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Radical Decarboxylative Functionalizations Enabled by Dual Photoredox Catalysis

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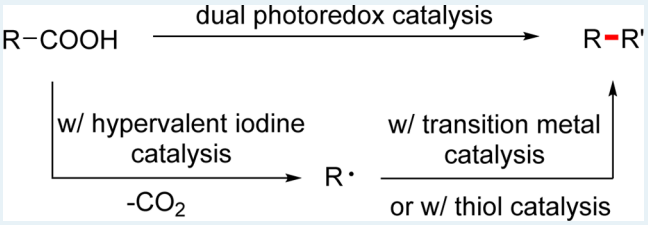
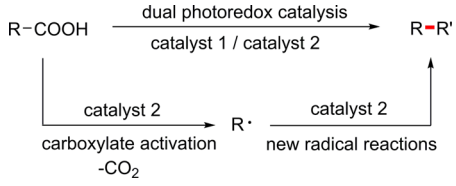
ABSTRACT: Organic carboxylates are readily available feedstock chemicals, and the carboxylate group is a latent activating group which can be easily removed by decarboxylation. The radical decarboxylative functionalization by photoredox catalysis undergoes rapid development recently, with which many difficult transformations can be achieved by dual photoredox catalysis. We summarize radical decarboxylative functionalizations via additional transition metal catalysts, thiol catalysts, or hypervalent iodine catalysts, which either activate the carboxylates or enable new radical transformations.



KEYWORDS: *photoredox catalysis, decarboxylation, dual catalysis, radical reaction, transition metal catalysis, thiol catalysis, hypervalent iodine catalysis*

Organic carboxylates are readily available and stable, and the carboxylate group is a latent activating group for organic synthesis which can be easily removed.[1] Radical decarboxylative functionalization is widely used in organic synthesis, with which the light irradiation or strong oxidative conditions are usually applied as radical initiation conditions.[2] Recently, radical decarboxylative reactions by photoredox catalysis are developed,[3] and their combination with additional catalysts (catalyst 2) enables transformations that are difficult to achieve by traditional radical decarboxylation (Scheme 1).[4] In this Perspective, we focus on radical decarboxylative functionalization by dual photoredox catalysis, in which catalyst 2 either activates the carboxylates in a novel way or enables new radical transformations.

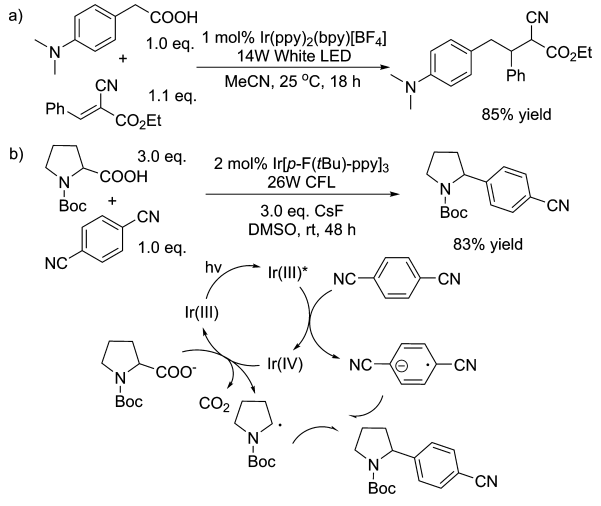
Scheme 1. Radical Decarboxylative Functionalization by Dual Photoredox Catalysis



I. INTRODUCTION OF DECARBOXYLATIVE FUNCTIONALIZATION ENABLED BY PHOTOREDOX CATALYSIS

The carboxylic acids or their derivatives can be oxidized or reduced by photoexcited photocatalysts or their oxidation/reduction adducts to induce radical decarboxylation.[3] Compared to traditional radical decarboxylations, these visible-light-induced decarboxylations are usually run under mild reaction conditions. In 2013, the Nishibayashi group reported the decarboxylative Michael addition reaction, and the carboxylic acid scope was limited to benzylic carboxylates with *para*-amino substitutions (Scheme 2a).[5] In 2014, the MacMillan group reported the decarboxylative addition of α-amino acids to electron-deficient arylnitriles, and arylnitriles were used as both oxidants and radical acceptors (Scheme 2b).[6] The mechanistic investigations suggest the oxidation of the photoexcited Ir(III)* to Ir(IV) by arynitriles, in which the resulting Ir(IV) oxidizes

