Supporting Information

Fixation of CO_2 as Carboxylic Acid Precursor by Microcrystalline Cellulose (MCC) Supported Ag NPs: A More Efficient, Sustainable, Biodegradable and Eco-friendly Catalyst

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Experimental

Materials

Without any further purification, analytical grade (AR) chemicals were used as purchased. Silver nitrate, terminal alkynes derivatives were purchased from Sigma Aldrich. Ethyl acetate, methanol, DMSO, DMF, acetonitrile were purchased from Finar Chemicals and hydrazine hydrate was purchased from Sigma Aldrich. Water used in all experiments was purified by Millipore-Q system. Freshly prepared 3:1 HCl/HNO_3 (aqua regia) was used to clean all glassware thoroughly cleaned before use.

Instrumentation

JEOL JEM 2100 instrument and were used for particle size measurement through High resolution transmission electron microscopy (HR-TEM) as well as Energy dispersive atomic X ray analysis (EDAX). A drop of methanol with dispersed catalyst was placed onto a 200 mesh carbon coated copper grid. The water was evaporated and particle size measurement was done. The powder XRD of the catalyst was recorded on Brucker D_2 Phaser using Cu Kα radiation (λ = 1.54184 Å) and a filter of nickel at 30 kV and 10 mA with step size 0.03 and count time 0.1s. Scanning Electron microscopy analysis (SEM) was carried out through JSM 6100 (JEOL) with acceleration voltage range 0.3 to 30 kV and working distance of 6 to 48 mm. IR spectra were recorded on Bruker FT-IR spectrophotometer using KBr pellets. The disc containing 1 mg of sample was scanned within a range of 600 to 3600 cm^{-1}. ^{1}H NMR spectra were measured in Bruker AV 400 MHz using $CDCl_3$, DMSO as solvent and TMS as internal standard. Mass spectra were recorded by injecting the samples in ESI ionizer of Shimadzu LCMS 2010 with single quadruple analyzer.

Preparation of Ag NPs/MCC

The resulting microcrystalline cellulose (MCC) support material was dispersed in methanol by sonication. A methanolic solution of silver nitrate [$Ag(NO_3)_2$] (12 mg) was added to the dispersed solution of MCC (500 mg) and after sonication the mixture was stirred for 3 h at room temperature. The resulting solution was reduced by adding hydrazine hydrate (0.5 ml) as reducing agent. The resulting solution was centrifuged and washed with methanol, and dried to afford Ag NPs/MCC catalyst.

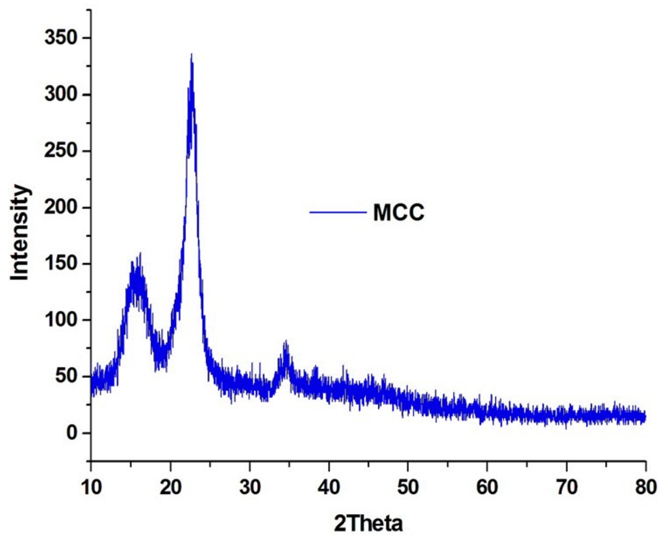


Figure S_1. PXRD of Micro crystalline cellulose (MCC).

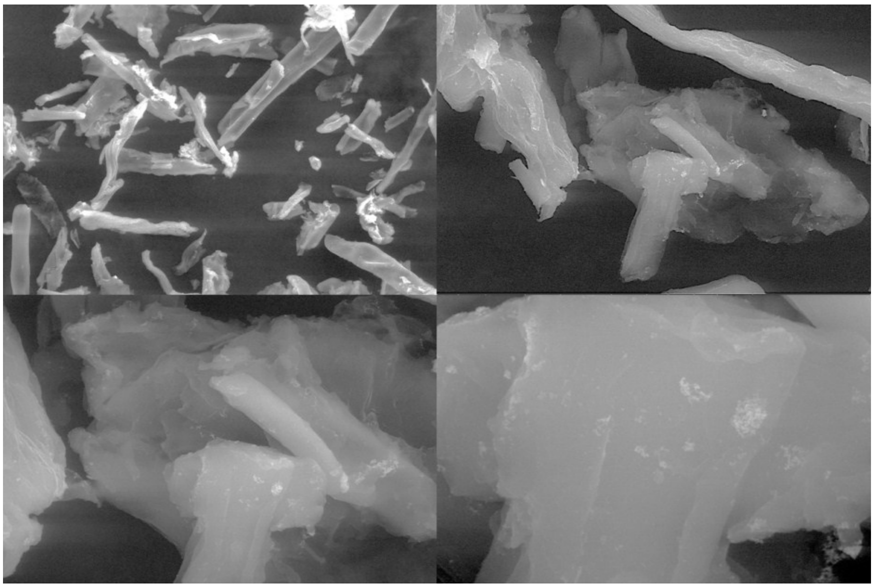


Figure S_2. SEM images of Micro crystalline cellulose (MCC).

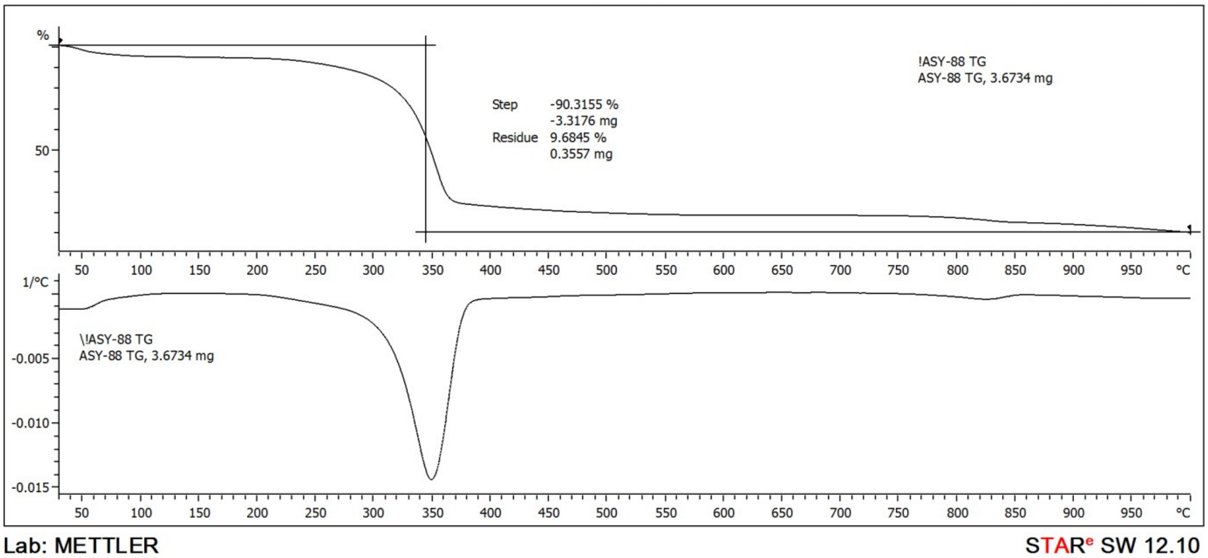


Figure S$_3$. TGA of Micro crystalline cellulose (MCC).

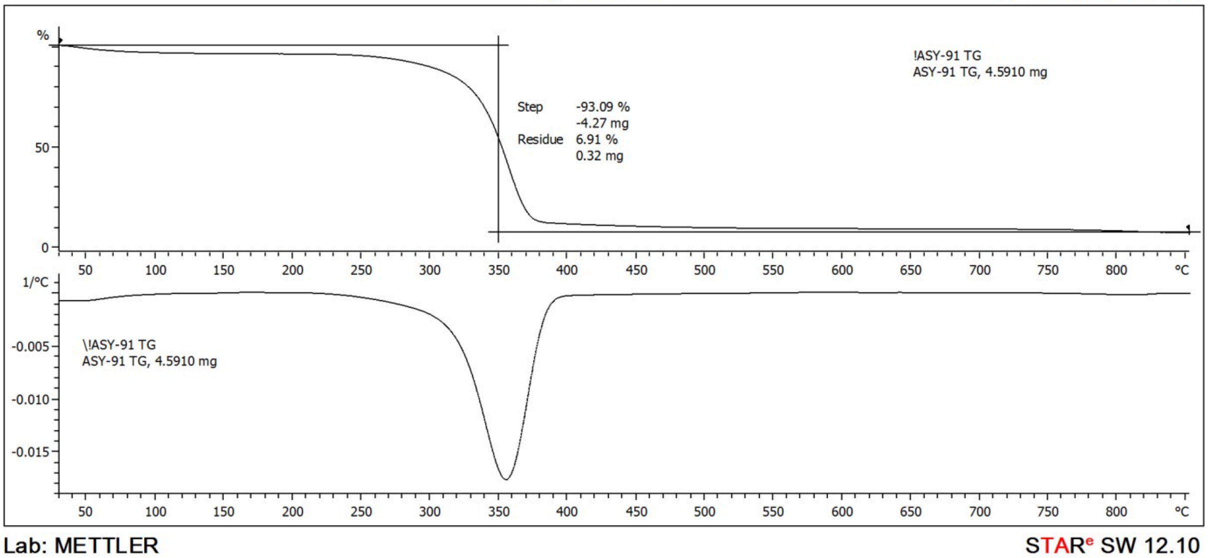


Figure S$_4$. TGA of Ag/MCC.

