthesis of alkyl aryl ethers using highly robust heterogeneous catalyst still represents a considerable synthetic challenge.

According to our research project objective, we have focused our attention toward synthesis of supported ionic liquid phase (SILP) catalyst based on hemicucurbituril support which is acronymed as HmCucSILP catalyst. A hemicucurbituril is a macrocycle composed of alternating methylene bridges (-CH₂- units) and *N*-substituted ethylene urea units. The heterogeneous nature and appreciable surface area prompted us to use hemicucurbituril as support for the synthesis of SILP catalyst. We opted to use Pd-acetate and X-PHOS as catalyst and ligand for the synthesis of SILP catalyst as they have been extensively employed as a catalyst and ligand in organic synthesis. 3-*N*-Butyl-1-methyl imidazolium chloride ([Bmim]Cl) was used as ionic liquid for anchoring Pd-acetate and X-PHOS on hemicucurbituril surface. In the synthesis of HmCucSILP catalyst, a mixture of hemicucurbituril, Pd-acetate, X-PHOS and [Bmim]Cl was stirred in ethanol at ambient temperature for 24 h (Scheme 7). The removal of the solvent under vacuum afforded the desired HmCucSILP catalyst in the form of a fine powder that was used for further studies without any further treatment. The amount of Pd-acetate in SILP was quantified by using energy dispersive X-ray (EDX) analysis. The confinement of [Bmim]Cl, Pd-acetate and X-PHOS on the hemicucurbituril matrix was confirmed by FT-IR and FT-Raman spectroscopy. The thermal stability of catalyst was studied using thermo-gravimetric analysis (TGA) while the morphology was assessed by scanning electron microscopy (SEM). The HmCucSILP catalyst was used as an efficient heterogeneous catalyst for the synthesis of aryl alkyl ethers from sodium alkoxide and aryl halides in THF as solvent (Scheme 8). The reactions proceeded smoothly offering aryl alkyl ethers as sole products. The advantages of the

reported protocol include relatively short reaction times, high product yields and its workability at ambient temperature.



Scheme 7



X = Cl, Br, I; R = -H, -CHO, -NH₂; R' = -CH₃, -C₂H₅, -CH(CH₃)₂

Scheme 8

The Manuscript writing is in progress. The manuscript will be communicated to the Journal of Supramolecular Chemistry.

Vth Scheme:

