



Recent synthetic applications of metal catalysis in combination of photocatalysis

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ABSTRACT

The metal catalysis and photocatalysis has recently emerged as a versatile platform for the development of new, highly enabling synthetic methodologies. Photoredox catalysis provides access to reactive radical species under mild conditions from abundant, native functional groups, and when combined with metal catalysis, this feature allows direct coupling of non-traditional nucleophile partners. Photocatalysis can aid fundamental organometallic steps through modulation of the oxidation state of metal complexes or through energy-transfer mediated excitation of intermediate catalytic species. This review discusses the recent synthetic applications in organic synthesis.

1. Introduction

Metal catalysis has long been recognized for its scientific and societal impact^[1-3]. During the period of more than two century research in the field of metal catalysis, has grown and evolved in remarkable ways. However, three fundamental aspects of catalyst structure have remained consistent as a focus: ligand design, manipulation of available oxidation states and electronic excitation have all continued to be fruitful areas of research in catalysis^[4]. It has long been appreciated that coordinating ligands can significantly alter the reactivity of metal complexes^[5]. Moreover, for any given metal catalysed organic reaction that has become widely adopted, there exists a foundation of extensive ligand design and development studies that underpin the final general catalyst system. As one prominent example, the transformation in pharmaceutical synthesis^[6]. The importance of the metal oxidation state in transition metal catalysis is well established. Indeed, it has long been noted that the acceleration of several elementary steps in coupling protocols can be observed on modulation of the oxidation state of the metal catalyst^[7-17]. Not surprisingly, these findings have inspired a renaissance in high-valent metal catalysis, which in turn has led to the development of valuable new bond-forming reactions^[18,19].

The photophysical and photochemical properties of metal complexes have been extensively studied for more than 50 years^[20]. In fact, the properties of metal species in their excited states have been exploited in many important applications: energy storage^[21,22], organic light-emitting diodes^[23] and dye-sensitized solar cells^[24], to name only a few. Interestingly, with the exception of photoredox catalysis^[25], the invocation of the excited state of a transition metal in organic transformations remains limited^[26-29]. As a recent exception, researchers have demonstrated that photoexcitation can be exploited^[30], a protocol

that overcomes the harsh operating conditions of traditional non-light mediated variants^[31]. These findings have triggered a resurgence of interest in identifying new bond-forming processes that proceed via the intermediacy of an excited state of a metal catalyst^[32,33]. In recent years, a generic mode of photocatalysis, termed photoredox catalysis, has been rapidly developed and adopted by the organic chemistry community^[25,34-56].

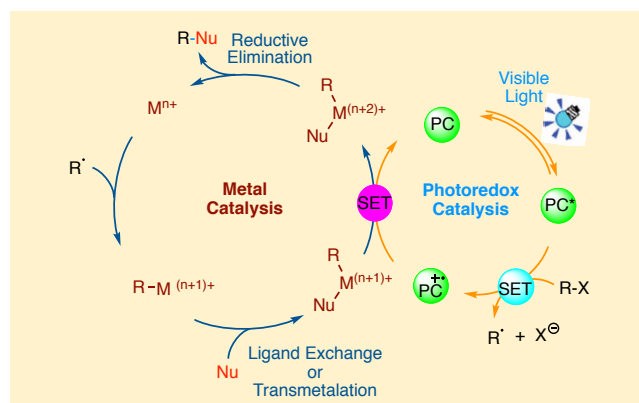


Fig. 1. Combination of metal catalysis and photocatalysis

One area of research that has been particularly fruitful within the field of photoredox catalysis is its merger with alternative modes of catalysis. These dual catalytic platforms have attracted attention from many research laboratories^[57,58]. Early publications in the area of organic photoredox catalysis demonstrated the potentially diverse nature of this dual activation strategy through the combination of photoexcited complexes with both organocatalysts and Lewis acids^[52,53]. More recently, the application of photoredox to the field of metal catalysis has received broad attention from the synthetic community and has

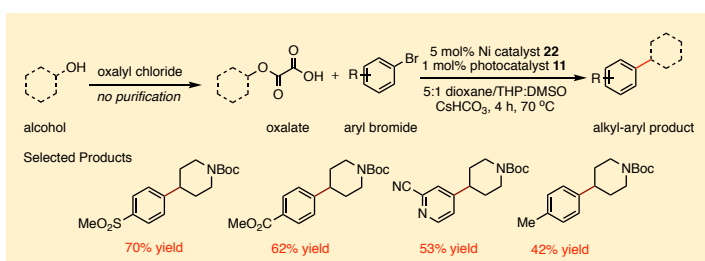
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enabled the development of many useful new C–C and C–heteroatom bond-forming protocols^[59,60] (Fig 1).

