Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Carboxylation of Terminal Alkynes at Ambient CO_2 Pressure in Ethylene Carbonate

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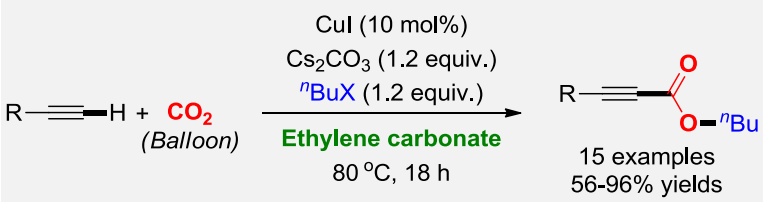


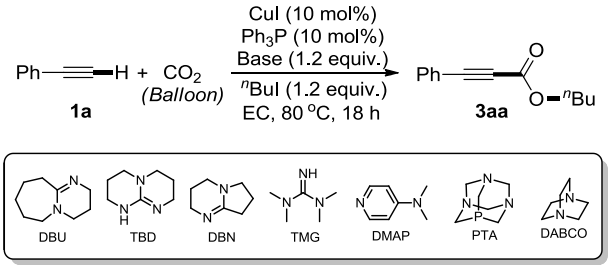
Contents Table

1. General Experimental Section

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 ^{o}C) and ethyl acetate. All compounds were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy, which are consistent with those reported in the literature. NMR spectra were determined on Bruker 400 in $CDCl_3$. ^{1}H NMR chemical shifts were referenced to residual solvent as determined relative to $CDCl_3$ (7.26 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (central peak is 77.0 ppm). ^{1}H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, *J*, are reported in Hertz (Hz). GC-MS data were performed on Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-17 30 m × 0.25 μm) using a flame ionization detector.

2. Optimization Studies

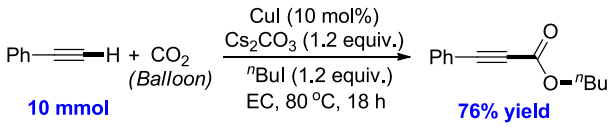
Table S1. Base effect on carboxylation of phenylacetylene



Entry	Base	Yield (%)
1	Cs_2CO_3	>99
2	K_2CO_3	42
3	KF	<1
4	KF/18-Crown-6	5
5	CsF	3
6	KOH	<1
7	NaOH	<1
8	^{t}BuOLi	4
9	^{t}BuOK	23
10	$NaNH_2$	<1
11	CsOAc	<1
12	Et_3N	<1
13	DBU	<1
14	TBD	38
15	DBN	6
16	TMG	<1
17	DMAP	<1
18	PTA	<1
19	DABCO	<1

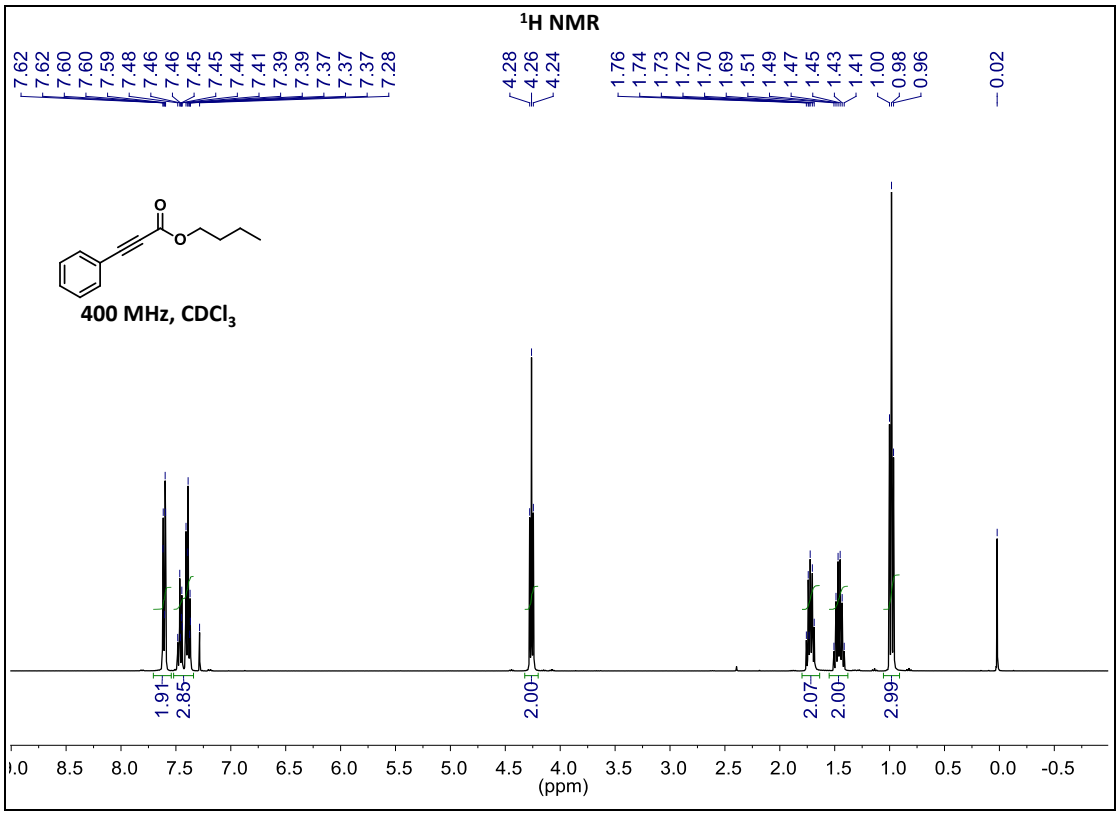
[a] Reaction conditions: Phenylacetylene (0.0511 g, 0.5 mmol), CuI (0.0095 g, 0.05 mmol), Ph_3P (0.0131 g, 0.05 mmol), base (0.6 mmol), *n*-BuI (0.1104 g, 0.6 mmol), EC (3 mL), CO_2 (99.999%, balloon), 80 ^{o}C, 18 h. [b] The yields were determined by GC with biphenyl as internal standard.

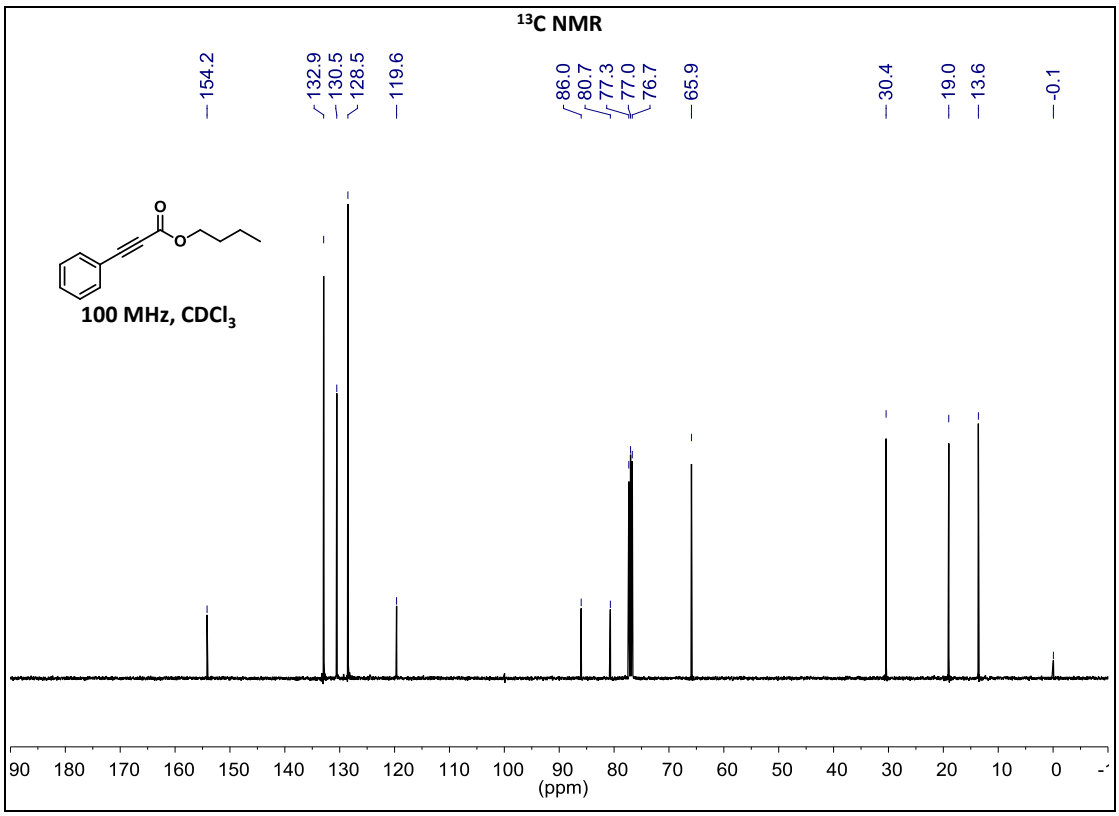
3. Gram Scale Synthesis of 3aa

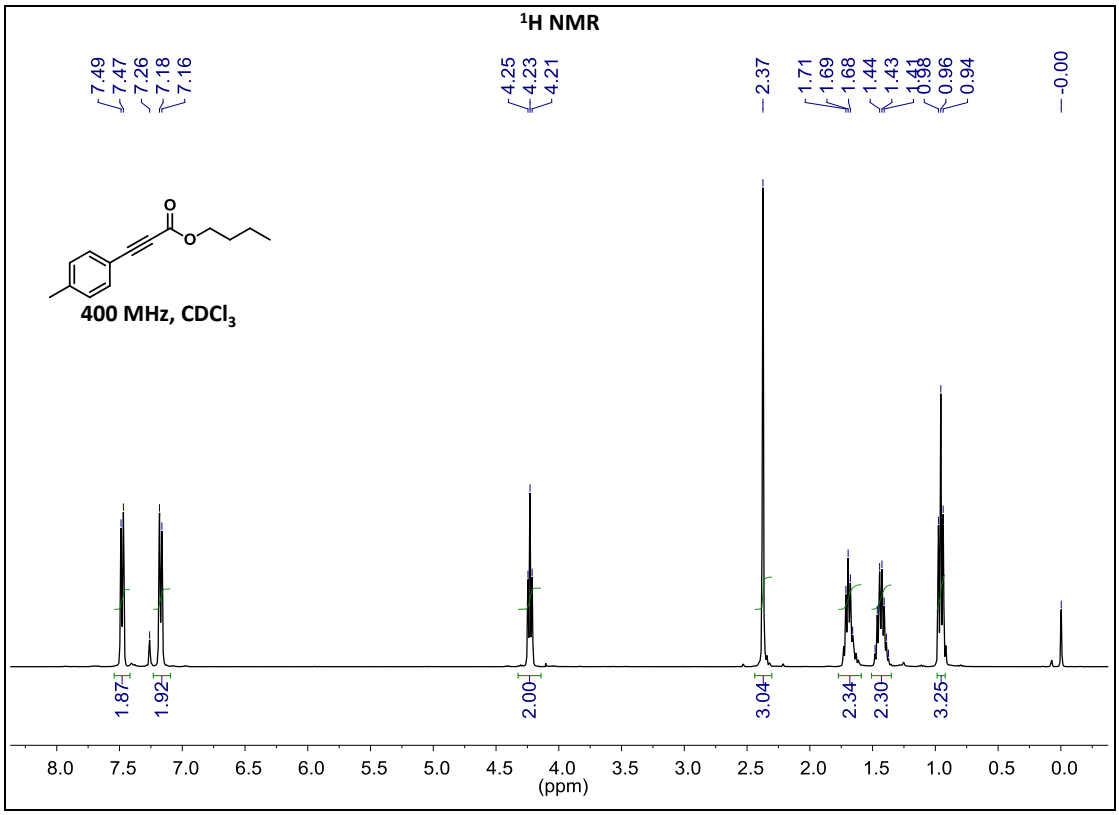


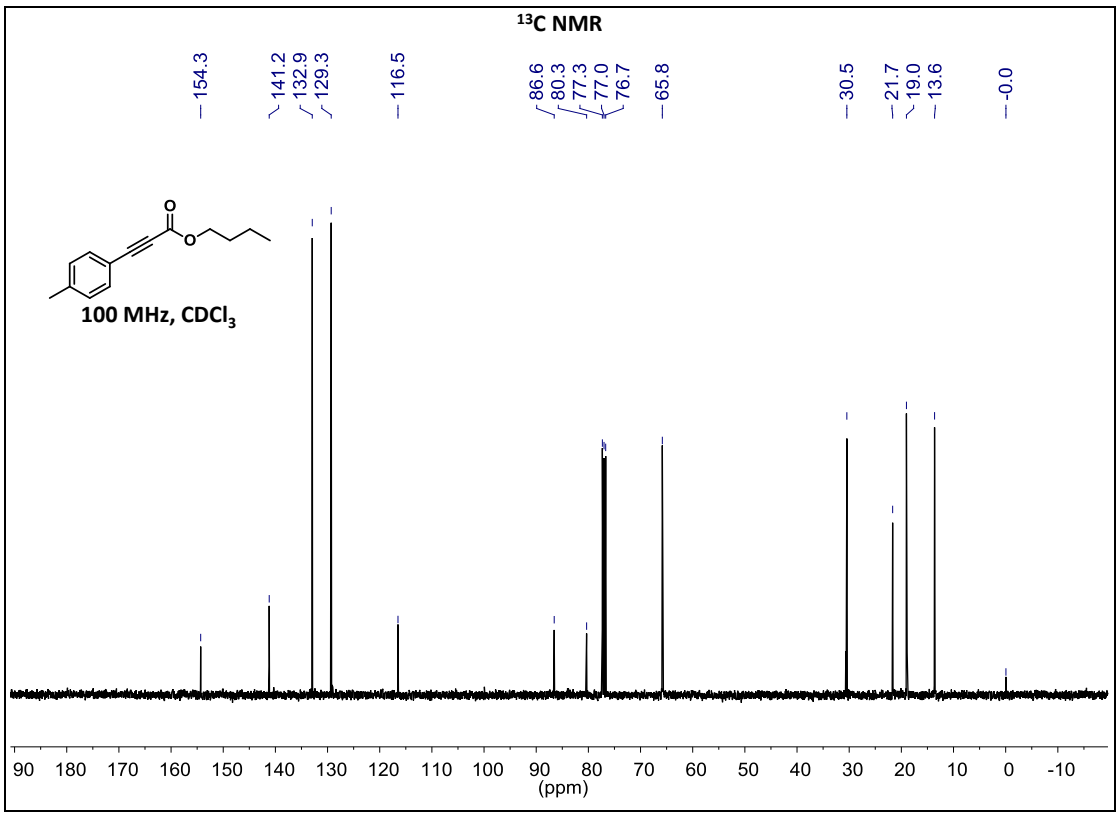
In a 200 mL Schlenk flask, Phenylacetylene (1.02 g, 10 mmol), CuI (0.19 g. 1 mmol), Cs_2CO_3 (3.91 g, 12 mmol), *n*-BuI (2.21 g, 12 mmol) and ethylene carbonate (15 mL) were added. The flask was capped with a stopper and sealed. Then the freeze-pump-thaw method was employed for gas exchanging process. The reaction mixture was stirred at 80 ^{o}C for desired time under the atmosphere of CO_2 (99.999%, balloon). After the reaction, the mixture was cooled to room temperature, extracted with *n*-hexane. The combined organic layers were washed with saturated NaCl solution then dried with anhydrous Na_2SO_4. The residue was purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford spectroscopically pure product **3aa** in the yield of 76%.

