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Electrogenerated Sm(II)-Catalyzed Carbon Dioxide Reduction for β -Hydrocarboxylation of Styrenes.

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KEYWORDS: *Samarium, Catalysis, Electrochemistry, Carbon dioxide reduction, Alkenes, Hydrocarboxylation.*

ABSTRACT: The synthesis of carboxylic acids from low-value materials such as alkenes using CO₂ as a C₁-building block remains a real challenge for synthetic chemists from both reactivity and selectivity perspective. Electrochemical carboxylations have been examined but they remain limited, still suffering from a crucial lack of selectivity. Herein we report a new catalytic protocol based on an electrogenerated Sm(II) catalyst as a powerful CO₂ reductant, able to perform exclusively *anti*-Markovnikov hydrocarboxylation of alkenes. This electrochemical approach overcomes several current limitations and allows direct β -hydrocarboxylation of styrene derivatives, in a regioselective manner.

INTRODUCTION

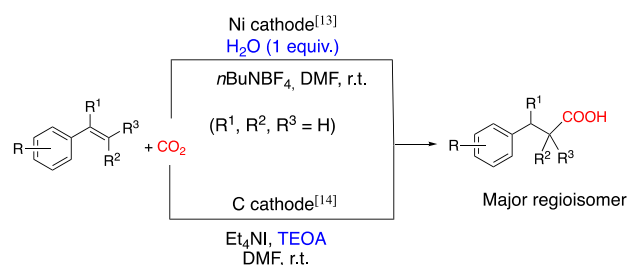
Carboxylation with carbon dioxide as an abundant and inexpensive C₁-building block has gained a tremendous boost in organic synthesis,¹ providing an extremely attractive way to access valuable carboxylic acids which are important motifs in pharmaceuticals.² Among these reactions, the carboxylation of unsaturated hydrocarbons using CO₂ 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 CO₂, requiring consequently the use of strong reducing agents in most cases and leading to additional constraints in terms of functional group tolerance.³ 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.⁴ Aliphatic alkenes are indeed transformed into alkanolic acids, whereas the high stability of η^3 -benzylic metal intermediates delivered mainly branched carboxylic acids from styrene derivatives. Therefore, organometallic catalysis faced a real obstacle in trying to shift the CO₂ fixation to the β -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 CO₂.⁵ Earlier attempts to selectively generate linear carboxylic acids from styrenes and phenylacetylenes derivatives were limited to the use of organoboranes,⁶ organozinc and Grignard reagents.⁷ The nickel-catalyzed hydrocarboxylation of unsaturated bonds has nevertheless been controlled by the group of Martín by using appropriate ligands for the metal center and water as a formal hydride source.⁸ Photochemical carboxylation was also recently proved successful as activation mode for the synthesis of linear carboxylic acids.⁹

The electrochemical carboxylation of hydrocarbons was considered as an alternative very early on, but its development

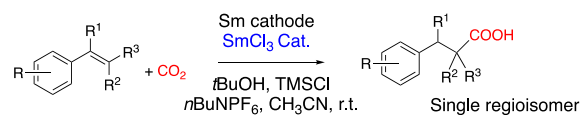
remained relatively limited due to the lack of selectivity.^{10,11} For styrene transformation, site-selective hydrocarboxylations are hardly achieved and a mixture of α - and β -hydrocarboxylation or dicarboxylation is mostly observed.¹² Major advances in selective electrochemical carboxylation reactions of styrenes using carbon dioxide have, however, been reported very recently (Scheme 1). Nam and co-workers indeed developed a direct electrochemical β -selective hydrocarboxylation of styrenes using CO₂ and water, in which the site selectivity was controlled between β -hydrocarboxylation and dicarboxylation.¹³ Malkov and Buckley also established an electrochemical protocol with triethanolamine as proton source delivering carboxylic acids from diversely substituted aryl-olefins with a high β -regioselectivity.¹⁴

Scheme 1. Electrochemical β -Hydrocarboxylation of Styrenes with CO₂.

