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Photocatalytic decarboxylation of free carboxylic acids and their functionalization

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Visible light mediated decarboxylative functionalization of carboxylic acids and their derivatives has recently emerged as a novel and powerful toolkit for small molecule activation in diverse carbon–carbon and carbon–hetero bond forming reactions. Naturally abundant highly functionalized bench-stable carboxylic acid analogs have been employed as promising alternatives to non-trivial organometallic reagents for mild and eco-benign synthetic transformation with traceless CO_2 by-products. In this highlight article, we focus on the development of various photodecarboxylative functionalization strategies along with intra/inter-molecular cyclization *via* concerted single electron transfer (SET) or energy transfer (ET) pathways. Moreover, widely explored carboxylic acids are systematically classified here into four categories; *i.e.*, α-keto, aliphatic, α,β-unsaturated, and aromatic analogs for a concise overview to the readership. The association of decarboxylative radical species with coupling partners to construct C–C and C–N/O/S/P/X bonds for each analogous acid has been presented in brief.

1. Introduction

Carboxylic acids are ubiquitous, structurally diverse and synthetically applicable as a synthon for important alkyl or aryl motifs in organic transformations.[1–3] The release of CO_2, known as decarboxylation, is a fundamental step in biological and chemical conversions for diverse carbon–carbon (C–C) and carbon–hetero (C–Het) bond formation.[4] Enzyme catalysed bio-decarboxylation facilitates many important bio-transformations, such as the conversion of pyruvic acid into acetyl-CoA by the pyruvate dehydrogenase complex, which is a crucial step of the Krebs cycle.[5,6] Inspired by Nature's toolbox, synthetic chemists have utilised decarboxylation protocols toward the regio-selective generation of highly reactive radical species to access complex molecularity.[7,8] Kolbe electrolysis[9] and Cu/Ag salt mediated thermal decarboxylations[10,11] are the earliest methods for CO_2 extrusion with limited applicability due to harsh conditions and low regio-selectivity. The subsequent advancement of transition

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metal-mediated decarboxylation was reported by the Sheppard, Nilsson and Myers groups from the mid-1900s but those suffered from the usage of stoichiometric metal salts and limited scope.[12–14] In 2006, Goossen and co-workers reported the first example of catalytic decarboxylation to access bi-aryl scaffolds using a bimetallic Pd/Cu system.[15] Thereafter, a significant advancement in transition metal catalysed decarboxylation for diverse C–C and C–hetero bond formation has gained much attention over the past decades.[16–19] However, the high temperature conditions and stoichiometric oxidant usage demand a green and sustainable catalytic pathway towards decarboxylative bond forming reactions.

Most recently, photocatalytic single electron or energy transfer has emerged as one of the fundamental synthetic protocols for remote functionalization, regio-selective cross-coupling reactions and C–H bond activations.[20–23] Subsequently, the merging of photoredox with transition metals, known as metallaphotoredox catalysis, unveiled a new mechanistic pathway that reconfigures the synthetic library to access unusual and complex molecular scaffolds.[8,24,25] Utilizing these photocatalytic plethoras, bench-stable aliphatic or aromatic carboxylic acids are functionalized by decarboxylation towards C–C/hetero bond formation at room temperature and under oxidant free conditions.[26–28]

To the best of our knowledge, the first photocatalytic decarboxylation was developed by Nishibayashi[29] and Lei[30] groups independently in 2013 using Ru and Ir photocatalysts. In the subsequent year, the MacMillan group reported decarboxylative arylation of α-amino acids *via* visible light mediated photoredox catalysis for $C(sp^2)$–$C(sp^3)$ cross-coupling.[31] A novel aliphatic carboxylic acid variant, known as acrylic acid, also underwent decarboxylation in the presence of hypervalent iodine towards a $C(sp^2)$–$C(sp^3)$ cross-coupling reaction under blue light-emitting diode (LED) irradiation.[32] These pioneering developments for aliphatic acid decarboxylation have leveraged new modes of coupling reactions for the construction of potent drugs and bio-relevant molecules. The remaining aryl carboxylic acid analogs are also bench-stable, structurally diverse precursors for various building blocks found in nature and commercial sources. Typically, the rate of decarboxylative aryl radical formation is lower than that of aliphatic carboxylic acids ($k_{Aro} = 10^6\ s^{-1}$ *vs.* $k_{Ali} = 10^9\ s^{-1}$).[33] Thus, aromatic acid decarboxylation is difficult to harness with the abovementioned photocatalytic methods. Most recently, the Ritter group has demonstrated a visible light-mediated ligand-to-metal-charge-transfer (LMCT) protocol to generate open-shell aryl radical species with low energy barrier and it opens up a new doorway of aromatic carboxylic acid functionalization.[34]

Overall, remarkable progress in the field of photocatalytic decarboxylation reactions has been devoted by the scientific

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community throughout the globe. To date, several reviews have been reported on the decarboxylative bond formations and few on substrate selective photo-decarboxylation reactions.[26,27,31,35] However, the complete development of photocatalytic decarboxylation has not been summarised in a single review. In this article, we present the development of visible light mediated decarboxylation reactions that have elevated vast modes of C–C, C–O, C–N, C–P and C–S cross-couplings, cyclizations, and functionalization. Regardless of various important architectural motifs, we have tried to cover up all varieties of carboxylic acids by dividing the substrate analogs into four categories; *i.e.*, α-keto acids; cyclic and acyclic aliphatic acids; α,β-unsaturated acids and aromatic acids. We are aware of numerous types of mechanistic pathways to construct a complex photocatalytic architecture, which is beyond the scope of this article. This highlight article intends to cover the year-wise evaluation of photo-decarboxylative functionalization, which will provide a comprehensive bond forming overview to the readers (Fig. 1).

2. Decarboxylation of α-keto acids

α-keto acids, a class of organic carboxylic acids containing the keto group at the α-position are significant acyl synthons used in synthetic organic chemistry. However, the decarboxylation of α-keto acids is limited to high temperatures and the usage of strong oxidants. In 2014, Lei and co-workers revealed an amazing breakthrough in the decarboxylation of carboxylic acids under photocatalytic conditions.[30]

2.1 C–C cross-coupling and cyclization

In 2008, Goossen and co-workers reported the first catalytic method for decarboxylative cross-coupling of α-keto acids with aryl halides using a Pd/Cu dual catalyst.[36] Due to the requirement of a high temperature, this reaction is incompatible with the synthesis of thermally labile organic compounds. Following Lei and Lan's pioneering work on photoredox-catalyzed decarboxylative amidation, MacMillan and his team developed a mild and straightforward method for synthesizing ketones (**2.1**). This approach involved the decarboxylation of α-keto acids for cross-coupling with aryl bromides, utilizing a combined Ir/Ni photocatalytic system (Fig. 2a).[37] Of late, several groups have explored versatile modes of arylation with α-keto acids and different aryl halides or boronic acids under different photocatalytic conditions.[38–42] In 2015, Chen and co-workers demonstrated decarboxylative ynonylation using a $[Ru(bpy)_3](PF_6)_2$ photocatalyst and hypervalent iodine(III) reagents (HIR).[43] This reaction represents the first example of merging photoredox/HIR catalysis for decarboxylation of α-keto acids, which leads to the formation of acyl radicals and their unprecedented addition to HIR-bound alkynes (Fig. 2b).

