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Visible-Light-Mediated Dual Decarboxylative Coupling of Redox-Active Esters with α,β-Unsaturated Carboxylic Acids

Jin-Jiang Zhang, Jun-Cheng Yang, Li-Na Guo, and Xin-Hua Duan*

Dedication ((optional))

Abstract: An efficient visible-light-induced decarboxylative coupling between α,β-unsaturated carboxylic acids and alkyl *N*-hydroxyphthalimide esters has been developed. A wide range of redox-active esters derived from aliphatic carboxylic acids (1°, 2° and 3°) proved viable in this dual decarboxylation process, affording a broad scope of substituted alkenes in moderate to excellent yields with good *E*/*Z* selectivities. This redox-neutral procedure was highlighted by its mild conditions, operational simplicity, easy accessibility of carboxylic acids, and excellent functional-group tolerance.

Transition-metal catalyzed cross-coupling reactions involving alkyl species have emerged as one of the powerful tools for construction of C_{sp3}−C bonds. While the easily available alkyl halides containing β hydrogen atoms are one of the most challenging substrates in such transformations due to their difficulty of oxidative addition and ease of β-hydrogen elimination.[1] During the past decade, significant progress has been made in this field. So far, alkyl halides have been developed to be efficient alkyl sources in C_{sp3}−C bond formation reactions.[1,2] In addition, a series of alkyl electrophiles including cyclic anhydrides,[3a] alkyl ethers,[3b,c] styrenyl epoxides[3d] even styrenyl aziridines,[3e] and cyclic sulfates[3f] have also been successfully exploited to construct the C_{sp3}−C bonds. Recently, redox-active esters derived from alkyl carboxylic acids and *N*-hydroxyphthalimide (NHPI) were demonstrated to be very efficient alkyl electrophiles in alkyl cross-coupling reactions.[4,5] For example, Baran and co-workers have successfully developed a series of Ni-catalyzed alkyl-aryl and alkyl-alkyl cross-coupling reactions using this redox-active esters as alkyl sources.[4a-c] Simultaneously, the group of Weix has also reported an efficient alkyl-aryl cross-electrophile coupling reaction using the *N*-hydroxyphthalimide esters (NHP esters).[5] Inspired by those results, we wish to develop a novel alkyl-vinyl cross-coupling reaction using NHP esters as an alkyl source for C_{sp3}-C_{sp2} bond formation.[4e]

In recent years, visible-light-mediated decarboxylative cross-couplings of carboxylic acids and their derivatives have attracted increasing attention owning to their sustainability, practicality and environmental friendliness.[6] Recently, MacMillan and Doyle reported the first direct decarboxylative coupling of alkyl carboxylic acids with aryl, vinyl and alkyl halides through merging photoredox and nickel catalysis.[7] In fact, visible-light-mediated decarboxylation of alkyl carboxylic acid derivatives can be dated back to 1990s. Pioneering work developed by Okada and co-workers revealed that redox-active NHP esters could undergo decarboxylative Michael addition with electron-deficient alkenes under photoredox catalytic conditions (Figure 1).[8] Later on, Overman et al employed this radical decarboxylative alkylation strategy for the construction of quaternary carbon centers.[9] In 2015, Chen and co-workers disclosed visible-light-induced reductive decarboxylative allylation and alkynylation of the NHP esters, respectively.[10] More recently, the group of König demonstrated an efficient metal-free decarboxylative alkylation of electron-deficient alkenes with the NHP esters under visible-light catalysis.[11] On the other hand, the oxidative decarboxylative alkylation of cinnamic acids have also been well documented, but the generation of these alkyl radical always requires the employment of strong stoichiometric peroxides and high temperature.[12a-f] Very recently, Chen has also reported a photoredox catalyzed decarboxylative alkylation of vinyl carboxylic acids using alkylboronic acids in the presence of stoichiometric hypervalent iodine reagents.[12g] However, the redox-neutral visible-light-induced decarboxylative alkylation of α,β-unsaturated carboxylic acids remains rare. On the basis of these elegant results as well as our ongoing interest in decarboxylative reactions,[6c,13] we report herein a concise visible-light-mediated dual decarboxylative couping between α,β-unsaturated carboxylic acids and redox-active NHP esters at room temperature, which provides an efficient route to substituted alkenes under redox-neutral conditions (Figure 1).

