Visible-Light-Driven Reductive Carboarylation of Styrenes with CO₂ and Aryl Halides

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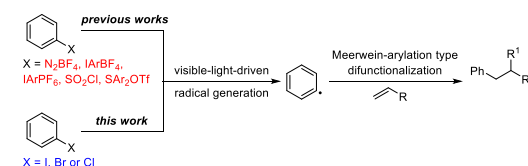*Supporting Information Placeholder*

ABSTRACT: The first example of visible-light-driven reductive carboarylation of styrenes with CO_2 and aryl halides in a regioselective manner has been achieved. A broad range of aryl iodides and bromides were compatible with this reaction. Moreover, pyridyl halides, alkyl halides and even aryl chlorides were also viable with this method. These findings may stimulate the exploration of novel visible-light-driven Meerwein arylation-addition reactions with user-friendly aryl halides as the radical sources and the photocatalytic utilization of CO_2.

Scheme 1. Visible-light-driven Difunctionalization of Alkenes

(a) visible-light-driven Meerwein-arylation type alkene difunctionalization

(b) visible-light-driven alkene carboxylative difunctionalization with CO_2 (*previous works*)

(c) visible-light-driven alkene carboarylation using aryl halides with CO_2 (*this work*)

Visible-light-driven photoredox catalysis (PRC) has proven to be a powerful method to access complex organic molecules under mild reaction conditions.[1] Difunctionalization of alkenes is a fruitful research filed that is valuable for building molecular complexity in a highly efficient manner, which could be achieved through PRC processes besides transition-metal-catalyzed or other radical-mediated pathways.[2-6] Particularly, the visible-light-driven Meerwein-arylation-type difunctionalization of alkenes, which generally utilizes aryl radical sources from aryl diazonium salts, diaryliodonium salts, arylsulfonyl chlorides and so on, has recently received much attention (Scheme 1a) and was pioneered by König.[1a,2,3] However, aryl halides, which are bench-stable, inexpensive and widely available, have not been successfully employed in this type of reaction to date.[1a,2,3] One of the challenges could be it is difficult to generate highly reactive aryl radicals from aryl halides with visible-light since much higher negative reduction potential is required for aryl halides than aryl diazonium salts, diaryliodonium salts or arylsulfonyl chlorides.[1a,2,7-9]

In recent years, the photocatalytic utilization of carbon dioxide (CO_2), which is an ideal one-carbon (C1) building block and sustainable, abundant, low-cost and nontoxic as well, has been a research topic of great interest in fine chemical synthesis.[10-13] Notably, a limited number of redox-neutral photocatalytic difunctionalizations of alkenes with CO_2 were achieved to provide rapid access to carboxylic acids that are important motifs in a number of biologically active molecules (Scheme 1b).[10] Consequently, visible-light-induced regioselective carbocarboxylation, silacarboxyaltion, phosphonocarboxylation as well as thiocarboxylation of alkenes have been developed with CO_2 and various radical precursors by the groups of Martin,[10a] Yu[10b,d] and Wu[10c]. However, these redox-neutral protocols should not be applicable for developing three-component carboarylation of alkenes with CO_2 and aryl halides, since a novel highly-reducing protocol is probably necessary for utilizing aryl halides in such type of visible-light-driven reaction. Due to this challenge, the Meerwein-arylation-type carboarylation
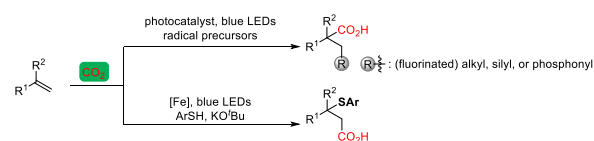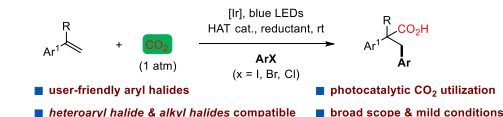
of alkenes with CO_2 via visible-light PRC has not been realized so far.[14,15] Inspired by previous studies by König,[2a,9d] Stephenson,[7a] Jui,[7h,i] and other groups,[7-9] herein, we report the development of the first visible-light-driven reductive carboarylation of styrenes with CO_2 and aryl halides in a highly regioselective manner using the readily available and low-cost HCO_2K as the terminal reductant, leading to the rapid access to valuable hydrocinnamic acid derivatives.[16] Notably, the scope of aryl halides is very broad, and pyridyl halides, alkyl halides and even aryl chlorides are also compatible with this reaction (Scheme 1c).