Scheme 2. Decarboxylative Functionalization of Carboxylic Acids by Photoredox Catalysis



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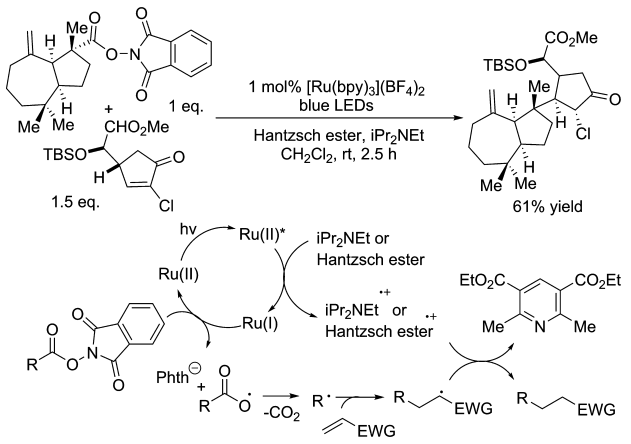
the deprotonated carboxylates to yield the α-aminoalkyl radical after decarboxylation. This α-aminoalkyl radical recombines with the arylnitrile radical anion to yield the alkyl arylation adduct. The decarboxylation of carboxylic acids are later expanded to simple aliphatic carboxylic acids and used for fluoronations,[7] alkenylations,[8] and alkynylations.[9]

In 1991, the Oda group discovered that the *N*-(acyloxy)-phthalimides underwent radical decarboxylation with single-electron reduction, and subsequent Michael addition reaction and other transformations were realized.[10] In 2012, the Overman group used this *N*-(acyloxy)-phthalimides decarboxylation strategy to achieve the total synthesis of aplyviolene (Scheme 3).[11] In this work, they found the commercially

Scheme 3. Decarboxylative Functionalization of Carboxylate Derivatives by Photoredox Catalysis

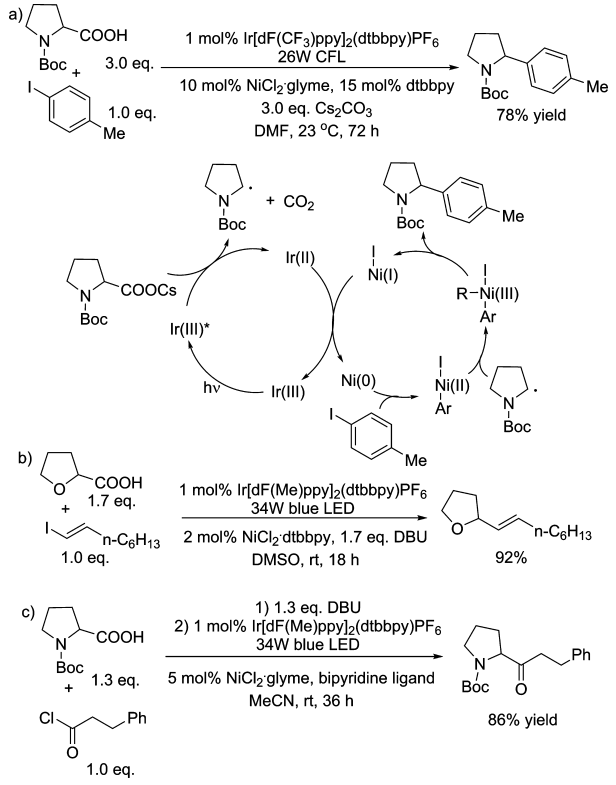


available diisopropylethylamine and Hantzsch ester were effective reductive quenchers for photoexcited Ru(II)*. The resulting Ru(I) reduced the *N*-(acyloxy)-phthalimides and yielded the alkyl radical after phthalimide elimination and decarboxylation. The decarboxylative alkynylations[12] and allylations[13] were later developed by reacting with corresponding radical acceptors.

