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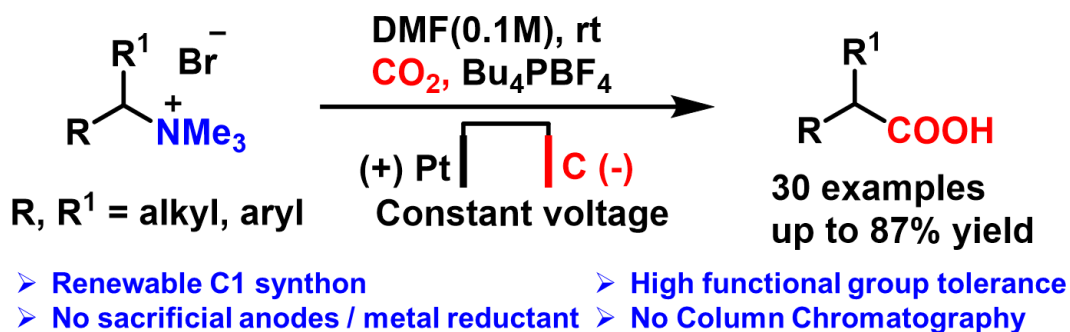## Direct Electrochemical Carboxylation of Benzylic C–N Bonds with Carbon Dioxide

Direct Electrochemical Carboxylation of Benzylic C-N Bonds with Carbon Dioxide

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ABSTRACT: We report a direct and efficient electrochemical carboxylation of benzylic C-N bonds with CO_2 at room temperature. The reaction has been successfully applied to both primary and secondary benzylic C-N bonds with compatibility of a variety of functional groups. This procedure does not require stoichiometric metals, external reducing agents, or sacrificial anodes, making column chromatography unnecessary for product purification. Differential

electrochemical mass spectrometry (DEMS) was used to elucidate key intermediates of the electrocarboxylation reaction.

Keywords: electrochemistry, carboxylation, carbon dioxide, carboxylic acids, C-N bond

1. INTRODUCTION

Carboxylic acids have drawn extensive attention due to their wide usage in the production of pharmaceuticals,[1] polymers,[2] and food additives.[3] Carboxylic acids are primarily synthesized from the oxidation of aldehydes/alcohols[4] and C-H bonds,[5] as well as carboxylation of carbon nucleophiles with CO_2;[6] the latter allows for extending carbon chain length. CO_2 is an ideal and green one-carbon (C1) building block for commodity chemical synthesis due to its abundance, low cost, and nontoxicity.[7] Many carboxylation methods have been developed using CO_2 and transition-metal catalysts.[8] Those carboxylation systems involving organic (pseudo)halides provide an alternative to traditional routes requiring reactive and unstable organometallic chemicals based on organolithium or Grignard reagents.[9] For instance, benzyl halides can be carbonylated with CO_2 by a Ni catalyst in the presence of Zn as the reducing agent (Scheme 1a).[10] A variety of other surrogates of halides, including sulfonates,[11] ester derivatives,[12] and allylic alcohols[13] have been conceived to enhance reaction scope. Notably, most transition-metal catalyzed carboxylation reactions require stoichiometric metal reagents based on Mn or Zn as reducing agents. Those reducing agents usually not only give rise to environmental concerns, but may also persist as trace metal residues in the final products. In addition, it should be noted that the current reductive carboxylation of benzyl derivatives with CO_2 is plagued by dimerization and β-hydride elimination of substrates.[10,12a,14] Transition-metal catalyzed carboxylation of

benzyl halides with CO_2 without any dimerization or β-hydride elimination by-products is still a challenge.

The air- and thermally stable benzyl ammonium salts can be readily prepared in one step from available benzyl bromide or benzyl amine precursors. A nickel-catalyzed cross-electrophile coupling reaction via C-N bond breaking/CO_2 insertion from benzylammonium iodide salts was reported to overcome this challenge (Scheme 1b).[15] Although this method can prevent dimerization and β-hydride elimination using new design of ligands, it still needs high temperature and stoichiometric manganese reductant. Very recently, an example of tetraalkyl ammonium salts undergoing a coupling reaction with carbonyl groups and CO_2 driven by visible-light photoredox was reported (Scheme 1c).[16]

Scheme 1. Carboxylation of organic halides and ammonium salts.

a) Nickel-catalyzed carboxylation of benzyl halides (Previous study)
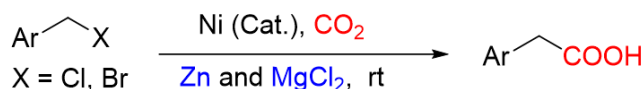
$$Ar\diagdown X \xrightarrow[\text{Zn and } MgCl_2, \text{ rt}]{\text{Ni (Cat.), } CO_2} Ar\diagdown COOH$$

