Supplementary Materials

$CuFe_2O_4@SiO_2@ZrO_2/SO_4^{2-}$/Cu nanoparticles: as an efficient magnetically recyclable multifunctional Lewis/Brønsted acid nanocatalyst for ligand- and Pd-free Sonogashira cross-coupling reaction in water

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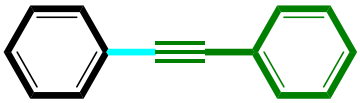
Table S1 Metal leaching tests over the model reaction of iodobenzene with phenyl acetylene under optimized conditions for each of nine runs using a ICP-MS instrument[a,b]

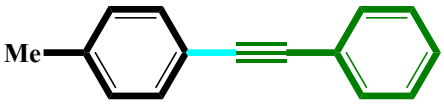
Run	Leaching amount ($\mu g.L^{-1}$)		
	Cu	Fe	Zr
1	0.000	0	0
2	0.000	0	0
3	0.000	0	0
4	0.000	0	0
5	0.006	0	0
6	0.005	0	0
7	0.005	0	0
8	0.006	0	0
9	0.005	0	0

[a] The analyses were taken at 324.754 nm, 259.940 nm, and 343.823 nm for Cu, Fe, and Zr respectively.
[b] The leaching tests were also carried out with a ICP-OES instrument and didn't found any detectable metal in the residues

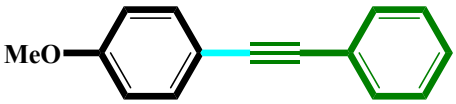
^{1}H NMR, ^{13}C NMR and Mass characterization data of the sonogashira products:



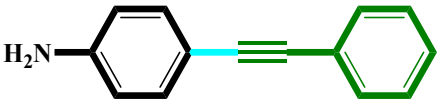
^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.23-7.28 (m, 6H), 7.43-7.47 (m, 4H) ppm; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 89.5, 123.3, 128.3, 129.2, 131.6 ppm; MS (m/e) = 178 [M^+]; Elemental Analysis: Calcd. C: 94.33, H: 5.67%, Found. C: 94.11, H: 5.89%.



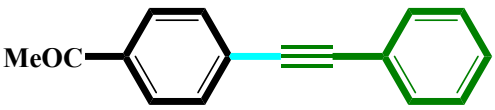
^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 2.22 (s, 3H, CH_3), 7.14 (d, 2H, J= 8.4 Hz, Ar-H), 7.19-7.42 (m, 7H, Ar-H) ppm; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 21.5, 88.7, 89.6, 120.2, 123.5, 128.1, 128.3, 129.1, 131.5, 131.7, 138.4 ppm; MS (m/e)= 192 [M^+]; Elemental Analysis: Calcd. C: 93.77, H: 6.30%, Found. C: 93.57, H: 6.23%.



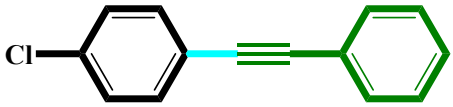
^{1}H-NMR (250 MHz, $CDCl_3$) δ: 3.76 (s, 3H, CH_3), 6.79 (d, 2H, J= 8.2 Hz, Ar-H), 7.21-7.25 (m, 3H, Ar-H), 7.37-7.44 (m, 4H, Ar-H) ppm; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 55.2, 88.0, 89.4, 114.0, 115.3, 123.6, 127.9, 128.3, 131.4, 133.0, 159.6 ppm; MS (m/e)= 208 [M^+]; Elemental Analysis: Calcd. C: 86.50, H: 5.82%, Found. C: 86.64, H: 5.71%.



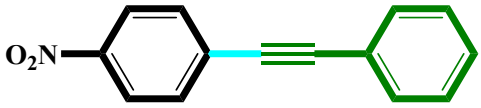
^{1}H-NMR (250 MHz, $CDCl_3$) δ: 3.62 (s, 2H, NH_2), 6.52 (s, 2H, Ar-H), 7.22-7.40 (m, 7H, Ar-H) ppm; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 87.3, 90.2, 112.5, 114.7, 123.9, 127.7, 128.3, 131.3, 132.9, 146.7 ppm.



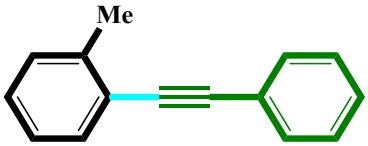
^{1}H-NMR (250 MHz, $CDCl_3$) δ: 2.51 (s, 3H, CH_3), 7.16-7.33 (m, 3H, Ar-H), 7.45-7.54 (m, 4H, Ar-H), 7.86 (d, 2H, *J*=7.5 Hz, Ar-H) ppm; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 27.0, 88.9, 92.9, 123.0, 128.2, 128.3, 128.8, 129.5, 132.0, 132.2, 136.5, 197.6 ppm.



^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.13-7.43 (m, 9H, Ar-H) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 88.2, 90.3, 121.8, 122.9, 128.4, 128.5, 128.7, 131.6, 132.8, 134.2 ppm.

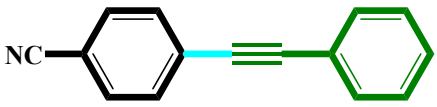


^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.37-7.41 (m, 3H, Ar-H), 7.54-7.57 (m, 2H, Ar-H), 7.68 (d, 2H, *J*= 12.5 Hz, Ar-H), 8.22 (d, 2H, *J*= 7.5 Hz, Ar-H) ppm; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 87.5, 94.7, 122.0, 123.6, 128.5, 129.2, 130.2, 131.8, 132.2, 146.9 ppm; MS (m/e)= 224 [M^+]; Elemental Analysis: Calcd. C: 75.32, H: 4.07, N: 6.27%, Found. C: 75.42, H: 4.21, N: 6.15%.

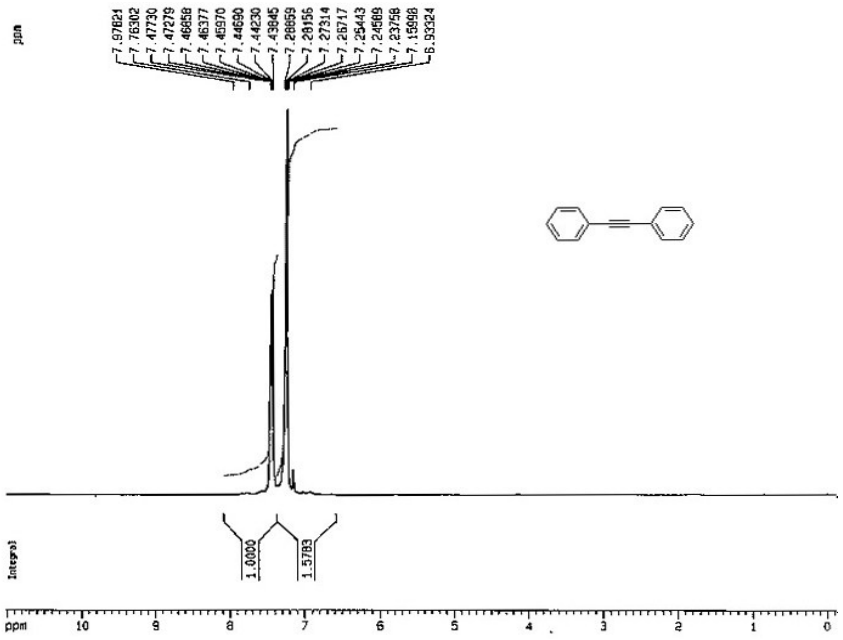


^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.44 (s, 3H, CH_3), 7.14-7.46 (m, 9H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 20.7, 86.01, 94.2, 123.0, 125.5, 128.1, 128.30, 128.35, 129.4, 131.5, 131.8, 140.1 ppm; MS (m/e)= 192 [M^+]; Elemental Analysis: Calcd. C: 93.70, H: 6.30%, Found. C: 93.82, H: 6.18%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 3.82 (s, 3H, CH_3), 6.87 (d, 2H, J= 7.25 Hz, Ar-H), 7.31-7.33 (m, 3H, Ar-H), 7.45-7.53 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ: 55.8, 85.6, 93.3, 110.6, 112.4, 120.4, 123.5, 128.0, 128.1, 129.7, 131.6, 133.5, 159.8 ppm.



