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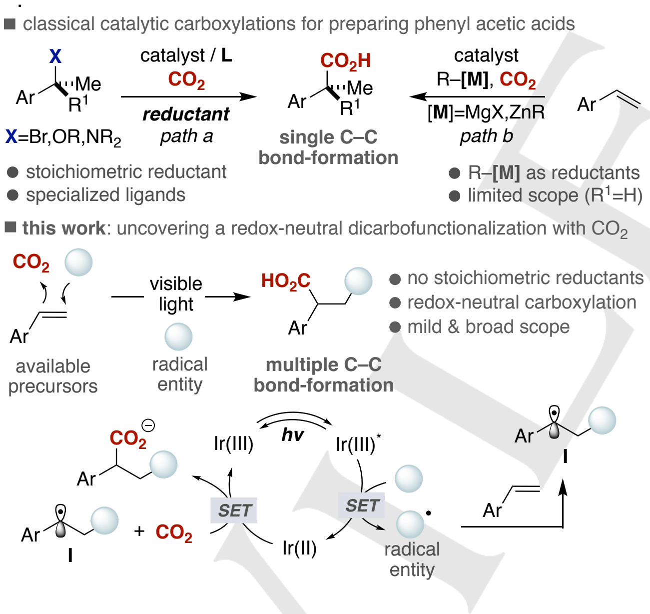
# Catalytic Intermolecular Dicarbofunctionalization of Styrenes with $CO_2$ and Radical Precursors

Veera Reddy Yatham, Yangyang Shen and Ruben Martin*

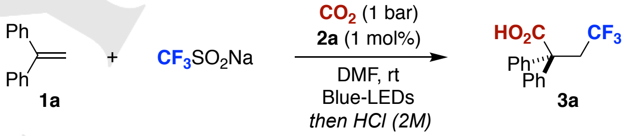
**Abstract:** A redox-neutral intermolecular dicarbofunctionalization of styrenes with $CO_2$ at atmospheric pressure and carbon-centered radicals is described. This mild protocol results in multiple C–C bond-forming reactions from simple precursors in the absence of stoichiometric reductants, thus exploiting a previously unrecognized opportunity that complements existing catalytic carboxylation events.

Driven by the abundance and inherent synthetic potential of carbon dioxide ($CO_2$) as C1 source,[1] chemists have been challenging to design catalytic C–C bond-formations en route to carboxylic acids, privileged motifs in a myriad of molecules that display significant biological properties.[2] Despite the considerable advances realized, the catalytic synthesis of valuable phenylacetic acids from $CO_2$ as C1 source remains confined to *single C–C bond formations* by using stoichiometric metal reductants with organic (pseudo)halides (Scheme 1, *path a*)[3,4] or stoichiometric amounts of well-defined, air-sensitive, organometallic reagents with styrenes as coupling counterparts (*path b*).[5] Unfortunately, specialized ancillary ligands are required in the former[4] whereas a limited set of substitution patterns are within reach in the latter,[5] thus reinforcing the need for a change in strategy.

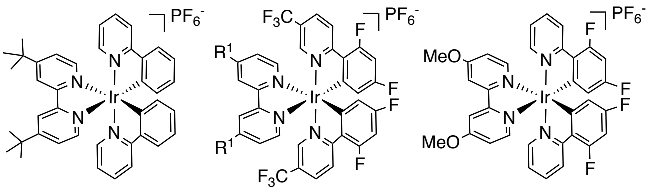


**Scheme 1.** Catalytic preparation of phenyl acetic acids from $CO_2$

As part of our ongoing interest in Ni-catalyzed reductive carboxylation techniques with $CO_2$,[6,7] we questioned whether a new design principle complementary to conventional carboxylation protocols with improved flexibility and versatility en route to phenyl acetic acids could ever be implemented. In particular, we speculated that a redox-neutral mechanism[8] might enable an intermolecular dicarbofunctionalization of styrenes with simple radical precursors via the intermediacy of **I** (Scheme 1, *bottom*), thus offering new vistas for an atom-economical incorporation of $CO_2$ into organic matter.[9] If successful, such a scenario might unravel a multifaceted challenge, not only providing the synergistic merger of visible light photoredox catalysis and $CO_2$ with $\pi$-systems,[10,11] but also offering an unrecognized opportunity in catalytic carboxylations to enable multiple, intermolecular C–C bond-formations.[12,13] Herein, we report the successful realization of this goal. This protocol operates at atmospheric pressure of $CO_2$ without the need for organic (pseudo)halides[4] or stoichiometric reductants.[5 The method is characterized by its mild conditions and wide substrate scope with a range of different radical precursors and/or styrenes possessing a diverse set of substitution patterns



