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## Educational Background

### Secondary

<b>Board</b>	West Bengal Board of Secondary Education (WBBSE)
<b>Marks (%)</b>	<b>85.4</b>
<b>Subjects</b>	Bengali, English, Mathematics, Physical Science, Biological Science, History, Geography

### Higher Secondary (10+2)

<b>Board</b>	West Bengal Council of Higher Secondary Education (WBCHSE)
<b>Marks (%)</b>	<b>80.6</b>
<b>Subjects</b>	Bengali, English, Chemistry, Physics, Mathematics, Biology

### Bsc. in Chemistry (Vidyasagar University)

<b>College</b>	Bajkul Milani Mahavidyalaya
<b>Marks (%)</b>	<b>73.5</b>

### Int. PhD

<b>Institute</b>	IISER Kolkata
<b>CGPA (upto 6<sup>th</sup> sem)</b>	<b>9.5</b>

## Teaching Assistantship

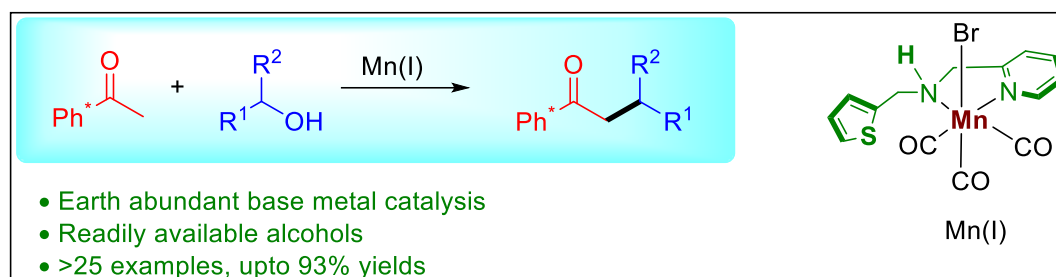
- Teaching Assistant for “CH2203- Synthesis and Characterization Laboratory”- 2 nd Year UG Students
- Teaching Assistant for “CH3104- Physical Organic Chemistry”- 3 rd Year UG Students
- Online Teaching at Jawahar Navodaya Vidyalaya (JNV), Kalyani, Nadia- XIth and XIIth Students
- Teaching Assistant for NPTEL course on research methodology.

## Awards & Achievement:

- SWAMI VIVEKANANDA MCM SCHOLARSHIP (2015-2018)
- JAM 2018
- CSIR-UGC NET (June 2018)
- GATE 2020
- PRIME MINISTER RESEARCH FELLOW (May 2020)

## Research Interest:

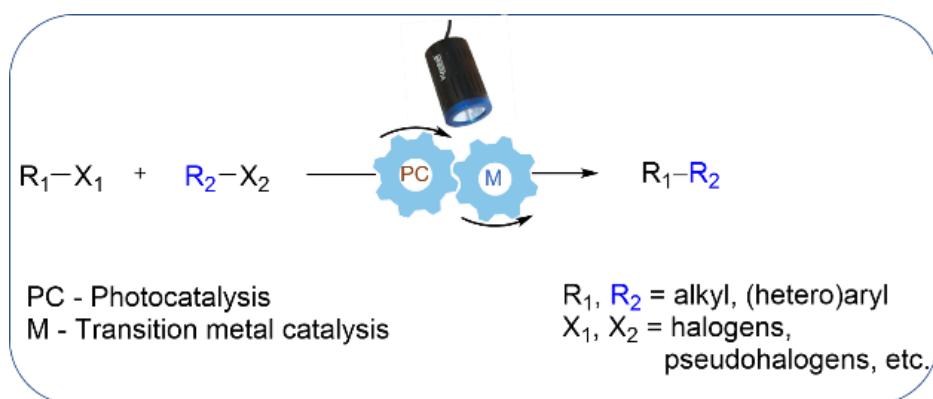
At my early research work I mainly focused on ‘‘borrowing hydrogen’’ (BH) catalysis to construct C-C bond. Here our primary goal was the replacement of precious metals by earth-abundant metals for this type of catalytic transformations. In this regard, lately, well-defined manganese(I) complexes have emerged as an attractive noble metal replacer in sustainable (de)hydrogenation reactions and other organic transformations.



