Supplementary Information (SI) for ChemComm.

# Supporting Information

# Silver Nanoparticle-Immobilized Benzimidazole-Linked Porphyrin Polymers for Efficient Carboxylation of Terminal Alkynes with $CO_2$

## 1. Methods

Fourier transform infrared (FT-IR) spectra of the samples were tested by a Nicolet 6700 research-based IR spectrometer at 4000-400 cm$^{-1}$. Solid-state carbon-13 cross-polarization magic angle spinning nuclear magnetic resonance ($^{13}$C CP/MAS NMR) spectroscopy was performed on a Bruker AVANCE III HD 600M digital superconducting NMR spectrometer. Thermogravimetric analysis (TGA) was employed to examine the composition of the samples. The X-ray photoelectron spectroscopy (XPS) data were acquired using a Thermo Fisher Escalab 250Xi instrument. The microstructural characterization was performed using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), while the elemental composition and distribution were determined by energy-dispersive X-ray spectroscopy (EDX) mapping. The silver content of the samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Thermo Scientific iCAP 7000 Series spectrometer. The textural properties of the samples were characterized by $N_2$ sorption measurements at 77 K using a Micromeritics ASAP 2020 analyzer. The specific surface area (SSA) was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution (PSD) was derived using non-local density functional theory (NLDFT).

## 2. Materials

4-Formylbenzoic acid, polyphosphoric acid (PPA), pyrrole, triptycene, 1,2,4,5-benzenetetraamine tetrahydrochloride (BTA·4HCl), stannous chloride dehydrate ($SnCl_2·2H_2O$), cesium carbonate ($Cs_2CO_3$) and propionic acid were purchased from Macklin Biochemical Technology (Shanghai) Co., Ltd.. Phenylacetylene (1a), 4-methylphenylacetylene (1b), 4-methoxyphenylacetylene (1c), 4-nitrophenylacetylene (1d), 4-bromophenylacetylene (1e), 4-chlorophenylacetylene (1f) and 3-ethynylthiophene (1g) were obtained from Sa'en Chemical Technology (Shanghai) Co., Ltd. (Energy Chemical). Other chemicals were obtained from commercial suppliers and directly used without further purification.

## 3. Experimental section

### 3.1 Synthesis of *5,10,15,20*-Tetrakis(4-carboxyphenyl)porphyrin (TCPP)

Under a nitrogen atmosphere, a mixture of 4-formylbenzoic acid (1 g, 6.7 mmol), and propionic acid (70 mL) was added to a 100 mL round-bottom flask. The mixture was gradually heated to 120 °C, followed by the addition of pyrrole (0.7 mL, 18.8 mmol) under reflux for 8 h. After cooling to room temperature, the resulting mixture was washed with petroleum ether and a small amount of methanol. Finally, a deep purple solid identified as **TCPP** was obtained (yield: 467 mg). 1H NMR (DMSO-$d_6$): 13.29 (s, 4H), 8.86 (s, 8H), 8.40 (d, 8H), 8.36 (d, 8H), -2.93 (s, 2H).

### 3.2 Synthesis of *2,3,6,7,12,13*-Hexaaminotriptycene Hexahydrochloride (HATP·6HCl)

Triptycene (1.7 g, 6.7 mmol) was suspended in fuming nitric acid (30 mL) at 0 °C, and then the mixture was heated at 85 °C for 4 h. After cooling to room temperature, the mixture was poured into deionized water (300 mL) and stirred for 1 h. The light yellow precipitate was collected by filtration, washed with water, and dried under vacuum to afford the crude product. The obtained solid was recrystallized in hot DMF. Subsequently, the resulting *2,3,6,7,12,13*-hexanitrotriptycene (1.25 g, 2.4 mmol) and $SnCl_2·2H_2O$ (12 g, 53.3mmol) were refluxed in a mixture of ethanol (140 mL) and concentrated hydrochloric acid (60 mL) for 24 h. After cooling to room temperature, the white precipitate was collected by filtration, washed with hydrochloric acid, and dried under vacuum to give a light yellow solid as HATP·6HCl (yield: 780 mg). 1H NMR (DMSO-$d_6$): 7.04 (s, 6H), 5.31 (s, 2H).

### 3.3 Synthesis of 2D-BzIm-Por, 3D-BzIm-Por and 3D-BzIm

Under a nitrogen atmosphere, **TCPP** (395 mg, 0.5 mmol) and PPA (30 mL) were charged into a 100 mL round-bottom flask. The mixture was heated to 100 °C under vigorous stirring. Then, HATP·6HCl (1.12 g, 2.0 mmol) was added portion-wise, and the reaction was stirred at 180 °C for 48 h. After the reaction, the mixture was carefully neutralized with saturated sodium bicarbonate solution to pH 8–9. The precipitate was collected by filtration and washed sequentially with dichloromethane and methanol. Finally, the polymer as **3D-BzIm-Por** was subjected to Soxhlet extraction for further purification and subsequently dried under vacuum at 80 °C for 12 h (yield: 580 mg). The synthesis of **2D-BzIm-Por** was carried out under identical conditions, except that BTA·4HCl (0.5 g, 2 mmol) was used in place of HATP·6HCl (yield: 530 mg). Similarly, **3D-BzIm** was also prepared following the same procedure, with biphenyl-4,4'-dicarboxylic acid (121.1 mg, 0.5 mmol) substituted for **TCPP**.

### 3.4. Synthesis of TPP-Por

Anhydrous aluminum chloride ($AlCl_3$, 29 mmol) was added slowly into a chloroform solution of 5,10,15,20-tetraphenylporphyrin (1.0 mmol) under stirring and the resulting mixture was heated at 60°C for 24 h. After the completion of reaction, the solid product was isolated by filtration, washed with dichloromethane and ethanol. The polymer was further purified by Soxhlet extraction in methanol for 12 h.

### 3.5 Synthesis of Ag/2D-BzIm-Por , Ag/3D-BzIm-Por and Ag/3D-BzIm

A solution of **3D-BzIm-Por** (100 mg) in DMSO (5 mL) was added to a 50 mL double-necked flask. After ultrasonic treatment for 30 min, a solution of AgNO3 (50 mg) in DMSO (5 mL) was slowly added. The mixture was stirred at room temperature for 2 h and then heated to 80 °C for 24 h in the dark. The dark solid was collected by filtration, washed with several organic solvents. Furthermore, **Ag/2D-BzIm-Por** and **Ag/3D-**

**BzIm** were synthesized following the aforementioned procedure, using **2D-BzIm-Por** or **3D-BzIm**, respectively, as a substitute for 3D-BzIm-Por.

### 3.6. Synthesis of Ag/TPP-Por

A solution of **TPP-Por** (100 mg) in DMSO (5 mL) was added to a 50 mL double-necked flask. After ultrasonic treatment for 30 min, a solution of $AgNO_3$ (50 mg) in DMSO (5 mL) was slowly added. The mixture was stirred at room temperature for 2 h and then heated to 80 °C for 24 h in the dark. The dark solid was collected by filtration, washed with several organic solvents.

### 3.7 Synthesis of Ag/3D-BzIm-Por'

Typically, $AgNO_3$ (50 mg) was dissolved in water (15 mL), followed by the addition of 3D-Bz-Por (100 mg) and sonication for 30 min. Under a $N_2$ atmosphere, an aqueous solution of $NaBH_4$ (110 mg in 5 mL water) was added dropwise. After reacting for 6 h, the dark solid was collected by filtration, washed with DMF and methanol.

### 3.8 General Procedure for Carboxylation of Terminal Alkynes with $CO_2$.

Phenylacetylene (**1a**) was selected as a model substrate to evaluate the catalytic performance under the standardized carboxylation conditions. Typically, **Ag/3D-BzIm-Por** (10 mg) was added to a mixture of **1a** (102 mg, 1 mmol) and $Cs_2CO_3$ (489 mg, 1.5 mmol) in DMSO (3 mL) in a 10 mL Schlenk tube. The reactor was evacuated and refilled with $CO_2$ three times to ensure complete gas exchange, then connected to a balloon filled with $CO_2$ (99.99%). The reaction mixture was stirred at 60 °C. After completion, the mixture was cooled to room temperature, washed with dichloromethane, and the aqueous layer was acidified with concentrated HCl to pH=1. The acidified aqueous solution was extracted with ethyl acetate ($3 \times 30$ mL). The combined organic extracts were washed with cold saturated NaCl solution, dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure to afford the desired products. The yields were determined via $^1H$ NMR spectroscopy by integration of the aromatic and alkyne proton signals of the remaining phenylacetylene. The nanosilver catalyst was recovered from the organic phase via centrifugation, washed three times with ethanol, and dried under vacuum at 60 °C. The resulting solid was then directly employed as the recycled catalyst in subsequent catalytic runs.

