Transition Metal Catalyzed Remote C-H Activation: *A New Direction Towards Site-Selective Chemical Reactions*

By Jayabrata Das, and Debabrata Maiti

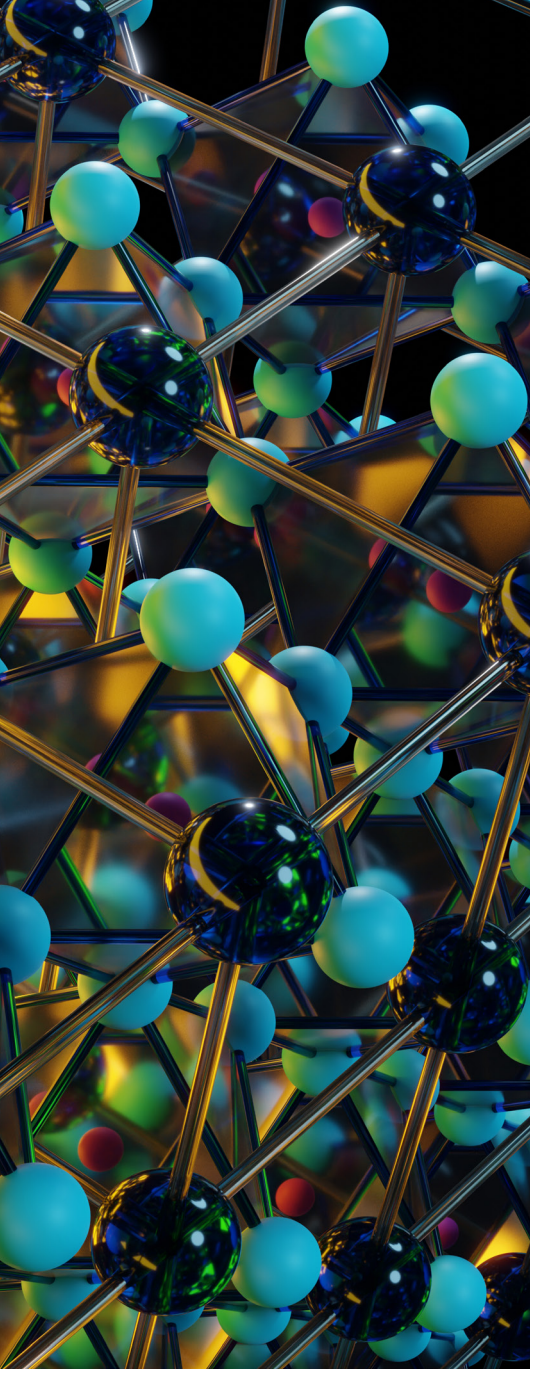
https://doi.org/10.51167/acm00036

Jayabrata Das
Jayabrata Das was born in India. He received his master's degree from the University of North Bengal in 2016. Then he moved to Indian Institute of Technology Bombay to pursue his Ph.D. In the group of Debabrata Maiti, he worked on transition metal catalyzed remote activation of aryl and aliphatic substrates. He received his Ph.D. degree in 2022. Currently, he is a post-doctoral fellow with Prof. Timothy Cernak at the University of Michigan. His work revolves around the interface of chemical synthesis and computer science.

Debabrata Maiti
Debabrata Maiti obtained his Ph.D. in 2003 from Johns Hopkins University, USA with Prof. Kenneth D. Karlin. Later he moved to Massachusetts Institute of Technology, USA to pursue post-doctoral studies with Prof. Steve Buchwald. In 2011, he joined Indian Institute of Technology Bombay as an assistant professor. He is now a full professor at Indian Institute of Technology Bombay. His research area revolves around catalysis and metal catalysed C-H activation of arenes, heteroarenes, aliphatic compounds, photocatalysis, electrocatalysis, artificial metalloenzyme, etc.

Transition metal catalyzed remote C-H activation offers a powerful tool to modify architecture of organic molecules. Remote or distal C-H activation of aromatic and aliphatic compounds presents more challenge than proximal sites due to the inaccessibility of these sites in formation of energetically favorable organometallic pre-transition states. Nonetheless, recent years have witnessed remarkable progress in reaching out and functionalizing distal C-H bonds. With the advancement of this field, synthetic modifications of organic molecules have become more step and atom economical, and have shown great promise to revolutionize synthetic organic chemistry.

