Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Understanding Photoelectrochemical Kinetics in a Model CO_2 Fixation Reaction

Bingju Zhong, ‡ Da He, ‡ Ruonan Chen, Tianyue Gao, Yuanxing Wang, Hongyu Chen, Yanhua Zhang and Dunwei Wang**

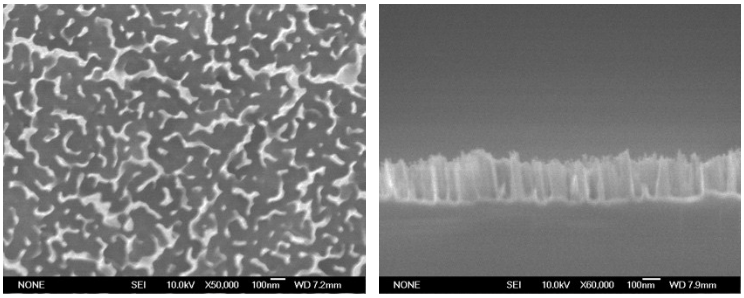
1. Materials and equipments

Acetonitrile (99.8%, for HPLC, Sigma-Aldrich) is purified and dried prior to use by passing through a solvent purification system. Trans-stilbene (>98.0%, TCI), tetrabutylammonium bromide (99%, Sigma-Aldrich), HF solution (48 wt. % in H_2O, Sigma-Aldrich) and $AgNO_3$ (>98%, Sigma-Aldrich) are used without further purification. P-Si (100) wafers (10^{15} cm^{-3} B doped, ρ: 10-20 Ω·cm, Wafernet) and Al foil (99.9995%, Alfa Aesar) are polished before use. CO_2 (99.9%) is purchased from Airgas, while Ag epoxy (MG Chemicals 8331) from SPI supplies and non-conductive hysol epoxy (EA615) from Loctite. All other reagents and materials, unless otherwise noted, are purchased from commercial vendors and used without further purification.

All non-aqueous reactions are carried out in oven-dried glassware with magnetic stirring. Except as otherwise indicated, all reactions are monitored by analytical thin-layer chromatography (TLC) performed on pre-coated TLC plates (silica gel, 0.2 mm, HSGF254). Visualization is accomplished with UV light (254 nm) and phosphomolybdic acid in ethanol by heating. Flash column chromatography is performed on silica gel (200-300 mesh, Huanghai Ltd.). Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted. Infrared spectra are obtained with KBr plates by using an IS10 FT-IR spectrometer (ThermoFisher Corp.).^1H NMR and ^{13}C NMR spectra are recorded on a JEOL 400 MHz spectrometer at ambient temperature. High resolution mass spectra (HRMS) are obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. Electrochemical data are recorded on AutoLab XM (Ameteck, PSTAT) ECS Electrochemical Test System. The sputtering of Al on Si plate is operated on radio frequency magnetron sputtering instrument (AJA International). Xenon lamp (300W, Newport, model 71228, CA, USA) equipped with an AM 1.5G filter served as simulated sunlight and illumination intensity is calibrated to 113 mW•cm^{-2} using Si photodiode. The morphology of SiNWs are imaged by a field-emission SEM (JEOL 4340F) at 10 kV.

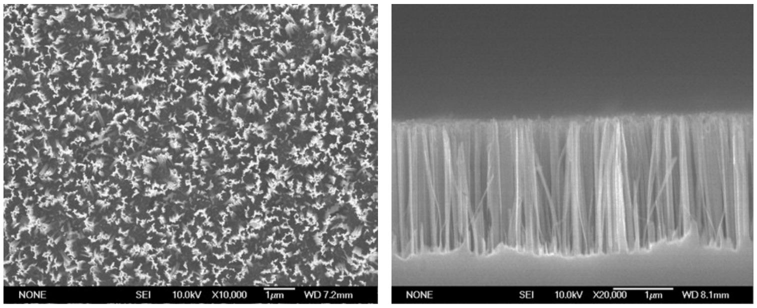
2. Synthesis of SiNWs electrode

SiNWs etching: A p-Si (100) wafer is cleaned sequentially by acetone, methanol, and isopropanol, followed by oxidation in H_2O_2/H_2SO_4 (1:3 v/v) at 90℃ for 15min to remove possible heavy metals and organic species on surface. After rinsing in deionized (DI) water and drying in air, the wafer is cut into small pieces with size of 1cm X 1cm and then immersed into $HF/AgNO_3$ solution at 50℃ to etch SiNWs of various length. Experimental results indicate that SiNWs length increases with the concentration of $AgNO_3$ and the etching time (**Fig. S1-S3**).



