



Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

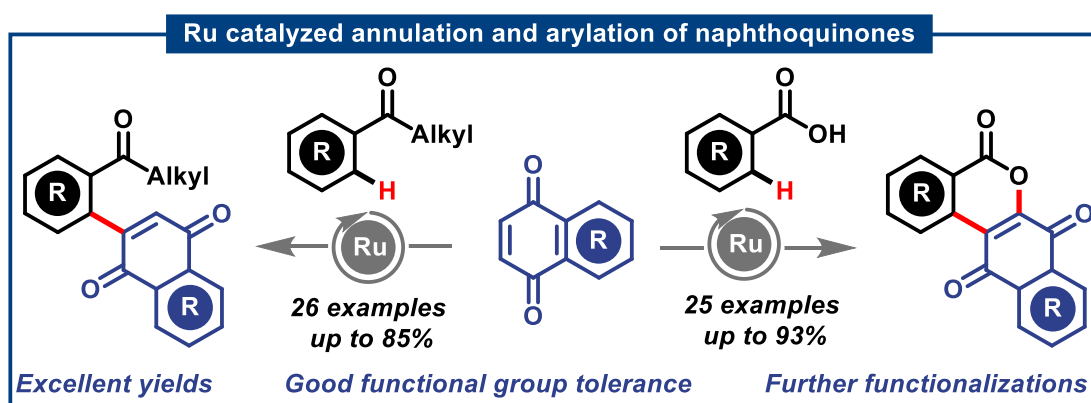
Ru(II)-Catalyzed [4+2]- Annulation and Arylation of 1,4-Naphthoquinones

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Naphthoquinones are the primary component of numerous medicines and organic products. As a result, combining 1,4 naphthoquinones with organic building blocks would be a simple method to produce biologically interesting scaffolds. In this context, we have developed 1,4-naphthoquinone-benzoic acid [4+2] annulation, which yields a variety of naphthoquinone lactones. Also demonstrated was the use of acetophenones in ketone-directed arylation of naphthoquinones under Ru (II)-catalysis. The extensive library of naphthoquinone derivatives could be obtained in good to exceptional yields under relatively benign conditions thanks to the feed-stock accessibility of these precursors. The execution of gram scale synthesis and other functionalizations supported the viability of these procedures. In order to better understand the response mechanism, early mechanistic studies were also conducted.



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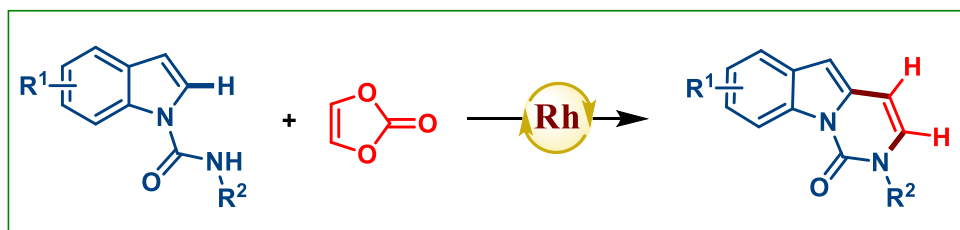
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Rh(III)-Catalyzed [4 + 2] Annulation of *N*-Carbamoylindoles with Vinylene Carbonate for syntheses of 3,4-Unsubstituted Pyrimidoindolones **Vikash Kumar, and Parthasarathy Gandeepan***

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Transition metal-catalyzed, chelation-assisted *ortho* C–H bond functionalization of (hetero)aromatics becomes an expedient tool in organic synthesis.¹ These methods provide atom-, step-and resource-economical ways to access diverse heterocyclic core moieties in various natural products, bioactive compounds, polymers, and functional materials.² Pyrimidoindolones are an important heterocyclic structural motif found in various natural products, bioactive compounds, polymers, functional materials and agrochemical industry.³ Direct synthesis of 3,4-unsubstituted pyrimidoindolones is not easily accessible. In this context, we have developed a rhodium(III)-catalyzed C–H/N–H activation and annulation approach for obtaining 3,4 unsubstituted pyrimidoindolones from *N* carbamoylindoles and vinylene carbonate. The protocol features high functional group compatibility, low catalyst loading, external oxidant-free reaction conditions and milder reaction conditions with short reaction time.



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Cp^{*}Rh(III)-catalysed C-H/C-H cross-coupling between heteroarenes to access diverse heterobiaryls

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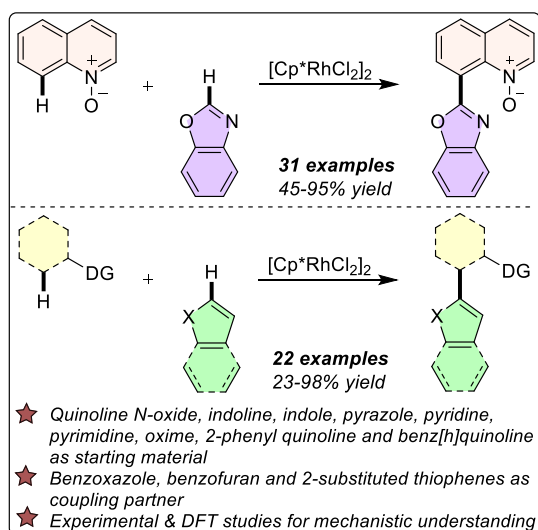
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The biheteroarenes are privileged scaffolds, extensively utilized in the pharmaceuticals, agrochemicals, ligands and optoelectronic materials.¹ In this perspective, the coupling between inert and unreactive C(sp²)-H bonds of two dissimilar heteroarenes is quite interesting, yet practically a challenging approach.² The transition metal-catalysed direct C-H/C-H coupling between two heteroarenes has been recognized as an efficient transformation for the synthesis of heterobiaryl frameworks.³ Herein, Rh(III)-catalysed, directing group-assisted site-selective C-H/C-H cross-coupling between *N*-heteroarenes has been disclosed.⁴ A plausible mechanism cycle has been described on the basis of mechanistic experiments and DFT studies.



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Cu-Catalyzed Alkylboration of Alkylidenecycloalkanes with Bis(pinacolato)diboron and Alkyl Iodides

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Small-carbocyclic cyclopropane and oxetane are frequently used as core structures in drug design¹. Medicinal chemists can build upon these scaffolds of restricted conformation to create libraries of compounds with diverse functional groups, optimizing the pharmacological properties of the resulting molecules.² Intrigued by the importance of tertiary cycloalkyl boronic esters as building blocks,³ the installation of both boron and alkyl functionalities across a C=C bond via the formation of B-Csp³ and Csp³-Csp³ bonds have received ample attention to build up 3D carbogenic complexity with concurrent decoration of boron functionality.⁴ In this poster, we discuss a regioselective Cu-catalyzed alkylboration of readily accessible strained benzylidenecycloalkanes (BCAs) with diboron reagent with alkyl iodides towards the synthesis of tertiary cycloalkylboronic esters.⁵ The versatility of organoboron compounds is explored by converting the so-formed tertiary cycloalkyl boronic esters into a variety of functionalities.

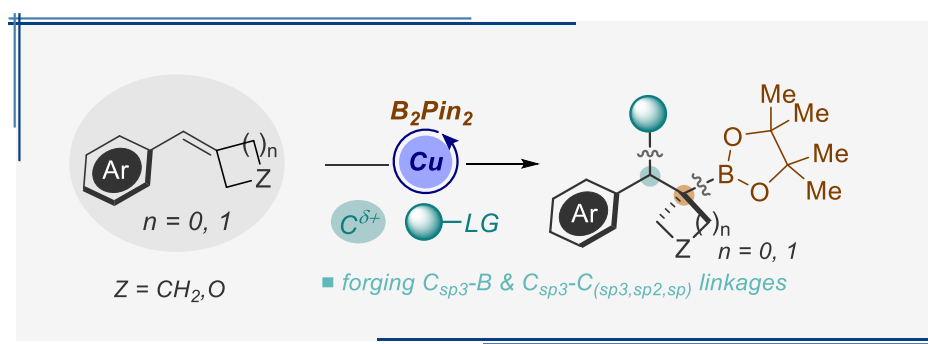


Figure 1. Cu-catalyzed alkylboration of alkylidenecycloalkanes

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Copper-catalyzed one pot cascade cyclization reaction to access pyrroloquinolines

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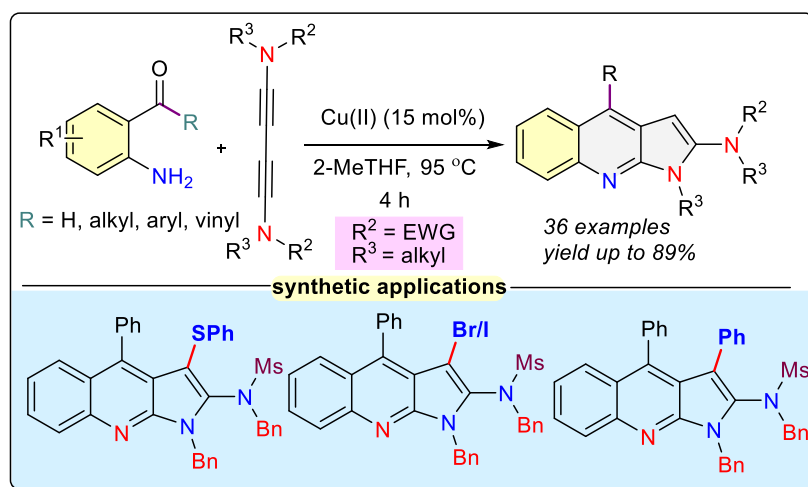
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Abstract: A straightforward and one pot protocol enabled by copper(II) catalyst to access pyrroloquinolines from 2-carbonyl-anilines and 1,3-butadiynes has been showcased. Interestingly, a large number of 2-carbonyl-anilines are well tolerated, furnishing a library of pyrroloquinolines in good to excellent yields. Subsequently, gram-scale synthesis of pyrroloquinolines has been carried out with excellent efficiency and a series of successful synthetic applications highlight the practical utility of the developed protocol. Moreover, control experiments highlight the significance of moisture in this reaction.



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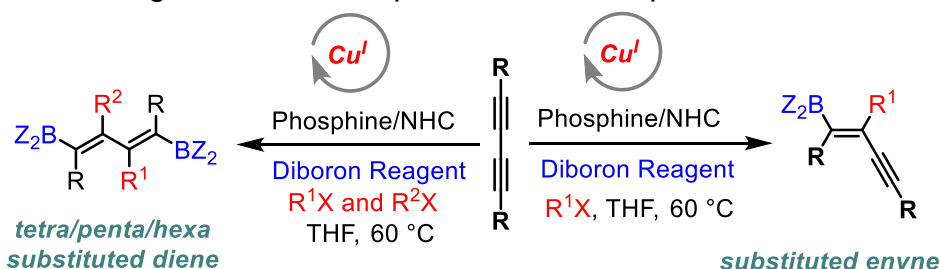
Copper-Catalyzed Proto/Carboboration of 1,3-Diynes: An Easy and Sustainable Access to Borylated Enynes and Dienes

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Targets with high structural complexity can be easily assembled using small, modular building blocks similar to a 'Lego' construction using iterative chemistry.³⁻⁴ Organoboron compounds have been in the spotlight as versatile building blocks in natural product synthesis. Here, we present a sustainable, glovebox-free regioselective protoboration of 1,3-diynes using a stable diboron source and Cu(I)/phosphine as a catalyst to access stable enynyl and dienyl boronate esters in a single operation. Then, we developed the first copper-catalyzed carboboration of 1,3-diynes, in which a simultaneous C–B and C–C bond formation was achieved in a single operation using Cu(I)/NHC catalyst. The methodology provides easy access to highly sterically encumbered penta- and hexasubstituted dienes. A wide range of electrophiles have been successfully employed. The introduction of allyl moiety provided access to skipped diene-yne boronate ester with excellent regioselectivity. DFT studies supported the regioselective incorporation of electrophiles.



Protoboration: $R^1=R^2=H$, when $R^1X=R^2X=MeOH$; L= phosphine

Carboboration: $R^1, R^2=$ alkyl, allyl; when $R^1X/R^2X=$ alkyl or allyl halide; L= NHC

Iterative Coupling Ready Modular Building Block High Regioselectivity
Broad Substrate Scope Tetra/Penta/Hexa substituted diene Glovebox Free

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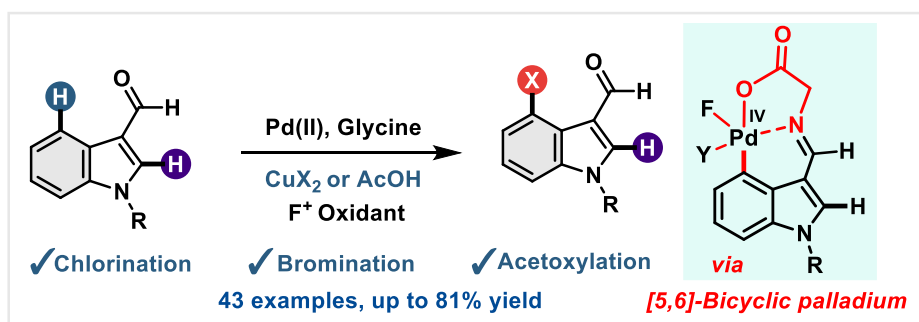
Pd(II)-Catalyzed Transient Directing Group-Assisted Regioselective Diverse C4–H Functionalizations of Indoles

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Indoles and their derivatives are found in many natural and unnatural products having biological and medicinal significance. The development of a rational strategy for achieving site-selective C4–H halogenation of indoles is an appealing yet challenging task. Recent years have witnessed the emergence of transition metal catalyzed C–H activation as a powerful synthetic tool in organic chemistry. In this context, we developed a Pd(II)-catalyzed transient directing group (TDG)-assisted methodology to access C-4 chlorination/bromination of indoles employing glycine as the TDG and NFSI as a bystanding oxidant. The use of inexpensive and commercially available CuX_2 as the halide source is the key highlight of this protocol. Furthermore, the TDG methodology was also extended to accessing C4 acetoxylation of indoles employing acetic acid as the acetate source and 1-fluoro-2,4,6-trimethylpyridinium triflate as the oxidant.



