Magnetically Separable Pd Catalyst for Carbonylative Sonogashira Coupling Reactions for the Synthesis of *α,β*-Alkynyl Ketones

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Supporting information

I. **Experimental Section:**

General

Nanoparticles Fe_3O_4 (<50nm) and phenylacetylene were purchased from Aldrich. Aryl iodides were obtained by Alfa Aesar. Solvents were freshly distilled and used. Carbon monoxide with a purity of 99.99% was commercially available. Other reagents were of analytical grade and were used as received.1. Synthesis Procedure & Characterization

1. Synthesis of the Pd/Fe_3O_4 catalyst

Pd/Fe_3O_4 was prepared according to the following procedures. Nanoparticles Fe_3O_4 were impregnated with Na_2PdCl_4 (1.0 %) aqueous solution and stirred 1h. After impregnation, the suspension was adjusted to pH 12 by adding sodium hydroxide (1 M) and stirred 6 h. The solid was washed by distilled water. The catalyst precursors were reduced by adding 0.2 M KBH_4 solution dropwise under gentle stirring in an ice-water bath 30 min until no obvious bubbles were observed in the solution. The resulting Pd/Fe_3O_4 was washed thoroughly with distilled water and subsequently with alcohol. The metal Pd content of catalyst determined by atomic absorption spectroscopy is 1.04%.

Characterization of the catalyst

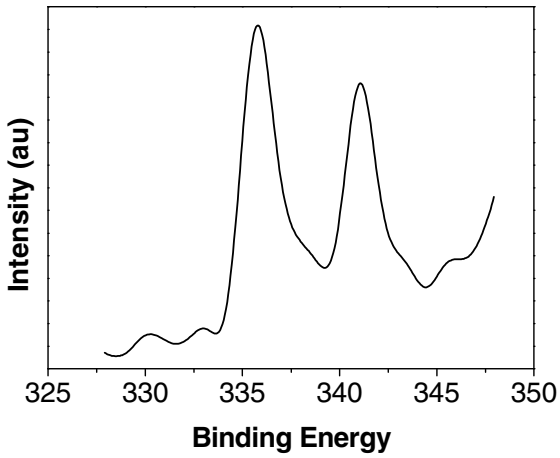


Fig. 2 Pd XPS spectra of Pd/ Fe_3O_4

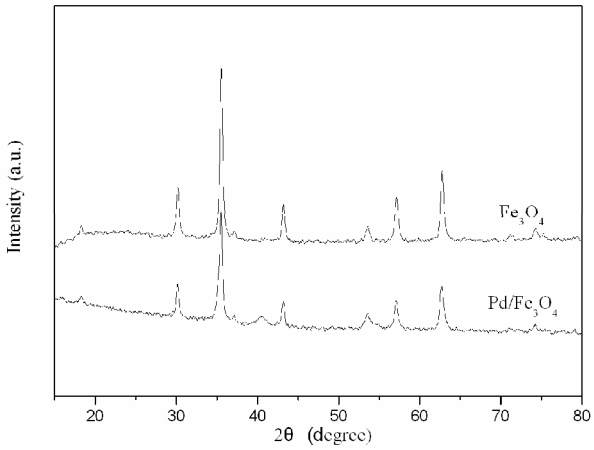


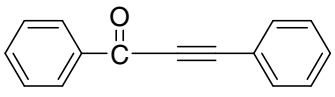
Fig. 3 XRD patterns of Pd/ Fe_3O_4

2. General procedure for carbonylative Sonogashira coupling reaction of aryl iodides by Pd/ Fe_3O_4.

All carbonylative Sonogashira coupling reaction experiments were carried out in a 100 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, known quantities of iodobenzene (2.5 mmol), phenylacetylene (3.0 mmol), Pd/Fe_3O_4 (50 mg, Pd, 1.04% wt%), Et_3N (7.2 mmol) and 5ml of toluene were charged into the reactor. The autoclave was closed, purged three times with CO, pressurized to 2.0 MPa with CO, and then stirred at 130 ^oC for 4 h. After reaction, carbon monoxide was purged carefully and the catalyst was obtained by magnetic separation. The catalyst could be directly reused for the next run after washed several times with ethanol and dried under vacuum, the base should be freshly added before the next carbonylation reaction. The reaction mixture was qualitatively and quantitatively analyzed by GC-MS (Agilent 6890/5973) and GC (Agilent 6820), respectively. The crude product was purified by column chromatography on silica gel (eluting solvent hexane: ethyl acetate) to give the desired products.

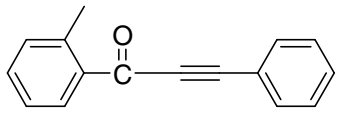
NMR data of *α,β*-alkynyl ketones.

1,3-diphenylprop-2-yn-1-one 3aa[2]



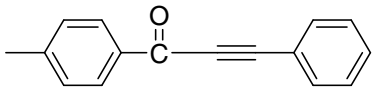
A yellowish solid, mp 46-48°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.43(m, 3H), 7.45-7.53(m, 2H), 7.60-7.64(m, 1H), 7.64-7.69 (m, 2H), 8.20-8.22(dd, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.86, 93.10, 120.10, 128.62, 128.68, 129.57, 130.79, 133.07, 134.12, 136.85, 178.03; EI-MS: *m/z* = 206 (M^+).

1-(2-toyl)-3-phenyl-2-yn-1-one 3ba[2]



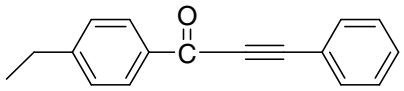
A yellowish oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 7.25-7.27 (d, 1H), 7.33-7.45 (m, 5H), 7.63-7.65 (t, 2H), 8.29-8.31 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.90, 88.29, 91.73, 120.23, 125.82, 128.57, 130.53, 132.10, 133.13, 135.59, 140.40, 179.68; EI-MS: *m/z* = 220 (M^+).

1-(4-toyl)-3-phenyl-2-yn-1-one 3ca[1]



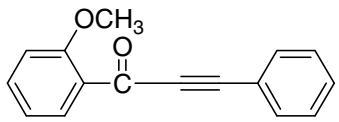
A yellowish solid, mp 68-70°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.29-7.31 (d, 2H), 7.38-7.48 (m, 3H), 7.65-7.68 (m, 2H), 8.09-8.11 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.84, 86.94, 92.59, 120.22, 128.64, 129.33, 129.70, 130.67, 133.01, 134.5
7, 145.24, 177.73; EI-MS: *m/z* = 220 (M^+).

1-(4-ethylphenyl)-3-phenylprop-2-yn-1-one 3da[6]



A yellowish oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24-1.28 (t, 3H), 2.70-2.75 (m, 2H), 7.18-7.31(d, 3H), 7.40-7.48(m, 2H), 7.65-7.68 (d, 2H), 8.12-8.14 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.14, 29.09, 86.96, 92.61, 120.23, 128.15, 128.63, 129.81, 130.66, 133.01, 134.76, 151.38, 177.76; EI-MS: *m/z* =234 (M^+).

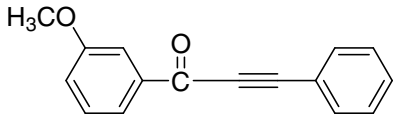
1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one 3ea[1]



A yellowish oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 6.98-7.05 (q, 2H), 7.35-7.44 (m, 3H), 7.49-7.54 (m, 1H), 7.59-7.61 (t, 2H), 8.05-8.08 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.83,

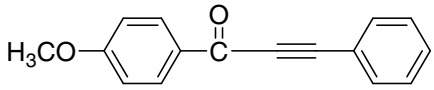
89.09, 91.51, 112.11, 120.22, 120.56, 126.57, 128.51, 130.38, 132.57, 132.89, 134.98, 159.73, 176.68; EI-MS: *m/z* = 236 (M^+).

1-(3-methoxyphenyl)-3-phenylprop-2-yn-1-one 3fa[1]



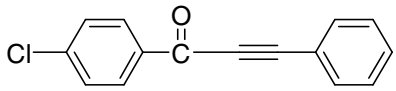
A yellowish solid, mp 59-61°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 7.14-7.17 (m, 1H), 7.37-7.48 (m, 4H), 7.64-7.68 (m, 3H), 7.83-7.85 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.41, 86.88, 92.94, 112.72, 120.00, 120.91, 122.81, 128.64, 129.60, 130.77, 133.02, 138.15, 159.72, 177.71; EI-MS: *m/z* = 236 (M^+).

1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one 3ga[1]



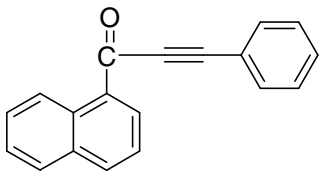
A yellowish solid, mp 97-99°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 6.96-6.98 (d, 2H), 7.38-7.46 (m, 3H), 7.64-7.67 (q, 2H), 8.17-8.19 (dd, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.59, 86.99, 92.30, 113.86, 120.33, 128.63, 130.27, 130.57, 131.98, 132.94, 164.46, 176.68; EI-MS: *m/z* = 236 (M^+).

1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one 3ha[1]



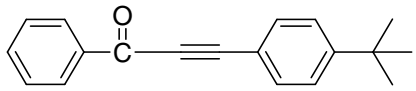
A yellowish solid, mp 103-105 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.43 (t, 2H), 7.47-7.50 (t, 3H), 7.66-7.68 (d, 2H), 8.13-8.15 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.55, 93.63, 119.86, 128.73, 129.00, 130.87, 130.99, 133.11, 135.27, 140.71, 176.68; EI-MS: *m/z* = 242 (M^+).

1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-one 3ia[1]



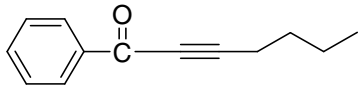
A yellowish solid, mp 92-94°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.49 (m, 3H), 7.55-7.61 (m, 2H), 7.65-7.70 (m, 3H), 7.89-7.91 (d, 1H), 8.08-8.10 (d, 1H), 8.63-8.65 (dd, 1H), 9.21-9.24 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.46, 91.69, 120.33, 124.47, 125.98, 126.76, 128.56, 128.65, 128.97, 130.60, 130.72, 132.95, 133.85, 134.54, 135.11, 179.75; EI-MS: *m/z* = 256 (M^+).

3-(4-tert-butylphenyl)-1-phenylprop-2-yn-1-one 3ab[5]



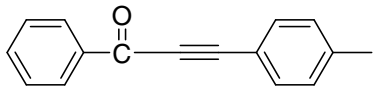
A yellowish oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 7.42-7.44 (d, 2H), 7.48-7.52 (t, 2H), 7.59-7.63 (t, 3H), 8.20-8.22 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.00, 35.06, 86.68, 93.79, 116.96, 125.73, 128.56, 129.51, 132.97, 133.98, 136.94, 154.55, 178.09; EI-MS: *m/z* = 262 (M^+).

1-phenylhept-2-yn-1-one 3ac[3]



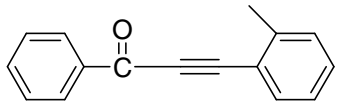
A yellowish oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92-0.95 (t, 3H), 1.43-1.52 (m, 2H), 1.60-1.67 (m, 2H), 2.46-2.49 (t, 2H), 7.43-7.46 (t, 2H), 7.55-7.58 (t, 1H), 8.10-8.12 (d,2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.46, 18.83, 22.00, 29.75, 79.58, 69.82, 128.41, 129.47, 133.81, 136.82, 178.21; EI-MS: *m/z* = 186 (M^+).

1-phenyl-4-toyl-2-yn-1-one 3ad[7]



A yellowish solid, mp 69-71°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s,3H), 7.24-7.31 (m, 2H), 7.39-7.48 (m, 3H), 7.66-7.68 (m, 2H), 8.09-8.11(dd, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.83, 86.92, 92.58, 120.21, 128.63, 129.32, 129.69, 130.66, 133.00, 134.56, 145.23, 177.72. EI-MS: 220(M^+).

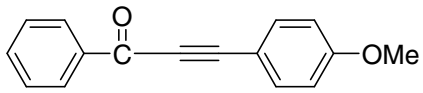
1-phenyl-3-*o*-toyl-2-yn-1-one 3ae[8]



A yellowish oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s 3H), 7.22-7.30 (m, 2H), 7.36-7.45 (m, 3H), 7.50-7.67 (m, 2H), 8.04-8.25 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.84, 90.77, 92.13, 120.03,

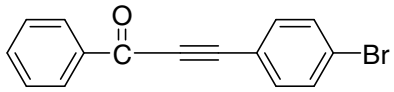
125.91, 128.26, 128.60, 129.51, 130.77, 132.74, 133.63, 1333.97, 137.14, 142.14, 178.00. EI-MS: 220(M^+).