To start our investigation, 1,1-diphenylethylene was employed as the model substrate, which reacted with iodobenzene under 30 W blue LEDs irradiation in the presence of commercially available [Ir(ppy)₂(dtbbpy)]PF₆ photocatalyst (PC) and an atmospheric pressure of CO_2 at ambient temperature (Table 1, see Supporting Information (SI) for photocatalyst optimization). After extensive investigation of the reaction conditions, the desired carboarylation product **1** was produced regioselectively in a 78% isolated yield in the presence of the hydrogen atom transfer (HAT) catalyst DABCO with HCO_2K as the terminal reductant and K_2CO_3 as the base in DMSO (entry 1). It should be mentioned that for the ease of analysis and product isolation, the original carboxylic acid product was converted to a methyl ester. Importantly, no product was detected

in the absence of either a photocatalyst or light, demonstrating the reaction was induced by light (entries 2 and 3). Slight decrease in the yield was observed when the reaction was carried out under nitrogen atmosphere (entry 4), suggesting that CO_2 could be also formed from oxidation of HCO_2K or possibly the acidification of K_2CO_3.[15j,17a] Notably, not any product can be detected without adding HCO_2K, which was the vital terminal reductant (entry 5, see SI for other reductant tested).[7a,i,17b-d] However, DABCO was also crucial for the reaction (entry 6), and it acted better than other amine HAT catalysts (entries 7-9). These results might suggest the combination of HCO_2K/DABCO is an effective electron donor for this reductive carboarylation. Moreover, it was found that K_2CO_3 was only slightly beneficial for the reaction (entry 10), and other bases such as Na_2CO_3 and Cs_2CO_3 were equally effective (entries 11 and 12). Finally, solvents were also evaluated, and DMSO was found to be the best out of a variety of solvents such as DMF and DMA (entries 13 and 14).

With the optimized reaction conditions in hand, the generality of this carboarylation was investigated with a variety of aryl iodides and bromides as well as some representative alkyl halides with 1,1-diphenylethylene (Table 2). First, cheaper bromobenzene was only slightly less effective than iodobenzene (**1**). Notably, a large number of substituents that are electron-donating such as methyl, methoxy and methylthio groups, or electron-withdrawing such as fluoro, choloro, boronate, trifluoromethyl, carbonyl and cyano groups were tolerated in this reaction without much difference in reactivity (**2**-**33**), delivering the target products in generally good yields. However, aryl iodides worked better than their bromide counterparts for some substrates with electron-donating groups such as halides for products **2**-**5**. Similarly, aryl bromides worked much better

Table 1. Optimization of Reaction Conditions[a]
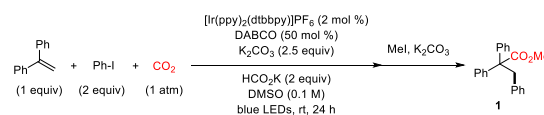
Entry	Deviation from standard conditions	Yield [%][b]
1	none	82 (78)[c]
2	without [Ir(ppy)$_2$(dtbbpy)]PF$_6$	N.D.
3	in the dark	N.D.
4	under a nitrogen atmosphere	76
5	without HCO$_2$K	N.D.
6	without DABCO	3
7	quinuclidine instead of DABCO	33
8	quinuclidin-3-yl acetate instead of DABCO	6
9	trisobutylamine instead of DABCO	64
10	without K$_2$CO$_3$	76
11	Na$_2$CO$_3$ instead of K$_2$CO$_3$	82
12	Cs$_2$CO$_3$ instead of K$_2$CO$_3$	82
13	DMF instead of DMSO	21
14	DMA instead of DMSO	13

