Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

CsF-Promoted Carboxylation of Aryl(Hetaryl)Terminal Alkynes with Atmospheric CO_2 at Room Temperature

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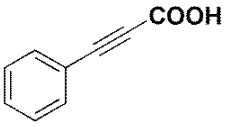
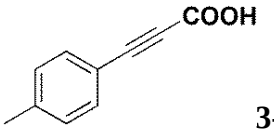
This file includes:

General information: Alkynes, trimethylsilylacetylene and other chemicals were purchased from J&K or Innochem. Carbon dioxide (99.999%), ^{13}C-labled carbon dioxide (purity>99.9%, ^{13}C 99%, ^{18}O<1%), terminal alkynes, and other reagents were used without further purification. All reactions were monitored by thin-layer chromatography (TLC) using UV light as cisualizing agent. Column chromatography was performed with 230-300 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AvanceII 400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^{1}H NMR and against the solvent ($CDCl_3$, 77.0 ppm) for ^{13}C NMR, respectively. Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*, Hz).

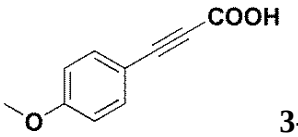
General procedure for carboxylation of terminal alkynes and characterization data: In a glovebox, the terminal alkynes (1.0 mmol), trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) was added in dry DMSO (2 ml) in a 10 mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox and the Ar gas inside the reactor was removed by CO_2. After a CO_2 ballon was connected, the reactor was moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 10 mL). The aqueous layer was acidified with aqueous HCl (6 M) and then extracted with diethyl ether (5 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the pure aromatic propiolic acid (for example, compound **3a**: 92%).



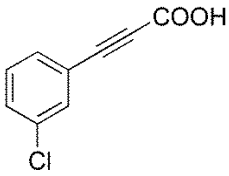
3-phenylpropiolic acid (3a) 133.3 mg, 92% , white solid, ^{1}H NMR (400 MHz, DMSO) δ 7.68 – 7.62 (m, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.81, 133.07, 131.36, 129.50, 119.53, 119.51, 85.03, 81.68.



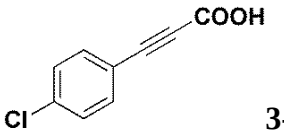
3-(p-tolyl)propiolic acid (3b) 114.1 mg, 77%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 17.4 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48, 141.61, 133.19, 129.40, 116.31, 88.54, 80.17, 21.72.



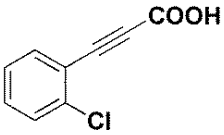
3-(4-methoxyphenyl)propiolic acid (3c) 108.8 mg, 71%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.85, 157.84, 135.25, 114.38, 111.06, 89.51, 79.80, 55.41.



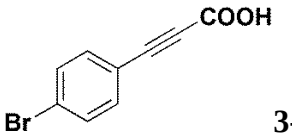
3-(3-chlorophenyl)propiolic acid (3d) 147.8 mg, 82%, yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.51 – 7.42 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.87, 134.58, 132.78, 131.18, 129.90, 121.14, 85.94, 81.16.



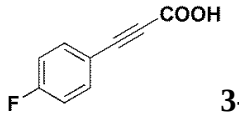
3-(4-chlorophenyl)propiolic acid (3e) 155.6 mg, 82%, yellow solid, ^{1}H NMR (400 MHz, DMSO) δ 7.36 (dd, *J* = 16.1, 4.6 Hz, 1H), 7.28 – 7.19 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 154.92, 136.35, 133.79, 128.76, 118.23, 83.58, 82.15.



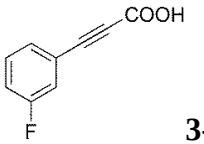
3-(2-chlorophenyl)propiolic acid (3f) 147.5 mg, 81%, yellow solid, ^{1}H NMR (400 MHz, DMSO) δ 7.75 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.56 (td, *J* = 7.8, 1.6 Hz, 1H), 7.45 (td, *J* = 7.6, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 153.49, 135.14, 134.15, 131.86, 129.12, 127.09, 118.49, 85.50, 79.89.



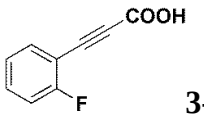
3-(4-fluorophenyl)propiolic acid (3g) 192.4 mg, 80%, yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.40, 134.21, 131.90, 125.08, 118.92, 84.23, 82.33.



3-(4-fluorophenyl)propiolic acid (3h) 147.2 mg, 85%, pale yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.25, 162.73, 156.67, 156.62, 140.02, 135.43, 135.34, 133.41, 133.33, 127.98, 127.90, 116.24, 116.02, 86.25, 86.19, 80.67.

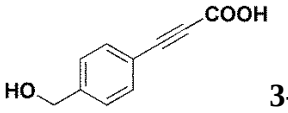


3-(3-fluorophenyl)propiolic acid (3i) 145.6 mg, 87%, yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.21 (ddd, *J* = 3.8, 2.1, 1.2 Hz, 1H), 7.10 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.45, 160.98, 156.86, 130.42, 130.34, 129.03, 129.00, 121.26, 121.17, 119.88, 119.65, 118.47, 118.26, 86.06, 86.03, 80.92.

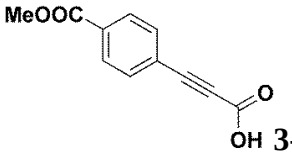


3-(2-fluorophenyl)propiolic acid (3j) 156 mg, 85%, yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 1H), 7.47 (ddd, *J* = 15.4, 5.3, 1.7 Hz, 1H), 7.21 – 7.10 (m, 2H). ^{13}C NMR

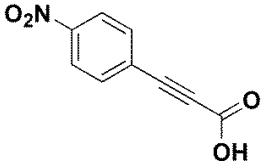
(101 MHz, $CDCl_3$) δ 164.12, 161.57, 156.50, 133.78, 132.10, 132.02, 123.35, 123.31, 115.05, 114.85, 107.28, 107.13, 83.66, 81.00.



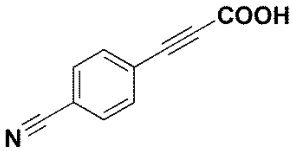
3-(4-hydroxymethylphenyl)propiolic acid (3k) 143.2 mg, 82%, yellow solid, ^{1}H NMR (400 MHz, DMSO) δ 13.62 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.41 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.79, 146.37, 132.94, 127.19, 117.47, 85.28, 81.89, 62.85.



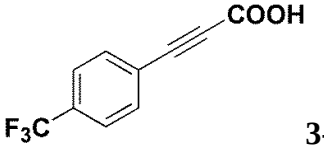
3-(3-(methoxycarbonyl)phenyl)propiolic acid (3l) 149.7 mg, 76%, yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ161.10, 155.15, 140.43, 132.81, 132.15, 131.66, 130.61, 129.59, 125.70, 124.30, 90.29, 82.86, 52.39



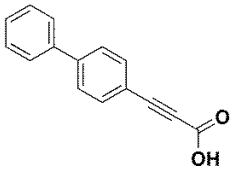
3-(nitrophenyl)propiolic acid (3m) 101.8 mg, 52%, brown solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.58, 153.77, 148.53, 133.68, 130.65, 126.42, 126.23, 123.71, 84.34, 83.22.



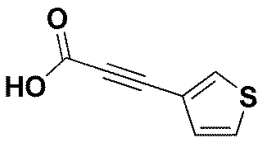
3-(4-cyanophenyl)propiolic acid (3n) 113.2 mg, 68%, brown solid, ^{1}H NMR (400 MHz, DMSO) δ 14.03 (s, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.29, 133.65, 133.22, 124.32, 118.72, 113.50, 85.47, 82.50.



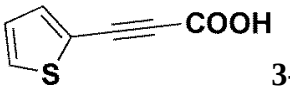
3-(2-(trifluoromethyl)phenyl)propiolic acid (3o) 167.1 mg, 77%, pale yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.87, 154.84, 133.20, 132.36, 132.03, 131.79, 126.56, 125.57, 125.54, 125.50, 125.46, 124.89, 123.51, 122.19, 84.60, 82.42.



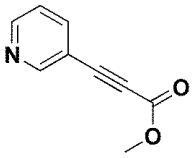
3-(biphenyl-4-yl)propiolic acid (3p) 140.4 mg, 65%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.57 (m, 4H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.93, 143.80, 139.76, 133.68, 128.97, 128.20, 127.28, 127.14, 118.05, 88.27, 80.85.



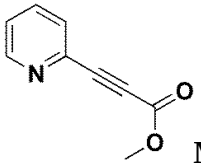
3-(thiophen-3-yl)propiolic acid (3q) 134.2 mg, 90%, brown solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 2.8, 0.9 Hz, 1H), 7.34 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.28 – 7.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 134.60, 130.29, 126.25, 118.53, 84.14, 80.26.



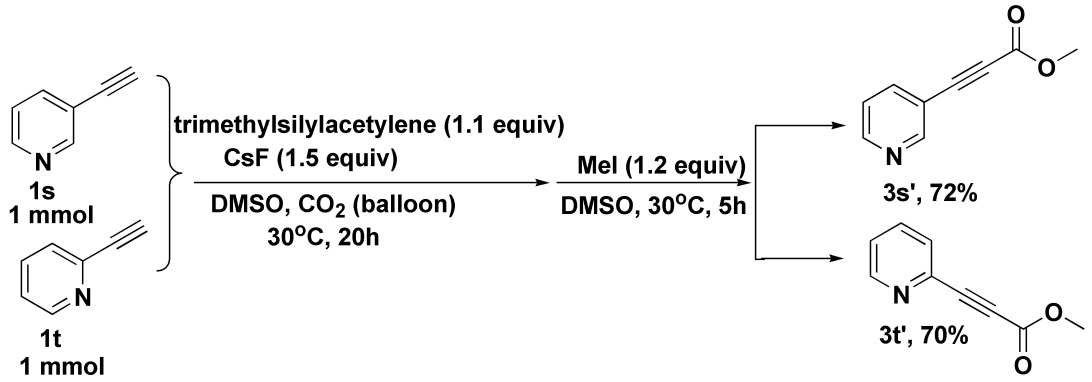
3-(thiophen-2-yl)propiolic acid (3r) 134.3 mg, 93%, dark solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.48 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.06 (dd, *J* = 5.0, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.84, 136.97, 131.59, 127.60, 119.24, 84.82, 81.88.



Methyl 3-pyridylpropiolate (3s') 115.6 mg, 78%, brown solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.3 Hz, 1H), 8.63 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.85 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.31 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.83 (s, 3H), ^{13}C NMR (101 MHz, CDCl3) δ 153.84, 153.25, 150.67, 139.74, 123.12, 116.90, 83.15, 82.67, 52.89.



Methyl 2-pyridylpropiolate (3t') 112.5mg, 76%, brown solid, 1H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.3 Hz, 1H), 7.72 (td, J = 7.7, 1.7 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.35 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.37, 150.18, 140.17, 135.99, 128.18, 124.33, 83.76, 78.40, 52.39.



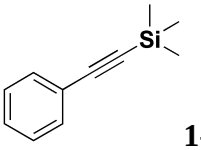
Scheme S1. Synthesis of 3s' and 3t' from carboxylation of 2- and 3-ethynylpyridine with CO_2 promoted by trimethylsilylacetylene/CsF

Control experiments:

Experiment of isotopically labled $^{13}CO_2$: In a glovebox, the terminal alkynes (1.0 mmol),

trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) was added in dry DMSO (2 ml) in a 10 mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox and a $^{13}CO_2$ ballon was connected to the reactor, which was then moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 10 mL). The aqueous layer was acidified with aqueous HCl (6 M) and then extracted with diethyl ether (5 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the pure aromatic propiolic acid in 90% isolated yield. The product was then analyzed by ^{13}C NMR spectroscopy (Figure 2).

Synthesis of alkynylsilane 4a: In a glovebox, phenylacetylene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) in a 10 mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox and a N_2 ballon was connected to the reactor, which was then moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude mixture. The residue was purified by silica gel flash column chromatography (Petroleum ether) to give the pure desired product as yellow liquid in 95% yield.



1-phenyl-2-trimethylsilylacetylene 95%, yellow liquid, ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.33 (dd, *J* = 5.1, 1.8 Hz, 3H), 0.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.96, 128.46, 128.19, 123.22, 105.21, 94.05, 0.00.

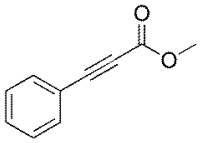
Next, **4a** (1.0 mmol) as starting substarte was added into DMSO solution of CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) in a 10 mL Schlenk tube with a magnetic stirrer. Then the tube was evacuated and back-filled with CO_2 for 3 times. After being stirred for 20h at 30°C, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 10 mL). The aqueous layer was acidified with aqueous HCl (6 M) and then extracted with diethyl ether (5 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the pure aromatic propiolic acid in 94% isolated yield.

Applications of the protocol

Synthesis of 3a in gram scale: In a glovebox, phenylacetylene (10.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (11 mmol), CsF (15 mmol) and 18-crown-6 (2 mmol) in a 100 mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox and evacuated and back-filled with CO_2 for 3 times. Then a CO_2 ballon was connected to the reactor, which was moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (200 mL), and was extracted with CH_2Cl_2 (3 × 50 mL). The aqueous layer was acidified with aqueous HCl (6 M) and then extracted with diethyl ether (5 × 50 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the pure **3a** in 88% isolated yield.

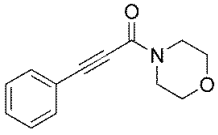
Synthesis of 6: In a glovebox, phenylacetylene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) in a 10 mL Schlenk

tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox, evacuated and back-filled with CO_2 for 3 times. Then a CO_2 ballon was connected to the reactor, which was then moved to a water bath of 30°C. After being stirred for 20h, the solution of MeI (1.2 mmol MeI in 2 ml anhydrous DMSO) was added via syringe. After 2h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude mixture, which was purified by silica gel flash column chromatography (Petroleum ether/EtOAc 10:1) to give the pure **6** as light yellow liquid in 90% yield.[1]



Methyl phenylpropiolate 90%, colorless liquid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H), 7.24 (t, *J* = 7.4 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.26, 132.83, 130.60, 128.52, 119.45, 86.27, 80.32, 52.57.

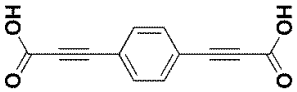
Synthesis of 7: In a glovebox, phenylacetylene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) in a 10 mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox, evacuated and back-filled with CO_2 for 3 times. Then a CO_2 ballon was connected to the reactor, which was then moved to a water bath of 30°C. After being stirred for 15 h, the solution of morpholine (1.1 mmol morpholine and 1.2 mmol HBTU (O-(1H-Benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate) in 3ml anhydrous DMF) was added via syringe. After 5h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude mixture, which was purified by silica gel flash column chromatography (Petroleum ether/EtOAc 5:1) to give pure **7** as light yellow powder in 56% yield.[2]



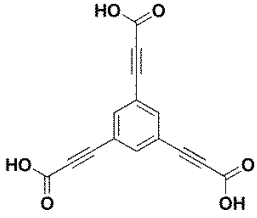
1-morpholino-3-phenylprop-2-yn-1-one 56%, light yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.35 (ddd, *J* = 16.0, 11.7, 4.5 Hz, 3H), 3.83 – 3.79 (m, 2H), 3.75 – 3.70 (m, 2H), 3.67 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.22, 132.35, 130.16, 128.52, 120.25, 91.23, 80.74, 47.32, 41.99.

Synthesis of 3u and 3v: In a glovebox, 1,4-diethynylbenzene or 1,3,5-triethynylbenzene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 equiv.), CsF (1.5 equiv.) and 18-crown-6 (0.2 equiv.) in a 10 mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox, evacuated and back-filled with CO_2 for 3 times. Then a CO_2 ballon was connected to the reactor, which was then moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 20 mL). The aqueous layer was acidified with aqueous HCl (6 M) and then extracted with diethyl ether (5 × 20 mL). The

combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give pure product in 75% and 62% isolated yield, respectively.[1]



3, 3'-(1,4-phenylene)dipropiolic acid (3u) 160.5 mg, 75%, pale yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.44, 133.41, 121.62, 84.29, 83.51.



