Carboxylation of terminal alkynes with CO_2 catalyzed by novel silver N-heterocyclic carbene complexes

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Electronic Supplementary Information

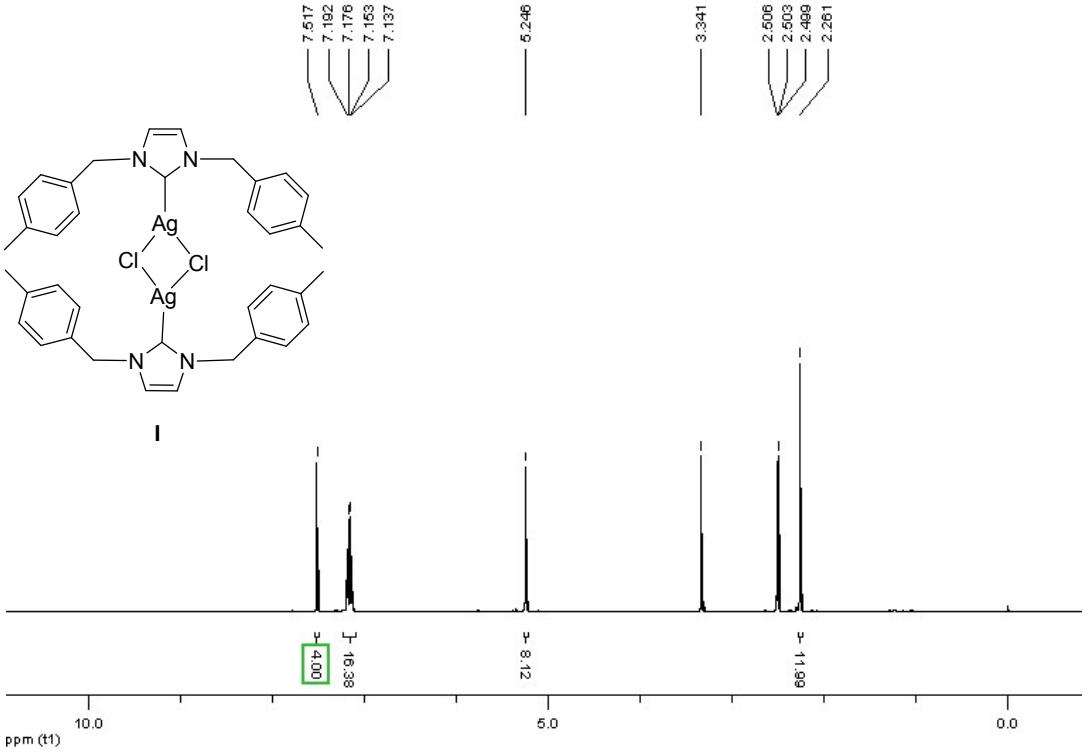
Table S1. Crystal data and refinement parameters for complex **I** and **II**

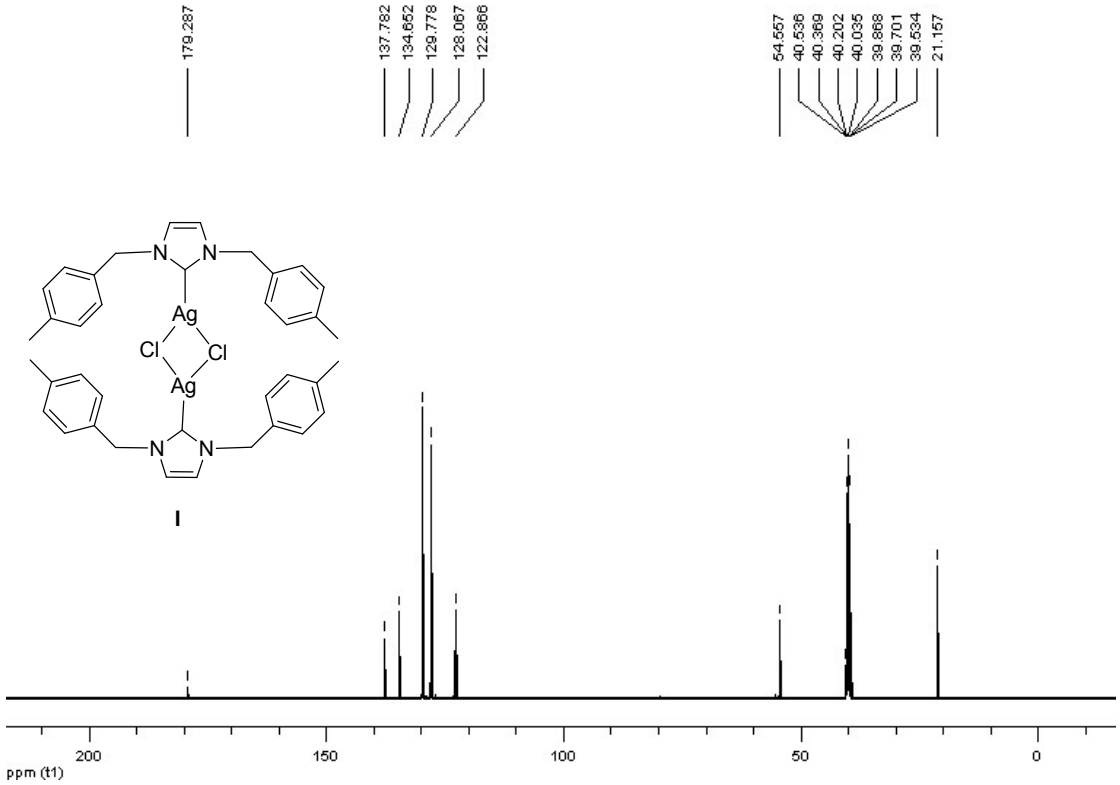
	Complex I	**Complex II**
Empirical Formula	$C_{38}H_{40}Ag_2Cl_2N_4$	$C_{19}H_{20}AgCl\,N_2O_2$
Formula weight	839.38	451.69
Temperature (K)	193(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/n
a (Å)	9.992(5)	14.281(3)
b (Å)	8.977(4)	8.041(2)
c (Å)	19.725(9)	17.283(4)
α (°)	90	90
β (°)	91.261(9)	107.309(4)
γ (°)	90	90
Volume ($Å^3$)	1768.9(14)	1894.8(8)
Z	2	4
Calculated density (mg/m^3)	1.576	1.583
Absorption coefficient (mm^{-1})	1.291	1.219
F(000)	848	912
Crystal size (mm^3)	0.130 x 0.050 x 0.040	0.400 x 0.130 x 0.120
θ Range (°)	1.03-26.56	1.630-27.253
Index ranges	-12 <= h <= 12, -10 <= k <= 11, -24 <= l <= 20	-17 <= h <= 18, -9 <= k <= 10, -22 <= l <= 19
Reflections collected	10996	12999
Independent reflections, R_{int}	3434, 0.0658	4199, 0.0318
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3576 / 0 / 211	4199 / 0 / 228
Goodness-of-fit on F^2	1.141	1.051
R [I>2sigma(I)]	0.1047, 0.2673	0.0314, 0.0886
R indices (all data)	0.1477, 0.2929	0.0469, 0.0961
Largest difference in peak and hole ($e\,Å^{-3}$)	3.095 and -1.200	0.553 and -0.615

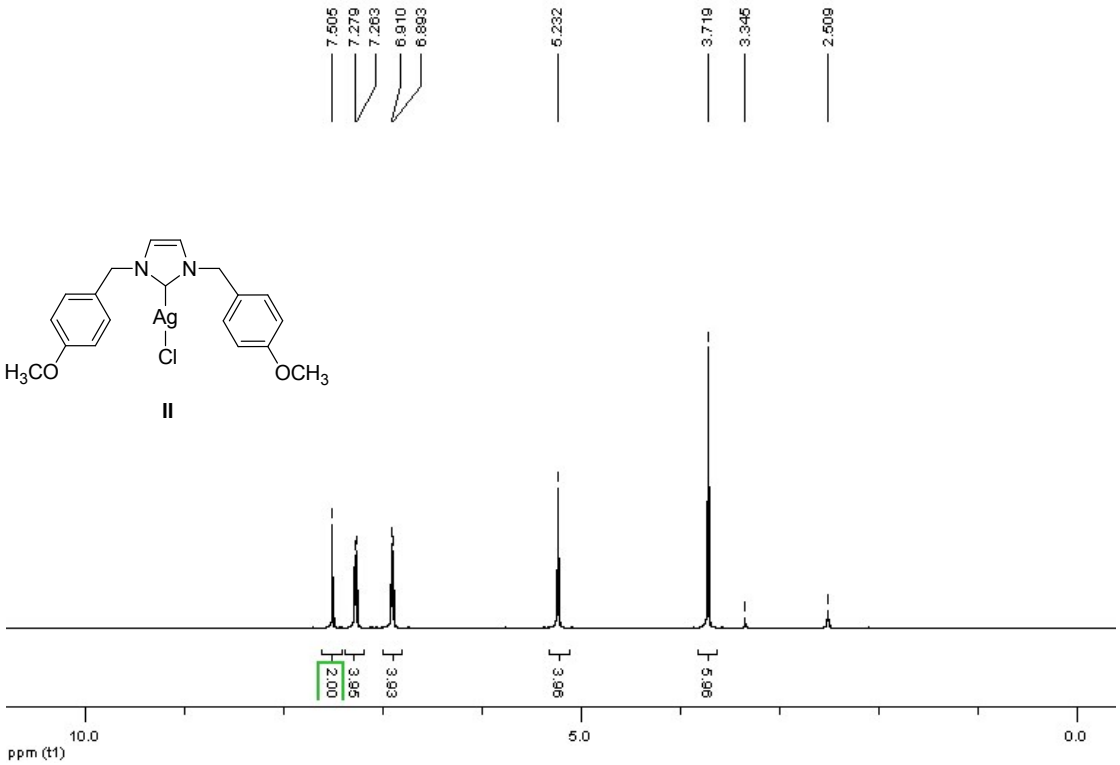
Table S2. Crystal data and refinement parameters for complex **III** and **IV**.

	Complex III	**Complex IV**
Empirical Formula	$C_{34}H_{28}Ag_2Cl_6N_4$	$C_{19}H_{20}AgClN_2O_2$
Formula weight	921.04	451.69
Temperature (K)	293(2)	203(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/c
a (Å)	9.757(3)	15.9786(19)
b (Å)	9.169(3)	7.8790(9)
c (Å)	19.300(5)	15.8991(18)
α (°)	90	90
β (°)	91.390(4)	114.739(2)
γ (°)	90	90
Volume ($Å^3$)	1726.2(8)	1817.9(4)
Z	2	4
Calculated density (mg/m^3)	1.772	1.650
Absorption coefficient (mm^{-1})	1.631	1.270
F(000)	912	912
Crystal size (mm^3)	0.200 x 0.080 x 0.060	0.180 x 0.140 x 0.040
θ Range (°)	2.088-25.998	2.572-27.488
Index ranges	-11 <= h <= 7, -10 <= k <= 11, -23 <= l <= 23	-19 <= h <= 20, -10 <= k <= 9, -20 <= l <= 17
Reflections collected	7656	12663
Independent reflections, R_{int}	3372, 0.0399	4129, 0.0306
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3372 / 0 / 208	4129 / 0 / 228
Goodness-of-fit on F^2	0.942	1.165
R [I>2sigma(I)]	0.0410, 0.0970	0.0373, 0.1230
R indices (all data)	0.0792, 0.1245	0.0484, 0.1293
Largest difference in peak and hole (e $Å^{-3}$)	0.628 and -0.560	0.754 and -0.676