II. DECARBOXYLATIVE FUNCTIONALIZATION ENABLED BY DUAL PHOTOREDOX/NICKEL CATALYSIS

Transition-metal-catalyzed cross-coupling reactions are highly effective for Csp^2–Csp^2 bond formations; however, their extension to Csp^3–Csp^2 bond formations are challenging. The alkylmetallic intermediates undergo facile β-hydride elimination, and it is difficult for oxidative addition and transmetalation on Csp^3 centers.[14] In 2014, the MacMillan and Doyle group reported the dual photoredox/nickel catalytic system to enable the cross-coupling reaction between alkyl carboxylic acids and aryl halides (bromides, iodides, Scheme 4a).[15] The mechanistic investigations suggest the formation of the Ni(II)-aryl species from the oxidative addition of the aryl halide to Ni(0). In the photoredox cycle, the alkyl carboxylic acid is oxidized by the photoexcited Ir(III)* and induces radical decarboxylation to generate the alkyl radical. The alkyl radical adds to the Ni(II)-aryl complex and generates alkyl-Ni(III)-aryl species, which can undergo reductive elimination to yield the Csp^3-Csp^2 coupling adducts and the Ni(I) species. Finally, this Ni(I) intermediate is reduced by the Ir(II) and provides the Ir(III) as well as the Ni(0) catalyst. The MacMillan group

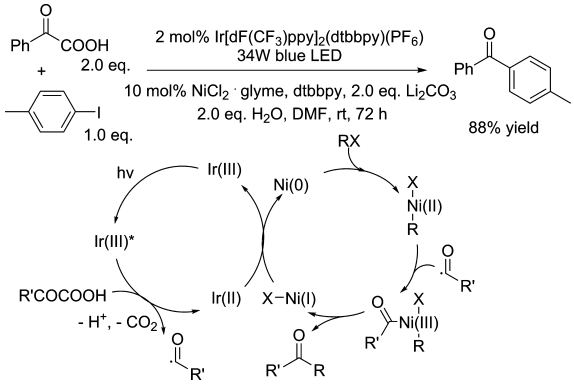
Scheme 4. Dual Photoredox/Nickel Catalysis for Alkyl Arylation, Alkenylation, and Acylation



further extended this dual photoredox/nickel catalytic system to vinyl halides, and they expanded the scope of alkyl carboxylic acids to simple hydrocarbon-substituted acids other than α-oxy and α-amino acids (Scheme 4b).[16] In 2015, they used alkyl carboxylic acids and acyl chlorides to form mixed anhydrides in situ and enabled the ketone formation (Scheme 4c).[17] In 2016, the MacMillan group collaborated with the Fu group to extend the alkyl arylation coupling reaction to be asymmetric and stereoconvergent by introducing the chiral ligand.[18]

In 2015, the MacMillan group discovered that the dual photoredox/nickel catalytic system could be applied to ketoacids, which reacted with aryl halides (bromides, iodides) to yield the aryl ketones (Scheme 5).[19] The mechanistic investigations indicate the formation of the Ni(II)-aryl species from the oxidative addition of the aryl iodides to Ni(0). The

Scheme 5. Dual Photoredox/Nickel Catalysis for Acyl Arylation



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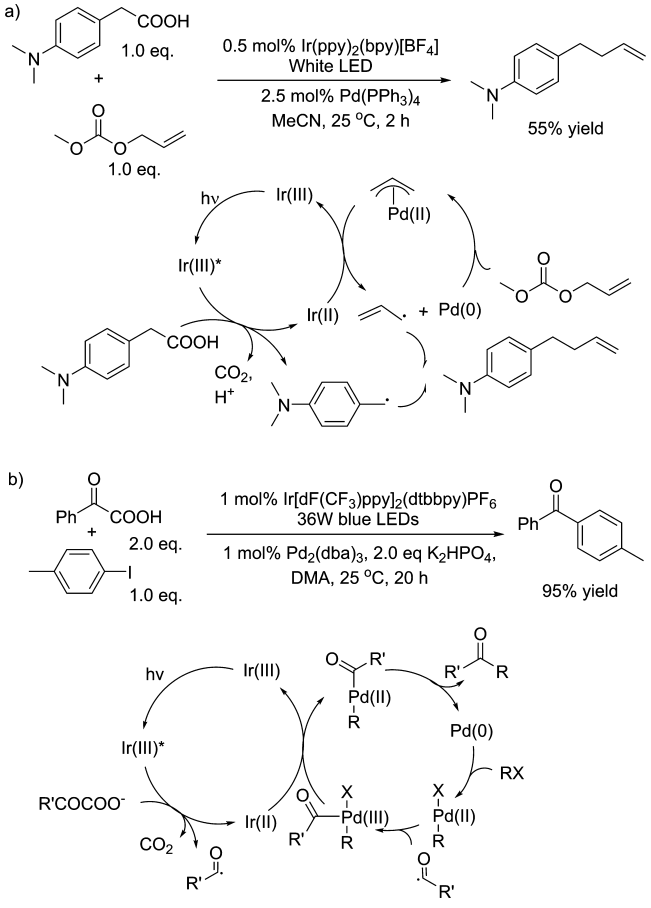
ketoacid is oxidized by the photoexcited Ir(III)* and induces radical decarboxylation to generate the acyl radical. The acyl radical adds to the Ni(II)-aryl complex and generates an acyl-Ni(III)-aryl species, which can undergo reductive elimination to yield the aryl ketone and the Ni(I) species. Finally, this Ni(I) intermediate is reduced by the Ir(II) and provides the Ni(0) as well as the Ir(III) catalyst.

