

# Catalytic direct hydrocarboxylation of styrenes with CO<sub>2</sub> and H<sub>2</sub>

Received: 22 October 2022

Accepted: 24 November 2022

Published online: 08 December 2022

Check for updates

Yushu Jin<sup>1</sup>, Joaquim Caner<sup>1</sup>, Shintaro Nishikawa<sup>1</sup>, Naoyuki Toriumi<sup>1</sup> & Nobuharu Iwasawa<sup>1</sup>✉

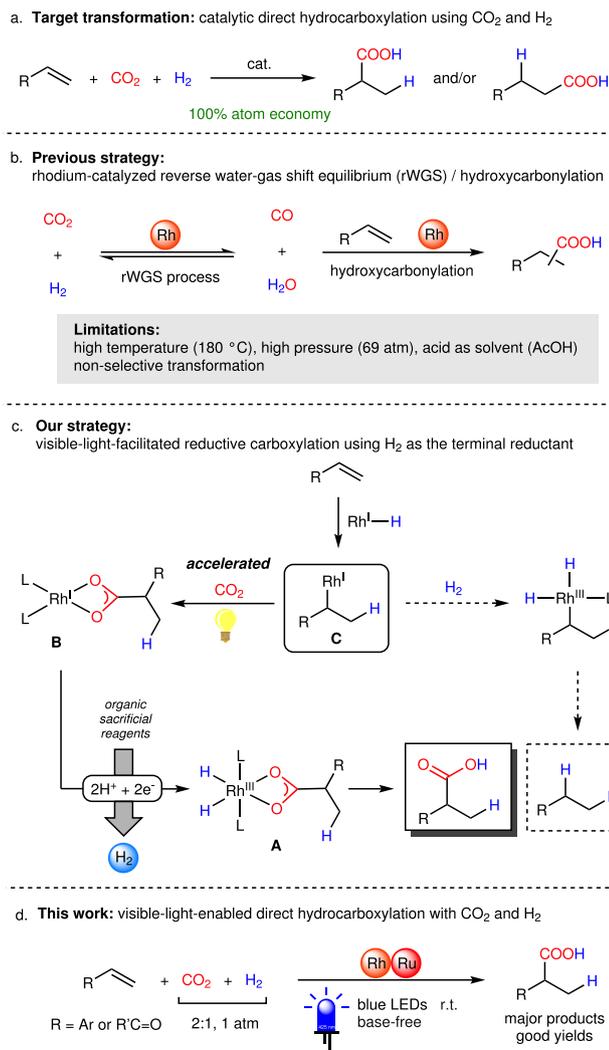
A three-component hydrocarboxylation of an olefin with CO<sub>2</sub> and H<sub>2</sub> could be regarded as a dream reaction, since it would provide a straightforward approach for the synthesis of aliphatic carboxylic acids in perfect atom economy. However, this transformation has not been realized in a direct manner under mild conditions, because boosting the carboxylation with thermodynamically stable CO<sub>2</sub> while suppressing the rapid hydrogenation of olefin remains a challenging task. Here, we report a rhodium-catalysed reductive hydrocarboxylation of styrene derivatives with CO<sub>2</sub> and H<sub>2</sub> under mild conditions, in which H<sub>2</sub> served as the terminal reductant. In this approach, the carboxylation process was largely accelerated by visible light irradiation, which was proved both experimentally and by computational studies. Hydrocarboxylation of various kinds of styrene derivatives was achieved in good yields without additional base under ambient pressure of CO<sub>2</sub>/H<sub>2</sub> at room temperature. Mechanistic investigations revealed that use of a cationic rhodium complex was critical to achieve high hydrocarboxylation selectivity.

The increasing demands for environmental friendliness and sustainable development inspired scientists to search new applications of utilizing renewable resources to industrial chemical feedstock<sup>1</sup>. During the past decades, great efforts have been made on transforming carbon dioxide (CO<sub>2</sub>), which is the critical compound for the greenhouse effect, into useful chemicals in the field of synthetic chemistry<sup>2–5</sup>. Dihydrogen (H<sub>2</sub>), regarded as one of the best and cleanest energy sources, has long been expected to be a potential partner with CO<sub>2</sub> in organic synthesis<sup>6</sup>, and extensive studies have been carried out for the reduction of CO<sub>2</sub> with H<sub>2</sub> to give formic acid, methanol, etc<sup>7,8</sup>. Catalytic production of carboxylic acids, alcohols, and alkanes with two or more carbons from CO<sub>2</sub> and H<sub>2</sub> has also been explored in recent years<sup>9</sup>. As a one-carbon (C<sub>1</sub>) source, another straightforward exit for CO<sub>2</sub> is converting it into carboxylic acid derivatives by the reaction with organic substrates<sup>10–17</sup>, however, the reaction of organic compounds in combination with CO<sub>2</sub> and H<sub>2</sub> has rarely been studied. Among these transformations, a three-component hydrocarboxylation, which is the addition of CO<sub>2</sub> and H<sub>2</sub> to an olefin, could be regarded as a dream reaction, because it would provide the corresponding aliphatic carboxylic acid with 100% atom economy (Fig. 1a), while the existing

examples of olefin hydrocarboxylations with CO<sub>2</sub> using Cu<sup>18–21</sup>, Rh<sup>22–24</sup>, Ti<sup>25</sup>, Ni<sup>26–28</sup>, Ru<sup>29</sup>, Fe<sup>30</sup>, Co<sup>31</sup>, Zr<sup>32</sup>, and Pd<sup>33,34</sup> catalysts or light energy<sup>35–38</sup> could hardly get rid of using a stoichiometric amount of base or metallic/organic reductants, which are out of the concept of green chemistry and sustainability. A pioneering work of Rh-catalysed formal hydrocarboxylation of olefins with CO<sub>2</sub> and H<sub>2</sub> has been described by Leitner's group in 2013, but the reaction was proved to proceed through a hydroxycarbonylation pathway with in situ generation of carbon monoxide (CO) and H<sub>2</sub>O via reverse water-gas shift equilibrium (rWGS) under high temperature (180 °C) and high pressure of CO<sub>2</sub>/H<sub>2</sub> (6:1, 69 atm) in strongly acidic conditions (Fig. 1b)<sup>39</sup>. Although computational calculation indicated that catalytic direct hydrocarboxylation of olefins with CO<sub>2</sub> and H<sub>2</sub> was thermodynamically feasible, the competing hydrogenation reaction, which usually proceeds rapidly, and complexity of the desired reaction pathway have made this dream reaction challenging<sup>40</sup>. To the best of our knowledge, hydrocarboxylation of olefins with CO<sub>2</sub> and H<sub>2</sub> via direct insertion of CO<sub>2</sub> has not yet been realized to date.

