Visible-Light-Driven Alkene Dicarboxylation with Formate and CO_2 Under Mild Conditions

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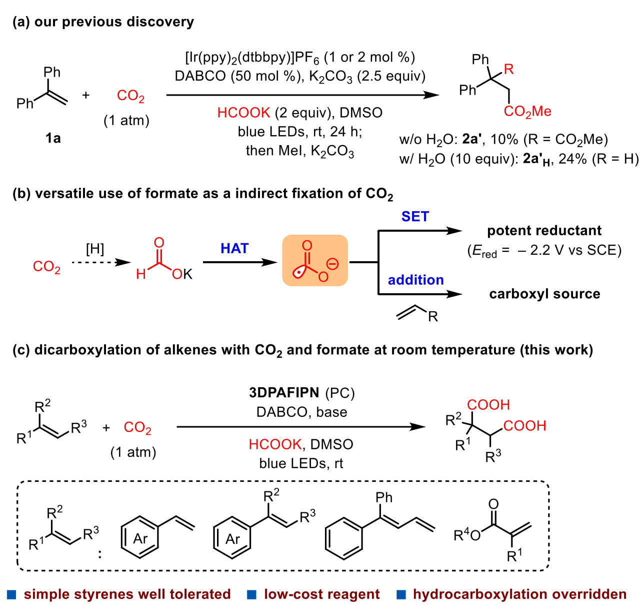
ABSTRACT: The low-cost formate salt was used as the reductant and part of the carboxyl source in a visible-light-driven dicarboxylation of diverse alkenes, including simple styrenes. The highly competing hydrocarboxylation side reaction was successfully overridden. Good yields of products were obtained under mild reactions at ambient temperature and pressure of CO_2. The dual role of formate salt may stimulate the discovery of a range of new transformations under mild and friendly conditions.

INTRODUCTION

Over the past decade, great progress has been made in the catalytic utilization of carbon dioxide (CO_2) using visible light.[1] However, many of these transformations require the use of stoichiometric reductant. Recently, we developed an arylcarboxylation of alkenes with CO_2 using formate salt as a low-cost terminal reductant and also as part of the CO_2 source.[2] In this study, it was first realized that the CO_2 radical anion ($CO_2^{\bullet-}$) ($E_{1/2}(CO_2/CO_2^{\bullet-}) = -2.2$ V vs SCE),[3] readily available from the formate via hydrogen atom transfer (HAT), could be used as a potent reductive intermediate for direct reduction of substrates in visible-light-induced organic synthesis, avoiding the need to generate a highly reductive photocatalyst (PC). This discovery has been employed in a series of photocatalytic reactions involving challenging reduction of substrates recently.[4-6] Moreover, in the control experiments of this work, we also discovered dicarboxylation and hydrocarboxylation of alkene **1a** in the absence of an aryl halide (Scheme 1a).[2] Afterwards, the groups of Jui,[4a] Wickens,[7] Li,[8] and Mita[9] also proved that $CO_2^{\bullet-}$ generated from formate could act as a source of carboxyl via Giese-type radical addition to alkenes and (hetero)aromatics to deliver hydrocarboxylation reactions.[10.11] Since formate could potentially be produced from CO_2, e.g. via hydrogenation, photoreduction and electroreduction,[12] the use of formate for the dicarboxylation of alkenes to produce diacids can be considered as an attractive indirect method for CO_2 fixation (Scheme 1b).[13]

Diacids such as succinic acid derivatives are important core structures of many bioactive molecules and useful monomers for polymers.[14] The production of diacids using CO_2 as the carboxyl source is a sustainable strategy, but only limited methods have been developed to date.[15] Traditionally, electrochemical dicarboxylation of alkenes with CO_2 has been investigated, but these processes generally require a sacrificial anode.[15,16] In addition, Martin and co-workers reported a Ni-catalyzed site-selective dicarboxylation of 1,3-dienes with CO_2, which used stoichiometric Mn as the reductant.[17] In 2021, the group of Yu reported an elegant dicarboxylation of alkenes with CO_2 via a sequential single electron transfer (SSET) process, in which the reduction of the alkene substrate to a radical anion intermediate was the key step.[18] Recently, the same group disclosed a remote dicarboxylation of alkene and benzylic C(sp^3)–H bond via an intramolecular HAT.[19] However, amine terminal reductants were necessary for these two transformations. Given the challenge of direct CO_2 reduction[3,15,20] and the low cost of the formate salt that possessed dual role in our preliminary results of dicarboxylation (Scheme 1a,b),[2] we envisioned using the formate for alkene dicarboxylation to obtain diacids in a redox-economical and practical manner.[21]

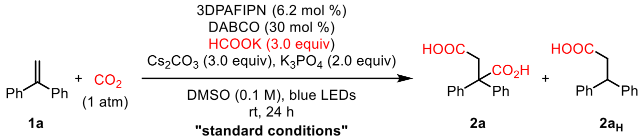
Scheme 1. The Development of Dicarboxylation of Alkenes with Formate and CO_2



Herein, we report a visible-light-induced dicarboxylation of diverse alkenes with CO_2 using formate as a low-cost reductant and part of the carboxyl source. Notably, simple styrenes were well tolerated, and the reaction could be performed under mild conditions at ambient temperature and pressure of CO_2. Importantly, the highly competing hydrocarboxylation side reaction was successfully overridden.

RESULTS AND DISCUSSION

Table 1. Optimization of Reaction Conditions[a]