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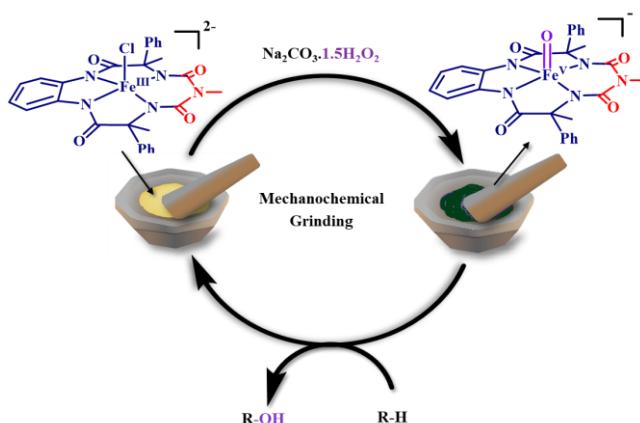
Solvent-free Hydroxylation of C-H bonds by Fe-complex: A Green Approach for Activation of Small Molecules and Polymers

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In the past few decades, there have been significant advances made in "solventless" solid-solid reactions. Such mechanochemically promoted processes often provide advantages over standard solvent-based methods, including higher yields, shorter reaction times, lower catalyst loadings, and mostly the avoidance of organic solvents and elevated reaction temperatures. Herein this report, we have successfully eliminated solvent from the reaction system and come up with a green mechanochemical approach for oxidizing a wide array of substrates, including hydrophobic molecules, to natural products and medicinal drugs by a biomimetic Fe-bTAML catalyst. This methodology was successfully implemented for functionalizing the polyolefins, a major contributor to the landfill. We employed sodium percarbonate as an oxidant, which is a green and cheap source of solid H₂O₂. This is a truly green process since both the catalyst and oxidant are known to be non-toxic, and the only purification required would be to wash the excess oxidant and inactivated catalyst in water, thus addressing the hazardousness of an organic solvent in the reaction. We were able to characterize the reactive intermediate by solid-state UV, solid-state EPR, and mass spectrometry. All these measurements predict our reactive intermediate as oxoiron(V).



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Cobalt(III)-catalyzed regioselective hydro-arylation of 1,6-diyne via weak-chelation assisted C-H bond activation

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Abstract: The 3d transition metal-catalyzed C-H bond activation using weakly coordinating directing groups such as aldehyde, ketone, esters and substituted amide are emerging and sustainable area.^{1,2} In this regard, we have developed various C-H bond functionalization utilizing earth-abundant cobalt catalysts and weak chelation.^{3,4} Herein, we have report cobalt(III)-catalyzed hydro-arylation functionalization of 1,6-diyne, which was never explored before. The *N*-aryl γ -lactam is the prime substrate that undergoes *sp*² C-H bond activation in a weakly coordinating manner. The reaction mechanism reveals the in-situ formation of a six-membered cobaltacycle which undergoes further functionalization with 1,6 diyne to give substituted enyne.

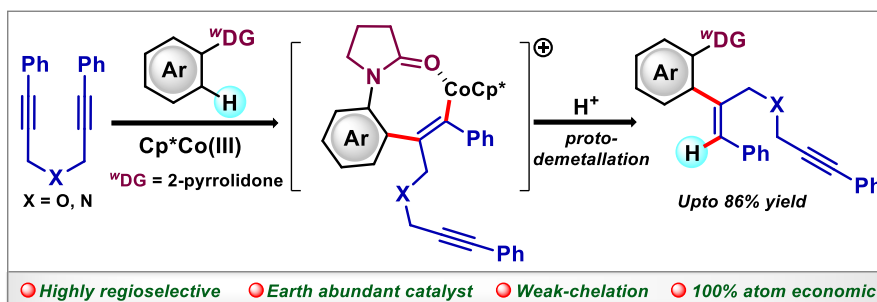


Figure: Synthesis of enyne through cobalt-catalyzed regioselective hydroarylation of 1,6-diyne.

Also, we have detected a six-membered cobaltacycle intermediate through high-resolution mass spectrometry (HRMS), which supports our proposed catalytic cycle. The radical scavengers' experiments suggest the non-involvement of the radical pathway for this transformation. In addition, the protocol worked well with the various substrate in good yield and high regioselectivity⁵.

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Site Selective C(sp²)-H functionalization of Isoquinolones

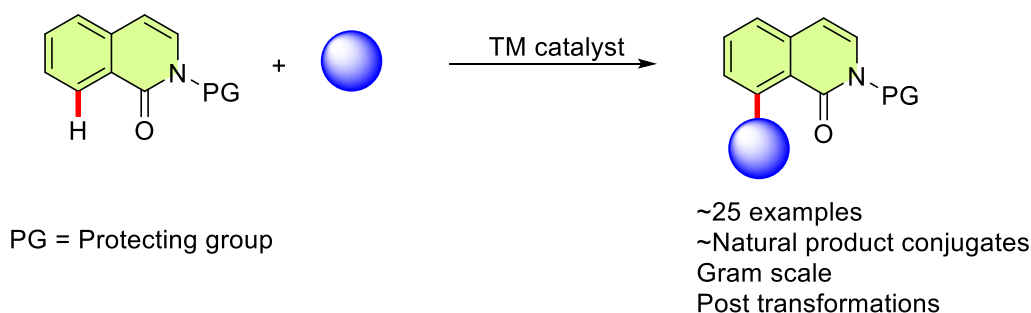
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Isoquinolones are one of the key scaffolds present in natural products and utilized for synthesizing various molecules of interest.¹ Transition metal catalyzed C-H activation has made it feasible to achieve the regioselective functionalization of the organic compounds.² Owing to the great importance of isoquinolones and C-H activation, we here present the regioselective C(sp²)-H functionalization of isoquinolones under very mild conditions to attain the site selective functionalization of the isoquinolones. Preliminary experiments were done to understand the mechanistic pathway of the developed methodology. Gram scale and post transformations of the synthesized product demonstrated the potential of the developed protocol.



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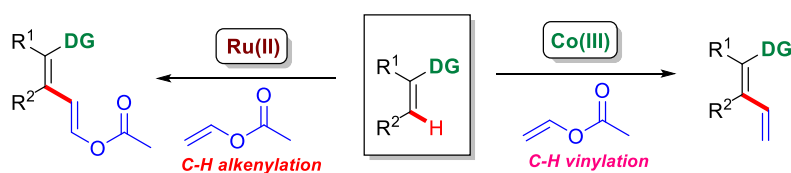
Effect of Transition Metals on Chemodivergent Cross-Coupling of Alkenes with Vinyl Acetate via C–H Activation

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Olefins are inexpensive, widely available feedstock and can be readily functionalized into complex organic molecules.¹ The unique reactivity of olefins has made alkene functionalization essential in organic synthesis. In particular, transition-metal-catalyzed C–H functionalization of alkenes has gained special attention because it can construct complex carbon skeletons in a high atom- and step-economical manner. However, most established methods are limited to activated olefins, and the direct olefinic C–H functionalization of electron-rich olefins remains rare.² Vinyl acetates are versatile building blocks and an ideal synthetic precursor for chemodivergent reactions.³ In this methodology, the difference in selectivity between the Co(III) and Ru(II) using vinyl acetate has been described. Under oxidative reaction conditions, these two metals show different reactivity as well as selectivity—the former results in β -acetate eliminated product, and the latter results in β -hydride eliminated product.⁴



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Palladium (II)-catalyzed Acyloxylation of C(sp²)-H Bond with Aldehyde and O₂

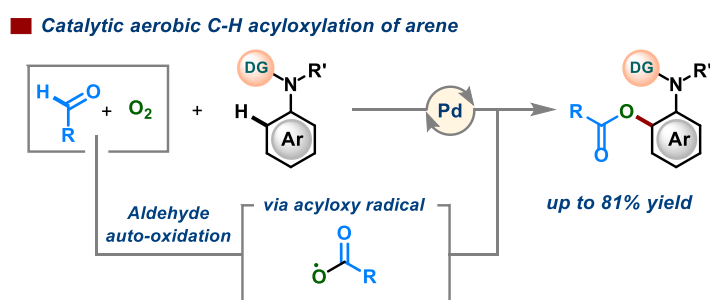
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Oxidative Pd-catalysis occupies an important place in organic synthesis enabling selective transformation of various feedstocks into high-value materials via direct functionalization of unactivated C-H bond. Indeed, many useful C-H functionalization reactions have been developed using oxidative Pd-catalysis. However, they often rely on the use of excess amount of synthetic oxidants like metal salt, peroxides, BQ, PIDA, and others that produces significant amount of chemical waste.¹ With increasing concern towards environmental issues, the development of new-generation Pd-catalyzed C-H functionalization reaction using green oxidants such as molecular oxygen (O₂), preferably at 1 atmospheric pressure, is in great demand.² Along with this line, our group has developed an aerobic method for the Pd-catalyzed arene C-H hydroxylation³ utilizing in-situ generated per-oxo radical via aldehyde auto-oxidation.⁴ Recently, we have developed an aerobic radical C-H acyloxylation of arenes via simultaneous cooperation of Pd-catalysis with aldehyde auto-oxidation.⁵ The method features O₂ as the sole oxidant, inexpensive aldehyde as the source of acyloxy radical and operational simplicity. In the poster, studies on the reaction development, substrate scope evaluation, and reaction mechanism of the catalytic process will be discussed in detail.



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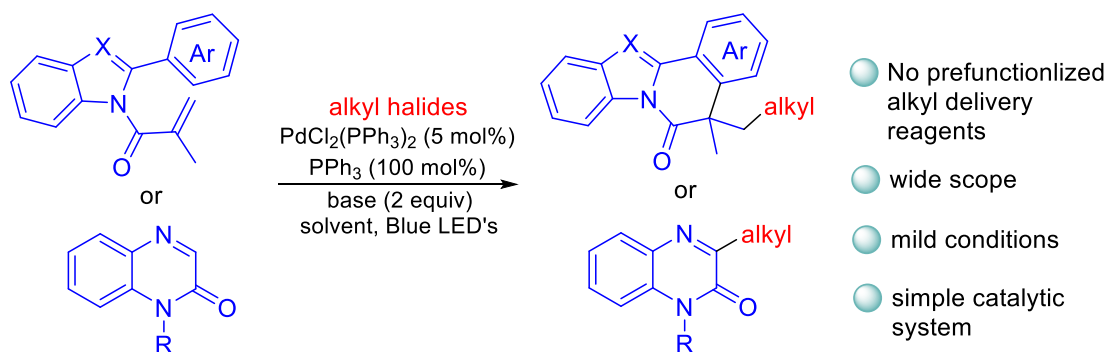
Pd-Catalyzed Photochemical Alkylative Functionalization of C=C and C=N Bonds

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The development of excited-state palladium-catalyzed alkylative cyclization of acrylamides and the alkylation of quinoxalinones is described. The application of a variety of primary, secondary, and tertiary unactivated alkyl halides as alkyl radical precursors and the use of a simple catalyst system are the highlights of this reactivity manifold. The reactions exhibit wide scope, occur under mild conditions, and furnish the products in excellent yields.



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Solid Silylzinc Reagents: Application to Aryl and Alkyl Trimethylsilane Synthesis

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Organosilanes have been widely used in various organic transformations over the years.¹ Transition metal catalysis employing disilanes² and silylboranes³ for synthesizing organosilanes circumvents the limitations of conventional hydrosilylations.⁴ While disilanes require special conditions, silylboranes are yet to be developed as TMS sources. Functional group compatibility renders silylzinc reagents highly desirable; however, their development is hindered due to their synthesis using pyrophoric silyllithium and dissolved lithium salts. Our novel solid $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ ⁵ circumvents these limitations and herein, we demonstrate its significance in the silylation of aryl and primary alkyl bromides. The methodology was used for the synthesis of various organotrimethylsilanes from aryl and primary alkyl bromides with wide functional group tolerance (free amines, alcohols). The same methodology was used for synthesis of silanes of various API derivatives (Ibuprofen, Probenecid, Gemfibrozil).