In 2015, Zu *et al.* explored the decarboxylative acylation of α-keto acids with electron-deficient olefins under visible-light induced photoredox catalysis (Fig. 2c).[44] They successfully employed this acyl radical to a series of Michael acceptors including aldehydes, ketones, amides, nitriles, α,β-unsaturated esters and sulfones towards 1,4-conjugate addition. Later, similar modes of transformation have been developed by several groups.[45–49] In the same year, Wang and co-workers proposed a novel approach for *ortho* acylation of acetanilide derivatives

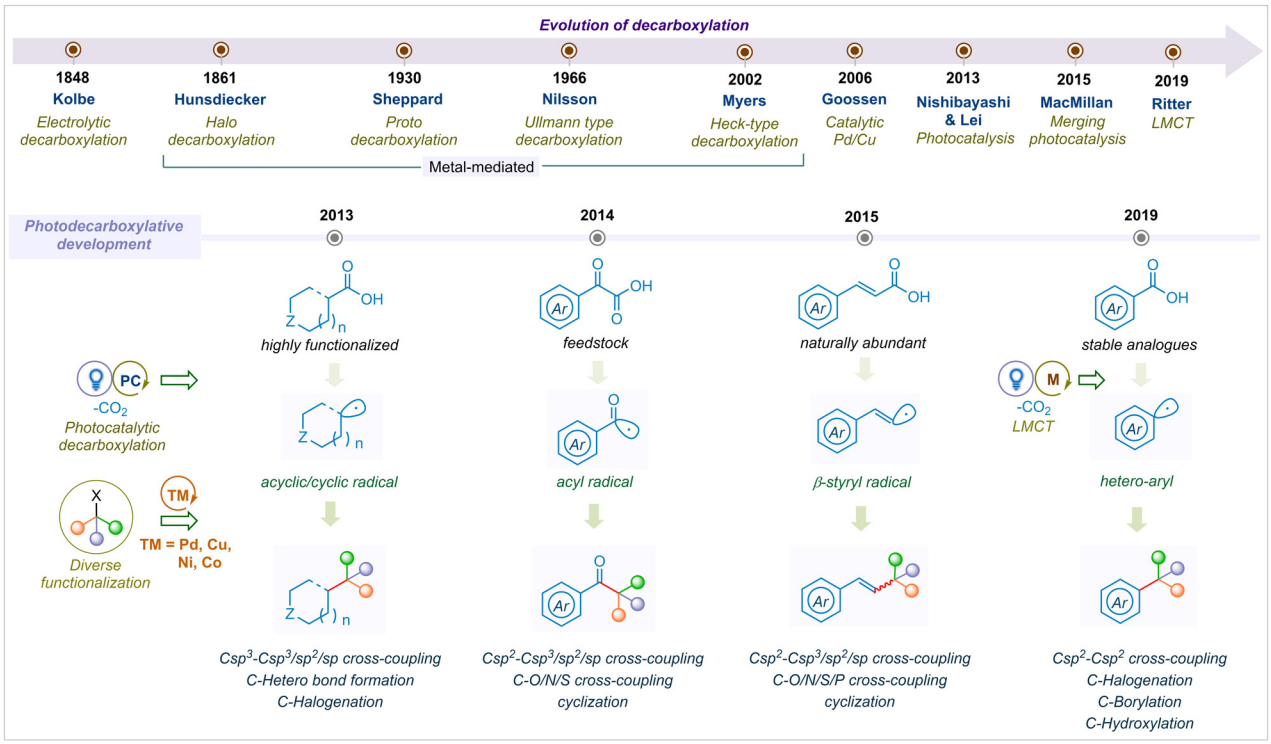

Fig. 1 Evolution of decarboxylation from electrocatalysis to photocatalysis for diverse functionalization.

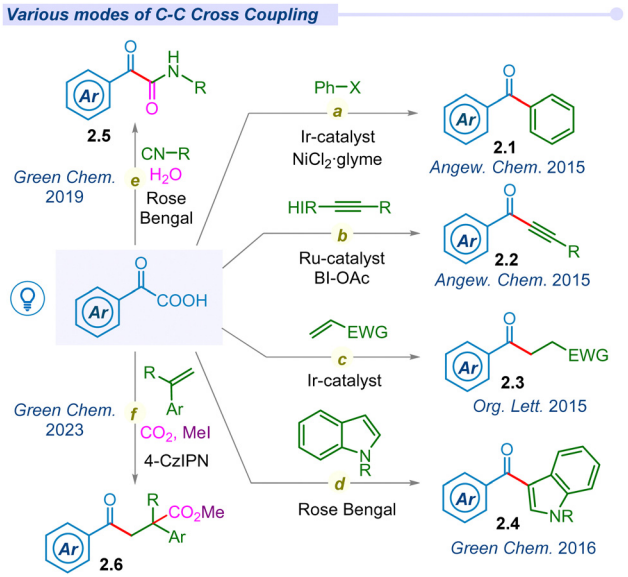

Fig. 2 Decarboxylative C–C cross-coupling of α-keto acids.

through decarboxylation of α-keto acids under a dual Eosin-Y/Pd-catalytic cycle.[50] α-Keto acids have been employed for C(sp^2)–C(sp^3) cross-coupling through C–H acylation of azo and azoxybenzene moieties, using acridinium salt as an effective organophotocatalyst under blue LED irradiation.[51]

In 2016, Wand and Gu independently synthesized 3-acylindoles (**2.4**) from feedstock indoles and α-keto acids under photocatalytic conditions (Fig. 2d).[52,53] In 2019, Wei and co-workers proposed a potent method for the synthesis of α-ketoamides (**2.5**) using α-keto acids, isocyanides and water as precursors under visible light conditions using the Rose Bengal photocatalyst (Fig. 2e).[54] These mild and metal-free conditions offer a unique and straightforward method for preparing α-ketoamides through decarboxylation, radical addition and hydration processes in a cascade manner from feedstock chemicals. Thereafter, Prabhu and co-workers applied this protocol for the acylation of various electron-deficient heteroarenes, such as pyridines, quinolones, isoquinoline and phenanthridine, to their respective analogs under visible light irradiation.[55] Similarly, the He group established decarboxylative acylation of quinoxalin-2-(1*H*)-ones using aerial oxygen as a sole oxidant under visible light conditions.[56] However, this photo-enabled protocol did not require any external photosensitizers, powerful oxidants or metal catalysts. The Chu group has developed Minisci-type reactions for pyridine *N*-oxides *via* decarboxylative cross-coupling using a new generation organophotocatalyst fluorescein dimethyl ammonium.[57]

Jana and co-workers developed a novel strategy for regioselective di-functionalization at the α- and β-positions of styrenes using CO_2 under metal-free conditions (Fig. 2f).[58] Mechanistic investigation revealed radical–radical cross-coupling and radical polar cross-over for acylative-benzylation and acylative-carboxylation to produce benzylic carbanions, which further act as nucleophiles towards carbon dioxide molecules.

Substantial development in the decarboxylative acylation of α-keto acids has leveraged the synthetic route of cross-couplings over the years. Apart from these seminal works, several groups have designed various efficient routes to employ the 'acyl' radical in one pot intra/inter-molecular cyclization reactions (Fig. 3). In 2016, Wang and co-workers unveiled a catalyst-free visible light irradiated approach for carbonyl-arylation of acrylamides with α-keto acids using HIR at room temperature (Fig. 3a).[59] Similarly, Chu *et al.* reported a one-pot photo-induced decarboxylative reaction for the synthesis of 4-aryl-2-quinolinones (**3.2**) through an intramolecular cyclization (Fig. 3b).[60] In 2020, the Yao group utilized the energy of visible light to develop an efficient route to synthesize 2-acylindoles (**3.3**) through decarboxylative cyclization of 2-alkenylarylisocyanides (Fig. 3c).[61] Mechanistic insights unfolded that the reaction proceeded through the sequential addition of acyl radical to 2-alkenylarylisocyanides, followed by the 5-exo-trig cyclization. The Miao group developed a photosensitizer-free decarboxylative cyclization reaction of 2-isocyanobiphenyls to access phenanthridin-6-yl(aryl)methanol (**3.4**) in a cascade manner (Fig. 3d).[62] Mechanistic analysis found that the decarboxylation process occurred *via* the formation of an electron donor–acceptor complex (EDA) under visible light irradiation. Su *et al.* utilized and employed Eosin-B and $(NH_4)_2S_2O_8$ oxidant for synthesizing acylated isoquinoline-1,3(2*H*,4*H*)-dione (**3.5**) derivatives through visible-light mediated decarboxylative cyclization of *N*-methacryloyl-*N*-methylbenzamide and α-keto acids (Fig. 3e).[63] In 2021, the Yu group disclosed a metal-free decarboxylative cyclization method for the construction of acylated heterocyclic derivatives (**3.6**).[64] They successfully synthesized indolo[2,1-*a*]isoquinolin-6(5*H*)-one, benzimidazo, thioflavone, aroylazaspiro[4.5]trienone derivatives using 4-CzIPN as a photocatalyst (Fig. 3f).