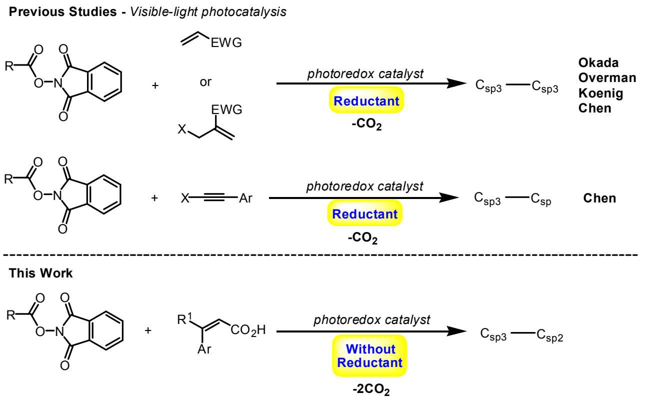

Figure 1. Visible-light-mediated decarboxylative coupling of *N*-hydroxyphthalimide esters with different reactants

We commenced our studies with the optimization of the coupling between *N*-acyloxyphthalimide **1a** and 4-bromo cinnamic acid (**2a**) under visible-light irradiation conditions

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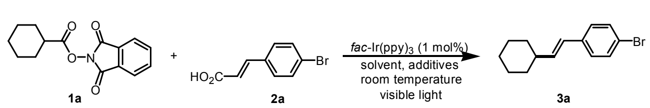
Table 1. Optimization of the Reaction Conditions.[a]



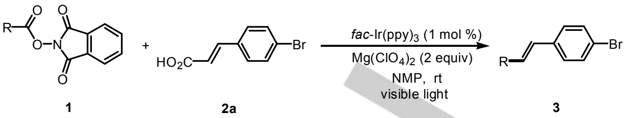
Entry	Solvent	Additives (equiv)	Yield [%][b]
1	NMP/H_2O (4:1)	-	42
2	DMF/H_2O (4:1)	-	11
3	dioxane/H_2O (4:1)	-	19
4	THF/H_2O (4:1)	-	33
5	DME/H_2O (4:1)	-	16
6	DCE/H_2O (4:1)	-	0
7	NMP/H_2O (1:4)	-	36
8	H_2O	-	<5
9	NMP	-	44
10	NMP	$Mg(ClO_4)_2$ (1)	55
11	NMP	$MgSO_4$ (1)	40
12	NMP	$MgCl_2 \cdot 6H_2O$ (1)	27
13	NMP	$Mg(NO_3)_2$ (1)	34
14	NMP	$Mg(ClO_4)_2$ (2)	64[c]
15	NMP	$Mg(ClO_4)_2$ (3)	42
16	NMP	$Mg(ClO_4)_2$ (1)	0[d]
17	NMP	$Mg(ClO_4)_2$ (1)	0[e]
18	NMP	$Mg(ClO_4)_2$ (1)	trace[f]

