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An Eco-Friendly Approach to C-H Functionalization in Modern Organic Synthesis: Green Photoredox Catalysis

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ABSTRACT

Synergistic integration of C–H activation and photoredox catalysis is creating a new potent approach to modern organic synthesis that transforms molecules selectively, efficiently, and sustainably. The production of reactive radical intermediates in mild conditions under visible light is accomplished through photoredox catalysis. Site-selective functionalization of inert C-H bonds can be accomplished through C-H activation when the conditions are favorable. It is possible to construct new bonds and functionalize functional groups late thanks to their combination, which also makes it possible to put complex chemicals, such as natural products, medicines, and heterocycles, into easy reach. Two-catalytic processes are made possible as a result of using this combination. The focus on eco-friendly processes, expanding the variety of substrates, and computationally guided reaction design are examples of recent advancements. This review delineates fundamental concepts, mechanistic insights, applications, problems, and current trends in synthetic chemistry, emphasizing its transformational potential through a dual approach.

Keywords: Photoredox catalysis, late-stage functionalization, visible-light processes, dual catalysis, C-H activation.

Introduction

For a long time, organic synthesis relied on the deliberate formation and conversion of carbon-hydrogen (C-H) bonds, which are among the most prevalent and inert bonds in organic compounds. Historically, organic compound functionalization has been associated with higher wastage, simpler synthetic pathways, less atom economy, and the need for pre-activated substrates or several steps (Noël & Zysman-Colman, 2022) . Furthermore, scientists have achieved a first with C-H activation, which

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efficiently and selectively converts C-H bonds to C-C, C-N, C-O, and other bonds. In addition to making synthetic routes easier, the approach also makes it possible to synthesize chemicals that were previously difficult or poorly produced (Itoh et al., 2019) . Significant progress has been made in the last 20 years regarding the development of catalysts for C-H activation by transition metals. In particular, catalysts made of palladium, rhodium, ruthenium, and iridium have demonstrated remarkable regio- and chemoselectivity within complicated molecular structures (Karataş et al., 2023).

Photoredox catalysis has also emerged as a powerful tool in modern organic chemistry alongside these advancements. Using visible light and photocatalysts, such as transition-metal complexes or organic dyes, photoredox catalysis can drive single-electron transfer (SET) reactions in moderate environments to generate very reactive radical intermediates (Udayakumar et al., 2024). Redox transformations are now much easier to carry out, and this technique has opened the door to new bond types that were previously impossible to achieve with thermal or metal-catalyzed redox transformations (Qiu et al., 2025) . The gentle reaction conditions, high function-group tolerance, and compatibility with sustainable energy sources make photoredox catalysis an incredibly attractive method for research and implementation in both academia and industry (Lepori et al., 2023).

An important step forward in the synthetical technique is the combining of C-H activation with photoredox catalysis. By combining them, chemists can take advantage of both approaches' strengths: site selectivity, the capacity to generate radicals and cover redox processes of photoredox systems, and the ability to create covalent bonds with C-H activation (Xu et al., 2024). The combination of these two forces has opened up new avenues for synthetic modification, allowing for the functionalization of complicated structures at a later stage, the direct arylation and alkylation of unactivated C-H bonds, and the facile access to heterocycles and bioactive compounds (Latchev et al., 2025).

This article aims to provide a synopsis of current advances in photoredox catalysis and C-H activation. We will discuss the fundamentals, the mechanisms, the practical applications in organic molecule synthesis, and the current state of the field,

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including its trends, problems, and upcoming technologies. With an emphasis on the revolutionary potential of merging these two powerful technologies, this review seeks to summarize key developments to direct researchers towards the creation of efficient and long-term solutions to complicated molecular construction (Latchev et al., 2025).

C–H Activation Principles

C–H activation represents a significant advancement in modern organic synthesis, enabling the direct functionalization of carbon-hydrogen bonds without the requirement for pre-functionalized starting materials. Historically, C-H bonds were considered chemically inert due to their high bond dissociation energies and non-polar nature, making selective transformation of these bonds particularly challenging (Mondal & van Gemmeren, 2022). With the advent of transition-metal catalysis, chemists have effectively mitigated these limitations, enabling selective cleavage and functionalization of C-H bonds with remarkable specificity. This methodology has simplified the synthesis of pathways, resulting in increased atom economy, minimized waste, and a reduction in the number of synthetic steps required to produce complex molecules (Niu et al., 2021).