Previous works: Direct β -Hydrocarboxylation



This work : Catalytic β -Hydrocarboxylation



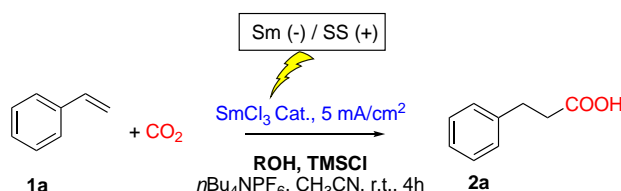
Building on our recent developments for catalytic reactions mediated by electrogenerated low valent samarium species¹⁵ and particularly on the electrochemical carboxylation of aryl halides¹⁶ and benzyl halides,¹⁷ we report here an alternative

electrocatalytic approach for the regioselective β -hydrocarboxylation of low value styrene derivatives.

RESULTS AND DISCUSSION

We began our investigation towards the hydrocarboxylation of styrene **1a** as a benchmark substrate using SmCl_3 as a precatalyst, a samarium rod as the cathode, and a stainless-steel grid as the anode at 5 mA/cm² current density (Table 1). The electrolysis was conducted in an undivided electrochemical cell according to the procedure developed for the carboxylation of aryl and benzyl halides.^{16,17} The optimization study was conducted in acetonitrile using $\text{CO}_{2(g)}$ (1 atm). Water was initially chosen as a proton source after the reported accomplishments using the $\text{SmI}_2\text{-H}_2\text{O}$ system for the reduction of challenging functional groups.¹⁸ 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 equivalents of H_2O (Table 1, entry 1).

Table 1. Optimization of the Reaction Conditions



Entry	SmCl_3 mol%	ROH (equiv)	TMSCl equiv.	2a (%) ^a
1	10	H_2O (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 ^b	10	<i>t</i> -BuOH (10)	8	65
9	10	<i>t</i> -BuOH (10) + H_2O (10)	8	45
10 ^c	10	<i>t</i> -BuOH (10)	8	-
11	5	<i>t</i> -BuOH (10)	8	30
12 ^d	10	<i>t</i> -BuOH (10)	8	-

^a Isolated yields. ^b $\text{CO}_{2(g)}$ was replaced by dry ice (1 atm). ^c reaction performed at -40°C . ^d no current applied, 24h.

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 equivalents led to a lower yield of the desired product (Table 1, entry 5) but 10 equivalents of *t*-BuOH were enough to produce exclusively the carboxylic acid **2a** with 37% yield (Table 1, entry 6). Finally increasing the quantity of TMSCl from 6 equivalents to 8 equivalents allowed to isolate the carboxylic acid with a maximal yield of 47% (entry 7). Eventually, we found that using dry ice as CO_2 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 bet-

ter yield of the reaction, as revealed by an electrolysis carried out at -40°C in the presence of $\text{CO}_{2(g)}$ (entry 10). The catalytic loading was also evaluated, and it was found that 10 mol% are 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 β -hydrocarboxylation of styrene derivatives (Scheme 2). Initially, different styrenes bearing various substituents on the aromatic moiety, were evaluated, and proved all (**1b-1f**) 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 β -hydrocarboxylated products. In the case of α -substituted styrenes **1h** and **1i**, the corresponding monocarboxylated products were produced in good yields.

As shown in Scheme 2, the hydrocarboxylation of β -substituted styrenes bearing a methyl substituent (**1j-m**, *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 α,β -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 reduce nitro functions.^{15a} 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**.

