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Transition metal-free decarboxylative olefination of carboxylic acid salts†

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The cost-effective and efficient synthesis of alkenes is highly significant due to their extensive applications in both synthetic and polymer industries. A transition metal-free approach has been devised for the chemoselective olefination of carboxylic acid salts. This modular approach provides direct access to valuable electron-deficient styrenes in moderate to good yields. Detailed mechanistic studies suggest anionic decarboxylation is followed by halogen ion transfer. This halogen transfer leads to an umpolung of reactant electronics, allowing for a rate-limiting rebound elimination.

Introduction

Alkenes are appealing, low-cost synthetic precursors. While unfunctionalized olefins are easily obtained in bulk quantities from petrochemical feedstocks,[1] the efficient and low-cost synthesis of electronically varied alkenes is of great interest because of their widespread application in synthesis and polymerization.[2] The rising demand and escalating financial costs of petroleum products[3] have emphasized the necessity of synthesizing functionalized alkenes from more oxidized, readily available intermediates, including those obtained from biomass. Carboxylic acids are particularly attractive oxidized feedstocks since a large number of carboxylic acids are prepared on an industrial scale and are commercially available.[4]

Decarboxylation is a burgeoning strategy for forming reactive intermediates that avoids preformed organometallic reactants by leveraging the extrusion of carbon dioxide, an innocuous by-product, to form carbanions, carbocations, and radicals (Scheme 1).[5] Since the pioneering work of Kolbe demonstrating the formation of carbon-centered radicals through decarboxylation from carboxylic acids,[6] decarboxylative strategies have been shown to provide access to a large variety of functionally interesting products.[7] Classically, the barton decarboxylation allows for the direct access of alkanes and arenes from carboxylic acids,[8] and the Hunsdiecker–Borodin reaction allows for the direct conversion of silver carboxylates into halides.[9] More recently, coupling reactions have utilized decarboxylative metalation to generate organometallics that couple to form new C–C, C–N, C–S, and C–O bonds, providing alternatives to traditional cross-coupling reactions.[7a,10] The decarboxylative

elimination of carboxylic acids to produce alkenes, on the other hand, still represents a relatively underexplored reaction class.

Kochi pioneered the direct conversion of carboxylic acids into olefins, although the method was limited by the requirement of a stoichiometric lead oxidant and forcing reaction conditions.[11] Building upon Kochi's work, more reports have
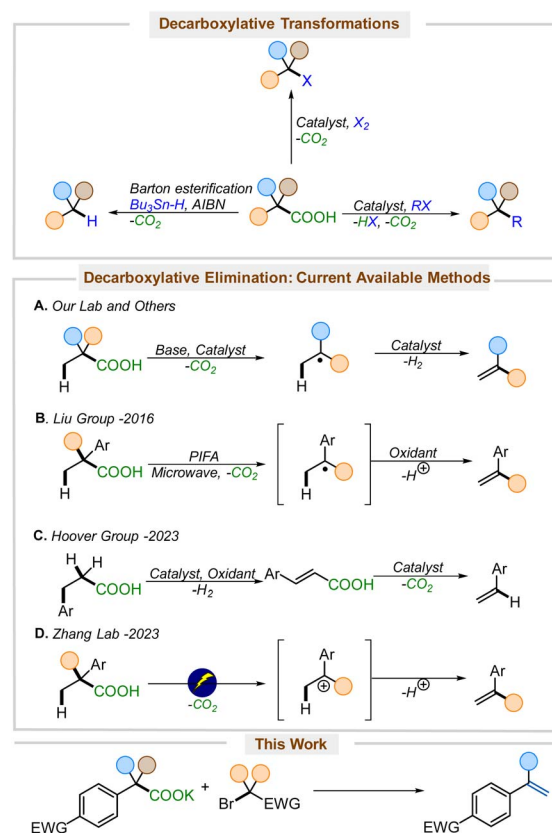
Scheme 1 Decarboxylative transformations.