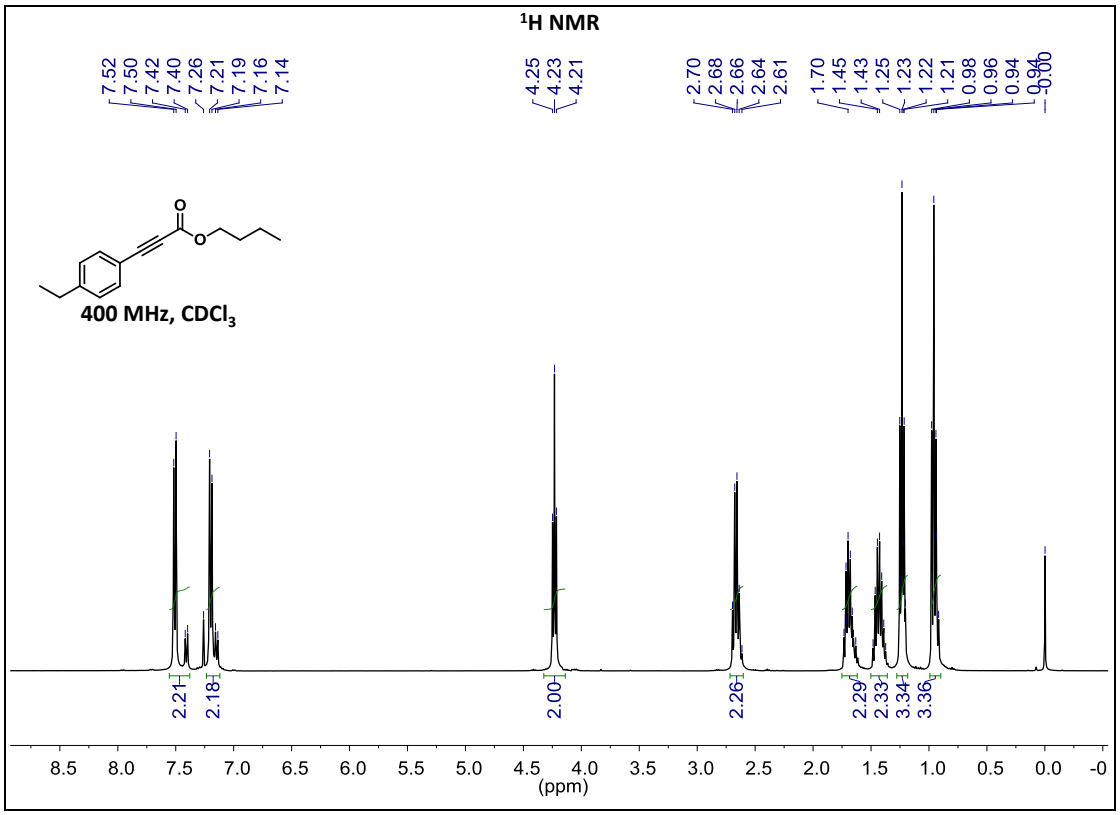
4. NMR Spectral Data of the Products

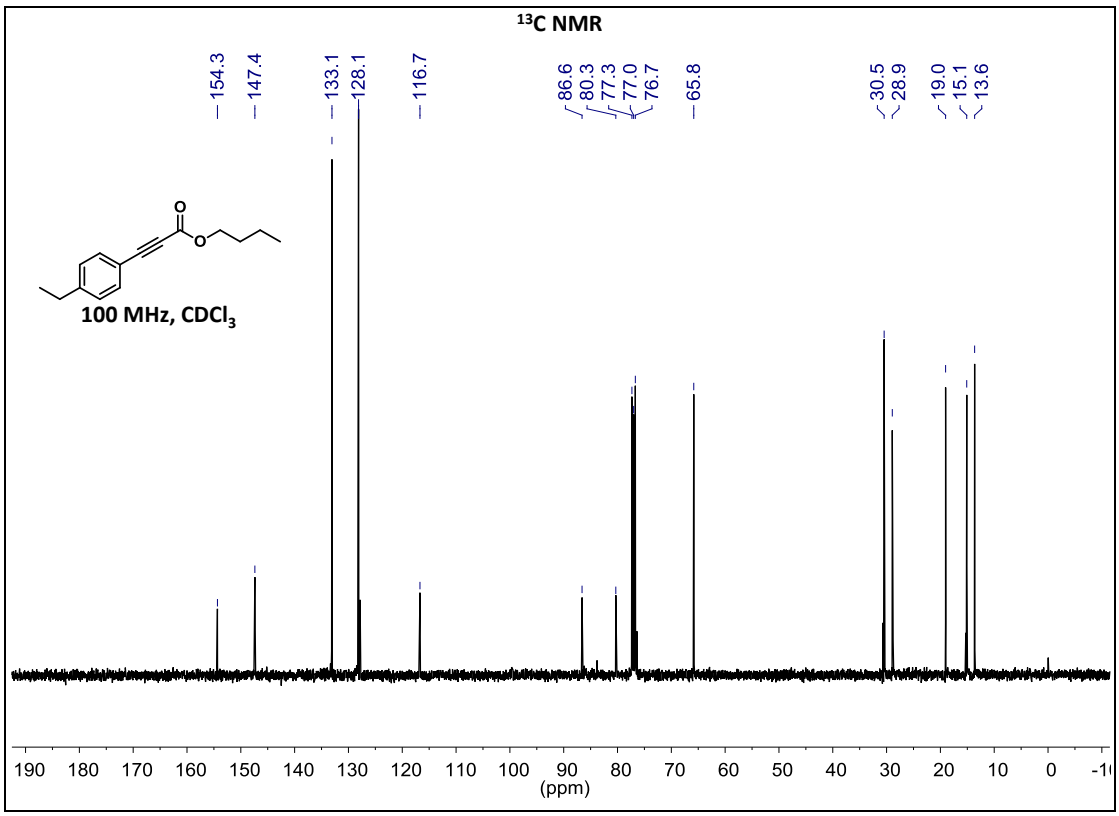


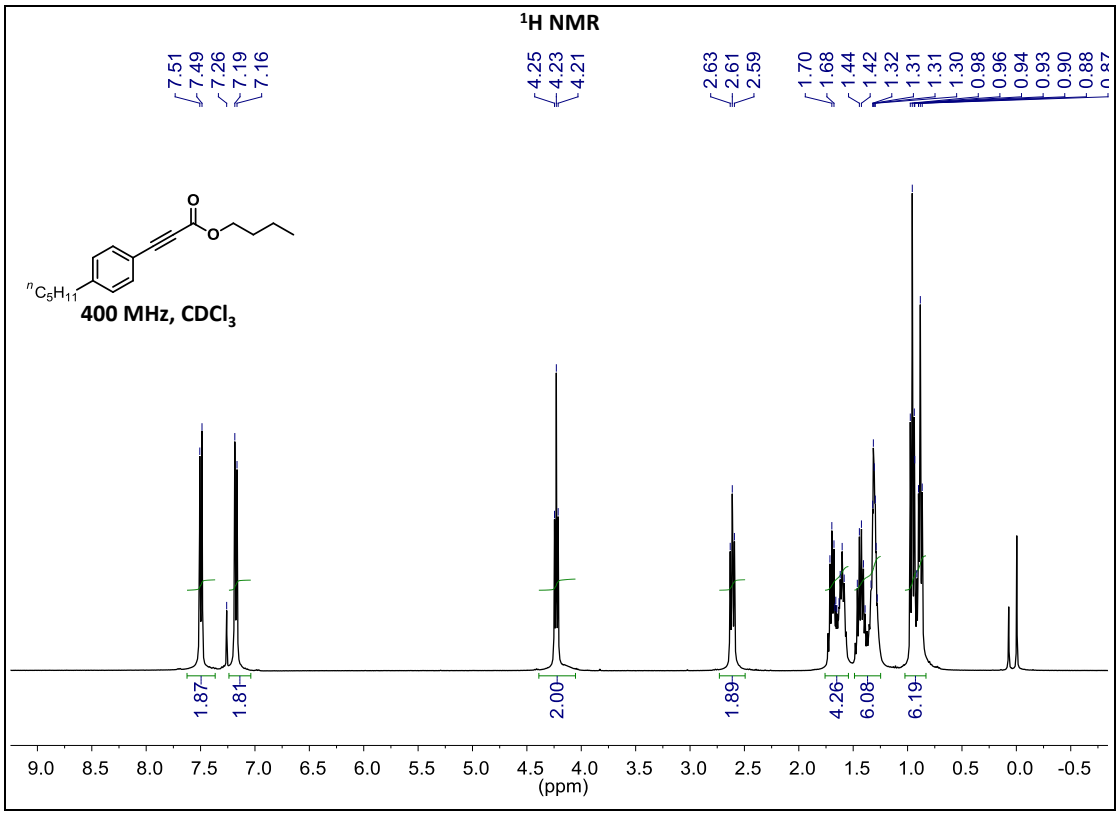


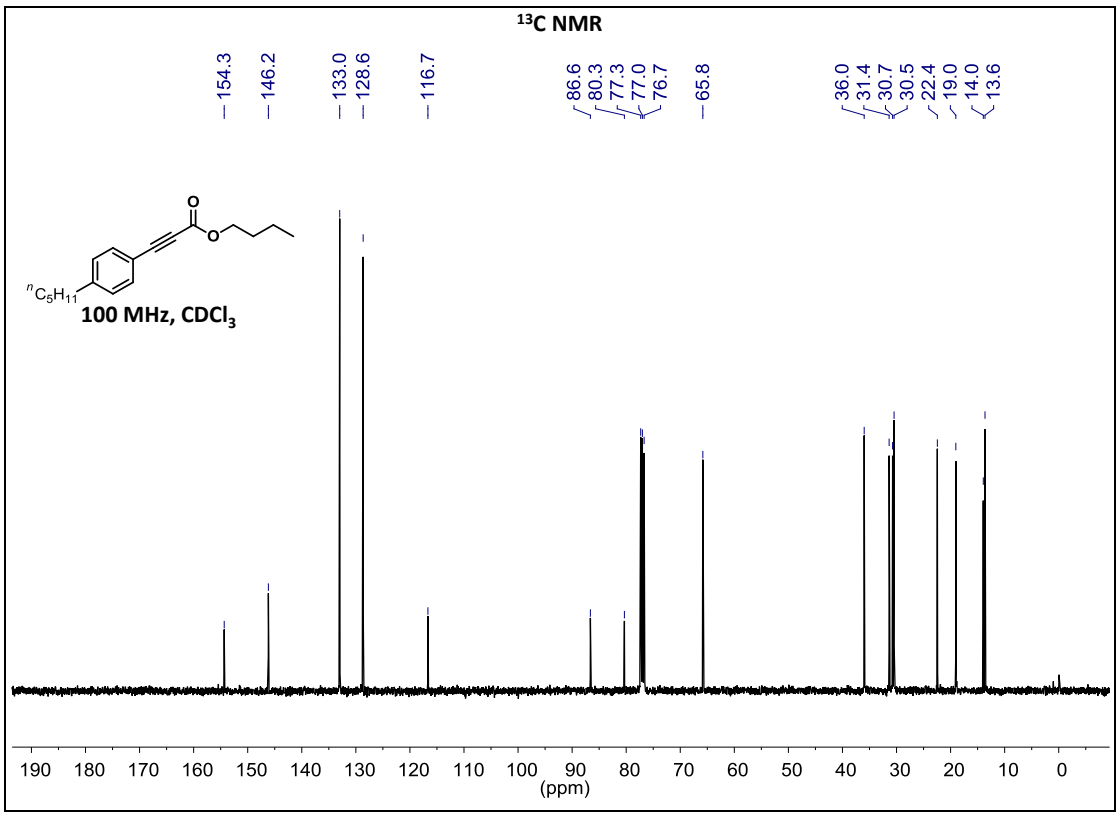


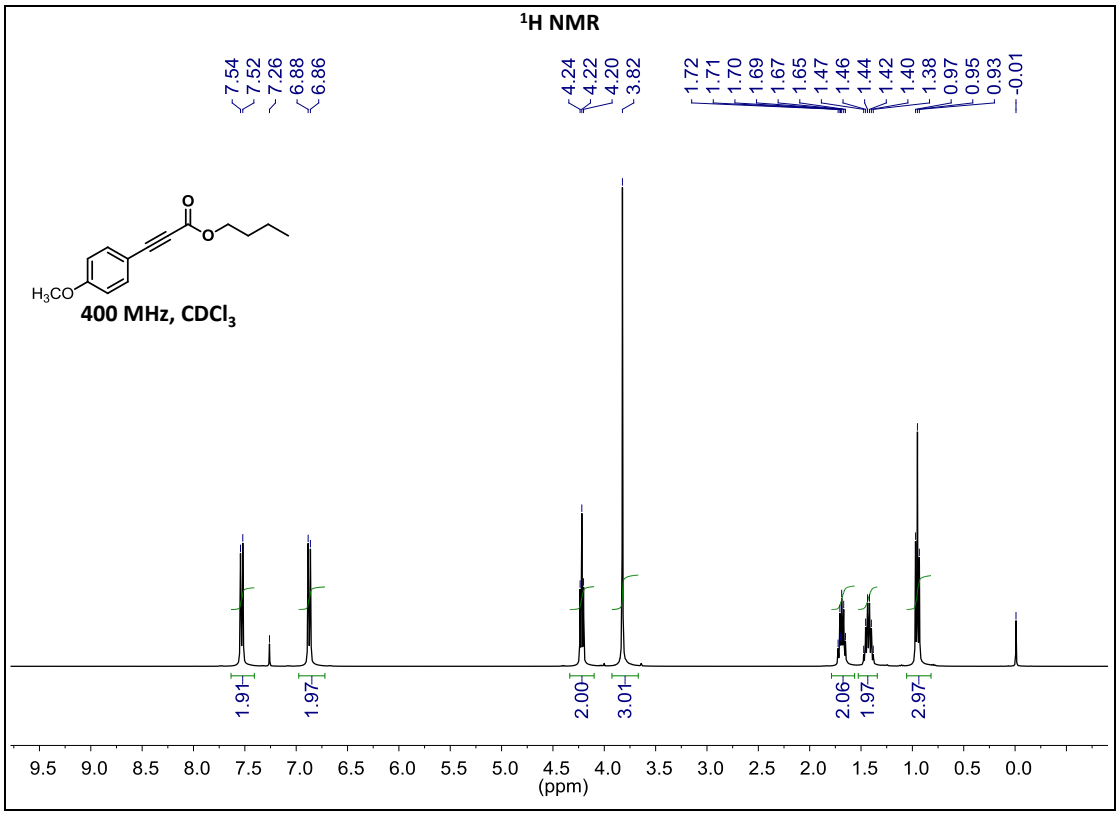


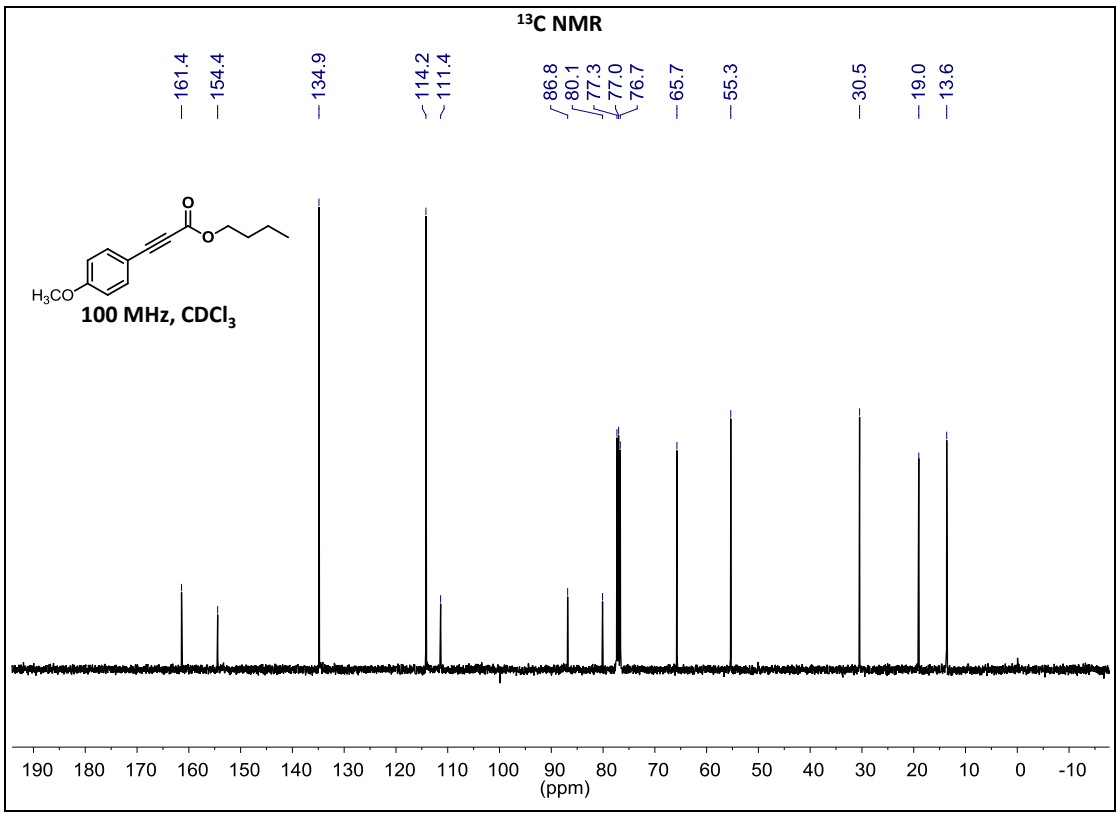


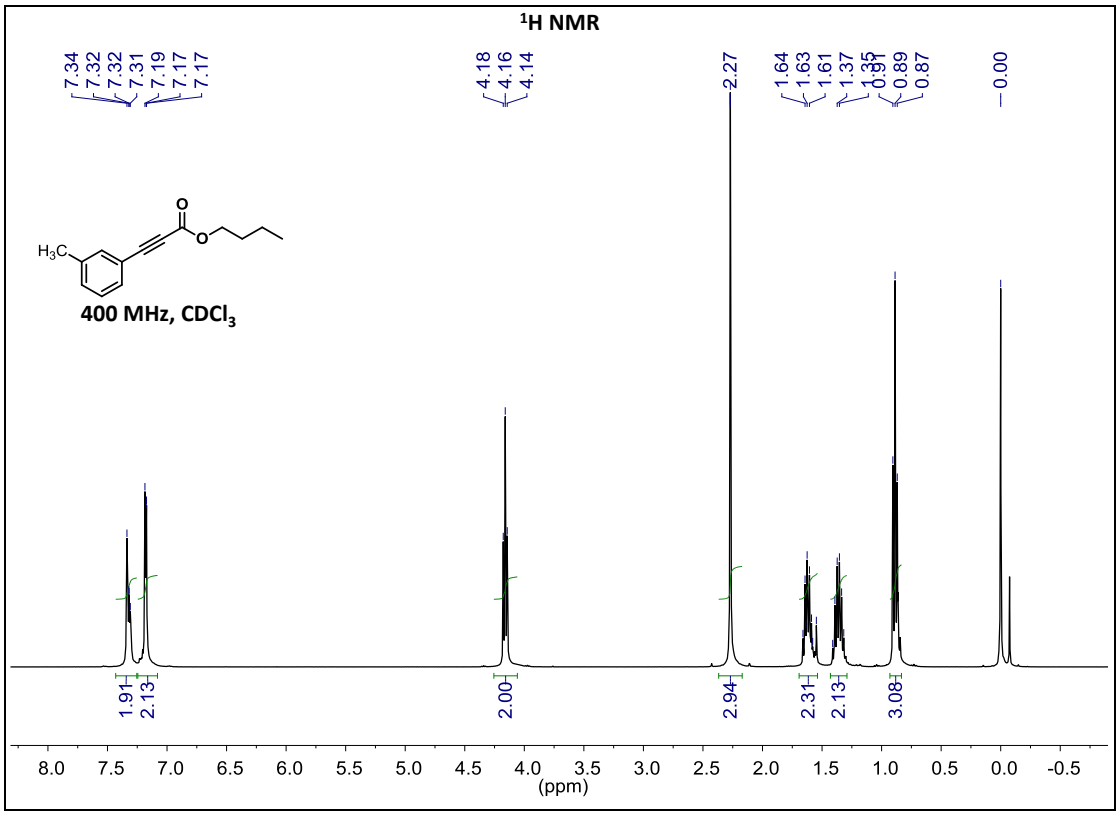


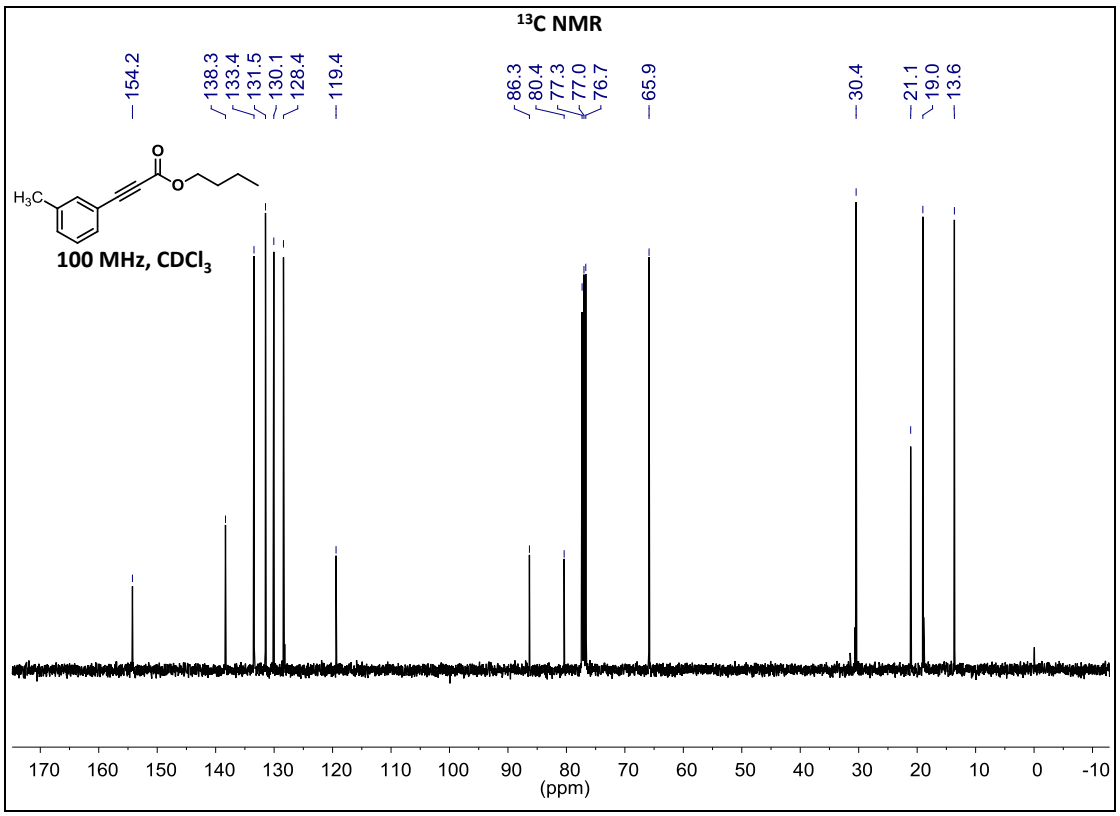


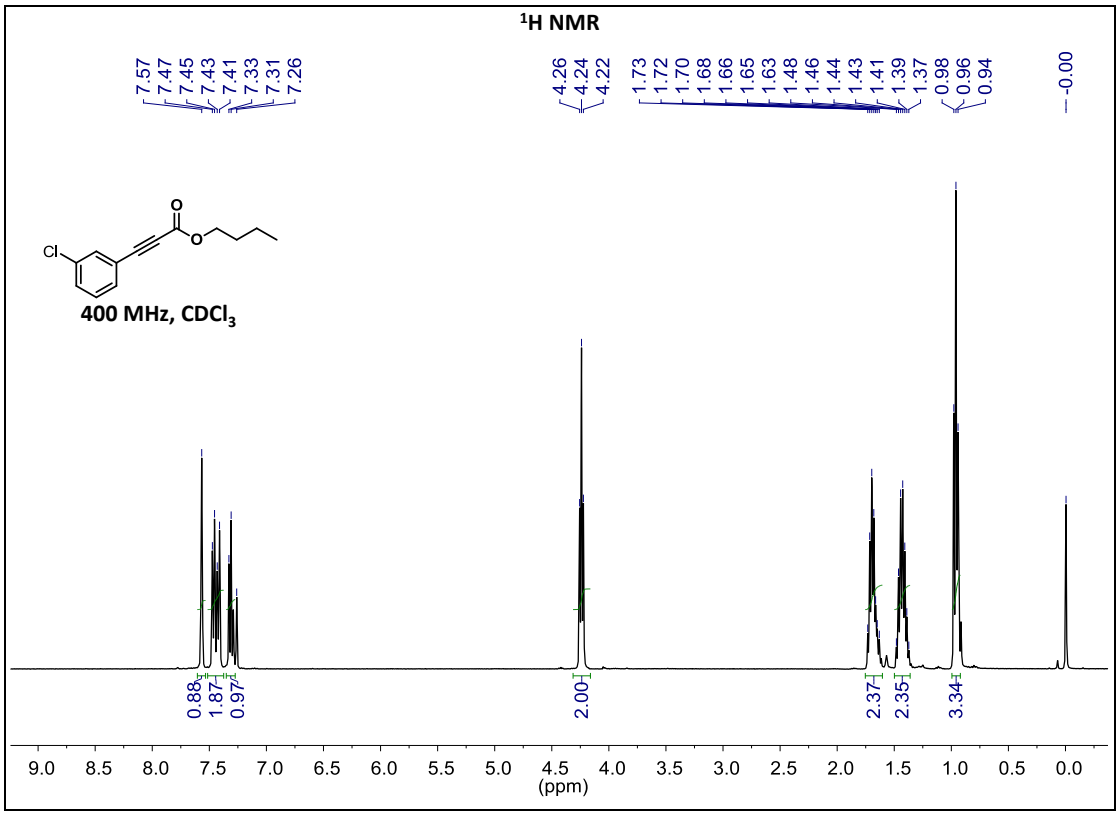

^{13}C NMR
154.3
146.2
133.0
