Direct electrochemical defluorinative carboxylation of $\alpha$-CF$_3$ alkenes with carbon dioxide

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1. General information

Reactions were monitored by thin layer chromatography using UV light, I₂ or KMnO₄ to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were obtained using Bruker DPX 400 or 500 MHz Spectrometer. Chemical shifts were reported in ppm with TMS as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

Unless mentioned, all reactions were performed under an atmosphere of N₂ and carried out with dry solvents. ²Bu₄NClO₄ were purchased from Macklin and used as received. α-Aryl α-trifluoromethyl alkenes were prepared by Suzuki cross coupling reaction of the corresponding arylboronic acid with 2-bromo-3,3,3-trifluoropropene.¹,² α-Alkyl α-trifluoromethyl alkenes were prepared by Wittig olefination of the corresponding ketone.¹ α-Alkynyl α-trifluoromethyl alkenes were prepared by Sonagashira coupling of the corresponding alkyne.³,⁴ Trisubstituted alkenes were prepared by Wittig olefination of the corresponding ketone.³,⁵ Substrates derived from bioactive compounds, such as fructose, β-D-glucose and estrone were prepared according to reported procedure.²,⁶,⁷

List of abbreviation:

| Entry | Chemical name                          | Abbreviation |
|-------|----------------------------------------|--------------|
| 1     | Petroleum ether                        | PE           |
| 2     | Ethyl acetate                          | EtOAc        |
| 3     | Tetrahydrofuran                        | THF          |
| 4     | N,N-Dimethylformamide                  | DMF          |
| 5     | N,N-Dimethylacetamide                  | DMA          |
| 6     | N-methyl-2-pyrrolidone                 | NMP          |
| 7     | Dimethyl sulfoxide                     | DMSO         |
| 8     | Hexamethyl phosphoryl triamide         | HMPA         |
2. Reaction condition optimization

The reaction of α-trifluoromethyl styrene 1a with CO$_2$ was selected as model reaction for condition optimization. We first examined the influence of electrode on the carboxylation of 1a, by conducting the reaction in DMF containing Et$_4$NOTs at constant current of 8 mA in an undivided cell under room temperature with CO$_2$ bubbling, as shown in Table S1. Of several typical non-sacrificial anode screened (entries 1-4), Pt-plate turned out to be the best, affording the desired γ-carboxylation product 2a in 57% yield (entry 1). The performance of sacrificial anode was also studied, and Mg-plate gave a slightly higher 60% yield (entries 5-7). Aiming to develop a non-sacrificial metal system, Pt-plate was selected as the anode. Further variation of cathode failed to give better results than that of Pt-plate (entries 8-12).

Table S1. Screening of anode and cathode

| Entry | Anode          | Cathode | Isolated yield (%) |
|-------|----------------|---------|--------------------|
| 1     | graphite       | Pt      | 32                 |
| 2     | RVC            | Pt      | 14                 |
| 3     | Pt             | Pt      | 57                 |
| 4     | glassy carbon  | Pt      | 45                 |
| 5     | Mg             | Pt      | 60                 |
| 6     | Fe             | Pt      | 41                 |
| 7     | Ni             | Pt      | 44                 |
| 8     | Pt             | graphite| 50                 |
| 9     | Pt             | RVC     | 38                 |
| 10    | Pt             | glassy carbon | 44        |
| 11    | Pt             | Ni      | 43                 |
| 12    | Pt             | Foam Ni | 28                 |

The influence of current intensity on the reaction was then studied, as shown in Table S2. It was found that under the current lower than 8 mA with the total charge less than 6 F/mol, the reaction yield decreased gradually due to the incomplete reaction. However, by increasing the current higher than 8 mA, there was almost no further influence on the reaction yield.
Table S2. Influence of electric current

| Entry | I (mA) | F/mol | Isolated yield (%) |
|-------|--------|-------|-------------------|
| 1     | 4      | 3.0   | 30                |
| 2     | 6      | 4.5   | 42                |
| 3     | 8      | 6.0   | 57                |
| 4     | 9      | 6.7   | 50                |
| 5     | 10     | 7.5   | 54                |
| 6     | 11     | 8.2   | 53                |

The supporting electrolyte is another important parameter in affecting the reaction outcome, as it could influence the local environment near the electrode as part of the electrical double-layer. By changing the electrolyte from Et₄NOTs to "Bu₄NOTs, a slightly higher 60% yield was obtained (Table S3, entry 1). Further varying the counter anions in the tetrabutylammonium family had a positive impact on the reaction (entries 2-5), and 72% yield could be achieved by using "Bu₄NClO₄ as electrolyte (entry 5). Other perchlorate, such as Et₄NClO₄, was also tried, but no better result was obtained (entry 6).

Table S3. Screening of supporting electrolyte

| Entry | Electrolyte     | Isolated yield (%) |
|-------|-----------------|--------------------|
| 1     | "Bu₄NOTs        | 60                 |
| 2     | "Bu₄NPF₆        | 62                 |
| 3     | "Bu₄NBr         | 27                 |
| 4     | "Bu₄NBF₄        | 53                 |
| 5     | "Bu₄NClO₄       | 72                 |
| 6     | Et₄NClO₄        | 61                 |
With $^4$Bu$_4$NClO$_4$ as electrolyte, the solvent effects were then examined with typical results shown in Table S4. The reaction conducted in DMA, NMP and HMPA gave lower yield than that in DMF (entries 1-4). No reaction occurred by using DMSO or CH$_3$CN as solvent (entries 5-6). DCE and THF could give 20% and 70% yield, respectively (entries 7-8). DMF was finally selected, not only because it could give higher reaction yield, but also due to its less volatility, especially under bubbling CO$_2$ condition. Further study revealed that the volume of solvent could also affect the reaction outcome. By performing the 0.2 mmol scale reaction in 7.0 mL DMF, 81% yield could be achieved (entries 9-12).

**Table S4. Screening of solvent.**

| Entry | Solvent | x (mL) | Isolated yield (%) |
|-------|---------|--------|-------------------|
| 1     | DMF     | 6.0    | 72                |
| 2     | DMA     | 6.0    | 59                |
| 3     | NMP     | 6.0    | 69                |
| 4     | HMPA    | 6.0    | 44                |
| 5     | DMSO    | 6.0    | Trace             |
| 6     | CH$_3$CN| 6.0    | Trace             |
| 7     | DCE     | 6.0    | 20                |
| 8     | THF     | 6.0    | 70                |
| 9     | DMF     | 3.0    | 56                |
| 10    | DMF     | 5.0    | 63                |
| 11    | DMF     | 7.0    | 81                |
| 12    | DMF     | 9.0    | 78                |

Subsequently, the concentration of electrolyte was studied to further improved the reaction outcome. As shown in Table S5, by increasing the concentration of $^4$Bu$_4$NClO$_4$ to 0.07 M, the desired carboxylic acid 2a could be obtained in 83% isolated yield (entry 3). Further increasing or decreasing the concentration gave no better results. Finally, we determined to perform the carboxylation of 1a (0.2 mmol) under room temperature in DMF (7.0 mL) containing $^4$Bu$_4$NClO$_4$ (0.07 M) at constant current of 8 mA in an undivided cell with CO$_2$ bubbling and Pt-plate as both cathode and anode.
Table S5. Screening of electrolyte concentration

During the investigation of substrate scope, we found that under the established optimal reaction condition for the reaction of 1a, the carboxylation of 1s bearing a 2-naphthyl gave only 23% yield. Considering that H₂O possessing an oxidation potential of 1.23V vs. SHE,⁸ which might be utilized as sacrificial oxidant to avoid unexpected oxidation, we tried using H₂O as additive to improve the reaction outcome. Fortunately, as shown in Table S6, the addition of 200 μL H₂O in 7 mL DMF could promote the carboxylation of 1s to give the desired 2s in 62% yield. Consequently, water was added for some substrates to improve the reaction yield.

Table S6. Influence of H₂O as additive for the reaction of 1s
3. Photographic guide for electrochemical reaction

Electrode electrochemical reactions were carried out using the following three kinds of equipment,

- In a 10 mL hydrogenation tube using Pt-plate (10 mm*10 mm*0.2 mm) as anode and cathode with the current supplied from a 36 V constant-current power supply purchased from Xiamen Bodong Biotechnology Ltd. (for 0.2 mmol scale).
- In a 10 mL electrochemical cell using corresponding Pt-plate as anode and cathode with the current supplied from an ElectraSyn 2.0 instrument purchased from IKA®-Werke GmbH & CO. KG. (for 0.2 mmol scale).
- In a 250 mL wild-mouth bottle using Pt-plate (30 mm*30 mm*0.1 mm) as anode and cathode with the current supplied from a 36 V constant-current power supply purchased from Xiamen Bodong Biotechnology Ltd. (for 6.0 mmol gram-scale reaction).

3.1 Photographic guide for first kind of equipment (0.2 mmol)

Step 0. Overview of materials used.

From left to right: 1) two Pt plates [anode and cathode, 10 mm*10 mm*0.2 mm]; 2) a 10 mL hydrogenation tube; 3) a rubber stopper; 4) two hypodermic needles (the longer one for intake, the shorter for exhaust)

Step 1. Assembling the cell

1) Pierce the rubber stopper with two Pt plates; 2) The stopper was fitted into the tube; 3) Pierce the rubber stopper with the two hypodermic needles (the longer one for intake, the shorter for exhaust).
Step 2. Electrolysis

After the addition of all materials, CO₂ was bubbled for 10 mins and then conducted constant current electrolysis (I = 8.0 mA) using a constant-current power supply under continuous bubbling of CO₂.

3.2 Photographic guide for the second kind of equipment (0.2 mmol, ElectraSyn 2.0)

Step 0. Overview of materials used.
From left to right: 1) electrochemical cell; 2) two Pt plates [anode and cathode]; 3) a hypodermic needle for intake; 4) cap.
Step 1. Assembling the cell

1) Install two Pt plates to the cap; 2) The cap was fitted into the cell; 3) Pierce the rubber of cap with the hypodermic needle for intake.

Step 2. Electrolysis

After the addition of all materials, CO$_2$ was bubbled for 10 mins and then conducted constant current electrolysis (I = 8.0 mA) using ElectraSyn 2.0 under continuous bubbling of CO$_2$.

3.3 Photographic guide for the third kind of equipment (for 6 mmol gram-scale reaction)

Step 0. Overview of materials used.

From left to right: 1) 250 mL wild-mouth bottle; 2) a rubber stopper with three holes; 3) a glass tube for intake; 4) two Pt plates [anode and cathode, 30 mm*30 mm*0.1 mm]
Step 1. Assembling the cell

1) Install two Pt plates and the glass tube to the rubber stopper; 2) The rubber stopper was fitted into the bottle.

Step 2. Electrolysis

After the addition of all materials, CO₂ was bubbled for 10 mins and then conducted constant current electrolysis (I = 72.0 mA) using a constant-current power supply under continuous bubbling of CO₂.
4. General Procedure for the Electrolysis

4.1 General procedure A. (for synthesis of acids 2a-2h, 2j-2k, 2m-2u, 3e-3k and 4a-4c.)

To a 10 mL hydrogenation tube or a cell of ElectraSyn 2.0 containing a stir bar were added $\text{Bu}_4\text{NClO}_4$ (167.5 mg, 0.49 mmol) and DMF (7.0 mL), followed by the addition of 1 (0.2 mmol). Then the tube was installed with two Pt-plates as cathode and anode. After bubbling of CO$_2$ gas into the electrolytes for 10 mins, the reaction mixture was electrolyzed under a constant current of 8 mA until the complete consumption of the starting materials as monitored by TLC (4-7 hours). After that, the reaction mixture was transferred to a 50 mL Erlenmeyer flask and acidized with HCl (2 N, 10 mL). The aqueous layer extracted with EtOAc (2 x 20 mL) and the combined organics were washed with sat. NH$_4$Cl (2 x 20 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The crude product was purified by column chromatography using PE/EtOAc (3:1, v/v) as the eluent to afford the desired product.

Note: for the synthesis of 2g, 2m-o, 2r-u, 3e and 4c, H$_2$O (200 μL) was added.

4.2 General procedure B. (for synthesis of esters 2i, 2l, 3a, 3b and 3d).

To a 10 mL hydrogenation tube or a cell of ElectraSyn 2.0 containing a stir bar were added $\text{Bu}_4\text{NClO}_4$ (167.5 mg, 0.49 mmol) and DMF (7.0 mL), followed by the addition of 1 (0.2 mmol). Then the tube was installed with two Pt-plates as cathode and anode. After bubbling of CO$_2$ gas into the electrolytes for 10 mins, the reaction mixture was electrolyzed under a constant current of 8 mA until the complete consumption of the starting materials as monitored by TLC (4-7 hours). After that, the reaction mixture was transferred to a 50 mL Erlenmeyer flask and acidized with HCl (2 N, 10 mL). The aqueous layer extracted with EtOAc (2 x 20 mL) and the combined organics were washed with sat. NH$_4$Cl (2 x 20 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The crude product was dissolved in the mixture solvent of Et$_2$O (2.0 mL) and MeOH (0.5 mL) and cooled to 0 °C. The hexane solution of
TMSCHN$_2$ (0.2 mL, 2 mol/L, 0.4 mmol) was added and the mixture was stirred at 0 °C for 30 mins. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography using PE/EtOAc (10:1, v/v) as the eluent to afford the desired product.

