

Rakesh Kumar Sharma
Department of Chemistry
Indian Institute of Technology Rajasthan
Old Residency Road
Jodhpur-342011
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Present position:

Assistant Professor at Chemistry department (COE-Energy and System Science), Indian Institute of Technology Rajasthan, Jodhpur from May, 2010 onwards.

Date of Birth: 1st July, 1976
Nationality: Indian

Current Running Projects

1. **Solar water splitting: Lanthanide complexes for hydrogen production.** (Funding Agency : DST-Technology (2011-2013))
2. **Molecular sensors : Synthesis and anion recognition studies** (Funding Agency: DST, (2012-2014))
3. **Asymmetric Hydrogenation on Carbon Nanotube Surface**(DST-RFBR ; Indo-Russia joint Research Proposal; 330K (2012-2014) (International Project with Prof. Irina P. Beletskaya, Moscow State University)

Project (under-consideration)

4. **Hectorite-supported ruthenium catalyst for hydrogenation of carbon dioxide and activation of small molecules** (Indo-swiss Joint Research call)
5. **Organically templated lanthanide based metal organic framework catalysts for energy, fuel and fine chemicals** (Indo-Portugal Joint Research Call)

Education

Post Doctoral Researcher: (Advisor: Prof. T V RajanBabu) Jan 2008 to May 2010
Department of Chemistry, The Ohio State University, Columbus, OHIO, USA

PhD: (Advisor: Prof. Ashoka. G. Samuelson) January 2008
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore
Thesis: "*Chiral Bisphosphinites for asymmetric catalysis*"

Master of Science in Organic Chemistry: July 1999
University of Rajasthan, Jaipur

Bachelor of Science in Chemistry: March 1997
University of Rajasthan, Jaipur

Honors and Fellowships

Rural talent search fellowship

1988

Conducted by the Department of Education, Ministry of human resources development (MHRD), Government of Rajasthan.

National Eligibility Test (NET-2002)

2002

Conducted by Council of Scientific and Industrial Research (CSIR), New Dehli, Government of India.

Previous Positions (after M.Sc.)

Sr. Research Chemist (Medicinal & Synthetic Chemistry)

May 2000 – July 2001

Zydus Research Centre, Zydus Cadila Healthcare Ltd. Ahmedabad.
www.zyduscadila.com

Research Assistant (Silicates and Catalysis Discipline)

July, 2001- July, 2002

Central Salt & Marine Chemicals Research Institute, Bhavnagar
www.csmcri.org

Conferences and Presentations

Green Catalysts for selective Friedel-Craft reactions

March 2002

Presentation at 7th national symposium on heterogeneous catalyst, Banaras Hindu University, Varanasi.

Chiral Phosphinites for Asymmetric Catalysis

Feb 2005

Poster presented in 7th CRSI National Symposium in Chemistry, Indian Association for the cultivation of Science, Kolkata.

Platinum catalyzed Hydrosilylation of Olefins

Dec 2005

Poster presentation in 11th Symposium on Modern Trends in Inorganic Chemistry (MTIC-XI) Indian Institute of Technology, Delhi.

News Chiral phosphinites for asymmetric catalysis

March 2007

Poster presentation in Annual In-house symposium in Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore (**BEST POSTER AWARD**)

Nature's chiral pool for asymmetric catalysis

July 2007

Invited talk at GE Global Research Center Bangalore.

Publications

"Hydrovinylation Reaction in organic Synthesis" T. V. RajanBabu* G. Adam Cox and **Rakesh K Sharma**, *Comprehensive Organic Synthesis*, 2012, XXX, XXXX. (Book Chapter)

"Room Temperature Water Splitting at the Surface of Yttrium iron garnet" Gurjot Singh and **Rakesh Kumar Sharma*** (manuscript)

"Biscyclometallated molecular switched based on thiohelicene and 1,5-naphthyridine" Amanpreet Hundal and **Rakesh Kumar Sharma*** (manuscript)

"Carbon Dioxide Reduction by Cobalt Hydrides at room temperature" **Rakesh Kumar Sharma***
ACS Catalysis (under revision) **2012**

"Highly enantioselective ascorbic acid derived bisphosphinites for asymmetric hydrosilylation of alkenes in solvent free conditions"; *Organic Letters*
Rakesh Kumar Sharma and A. G. Samuelson* (under revision) **2012**

"Asymmetric Hydrovinylation of Unactivated Linear 1,3-Dienes"
Rakesh K Sharma and T. V. RajanBabu* *J. Am. Chem. Soc.* **2010**, *132*, 3295

