

# Supporting Information

## Silver encapsulated copper salen complexes: Highly efficient catalyst for electrocarboxylation of cinnamyl chloride with CO<sub>2</sub>

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## 1. Materials and Instrument

Galvanostatic electrosynthesis was performed using a digital direct current-regulated power supply (HY3005MT, HYElec® China). Voltammetric measurements were conducted using electrochemical station (CHI650C, Chenhua) in a conventional three-electrode cell. The product yield was determined by high-performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) (Thermo Scientific, Germering, Germany) equipped with a UV (RS Variable Wavelength) (Thermo Scientific, Germering, Germany) detector. Microstructure and morphology of [M]@Ag were analyzed using Hitachi S4800 field-emission scanning electron microscope (FE-SEM) (Hitachi, Tokyo, Japan) equipped with an energy dispersive X-Ray fluorescence spectrometer (Ametek, Oxford, UK). X-ray diffraction (XRD) (Rigaku Corporation, Tokyo, Japan) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu K $\alpha$  radiation ( $k = 1.5406 \text{ \AA}$ ).  $^1\text{H}$ NMR spectra were recorded on an AVANCE 500 (500 MHz, Bruker, Germany) spectrometer in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as an internal standard. The calculation of energy was performed in Gaussian 09 D.01 using B3LYP method with 6-31+G(d,p) set. All substrates, vinylacetic acid (**2d**) and Co-salen were used as received (Energy chemical, China). MeCN were kept over 4  $\text{\AA}$  molecular sieves.

## 2. General procedure

### 2.1 Preparation of cathodes

The synthesis process of [M]@Ag cathode was shown in Scheme S1.

Synthesis of [Cu]@Ag: In typical procedure, 16 mg Cu-salen prepared as described in literature<sup>1</sup> and 0.5 g sodium dodecyl sulfate (SDS) were added into a solution of 0.85 g  $\text{AgNO}_3$  and 50 mL distilled water. After stirring for 30 min, 0.17 g zinc powder was slowly added into the reaction system and then the solution was stirred for 8 hours at room temperature. The product was collected by centrifuging, washed with 5 mL of 1 M HCl for 2 times to remove remaining zinc powder, then washed with distilled water and ethanol for many times and dried under vacuum overnight. Finally, the powder was pressed into a coin ( $d = 2 \text{ cm}$ ) and used as cathode.



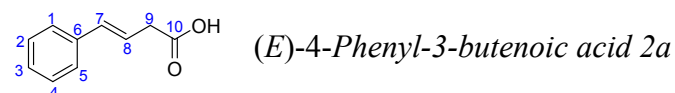
Scheme S1. Synthesis Process of [M]@Ag cathode

[Co]@Ag and Ag NPs were prepared in the same way. In case of [Co]@Ag, 16 mg of Co-salen was added into the reaction system instead of Cu-salen. In case of Ag NPs, no metal salen complex was added.

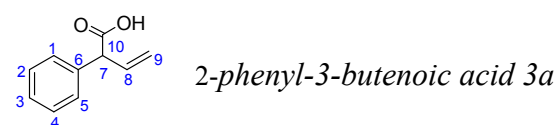
## 2.2 Electrochemical study

Electrochemical measurements were performed in a conventional three-electrode cell at a electrochemical workstation (CHI 650C). Typically, 10 mg of synthetic powder was suspended in the mixture solution of 40 uL Nafion solution (5 wt%), 750 uL deionized water and 250 uL ethanol, and a homogeneous ink was formed by ultrasound for 1 h. Then, 6 uL of the ink was loaded onto a glassy carbon electrode (GC) with 1 mm radius. The electrochemical behavior of **1a** was scanned at different cathodes ([Cu]@Ag, [Co]@Ag, Ag NPs) in tetraethylammonium chloride-acetonitrile (TEACl-MeCN) solution with a sweep rate of 0.2 V s<sup>-1</sup> in a nitrogen atmosphere. The counter and the reference electrodes were the platinum sheet (1 cm × 2 cm) the Ag/AgI/0.1 mol L<sup>-1</sup> TBAI respectively.