III. DECARBOXYLATIVE FUNCTIONALIZATION ENABLED BY DUAL PHOTOREDOX/PALLADIUM CATALYSIS

Palladium is a widely used transition metal catalyst in cross-coupling reactions, and it has been used in dual photoredox catalysis.[20] In 2014, the Tunge group combined the palladium catalyst with the photoredox catalysis to enable the decarboxylative allylation of α-amino acids and phenylacetic acids (Scheme 6a).[21] The allyl−allyl coupling and benzyl−

Scheme 6. Dual Photoredox/Palladium Catalysis for Alkyl Allylation and Acyl Arylation

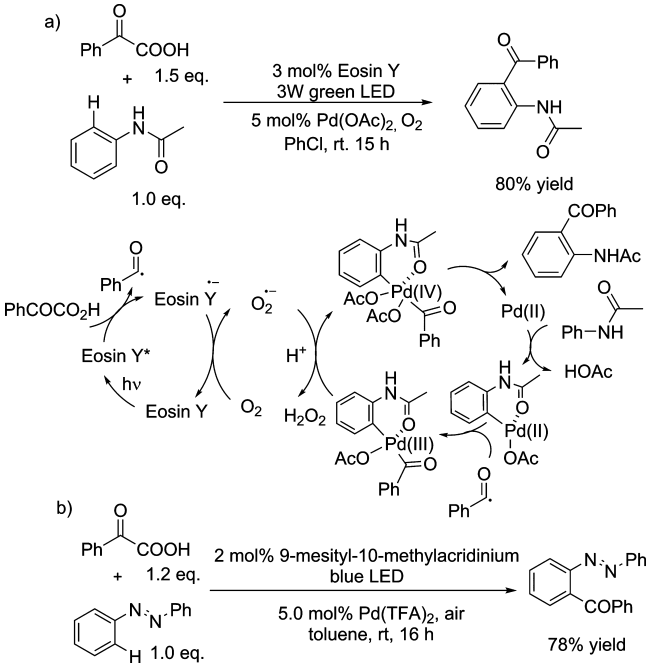


benzyl dimer products were observed as the byproducts. The mechanistic investigations suggest the formation of the Pd(II)-π-allyl species from the oxidative addition of the allyl ester to Pd(0). The carboxylate is oxidized by the photoexcited Ir(III)* and induces radical decarboxylation. The Pd(II)-π-allyl species is then reduced by the Ir(II) and provides an allyl radical and the Pd(0) catalyst. Alternatively, the benzyl radical may add to the Pd(II)-π-allyl complex and generates a benzyl-Pd(III)-allyl species, which can be reduced by the Ir(II) and undergoes reductive elimination. In either case, the electron shuttling mechanism by the photocatalyst is crucial.

In 2015, the Fu group utilized the dual photoredox/palladium catalytic system to realize the cross-coupling reaction between ketoacids and aryl halides (bromides, iodides, Scheme 6b).[22] The authors propose the acyl radical adds to the Pd(II)-aryl complex and generates the acyl-Pd(III)-aryl species based on DFT calculations, which is then reduced by the Ir(II) and undergoes reductive elimination. The alkyl and aryl substituted ketoacids, as well as the oxalates are all applicable for the reaction.