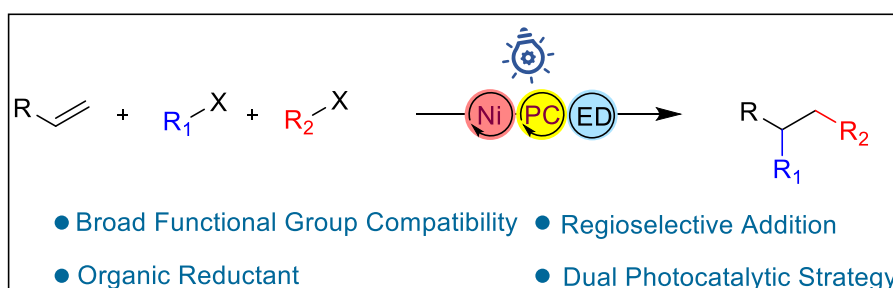
At present I'm working on 'Visible-Light-Mediated C-C Bond Formation Reaction via Transition Metal/Photoredox Dual Catalysis'. Here also the formation of the C-C bond is one of the central goal and photoredox/transition metal catalysis is an alternative to the traditional methods. We wish to use visible light as the sole energy source to drive these reactions. Abundant and less toxic organic reductants will be utilized as the sacrificial reductant. The method will be applied for making C<sub>sp3</sub>-C<sub>sp2</sub>, C<sub>sp2</sub>-C<sub>sp2</sub>, and C<sub>sp3</sub>-C<sub>sp3</sub> bonds and other reductive functionalization reactions. We envisioned that the mildness of the developed protocol would accommodate larger functional groups. It will also enable the synthesis and late-stage functionalization of targeted bioactive molecules. Transition-metal-catalyzed cross-coupling reaction between C-X electrophiles (X = Cl, Br, OTf, etc.) and C-M nucleophiles (M = Mg, Zn, B, Si, Sn) is one of the most powerful tools in organic synthesis. It played a vital role in the preparation of complex medicinal drugs, designing functional ligands, molecular materials, including industrial applications. However, unavailability of the organometallic C-M nucleophiles, their cost, handling issues under ambient conditions, and generation of copious waste demanded an alternative of traditional cross-coupling reaction. In recent years, a conceptually different approach that is the reductive cross-coupling reaction between two electrophiles has emerged. The method utilizes bench-stable high-valent late-transition metal salts (such as Pd, Ni, Co, Fe, Cr) as a catalyst and excess amount metallic terminal reductants (such as Zn, Mn, In, Sm, Mg). Importantly, these protocols avoid the individual preparation of hazardous organometallics reagents and offered wide availability of diverse electrophiles for

coupling. However, the use of an excessive amount of metallic powder as a reductant generates an over-stoichiometric amount of metal salts as waste that not only complicates the work-up and purification procedure but also creates environmental concern over waste disposal. Not only that, reductant-derived metal salts often reduce the catalytic performance of the low-valent catalysts by coordination to the active sites. Additionally, functional group tolerance is not too much due to the presence of an external metal reductant. To overcome these concerns, an alternative catalytic method of activation is in high demand.

Visible light photoredox catalysis has emerged as a powerful arsenal in organic synthesis. It leverages abundant visible light for the bond activation process in a controlled manner without the need for toxic and hazardous reagents. Upon excitation with visible light, a photoredox catalyst can simultaneously act as a powerful oxidant and reductant. We envision that merging photoredox catalysis with transition metal catalysis in a dual-catalysis fashion might address the challenges of the classical cross-coupling reaction and might pave the way for the development of the novel bond formation reactions.

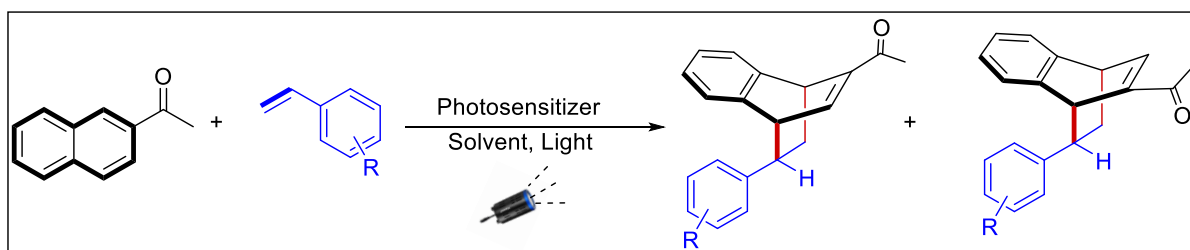


Nickel and photoredox dual catalysis proved to be one of the most versatile approaches to accessing diverse organic transformations using basic starting materials. In this synergistic strategy, one reactive open shell species generated by photocatalysis can be trapped by the Ni catalyst and used to perform further reactions. Keeping this in our mind we have designed a three-component coupling reaction using olefin, alkyl halide and aryl halide. Because of different reactivity of all three component, they add to nickel cycle selectively and gives back desired difunctionalised product.