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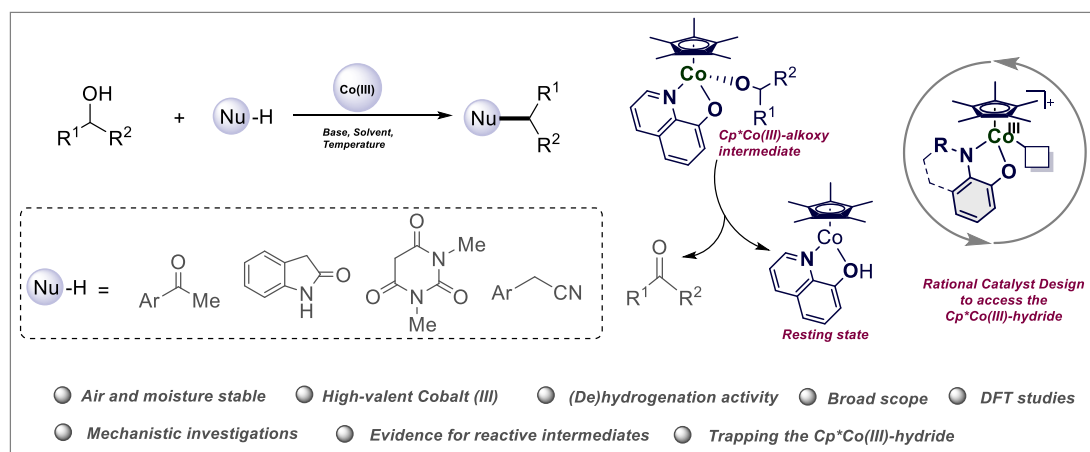
Half-Sandwich Cp*Co(III) Complexes in (De)hydrogenative Functionalization: Catalytic Evaluation and Mechanistic Landscape

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An atom-economical methodology for upgrading small molecules into higher order products are dehydrogenative reactions, wherein, the initial dehydrogenation reaction reveals a more reactive organic synthon that can undergo tandem functionalization reactivity.^{[1][2]} Although in the past decade, significant advances using earth abundant metals have been made, use of a high valent catalytic system is rare and the exploration of the possible catalytic intermediates remains unexplored. High-valent Cp*Ir(III) complexes are known to be active for hydrogen auto-transfer reactions and involved catalytic intermediates are established. Whether its analogous Cp*Co(III) gives the same reactivity? In this regard, we have described the use of high valent Cp*Co(III) system in one-step alkylation reactions with secondary alcohols.^{[3][4]} DFT and experimental investigations sheds light on the involvement of a new paradigm in the oxidative activation of alcohols unlike its high-valent noble metal analogues.^[5] The mechanistic landscape of Cp*Co(III) catalysts and trapping of reactive intermediates with the aid of a rational catalyst design^[6] will be presented and discussed in detail.



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Weak-chelation assisted regioselective alkylation of *N*-heterocyclic compound via six-membered cobaltacycle intermediate

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Abstract: *N*-Heterocyclic compounds have gained a lot of attention because of their diverse medical and biological uses found in 90% of marketed drugs, bridging the gap between chemistry and biology. Therefore, the functionalization of *N*-heterocyclic moiety has much synthetic value. In this context, transition metal-catalyzed C-H activation is a compelling tool for the late-stage modification and functionalization of biologically active compounds. Here we mention a highly regioselective alkylation of the *N*-heterocyclic compound utilizing earth-abundant cobalt(III)-catalyst (Figure 1.). Alkylation of *N*-heterocyclic compound has a good synthetic application because many vital heterocyclic compound building blocks are made with alkyne moieties. Also, readily available (haloalkynyl)benzene was found to be an effective alkylating agent for this transformation. To get cobaltacycle intermediate various weakly coordinating chelating group like ester, ketone, amide has been screened. Also, we have detected a six-membered cobaltacycle intermediate through high-resolution mass spectrometry (HRMS), which supports our proposed catalytic cycle. The radical scavengers' experiments suggest the non-involvement of the radical pathway for this transformation. In addition, the protocol worked well with the various substrate in good yield with high regioselectivity.

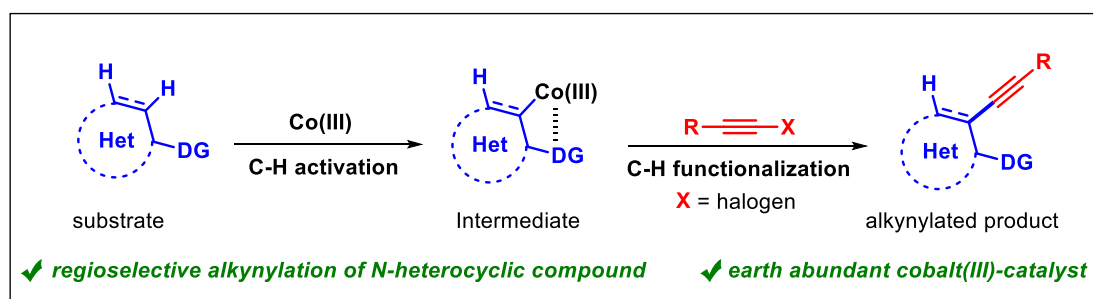


Figure 1. General approach for cobalt(III)-catalyzed C-H bond ethynylation of *N*-heterocycles.

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Palladium Catalyzed Asymmetric Desymmetrization Approach to Enantioenriched 1,3- disubstituted Isoindolines

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Enantioselective C-H functionalization especially where asymmetry is created during the C-H activation are highly challenging. Herein, we report the first palladium/MPAA catalyzed enantioselective C-H activation/[4+1] annulation of diarylmethyltriflamide and olefins to construct chiral *cis*-1,3- disubstituted isoindoline derivatives. The use of readily accessible mono N-protected amino acid as a chiral ligand improves the efficiency and enantioselectivity of the catalytic transformation. The developed method provides access to both enantiomers of a product using either D or L-phenylalanine derivative as a chiral ligand facilitating synthesis of both optically active 1,3- disubstituted isoindoline derivatives.

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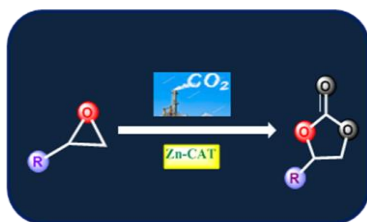
Preparation of Cyclic carbonate from CO₂ and Epoxides using Zinc-Imidazolium)-ylidene Complexes as Catalysts

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The rapid development in modern times has significantly impacted climatic changes, which were believed to be due to greenhouse gas emissions, such as CO₂ gas at large. Thus, the catalytic conversion of CO₂ into valuable products is essential to achieve carbon neutrality and long-term sustainability. Since CO₂ is a plentiful, inexpensive, non-toxic renewable C1 resource, it is an excellent choice for developing a circular economy based on value and environmentally beneficial goods such as organic acids, amides, alcohols, cyclic organic carbonates (COC), polycarbonates, and so on.¹ Several metal complexes based on salen, salophen, and phenolate as spectator ligands have been described to produce COCs. Instead, metal-ligand cooperativity using hemilabile ligands could pave the way for activating the substrates and reducing the overall experimental time for the COC preparation. We have been working with metal-NHC complexes containing mono-substituted hydroxypyridine, which serve as a hemi-labile ligand during the aerobic alcohol oxidation and Kumada-Tamao-Corriu catalytic reactions.² Extending the work herein zinc-NHC complexes containing hydroxypyridine arms of come a long way as polymerization catalysts for various ring-opening polymerization reactions and have been subsequently utilized for many reactions like C-H Borylation, Allylic Alkylation, and Hydroboration of carbon dioxide as well.³ Herein, we discussed the synthesis of various zinc-imidazolium)-ylidene complexes and their utility as catalysts for CO₂ cycloaddition reaction with different epoxides at room/elevated temperatures.



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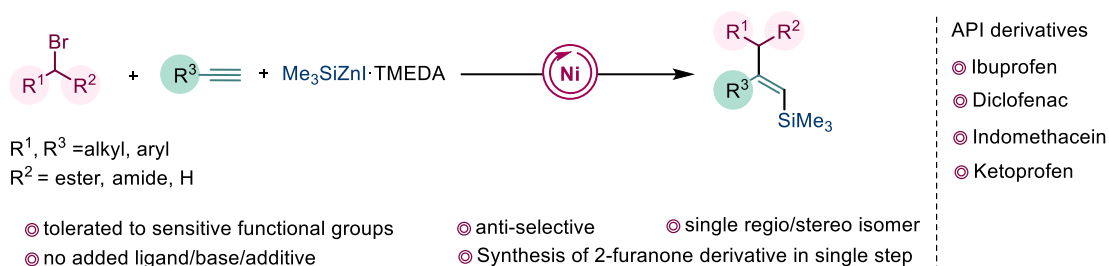
10-13 December 2023

Nickel Catalyzed Anti-Selective Silylalkylation of Alkyne

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Vinylsilane is an attractive synthetic building block in the organic transformation and synthesis of complex natural/bio-active molecules. Hydrosilylation of the alkyne is well-known to produce vinylsilane. However, the gaseous and pyrophoric nature of trimethyl silane (TMSH) and the requirement of special ligands for controlling regio- and stereoselectivity limit this methodology. The addition of silyl nucleophiles across to the triple-bond of alkyne is an alternative method; silylzinc reagents are mild and owing the functional group tolerance. We describe the nickel-catalyzed cross-coupling of alkyne, α -bromocarbonyl compound, and trimethylsilyl zinc iodide for synthesizing 1,2,2-trisubstituted vinylsilane. The unusual anti-selective trisubstituted vinylsilane is obtained through the isomerization of the vinyl nickel intermediate. The methodology is applied for the synthesis of 2-furanone derivatives in a single step.



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Enantioselective Synthesis of Room Temperature Stable P-Stereogenic Supramolecular Phosphines

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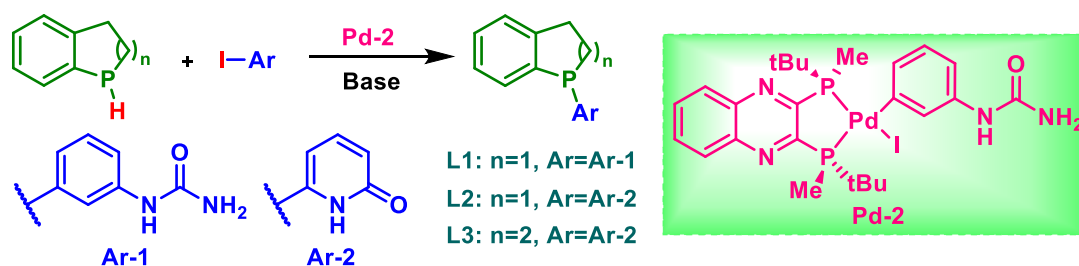
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P-stereogenic phosphine ligands play a pivotal role in asymmetric transformations, but their synthesis is highly challenging.¹ Coupling of a secondary phosphine with alkyl or aryl halide offers a direct and one-step method for their preparation. Here we present a palladium (Pd-2) catalyzed direct P-C coupling of 2, 3-dihydro-1-H-phosphindole/1,2,3,4-tetrahydrophosphinoline (secondary phosphine) and 1-(3-iodophenyl)urea/6-iodopyridin-2(1H)-one (aryl halide) to yield P-stereogenic supramolecular phosphines (L1-L3).²⁻³ P-stereogenic supramolecular phosphines with a very high enantiomeric excess of up to 99% have been prepared at room temperature (25 °C). The newly designed ligand L2 is stable at room temperature and do not oxidize on exposure to air. The enantiomeric excess (95%) in this supramolecular phosphine is retained even at higher temperatures (150 °C). The utility of this P-chiral ligand L2 is demonstrated in the Rh-catalyzed asymmetric hydrogenation of functionalized olefins 99% with enantioselectivity of upto 72%.



Scheme 1. Palladium catalyzed direct P-C coupling.

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Photoredox Minisci-type hydroxyfluoroalkylation of isoquinolines

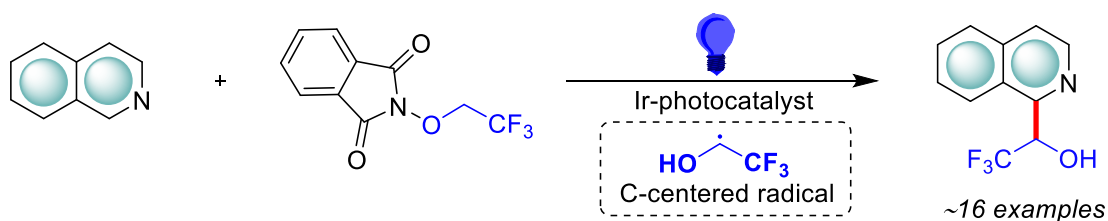
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Isoquinolines are always versatile key substructures for natural product designs and pharmaceutical target synthesis. Owing to its great importance in organic synthesis, an efficient photocatalytic approach was designed to incorporate hydroxyfluoroalkyl unit onto the isoquinolines. We here report the *N*-trifluoroethoxyphthalimide as trifluoroethanol radical precursor that enables the construction of hydroxyfluoroalkylated isoquinolines. Quenching experiments were carried out to confirm the involvement of radical pathways. Moreover, the intramolecular 1,2-HAT reactivity of *O*-centered trifluoroethoxy radical to *C*-centered trifluoroethanol radical was also examined by DFT. Based on these preliminary studies, a photocatalytic cycle was also outlined.



