

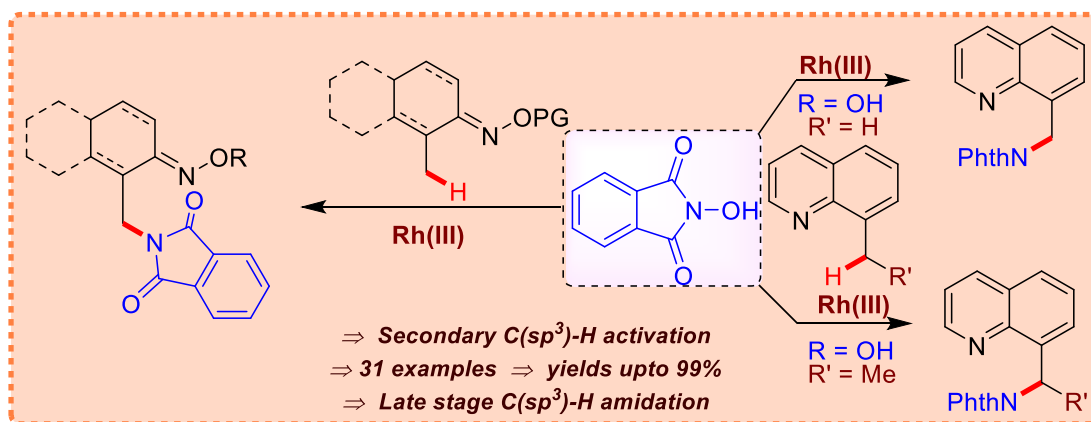
Cp*Rh(III)-catalyzed amidation of C(sp³)-H bonds using *N*-hydroxyphthalimides

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The construction of carbon-nitrogen (C-N) bonds holds a great importance in organic chemistry.¹ In this context the transformation of C(sp³)-H bond to C(sp³)-N is fascinating yet a challenging task due to complex reactivity associated with C-H bonds.² Herein, we disclose Rh(III) catalyzed amidation of C(sp³)-H bond using *N*-hydroxyphthalimides.³ The developed methodology does not require any external oxidant as *N*-O bond acts as an internal oxidant. The amidation of both primary and secondary C-H bonds have been achieved successfully. The key feature of the reaction was late stage functionalization of carvone and santonin derivatives to get the desired amidated product. A plausible mechanism has been depicted on the basis of some preliminary mechanistic experiments.



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Rh(III)-catalyzed C(sp³)-H functionalization of oxabenzonorbornadienes

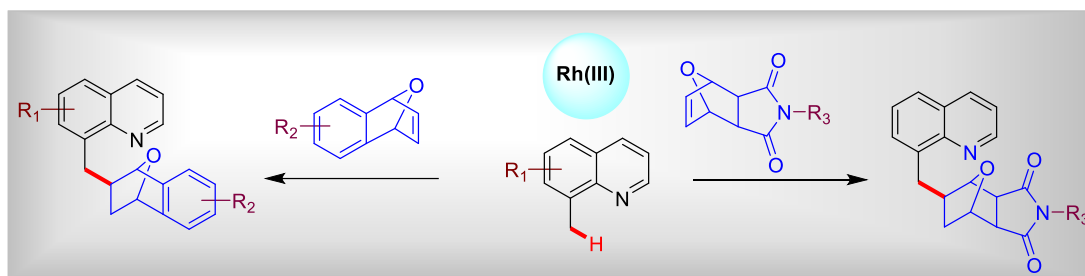
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Heterobicyclic structures are one of the most vital and influential scaffolds existing in biological molecules.¹ Oxabenzonorbornadienes are significant heterobicyclic moiety, isolated from natural sources and also used in pharmaceuticals.² Herein, we have disclosed Rh-catalyzed regioselective C-H alkylation of 8-methylquinolines with oxabenzonorbornadienes scaffolds with ring retention of the oxabenzonorbornadiene skeleton. Mechanistic experiments were carried out to get an insight into the reaction mechanistic pathway. The scale-up reactions and post-transformations were explored to the versatility of the developed methodology.



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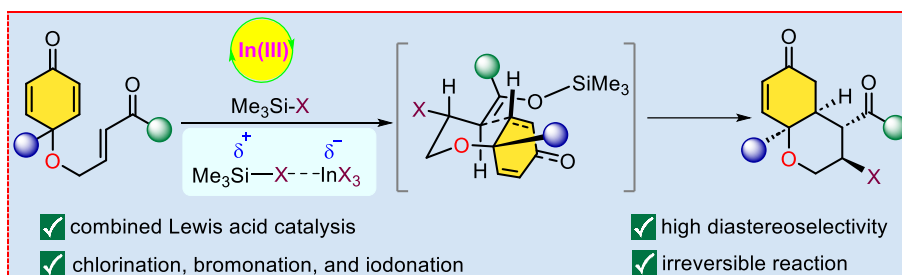
Combined Lewis acid Catalyzed diastereoselective halogenative cascade annulation of enone-tethered cyclohexadienones

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The cascade di-functionalization of α,β -unsaturated carbonyls by nucleophilic halogenation followed by enolate trapping with other electrophiles is highly challenging in synthetic organic chemistry. Herein, we report a chemo- and diastereoselective cascade annulation of enone-tethered cyclohexadienones by using unconventional combined Lewis acid catalyzed halogenation reaction in the presence of In(III)-catalysis and trimethylsilyl halide. The reaction provides highly functionalized bicyclic enones with four contiguous stereocenters.



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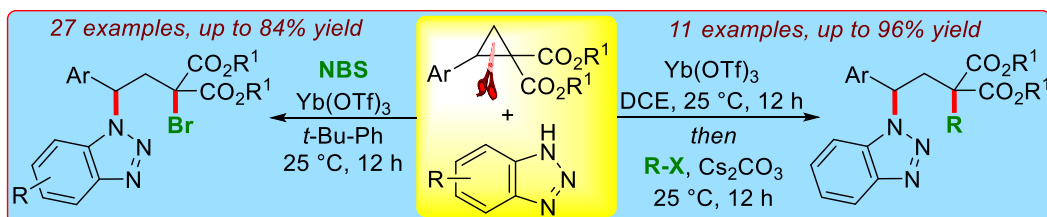
Benzotriazole-Triggered, Three-Component, Lewis Acid-Catalyzed Ring-Opening 1,3-Aminofunctionalization of Donor-Acceptor Cyclopropanes

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Functionalized cyclopropanes with donor and acceptor moieties at the vicinal positions, known as donor-acceptor (D-A) cyclopropanes are valuable three-carbon building blocks in organic synthesis.¹ Although the annulation reactions employing D-A cyclopropanes are well-explored, the 1,3-bisfunctionalization of D-A cyclopropanes are relatively less reported.² These types of reactions usually proceed either via multi-component coupling reactions, or by the insertion of a heteroatom-heteroatom bond to D-A cyclopropanes. In this context, the use of benzotriazoles as nucleophilic trigger in the three-component, Yb(OTf)₃-catalyzed ring-opening 1,3-aminofunctionalization of donor-acceptor (D-A) cyclopropanes is being presented.² Using N-bromo succinimide (NBS) as the third component, the reaction afforded the 1,3-aminobromination in up to 84% yield. Moreover, the use of alkyl halides or Michael acceptors as third components, the 3,1-carboamination products are formed in up to 96% yield in a one-pot operation. Employing Selectfluor as the electrophile furnished the 1,3-aminofluorination product in 61% yield. The reaction presented using enantiopure D-A cyclopropane suggested that the ring-opening is stereospecific and advances in an S_N2 fashion. Product functionalizations were carried out to demonstrate the synthetic utility of this present methodology.



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Enantioselective Cu(I)-Catalyzed Allylation of Anhydrides to Access α -Hydroxyketones

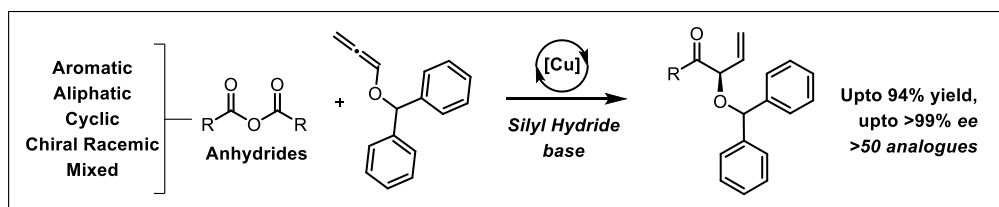
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Chiral α -hydroxyketones have always been of interest within the scientific community due to their use as chiral synthons, and high functionality to produce several complex molecules and natural products. Our group currently focuses on Cu-catalyzed enantioselective transformations to generate chiral highly-functionalized small molecules and natural products.^{1,2} Herein, Cu-catalyzed asymmetric allylation of anhydrides from allene-generated nucleophile³ has been described. This method has a broad substrate scope with several classes of anhydrides compatible with it providing α -hydroxyketones with high enantioselectivity and yields. This method also allows the Dynamic Kinetic Resolution (DKR) of α -substituted *rac*-anhydrides with excellent results.



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Enantioselective Amination of 3-Substituted-2-benzofuranones via Non-covalent N-Heterocyclic Carbene Catalysis

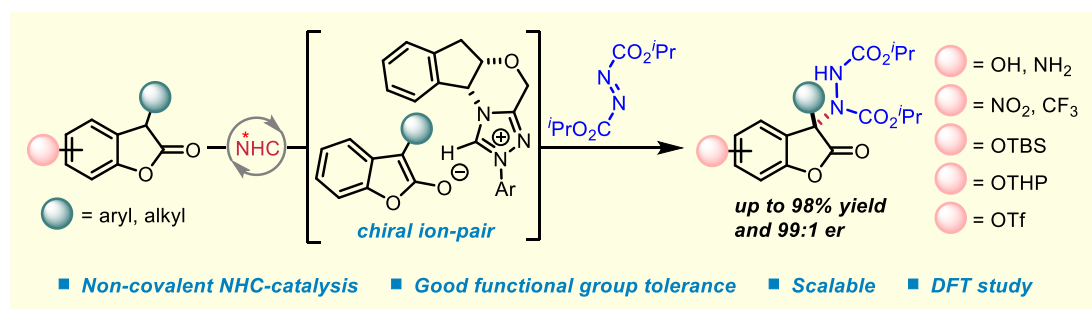
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Abstract: N-heterocyclic carbenes (NHCs) have received significant interest in asymmetric organocatalysis due to their ability to activate a wide range of substrates via both covalent and non-covalent interactions.¹ While, asymmetric NHC catalysis is mainly dominated by substrate/NHC covalent interaction, the interest in developing new asymmetric transformations with NHC, involving non-covalent interaction, is constantly rising.² In this line, we have recently developed an efficient catalytic method for the asymmetric α -amination of 2-benzofuranones with NHC involving non-covalent interaction with substrates. The process enables synthesis of enantioenriched 2-benzofuranones having amine substituted quaternary stereocenter, which constitutes the core of many important bioactive molecules.³ The reaction exhibits a board substrate scope. DFT calculations predict the origin of stereoselectivity of the product from a favoured diastereomeric transition state having 1.13 kcal/mol lower energy. In the poster, the development of the catalytic asymmetric amination reaction, substrate scope and reaction mechanism will be presented.

Scheme:



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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Development of Novel BINOL-Bipyridine Ligands for Remote Enantioselective Desymmetrization of Diarylacetic Acid Derived Amides *via* Iridium Catalyzed C–H Borylation

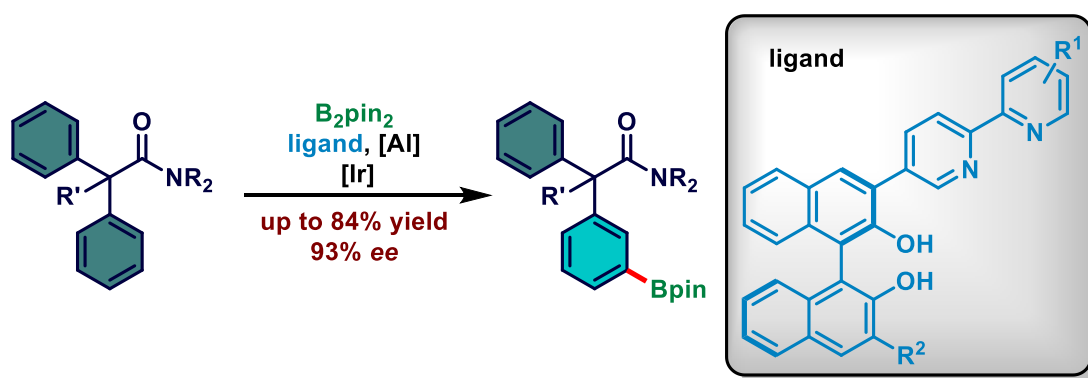
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Abstract

Despite the versatile abilities of 2,2'-bipyridines as ligands in metal catalyzed reactions, the enantioselective reactions utilizing them remains rare owing to their planar core structure. Traditionally, oxazoline-based N,N-bidentate ligands are being extensively used for enantioselective metal catalyzed reactions. However, these ligands are often unable to replicate the reactivities of 2,2'-bipyridine ligands due to their different electronic properties and bite angles. Herein, we report a novel strategy to perform desymmetrization of diphenyl acetic acid derived amides in an enantioselective and regioselective manner *via* remote C–H borylation using a 2,2'-bipyridine ligand having a chiral side-arm. The chiral side-arm, BINOL, holds a Lewis acid like aluminium and interacts with the Lewis basic substrate to control the reaction outcome. The strategy enables effective transfer of the chiral information overcoming the challenges of long-range asymmetric induction presumably due to closer proximity of the chiral part of the ligand and the prochiral center of the substrate. In principle, a wide class of geminal diaryl substrates can be desymmetrized or kinetically resolved using the developed ligands.