Note: 1) for the synthesis of 3a and 3b, graphite was used as anode; 2) H$_2$O (200 μL) was added for the synthesis of 3d.

4.3 General procedure C. (for synthesis of amide 3c)

To a 10 mL hydrogenation tube or a cell of ElectraSyn 2.0 containing a stir bar were added $^a$Bu$_4$NClO$_4$ (167.5 mg, 0.49 mmol) and DMF (7.0 mL), followed by the addition of 1 (0.2 mmol). Then the tube was installed with Pt-plate as cathode and graphite as anode. After bubbling of CO$_2$ gas into the electrolytes for 10 mins, the reaction mixture was electrolyzed under a constant current of 8 mA until the complete consumption of the starting materials as monitored by TLC analysis (4-7 hours). After that, the reaction mixture was transferred to a 50 mL Erlenmeyer flask and acidized with HCl (2 N, 10 mL). The aqueous layer extracted with EtOAc (2 x 20 mL) and the combined organics were washed with sat. NH$_4$Cl (2 x 20 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The crude residue was dissolved in DMF (2 mL), then p-anisidine (36.9 mg, 0.3 mmol), Et$_3$N (60.7 mg, 0.6 mmol), and o-(7-azabenzotriazol-1-yl)-N,N',N'-trimethyluronium hexafluorophosphate (HATU, 152.0 mg, 0.4 mmol) were added. The resulting mixture was stirred for 5 h at room temperature. The reaction was quenched with H$_2$O and extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography using PE/EtOAc (5:1, v/v) as the eluent to afford the desired product.

4.4 General procedure for the gram-scale reaction.

To a 250 mL wild-mouth bottle containing a stir bar were added $^a$Bu$_4$NClO$_4$ (5.0 g, 14.7 mmol) and DMF (210 mL), followed by the addition of 1a (1.03 g, 6.0 mmol). Then the tube was installed with two Pt-plates (30 mm x 30 mm x 0.1 mm) as cathode and anode. After bubbling of CO$_2$ gas into the electrolytes for 10 mins, the reaction mixture was electrolyzed under a constant current of 72 mA until the complete consumption of the starting materials as monitored by TLC (20 hours). After that, the
reaction mixture was transferred to a 500 mL round-bottom flask and then removing most of the solvent by distillation in vacuum. The residue was diluted with 50 mL EtOAc, and acidized with HCl (2 N, 40 mL). After separation of organic layer, the aqueous layer was extracted with EtOAc (2 x 40 mL) and the combined organics were washed with sat. NH₄Cl (2 x 40 mL), dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography using PE/EtOAc (3:1, v/v) as the eluent to afford the desired 2a in 0.93 g with 78% yield.

4.5 Characterization data of products

Product 2a was obtained in 32.8 mg (83% yield) as colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.33 (m, 4H), 7.31-7.27 (m, 1H), 3.45 (t, J = 2.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 176.38, 155.00 (dd, J = 291.3 Hz, 287.7 Hz, 1C), 132.72 (t, J = 3.8 Hz, 1C), 128.60, 127.80 (t, J = 3.5 Hz, 1C), 127.69, 86.62 (dd, J = 21.5 Hz, 18.0 Hz, 1C), 33.60 (d, J = 2.8 Hz, 1C); ¹⁹F NMR (376 MHz, CDCl₃): δ -87.13 (d, J = 33.5 Hz, 1F), -88.55 (d, J = 33.8 Hz, 1F); IR (ATR) ν 2972.3, 2887.4, 1728.2, 1712.8, 1498.7, 1413.8, 1247.9, 1176.6, 1128.4, 1006.8 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₀H₈F₂NaO₂ [M+Na]⁺: 221.0385, found: 221.0383.

Product 2b was obtained in 35.6 mg (84% yield) as light yellow solid; Mp 52-54 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.24-7.22 (m, 2H), 7.18-7.16 (m, 2H), 3.43 (t, J = 2.0 Hz, 2H), 2.35 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 176.34, 154.85 (dd, J = 290.8 Hz, 287.4 Hz, 1C), 137.52, 129.63 (t, J = 3.8 Hz, 1C), 129.30, 127.60 (t, J = 3.5 Hz, 1C), 86.39 (dd, J = 21.1 Hz, 18.0 Hz, 1C), 33.56, 21.12; ¹⁹F NMR (376 MHz, CDCl₃): δ -87.67 (d, J = 35.0 Hz, 1F), -88.91 (d, J = 35.0 Hz, 1F); IR (ATR) ν 2970.3, 1716.6, 1516.0, 1415.7, 1382.9, 1238.3, 1107.1, 1004.9, 879.5 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₁H₁₀F₂NaO₂ [M+Na]⁺: 235.0541, found: 235.0542.

Product 2c was obtained in 30.9 mg (73% yield) as light yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.22 (m, 1H), 7.14-7.08 (m, 3H), 3.42 (t, J = 2.4 Hz, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 176.56 (dd, J = 4.4 Hz, 2.8 Hz, 1C), 154.94 (dd, J = 291.0 Hz, 287.6 Hz, 1C), 138.23, 132.63 (t, J = 3.8 Hz, 1C), 128.48, 128.46, 128.42, 124.85 (t, J = 3.5 Hz, 1C), 86.63 (dd, J = 21.0 Hz, 18.0 Hz, 1C), 33.66 (d, J = 2.8 Hz, 1C), 21.40; ¹⁹F NMR (376 MHz, CDCl₃): δ -87.34 (d, J = 33.8 Hz, 1F), -88.64 (d, J = 34.2 Hz, 1F); IR (ATR) ν 3020.5, 1716.6, 1695.4, 1604.7, 1490.9, 1413.8, 1311.5, 1240.2, 1182.3, 912.3 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₁H₁₀F₂NaO₂ [M+Na]⁺: 235.0541, found: 235.0539.
Product 2d was obtained in 34.3 mg (76% yield) as light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.94-6.93 (m, 3H), 3.42 (t, $J$ = 2.0 Hz, 2H), 2.31 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 176.70, 154.91 (dd, $J$ = 290.9 Hz, 287.5 Hz, 1C), 138.10, 132.50 (t, $J$ = 3.8 Hz, 1C), 129.44, 125.54 (t, $J$ = 3.4 Hz, 1C), 86.58 (dd, $J$ = 20.7 Hz, 18.2 Hz, 1C), 33.67 (d, $J$ = 9.8 Hz, 1C), 21.28; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -87.50 (dd, $J$ = 32.7 Hz, 1F), -88.65 (d, $J$ = 34.6 Hz, 1F), -116.80 (s, 1F); IR (ATR) $\nu$ 2987.7, 1716.6, 1602.8, 1411.8, 1259.5, 1176.5, 1062.7, 918.1, 850.6, 821.6 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{12}$H$_{12}$F$_2$NaO$_2$ [M+Na]$^+$: 249.0698, found: 249.0701.

Product 2e was obtained in 32.6 mg (71% yield) as light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.16 (t, $J$ = 8.0 Hz, 1H), 7.02 (d, $J$ = 4.8 Hz, 1H), 7.00 (s, 1H), 3.41 (t, $J$ = 2.4 Hz, 2H), 2.26 (d, $J$ = 1.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 176.11, 161.15 (d, $J$ = 243.4 Hz, 1C), 155.04 (dd, $J$ = 291.9 Hz, 288.0 Hz, 1C), 132.04-131.88 (m, 1C), 131.53 (d, $J$ = 5.6 Hz, 1C), 124.42 (d, $J$ = 17.2 Hz, 1C), 123.04 (dd, $J$ = 7.1 Hz, 3.5 Hz, 1C), 114.47 (ddd, $J$ = 23.7 Hz, 4.6 Hz, 3.1 Hz, 1C), 114.47 (ddd, $J$ = 21.9 Hz, 17.6 Hz, 2.2 Hz, 1C), 33.38 (d, $J$ = 2.8 Hz, 1C), 14.24 (d, $J$ = 3.4 Hz, 1C); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -86.51 (d, $J$ = 32.7 Hz, 1F), -87.50 (d, $J$ = 32.7 Hz, 1F), -116.80 (s, 1F); IR (ATR) $\nu$ 2546.0, 1728.2, 1695.4, 1570.0, 1423.4, 1317.3, 1253.7, 1180.4, 1026.1, 848.6 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{11}$H$_9$F$_3$NaO$_2$ [M+Na]$^+$: 253.0447, found: 253.0457.

Product 2f was obtained in 35.6 mg (70% yield) as white solid; Mp 55-57 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40-7.37 (m, 2H), 7.30-7.27 (m, 2H), 3.44 (t, $J$ = 2.0 Hz, 2H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 176.43, 155.00 (dd, $J$ = 291.2 Hz, 287.4 Hz, 1C), 150.66, 129.66 (t, $J$ = 3.8 Hz, 1C), 127.35 (t, $J$ = 3.8 Hz, 1C), 125.54, 86.35 (dd, $J$ = 21.1 Hz, 17.8 Hz, 1C), 34.54, 33.51 (d, $J$ = 2.9 Hz, 1C), 31.22; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -87.31 (d, $J$ = 34.6 Hz, 1F), -88.65 (d, $J$ = 34.2 Hz, 1F); IR (ATR) $\nu$ 2976.1, 1732.0, 1614.4, 1317.3, 1249.8, 1178.5, 1049.2, 1004.9, 881.4, 833.2 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{14}$H$_{16}$F$_2$NaO$_2$ [M+Na]$^+$: 277.1011, found: 277.1013.

Product 2g was obtained in 41.6 mg (76% yield) as white solid with 200 μL H$_2$O as additive; Mp 120-122 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62-7.59 (m, 4H), 7.48-7.43 (m, 4H), 7.39-7.35 (m, 1H), 3.50 (t, $J$ = 2.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 176.45, 155.07 (dd, $J$ = 291.8 Hz, 288.2 Hz, 1C), 140.50, 140.35, 131.58 (t, $J$ = 3.9 Hz, 1C), 128.80,
128.10 (t, J = 3.7 Hz, 1C), 127.49, 127.27, 127.00, 86.39 (dd, J = 21.5 Hz, 17.9 Hz, 1C), 33.48 (d, J = 2.8 Hz, 1C); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -86.53 (d, J = 32.7 Hz, 1F), -87.91 (d, J = 32.7 Hz, 1F); IR (ATR) \(\nu\) 2972.3, 1734.0, 1693.5, 1489.0, 1417.6, 1404.1, 1249.8, 1078.2, 952.8, 839.0 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{16}\)H\(_2\)F\(_2\)NaO\(_2\) [M+Na\(^+\)]: 297.0698, found: 297.0693.

Product 2h was obtained in 45.2 mg (72% yield) as light yellow solid; Mp 125-127 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.72-7.68 (m, 2H), 7.44-7.41 (m, 2H), 7.35-7.30 (m, 3H), 3.50 (t, J = 2.4 Hz, 2H), 1.48 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 176.46, 155.02 (dd, J = 291.2 Hz, 287.9 Hz, 1C), 153.90, 153.80, 138.84, 138.50, 131.50 (t, J = 3.8 Hz, 1C), 127.49, 127.01, 126.61 (t, J = 3.6 Hz, 1C), 122.58, 122.04 (dd, J = 4.6 Hz, 3.1 Hz, 1C), 120.10, 120.04, 87.03 (dd, J = 21.1 Hz, 17.8 Hz, 1C), 46.88, 33.84 (d, J = 2.7 Hz, 1C), 27.04.; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -86.97 (d, J = 33.8 Hz, 1F), -88.21 (d, J = 34.2 Hz, 1F); IR (ATR) \(\nu\) 3483.4, 3251.9, 1712.7, 1409.9, 1313.5, 1228.6, 1016.4, 900.7, 819.7, 783.1 cm\(^{-1}\); HRMS (EI): Exact mass calcd for C\(_{19}\)H\(_{16}\)O\(_2\)F\(_2\) [M]: 314.1118, found: 314.1116.