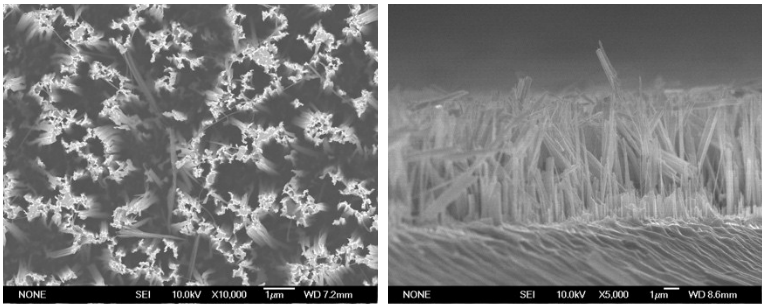
(a) (b)

Figure S1. SEM images of SiNWs etched in $HF/AgNO_3$ solution (4.6 M HF and 0.01 M $AgNO_3$) for 30 min at 50℃. The length obtained is about 200nm. (a) Top view, (b) side view.



(a) (b)

Figure S2. SEM images of SiNWs etched in $HF/AgNO_3$ solution (4.6 M HF and 0.02 M $AgNO_3$) for 30 min at 50℃. The length obtained is about 2000nm. (a) Top view, (b) side view.



(a) (b)

Figure S3. SEM images of SiNWs etched in HF/$AgNO_3$ solution (4.6 M HF and 0.02 M $AgNO_3$) for 60 min at 50℃. The length obtained is about 8000nm. (a) Top view, (b) side view.

SiNWs electrode fabrication: After throughout cleaning, the substrates containing SiNWs are immersed in HF (aqueous, 5%) for 2 min and then dried in a stream of N_2. A film of Al (300 nm) is then sputtered onto the backside of the SiNWs' substrate by radio frequency magnetron sputtering. The resulted samples are then annealed in Ar (flow rate: 5000 standard cubic centimeter per minute, SCCM) at 450℃ for 5 min. Afterward, tinned Cu wires are fixed to the Al film by Ag epoxy. Finally, non-conductive hysol epoxy is used to seal the entire substrates except for the regions where SiNWs reside.

3. Experimental procedures

Experimental instrument: As shown in **Fig. S4**, photoelectro-catalysis (PEC) system applied herein includes Xe lamp as light source and three-electrode electrochemical working station. Ag/AgBr reference electrode is soaked in a solution of 0.1 M tetrabutylammonium bromide and 0.01 M $AgNO_3$ in acetonitrile. A piece of high-pure Al foil serves as counter electrode. Fabricated SiNWs electrode is used as working electrode. And carbon dioxide is bubbled into the vessel continuously with controlled flow rate.

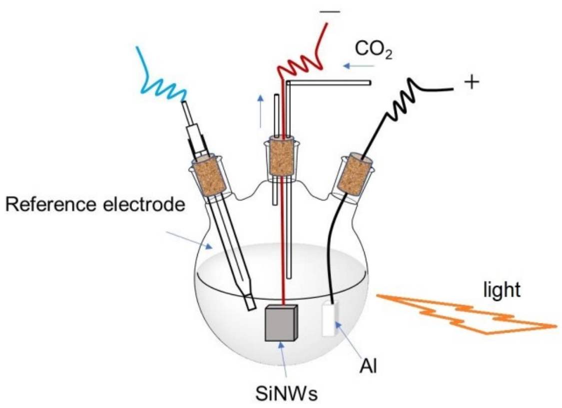
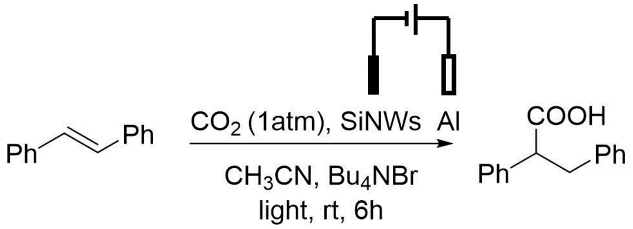


Figure S4. Three-electrode PEC configuration.

