Supporting Information

Photoelectrochemical Dicarboxylation of Styrene with CO_2 to Phenylsuccinic Acid on Ni-Decorated Silicon Photocathode

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Experimental Section

Materials and Reagents

Single polished p-Si (B doped, ρ=1-5 Ω cm^{-2}, thickness 500 μm, <100>) and were purchased from Suzhou Crystal Silicon Electronic & Technology Co., Ltd. Nickel sulfate hexahydrate ($Ni_2SO_4 \cdot 6H_2O$, 99%), Boric acid (H_3BO_3, 99%), Potassium Chloride (KCl, 99.5%), Phosphoric Acid (H_3PO_4, 85%), and Gallium Indium eutectic (Ga-In, 99.99%) were purchased from Aladdin Reagent, Shanghai, China. Tetrabutylammonium bromide ($C_{16}H_{36}Br$, 98%) was purchased from Bidepharm Reagent, Shanghai, China. Anhydrous acetonitrile (CH_3CN) was purchased from Innochem Reagent, Beijing, China. All aqueous solutions were prepared with high-purity deionized water (Milli-Q, resistance 18.2 MΩ cm^{-1}). All the reagents were commercially available and used as received.

Physical characterizations

The morphology and composition of the fabricated films were characterized by field emission scan electron microscopy (FE-SEM, HITACHI SU8220) equipped with energy dispersive X-ray (EDX) microanalysis (Oxford EDS Inca Energy Coater 300, operated at 20 kV). The surface composition of the electrode films and the depth profiles were investigated using X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi (Thermo Scientific™). X-ray diffraction (XRD) patterns were obtained on a Smart Lab 9KW diffractometer using Cu Kα radiation (Rigaku Corp, Japan). The pH of the electrolyte was measured at 914 pH/conductometer (Metrohm™). NMR spectra were recorded on a Bruker Avance NEO 400 MHz NMR Spectrometer. High-resolution mass spectrometry measurements were performed on an Agilent TOF spectrometer. High-performance liquid chromatography (HPLC, 1100 II Agilent) was employed to detect the contents of hydrocinnamic acid and phenylsuccinic acid. The succinic acid

derivatives were separated by using a Shimadzu LC-20A ultraviolet detector. High resolution mass spectra (HRMS) were obtained on an Agilent HPLC-APCI-TOF mass spectrometer (Agilent G6224A). EPR spectra were obtained on an A300 spectrometer (Bruker, Germany).

Preparation of p-Si Photocathode

A commercial p-type silicon wafer was sectioned into 1 cm × 1 cm. Before the etching process, the p-type silicon substrates were ultrasonically cleaned in an ethanol/acetone solution (1:1, v/v) for 20 minutes to remove organic contaminants. Subsequently, the p-type silicon substrates were rinsed with deionized water and further cleaned with a piranha solution of H_2SO_4/H_2O_2 (3:1, v/v) at 95 °C for 30 min to thoroughly eliminate the insoluble organic impurities. Finally, the silicon substrates were washed with deionized water and then immersed in a 5% HF aqueous solution for 5 min to etch the surface oxide layer. Following thorough cleaning with deionized water, the silicon substrates then underwent surface texturing to form micro-pyramid structures via anisotropic chemical etching in an alkaline solution comprising 1.5 wt% NaOH, 1.5 wt% Na_2SiO_3, and 5 vol% isopropanol at 85 °C for 30 min.[1] After cleaning with deionized water, Ga-In eutectic alloy was rubbed at the backsides of the micropyramid silicon substrates to establish ohmic contact. Then, a copper chip was bonded to the Ga-In alloy interface by silver conductive paint (SPI, 99%). After drying in air, the edges and backside of micropyramid silicon substrates were encapsulated by epoxy resin (LOCTITE EA 9462 Henkel) to insulate and protect the back contact of these electrodes.[2]

Several alternative solutions for industrial applications have been provided, prioritizing green and sustainable production processes. In the semiconductor and photovoltaic industries, the traditional silicon wafer cleaning process primarily employs strong acid sulfuric peroxide mixture (H_2SO_4:H_2O_2=4:1, 120-

150 °C) solution. As an environmentally friendly alternative, ozone water (O_3/H_2O), with its strong oxidizing properties, can effectively remove contaminants from silicon wafer surfaces while significantly reducing the use of hazardous chemicals.[3] For silicon dioxide etching, in addition to traditional wet etching methods (such as diluted hydrofluoric acid or buffered oxide etchant), dry plasma etching techniques including NF_3/NH_3 and OF_2/NH_3 can significantly reduce environmental impact while maintaining excellent etching performance.[4, 5] In the context of surface texturization, crystalline silicon with a structure of micro-pyramid array has been widely used in photovoltaic industry. Among various approaches, alkaline wet etching remains the most widely implemented technique at the commercial scale.[2]

Preparation of Ni/p-Si Photocathodes

Right before deposition, the micropyramid silicon substrates were cleaned with HF aqueous solution and deionized water to remove native oxides on the surface. The Ni catalyst was deposited on the surface of the p-Si photocathode via a photoelectrodeposition method. Briefly, the photoelectrodeposition process was implemented in a standard three-electrode cell with the p-Si photocathode as working electrode, Ag/AgCl as reference electrode, graphite as counter electrode, and the solution containing $Ni_2SO_4 \cdot 6H_2O$ (0.5 M), KCl (0.4 M), and H_3BO_3 (0.3 M) as electrolyte. A constant potential of −0.6 V vs. Ag/AgCl was passed through in the passage of 0.1 C cm^{-2}. After Ni deposition, the resulting electrodes were carefully washed with deionized water.

PEC Measurements

All photoelectrochemical measurements were conducted at room temperature with a CHI 760E electrochemical workstation without iR correction. The simulated solar illumination was generated by a 300 W xenon arc lamp (EXCELITAS, PE300BFA) equipped with an AM 1.5G filter (class A spectral

match). The system provides a spectral output of 300-1100 nm that fully complies with the ASTM G173-03 standard for AM 1.5G solar spectrum. The light intensity was precisely calibrated to 100 mW cm^{-2} (1 sun) using a certified silicon photodiode power meter (PM 100D, Thorlabs), ensuring reliable and reproducible illumination conditions for measurements. All photoelectrochemical measurements were performed in a standard three-electrode undivided cell with quartz windows, Ni/p-Si as the working electrode, graphite as the counter electrode, and Ag/AgCl as reference electrode. All potentials presented in this work were referred to Ag/AgCl electrode. Anhydrous acetonitrile (CH_3CN) with 0.1 M tetrabutylammonium bromide (TBAB) was used as electrolyte. Before testing, CO_2 was continuously bubbled into the electrolyte for 20 minutes to saturate the solution. Liner sweep voltammetry (LSV) curves were held at a potential range from −1.2 V to −2. 5 V vs. Ag/AgCl electrode with a scan rate of 20 mV s^{-1}.

Quantification of styrene carboxylation products

The styrene carboxylation products were determined and analyzed by HPLC (Agilent 1100 II) equipped with a C18 column and a UV detector set at 220 nm. The separation was performed using a binary gradient elution system with 0.1% phosphoric acid in water (Mobile Phase A) and acetonitrile (Mobile Phase B). The elution program was set as follows: 0–10 min, isocratic elution with 40% B; 10–20 min, a linear gradient to 100% B. The flow rate was maintained at 1.0 mL/min throughout the analysis. The peaks identification of **2COOH** and **1COOH** were assessed using standard **2COOH** and **1COOH** (Chromatographic peaks: **2COOH** at 4.5 min, **1COOH** at 8.5 min, styrene at 15.7min of retention time). Different concentrations of commercial **2COOH, 1COOH** and styrene were measured to determine the

linear relation between peak area and concentration.

Faraday efficiency and yield calculation

The faradaic efficiency (FE) was calculated as the following equation:

$$FE(\%) = \frac{nFCV}{Q_{i-t}} \times 100\% \qquad \textit{Eq. S1}$$

Where ***n*** is the number of electrons transferred in carboxylation reactions (n=2), ***F*** is the Faraday constant (96485 C mol^{-1}), ***C*** is the molar concentration of the carboxylation product, ***V*** is electrolyte volume (10 cm^3), $\boldsymbol{Q_{i-t}}$ is the amount of charge passing through the electrode during the PEC reaction.

The yield rate was calculated as the following equation:

$$Yield\ rate = \frac{CVM}{AT} \qquad \textit{Eq. S2}$$

Where ***C*** is the molar concentration of the carboxylation product, ***V*** is electrolyte volume, and ***M*** is the relative molecular mass of the carboxylation product. ***A*** is the area of the Ni/p-Si electrode. ***T*** Photoelectrocatalytic electrolysis time.

The selectivity of **2COOH** was calculated as the following equation:

$$Selectivity(\%) = \frac{N_{2COOH}}{N_{styrene}} \times 100\% \qquad \textit{Eq. S3}$$

Where $\boldsymbol{N_{2COOH}}$ and $\boldsymbol{N_{styrene}}$ correspond to the molar amounts of produced **2COOH** and consumed styrene in the PEC reaction, respectively.

The Incident Photon to Current Efficiency (IPCE)

The IPCE measurements of photocathodes were directly measured by the photoelectrochemical

workstation (CIMPS-2, Zahner) at a constant applied potential of −2.4 V vs. Ag/AgCl. The integral current was calculated by the ***Eq. S3*** to compare with the corresponding photocurrent in PEC measurement. (Where λ is from 365 nm to 1020 nm)

$$Integral_j = \int_{\lambda} \frac{1}{1240} \times IPCE \times P_{mono} \cdot d\lambda \qquad \textbf{Eq. S3}$$

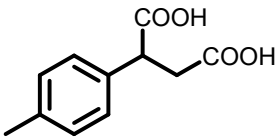
Photoelectrochemical Impedance Spectroscopy (PEIS).

PEIS measurements of p-Si and Ni/p-Si photocathodes were performed by applying 1000K to 0.1 Hz frequency range with an AC voltage amplitude (5 mV) in a 0.1 M TBAB anhydrous acetonitrile electrolyte at a bias of −2.4 V vs. Ag/AgCl under solar-simulator illumination (100 mW cm^{-2}).