3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one 3af [2]



A colorless solid, mp 80-81°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 6.96-6.98 (d, 2H), 7.53-7.57 (t, 2H), 7.64-7.70 (m, 3H), 8.25-8.26 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.43, 86.89, 94.25, 111.98, 114.45, 128..54, 129.47, 133.85, 135.11, 137.14, 161.77, 178.00. EI-MS: 236 (M^+).

3-(4-bromophenyl)-1-phenylprop-2-yn-1-one 3ag[7]



A yellowish solid, mp 115-116°C ^{1}H NMR (400 MHz, $CDCl_3$) δ7.50-7.59 (m, 6H) 7.63-7.67 (m, 1H), 8.20-8.22 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 87.14, 91.57, 119.10, 125.57, 128.66, 129.56, 132.10, 134.22, 134.31, 136.80, 177.76. EI-MS: 286 (M^+)

Reference:

(1) Ahmed, M. S. M.; Mori, A. *Org. Lett*. **2003**, *5*, 3057.

(2) Fukuyama,T.; Yamaura, R.; Ryu, I. *Can. J. Chem*. **2005** ,*83*, 71.

(3) Liang, B.; Huang, M. W.; You, Z. J. Xiong, Z. C.; Lu, K.; Fathi, R.; Chen J. H.; Yang, Z. *J. Org. Chem.* **2005**, *70*, 6097.

(4) Sans, V.; Trzeciak, A. M.; Luis, S. ; Ziółkowski, J. J. *Catal. Lett.* **2006**, *109*, 37.

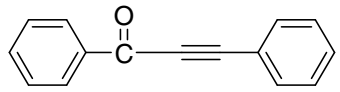
(5) Liu, J. H.; Chen, J.; Xia, C. G. *J. Catal.* **2008**, *258*, 50.

(6) Rao, P. N. P. ; Uddin, M. J.; Knaus, E. E. *J. Med. Chem.* **2004**, *47*, 3972.

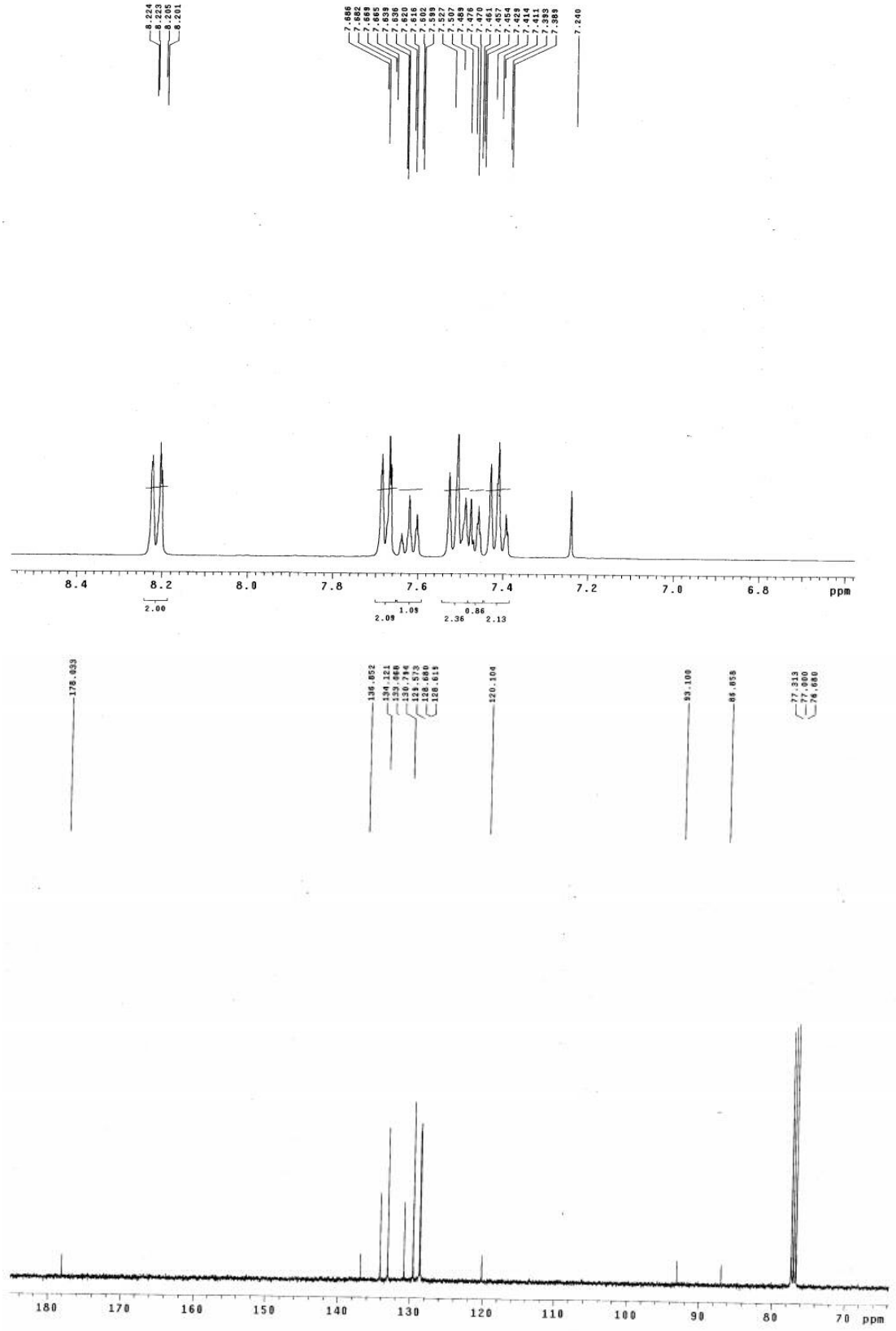
(7) Chen, L.; Li, C. J. *Org. Lett*. **2004**, *6*, 3151.

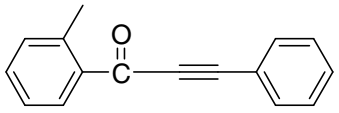
(8) Fontaine, M.; Chauvelier, J.;Barchewitz, P. *Bull. Soc. Chim. Fr*. **1962**, 2145.

II. Copy of NMR spectra of *α,β*-alkynyl ketones.



3aa





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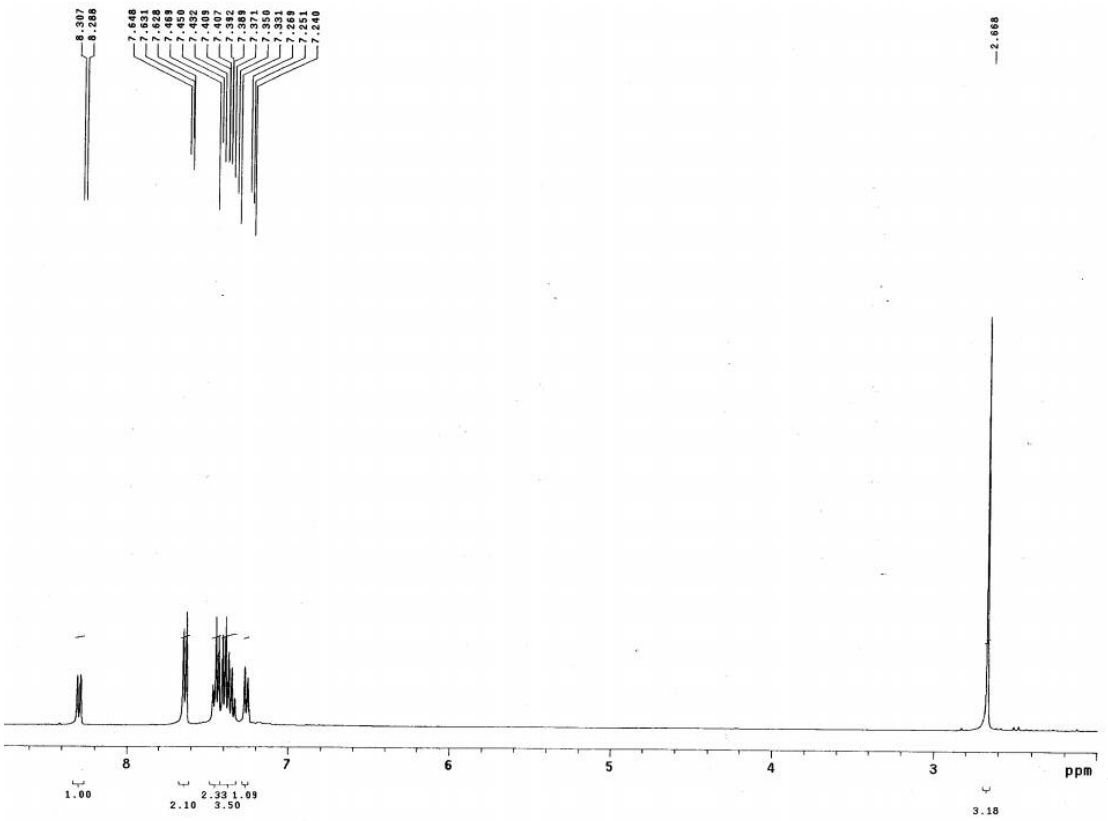
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7.350
7.331
7.269
7.251
7.240
2.668
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7
6
5
4
3
ppm
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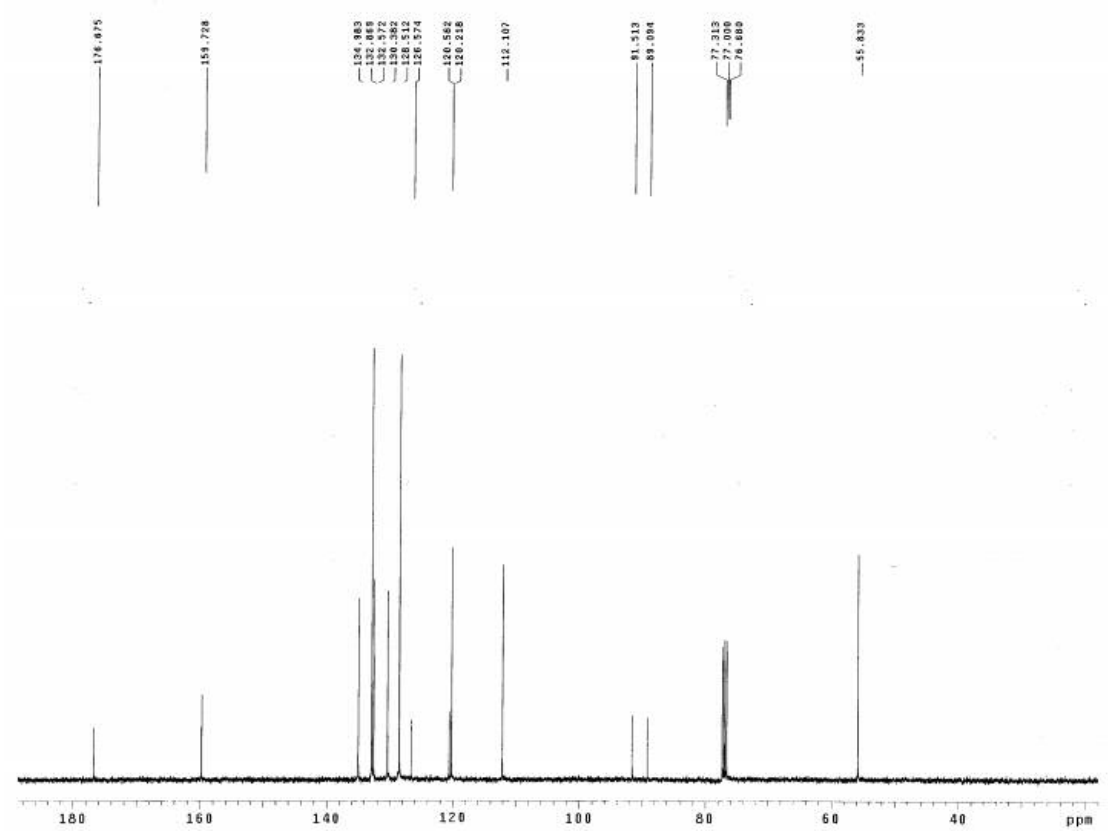
2.10
2.33
1.09
3.50
3.18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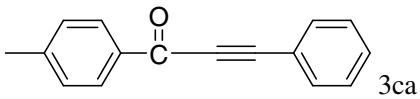