Catalytic activity characterization

General experimental procedure for carbonylation of terminal alkynes

In a 10 ml glass vessel, terminal alkyne (0.116 g, 1 mmol), Cs_2CO_3 (0.489 g, 1.5 mmol), Ag NPs/MCC (30 mg) and DMSO (5 ml) were added. The glass vessel was capped with a septum and sealed. Then the "freeze-pump-thaw" method was employed for gas exchanging process. The CO_2 balloon (99.99 %) is attached with the vessel. The reaction mixture was stirred at 50 ˚C for desired time under the atmosphere of CO_2. The progress of the reaction was monitored by LC-MS analysis. After the completion of the reaction, the reaction mixture was cooled to room temperature. After that the reaction mixture was partitioned between water (50 ml) and diethyl ether (50 ml). Then aqueous layer was acidified using 1N HCl (10 ml, 1N) and extracted in diethyl ether (2×50 ml). After that the solvent was completely evaporated under a rotary evaporator. The obtained curded product was purified in reverse phase (C18 silica gel) with using 0-95 % acetonitrile: water to get the final desired product.

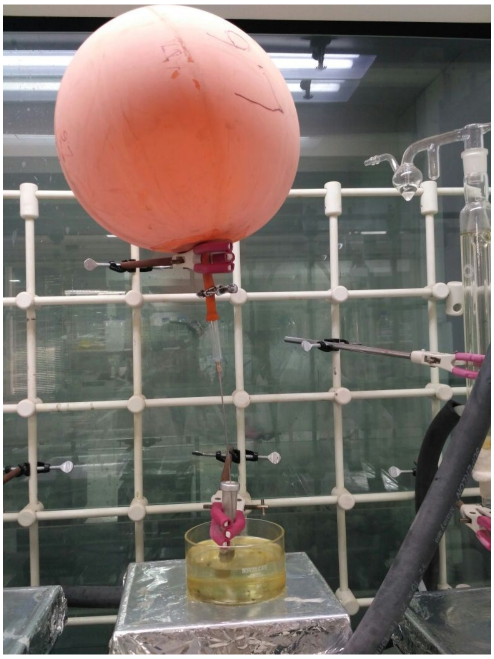


Figure S_5. Experimental Setup for the carbonylation of the terminal acetylene.

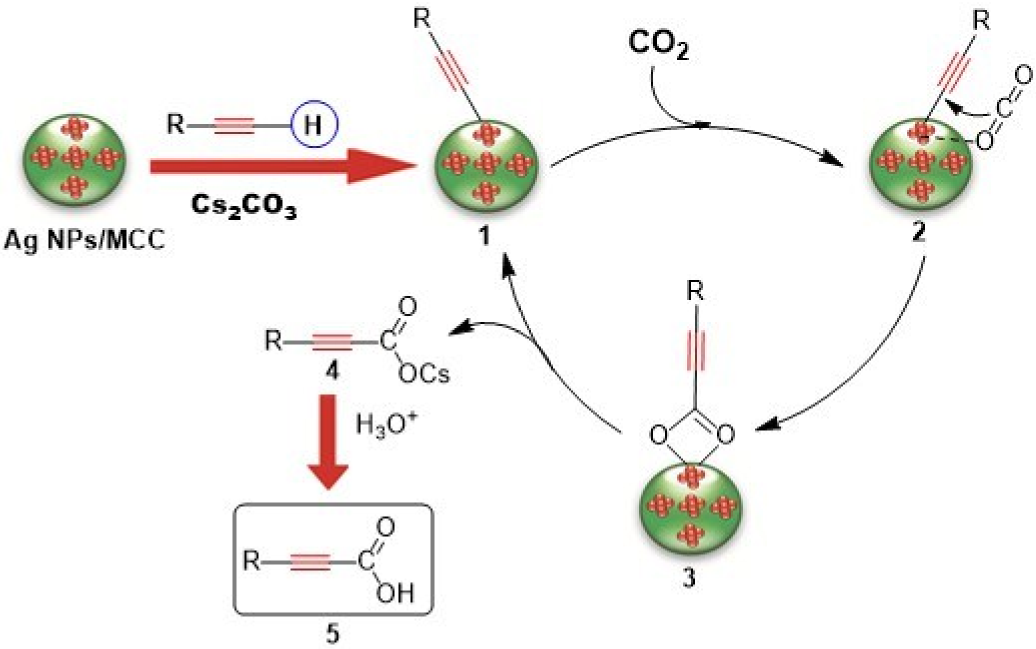


Figure S6. Possible reaction mechanism for the Ag NPs/MCC catalyzed carboxylation of phenyl acetylene via C-H activation.

Computational Studies

All the calculations have been performed at Density Functional Theory (DFT) level using the B3LYP functional. The CEP-121G basis set with effective core potentials (ECPs) were employed for Ag, and the 6-311+G(d) basis set was used for H, C and O. Geometry optimization, vibrational calculations followed by single point energies were computed to calculate the total energies of the structures represented in above figure. Transition state was characterized by the absence of one negative imaginary frequency. Thereafter, considering the total energies of reactants in toluene, the relative energies in kcal/mol were depicted in order to showcase the reaction energetics.

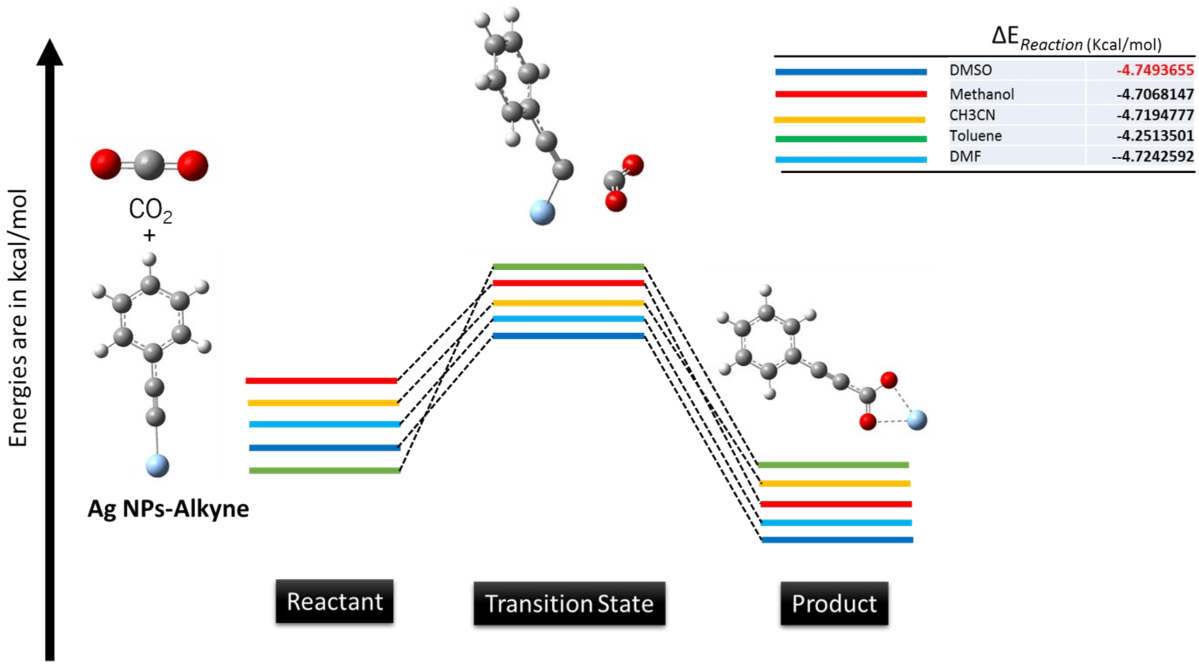


Figure S7. Relative free energies of the energy barrier (ΔE) for the Ag NPs-catalyzed electrophilic attack in various solvents.

Table S_1. Relative Free energies of the energy barrier for the Ag NPs-catalyzed electrophilic attack in various solvents.

	Relative Energy (Kcal/mol)			
Solvents	Reactant	Transition State	Product	**ΔE** ***reaction (Kcal/mol)***
DMSO	-10.0789	3.753642	-14.8283	-4.7493655
Methanol	-9.81918	4.07122	-14.5260	-4.7068147
CH_3CN	-9.89279	3.981174	-14.6123	-4.7194777
Toluene	0	16.71164	-4.25138	-4.2513501
DMF	-9.9241	3.94183	-14.6484	-4.7242592

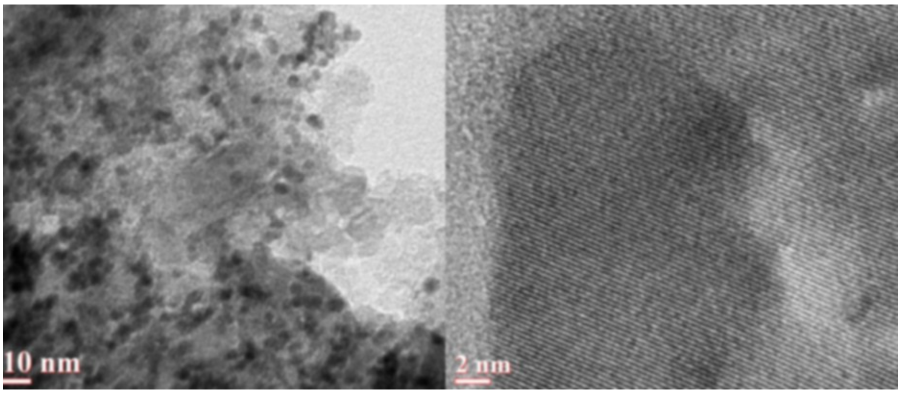


Figure S_8. TEM and HR-TEM images of Ag NPs/MCC.