X = Cl, Br

b) Nickel-catalyzed carboxylation of benzyl C-N bonds (Previous study)

$$Ar\diagdown \overset{+}{N}Me_3 \; I^- \xrightarrow[\text{Mn, 90 °C}]{\text{Ni (Cat.), } CO_2} Ar\diagdown COOH$$
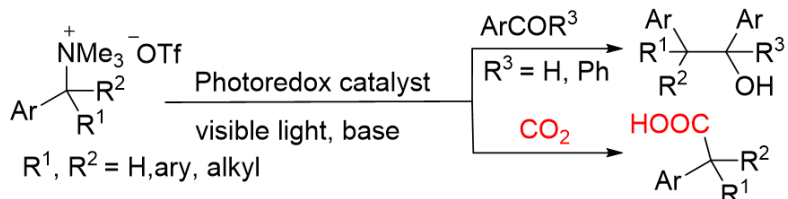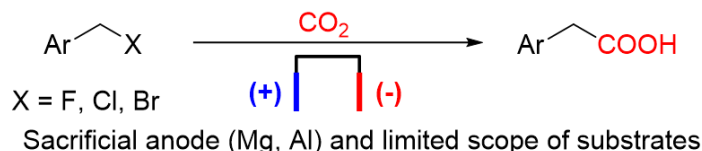
c) Visible-light-driven carboxylation of benzyl C-N bonds (Previous study)

$$Ar\diagdown \overset{\overset{+}{N}Me_3 \; ^-OTf}{\underset{R^1}{\overset{R^2}{|}}} \xrightarrow[\text{visible light, base}]{\text{Photoredox catalyst}}$$

$$\xrightarrow{ArCOR^3, R^3 = H, Ph} \quad \overset{Ar}{\underset{R^2}{R^1}}\diagup\diagdown\overset{Ar}{\underset{OH}{R^3}}$$

$$\xrightarrow{CO_2} \quad HOOC\diagdown \overset{Ar}{\underset{R^1}{\overset{R^2}{|}}}$$

R¹, R² = H, ary, alkyl

d) Electrochemical carboxylation of benzyl halides (Previous study)

$$Ar\diagdown X \xrightarrow[\text{(+) } \quad \text{(-)}]{CO_2} Ar\diagdown COOH$$

X = F, Cl, Br

Sacrificial anode (Mg, Al) and limited scope of substrates
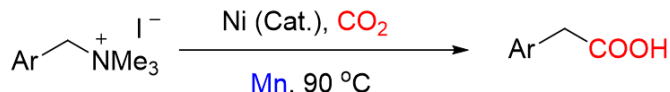
e) Electrochemical carboxylation of benzyl C-N bonds (this study)

$$\overset{\overset{+}{N}Me_3 \; ^-Br}{\underset{R^1 \quad R^2}{|}} \xrightarrow[\text{(+) Pt/C} \quad \text{C (-)}]{CO_2} \overset{COOH}{\underset{R^1 \quad R^2}{|}}$$

R¹ = aryl, heteroaryl; R² = H, alkyl, aryl
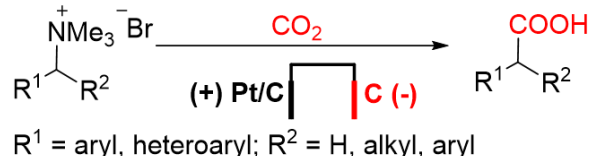
✓ No sacrificial anodes   ✓ No column chromatography
✓ No metal reducing agent ✓ High functional group tolerance

Electrochemical methods can allow for eliminating toxic or hazardous redox reagents with direct redox reaction at an electrode surface; moreover, the electricity can be of renewable origin, such as solar or wind, helping to improve sustainability.[17] Electrochemical carboxylation with CO_2 is regarded as one of the most sustainable and efficient approaches to generate valuable carboxylic acids.[18] Electrocarboxylation usually involves the reduction of substrate and/or CO_2, leading to the generation of carboxylate anions. Most electrocarboxylation reactions are conducted with limited scope of substrates in the presence of a sacrificial anode, like aluminum or magnesium, because the existence of the sacrificial anode allows for maintaining high current

efficiencies, as the oxidative dissolution of anode materials provides the counterions which prevent substrates or products from undesired over-oxidation.[18] In the previous work, electroreduction of benzyl halides has been mainly focused on the detailed study of mechanism with several representative examples (Scheme 1d).[19]

Our work provides a new design strategy for electrochemical carboxylation which utilizes the benzyltrimethylammonium bromide intermediate as a substrate for carboxylation (Scheme 1e). Compared to previous transition-metal catalyzed carboxylations (Scheme 1a-b), our electrochemical method does not require stoichiometric metals as reducing agents. The fact that there is no sacrificial anode required in this approach differentiates our work from traditional electrocarboxylation (Scheme 1d), because trimethylamine generated in situ by the substrate can act as the sacrificial agent to be oxidized at the anode. Compared to visible-light driven carboxylation of benzyl C-N bonds (Scheme 1c), our work does not require metal complexes, external base, or column chromatography.