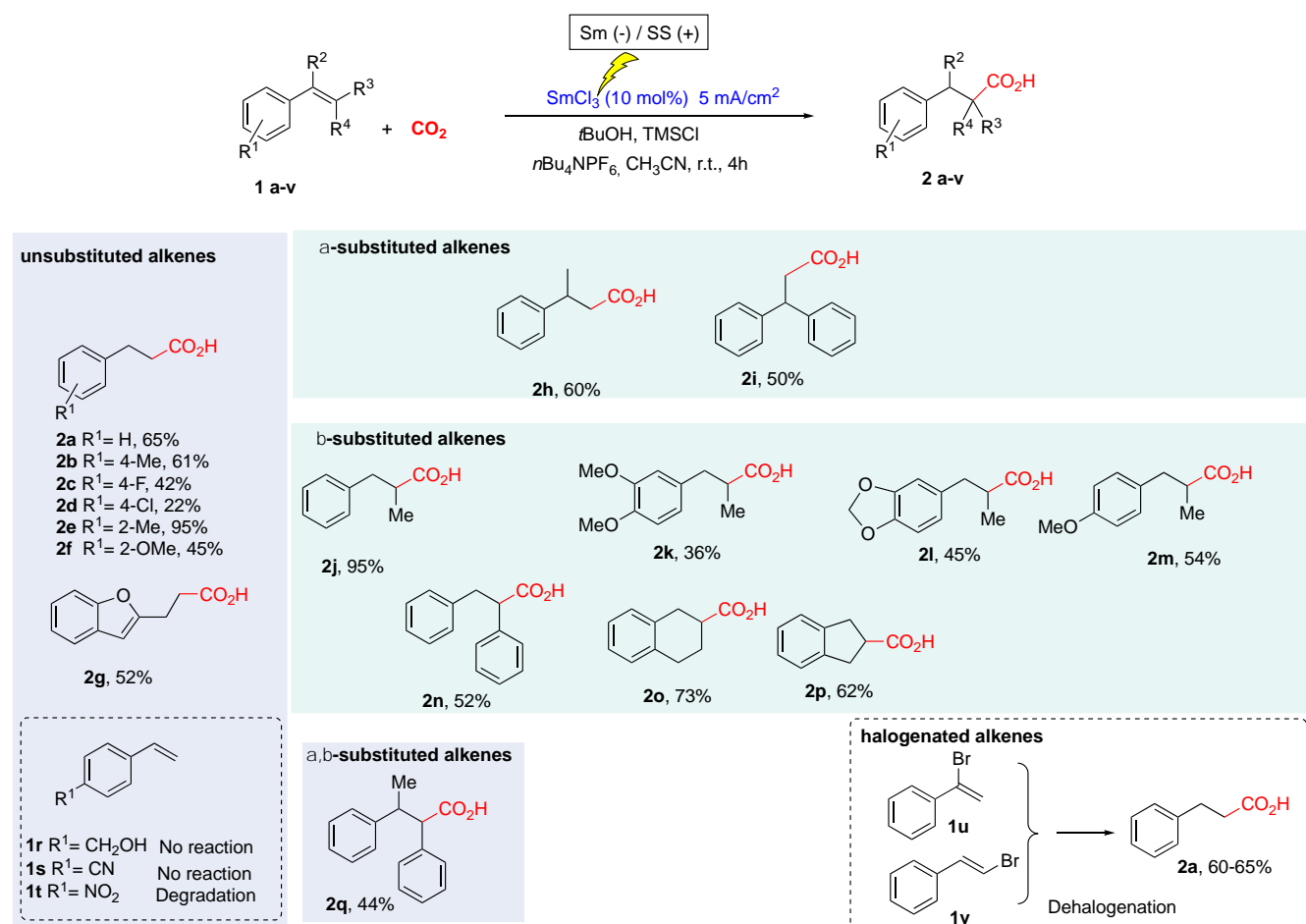
We then investigated the mechanism of this electrocatalytic hydrocarboxylation. Our studies were first focused on assigning the role of each component present in the electrochemical cell. Without the catalyst or *t*-BuOH, the transformation of styrenes showed inertia with respect to direct electrocarboxylation; 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_3 also resulted in complete degradation of the substrate. This is in line with our previous studies,^{15b} 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 exper-

iments indicate that, in our case, the samarium activation of CO₂ is mandatory to perform the electrocarboxylation of such unsaturated products.