In 2015, the Wang group discovered that the organic photocatalyst eosin Y also engaged in the dual catalytic reaction with the palladium catalyst (Scheme 7a).[23] With molecular

Scheme 7. Dual Photoredox/Palladium Catalysis for C−H Acylation



oxygen as the external oxidant, the oxidative coupling reaction between ketoacids and the aryl-H bond of the arylacetanilide were achieved. This reaction is initiated by green light irradiation to generate the photoexcited eosin Y*, which can oxidize the ketoacids to yield the acyl radical after decarboxylation. The resulting eosin Y·$^-$ is oxidized by the molecular oxygen to regenerate the eosin Y and yields the O_2·$^-$. On the palladium catalytic cycle, the palladium does the C−H insertion reaction facilitating by the neighboring acetanilide coordination. This Pd(II)-aryl species undergoes an acyl radical addition to yield the acyl-Pd(III)-aryl intermediate. This acyl-Pd(III)-aryl intermediate is then oxidized by the O_2·$^-$ to yield the C−H acylation adduct after reductive elimination. The azo- or azoxy-benzenes could also engage in the aryl C−H acylation by dual catalysis with 9-mesityl-10-methylacridinium (Mes-Acr-Ph) as the photocatalyst, and the presence of O_2·$^-$ was detected by EPR analysis (Scheme 7b).[24]

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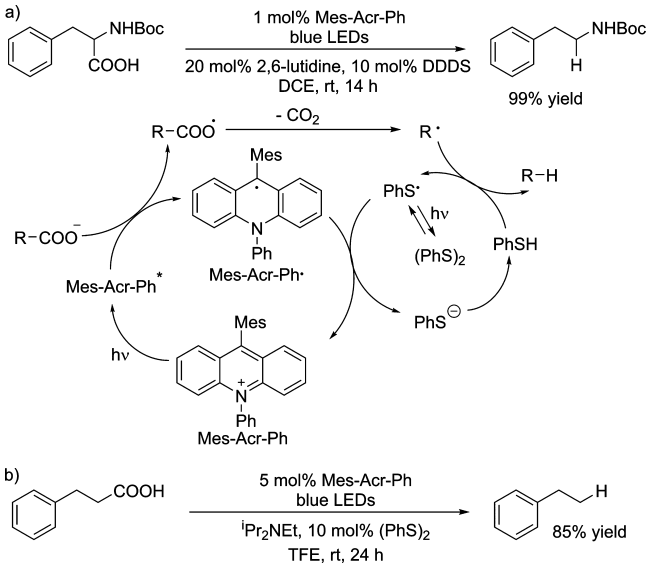
IV. DECARBOXYLATIVE FUNCTIONALIZATION ENABLED BY DUAL PHOTOREDOX/THIOL CATALYSIS

The hydrodecarboxylation strategy allows for the use of carboxyl groups as the traceless hydrogen surrogates. In 2014, the Wallentin group reported a dual photoredox/thiol catalysis method for the hydrodecarboxylation of stabilized carboxylic acids, such as protected amino acid derivatives and phenyl acetic acid derivatives (Scheme 8a).[25] The reaction is initiated

Scheme 8. Dual Photoredox/Thiol Catalysis for Hydrodecarboxylation



by the oxidation of deprotonated carboxylic acid by photoexcited Mes-Acr-Ph*, which forms the alkyl radical after decarboxylation. The hydrogen atom abstraction from thiophenol furnishes the hydrodecarboxylation adduct. The thiyl radical then reoxidizes the reduced catalyst and regenerates the hydrogen atom donor after protonation. However, aliphatic carboxylic acids were not viable substrates in this report.