Chemical synthesis has been one of the most significant inceptions in the human history. The modern civilization relies heavily on the efficiency of doing chemical synthesis for the sustainable future of humankind. The discovery of new drugs, organic materials, agrochemicals, etc. depend on the ease and effectiveness of carrying out chemical reactions. For the same reason, the pursuit of inventing new strategies that could make synthetic chemistry more potent has always received tremendous importance in Chemistry. A functional group is the most active moiety in an organic molecule. Synthetic Chemistry in the earlier days started with the functional



group conversion in organic molecules. Gradually, Chemistry of C-H functionalization took off. Cross coupling reactions such as Heck, Suzuki, Sonogashira, Hiyama, Kumada, etc. discovered in 1970s impacted the synthetic chemistry significantly.[1] Coupling between two organic compounds became easier by utilizing cross-coupling reactions. Nonetheless, there remain some problems to be solved in cross-coupling reactions. A prefunctionalized substrate as starting material is necessary in aforementioned reactions which hampers the atom as well as step economy and cost-associated with the reactions. Add with this the waste generated in cross coupling reactions that often become problematic in industrial large scale reactions. A more effective and simpler strategy was required to tackle these problems. C-H activation came with tremendous promise to solve the limitations of previous approaches of doing chemical reactions. C-H bond which is the most abundant part in any organic compound is being utilized in C-H activation to make a new bond, making it a lucrative approach of performing chemical reactions. In this strategy, a particular C-H bond is being broken (activated) by a metal to form a metallacycle (an inner sphere mechanism). Further, an external coupling partner adds to the metallacycle to provide a functionalized product.[2] Although the concept of C-H activation is known from 1960s or 70s through the work of Shilov, Murahashi, Bergmann, etc., the first example of catalytic C-H active reaction was reported by Murai in 1993.[3] Since then a remarkable progress have been witnessed in this domain. Although enormous amount of work have been carried out to improve C-H activation, most reported works outlines the selective C-H activation in the proximal sites of organic molecules. For example, ***ortho*** C-H bond in an aromatic compound is considered proximal but ***meta*** and ***para*** as distal or remote bond. Similarly, α and β C-H bonds of aliphatic substrates are considered nearby or proximal, but, γ δ, ε, etc. as remote C-H bonds. Carrying out reactions at proximal sites are relatively easier as the reactions require formation of thermodynamically favorable metallacycle in transition metal catalyzed reactions. However, the reaction at remote sites requires intermediacy of larger and less favorable metallacycle which make such reactions more challenging to carry out. Over the last few years, our focus has been to address these challenges and take remote C-H activation to a level where it could be routinely applied in academic and industrial settings.[4-7]

Transition Metal Catalyzed Remote C(sp^2)-H Activation

Aromatic compounds are prevalent in nature in the form of pharmacoactives, agrochemicals, fragrance molecules, etc. C-H functionalization of these molecules is of utmost importance to improve their utility and significance. In the past, the traditional methods such electrophilic or nucleophilic substitution reactions were utilized to insert a functionality into an organic molecule (Figure 1A). These reactions had limitations such as selectivity, functional group tolerance, waste generation, etc. To circumvent the drawbacks, cross coupling reactions were preferred by synthetic chemists after 1970s (Figure 1B). In this realm, C-H activation comes with a promise to make synthesis greener and more efficient. Although activation of proximal ***ortho***-C-H bond in aryl compounds have been well-known since 1990s, activation of distal ***meta*** or ***para*** C-H bond have not been explored until 2012. The difficulty in reaching out ***meta*** or ***para*** positions lies in the formation of larger metallacycle formation. Whereas, ***ortho*** C-H activation require favorable five or six membered metallacycle formation, ***meta*** or ***para*** present challenge to form less favorable 13-17 membered metallacycle. Nonetheless, in the last decade several strategies have been devised for regioselective distal functionalization of different arenes. These includes (1) σ-bond activation–assisted remote C–H functionalization, in which initial ***ortho***-cycloruthenation plays a significant role in favoring selectively at the ***meta*** or ***para*** position (Figure 1C).[8] (2) template-assisted remote C–H Functionalization (Figure 1D).[9-10] (3) bifunctional template for remote C–H activation of heteroarenes (Figure 1E). (4) noncovalent interaction enabled remote C–H functionalization (Figure 1F).[4] (5) palladium/transient mediator cooperative catalysis for remote C(sp^2) -H functionalization.[11] (6) transient template approach for remote functionalization (Figure 1G). The exploration in this field started with template assisted approaches in the beginning years. Activating remote C-H bonds in aromatic compounds require meticulous design of templates that could assist in holding a metal in the proximity of remote C-H bonds. Yu and coworkers in 2012 outlined ***meta*** C-H activation of toluene and hydrocinnamic acid derivatives by employing a U-shaped template containing a nitrile group (Figure 2a).[12] The weak end-on interaction between nitrile group and palladium aided the ***meta*** C-H activation in this case. This U-shaped template overrides the intrinsic electronic and steric biases as well as ***ortho***-directing effects substrates utilized in this case. We have later designed another nitrile based template to extend the selective meta-C-H functionalization. Not only ***meta,*** but the furthest ***para*** C-H bond could also be exploited for C-H activation. A D-shaped biphenyl template was engineered by our group to serve the purpose (Figure 2b).[13] Selective ***para*** olefination reaction was achieved without affecting ***ortho*** or ***meta*** C-H bond of substrates. Although weak coordination of nitrile group provided excellent results for selective ***meta*** or even ***para*** C-H activation but the number of transformations that could be achieved was limited. Olefination found to be the most viable reaction with weak coordinating template. Later, we also showcased silylation and germanylation at ***meta*** position of aryl compounds. To extend the diversity of reactions that could be performed at remote ***meta*** and ***para*** sites, a better design of the template was essential. We came up with a biphenyl pyrimidine template that offers strong coordination to metal for doing diverse chemical reactions at ***meta*** C-H bond.[5] A plethora of ***meta***-selective reactions such as cyanation, alkylation,