The first example was reported by Osawa^[61] in 2007. The role of the photocatalyst was not elucidated and, consequently, the significance of combining photoredox and metal catalysis was not fully appreciated until the seminal report of Sanford and co-workers^[62,63]. Subsequently, Rueping demonstrated that photoredoxcatalysis could also aid Ru and Rh-catalyzed oxidative Heck reactions in a mechanistically analogous manner^[64–66].

1. Synthesis of sp^3 – sp^2 cross-coupling of oxalates with aryl halides

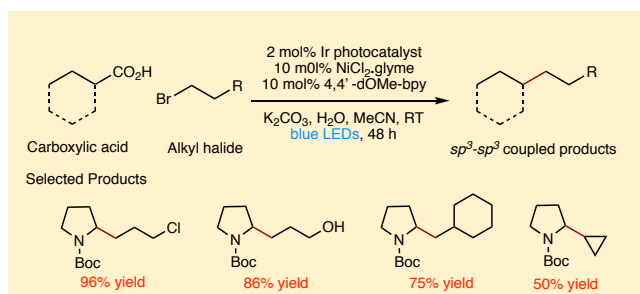
Xiaheng Zhang and David W. C. MacMillan illustrated the first general route for efficiently converting a variety of alcohols via their corresponding oxalates into Csp^3 – Csp^2 coupled products with aryl halides by way of the synergistic action of Ni and photoredox catalysis. The mechanistic details of this transformation are outlined in (Scheme 1)^[67].



Scheme 1. Synthesis of sp^3 – sp^2 cross-coupling of oxalates with aryl halides

2. Synthesis of sp^3 – sp^3 cross coupling of carboxylic acids with alkyl halides

Craig P. Johnston and co-workers have established a robust strategy for the direct formation of sp^3 – sp^3 bonds from abundant carboxylic acids and alkyl halides. This new platform for carbon–carbon bond construction is enabled by the catalytic activation of both coupling partners through the synergistic merger of photoredox and nickel catalysis. The benign nature of the reaction conditions has been exemplified by the breadth of functional groups tolerated in this transformation. The generality of this methodology and the ready availability of the starting materials used will aid the uptake of sp^3 – sp^3 cross-coupling across several fields of synthetic organic chemistry. A detailed mechanism for the proposed decarboxylative sp^3 – sp^3 coupling is delineated in (Scheme 2)^[68].

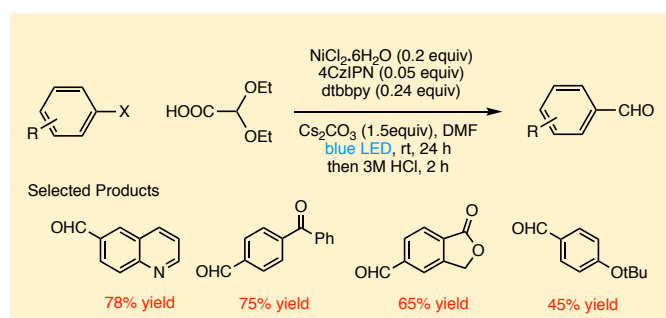


Scheme 2. Synthesis of sp^3 – sp^3 cross coupling of carboxylic acids with alkyl halides

3. Formylation of aryl halides and triflates

Wei Wang and co-workers^[71] reported a simple formylation reaction of aryl halides, aryltriflates, and vinyl bromides under synergistic nickel- and organic-dye-mediated photoredox catalysis. The photoredox-mediated single-electron-transfer

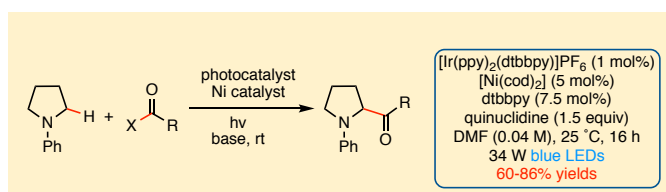
(SET) oxidation of glyoxylic acid or its acetals, followed by the loss of CO_2 , would form a formyl radical equivalent (**Scheme 3**).



