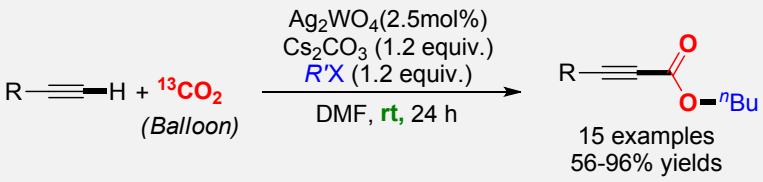
Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Silver tungstate: A single-component bifunctional catalyst for carboxylation of terminal alkynes with CO_2 in ambient conditions †

Chun-Xiang Guo, Bing Yu, Jia-Ning Xie, Liang-Nian He*



Contents Table

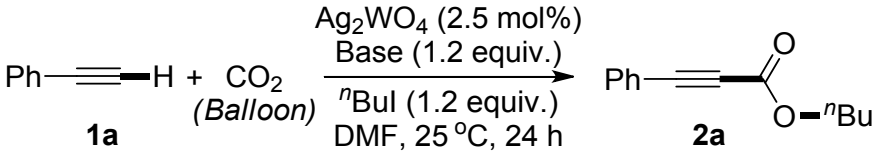
1. General Experimental Section

The starting materials were commercially available and were used without further purification. 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 Shimadzu GCMS-QP2010 SE. 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.

The general procedure for the carboxylation of terminal alkynes in DMF is like this: The terminal alkyne (1.0 mmol), Ag_2WO_4 (0.0116 g, 0.025 mmol), Cs_2CO_3 (0.3910 g, 1.2 mmol), ^{n}BuI (0.2208 g, 1.2 mmol) and DMF (3 mL) were added in a 10 mL Schlenk flask. The flask was capped and sealed. Then gas exchanging process was conducted with the "freeze-pump-thaw" method. The reaction mixture was stirred at 25 °C for 24h under an atmosphere of CO_2 (99.999%, balloon). After reaction, added water to the mixture and extracted with acetic ether for 5 times. The combined organic layer was washed with sat. NaCl aq. and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product and the residue was purified by column chromatography (silica gel, petroleum ether-EtOAc).

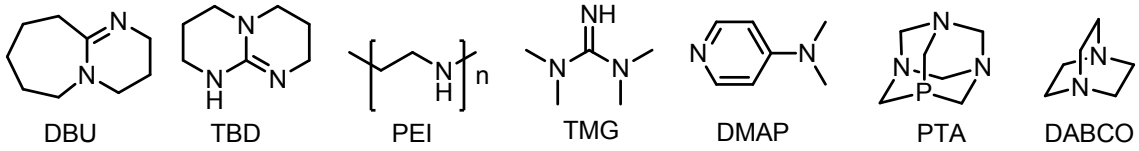
2. Optimization Studies

Table S1. Base effect on carboxylation of phenylacetylene[a]



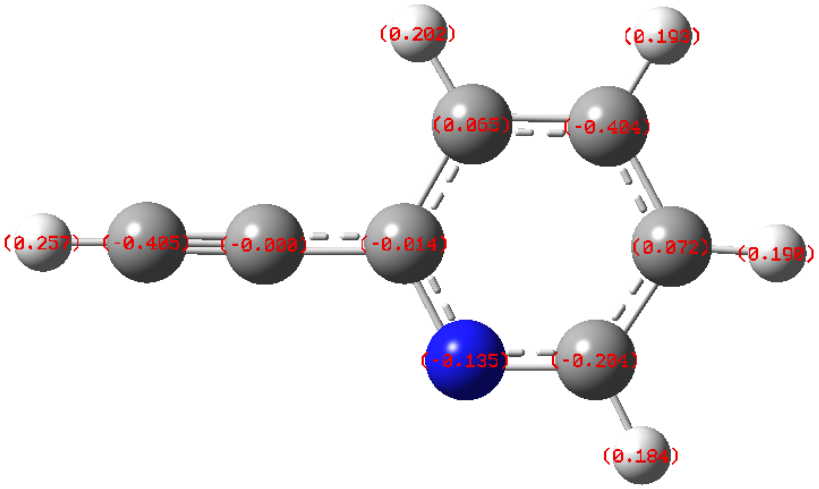
Entry	Base	Yield (%)[b]
1	0	<1
2[c]	Cs_2CO_3	76
3[d]	Cs_2CO_3	<1
4	Cs_2CO_3	<1
5	K_2CO_3	5
6	Na_2CO_3	<1
7	$NaNH_2$	<1
8	^{t}BuOLi	2
9	^{t}BuOK	<1
10	^{t}BuONa	<1
11	KOH	<1
12	NaOH	<1
13	LiOH	<1
14	CsF	<1
15	KF	<1
16	CsOAc	<1
17	KOAc	<1
18	CsF+K_2CO_3	7
19	TBD	21.2
20	DBU	<1
21	PEI_{600}	<1
22	DMAP	<1
23	TMG	<1
24	Et_3N	<1
25	PTA	<1

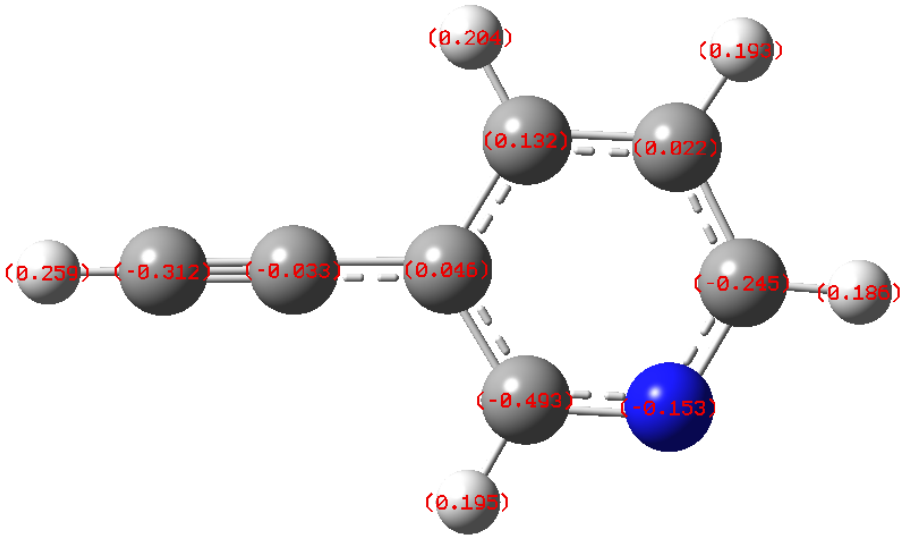
[a]Reaction conditions: Phenylacetylene (0.0511 g, 0.5 mmol), Ag_2WO_4 (0.0056 g, 0.0013 mmol), base (0.6 mmol), *n*-BuI (0.1104 g, 0.6 mmol), DMF (3 mL), CO_2 (99.999%, balloon), 25 °C, 12 h. [b]The yields were determined by GC with biphenyl as internal standard. [c]without Ag2WO4, [d]Ar balloon instead of CO_2 balloon



3. DFT Calculations

The calculations were carried out by performing DFT by use of the B3LYP functional with the 6-31+G(d) basis set as implemented in Gaussian 09 program package. The negative charge at terminal carbon of 2-ethynylpyridine is -0.405 and that of 3-ethynylpyridine was -0.312

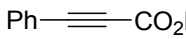




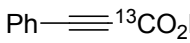
4. NMR and MS Spectral Data of the Products


2a

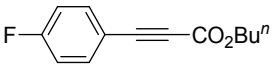
Compound **2a**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58-7.57 (d, J = 4.0 Hz, 2H), 7.45-7.34 (m, 3H), 4.23 (t, J = 6.7 Hz, 2H), 1.73-1.66 (m, 2H), 1.48-1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 154.1, 132.9, 130.5, 128.5, 119.6, 86.0, 80.7, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z(%): 129.15 (100), 201.20 (11.72) [M^+].


2ab

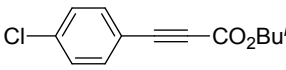
Compound **2ab**. Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48-7.45 (m, 2H), 7.04 (s, 1H), 4.23 (t, J = 6.6 Hz, 2H), 1.71-1.67 (m, 2H), 1.46-1.40 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 154.0, 136.4, 131.0, 127.5, 119.4, 84.9, 80.0, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z(%): 129.15 (100), 173.97 (5) [M^+].


2ac

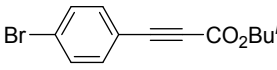
Compound **2ac.** Colorless oil; ^{13}C NMR (100 MHz, $CDCl_3$, NS=1) δ(ppm): 154.2. HRMS (ESI): $C_{12}{}^{13}CH_{15}O_2$ for $[M + H]^+$ calculated 204.1100, found 204.1102.


2b

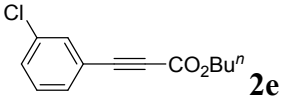
Compound **2b**.Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):: 7.57-7.54 (m, 2H), 7.06-7.02 (m, 2H), 4.21 (t, J= 6.6 Hz, 2H), 1.70-1.64 (m, 2H), 1.45-1.36 (m, 2H), 0.93 (t, J = 7.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 165.0, 162.6, 154.0, 135.2, 116.1, 115.9, 84.9, 80.6, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z(%):147.20 (100), 220.15 (6) [M^+].


2c

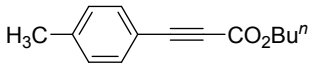
Compound **2c**.Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 (d, J =8.4Hz,2H), 7.34 (d, J = 8.5 Hz, 2H), 4.22 (t, J=6.7 Hz, 2H), 1.71-1.65 (m, 2H), 1.46-1.37 (m, 2H), 0.94 (t, J=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 153.9, 136.9, 134.1, 129.0, 118.1, 84.6, 81.5, 66.0, 30.4, 19.0, 13.6; EI-MS, m/z(%): 163.05 (100), 236.10 (10) [M^+].


2d

Compound **2d**. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J= 8.5 Hz, 2H), 7.42 (d, J= 8.5 Hz, 2H), 4.22 (t, J = 6.7 Hz, 2H), 1.69-1.66 (m, 2H), 1.44-1.39 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 153.9, 134.2, 131.9, 125.3, 118.6, 84.6, 81.6, 66.0, 30.4, 19.0, 13.6; EI-MS, m/z(%):180.10 (100), 280.20 (14) [M^+].

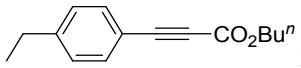

2e

Compound **2e**.Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (s, 1H), 7.47-7.41 (m, 2H), 7.33-7.29 (m, 1H), 4.24 (t, J = 6.6 Hz, 2H), 1.73-1.63 (m, 2H), 1.48-1.37 (m, 2H), 0.96 (t, J= 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 153.8, 134.5, 132.6, 131.0, 130.9, 129.8, 121.4, 84.1, 81.4, 66.1, 30.4, 19.0, 13.6; EI-MS, m/z(%):163.10 (100), 235.10 (10) [M^+].



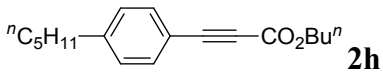
2f

Compound **2f**. Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (d, J = 7.5 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 4.23 (t, J = 6.6 Hz, 2H), 2.37 (s, 3H), 1.73-1.66 (m, 2H), 1.48-1.39 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 154.3, 141.2, 132.9, 129.3, 116.5, 86.5, 80.3, 65.8, 30.4, 21.6, 19.0, 13.6; EI-MS, m/z(%): 116.15 (100), 216.20 (13) [M^+].



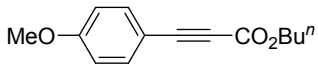
2g

Compound **2g**. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J = 7.5 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 4.22 (t, J = 6.7 Hz, 2H), 2.69-2.63 (m, 2H), 1.71-1.67 (m, 2H), 1.46-1.40 (m, 2H), 1.22 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 154.3, 147.3, 133.0, 128.1, 116.7, 86.5, 80.3, 65.8, 30.4, 28.9, 19.0, 15.0, 13.6; EI-MS, m/z (%): 130.20 (100), 230.15 (15) [M^+].



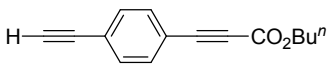
2h

Compound **2h**. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 (d, J= 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 4.23 (t, J = 6.7 Hz, 2H), 2.63-2.59 (m, 2H), 1.73-1.58 (m, 4H), 1.46-1.31 (m, 6H), 0.97-0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 154.3, 146.2, 133.0, 128.6, 116.7, 86.6, 80.3, 65.8, 36.0, 31.4, 30.7, 30.5, 22.4, 19.0, 14.0, 13.6; EI-MS, m/z (%): 172.20 (100), 272.25 (15) [M^+].



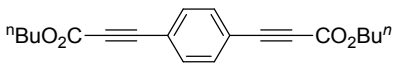
2i

Compound **2i.** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.22 (t, J = 6.7 Hz, 2H), 3.82 (s, 3H), 1.69 (dt, J = 14.7, 6.8 Hz, 2H), 1.44 (dq, J = 14.7, 7.4 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 161.5, 154.4, 134.9, 114.2, 111.4, 86.8, 80.1, 65.7, 55.5, 30.5, 19.0, 13.6; EI-MS, m/z(%): 132.20 (100), 232.20 (18) [M^+].



2ja

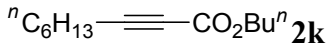
Compound **2ja.** Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 4.23 (t, J = 6.7 Hz, 2H), 3.23 (s, 1H), 1.73-1.62 (m, 2H), 1.47-1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 154.0, 132.7, 132.1, 124.4, 120.0, 85.0, 82.6, 82.1, 80.2, 66.0, 30.4, 19.0 13.6; EI-MS, m/z (%): 126.15 (100), 326.25 (16) [M^+].



2jb

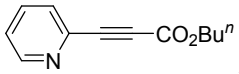
Compound **2jb.** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (s, 4H), 4.24 (t, J = 6.7 Hz, 2H), 1.73-66 (m, 4H), 1.47-1.38 (m, 8H), 0.95 (t, J = 7.4 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 153.8, 132.8, 121.79, 84.4, 82.9, 30.4, 19.0, 13.6; EI-MS, m/z (%): 126.10 (100), 226.10 (16) [M^+].



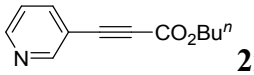
2k

Compound **2k**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.13 (t, J = 6.7 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.65-1.52 (m, 4H), 1.42-1.25 (m, 8H), 0.94-0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.0, 89.4, 73.1, 65.5, 31.1, 30.4, 28.5, 27.4, 22.4, 19.0, 18.6, 13.9, 13.6; EI-MS, m/z (%): 155.15 (100), 195.20 (1) [M^+].



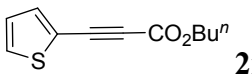
2l

Compound **2l**. Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (t, J = 6.7 Hz, 1H), 7.72-7.68 (m, 1H), 7.57 (d, J =4.0 Hz, 1H), 7.35-7.31 (m, 1H), 4.23 (t, J =6.7, 2H), 1.70-1.63 (m, 2H), 1.44-1.36 (m, 5H), 0.93 (t, J =7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.5, 1510.5, 140.6, 128.5, 124.5, 83.7, 79.2, 66.1, 30.3, 18.9, 13.5; EI-MS, m/z (%): 130.10 (100), 202.10 (2) [M^+].



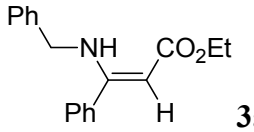
2m

Compound **2m.** Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.87 (s, 1H), 8.62 (d, J =4.0, 1H), 7.84-7.82 (m, 1H), 7.31-7.26 (m, 1H), 4.24 (t, J = 6.7 Hz, 2H) 1.68-1.64 (m, 2H), 1.43-1.37 (m, 2H), 0.92 (t, J =7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 154.0, 89.4, 73.1, 65.5, 31.1, 30.4, 28.5, 27.4, 22.4, 19.0, 18.6, 13.9, 13.6; EI-MS, m/z (%): 130.15 (100), 202.15 (10) [M^+].



2n

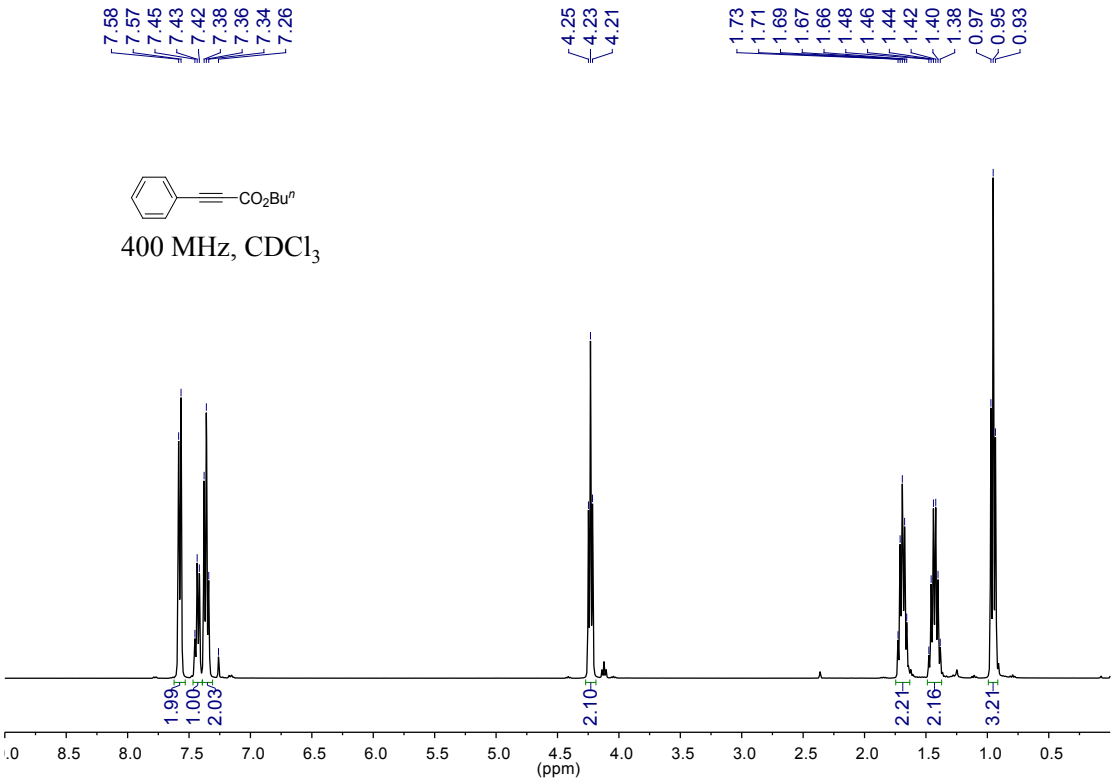
Compound **2n**. Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47-7.44 (m, 2H), 7.04-7.02 (m, 1H), 4.22 (t, J = 6.6 Hz, 2H), 1.72-1.65 (m, 2H), 1.47-1.36 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.0, 136.4, 131.0, 127.4, 119.4, 84.9, 80.0, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z(%): 108.10 (100), 208.15 (15) [M^+].