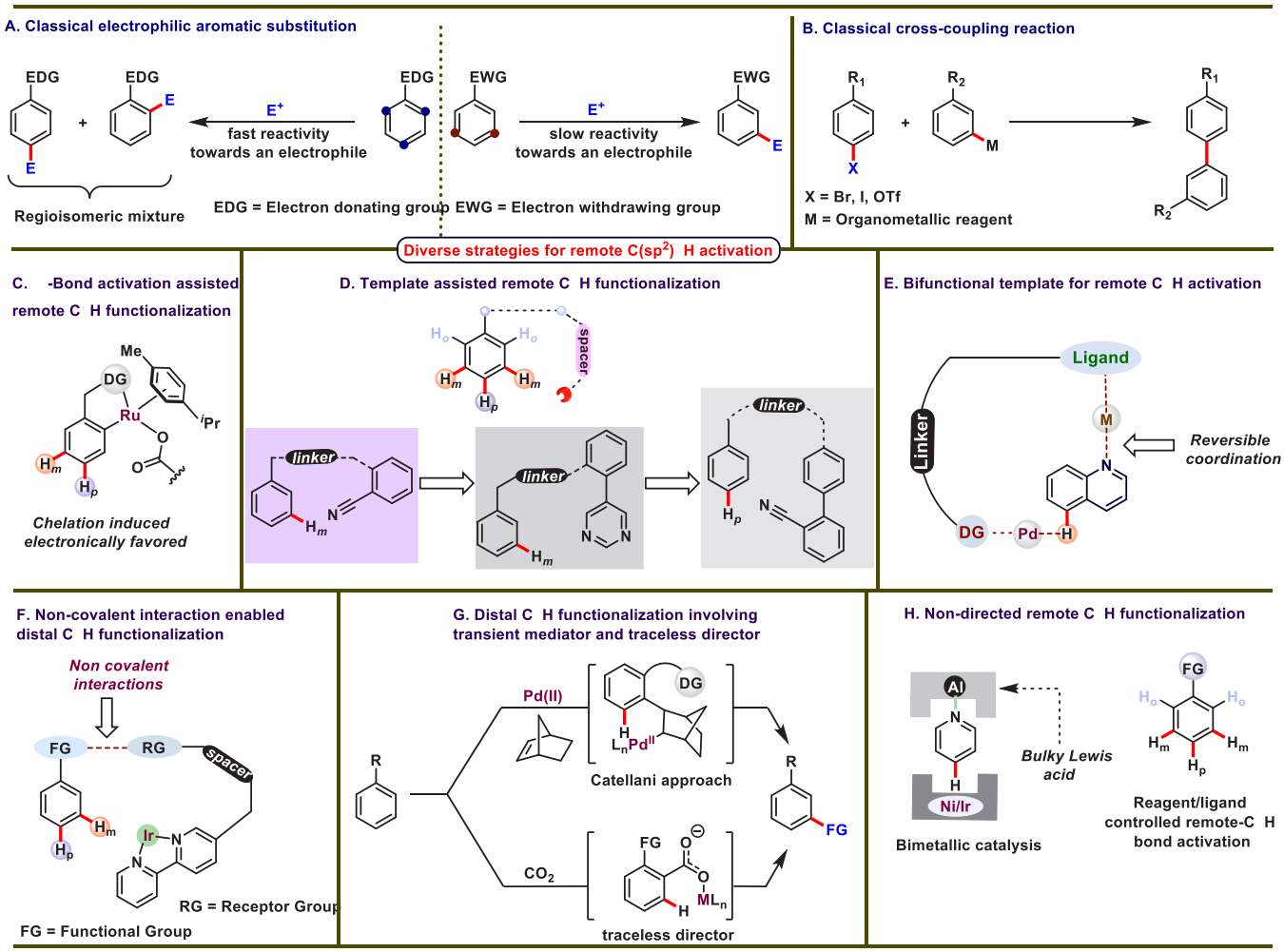


Figure 1. Overview of various strategies for remote C(sp^2)–H activation

allylation deuteration, perfluoroalkylation, etc. were carried out using the pyrimidine template (Figure 2d). We also developed our 2nd generation template for *para* C-H activation by introducing electron richness in the biphenyl-D-shaped template. Reactions such as silylation, carboalkylation, cyanation, etc. were performed with the 2nd generation template.[4] The remote C(sp^2)-H activation reactions are catalyzed most often by Pd catalysts. This overdependency on Pd catalyst made it necessary to expand the horizon of transition metals from Pd to other abundant metals for distal C-H functionalization. In 2017, we reported the *meta*-olefination and alkynylation of arenes catalyzed by rhodium (Figure 2g).[14,15] Later we expanded rhodium catalysis for *para*-olefination of arenes using our D-shaped template.[16] Although template assisted strategy is great for establishing proof of concept in remote C(sp^2) -H functionalization, but when it comes to practical applications, template approach present limitations, mainly the need of an extra template which need to be added and removed pre and post functionalization, limiting the step and atom economy of the reaction. To counter such drawbacks, non-covalent interactions or transient directing group approaches have been employed in recent years. In these cases, the substrate and the template need not be attached in a covalent fashion thus resolve the problem of addition and removal of template, hence improve the step economy. Groups of Phipps and Chattyopadhaya have designed templates (or ligands) that take part in non-covalent interactions such as hydrogen bonding, ion-pair interaction, etc. with the substrates and place the metal in the close vicinity of remote C-H bond, thus activate and functionalize these bonds.