128.6
116.7
86.6
80.3
77.3
77.0
76.7
65.8
36.0
31.4
30.7
30.5
22.4
19.0
14.0
13.6
$^{n}C_5H_{11}$
100 MHz, CDCl$_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

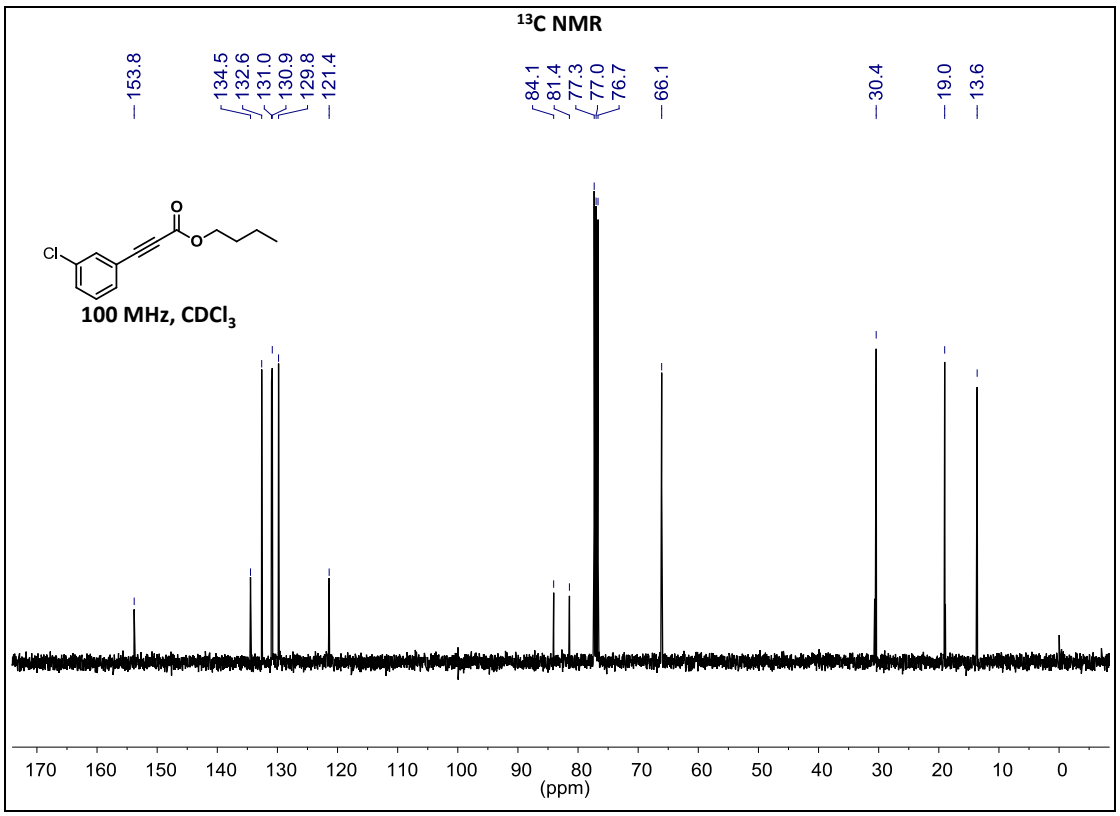

^{1}H NMR
7.54
7.52
7.26
6.88
6.86
4.24
4.22
4.20
3.82
1.72
1.71
1.70
1.69
1.67
1.65
1.47
1.46
1.44
1.42
1.40
1.38
0.97
0.95
0.93
-0.01
H_3CO
400 MHz, CDCl$_3$
1.91
1.97
2.00
3.01
2.06
1.97
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