In our goal of developing novel and sustainable catalytic systems for the utilization of CO<sub>2</sub>, the potential of rhodium hydride as a catalyst

<sup>1</sup>Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan. ✉e-mail: [niwasawa@chem.titech.ac.jp](mailto:niwasawa@chem.titech.ac.jp)



**Fig. 1 | Carboxylation of olefinic compounds using CO<sub>2</sub> and H<sub>2</sub>.** **a** Target transformation: catalytic direct hydrocarboxylation of olefins using CO<sub>2</sub> and H<sub>2</sub>, a 100% atom economical reaction. **b** Previous strategy: rhodium-catalysed reverse water-gas shift equilibrium (rWGS)/hydroxycarbonylation. **c** Our strategy: visible-light-facilitated reductive carboxylation using H<sub>2</sub> as the terminal reductant. **d** This work: visible-light-enabled direct hydrocarboxylation with CO<sub>2</sub> and H<sub>2</sub>. LED, light-emitting diode.

for C–C bond formation<sup>41</sup>, as well as our recent studies on rhodium-catalysed reductive hydrocarboxylation of activated olefins<sup>23,24</sup> inspired us to tackle this reaction not only under mild conditions but also with high efficiency. In our previous research, we have found that rhodium(III)-dihydride-carboxylate species **A** could be generated from rhodium(I) carboxylate **B**, which was formed by CO<sub>2</sub> insertion into alkylrhodium(I) species **C** with the support of light energy, using organic sacrificial reagents (i.e. diisopropylethylamine<sup>23</sup> and BI(OH)H (1,3-dimethyl-2-(*o*-hydroxyphenyl)-2,3-dihydro-1*H*-benzo[*d*]imidazole<sup>24</sup>) as both proton and electron donors (Fig. 1c). From the mechanistic point of view, in principle, two protons and two electrons (2H<sup>+</sup> + 2e<sup>-</sup>) can formally be replaced by molecular H<sub>2</sub>, thus providing the opportunity to employ H<sub>2</sub> as the terminal reductant in our catalytic system. Furthermore, we also envisioned that selective hydrocarboxylation over the undesired hydrogenation may become possible, because the carboxylation process would be boosted under light irradiation.

Here we describe an example of base-free catalytic hydrocarboxylation of styrene derivatives with CO<sub>2</sub> and H<sub>2</sub> under mild

conditions (Fig. 1d). Our catalytic system allowed the synthesis of aliphatic carboxylic acids under ambient pressure of a CO<sub>2</sub>/H<sub>2</sub> gas at room temperature with visible light irradiation. Furthermore, it is worth mentioning that base is no longer required in our catalytic system, while conventional reductive carboxylations under base-free conditions have been elusive<sup>42,43</sup>.

## Results and discussion

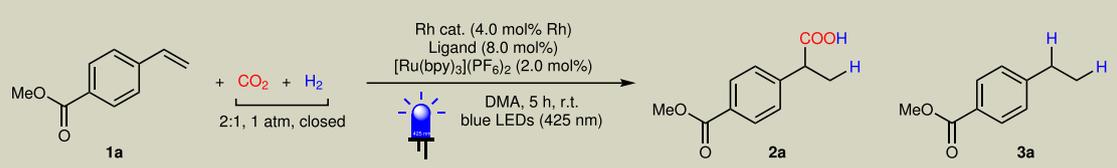
### Optimization of reaction conditions

We started our investigation with modified conditions based on our previous research<sup>23</sup>. Methyl 4-vinylbenzoate (**1a**) was selected as the model substrate, and our first trial was conducted under an ambient pressure of CO<sub>2</sub>/H<sub>2</sub> (2:1 ratio) at room temperature in DMA (*N,N*-dimethylacetamide) solvent in the presence of 2.0 mol% of [Rh(OAc)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> (4.0 mol% of Rh atom) as the rhodium precursor, 8.0 mol% of P(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> as the ligand, and 2.0 mol% of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate) as the photosensitizer with blue LEDs (425 nm) irradiation. After 5 h, the hydrocarboxylation product **2a** was actually observed in 5% yield, although hydrogenation (**3a**, 74% yield) dominated the reaction (Table 1, entry 1).

After an intensive screening of various kinds of ligands (Supplementary Table 1), we turned our eyes on testing various kinds of Buchwald-type ligands for hydrocarboxylation (Table 1, entries 2–6). It was found that when using DavePhos (2-dicyclohexylphosphino-2'-(*N,N*-dimethylamino)biphenyl) as the ligand, carboxylic acid **2a** was obtained in 35% yield with reduced amount of hydrogenation product **3a** (Table 1, entry 4). The choice of rhodium precursor also appeared to play a pivotal role in the selectivity between carboxylation and hydrogenation (Table 1, entries 7–10, see Supplementary Table 2 for details). Considering the fact that formation of rhodium-dihydride species from a Buchwald-type ligand coordinated cationic Rh-complex was very slow even under high pressure of H<sub>2</sub><sup>44</sup>, consequently, a DavePhos ligated cationic rhodium complex, [Rh(C<sub>2</sub>H<sub>4</sub>)(DavePhos)]<sup>+</sup>(OTf)<sup>-</sup> (Supplementary Data 1), was found to be not only highly reactive, but also selective for the hydrocarboxylation, providing the desired branched carboxylic acid **2a** in 75% yield, while only 23% yield of **3a** was generated (Table 1, entry 10). Additional amount of DavePhos ligand was critical to achieve high yield (Table 1, entry 11). A slightly higher yield of **2a** (84%) was achieved when the reaction was conducted in the presence of LiOTf (100 mol%, lithium trifluoromethanesulfonate) as an additive (Table 1, entry 12, see Supplementary Table 3 for details). We have confirmed that rhodium catalyst, light irradiation, photocatalyst, and H<sub>2</sub> atmosphere were all essential to this transformation (Table 1, entries 13–16). Finally, the reaction didn't proceed in the presence of H<sub>2</sub>O (500 mol%) under CO atmosphere (Table 1, entry 17), providing strong evidence that our reaction is not occurring through the rWGS pathway<sup>39</sup>. Although catalytic hydroxycarbonylations using CO/H<sub>2</sub>O are useful to obtain this type of carboxylic acids from vinyl arenes<sup>45–47</sup>, use of non-toxic CO<sub>2</sub> gas would make this type of reaction more sustainable and environmentally friendly.

