

# Electrogenerated Sm(II)-Catalyzed Carbon Dioxide Reduction for $\beta$ -Hydrocarboxylation of Styrenes

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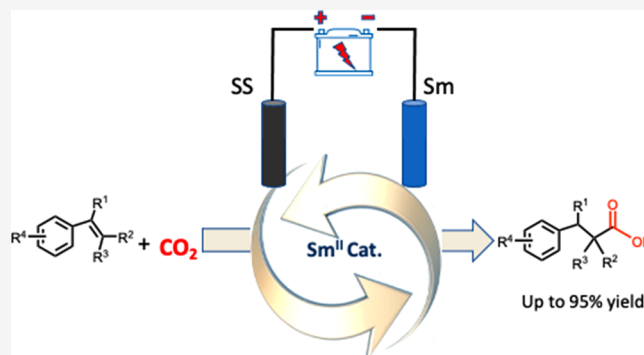


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**ABSTRACT:** The synthesis of carboxylic acids from low-value materials such as alkenes using CO<sub>2</sub> as a C<sub>1</sub>-building block remains a real challenge for synthetic chemists from both reactivity and selectivity perspectives. Electrochemical carboxylations have been examined but they remain limited, still suffering from a crucial lack of selectivity. Herein we report a catalytic protocol based on an electrogenerated Sm(II) catalyst as a powerful CO<sub>2</sub> reductant, able to perform exclusively *anti*-Markovnikov hydrocarboxylation of alkenes. This electrochemical approach overcomes several current limitations and allows direct  $\beta$ -hydrocarboxylation of styrene derivatives, in a regioselective manner.



## INTRODUCTION

Carboxylation with carbon dioxide as an abundant and inexpensive C<sub>1</sub>-building block has gained a tremendous boost in organic synthesis,<sup>1</sup> providing an extremely attractive way to access valuable carboxylic acids which are important motifs in pharmaceuticals.<sup>2</sup> Among these reactions, the carboxylation of unsaturated hydrocarbons using CO<sub>2</sub> is a particularly attractive route. Ongoing efforts to develop robust chemical protocols for this direct hydrocarboxylation reaction were, however, hampered by the high kinetic and thermodynamic stability of CO<sub>2</sub>, requiring consequently the use of strong reducing agents in most cases and leading to additional constraints in terms of functional group tolerance.<sup>3</sup> In this context, tangible improvements have been made by transition-metal catalysis and photocatalysis, with the control of the regioselectivity of the addition intimately linked to the structure of the considered olefin.<sup>4</sup> Aliphatic alkenes are indeed transformed into alkanolic acids, whereas the high stability of  $\eta^3$ -benzylic metal intermediates delivered mainly branched carboxylic acids from styrene derivatives. Therefore, organometallic catalysis faced a real obstacle in trying to shift the CO<sub>2</sub> fixation to the  $\beta$ -position for the latter. Recent reports have demonstrated that a specific design of organometallic nucleophiles is a primary requisite for the modulation of site selectivity and extension of substrates in hydrocarboxylation with CO<sub>2</sub>.<sup>5</sup> Earlier attempts to selectively generate linear carboxylic acids from styrenes and phenylacetylenes derivatives were limited to the use of organoboranes,<sup>6</sup> organozinc and Grignard reagents.<sup>7</sup> The nickel-catalyzed hydrocarboxylation of unsaturated bonds has nevertheless been controlled by the group of Martin by using appropriate ligands for the metal

center and water as a formal hydride source.<sup>8</sup> Photochemical carboxylation was also recently proved successful as activation mode for the synthesis of linear carboxylic acids.<sup>9</sup>

The electrochemical carboxylation of hydrocarbons was considered as an alternative very early on, but its development remained relatively limited due to the lack of selectivity.<sup>10,11</sup> For styrene transformation, site-selective hydrocarboxylations are hardly achieved, and a mixture of  $\alpha$ - and  $\beta$ -hydrocarboxylation or dicarboxylation is mostly observed.<sup>12</sup> Major advances in selective electrochemical carboxylation reactions of styrenes using carbon dioxide have, however, been reported very recently (Scheme 1). Nam and co-workers indeed developed a direct electrochemical  $\beta$ -selective hydrocarboxylation of styrenes using CO<sub>2</sub> and water, in which the site selectivity was controlled between  $\beta$ -hydrocarboxylation and dicarboxylation.<sup>13</sup> Malkov and Buckley also established an electrochemical protocol with triethanolamine as proton source delivering carboxylic acids from diversely substituted aryl-olefins with a high  $\beta$ -regioselectivity.<sup>14</sup>

Building on our recent developments for catalytic reactions mediated by electrogenerated low valent samarium species<sup>15</sup> and particularly on the electrochemical carboxylation of aryl halides<sup>16</sup> and benzyl halides,<sup>17</sup> we report here an alternative

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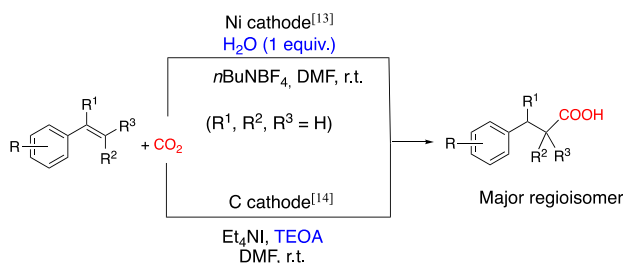
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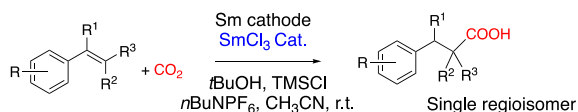


### Scheme 1. Electrochemical $\beta$ -Hydrocarboxylation of Styrenes with CO<sub>2</sub>

#### Previous works: Direct $\beta$ -Hydrocarboxylation



#### This work: Catalytic $\beta$ -Hydrocarboxylation



electrocatalytic approach for the regioselective  $\beta$ -hydrocarboxylation of low value styrene derivatives.