^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.28-7.31 (m, 3H, Ar-H), 7.44-7.53 (m, 6H, Ar-H) ppm; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 87.7, 93.7, 111.4, 118.5, 122.2, 128.2, 128.5, 129.1, 131.7, 132.03, 132.06 ppm; MS (m/e)= 203 [M^+]; Elemental Analysis: Calcd. C: 88.64, H: 4.47, N: 6.89%, Found. C: 88.77, H: 4.57, N: 6.66%.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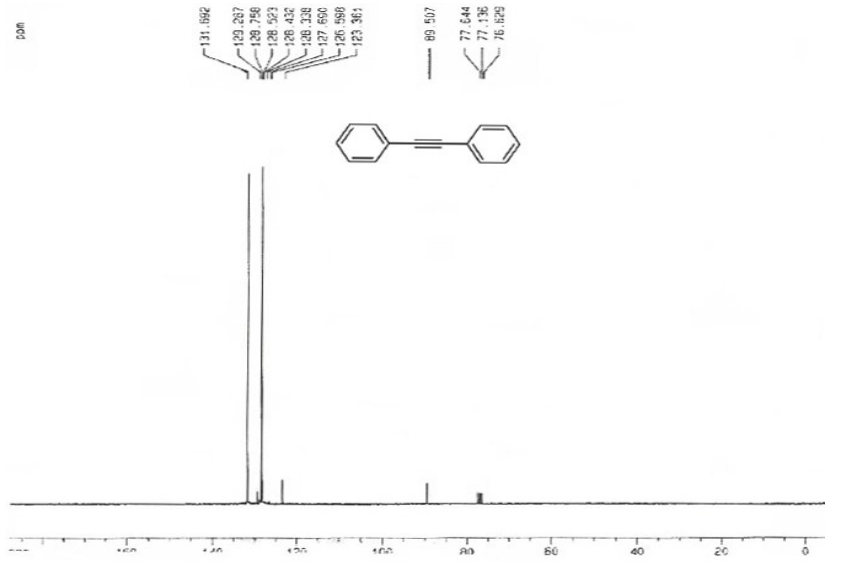
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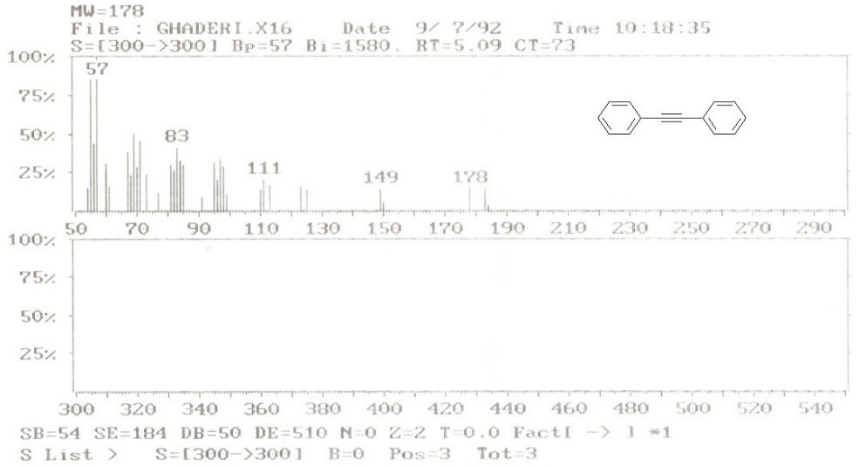
76.629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50%
25%
57
83
111
149
178
50 70 90 110 130 150 170 190 210 230 250 270 290
300 320 340 360 380 400 420 440 460 480 500 520 540
