Ni-Fe_3O_4 Magnetic Nanoparticles Supported on Multiwalled Carbon Nanotubes: Effective Catalyst in Suzuki Cross Coupling Reactions

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Supporting Information

General Methods

All organic reagents were purchased from Sigma-Aldrich and used without further modification. Multiwalled carbon nanotubes were purchased from Graphene Supermarket. High resolution ^{1}H and ^{13}C NMR acquisition was performed on JEOL 400 MHz Nuclear Magnetic Resonance Spectrometer (NMR). Transmission Electron Microscopy (TEM) was completed at Analytical Instrumentation Facilities (AIF) at North Carolina University on Talos F200X G2 with a 200 kV FEG (Field Emission Gun) Analytical Scanning Transmission Electron Microscope (S/TEM). X-ray Diffraction (XRD) was performed at Southeastern North Carolina Regional Microanalytical and Imaging Center (SENCR-MIC) at Fayetteville State University on Rigaku MiniFlex 600 X-ray Diffractometer.

Preparation of Ni-Fe_3O_4/MWCNTs

Nickel acetate tetrahydrate (50.9 mg, 12%), iron(II,III) oxide (39 mg, 28%), and MWCNTs (60 mg, 60%) were added to a 20 mL volume zirconium ceramic vial (SPEX CertiPrep). Two ceramic balls (d ¼ 1.3 cm) were added and the vial was subjected to mechanical shaking in a ball-mill mixer (SPEX CertiPrep 8000M High-Energy Shaker Mill) for 45 min to afford the final product of Ni/Fe_3O_4-MWCNTs. The SPEX CertiPrep 8000M ball-mill mixer typically provides mechanical motions of 1060 lateral cycles per minute with 5.9 cm back-and-forth and 2.5 cm side-to-side.

Procedure for the Suzuki Cross Coupling Reactions

Aryl iodide and bromide (0.25 mmol, 1 eq.) was dissolved in a mixture of 4 mL H_2O:EtOH 1 : 1 and placed in a 10 mL Monowave 50 tube. To this was added the arylboronic acid (0.3 mmol, 1.2 eq.) and potassium carbonate (0.75 mmol, 3 eq.). The catalyst Ni-Fe_3O_4/MWCNTs (1.20 mg, 2.45 µmol, 1 mol%) was then added, and the tube was sealed and heated using Monowave 50 heating reactor at 120 ^{o}C for 15 minutes. After completion of the reaction time, the reaction mixture was diluted with H_2O (30 mL) and extracted with dichloromethane (CH_2Cl_2 3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The solvent in the filtrate was then removed in vacuo to give a solid which was further purified by flash chromatography using hexane– ethyl acetate as eluent.

Procedure for recycling the Ni-Fe_3O_4/MWCNT

Iodobenzene (50 mg, 0.25 mmol, 1 eq.) was dissolved in a mixture of 4 mL H_2O:EtOH (1 : 1) and placed in a 10 mL Monowave 50 tube. To this was added phenyl boronic acid (36 mg, 0.30 mmol, 1.2 eq.), potassium carbonate (101.4 mg, 0.735 mmol, 3eq.). Ni-Fe_3O_4/MWCNTs (3.59 mg, 7.35 µmol, 3 mol%) were then added, the tube was sealed, and heated at 120 ^{o}C for 10 min using

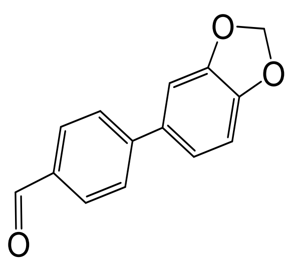
Monowave 50 heating reactor. After completion of the reaction, the mixture was diluted with 10 mL of EtOH and shaken to dissolve all the organic materials. The Ni-Fe_3O_4/MWCNTs nanoparticles were removed by an external magnet and transferred to another Monowave 50 vial where fresh reagents were introduced and heated to the above-mentioned temperature. This procedure was repeated for every run and the percent conversion of product was determined by means of GC-MS spectroscopy.

Spectroscopic Data for Table 3:

1a: 4-(2H-1,3-benzodioxol-5-yl)benzaldehyde ($C_{14}H_{10}O_3$), $M^{\cdot+}$: 226.06 *m/z*

1H-NMR (400 MHz, CHLOROFORM-D) δ 10.02 (s, 1H), 7.90 (d, J = 7.3 Hz, 2H), 7.66 (d, J = 7.3 Hz, 2H), 7.11 (m, J = 10.5 Hz, 2H), 6.90 (d, J = 7.5 Hz, 1H), 6.02 (s, 2H).

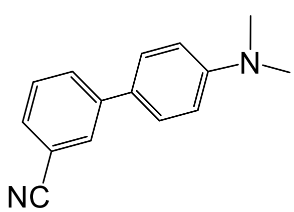
13C-NMR (101 MHz, CHLOROFORM-D) δ 191.94, 148.51, 148.20, 146.90, 134.95, 133.97, 130.39, 127.35, 121.36, 108.89, 107.73, 101.53.



1b: 4'-(Dimethylamino)[1,1'-biphenyl]-3-carbonitrile ($C_{15}H_{14}N_2$) $M^{\cdot+}$: 222.12 *m/z*

1H-NMR (400 MHz, CHLOROFORM-D) δ 7.809-7.806 (m, 1H), 7.63-7.44 (m, 1H), 7.49-7.45 (m, 4H), 6.80-6.78 (d, J = 8.7 Hz, 2H), 3.01 (s, 6H).

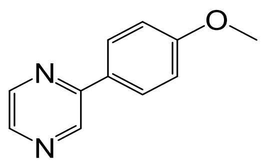
13C-NMR (101 MHz, CHLOROFORM-D) δ 150.08, 142.5, 130.47, 129.70, 129.51, 129.32, 127.74, 126.4, 119.7, 112.73, 112.75, 40.49.



1c: 2-(4-Methoxyphenyl)pyrazine ($C_{11}H_{10}N_2O$) $M^{\cdot+}$: 186.08 *m/z*

1H-NMR (400 MHz, CHLOROFORM-D) δ 8.94 (s, 1H), 8.55 (s, 1H), 8.40 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 3.84 (s, 3H).

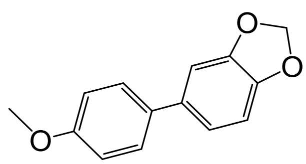
13C-NMR (101 MHz, CHLOROFORM-D) δ 161.28, 152.67, 144.14, 141.99, 141.58, 128.77, 128.39, 114.56, 55.45.