(Abstract: Monosubstituted acyclic (E)-1,3-dienes undergo efficient hydrovinylation giving (Z)-3-alkylhexa-1,4-dienes upon treatment with catalytic amounts of bidentate phosphine-CoCl₂ complexes {[P~P](CoCl₂)} and Me₃Al in an atmosphere of ethylene. The regioselectivity of the reaction (i.e., 1,4- or 1,2-addition) depends on the nature of the ligand and temperature at which the reaction is carried out. Complexes derived from (RR)-DIOP and (SS)-BDDP at -45 °C give very high enantioselectivities for several prototypical 1,3-dienes. In sharp contrast to the corresponding Ni(II)-catalyzed hydrovinylation, 1-aryl-substituted 1,3-dienes give almost exclusively achiral linear 1,4-addition products, unless the 2-position is also substituted. Solid-state structures of the precatalysts are presented.)

"Asymmetric allylic alkylation by palladium-bisphosphinites"; **2008**
Rakesh K Sharma, Munirathnam Nethaji, Ashoka G. Samuelson* *Tetrahedron: Asymmetry* **2008**, *19*, 655.

(Abstract: A series of new chiral palladium-bisphosphinite complexes have been prepared from readily available, Naturally occurring chiral alcohols. The complexes were used to efficiently carry out catalytic allylic alkylation of 1,3 diphenylpropene-2-yl acetate with dimethyl malonate. The complexes based on derivatives of ascorbic acid carry out enantioselective alkylations, one of which showed an ee as high as 97%. Based on the structural characterization, it can be surmised that strategic placement of phenyl groups is key to higher enantioselectivities.)

"Asymmetric allylation of aldehydes with chiral platinum phosphinite complexes"
Rakesh K Sharma and Ashoka G. Samuelson* *Tetrahedron: Asymmetry* **2007**, *18*, 2387 **2007**

(Abstract: Platinum phosphinite complexes made from chiral diols catalyze the enantioselective allylation of cinnamaldehyde. This reaction proceeds with better yields at shorter reaction times in the presence of acetic acid. Enantiomeric excesses were greater when reactions were carried out with phosphinite ligands having hydrogen bond donors or acceptors.)

"On the key role of water in the allylic activation catalyzed by Pd (II) bisphosphinites"
Rakesh K Sharma and Ashoka. G. Samuelson* *J.Chem. Sci* **2006**, *118*, 569. **2006**

(Abstract. Palladium and platinum complexes of bisphosphinites and bisphosphines derived from mandelic acid have been prepared and characterized. Their ability to catalyze allylation of imines with allyltributylstannane has been studied. Bisphosphinite complexes of Pd (II) are shown to be ideal and they work best in the presence of one equivalent of water. The near neutral conditions employed make the catalysts suitable for a wide variety of substrates.)

Research Summary

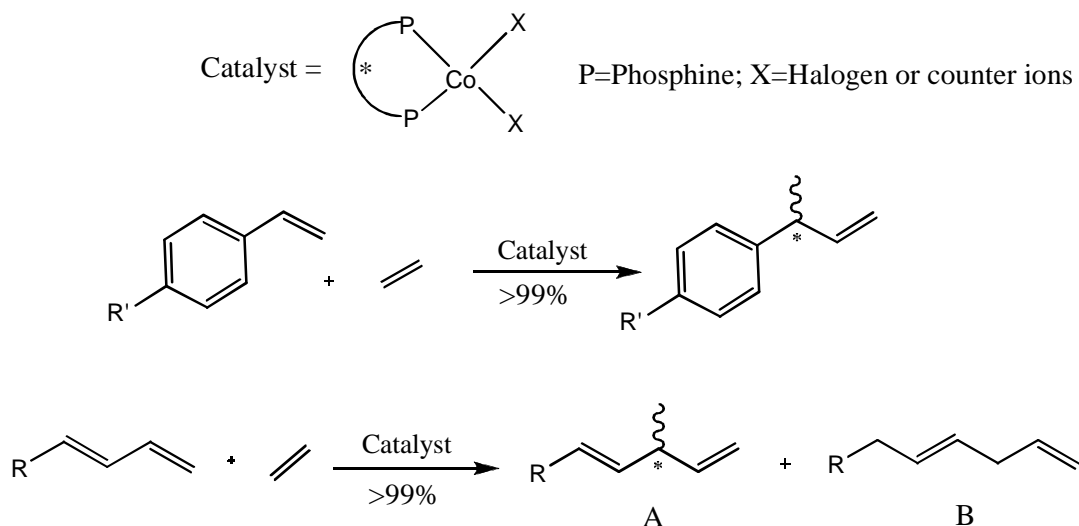
Rakesh Kumar Sharma and T. V. RajanBabu

Department of Chemistry, Ohio State University, Columbus OH-43210

Cobalt catalyzed asymmetric hydrovinylation of alkenes and 1,3-dienes: development of new catalytic system and mild reaction conditions for sensitive reaction¹