General Procedure for carboxylation of styrene Derivatives

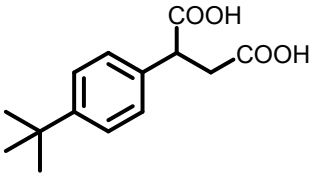
All reactions were conducted according to the following procedure. Photoelectrolysis of 0.1 M styrene derivatives was carried out in a CO_2-saturated acetonitrile electrolyte containing 0.1 M TBAB, using a Ni/p-Si photocathode and a graphite counter electrode. The reaction was conducted under constant potential for 10 h at each tested voltage at room temperature. The reactants were then treated with 1 mL HCl (2 M, aq) and concentrated in vacuo. The succinic acid derivatives were chromatographically separated using a Shimadzu LC-20A HPLC system equipped with a C18 column and a UV detector set at 220 nm. The mobile phase comprised 30% aqueous 0.1% phosphoric acid and 70% acetonitrile at a flow rate of 20 mL/min. The obtained eluent was concentrated in vacuo, acidified with 2 M HCl, and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give the pure desired product.

2-(p-tolyl)succinic acid



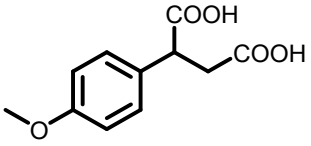
^{1}H NMR (400 MHz, CD_3CN) δ 7.21 – 7.14 (m, 4H), 3.94 (dd, J = 10.0, 5.3 Hz, 1H), 3.04 (dd, J = 17.1, 10.0 Hz, 1H), 2.60 (dd, J = 17.1, 5.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 174.16, 172.70, 137.98, 135.71, 129.96, 128.27, 46.79, 37.32, 20.62. HRMS(ESI, m/z): $[M-H]^-$ calcd for $C_{11}H_{11}O_4$, 207.0736, found 207.0663.

2-(4-(tert-butyl)phenyl)succinic acid



^{1}H NMR (400 MHz, CD_3CN) δ 7.40 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 3.96 (dd, J = 10.0, 5.3 Hz, 1H), 3.06 (dd, J = 17.2, 10.0 Hz, 1H), 2.62 (dd, J = 17.2, 5.3 Hz, 1H), 1.30 (s, 10H). ^{13}C NMR (101 MHz, CD_3CN) δ 174.24, 172.85, 151.15, 135.69, 128.09, 126.32, 46.69, 37.19, 34.69, 31.08. HRMS(ESI, m/z): $[M-H]^-$ calcd for $C_{14}H_{18}O_4$, 249.1205, found 249.1132.

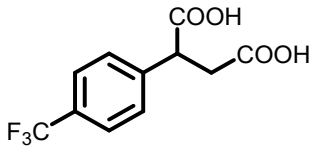
2-(4-methoxyphenyl)succinic acid



^{1}H NMR (400 MHz, CD_3CN) δ 7.22 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 3.92 (dd, J = 10.0, 5.3 Hz, 1H), 3.77 (s, 3H), 3.03 (dd, J = 17.1, 10.0 Hz, 1H), 2.59 (dd, J = 17.1, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 174.46, 172.91, 159.91, 130.83, 129.69, 114.87, 55.68, 46.54, 37.59. HRMS(ESI, m/z):

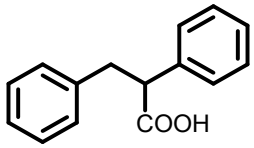
[M-H]$^-$ calcd for $C_{11}H_{11}O_5$, 223.0684, found 223.0612.

2-(4-(trifluoromethyl)phenyl)succinic acid



^{1}H NMR (400 MHz, CD_3CN) δ 9.26 (s, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 4.11 (dd, J = 9.7, 5.5 Hz, 1H), 3.10 (dd, J = 17.2, 9.7 Hz, 1H), 2.68 (dd, J = 17.2, 5.5 Hz, 1H). ^{19}F NMR (376 MHz, CD_3CN) δ -63.11. ^{13}C NMR (101 MHz, CD_3CN) δ 173.4, 172.48, 143.27, 129.65 (q, J = 32.1 Hz), 129.29, 126.19 (q, J = 3.9 Hz), 123.56 (q, J = 275.1 Hz), 47.23, 37.17. HRMS(ESI, m/z): [M-H]$^-$ calcd for $C_{11}H_8F_3O_4$, 261.0453, found 261.0380.

2,3-diphenylpropanoic acid



^{1}H NMR (400 MHz, CD_3CN) δ 7.56 – 6.90 (m, 10H), 3.91 (t, J = 7.9 Hz, 1H), 3.35 (dd, J = 13.8, 8.2 Hz, 1H), 3.02 (dd, J = 13.9, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 174.58, 139.89, 139.45, 129.54, 129.16, 128.79, 128.62, 127.89, 126.83, 53.11, 39.27. HRMS(ESI, m/z): [M-H]$^-$ calcd for $C_{15}H_{13}O_2$, 225.0994, found 225.0921.

Application of the PEC carboxylation strategy

2-phenylsuccinic acid (**2COOH, 1a**, 116 mg, 0.6 mmol) was charged into a dried 100 mL three-neck round-bottom flask under a nitrogen atmosphere. Dichloromethane (20 mL) and sulfonyl chloride (0.58 mL, 0.72 mmol) were added sequentially, and the mixture was heated to 75 °C. After complete dissolution of **1a**, the solvent was removed under reduced pressure using a Dean-Stark apparatus. The system was

then charged with 1,2-dichloroethane (20 mL), followed by portionwise addition of $AlCl_3$(160 mg, 1.2 mmol). The reaction mixture was stirred at room temperature for 12 h and subsequently heated to 60 °C for an additional 5 h. The reaction was quenched with 6 N HCl (5 mL) and water (20 mL), extracted with ethyl acetate, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 2:1) to afford the desired product (95 mg, 90% yield). ^{1}H NMR (400 MHz, DMSO) δ 12.92 (s, 1H), 7.74 (t, J = 4.0 Hz, 2H), 7.67 (d, J = 7.6 Hz, 1H), 7.54 – 7.49 (m, 1H), 4.33 (dd, J = 6.6, 4.5 Hz, 1H), 2.88 (dd, J = 5.5, 2.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 204.69, 173.74, 152.49, 136.37, 135.48, 129.05, 127.17, 123.51, 43.96, 40.06. HRMS(ESI, m/z): $[M-H]^-$ calcd for $C_{10}H_7O_3$, 175.0473, found 175.0401.

EPR measurement

The existence of styrene radicals was verified by EPR measurement. The Photoelectrolysis was conducted by controlled-potential electrolysis in a three-electrode single cell. The electrolyte was composed of 5 mL 0.1 M TBAB acetonitrile solution. Photoelectrolysis was run at –2.4 V vs. Ag/AgCl for 5 min, then 50 μL DMPO was injected into the electrolyte near the working electrode. After 10 min electrolysis, a 0.3 mL solution sample was extracted using a capillary tube (120 mm for length, 0.9 mm for inner diameter, and 1.1 mm for outer diameter), with both ends sealed by petroleum jelly. Measurement conditions: Frequency 9.8525 GHz; Power 19.45 mW; Center Field 3500 G; Sweep Width 200 G, Modulation Width 1.000 G; Sweep time 30 s.

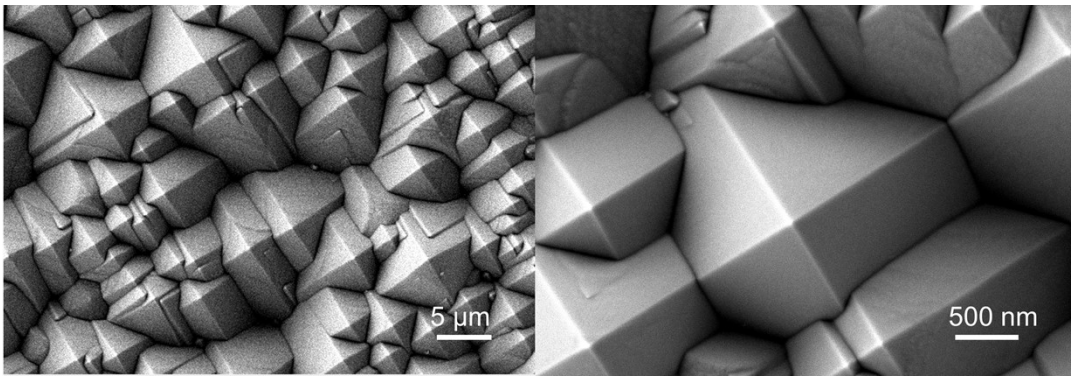


Figure S1. SEM images of bare p-Si at different magnifications.