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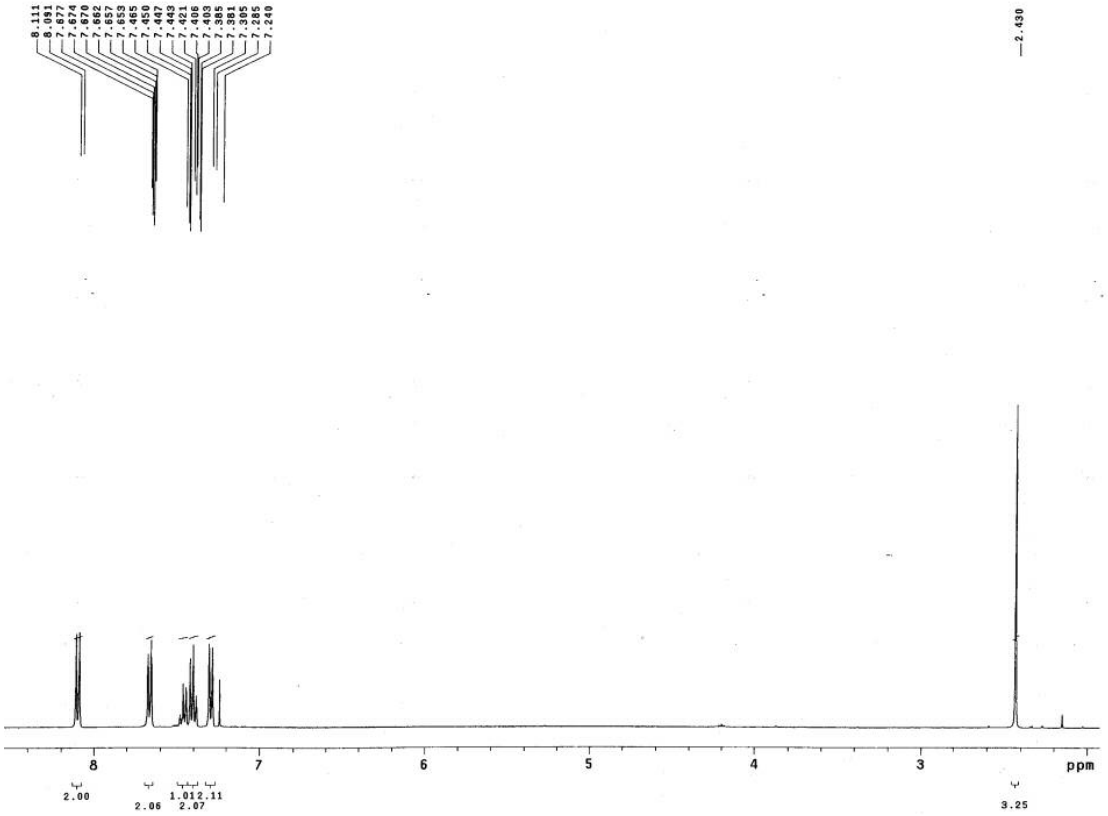
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7.421
7.406
7.403
7.385
7.381
7.365
7.285
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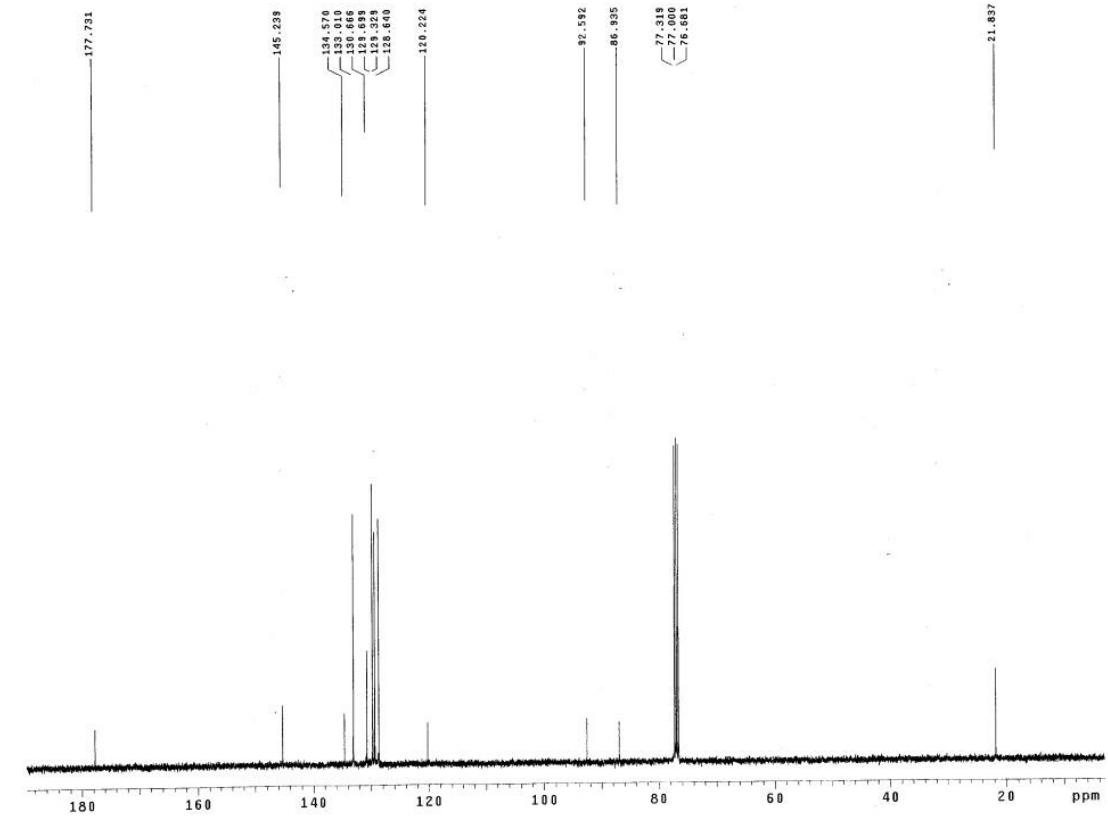
3.25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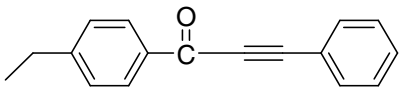
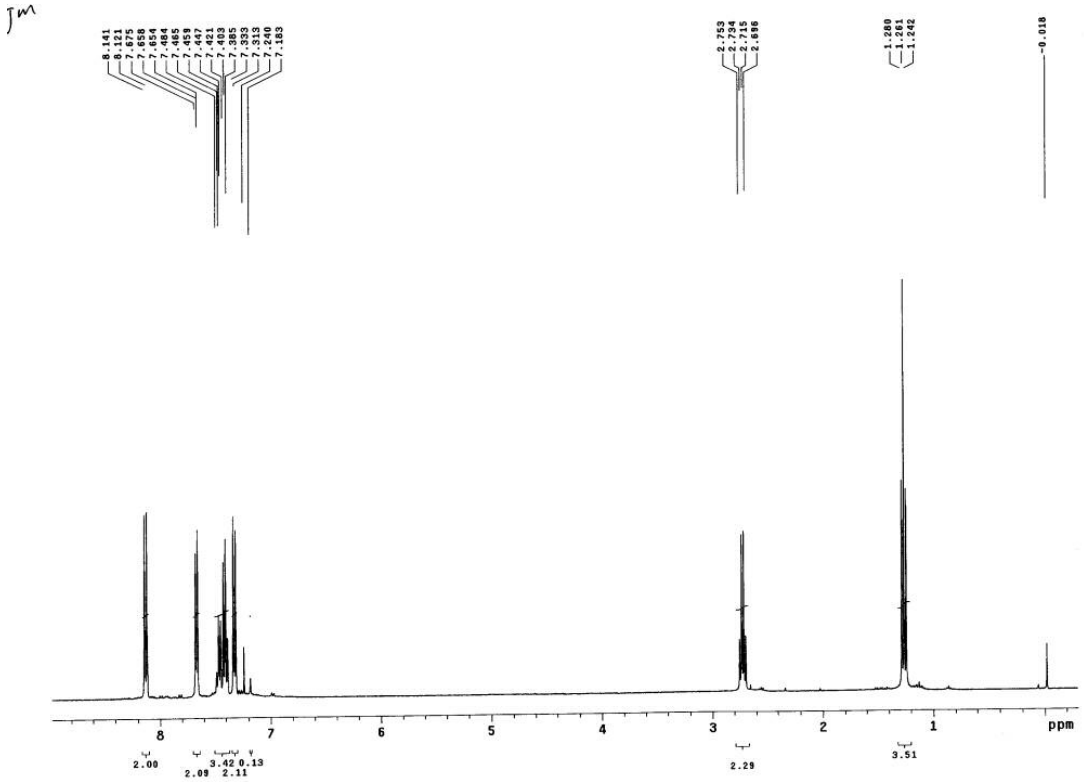
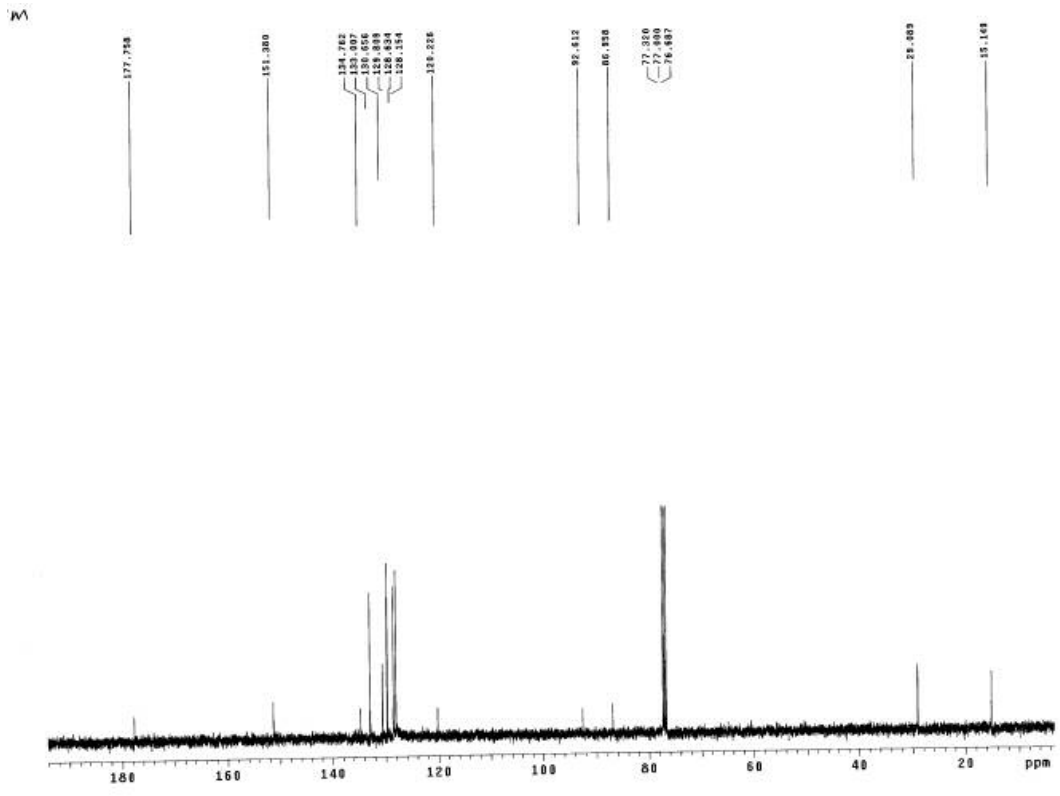
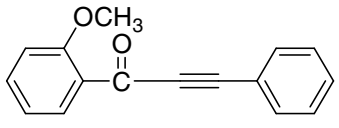