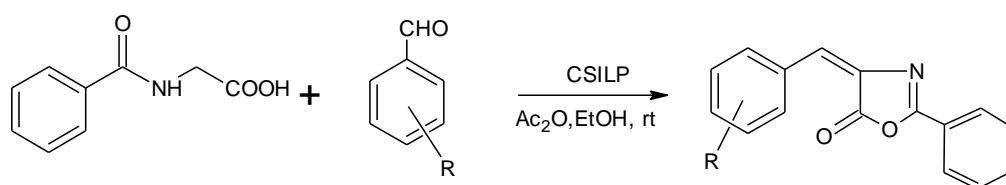
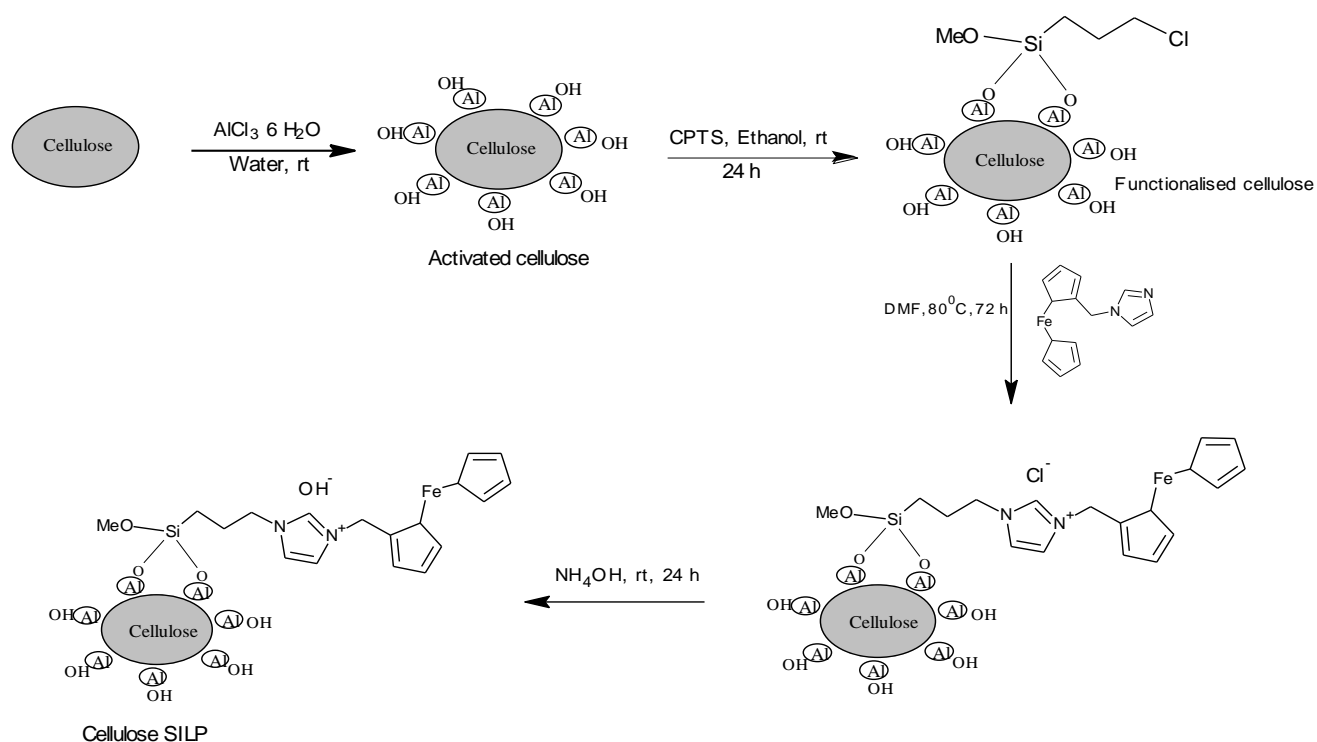
The past few decades have seen a rapid increase in the number of studies devoted to develop potent, selective therapeutic agents of high molecular divergence in balanced and decisive ways. Moreover, the ability of scientist to reform newly discovered lead compounds, as well as to produce cognate or mimics of biologically active natural products entrust upon the advancement of synthetic technologies.^[27] In this regard, potent heterocyclic compounds are one of the main topic of concern for the scientists as they are of pharmacological as well as industrial relevance.^[28] For such intension, azlactones (2,4-disubstituted oxazolin-5-ones) have been enticing as they can be used in the synthesis of natural or synthetic bioactive molecules because they may serve as protected amino acids.^[29] Recently it is proved that,

azlactones acts as carbon based nucleophiles for enantioselective organocatalysis.^[30] Azlactones are important intermediates in the preparation of several fine chemicals, including amino acids,^[31] carboxylic acids,^[32] peptides, herbicides and fungicides,^[33] skin sensitizers,^[34] and photosensitizers.^[35] Erlenmeyer azlactone derivatives possess important properties such as antimicrobial, antifungal,^[36a] and anticancer ^[36b] activities. Azlactone grafted MNPs are used as efficient drug delivery vehicles, particularly for cancer treatment,^[36c] anti-inflammatory,^[36d] antiallergic,^[36e] efficient cell permeable molecules,^[36f] anticonvulsants,^[36g] antiangiogenic,^[36h] insecticidal^[36i] and antioxidants^[36j] compounds. Although there are several methods for the synthesis of azalactones, the classical and most widely used strategy for their synthesis is through the Erlenmeyer reaction, which involves cyclodehydration of hippuric acid, followed by condensation with an aldehyde in the presence of acetic anhydride to give azalactones.^[37]