## RESULTS AND DISCUSSION

We began our investigation toward the hydrocarboxylation of styrene **1a** as a benchmark substrate using SmCl<sub>3</sub> as a precatalyst, a samarium rod as the cathode, and a stainless-steel grid as the anode at 5 mA/cm<sup>2</sup> current density (Table 1). The

Table 1. Optimization of the Reaction Conditions

Entry	SmCl <sub>3</sub> mol %	ROH (equiv)	TMSCl equiv	<b>2a</b> (%) <sup>a</sup>
1	10	H <sub>2</sub> O (20)	6	21
2	10	MeOH (20)	6	9
3	10	EtOH (20)	6	13
4	10	<i>t</i> -BuOH (20)	6	32
5	10	<i>t</i> -BuOH (3)	6	21
6	10	<i>t</i> -BuOH (10)	6	37
7	10	<i>t</i> -BuOH (10)	8	47
8 <sup>b</sup>	10	<i>t</i> -BuOH (10)	8	65
9	10	<i>t</i> -BuOH (10) + H <sub>2</sub> O (10)	8	45
10 <sup>c</sup>	10	<i>t</i> -BuOH (10)	8	–
11	5	<i>t</i> -BuOH (10)	8	30
12 <sup>d</sup>	10	<i>t</i> -BuOH (10)	8	–

<sup>a</sup>Isolated yields. <sup>b</sup>CO<sub>2(g)</sub> was replaced by dry ice (1 atm). <sup>c</sup>Reaction performed at –40 °C. <sup>d</sup>No current applied, 24 h.

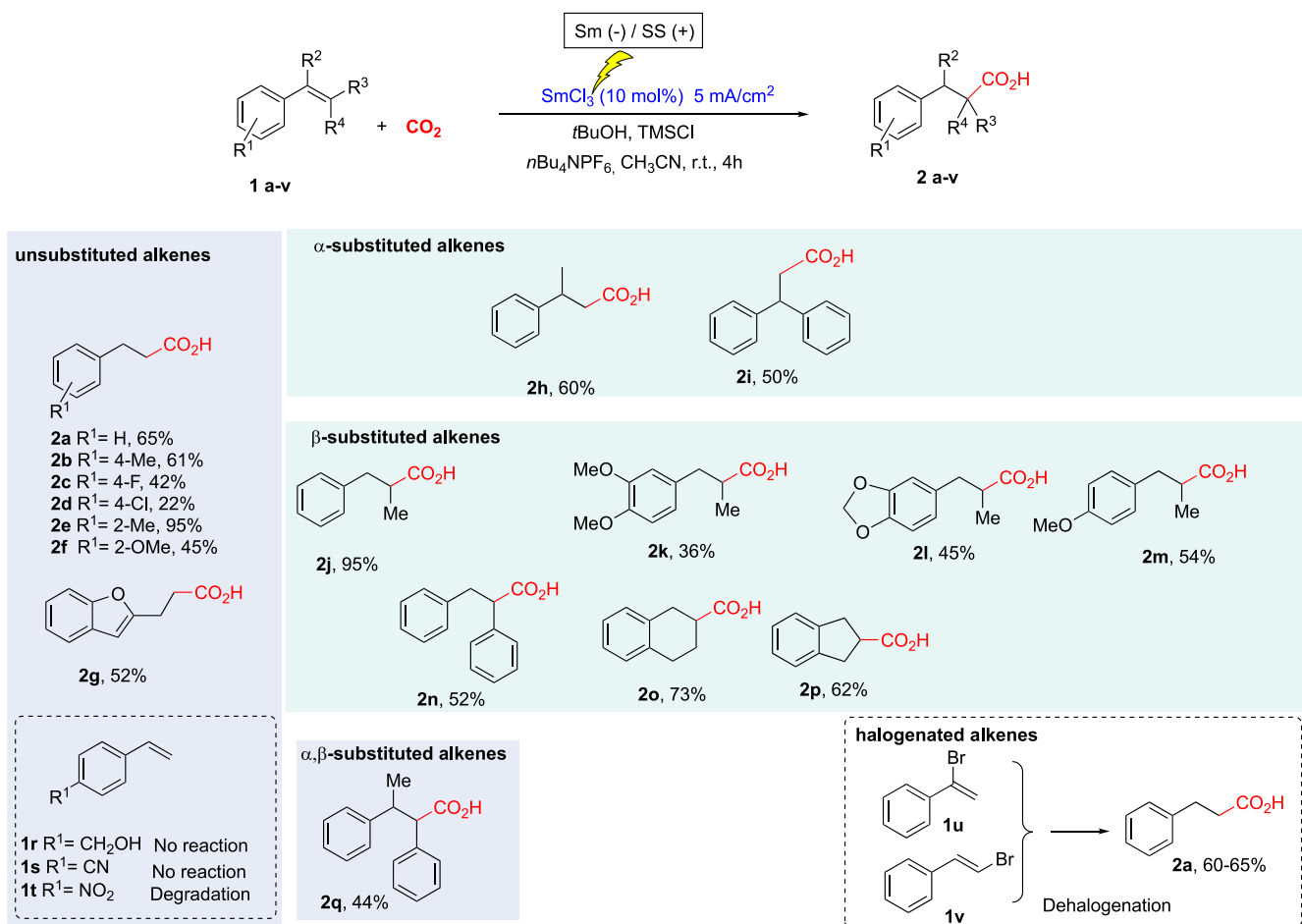
electrolysis was conducted in an undivided electrochemical cell according to the procedure developed for the carboxylation of aryl and benzyl halides.<sup>16,17</sup> The optimization study was conducted in acetonitrile using CO<sub>2(g)</sub> (1 atm). Water was initially chosen as a proton source after the reported accomplishments using the SmI<sub>2</sub>-H<sub>2</sub>O system for the reduction of challenging functional groups.<sup>18</sup> Even though a large quantity of the starting material was recovered, the monocarboxylic acid **2a** was isolated as a unique product with 21% yield using 20 equiv of H<sub>2</sub>O (Table 1, entry 1).