NMR spectra of I-IV



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6.910
6.893
5.232
3.719
3.345
2.509
N
N
Ag
Cl
H3CO
OCH3
II
2.00
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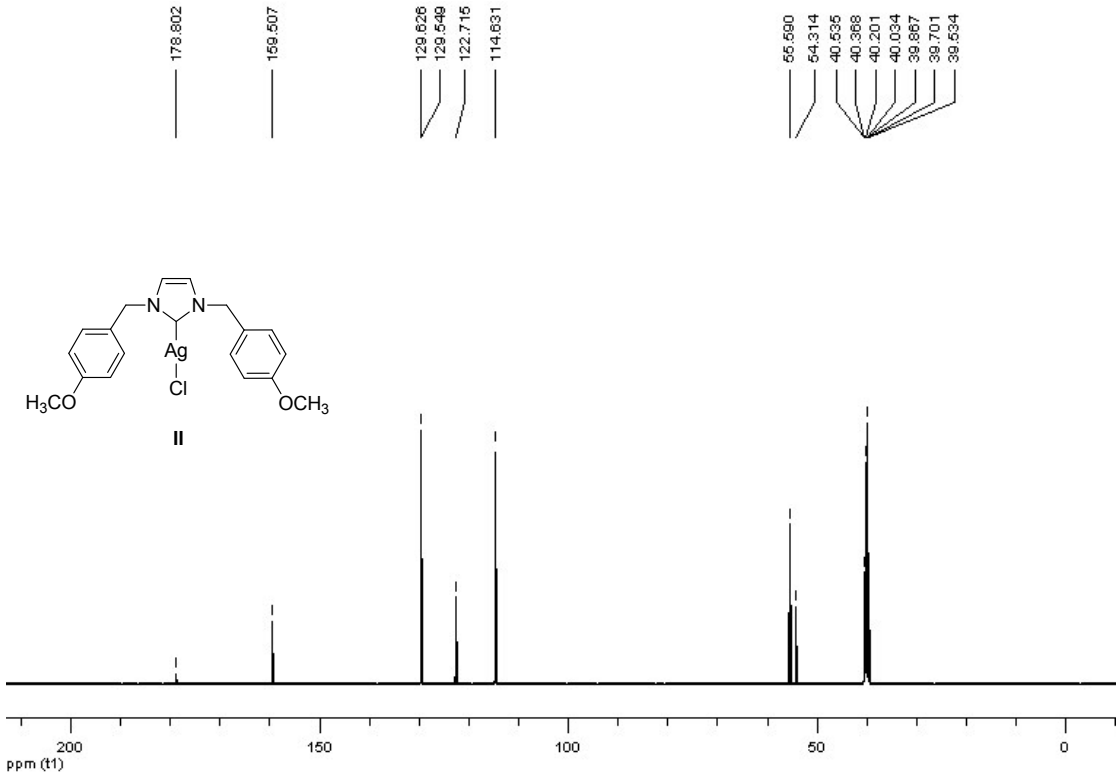
3.93
3.96
6.96
10.0
5.0
0.0
ppm (t1)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129.626
129.549
122.715
114.631
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54.314
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39.701
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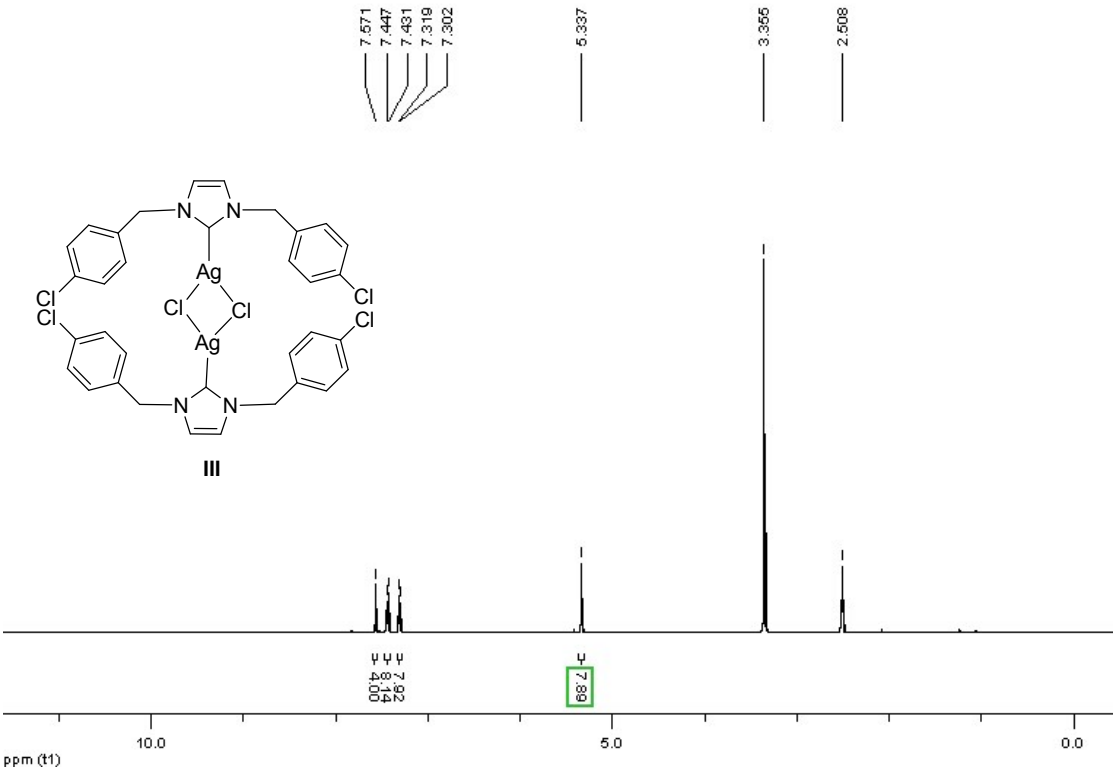
N
Ag
Cl
H3CO
OCH3
II
200
150
100
50
0
ppm (t1)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7.431
7.319
7.302
5.337
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2.508
Ag
Cl
Cl
Ag
N
N
N
N
Cl
Cl
Cl
Cl
III
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1.84
2.92
7.89
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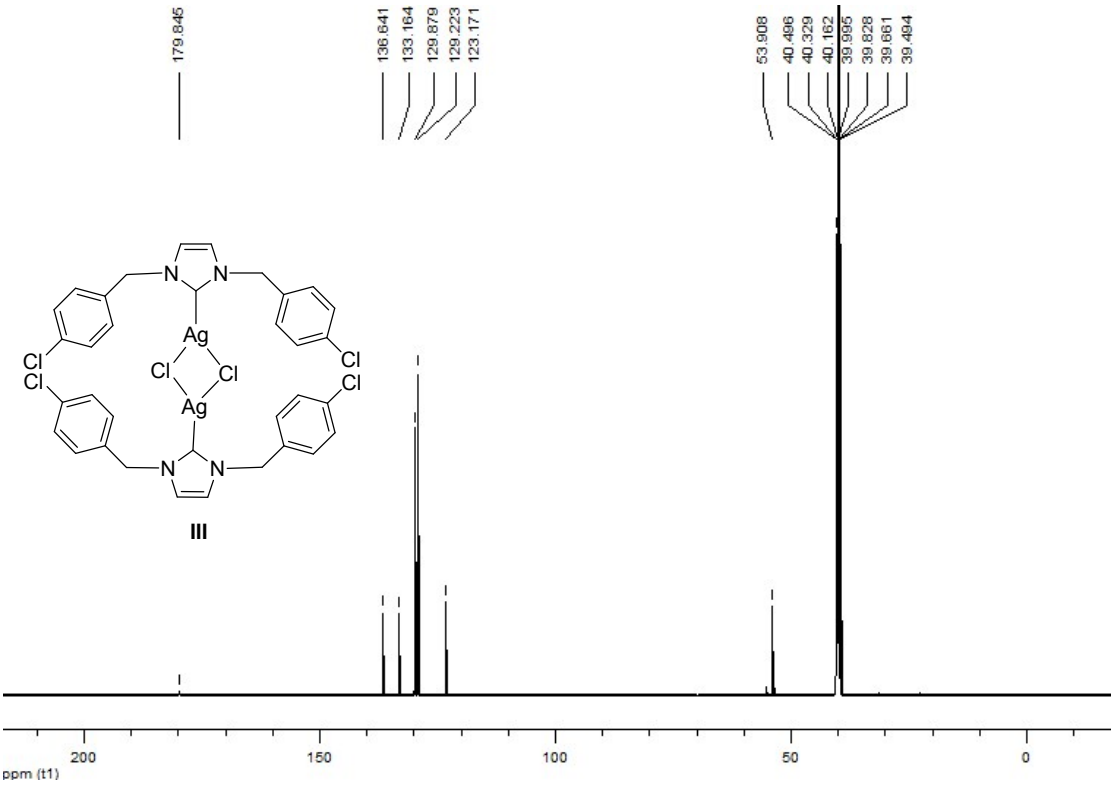
5.0
0.0
ppm (t1)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133.164
129.879
129.223
123.171
53.908
40.496
40.329
40.162
39.995
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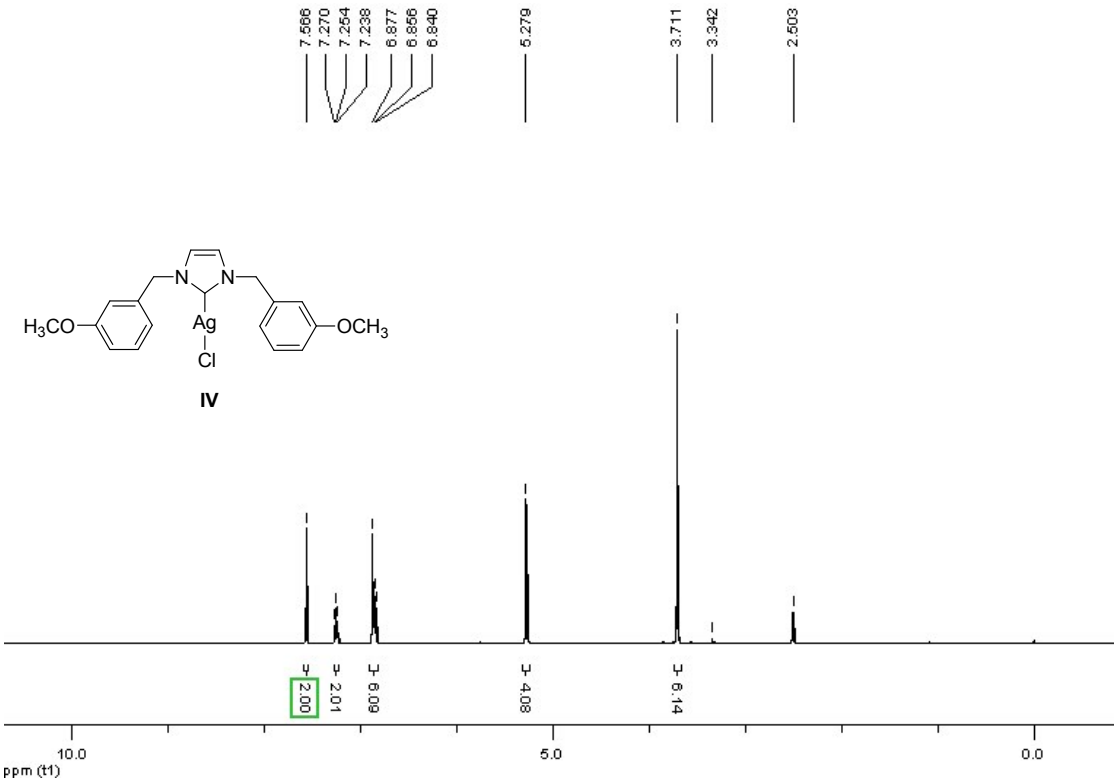
39.661
39.494
Ag
Cl
Cl
Ag
N
N
N
N
Cl
Cl
Cl
Cl
III
200
150
100
50
0
ppm (t1)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7.254
7.238
6.877
6.856
6.840
5.279
3.711
3.342
2.503
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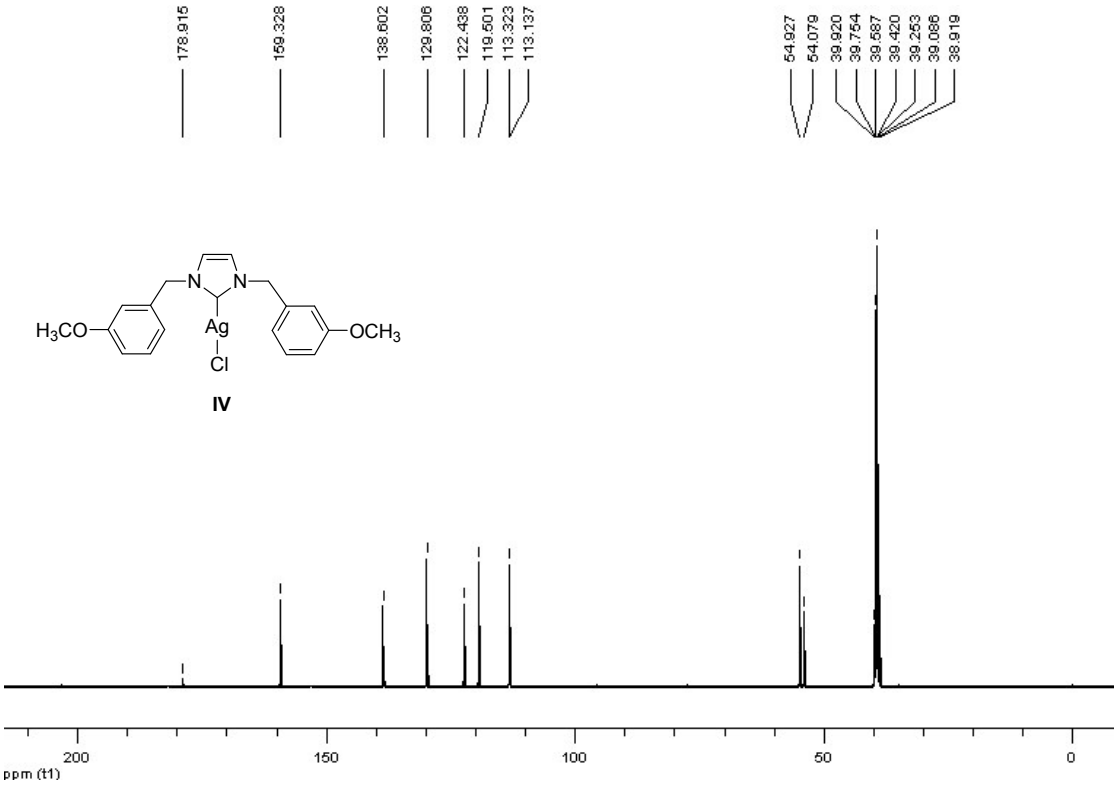
N
Ag
Cl
H3CO
OCH3
2.00
2.01
6.09
4.08
6.14
10.0
5.0
0.0
ppm (t1)

IV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122.438
119.501
113.323
113.137
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54.079
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39.587
39.420
39.253
39.086
38.919
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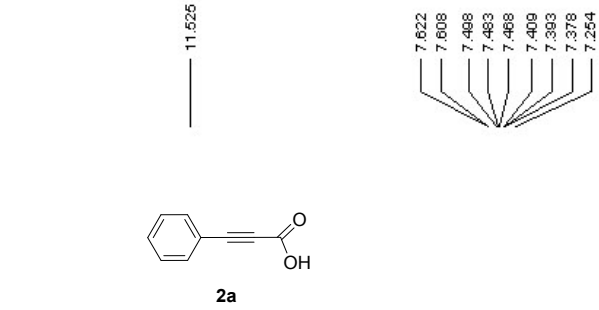
Ag
Cl
H3CO
OCH3
200
150
100
50
0
ppm (t1)

IV

NMR spectra of 2a-2t



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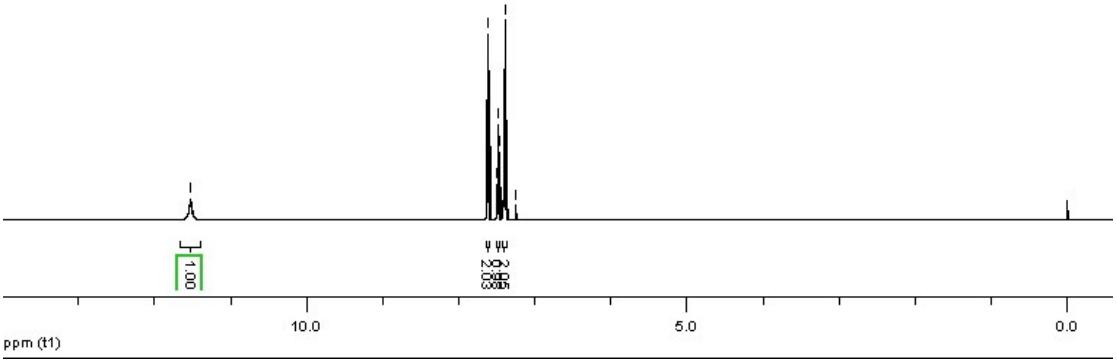
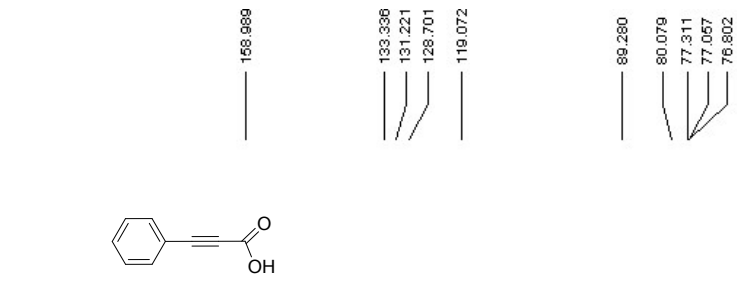
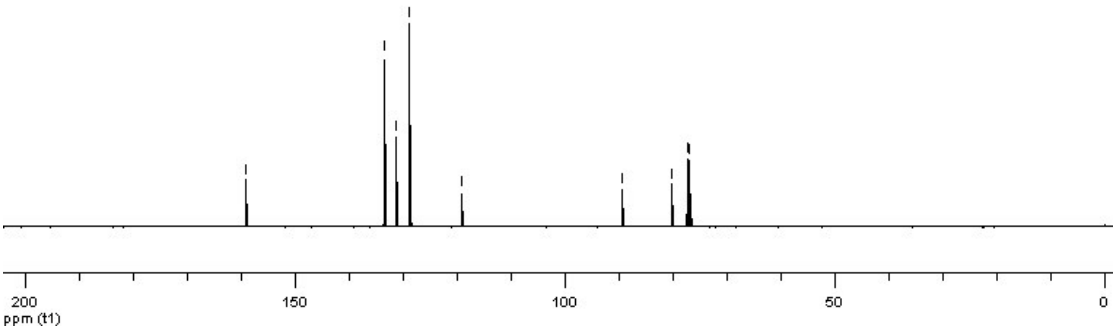
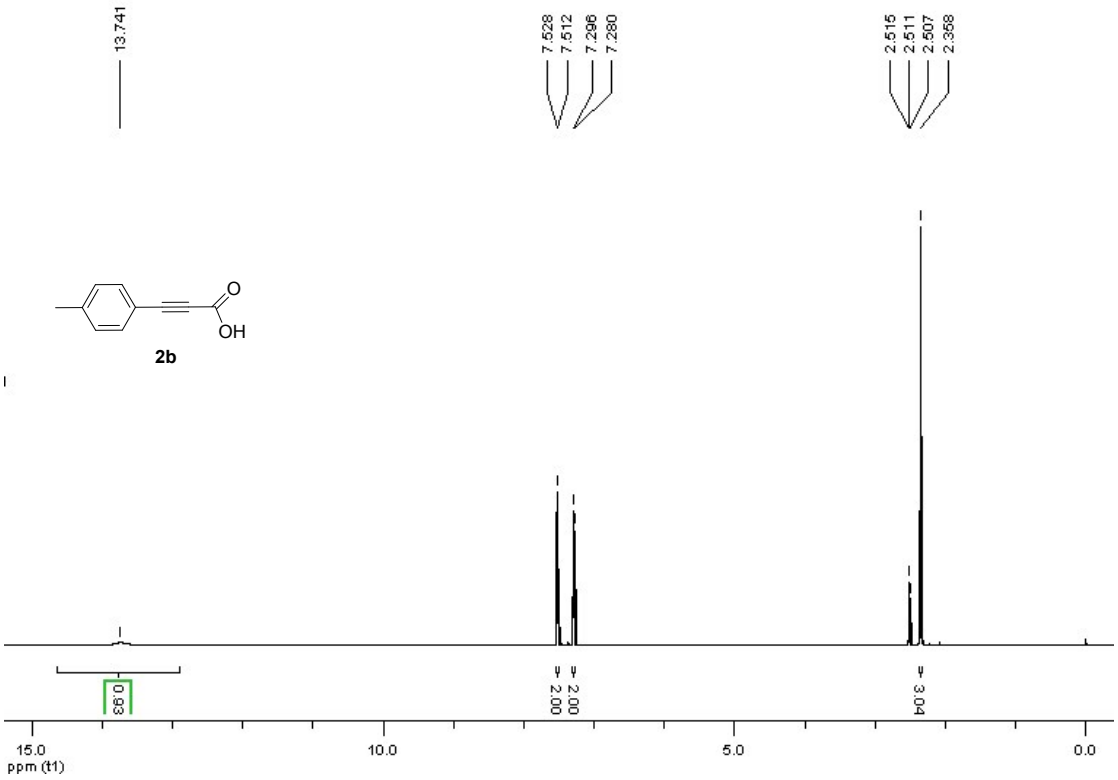




