Supporting Information for

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

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1. General Methods

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on Bruker Avance 400 and 500 instruments and were calibrated using residual undeuterated solvent as an internal reference (CDCl$_3$: 7.26 ppm $^1$HNMR, 77.16 ppm $^{13}$C NMR; (CD$_3$)$_2$CO: 2.05 ppm $^1$HNMR, 29.84 and 206.26 ppm $^{13}$C NMR; (CD$_3$)$_2$SO: 2.50 ppm $^1$HNMR, 39.52 ppm $^{13}$C NMR). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d= doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. DEMS data were recorded on a Shanghai Linglu Instruments Differential Electrochemical Mass Spectrometer. Ion chromatography were recorded on a Thermofisher ICS1100 Ion chromatography. $N,N$-Dimethylformamide (DMF) was purchased from Sigma-Aldrich (anhydrous,99.8%, 227056-2L) and dried with molecular sieves overnight prior to use. Tetrabutylphosphonium tetrafluoroborrate (Bu$_4$PBF$_4$, >97%, T2006) and trimethylphenylammonium bromide (>98%, P0243) were purchased from TCI Chemicals. Benzyltrimethylammonium bromide was purchased from Aldrich Chemistry (97%, 147117-25G). Platinum on carbon (Paper GDE -0.5mg/cm$^2$ PtC 60%, SKU: 1610005), carbon papers (Freudenberg H14 (SKU: 15910014), Sigracet 39 BC (SKU: 15920007)) were purchased from FuelCellStore. Toray Carbon Paper 060 (TGPH060-4005) was purchased from Fuel Cell Earth. CO$_2$ cylinder (99.999% research grade) was purchased from Airgas. Leak free Ag/AgCl electrode (Innovative Instruments) was used as a reference electrode, which was calibrated using ferrocene.

2. Synthesis of Substrates and Characterization

2.1 Synthesis of Benzyl Ammonium

All the benzylic ammonium salts were synthesized according to literature procedures$^1$; to a solution of benzyl halide (1 equiv.) in THF (30 ml/g benzyl halide) were added trimethylamine (1.5 equiv., 33 wt% in EtOH). The resulting solution was stirred at room temperature for 12 hours, during which the product precipitated as a white/yellow solid. The resulting suspension was cooled to 0 °C, filtered, washed with ice-cold Et$_2$O and dried in vacuo to yield benzyl ammonium salt.
1-(4-(tert-butyl)phenyl)-N,N,N-trimethylmethanaminium bromide (2a)  

The product 2a was synthesized following Synthesis of Benzyl Ammonium as white solid (85% yield).

\[ ^1H \text{NMR (400 MHz, DMSO-}d_6\text{)} \delta 7.51 (s, 4H), 4.75 - 4.44 (m, 2H), 3.08 (s, 9H), 1.28 (s, 9H). ^{13}C \text{NMR (101 MHz, DMSO-}d_6\text{)} \delta 152.66, 132.54, 125.60, 125.56, 66.96, 51.50 (t, }J = 3.9 \text{ Hz), 34.47, 30.92.} \]

N,N,N-trimethyl-1-(o-tolyl)methanaminium bromide (3a)  

The product 3a was synthesized following Synthesis of Benzyl Ammonium as white solid (95% yield).

\[ ^1H \text{NMR (400 MHz, DMSO-}d_6\text{)} \delta 7.53 (dd, }J = 7.7, 1.4 \text{ Hz, 1H), 7.41 (td, }J = 7.5, 1.4 \text{ Hz, 1H), 7.37 - 7.24} (m, 2H), 4.67 (s, 2H), 3.11 (s, 9H), 2.45 (s, 3H). ^{13}C \text{NMR (101 MHz, DMSO-}d_6\text{)} \delta 139.85, 134.28, 131.46, 130.26, 126.87, 125.98, 64.74, 51.73 (t, }J = 3.6 \text{ Hz), 19.78.} \]

N,N,N-trimethyl-1-(m-tolyl)methanaminium bromide (4a)  

The product 4a was synthesized following Synthesis of Benzyl Ammonium as white solid (94% yield).

\[ ^1H \text{NMR (400 MHz, DMSO-}d_6\text{)} \delta 7.44 - 7.26 (m, 4H), 4.59 (s, 2H), 3.07 (s, 9H), 2.35 (s, 3H). ^{13}C \text{NMR (101 MHz, DMSO-}d_6\text{)} \delta 138.12, 133.25, 130.81, 129.89, 128.71, 128.34, 67.45 (t, }J = 2.5 \text{ Hz), 51.65 (t, }J = 2.5 \text{ Hz), 20.89.} \]

1-(3-methoxyphenyl)-N,N,N-trimethylmethanaminium bromide (5a)  

The product 5a was synthesized following Synthesis of Benzyl Ammonium as white solid (89% yield).

\[ ^1H \text{NMR (400 MHz, DMSO-}d_6\text{)} \delta 7.43 (t, }J = 7.9 \text{ Hz, 1H), 7.17 (dd, }J = 2.5, 1.6 \text{ Hz, 1H), 7.14 - 7.05} (m, 2H), 4.59 (s, 2H), 3.79 (s, 3H), 3.07 (s, 9H). ^{13}C \text{NMR (101 MHz, DMSO-}d_6\text{)} \delta 159.24, 129.95, 129.74, 124.83, 118.46, 115.63, 67.38, 55.28, 51.80 (t, }J = 3.7 \text{ Hz).} \]
1-(3-methoxyphenyl)-N,N,N-trimethylmethanaminium bromide (6a) \(^1\)

The product \(6a\) was synthesized following *Synthesis of Benzyl Ammonium* as white solid (90% yield).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.50 (d, \(J = 8.7\) Hz, 2H), 7.05 (d, \(J = 8.7\) Hz, 2H), 4.59 (s, 2H), 3.79 (s, 3H), 3.04 (s, 9H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 160.51, 134.20, 120.30, 114.20, 68.37 – 64.54 (m), 55.30, 52.64 – 49.10 (m).

1-([1,1'-biphenyl]-4-yl)-N,N,N-trimethylmethanaminium bromide (7a) \(^1\)

The product \(7a\) was synthesized following *Synthesis of Benzyl Ammonium* as white solid (80% yield).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.82 (d, \(J = 8.1\) Hz, 2H), 7.72 (d, \(J = 7.4\) Hz, 2H), 7.67 (d, \(J = 8.0\) Hz, 2H), 7.49 (t, \(J = 7.6\) Hz, 2H), 7.40 (t, \(J = 7.3\) Hz, 1H), 4.69 (s, 2H), 3.11 (s, 9H).