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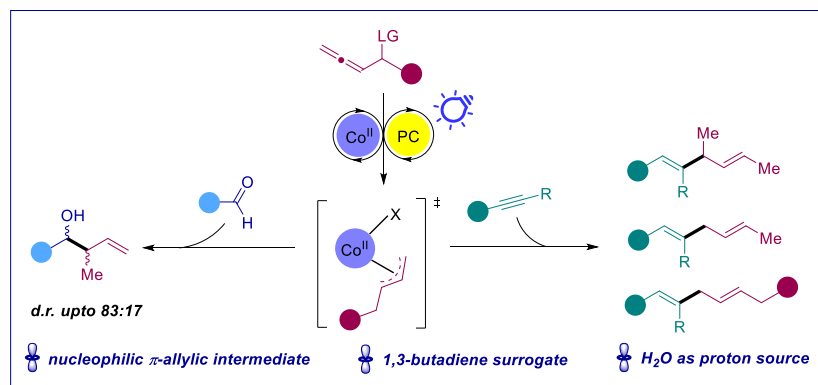
Allenyl Carbonate as Butadiene Surrogate for Cobalt-Catalyzed Reductive Coupling of Alkynes and Aldehydes

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The structural motif of skipped dienes is prevalent in fatty acids and bioactive compounds.¹ In general, these structural motifs are synthesised *via* hydrovinylation of 1,3-butadienes with alkene² or by reductive cross-coupling of alkyne with vinylcyclopropanes (or vinylsilanes) under thermal conditions,³ which needs a toxic metal-based reductant to form a low-valent metal centre. In contrast, researchers have shown in recent years that such a low-valent metal centre may be produced *in situ* under photocatalytic conditions to accomplish regio, stereo, and enantioselective organic transformations under mild, oxidant/reductant-free conditions.⁴ In this context, we have demonstrated cobalt-catalyzed reductive coupling of aldehyde with allenyl carbonate to access homoallylic alcohols utilising allenyl carbonate as 1,3-butadiene surrogate.⁵ Expanding the breadth of such reductive coupling methods, we describe photocatalytic reductive coupling of allenyl carbonate with alkynes to produce stereo and regiospecific skipped dienes. DFT calculations and a comprehensive mechanistic investigation were performed to understand the reaction pathway.



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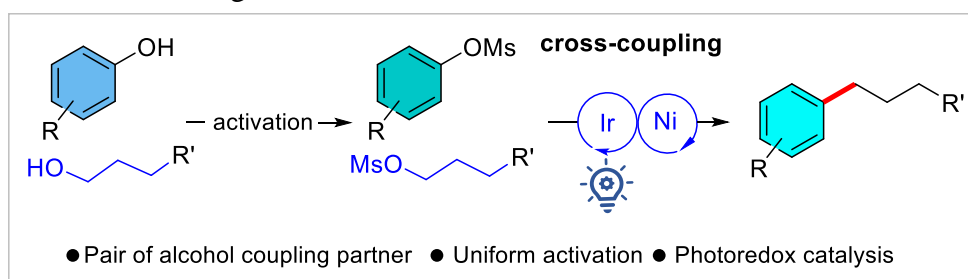
Photoredox/Nickel Dual Catalysis for C(sp²)-C(sp³) Cross Electrophile Coupling Reaction Using Alcohols as the Latent Electrophile Sources

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Abstract: Forming the C–C bond is one of the central goals in synthetic organic chemistry. The drawbacks of the traditional cross-coupling reaction between an electrophile with an organometallic nucleophile demanded an alternative synthetic protocol. In the last decade, visible light photoredox catalysis has emerged as a powerful arsenal in organic synthesis.¹ Cross-electrophile coupling has rapidly become essential to synthesizing C(sp²)-C(sp³) bonds, ubiquitous in various natural products and drug molecules.² Primarily, aryl halides with a different alkyl radical precursor make the C(sp²)-C(sp³) bond. Alcohol is a ‘native’ functional group, and the utilization of alcohol as an alkyl coupling partner is advantageous in terms of its commercial availability and inert reactivity.³ Herein, we describe a photoredox/nickel dual catalytic strategy for alkyl-aryl cross-electrophile coupling. Two alcohol coupling partners were taken, activated by mesylation, and utilized in a cross-coupling reaction.⁴ Besides several challenges to activating similar coupling partners with equal reactivity, we are pleased to have archived our cross-coupled product with an excellent yield. A dual ligand with a suitable nickel catalyst and an appropriate photocatalyst combination furnishes fruitful results. Several phenol and alkanol derivatives give the desired product a good to excellent yield, irrespective of their steric and electronic nature. We describe our aryl mesylates be a native functional group in well-known cross-coupling reactions like Suzuki, Sille, Negishi, Sonogashira, Heck etc. For the synthetic utility of the response, we have employed this strategy in various drug and natural product synthesis, starting from alcohol. Mechanistic studies reveal the photocatalytic SET event and formation of alkyl radicals in our reaction. Overall, the work will shed on using both alcohols as a carbon source for C-C bond formation.



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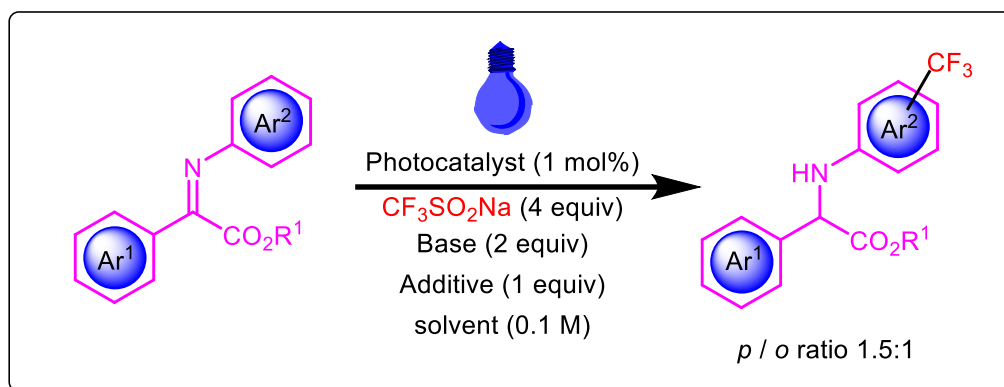
Photoredox Catalyzed Reductive Trifluoromethylation

Hrishikesh Paul[†], SK Ariyan[†], Suman Pradhan[†], Indranil Chatterjee^{†*}

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The trifluoromethyl-substituted amino acids are biologically active compounds and useful building blocks. Various research group exploited the Langlois reagent ($\text{CF}_3\text{SO}_2\text{Na}$) as the radical precursor for functionalizing various olefins and aromatic systems.¹⁻⁵ This protocol describes the visible-light-induced reductive trifluoromethylation of α -iminoesters via umpolung strategy generate N-centered radical to C-centered radical. On the other hand, trifluoromethyl radical was generated using commercially available Langlois reagent in presence of Ir(III) photocatalyst, followed by radical-radical coupling to form C-C bond. The resulting products were successfully transformed into various valuable fluorine-containing unnatural amino acids (Scheme 1).⁶



Scheme 1: Photoredox catalyzed C-C bond formation via N-centered radical.

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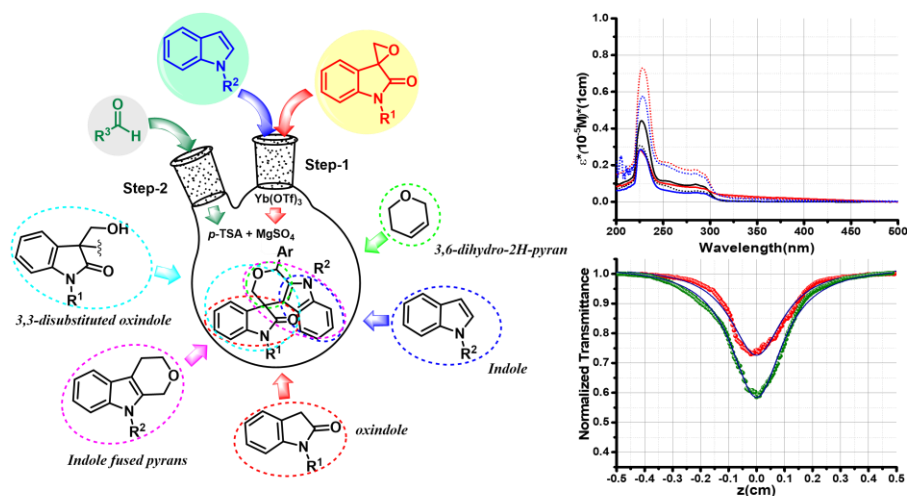
A Synthetic Route to Polyheterocyclic *spiro*-Oxindoles via Friedel-Craft type C-3 Alkylation/Pictet-Spengler Reactions of Indoles with *spiro*-Epoxy oxindoles/Aldehydes, and Study of their *three*-Photon Absorption *non*Linear Properties

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One-Pot two-step synthetic route to polyheterocyclic *spiro*-oxindoles by Lewis-acid catalyzed Friedel-Craft type C-3 alkylation of Indoles via nucleophilic ring-opening of *spiro*-epoxy oxindoles in a regioselective fashion, followed by *p*-TSA catalyzed Pictet-Spengler reaction in *6-endo-trig* fashion with aldehydes has been reported. A study of their *three*-photon absorption *non*linear properties has been reported. To the best of our knowledge, we are the first going to demonstrate that two diastereomeric pair may have different *three*-Photon Absorption *non*Linear Properties. The scope and generality of our protocol have been demonstrated by the synthesis of 19 diastereomeric pairs and the study of their *three*-photon absorption *non*linear properties.



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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Photocatalytic Electrocyclization for Synthesis of Dihydrophenanthrenes

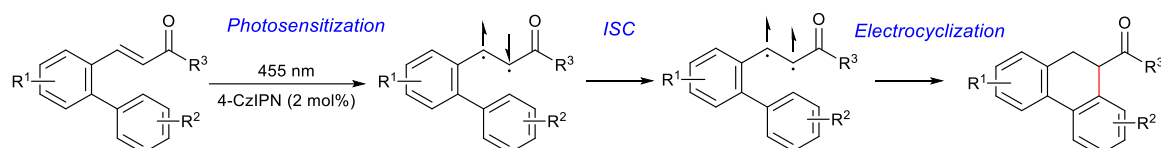
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An organo-photocatalyzed access of 9,10-dihydrophenanthrenes derivatives, motifs present in various natural products like lusianthridin, coelonin, juncusol etc., has been reported.¹ Traditionally, this scaffold is accessed through metal catalyzed reactions or via electrocyclization under UV irradiation.² A visible light mediated photocatalytic protocol for the synthesis of 9,10-dihydrophenanthrene scaffolds in a greener and sustainable manner is discussed. Mechanistic experiments lead towards a 6π electrocyclization followed by 1,5 H-shift.



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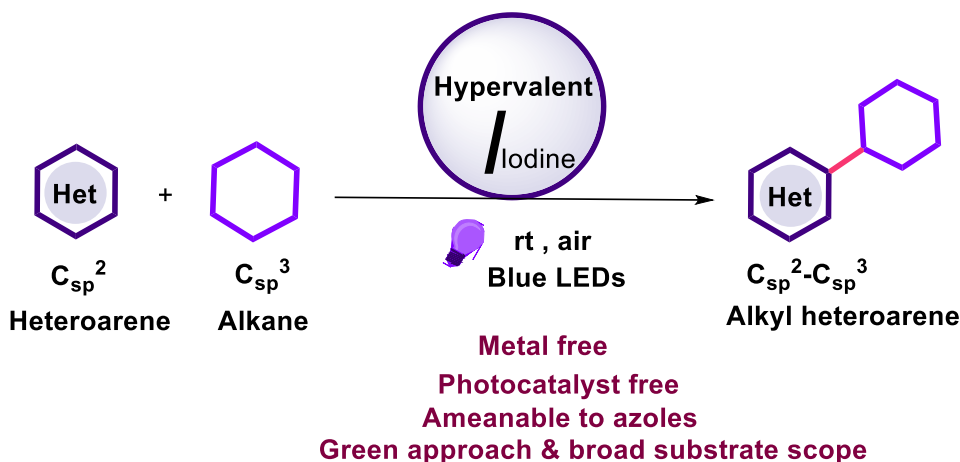
Visible Light-Mediated C–H Alkylation of Heteroarenes with Ethers and Alkanes

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We are reporting the direct alkylation of heteroarenes with simple ethers and alkanes through a photo-redox-mediated C–H functionalization pathway (Figure 1).¹⁻² Transiently generated α -oxoalkyl radicals and alkyl radicals from various ethers and alkanes, respectively, through hydrogen atom transfer (HAT) were coupled with a range of electron-deficient and electron-rich heteroarenes in a Minisci-type mechanism.³ This mild, visible light-driven protocol allows direct access to medicinal pharmacophores of broad utility using feedstock substrates and a commercially available hypervalent iodine reagent as the oxidant.



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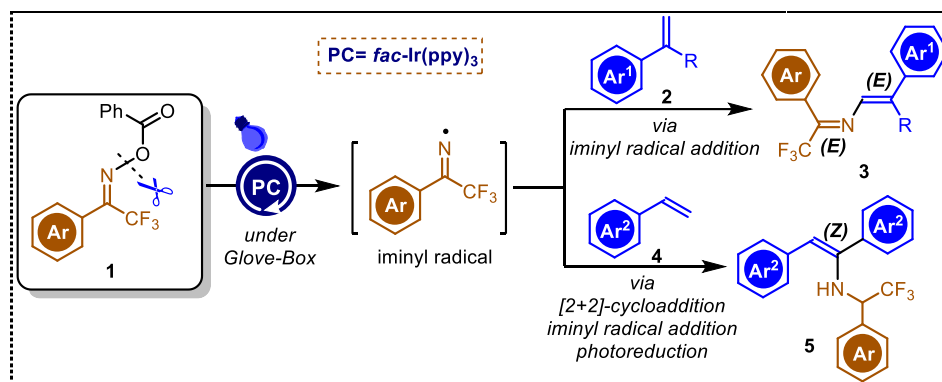
A Multitasking Photoredox-Catalysis for Stereoselective C–N Bond Formation

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Herein, we have disclosed a new C–N bond formation strategy via the generation of iminyl radicals. We have used easily synthesizable oxime esters as the radical precursor, readily generating *N*-centered iminyl radicals under blue LED irradiation in the presence of an Ir(III) photocatalyst.¹⁻³ Iminyl radicals have been used so far for the difunctionalization of olefins by Glorius *et al.*,¹ Han *et al.*² or rearranged to generate other radicals by Chen *et al.*³ and others. On the other hand, [2+2]-photocycloaddition was well known via energy transfer mechanism.⁴ Our thought process comprises of the simultaneous [2+2]-photocycloaddition and iminyl radical addition in a multifunctional way to generate aminated or iminated olefins. After a prolonged screening, we successfully achieved the *E*-selective imine addition product **3** (configuration *E, E*) using α , α' -disubstituted olefins **2**, and most interestingly, *Z*-selective aminated stilbene derivatives **5** using simple styrenes **4** via energy transfer and photoredox catalysis altogether.⁵



Scheme 1. Photoredox catalyzed C–N bond formation via N–O bond cleavage.