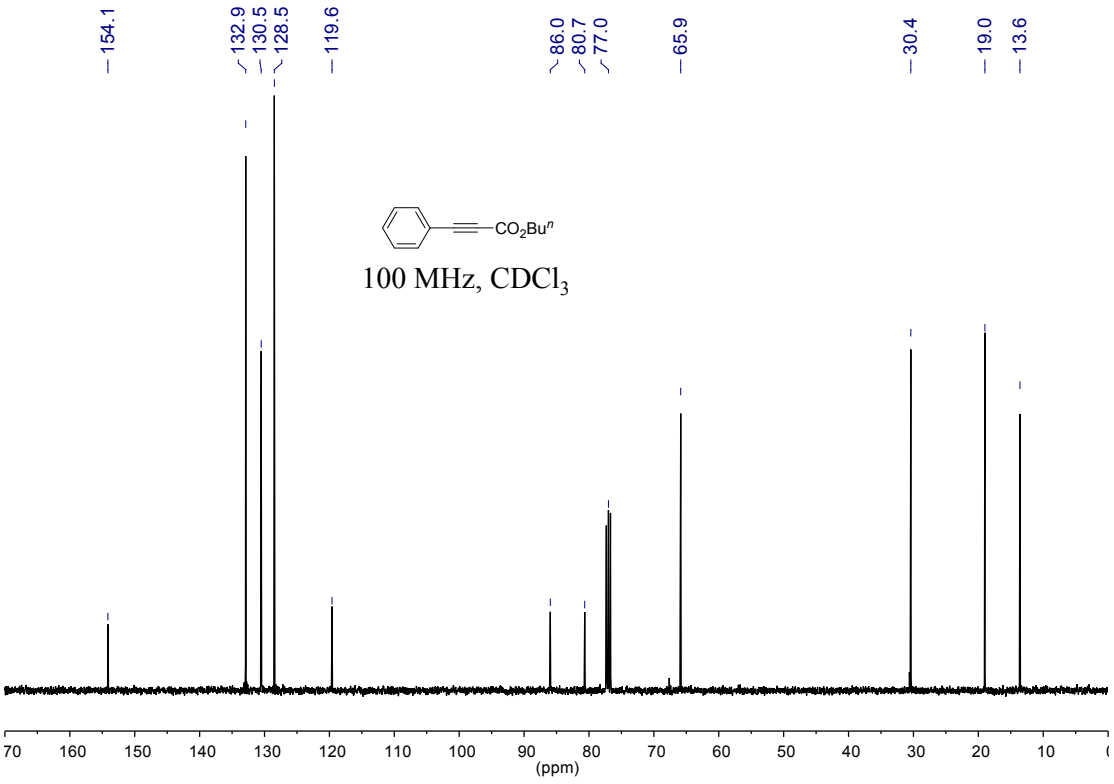


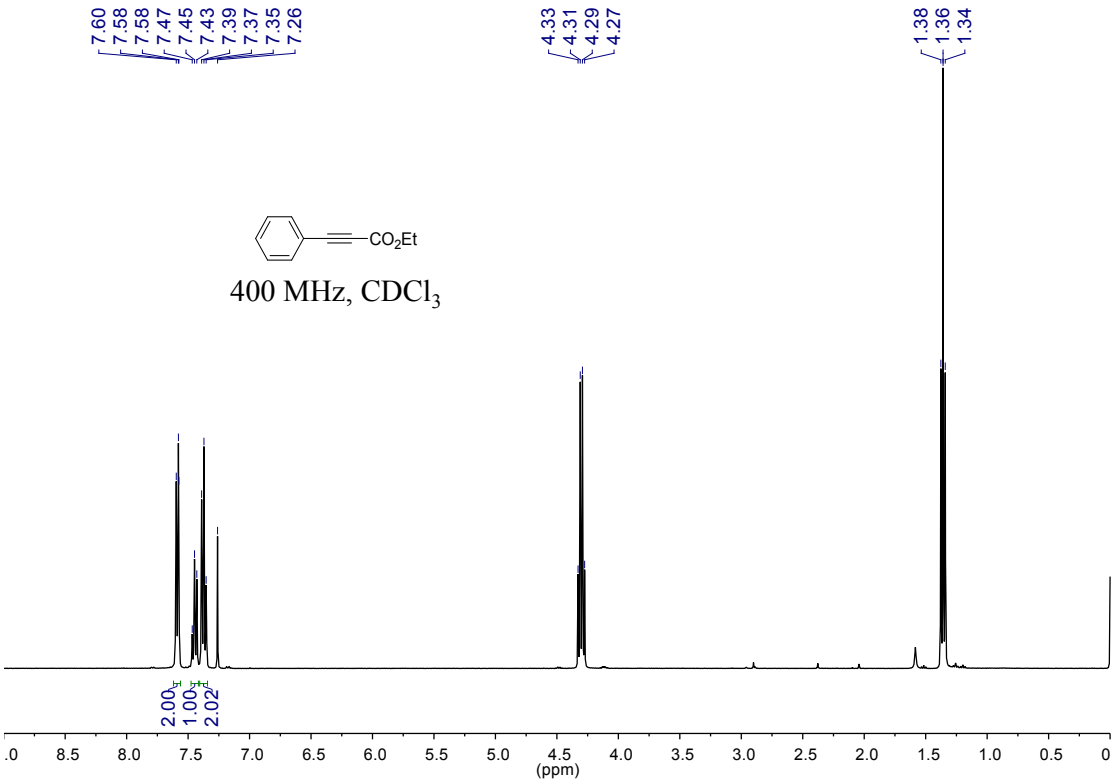
3a

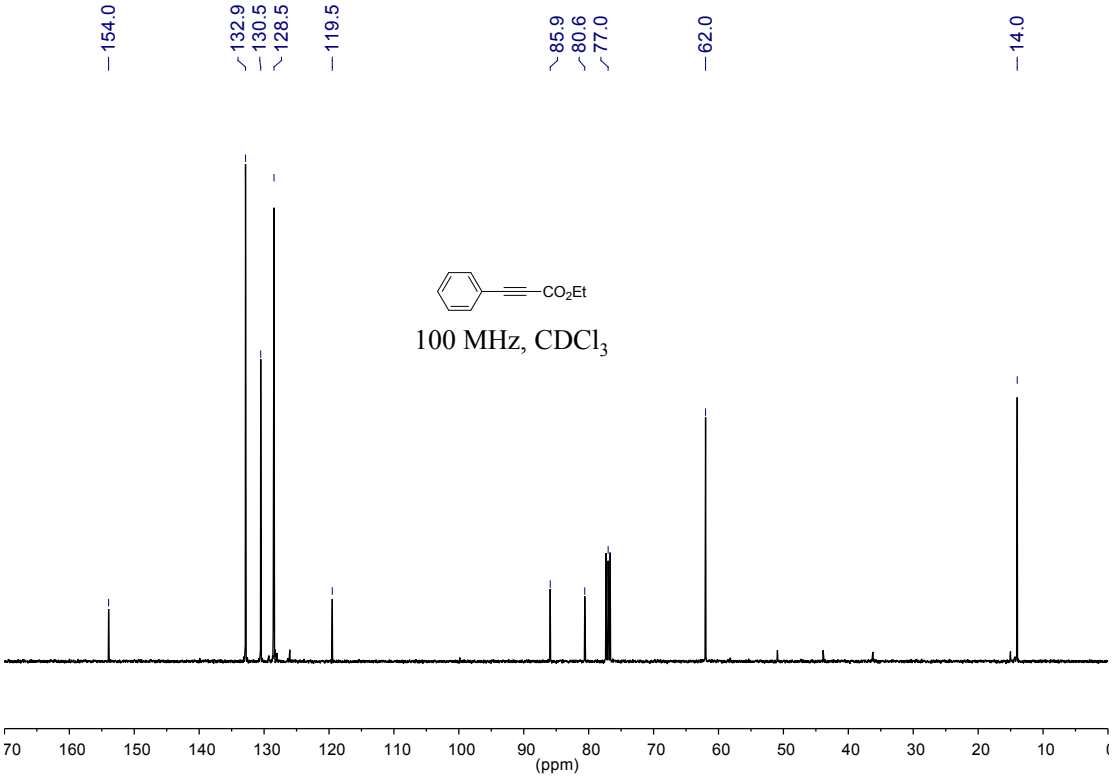
Compound **3a**. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.92 (s, 1H), 7.28-7.16 (m, 10H), 4.68 (s, 1H), 4.27 (d, J = 6.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 1.27 (t, J =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 170.1, 164.7, 139.1, 135.9, 129.2 128.6, 128.3, 137.8, 127.1, 126.7, 86.2, 58.7, 48.3, 14.5; HRMS (ESI): $C_{18}H_{20}NO_2$ for $[M + H]^+$ calculated 282.1494, found 282.1495.

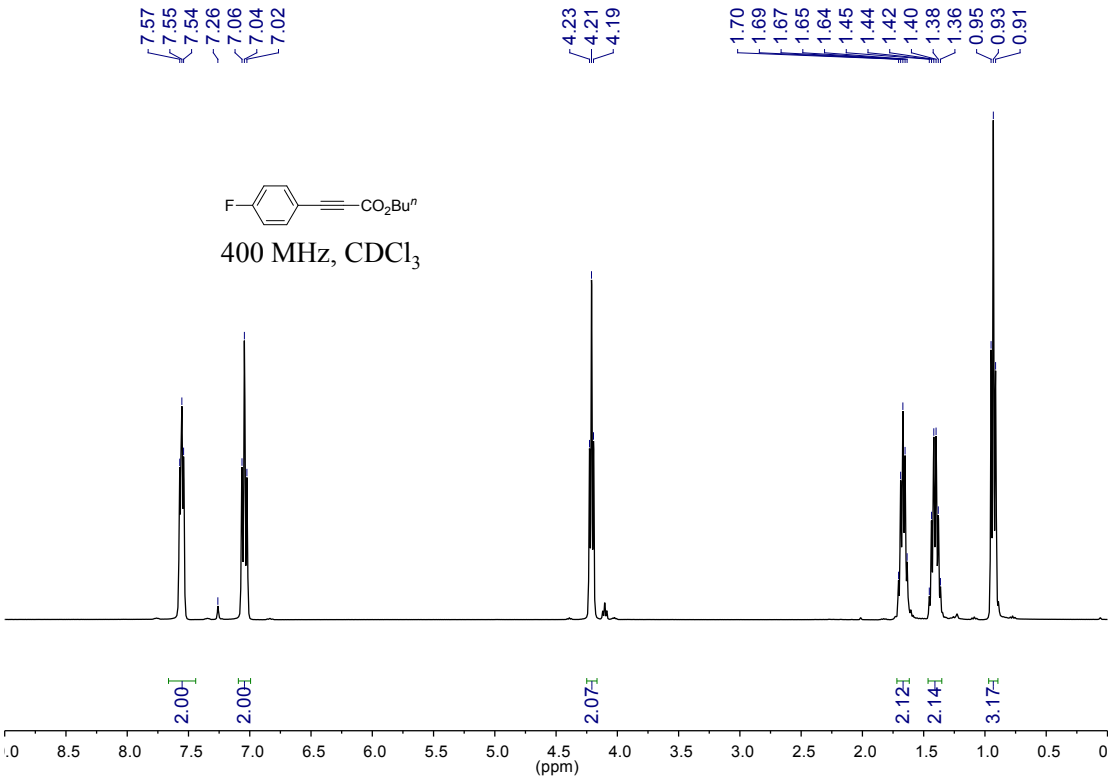
5. NMR spectrum of the Products

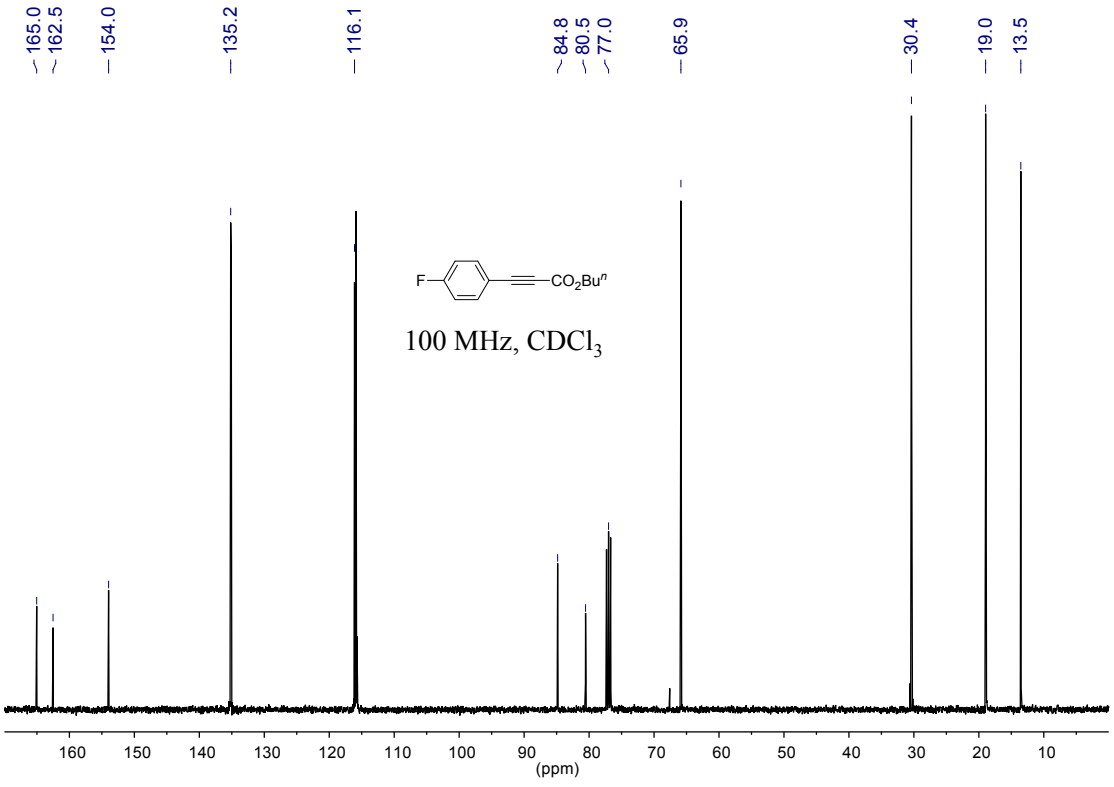


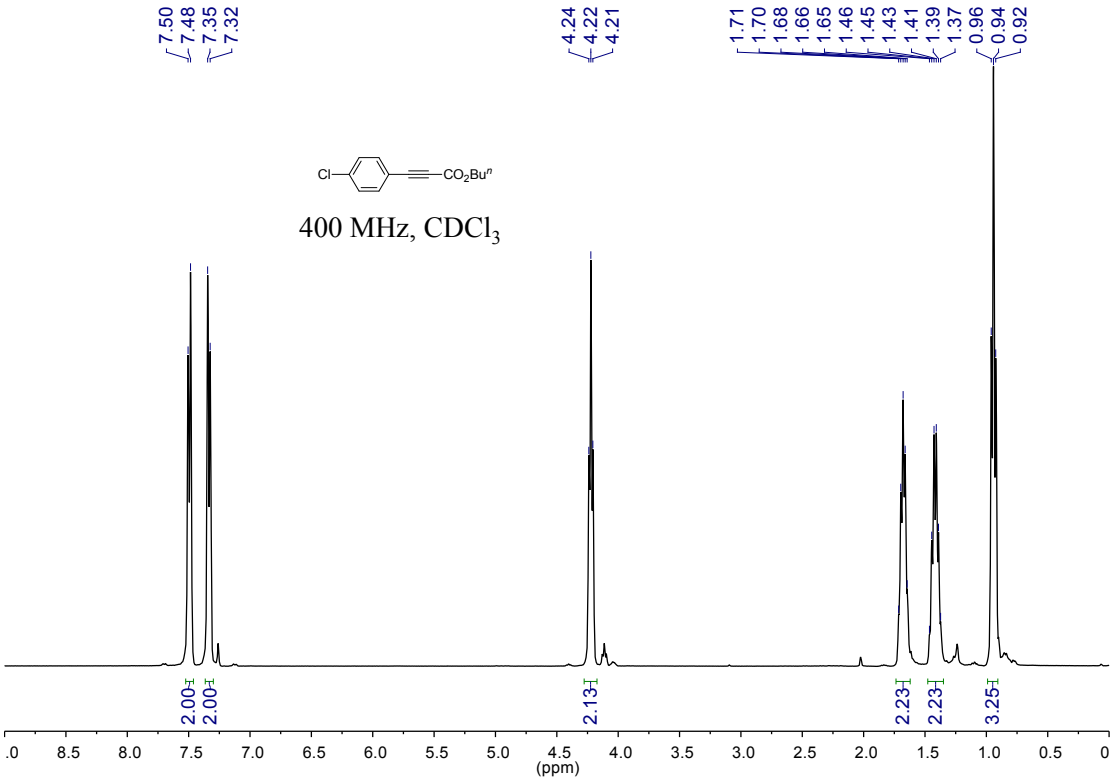


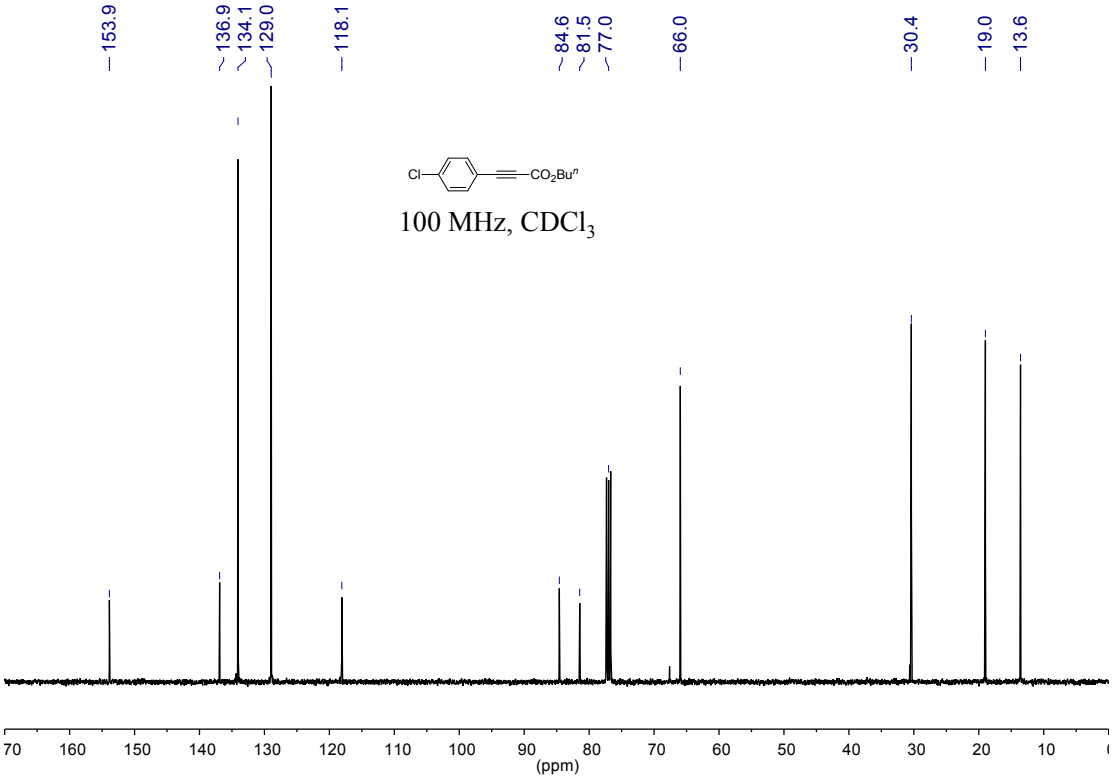

7.60
7.58
7.58
7.47
7.45
7.43
7.39
7.37
7.35
7.26
4.33
4.31
4.29
4.27
1.38
1.36
1.34
CO2Et
400 MHz, CDCl3
2.00
1.00
2.02
(ppm)