[4] In 2021, our group outlined a transient directing group approach for *meta*-C-H olefination of biphenyl aldehyde and amines (Figure 2e).[17] A pyrimidine template containing either -NH_2 or –CHO have been employed as the transient template to form an imine intermediate *in situ*. The imine intermediate form within the reaction directs the metal to *meta*-position of the substrate and hydrolyzes after functionalization by addition of simple acid. Thus this approach discard the necessity to attach and remove an exogenous template, making the approach more efficient and practical. A complementary strategy for remote C(sp^2)-H functionalization involve a transient mediator that facilitates palladium relay chemistry, has emerged as a productive research field in recent years. The Pd-relay process in conjunction with norbornene (NBE) as transient mediator is famously named after Prof. Marta Catellani, who introduced the methodology.[8] Groups of Yu and Dong have shown beautifully the utility of norbornene as mediator for remote functionalization of arenes. Simultaneously, we have reached the *para* C-H bond of arenes employing norbornene derivative as a transient mediator. We have utilized our *meta* directing group that first bind with Pd and activate meta C-H bond (Figure 2h).[18] Further a Pd-relay process invoked by the norbornene assist to activate the *para*-C-H bond. Substantial effort has been also devoted towards non-directed distal C-H functionalization that overrides the inherent electronic bias of the arenes. This strategy allows to insert a number of functionality into arenes in a straightforward manner. Steric effect controlled non-directed C-H functionalization of 1,2- or 1,3-disubstitued benzenes has been developed by several research groups. However, in recent times most popular approach has been to