Synthesis of three-dimensional molecular scaffolds from simple molecules is highly challenging, yet have significant impact in organic synthesis in terms of medicinal chemistry. Cycloaddition reaction perhaps is the representative example that provides three dimensional

architectures. Notably, in (4+2) cycloadditions, two single (sigma) bonds and one new (Pi) bond are formed in a three dimensional six-membered ring structure from two unsaturated reaction components. Polycyclic aromatic hydrocarbons contain alternating double bonds, but their use in cycloaddition reactions presents additional challenges as a result of their increased stabilization conferred by aromaticity. In this context we have performed a photocatalyzed (4+2) cycloaddition reaction using visible light mediated energy transfer by a suitable photosensitizer. We anticipate that the protocol will further illuminate the EnT catalysis for designing complex molecular scaffolds.



## Publication:

- Waiba, S.; Jana, S. K.; Jati, A.; Jana, A.; Maji, B., Manganese complex-catalysed  $\alpha$ -alkylation of ketones with secondary alcohols enables the synthesis of  $\beta$ -branched carbonyl compounds. *Chem. Commun.* **2020**, 56 (60), 8376-8379.
- **Jana, S. K.**; Maiti, M.; Dey, P.; Maji, B., Photoredox/Nickel Dual Catalysis Enables the Synthesis of Alkyl Cyclopropanes via C(sp<sup>3</sup>)-C(sp<sup>3</sup>) Cross Electrophile Coupling of Unactivated Alkyl Electrophiles. *Org. Lett.* **2022**, 24, 1298-1302.
- Rai P, Maji K, **Jana SK**, Maji B. Intermolecular Dearomative [4+2] Cycloaddition of Naphthalenes via Visible-Light Energy-Transfer-Catalysis. *Manuscript under revision*.
- Di-Carbofunctionalization of Un-Activated Alkenes via Photoredox/Nickel Dual Catalysis. *Manuscript under Preparation*.

**Manganese complex-catalysed  $\alpha$ -alkylation of ketones with secondary alcohols enables the synthesis of  $\beta$ -branched carbonyl compounds†**

Satyadeep Waiba,† Sayan K. Jana,† Ayan Jati, Akash Jana and Biplab Maji\*†

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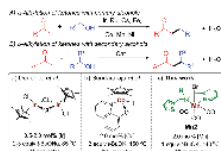
DOI: 10.1039/C9CC04600e

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Herein,  $\beta$ -branched carbonyl compounds were synthesized via the  $\alpha$ -alkylation of ketones with secondary alcohols under "borrowing hydrogen" catalysis. A wide range of secondary alcohols, including various cyclic, acyclic, symmetrical, and unsymmetrical alcohols, have been successfully applied under the developed reaction conditions. A manganese complex bearing a phosphine-free multifunctional ligand catalysed the reaction and produced water as the sole byproduct.

The development of catalytic methods for the construction of C–C bonds is one of the central goals in organic synthesis. The delicacy of "borrowing hydrogen" (BH) catalysis lies in the fact that it utilizes alcohol as an alternative carbon source for such processes under eco-friendly conditions avoiding substrate prefunctionalization, organohalides, cyrogenic temperature, etc.<sup>1</sup> In this process, alcohols get activated by dehydrogenation for a reaction with a nucleophile, which is then followed by hydrogenation of the resulting unsaturated intermediate by the "borrowed hydrogen", thereby making the whole process atom economical, and benign.

In the recent past, BH catalysis has widely been applied for the  $\alpha$ -alkylation of ketones with primary alcohols (Scheme 1A).<sup>2a,c,p</sup> On the other hand, the use of secondary alcohols under BH catalysis to generate the  $\beta$ -branched molecular architecture is limited (Scheme 1B).<sup>2</sup> Commonly, the  $\beta$ -branched ketones were made in the presence of lithium bases by using secondary alkyl halides as an electrophile and this unavoidably produced a large amount of waste.<sup>4</sup> In a pioneering work, Donohoe and coworkers reported the  $\alpha$ -alkylation of ketones with secondary alcohols leading to  $\beta$ -branched products using [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (Cp\* = C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>) as a catalyst (Scheme 1Ba).<sup>2a</sup> The steric factor of the used carbonyl substrate was exploited to limit the self-condensation of the carbonyl substrate used and the ketone,