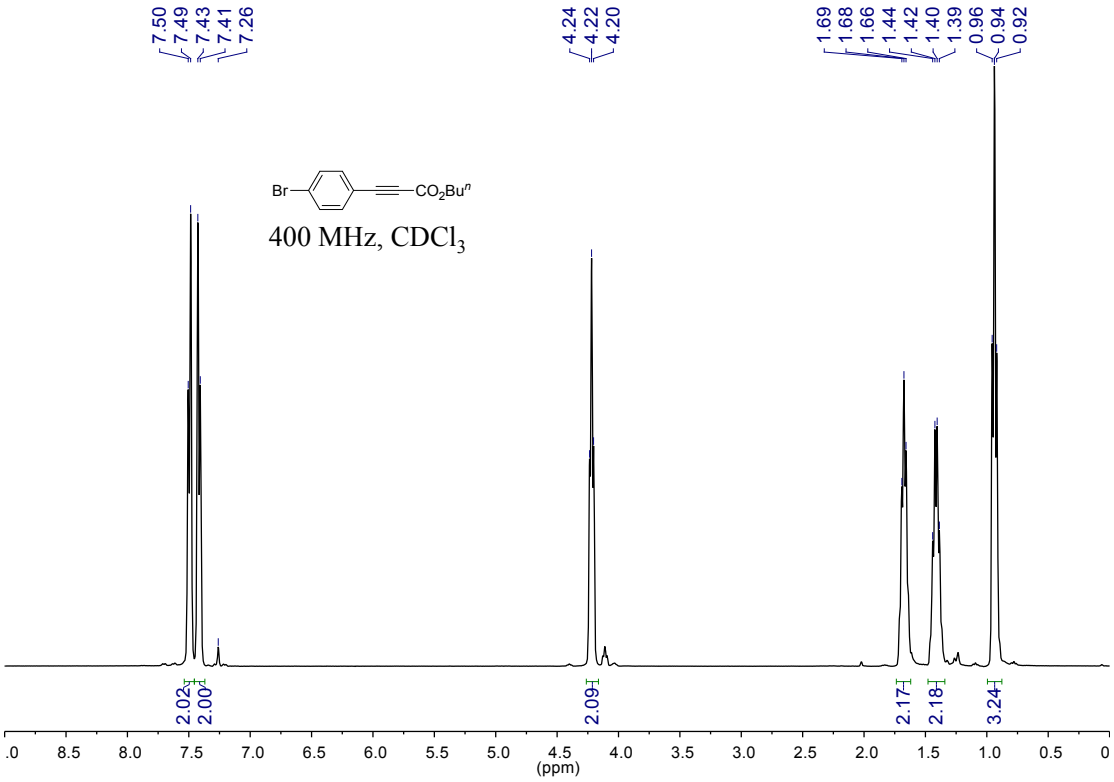

154.0
132.9
130.5
128.5
119.5
85.9
80.6
77.0
62.0
14.0
CO2Et
100 MHz, CDCl3
(ppm)

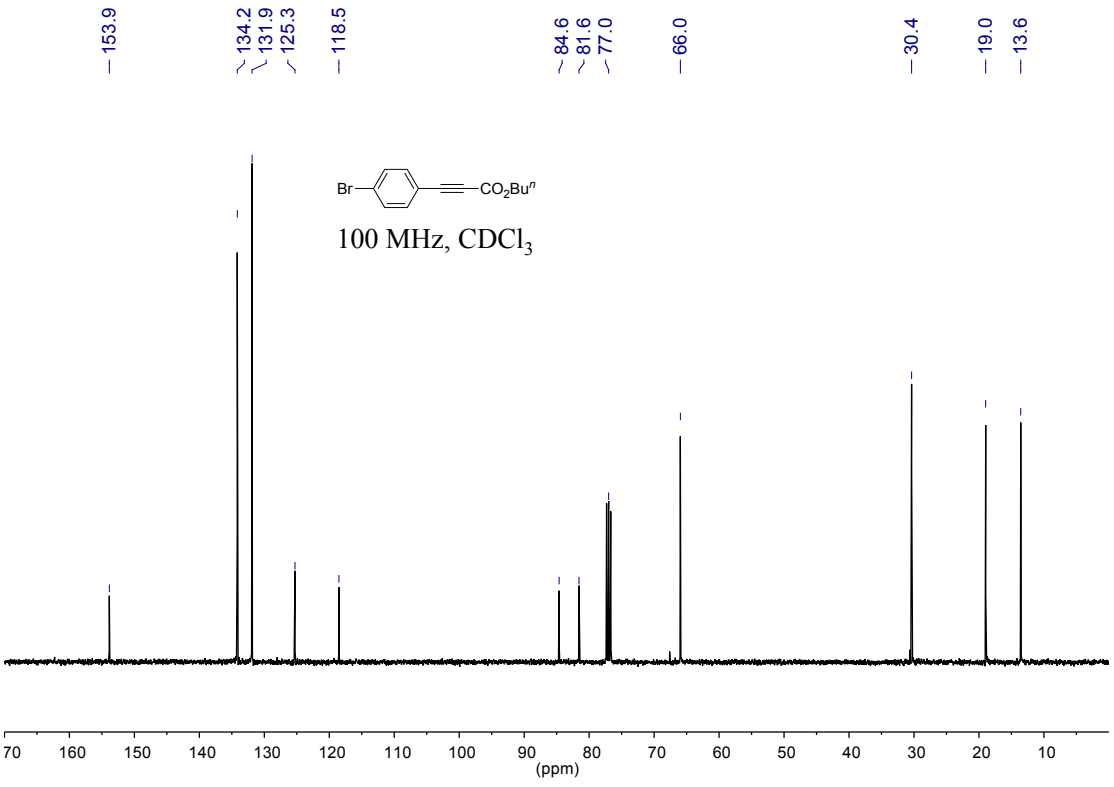

7.57
7.55
7.54
7.26
7.06
7.04
7.02
4.23
4.21
4.19
1.70
1.69
1.67
1.65
1.64
1.45
1.44
1.42
1.40
1.38
1.36
0.95
0.93
0.91
F
CO2Bun
400 MHz, CDCl3
2.00
2.00
2.07
2.12
2.14
3.17
(ppm)

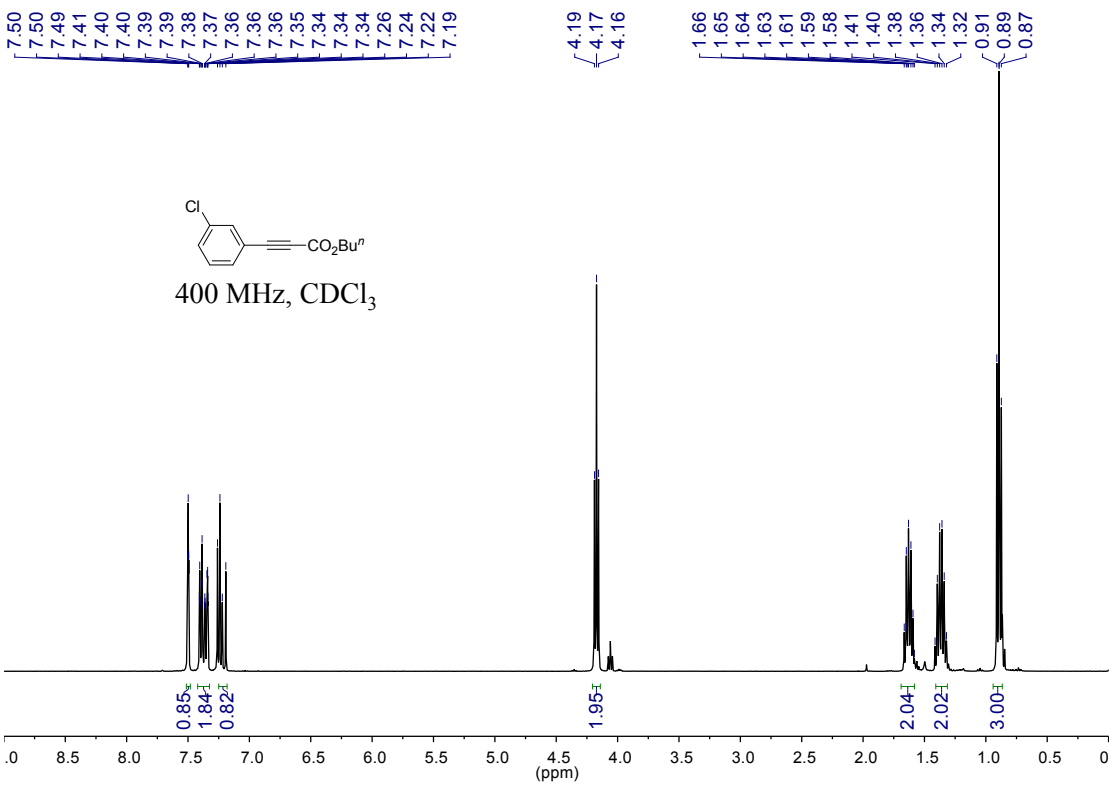

165.0
162.5
154.0
135.2
116.1
84.8
80.5
77.0
65.9
30.4
19.0
13.5
F
CO2Bun
100 MHz, CDCl3
(ppm)

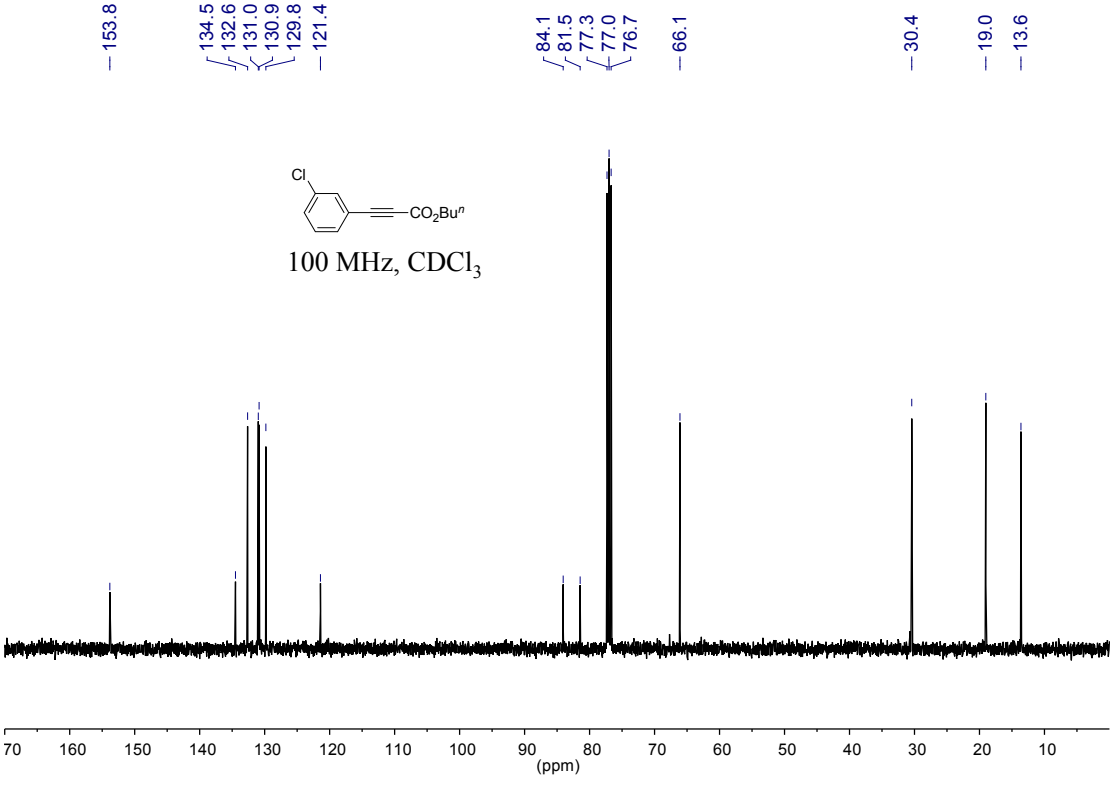

7.50
7.48
7.35
7.32
4.24
4.22
4.21
1.71
1.70
1.68
1.66
1.65
1.46
1.45
1.43
1.41
1.39
1.37
0.96
0.94
0.92
Cl
CO2Bun
400 MHz, CDCl3
2.00
2.00
2.13
2.23
2.23
3.25
(ppm)

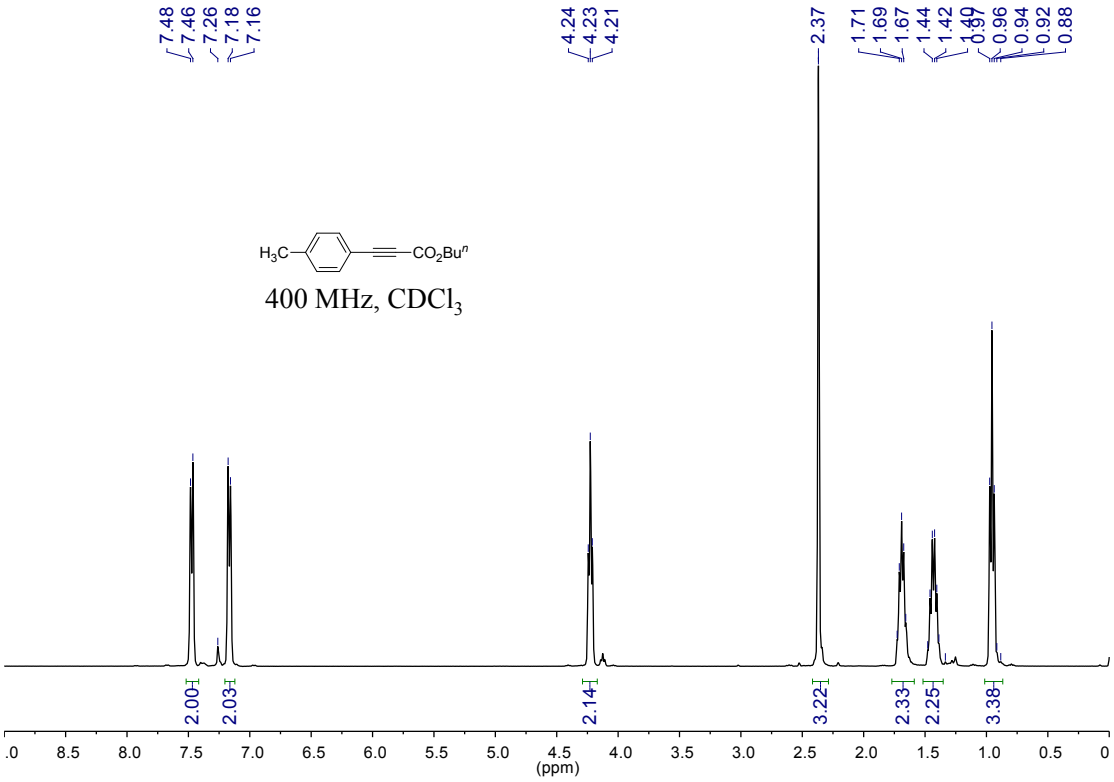

153.9
136.9
134.1
129.0
118.1
84.6
81.5
77.0
66.0
30.4
19.0
13.6
Cl
CO2Bun
100 MHz, CDCl3
(ppm)

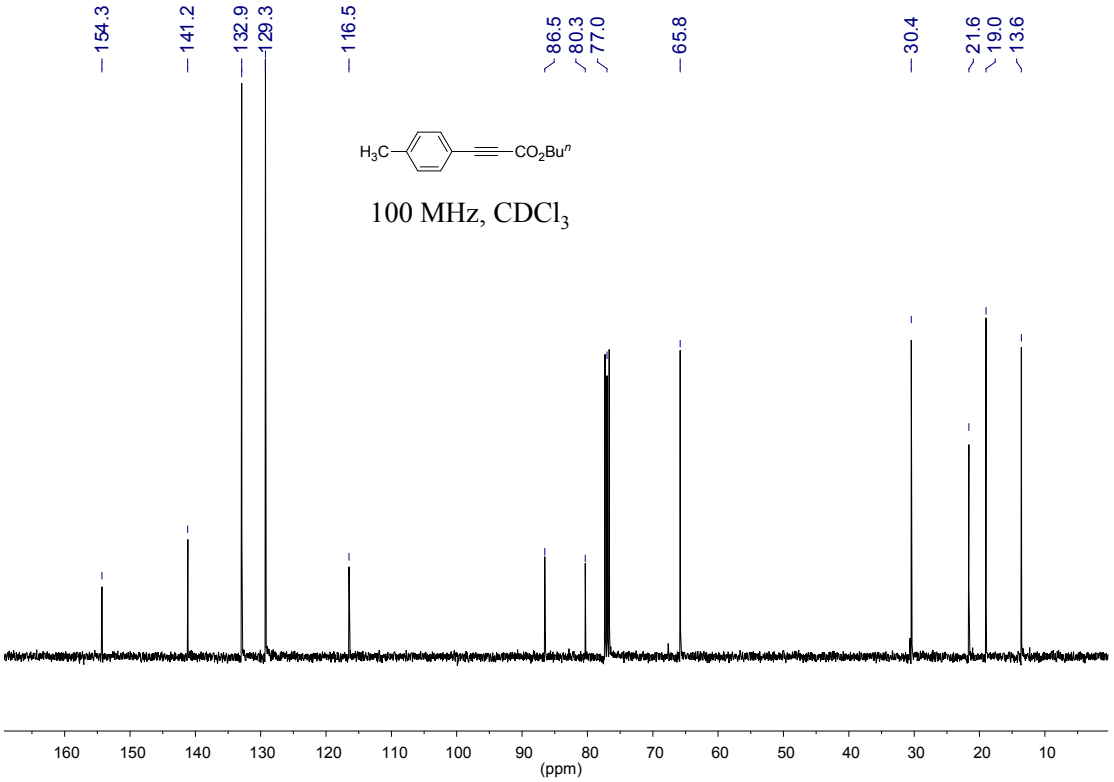

7.50
7.49
7.43
7.41
7.26
4.24
4.22
4.20
1.69
1.68
1.66
1.44
1.42
1.40
1.39
0.96
0.94
0.92
Br
CO2Bun
400 MHz, CDCl3
2.02
2.00
2.09
2.17
2.18
3.24
(ppm)