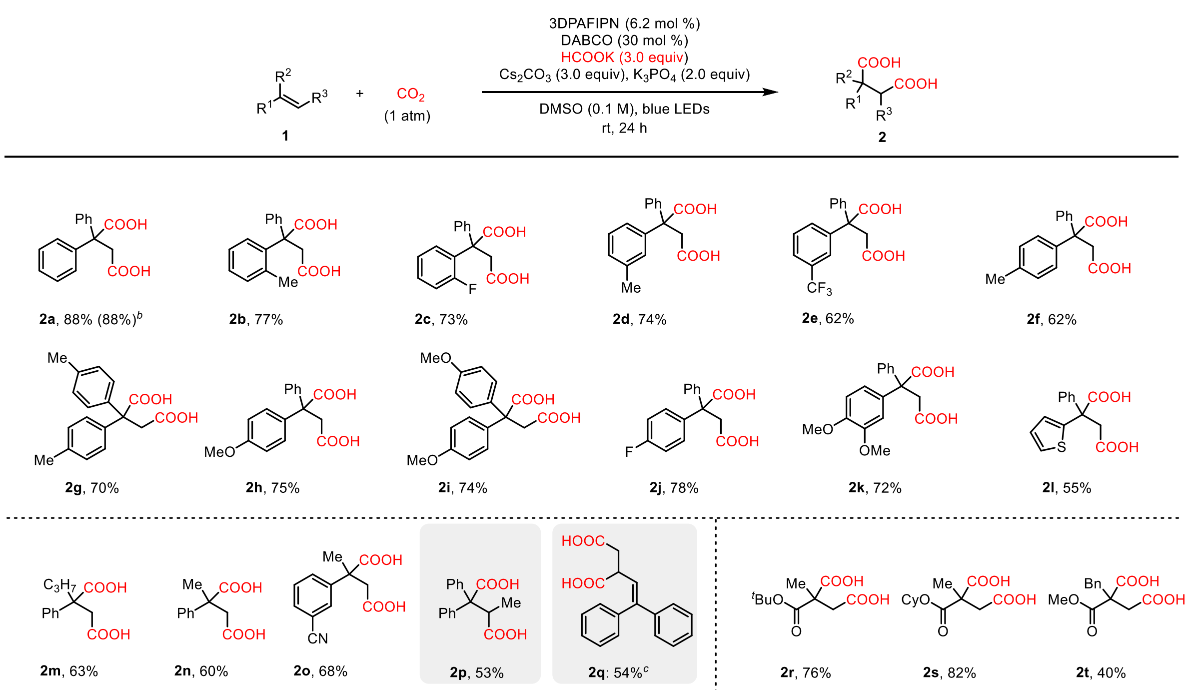
entry	deviations from standard conditions	**2a** yield [%]	**2a$_H$** yield [%]
1	none	91%[b]	--
2	in the dark	--	--
3	w/o 3DPAFIPN	--	--
4	w/o HCOOK	--	--
5	w/o DABCO	32%	28%
6	w/o CO_2 (N_2 atmosphere)	--	76%
7	w/o K_3PO_4	40%	12%
8	w/o Cs_2CO_3; K_3PO_4 (3 equiv)	44%	50%
9	w/o Cs_2CO_3 and K_3PO_4	11%	66%
10	HCOONa instead of HCOOK	70%	--
11	quinuclidine instead of DABCO	40%	--
12	4DPAIPN instead of 3DPAFIPN	65%	--
13	4CzIPN instead of 3DPAFIPN	39%	--
14	3DPAFIPN (2.0 mol %)	70%	--
15	3DPAFIPN (4.0 mol %)	86%	--
16	THF instead of DMSO	16%	--
17	DMA instead of DMSO	17%	--

[a]Reaction conditions: **1a** (0.2 mmol), 3DPAFIPN (6.2 mol %), DABCO (0.06 mmol), Cs_2CO_3 (0.6 mmol), K_3PO_4 (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs, rt (25-33 ºC), 24 h; then treated with 2 mL of HCl (2 N). Yield was determined by ^{1}H NMR with CH_2Br_2 as internal standard. [b]Isolated yield was 88%. 3DPAFIPN = 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile; DABCO = triethylenediamine.

Our investigation began with using 1,1-diphenylethylene (**1a**) as the model substrate, which was treated with 30 W blue LEDs irradiation in the presence of a PC and an atmospheric pressure of CO_2 at ambient temperature (Table 1). After extensive investigation of the reaction conditions, the desired dicarboxylation product **2a** was generated in an 88% isolated yield using 3DPAFIPN as the PC in the presence of the HAT catalyst DABCO with HCOOK as the terminal reductant and Cs_2CO_3 and K_3PO_4 as the cooperative bases in DMSO (entry 1).[22] No product was found in the absence of either visible light or the PC, indicating the reaction was a photocatalytic reaction (entries 2 and 3). Importantly, HCOOK was essential for the reaction (entry 4). Surprisingly, in the absence of DABCO, a modest yield of the desired product **2a** was obtained along with some hydrocarboxylation side-product **2a$_H$**, suggesting that more than one HAT processes might be involved in this reaction (entry 5). Interestingly, only hydrocarboxylation product was received under nitrogen atmosphere without adding CO_2 (entry 6), suggesting HCOOK was also one of the carboxyl sources. Moreover, the addition of suitable bases was important to achieve a high yield of the desired product (entries 7-9, also see Supporting Information (SI) for screening of other bases). Other formates such as HCOONa were also used, but they were less effective than HCOOK (entry 10). Other HAT catalysts such as quinuclidine were also evaluated, but they were inferior to DABCO (entry 11).[23] Other PCs such as 4DPAIPN and 4CzIPN were also tested, but worse results were obtained (entries 12 and 13). In addition, lower yields were delivered while reducing the loading of 3DPAFIPN (entries 14 and 15). Finally, DMSO was the best solvent of all those used such as THF and DMA (entries 16 and 17).

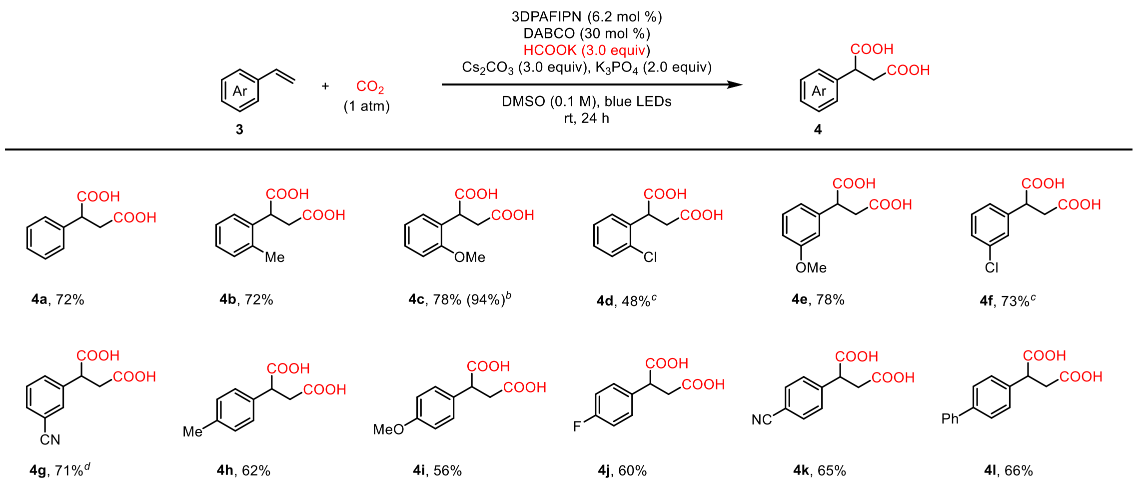
With the optimized reaction conditions in hand, we first examined this protocol with a variety of 1,1-disubstituted ethylenes (Table 2). Good to excellent yields of desired dicarboxylation products were received with model substrate **1a** and mono- or di-substituted 1,1-diarylethylenes bearing a list of functional groups at *ortho*-, *meta*- or *para*-positions of the phenyl groups (**2a**-**2k**). Both electron-donating methyl (**2b**, **2d**, **2f**, and **2g**), methoxy (**2h**, **2i**, and **2k**) substituents and electron-