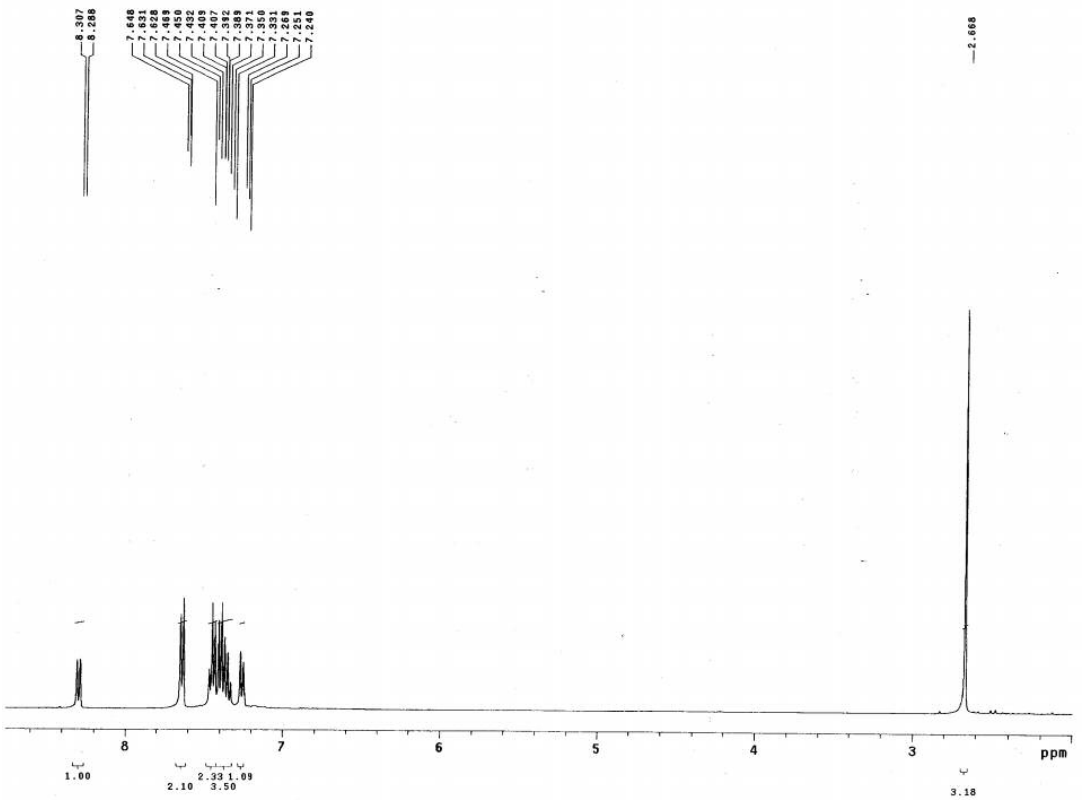
3da






OCH3
O
C

3ea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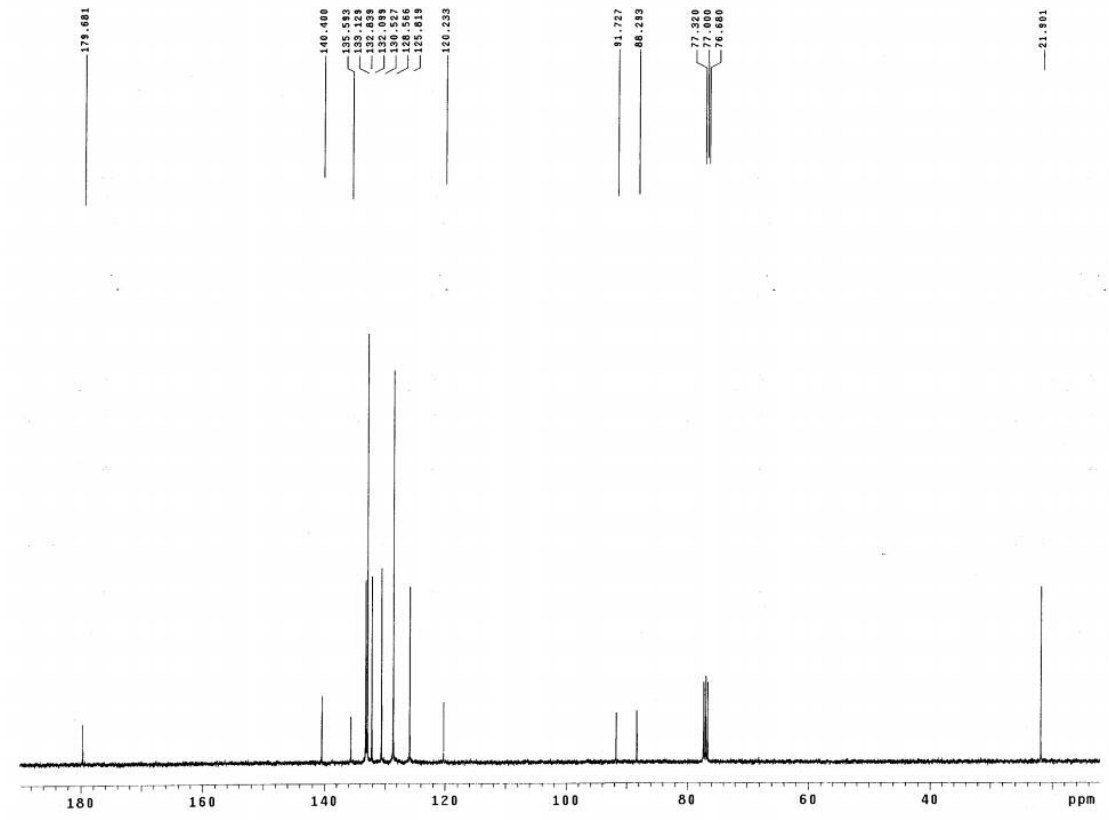
8.288
7.648
7.631
7.618
7.468
7.450
7.432
7.409
7.407
7.392
7.388
7.371
7.356
7.331
7.269
7.251
7.240
2.668
8
7
6
5
4
3
ppm
1.00
2.10
2.33
3.50
1.09
3.18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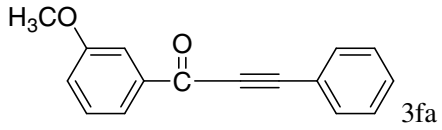
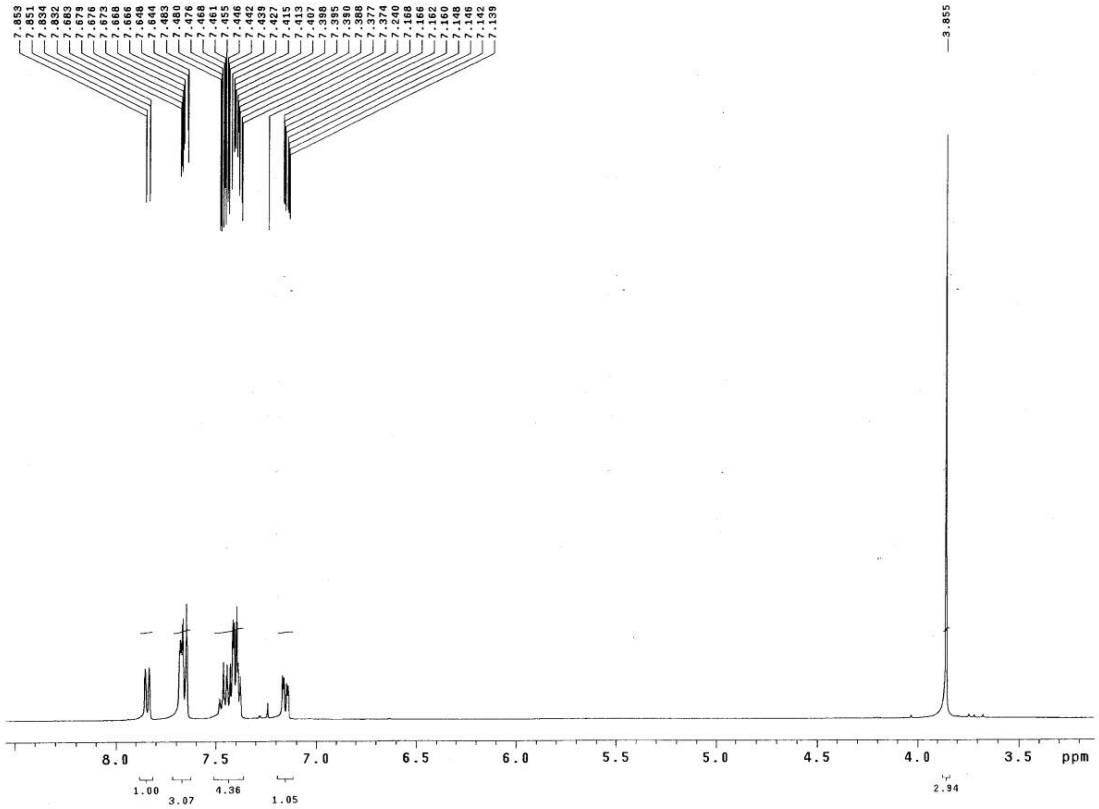
140.400
135.583
133.129
132.839
132.099
130.527
128.566
125.819
120.233
91.727
88.293
77.320
77.000
76.680
21.901
180
160
140
120
100
80
60
40
ppm


H3CO
O
C

3fa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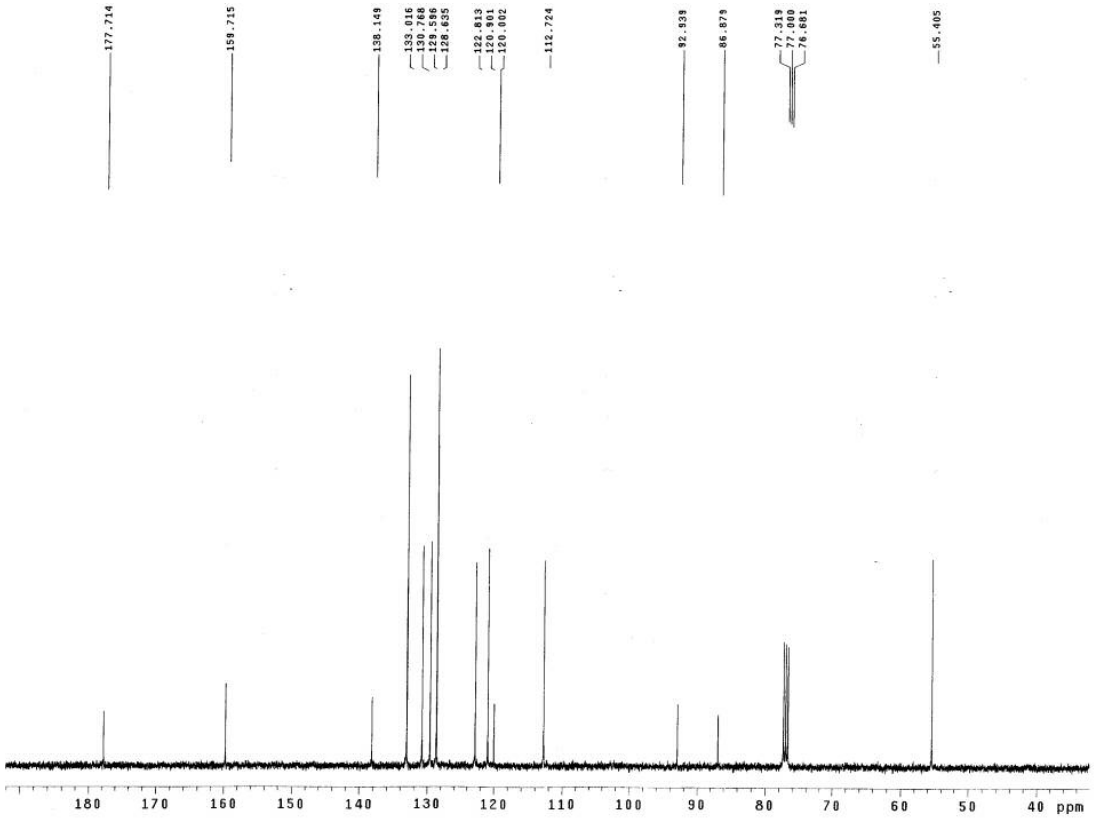
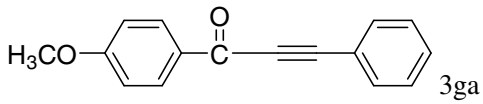
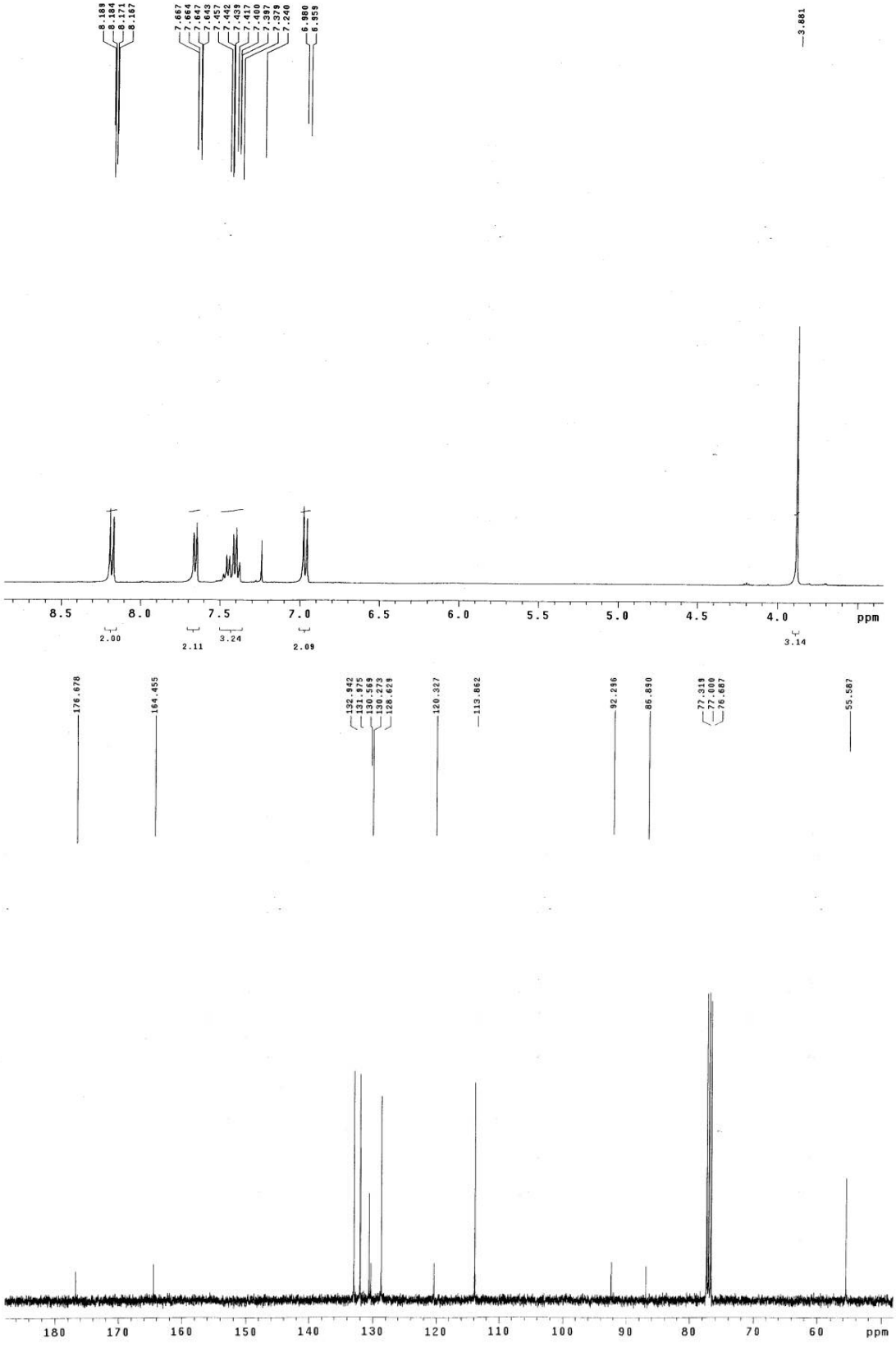
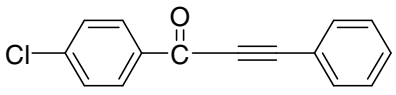
7.851
7.834
7.832
7.683
7.679
7.676
7.673
7.668
7.666
7.648
7.644
7.483
7.480
7.476
7.468
7.461
7.455
7.446
7.442
7.439
7.427
7.415
7.413
7.407
7.398
7.395
7.390
7.388
7.377
7.374
7.240
7.168
7.166
7.162
7.160
7.148
7.146
7.142
7.139
3.855
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
1.00
3.07
4.36
1.05
2.94