## 4. Schemes, Figures and Tables

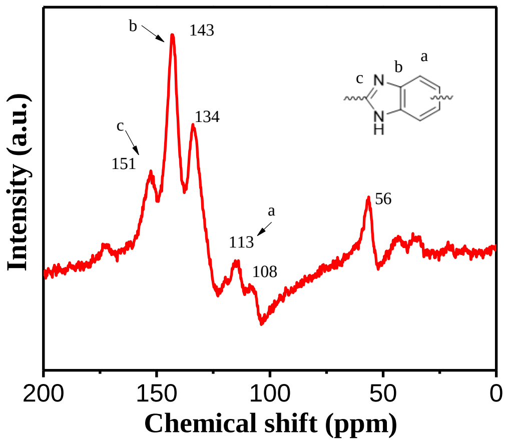


**Figure S1.** Solid-state $^{13}$C MAS NMR spectrum of **3D-BzIm-Por**

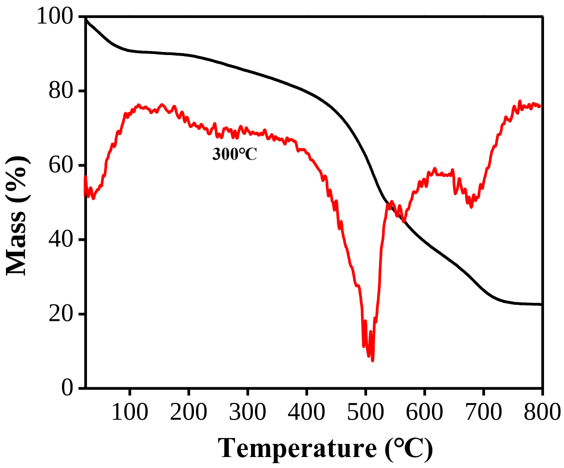


**Figure S2.** TGA curve of **3D-BzIm-Por**

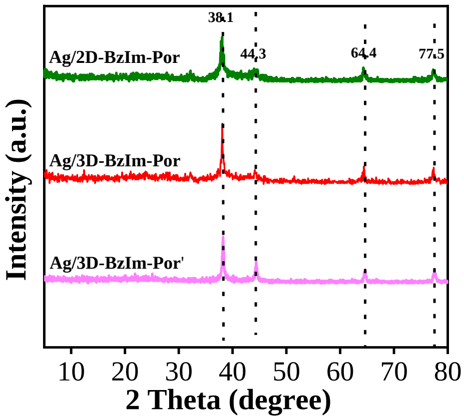


**Figure S3.** Powder XRD curves of **Ag/2D-BzIm-Por**, **Ag/3D-BzIm-Por** and **Ag/3D-BzIm-Por'**

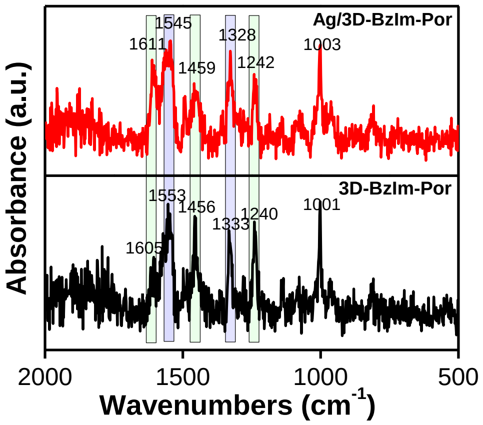


**Figure S4.** Raman spectra of **3D-BzIm-Por** and **Ag/3D-BzIm-Por**

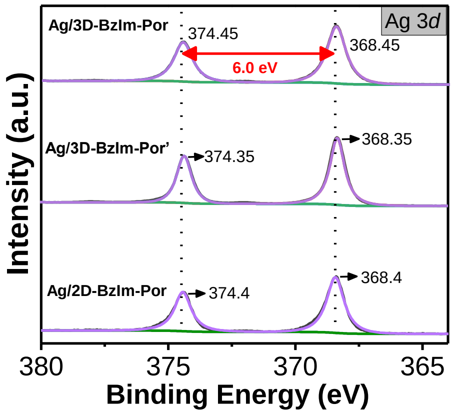


**Figure S5.** Ag3*d* XPS spectra of **Ag/2D-BzIm-Por**, **Ag/3D-BzIm-Por** and **Ag/3D-BzIm-Por'**

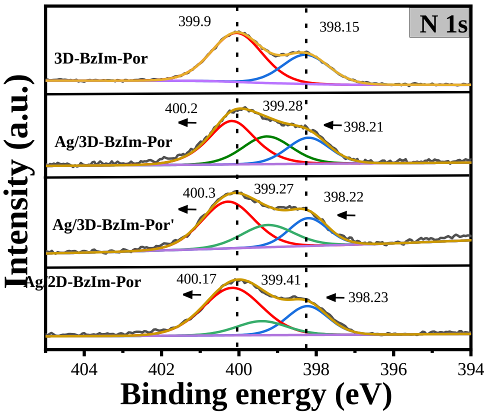


**Figure S6.** N1*s* spectra of **Ag/2D-BzIm-Por**, **Ag/3D-BzIm-Por** and **Ag/3D-BzIm-Por'**

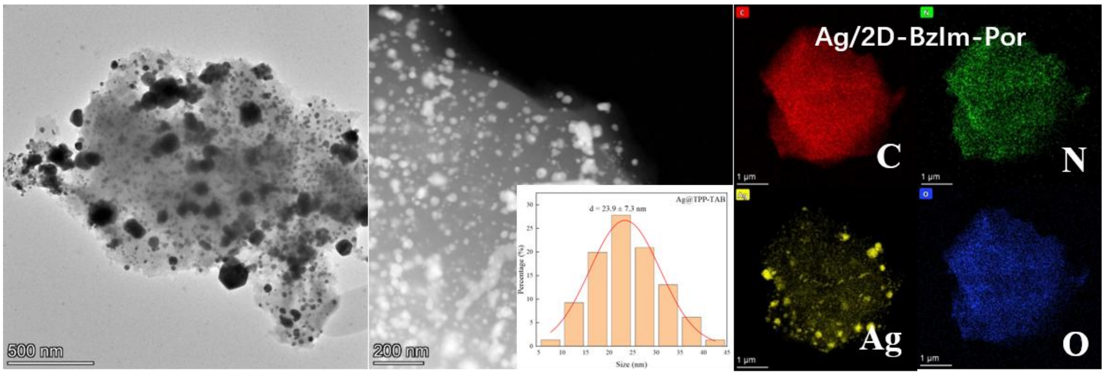


**Figure S7.** HAADF-STEM and EDX elemental mapping images of **Ag/2D-BzIm-Por**

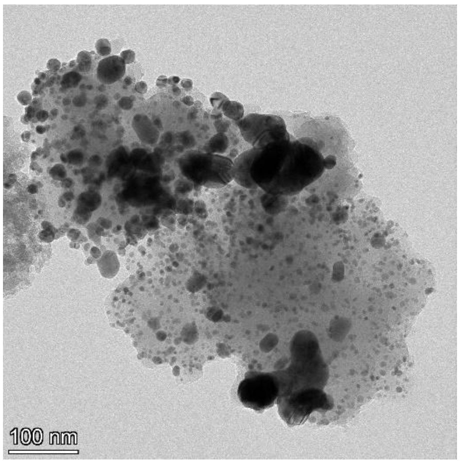


**Figure S8.** HAADF-STEM image of **Ag/3D-BzIm-Por'**

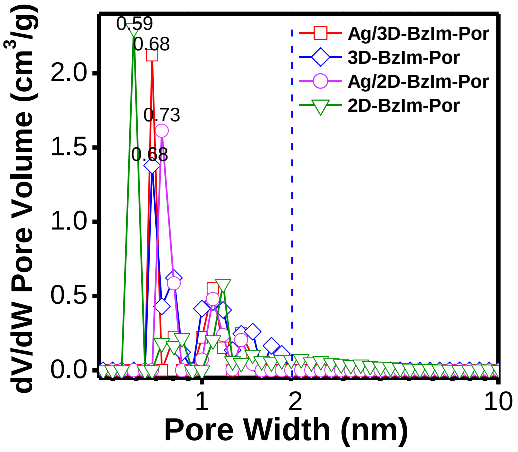


**Figure S9.** PSDs of **2D-BzIm-Por**, **3D-BzIm-Por**, **Ag/2D-BzIm-Por** and **Ag/3D-BzIm-Por**

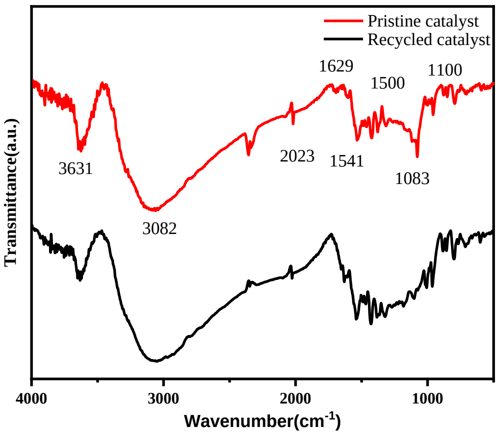
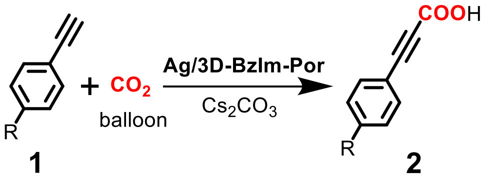


