The Fujiwara-Moritani reaction has had a profound contribution in the emergence of contemporary C–H activation protocols. Despite the applicability of the traditional approach in different fields, the associated reactivity and regioselectivity issues had rendered it redundant. The revival of this exemplary reaction requires the development of a mechanistic paradigm that would have simultaneous control on both the reactivity and regioselectivity. Often high thermal energy required to promote olefination leads to multiple site functionalization. To this aim we established a photoredox catalytic system constituting a merger of palladium/organo-photocatalyst that forges oxidative olefination in an explicit regioselective fashion of diverse arenes and heteroarenes. Visible light plays a significant role in executing ‘regio-resolved’ Fujiwara-Moritani reaction without the requirement of silver salts and thermal energy. The catalytic system is also amenable towards proximal and distal olefination aided by respective directing groups (DGs), which entails the versatility of the protocol in engaging the entire spectrum of C(sp)2–H olefination. Furthermore, streamlining the synthesis of natural products, chiral molecules, drugs and diversification through late-stage functionalization’s underscore the importance of this sustainable protocol. The photoinduced olefination of this regioselective transformation is mechanistically established through control reactions, kinetic studies and theoretical calculations.

The inception of Fujiwara-Moritani reaction had established a profound platform in the area of oxidative C–H functionalizations (Fig. 1a). This exemplary reaction, although inherits the advantages of a C–H activation process, falls apart in regioselectivity and reactivity. Very recently ligand approaches have been devised which helped in overcoming the reactivity issue and expanded the scope to various arenes and heteroarenes (Fig. 1b)13. However, the regioselectivity with most arenes still remains problematic, unless the (hetero)arene is sterically or electronically biased. A mechanistic scrutiny of the Fujiwara-Moritani reaction reveals that oxidative olefination occurs via initial electrophilic palladation. Thus, palladation is expected to occur at the more nucleophilic position of the arene guided by the intrinsic stereo-electronic factors. However, available thermal energy to promote the reaction is sufficiently high to perturb the regio-selection as multiple C–H bonds of arenes are prone to undergo activation which results in multiple unwanted products formations. This genre of non-directed C–H functionalization in general could herald the next phase of modern catalysis particularly in expanding the chemical space through late-stage functionalization; provided there is no compromise on the regioselectivity14,15. Presumably, along with the ligand assistance, a milder energy source is required which would be sufficient for the C–H activation while allowing the desired regio-selection only through kinetically driven process. In addition, a directing group strategy can be employed in conjunction with mild condition (Fig. 1c)15,16.

The paradigm of merging transition metal catalysis with photocatalysis has invoked mechanistic wonders in cross-coupling reactions17,18. This redifining of chemistry is forged either by a modulated oxidation state or in situ generation of an excited catalytic species through energy transfer19. Despite the economic and operational benefits19, its application in C–H activation with palladium catalysis remains elusive20. Converging the appealing properties and complementary reactivities of palladium catalysis with photocatalysis17,18 has the potential of creating diverse C–H activation manifolds in a sustainable manner, and this combination fits aptly in the current context of regioselective Fujiwara-Moritani reaction (Fig. 1d). Here, we describe how Pd/organic photocatalysis can achieve the regioselective olefination of arenes and heteroarenes (Fig. 1f and 1g). As per an intuitive mechanistic postulate, Pd/ligand combination serves the purpose of the C–H activation while bypassing the thermal activation mode (Fig. 1e). Presumably, the photocatalysis of Pd species upon energy transfer in the presence of a photocatalyst and visible light source attribute to the C–H activation process. The mildness of the light energy allows the regioselective palladation to occur at the most electron-rich site. The same photocatalyst/light merger is also effective for the regeneration of Pd(II) from Pd(0) to continue the cycle21. Since the redox potential has a crucial role to play in the dual functioning of activation and oxidation, a prudent choice of organo-photocatalyst is necessary. Most notably, the present catalytic system obviates the use of super-stoichiometric silver salt as the oxidant, although it is known to play a pivotal role to regenerate the active catalyst in the reaction under thermal conditions22.