Table 2. Scope of 1,1-disubstituted ethylenes and acrylates[a]



[a]Reaction conditions: **1** (0.2 mmol), 3DPAFIPN (6.2 mol %), DABCO (0.06 mmol), Cs_2CO_3 (0.6 mmol), K_3PO_4 (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs, rt (25-33 ºC), 24 h; then treated with 2 mL of HCl (2 N). Isolated yields. [b]Yield of 1 mmol scale reaction (52 h). [c]Major product 3,4-dicarboxylation product (**2q$_a$**, 37%) displayed; minor product: 1,4-dicarboxylation product (**2q$_b$**, 17%).

Table 3. Scope of Styrenes[a]



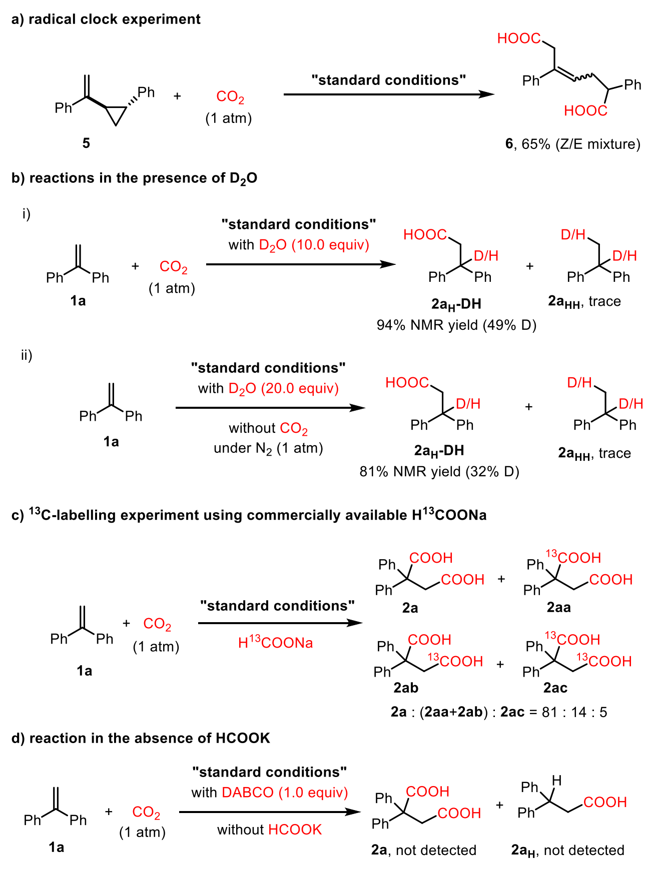
[a]Reaction conditions: **3** (0.2 mmol), 3DPAFIPN (6.2 mol %), DABCO (0.06 mmol), Cs_2CO_3 (0.6 mmol), K_3PO_4 (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs, rt (25-33 ºC), 24 h; then treated with 2 mL of HCl (2 N). Isolated yields. [b]Reaction temperature: 40-45 ºC. [c]Desired product displayed; de-chlorination product (18% for **4d**, 16% for **4f**) not shown. [d]About 6% hydrocarboxylation side product.

withdrawing fluoro (**2c** and **2j**), trifluoromethyl (**2e**) ones were tolerated. Moreover, thiofuran group was also compatible with this method. Other di-substituted ethylenes (**2m**, **2n**, and **2o**) and even a tri-substituted one (**2p**) were also viable to deliver acceptable yields of products. Note that the reaction with a diene substrate (**1q**) would give both 3,4-dicarboxylation and 1,4-dicarboxylation products. Finally, good results were obtained with methacrylates (**2r** and **2s**), although only a modest yield was obtained with a 2-benzylacrylate (**2t**).

We then moved on to investigate the scope of the more challenging simple styrenes, leading to generally good yields with a variety of substituted styrenes regardless of the electronic property and the position of the substituent on the aromatic ring. It should be noted that in Zhu's work, only very narrow scope of simple styrenes were tolerated with low yields.[22] As shown in Table 3, the un-substituted styrene **3a** and the *ortho*-substituted styrenes with electron-donating methyl (**3b**) and methoxyl (**3c**) groups proceeded smoothly and gave good yields of the desired products. Notably, the yield of **4c** could be increased to 94% by slightly elevating the reaction temperature to 40-45 ºC. Moderate yield was obtained with substrate **3d** bearing an *ortho*-chloro group, since some de-chlorination occurred. In addition, both electron donating (**4e**) and withdrawing (**4f** and **4g**) groups were well tolerated at the *meta*-position. Finally, good results were also obtained with substrates containing several representative substituents at the *para*-position of the phenyl ring (**4h**-**4l**). It is noteworthy that the hydrocarboxylation side product was not detected or only in trace amounts, and only substrate **3g** led to 6% of the hydrocarboxylation side product.