\(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 141.73, 139.02, 133.42, 129.05, 128.03, 127.50, 127.00, 126.80, 67.10, 51.68 (t, \(J = 3.6\) Hz).

1-([1,1'-biphenyl]-3-yl)-N,N,N-trimethylmethanaminium bromide (8a)

The product \(8a\) was synthesized following *Synthesis of Benzyl Ammonium* as white solid (80% yield).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.91 (t, \(J = 1.8\) Hz, 1H), 7.83 (dt, \(J = 7.0, 2.0\) Hz, 1H), 7.75 – 7.67 (m, 2H), 7.64 – 7.54 (m, 2H), 7.49 (dd, \(J = 8.4, 6.9\) Hz, 2H), 7.44 – 7.33 (m, 1H), 4.75 (s, 2H), 3.13 (s, 9H). \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 140.68, 139.22, 131.71, 131.21, 129.46, 129.16, 128.98, 128.43, 127.86, 126.85, 67.32, 51.77.

1-(4-fluorophenyl)-N,N,N-trimethylmethanaminium bromide (9a) \(^1\)

The product \(9a\) was synthesized following *Synthesis of Benzyl Ammonium* as white solid (95% yield).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.71 – 7.49 (m, 2H), 7.49 – 7.23 (m, 2H), 4.66 (s, 2H), 3.07 (s, 9H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 163.13 (d, \(J = 247.2\) Hz), 135.16 (d, \(J = 8.8\) Hz), 124.86 (d, \(J = 3.4\) Hz), 115.87 (d, \(J = 21.7\) Hz), 66.37, 53.62 – 48.33 (m). \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)) \(\delta\) -110.91 (ddd, \(J = 14.4, 9.1, 5.4\) Hz).
1-(3-chlorophenyl)-N,N,N-trimethylmethanaminium bromide (10a)  

The product 10a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (85% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.71 (t, $J = 1.4$ Hz, 1H), 7.60 (tt, $J = 9.0$, 1.9 Hz, 1H), 7.57 – 7.51 (m, 2H), 4.70 (s, 2H), 3.10 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 133.32, 132.43, 131.55, 130.72, 130.23, 66.28, 51.77.

1-(4-bromophenyl)-N,N,N-trimethylmethanaminium bromide (11a)  

The product 11a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (95% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.73 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 4.62 (s, 2H), 3.06 (s, 9H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 134.87, 131.89, 127.75, 124.09, 66.54, 51.67 (t, $J = 3.6$ Hz).

N,N,N-trimethyl-1-(4-(trifluoromethyl)phenyl)methanaminium bromide (12a)  

The product 12a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (94% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.86 (q, $J = 8.3$ Hz, 4H), 4.82 (s, 2H), 3.13 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 133.77, 132.96, 130.85 - 129.90 (q, $J = 32$ Hz), 125.74-125.27 (q, $J = 3.5$ Hz), 127.98-119.85 (q, $J = 275$ Hz), 66.19, 51.81. $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ -61.38.

1-(4-cyanophenyl)-N,N,N-trimethylmethanaminium bromide (13a)  

The product 13a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (90% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.01 (d, $J = 8.2$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 4.78 (s, 2H), 3.10 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 133.77, 133.57, 132.69, 118.27, 112.92, 66.28, 51.88.
1-(3-cyanophenyl)-N,N,N-trimethylmethanaminium bromide (14a)

The product 14a was synthesized following Synthesis of Benzyl Ammonium as white solid (90% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.09 (d, $J = 1.8$ Hz, 1H), 8.02 (dt, $J = 7.9, 1.4$ Hz, 1H), 7.95 (dt, $J = 8.0, 1.4$ Hz, 1H), 7.73 (t, $J = 7.8$ Hz, 1H), 4.76 (s, 2H), 3.11 (s, 9H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 137.63, 136.28, 133.88, 130.14, 129.93, 118.27, 111.94, 66.00, 51.83.

1-(4-(methoxycarbonyl)phenyl)-N,N,N-trimethylmethanaminium bromide (15a)  5

The product 15a was synthesized following Synthesis of Benzyl Ammonium as white solid (88% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.06 (d, $J = 8.3$ Hz, 2H), 7.73 (d, $J = 8.3$ Hz, 2H), 4.74 (s, 2H), 3.88 (s, 3H), 3.10 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 165.73, 133.34, 133.27, 131.07, 129.46, 66.62, 52.42, 51.85.

1-(4-acetylphenyl)-N,N,N-trimethylmethanaminium bromide (16a)  6

The product 16a was synthesized following Synthesis of Benzyl Ammonium as white solid (88% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.06 (d, $J = 8.3$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 4.78 (s, 2H), 3.12 (s, 9H), 2.61 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 197.72, 137.82, 133.21, 133.17, 128.45, 66.52, 51.82, 26.95.

$N,N,N$-trimethyl-1-(naphthalen-2-yl)methanaminium bromide (17a)  1

The product 17a was synthesized following Synthesis of Benzyl Ammonium as white solid (93% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.16 (d, $J = 1.7$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 8.02 – 7.96 (m, 2H), 7.68 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.65 – 7.56 (m, 2H), 4.82 (s, 2H), 3.14 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 133.29, 132.97, 132.41, 129.32, 128.38, 128.29, 127.64, 127.46, 126.78, 125.97, 67.56, 51.75 (t, $J = 3.6$ Hz).
\[ N,N,N\text{-trimethyl}-1\text{-}(naphthalen-1\text{-yl})\text{methanaminium bromide (18a)} \]

The product \textit{18a} was synthesized following \textit{Synthesis of Benzyl Ammonium} as white solid (90\% yield).

\[ ^{1}H\text{ NMR (400 MHz, DMSO-\textit{d}_6) \delta 8.59 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.05 (dd, J = 8.0, 1.4 Hz, 1H), 7.84 (dd, J = 7.1, 1.3 Hz, 1H), 7.72 - 7.52 (m, 3H), 5.16 (s, 2H), 3.15 (s, 9H).} \]

\[ ^{13}C\text{ NMR (101 MHz, DMSO-\textit{d}_6) \delta 133.64, 133.58, 132.81, 131.27, 128.96, 127.27, 126.22, 125.21, 124.64, 124.20, 63.62, 52.12.} \]

\[ N,N,N\text{-trimethyl}-1\text{-}(3\text{-methylbenzo}[b]\text{thiophen-2\text{-yl})\text{methanaminium bromide (19a)} \]