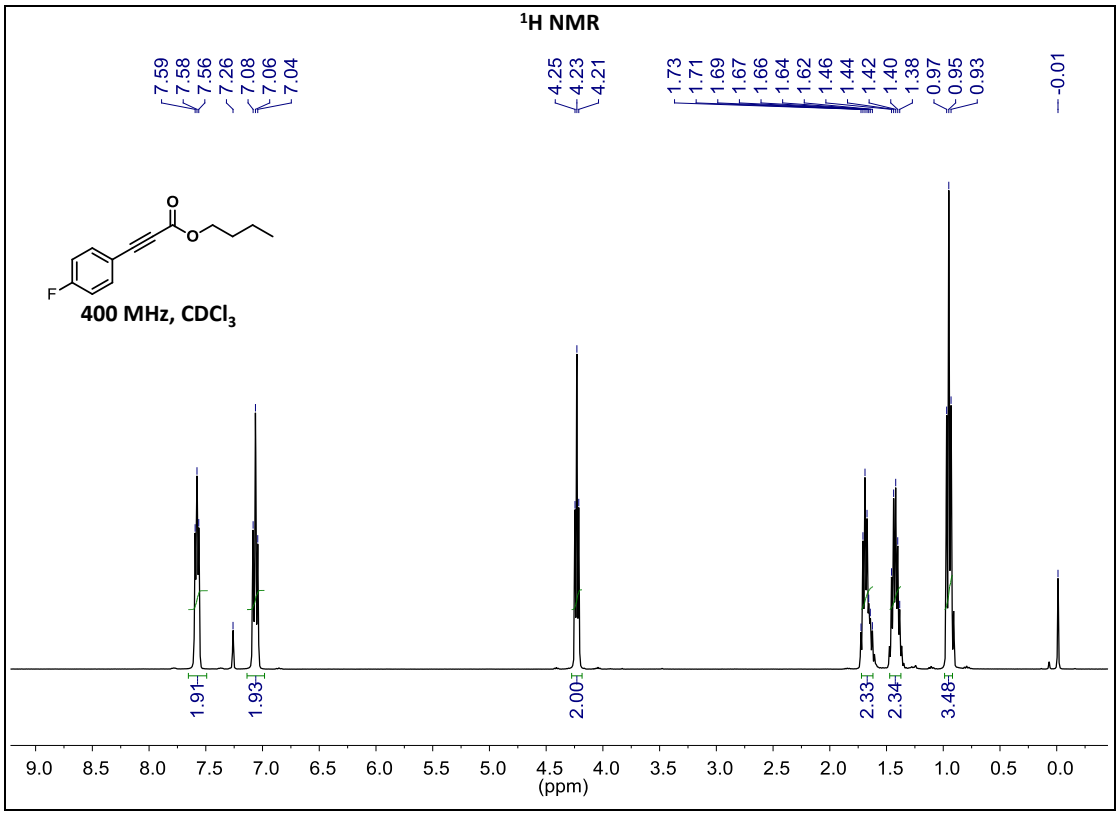


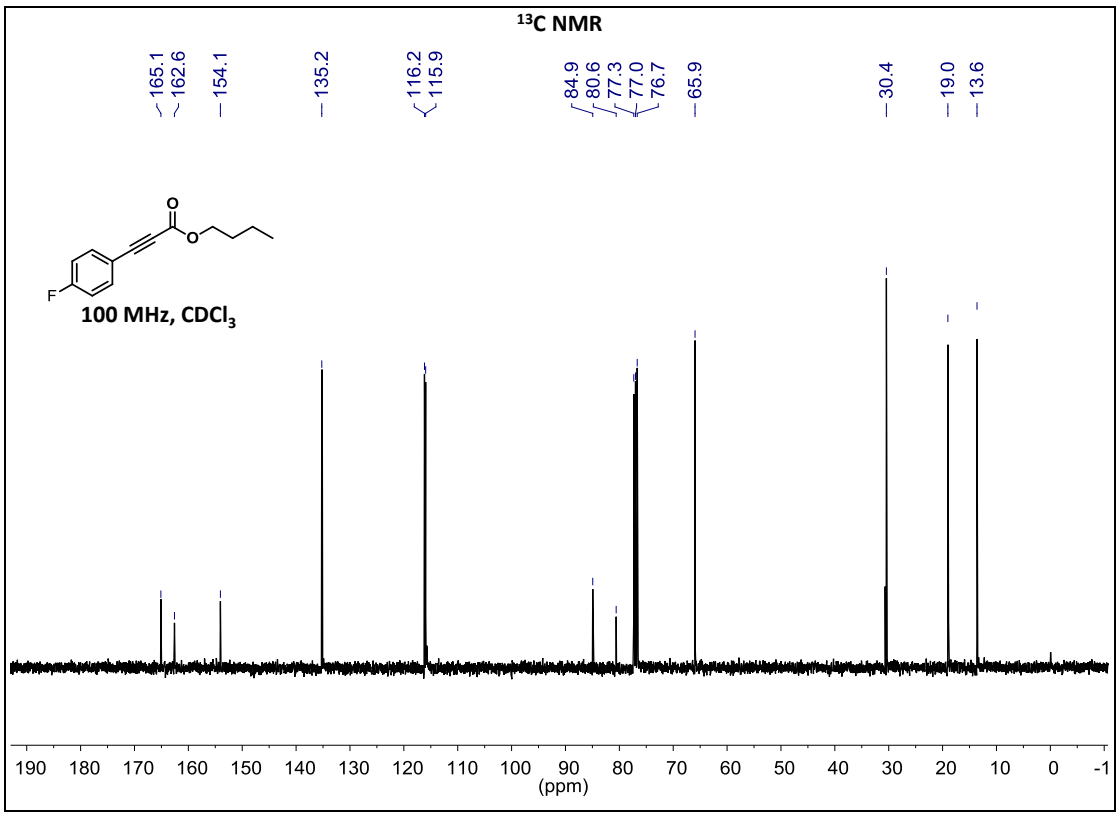


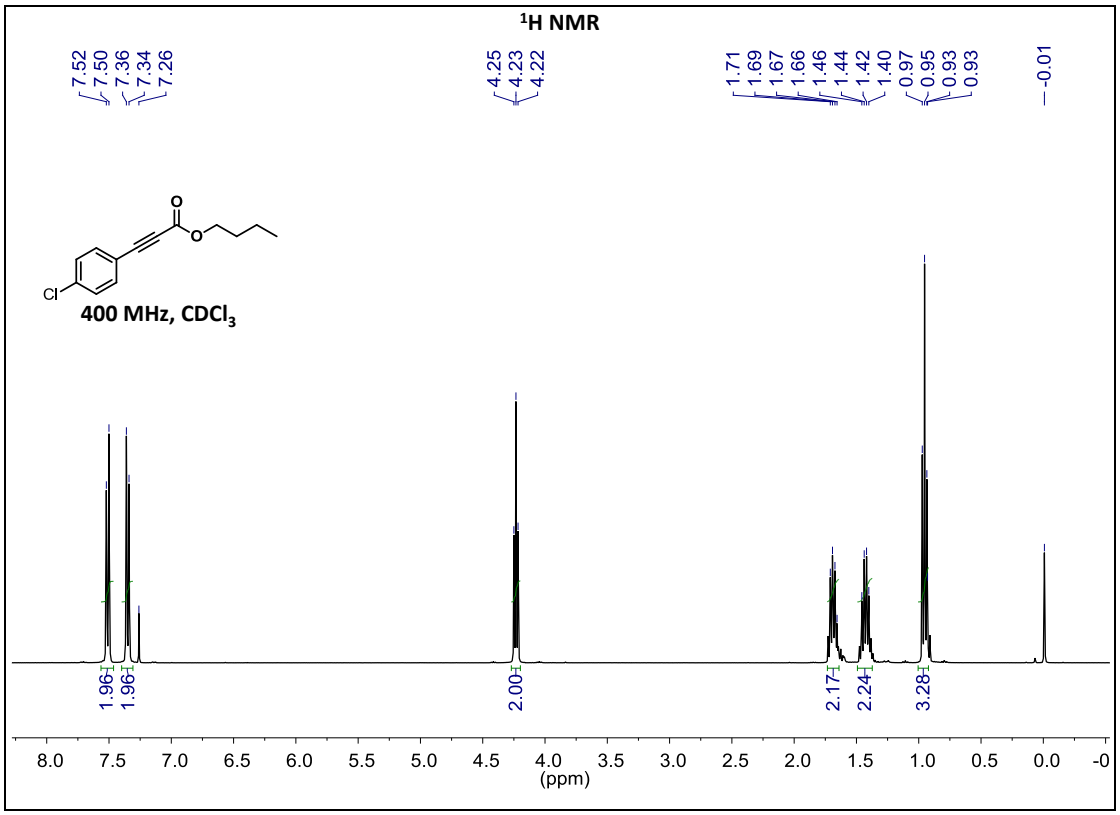


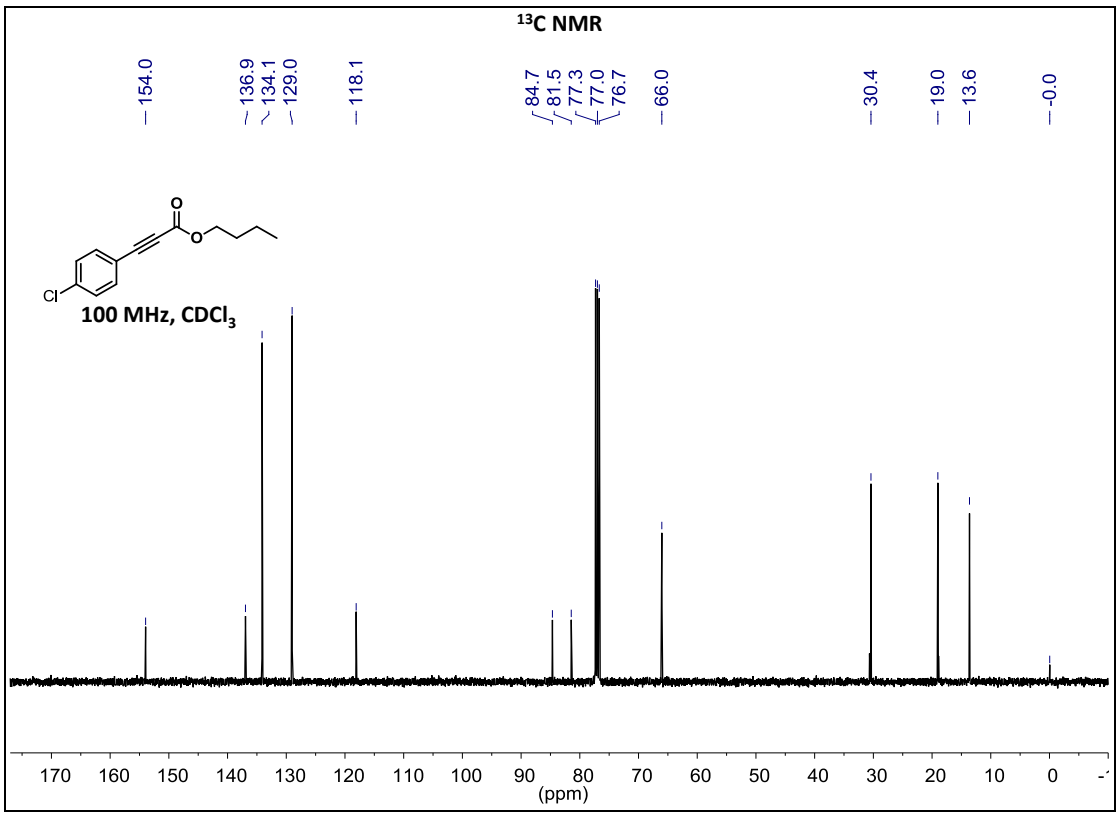


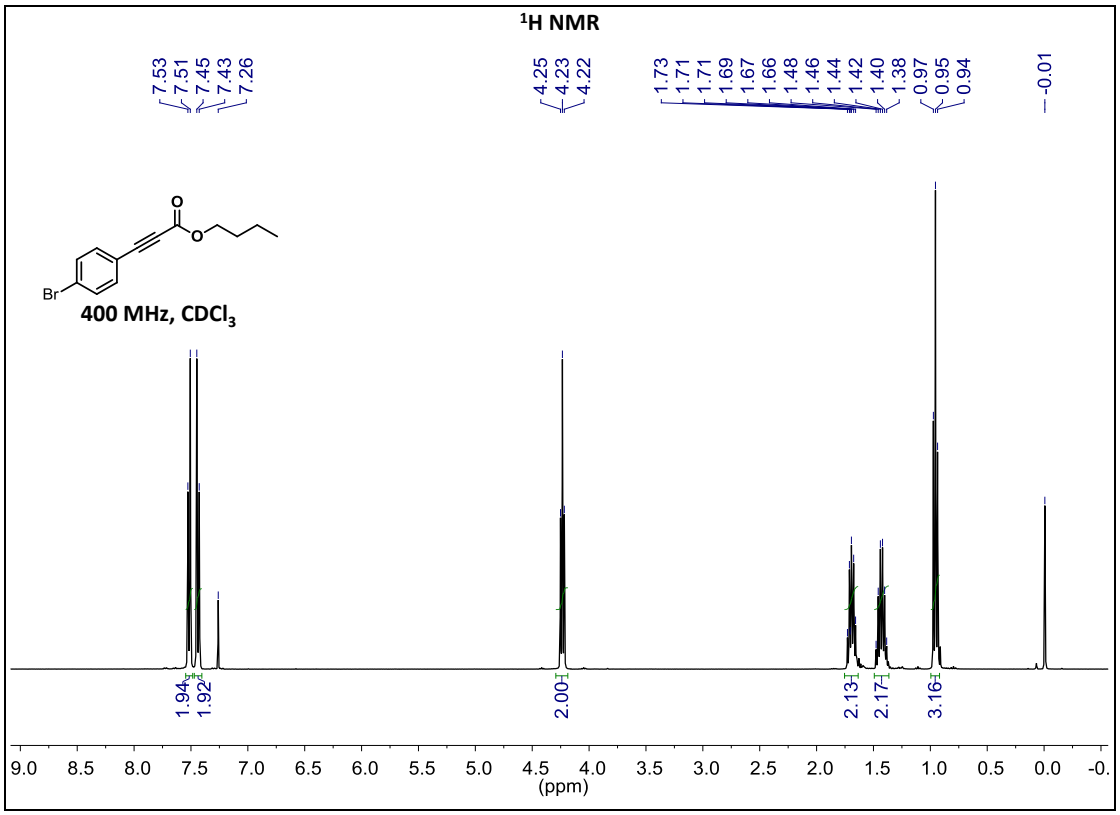


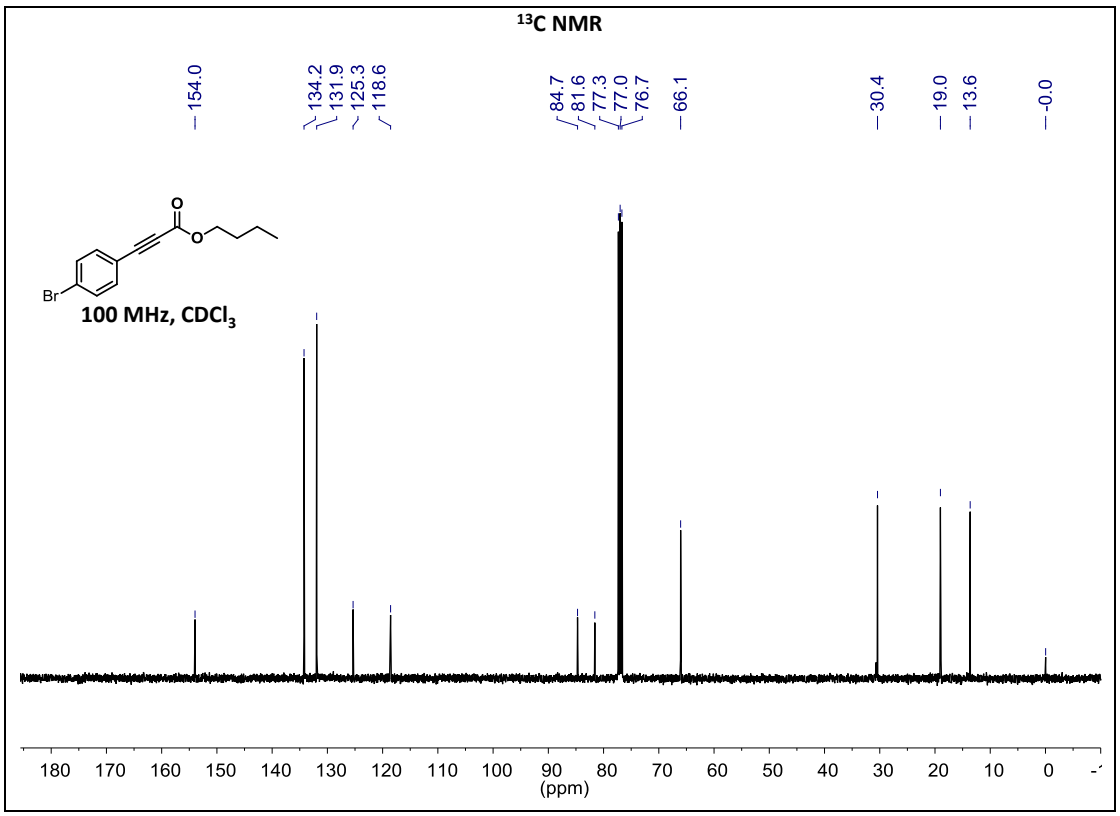


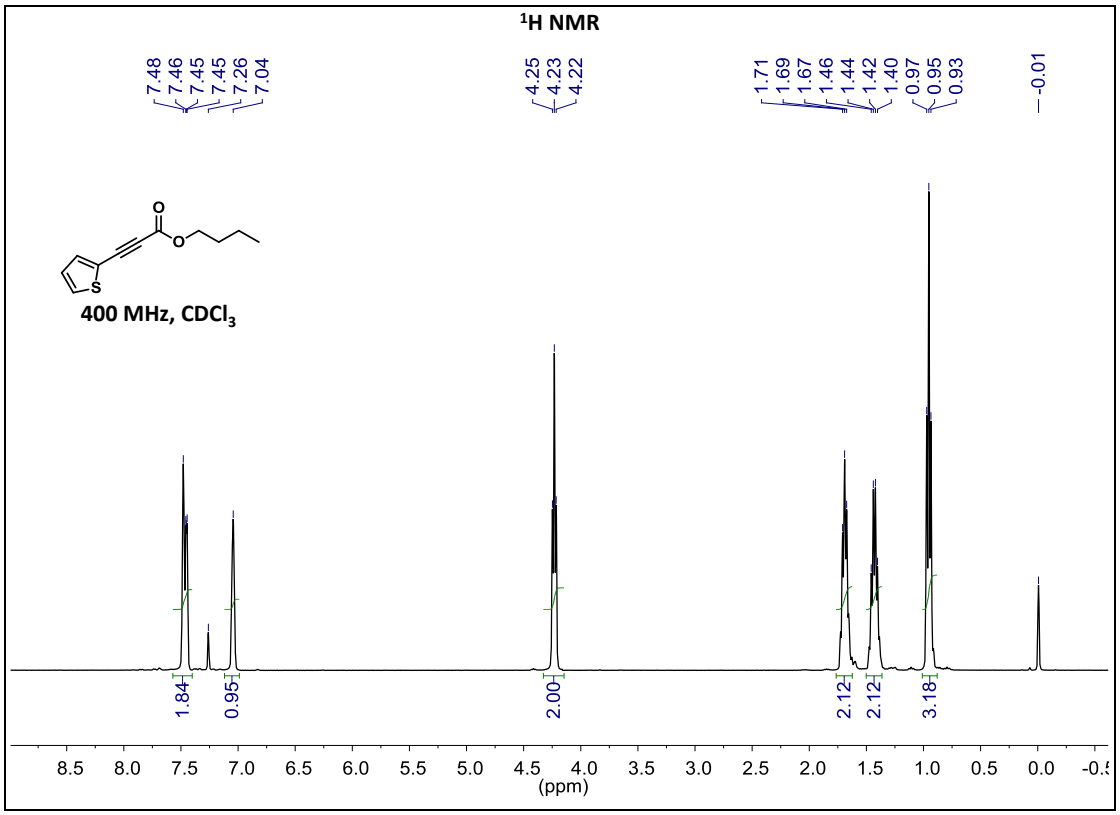


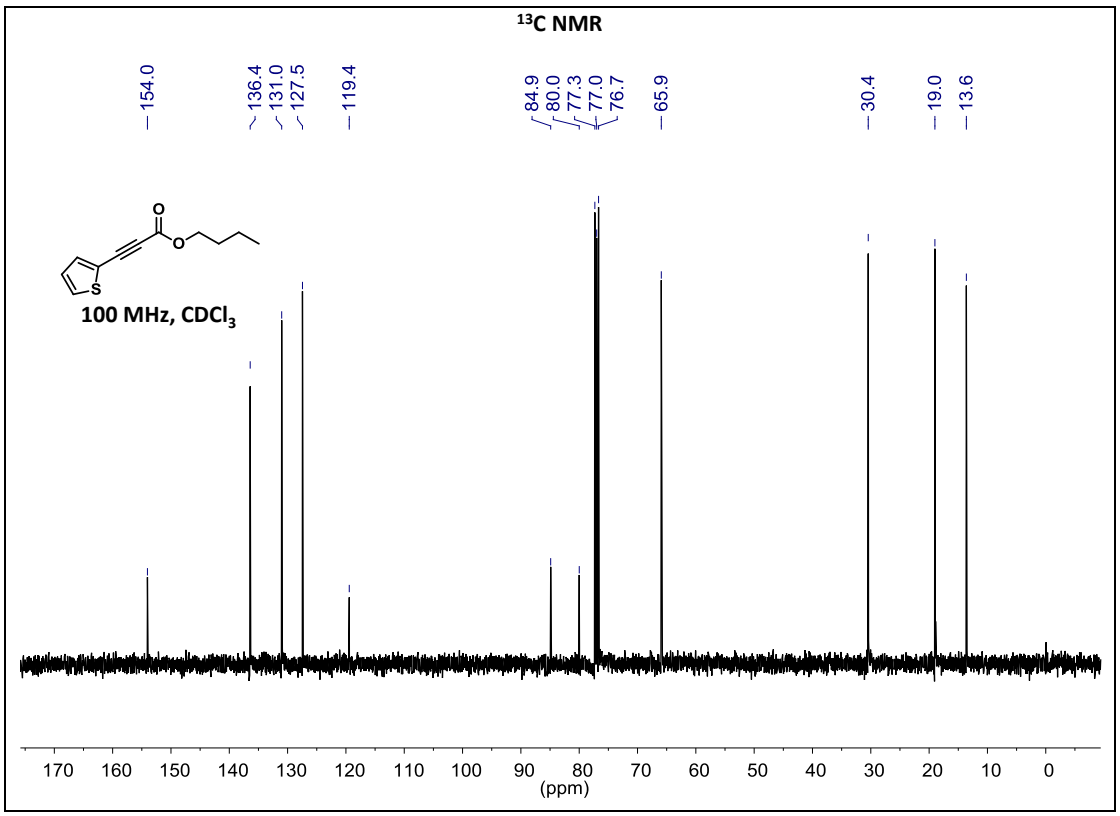