Water was then replaced by various alcohols and *t*-BuOH promoted the targeted transformation, providing the best result with up to 32% yield for **2a** (Table 1, entries 2–4). The effect of the amount of *t*-BuOH turned out to be crucial, since 3 equiv led to a lower yield of the desired product (Table 1, entry 5), but 10 equiv of *t*-BuOH was enough to produce exclusively the carboxylic acid **2a** with 37% yield (Table 1, entry 6). Finally increasing the quantity of TMSCl from 6 equiv to 8 equiv allowed to isolate the carboxylic acid with a maximal yield of 47% (entry 7). Eventually, we found that using dry ice as CO<sub>2</sub> source was beneficial since the yield is significantly improved to 65% without modifications in the operating conditions (entry 8). At this stage, it was verified that the increase in the efficiency of the reaction was not due to a possible addition of water to the reaction medium in the presence of dry ice (entry 9). The drop in temperature linked to the addition of dry ice is not responsible for the better yield of the reaction, as revealed by an electrolysis carried out at –40 °C in the presence of CO<sub>2(g)</sub> (entry 10). The catalytic loading was also evaluated, and it was found that 10 mol % is necessary to obtain the best results (compare in Table 1, entries 7 and 11). The electrochemical nature of the reduction was proven by a blank experiment with no current applied, all other things being equal, which did not lead to any conversion (entry 12). It was observed that the stainless-steel electrode is not sacrificially oxidized; instead, chloride oxidation is likely at the anode.

Encouraged by these results, we set out to investigate the preparative scope of the Sm(II)-catalyzed regioselective  $\beta$ -hydrocarboxylation of styrene derivatives (Scheme 2). Initially, different styrenes bearing various substituents on the aromatic moiety were evaluated, and all (**1b–1f**) proved to be compatible with the electrochemical conditions, affording the corresponding carboxylic acids with a complete regioselectivity. Nevertheless, the chlorinated derivative **1d** suffered a dramatic decrease in the isolated yield of the targeted product (22%), probably due to undesired dehalogenation reaction. To our delight, a (hetero)aromatic reagent such as 2-vinylbenzofuran **1g** was also tolerated and gave 3-(1-benzofuran-2-yl) propionic acid **2g** with 52% isolated yield. These electrochemical conditions also accept substituents on the vinyl group of styrene, providing exclusively  $\beta$ -hydrocarboxylated products. In the case of  $\alpha$ -substituted styrenes **1h** and **1i**, the corresponding monocarboxylated products were produced in good yields.

As shown in Scheme 2, the hydrocarboxylation of  $\beta$ -substituted styrenes bearing a methyl substituent (**1j–1m**, *trans*-configuration) or cyclic ones (**1o** and **1p**) delivered also the corresponding carboxylic acids in moderate to excellent yields (36–95%). A stilbene derivative (**1n**) underwent the transformation smoothly and provided the desired carboxylic acid, although in a moderate yield, probably due to steric hindrance. Moreover, the more sterically demanding  $\alpha,\beta$ -disubstituted styrene **1q** was also reactive under these conditions. It was however found that the presence of a hydroxymethyl or a cyano group on the substrate (**1r** and **1s**) fully inhibited the reaction and returned significant amounts of starting materials. This observation can be rationalized with the high tendency of samarium to strongly coordinate to such substituents, which may lead to catalyst quenching. In the case of substrate **1t** bearing a nitro group, substantial conversion to degradation products was detected in the crude. These side reactions were attributed to the propensity of Sm species to

## Scheme 2. Substrate Scope of Styrene Derivatives

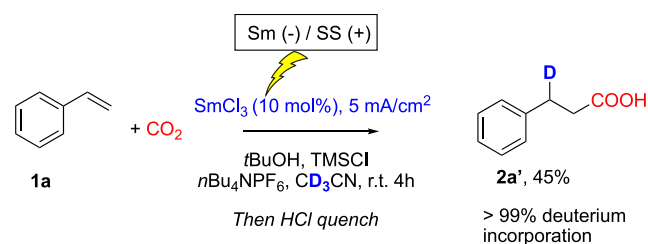


reduce nitro functions.<sup>15a</sup> Interestingly, vinyl bromides **1u** and **1v** were also prone to dehalogenation, furnishing exclusively **2a** as final product with comparable yields to the one obtained from **1a**.

We then investigated the mechanism of this electrocatalytic hydrocarboxylation. Our studies were first focused on assigning the role of each component present in the electrochemical cell. Without the catalyst or *t*-BuOH, the transformation of styrenes showed inertia with respect to direct electrocarboxylation; it led indeed to considerable degradation but without any formation of carboxylic acid. In the absence of TMSCl, only 8% of **2a** were produced. Replacing the samarium cathode with a glassy carbon one in the presence of SmCl<sub>3</sub> also resulted in complete degradation of the substrate. This is in line with our previous studies,<sup>15b</sup> in which screening of cathode materials for reduction of Sm(III) salts was found to be possible only with Sm as the cathode. These blank experiments indicate that, in our case, the samarium activation of CO<sub>2</sub> is mandatory to perform the electrocarboxylation of such unsaturated products.

Deuterium labeling experiments were then conducted to elucidate the protonation step. We first explored the hydrocarboxylation of **1a** followed by DCl quench but **2a** was isolated without any deuterium fixation. Surprisingly, the addition of *t*-BuOD, supposed to be the proton donor, also delivered the deuterium-free product. Lastly, the reaction was performed in CD<sub>3</sub>CN, and interestingly **2a'** was isolated with more than 99% deuterium incorporation on the benzylic position (Scheme 3). At this point, we hypothesized that this

## Scheme 3. Deuterium Labeling Experiments

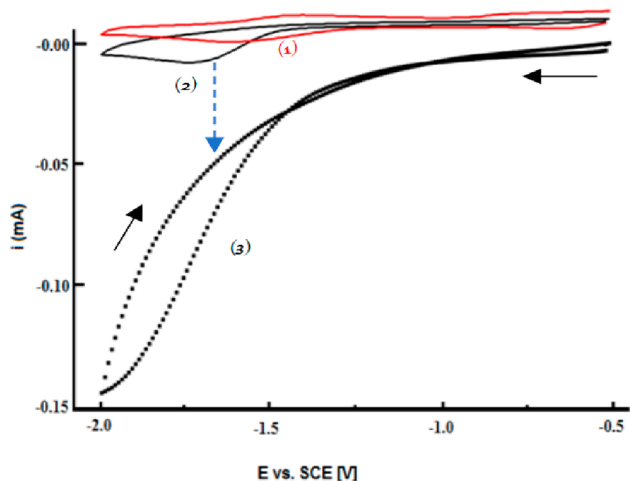


specific behavior of acetonitrile was triggered by its coordination at the Sm center, which makes the protons much more acidic and thus explains the observed proton-donating character. Noteworthy, this behavior was also reported with transition-metal based catalysts.<sup>19</sup> We accordingly propose that after CH<sub>3</sub>CN deprotonation, the simple coordination of Sm(III) via the nitrogen atom (Sm-NCCH<sub>3</sub>) is transformed into a strong Sm-CH<sub>2</sub>CN bond. At this stage, *t*-BuOH, known as noncoordinating alcohol<sup>20</sup> and activated by TMSCl, can therefore be deprotonated by the generated carbanion, thus leading to the dissociation of the Sm(III) species.