2a

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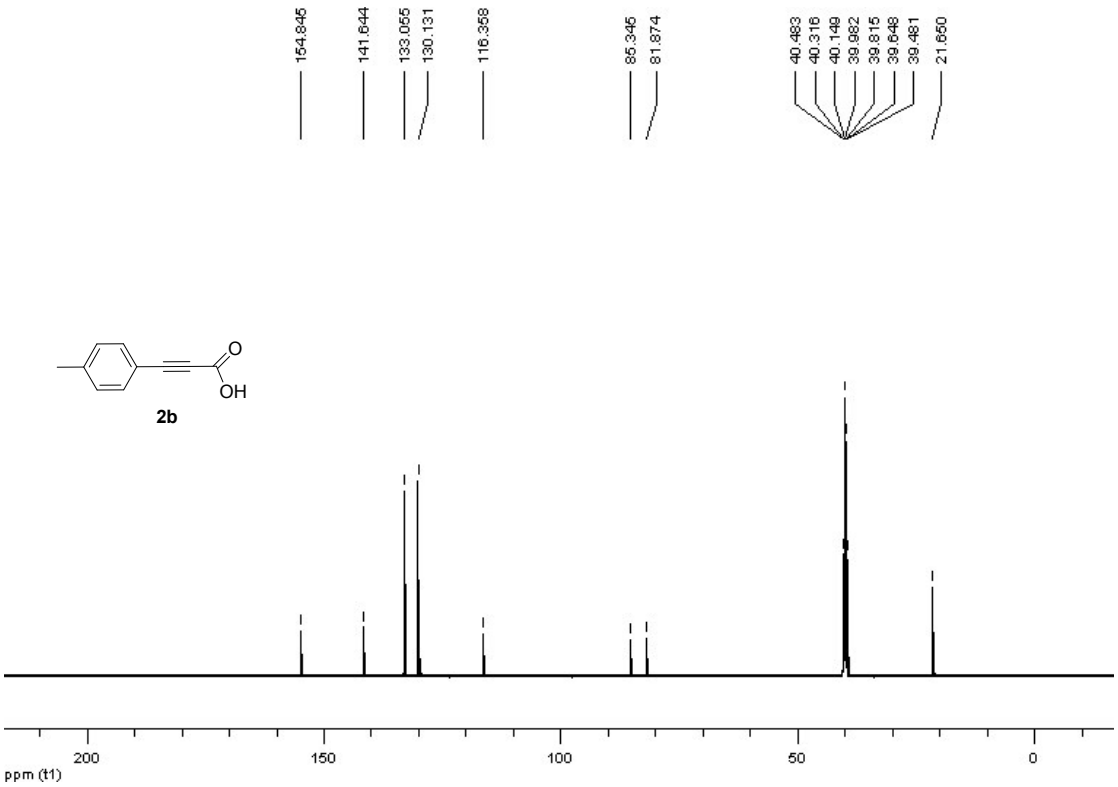
7.512
7.296
7.280
2.515
2.511
2.507
2.368
O
OH
2b
0.93
2.00
2.00
3.04
15.0
10.0
5.0
0.0
ppm (t1)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133.055
130.131
116.358
85.345
81.874
40.483
40.316
40.149
39.982
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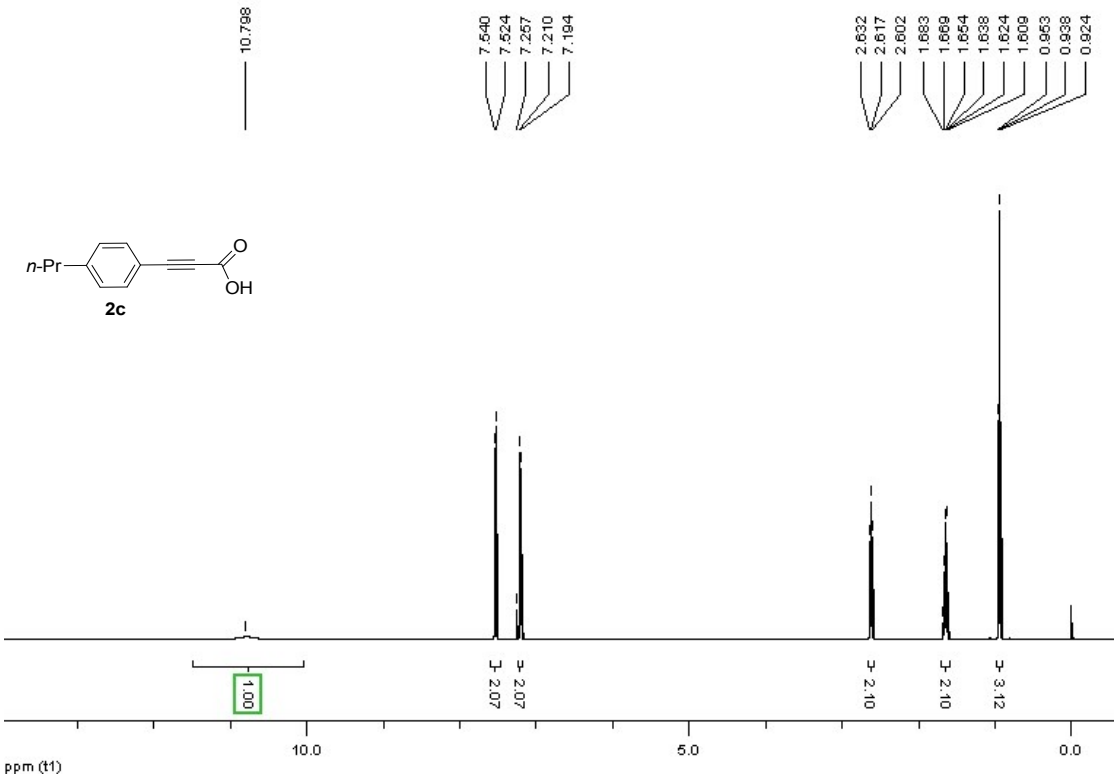
39.648
39.481
21.650
O
OH
2b
200
150
100
50
0
ppm (t1)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7.194
2.632
2.617
2.602
1.683
1.669
1.654
1.638
1.624
1.609
0.953
0.938
0.924
n-Pr
O
OH
2c
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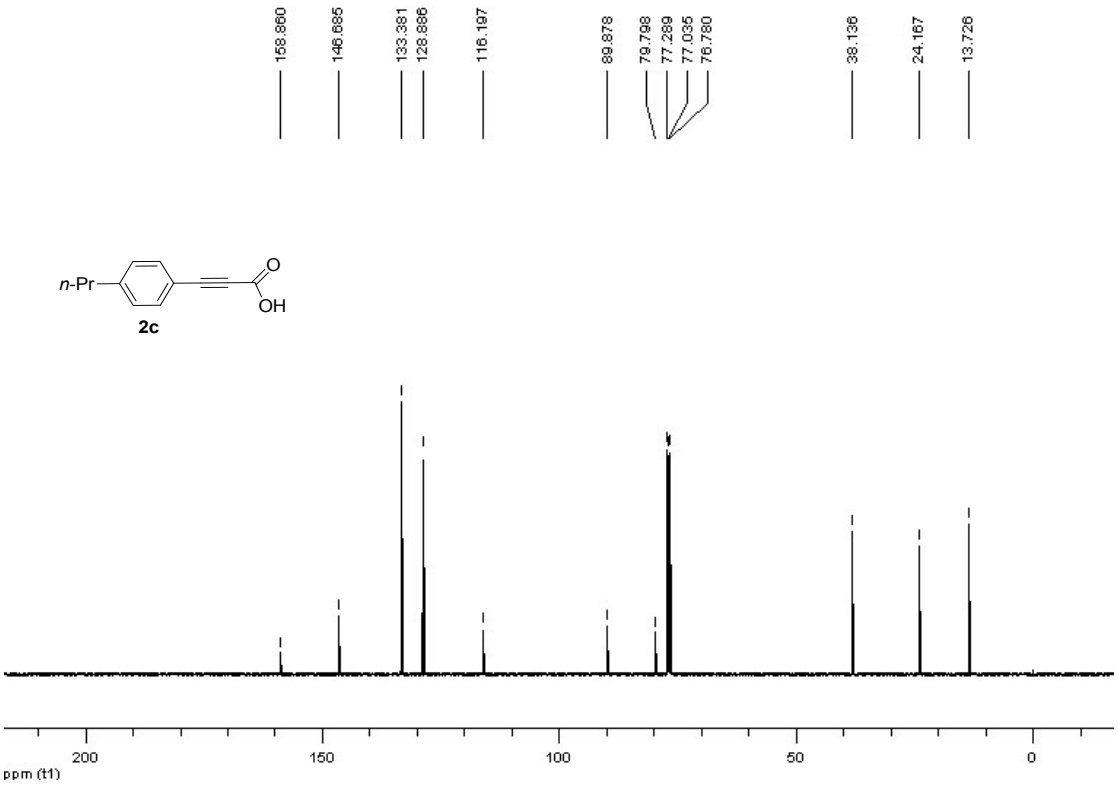
2.07
2.07
2.10
2.10
3.12
10.0
5.0
0.0
ppm (t1)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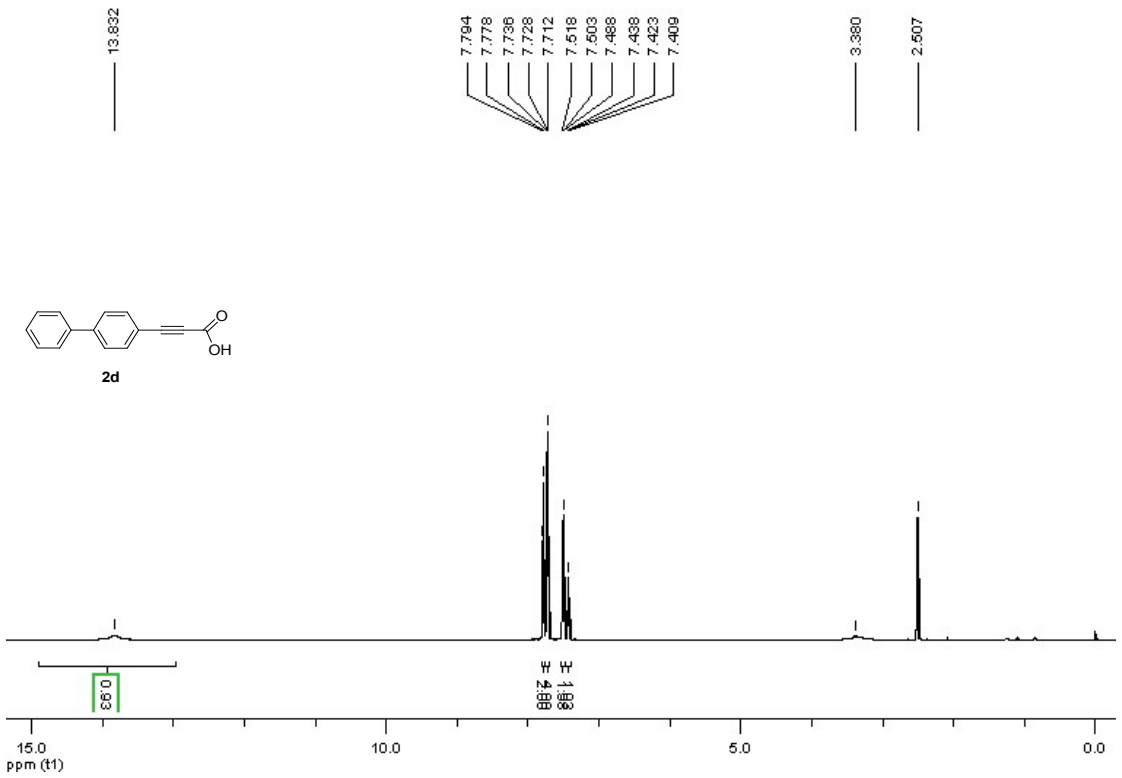
133.381
128.886
116.197
89.878
79.798
77.289
77.035
76.780
38.136
24.167
13.726
n-Pr
O
OH
2c
200
150
100
50
0
ppm (t1)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7.778
7.736
7.728
7.712
7.518
7.503
7.488
7.438
7.423
7.409
3.380
2.507
O
OH
2d
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4.00
1.89
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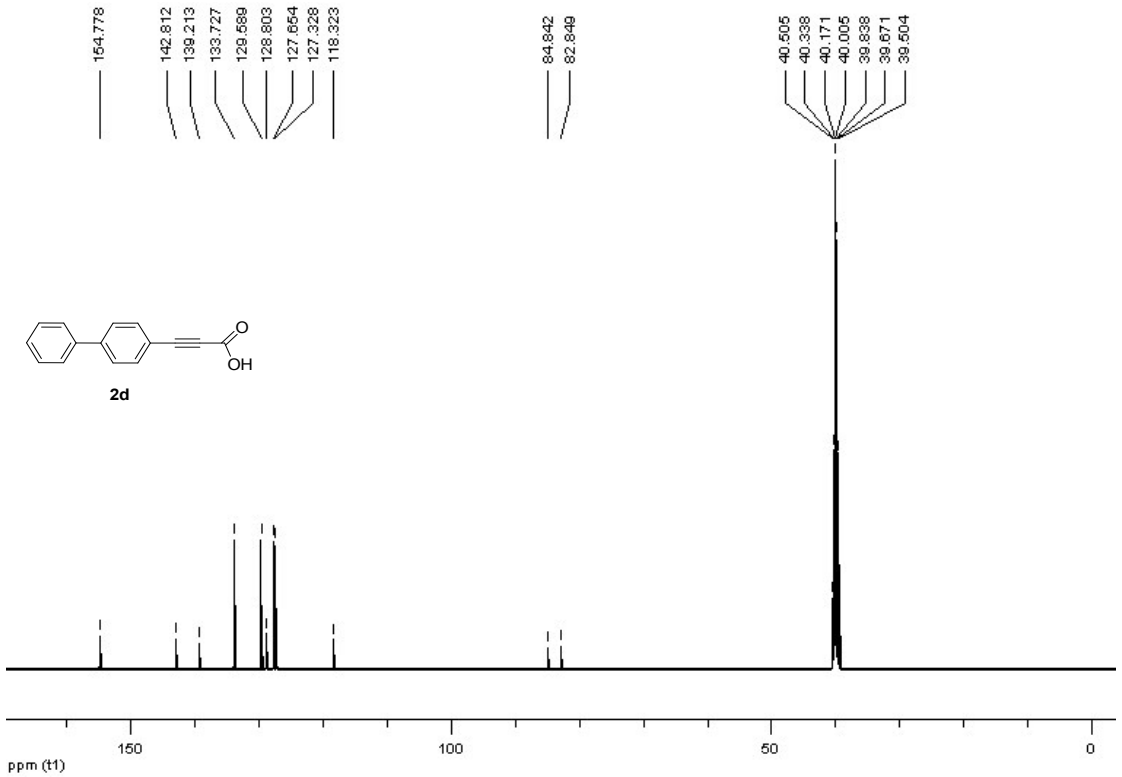
10.0
5.0
0.0
ppm (t1)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133.727
129.589
128.803
127.654
127.328
118.323
84.842
82.849
40.505
40.338
40.171
40.005
39.838
39.671
39.504
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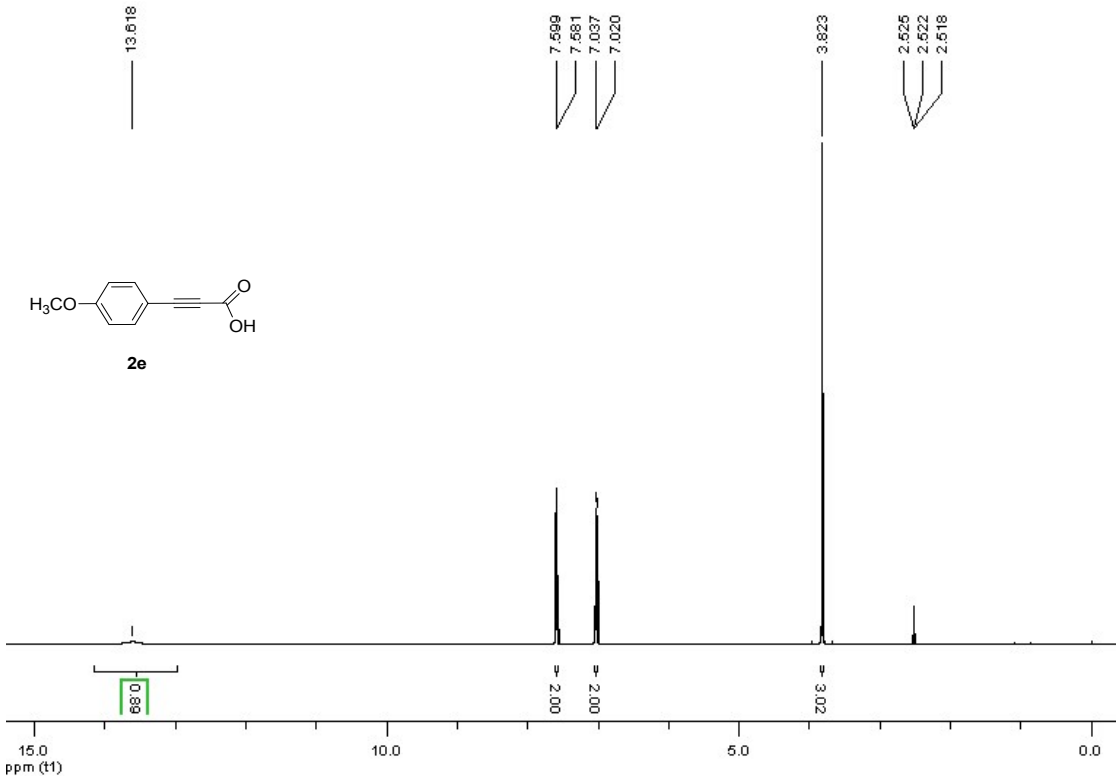
OH
2d
150
100
50
0
ppm (t1)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7.581
7.037
7.020
3.823
2.525
2.522
2.518
H3CO
O
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2e
0.89
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2.00
3.02
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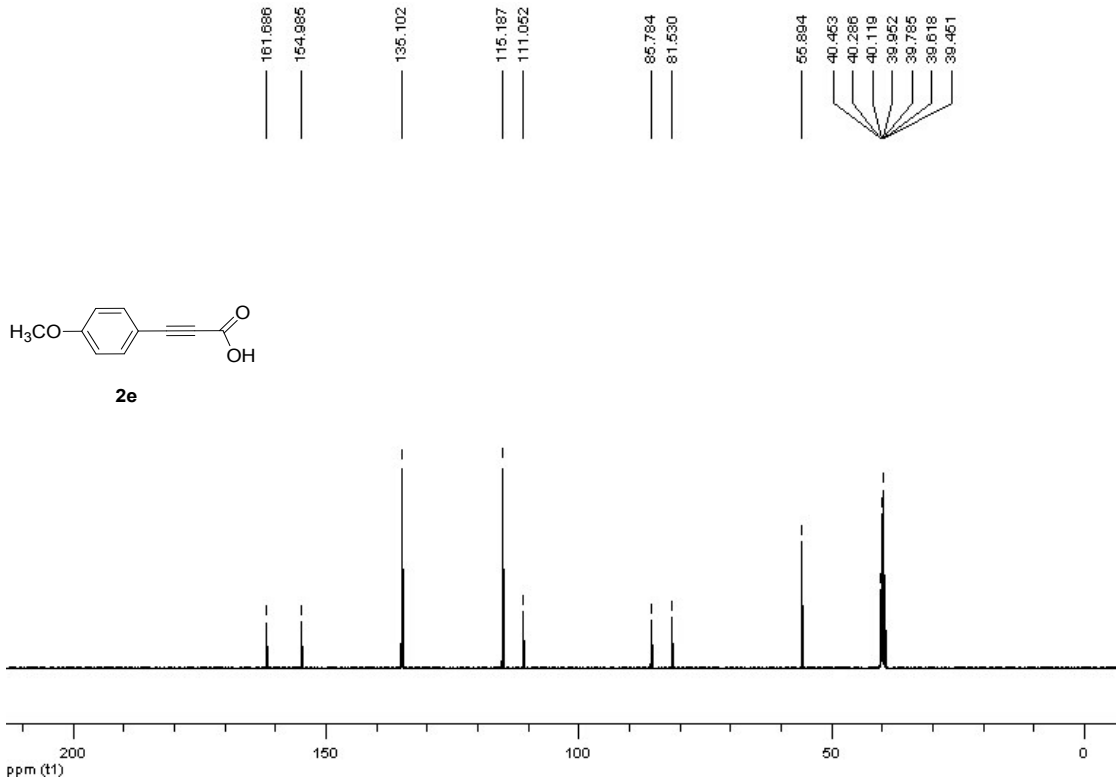
10.0
5.0
0.0
ppm (t1)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111.052
85.784
81.530
55.894
40.453
40.286
40.119
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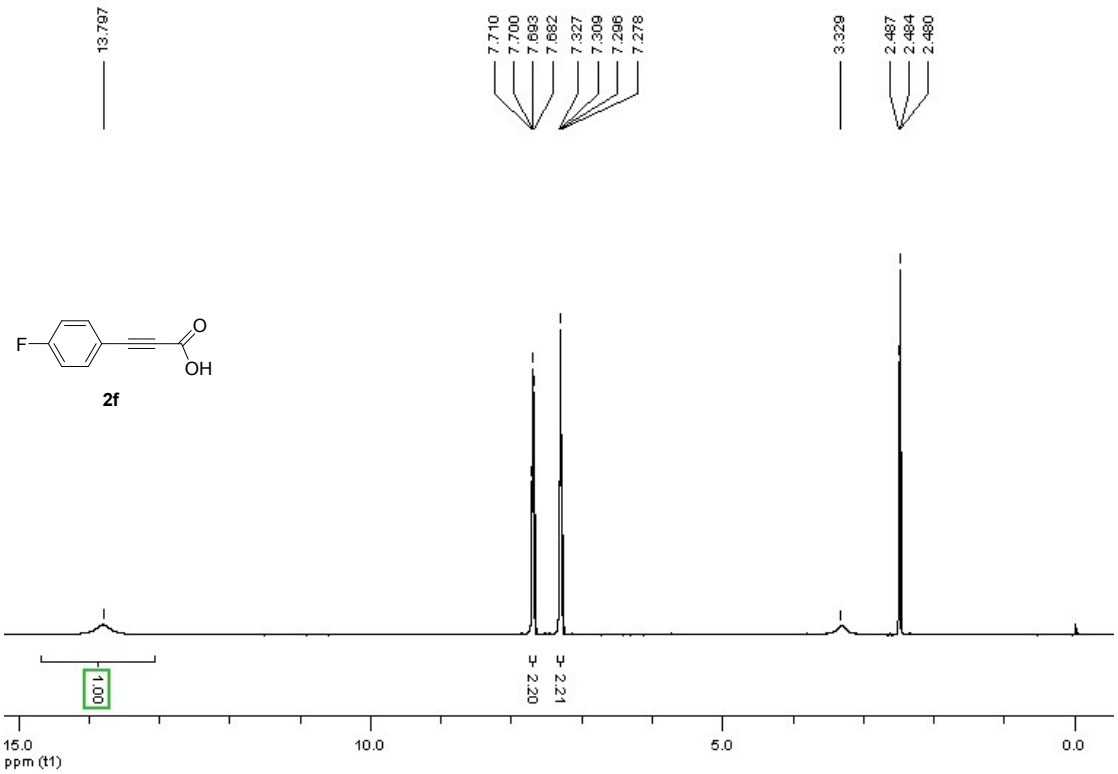
39.785