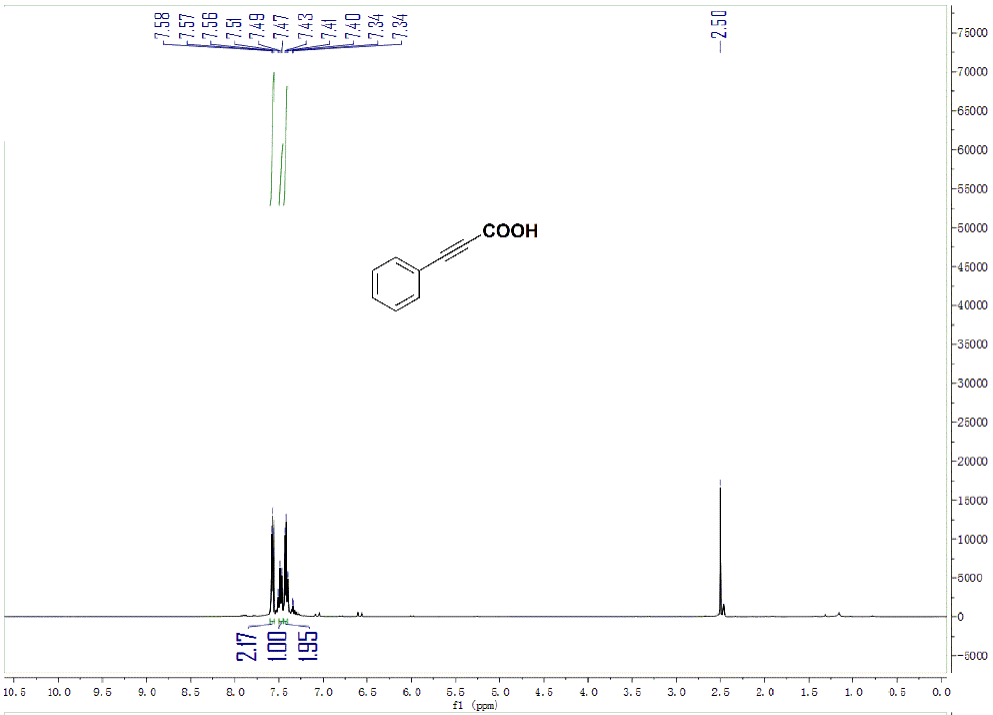
3, 3',3''-(1,3,5-phenylene)tripropiolic acid (3v) 174.8 mg, 62%, yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.26, 137.97, 121.54, 83.63, 81.65.

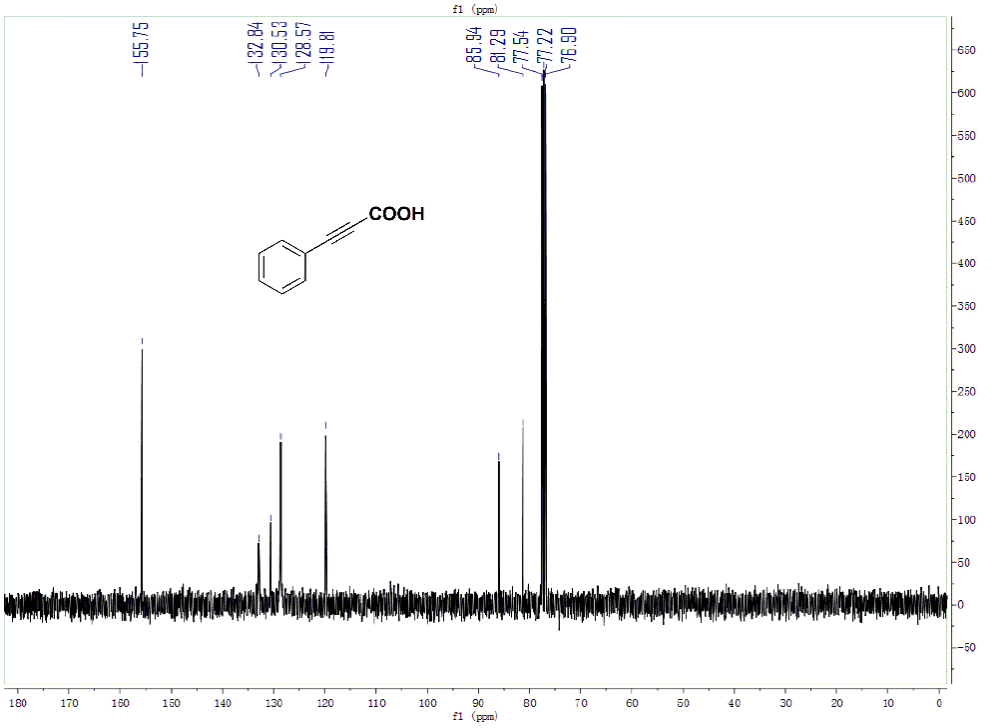
Reference:

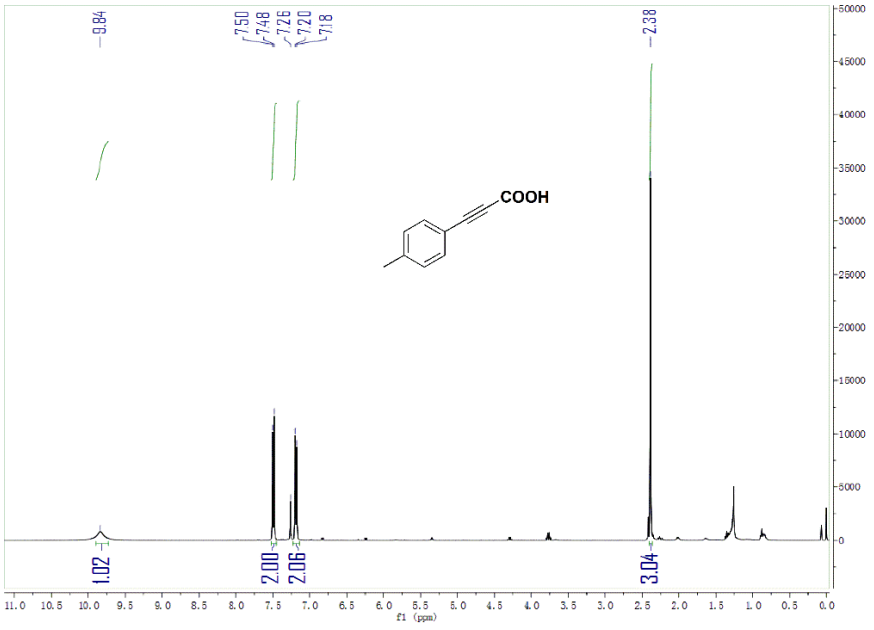
(1) Yu, B.; Xie, J. N.; Zhong, C. L.; Li, W.; He, L. N. *ACS Catal.*, **2015**, 5, 3940-3944

(2) Goodreid, J. D.; Duspara, P. A.; Bosch, C.; Batey, R. A. *J. Org. Chem*., **2014**, 79, 943-954.