Product 2i was obtained in 26.6 mg (45% yield) as colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.26-7.23 (m, 2H), 6.89-6.86 (m, 2H), 5.90-5.80 (m, 1H), 5.09-5.03 (m, 1H), 5.02-4.98 (m, 1H), 3.96 (t, J = 6.4 Hz, 2H), 3.67 (s, 3H), 3.37 (t, J = 2.4 Hz, 2H), 2.26-2.21 (m, 2H), 1.91-1.84 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 170.77, 158.37, 154.64 (t, J = 286.4 Hz, 1C), 137.73, 128.95 (t, J = 3.5 Hz, 1C), 124.93, 115.22, 114.53, 86.57 (t, J = 19.1 Hz, 1C), 67.13, 52.17, 33.76, 30.08, 28.37; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -89.00 (d, J = 38.0 Hz, 1F), -90.00 (d, J = 38.0 Hz, 1F); IR (ATR) \(\nu\) 2978.0, 1743.6, 1610.5, 1516.0, 1436.9, 1346.3, 1246.0, 1174.6, 914.2, 831.3 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{16}\)H\(_{18}\)F\(_2\)NaO\(_3\) [M+Na\(^+\)]: 319.1116, found: 319.1119.

Product 2j was obtained in 33.4 mg (72% yield) as light yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.34-7.32 (m, 2H), 7.28-7.25 (m, 2H), 3.42 (t, J = 2.4 Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 176.35, 154.95 (dd, J = 291.7 Hz, 288.7 Hz, 1C), 133.64, 131.10 (t, J = 3.9 Hz, 1C), 129.12 (t, J = 3.7 Hz, 1C), 128.84, 85.89 (dd, J = 21.9 Hz, 17.9 Hz, 1C), 33.43 (d, J = 2.6 Hz, 1C); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -86.38 (d, J = 32.3 Hz, 1F), -87.69 (d, J = 32.3 Hz, 1F); IR (ATR) \(\nu\) 2972.3, 1712.7, 1496.7, 1423.4, 1342.4, 1317.3, 1238.3, 1093.6, 1002.9, 912.3 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{10}\)H\(_7\)ClF\(_2\)NaO\(_2\) [M+Na\(^+\)]: 254.9995, found: 254.9993.
Product 2k was obtained in 31.9 mg (74% yield) as colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.32-7.29 (m, 2H), 7.08-7.02 (m, 2H), 3.42 (t, $J = 2.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 176.17, 162.10 (d, $J = 246.2$ Hz, 1C), 154.94 (t, $J = 289.7$ Hz, 1C), 129.73-129.58 (m, 1C), 128.62 (dd, $J = 7.3$ Hz, 3.6 Hz, 1C), 115.63 (d, $J = 21.6$ Hz, 1C), 85.90 (dd, $J = 21.9$ Hz, 18.6 Hz, 1C), 33.71 (d, $J = 2.6$ Hz, 1C); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -87.39 (dd, $J = 34.2$ Hz, 2.2 Hz, 1F), -88.70 (d, $J = 34.2$ Hz, 1F), -113.81 (d, $J = 1.9$ Hz, 1F); IR (ATR) ν 2999.3, 2563.4, 1747.5, 1722.4, 1604.7, 1510.2, 1417.6, 1313.5, 1247.9, 1006.8 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{10}$H$_7$F$_3$NaO$_2$ [M+Na]$^+$: 239.0290, found: 239.0282.

Product 2l was obtained in 43.8 mg (74% yield) as colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38-7.36 (m, 2H), 7.22-7.19 (m, 2H), 3.69 (s, 3H), 3.40 (t, $J = 2.4$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 170.39 (dd, $J = 4.5$ Hz, 2.4 Hz, 1C), 154.95 (dd, $J = 291.1$ Hz, 288.1 Hz, 1C), 148.43, 131.66 (t, $J = 4.1$ Hz, 1C), 129.35 (t, $J = 3.5$ Hz, 1C), 120.96, 120.42 (q, $J = 255.8$ Hz, 1C), 86.28 (dd, $J = 22.2$ Hz, 17.6 Hz, 1C), 52.22, 33.48 (d, $J = 2.8$ Hz, 1C); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -57.88 (s, 3F), -86.86 (d, $J = 33.1$ Hz, 1F), -88.16 (d, $J = 32.3$ Hz, 1F); IR (ATR) ν 3523.9, 2976.1, 1743.6, 1610.5, 1512.1, 1438.9, 1352.1, 1159.2, 1006.8, 852.5 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{12}$H$_9$F$_5$NO$_3$ [M+Na]$^+$: 319.0364, found: 319.0361.

Inseparable mixture 2m and 2m' was obtained in 29.8 mg (2m, 61% yield; 2m', 6% yield) as light yellow oil with 200 μL H$_2$O as additive; Selectivity (desired C-F cleavage product : byproduct) = 10:1. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.65 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 3.47 (t, $J = 2.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 175.35, 155.34 (dd, $J = 294.2$ Hz, 290.5 Hz, 1C), 137.57 (t, $J = 4.4$ Hz, 1C), 132.37, 128.38 (t, $J = 3.2$ Hz, 1C), 118.36, 111.42, 86.11 (dd, $J = 22.4$ Hz, 16.9 Hz, 1C), 32.94; $^{19}$F NMR (376 MHz, CDCl$_3$) (2m): δ -83.32 (d, $J = 25.9$ Hz, 1F), -85.07 (d, $J = 25.9$ Hz, 1F); $^{19}$F NMR (376 MHz, CDCl$_3$) (2m'): -69.98 (s, 3F); IR (ATR) ν 3408.2, 2225.8, 1718.5, 1606.7, 1411.8, 1313.5, 1251.8, 1157.2, 1109.0, 1004.9 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{11}$H$_7$F$_2$NO$_2$ [M+Na]$^+$: 246.0337, found: 246.0334. The by-product might be formed via a β-hydrocarboxylation as recently reported by Malkov & Buckley$^9$a and Nam$^9$b, respectively.
Product 2n was obtained in 27.6 mg (54% yield) as white solid with 200 μL H2O as additive; Mp 77-79 °C; 1H NMR (400 MHz, CDCl3): δ 8.03-8.01 (m, 2H), 7.42-7.40 (m, 2H), 3.91 (s, 3H), 3.47 (t, J = 2.0 Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 175.77 (t, J = 3.2 Hz, 1C), 166.64, 155.22 (dd, J = 293.5 Hz, 289.5 Hz, 1C), 137.41 (t, J = 4.2 Hz, 1C), 129.83, 129.22, 127.65 (t, J = 3.8 Hz, 1C), 86.39 (dd, J = 21.8 Hz, 17.1 Hz, 1C), 52.21, 33.16 (d, J = 2.6 Hz, 1C); 19F NMR (376 MHz, CDCl3): δ -84.63 (d, J = 28.6 Hz, 1F), -86.15 (d, J = 28.6 Hz, 1F); IR (ATR) ν 2980.0, 2576.9, 1724.3, 1699.2, 1608.6, 1435.0, 1284.5, 1249.8, 1105.2, 945.1 cm⁻¹; HRMS (ESI): Exact mass calcd for C12H10F2NaO4 [M+Na]⁺: 279.0439, found: 279.0440.

Product 2o was obtained in 40.9 mg (77% yield) as white solid with 200 μL H2O as additive; Mp 88-90 °C; 1H NMR (400 MHz, CDCl3): δ 7.62 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 3.47 (t, J = 2.4 Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 176.07, 155.28 (dd, J = 292.9 Hz, 289.2 Hz, 1C), 136.43, 129.80 (q, J = 32.5 Hz, 1C), 128.12 (t, J = 3.6 Hz, 1C), 125.58 (q, J = 3.8 Hz, 1C), 123.88 (q, J = 270.4 Hz, 1C), 86.10 (dd, J = 22.2 Hz, 17.8 Hz, 1C), 33.32; 19F NMR (376 MHz, CDCl3): δ -112.48 (s, 1F), -85.74 (d, J = 30.8 Hz, 1F), -86.93 (d, J = 30.5 Hz, 1F), -85.85 (d, J = 30.5 Hz, 1F); IR (ATR) ν 2976.1, 1751.3, 1734.0, 1616.3, 1498.6, 1328.9, 1246.0, 1161.1, 1008.7, 846.7 cm⁻¹; HRMS (ESI): Exact mass calcd for C11H7F5NaO2 [M+Na]⁺: 289.0258, found: 289.0256.

Product 2p was obtained in 34.1 mg (79% yield) as colorless oil; 1H NMR (400 MHz, CDCl3): δ 7.36-7.30 (m, 1H), 7.13-7.06 (m, 2H), 6.99 (td, J = 8.4 Hz, 2.4 Hz, 1H), 3.44 (t, J = 2.0 Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 176.43 (t, J = 3.2 Hz, 1C), 162.74 (d, J = 244.5 Hz, 1C), 155.16 (dd, J = 292.5 Hz, 288.5 Hz, 1C), 134.89-134.72 (m, 1C), 130.11 (d, J = 8.4 Hz, 1C), 123.38 (dd, J = 6.9 Hz, 3.4 Hz, 1C), 114.93 (ddd, J = 22.7 Hz, 4.4 Hz, 3.1 Hz, 1C), 114.80, 86.27-85.85 (m, 1C), 33.37 (d, J = 2.6 Hz, 1C); 19F NMR (376 MHz, CDCl3): δ -85.74 (d, J = 30.8 Hz, 1F), -86.93 (d, J = 30.5 Hz, 1F), -112.48 (s, 1F); IR (ATR) ν 3560.5, 1724.3, 1614.4, 1585.4, 1490.9, 1411.8, 1253.7, 1120.6, 1022.2, 921.9 cm⁻¹; HRMS (ESI): Exact mass calcd for C10H7F3NaO2 [M+Na]⁺: 239.0290, found: 239.0290.

Product 2q was obtained in 29.2 mg (63% yield) as light yellow oil; 1H NMR (400 MHz, CDCl3): δ 7.37-7.28 (m, 3H), 7.23-7.21 (m, 1H), 3.43 (t, J = 2.0 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 175.76, 155.13 (dd, J = 292.3 Hz, 288.9 Hz, 1C), 134.53-134.46 (m, 129.84, 128.00-127.92 (m), 125.97 (t, J = 3.5 Hz, 1C), 85.92 (dd, J = 22.1 Hz, 17.9 Hz,
1C), 33.32 (d, J = 2.0 Hz, 1C); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -85.73 (d, J = 30.8 Hz, 1F), -87.03 (d, J = 30.8 Hz, 1F); IR (ATR) ν 3660.8, 2993.5, 2623.1, 1712.7, 1566.2, 1409.9, 1247.9, 1128.3, 1080.1, 881.4 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{10}$H$_7$CLF$_2$NaO$_2$ [M+Na]$^+$: 254.9995, found: 254.9990.

Product 2r was obtained in 37.9 mg (64% yield) as light yellow oil with 200 μL H$_2$O as additive; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.39 (t, J = 8.0 Hz, 1H), 7.28-7.26 (m, 1H), 7.21 (s, 1H), 7.17-7.14 (m, 1H), 3.44 (t, J = 2.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 175.85, 155.22 (dd, J = 292.6 Hz, 289.0 Hz, 1C), 149.38 (d, J = 1.9 Hz, 1C), 134.80 (t, J = 4.0 Hz, 1C), 129.97, 126.12 (t, J = 3.6 Hz, 1C), 120.58 (t, J = 3.5 Hz, 1C), 120.43 (q, J = 255.9 Hz, 1C), 120.07, 85.99 (d, J = 30.1 Hz, 1F), -86.76 (d, J = 30.1 Hz, 1F); IR (ATR) ν 2985.8, 2875.8, 1732.0, 1716.6, 1583.5, 1423.4, 1321.2, 1253.7, 1155.3, 1041.5 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{11}$H$_7$F$_5$NaO$_3$ [M+Na]$^+$: 305.0208, found: 305.0205.

Product 2s was obtained in 30.7 mg (62% yield) as light yellow solid with 200 μL H$_2$O as additive; Mp 78-80 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.84-7.81 (m, 3H), 7.79 (s, 1H), 7.51-7.46 (m, 3H), 3.55 (t, J = 2.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 176.76 (dd, J = 4.3 Hz, 2.7 Hz, 1C), 155.16 (dd, J = 291.6 Hz, 288.2 Hz, 1C), 133.14, 132.53, 130.04 (t, J = 3.8 Hz, 1C), 128.27, 128.00, 127.55, 126.93 (t, J = 3.7 Hz, 1C), 126.38, 126.35, 125.44 (dd, J = 4.5 Hz, 2.6 Hz, 1C), 86.74 (dd, J = 21.3 Hz, 17.9 Hz, 1C), 33.66 (d, J = 2.8 Hz, 1C); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -86.54 (d, J = 33.1 Hz, 1F), -88.15 (d, J = 32.7 Hz, 1F); IR (ATR) ν 3412.1, 2976.2, 1708.9, 1523.7, 1415.7, 1259.5, 1230.5, 1118.7, 935.4, 815.8 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{14}$H$_{10}$F$_2$NaO$_3$ [M+Na]$^+$: 271.0541, found: 271.0538.