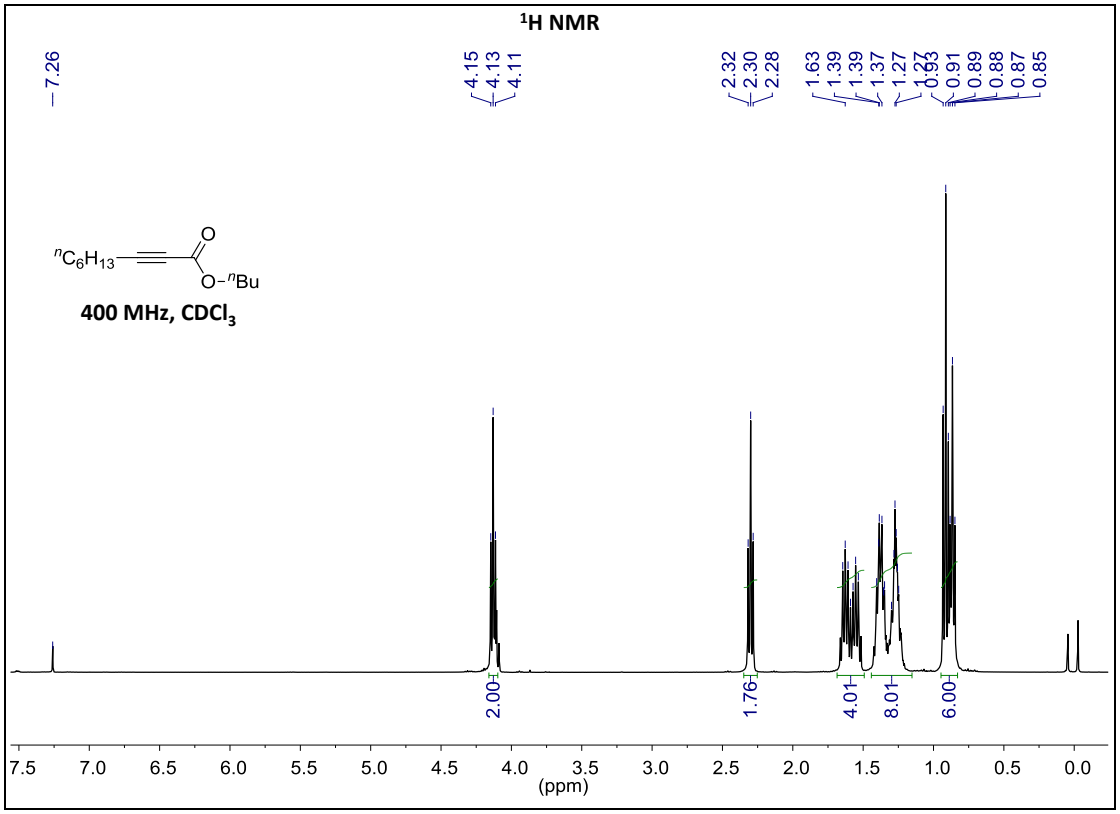


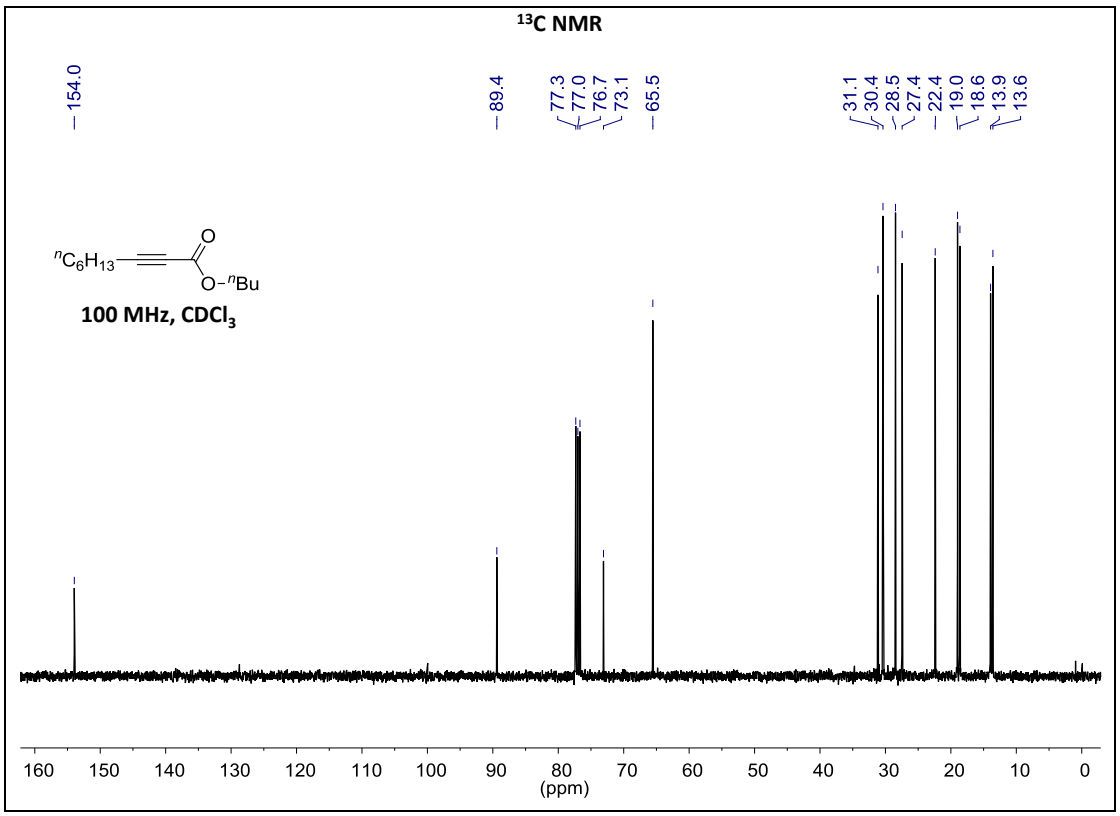


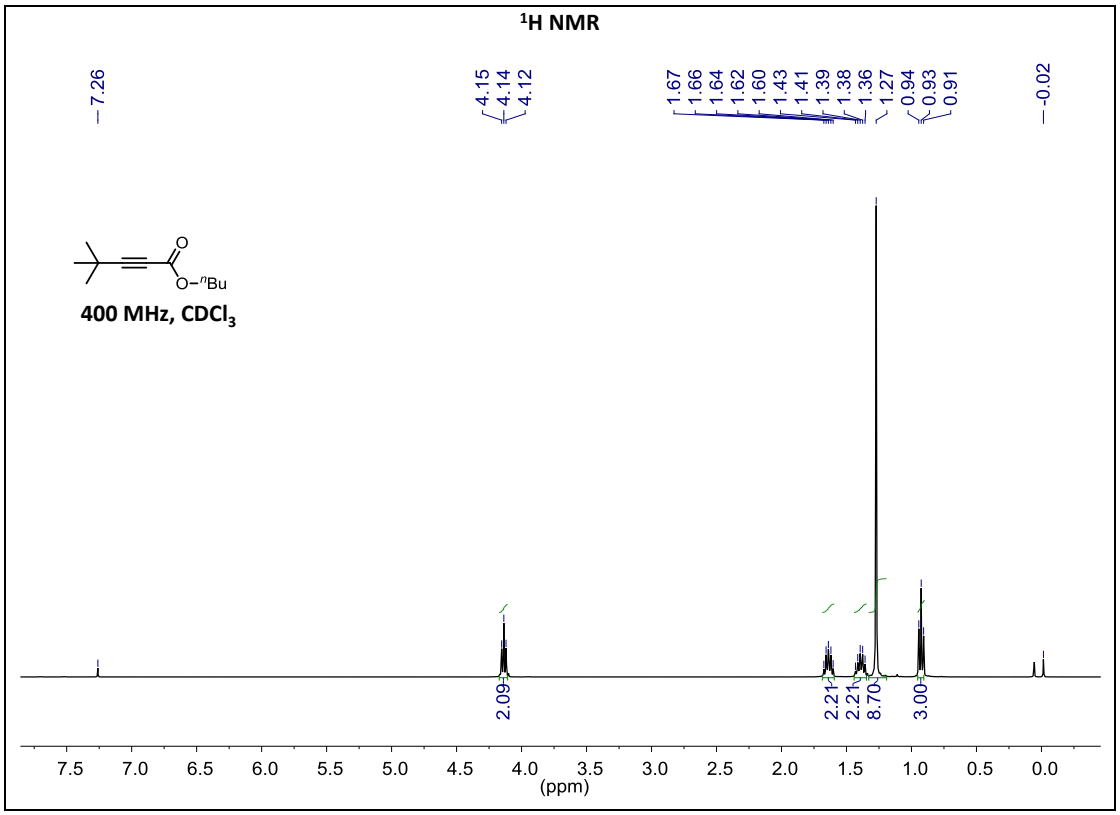


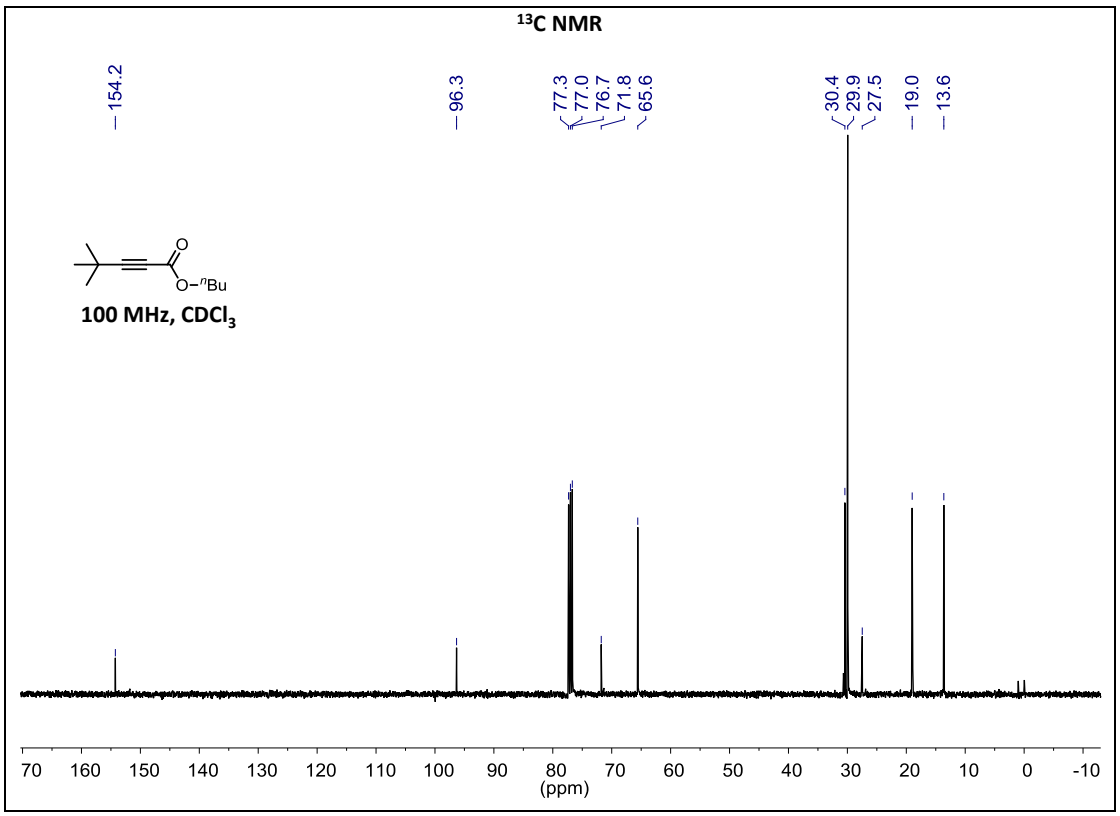



13C NMR
154.0
136.4
131.0
127.5
119.4
84.9
80.0
77.3
77.0
76.7
65.9
30.4
19.0
13.6
100 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

