Prayogik Rasayan

Ruthenium(II)-Catalyzed C–H Bond Activation/Functionalization Reactions with Aromatic Acids

Chandan Kumar Giri, Nityananda Ballav, and Mahiuddin Baidya*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
Email: mbaidya@iitm.ac.in

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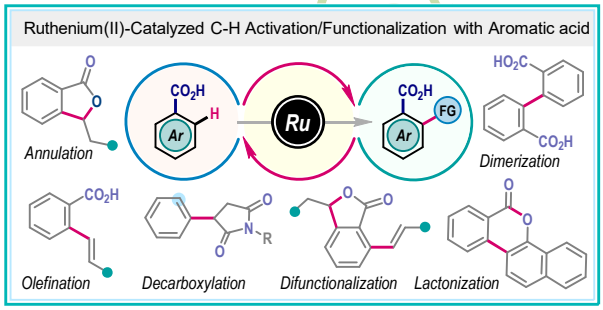
Abstract

Aromatic acids are feedstock molecules and their site-selective transformations employing the C–H bond provide a convenient avenue to assemble high-value molecular scaffolds. The acid functionality can also be judicially engaged in situ as well as ex situ synthetic manipulations including decarboxylation-based strategy, offering a unique opportunity to fetch further molecular complexity. In this account article, we showcased a variety of C–H bond activation and functionalization reactions of benzoic acids developed by our research group. Notably, these reactions are catalyzed by cost-effective ruthenium(II) catalysts, making them particularly compelling. Challenges in reaction design and mechanistic rationale were critically discussed for a comprehensive understanding.



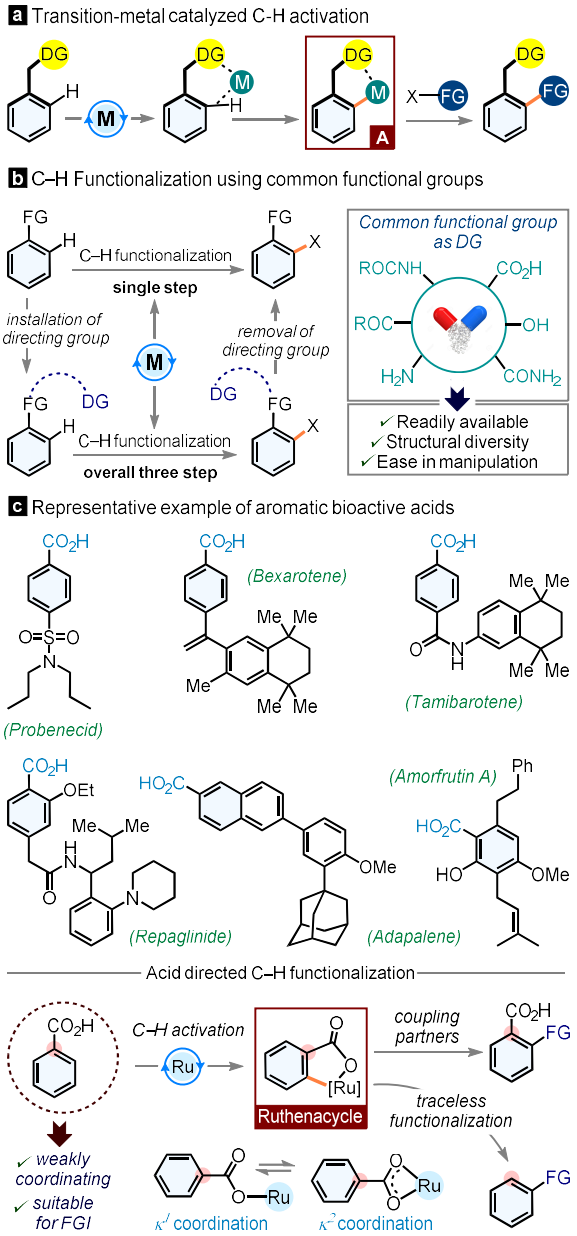
Keywords: Ruthenium catalysis, C–H activation, Cross-Dehydrogenative coupling, Aromatic Acids, Carbenes