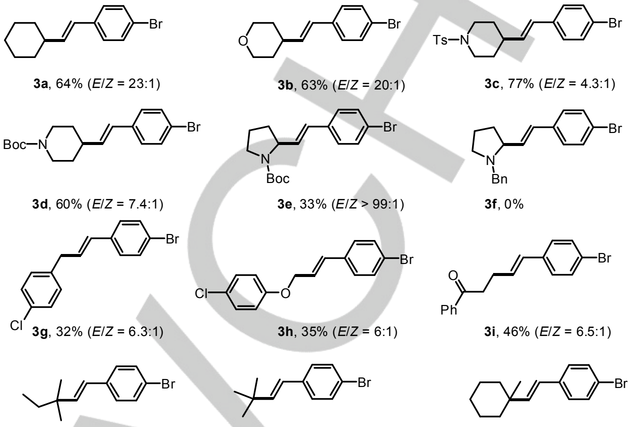
[a] Reaction conditions: **1a** (0.25 mmol, 1.0 equiv), **2a** (0.375 mmol, 1.5 equiv), additives and *fac*-Ir(ppy)$_3$ (1 mol%), in 2.5 mL of solvent at room temperature were irradiated by a 23 W compact fluorescent light (CFL) bulb for 36 h under N_2, *E*/*Z* = 23:1, the *E*/*Z* ratio was determined by ^{1}HNMR spectroscopy of the crude product. [b] Yield of isolated product. [c] Phthalimide was isolated as the major byproduct in 97% yield. [d] No photocatalyst. [e] In the dark. [f] Under air.

(Table 1). To our delight, the desired decarboxylative coupling product **3a** was isolated in 42% yield in the presence of 1 mol% *fac*-Ir(ppy)$_3$ as photocatalyst (Table 1, entry 1).[14] Other Ir(III) complexes such as Ir(ppy)$_2$dtbbpy were less effective than the *fac*-Ir(ppy)$_3$ catalyst. In contrast, Ru(bpy)$_3$Cl$_2$, Cu(dap)$_2$Cl and some representative organic dyes including Eosin Y, Fluorescein, Rhodamine B and 1,6-bis(dimethylamino)pyrene were completely inactive (See the Supporting Information). Solvent screening revealed that NMP/H_2O (4:1, NMP = *N*-methylpyrrolidone) was superior to other mixed solvents (entries 1-6). Changing the ratio of NMP/H_2O from 4:1 to 1:4 did not significantly affect the yield of product **3a** (entry 7). It was found that using NMP as the sole solvent also resulted in a similar yield compared (entry 9). To further enhance the reaction efficiency, some additives were next examined. Satisfactorily, addition of 1.0 equiv of $Mg(ClO_4)_2$ significantly enhanced the yield of the desired product **3a** (entry 10).[15] However, other magnesium salts were found to be inferior for this transformation (entries 11-13). Increasing the amount of $Mg(ClO_4)_2$ to 2.0 equiv further enhanced the yield to 64%, while further increasing the amount of additive led to a diminished yield (entries 14 and 15). Other Lewis or Brønsted acids such as $AlCl_3$, $ZnCl_2$, AcOH or HCl were also tested, but none of them gave higher yields than $Mg(ClO_4)_2$. Furthermore, benziodoxole reagent (BIOH) was also proved to be ineffective for this reaction (see the Table S1 in Supporting Information). A series of contrast experiments revealed that both the photocatalyst and light were essential for the success of this decarboxylative coupling reaction (entries 16 and 17). Of note, the reaction must be carried out under an inert atmosphere (entry 18).

With the optimal reaction conditions in hand, we then examined the scope of the *N*-hydroxyphthalimide esters in the coupling with 4-bromocinnamic acid **2a** (Table 2). The reactions of various alkyl NHP esters proceeded efficiently to afford the desired products **3** in moderate to good yields with good to excellent *E*/*Z* selectivity (Table 2). Satisfactorily, secondary alkyl NHP esters containing heteroatoms (O or N) on the aliphatic ring also worked well to give the desired products in good yields (**3b**-**3d**). It is noteworthy that the protecting groups on the N atom exhibited a significant influence on the reaction efficiency. For example, *N*-Boc- and *N*-Ts-protected substrates underwent the decarboxylation process smoothly to furnish the corresponding products **3c** and **3d** in 77% and 60% yields, respectively. However, Bn-protected substrate **1f** was inactive toward this photoredox catalytic system. Besides secondary NHP esters, the primary esters **1g**-**i** were also effective substrates for this reaction, albeit with relatively low yields. Notably, the carbonyl group also survived in this procedure (**3i**). Compared with the primary and secondary esters, the tertiary alkyl NHP esters showed higher catalytic reaction activity, delivering the products **3j**-**l** in 66-78% yields.