### Scope of substrates

With the optimized conditions in hand (Table 1, entries 10 and 12), we next investigated the substrate scope for the hydrocarboxylation using CO<sub>2</sub> and H<sub>2</sub> (Fig. 2). Generally speaking, although the hydrocarboxylation proceeded smoothly under standard conditions for most electron-deficient styrene derivatives (Fig. 2, **1a–o**), it was found that slightly higher yields could be obtained by employing LiOTf (100 mol%) as the additive for many of the substrates. We assumed that either the carbonyl group in substrates or CO<sub>2</sub> were activated by LiOTf due to its Lewis acidity<sup>48</sup>. Substrates bearing esters (**1a–d**, **1l**), ketones (**1f–j**, **1m**, **1n**), methoxy (**1g**), fluoride (**1h**), and nitrile (**1k**) moieties provided the target aliphatic carboxylic acids in moderate to good yields. The benzylic (**2c**) and prenylic ester (**2d**) scaffolds tolerated from potential ester hydrogenolysis under both acidic and H<sub>2</sub>

**Table 1 | Optimization of reaction conditions and control experiments**


Entry	Rh catalyst	Ligand	Yield of 2a (%)	Yield of 3a (%)
1	[Rh(OAc)(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub>	P(4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	5	74
2	[Rh(OAc)(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub>	JohnPhos	7	6
3	[Rh(OAc)(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub>	CyJohnPhos	16	61
4	[Rh(OAc)(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub>	DavePhos	35	48
5	[Rh(OAc)(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub>	PhDavePhos	3	30
6	[Rh(OAc)(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub>	CPhos	17	38
7	[RhCl(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub>	DavePhos	4	>95
8	[Rh(cod) <sub>2</sub> ](OTf)	DavePhos	18	80
9	[Rh(OAc)(DavePhos)]	DavePhos <sup>a</sup>	38	27
10	[Rh(C <sub>2</sub> H <sub>4</sub> )(DavePhos)](OTf) ( <b>4</b> )	DavePhos <sup>a</sup>	75 (70)	23
11	[Rh(C <sub>2</sub> H <sub>4</sub> )(DavePhos)](OTf) ( <b>4</b> )	–	10	9
12 <sup>b</sup>	[Rh(C <sub>2</sub> H <sub>4</sub> )(DavePhos)](OTf) ( <b>4</b> )	DavePhos <sup>a</sup>	84 (81)	16
13	–	DavePhos <sup>a</sup>	n.d.	n.d.
14 <sup>c</sup>	[Rh(C <sub>2</sub> H <sub>4</sub> )(DavePhos)](OTf) ( <b>4</b> )	DavePhos <sup>a</sup>	n.d.	13
15 <sup>d</sup>	[Rh(C <sub>2</sub> H <sub>4</sub> )(DavePhos)](OTf) ( <b>4</b> )	DavePhos <sup>a</sup>	n.d.	10
16 <sup>e</sup>	[Rh(C <sub>2</sub> H <sub>4</sub> )(DavePhos)](OTf) ( <b>4</b> )	DavePhos <sup>a</sup>	n.d.	n.d.
17 <sup>f</sup>	[Rh(C <sub>2</sub> H <sub>4</sub> )(DavePhos)](OTf) ( <b>4</b> )	DavePhos <sup>a</sup>	n.d.	n.d.

Reaction conditions: **1a** (50 μmol), CO<sub>2</sub>/H<sub>2</sub> (2:1 mix gas, 1 atm, closed), Rh catalyst (2.0 μmol of Rh), ligand (4.0 μmol), [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (1.0 μmol), DMA (1.0 mL), blue LEDs (425 nm), room temperature, 5 h. Yields were determined by <sup>1</sup>H NMR spectroscopy with 1,1,2,2-tetrachloroethane as the internal standard; isolated yields in parenthesis.

Me methyl, bpy bipyridine, Ac acetyl, Cy cyclohexyl, cod 1,5-cyclooctadiene, OTf trifluoromethanesulfonate.

<sup>a</sup>DavePhos (4.0 mol%) was used.

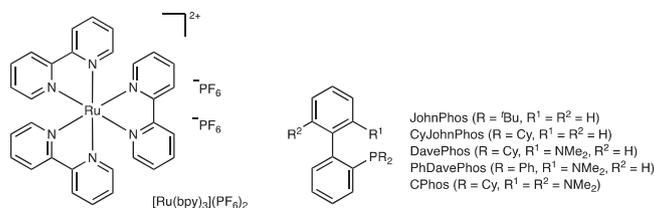
<sup>b</sup>With LiOTf (100 mol%).

<sup>c</sup>Under dark.

<sup>d</sup>Without Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>.

<sup>e</sup>Under CO<sub>2</sub> (1 atm, closed) atmosphere.

<sup>f</sup>Under CO (1 atm, closed) atmosphere with H<sub>2</sub>O (500 mol%).



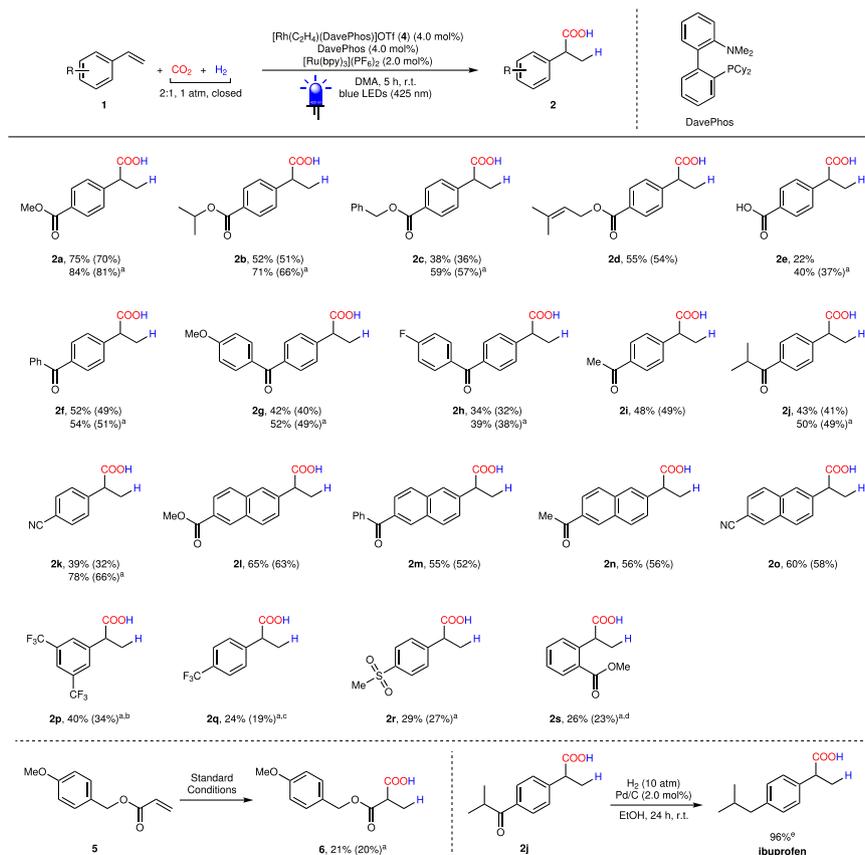
conditions. Owing to the base-free feature of our method, dicarboxylic acid **2e** could be prepared from 4-vinylbenzoic acid (**1e**) under CO<sub>2</sub>/H<sub>2</sub> in synthetically useful yield (37%, with LiOTf) without protection. The hydrocarboxylation proceeded smoothly with 4-vinylbenzonitrile (**1k**) as the starting material, providing the benzylic carboxylic acid **2k** in good yield (66%), while the cyano group remained intact. As expected, hydrogenation products **3** were found to be the major side products (see Supplementary Table 6 for details). On the other hand, we also observed polymerization competing with the hydrocarboxylation and hydrogenation for some of the styrene substrates. For example, the hydrocarboxylation of trifluoromethyl substituted styrenes (**1p** and **1q**) suffered from serious polymerization under light irradiation and only low yields were obtained even with the addition of polymerization inhibitors (see Supplementary Table 5 for details). An acrylate substrate **5** was also examined under standard conditions. Unfortunately, only 20% yield of product **6** was obtained due to undesired hydrogenation and polymerization. Considering the importance of 2-arylpropionic acids in pharmaceuticals<sup>49</sup>, product **2j** was treated with