2. RESULTS AND DISCUSSION

2.1 Screening of Reaction Conditions. We initially investigated the electrochemical carboxylation of benzyltrimethylammonium bromide (**1a**) as the model substrate (Table 1). Commercially available carbon cloth (Freudenberg H14) and platinum on carbon (Pt/C) were chosen as cathode and anode, respectively. A solution of benzyltrimethylammonium bromide (**1a**) with tetrabutylphosphonium tetrafluoroborate (Bu_4PBF_4) in DMF with CO_2 bubbling was used. At -4.5 V constant cell voltage, phenylacetic acid was produced in 70% yield after workup with aqueous HCl (entry 1, Table 1). The simple system and clean conversion are believed to be the key reason for the high yield of the carboxylic acids. The fact that the purification process does not require column chromatography could also decrease losses of the product during

purification. Controlled current electrolysis and other potentials resulted in dramatic decreases in yields (entries 2-6). When -2.6 V (vs Fc^+/Fc) was applied to the cathode (entry 5), which is close to the reduction onset of the substrate and yields a much lower current, the product **1b** was obtained in only 40% yield even after 48 hours of electrolysis. When the voltage of the cathode was held at -3.07 V (vs Fc^+/Fc) (entry 6), which corresponds to -4.5 V of cell voltage at the beginning of the electrolysis, the product **1b** was obtained in only 42% yield. The lower yield of **1b** was probably caused by the dramatically increasing voltage at the anode during the electrolysis process when constant cathode potential was applied, compared to applying constant cell potential (Figure S1 and S2); this could cause the oxidation of the generated product at the anode. Therefore, holding the applied cell voltage constant is preferable not only because it is easier to achieve in practical systems, but also because a system controlled in this way has been demonstrated to exhibit superior performance. Considering that substrate **1a** itself can act as an electrolyte, electrolysis of substrate **1a** without electrolyte also generated the desired product in 30% yield (entry 8). The lower yield was probably caused by decreased conductivity with the consumption of the substrate, leading to large electrolyte resistance, which could be potentially solved using a flow cell.[20] Therefore, the approach described in entry 8 is still very appealing since there was nothing else used in the system besides substrate and solvent, which can further simplify the product purification procedure. The anodic Me_3N oxidation reaction, which generates cations to stabilize carboxylate anions, is also important. Since in situ generated trimethylamine (Me_3N) was regarded as the sacrificial agent to be oxidized at the anode, an external sacrificial agent triethylamine (Et_3N) was added to the reaction solution, but this did not lead to higher yield (entry 9). This may be because the oxidation of triethylamine could generate protons even after depletion of in situ generated trimethylamine; these protons could then

compete with CO_2 to attack the benzyl anion. Differences in the type of cathode materials have also been found to have a significant impact on yields (entries 11-15). A fresh glassy carbon cathode produced comparable product in 64% yield (entry 14); however, the yield tended to decrease when glassy carbon was reused several times. Raman spectroscopy was used to investigate the surface differences of different carbon materials (see Figure S4), which indicates that the higher product yield using glassy carbon and Freudenberg carbon cloth is correlated with a larger number of defects. When the Pt/C carbon paper anode was replaced by carbon cloth (Freudenberg H14), there was a decrease in the yield of the product (entry 16). Different substrate anions have been studied (entries 17-19); and bromide as the counter ion gave the highest yield. Control experiments revealed that passing current was essential for this transformation to occur (entry 20).

Table 1. Screening of reaction conditions.
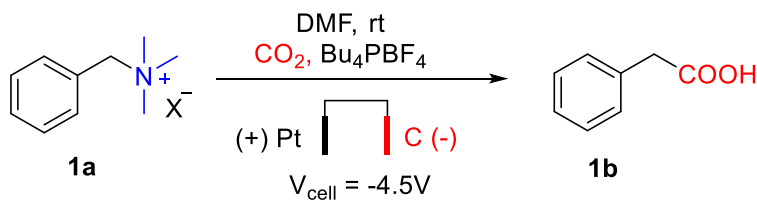
Entry	Deviation from standard conditions	Yield [a]
1	None	70%
2	$I = 10$ mA/cm^2 (constant current)	43%
3	$V_{cell} = -4.0$ V [c]	13%
4	$V_{cell} = -5.0$ V [c]	55%
5	$V_{cathode} = -2.6$ V (vs Fc^+/Fc) [b]	40%

6	$V_{cathode}$ = -3.07 V (vs Fc$^+$/Fc) [b]	40%
7	Electrolyte = Bu$_4$NBF$_4$	60%
8	No Electrolyte	30%
9	Et$_3$N as additive	54%
10	CsCO$_3$ as additive	15%
11	Pt/C as cathode	25%
12	Ag foil as cathode	20%
13	Ni foil as cathode	27%
14	Glassy carbon as cathode	64%
15	Toray Carbon Paper 060 as cathode	13%
16	Freudenberg H14 carbon cloth as anode	44%
17	X = I	25%
18	X = Cl	50%
19	X = BF$_4$	46%
20	No current	0%

Reaction conditions: **1a** (X = Br, 0.15 mmol), Bu$_4$PBF$_4$ (0.15 mmol), CO_2 bubbling in DMF (1.5 mL). [a] Yields determined by ^{1}H NMR using trimethoxybenzene as internal standard. [b] Voltage of cathode is held constant. [c] Voltage of cell is held constant.

