Single-Step Synthesis of γ–Ketoacids through a Photoredox-Catalyzed Dual Decarboxylative Coupling of α–Oxo Acids and Maleic Anhydrides

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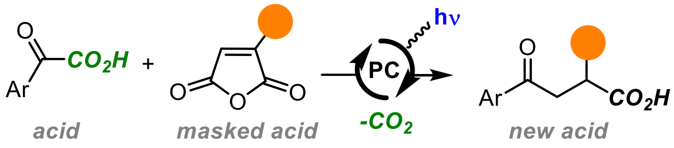
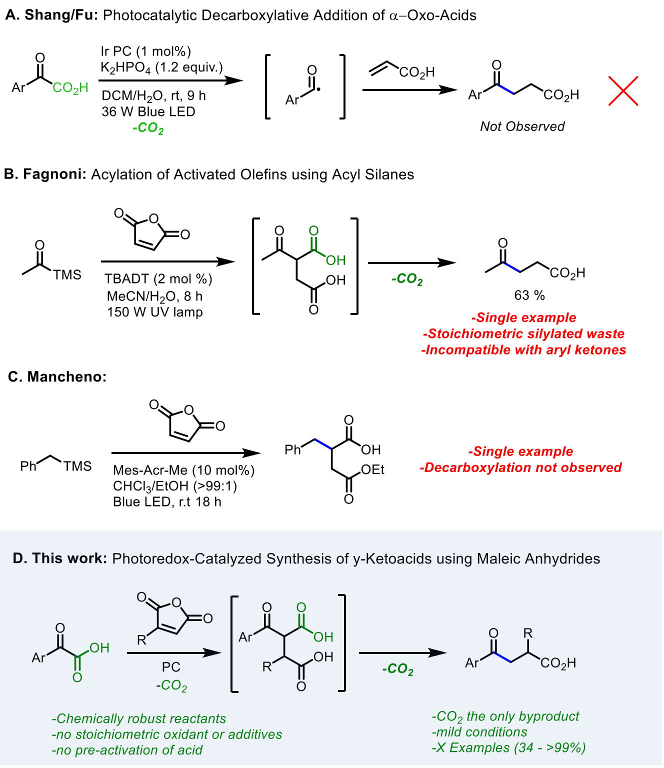


ABSTRACT: A photocatalytic methodology for the single step synthesis of γ–ketoacids from α–ketoacids has been developed. This method employs maleic anhydrides as traceless synthetic equivalents of acrylic acids, achieving a selective cross-coupling *via* a dual decarboxylative strategy, where molecular CO_2 is released as the only waste by-product. The method has also been expanded to incorporate a highly regioselective, 3-component coupling with various alcohols to access functionalized γ–ketoesters.

Efficient methodologies for the synthesis of 1,4-ketoacids are highly sought-after transformations due to their role as versatile chemical building blocks[1] and as core scaffolds for many biologically relevant compounds.[2] However, due to the innate reactivity that carboxylic acid moieties possess, accessing unprotected ketoacids in a single synthetic step is often challenging. A common strategy is to synthesize carboxylic acid derivatives (like esters or nitriles) before unmasking the acid in subsequent steps, rendering these transformations inefficient. The Stetter reaction is an early example of carbonyl umpolung chemistry and remains the most widely used method for preparing 1,4-ketoacids upon acidic aqueous work up, although it necessitates highly toxic cyanide salts.[3] Friedel-Crafts strategies have also been developed for the preparation of aryl ketoacids that often suffer from poor functional group compatibility and produce stoichiometric amounts of metal waste.[4] Recently, acyl radicals have emerged as excellent candidates to partake in carbonyl umpolung chemistry due to their nucleophilic nature.[5] Their ease of generation under photocatalytic conditions has also greatly enhanced their utility, and have been employed in the synthesis of 1,4-dicarbonyl compounds via Giese additions with activated olefins.[6] Aldehydes,[7] acid chlorides,[8] acyl silanes,[9] carboxylic acids and anhydrides[10] are all reliable sources of acyl radicals under photolytic conditions when coupled with stoichiometric atom-transfer reagents or internal oxidants. However, α–oxo-acids provide an appealing alternative as they produce acyl radicals through a facile decarboxylation without the need for additional reagents,[11] and thus have been used as powerful acylating agents.[12]