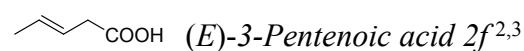
Typical electrocatalytic carboxylation was conducted in a mixture of 50 mM cinnamyl chloride (**1a**), 0.1 M TEACl and 10 mL MeCN saturated with CO<sub>2</sub> (1 atm) in an undivided cell equipped with [Cu]@Ag cathode and Mg rod anode in One-compartment electrolytic cell. During the electrolysis process, CO<sub>2</sub> bubbles are always bubbling into the reaction system. The electrolysis was stopped after the consumption of 2.0 F/mol of **1a**. At the end of the electrolysis, MeCN was removed under reduced pressure, the rest was hydrolyzed with hydrochloric acid (0.2 M, 15 mL) and extracted with Et<sub>2</sub>O (15 mL) for 4 times. Combined ethereal layers and dried with MgSO<sub>4</sub> for 4 h, after then remove the solvent under reduced pressure, products **2a** and **3a** were purified using flash chromatography (Petroleum ether-ethyl acetate 16:1) and characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR. The yields were determined by high-performance liquid chromatography (HPLC).



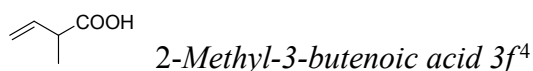
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43-7.38 (m, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.28-7.24 (m, 1H), 6.55 (d, J = 15.9 Hz, 1H), 6.31 (dt, J = 15.9, 7.1 Hz, 1H), 3.33 (dd, J = 7.1, 1.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.24 (C-10), 136.66 (C-6), 134.05 (C-7), 128.60 (C-2, C-4), 127.74 (C-3), 126.37 (C-1, C-5), 120.80 (C-8), 38.08 (C-9) ppm.



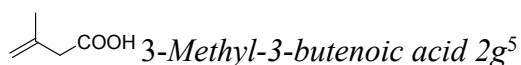
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.44 -7.29 (m, 5H), 6.24 (ddd, J = 17.7, 10.2, 8.0 Hz, 1H), 5.40-5.05 (m, 2H), 4.36 (d, J = 8.0 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.71 (C-10), 137.40 (C-6), 135.00 (C-8), 128.86 (C-2, C-4), 128.15 (C-1, C-5), 127.67 (C-3), 118.15 (C-9), 55.58 (C-7) ppm.



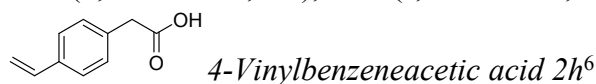
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.55 (s, 1H), 5.82-5.40 (m, 2H), 3.12 (dd, J = 6.9, 6.6 Hz, 2H), 1.79-1.56 (m, 3H) ppm.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.69 (s, 1H), 5.94 (ddd, J = 17.4, 10.3, 7.4 Hz, 1H), 5.27-5.09 (m, 2H), 3.19 (pt, J = 7.1, 1.2 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H) ppm.



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.98 (p, J = 1.6 Hz, 1H), 4.91 (t, J = 1.5 Hz, 1H), 3.11 (d, J = 1.2 Hz, 2H), 1.86 (s, J = 1.1 Hz, 3H) ppm.



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43-7.25 (m, 3H), 7.25-7.10 (m, 1H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (ddd, J = 17.6, 8.9, 0.9 Hz, 1H), 5.27 (ddd, J = 10.9, 9.0, 0.9 Hz, 1H), 3.67 (d, J = 3.2 Hz, 2H) ppm.

### 3. Summary and comparison of different ways to synthesize β,γ-unsaturated carboxylic acids

Table S1 Summary and comparison of different methods for the preparation of β,γ-unsaturated carboxylic acids

Entry	Model substrate	Catalyst	Reductant	Yield /% (L:B) <sup>a</sup>	Ref
1		NiBr <sub>2</sub> ·glyme	Mn & Zn (2.4 equiv.)	77 (99:1)	7
2		Ni(acac) <sub>2</sub>	Mn (2.0 equiv.)	88 (L)	8
3		PdCl <sub>2</sub>	Et <sub>2</sub> Zn (3.0 equiv.)	94 (B)	9
4		NiBr <sub>2</sub> ·glyme	Zn (4 equiv.)	70 (99:1)	10
5		-	In (0.67equiv.)	72 (L)	11
6		-	Zn (1.05 equiv.)	87 (B)	12
7		Pd(OAc) <sub>2</sub>	Electric current	85 (1:20)	13
8		[Cu]@Ag electrode	Electric current	98 (3:1)	This work

<sup>a</sup> L = Linear structure, B = Branch structure.