The product \textit{19a} was synthesized following \textit{Synthesis of Benzyl Ammonium} as white solid (90\% yield).

\[ ^{1}H\text{ NMR (400 MHz, DMSO-\textit{d}_6) \delta 8.09 - 7.94 (m, 1H), 7.94 - 7.79 (m, 1H), 7.56 - 7.38 (m, 2H), 4.99 (s, 2H), 3.20 (s, 9H), 2.55 (s, 3H).} \]

\[ ^{13}C\text{ NMR (101 MHz, DMSO-\textit{d}_6) \delta 139.45, 139.28, 137.64, 126.09, 124.63, 123.84, 123.20, 122.44, 60.52, 51.88, 12.64.} \]

\[ 1\text{-}(furan-2\text{-yl})\text{-}N,N,N\text{-trimethylmethanaminium bromide (20a)} \]

The product \textit{20a} was synthesized following \textit{Synthesis of Benzyl Ammonium} as yellow solid (81\% yield).

\[ ^{1}H\text{ NMR (400 MHz, DMSO-\textit{d}_6) \delta 7.89 (d, J = 1.8 Hz, 1H), 6.84 (d, J = 3.2 Hz, 1H), 6.60 (dd, J = 3.3, 1.8 Hz, 1H), 4.77 (s, 2H), 3.09 (s, 10H).} \]

\[ ^{13}C\text{ NMR (101 MHz, DMSO) \delta 145.90, 143.43, 116.18, 111.30, 60.03, 51.79 (t, J = 3.6 Hz).} \]

\[ N,N,N\text{-trimethyl-1\text{-phenylethan-1-aminium bromide (21a)} \]

The product \textit{21a} was synthesized following \textit{Synthesis of Benzyl Ammonium} as white solid (85\% yield).

\[ ^{1}H\text{ NMR (400 MHz, DMSO-\textit{d}_6) \delta 7.69 - 7.59 (m, 2H), 7.48 (dd, J = 5.1, 1.9 Hz, 3H), 4.97 (q, J = 7.1 Hz, 1H), 3.03 (s, 9H), 1.71 (dt, J = 7.1, 1.8 Hz, 3H).} \]

\[ ^{13}C\text{ NMR (101 MHz, DMSO) \delta 133.62, 130.47, 130.06, 128.76, 72.10, 50.37 (t, J = 3.6 Hz), 14.58.} \]

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**N,N,N-trimethyl-1-(p-tolyl)ethan-1-aminium bromide (22a)**

The product 22a was synthesized following Synthesis of Benzyl Ammonium as white solid (86% yield).

\[
\begin{align*}
\text{N} & \text{Br}^- \\
\text{C}_8H_7 & \\
\text{N} & \text{Br}^-
\end{align*}
\]

\[^1\text{H NMR (400 MHz, DMSO-d}_6\text{)} \delta 7.51 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 4.89 (tt, J = 8.7, 7.0, 2.9 Hz, 1H), 3.00 (s, 9H), 2.33 (s, 3H), 1.68 (dt, J = 7.1, 1.8 Hz, 3H). ^{13}\text{C NMR (101 MHz, DMSO-d}_6\text{)} \delta 139.64, 130.64, 130.37, 129.29, 71.97, 50.28 (t, J = 3.6 Hz), 20.74, 14.60.\]

**N,N,N-trimethyl-1-(3-(trifluoromethyl)phenyl)ethan-1-aminium bromide (23a)**

The product 23a was synthesized following Synthesis of Benzyl Ammonium as white solid (83% yield).

\[
\begin{align*}
\text{N} & \text{Br}^- \\
\text{C}_8H_7 & \\
\text{N} & \text{Br}^-
\end{align*}
\]

\[^1\text{H NMR (400 MHz, DMSO-d}_6\text{)} \delta 8.02 (d, J = 2.3 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.75 (t, J = 7.8 Hz, 1H), 5.06 (q, J = 7.0 Hz, 1H), 3.04 (s, 10H), 1.76 (d, J = 7.0 Hz, 3H). ^{13}\text{C NMR (101 MHz, DMSO-d}_6\text{)} \delta 134.95, 134.49 (br), 130.07, 129.49 (q, J = 33 Hz), 127.38, 126.90 (q, J = 3.6 Hz), ~123.50 (q, J = 272 Hz). ^{19}\text{F NMR (376 MHz, DMSO)} \delta -111.19.\]

**1-(4-fluorophenyl)-N,N,N-trimethylethan-1-aminium bromide (24a)**

The product 24a was synthesized following Synthesis of Benzyl Ammonium as white solid (82% yield).

\[
\begin{align*}
\text{N} & \text{Br}^- \\
\text{C}_8H_7 & \\
\text{N} & \text{Br}^-
\end{align*}
\]

\[^1\text{H NMR (400 MHz, DMSO-d}_6\text{)} \delta 7.80 – 7.62 (m, 2H), 7.40 – 7.22 (m, 2H), 5.00 (qd, J = 7.0, 1.4 Hz, 1H), 3.02 (s, 9H), 1.70 (dt, J = 7.0, 1.8 Hz, 3H). ^{13}\text{C NMR (101 MHz, DMSO-d}_6\text{)} \delta 162.84 (d, J = 247.6 Hz), 132.87, 129.95 (d, J = 3.0 Hz), 115.72 (d, J = 21.3 Hz), 71.27, 52.16 – 48.62 (m), 14.65. ^{19}\text{F NMR (376 MHz, DMSO-d}_6\text{)} \delta -111.19 (ddd, J = 14.3, 9.1, 5.4 Hz).\]
\[
\text{N,N,N-trimethyl-1-(naphthalen-2-yl)ethan-1-aminium bromide (25a)}
\]

The product 25a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (80% yield).