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emerged demonstrating more efficient and practical versions of decarboxylative elimination.[12] Our lab and others have developed a decarboxylative-dehydrogenation strategy for the direct conversion of carboxylic acids to alkenes (Scheme 1A).[12b,13] However, these methods rely on a single-electron-transfer pathway, which often requires expensive iridium-based[14] or specialized photocatalysts,[15] that also engage styrenes and thus are often incompatible with the formation of styrene products. In 2016, Liu and co-workers reported a metal-free microwave-assisted approach for the synthesis of styrenes from carboxylic acids (Scheme 1B).[12a] Later in 2023, the Hoover group developed a copper-catalyzed decarboxylative elimination of carboxylic acids to styrenes (Scheme 1C).[16] These important contributions do, however, suffer from several drawbacks. PIFA is a relatively high molecular weight oxidant that promotes the formation of radicals and cations, and thus is not effective for the generation of electron-deficient styrenes;[12a] electrochemical decarboxylative elimination is similarly limited (Scheme 1D).[12e,f] In contrast, copper-catalyzed elimination works well for the synthesis of nitrostyrenes, but it also involves intermediate radicals and is mechanistically limited by the need for benzylic deprotonation with LiOAc.[16]

We set forth to develop a metal-free reagent for decarboxylative elimination that would be compatible with the formation of electron-deficient styrenes. Here, we envisioned an anionic intermediate, generated by thermal decarboxylation, could undergo oxidation *via* halogen ion transfer.[17] The resulting umpoled intermediates would be poised for elimination to furnish styrenes (Scheme 2). The key to unlocking this methodology would lie in the selection of an appropriate reagent that would initially serve as a halogen source, generating a stabilized anion, which could rebound to effect an E2-elimination. While there are numerous reports of decarboxylative halogenation reactions in the literature,[8a,18] none leverage this one-pot halogenation-rebound elimination approach starting directly from carboxylic acids.

## Results and discussion

Initial optimizations

To evaluate the feasibility of umpolung elimination, we initiated our investigations by screening reagents that would serve as the halogen ion donor. We chose NBS as our initial reagent,

and fortunately we were able to observe the corresponding styrene **3a** in 39% yield (Table 1). We hypothesized that the low yield was due to the relatively low basicity of the succinimide anion (conj. acid pK_a 14.7) formed after the initial halogen ion transfer. With this in mind, 2-bromo-2-nitropropane[19] (nitronate pK_a *ca.* 17) was chosen as the halogen ion transferring reagent,[17,20] and styrene **3a** was furnished in 77% yield. Interestingly, a further increase in the conjugate basicity of the halogen source resulted in a preferential substitution rather than the expected elimination. Specifically, when ethyl 2-bromoisobutyrate (pK_a *ca.* 29) was utilized, hindered substitution product **4a** was isolated in good yield (Table 1).

With elimination conditions in hand, control studies confirmed the necessity of bromo nitropropane **2a** for effective reaction (Table 2A, entry 2). Acetonitrile was found to be the best solvent for the reaction, although dry MeCN was necessary for the efficient formation of **3a** (Table 2A, entries 3 & 4). Furthermore, a more dilute reaction concentration led to drastic yield decrement (Table 2A, entry 5). Additionally, we found that the temperature and reaction time had a significant influence on the yield of the decarboxylative elimination reaction. For example, running the reaction for shorter periods or at lower temperatures resulted in a considerable amount of the brominated product **3a′** (Table 2A, entries 6 & 7). Furthermore, increasing the loading of **2a** to 1.2 equiv with respect to the carboxylate salt gave the best results: 83% isolated yield of α-methyl-4-nitrostyrene (Table 2A, entry 8). Additionally, different counter cations of **1a** were screened, although K⁺ was found to be better compared to Cs⁺, Na⁺ or Li⁺ (see Table S6, ESI†). Moreover, these conditions provide superior results compared to the state-of-the-art photochemical[13c] or microwave[12a] methods for synthesizing electron-deficient styrenes from carboxylic acids (Table 2B, entries 10 & 11) (see ESI† for more details). Only the copper-catalyzed elimination is comparable (Table 2B, entry 12), but that reaction requires isomeric β-nitroaryl acids and has lower atom economy.[16]