2.2. Scope of Electrochemical Carboxylation of Ammonium Salts.

### Table 2. Electrochemical carboxylation of primary ammonium salts.
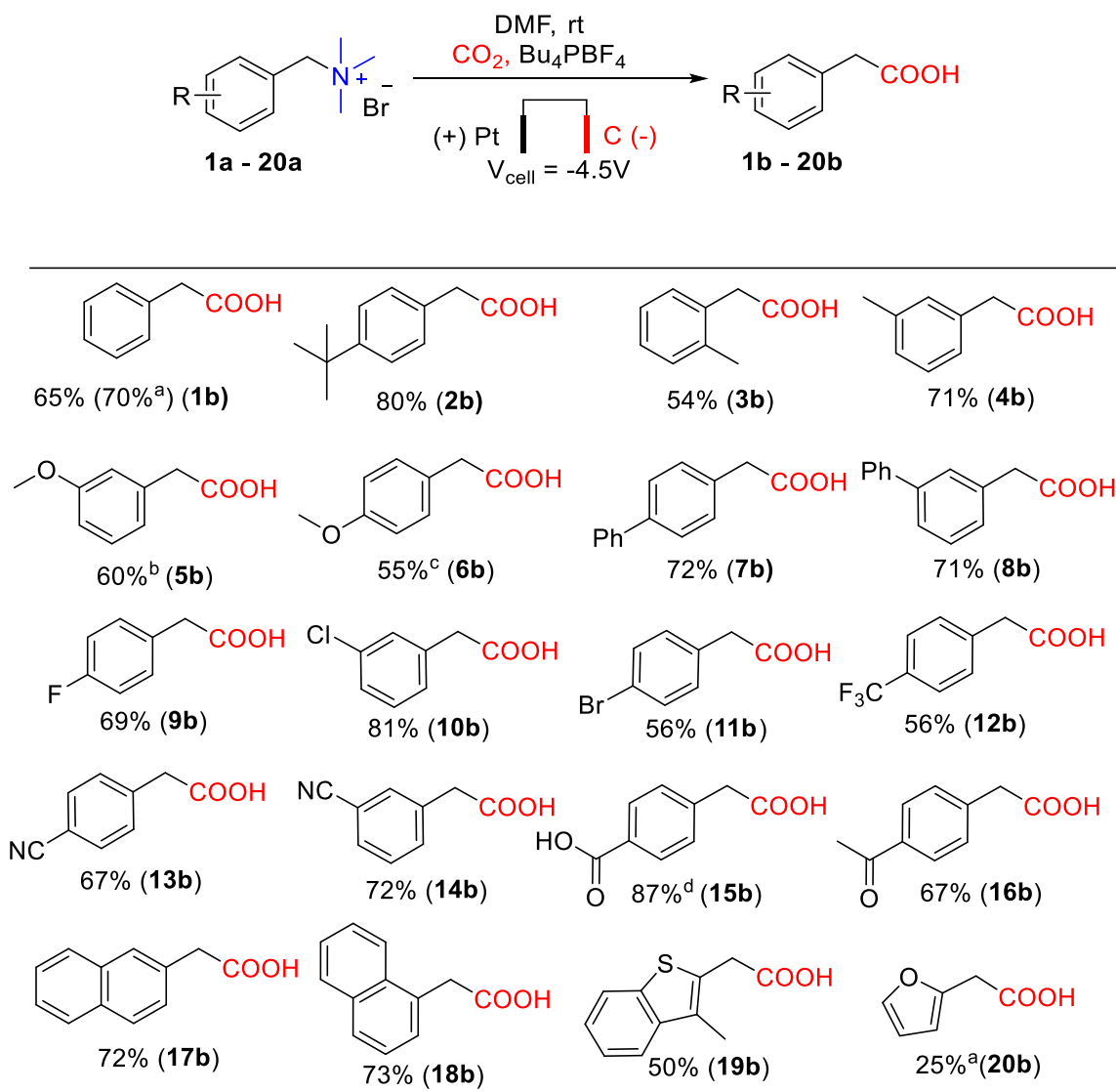
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Reaction scheme: R—(aryl)—CH$_2$—N$^+$(CH$_3$)$_3$ Br$^-$ (**1a - 20a**), DMF, rt, CO$_2$, Bu$_4$PBF$_4$, (+) Pt | C (-), V_{cell} = -4.5V → R—(aryl)—CH$_2$COOH (**1b - 20b**)

65% (70%[a]) (**1b**)

80% (**2b**)

54% (**3b**)

71% (**4b**)

60%[b] (**5b**)

55%[c] (**6b**)

72% (**7b**)

71% (**8b**)

69% (**9b**)

81% (**10b**)

56% (**11b**)

56% (**12b**)

67% (**13b**)

72% (**14b**)

87%[d] (**15b**)

67% (**16b**)

72% (**17b**)

73% (**18b**)

50% (**19b**)

25%[a] (**20b**)

Reaction conditions: benzylammonium salt (0.15 mmol), Bu$_4$PBF$_4$ (0.15 mmol), anhydrous DMF (1.5 mL), CO$_2$ bubbling, -4.5 V cell voltage, room temperature; and yields of isolated products are given. [a] Yields determined by NMR using 1,3,5-trimethoxybenzene as internal standard. [b] The anion of this substrate was BF$_4^-$ instead of Br$^-$. [c] The ratio of **6b** and **6b-Br** was 3:1 (55%: 13.4%). [d] 2-(4-(methoxycarbonyl)phenyl)acetic acid was hydrolyzed to 4-(carboxymethyl)benzoic acid during purification.