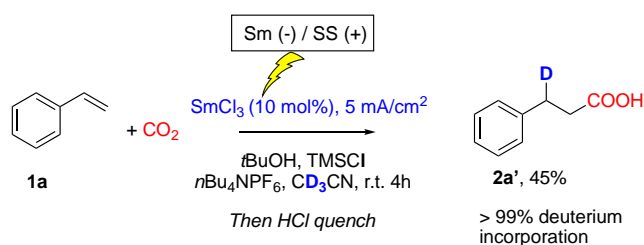
Deuterium labeling experiments were then conducted to elucidate the protonation step. We first explored the hydrocarboxylation of **1a** followed by DCl quench but **2a** was isolated without any deuterium fixation. Surprisingly, the addition of

t-BuOD, supposed to be the proton donor, also delivered the deuterium-free product. Lastly, the reaction was performed in CD₃CN and interestingly, **2a'** was isolated with more than 99% deuterium incorporation on the benzylic position (Scheme 3). At this point, we hypothesized that this specific behavior of acetonitrile was triggered by its coordination at the Sm center, which makes the protons much more acidic and

Scheme 2: Substrate Scope of Styrene Derivatives.



Scheme 3: Deuterium Labeling Experiments.



thus explains the observed proton-donating character. Noteworthy, this behavior was also reported with transition-metal based catalysts.¹⁹ We accordingly propose that after CH₃CN deprotonation, the simple coordination of Sm(III) via the nitrogen atom (Sm-NCCH₃) is transformed into a strong Sm-CH₂CN bond. At this stage, *t*-BuOH, known as non-coordinating alcohol²⁰ 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 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 hours 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,¹⁶ this result shows that the radical scavenger did not deactivate the catalyst. We rather propose that it was initially neutralized by the CO₂^{•-} 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⁺.¹³ 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 SmCl₂ electrogenerated from SmCl₃ in CH₃CN containing *n*Bu₄NPF₆ as supporting electrolyte is presented in Figure 1. It shows a quasi-reversible system with a redox potential around -1.5 V/SCE (Red curve (1) in Figure 1). Addition of CO₂ caused the loss of the oxidation wave of SmCl₂ 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 is taking place between CO₂ and Sm(II), releasing another Sm(III) complex. Moreover, when adding a solution (1 mL) containing styrene **1a** (3.10^{-3} M), *t*-BuOH (10 equiv.) and TMSCl (8 equiv.) in CH₃CN, 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 SmCl₂.²¹

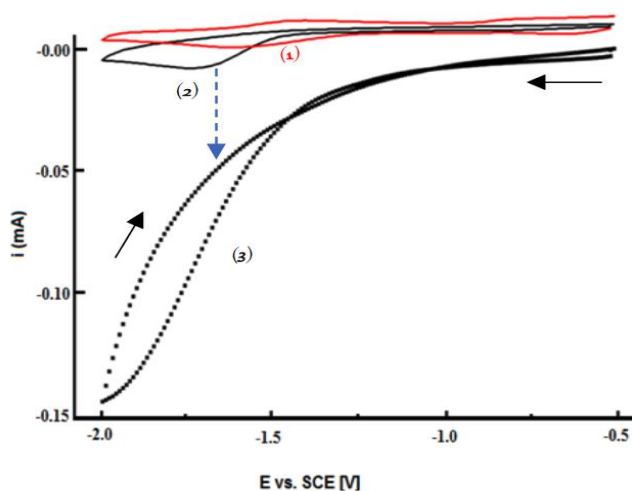
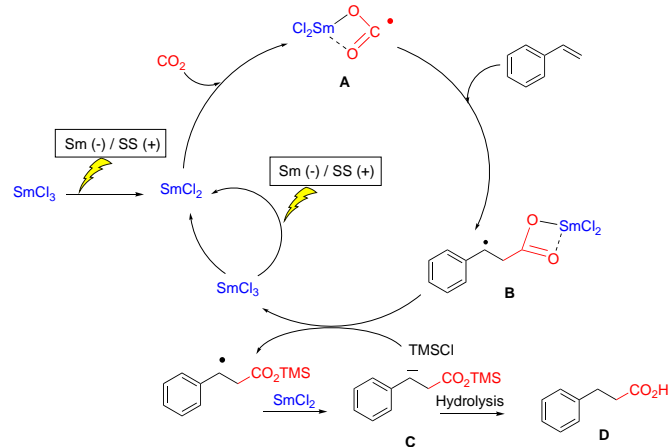