Scheme 1 Alkylation of ketones.

derived during the reaction from the secondary alcohol.<sup>2a,c</sup> The replacement of precious metals by earth-abundant metals for this type of catalytic transformations is highly attractive in terms of toxicity, cost, and sustainability.<sup>5</sup> In this regard, the only base metal-catalysed reaction of this type was reported by the Sundamraju group using [Cp\*Co(N,O)] (N,O = quinolin-8-olate) as a catalyst (Scheme 1Bb).<sup>2b</sup> However, the recent European Commission's list of critical raw materials (CRMs) suggested that except cobalt, all first-row transition metals exceed the economic importance threshold while their abundance is below the supply risk threshold.<sup>7</sup> In this regard, lately, well-defined manganese complexes have emerged as an attractive noble metal replacers in sustainable (de)hydrogenation reactions and other organic transformations.<sup>8</sup> Manganese is the third-most abundant transition metal in the earth's crust (after iron and titanium) and it is less toxic than its higher analogs. Not long ago, selective  $\alpha$ -alkylations of ketones was achieved by using Mn(cy) catalysis by Beller,<sup>2a</sup> Rueping,<sup>2f</sup> Sortais,<sup>2m</sup> and our groups.<sup>2g</sup> Alkylations of esters and amides with primary alcohols were also disclosed under manganese catalysis.<sup>9</sup> We have also reported the alkylations of nitriles using a well-defined phosphine-free manganese complex.<sup>10</sup> However, to the best of our knowledge, manganese complex-catalysed alkylations of methyl ketones with

† Electronic supplementary information (ESI) available: See DOI: 10.1039/C9CC04600e. ‡ The authors contributed equally.

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Letter

**Photoredox/Nickel Dual Catalysis Enables the Synthesis of Alkyl Cyclopropanes via C(sp<sup>3</sup>)–C(sp<sup>3</sup>) Cross Electrophile Coupling of Unactivated Alkyl Electrophiles**Sayan K. Jana, Mamata Maiti,<sup>2</sup> Purusattam Dey,<sup>2</sup> and Biplab Maji\*Cite This: *Org. Lett.*, 2022, 24, 1298–1302

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**ABSTRACT:** A facile synthesis of mono-, 1,1- and 1,2-disubstituted cyclopropanes via visible light-mediated photoredox/nickel dual catalysis is demonstrated. The challenging intramolecular C(sp<sup>3</sup>)–C(sp<sup>3</sup>) cross-electrophile coupling of readily available unactivated 1,3-alkyl electrophiles was performed under mild conditions that allowed traditionally reactive functional groups to be included. Mechanistic inspection and control experiments revealed the importance of dual catalysis and that the reaction proceeds via a stepwise oxidative addition followed by an intramolecular S<sub>N</sub>2 reaction.



Cyclopropane is an enthralling molecule with high strain and unusual electronic attributes due to its bent, shorter, and planar three-membered C–C framework.<sup>1</sup> Consequently, it has been contributed to many seminal discoveries in chemical structure and bonding.<sup>2</sup> The cyclopropane fragment has also been endowed largely by Nature,<sup>3</sup> and is privileged in various secondary metabolites and manufactured drugs.<sup>4</sup> Besides, numerous synthetic applications of cyclopropanes as a synthon or key intermediate have been reported.<sup>5</sup> Cyclopropane synthesis received deserved attention (Scheme 1a). The [2 + 1] cycloaddition of olefins with carbenoids or diazo-compound derived metal carbenes represented an elegant classical approach.<sup>6</sup> Two-step nucleophilic addition-ring closure sequences have also been reported for the cyclopropanation of activated olefins.<sup>7</sup> However, most venerable state-of-the-art approaches frequently lack broad functional group compatibility and operational simplicity and rarely apply mild conditions. Recently, Molander, Aggarwal, Suero, Tambar and others have reported three-membered ring synthesis using a photoredox active C1 source with certain olefins and photoisomerization reactions.<sup>8</sup>