We initiated our investigations with the photo-induced olefination of arenes via non-directed approach. From the established redox potentials of organo-photocatalyst eosin-Y23 and Pd(II)/Pd(0), the regeneration of the active catalyst can be conceived. However, the point of uncertainty was the feasibility of initial C–H activation step through energy transfer excitation of the Pd species. To proceed with the validation of the photoinduced C–H activation step, a palladium complex with the pyridone ligand (L1) was structurally characterized by X-ray crystallography (Fig. 1h). The competency of this photocatalyst in effectuating C–H activation was adjudged by the absorption experiments, which showed the maxima in the visible light region, complying with the mechanistic hypothesis (Fig. 1i). Besides, absorption studies performed at an interval of 5 min on mixing the individual components of the standard reaction without olefin also indicated the formation of a similar type of Pd species which too shows absorption in the visible light region (see Supplementary Information for details). To verify all these observations in an experimental set up, α-xylene, bearing two distinct reaction sites (α and β), was subjected to olefination employing the Pd(OAc)2/eosin-Y/visible light combination at room temperature under air. The outcome of this reaction was encouraging, indicating the actual path is in line with the mechanistic postulate. The Pd-photocatalyst was also found to be catalytically competent in promoting the photoinduced olefination (see Supplementary Information for details). This led to a survey of various combinations of Pd salts, photocatalysts in presence of a CFL lamp (23 W) as the visible light source. It turned out that fluorescein rendered near explicit β-regioselectivity along side high yield of the olefinated product (1). The pyridone-based ligand played a decisive role in improving regioselectivity and reactivity of arenes towards photoinduced Fujiwara-Moritani reaction. However, it may be noted here that pyridine and quinoline based ligands examined for this transformation provided inferior results pertaining to regioselectivity. An extensive study of different parameters finally accomplished a reaction condition that afforded 88% of the olefinated product (1) with β α selectivity>25:1 (for optimization details see Supplementary Information). A minimal requirement of a catalytic Pd(OAc)2/ligand photocatalyst to perform olefination at room temperature with a commercially available CFL lamp established an ideal set of conditions for interrogating the generality of this process in terms of scope and regioselectivity.

The optimal conditions were then implemented to explore the scope of olefins as coupling partners of α-xylene (Fig. 2a). An array of diversely substituted acrylates served as effective coupling partners for this transformation giving excellent yields of the desired olefinated products and maintaining high degree of β-selectivity (2-6). The present catalytic system was amenable to olefins possessing free carboxylic acid (7), ketone (8), nitrile (9), phosphonate (10) and sulfone (11), with equivalent efficiency as acrylates. With a cyclic α,β-unsaturated ester, an allylic product was obtained in a synthetically useful yield and high β-regioselectivity (12). In general, it is observed that acrylic acid is often incompatible in a Fujiwara-Moritani reaction; albeit defined in present transformation. We next evaluated simple arenes which are deemed as problematic substrates in a non-directed approach owing to the formation of regioisomeric mixture of products. An exclusive formation of a single regioisomer was observed in all cases of mono-substituted arenes irrespective of their electronic nature (Fig. 2i). While toluene (14), anisole (15) and chlorobenzene (16) provided exclusive para-selectivity; nitrobenzene (18), trifluoromethyl benzene (19) and benzyaldheyde (20) gave exclusive meta-selectivity and that with fluorobenzene (21) exclusive ortho-selectivity was observed. Noteworthy that even with highly electron-withdrawing effects of –NO2 and –CF3 the reactivity and regioselectivity were not hampered. The intriguing aspects continued with exclusive para-olefination of free phenol (17) obviating the prior protection protocol. A comparison of regioselectivity with these arenes under a similar thermally controlled condition establishes the superiority of the present one. Even with disubstituted arenes having different substitution patterns (22,25), regiospecific olefination occurred to provide the respective products in synthetically useful yields. The selectivity in all these arenes are expected to be primarily dictated by the electron density where palladation is favored together with the steric influence imparted by substituents and