Figure 1. Electrochemical behavior of SmCl₃ with styrene **1a**. Cyclic voltammetry performed using a GC electrode (20 mm²) and a Pt wire as counter electrode with a scanning potential between -0.5 and -2 V vs. SCE in CH₃CN with *n*Bu₄NPF₆ [0.1 M]. Scan rate: 100 mV/s. Red curve (1): 0.02 M SmCl₃ in 0.1 M *n*Bu₄NPF₆ in CH₃CN; black curve (2): after introduction of CO₂; dashed curve (3): addition of 1 mL of *t*-BuOH/TMSCl/**1a** (10/8/1).

Consequently, we propose the following mechanism for the hydrocarboxylation of alkenes (Scheme 4). Firstly, the electrogenerated Sm(II) species reduces selectively the CO₂ and generates the corresponding radical anion **A** as a samarium carboxylate.²² This latter undergoes an anti-Markovnikov addition onto the unsaturated substrate to produce the benzylic radical **B** which after transmetalation with TMSCl is rapidly reduced by a second equivalent of Sm(II) to the carbanion **C**. In the mixture, the *t*-BuOH, activated by TMSCl, is essential for the reaction. Therefore, we suggest a mechanism displaying two successive proton donations: the first one involves the

solvent CH₃CN that after its activation by the catalyst transfers one proton to form the product **D** after hydrolysis. The CH₂CN⁻ anion extracts the nearest activated proton, from the *t*-BuOH-TMSCl adduct, to restore its original structure and dissociate the 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*-BuOH and acetonitrile could not be excluded under the reaction conditions.

Scheme 4: Proposed Mechanism for the Catalytic β -Hydrocarboxylation of Alkenes.



CONCLUSION

In summary, we have developed the regioselective hydrocarboxylation of styrene derivatives via CO₂ activation, catalyzed by a reductive SmCl₂ 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 SmCl₂ catalyzes this reaction assisted by acetonitrile and *t*-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*Bu₄NPF₆ (1 mmol, 387 mg) in acetonitrile (40 mL), equipped with a samarium rod as the cathode and a stainless-steel as the anode, was used. The electrogeneration of Sm²⁺ from SmCl₃ (0.1 mmol, 26 mg) was started by setting the chronopotentiometry mode for 15000 seconds with $i = 5$ mA/cm². The dry ice was carefully added to the mixture in small pieces followed by the alkene (1.0 mmol, 104 mg in the case of styrene), *t*-BuOH (10 mmol, 741 mg) and trimethylsilyl chloride (8 mmol, 869 mg). During the electrolysis, small pieces of dry ice were added each 15 min. After 4 hours of electrolysis, the reaction was quenched with diethyl ether Et₂O (10 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 Et₂O (2 x 30 mL). The combined organic phase was washed with water and brine and dried over anhydrous MgSO₄. 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%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (75 MHz, CDCl₃) δ 177.8, 140.1, 128.5, 128.2, 126.3, 35.3, 30.5. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

3-phenylpropanoic acid (**2a**): 90.0 mg (0.60 mmol, 60 %) was also prepared starting from **1u** (183.0 mg, 1 mmol) or 97.5 mg (0.65 mmol, 65%) from **1v** (183.0 mg, 1 mmol).

3-(*p*-tolyl)propanoic acid (**2b**): 100 mg (0.61 mmol, 61%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) δ 179.6, 137.1, 135.9, 129.3, 128.2, 35.8, 30.2, 21.0. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

3-(4-fluorophenyl)propanoic acid (**2c**): 70.5 mg (0.42 mmol, 42%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) 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 ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

3-(4-chlorophenyl)propanoic acid (**2d**): 40.5 mg (0.22 mmol, 22%). ¹H NMR (360 MHz, CDCl₃) δ 7.42 – 7.15 (m, 4H), 3.02 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (91 MHz, CDCl₃) δ 178.6, 140.1, 128.5, 128.2, 126.3, 35.5, 30.5. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