39.618
39.451
H3CO
O
OH
2e
200
150
100
50
0
ppm (t1)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7.327
7.309
7.296
7.278
3.329
2.487
2.484
2.480
F
O
OH
2f
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2.21
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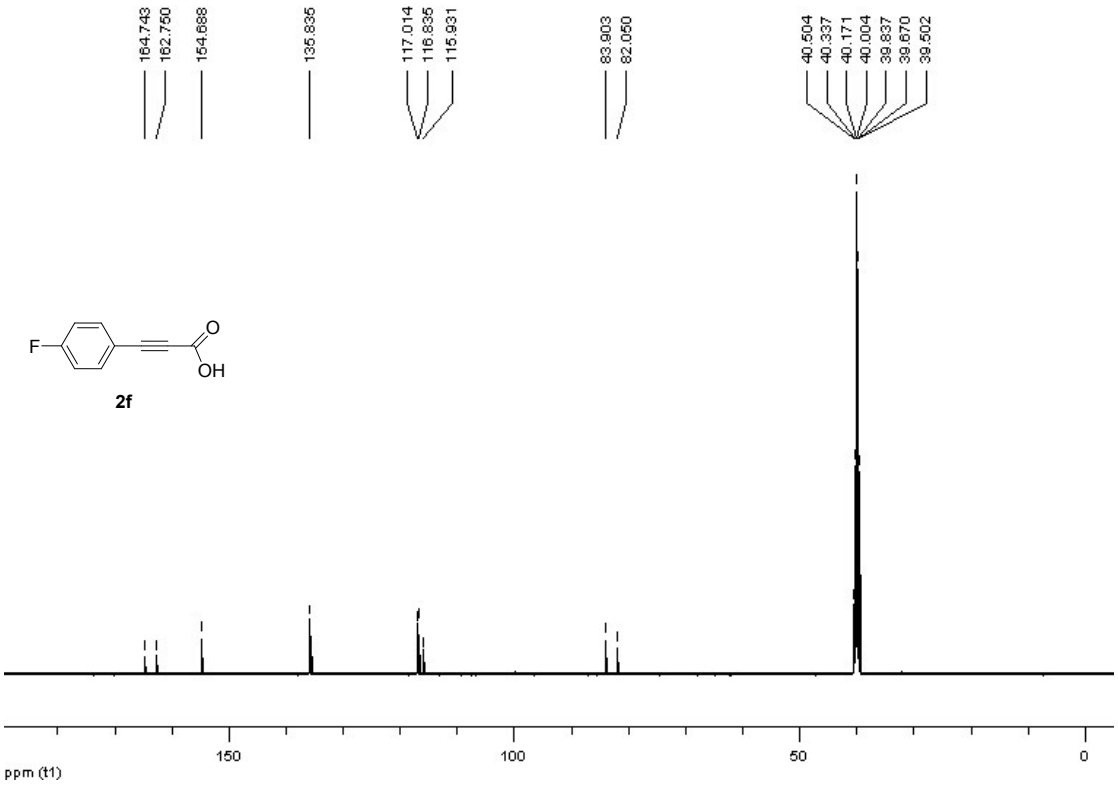
10.0
5.0
0.0
ppm (t1)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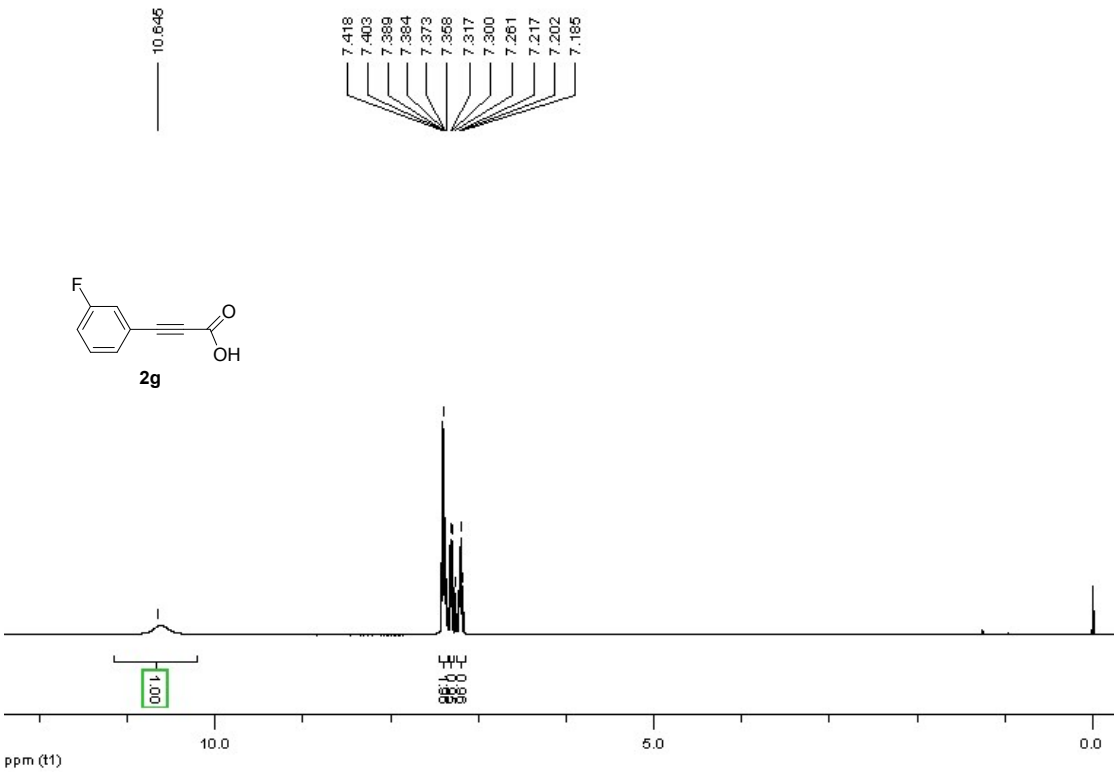
154.688
135.835
117.014
116.835
115.931
83.903
82.050
40.504
40.337
40.171
40.004
39.837
39.670
39.502
F
O
OH
2f
150
100
50
0
ppm (t1)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7.384
7.373
7.358
7.317
7.300
7.261
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7.202
7.185
F
O
OH
2g
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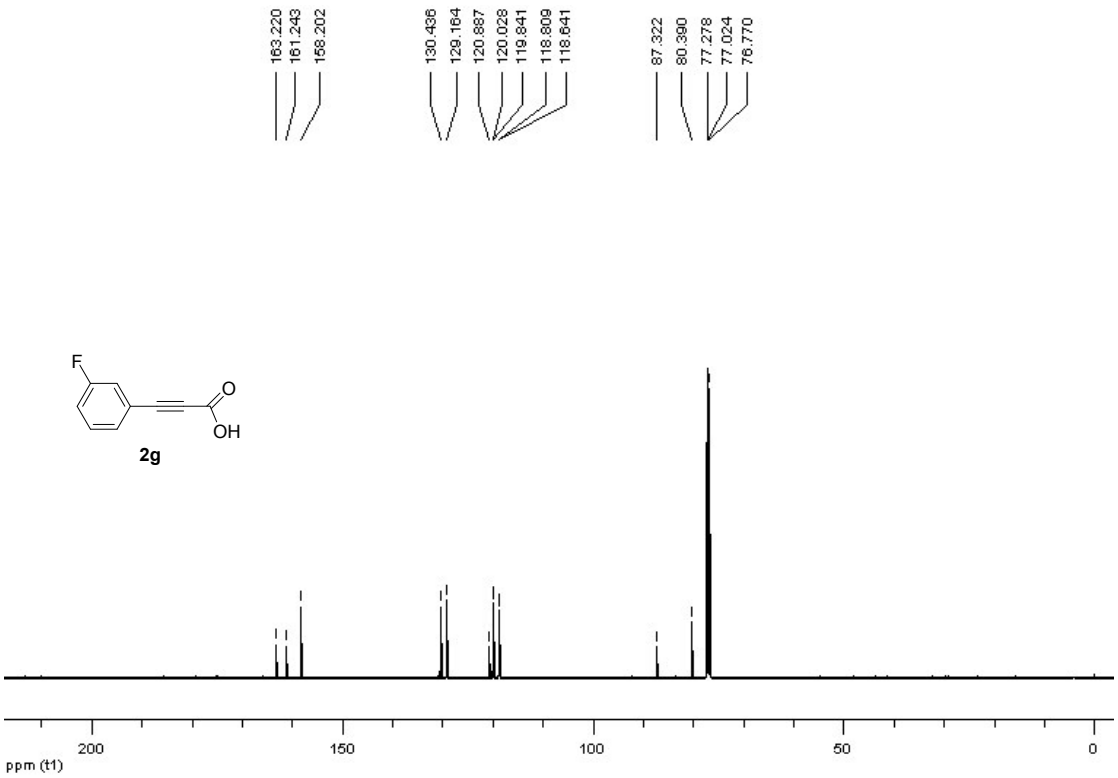
5.0
0.0
ppm (t1)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129.164
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120.028
119.841
118.809
118.641
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77.024
76.770
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O
OH
2g
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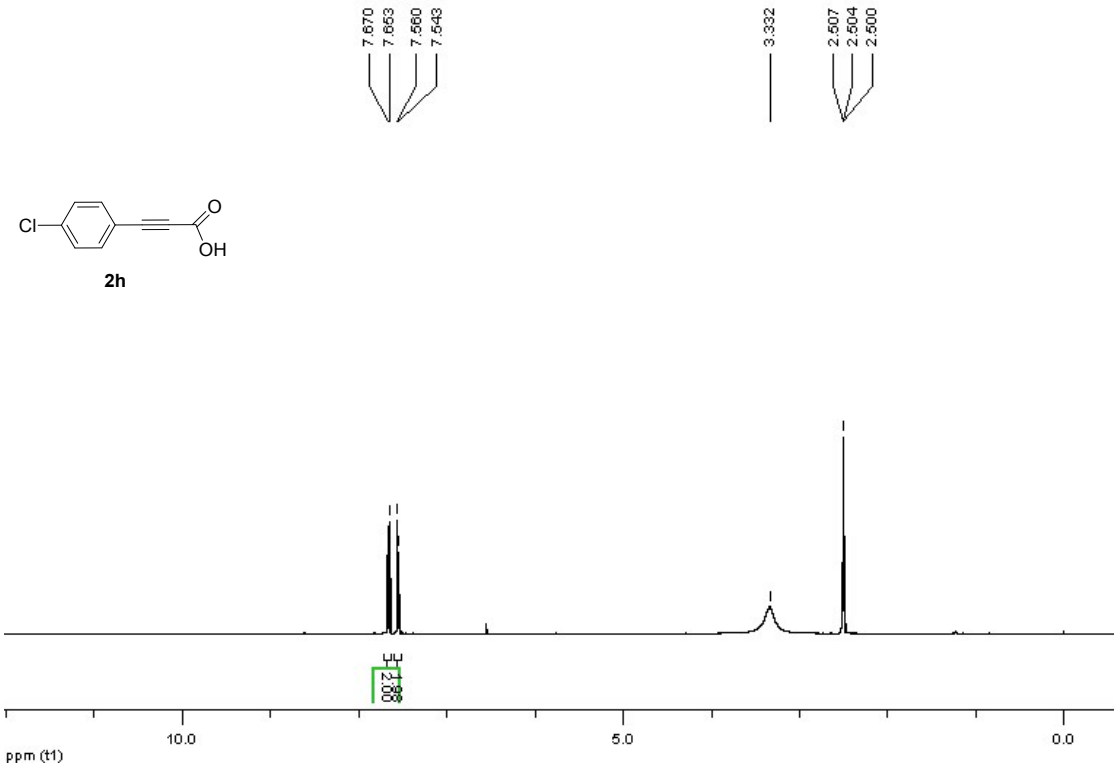
150
100
50
0
ppm (t1)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7.543
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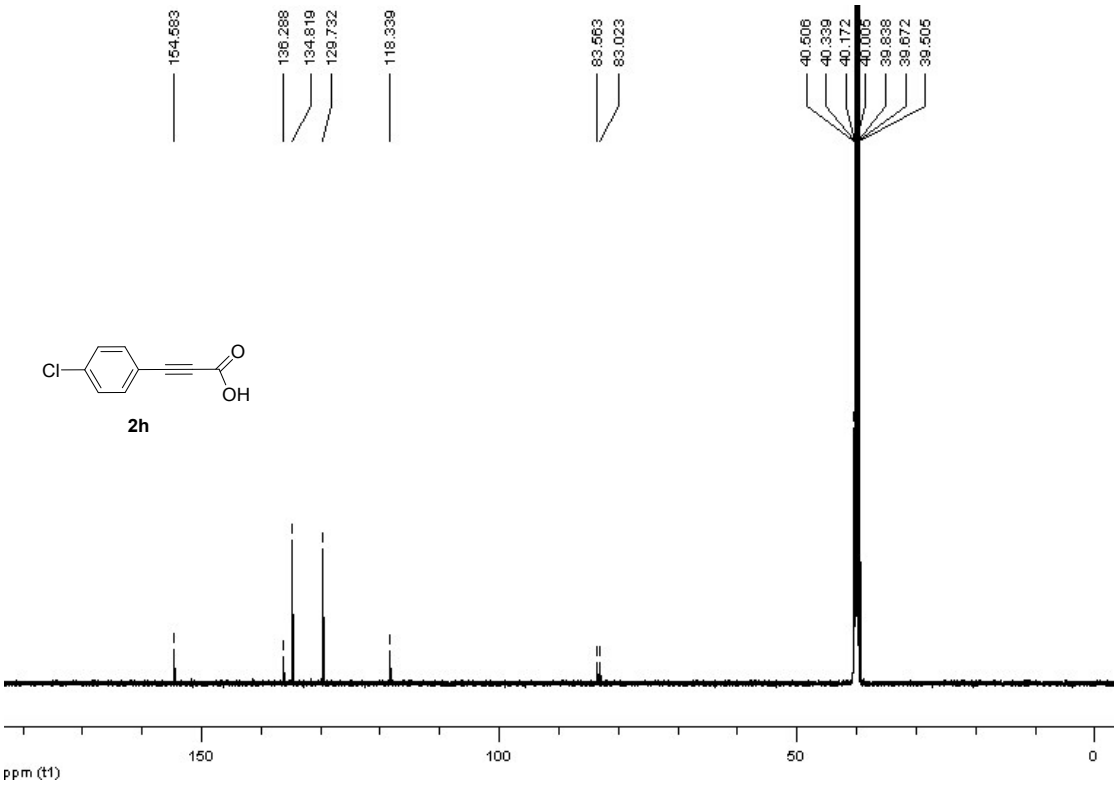
2.504
2.500
Cl
O
OH
2h
10.0
5.0
0.0
ppm (t1)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83.563
83.023
40.506
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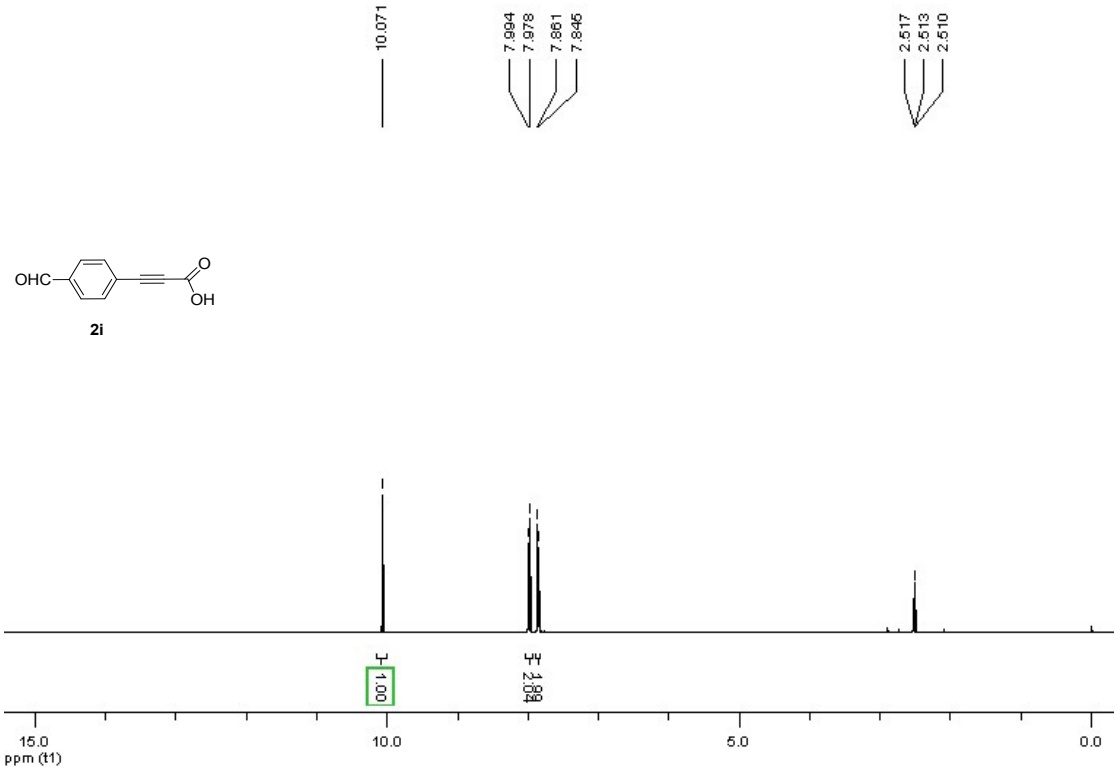
39.838
39.672
39.505
Cl
O
OH
2h
150
100
50
0
ppm (t1)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2.513
2.510
OHC
O
OH
2i
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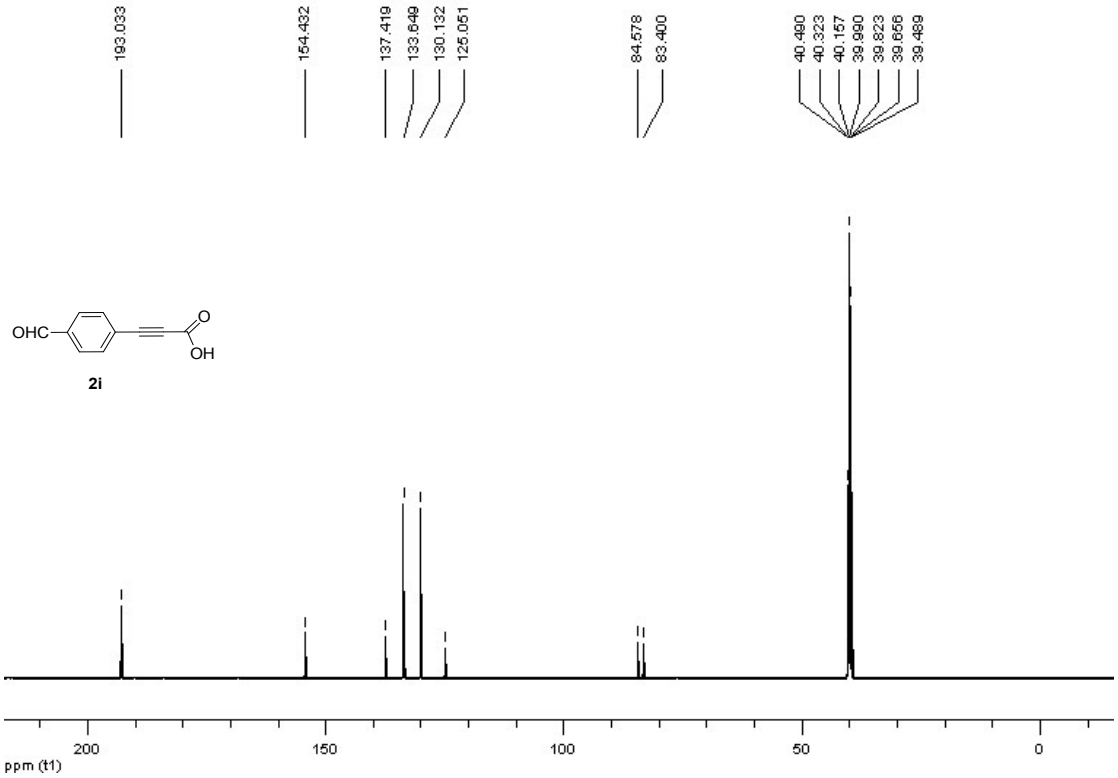
2.08
15.0
ppm (t1)
10.0
5.0
0.0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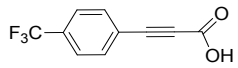
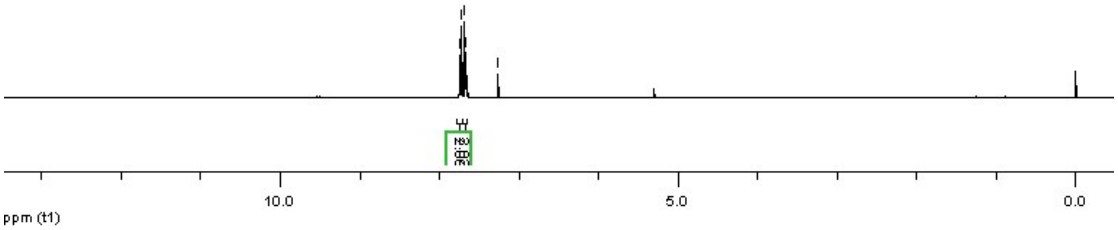
130.132
125.051
84.578
83.400
40.490
40.323
40.157
39.990
39.823
39.656
39.489
OHC
O
OH
2i
200
150
100
50
0
ppm (t1)