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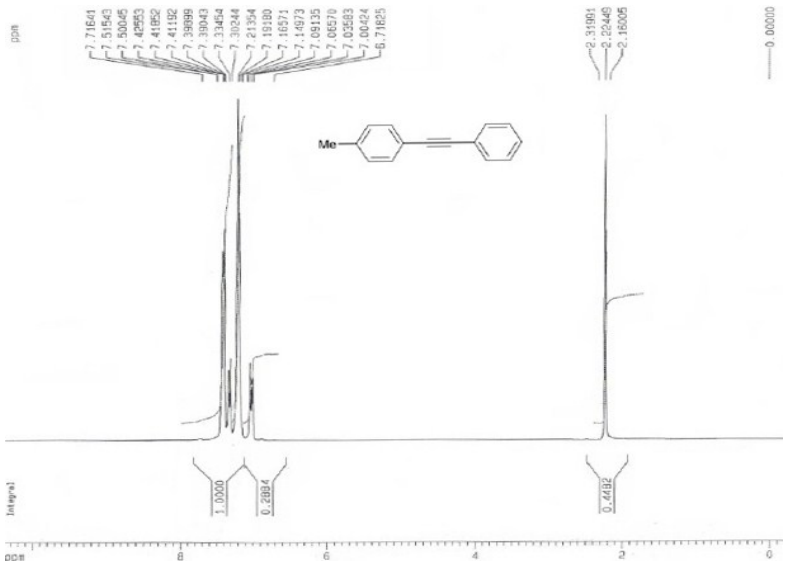
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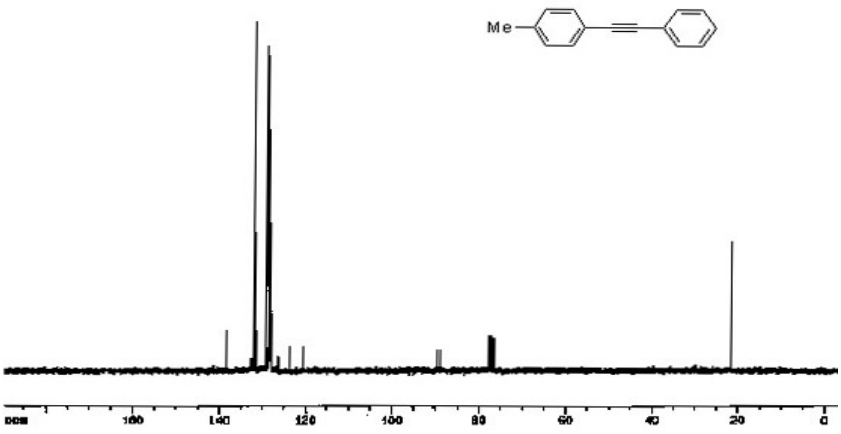
ppm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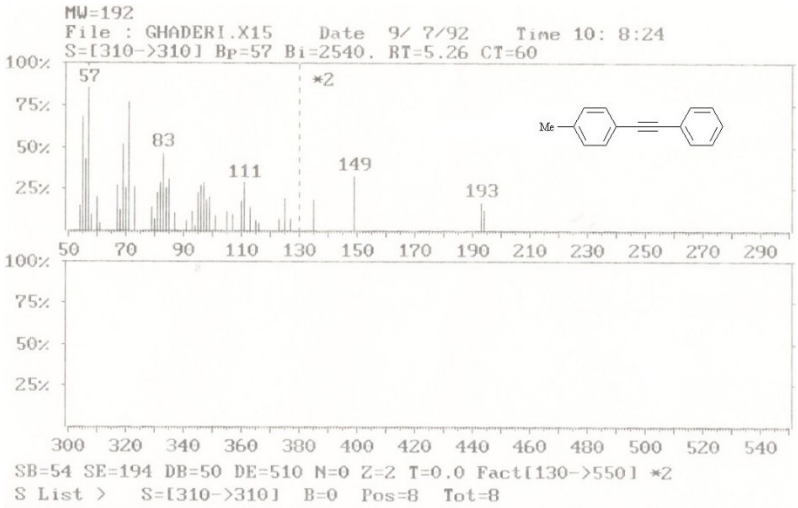
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25%
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*2
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111
149
193
Me
50 70 90 110 130 150 170 190 210 230 250 270 290
300 320 340 360 380 400 420 440 460 480 500 520 540
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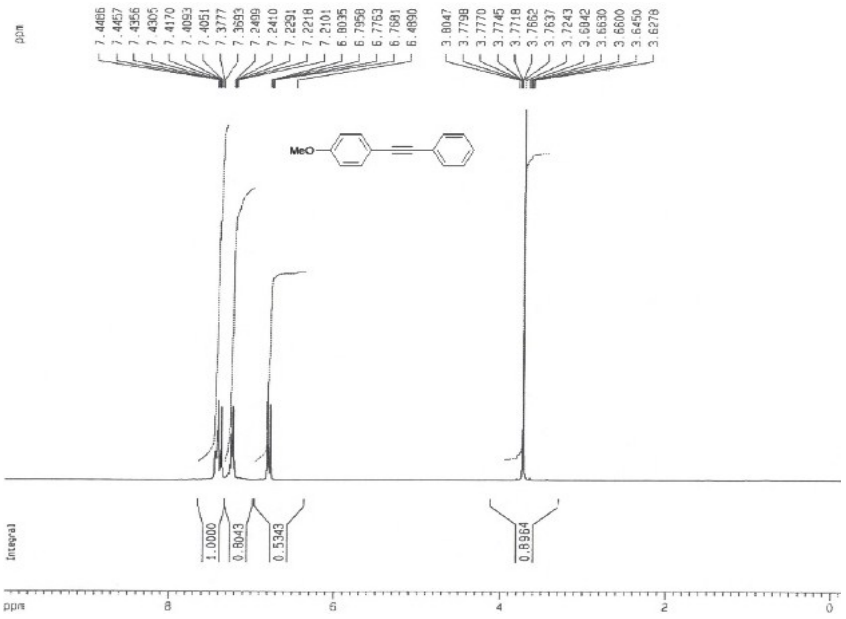
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7.2101
6.8035
6.7958
6.7763
6.7681
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3.8047