\[
\text{1H NMR (400 MHz, DMSO-\text{d}_6) } \delta 8.26 \text{ (s, 1H), } 8.06 - 7.93 \text{ (m, 3H), } 7.75 \text{ (dd, } J = 8.6, 1.8 \text{ Hz, 1H), } 7.65 - 7.54 \text{ (m, 2H), } 5.12 \text{ (qd, } J = 7.0, 2.7 \text{ Hz, 1H), } 3.09 \text{ (s, 9H), } 1.82 \text{ (d, } J = 6.9 \text{ Hz, 3H).}
\]

\[
\text{13C NMR (101 MHz, DMSO-\text{d}_6) } \delta 133.28, 132.37, 131.06, 130.57, 128.35, 128.28, 127.54, 127.35, 127.23, 126.74, 72.29, 50.51 \text{ (t, } J = 3.6 \text{ Hz), 14.77.}
\]

\[
\text{N,N,N-trimethyl-1,2,3,4-tetrahydronaphthalen-1-aminium bromide (26a)}
\]

The product 26a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (81% yield).

\[
\text{1H NMR (400 MHz, DMSO-\text{d}_6) } \delta 7.52 \text{ (dd, } J = 7.3, 1.7 \text{ Hz, 1H), } 7.42 \text{ (td, } J = 7.4, 1.3 \text{ Hz, 1H), } 7.31 \text{ (t, } J = 7.3 \text{ Hz, 2H), } 5.02 \text{ (dt, } J = 8.3, 4.0 \text{ Hz, 1H), } 3.02 \text{ (s, 9H), } 2.76 - 2.66 \text{ (m, 2H), } 2.49 - 2.37 \text{ (m, 1H), } 2.15 \text{ (dq, } J = 14.6, 6.9 \text{ Hz, 1H), } 2.09 - 1.94 \text{ (m, 1H), } 1.44 \text{ (dddd, } J = 15.4, 13.1, 9.0, 6.4 \text{ Hz, 1H).}
\]

\[
\text{13C NMR (101 MHz, DMSO-\text{d}_6) } \delta 142.72, 133.59, 130.00, 129.49, 127.00, 71.48, 50.52 \text{ (t, } J = 3.6 \text{ Hz), 27.90, 22.73, 21.10.}
\]

\[
\text{N,N,N-trimethyl-1,1-diphenylmethanaminium bromide (27a)}
\]

The product 27a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (60% yield).

\[
\text{1H NMR (400 MHz, DMSO-\text{d}_6) } \delta 8.01 - 7.83 \text{ (m, 4H), } 7.58 - 7.37 \text{ (m, 6H), } 6.20 \text{ (m, 1H), } 3.11 \text{ (s, 9H).}
\]

\[
\text{13C NMR (101 MHz, DMSO-\text{d}_6) } \delta 132.89, 131.00, 129.97, 129.27, 79.77, 51.64.
\]

\[
\text{1-(4-isobutylphenyl)-N,N,N-trimethylethan-1-aminium bromide (28a)}
\]

The product 28a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (90% yield from 1-(4-isobutylphenyl)ethan-1-ol).

\[
\text{1H NMR (400 MHz, DMSO-\text{d}_6) } \delta 7.55 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 7.28 \text{ (d, } J = 8.0 \text{ Hz, 2H), } 4.90 \text{ (q, } J = 7.0 \text{ Hz, 1H), } 3.01 \text{ (s, 9H), } 2.49 \text{ (d, } J = 7.2 \text{ Hz, 2H), } 1.85 \text{ (dh, } J = 13.5, 6.8 \text{ Hz, 1H), 1.71}
\]
(dt, $J = 7.0, 1.8$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 143.24, 130.90, 130.24, 129.26, 72.08, 50.32 (t, $J = 3.6$ Hz), 44.12, 29.46, 22.11, 14.55.

**Step 1:** Sodium borohydride (0.32 g, 8.52 mmol) was added portion-wise to a stirred solution of 4-isobutylacetophenone (1 g, 5.68 mmol) in methanol (7 mL). After 1 h of refluxing, the mixture was cooled at room temperature and 1 M HCl (5 mL) was added and the solvent distilled off. The resulting aqueous acid phase was extracted with EtOAc (3 × 5 mL) and the combined extract was washed with brine (2 × 15 mL) and dried over Na$_2$SO$_4$. Removal of the solvent under reduced pressure afforded the pure 1-hydroxy-1-(4-isobutylphenyl)ethane (0.9 g, 98%) as a colorless oil.

**Step 2:** To a solution of the resulting alcohol from **Step 1** (0.9 g, 5.06 mmol) in dry ether (20 mL) was added PBr$_3$ (0.6 mL, 5.06 mmol) at room temperature. The mixture was stirred for 1 h at this temperature. The resulting solution was treated with H$_2$O and extracted with Et$_2$O three times. The combined organic layer was washed with brine, dried over MgSO$_4$ and filtered. The filtrate was added with THF (50 mL) and Et$_2$O was removed under reduced pressure on a rotary evaporator (0 °C) to obtain a solution of 1-(1-bromoethyl)-4-isobutylbenzene in THF, which was directly used to next step.

**N,N,N-trimethyl-2-phenylethan-1-aminium bromide (30a)**

The product 30a was synthesized following *Synthesis of Benzyl Ammonium* as white solid (60% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.34 (d, $J = 4.4$ Hz, 4H), 7.26 (ddd, $J = 8.7, 5.0, 3.8$ Hz, 1H), 3.67 – 3.56 (m, 2H), 3.19 (s, 9H), 3.11 – 3.00 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 136.32, 128.97, 128.60, 126.86, 65.62 (t, $J = 3.1$Hz), 52.18 (t, $J = 3.6$ Hz), 28.47.
3. Graphical Guide for the Assembly of a Cell

Depicted here is our setup for 0.15 mmol scale experiments.

Overview of materials used.

1) Aluminum current collector; 2) piece of platinum foil (used to connect electrode, prevent aluminum from oxidation); 3) working electrode (Freudenberg carbon cloth unless otherwise stated, diameter is 12 mm); 4) counter electrode (Pt/C, Pt side faces the electrolyte, diameter is 12 mm); 5) O-ring.