Scope of decarboxylative elimination

With the optimized conditions in hand, a series of substituted styrenes were made starting from different carboxylate salts
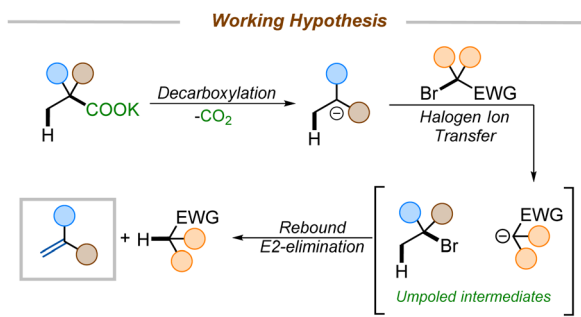

Scheme 2 Our working hypothesis.

Table 1 Reaction discovery

Reagent:	NBS	2-bromo-2-nitropropane	ethyl 2-bromoisobutyrate
Product:	**3a**, 39%[a]	**3a**, 77%[a]	**4a**, 70%[a]

[a] Yields determined by quantitative ¹H NMR analysis using anisole as a standard. Reaction conditions: **1a** (1 equiv), reagent (1 equiv), CH₃CN (0.1 M), 95 °C, 3 h.

Table 2 Initial optimizations and comparison against state-of-the-art conditions

A: Optimizations
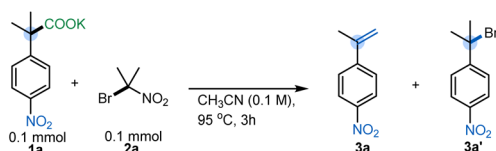
Entry	Variation in conditions	% Yield[a]a
1	—	77:–
2	No **2a**	—
3	DMF, DCM, THF instead of MeCN	<36:–
4	Wet CH$_3$CN	60:–
5	0.05 M instead of 0.1 M	39:–
6[b]	90 min instead of 3 h	73:10
7	70 °C instead of 95 °C	47:27
8	0.12 mmol of **2a**	88(83):–

B: State-of-the-art-conditions

Entry	Elimination	Reaction conditions	% Yield (**3a**)[a]
9	This work	**2a** (1.2 equiv), CH$_3$CN, 95 °C, 3 h	88(83)
10	Co/Acr hν, (ref. 13c)	[Co] cat., [Acr] cat., STAB cat., Na$_2$CO$_3$ cat., H$_2$O cat., MeOH, blue LED, rt, 18 h	6
11	PIFA μW, (ref. 12a)	PIFA (1.2 equiv), CH$_3$CN, μW 120 °C, 20 min	—
12	Cu/oxidant, (ref. 16)	[Cu] cat., [bpy] cat., MnO$_2$ (2 equiv), LiOAc (2 equiv), 120 °C, 24 h	89(80)

[a] Yields determined by quantitative ^{1}H NMR analysis using anisole as a standard. Numbers in parenthesis are isolated yields. [b] 0.12 mmol of **2a** instead of 0.1 mmol.

(Scheme 3). Several different 4-nitrophenylacetic acid salts bearing alkyl or aryl substituents in the benzylic position were screened under our reaction conditions. Remarkably, in all cases the alkene formation was chemoselective. An electron-rich vinyl ether (**3c**), often prone to electrochemical or photochemical oxidation,[21] was readily synthesized using the current method. Additionally, a wide range of substituted 1,1-diphenylethylenes was also rapidly accessed using the current protocol (**3d–3h**). The internal alkene, resulting from an α,α-diethyl carboxylate provided product in excellent yield, but resulted in a stereoisomeric mixture of alkene (**3i**). Carboxylate salts bearing other important functional groups such as nitrile (**3j**; 91%), keto (**3k**; 71%), and ester groups (**3l**; 76%) were all tolerated well under the reaction conditions, furnishing the internal alkenes selectively. Notably, as the steric bulk of the substituent increased, the *Z* alkene isomer diminished, providing the *E* alkene exclusively (**3j–l**). Interestingly, the ethyl-substituted salt **1m** gave a regioisomeric mixture of the internal and external olefin (76 : 24) along with the *E* and *Z* isomers (89 : 11) for the internal alkene (see ESI† for details). However, as the chain length increased, the selectivity for the internal to the external alkene decreased (**3n** and **3o**). While a steric influence in the elimination is clear, a slight electronic bias resulted in controlled formation of internal alkenes. Specifically, alkyl chains with more acidic hydrogens (**3j–3l**) provided the

conjugated olefins, as did allyl (**3p**), benzyl (**3q**), naphthyl (**3r**), and propargyl (**3s**) substituted carboxylates. Moreover, further isomerization studies have revealed that the regioisomeric and geometric mixtures of olefins stem from E2 elimination, as very minimal isomerization was observed when the alkenes were subjected to basic conditions (see ESI† for more details).