3.7798
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3.7745
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2
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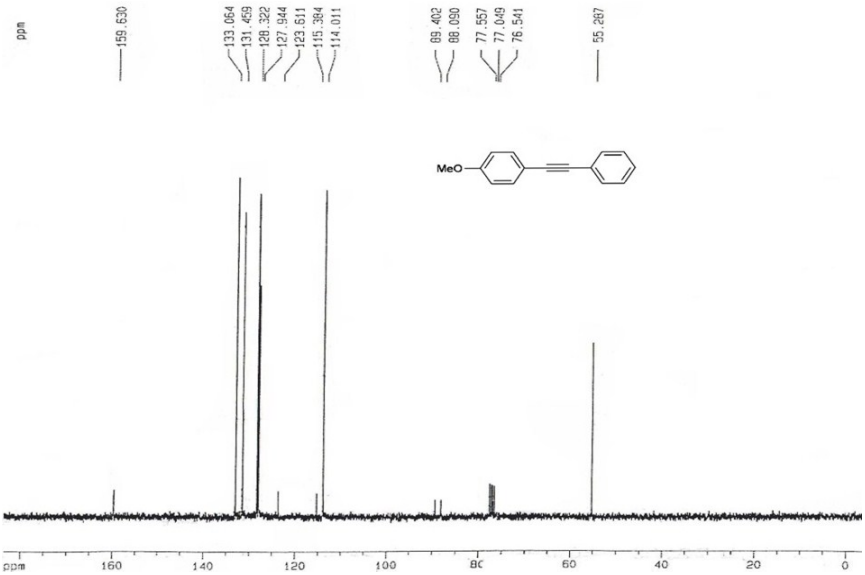
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60
40
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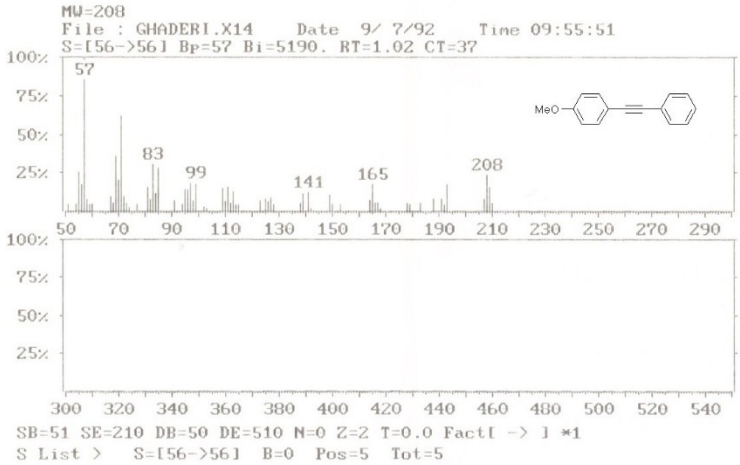
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165
208
MeO
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300 320 340 360 380 400 420 440 460 480 500 520 540
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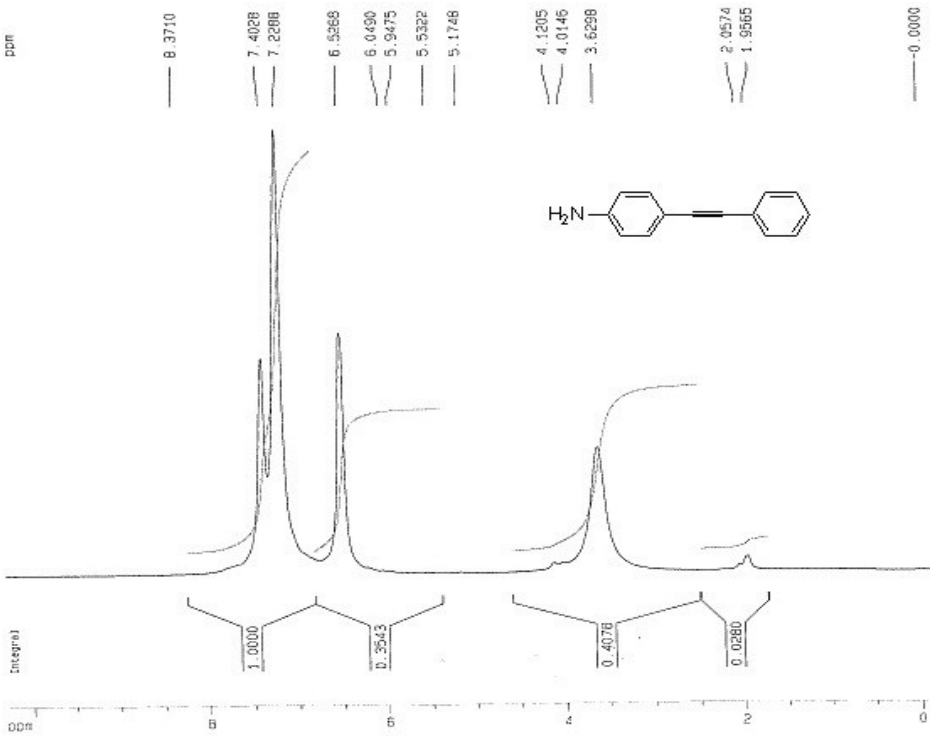
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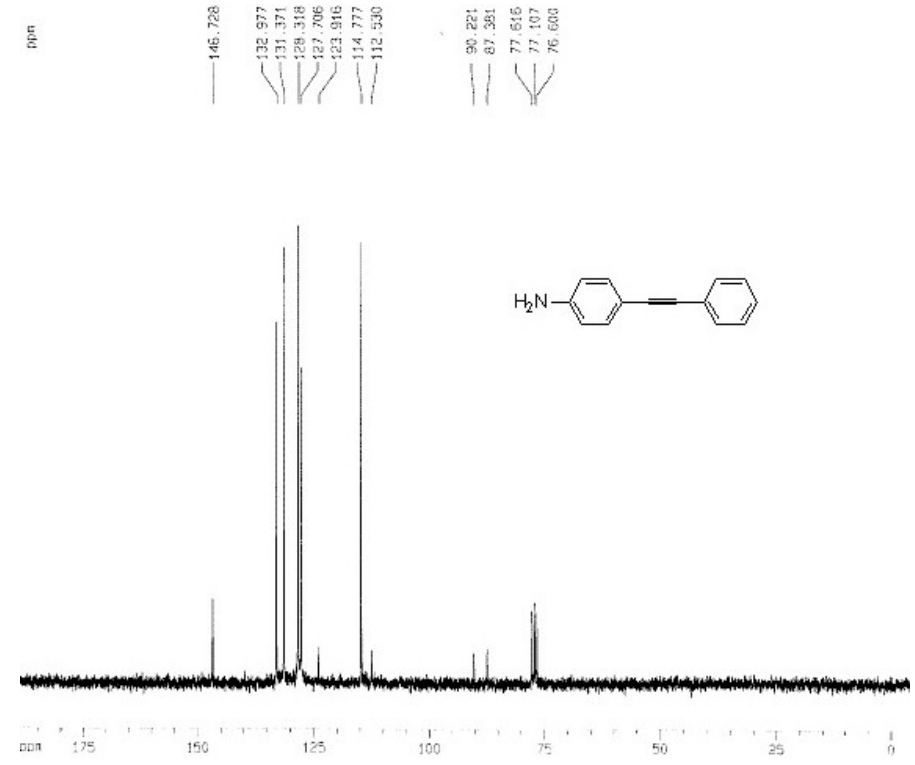