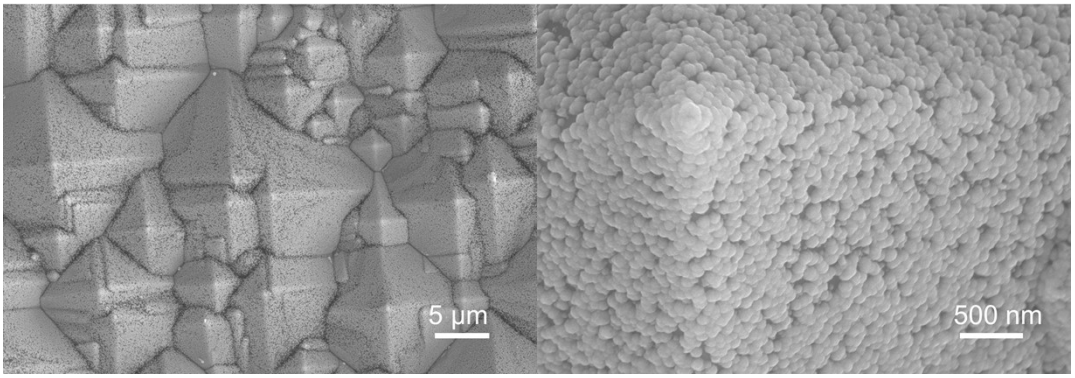
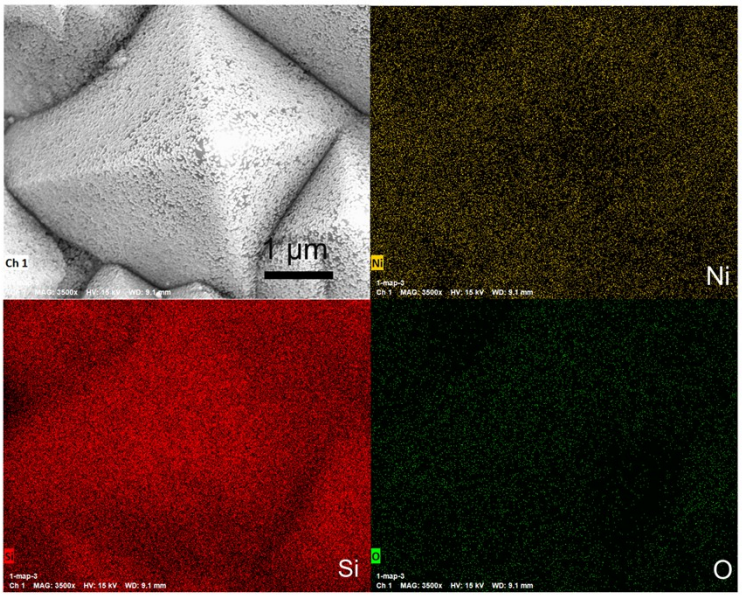


Figure S2. SEM images of Ni/p-Si at different magnifications.

a



b

Element	Weight%	Atom%
Si	83.288	89.853
O	1.104	2.090
Ni	15.608	8.057

c

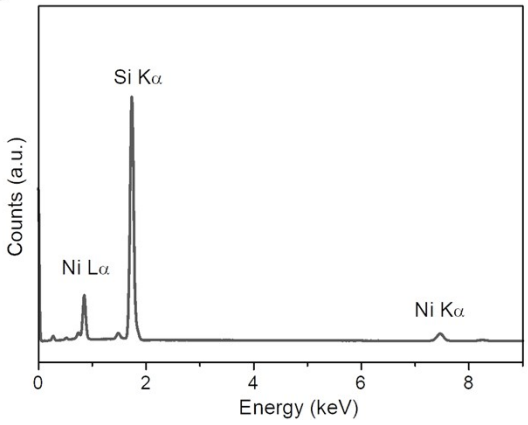


Figure S3. (a) SEM image and corresponding EDS mapping of Ni/p-Si. (b) The corresponding element contents. (c) EDS spectrum of Ni/p-Si.

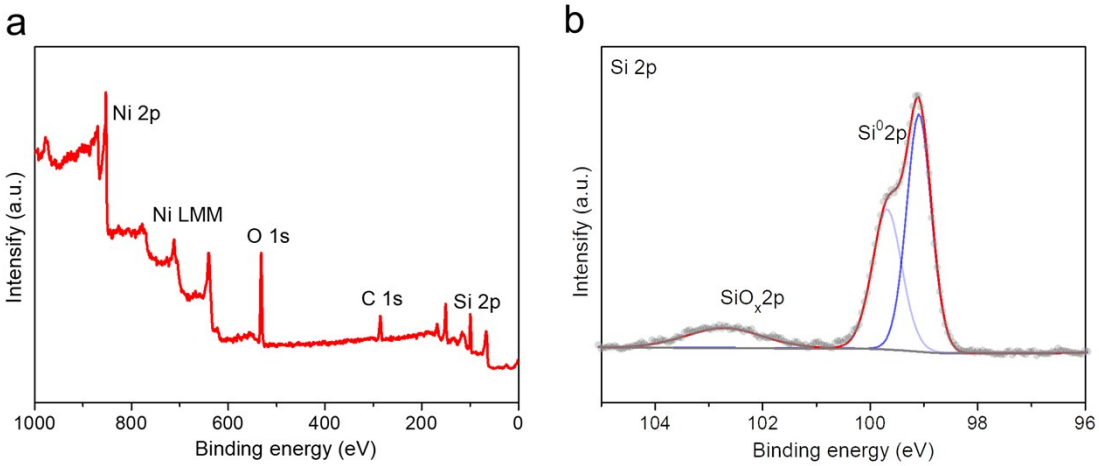


Figure S4. (a) XPS survey spectrum of Ni/p-Si. (b) High-resolution XPS spectra of Si 2p region.

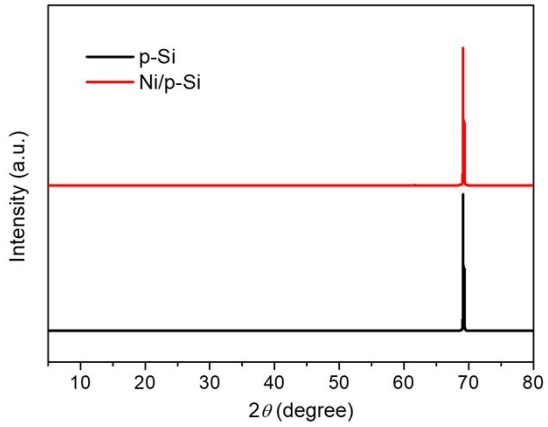


Figure S5. XRD pattern of p-Si and as-prepared Ni/p-Si.

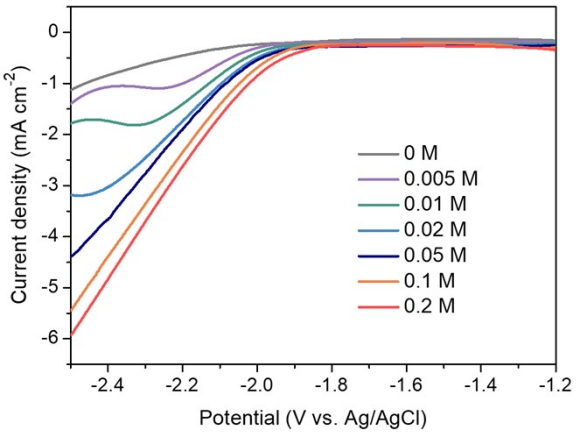


Figure S6. Cathodic linear sweep voltammetry curves of the Ni/p-Si photocathode in CO_2-saturated electrolyte containing varying concentrations of styrene (0 to 0.2 M), recorded at a scan rate of 20 mV s^{-1}.

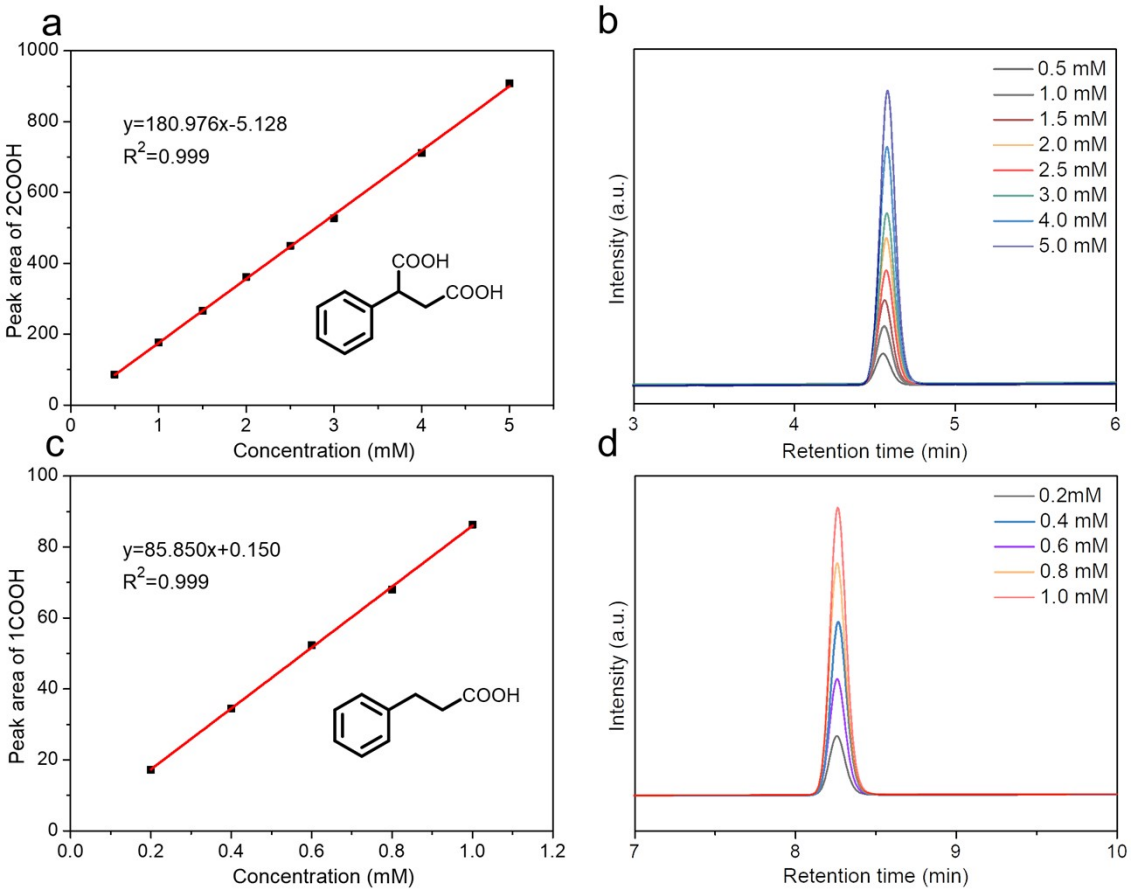


Figure S7. (a) HPLC chromatograms showing peak intensities for different concentrations of **2COOH**.

(b) Calibration curve of **2COOH** concentration vs. chromatographic peak area. (c) HPLC chromatograms showing peak intensities for different concentrations of **1COOH**. (d) Calibration curve of **1COOH** concentration vs. chromatographic peak area.