2.2 C–hetero cross-coupling and cyclization

In 2014, Lei and co-workers pioneered room temperature visible light-mediated aerobic decarboxylative amidation of

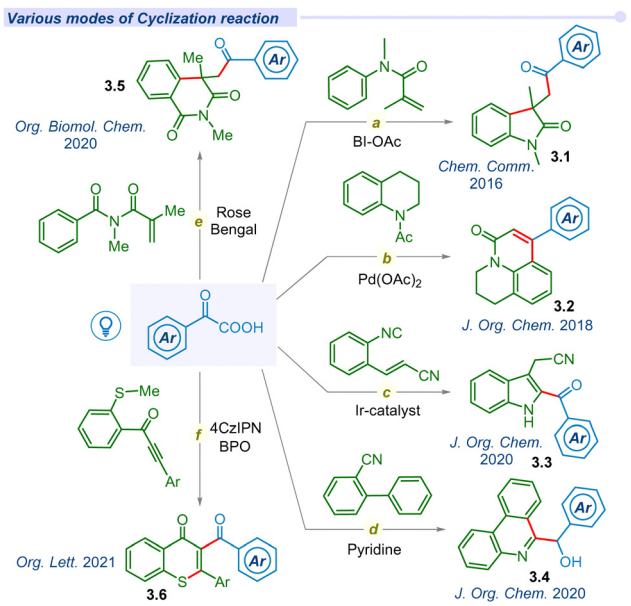

Fig. 3 Decarboxylative cyclization of α-keto acids.

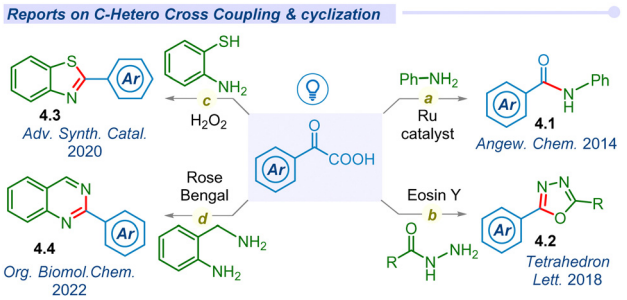

Fig. 4 Decarboxylative C–hetero cross-coupling and cyclization of α-keto acids.

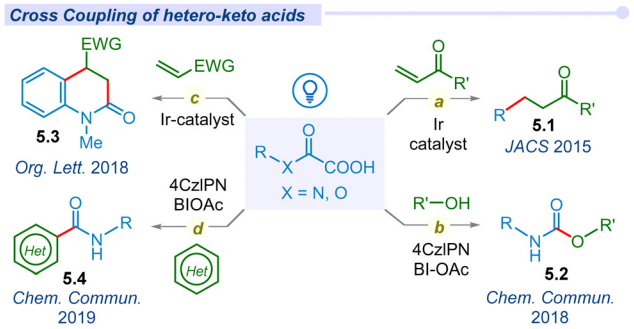

Fig. 5 Decarboxylative cross-coupling as well as cyclization of β-hetero-α-keto acids.

α-keto acids with amines using a ruthenium photocatalyst, to unveil new avenues for complex molecular construction *via* decarboxylation of carboxylic acids (Fig. 4a).[30] Later, Xu and co-workers developed a photocatalyst-free singlet oxygen mediated *N*-acylation (**4.1**) of amines with α-keto acids.[65]

In 2018, Guo and He groups reported the decarboxylative cyclization of α-keto acids for the production of 2,5-diaryl-1,3,4-oxadiazoles (**4.2**) using acylhydrazines under visible light conditions (Fig. 4b).[66,67] Later on, Sharma and co-workers developed metal and photocatalyst-free cyclization of α-keto acids with 2-amino thiophenol to synthesize benzothiazoles (**4.3**) under blue LED conditions (Fig. 4c).[68] Similarly, the Le group synthesized quinazoline derivatives (**4.4**) *via* cyclization of α-keto acids with 2-amino benzylamine under blue LED irradiation (Fig. 4d).[69]

2.3 Decarboxylation of β-hetero-α-keto acids

The decarboxylation of β-hetero-α-keto acids was achieved in 2013, when Overman and co-workers proposed a novel approach for the exclusive generation of a quaternary carbon center *via* cross-coupling between Michael acceptors and *N*-phthalimidoyl oxalate derivatives of tertiary alcohols under photoredox conditions.[70] Later in 2014, the MacMillan group reported a redox-neutral approach for quaternary carbon center formation through the cross-coupling of *in situ* generated alkyl radicals from decarboxylation of carboxylic acids and Michael acceptors with the $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ photocatalyst.[71] In 2015, Overman and MacMillan merged these two features and developed a simple and efficient route for the synthesis of quaternary carbons (**5.1**) through the cross-coupling of simple oxalate salts of tertiary alcohols with electron-deficient alkenes under photocatalytic conditions (Fig. 5a).[72] Thereafter, in 2018 the Landais group reported oxidative decarboxylative generation of a carbamoyl radical from oxamic acids under metal-free conditions.[73] They successfully employed the carbamoyl radical to synthesize urethanes and ureas (**5.2**) from alcohols and amines respectively by using an organo-photocatalyst and HIR (BI-OAc) as an oxidant (Fig. 5b). Similarly, they also coupled this carbamoyl radical into the heteroarenes to afford the corresponding enantiopure amides.[74] In the same year, Feng and co-workers utilized this carbamoyl radical for cyclization with electron deficient olefins to unveil an efficient route for the synthesis of 3,4-dihydroquinolin-2(1*H*)-ones (**5.3**) (Fig. 5c).[75] Mechanistic insight revealed the steps involved in the sequential addition of carbamoyl radical, cyclization, and aromatization in a cascade manner. Recently, the Landais group further coupled this carbamoyl radical into imines for the synthesis of amino acid amides (**5.4**) under a ferrocene-based photocatalyst (Fig. 5d).[76]

3. Decarboxylation of $C(sp^3)$-aliphatic acids

3.1 $C(sp^3)$–Csp^2(aromatic) cross-coupling

Developing strategies for $C(sp^3)$–$C(sp^2)$ bond formation expands to access a broader chemical space, which is essential for addressing complex synthetic targets such as natural products and potential drug candidates.[77] The decarboxylation of aliphatic carboxylic acids has a long-standing history of centuries and is currently undergoing a resurgence through a photocatalytic single electron transfer pathway.

Due to the potential application of the $C(sp^3)$–$C(sp^2)$ coupling reaction, the MacMillan group pioneered photocatalyzed decarboxylative coupling of α-amino acids with cyanoarene moieties in 2014 (Fig. 6a).[78] The irradiation of iridium photocatalyst with a compact fluorescent lamp (CFL) in the presence of CsF as a base, α-amino acids and cyanoarenes afforded the racemic mixture of benzylic amines (**6.1**). This cross-coupling is also well tolerated for various α-amino and α-oxy acids with electronically diverse cyanoarene derivatives.