### 4. EDX Spectrum of [Cu]@Ag and [Co]@Ag

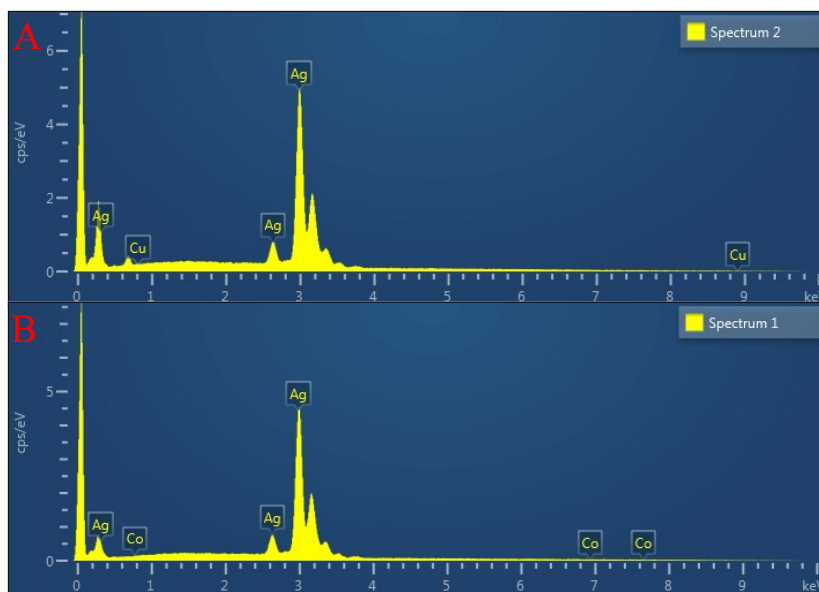


Figure S1. EDX Spectrum of [Cu]@Ag (A); [Co]@Ag composite (B)

## 5. Energy of product in gas phase

Table S2 Energy of product in gas phase<sup>a</sup>

Entry	Product	Energy/Hartree <sup>b</sup>
1	<chem>C=C(Cc1ccccc1)CC(=O)O</chem> <b>2a</b>	-537.573
2	<chem>C=C(C(=O)O)c1ccccc1</chem> <b>3a</b>	-537.562
3	<chem>C=C(C)CC(=O)O</chem> <b>2f</b>	-345.825
4	<chem>C=C(C)C(=O)O</chem> <b>3f</b>	-345.819

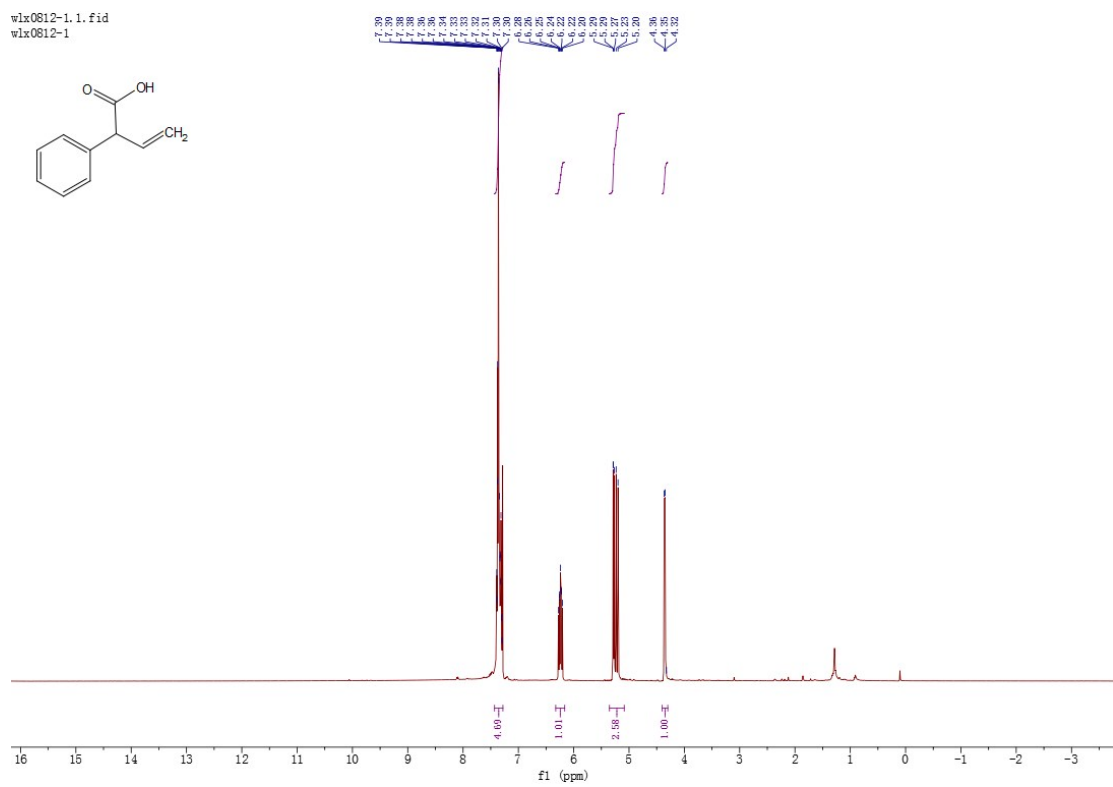
<sup>a</sup>: Calculations were performed in Gaussian 09 D.01 using B3LYP method with 6-31+G(d,p) set.