^{1}H and ^{13}C NMR spectrum of the isolated products



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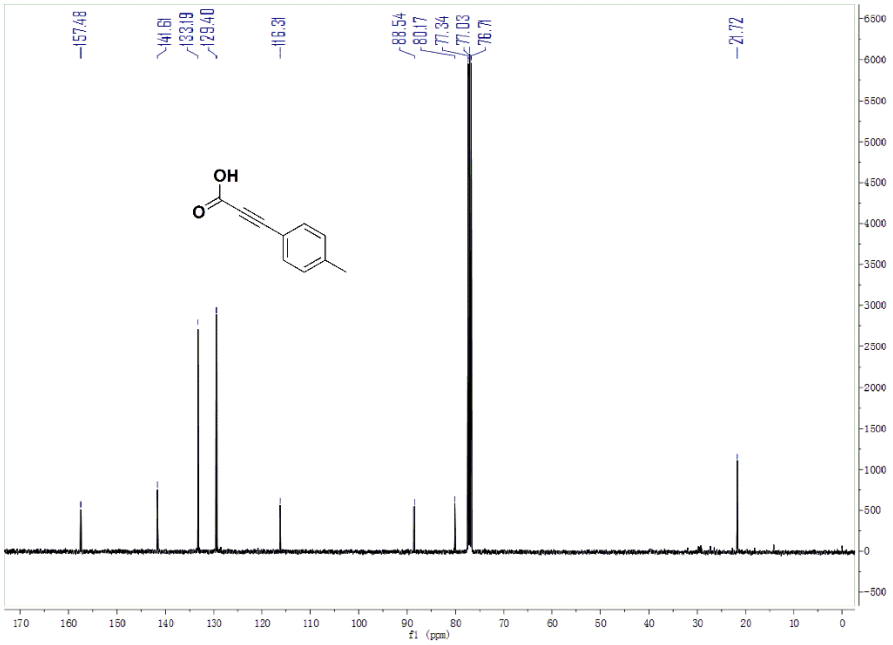
2.00
2.06
3.04
f1 (ppm)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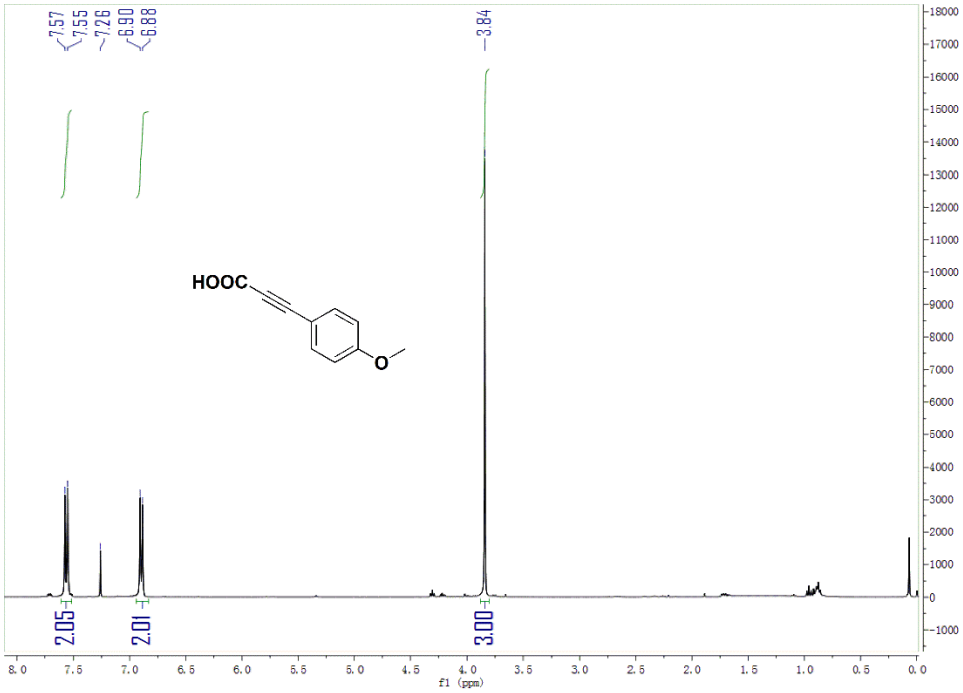
77.03
76.71
21.72
OH
O
f1 (ppm)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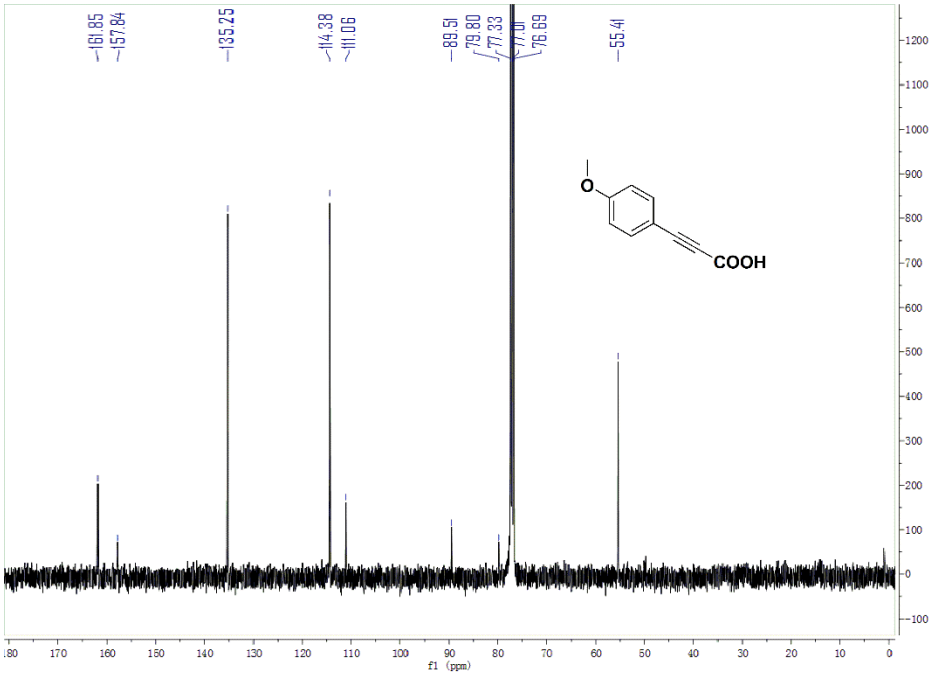
f1 (ppm)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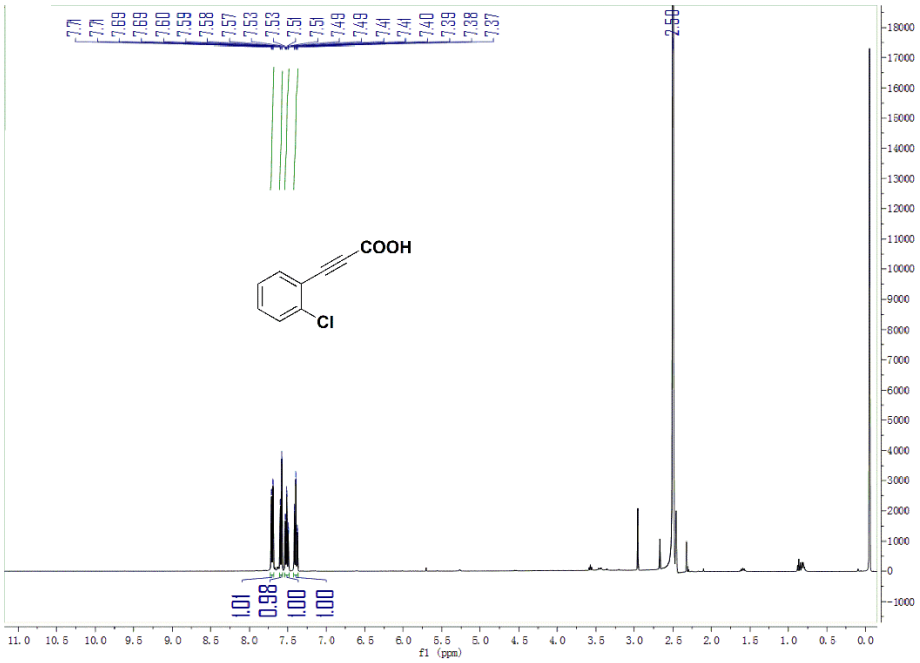
COOH
f1 (ppm)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7.49
7.41
7.41
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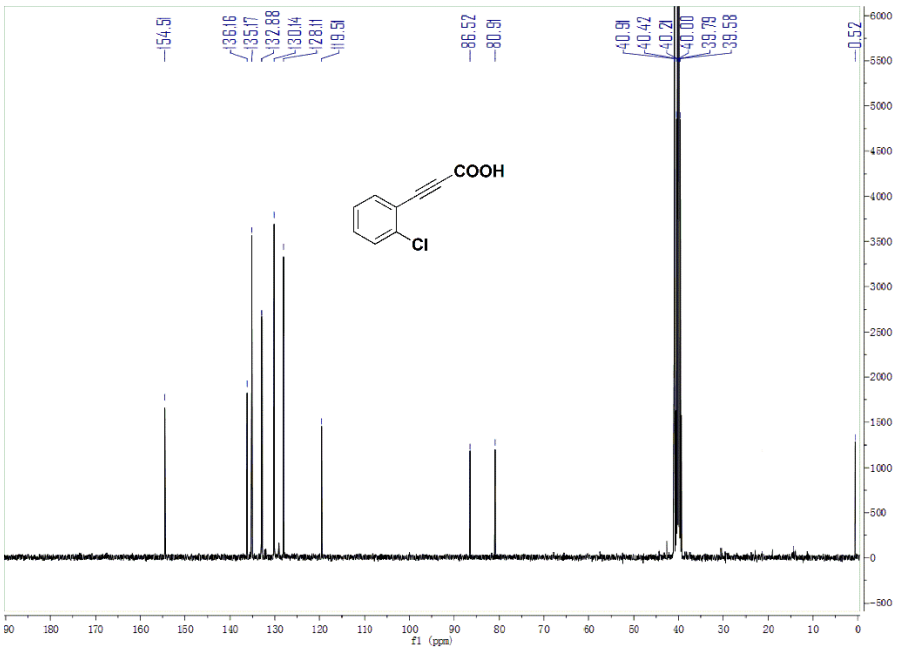
f1 (ppm)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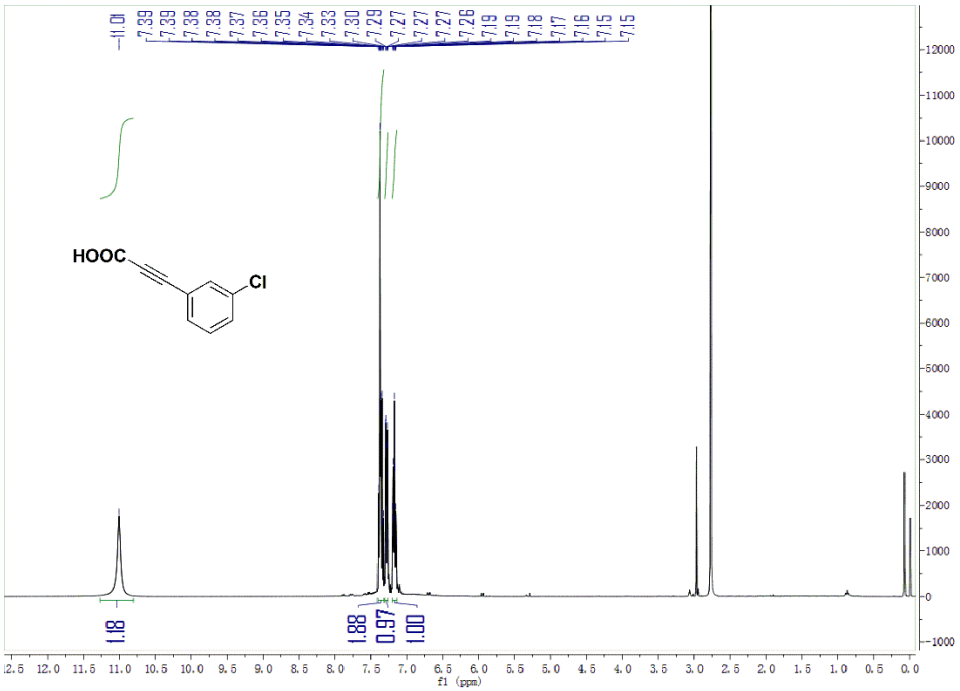
COOH
Cl
f1 (ppm)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7.27
7.26
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7.19
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Cl
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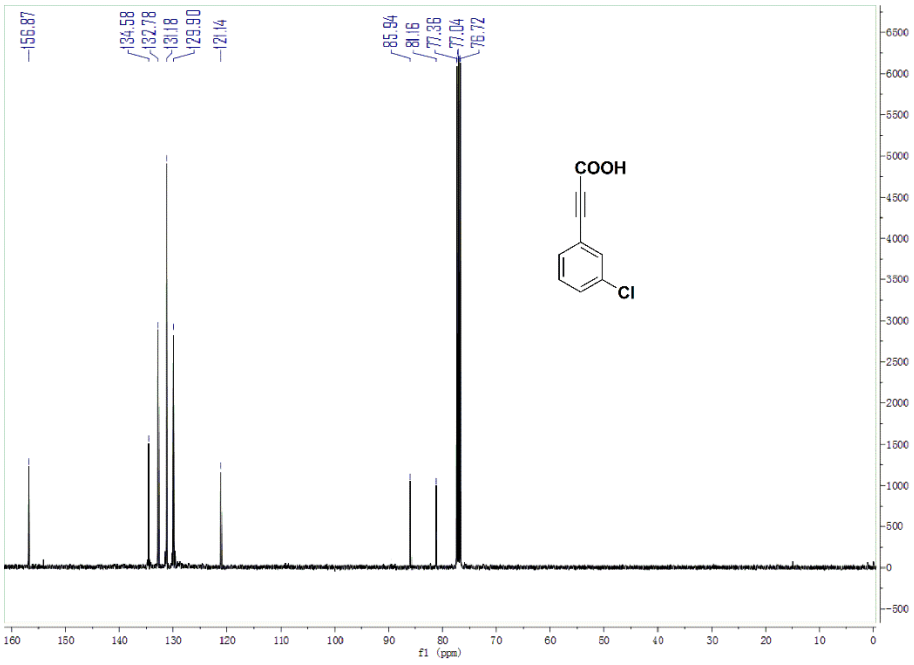
f1 (ppm)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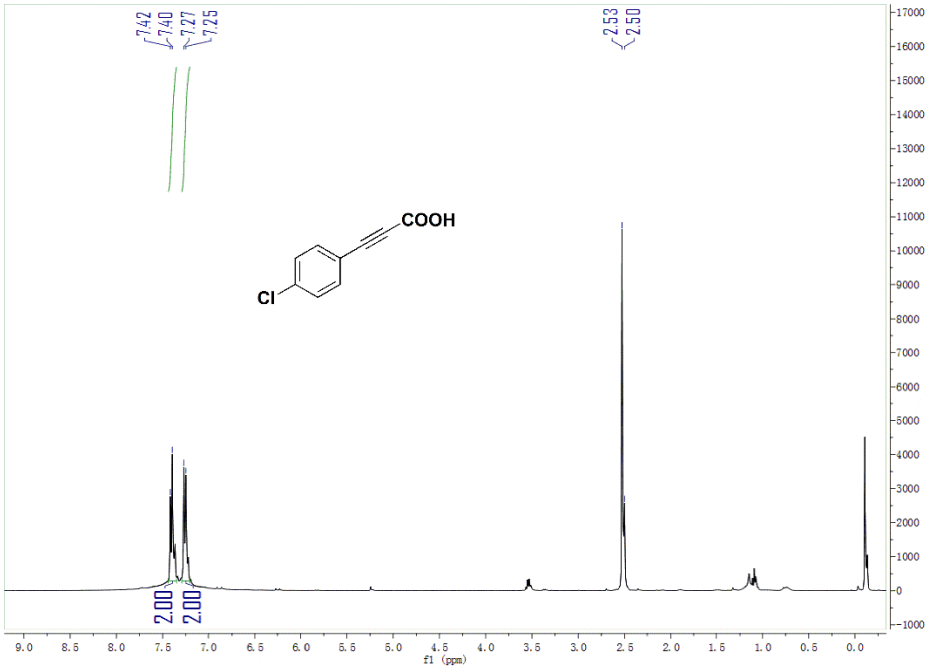