177.714
159.715
138.149
133.016
130.768
129.586
128.635
122.813
120.901
120.002
112.724
92.539
86.879
77.319
77.000
76.681
55.405
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40 ppm

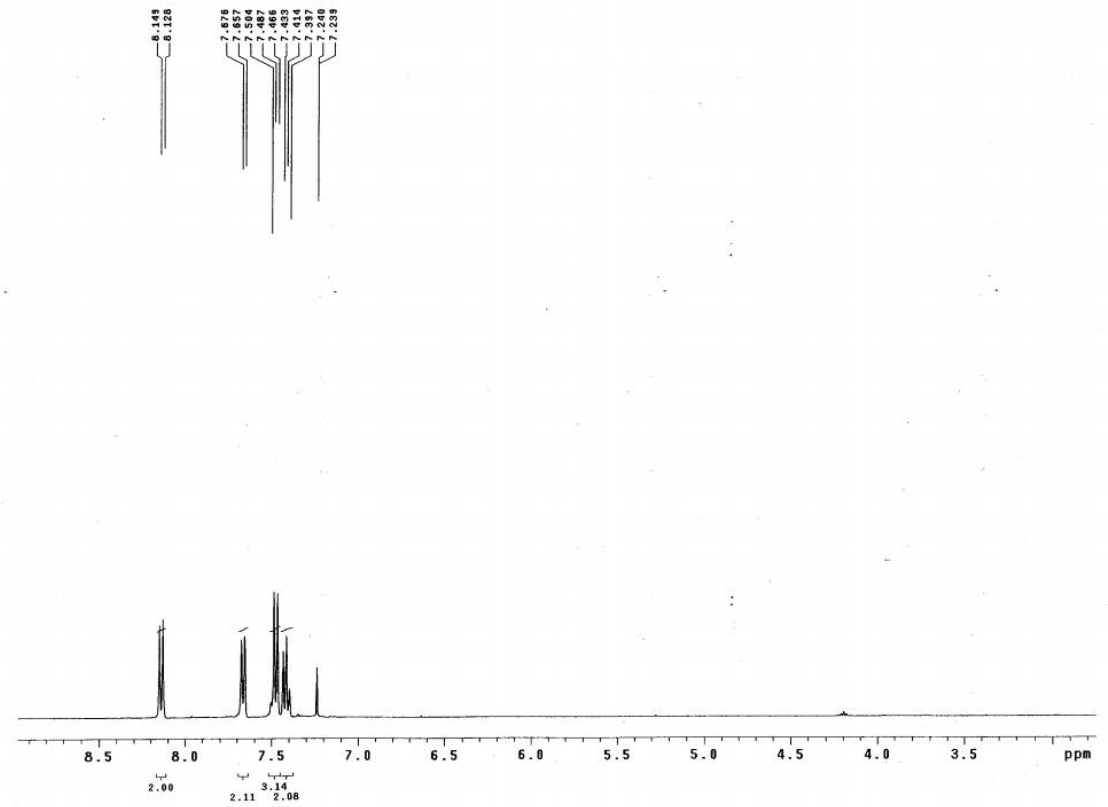

H3CO
O
C

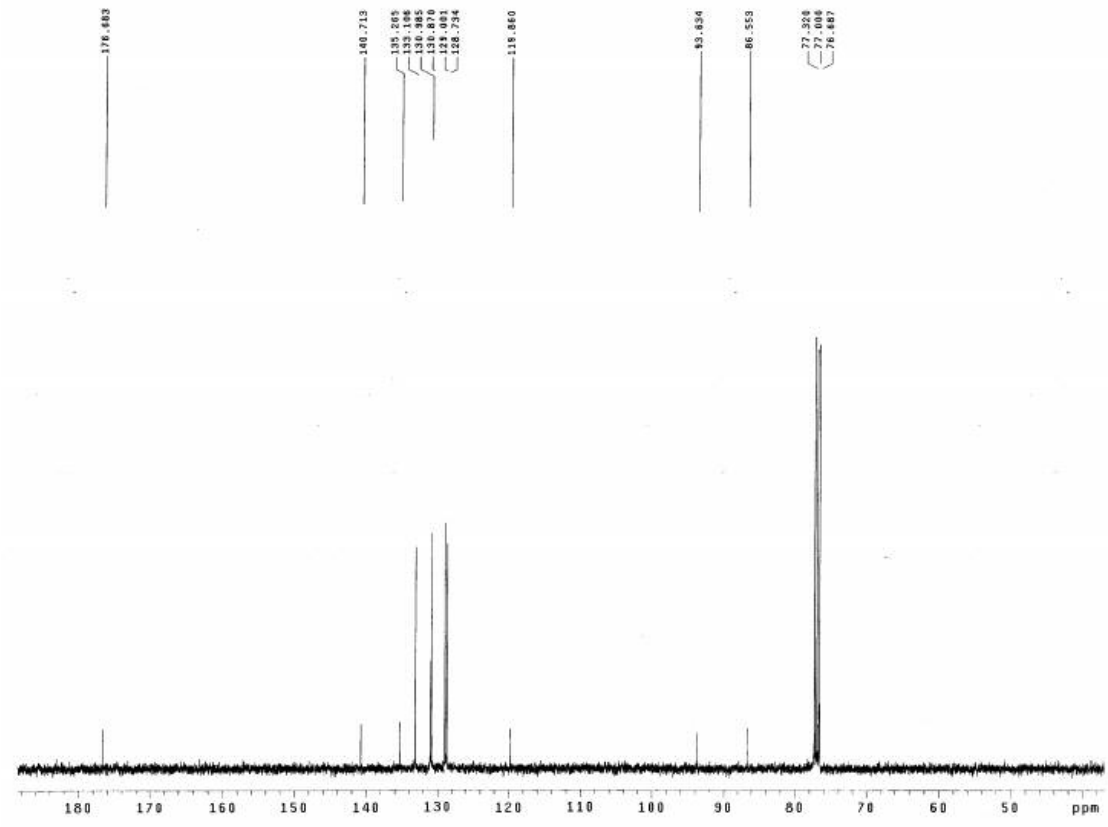
3ga

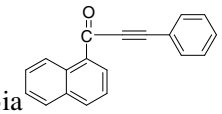

8.188
8.184
8.171
8.167
7.667
7.664
7.647
7.643
7.457
7.442
7.439
7.417
7.400
7.397
7.379
7.240
6.980
6.959
3.881
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
2.00
2.11
3.24
2.09
3.14
176.678
164.455
132.942
131.975
130.569
130.273
128.629
120.327
113.862
92.296
86.890
77.319
77.000
76.687
55.587
180
170
160
150
140
130
120
110
100
90
80
70
60
ppm


