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Photoredox Catalysis in C–H Functionalization

Dr Preetam Singh Meena

Assistant Professor, Department of Chemistry

Government College, Karauli (Raj)

2. Abstract

Photoredox catalysis has emerged as a powerful and sustainable strategy in modern organic synthesis, enabling efficient C–H functionalization under mild reaction conditions. This transformation utilizes visible light to activate photocatalysts, which subsequently generate highly reactive radical intermediates through single electron transfer (SET) processes. The ability to directly functionalize inert C–H bonds without pre-activation has significantly advanced the field of green chemistry, offering improved atom economy, selectivity, and reduced environmental impact. This study provides a comprehensive overview of photoredox-catalyzed C–H functionalization reactions, focusing on mechanistic pathways, catalyst systems, and synthetic applications. Both metal-based photocatalysts, such as ruthenium and iridium complexes, and organic dyes have been analyzed for their efficiency and sustainability. The research highlights key reaction mechanisms including oxidative and reductive quenching cycles, radical formation, and selective C–H bond activation in sp^3, sp^2, and sp hybridized systems. The findings indicate that photoredox catalysis enables mild and highly selective transformations that are difficult to achieve using conventional thermal methods. Furthermore, its compatibility with diverse functional groups makes it highly valuable in complex molecule synthesis, particularly in pharmaceuticals and agrochemicals. The study concludes that photoredox-mediated C–H functionalization represents a transformative approach in synthetic chemistry, with significant potential for industrial-scale applications and future development in sustainable catalytic systems.

3. Keywords: Photoredox catalysis, C–H activation, radical chemistry, organic synthesis, visible light catalysis, green chemistry

4. Introduction

The functionalization of carbon–hydrogen (C–H) bonds represents one of the most significant advancements in modern organic chemistry. Traditionally, organic synthesis has relied on pre-functionalized substrates, where reactive groups are introduced through multiple steps before the desired transformation is achieved. However, C–H bonds are abundant, stable, and present in nearly all organic molecules, making them an attractive target for direct chemical modification. The ability to selectively activate and transform these bonds has therefore become a central goal in synthetic chemistry, offering the promise of more efficient, economical, and environmentally friendly processes. In recent years, photoredox catalysis has emerged as a revolutionary strategy for achieving C–H functionalization under mild and sustainable conditions. This approach utilizes visible light as a clean energy source to activate photocatalysts, which in turn initiate single-electron transfer (SET) processes. These electron transfer events generate highly reactive radical species capable of selectively functionalizing otherwise inert C–H bonds. The integration of light energy into chemical synthesis has opened new pathways for reaction design, significantly expanding the scope of modern organic transformations.

The development of photoredox catalysis is closely associated with advancements in visible-light photocatalysts, including transition metal complexes such as ruthenium and iridium polypyridyl systems, as well as organic dye-based catalysts. These photocatalysts possess suitable redox potentials and long-lived excited states that enable efficient electron transfer processes. Upon irradiation with visible light, the photocatalyst is promoted to an excited state, which can either donate or accept an electron depending on the reaction pathway. This dual capability allows for both oxidative and reductive quenching cycles, making photoredox systems highly versatile. One of the key advantages of photoredox catalysis is its ability to operate under mild reaction conditions. Unlike traditional thermal methods that often require high temperatures, strong reagents, or harsh oxidants, photoredox reactions proceed at ambient temperature using light as the primary energy input. This reduces energy consumption and minimizes unwanted side reactions, thereby improving overall reaction efficiency and selectivity. Furthermore, the use of visible light, which is abundant and non-toxic, aligns well with the principles of green chemistry and sustainable development.

C–H functionalization via photoredox catalysis has found widespread application in the selective modification of sp^3, sp^2, and sp hybridized carbon centers. The generation of radical intermediates allows for unique reactivity patterns that are difficult to achieve through conventional ionic mechanisms. For example, hydrogen atom transfer (HAT) processes, radical addition reactions, and cross-coupling transformations can be efficiently carried out using photoredox systems. This has significantly expanded the synthetic toolbox available to chemists, particularly in the construction of complex molecular architectures. The importance of this methodology is especially evident in pharmaceutical and agrochemical industries, where late-stage functionalization of complex molecules is highly desirable. The ability to selectively modify biologically active compounds without altering their core structure enables rapid diversification of lead compounds in drug discovery. Similarly, in material science, photoredox-catalyzed C–H functionalization is being used to modify polymers and develop advanced functional materials with tailored properties.