Scheme 3. Formylation of aryl halides and triflates

4. Direct acylation of $C(sp^3)$ -H bonds

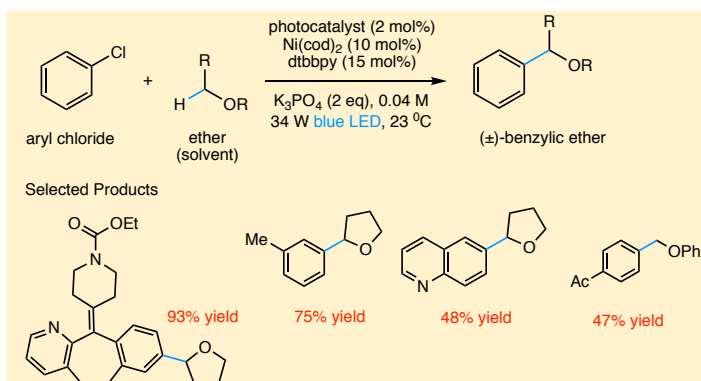
Candice L. Joe and Abigail G. Doyle^[72] have developed a novel method for $C(sp^3)$ C-H acylation mediated by nickel and photoredox catalysis. This protocol enables the direct synthesis of amino-ketones from simple N-aryl amines and acyl donors. Importantly, this method can be extended to late-stage coupling of complex and biologically relevant partners. More generally, this work demonstrates that metallaphotoredoxcatalysis can afford a strategic alternative for $C(sp^3)$ -H functionalization and precludes the need for traditional metal-coordinating directing groups on the C-H partner, and features uncommonly mild reaction conditions (**Scheme 4**).



Scheme 4. Metallaphotoredox $C(sp^3)$ -H cross-coupling with acyl electrophiles

5. Direct $C(sp^3)$ -H cross coupling

B. J. Shields and A. G. Doyle^[73] reported the development of a $C(sp^3)$ -H cross-coupling platform enabled by the catalytic generation of chlorine radicals by nickel and photoredoxcatalysis.



Scheme 5. Proposed catalytic cycle.

Aryl chlorides serve as both cross-coupling partners and the chlorine radical source for the α -oxy $C(sp^3)$ -H arylation of cyclic and acyclic ethers. Mechanistic studies suggest that photolysis of a Ni(III) aryl chloride intermediate, generated by photoredox-mediated single-electron oxidation, leads to elimination of a chlorine radical in what amounts to the sequential capture of two photons. Arylations of a benzylic $C(sp^3)$ -H bond of toluene and a completely unactivated $C(sp^3)$ -H bond of cyclohexane demonstrate the broad implications of this manifold for

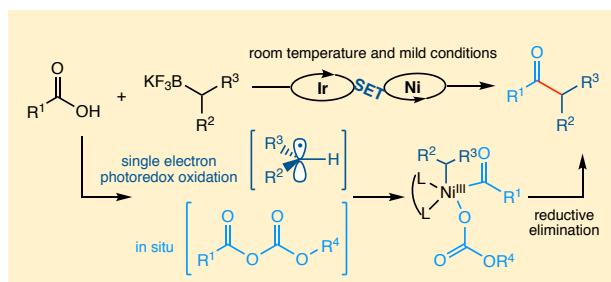
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accomplishing numerous C(sp³)-H bond functionalizations under exceptionally mild conditions (**Scheme 5**).

6. Direct conversion of carboxylic acids to alkyl ketones

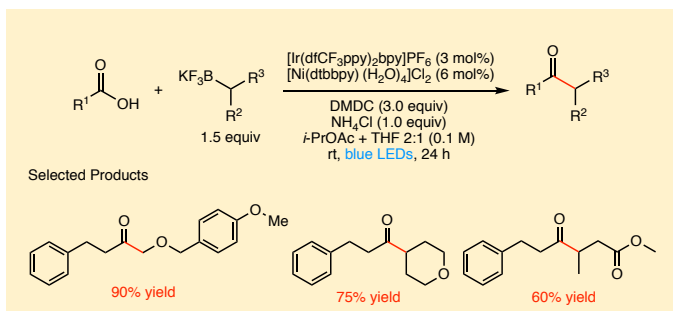
J. Amani and G. A. Molander^[74] have developed an efficient and mild method for acyl-Csp³ bond formation based on the direct conversion of carboxylic acids. This protocol is enabled by the synergistic, Ir-photoredox/nickel catalytic cross-coupling of in-situ activated carboxylic acids and alkyl trifluoroborates. This versatile method is amenable to the cross-coupling of structurally diverse carboxylic acids with various potassium alkyl trifluoroborates, affording the corresponding ketones with high yields. In this operationally simple cross-coupling protocol, aliphatic ketones are obtained in one step from bench stable, readily available carboxylic acids.