Mechanistically, C-H activation often relies on a metal catalyst that establishes a transient bond with the substrate. Palladium, rhodium, ruthenium, iridium, and cobalt, classified as transition metals, have been extensively researched due to their unique electronic properties, which enable them to catalyze oxidative addition, σ-bond metathesis, or concerted metalation-deprotonation reactions (Deufel & van Gemmeren, 2024). These pathways facilitate the cleavage of otherwise inert C-H bonds, enabling subsequent formation of C-C, C-N, C-O, or C-X (halogen) bonds. Metals, ligands, and reaction conditions significantly influence the reactivity and selectivity of reactions, facilitating site-specific functionalization of complex molecules (Sharma et al., 2025).

This represents a primary concern in C–H activation: selectivity. However, various C-H bonds presence with similar electronic and steric characteristics often leads to competing pathways, making regioselective functionalization difficult. To address this challenge, chemists have developed the concept of directing-group

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reactions, wherein an organizing functional group guides the metal catalyst to a specific C–H bond, thereby achieving a high degree of positional selectivity (Sharma et al., 2025) . Ligand design, steric tuning, and transient mediators have expanded the scope of selective C–H functionalization, facilitating the realization of previously inaccessible molecular architectures (Gorgas et al., 2024).

The impact of C-H activation extends beyond simple bond alterations. It has facilitated the functionalization of complex natural products and pharmaceuticals at later stages, enabling rapid diversification of lead compounds and expediting drug discovery (Rodrigalvarez & Gaunt, 2024) . Furthermore, it has achieved access to sustainable synthesis by reducing the reliance on pre-activated substrates and minimizing hazardous reagents. C-H activation provides a versatile and effective toolkit that has become fundamental to modern organic chemistry, particularly when integrated with complementary techniques such as photoredox catalysis, thereby enhancing synthetic capabilities.

Photoredox Catalysis Principles

This photoredox catalysis represents a novel method in organic synthesis, enabling unprecedented control over chemical reactivity through the utilization of visible light to facilitate redox transformations. Photoredox catalysis, unlike traditional thermal or metal-catalyzed reactions, occurs under relatively mild conditions, typically at room temperature and atmospheric pressure. This approach enhances the tolerance of functional groups to reactants and reduces energy consumption. Photoredox catalysis operates on a fundamental mechanism where light induces the absorption of a photocatalyst, resulting in the generation of an excited state. This excited state can facilitate single-electron transfer (SET) reactions, leading to the formation of highly reactive radical intermediates capable of participating in diverse bond-forming reactions (Rodrigalvarez & Gaunt, 2024).

Photocatalysts utilized in these reactions primarily fall into two main categories: transition-metal complexes and organic dyes. Transition-metal complexes, such as those containing ruthenium and iridium, exhibit high-lying excited states, tunable redox potentials, and efficient light absorption properties. The eosin Y, acridinium salts, and flavins are organic photocatalysts that exhibit

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comparable reactivity to metal-based catalysts, aligning with the principles of green chemistry by eliminating the use of metals. Upon light excitation, the photocatalyst alters its oxidative or reductive potential, becoming excited and exhibiting enhanced reduction or oxidation capabilities relative to its ground state. This has facilitated the production of reactive radical species from stable organic compounds, enabling various transformations such as C-C, C-N, and C-O bonding (Tay et al., 2022).

One significant advantage of photoredox catalysis is the ability to control reaction pathways that are inaccessible through traditional methods. Selective radical production allows chemists to perform highly site-selective reactions, including the functionalization of unactivated C-H bonds, cross-coupling, and two-step reactions [22]. Furthermore, photoredox processes can be integrated with various catalytic systems, such as organocatalysis, transition-metal catalysis, and notably, C-H activation. This integration facilitates synergistic reaction designs, thereby expanding the range of synthetic possibilities (Cauwenbergh & Das, 2022).