Product 2t was obtained in 16.3 mg (40% yield) as light yellow solid with 200 μL H$_2$O as additive; Mp 70-72 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.31-7.29 (m, 1H), 7.05-7.01 (m, 2H), 3.48 (t, J = 2.0 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 176.26 (dd, J = 3.8 Hz, 3.1 Hz, 1C), 154.74 (dd, J = 294.5 Hz, 288.6 Hz, 1C), 134.55 (dd, J = 7.2 Hz, 2.9 Hz, 1C), 127.13, 125.44 (dd, J = 6.8 Hz, 3.0 Hz, 1C), 125.34 (dd, J = 5.9 Hz, 4.0 Hz, 1C), 83.26 (dd, J = 25.8 Hz, 18.5 Hz, 1C), 33.29 (d, J = 3.4 Hz, 1C); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -82.37 (d, J = 27.1 Hz, 1F), -88.53 (d, J = 26.7 Hz, 1F); IR (ATR) ν 2991.5, 1724.3, 1693.5, 1406.1, 1354.0, 1253.7, 1101.3, 1053.1, 869.9, 690.5 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_8$H$_6$F$_2$NaO$_2$S [M+Na]$^+$: 226.9949, found: 226.9948.
Product 2u was obtained in 20.0 mg (42% yield) as light yellow solid with 200 μL H₂O as additive; Mp 92-94 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.53-7.51 (m, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.25-7.18 (m, 2H), 6.74 (s, 1H), 3.54 (t, J = 2.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 175.98 (dd, J = 3.9 Hz, 3.0 Hz, 1C), 155.60 (dd, J = 298.2 Hz, 289.4 Hz, 1C), 154.27, 148.27 (dd, J = 7.2 Hz, 5.0 Hz, 1C), 128.57, 124.34, 123.11, 120.85, 111.08, 104.53 (dd, J = 9.4 Hz, 5.5 Hz, 1C), 81.19 (dd, J = 27.5 Hz, 16.9 Hz, 1C), 30.28 (d, J = 2.8 Hz, 1C); ¹⁹F NMR (376 MHz, CDCl₃): δ -78.30 (d, J = 18.4 Hz, 1F), -84.86 (d, J = 18.4 Hz, 1F); IR (ATR) ν 2974.2, 1755.2, 1612.4, 1516.0, 1352.1, 1253.7, 1172.7, 1018.4, 935.4, 750.3 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₂H₈F₂NaO₃ [M+Na]⁺: 261.0334, found: 261.0337.

Product 3a was obtained in 25.9 mg (54% yield) as colorless oil with graphite rod as anode; ¹H NMR (400 MHz, CDCl₃): δ 7.23-7.19 (m, 2H), 7.14-7.09 (m, 3H), 3.62 (s, 3H), 2.91 (t, J = 2.0 Hz, 2H), 2.65-2.61 (m, 2H), 2.33-2.28 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 170.85 (dd, J = 4.1 Hz, 3.0 Hz, 1C), 154.54 (dd, J = 284.7 Hz, 283.7 Hz, 1C), 140.78, 128.42, 128.27, 126.16, 83.59 (dd, J = 22.3 Hz, 16.5 Hz, 1C), 52.04, 33.52, 31.94, 28.52 (d, J = 1.8 Hz, 1C), 12.96 (t, J = 2.6 Hz, 1C), 28.72 (t, J = 1.7 Hz, 1C), 26.36 (d, J = 1.7 Hz, 1C); ¹⁹F NMR (376 MHz, CDCl₃): δ -92.55 (d, J = 48.1 Hz, 1F), -92.90 (d, J = 47.0 Hz, 1F); IR (ATR) v 3736.1, 3066.8, 2958.8, 1753.2, 1604.7, 1436.9, 1350.1, 1257.5, 1172.7, 1064.7 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₃H₁₄F₂NaO₂ [M+Na]⁺: 263.0854, found: 263.0858.

Inseparable mixture 3b and 3b’ was obtained in 30.9 mg (3b, 57% yield; 3b’, 4% yield) as light yellow oil with graphite rod as anode; Selectivity (desired C-F cleavage product : byproduct) = 13:1; ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 3.68 (s, 3H), 2.99 (t, J = 2.0 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.13-2.08 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 170.88 (dd, J = 4.3 Hz, 2.7 Hz, 1C), 154.42 (dd, J = 284.5 Hz, 283.1 Hz, 1C), 141.73, 128.32, 128.30, 125.85, 83.73 (dd, J = 22.6 Hz, 16.1 Hz, 1C), 51.99, 35.24, 31.78 (d, J = 3.5 Hz, 1C), 28.72 (t, J = 2.6 Hz, 1C), 26.36 (d, J = 1.7 Hz, 1C); ¹⁹F NMR (376 MHz, CDCl₃) (3b): δ -92.55 (d, J = 48.1 Hz, 1F), -93.38 (d, J = 48.1 Hz, 1F); ¹⁹F NMR (376 MHz, CDCl₃) (3b’): δ -71.31 (s, 3F); IR (ATR) v 3028.2, 2953.0, 1755.2, 1604.7, 1496.7, 1352.1, 1278.8, 1170.7, 1093.6, 991.4 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₄H₁₇O₂F₂ [M+H]⁺: 255.1191, found: 255.1182. The by-product might be formed via a β-hydrocarboxylation as recently reported by Malkov & Buckley⁹a and Nam⁹b, respectively.
Product 3c was obtained in 32.5 mg (46% yield) as light yellow oil with graphite rod as anode; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.40-7.35 (m, 3H), 6.86-6.82 (m, 2H), 3.78 (s, 3H), 3.03 (t, \(J = 2.4\) Hz, 2H), 2.12-2.07 (m, 2H), 1.46-1.39 (m, 2H), 1.29-1.25 (m, 12H), 0.87 (t, \(J = 6.8\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 167.59-167.52 (m, 1C), 156.64, 154.49 (t, \(J = 284.4\) Hz, 1C), 130.58, 122.00, 114.11, 85.16 (dd, \(J = 20.8\) Hz, 15.8 Hz, 1C), 55.42, 35.07 (d, \(J = 2.6\) Hz, 1C), 31.81, 29.47, 29.28, 29.22, 29.08, 27.20 (t, \(J = 2.5\) Hz, 1C), 26.66, 22.61, 14.03; \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -92.58 (d, \(J = 48.9\) Hz, 1F), -92.82 (d, \(J = 48.9\) Hz, 1F); IR (ATR) \(\nu\) 3267.4, 2854.6, 1753.2, 1649.1, 1531.4, 1413.8, 1246.0, 1170.7, 1026.1, 827.4 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{20}\)H\(_{30}\)O\(_2\)NF\(_2\)[M+H]\(^+\): 354.2239, found: 354.2228.

Product 3d was obtained in 27.6 mg (48% yield) as light yellow oil with 200 \(\mu\)L H\(_2\)O as additive; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 4.15 (t, \(J = 6.8\) Hz, 2H), 3.72 (s, 3H), 3.06 (t, \(J = 2.0\) Hz, 2H), 2.64 (tt, \(J = 6.4\) Hz, 1.2 Hz, 2H), 1.20 (s, 9H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 178.25, 169.62 (dd, \(J = 4.1\) Hz, 3.0 Hz, 1C), 160.13 (dd, \(J = 294.1\) Hz, 292.4 Hz, 1C), 90.52 (t, \(J = 5.8\) Hz, 1C), 73.07 (dd, \(J = 34.0\) Hz, 21.0 Hz, 1C), 72.56 (dd, \(J = 7.4\) Hz, 4.4 Hz, 1C), 61.82, 52.27, 38.71, 33.18, 27.07, 19.91; \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -79.67 (d, \(J = 12.8\) Hz, 1F), -83.65 (d, \(J = 12.8\) Hz, 1F); IR (ATR) \(\nu\) 3522.0, 2978.0, 2879.7, 2243.2, 1728.2, 1438.9, 1352.1, 1286.5, 1151.5, 983.7 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{14}\)H\(_{18}\)F\(_2\)NaO\(_4\)[M+Na]\(^+\): 311.1065, found: 311.1058.

Product 3e was obtained in 28.8 mg (65% yield) as light yellow oil with 200 \(\mu\)L H\(_2\)O as additive; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.46-7.42 (m, 2H), 7.33-7.29 (m, 3H), 3.67 (q, \(J = 7.2\) Hz, 1H), 1.32 (d, \(J = 7.2\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 174.74, 154.34 (t, \(J = 288.7\) Hz, 1C), 131.87 (d, \(J = 1.9\) Hz, 1C), 129.22 (t, \(J = 2.6\) Hz, 1C), 128.46, 127.96, 92.68 (t, \(J = 19.0\) Hz, 1H), 1.32 (d, \(J = 7.2\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 179.15, 154.34 (t, \(J = 288.7\) Hz, 1C), 131.87 (d, \(J = 1.9\) Hz, 1C), 129.22 (t, \(J = 2.6\) Hz, 1C), 128.46, 127.96, 92.68 (t, \(J = 19.0\) Hz, 1H), 1.32 (d, \(J = 7.2\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 179.15, 154.34 (t, \(J = 288.7\) Hz, 1C), 131.87 (d, \(J = 1.9\) Hz, 1C), 129.22 (t, \(J = 2.6\) Hz, 1C), 128.46, 127.96, 92.68 (t, \(J = 19.0\) Hz, 1H).
Product 3g was obtained in 23.0 mg (51% yield) as light yellow solid; Mp 90-92 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.16 (s, 4H), 3.65 (q, $J$ = 7.5 Hz, 1H), 2.35 (s, 3H), 1.30 (d, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 178.90-178.83 (m, 1C), 154.24 (t, $J$ = 288.4 Hz, 1C), 137.78, 129.18, 129.06 (t, $J$ = 2.8 Hz, 1C), 128.71 (d, $J$ = 2.8 Hz, 1C), 92.43 (t, $J$ = 19.0 Hz, 1C), 38.96, 21.17, 14.91; $^{19}$F NMR (376 MHz, CDCl$_3$): δ -89.10 (s, 1F), -89.11 (s, 1F); IR (ATR) ν 2980.0, 2617.4, 1728.2, 1697.3, 1516.0, 1450.4, 1317.3, 1236.3, 1053.1, 935.4 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{11}$H$_{10}$F$_2$NaO$_2$ [M+Na]$^+$: 235.0541, found: 235.0541.

Product 3h was obtained in 24.8 mg (41% yield) as light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38-7.32 (m, 3H), 7.29-7.23 (m, 4H), 7.20-7.16 (m, 1H), 7.09-7.07 (m, 2H), 3.53 (dd, $J$ = 8.8 Hz, 6.4 Hz, 1H), 2.71-2.56 (m, 2H), 2.26-2.17 (m, 1H), 1.92-1.83 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 178.35-178.29 (m, 1C), 154.83 (t, $J$ = 289.5 Hz, 1C), 140.75, 131.64 (dd, $J$ = 4.1 Hz, 2.1 Hz, 1C), 129.22 (t, $J$ = 2.7 Hz, 1C), 128.52, 128.44, 128.39, 128.03, 126.14, 91.17 (dd, $J$ = 19.2 Hz, 18.2 Hz, 1C), 43.69, 33.32, 30.60 (t, $J$ = 2.1 Hz, 1C); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -87.45 (d, $J$ = 35.0 Hz, 1F), -87.88 (d, $J$ = 34.6 Hz, 1F); IR (ATR) ν 2904.8, 2617.4, 1728.2, 1697.3, 1516.0, 1450.4, 1317.3, 1236.3, 1053.1, 935.4 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{18}$H$_{16}$F$_2$NaO$_2$ [M+Na]$^+$: 325.1011, found: 325.1011.