Encouraged by these results, we determined the preparative scope of our direct electrochemical carboxylation of primary benzylammonium substrates with CO$_2$ (Table 2). All the substrates can be prepared from corresponding benzyl bromides in one step and purified by filtration, as shown in Supporting Information. All of the generated products were purified via

simple extraction without the usage of column chromatography (see SI for details). A range of *meta-*, *ortho-*, and *para-*alkyl group substituted benzylammonium salts (**1a** - **4a**) reacted with CO_2 to afford carboxylic acids in moderate to excellent yields. Notably, both electron-donating and electron-withdrawing functional groups were tolerated under the reaction conditions. For the electron donating methoxy group, both product (**5b**) and brominated by-product (**5b-Br**) were observed with a ratio of 2:3 in 89% total yield (see SI). This problem can be prevented by changing the anion from Br^- to BF_4^- in the 3-methoxybenzyltrimethylammonium salt (**5a**), which resulted in product **5b** in 60% yield. For substrate **6a**, the ratio of product **6b** and **6b-Br** was 3:1. However, this strategy of switching anions did not work for the 4-methoxybenzyltrimethylammonium salt (**6a**), instead resulting in unidentifiable products. The position of phenyl substitution of benzylammonium bromides **7a** and **8a** did not show any effect on yields of compounds **7b** and **8b**. A variety of electron-withdrawing functional groups including halides (F **9b**, Cl **10b**, Br **11b**), trifluoromethyl (**12b**), cyano (**13b** and **14b**), carboxylate (**15b**) and ketone (**16b**) were tolerated under the reaction conditions. In addition to product **11b**, **11a** also generated 4-(carboxymethyl)benzoic acid in 10% yield through the electrochemical carboxylation of bromide. Regardless of functional groups prone to oxidation or reduction, products containing cyano (**13b** and **14b**), carboxylate ester (**15b**) and ketone (**16b**) were obtained from 67% - 87% yields. In literature, in order to isolate as the corresponding methyl ester, the reaction solution was treated with $TMSCHN_2$.[15] In our case, we let the product completely hydrolyze to its corresponding carboxylic acid form (**15b**) during the extraction process. The electrochemical carboxylation method was also compatible with naphthalene aromatic fused rings (**17b** and **18b**) and heteroaromatic rings, including benzothiophene (**19b**) and furan (**20b**). However, the product furanacetic acid (**20b**) was only obtained in low yield

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using internal standard, because furanacetic acid decomposed if basic conditions were used for purification.

Table 3. Electrochemical carboxylation of secondary ammonium salts.
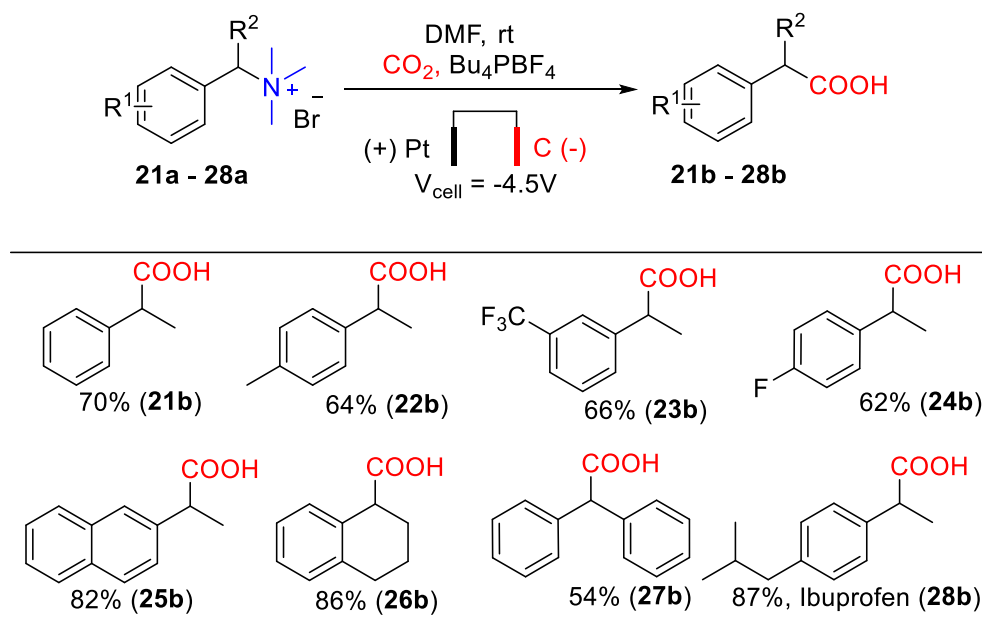
Reaction conditions: benzylammonium salt (0.15 mmol), Bu_4PBF_4 (0.15 mmol), anhydrous DMF (1.5 mL), CO_2 bubbling, -4.5 V cell voltage, room temperature; and yields of isolated products are given.
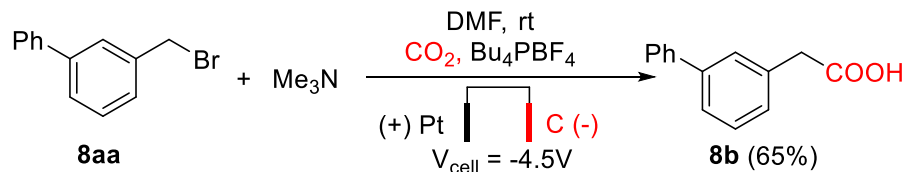
The tendency of secondary benzyl halides to undergo valueless β-hydride elimination makes the synthesis of α-substituted phenylacetic acids challenging. Our method still has excellent selectivity toward α-substituted phenylacetic acids (Table 3). The reaction was not hampered when substrates contained a β-methyl group (**21a** – **25a**), giving good to excellent yields of corresponding secondary carboxylic acids. Surprisingly, benzylammonium salts bearing sterically encumbered backbones, such as **26a** and **27a** which contained a β-alkyl chain and β-phenyl group respectively, could be utilized in our electrocarboxylation method as well. In particular, ibuprofen (**28b**) was electrochemically synthesized in high yield from the readily available and cheap starting material 4'-isobutylacetophenone and isolated without column