Step 1. Assembly of the components.
Step 2. Connection of CO$_2$ and potentiostat.
4. General Procedure for Electrochemical Carboxylation

To a clean centrifuge tube or vial was added electrolyte Bu₄PBF₄ (0.15 mmol, 52 mg), benzyl ammonium bromide (0.15 mmol), and anhydrous DMF (0.1M, 1.5 mL). The resulting suspension was sonicated until the dissolution of all solids. The solution was transferred to the assembled cell with a carbon paper cathode and a Pt/C anode (see 3. Graphical Guide for the Assembly of a Cell). The reaction mixture was degassed and saturated by bubbling CO₂ for 5 min before constant voltage electrolysis (cell voltage = -4.5 V, VMP3 Multi-channel potentiostat) was conducted for 12 h or the current decreased to -2 mA under CO₂ bubbling (Flow rate = 20 sccm). The resulting mixture was transferred back into the centrifuge tube or vial which was used to prepare the reaction solution at the beginning. The cell was washed with ethyl acetate (1.5 mL x 2) twice. The combined organic solution was acidified (pH < 2) by addition of 2 M HCl and extracted with ethyl acetate (3x3 mL). The combined organic layers were washed with water, dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was re-dissolved in diethyl ether (5 mL) and extracted with 1 M NaOH (3x3 mL). Finally, the aqueous fractions were combined, washed by diethyl ether before acidified (pH < 2) by adding 5 M HCl and extracted with ethyl acetate (3x4 mL). The combined organic layers were washed by 5 M HCl and water, dried with MgSO₄, filtered, and concentrated in vacuo to give the final product.
5. Graphical Guide for Electrochemical Carboxylation with *ElectraSyn 2.0*

To an oven-dried, undivided electrochemical vial equipped with a magnetic stir bar was added electrolyte Bu₄PBF₄ (0.30 mmol, 104 mg), benzyl ammonium bromide (0.30 mmol), and anhydrous DMF (0.1M, 3.0 mL). The resulting suspension was sonicated until the dissolution of all solids. The reaction mixture was degassed and saturated by bubbling CO₂ for 5 min before constant voltage electrolysis (cell voltage = -4.5 V, ElectraSyn 2.0, with a carbon paper cathode and a Pt foil anode) was conducted for 20 h under CO₂ bubbling (Flow rate = 20 sccm). The reaction solution was acidified (pH < 2) by addition of 2 M HCl and extracted with ethyl acetate (3x3 mL). The combined organic layers were washed with water, dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was re-dissolved in diethyl ether (5 mL) and extracted with 1 M NaOH (3x3 mL). Finally, the aqueous fractions were combined, washed by diethyl ether before acidified (pH < 2) by adding 5 M HCl and extracted with ethyl acetate (3x4 mL). The combined organic layers were washed by 5 M HCl and water, dried with MgSO₄, filtered, and concentrated in vacuo to give the final product.
6. Optimization of Reaction Conditions

Figure S1. Constant cathode potential applied at -3.1 V (vs. Fc+/Fc). The cell voltage was recorded, which increased from -4.5V to -5.3V within 3 hours electrolysis, indicating that the anode potential increased from +1.8V to +2.6V (~0.8V increase).
Figure S2. Constant cell voltage applied at -4.5V. Both cathode potential (top) and anode potential (bottom) were recorded. Although the anode potential increased, it only increased 0.25V.
Figure S3. A control reaction of our substrate benzylammonium bromide with a Grignard reagent benzylmagnesium chloride that can act as a benzyl anion. According to the GC-MS, the homodimer by-product was present in less than 5% yield. Meanwhile, we did not observe homodimer by-product at -4.5 V under our optimized condition. These results indicate that homodimer by-product formed from S_{N}2 reaction is negligible.
7. Characterization Data of Products

2-phenylacetic acid (1b)\textsuperscript{8}

\[ \text{Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 1b as white solid (14.1 mg, 65\% yield).} \]

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 7.43 – 7.19 \text{ (m, 5H), 3.66 (s, 2H).} \)

\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta 177.34, 133.42, 129.51, 128.79, 127.49, 41.12.} \)

2-(4-(tert-butyl)phenyl)acetic acid (2b)\textsuperscript{8}

\[ \text{Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 2b as colorless oil (24.4 mg, 80\% yield).} \]

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 7.36 (d, J = 8.3 \text{ Hz, 2H}), 7.22 (d, J = 8.4 \text{ Hz, 2H), 3.62 (s, 2H), 1.31 (s, 9H).} \)

\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta 177.64, 150.38, 130.34, 129.16, 125.75, 40.61, 34.63, 31.47.} \)

2-(o-tolyl)acetic acid (3b)\textsuperscript{8}

\[ \text{Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 3b as white solid (12.2 mg, 54\% yield).} \]

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 7.23 – 7.14 \text{ (m, 4H), 3.67 (s, 2H), 2.33 (s, 3H).} \)

\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta 177.31, 137.08, 132.15, 130.57, 130.43, 127.84, 126.36, 38.93, 19.71.} \)

2-(m-tolyl)acetic acid (4b)\textsuperscript{9}

\[ \text{Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 1b as white solid (16.0 mg, 71\% yield).} \]

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 7.25 – 7.18 \text{ (m, 1H), 7.14 – 7.05 (m, 3H), 3.61 (s, 2H), 2.35 (s, 3H).} \)

\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta 177.62, 138.49, 133.28, 130.25, 128.69, 128.26, 126.51, 41.08, 21.49.} \)
2-(3-methoxyphenyl)acetic acid (5b) 

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 5b as white solid (15 mg, 60% yield).

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.30 – 7.20 (m, 1H), 6.90 – 6.79 (m, 3H), 3.80 (s, 3H), 3.63 (s, 2H). \]

13C NMR (101 MHz, CDCl$_3$) δ 176.74, 134.85, 129.78, 121.84, 115.18, 113.01, 55.36, 41.10.

2-(4-methoxyphenyl)acetic acid (6b)

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 6b and 6b-Br as white solid (20.6mg, 6b:6b-Br = 3:1; 6b: 55% yield; 6b-Br: 13.4% yield).

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.20 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.59 (s, 2H). \]

13C NMR (101 MHz, CDCl$_3$) δ 177.42, 159.01, 130.56, 125.45, 114.24, 55.42, 40.15.

2-([1,1'-biphenyl]-4-yl)acetic acid (7b)

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 7b as white solid (23 mg, 72% yield).

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.58 (dt, J = 8.1, 2.8 Hz, 4H), 7.44 (t, J = 7.7 Hz, 2H), 7.36 (dd, J = 7.6, 5.6 Hz, 3H), 3.71 (s, 2H). \]

13C NMR (101 MHz, CDCl$_3$) δ 177.22, 140.84, 140.54, 132.36, 129.94, 128.91, 127.57, 127.48, 127.24, 40.70.
2-[(1,1'-biphenyl)-3-yl]acetic acid (8b) \(^8\)

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give \(8\)\(b\) as white solid (22.5 mg, 71\% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (d, \(J = 7.6\) Hz, 2H), 7.51 (m, \(J = 7.7\) Hz, 2H), 7.39 (m, 7.4 Hz, 4H), 7.26 (m, \(J = 4.0\) Hz, 1H), 3.70 (s, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.57, 141.81, 140.94, 133.89, 129.19, 128.89, 128.42, 128.38, 127.54, 127.34, 126.34, 41.25.