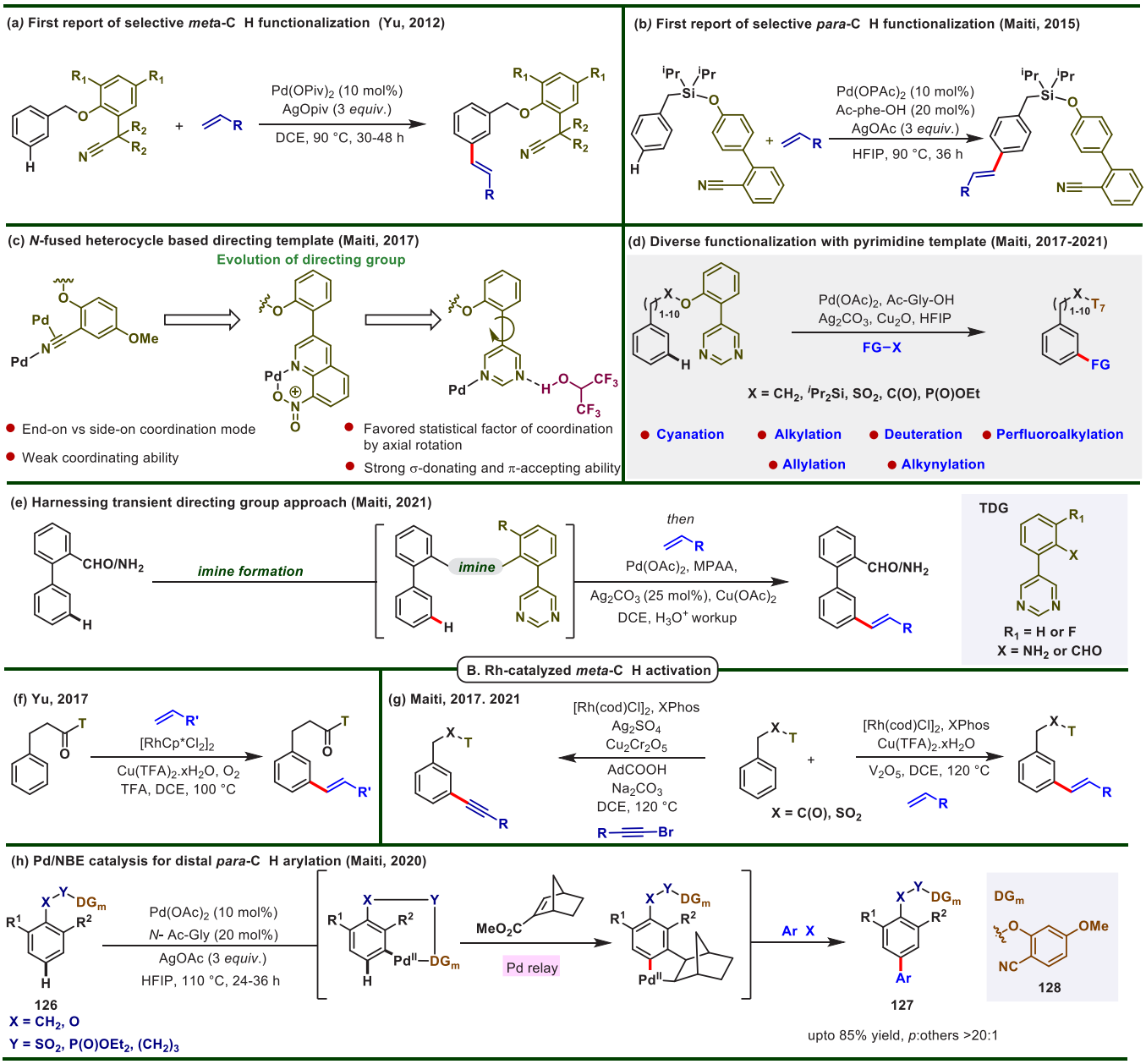


Figure 2. Diverse approaches developed for meta or para C(sp^2)–H functionalization

utilize a suitable ligand for controlling the regioselectivity of arenes. In this realm, Yu group in 2017 reported regioselective olefination of various arenes employing 3,5-bis(trifluoromethyl)pyridin-2-ol ligand as an external ligand. Later van Gemmeren and Ritter group gave also contributed in this field. Our group is also actively involved in exploring this research domain. In 2021, we showcased a phocatalysed C-H olefination of arene and heteroarenes that overcame a lot of previous selectivity issues.[19] In 2022, thioarylation of arenes/hetroarenes has been achieved using suitable pyridone ligands.[20]

Transition Metal Catalyzed Remote C(sp^3)-H Activation

Although remote C(sp^2)-H activation has been well-explored over the last two decades, distal C(sp^3)-H activation in aliphatic compounds remains elusive. The challenge associated with C(sp^3)-H activation are greater than with C(sp^2)-H activation due to inert nature of aliphatic C-H bond, fluxional nature of aliphatic compounds, and lack of assistance from π groups that could interact with transition metal centers. All of these together make sp3 C-H bond activation more strenuous. It is worth mentioning that remote activation of aliphatic substrates requires intermediacy of six or over six-membered metallacycle that are considered thermodynamically less favorable and challenging to form. Instead of these challenges, the area of remote C(sp^3) -H Activation has progressed remarkably in the last decade.[7] The initial reports of remote C(sp^3) -H functionalization came from the groups of Daugulis and Corey in the years 2005-2007. A strong coordinating external auxiliary or directing group such as 8-amino quinolone, 2-picolinic acid, etc. were utilized to activate inert sp^3 C-H bonds. Later the diversity of functionalizations were extended by employing other directing groups like oxazole, triazole, etc. We have also contributed significantly in this challenging field of remote C(sp^3) -H Activation. In 2017, we devised a γ-arylation strategy for aliphatic acid using 8-amino quinoline as the directing group.[21] Later, olefination was carried out in the same substrate class (Figure 3b). Despite impressive progress in remote C(sp^3)-H functionalization, most reports were limited up to C-C and C-O bond formation.[22] Forming other class of bonds such as C-N, C-S, C-X (X = halogen), etc. are crucial for further applications of aliphatic C-H