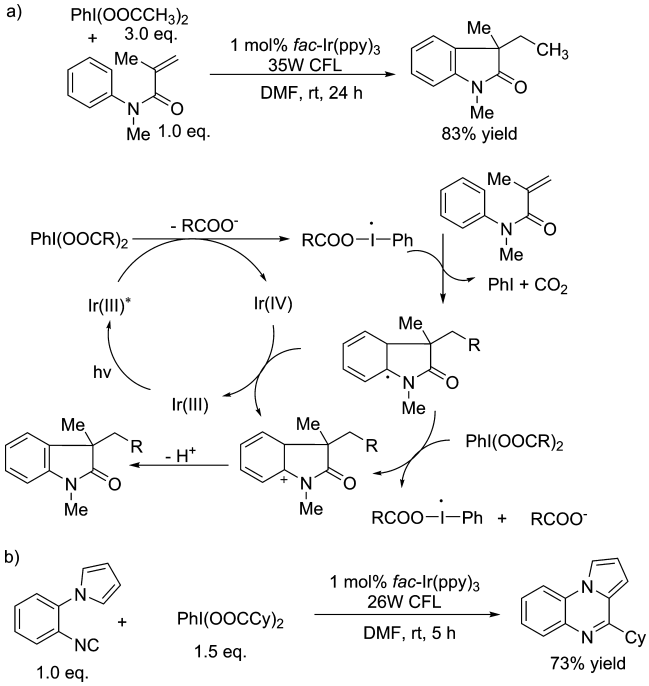
In 2015, the Nicewicz group extended the catalytic system to realize the direct hydrodecarboxylation of aliphatic carboxylic acids and malonic acid derivatives (Scheme 8b).[26] In the hydrodecarboxylation of single aliphatic carboxylic acids, the *N,N*-diisopropylethylamine was employed, although it might form aminium radical cations. However, they predominately existed in solution as the ammonium salts and insulated from oxidation. In the case of malonic acid derivatives, the second acid moiety increased the oxidation potential of the carboxylate due to the hydrogen bonding such that the strong base KO^{t}Bu was needed. The use of trifluoethanol (TFE) as solvent was not contributing as a hydrogen atom donor, instead it increased the excited state lifetime of Mes-Acr-Ph.

V. DECARBOXYLATIVE FUNCTIONALIZATION ENABLED BY PHOTOREDOX CATALYSIS AND HYPERVALENT IODINE REAGENTS

Hypervalent iodine reagents (HIR) are not only excellent oxidizing agents but also demonstrate reactivity similar to transition metals due to a weak and highly polarized hypervalent bond between the iodine atom and the ligands.[27]

In 2013, the Zhu group reported that phenyliodine(III) diacetate (PhI(OAc)2, DIB) underwent decarboxylation by photoredox catalysis (Scheme 9a).[28] This methodology

Scheme 9. Photoredox Catalysis and Hypervalent Iodine Reagents for Michael Addition and C−H Activation Cascade



extended to other carboxylates bound to the phenyliodine(III), which yielded the corresponding alkyl radical for addition to *N*-methyl-*N*-phenylmethacylamide. The mechanistic investigations indicate that the carboxylate bound to phenyliodine(III) are readily reduced by photoexcited Ir(III)* and affords the I(II) radical. This I(II) radical anion facilitates the alkyl radical addition to the alkene by coordinating the *N*-methyl-*N*-phenylmethacylamide. After radical C−H functionalization cascade, the resulting radical is oxidized by Ir(IV) to yield the carbocation and undergoes deprotonation to yield the final adduct. In 2014, the Jamison group used the similar phenyliodine(III) activation to realize the alkyl radical cyclization on arylisocyanides by photoredox catalysis (Scheme 9b).[29] In 2014, the Zhu group reported a visible-light-induced decarboxylative trifluoromethylation of α,β-unsaturated carboxylic acids.[30] The effectiveness of the Togni reagent compared to other trifluoromethylation reagents such as Umemoto reagent or CF_3SO_2Cl indicated that the hypervalent iodine reagent was crucial.

In 2015, our group discovered a novel deboronative/decarboxylative alkenylation reaction by photoredox catalysis with hypervalent iodine activation.[31] The hypervalent iodine was not just the oxidant evidenced by the lack of reactivity by strong oxidant persulfates (entry 1 in Scheme 10a). In addition, the commonly used noncyclic HIRs such as PhIO and PhI(OAc)2 were not effective (entries 2 and 3), while the cyclic HIRs such as hydroxybenziodoxole (BI−OH) and acetoylbenziodoxole (BI-OAc) gave excellent results (entries 4 and 5). The mechanistic investigations indicate the formation of the benziodoxole-vinyl carboxylic acid complex (BI−OOCCH=CHR′), which is characterized by X-ray crystallography (Scheme 8b). The BI−OOCCH=CHR′ has an