Keeping in mind the objectives of the research project, we have designed a novel cellulose supported ionic liquid phase catalyst (CSILP) containing hydroxide anion. The CSILP catalyst was prepared by multi-step synthesis involving quaternization of ferrocenylmethyl imidazole with functionalized cellulose followed by treatment with NH₄OH (Scheme 9). The confinement of organic moieties on cellulose matrix in CSILP was confirmed by FT-IR spectroscopy. The elemental analysis was performed by using energy dispersive X-ray (EDX) analysis which helped to quantify the functional groups and catalytically active hydroxyl anion. The thermal stability and morphology of catalyst was studied using Thermo gravimetric analysis (TGA) and scanning electron microscopy (SEM) respectively.

The CSILP catalyst was employed for the synthesis of azlactones by reacting hippuric acid and acetic anhydride with various aryl aldehydes using ethanol as solvent (Scheme 10). The reactions proceeded smoothly offering corresponding azlactones in excellent yields in

short reaction times. The main advantage of CSILP catalyst is that, it can be separated by simple filtration and can be reused without any significant loss in chemical yield of the products upto six cycles. All the products were characterized by IR, ^1H NMR, ^{13}C NMR and mass spectroscopy. The physical and spectroscopic data are consistent with the proposed structures and are in harmony with the literature values. Simple work up procedure, high yields and easy recovery and reusability of the catalyst are the salient features of this method.

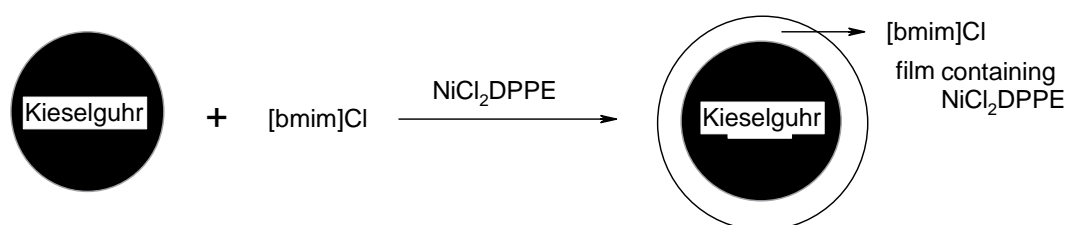


VIth Scheme:

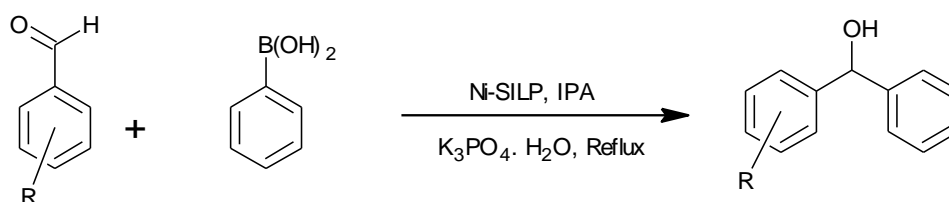
Delivering pure substances for the pharmaceutical industry, combined with the common obstacles and costs of separations, has led to new synthetic methods for the designing of various intermediates in drug synthesis.^[38] The diarylmethanols have attracted considerable interest over past two decades, since these are valuable intermediates for the synthesis of biologically active molecules.^[39] They are precursors of numerous molecules with important pharmacological properties, such as antihistaminic, antiarrhythmic, diuretic, laxative, antidepressive, local-anesthetic and anticholinergic.^[40] The synthesis of diarylmethanols thus has been the focus of many catalytic studies. The syntheses of diarylmethanols commonly involve of two strategies: The first strategy involves addition of suitable aryl nucleophiles to aromatic aldehydes or the reduction of diaryl ketones^[41] while the second strategy involves nucleophilic addition of organometallic compounds to aldehydes.^[42] Catalytic arylation of aromatic aldehydes with arylating reagents is one of the most useful reactions used to synthesize diarylmethanols. From the view point of modern organic synthesis, the use of heterogeneous catalysts and reagents is desirable. To date, many successful examples of catalytic arylation using various catalysts have been reported by various groups.^[43] However, new protocols employing new heterogeneous catalytic systems can be a worthy contribution in this field.