To obtain insights into the reaction mechanism, several control experiments were then carried out (Scheme 2). Ring-opening product **6** was afforded in the radical clock experiment, indicating a benzyl radical might be generated after $CO_2^{\bullet-}$ addition to the alkene (Scheme 2a). When the reaction was run in the presence of D_2O, hydrocarboxylation product **2a$_H$-DH** was produced instead of dicarboxylation with traces of reduction product **2a$_{HH}$**, indicating the formation of a benzylic anion intermediate and that the formation of anion at the alkene terminal position was trivial (Scheme 2bi). Similar results were received while the reaction was carried out without the addition of CO_2 gas (Scheme 2bi). The low deuteration ratio at the benzylic position in these two reactions (49% and 32%, respectively) might suggest a HAT process between benzylic radical and formate was also involved except the protonation of the benzylic anion under current reaction conditions. In addition, four possible dicarboxylation products were obtained when using ^{13}C-labelled formate (i.e. commercially available $H^{13}COONa$),[24] suggesting

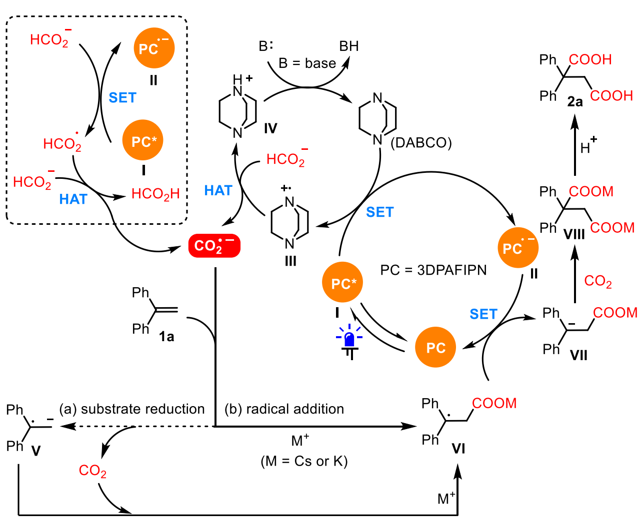
Scheme 2. Mechanistic Study Experiments



formate was also part of the carboxyl source (Scheme 2c). Moreover, no carboxylation products were detected when the reaction was performed using a stoichiometric amount of DABCO without formate, indicating the reduced 3DPAFIPN could not reduce the substrate **1a** or CO_2 to initiate the reaction (Scheme 2d). Finally, the Stern-Volmer quenching experiments showed the activated catalyst (PC*) was mainly quenched by DABCO, but it could also be slightly quenched by HCOOK (see SI).

Based on the above mechanistic studies, a possible catalytic cycle was proposed (Scheme 3). Upon blue light irradiation, the excited PC* (**I**) is generated and then quenched by DABCO to form $PC^{\bullet-}$ (**II**) ($E_{1/2}$ ($PC^*/PC^{\bullet-}$) = +1.09 V vs SCE in MeCN)[25] and radical cation of DABCO (**III**). A HAT between radical **III** and HCO_2^- produces $CO_2^{\bullet-}$ and cation **IV**. Alternatively, $CO_2^{\bullet-}$ can be partially generated by a HAT process between HCO_2^- and $HCO_2^{\bullet}$ that is produced by reducing PC* with HCO_2^- (E_{ox} ($HCO_2^{\bullet}/HCO_2^-$) = +1.25 V vs SCE),[4b] considering the results of Stern-Volmer quenching experiments with formate (see Figure S5 of SI) and the fact that some product could be received without DABCO (see entry 5 in table 1). Subsequently, $CO_2^{\bullet-}$ may reduce the substrate (E^o = −2.25 V vs SCE for **1a**)[26] to give radical anion **V**, considering product **2a** was the major product in the ^{13}C-labelling experiment of Scheme 2c. However, the direct addition of $CO_2^{\bullet-}$ to the double bond of **1a** to afford intermediate **VI** is more likely based on the results in Scheme 2b. In this scenario, a potential facile electron transfer between $^{13}CO_2^{\bullet-}$ and the excess CO_2 may account for the observation of **2a** as the main product in Scheme 2c. Moreover, since the reduction of simple styrenes ($E_{1/2}$ = −2.58 V vs SCE in DMF for **3a**)[27] is more demanding than **1a**, direct $CO_2^{\bullet-}$ addition is possibly the predominant pathway for substrates in Table 3. The radical intermediate **VI** was then reduced by $PC^{\bullet-}$ (**II**) to give the anion **VII**, which undergoes nucleophilic attack of CO_2 to afford the final product **2a** after acidification of the salt intermediate **VIII**.

Scheme 3. Proposed Catalytic Cycle



CONCLUSIONS

In conclusion, we have developed a visible-light-driven alkene dicarboxylation using formate and CO_2, overriding the highly competing hydrocarboxylation side reaction successfully. Good yields of products were obtained with diverse alkenes including simple styrenes under mild reactions at ambient temperature. The dual role of the low-cost formate as a reductant and the C1 source may open up the discovery of a range of new transformations including indirect utilization of CO_2 under mild and friendly conditions.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/xxxxxx.

Detailed experimental procedures, characterization data for new compounds, and computational study details (PDF)