Product 3i was obtained in 19.2 mg (40% yield) as colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.39-7.32 (m, 3H), 7.31-7.27 (m, 2H), 3.54 (dd, $J$ = 8.4 Hz, 6.4 Hz, 1H), 1.90-1.81 (m, 1H), 1.62-1.52 (m, 1H), 1.44-1.34 (m, 2H), 0.90 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 179.04 (t, $J$ = 3.0 Hz, 1C), 154.75 (t, $J$ = 289.0 Hz, 1C), 131.86 (dd, $J$ = 4.2 Hz, 2.2 Hz, 1C), 129.24 (t, $J$ = 2.8 Hz, 1C), 128.44, 127.93, 91.26 (dd, $J$ = 19.4 Hz, 18.4 Hz, 1C), 44.32 (d, $J$ = 1.9 Hz, 1C), 30.90 (t, $J$ = 2.1 Hz, 1C), 20.49, 13.67; $^{19}$F NMR (376 MHz, CDCl$_3$): δ -87.81 (d, $J$ = 36.1 Hz, 1F), -88.53 (d, $J$ = 36.1 Hz, 1F); IR (ATR) ν 2962.6, 1734.0, 1705.0, 1496.7, 1409.9, 1244.0, 1176.5, 1010.7, 948.9 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{13}$H$_{14}$F$_2$NaO$_2$ [M+Na]$^+$: 263.0854, found: 263.0857.
Product **3j** was obtained in 23.3 mg (52% yield) as white solid; Mp 100-102 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.62-7.59 (m, 1H), 7.23-7.11 (m, 3H), 3.78 (td, \(J = 5.2\) Hz, 2.4 Hz, 1H), 2.93-2.85 (m, 1H), 2.74 (dt, \(J = 16.4\) Hz, 4.8 Hz, 1H), 2.31-2.24 (m, 1H), 2.12-2.04 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 178.13 (dd, \(J = 3.6\) Hz, 2.7 Hz, 1C), 154.27 (dd, \(J = 297.1\) Hz, 285.4 Hz, 1C), 136.49 (dd, \(J = 6.2\) Hz, 0.9 Hz, 1C), 128.78, 127.46-127.36 (m, 1C), 127.22 (d, \(J = 0.5\) Hz, 1C), 127.02 (t, \(J = 2.0\) Hz, 1C), 126.54, 87.32 (dd, \(J = 22.4\) Hz, 11.5 Hz, 1C), 39.34 (t, \(J = 2.3\) Hz, 1C), 27.07, 25.01; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -84.32 (d, \(J = 33.8\) Hz, 1F), -86.08 (d, \(J = 33.8\) Hz, 1F); IR (ATR) \(\nu\) 3026.3, 2802.5, 2601.9, 1707.0, 1489.0, 1417.6, 1317.3, 1165.0, 991.4 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{12}\)H\(_{10}\)F\(_2\)NaO\(_2\) [M+Na]\(^+\): 247.0541, found: 247.0541.

Product **3k** was obtained in 26.2 mg (55% yield) as light yellow solid; Mp 128-130 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.42 (t, \(J = 2.0\) Hz, 1H), 7.04-6.98 (m, 2H), 3.79-3.76 (m, 1H), 2.88-2.80 (m, 1H), 2.74-2.68 (m, 1H), 2.34 (s, 3H), 2.29-2.24 (m, 1H), 2.11-2.02 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 179.23 (dd, \(J = 3.5\) Hz, 2.4 Hz, 1C), 154.14 (dd, \(J = 297.0\) Hz, 285.1 Hz, 1C), 135.96, 133.47 (d, \(J = 6.1\) Hz, 1C), 128.64, 127.96 (t, \(J = 2.0\) Hz, 1C), 127.71 (dd, \(J = 13.9\) Hz, 0.8 Hz, 1C), 127.14 (dd, \(J = 6.2\) Hz, 3.2 Hz, 1C), 87.36 (dd, \(J = 22.1\) Hz, 11.5 Hz, 1C), 39.36 (t, \(J = 2.5\) Hz, 1C), 26.63, 25.16, 21.25; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -84.58 (d, \(J = 34.2\) Hz, 1F), -86.13 (d, \(J = 34.2\) Hz, 1F); IR (ATR) \(\nu\) 3033.3, 1747.5, 1697.3, 1496.7, 1417.6, 1317.3, 1246.0, 1166.9, 1076.2, 937.4 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{13}\)H\(_{12}\)F\(_2\)NaO\(_2\) [M+Na]\(^+\): 261.0698, found: 261.0697.

Product **4a** was obtained in 73.6 mg (50% yield) as light yellow solid; Mp 108-110 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.34-7.22 (m, 20H), 7.19-7.16 (m, 2H), 7.06-7.04 (m, 2H), 5.02-4.98 (m, 2H), 4.96-4.93 (m, 1H), 4.85-4.80 (m, 3H), 4.59-4.54 (m, 2H), 4.52-4.49 (m, 1H), 3.80-3.73 (m, 3H), 3.69-3.65 (m, 2H), 3.62-3.58 (m, 1H), 3.39 (t, \(J = 2.0\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 175.92-175.85 (m, 1C), 156.63, 154.81 (dd, \(J = 290.7\) Hz, 287.4 Hz, 1C), 138.40, 138.08, 137.97, 137.90, 129.02 (t, \(J = 3.7\) Hz, 1C), 128.38, 128.36, 128.29, 128.19, 127.94, 127.84, 127.80, 127.76, 127.70, 127.64, 127.58, 126.88 (t, \(J = 3.9\) Hz, 1C), 116.90, 101.42, 86.08 (dd, \(J = 21.5\) Hz, 18.0 Hz, 1C), 84.59, 81.87, 77.60, 75.74, 75.09, 75.03, 75.02, 73.44, 68.72, 33.59; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -87.66 (d, \(J = 35.3\) Hz, 1F), -89.05 (d, \(J = 35.3\) Hz, 1F); IR (ATR) \(\nu\) 3030.1, 2362.8, 1720.5, 1516.0, 1423.4, 1240.2, 1066.6, 831.3 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{44}\)H\(_{42}\)F\(_2\)NaO\(_8\) [M+Na]\(^+\): 759.2740, found: 759.2748.
Product 4b was obtained in 39.6 mg (53% yield) as light yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 3.43 (t, J = 2.0 Hz, 2H), 2.92 (d, J = 4.0 Hz, 1H), 2.90 (d, J = 4.4 Hz, 1H), 2.55-2.48 (m, 1H), 2.44-2.39 (m, 1H), 2.32-2.26 (m, 1H), 2.20-2.11 (m, 1H), 2.10-1.95 (m, 3H), 1.66-1.43 (m, 6H), 0.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 175.88 (t, J = 2.8 Hz, 1C), 154.90 (dd, J = 290.9 Hz, 287.3 Hz, 1C), 139.34, 136.74, 130.08 (t, J = 3.7 Hz, 1C), 128.22 (t, J = 3.5 Hz, 1C), 125.58, 125.06 (t, J = 3.5 Hz, 1C), 86.31 (dd, J = 21.0 Hz, 17.9 Hz, 1C), 50.46, 47.98, 44.29, 37.98, 35.82, 33.42 (d, J = 2.8 Hz, 1C), 31.51, 29.36, 26.39, 25.55, 21.55, 13.79; ¹⁹F NMR (376 MHz, CDCl₃): δ -87.31 (d, J = 34.6 Hz, 1F), -88.63 (d, J = 34.6 Hz, 1F); IR (ATR) ν 3419.7, 1735.9, 1516.0, 1406.1, 1288.4, 1247.9, 1087.8, 1008.7, 912.3, 881.4 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₂H₂₄F₂NaO₃ [M+Na]⁺: 397.1586, found: 397.1585.

Inseparable mixture 4c and 4c‘ was obtained in 44.5 mg (4c, 41% yield; 4c‘, 5% yield) as light yellow oil with 200 μL H₂O as additive; Selectivity (desired C-F cleavage product : byproduct) = 8:1; ¹H NMR (400 MHz, CDCl₃): δ 8.06-8.04 (m, 2H), 7.43-7.40 (m, 2H), 4.68-4.62 (m, 2H), 4.44 (d, J = 2.4 Hz, 1H), 4.34-4.31 (m, 1H), 4.27-4.25 (m, 1H), 3.97-3.93 (m, 1H), 3.82-3.78 (m, 1H), 3.46 (t, J = 2.0 Hz, 2H), 1.55 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 174.49, 165.46, 155.20 (dd, J = 282.6 Hz, 278.2 Hz, 1C), 137.91-137.82 (m, 1C), 129.93, 128.83, 127.69-127.62 (m, 1C), 109.17, 108.84, 101.58, 86.67 (dd, J = 21.9 Hz, 16.6 Hz Hz, 1C), 70.73, 70.50, 70.03, 65.40, 61.30, 49.49, 33.43, 33.23, 26.44, 25.78, 25.48, 23.96; ¹⁹F NMR (376 MHz, CDCl₃) (4c): δ -84.41 (d, J = 28.2 Hz, 1F), -86.01 (d, J = 28.2 Hz, 1F); ¹⁹F NMR (376 MHz, CDCl₃) (4c‘): δ -70.05 (d, J = 3.4 Hz, 3F); IR (ATR) ν 3408.2, 2989.6, 1720.5, 1610.5, 1456.2, 1375.2, 1276.8, 1163.0, 1066.6, 887.2 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₃H₂₆F₂NaO₉ [M+Na]⁺: 507.1437, found: 507.1436. The by-product might be formed via a β-hydrocarboxylation as recently reported by Malkov & Buckley⁹ᵃ and Nam⁹ᵇ, respectively.
5. Product elaboration

A 10 mL flask containing 2a (0.2 mmol, 39.6 mg), Pd/C (5.0 mg, 10 wt%) and EtOAc (3.0 mL) was charged with H₂ balloon. The reaction mixture was stirred for 5 h at room temperature and monitored by TLC until full conversion of 2a. Then the reaction mixture was diluted with EtOAc, filtered, and dried with Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography using PE/EtOAc (1:1, v/v) as the eluent to afford 5 in 36 mg with 90% yield as colorless oil. 

\[ \begin{align*}
\delta & = 7.37 - 7.33 \text{ (m, 2H)}, 7.32 - 7.29 \text{ (m, 1H)}, 7.28 - 7.27 \text{ (m, 1H)}, 7.26 - 7.25 \text{ (m, 1H)}, 5.91 \text{ (td, } J = 56.4 \text{ Hz, 3.2 Hz, 1H)}, 3.65 - 3.53 \text{ (m, 1H)}, 3.00 \text{ (dd, } J = 16.8 \text{ Hz, 5.6 Hz, 1H)}, 2.81 \text{ (dd, } J = 16.8 \text{ Hz, 8.8 Hz, 1H});
\end{align*} \]


To a 10 mL flask were added 2a (0.2 mmol, 39.6 mg), Et₂O (2.0 mL) and MeOH (0.5 mL), and the hexane solution of TMSCHN₂ (0.2 mL, 2 mol/L, 0.4 mmol) was added at 0 °C. The mixture was stirred at that temperature for another 30 mins. Then the solvent was removed under reduced pressure, and the crude residue was dissolved in DMF (1 mL) and cooled to 0 °C, followed by the addition of 0.24 mL of TBAF (0.24 mmol, 1.0 M in THF). The resulting mixture was slowly warmed to room temperature and stirred for 24 h. After monitored by TLC till full conversion to the product, the reaction was quenched by saturated aqueous solution of NaCl (5 mL) and extracted with Et₂O (5 mL x 3). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography using PE/EtOAc (10:1, v/v) as eluent to afford 6 in 33.0 mg with 78% yield as light yellow oil. 

\[ \begin{align*}
\delta & = 7.42 - 7.40 \text{ (m, 3H)}, 7.28 - 7.26 \text{ (m, 2H)}, 6.37 \text{ (t, } J = 2.0 \text{ Hz, 1H)}, 6.25 \text{ (t, } J = 55.6 \text{ Hz, 1H)}, 3.61 \text{ (s, 3H)}; \]


\[ \begin{align*}
\delta & = 165.07, 147.34 \text{ (t, } J = 20.0 \text{ Hz, 1C)}, 132.36, 129.01, 128.24, 128.20, 122.30 \text{ (t, } J = 8.9 \text{ Hz, 1C)}, 114.12 \text{ (t, } J = 241.4 \text{ Hz, 1C)}, 51.76; \]


\[ \begin{align*}
\delta & = -116.38 \text{ (s, 2F)}; \]


\[ \begin{align*}
\text{HRMS (EI): Exact mass calcd for C}_{11}\text{H}_{10}\text{O}_2\text{F}_2 [M]^+: 212.0649, \text{ found: 212.0652.} \]
\]
The carboxylic acid 2a (0.2 mmol, 39.6 mg) was dissolved in DMF (2 mL), then sec-butylamine (21.9 mg, 0.3 mmol), o-(7-Azabenzotriazol-1-yl)-N,N,N',N'-trimethyluronium hexafluorophosphate (HATU, 152.0 mg, 0.4 mmol) and Et₃N (60.7 mg, 0.6 mmol) were added. The resulting mixture was stirred for 5 h at room temperature till full conversion of 2a. Then the reaction was quenched with H₂O and extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography using PE/EtOAc (2:1, v/v) as eluent to afford 7 in 46.2 mg with 92% yield as white solid. Mp 85-87 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.34 (m, 4H), 7.32-7.27 (m, 1H), 5.31 (br, 1H), 3.90-3.80 (m, 1H), 3.31 (t, J = 2.4 Hz, 2H), 1.40-1.28 (m, 2H), 1.00 (d, J = 6.8 Hz, 3H), 0.74 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.12, 154.75 (dd, J = 289.5 Hz, 286.0 Hz, 1C), 132.59 (t, J = 3.8 Hz, 1C), 128.72, 127.78 (d, J = 4.0 Hz, 1C), 127.74 (d, J = 3.4 Hz, 1C), 87.89 (dd, J = 21.0 Hz, 15.6 Hz, 1C), 46.82, 35.98 (d, J = 3.8 Hz, 1F), -87.73 (d, J = 3.8 Hz, 1F); IR (ATR) ν 3900.0, 2968.4, 1747.5, 1633.7, 1448.5, 1309.6, 1232.5, 1159.2, 1080.1, 881.4 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₄H₁₇F₂NNaO [M+Na]⁺: 276.1170, found: 276.1179.