As per our proposed work, we have synthesized novel SILP catalyst for the synthesis of diarylmethanols. The SILP catalyst was synthesized using Kieselguhr as a support. Kieselguhr, a diatomaceous earth (diatomite), is a form of silica composed of the siliceous shells of unicellular aquatic plants of microscopic size. The heterogeneous nature and highly porous nature of Kieselguhr prompted us to use as support in the synthesis of SILP catalyst for the synthesis of diarylmethanols. The Kieselguhr based SILP catalyst (acronymed as KSILP) was synthesized by depositing ionic liquid 3-*N*-butyl-1-methyl imidazolium chloride

([Bmim]Cl) containing NiCl₂DPPE (1,2-Bis(diphenylphosphino)ethane nickel(II) chloride) on mesoporous Kieselguhr (Scheme 11). The confinement of [Bmim]Cl and NiCl₂DPPE in the mesoporous matrix was confirmed by FTIR spectroscopy. The amount of Ni in the SILP catalyst was quantified by using energy dispersive X-ray (EDX) analysis. The size and morphology of the Ni-SILP catalyst was studied by scanning electron microscopy (SEM). The thermal stability of catalyst was studied using thermo gravimetric analysis (TGA). The catalytic activity of synthesized Ni-SILP catalyst was studied in the synthesis of diarylmethanols from phenyl boronic acid and aryl aldehydes (Scheme 12).



Scheme 11



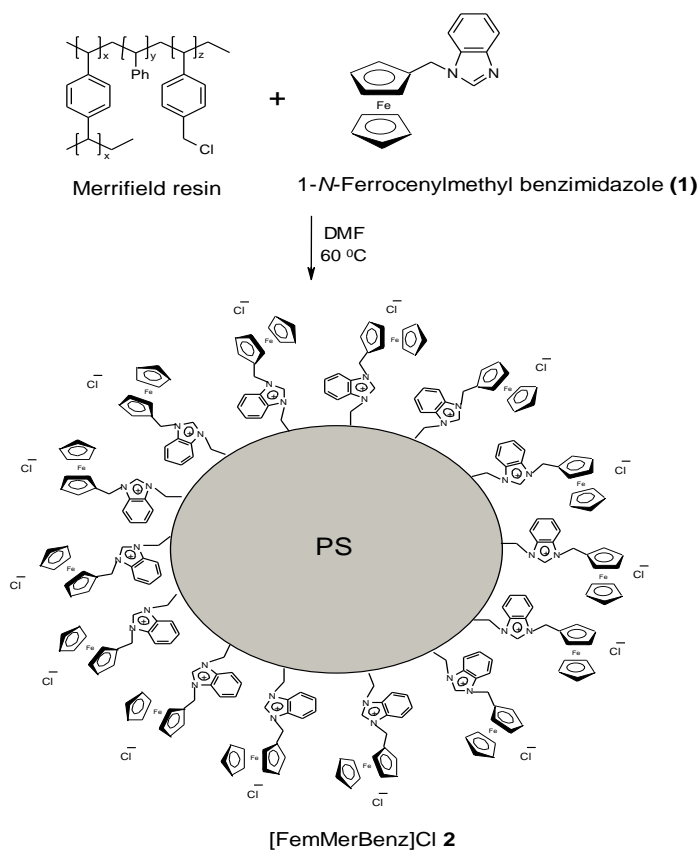
Scheme 12

The generality of the protocol was assessed by reacting variety of structurally diverse aldehydes with phenyl boronic acid using Ni-SILP catalyst. The aryl aldehydes with both electro donating as well as electron withdrawing groups reacted efficiently offering the corresponding diarylmethanols in excellent yields. The reusability of the Ni-SILP catalyst was investigated and it was found that it showed a remarkable recyclability as the yields of the products did not changed significantly till the fifth run.