2-(4-fluorophenyl)acetic acid (9b) \(^8\)

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give \(9\)\(b\) as white solid (16 mg, 69\% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.24 (t, \(J = 8.5\) Hz, 2H), 7.02 (t, \(J = 8.5\) Hz, 2H), 3.62 (s, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 176.85, 163.51, 161.07, 131.14, 131.06, 129.08, 115.79, 115.58, 40.17. \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -115.41.

2-(3-chlorophenyl)acetic acid (10b) \(^11\)

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give \(10\)\(b\) as white solid (20.7 mg, 81\% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29 (m, 1H), 7.27 – 7.23 (m, 2H), 7.16 (m, 1H), 3.63 (s, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.03, 135.15, 134.57, 130.00, 129.71, 127.77, 127.75, 40.68.

2-(4-bromophenyl)acetic acid (11b) \(^11\)

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give \(11\)\(b\) as white solid (18.1 mg, 56\% yield).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 2H), 3.62 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.87, 132.32, 131.92, 131.24, 121.63, 40.30.

2-(4-((trifluoromethyl)phenyl)acetic acid (12b) $^9$

![trifluoromethylphenylacetic acid](image)

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 12b as white solid (17.2 mg, 56% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 3.72 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.63, 137.23, 129.95, 125.74 (q, $J = 3.9$ Hz), 122.84, 40.80. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.64.

2-(4-cyanophenyl)acetic acid (13b) $^9$

![cyanophenylacetic acid](image)

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 13b as white solid (16.1 mg, 67% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 3.72 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.02, 138.56, 132.55, 130.42, 118.67, 111.65, 40.98.

2-(3-cyanophenyl)acetic acid (14b) $^9$

![cyanophenylacetic acid](image)

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 14b as white solid (17.4 mg, 72% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (m, 2H), 7.53 (dt, $J = 7.9$, 1.6 Hz, 1H), 7.45 (t, $J = 7.9$ Hz, 1H), 3.70 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.41, 134.73, 134.11, 133.12, 131.30, 129.59, 118.58, 112.96, 40.45.
**4-(carboxymethyl)benzoic acid (15b)**

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give **15b** as white solid (23.0 mg, 87% yield).

1H NMR (400 MHz, (CD$_3$)$_2$CO) δ 8.00 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 8.1$ Hz, 2H), 3.75 (s, 2H). 13C NMR (101 MHz, (CD$_3$)$_2$CO) δ 174.48, 172.18, 167.46, 141.18, 130.49, 129.98, 41.12.

**2-(4-acetylphenyl)acetic acid (16b)**

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give **16b** as yellow oil (18.0 mg, 67% yield).

1H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 3.72 (s, 2H), 2.59 (s, 3H). 13C NMR (101 MHz, CDCl$_3$) δ 197.93, 176.35, 138.72, 136.35, 129.84, 128.85, 40.97, 26.76.

**2-(naphthalen-2-yl)acetic acid (17b)**

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give **17b** as white solid (20 mg, 72% yield).

1H NMR (400 MHz, CDCl$_3$) δ 7.81 (t, $J = 8.2$ Hz, 3H), 7.74 (s, 1H), 7.47 (qd, $J = 6.5$, 3.3 Hz, 2H), 7.41 (dd, $J = 8.4$, 1.7 Hz, 1H), 3.82 (s, 2H). 13C NMR (101 MHz, CDCl$_3$) δ 177.19, 133.55, 132.71, 130.83, 128.50, 128.34, 127.82, 127.44, 126.40, 126.11, 41.24.

**2-(naphthalen-1-yl)acetic acid (18b)**

Electrolysis was conducted following the *General Procedure for Electrochemical Carboxylation*. The product was purified by extraction to give **18b** as white solid (20.4 mg, 73% yield).
NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.2 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.83 – 7.75 (m, 1H), 7.57 – 7.46 (m, 2H), 7.43 (d, J = 7.6 Hz, 2H), 4.09 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 177.57, 133.95, 132.15, 129.92, 128.92, 128.49, 128.34, 126.64, 126.01, 125.59, 123.81, 38.90.

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 19b as yellow solid (15.4 mg, 50% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.75 (m, 1H), 7.68 – 7.63 (m, 1H), 7.29-7.39 (m, 2H), 3.91 (s, 2H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.25, 140.39, 138.90, 130.40, 128.48, 124.54, 124.21, 122.35, 121.97, 33.81, 11.85.

2-(furan-2-yl)acetic acid (20b)

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. Product 20b was not compatible to our purification procedure. The yield was determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard, after work-up by 2M HCl.

¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 1.9 Hz, 1H), 6.32 (dd, J = 3.2, 1.9 Hz, 1H), 6.23 (d, J = 3.0 Hz, 1H), 3.70 (s, 2H).

2-phenylpropanoic acid (21b)

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 21b as colorless oil (15.8 mg, 70% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 3.74 (q, J = 7.1 Hz, 1H), 1.52 (d, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 180.22, 139.89, 128.83, 127.73, 127.54, 45.40, 18.27.
2-(p-tolyl)propanoic acid (22b)  
Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 22b as colorless oil (15.7 mg, 64% yield).

\[
{\text{H NMR (400 MHz, Chloroform-}d{\text{)}} \delta 7.21 \text{ (d, } J = 7.9 \text{ Hz, 2H), 7.14 \text{ (d, } J = 7.9 \text{ Hz, 2H), 3.71 \text{ (q, } J = 7.2 \text{ Hz, 1H), 2.33 \text{ (s, 3H), 1.49 \text{ (d, } J = 7.1 \text{ Hz, 3H). C NMR (101 MHz, CDCl}_3{\text{)}} \delta 180.15, 137.23, 136.95, 129.51, 127.58, 44.96, 21.20, 18.27.}}}
\]

2-(3-(trifluoromethyl)phenyl)propanoic acid (23b)  
Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 23b as white solid (21.5 mg, 66% yield).