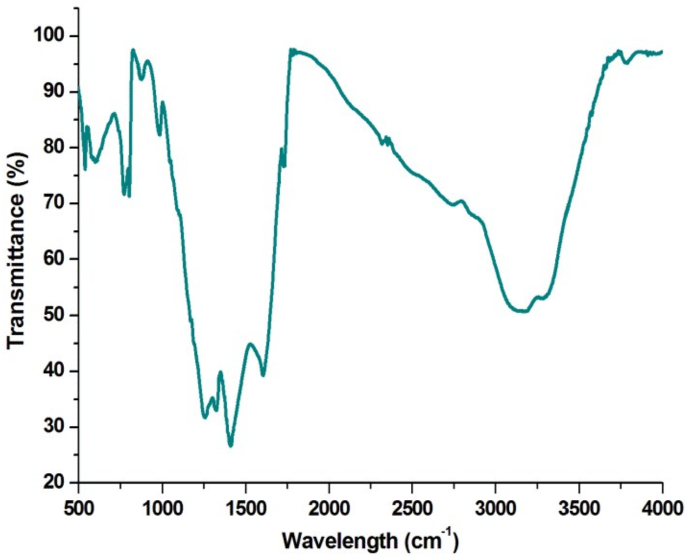


Figure S_9. IR spectrum of recycled Ag NPs/MCC.

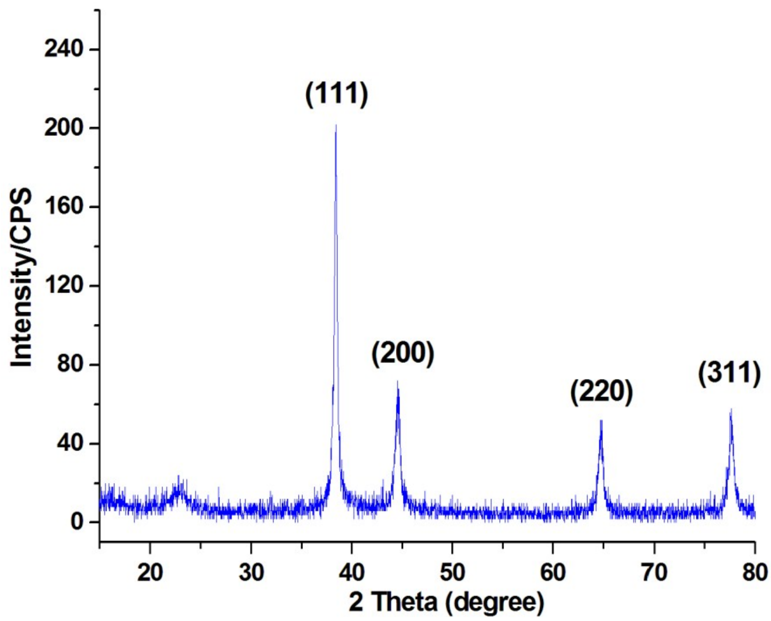
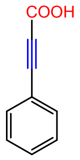


Figure S_{10}. XRD spectrum of recycled Ag NPs/MCC.

Table S_2. Synthesis of 3-phenylpropiolic acid from carboxylation of 1-ethynylbenzene via C-H bond activation with different catalysts material.

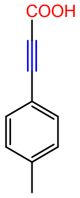
Catalyst	Solvent	T (˚C)	Time (h)	Ag (mol %)	CO_2 (atm)	Yield	Ref.
Ag@P-NHC	DMF	25	20	0.30	1.0	98	1
Ag@MIL-101	DMF	50	15	2.70	1.0	97	2
Ag/F-Al_2O_3	DMSO	50	18	5.16	60.0	62	3
Ag/Schiff-SiO_2	DMSO	60	24	1.45	1.0	98	4
Ag/KAPs-P	DMSO	60	10	0.01	1.0	92	5
Ag NPs/Co-MOF	DMF	80	14	4.40	1.0	98	6
Ag NPs/MCC	DMSO	50	16	2.50	1.0	99	This Work

1. Phenylpropiolic acid



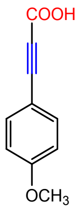
^{1}H NMR (400 MHz, DMSO): δ 13.86 (s, 1H), 7.58 (m, J = 8.4 Hz, 2H, Ar-H), δ 7.55 (m, J = 7.5 Hz, 1H, Ar-H), 7.47 (m, J = 7.5 Hz, 2H, Ar-H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 158.69, 133.34, 131.21, 128.713, 119.114, 89.14, 80.10 ppm.

2. 4-Methyl phenyl propiolic acid



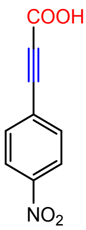
^{1}H NMR (400 MHz, CDCl3): δ = 7.58 (d, J = 8.1 Hz, 2H, Ar-H), 7.23 (d, J = 8.0 Hz, 2H, Ar-H), 2.35 (s, 3H, CH_3), **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.11, 141.74, 133.12, 130.33, 116.38, 85.49, 82.00 ppm.

3. 4-Methoxy phenyl propiolic acid



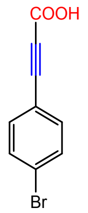
^{1}H NMR (400 MHz, CDCl3): δ = 7.56 (d, J = 8.9 Hz, 2H, Ar-H), 6.92 (d, J = 8.9 Hz, 2H, Ar-H), 3.81 (s, 3H, CH_3), **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.79, 155.18, 135.21, 115.33, 111.12, 85.92, 81.68, 56.01ppm.

4. 4-Nitro phenylpropiolic acid



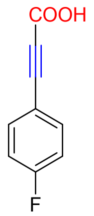
^{1}H NMR (400 MHz, DMSO): δ = 13.78 (s, 1H, COOH), 8.13 (d, J = 8.8 Hz, 2H, Ar-H), 7.78 (d, J = 8.8 Hz, 2H, Ar-H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.34, 149.09, 136.03, 134.30, 124.55, 85.51, 82.18 ppm.

5. 4-Bromo phenylpropiolic acid



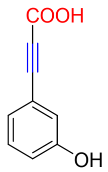
¹H NMR (400 MHz, DMSO): δ = 13.80 (s, 1H, COOH), 7.54 (d, J= 8.2 Hz, 2H, Ar-H), 7.34 (d, J= 7.8 Hz, 2H, Ar-H) **¹³C NMR (100 MHz, $CDCl_3$):** δ = 153.81, 134.60, 131.44, 122.70, 121.70, 121.65, 89.16, 88.07 ppm.

6. 4-Fluoro phenylpropiolic acid



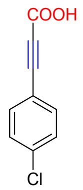
¹H NMR (400 MHz, DMSO): δ = 13.80 (s, 1H), 7.50 (m, 2H, Ar-H), 6.99 (m, 2H, Ar-H) **¹³C NMR (100 MHz, $CDCl_3$):** δ = 165.20, 162.73, 155.33, 135.01, 115.92, 84.06, 80.07 ppm.

7. 3-Hydroxy phenylpropiolic acid



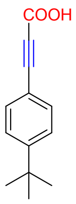
¹H NMR (400 MHz, $CDCl_3$): δ = 13.51 (br, s, 1H), 7.52 (s, 1H, OH), 7.02-7.03 (m, 1H, Ar-H), 7.05 (m, 1H, Ar-H), 6.81 (m, 2H, Ar-H) **¹³C NMR (100 MHz, $CDCl_3$):** δ = 157.96, 154.84, 130.74, 122.82, 120.06, 118.96, 118.85, 85.05, 81.59 ppm.

8. 4-Chloro phenylpropiolic acid



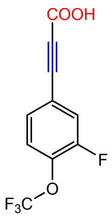
¹H NMR (400 MHz, DMSO): δ = 13.41 (s, 1H, COOH), 7.41 (2H, Ar-H), 7.29 (2H, Ar-H), **¹³C NMR (100 MHz, $CDCl_3$):** δ = 154.36, 136.38, 135.93, 129.82, 118.40, 83.66, 83.11 ppm.

9. 4-tert-Butylphenylpropiolic acid



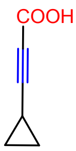
^{1}H NMR (400 MHz, DMSO): δ = 13.54 (s, 1H, COOH), 7.54 (d, J = 8.5 Hz, 2H, Ar-H), 7.34 (d, J = 8.5 Hz, 2H, Ar-H), 1.41 (s, 9H, CH_3), **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 159.16, 155.02, 133.31, 125.80, 116.01, 89.82, 79.82, 35.12, 31.02 ppm.

10. 3-Fluoro-4-(trifluoromethoxy) phenylpropiolic acid



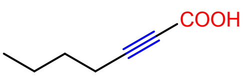
^{1}H NMR (400 MHz, DMSO): δ = 14.08 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.602 (d, 1H, J = 8.5 Hz) **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.305, 150.502, 136.944, 131.185, 130.065, 124.219, 70.254 ppm.

11. 3-Cyclo propylpropiolic acid



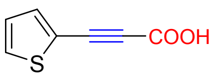
^{1}H NMR (400 MHz, DMSO): δ = 13.51 (s, 1H, COOH), 1.26 (m, 1H), 0.86 (m, 2H), 0.68 (m, 2H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 158.55, 96.79, 68.09, 9.56, 0.48 ppm.

12. Hept-2-ynoic acid



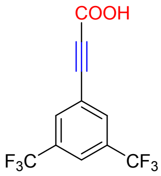
^{1}H NMR (400 MHz, DMSO): δ = 13.84 (s, 1H, COOH), 2.34 (t, 3H), 1.45-1.54 (m, 4.0 H), 0.99 (t, 3H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.28, 88.36, 29.17, 21.36, 17.34, 13.33 ppm.

13. 3-(thiophen-2-yl)propiolic acid

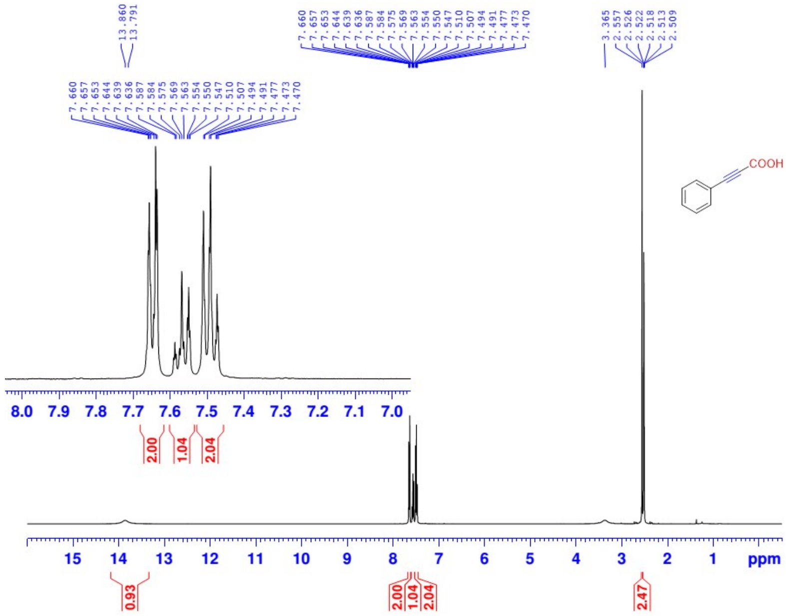


^{1}H NMR (400 MHz, DMSO): δ = 13.51 (s, 1H, COOH), 7.51 (s, 1.0H), 7.34 (d, 1.0H), 7.29 (d, 1.0H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.12, 135.95, 130.49, 128.47, 118.34, 82.11, 80.84 ppm.