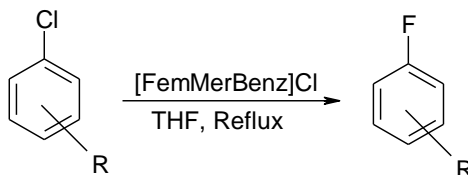
VIIth Scheme:

The fluorinated organic compounds play a vital role in pharmaceuticals, agrochemicals, materials and tracers for positron tomography.^[44] Fluorine substituent's have an unique and often profound impact on the structure, energy and chemical as well as physical properties of organic compounds.^[45] It has been well established that the incorporation of fluorine in organic compound can impart interesting properties such as lipophilicity and metabolic stability that can change in vivo drug transport and absorption rates.^[46] According to latest report, around one third of agrochemicals and one fifth of pharmaceuticals contain fluorine including drugs such as Lipitor, Ciprofloxacin, Prozac and Lexapro.^[47] There has been keen interest in selective incorporation of fluorine into organic compounds. The halogen exchange fluorination (Halex) is one of the most important and frequently used methods to synthesize fluorinated organic compounds.^[48] In the halex reaction, halogen atom serve as leaving group and inexpensive organic fluorides such as KF are used as nucleophiles. While many different protocols for the halex reaction have been invented over the past decades,^[49] an efficient, high yielding protocol using a robust heterogeneous catalyst is still a significant challenge in synthetic chemistry.

As per the proposed outline in our project, we have synthesized, a novel supported ionic liquid phase catalyst (SILP) for halex reaction (Scheme 13). The SILP catalyst was synthesized by quaternization of ferrocenylmethylbenzimidazole with Merrifield resin. The SILP catalyst was characterized by FTIR and FT Raman spectroscopy. The SILP catalyst proved to be an effective heterogeneous reagent for the halex reaction of structurally diverse aryl chlorides (Scheme 14). Simple work up procedure, high yields and easy recovery and reusability of the catalyst are the salient features of the method.



Scheme 13



Scheme 14

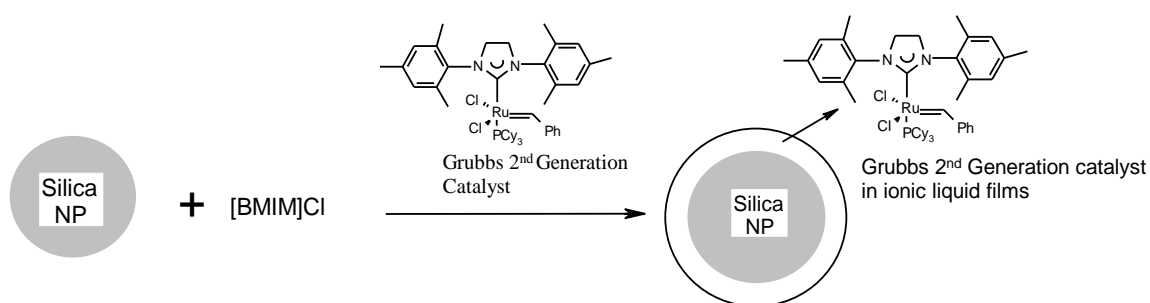
The Manuscript is communicated to Journal of Fluorine Chemistry.