Pd/C under a H<sub>2</sub> atmosphere to provide the nonsteroidal anti-inflammatory drug ibuprofen in 96% yield.

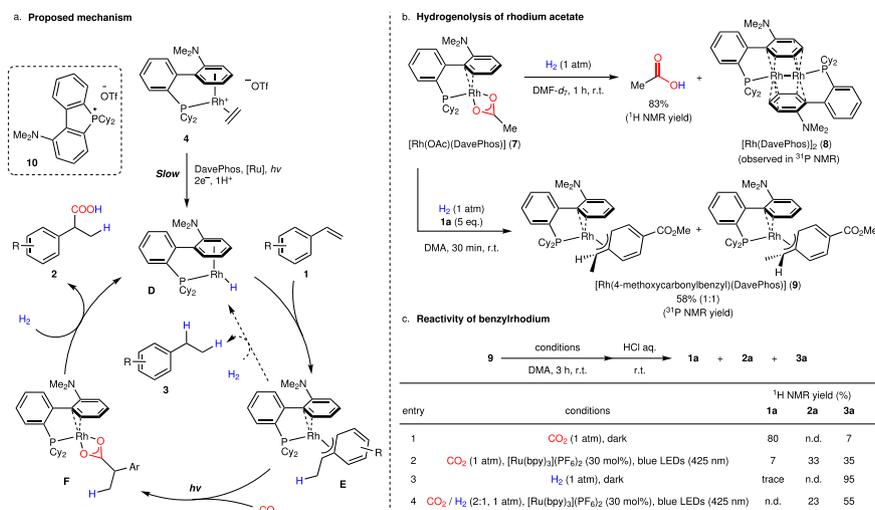
### Mechanistic investigations

To get mechanistic insight for this reaction, some control experiments were firstly performed. Hydrocarboxylation product **2a** was not observed at all when the reaction of styrene **1a** was conducted at high temperature (110 °C) in dark in the absence of photocatalyst (see Supplementary Information, Section 6.1), proving that there is no thermal background reaction. Benzylic C–H bond carboxylation didn't proceed at all when ethylbenzene **3a** was used as the substrate under the standard conditions (see Supplementary Information, Section 6.2), indicating that the hydrogenation-benzylic C–H bond photocarboxylation<sup>42</sup> pathway is not likely.

Then, the mechanism of this reaction is assumed based on our previous report on rhodium-catalysed hydrocarboxylation using amine as a reductant<sup>23,24</sup>. The postulated mechanism is shown in Fig. 3a, which consists of conversion of [Rh(C<sub>2</sub>H<sub>4</sub>)(DavePhos)](OTf)



**Fig. 2 | Scope of substrates.** Reaction conditions: **1** or **5** (50  $\mu$ mol), CO<sub>2</sub>/H<sub>2</sub> (2:1, 1 atm, closed), [Rh(C<sub>2</sub>H<sub>4</sub>)(DavePhos)](OTf) (2.0  $\mu$ mol), DavePhos (4.0  $\mu$ mol), [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (1.0  $\mu$ mol), DMA (1.0 mL), blue LEDs (425 nm), room temperature, 5 h. NMR yields were shown, which were estimated by <sup>1</sup>H NMR spectroscopy with 1,1,2-tetrachloroethane as the internal standard; isolated yields in parenthesis. <sup>a</sup>With LiOTf (100 mol%). <sup>b</sup>With TEMPO (10 mol%). <sup>c</sup>With phenothiazine (10 mol%). <sup>d</sup>10 h. <sup>e</sup>Reaction conditions: **2j** (49  $\mu$ mol), H<sub>2</sub> (10 atm), Pd/C (10 wt% Pd, 5 wt% H<sub>2</sub>O) (1.0  $\mu$ mol), EtOH (1.0 mL), room temperature, 24 h.



**Fig. 3 | Experimental mechanistic studies.** **a** Proposed mechanism. **b** Hydrogenolysis of rhodium acetate **7** with H<sub>2</sub>. **c** Reactivity of benzylrhodium **9**.

(**4**) to rhodium(I) hydride **D**, insertion of styrene to **D** to give benzylrhodium(I) **E**, carboxylation of **E** to yield rhodium(I) carboxylate **F**, and reduction of **F** to regenerate rhodium(I) hydride **D**. Under the catalytic reaction conditions, the initial generation of the active catalyst **D** from the cationic rhodium precursor **4** would involve the additional amount of DavePhos, since the hydrocarboxylation did

not proceed efficiently in the absence of DavePhos (Table 1, entry 11). The kinetic time course showed the presence of an induction period (-1 h) on the generation of carboxylic acid (see Supplementary Fig. 5), suggesting slow conversion of **4** to **D**. We have observed a phosphonium salt **10** generated from DavePhos in the reaction conditions, and diisopropylethylamine or BI(OH)H as a catalytic additive

instead of DavePhos was also effective for the hydrocarboxylation (see Supplementary Table 3, entries 5 and 6). These results indicated that the additional DavePhos may act as a sacrificial electron donor to reduce rhodium cation **4** to rhodium hydride **D**. On the other hand, **D** could also be generated by oxidative addition of H<sub>2</sub> to Rh(I) species, followed by a base-induced deprotonation, in which DavePhos may serve as a base. To further confirm the function of DavePhos in this step, **4** and DavePhos were mixed in a H<sub>2</sub> atmosphere under dark. As a result, both cationic rhodium complex **4** and DavePhos remained intact for long time (-9 h) (see Supplementary Information, Section 6.4 for details), suggesting that DavePhos is more likely to work as a sacrificial electron donor than as a base. Nevertheless, based on the facts that using a catalytic amount of Cs<sub>2</sub>CO<sub>3</sub> instead of DavePhos also provided **2a** in 38% yield (Supplementary Table 3, entry 2), the possibility that DavePhos works as a base could not be completely ruled out (see also Supplementary Information, Section 6.5).