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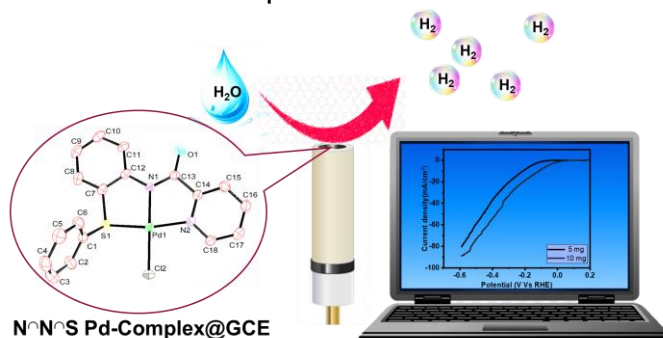
Palladium Complexes Derived From N²N²S Pincer ligands: An Efficient Electrocatalysts for Hydrogen Evolution Reaction

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The demand for sustainable and effective production methods using renewable resources is expanding along with interest in the hydrogen economy. Among the options, electrochemical hydrogen evolution reaction (HER) is regarded as an effective and sustainable method for producing green hydrogen gas from water through proton reduction.^[1] The development of alternative to Pt based electrocatalysts for the hydrogen evolution reaction (HER) is a pre-requisite for the generation of hydrogen, a feasible and cost-effective source of hydrogen.^[2] Among others, the development of palladium-based electrocatalysts is scarce probably due to surface damage during the adsorption of hydrogen, which makes the catalyst unstable and degradable. Viable strategies to overcome this issue is to use palladium organometallic/coordination complexes.

In this regard, herein we report the synthesis, characterization of pincer palladium (II) derived from N²N²S ligands and its application in the electrochemical hydrogen evolution reaction. The results are impressive which shows over potential around 120 mV. The detailed synthetic procedure and other electrochemical data will be presented.



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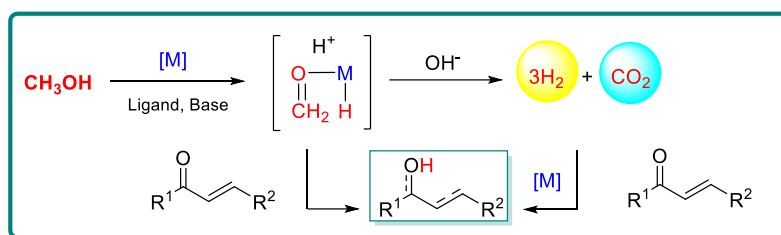
Ir^{III}-catalyzed Dehydrogenative Methanol Activation and its applications: A success towards Hydrogen Economy

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Liquid Organic Hydrogen Carriers (LOHC) are an attractive solution towards long-term hydrogen storage and straightforward transportation, unlike liquified hydrogen (high security requirements) and metal hydrides (packing limitations and limited reversibility).¹ Among various LOHCs, methanol has high hydrogen content (12.5% w/w) and provides abundant possibilities for hydrogen production. However, its endothermic dehydrogenation (63 kJ/mol) and the purification of the liberated hydrogen from the CO₂ and CO co-products are a concern.² The selection of a suitable transition-metal catalyst could help the development of a CO/CO₂-free hydrogen production at mild temperatures.² Transition metal-catalyzed hydrogen transfer reactions are viable practical alternatives to direct hydrogenation reactions as they avoid using special reactors, hazardous gas, *etc.* In this regard, we have recently reported the homogeneous Ir^{III}-bipyridonate-catalyzed chemoselective transfer hydrogenation of ketones and chalcones in the presence of catalytic amount of base using methanol under mild reaction conditions; including its application in late-stage functionalisation.³⁻⁴ Our more recent work has addressed the detailed mechanism of these reactions, including spectroscopic, kinetic and computational work. Notably, a pH-dependent reversible interconversion between two metal-hydride species is noticed.⁵



Scheme: Ir (III)-catalyzed transfer hydrogenation using methanol as LOHC.

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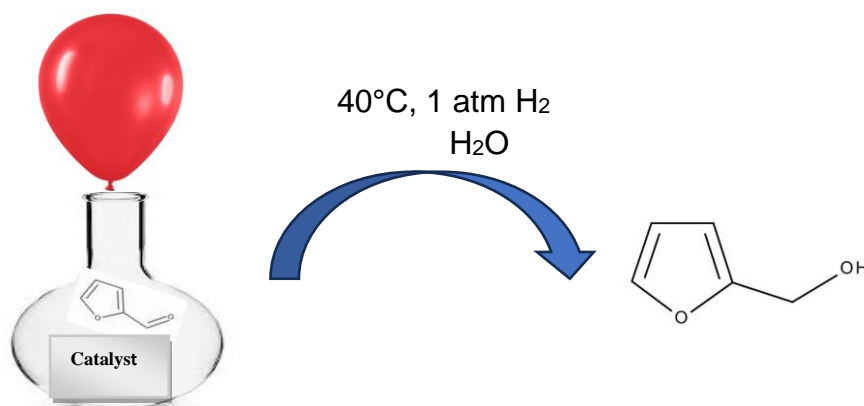
Aqueous phase highly selective hydrogenation of furfural to furfuryl alcohol at atmospheric pressure

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In order to diversify energy sources and the depletion of fossil fuel reserves, the use of biomass for its conversion into fuels and chemicals is growing in popularity. Furfural (FF), is a crucial platform molecule among different derived molecules from biomass. Furfural can be used to create a variety of value-added compounds and gasoline additives. Among the several compounds derived from Furfural, furfuryl alcohol (FA) is significant molecule. Although it is known that heterogeneous catalyst-based processes can produce FA from diluted solutions of FF, these processes often take place at high temperatures, high hydrogen pressures, and in the presence of organic solvents. The information about the selective hydrogenation of furfural in water as well as at atmospheric pressure is nearly completely absent from the literature. The majority of the studies on Cu-Zn-Al precursors have been concentrated on the production of methanol and water gas shift reaction only. In this work, we employ Pd supported Cu-Zn-Al catalyst with varying metal concentration to attain the highest furfuryl alcohol yield possible at 40 °C under 1 atmospheric H₂ pressure. The catalyst 4% Pd supported on Cu-Zn-Al exhibit at 40 °C and under 1 atm H₂ almost complete conversion of furfural and higher than 99% selectivity toward furfuryl alcohol after 15 hr of reaction. Additionally, effective catalyst recycling was seen during at least four runs with only a little activity loss without extra catalyst treatment or reactivation. We assume that, in the activation of the C=O group in furfural, the Cu sites take role. The performance of the catalyst is also influenced by the interaction of the active metal species with the support.



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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Palladium-Catalyzed Direct Aerobic Dehydrogenation of Acids and Amides

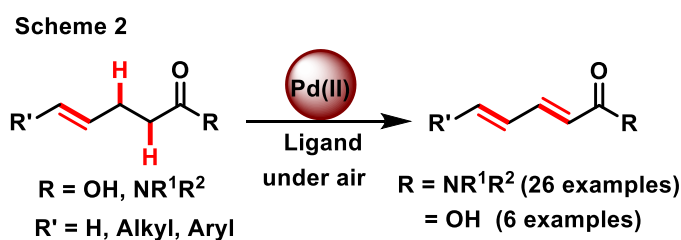
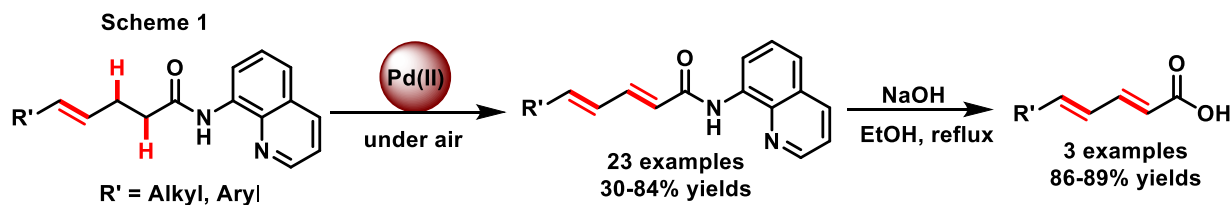
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α , β -Unsaturated carbonyl compounds are interesting structural moieties present in various pharmaceuticals and natural products and possess diverse reactivity.¹ The direct dehydrogenation of saturated carbonyl compounds is a convenient method to access this important class of molecules. Owing to the weak acidity of α -C H bonds to form metal-enolate intermediate, aerobic dehydrogenation of amides and acids is far more challenging.² In spite of significant advances in C H functionalization reactions in recent years, the dehydrogenation reactions has not been well explored.

Our continuous interest in developing new synthetic transformations prompted us to introduce a bis-chelating 8-aminoquinoline directing group for the selective dehydrogenation in the presence of a palladium catalyst (Scheme 1).^{3a} In continuation, we have further developed a direct and atom-economical approach towards aerobic dehydrogenation of the challenging amides and acids using palladium catalyst in the presence of ligand (Scheme 2).^{3b} The plausible reaction mechanism was proposed and supported by deuterium labelling study.



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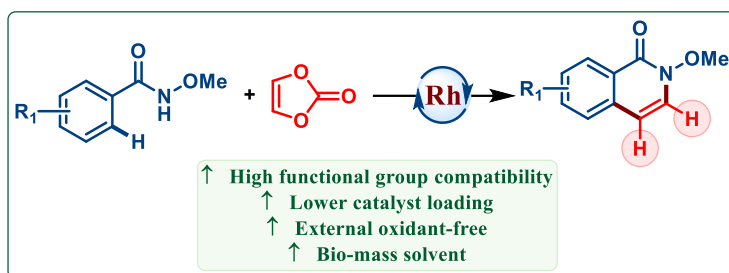
10-13 December 2023

Rhodium-Catalyzed C–H/N–H Activation and Annulation for the Synthesis of 3,4-Unsubstituted Isoquinolones

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Isoquinolones are important heterocyclic motifs often found in natural and bioactive compounds.¹ However, the existing methods are not suitable for accessing 3,4-unsubstituted isoquinolones. In this context, we have devised an efficient C–H activation²⁻⁴ approach to synthesize 3,4-unsubstituted isoquinolones from benzamides with vinylene carbonate. The reaction was conveniently achieved using versatile rhodium(III) catalyst [Cp*RhCl₂]₂ under mild reaction conditions. The C–H/N–H activation and annulation manifold proceeded with a broad substrate scope and high regioselectivities. Diversification of 3,4-unsubstituted has been demonstrated to access 3,4-unsubstituted isoquinolones and 4-substituted isoquinolones, complementing the existing methods. Based on the mechanistic studies, a plausible catalytic cycle was proposed.



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Weak Coordination Assisted Ru(II)-Catalyzed Annulation and Heck-Type Olefination of Arenes with Unactivated Olefins

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Arenes constitute the fundamental backbone in majority of the organic molecules including pharmaceuticals, clinical drug candidates, agrochemicals, and functional materials. Consequently, devising succinct protocols with minimal synthetic steps and byproducts for the functionalization of arenes has always been the key interest of organic chemistry research. In this realm, the common organic functional group-assisted bench-stable and less-expensive ruthenium-catalyzed catalyzed cross-dehydrogenative coupling (CDC) reactions strategy has emerged as a powerful synthetic manoeuvre.¹ However, breakthroughs of this strategy are largely confined to electronically activated olefins like acrylates, acrylonitrile, styrene, etc. and the progress to integrate electronically unbiased olefins for this purpose remains immature owing to poor reactivity and stereoselectivity issues. Considering this synthetic space, we have developed a Ru(II)-catalyzed oxidative cross-dehydrogenative Heck-type olefination of amides and ketones with unactivated olefins.² This regioselective reaction delivers alkenyl aromatics in high yields with exclusive *E*-selectivity, tolerates a large number of functional groups, and is also effective in the presence of steroid, commercial drug, and amino acid frameworks. The synthetic utilities were also highlighted through the downstream product diversifications leading to high-value 2,3-benzodiazepine, 1,2-diacetyl arenes, substituted anthracene, and 2,3-unsubstituted benzothiophene motifs.

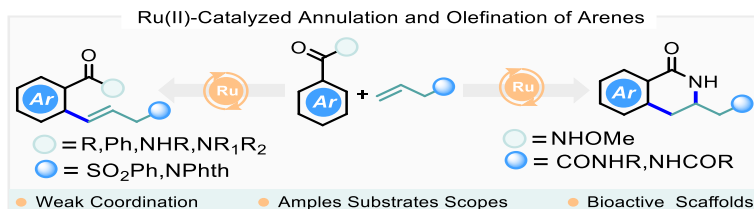


Fig 1. Ru(II)-Catalyzed Annulation and Olefination Of Arenes with Unactivated olefins.