VIIIth Scheme:

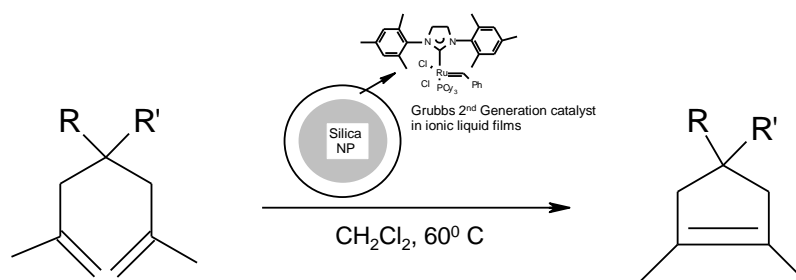
In recent years, olefin metathesis that involve a transition metal-catalyzed interexchange reaction of alkylidene units between two substituted alkenes has emerged as an effective and useful method for constructing carbon–carbon double bonds.^[50] As remarkable olefin metathesis catalysts, ruthenium-based carbene complexes developed by Grubbs^[51] have significantly broadened the scope of the olefin metathesis reaction. Lately, several modified Grubbs-type catalysts have also been developed and intensively studied. Most of homogeneous Grubbs-type catalysts are hard to be reused and recycled after reactions.

Furthermore, the homogeneous systems suffer the difficulty of removing residual ruthenium byproducts from the reaction products. Nowadays, the use of environmentally friendly heterogeneous catalysts have become an important research target for green chemistry. Immobilizing homogeneous catalytic species on solid supports and scavenging residual catalysts are the most effective ways to solve the problems. Several immobilized Grubbs-type catalysts have been reported by using polymer supports.^[52] Although various attempts have been made for the synthesis of immobilized Grubbs catalysts, no attempt has been made for heterogenize them using concept of SILP catalysts.

In this study, with purpose to prepare active and stable heterogeneous Grubbs catalysts, we synthesized a supported ionic liquid phase catalyst by immobilizing Grubbs second generation catalyst on silica support using ionic liquid [bmim]Cl (Scheme 15). The ruthenium content in SILP catalyst is determined by inductively coupled plasma (ICP) analysis. The ATR spectrum of SILP revealed that there are no obvious changes in the structure of Grubbs catalyst on immobilization in SILP catalyst. The SILP catalyst containing Grubbs catalyst was employed for olefin metathesis reactions (Scheme 16). Variety of dienes underwent smooth reaction using synthesized SILP catalyst in CH₂Cl₂ affording corresponding metathesis products in good yields under inert atmosphere. The SILP catalyst showed good activity as compared to other heterogeneous catalyst containing Grubbs second generation catalyst.



Scheme 15



Scheme 16

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PUBLICATIONS IN JOURNALS

1. Ferrocene tagged functional polymer: A robust solid-phase reagent for O-demethylation. Rajanikant Kurane, Vipul Gaikwad, Jagannath Jadhav, Rajashri Salunkhe, Gajanan Rashinkar*, **Tetrahedron Letters**, 2012, *53*, 6361–6366.
2. Synergistic catalysis by an aerogel supported ionic liquid phase (ASILP) in the synthesis of 1,5-benzodiazepines, Rajanikant Kurane, Jagannath Jadhav, Sharanabasappa Khanapure, Rajashri Salunkhe, Gajanan Rashinkar*, **Green Chemistry**, 2013, *15*, 1849–1856.

PRESENTATIONS IN CONFERENCE/SEMINAR/SYMPOSIUM

1. Poster presentation on 'New task specific supported ionic liquid phase catalyst for *O*-demethylation' in National seminar on 'Recent Advances in Synthetic Chemistry and Nanomaterials' (RASCN 2012) to be held at Shivaji University in 21st and 22nd Jan. 2012.
2. Poster presentation on "Halex Reaction in supported Ionic Liquid Phase Catalyst" in 2nd international conference on 'Emerging Trends in Chemical Sciences' (ETCS 2012) to be held at Solapur University in 2nd- 4th Oct. 2012.
3. Poster presentation on 'Aerogel Supported Ionic Liquid Phase (ASILP) Catalyst in the synthesis of 1,5-benzodiazepines' in National conference on 'Current Research in Chemical Sciences' (CRCS 2013) to be held at Shivaji University in 22nd- 23rd Jan. 2013.
4. Poster presentation on 'Efficient Oxidation of alcohols by Supported Ionic Liquid Phase (SILP) Catalysts' in National conference on 'Drug Designing and Discovery' (DDD-2013) to be held at Devchand College, Arjunnagar MS (India) in 6th and 7th Sept. 2013.
5. Poster presentation on 'Efficient Synthesis of Alky aryl ethers by Hemicucrbituril Supported Ionic Liquid Phase (HSILP) Catalyst' in International conference on 'Emerging Horizons in Biochemical Sciences and Nanomaterials' (EHBCSN-2013) organized by Shri Shivaji Mahavidyalay, Barshi on 28th- 30th Nov. 2013.