14. 3-(3,5-bis(trifluoromethyl)phenyl)propiolic acid



^{1}H NMR (400 MHz, DMSO): δ = 13.84 (s, 1H, COOH), 8.38 (d, 2H, Ar-H), 8.28 (d, J = 8.5 Hz, 1H, Ar-H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ =154.23, 133.64, 131.92, 131.62, 131.31, 131.25, 130.93, 124.52, 82.11, 80.79 ppm.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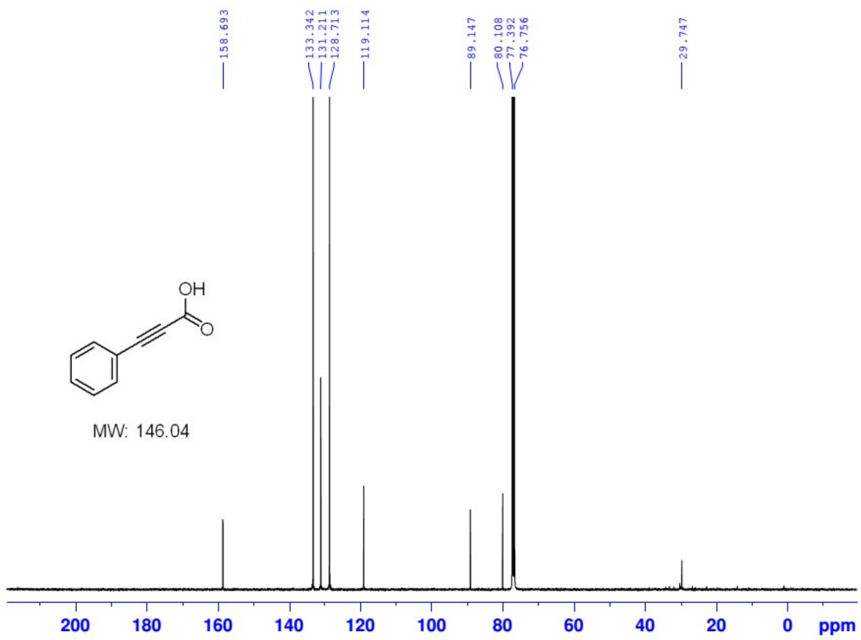
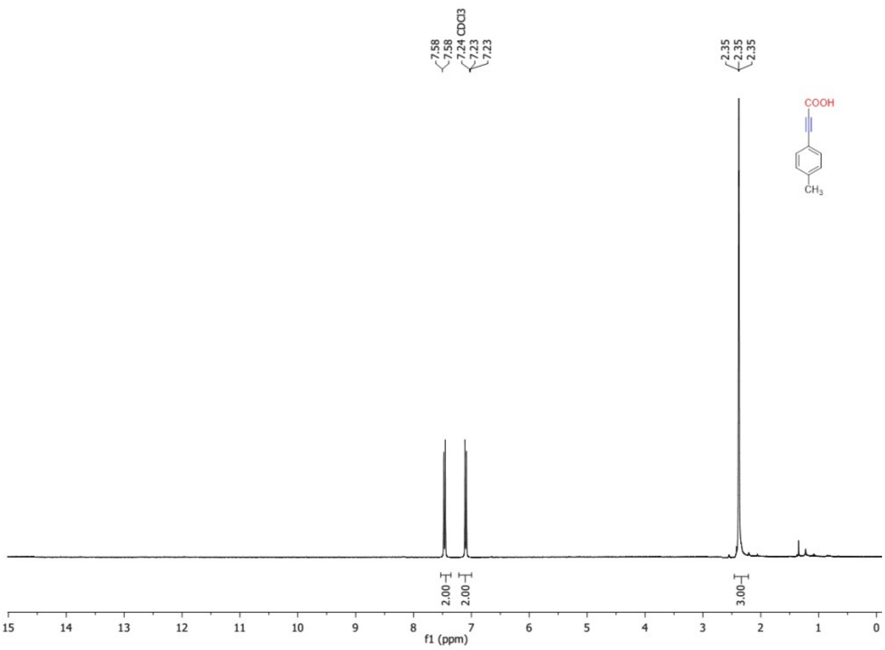
ppm


OH
O
MW: 146.04
ppm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5
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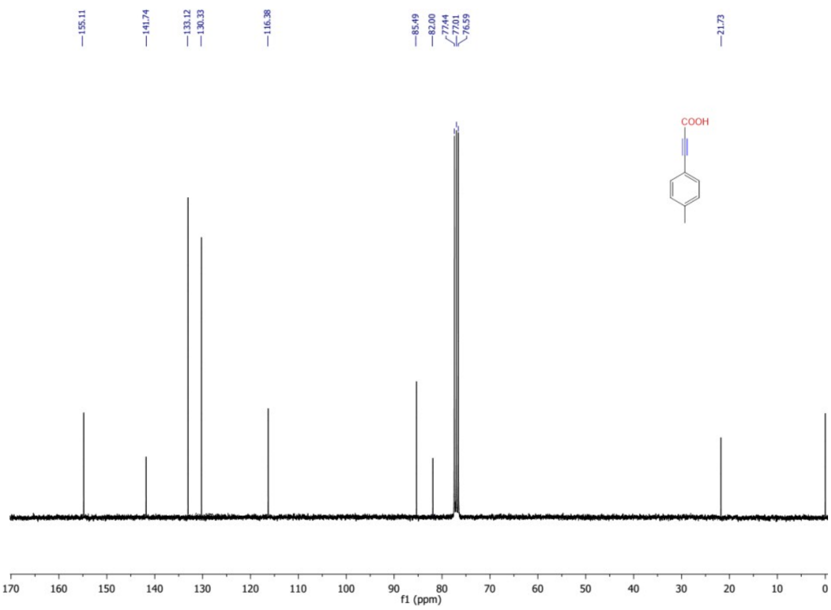
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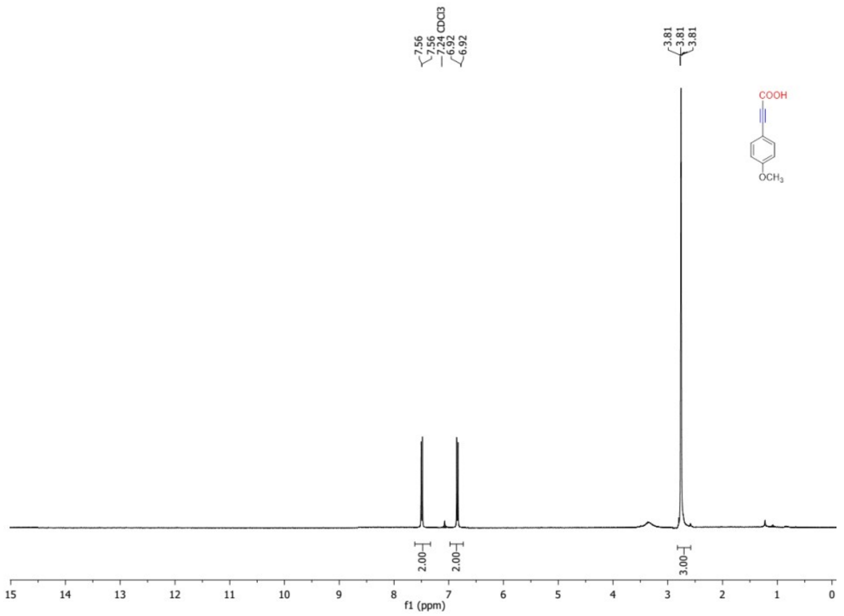
f1 (ppm)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15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
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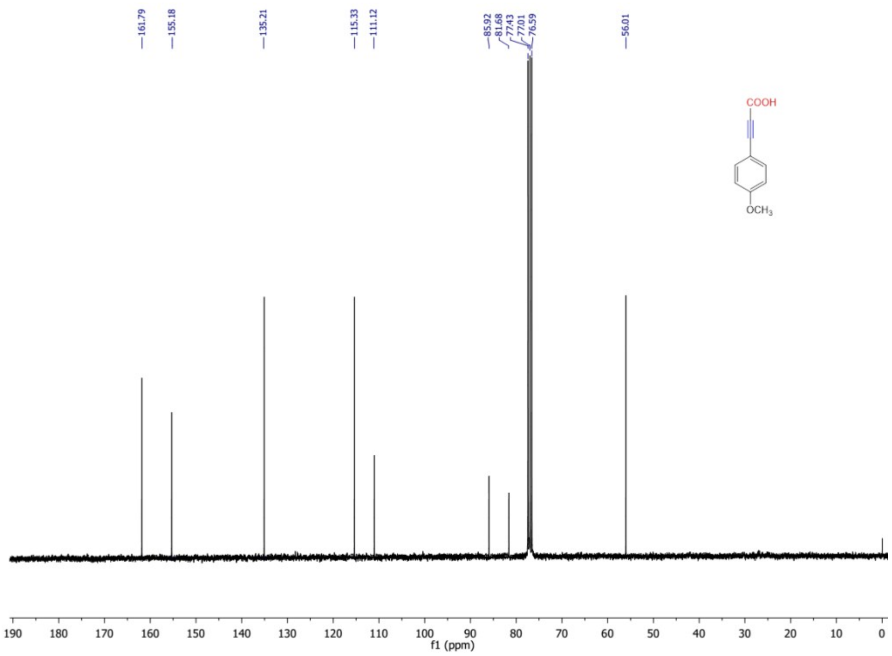
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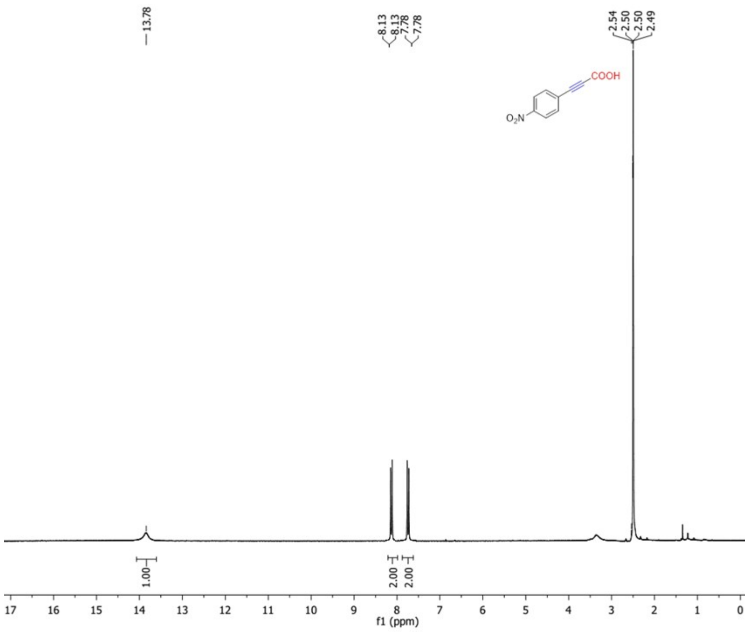