\[
{\text{H NMR (400 MHz, CDCl}_3{\text{)}} \delta 7.57 \text{ (s, 1H), 7.53 \text{ (t, } J = 8.2 \text{ Hz, 2H), 7.46 \text{ (t, } J = 7.7 \text{ Hz, 1H), 3.81 \text{ (q, } J = 7.2 \text{ Hz, 1H), 1.55 \text{ (d, } J = 7.2 \text{ Hz, 3H). C NMR (101 MHz, CDCl}_3{\text{)}} \delta 179.72, 140.66, 131.24, 129.31, 124.67 \text{ (q, } J = 4.0 \text{ Hz), 124.50 \text{ (q, } J = 3.8 \text{ Hz), 123\text{(q, } J = 278 \text{ Hz), 45.25, 18.23. F NMR (376 MHz, CDCl}_3{\text{)}} \delta -62.60.}}}
\]

2-(4-fluorophenyl)propanoic acid (24b)  
Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 24b as colorless oil (15.5 mg, 62% yield).

\[
{\text{H NMR (400 MHz, CDCl}_3{\text{)}} \delta 7.29 \text{ (dd, } J = 8.4, 5.3 \text{ Hz, 2H), 7.02 \text{ (t, } J = 8.6 \text{ Hz, 2H), 3.73 \text{ (q, } J = 7.2 \text{ Hz, 1H), 1.50 \text{ (d, } J = 7.2 \text{ Hz, 3H). C NMR (101 MHz, CDCl}_3{\text{)}} \delta 180.15, 162.23 \text{ (d, } J = 245.8 \text{ Hz), 135.54 \text{ (d, } J = 3.3 \text{ Hz), 129.31 \text{ (d, } J = 8.1 \text{ Hz), 115.67 \text{ (d, } J = 21.3 \text{ Hz), 44.65, 18.38. F NMR (376 MHz, CDCl}_3{\text{)}} \delta -115.20 \text{ to -115.31 (m).}}}
\]
2-(naphthalen-2-yl)propanoic acid (25b)\(^8\)

\[
\text{COOH} \quad \begin{array}{c}
\text{\includegraphics[width=1cm]{naphthalen-2-yl-propionate.png}}
\end{array}
\]

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 25b as yellow solid (24.6 mg, 82% yield).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 7.87 - 7.79\) (m, 3H), 7.77 (d, \(J = 1.8\) Hz, 1H), 7.52 – 7.41 (m, 3H), 3.93 (q, \(J = 7.1\) Hz, 1H), 1.62 (d, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 180.47, 137.30, 133.53, 132.80, 128.55, 127.95, 127.76, 126.48, 126.36, 126.07, 125.82, 45.57, 18.27.\)

1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (26b)\(^9\)

\[
\text{COOH} \quad \begin{array}{c}
\text{\includegraphics[width=1cm]{1,2,3,4-tetrahydronaphthalene-1-carboxylic-acid.png}}
\end{array}
\]

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 26b as colorless oil (22.7 mg, 86% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.33 - 7.08\) (m, 4H), 3.85 (t, \(J = 5.7\) Hz, 1H), 2.91 – 2.67 (m, 2H), 2.29 – 2.11 (m, 1H), 2.01 (dt, \(J = 20.4, 9.9, 4.8, 2.4\) Hz, 2H), 1.87 – 1.70 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 181.33, 137.43, 132.62, 129.76, 129.61, 127.23, 125.95, 44.58, 29.20, 26.62, 20.55.\)

2,2-diphenylacetic acid (27b)\(^10\)

\[
\text{COOH} \quad \begin{array}{c}
\text{\includegraphics[width=1cm]{2,2-diphenylacetic-acid.png}}
\end{array}
\]

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 27b as white solid (17.1 mg, 54% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.45 - 7.16\) (m, 10H), 5.06 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 178.11, 138.06, 128.81, 127.64, 57.06.\)

2-(4-isobutylphenyl)propanoic acid (28b)\(^10\)

\[
\text{COOH} \quad \begin{array}{c}
\text{\includegraphics[width=1cm]{2-(4-isobutylphenyl)propanoic-acid.png}}
\end{array}
\]

Electrolysis was conducted following the General Procedure for Electrochemical Carboxylation. The product was purified by extraction to give 28b as white solid (27.0 mg, 87% yield).
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.22 (d, $J = 7.7$ Hz, 2H), 7.10 (d, $J = 7.7$ Hz, 2H), 3.71 (q, $J = 7.2$ Hz, 1H), 2.44 (d, $J = 7.2$ Hz, 2H), 1.84 (hept, $J = 6.8$ Hz, 1H), 1.50 (d, $J = 7.2$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.29, 140.94, 137.22, 129.51, 127.42, 45.19, 45.07, 30.30, 22.53, 18.29.

Figure S4. Raman spectra of glassy carbon, Freudenberg H14 carbon cloth and Toray 060 carbon paper. Two peaks at 1310 and 1580 cm\(^{-1}\) can be assigned to the D band and the G band, originating from the disorder-induced C-C vibration and the tangential E\(_{2g}\) sp\(^3\) bonded C=C stretching vibration, respectively.\(^{13}\) The higher intensity ratio of the D to the G peak (ID/IG) of glassy carbon and Freudenberg H14 carbon cloth indicates that the higher performance of glassy carbon and Freudenberg H14 carbon cloth is probably caused by the larger number of defects. (Glassy carbon ID/IG = 6.70, Freudenberg H14 ID/IG = 9.74, Toray 060 ID/IG = 1.35.)
9. Some Unsuccessful Substrates

The following substrates did not lead to clean conversion to the corresponding carboxylic acid:

The following substrate gave protonated product rather than the corresponding carboxylic acid:

\[
\text{DMF, rt, CO}_2, \text{Bu}_4\text{PF}_4, (+) \text{Pt, } C (-) \quad V_{\text{cell}} = -4.5V
\]
10. In situ Differential Electrochemical Mass Spectrometry (DEMS)

The DEMS cell is optimized for ease of use and flexible experimentation setup (Figure S5). This configuration combines differential electrochemical mass spectrometry with hydrodynamic flow consisting of an impinging jet in a wall-tube configuration. This assembly allows simultaneous detection of electrochemical signals along with monitoring of dissolved gas species using differential electrochemical mass spectrometry under well-defined hydrodynamic conditions and over a wide range of mass transfer rates. Depending on application, the electrocatalyst can be deposited on the bottom side of the glassy carbon electrode (GCE) used as an inert electrode.