Similarly, we developed a ruthenium-catalyzed (4+2) annulation reaction using aromatic hydroxamic acid esters as an oxidizing directing group and allylic amides as coupling partners, offering valuable aminomethyl isoquinolinones in good to excellent yields.³ This annulation is distinctive as allylic congeners typically result in allylation and not the annulation. Synthetic applications were demonstrated through the production of amino acid derivatives and late-stage derivatization of a steroid molecule.

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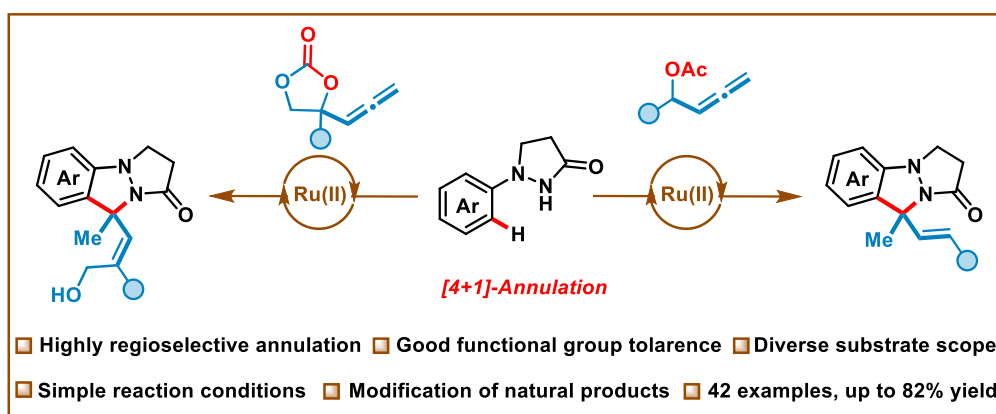
Ru(II)-Catalyzed Regioselective [4+1]-Annulation of 1-Aryl pyrazolidinones with Allenes: Access to Pyrazoloindazolones

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The TM-catalyzed regioselective annulations of allenes via C-H activation represent robust routes toward the construction of valuable cyclic/acyclic scaffolds. Considering the importance of allenes in the synthetic community herein we have developed unprecedented Ru(II)-catalyzed highly regioselective redox-neutral C-H bond activation/[4+1] annulation of 1-aryl pyrazolidinones with allenyl acetates to access pyrazoloindazolones. Additionally, allenyl cyclic carbonates have also been utilized to construct pyrazoloindazolones with a pendent alcoholic functionality. Remarkably, the bisfunctionalization has been achieved by simple modification in reaction conditions. The synthetic importance of this methodology was further achieved by late-stage modification of natural products, broad substrate scope, gram-scale synthesis, and post-functionalizations.



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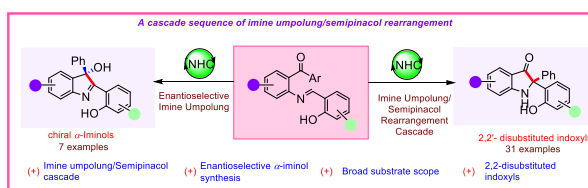
N-Heterocyclic Carbene-Catalyzed Aldimine Umpolung for the Synthesis of Indoxyls and Tetracyclic Indoles

Rohan Chandra Das, and Akkattu T. Biju*

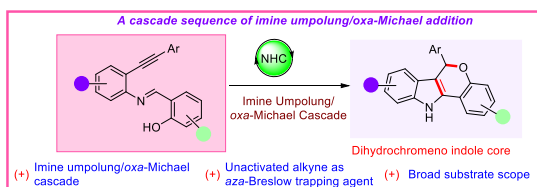
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N-Heterocyclic carbenes (NHC) are well known for polarity reversal of aldehydes and can lead to various unconventional disconnections, but NHC-catalyzed imine umpolung is underexplored.¹ In this context, and given our interest in the NHC-catalyzed umpolung of aldimines,² we have developed the NHC-catalyzed umpolung of aldimines for the synthesis of biologically important 2,2-disubstituted indoxyl derivatives.³ This NHC-catalyzed imine umpolung and semipinacol rearrangement cascade proceeds via the intermediacy of *aza*-Breslow intermediates. We have also demonstrated an enantioselective imine umpolung strategy for the synthesis of chiral α -iminol derivatives with excellent enantioselectivities. Intramolecular trapping of *aza*-Breslow intermediates by carbonyl electrophiles and broad substrate scope are the key highlights of this work.



Encouraged by this work and given the fact that there are no reports of trapping of *aza*-Breslow intermediates by unactivated alkyne electrophiles intramolecularly, we have developed the NHC-catalyzed imine umpolung and *oxa*-Michael cascade strategy for the synthesis of tetracyclic dihydrochromeno indole cores.³ The details of these works will be presented.



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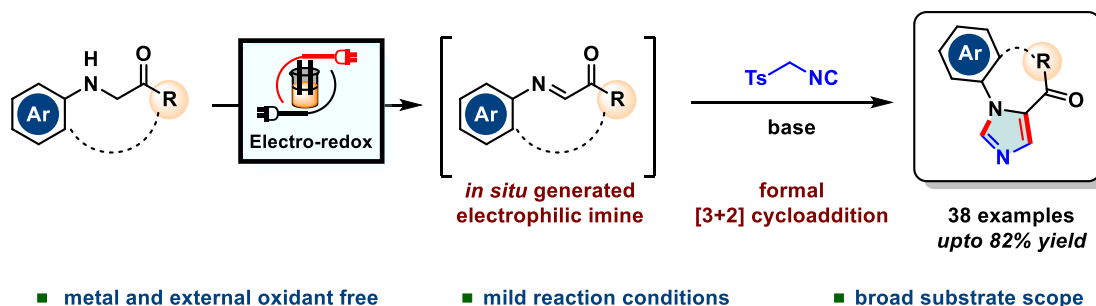
Electrochemical [3+2] Cycloaddition Between α -Amino Carbonyls and Tosmic, *en route* to Substituted Imidazoles

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Electrochemistry is one of the most versatile and environmentally benign platforms for redox-mediated transformations in organic synthesis.¹ This electro-synthetic strategy is now globally accepted as a smart alternative for stoichiometric redox reagents and successfully excludes chemical wastes and toxic byproducts. In addition, the selectivity and efficacy of the redox processes can be controlled by fine-tuning of the current flow and applied potential.² Herein, we unveil a metal and mediator free electrochemical [3+2] cycloaddition approach between α -amino carbonyls and tosylmethyl isocyanide fabricating substituted imidazole scaffolds.³ Mechanistic studies suggest electrochemical oxidation of secondary amines to their corresponding imines followed by consecutive C–C and C–N bond-forming events. A wide variety of different functionalities are well tolerated under this mild, robust, and scalable reaction condition contributing to a broad substrate scope and practical applicability of this developed methodology.



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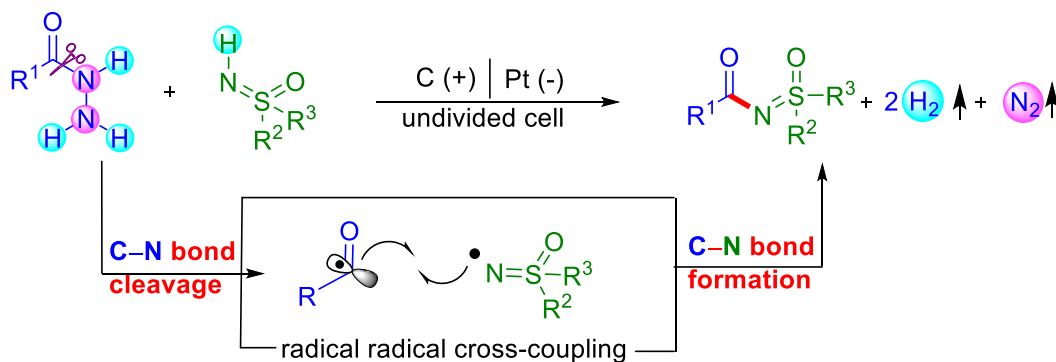
Electrochemical *N*-arylation of sulfoximine using benzoyl hydrazine as benzoyl source with H₂ generation

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Herein, we disclose a robust electrochemical cross-coupling of benzoyl hydrazine with sulfoximine through concomitant cleavage and formation of the C(sp²)-N bond. The protocol is sustainable, proceeds at room temperature, and avoids using toxic reagents. Mechanistic studies suggest that the reaction proceeds via the generation of acyl and sulfoximidoyl radicals by anodic oxidation under the constant current electrolysis (CCE), affording sulfoximination product. In addition, the present methodology is mild, high functional group tolerance, with broad substrate scope. The reaction is applied to late-stage diversification of complex molecular architectures, including derivatives of marketed drugs such as probenecid, L-menthol, (-) borneol, ibuprofen, flurbiprofen, D-glucose, vitamin E, ciprofibrate, sulindac, and peptide. More importantly, nitrogen and hydrogen gas would be produced as the only by-products, which can be used as a clean energy source.



- metal and exogenous oxidant-free
- H₂ and N₂ as by-product
- concomitant cleavage and formation of C-N bond
- wide substrate compatibility
- late-stage functionalization
- details mechanistic study

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Development of trimetallic catalyst for CO₂ valorization

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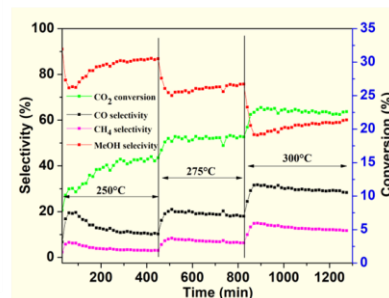
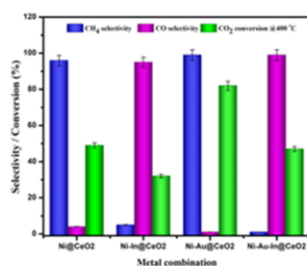
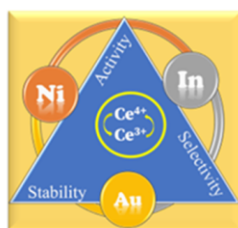
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CO₂ hydrogenation to CO is thermodynamically favored at higher temperatures but the catalyst deactivates due to the sintering of metal nanoparticles. In our work, we have developed a trimetallic catalyst that can tune selectivity from methane to CO with high CO selectivity at lower temperatures (200-400 °C) and ambient pressure conditions with very good rate. Further, we demonstrate that the same catalyst can convert CO₂ to methanol at high pressures with excellent space time yield (STY).



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π -Coordination over *O*-coordination: Reversal in reactivity of cyclopropenones

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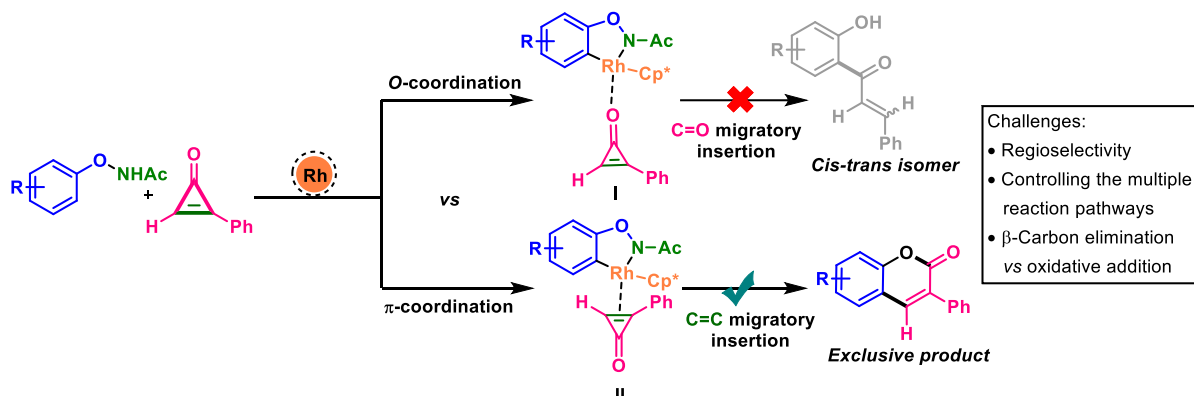
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Herein, we have disclosed the reversal in reactivity of cyclopropenone, where the selective π -coordination mode of cyclopropenone operates to deliver the 3-phenyl coumarin derivatives. Cyclopropenone exhibits its aromaticity primarily because of its 2π electron, resulting in the concentration of negative charge predominantly on the oxygen atom, facilitating its coordination with the metal. Herein, the π -coordination mode is dominant over the *O*-coordination mode, which has been proven by mechanistic studies. Moreover, the key intermediate involved has been established by high-resolution mass spectrometry (HRMS).