Cl
O
C

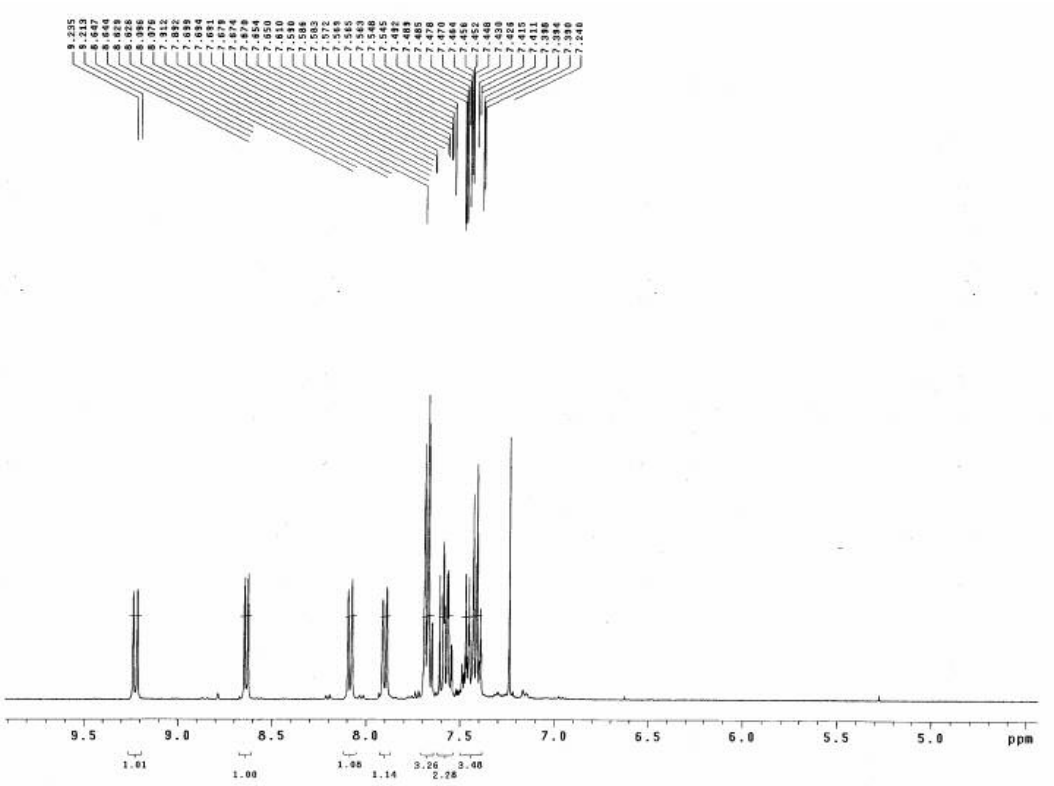
3ha

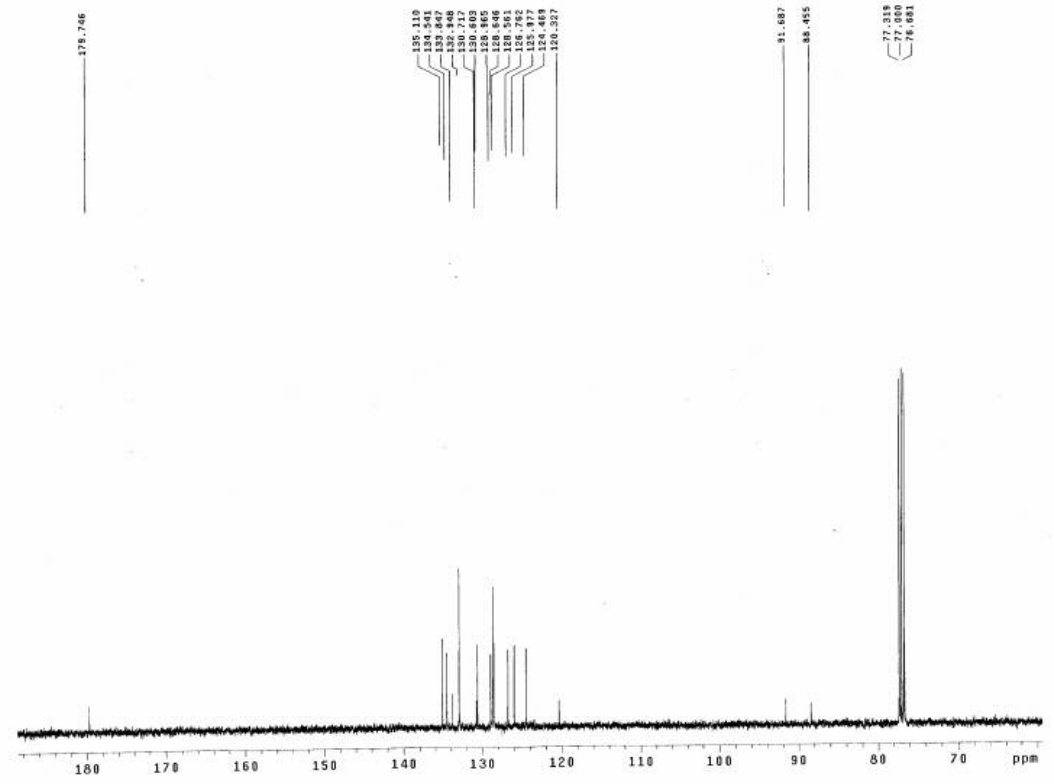

8.149
8.128
7.676
7.657
7.507
7.487
7.466
7.433
7.414
7.397
7.240
7.238
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
2.00
2.11
3.14
2.08

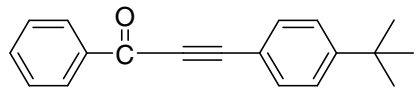

176.683
140.713
135.265
133.186
130.995
130.870
129.081
128.734
119.860
93.634
86.553
77.320
77.004
76.687
180
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm



3ia


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm
1.01
1.00
1.08
1.14
3.26
2.28
3.48


180
170
160
150
140
130
120
110
100
90
80
70
ppm



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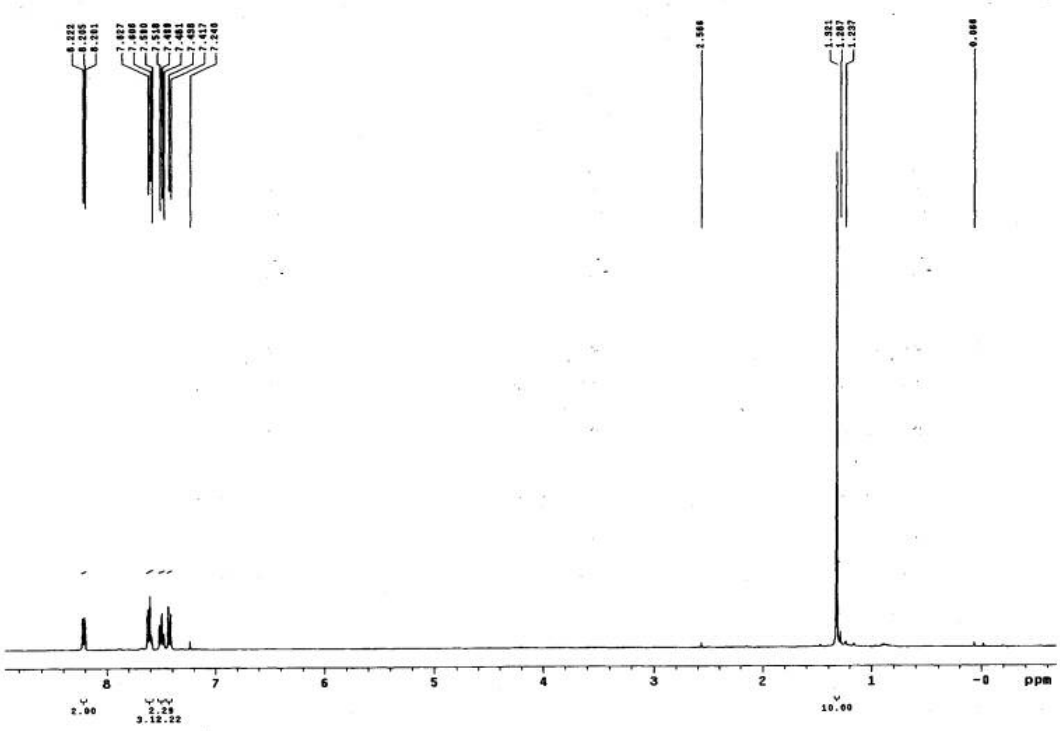
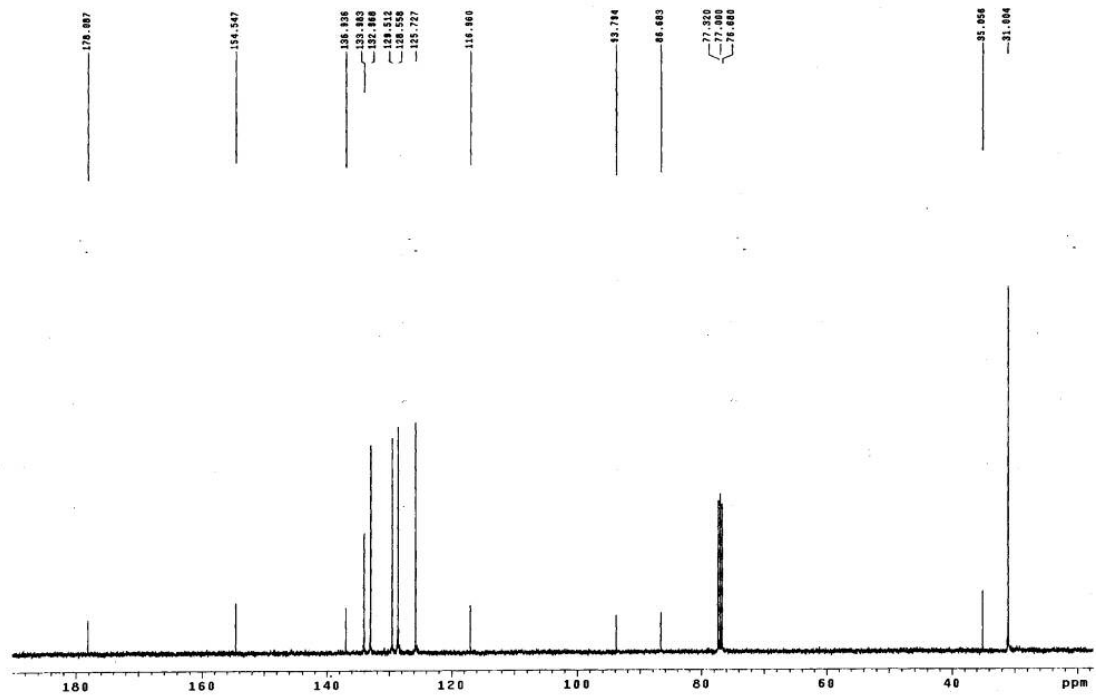
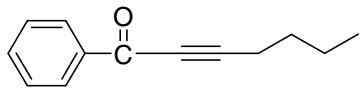
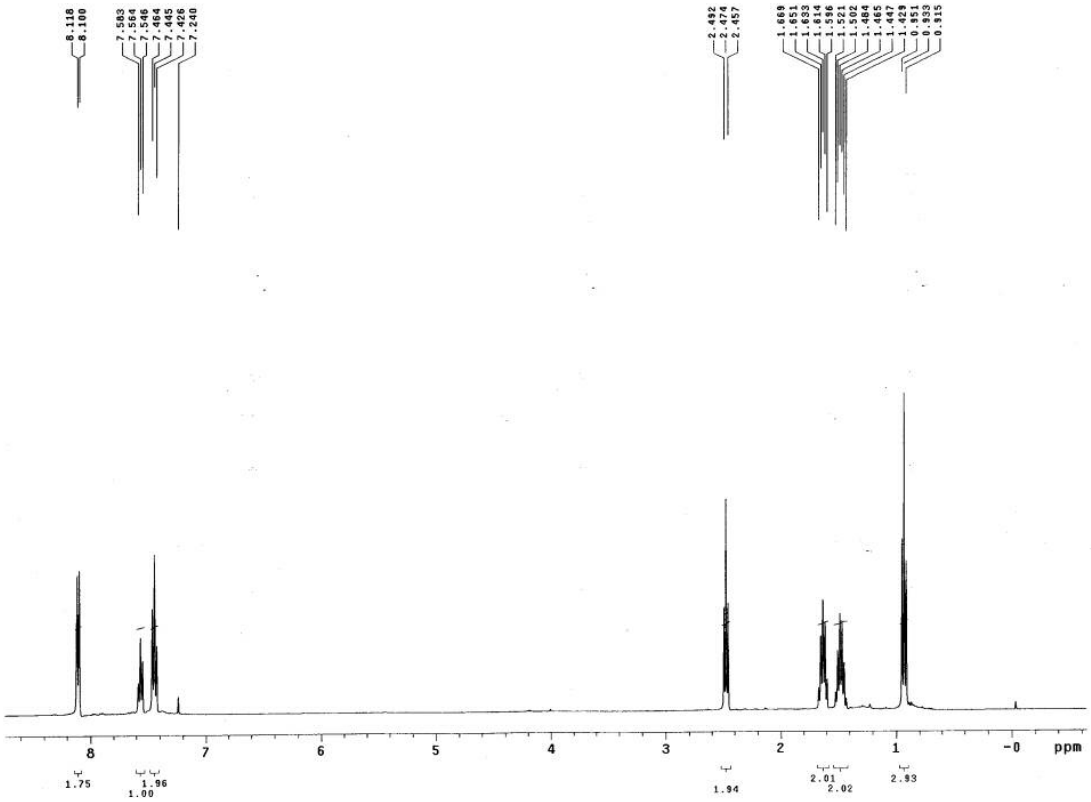