To further clarify the mechanism, attempts to quench a radical intermediate were made with indene **1p** as the starting material. In this case, the addition of a specific amount of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl TEMPO (2 equiv) led to complete inhibition of the hydrocarboxylation. Extending

the reaction time to 8 h of electrocatalysis made it possible to restore the reactivity, and finally, the expected product **2p** was isolated with the same yield as without TEMPO (see SI). As already described in our previous work,<sup>16</sup> this result shows that the radical scavenger did not deactivate the catalyst. We rather propose that it was initially neutralized by the  $\text{CO}_2^{\bullet-}$  radical anion formed to lead to an unstable, not isolable intermediate, to explain the reactivity found after complete consumption of TEMPO.

To gain insight into the electrochemical behavior of the species present in the solution, a series of cyclic voltammetry experiments were carried out. These studies were initiated by determining the behavior of each reactant in the electrochemical medium. The reduction potentials of various styrene derivatives have been described, with potential values lower than  $-2.4$  V vs Ag/Ag<sup>+</sup>.<sup>13</sup> These values have been nevertheless determined in our electrochemical conditions (see SI), confirming that all substrates are more difficult to reduce than the Sm(III) species. The cyclic voltammogram of  $\text{SmCl}_2$  electrogenerated from  $\text{SmCl}_3$  in  $\text{CH}_3\text{CN}$  containing  $n\text{Bu}_4\text{NPF}_6$  as supporting electrolyte is presented in Figure 1. It shows a

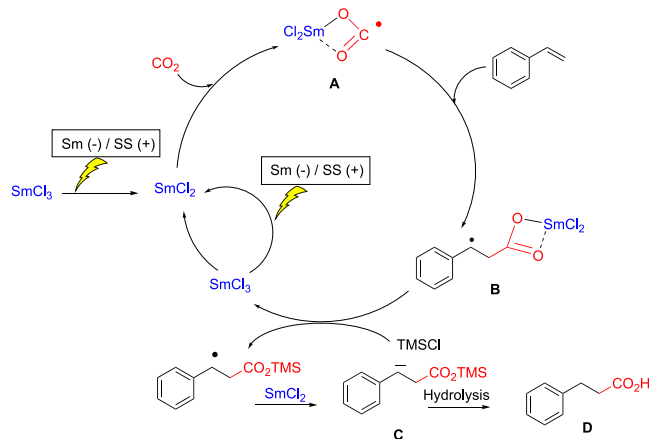


**Figure 1.** Electrochemical behavior of  $\text{SmCl}_3$  with styrene **1a**. Cyclic voltammetry performed using a GC electrode ( $20 \text{ mm}^2$ ) and a Pt wire as counter electrode with a scanning potential between  $-0.5$  and  $-2$  V vs SCE in  $\text{CH}_3\text{CN}$  with  $n\text{Bu}_4\text{NPF}_6$  [ $0.1 \text{ M}$ ]. Scan rate:  $100 \text{ mV/s}$ . Red curve (1):  $0.02 \text{ M SmCl}_3$  in  $0.1 \text{ M } n\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$ ; black curve (2): after introduction of  $\text{CO}_2$ ; dashed curve (3): addition of  $1 \text{ mL}$  of  $t\text{-BuOH/TMSCl/1a}$  ( $10/8/1$ ).

quasi-reversible system with a redox potential around  $-1.5$  V/SCE (red curve (1) in Figure 1). Addition of  $\text{CO}_2$  caused the loss of the oxidation wave of  $\text{SmCl}_2$ , while the reduction wave persisted with a slight cathodic shift to  $-1.6$  V/SCE (black curve (2) in Figure 1). This result indicates that a chemical reaction took place between  $\text{CO}_2$  and  $\text{Sm(II)}$ , releasing another  $\text{Sm(III)}$  complex. Moreover, when adding a solution ( $1 \text{ mL}$ ) containing styrene **1a** ( $3 \times 10^{-3} \text{ M}$ ),  $t\text{-BuOH}$  ( $10$  equiv) and  $\text{TMSCl}$  ( $8$  equiv) in  $\text{CH}_3\text{CN}$ , a massive reduction wave emerged (dashed black curve (3) in Figure 1). This electrochemical behavior shows the existence of a catalytic current, proving that the hydrocarboxylation was catalyzed by  $\text{SmCl}_2$ .<sup>21</sup>

Consequently, we propose the following mechanism for the hydrocarboxylation of alkenes (Scheme 4). First, the electrogenerated  $\text{Sm(II)}$  species reduces selectively the  $\text{CO}_2$  and

#### Scheme 4. Proposed Mechanism for the Catalytic $\beta$ -Hydrocarboxylation of Alkenes



generates the corresponding radical anion **A** as a samarium carboxylate.<sup>22</sup> This latter undergoes an anti-Markovnikov addition onto the unsaturated substrate to produce the benzylic radical **B** which after transmetalation with  $\text{TMSCl}$  is rapidly reduced by a second equivalent of  $\text{Sm(II)}$  to the carbanion **C**. In the mixture, the  $t\text{-BuOH}$ , activated by  $\text{TMSCl}$ , is essential for the reaction. Therefore, we suggest a mechanism displaying two successive proton donations: The first one involves the solvent  $\text{CH}_3\text{CN}$  that after its activation by the catalyst transfers one proton to form the product **D** after hydrolysis. The  $\text{CH}_2\text{CN}^-$  anion extracts the nearest activated structure, from the  $t\text{-BuOH-TMSCl}$  adduct, to restore its original structure and dissociate the  $\text{Sm(III)}$  to be regenerated on the cathode. This mechanistic proposal is based in particular on the deuterium labeling experiments that were carried out. However, possible H/D exchanges between  $t\text{-BuOH}$  and acetonitrile could not be excluded under the reaction conditions.