Typical experimental procedure:



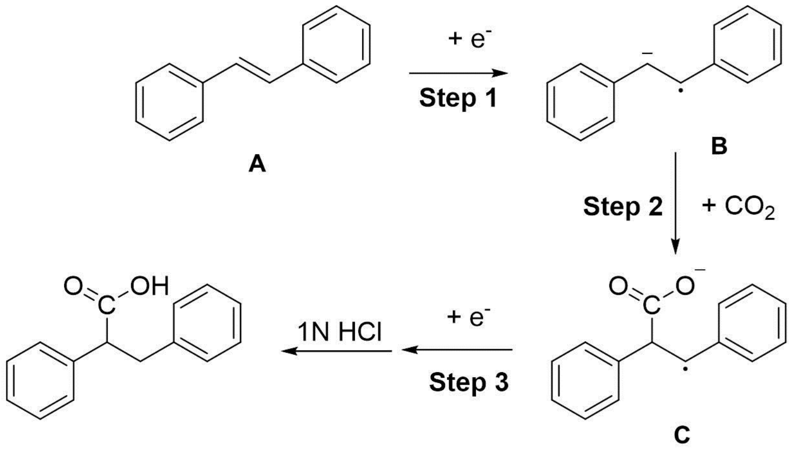
To an oven-dried three-neck round-bottom flask equipped with magnetic stir bar are charged with tetrabutylammonium bromide (3.320 g,10.0 mmol), trans-stilbene (0.072 g, 0.40 mmol) and acetonitrile (20 mL) under Ar. Then the flask is set up in photoelectro-catalysis system and a suitable potential is applied with light irradiation and vigorously stirring overnight. The crude mixture is concentrated in vacuo and quenched with 1 N HCl (3 mL), followed by extraction with diethyl ether (3 x 20 mL). The combined organic layers are dried over $MgSO_4$, filtered, and concentrated in vacuo to afford the crude product. After purification on column chromatography (Hexane/Ethyl acetate), pure 2,3-diphenylpropanoic acid is isolated as colorless solid with yield of 68.4%. **^{1}H NMR** (d^6-DMSO, 400 MHz) δ 12.37 (s, 1H), δ 7.36 – 7.13 (m, 10H), 3.86 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.29 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.94 (dd, *J* = 13.6, 6.8 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 125 MHz) δ 174.32, 139.38, 139.29, 128.94, 128.51, 128.19, 127.96, 127.11, 126.17, 52.62, 38.82; **IR** (film, cm^{-1}) 3430, 3029, 1701, 1494, 1454, 1250, 1222, 744, 696; **Exact mass calcd** for [MH$^+$] requires *m/z* 227.1072 Found 227.1073 (ES+).

Tafel test procedure: Tafel test is conducted in photoelectro-catalysis system described above with three-electrode configuration. The studied reaction solution consists of 0.5 M of Bu_4NBr and 0.40 mmol of trans-stilbene in acetonitrile (20 mL) into which CO_2 is continuously bubbled. At a certain potential and light illumination, the corresponding current is observed and recorded. Before analysis, the real potential values should be corrected according to Ohmic loss ($E_{real} = E_{measured} - iR_u$, i: current, R_u: electric resistance of solution). Then the relationship between overpotential (η) and current density (j) is concluded and Tafel slope is extracted.

Reaction order determination: To determine the reaction order (i.e., the dependence of the reaction rate on the substrate concentration), a series of j/η plots were obtained firstly at certain substrate concentration, which is similar to Tafel test procedure described above. Then plots of $\log j$ versus $\log C_{Sub}$ at different overpotentials (η) were derived. For every condition, the data was measured three times. The obtained plots ($\log j$ *vs.* $\log c$) showed identically linear at various overpotentials, and the slope reported on the reaction order.

4. Derivation of formula

The possible reaction pathway can be written step by step as shown below.