**Figure S10.** FT-IR spectrum of **Ag/3D-BzIm-Por**



|  | 2a | 2b | 2c | 2d | 2e | 2f | 2g | 2h |
|---|---|---|---|---|---|---|---|---|
| **R=** | -H | -Me | -OMe | -NO$_2$ | -Br | -Cl | -CF$_3$ | -F |
| **Time** | 6 h | 6 h | 8 h | 6 h | 12 h | 12 h | 6 h | 8 h |
| **Yield** | 95% | 83% | 81% | 99% | 90% | 93% | 91% | 93% |

**Figure S11.** Substrate scope for the carboxylation of various terminal alkynes with CO$_2$ over **Ag/3D-BzIm-Por**

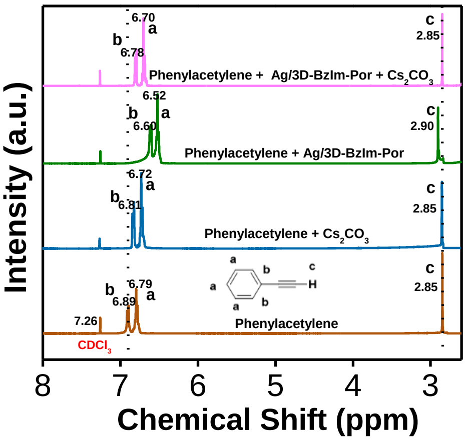


**Figure S12.** $^1$H NMR spectra of phenylacetylene (green), the mixture of phenylacetylene and Cs$_2$CO$_3$ (blue), the mixture of phenylacetylene and **Ag/3D-BzIm-Por** (pink), the mixture of phenylacetylene, **Ag/3D-BzIm-Por** and Cs$_2$CO$_3$ (red);

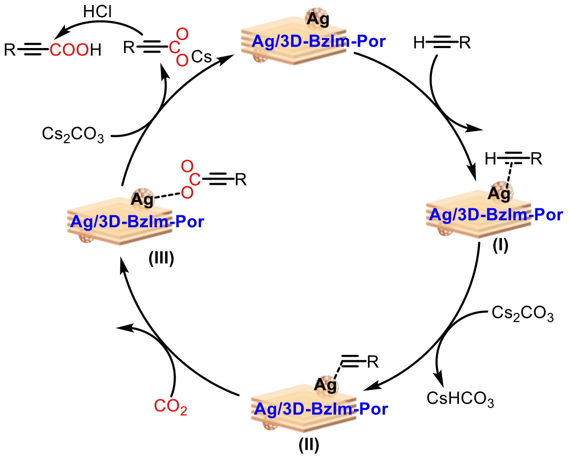
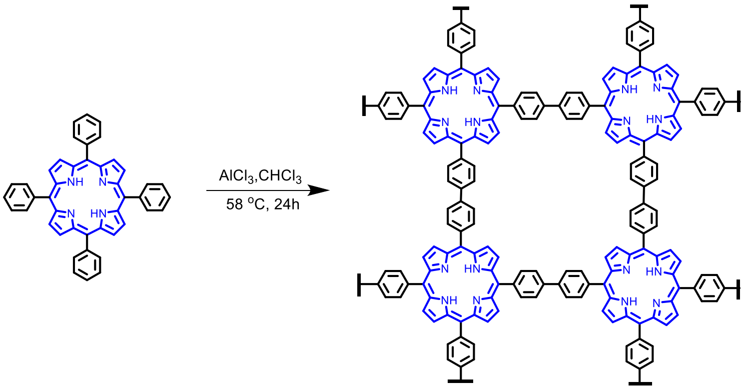
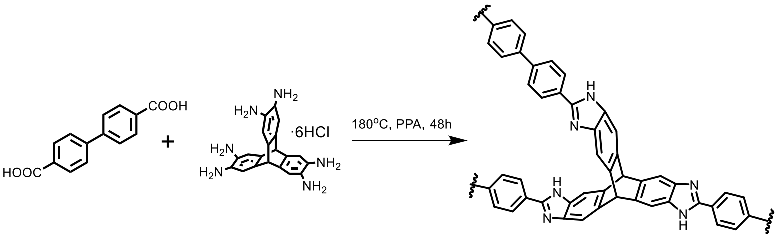


**Figure S13.** Possible mechanism for the carboxylation of terminal alkynes with $CO_2$ over **Ag/3D-BzIm-Por**



**Scheme S1.** Synthesis of **TPP-Por**



**Scheme S2.** Synthesis of **3D-BzIm**

**Table S1.** Comparison of catalytic activity of **Ag/3D-BzIm-Por** with previously reported heterogeneous catalysts for the carboxylation of terminal alkynes.

| **Entry** | **Catalyst** | **Amount /mol%** | **Silver Reduction Strategy** | **P /atm** | **T/°C** | **T /h** | **Yield /%** | **TOF[c] /h$^{-1}$** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|
| Inorganic materials as supports | | | | | | | | | |
| 1 | Ag/F-$Al_2O_3$ | 5.16 | $AgNO_3/H_2$, 450 °C | 60 | 50 | 18 | 62.1 | 0.67 | 1 |
| 2 | $CeO_2$-Ag | 11.8 | $AgNO_3$/DMP | 1 | 80 | 12 | 98 | 0.69 | 2 |
| 3 | AgNPs@m-MgO | 2.1 | $AgNO_3/NaBH_4$ | 1 | 70 | 12 | 98 | 3.89 | 3 |
| 4 | Ag/Schiff-$SiO_2$ | 0.14 | $AgNO_3$/MeOH | 1 | 60 | 24 | 98 | 29.17 | 4 |
| 5 | 0.2Ag@$SiO_2$ | 0.78 | $AgNO_3/N_2H_4\cdot H_2O$ | 1 | 70 | 20 | 92.5 | 5.94 | 5 |
| 6 | Ag/tert-GO | 1.3 | $AgNO_3$/DMF, 60°C | 1 | 40 | 24 | 97.2 | 3.12 | 6 |
| Organic-inorganic hybrid materials as supports | | | | | | | | | |
| 7 | Ag@MIL-101(Cr) | 2.7 | $AgNO_3/NaBH_4$ | 1 | 50 | 15 | 96.5 | 2.38 | 7 |
| 8 | Ag@MIL-100(Fe) | 2.2 | $AgNO_3$/DMF, 120°C | 1 | 50 | 15 | 94.6 | 2.87 | 8 |
| 9 | Ag@UIO-66(Zr) | 4.6 | $AgNO_3$/DMF, 120°C | 1 | 50 | 15 | 97.7 | 1.42 | 8 |
| 10 | Ag/Co-MOF | 2 | $AgNO_3/NaBH_4$ | 1 | 80 | 14 | 96 | 3.43 | 9 |
| Organic materials as supports | | | | | | | | | |
| 11 | Ag@p-CTF-250 | 4 | $AgNO_3/NaBH_4$ | 1 | 50 | 16 | 96 | 1.5 | 10 |
| 12 | Ag@CTFN | 0.76 | $AgNO_3/NaBH_4$ | 1 | 60 | 24 | 97 | 5.32 | 11 |
| 13 | Ag@FeNT | 1.57 | $AgNO_3/NaBH_4$ | 1 | 60 | 15 | 70 | 2.97 | 12 |
| 14 | AgNPs(2.5%)/Melamine-based POPs | 2.78 | $AgNO_3/NaBH_4$ | 1 | 50 | 15 | 93 | 4.9 | 13 |
| 15 | Ag-HMP-2 | 1.2 | $AgNO_3/NaBH_4$ | 1 | 80 | 12 | 98 | 6.81 | 14 |
| **16** | **Ag/3D-BzIm-Por** | **1.5** | **$AgNO_3$/DMSO, 80°C** | **1** | **60** | **6** | **95** | **10.39** | **This work** |
| **17** | **Ag/3D-BzIm-Por** | **0.15** | **$AgNO_3$/DMSO, 80°C** | **1** | **60** | **6** | **62** | **68.9** | **This work** |

Base: $Cs_2CO_3$; TOF = moles of product/mole of metal in the catalyst/time.