1. Introduction

Catalytic synthetic protocols that harvest molecular complexity from abundant and readily available feedstock molecules in an operationally simple procedure and with desired selectivity are highly intriguing. In this context, the transition metal-catalyzed C–H bond activation strategy received significant attention from the synthetic community (Scheme 1a).[1-5] The C–H bonds are abundant in organic molecules, and their direct engagement in regio- and stereoselective transformations greatly expands the synthetic space and also upholds favorable atom-economy and sustainability features that are not apparent from the classical cross-coupling reactions. In this reaction blueprint, substrates are often connected to a suitable heteroatom-containing functional group, the so-called directing group (DG), which coordinates with the metal catalyst and brings it in proximity to a specific C–H bond for activation, resulting in the key organometallic complex **A** (Scheme 1a).[6-9] This metal complex is called metalacycle which can react with available coupling partners to materialize a desired transformation. While a number of directing groups are currently known in the literature, the employment of common organic functional groups such as amides, acids, esters, etc. as directing groups is highly beneficial as they are part of the substrate and thus, the step-economy bias stemming from the installation of an external DG before the C–H bond activation reaction and its removal after the desired functionalization can be avoided (Scheme 1b).

The choice of metal catalysts is also significant. The breakthroughs in the C–H activation strategy have majorly been realized by using 4d and 5d transition metal catalysts. However, they are expensive and less abundant in the earth's crust. On the other hand, 3d transition metal-based catalysts are promising given their cost and abundance on the earth's crust, while their reactivity in general is poor in comparison to 4d transition metal catalysts.[10-11] Nonetheless, the ruthenium metal-based catalysts attracted our attention as ruthenium metal is relatively less expensive than other 4d and 5d metals such as rhodium, palladium, and iridium, and exhibits comparable reactivity in the C–H activation strategy. Also, ruthenium(II) catalysts, for example $[Ru(p\text{-cymene})Cl_2]_2$, can be readily prepared and bench-stable. In fact, many of the C–H bond activation reactions can be performed in aqueous conditions in the presence of air or oxygen, highlighting operational simplicity.[12-14]

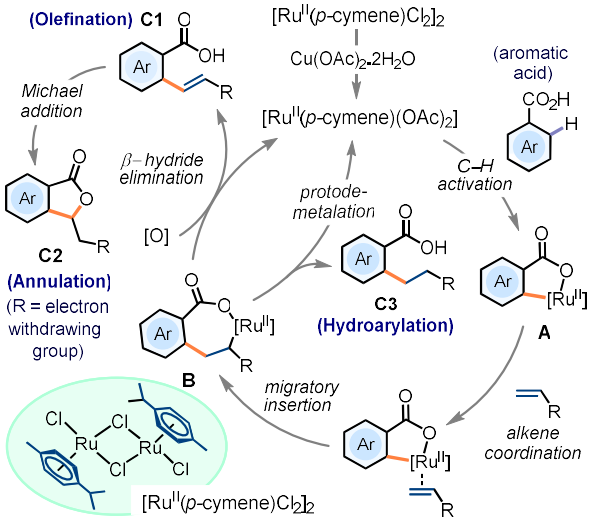
Carboxylic acids are one of the most ventured molecules in organic synthesis. They are available in wide structural diversity and serve as the integral component of numerous pharmaceutical compounds. The acid functionality can also be easily transformed into other useful organic functionalities and can be tracelessly removed employing known procedures. Most notably, it is weakly coordinating and has two distinct binding modes - κ^1 and κ^2. It binds to metal catalysts weakly to facilitate regioselective C–H bond activation and also endorses the release of the metal catalyst to continue the catalytic cycle (Scheme 1c). These characteristics prompted us to explore the C–H activation reaction of aromatic acids.[15-21] In recent years, we have established various C–H bond activation-guided cogent functionalization reactions of aromatic acids employing inexpensive ruthenium(II) catalysts, which range from annulation reactions to Heck-type olefinations and cross-dehydrogenative dimerizations. In this personal account article, we have highlighted a few of these findings from our laboratory. We expect this overview will attract young minds for further advancements of the C–H activation strategy for contemporary organic synthesis.