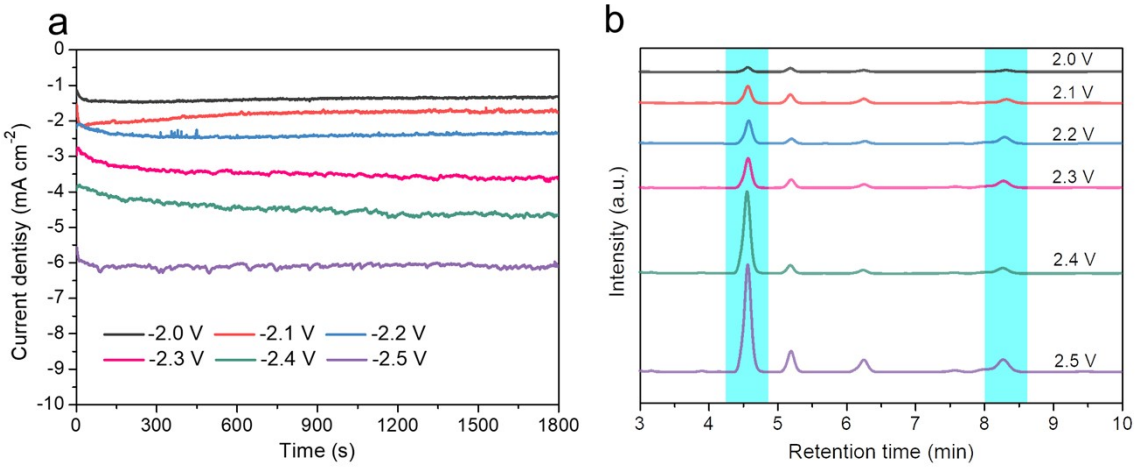


Figure S8. (a) Chronoamperometry curves of Ni/p-Si photocathode recorded at different applied potentials. (b) HPLC chromatogram of PEC carboxylation products on the Ni/p-Si photocathode.

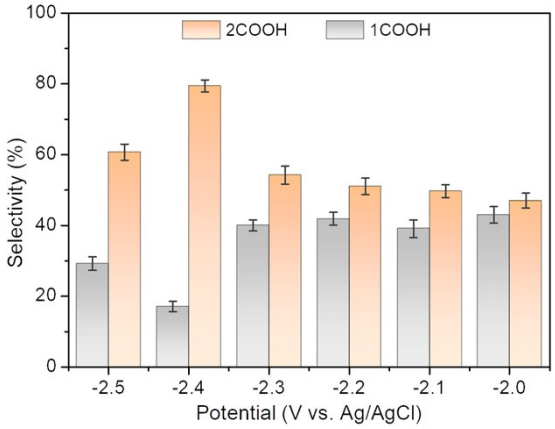


Figure S9. Selectivity for Ni/p-Si at different applied potentials.

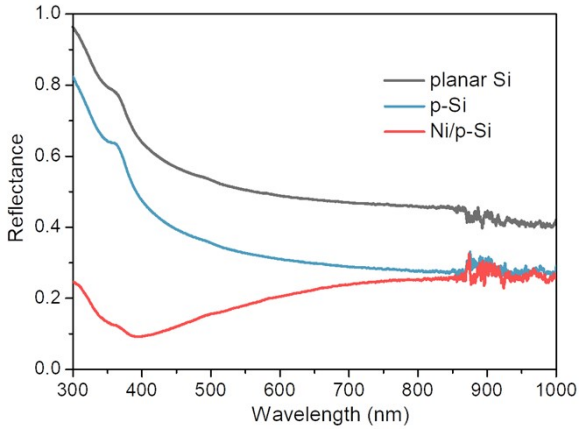


Figure S10. UV−vis diffuse reflectance spectra of planar Si, p-Si, and Ni/p-Si.

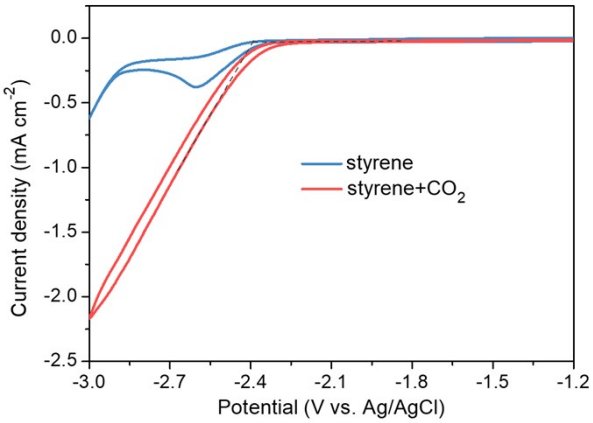


Figure S11. Cyclic voltammetry curves of 0.1 M styrene in 0.1 M TBAB acetonitrile solution with and without CO_2, recorded on a glassy carbon electrode.

Table S1. Fitted parameter values obtained from PEIS tests

	R_S (Ω)	R_{SC} (Ω)	C_{SC} (μF)	R_{CT} (Ω)	C_H (μF)
p-Si	13.11	56.35	0.43	128.50	5.29
Ni/p-Si	10.79	44.48	0.47	34.53	10.05

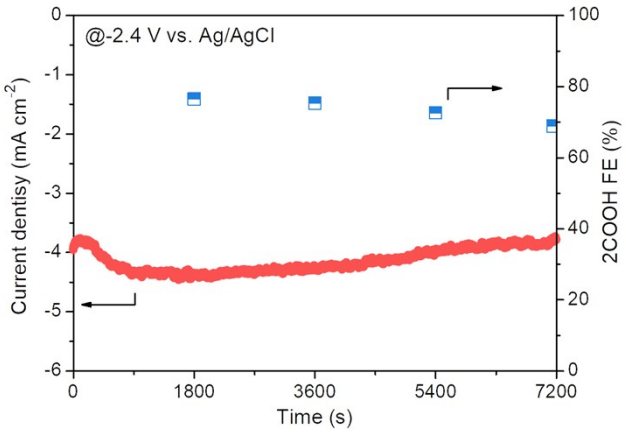


Figure S12. Photocurrent-time (*I-t*) curve of the Ni/p-Si photocathode under continuous light irradiation at a constant potential of −2.4 V vs. Ag/AgCl for 2 h, and the corresponding FE of **2COOH**.

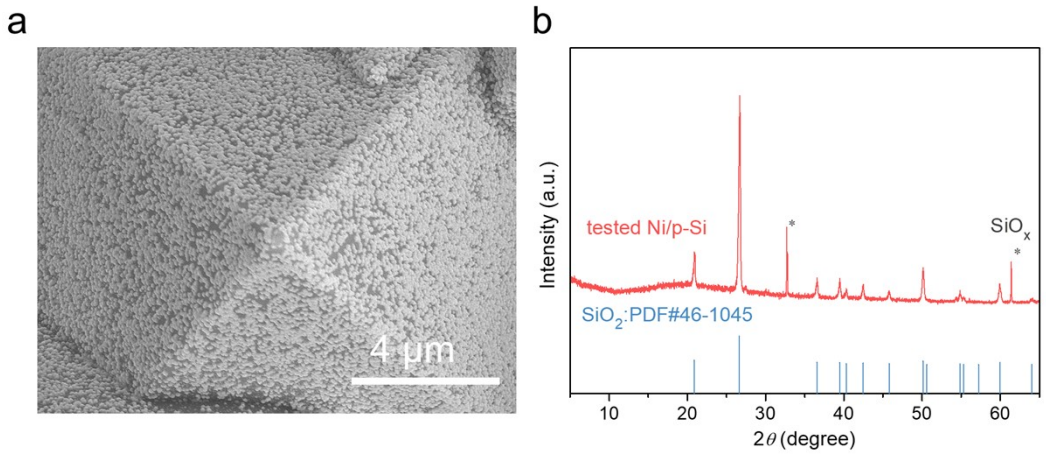


Figure S13. (a) SEM image and (b) XRD pattern of tested Ni/p-Si photocathode. * denotes the peak of SiO_x.

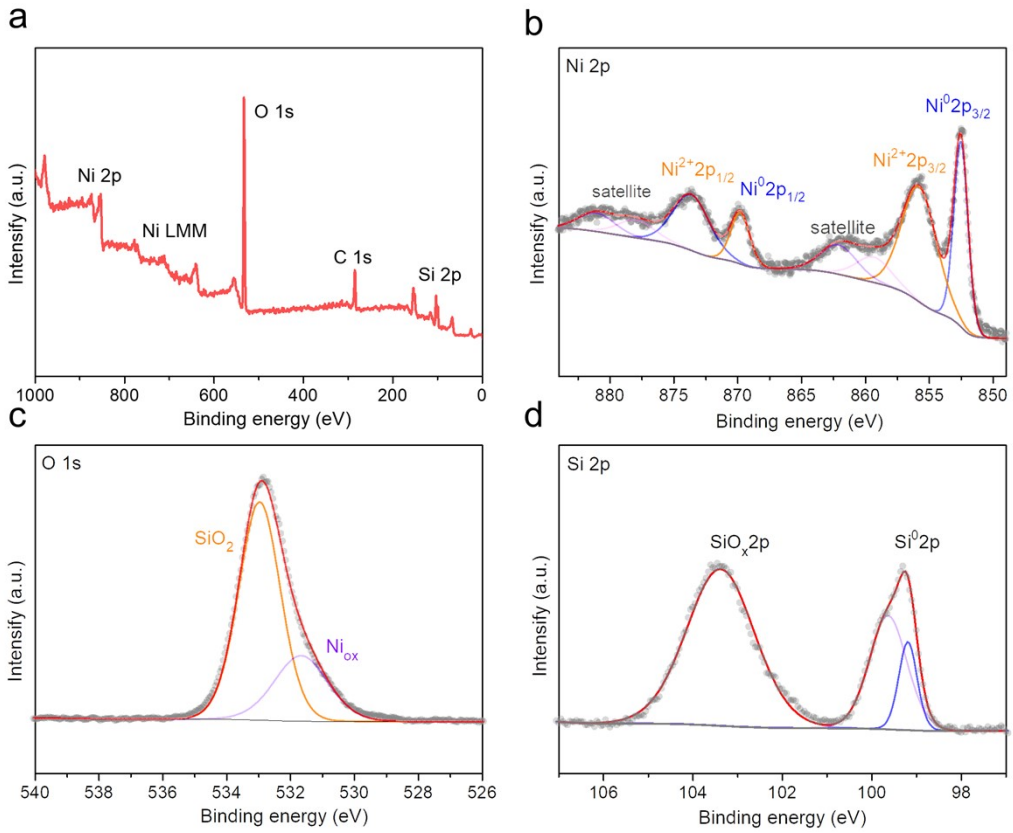


Figure S14. (a) XPS survey spectrum of Ni/p-Si after 2 h stability test. High-resolution XPS spectra of (b) Ni 2p (c) O 1s (d) Si 2p regions for Ni/p-Si after the PEC carboxylation test.