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8.13
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7.78
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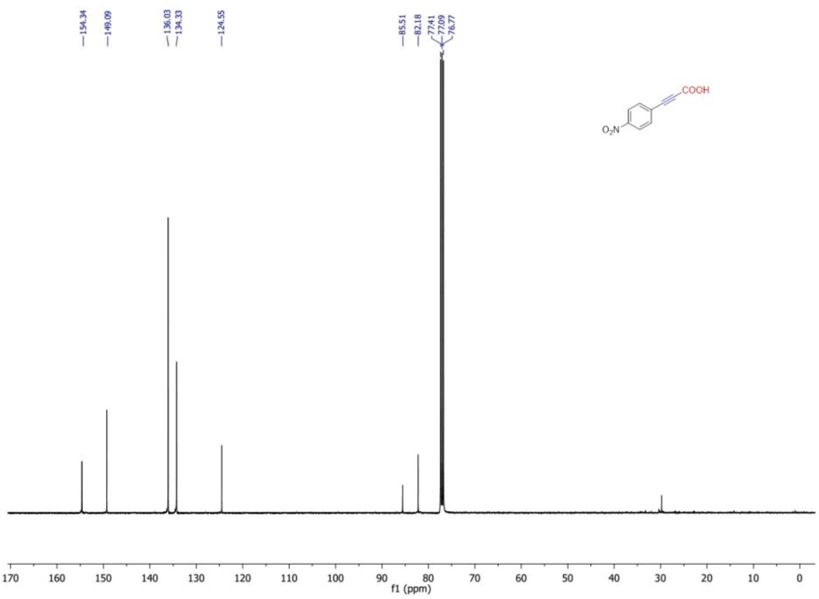
2.00
2.00
f1 (ppm)



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77.09
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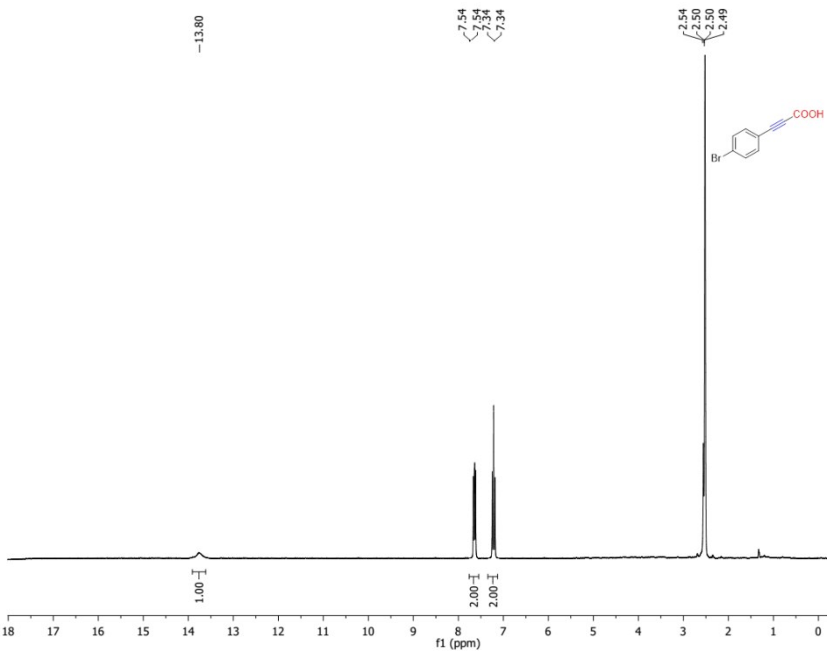
COOH
O2N
f1 (ppm)



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7.54
7.34
7.34
2.54
2.50
2.50
2.49
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Br
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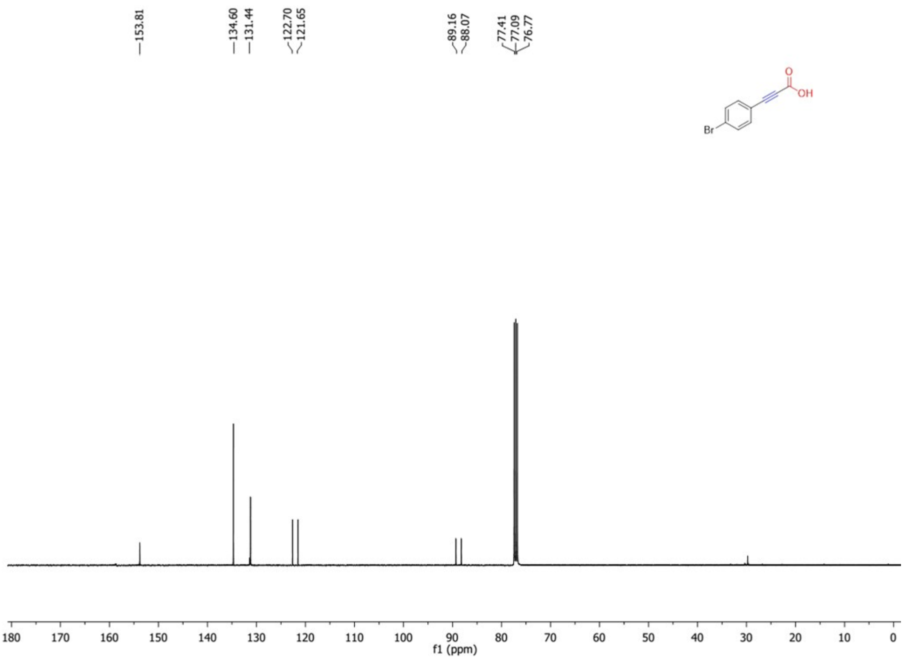
2.00
2.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)