## References

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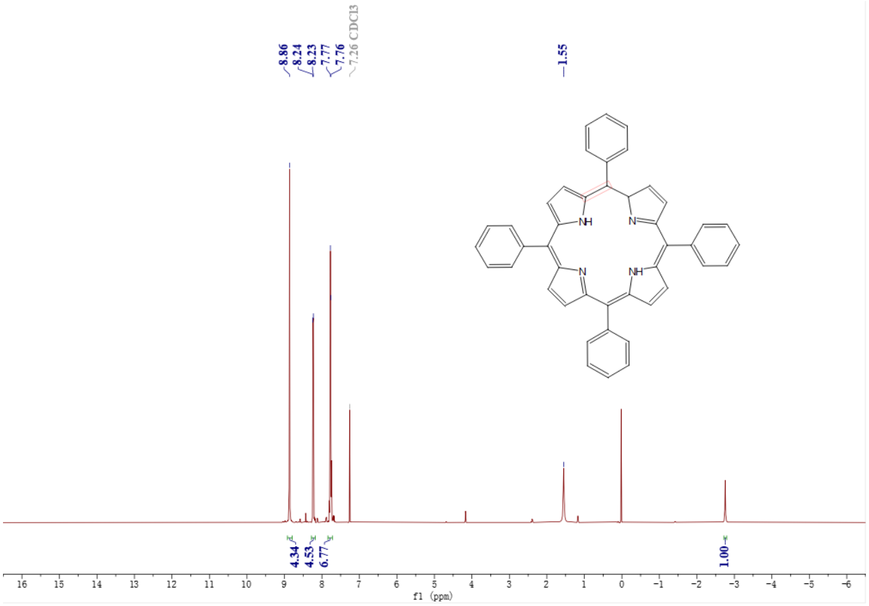
# NMR Spectra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6.77
1.00
16
15
14
13
12
11
10
9
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7
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5
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−3
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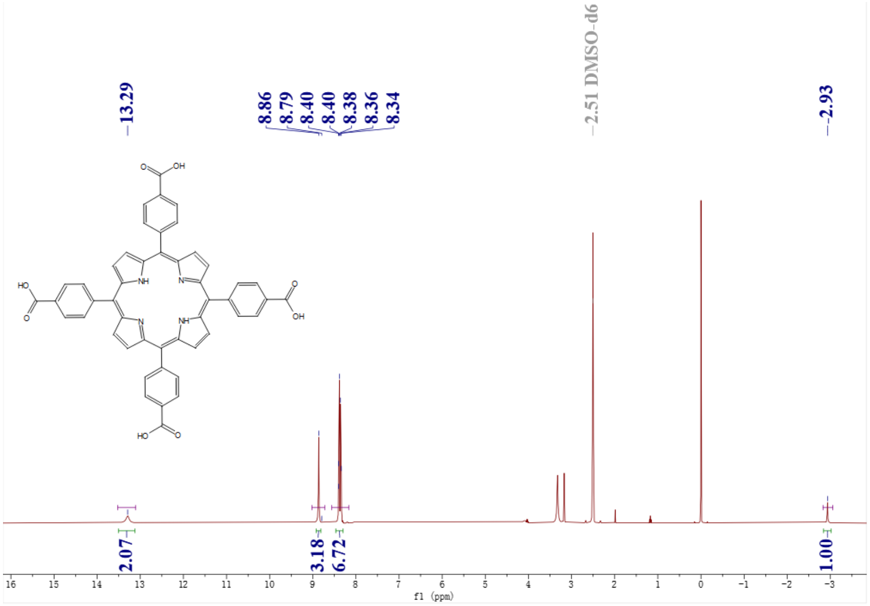
−6
f1 (ppm)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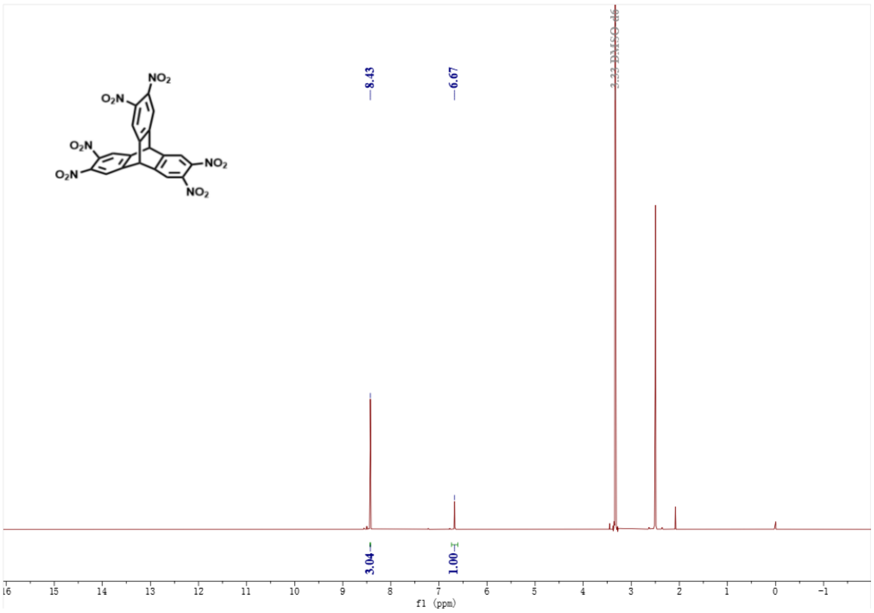
f1 (ppm)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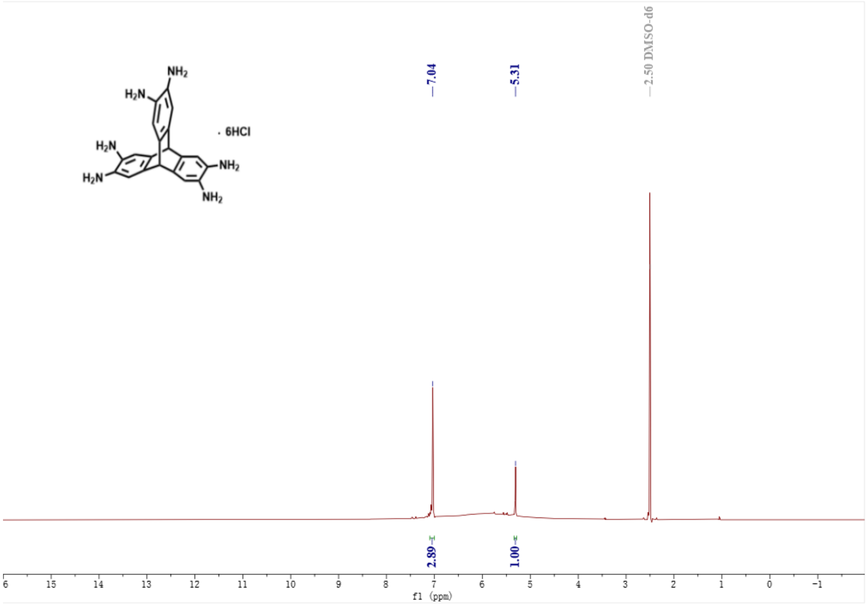