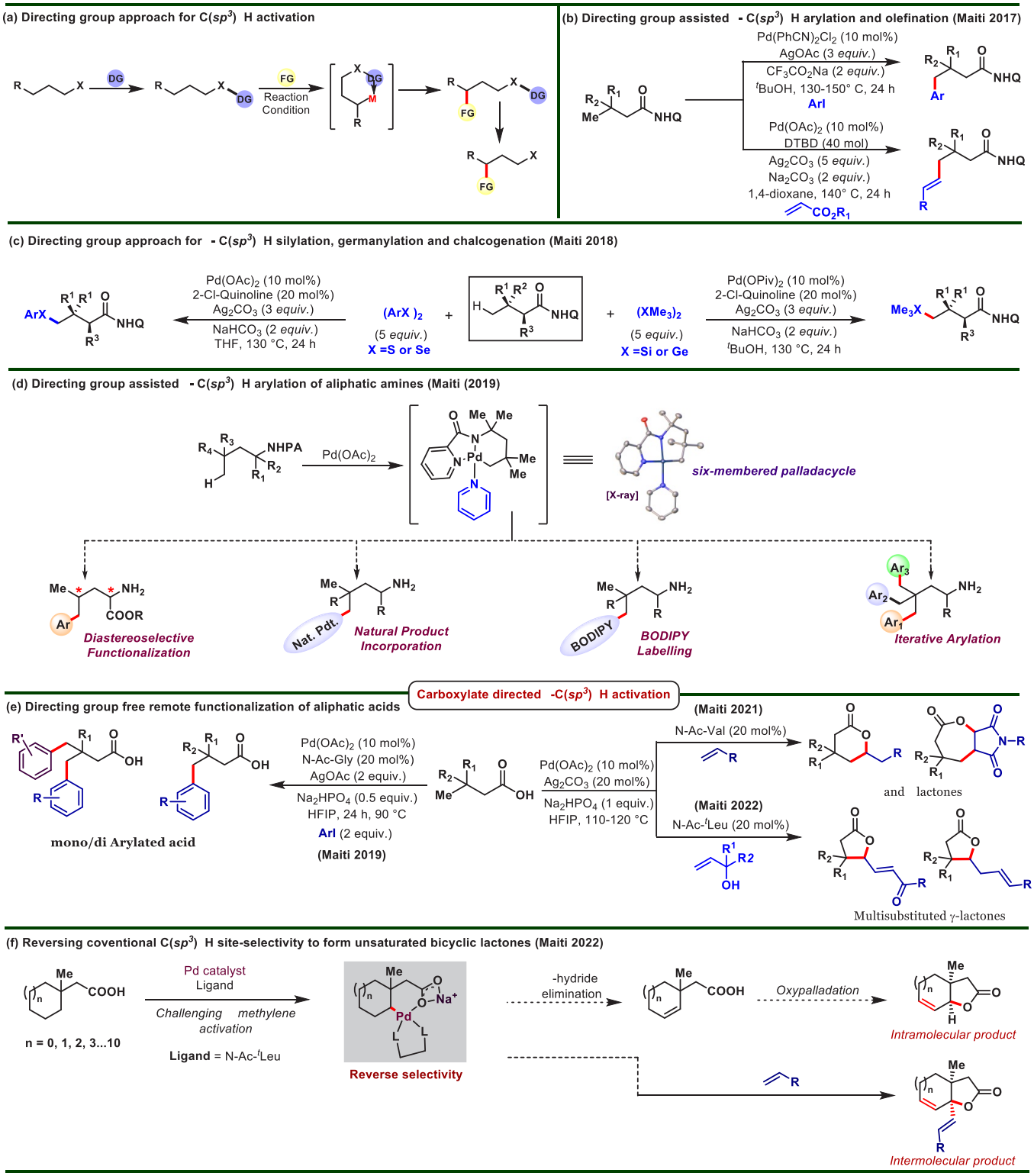


Figure 3. Divergent approaches for transition metal catalyzed remote C(sp^3)–H functionalization

activation. In this regard, we have reported the formation of C-S, C-Se, C-Si, and C-Ge bonds starting from aliphatic acid substrates (Figure 3c).[23, 24] These protocols enable the synthesis of bioactive chalcogen containing α-amino acids in fewer steps. Further, distal δ-(sp^3)-H bond of aliphatic amines have also been activated by our group and group of Shi. In 2019, we showed δ-(sp^3)-H arylation of a number of aliphatic amines (Figure 3d).[25] Notably, the activated six-membered palladacycle was characterized *via* X-ray crystallography. A number of aryl coupling partners including aryl iodides, natural product containing iodides, BODIPY derivatives were utilized as coupling partners in the reaction. Not just mono arylation, but even sequential di or tri arylation of amines have been performed using the same protocol.

Instead of these success stories, one of the major criticism in this domain has been the usage of external directing group which has to be attached and detached pre and post functionalization. An ideal approach would be to perform the reaction

with same efficiency but without using any extra auxiliary. In this realm, transient directing group approaches have come up as an alternative for amine, aldehyde, and ketone substrates where imine intermediate forms ***in situ*** and breaks down after the functionalization, omitting the need to covalently attach the directing group.[26] However, this approach is limited only to ketone, aldehyde, and amine substrates to some extent. However, a practical and preferred approach would be one where no usage of extra directing group is necessary. In other words, native functional group such as amine, acid, etc. present in the substrate could coordinate with the metal and assist in activating C-H bonds of the substrates.[27] In 2019, we reported for the first time that carboxylate group could activate the γ-(sp^3)-H bond of aliphatic acid substrate.[28] Employing various aryl iodides, γ-(sp^3)-H mono as well as diarylation was achieved. Later, we expanded this strategy to unsaturated systems such as alkene and allyl alcohol (Figure 3e). Whereas, alkene with aliphatic acid provided six and seven membered lactones, usage of allyl alcohols furnished multisubstituted five membered lactones ***via*** dual γ-(sp^3)-H activation.[29, 30] Although, carboxylate group found to be effective for methyl group activation but the activation of methylene group in a aliphatic substrate present a bigger challenge due to steric hindrance. Very recently, we devised a new strategy to reverse the site-selectivity in aliphatic substrates. Utilizing a bulky amino acid ligand N-acetyl tertiary leucine, γ-methylene group of cycloalkane acetic acid have been activated in presence of more facile γ-methyl group.[31] More interestingly, unsaturated bicyclic lactones form in absence of any coupling partner in the reaction, whereas, in presence of alkene or allyl alcohol as coupling partner olefinated bicyclic lactones form (Figure 3f). Thus a quaternary center forms in a single step from a methylene center in the substrate. There are a plethora of natural products and bioactive compounds that requires synthesis of such bicyclic lactones. Our developed methodology provides access to these lactones in a straightforward manner than previously utilized approaches.