The procedure for the in situ DEMS experiment: a solution of electrolyte Bu₄PBF₄ (0.15 mmol) and benzyl ammonium bromide (0.15 mmol) in anhydrous DMF (0.1M) was added to the assembled cell with a carbon paper cathode and a Pt/C anode. The reaction mixture was degassed and saturated by bubbling CO₂ for 5 min before 30 min constant voltage electrolysis under CO₂ bubbling. The mass spectra (MS) shown here (Figure S6) represent full scans of the sampled electrolyte at both -4.5 V cell potential and open circuit. The CV scan (Figure 1a) started under CO₂ atmosphere instead of bubbling, and the ion currents for m/z = 91 (Figure 1b) and m/z = 58 (Figure 1c) were recorded. After completion of CV scan under CO₂, the solution was purged with helium. The second CV scan (Figure S8a) started under helium atmosphere, and the ion currents for m/z = 91 (Figure S8b) and m/z = 58 (Figure S8c) were recorded.
Figure S5. Schematic representation of the DEMS system.
Figure S6. The mass spectra (MS) full scan of reaction at cathode at -4.5 V cell potential (red) and at open circuit (black).

Figure S7. Ion chromatography indicating the formation of product after 1 hour electrolysis at -4.5 V under CO₂.
Figure S8 Simultaneously recorded cyclic voltammogram (CV) (a) under helium, 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 Bu$_4$PBF$_4$ at a potential scan rate = 5 mV/s.
11. Cyclic Voltammetry and Tafel Plot

Figure S9. Cyclic voltammetry study. The sandwich cell was used for cyclic voltammetry in order to keep consistent to the real reaction. A Freudenberg carbon cloth (diameter: 10 mm) was used as a working electrode. A Pt/C electrode (diameter: 10 mm) was used as a counter electrode. Leak free Ag/AgCl electrode was used as a reference electrode. Electrolyte: 0.1 M Bu4PBF4 in DMF. Scan rate: 100mV/s. E(Fc+/Fc) = 0.4 V vs. Ag/AgCl. (N2: 0.1 M Bu4PBF4 in DMF under N2. 1a + N2: 0.1 M substrate 1a and 0.1 M Bu4PBF4 in DMF under N2. 1a + CO2: 0.1 M substrate 1a and 0.1 M Bu4PBF4 in DMF under CO2. CO2: 0.1 M Bu4PBF4 in DMF under CO2.)
Figure S10. Cyclic voltammetry of 1a in DMF (0.1 M) without electrolyte in the presence and absence of CO$_2$. A glassy carbon disk electrode (diameter: 3.0 mm) was used as a working electrode. A platinum wire was used as a counter electrode. Leak free Ag/AgCl electrode was used as a reference electrode. Scan rate: 100mV/s. $E(Fc+/Fc) = 0.4$ V vs. Ag/AgCl.
Figure S11. Cyclic voltammetry of 1a, Me₃N and TBABr in DMF (0.1 M). A glassy carbon disk electrode (diameter: 3.0 mm) was used as a working electrode. A platinum wire was used as a counter electrode. Leak free Ag/AgCl electrode was used as a reference electrode. Scan rate: 100mV/s. E(Fc⁺/Fc) = 0.4 V vs. Ag/AgCl. For Me₃N, 0.1 M Bu₄PBF₄ was used for electrolyte. For 1a and TBABr, there were no external electrolyte. Both substrate 1a and TBABr contain bromide, therefore the oxidation peak should be the oxidation of bromide.
Figure S12. Tafel plot for substrate 1a.
12. NMR Data

12.1  NMR Spectra of Substrates

12.1.1  NMR Spectra of Substrate 2a
12.1.2 NMR Spectra of Substrate 3a
12.1.3 NMR Spectra of Substrate 4a
12.1.4 NMR Spectra of Substrate 5a
12.1.5 NMR Spectra of Substrate 6a
12.1.6 NMR Spectra of Substrate 7a
12.1.7 NMR Spectra of Substrate 8a
12.1.8 NMR Spectra of Substrate 9a
12.1.9 NMR Spectra of Substrate 10a
12.1.10 NMR Spectra of Substrate 11a
12.1.11 NMR Spectra of Substrate 12a
12.1.12 NMR Spectra of Substrate 13a
12.1.13 NMR Spectra of Substrate 14a
12.1.14 NMR Spectra of Substrate 15a
12.1.15 NMR Spectra of Substrate 16a
12.1.16 NMR Spectra of Substrate 17a
12.1.17 NMR Spectra of Substrate 18a
12.1.18 NMR Spectra of Substrate 19a
12.1.19 NMR Spectra of Substrate 20a
12.1.20 NMR Spectra of Substrate 21a
12.1.21 NMR Spectra of Substrate 22a
12.1.22 NMR Spectra of Substrate 23a
12.1.23 NMR Spectra of Substrate 24a
12.1.24 NMR Spectra of Substrate 25a
12.1.25 NMR Spectra of Substrate 26a
12.1.26 NMR Spectra of Substrate 27a
12.1.27 NMR Spectra of Substrate 28a
12.1.28 NMR Spectra of Substrate 30a
12.2 NMR Spectra of Products

12.2.1 NMR of Product 1b
12.2.2 NMR of Product 2b
12.2.3 NMR of Product 3b
12.2.4 NMR of Product 4b
12.2.5 NMR of Product 5b
12.2.6 NMR of Product 6b and 6b-Br
12.2.7 NMR of Product 7b
12.2.8 NMR of Product 8b

Ph

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\text{COOH}
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9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

90 80 70 60 50 40 30 20 10 0

Ph

\[
\text{COOH}
\]
12.2.9 NMR of Product 9b
12.2.10  NMR of Product 10b

![NMR Spectra Image](image)

![NMR Spectra Image](image)
12.2.11 NMR of Product 11b
12.2.12 NMR of Product 12b
12.2.13 NMR of Product 13b
12.2.14 NMR of Product 14b
12.2.15  NMR of Product 15b
12.2.16  NMR of Product 16b
12.2.17 NMR of Product 17b
12.2.18  NMR of Product 18b
12.2.19  NMR of Product 19b
12.2.20  NMR of Product 20b
12.2.21  NMR of Product 21b
12.2.22 NMR of Product 22b
12.2.23 NMR of Product 23b
12.2.24 NMR of Product 24b
12.2.25 NMR of Product 25b
12.2.26  NMR of Product 26b
12.2.27  NMR of Product 27b
12.2.28  NMR of Product 28b
13. References