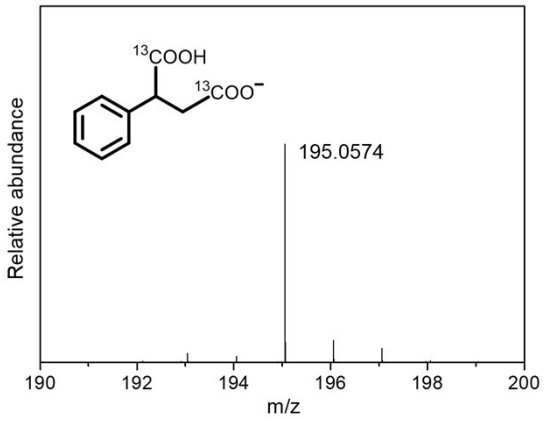


Figure S15. Time-of-flight liquid chromatography-mass spectrometry (TOF LC/MS) result from the ^{13}C labeling experiment.

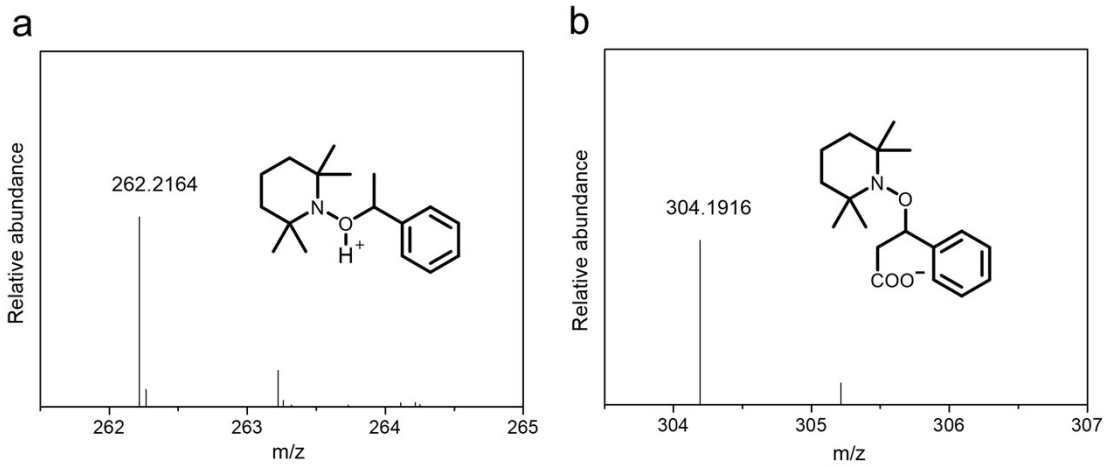


Figure S16. TOF LC/MS results from the radical trapping experiment.

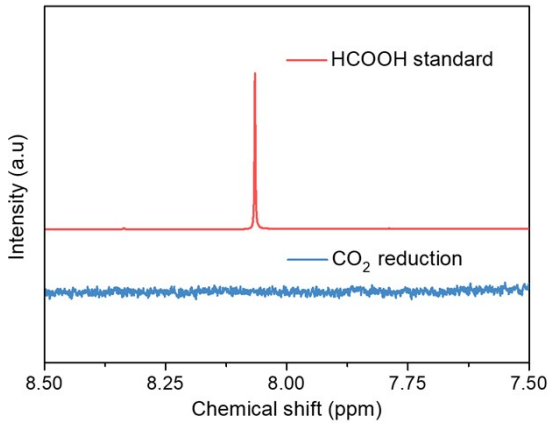


Figure S17. ^{1}H NMR spectra of HCOOH standard and the product from CO_2 reduction.

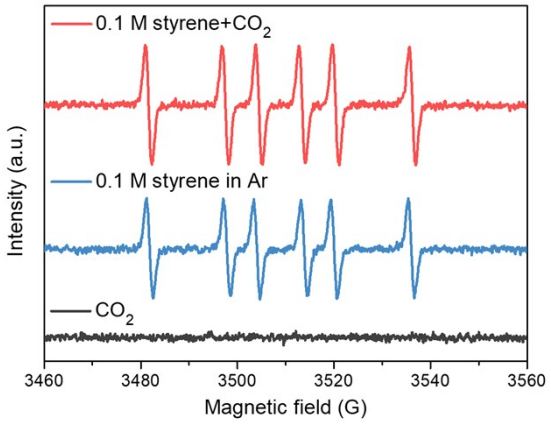
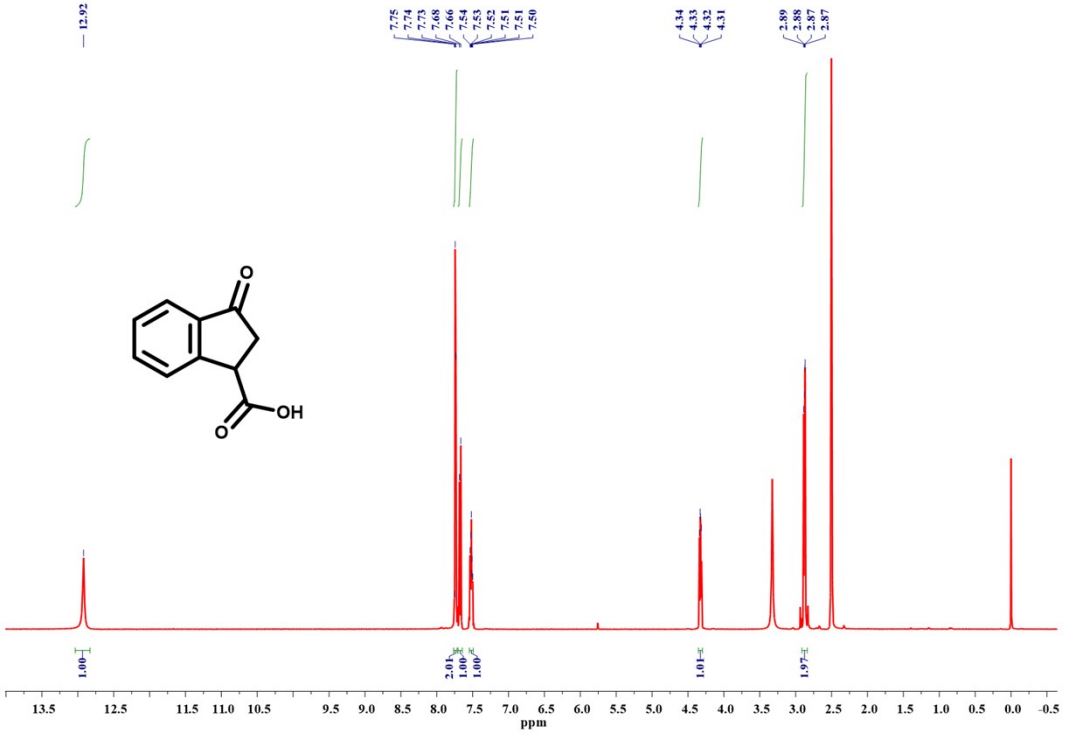
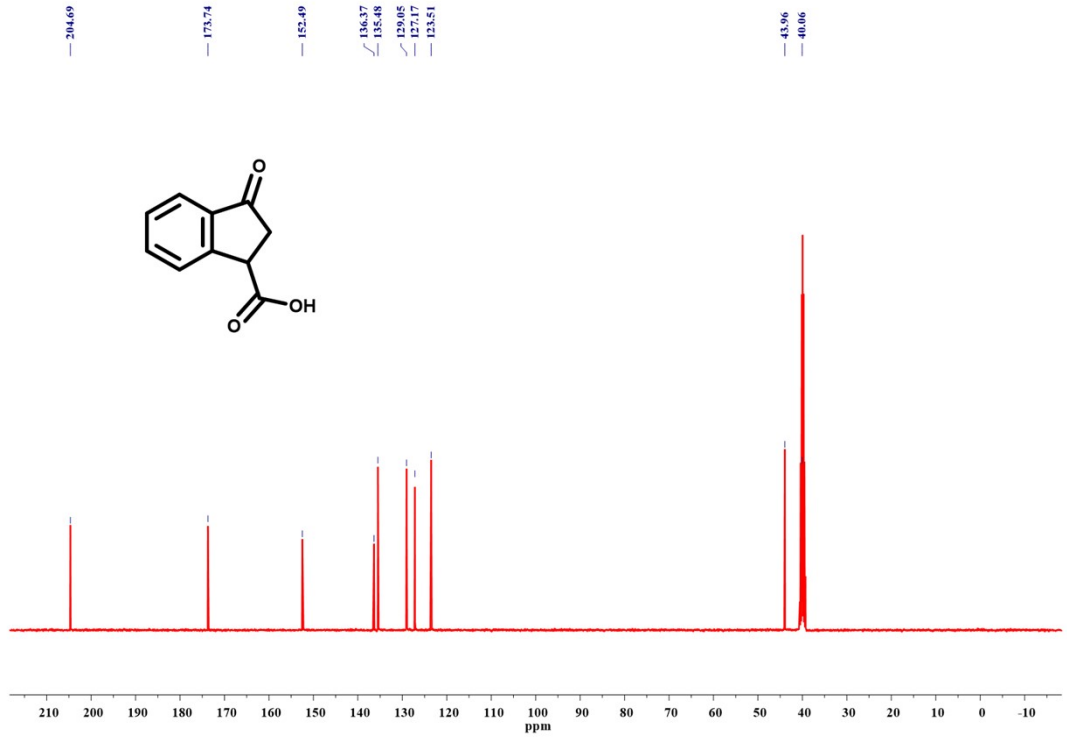


Figure S18. Probing the involvement of radical intermediates by EPR.