While 1,4 acyl radical additions into Michael acceptors are abundant, direct additions into acrylic acids for the synthesis of γ–ketoacids are significantly more challenging. In 2015, Shang and Fu reported the first example of trapping photocatalytically generated acyl radicals from α–oxo acids with a variety of activated olefins.[13] Although α,β-unsaturated esters, ketones, aldehydes, amides, nitriles, and sulfones afforded the respective

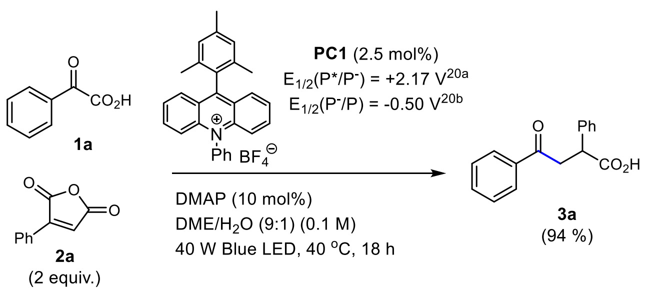
Scheme 1. Previous Work



1,4-dicarbonyl derivatives in good yields, no cross coupling was observed when acrylic acid was employed (**Scheme 1a**). It's hypothesized the presence of the additional carboxylic acid moiety offers an alternate quenching pathway for the excited state photocatalyst, inhibiting reactivity. Diminished yields with acrylic acids are regularly observed in similar cross-coupling reactions, due to their high propensity to polymerization and their ability to participate other off-cycle reaction pathways.[14] Consequently, reaction conditions need to be tailored to specifically accommodate acrylic acids.[15] Alternatively, strategies that protect carboxylic acids *in situ* are also employed.[16] With these limitations in mind, the development of an efficient, one-pot synthesis toward γ-ketoacids from α–oxo-acids and maleic anhydrides is described herein (**Scheme 1d**). Here maleic anhydrides are employed as traceless synthetic equivalents for acrylic acids, where the desired carboxylic acid moieties are unmasked *in situ* by hydrolysis and a second decarboxylation. This obviates the issues associated with using acrylic acids directly, while providing γ–ketoacids in a single regioselective transformation, where molecular CO_2 is the only stoichiometric by-product. Additionally, these products can be isolated in high yields and high levels of purity after a simple extraction (*Supporting information* Figure S1).

In 2018, Fagnoni reported that acyl silanes could be used as acyl radical equivalents, which were subsequently subjected to 1,4-additions.[9] As part of the substrate scope, Fagnoni observed the formation of levulinic acid when maleic anhydrides were employed, analogous to the reactivity discussed herein (**Scheme 1b**). However, this was not investigated further and only a single example was reported. Also, Fagnoni's method could only be applied for the synthesis of alkyl ketones, as aryl derivatives were incompatible. Mancheno and co-workers developed an extension of Fagnoni's work by using benzyl silanes.[17] Again a single example with maleic anhydride was reported and a similar ring opened product was observed, however, decarboxylation did not occur in this case such that the maleic acid adduct was formed (**Scheme 1c**). In 2020, Zhang reported a decarboxylative amino-alkylation of maleic anhydrides by using anilines as the nucleophile to open maleic anhydride.[18] Zhang observed that the second decarboxylation occurs via a radical process that reinstalls the olefin for the synthesis of acrylamides; similar olefin formation is not observed in our reaction.