#### CONCLUSION

In summary, we have developed the regioselective hydrocarboxylation of styrene derivatives via  $\text{CO}_2$  activation, catalyzed by a reductive  $\text{SmCl}_2$  complex in acetonitrile. This reaction showed remarkable anti-Markovnikov selectivity to give the aliphatic carboxylic acids in good to excellent yields. Several experimental investigations allowed identifying the role of each species present in this reaction. Foremost, after various blank tests, it was proven that  $\text{SmCl}_2$  catalyzes this reaction assisted by acetonitrile and  $t\text{-BuOH}$ . Electrochemical measurements confirmed the existence of a catalytic process.

#### EXPERIMENTAL SECTION

**General Procedure for the Catalytic Carboxylation of Styrene Derivatives.** An undivided cell charged with tetrabutylammonium hexafluorophosphate  $n\text{Bu}_4\text{NPF}_6$  ( $1 \text{ mmol}$ ,  $387 \text{ mg}$ ) in acetonitrile ( $40 \text{ mL}$ ), equipped with a samarium rod as the cathode and a stainless-steel as the anode, was used. The electrogeneration of  $\text{Sm}^{2+}$  from  $\text{SmCl}_3$  ( $0.1 \text{ mmol}$ ,  $26 \text{ mg}$ ) was started by setting the chronopotentiometry mode for  $15000 \text{ s}$  with  $i = 5 \text{ mA/cm}^2$ . The dry ice was carefully added to the mixture in small pieces followed by the alkene ( $1.0 \text{ mmol}$ ,  $104 \text{ mg}$  in the case of styrene),  $t\text{-BuOH}$  ( $10 \text{ mmol}$ ,  $741 \text{ mg}$ ) and trimethylsilyl chloride ( $8 \text{ mmol}$ ,  $869 \text{ mg}$ ). During the electrolysis, small pieces of dry ice were added each  $15 \text{ min}$ . After  $4 \text{ h}$  of electrolysis, the reaction was quenched with diethyl ether  $\text{Et}_2\text{O}$  ( $10 \text{ mL}$ ), and the solvent was evaporated. To the obtained solid, a

solution of HCl (2 M) was added, and the aqueous solution was extracted with Et<sub>2</sub>O (2 × 30 mL). The combined organic phase was washed with water and brine and dried over anhydrous MgSO<sub>4</sub>. The solvent evaporation under vacuo furnished the product that was purified by column chromatography on silica gel (90/10 then 50/50 PE/EtOAc).

**3-Phenylpropanoic Acid (2a).** 97.5 mg (0.65 mmol, 65%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 11.31 (br, 1H), 7.42–7.32 (m, 5H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 177.8, 140.1, 128.5, 128.2, 126.3, 35.3, 30.5. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**3-Phenylpropanoic Acid (2a).** 90.0 mg (0.60 mmol, 60%) was also prepared starting from **1u** (183.0 mg, 1 mmol) or **1v** (183.0 mg, 1 mmol).

**3-(*p*-Tolyl)propanoic Acid (2b).** 100 mg (0.61 mmol, 61%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.19 (m, 4H), 3.00 (t, *J* = 7.8 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.41 (s, 3H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 179.6, 137.1, 135.9, 129.3, 128.2, 35.8, 30.2, 21.0. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**3-(4-Fluorophenyl)propanoic Acid (2c).** 70.5 mg (0.42 mmol, 42%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.22–7.11 (m, 2H), 7.04–6.91 (m, 2H), 2.93 (t, *J* = 7.7 Hz, 2H), 2.67 (t, *J* = 7.7 Hz, 2H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 179.2, 161.4 (d, *J* = 257.6 Hz), 135.7 (d, *J* = 3.6 Hz), 129.6 (d, *J* = 7.9 Hz), 115.3 (d, *J* = 21.2 Hz), 35.6, 29.6. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**3-(4-Chlorophenyl)propanoic Acid (2d).** 40.5 mg (0.22 mmol, 22%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.42–7.15 (m, 4H), 3.02 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 178.6, 140.1, 128.5, 128.2, 126.3, 35.5, 30.5. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**3-(*o*-Tolyl)propanoic Acid (2e).** 156 mg (0.95 mmol, 95%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 11.56 (br, 1H), 7.24 (m, 4H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.80–2.67 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 179.8, 138.3, 136.0, 130.4, 128.5, 126.6, 126.2, 34.4, 28.0, 19.3. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>23</sup>

**3-(2-Methoxyphenyl)propanoic Acid (2f).** 81 mg (0.45 mmol, 45%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.30–7.14 (m, 2H), 6.90 (dd, *J* = 14.3, 7.6 Hz, 2H), 3.85 (s, 3H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 179.8, 157.4, 129.9, 128.4, 127.7, 120.4, 110.2, 55.1, 34.0, 25.8. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>23</sup>

**3-(Benzofuran-2-yl)propanoic Acid (2g).** 99 mg (0.52 mmol, 52%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.52–7.45 (m, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.20 (td, *J* = 14.1, 7.1 Hz, 2H), 6.45 (s, 1H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 177.2, 156.8, 154.6, 128.5, 123.4, 122.6, 120.5, 110.8, 102.6, 31.8, 23.7. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**3-Phenylbutanoic Acid (2h).** 94.5 mg (0.60 mmol, 60%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.49–7.13 (m, 5H), 3.41–3.24 (m, 1H), 2.76–2.59 (m, 2H), 1.37 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 178.7, 145.4, 128.5, 126.7, 126.5, 42.6, 36.1, 21.8. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**3,3-Diphenylpropanoic Acid (2i).** 113 mg (0.50 mmol, 50%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.55–7.08 (m, 10H), 4.58 (t, *J* = 7.9 Hz, 1H), 3.14 (d, *J* = 7.9 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 178.0, 143.1, 128.6, 127.5, 126.6, 46.6, 40.4. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**2-Methyl-3-phenylpropanoic Acid (2j).** 156 mg (0.95 mmol, 95%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 10.70 (br, 1H), 7.50–7.14 (m, 5H), 3.14 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.82 (dq, *J* = 13.2, 6.8 Hz, 1H), 2.73 (dd, *J* = 13.3, 8.0 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 182.8, 139.1, 129.0, 128.5, 126.5, 41.3, 39.3, 16.5. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**3-(3,4-Dimethoxyphenyl)-2-methylpropanoic Acid (2k).** 80 mg (0.36 mmol, 36%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 6.76 (m, 3H), 3.85 (s, 6H), 3.01 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.73 (dq, *J* = 13.5, 6.9 Hz, 1H), 2.63 (dd, *J* = 13.4, 7.8 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 182.3, 148.7, 147.5, 131.5, 121.0, 112.1, 111.1, 55.8, 55.7, 41.4, 38.9, 16.4. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>24</sup>