Argha Saha1, Srimita Guin1, Wajid Ali1, Trisha Bhattacharyya1, Sheuli Sasmal1, Nupur Goswami1, Gaurav Prakash1, Soumya Kumar Sinha1, Hidyabala B. Chandrashekar1, S. S. Anjana2 & Debabrata Maiti1*
lipid. For naphthalene the maximum $\beta$ is selectivity that could be attained was at $100^\circ$C; using enantiomer-purified (L3) as the suitable ligand (L3) (26). The compatibility was further showcased by the regiocontrolled olefination of ferrocene derivative (27).

As with the amines, the heteroarenes also possess multiple reaction sites (Fig. 2c). Scutari of literature reports unveils C-H olefination of common five- and six-membered heterocycles such as furan, thiophene and phenothiazine. In contrast to multiple regioselective products in the present case the same heterocycles afforded exclusive C3-olefinated products, unattainable thus far (28-29, 34-36). With C2/C3 substituted furan anilide olefination was observed (30-32); regioselectivity being governed by the steric contribution of the substituent. Moreover, the unprotected imidazole was competent as substrate for the photoinduced olefination at C5 position selectively (33). Usually the presence of free NH group on or off the catalytic cycle or even gives rise axial chirality when proficient under the current system; depicting the tolerance level of the transformation. With pyrimidine, a C2 selective olefination was achieved.

Olefination of naphthalene systems under the present photocatalytic conditions (Fig. 3c) (20), usually it has been noticed that the first photoinduced axial chirality at the biaryls by dynamic kinetic resolution (Supplementary Information) is observed. The viability of acrylates and acrylic acid leaves the scope of tethering natural products into them. Indeed, a host of acrylates with complex natural product patterns viz. cholesterol (40); ergosterol (41); and citronelol (52) underwent facile reactions with arylene and heteroaromatic systems irrespective of any compromise in regioselectivity (20). The generation of a library of structurally diverse natural products clearly demonstrate the robustness of the protocol.

Despite the inherent advantages of non-directed approach, assistance of a directing group will continue to persist as the quintessential part for obtaining complementary regioselectivity. This propelled the implementation of photoinduced irreversible olefination of acrylates with focus on weak coordinating DG such as acetonide and silanol (Fig. 3a) (22). Noteworthy, a combined photo-thermal approach is reported for the synthesis of indole by oxidative olefination, restricted to intramolecular approach only (23). For anilide a slightly revised reaction conditions enabled the oxidative olefination to occur in a mono-selective fashion and high yields. An array of acrylates (53-55, 58), $\alpha,\beta$-unsaturated ketones (56) and sulfones (57 and 59) could be incorporated at ortho-position with the aid of photocatalysis. The transformation worked with equal efficiency for substituted acetonides irrespective of their position and electronic nature (57-59). Even pivalamide as a DG proved efficient for ortho-olefination of naphtalene system under the present photocatalytic conditions (60 and 61). With benzil silanol system, eosin-Y provided superior results over other organo-photo catalysts (for optimization details see Supplementary Information). The modified conditions led to high reactivity for olefination even at room temperature despite the weak electron withdrawing nature of DG (62-64). The big lead that evolved out of the ortho strategy is the first photoinduced axial chirality at the biaryls by dynamic kinetic resolution (Fig. 3c). In presence of (L)-N-Methyl maleimide as the chiral ligand and the heteroleptic iridium photocatalyst facile olefination occurred at the targeted position of the biaryl system leading to atropisomers with high degree of enantiopurity (65-66).