Dominance of π -coordination in the synthesis of 3-phenyl coumarin (our work)



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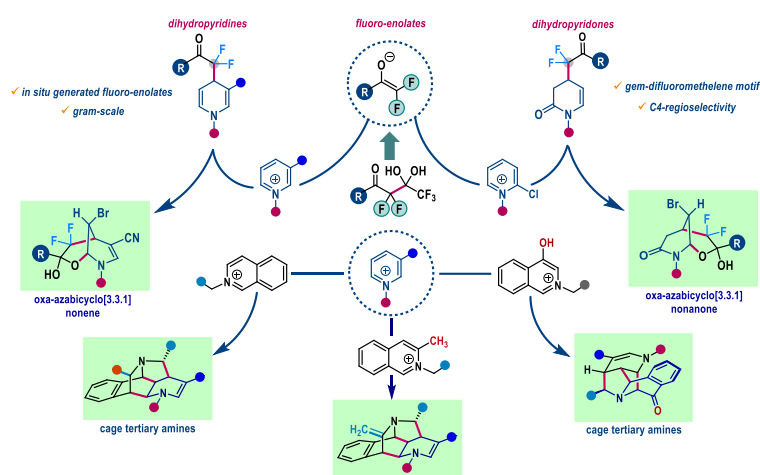
Divergent Reactivity of *N*-activated Pyridines towards Fluorine-Rich Molecules and Caged Tertiary Amines

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Nitrogen heterocycles are ready-stock molecules that serve as pivotal building blocks in organic synthesis. In this realm, major advancements have been realized in the form of substitution reactions without disrupting the aromatic character of these molecules. However, situation becomes increasingly challenging when functionalization of these heterocycles necessitates the dearomatization strategy useful to transform planner 2D framework to complex 3D scaffolds. Further, owing to the presence of more than one electrophilic centre, attempts are typically leads to regio-isomeric products with poor synthetic utility. We have addressed these challenges through the careful activation of pyridines and isoquinolines by converting them to respective azolium salts. We have accomplished the synthesis of high-value *gem*-difluoro substituted dihydropyridines and pyridones by exploiting fluoro-enolate chemistry. The concept is also upgraded by proper designing which allows the assembly of isoquinolinium salts with pyridinium salts, offering cage tertiary amines framework in a high yield with excellent diastereoselectivity. Notably, such complex frameworks are represented by many natural products with promising bio-activities, albeit their succinct synthetic strategy is currently limited. Our finding provides the pivotal stepping stone for future developments.



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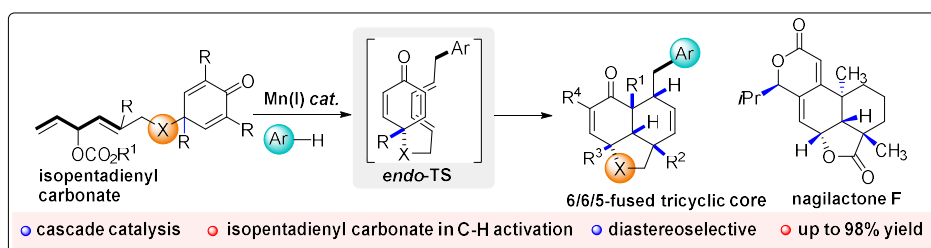
Robust Synthesis of Terpenoid Scaffolds under Mn(I)-Catalysis

Athira Parammal,[‡] Shubham Singh,[‡] Manoj Kumar, Joe Sam Xavier and Parthasarathi Subramanian*

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The 6/6/5-fused tricyclic scaffold is a central feature of structurally complex terpenoid natural products. A step economical cascade transformation that leads to a complex molecular skeleton is regarded as a sustainable methodology. Therefore, we reported the first Mn(I)-catalyzed C(*sp*²)-H chemoselective in situ dienylation and diastereoselective intramolecular Diels-Alder reaction using *iso*-pentadienyl carbonate to access 6/6/5-fused tricyclic scaffolds. The broad substrate scope of this method demonstrates a wide range of functional group tolerances with a high-yielding synthesis of nagilactone-type1 6/6/5-fused tricyclic core with a THF ring and endiandric acid A-type2 6/6/5-fused carbo-tricyclic core natural products. The main attractions of our methodology include: (i) no prior reports using *iso*-pentadienyl carbonate as a reactant in C-H activation catalysis, (ii) a favorable conditions to be established for achieving regio-, stereo-, and chemo-selective arylmanganese(I) insertion on terminal olefin of tetra-olefin containing substrate to obtain 1,3-dienes, and (iii) final product, homo-aryl 6/6/5-fused tricyclic scaffold contains five contiguous chiral centers, including an epimerizable α -center at the ring junction. Further, extensive mechanistic studies, including isolation of catalytically active organo-manganese(I) complex, 1,3-dienyl-intermediates, and isotopic labeling experiments, have supported the proposed mechanisms of both methodologies. Moreover, the late-stage diversification of these products led to several valuable new transformations.



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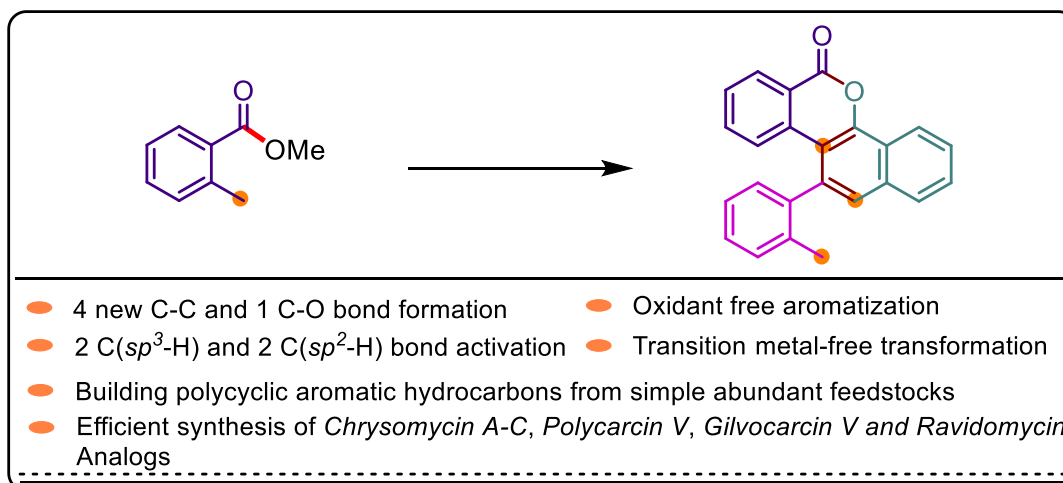
APEX-LAC (Annulative π -Extension Lactonization) of Methyl Arenes

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Here we report, the term APEX-LAC (Annulative π -Extension Lactonization) a new terminology in stitching molecules at room temperature. APEX (Annulative π -Extension) is a burgeoning methodology in synthesizing new polycyclic aromatic hydrocarbons incorporated with heteroatom.¹ On the other hand, lactonization of acids and introduction of lactone skeleton into arenes is a challenging task for chemists to produce biologically important lactones.² Along the line, drugs like *Chrysomycin A-C*, *Polycarcin V*, *Gilvocarcin V* and *Ravidomycin* bearing lactone with two-three annulated rings find to be potent drugs for the treatment of Tuberculosis. Among them *Chrysomycin A* is a rare C-aryl glycoside first discovered over 60 years ago and obtained in low yields from fermentation of *Streptomyces*.³ In addition, the available synthetic route to these drugs were over 10 steps till date.⁴ Here we developed a single step synthesis of *Chrysomycin A-C*, *Polycarcin V*, *Gilvocarcin V* and *Ravidomycin* analogs bearing 90% similarity by functionalizing γ - sp^3 C-H bond of methyl arenes (petrochemical feedstock) by the use of regenerative cyclisation strategy.



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Synthesis of Efficient Co-initiator via Base Catalysed Sequential Conjugate Addition Reaction: Application in Photoinduced Radical Polymerisation

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Abstract: Photochemistry is becoming an essential tool both in academia and industry due to its operational simplicity, environmentally friendly and economically sustainable nature in comparison to its thermochemistry.^[1] Particular scientific community are attracted towards photoinduced radical polymerisation (PRP) reaction due to its various applications in the areas of dental restoration process, tissue engineering, artificial bone generation and 3D-Printing.^[2] Herein we report the design and synthesis of a new efficient co-initiator for type-II photoinitiator promoted PRP reaction via barrierless sequential conjugate addition reaction.

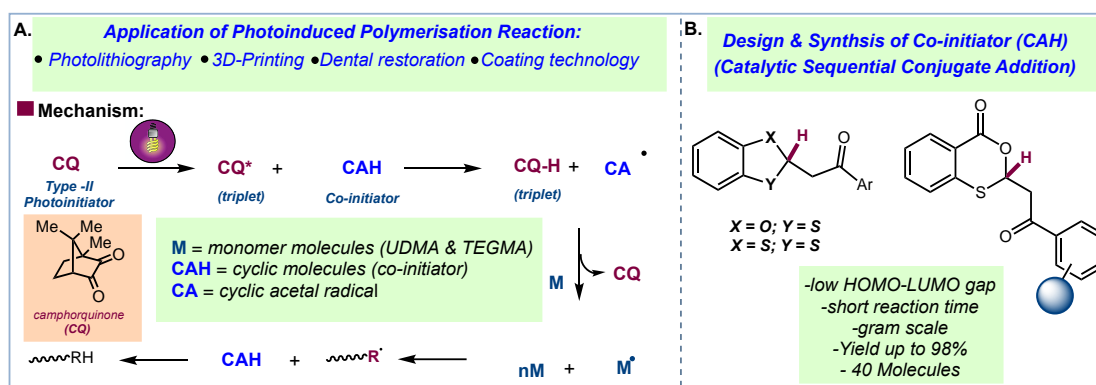


Figure: A. Application & mechanism of PRP reaction; B. Newly designed co-initiator.

Newly synthesised 1,2-benzenedithiol (DTH) based co-initiator promoted polymerisation of diurethane dimethacrylate (UDMA, 70%) and triethylene glycol dimethacrylate (TEGDMA, 30%) in presence of 450 nm LED (15 W) under the aerobic conditions turned out to be very efficient (38 seconds) and the resultant polymeric material has excellent physical properties.^[3]

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Solar-driven bio-refinery and fuels: Concepts for Sustainability

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Expeditious fossil fuel consumption by modern society setting up a deep concern for the global energy crisis in the near future. Extensive mining and burning of non-renewable sources (fossil fuels) apparently pile up the carbon dioxide (CO₂) level into the atmosphere which is an alarming call for global warming and has an adverse impact on the environment. Therefore, it is urgent to mitigate the anthropogenic emission of CO₂ in the atmosphere and to hunt for alternative renewable fuels to fossil fuels. Asserting the production of hydrogen (H₂) fuel via proton reduction and CO₂ reduction to high-value CO (viably utilized in the Fischer-Tropsch process) via renewable solar light assistance provides an exceptional platform to solve the energy-crisis impact globally.

However, the above-mentioned half-reduction reactions are hampered by thermodynamically and kinetically sluggish H₂O oxidation half-reactions. Replacing the H₂O oxidation half-reaction by organic transformation is quite meaningful and makes use of photo-excited holes for purposeful oxidation processes. In that sense, the oxidation of abundant biomass-based organic fractions to value-added chemicals in synergy with the proton reduction to H₂ and CO₂ reduction to CO under solar irradiation could be a green and sustainable route to boost the bio-chemical economy. Therefore, herein, we focus on solar-driven production of fuels (H₂ and CO) and oxidation of biomass-based precursors to high-value-added fine chemicals by using mesoporous carbon nitride-based photocatalytic systems. This offers a most fascinating process that features in effective utilization of photogenerated electrons and holes to meet the criteria of sustainability and chemical economy, overwhelmingly.

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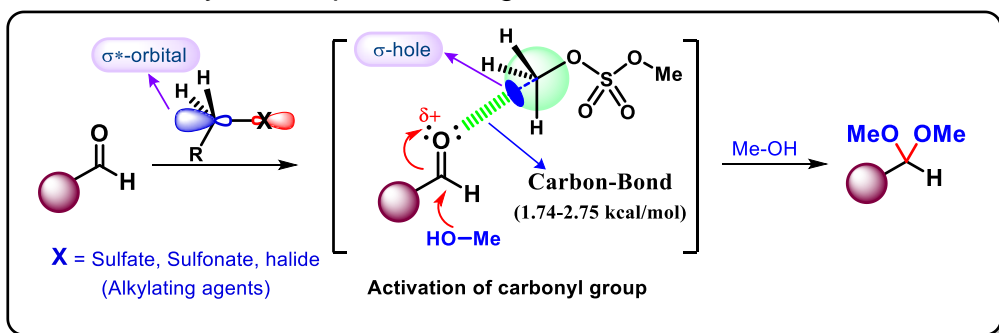
Carbon Bond Catalysis: Dialkyl Sulfates, Alkyl Sulfonates and Alkyl Halides as Catalysts in Acetal Forming and Related Reactions

Tanmay Sarkar, Reyno R. S., Keerthana S., Goreti Rajendar*

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This study demonstrates a previously unexplored facet of carbon electrophiles (or alkylating agents): their potential for catalytic applications involving noncovalent carbon bond interactions. Role of NCIs by carbon electrophiles (having polar Csp³-X bonds) in stabilizing conformations of small molecules and biomolecules has recently been discovered, nonetheless, their catalytic behavior in small molecule activation has never been observed. As the “X” becomes good leaving group carbon electrophiles convert strong alkylating agents, and they develop a positive potential (σ -hole) on carbon atom. Conversely, small atomic size and steric crowding by four groups around the carbon make it difficult to have strong σ -hole interactions with nucleophilic acceptors. This peculiar behavior of alkyl electrophiles has kept chemists away from thinking about their catalytic potential in chemical transformations. For the first time, we showed that alkyl electrophiles operate as Lewis acid catalysts in carbonyl activation towards acetal forming and related reactions through NCIs. Our experimental and theoretical investigations supported the novel catalytic implications of alkyl electrophiles through carbon bond interactions.