chromatography (See SI), which could be considered as a potential industrial approach for synthesizing ibuprofen.[1] This showcases that our method demonstrates great potential in practical applications.
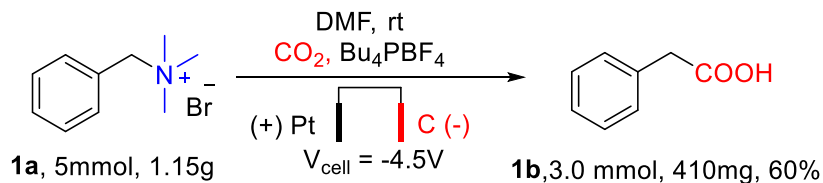
To further simplify this electrochemical carboxylation and avoid the purification of ammonium bromide, we investigated a one-pot reaction of 4-phenylbenzyl bromide **8aa** with Me_3N under CO_2 bubbling to give **8b** in 65% yield (Scheme 2a). We then tested the scalability of this straightforward electrochemical carboxylation. The reaction with 1.15 grams (5 mmol) of **1a** was conducted under constant cell voltage at -4.5 V for 48 hours (Scheme 2b), leading to the carboxylic acid **1b** in 60% yield.

Scheme 2. One-pot reaction and gram-scale reaction.

(a) One-pot process to generate carboxylic acid

DMF, rt
CO_2, Bu_4PBF_4

(+) Pt   C (-)
V_{cell} = -4.5V

8aa + Me_3N → Ph COOH **8b** (65%)

(b) Gram-scale reaction

DMF, rt
CO_2, Bu_4PBF_4

(+) Pt   C (-)
V_{cell} = -4.5V

1a, 5mmol, 1.15g → COOH **1b**, 3.0 mmol, 410mg, 60%

We also investigated the effect of carbon chain length between the phenyl group and carboxylic acid. Phenyltrimethylammonium bromide (**29a**) and phenylethyltrimethyl ammonium bromide (**30a**) also generated benzoic acid (**29b**) and 3-phenylpropanoic acid (**30b**), respectively, under our optimized conditions (Scheme 3). While the yields of these two types of substrates were low, the fact that products were isolated indicates that our method is not only limited to

benzylammonium salts, but could also possibly be extended to other types of ammonium salt substrates (e.g. aromatic and aliphatic ammonium salts) with future work.

Scheme 3. Electrochemical carboxylation of phenyl and phenylethyl ammonium salts.
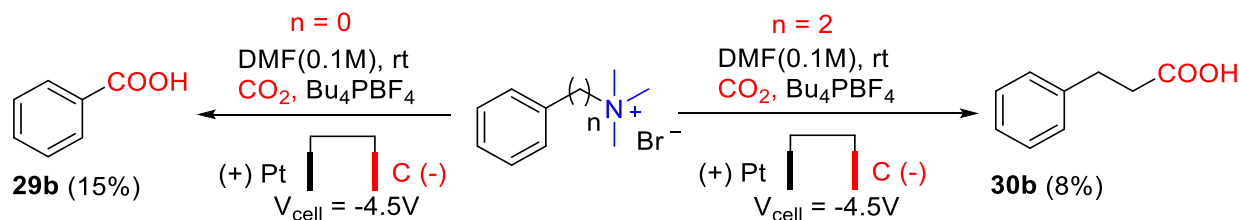
**2.3. Mechanistic Studies.** In preliminary mechanistic studies, to investigate the formation of the concomitant homodimerization by-product, 4-*tert*-butylbenzyltrimethylammonium bromide (**2a**) was used as a model substrate due to its simple ^{1}H NMR splitting pattern. The dimerization by-product (**2c**) was observed when a higher cell voltage was applied (-5.0 V), leading us to believe that higher potentials lead to the generation of benzyl radical; at a high enough local concentration that dimerization is favored (Scheme 4). To determine if a S_N2 reaction could lead to **2c**, we conducted a control reaction of benzyltrimethylammonium bromide with benzylmagnesium chloride (acting as the benzyl anion) in DMF, which only generated less than 5% yield of the homodimer (See Figure S3). Furthermore, the homodimer by-product only forms at more reductive potentials at which the radical is present at high enough concentrations to promote the bimolecular radical-radical coupling reaction. These results indicate that formation of a homodimer by-product through an S_N2 reaction is negligible.