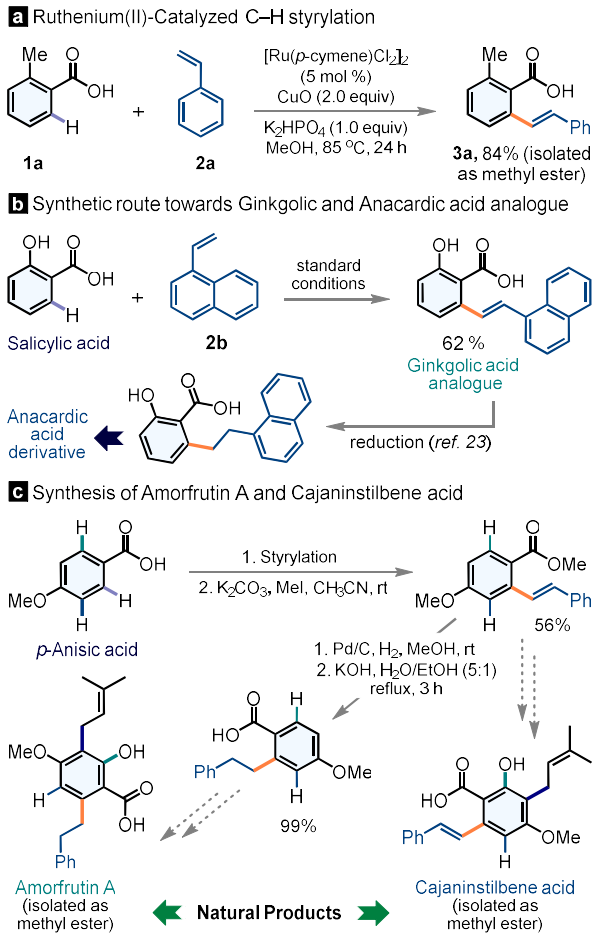
Scheme 1: The C–H bond activation reactions and the carboxylic acid functionality as a directing group.

2.1 Olefination and Annulation Reactions

Ruthenium(II)-catalyzed arene C–H bond activation reactions have been extensively explored with olefin coupling partners. A general catalytic cycle is depicted in Scheme 2 for an aromatic acid substrate considering $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst and $Cu(OAc)_2$ as an additive. The coordination-guided *ortho* C–H activation step forms the key ruthenacycle **A**. It then undergoes insertion reaction with the olefin coupling partner and generates the intermediate **B** from where various reactions are feasible leading to a diverse class of products. For example, a β-hydride elimination step would furnish the olefination product **C1**. If the R functionality in olefin is an electron-withdrawing group, oxa-Michael addition takes place promptly, offering formal annulation product **C2**. Alternatively, a protometalation step would lead to C–H alkylation (or hydroarylation) product **C3**.



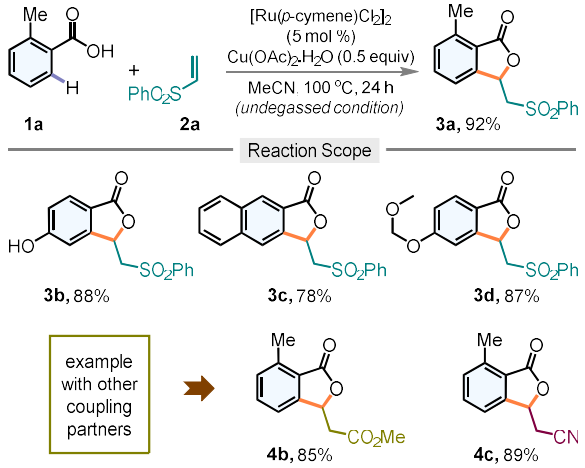
Scheme 2: Ruthenium(II)-catalyzed C–H bond activation and functionalization reactions with aromatic carboxylic acids.



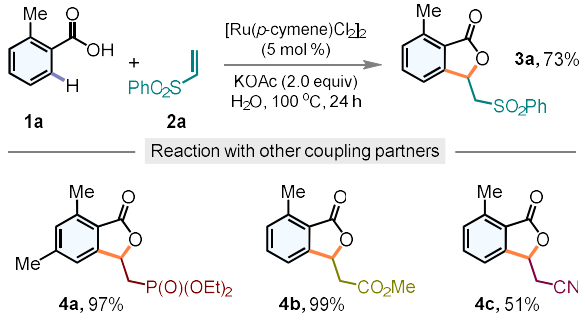
Scheme 3: Regioselective C–H olefination of aromatic acids.