Conclusion

In essence, the field is transition metal catalyzed remote C-H activation witnessing tremendous growth due to its potential to streamline chemical synthesis. Remote functionalization of both C(sp^2)-H and C(sp^3)-H have achieved tremendous advances in terms of designing directing templates, catalysts, and ligands. The major challenges associated with increasing the practicality of this research domain is to discover more environmentally benign, cost-effective, scalable, and sustainable catalytic systems with very high turnover number. In this realm, usage of abundant 3d transition metals like Fe, Ni, Cu, etc. for catalysis are getting more popular. To improve the practical applications, directing group free approaches have been invented both in the realm of sp^2 and sp^3 activation. Given the remarkable progress remote C-H functionalization has made in the last two decades, these strategies are expected to expand the toolbox of synthetic chemists and facilitate the discovery of pharmaceuticals, agrochemicals, and other desired materials.

References:

1. Biffis, A.; Centomo, P.; Zotto, A, D.; Zecca, M. Pd Metal Catalysts for Cross-Couplings and Related Reactions in the 21st Century: A Critical Review. *Chem. Rev.* **2018**, *118*, 2249–2295.
2. Crabtree, R. H.; Lei, A. Introduction: CH Activation. *Chem. Rev.* **2017**, *117*, 8481–8482.
3. Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. Efficient catalytic addition of aromatic carbon-hydrogen bonds to olefins. *Nature* **1993**, *366*, 529-531.
4. Sinha, S. K.; Guin, S.; Maiti, S.; Biswas, J. P.; Porey, S.; Maiti, D. Toolbox for Distal C-H Bond Functionalizations in Organic Molecules. *Chem. Rev.* **2022**, *122*, 5682–5841.
5. Dutta, U.; Maiti, D. Emergence of Pyrimidine as meta-Directing Group: Journey from Weak to Strong Coordination in Diversifying meta-C–H Functionalization. *Acc. Chem. Res.* **2022**, *55*, 354–372.
6. Dutta, U.; Maiti, S.; Bhattacharya, T.; Maiti, D. Arene Diversification via Distal C(sp^2)-H Functionalization. *Science*, **2021**, *372*, 701-715.
7. Das, J.; Guin, S.; Maiti, D. Diverse Strategies for Transition Metal Catalyzed Distal C(sp^3)-H Functionalizations. *Chem. Sci.*, **2020**,*11*, 10887-10909.
8. Leitch, J. A.; Frost, C. G. Ruthenium-catalysed σ-activation for remote meta-selective C–H functionalisation. *Chem. Soc. Rev.* **2017**, *46*, 7145-7153.
9. Dey, A.; Sinha, S.K.; Achar, T. K.; Maiti, D. Accessing remote meta- and para-C(sp^2)-H bonds with covalently attached directing groups. *Angew. Chem. Int. Ed.* **2019**, *58*, 10820-10843.
10. Mihai, M. T.; Genova, G. R.; Phipps, R. J. Access to the meta position of arenes through transition metal catalysed C–H bond functionalisation: a focus on metals other than palladium. *Chem. Soc. Rev.* 2018, 47, 149-171.
11. Wang, J.; Dong, G. Palladium/Norbornene cooperative catalysis. *Chem. Rev.* **2019**, *119*, 7478–7528.
12. Leow, D.; Li, G.; Mei, T.-S.; Yu, J.-Q. Activation of remote meta-C-H bonds assisted by an end-on template. *Nature*. **2012**. 486. 518-522.
13. Bag, S.; Patra, T.; Modak,A.; Deb, A.; Maity, S.; Dutta, U.; Dey, A.; Kancherla, R.; Maji, A.; Hazra, A.; Bera, M.; Maiti, D. Remote para-C-H Functionalization of Arenes by a D-Shaped Biphenyl Template-Based Assembly. *J. Am. Chem. Soc*. **2015**, *137*, 11888-11891.
14. Bera, M.; Agasti, S.; Chowdhury, R.; Mondal, R.; Pal, D.; Maiti, D. XPhos Ligated Rhodium Catalyzed meta-C-H Functionalization of Arenes. *Angew. Chem. Int. Ed*. **2017**, *56*, 5272-5276.
15. Sasmal, S.;Prakash, G.;Dutta, U.;Laskar, R.; Lahiri, G. K.; Maiti, D. Directing Group Assisted Rhodium Catalyzed meta-C-H Alkynylation of Arenes. *Chem. Sci.,* **2022**,*13*, 5616-5621.