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REFERENCES

(1) (a) Cao, Y.; He, X.; Wang, N.; Li, H.-R.; He, L.-N. Photochemical and Electrochemical Carbon Dioxide Utilization with Organic Compounds. *Chin. J. Chem.* **2018**, *36*, 644. (b) Tan, F.; Yin, G. Homogeneous Light-Driven Catalytic Direct Carboxylation with CO_2. *Chin. J. Chem* . **2018**, *36*, 545. (c) Zhang, Z.; Ye, J.-H.; Ju, T.; Liao, L. L.; Huang, H.; Gui, Y. Y.; Zhou, W. J.; Yu, D.-G. Visible-Light-Driven Catalytic Reductive Carboxylation with CO_2. *ACS Catal.* **2020**, *10*, 10871. (d) He, X.; Qiu, L.-Q.; Wang, W.-J.; Chen, K.-H.; He, L.-N. Photocarboxylation with CO_2: an appealing and sustainable strategy for CO2 fixation. *Green Chemistry* **2020**, *22*, 7301. (e) Fan, Z.; Zhang, Z.; Xi, C. Light-Mediated Carboxylation Using Carbon Dioxide. *ChemSusChem* **2020**, *13*, 6201. (f) Schmalzbauer, M.; Svejstrup, T. D.; Fricke, F.; Brandt, P.; Johansson, M. J.; Bergonzini, G.; König, B. Redox-Neutral Photocatalytic C−H Carboxylation of Arenes and Styrenes with CO_2. *Chem* **2020**, *6*, 2658. (g) Ye, J.-H.; Ju, T.; Huang, H.; Liao, L.-L.; Yu, D.-G. Radical Carboxylative Cyclizations and Carboxylations with CO_2. *Acc. Chem. Res.* **2021**, *54*, 2518. (h) Cai, B.; Cheo, H. W.; Liu, T.; Wu, J. Light-Promoted Organic Transformations Utilizing Carbon-Based Gas Molecules as Feedstocks. *Angew. Chem. Int. Ed.* **2021**, *60*, 18950. (i) Davies, J.; Lyonnet, J. R.; Zimin, D. P.; Martin, R. The road to industrialization of fine chemical carboxylation reactions. *Chem* **2021**, *7*, 2927. (j) Wang, S.; Konig, B. Catalytic Generation of Carbanions through Carbonyl Umpolung. *Angew. Chem. Int. Ed.* **2021**, *60*, 21624. (k) Bertuzzi, G.; Cerveri, A.; Lombardi, L.; Bandini, M. Tandem Functionalization-Carboxylation Reactions of Π-Systems with CO_2. *Chin. J. Chem.* **2021**, *39*, 3116. (l) Jung, J.; Saito, S. Recent Advances in Light-Driven Carbon–Carbon Bond Formation via Carbon Dioxide Activation. *Synthesis* **2021**, *53*, 3263. (m) Gao, Y.; Wang, H.; Chi, Z.; Yang, L.; Zhou, C.; Li, G. Spirocyclizative Remote Arylcarboxylation of Nonactivated Arenes with CO_2 via Visible-Light-Induced Reductive Dearomatization. *CCS Chem.* **2022**, *4*, 1565.
(2) Wang, H.; Gao, Y.; Zhou, C.; Li, G. Visible-Light-Driven Reductive Carboarylation of Styrenes with CO_2 and Aryl Halides. *J. Am. Chem. Soc.* **2020**, *142*, 8122.
(3) Koppenol, W. H.; Rush, J. D. Reduction potential of the carbon dioxide/carbon dioxide radical anion: a comparison with other C1 radicals. *J. Phys. Chem.* **1987**, *91*, 4429.
(4) For direct reduction of substrates with $CO_2^{\bullet-}$ generated from formate: (a) Hendy, C. M.; Smith, G. C.; Xu, Z.; Lian, T.; Jui, N. T. Radical Chain Reduction via Carbon Dioxide Radical Anion ($CO_2^{\bullet-}$). *J. Am. Chem. Soc.* **2021**, *143*, 8987. (b) Chmiel, A. F.; Williams, O. P.; Chernowsky, C. P.; Yeung, C. S.; Wickens, Z. K. Non-innocent Radical Ion Intermediates in Photoredox Catalysis: Parallel Reduction Modes Enable Coupling of Diverse Aryl Chlorides. *J. Am. Chem. Soc.* **2021**, *143*, 10882. (c) Campbell,

M. W.; Polites, V. C.; Patel, S.; Lipson, J. E.; Majhi, J.; Molander, G. A. Photochemical C-F Activation Enables Defluorinative Alkylation of Trifluoroacetates and -Acetamides. *J. Am. Chem. Soc.* **2021**, *143*, 19648. (d) Liao, L.-L.; Song, L.; Yan, S.-S.; Ye, J.-H.; Yu, D.-G. Highly reductive photocatalytic systems in organic synthesis. *Trends Chem.* **2022**, *4*, 512. (e) Bo, Z.-Y.; Yan, S.-S.; Gao, T.-Y.; Song, L.; Ran, C.-K.; He, Y.; Zhang, W.; Cao, G.-M.; Yu, D.-G. Visible-light photoredox-catalyzed selective carboxylation of C(sp2)−F bonds in polyfluoroarenes with CO_2. *Chin. J. Catal.* **2022**, *43*, 2388. (f) Ye, J. H.; Bellotti, P.; Heusel, C.; Glorius, F. Photoredox-Catalyzed Defluorinative Functionalizations of Polyfluorinated Aliphatic Amides and Esters. *Angew. Chem. Int. Ed.* **2022**, *61*, e202115456. (g) Zhang, M.; Yang, L.; Zhou, C.; Fu, L.; Li, G. Visible-Light-Induced Arylcarboxylation of Enamides with CO_2 and Aryl Iodides to Synthesize α-Amino Acids. *Asian J. Org. Chem.* **2022**, *11*, e202200087. (h) Xu, P.; Wang, X. Y.; Wang, Z.; Zhao, J.; Cao, X. D.; Xiong, X. C.; Yuan, Y. C.; Zhu, S.; Guo, D.; Zhu, X. Defluorinative Alkylation of Trifluoromethylbenzimidazoles Enabled by Spin-Center Shift: A Synergistic Photocatalysis/Thiol Catalysis Process with $CO_2^{\bullet-}$. *Org. Lett.* **2022**, *24*, 4075. (i) Liu, C.; Shen, N.; Shang, R. Photocatalytic defluoroalkylation and hydrodefluorination of trifluoromethyls using o-phosphinophenolate. *Nat. Commun.* **2022**, *13*, 354. (j) Zhou, C.; Wang, X.; Yang, L.; Fu, L.; Li, G. Visible-light-driven regioselective carbocarboxylation of 1,3-dienes with organic halides and CO_2. *Green Chem.* **2022**, *24*, 6100. (k) Wang, B.; Wang, C. T.; Li, X. S.; Sun, W. H.; Liu, X. Y.; Liang, Y.-M. Visible-light-mediated C-F bond cleavage for the synthesis of polyfluorinated compounds. *Org. Chem. Front.* **2023**, *10*, 3341. (l) Zeng, L.; Qin, J. H.; Lv, G. F.; Hu, M.; Sun, Q.; Ouyang, X. H.; He, D. L.; Li, J. H. Electrophotocatalytic Reductive 1,2-Diarylation of Alkenes with Aryl Halides and Cyanoaromatics. *Chin. J. Chem* . **2023**, *41*, 1921.