(1) If step 1 is rate-limiting step, the electron acceptance process is considered irreversible and the mass transport limitation is negligible. The relationship between

current and overpotential could be derived as below (**eq. (S1)**) from Butter-volmer equation.

$$I = 2Fk_1C_{sub}e^{\frac{\alpha\eta F}{RT}} \quad (\alpha = 0.5) \qquad \text{(S1)}$$

In this formula, *F* as Faraday constant, *R* as universal gas constant and k_1 as potential-independent rate constant are fixed values for the first active step, as while as C_{sub} as the substrate concentration. *I* is the exchange current recorded at different overpotential *(η)* and α is the transfer coefficient directly related to the Tafel slope. At room temperature (*T* = 298K), Tafel slope is about 120 mV/dec with common α value of 0.5.

(2) If step 2 is the rate-limiting step, step 1 is assumed to reach quasi-equilibrium and the equilibrium constant should be expressed as **eq. (S2)**.

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[B]}{C_{sub}e^{\frac{\alpha\eta F}{RT}}} \quad (\alpha = 1) \qquad \text{(S2)}$$

k_1 and k_{-1} are forward and reverse reaction rate constant, respectively. [*B*] is the concentration of radical intermediate from step 1. Based on the rate law of step 2 (**eq. (S3)**), the final expression is derived as **eq. (S4)** after substitution for [*B*].

$$I = 2Fk_2[B]P_{CO_2} \qquad \text{(S3)}$$

$$I = 2F\frac{k_1}{k_{-1}}k_2C_{sub}P_{CO_2}e^{\frac{\alpha\eta F}{RT}} \ (\alpha = 1) \qquad \text{(S4)}$$

k_2 is the reaction rate constant of step 2 and P_{CO_2} is the partial pressure of CO_2. According to **eq. (S4)**, Tafel slope is about 60 mv/dec with a common α value of 1 at room temperature.

(3) If step 3 is the rate-limiting step, step 1 and step 2 are both assumed to reach quasi-equilibrium and the equilibrium constant should be expressed as **eq. (S2)** and **eq. (S5)**, respectively, in which [*C*] is the concentration of carboxylated radical intermediate from

step 2. After substitution for [*B*] and [*C*] in the rate law of step 3 (**eq. (S6)**), the final equation is obtained as **eq. (S7)**.

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[C]}{[B]P_{CO_2}} \qquad \text{(S5)}$$

$$I = 2Fk_3[C]e^{\frac{\alpha' \eta F}{RT}} \; (\alpha' = 0.5) \qquad \text{(S6)}$$

$$I = 2F\frac{k_2}{k_{-2}}\frac{k_1}{k_{-1}}k_3 C_{sub} P_{CO_2} e^{\frac{\alpha_t \eta F}{RT}} \; (\alpha_t = \alpha + \alpha' = 1.5) \qquad \text{(S7)}$$

k_3 is the reaction rate constant of step 3, and the corresponding Tafel slope is about 40 mv/dec when applying final α value (α_t) of 1.5.

By analysis of logarithms of **eq. (S1)**, **eq. (S4)** and **eq. (S7)**, a common equation to show the relationship between overpotential η and current density j is concluded as below which is indicated in main text (**eq. (1)**):

$$\eta = \frac{2.303RT}{\alpha F}\log j + A \qquad \text{(1)}$$

Moreover, extracted Tafel slope (η vs. $\log j$) is inversely proportional to the transfer coefficient (α), as shown in **equation (S8).**

$$\text{Tafel slope} = \frac{2.303\text{RT}}{\alpha\text{F}} \qquad \text{(S8)}$$