[a]Reaction conditions: 1,1-diphenylethylene (0.2 mmol), iodobenzene (0.4 mmol), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (2 mol %), DABCO (0.1 mmol), K$_2$CO$_3$ (0.5 mmol), HCO$_2$K (0.4 mmol), DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs, rt, 24 h; then MeI (2.0 mmol), K$_2$CO$_3$ (1.0 mmol), acetone (10 mL), 70 °C, 2 h. [b]Yield was determined by ^{1}H NMR with CH$_2$Br$_2$ as internal standard. [c]Yield of isolated products in parentheses. DABCO = triethylenediamine; N.D. = not detected.

Table 2. Scope of of Aryl Halides and Alkyl Halides[a]
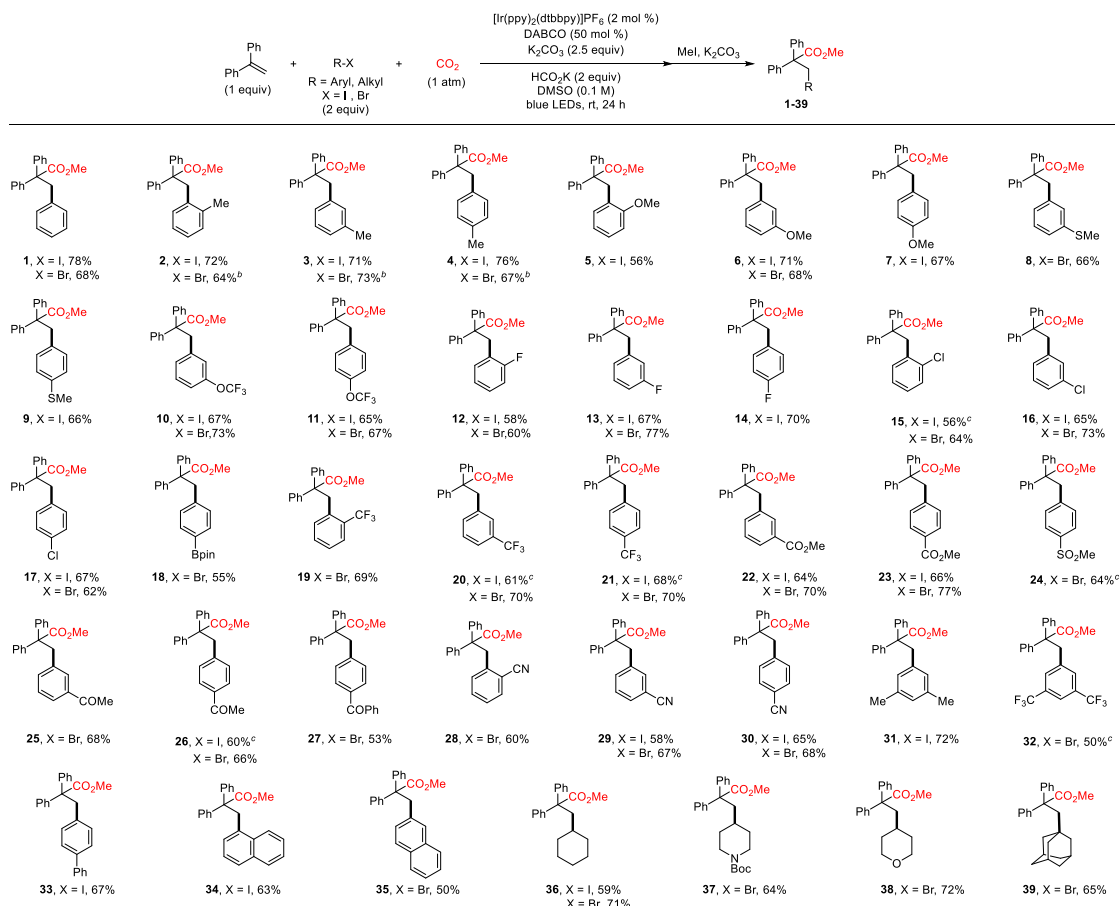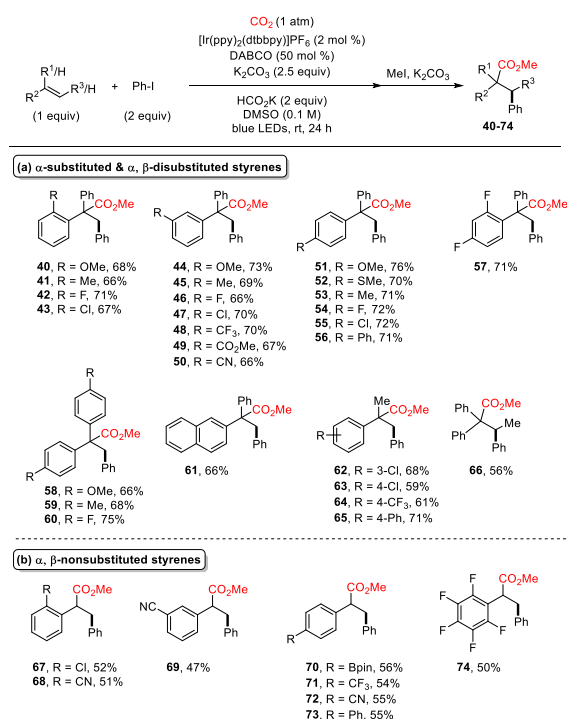