3ac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7.546
7.464
7.445
7.426
7.240
2.492
2.474
2.457
1.668
1.651
1.633
1.614
1.596
1.521
1.502
1.484
1.465
1.447
1.429
0.951
0.933
0.915
8
7
6
5
4
3
2
1
-0
ppm
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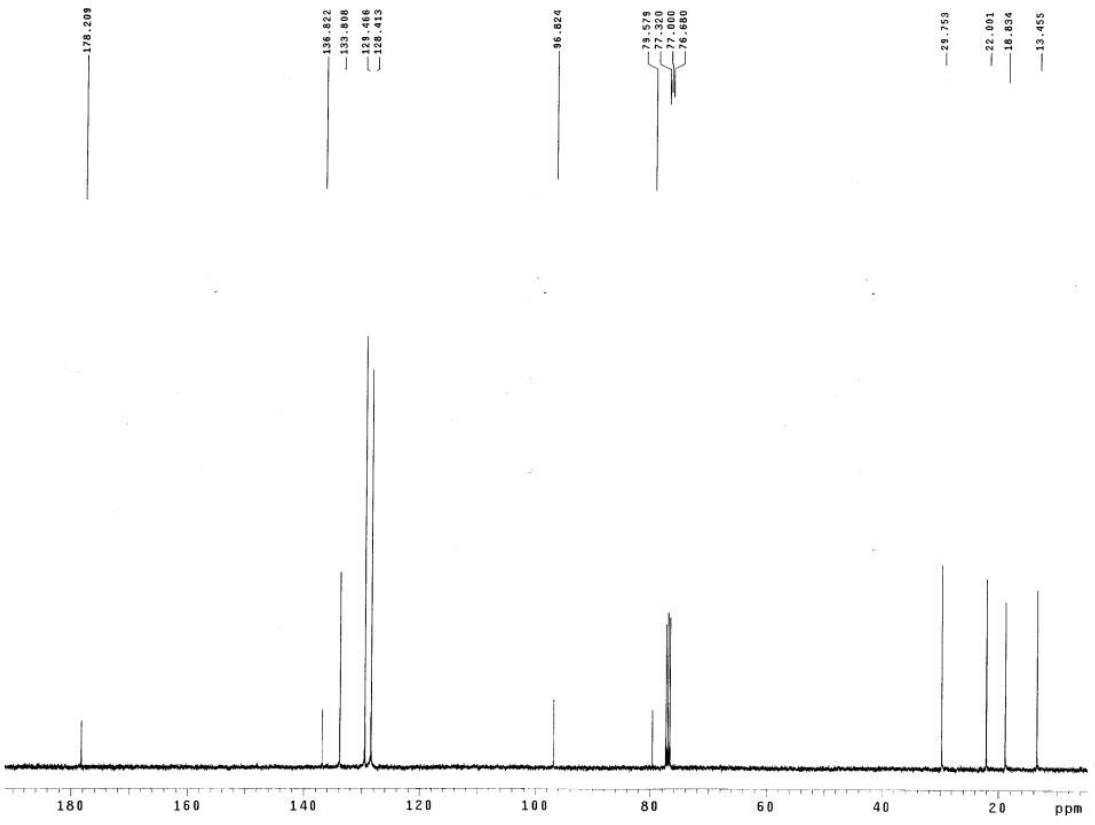
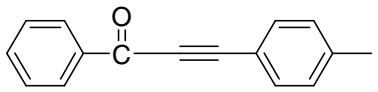
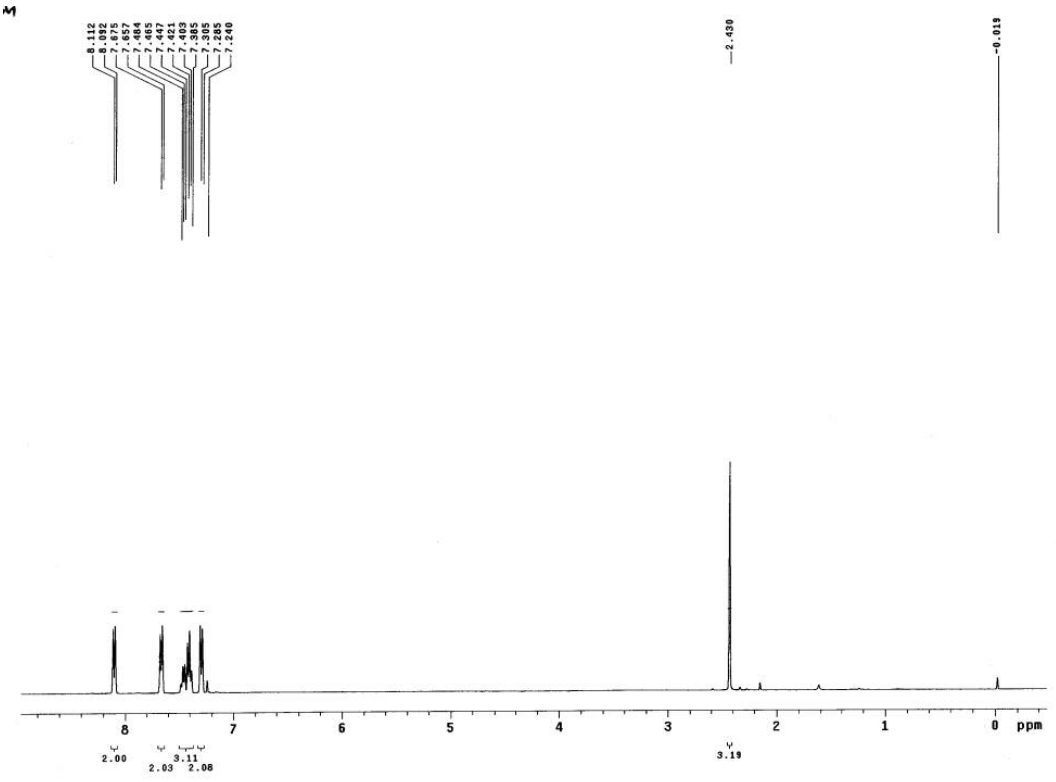
1.96
1.00
1.94
2.01
2.02
2.93


178.209
136.822
133.808
129.466
128.413
96.824
79.578
77.320
77.000
76.680
29.753
22.001
18.834
13.455
180
160
140
120
100
80
60
40
20
ppm



3ad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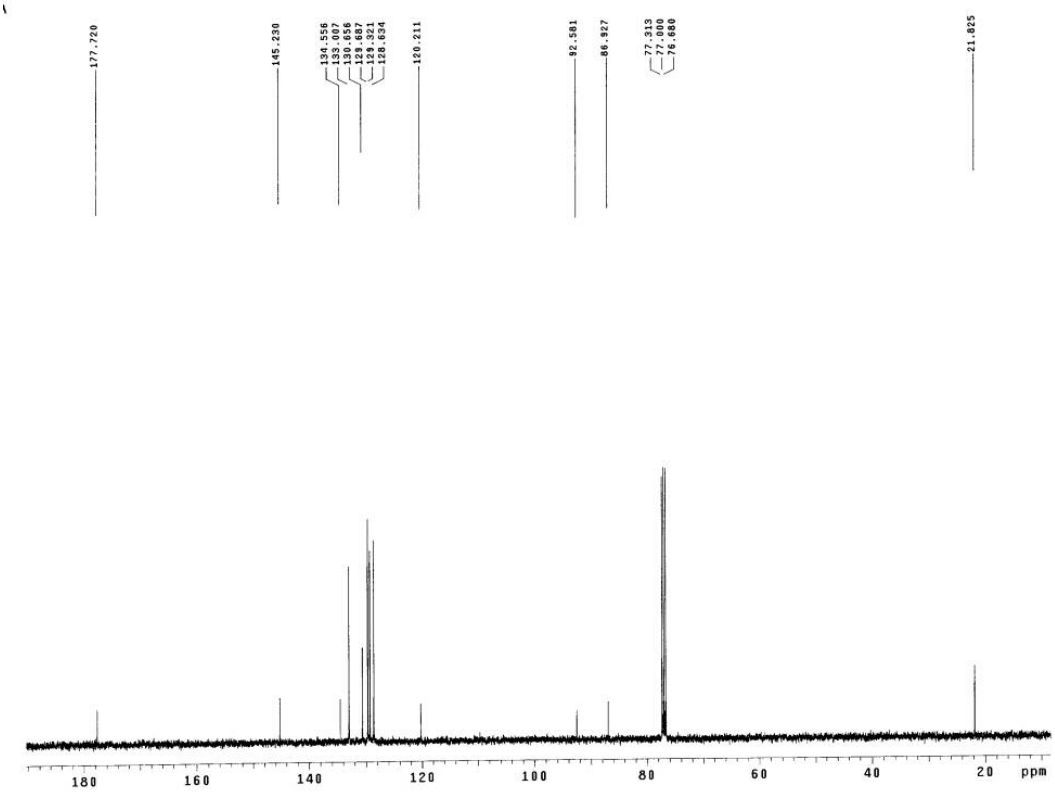
8.092
7.675
7.657
7.484
7.465
7.447
7.421
7.403
7.385
7.305
7.285
7.240
2.430
0.019
8
7
6
5
4
3
2
1
0
ppm
2.00
3.11
2.03
2.08
3.19


177.720
145.230
134.556
132.037
130.656
129.687
129.321
128.634
120.211
92.581
86.927
77.313
77.000
76.680
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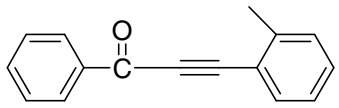
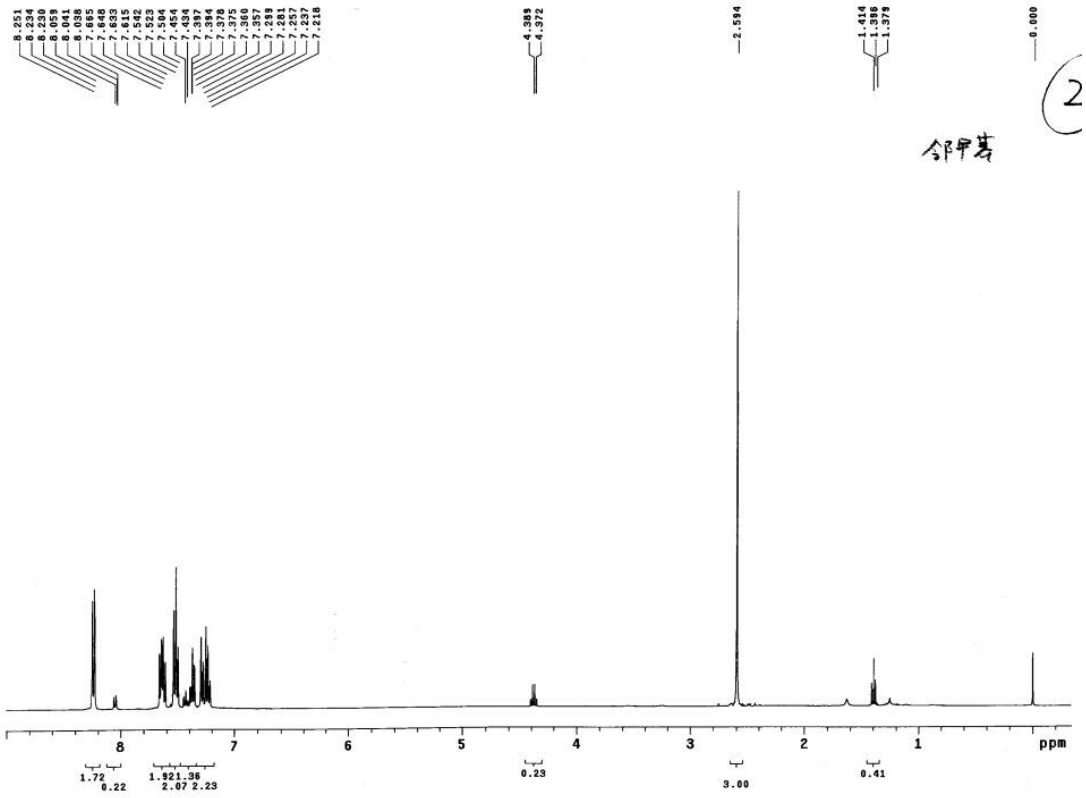
180
160
140
120
100
80
60
40
20
ppm