In the same year, MacMillan and Doyle significantly expanded the decarboxylative cross-coupling protocol with the groundbreaking approach of merging photoredox with nickel catalysis for a wide range of substituted (hetero)aryl halides in synthetic transformations (Fig. 6b).[79] They explored the decarboxylative cross-coupling between amino acids or α-*O*-carboxylic acids and aryl halides. Subsequently, they developed an asymmetric decarboxylative $C(sp^3)$–$C(sp^2)$ cross-coupling under a dual Ir-photocatalyst and a chiral nickel co-catalyst.[80] In 2016, the Zhang group developed an alternative and cost-effective organo-fluorophore based photocatalyst (4-CzIPN) to replace the iridium polypyridyl catalyst in merging photoredox/Ni catalytic cross-coupling reactions (Fig. 6c).[81] Furthermore,

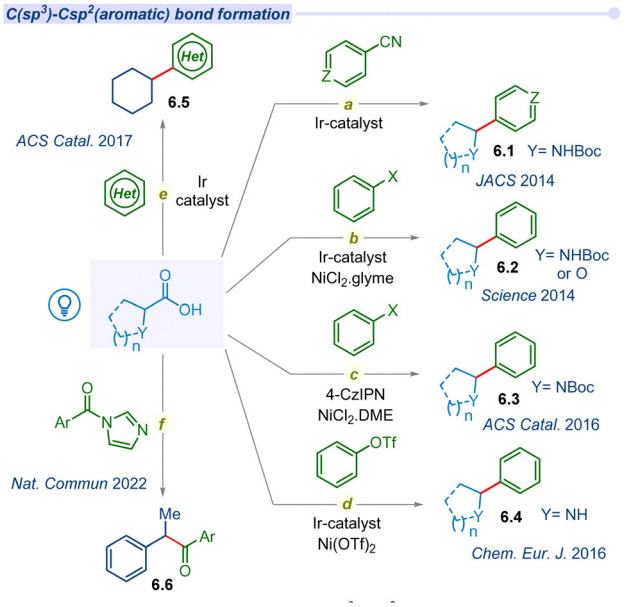

Fig. 6 Decarboxylation of aliphatic acids for C(sp^3)–Csp^2(aromatic) cross-coupling.

the Rueping group explored the arylation agents for C(sp^3)–C(sp^2) bond forming decarboxylation reactions beyond aryl halides to aryl triflates in dual iridium/nickel photocatalysis (Fig. 6d).[82]

Despite the various methods of decarboxylative C–H functionalization of heteroarenes, a visible light-mediated mild and efficient protocol remains elusive. In 2017, the Glorius group reported visible light irradiated direct C–H alkylation of heteroarenes with aliphatic carboxylic acids using iridium photocatalyst and ammonium persulfate as an additive for the first time (Fig. 6e).[83] This effective method is used to alkylate a variety of *N*-heterocycles, including pyridines, isoquinoline, benzothiazole, phthalazine, and other derivatives with cyclic or acyclic carboxylic acids, as well as different kinds of amino acids and fatty acids. A similar type of alkylation of heteroarenes was developed by the Li group using an oxidant-free dual Ir/Co photocatalytic system.[84] Thereafter, significant advancements in decarboxylative C(sp^3)–C(sp^2) coupling with aryl halides using an iridium based photocatalyst and nickel catalyst were reported by several groups. These couplings are also extended towards the synthesis of heteroaryl-C-nucleosides,[85] bioconjugation,[86,87] and polyfluoroarylation.[88,89]

Merging of *N*-heterocyclic carbene (NHC) and photocatalyst based cross-coupling between a radical precursor and an acyl electrophile is emerging as an attractive method for ketone synthesis. However, the previous reports are mostly focused on the synthesis of prefunctionalized radical precursors and their subsequent two-component coupling process. In 2022, Chi and co-workers developed a straightforward method for the synthesis of ketones *via* cross-coupling of acyl imidazoles and carboxylic acids using the merger of Ir/NHC photocatalysts (Fig. 6f).[90] This report also provides a one pot strategy for the synthesis of ketones from two different carboxylic acid derivatives through *in situ* generated acyl imidazole intermediates. Since then, a myriad of developments on photodecarboxylative C(sp^3)–C(sp^2) has gained considerable interest within the synthetic community.[91–93]

3.2 C(sp^3)–Csp^2(alkene) cross-coupling

Alkenes and their derivatives are among the most fundamental synthetic intermediates and adaptable building blocks, capable of transforming into complex molecular scaffolds with a wide range of applications. Recently, alkenyl C(sp^3)–C(sp^2) bond-forming reactions utilizing C(sp^3)–alkyl carboxylic acids have drawn significant interest in synthetic methodology *via* a decarboxylative pathway. In 2014, MacMillan introduced a C(sp^3)–C(sp^2) cross-coupling reaction between *N*-Boc-α-amino acids with vinyl sulfones (Fig. 7a).[94] Under 26 W CFL irradiation this decarboxylative reaction proceeds rapidly in the presence of iridium polypyridyl photocatalyst and $CsHCO_3$ additive. In addition, the same group also reported a decarboxylative vinylation using vinyl halides by altering the coupling partners with alkyl carboxylic acids (Fig. 7b).[95] In this reaction, different α-heteroatoms containing alkyl carboxylic acids (α-oxy and α-amino acids) are reacted with vinyl bromides or iodides to produce an important class of allylamine or allylether motifs using dual photoredox/Ni catalysis.

In 2017, the Fu group disclosed a similar approach for the vinylation of *N*-protected α-amino acids using *gem*-difluoro styrene derivatives (Fig. 7c). All the defluorinated mono-fluoro allylamine products (**7.3**) with a mixture of (*E*)- and (*Z*)-isomers are reported.[96] Surprisingly, Shang and co-workers reported a *stereo*-selective (*Z*)-olefinated decarboxylative cross-coupled product from styrene derivatives.[97]

Of late, MacMillan and co-workers developed a new decarboxylative migratory insertion coupling protocol of carboxylic acids with alkynes under visible light irradiation to afford C(sp^3)–C(sp^2) cross-coupling products **7.4** (Fig. 7d).[98]

3.3 C(sp^3)–C(sp^3) cross-coupling

In 2014, MacMillan and co-workers used carboxylic acids as traceless activating groups for radical formation and their 1,4-conjugate addition to a Michael acceptor under visible light-irradiation (Fig. 8a).[99] This is the first report of a photodecarboxylative C(sp^3)–C(sp^3) bond-forming protocol. Most importantly, this newly established approach provides an alternate

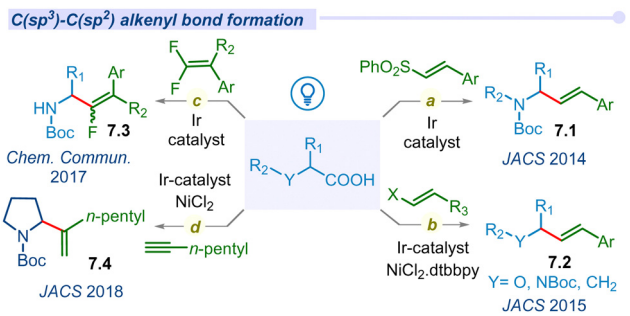

Fig. 7 Decarboxylation of aliphatic acids for C(sp^3)–Csp^2(alkenyl) cross-coupling.