Having established the feasibility of our elimination conditions with respect to nitrophenyl acetates, the scope of other weakly activated aryl acetic acid salts was explored. Functional groups that provide adequate stabilization of an anionic intermediate formed after decarboxylation, such as SO$_2$Me ($\sigma_p^- = 1.13$), CN ($\sigma_p^- = 1.00$), keto ($\sigma_p^- = 0.84$), pyridyl ($\sigma_p^- = 0.81$) and ester groups ($\sigma_p^- = 0.75$) were expected to undergo the elimination between temperature range of 110 and 150 °C.[10d,22] However, at the higher temperatures, required for decarboxylation of these substrates, it was observed that the parent carboxylic acids were recovered from the reaction mixture, with minimal to no elimination occurring (Scheme 4a). This was attributed to competitive E2-elimination to form 2-nitropropene with the carboxylates serving as the base (Scheme 4b). Thus, it was anticipated that choosing a *gem*-bromonitro alkane that could not undergo such an elimination should facilitate the elimination of **1y** (Scheme 4c). In support of this hypothesis, utilization of an adamantane-derived *gem*-bromonitro alkane (**2b**) led to decarboxylative elimination of **1y** in 77% yield (Scheme 4d).

With the newer reagent, the decarboxylative elimination of 4-SO$_2$CF$_3$-phenylacetic acid salt (**1t**) and other aryl acetic acids were evaluated (Scheme 3). The reaction with **1t** delivered the corresponding styrene **3t** in good yield (79%). Other activating groups such as –SO$_2$Et (**3u**; 65%), –CN (**3y**; 77%), –CHO (**3ac**; 61%), –COR (**3ad**; 62%), –pyridine (**3ae**; 70%), and –CO$_2$Me (**3af**; 72%) gave moderate to good yields for the corresponding styrenes. Overall, the observed functional group tolerance can, in part, be attributed to use of bromonitroalkanes as mild oxidants.

Importantly, the method was readily scaled to gram-scale, yielding **3a** in 78% yield (Scheme 5a). To further illustrate the utility of this decarboxylative elimination approach, we subjected **3a** to several different transformations (Scheme 5b). Specifically, **3a** was subjected to radical cyclization under oxidative conditions to furnish the dihydrofuran derivative **4c** in 61% yield.[23] Additionally, dimerization was achieved under acidic conditions (**4e**, 50%),[24] and allylic halogenation was performed using NBS (**4b**, 42%).[25] Nucleophilic addition to styrene **3a** was achieved under basic conditions to deliver **4d** in 67% yield.[26]