7.743
7.726
7.681
7.665
7.260


F3C
O
OH

2j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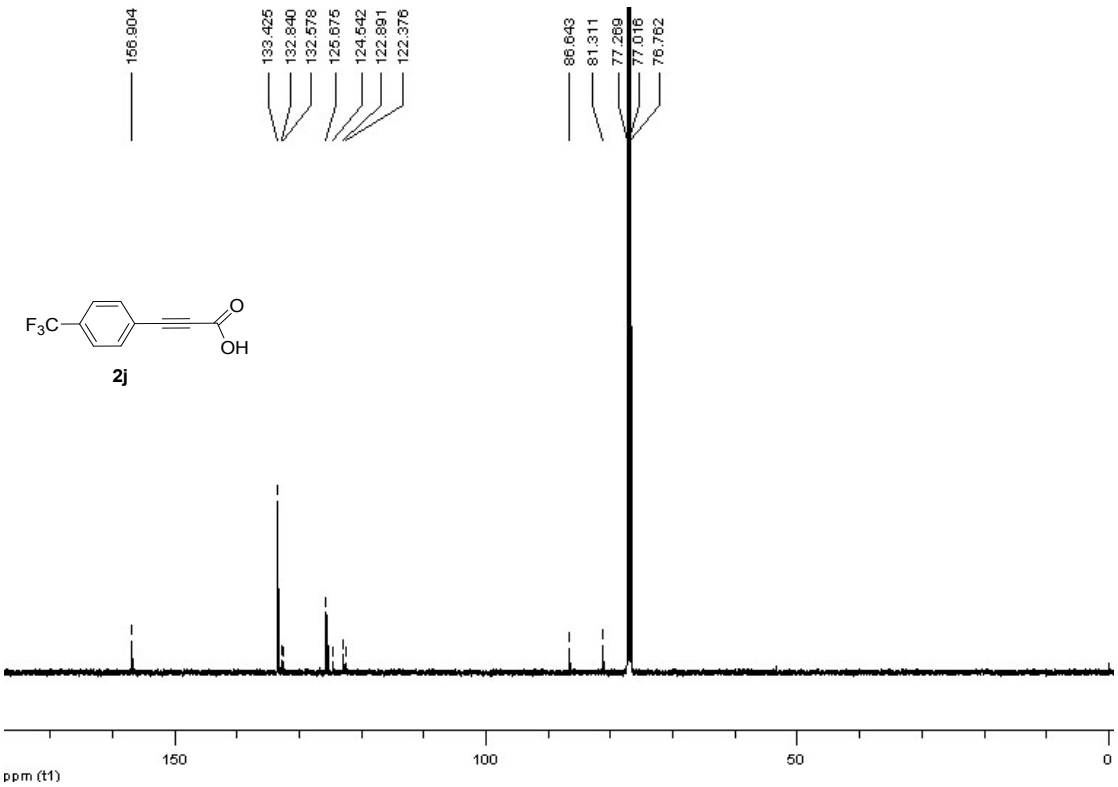
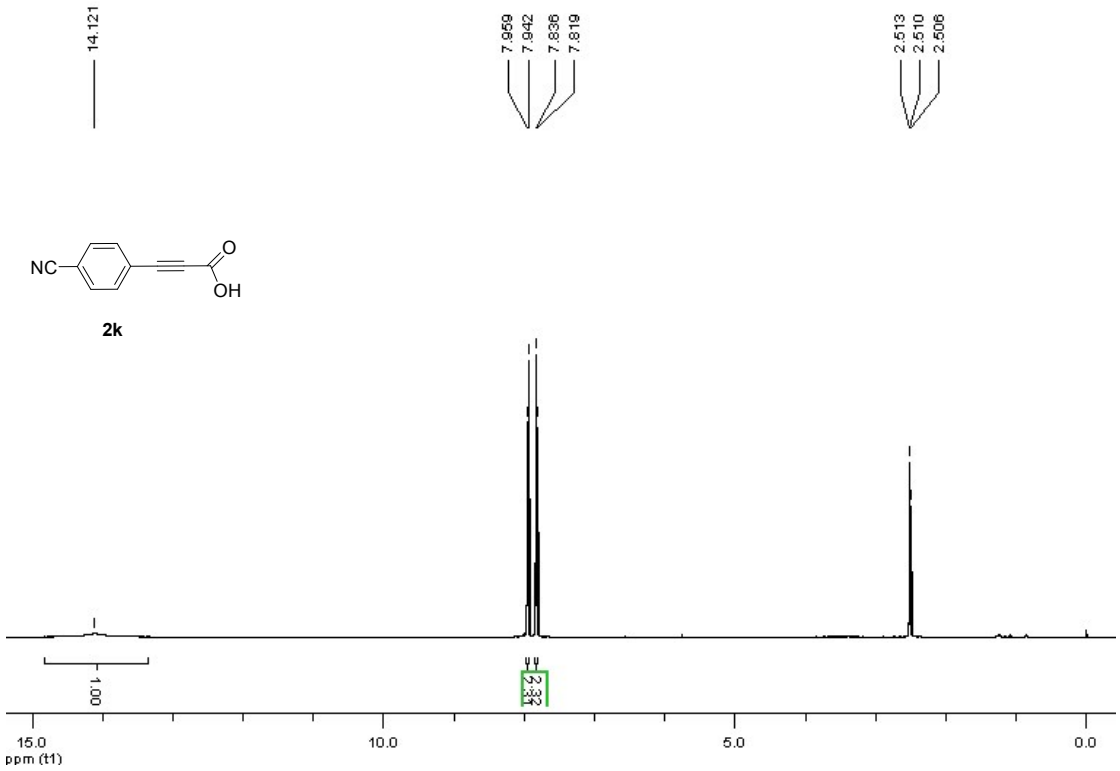
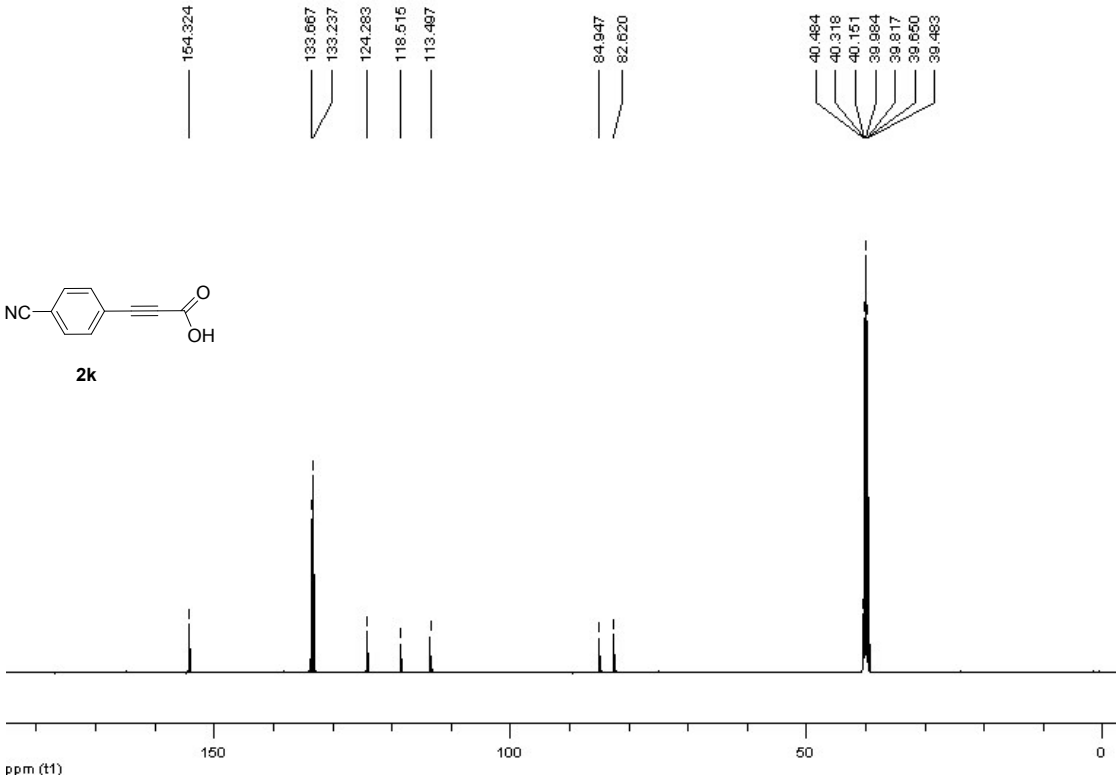
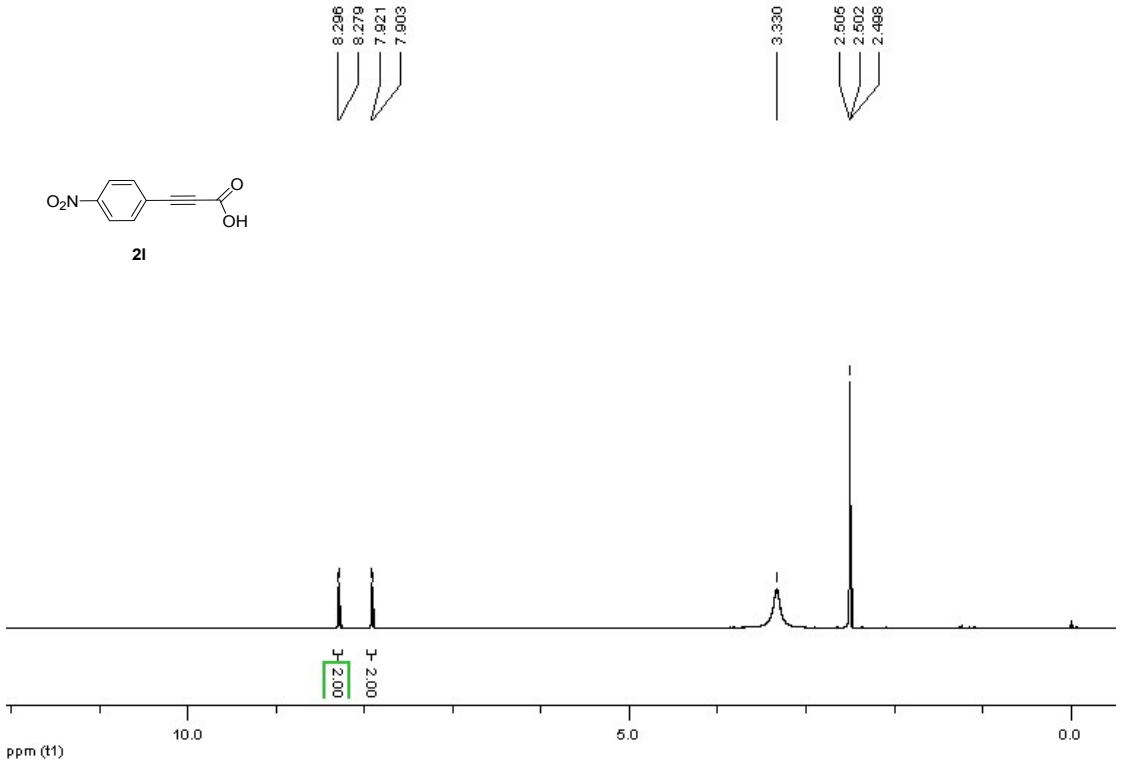