A general, robust method for the direct synthesis of alkyl ketones from carboxylic acids via Csp³-acyl bond construction under mild conditions and without the limitations of the more traditional two-electron protocols would be highly valued. For realization of this idea and to expand the scope of the photoredox/Ni dual catalysis cross-coupling strategy, they investigated the potential of the coupling of carboxylic acids with alkyl trifluoroborates via in-situ activation of the carboxylic acids (**Scheme 6**).



Scheme 6. Photoredox/Ni dual catalysis cross-coupling of carboxylic acids with alkyltrifluoroborates.

The investigations revealed the feasibility of the cross-coupling reaction by using dimethyl dicarbonate (DMDC) as the activator. It was satisfying to observe that DMDC, which is a commodity chemical used as a beverage preservative, would serve as a nearly ideal activating agent that generates an activated carbonic anhydride in situ. Upon reaction, the by products of the subsequent acylation include gaseous CO₂ and two equivalents of methanol, neither of which interferes with the separation of the produced ketones. (**Scheme 7**) shows the proposed mechanistic cycle for this acyl-sp³ coupling protocol adapted from their studies on cross-coupling of potassium alkyltrifluoroborates with aryl halides.

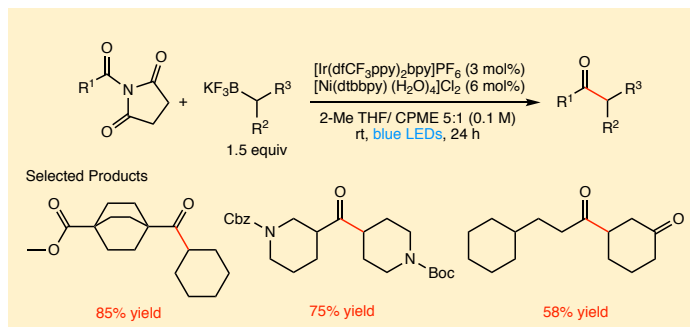


Scheme 7. Proposed mechanism for the acyl-sp³ cross-coupling

7. Cross-coupling of *N*-acylpyrrolidine-2,5-diones with alkyl-BF₃K

A visible-light photoredox/Ni electrophilic imide-based acyl transfer cross-coupling reaction have been reported by Gary A.

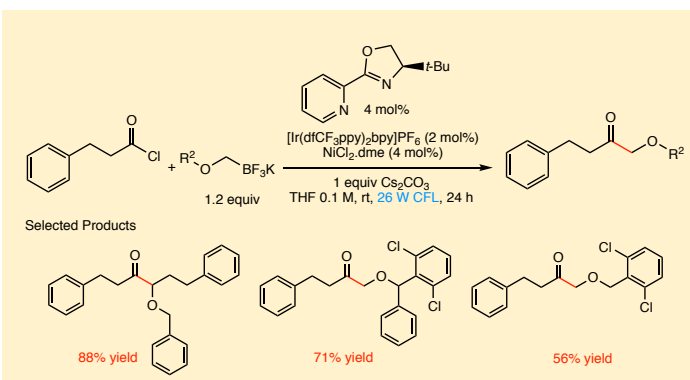
Molander and coworkers^[75] to access a variety of aliphatic ketones in high yields. In this protocol, *N*-acylpyrrolidine-2,5-diones have been used as electrophilic reagents in transition-metal-catalyzed selective N-C bond cleavage. These imides are readily accessed from the corresponding carboxylic acids and are more stable and more easily handled than the corresponding acyl chlorides or anhydrides. This transformation developed proceeds under extremely mild conditions using visible light without any additive and exhibits tolerance of a variety of functional groups in both coupling partners. This cross-coupling protocol thus represents an expansion of the synergistic photoredox/Ni catalytic paradigm into new electrophile space (**Scheme 8**).