Meanwhile, 4-(*tert*-butyl)toluene (**2d**) was detected as an additional by-product which was attributed to the protonation of the intermediate 4-(*tert*-butyl)toluene anion. The by-product 4-(*tert*-butyl)toluene (**2d**) was detected in lower quantities when a higher flow rate of CO_2 was

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applied. This indicates that there is competition between protons and CO_2 for the generated anion intermediate. To further confirm the existence of the 4-(*tert*-butyl)toluene anion, when the electrolysis at our optimized condition was conducted under N_2 bubbling instead of CO_2 bubbling, 4-(*tert*-butyl)toluene (**2d**) was obtained in 14% yield. The proton probably comes from the oxidation of trimethylamine and/or trace water in the solution. Therefore, it is hypothesized that the benzyl radical and benzyl anion are generated in our system. The yield of protonated product **2d** under N_2-bubbling conditions was much lower than that of carboxylation under CO_2-bubbling conditions, which suggests the in situ generated protons from trimethylamine may be used in some other process, like hydrogen evolution reaction (HER). We also observed similar currents when bubbling through either N_2 or CO_2 in the absence of substrate, suggesting that direct, outer-sphere reduction of CO_2 can be ruled out. The current efficiency of carboxylation of substrate **1a** under optimized conditions was determined to be ~25%; the relatively lower current efficiency is likely caused by HER or the reduction of the amine radical cations.[21]

Scheme 4. Side reactions of 2a.
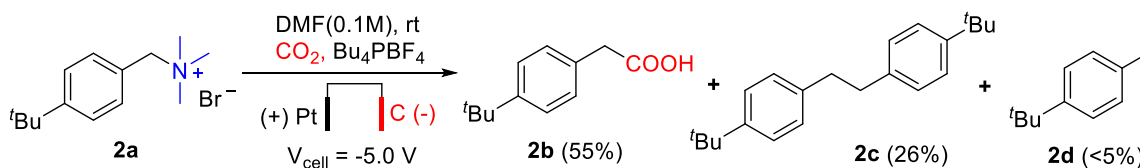
Due to the small amount of species generated at electrode surfaces, the real-time detection of electrochemical reaction intermediates and products is often difficult. Differential electrochemical mass spectrometry (DEMS) has proven useful for in situ detection of gaseous or volatile electrochemical reactants, reaction intermediates, and products.[22] Here we used DEMS to elucidate some key intermediates in our reaction. After constant cell voltage -4.5 V was applied

to the reaction for 30 min, a cyclic voltammogram (CV) was recorded for the reduction of benzyltrimethylammonium bromide (**1a**) at carbon paper cathode from -1 to -5 V of cell potential under CO_2 atmosphere (Figure 1a). The selected scan rate for the CV was 5 mV/s in order to obtain mass signals that correspond to the applied potential. As this CV scan was conducted, products generated at the working electrode were instantaneously sampled by a surface probe held under negative pressure. Products taken in by this probe were vaporized and sent to be detected at the MS. The ion currents for $m/z = 91$ (Figure 1b) and $m/z = 58$ (Figure 1c) were recorded, which represent toluene and trimethylamine, respectively. No other mass signals (aside from $m/z = 73$ related to solvent DMF) were observed (for the full scan of MS, see Figure S6 in SI). Although the carboxylated product was not observed by DEMS due to its low volatility, we confirmed its formation under the conditions of the DEMS experiment by measuring the products post-electrolysis using ion chromatography (see Figure S7 in SI). The ion currents of toluene ($m/z = 91$) and trimethylamine ($m/z = 58$) followed the trend of the CV scan. CV scans under helium atmosphere showed similar behavior in terms of currents and mass spectra, as expected for the early intermediates in the reaction which do not involve CO_2 (see Figure S8 in SI).