3ae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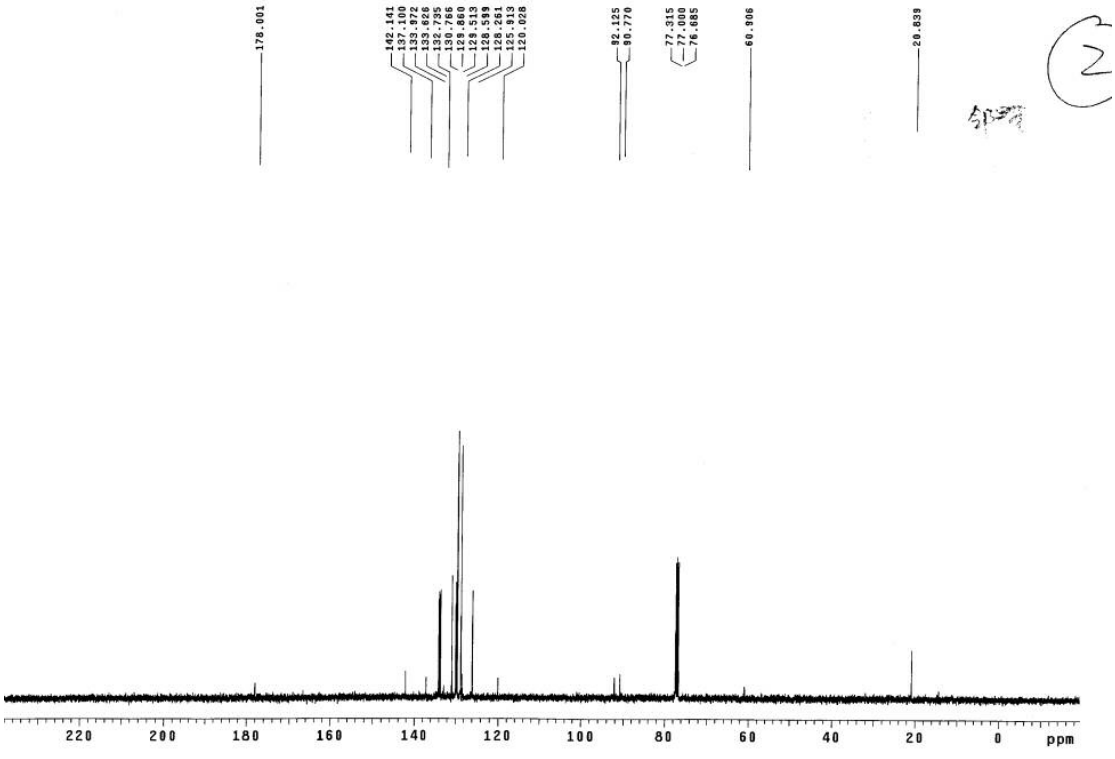
8.230
8.059
8.041
8.038
7.665
7.648
7.633
7.615
7.542
7.523
7.504
7.454
7.434
7.397
7.384
7.378
7.375
7.360
7.357
7.299
7.281
7.257
7.237
7.218
4.389
4.372
2.594
1.414
1.396
1.379
0.000
邻甲基
8
7
6
5
4
3
2
1
ppm
1.72
0.22
1.92
1.36
2.07
2.23
0.23
3.00
0.41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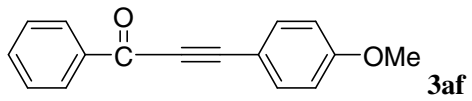
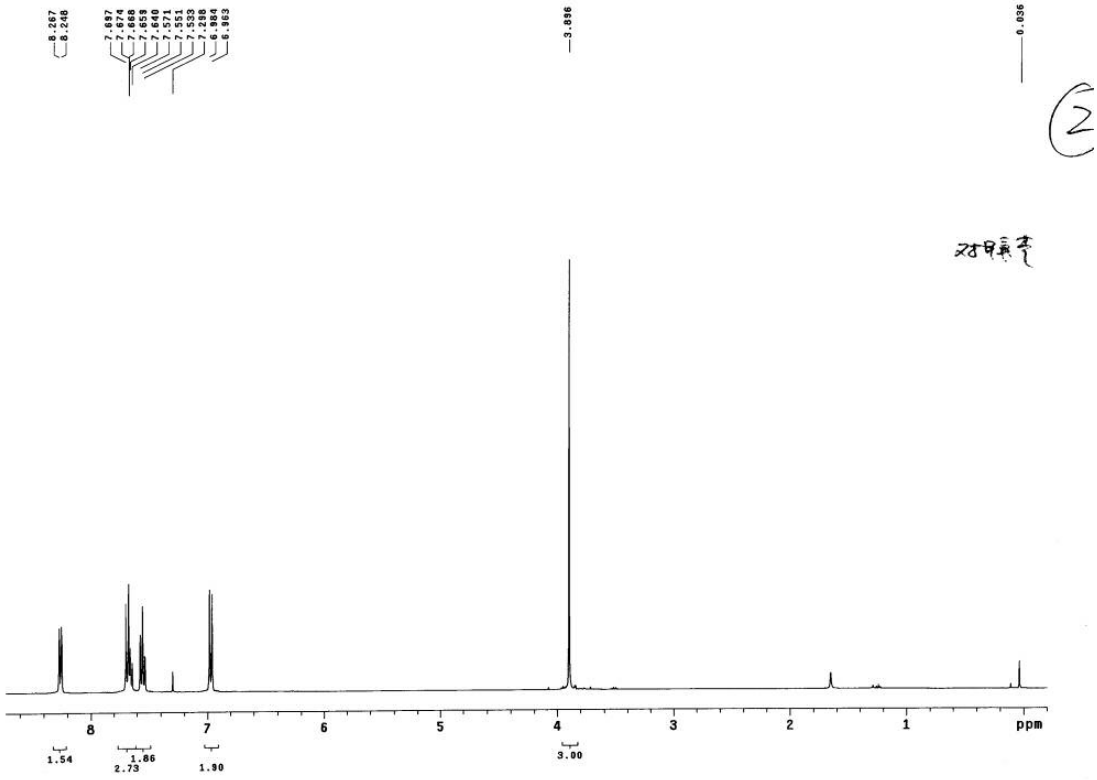
137.100
133.972
133.628
132.795
130.765
129.860
129.513
128.599
128.261
125.913
120.028
92.125
80.770
77.315
77.000
76.685
60.806
20.838
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
C
OMe

3af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7.697
7.674
7.668
7.659
7.640
7.571
7.551
7.533
7.288
6.984
6.963
3.856
0.036
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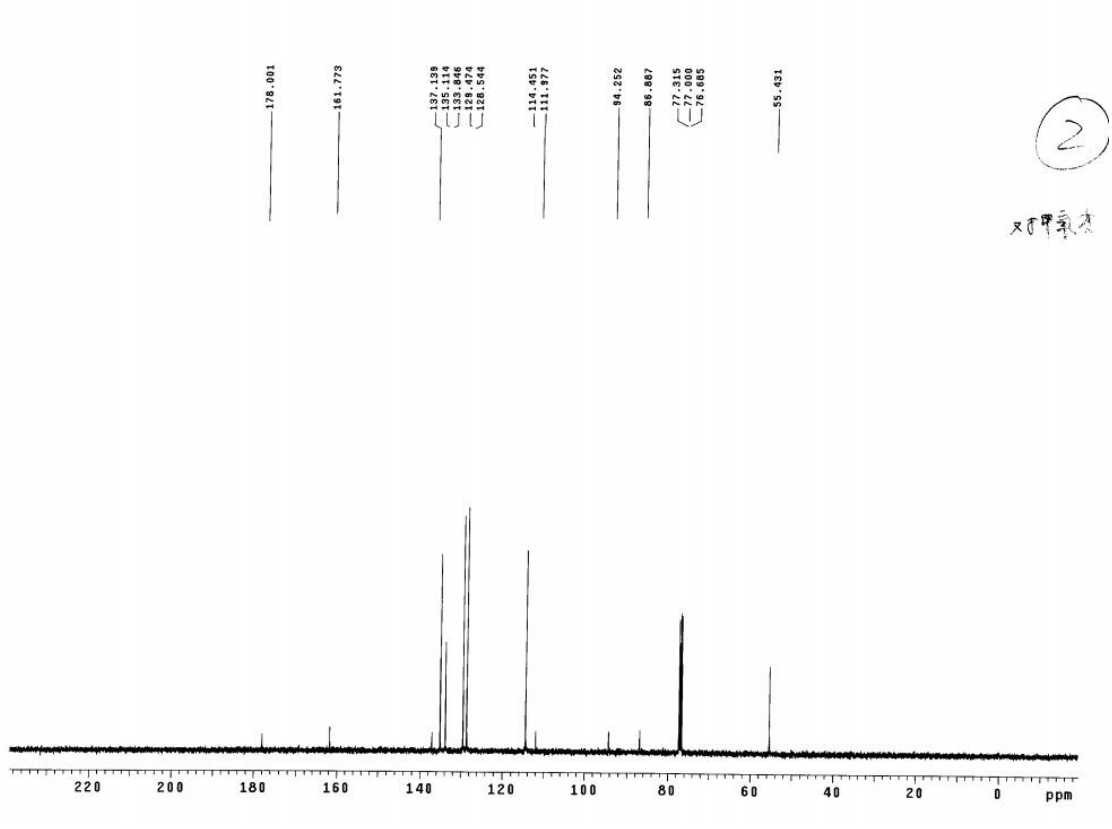
7
6
5
4
3
2
1
ppm
1.54
1.86
2.73
1.90
3.00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137.198
135.114
133.846
129.474
128.544
114.451
111.877
94.252
86.887
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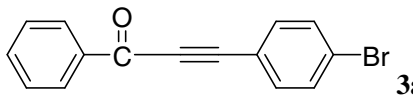
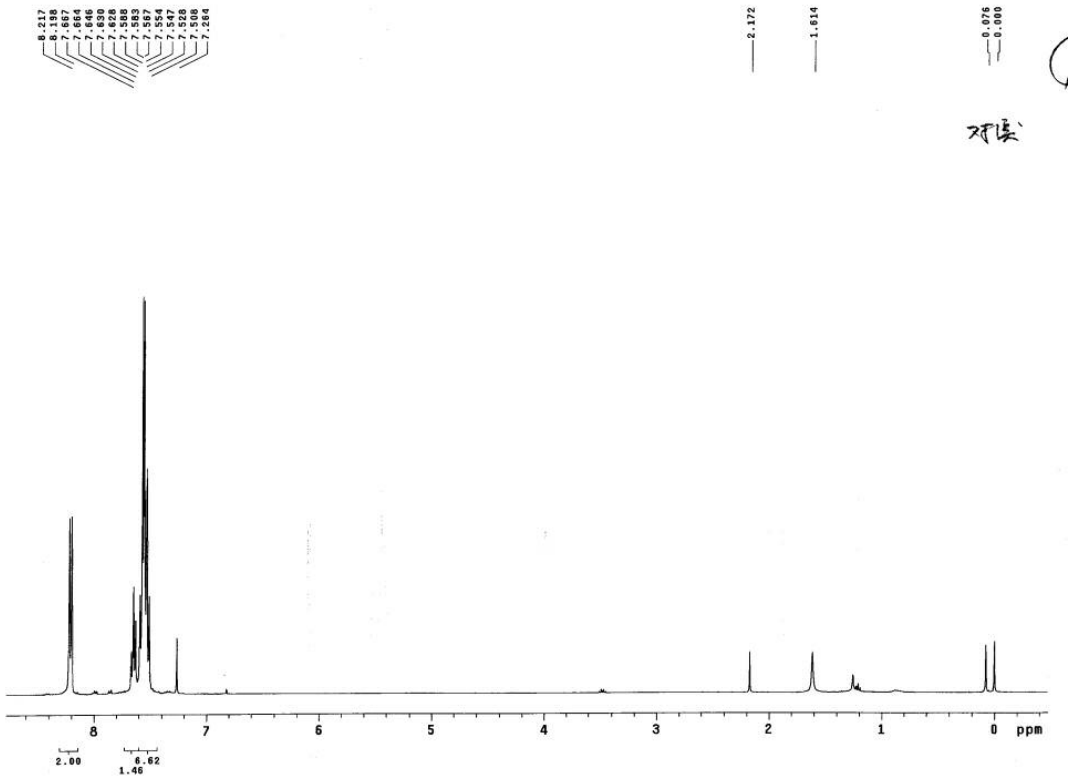
77.000
76.685
55.431
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
C
Br

3ag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7.630
7.609
7.588
7.583
7.567
7.554
7.547
7.528
7.508
7.284
2.172
1.614
0.076
0.000
8
7
6
5
4
3
2
1
0
ppm
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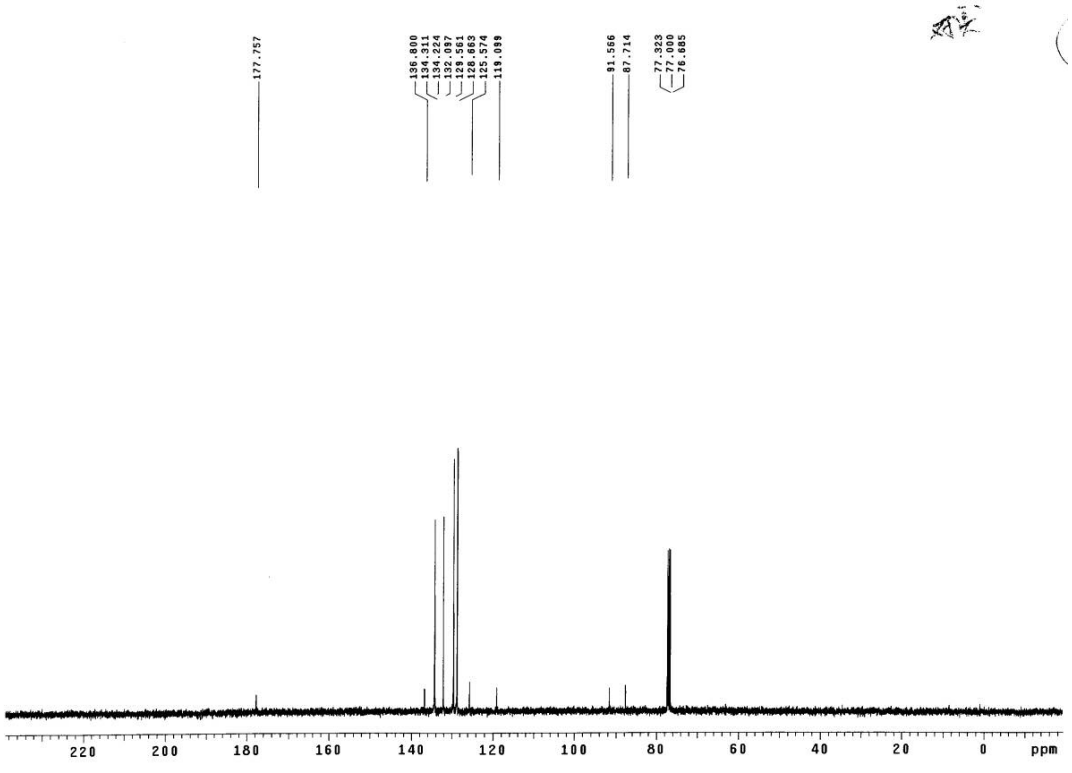
6.62
1.46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134.224
132.097
129.561
128.663
125.574
119.099
91.566
87.714
77.323
77.000
76.685
220
200
180
160
140
120
100
80
60
40
20
0
ppm