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Solar Light Induced Chemical Bond Activation: Utilizing Hot Electrons of Plasmonic Black Gold-Nickel

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Localized surface plasmon resonance (LSPR) enables challenging reactions to be catalyzed by generating highly energetic charge carriers on nanoparticle surfaces, leading to the emergence of novel reaction pathways.^{1,2} In this work, using dendritic fibrous nanosilica (DFNS)³ based black gold,⁴ we have synthesized nickel-laden black gold (black gold-Ni).^{5,6} The photocatalytic CO₂ hydrogenation activities of black gold-Ni increased dramatically to the extent that measurable photoactivity was only observed with the black gold-Ni catalyst, with a very high photocatalytic CO production rate (2464 ± 40 mmol g_{Ni}⁻¹ h⁻¹) and 95% selectivity. The catalyst was stable for at least 100 h. Photocatalytic reaction rates on excited black gold-Ni showed a superlinear power law dependence on the light intensity, with a power law exponent of 5.6. Photocatalytic quantum efficiencies increased with an increase in light intensity and reaction temperature, which indicated the hot-electron-mediated mechanism. The kinetic isotope effect (KIE) in light (1.91) was higher than that in the dark (~1), which further indicated the electron-driven plasmonic CO₂ hydrogenation. Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) showed that CO₂ hydrogenation took place by a direct dissociation path via linearly bonded Ni–CO intermediates.⁵ Black gold-Ni also demonstrated excellent activity in other reactions such as hydrodechlorination of dichloromethane and hydrogenations of propene and acetylene.⁶ The outstanding catalytic performance of black gold-Ni may provide a way to develop plasmonic catalysts for CO₂ reduction and other catalytic processes using black gold.

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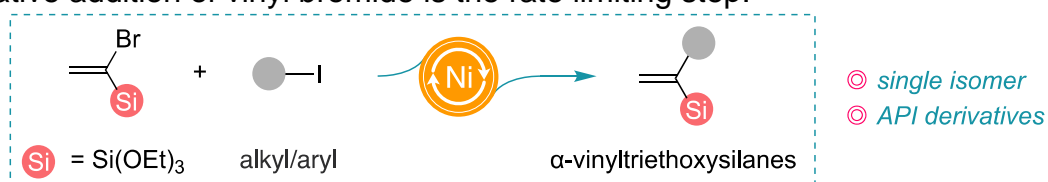
Synthesis of α -Vinyltrialkoxysilanes via Nickel Mediated Cross-Electrophile Coupling Reactions

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Unsaturated organosilanes are of important class of reagents utilized in organic synthesis, silicone industry and as π -acceptor ligands. In particular, they serve as nucleophiles in cross-coupling reactions. Hydrosilylation of alkynes is a highly atom-economical process that efficiently yields unsaturated organosilanes; yet the reaction can produce three distinct isomers, namely β -E, β -Z, and α -isomers, the synthesis of α -isomer as primary product is relatively challenging. Cross electrophile coupling reactions on the other hand are particularly desirable since they do not require the use of highly reactive organometallic reagents, particularly cross $C(sp^2)$ - $C(sp^2)$ coupling of two halides is challenging to achieve due to undesirable homo-coupling reactions. For the first time, we report the synthesis of α -vinyltrialkoxysilanes via cross-electrophile $C(sp^2)$ - $C(sp^2)$ coupling between bromoalkenes and aryl iodides. The scope was extended to alkyl iodides, benzyl bromides with broader functional group tolerance and API derivatives. The gram-scale synthesis of most substrates is impressive. The intermediacy vinyl-iodide and radical escape rebound path are supported by mechanistic studies. Kinetic analysis of the reaction was performed using variable-time normalization analysis (VTNA) developed by Burés and we found that oxidative addition of vinyl bromide is the rate limiting step.



⊙ gram-scale synthesis of preponderance substrates ⊙ radical transcend rebound
⊙ challenging cross $C(sp^2)$ - $C(sp^2)$ electrophile coupling ⊙ vinyl iodide intermediate

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A facile green synthesis-based study of tri-carboxylate-based metal-organic frameworks: Adsorption and selectivity aspects

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A significant drawback of conventional MOF synthesis is using toxic organic solvents to solubilize various organic linkers and to grow the MOF framework. Such an approach requires longer MOF growth time and it also consumes energy¹. In this work, we report the synthesis of Fe, Cu- based metal-organic frameworks using benzene tri-carboxylate (BTC) as a linker via a facile route under environment-friendly conditions without requiring any toxic solvent and temperature. Water has been used as a solvent and NaOH has been used as a stoichiometric deprotonating agent for the aromatic carboxylic acid groups in the linker to facilitate linker solubility and interaction with metal ions². The synthesized MOFs were characterized by BET, PXRD, SEM, TGA, and FTIR, and isotherms were measured for different gases (N₂, propylene, propane). The Ideal Adsorbed Solution Theory (IAST) is used to predict binary selectivity from single-component isotherm data. The selectivity of the prepared Fe-BTC in an aqueous medium was five times higher than the conventional MIL-100-Fe for the propylene/nitrogen separations and the selectivity of the prepared Cu-BTC was 45% higher than the conventional Cu-BTC for propylene/propane separation.

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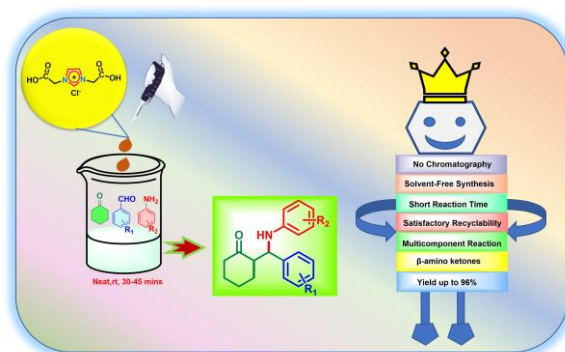
[BCMIM][Cl] Ionic Liquid Catalyzed Diastereoselective Synthesis of β -Amino Ketones via Facile, One-pot, Multicomponent Mannich Reaction under Solvent-Free Condition

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In this work, by utilizing 6 mol% of 1,3-bis(carboxymethyl)imidazolium chloride [BCMIM][Cl] ionic liquid as a catalyst, a highly effective diastereoselective one-pot multicomponent Mannich reaction has been established. The three components, namely, cyclohexanone, substituted aromatic aldehydes, and substituted aromatic amines, underwent the Mannich reaction efficiently under the solvent-free condition at room temperature in the presence of 6 mole % [BCMIM][Cl] catalyst to afford the desired β -amino ketones. Excellent diastereoselectivity, rapid reaction times, high yields, and no purification by column chromatography are the key characteristics of these processes. Moreover, the catalytic activity of the [BCMIM][Cl] ionic liquid catalyst was maintained after being reprocessed and used three times.



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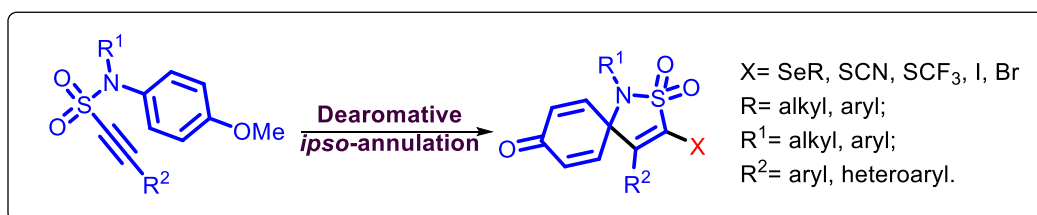
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Dearomative *ipso*- Annulation of Aryl Alkynyl Sulfonamides towards Unique Spirocyclic sultams

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Abstract: Spirocyclic compounds having thio/halo-functionalized bond are found in many bioactive molecules.¹ Hence, the development of new methods for the synthesis of various spirocycles² is always an attractive target for synthetic organic chemists.² We have established a simple and novel synthetic strategy involving oxidative dearomatization/*ipso*-annulation of aryl alkynyl sulfonamides to afford uniquely functionalized spirocyclic sultams.³ The detailed results⁴ will be presented in the poster.



Keywords: *ipso*-annulation, Spirocyclic sultam.

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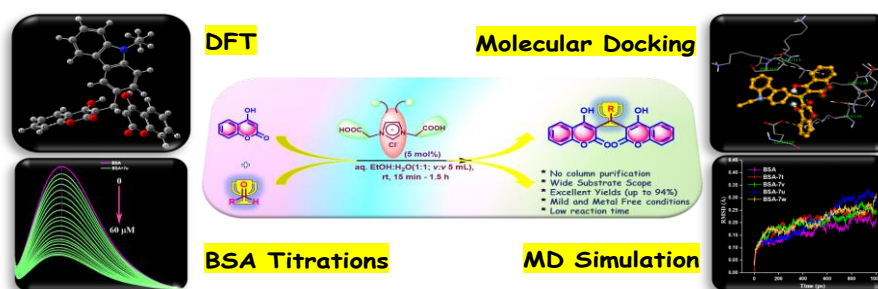
Facile synthesis of bis-coumarins using [BCMIM][Cl] zwitter ionic liquid and their binding with bovine serum albumin

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Herein, we report a synthetic pathway for synthesizing bis-coumarins using 5 mol% [BCMIM][Cl] ionic liquid via the facile, one-pot, metal-free synthesis in aqueous ethanol at room temperature. A series of 24 derivatives were furnished in up to 94% yields in 15 min to 1.5 h and were characterized using different spectroscopic techniques. The photophysical properties of bis-coumarin derivatives were explored through UV-Visible and fluorescence spectroscopy. The absorption and emission spectra demonstrate a peak wavelength (λ_{max}), within the range of 297–311 nm and 486–505 nm, respectively. An analogous pattern to the experimental results is seen in density functional calculations. The binding affinities of all the synthesized derivatives with Bovine Serum Albumin (BSA) were determined using AutoDock Vina which exhibited a range from -8.4 to -11.5 kcal mol⁻¹. The computed binding constant (K_{BSA}) by tryptophan (Trp) emission quenching values illustrate strong binding interactions of the selected ligands in the order of 10⁴. The calculated binding affinities were validated by performing molecular dynamics simulations of the best docking pose using GROMACS software over a period of 1 ns for studying the stability of protein-ligand complexes.



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Triphenylamine and Terpyridine–Zinc (II) Complex Based Donor–Acceptor Soft Hybrid as a Visible Light-Driven Hydrogen Evolution Photocatalyst.

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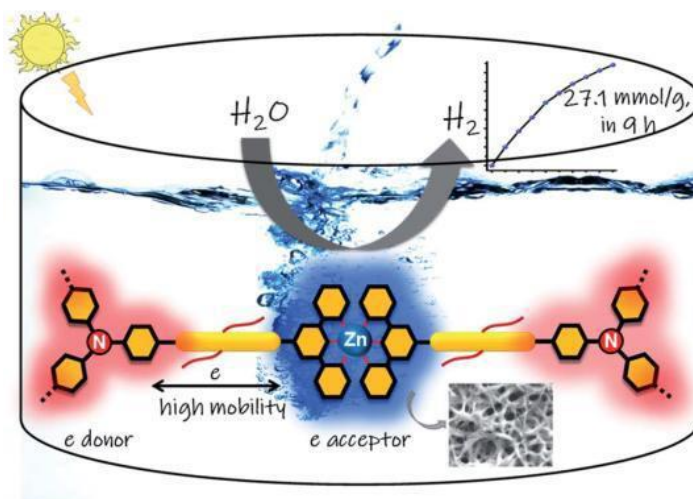
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A donor–acceptor coordination polymer (TPA-Zn) was synthesized by Zn(II)-assisted self-assembly of an in situ generated triphenylamine (TPA) cored terpyridine ligand. The polymer absorbs a broad- spectrum of light and exhibits visible light-assisted hydrogen generation (27.1 mmol g^{-1} over 9 h) from water with 2.9% quantum efficiency at 400 nm. The microscopy images show a mesoscale fibrous morphology and the Brunauer–Emmett–Teller (BET) analysis reveals the porous nature of TPA-Zn (surface area: $234.5 \text{ m}^2\text{g}^{-1}$; $d = 6.98 \text{ nm}$), both of which are helpful for substrate diffusion during catalysis



Scheme: Schematic representation of the present work showing visible light-induced dihydrogen production by the mesoscale coordination polymer TPA-Zn.