In 2018, we first reported the Ru(II)-catalyzed coupling of aromatic acids with styrenes to access valuable 2-styrylbenzoic acids (Scheme 3a).[22] Interestingly, the reaction was effective with salicylic acid to dispense ginkgolic acid analog which can be transformed to anacardic acid derivative through reduction (Scheme 3b). The methodology was further employed in the total synthesis of the natural product Amorfruit A, a lead molecule in type II diabetes drug discovery (Scheme 3c).[24]

In the same year, we also reported the annulative coupling of aromatic acids with electron-deficient olefins. Employing vinyl sulfone in the presence of 5 mol% Ru-catalyst, an array of phthalide scaffolds was prepared in high yields (Scheme 4).[25] Later, it was identified that this annulation can be performed under aerobic conditions in an aqueous reaction medium without compromising the reaction efficacy and selectivity (Scheme 5).[26]

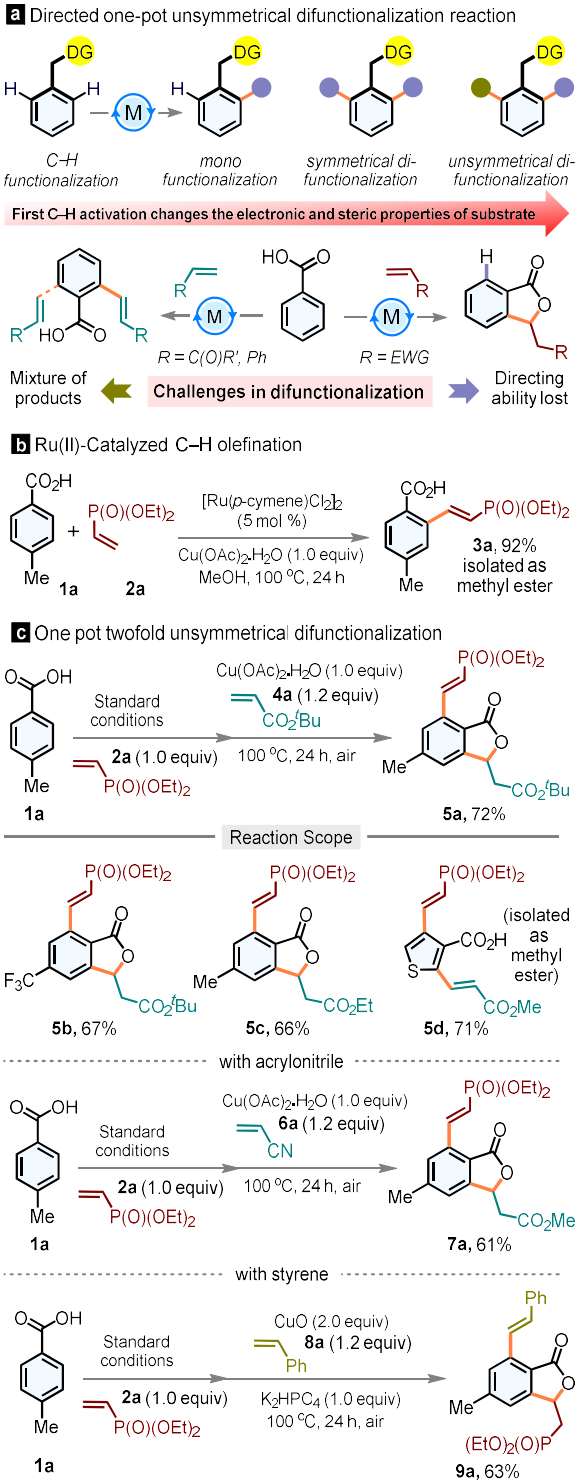


Scheme 4: Ruthenium(II)-catalyzed C–H bond activation and annulation reaction with aromatic acids.



Scheme 5: Ruthenium(II)-catalyzed annulation reaction in water.

While mono-selective C–H olefination is very common, ascending this methodology for twofold C–H olefination, particularly in an unsymmetrical manner under a single catalytic system is a challenging task (Scheme 6a).[27] With benzoic acid, the scenario becomes more cumbersome as the acid group loses its directing ability after oxa-Michael addition step.

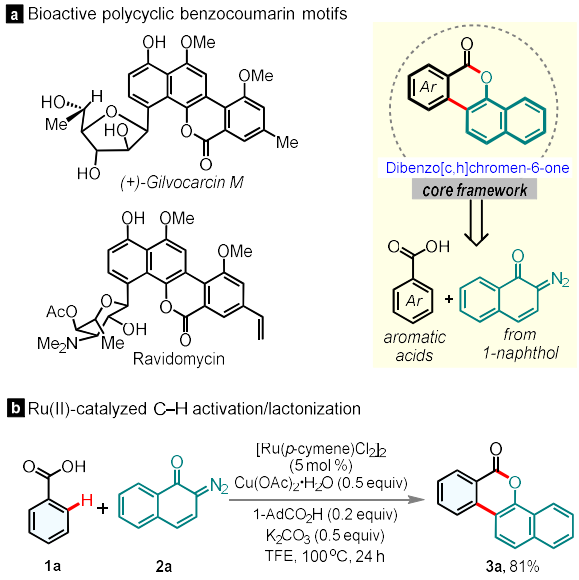


Scheme 6: Ruthenium(II)-catalyzed one-pot twofold unsymmetrical difunctionalization of benzoic acids.