The merger of palladium catalysis with photocatalysis was pursued further with the aim of performing DG assisted distal meta- and para-C-H olefination; the genre which remains completely unprecedented till date. Usually it has been noticed that for a successful outcome of Pd catalyzed olefination at distal positions, the requirement of silver salt is apparent. In this aspect several computational studies have been carried out that hints towards the formation of Ag-Pd heterobimetallic system which is responsible for a better distal regioselectivity (67). A fascinating fact observed from the present strategy is the attainment of exclusive distal selectivity at room temperature even in the absence of silver salt (Fig. 3c). In the context of meta-C-H olefination, 4-methoxy-2- cyano-phenol was utilized as the directing group with linkers such as sulfonfyl (67-72), silyl (73-74), phosphonate (75-76), and trifluoromethyl (77-84). Diverse ortho-substrates were well tolerated and provided excellent meta-selectivity with good yields of the respective olefinated products using eosin-Y as the optimal photoredox catalyst. The catalytic system was suitable in accessing unsaturated acrylates, vinyl ketones, sulfones, phosphonates and phthalimides. Even with the extended linker length there was no drop in regioselectivity (78-80). The biphenyl carboxylic acid was also suitable as substrate in providing the desired olefination even with cofacial N,N dimethylmaleimide (81). This photocatalyst marks the use of 2-amino benzonitrile as an effective DG for meta-olefination of phenyl acetic acid derivatives (82). Finally marketed drugs and analogues were subjected to late-stage functionalization by the present catalytic system. Ibuprofen (NSAID) and clofibrate (herbicide) were transformed to their meta-olefinated derivatives in useful selectivities (83-84). The photoinduced para-C-H olefination was next sought after using our recently developed second-generation para-DG (Fig. 3d). The results obtained were exceedingly satisfying; in most cases the para-selectivity was observed. The optimal B-Pd-Aux of 10:1 using enantiomer-purified (L3) as the suitable ligand (L3) (26). The compatibility was further showcased by the regiocontrolled olefination of ferrocene derivative (27).

The development of benign reaction conditions for highly regioselective oxidative olefination by non-directed approach gives ample opportunity to explore the potential of drug discovery with the help of improved functionalization of bio-relevant molecules. Such an approach is expected to broaden the scope for encompassing molecules which are inaccessible for functionalization by DG-ligated diazo compounds. Ibuprofen, a COX-2 selective non-steroidal anti-inflammatory drug was employed with the help of palladium catalysis to prepare aza-olefination products (Fig. 4a). The newly developed photoredox system expedites the synthesis of caffeic acid (95), curcumin (100), plicatin B (101), drupamine (102), artemisinin C (103) and others (98-99); synthesis of which in a directed strategy demands inclusion of multistep procedures (Fig. 1j). The late-stage functionalizations of various bioactive compounds (99) under the present photocatalytic conditions (Fig. 4a) will continue to persist for details (Supplementary Information for deta) were characterized for their role in regenerating the active C-H olefination observed for (Fig. 1j). High reactivity with the most electron dense site having led to high reactivity with the most electron dense site having (Fig. 1j). Directing approaches clearly demonstrate the robustness of the protocol.

Based on our proposed design plan, the fundamental part of this metallophotoredox transformation is the dual role of visible light as an oxidant and activator. In order to probe that, a series of control experiments were performed in a step wise manner. In absence of either the photocatalyst or visible light, a minimal conversion was observed which suggests that in the oxidation step their role is imperative in regenerating the active catalyst (Fig. 4c, eqn. 1 and 2). A standard reaction was carried out with deoxygenated solvent and liquid components under argon atmosphere that led to trace amount of the product (Fig. 4c, eqn. 3). The same reaction with 100 fold of the photocatalyst catalyst (TEMPO), phenyl n-Butyryl thionine (PNTB) and butylated hydroxytoluene (BHT), respectively. None of these reactions exhibited any noticeable impediment of catalytic activity, referring that radical reaction is unlikely to be operative. Further, a higher value of KIE for both non-directed and directed reactions implies the C-H activation step is facilitated by photophysical energy.