Scheme 2: Optimized Reaction Conditions

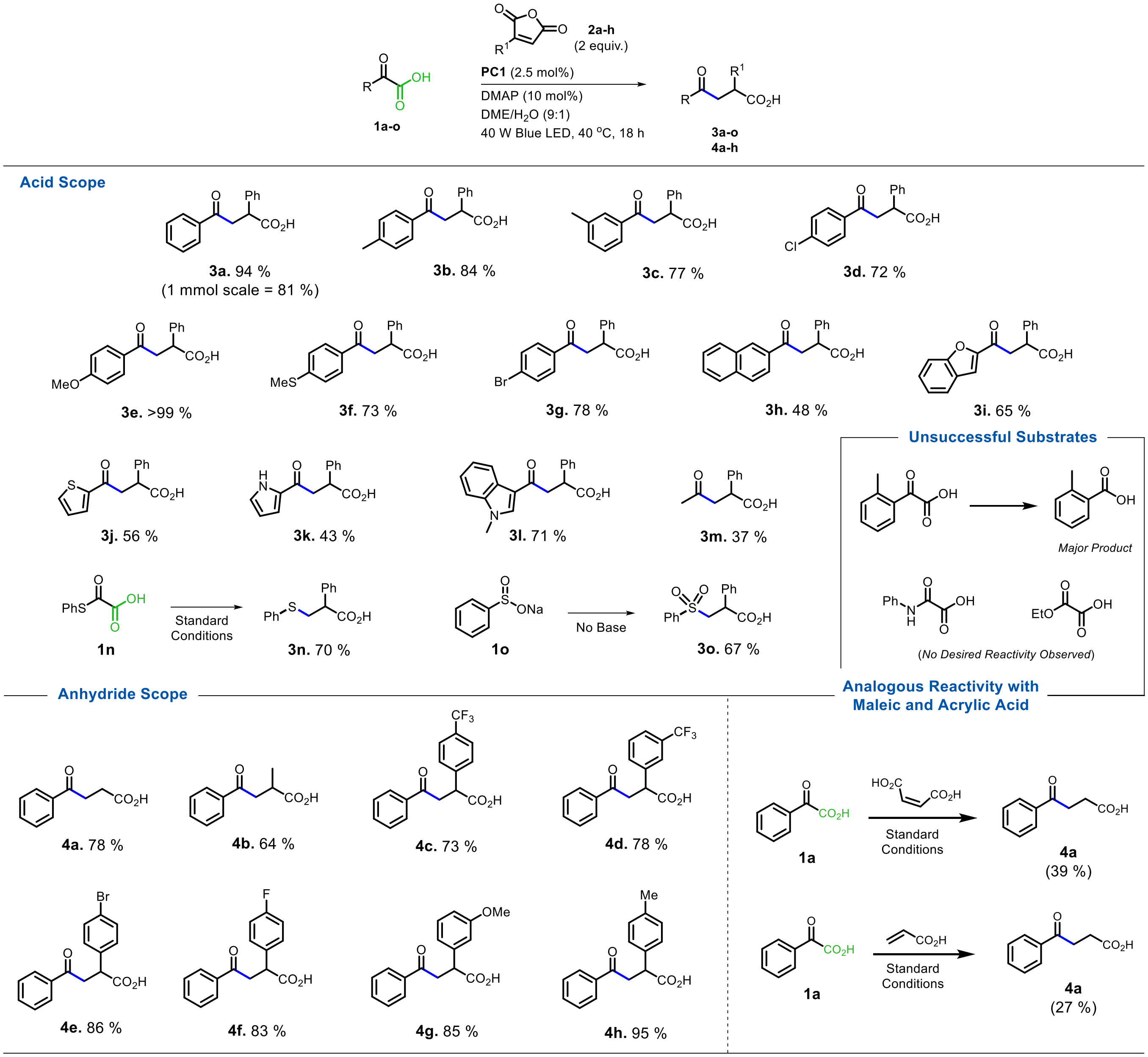


Reaction Optimization. The commercially available phenylglyoxylic acid **1a** and phenyl maleic anhydride **2a** were selected as model substrates for exploring this transformation. The determined optimal reaction conditions were based on our previously reported successful system,[19] with minor adaptations that included lowering the photocatalyst loading to 2.5 mol% (**PC1 -** Mes-Acr-Ph$^+$ BF_4) and employing dimethylaminopyridine (DMAP) as the substoichiometric base for inducing the initial decarboxylation. Adding sufficient water as a cosolvent was also necessary for aiding hydrolysis. (*see supporting information for extensive optimization results*). Under the conditions detailed in **scheme 2**, γ-ketoacid **3a** was isolated in 94 % yield.