<sup>b</sup>: 1 Hartree = 627.51 Kcal mol<sup>-1</sup>.

## 6. NMR characterization

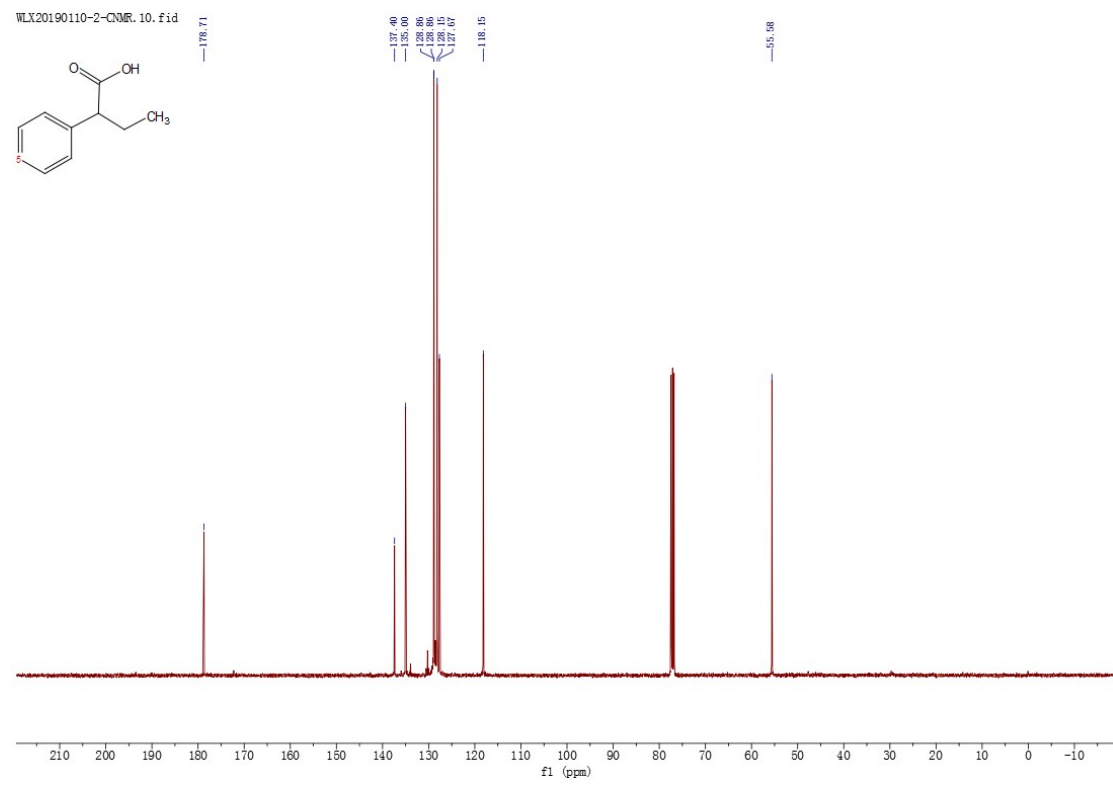


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wlx0812-1

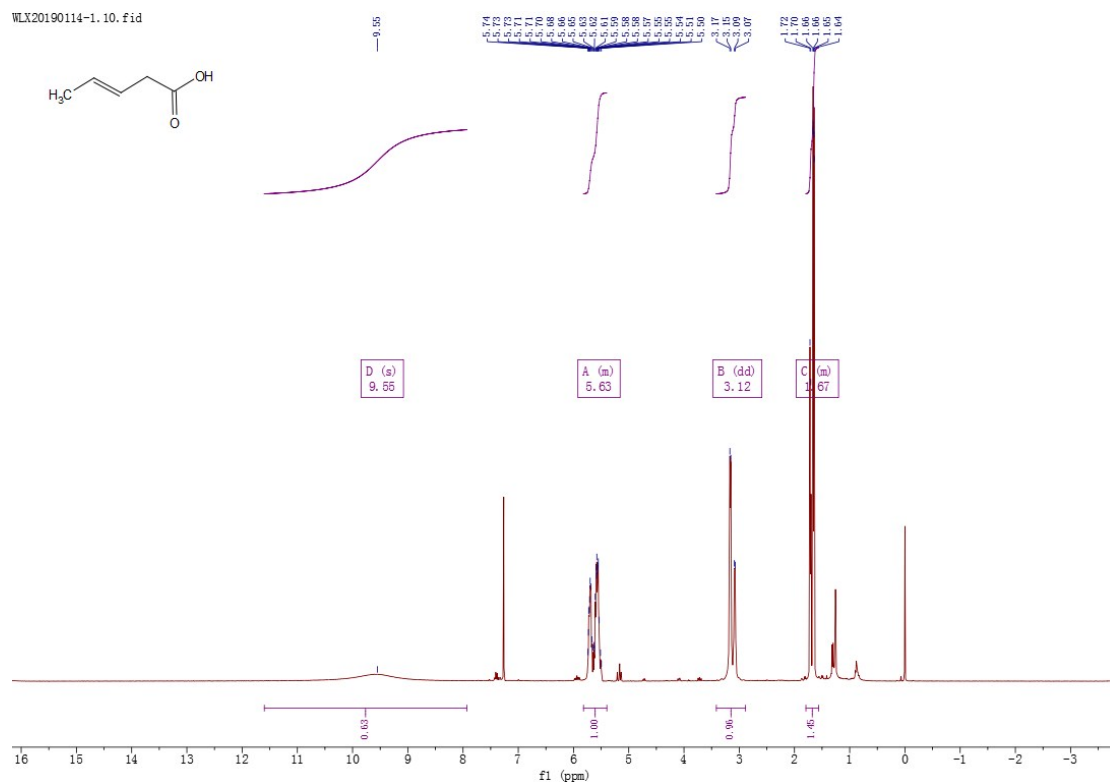


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-phenyl-3-butenoic acid **3a**