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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Brønsted Acid Catalyzed Photoinduced Radical Addition to Quinone Methides

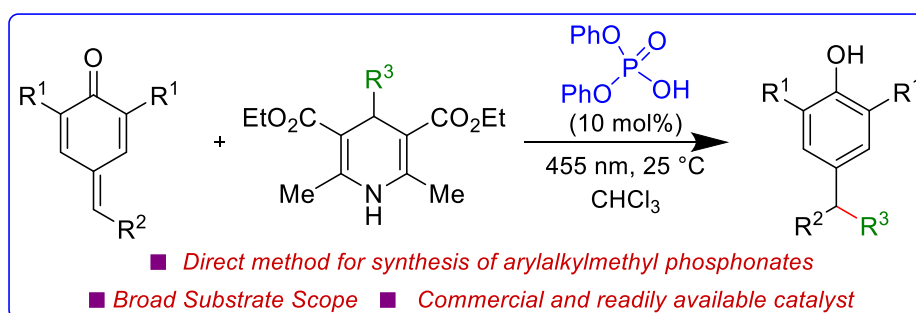
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A photoinduced radical addition to quinone methides yielding aryl methane derivatives via Brønsted acid catalysis is discussed¹. In contrast to the previous procedures where transition metals² or external photocatalysts³ were required, this methodology utilizes inexpensive and readily available DPP as a catalyst. Mechanistic investigations support formation of electron donor-acceptor complex with a pivotal role of phosphoric acid. This protocol is also successfully utilized in the synthesis of Lp(a) and cholesterol lowering agent.



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Metallaphotoredox Mediated C(sp³) – C(sp³) Cross-Coupling of Alkyl Halides and Unactivated Alkanes

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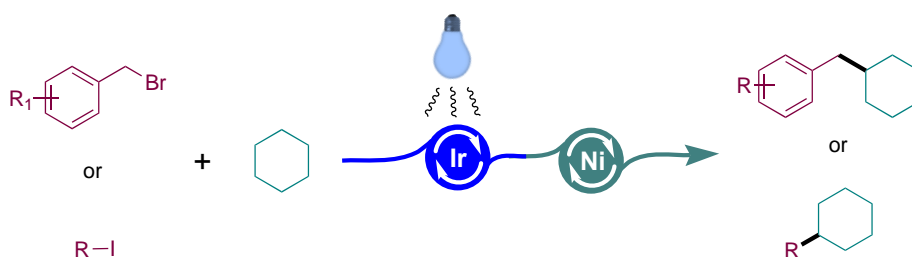
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In the past decade, merger of photocatalysis and transition metal mediated catalysis evolved to be highly successful as this evades the usage of organometallic reagents. Further, both the catalysts could be regenerated synergistically.

Hydrogen atom transfer (HAT) allows for the activation of C–H bonds to generate reactive alkyl radical species without the requirement for pre-functionalization. Macmillan and co-workers recently developed a protocol for aryl–alkyl cross-coupling from aryl halides and unactivated alkanes using photocatalyzed HAT merged with nickel¹ and this could be applied to various coupling partners as well.

Alkyl–alkyl cross-coupling reactions are highly challenging because of their susceptibility towards β -hydride elimination, protodehalogenation and dimerization. This practical limitation led to almost no exploration in forging alkyl–alkyl cross-coupling using HAT except for an attempt by Rueping with poor yield.²

We developed a robust TBADT mediated protocol for challenging C(sp³)–C(sp³) coupling of alkyl halides and alkanes. This methodology was found to be compatible with various sensitive functional groups such as free carboxylic acids, BPin etc. which could find potential applications in further functionalization. Catalyst recycling experiments revealed the potential utility of scaling up this method. Radical trap experiments revealed that both substrates are activated to generate respective radicals.³



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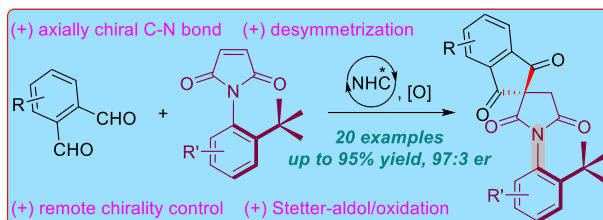
N-Heterocyclic Carbene (NHC)-Catalyzed Atroposelective Synthesis of C–N Axially Chiral Molecules via Desymmetrization and Kinetic Resolution Strategies

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A type of stereoisomer, where the chirality comes from restricted rotation around the stereogenic axis called atropisomer represents a fundamentally important chirality element in nature. Although the construction of axially chiral C–C bonds is widely known, the related synthesis of compounds bearing the C–N stereogenic axis is underdeveloped¹. The molecules bearing C–N chiral axis have found widespread application as natural products, pharmaceuticals, agrochemicals, and ligands. So, the synthesis of such molecules is highly desirable. We have recently disclosed



N-heterocyclic carbene (NHC) catalyzed atroposelective synthesis of *N*-aryl succinimides via desymmetrization of *N*-arylmaleimides (see scheme)². The NHC was involved in an intermolecular Stetter-aldol cascade of dialdehydes with prochiral *N*-aryl maleimides, followed by oxidation, which resulted in the formation of C–N axially chiral *N*-aryl succinimides. Preliminary studies on the rotation barrier for the C–N bond, temperature dependence, and detailed DFT studies on the mechanism are being presented.

The rotation along the C_{Ar}–N single bond in 2-*tert*-butyl aryl maleimides is restricted, which gives rise to two non-equivalent atropotopic faces, and the molecule is prochiral. Introduction of the amino group at the olefin carbon breaks the symmetry and makes the *N*-aryl aminomaleimides racemic with a chiral C–N axis. We have also reported the kinetic resolution of *N*-aryl aminomaleimides utilizing the possibility of an [3+3] annulation of the enamine moiety with α,β -unsaturated acylazoliums generated from 2-bromoenals³.

In addition, the first organocatalytic atroposelective synthesis of *N*-aryl phthalimides via the traditional *N*-C_{=O} disconnection under mild conditions also will be presented.

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Sequential Organo and Metal Catalyzed Reaction Between 3-Pyrrolyloxindoles and Linear Nitroenynes: Access to Cyclic Aza-Spirooxindoles

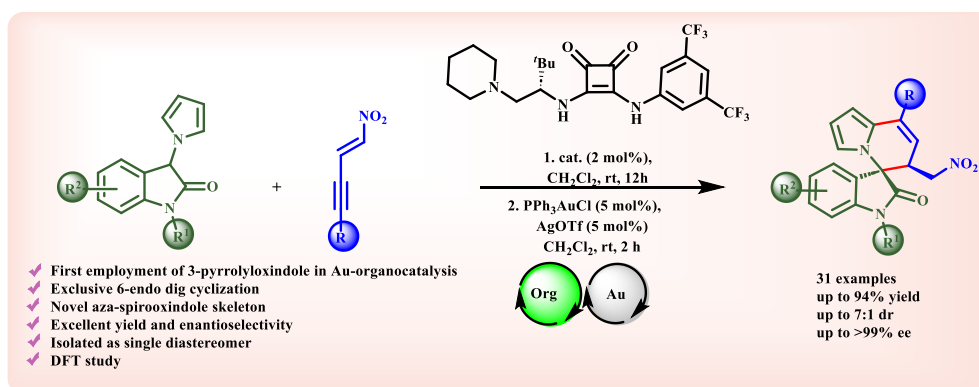
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An asymmetric Michael addition/Friedel-Crafts reaction sequence, catalyzed by a sequential catalytic system consisting of a squaramide and a combination of silver and gold salts, provides a new series of cyclic aza-spirooxindole derivatives in excellent yields (up to 94%) and high diastereo- and enantioselectivities (up to 7:1 dr, up to >99% ee). Computational study has also been performed.



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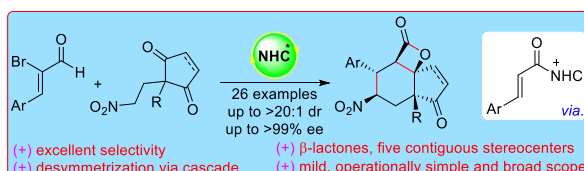
N-Heterocyclic Carbene Catalyzed Enantioselective Synthesis of Tricyclic β -Lactones and Pyrazoloquinolin-3-one Derivatives

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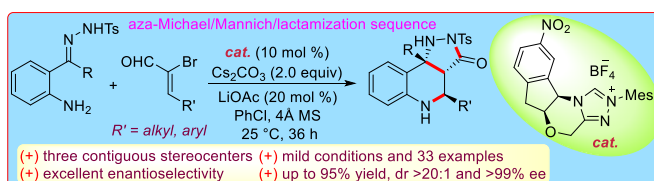
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Although N-heterocyclic carbenes (NHCs) are well known for the umpolung of aldehydes and related electrophiles, these catalysts can catalyze transformations in normal mode proceeding via α,β -unsaturated acylazoliums.¹ In this context, we have developed the NHC-catalyzed desymmetrization of cyclic 1,3-diketones, allowing the enantioselective construction of tricyclic β -lactones with five contiguous stereocenters, including two quaternary centers (Scheme 1). This Michael-aldol-lactonization cascade afforded the desired biologically relevant cyclohexane-fused β -lactones in moderate to good yields and excellent stereoselectivities. Mildness, operational simplicity, broad scope, step economy, and high selectivity are the notable features of this reaction.²



Scheme 1: Desymmetrization of cyclic 1,3-diketones via α,β -unsaturated acylazoliums

The key α,β -unsaturated acylazolium intermediate has also been found to mediate other effective cascades for synthesizing various carbocycles and heterocycles. In this regard, given the wide range of pharmacological properties of the pyrazolo-[4,3-c] quinolone core structure, we demonstrated the enantioselective synthesis of functionalized pyrazoloquinolin-3-ones via an NHC-catalyzed cascade reaction of α -bromoaldehydes with 2-aminoaryl N-tosyl hydrazones. The in situ-generated α,β -unsaturated acylazolium intermediates undergo an aza-Michael-Mannich-lactamization cascade, delivering the tricyclic products bearing three contiguous stereocenters, including a sterically demanding quaternary stereocenter, with high enantioselectivities (Scheme 2). Highly enantioselective construction of biologically relevant nitrogen-containing tricycles, mild reaction conditions, and broad scope are the noteworthy features of this domino reaction.³



Scheme 2: NHC-Catalyzed Enantioselective Synthesis of Pyrazoloquinolinones

Moreover, the preliminary studies on NHC-catalyzed synthesis of C-O axially chiral molecules also will be presented.

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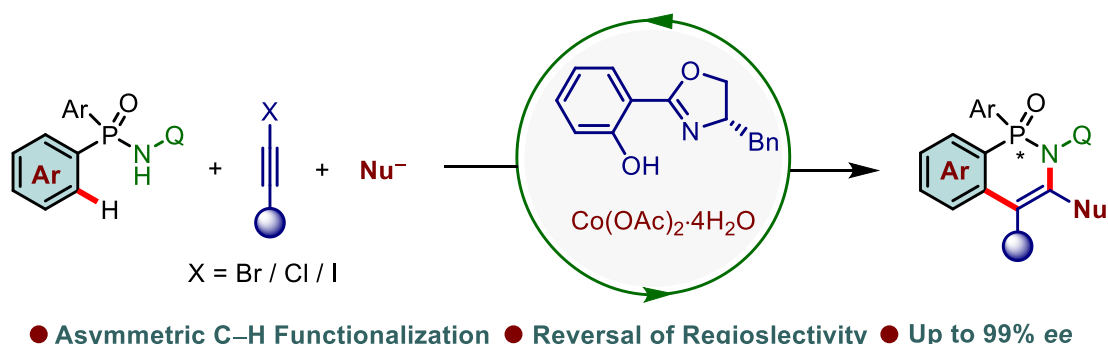
Reversing the Regioselectivity of Asymmetric C-H Bond Annulation with Bromoalkynes Under Cobalt Catalysis

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In the context of sustainable catalysis, it is essential to fulfill present needs without compromising those of the future.^[1] In this regard, the application of commercially available cobalt salts in enantioselective C–H bond functionalization for synthesizing enantiopure scaffolds has brought about a transformative shift in the landscape of asymmetric C–H bond functionalizations.^[2] In this study, we present an unconventional protocol for achieving regio-reversal and enantioselective C–H and N–H bond annulation of phosphinamide with bromoalkyne through desymmetrization.^[3] The reaction proceeds through ligand-assisted cyclocobaltation, followed by the regioselective insertion of bromoalkyne between Co–C, subsequent reductive elimination, and halogen exchange with carboxylate, providing access to various P-stereogenic compounds with excellent enantiomeric excess (up to 99%) and high yield. Moreover, the isolation of a competent reaction intermediate, along with various control experiments and a DFT study, supports the proposed reaction pathway.