Cross-electrophile coupling (XEC) reaction is an intriguing strategy for constructing C–C bonds under mild conditions. The field has been advanced with activated electrophiles or substrates having different oxidative addition rates to favor cross-selectivity.<sup>9</sup> However, the coupling between two unactivated substrates with the same reactivity is challenging.<sup>10</sup> In this regard, the Wurtz coupling between alkyl halides employing stoichiometric alkali metal reductants such as Na, Mg, Ca, Mn, or electricity generally led to poor functional group tolerance, minimum substrate scope, and low yields.<sup>11</sup> In 2016, Gong explored a nickel catalyzed intramolecular Wurtz cyclization reaction to synthesize cycloalkanes.<sup>12</sup> Although the

protocol successfully synthesized higher cycloalkanes, it failed to make a cyclopropane ring from a primary alkyl 1,3-dibromide substrate (Scheme 1b). In 2020, Jarvo disclosed an elegant synthesis of alkyl cyclopropanes via nickel-catalyzed XEC of 1,3-dimesylates (Scheme 1c).<sup>13</sup> The reaction proceeds via 1,3-diolides formation followed by preferential radical oxidative addition at the secondary alkyl position. However, using a stoichiometric amount of Grignard reagent as a reductant limits the functional group tolerance and reaction's utility. Besides, cyclopropane synthesis via XEC reaction required a secondary alkyl electrophile to favor oxidative addition via a more stable secondary radical.<sup>14</sup> The intramolecular XEC of unactivated primary alkyl electrophiles delivering cyclopropanes is challenging.

Of late, photoredox/transition-metal dual catalysis, leveraging the visible light's energy, has emerged as a powerful arsenal in organic synthesis for chemical bond activation and transformation under mild conditions.<sup>15</sup> We have instigated that metallaphotoredox catalysis can be a prominent strategy to make the cyclopropane ring via an intramolecular C(sp<sup>3</sup>)–C(sp<sup>3</sup>) cross-coupling of 1,3-alkyl electrophiles (Scheme 1c). It is reasoned that a reductively quenched photoredox catalyst PC\* could provide the requisite reductive equivalent for the nickel-catalyzed XEC reaction in a controlled manner sacrificing an organic electron donor (ED) under visible light irradiation.<sup>16</sup> The decisive advantage of such a photodriver

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# Intermolecular Dearomative [4+2] Cycloaddition of Naphthalenes via Visible-Light Energy-Transfer-Catalysis

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Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur 741246, India.

**ABSTRACT:** Dearomative cycloaddition reaction serves as a blueprint for creating three-dimensional molecular topology from flat-aromatic compounds. However, severe reactivity and selectivity issues make this process challenging. Herein, we describe visible-light energy-transfer catalysis for the intermolecular dearomative [4+2] cycloaddition reaction of feed-stock naphthalene molecules with vinyl benzenes. Tolerating a wide range of functional groups, a variety of structurally diverse 2-acyl naphthalenes and styrenes could easily be converted to a diverse range of bicyclo[2.2.2]octa-2,5-diene scaffolds in high yields and selectivities. The late-stage modification of pharmaceutical agents further demonstrated the broad potentiality of this methodology. The efficacy of the introduced methods was further highlighted by the post-synthetic diversification of the products. Furthermore, photoluminescence, electrochemical, kinetic, and control experiments support the energy transfer catalysis