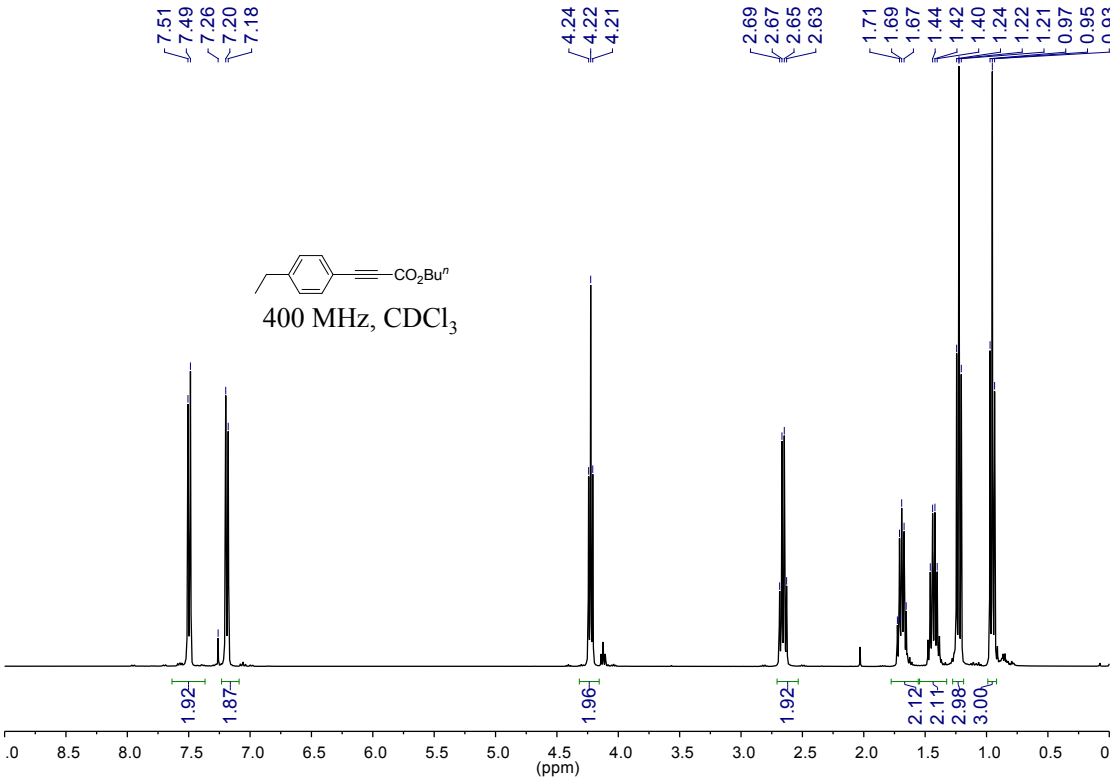

153.9
134.2
131.9
125.3
118.5
84.6
81.6
77.0
66.0
30.4
19.0
13.6
Br
CO2Bun
100 MHz, CDCl3
(ppm)

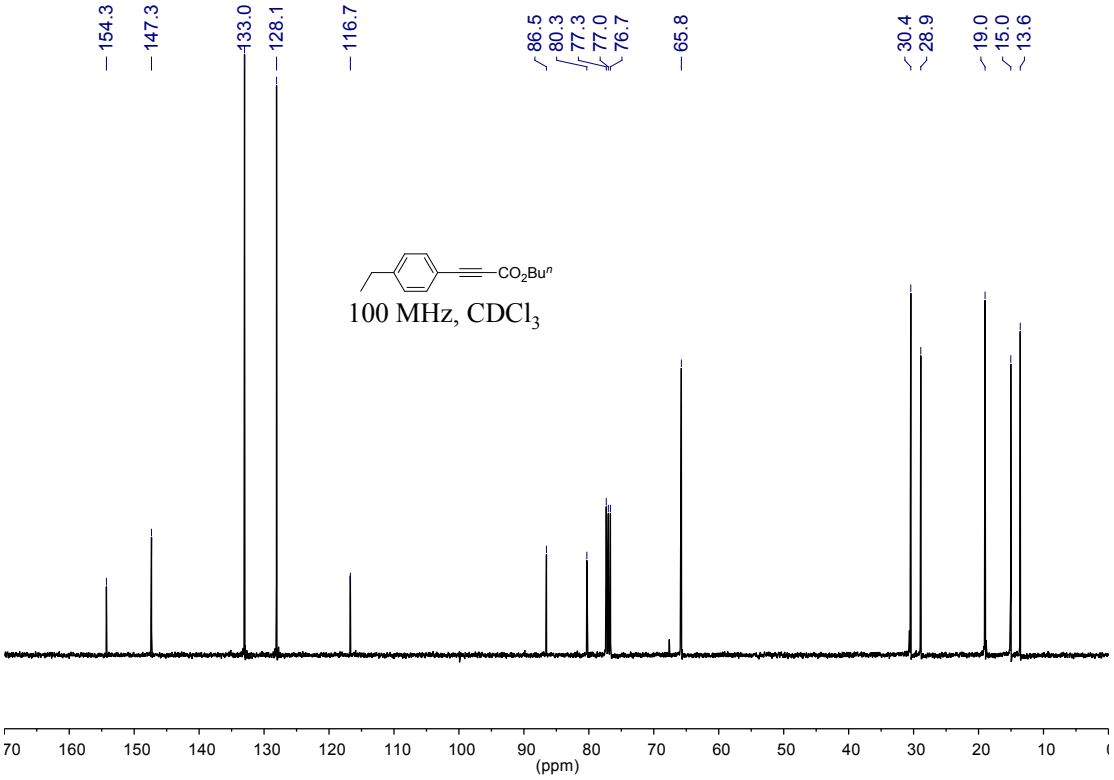

7.50
7.50
7.49
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.34
7.26
7.24
7.22
7.19
4.19
4.17
4.16
1.66
1.65
1.64
1.63
1.61
1.59
1.58
1.41
1.40
1.38
1.36
1.34
1.32
0.91
0.89
0.87
Cl
CO2Bun
400 MHz, CDCl3
0.85
1.84
0.82
1.95
2.04
2.02
3.00
(ppm)

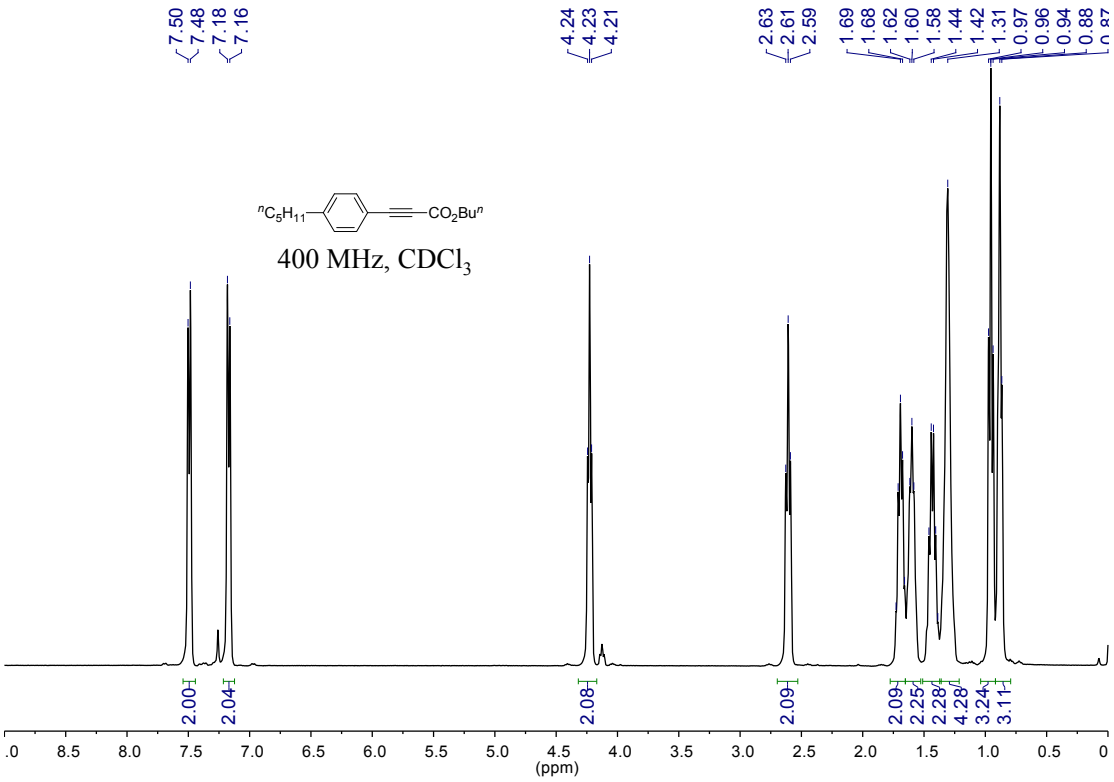

153.8
134.5
132.6
131.0
130.9
129.8
121.4
84.1
81.5
77.3
77.0
76.7
66.1
30.4
19.0
13.6
Cl
CO2Bun
100 MHz, CDCl3
(ppm)

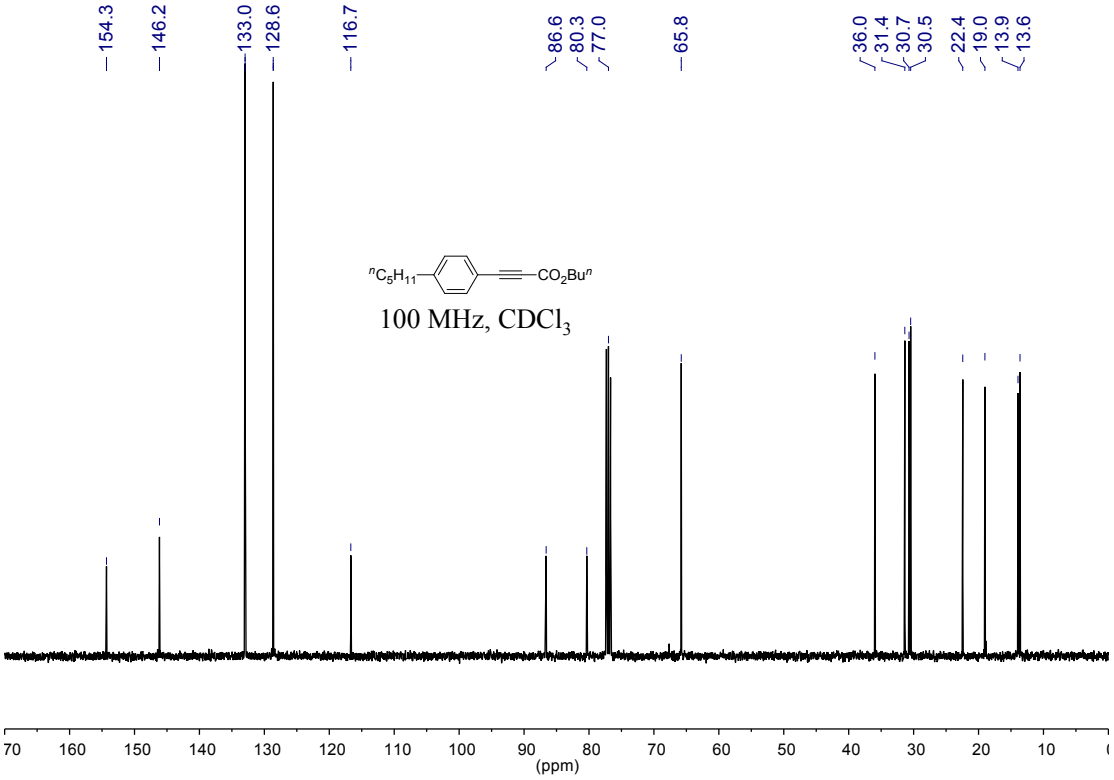

7.48
7.46
7.26
7.18
7.16
4.24
4.23
4.21
2.37
1.71
1.69
1.67
1.44
1.42
0.97
0.96
0.94
0.92
0.88
H3C
CO2Bun
400 MHz, CDCl3
2.00
2.03
2.14
3.22
2.33
2.25
3.38
(ppm)

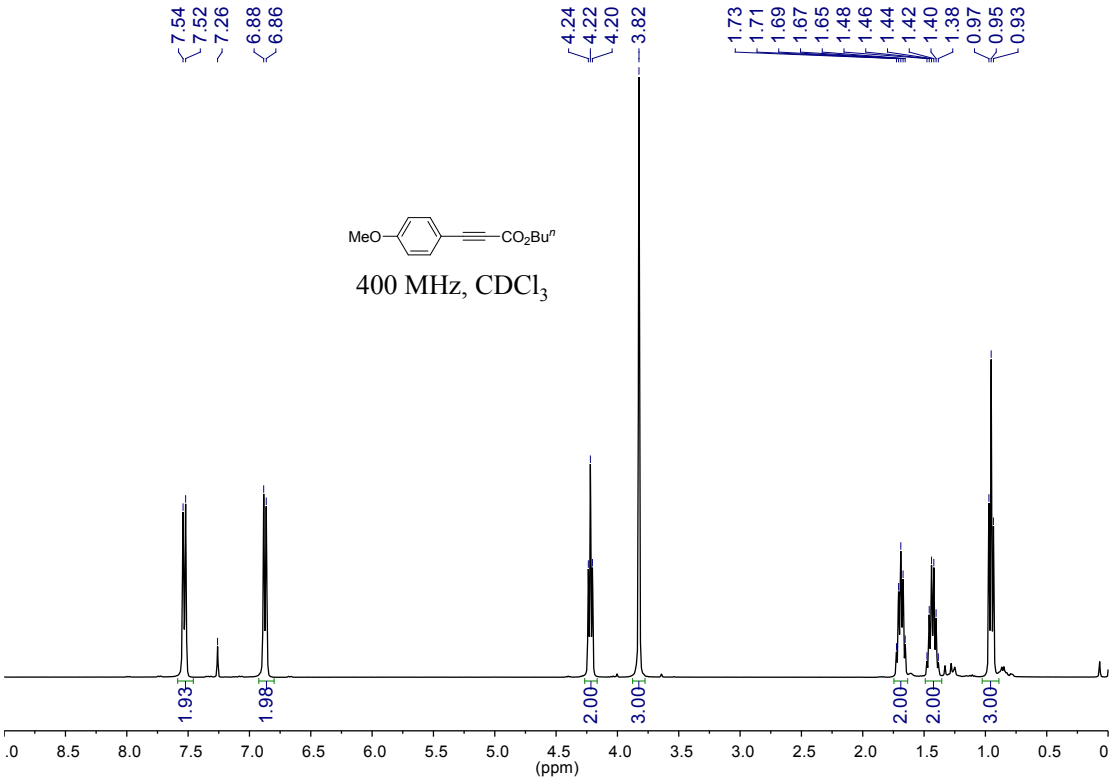

154.3
141.2
132.9
129.3
116.5
86.5
80.3
77.0
65.8
30.4
21.6
19.0
13.6
H3C
CO2Bun
100 MHz, CDCl3
(ppm)

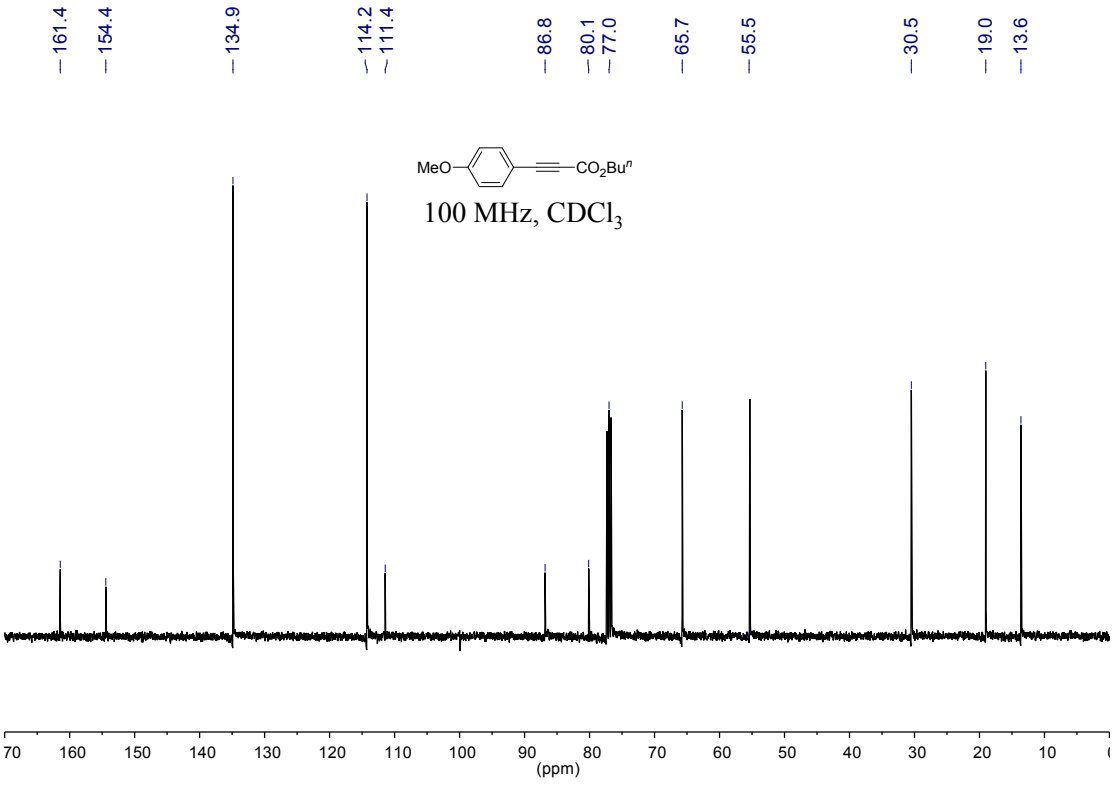

7.51
7.49
7.26
7.20
7.18
4.24
4.22
4.21
2.69
2.67
2.65
2.63
1.71
1.69
1.67
1.44
1.42
1.40
1.24
1.22
1.21
0.97
0.95
CO2Bun
400 MHz, CDCl3
1.92
1.87
1.96
1.92
2.12
2.11
2.98
3.00
(ppm)

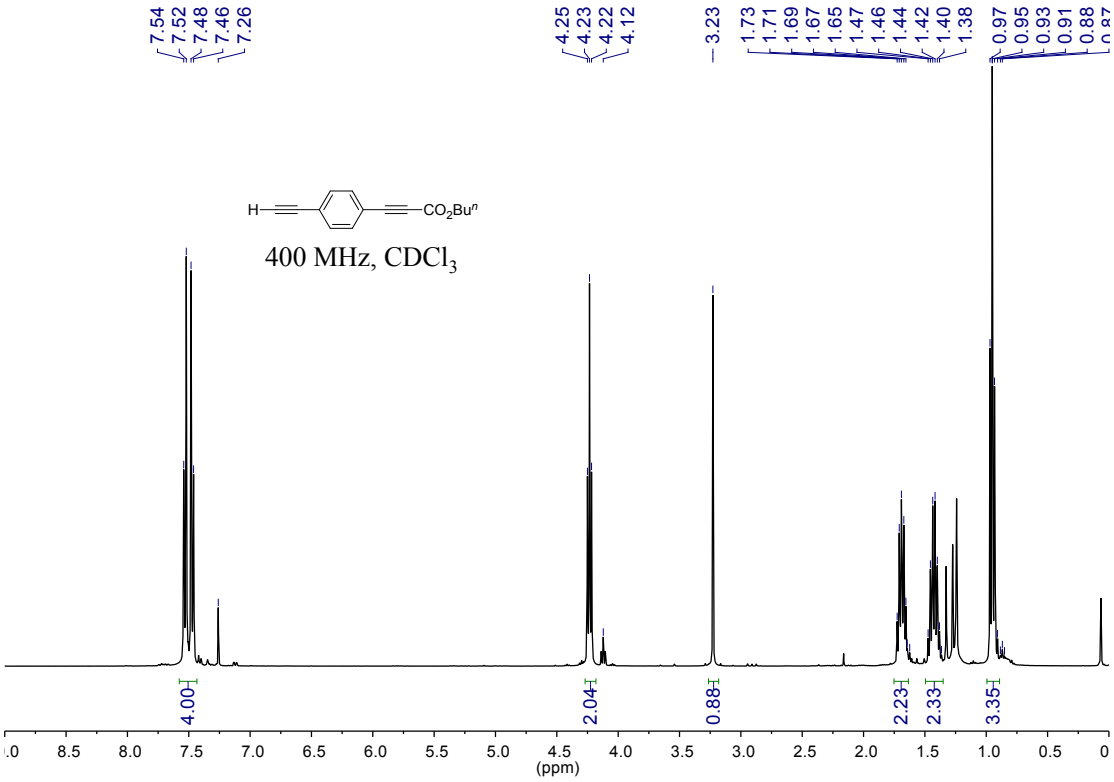

154.3
147.3
133.0
128.1
116.7
86.5
80.3
77.3
77.0
76.7
65.8
30.4
28.9
19.0
15.0
13.6
CO2Bun
100 MHz, CDCl3
(ppm)