Mechanistic studies

Despite our reaction design, we considered three possible pathways for the formation of alkenes under the reaction conditions (Scheme 6). Pathway A involves a thermal decarboxylation followed by Halogen-ion-transfer from 2-bromo-2-nitropropane and a rebound E2-elimination to furnish the styrene. Pathway B would involve a thermal decarboxylation followed by a single-electron-transfer (SET) to 2-bromo-2-
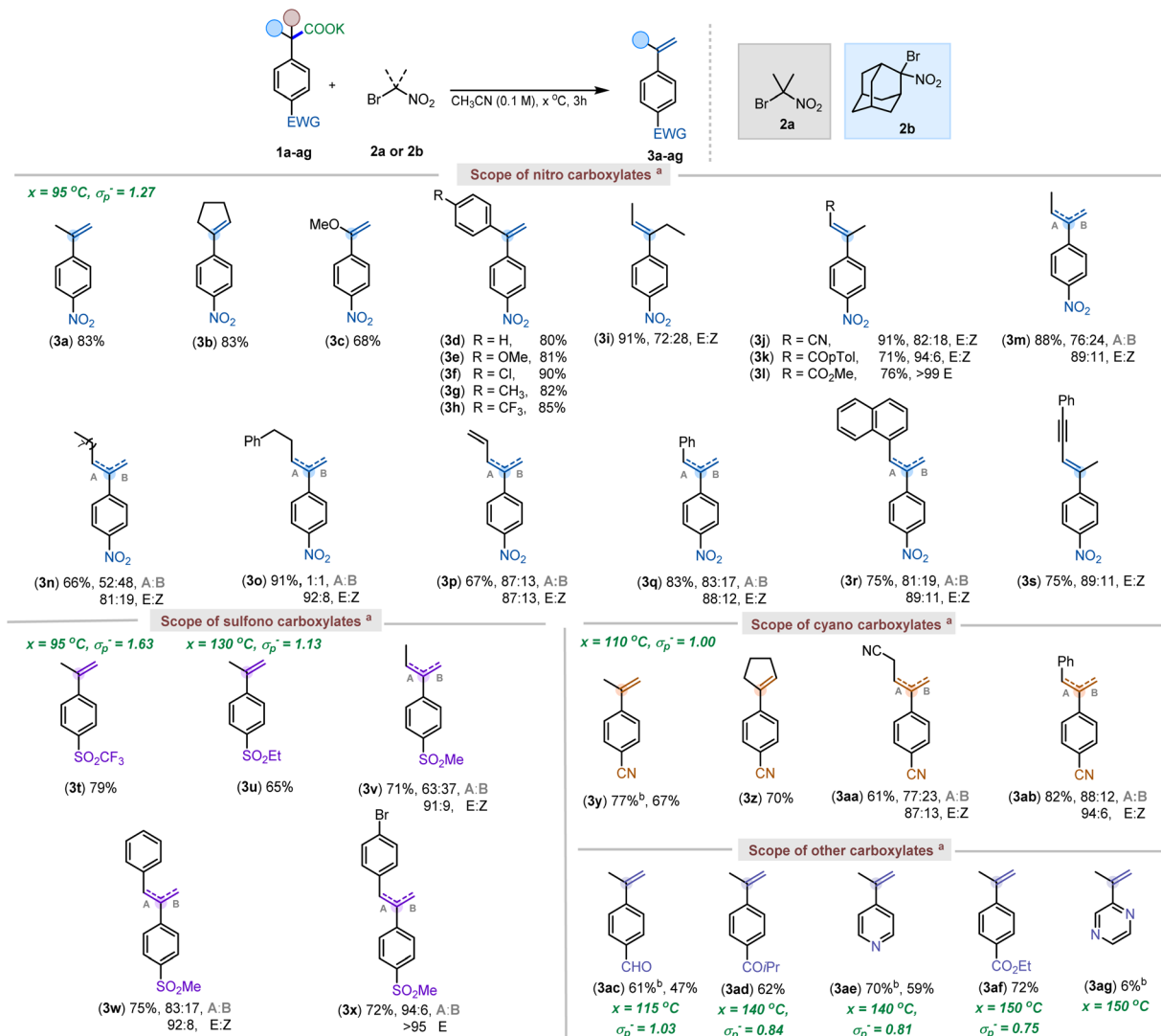
Scheme 3 Scope of carboxylates. [a]Reactions were run on a 0.1–0.2 mmol scale, and yields reported are isolated, unless otherwise denoted. Regioisomer ratio was determined using ¹H NMR & COSY. [b]Yields reported are quantitative ¹H NMR yields with anisole as the internal standard. Reaction conditions: **1a–1ag** (1 equiv), **2a** or **2b** (1.2 equiv), CH$_3$CN (0.1 M), 3–6 hours, temperature as specified in ESI.†

nitropropane followed by hydrogen-atom-transfer (HAT). SETs to *gem*-bromonitroalkanes are known and are a common pathway in radical nucleophilic substitution ($S_{RN}1$) reactions.[27] Another possible pathway, pathway C, would begin with a halogen ion exchange to form an acyl hypohalide, as in the Hunsdiecker–Borodin reaction.[9c] Subsequent bond homolysis, radical decarboxylation, and recombination would form a halide intermediate. This intermediate would then undergo elimination to generate the olefin.