5. Supplementary Figures

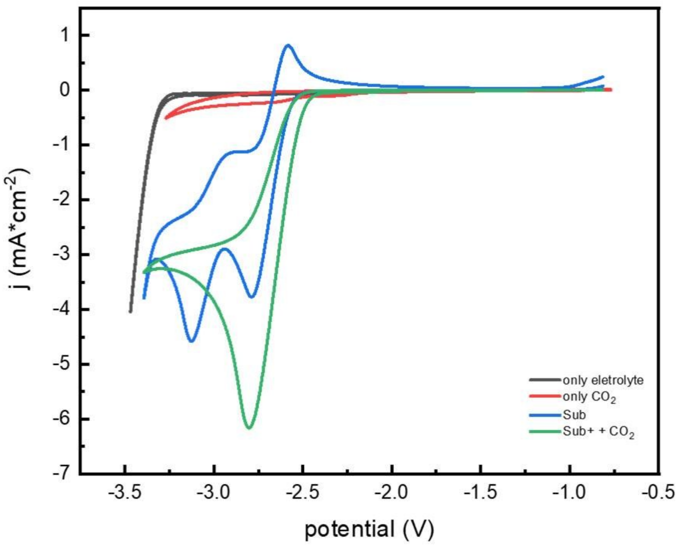


Figure S5. Cyclic voltammograms (E *vs.* Ag/AgBr) on glassy carbon electrode of only electrolyte (0.5 M of Bu_4NBr in acetonitrile, black trace), electrolyte (0.5 M of Bu_4NBr) with CO_2 bubbling (red trace), electrolyte (0.5 M of Bu_4NBr) containing substrate (20 mM in acetonitrile, blue trace) and electrolyte (0.5 M of Bu_4NBr) containing substrate with CO_2 bubbling (20 mM in acetonitrile, green trace).

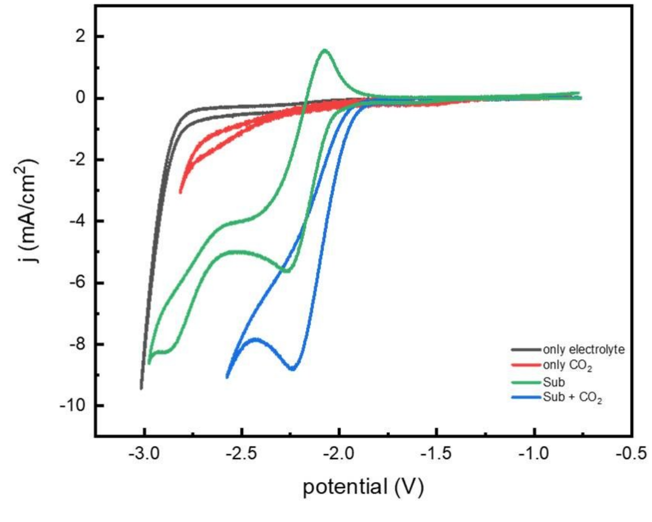


Figure S6. Cyclic voltammograms (E *vs.* Ag/AgBr) on SiNWs electrode of only electrolyte (0.5 M of Bu_4NBr in acetonitrile, black trace), electrolyte (0.5 M of Bu_4NBr) with CO_2 bubbling (red trace), electrolyte (0.5 M of Bu_4NBr) containing substrate (20 mM in acetonitrile, green trace) and electrolyte (0.5 M of Bu_4NBr) containing substrate with CO_2 bubbling (20 mM in acetonitrile, blue trace).

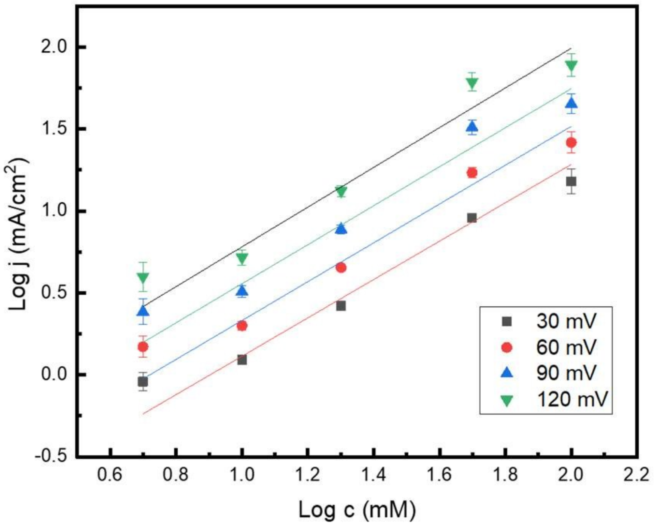


Figure S7. Current density *vs.* substrate concentration at different over potential on glassy carbon electrode (reaction order ≈ 1). The reaction solution consists of 0.5 M of Bu_4NBr and various amount (5, 10, 20, 50 and 100 mM) of trans-stilbene in 20.0 mL of acetonitrile with CO_2 bubbling.