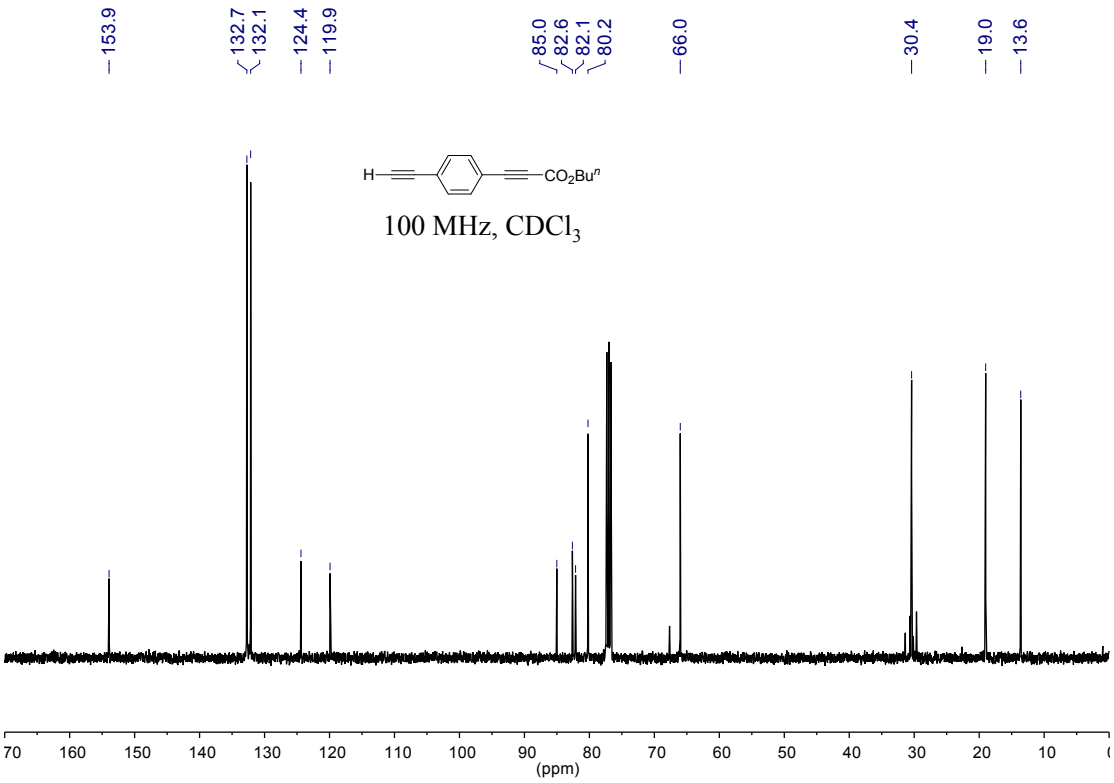

7.50
7.48
7.18
7.16
4.24
4.23
4.21
2.63
2.61
2.59
1.69
1.68
1.62
1.60
1.58
1.44
1.42
1.31
0.97
0.96
0.94
0.88
$^{n}C_5H_{11}$—≡—CO_2Bu^{n}
400 MHz, $CDCl_3$
2.00
2.04
2.08
2.09
2.09
2.25
2.28
4.28
3.24
3.11
(ppm)

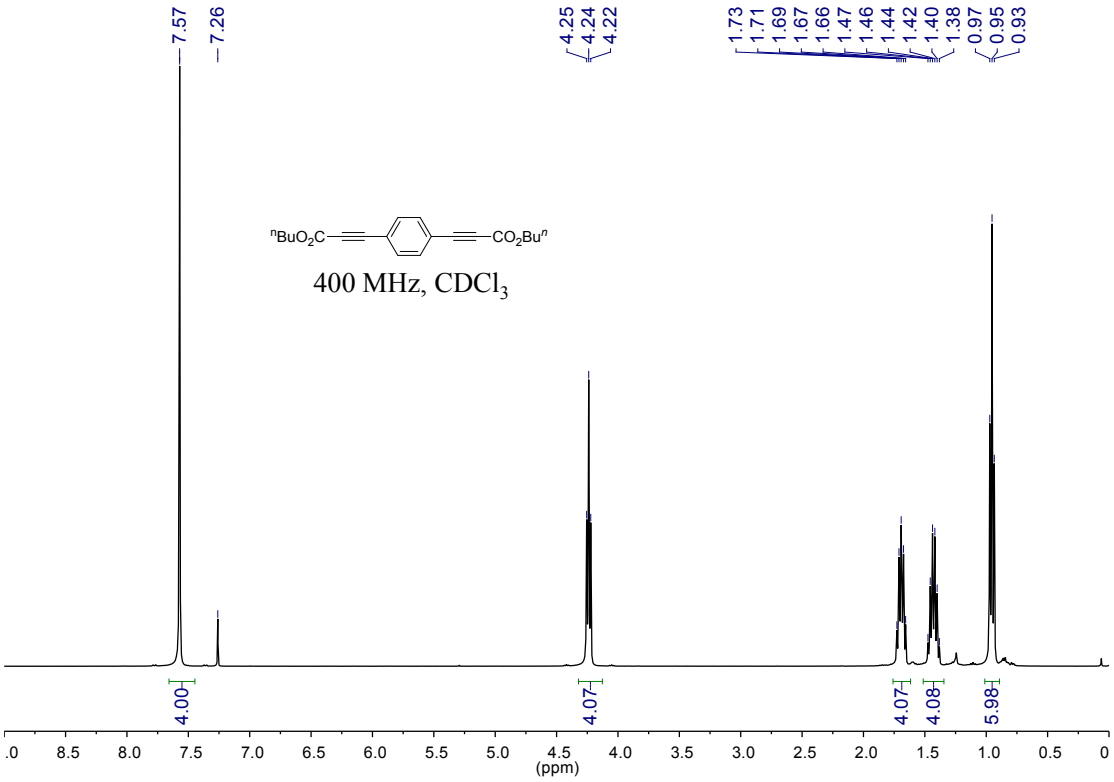

154.3
146.2
133.0
128.6
116.7
86.6
80.3
77.0
65.8
36.0
31.4
30.7
30.5
22.4
19.0
13.9
13.6
$^{n}C_5H_{11}$—≡—CO_2Bu^{n}
100 MHz, $CDCl_3$
(ppm)

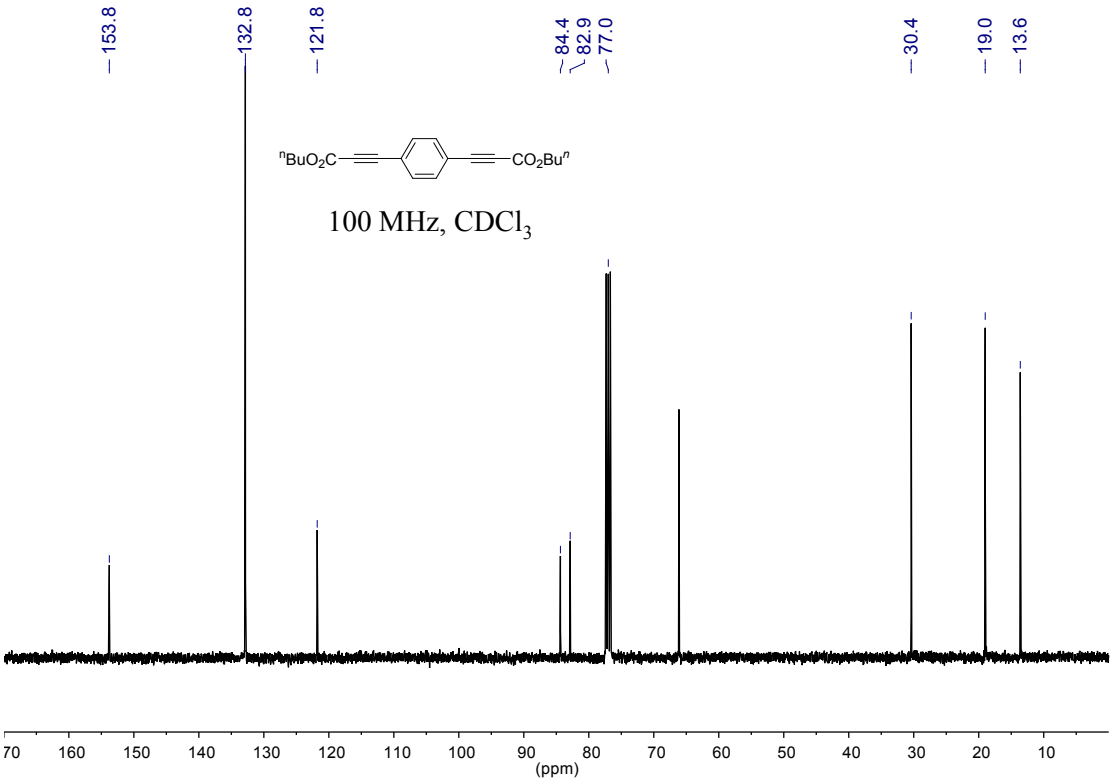

7.54
7.52
7.26
6.88
6.86
4.24
4.22
4.20
3.82
1.73
1.71
1.69
1.67
1.65
1.48
1.46
1.44
1.42
1.40
1.38
0.97
0.95
0.93
MeO
CO2Bun
400 MHz, CDCl3
1.93
1.98
2.00
3.00
2.00
2.00
3.00
(ppm)

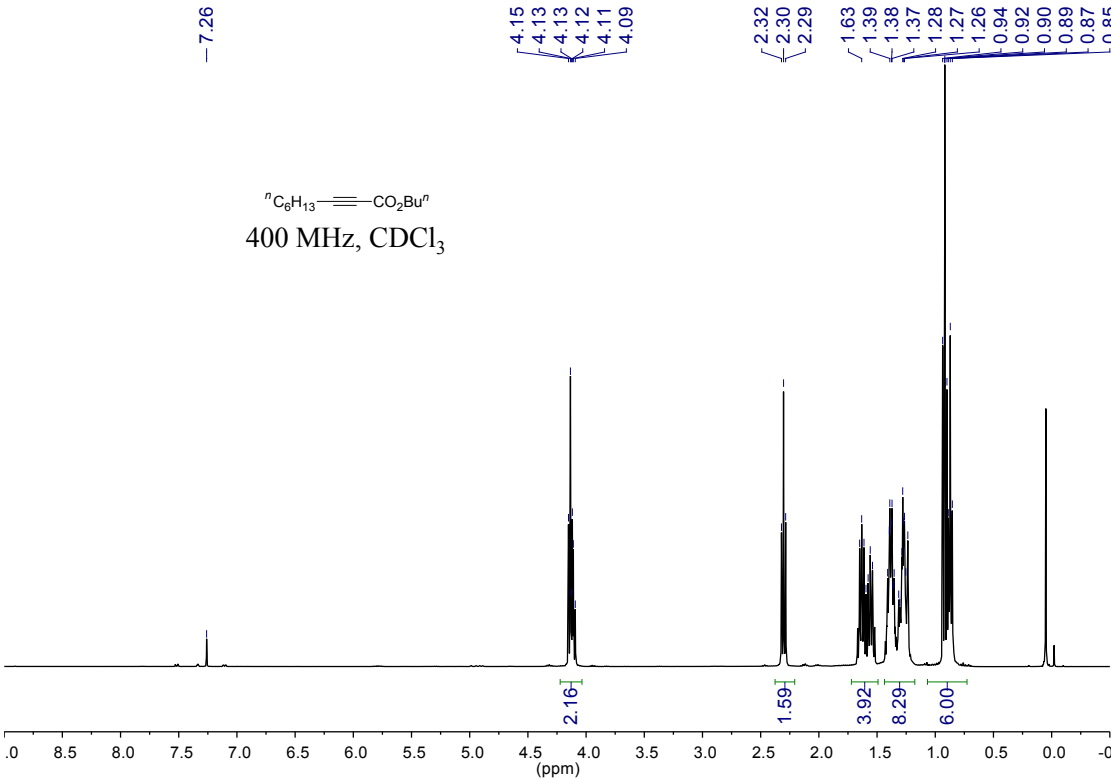

161.4
154.4
134.9
114.2
111.4
86.8
80.1
77.0
65.7
55.5
30.5
19.0
13.6
MeO
CO2Bun
100 MHz, CDCl3
(ppm)

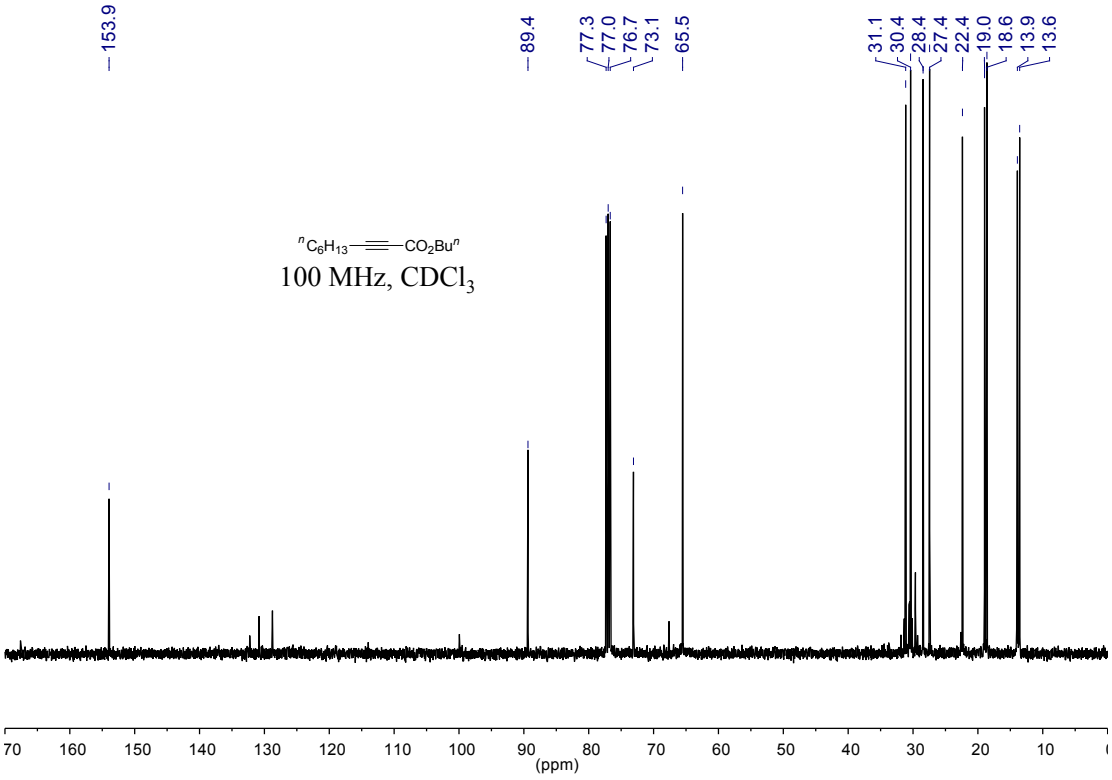

7.54
7.52
7.48
7.46
7.26
4.25
4.23
4.22
4.12
3.23
1.73
1.71
1.69
1.67
1.65
1.47
1.46
1.44
1.42
1.40
1.38
0.97
0.95
0.93
0.91
0.88
H
CO2Bun
400 MHz, CDCl3
4.00
2.04
0.88
2.23
2.33
3.35
(ppm)

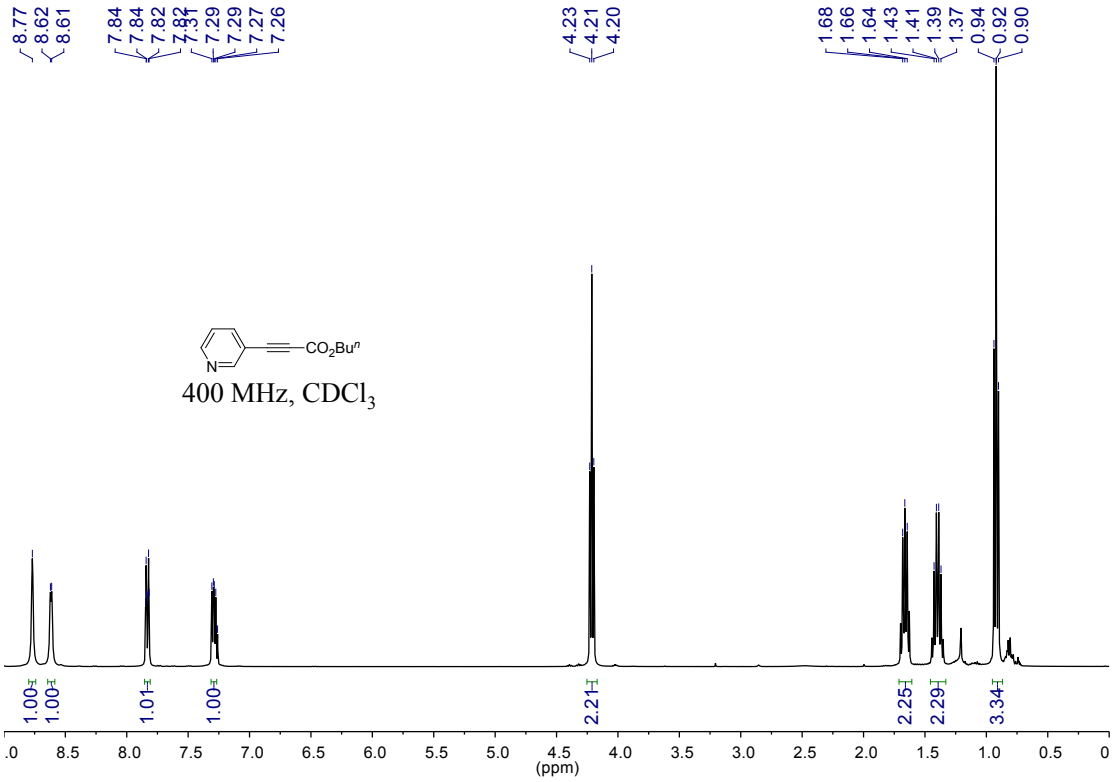

153.9
132.7
132.1
124.4
119.9
85.0
82.6
82.1
80.2
66.0
30.4
19.0
13.6
H
CO2Bun
100 MHz, CDCl3
(ppm)