Table 2. Scope of N-Hydroxyphthalimide Esters.



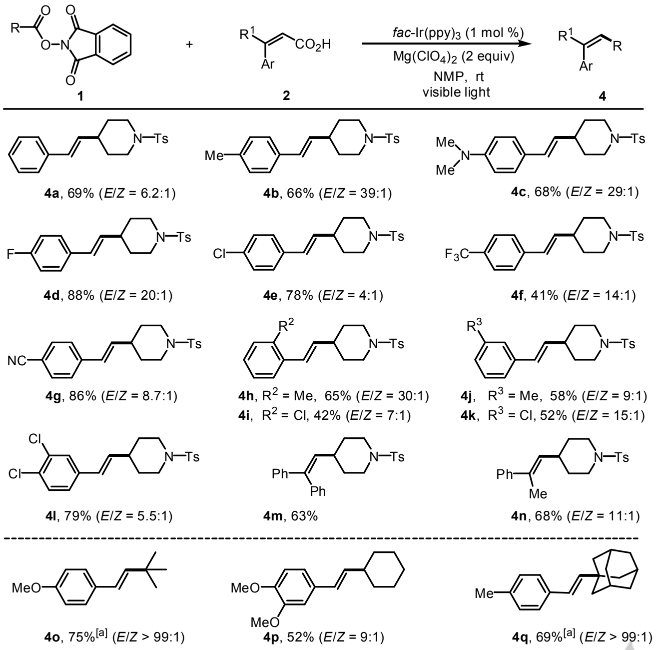


3a, 64% (*E*/*Z* = 23:1)
3b, 63% (*E*/*Z* = 20:1)
3c, 77% (*E*/*Z* = 4.3:1)
3d, 60% (*E*/*Z* = 7.4:1)
3e, 33% (*E*/*Z* > 99:1)
3f, 0%
3g, 32% (*E*/*Z* = 6.3:1)
3h, 35% (*E*/*Z* = 6:1)
3i, 46% (*E*/*Z* = 6.5:1)
3j, 72%[a] (*E*/*Z* > 99:1)
3k, 78%[a] (*E*/*Z* > 99:1)
3l, 66%[a] (*E*/*Z* > 99:1)

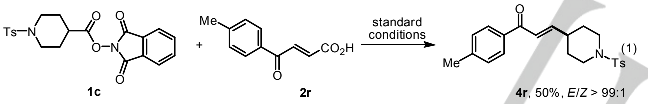
[a] 1.0 equiv of $Mg(ClO_4)_2$ was used.

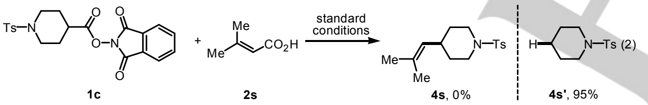
Subsequently, we explored the scope of acrylic acids **2** in this decarboxylative reaction. As given in Table 3, a wide range of cinnamic acids bearing electron-donating and -withdrawing groups at the *para*-position of the phenyl ring all reacted smoothly with **1d** to give the corresponding alkenes **4b-g** in satisfied yields. More importantly, some functional groups such as dimethylamino (**4c**), halogens (**4d** and **4e**), and cyano (**4g**) were well tolerated. Furthermore, the sterically congested *ortho*-substituted cinnamic acids were also suitable substrates, furnishing the corresponding products **4h** and **4i** in 65% and 42% yields, respectively. In addition, *meta*-substituted (**2j** and **2k**) and disubstituted (**2l**) cinnamic acids also resulted in satisfactory yields. Furthermore, the cinnamic acid was successfully extended to other α,β-unsaturated carboxylic acids such as 3,3-diphenylacrylic acid (**2m**) and 3-methyl-3-phenylacrylic acid (**2n**), providing the corresponding trisubstituted alkenes **4m** and **4n** in 63% and 68% yields, respectively. The alkyl NHP esters **1** could also react smoothly with different cinnamic acids to give the 1,2-disubstituted alkenes **4o-q** in moderate to good yields. To our delight, 3-(4-methylbenzoyl)-2-propenoic acid (**2r**) was also an effective substrate in this protocol, and the desired product **4r** was isolated in 50% yield [Eq. (1)]. In contrast, when 3,3-dimethylacrylic acid (**2s**) was subjected to the reaction, only *N*-(*p*-tolylsulfonyl)piperidine (**4s'**) was isolated as major product and no desired coupled product **4s** was detected [Eq. (2)].[16]