| Entry | Deviation from standard conditions | **3a** (%)[a] |
|---|---|---|
| ***1*** | ***none*** | ***90** (86)[b]* |
| 2 | **2b** instead of **2a** | 29 |
| 3 | **2c** instead of **2a** | 50 |
| 4 | **2d** instead of **2a** | 57 |
| 5 | THF instead of DMF | 40 |
| 6 | DMSO instead of DMF | 70 |
| 7 | MeCN instead of DMF | 18 |
| 8 | PhMe instead of DMF | 56 |
| 9 | No **2a** | 0 |
| 10 | In the dark | 0 |



**2a**

**2b** (R = H),
**2c** (R = *t*-Bu)

**2d**

**Scheme 2.** Optimization of the reaction conditions. **1a** (0.20 mmol), $CF_3SO_2Na$ (0.24 mmol), Ir photocatalyst (1 mol%), $CO_2$ (1 bar), DMF (0.10 M) at rt for 15 h, followed by HCl (2M) quench. [a] NMR yields using $PhCF_3$ as internal standard. [b] Isolated yield. Redox potentials of Ir photocatalysts: **2a** ($E_{red}$ [$Ir^{III}/Ir^{II}$] = -1.51V *vs* SCE in MeCN); **2b** ($E_{red}$ [$Ir^{III}/Ir^{II}$] = -1.37V *vs* SCE in MeCN); **2c** ($E_{red}$ [$Ir^{III}/Ir^{II}$] = -1.37V *vs* SCE in MeCN); **2d** ($E_{red}$ [$Ir^{III}/Ir^{II}$] = -1.41V *vs* SCE in MeCN).