Cl
f1 (ppm)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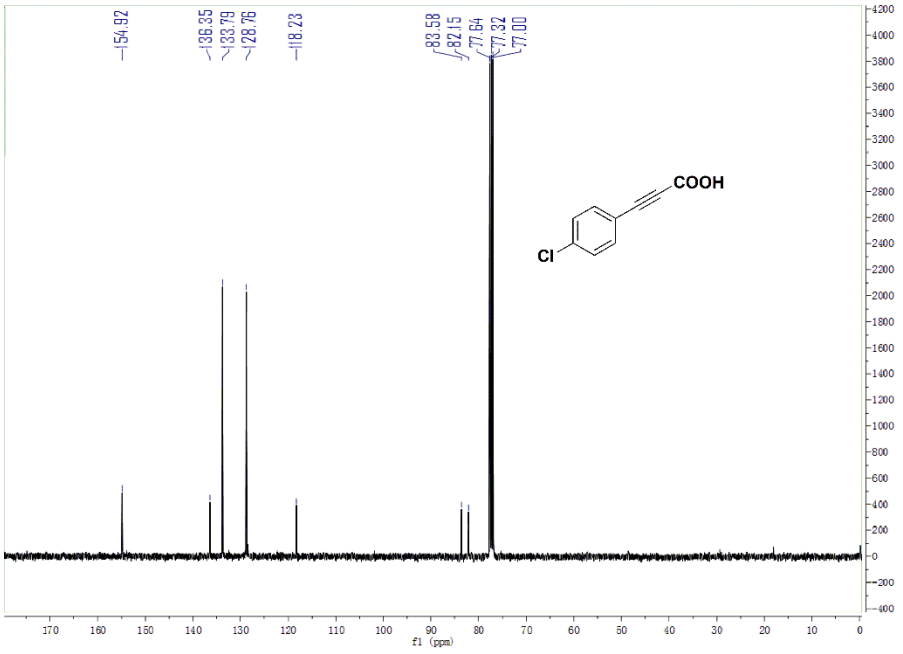
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Cl
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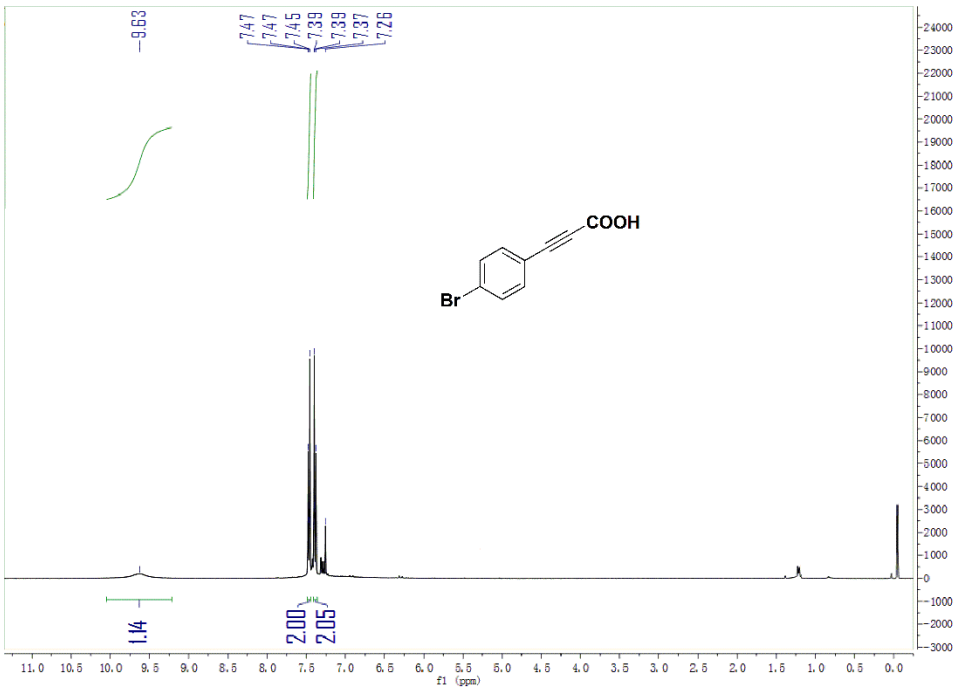
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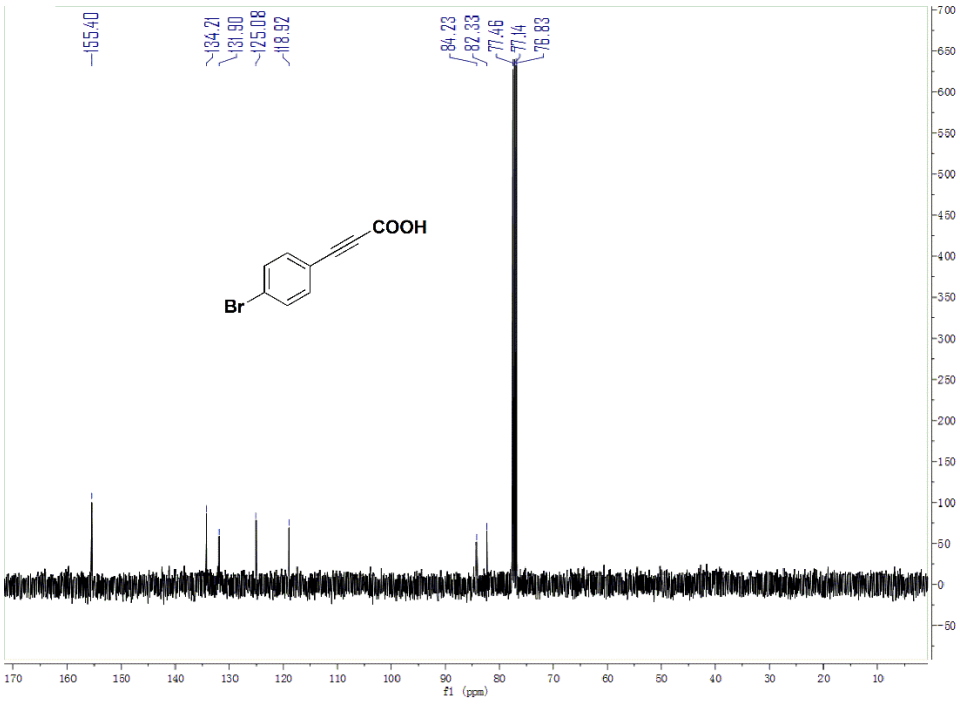
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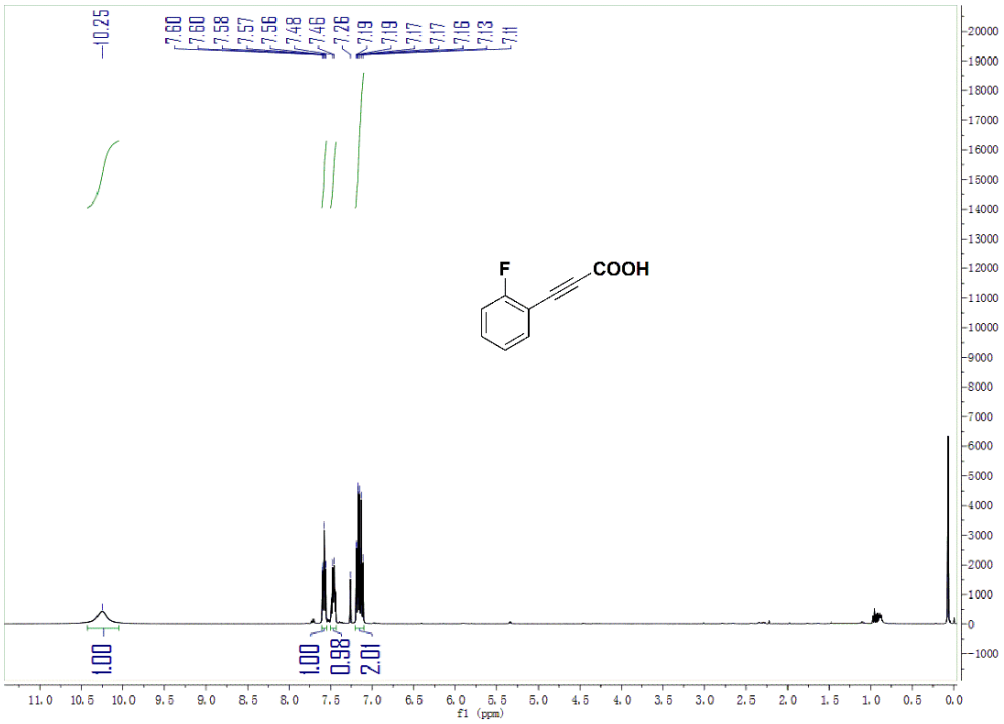
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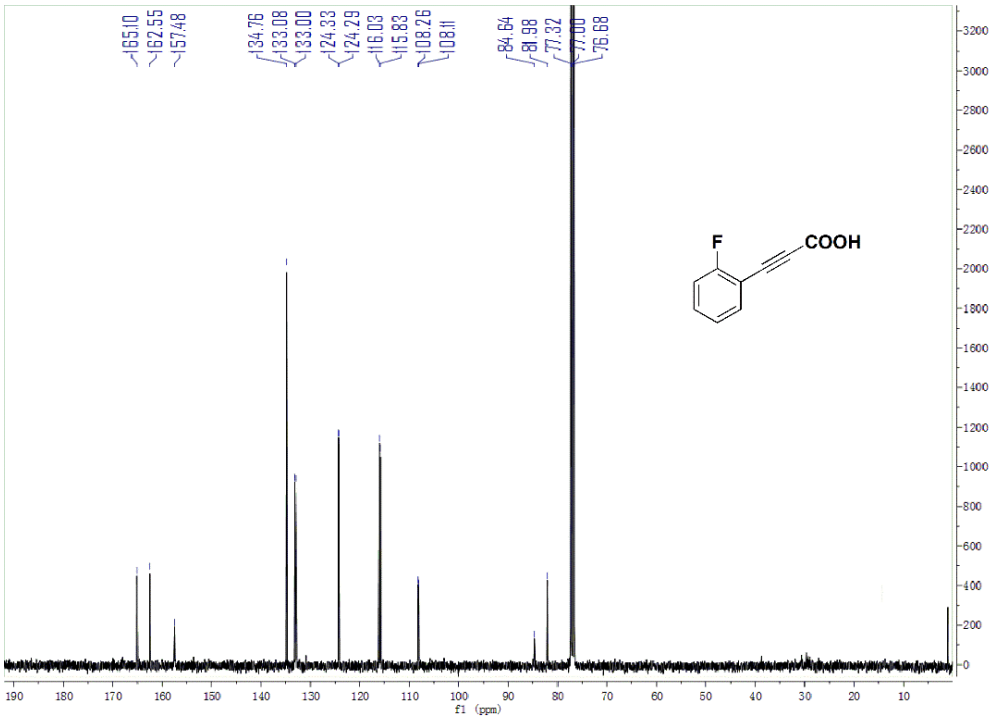
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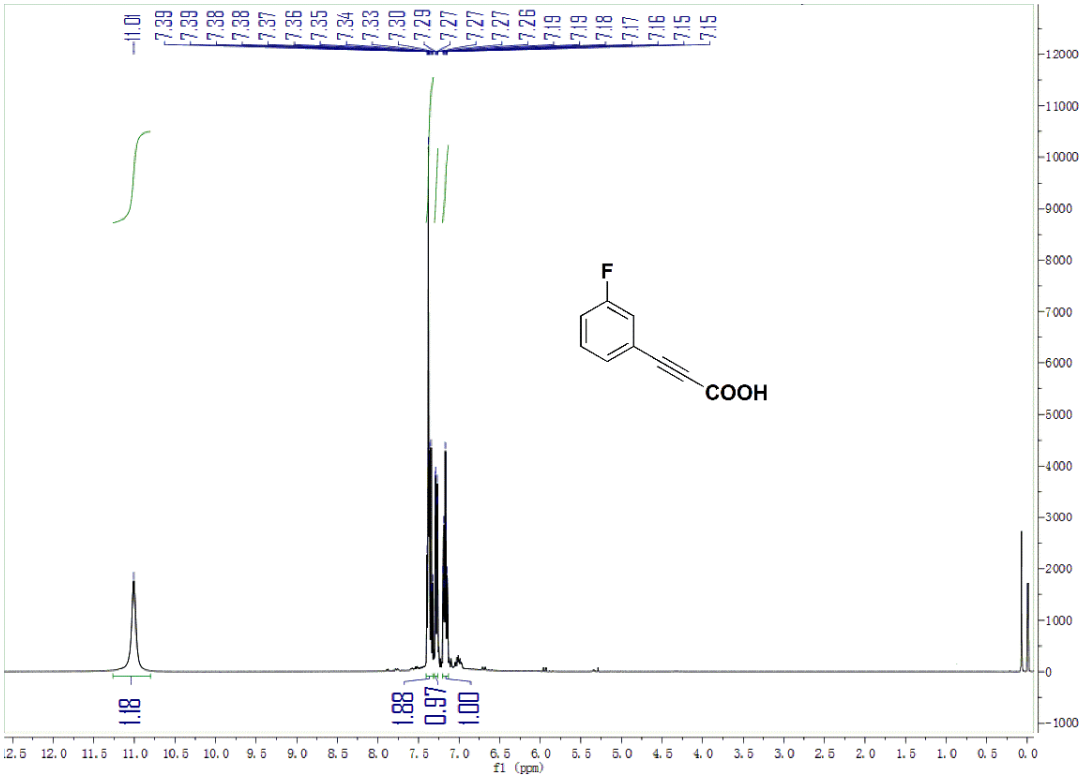
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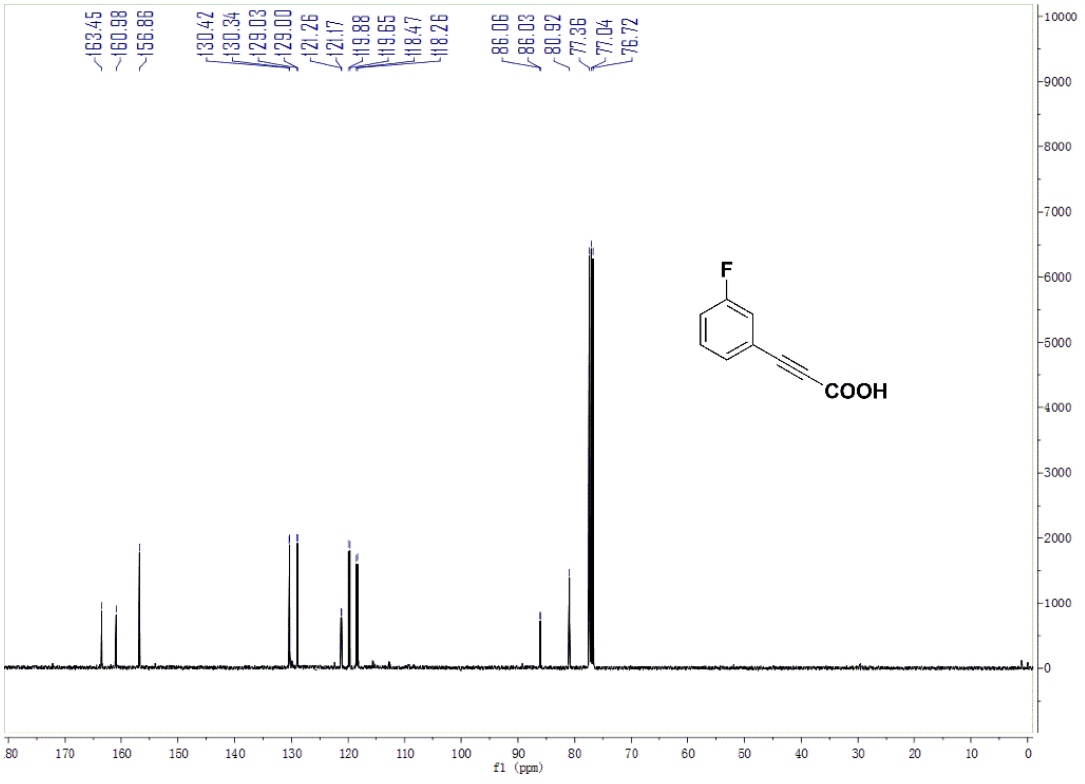
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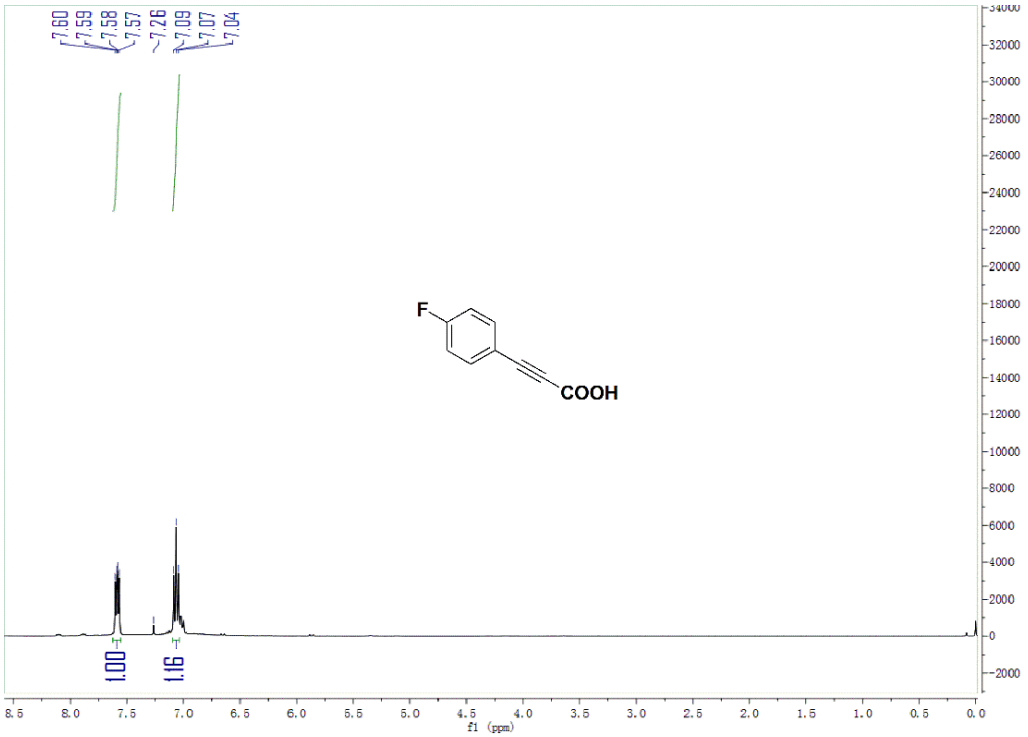
f1 (ppm)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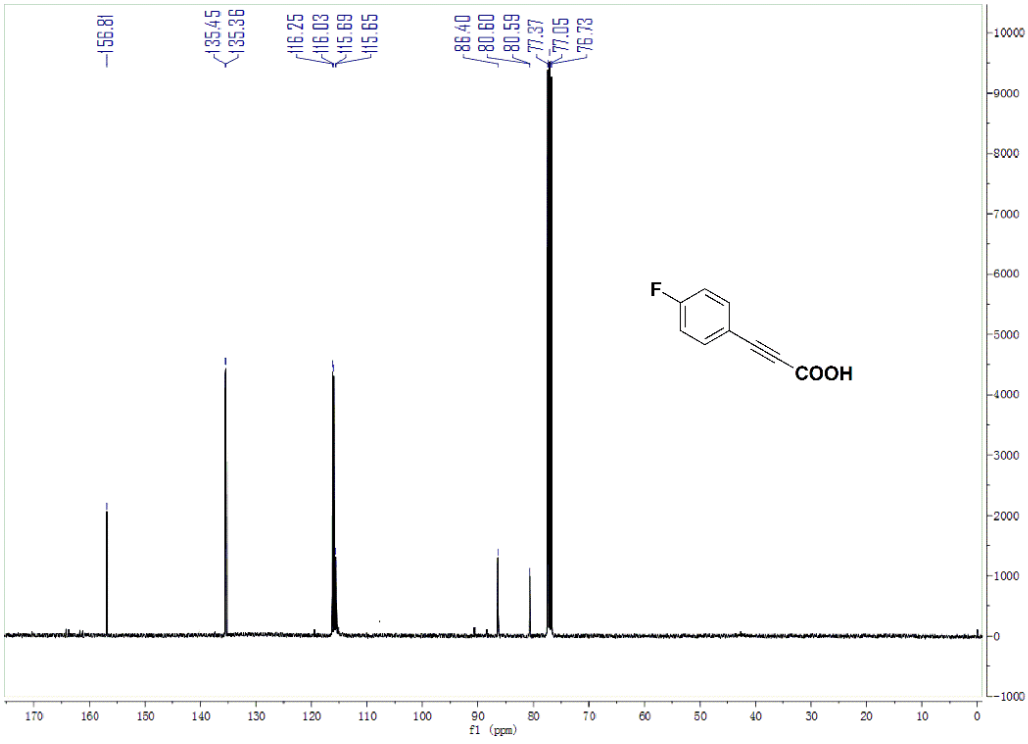
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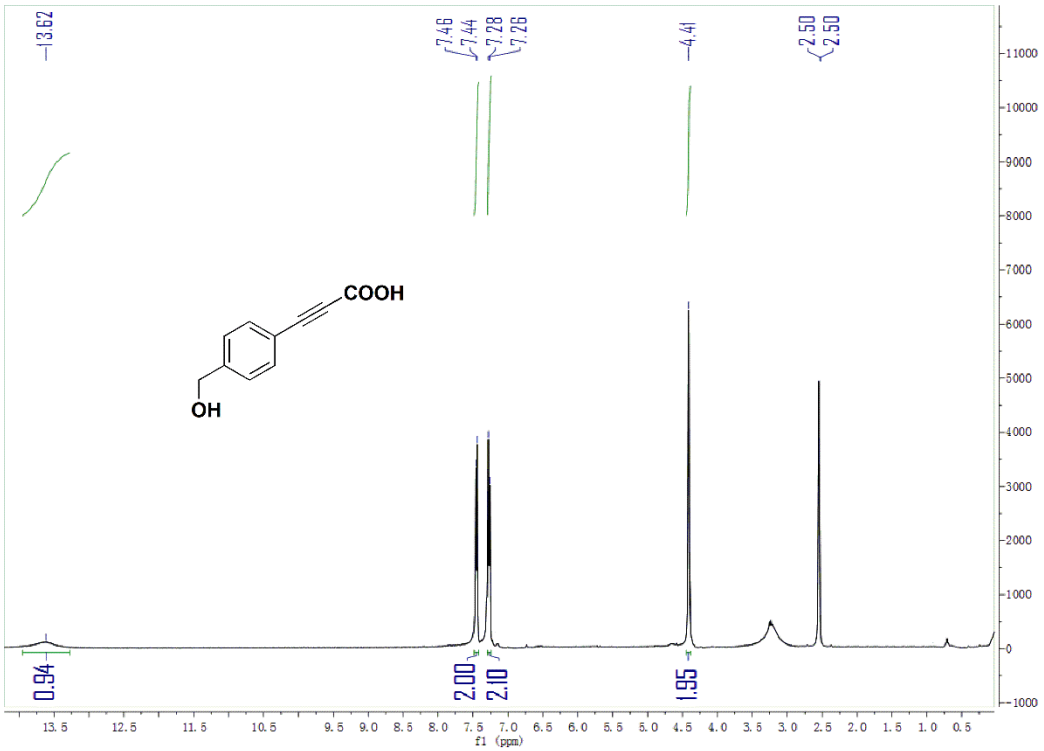
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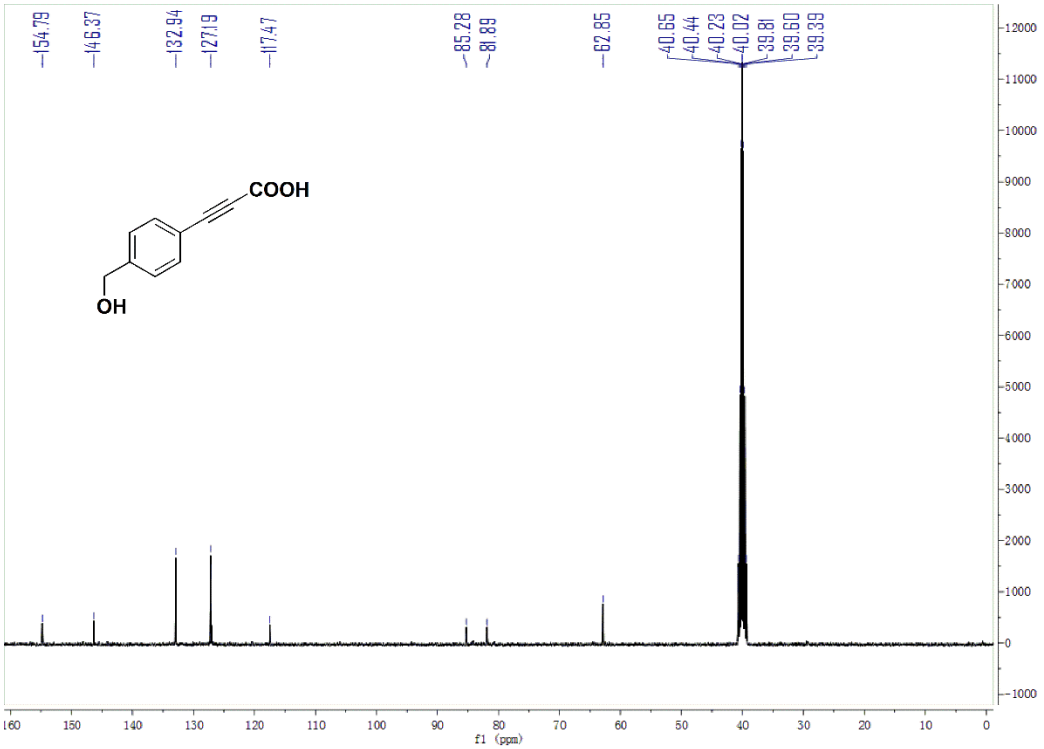