Table 3. Scope of α,β-Unsaturated Carboxylic Acids and N-Hydroxyphthalimide Esters.

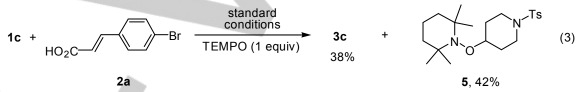


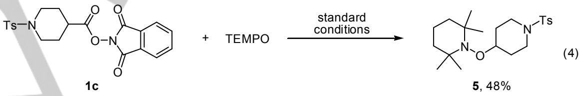
[a] 1.0 equiv of $Mg(ClO_4)_2$ was used.

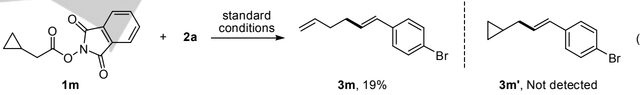


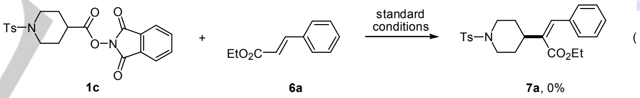


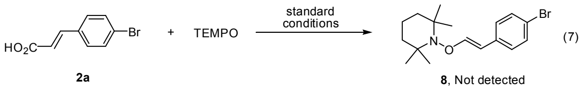
To gain mechanistic insight into this process, some control experiments were conducted (Also see the Supporting Information). As shown in Eq. 3, when TEMPO, a typical radical scavenger was added to the reaction of **1c** with **2a**, **3c** was obtained in only 38% yield, along with 42% yield of alkyl-TEMPO adduct **5** isolated. In addition, the reaction of TEMPO with redox-active ester **1c** also directly afforded the adduct **5** in 48% yield [Eq. (4)]. These results suggest that alkyl radical intermediate might be involved in this transformation. Moreover, treatment of cyclopropylmethyl substituted NHP ester **1m** with **2a** under the standard conditions furnished the ring-opening product **3m** in 19% yield [Eq. (5)]. The formation of **3m** also suggests a radical process. It should be mentioned that the alkyl substituted cinnamic acid could not be detected in all cases under the optimized reaction conditions. Furthermore, when ethyl cinnamate **6a** was employed instead of the cinnamic acid, no reaction occurred, indicative of the necessity of the COOH group [Eq. (6)]. Given the strong reduction potential of the catalyst *fac*-$Ir(ppy)_3$ ($E_{1/2}^{IV/*III}$ = -1.73 V vs. SCE), it is sufficient to reduce the ester **1a** ($E_{1/2}^{red}$ = -1.2 V vs. SCE in MeCN) to afford an alkyl radical.[8-10,17] Meanwhile, cinnamic acid can not be oxidized by the excited *Ir (III) complex ($E_{1/2}^{*III/II}$ = +0.31 V vs. SCE)[14] because of their comparatively high oxidation potentials (for cinnamic acid **2b**, $E_{1/2}^{ox}$ = +2.01 V vs. SCE in MeCN).[17] In addition, treatment of vinyl carboxylic acid **2a** with TEMPO under standard conditions did not afford any alkene-TEMPO adduct [Eq. (7)], which excludes a vinyl radical intermediate through direct decarboxylation of cinnamic acids in this transformation.[12] Based on these results and previous reports,[8-11] a possible reaction mechanism was proposed in Scheme 1. Initially, the photocatalyst PC is excited to a strongly reducing excited state (PC*) by visible light irradiation. Next, a single electron transfer (SET) from this species to NHP esters **1** generates PC^+ and a radical anion **I**, which then fragments followed by extrusion of CO_2, thereby producing an alkyl radical and the phthalimide anion **II**. Subsequently, the alkyl radical attacks the C=C bond of acrylic acids **2** to give the radical **III**. Deprotonation of **III** with **II** to give phthalimide and β-radical carboxylate **IV**, which might be oxidized by PC^+ to a radical **V**. Then intermediate **V** could release CO_2 to deliver the desired product. Oxidative quenching of *fac*-$Ir(ppy)_3$ generates the oxidizing species ($[Ir(ppy)_3]^+$ ($E_{1/2}^{IV/III}$ = 0.77 V vs. SCE),[14] which is suited to single-electron oxidation of radical anion **IV** to deliver the radical intermediate **V** (for alkyl carboxylate, $E_{1/2}^{ox}$ = +0.80 ~ +1.2 V vs. SCE).[7b,18]