156.904
133.425
132.840
132.578
125.675
124.542
122.891
122.376
86.843
81.311
77.269
77.016
76.762
150
100
50
0
ppm (t1)

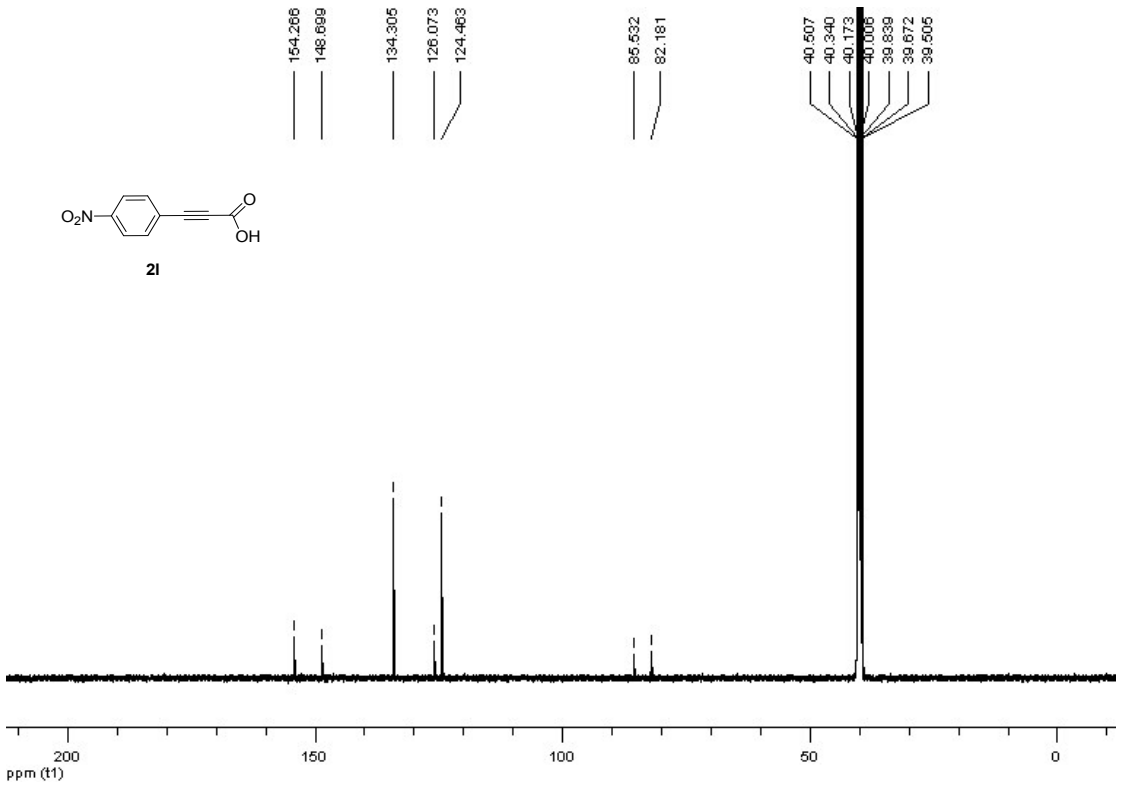
F3C
O
OH

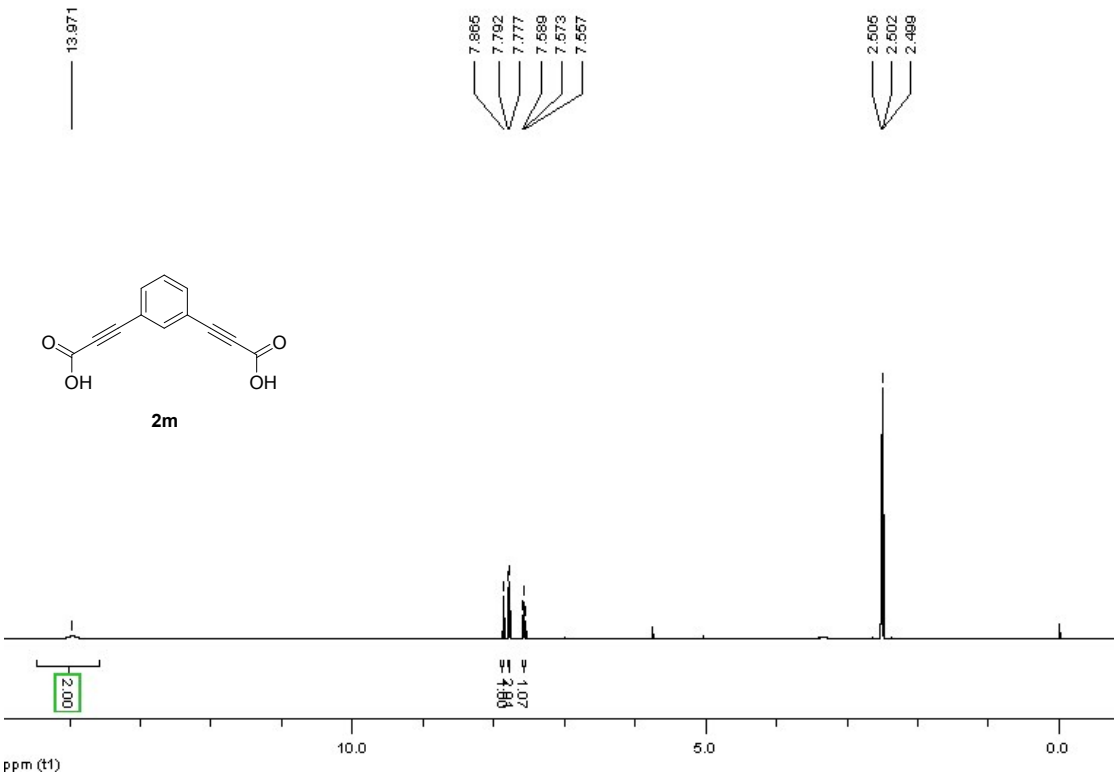
2j

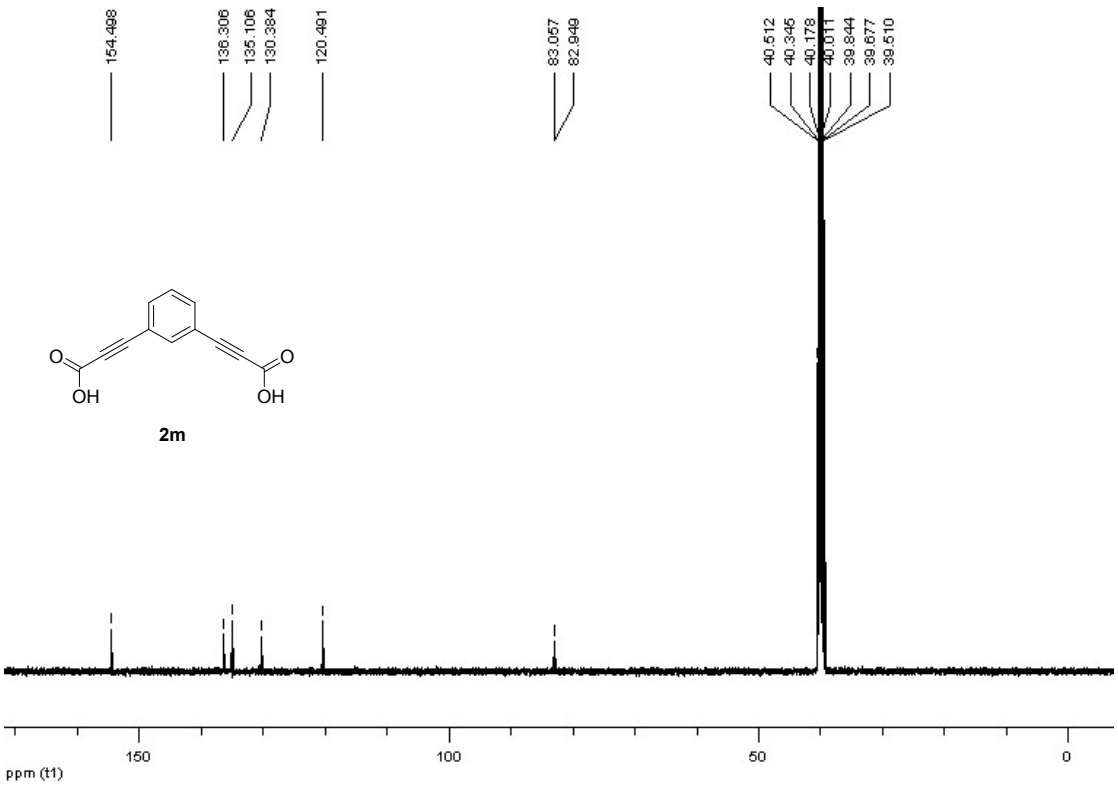

14.121
7.959
7.942
7.836
7.819
2.513
2.510
2.506
NC
O
OH
2k
1.00
2.33
15.0
10.0
5.0
0.0
ppm (t1)

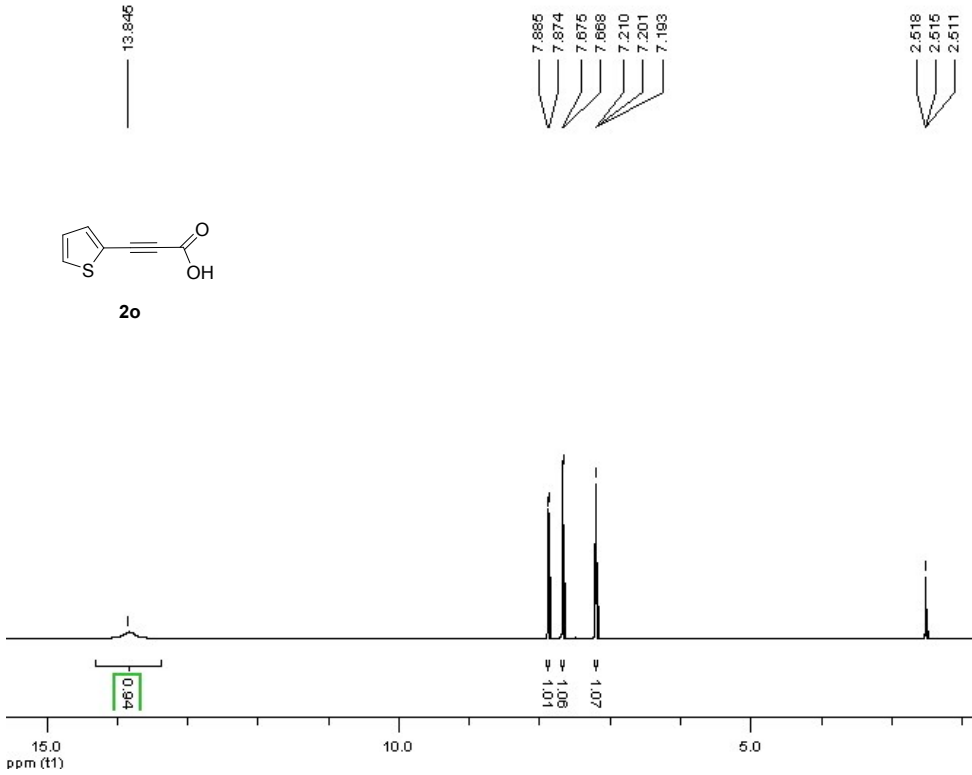

154.324
133.667
133.237
124.283
118.515
113.497
84.947
82.620
40.484
40.318
40.151
39.984
39.817
39.650
39.483
NC
O
OH
2k
150
100
50
0
ppm (t1)


8.296
8.279
7.921
7.903
3.330
2.505
2.502
2.498
O2N
O
OH
2l
2.00
2.00
10.0
5.0
0.0
ppm (t1)

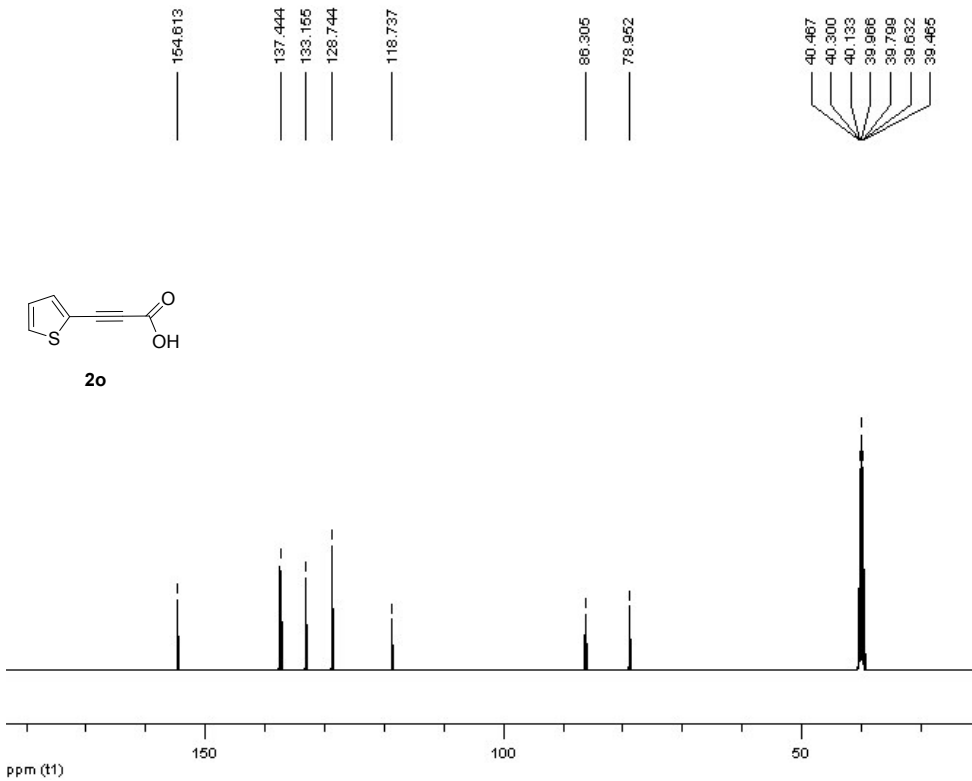

154.266
148.699
134.305
126.073
124.463
85.532
82.181
40.507
40.340
40.173
40.006
39.839
39.672
39.505
O2N
O
OH
2l
200
150
100
50
0
ppm (t1)


13.971
7.865
7.792
7.777
7.589
7.573
7.557
2.505
2.502
2.499
O
OH
O
OH
2m
2.00
2.14
1.07
10.0
5.0
0.0
ppm (t1)

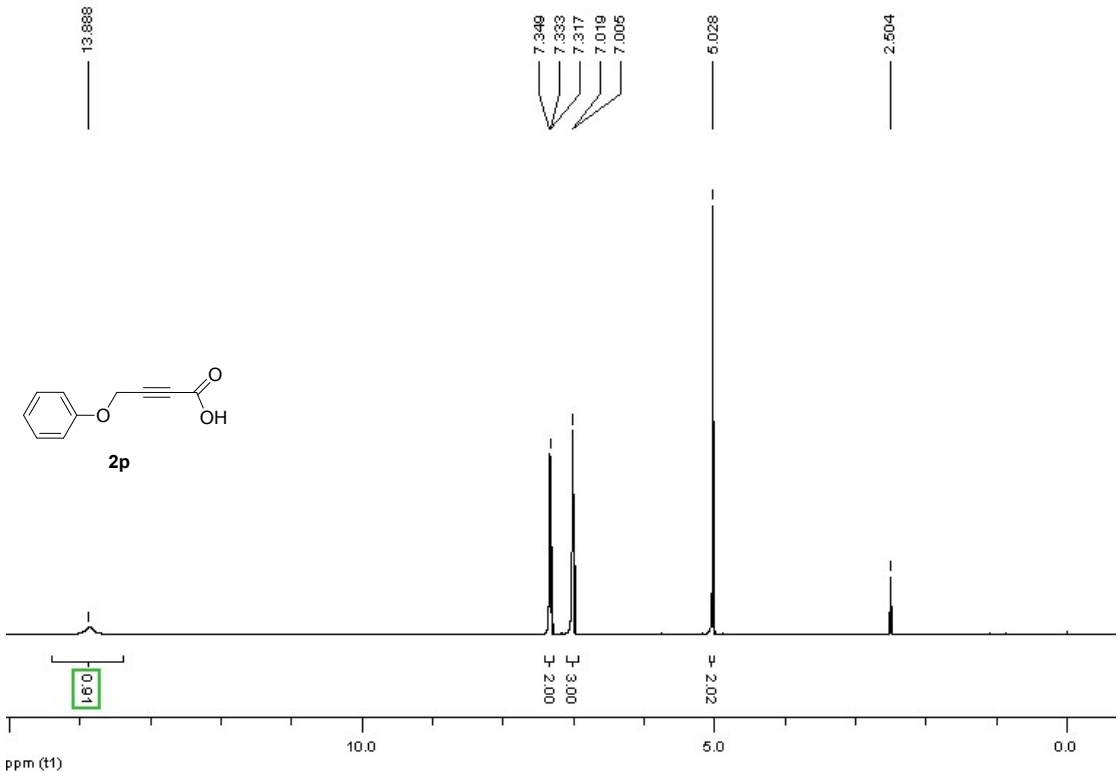

154.498
136.306
135.106
130.384
120.491
83.057
82.949
40.512
40.345
40.178
40.011
39.844
39.677
39.510
O
OH
O
OH
2m
150
100
50
0
ppm (t1)