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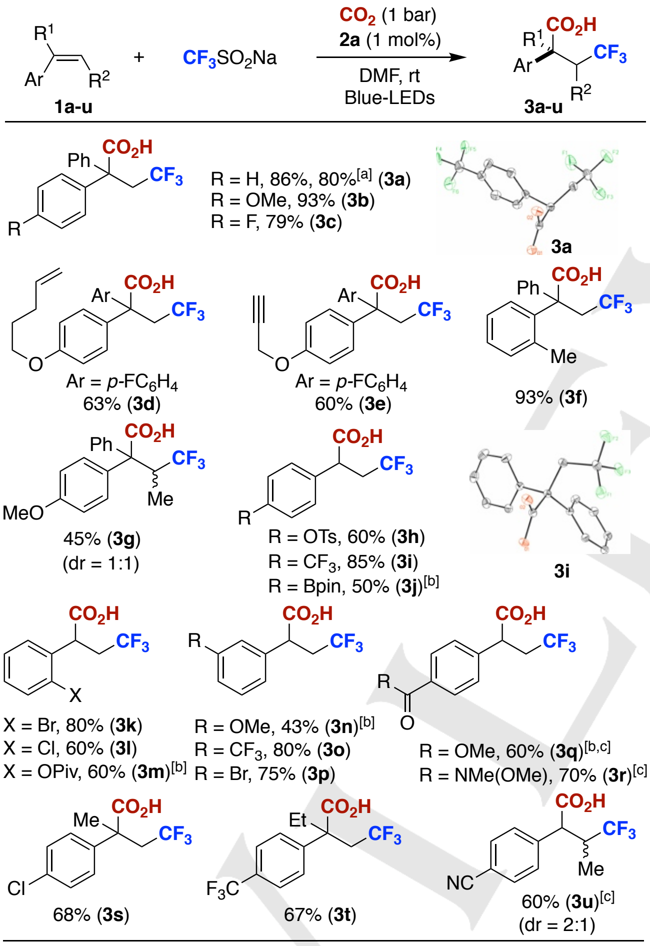
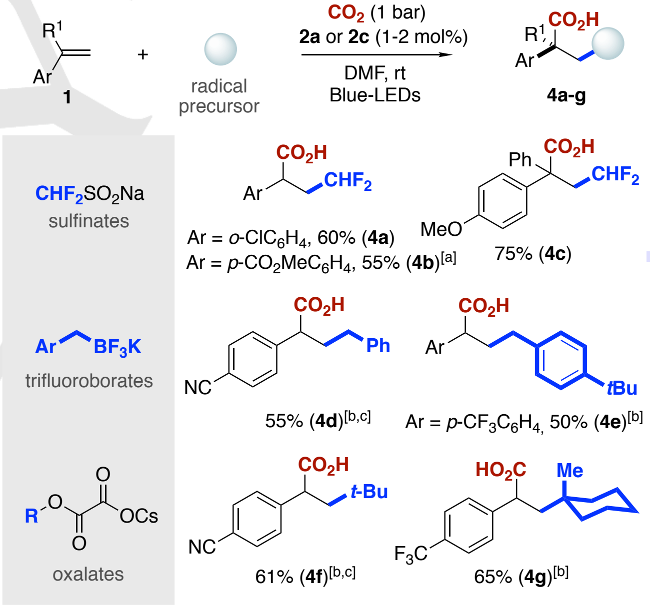
Prompted by the inherent interest of perfluorinated alkyl groups in drug discovery, particularly the trifluoromethyl group,[14] our investigations started by studying the catalytic redox-neutral trifluoromethylcarboxylation reaction of **1a** with Langlois reagent ($CF_3SO_2Na$) and $CO_2$ (1 bar) under blue light-emitting diodes (LEDs) irradiation at room temperature (Scheme 2).[15,16] As anticipated, the nature of the photocatalyst markedly influenced the reaction outcome, with **2a** providing the best results (entry 1).[17] Intriguingly, the use of **2b-2d** resulted in significant lower yields of **3a**. These findings might be interpreted on the basis of a more efficient SET from the reduced photocatalyst **2a** $E_{red}$ [$Ir^{III}/Ir^{II}$] = -1.51V *vs* SCE in MeCN)[18] to 1,1-diphenyl 3,3,3-trifluoropropane radical ($E_{red}$ = –1.34V *vs* SCE in MeCN)[19] prior to $CO_2$ insertion (Scheme 1, *bottom*).[20] As shown in entries 5-8, the employment of solvents other than DMF had a deleterious effect, resulting in lower yields of **3a**. Rigorous control experiments revealed that all of the reaction parameters were crucial for the transformation to occur; indeed, not even traces of **3a** were found in the absence of light or **2a** (entries 9 and 10).



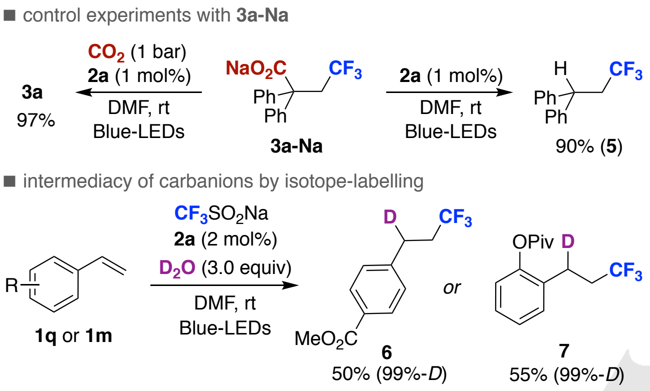
**Scheme 3.** Redox-neutral trifluoromethylcarboxylation of styrenes. Reaction conditions: as in Scheme 2 (entry 1). Isolated yields, average of at least two independent runs. [a] Reaction performed at 1.0 mmol scale (**1a**). [b] **2a** (2 mol%), $CF_3SO_2Na$ (2.0 equiv) in DMF at 5 ºC for 15 h. [c] Isolated as the corresponding methyl ester upon exposure to $TMSCHN_2$.