[a]Reaction conditions: standard conditions (Table 1, entry 1). [b]48h. [c]Trisobutylamine (50 mol %) was used instead of DABCO.

than their iodide counterparts for some substrates with electron-withdrawing groups such as bromides for products **25**, **28** and **32**. Moreover, *ortho*-substituted aryl halides generally gave lower yields than their *meta*- and *para*-substituted counterparts such as **5**-**7**, **12**-**14** and **28**-**30**. In addition, iodo- and bromonaphthalenes were also viable in this reaction (**34** and **35**). It is noteworthy that the aryl iodides/bromides bearing a chloro or boronate group were feasible for our carboarylation (**15**-**18**), leaving the opportunity for further derivatization. Stimulated by the success in using aryl halides, we examined the feasibility of alkyl halides. Pleasingly, representative secondary alkyl halides (**36**-**38**) proceeded smoothly under the optimized conditions. Finally, tertiary bromide (**39**) could also be employed in this method. However, primary halides did not work well at present.

The scope of styrenes was studied subsequently (Table 3). The α-substituted styrenes including α-methyl styrenes (**62**-**65**) were excellent substrates (**40**-**65**), regardless of the electronic nature and the position of substituents on the aromatic ring. Notably, hindered α,β-disubstituted styrene (**66**) also delivered the expected products in a moderate yield. However, α,β-nonsubstituted styrene derivatives were less effective, leading to generally moderate yields of products with electron-deficient substrates (**67**-**74**). Notably, synthetically useful boronate group (**70**) was also tolerated. However, aliphatic alkenes were not compatible with this method at this stage.

Table 3. Scope of Styrenes[a]

(a) α-substituted & α, β-disubstituted styrenes

40, R = OMe, 68%
41, R = Me, 66%
42, R = F, 71%
43, R = Cl, 67%

44, R = OMe, 73%
45, R = Me, 69%
46, R = F, 66%
47, R = Cl, 70%
48, R = CF₃, 70%
49, R = CO₂Me, 67%
50, R = CN, 66%

51, R = OMe, 76%
52, R = SMe, 70%
53, R = Me, 71%
54, R = F, 72%
55, R = Cl, 72%
56, R = Ph, 71%