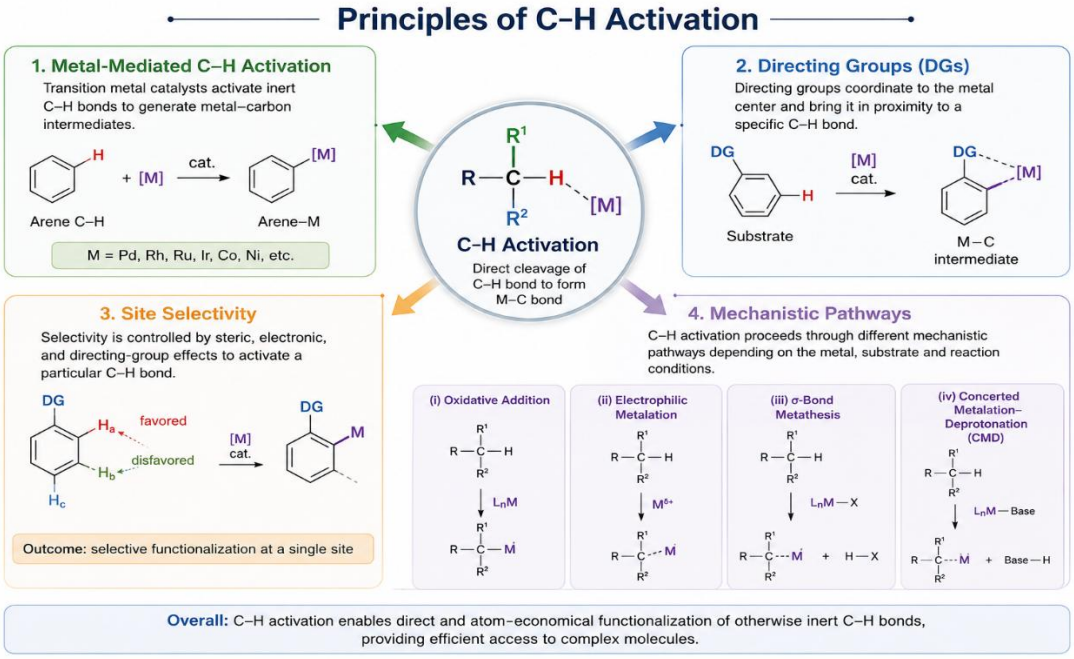

Figure 1 : Principle of C-H Activation

Sustainability and energy efficiency have been the focus of recent advancements. Photoredox catalysis aligns with the principles of green chemistry by utilizing visible light from inexpensive LEDs or sunlight, thereby reducing reliance on

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hazardous reagents and high-energy inputs. Mechanistic studies, including time-resolved spectroscopy and computational models, have enhanced the understanding of radical generation, electron-transfer processes, and catalyst design. These approaches facilitate the rational optimization of reaction conditions and improve selectivity (Niu et al., 2021; Qiu et al., 2025).

Overall, the domain of photoredox catalysis offers a versatile and effective framework for contemporary organic synthesis. Its mild operating environment, compatibility with various functional groups, and ability to generate reactive radical intermediates render it a favorable option for complementary strategies, including C-H activation, facilitating efficient and sustainable molecular construction (Singh et al., 2024).