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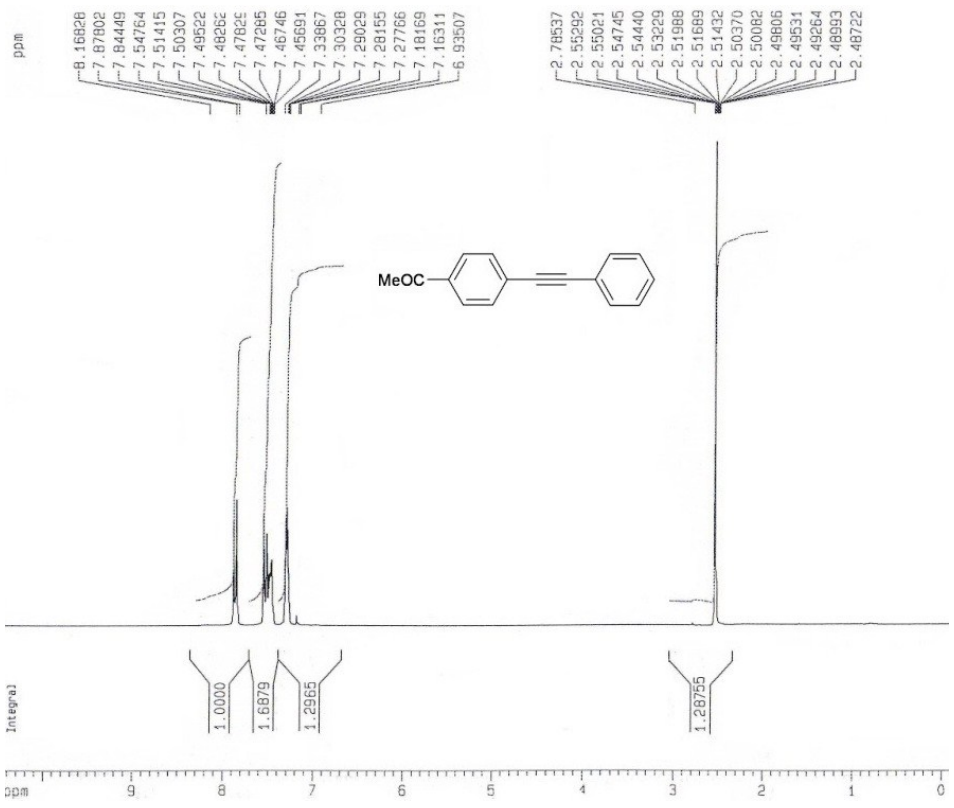
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2.51689
2.51432
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2.49531
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7
6
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3
2
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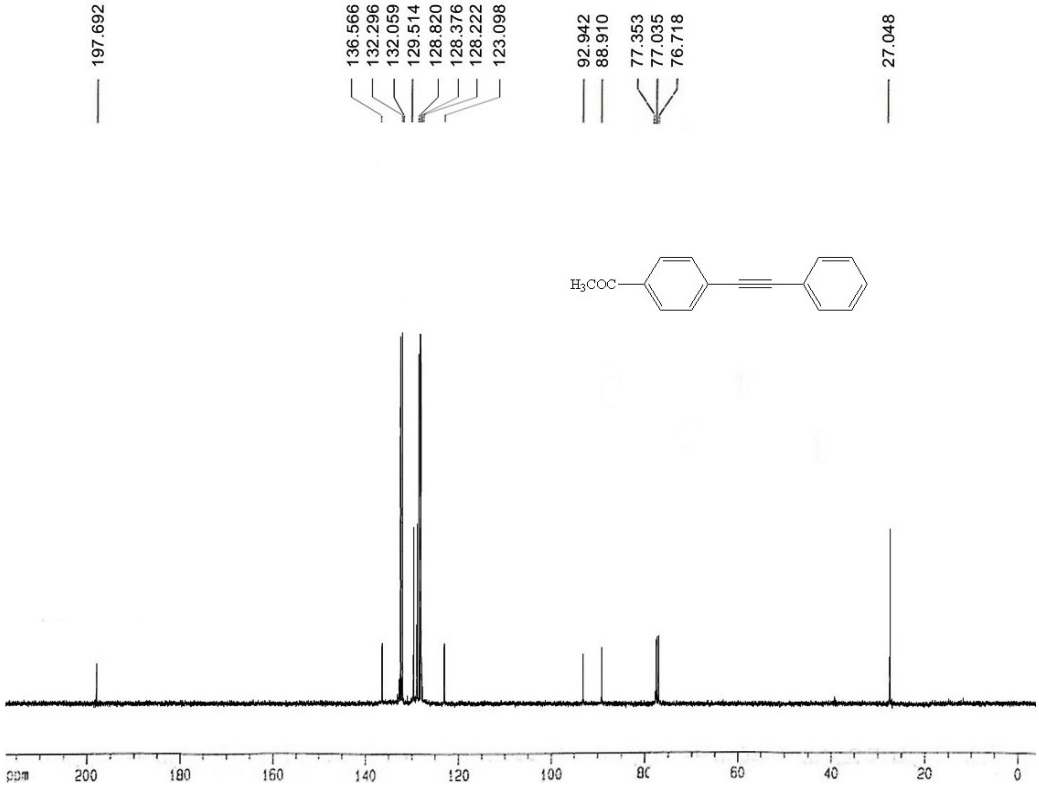
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140
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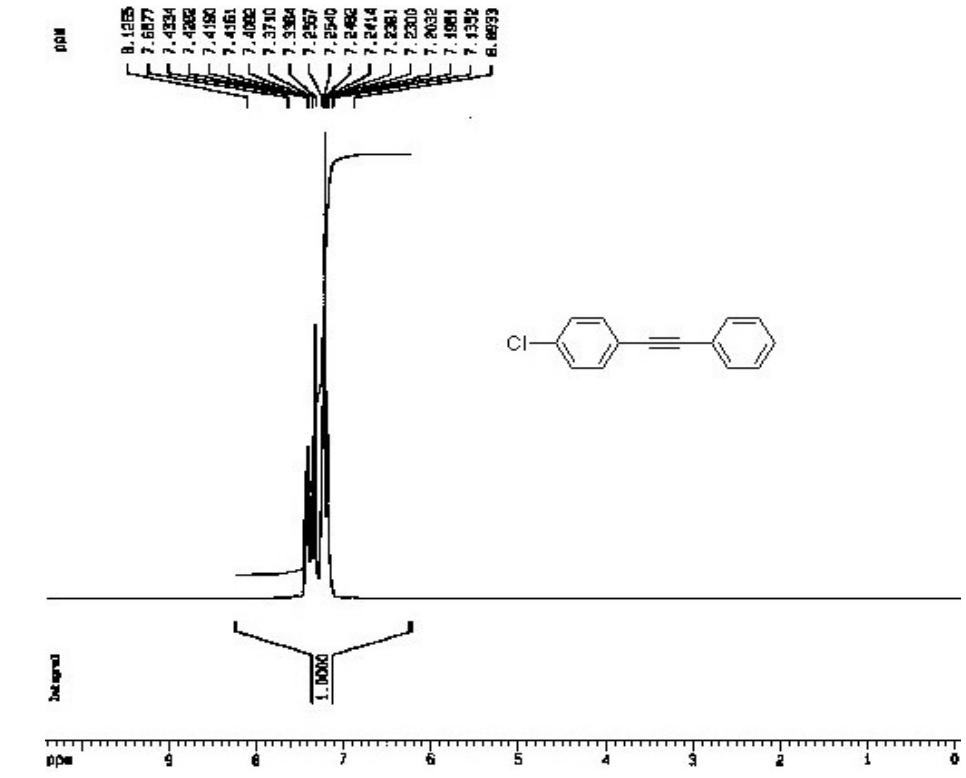
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7.2032
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2
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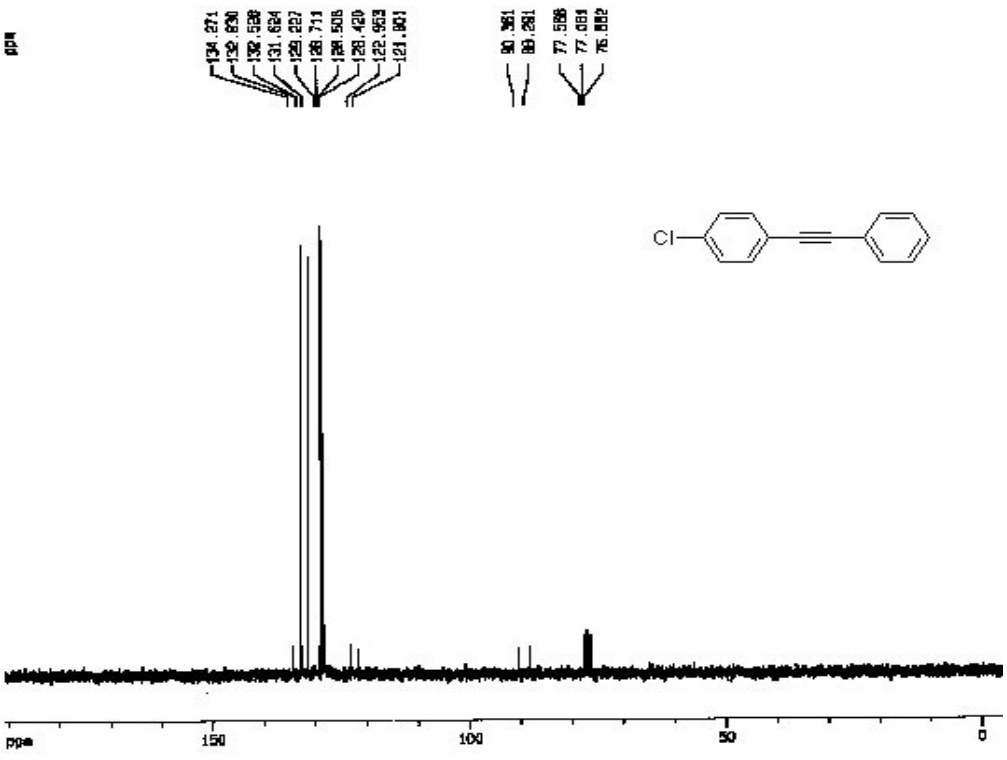