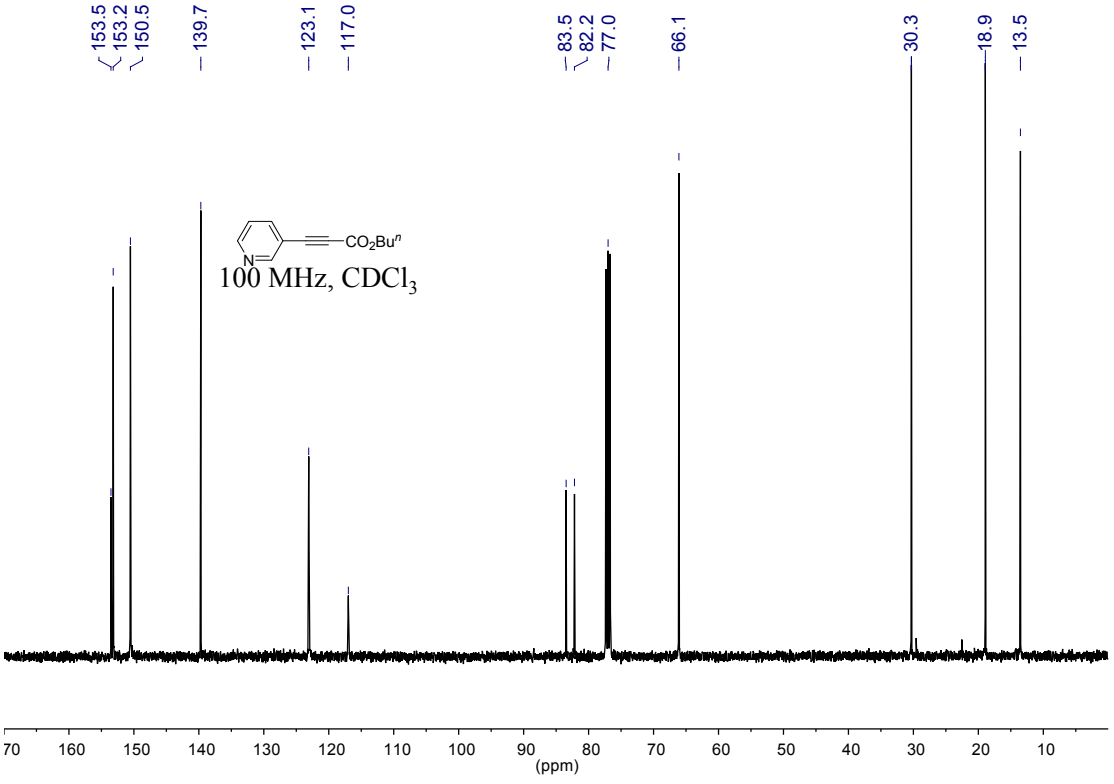

7.57
7.26
4.25
4.24
4.22
1.73
1.71
1.69
1.67
1.66
1.47
1.46
1.44
1.42
1.40
1.38
0.97
0.95
0.93
nBuO2C
CO2Bun
400 MHz, CDCl3
4.00
4.07
4.07
4.08
5.98
(ppm)

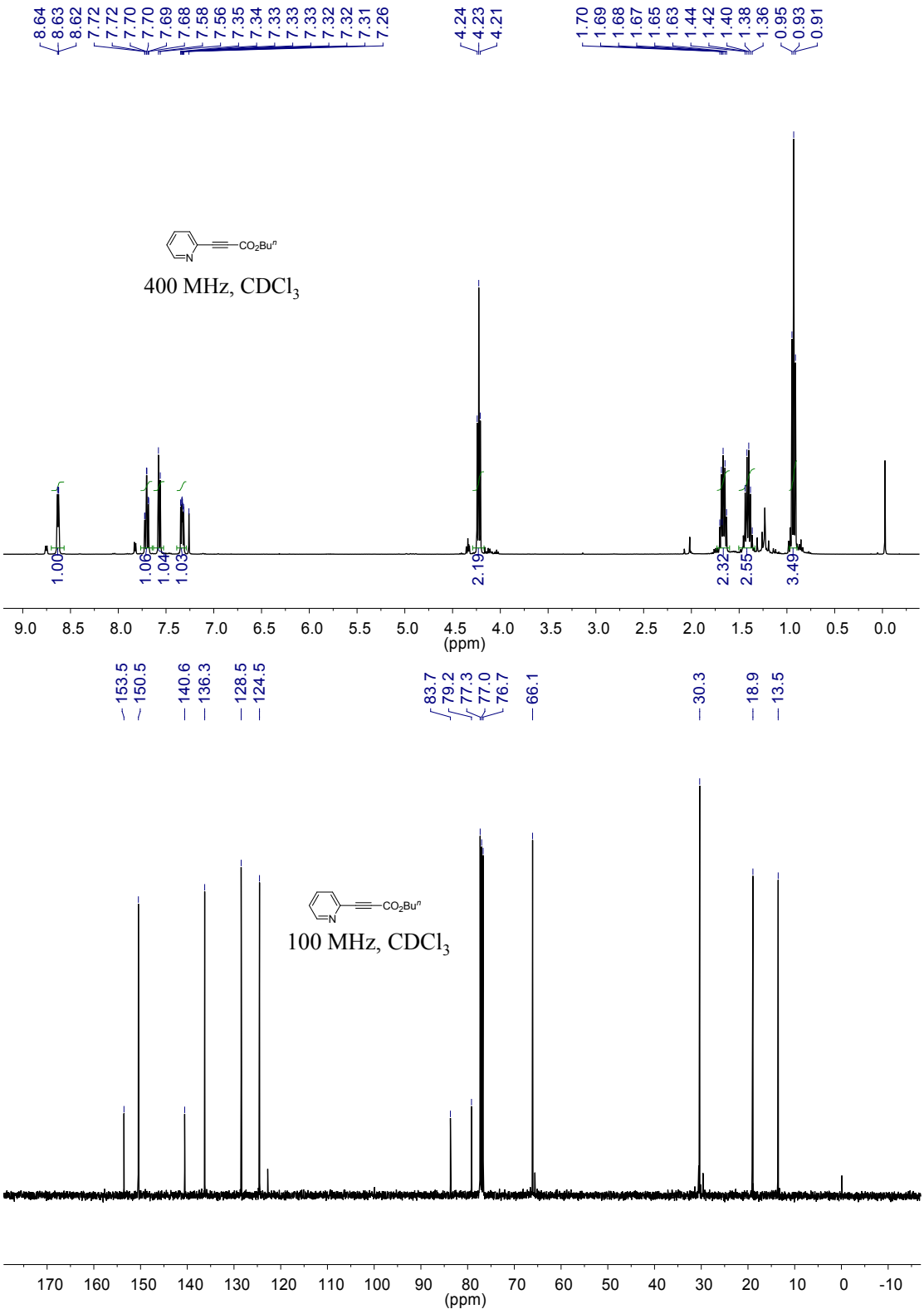

153.8
132.8
121.8
84.4
82.9
77.0
30.4
19.0
13.6
nBuO2C
CO2Bun
100 MHz, CDCl3
(ppm)

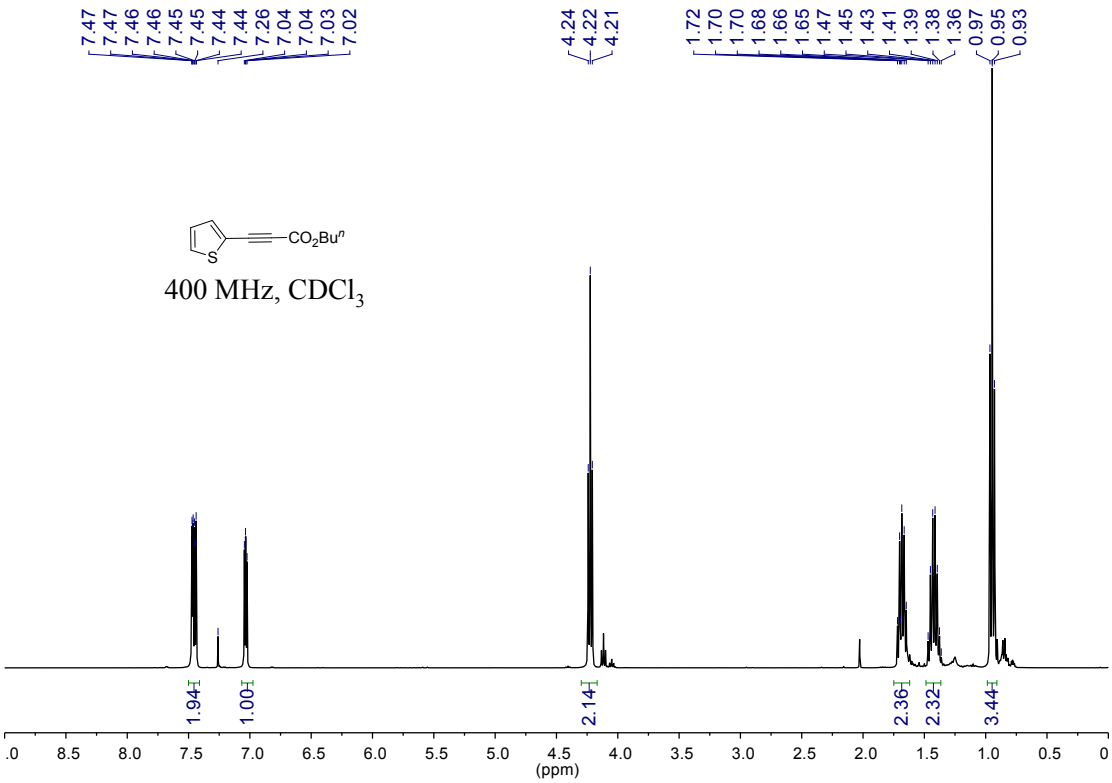

7.26
4.15
4.13
4.13
4.12
4.11
4.09
2.32
2.30
2.29
1.63
1.39
1.38
1.37
1.28
1.27
1.26
0.94
0.92
0.90
0.89
0.87
$^{n}C_6H_{13}$—≡—CO_2Bu^{n}
400 MHz, $CDCl_3$
2.16
1.59
3.92
8.29
6.00
(ppm)

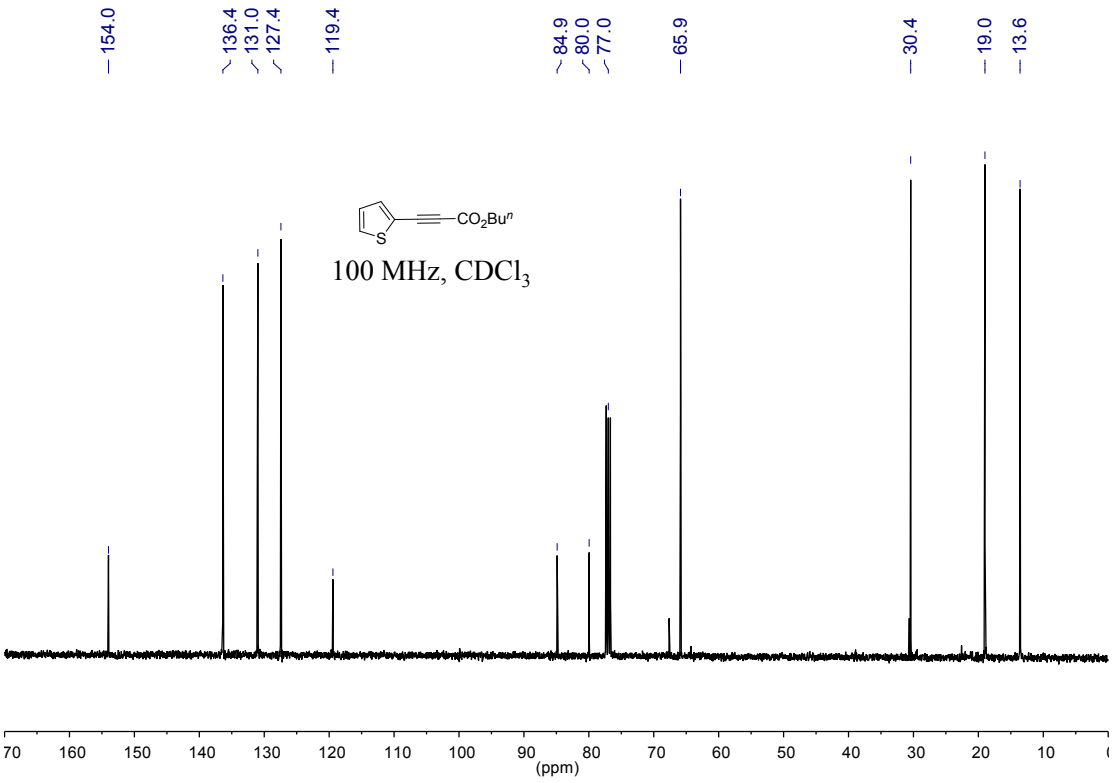

153.9
89.4
77.3
77.0
76.7
73.1
65.5
31.1
30.4
28.4
27.4
22.4
19.0
18.6
13.9
13.6
$^{n}C_6H_{13}$—≡—CO_2Bu^{n}
100 MHz, $CDCl_3$
(ppm)

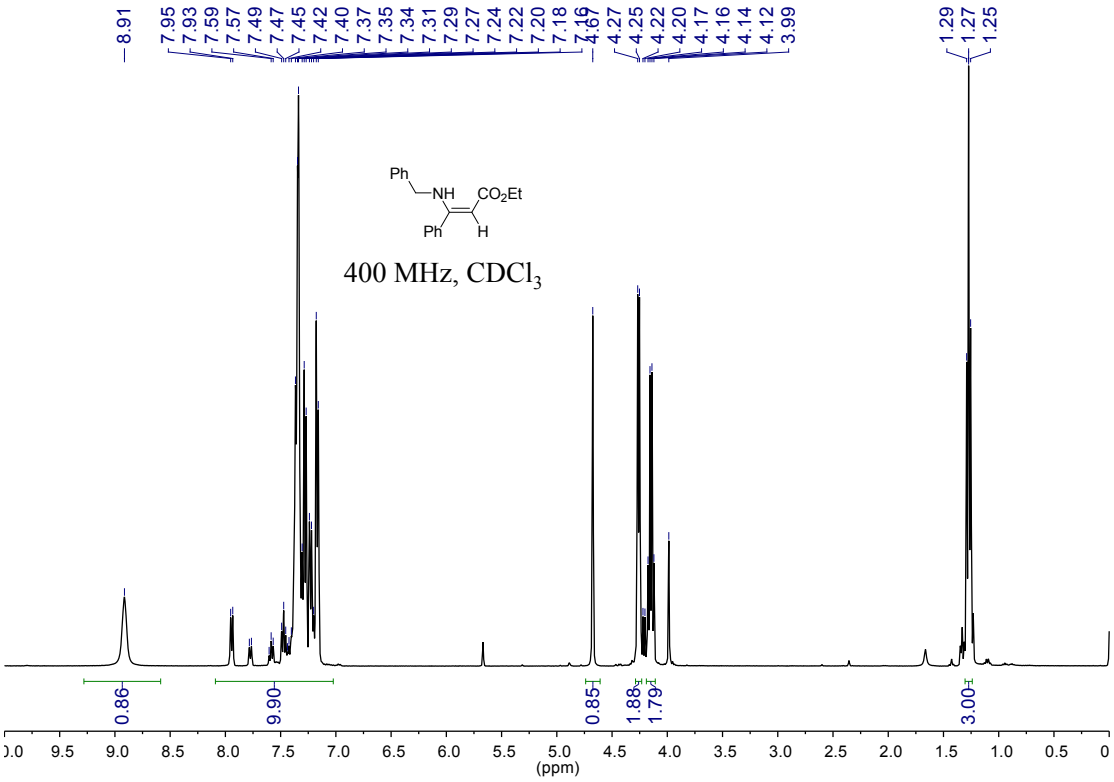

8.77
8.62
8.61
7.84
7.84
7.82
7.31
7.29
7.29
7.27
7.26
4.23
4.21
4.20
1.68
1.66
1.64
1.43
1.41
1.39
1.37
0.94
0.92
0.90
CO2Bun
N
400 MHz, CDCl3
1.00
1.00
1.01
1.00
2.21
2.25
2.29
3.34
(ppm)

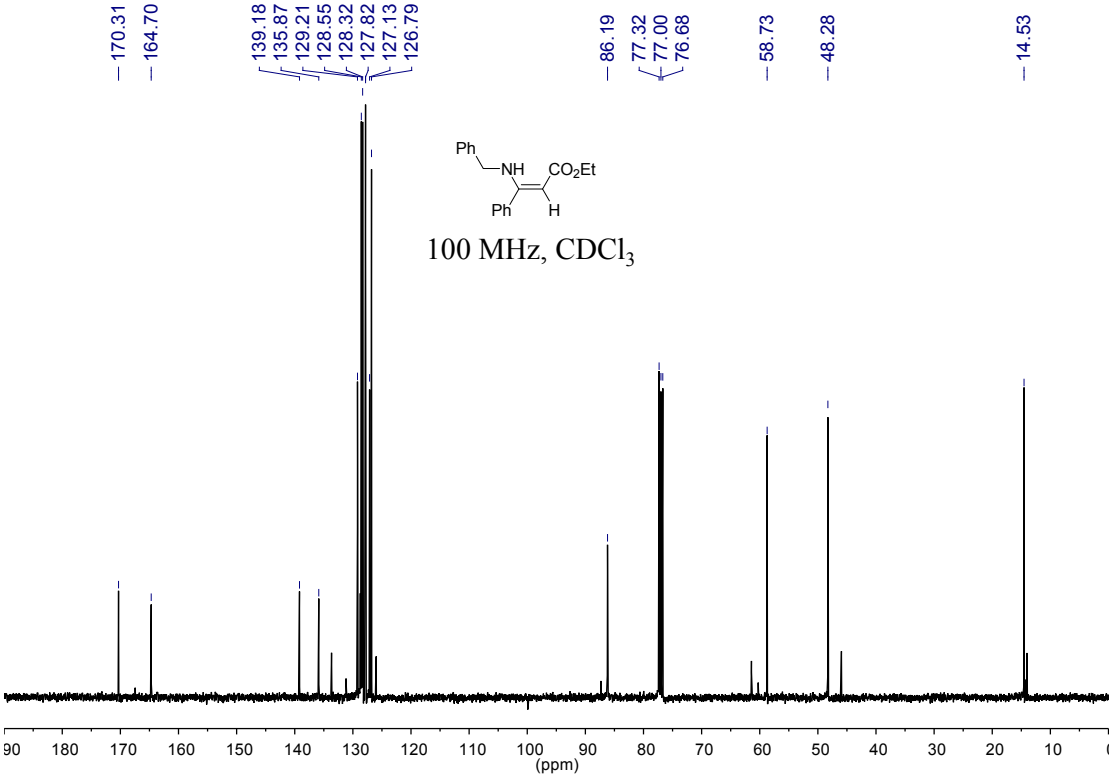

153.5
153.2
150.5
139.7
123.1
117.0
83.5
82.2
77.0
66.1
30.3
18.9
13.5
CO2Bun
N
100 MHz, CDCl3
(ppm)


8.64
8.63
8.62
7.72
7.72
7.70
7.70
7.69
7.68
7.58
7.56
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.26
4.24
4.23
4.21
1.70
1.69
1.68
1.67
1.65
1.63
1.44
1.42
1.40
1.38
1.36
0.95
0.93
0.91
CO2Bun
400 MHz, CDCl3
1.00
1.06
1.04
1.03
2.19
2.32
2.55
3.49
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)
153.5
150.5
140.6
136.3
128.5
124.5
83.7
79.2
77.3
77.0
76.7
66.1
30.3
18.9
13.5
CO2Bun
100 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