A series of mechanistic experiments were conducted to eliminate one or more of these potential mechanistic pathways (Scheme 7). To examine the possibility of radical intermediates, we employed TEMPO as radical trapping agent. Addition of TEMPO into the reaction mixture did not yield any TEMPO trapped product nor did TEMPO inhibit the reaction (Scheme 7a). Next, a radical clock experiment was performed to probe for the formation of nitro-alkyl radicals. However, no ring-opened

products were observed when **2c** was subjected to our reaction. Instead, **3a** and **2c′** were isolated in 71% and 70% yield, respectively (Scheme 7b). This lies in contrast with existing decarboxylative eliminations, where radicals are involved;[12,13] for example the Liu group observed the formation of cyclopropyl ring-opened products in their decarboxylation methodology.[12a] Moreover, if pathway B were operating, the competitive $S_{RN}1$ reaction products were expected to be observed in addition to the olefins.[27b] However, no such products were observed under our reaction conditions (see ESI† for details). Additionally, we were able to isolate and characterize the intermediate halide **3a′** (Scheme 7B), which is inconsistent with reaction through pathway B. Finally, the reaction with 2-phenyl-isobutyric acid salt failed to give the corresponding styrene **4aj** (Scheme 7c), suggesting the need for an electron withdrawing group to facilitate reaction. In contrast, the Hunsdiecker–Borodin reaction is known to proceed with unactivated
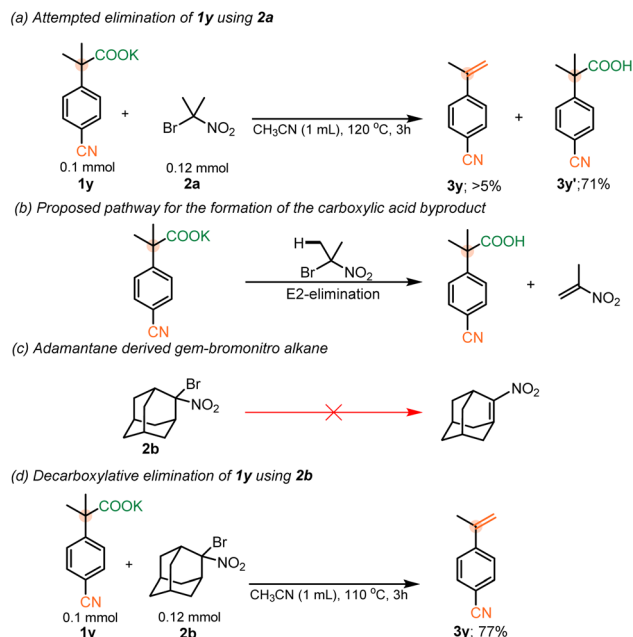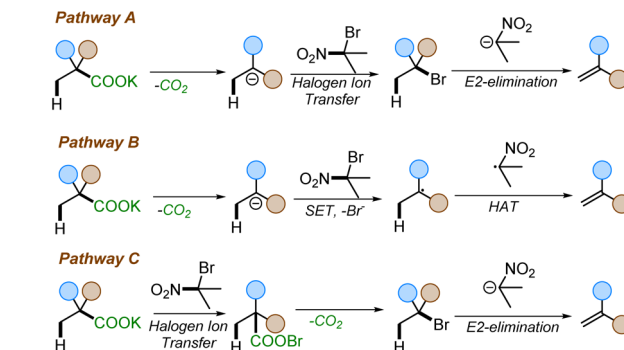
Scheme 4 (a) Attempted elimination of **1y** with **2a**. (b) Mechanistic proposal for the formation of **3y'**. (c) Anti-bredt olefin formation from **2b**. (d) Elimination of **1y** using **2b**.
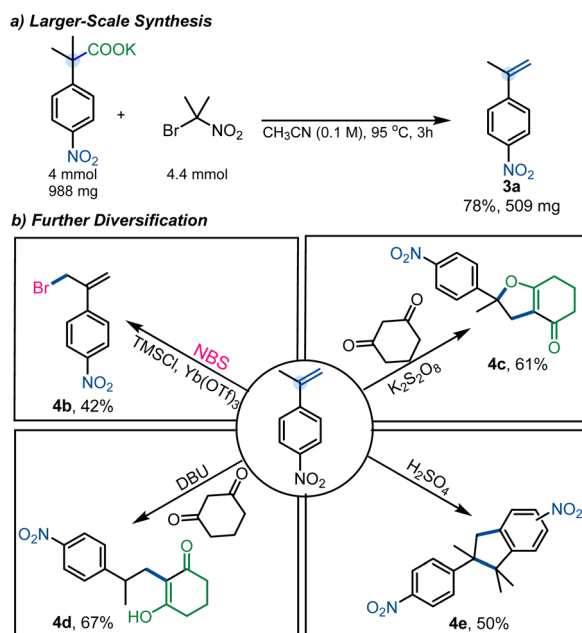
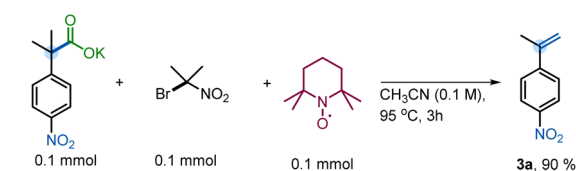Scheme 5 (a) Larger-scale synthesis. (b) Diversification.