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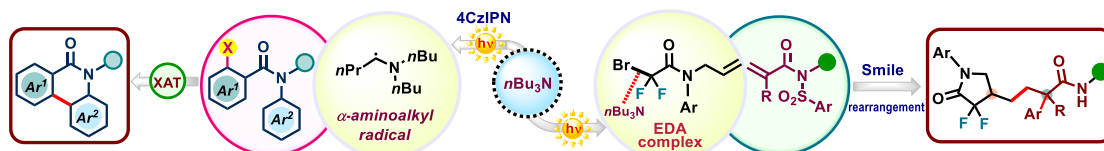
Visible Light Induced α -Aminoalkyl Radical Mediated Cascade Processes: Demonstration of XAT and SET Events

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Abstract



Visible light-induced photocatalysis is fundamental in organic chemistry, garnering significant attention from the synthetic community. In this context, we have developed a XAT strategy utilizing α -aminoalkyl radicals¹ for the generation of aryl radicals at room temperature, which is applied for intramolecular cyclization reactions *en route* to biologically relevant alkaloids. Starting from simple halogen-substituted benzamides under visible light irradiation in the presence of an organophotocatalyst (4CzIPN) and $n\text{Bu}_3\text{N}$ allows the modular construction of the phenanthridinone core, offering facile access to drug analogs and alkaloids from the Amaryllidaceae family. The reaction pathway most likely involves a quantum mechanical tunneling-enabled transfer event to achieve aromatization-halogen atom transfer.² Meanwhile a photocatalyst-free visible-light-induced EDA-based³ radical cascade reaction of *N*-allylbromodifluoroacetamides and *N*-alkylacrylsulfonamide, featuring a radical Truce-Smiles arrangement, is identified for the modular construction of the difluoroamid pyrolidone core.⁴

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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Catalytic pyrolysis of high density polyethylene to petrochemical products with M-zeolite based catalysts

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Chemical recycling of waste plastics has been proposed as one of the possible ways to obtain petroleum-derived products (fuels and chemicals) from waste plastics in a sustainable and commercially feasible way however, there is a lack of deep understanding of the effect of different silica alumina ratio catalysts on the plastic pyrolysis oil. Zeolites are used as catalysts, absorbents and desiccants in gas purification, and separation processes. Changing the silica-alumina ratio of these zeolite catalysts affects the composition of plastic pyrolysis oil. These zeolite catalysts with different silica-alumina ratios are synthesized with the help of the hydrothermal process of catalyst synthesis. The synthesized catalyst has been characterized by the help of different techniques like TGA, XRD, BET and NMR. TGA analysis shows the high thermal stability of these catalysts, XRD analysis confirms the crystalline structure of all the catalysis, and BET analysis shows porosity and the high surface area of the catalysts. The synthesized catalysts have been used to carry out the pyrolysis reactions. The pyrolysis process is carried out in a batch reactor at a temperature range of 400-500°C with high density polyethylene (HDPE). The recovery of pyrolysis is around 70%. The products like pyrolysis oil, gases and residue can be further characterized with the help of different analytical techniques to understand the effect of variation of silica-alumina ratio on the pyrolysis product yield and compositions.



Ru-Pt Laden 'Black gold' as Air Stable Plasmonic Catalysts for Acetylene Semi Hydrogenation

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Abstract

In general, catalysts for reduction are unstable in the presence of air. A plasmonic reduction catalyst that is stable only in air has been described in this work. A highly active, selective and particularly air-stable plasmonic reduction catalyst for acetylene semi-hydrogenation was developed by loading Pt-doped Ru nanoparticles¹ on 'dendritic plasmonic colloidosomes (DPC)', also known as black gold². With over 90% selectivity and productivity of 320 mmol g⁻¹ h⁻¹ of ethene, the DPC/RuPt catalyst outperformed nearly all previously reported catalysts. The critical role of co-existing metal oxide and metal phase was evidenced by high catalytic activity and long-term stability for at least 100 h, which could only be achieved by providing continuous airflow along with the reactant feed. Plasmon-mediated simultaneous reduction and oxidation of the active site during the reaction were responsible for the unprecedented stability of the catalyst which was demonstrated by various spectroscopic analyses (XPS, EXAFS, and XANES). FDTD simulations showed a five-fold enhancement in the electric field as compared to pristine DPC due to the near-field coupling between the RuPt nanoparticles and DPC. The KIE measured in light was larger than in the dark at all temperatures, implying the contribution from the non-thermal effects along with the photothermal activation of the reactants as a result of plasmonic activation.³⁻⁶ In-situ FTIR studies provided insight into the molecular reaction mechanism over the oxide surface and highlighted the role of the intermediates in determining selectivity.

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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Effect of alkaline treatment of zeolite catalyst in the catalytic cracking of high-density polyethylene in a lab-scale reactor

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Global plastics production increased vigorously in the last few decades and Plastic waste has become one of the biggest global environmental issues thus recycling such massive quantities is targeted. Low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) are considered among the main types of plastic waste. Some alternative measures have been developed to manage waste plastics, like recycling and energy recovery methods. Chemical recycling through pyrolysis is the preferable method to resolve waste plastic management as it allows the production of various products like fuels and chemicals. In the present study, the effect of desilication of zeolite catalyst on the product distribution in catalytic cracking of HDPE has been studied. The catalyst has been characterized by XRD, SEM, and, BET while liquid products have been characterized by GC-MS, FTIR, and proton NMR analysis for identifying molecular spectra. Post-treatment of the catalyst results in higher liquid and low gaseous conversion than catalytic (without treatment) cracking. Along with this post-treatment of the catalyst results in higher olefinic content than thermal pyrolysis of HDPE. All these hydrocarbons can be used for different applications like fuels and chemical intermediates etc.



Nickel Oxide Loaded Antimony Doped Tin Oxide as a Photo-electrochemical Oxygen Evolution Catalyst

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The oxygen evolution reaction (OER) is considered as the bottleneck in water splitting as it is kinetically slow and requires high overpotentials to reach substantial current densities.¹ IrO₂ and RuO₂ are well known OER catalysts, however these traditional catalysts are expensive and not sustainable for long term utilization.² Hence, researchers are towards identifying cheap and efficient electrocatalysts such as oxides and hydroxides of earth abundant metals such as Nickel (Ni).³ In this current work, we have synthesized Nickel

Oxide (NiO) nanoparticles (NPs) in-situ with Antimony Doped Tin Oxide (ATO) NPs via a modified one pot sol-gel method. Here the template, porous ATO enhances the active surface area and provides a photo-assisted OER platform for NiO. The prepared catalyst has shown excellent electrochemical oxygen evolution reaction from an alkaline electrolyzer (1M NaOH) with a recorded onset potential of 1.59 V at 10 mAcm⁻². Further, considering the good photo-absorption of ATO nanoparticles in the visible range, we have studied the effect of visible light irradiation upon catalyst. The catalyst showed remarkable enhancement in current densities and considerable reduction in onset overpotential (1.51 V at 10 mAcm⁻²) under this photo-electrochemical condition. The integration of n-type ATO with p-type NiO has led to the improved photoinduced charge separation enabling enhanced OER activity of the NiO/ATO catalyst.

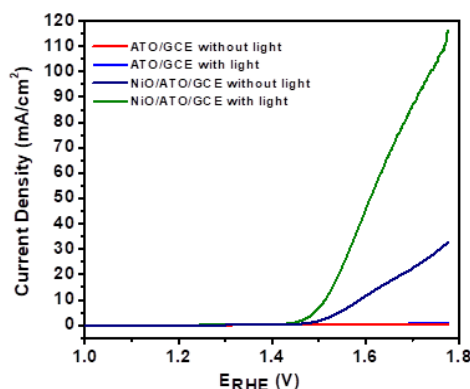


Figure 1. Comparison of OER polarization curves for ATO and NiO/ATO catalysts without and with irradiation on GCE in N₂ saturated 1M NaOH at a scan rate of 10 mV/S

The catalyst showed remarkable enhancement in current densities and considerable reduction in onset overpotential (1.51 V at 10 mAcm⁻²) under this photo-electrochemical condition. The integration of n-type ATO with p-type NiO has led to the improved photoinduced charge separation enabling enhanced OER activity of the NiO/ATO catalyst.

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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

One Pot Synthesis of Sponge-Like Amine Functionalized Silica for CO₂ Utilization into Carbonates at Ambient Pressure

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The abrupt rise in temperature with the irregular seasonal change is strong evidence of losing the homeostasis balance of nature, one of the reasons is supposed to be the anthropogenic CO₂ emission. At this cutting edge, CO₂ capture and utilization have become one of the foremost concerns of research worldwide to suppress global warming and its adverse effects. Amine-based CO₂ capture is a well-known technology but the carbon capture and storage (CCS) technique involves large capital investment. Whereas utilization of CO₂ as fuel like methanol requires a green hydrogen source which is a big challenge. Converting CO₂ into industrially valuable chemicals like carbonates, polycarbonates, etc. will be a good alternative in the field of carbon capture and utilization (CCU). This work demonstrates the heterogeneous catalysis of sponge-like mesoporous amine-functionalized silica catalysts with high surface area (541 m²/g) in the conversion of styrene oxide to styrene carbonate at ambient pressure of CO₂ at 120°C in the presence of co-catalyst tetrabutylammonium bromide (TBAB). Styrene carbonate has the potential application in the field of organic electrolytes in lithium-ion batteries, as intermediate for biomedical and pharmaceutical fine chemical synthesis, and in the agriculture industry as herbicide and disinfectant. The optimum ratio of the Lewis acidic and basic surface silanol and amine groups and the high surface area make this catalyst efficient for conversion (90 %) of styrene oxide to styrene carbonate (99 %) at balloon pressure of CO₂.



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Polystyrene stabilized nano-catalyst development and its applications for carbonylative transformation using oxalic acid as C1 source

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The development of heterogeneous transition metal nano-catalyst and their applications have gained immense interest due to their exceptional features such as sustainability, high reactivity and selectivity, ease of handling and significant recyclability. In this context, our research group is continuously developing mono as well as bimetallic polystyrene (PS) supported transition metal nano-catalysts which are well characterized by SEM, HR-TEM, SEM-EDX, ICP-AES, P-XRD, XPS analysis and exploring them in different fields of organic synthesis including carbonylative transformations.¹ The utilization of CO has gained the immense interest of scientific community for the synthesis of various valuable molecules. However, CO gas being colourless, odourless, and highly toxic in nature is very tough to handle and requires sophisticated equipment. To overcome these challenges, we have explored oxalic acid as a solid, economic and efficient *in-situ* as well as *ex-situ* CO source which exhibits remarkable synergistic effects with polystyrene stabilized nano catalyst in different carbonylative transformations.² Recently, we have applied polystyrene supported palladium (Pd@PS) nano-catalyst for carbonylative Suzuki-Miyaura reaction for the synthesis of diversely substituted biaryl ketones using oxalic acid as an *ex-situ* C1 source. The reaction has been carried out in ppm-level catalyst loading under ligand and additive free conditions. Interestingly, carbonylative as well as di-carbonylative Suzuki-Miyaura cross-coupling products were also obtained in moderate to excellent yields. Furthermore, we explore Pd@PS for tandem aminocarbonylative coupling of benzoxazole with aryl iodides to synthesize *N*-(2-hydroxyphenyl)benzamides. This protocol involves the ring opening of benzoxazole to 2-aminophenol followed by aminocarbonylative coupling with aryl iodides.

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Reductive Depolymerization of Lignin using Ni-Co/Al₂O₃ Catalysts for the Production of Aromatic Based Chemicals

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Abstract

The global energy crisis and related harmful effects to environment have stimulated extensive R&D programs on efficient biomass conversion. The most abundant lignocellulosic biomass (LCB) has been anticipated as a potential substitute of non-renewable fuels and chemicals. In past decades, there has been huge technological progress in the conversion of sugars to fuels and fine chemicals. However, complete usage of LCB is still rely on the third component, 'lignin'. In the present study reductive depolymerization reaction of lignin was investigated using Ni-Co/ γ Al₂O₃ catalyst under varying reaction conditions. The xNi_yCo/Al₂O₃ was prepared by co-impregnation method and characterized by using BET, XRD, FTIR and UV-Vis Spectrophotometer. The characterization results revealed the formation of Ni-Co alloy depending on Ni/Co mole ratio. The primary products formed during lignin depolymerization reaction were guaiacol, pyro-catechol, and phenols. The Ni/Co mole ratio and reaction conditions have significant effect on lignin conversion and guaiacol yield. It was observed that the guaiacol selectivity increases with the increase in Ni/Co mole ratio. The maximum yield of guaiacol (80.78%) was obtained at optimized reaction conditions: Ni-Co mole ratio= 1:1, total metal loading=20%, reaction time=2 h, reaction temperature=533 K, water-THF ratio=1:1, catalyst to lignin ratio=1:6, NaOH-lignin ratio=0.1:1, and solvent-lignin ratio=150:1. The plausible lignin depolymerization pathway was also proposed by considering the product distribution obtained under various process parameters.