Encouraged by these results, we turned our attention to examine the generality of our trifluoromethylcarboxylation with **2a** and $CF_3SO_2Na$ (Scheme 3).[21,22] As shown, a host of differently substituted styrene derivatives could be used for our purposes. Particularly noteworthy was the observation that the reaction could be equally extended to α- or β-substituted styrenes, with the former resulting in quaternary carbon centers (**3a-3g, 3s** and **3t**). These findings certainly constitute a bonus when compared to classical hydrocarboxylation reactions with $CO_2$ that require either stoichiometric reductants or a rather limited set of substitution patterns on the styrene backbone.[5,11] The chemoselectivity profile of our trifluoromethylcarboxylation was illustrated by the tolerance of a variety of functional groups such as alkenes (**3d**),[23] alkynes (**3e**), nitriles (**3u**), esters (**3m, 3q**) or amides (**3r**), delivering the targeted phenyl acetic acids in good to excellent yields. While the use of aryl chlorides (**3l, 3s**), bromides (**3k**, **3p**), tosylates (**3h**) or even aryl pivalates (**3m**) as coupling partners have become routine,[24] including related carboxylation events,[25] we found that the presence of these electrophilic sites did not compete with the efficacy of our reaction. Similarly, aryl boronates did not interfere, albeit in lower yields (**3j**).[26] These observations are particularly noteworthy, providing ample room for further derivatization via either C–B or C-X (X = Br, Cl, OTs or OPiv) bond-cleavage, suggesting the viability for implementing orthogonal cross-coupling techniques. Importantly, the reaction can be conducted at 1 mmol scale without a significant erosion in yield of **3a**.



**Scheme 4.** Dicarbofunctionalization of styrene derivatives using a diverse set of carbon-centered radical precursors. Reaction conditions: as in Scheme 2 (entry 1). Isolated yields, average of at least two independent runs. [a] **2a** (2 mol%), $CHF_2SO_2Na$ (2.0 equiv) at 5 ºC. [b] **2c** (2 mol%). [c] Isolated as the methyl ester upon exposure to $TMSCHN_2$.

In light of these results, we wondered whether our redox-neutral dicarbofunctionalization reaction of styrenes with $CO_2$ could be extended to radical precursors other than $CF_3SO_2Na$.[27] As shown in Scheme 4, this turned out to be the case. Specifically, we found that difluoromethyl-containing phenyl acetic acids are easily within reach when using $CHF_2SO_2Na$ under otherwise identical reaction conditions to those shown for $CF_3SO_2Na$ (**4a-4c**). In light of these results, we questioned whether non-fluorinated radical analogues could also be used for similar purposes. Indeed, we found that easily accessible benzyl trifluoroborates ($E_{ox}$ = +1.1V *vs* SCE in MeCN)[28] and *tert*-butyl oxalates ($E_{ox}$ = +1.28V *vs* SCE in MeCN)[29] could be employed in our dicarbofunctionalization reaction. In this case, however, the more strongly oxidizing photocatalyst **2c** ($E_{red}$ [$Ir^{III*}/Ir^{II}$] = +1.21V *vs* SCE in MeCN) was required, cleanly delivering **4d-4g** in moderate to good yields.[30] Taken together, the results compiled in Schemes 3 and 4 stand as a testament to the prospective potential of redox-neutral catalysis for enabling dicarbofunctionalization reactions of π-components with $CO_2$ and radical precursors, representing a different, yet complementary, reactivity mode to existing catalytic carboxylation events.[31] We anticipate that these findings might open up new vistas for effecting otherwise inaccessible coupling processes involving $CO_2$ as coupling partner.