1d: 5-(4-methoxyphenyl)-2H-1,3-benzodioxole ($C_{14}H_{12}O_3$) $M^{\cdot+}$: 228.08 *m/z*

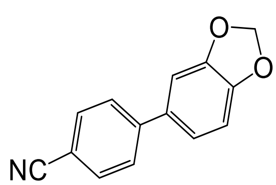
1H-NMR (400 MHz, CHLOROFORM-D) δ 7.43 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 13.3 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 7.8 Hz, 1H), 5.98 (s, 2H), 3.83 (s, 3H).

13C-NMR (101 MHz, CHLOROFORM-D) δ 158.93, 148.13, 146.65, 135.37, 133.64, 127.98, 120.17, 114.23, 108.62, 107.47, 101.15, 55.43.



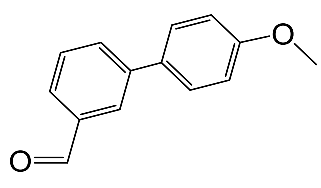
1e: 4-(2H-1,3-benzodioxol-5-yl)benzonitrile ($C_{14}H_9NO_2$) $M^{\cdot+}$: 223.06 *m/z*
1H-NMR (400 MHz, CHLOROFORM-D) δ 7.67 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.04-7.07 (m, 2H), 6.90 (d, J = 7.8 Hz, 1H), 6.02 (s, 2H).

13C-NMR (101 MHz, CHLOROFORM-D) δ 148.59, 148.33, 145,38, 133.45, 132.66, 127.42, 121.25, 119.07, 110.52, 108.95, 107.59, 101.58.



1f: 4'-methoxy-[1,1'-biphenyl]-3-carbaldehyde ($C_{14}H_{12}O_2$) $M^{\cdot+}$: 212.08 *m/z*
1H-NMR (400 MHz, CHLOROFORM-D) δ 10.15-9.94 (1H), 8.21-7.94 (1H), 7.86-7.67 (2H), 7.65-7.44 (3H), 7.11-6.82 (2H), 3.95-3.74 (3H).

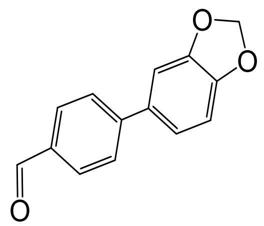
13C-NMR (101 MHz, CHLOROFORM-D) δ 192.56, 159.78, 142.02, 136.98, 136.8, 132.69, 129.53, 128.29, 128.18, 127.72, 114.52, 55.47.



1g: 4-(2H-1,3-benzodioxol-5-yl)benzaldehyde ($C_{14}H_{10}O_3$), $M^{\cdot+}$: 226.06 *m/z*

1H-NMR (400 MHz, CHLOROFORM-D) δ 10.02 (s, 1H), 7.90 (d, J = 7.3 Hz, 2H), 7.66 (d, J = 7.3 Hz, 2H), 7.11 (d, J = 10.5 Hz, 2H), 6.90 (d, J = 7.5 Hz, 1H), 6.02 (s, 2H).

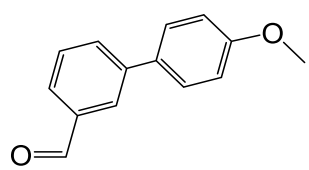
13C-NMR (101 MHz, CHLOROFORM-D) δ 191.94, 148.51, 148.20, 146.90, 134.95, 133.97, 130.39, 127.35, 121.36, 108.89, 107.73, 101.53.



1h: 4'-methoxy-[1,1'-biphenyl]-3-carbaldehyde ($C_{14}H_{12}O_2$) $M^{\cdot+}$: 212.08 *m/z*

1H-NMR (400 MHz, CHLOROFORM-D) δ 10.15-9.94 (1H), 8.21-7.94 (1H), 7.86-7.67 (2H), 7.65-7.44 (3H), 7.11-6.82 (2H), 3.95-3.74 (3H)

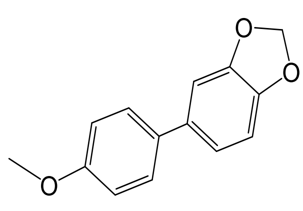
13C-NMR (101 MHz, CHLOROFORM-D) δ 192.56, 159.78, 142.02, 136.98, 136.8, 132.69, 129.53, 128.29, 128.18, 127.72, 114.52, 55.47.



1i: 5-(4-methoxyphenyl)-2H-1,3-benzodioxole ($C_{14}H_{12}O_3$) $M^{\cdot+}$: 228.08 *m/z*

1H-NMR (400 MHz, CHLOROFORM-D) δ 7.45-7.43 (d, J = 6.9, 2.1 Hz, 2H), 7.039-7.02 (m, 2H), 6.96-6.94 (d, 2H), 6.87-6.85 (d, 1H), 5.98 (s, 2H), 3.84 (s, 3H)

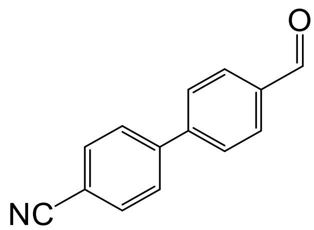
13C-NMR (101 MHz, CHLOROFORM-D) δ 158.97, 148.16, 146.69, 135.40, 133.66, 127.98, 120.17, 114.26, 108.62, 107.47, 101.16, 55.42.



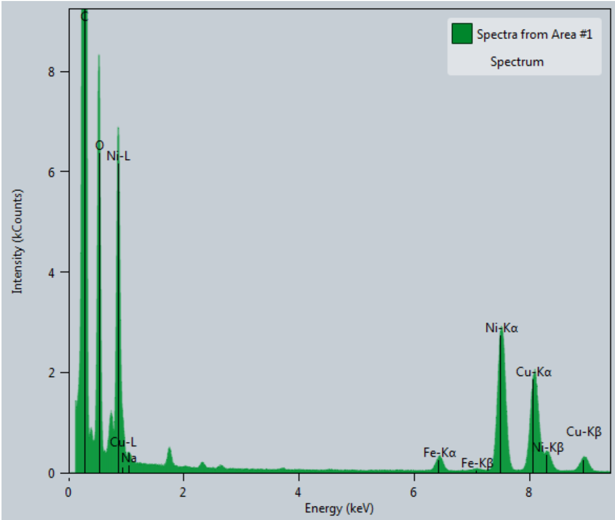
1j: 4'-cyano-[1,1'-biphenyl]-4-carbaldehyde ($C_{14}H_9NO_4$) $M^{\cdot+}$: 207.07 *m/z*

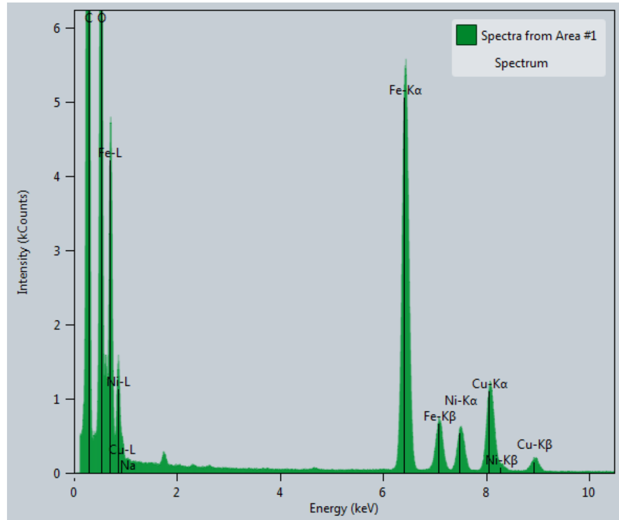
1H-NMR (400 MHz, CHLOROFORM-D) δ 10.07 (s, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.74 (m, J = 16.8, 8.1 Hz, 6H).