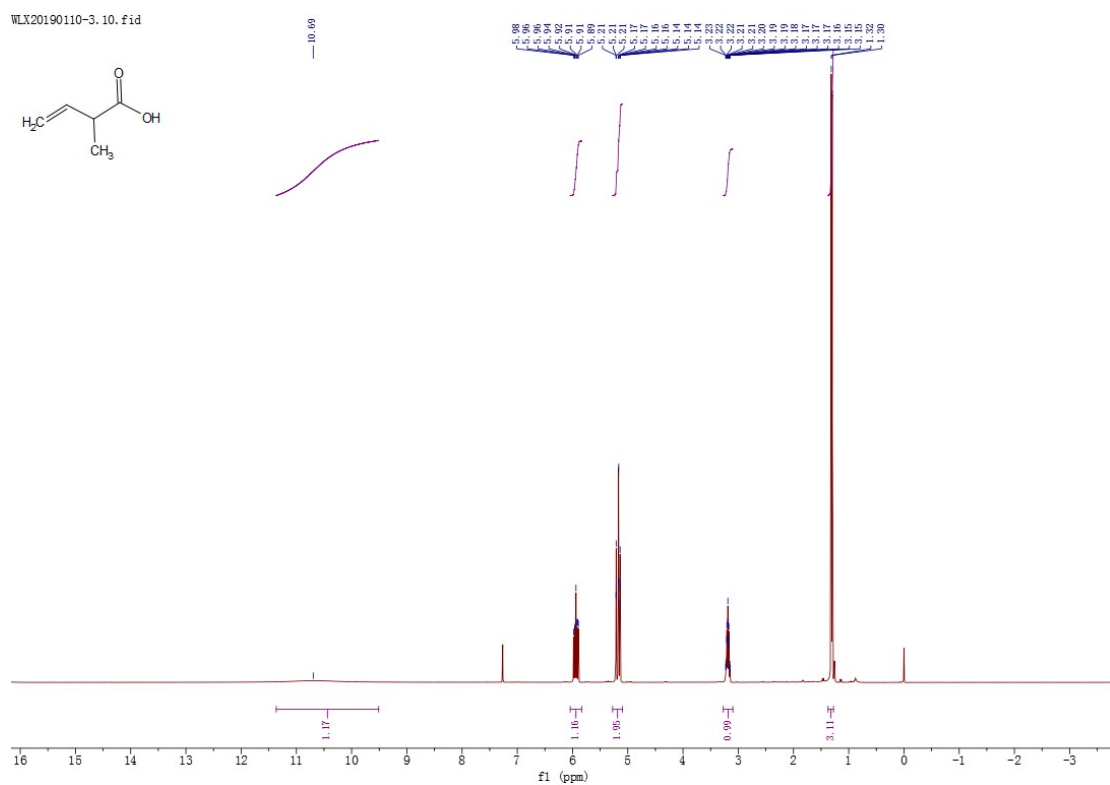
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<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 