Scheme 8. Proposed mechanism for the photoredox cross-coupling of *N*-acylpyrrolidine-2,5-diones with alkyl-BF₃K

8. Synthesis of α -alkoxyketones

A visible-light, single-electron-transfer (SET), photoredox cross coupling for the synthesis of α -alkoxyketones have been developed by Gary A. Molander and coworkers^[76]. In this method, various aliphatic and aromatic acylchlorides were successfully coupled with structurally diverse potassium alkoxymethyltrifluoroborates, producing the corresponding α -alkoxyketones with high yields. In this operationally simple and mild cross-coupling protocol, the desired ketones were obtained in one step from bench stable starting materials by a bond connection that is unique to both alkylboron chemistry and photoredox/Ni catalysis (**Scheme 9**).

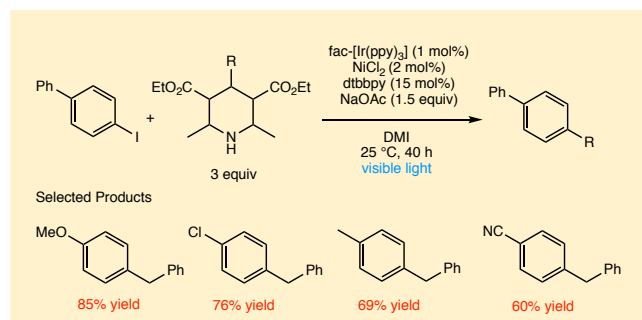


Scheme 9. Proposed mechanism for the synthesis of α -alkoxyketones

9. Cross-coupling reactions of aryl halides with 4-alkyl-1,4-dihydropyridines

Yoshiaki Nishibayashi and coworkers^[77] have reported novel cross-coupling reactions of aryl halides with 4-alkyl-1,4-dihydropyridines. In this reaction system, 4-alkyl-1,4-dihydropyridines can be used as formal nucleophilic alkylation reagents in transition-metalcatalyzed cross-coupling reactions. These results provide an alternative to the use of classical organometallic reagents as carbon-centered nucleophilic reagents. They consider that the method described herein opens up a novel synthetic strategy for the use of 4-alkyl-1,4-

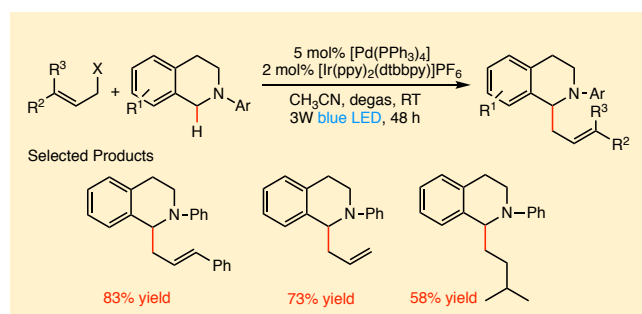
dihydropyridines as formal nucleophilic alkylation reagents in transition-metal-catalyzed transformations (**Scheme 10**).



Scheme 10. A plausible reaction pathway

10. α -Allylation of amines

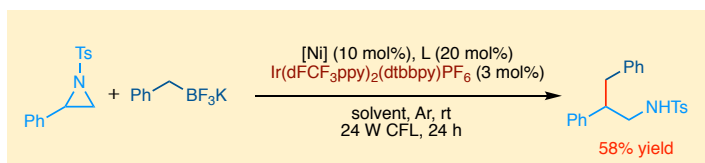
Jing Xiao and coworkers^[79] illustrated the catalytic generation of an allyl radical from a π -allylpalladium complex by combining visible-light-induced photoredox catalysis and palladium catalysis. The α -amino radical derived from the same catalytic cycle can react with the allyl radical through a cross-coupling process to afford various α -allylation products of amines in high yields (**Scheme 11**).



Scheme 11. Plausible reaction mechanism of α -allylation of amines

11. Cross-coupling of 2-arylaziridines and potassium benzyltrifluoroborates

Wen-Jing Xiao and coworkers^[80] have developed the first example of dual photoredox and nickel-catalyzed cross-coupling of aziridines and potassium alkyltrifluoroborates. This protocol features broad substrate scope, high functional group tolerance, exclusive regioselectivity, and mild redox-neutral conditions, providing complementary access to β -substituted amines (**Scheme 12**).