Constructing three-dimensional (3D) molecular scaffolds from two-dimensional (2D) molecules is highly challenging yet significantly impacts organic synthesis and drug discovery programs.<sup>1-4</sup> The cycloaddition reactions that convergently and predictably join multiple molecular fragments have been recognized as a powerful tool for this purpose (Figure 1).<sup>5-8</sup> Notably, in [4+2] cycloaddition reaction, two new  $\sigma$ -bonds, and one  $\pi$ -bond are formed in a 3D six-membered ring topology from two simple unsaturated reaction components, *diene*, and *dienophile* (Figure 1a).<sup>9,10</sup> In fact, this thermally allowed process has been a fundamental reaction type demonstrating its molecular complexity generating power for many years.<sup>11-13</sup> In this context, polycyclic aromatic hydrocarbon such as naphthalene also contains alternating double bonds. Besides, they are abundant and inexpensive feed-stock chemicals (present at about 10% in typical coal tar).<sup>14</sup> However, these 2D molecules displayed limited application in 3D complexity generating cycloadditions reactions due to severe challenges associated with breaking the increased stabilization conferred by aromaticity (resonance energy = 80.3 kcal mol<sup>-1</sup>) and selectivity (Figure 1b,c).<sup>15,16</sup> A typical thermal dearomative [4+2] cycloaddition with naphthalenes required harsh reaction conditions (high temperature up to 210 °C, pressure up to 10<sup>3</sup> atm),<sup>17</sup> specially designed reaction conditions,<sup>18-20</sup> or reactive *dienophile*<sup>21,22</sup> (hereafter called *arenophile*) to overcome the high kinetic barrier (Figure 1c).<sup>23,24</sup> However, since the free energy is often positive for such a reaction, the reverse reaction is thermodynamically preferred resulting in lower product yields (Figure 1d, blue curve).<sup>25,26</sup> Photochemistry provides alternative strategies for achieving challenging and unusual chemical transformations in this context.<sup>25,26,27</sup> However, since most organic molecules are incapable of absorbing visible light efficiently, direct high-energy ultraviolet (UV) light irradiation is required. Indeed, the UV-light mediated dearomative [4+2] cycloaddition with naphthalenes is known.<sup>28,29</sup> However, their utility in organic synthesis is minimal due to the requirement of specific *arenophiles*, meager product yields, and unpredictable side reactions conferred by UV light (Figure 1c). Eliminating UV irradiation should ideally broaden the synthetic applicability of this process with enriched structural diversity. The recent renaissance of visible-light photocatalysis provides a new space for dearomative [4+2] cycloaddition reaction via sensitization induced energy transfer (EnT) catalysis<sup>30,31</sup> or direct visible-light excitation of the *dienophile* in some cases.<sup>21</sup> Conceptually, the EnT process can selectively excite a ground state of a polycyclic hydrocarbon by using an appropriate photosensitizer to a higher triplet state (naphthalenes exhibit E<sub>1</sub>s of 54–60 kcal mol<sup>-1</sup>),<sup>32</sup> lowering the kinetic barriers significantly compared to thermal processes (Figure 1d, black curve).<sup>33</sup> Furthermore, the milder reaction conditions and substantially higher E<sub>T</sub> of the dearomatized product prevent the reverse reaction resulting in higher product yields.

Recently, Glorius and coworkers demonstrated dearomative [4+2] cycloaddition of pyridines (intramolecular)<sup>30</sup> and bicyclic azarenes (intermolecular, Figure 1e)<sup>31</sup> via visible-light EnT catalysis. A stoichiometric Brønsted acid additive was shown to play a vital role in the latter reaction to increase the reactivity of quinolines' triplet state toward olefins.<sup>31</sup> You and coworkers reported intramolecular dearomative cycloaddition of indole tethered naphthalenes (Figure 1f).<sup>34</sup> The dearomative intramolecular [2+2] cycloaddition of 1-naphthol derivatives via visible-light EnT catalysis was recently developed by Glorius.<sup>35</sup> The intramolecularity prepaid the entropic requirements for the last two reactions. Besides, various groups demonstrated the application of the EnT process in diverse chemical transformations.<sup>36-62</sup> However, to the best of our knowledge, intermolecular dearomative [4+2] cycloaddition reactions of naphthalenes with unactivated alkenes have not been documented yet. Herein,



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### Academic background

- Ph.D. (2012). Ludwig-Maximilians-Universität München, Germany. (Supervisor: Prof. Dr. Herbert Mayr,) Grade: Summa cum laude
- M.Sc. (2009). Indian Institute of Technology Kanpur (IIT K), India (M.Sc. thesis supervisor: Prof. Manas. K. Ghorai)
- B.Sc. (2007). Ramakrishna Mission Vidyamandira, University of Calcutta, India

### Professional Career

- Associate Professor (Since May 2021) Indian Institute of Science Education and Research (IISER) Kolkata, India
- Assistant Professor (July 2016-May 2021). Indian Institute of Science Education and Research (IISER) Kolkata, India
- Alexander von Humboldt Postdoctoral fellowship (2016) Westfälische Wilhelms-Universität Münster, Germany (Supervisor: Prof. Frank Glorius)
- Postdoctoral Research (2013-2015). Molecular Catalyst Research Center, Japan (Supervisor: Professor Hisashi Yamamoto)

### Awards

- 2021: Associate of the Indian Academy of Sciences (IASc)
- 2020: NASI-Young Scientist Platinum Jubilee Award (2020) in Chemical Sciences
- 2019: Thieme Journal Award
- 2017: Early Career Research Award, DST-SERB
- 2016: INSPIRE Faculty Award, DST
- 2015: Alexander von Humboldt Postdoctoral Fellowship
- 2013: "Förderpreis 2013" for best Ph.D. thesis, Ludwig-Maximilians-Universität München
- 2012: Award of the Dr. Klus Römer-Stiftung for Ph.D. students