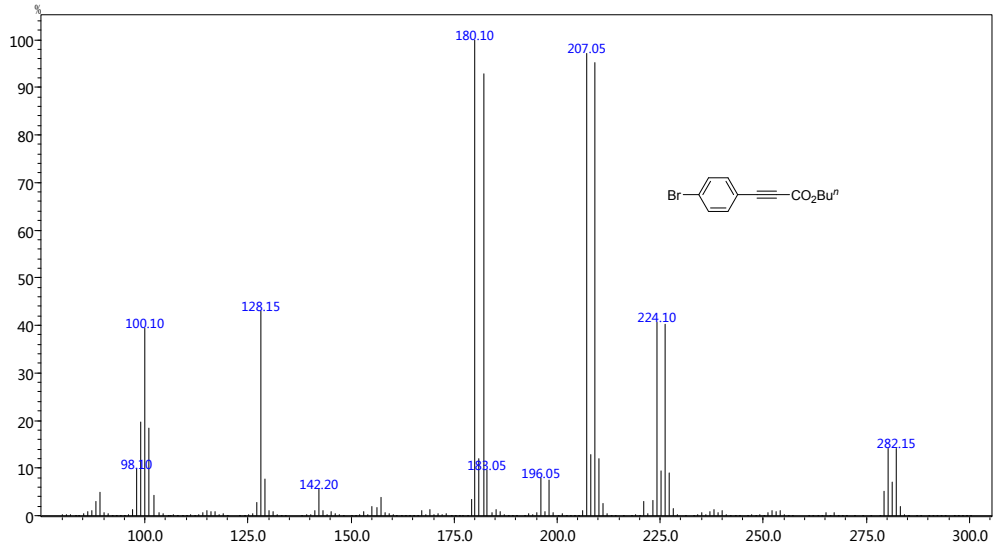

7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.26
7.04
7.04
7.03
7.02
4.24
4.22
4.21
1.72
1.70
1.70
1.68
1.66
1.65
1.47
1.45
1.43
1.41
1.39
1.38
1.36
0.97
0.95
0.93
CO2Bun
400 MHz, CDCl3
1.94
1.00
2.14
2.36
2.32
3.44
(ppm)

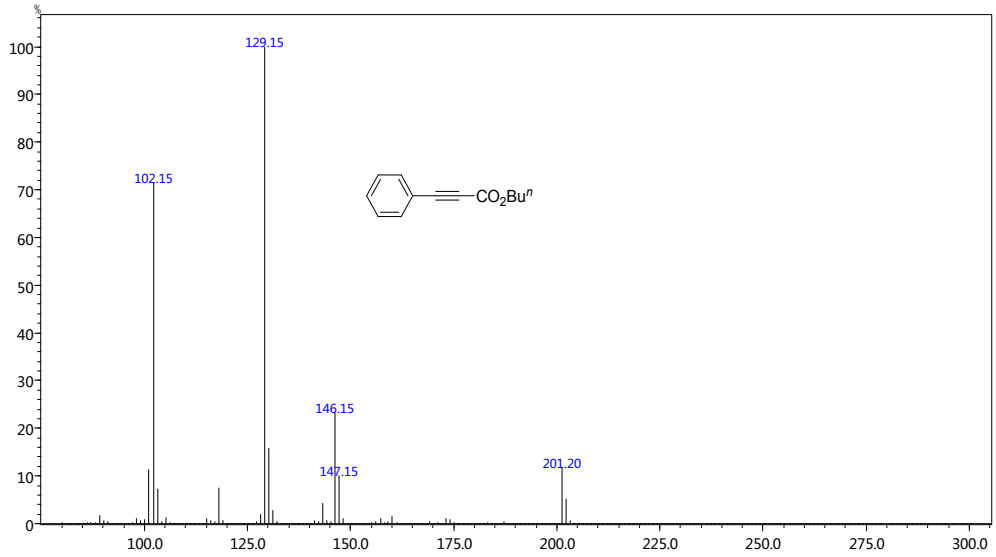

154.0
136.4
131.0
127.4
119.4
84.9
80.0
77.0
65.9
30.4
19.0
13.6
CO2Bun
100 MHz, CDCl3
(ppm)

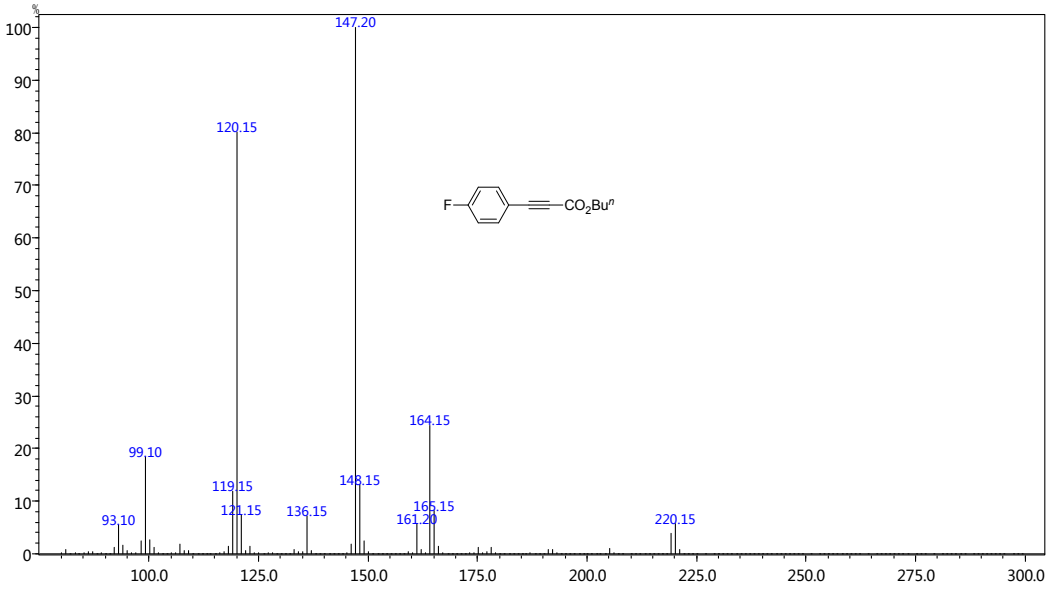

8.91
7.95
7.93
7.59
7.57
7.49
7.47
7.45
7.42
7.40
7.37
7.35
7.34
7.31
7.29
7.27
7.24
7.22
7.20
7.18
4.67
4.27
4.25
4.22
4.20
4.17
4.16
4.14
4.12
3.99
1.29
1.27
1.25
Ph
NH
CO2Et
Ph
H
400 MHz, CDCl3
0.86
9.90
0.85
1.88
1.79
3.00
(ppm)

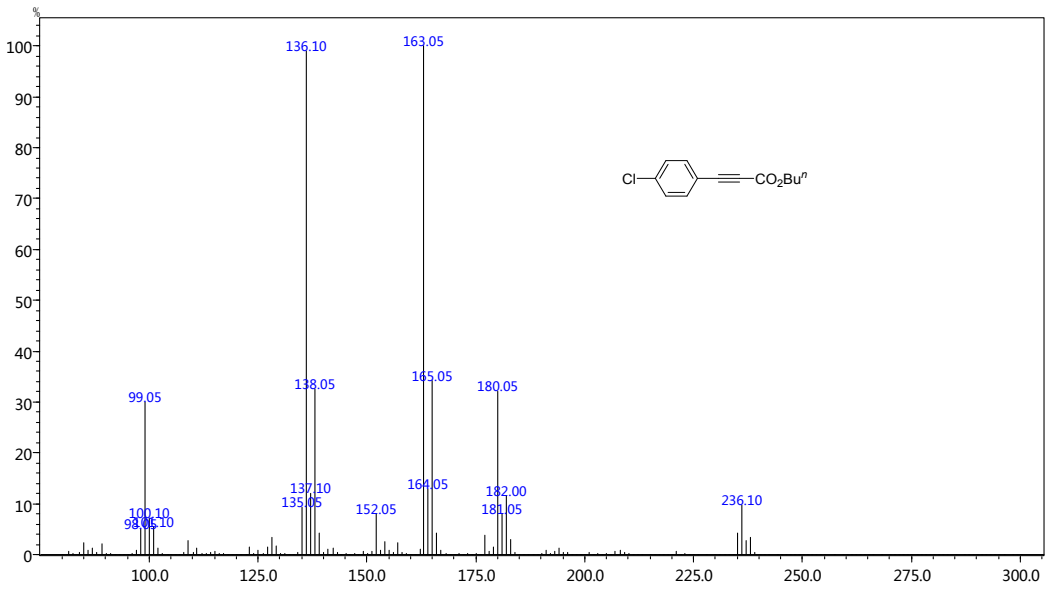

170.31
164.70
139.18
135.87
129.21
128.55
128.32
127.82
127.13
126.79
86.19
77.32
77.00
76.68
58.73
48.28
14.53
Ph
NH
CO2Et
Ph
H
100 MHz, CDCl3
(ppm)

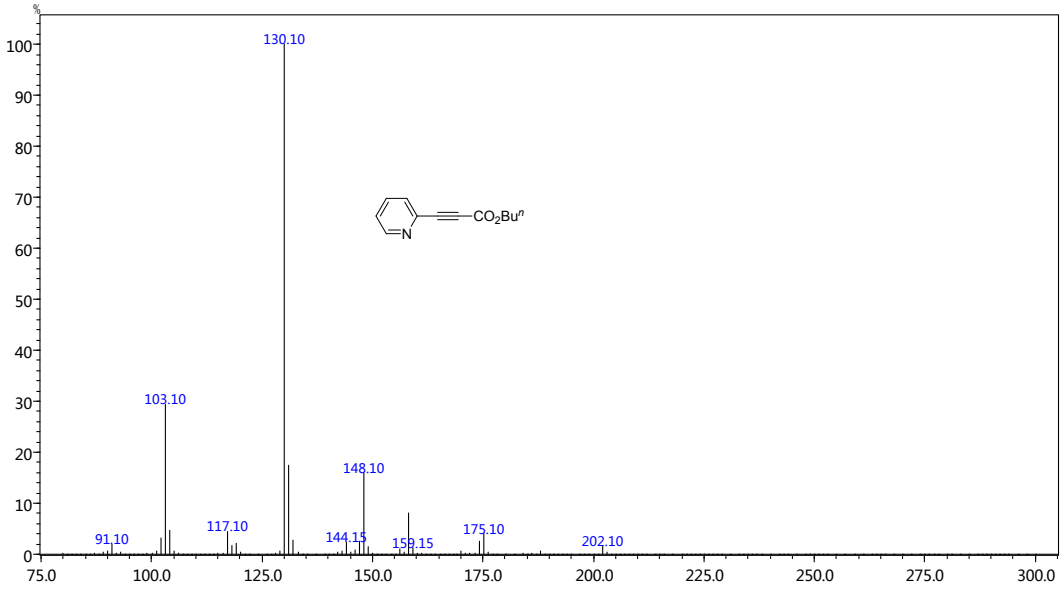
6. GC-MS spectrum of the Products

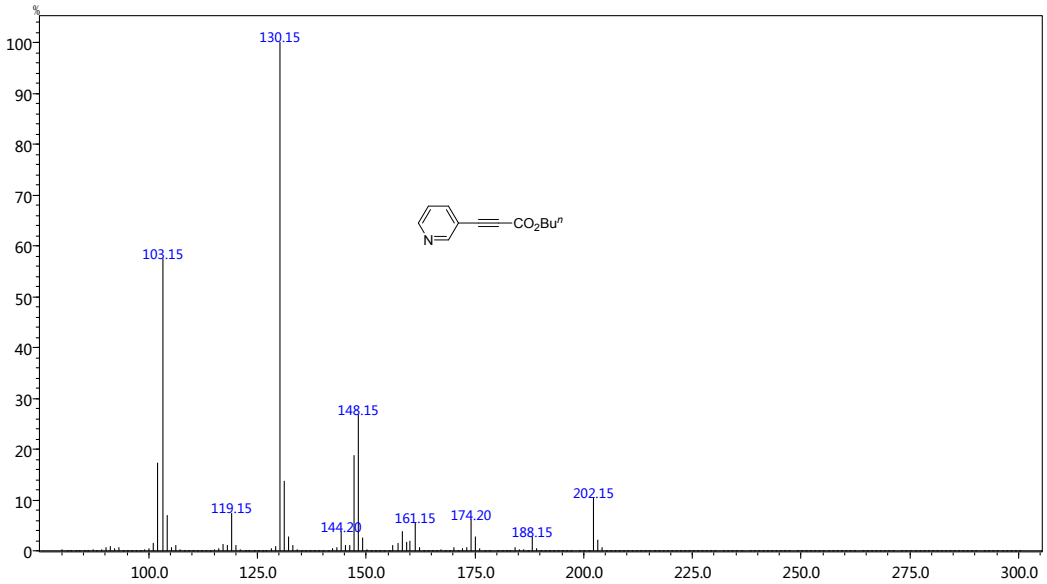


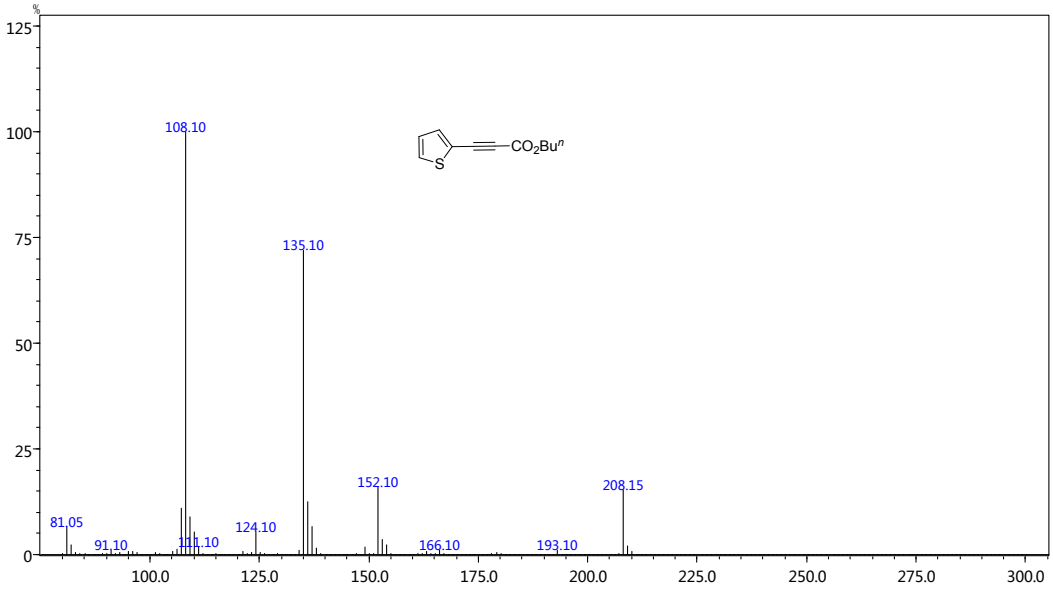


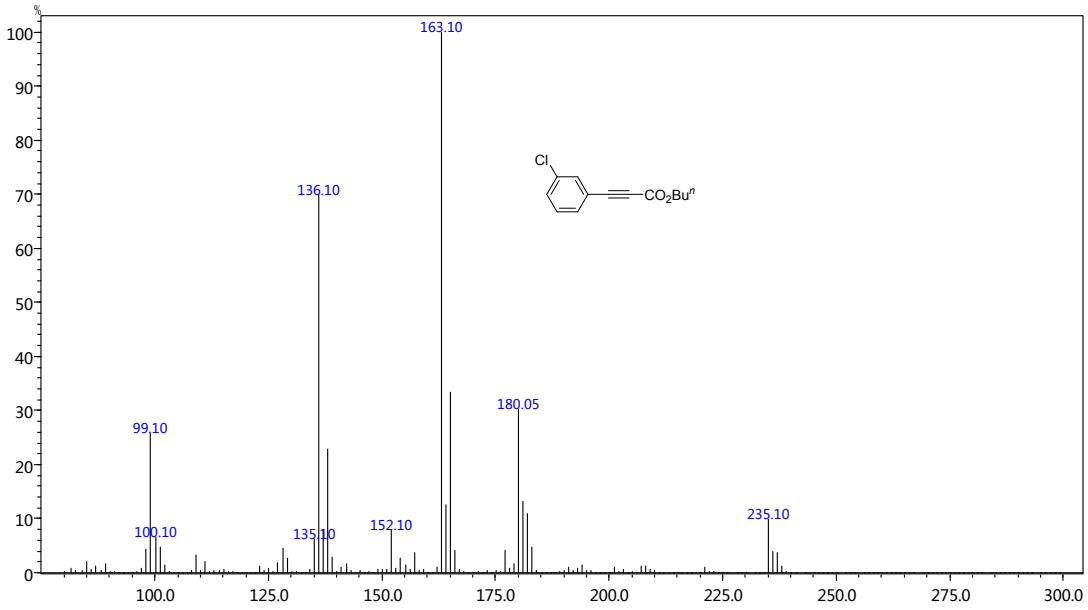

%
147.20
120.15
F
CO2Bun
164.15
99.10
119.15
148.15
121.15
136.15
165.15
93.10
161.20
220.15
100
90
80
70
60
50
40
30
20
10
0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0

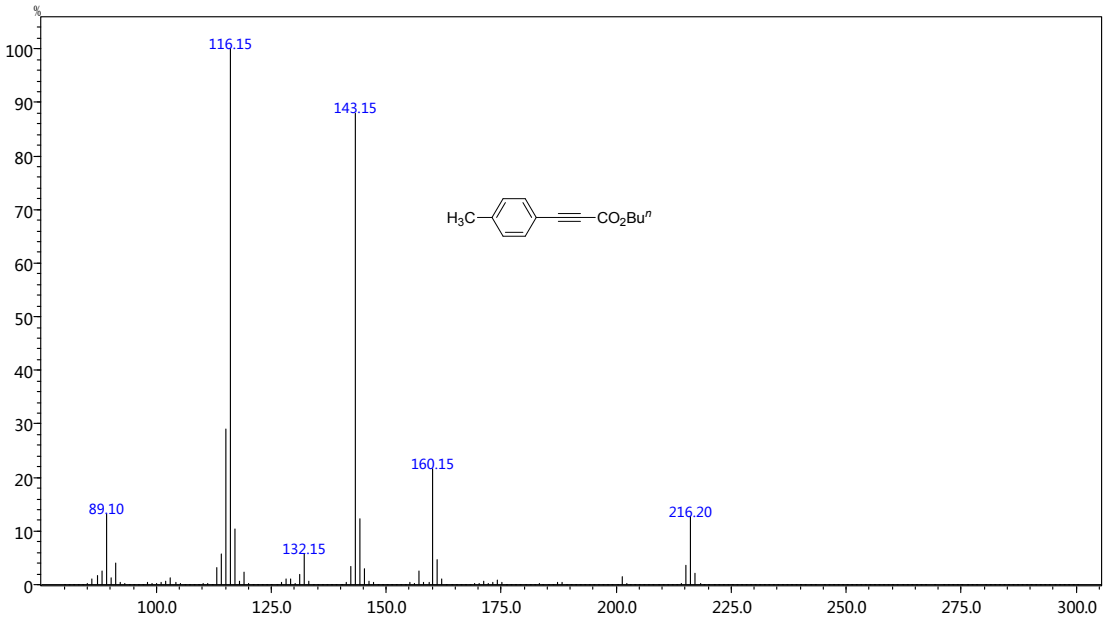

%
136.10
163.05
Cl
CO2Bun
138.05
165.05
180.05
99.05
137.10
135.05
164.05
182.00
181.05
152.05
236.10
100.10
100
90
80
70
60
50
40
30
20
10
0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0