A variety of CVs using three electrodes were conducted in order to investigate the redox potentials of relevant species, as shown in SI. Since it was found that the carbon materials of the cathode electrode had significant influence on yield of the reaction, we used Freudenberg carbon paper for the cathode in CV experiments. We did not observe well resolved reduction peaks. The Tafel slope we obtained is 300 mV dec^{-1} (see Figure S12), higher than 120 mV dec^{-1}. If we interpret this assuming that a first electron transfer (ET) is likely the rate limiting step, we can determine the corresponding transfer coefficient. The transfer coefficient (α) is used to probe the

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mechanistic nature of the first ET in a dissociative process. Previous studies of dissociative electron transfer have found that concerted ETs, where a bond is broken at the same time as the electron transferred, have small values of α (often significantly smaller than 0.5). In our carboxylation of ammonium salts, α = 0.2, which is similar to previous studies of reduction of benzyl halides.[19]
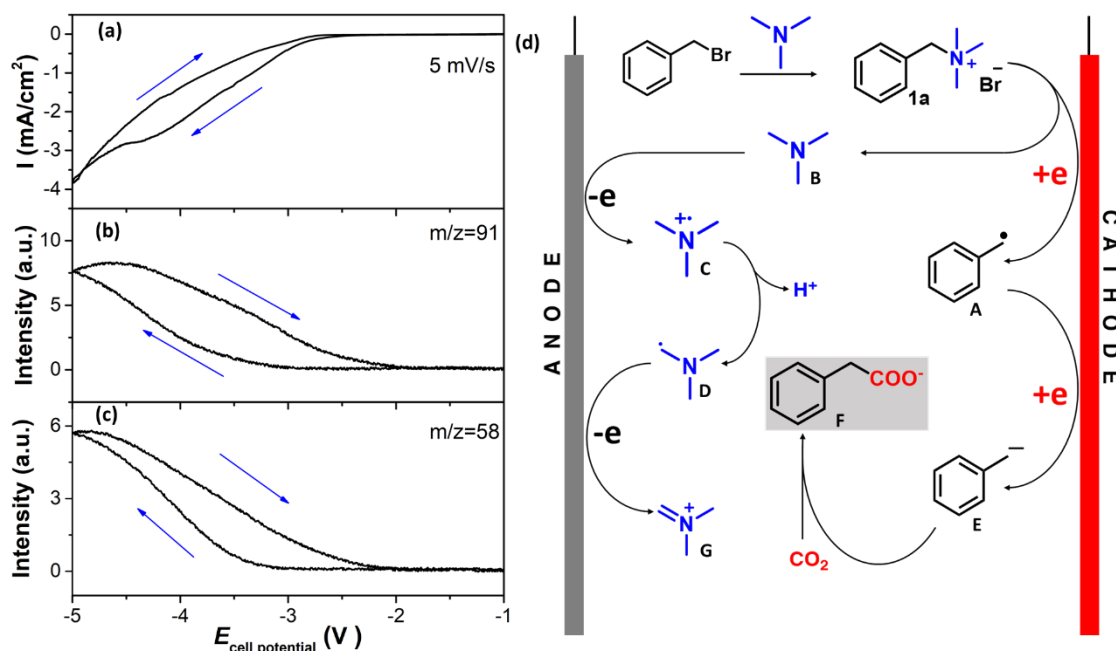
Figure 1. Simultaneously recorded cyclic voltammogram (CV) (a), mass spectrometric CV (MSCV) for m/z = 91 (b), and MSCV for m/z = 58 (c) on carbon paper cathode in 0.1 M DMF + 0.1 M Bu4PBF4 at a scan rate of 5 mV/s, and proposed reaction mechanism (d).

On the basis of these results, we propose the following mechanism (Figure 1d): first, benzyl radical (**A**) is generated through reduction of benzylammonium (**1a**) at the cathode. Meanwhile, trimethylamine (**B**) is produced during reduction through C-N bond breaking, which can then diffuse to the anode to be oxidized to the trimethylamine radical cation (**C**). However, due to similar oxidation potentials of bromide anion and trimethylamine (see Figure S11 in SI), we

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could not exclude the possibility of Br-mediated trimethylamine oxidation. We infer that both processes exist in the reaction based on the fact that they have similar oxidation potentials, observation of brominated by-products, and since the carboxylated products still form when bromide is entirely excluded through use of a different anion (BF_4^-) for the substrate. This trimethylamine radical cation (**C**) tends to release one proton with the formation of the imine radical (**D**).[23] The function of generated trimethylamine was similar to a recent work (Scheme 1c);[16] that is, the in situ generated trimethylamine loses two electrons and one proton during the redox process. The benzyl radical (**A**) can gain one more electron to form benzyl anion (**E**) at the cathode, which can be trapped by CO_2 generating the 2-phenylacetate anion (**F**). Meanwhile, at the anode, the imine radical (**D**) loses one electron to form the imine cation (**G**) that can form an ion-pair with the 2-phenylacetate anion (**F**).

3. CONCLUSIONS

We have developed a new, efficient, and mild strategy for electrochemical carboxylation of benzylammonium salts through C-N bond cleavage/CO_2 insertion without the usage of stoichiometric metals as reducing agent or sacrificial anode and without column chromatography for purification. Both primary and secondary benzylammonium substrates had high selectivity and moderate to excellent yields. A broad range of functional groups were tolerated under this direct electrochemical carboxylation. These features show that this user-friendly and simple system could be applied in the future to the synthesis of a broader range of aliphatic carboxylic acids and dicarboxylic acids. In addition, DEMS may be more widely used to investigate the mechanism of organic electrosynthesis reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Additional information including reagent information, analytical information, experimental protocols and NMR spectra.

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Notes

Any additional relevant notes should be placed here.

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