f1 (ppm)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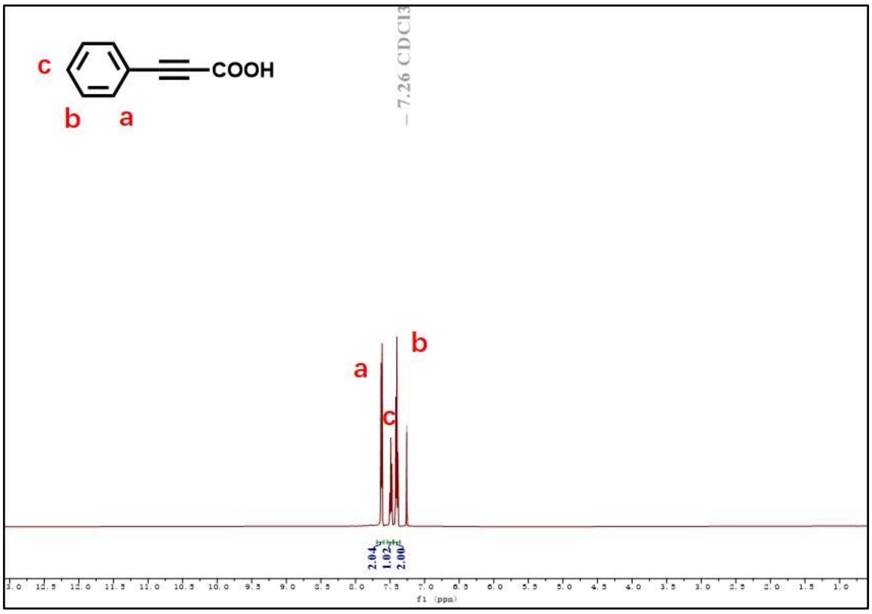
f1 (ppm)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1.0
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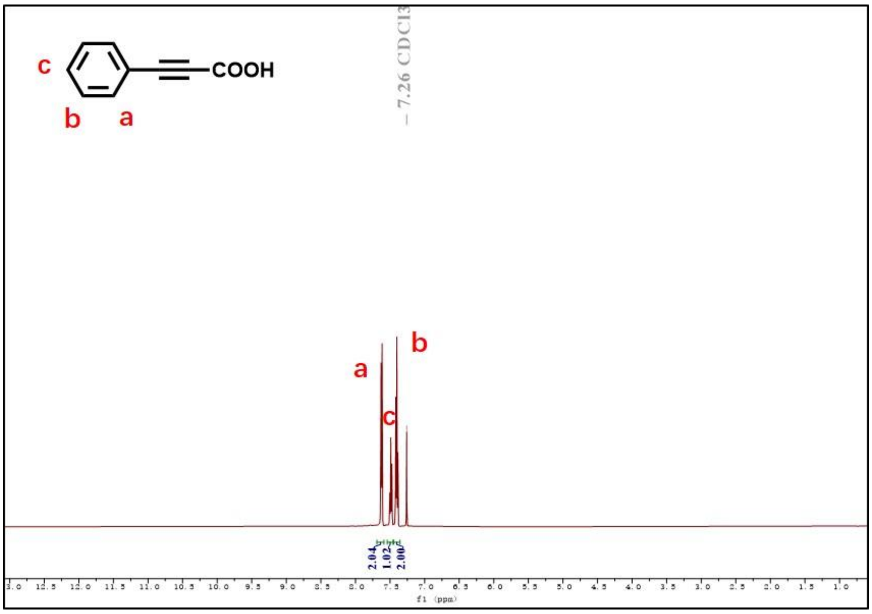
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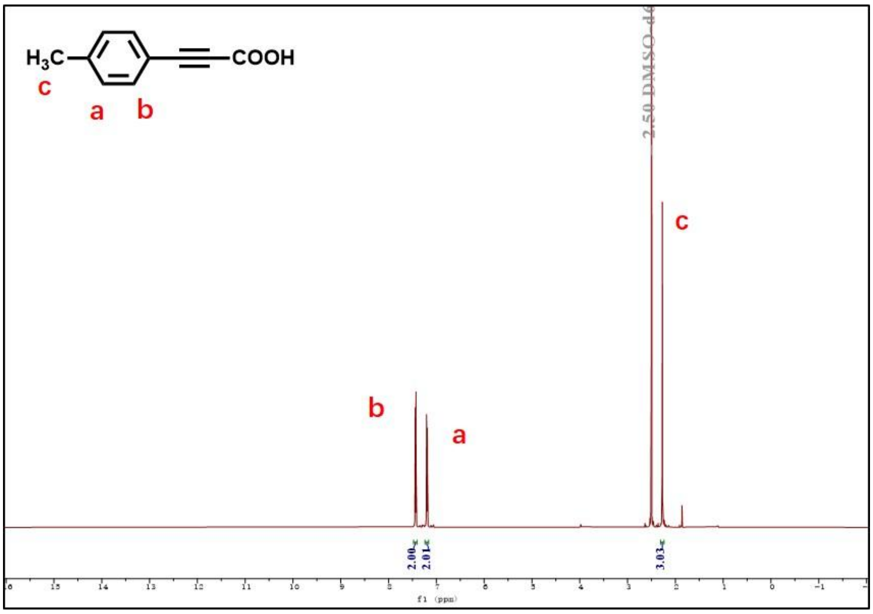
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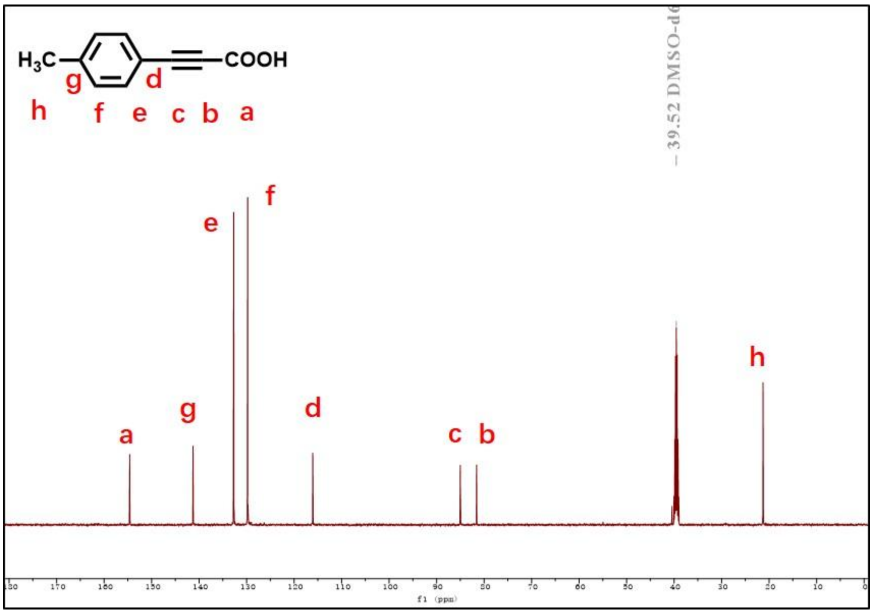
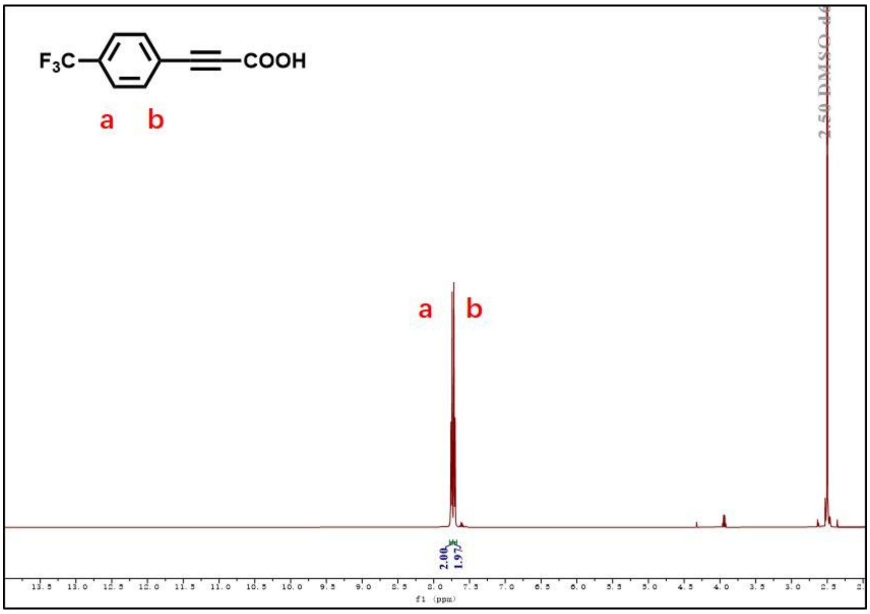
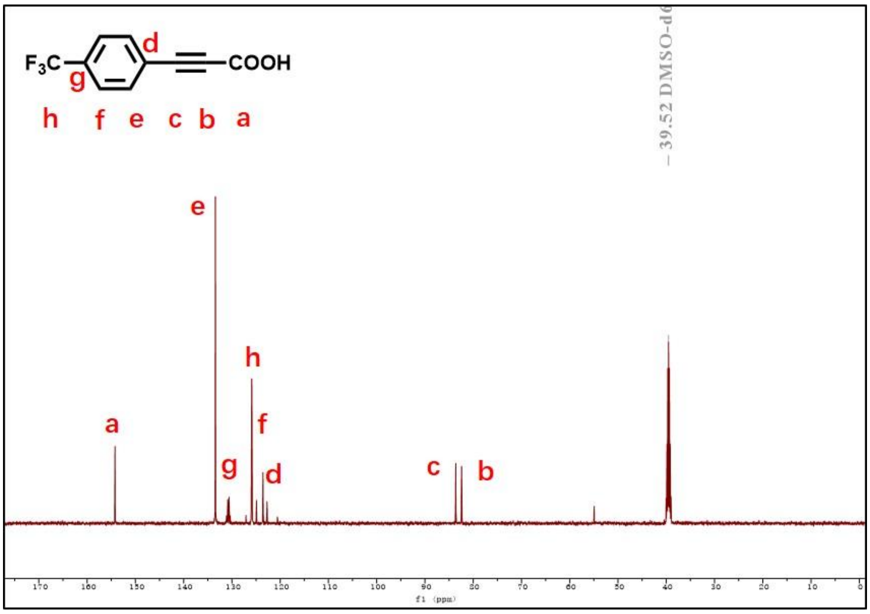
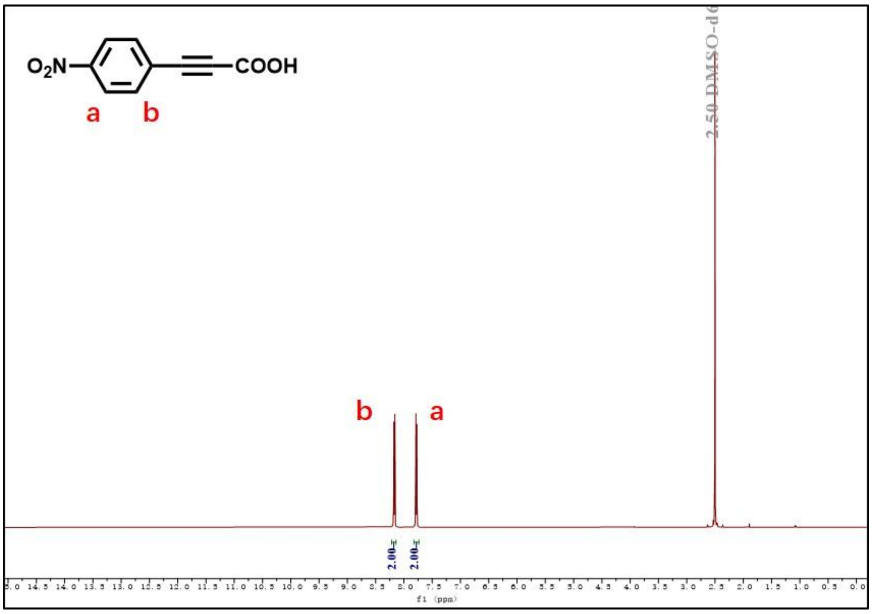
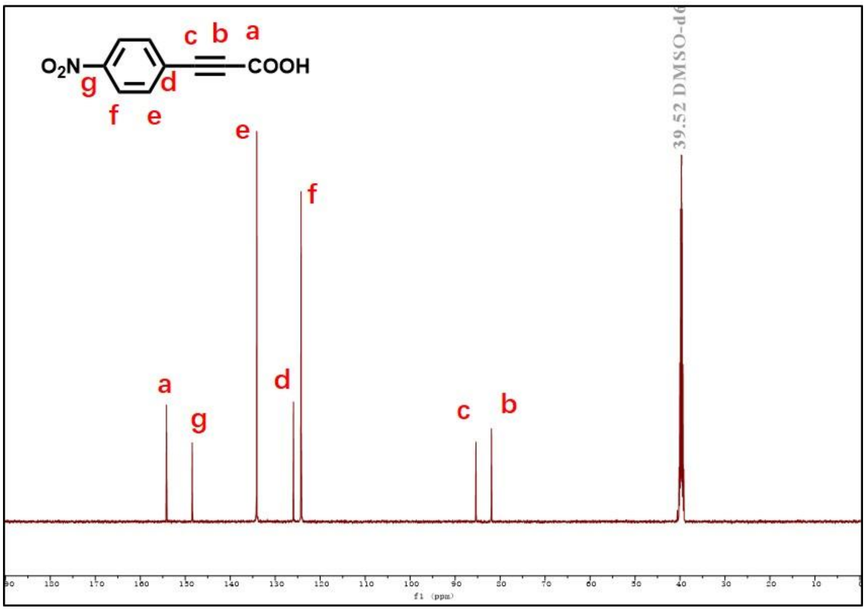
-1
f1 (ppm)