**3-(Benzo[d][1,3]dioxol-5-yl)-2-methylpropanoic Acid (2l).** 93 mg (0.45 mmol, 45%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 6.69 (m, 3H), 5.94 (s, 2H), 3.00 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.71 (m, 1H), 2.62 (dd, *J* = 13.4, 7.8 Hz, 2H), 1.19 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 182.4, 147.6, 146.1, 132.7, 121.9, 109.3, 108.1, 100.8, 41.4, 39.0, 16.4. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>25</sup>

**3-(4-Methoxyphenyl)-2-methylpropanoic Acid (2m).** 105 mg (0.54 mmol, 54%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.05 (dd, *J* = 13.3, 6.3 Hz, 1H), 2.85–2.71 (m, 1H), 2.67 (dd, *J* = 13.3, 7.8 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 179.6, 158.2, 131.1, 129.9, 113.9, 55.2, 41.4, 38.4, 16.4. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>26</sup>

**2,3-Diphenylpropanoic Acid (2n).** 158 mg (0.7 mmol, 70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.16 (br, 1H), 7.65–6.97 (m, 10H), 3.94 (t, *J* = 7.7 Hz, 1H), 3.49 (dd, *J* = 13.8, 8.3 Hz, 1H), 3.11 (dd, *J* = 13.8, 7.1 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 179.6, 138.7, 137.9, 128.9, 128.7, 128.4, 128.1, 127.6, 126.5, 53.5, 39.3. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>27</sup>

**1,2,3,4-Tetrahydronaphthalene-2-carboxylic Acid (2o).** 126 mg (0.73 mmol, 73%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 11.42 (br 1H), 7.38–7.03 (m, 4H), 3.13 (d, *J* = 7.3 Hz, 2H), 3.01–2.81 (m, 3H), 2.34 (m, 1H), 1.98 (m, 1H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 181.4, 135.6, 134.6, 129.1, 128.9, 126.0, 125.9, 39.7, 31.3, 28.4, 25.6. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**2,3-Dihydro-1H-indene-2-carboxylic Acid (2p).** 100 mg (0.62 mmol, 62%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.35–7.13 (m, 4H), 3.49–3.23 (m, 5H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 182.0, 141.3, 126.7, 124.4, 43.4, 36.0. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with those reported in the literature.<sup>9c</sup>

**2,3-Diphenylbutanoic Acid (2q).** 166 mg (0.44 mmol, 44%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.76–6.87 (m, 10H), 3.72 (d, *J* = 11.2 Hz, H), 3.54–3.33 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (91 MHz, CDCl<sub>3</sub>) δ 178.2, 144.5, 137.0, 130.4, 128.4, 127.7, 127.3, 126.4, 59.1, 42.9, 19.9. HRMS (*m/z*) [*M* + Na]<sup>+</sup> calculated 263.1048, found 263.0995.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.3c00076>.

Experimental procedures, cyclic voltammograms, compounds data and spectra (PDF)

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### Author Contributions

S.B. and L.H. collected the data and performed the analyses. S.B., E.S., and M.M. conceived and designed the work and contributed to the writing of the manuscript.

### Notes

The authors declare no competing financial interest.

