1. **Imine as a linchpin approach for *meta*-C–H functionalization.**
   Bag, S.; Jana, S.; Pradhan, S.; Bhowmick, S.; Goswami, N.; Sinha, S. K.; Maiti, D. *Nat. Commun.*, **2021**, *12*, 1393. (Google Scholar Citation: 6)

   Despite the widespread applications of C–H functionalization, controlling site selectivity remains a significant challenge. Covalently attached directing groups (DGs) served as ancillary ligands to ensure *ortho*-, *meta*- and *para*-C–H functionalization over the last two decades. These covalently linked DGs necessitate two extra steps for a single C–H functionalization: introduction of DG prior to C–H activation and removal of DG post-functionalization. Here we report a temporary directing group (TDG) for *meta*-C–H functionalization via reversible imine formation. By overruling facile *ortho*-C–H bond activation by imine-*N* atom, a suitably designed pyrimidine-based TDG successfully delivered selective *meta*-C–C bond formation. Application of this temporary directing group strategy for streamlining the synthesis of complex organic molecules without any necessary pre-functionalization at the *meta*-position has been explored.

2. **An Alkyne Linchpin Strategy for Drug: Pharmacophore Conjugation: Experimental and Computational Realization of a meta-selective Inverse Sonogashira Coupling.**
   Porey, S.; Zhang, X.; Bhowmick, S.; Singh, V. K.; Guin, S.; Paton, R. S.; **Maiti. D.** *J. Am. Chem. Soc,* **2020**, *142*, 3762. (Google Scholar Citation: 42)

   The late-stage functionalization (LSF) of pharmaceutical and agrochemical compounds by the site-selective activation of C−H bonds provides access to diverse structural analogs and expands synthetically-accessible chemical space. We report a C−H functionalization LSF strategy that hinges on the use of an alkyne linchpin to assemble conjugates of sp^2 -rich marketed pharmaceuticals and agrochemicals with sp3 -rich 3D fragments and natural products. This is accomplished through a template-assisted inverse Sonogashira reaction that displays high levels of selectivity for the meta position. This protocol is also amenable to distal structural modifications of α-amino acids. The transformation of alkyne functionality to other functional groups further highlights the applicative potential. Computational and experimental mechanistic studies shed light on the detailed mechanism. Turnover-limiting 1,2-migratory insertion of the bromoalkyne coupling partner occurs after relatively fast C−H activation. While this insertion occurs unselectively, regioconvergence results from one of the adducts undergoing a 1,2-trialkylsilyl migration to form the alkynylated product. A heterobimetallic Pd−Ag transition structure is essential for product formation in the β-bromide elimination step.

3. **H-Bonded Template Assisted *para*-Selective Carboalkylation Using Soft Electrophilic Vinyl Ether**
   Maji, A.; Dahiya, A.; Lu, G.; Bhattacharya, T.; Liu, P.; Zanoni, G.; **Maiti, D**. *Nat Commun,* **2018**, 9, 3582. (Google Scholar Citation: 41)

   In nature, enzymatic pathways generate C_{aryl}−C(O) bonds in a site-selective fashion. Synthetically, C_{aryl}−C(O) bonds are synthesised in organometallic reactions using prefunctionalized substrate materials. Electrophilic routes are largely limited to electron-rich systems, non-polar medium, and multiple product formations with a limited scope of general application. Herein we disclose a directed para-selective ketonisation technique of arenes, overriding electronic bias and structural congestion, in the presence of a polar protic solvent. The concept of hard–soft interaction along with in situ activation techniques is utilised to suppress the competitive routes. Mechanistic pathways are investigated both experimentally and computationally to establish the hypothesis. Synthetic utility of the protocol is highlighted in formal synthesis of drugs, drug cores, and bioactive molecules.

4. **Remote *meta*-C–H Cyanation of Arenes Enabled by Pyrimidine Based Auxiliary**
Bag, S.; Jayarajan, R.; Dutta, U.; Chowdhury, R.; Mondal, R.; **Maiti, D**. *Angew. Chem. Int. Ed.* **2017**, *56*, 12538. (Google Scholar Citation: 88)

   An easily removable pyrimidine-based auxiliary has been employed for the remote meta-C−H cyanation of arenes. The scope of this Pd-catalyzed cyanation reaction using copper(I) cyanide as the cyanating agent was demonstrated with benzylsilanes, benzylsulfonates, benzylphophonates, phenethylsulfonates, and phenethyl ether derivatives. The method was utilized for the synthesis of pharmaceutically valuable precursors.

5. **Palladium-Catalyzed Directed *para*-C–H Functionalization of Phenols**
Patra, T.; Bag, S.; Kancherla, R.; Mondal, A.; Dey, A.; Pimparkar, S.; Agasti, S.; Modak, A.; **Maiti, D**. *Angew. Chem. Int. Ed.*, **2016**, *55*, 7751. (Google Scholar Citation: 151)

   Various practical methods for the selective C¢H functionalization of the ortho and recently also of the meta position of an arene have already been developed. Following our recent development of the directing-group-assisted para C¢H functionalization of toluene derivatives, we herein report the first remote para C¢H functionalization of phenol derivatives by using a recyclable silicon-containing biphenylbased template. The effectiveness of this strategy was illustrated with different synthetic elaborations and by the synthesis of various phenol-based natural products.