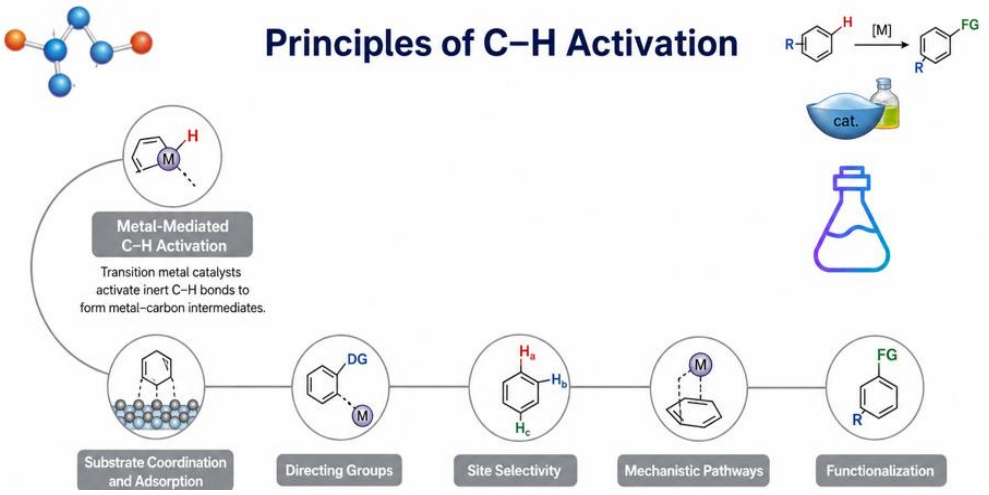

Figure 2: Catalysis Principle

C-H activation combined photoredox catalysis represents a significant advancement in contemporary organic synthesis, enhancing the capabilities of two highly versatile methodologies to achieve transformations that were previously challenging or unattainable. While C-H functionalization allows for site-selective modification of unactivated C-H bonds through C-H activation, photoredox catalysis serves as a mild, light-driven approach to generate reactive radical intermediates. When integrated, these methods facilitate precise bonding under environmentally friendly conditions, thereby improving efficiency and sustainability in synthetic chemistry (Zhou et al., 2022).

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Mechanistically, the synergy between C-H activation and photoredox catalysis typically involves two independent catalytic cycles functioning in tandem. In an optimal scenario, a transition-metal catalyst facilitates the selective cleavage of a C-H bond, resulting in the formation of a metal-carbon intermediate. Simultaneously, a photocatalyst can absorb visible light and become excited to an active state, enabling it to perform single-electron transfer (SET) reactions (Cauwenbergh & Das, 2022). The resulting radical species subsequently reacts with the metal-bound intermediate or participates in other steps related to bond formation, thereby linking the two catalytic cycles. This complementary process enables a diverse range of transformations, including arylation, alkylation, amination, and oxygenation, often exhibiting high regio- and chemoselectivity (Sharma et al., 2025).

One of the primary advantages of the dual method is its ability to functionally replicate complex molecules in advanced stages. Pharmaceuticals, natural products, and other bioactive compounds can be strategically modified at positions that are typically inert or sterically hindered to accelerate drug discovery and development. Furthermore, the mild conditions employed in photoredox catalysis prevent the degradation of sensitive functional groups, a limitation often associated with numerous conventional C-H activation methods (Latchev et al., 2025).