13C-NMR (101 MHz, CHLOROFORM-D) δ 191.73, 144.98, 144.22, 136.20, 132.88, 130.52, 128.13, 128.01, 118.65, 112.23.

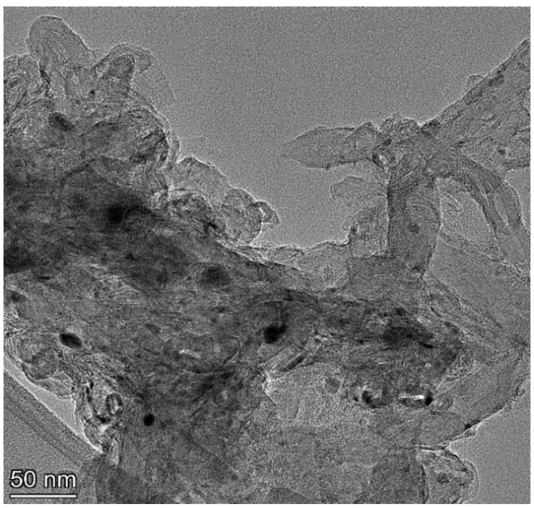


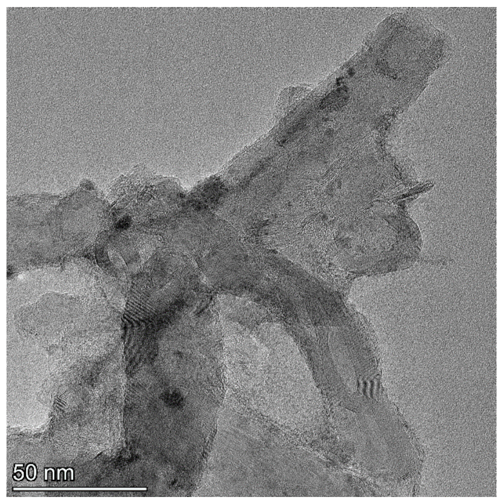
EDS Images of Ni-Fe_3O_4/MWCNTs:





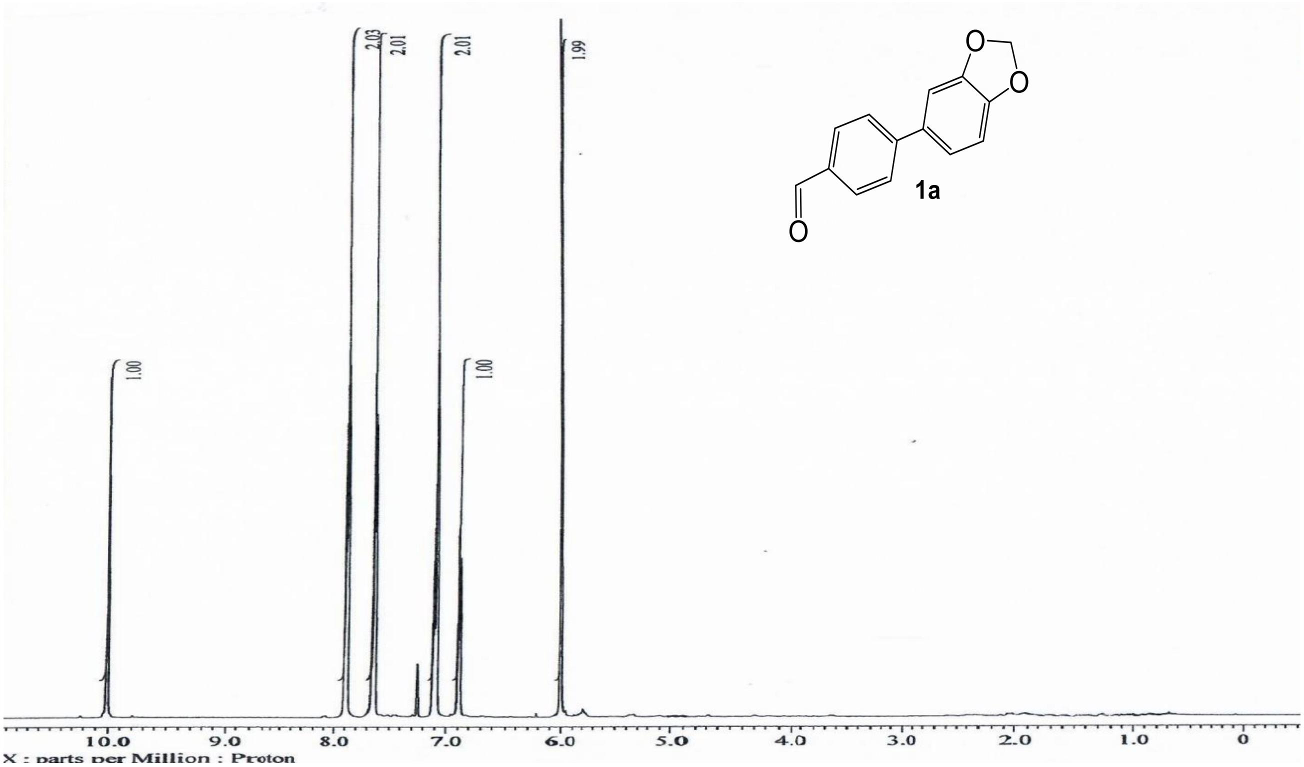
Additional TEM Images of Ni-Fe_3O_4/MWCNTs:

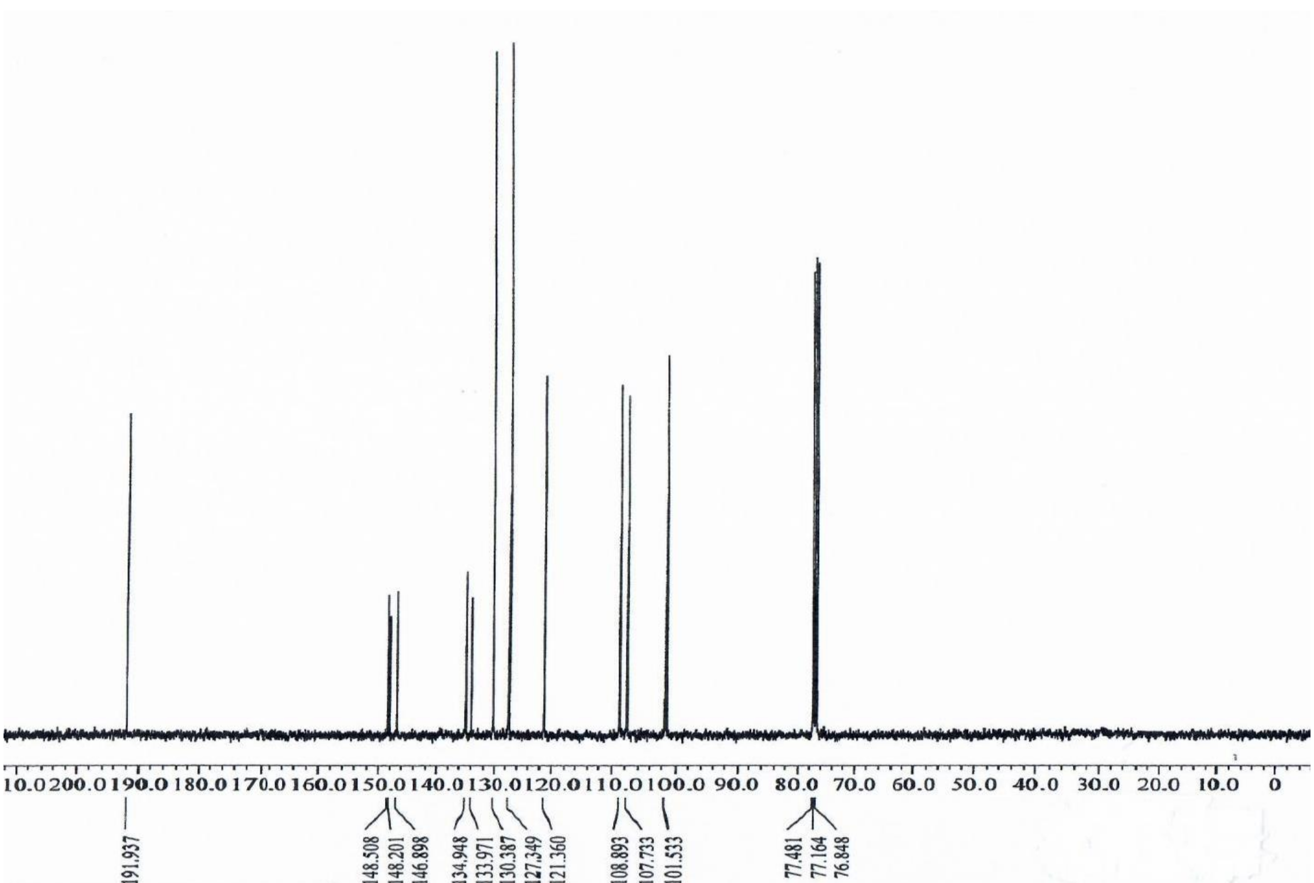


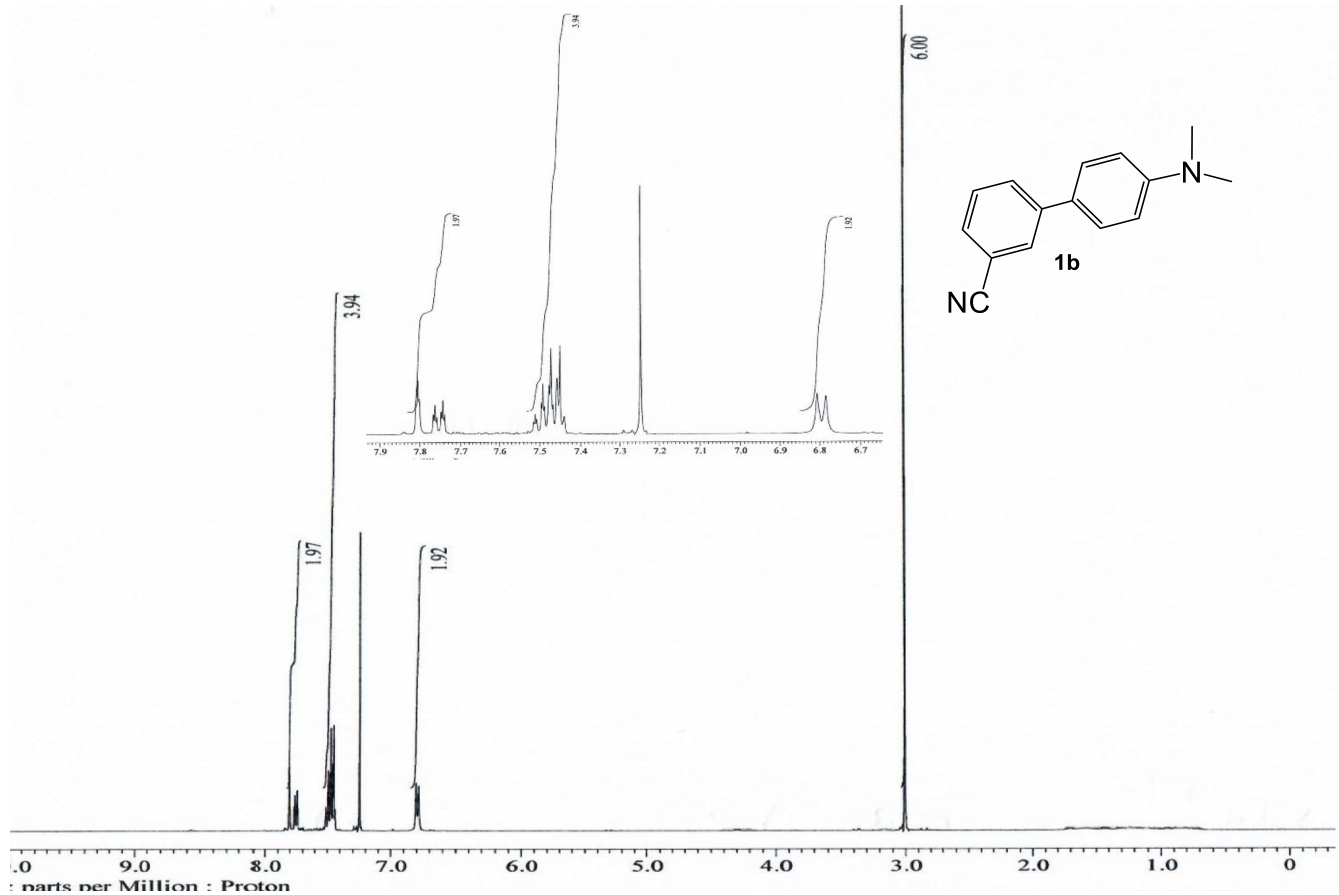


Monowave 50 Heating Reactor

^{1}H and ^{13}C NMR Spectra of Compounds in Table 3:







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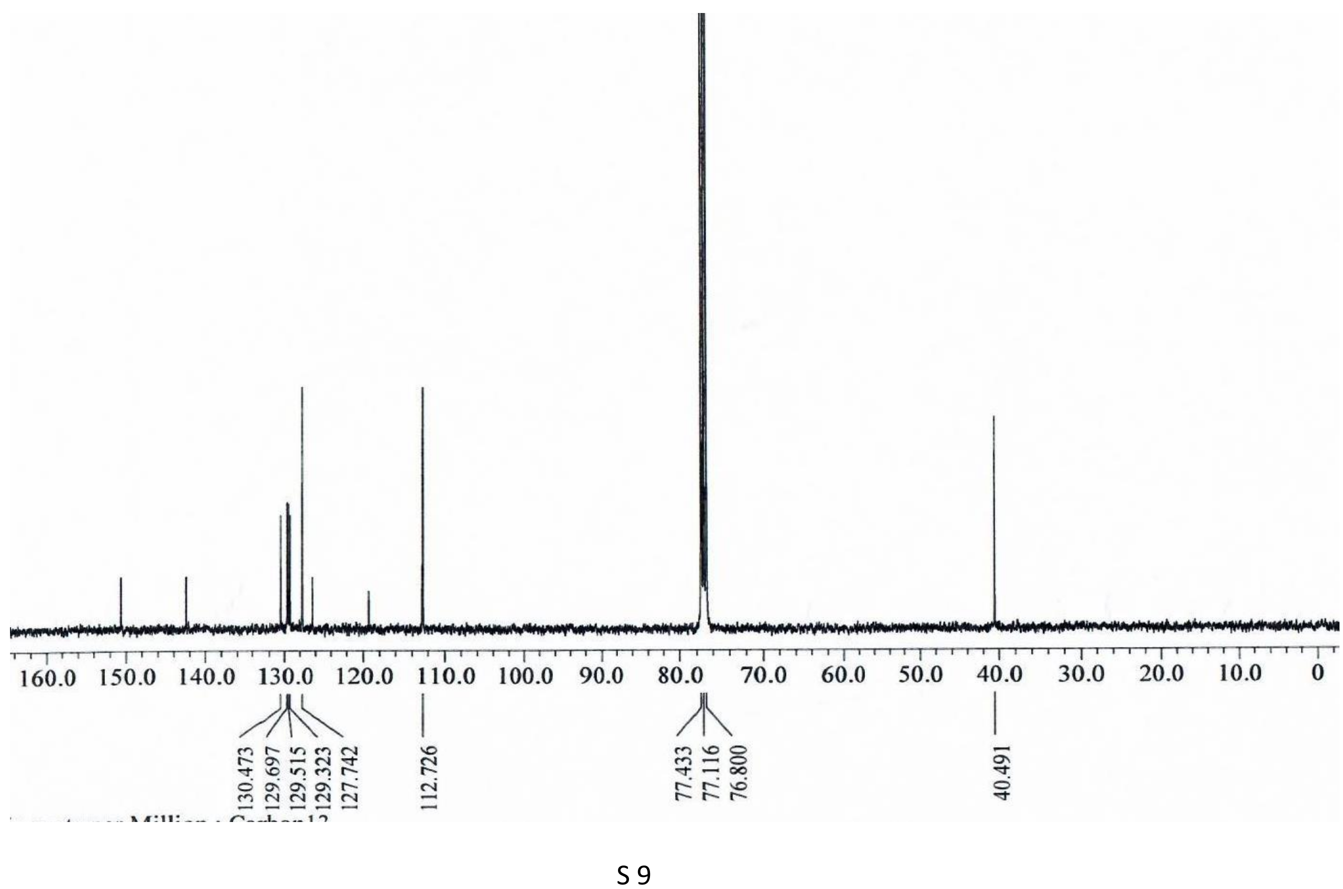
3.0
2.0
1.0
0
parts per Million : Proton



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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
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40.0
30.0
20.0
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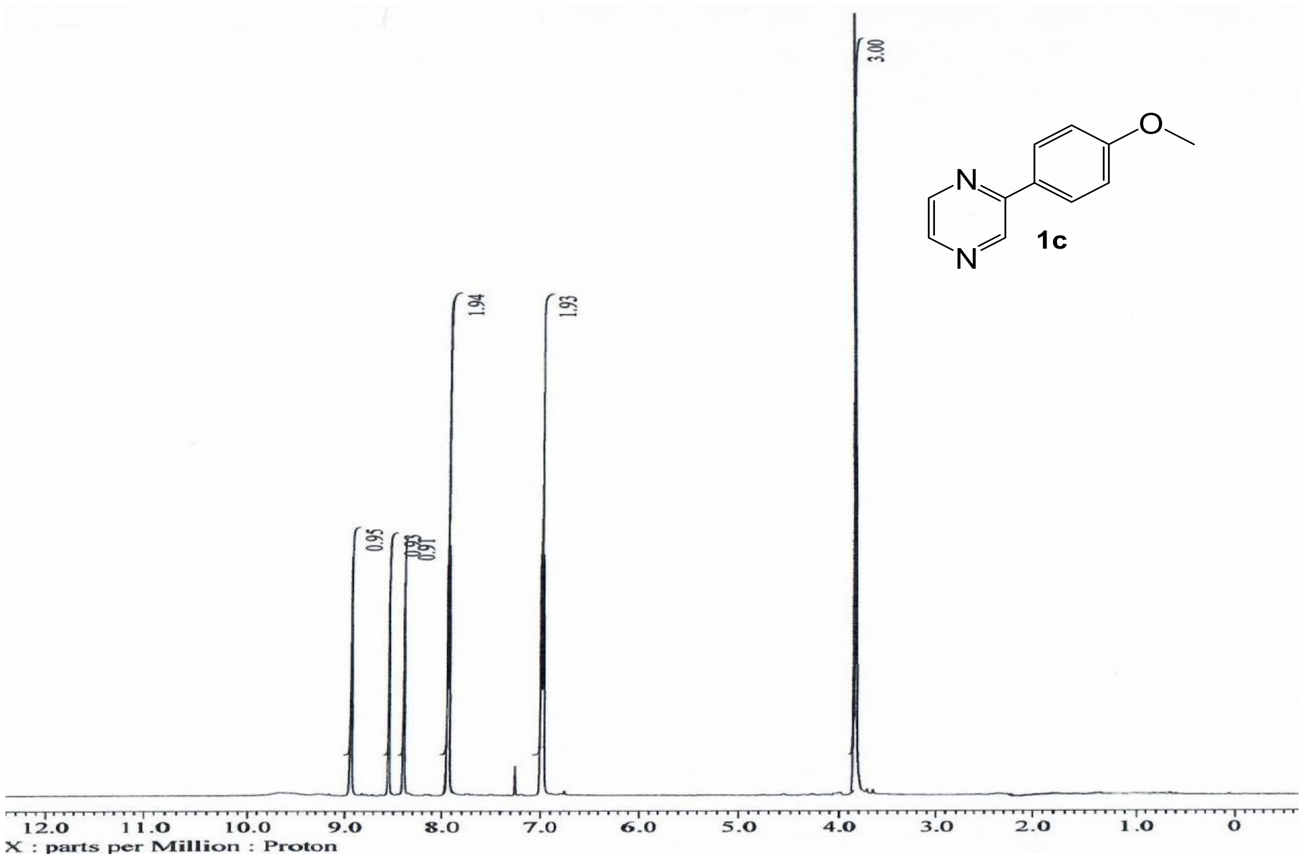