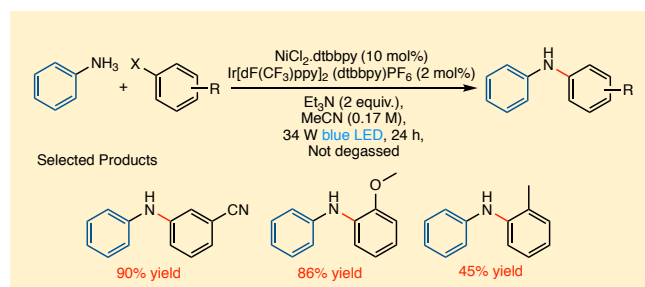


Scheme 12. Plausible reaction mechanism

12. Cross-coupling of primary aryl amines with aryl halides

Martins S. Oderinde and coworkers^[81] have reported a mild, highly chemoselective photoinduced Ir/Ni dual-catalyzed procedure for the cross-coupling of primary aryl amines with aryl and hetero arylhalides, which, probably the best of knowledge, is the first method of its kind. In terms of practical utility, this dual catalyzed C-N coupling procedure operates with high efficiency in the presence of molecular oxygen using a simple and readily available Ni-based catalyst. They also demonstrate the tolerance of synthetically useful functional groups, including alcohol, fluoride, chloride, aldehyde, organoboronate, vinyl, ketone, carbamate, ester, cyano, methyl, methoxy, thioether, and

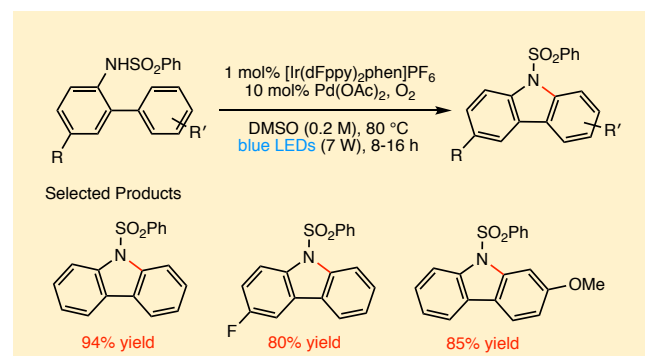
acetylene, using this mild procedure. Mechanistic studies and experimental evidence suggest that the reaction proceeds through an aminyl radical and a stepwise oxidative addition process. This synthetic method should find use in the synthesis of nitrogen-containing drug molecules and the mechanistic insights provided should promote interest and further development (**Scheme 13**).



Scheme 13. Proposed C-N coupling mechanism

13. Synthesis of carbazoles

Eun Jin Cho and coworkers^[82] reported an efficient method for the synthesis of *N*-substituted carbazoles, which involves intramolecular C-H bond amination of *N*-substituted 2-amidobiaryls. The strategy employed in this study, which combines transition metal catalysis and photocatalysis and negates the use of stoichiometric amounts of harsh or potentially toxic chemical additives, might be applicable in the formation of other environmentally benign reactions.

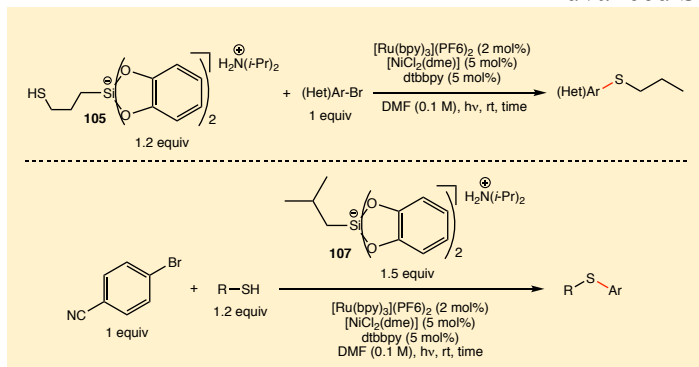


Scheme 14. Proposed mechanism for the synthesis of carbazoles

Similarly, David W. C. MacMillan and coworkers^[83] reported a highly efficient method for nickel-catalyzed C-N bond formation between sulphonamides and aryl electrophiles. This technology provides generic access to a broad range of *N*-aryl and *N*-heteroaryl sulphonamide motifs, which are widely represented in drug discovery.

14. Thioetherification

A mild, S-selective method for the thioetherification of aryl bromides using photoredox/Ni-dual catalysis was given by Gary A. Molander and coworkers^[84]. Although alkylthiosilicates can be used directly, the reaction scope was extended to include simple thiols by way of an intermolecular HAT pathway using alkylsilicates as H-atom abstractors. This base-free, room-temperature reaction tolerates a variety of aryl and heteroaryl bromides. Additionally, protic (even those containing acidic moieties) and sterically congested thiols were all competent toward thioetherification. The broad tolerance and mild nature of the described reaction could potentially be employed to prepare sulfides with biological relevance or for bioconjugation. Moreover, it provides unprecedented access to new chemical space for thioethers, unlocking their potential for examination by drug discovery groups or agroscience.