0
Cl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77.084
76.882
Cl
ppm
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50
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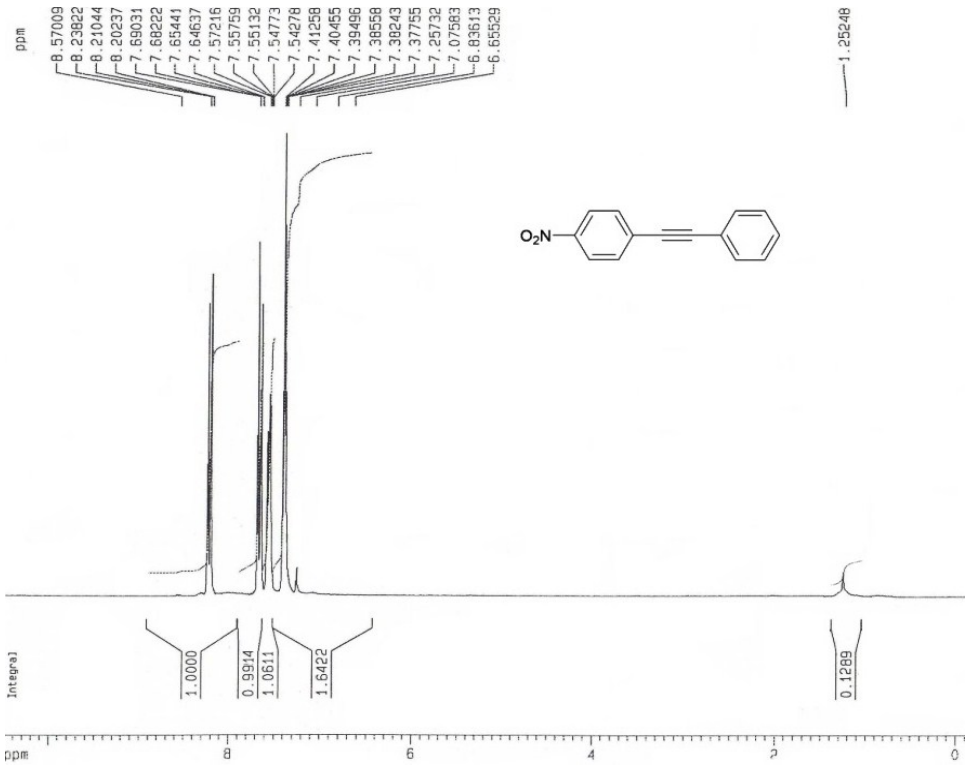
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7.25732
7.07583
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2
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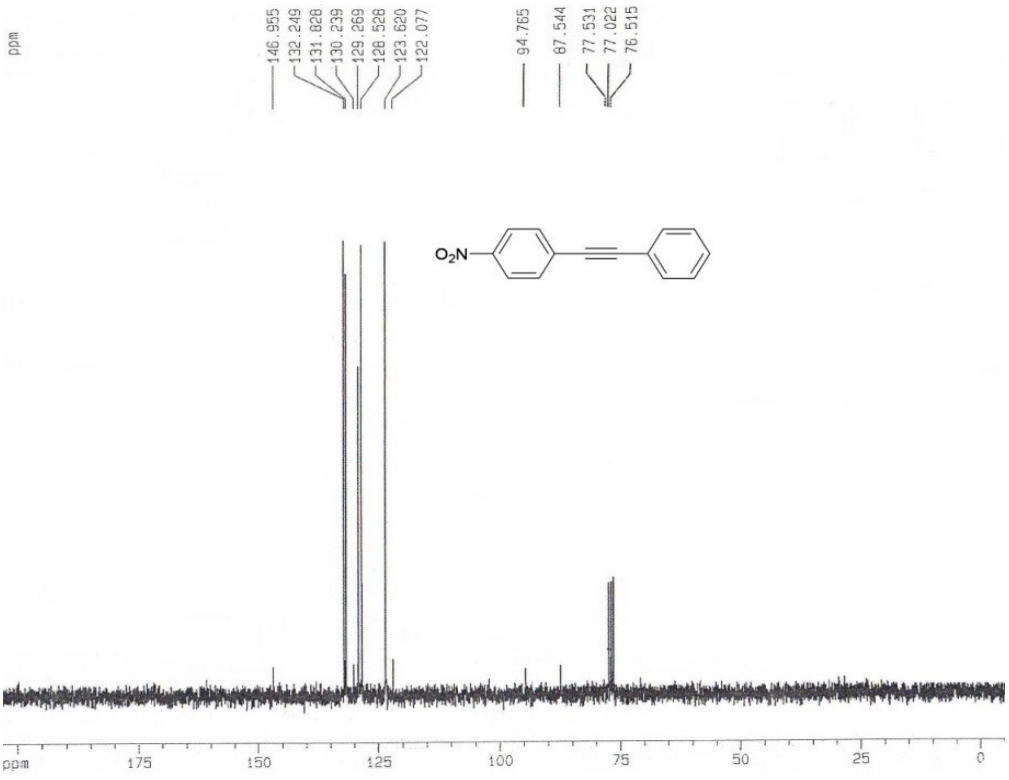
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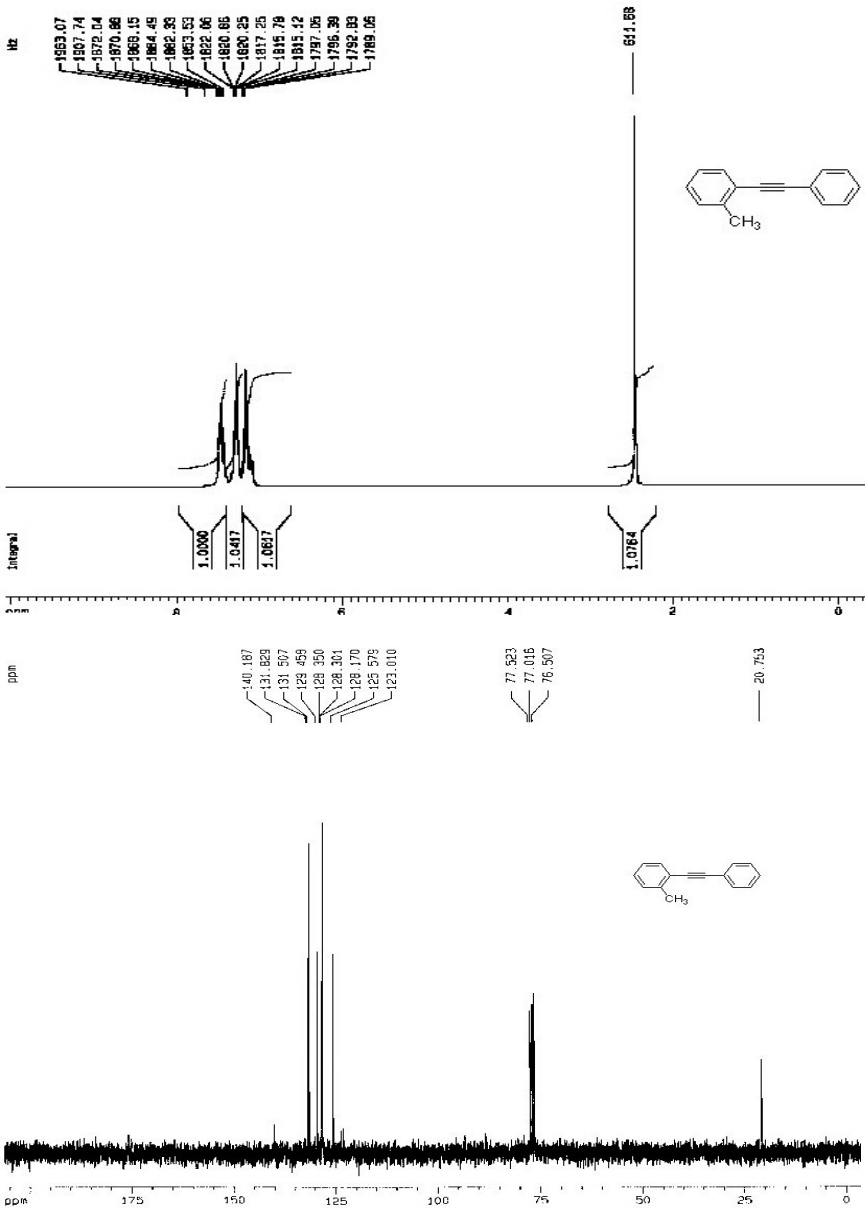
75
50
25
0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1868.15
1864.49
1862.36
1853.53
1822.06
1820.66
1820.25
1817.25
1815.78
1815.12
1797.05
1795.30
1792.83
1789.06
611.68
CH3
Integral