(5) For previous works on using the formate as a reductant for PC rather than substrate to produce highly reductive PC: (a) Nguyen, J. D.; D'Amato, E. M.; Narayanam, J. M.; Stephenson, C. R. Engaging unactivated alkyl, alkenyl and aryl iodides in visible-light-mediated free radical reactions. *Nat. Chem.* **2012**, *4*, 854. (b) Discekici, E. H.; Treat, N. J.; Poelma, S. O.; Mattson, K. M.; Hudson, Z. M.; Luo, Y.; Hawker, C. J.; Read de Alaniz, J. A highly reducing metal-free photoredox catalyst: design and application in radical dehalogenations. *Chem. Commun.* **2015**, *51*, 11705. (c) Wang, H.; Jui, N. T. Catalytic Defluoroalkylation of Trifluoromethylaromatics with Unactivated Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 163. (d) Boyington, A. J.; Seath, C. P.; Zearfoss, A. M.; Xu, Z.; Jui, N. T. Catalytic Strategy for Regioselective Arylethylamine Synthesis. *J. Am. Chem. Soc.* **2019**, *141*, 4147. (e) Vogt, D. B.; Seath, C. P.; Wang, H.; Jui, N. T. Selective C-F Functionalization of Unactivated Trifluoromethylarenes. *J. Am. Chem. Soc.* **2019**, *141*, 13203.

(6) For generation of $CO_2^{\bullet-}$ via hydride-transfer reduction and HAT: Yan, S.-S.; Liu, S.-H.; Chen, L.; Bo, Z.-Y.; Jing, K.; Gao, T.-Y.; Yu, B.; Lan, Y.; Luo, S.-P.; Yu, D.-G. Visible-light photoredox-catalyzed selective carboxylation of C(sp3)−F bonds with CO_2. *Chem* **2021**, *7*, 3099.

(7) (a) Alektiar, S. N.; Wickens, Z. K. Photoinduced Hydrocarboxylation via Thiol-Catalyzed Delivery of Formate Across Activated Alkenes. *J. Am. Chem. Soc.* **2021**, *143*, 13022. (b) Mikhael, M.; Alektiar, S. N.; Yeung, C. S.; Wickens, Z. K. Translating Planar Heterocycles into Three-Dimensional Analogs by Photoinduced Hydrocarboxylation. *Angew. Chem. Int. Ed.* **2023**, *62*, e202303264. (c) Alektiar, S. N.; Han, J.; Dang, Y.; Rubel, C. Z.; Wickens, Z. K. Radical Hydrocarboxylation of Unactivated Alkenes via Photocatalytic Formate Activation. *J. Am. Chem. Soc.* **2023**, *145*, 10991.

(8) (a) Huang, Y.; Hou, J.; Zhan, L.-W.; Zhang, Q.; Tang, W.-Y.; Li, B.-D. Photoredox Activation of Formate Salts: Hydrocarboxylation of Alkenes via Carboxyl Group Transfer. *ACS Catal.* **2021**, *11*, 15004. (b) Huang, Y.; Zhang, Q.; Hua, L.-L.; Zhan, L.-W.; Hou, J.; Li, B.-D. A versatile catalyst-free redox system mediated by carbon dioxide radical and dimsyl anions. *Cell Rep. Phys. Sci.* **2022**, *3*, 100994. (c) Li, B.; Hou, J.; Zhan, L.; Zhang, Q.; Huang, Y. Hydrocarboxylation of Alkenes with Formate Salts via Photocatalysis. *Chin. J. Org. Chem.* **2022**, *42*.

(9) Mangaonkar, S. R.; Hayashi, H.; Takano, H.; Kanna, W.; Maeda, S.; Mita, T. Photoredox/HAT-Catalyzed Dearomative Nucleophilic Addition of the CO_2 Radical Anion to (Hetero)Aromatics. *ACS Catal.* **2023**, *13*, 2482.

(10) For hydrocarboxylation by generating $CO_2^{\bullet-}$ via other methods rather than using formate: (a) Seo, H.; Liu, A.; Jamison, T. F. Direct beta-Selective Hydrocarboxylation of Styrenes with CO_2 Enabled by Continuous Flow Photoredox Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 13969. (b) Alkayal, A.; Tabas, V.; Montanaro, S.; Wright, I. A.; Malkov, A. V.; Buckley, B. R. Harnessing Applied Potential: Selective beta-Hydrocarboxylation of Substituted Olefins. *J. Am. Chem. Soc.* **2020**, *142*, 1780. (c) Huang, H.; Ye, J.-H.; Zhu, L.; Ran, C.-K.; Miao, M.; Wang, W.; Chen, H.; Zhou, W.-J.; Lan, Y.; Yu, B.; Yu, D.-G. Visible-Light-Driven Anti-Markovnikov Hydrocarboxylation of Acrylates and Styrenes with CO_2. *CCS Chem.* **2021**, *3*, 1746. (d) Kang, G.; Romo, D. Photocatalyzed, β-Selective Hydrocarboxylation of α,β-Unsaturated Esters with CO2 under Flow for β-Lactone Synthesis. *ACS Catal.* **2021**, *11*, 1309. (e) Sheta, A. M.; Alkayal, A.; Mashaly, M. A.; Said, S. B.; Elmorsy, S. S.; Malkov, A. V.; Buckley, B. R. Selective Electrosynthetic Hydrocarboxylation of alpha,beta-Unsaturated Esters with Carbon Dioxide. *Angew. Chem. Int. Ed.* **2021**, *60*, 21832. (f) Wu, Z. G.; Wu, M. Y.; Zhu, K.; Wu, J.; Lu, Y. X. Photocatalytic coupling of electron-deficient alkenes using oxalic acid as a traceless linchpin. *Chem* **2023**, *9*, 978. (g) Yuan, T.; Wu, Z.; Zhai, S.; Wang, R.; Wu, S.; Cheng, J.; Zheng, M.; Wang, X. Photosynthetic Fixation of CO_2 in Alkenes by Heterogeneous Photoredox Catalysis with Visible Light. *Angew. Chem. Int. Ed.* **2023**, *62*, e202304861.

(11) For other hydrocarboxylation reactions: (a) Zhu, C.; Takaya, J.; Iwasawa, N. Use of formate salts as a hydride and a CO_2 source in PGeP-palladium complex-catalyzed hydrocarboxylation of allenes. *Org. Lett.* **2015**, *17*, 1814. (b) Murata, K.; Numasawa, N.; Shimomaki, K.; Takaya, J.; Iwasawa, N. Construction of a visible light-driven hydrocarboxylation cycle of alkenes by the combined use of Rh(i) and photoredox catalysts. *Chem. Commun.* **2017**, *53*, 3098. (c) Takaya, J.; Miyama, K.; Zhu, C.; Iwasawa, N. Metallic reductant-free synthesis of alpha-substituted propionic acid derivatives through hydrocarboxylation of alkenes with a formate salt. *Chem. Commun.* **2017**, *53*, 3982. (d) Gaydou, M.; Moragas, T.; Julia-Hernandez, F.; Martin, R. Site-Selective Catalytic Carboxylation of Unsaturated Hydrocarbons with CO_2 and Water. *J. Am. Chem. Soc.* **2017**, *139*, 12161. (e) Meng, Q. Y.; Wang, S.; Huff, G. S.; Konig, B. Ligand-Controlled Regioselective Hydrocarboxylation of Styrenes with CO_2 by Combining Visible Light and Nickel Catalysis. *J. Am. Chem. Soc.* **2018**, *140*, 3198. (f) Ren, W.; Chu, J.; Sun, F.; Shi, Y. Pd-Catalyzed Highly Chemo- and Regioselective Hydrocarboxylation of Terminal Alkyl Olefins with Formic Acid. *Org. Lett.* **2019**, *21*, 5967.