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Br
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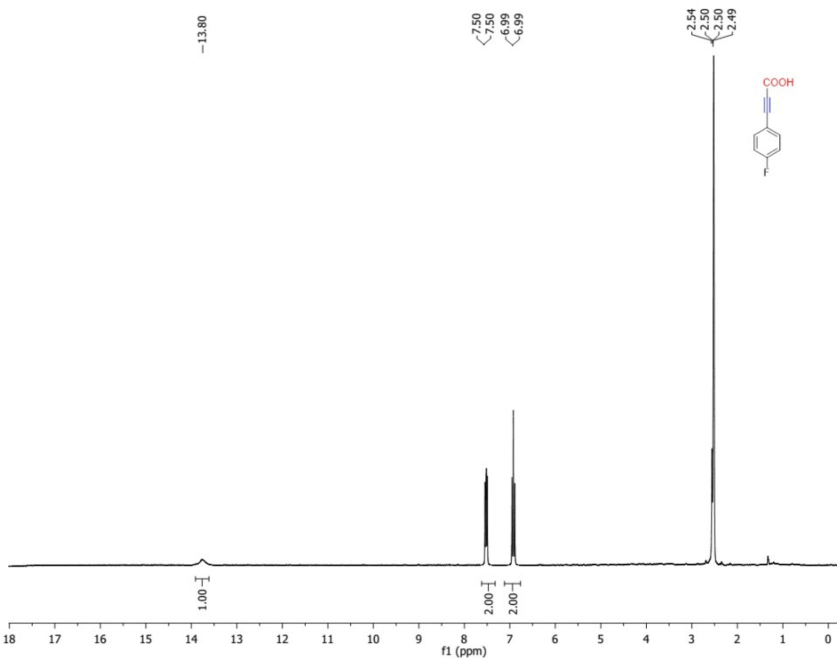
f1 (ppm)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F
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18
17
16
15
14
13
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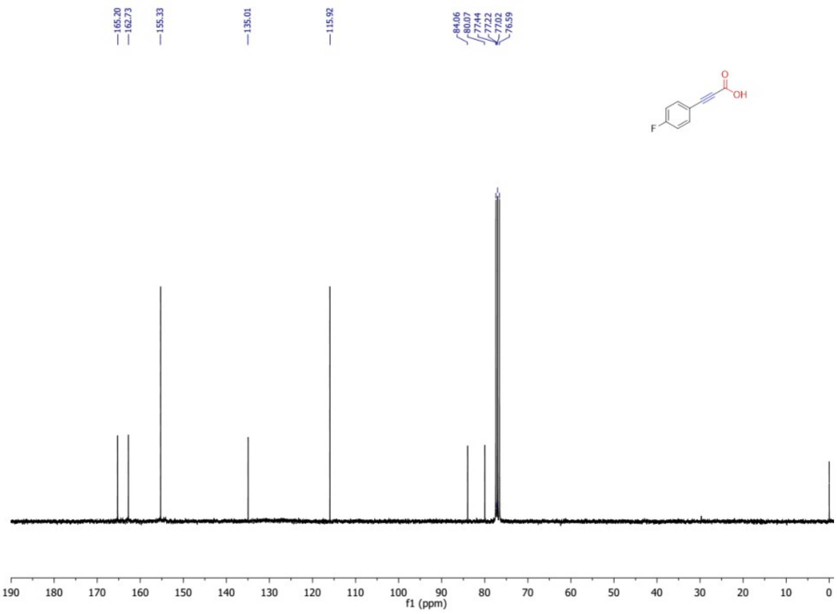
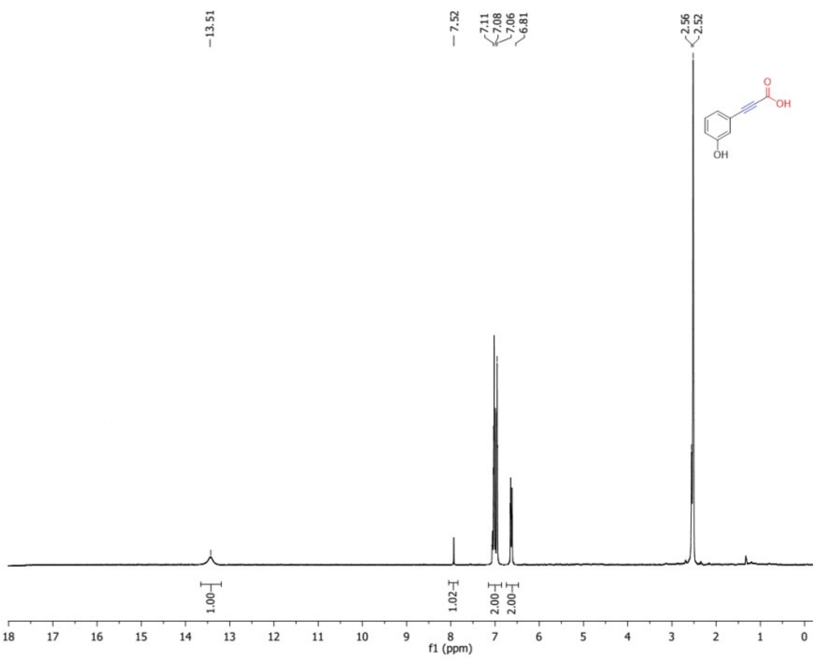
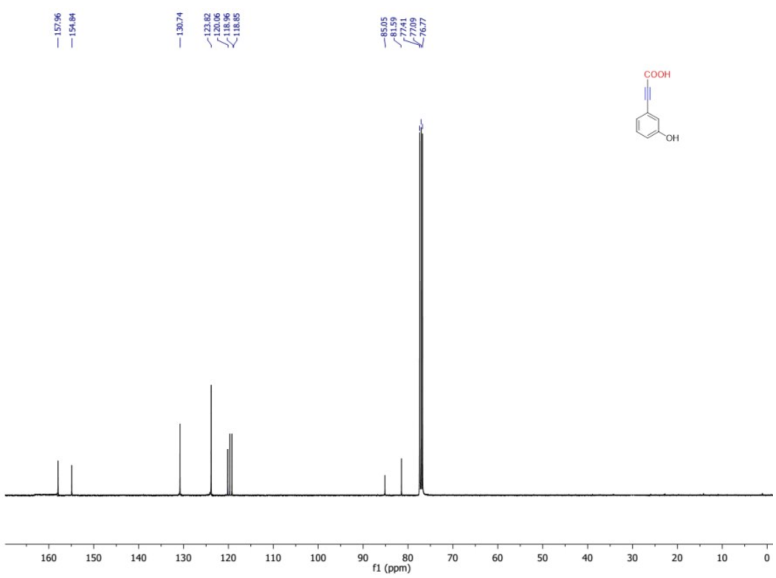
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

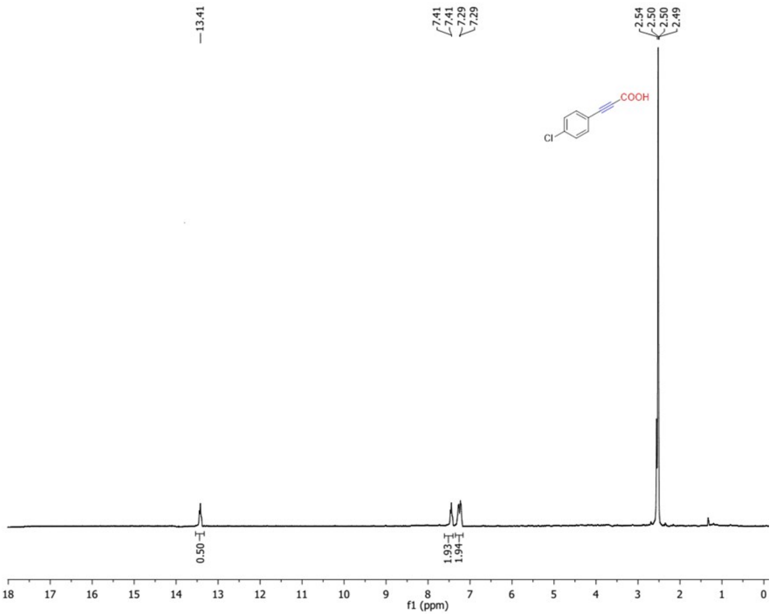

165.20
162.73
155.33
135.01
115.92
84.06
80.07
77.44
77.22
77.02
76.59
O
OH
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

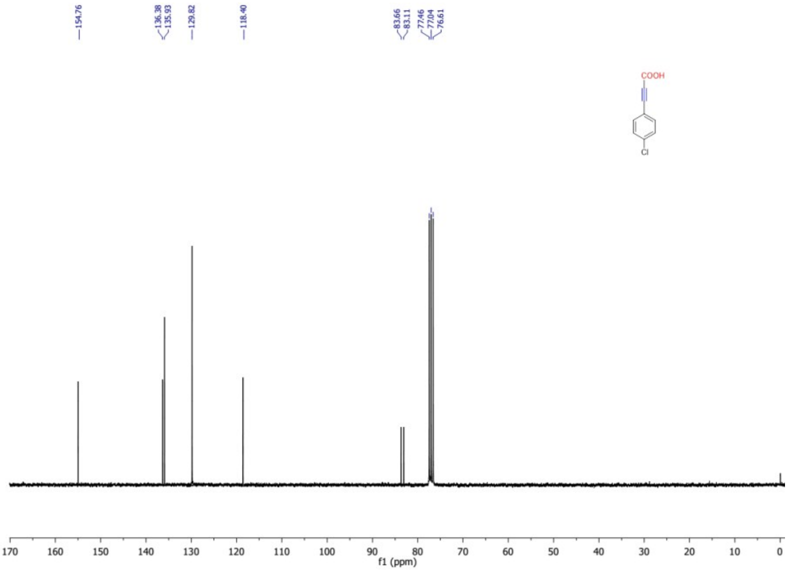


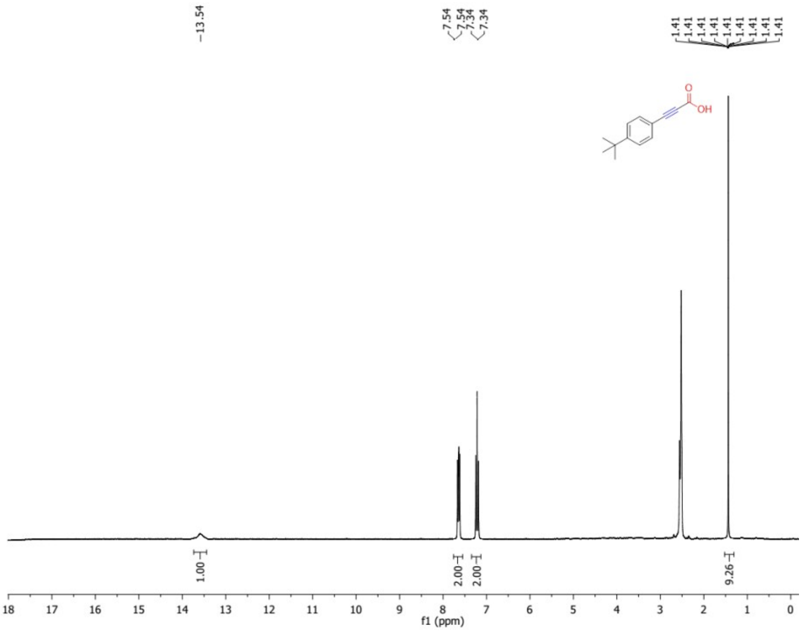
13.51
7.52
7.11
7.08
7.06
6.81
2.56
2.52
O
OH
OH
1.00
1.02
2.00
2.00
f1 (ppm)