Development of new air stable bidentate cobalt based catalysts for asymmetric hydrovinylation of alkenes is the main goal of these studies. The present successful nickel based catalysts are not air stable and required drybox to perform every single experiment. Also the nickel based catalysts are monodentate that have limited control on stereochemistry and design.

A series of new chiral and achiral cobalt phosphine complexes are synthesized and screened for various alkenes and 1,3-dienes. Under optimized reaction conditions cobalt complexes work tremendously well and gave 100% conversion for styrenes and its derivatives. More interesting results were obtained when 1,3-dienes are used as substrate, a ligand directing 1,2-**A** (>99%) or 1,4-**B** hydrovinylation (>99%) reactions were observed with excellent enantioselectivity (>99%).



R, R' = Phenyls, alkyls, halogen, amines, ethers and esters

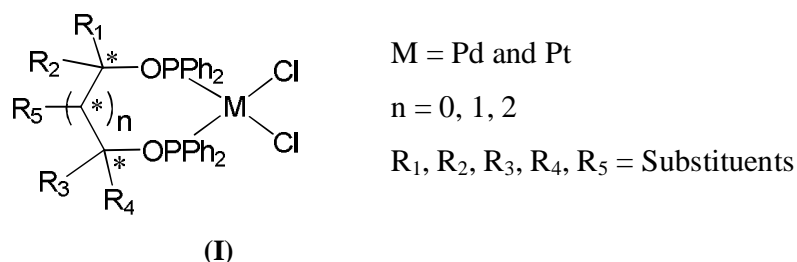
Research Summary

Rakesh Kumar Sharma and A. G. Samuelson

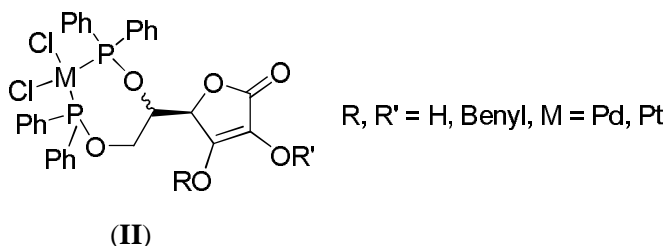
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore

New bisphosphinites from naturally occurring chiral sources: modified template method for direct synthesis of metal complexes from diols²

The objective of this research is to develop new chiral catalysts derived from natural chiral pool for application as chiral auxiliaries in several important asymmetric catalytic reactions. In this respect synthesis of new chiral bisphosphinites and their palladium and platinum complexes with framework **I**, from inexpensive natural chiral compounds was intended. The modular construction of these ligands enable one to study the effect of (a) steric and electronic effect of substituents R₁-R₅ in order to improve selectivity of these reactions (b) Hydrogen bonding effects on selectivity if the substituents are hydrogen bond donors or acceptors.



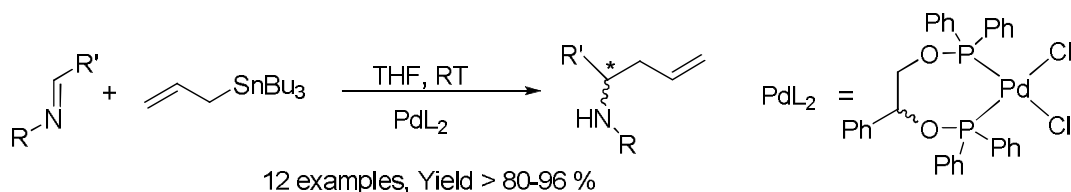
Most complexes are synthesized with a modified template procedure. In this method, alcohols are directly treated with $M(PPh_2Cl)_2Cl_2$, generated *in situ* from $[M(COD)Cl_2]$ (M = Pd/Pt) and PPh_2Cl_2 . **Forty two** new complexes are prepared with different ring sizes and functional group tolerance. Synthetically difficult bimetallic complexes are synthesized with ease using the modified template procedure. Seventeen complexes are found to be suitable for X-ray diffraction studies. Crystal structures show distorted square planar geometry around the metal with a twist half boat conformation. The diols are chosen based on the backbone functionalities such as hydrogen bond donors/acceptors and steric demand. Particularly, ascorbic and isoascorbic acid derived bisphosphinites are systematically edited to understand the influence of hydrogen bonding and steric interactions in asymmetric transformations (II).