Scope of Olefin Aroylation. With the optimized conditions in hand, an extensive scope of compatible α–oxo acids and maleic anhydride coupling partners for the synthesis of the corresponding γ–ketoacids were explored (scheme 3). The transformation was tolerant to a broad range of functional groups, providing the γ–ketoacids in good to excellent yields. In the presence of catalytic quantities of DMAP, the reaction with benzoyl formic acid now provided the desired product **3a** in 94 % yield, compared to 87 % yield without base. With regards to steric influences, it was observed that steric hindrance close to the reactive benzoyl center decreased yields significantly; **3b** (*p*-Me) was obtained in 84 % yield compared to just 37 % (NMR yield) with *o*-Me. Notably, the major product isolated in the reaction with the *o*-Me ketoacid was 2-methylbenzoic acid, presumably a result of water intercepting the acyl electrophile. As acyl radicals are nucleophilic in nature,[5] it is unsurprising that aryl groups with electron donating substituents performed better than the corresponding electron deficient derivatives. 4-Chlorophenyl glyoxylic acid provided the corresponding γ–ketoacid **1d** in 71 % yield, whereas **3e** (4-OMe) was obtained in quantitative yield. Sulfur containing compounds were also well tolerated (**3f;** 73 %) and halogens could also be employed without observation of extensive dehalogenation (**3g;** 78 %). Extended aryl systems like naphthalene were also compatible (**3h**; 48 %). Gratifyingly a broad range of heteroaromatic systems were also well tolerated in this reaction including benzofurans (**3i**; 65 %) and thiophenes (**3j**; 56 %). With regards to the nitrogen heterocycles, the N-protected indole derivative (**3l;** 71 %) greatly outperformed the unprotected pyrrole (**3k**; 43 %) though both substrates were tolerated.

Pyruvic acid could also be employed in this system, providing the 2-phenyl levulinic acid **3m** in 37 % yield. A common observation in these photocatalytic decarboxylative protocols is that alkyl oxo acids generally provide lower product yields than the analogous aryl acids. The acyl radical formed in these cases have been observed to undergo decarbonylation to the subsequent carbon centered radical.[19] Similarly, when the thioester derivative of an α–oxo-acid was used, this subsequent decarbonylation was observed, yielding the sulfide **3n** as a product of thiophenoxy radical addition. An interesting observation is that this substrate still underwent the second decarboxylation providing the mono-acid product in 70 % yield. Potentially a single electron oxidation of the sulfide may induce a facile decarboxylation,[21] though the exact mechanism is unclear at this point. Finally, the sodium salt of phenylsulfinic acid could also be employed,[22] yielding the aryl sulfonylation product **3o** in 61 % yield, allowing access to analogous products with differing oxidation states of sulfur. Benzoylation of a variety of maleic anhydride derivatives proceeded in good to excellent yields for most substrates. Simple maleic anhydride as the reaction partner provided 78% yield of the acylated product **4a**. Reaction with citraconic anhydride provided the corresponding γ-ketoacid **4b** in 64% yield. Next, a series of substituted aryl maleic anhydrides was tested. Electron withdrawing groups on the substituent benzene ring were tolerated, including fluorine (**4f**; 83%), bromine (**4e**; 86%), trifluoromethyl (**4c**; 73% and **4d**;