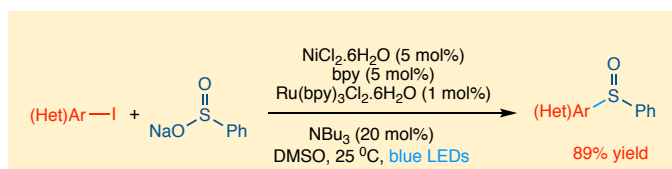


Scheme 15. Plausible catalytic cycle for thioetherification

15. Cross coupling of sulfinic acid salts with aryl iodides

G. Manolikakes and coworkers^[85] have reported a cross-coupling of sodium and lithium sulfinates with (hetero)aryl iodides promoted by a photoredox/nickel dual catalyst system. This method enables an efficient and mild synthesis of a wide range of aryl sulfones in good yields (**Scheme 16**).

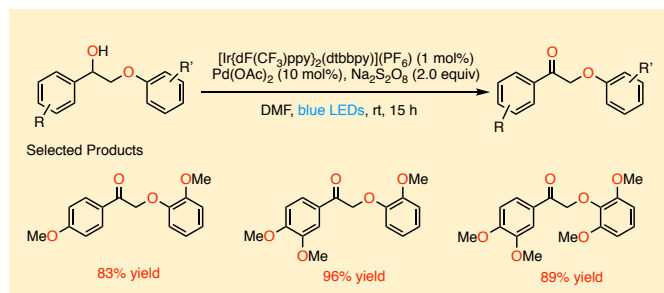
Similarly, G. A. Molander and coworkers^[86] reported the development and implementation of a strategy to construct aryl- and heteroaryl sulfones via Ni/photoredox dual catalysis. Using aryl sulfinate salts, the C–S bond can be forged at room temperature under base-free conditions. An array of aryl- and heteroaryl halides are compatible with this approach.



Scheme 16. Cross coupling of sulfinic acid salts with aryl iodides

16. Oxidation of lignin model systems

C. R. J. Stephenson and co-workers^[87] postulated that a novel approach toward the valorization of lignin and related systems has been developed by combining photoredox and Pd catalysis.

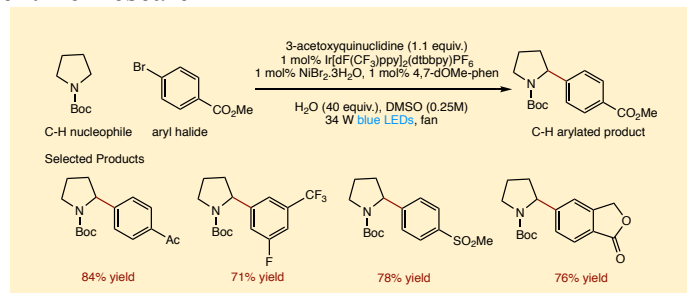


Scheme 17. Oxidation of lignin model systems

This unique cooperative interplay of photoredox and Pd catalysis has allowed for the efficient oxidation of lignin related systems at room temperature and constitutes a vital step toward converting lignin to value-added, low-molecular weight aromatics. Current efforts to improve this process and to develop further the use of dual catalytic systems incorporating visible-light active complexes are underway (**Scheme 17**).

17. Cross-coupling of aryl halide and C–H nucleophile

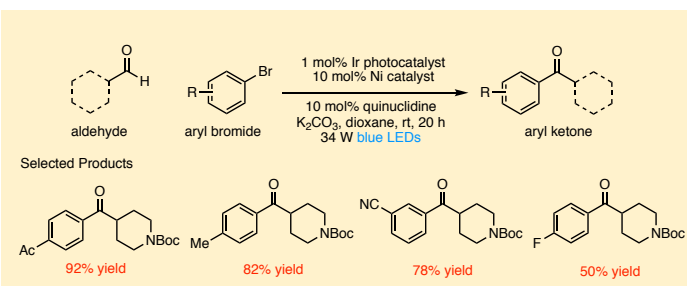
Megan H. Shaw and co-workers^[88] have developed a highly selective and general C–H arylation protocol that activates a wide array of C–H bonds as native functional handles for cross-coupling. This protocol will gain widespread use within the synthetic community as a complement to existing cross-coupling technologies (**Scheme 18**).