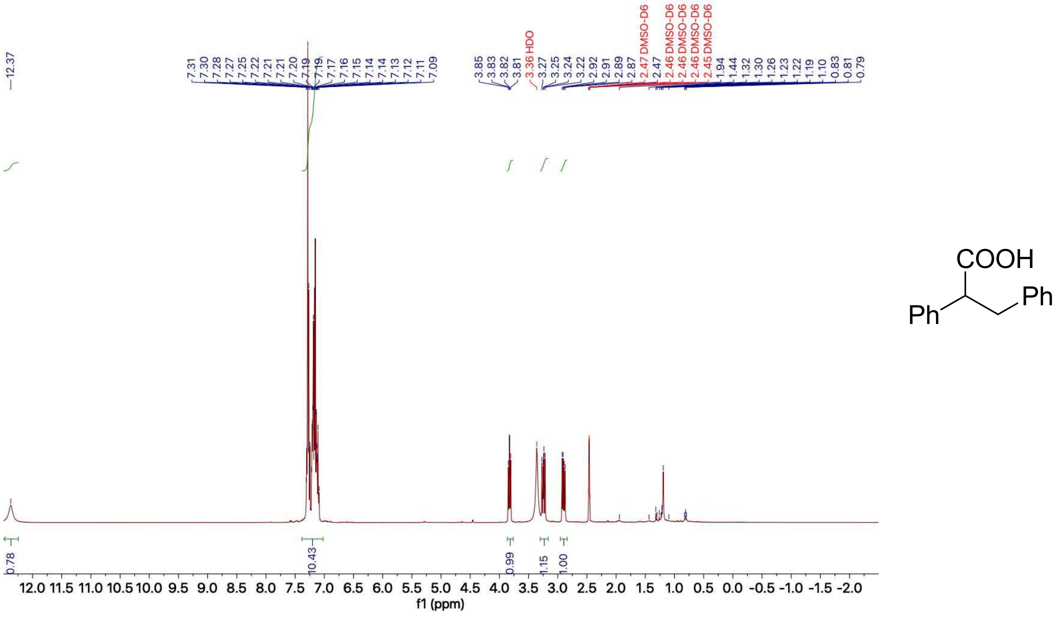


Figure S8. ^{1}H NMR (d^6-DMSO, 400 MHz) of 2,3-diphenylpropanoic acid.

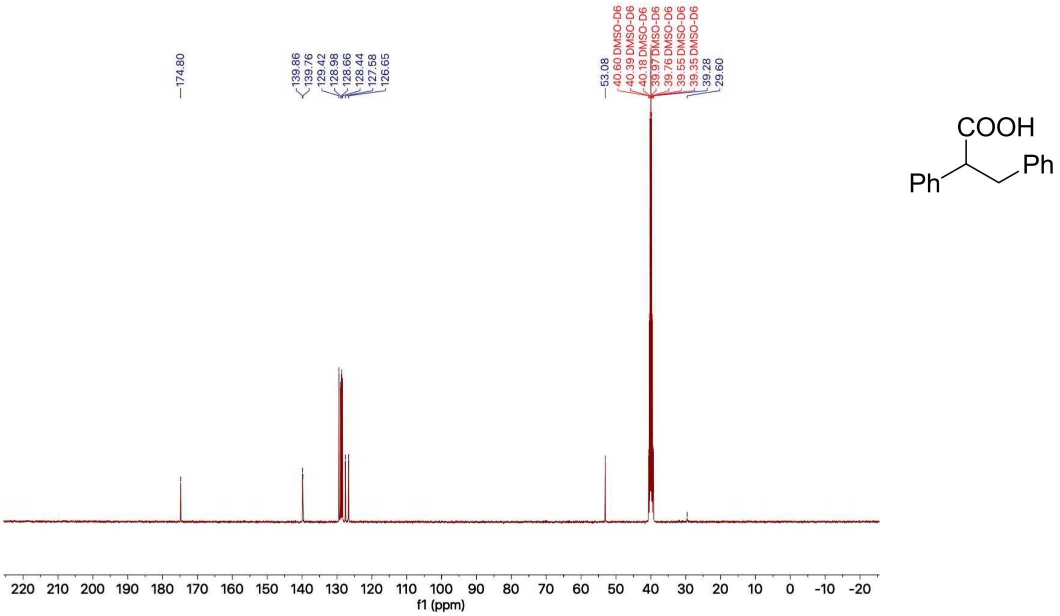


Figure S9. ^{13}C NMR (d^6-DMSO, 125 MHz) of 2,3-diphenylpropanoic acid.