Scheme 3: Scope of Acid and Anhydride Coupling Partners



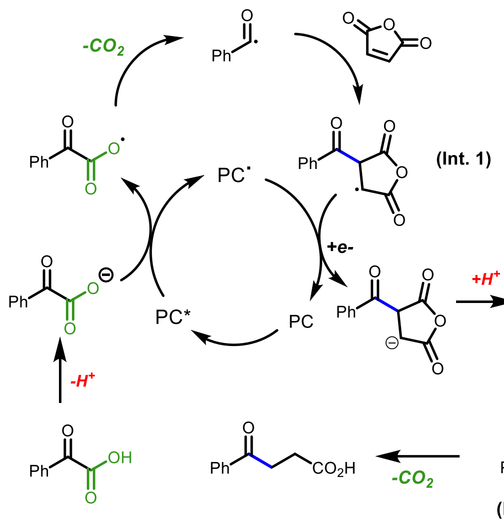
[a]Reactions were run on a 0.2 mmol scale with respect to α-oxo acids. [b] Yields reported are isolated yields.

78%), and *m*-methoxy (**4g**; 85%). The electron donating tolyl group was tolerated as well, giving product **4h** in 95% yield. Finally, to assess the practical utility of this methodology, a scaled-up synthesis was performed under the standard reaction conditions. To our delight, **3a** was obtained in 81% isolated yield for a 1 mmol scale reaction of **1a** and **2a**.

Reaction Mechanism. The general mechanism that can be proposed for this reaction is depicted in **Scheme 4**. Upon irradiation with blue light, the acridinium photocatalyst Mes-Acr-Ph$^+$ can be elevated to its excited state Mes-Acr-Ph^{+*} ($E_{1/2}$(PC*/PC$^-$) = +2.17 V).[20a] A single electron transfer (SET) from the deprotonated carboxylic acid to the highly oxidizing Mes-Acr-Ph^{+*} would generate the carboxyl radical intermediate. This would then undergo a facile decarboxylation to furnish the acyl radical. This acyl radical would then undergo a Giese-like 1,4-addition into the maleic anhydride, generating the radical intermediate (**A**). The reduced photocatalyst would then be returned to its ground state via reductive quenching, through a SET to **A**, generating the corresponding enolate. This can then be protonated by another molecule of the carboxylic acid as proposed by Shang and Fu.[13] Reversible hydrolysis of the formed dihydrofurandione would lead to **B**, which can then undergo a second decarboxylation under thermal conditions to generate the desired γ–ketoacid product. One potential deviation from this mechanism is if the hydrolysis of maleic anhydride occurs before the radical addition of the aroyl group. To test whether this was a viable reaction pathway, the analogous reaction was carried out in the presence of maleic acid (**Scheme 3**). Here, **4a** was obtained in 39 % yield, suggesting that this pathway may well contribute somewhat to product formation but is unlikely to be the dominant route. The lower yield with maleic acid could be attributed to the presence of multiple, unprotected carboxylic acid moieties, which offers alternate quenching pathways for the excited state photocatalyst.