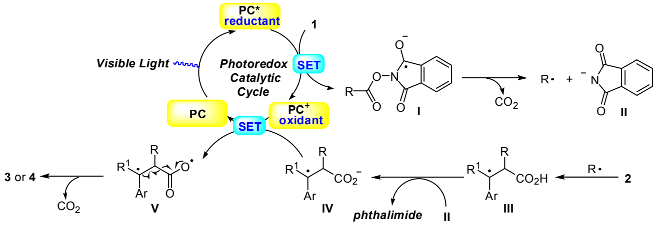












Scheme 1. Proposed Mechanism.

In summary, we have realized an efficient visible-light-mediated redox-neutral, and decarboxylative coupling between the alkyl NHP esters and α,β-unsaturated carboxylic acids. This sequential decarboxylation procedure provided a facile and efficient method for the preparation of structurally diverse alkenes. Remarkably, this redox-neutral protocol features mild conditions, simple operation, good functional group tolerance and good to excellent stereoselectivity.

Experimental Section

Representative Procedure for the Decarboxylative Coupling of α,β-Unsaturated Carboxylic Acids with Redox-Active Esters

A 10 mL oven-dried Schlenk-tube equipped with a magnetic stir bar under a nitrogen atmosphere was charged with *fac*-Ir(ppy)$_3$ (1.64 mg, 1 mol%) and Mg(ClO$_4$)$_2$ (0.5 mmol, 2.0 equiv). Then NHP ester **1** (0.25 mmol, 1.0 equiv), α,β-unsaturated carboxylic acids **2** (0.375 mmol, 1.5 equiv) in 2.5 mL of NMP were added by syringe. The tube was then sealed and the mixture was stirred under the irradiation of a 23 W compact fluorescent light (CFL) bulb at room temperature for 36 h. The mixture was then quenched with H_2O and transferred to a separatory funnel with EtOAc (2 mL). The aqueous layer was extracted with EtOAc (3 x 5 mL), then the organic phases were combined and washed with brine (10 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/100 to 1/50) to give the corresponding products **3** or **4** in yields listed in Table 2 and 3.

Acknowledgements

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Keywords: Photoredox Catalysis • Visible Light • Decarboxylative Coulping • Redox-Active Esters • α,β-Unsaturated Carboxylic Acids

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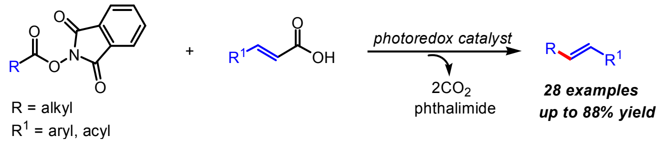

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