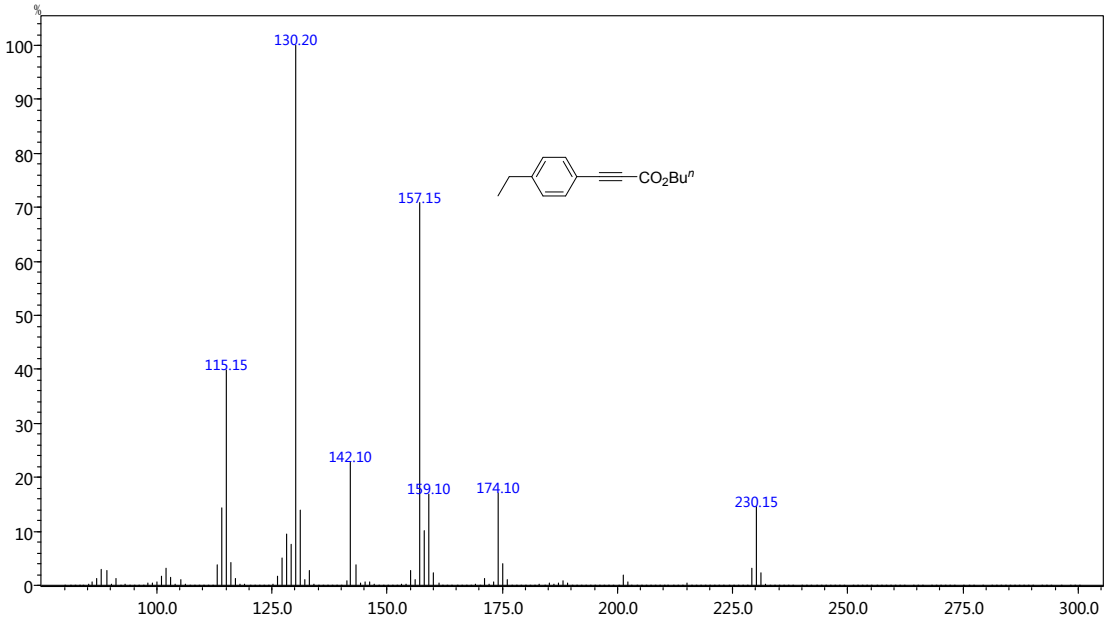

%
100
90
80
70
60
50
40
30
20
10
0
130.10
103.10
148.10
91.10
117.10
144.15
158.15
175.10
202.10
N
CO2Bun
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0

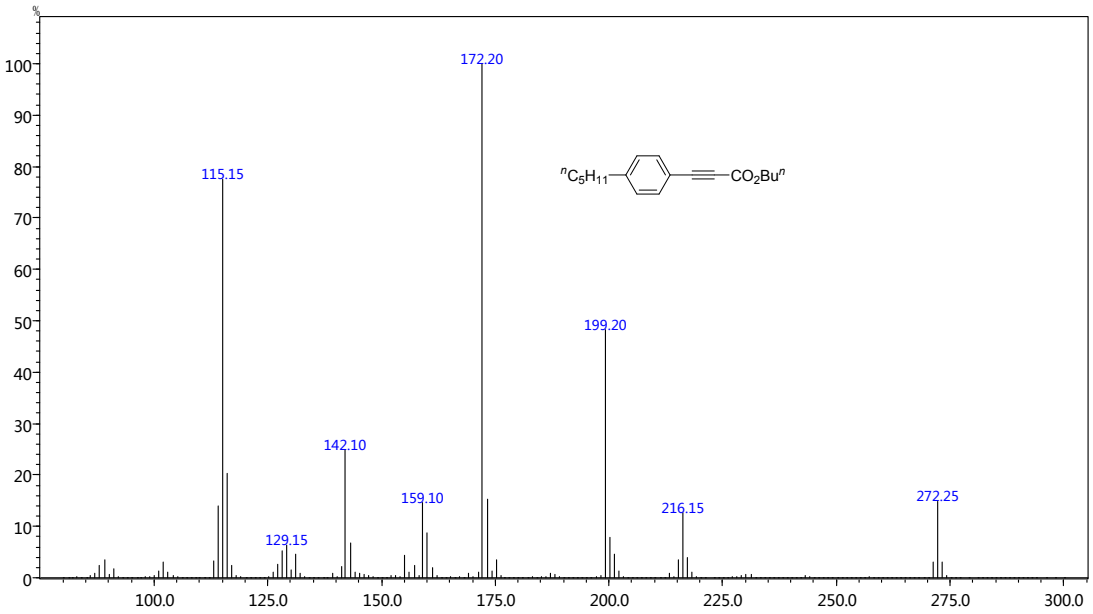

%
100
90
80
70
60
50
40
30
20
10
0
130.15
103.15
148.15
119.15
144.20
161.15
174.20
188.15
202.15
N
CO2Bun
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0

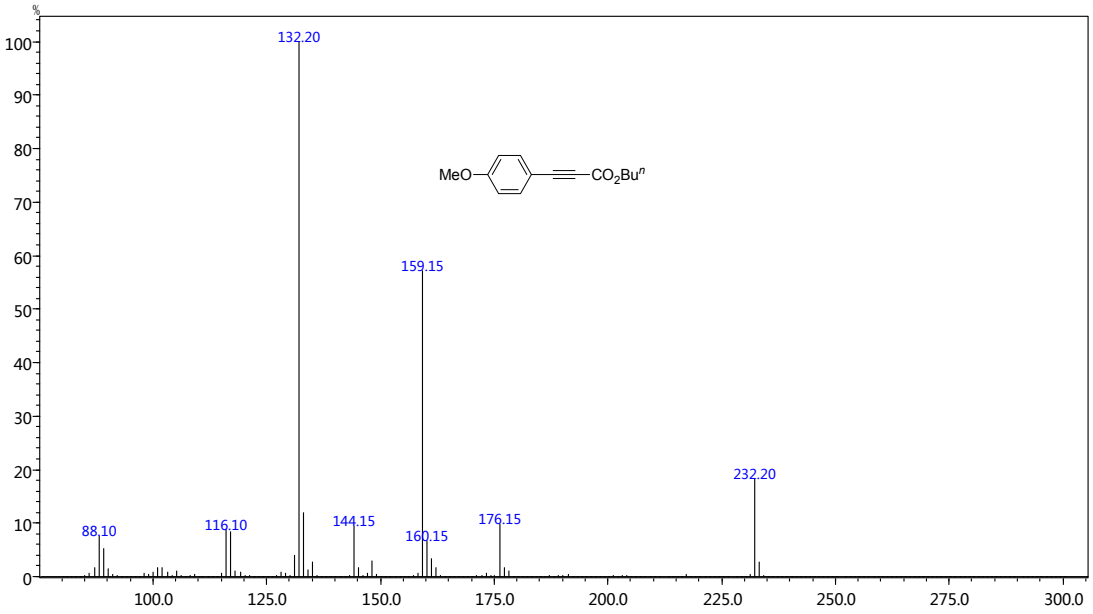

%
125
100
75
50
25
0
108.10
135.10
152.10
208.15
81.05
91.10
111.10
124.10
166.10
193.10
S
CO2Bun
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0

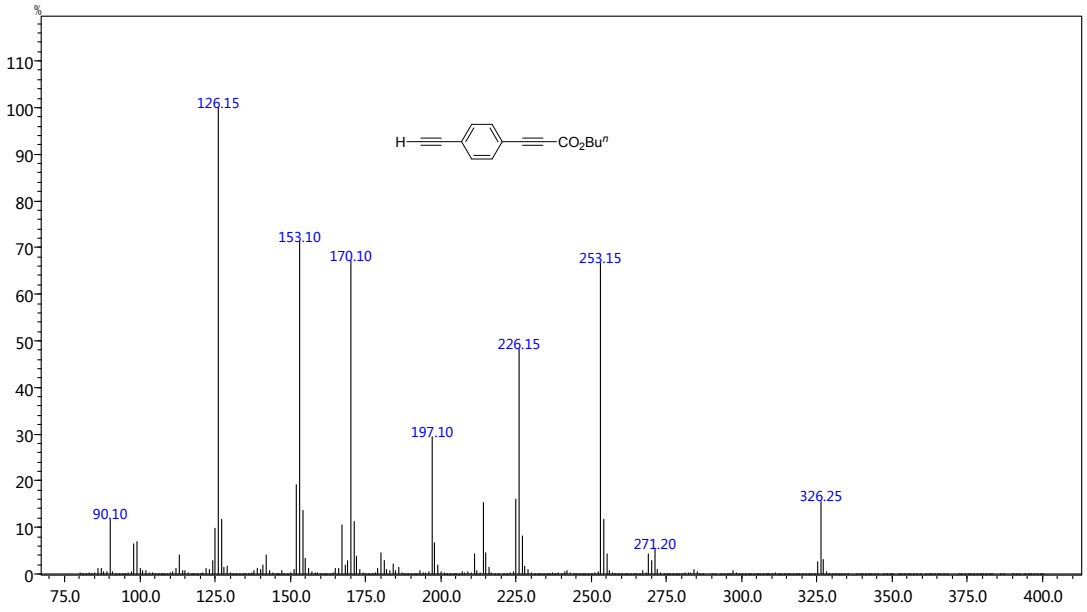

%
100
90
80
70
60
50
40
30
20
10
0
163.10
136.10
180.05
99.10
100.10
135.10
152.10
235.10
Cl
CO2Bun
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0

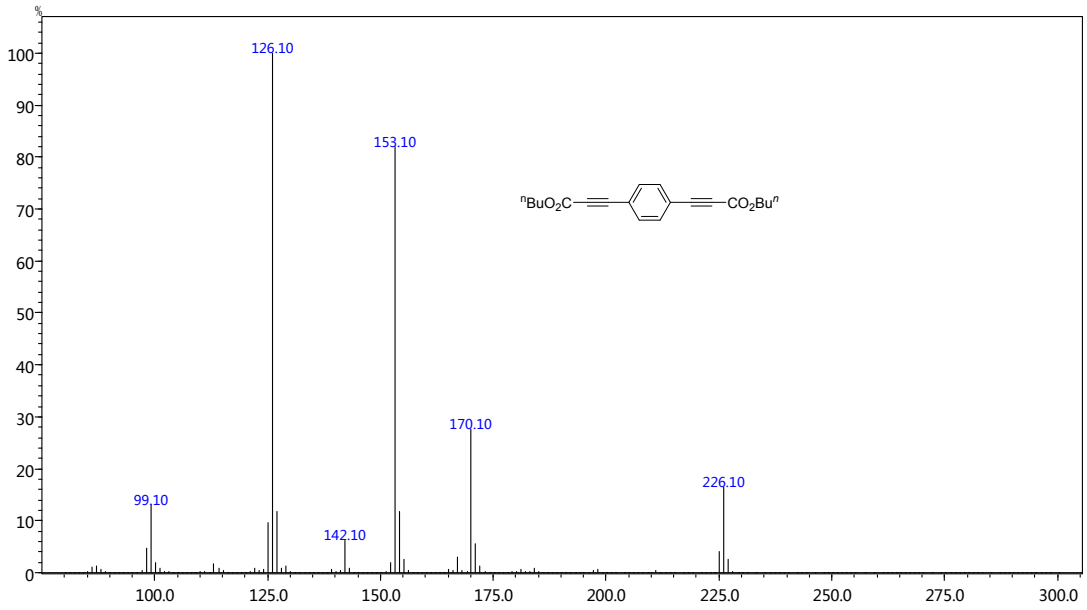

116.15
143.15
160.15
89.10
216.20
132.15
H3C
CO2Bun

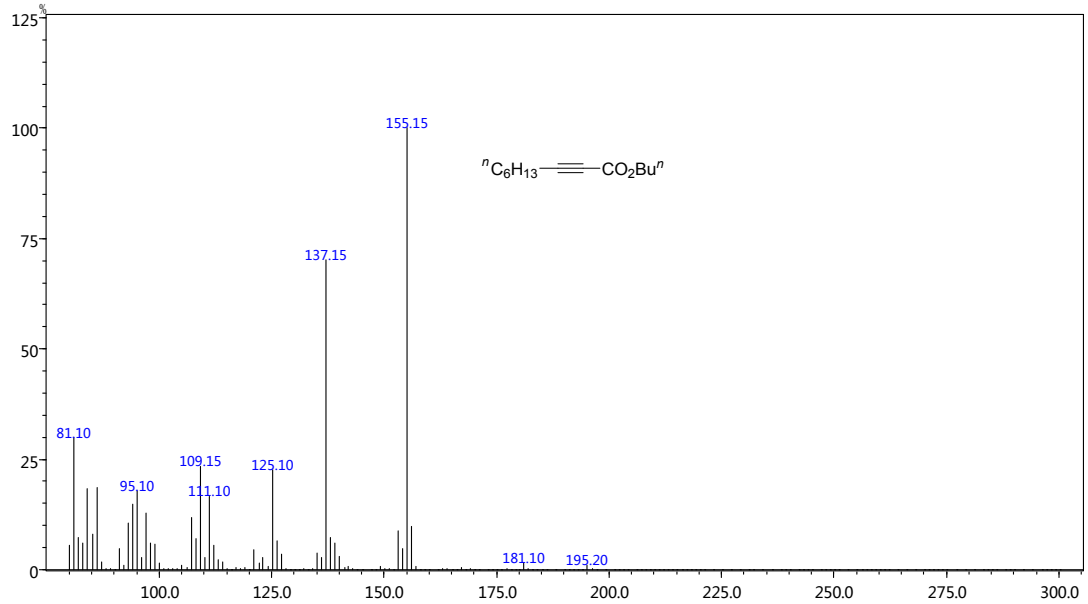

130.20
157.15
115.15
142.10
159.10
174.10
230.15
CO2Bun

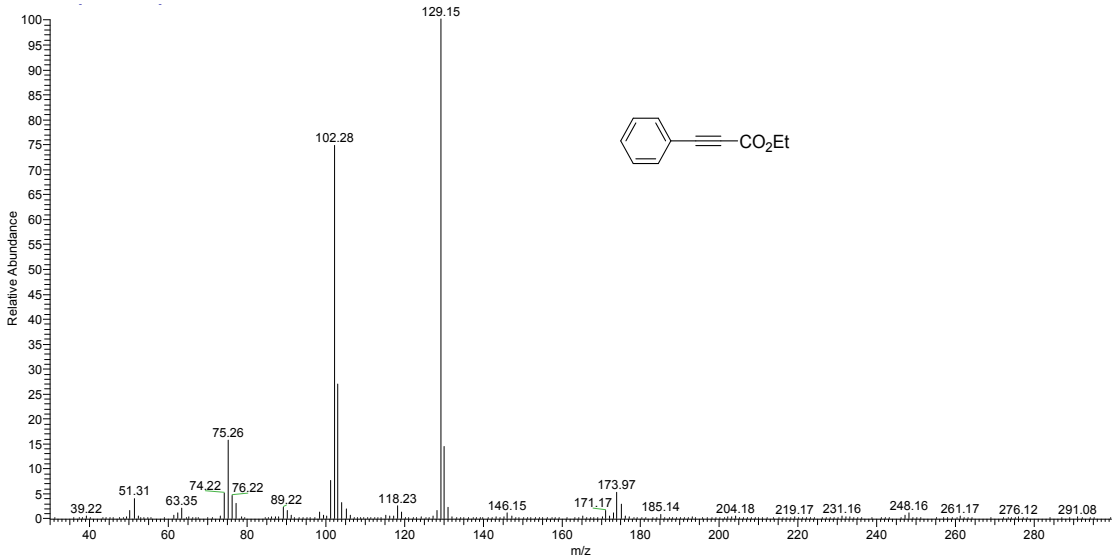

%
100
90
80
70
60
50
40
30
20
10
0
172.20
115.15
199.20
142.10
159.10
216.15
272.25
129.15
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
$^{n}C_5H_{11}$
CO_2Bu^n

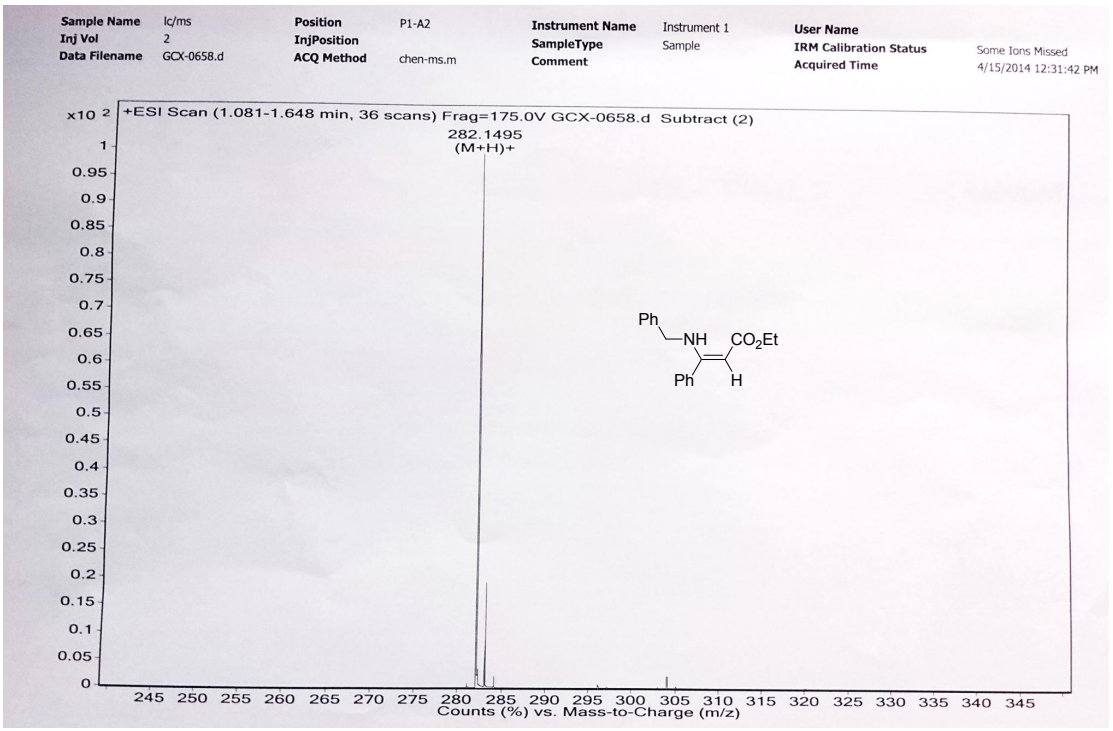

%
100
90
80
70
60
50
40
30
20
10
0
132.20
159.15
232.20
88.10
116.10
144.15
160.15
176.15
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
MeO
CO_2Bu^n


%
110
100
90
80
70
60
50
40
30
20
10
0
126.15
153.10
170.10
253.15
226.15
197.10
326.25
90.10
271.20
H
CO2Bun
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0


%
100
90
80
70
60
50
40
30
20
10
0
126.10
153.10
170.10
226.10
99.10
142.10
nBuO2C
CO2Bun
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0


%
125
100
75
50
25
0
155.15
137.15
81.10
109.15
125.10
95.10
111.10
181.10
195.20
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
$^{n}C_6H_{13}$—≡—CO_2Bu^{n}


Relative Abundance
129.15
102.28
75.26
CO_2Et
39.22
51.31
63.35
74.22
76.22
89.22
118.23
146.15
171.17
173.97
185.14
204.18
219.17
231.16
248.16
261.17
276.12
291.08
m/z


Sample Name lc/ms
Inj Vol 2
Data Filename GCX-0658.d
Position P1-A2
InjPosition
ACQ Method chen-ms.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Some Ions Missed
Acquired Time 4/15/2014 12:31:42 PM
+ESI Scan (1.081-1.648 min, 36 scans) Frag=175.0V GCX-0658.d Subtract (2)
282.1495
(M+H)+
x10 2
Ph
NH
CO2Et
Ph
H
Counts (%) vs. Mass-to-Charge (m/z)