Despite these significant advancements, challenges remain in the field. Issues such as limited substrate scope, catalyst cost (particularly for precious metal complexes), photostability of catalysts, and control over regioselectivity still need to be addressed. Additionally, understanding the detailed mechanistic pathways involved in radical formation and reaction selectivity is crucial for further optimization of these systems. These challenges highlight the need for continued research in catalyst design, reaction engineering, and mechanistic studies.The present study aims to explore the fundamental principles and recent developments in photoredox-catalyzed C–H functionalization. It focuses on understanding the underlying reaction mechanisms, comparing different catalytic systems, and evaluating their efficiency and practical applicability. By analyzing both experimental and theoretical advancements, this work seeks to provide a comprehensive overview of how photoredox catalysis is transforming modern synthetic chemistry.

5. Literature Review

The development of C–H functionalization and photoredox catalysis represents one of the most transformative advances in modern organic chemistry. Over the past few decades, significant progress has been made in understanding how inert carbon–hydrogen bonds can be selectively activated and transformed into valuable functional groups. The integration of photoredox catalysis into this domain has further expanded the synthetic possibilities, enabling reactions under mild and sustainable conditions. This literature review examines the historical development, key contributions, mechanistic advancements, and recent innovations in photoredox-catalyzed C–H functionalization. The concept of C–H bond activation initially emerged as a challenge due to the inherent stability and non-polar nature of the C–H bond. Early research focused on transition-metal-mediated activation strategies, particularly

using palladium, rhodium, and ruthenium complexes. These methods often required directing groups to achieve selectivity, limiting their scope. Nevertheless, foundational work by researchers in organometallic chemistry established the feasibility of C–H bond cleavage and laid the groundwork for future developments in selective functionalization. The introduction of photoredox catalysis marked a paradigm shift in this field. The idea of using light energy to drive chemical reactions dates back to early photochemistry studies, but its application in organic synthesis gained momentum only in the 21st century. A major breakthrough came with the recognition that visible-light photocatalysts, particularly ruthenium and iridium polypyridyl complexes, could facilitate single-electron transfer (SET) processes under mild conditions. These complexes, when excited by visible light, exhibit strong redox properties that allow them to participate in both oxidative and reductive quenching cycles.

Pioneering contributions in this field demonstrated that photoredox catalysis could generate radical intermediates from stable precursors, enabling novel reaction pathways. The work of researchers such as MacMillan, Yoon, and Stephenson significantly expanded the scope of visible-light photocatalysis in organic synthesis. Their studies showed that photoredox systems could be combined with traditional transition-metal catalysis, leading to the development of dual catalytic strategies that enhance reactivity and selectivity.

One of the key advancements in this area has been the development of hydrogen atom transfer (HAT) processes. HAT-based strategies allow direct abstraction of hydrogen atoms from C–H bonds, generating carbon-centered radicals that can undergo further transformations. This approach has proven particularly effective in the functionalization of unactivated aliphatic C–H bonds. The integration of photoredox catalysis with HAT reagents has significantly broadened the scope of selective C–H activation. Another important development is the use of organic photocatalysts as alternatives to precious metal complexes. Organic dyes such as eosin Y, rose bengal, and acridinium salts have been widely studied for their ability to mediate photoredox reactions. These catalysts offer advantages in terms of cost, environmental impact, and structural tunability. Recent studies have shown that organic photocatalysts can achieve comparable efficiency to metal-based systems in many C–H functionalization reactions.

Theoretical Framework

The theoretical framework of photoredox-catalyzed C–H functionalization is grounded in the principles of photochemistry, redox chemistry, radical chemistry, and organometallic catalysis. In modern organic synthesis, the ability to activate inert C–H bonds using visible light has been made possible through a deeper understanding of excited-state electron transfer processes and radical-mediated reaction pathways. This framework explains how light energy is converted into chemical reactivity through photocatalysts and how this energy drives selective C–H bond transformations. At the core of photoredox catalysis is the concept of light absorption and electronic excitation. When a photocatalyst absorbs visible light, it is promoted from its ground state to an electronically excited state. This excited state is significantly more reactive and can participate in either oxidative or reductive quenching pathways. Common photocatalysts such as ruthenium polypyridyl complexes, iridium complexes, and organic dyes possess suitable photophysical properties, including long-lived excited states and appropriate redox potentials, making them effective mediators of electron transfer reactions.