Allylation of imines: key role of water in the allylic activation catalyzed by Pd (II) bisphosphinites²

In initial attempts nucleophilic allylation reaction and the effect of promoters on chemical and optical conversion were investigated. An important role of water is observed in allylation of imines using palladium bisphosphinite complexes (Scheme I) derived from mandelic acid.

It is found that one equivalent of water reduces the reaction time and enhances the yield. Allylation of diverse imines were carried out in essentially neutral condition in contrast to the Lewis acid catalyzed reaction.

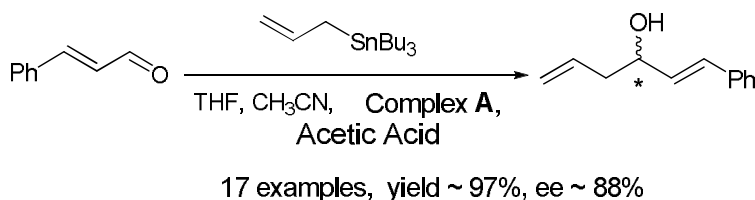


(Scheme I)

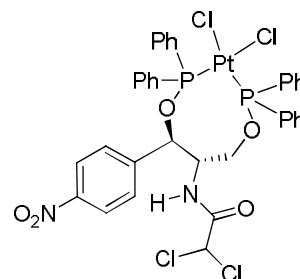
Allylation of aldehydes: Acetic acid promoted asymmetric induction in synthesis of homoallylic alcohols³

In contrast to imines nucleophilic allylation of aldehydes is catalyzed by Pt-bisphosphinites (Scheme II). Acetic acid is found to be the best promoter among the promoters tested. High yield and enantioselectivity (> 88% ee)

are observed with complex **A** derived from chloramphenicol. Ligands based on ascorbic acid and isoascorbic acid show good potential for enantioselective allylation of carbonyl compounds.



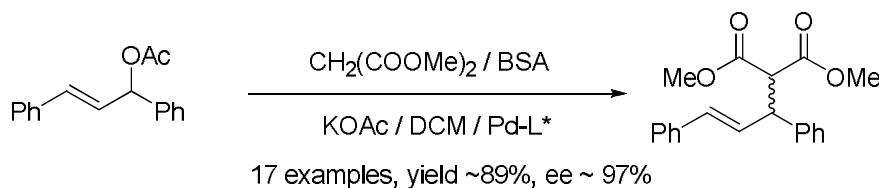
(Scheme II)



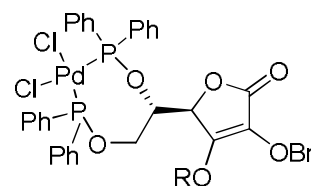
(A)

Tsuji-Trost reaction: effect of ligand design on enantioselectivity⁴

In another study of asymmetric allylic alkylation (AAA) reaction of rac-1,3-diphenyl-3-acetoxy-1-ene with a series of Pd-bisphosphinite complexes under the standard Tsuji-Trost condition (Scheme III). The Pd-bisphosphinites are having good potential for catalyzing AAA reaction. Bulky and hydrogen bond donor groups are having a positive effect on enantioselectivity. Among the catalysts screened, the 3-O-benzyl substituted ascorbic acid derived complex **B** gives highest enantioselectivity 97%.



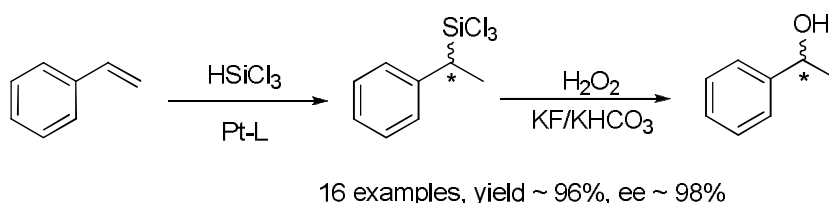
(Scheme III)