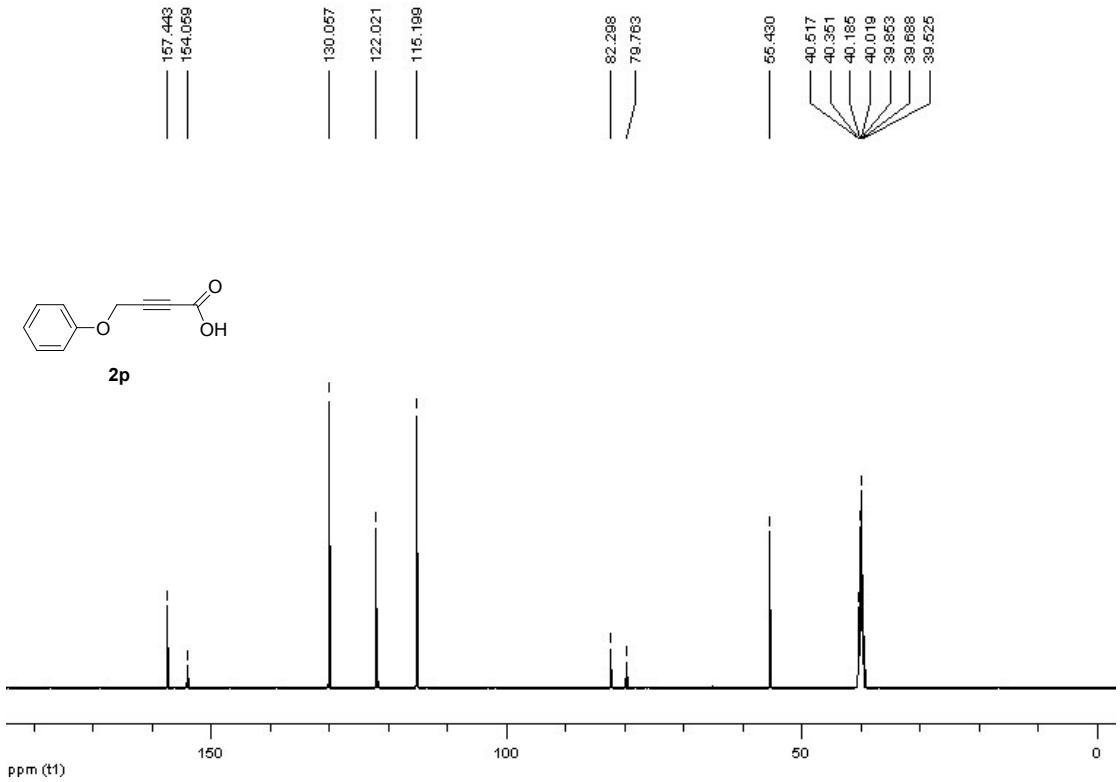

13.845
7.885
7.874
7.675
7.668
7.210
7.201
7.193
2.518
2.515
2.511
O
S
OH
0.94
1.01
1.06
1.07
15.0
10.0
5.0
0.0
ppm (t1)

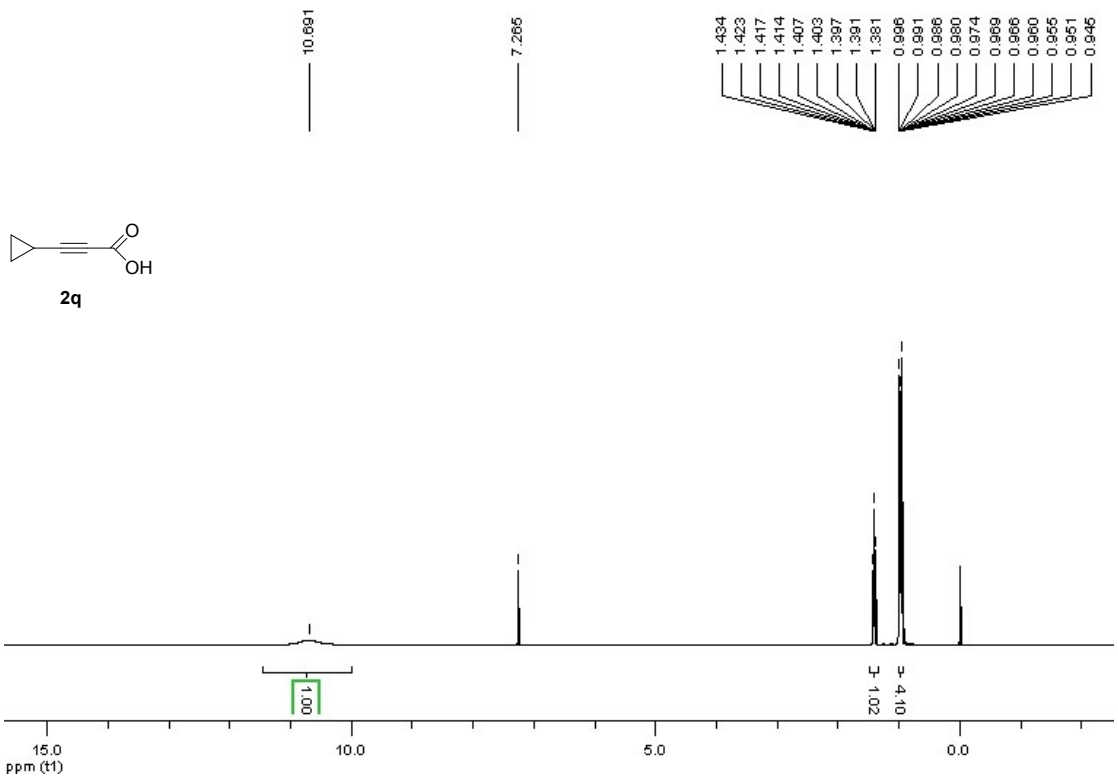
2o


154.613
137.444
133.155
128.744
118.737
88.305
78.952
40.467
40.300
40.133
39.966
39.799
39.632
39.465
O
S
OH
150
100
50
0
ppm (t1)

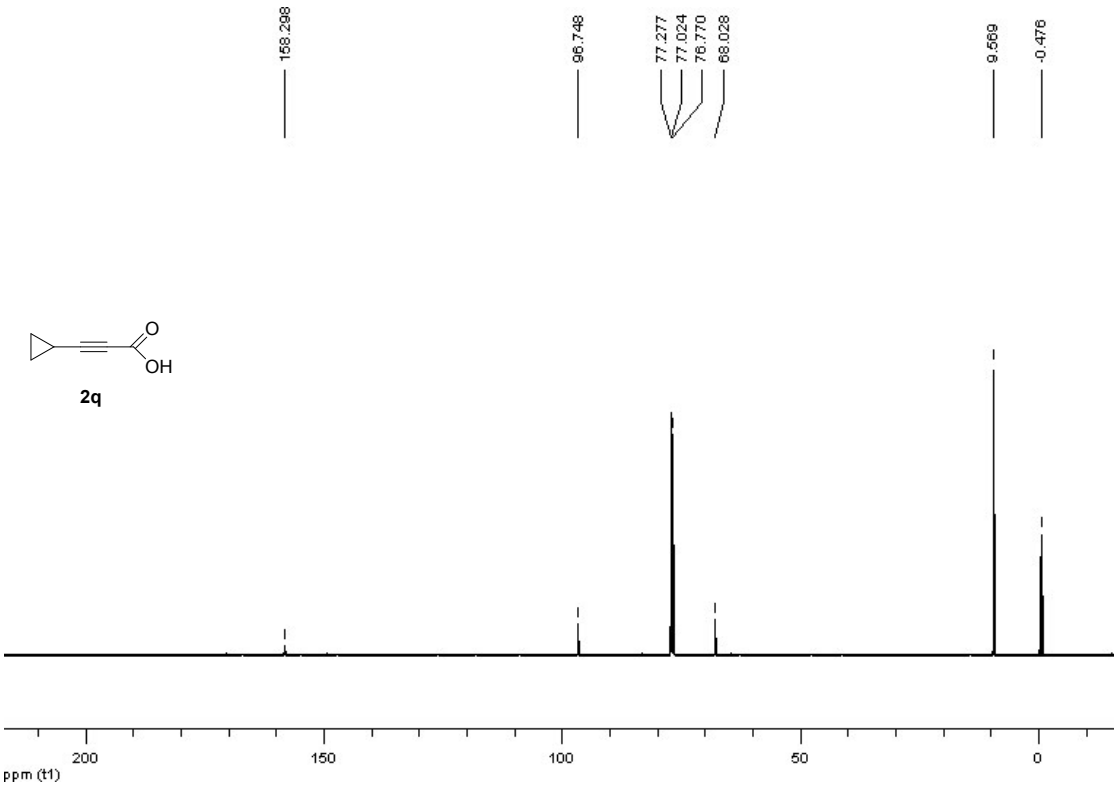
2o


13.888
7.349
7.333
7.317
7.019
7.005
5.028
2.504
O
O
OH
2p
0.91
2.00
3.00
2.02
10.0
5.0
0.0
ppm (t1)

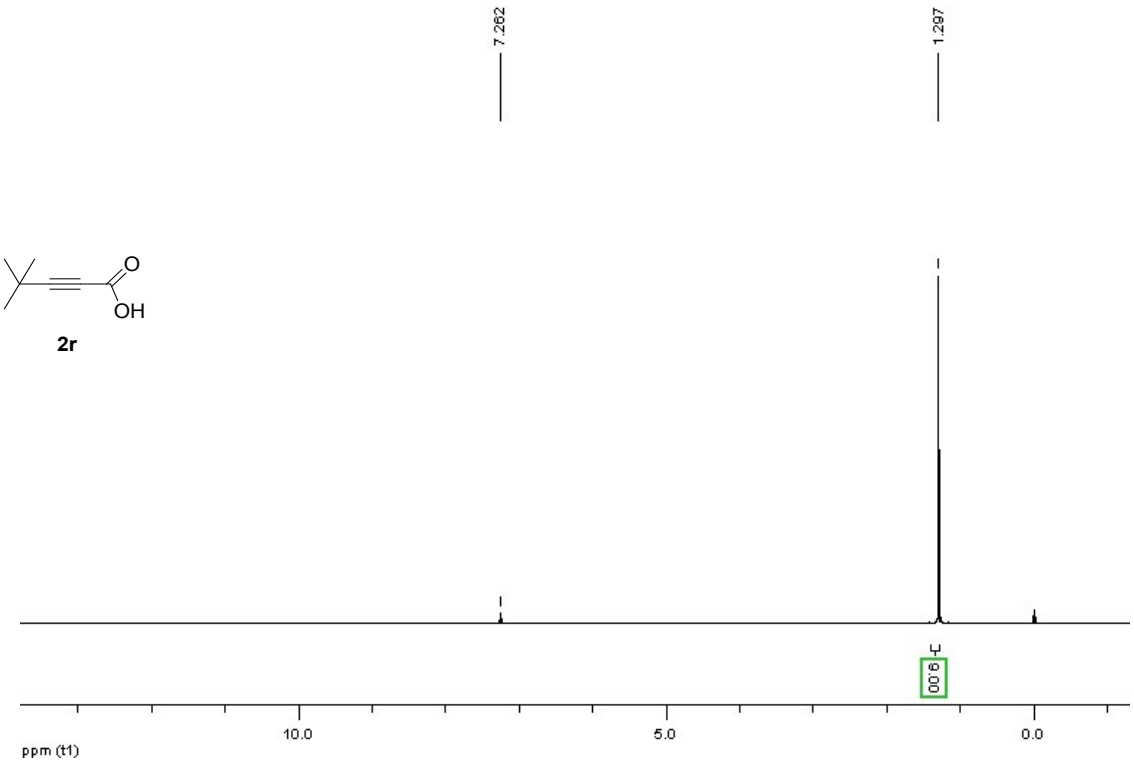

157.443
154.059
130.057
122.021
115.199
82.298
79.763
55.430
40.517
40.351
40.185
40.019
39.853
39.688
39.525
O
O
OH
2p
150
100
50
0
ppm (t1)

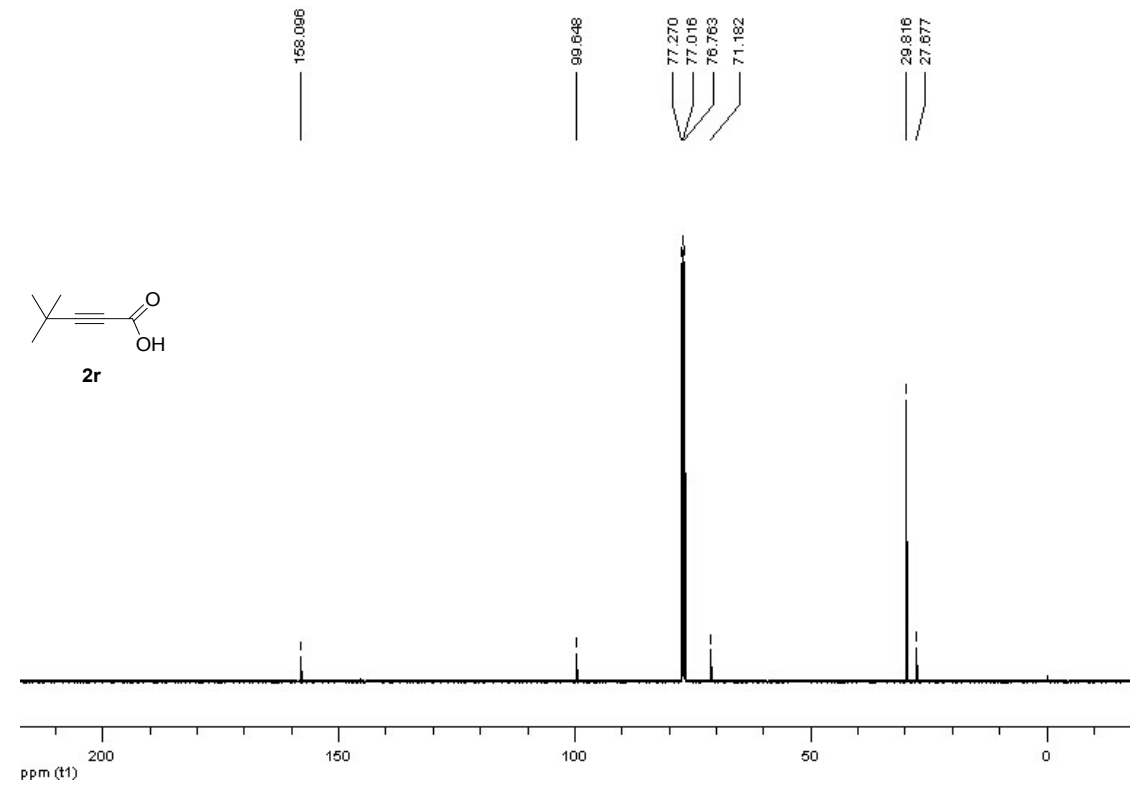

10.691
7.265
1.434
1.423
1.417
1.414
1.407
1.403
1.397
1.391
1.381
0.996
0.991
0.986
0.980
0.974
0.969
0.966
0.960
0.955
0.951
0.945
O
OH
1.00
1.02
4.10
15.0
ppm (t1)
10.0
5.0
0.0