Next, we investigated the reactivities of the possible rhodium intermediates **D–F** to clarify the catalytic cycle. To confirm hydrogenolysis of rhodium carboxylate **F**, which is one of the key steps in this reaction (Fig. 1c), [Rh(OAc)(DavePhos)] (**7**) was synthesized as a model complex (see Supplementary Information, Section 6.3 for details). Treatment of **7** with H<sub>2</sub> gas gave AcOH in high yield, simultaneously generating [Rh(DavePhos)]<sub>2</sub> (**8**) (Supplementary Data 2), which would be produced by dehydrogenative dimerization of unstable rhodium hydride **D** (Fig. 3b). The release of carboxylic acid from rhodium carboxylate with H<sub>2</sub> in the absence of base is known for a rhodium(III) acetate complex<sup>50</sup>, but has not been reported for rhodium(I) carboxylate complexes to the best of our knowledge. The hydrogenolysis of **7** in the presence of styrene **1a** afforded [Rh(4-methoxycarbonylbenzyl)(DavePhos)] **9**, which indicated rapid insertion of **1a** to rhodium hydride **D** before the dimerization of **D** proceeded.

The reactivity of benzylrhodium **9** towards CO<sub>2</sub> and H<sub>2</sub> is critical to realize selective hydrocarboxylation over hydrogenation (Fig. 1c). Similarly to our previous report<sup>24</sup>, **9** reacted with CO<sub>2</sub> in the presence of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> under irradiation to give carboxylic acid **2a** (Fig. 3c, entry 2), while **2a** was not observed at all without irradiation (Fig. 3c, entry 1). We have found that **9** underwent complete hydrogenolysis under a H<sub>2</sub> atmosphere without irradiation (Fig. 3c, entry 3), indicating one plausible pathway to yield hydrogenated byproduct **3** in this reaction system. On the other hand, carboxylation did proceed under a CO<sub>2</sub>/H<sub>2</sub> atmosphere upon irradiation although hydrogenolysis was faster (Fig. 3c, entry 4), which clearly demonstrates the photoenhanced carboxylation reaction in the presence of H<sub>2</sub>. The modest selectivity towards carboxylation observed here seems to be contradictory to the result of the catalytic reactions, where hydrocarboxylation of styrenes was preferred compared with hydrogenation. This discrepancy could be ascribed to the difference in excitation efficiency of benzylrhodium **9**. The relatively high concentration of **9** would hamper its excitation by [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and cause hydrogenation in the investigation of the reactivity of **9** (Fig. 3c, entry 4). However, the existence of the induction period in the catalytic conditions would lower the concentration of active species **9**, making the photocarboxylation step much more selective.

In order to verify the existence of these possible intermediates in the hydrocarboxylation, we used rhodium acetate **7** or benzylrhodium **9** as a catalyst instead of cationic rhodium complex **4** (see Supplementary Information, Section 6.10 for details). Although the ratio of hydrogenation was somewhat increased, hydrocarboxylation proceeded smoothly without the addition of DavePhos, further supporting the role of these complexes as the reaction intermediates.

### Computational analysis

To investigate the energy profile of this hydrocarboxylation, density functional theory (DFT) calculation of the proposed cycle was

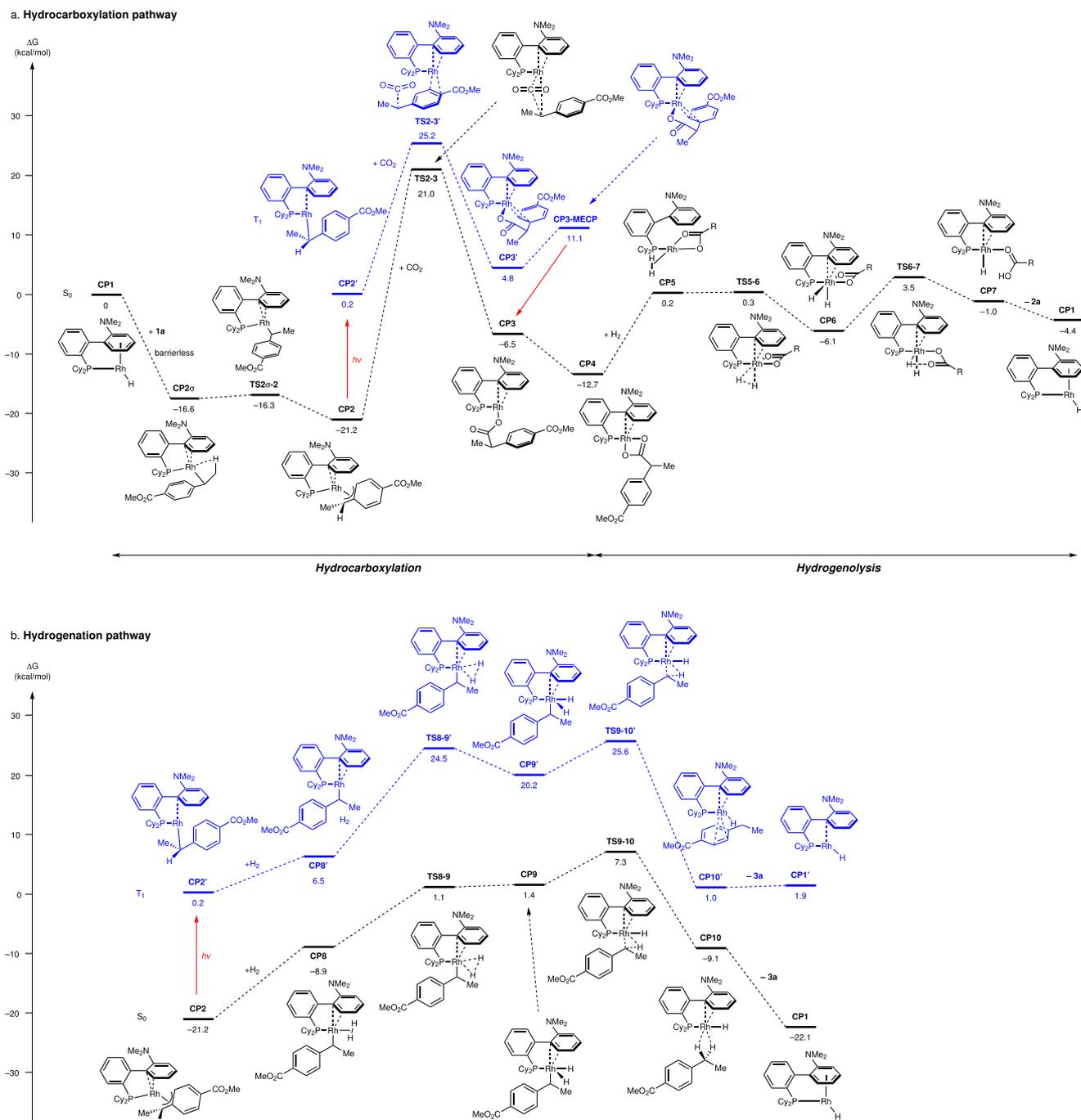
conducted starting from RhH(DavePhos) **CP1** and styrene **1a** (Fig. 4). The insertion of **1a** to **CP1** proceeds barrierlessly to afford  $\sigma$ -benzylrhodium **CP2 $\sigma$**  (-16.6 kcal/mol), which isomerize to give more stable  $\pi$ -benzylrhodium **CP2** (-21.2 kcal/mol) (Fig. 4a and Supplementary Fig. 6). The CO<sub>2</sub> insertion to **CP2** needs quite high activation energy in the ground state (S<sub>0</sub>) (**CP2** to **TS2-3**: 42.2 kcal/mol)<sup>51</sup>, but proceeds smoothly in the lowest triplet excited state (T<sub>1</sub>) (**CP2'** to **TS2-3'**: 25.0 kcal/mol) to yield rhodium carboxylate **CP4** (-12.7 kcal/mol) after deactivation to the ground state. **CP4** undergoes hydrogenolysis via oxidative addition of H<sub>2</sub> and reductive elimination of carboxylic acid **2a** with the low activation barrier (**CP4** to **TS6-7**: 16.2 kcal/mol) to regenerate **CP1** (-4.4 kcal/mol), which is endothermic by 8.3 kcal/mol. This increase of the energy is compensated in the presence of styrene **1a** by the generation of highly stable benzylrhodium **CP2**, realizing the base-free conditions. We also calculated on hydrogenation of **1a** to give alkane **3a** (Fig. 4b). **CP2** undergoes hydrogenolysis via oxidative addition of H<sub>2</sub> and reductive elimination of **3a** with a slightly higher activation energy (**CP2** to **TS9-10**: 28.5 kcal/mol) than that of hydrocarboxylation in T<sub>1</sub> (**CP2'** to **TS2-3'**: 25.0 kcal/mol). Notably, hydrogenation is not significantly accelerated in T<sub>1</sub>, where the activation barrier (**CP2'** to **TS9-10'**: 25.4 kcal/mol) is slightly higher than that of hydrocarboxylation. Although the difference of the activation energy between hydrocarboxylation and hydrogenation in T<sub>1</sub> is relatively small (0.4 kcal/mol), these computational results are consistent with the experimental results, supporting the validity of the proposed catalytic cycle. The energy of product **2a** is 4.4 kcal/mol more stable than that of the starting materials (**1a** + H<sub>2</sub> + CO<sub>2</sub>), which is consistent with the previous calculation<sup>40</sup>.