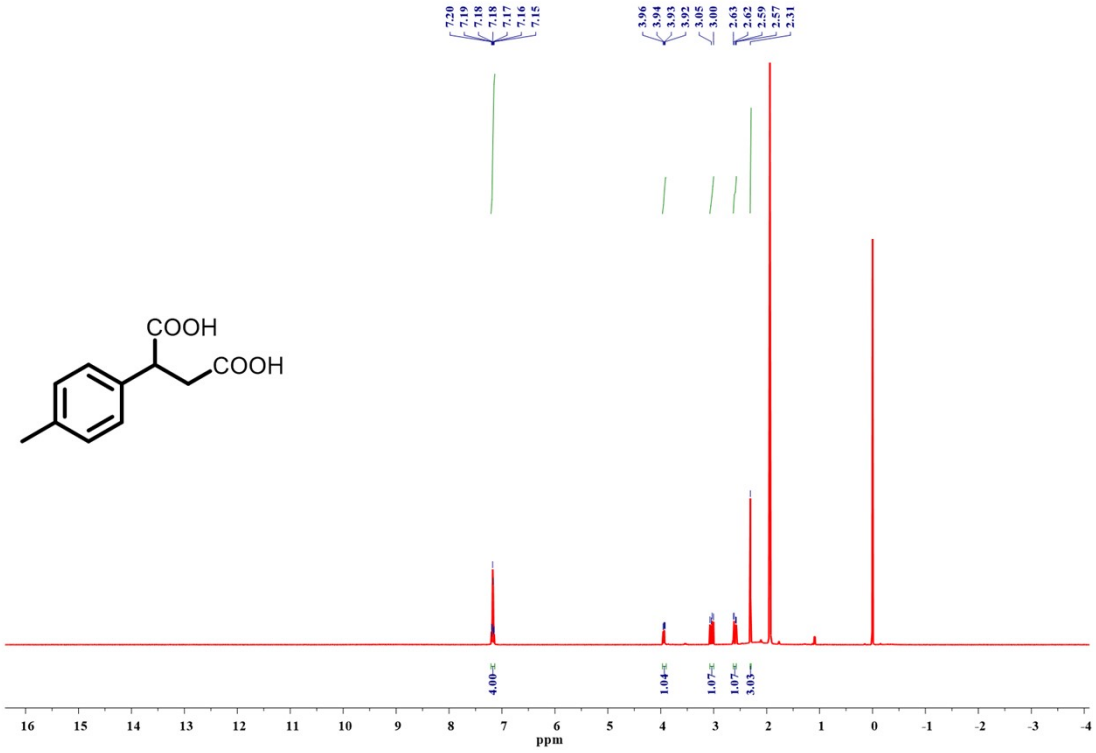
NMR spectra

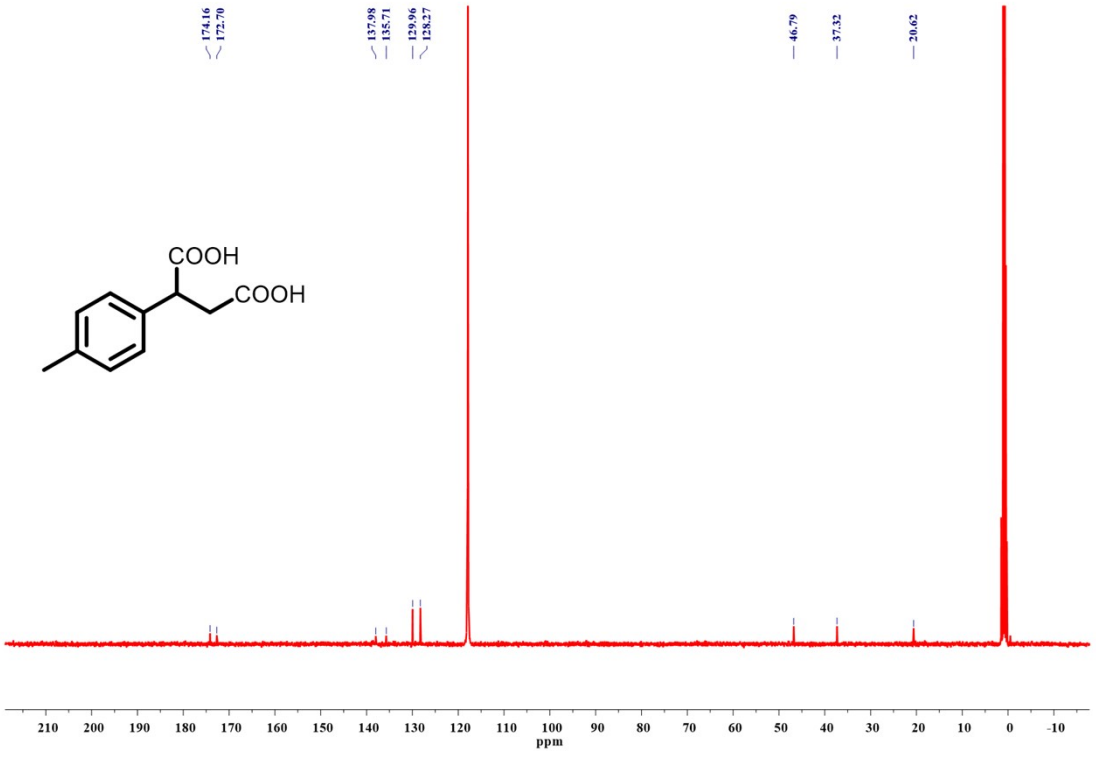
3-Oxoindan-1-carboxylic acid



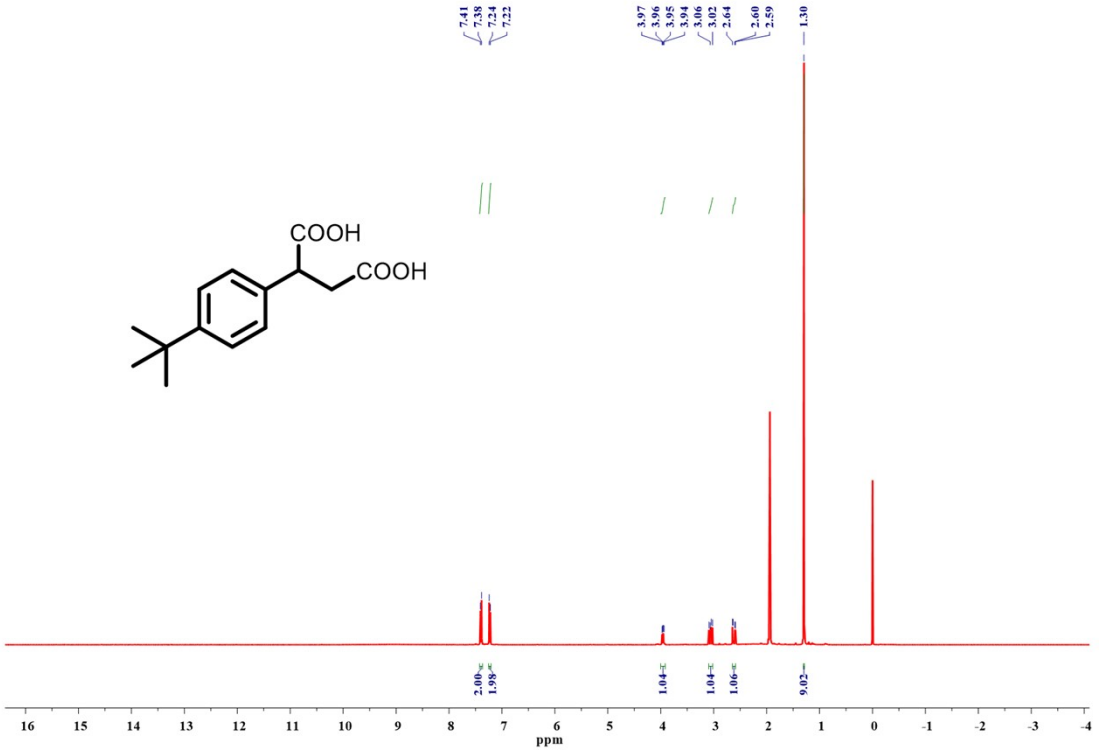


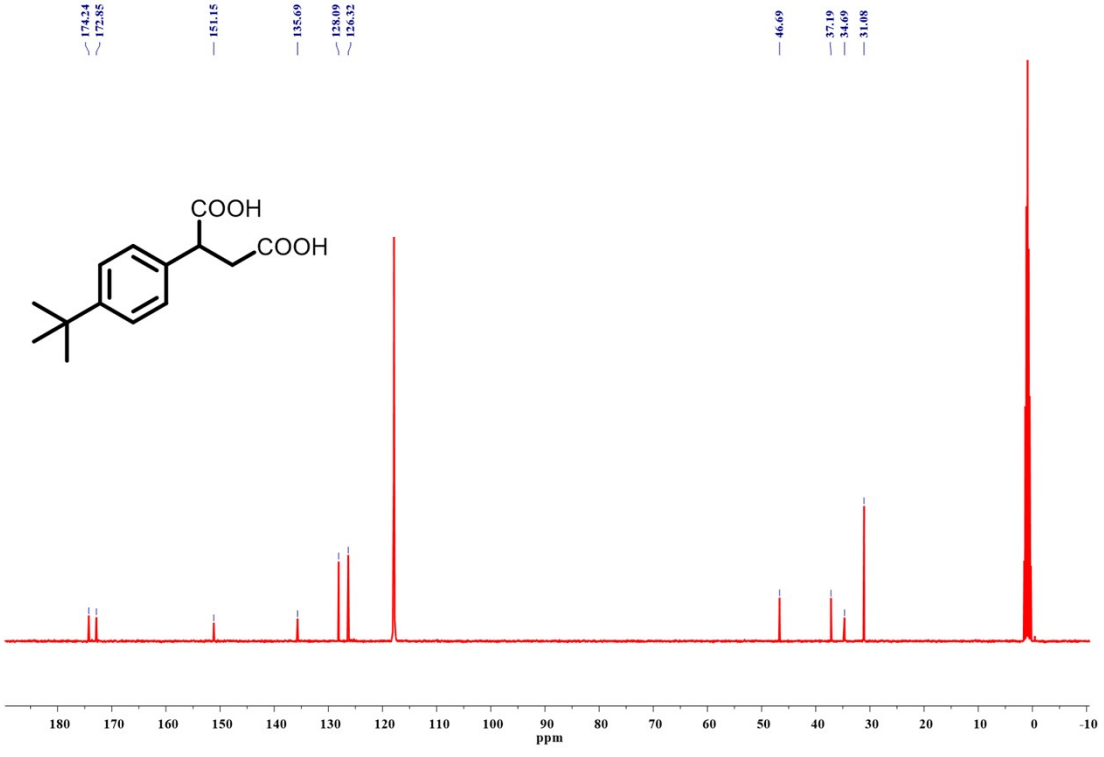
2-(p-tolyl)succinic acid