Scheme 18. Cross-coupling of aryl halide and C–H nucleophile

18. Direct aldehyde C–H arylation and alkylation

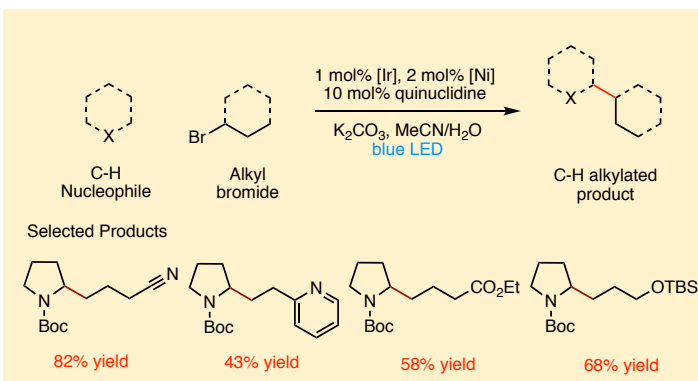
Xiaheng Zhang and David W. C. MacMillan^[89] illustrated the direct aldehyde C–H functionalization via the synergistic merger of photoredox, nickel, and hydrogen atom transfer catalysis. This mild, operationally simple protocol transforms a wide variety of commercially available aldehydes, along with aryl or alkyl bromides, into the corresponding ketones in excellent yield. This C–H abstraction coupling technology has been successfully applied to the expedient synthesis of the medicinal agent haloperidol. The mechanistic details of their proposed transformation are outlined in (**Scheme 19**).



Scheme 19. Direct aldehyde C–H arylation and alkylation

19. sp³ C–H alkylation

Chip Le and co-workers^[90] described the functionalization of carbon hydrogen (C–H) bonds is one of the most attractive strategies for molecular construction in organic chemistry.

Scheme 20. sp³ C–H alkylation

The hydrogen atom is considered to be an ideal coupling handle, owing to its relative abundance in organic molecules and its availability for functionalization at almost any stage in a synthetic sequence. Although many C–H functionalization reactions involve C(sp³)–C(sp²) coupling, there is a growing demand for C–H alkylation reactions, wherein sp³ C–H bonds are replaced with sp³ C–alkyl groups. Here they describe a polarity-match-based selective sp³ C–H alkylation via the combination of photoredox, nickel and hydrogen-atom transfer catalysis. This methodology simultaneously uses three catalytic cycles to achieve hydridic C–H bond abstraction (enabled by polarity matching), alkyl halide oxidative addition, and reductive

elimination to enable alkyl–alkyl fragment coupling. The sp^3 C–H alkylation is highly selective for the α -C–H of amines, ethers and sulphides, which are commonly found in pharmaceutically relevant architectures. This cross-coupling protocol should enable broad synthetic applications in de novo synthesis and late-stage functionalization chemistry (**Scheme 20**).

Conclusion

In recent years, the application of metal in conjugation with photocatalysis has come to the forefront in organic chemistry. A dual catalytic platform that has recently attracted great interest from the synthetic community is the combination of photoredox and metal catalysis. Photoredox catalysis offers access to a broad range of carbon-centred and heteroatom-centred radicals, and these species have been used as nucleophilic coupling partners in metal-photocatalytic transformations. The advantages of combining photoredox and metal catalysis extend far beyond the singular aspect of radical generation. Photoredox catalysis provides a unique reaction environment, as the light harvesting catalysts are simultaneously oxidizing and reducing in nature. The photoredox catalysts can be of use in challenging mechanistic steps by either direct modification of the oxidation state of the transition metal via SET, or generation of excited-state metal complexes through energy transfer.

The combination of photoredox and metal catalysis has been demonstrated as a highly versatile platform for the development of new methodologies. By combining these individually powerful catalytic manifolds, synthetic chemists can strive to achieve transformations that are not currently possible using a single catalyst system. As such, on the basis of our previous work^[91–99] on photocatalysed organic synthesis, we anticipate that the field of merging metals with photocatalysis will continue to grow at a remarkable pace, providing the organic community with new synthetic tools for streamlined access to valuable chemical building blocks. Considering these advances and the potential impact of further work in this field, the pharmaceutical industry has chosen to adopt these technologies at an unprecedented rate.

Acknowledgements

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