In summary, we have demonstrated an example of catalytic hydrocarboxylation of styrenes with CO<sub>2</sub> and H<sub>2</sub> under mild conditions using light energy. In the presence of rhodium/ruthenium dual catalysts and DavePhos, our catalytic system allowed the synthesis of various kinds of aliphatic carboxylic acids under ambient pressure of a CO<sub>2</sub>/H<sub>2</sub> atmosphere at room temperature with visible light irradiation. Furthermore, we also discovered that base is no longer required under current reaction conditions. Mechanistic studies revealed that DavePhos has multiple functions in this reaction system. It not only played a role as a ligand, but also served as an electron donor, which supported the generation of Rh–H species for entering the catalytic cycle. The result of DFT calculations indicated that the activation barrier of the hydrogenation pathway is higher than that of the carboxylation, which rationalized the reason for the selectivity of hydrocarboxylation over hydrogenation under our catalytic system. We anticipate that our method would extend the toolbox for developing more sustainable catalytic methodologies in the future.

## Methods

### Procedure for the preparation of [Rh(C<sub>2</sub>H<sub>4</sub>)(DavePhos)](OTf) complex (**4**)

In an argon-filled glovebox, a THF solution (5 mL) of [RhCl(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> (78 mg, 0.20 mmol) was stirred in a 30 mL Schlenk flask at room temperature. AgOTf (103 mg, 0.40 mmol) was added to the solution in small portions. White precipitate appeared immediately, and the mixture was kept stirring for 1 h. After all the volatiles were removed in vacuo, CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to the residue and the mixture was filtered with celite. The organic filtrate was evaporated again under reduced pressure to remove all the volatiles. DavePhos (157 mg, 0.40 mmol) was added to the residue and the flask was charged with CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The solution was kept stirring at room temperature for overnight to ensure complete complexation. The resulting mixture was filtered through celite again, and the filtrate was evaporated under reduced pressure. The product was recrystallized from slowly adding Et<sub>2</sub>O to CH<sub>2</sub>Cl<sub>2</sub> solution to provide the target complex [Rh(C<sub>2</sub>H<sub>4</sub>)(DavePhos)](OTf) (**4**, 177 mg, 0.26 mmol, 66%) as orange yellow crystals.



**Fig. 4 | Computational studies.** Free-energy diagram of **a** hydrocarboxylation and **b** hydrogenation of **1a** with RhH(Davephos) **7** (**CP1**) as a catalyst computed at the M06/SDD(Rh)&6-311 + G(d,p)(C, H, N, O, P), SMD(DMA)//LANL2DZ(Rh)&6-

31G(d,p)(C, H, N, O, P) level. Potential energy values relative to **CP1** (kcal/mol) are shown in the diagram.

### General procedure for the catalytic hydrocarboxylation of styrenes with CO<sub>2</sub> and H<sub>2</sub>

In an argon-filled glove box, [Rh(C<sub>2</sub>H<sub>4</sub>)(DavePhos)](OTf) (**4**, 1.4 mg, 2.0 μmol), DavePhos (0.8 mg, 2.0 μmol), [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.9 mg, 1.0 μmol), additive if any (0.05 mmol), and styrene substrate **1** (0.05 mmol) were placed in an oven-dried glass tube (ϕ = 1.7 cm, 18 cm). To the mixture was added anhydrous *N,N*-dimethylacetamide (DMA, 1.0 mL). The tube was sealed with a three-way cock and removed from the glove box. A mix gas of CO<sub>2</sub>/H<sub>2</sub> (1 atm) was charged into the glass tube through the three-way cock. The mixture was then subjected to a blue LED (425 nm) irradiation (two sockets) with

vigorous stirring. After 5 h, 1N HCl aq. (1.0 mL) was added to the mixture, and was extracted with Et<sub>2</sub>O for three times. The crude mixture was analysed by <sup>1</sup>H NMR to determine the yields of **2** and **3** using 1,1,2,2-tetrachloroethane as internal standard. Then the crude was diluted in Et<sub>2</sub>O and extracted with 1N NaOH aq. (2.0 mL). The basic water phase was then acidified with 1N HCl aq. until pH ≈ 1, and was extracted again with Et<sub>2</sub>O twice. The combined organic layer was dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified with preparative thin layer chromatography (PTLC) on silica gel (elution: hexane/EtOAc + 1% AcOH) to give the desired carboxylic acid product.