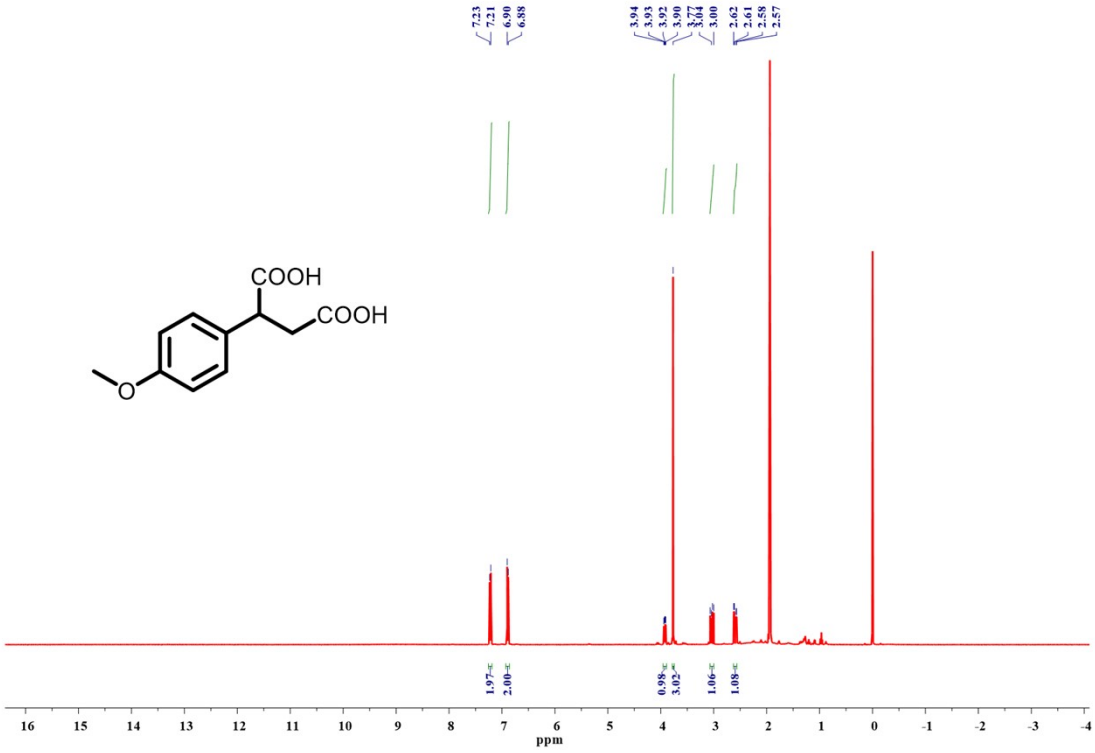


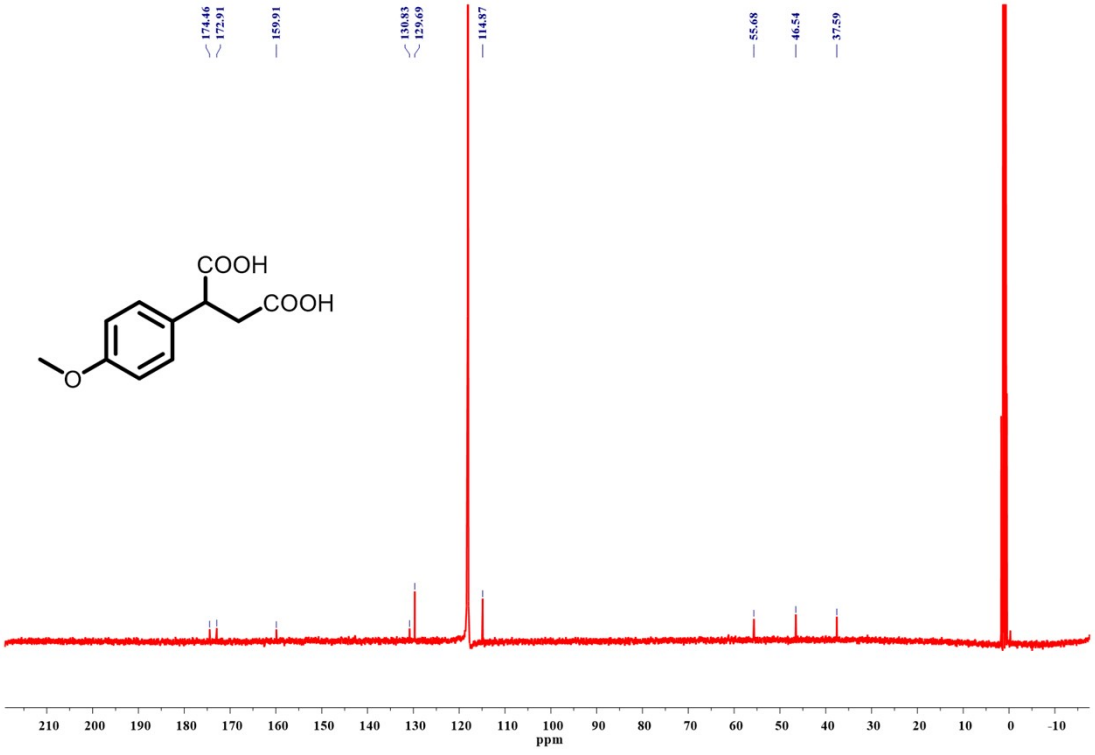
2-(4-(tert-butyl)phenyl)succinic acid



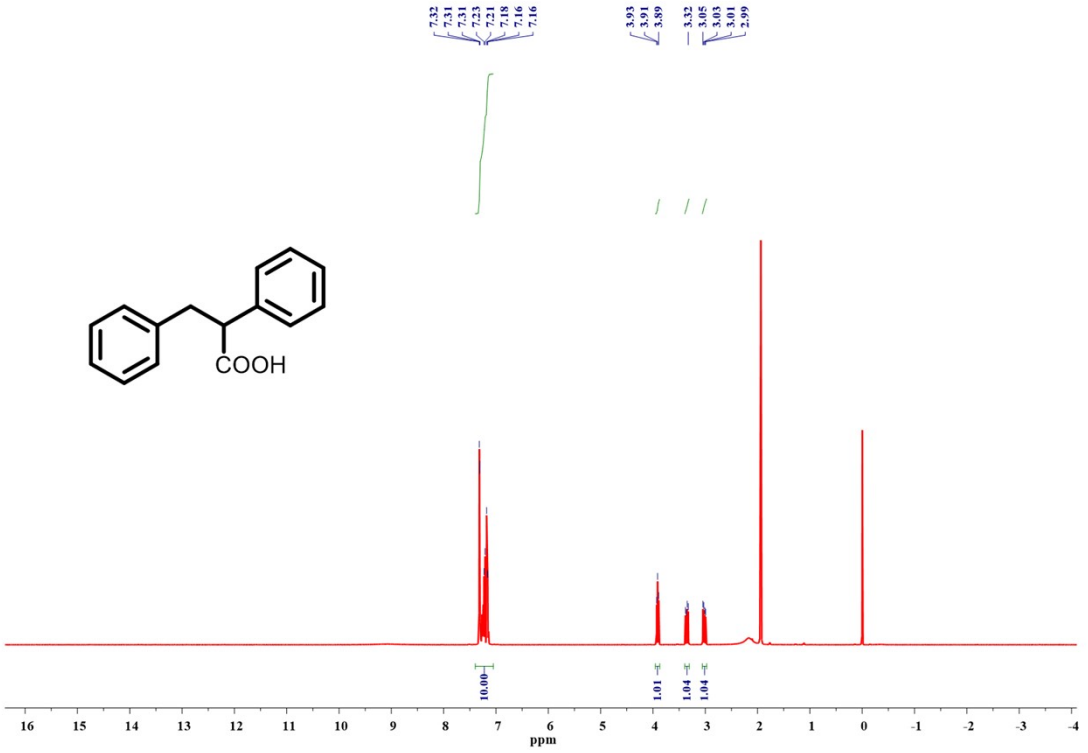


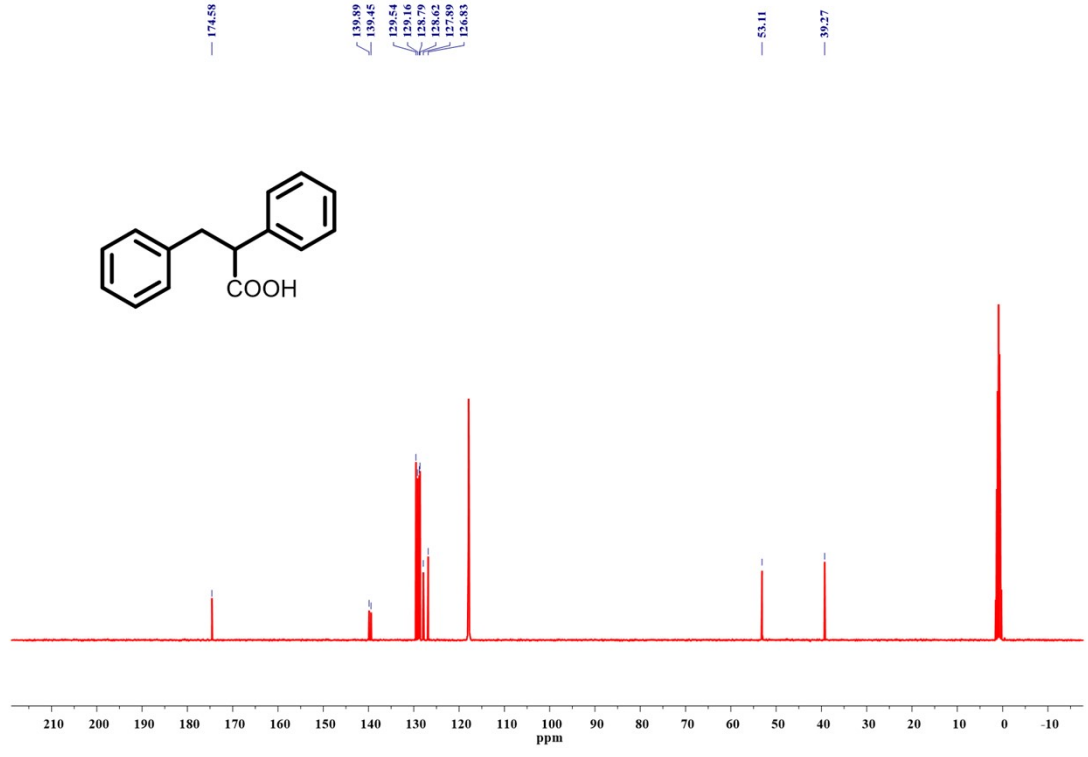
2-(4-methoxyphenyl)succinic acid



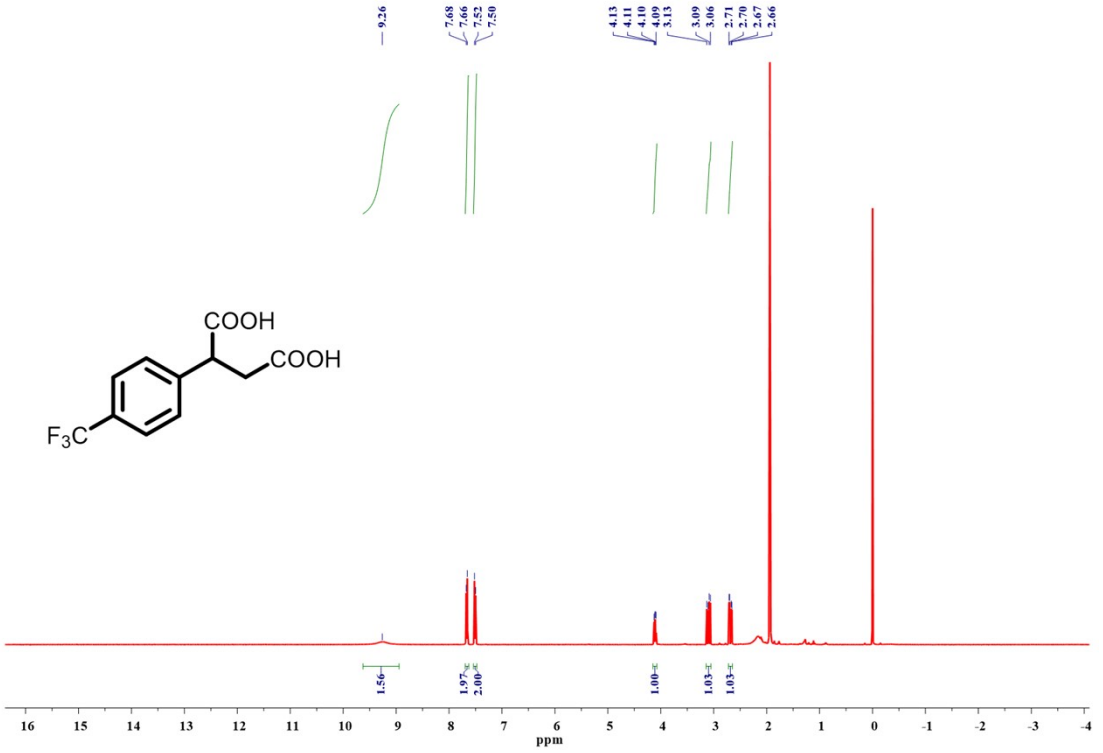