Open Chain Conjugated Azomethine Copper Complex Based Sensor For Dual Mode Fluorescence as well as RGB Color Sensing of Histamine in Diverse Biological Fluids and Fish Samples

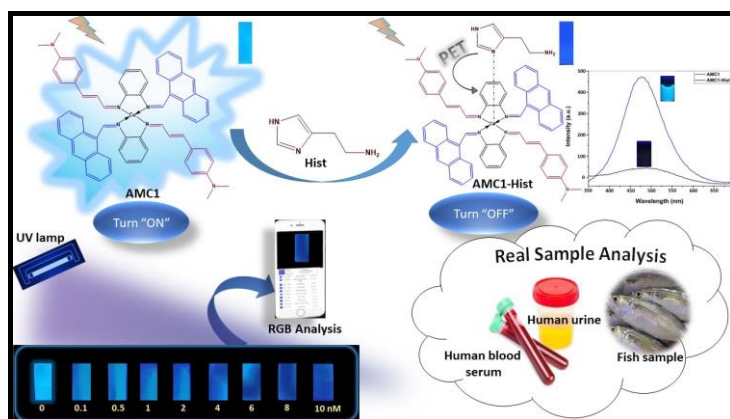
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Histamine (Hist), the molecule attributed to food poisoning, is nowadays recognized as a legitimate indicator of seafood freshness, thus consequently, its quick and simple quantification seems critical. In the current work, a quick and straightforward analytical method has been designed to determine Hist as an indirect strategy to check the amount of food freshness. Fluorescent Hist sensor with open chain conjugated azomethine derived copper(II) complex (AMC1) deposited onto silica coated alumina based test strips was fabricated and was depicted to respond effectively to Hist. The AMC1-Hist binding generated reduction of the fluorescent signal. Under the optimal parameters of the reaction condition, the designed sensor can determine LOD upto 0.404 nM/ 404.9 pM with in the linear range between 0-20 nM ($R^2 = 0.9987$). Fluorophore AMC1 exhibited high affinity for Hist binding constant ($K_b = 2.580 \times 10^7 \text{ M}^{-1}$). The detailed investigation revealed that such a high sensitivity of the designed sensor towards Hist is attributable to the existence of PET mechanism. The stern volmer plots, Job's plot, Benesi-Hildebrand plot and ¹H-NMR titrations as well indicated the existence of substantial interactions between AMC1 and Hist. The conducted selectivity tests provided distinguishable selectivity for Hist detection over various other bioanalytes. Furthermore, this work was subsequently applied for the estimation of Hist in the complex biological milieu such as human blood serum and urine samples. Additionally, the presented sensing assay was also applied to quantify the Hist residues in seafood samples (*Tuna* and *Mackerel* fish) acquiring a satisfactory precision and accuracy with recovery rates ranging from 95.681 to 105.935%. In addition, the sensor coated fluorescence paper based test strips were also fabricated for the on-site detection of Hist. Additionally, the applicability of smartphone relied RGB analysis significantly streamlined the operation process and speeds up the detection procedure. With excellent stability and ultra-sensitivity, these strips can be used to monitor the quality change of canned fish at different temperatures, so that people can avoid suffering from Hist poisoning, suggesting that it holds great potential in the intelligent system for on-site detection and real-time monitoring.



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Morphology-controlled perovskites synthesis and application

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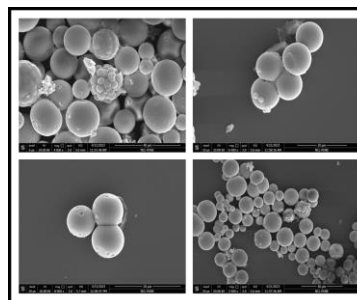
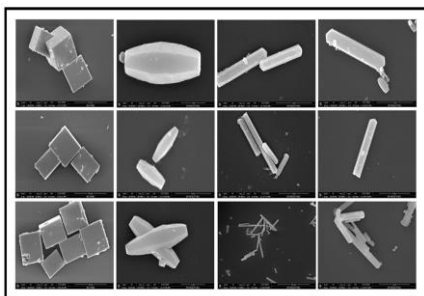
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Shape-controlled synthesis and activity of the metal nanoparticles are well explored in material science. In the same scenario, mixed metal oxides are also explored in the field of catalysis, where synergistic effects among two metals clearly play roles in the activity of the materials. Still, shape or facet-dependent synthesis and activity have yet to be explored for the mixed metal oxides. It can open several ways for the scientific community to apply the mixed metal oxide material. In mixed metal oxides, Perovskites are a class of inorganic materials that have attracted considerable attention in other areas of materials chemistry but have yet to be much explored in catalysis. They are well known for stability and, with easy and scalable preparation routes, are the ideal choice as catalysts for fine chemical synthesis. We have synthesized the shaped perovskites with the combination of Lanthanum and transition metal (Fe, Cu, Mn etc.) using the hydrothermal method with various morphology. The poster presentation will discuss shape-dependent catalysis (Oxidation/reduction).



Indian patent entitled “SHAPED METAL OXIDES (PEROVSKITES) AND PROCESS FOR PREPARATION THEREOF” Provisional application no. – 02311033445

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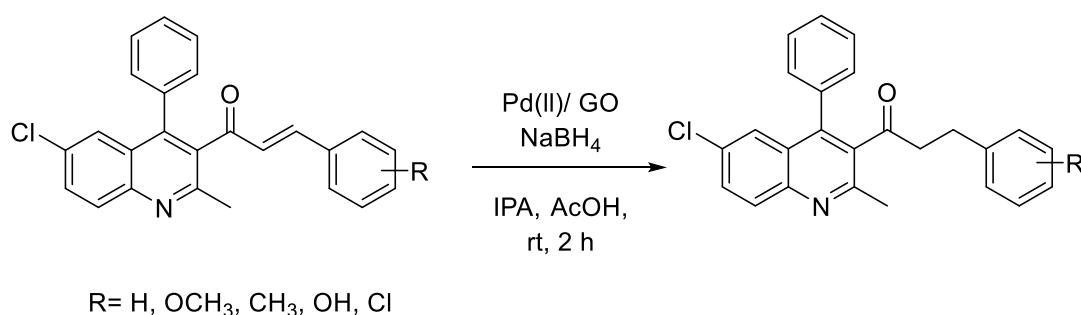
Selective reduction of α,β -unsaturated carbonyl compounds via transfer hydrogenation using Palladium/GO catalyst

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Herein we reported a chemoselective reduction of alkenes over ketones using a sustainable Pd/GO heterogeneous catalyst for transfer hydrogenation of α, β -unsaturated ketones.¹⁻² The amount of Pd loading in the catalyst is 20% also it is well characterized using powder XRD, UV-DRS, IR and TEM. The catalyst is applied to the chemoselective reduction of quinoline scaffolds which possess promising biological applications in the field of medicine.^{3,4} The catalyst is recyclable up to three cycles without erosion in the yield. The compatibility of the substrate scope, ambient room temperature and shorter reaction time are the highlights of this study. A detailed mechanistic study was conducted to elucidate the plausible reaction mechanism.



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Methane dehydroaromatization using Molybdenum-supported coal waste material catalyst

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Methane is 21 times more potential greenhouse gas¹ than CO₂, and its amount in the atmosphere increases yearly. There are so many direct and indirect routes for methane conversion. An indirect way of methane is energy intensive and complex. The indirect ways for methane conversion include dry reforming, steam reforming, bi-reforming, tri-reforming, and partial oxidation of methane (POM). Methane dehydroaromatization (MDA) is a direct way to convert methane into aromatics². Aromatics are employed to make plastics polymers, Polystyrenes and styrenic products such as SBR latex & ABS, phenol & cyclohexane and nitrobenzene production. This work utilizes a molybdenum-supported coal waste material catalyst (CWM). Here the coal waste material is the source of silica & alumina³. The methane conversion is 8%, and the selectivity for the benzene is more than 85% at 700°C & GHSV 1700 mlg⁻¹h⁻¹ with 0.3gm catalyst. The feed ratio for the reaction CH₄:N₂=4:1 & total flow for the reaction is 8.5ml/min. The coke deposition in our catalyst is lesser compared to the well-known catalyst Mo/ZSM-5 for MDA reaction. The MDA reaction gives byproducts, including carbon monoxide, ethane, ethylene, propylene, and hydrogen.

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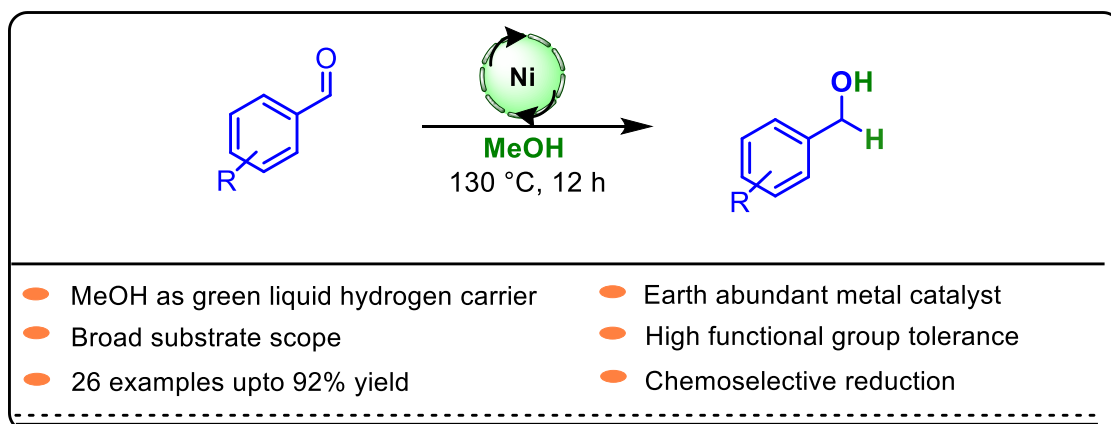
Earth abundant Ni-Catalysed Transfer Hydrogenation of Benzaldehyde Using Methanol as a Liquid Hydrogen Carrier.

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The creation of a clean and renewable energy source has gained importance in recent years. Additionally, a novel catalytic system that uses both cheap and abundant catalysts and environmentally friendly solvents is very desirable from the standpoint of practical and sustainable chemistry.¹ Along the line, here we unveiled a mild catalyst for the selective reduction of aldehydes and its derivatives has been investigated using the widely available Ni metal supported on graphitic carbon nitride (Ni/GCN) using methanol as both hydrogen source.² Methanol acts as a liquid hydrogen carrier with its high hydrogen content (12.6 wt %), low cost, and ready availability which makes it attractive and alternate to existing hydrogen sources.^{3, 4}



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Defect-Engineered Nickel Supported Ceria as an Efficient Catalyst for Reverse Water Gas Shift Reaction

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The importance of developing strategies to utilize CO₂ for carbon valued products has increased significantly due to the negative impact of global warming and climate change on human well-being. There is an urgent need for an inexpensive and efficient novel catalyst with the ability to convert CO₂ into fuels and chemicals of industrial significance, thereby serving as a double-edged sword against serious environmental issues, by creating a carbon neutral cycle, and energy crisis. To address this, defected catalyst ceria (CeO₂) with oxygen vacancies was synthesised using protocol similar to DFNS^[1] loaded with Ni using wet impregnation protocol.^[2] The synthesized catalysts were tested for Reverse Gas Water Shift (RWGS) reaction at various temperatures. To enhance their productivity at lower temperatures several catalysts with different loadings of Ni on ceria were explored. Different characterisation techniques like pXRD, SEM, TEM, ICPMS, EDX, BET, UV-DRS, TGA, H₂-TPR were employed to understand the physical and chemical properties of these catalysts. Attempts were made to understand the effect defects in ceria and different Ni loadings on ceria to enhance the catalytic performance (activity and selectivity).

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Plasmon Assisted Efficient Photo-Electrochemical Water Splitting By Au-MoS₂/NiO/Ni Foam Hybrid

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Rational design of bi-functional catalysts for efficient water splitting in alkaline medium under photo-electrocatalytic conditions through the coupling of photo-electron transfer and surface catalytic reaction holds great promise for sustainable energy conversion. Hydrogen evolution reaction (HER) in alkaline medium is challenging due to the requirement of an additional water dissociation step.¹ The porous NiO/Ni foam structures provide active sites for water dissociation with high oxygen evolution reaction (OER) activity. However, their HER activity is limited presumably due to the lack of H-adsorption sites. Hence, here we demonstrate a simple strategy to develop a hybrid catalyst for overall water splitting by in-situ coupling of plasmonic Au nanoparticles-decorated MoS₂ nanosheets with NiO/Ni foam (Au-MoS₂/NiO/Ni foam), through which the combination of active sites for both water dissociation and hydrogen adsorption can be achieved.² Hence, our designed Au-MoS₂/NiO/Ni foam hybrid exhibits superior alkaline HER and OER performance with lower overpotentials compared to the template catalysts under both electro- and photoelectro-catalytic conditions. The plasmonic excitation with white light irradiation has significantly improved the overall water-splitting performance by strong plasmon-exciton coupling in the Au-MoS₂/NiO/Ni foam hybrid catalyst.

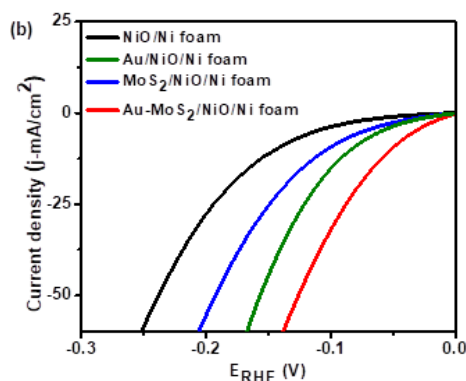


Figure 1 Cathodic LSV curves for various catalysts under white light irradiation in N₂ saturated 1 M NaOH at a scan rate of 10 mV/s

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Indo-French Seminar on Catalysis for Sustainability

10-13 December 2023

Utilization of agro-waste, waste paper, cotton, and poly/monomeric carbohydrates into 5-hydroxymethylfurfural and furfural

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Lignocellulosic biomass is one of the widely distributed, naturally abundant, renewable, and sustainable feedstock that has attracted considerable attention as a promising aspirant for the alternative to fossil carbon sources. In this perspective, 5-Hydroxymethylfurfural (HMF) and furfural are envisioned as key molecules derived from biomass and found direct applications in textile, resin, drug (APIs production), bio-polymer, and biofuel industries.¹ The complex structure of such biomass generally makes them recalcitrant for their further conversion to high value furan based molecules and assumed a challenging issue for the scientific community. In this context, last few years our research group has been working diligently for the development of new processes for economical, highly selective, and scalable production of 5-HMF and furfural.² Under this framework, we have developed a one-pot greener approach for the direct utilization of agricultural waste (corn-cob, sugarcane bagasse, rice-straw, and corn-straw), various waste papers (cardboard, newspaper, tissue paper, white paper), cotton, and poly/monomeric carbohydrates into 5-HMF and furfural under a hydrothermal reactor system.³ The synergistic behavior of reagent system was critically optimized to procure good yields of desired products with ~90-95% UPLC purity without any tedious purifications. Overall, the developed process is highly selective, non-hazardous, cost-effective, and avoids pre-treatment steps with high yields of 5-HMF and furfural.