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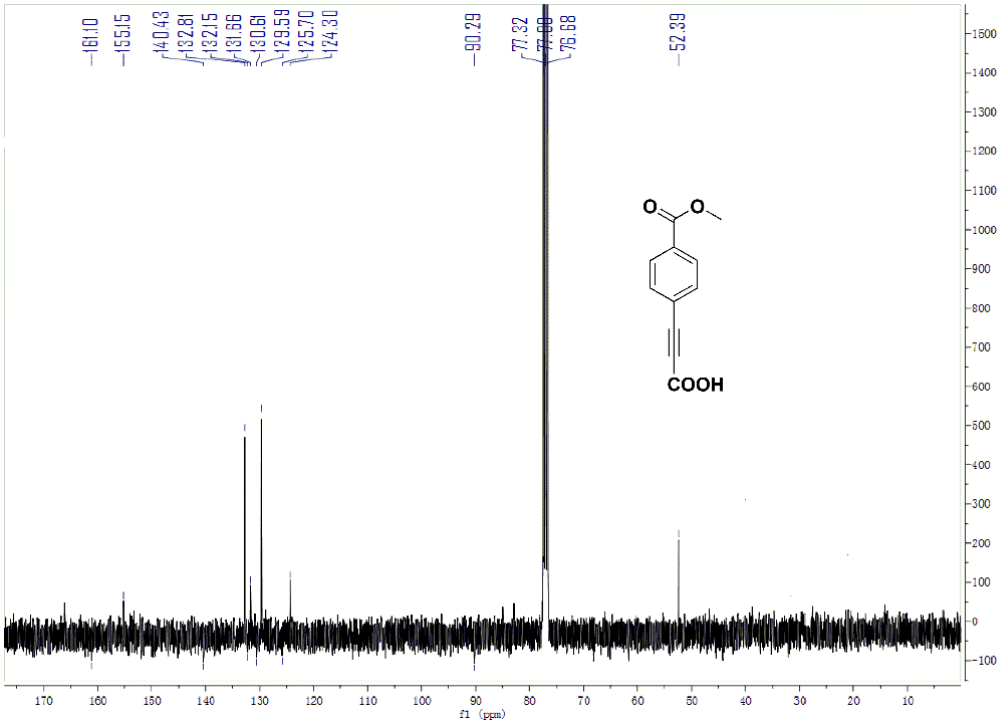
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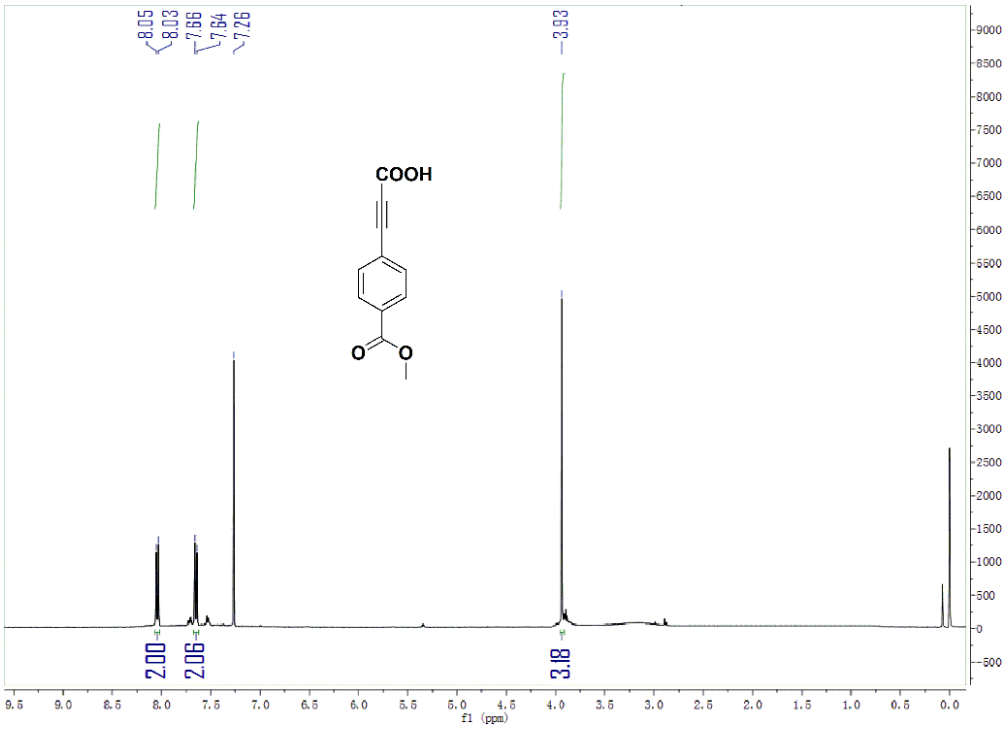
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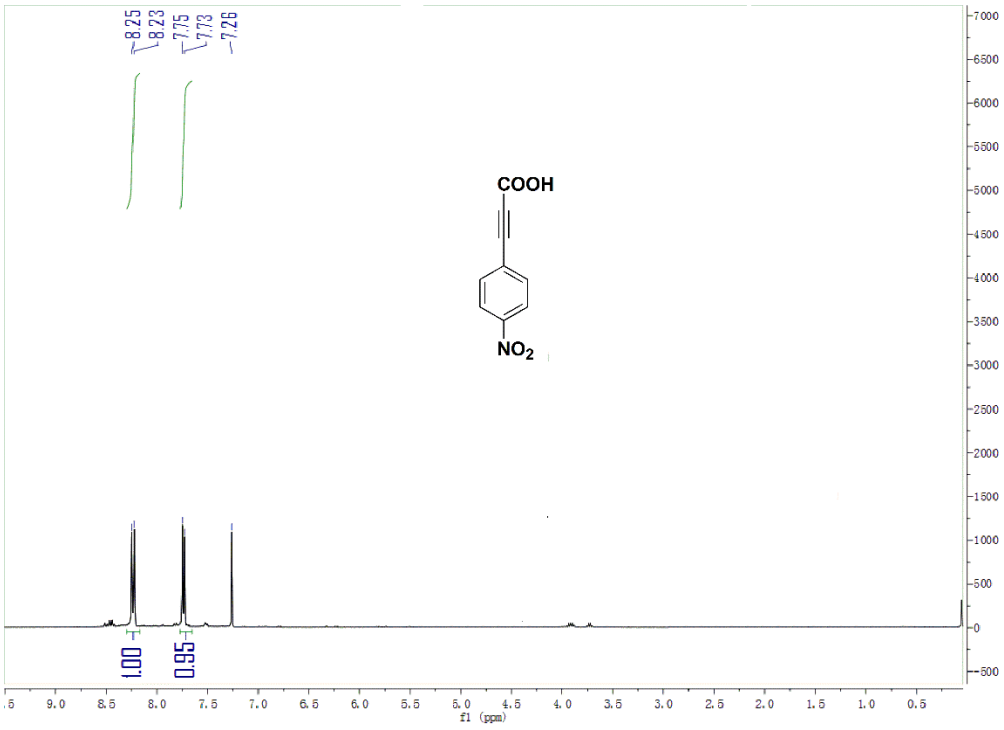
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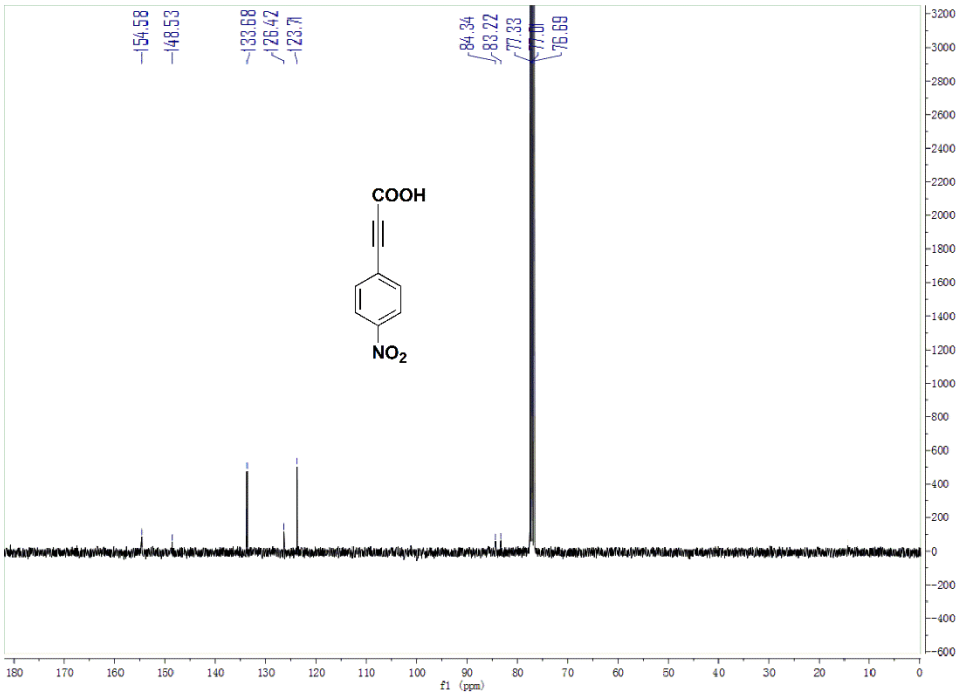
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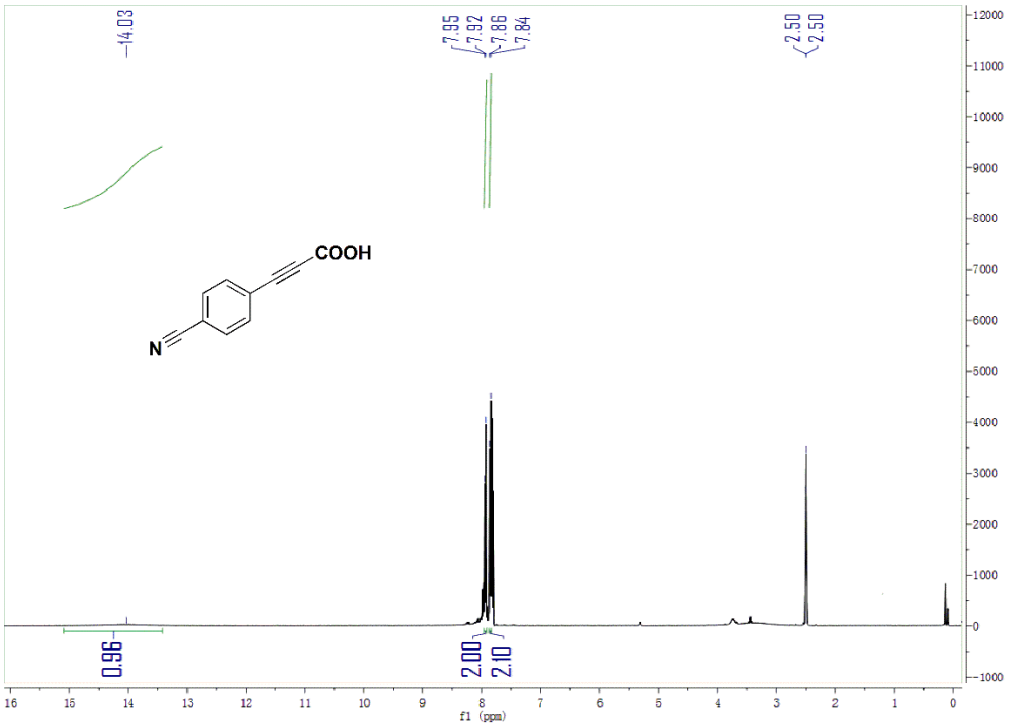
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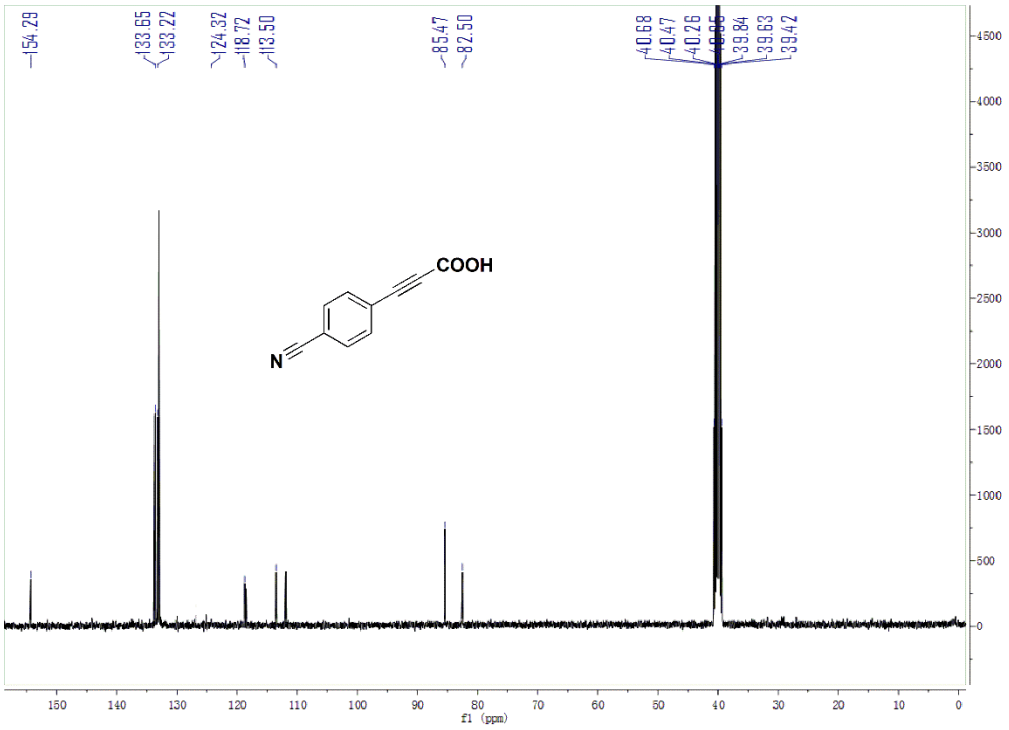
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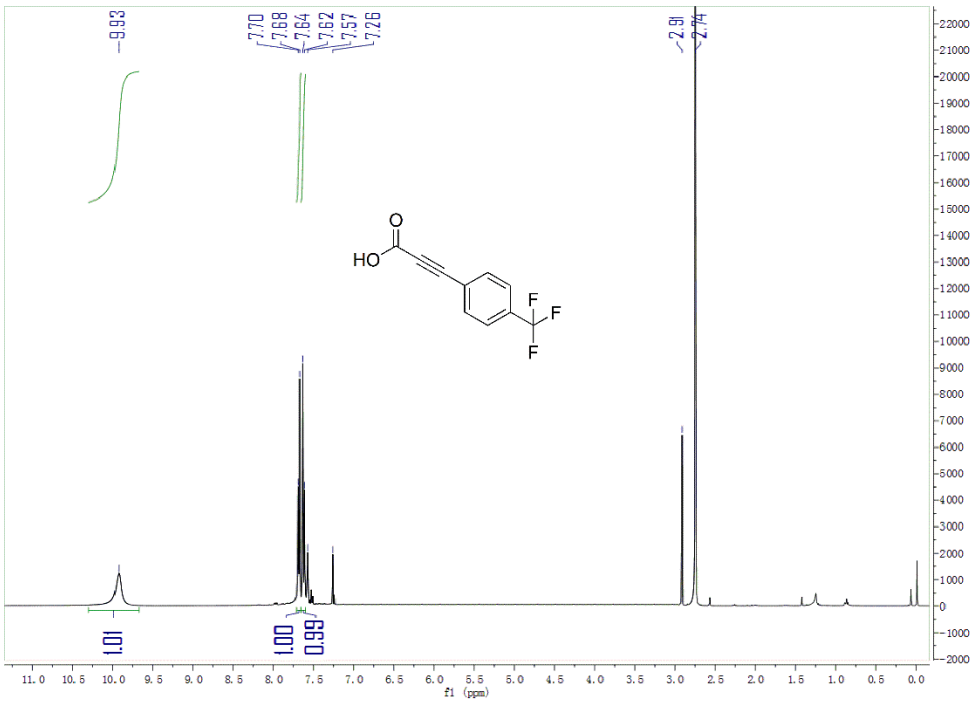
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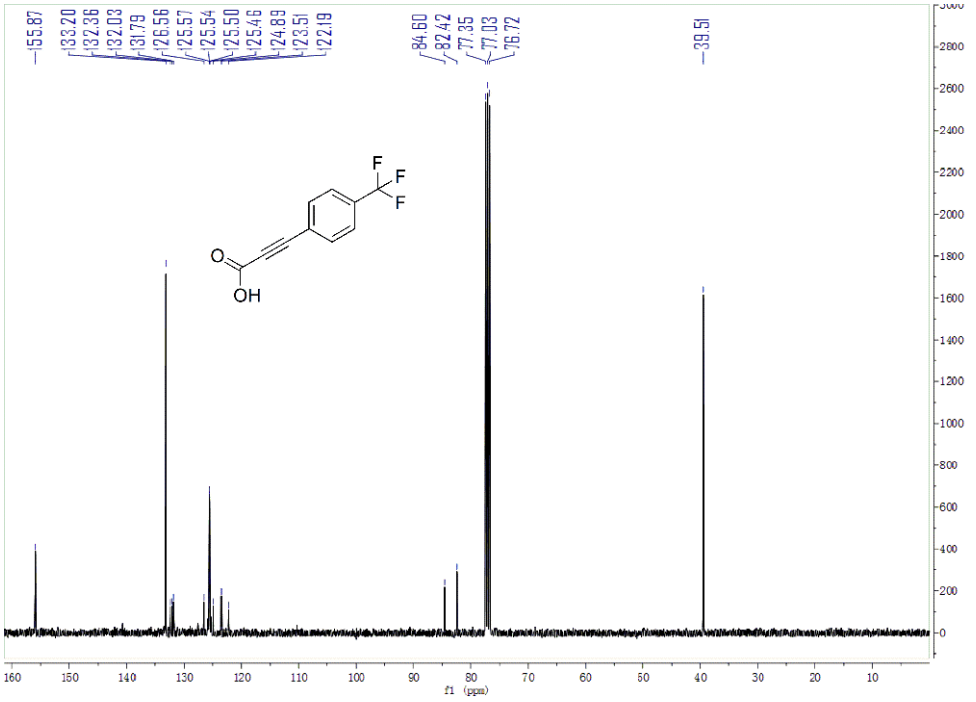
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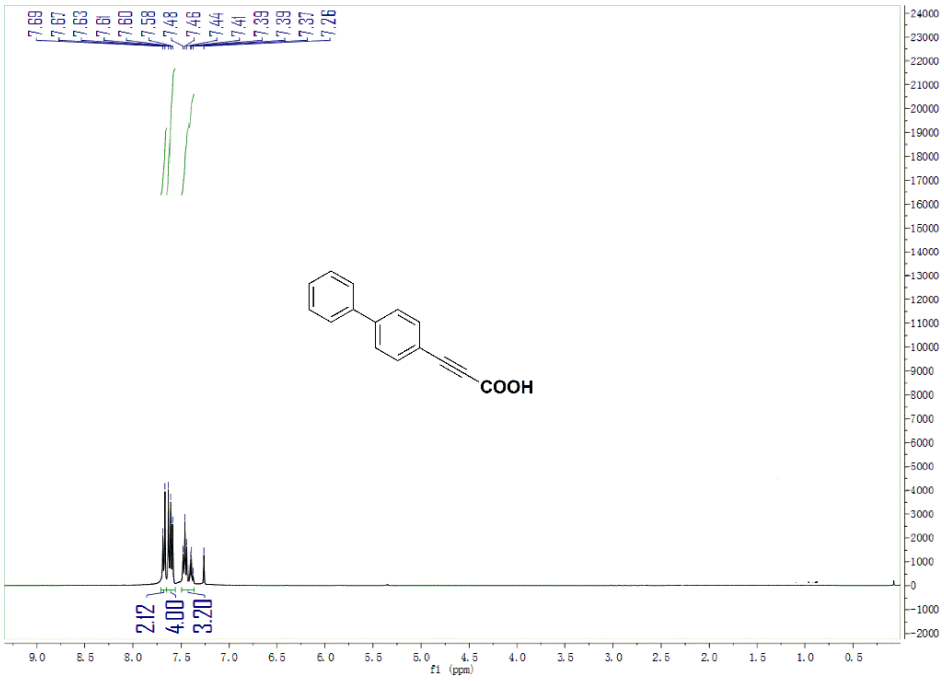
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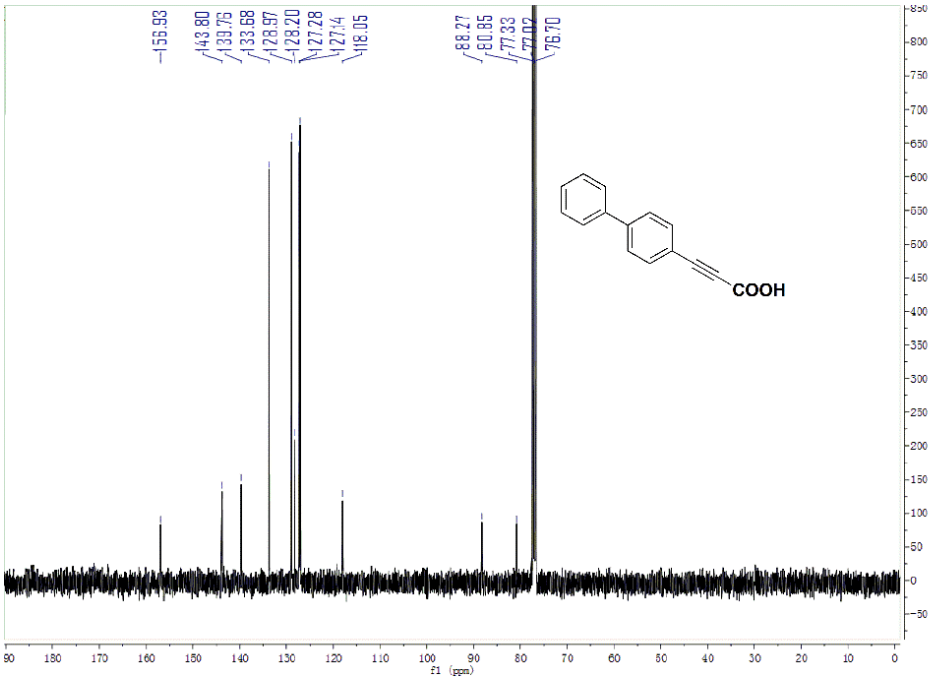
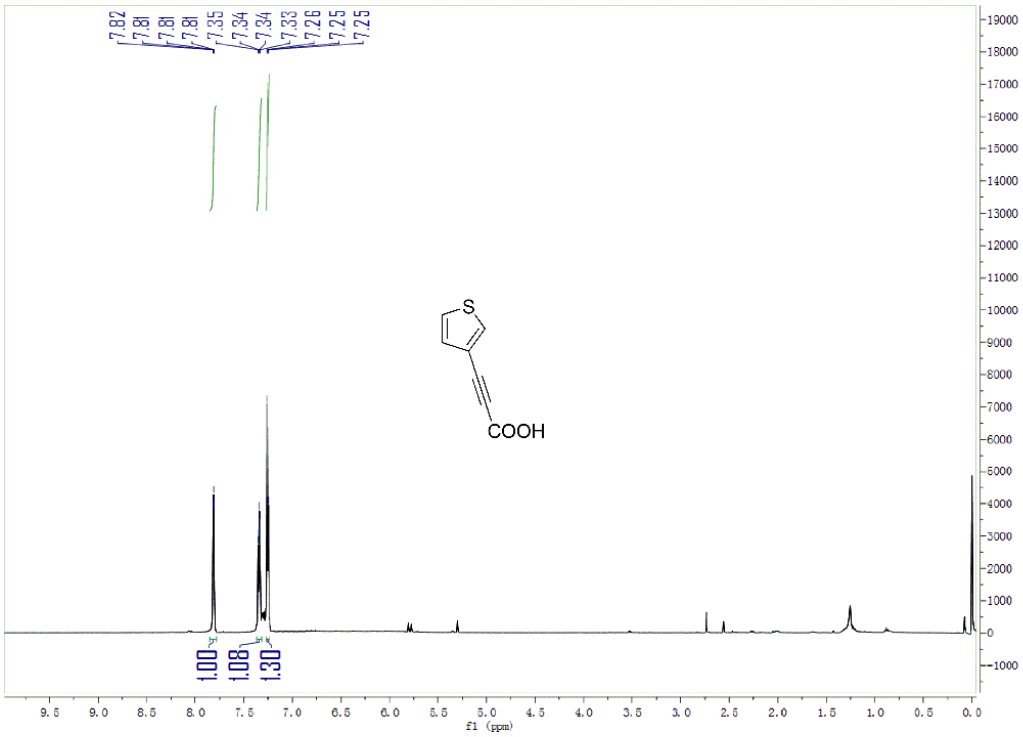
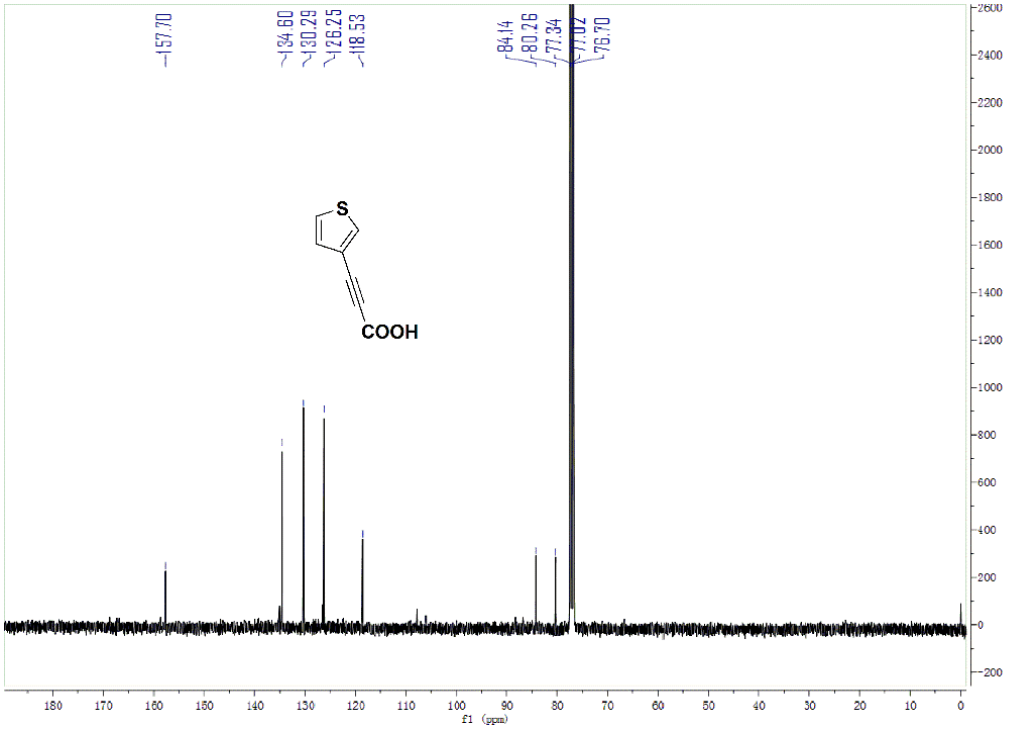
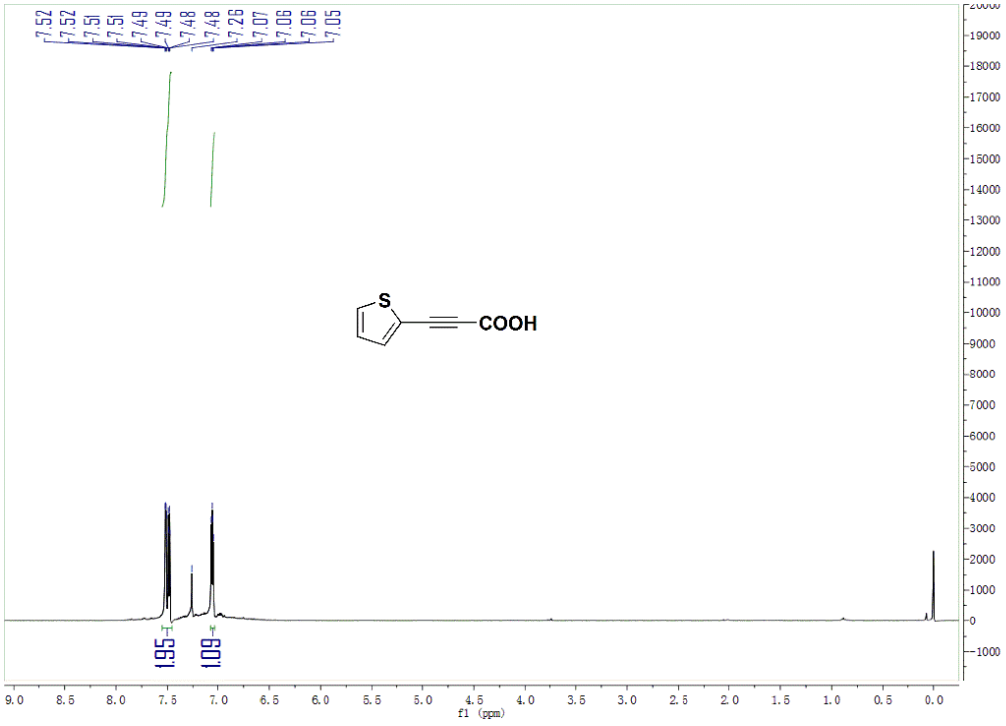
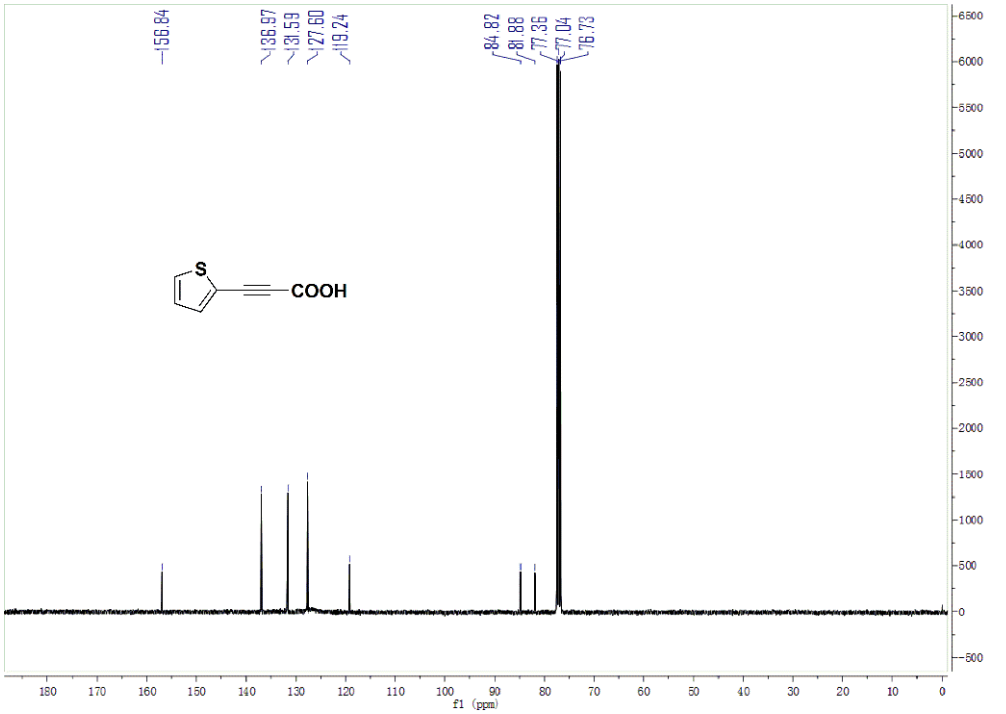
7.39
7.37
7.26
COOH
2.12
4.00
3.20
f1 (ppm)