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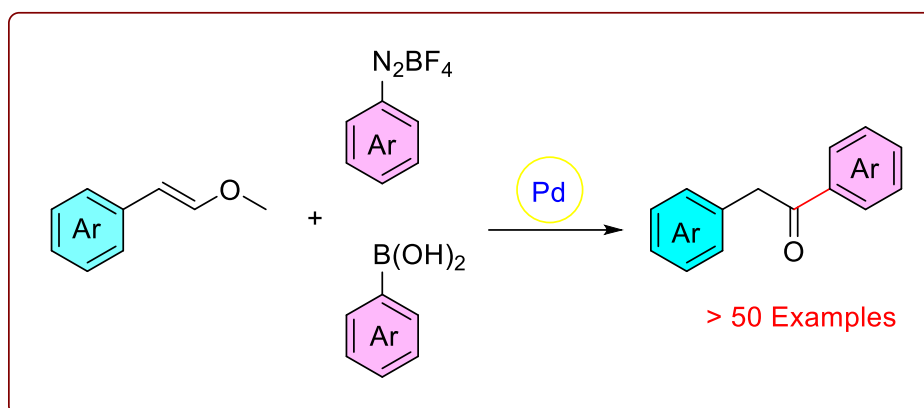
Palladium-catalyzed synthesis of α -aryl acetophenones from styryl ethers, aryldiazonium salts and arylboronic acids under mild conditions

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α -Aryl acetophenones are important precursors in organic synthesis, and they have been used in the preparation of various bioactive molecules, heterocycles (e.g., indoles, isoxazoles and pyrazoles) and natural products.¹⁻² Moreover, α -aryl acetophenones are the structural motifs of some drugs and bioactive molecules.³⁻⁴ In this context, here we report the palladium-catalyzed synthesis of α -aryl acetophenones from styryl ethers, aryldiazonium salts and arylboronic acids via Heck and Suzuki coupling reactions. The developed method is highly attractive in terms of reaction conditions, substrate scope, functional group tolerance and yields. Synthetic applications of the present method are demonstrated by preparing α -aryl indoles and 3-aryl isocoumarin from styryl ethers.⁵



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Indo-French Seminar on Catalysis for Sustainability

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Nitrogen-Atom Transfer Enables (5 + 1) Annulation Reaction to Access Aminoisoquinolines

Gayyur,[†] Shivani Choudhary,[‡] Ruchir Kant[‡] and Nayan Ghosh^{†*}

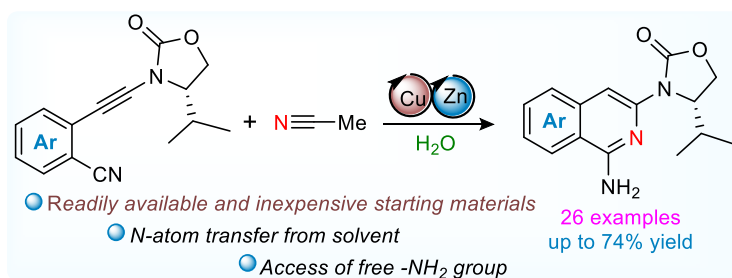
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Isoquinolines are the core structure of many natural products, biologically active molecules and functional materials. So, we have developed a catalytic synthetic transformation offering a series of $-NH_2$ group bearing 1-aminoisoquinoline with moderate to good yields. This (5+1) annulation reaction shows broad substrate variation. Prominently, acetonitrile act as a solvent and reactant in this reaction. Furthermore, the derivatization of isoquinoline core via functional group interconversions has been carried out successfully. The gram-scale synthesis of 1-aminoisoquinoline proves the practicality of this protocol.



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Iron-Catalysed Highly Selective Hydroalkoxycarbonylation of Alkynes Using CO as a C1 Source

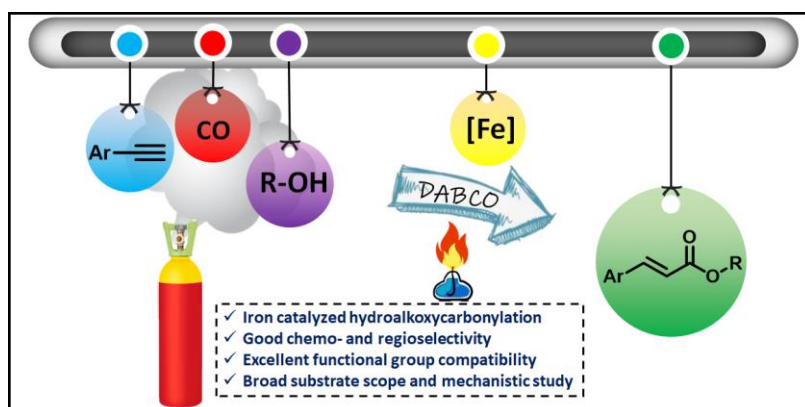
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Late-transition metals have been extensively used in metal-catalysed transformations.¹ But late-transition metals are rare, precious and costly. On the contrary, base metals are cheap, and available abundantly. Their practical utilization in carbonylation reactions is rarely explored.² Here, we report iron-catalyzed hydroalkoxycarbonylation of alkynes to α , β -unsaturated esters in one pot.³ Readily available iron precursor $[\text{Fe}_2(\text{CO})_9]$ in the presence of a diimine ligand catalyzes the conversion of alkynes to α , β -unsaturated esters under 10 bar CO pressure. This operationally simple protocol tolerates various functional groups and allows facile access to about 40 α , β -unsaturated esters. The kinetic study suggests that the reaction shows positive rate order with respect to the iron catalyst. Mechanistic investigations indicated the existence of $[\text{Fe-H}]$ intermediate, and control experiments suggest the absence of any radical species.



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Rh-Catalyzed Cascade Cyclization of Dienal Diazo Esters and Enamino Ketones: Construction of 9,9a-Dihydropyrano[2,3-b]azepines

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The first diazocarbonyl compound was reported by Curtius in 1883 where they synthesized ethyl diazoacetate by diazotization of simple glycine. Designing a bench stable synthetically important diazoenal compounds are more challenging. Nowadays researchers are excited towards this emerging field for synthesizing novel diazoenal compounds having a potential synthetic application. We developed a unique class of diazo dienal compounds, installed with both dienal and diazo functionalities. The reported system involve Rh-catalyzed cascade cyclization with enamino ketone for the construction of 9,9a-dihydropyrano[2,3-b]azepine. The reaction includes N-H insertion into dienalcarbenoid, intramolecular Michael addition, and ring-rearrangement. However, both pyran and azepine systems have wide range of biological applications but we are keen to study their simultaneous effect on biological applications. Hence, in this poster I will be focusing on their novel synthetic methodology.

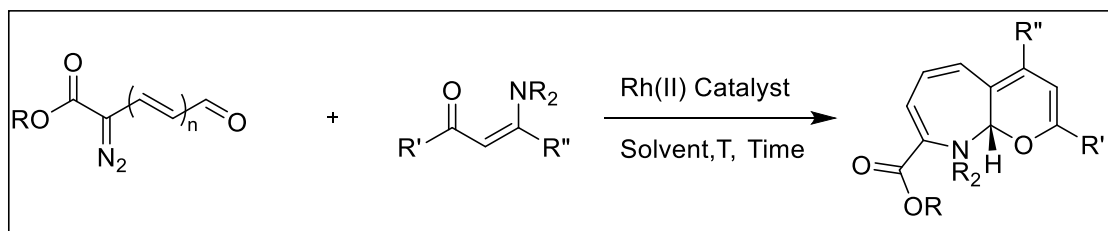


Figure: General synthesis of 9,9a-dihydropyrano[2,3-b]azepine

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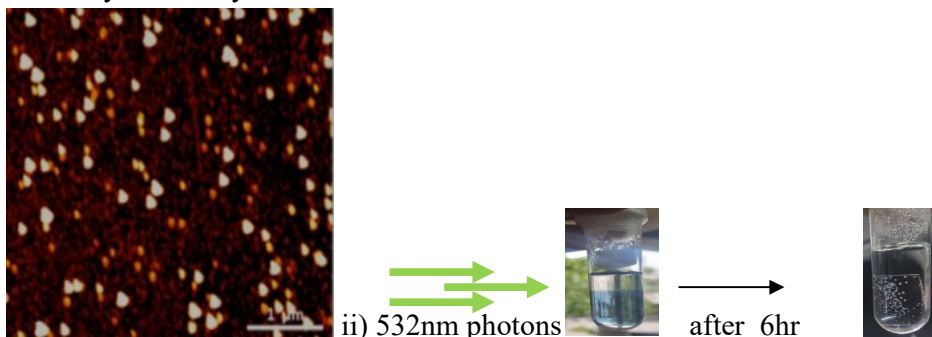
10-13 December 2023

Plasmon-enhanced ligand mediated photocatalytic D-glucose oxidation

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Abstract: Plasmonic nanostructures are identified as a good candidate to drive direct photocatalysis utilizing visible-NIR photons due to their superb light absorbance capability and the hot carrier generation. However, due to the fast recombination of hot carriers, the plasmonic nanostructures suffer in chemical reactivity. Here, we have shown the photocatalytic glucose oxidation using the plasmonic gold triangular nanostructures (AuTP) functionalized with various p-substituted benzene thiol ligands. The catalytic activity of the glucose oxidation. Here, we have found that the p-substitute group present on the ligand plays a critical role in photocatalytic efficiency. The hot carriers efficiently channel through the ligand and enhance the charge separation, resulting in improved photocatalysis. The photocatalytic glucose oxidation under 532 nm laser excitation results in the organic acid and produces H₂, CO, and CO₂. The catalytic activity of the substrates is quantified with the amount of glucose converted into CO and CO₂ through complete degradation. It was found that photocatalytic glucose oxidation is enhanced by several factors when the AuTP is functionalized with the NO₂-substituted benzenethiol compared to bare AuTP and other substitutes such as Br and OH the attachment of appropriate ligand will enhance the catalytic activity.



i) Is AFM image of AuTP on glass surface ii) Is Schematic representation of photocatalysis under 532nm LASER FOR 6hrs .

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Coupling of M_3 -POM supported on CuNi-SAD/g- C_3N_4 for overall water splitting

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Abstract Texts

Single metal atom photocatalyst has become a widespread catalyst in photochemical and electrochemical application because of its rational use and maximum atomic efficiency. Nitrogen enriched graphitic carbon nitride have been widely used to anchor single metal atom. However, further modification and utilization of single metal catalyst is limited due to its simplicity. Bimetallic single metal atom dimer (SAD) structure can reform the electronic structure of single metal atom with additional synergistic interaction enhancing the catalytic activity compared to single metal atom. The first principle investigation indicates that interaction between single metal atom dimer up-shifts the d-band center, facilitates the water dissociation and H^+ -adsorption which accelerates hydrogen evolution reaction. Herein, we have developed composite of CuNi-SAD on g- C_3N_4 and M_3 -POM (M: Cu, Ni, Co; POM: $Na_9[\alpha-SbW_9O_{33}].19H_2O$). The single metal atom dimer co-ordinated with nitrogen atom on g- C_3N_4 exhibit hydrogen evolution and oxygen evolution reaction occurs on M_3 -POM. The formation of SAD was confirmed by HAADF and EXAFS analysis and the Co-ordination chemistry of SAD was confirmed by XANES analysis. The obtained CuNi-SAD/g- C_3N_4 / M_3 POM exhibited excellent activity and stability for overall water-splitting both in photocatalytic and electro-catalytic reaction. This work paves the way to design single metal dimer based catalyst for remarkable activity and stability.

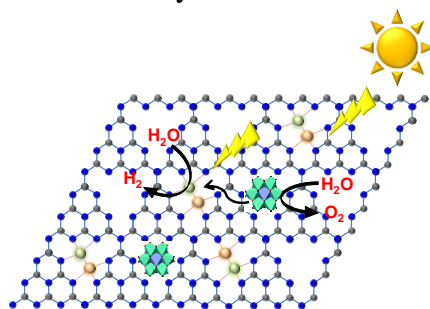


Figure. Proposed mechanism of photocatalytic water splitting reaction.

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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Asymmetric Ru/Cinchonine Dual Catalysis for the One-Pot Synthesis of Optically Active Phthalides from Benzoic Acids and Acrylates

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I'll be presenting, the asymmetric Ru/cinchonine dual catalysis that provides straightforward access to enantioselective synthesis of C-3 substituted phthalides via tandem C–H activation/Michael addition cascade. The use of readily accessible and less expensive $[\text{RuCl}_2(\text{p-cym})]_2$ and cinchonine catalyst for the one-pot assembly of chiral phthalides greatly overcomes the present trend of using highly sophisticated catalysts. The developed method provides access to both enantiomers of a product using pseudoenantiomeric cinchona alkaloids as catalysts streamlining the synthesis of phthalide in both the optically active forms.

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Heterogenous ppm level palladium catalysed C-N cross coupling in aqueous micellar condition

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Abstract

Ligated palladium has been and continues to be a privileged catalyst in the realm of organic synthesis [1]. Palladium-catalysed aminations have been pursued actively in fields ranging from pharmaceuticals and agrochemicals to others in the fine chemical industry. The versatility and utility of such aminations has also made it among the more reliable methods for construction of C-N bonds that are so prevalent in many target molecules. Mostly C-N cross coupling carried harsh environment under homogenous conditions with use of high temperature, toxic solvent like 1,4-dioxane, DMF and high catalyst loading.

In present study, we have synthesized hyper crosslinked polymer (HCP) with catalytic sites for the stabilization of Pd pre-catalyst. Due to the inherent hydrophobic nature of these HCP catalysts, the cooperative effect of micelles and metal HCPs was harnessed to construct C-N bonds in water under very mild conditions. Hypercrosslinked polymer [2] come under the category of porous organic polymer, requires mild conditions and inexpensive reagents during its preparation, it has great advantage over other porous materials in terms of large-scale preparation [3], suitable ligand and linker was used to form hypercrosslinked porous organic polymer with highly active sites in which the Pd pre-catalyst loading was found to be in ppm range (500-1500 ppm). The material was found to be recyclable, stable and water dispersible under ambient conditions. The catalysts were characterized by various spectroscopic/imaging techniques (HR-TEM, SEM, XPS, PXRD, BET, Solid state-NMR, AFM).