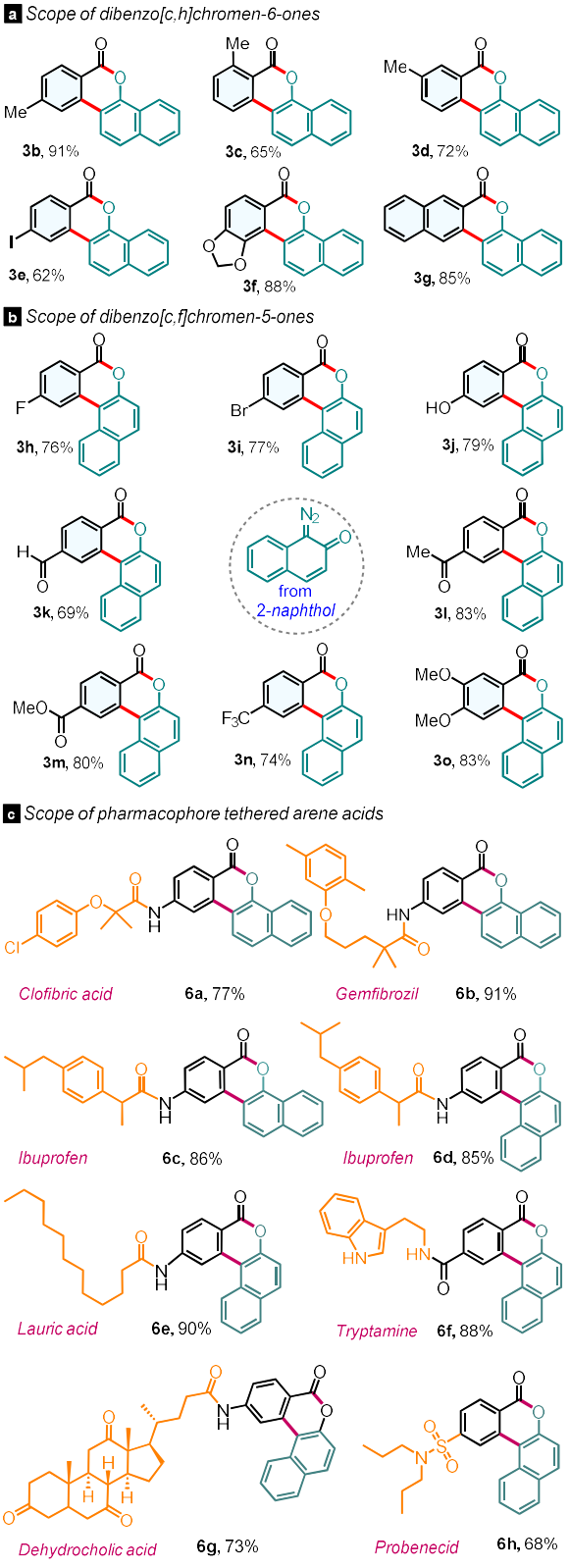
In 2019, we identified that Ru(II)-catalyzed coupling of vinyl phosphonate and benzoic acids in MeOH solvent proceeds without oxa-Michael addition step, and the olefination products were isolated solely instead of phthalide molecules (Scheme 6b).[28] Thus, the directing ability of the acid group

can be engaged to materialize a sequential twofold C–H activation reaction leading to 2,6-unsymmetrical difunctionalization of benzoic acids. To validate the concept, after completion of the first *ortho* C−H olefination with vinyl phosphonate (1 equiv), *t*-butyl acrylate (1.2 equiv) and $Cu(OAc)_2 \cdot H_2O$ (1 equiv) were added to the reaction flask and stirred at 100 °C for an additional 24 h. Pleasingly, unsymmetrical difunctionalization proceeded smoothly, delivering the desired product **5a** in 72% isolated yield (Scheme 6c). The protocol is quite general covering various electron-donating and electron-withdrawing substituted aromatic acids. This sequential difunctionalization was also successful with acrylonitrile; however, the nitrile group was hydrolyzed to methyl ester under the reaction conditions (Scheme 6c). Styrene was also effectively employed as a second olefinic coupling partner in the presence of CuO oxidant and K_2HPO_4 base. Of note, in these unsymmetrical difunctionalization reactions, the first C−H functionalization took place at the less hindered and most reactive position of the aromatic acid, and the annulation via oxa-Michael addition occurred at the alkene functionality having a stronger electron-deficient group, validating our working hypothesis.