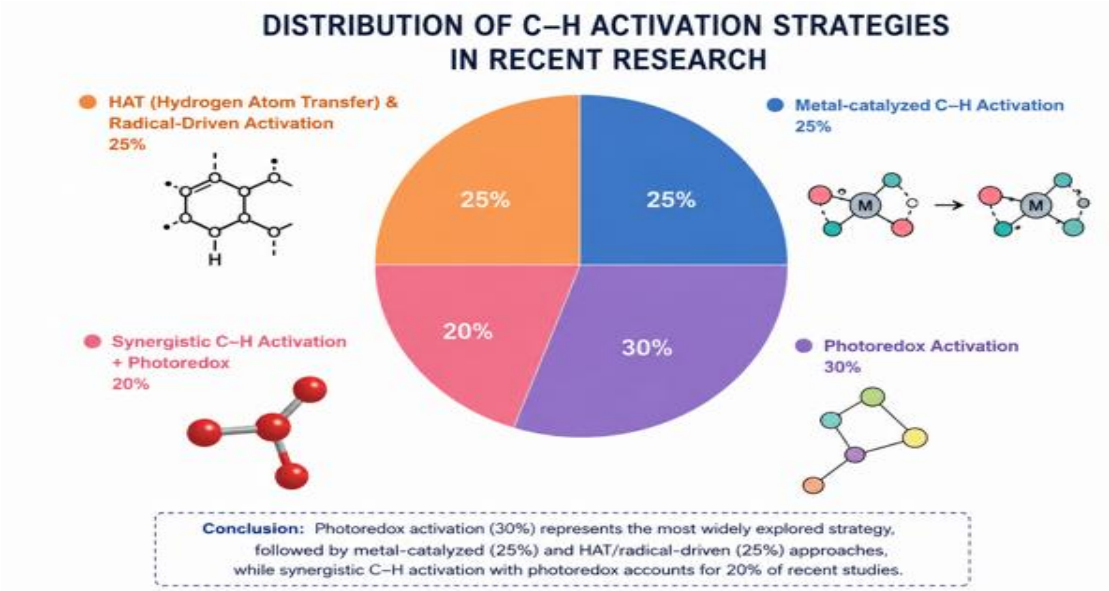

Figure 3: C-H activation strategies in research

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Utilizing radical relay for remote C–H functionalization, direct cross-coupling of unactivated C–H bonds with heteroaryl or alkylic partners, and stereoselective metathesis with chiral ligands in the metal-catalyzed cycle are just some of the innovative uses that have emerged as a result of recent research. Computational and mechanistic investigations have enhanced the understanding of these systems and identified factors influencing selectivity, reaction efficiency, and radical stability (Latchev et al., 2025). The integration of C–H activation with photoredox catalysis aligns with the principles of green chemistry. The synergistic method of synthesis is sustainable due to its minimal pre-functionalization, reduced waste generation, and utilization of visible light as a renewable energy source, among other factors. Overall, the dual catalysis paradigm represents a significant approach in modern organic chemistry, facilitating the development of efficient, selective, and environmentally sustainable pathways for the synthesis of complex molecular structures, thereby expanding the range of synthetic methodologies available to chemists (Itoh et al., 2019; Noël & Zysman-Colman, 2022).

Applications of Organic synthesis, Molecular scale and Reactor scale

The integration of CH activation with photoredox catalysis has significantly expanded the possibilities in organic synthesis, enabling transformations that are characterized by high selectivity, efficiency, and the construction of complex molecular scaffolds. It is primarily utilized in the synthesis of complex molecules and natural products. Direct functionalization of unactivated C-H bonds allows chemists to construct complex molecular structures with reduced synthetic operations, necessitating fewer pre-functionalized substrates and protecting groups (Shuaib Ahmed et al., 2023). This method optimizes time and resource utilization, thereby improving the overall atom economy. Consequently, synthetic routes are rendered more sustainable and cost-effective. The strategy's versatility and broad applicability have been evidenced in recent studies, which indicate its utility in the total synthesis of alkaloids, terpenes, and other bioactive natural products (Noël & Zysman-Colman, 2022).

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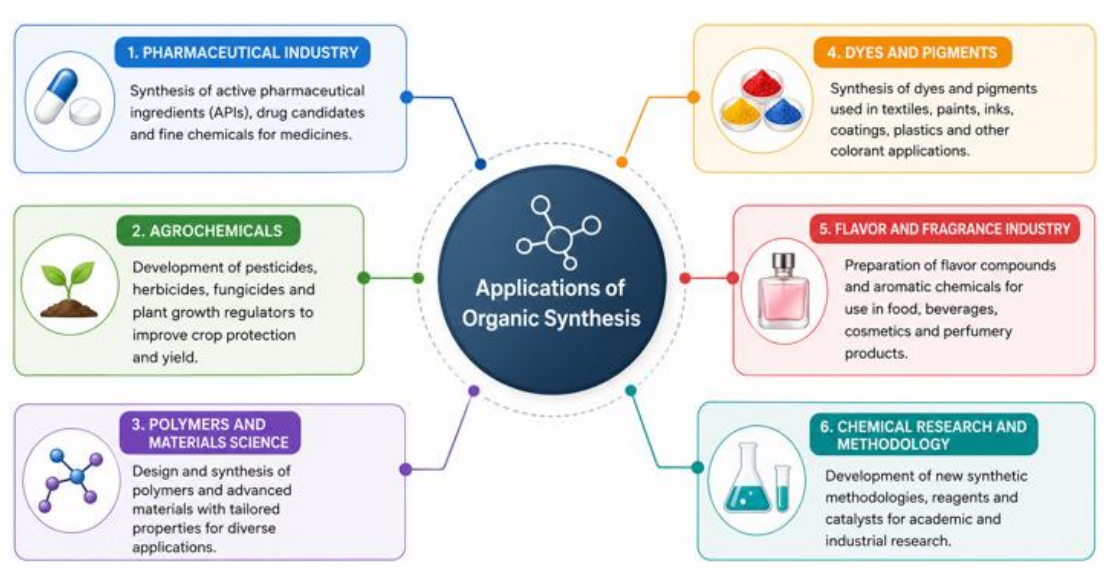

Figure: 4 showing Applications of organic synthesis

The other notable application area is late-stage functionalization, which has become increasingly important in drug discovery and medicinal chemistry. Chemists can produce analogs for structure-activity relationship (SAR) studies by selectively modifying C-H bonds in complex pharmaceuticals, eliminating the need for de novo synthesis (Docherty et al., 2023) . Photoredox-based carbon transformations -H functionalization facilitates the introduction of various functional groups, including aryl, alkyl, amino, and oxygen-containing groups, under mild conditions that preserve sensitive functional groups and stereochemistry. The ability is significant, particularly in optimizing biological activity and rapidly exploring chemical space through the modification of drug candidates (Akita & Koik, 2016).