Scheme 6 Possible mechanistic pathways.
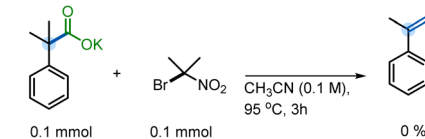
Scheme 7 Mechanistic experiments. (A) Radical probing. (B) Intermediate analysis.

phenylacetic acid salts.[28] The observed requirement for higher temperatures to effect reaction of substrates with less electron-withdrawing activating groups further suggests that pathway C may not be operative.[22] Thus, we favor pathway A as it is consistent with the observation of the intermediate halide **3a'** and the temperature dependence for attaining the decarboxylation with other weakly activating groups.

With the goal of obtaining further insight into the mechanism of the reaction, KIE experiments were undertaken. Kinetic isotopic effects were obtained for a series of substrates (**1a, 1d** and **1h**) and their deuterated derivates through the analysis of initial rates of independent reactions. For **1a** and **1a**-d_6, independent rate studies derived a KIE of 2.8, and the intermolecular competition experiment resulted in a KIE of 2.0 (Scheme 8a and b). These values suggest the elimination to be the rate-determining step in pathway A. Furthermore, these KIE values are consistent with those reported in the literature for the elimination reaction of α-phenylethyl bromide systems.[29]

Independent rate studies of **1d** and **1d**-d_3 revealed a KIE of 2.67, again suggesting a rate-determining elimination (Scheme 8c).

To further gain an understanding of the mechanism and the nature of the transition state of this elimination reaction, we conducted a Hammett competition study of various 4-substituted-2,2-diphenylpropanoate salts (Scheme 9). The competition studies were carried out under the standard conditions reported in Table 1, although an excess of the competing 4-substituted-2,2-diphenylpropanoate salts was added to the reaction mixture (5 equivalents each) to ensure that reactant concentration did not affect product selectivity (see ESI† for more details). The Hammett competition study suggests positive charge buildup in the product-determining transition state ($\rho = -1.63$). Such negative slopes have previously been observed in the gas phase elimination of substituted 1-phenylethyl chlorides[30] and is indicative of a moderate degree of charge separation through an E2 transition state with significant E1 character.