In order to rationalize the excellent regioselectivity observed for the C-H olefination of various amines in the present transformation, we determined Fukui values for several (hetero)amines by computing a population analysis for each amine (see Supporting Information for details). As shown in Fig. 4e, the electron-density map of partial charges correlates to the observed regioselectivity of (hetero)amines; with the most electron dense site having the highest probability for oxidative functionalization. The conversion profile of the reaction was monitored through an on/off experiment (see Supplementary Information for details). A suppression in the product formation when the CFL was switched off indicates the requirement of constant photoexcitation for an effective transformation (see Supplementary Information for details). In order to analyze the mode of reaction, three independent reactions were performed with three equivalence of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), phenyl n-Butyryl thionine (PNTB) and butylated hydroxytoluene (BHT), respectively. None of these reactions exhibited any noticeable impediment of catalytic activity, referring that radical reaction is unlikely to be operative. Further, a higher value of KIE for both non-directed and directed reactions implies the C-H activation step is facilitated by photophysical energy during the rate-determining step (see Supplementary Information for details).

In summary, we have devised a palladium photoredox protocol for accessing photoinduced Fujiwara-Moritani reaction by both the non-directed and directed approaches without the requirement of silver salts and thermal energy. Present transformation highlights the C-H scissoring visible as an oxidant and activator in enabling the following: (a) highly regioselective olefination of (hetero)amines via non-directed approach; (b) expedite the synthetic routes to phenolic natural products; (c) photoinduced axial chirality by dynamic kinetic resolution of biaryls (d) first distal functionalization by photocatalysis and (e) late-stage functionalization of bio-relevant molecules. The mechanistic finding brings forward an elusive form of this transformation occurs in dark (Fig. 3d). The formation of selective meta dimer through oxidative coupling upon light irradiation indicates the energy required for C-H activation step is fulfilled by photophysical energy.
into light through the photocatalysis of palladium catalyst and is expected to create a paradigm for wide scale industrial and biological applications.

**Received** (to be inserted automatically)

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Figure 1 | Evolution of Fujiwara-Moritani reaction. a. Traditional approach for oxidative olefination. b. Directing group assisted proximal and distal C–H activation. c. Ligand enabled Fujiwara-Moritani reaction. d. Photoinduced vs thermal Fujiwara-Moritani reaction. e. Mechanistic hypothesis for the photoinduced Fujiwara-Moritani reaction. f. A comparative study of regioselectivity for selected arene substrates under thermal and photoredox conditions. g. A comparative study of regioselectivity for selected arene substrates under thermal and photoredox conditions. h. Crystal structure of Pd-precatalyst. i. UV absorption studies of reaction components. j. A comparison of steps required to synthesize a phenolic drug via photoinduced Fujiwara-Moritani reaction in a non-directed strategy vs the directing group strategy.
Figure 2: Photoinduced olefination by non-directed approach.  

### a. Olefin variation

| Entry | Scope of olefins for photoinduced olefination of o-xylene. | Isolated yields |
|-------|----------------------------------------------------------|-----------------|
| 1     | 85% (β/α > 25:1)                                         |                |
| 2     | 90% (β/α > 25:1)                                         |                |
| 3     | 95% (β/α > 25:1)                                         |                |
| 4     | 92% (β/α > 25:1)                                         |                |
| 5     | 93% (β/α > 25:1)                                         |                |
| 6     | 90% (β/α > 25:1)                                         |                |
| 7     | 81% (β/α > 25:1)                                         |                |
| 8     | 86% (β/α > 25:1)                                         |                |
| 9     | 85% (β/α > 25:1)                                         |                |
| 10    | 87% (β/α > 25:1)                                         |                |
| 11    | 71% (β/α > 25:1)                                         |                |
| 12    | 79% (β/α > 25:1)                                         |                |