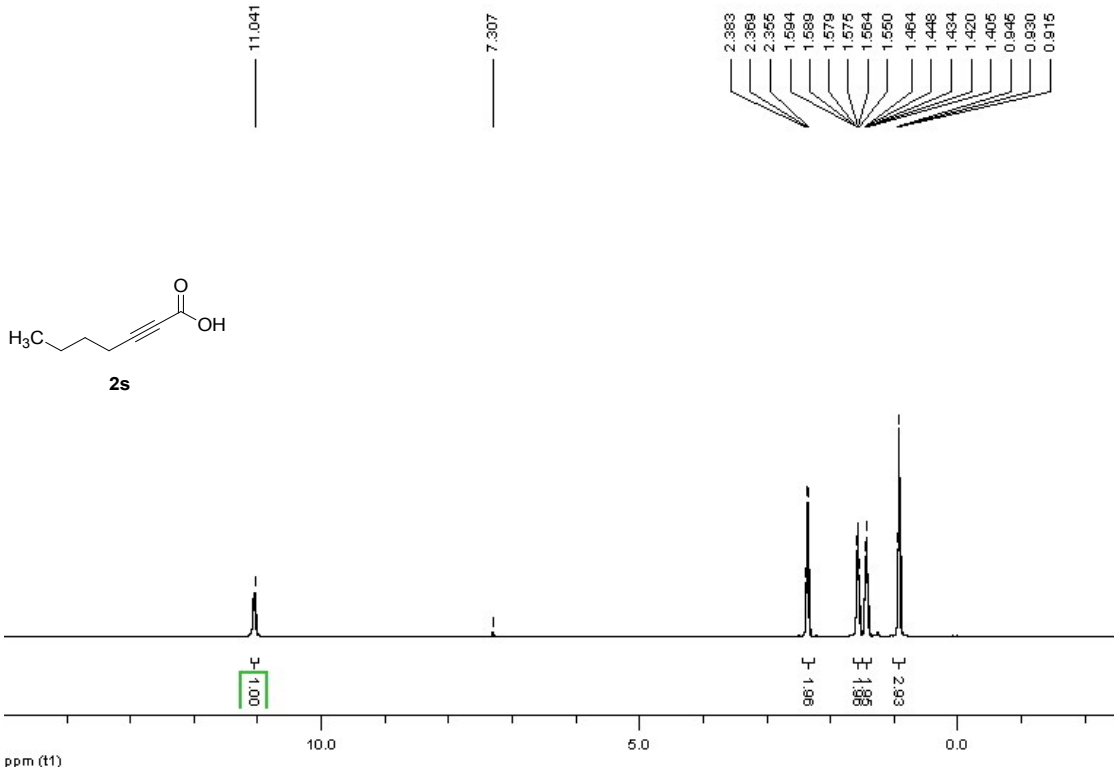
2q

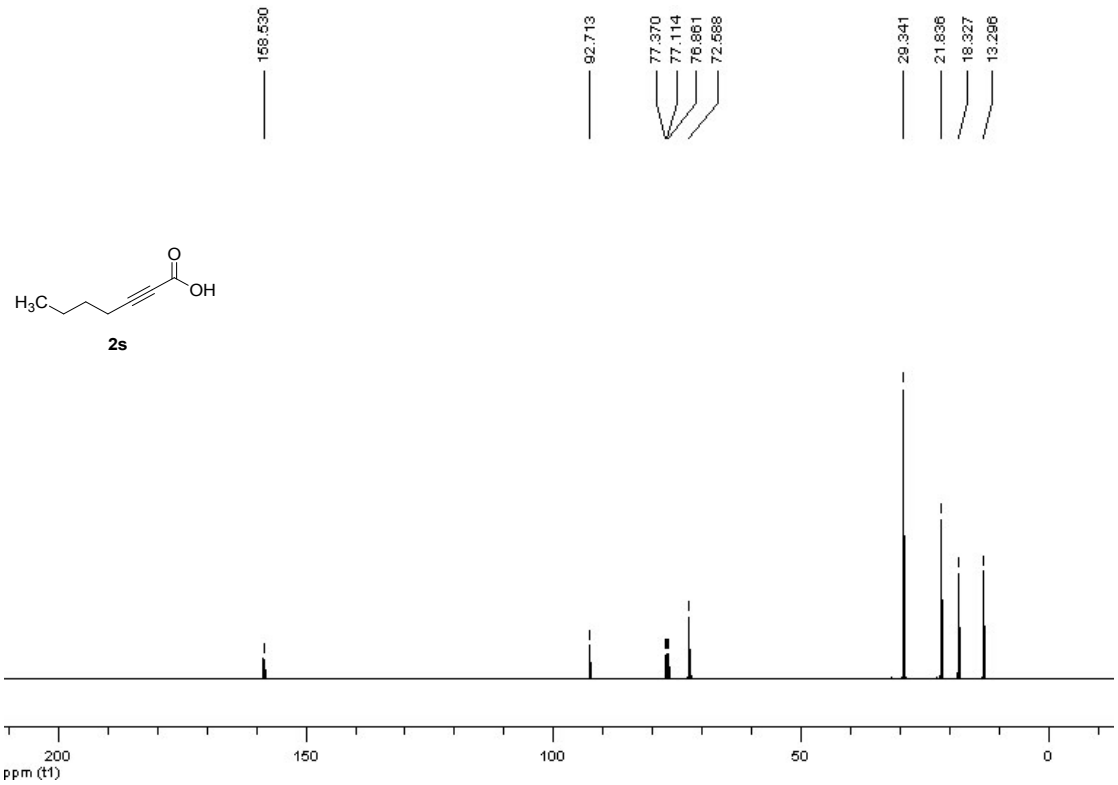

158.298
96.748
77.277
77.024
76.770
68.028
9.569
-0.476
O
OH
200
ppm (t1)
150
100
50
0

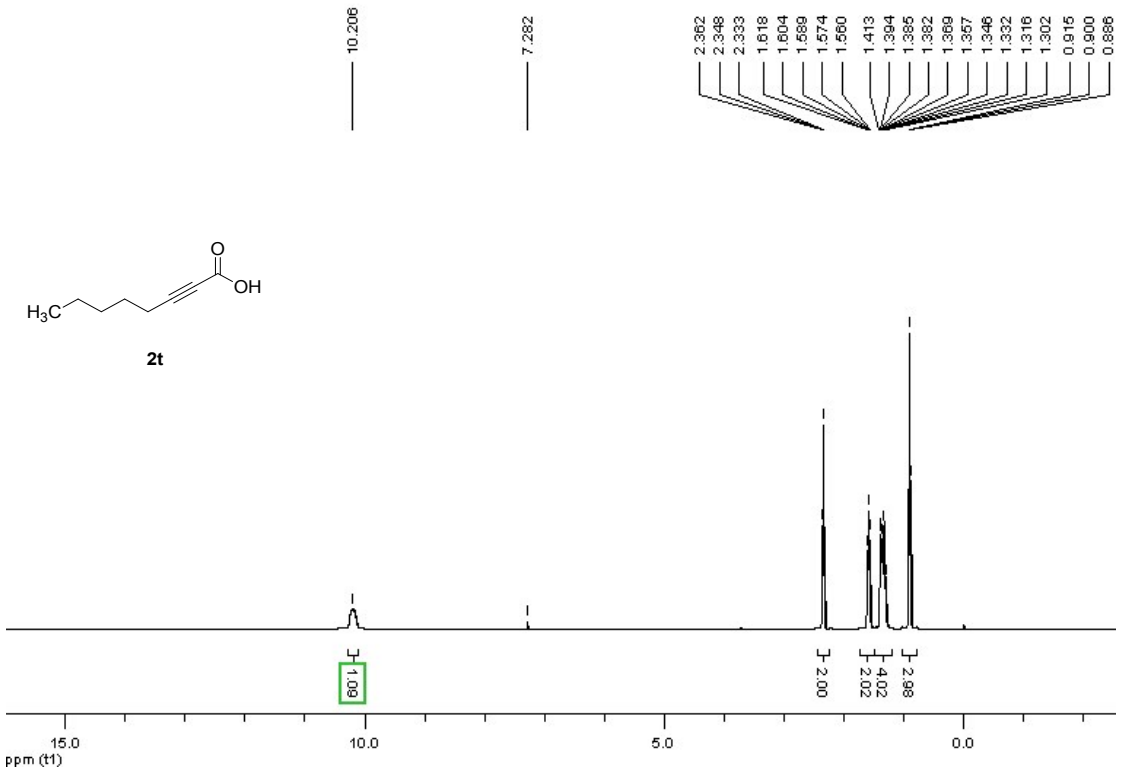
2q


7.262
1.297
O
OH
2r
9.00
10.0
5.0
0.0
ppm (t1)

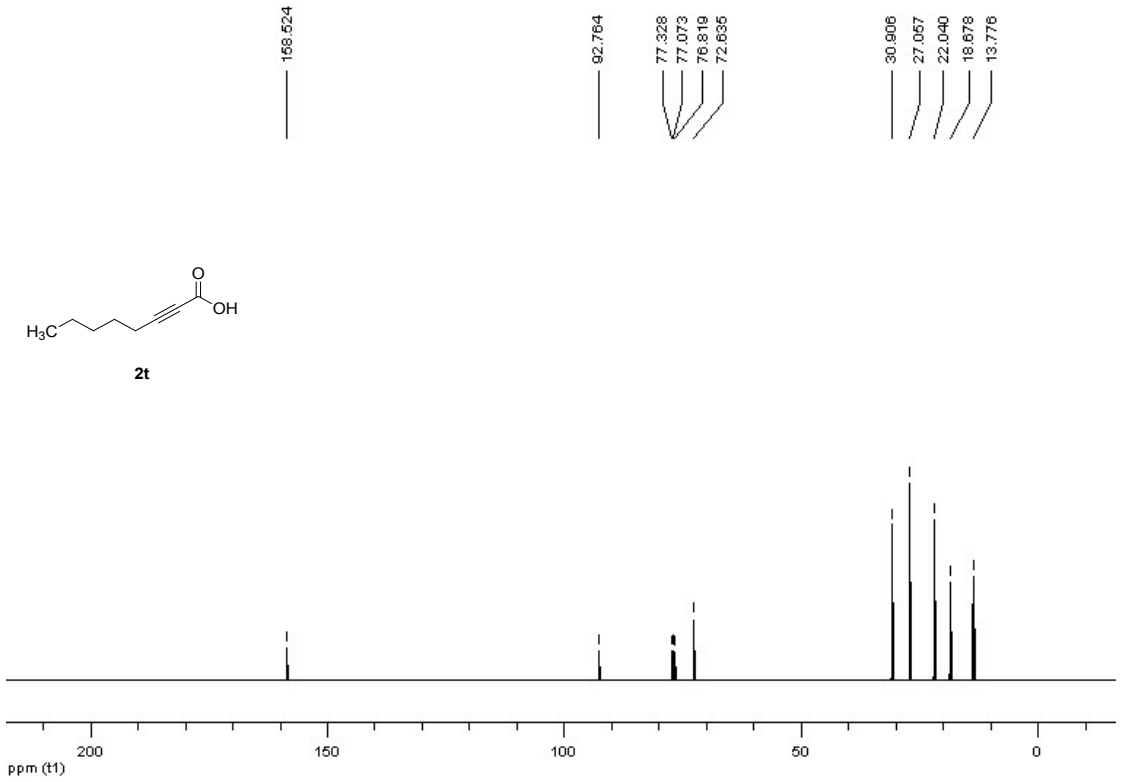

158.096
99.648
77.270
77.016
76.763
71.182
29.816
27.677
O
OH
2r
200
150
100
50
0
ppm (t1)


11.041
7.307
2.383
2.369
2.355
1.594
1.589
1.579
1.575
1.564
1.550
1.464
1.448
1.434
1.420
1.405
0.945
0.930
0.915
O
OH
H3C
2s
1.00
1.96
1.98
2.93
10.0
5.0
0.0
ppm (t1)

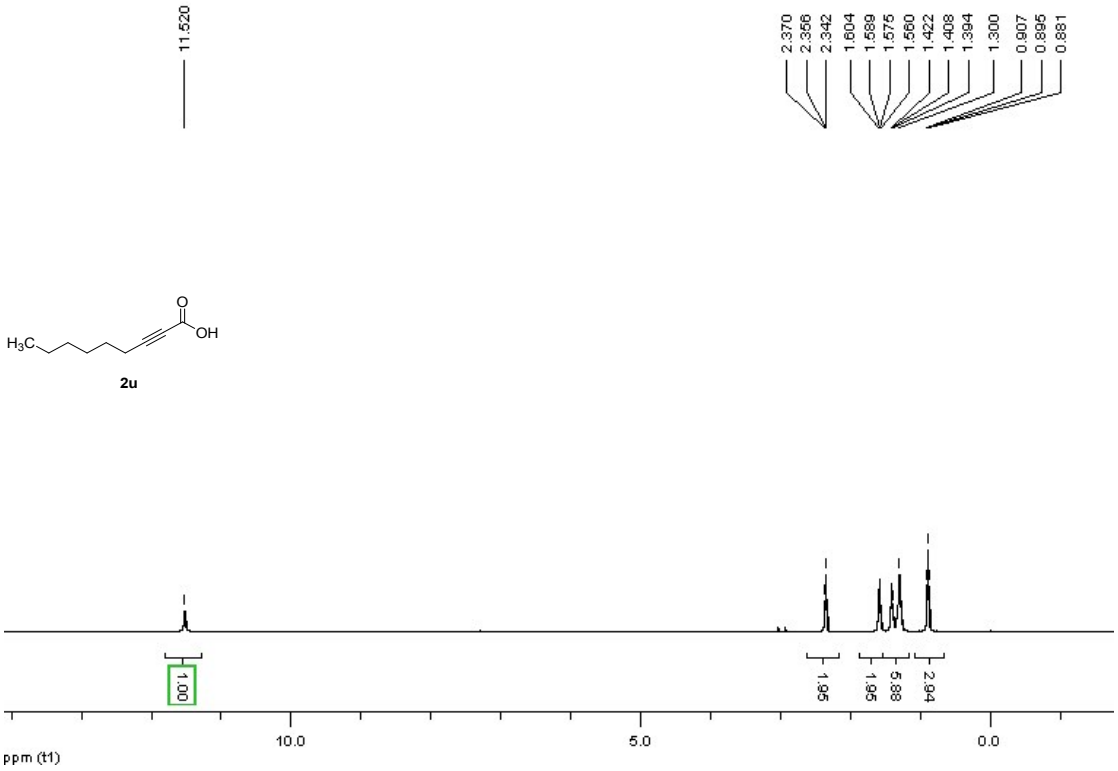

158.530
92.713
77.370
77.114
76.861
72.588
29.341
21.836
18.327
13.296
O
OH
H3C
2s
200
150
100
50
0
ppm (t1)

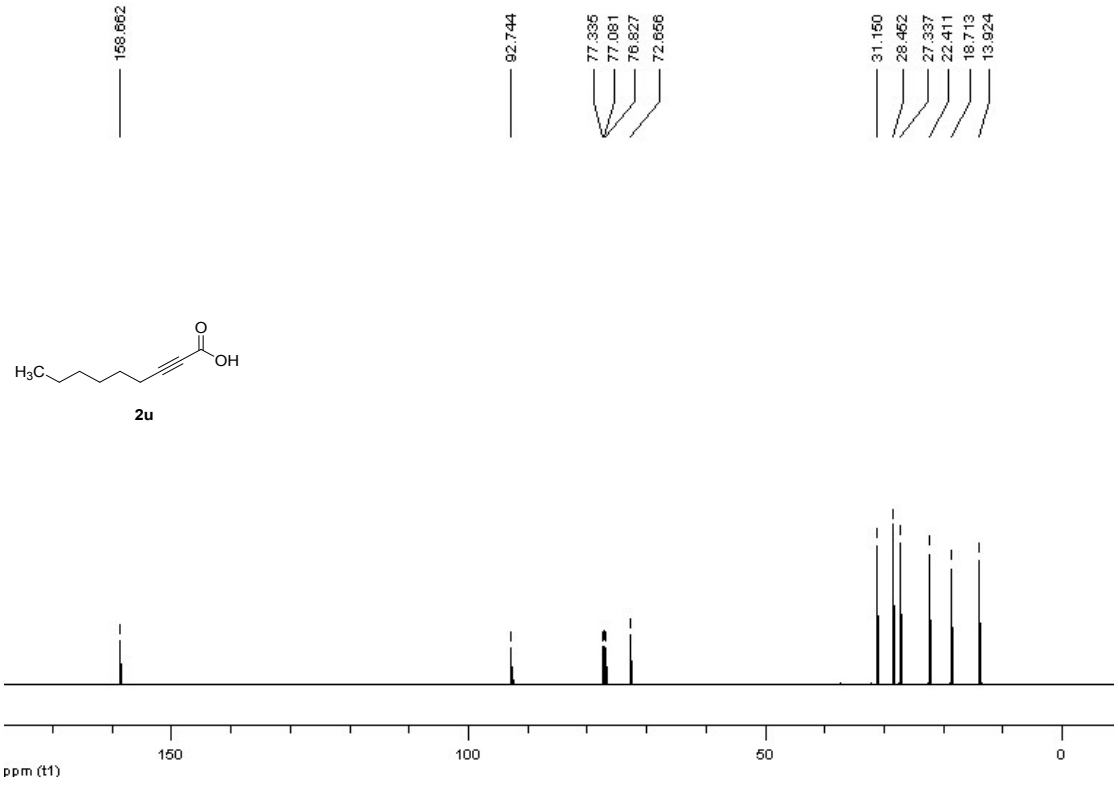

10.206
7.282
2.362
2.348
2.333
1.618
1.604
1.589
1.574
1.560
1.413
1.394
1.385
1.382
1.369
1.357
1.346
1.332
1.316
1.302
0.915
0.900
0.886
O
OH
H3C
1.09
2.00
2.02
4.02
2.98
15.0
10.0
5.0
0.0
ppm (t1)

2t


158.524
92.764
77.328
77.073
76.819
72.635
30.906
27.057
22.040
18.678
13.776
O
OH
H3C
200
150
100
50
0
ppm (t1)

2t


11.520
2.370
2.356
2.342
1.604
1.589
1.575
1.560
1.422
1.408
1.394
1.300
0.907
0.895
0.881
O
OH
H3C
2u
1.00
1.95
1.95
5.88
2.94
10.0
5.0
0.0
ppm (t1)


158.662
92.744
77.335
77.081
76.827
72.656
31.150
28.462
27.337
22.411
18.713
13.924
O
OH
H3C
2u
150
100
50
0
ppm (t1)