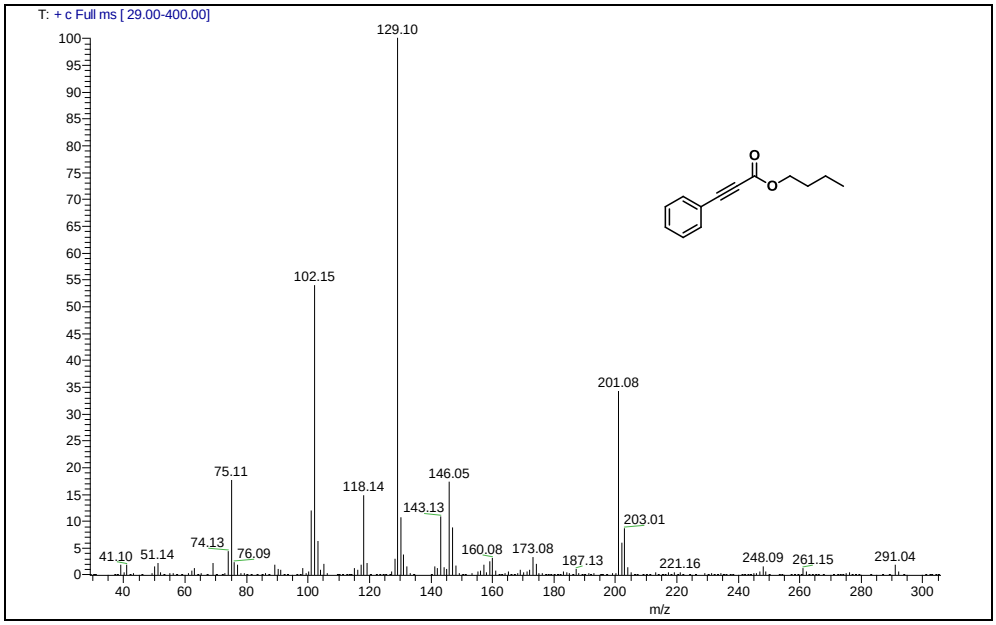

1H NMR
7.26
4.15
4.13
4.11
2.32
2.30
2.28
1.63
1.39
1.39
1.37
1.27
0.91
0.89
0.88
0.87
0.85
nC6H13
O-nBu
400 MHz, CDCl3
2.00
1.76
4.01
8.01
6.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

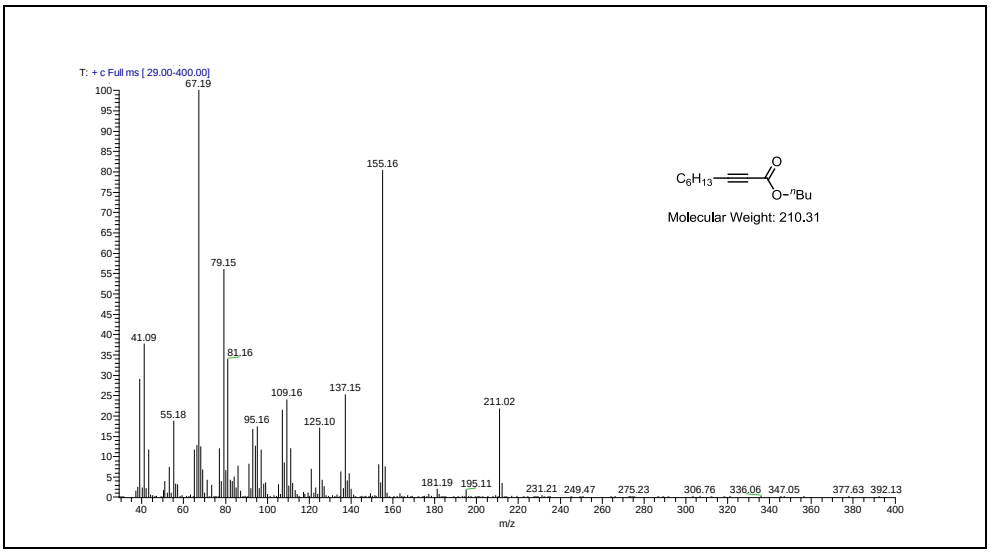

^{13}C NMR
154.0
89.4
77.3
77.0
76.7
73.1
65.5
31.1
30.4
28.5
27.4
22.4
19.0
18.6
13.9
13.6
^{n}C$_6$H$_{13}$
O
O–^{n}Bu
100 MHz, CDCl$_3$
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


^{1}H NMR
7.26
4.15
4.14
4.12
1.67
1.66
1.64
1.62
1.60
1.43
1.41
1.39
1.38
1.36
1.27
0.94
0.93
0.91
-0.02
O
O–^{n}Bu
400 MHz, CDCl$_3$
2.09
2.21
2.21
8.70
3.00
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
(ppm)



5. GC-MS Spectral Data of the Products




T: + c Full ms [29.00-400.00]
67.19
155.16
79.15
41.09
81.16
109.16
137.15
55.18
95.16
125.10
211.02
181.19
195.11
231.21
249.47
275.23
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347.05
377.63
392.13
m/z
C_6H_{13}
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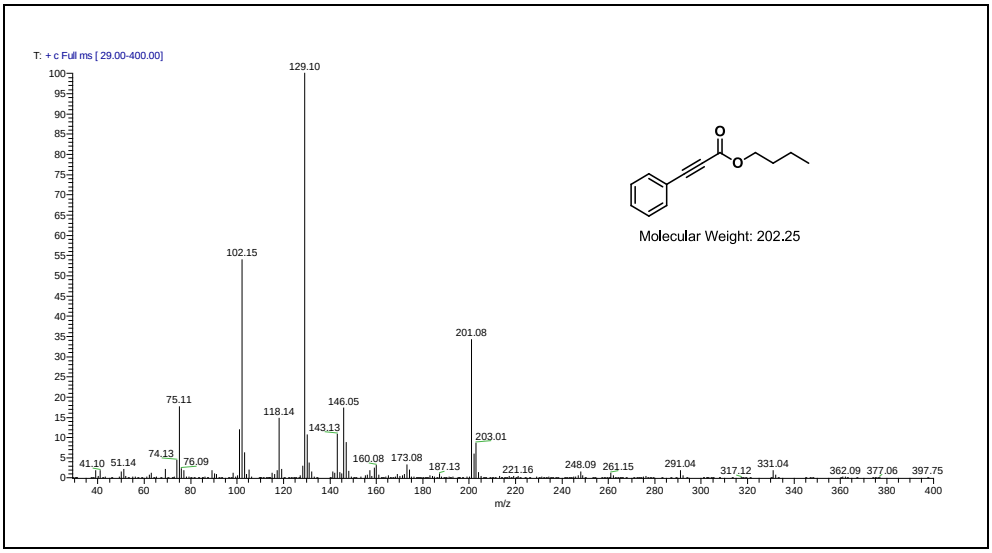
O-^{n}Bu
Molecular Weight: 210.31


T: + c Full ms [29.00-400.00]
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102.15
201.08
75.11
118.14
146.05
143.13
203.01
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51.14
74.13
76.09
160.08
173.08
187.13
221.16
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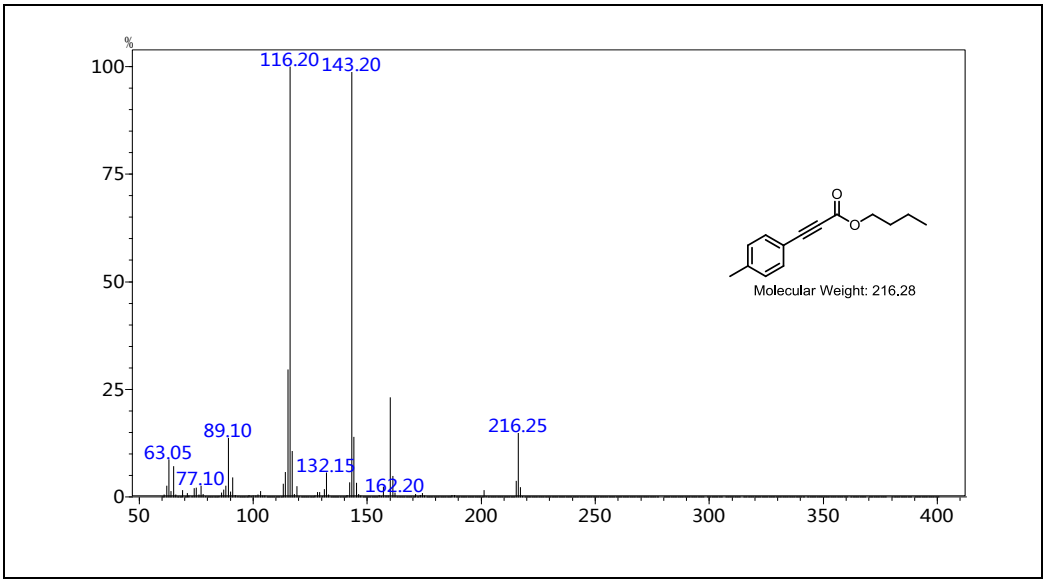
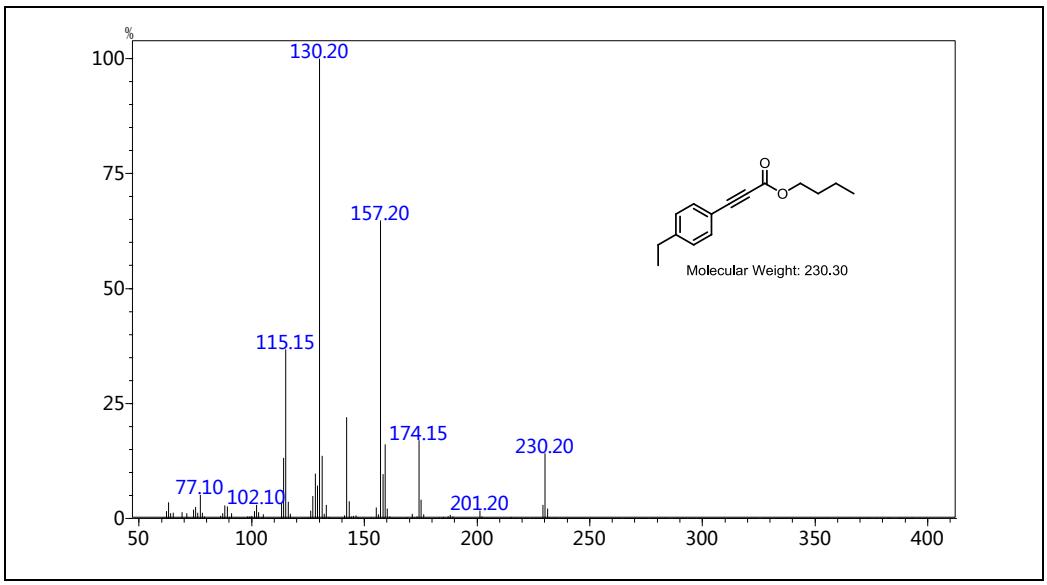
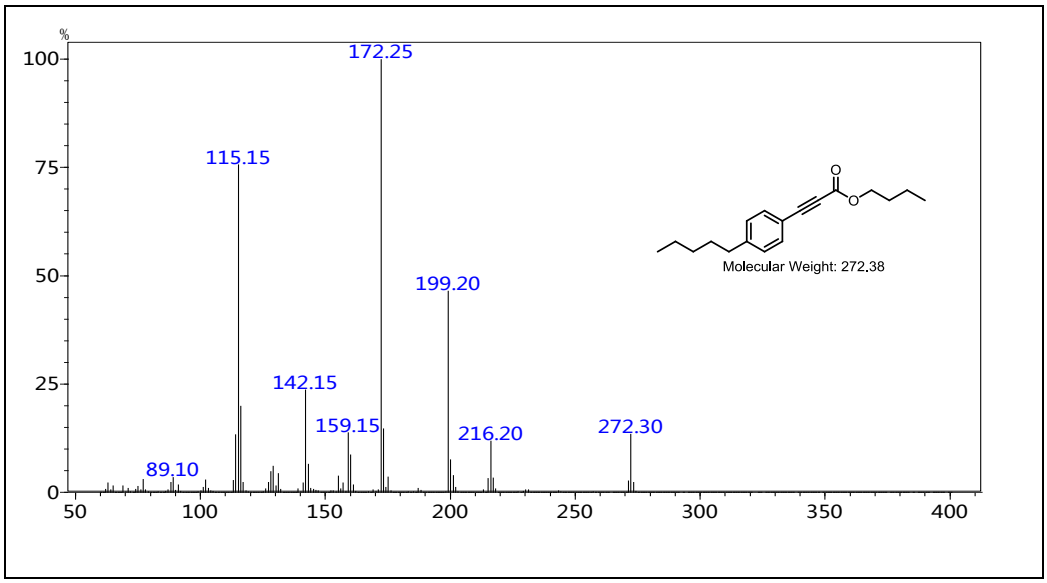
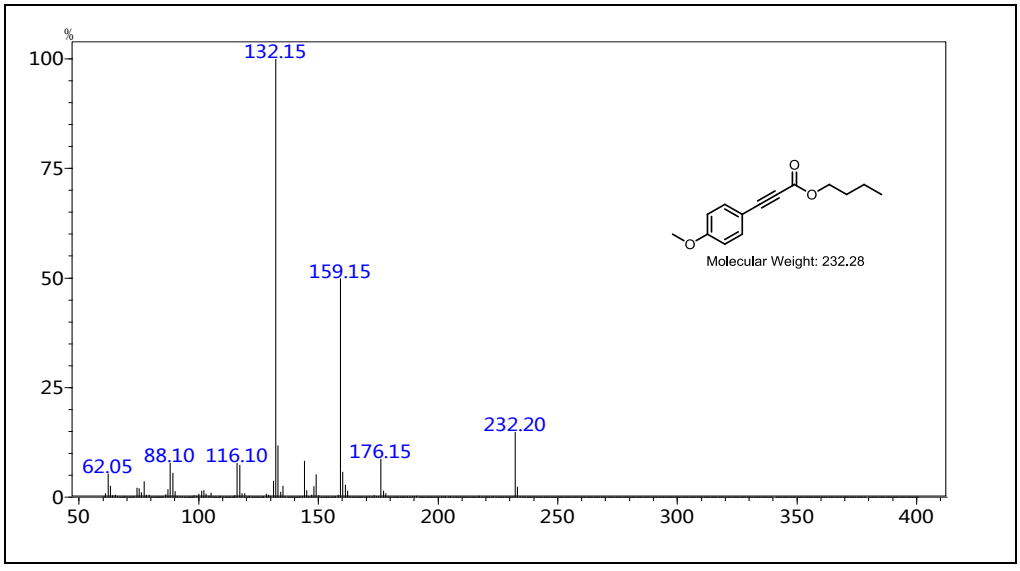
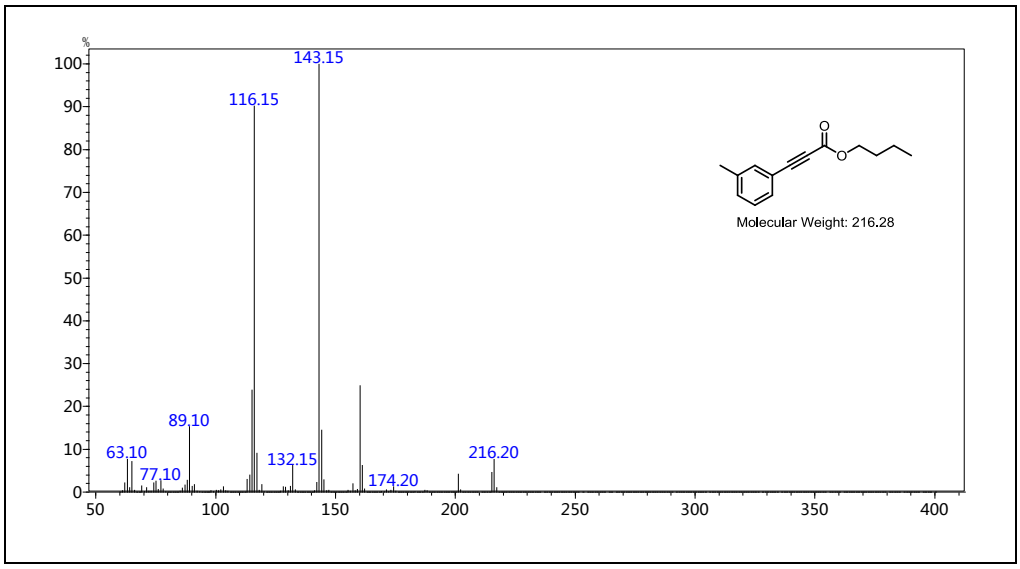
377.06
397.75
m/z
O
O
Molecular Weight: 202.25