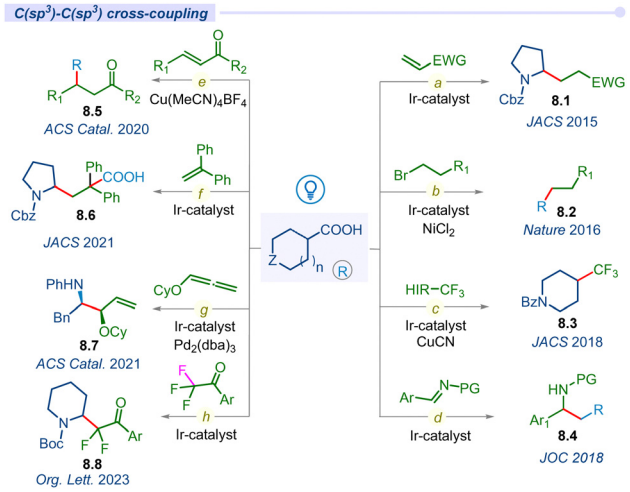

Fig. 8 Decarboxylation of aliphatic acids for C(sp^3)–C(sp^3) cross-coupling.

route to produce Michael donors that does not require organometallic activation or propagation. Lately, the same group developed a highly efficient challenging methodology to form a C(sp^3)–C(sp^3) bond using an unactivated alkyl halide coupling partner under Ir/Ni merging catalysis (Fig. 8b).[100]

The incorporation of CF_3 groups can enhance therapeutic efficacy by modifying protein–ligand interactions and enhancing membrane permeance. Although significant advancements have been developed for accessing aryl-CF_3 motifs, aliphatic C(sp^3)–CF_3 bond forming methods remain elusive. In this regard, in 2018, the MacMillan group disclosed decarboxylative trifluoromethylation of aliphatic acids using a merging Ir/Cu-system and Togni's reagent as a source of CF_3 (Fig. 8c).[101]

In the same year, the Lu group developed a decarboxylative photo-irradiated benzylation of imines using arylacetic acids (Fig. 8d).[102] This reaction tolerates a variety of functional groups, showcasing a broad substrate scope of primary, secondary, and tertiary aliphatic acid precursors. Similarly, they also developed a decarboxylative conjugate addition reaction of carboxylic acids with *para*-quinone methides (*p*-QMs) using an organo-photoredox catalyst to synthesize 1,1,2-triarylethanes.[103] Subsequently, Larionov and other groups developed direct decarboxylative conjugate addition of a variety of carboxylic acids with different Michael acceptors under visible light conditions for the construction of diverse C(sp^3)–C(sp^3) bond forming methodologies (Fig. 8e).[104–106]

For the first time, Yu and co-workers introduced carboxylic acids as bifunctional reagents for a redox-neutral carbocarboxylation reaction of activated alkenes under photoredox catalysis (Fig. 8f).[107] This study represents a unique approach for the usage of both carboxyl and alkyl segments of carboxylic acids simultaneously. In 2021, the Breit group disclosed an asymmetric merging Ir/Pd-catalyzed decarboxylative hydroaminoalkylation of alkoxylallenes for accessing regio- and enantioselective vinyl 1,2-amino ether products **8.7** (Fig. 8g).[108] Recently, the Xing group developed a simultaneous decarboxylation and defluorination approach to achieve difluoroalkylation in amino acids by using readily available amino acids and trifluoroacetophenones as key starting materials (Fig. 8h).[109]

3.4 C(sp^3)–C(sp) cross-coupling

n recent years, there has been a lot of interest in using photoredox catalysis with hypervalent iodine reagents in visible light-mediated synthetic transformation to decarboxylate carboxylic acids. In 2015, Xiao and co-workers developed unprecedented photocatalytic direct radical decarboxylative alkynylation of carboxylic acids under visible-light irradiation (Fig. 9a).[110] This methodology efficiently produced various types of alkynes (**9.1**) and ynone using iridium photocatalyst and ethynylbenziodoxolones (EBX) as the alkynylating agent. Similarly, the Cheng group also developed a metal-free photocatalytic method for decarboxylative alkynylation of carboxylic acids using 9,10-dicyanoanthracene as a photoredox catalyst.[111]

In 2017, Waser and co-workers developed a one-step transformation of aliphatic acids to their corresponding nitriles under visible light mediated merging Ir/HIR-reagent cyanobenziodoxolones (CBX) (Fig. 9b).[112] This approach potentially cyanated a wide variety of amino acids. Later, a similar type of transformation was discovered by the Gomez group in 2019, using a less expensive organo-photocatalyst riboflavin tetraacetate.[113]

Messaoudi and co-workers developed the dual photoredox/copper catalytic alkynylation approach for the synthesis of anomeric furanosyls using various terminal alkynes (Fig. 9c).[114] This reaction offers an extraordinary output for alkynyl C-nucleosides with high efficiency and diastereo-selectivity under mild conditions. In 2022, Zhang and co-workers further reported a sustainable protocol for the synthesis of alkynyl C-glycosides (**9.4**) with high stereoselectivity with broad substrate scope and good functional group compatibility (Fig. 9d).[115]

3.5 C(sp^3)–halo/hetero cross-coupling

Fluorinated compounds are important structural motifs widely found in pharmaceuticals, agrochemicals, and radiochemical applications. In this regard, Paquin and co-workers developed the pioneering photocatalytic C–F bond formation of aryloxyacetic derivatives using a Selectfluor and ruthenium photocatalyst in 2015.[116] Furthermore, the MacMillan group developed a highly regiospecific, bond strength-independent decarboxylative fluorination of aliphatic carboxylic acids using the iridium photocatalyst (Fig. 10a).[117] This operationally simple fluorination reaction involved formation of carboxyl radicals from carboxylic acids and the addition to $F^{\bullet}$ from the fluorinating reagent affording the desired fluoroalkane products **10.1**.

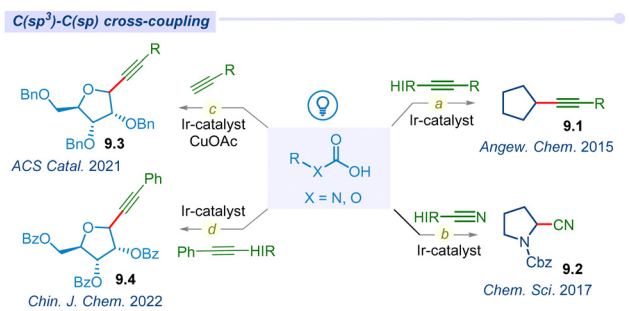

Fig. 9 Decarboxylation of aliphatic acids for C(sp^3)–C(sp) cross-coupling.

Alkyl halides are commonly used substrates in electrophilic substitution and cross-coupling reactions. Due to the synthetic utility of alkyl halides, the Glorius group developed a simple decarboxylative halogenation (chlorination, bromination and iodination) of aliphatic carboxylic acids by employing an iridium photocatalyst (Fig. 10b).[118] Afterwards, a similar type of halide transformation was developed by Hu and co-workers by introducing an iron salt as a photocatalyst.[119]

Nitrogen-containing organic scaffolds are commonly found in natural products, pharmaceuticals, dyes and functional materials. The Buchwald–Hartwig coupling reaction is one of the most traditional reactions for the construction of a C–N bond but suffers from its elevated temperature.[120] In 2016, Guan and co-workers disclosed a room temperature photo-induced amination of indoline-2-carboxylic acids and azodicarboxylate ester using metal-free Rose Bengal as a photocatalyst.[121] Significant progress has been observed in the construction of diverse C(sp^2)–N bonds using a variety of transition metal catalysis strategies but the formation of C(sp^3)–N bonds remains the most daunting task in the field of cross-coupling chemistry. In 2018, MacMillan and co-workers addressed this challenge of the C(sp^3)–N bond *via* decarboxylative cross-coupling of naturally abundant alkyl carboxylic acids and feedstock nitrogen nucleophiles as coupling partners under the merging Ir/Cu-photocatalysis pathway (Fig. 10c).[122] Lately, in 2020, Larionov and co-workers described a visible-light-enabled *N*-alkylation of various amines including heterocyclic amines and carboxylic acids using acridine as a photocatalyst with a copper co-catalyst (Fig. 10d).[123] They also developed a direct access to sulfonamides and sulfonyl azides from carboxylic acids under visible light conditions.[124]

Furthermore, the Leonori group also disclosed another visible light induced decarboxylative azidation reaction of cyclic α-amino acids using the Rhodamine 6G organo-photocatalytic pathway.[125] In the report, they successfully synthesized new α-N-Boc-amino-azide building blocks and also selectively modified the *N*-terminal proline residues of dipeptides.