The carboxylic acid 2a (0.2 mmol, 39.6 mg) was dissolved in Et₂O (2 mL) and cooled to 0 °C. Then LiAlH₄ (7.6 mg, 0.2 mmol, 1.0 equiv) was added. The resulting mixture was stirred for 0.5 h at 0 °C. After full conversion of 2a monitored by TLC, the reaction was quenched by H₂O and extracted with Et₂O (10 mL). The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography using PE/EtOAc (10:1, v/v) as eluent to afford 8 in 30.2 mg with 82% yield as colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 7.38-7.33 (m, 4H), 7.31-7.28 (m, 1H), 3.66 (t, J = 7.0 Hz, 2H), 2.68-2.66 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 154.26 (dd, J = 289.5 Hz, 286.0 Hz, 1C), 133.14 (t, J = 3.4 Hz, 1C), 128.54, 128.22 (t, J = 3.1 Hz, 1C), 127.47, 89.28 (dd, J = 21.4 Hz, 14.4 Hz, 1C), 60.46 (dd, J = 3.4 Hz, 2.6 Hz, 1C), 31.20 (d, J = 1.8 Hz,
1C); $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -89.68 (d, $J = 41.0$ Hz, 1F), -90.57 (d, $J = 41.0$ Hz, 1F).

The carboxylic acid 2a (0.2 mmol, 39.6 mg) was dissolved in Et$_2$O (2 mL) and cooled to 0 °C. Then LiAlH$_4$ (7.6 mg, 0.2 mmol, 1.0 equiv) was added. The resulting mixture was stirred for 0.5 h at 0 °C. After the full conversion of 2a monitored by TLC analysis, the reaction was quenched with H$_2$O and extracted with Et$_2$O (10 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Then the crude residue was dissolved in CH$_3$CN (2 mL) and KOH (13.4 mg, 0.24 mmol) with H$_2$O (60 µL) were added. The resulting mixture was stirred for 3 days at 60 °C. After the full transformation to final product by TLC analysis, the reaction was quenched with H$_2$O and extracted with Et$_2$O (10 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure at 0 °C. The residue was purified by column chromatography using PE as eluent to afford 9 in 13.0 mg with 40% yield as colorless oil. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.38-7.31 (m, 1H), 7.31-7.29 (m, 1H), 7.28-7.26 (m, 2H), 7.14-7.10 (m, 1H), 4.54 (t, $J = 8.8$ Hz, 2H), 3.07 (td, $J = 9.2$ Hz, 3.6 Hz, 2H); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta$ 157.36 (d, $J = 275.8$ Hz, 1C), 132.59 (d, $J = 6.2$ Hz, 1C), 128.39, 124.90 (d, $J = 1.9$ Hz, 1C), 124.55 (d, $J = 5.8$ Hz, 1C), 81.37 (d, $J = 10.9$ Hz, 1C), 67.67 (d, $J = 4.2$ Hz, 1C), 29.26 (d, $J = 3.2$ Hz, 1C); $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta$ -108.47 (s, 1F). HRMS (EI): Exact mass calcd for C$_{10}$H$_9$OF [M]$^+$: 164.0637, found: 164.0640.

Note: The final product 9 should be very volatile, as it can be removed by water pump under room temperature, so the concentration is suggested to be performed at low temperature.
6. Mechanistic studies

6.1 Cyclic voltammetry (CV) analysis

Cyclic voltammograms were recorded with a Bio-logic VSP Potentiostat/Galvanostat equipped with electrochemical analysis software at room temperature in DMF. n-Bu₄NClO₄ (0.07 M) was used as the supporting electrolyte, and a Pt disk electrode was used as the working electrode. The auxiliary electrode was a Pt pillar. All potentials are referenced against the Ag/AgNO₃ (0.1 M in CH₃CN) redox couple. The scan rate is 100 mV s⁻¹.

Figure S1. CV analyses of 1a. (a) DMF containing 0.07 M n-Bu₄NClO₄; (b) DMF containing 0.07 M n-Bu₄NClO₄ with CO₂ saturated; (c) DMF containing 0.07 M n-Bu₄NClO₄ after addition of 0.02 M 1a; (d) DMF containing 0.07 M n-Bu₄NClO₄ after addition of 0.02 M 1a and CO₂ saturated.

For the CV of α-trifluoromethyl styrene 1a (Figure S1), a one-electron reduction peak in the potential at -2.69 V and a second one at -2.94 V was observed (green line), whereas at the potential of -2.69 V, the reduction current of CO₂ was less than 0.1 mA (blue line), indicating that 1a should be easier to reduce than CO₂. After the solution of 1a was saturated with CO₂ (pink line), only one reduction peak was observed at -2.81 V with an associated peak current increase from 0.21 to 0.36 mA (ca. 1.7 times). These results suggested that an ECEC process might be involved, in which a radical anion might be generated after the first one-electron electroreduction, that could react immediately with CO₂, then the second electron transfer is facilitated at a less negative potential thus leading to a significant increase in
current observed. Accordingly, since a different species is being reduced in the presence of CO\textsubscript{2}, the second peak at -2.94 V is not observed.

**Figure S2.** CV analyses of 1n. (a) DMF containing 0.07 M \textit{n}-Bu\textsubscript{4}NClO\textsubscript{4}; (b) DMF containing 0.07 M \textit{n}-Bu\textsubscript{4}NClO\textsubscript{4}, after addition of 0.02 M 1n; (c) DMF containing 0.07 M \textit{n}-Bu\textsubscript{4}NClO\textsubscript{4}, after addition of 0.02 M 1n and 55 M H\textsubscript{2}O; (d) DMF containing 0.07 M \textit{n}-Bu\textsubscript{4}NClO\textsubscript{4}, after addition of 0.02 M 1n, 55 M H\textsubscript{2}O and CO\textsubscript{2} saturated.

Considering that H\textsubscript{2}O could promote the electro-carboxylation reaction of 1n to give a higher 54% yield (without H\textsubscript{2}O, 28% yield), the CV analysis of 1n was then conducted. As shown in Figure S2, a one-electron reduction peak in the potential at -2.30 V and a second one at -2.49 V was observed (blue line). After addition of H\textsubscript{2}O, there was no obvious changes on its first single-electron reduction process, but the current was increased from 0.28 to 0.32 mA at the second reduction wave (red line). These results indicate that H\textsubscript{2}O might be able to react with the intermediate formed after two-electron transfer. After the solution of 1n containing H\textsubscript{2}O was saturated with CO\textsubscript{2}, the first reduction peak disappeared and only one reduction peak was observed at -2.40 V with the peak current increased from 0.20 to 0.34 mA (ca. 1.7 times) (green line), which indicated that a fast chemical reaction might be occurred between CO\textsubscript{2} with the intermediate generated after the first single-electron reduction.
6.2 Controlled-potential electrolysis

Since there are two reduction peaks (-2.69 V and -2.94 V) were observed for the CV analysis of 1a, the influence of potential on the reaction was further studied via controlled-potential electrolysis, which was conducted on Bio-logic VSP Potentiostat/Galvanostat, using a three electrodes system, with Pt-plate as working cathode and counter anode, the Ag/AgNO₃ (0.1 M in CH₃CN) as a reference electrode.

As shown in Table S7, when the potential less than -2.7 V (vs Ag/AgNO₃) was applied to the cathode, the efficiency of the reaction decreased precipitously with only 14% and 33% yield obtained at -2.5 V and -2.6 V, respectively (entries 1 and 2). At the potential of -2.7 V, the carboxylic acid could be obtained in 78% yield (entry 3). By increasing the potential to -2.8 V, a higher 88% yield was achieved (entry 4). Further enhancing the potential to -3.1 or 3.4 V only gave slightly increase of the reaction yield (entries 5-6). These results suggested that the first one-electron reduction process was critical to the reaction, and the thus generated radical anion should be the real species that reacted with CO₂.

Table S7. The influence of potential.

| Entry | V<sub>cathode</sub> (x V) | Isolated yield (%) |
|-------|-----------------|-------------------|
| 1     | -2.5            | 14                |
| 2     | -2.6            | 33                |
| 3     | -2.7            | 78                |
| 4     | -2.8            | 88                |
| 5     | -3.1            | 87                |
| 6     | -3.4            | 90                |
6.3 Radical capture experiments

To get more evidence for the intermediacy of possible radical species, the following radical capture experiments in the presence or absence of CO$_2$ was performed.

At first, the capture of possible radical intermediates generated after the addition of CO$_2$ was conducted based on the following procedure: To a 10 mL hydrogenation tube containing a stir bar were added $^+$Bu$_4$NClO$_4$ (167.5 mg, 0.49 mmol), DMF (7.0 mL) and TEMPO (62.4 mg, 0.4 mmol), followed by the addition of 1a (34.4 mg, 0.2 mmol). Then the tube was installed with two Pt plates (10 mm x 10 mm x 0.2 mm) as cathode and anode. After bubbling of CO$_2$ gas into the electrolytes for 10 min, the reaction mixture was electrolyzed under a constant current of 8 mA for 7 hours. The reaction mixture was separated into two portions, one was analyzed by HRMS directly and the other was analyzed after acidification. Unfortunately, both of which showed no incorporation of TEMPO, just unreacted styrene 1a, carboxylation product 2a, TEMPOH and (TEMPO)$_2$ were detected.

Then the reaction in the absence of CO$_2$ was conducted and a TEMPO adduct 10 of allyl radical was obtained based on the following procedure: To a 10 mL hydrogenation tube containing a stir bar were added $^+$Bu$_4$NClO$_4$ (167.5 mg, 0.49 mmol, 0.07 M), DMF (7.0 mL) and TEMPO (62.4 mg, 0.4 mmol), followed by the addition of 1a (34.4 mg, 0.2 mmol). Then the tube was installed with two Pt plates (10 mm x 10 mm x 0.2 mm) as cathode and anode. The reaction mixture was electrolyzed under a constant current of 8 mA for 7 hours. The reaction mixture was transferred to a 50 mL Erlenmeyer flask and acidized with HCl (2 N, 10 mL). The aqueous layer extracted with EtOAc (2 x 20 mL) and the combined organics were washed with sat. NH$_4$Cl (2 x 20 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by column chromatography by using PE as eluate to afford 10 in 24.7 mg with 40% yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45-7.43 (m, 2H), 7.38-7.34 (m, 2H), 7.31-7.26
(m, 1H), 4.55 (t, J = 2.8 Hz, 2H), 1.47-1.32 (m, 6H), 1.14 (s, 6H), 1.07 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.62 (dd, J = 291.7 Hz, 289.8 Hz, 1C), 133.27 (dd, J = 3.9 Hz, 3.4 Hz, 1C), 128.71 (t, J = 3.2 Hz, 1C), 128.22, 127.38, 90.87 (dd, J = 20.2 Hz, 14.6 Hz, 1C), 72.72 (d, J = 5.0 Hz, 1C), 59.95, 39.79, 32.90, 20.11, 17.08; $^{19}$F NMR (376 MHz, CDCl$_3$): δ -87.34 (d, J = 32.0 Hz, 1F), -88.46 (d, J = 31.6 Hz, 1F); HRMS (EI): Exact mass calcd for C$_{18}$H$_{25}$NOF$_2$ [M]$^+$: 309.1904, found: 309.1899.

A S$_{N}$2'-type reaction of 1a with TEMPO anion generated via electroreduction might also give the TEMPO adduct 10. To rule out this possibility, we further conducted the reaction in the absence of CO$_2$ and TEMPO, and an allyl radical dimerization product 11 was successfully obtained based on the following procedure: To a 10 mL hydrogenation tube containing a stir bar were added nBu$_4$NClO$_4$ (167.5 mg, 0.49 mmol), DMF (7.0 mL), followed by the addition of 1a (34.4 mg, 0.2 mmol). Then the tube was installed with two Pt plates (10 mm x 10 mm x 0.2 mm) as cathode and anode. The reaction mixture was electrolyzed under a constant current of 8 mA. After 2 hours, the reaction mixture was transferred to a 50 mL Erlenmeyer flask and acidized with HCl (2 N, 10 mL). The aqueous layer extracted with EtOAc (2 x 20 mL) and the combined organics were washed with sat. NH$_4$Cl (2 x 20 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by column chromatography by using PE as eluate to afford 11 in 10.1 mg with 33% yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.36-7.32 (m, 4H), 7.30-7.27 (m, 2H), 7.22-7.20 (m, 4H), 2.48 (t, J = 1.6 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.73 (dd, J = 289.4 Hz, 285.6 Hz), 133.12 (dd, J = 4.3 Hz, 3.2 Hz), 128.43, 128.17 (t, J = 3.3 Hz), 127.35, 91.53 (dd, J = 21.3 Hz, 13.7 Hz), 26.24-26.17 (m); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -90.72 (d, J = 41.4 Hz, 1F), -90.14 (d, J = 41.4 Hz, 1F); HRMS (EI): Exact mass calcd for C$_{18}$H$_{14}$F$_4$ [M]$^+$: 306.1032, found: 306.1030.