2-phenyl-3-butenoic acid **3a**



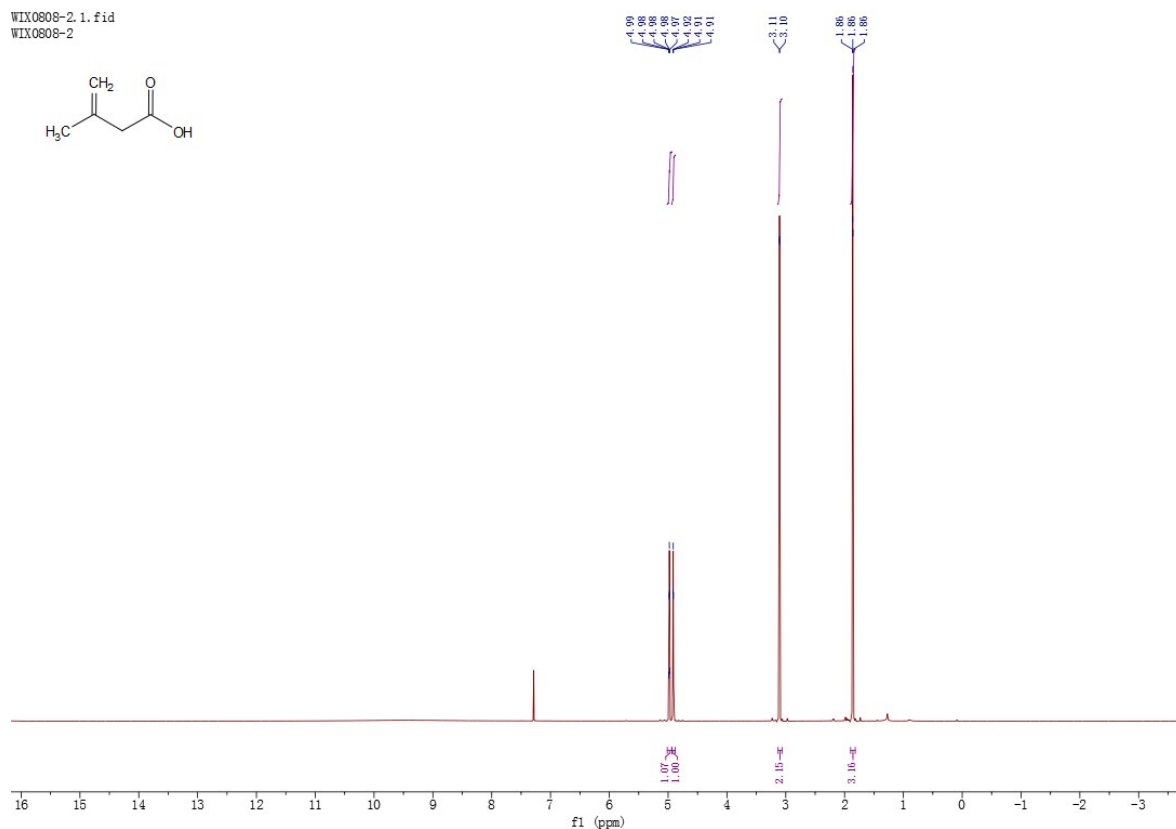
<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>) of (*E*)-3-pentenoic acid **2f**