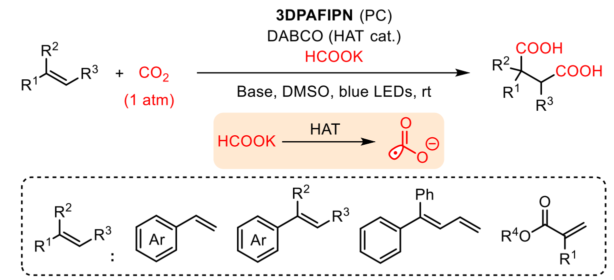
(12) (a) He, M.; Sun, Y.; Han, B. Green carbon science: scientific basis for integrating carbon resource processing, utilization, and recycling. *Angew. Chem. Int. Ed.* **2013**, *52*, 9620. (b) Alvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A. V.; Wezendonk, T. A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO_2 Hydrogenation Processes. *Chem. Rev.* **2017**, *117*, 9804. (c) Philips, M. F.; Gruter, G.-J. M.; Koper, M. T. M.; Schouten, K. J. P. Optimizing the Electrochemical Reduction of CO_2 to Formate: A State-of-the-Art Analysis. *ACS Sustainable Chem. Eng.* **2020**, *8*, 15430. (d) Sampaio, R. N.; Grills, D. C.; Polyansky, D. E.; Szalda, D. J.; Fujita, E. Unexpected Roles of Triethanolamine in the Photochemical Reduction of CO_2 to Formate by Ruthenium Complexes. *J. Am. Chem. Soc.* **2020**, *142*, 2413.

(13) (a) Bushuyev, O. S.; De Luna, P.; Dinh, C. T.; Tao, L.; Saur, G.; van de Lagemaat, J.; Kelley, S. O.; Sargent, E. H. What Should We Make with CO_2 and How Can We Make It? *Joule* **2018**, *2*, 825. (b) Xia, S.-M.; Yang, Z.-W.; Chen, K.-H.; Wang, N.; He, L.-N. Efficient hydrocarboxylation of alkynes based on carbodiimide-regulated in situ CO generation from HCOOH: An alternative indirect utilization of CO_2. *Chin. J. Catal.* **2022**, *43*, 1642. (c) Huang, W.-B.; Yang, M.; He, L.-N. Metal-Free Hydroxymethylation of Indole Derivatives with Formic Acid as an Alternative Way to Indirect Utilization of CO_2. *J. Org. Chem.* **2022**, *87*, 3775. (d) Wang, L.; Neumann, H.; Beller, M. A General, Activator-Free Palladium-Catalyzed Synthesis of Arylacetic and Benzoic Acids from Formic Acid. *Angew. Chem. Int. Ed.* **2018**, *57*, 6910.

(14) (a) Whittaker, M.; Floyd, C. D.; Brown, P.; Gearing, A. J. H. Design and Therapeutic Application of Matrix Metalloproteinase Inhibitors. *Chem. Rev.* **1999**, *99*, 2735. (b) Carnahan, M. A.; Grinstaff, M. W. Synthesis and Characterization of Poly(glycerol−succinic acid) Dendrimers. *Macromolecules* **2001**, *34*, 7648. (c) Liu, J.; Dong, K.; Franke, R.; Neumann, H.; Jackstell, R.; Beller, M. Selective Palladium-Catalyzed Carbonylation of Alkynes: An Atom-Economic Synthesis of 1,4-Dicarboxylic Acid Diesters. *J. Am. Chem. Soc.* **2018**, *140*, 10282.

(15) (a) Ran, C.-K.; Xiao, H.-Z.; Liao, L.-L.; Ju, T.; Zhang, W.; Yu, D.-G. Progress and challenges in dicarboxylation with CO_2. *Natl. Sci. Open* **2022**, *2*, 20220024. (b) Yu, Z.; Shi, M. Recent advances in the electrochemically mediated chemical transformation of carbon dioxide. *Chem. Commun.* **2022**, *58*, 13539. (c) Liu, X.-F.; Zhang, K.; Tao, L.; Lu, X.-B.; Zhang, W.-Z. Recent advances in electrochemical carboxylation reactions using carbon dioxide. *Green Chem. Eng.* **2022**, *3*, 125. (d) Liao, L.-L.; Wang, Z. H.; Cao, K. G.; Sun, G. Q.; Zhang, W.; Ran, C. K.; Li, Y.; Chen, L.; Cao, G. M.; Yu, D.-G. Electrochemical Ring-Opening Dicarboxylation of Strained Carbon-Carbon Single Bonds with CO_2: Facile Synthesis of Diacids and