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### REFERENCES

- (1) (a) Gui, Y.-Y.; Zhou, W.-J.; Ye, J.-H.; Yu, D.-G. Photochemical Carboxylation of Activated C(sp<sup>3</sup>)-H Bonds with CO<sub>2</sub>. *ChemSusChem* **2017**, *10*, 1337–1340. (b) Börjesson, M.; Moragas, T.; Gallego, D.; Martin, R. Metal-Catalyzed Carboxylation of Organic (Pseudo)halides with CO<sub>2</sub>. *ACS Catal.* **2016**, *6*, 6739–6749. (c) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using Carbon Dioxide as a Building Block in Organic Synthesis. *Nat. Commun.* **2015**, *6*, 5933. (d) Tsuji, Y.; Fujihara, T. Carbon Dioxide as a Carbon Source in Organic Transformation: Carbon–Carbon Bond Forming Reactions by Transition-Metal Catalysts. *Chem. Commun.* **2012**, *48*, 9956–9964. (e) Martín, R.; Kleij, A. W. Myth or Reality? Fixation of Carbon Dioxide into Complex Organic Matter Under Mild Conditions. *ChemSusChem* **2011**, *4*, 1259–1263. (f) Huang, K.; Sun, C.-L.; Shi, Z.-J. Transition-Metal-Catalyzed C-C Bond Formation Through the Fixation of Carbon Dioxide. *Chem. Soc. Rev.* **2011**, *40*, 2435–2452. (g) Correa, A.; Martín, R. Metal-Catalyzed Carboxylation of Organometallic Reagents with Carbon Dioxide. *Angew. Chem., Int. Ed.* **2009**, *48*, 6201–6204. (h) Sakakura, T.; Choi, J.-C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365–2387. (i) Braunstein, P.; Matt, D.; Nobel, D. Reactions of Carbon Dioxide with Carbon–Carbon Bond Formation Catalyzed by Transition-Metal Complexes. *Chem. Rev.* **1988**, *88*, 747–764.
- (2) (a) Maag, H. In *Prodrugs. Biotechnology: Pharmaceutical Aspects*; Stella, V.J.; Borchardt, R. T.; Hageman, M. J.; Oliyai, R.; Maag, H.; Tilley, J. W., Eds.; Springer, New York, 2007; Vol V. (b) *The Chemistry of Acid Derivatives*; Patai, S. Ed.; John Wiley & Sons, New York, 1992; Supplement B, Vol. 2.
- (3) (a) Zhang, Y.; Riduan, S. N. Catalytic Hydrocarboxylation of Alkenes and Alkynes with CO<sub>2</sub>. *Angew. Chem., Int. Ed.* **2011**, *50*, 6210–6212.
- (4) (a) Yatham, V. R.; Shen, Y.; Martin, R. Catalytic Intermolecular Dicarbofunctionalization of Styrenes with CO<sub>2</sub> and Radical Precursors. *Angew. Chem., Int. Ed.* **2017**, *56*, 10915–10919. (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*, 3098–3101. (c) Kawashima, S.; Aikawa, K.; Mikami, K. Rhodium-Catalyzed Hydrocarboxylation of Olefins with Carbon Dioxide. *Eur. J. Org. Chem.* **2016**, *2016*, 3166–3170. (d) 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.* **2016**, *18*, 2050–2053. (e) Tanaka, S.; Tanaka, Y.; Chiba, M.; Hattori, T. Lewis Acid-Mediated  $\beta$ -Selective Hydrocarboxylation of  $\alpha,\alpha$ -Diaryl- and  $\alpha$ -Arylalkenes with R<sub>3</sub>SiH and CO<sub>2</sub>. *Tetrahedron Lett.* **2015**, *56*, 3830–3834. (f) Williams, C. M.; Johnson, J. B.; Rovis, T. Nickel-Catalyzed Reductive Carboxylation of Styrenes Using CO<sub>2</sub>. *J. Am. Chem. Soc.* **2008**, *130*, 14936–14937.
- (5) (a) Luan, Y.-X.; Ye, M. Transition Metal-Mediated or Catalyzed Hydrocarboxylation of Olefins with CO<sub>2</sub>. *Tetrahedron Lett.* **2018**, *59*, 853–861. (b) Kirillov, E.; Carpentier, J.-F.; Bunel, E. Carboxylic Acid Derivatives via Catalytic Carboxylation of Unsaturated Hydrocarbons: Whether the Nature of a Reductant May Determine the Mechanism of CO<sub>2</sub> Incorporation? *Dalton Trans.* **2015**, *44*, 16212–16223. (c) Juhl, M.; Laursen, S. L. R.; Huang, Y.; Nielsen, D. U.; Daasbjerg, K.; Skrydstrup, T. Copper-Catalyzed Carboxylation of Hydroborated Disubstituted Alkenes and Terminal Alkynes with Cesium Fluoride. *ACS Catal.* **2017**, *7*, 1392–1396. (d) 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.* **2011**, *50*, 8114–8117. (e) Ohmiya, H.; Tanabe, M.; Sawamura, M. Copper-Catalyzed Carboxylation of Alkylboranes with Carbon Dioxide: Formal Reductive Carboxylation of Terminal Alkenes. *Org. Lett.* **2011**, *13*, 1086–1088. (f) Greenhalgh, M. D.; Thomas, S. P. Iron-Catalyzed, Highly Regioselective Synthesis of  $\alpha$ -Aryl Carboxylic Acids from Styrene Derivatives and CO<sub>2</sub>. *J. Am. Chem. Soc.* **2012**, *134*, 11900–11903.
- (6) (a) Juhl, M.; Moragas, T.; Juliá-Hernández, F.; Martín, R. Site-Selective Catalytic Carboxylation of Unsaturated Hydrocarbons with CO<sub>2</sub> and Water. *J. Am. Chem. Soc.* **2017**, *139*, 12161–12164. (b) 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.* **2018**, *140*, 3198–3201. (c) Seo, H.; Liu, A.; Jamison, T. F. Direct  $\beta$ -Selective Hydrocarboxylation of Styrenes with CO<sub>2</sub> Enabled by Continuous Flow Photoredox Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 13969–13972.
- (7) (a) Senboku, H. Electrochemical Fixation of Carbon Dioxide: Synthesis of Carboxylic Acids. *Chem. Rec.* **2021**, *21*, 2354–2374. (b) Yang, Z.; Yu, Y.; Lai, L.; Zhou, L.; Ye, K.; Chen, F.-E. Carbon Dioxide Cycle via Electrocatalysis: Electrochemical Carboxylation of CO<sub>2</sub> and Decarboxylative Functionalization of Carboxylic Acids. *Green Synth. Catal.* **2021**, *2*, 19–26. (c) Baran, P. S.; Kawamata, Y.; Yan, M. Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. *Chem. Rev.* **2017**, *117*, 13230–13319. (d) Senboku, H.; Katayama, A. Electrochemical Carboxylation with Carbon Dioxide. *Curr. Opin. Green Sust. Chem.* **2017**, *3*, 50–54. (e) Matthesen, R.; Fransær, J.; Binnemans, K.; De Vos, D. E. Electrocarboxylation: Towards Sustainable and Efficient Synthesis of Valuable Carboxylic Acids. *Beilstein J. Org. Chem.* **2014**, *10*, 2484–2500. (f) Silvestri, G.; Gambino, S.; Filardo, G.; et al. Use of Sacrificial Anodes in Synthetic Electrochemistry. Processes Involving Carbon Dioxide. *Acta Chem. Scand.* **1991**, *45*, 987–992.
- (8) (a) Yuan, G.-Q.; Jiang, H.-F.; Lin, C.; Liao, S.-J. Efficient Electrochemical Synthesis of 2-Arylsuccinic Acids from CO<sub>2</sub> and Aryl-Substituted Alkenes with Nickel as the Cathode. *Electrochim. Acta* **2008**, *53*, 2170–2176. (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*, 913–916. (c) 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*, 418–420.
- (9) (a) Ballivet-Tkatchenko, D.; Folest, J. C.; Tanji, J. Electrocatalytic Reduction of CO<sub>2</sub> for the Selective Carboxylation of Olefins. *Appl. Organomet. Chem.* **2000**, *14*, 847–849. (b) Dérien, S.; Clinet, J. C.; Duñach, E.; Périchon, J. Electrochemical Incorporation of Carbon Dioxide into Alkenes by Nickel Complexes. *Tetrahedron* **1992**, *48*, 5235–5248. (c) Gambino, S.; Gennaro, A.; Filardo, G.; Silvestri, G.;

Vianello, E. Electrochemical Carboxylation of Styrene. *J. Electrochem. Soc.* **1987**, *134*, 2172–2174.