Diazonaphthoquinones are high-value synthons, serving as a central source of carbene species in organic synthesis. However, their reaction in the C–H activation regime is limited and particularly very immature under Ru(II)-catalysis. We envisioned that they could be utilized for C–H bond activation and annulation reaction with benzoic acids which may furnish polycyclic benzocoumarin motifs that are prevalent in natural products (Scheme 7a). In 2023, we developed an operationally simple Ru(II)-catalyzed protocol for this purpose. The methodology leverages migratory insertion of quinoid carbene species and an *in situ* lactonization process to fabricate biologically relevant dibenzo[c,h]chromen-6-ones in high yields (Scheme 7b).[29] Using regioisomeric diazonaphthoquinones derived from β-naphthol, dibenzo[c,f]chromen-5-one frameworks were also prepared in high yields (Scheme 8b).



Scheme 7: The C–H bond activation and annulation reaction of aromatic acids through ruthenium-carbenoid species.



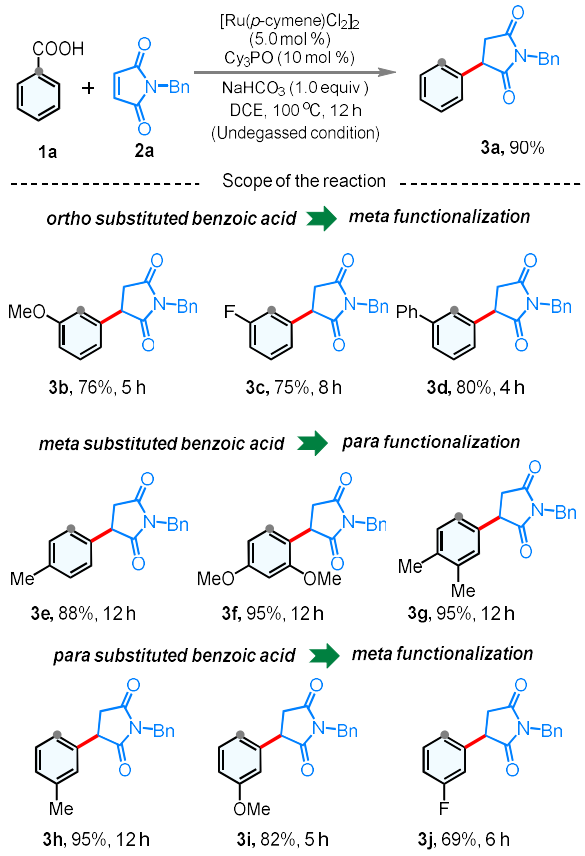
Scheme 8: Substrate generality and tolerance of pharmacophore scaffolds.

The protocol tolerates many valuable functional groups such as aldehyde, ketone, ester, free hydroxy, and halogen

functionality. The methodology is also effective in the presence of bio-relevant frameworks such as steroids and commercial drugs, highlighting wider substrate generality and application prospects in pharmaceutical industries (Scheme 8).

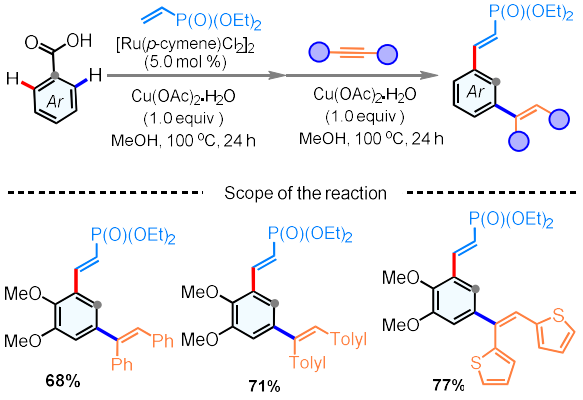
2.2 C–H activation and Decarboxylation

While acid functionality serves as a promising directing group to facilitate the regioselective C–H functionalization, we wonder when it can be removed in the form of a decarboxylation reaction after the completion of the C–H functionalization event. It would be much more beneficial if the decarboxylation event took place under the same catalytic system.