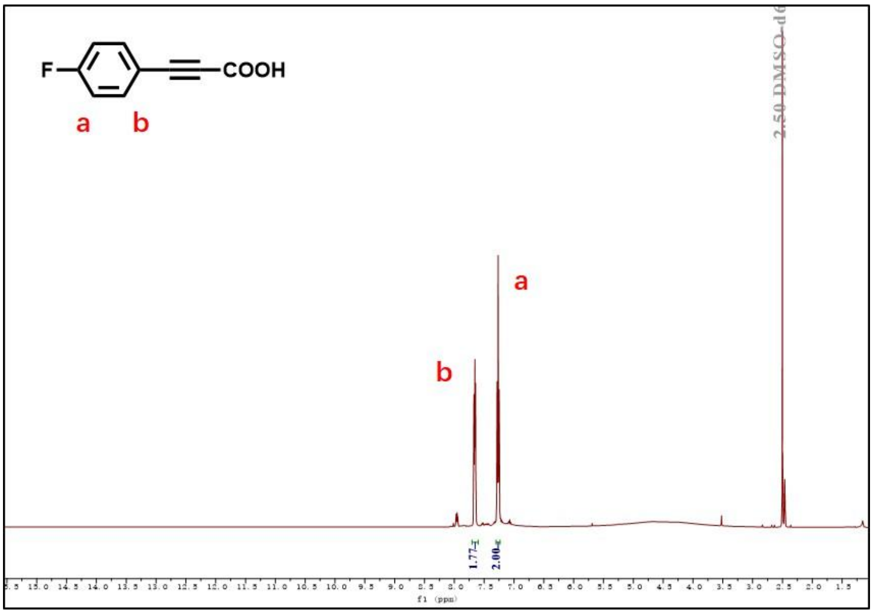

$H_3C$
COOH
g
d
h
f
e
c
b
a
39.52 DMSO-d6
f
e
h
g
d
a
c
b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

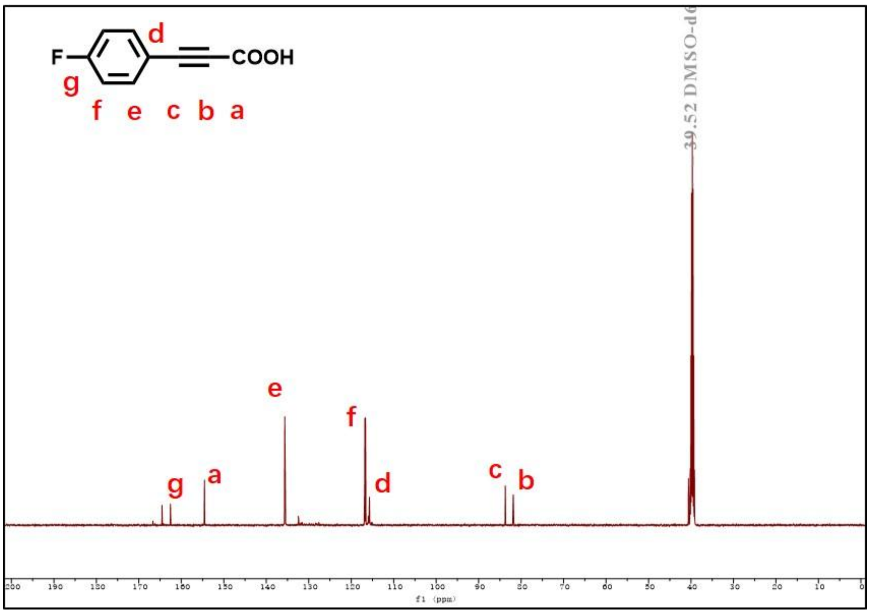

F$_3$C
COOH
a
b
a
b
2.50 DMSO-d
2.00
1.97
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

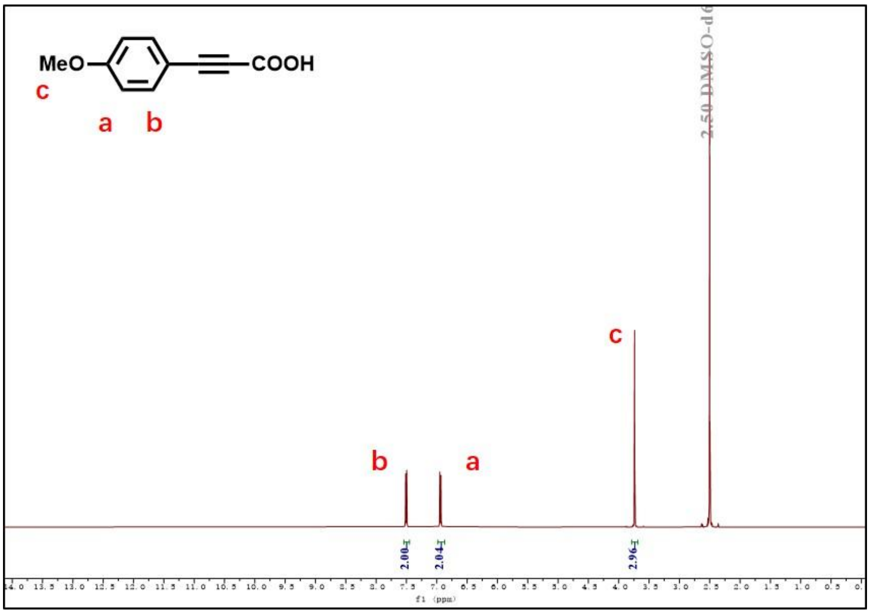

F$_3$C
COOH
d
g
h f e c b a
– 39.52 DMSO-d6
e
h
a
f
g
d
c
b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

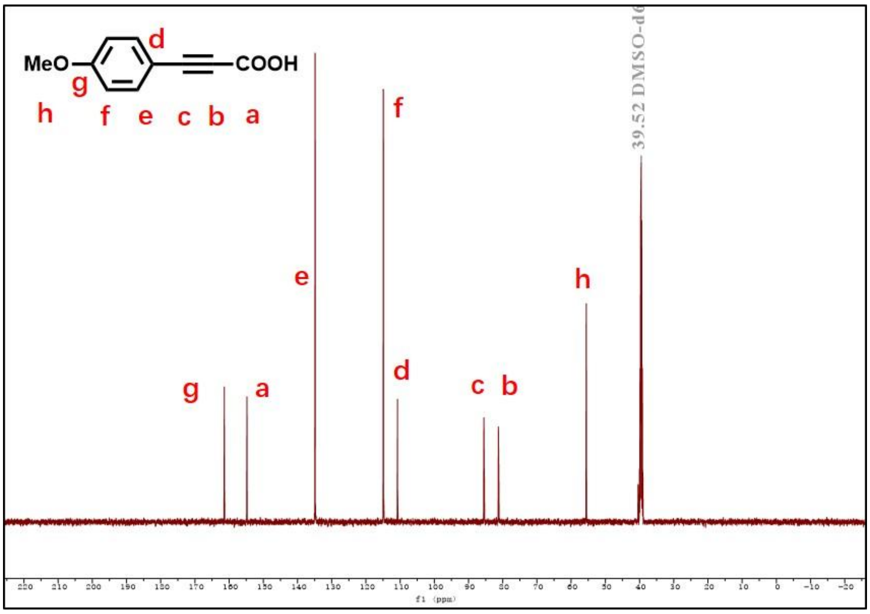

O2N
COOH
a
b
2.50 DMSO-d6
b
a
2.00
2.00
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