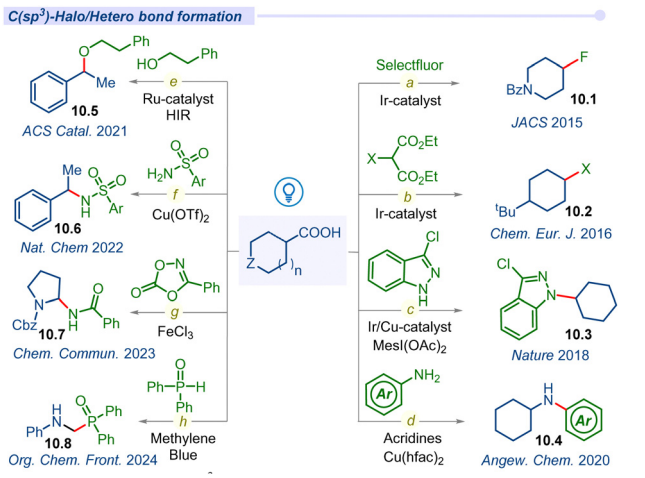

Fig. 10 Decarboxylative C(sp^3)–halo/hetero cross-coupling of aliphatic carboxylic acids.

In 2021, Terrett and co-workers used a dual Ru-photoredox/iodine(III) platform to form carbon–oxygen bonds between simple alcohols and carboxylic acids (Fig. 10e).[126] They overcame the electronically mismatched nature of previous radical-based decarboxylative couplings. Next year, the Yoon group developed a ligand-to-metal charge transfer (LMCT) decarboxylative nucleophilic cross-coupling reaction of carboxylic acids with various carbon, nitrogen and oxygen nucleophiles under visible-light irradiation (Fig. 10f).[127] In mechanistic investigation, they proposed a photoactive Cu(II) carboxylate as a chromophore which formed *in situ via* interaction between $Cu(OTf)_2$ and a carboxylic acid. Photoexcitation of the LMCT state creates a dissociative carboxyl radical, which can readily decarboxylate to form the corresponding alkyl radical species that facilitated the cross-coupling process.

The Bao group developed an efficient method for the synthesis of amide derivatives *via* C–N cross-coupling between α-amino acids and dioxazolones (Fig. 10g).[128] This method effectively converted α-amino acids to their corresponding amides (**10.7**) using iron(III) chloride under visible light irradiation.

Most recently Yang and co-workers introduced a simple method for α-amino phosphine oxides *via* decarboxylative cross-coupling of *N*-aryl glycines with diarylphosphine oxides using methylene blue (MB) as a photocatalyst (Fig. 10h).[129] Similarly, different kinds of decarboxylative C–S/C–Se cross-coupling have also been explored by several groups in the recent past.[130–133]

3.6 Cyclization of aliphatic acids

Decarboxylative cyclization through multiple C–C and C–Het bonds forming concerted processes manifold a wide range of biologically and pharmaceutically important organic scaffolds. In this perspective, the Studer group in 2017 introduced readily accessible and highly efficient α-imino-oxy propionic acid precursors to synthesize pyrroline derivatives (**11.1**) using Michael acceptors through SET reduction (Fig. 11a).[134] An iridium based photocatalyst accomplished this cascade reaction through sequential intra/inter-molecular C–N and C–C bond formation under mild conditions with a wide range of functional groups tolerance. Subsequently, the Zhou group also reported *diastereo*- and regio-selective fluorinated benzo[*a*]quinolizidines (**11.2**) by the combination of dihydroisoquinoline acetic acids and trifluoromethyl alkenes under visible light conditions (Fig. 11b).[135] This decarboxylative cyclization reaction proceeded through a one-pot sequential defluorinative cross-coupling and intramolecular C–H functionalization pathway.

In 2019, the Jiang group developed a unique route for the synthesis of pharmaceutically important and bioactive isoxazolidine derivatives (**11.3**) from naturally abundant amino acids (Fig. 11c).[136] This photoinduced transition-metal free cyclization followed concerted difunctionalization of activated alkenes with the decarboxylative α-amino radicals of amino acids. This is the first report of isoxazolines dismissing the traditional 1,3-dipolar or hydroxylamine cyclization route and emerges as an alternative method for a heterocyclic scaffold under an environmentally friendly and atom efficient pathway.

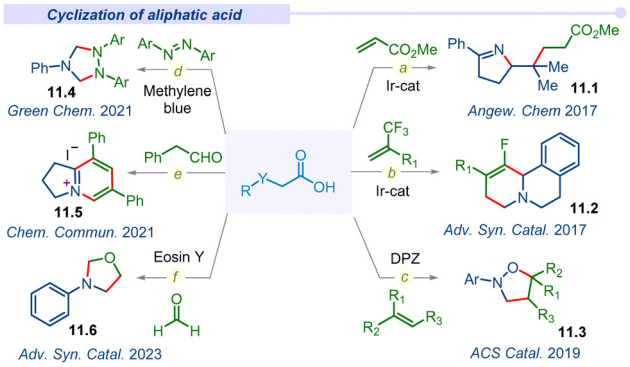

Fig. 11 Decarboxylative cyclization of aliphatic carboxylic acids.

In 2021, the Wang group developed a visible-light-driven cyclization strategy of *N*-aryl glycines with azobenzenes through a decarboxylation pathway for the formation of 1,2,4-triaryl-1,2,4-triazolidines (**11.4**) (Fig. 11d).[137] Commercially available organic photocatalyst methylene blue was irradiated under visible-light and afforded room temperature triazolidine products with excellent yields. Apart from the previously described metal-catalyzed activation/cascade cyclization *via ortho* C–H bond activation is the first metal-free example of direct *N*-heterocycle synthesis by the addition and cyclization of the *azo* bond of azobenzenes.

Furthermore, the Xia group demonstrated a method for the synthesis of chichibabin pyridinium (**11.5**) *via* cross-coupling between α-amino acids and aldehydes under visible light irradiation (Fig. 11e).[138] The oxidative decarboxylation of *in situ* generated electron-rich enamine and sequential new bond formation afforded the desired chichibabin product. Recently in 2023, a complementary approach to acquire oxazolidine derivatives was developed by the Singh group under a visible light irradiated tandem decarboxylation–cyclization plethora using organophotocatalysts.[139] Furthermore, subsequent development of various visible light mediated decarboxylative cyclizations was observed by several groups with broad and functional group tolerance.[140–144]

4. Decarboxylation of α,β-unsaturated acids

α,β-unsaturated acids or acrylic acids are important feedstock chemicals found in Nature in various forms. In particular, 3-phenylacrylic acids, popularly known as cinnamic acids, have drawn lots of attention from organic chemists in the past decades.[145,146] The versatility of such moiety to transform into alkyl, β-styryl, β-keto, and α,β-diketo fragments has been employed to develop many underexplored catalytic methods under blue LED conditions. The preparation, availability, thermal stability and natural abundance make this carboxylic acid one of the most explored chemical architectures for decarboxylation to access new C–C/Het bonds under mild and eco-benign conditions.