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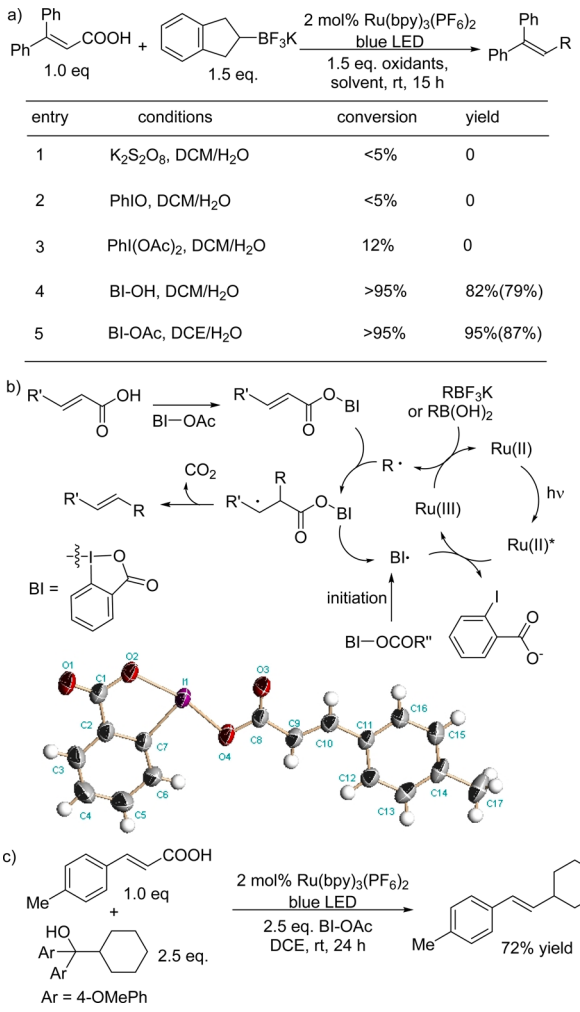
Scheme 10. Photoredox Catalysis and Hypervelent Iodine Reagents for Alkyl Alkenylation



entry	conditions	conversion	yield
1	$K_2S_2O_8$, DCM/H_2O	<5%	0
2	PhIO, DCM/H_2O	<5%	0
3	$PhI(OAc)_2$, DCM/H_2O	12%	0
4	BI-OH, DCM/H_2O	>95%	82%(79%)
5	BI-OAc, DCE/H_2O	>95%	95%(87%)

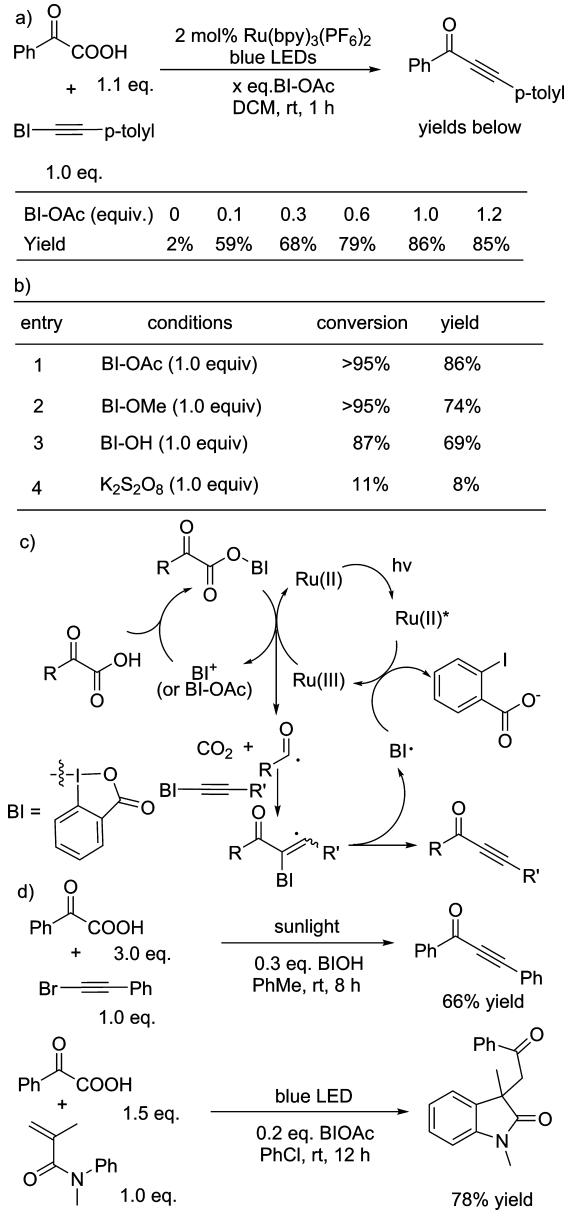
oxygen−iodine bond (2.12 Å) between the vinyl carboxylic acid and the benziodoxole moiety, which is similar to the oxygen−iodine bond (2.12 Å) in the benziodoxole moiety.