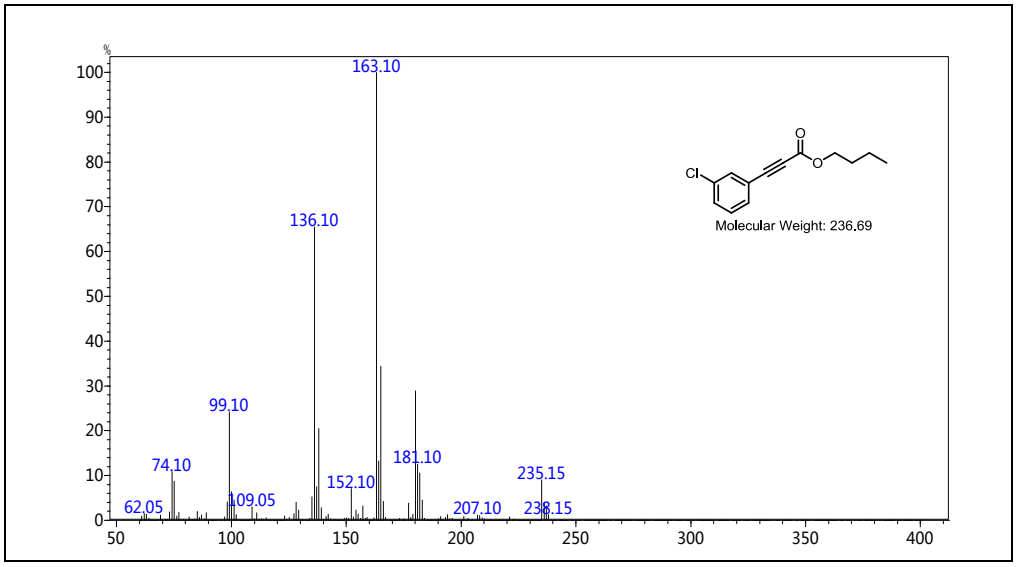

%
116.20
143.20
89.10
63.05
77.10
132.15
162.20
216.25
O
O
Molecular Weight: 216.28

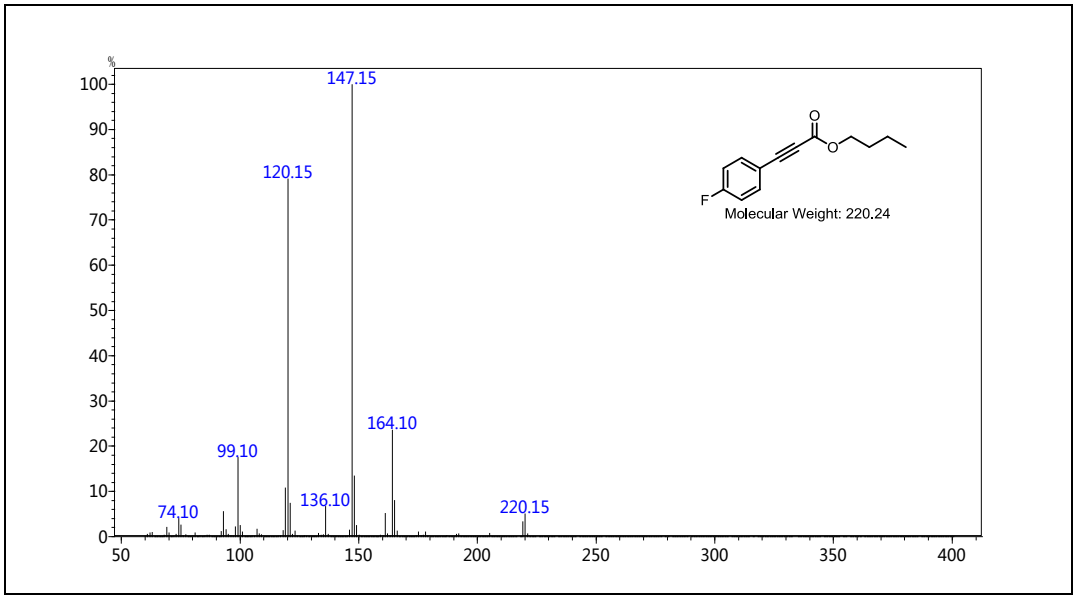







143.15
116.15
89.10
63.10
77.10
132.15
174.20
216.20
Molecular Weight: 216.28


163.10
136.10
99.10
74.10
62.05
109.05
152.10
181.10
207.10
235.15
238.15
Cl
Molecular Weight: 236.69


147.15
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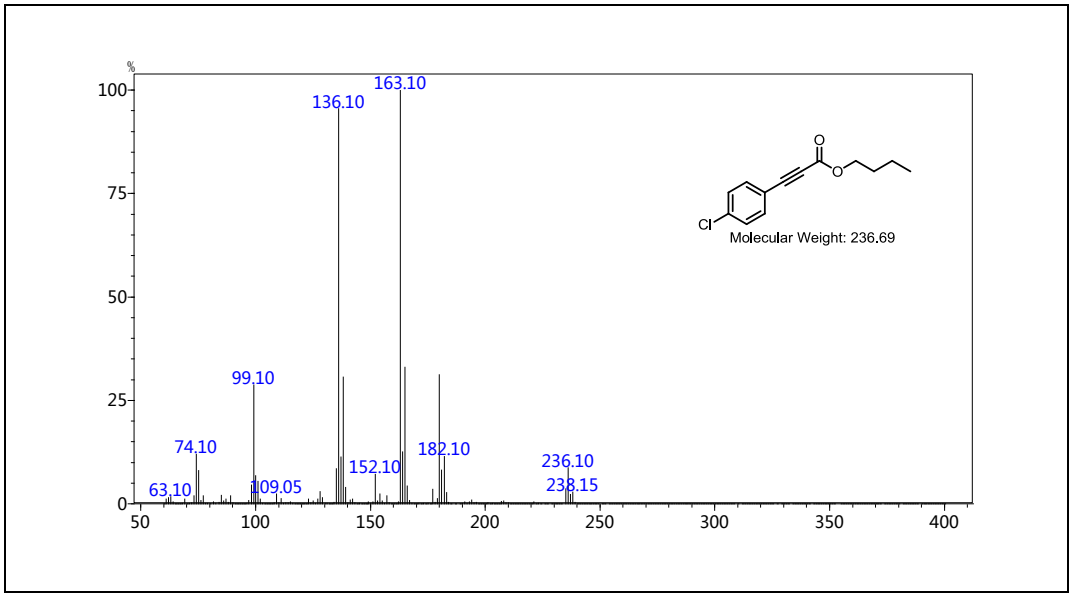
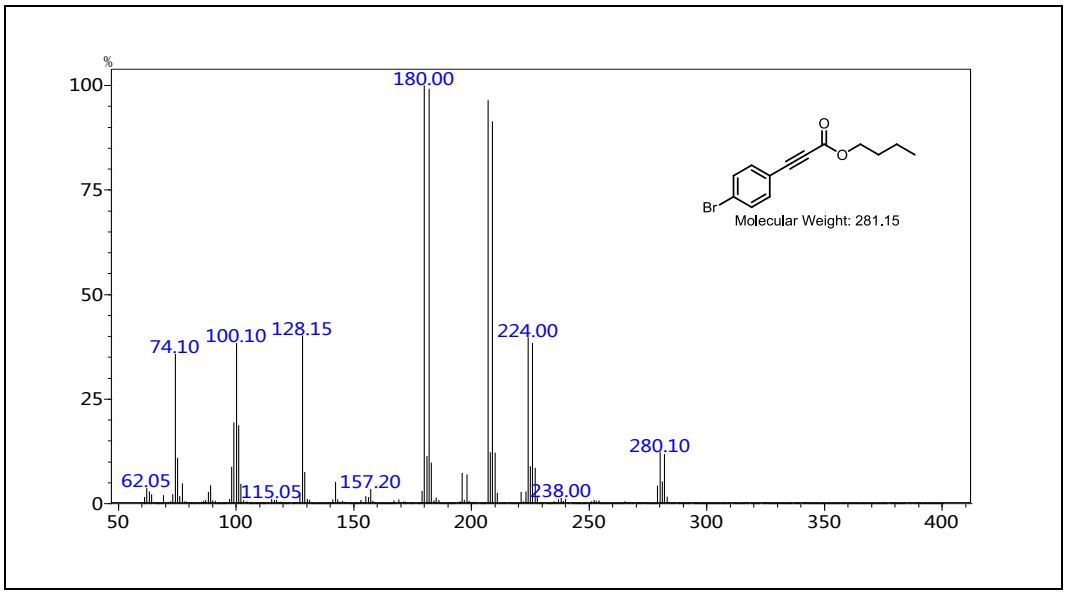
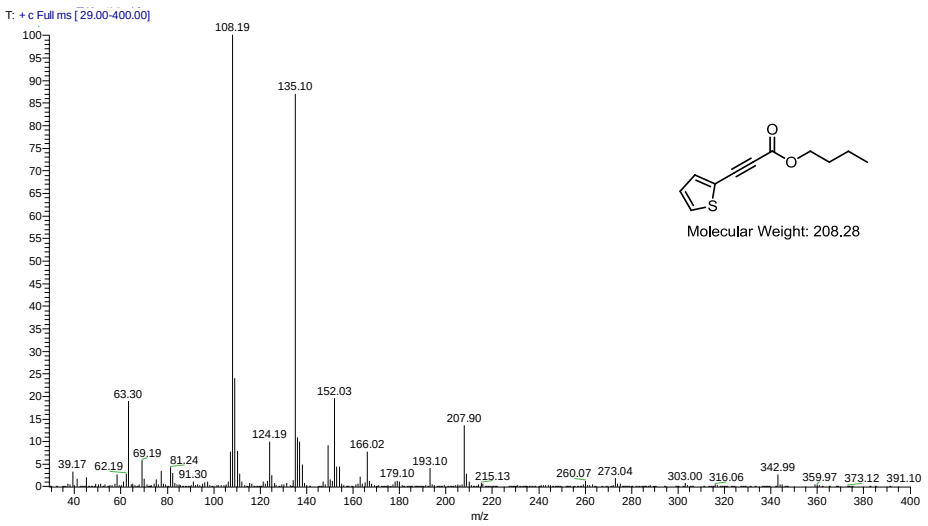
99.10
74.10
136.10
164.10
220.15
F
Molecular Weight: 220.24


%
100
75
50
25
0
50
100
150
200
250
300
350
400
163.10
136.10
99.10
74.10
63.10
109.05
152.10
182.10
236.10
238.15
O
O
Cl
Molecular Weight: 236.69


%
100
75
50
25
0
50
100
150
200
250
300
350
400
180.00
74.10
100.10
128.15
224.00
62.05
115.05
157.20
238.00
280.10
O
O
Br
Molecular Weight: 281.15

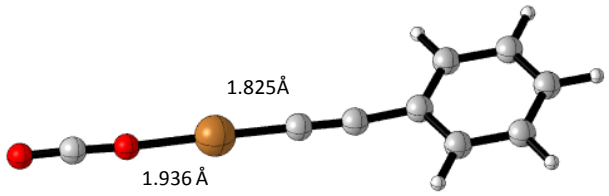


6. DFT Calculations

The calculations were carried out by performing DFT by use of the B3PW91functional with the 6-311++G (d, p) (C, H, N, O) and LANL2DZ (Cu) basis set as implemented in Gaussian 09 program package. All the final structures were confirmed by frequency calculation to be the real minima without any imaginary frequency using the same level of theory. All transition-state (TS) geometries were characterized by the presence of a single imaginary frequency, and intrinsic reaction coordinates (IRC) were examined to ensure smooth connection of reactants and products. All the bond lengths are in angstroms (Å). Structures were generated using CYLview.[1]

[1] CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009 (http://www.cylview.org).

The cartesian coordinates



(H: white, C: gray, O: red, Cu: golden. Bond lengths and distances in Å.)

C	4.61641300	-1.19858300	0.07646200
C	3.22736900	-1.20982100	-0.01074100
C	2.50141800	-0.00574400	-0.05874800
C	3.21280600	1.20705600	-0.01358700
C	4.60185600	1.21241000	0.07359200
C	5.30813900	0.01117200	0.12206200
H	5.15081300	-2.14101100	0.10484200
H	2.69442800	-2.15187700	-0.05769100
H	2.66868800	2.14252300	-0.06277600
H	5.12488400	2.16131000	0.09967000
H	6.38925300	0.01778800	0.19519800
C	1.07695400	-0.01387300	-0.18586500
C	-0.14533800	-0.00788700	-0.12234600
Cu	-1.96859900	-0.00221800	-0.04467000
O	-6.21519800	0.01191300	0.14261900
C	-5.06370700	0.00442400	0.10361300
O	-3.90407300	-0.00683000	-0.00392500

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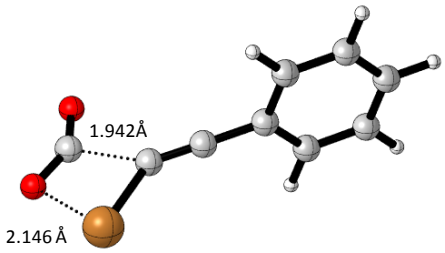

TS1

(H: white, C: gray, O: red, Cu: golden. Bond lengths and distances in Å.)