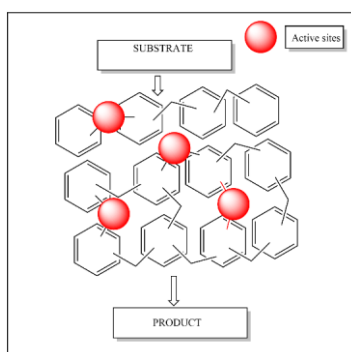
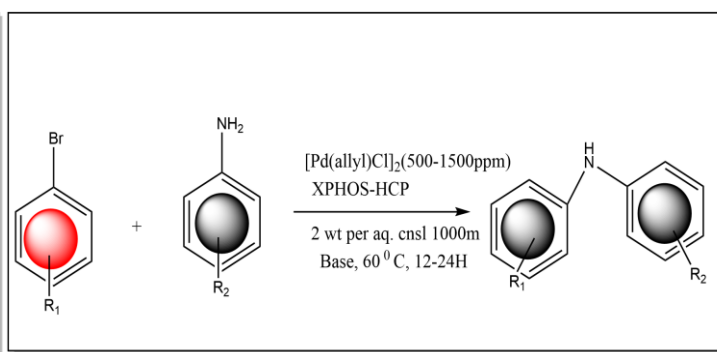


Figure 1



Scheme 1

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Ni₃V₂O₈@g-CN nanocomposite based p-n heterojunction: Mechanistic insights on photocatalytic activation of inert C(sp³)-H bond

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Selective oxidation of C(sp³)-H bonds of aliphatic hydrocarbons to form value-added chemicals is still a challenging task being pursued. Herein, a p-n heterojunction based Ni₃V₂O₈@g-CN (NVO@g-CN) nanocomposite as a visible light active photocatalyst have been successfully reported for the activation and oxidization of inert C(sp³)-H bond of cyclohexane under mild reaction conditions. Moreover, p-n heterojunction formed enhances the charge separation at the interface leading to higher photocatalytic activity. Amid all composites, NVO-1@g-CN showed excellent performance towards the production of cyclohexanone with 93.4 % selectivity. The plausible photooxidation mechanism was validated by EPR and UV-Vis spectroscopy along with the scavenger experiments. Further mechanistic investigation using techniques like photocurrent density and photoluminescence experiments elucidate that the p-n heterojunction formed at the interface of the catalyst accelerates the charge separation by suppressing the recombination of photogenerated charge carriers. Thus, the p-n heterojunction based NVO@g-CN nanocomposite provides an efficient and sustainable approach for the selective photooxidation of cyclohexane.

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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Highly efficient production of 2,3-Pentanedione from Condensation of Bio-Derived Lactic Acid over Polymorphic ZrO₂

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Much attention has recently been paid to the usage of renewable biomass due to the energy and environmental crises. Thus Biomass research has thus been widely conducted. Catalytic conversion produces chemicals and fuels from abundant, renewable biomass and its byproducts, providing a viable alternative to our reliance on depleting fossil fuels^{1,2}. Lactic acid (LA) is particularly appealing due to its simple synthesis via biomass fermentation and chemical conversion of glycerol, as well as the expected increased availability and lower cost³. Here is a promising opportunity to replace petroleum-based feedstock with renewable lactic acid for greener and more sustainable 2,3-pentane dione production. The primary causes driving the change to bio-based chemicals are rising crude oil prices and growing worries about carbon emissions. 2,3-Pentanedione is a high-value fine chemical that is currently manufactured in modest quantities by multi-stage chemical synthesis or extracted from milk waste. We present a green method for producing 2,3-Pentanedione directly from crude lactic acid vapor-phase condensation over polymorphic ZrO₂. The catalyst is extremely selective, active, and stable for the direct condensation of raw lactic acid to 2,3-Pentanedione, with a conversion rate of 99.7% and a selectivity of 95.5%.

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10-13 December 2023

Utilizing the undesirable oxidation of Lead-free hybrid halide perovskite nanosheets for solar-driven photocatalytic C(sp³)–H activation: Unraveling the serendipity

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Hybrid halide perovskites (HHPs), whose every branch generates intrusiveness, have been utilized in solar cells from a wider perspective. However, the inclusiveness of employing HHP as a photocatalyst is in its initial stage. This study mainly focuses on the unexpected utilization of so far undesirable material vacancy-ordered MA₂SnBr₆ quantum dots synthesized from MASnBr₃ nanosheets. Here, the quantum confinement grounded a large blue shift in UV and PL spectra with a Stokes shift of 420 meV, where the band gap increment is observed as size decreases in MA₂SnBr₆. Remarkably, MA₂SnBr₆ exhibits air and moisture stability, better charge transfer, and high oxidation potential in comparison to MASnBr₃. The first principle-based atomistic computations reveal the strain relaxation in the Sn-Br framework that structurally stabilizes the MA₂SnBr₆ lattice. Furthermore, direct bandgap and strongly localized valence band edge give rise to new potential visible-light active photocatalyst MA₂SnBr₆ for efficient solar-driven C(sp³)–H activation of cyclohexane and toluene under ambient conditions.



Hydrodifluoromethylation of unactivated alkenes enabled by Visible-Light Photocatalysis

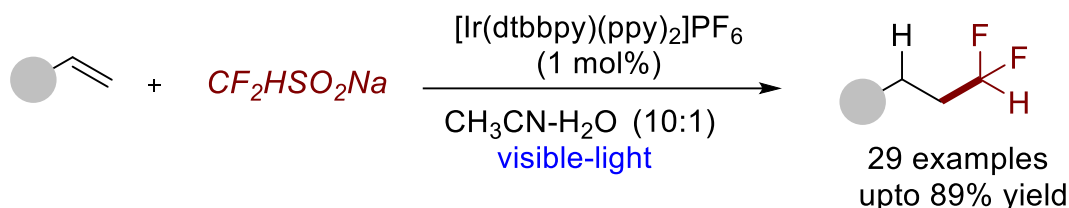
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The development of an inexpensive catalytic approach that will allow the building of pharmaceutical-relevant difluoro methylated alkanes has attracted considerable attention, due to the insertion of [CF₂H]-group can alter the physicochemical and biological properties of the molecules.^[1] Also, a unique feature associated with introducing the [CF₂H]-group is the ability to act as a hydrogen-bond donor and thus a potential bioisostere for hydroxyl, amino or thiol groups.^[2] Due to these remarkable features, difluoromethyl (CF₂H) group-containing compounds have emerged as promising pharmaceuticals and agrochemicals candidates.^[1] In this work, we have developed a general catalytic strategy that can utilize the commercially available radical difluoromethylating reagent (CF₂HSO₂Na) for hydro-difluoromethylation of unactivated alkenes. A variety of unactivated alkenes including several pharmaceutically relevant drugs are transformed to corresponding difluoromethylated alkenes in good yields.

This work



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Photocatalytic Aerobic Oxidation of Sulfides and Enaminones by Acridone Based Zn-Metal-Organic Framework (Zn-MOF) Under Visible Light Irradiation

Parag Tamuly,^a and Jarugu Narasimha Moorthy^{a,b*}

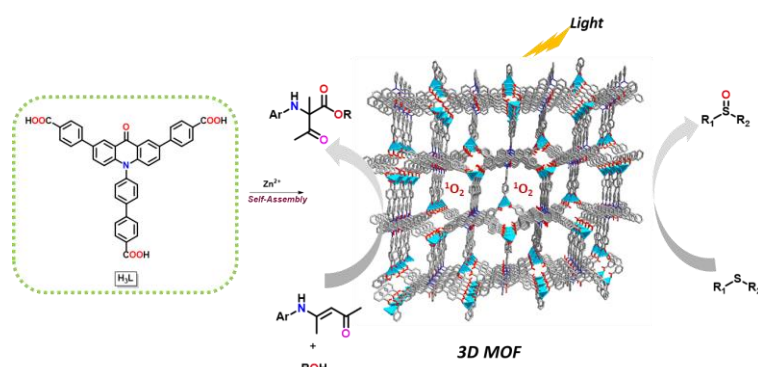
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Visible light photocatalysis has emerged as an effective tool for organic transformation due to its sustainable and green approach [1]. Among the various heterogeneous photocatalyst, metal-organic frameworks (MOFs) have been on demand because of (i) their structural tunability that permits the embedding of photosensitizers as linkers (ii) high surface area that allows mass transfer (iii) easily accessible active sites and (iv) recyclable nature [2].

In this regard, A two-fold interpenetrated 3D zinc metal-organic framework, i.e. **Zn-AcBP** was accessed from a rationally designed photosensitive 3-connecting triacid linker i.e. **H₃AcBP** based on acridone as a core. The Zn-AcBP MOF exhibits visible light absorption and is exploited as a heterogeneous photocatalyst for the photocatalytic aerobic oxidation of various sulfides and enaminones in a recyclable manner. Mechanistic insights demonstrate that singlet oxygen serves as reactive oxygen species for the photooxidation reactions. It is the first demonstration of the grafting of acridone photosensitizer as a linker for the construction of MOF which can be used for photocatalysis in the presence of green, inexpensive oxygen for organic transformations.



Scheme1. Visible light induced photocatalysis by **Zn-AcBP** MOF.

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Metal–Organic Framework-Encaged Monomeric Cobalt(III) Hydroperoxides Enable Chemoselective Methane Oxidation to Methanol

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Developing highly efficient catalysts for chemoselective oxidation of methane to methanol under mild conditions is a grand challenge. We reported the successful design and synthesis of a heterogeneous single-site cobalt hydroxide catalyst [Ce-UiO-Co(OH)] supported by the nodes of a cerium metal–organic framework (Ce-UiO-66 MOF), which is efficient in partial methane oxidation using hydrogen peroxide at 80 °C, giving an extraordinarily high methanol yield of 2166 mmol gcat⁻¹ in 99% selectivity with a turnover number of 3250. The Ce-UiO-Co catalyst is significantly more active and selective than its iso-structural zirconium analogue Zr-UiO-Co in methane to methanol conversion. Experimental and computational studies suggested the formation of the Co^{III}(η^2 -hydroperoxide) intermediate coordinating with one μ_4 -O⁻ and two neutral carboxylate oxygens of Ce⁴⁺ oxo nodes within the pores of Ce-UiO-66, which undergoes σ -bond metathesis with the methane C–H bond in the turnover limiting step of the catalytic cycle. The significantly lower activation energy of Ce-UiO-Co than Zr-UiO-Co is due to the highly electron-deficient nature of the cobalt ion of the Co(η^2 -O₂H) species supported by the Ce-UiO nodes, which promotes facile C–H activation of methane via σ -bond metathesis. This MOF-based catalyst design holds promise in developing molecular electrophilic abundant metal catalysts for chemoselective functionalization of saturated hydrocarbons. This research was funded by CSIR-HRDG [01(3040)/21/EMR-II]. The authors acknowledge the Central Research Facility, IIT Delhi, for instrument facilities.

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Conversion of Methane to Methanol over Ceria-ZSM-5 supported Copper oxide catalysts

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Direct Conversion of methane to methanol (DMTM) is an alternative way of utilizing abundant CH₄ in natural gas. However, DMTM process has challenges of methane activation and overoxidation of methanol resulting in low methanol yield. Hence, developing an efficient and selective catalyst is necessary to overcome these challenges. The present study demonstrates the DMTM conversion in a fixed bed reactor under varying process parameters over CeO₂-ZSM-5 supported Copper oxide catalysts prepared by incipient wetness impregnation method. The prepared catalysts were well characterized by several techniques including N₂ adsorption-desorption, XRD, FTIR, Pyridine -FTIR, XPS, UV-vis and H₂-TPR and CO DRIFT studies to unravel the physicochemical properties.

The detailed characterization results confirm the presence of Cu⁺ and Cu²⁺ and coexistence of Ce³⁺ & Ce⁴⁺ indicative of its redox behaviour. Moreover, the O1s XPS spectra of supported copper catalysts revealed the presence of lattice and adsorbed oxygen species. The UV-vis analysis confirmed the presence of either bis(μ-oxo) dicopper or mono(μ-oxo) dicopper species which are considered as active site for DMTM. The supported Cu catalysts were capable of activating the methane molecule at the reaction temperature of 673 K and the variation of reaction parameters had significant effect on the product distribution. The role of surface Cu²⁺ species and the ratio of lattice to adsorbed oxygen species played a crucial role on the yield of methanol. The highest yield of methanol of about 2.4% was obtained in our study. The physico-chemical and structural properties obtained from detailed characterization results were correlated to establish the structure-property correlation.