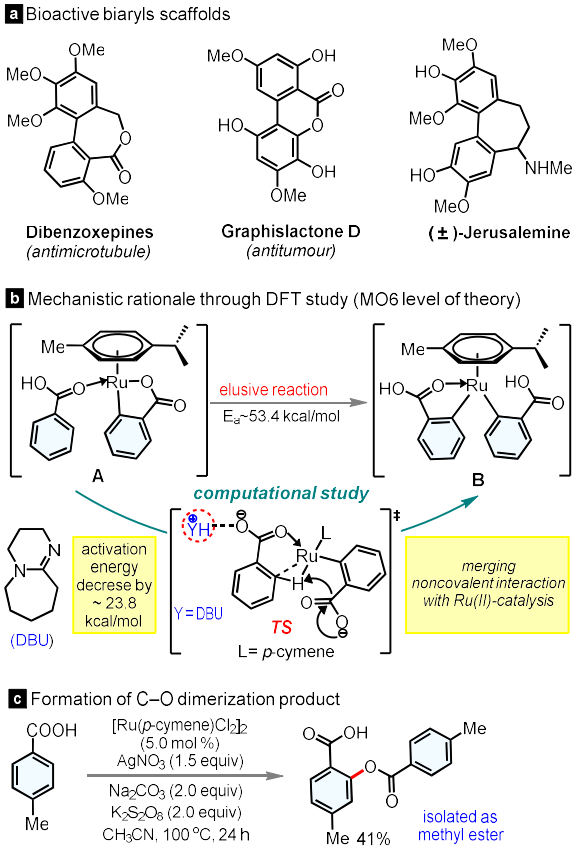
Scheme 9: Demonstration of ruthenium(II)-catalyzed C–H bond activation and concomitant decarboxylation reaction of aromatic acids.

In 2017, we found such an intriguing scenario during the investigation of the coupling reaction between benzoic acid and *N*-substituted maleimide. When the parent benzoic acid was treated with *N*-benzyl maleimide in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), Cy_3PO (10 mol %), $NaHCO_3$ (1 equiv) in DCE solvent at 100 °C, we obtained hydroarylation product **3a** in 90% yield with concomitant decarboxylation (Scheme 9).[30] This C–H activation coupled decarboxylation reaction became more enthralling when substituted benzoic acids were employed as it resulted in formal *meta*- and *para*-difunctionalization of arenes, which is a daunting task. Under the standard reaction conditions, ortho- and para-substituted benzoic acids offer the protocol meta-functionalized products while para-functionalized adducts were obtained from meta-substituted benzoic acids (Scheme 9). Later, we also disclosed a one-pot sequential difunctionalization and concomitant decarboxylation cascade to access challenging unsymmetrical *meta*-bis-olefinated arenes in high yields (Scheme 10).[28]



Scheme 10: Application toward one-pot unsymmetrical *meta*-bis-olefination under ruthenium catalysis.

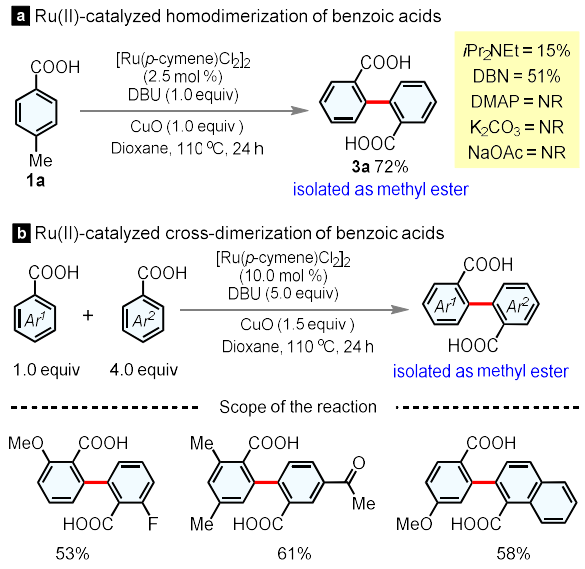
2.3 Cross-Dehydrogenative Dimerization



Scheme 11: Challenges in dimerization reaction of aromatic acids.