## Data availability

The data supporting the findings of this study are available within the paper and its Supplementary Information. Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under accession code CCDC 2160650 (4) and CCDC 2160651 (8). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: +44(0) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk). Cartesian coordinates of the optimized structure are available in Supplementary Data 3.

## References

1. Aresta, M., Dibenedetto, A. & Angelini, A. Catalysis for the valorization of exhaust carbon: from CO<sub>2</sub> to chemicals, materials and fuels. Technological use of CO<sub>2</sub>. *Chem. Rev.* **114**, 1709–1742 (2014).
2. Das S. CO<sub>2</sub> as Building Block in Organic Synthesis (WILEY-VCH GmbH, Boschstr. 2020).
3. Dabral, S. & Schaub, T. The use of carbon dioxide (CO<sub>2</sub>) as a building block in organic synthesis from an industrial perspective. *Adv. Synth. Catal.* **361**, 223–246 (2019).
4. Seo, H., Nguyen, L. V. & Jamison, T. F. Using carbon dioxide as a building block in continuous flow synthesis. *Adv. Synth. Catal.* **361**, 247–264 (2019).
5. Liu, Q., Wu, L., Jackstell, R. & Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **6**, 5933 (2015).
6. Klankermayer, J. & Leitner, W. Love at second sight for CO<sub>2</sub> and H<sub>2</sub> in organic synthesis. *Science* **350**, 626–630 (2015).
7. Wang, W.-H., Hameda, Y., Muckerman, J. T., Manbeck, G. F. & Fujita, E. CO<sub>2</sub> hydrogenation to formate and methanol as an alternative to photo- and electrochemical CO<sub>2</sub> reduction. *Chem. Rev.* **115**, 12936–12973 (2015).
8. Wang, D., Xie, Z., Porosoff, M. D. & Chen, J. G. Recent advances in carbon dioxide hydrogenation to produce olefins and aromatics. *Chem.* **7**, 2277–2311 (2021).
9. Bediako, B. B. A., Qian, Q. & Han, B. Synthesis of C2+ chemicals from CO<sub>2</sub> and H<sub>2</sub> via C–C bond formation. *Acc. Chem. Res.* **54**, 2467–2476 (2021).
10. Zhang, G., Cheng, Y., Beller, M. & Chen, F. Direct carboxylation with carbon dioxide via cooperative photoredox and transition-metal dual catalysis. *Adv. Synth. Catal.* **363**, 1583–1596 (2021).
11. Ran, C.-K., Liao, L.-L., Gao, T.-Y., Gui, Y.-Y. & Yu, D.-G. Recent progress and challenges in carboxylation with CO<sub>2</sub>. *Cur. Opin. Green. Sustain. Chem.* **32**, 100525 (2021).
12. Ye, J.-H., Ju, T., Huang, H., Liao, L.-L. & Yu, D.-G. Radical carboxylative cyclizations and carboxylations with CO<sub>2</sub>. *Acc. Chem. Res.* **54**, 2518–2531 (2021).
13. Zhang, Z. et al. Visible-light-driven catalytic reductive carboxylation with CO<sub>2</sub>. *ACS Catal.* **10**, 10871–10885 (2020).
14. Yeung, C. S. Photoredox catalysis as a strategy for CO<sub>2</sub> incorporation: direct access to carboxylic acids from a renewable feedstock. *Angew. Chem. Int. Ed.* **58**, 5492–5502 (2019).
15. Tortajada, A., Juliá-Hernández, F., Börjesson, M., Moragas, T. & Martin, R. Transition-metal-catalyzed carboxylation reactions with carbon dioxide. *Angew. Chem. Int. Ed.* **57**, 15948–15982 (2018).
16. Luo, J. & Larrosa, I. C–H carboxylation of aromatic compounds through CO<sub>2</sub> fixation. *ChemSusChem* **10**, 3317–3332 (2017).
17. Tommasi, I. Direct carboxylation of C(sp<sup>3</sup>)–H and C(sp<sup>2</sup>)–H bonds with CO<sub>2</sub> by transition-metal-catalyzed and base-mediated reactions. *Catalysts* **7**, 380 (2017).
18. Ohmiya, H., Tanabe, M. & Sawamura, M. Copper-catalyzed carboxylation of alkylboranes with carbon dioxide: formal reductive carboxylation of terminal alkenes. *Org. Lett.* **13**, 1086–1088 (2011).
19. Ohishi, T., Zhang, L., Nishiura, M. & Hou, Z. Carboxylation of alkylboranes by N-heterocyclic carbene copper catalysts: synthesis of carboxylic acids from terminal alkenes and carbon dioxide. *Angew. Chem. Int. Ed.* **50**, 8114–8117 (2011).
20. Juhl, M. et al. Copper-catalyzed carboxylation of hydroborated disubstituted alkenes and terminal alkynes with cesium fluoride. *ACS Catal.* **7**, 1392–1396 (2017).
21. Zhang, P., Zhou, Z., Zhang, R., Zhao, Q. & Zhang, C. Cu-catalyzed highly regioselective 1,2-hydrocarboxylation of 1,3-dienes with CO<sub>2</sub>. *Chem. Commun.* **56**, 11469–11472 (2020).
22. Kawashima, S., Aikawa, K. & Mikami, K. Rhodium-catalyzed hydrocarboxylation of olefins with carbon dioxide. *Eur. J. Org. Chem.* 3166–3170 (2016).
23. 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.* **53**, 3098–3101 (2017).
24. Murata, K., Numasawa, N., Shimomaki, K., Takaya, J. & Iwasawa, N. Improved conditions for the visible-light driven hydrocarboxylation by Rh(I) and photoredox dual catalysts based on the mechanistic analyses. *Front. Chem.* **7**, 371 (2019).
25. Shao, P., Wang, S., Chen, C. & Xi, C. Cp<sub>2</sub>TiCl<sub>2</sub>-catalyzed regioselective hydrocarboxylation of alkenes with CO<sub>2</sub>. *Org. Lett.* **18**, 2050–2053 (2016).
26. Williams, C. M., Johnson, J. B. & Rovis, T. Nickel-catalyzed reductive carboxylation of styrenes using CO<sub>2</sub>. *J. Am. Chem. Soc.* **130**, 14956–14937 (2008).
27. Gaydou, M., Moragas, T., Juliá-Hernández, F. & Martin, R. Site-selective catalytic carboxylation of unsaturated hydrocarbons with CO<sub>2</sub> and water. *J. Am. Chem. Soc.* **139**, 12161–12164 (2017).
28. Meng, Q.-Y., Wang, S., Huff, G. S. & König, B. Ligand-controlled regioselective hydrocarboxylation of styrenes with CO<sub>2</sub> by combining visible light and nickel catalysis. *J. Am. Chem. Soc.* **140**, 3198–3201 (2018).
29. Wu, L., Liu, Q., Fleischer, I., Jackstell, R. & Beller, M. Ruthenium-catalyzed alkoxy-carboxylation of alkenes with carbon dioxide. *Nat. Commun.* **5**, 3091 (2014).
30. Greenhalgh, M. D. & Thomas, S. P. Iron-catalyzed, highly regioselective synthesis of α-aryl carboxylic acids from styrene derivatives and CO<sub>2</sub>. *J. Am. Chem. Soc.* **134**, 11900–11903 (2012).
31. Hayashi, C., Hayashi, T., Kikuchi, S. & Yamada, T. Cobalt-catalyzed reductive carboxylation on α,β-unsaturated nitriles with carbon dioxide. *Chem. Lett.* **43**, 565–567 (2014).
32. Shao, P., Wang, S., Chen, C. & Xi, C. Zirconocene-catalyzed sequential ethylcarboxylation of alkenes using ethylmagnesium chloride and carbon dioxide. *Chem. Commun.* **51**, 6640–6642 (2015).
33. Takaya, J., Sasano, K. & Iwasawa, N. Efficient one-to-one coupling of easily available 1,3-dienes with carbon dioxide. *Chem. Commun.* **51**, 6640–6642 (2015).
34. Takaya, J. & Iwasawa, N. Hydrocarboxylation of allenes with CO<sub>2</sub> catalyzed by silyl pincer-type palladium complex. *J. Am. Chem. Soc.* **130**, 15254–15255 (2008).
35. Seo, H., Liu, A. & Jamison, T. F. Direct β-selective hydrocarboxylation of styrenes with CO<sub>2</sub> enabled by continuous flow photoredox catalysis. *J. Am. Chem. Soc.* **130**, 13969–13972 (2017).
36. Ju, T. et al. Selective and catalytic hydrocarboxylation of enamides and imines with CO<sub>2</sub> to generate α,α-disubstituted α-amino acids. *Angew. Chem. Int. Ed.* **57**, 13897–13901 (2018).
37. Huang, H. et al. Visible-light-driven anti-markovnikov hydrocarboxylation of acrylates and styrenes with CO<sub>2</sub>. *CCS Chem.* **2**, 1746–1756 (2020).
38. Kang, G. & Romo, D. Photocatalyzed, β-selective hydrocarboxylation of α,β-unsaturated esters with CO<sub>2</sub> under flow for β-lactone synthesis. *ACS Catal.* **11**, 1309–1315 (2021).
39. Ostapowicz, T. G., Schmitz, M., Krystof, M., Klankermayer, J. & Leitner, W. Carbon dioxide as a C1 building block for the formation