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Copper Oxidases: Emergence of Copper(II) Complexes as Functional Models

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Copper oxidases such as ascorbate oxidase (AO) or amine oxidase (AmO) (type-2 copper) catalytically convert ascorbic acid to dehydroascorbate or amine to aldehyde and catechol oxidase (CO) (type-3 copper) catalyzes the conversion of catechol to o-quinone in the presence of dioxygen. Copper-containing metalloenzymes are constantly being studied in terms of their structural or functional models. The ability to mimic not only the active site but also the secondary interactions of these enzymes could lead to the formation of new complexes, which could improve the catalytic activity of mimic models. Thus, the ternary copper(II) complexes of the type [Cu(pbp/pbtp)-(pybzim)](ClO₄) (where Hpbp or Hpbtp is the tridentate N₂O or NSO Schiff bases respectively, derived from the condensation of salicylaldehyde and 2-(2-amino-phenyl)benzimidazole (Hpbp) or 2-(2-aminophenyl)benzothiazole (Hpbtp) and pybzim is 2-(2-pyridyl)benzimidazole) were synthesized. Crystal structure of [Cu(pbp)(pybzim)](ClO₄) displays distorted square pyramidal (4+1) geometry (τ , 0.31) with CuN₄O chromophore. Interestingly, it is associated in pairs due to intermolecular N-H...O hydrogen bonding interaction between bzim nitrogen and phenolate oxygen. They show a d-d band (697-709 nm) and a charge transfer band (414-425 nm) in methanol. The EPR spectra at 77 K are axial suggesting the square-based geometry with CuN₄O chromophore. They are redox active and exhibit a quasi-reversible Cu^{II}/Cu^I couple (methanol vs. SCE). They are catalytically active in the oxidation of ascorbic acid (H₂A) in the presence of dioxygen, Remarkably, catalytic oxidation of H₂A to dA (dehydroascorbic acid) is highly effective at [H₂A]:[complex] mole ratio of 1:200. The catalytic efficacy of the complex for the conversion of amine to aldehyde by H₂O₂ was investigated with benzylamine in MeOH:H₂O mixture (4:1 v/v). No observable benzaldehyde formation occurs in the reaction between the complex and benzylamine or benzylamine and H₂O₂ in the absence of the complex. However, the deamination of benzylamine catalyzed by the complex in the presence of H₂O₂ induces the conversion of benzaldehyde with good yield (>80%). Also, the complexes effectively catalyze the oxidation of 3,5-DTBC (methanol or buffer solution pH 7.6) to the corresponding 3,5-DTBQ with significant K_{cat} values in the range of 10³ to 10⁵, which are comparable to the best values reported in the literature. The high catalytic efficiency is due to the presence of weak self-assembled intermolecular association, availability of labile phenolate oxygen donor, and reversible redox process with positive potential.

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Redox-Neutral Decarboxylative Cross-Coupling of Oxamates with Aryl Bromides

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Dual Nickel-photo redox enabled the direct synthesis of amides through cross-coupling of Cesium oxamates with aryl bromides has been developed. This methodology's key advantages are mild reaction conditions, utilizing organic dye as a photocatalyst and employing readily available starting chemicals as coupling partners. Furthermore, the synthetic utility of the methodology was successfully implemented for the carbamoylation of biologically relevant molecules.

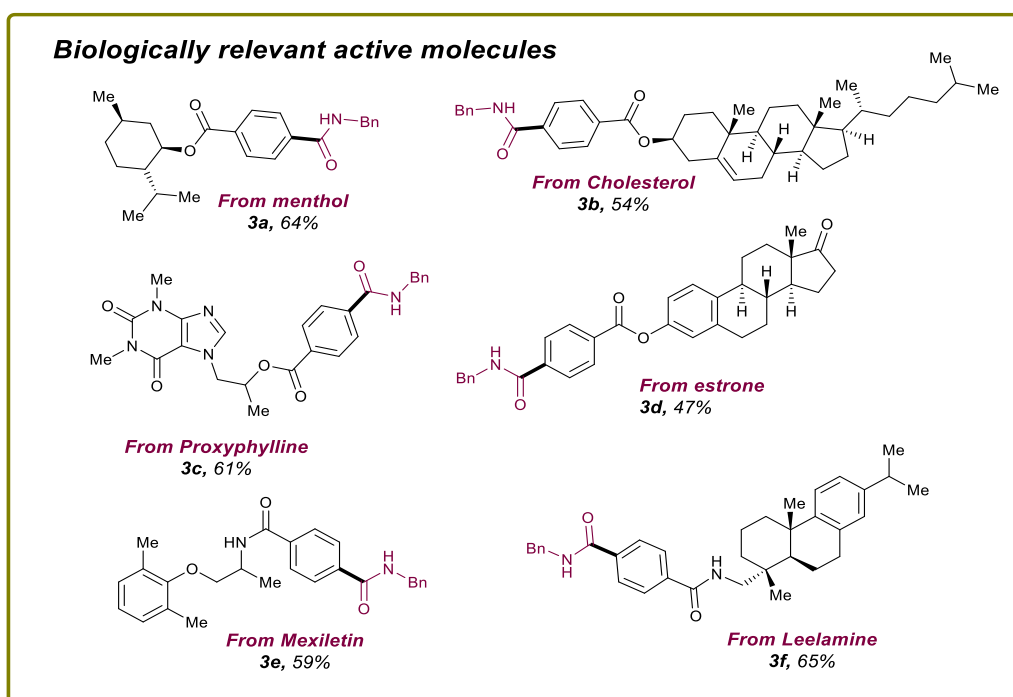


Figure 1: Late-stage functionalization of biologically active molecules.

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BINOL-3,3'-dicarboxylic acid derived chiral molecules

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Chiral 3,3'-diaryl BINOLs with their unique structural features such as C₂-symmetry are known to possess high level of stereodifferential ability, which in turn play a vital role as chiral inducer in ubiquitous modern asymmetric catalysis.¹ As a result, plenty of strategies have been devised to synthesize chiral 3,3'-diaryl BINOL derivatives.^{2a} There are two elegant synthetic protocols that have been utilized to accomplish the synthesis of 3,3'-diaryl BINOLs; (i). oxidative coupling of 3-aryl-2-naphthols^{2b}, (ii) cross coupling reactions^{2c,d}

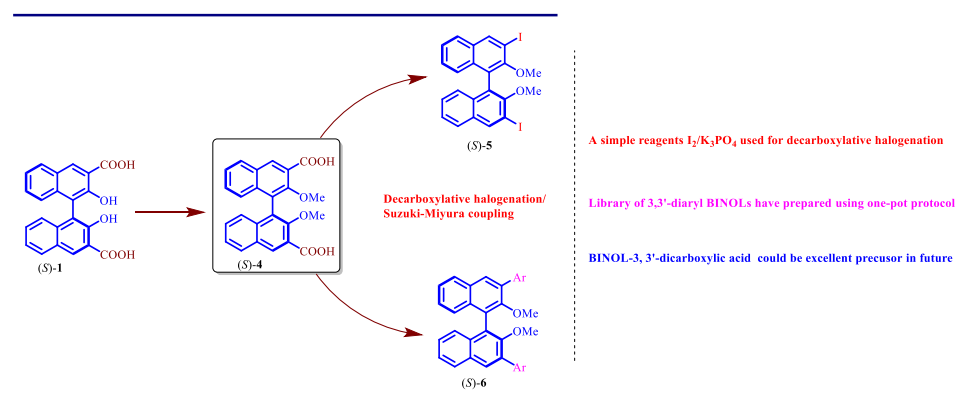


Figure 1

we herein report the direct conversion of BINOL-3,3'-dicarboxylic acid to corresponding 3,3'-diaryl BINOL via decarboxylative iodination and Suzuki-Miyaura coupling sequences in a one pot manner.³ Decarboxylative halogenation/cross coupling are classic protocol to synthesize aryl halide and biaryl molecules in organic synthesis.⁴ Chiral BINOL-3,3'-dicarboxylic acid has been successfully utilized for preparing chiral BINOL derivatives using our research methodologies (Figure 1)⁵.

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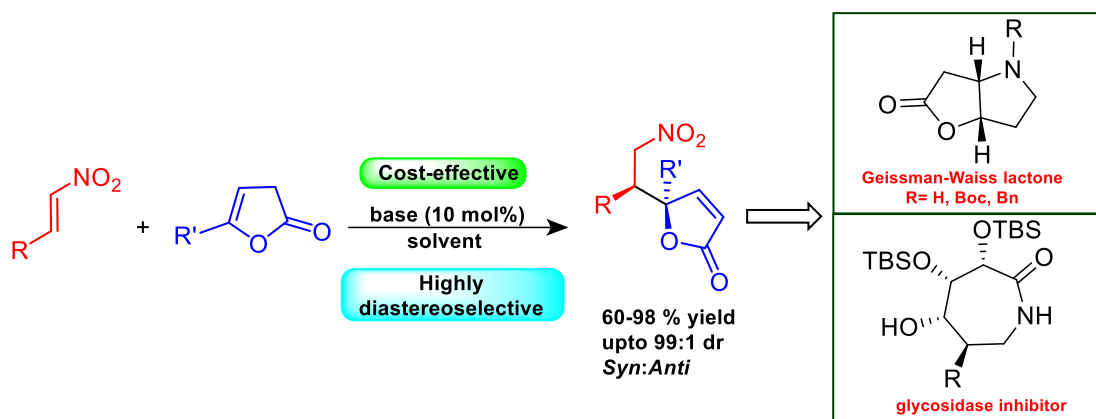
Base-Catalyzed Diastereoselective Michael Addition of Butenolides to Nitroalkenes

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Five-membered unsaturated cyclic lactones well known as butenolides are ubiquitous scaffolds found in naturally occurring products, like alkaloids and biologically active compounds, and are also employed to create therapeutic compounds that have potent effects on the neurological system and exhibit antiviral, anticancer, and antitumor activity, etc.¹⁻³ Furthermore, butenolides-containing molecules can be easily converted into azepanones derivatives, recognized as potent glycosidase inhibitors.^{3,4} Due to the broad abundance and wide applications, butenolide and butenolide-containing moiety used as a potent nucleophilic partner in several organic reactions. Herein, we demonstrate a base-catalyzed reaction between butenolides and nitroalkenes to obtain Michael addition products up to 98% yield with excellent diastereoselectivity (up to 99:1).⁵ Our method offers the broad substrate scope and several notable advantages over the existing reports, for example, cost-effective catalyst and mild reaction condition, *syn*-selective, etc. These Michael adducts allow rapid access to synthesis of several natural products as well as bio-active compounds.



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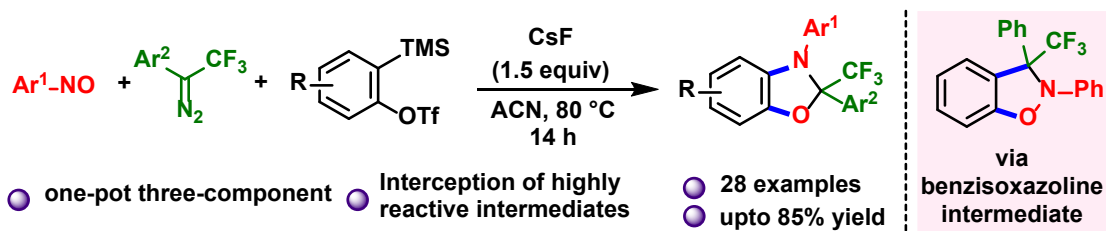
10-13 December 2023

Trapping of arynes with *in situ* generated aryltrifluoromethylnitrones enables facile access to trifluoromethylated benzoxazolines

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Trifluorodiazaoethane (CF_3CHN_2) has emerged as a versatile reagent for the rapid construction of vital CF_3 -containing subunits.¹ Consequently, our group and several others have employed this reagent to access diverse trifluoromethylated heterocycles.² Further, the swift generation of trifluoromethylnitron from trifluorodiazaoethane and nitrosobenzene has opened new avenues to access fluorinated motifs in one step.³ Recently, we developed an efficient method to access fused tricyclic trifluoromethylated isoxazolidines involving the [3+2] cycloaddition of trifluoromethylnitron generated *in situ* from trifluorodiazaoethane and nitrosobenzene with oxabicyclic alkenes.⁴ Recently, we have developed a one-pot, three-component protocol for the synthesis of trifluoromethylated benzoxazolines *via* the [3+2] cycloaddition of phenyltrifluoromethylnitron generated *in situ* from phenyltrifluorodiazaoethane and nitrosobenzene with arynes. This reaction involves the initial formation of trifluoromethylated benzisoxazoline, which surprisingly undergoes a thermal rearrangement *via* N–O bond cleavage to afford trifluoromethylated benzoxazoline.⁵ The result of this investigation will be presented.



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