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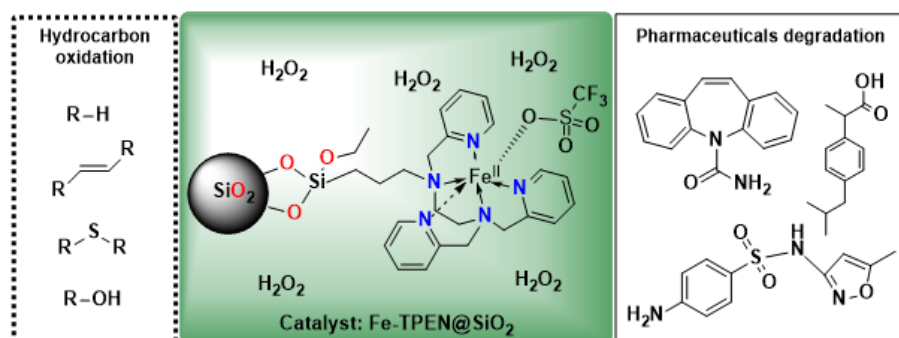
Iron (II)-polypyridyl complex immobilized on silica beads as versatile catalyst for hydrocarbon oxidation: Application towards organic pollutant removal

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The development of environmentally friendly cheap catalyst for selective and efficient oxidation is one of the great challenges in chemistry, with popular methodologies involving precious-metal catalysts. In recent years, iron catalysts have emerged as a possible alternative to the precious metal catalysts, owing to its high abundance, low cost and environment friendly nature.^[1] In this direction a versatile oxidation catalyst has been synthesized by tethering a nonheme Iron(II) complex on silica beads. The catalyst has been well characterized by solid state characterization technique such as XPS, TGA etc. The developed catalyst was studied in oxidation of sulphide, alcohol and hydrocarbons mainly in polar solvents (like Acetonitrile). Particularly the concentration of hydrogen peroxide (oxidant) governs the selectivity, observed in ¹H-NMR and GC spectrum. The catalyst was further used as an oxidation catalyst for degradation of various pharmaceutical products that are known to pose potential threat to bio-community if left untreated.^[2] The complexing ability of TPEN avoided the precipitation of an iron derived basic sludge and accelerated the electron transfer among oxidant and iron, where the iron-oxo species, as major reactive species, was generated.^[3] The carrier SiO₂ contributed to both separating the active sites on the surface of catalyst and avoiding the self-decomposition of Fe(II)-complex.



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Indo-French Seminar on Catalysis for Sustainability

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An Encapsulation of Palladium Nanoclusters in Surface-modified porous silica for the Study of Oxidation reactions

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Abstract: There has been a great deal of excitement about metal nanoclusters (1-2nm) in heterogeneous catalysis due to their superior physical, optical and chemical properties. Since they have an extremely high surface energy, they are easily deactivated by migration and coalescence during catalysis. A solution to this problem found by enclosing active metal nanoparticles inside porous silica matrix. Pd nanocluster with sizes less than 2 nm prepared using functionalized thiol ligands which can further encapsulate inside silica with the aid of TEOS by simple hydrolysis method. Altering the properties of encapsulating materials can improve the activity and selectivity towards various reactions. MFI zeolite is recognized as a significant catalyst for selective catalytic reactions because of its straight-line channel and sinusoidal channel systems. The potential for creating catalysts with outstanding selectivity and high activity for different oxidation processes is very significant. Through the use of a steam-assisted conversion technique, we are able to change the porosity of the silica matrix that surrounds the palladium nanocluster by converting silica matrix to silicalite without affecting the original size of palladium. In this catalyst the metal nanoclusters serve as catalytic active sites, and the crystalline silicalite which have both micropores and mesopores can control the product selectivity by altering molecular diffusion. This improved Pd@Silicalite has acidic sites and hierarchical nature. The prepared catalyst is testing for higher temperature oxidation reactions.

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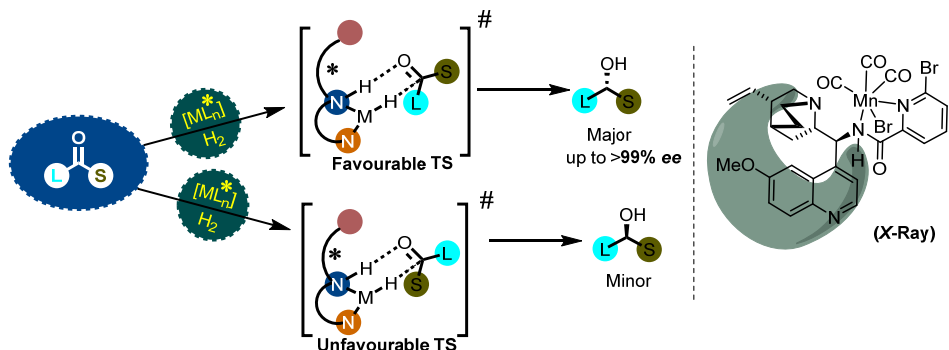
Rationally designed Mn(I) Cinchona Catalysed Asymmetric Hydrogenation of Ketones and its Derivative in water towards High Enantio-induction.

Soumen Paira, Debarsee Adhikari, Nupur Jain, Raghavan B. Sunoj*, Basker Sundararaju*

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Asymmetric hydrogenation (AH) of an unsaturated compound is the most straight forward process to generate chiral molecules from prochiral substrates. Rhodium, ruthenium, and iridium have monopolized industrial procedures in the fabrication of chiral molecules with exceptional activity and resilience [1]. Due to the high reactivity, low toxicity, and high abundance of Mn salts provide opportunity to replace the noble metals in AH and has the potential to dominate this field [2] [3]. Here in, we have synthesized a mini library of Cinchona based chiral ligands and utilized them in AH. We accomplished a phosphine free bidentate Mn(I) cinchona catalysed AH of ketones, β -keto ester, and β -keto amines to harness corresponding chiral secondary alcohol (up to >99% ee), β -hydroxy ester (up to >99% ee), γ -amino alcohol (up to 95% ee), in water towards a highly sustainable processes [4]. Additionally, an enantiocontrol model for ketone hydrogenation has been established via DFT calculations, in which the π - π stacking interaction between the catalyst and the substrate plays an important role.



Scheme: Mn(I)-Cinchona Catalyzed Asymmetric Hydrogenation of Ketones and their derivatives.

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4. Soumen Paira, Debarsee Adhikari, Nupur Jain, R.B. Sunoj*, Basker Sundararaju* (manuscript under preparation).



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METHANE TRANSFORMATION TO C₂ HYDROCARBONS USING NANOCRYSTALLINE Li/MgO CATALYST

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One of the ongoing difficulties in catalysis is the development of highly efficient and financially viable methods of using natural gasses like CH₄ to synthesize chemicals and other fuels. We have created Li/MgO catalysts in this work using sequential deposition-sublimation techniques, and they demonstrated excellent stability and activity for selective oxidation and conversion of methane to C₂ hydrocarbons. A solvothermal method assisted by CTAB as a surfactant was adopted to synthesize Magnesium Oxide as a support, then Li was deposited onto it by successive sublimation-deposition method, where initially deposited Li on the support was sublimated at 900 °C and the final Li doped MgO catalyst was obtained by repeating this process three times. For comparison purposes, different percentages of Li were loaded by deposition method only. Transmission electron microscope (TEM), X-ray diffractometer analysis (XRD), temperature-programmed desorption (TPD), and various other spectroscopic methods were used to characterize the produced catalysts. At 700 °C, the deposition-sublimation technique catalyst (3.6Li/MgODep-Sub) demonstrated a maximum methane conversion of 38% and total C₂ selectivity of 78% with 55% ethylene and 23% ethane selectivity. Our future plans are to enhance the stability of our catalyst up to 200 hr with better conversion and selectivity.



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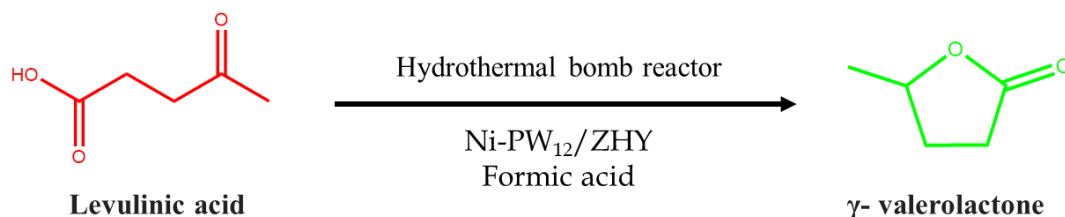
Ni exchanged supported 12-tungstophosphoric acid for the hydrogenation of Levulinic acid without external H₂ source

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Hydrogenation reaction of carbonyl and carboxyl groups containing molecules have boundless industrial application as the obtained products are directly used in petroleum industry, food industry, solvents preparation, used in polymer synthesis and other chemicals [1]. In recent years, hydrogenation of bio mass based molecules gained tremendous attention because their applications are widely utilized in biobased chemicals which would be helpful in building up the bio-based economy. In this direction to achieve the goal generally precious metals such as Pd, Pt, Au based catalyst have been used to carry out these reactions. By replacing these precious metal-based catalysts with less expensive metal-based catalysts is a real sound of research work [2]. In this sense, transition metal exchanged supported polyoxometalates are excellent catalysts because they combine the benefits of both transition metals and supported heteropolyacids.



Scheme 1. Hydrogenation of LA to GVL

In this work we demonstrate the designing of a bifunctional catalyst comprising Ni and 12-tungstophosphoric acid supported into Zeolite Y. Different physiochemical techniques such as acidity measurement, FTIR, TGA, BET, XRD, ³¹P NMR, and HRTEM were used to characterize the synthesized catalyst. The hydrogenation of levulinic acid with formic acid as internal hydrogen source was carried out in hydrothermal bomb reactor by varying different reaction parameters such as time, temperature, mole ratio and amount of the catalysts. Obtained results shows significant conversion (80%) and complete selectivity (100%) towards GVL without any external H₂ source. The catalyst was recycled by simple centrifugation method and reused to check sustainability of the catalyst.

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A heterogeneous catalyst prepared from red mud for the conversion of Benzene to Phenol

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In recent years the synthesis of benzene to phenol attracted genuine scientific interest among researchers from an environmental and economic standpoint worldwide. In this research work, we have synthesised Cu-nanoparticles supported on red mud as catalyst material for the benzene to phenol oxidative conversion. In the chemical industry, Phenol is a crucial intermediate for the diverse production of critical chemicals/intermediate/products such as pesticides, pharmaceuticals, resin, agrochemicals etc. XRD and TEM were used to demonstrate how the Cu-nanoparticles formed. The peaks in the X-ray Diffraction pattern match the typical values of the face-centred cubic structure of metallic copper, and no other peaks of impurity crystalline phases were found. Spherical nanoparticles with diameters between 2 and 18 nm are visible through TEM examination. FTIR, SEM, TGA-DTG, and BET surface area analyzers were also used to characterize the catalyst. The H₂-TPR approach was used to study the qualities of the catalyst that can be reduced. The one-pot hydroxylation reaction exhibits benzene conversion of 96% and selectivity of phenol up to 99% when conducted at 70 °C under ideal reaction conditions. The material's reusability tests up to four batch cycles in a row show that selectivity (99%) and conversion efficiency (96%) were retained, making it ideal for future commercial development in accordance with the green chemistry philosophy.

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“Liq. Hydrogen carrier and C1 source – Methanol” mediated selective N-Methylation of Urea via Transfer Hydrogenation catalyzed by Pd-Serine heterogenous catalyst

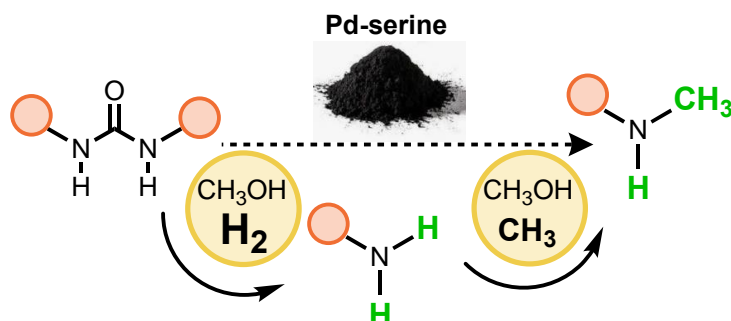
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ABSTRACT

We report the catalytic transfer hydrogenation of urea derivatives using green hydrogen from methanol, which is the most ambitious effort in this hydrogenation world. On enlarging this methodology, selective *N*-methylated amines achieved from urea which are widely featured in drugs, natural products, paints etc. Moreover, this methodology making a sustainable alternative pathway for the synthesis of selective methylated derivative from CO₂ derived compound. The key to the success of this transformation is the use of Pd-serine heterogenous catalyst and Methanol which act as both H₂ and C1 sources. In addition, several control experiments with the plausible intermediates were performed to analyze this novel pathway. This transformation proceeds in an environmentally friendly greener protocol and high atom-economy.



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Microwave-assisted synthesis of E-aldimines, N-heterocycles and H₂ by dehydrogenative coupling of benzyl alcohol and aniline derivatives using CoCl₂ as catalyst

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The acceptorless dehydrogenative coupling (ADC) between alcohols and amines to produce imines has been achieved mostly by employing precious-metal-based complexes, or complexes of earth-abundant metal ions with sensitive and complicated ligand systems as catalysts mostly under harsh reaction conditions. Methodologies using readily available earth-abundant metal salts as catalysts without the requirement of ligand, oxidant or any external additives are not explored. We report an unprecedented microwave-assisted CoCl₂-catalyzed acceptorless dehydrogenative coupling of benzyl alcohol and amine for the synthesis of E-aldimines, N-heterocycles and H₂ under mild condition, without any complicated exogenous ligand template, oxidant, or other additives. This environmentally benign methodology exhibits broad substrate scope (43 including 7 new products) with fair functional-group tolerance on the aniline ring. Detection of metal-associated intermediate by gas chromatography (GC) and HRMS, H₂ detection by GC and kinetic isotope effect reveal the mechanism of this CoCl₂ catalyzed reaction to be via ADC. Furthermore, kinetic experiments, and Hammett analysis with variation in nature of substituents over the aniline ring reveal the insight of the reaction mechanism with different substituents.