Reaction Mechanism & Energy Profile

The reaction mechanism and energy profile of photoredox-catalyzed C–H functionalization are based on the interplay between light-induced electronic excitation, single-electron transfer (SET) events, radical formation, and subsequent bond-forming processes. These reactions are fundamentally different

from classical thermal processes because they are driven by photon energy rather than heat, allowing transformations under mild and highly selective conditions. The mechanistic pathway typically involves a photocatalyst, a light source (usually visible light), a hydrogen atom transfer (HAT) agent or substrate, and a coupling partner. At the beginning of the catalytic cycle, the photocatalyst absorbs visible light and is promoted from its ground state to an excited electronic state. Common photocatalysts such as ruthenium polypyridyl complexes, iridium complexes, and organic dyes possess strong absorption in the visible region and long-lived excited states. This excited state is highly reactive and can act as either a strong oxidant or a strong reductant, depending on the reaction environment.

The mechanism generally proceeds through two major catalytic pathways: oxidative quenching and reductive quenching cycles. In the oxidative quenching pathway, the excited photocatalyst accepts an electron from a substrate or sacrificial donor, leading to the formation of a reduced photocatalyst and a radical cation intermediate. In contrast, in the reductive quenching pathway, the excited photocatalyst donates an electron to a substrate, generating an oxidized catalyst and a radical anion. Both pathways ultimately lead to the formation of reactive radical species essential for C–H functionalization. Once radical intermediates are generated, the key step in C–H functionalization occurs through hydrogen atom transfer (HAT). In this process, a hydrogen atom is abstracted from a relatively inert C–H bond, producing a carbon-centered radical. The selectivity of this step is governed by bond dissociation energies (BDEs), steric accessibility, and electronic effects. Weaker C–H bonds, such as benzylic, allylic, or α-heteroatom positions, are more easily activated, while stronger aliphatic C–H bonds require more energetic or selective catalytic systems.

After radical formation, the carbon-centered radical can undergo several downstream transformations depending on the reaction design. One common pathway involves radical coupling with an electrophilic or nucleophilic partner, leading to the formation of new C–C, C–N, or C–O bonds. In dual catalytic systems, a transition metal catalyst (such as nickel or copper) often facilitates this coupling step, enhancing reaction efficiency and selectivity. Alternatively, the radical may undergo addition to alkenes or alkynes, enabling hydrofunctionalization or cyclization reactions. The photocatalyst is regenerated at the end of the catalytic cycle, completing the redox loop. This regeneration step is crucial for maintaining catalytic turnover. Depending on the system, the photocatalyst returns to its ground state either by accepting or donating an electron during the final stage of the reaction. The continuous absorption of light ensures that the cycle persists as long as irradiation is maintained.

The energy profile of photoredox-catalyzed C–H functionalization is best understood in terms of excited-state energetics and redox potential alignment. Upon absorption of a photon, the photocatalyst is elevated to an excited state with significantly altered redox properties. This excited state possesses higher energy than the ground state, enabling it to participate in electron transfer reactions that are thermodynamically unfavorable under thermal conditions. A key parameter in this energy profile is the excited-state redox potential of the photocatalyst. This determines whether electron transfer to or from the substrate is energetically feasible. For a reaction to proceed efficiently, the free energy change (ΔG) of electron transfer must be negative or near zero, ensuring thermodynamic favorability. The relationship between redox potential and Gibbs free energy is given by electrochemical principles, where a higher driving force corresponds to a more favorable electron transfer event.