### b. Arene variation

| Entry | Scope of mono- and di-substituted arenes. | Isolated yields |
|-------|-------------------------------------------|-----------------|
| 13    | 95% (p-exclusive)                         |                |
| 14    | 85% (p-exclusive)                         |                |
| 15    | 65% (p-exclusive)                         |                |
| 16    | 73% (p-exclusive)                         |                |
| 17    | 74% (p-exclusive)                         |                |
| 18    | 45% (m-exclusive)                         |                |
| 19    | 69% (m-exclusive)                         |                |
| 20    | 50% (m-exclusive)                         |                |
| 21    | 68% (p-exclusive)                         |                |
| 22    | 67% (p-exclusive)                         |                |
| 23    | 62% (p-exclusive)                         |                |
| 24    | 66% (exclusive)                           |                |

### c. Heteroarene variation

| Entry | Scope of heteroarenes towards photoinduced olefination. | Isolated yields |
|-------|---------------------------------------------------------|-----------------|
| 25    | 74% (exclusive)                                         |                |
| 26    | 79% (β/α 14:1)                                          |                |
| 27    | 81% (exclusive)                                         |                |
| 28    | 70% (C3-exclusive)                                      |                |
| 29    | 74% (C3-exclusive)                                      |                |
| 30    | 77% (C5-exclusive)                                      |                |
| 31    | 80% (C5-exclusive)                                      |                |
| 32    | 55% (C5-exclusive)                                      |                |
| 33    | 69% (C5-exclusive)                                      |                |
| 34    | 70% (C3-exclusive)                                      |                |
| 35    | 72% (C3-exclusive)                                      |                |
| 36    | 85% (C3-exclusive)                                      |                |
| 37    | 65% (C2-exclusive)                                      |                |
| 38    | 69% (C3-exclusive)                                      |                |
| 39    | 72% (C3-exclusive)                                      |                |
| 40    | 60% (C2-exclusive)                                      |                |
| 41    | 56% (C3-exclusive)                                      |                |

### d. Natural product pendant olefin

| Entry | Source of natural product pendants. | Isolated yields |
|-------|-------------------------------------|-----------------|
| 42    | from geraniol                        | 72% (p-exclusive) |
| 43    | from cholesterol                     | 74% (p-exclusive) |
| 44    | from fenchyl alcohol                 | 85% (p-exclusive) |
| 45    | from 5-tocopherol                    | 78% (p-exclusive) |
| 46    | from olaic acid                      | 69% (p-exclusive) |
| 47    | from γ-oryzonal                      | 66% (p-exclusive) |
| 48    | from pregnaolone                     | 82% (exclusive)  |
| 49    | from ergosterol                      | 69% (p-exclusive) |
| 50    | from estrone                         | 67% (p-exclusive) |
| 51    | from geraniol                        | 73% (p-exclusive) |
| 52    | from citronellol                     | 71% (p-exclusive) |

Condition: Pd(OAc)$_2$ (10 mol%), l-glycine (20 mol%), fluorescein (3 mol%), HfIP (1 mL), CFL (23 W), RT, 28 h.
Figure 3: Photoinduced olefination by directing group strategy. a. Ortho-olefination of anilides and benzyl silanols. b. Dynamic kinetic resolution of biaryls by photoinduced olefination. c. Meta-olefination of arenes. The isolated yields are reported and ratios of meta:others are shown. d. Photoinduced para-olefination of arenes. The isolated yields are reported and ratios of para:others are shown. See Supplementary Information for experimental details.
Figure 4: Applications and mechanistic investigations. a. Short-step synthesis of phenolic drugs and natural products. b. Late-stage functionalizations of bio-relevant molecules. c. Role of light in oxidation step. d. Role of light in C–H activation. e. Fukui values of different (hetero)arenes.