1.0000
1.0417
1.0817
1.0764
ppm
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131.507
129.456
128.350
128.301
128.170
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CH3
ppm
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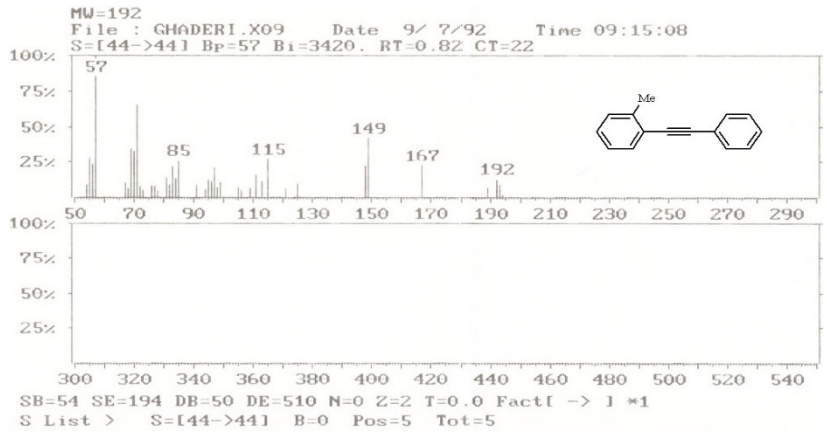
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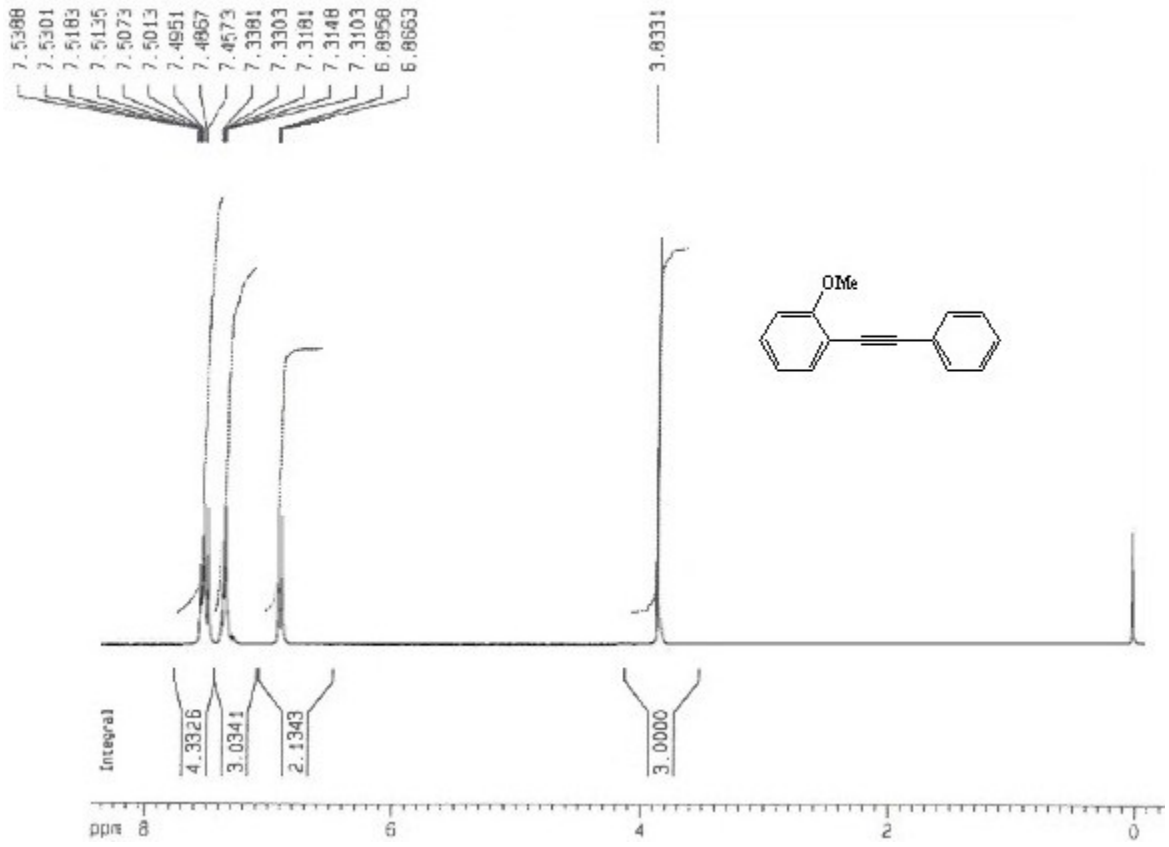
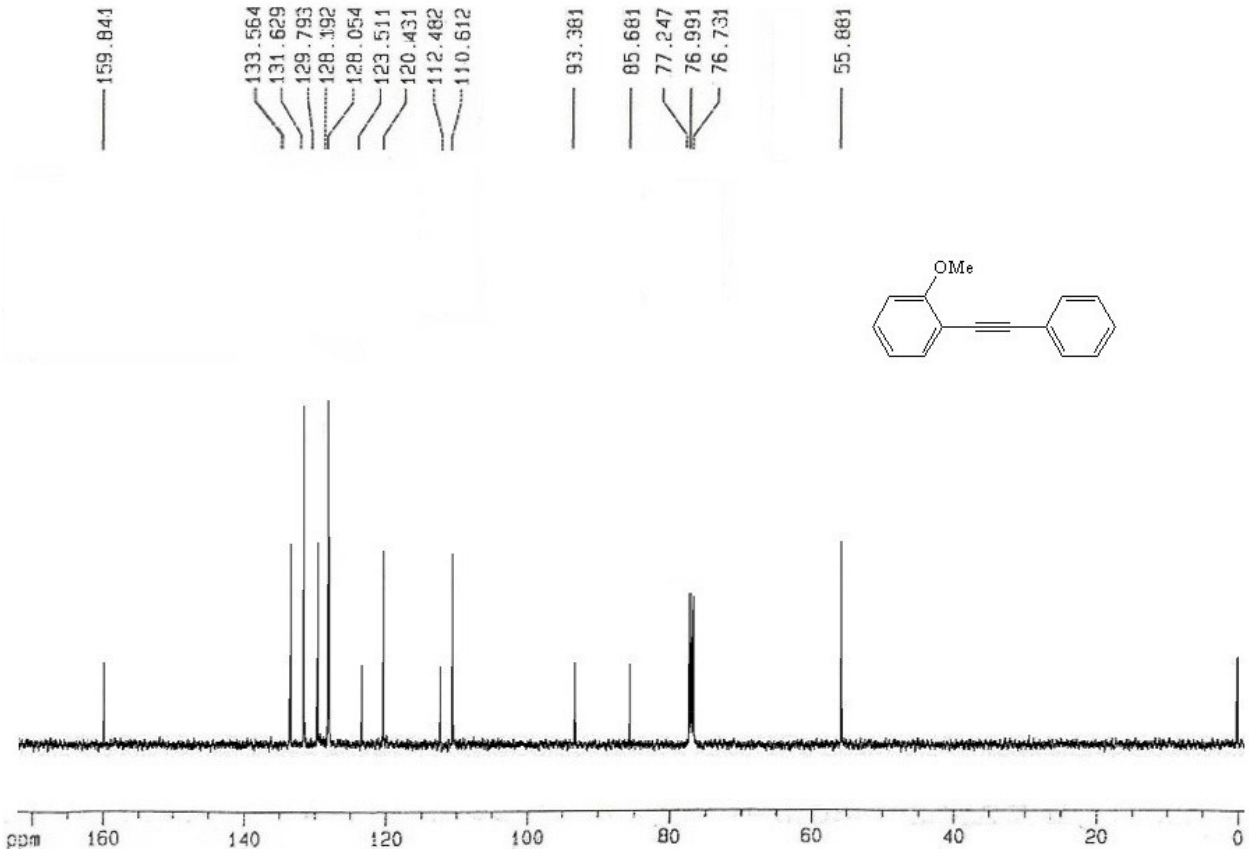
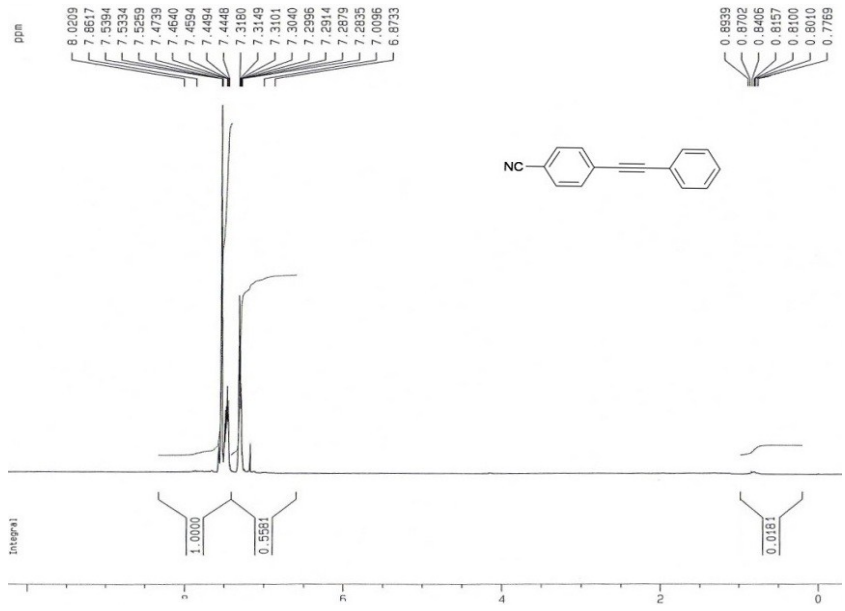
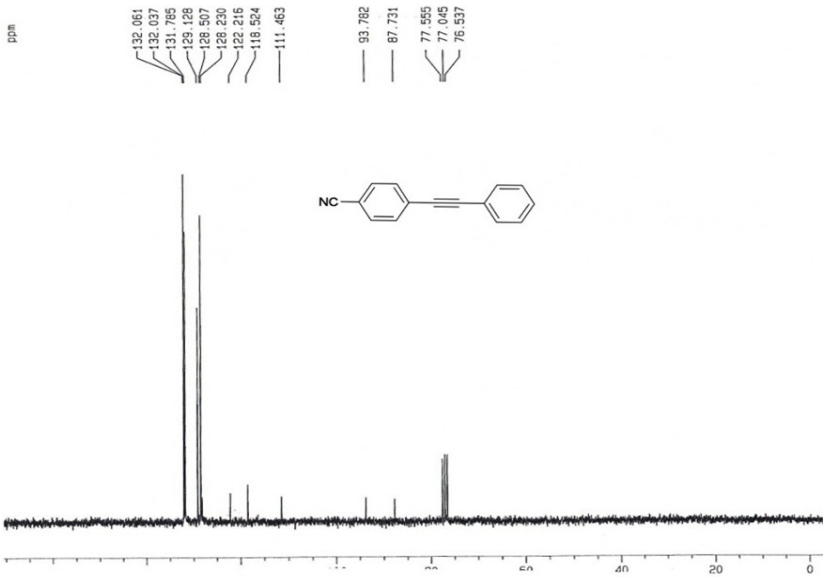
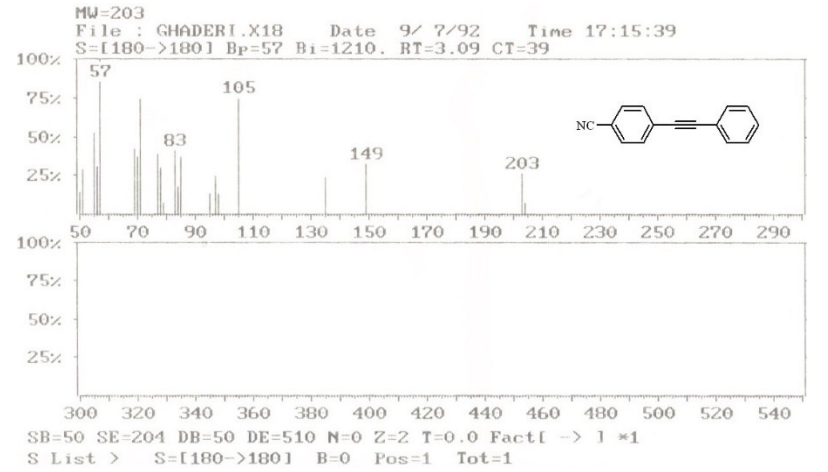
50%
25%
57
85
115
149
167
192
Me
50 70 90 110 130 150 170 190 210 230 250 270 290
300 320 340 360 380 400 420 440 460 480 500 520 540
SB=54 SE=194 DB=50 DE=510 N=0 Z=2 T=0.0 Fact[->] *1
S List > S=[44->44] B=0 Pos=5 Tot=5