Dual C–H activation and photoredox activation methods have been employed in the synthesis of heterocycles relevant to pharmaceutical and material chemistry, particularly concerning structural motifs found in drugs, agrochemicals, and functional materials. The methodology facilitates the functionalization of C-H bonds through direct catalysis, enabling the formation of five- and six-membered heterocycles via subsequent cyclization, typically under ambient conditions. Additionally, it has been employed in the preparation of complex polymeric structures, organic dyes, and molecular cages with specific functionalization patterns, and has demonstrated utility in other domains, including the synthesis of small

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molecules (Gorgas et al., 2024).

Furthermore, the selective and mild characteristics of these transformations allow for functional group tolerance, accommodating alcohols, amines, carboxylic acids, and other sensitive moieties that often exhibit incompatibility with traditional C-H functionalization methods. Together with the principles of green chemistry, such as activation by visible light and reduced waste production, these methodologies enhance the environmental sustainability of synthetic operations (Niu et al., 2021; Rodrigalvarez & Gaunt, 2024). In general, C–H activation and photoredox catalysis have diverse applications in organic synthesis, encompassing total synthesis, late-stage functionalization, drug discovery, and materials science. The integration of selectivity, efficiency, and sustainability positions this dual method as a cornerstone of contemporary organic chemistry, facilitating the rapid and convenient design of complex molecular structures (Mondal & van Gemmeren, 2022).

Recent Innovations and New Trends

In recent years, the field of CH activation combined with photoredox catalysis has experienced significant advancements, driven by a growing interest in developing sustainable, efficient, and highly selective synthetic methodologies. One notable advancement is the integration of visible-light photoredox catalysis with transition-metal-mediated C–H activation, which allows chemists to create bonds that were previously unattainable (Joy et al., 2025) . This bifunctional catalytic approach leverages the site-selectivity of C-H activation alongside the weak radical-generating capacity of photoredox systems to facilitate transformations under ambient conditions, demonstrating significant functional group tolerance. These advancements have enabled the development of new reactions, including remote C-H functionalization, radical relay reactions, and direct cross-coupling of unactivated C-H bonds with heteroaryl or alkyl partners (Joy et al., 2025).

Another emerging trend is the focus on green and sustainable practices. In alignment with environmentally sustainable practices, researchers are employing metal-free organic photocatalysts, renewable light sources such as LEDs or sunlight, and strategies that minimize solvent usage. Green photoredox catalysis involving C-H functionalization reduces the reliance on hazardous reagents and minimizes waste

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production, a factor of particular importance in large-scale pharmaceutical and industrial applications (Docherty et al., 2023) . Moreover, advancements in mechanistic understanding, facilitated by computational modeling and time-resolved spectroscopies, have enabled the rational design and optimization of reactions. These developments have provided valuable insights into radical formation, reaction kinetics, and selectivity (Zhou et al., 2022).

The recent research articles demonstrate the use of dual-functional ligands and transient directing groups to enhance regio- and chemoselectivity in C-H activation reactions. These technologies facilitate the precise functionalization of complex molecules, including natural products, pharmaceuticals, and functional materials, without the need for pre-functionalization. Furthermore, the incorporation of asymmetric photoredox catalysis has facilitated enantioselective reactions, allowing for the formation of highly stereocontrolled chiral centers (Banerjee et al., 2024).

The other significant development is the synergistic integration with computational and AI-assisted methods. Machine learning and predictive modeling are increasingly utilized to identify optimal reaction conditions, predict reactive sites in C-H functionalization, and develop novel photocatalysts. This integrative approach combining synthetic methodology with computational tools enhances the rate of new transformations and improves the efficiency of reaction optimization (Zhou et al., 2022). Overall, these recent developments and trends indicate a rapid transformation of the field, emphasizing efficiency, selectivity, sustainability, and innovation. The discovery of novel catalysts, reaction design, and computational methods continues to expand the scope of C–H activation and photoredox catalysis, establishing them as transformative technologies in contemporary organic synthesis (Singh et al., 2024).