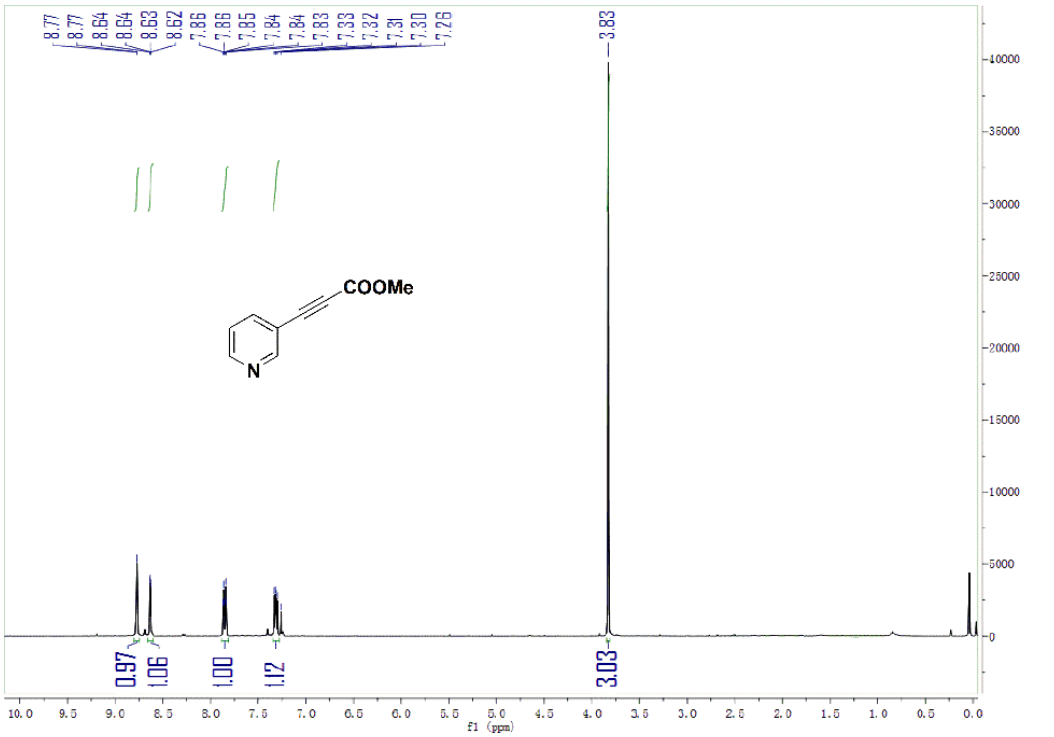

156.93
143.80
139.75
133.68
128.97
128.20
127.28
127.14
118.05
88.27
80.85
77.33
77.02
76.70
COOH
f1 (ppm)