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1.93
0.95
0.91
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11.0
10.0
9.0
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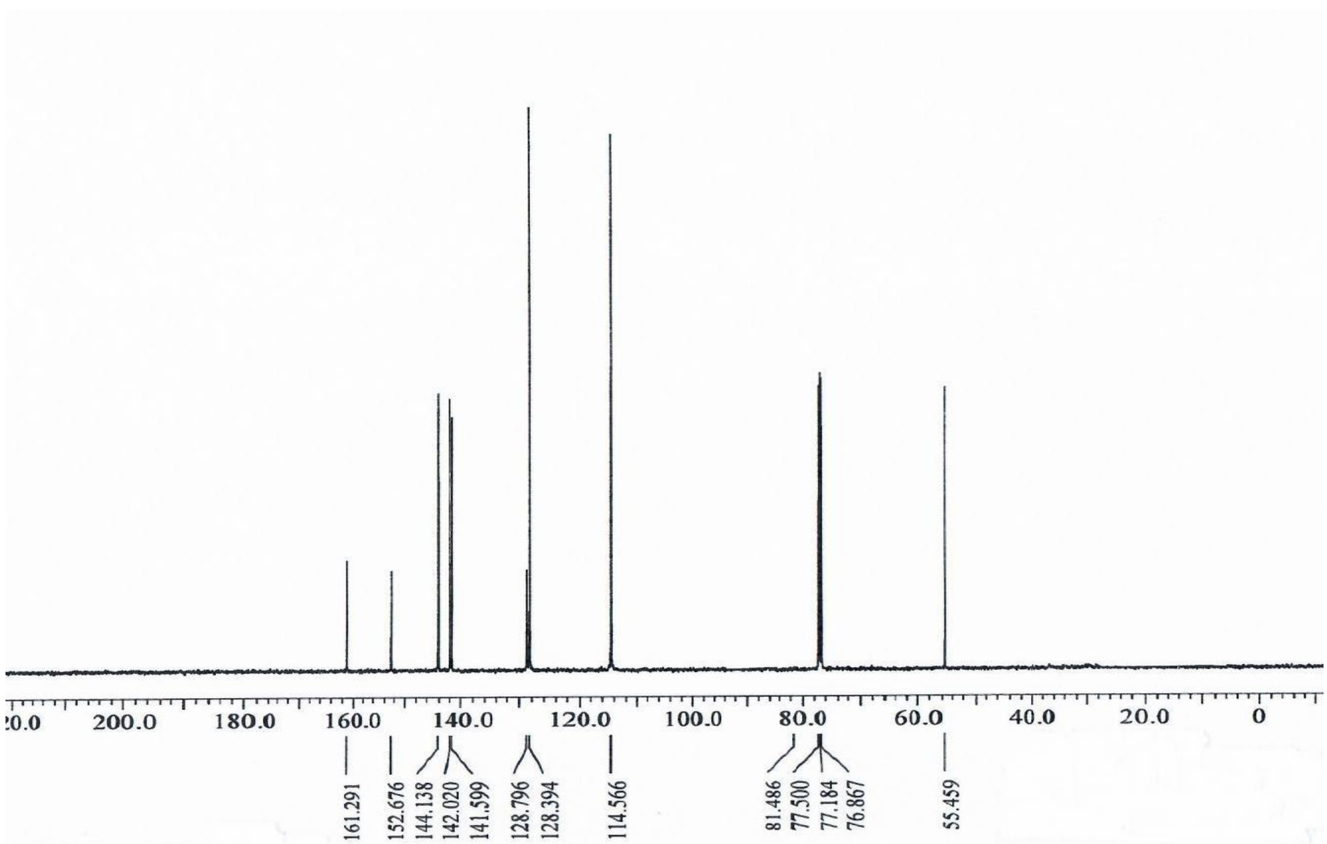
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton



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0
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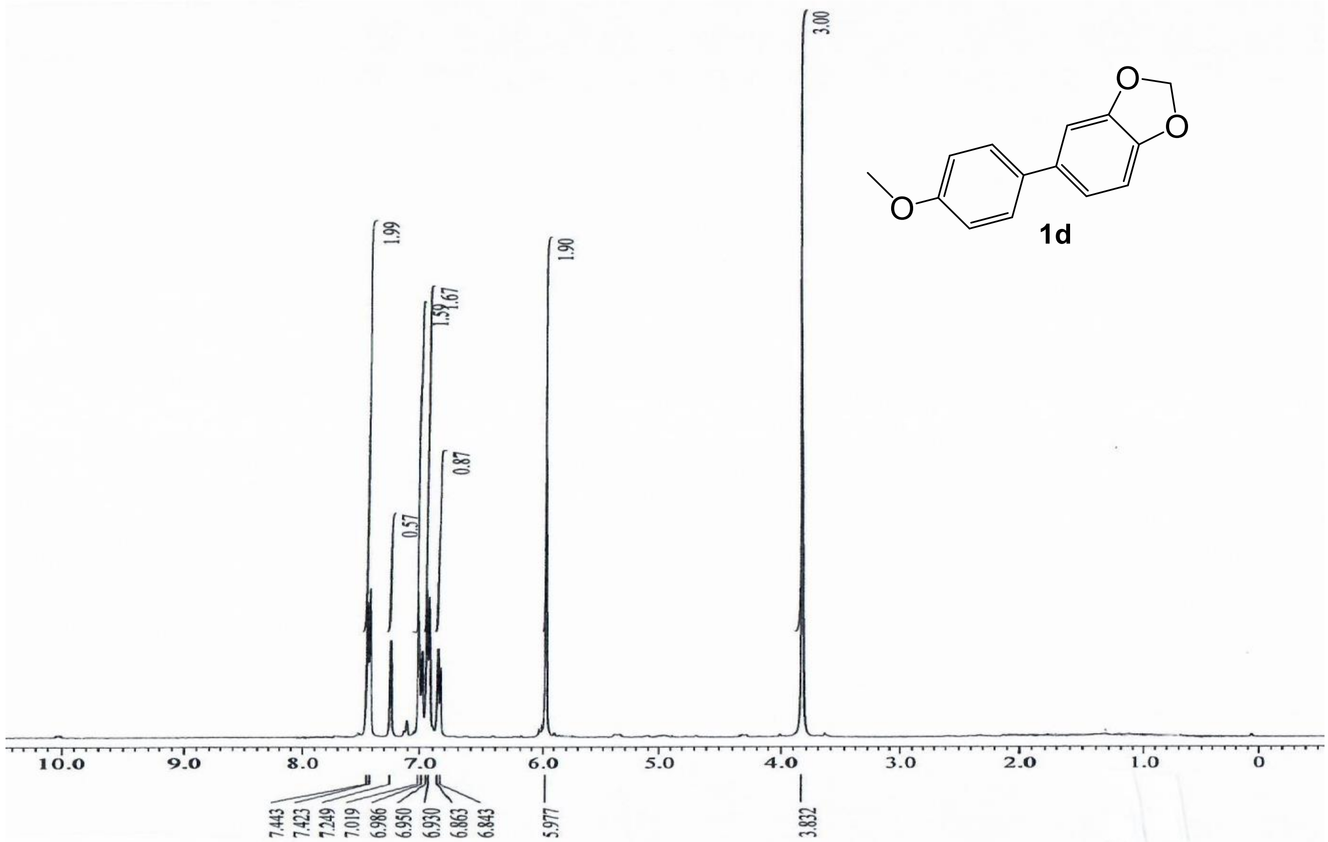
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2.0
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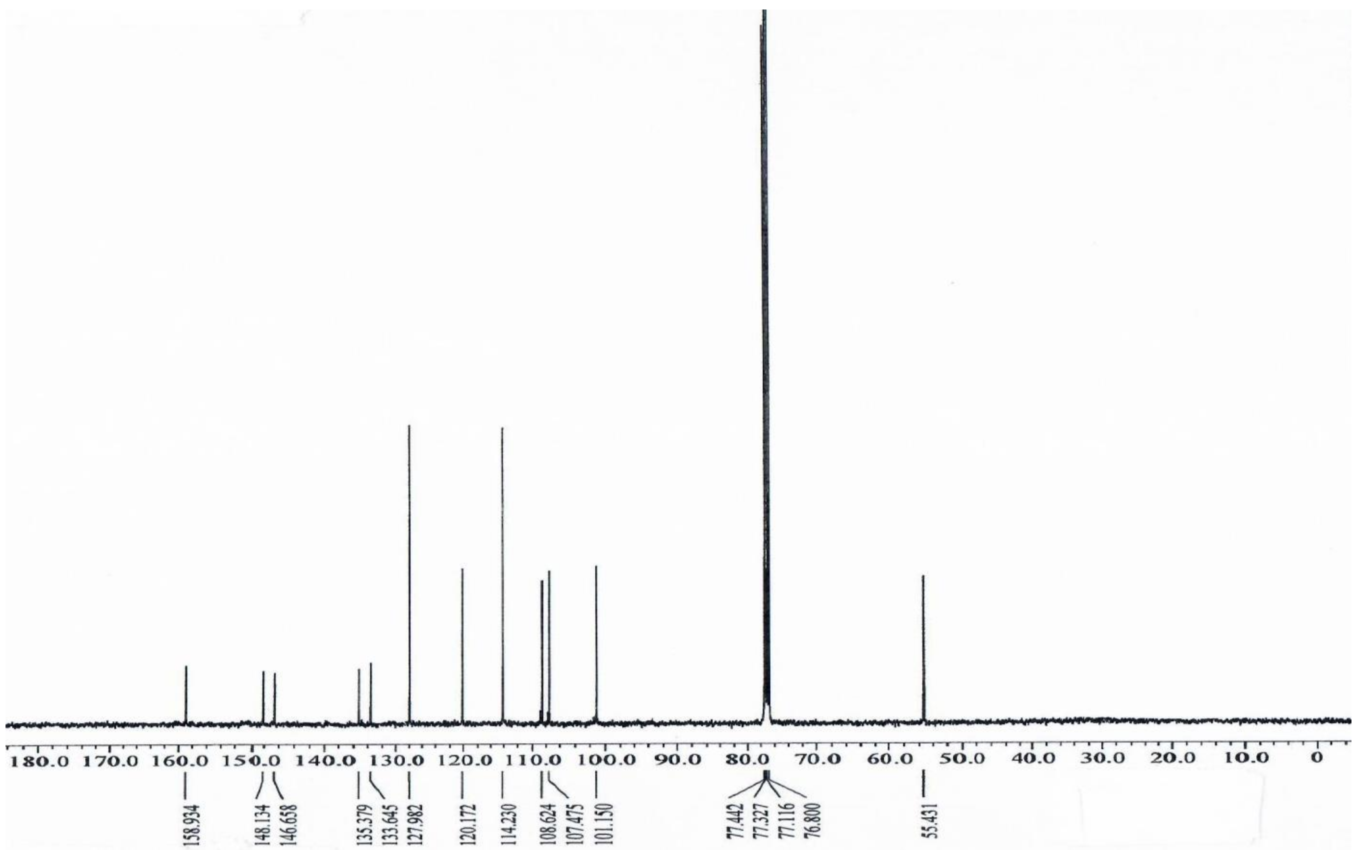
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40.0
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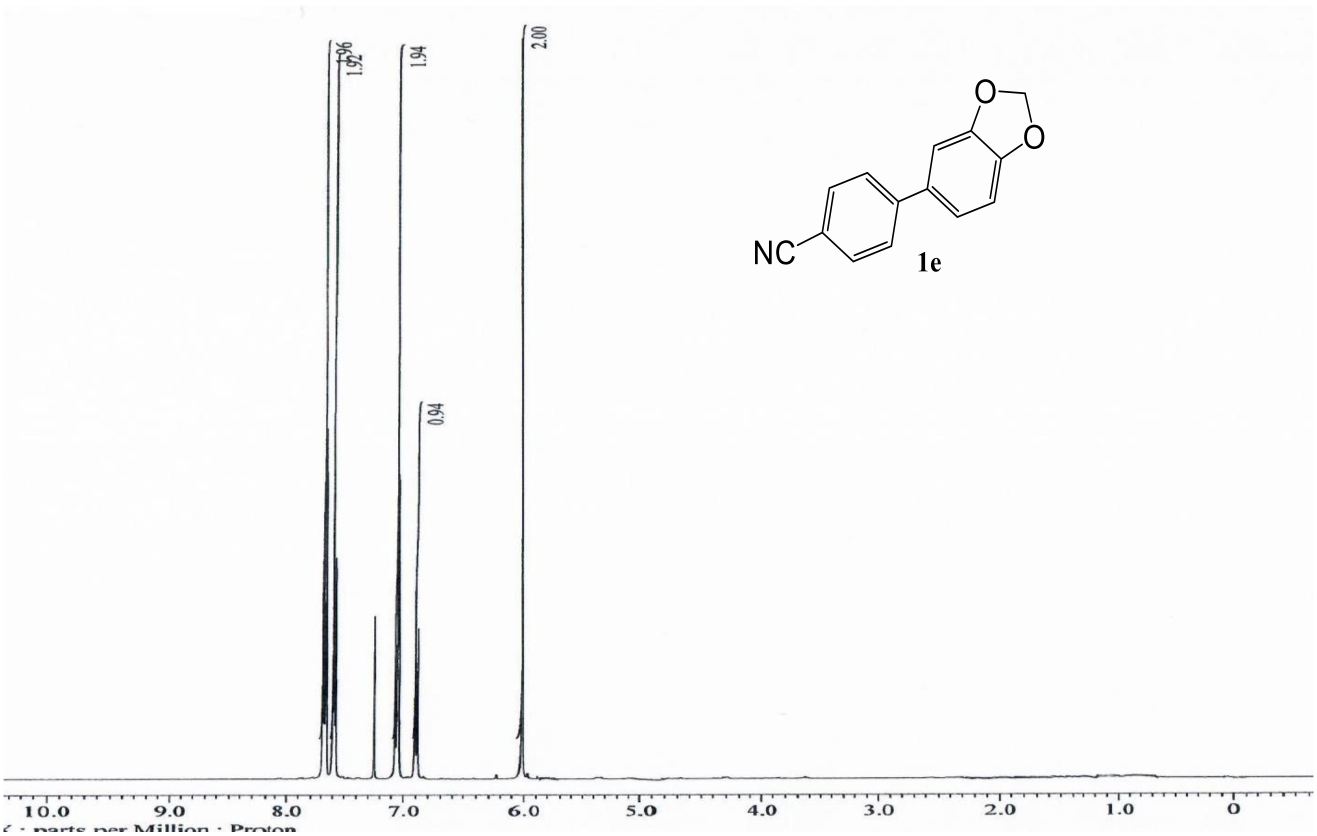