In reaction conditions, the vinyl carboxylic acid and BI-OAc generate the BI−OOCCH═CHR′ in situ, which then oxidize the photoexcited Ru(II)* to Ru(III) for reaction initiation (Scheme 10b). The alkyl trifluoroborate is oxidized by Ru(III) to alkyl R radical after deboronation and regenerates Ru(II). The alkyl R radical does α-addition to BI−OOCCH═CHR′, and the adduct undergoes benziodoxole-facilitated decarboxylation to release the benziodoxole radical and yields the alkene product. The exclusive *trans*-alkene product formation suggested the formation of the carbocation intermediate. In 2016, our group further discovered that the cyclic HIRs facilitated both alkoxyl radical formation and radical decarboxylation to enable the C−C bond-cleavage/alkenylation reaction (Scheme 10c).[32]

VI. DECARBOXYLATIVE FUNCTIONALIZATION ENABLED BY DUAL PHOTOREDOX/HYPERVALENT IODINE CATALYSIS

With the catalytic use of hypervalent iodine reagents, the dual photoredox/hypervalent iodine catalysis can be achieved. In 2015, our group discovered that the acetoylbenziodoxole (BI-OAc) enabled the decarboxylative ynonylation by photoredox catalysis, and even a catalytic amount of BI-OAc was suitable for the reaction (Scheme 11a).[33] The mechanistic inves-

Scheme 11. Dual Photoredox/Hypervelent Iodine Catalysis for Ynonylation and Michael Addition



BI-OAc (equiv.)	0	0.1	0.3	0.6	1.0	1.2
Yield	2%	59%	68%	79%	86%	85%

b)

entry	conditions	conversion	yield
1	BI-OAc (1.0 equiv)	>95%	86%
2	BI-OMe (1.0 equiv)	>95%	74%
3	BI-OH (1.0 equiv)	87%	69%
4	$K_2S_2O_8$ (1.0 equiv)	11%	8%

tigations indicate that other cyclic HIRs are also effective including BI-OMe and BI-OH; however, the BI-OAc is the most effective for the easy dissociation of the acetate (entries 1−3 in Scheme 11b). The persulfate is not suitable for the reaction (entry 4). This reaction is initiated by the ligand exchange between the ketoacid and the BI-OAc, which yields the BI-ketoacid intermediate. This intermediate can be independently prepared and suitable for the ynonylation. In the photoredox catalytic cycle, the photoexcited Ru(II)* is oxidized by the BI radical to generate the Ru(III), which can further oxidize the BI-ketoacid for decarboxylative acyl radical formation (Scheme 11c). In the meantime, the BI-OAc (or BI^+) is recovered for the new hypervalent iodine catalytic cycle. The alkyl and aryl substituted ketoacids, as well as the oxalates and oxalimide are all applicable for the reaction. In 2015, the

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Wang group discovered the similar BI-ketoacid intermediate enabled the acyl radical formation, and no photocatalyst was needed under sunlight irradiation (Scheme 11d).[34] The bromoalkyne and *N*-methyl-*N*-phenylmethacylamide were used as the radical acceptors for alkynylations and Michael addition reactions.

VII. CONCLUSION AND OUTLOOK

In conclusion, we have summarized radical decarboxylative functionalization enabled by dual photoredox catalysis, with the focus on their mechanistic insights. The additional catalysts used for dual catalysis have the following roles: (i) the transition metal catalysts enable radical reactions that are inaccessible by traditional radical reactions; (ii) the thiol catalysts facilitate the hydrogen transfer which is traditionally slow or difficult; and (iii) the hypervalent iodine catalysts activate the carboxylates with transition-metal-like reactivity. We envision the future radical decarboxylative functionalization by dual photoredox catalysis will enable reactions for carboxylate categories inaccessible by current methods and achieve other new radical transformations.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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