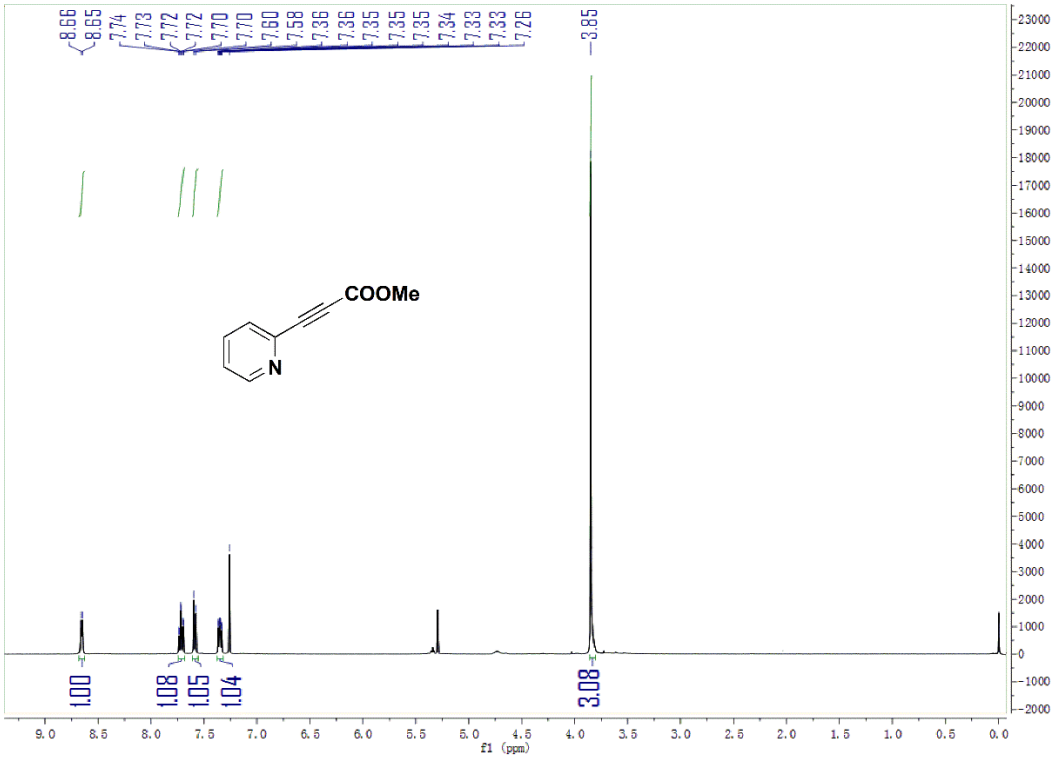

7.82
7.81
7.81
7.81
7.81
7.35
7.34
7.34
7.33
7.26
7.25
7.25
S
COOH
1.00
1.08
1.30
f1 (ppm)

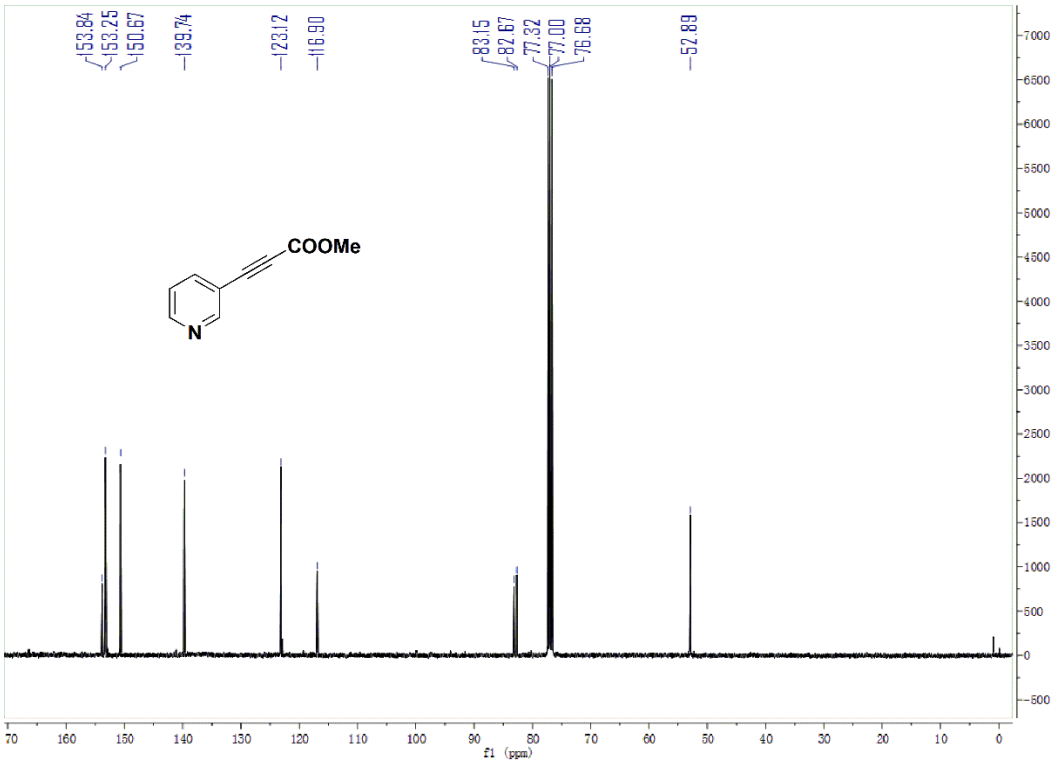

157.70
134.60
130.29
126.25
118.53
84.14
80.26
77.34
77.02
76.70
S
COOH
f1 (ppm)

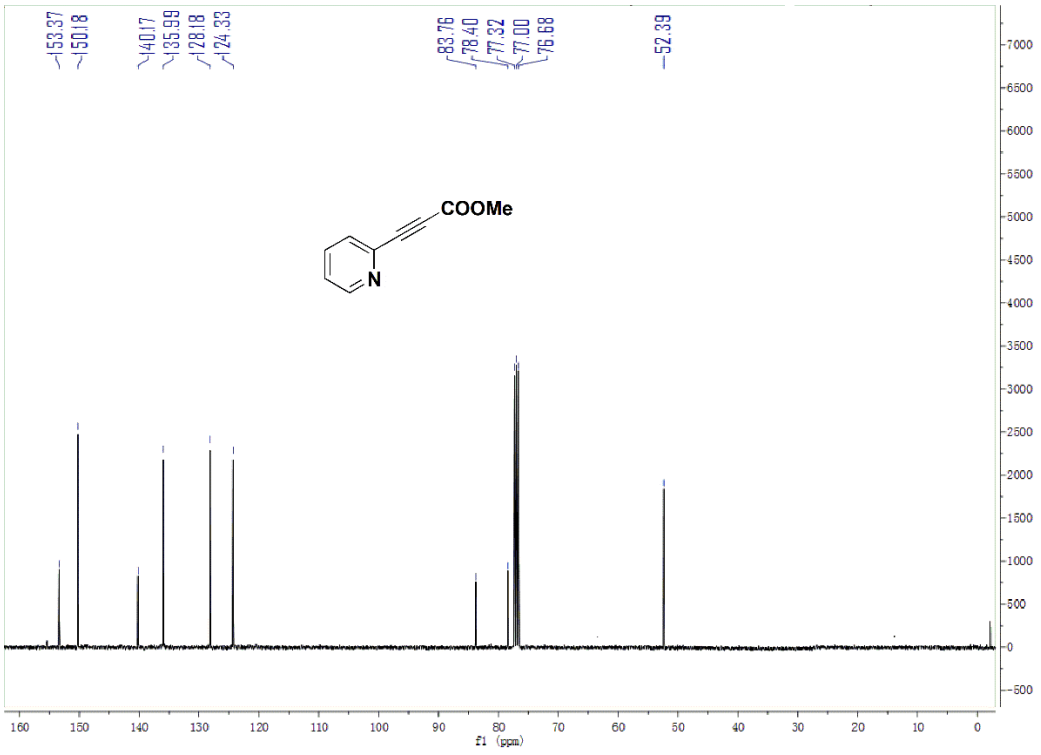

7.52
7.52
7.51
7.51
7.49
7.49
7.48
7.48
7.26
7.07
7.06
7.06
7.05
S
COOH
1.95
1.09
f1 (ppm)

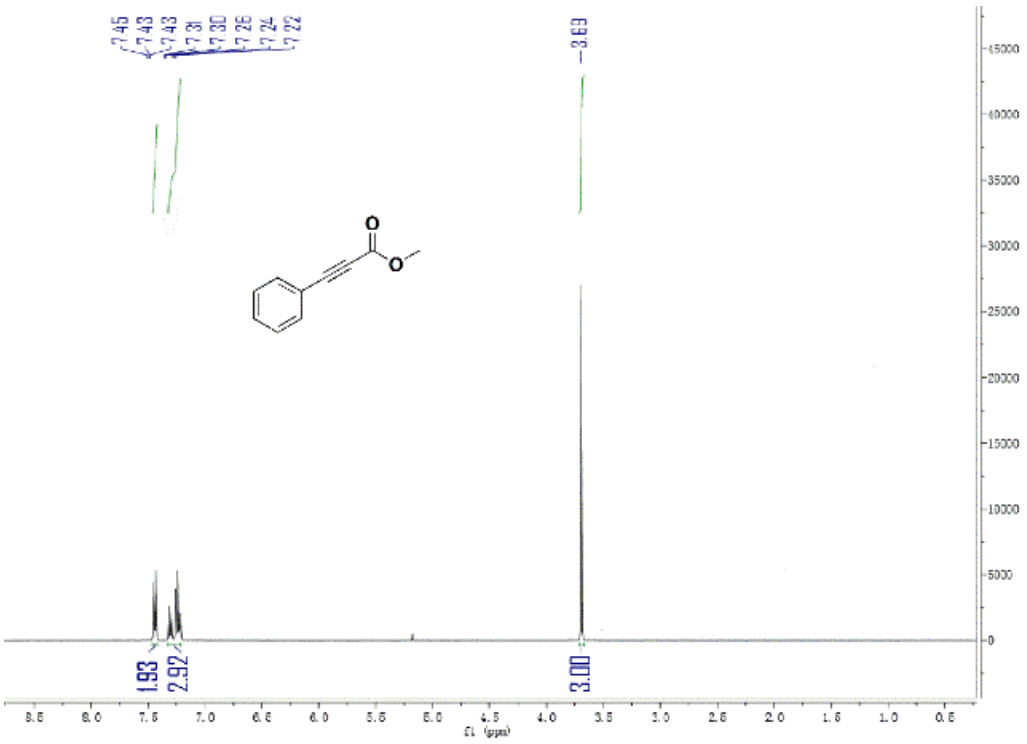

156.64
136.97
131.59
127.60
119.24
84.82
81.88
77.36
77.04
76.73
S
COOH
f1 (ppm)

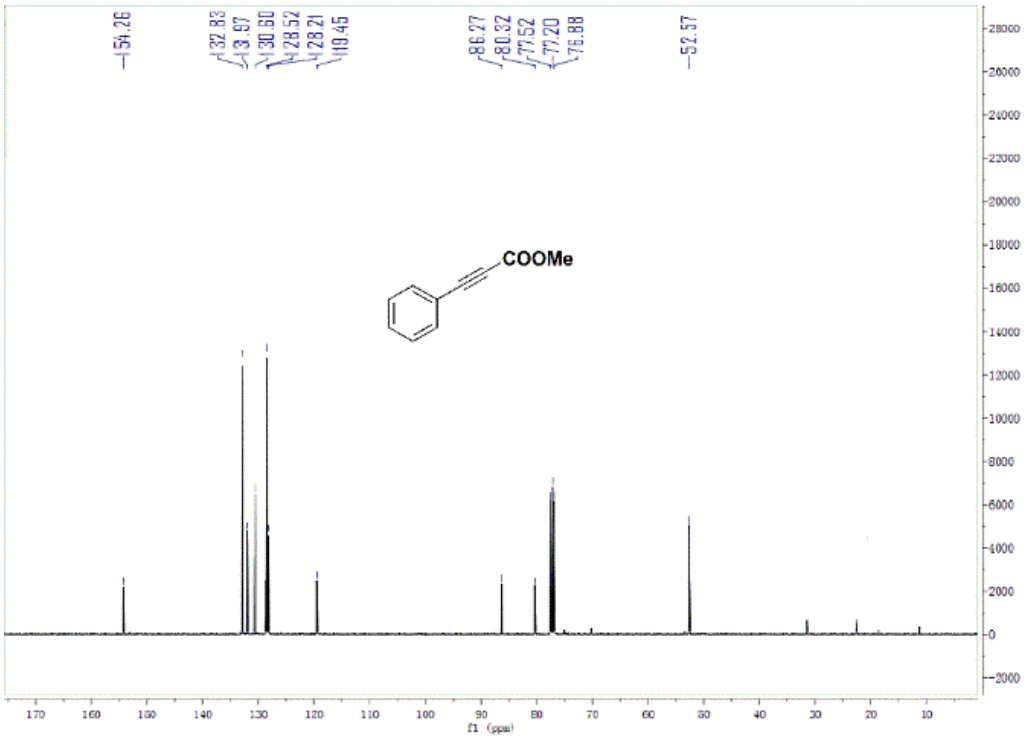

8.77
8.77
8.64
8.64
8.63
8.62
7.86
7.86
7.85
7.84
7.84
7.83
7.33
7.32
7.31
7.30
7.26
3.83
COOMe
N
0.97
1.06
1.00
1.12
3.03
f1 (ppm)

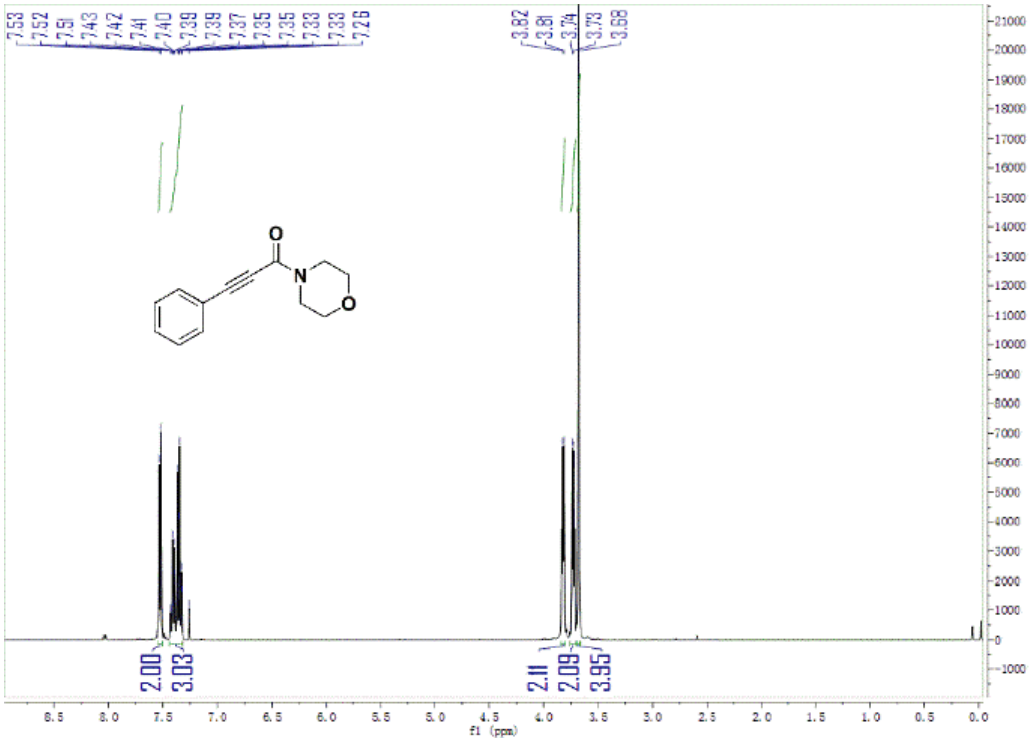

8.66
8.65
7.74
7.73
7.72
7.72
7.70
7.70
7.60
7.58
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.26
3.85
COOMe
N
1.00
1.08
1.05
1.04
3.08
f1 (ppm)