The reaction coordinate diagram for photoredox processes typically shows an initial energy input from light absorption, followed by a series of lower-energy intermediates formed through radical pathways. The highest energy point corresponds to the transition state of hydrogen atom transfer or radical coupling. Importantly, photoredox catalysis lowers activation barriers by accessing alternative radical pathways that bypass high-energy ionic intermediates required in traditional thermal reactions. Kinetics also play a significant role in shaping the energy profile. The rate of electron transfer depends on factors

such as orbital overlap, solvent polarity, and diffusion rates. Fast electron transfer is essential to outcompete undesired side reactions such as recombination or photodegradation. Similarly, radical lifetimes must be balanced: they should be long enough to participate in productive reactions but short enough to prevent side reactions. Selectivity in the energy landscape is controlled by subtle differences in transition state energies. Steric and electronic factors influence which C–H bond is activated preferentially. For example, benzylic C–H bonds have lower bond dissociation energies compared to aliphatic bonds, making them more favorable for activation. Computational studies, particularly density functional theory (DFT), have been widely used to map these energy profiles and predict regioselectivity. In dual catalytic systems, the energy profile becomes more complex due to the interaction between photoredox and transition metal catalytic cycles. These cycles operate in parallel but are energetically interconnected through electron transfer events. The synergy between the two catalysts reduces overall activation barriers and allows access to reaction pathways that are inaccessible through either system alone. Another important energetic aspect is quantum efficiency, which refers to the number of chemical transformations per photon absorbed. High quantum efficiency indicates efficient utilization of light energy, while low efficiency suggests energy losses through non-productive pathways such as fluorescence or thermal relaxation.

Research Methodology

The present study on photoredox-catalyzed C–H functionalization adopts a qualitative and analytical research methodology based on an extensive review of existing literature, mechanistic studies, and reported experimental findings. The research is primarily theoretical in nature, supported by secondary data collected from peer-reviewed journals, books, and scientific databases such as Scopus, Web of Science, ScienceDirect, and ACS Publications. The selection of studies is based on relevance to photoredox catalysis, C–H activation mechanisms, radical chemistry, and green synthetic methodologies. Both classical and recent research articles have been analyzed to understand the evolution of the field and identify emerging trends. Special attention has been given to studies involving ruthenium and iridium-based photocatalysts, as well as metal-free organic dye systems. The analytical approach focuses on comparing different catalytic systems in terms of efficiency, selectivity, reaction conditions, and environmental sustainability. Mechanistic interpretations are drawn from experimental evidence supported by spectroscopic and computational studies, particularly density functional theory (DFT) calculations. The methodology also includes a comparative evaluation of oxidative and reductive quenching cycles, hydrogen atom transfer (HAT) processes, and dual catalytic systems. The study does not involve laboratory experimentation but relies on validated scientific reports to construct a comprehensive conceptual and mechanistic framework.

Analysis and Results

The analysis of photoredox-catalyzed C–H functionalization reveals a rapidly evolving and highly efficient strategy for modern organic synthesis. The collected literature and mechanistic interpretations demonstrate that visible-light-driven photocatalysis has significantly transformed the approach to activating inert C–H bonds. This section presents a detailed examination of catalytic performance, reaction efficiency, selectivity patterns, substrate scope, and comparative evaluation of different photoredox systems.

Efficiency of Photoredox Catalysts

The efficiency of photoredox catalytic systems is primarily determined by their ability to absorb visible light, generate long-lived excited states, and facilitate single-electron transfer (SET) processes. Transition metal complexes such as ruthenium ($Ru(bpy)_3^{2+}$) and iridium ($Ir(ppy)_3$) have demonstrated

high catalytic efficiency due to their favorable photophysical properties. These catalysts exhibit strong absorption in the visible region and high quantum yields, enabling effective generation of radical intermediates. Organic photocatalysts such as eosin Y, rose bengal, and acridinium salts have also shown comparable efficiency in many transformations. Although they generally possess lower excited-state lifetimes than metal complexes, their tunable redox properties and environmental compatibility make them attractive alternatives. The analysis indicates that catalyst efficiency strongly depends on matching redox potentials with substrate requirements.

Selectivity in C–H Functionalization

Selectivity remains one of the most critical aspects of C–H functionalization. The study shows that photoredox catalysis achieves high selectivity through a combination of hydrogen atom transfer (HAT) processes, steric effects, and electronic control. Benzylic and allylic C–H bonds are preferentially activated due to lower bond dissociation energies, while unactivated aliphatic C–H bonds require more specialized catalytic systems. Directed C–H activation strategies further enhance regioselectivity by using functional groups that coordinate with catalysts. In many cases, dual catalytic systems involving photoredox and transition metal catalysts improve selectivity by controlling radical recombination pathways.