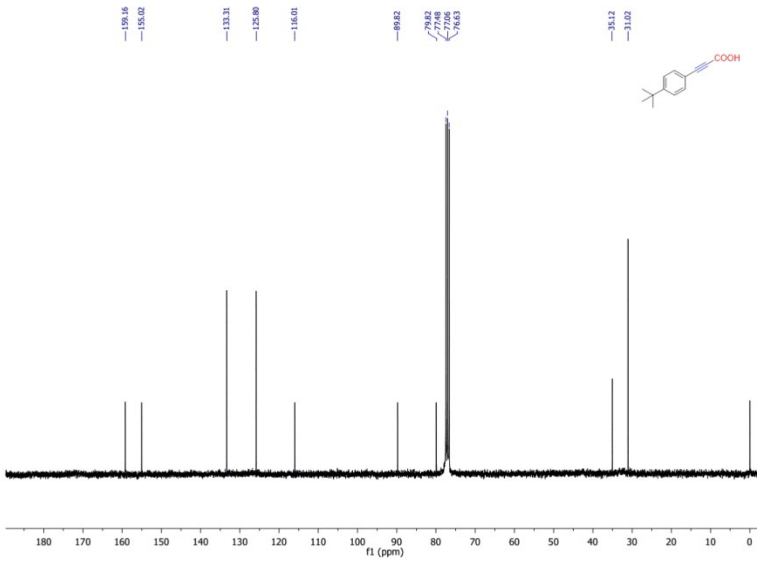


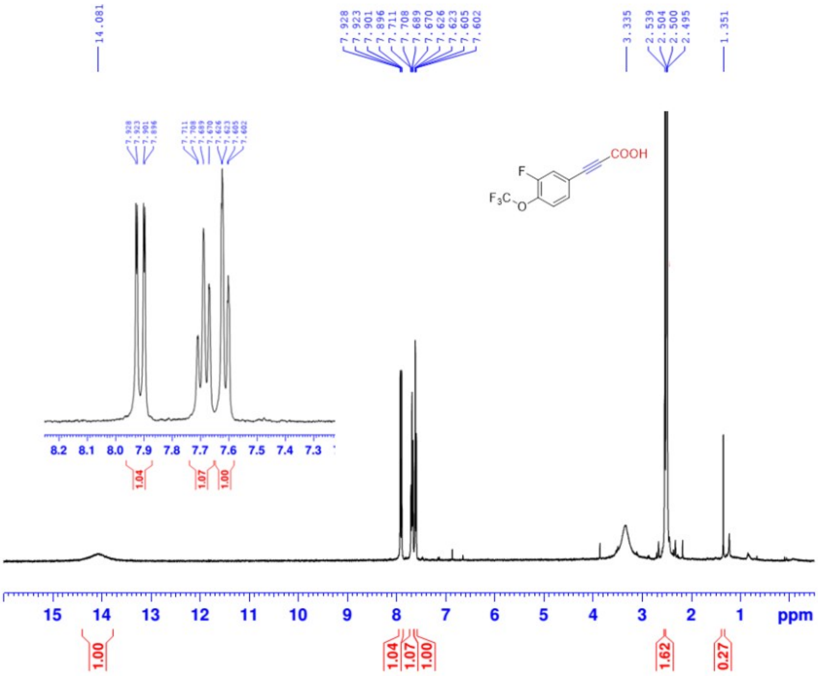
157.96
154.84
130.74
123.82
120.06
118.96
118.85
85.05
81.59
77.41
77.09
76.77
COOH
OH
f1 (ppm)

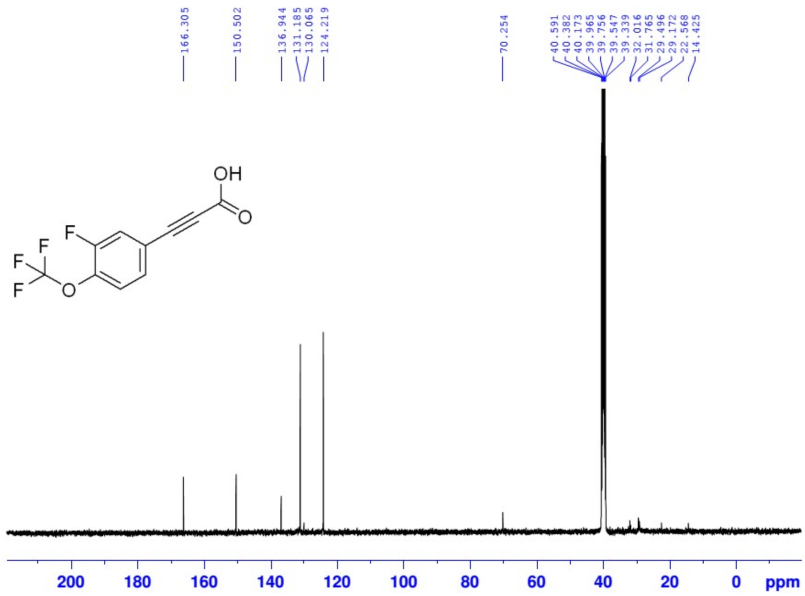

13.41
7.41
7.41
7.29
7.29
2.54
2.50
2.50
2.49
COOH
Cl
0.50
1.93
1.94
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


154.76
136.38
135.93
129.82
118.40
83.66
83.11
77.46
77.04
76.61
COOH
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


13.54
7.54
7.54
7.34
7.34
1.41
1.41
1.41
1.41
1.41
1.41
1.41
1.41
1.41
O
OH
1.00
2.00
2.00
9.26
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


159.16
155.02
133.31
125.80
116.01
89.82
79.82
77.48
77.06
76.63
35.12
31.02
COOH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


14.081
7.928
7.923
7.901
7.896
7.711
7.708
7.689
7.670
7.626
7.623
7.605
7.602
3.335
2.539
2.504
2.500
2.495
1.351
COOH
F
F_3C
O
1.04
1.07
1.00
1.62
0.27
ppm


166.305
150.502
136.944
131.185
130.065
124.219
70.254
40.591
40.382
40.173
39.965
39.756
39.547
39.339
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31.765
29.496
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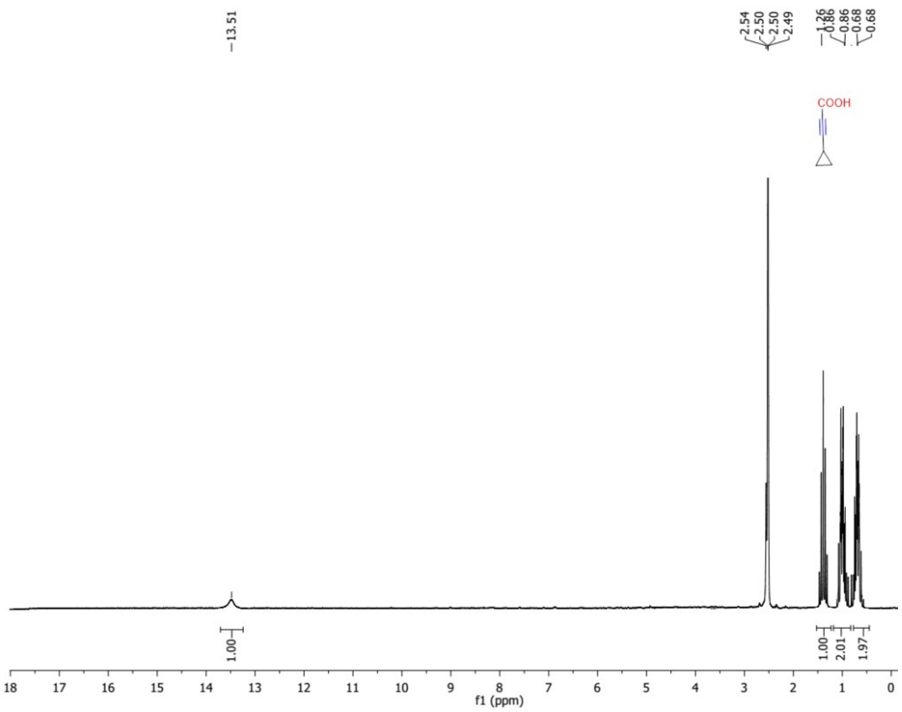
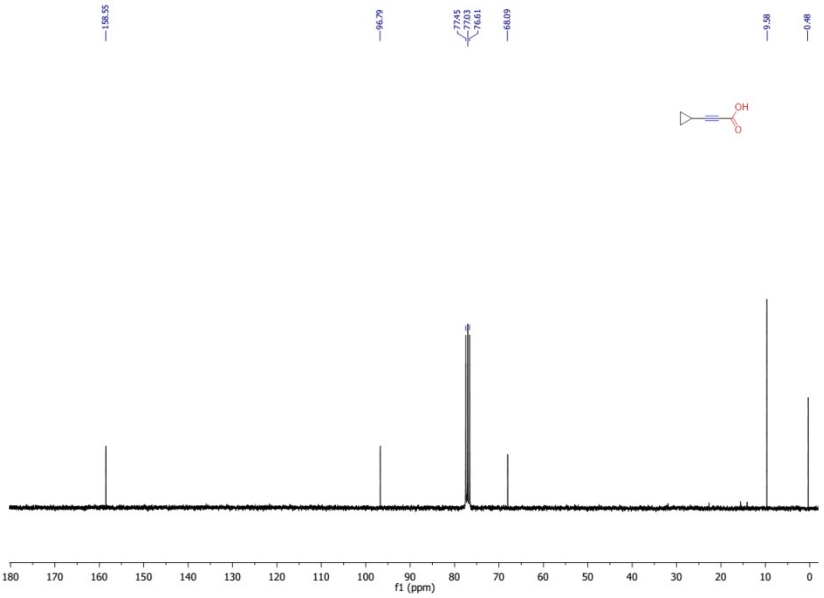
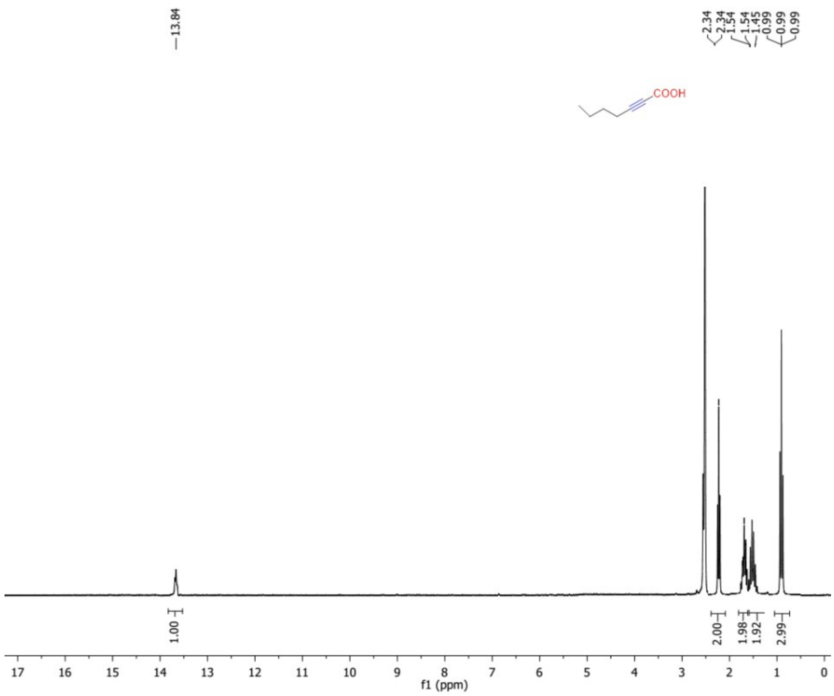
OH
O
F
F
F
F
O
ppm