6. **Pd(II)-Catalyzed *meta*-C–H Olefination: Constructing Multi-substituted Arenes through Homo-diolefination and Sequential Hetero-diolefination**
Bera, M; Maji, A.; Sahoo, S. K.; **Maiti, D**. *Angew. Chem. Int. Ed.* **2015**, *54*, 8515. (Google Scholar Citation: 195)

   Divinylbenzene derivatives represent an important class of molecular building blocks in organic chemistry and materials science. Reported herein is the palladium-catalyzed synthesis of divinylbenzenes by meta-C–H olefination of sulfone-based arenes. Successful sequential olefinations in a position-selective manner provided a novel route for the synthesis of hetero-dialkenylated products, which are difficult to access using conventional methods. Additionally, 1,3,5- trialkenylated compounds can be generated upon successful removal of the directing group.

7. **Remote *para*-C–H Functionalization of Arenes by a D-Shaped Biphenyl Template-Based Assembly**
Bag, S.; Patra, T.; Modak, A.; Deb, A.; Maity, S.; Dutta, U.; Dey, A.; Kanchrela, R.; Maji, A.; Hazra, A.; Bera, M.; **Maiti, D**. *J. Am. Chem. Soc*., **2015**, *137*, 11888. (Google Scholar Citation: 242)

   Site-selective C−H functionalization has emerged as an efficient tool in simplifying the synthesis of complex molecules. Most often, directing group (DG)- assisted metallacycle formation serves as an efficient strategy to ensure promising regioselectivity. A wide variety of ortho- and meta-C−H functionalizations stand as examples in this regard. Yet despite this significant progress, DG-assisted selective para-C−H functionalization in arenes has remained unexplored, mainly because it involves the formation of a geometrically constrained metallacyclic transition state. Here we report an easily recyclable, novel Si-containing biphenyl-based template that directs efficient functionalization of the distal p-C−H bond of toluene by forming a D-shaped assembly. This DG allows the required flexibility to support the formation of an oversized pre-transition state. By overcoming electronic and steric bias, para-olefination and acetoxylation were successfully performed while undermining oand m-C−H

activation. The applicability of this D-shaped biphenyl template-based strategy is demonstrated by synthesizing various complex molecules.

8. **Palladium Catalyzed Aryl C–H Olefination with Unactivated, Aliphatic Alkenes.**
Deb, A.; Bag, S.; Kancherla, R.; **Maiti, D**. *J. Am. Chem. Soc.*, **2014**, *136*, 13602. (Google Scholar Citation: 180)

Palladium-catalyzed coupling between aryl halides and alkenes (Mizoroki−Heck reaction) is one of the most popular reactions for synthesizing complex organic molecules. The limited availability, problematic synthesis, and higher cost of aryl halide precursors (or their equivalents) have encouraged exploration of direct olefination of aryl carbon−hydrogen (C−H) bonds (Fujiwara−Moritani reaction). Despite significant progress, the restricted substrate scope, in particular noncompliance of unactivated aliphatic olefins, has discouraged the use of this greener alternative. Overcoming this serious limitation, we report here a palladium-catalyzed chelation-assisted ortho C−H bond olefination of phenylacetic acid derivatives with unactivated, aliphatic alkenes in good to excellent yields with high regio- and stereoselectivities. The versatility of this operationally simple method has been demonstrated through drug diversification and sequential C−H olefination for synthesizing divinylbenzene derivatives.

9. **Palladium-Catalyzed Synthesis of Benzofurans and Coumarins from Phenols and Olefins.**
Sharma, U.; Togati, N.; Maji, A.; Manna, S.; and **Maiti, D.** *Angew. Chem. Int. Ed.*, **2013,** *52*, 12669. (Google Scholar Citation: 179)

Benzofuran derivatives are ubiquitous in natural products, agrochemicals, pharmaceuticals, and organic materials. Particularly, 2-arylbenzofurans are widely distributed in nature, and possess a number of biological activities. Over the years, several effective strategies involving transition-metal-catalyzed inter/intramolecula heteroannulation reactions have been reported for synthesizing benzofuran scaffolds. However, synthesis of 2-substituted benzofuran by simply reacting phenol and an unactivated olefin has yet to be reported. Another "privileged scaffold", coumarin, possesses various interesting biological activities. The most common approach for their synthesis is the Pechmann condensation wherein phenol is reacted with a β-ketoester or acid under strongly acidic conditions. Despite having a number of effective alternative methods (mainly for electron-rich phenols), the synthesis of coumarins from phenol and methyl acrylate remains attractive. This paper describes a palladium-catalyzed C–O/C–C bond formation sequence between phenol and an olefin for the convenient synthesis of benzofurans and coumarins.

10. **Efficient and Stereoselective Nitration of Mono- and Disubstituted Olefins with $AgNO_2$ and TEMPO**
Maity, S.; Manna, S.; Rana, S.; Togati, N.; Mallick, A; **Maiti, D**. *J. Am. Chem. Soc.*, **2013**, *135*, 3355. (Google Scholar Citation: 181)

Nitroolefin is a common and versatile reagent. Its synthesis from olefin is generally limited by the formation of mixture of *cis* and *trans* compounds. Here we report that silver nitrite ($AgNO_2$) along with TEMPO can promote the regio- and stereoselective nitration of a broad range of olefins. This work discloses a new and efficient approach wherein starting from olefin, nitroalkane radical formation and subsequent transformations lead to the desired nitroolefin in a stereoselective manner.