Contribution to the Society

The synthesis and applications of SILP catalysts employed in the current project obeys principles of green chemistry and thus helps in minimizing pollution associated with chemical processes and thus has important contribution to society. The important aspects of the project that are directly or indirectly contribute to society are listed below.

Lower Levels of Toxicity of Supported Ionic Liquid Phase Catalysts and its contribution to Green Chemistry: *Low toxicity of SILP catalysts:* The toxicity of Ionic Liquids (ILs) is questionable. Contemporary studies have revealed that some of the ILs are even more toxic for aquatic organisms than the classical organic solvents that they are aiming to replace. We have assessed the toxicological impact of the synthesized SILP catalysts by comprehensive antimicrobial toxicity studies and biodegradation experiments. The toxicity was investigated using two Gram positive bacteria *Bacillus subtilis* and *Staphylococcus aureus*, and one Gram negative bacteria *Escherichia coli*. The investigated SILP catalysts displayed predominantly no or just minor toxic effects on all of the studied bacteria confirming their environmentally benign nature. The studies reveal that SILP catalysts can be tagged as biodegradable and have a considerable potential to contribute to the development of more sustainable processes. These findings suggest that commercial and large scale applications of SILP catalysts will help in decreasing pollution due to disposal of SILP catalyst that will directly help society.

Benefits of processes using SILP catalysis: SILP catalysts are very active and are easy to handle. There is no leaching of IL like units in the reaction mixture which helps to prevent environmental pollution caused by residual entities in the waste. The built-in heterogeneous nature of SILP catalyst allows for easy separation simply by filtration. The SILP catalysts are reused for number of times with constant activity.

The comparison of our technology with other technologies:

The use of SILP catalysts over traditional ionic liquids has number of benefits. ILs are very costly and their recyclability induces energy consumption. The purity of ILs is a big problem. On the other hand, SILP catalysts are not costly to prepare. They can be separated without energy consumption as simple filtration is required for their separation from reaction

mixture. The SILP catalysts show superior performance in selectivity as well as reactivity over traditional ILs.

Current and planned commercialization:

The SILP based systems have significant applications for large scale processes utilising ionic liquids. In many cases, the ionic liquid is an expensive capital cost and the use of the SILP catalysts allows efficient recycle of the ionic liquid as well as increasing the surface area of the active phase. The major disadvantages of heterogeneous catalysts for fine chemical and pharmaceutical transformations is concerned with selectivity. This is alleviated to a large extent by utilising homogeneous catalysts; however, separation then becomes the major issue. A common method of heterogenisation these systems to aid workup is to covalently attach the homogeneous catalyst onto a support; however, this method often leads to changes in catalytic performance. The SILP catalysis provides a method by which the catalyst behaves similarly to that found under homogeneous reaction conditions due to the solvation of the metal complex by the ionic liquid with the reaction taking place in the thin liquid film. Furthermore this technique provide the opportunity of utilising homogeneous catalysts in the gas phase as well developing continuous processes from traditional batch systems. The field of SILP catalysis provides an opportunity to expand the educational toolbox and allow engineers and scientists more freedom in the planning and implementation of green catalytic technologies in all areas of the chemical industry. The research on the expansion of these horizons of SILP catalysis is underway in our laboratory.