Difficulties and Future Discussions

Despite the significant advancements in C–H activation and photoredox catalysis, several challenges remain that limit the application of these techniques in complex organic synthesis. Regio- and chemoselectivity represent significant challenges in the field. Most organic molecules contain multiple carbon bonds that exhibit similar

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steric and electronic environments, making selective functionalization challenging (Asadov et al., 2015) . While directing groups and ligand-directed strategies have improved site selectivity, the creation of universal methods capable of targeting specific C-H bonds in complex molecules remains a significant challenge. Selectivity is crucial, and a researcher is attempting to achieve precise selectivity without significantly altering its substrates (Li et al., 2024).

Additional concerns pertain to the stability and compatibility of the catalysts. In dual catalysis involving photoredox and transition-metal catalysts, it is essential that both catalysts operate synergistically without compromising each other's activity. The degradation of photocatalysts due to prolonged light exposure, along with the deactivation of catalysts from side reactions, may reduce the effectiveness and reproducibility of the reaction. The primary challenge in scaling up these reactions for industrial application is the development of robust and durable catalysts that maintain high activity across a diverse range of substrates and reaction conditions (Dang et al., 2024; Joy et al., 2025).

Reaction efficiency and substrate scope present significant challenges. Despite demonstrating effective transformation in laboratory settings, the scaling up of these reactions often encounters challenges such as low yield, prolonged reaction times, or functional group intolerance under standard conditions. Improving the assortment of substrates and utilizing a greater variety of sterically hindered molecules remains essential (Tay et al., 2022) . In the future, computation and AI-assisted methods are likely to provide effective solutions to numerous challenges. Machine learning models can predict the location of reactive sites, optimize reaction conditions, and design new photocatalysts, thereby reducing the trial and error associated with reaction development. Combining experimental results with computational predictions will expedite the identification of effective, selective, and sustainable C-H functionalization reactions (Akita & Koik, 2016; Banerjee et al., 2024).

The future trends will be characterized by enantioselective conversions, innovative strategies for remote and late-stage functionalization, and the development of green, metal-free systems aligned with sustainable chemistry

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principles. Disperse. The implementation of innovative light sources, advanced reactor design, and continuous-flow photochemistry will enhance scalability and operational efficiency. The field of C–H activation and photoredox catalysis is expected to advance further, notwithstanding the current challenges (Wallace & Reamer, 2014) . Addressing these limitations through innovative catalyst design, mechanistic insights, and the integration of computational techniques will enhance the generalizability of these methodologies, thereby reinforcing their significance as a transformative strategy in modern organic synthesis (Dang et al., 2024).

Conclusion

The interaction between C–H activation and photoredox catalysis represents a significant advancement in modern organic synthesis, providing chemists with enhanced capabilities for selective, efficient, and sustainable molecular synthesis. Both methodologies have evolved over the past two decades to address critical challenges in synthetic chemistry. C–H activation enables the direct functionalization of unactivated carbon-hydrogen bonds, eliminating the need for pre-functionalized substrates and streamlining the synthesis process. Photoredox catalysis has utilized visible light to generate highly reactive radical intermediates under mild and environmentally friendly conditions. The integration of the two as a synergistic strategy has notably expanded the synthetic toolkit, enabling the construction of more complex bonds that are not achievable through traditional methods.

This review elucidates the principles of C-H activation and photoredox catalysis, encompassing the mechanisms involved, catalyst development, and reaction optimization. C–H activation involves the cleavage of reactive C–H bonds through a highly regio- and chemoselective reaction facilitated by transition-metal catalysts, often guided by a directing group or ligand modification. Photoredox catalysis utilizes photocatalysts, such as metal complexes or organic dyes, to facilitate single-electron transfer processes that generate radical intermediates. These intermediates can subsequently participate in various transformations, including the formation of C–C, C–N, and C–O bonds. A combination of the two techniques allows for the selective reaction of radical products generated by

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photoredox catalysis with metal-bound products, facilitating the implementation of dual-catalytic cycles to enhance reaction efficiency, selectivity, and scope.

