In order of Importance, list of 10 best papers of the applicant highlighting the important discoveries/contributions described in them briefly (Max: 1 MB)

List of 10 best Publications:

1) A. Das, S. Kumaran, H. S. Ravi Shankar, J. R. Premkumar, B. Sundararaju. "A Dual Cobalt-Photoredox Catalytic Approach for Asymmetric Dearomatization of Indoles with Aryl Amides via C-H Activation"
Angew. Chem. Int. Ed. 2024, e202406195. *Chemrxiv*. 2024, 10.26434/chemrxiv-2024-dxz34

Description: *This study introduces a pioneering approach for the asymmetric dearomatization of indoles coupled with direct activation of carbon-hydrogen bond using cobalt/photoredox catalysis. By strategically activating C–H bonds in amides and facilitating the migratory insertion of π-bonds in indoles, the researchers achieve the synthesis of syn-selective tetrahydro-5H-indolo[2,3-c]isoquinolin-5-one derivatives. This method not only offers high yields but also achieves remarkable enantiomeric excesses exceeding 99%. This advancement represents a significant leap in disrupting aromaticity to create novel molecular architectures, showcasing a powerful strategy to harness and transform widely available aromatic hydrocarbons into valuable, complex structures.*

2) A. Das, R. Mandal, H. Subramanian, S. Kumaran, B. Sundararaju,* "Reversing the Regioselectivity of Asymmetric C–H Bond Annulation with Bromoalkynes Under Cobalt(III)-Catalysis"
Angew. Chem. Int. Ed. 2024, 63, e202315005. *ChemRxiv*. **2023** 10.26434/chemrxiv-2023-1rqz1

Description: *This study presents a novel protocol for the enantioselective C–H bond annulation of phosphinamides with bromoalkynes, leveraging Co(II) salts and chiral-Salox ligands. This method achieves regio-reversal and high enantioselectivity through a sequence involving ligand-assisted cyclocobaltation, regioselective insertion of bromoalkyne, reductive elimination, and halogen exchange with carboxylates. The process yields P-chiral compounds with exceptional optical purity, exceeding 99% enantiomeric excess. This advancement in asymmetric C–H bond functionalization is highly relevant to the pharmaceutical industry, offering a step- and atom-economical approach to synthesize chiral molecules essential for drug development and synthesis.*

3) S. Pradhan, D. Satav, S. Dutta, B. Maity, L. Cavallo, B. Sundararaju,* "Efficient Access to Skipped Dienes and Trienes by Cobalt-Catalyzed Reductive Coupling of Alkynes and Allenyl Carbonates"
Nat. Commun. 2024, minor revision. *ChemRxiv.* **2023**, DOI: 10.26434/chemrxiv-2023-1c4px-v2

Description: *This study introduces a novel one-step reductive protocol utilizing Co/PC catalysis to synthesize 1,4-dienes with high regio- and stereoselectivity, employing allenyl carbonates as 1,3-butadiene surrogates. This method efficiently constructs diverse skipped dienes from a variety of alkynes, including terminal and internal types. By mimicking biosynthetic pathways, the approach enables the iterative extension of three-carbon building blocks from geraniol derivatives, producing bio-mimetic synthetic terpenes. This technique's relevance to pharmaceuticals lies in its ability to generate structurally diverse isoprenoid compounds, crucial for drug development, and in mimicking natural metabolic processes to create valuable medicinal compounds and bioactive terpenes.*

4) N. Garg, A. H. Chowdhury, B. Sundararaju,* "Chemoselective Hydrogenation of Nitroarenes over 3D-COF derived Co-nanocarbon catalyst"
Tetrahedron Green Chem, 2024, 3, 100043.

Description: *Amines are one of the most ubiquitous functional groups in bioactive natural products and pharmaceuticals. Of the >4000 unique small-molecule drugs approved by the US Food and Drug Administration by 2022, >1800 contained at least one nitrogen atom and >1000 contained at least one N-heterocycle. This study showcases a novel 3D-COF nano catalyst for the chemoselective reduction of nitroarenes to amines using molecular hydrogen under mild conditions, without additives or bases. This method is highly relevant to the pharmaceutical industry due to its ability to efficiently convert nitroarenes into primary and secondary amines, essential building blocks in drug development. The approach offers high yields and maintains selectivity in the presence of various reducible functional groups, including ketones and carboxylic acids. By enabling the synthesis of biologically significant amines with precision, this technique supports the modification and optimization of pharmaceutical compounds at the late stage.*

5) B. Garai, M. Rahamat Ali, R. Mandal, B. Sundararaju,* "Cp*Co(III)-catalyzed C(8)-Nucleophilic cascade cyclization of quinoline-N-oxide with 1,6-enyne"
Org. Lett. 2023, 25, 2018-2023.

Description: *Bicyclic hydrobenzofuran moieties, integral to natural products and pharmaceuticals, are exemplified by huperzine A (Alzheimer's treatment) and dactinomycin (anticancer). Their stability and versatility enhance drug efficacy. We have developed a novel Cp*Co(III)-catalyzed protocol for synthesizing hydrobenzofuran tethered at the C(8) position of quinoline. This method uses quinoline N-oxide and 1,6-enynes, demonstrating excellent tolerance to various functional groups. The approach covers a broad range of substrates and allows for further transformation of the hydrobenzofuran scaffold into diverse, value-added products, expanding its utility in medicinal chemistry and drug development.*

6) P. Chakraborty, S. Pradhan, J. Richard Premkumar, B. Sundararaju,* "Valorization of terpenols under Iron catalysis"
J. Catal. 2023, 421, 309-318.