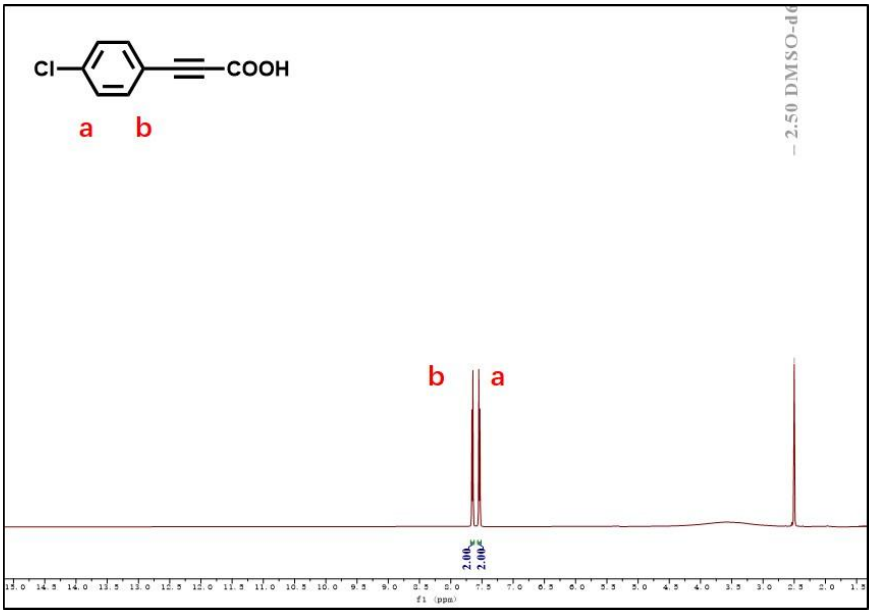

c b a
O2N
COOH
g
d
f e
39.52 DMSO-d6
e
f
a
g
d
c
b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

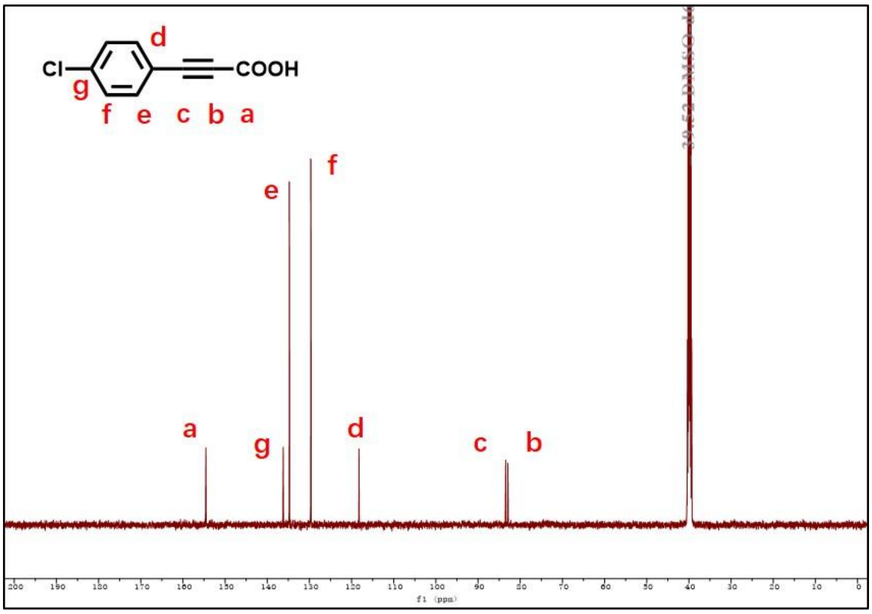

F
COOH
a
b
2.50 DMSO-d6
a
b
1.77
2.00
15.0
14.5
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

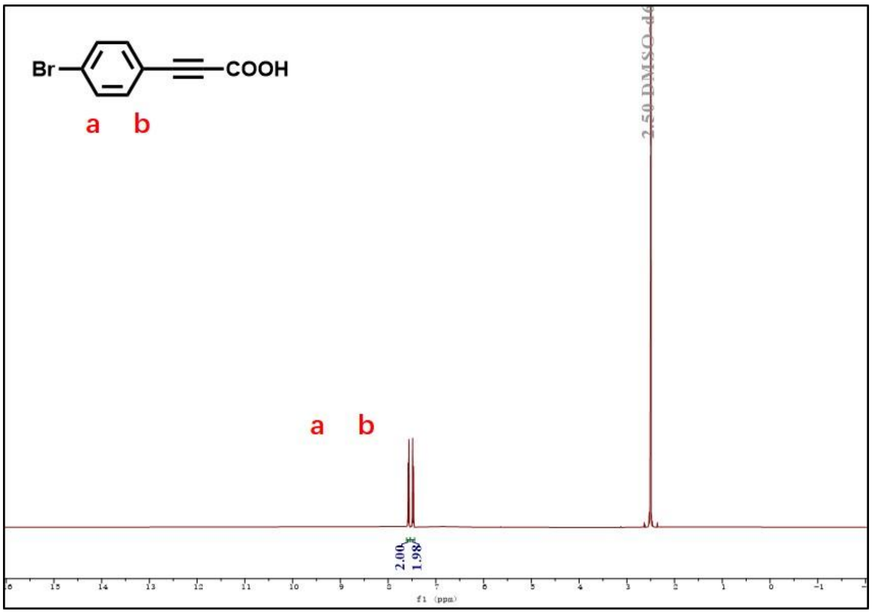

F
d
COOH
g
f
e
c
b
a
39.52 DMSO-d6
e
f
g
a
d
c
b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

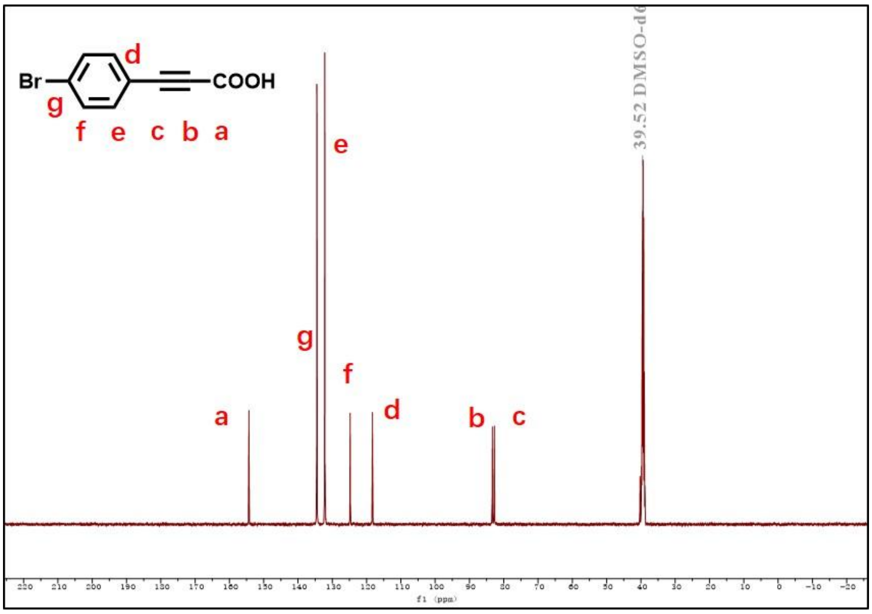

MeO
COOH
c
a
b
2.50 DMSO-d6
b
a
c
2.00
2.04
2.96
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

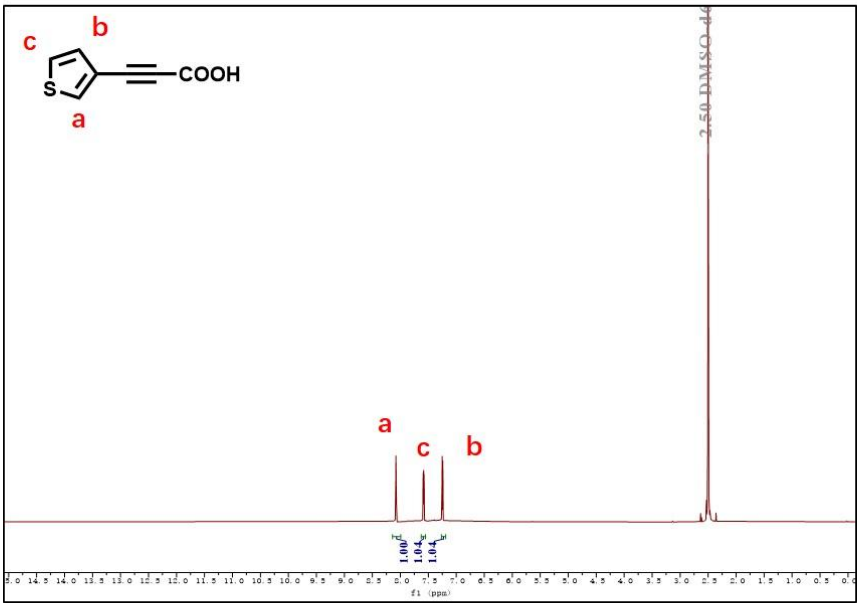

MeO
COOH
d
g
h
f
e
c
b
a
39.52 DMSO-d6
e
f
h
d
g
a
c
b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