C	3.82890100	-0.02298900	-1.20871700
C	2.44020500	0.00986600	-1.21395600
C	1.72497300	0.02675900	-0.00012300
C	2.43990100	0.00929500	1.21388000
C	3.82859900	-0.02356400	1.20897200
C	4.52611000	-0.04044500	0.00021100
H	4.37029600	-0.03294400	-2.14775700
H	1.89235400	0.02778600	-2.14814500
H	1.89181800	0.02677000	2.14794200
H	4.36975800	-0.03396800	2.14814300
H	5.60990900	-0.06484300	0.00034100
C	0.30699000	0.07123500	-0.00028700
C	-0.92504800	0.13638200	-0.00034900
Cu	-2.37318200	-1.18510600	-0.00015500
O	-2.02912400	2.47924500	0.00020100
C	-2.42700500	1.36762700	0.00020100
O	-3.44257900	0.67579000	0.00042200

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5 6 1.5 10 1.0
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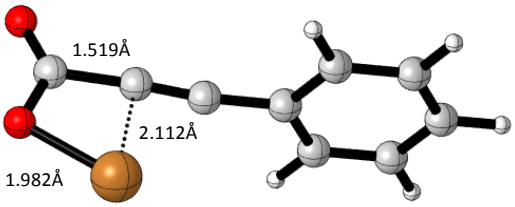

(H: white, C: gray, O: red, Cu: golden. Bond lengths and distances in Å.)

C	3.57859500	0.06813600	-1.20706400
C	2.19710500	0.22504900	-1.21285000
C	1.49156400	0.30524300	0.00018400
C	2.19734500	0.22411200	1.21303300
C	3.57882600	0.06722300	1.20686700
C	4.27308100	-0.01285900	-0.00020200
H	4.11449800	0.01214200	-2.14754500
H	1.65696800	0.29584400	-2.14927300
H	1.65738000	0.29417600	2.14961100
H	4.11491800	0.01050600	2.14719700
H	5.35006700	-0.13412200	-0.00035100
C	0.07063400	0.47861400	0.00038600
C	-1.11817400	0.77883100	0.00036500
Cu	-1.67288300	-1.25971700	-0.00020200
O	-3.03032600	2.18733400	0.00048000
C	-2.61252400	1.05347500	0.00016900
O	-3.25954300	-0.07154600	-0.00037000

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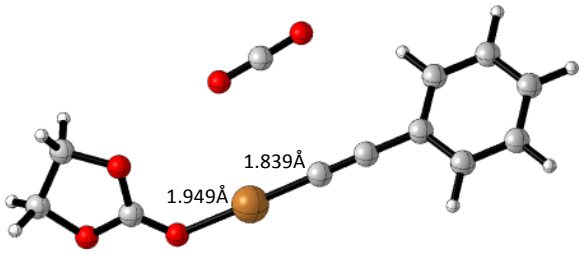

(H: white, C: gray, O: red, Cu: golden. Bond lengths and distances in Å.)

C	5.80028900	-1.37351800	0.35427500
C	4.42680100	-1.54273100	0.21551300
C	3.57265800	-0.42989900	0.08858700
C	4.14777600	0.85570100	0.10521900
C	5.52241600	1.01738400	0.24439500
C	6.35646700	-0.09395100	0.36996100
H	6.44018400	-2.24425700	0.45039400
H	3.99539000	-2.53657400	0.20311100
H	3.50146400	1.71935100	0.00626200
H	5.94522400	2.01642200	0.25410100
H	7.42765900	0.03538300	0.47777100
C	2.16423000	-0.60395800	-0.05288000
C	0.95783100	-0.77150700	-0.17490700
Cu	-0.85612800	-1.01804100	-0.35739800
O	1.10311600	3.06140400	-0.39551500
C	0.00293100	2.70044800	-0.43957900
O	-1.11247600	2.37393300	-0.48488000
C	-5.84347100	-0.06817100	0.40497900
C	-4.87399600	0.82698300	1.18316100
H	-6.33114500	-0.81756600	1.03024600
H	-6.58385800	0.47838500	-0.17477500
H	-5.06393800	0.86234000	2.25345600
H	-4.80041300	1.83704100	0.77793100
O	-4.96499600	-0.75709200	-0.51765500
O	-3.60331800	0.16693300	0.96960700
C	-3.70828600	-0.64511200	-0.08311100
O	-2.77941900	-1.22734700	-0.59751100

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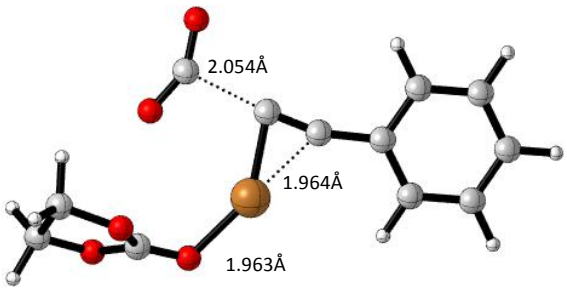

TS2

(H: white, C: gray, O: red, Cu: golden. Bond lengths and distances in Å.)

C	4.69520700	-1.68182600	0.10791400
C	3.36140300	-1.29436800	0.02581000
C	3.01140000	0.06483400	0.02764600
C	4.03473600	1.02683300	0.11462000
C	5.36514900	0.63259600	0.19663200

C	5.70205000	-0.72146700	0.19338200
H	4.94831000	-2.73610200	0.10455000
H	2.58163000	-2.04482600	-0.04113000
H	3.77165900	2.07755800	0.11597700
H	6.14246700	1.38565600	0.26256400
H	6.74073900	-1.02502900	0.25690300
C	1.64455300	0.50613000	-0.05891900
C	0.60732700	1.20082000	-0.12293200
Cu	-0.16035300	-0.60532900	-0.20569200
O	-0.52592700	3.56116900	-0.17915700
C	-0.99960400	2.47827700	-0.19398800
O	-1.96804700	1.77145000	-0.22667400
C	-5.02872400	-0.47986600	-0.12089100
C	-4.32546800	0.10703400	1.10759800
H	-5.73804800	-1.27315300	0.11946300
H	-5.49475400	0.26798100	-0.75811500
H	-4.85118000	-0.06162000	2.04446300
H	-4.05397000	1.15467900	0.98462400
O	-3.93033500	-1.07480500	-0.86044400
O	-3.08923700	-0.65280000	1.14117500
C	-2.86850600	-1.14966600	-0.06862800
O	-1.81067500	-1.64583900	-0.42161300

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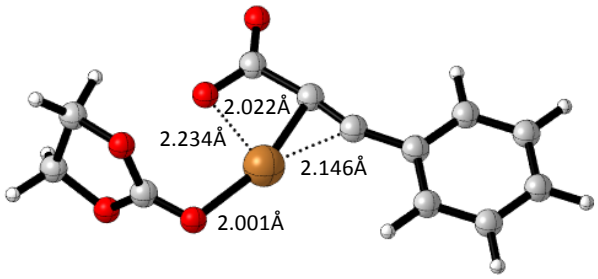

(H: white, C: gray, O: red, Cu: golden. Bond lengths and distances in Å.)

C	4.53875600	-1.75308300	0.04929800
C	3.22605500	-1.29428600	0.01813100
C	2.95654400	0.08267800	-0.00109600
C	4.03106200	0.99107700	0.01129800
C	5.33963400	0.52472800	0.04267800
C	5.59787500	-0.84656000	0.06166400
H	4.73457200	-2.81903900	0.06378700
H	2.40095200	-1.99699000	0.00832300
H	3.82583000	2.05452400	-0.00368900
H	6.16040600	1.23273300	0.05212600
H	6.62019400	-1.20616700	0.08596400
C	1.61308100	0.59202700	-0.03382000
C	0.66170600	1.38374400	-0.06493900
Cu	-0.28914700	-0.40132000	-0.04946000
O	-0.56194300	3.41094600	-0.10029600
C	-0.61904700	2.19662900	-0.09065400
O	-1.61808000	1.39442100	-0.09324000
C	-4.83918900	-0.30655200	-0.53633600
C	-4.39205200	0.18387500	0.84489400
H	-5.67421700	-1.00802500	-0.50463400
H	-5.04093600	0.49866000	-1.23886800
H	-5.14512100	0.07811100	1.62216700
H	-3.97096800	1.18879000	0.81909200
O	-3.67072200	-1.02688800	-1.00890600
O	-3.29825300	-0.72204300	1.14831300
C	-2.83389600	-1.20669900	0.00480800

O	-1.75207700	-1.76515800	-0.10905800

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24 26 1.5
25 26 1.5
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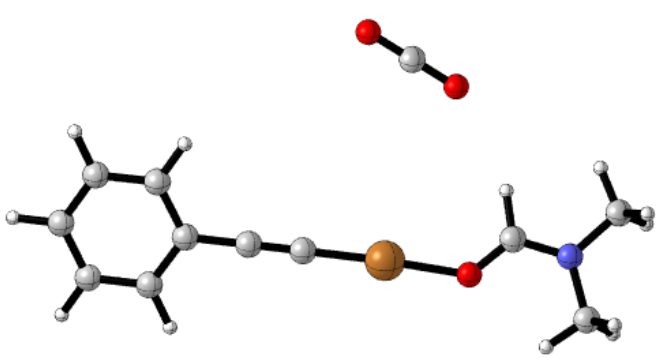
Bonding Energy (CO_2 and EC) = 1.85 kcal mol^{-1}
Bonding Energy (PhC≡CCu and EC) = 26.86 kcal mol^{-1}



(H: white, C: gray, N: blue, O: red, Cu: golden. Bond lengths and distances in Å.)

C	-5.94098700	-1.37867700	-0.32899400
C	-4.55622900	-1.51936500	-0.32296400
C	-3.72219900	-0.43075200	0.00263700
C	-4.32921900	0.80101700	0.32025800
C	-5.71466300	0.93505800	0.31233500
C	-6.52786600	-0.15239500	-0.01170200
H	-6.56415600	-2.22939200	-0.58205500
H	-4.10593000	-2.47376300	-0.56979400
H	-3.70268800	1.64848600	0.57285800
H	-6.16112600	1.89178100	0.56017200
H	-7.60656600	-0.04547300	-0.01678200
C	-2.30010500	-0.57312900	0.01226600
C	-1.07937000	-0.69978300	0.02390200
Cu	0.75835800	-0.89583500	0.04867300
O	0.32872200	4.18880100	0.09061300
C	1.30574800	3.59599400	-0.10885300
O	2.28454500	3.00388800	-0.30834000
O	2.64371000	-1.18250800	0.09119400
C	3.60276900	-0.38206300	-0.03074000
H	3.43488800	0.68739400	-0.17917400
N	4.87491500	-0.74935000	0.00917600
C	5.94910900	0.23119900	-0.14320000
H	6.58169400	0.22875200	0.74700100
H	6.55885900	-0.02043900	-1.01360900
H	5.52659200	1.22551600	-0.27851300
C	5.27075100	-2.14401900	0.20050700
H	5.89013000	-2.22764600	1.09612500
H	4.38170200	-2.75839600	0.31077900
H	5.84755700	-2.48209600	-0.66320900

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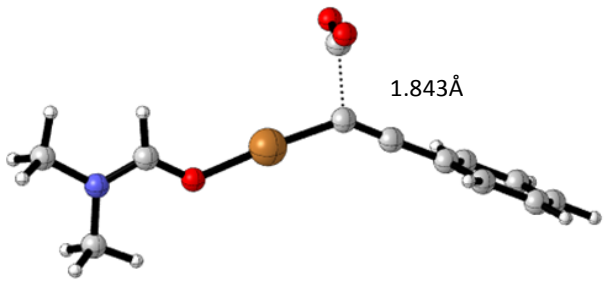

TS3

(H: white, C: gray, N: blue, O: red, Cu: golden. Bond lengths and distances in Å.)

C	5.18923600	-1.14794400	-1.18751800
C	3.90284000	-0.62351700	-1.20358700
C	3.22798000	-0.35963500	0.00706500
C	3.87669800	-0.63778500	1.22878000
C	5.16308500	-1.16245500	1.23427100
C	5.82082000	-1.41784400	0.02876600
H	5.70141300	-1.34781500	-2.12136100
H	3.40630800	-0.41307800	-2.14295000
H	3.36002700	-0.43832300	2.15964300
H	5.65492700	-1.37363700	2.17652000
H	6.82424000	-1.82767100	0.03714000
C	1.91625200	0.17555300	-0.00391900
C	0.78183700	0.67624700	-0.01323900
Cu	-1.01111600	0.06459300	-0.02757300
O	0.60437900	2.90857100	1.13158300

C	0.64509100	2.51427300	-0.01063100
O	0.62476100	2.91310700	-1.15179000
O	-2.77020200	-0.67695200	-0.04171500
C	-3.88793300	-0.10912600	0.03213700
H	-3.96903400	0.97762500	0.11068200
N	-5.04283900	-0.75546500	0.02170000
C	-6.31233600	-0.03402000	0.10791800
H	-6.91358500	-0.23697300	-0.78075800
H	-6.86302200	-0.35971400	0.99277900
H	-6.12613900	1.03662100	0.17659200
C	-5.11132900	-2.21307100	-0.07899100
H	-5.66209700	-2.49142400	-0.98014300
H	-4.10447500	-2.61816800	-0.12487000
H	-5.63128900	-2.61423900	0.79351500

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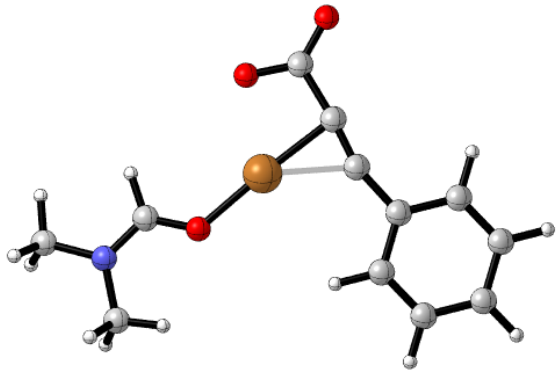

(H: white, C: gray, N: blue, O: red, Cu: golden. Bond lengths and distances in Å.)

C	3.12929300	-2.78576100	-0.00013800
C	2.19278500	-1.75678900	-0.00004700
C	2.61531800	-0.41749200	-0.00007000
C	3.99383100	-0.12971300	-0.00018300
C	4.92205200	-1.16447200	-0.00027700
C	4.49353400	-2.49338500	-0.00025400
H	2.79365300	-3.81612800	-0.00011900
H	1.13321900	-1.98182500	0.00004100
H	4.32348100	0.90207500	-0.00020000
H	5.98108200	-0.93435700	-0.00036700
H	5.22049100	-3.29725900	-0.00032700
C	1.67953500	0.67051300	0.00002300
C	1.16445500	1.79193400	0.00006800
Cu	-0.48981000	0.60919600	0.00004600
O	1.06077800	4.15283700	0.00022300
C	0.42956200	3.09287300	0.00010600
O	-0.82754900	2.89652500	0.00004500
O	-1.99896600	-0.60349500	0.00014700
C	-3.21798400	-0.30392700	0.00011000
H	-3.54651900	0.73887200	-0.00009600
N	-4.19619600	-1.19633700	0.00005200
C	-5.59829000	-0.78018100	-0.00015700
H	-6.09928900	-1.16831300	-0.88937200
H	-6.09949300	-1.16818600	0.88899700
H	-5.66169000	0.30682600	-0.00024200
C	-3.92822300	-2.63430000	0.00016600
H	-4.37082200	-3.08879800	-0.88888600
H	-2.85453900	-2.79926100	0.00030500
H	-4.37103300	-3.08869100	0.88916700

1 2 1.5 6 1.5 7 1.0

2 3 1.5 8 1.0
3 4 1.5 12 1.5
4 5 1.5 9 1.0
5 6 1.5 10 1.0
6 11 1.0
7
8
9
10
11
12 13 3.0
13 14 1.0 16 1.0
14 18 1.0
15 16 2.0
16 17 2.0
17
18 19 2.0
19 20 1.0 21 1.5
20
21 22 1.0 26 1.0
22 23 1.0 24 1.0 25 1.0
23
24
25
26 27 1.0 28 1.0 29 1.0
27
28
29