7.5388
7.5301
7.5183
7.5135
7.5073
7.5013
7.4951
7.4867
7.4573
7.3381
7.3303
7.3181
7.3148
7.3103
6.8958
6.8663
3.8331
OMe
Integral
4.3326
3.0341
2.1343
3.0000
ppm 8 6 4 2 0


159.841
133.564
131.629
129.793
128.192
128.054
123.511
120.431
112.482
110.612
93.381
85.681
77.247
76.991
76.731
55.681
OMe
ppm
160
140
120
100
80
60
40
20
0


ppm
8.0209
7.8617
7.5394
7.5334
7.5259
7.4739
7.4640
7.4594
7.4494
7.4448
7.3180
7.3149
7.3101
7.3040
7.2996
7.2914
7.2879
7.2835
7.0096
6.8733
0.8939
0.8702
0.8406
0.8157
0.8100
0.8010
0.7769
NC
Integral
1.0000
0.5581
0.0181
6
4
2
0


ppm
132.061
132.037
131.785
129.128
128.507
128.230
122.216
119.524
111.463
93.782
87.731
77.555
77.045
76.537
NC
50
40
20
0


MW=203
File : GHADERI.X18 Date 9/ 7/92 Time 17:15:39
S=[180->180] Bp=57 Bi=1210. RT=3.09 CT=39
100%
75%
50%
25%
57
105
83
149
203
NC
50 70 90 110 130 150 170 190 210 230 250 270 290
100%
75%
50%
25%
300 320 340 360 380 400 420 440 460 480 500 520 540
SB=50 SE=204 DB=50 DE=510 N=0 Z=2 T=0.0 Fact[->] *1
S List > S=[180->180] B=0 Pos=1 Tot=1