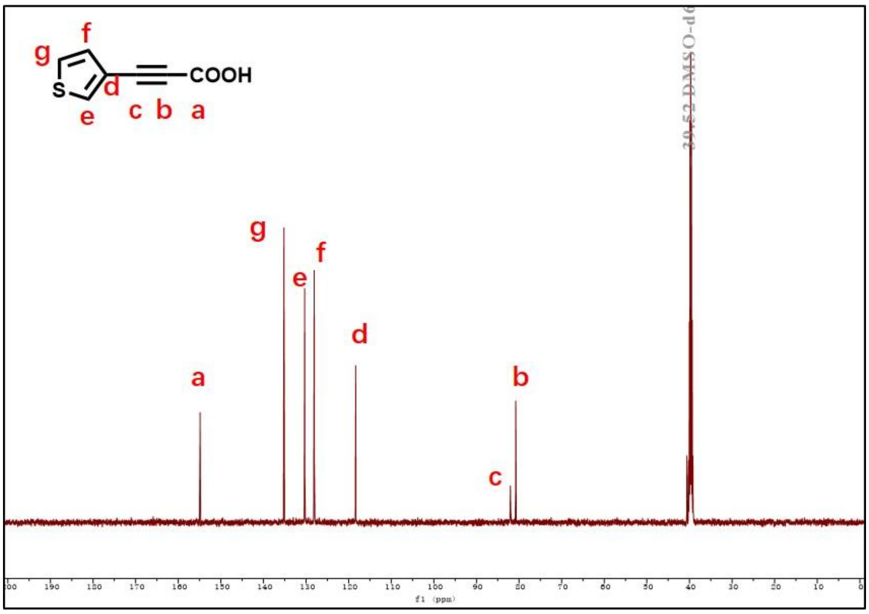

Cl
COOH
a
b
– 2.50 DMSO-d6
b
a
2.00
2.00
15.0
14.5
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

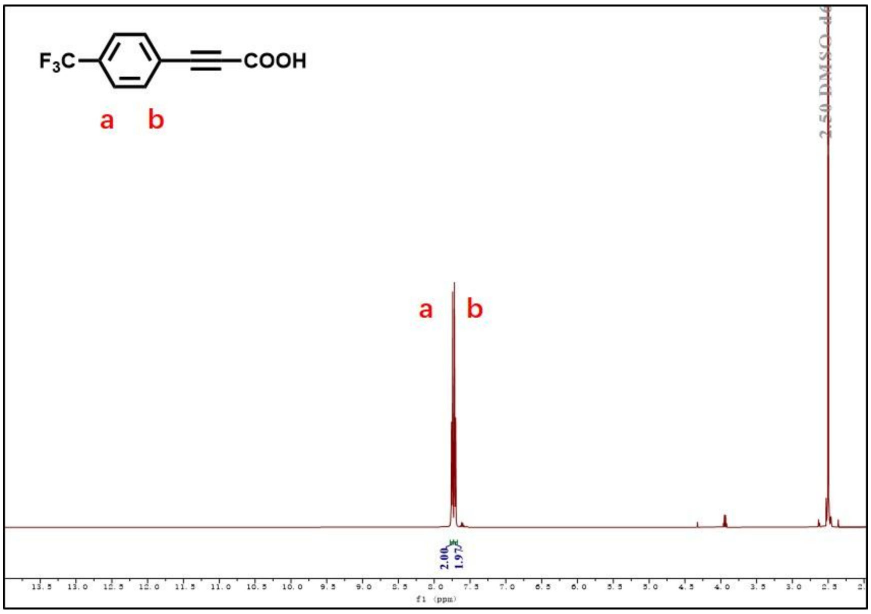

Cl
COOH
d
g
f
e
c
b
a
39.52 DMSO-d6
e
f
a
g
d
c
b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

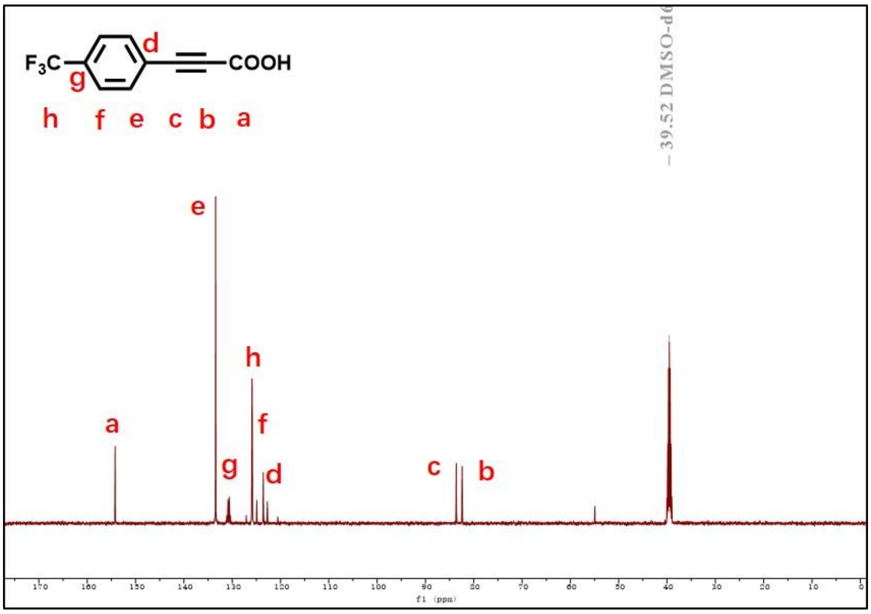

Br
COOH
a
b
a
b
2.50 DMSO-d6
2.00
1.98
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

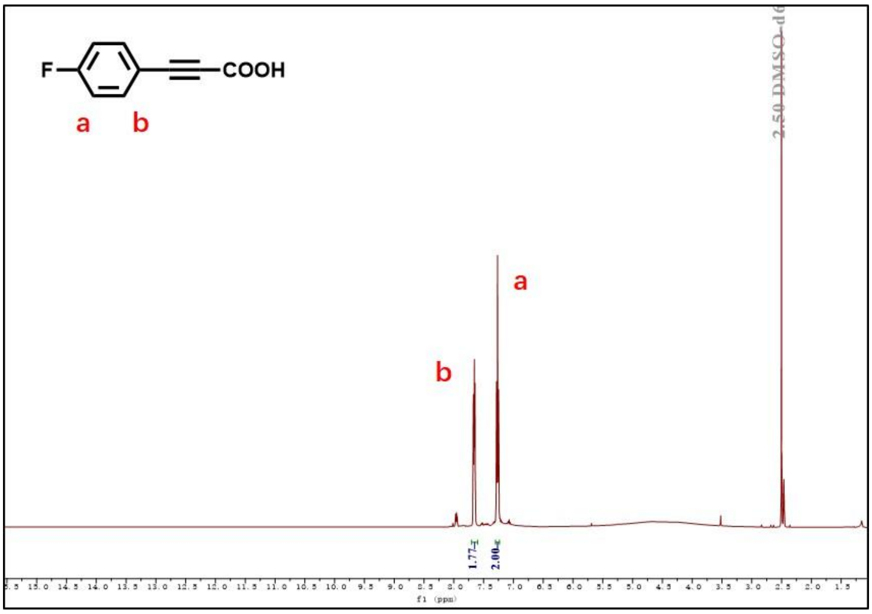

Br
COOH
d
g
f
e
c
b
a
e
39.52 DMSO-d6
g
f
a
d
b
c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

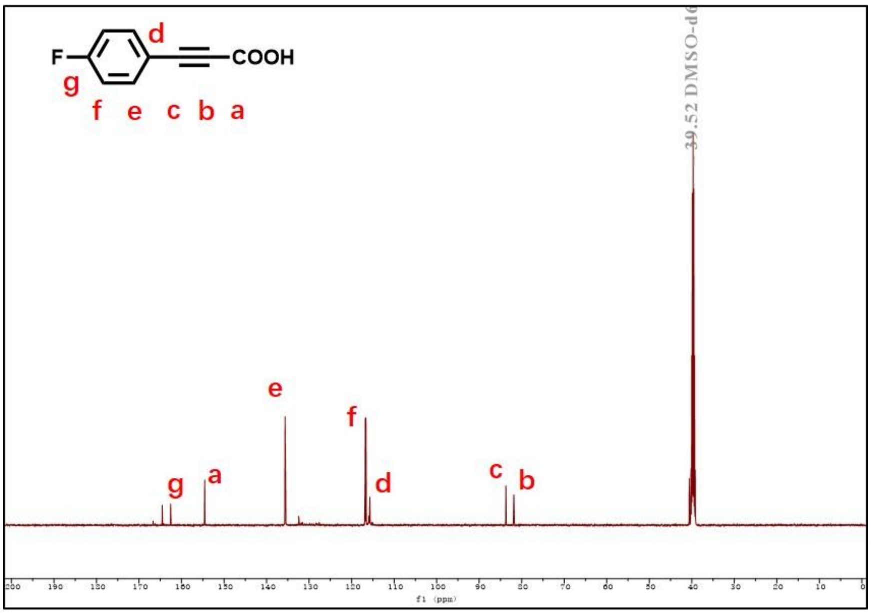

c
b
S
COOH
a
2.50 DMSO-d6
a
c
b
1.00
1.04
1.04
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


f
g
S
d
COOH
e
c b a
39.52 DMSO-d6
g
f
e
d
a
b
c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F3C
COOH
a
b
2.50 DMSO-d6
a
b
2.00
1.97
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2
f1 (ppm)


F3C
COOH
d
g
h
f
e
c
b
a
39.52 DMSO-d6
e
h
a
f
g
d
c
b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
COOH
a
b
2.50 DMSO-d6
a
b
1.77
2.00
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


F
COOH
d
g
f
e
c
b
a
39.52 DMSO-d6
e
f
g
a
d
c
b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)