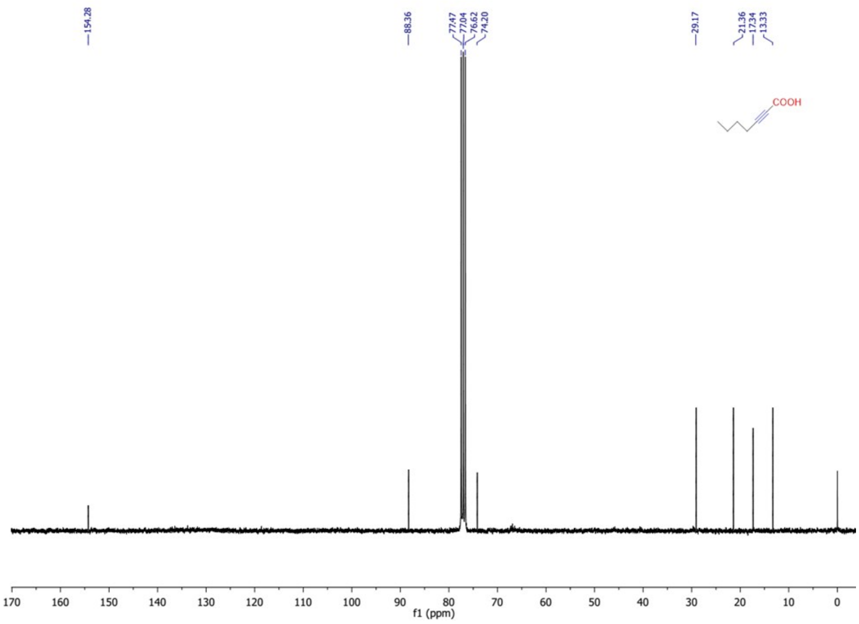


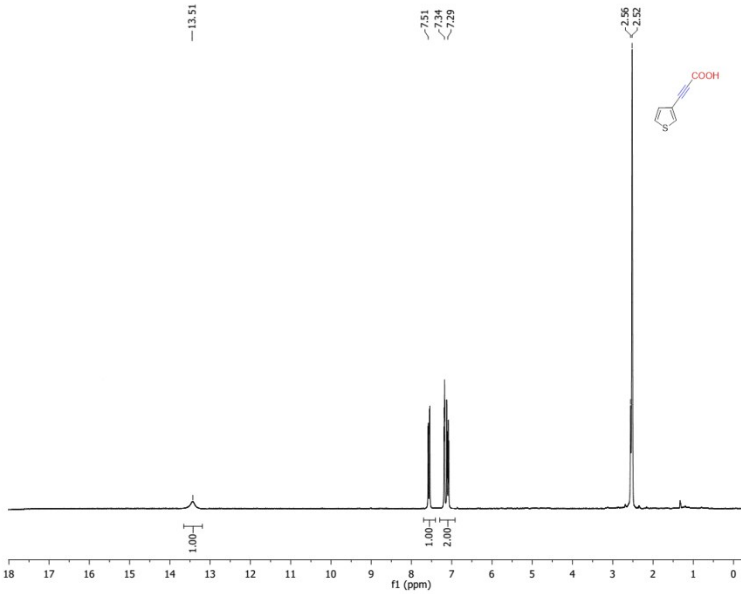
13.51
2.54
2.50
2.50
2.49
1.26
0.86
0.86
0.68
0.68
COOH
1.00
1.00
2.01
1.97
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

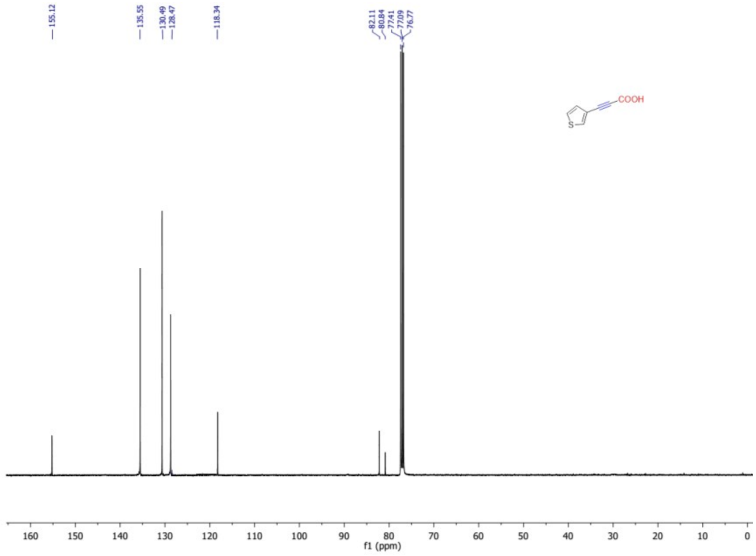


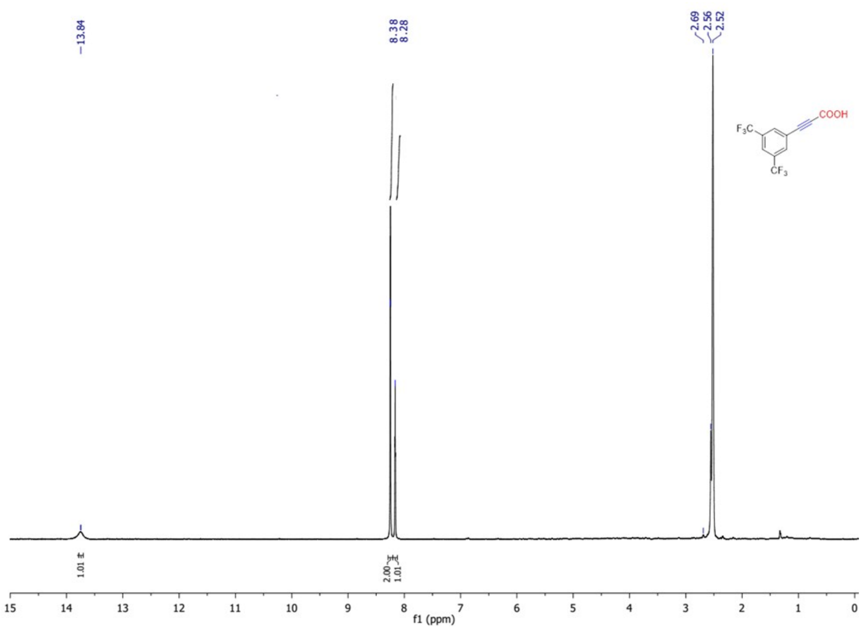
158.55
96.79
77.45
77.03
76.61
68.09
9.58
0.48
OH
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

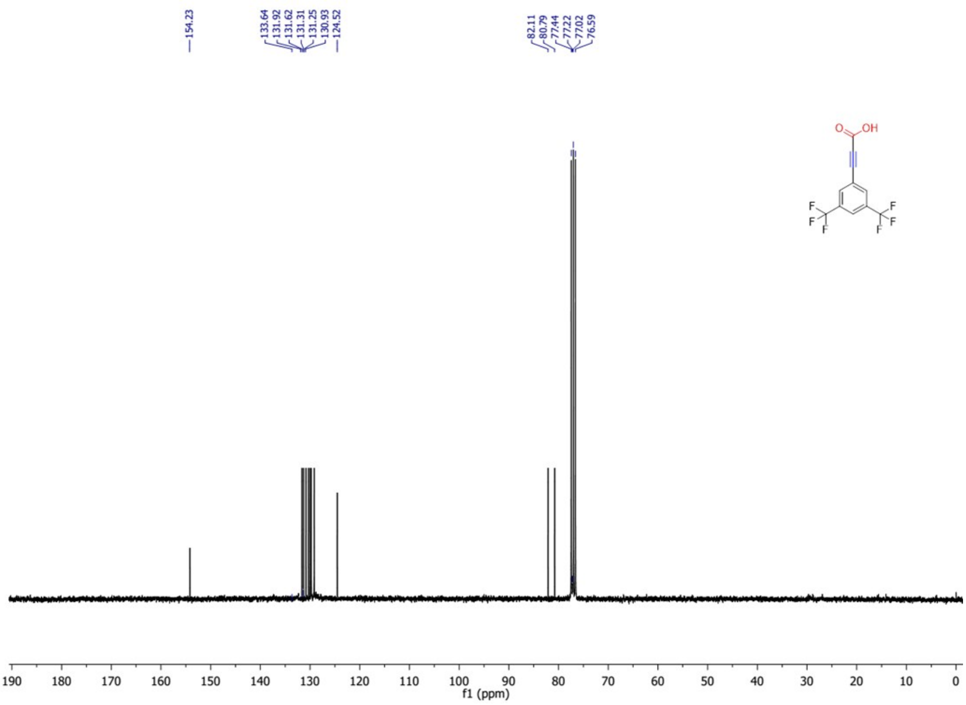

13.84
2.34
2.34
1.54
1.54
1.45
0.99
0.99
0.99
COOH
1.00
2.00
1.98
1.92
2.99
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


154.28
88.36
77.47
77.04
76.62
74.20
29.17
21.36
17.34
13.33
COOH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


13.51
7.51
7.34
7.29
2.56
2.52
COOH
S
1.00
1.00
2.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


155.12
135.55
130.49
128.47
118.34
82.11
80.84
77.41
77.09
76.77
COOH
S
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


13.84
8.38
8.28
2.69
2.56
2.52
F3C
COOH
CF3
1.01
2.00
1.01
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


154.23
133.64
131.92
131.62
131.31
131.25
130.93
124.52
82.11
80.79
77.44
77.22
77.02
76.59
O
OH
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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