Description: *Transferase enzymes facilitate the transfer of terpenyl units, creating significant macromolecular terpenoids like farnesylated proteins, which play crucial roles in cellular processes. Mimicking this natural terpenylation using synthetic methods is valuable for pharmaceutical applications. We present a method employing oxidized terpenes, such as those from essential oils, for the direct alkylation of oxindoles using a low-valent iron complex. This approach is versatile, accommodating a range of natural and synthetic terpenols, including geraniol, farnesol, and solanesol. This technique not only replicates natural biosynthetic pathways but also enables the development of bioactive compounds with potential therapeutic applications.*

7) R. Mandal, B. Garai, and B. Sundararaju,* "Weak-Chelation In C-H Bond Functionalization using 3d Metals"
ACS Catal. 2022, 12, 3452.

Description: *C–H functionalization marks a revolutionary shift in organic synthesis, moving from traditional functional group manipulation to the precise modification of C–H bonds, even amidst more*

reactive groups. Advances in organometallic chemistry have transformed C–H functionalization from a challenge of simple hydrocarbons to a robust strategy for complex target synthesis. This modern approach has paved the way for late-stage functionalization (LSF) in medicinal chemistry, allowing for rapid structure-activity relationship exploration, generation of oxidized metabolites, and creation of biological probes. This article provides a comprehensive toolkit for applying regioselective C–H functionalization to drug-like molecules, enhancing the development of innovative pharmaceuticals.

8) P. Chakraborty, N. Garg, E. Manoury, R. Poli, B. Sundararaju,* "C-Alkylation of Various Carbonucleophiles Under Co^{III}-Catalysis"
ACS Catal. 2020, 10, 8023-8031.

Description: *In contemporary science, the exploration of fundamental feedstocks for sustainable chemical transformations is crucial. Heterocyclic scaffolds, prominent in natural products and pharmaceuticals, are key targets for selective alkylation. Notably, oxindoles, benzyl cyanides, and barbituric acids, which are central to various alkaloids and drugs, benefit from this approach. Our recent discovery of active cobalt catalytic system under Cp*Co(III) catalysis have enabled efficient α-alkylation of oxindoles with diverse secondary alcohols, and this method has been extended to N,N-dimethyl barbituric acid and benzyl cyanides. These developments enhance the synthesis of C-alkylated heterocycles, supporting the creation of novel chemical libraries for drug discovery and development without any waste generation.*

9) D. Kalsi, S. Dutta, N. Barsu, M. Rueping, B. Sundararaju,* "Room Temperature C-H bond Functionalization by Merging Cobalt- and Photo-redox Catalysis"
ACS Catal. 2018, 8, 8115-8120.

Description: *Innovations in synthetic methodology, such as visible light photocatalysis, have revolutionized pharmaceutical development by expanding chemical diversity and enhancing drug discovery. A notable advance is the non-noble metal-free protocol for C–H bond functionalization at room temperature, integrating cobalt-mediated catalysis with photocatalysis. The present method utilizes visible light and oxygen as the sole oxidant, operating under redox-neutral conditions. The photocatalyst facilitates electron transfer, enabling efficient C–H and N–H bond annulations with various coupling partners. This approach not only broadens the scope of cobalt catalysis but also offers a sustainable and versatile tool for creating novel drug candidates and fine chemicals.*

10) N. Barsu, S. K. Bolli, B. Sundararaju,* "Cobalt Catalyzed Carbonylation of Unactivated C(sp^3)-H bonds"
Chem. Sci. 2017, 8, 2431-2435.

Description: *The development of efficient and environmentally friendly synthesis methods is crucial for advancing green chemistry in pharmaceuticals and fine chemicals. Catalysis, particularly carbonylation, plays a vital role in this effort. Despite its industrial significance, carbonylation has seldom been applied to complex pharmaceutical synthesis. We present a pioneering cobalt-catalyzed carbonylation method that efficiently regioselectively functionalizes unactivated C(sp3)–H bonds in aliphatic amides using atmospheric carbon monoxide (1–2 atm). This approach allows for the synthesis of α-spiral succinimides and marks the first reported carbonylation of sp3 C–H bonds, including β-C–H bonds of various carbons and internal β-C–H bonds. Additionally, the procedure is adaptable for using CO2 as a CO source, enabling site-selective synthesis of cyclic imides and spirocycles from aromatic, hetero-aromatic, and aliphatic carboxamides. This method was successfully applied to the late-stage derivatization of Telmisartan and Gemfibrozil and*

demonstrated general applicability with pharmacologically important scaffolds such as xanthone, coumarin, and isatin.

In addition to the aforementioned significant contributions, our group has consistently developed several cost-effective catalytic systems for regio-, stereo-, and enantioselective transformations. These advancements have the potential to streamline targeted synthesis, reducing the need for multistep traditional organic synthesis methods. These articles are either directly or indirectly used by various applications. see, *J. Org. Chem.* ***2023****, 88, 5893, Science of Synthesis,* ***2023****, 2, 149, Org. Lett.* **2022,** 24, 6219, *Adv. Synth. Catal.* ***2022****, 364, 2642, Chem. Commun.* ***2022****, 58, 9930, Chem. Commun.* ***2021****, 57, 13075, ChemCatChem,* ***2020****, 12, 3472, Chem. Commun.* ***2019****, 55, 11626, ChemSusChem,* ***2019****, 12, 3463, Org. Chem. Front.* ***2019****, 6, 852, ChemSusChem.* ***2019****, 12, 3089, Catal. Sci. Technol.* ***2018****, 8, 5963, Org. Lett.* ***2018****, 20, 2835, Org. Lett,* ***2017****, 19, 3699, Org. Lett.,* ***2017****, 19, 2544, Org. Lett.* ***2017****, 19, 6, Org. Lett.* ***2016****, 18, 4198, Org. Lett.* ***2015****, 17, 6118 & ACS Catal,* ***2016****, 6, 2792.*

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