Since Hammett competition experiments only reflect electronic differences in the product-determining step, additional kinetic investigations were conducted to verify that the rate-determining step (RDS) and the step governing product formation (PDS) are identical (see ESI† for additional details).
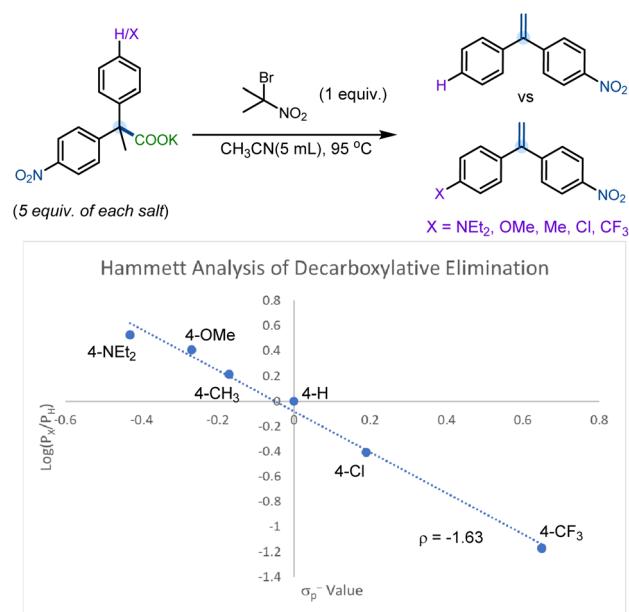
Scheme 9 Hammett plot.

Here, it was evident that the individual rate of reaction of **1g** (4-CH$_3$) was much faster rate than that of **1d** (4-H) and, it was also evident, that the rate decreased drastically for **1f** (4-Cl) and **1h** (4-CF$_3$) (see ESI† for details). These relative rates are consistent with a negative slope for the Hammett study. Thus, it was confirmed that the 'E1-like' E2-elimination was indeed the rate-determining step of this decarboxylative elimination reaction, as outlined in the Bunnett spectrum.[31]

Conclusions

In summary, we have developed a simple and efficient method for the olefination of potassium salts of carboxylic acids. This transition metal free approach allows for the facile construction of olefins in a chemoselective fashion in moderate to good yields. The green approach proceeds with good efficacy, good functional group tolerance, and broad substrate scope. Mechanistic studies demonstrated decarboxylation, followed by a halogen ion transfer and rebound E2 elimination as the likely pathway for this transformation. KIE and Hammett studies revealed a rate-determining 'E1-like' transition state for the E2-elimination.
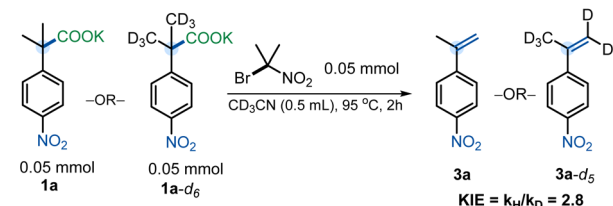
Data availability

The data underlying this study are available in the published article and its ESI.†
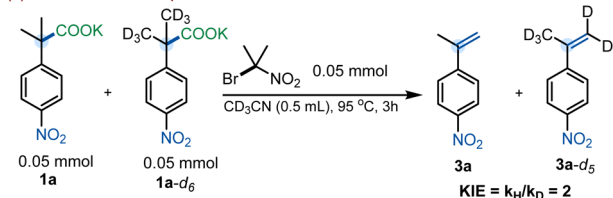
Author contributions

J. T. and E. J. conceptualized and initiated the project. E. J., D. B. & G. S. performed the experiments and analyzed the data. J. T. and E. J. co-wrote the paper.
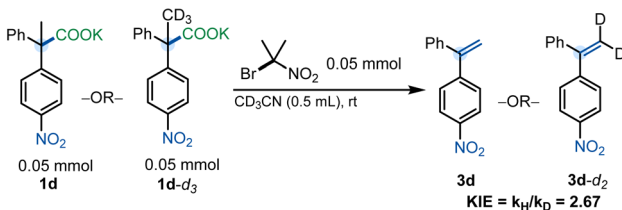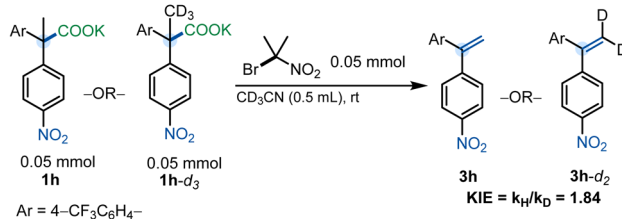
Scheme 8 Kinetic isotopic studies.

Conflicts of interest

The authors declare no conflict of interest.

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