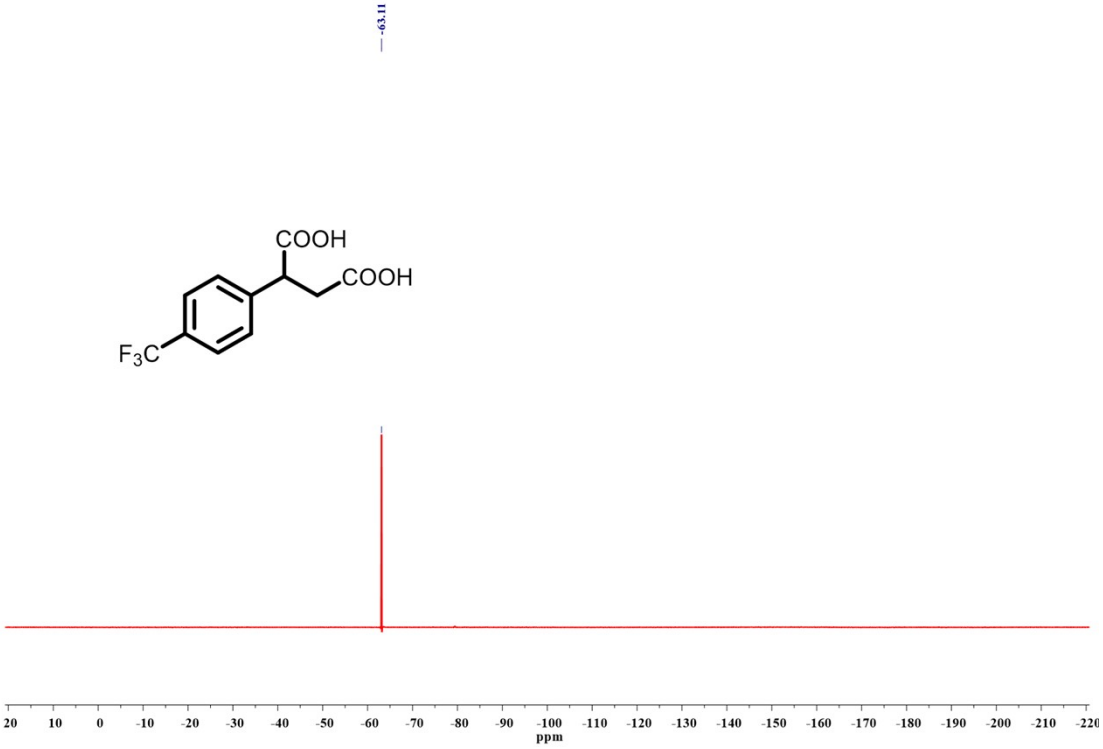
2,3-diphenylpropanoic acid

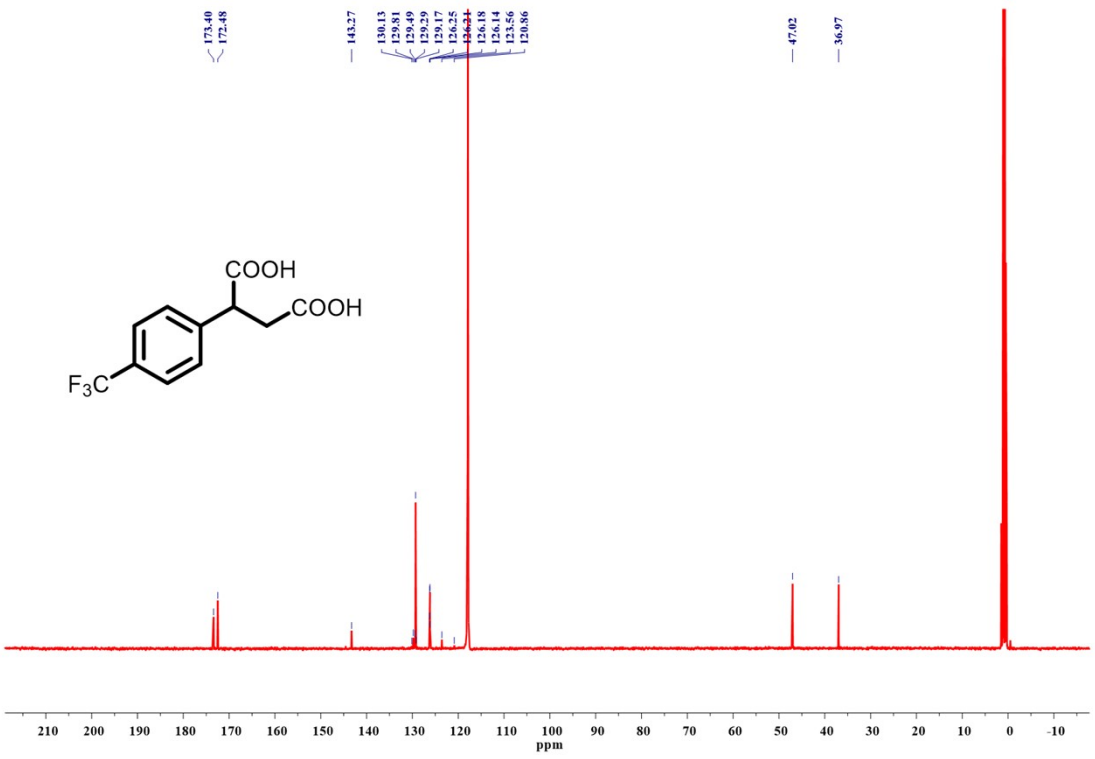




2-(4-(trifluoromethyl)phenyl)succinic acid







Supplementary Reference

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