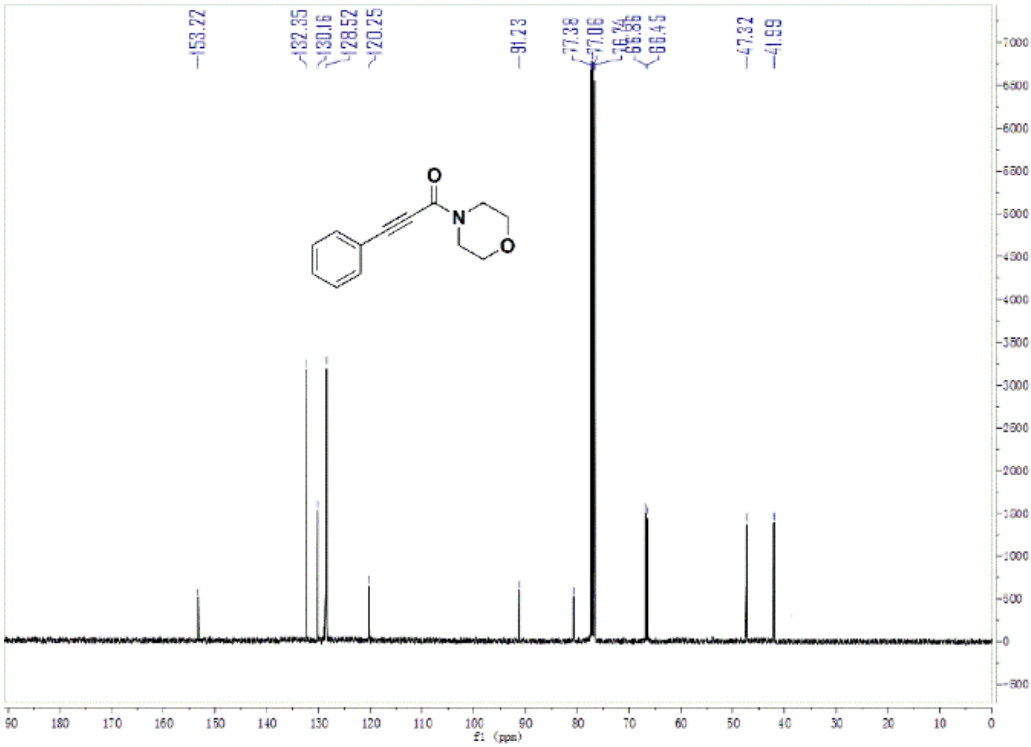

153.84
153.25
150.67
139.74
123.12
116.90
83.15
82.67
77.32
77.00
76.68
52.89
COOMe
N
f1 (ppm)

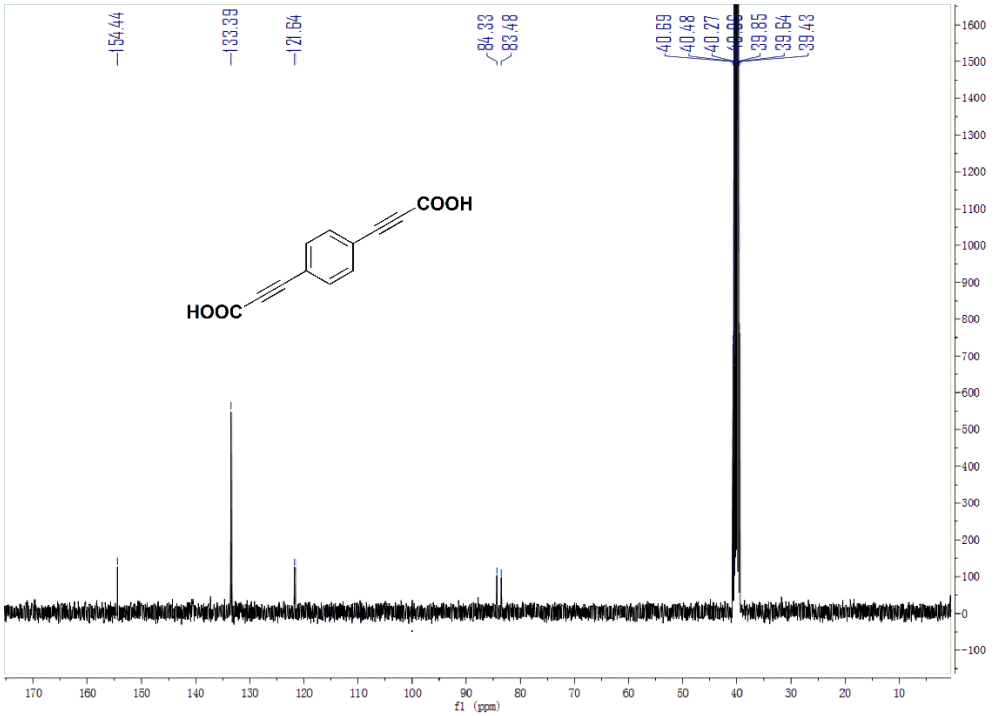

153.37
150.18
140.17
135.98
128.18
124.33
83.76
78.40
77.32
77.00
76.68
52.39
COOMe
N
f1 (ppm)

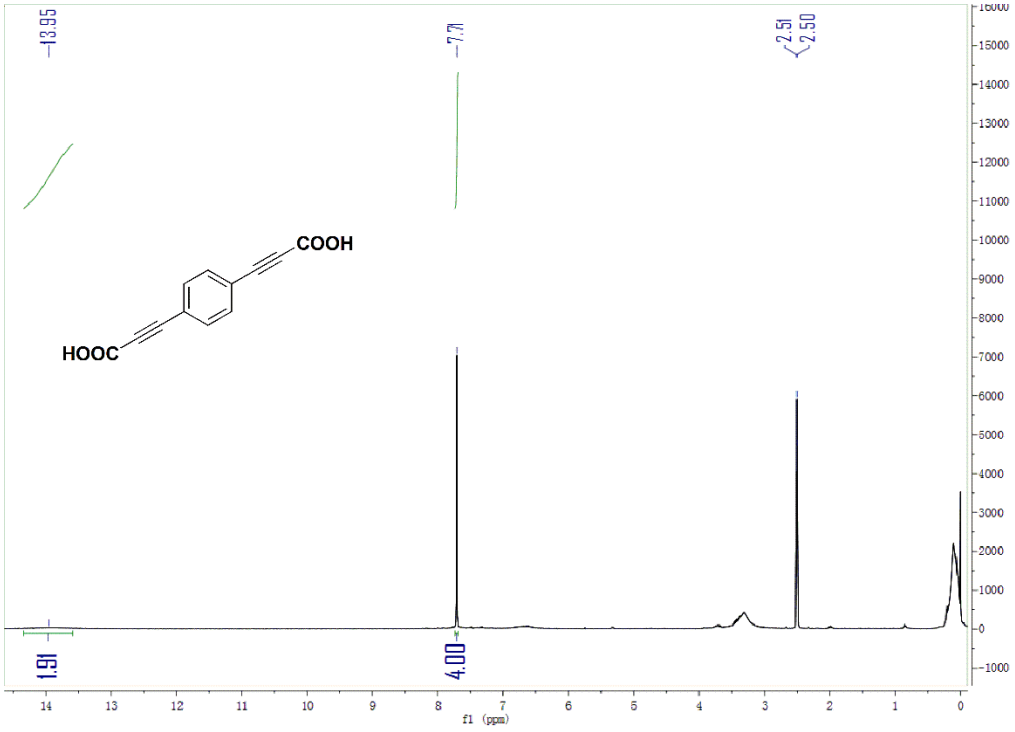

7.45
7.43
7.43
7.31
7.30
7.26
7.24
7.22
3.69
O
O
1.93
2.92
3.00
f1 (ppm)

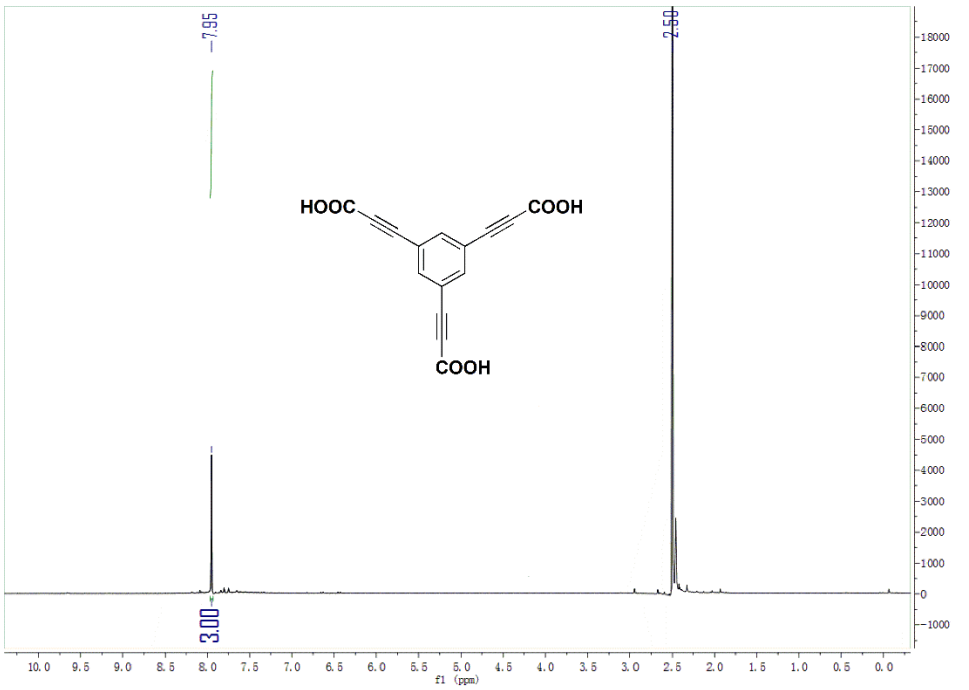

154.26
132.83
131.97
130.60
128.52
128.21
119.45
86.27
80.32
77.52
77.20
76.88
52.57
COOMe
f1 (ppm)

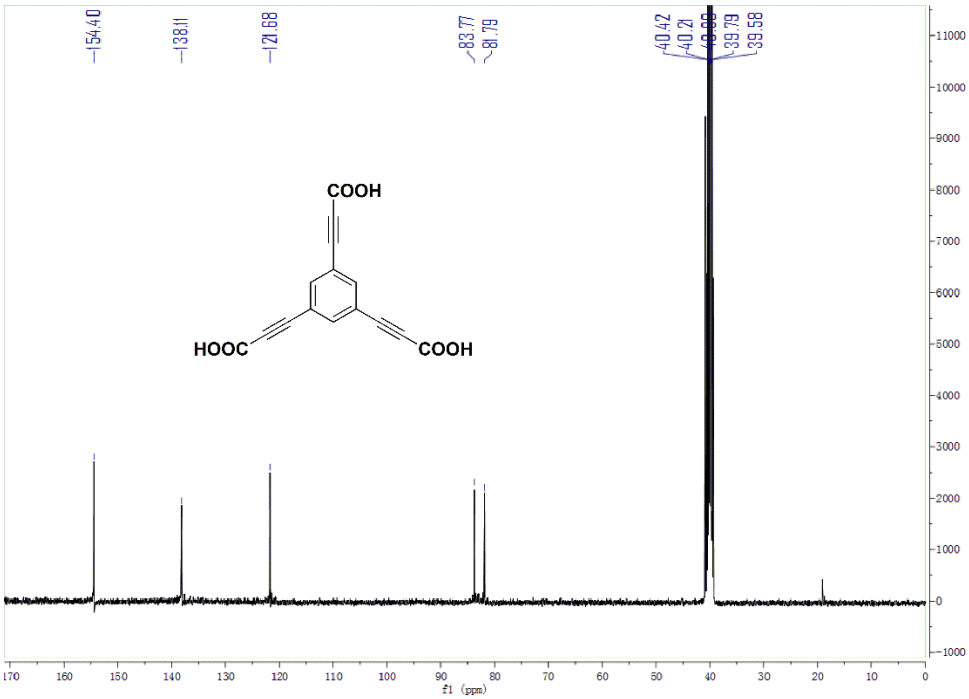

7.53
7.52
7.51
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.35
7.35
7.33
7.33
7.26
3.82
3.81
3.74
3.73
3.68
O
N
O
2.00
3.03
2.11
2.09
3.95
f1 (ppm)


153.72
132.55
130.16
128.52
120.25
91.23
77.38
77.06
76.74
66.86
66.45
47.32
41.99
O
N
O
f1 (ppm)

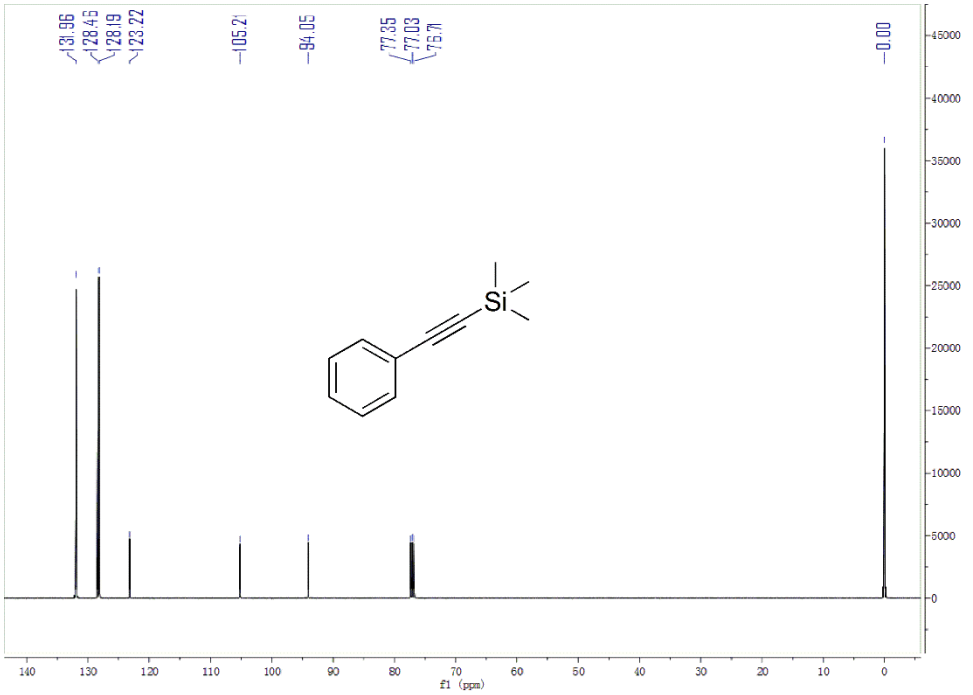

154.44
133.39
121.64
84.33
83.48
40.69
40.48
40.27
39.85
39.64
39.43
COOH
HOOC
f1 (ppm)


13.95
7.71
2.51
2.50
COOH
HOOC
1.91
4.00
f1 (ppm)


7.95
2.60
HOOC
COOH
COOH
3.00
f1 (ppm)


154.40
138.11
121.68
83.77
81.79
40.42
40.21
39.79
39.58
COOH
HOOC
COOH
f1 (ppm)


7.53
7.52
7.52
7.51
7.34
7.33
7.32
7.32
7.25
0.32
0.32
0.31
Si
2.00
3.01
9.11
f1 (ppm)


131.96
128.45
128.19
123.22
105.21
94.05
77.35
77.03
75.71
0.00
Si
f1 (ppm)