**Scheme 5.** Preliminary mechanistic studies

The efficiency of our dicarbofunctionalization of styrenes with $CO_2$ prompted us to conduct preliminary mechanistic studies (Scheme 5). As anticipated, "light-dark" experiments confirmed that our reaction required continuous visible light irradiation.[17] Stern-Volmer luminiscence studies demonstrated that the excited stated of **2a** was quenched by $CF_3SO_2Na$ ($E_{ox}$ = +1.05V *vs* SCE in MeCN)[15c] but not by **1a** ($E_{ox}$ = +1.81V *vs* SCE in MeCN).[17,19a,32] These results suggested the involvement of a reductive quenching photocatalytic cycle, in which a transient carbon-centered radical, generated upon single electron transfer (SET) with the excited state of the photocatalyst, is added across the styrene backbone. A subsequent SET from the reduced photocatalyst to **I** (Scheme 1, *bottom*) might give rise to a benzylic carbanion that rapidly reacts with $CO_2$.[33,34] Although control experiments *in the absence* of $CO_2$ resulted in competitive decarboxylation from **3a-Na** ($E_{ox}$ = +1.05V *vs* SCE in MeCN),[35] trace amounts of **5**, if any, were observed *in the presence* of $CO_2$ (Scheme 5, *top pathways*). The intermediacy of transient benzyl anionic species via SET from the reduced photocatalyst **2a** was indirectly confirmed by isotope-labelling studies (Scheme 5, *bottom*). Specifically, **6** and **7** (99%-*D*) were exclusively obtained upon exposure of **1m** and **1q** to $CF_3SO_2Na$ under visible light irradiation with **2a** and $D_2O$ in the absence of $CO_2$, thus ruling out the participation of hydrogen atom transfer (HAT) with DMF. Note, however, that the available data do not allow us to rigorously rule out an alternative mechanistic scenario in which the transient benzyl radical intermediate reacts reversibly with $CO_2$ followed by SET from the reduced photocatalyst **2a** to the carboxyl radical intermediate, leading the final sodium carboxylate. Further mechanistic studies to unravel the intricacies of this transformation are ongoing.

In summary, we have documented a catalytic intermolecular dicarbofunctionalization of styrenes with $CO_2$ as C1 source and radical precursors. This mild and versatile protocol offers a reactivity principle that is complementary to classical catalytic carboxylations, unlocking previously inaccessible scenarios in the carboxylation arena based on multiple C–C bond-forming events from π-components and in the absence of stoichiometric reductants. Further work along these lines is currently underway in our laboratories.

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**Keywords:** carbon dioxide • radical • catalysis • C–C bond-formation • difunctionalization

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[30] The lower yields found for **4d**-**4g** account for unreacted starting material, reduced product upon HCl quench and dimerization.

[31] Unfortunately, the use of unactivated $\alpha$-olefins such as 1-octene or 4-phenyl-1-butene as coupling partners resulted in recovered starting material as well as reduced trifluoromethylated products.

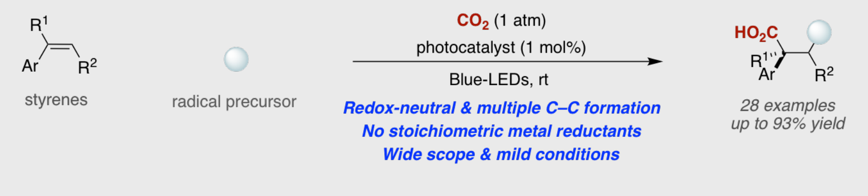
[32] At present, we believe that the reaction is likely driven by the rapid addition of CF$_3$ radical across the styrene and the formation of two strong C–C sigma bonds.

[33] A. J. Musacchio, L. Q. Nguyen, G. H Beard, R. R. Knowles. *J. Am. Chem. Soc.* **2014**, *136*, 12217-12220.

[34] Our results suggest that the addition of CF$_3$ radicals to styrenes is considerably faster than a possible reduction to CF$_3$ anion by the reduced Ir(II) photocatalyst. Notably, traces of benzylic dimerization were observed, indicating a lower concentration of benzyl radicals in solution under CO$_2$ atmospheres.

[35] For selected photoredox decarboxylation techniques: (a) L. Candish, M. Teders, F. Glorius, *J. Am. Chem. Soc.* **2017**, *139*, 7440-7443. (b) C. P. Johnston, R. T. Smith, S. Allmendinger, D. W. C. MacMillan, *Nature* **2016**, *536*, 322-325. (c) Z. Zuo, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 5257-5260. (d) Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle, D. W. C. MacMillan, *Science* **2014**, *345*, 437-440. The carboxylation of **1a** was not inhibited in the presence of **3a-Na**.

# COMMUNICATION



A catalytic, redox-neutral dicarbofunctionalization of readily available styrenes with $CO_2$ at atmospheric pressure has been developed. This mild protocol unlocks a previously inaccessible scenario that enables dicarbofunctionalization reactions of π-components with $CO_2$ and radical precursors without stoichiometric reductants, thus offering a complementary reactivity mode to existing carboxylation events.

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**Title**

**Catalytic intermolecular dicarbofunctionalization of styrenes with $CO_2$ and radical precursors**