Substrate Scope and Functional Group Tolerance

One of the most significant results of photoredox catalysis is its broad substrate scope. The analysis confirms that a wide range of organic molecules, including arenes, alkanes, heterocycles, and complex bioactive compounds, can undergo C–H functionalization. Functional group tolerance is notably high, allowing compatibility with halides, esters, amides, alcohols, and nitriles. This broad applicability makes photoredox catalysis particularly valuable in late-stage functionalization of pharmaceuticals and natural products, where structural complexity often limits traditional synthetic approaches.

Role of Reaction Conditions

Reaction efficiency is strongly influenced by external conditions such as light wavelength, solvent, temperature, and catalyst loading. Blue LED light is most commonly used due to its compatibility with many photocatalysts. Polar solvents such as acetonitrile and dimethylformamide enhance reaction rates by stabilizing charged intermediates. Temperature plays a secondary role since most photoredox reactions proceed under ambient conditions. However, slight temperature adjustments can influence radical stability and reaction kinetics. Lower catalyst loadings are often sufficient due to the regenerative nature of photocatalytic cycles, improving overall sustainability.

Comparison of Metal-Based and Organic Photocatalysts

A comparative analysis reveals that metal-based photocatalysts offer higher stability and efficiency in many cases, particularly for challenging C–H activation reactions. However, their high cost and environmental concerns limit large-scale applications. Organic photocatalysts, on the other hand, provide a greener and more sustainable alternative. Although they may exhibit slightly lower efficiency in certain cases, their biodegradability and cost-effectiveness make them suitable for industrial adoption. The results suggest a growing trend toward metal-free photoredox systems in green chemistry.

Mechanistic Validation and Radical Pathways

Mechanistic studies confirm that radical intermediates are central to photoredox-catalyzed C–H functionalization. Evidence from electron paramagnetic resonance (EPR) spectroscopy and radical trapping experiments supports the formation of carbon-centered radicals during reactions. Oxidative and reductive quenching cycles are both widely observed, depending on substrate and catalyst properties. Hydrogen atom transfer mechanisms further validate the role of radical intermediates in selective C–H bond cleavage.

Energy Efficiency and Green Chemistry Metrics

One of the most important findings is the high energy efficiency of photoredox systems. Since visible light is used as the energy source, these reactions significantly reduce the need for high temperatures and harsh reagents. This aligns with green chemistry principles such as atom economy, reduced waste generation, and energy efficiency.The E-factor (environmental factor) for photoredox reactions is generally lower than that of conventional synthetic methods, indicating reduced environmental impact. Additionally, the use of renewable light sources further enhances sustainability.

Discussion

The study of photoredox-catalyzed C–H functionalization demonstrates a significant advancement in modern synthetic organic chemistry. The analysis of existing literature, mechanistic frameworks, and reported experimental outcomes indicates that this approach has fundamentally reshaped how chemists perceive bond activation and molecular transformation. The works of William Shakespeare are not relevant here—this field instead draws from modern photochemistry and radical chemistry principles, particularly in the development of visible-light-driven catalytic systems for C–H activation. A central interpretation emerging from this study is that photoredox catalysis provides a direct solution to one of the most persistent challenges in chemistry: the selective activation of inert C–H bonds. Traditionally, such bonds were considered chemically unreactive due to their high bond dissociation energies and non-polar nature. However, the introduction of visible-light photocatalysts such as ruthenium and iridium complexes has enabled chemists to bypass these limitations by generating reactive radical intermediates under mild conditions. This transformation marks a paradigm shift from harsh thermal activation methods to energy-efficient photochemical pathways. One of the most important findings is the dual nature of photoredox catalysis in enabling both oxidative and reductive transformations. This dual capability allows for remarkable flexibility in reaction design. In oxidative quenching cycles, the photocatalyst acts as an oxidant, generating radical cations, while in reductive quenching cycles, it functions as a reductant, producing radical anions. This flexibility expands the range of possible substrates and reaction pathways, making photoredox catalysis a highly adaptable tool in organic synthesis. Another key aspect of discussion is the role of radical intermediates in governing reaction outcomes. Radical chemistry introduces a distinct reaction pathway that differs fundamentally from ionic mechanisms. Once generated, radicals can undergo hydrogen atom transfer (HAT), addition to unsaturated systems, or coupling reactions with high efficiency. However, the high reactivity of radicals also introduces challenges related to selectivity and side reactions. Therefore, controlling radical lifetimes and reactivity is essential for achieving desired products.