There results suggested that the radical anion should be generated during the reaction via one-electron reduction of α-trifluoromethyl alkenes, which could react with CO$_2$ immediately. While in the absence of CO$_2$, a defluorination process occurred to give the allyl radical.
As suggested by one reviewer, to identify the possibility for the generation of a CO₂ radical anion via the direct reduction of CO₂, one equivalent of styrene or 1,1-diphenylethylene was added to the reaction of 1a. It was found that there was almost no influence on the carboxylation of 1a, and no carboxylation product of styrene or 1,1-diphenylethylene was detected by NMR and LC-MS analysis. To avoid the possibility of carboxylic acids decomposing at the anode, the reaction using Mg instead of Pt-plate as anode was also performed, with similar phenomena observed. These results suggested that the CO₂ radical anion might not be involved during the reaction course.
6.4 DFT calculation

To better understand the reaction mechanism, three possible reaction channels of the radical anion generated via the one-electron reduction of α-trifluoromethyl alkenes were studied by the theoretical calculations. The density functional theory (DFT) calculations were performed with Gaussian 09 program. The Truhlar's M06-2X exchange-correlation functional were used with the standard 6-311++G(d,p) basis set. The geometries of reactant, transition states, and product were fully optimized, followed by vibrational frequency calculations at the same levels of theory to obtain the zero-point energies (ZPE) and verify whether it is a transition state on the potential energy surfaces (PES). To estimate the bulk solvent effects on the reaction, all the structures were optimized in the DMF solvent with the polarized continuum model using the integral equation formalism variant (IEFPCM). The temperature-dependent enthalpy corrections and the entropy effects are computed at 298K and 1 atmosphere of pressure. Natural bond orbital (NBO) analysis are also performed to compute the charge and spin distribution on the radical anion intermediate II.

![Figure S3](image)

**Figure S3.** DFT calculation, Gibbs free energy profile for possible reaction channels at the IEFPCM-M06-2X/6-311++G(d,p) level in solvent DMF.

Three possible reaction pathways have been identified and the corresponding potential energy profile has been shown in Figure S3. The optimized structures of the reaction species were present in Figure S4. As shown in Figure S3, the addition of CO₂ to I has a low free energy barrier of 8.4 kcal/mol. More importantly, the reaction Gibbs free energy change ΔG of this reaction channel is negative, which indicates that the reaction via the pathway is thermodynamic spontaneous. But for the other two
pathways, fluorine anion releasing and H$_2$O addition pathways, their free energy barriers are 4.9 and 10.9 kcal/mol higher than that of the CO$_2$ addition pathway, respectively. In addition, the two pathways have positive the reaction Gibbs free energy change ($+2.8$ and $+12.2$ kcal/mol). Thus, the two reaction pathways should be not thermodynamic spontaneous. The present calculated results show that the reaction prefers to proceed though the CO$_2$ addition pathway, which are in good agreement with the experimental data.

Figure S4. Optimized geometries of the reaction species at the IEFPCM-M06-2X/6-311++G(d,p) level in solvent DMF. The bond distances are in angstroms and the bond angles are in degrees. Carbon atoms are in grey, oxygen in red, hydrogen in white, and fluorine in grey blue.
In order to figure out where the radical and anion are situated in the intermediate II, the NBO analysis of which is performed. The nature charges and spins of the II are shown in Figure S5. The calculated charges show that the most negative charge located on the carboxylic group. Carbon atom C1 (see numbers in Figure S5) has a positive charge 0.81 but its two adjacent oxygen atoms have negative charge -0.82. Thus, the total net charges of the three atoms are -0.83. For the other carbon atoms, when the charges of their adjacent atoms such as hydrogen or fluorine atom were added to them, the total net charges of the corresponding group are very small. As a result, the most negative charge of molecule II is situated in the carboxylic group. In addition, NBO analysis also shows that the carbon atom C2 has the largest nature spin of 0.68, the single electron of radical should locate in the C2. According to the NBO analysis, we can speculate the structure of II should be more rational than that of II'.

![Figure S5](image)

**Figure S5.** Nature charges and spins (in parenthesis) of the molecule II computed by NBO analysis at the IEFPCM-M06-2X/6-311++G(d,p) level in solvent dimethylformamide.

**Coordinates for the optimized IMs and TSs at the IEFPCM-M06-2X/6-311++G(d,p).**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               |               |             | X          | Y           | Z          |
| 1             | 6             | 0           | -6.233394  | -0.711006  | 0.207779   |
| 2             | 6             | 0           | -4.855728  | -0.732281  | 0.192644   |
|   |   |   |      |      |     |
|---|---|---|------|------|-----|
| 3 | 6 | 0 | -4.096678 | 0.469424 | 0.068836 |
| 4 | 6 | 0 | -4.823112 | 1.698986 | -0.038919 |
| 5 | 6 | 0 | -6.227800 | 1.688194 | -0.020415 |
| 6 | 6 | 0 | -6.938315 | 0.504180 | 0.100977 |
| 7 | 1 | 0 | -2.183452 | -0.476462 | 0.135046 |
| 8 | 1 | 0 | -6.782587 | -1.641851 | 0.303152 |
| 9 | 1 | 0 | -4.324213 | -1.675411 | 0.275706 |
|10 | 6 | 0 | -2.688400 | 0.478114 | 0.050268 |
|11 | 6 | 0 | -4.058964 | 2.906412 | -0.163073 |
|12 | 1 | 0 | -6.754859 | 2.634435 | -0.103795 |
|13 | 1 | 0 | -8.021539 | 0.510084 | 0.113825 |
|14 | 6 | 0 | -2.694520 | 2.891487 | -0.178985 |
|15 | 6 | 0 | -1.935739 | 1.675854 | -0.073363 |
|16 | 1 | 0 | -4.589227 | 3.850206 | -0.245680 |
|17 | 1 | 0 | -2.180990 | 3.840221 | -0.275327 |
|18 | 6 | 0 | -0.500640 | 1.648161 | -0.089449 |
|19 | 6 | 0 | 0.218596  | 2.950103 | -0.222467 |
|20 | 6 | 0 | 0.284678  | 0.512515 | 0.007667 |
|21 | 1 | 0 | -0.157432 | -0.467831 | 0.106319 |
|22 | 1 | 0 | 1.362664  | 0.569532 | -0.011807 |
|23 | 9 | 0 | 1.559457  | 2.829371 | -0.228486 |
|24 | 9 | 0 | -0.081270 | 3.625998 | -1.365347 |
|25 | 9 | 0 | -0.053288 | 3.829925 | 0.779727 |

Zero-point correction= 0.182088 (A.U.)
Thermal correction to Gibbs Free Energy= 0.141857 (A.U.)
Sum of electronic and thermal Free Energies=-800.200311 (A.U.)
The number of imaginary frequencies: 0
| Center Number | Atomic Number | Type | X       | Y       | Z       |
|---------------|---------------|------|---------|---------|---------|
| 1             | 6             | 0    | 4.463917| 1.265501| -0.129787|
| 2             | 6             | 0    | 3.123371| 1.495573| -0.306577|
| 3             | 6             | 0    | 2.186064| 0.433567| -0.190679|
| 4             | 6             | 0    | 2.661022|-0.871416| 0.114107 |
| 5             | 6             | 0    | 4.048225|-1.080031| 0.290506 |
| 6             | 6             | 0    | 4.932624|-0.034852| 0.171541 |
| 7             | 1             | 0    | 0.464820| 1.653474| -0.581222|
| 8             | 1             | 0    | 5.171631| 2.080965| -0.220521|
| 9             | 1             | 0    | 2.759280| 2.490970| -0.537587|
| 10            | 6             | 0    | 0.799993| 0.644887| -0.367794|
| 11            | 6             | 0    | 1.710673|-1.927439| 0.233187 |
| 12            | 1             | 0    | 4.402622|-2.078683| 0.522657 |
| 13            | 1             | 0    | 5.994151|-0.203164| 0.308990 |
| 14            | 6             | 0    | 0.378297|-1.706023| 0.063337 |
| 15            | 6             | 0    | -0.127009| -0.393474| -0.251473|
| 16            | 1             | 0    | 2.069094|-2.925236| 0.463019 |
| 17            | 1             | 0    | -0.305396|-2.539391| 0.154776 |
| 18            | 6             | 0    | -1.518392| -0.130133| -0.437512|
| 19            | 6             | 0    | -2.506834| -1.194716| -0.097270|
| 20            | 6             | 0    | -2.028030| 1.197973| -0.867995|
| 21            | 1             | 0    | -1.394297| 1.624207| -1.646043|
| 22            | 1             | 0    | -3.032186| 1.109121| -1.286690|
| 23            | 9             | 0    | -3.776940| -0.774209| -0.185652|
| 24            | 9             | 0    | -2.415604| -2.274436| -0.916675|
| 25            | 9             | 0    | -2.356128| -1.682961| 1.154070 |
| 26            | 6             | 0    | -2.140158| 2.239940| 0.301325 |
Zero-point correction = 0.198594 (A.U.)
Thermal correction to Gibbs Free Energy = 0.153026 (A.U.)
Sum of electronic and thermal Free Energies = -988.798975 (A.U.)
The number of imaginary frequencies: 0

III

| Center Number | Atomic Number | Atomic Type | X        | Y        | Z        |
|---------------|---------------|-------------|----------|----------|----------|
| 1             | 6             | 0           | -3.917162| 1.055080 | -0.462074|
| 2             | 6             | 0           | -2.613393| 1.476590 | -0.445087|
| 3             | 6             | 0           | -1.568603| 0.578157 | -0.101408|
| 4             | 6             | 0           | -1.893168| -0.766905| 0.222468 |
| 5             | 6             | 0           | -3.252675| -1.174641| 0.197617 |
| 6             | 6             | 0           | -4.240789| -0.285480| -0.137008|
| 7             | 1             | 0           | 0.032382 | 2.011969 | -0.337376|
| 8             | 1             | 0           | -4.708993| 1.746654 | -0.724261|
| 9             | 1             | 0           | -2.360977| 2.502190 | -0.692934|
| 10            | 6             | 0           | -0.210205| 0.986215 | -0.077919|
| 11            | 6             | 0           | -0.842985| -1.659494| 0.564376 |
| 12            | 1             | 0           | -3.494445| -2.202466| 0.447036 |
| 13            | 1             | 0           | -5.276267| -0.604594| -0.154391|
| 14            | 6             | 0           | 0.458818 | -1.239054| 0.579864 |
| 15            | 6             | 0           | 0.790139 | 0.105105 | 0.253784 |
| 16            | 1             | 0           | -1.089240| -2.684381| 0.820872 |
| 17            | 1             | 0           | 1.248365 | -1.928541| 0.855677 |
| 18            | 6             | 0           | 2.204083 | 0.573363 | 0.302322 |
| 19            | 6             | 0           | 3.164825 | -0.190944| -0.306131|
Zero-point correction=  0.180031  (A.U.)
Thermal correction to Gibbs Free Energy=  0.140494  (A.U.)
Sum of electronic and thermal Free Energies=  -700.204179  (A.U.)
The number of imaginary frequencies: 0

IV

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               | Atomic Number |             | X           | Y           | Z             |
| 1             | 6             | 0           | 4.305698    | 0.984818    | -0.000087     |
| 2             | 6             | 0           | 3.022671    | 1.469447    | -0.000154     |
| 3             | 6             | 0           | 1.915080    | 0.579340    | -0.000081     |
| 4             | 6             | 0           | 2.157771    | -0.821522   | 0.000050      |
| 5             | 6             | 0           | 3.489956    | -1.293154   | 0.000119      |
| 6             | 6             | 0           | 4.543008    | -0.409662   | 0.000054      |
| 7             | 1             | 0           | 0.430879    | 2.125600    | -0.000246     |
| 8             | 1             | 0           | 5.145185    | 1.669721    | -0.000141     |
| 9             | 1             | 0           | 2.835392    | 2.537828    | -0.000259     |
| 10            | 6             | 0           | 0.584380    | 1.053143    | -0.000119     |
| 11            | 6             | 0           | 1.036830    | -1.703414   | 0.000100      |
| 12            | 1             | 0           | 3.667489    | -2.363197   | 0.000222      |
| 13            | 1             | 0           | 5.561581    | -0.778925   | 0.000113      |
| 14            | 6             | 0           | -0.239454   | -1.231786   | 0.000049      |
| 15            | 6             | 0           | -0.511317   | 0.184964    | -0.000029     |
Zero-point correction= 0.196048  (A.U.)
Thermal correction to Gibbs Free Energy= 0.154893  (A.U.)
Sum of electronic and thermal Free Energies= -800.682324  (A.U.)