(13) Kim, Y.; Park, G. D.; Balamurugan, M.; Seo, J.; Min, B. K.; Nam, K. T. Electrochemical  $\beta$ -Selective Hydrocarboxylation of Styrene Using CO<sub>2</sub> and Water. *Adv. Sci.* **2020**, *7*, 1900137.

(14) 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*, 1780–1785.

(15) (a) Zhang, Y.-F.; Mellah, M. Convenient Electrocatalytic Synthesis of Azobenzenes from Nitroaromatic Derivatives Using SmI<sub>2</sub>. *ACS Catal.* **2017**, *7*, 8480–8486. (b) Sun, L.; Sahloul, K.; Mellah, M. Use of Electrochemistry to Provide Efficient SmI<sub>2</sub> Catalytic System for Coupling Reactions. *ACS Catal.* **2013**, *3*, 2568–2573.

(16) Bazzi, S.; Le Duc, G.; Schulz, E.; Gosmini, C.; Mellah, M. CO<sub>2</sub> Activation by Electrogenerated Divalent Samarium for Aryl Halide Carboxylation. *Org. Biomol. Chem.* **2019**, *17*, 8546–8550.

(17) Bazzi, S.; Schulz, E.; Mellah, M. Electrogenerated Sm(II)-Catalyzed CO<sub>2</sub> Activation for Carboxylation of Benzyl Halides. *Org. Lett.* **2019**, *21*, 10033–10037.

(18) (a) Ramírez-Solís, A.; Bartulovich, C. O.; León-Pimentel, C. I.; Saint-Martin, H.; Boekell, N. G.; Flowers, R. A. Proton Donor Effects on the Reactivity of SmI<sub>2</sub>. Experimental and Theoretical Studies on Methanol Solvation vs. Aqueous Solvation. *Dalton Trans.* **2020**, *49*, 7897–7902. (b) Ramírez-Solís, A.; Bartulovich, C. O.; León-Pimentel, C. I.; Saint-Martin, H.; Anderson, W. R., Jr; Flowers, R. A. Experimental and Theoretical Studies on the Aqueous Solvation and Reactivity of SmCl<sub>2</sub> and Comparison with SmBr<sub>2</sub> and SmI<sub>2</sub>. *Inorg. Chem.* **2019**, *58*, 13927–13932. (c) Bartulovich, C. O.; Flowers, R. A. Coordination-Induced O–H Bond Weakening in Sm(II)-Water Complexes. *Dalton Trans.* **2019**, *48*, 16142–16147. (d) Szostak, M.; Spain, M.; Parmar, D.; Procter, D. J. Selective Reductive Transformations Using Samarium Diiodide-Water. *Chem. Commun.* **2012**, *48*, 330–346.

(19) Bissember, A. C.; Gardiner, M. G.; Wierenga, T. S.  $\alpha$ -CyanoCarbanion Complexes and their Application in Synthesis. *J. Organomet. Chem.* **2018**, *869*, 213–226.

(20) (a) Chopade, P. R.; Prasad, E.; Flowers, R. A. The Role of Proton Donors in SmI<sub>2</sub>-Mediated Ketone Reduction: New Mechanistic Insights. *J. Am. Chem. Soc.* **2004**, *126*, 44–45. (b) Hutton, T. K.; Muir, K. W.; Procter, D. J. Switching Between Novel Samarium(II)-Mediated Cyclizations by a Simple Change in Alcohol Cosolvent. *Org. Lett.* **2003**, *5*, 4811–4814.

(21) For a recent example of electrochemical reduction of SmI<sub>3</sub> into SmI<sub>2</sub> see: Arashiba, K.; Kanega, R.; Himeda, Y.; Nishibayashi, Y. Electrochemical Reduction of Samarium Triiodide into Samarium Diiodide. *Chem. Lett.* **2020**, *49*, 1171–1173.

(22) (a) Willauer, A. R.; Toniolo, D.; Fadaei-Tirani, F.; Yang, Y.; Laurent, M.; Mazzanti, M. Carbon Dioxide Reduction by Dinuclear Yb(II) and Sm(II) Complexes Supported by Siloxide Ligands. *Dalton Trans.* **2019**, *48*, 6100–6110. (b) Castro, L.; Labouille, S.; Kindra, D. R.; Ziller, J. W.; Nief, F.; Evans, W. J.; Maron, L. Insights into the Mechanism of Reaction of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm<sup>II</sup>(thf)<sub>2</sub>] with CO<sub>2</sub> and COS by DFT Studies. *Chem.—Eur. J.* **2012**, *18*, 7886–7895.

(23) Shabbir, S.; Lee, S.; Lim, M.; Lee, H.; Ko, H.; Lee, Y.; Rhee, H. Pd Nanoparticles on Reverse Phase Silica Gel as Recyclable Catalyst for Suzuki-Miyaura Cross Coupling Reaction and Hydrogenation in Water. *J. Organomet. Chem.* **2017**, *846*, 296–304.

(24) Cueva, J. P.; Gallardo-Godoy, A.; Juncosa, J. I.; Vidi, P. A.; Lill, M. A.; Watts, V. J.; Nichols, D. E. Probing the Steric Space at the Floor of the D1 Dopamine Receptor Orthosteric Binding Domain:  $7\alpha$ -,  $7\beta$ -,  $8\alpha$ -, and  $8\beta$ -Methyl Substituted Dihydropyridine Analogues. *J. Med. Chem.* **2011**, *54*, 5508–5521.

(25) Schulze, M. Synthesis of 2-Arylethylamines by the Curtius Rearrangement. *Synth. Commun.* **2010**, *40*, 1461–1476.

(26) Zhu, Y.; Chen, X.; Yuan, C.; Li, G.; Zhang, J.; Zhao, Y. Pd-Catalyzed Ligand-Enabled Carboxylate-Directed Highly Regioselective Arylation of Aliphatic Acids. *Nature Commun.* **2017**, *8*, 14904.

(27) Meng, Q.-Y.; Schirmer, T. E.; Berger, A. L.; Donabauer, K.; König, B. Photocarboxylation of Benzylic C–H Bonds. *J. Am. Chem. Soc.* **2019**, *141*, 11393–11397.