57, 71%

58, R = OMe, 66%
59, R = Me, 68%
60, R = F, 75%

61, 66%

62, R = 3-Cl, 68%
63, R = 4-Cl, 59%
64, R = 4-CF₃, 61%
65, R = 4-Ph, 71%

66, 56%

(b) α, β-nonsubstituted styrenes

67, R = Cl, 52%
68, R = CN, 51%

69, 47%

70, R = Bpin, 56%
71, R = CF₃, 54%
72, R = CN, 55%
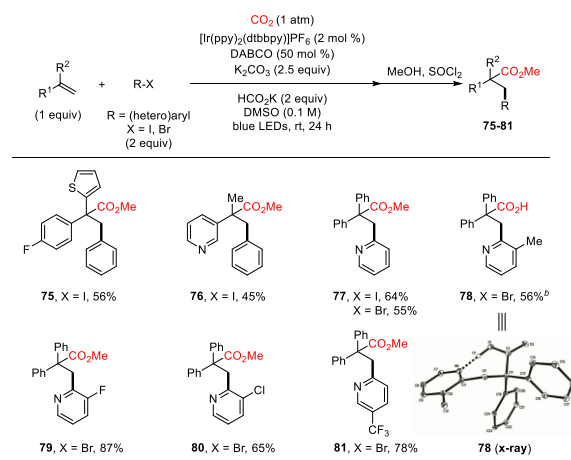**73**, R = Ph, 55%

74, 50%

[a]Reaction conditions: standard conditions (Table 1, entry 1).

In light of these results, we turned our attention to test heterocyclic substrates, especially the challenging electron-deficient pyridyl halides. As shown in Table 4, alkenes with a thiofuryl or pyridyl group could afford the desire products (**75** and **76**) in modest yields. Remarkably, this reaction also proceeded efficiently with several pyridyl halides to give corresponding products (**77**-**81**) in generally good yields. In addition, unambiguous proof of the structure of **78** was achieved by single-crystal X-ray analysis.

To demonstrate the potential of this reaction, we tested the viability of aryl chlorides that are generally much less reactive in visible-light driven photocatalytic reactions (Table 5).[7i,9c,d,l-n,q]

Table 4. Scope of Heterocyclic Substrates[a]

75, X = I, 56%

76, X = I, 45%

77, X = I, 64%
X = Br, 55%

78, X = Br, 56%[b]

79, X = Br, 87%

80, X = Br, 65%

81, X = Br, 78%

78 (x-ray)

[a]Reaction conditions: standard conditions (Table 1, entry 1); methylation conditions (**75** used standard conditions): SOCl₂ (0.4 mL), MeOH (4 mL), 100 ºC, 6 h, see SI for details. [b]The methyl ester of **78** was transferred to acid **78** while isolating with silical gel.

Table 5. Scope of Aryl Chlorides[a]

19, 48%[b]

23, 70%

24, 62%

28, 64%

29, 54%

30, 72%

81, 68%[c]

82, 56%[c]
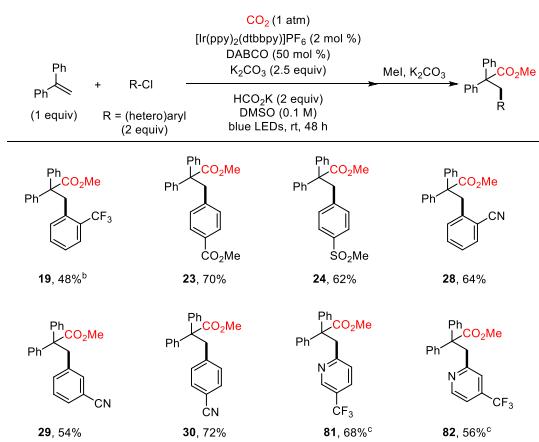
[a]Reaction conditions: standard conditions (Table 1, entry 1) in 48 h. [b]4 equiv aryl chloride were employed. [c]methylation conditions: SOCl₂ (0.4 mL), MeOH (4 mL), 100 ºC, 6 h, see SI for details.

Remarkably, the carboarylation could be successfully extended to several electron-deficient (hetero)aryl chlorides that are often much cheaper than corresponding bromides and iodides (Table 5).