Derivatization into Polyesters. *J. Am. Chem. Soc.* **2022**, *144*, 2062. For an early example: (e) Wright, G. F. Addition of Alkali Metals to the Stilbenes. *J. Am. Chem. Soc.* **1939**, *61*, 2106.
(16) (a) Senboku, H.; Komatsu, H.; Fujimura, Y.; Tokuda, M. Efficient Electrochemical Dicarboxylation of Phenyl-substituted Alkenes: Synthesis of 1-Phenylalkane-1,2-dicarboxylic Acids. *Synlett* **2001**, *2001*, 0418. (b) Wang, H.; Lin, M.-Y.; Fang, H.-J.; Chen, T.-T.; Lu, J.-X. Electrochemical Dicarboxylation of Styrene: Synthesis of 2-Phenylsuccinic Acid. *Chin. J. Chem .* **2007**, *25*, 913. (c) Yuan, G.-Q.; Jiang, H.-F.; Lin, C.; Liao, S.-J. Efficient electrochemical synthesis of 2-arylsuccinic acids from CO2 and aryl-substituted alkenes with nickel as the cathode. *Electrochim. Acta* **2008**, *53*, 2170. (d) Li, C.-H.; Yuan, G.-Q.; Ji, X.-C.; Wang, X.-J.; Ye, J.-S.; Jiang, H.-F. Highly regioselective electrochemical synthesis of dioic acids from dienes and carbon dioxide. *Electrochim. Acta* **2011**, *56*, 1529. (e) You, Y.; Kanna, W.; Takano, H.; Hayashi, H.; Maeda, S.; Mita, T. Electrochemical Dearomative Dicarboxylation of Heterocycles with Highly Negative Reduction Potentials. *J. Am. Chem. Soc.* **2022**, *144*, 3685. (f) Zhang, W.; Liao, L. L.; Li, L.; Liu, Y.; Dai, L. F.; Sun, G. Q.; Ran, C. K.; Ye, J. H.; Lan, Y.; Yu, D.-G. Electroreductive Dicarboxylation of Unactivated Skipped Dienes with CO_2. *Angew. Chem. Int. Ed.* **2023**, *62*, e202301892.
(17) Tortajada, A.; Ninokata, R.; Martin, R. Ni-Catalyzed Site-Selective Dicarboxylation of 1,3-Dienes with CO2. *J. Am. Chem. Soc.* **2018**, *140*, 2050
(18) Ju, T.; Zhou, Y.-Q.; Cao, K.-G.; Fu, Q.; Ye, J.-H.; Sun, G.-Q.; Liu, X.-F.; Chen, L.; Liao, L.-L.; Yu, D.-G. Dicarboxylation of alkenes, allenes and (hetero)arenes with CO_2 via visible-light photoredox catalysis. *Nat. Catal.* **2021**, *4*, 304.
(19) Song, L.; Wang, W.; Yue, J.-P.; Jiang, Y.-X.; Wei, M.-K.; Zhang, H.-P.; Yan, S.-S.; Liao, L.-L.; Yu, D.-G. Visible-light photocatalytic di- and hydro-carboxylation of unactivated alkenes with CO_2. *Nat. Catal.* **2022**, *5*, 832.
(20) Seo, H.; Katcher, M. H.; Jamison, T. F. Photoredox activation of carbon dioxide for amino acid synthesis in continuous flow. *Nat. Chem.* **2017**, *9*, 453.
(21) For selected difunctionalization of alkenes with CO_2: (a) Yatham, V. R.; Shen, Y.; Martin, R. Catalytic Intermolecular Dicarbofunctionalization of Styrenes with CO2 and Radical Precursors. *Angew. Chem. Int. Ed.* **2017**, *56*, 10915. (b) Ye, J.-H.; Miao, M.; Huang, H.; Yan, S. S.; Yin, Z. B.; Zhou, W. J.; Yu, D.-G. Visible-Light-Driven Iron-Promoted Thiocarboxylation of Styrenes and Acrylates with CO_2. *Angew. Chem. Int. Ed.* **2017**, *56*, 15416. (c) Hou, J.; Ee, A.; Cao, H.; Ong, H. W.; Xu, J. H.; Wu, J. Visible-Light-Mediated Metal-Free Difunctionalization of Alkenes with CO2 and Silanes or C(sp(3))-H Alkanes. *Angew. Chem. Int. Ed.* **2018**, *57*, 17220. (d) Zhang, B.; Yi, Y.; Wu, Z.-Q.; Chen, C.; Xi, C. Photoredox-catalyzed dicarbofunctionalization of styrenes with amines and CO_2: a convenient access to γ-amino acids. *Green Chem.* **2020**, *22*, 5961. (e) Zhang, W.; Lin, S. Electroreductive Carbofunctionalization of Alkenes with Alkyl Bromides via a Radical-Polar Crossover Mechanism. *J. Am. Chem. Soc.* **2020**, *142*, 20661. (f) Liao, L.-L.; Cao, G. M.; Jiang, Y. X.; Jin, X. H.; Hu, X. L.; Chruma, J. J.; Sun, G. Q.; Gui, Y. Y.; Yu, D.-G. alpha-Amino Acids and Peptides as Bifunctional Reagents: Carbocarboxylation of Activated Alkenes via Recycling CO_2. *J. Am. Chem. Soc.* **2021**, *143*, 2812. (g) Hang, W.; Xi, C. Rh(I)-Catalyzed Regioselective Arylcarboxylation of Acrylamides with Arylboronic Acids and CO_2. *Chin. J. Org. Chem.* **2021**, *41*, 425.
(22) When we were close to finish our study, Gao and Zhu's group disclosed a closely related work with 4CzIPN as the PC based on our previously study. In this work, only 3 examples of simple styrenes substrates were viable with low (about 40%) yields, and elevating reaction temperature was required: Xu, P.; Wang, S.; Xu, H.; Liu, Y.-Q.; Li, R.-B.; Liu, W.-W.; Wang, X.-Y.; Zou, M.-L.; Zhou, Y.; Guo, D.; Zhu, X. Dicarboxylation of Alkenes with CO_2 and Formate via Photoredox Catalysis. *ACS Catal.* **2023**, *13*, 2149.
(23) Xiao, W.; Wang, X.; Liu, R.; Wu, J. Quinuclidine and its derivatives as hydrogen-atom-transfer catalysts in photoinduced reactions. *Chin. Chem. Lett.* **2021**, *32*, 1847.
(24) $H^{13}COOK$ was not commercially available.
(25) Speckmeier, E.; Fischer, T. G.; Zeitler, K. A Toolbox Approach To Construct Broadly Applicable Metal-Free Catalysts for Photoredox Chemistry: Deliberate Tuning of Redox Potentials and Importance of Halogens in Donor-Acceptor Cyanoarenes. *J. Am. Chem. Soc.* **2018**, *140*, 15353.
(26) Czyz, M. L.; Taylor, M. S.; Horngren, T. H.; Polyzos, A. Reductive Activation and Hydrofunctionalization of Olefins by Multiphoton Tandem Photoredox Catalysis. *ACS Catal.* **2021**, *11*, 5472.
(27) Filardo, G.; Gambino, S.; Silvestri, G.; Gennaro, A.; Vianello, E. Electrocarboxylation of styrene through homogeneous redox catalysis. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *177*, 303.



■ **simple styrenes tolerated** ■ **low-cost reagent** ■ **hydrocarboxylation overridden**