This dual approach has extensive and effective applications. These strategies enhance atom economy and reduce the number of steps required for the construction of complex natural products and bioactive molecules in total synthesis. Late-stage functionalization has demonstrated significant efficacy in medicinal chemistry, as it allows for the selective modification of drug candidates and facilitates structure-activity relationship studies without the necessity of large-scale resynthesis of the compound. The dual method has also been applied in material chemistry, including the synthesis of heterocycles, molecular cages, and polymeric architectures, demonstrating that this technology extends beyond the synthesis of small molecules. The recent advancements highlight the growing importance of sustainability and green chemistry, including metal-free photocatalysts, environmentally friendly light sources, and solvent-efficient methods. Computational modeling and reaction design utilizing AI have become integral components, offering predictive capabilities regarding reactivity, selectivity, and optimal reaction conditions. These inventions facilitate the rapid discovery of new transformations while enabling scalable and environmentally sustainable processes applicable across various industries.

Despite significant advancements, further efforts are required to achieve universal regioselectivity, expand substrate range, enhance catalyst durability, and improve scalability. Addressing these weaknesses will require advancements in catalyst design, enhanced mechanistic understanding, and the integration of computational tools. Furthermore, emerging avenues such as enantioselective C–H functionalization, remote C–H activation, and hybrid photochemical methods hold considerable promise for future developments.

In summary, the integration of C-H activation with photoredox catalysis has introduced a novel aspect to contemporary organic synthesis. These methodologies integrate selectivity, efficiency, and sustainability to synthesize complex molecules with high precision. This dual-catalytic strategy will serve as a crucial tool in both academia and industry, as mechanistic insights gain prominence and new technologies are integrated. It will underpin innovations in pharmaceuticals, natural

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product synthesis, and materials science. The recent advancements in this discipline underscore its transformative potential and the critical importance of this field in shaping the future of synthetic chemistry.

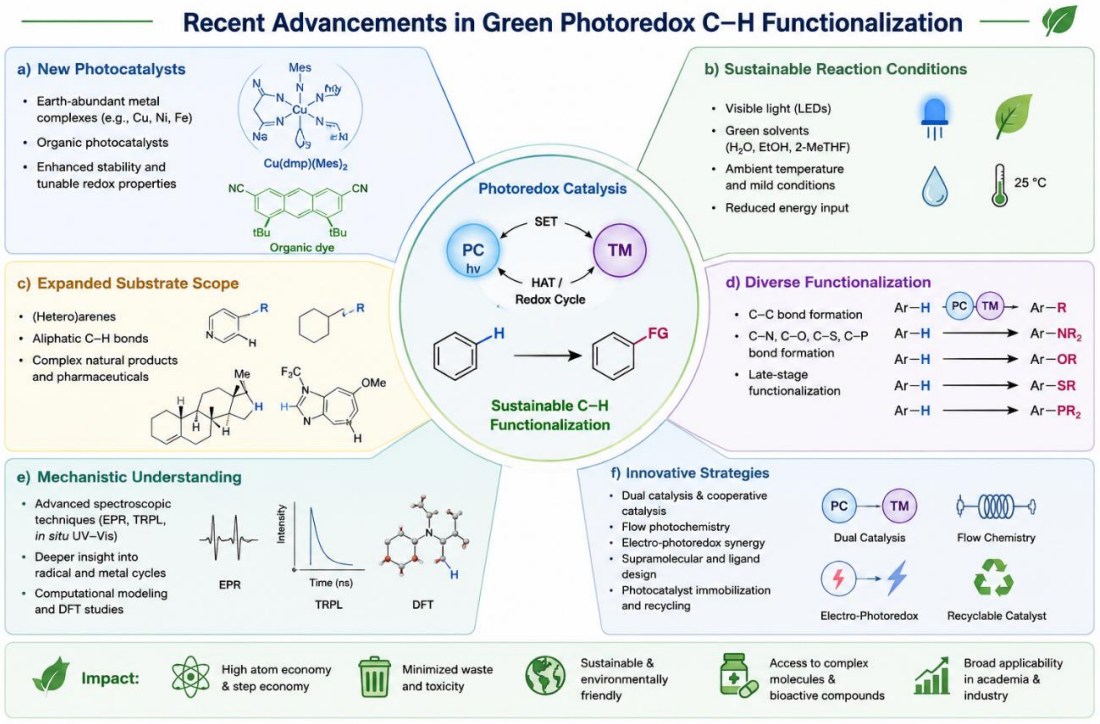

Figure 5: Recent Advancement

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