4.1 C–C cross-coupling

In 2014, hypervalent iodine mediated first decarboxylative trifluoromethylation of α,β-unsaturated acids was developed by the Zhu group using Togni's reagent to access fluoromethylated alkene moieties (**12.1**) under *fac*-Ir(ppy)$_3$ photocatalytic conditions (Fig. 12a).[32] The following year, Chen and co-workers also developed hypervalent acetoxybenziodoxole (BI-OAc) induced *chemo*-selective C(sp^3)–C(sp^2) coupling of α,β-unsaturated acids with alkyl trifluoroborate using a ruthenium photocatalyst.[147]

In 2017, Timothy Noel and his group developed a novel method to access difluoromethylated styrenes (**12.1**) using *fac*-Ir(ppy)$_3$ and ethyl bromodifluoroacetate in both batch and continuous flow processes (Fig. 12a).[148] Notably, β-styryl derivatives were synthesized by other groups under similar photocatalytic conditions.[149–152] Later, Singh *et al.* used a metal-free perylenebisimide(PDI) photocatalyst to synthesize benzil derivatives (**12.2**) from cinnamic acids using iodobenzene and peroxide (Fig. 12b).[153] The same group synthesized highly strained stereospecific epoxides (**12.3**) using diazonium salts, Eosin-Y and peroxide under mild photocatalytic conditions (Fig. 12c).[154] Furthermore, they also developed a synthetic route for benzophenone derivatives (**12.4**) using diazonium salt under cobalt mediated photo-conditions (Fig. 12d).[155] Most recently, our group developed dual decarboxylative *chemo*-selective C(sp^3)–C(sp^2) coupling from α,β-unsaturated acids and glyoxalic acid under an iridium–palladium dual catalytic system to access (*E*)-chalcones **12.5** (Fig. 12e).[156] In 2024, Datta, Pradhan and Ghosh groups jointly pioneered a dodecahedron shaped heterogeneous photocatalyst $CsPbBr_3$ to access 2-oxyalkylated ketones (**12.6**) from cinnamic acid and cyclic ethers under transition metal-free conditions (Fig. 12f).[157] This report explored the semiconductor–metal heterostructures of $CsPbBr_3$ nanocrystals and their facets dependent photocatalytic behaviour for selective C(sp^3)–C(sp^3) cross-coupled products.

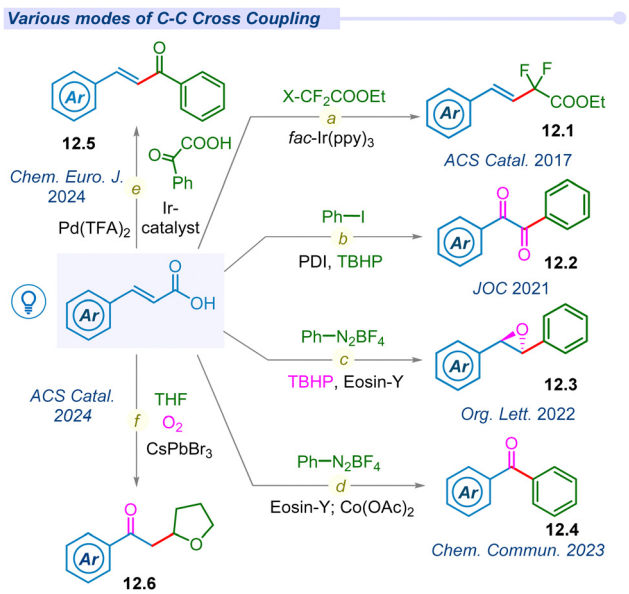

Fig. 12 Decarboxylative C–C cross-coupling of unsaturated acids.

4.2 C–hetero cross-coupling

Apart from C–C cross-coupling, various modes of decarboxylative C–Het coupling have been reported in recent years. In 2016, the Weng group established α,β-unsaturated acids as β-styryl synthons with sulfonylhydrazides to access vinyl sulfones under metal-free conditions (Fig. 13).[158–162] Lately, in 2020, Singh used KSCN as a source of ˙SCN to access (*E*)-vinylthiocyanate derivatives (Fig. 13).[163]

Surprisingly, other crucial heteroatoms such as phosphorus, oxygen, and nitrogen mostly oxidize such alkene bonds and afford the β-keto or α,β-diketo system under mild conditions. In 2017, the Zou group reported decarboxylative C–P bond forming β-ketophosphine oxide (**13.3**) from diarylphosphine oxides with Rose Bengal using a CFL bulb under an oxygen atmosphere (Fig. 13c).[164] In this report, a mechanistic investigation revealed that aerial oxygen is oxidizing alkene bonds to access β-keto analogues.

Recently, our group developed decarboxylative C–O cross-coupling of benzoic acids with unsaturated acids to afford the corresponding *O*-alkylated ester product (**13.4**) under dual iridium–palladium merging photocatalytic conditions (Fig. 13d).[165] Mechanistic investigation revealed that the ketone oxygen source was molecular water whereas aerial oxygen acted as an oxidant in this green and sustainable methodology. Patel and co-workers developed an NIS-initiated oxidative decarboxylative sulfoximidation (**13.5**) reaction (Fig. 13e).[166] This C–N cross-coupling process under blue LED facilitates oxidation upon the alkene bond for dual C=O formation in the desired product. Mechanistic investigation revealed that the source of β-keto oxygen is molecular oxygen and other oxygens are contributed by water molecules.

5. Decarboxylation of aromatic acids

Over the centuries, enormous efforts have been committed to the functionalization of aromatic carboxylic acids for the construction of diverse carbon–carbon (C–C) and carbon–hetero (C–X) bonds *via* decarboxylative processes.[167–175] Usually, aromatic acid decarboxylation leads to an unstable aryl radical intermediate and its CO_2 extrusion requires higher activation energy due to the partial double bond character of the C(*Ar*)–C(CO_2) bond. Therefore, decarboxylation of aromatic carboxylic acid requires unusual photocatalytic conditions.

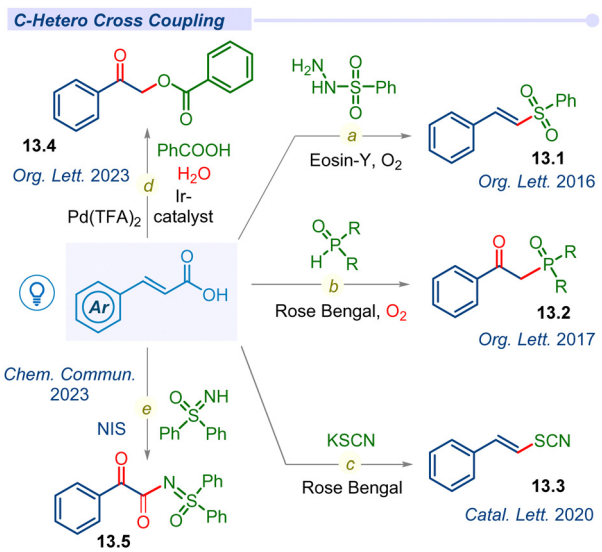

Fig. 13 Decarboxylative C–hetero cross-coupling of unsaturated acids.

5.1 Photo-induced decarboxylation of aromatic acids

In 2017, the Glorius group first reported visible light mediated photoredox catalysis for decarboxylative aryl radical formation using dimethyl 2-bromo-2-methylmalonate oxidant through an *in situ* hypobromite intermediate under mild thermal conditions to afford biaryl motifs (**14.1**) (Fig. 14a).[176] Following this pioneering report, photo-decarboxylative iodination of aromatic carboxylic acids was developed by the Fu group under mild conditions using stoichiometric amounts of oxidants.[177] Seminal work on thermally photoinduced benzoic acid decarboxylation reactions with electron deficient alkenes, diboranes, and acetonitrile using organic photocatalysts biphenyl (BP) and 9,10-dicyanoanthracene (DCA) or 1,4-dicyanonaphthalene (DCN) was reported by Yoshimi and co-workers in 2020 (Fig. 14b).[178] The yield of resulting alkylated adducts, arylboronate esters and protodecarboxylative products was enhanced upon visible light irradiation instead of initial sunlight irradiation.