3-(*o*-tolyl)propanoic acid (**2e**): 156 mg (0.95 mmol, 95%). ¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (75 MHz, CDCl₃) δ 179.8, 138.3, 136.0, 130.4, 128.5, 126.6, 126.2, 34.4, 28.0, 19.3. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.²³

3-(2-methoxyphenyl)propanoic acid (**2f**): 81 mg (0.45 mmol, 45%). ¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (75 MHz, CDCl₃) δ 179.8, 157.4, 129.9, 128.4, 127.7, 120.4, 110.2, 55.1, 34.0, 25.8. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.²³

3-(benzofuran-2-yl)propanoic acid (**2g**): 99 mg (0.52 mmol, 52%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) δ 177.2, 156.8, 154.6, 128.5, 123.4, 122.6, 120.5, 110.8, 102.6, 31.8, 23.7. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

3-phenylbutanoic acid (**2h**): 94.5 mg (0.60 mmol, 60%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) δ 178.7, 145.4, 128.5, 126.7, 126.5, 42.6, 36.1, 21.8. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

3,3-diphenylpropanoic acid (**2i**): 113 mg (0.50 mmol, 50%). ¹H NMR (360 MHz, CDCl₃) δ 7.55 – 7.08 (m, 10H), 4.58 (t, *J*

= 7.9 Hz, 1H), 3.14 (d, *J* = 7.9 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 178.0, 143.1, 128.6, 127.5, 126.6, 46.6, 40.4. The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

2-methyl-3-phenylpropanoic acid (**2j**): 156 mg (0.95 mmol, 95%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) δ 182.8, 139.1, 129.0, 128.5, 126.5, 41.3, 39.3, 16.5. ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

3-(3,4-dimethoxyphenyl)-2-methylpropanoic acid (**2k**): 80 mg (0.36 mmol, 36%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) 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. ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.²⁴

3-(benzo[d][1,3]dioxol-5-yl)-2-methylpropanoic acid (**2l**): 93 mg (0.45 mmol, 45%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) δ 182.4, 147.6, 146.1, 132.7, 121.9, 109.3, 108.1, 100.8, 41.4, 39.0, 16.4. ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.²⁵

3-(4-methoxyphenyl)-2-methylpropanoic acid (**2m**): 105 mg (0.54 mmol, 54%). ¹H NMR (360 MHz, CDCl₃) 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). ¹³C NMR (91 MHz, CDCl₃) δ 182.4, 158.2, 131.1, 129.9, 113.9, 55.2, 41.4, 38.4, 16.4. ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.²⁶

2,3-diphenylpropanoic acid (**2n**): 158 mg (0.7 mmol, 70%). ¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (75 MHz, CDCl₃) δ 179.6, 138.7, 137.9, 128.9, 128.7, 128.4, 128.1, 127.6, 126.5, 53.5, 39.3. ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.²⁷

1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (**2o**): 126 mg (0.73 mmol, 73%). ¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (63 MHz, CDCl₃) δ 181.4, 135.6, 134.6, 129.1, 128.9, 126.0, 125.9, 39.7, 31.3, 28.4, 25.6. ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

2,3-dihydro-1H-indene-2-carboxylic acid (**2p**): 100 mg (0.62 mmol, 62%). ¹H NMR (360 MHz, CDCl₃) δ 7.35 – 7.13 (m, 4H), 3.49 – 3.23 (m, 5H). ¹³C NMR (63 MHz, CDCl₃) δ 182.0, 141.3, 126.7, 124.4, 43.4, 36.0. ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.^{9c}

2,3-diphenylbutanoic acid (**2q**): 166 mg (0.44 mmol, 44%). ¹H NMR (360 MHz, CDCl₃) δ 7.76 – 6.87 (m, 10H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.54 – 3.33 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (91 MHz, CDCl₃) 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]⁺ calculated 263.1048, found 263.0995.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at <https://...>. Experimental procedures, cyclic voltammograms, compounds data and spectra (PDF).

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SB and LH collected the data and performed the analyses. SB, ES and MM conceived and designed the work and contributed to the writing of the manuscript.

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