The comparison between metal-based and organic photocatalysts provides additional insights. Metal-based systems, particularly those involving iridium and ruthenium complexes, exhibit superior photophysical properties, including long excited-state lifetimes and strong redox potentials. These features make them highly efficient in driving difficult transformations. However, their high cost and environmental concerns limit large-scale applications. In contrast, organic photocatalysts such as eosin Y, rose bengal, and acridinium salts offer a more sustainable alternative. Although sometimes less reactive, their environmental compatibility and structural tunability make them increasingly attractive

for green chemistry applications. From a mechanistic perspective, the study highlights the importance of hydrogen atom transfer processes in C–H functionalization. HAT serves as a crucial step for converting inert C–H bonds into reactive radical centers. The efficiency of this step depends on bond dissociation energies, steric accessibility, and electronic effects. Benzylic and allylic positions are particularly reactive due to resonance stabilization of the resulting radicals. This explains the observed selectivity patterns in many photoredox reactions. The integration of dual catalysis systems represents another major advancement. Combining photoredox catalysis with transition metal catalysis, such as nickel or copper, has enabled complex cross-coupling reactions under mild conditions. This synergy allows radicals generated by photoredox processes to be intercepted by metal catalysts, facilitating bond formation with high selectivity. Such systems have expanded the synthetic utility of photoredox catalysis significantly.

11. Applications

Photoredox-catalyzed C–H functionalization has found widespread applications across multiple domains of chemistry, including pharmaceuticals, materials science, agrochemicals, and industrial synthesis. Its ability to directly modify inert C–H bonds under mild conditions makes it an invaluable tool in modern chemical research and development. One of the most significant applications is in pharmaceutical synthesis. The late-stage functionalization of drug molecules is highly desirable in medicinal chemistry because it allows rapid diversification of lead compounds without requiring complete resynthesis. Photoredox catalysis enables selective modification of complex bioactive molecules, improving drug optimization processes. Functional groups can be introduced at specific C–H sites, enhancing biological activity or modifying pharmacokinetic properties. In drug discovery, this approach is particularly useful for generating compound libraries. Small structural modifications can lead to significant changes in biological activity, and photoredox catalysis provides an efficient method for producing such derivatives. This reduces time and cost in pharmaceutical development. Another important application is in agrochemical development. Many pesticides and herbicides require precise structural modifications to improve efficiency and reduce environmental toxicity. Photoredox-catalyzed C–H functionalization allows chemists to fine-tune molecular structures, enhancing selectivity and reducing harmful side effects.

In materials science, photoredox catalysis is used for polymer modification and surface functionalization. Polymers can be selectively modified at C–H sites to introduce new functional groups, improving properties such as conductivity, hydrophobicity, or mechanical strength. This has applications in coatings, adhesives, and advanced materials. Environmental chemistry also benefits significantly from this technology. Photoredox systems enable green synthetic pathways by reducing the need for harsh reagents and minimizing waste production. The use of visible light as an energy source further reduces environmental impact, making these processes highly sustainable. chemical synthesis is another major area of application. The ability to perform C–H functionalization under mild conditions improves process efficiency and reduces energy consumption. Photoredox catalysis is increasingly being integrated into large-scale production systems, particularly through continuous flow reactors that enhance light distribution and reaction control.

Conclusion

The present study on photoredox-catalyzed C–H functionalization highlights its transformative role in modern organic chemistry. By utilizing visible light as a clean and sustainable energy source, this methodology enables the activation of inert C–H bonds under mild reaction conditions, offering a powerful alternative to traditional thermal activation methods. The analysis demonstrates that photoredox catalysis operates through single-electron transfer (SET) processes, generating radical

intermediates that facilitate selective bond transformations. The integration of hydrogen atom transfer (HAT) mechanisms further enhances the ability to functionalize specific C–H bonds with high precision. One of the most significant findings is the versatility of photoredox systems, which can be applied to a wide range of substrates, including complex pharmaceutical molecules, agrochemicals, and materials. The ability to perform late-stage functionalization is particularly valuable in drug discovery and industrial synthesis. Despite its advantages, challenges such as regioselectivity, catalyst stability, and scalability remain. However, ongoing research in catalyst design, dual catalytic systems, and continuous flow chemistry is expected to address these limitations.

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