5.2 LMCT mediated decarboxylation of aromatic acids

In contrast to exogenous reductants or oxidants in Ru or Ir-based polypyridyl photoredox catalysis, regulating the redox state of the metal in photoinduced metal–ligand complexes *via* ligand-to-metal charge transfer (LMCT) represents a significant advancement in photocatalytic research without the need for a photocatalyst. In 2016, the Doyle group pioneered photocatalytic LMCT for chlorine radical formation to functionalize the inert C(sp^3)–H bond.[179] Similarly, Wu and Zho groups independently utilized this LMCT strategy to catalyze the formation of chlorine and alkoxy radical for hydroalkylation of alkynes and distal functionalization of primary alcohols.[180,181]

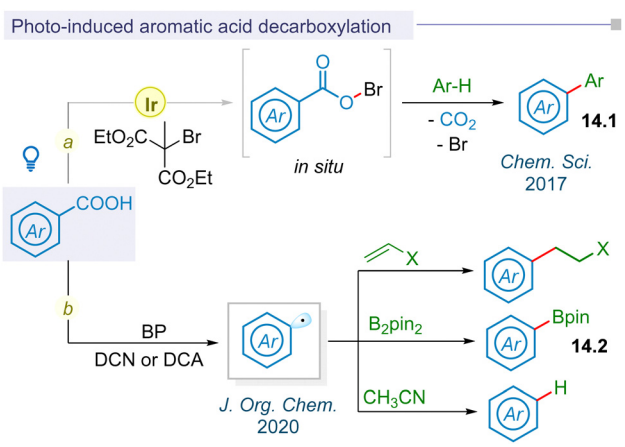

Fig. 14 Photoinduced C–C and C–hetero bond formation of aromatic acids.

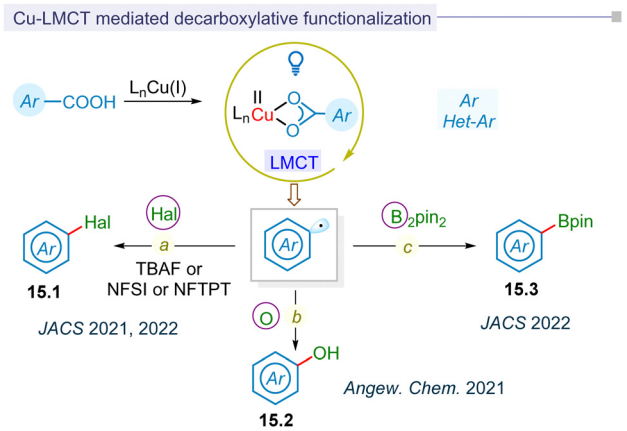

Fig. 15 MLCT based C–C and C–hetero bond formation of aromatic acids.

Following this development, the Ritter group reported for the first time LMCT-enabled radical decarboxylation of aromatic acids in 2021 (Fig. 15a).[34] This strategy of low-barrier decarboxylative carbometallation proceeded *via* a highly reactive aryl-copper(III) complex. This complex underwent reductive elimination, thereby regenerating the copper(I) pre-catalyst, along with decarboxylative fluorination (**15.1**) of the aryl carboxylic acids. In the same year, Ritter reported the decarboxylative hydroxylation of benzoic acids for synthesizing phenols (**15.2**) (Fig. 15b).[182] This method utilized photoinduced LMCT to facilitate charge transfer, initiating the transformation from C–F bonds to C–O bonds. In this LMCT-based decarboxylative functionalization of aromatic carboxylic acids, an excess amount of $[Cu(MeCN)_4]BF_4$ and $Cu(OTf)_2$ salts were typically employed.

The MacMillan group reported the first catalytic photoinduced LMCT-strategy for synthesizing (hetero)arylboronic esters (**15.3**) from (hetero)aryl carboxylic acids in 2022 (Fig. 15c).[183] The report highlighted a catalytic process involving $[Cu(MeCN)_4]BF_4$ that facilitated borylation at ambient temperature. This process was extended to one-pot reactions, including arylation, vinylation, and alkylation by integrating ligand-to-metal charge transfer (LMCT)-borylation with Suzuki–Miyaura cross-coupling. The method demonstrated broad applicability to (hetero)aryl and pharmaceutical substrates. In a similar vein, the decarboxylative halogenation of (hetero)aryl carboxylic acid precursors *via* a catalytic LMCT-concept was pioneered by the MacMillan group, showcasing a broad substrate scope (Fig. 15a).[184] Mechanistically, the process involved the reductive elimination of an aryl-copper(III) intermediate, resulting in fluorination or chlorination. Additionally, an atom transfer pathway facilitated the bromination or iodination of (hetero)aryl carboxylic acids.

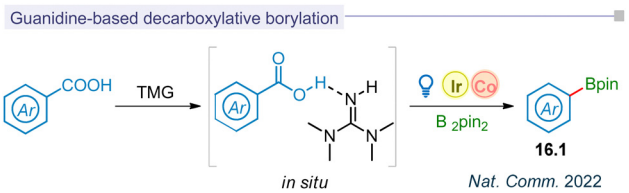

Fig. 16 Guanidine based decarboxylative borylation of aromatic acids.

5.3 Guanidine based decarboxylative borylation

Photodecarboxylative aryl radical formation and its functionalization have been limited to halogenation, hydroxylation, and borylation, typically achieved through thermal photoredox catalysis or the LMCT concept. Among the various methods for photodecarboxylative aryl radical formation, biomimetic decarboxylation was most recently reported by the Liu group. This innovative approach utilized a guanidine-based transition state (**16.1**) to achieve the decarboxylative borylation process through visible-light catalysis (Fig. 16).[185] This biomimetic merging of iridium and cobalt catalysis improved the kinetics of decarboxylation and resulted in the borylation (**16.2**) for carbocyclic and medicinal substrates.

Summary and outlook

As discussed, photo-decarboxylative functionalization of carboxylic acids has gained significant attention due to its diverse applications in various fields with traceless CO_2 by-products. In this highlight article, we summarize the complete development of photocatalytic decarboxylation *via* a concerted single electron transfer (SET) or energy transfer (ET) pathway. This article systematically compiles photodecarboxylative C–C, C–N, C–O, C–S, and C–P cross couplings, along with intra/inter-molecular cyclization of α-keto acids; cyclic and acyclic aliphatic acids; α,β-unsaturated acids and aromatic acids. As decarboxylation is a promising synthetic toolkit for underexplored functionalization/cyclization of various organic molecules, it can easily leverage the molecular library of bio-active scaffolds. A recent upsurge of photomediated protocols has successfully revealed that it can be used for the regio-selective C–H functionalization and cross-coupling. In recent times, considerable progress and rapid access to decarboxylative cross-coupled products disclosed some of the underexplored corners of organic methodology. Although there are numerous reports on C–C cross-coupling, C–Het bond formation is limited for most of the carboxylic acids. Notably, various heteroatoms can influence a reaction for new modes of activation and cyclization in bond-forming methodologies. Interestingly, aryl carboxylic acids are difficult to harness at room temperature and thus LMCT has been employed for decarboxylative functionalization through a lower energy barrier transition state. We hope this article will help the readers gain an insight into the photodecarboxylative functionalization of carboxylic acids over the years.

Data availability

This Feature article does not contain any new data.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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