The number of imaginary frequencies: 0

TS-CO$_2$

| Center | Atomic Number | Atomic Type | X       | Y       | Z       |
|--------|--------------|-------------|---------|---------|---------|
| 1      | 6            | 0           | 4.471396| 1.225707| -0.264241|
| 2      | 6            | 0           | 3.134728| 1.430596| -0.509597|
| 3      | 6            | 0           | 2.179802| 0.396037| -0.294199|
| 4      | 6            | 0           | 2.654120| -0.859727| 0.187962|
| 5      | 6            | 0           | 4.032282| -1.042624| 0.428627|
| 6      | 6            | 0           | 4.933692| -0.022898| 0.209335|
| 7      | 1            | 0           | 0.479279| 1.557798| -0.882142|
| 8      | 1            | 0           | 5.180490| 2.028326| -0.434729|
| 9      | 1            | 0           | 2.786030| 2.392115| -0.873567|
| 10     | 6            | 0           | 0.800306| 0.582309| -0.535839|
Zero-point correction= 0.194700  (A.U.)
Thermal correction to Gibbs Free Energy= 0.148535  (A.U.)
Sum of electronic and thermal Free Energies= -988.773493  (A.U.)
The number of imaginary frequencies: 1
Imaginary frequency  -313.5464  cm\(^{-1}\); IR Intensity  3260.3165  KM/Mole

TS-F

| Center | Atomic Number | Atomic Number | Type | X        | Y        | Z        |
|--------|---------------|---------------|------|----------|----------|----------|
| 1      | 6             | 0             |      | -4.309307| 0.938599 | 0.199774 |
| 2      | 6             | 0             |      | -3.037239| 1.450941 | 0.193669 |
|   |   |   |          |          |          |
|---|---|---|----------|----------|----------|
| 3 | 6 | 0  | -1.910476| 0.597659 | 0.043111 |
| 4 | 6 | 0  | -2.126362| -0.800466| -0.098729|
| 5 | 6 | 0  | -3.453131| -1.301915| -0.090755|
| 6 | 6 | 0  | -4.521851| -0.454300| 0.055425 |
| 7 | 1 | 0  | -0.434144| 2.167606 | 0.164331 |
| 8 | 1 | 0  | -5.159929| 1.600419 | 0.314432 |
| 9 | 1 | 0  | -2.872391| 2.517923 | 0.303116 |
|10 | 6 | 0  | -0.584249| 1.100052 | 0.038478 |
|11 | 6 | 0  | -0.994825| -1.646752| -0.249674|
|12 | 1 | 0  | -3.607969| -2.370339| -0.201635|
|13 | 1 | 0  | -5.532177| -0.845871| 0.061776 |
|14 | 6 | 0  | 0.273269 | -1.134769| -0.255079|
|15 | 6 | 0  | 0.505602 | 0.266294 | -0.101734|
|16 | 1 | 0  | -1.154368| -2.713029| -0.374871|
|17 | 1 | 0  | 1.128110 | -1.784757| -0.402585|
|18 | 6 | 0  | 1.879264 | 0.810524 | -0.144395|
|19 | 6 | 0  | 2.912420 | -0.006010| 0.308218 |
|20 | 6 | 0  | 2.160706 | 2.056285 | -0.718693|
|21 | 1 | 0  | 1.383332 | 2.614211 | -1.222315|
|22 | 1 | 0  | 3.164554 | 2.457200 | -0.720254|
|23 | 9 | 0  | 4.124761 | 0.517623 | 0.465028 |
|24 | 9 | 0  | 2.701874 | -0.917303| 1.259444 |
|25 | 9 | 0  | 3.431371 | -1.255899| -0.946659 |

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Zero-point correction= 0.194700 (A.U.)
Thermal correction to Gibbs Free Energy= 0.148535 (A.U.)
Sum of electronic and thermal Free Energies= -800.179095 (A.U.)
The number of imaginary frequencies: 1
Imaginary frequency -313.5464 cm⁻¹; IR Intensity 3260.3165 KM/Mole
## TS-H₂O

| Center Number | Atomic Number | Atomic Number | Atomic Type | X           | Y           | Z           |
|---------------|---------------|---------------|-------------|-------------|-------------|-------------|
| 1             | 6             | 0             | 4.357809    | 0.979362    | -0.193000  |
| 2             | 6             | 0             | 3.050325    | 1.359262    | -0.362313  |
| 3             | 6             | 0             | 1.994664    | 0.418504    | -0.212374  |
| 4             | 6             | 0             | 2.322092    | -0.924845   | 0.120862   |
| 5             | 6             | 0             | 3.678081    | -1.289327   | 0.288025   |
| 6             | 6             | 0             | 4.678660    | -0.359180   | 0.135341   |
| 7             | 1             | 0             | 0.418050    | 1.822409    | -0.609419  |
| 8             | 1             | 0             | 5.152695    | 1.706622    | -0.311239  |
| 9             | 1             | 0             | 2.802726    | 2.385340    | -0.614268  |
| 10            | 6             | 0             | 0.640130    | 0.786575    | -0.379744  |
| 11            | 6             | 0             | 1.255666    | -1.857792   | 0.276016   |
| 12            | 1             | 0             | 3.915689    | -2.317898   | 0.540183   |
| 13            | 1             | 0             | 5.715142    | -0.646536   | 0.265863   |
| 14            | 6             | 0             | -0.044593   | -1.485167   | 0.111860   |
| 15            | 6             | 0             | -0.402267   | -0.131947   | -0.231325  |
| 16            | 1             | 0             | 1.496455    | -2.885749   | 0.527429   |
| 17            | 1             | 0             | -0.818641   | -2.232102   | 0.231963   |
| 18            | 6             | 0             | -1.759057   | 0.286681    | -0.429026  |
| 19            | 6             | 0             | -2.849399   | -0.641380   | -0.024293  |
| 20            | 6             | 0             | -2.107983   | 1.623974    | -0.890214  |
| 21            | 1             | 0             | -1.454854   | 1.967144    | -1.696776  |
| 22            | 1             | 0             | -3.150393   | 1.719341    | -1.188264  |
| 23            | 9             | 0             | -4.068270   | -0.079659   | -0.074526  |
| 24            | 9             | 0             | -2.927175   | -1.754413   | -0.806384  |
| 25            | 9             | 0             | -2.716756   | -1.116954   | 1.240905   |
| 26            | 8             | 0             | -1.612963   | 3.366620    | 1.112129   |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 27 | 1 | 0 | -1.902695 | 2.420892 | 0.027719 |
| 28 | 1 | 0 | -0.745415 | 3.098499 | 1.430935 |

Zero-point correction= 0.202795 (A.U.)
Thermal correction to Gibbs Free Energy= 0.158578 (A.U.)
Sum of electronic and thermal Free Energies= -876.594417 (A.U.)
The number of imaginary frequencies: 1

Imaginary frequency -707.1457 cm\(^{-1}\); IR Intensity 7788.7992 KM/Mole
6.5 Anodic Oxidation.

Since a non-sacrificial anode was employed, to identify the real sacrificial oxidant on anode, we analyzed the reaction mixture directly without acidification, based on the following procedure: To a 10 mL hydrogenation tube containing a stir bar were added $^+$Bu$_4$NCIO$_4$ (167.5 mg, 0.49 mmol), DMF (7.0 mL), followed by the addition of 1a (0.2 mmol). Then the tube was installed with two Pt-plates as cathode and anode. After bubbling of CO$_2$ gas into the electrolytes for 10 min, the reaction mixture was electrolyzed under a constant current of 8 mA for 7 hours. After that, the reaction mixture was transferred to a 50 mL Erlenmeyer flask and quenched with sat. NaCl (20 mL). The aqueous layer extracted with EtOAc (20 mL) and dried over Na$_2$SO$_4$. After concentrated in vacuo, the residue was analyzed by $^1$H NMR with benzotrifluoride (29.3 mg, 0.2 mmol) as internal standard. As shown in Figure S6, the formation of carboxylate 12 was detected in 14% yield, along with the generation of carboxylic acid 2a in 76% yield, which indicated that a Shono oxidation of DMF might be occurred.

![Figure S6. $^1$H NMR of reaction mixture without acidification](image-url)
Product 12 could be obtained by column chromatography with CH$_2$Cl$_2$/Et$_2$O (9:1, v/v) as eluate, which is colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.16 (s, 1H), 7.31-7.27 (m, 2H), 7.26-7.19 (m, 3H), 5.18 (s, 2H), 3.38 (t, $J$ = 2.4 Hz, 2H), 2.72 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 169.86 (dd, $J$ = 4.3 Hz, 2.6 Hz, 1C), 163.76, 154.82 (dd, $J$ = 291.6 Hz, 288.0 Hz, 1C), 132.49 (t, $J$ = 3.8 Hz, 1C), 128.70, 127.86, 127.72 (t, $J$ = 3.4 Hz, 1C), 86.72 (dd, $J$ = 21.1 Hz, 18.2 Hz, 1C), 74.19, 33.76 (d, $J$ = 2.7 Hz, 1C), 29.60; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -87.44 (d, $J$ = 34.2 Hz, 1F), -88.53 (d, $J$ = 33.8 Hz, 1F); IR (ATR) ν 3495.0, 2980.0, 1743.6, 1683.8, 1498.6, 1394.5, 1311.5, 1244.0, 1155.3, 1070.4 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{13}$H$_{13}$F$_2$NNaO$_3$ [M+Na]$^+$: 292.0756, found: 292.0755.

**Figure S7. Oxygen capture experiment**

Inspired by the Cheng’s latest work,$^{16}$ the capture of oxygen generated via the potential anode oxidation of H$_2$O was conducted by using labeled H$_2$O$^{18}$O. As shown in Figure S7, if $^{18}$O$_2$ generated through the anode oxidation of H$_2$O$^{18}$O, it could oxidize PPh$_3$ to $^{18}$O=PPh$_3$, which could be detected by MS analysis. Unfortunately, the formation of O=PPh$_3$ was detected instead of $^{18}$O=PPh$_3$. Meanwhile, GC-MS analysis revealed that H$_2$O$^{18}$O in the reaction system was disappeared and replaced by H$_2$O. It was speculated that during the reaction course, the reversible reaction of H$_2$O$^{18}$O and bubbling CO$_2$ lead to the generation of H$_2$O and C$^{18}$O$_2$, and ultimately resulted in the formation of O=PPh$_3$. As O$_2$ penetrating plastic tube readily, the influence of environment O$_2$ could not be excluded. However, based on the fact that H$_2$O possesses lower oxidation potential than DMF (1.23 and 1.9 V vs. SHE, respectively),$^{17}$ it was more likely act as sacrificial oxidant.
gxt-gh-114 H

$\text{Me} \quad \text{CO}_2\text{H}$

2b
gxt-gh-114 F

2b

CO₂H

Me

87.629
87.721
88.966
88.959

f1 (ppm)
gxt-gh-16-1014 F

![NMR spectrum of compound 2d](image-url)
gxt-gg-120cuiqu H

\[
\text{Ph} \quad \text{g} \quad \text{CO}_2\text{H}
\]

\[
\begin{align*}
\text{f1 (ppm)} & : 4.07, 1.07, 2.00 \\
\end{align*}
\]
2m: major

byproduct 2m': minor
gxt-gh-123 F

2m: major
byproduct 2m*: minor
gxt-gh-109 C

2n

$\text{MeO}_2\text{C}$

$\text{CO}_2\text{H}$

$f_1 (\text{ppm})$

$\begin{align*}
175.800 & \quad 175.774 & \quad 166.636 \\
157.548 & \quad 152.322 & \quad 65.885 \\
137.448 & \quad 137.378 & \quad 129.628 \\
129.222 & \quad 127.679 & \quad 127.618 \\
68.849 & \quad 88.375 & \quad 86.237 \\
77.254 & \quad 77.000 & \quad 70.140 \\
33.467 & \quad 33.146 & 
\end{align*}$

86
gxt-gh-30-cuiqu H

---

Chemical structure and NMR spectrum of compound 2r.
gxt-gi-53-CO2Me H

3b: major

by product 3b': minor
gxt-gi-53-CO2Me C

3b: major
by product 3b': minor
gxt-gi-53-CO2Me F

3b: major

by product 3b*: minor
gxt-gi-52 F

3c
gxt-gi-15-zhihua F

$3d$

$\text{CO}_2\text{Me}$

$\text{PivO}$
gxt-gh-125 H

121
143
gxt-gh-131 H

4c: major

byproduct 4c': minor

[Chemical structures and spectra]
4c: major

byproduct 4c': minor
gxt-gi-17 F
gxt-gi-0610 H

with n-hexane

163
gxt-gh-92-0611 F

11

f1 (ppm)
gxt-gi-46 H

![Chemical Structure Image]

- 1.0 9.0 9.5 10.0 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
- 2.02 3.00 2.00 3.18 2.22 0.97
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