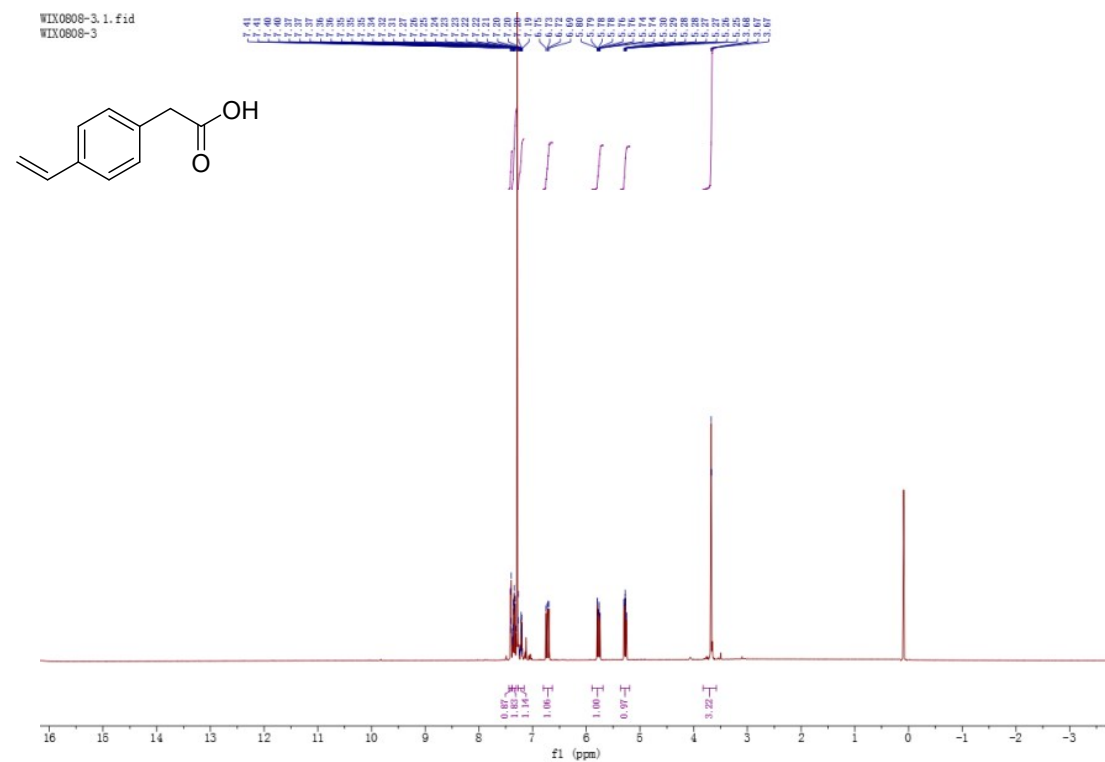
<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>) of 2-Methyl-3-butenoic acid **3f**



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$^1\text{H}$ NMR (500 MHz,  $\text{CDCl}_3$ ) 3-Methyl-3-butenoic acid **2g**



$^1\text{H}$ NMR (500 MHz,  $\text{CDCl}_3$ ) 4-Vinylbenzeneacetic acid **2h**

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