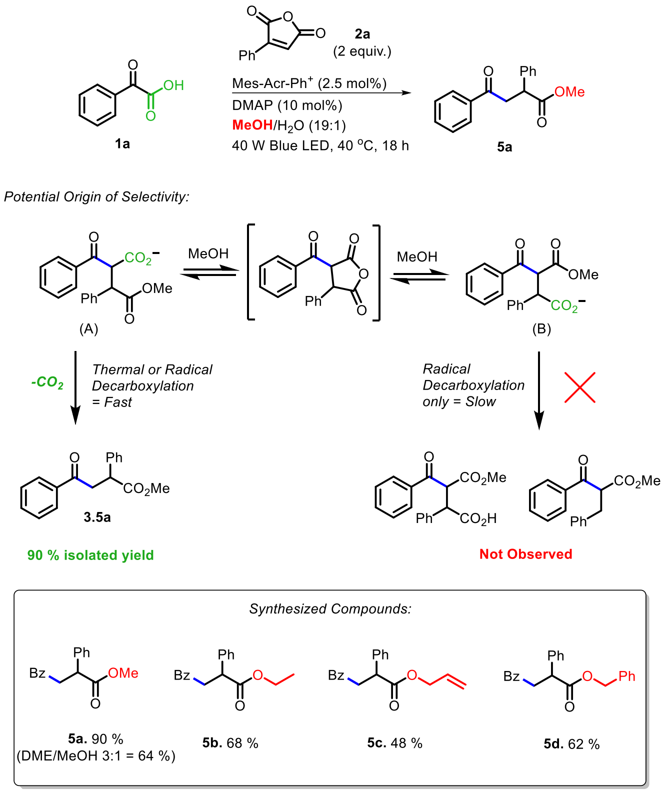
Interestingly, maleic acid still outperformed simple acrylic acid under these conditions (27 %). This could be a result of acrylic acids higher propensity to polymerize, or the innate hydrogen bonding interaction exhibited by the mono-deprotonated maleic acid may lessen the extent to which it is able to quench the photocatalyst.

Scheme 4. Potential Mechanism



Pathway to γ–Ketoesters. During the reaction optimization, an interesting observation was made when the reaction was carried out in methanol. Protic solvents weren't anticipated to be compatible for the formation of ketoacids since the presence large quantities of alcohol would outcompete hydrolysis to potentially undergo a series of esterifications. However, a nuance that presented itself was that even though esterification did occur, decarboxylation of the ring opened maleic anhydride still proceeded, selectively forming the ester at the terminal position only (**5a**). This product was eventually isolated in a 90 % yield. This product is analogous to a 1,4-addition of the corresponding acrylate, however we envision a practical benefit of forming 1,4-dicarbonyl compounds through this 3-component coupling is this method obviates the need of pre-synthesizing the acrylates and could be used for efficient library derivatization of compounds. The origin of selectivity could arise from the fact the nucleophilic ring opening of the maleic anhydride is likely to be reversible (**Scheme 5**). This reversibility would instigate a Curtin-Hammett scenario within the system, where the carboxylate can be formed interchangeably from being situated at the α–position of the benzoyl group (intermediate A) or phenyl group (intermediate B) respectively. For the decarboxylation to occur from intermediate B, this must proceed through a radical decarboxylation pathway initiated through oxidation by the photocatalyst. Whilst it's logical to assume this pathway is viable under the reaction conditions, it is not observed to occur to any significant extent. However, decarboxylation from intermediate A is facile and readily occurs under thermal conditions, which drives the equilibrium toward the formation of **5a**. A small scope of compatible alcohols was composed without further optimization of the reaction conditions (Scheme 3). It was found that the alcohols needed to be employed as the reaction solvent for high yields. For the reaction in methanol, **5a** was obtained in a 90 % yield, which dropped to 64 % when methanol was used as a co-solvent with DME (DME/MeOH = 3:1). The ethyl ester was also obtained in good yields (**5b;** 68 %) though the greater steric hinderance around the alcohol moiety decreased yields, presumably due to the slower rate of nucleophilic addition. Gratifyingly, the ester products from allyl alcohol (**5c;** 48 %) and benzyl alcohol (**5d**; 62 %) could both be formed under these conditions in reasonable yields, which are products that can be employed in radical decarboxylative allylation and benzylation reactions. [23]

Scheme 5. Selective Esterification in the Presence of Alcohols



Conclusion. The development of an efficient, single-step synthesis toward γ–ketoacids from α–oxo-acids and maleic anhydrides under photoredox conditions has been described. Here maleic anhydrides are employed as traceless synthons of acrylic acids, obviating the issues associated with direct 1,4-additions into acrylic acids. A wide range of γ–ketoacids can be prepared under mild conditions in good to excellent yields and with high levels of purity after a simple acid-base extraction.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, spectral data and copies of NMR spectra for all new compounds (PDF)

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