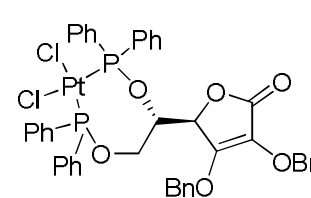
(B)

Hydrosilylation of alkenes: a novel solvent free highly enantioselective reaction for synthesis of chiral silicon masked compounds⁵

To see the activity of bisphosphinites in addition reactions, Pt-bisphosphinite catalyzed hydrosilylation of styrene with trichlorosilane in solvent free conditions (Scheme IV). The results show that enantioselectivities of product depend strongly on the type of functional groups that exist on the backbone of the ligand. The enantioselectivities are high with complexes that contain a hydrogen bond donor group and those with sterically demanding groups. Ascorbic acid based complexes show superior catalytic activity among the complexes tested, dibenzylated ascorbic acid derived platinum complex **C** gives highest enantiomeric excess as high as 98 %.



(Scheme IV)



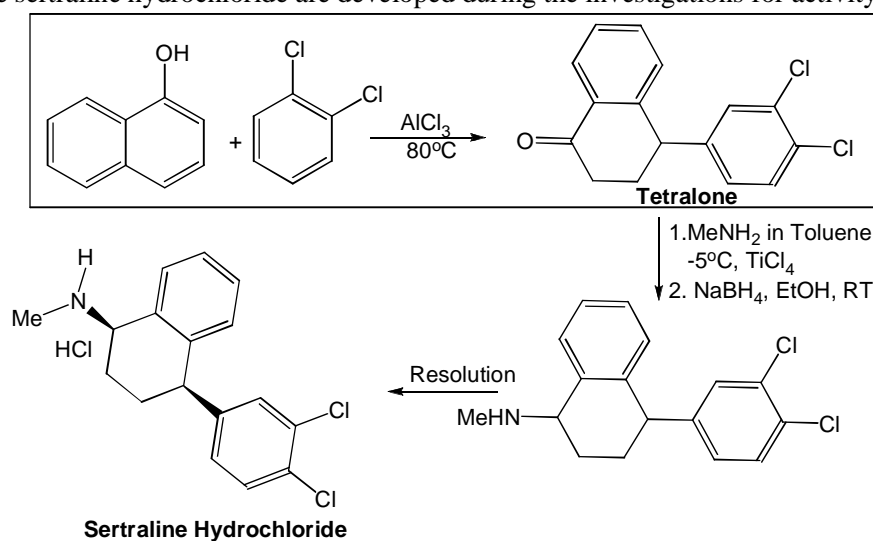
(C)

Research Summary

Rakesh Kumar Sharma and Bipin Pandey
Zydus Research Center, Zydus Cadila Healthcare, Ahmadabad

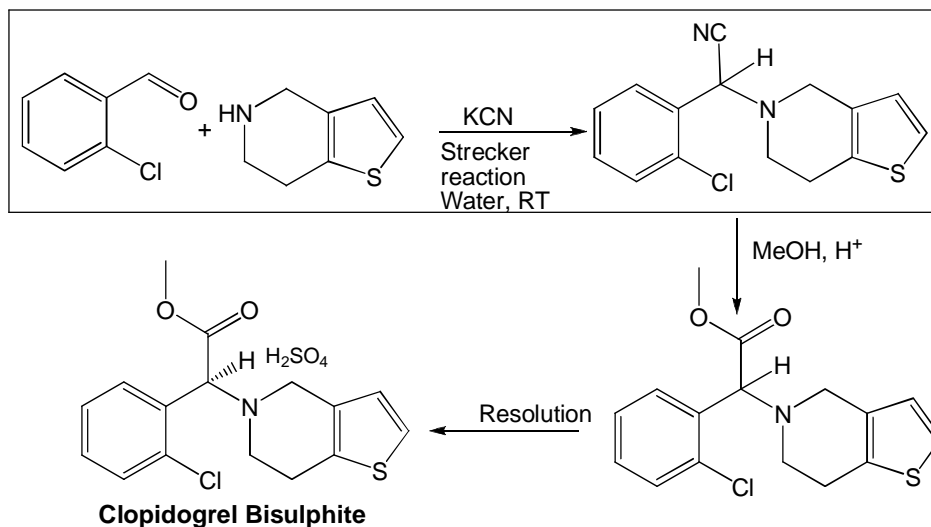
A catalytic phenylation and hydrolysis process for the preparation of 4-[(un)substituted phenyl]-3,4-dihydro-1-(2H)-naphthalene-1-ones from 1-alkoxynaphthalenes and 1,2-disubstituted benzenes⁶