To determine the carboxyl source of the product, ¹³CO₂ (99% ¹³C) gas was employed and 74% ¹³C incorporation was found in the carboxyl of the product, indicating that CO_2 is mainly from the CO_2 gas but part of the CO_2 could be generated from HCO_2K or K_2CO_3 (Scheme 2a). Moreover, the reaction could be easily scaled up to 5 mmol without significant decrease in the yield of **1** (Scheme 2b).

Finally, the proposed mechanism for the carboarylation process is depicted in Scheme 3 based on Stern-Volmer luminescence studies (see SI) and previous reports.[7a,b,10a,13i] Upon blue light irradiation, the excited PC* (**A**) is produced and subsequently quenched reductively by DABCO to give radical anion of PC (**B**) and radical cation of DABCO (see SI for Stern-Volmer luminescence studies). Then an electron is transferred from **B** to the aryl halide, leading to an aryl radical (**C**) by scission of the C−X bond. The aryl radical undergoes regioselective addition to alkene affording a benzyl radical (**D**), which can be reduced to a benzyl anion (**E**) by **B**.[10a,13i] Then **E** undergoes nucleophilic addition to CO_2 to produce the carboxylate **F** which was then converted to methyl ester after methylation.

Scheme 2. Determination the Source of CO₂ and the Scaled-up Reaction.

(a) reaction using ¹³CO₂

(b) gram-scale synthesis
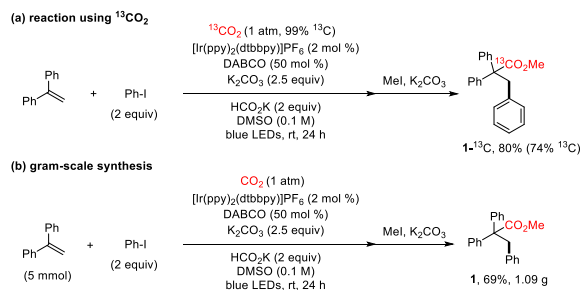
Scheme 3. Proposed Catalytic Cycle.
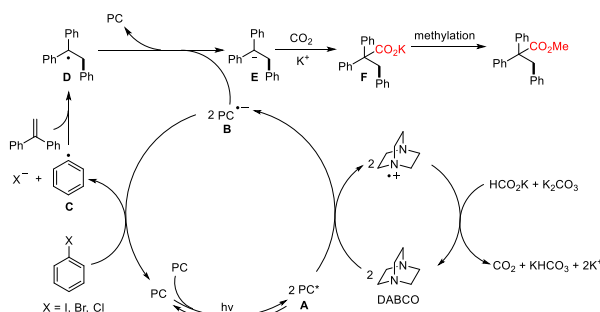
In conclusion, we have developed the first effective reductive protocol of regioselective visible-light-driven carboarylation of styrenes with CO_2 and aryl halides, leading to an efficient method for producing valuable hydrocinnamic acid derivatives. Notably, this highly-reducing protocol allows the use of a wide range of aryl halides, including electron-deficient and low-cost aryl chlorides. Moreover, pyridyl halides as well as alkyl halides were also viable with this method. These findings may open up a new opportunity for exploring novel visible-light-driven Meerwein type arylation-addition reactions employing user-friendly aryl halides as the radical sources, as well as developing new photocatalytic utilization reactions of CO_2. Further exploration of this discovery is under way in our laboratory and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization data for new compounds (PDF)

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Notes

The authors declare no competing financial interests.

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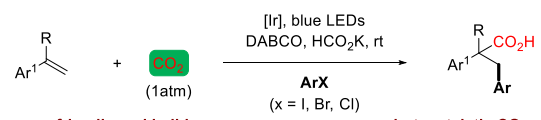
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Ar^1—C(R)=CH₂ + CO₂ (1atm) → [Ir], blue LEDs; DABCO, HCO₂K, rt; ArX (x = I, Br, Cl) → Ar¹—C(R)(CO₂H)—CH₂—Ar

- ■ **user-friendly aryl halides**
- ■ *heteroaryl halide & alkyl halides* **compatible**
- ■ **photocatalytic CO₂ utilization**
- ■ **broad scope & mild conditions**