16. Dutta, U.; Maiti, S.; Pimparkar, S.; Maiti, S.; Gahan, L. R.; Krenske, E. H.; Lupton, D. W.; Maiti, D. Rhodium Catalyzed Template-Assisted Distal para-C-H Olefination. *Chem. Sci*. **2019**, *10*, 7426-7429.
17. Bag, S.; Jana, S.; Pradhan, S.; Bhowmick, S.; Goswami, N.; Sinha, S. K.; Maiti, D. Imine as a linchpin approach for meta-C–H functionalization. *Nat. Commun.* **2021**, *12*, 1393-1398.
18. Dutta, U; Porey, S; Pimparkar, S.; Mandal, A; Grover, J; Koodan, A; Maiti, D. Para-Selective Arylation of Arenes: A Direct Route to Biaryls by Norbornene Relay Palladation. *Angew. Chem. Int. Ed.* **2020**, *59*, 20831-21022.
19. Saha, A.; Guin, S.; Ali, W.; Bhattacharya, T.; Sasmal, S.; Goswami, N.; Prakash, G.; Sinha, S. K.; Chandrashekar, H. B.; Panda, S.; Anjana, S. S.; Maiti, D. Photoinduced Regioselective Olefination of Arenes at Proximal and Distal Sites. *J. Am. Chem. Soc*. **2022**, *144*, 1929–1940.
20. Sinha, S. K.; Panja, S.; Grover, J.;† Hazra, P. S.; Pandit, S.; Bairagi, Y.; Zhang, X.; Maiti, D. Dual Ligand Enabled Non-Directed C–H Chalcogenation of Arenes and Heteroarenes. *J. Am. Chem. Soc.*, **2022**, *144*, 12032-12039.
21. Dey, A.; Pimparkar, S.; Deb, A.; Guin, S.; Maiti, D. Chelation assisted palladium catalyzed arylation of aliphatic carboxylic acid derivatives. *Adv. Synth. Catal.* **2017**, *359*, 1301-1307.
22. Thrimurtulu, N.; Khan, S.; Maity, S.; Volla, C. M. R.; Maiti, D. Palladium catalyzed direct aliphatic C(sp3)–H alkenylation with alkenes and alkenyl iodides. *Chem. Commun*.. 2017. 53. 12457-12460.
23. Deb, A.; Singh, S.; Seth, A.; Pimparkar, S.; Bhaskararao, B.; Guin, S.; Sunoj, R. B.; Maiti, D. Experimental and Computational Studies on Remote γ-C(sp^3)–H Silylation and Germanylation of Aliphatic Carboxamides. *ACS Catal.* **2017**, *7*, 8171-8175.
24. Guin, S.; Deb, A.; Dolui, P.; Chakraborty, S.; Singh, V.K.; Maiti, D. Promoting Highly Diastereoselective γ-C–H Chalcogenation of α-Amino Acids and Aliphatic Carboxylic Acids. *ACS Catal.* **2018**, *8*, 2664–2669.
25. Guin, S.; Dolui, P.; Zhang, X.; Paul, S.; Singh, V. K; Pradhan, S.; Chandrashekar, H. B.; S. S. Anjana.; Paton, R. S.; Maiti, D. Iterative Arylation of Amino Acids and Aliphatic Amines via-C(sp3)-H Activation: Experimental and Computational Exploration. *Angew. Chem. Int. Ed*. **2019**, *58*, 5633-5638.
26. Goswami, N.; Bhattacharya, T.; Maiti. D. Transient directing ligands for selective metal-catalyzed C-H activation. *Nat Rev Chem*. **2021**, *5*, 646–659.
27. Das, J.; Mal, D. K.; Maji, S.; Maiti, D. .Recent Advances in External Directing Group Free C-H Functionalization of Carboxylic Acids Without Decarboxylation. *ACS Catal*. **2021**, *11*, 7, 4205–4229.
28. Dolui, P.; Das, J.; Chandrashekar, H. B.; Anjana, S. S.; Maiti, D. Ligand-Enabled Pd(II)-Catalyzed Iterative γ-C(sp3)-H Arylation of Free Aliphatic Acid. *Angew. Chem. Int. Ed.* **2019**, *58*, 13773-13777.
29. Das, J.; Dolui, P.; Ali, W.; Biswas, J. P.; Chandrashekar, H. B.; Prakash, G; Maiti, D. A Direct Route to Six and Seven Membered Lactones via γ-C(sp3)-H Activation: A Simple Protocol to Build Molecular Complexity. *Chem. Sci.,* **2020**, 11, 9697-9702.
30. Das, J.; Pal, T.; Ali, W.; Sahoo, S. R.; Maiti, D. Pd Catalyzed Dual-γ-1,1-C(sp3)-H Activation of Free Aliphatic Acids With Allyl-O Moieties. *ACS Catal.*, **2022**, *12*, 11169-11176.
31. Das, J.; Ali, W.; Ghosh, A.; Pal, A, Mandal, A.; Teja, C.; Dutta, S.; Pothikumar, R. Ge, H.; Zhang, X, Maiti, D. Access to Unsaturated Bicyclic Lactones by Overriding Conventional C(sp^3)-H Site Selectivity. Chemrxiv. DOI: 10.26434/chemrxiv-2022-4brs3.