Biaryls are represented by a wide range of natural products, catalysts, ligands, and materials with useful properties, and their straightforward synthesis remains the focus of general

interest. Biaryl derivatives particularly those bearing tunable 2,2-substitution are fundamental as they are the cornerstone building blocks to adron further molecular complexity (Scheme 11a). The carboxylic acid functionality being a versatile functional group, we surmised that oxidative C–C dimerization reaction between two benzoic acids could be a cogent protocol. However, such C–C dimerization demands the breaking of the stable metalacycle **A** to give intermediate **B** from which reductive elimination will produce the desired product and it is an energetically uphill process(Scheme 11b).[31] In fact, the majority of our early attempts with Ru(II)-catalysts led to competitive C–O dimerization products (Scheme 11c). Through computational study, we have realized that the presence of a suitable organic base would reduce the activation barrier through a noncovalent ion-pair interaction. Accordingly, we performed the reaction using 1 equiv. of iPr$_2$NEt where the desired C–C dimerization product was obtained in 15% yield. Further optimization resulted in DBU as the optimal base additive for this reaction, offering **3a** in 72% yield (Scheme 12a). The protocol accommodates a range of aromatic carboxylic acids bearing electron-donating as well as electron-withdrawing functionalities. Thrillingly, this C–C dimerization can be advanced from the symmetrical to the unsymmetrical mode by controlling the reaction kinetics. When the electron-deficient benzoic acid was used in excess of up to four equiv. along with an electron-rich aromatic acid, the cross C–C dimerization took place efficiently, offering unsymmetrical biaryl frameworks in synthetically useful yields (Scheme 12b).



Scheme 12: Ruthenium(II)-catalyzed dimerization reaction of aromatic acids.

3. Conclusions

In this article, we have elucidated the C–H bond activation reactions of aromatic carboxylic acid using cost-effective ruthenium(II) catalysis. A range of annulation, olefination, and dimerization reactions are discussed, and the exciting decarboxylation phenomenon of carboxylic acid functionality is highlighted. At present, most of these reactions are conducted in a racemic form, making the development of an enantioselective version highly desirable. Further, efforts should be dedicated to engaging the decarboxylation step for a carbon-carbon or carbon-heteroatom bond-forming reaction. If successful, the methodology would provide the stepping stone for the challenging C–C activation and functionalization strategy, which is a rare event, particularly under ruthenium catalysis. We believe adopting the C–H activation strategy will expand the horizon of organic synthesis in a sustainable way and be very compelling for the total synthesis of bioactive compounds.

5. Acknowledgements

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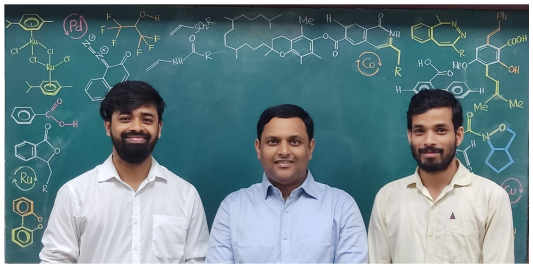
7. About the author(s)



Chandan Kumar Giri (right), was born in Odisha, India, in 1995. He received his bachelor's degree in Chemistry (Honours) from U. N. College, Soro, Odisha (Gold Medallist, F. M. University). In 2017, he completed his M.Sc. degree in Chemistry from Sambalpur University, Odisha, India. Since January 2019, he has been a research scholar at the Indian Institute of Technology Madras, under the supervision of Prof. Mahiuddin Baidya. His research focuses on the transition-metal catalyzed C–H bond activation reactions and their applications in the synthesis of therapeutically important molecules.

Nityananda Ballav (left), was born in West Bengal, India, in 1996. He received his bachelor's degree in Chemistry (Honours) from Krishnath College, University of Kalyani, West Bengal. In 2020, he completed his M.Sc. degree in Chemistry from Banaras Hindu University, Varanasi. India. Since July 2020, he has been a research scholar at the Indian Institute of Technology Madras, under the supervision of Prof. Mahiuddin Baidya. His research focuses on palladium-catalyzed unbiased olefin functionalization and applications in the synthesis of alkaloid scaffolds.

Mahiuddin Baidya (middle), born in 1983 in West Bengal, India, studied Chemistry at the Indian Institute of Technology Kanpur. He received his Ph.D. in 2009 from Ludwig-Maximilians-Universität München, Germany, under the supervision of Prof. Herbert Mayr, where he worked in the area of Physical-Organic-Chemistry. After post-doctoral studies with Prof. Hisashi Yamamoto at the University of Chicago, USA and Molecular Catalyst Research Center, Chubu University, Japan (JSPS postdoctoral fellowship), he joined the Department of Chemistry, Indian Institute of Technology Madras in 2014. Currently, he holds the Professor position in the same department. His research endeavors revolve around pioneering concepts in transition-metal catalysis, organocatalysis, photo-redox catalysis, and the synthesis of bioactive molecules.

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