Sertraline hydrochloride is an antidepressant of the selective serotonin reuptake inhibitor (SSRI) class. Sertraline is primarily used to treat major depression in adult outpatients as well as obsessive-compulsive, panic, and social anxiety disorders in both adults and children. For the total synthesis of sertraline, the intermediate tetralone is most important and there are 4 steps are needed for its synthesis. During my research, it is found that optimized reaction conditions using AlX_3 as catalyst give excellent yield (> 93%) and regioselectivity (> 96%), the unwanted isomer could be avoided using recrystallization methods. Novel highly active new polymorphs of the sertraline hydrochloride are developed during the investigations for activity studies.



(S)-(+)-clopidogrel: Development of new aqueous Strecker reaction⁷

The other project was total synthesis of Clopidogrel which is an oral antiplatelet to inhibit blood clots in coronary artery disease, peripheral vascular disease, and cerebrovascular disease. It works by irreversibly inhibiting a receptor called P2Y_{12} . The most significant contribution is the development of Strecker synthesis in water at room temperature. A good use of sodium bisulphate adduct of ortho-chloro benzaldehyde is used to dissolve in water. The reaction is fast and product precipitates during the reaction to give quantitative yield.

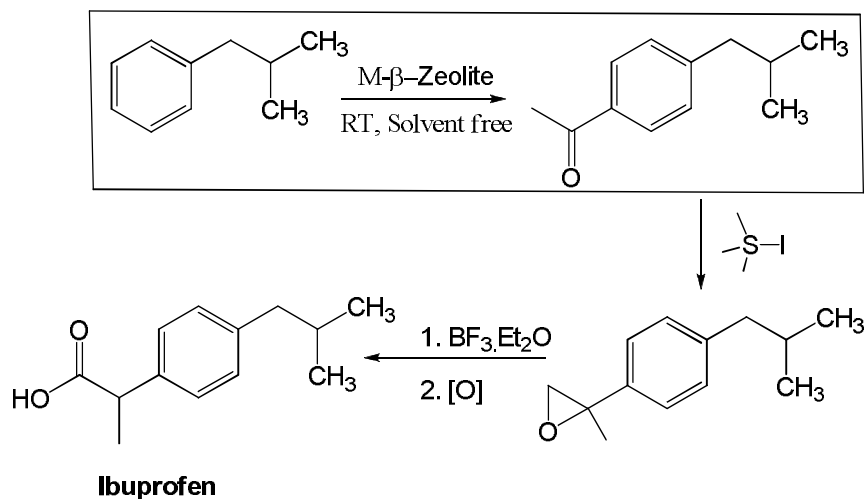


Research Summary

Rakesh Kumar Sharma and R.V. Jasra
Central Salt & Marine Chemicals Research Institute, Bhavnagar

Green catalysts for Friedel-Craft acylation⁸

This project is to develop green catalysts for synthesis of a key intermediate of Iso-butyl-propanoic-phenolic acid popularly known as Ibuprofen. Ibuprofen is a non-steroidal anti-inflammatory drug (NSAID). It is used for relief of symptoms of arthritis, primary dysmenorrhea, fever, and as an analgesic, especially where there is an inflammatory component. Ibuprofen is a core medicine in the World Health Organization's "Essential Drugs List". Various Zeolite, clay based catalysts are synthesized and modified for the acylation of isobutyl benzene that is a key intermediate in this synthesis. The highlights of the work is to replace environmentally hazardous aluminum chloride with transition metal (Sc, Yb, Y and Hf) triflate impregnated β -Zeolite which give moderate to high conversions



References:

1. **Rakesh K Sharma** and T. V. RajanBabu* *J. Am. Chem. Soc.* **2010**, *132*, 3295.
2. **Rakesh K Sharma** and Ashoka. G. Samuelson* *J.Chem. Sci* **2006**, *118*, 569.
3. **Rakesh K Sharma** and Ashoka G. Samuelson* *Tetrahedron: Asymmetry* **2007**, *18*, 2387
4. **Rakesh K Sharma**, Munirathnam Nethaji, Ashoka G. Samuelson* *Tetrahedron: Asymmetry* **2008**, *19*, 655.
5. Unpublished results.
6. Indian Patent IN 194118, **2004**.
7. PCT Int. Appl. WO 2007144895, **2007**.
8. Unpublished results.