- of carboxylic acids by formal catalytic hydrocarboxylation. *Angew. Chem. Int. Ed.* **52**, 12119–12123 (2013).
40. Ostapowicz, T. G., Hölscher, M. & Leitner, W. Catalytic hydrocarboxylation of olefins with CO<sub>2</sub> and H<sub>2</sub> – a DFT computational analysis. *Eur. J. Inorg. Chem.* 5632–5641 (2012).
  41. Santana, G. C. & Krische, M. J. From hydrogenation to transfer hydrogenation to hydrogen auto-transfer in enantioselective metal-catalyzed carbonyl reductive coupling: past, present and future. *ACS Catal.* **11**, 5572–5585 (2021).
  42. Meng, Q.-Y., Schirmer, T. E., Berger, A. L., Donabauer, K. & König, B. Photocarboxylation of Benzylic C–H bonds. *J. Am. Chem. Soc.* **141**, 11393–11397 (2019).
  43. Matsumoto, T., Uchijo, D., Koike, T., Namiki, R. & Chang, H.-C. Direct photochemical C–H carboxylation of aromatic diamines with CO<sub>2</sub> under electron-donor- and base-free conditions. *Sci. Rep.* **8**, 14623 (2018).
  44. O'Connor, A. R., Kaminsky, W., Heinekey, D. M. & Goldberg, K. I. Synthesis, characterization, and reactivity of arene-stabilized rhodium complexes. *Organometallics* **30**, 2105–2166 (2011).
  45. Seayad, A., Jayasree, S. & Chaudhari, R. V. Carbonylation of vinyl aromatics: convenient regioselective synthesis of 2-arylpropanoic acids. *Org. Lett.* **1**, 459–461 (1999).
  46. Huang, Z. et al. Regioselectivity inversion tuned by iron(III) salts in palladium catalyzed carbonylations. *Chem. Commun.* **54**, 3967–3970 (2018).
  47. Yao, Y.-H. et al. Palladium-catalyzed asymmetric Markovnikov hydroxycarbonylation and hydroalkoxycarbonylation of vinyl arenes: synthesis of 2-arylpropanoic acids. *Angew. Chem. Int. Ed.* **60**, 23117–23122 (2021).
  48. Heimann, J. E., Bernskoetter, W. H. & Hazari, N. Understanding the individual and combined effects of solvent and Lewis acid on CO<sub>2</sub> insertion into a metal hydride. *J. Am. Chem. Soc.* **141**, 10520–10529 (2019).
  49. Maag, H. *Prodrugs of Carboxylic Acids* (Springer, New York, 2007).
  50. King, R. E. III, Busby, D. C. & Hawthorne, M. F. Reactions at the rhodium vertex of isomeric closo-bis(triphenylphosphine)hydridorhodacarboranes, alkenyl acetate cleavage and subsequent reactions. *J. Organomet. Chem.* **279**, 103–114 (1985).
  51. Pavlovic, L., Vaitra, J. C., Bayer, A. & Hopmann, K. H. Rhodium-catalyzed hydrocarboxylation: mechanistic analysis reveals unusual transition state for carbon–carbon bond formation. *Organometallics* **37**, 941–948 (2018).

## Acknowledgements

This research was supported by JSPS KAKENHI Grant Number 15H05800 and 17H06143. We thank Prof. Dr. Laurean Ilies (RIKEN) and

Prof. Dr. Masanobu Uchiyama (The University of Tokyo) for kindly providing technical support.

## Author contributions

Y.J. and N.I. conceived the work and designed the experiments. Y.J., J.C. and S.N. conducted the experiments and analysed the data. N.T. performed the computational calculations. N.I. supervised the research. Y.J., N.T. and N.I. co-wrote the manuscript. All authors contributed to discussion.

## Competing interests

The authors declare no competing interests.

## Additional information

**Supplementary information** The online version contains supplementary material available at <https://doi.org/10.1038/s41467-022-35293-3>.

**Correspondence** and requests for materials should be addressed to Nobuharu Iwasawa.

**Peer review information** *Nature Communications* thanks the anonymous reviewers for their contribution to the peer review of this work.

**Reprints and permissions information** is available at <http://www.nature.com/reprints>

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2022