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1.92
1.94
0.94
2.00
O
O
NC
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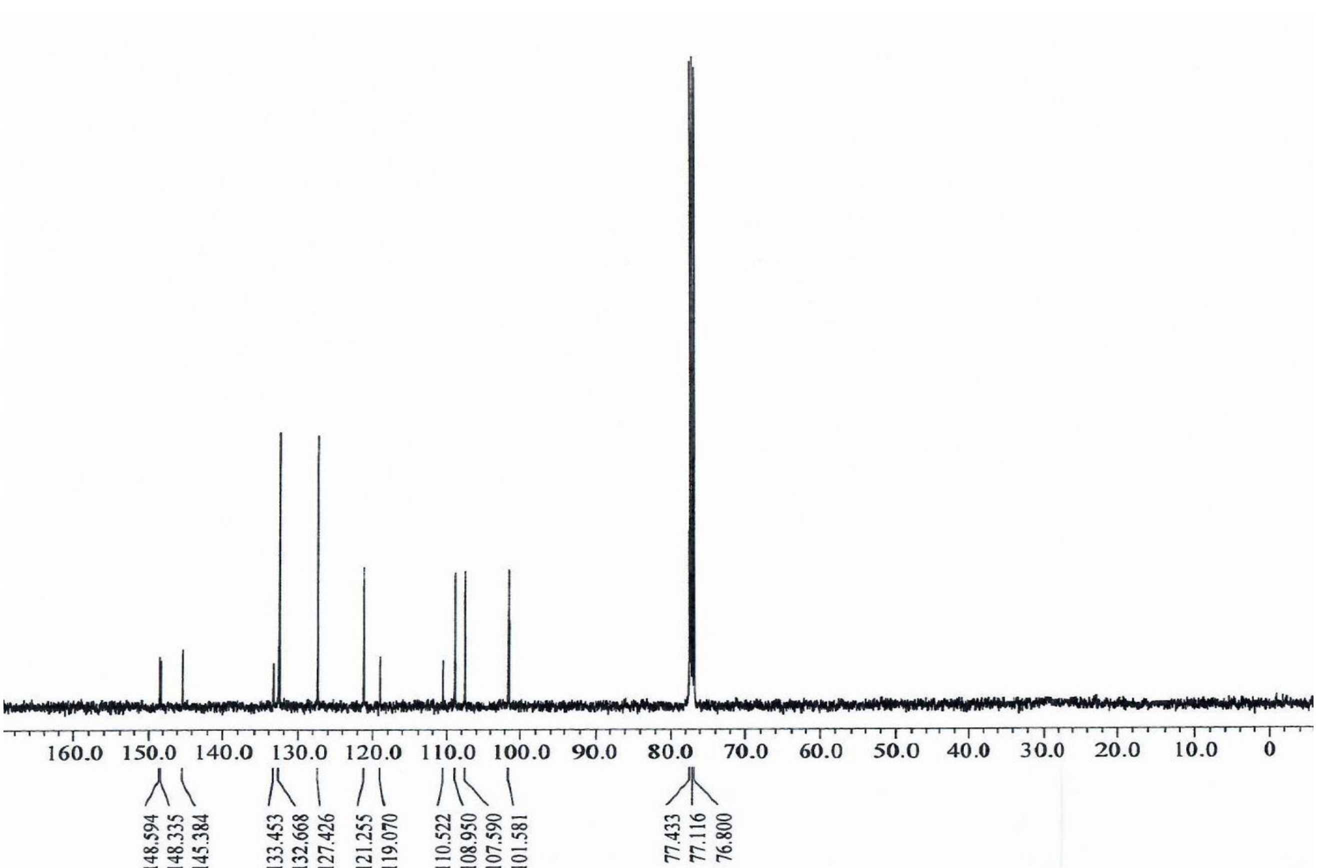
: parts per Million : Proton



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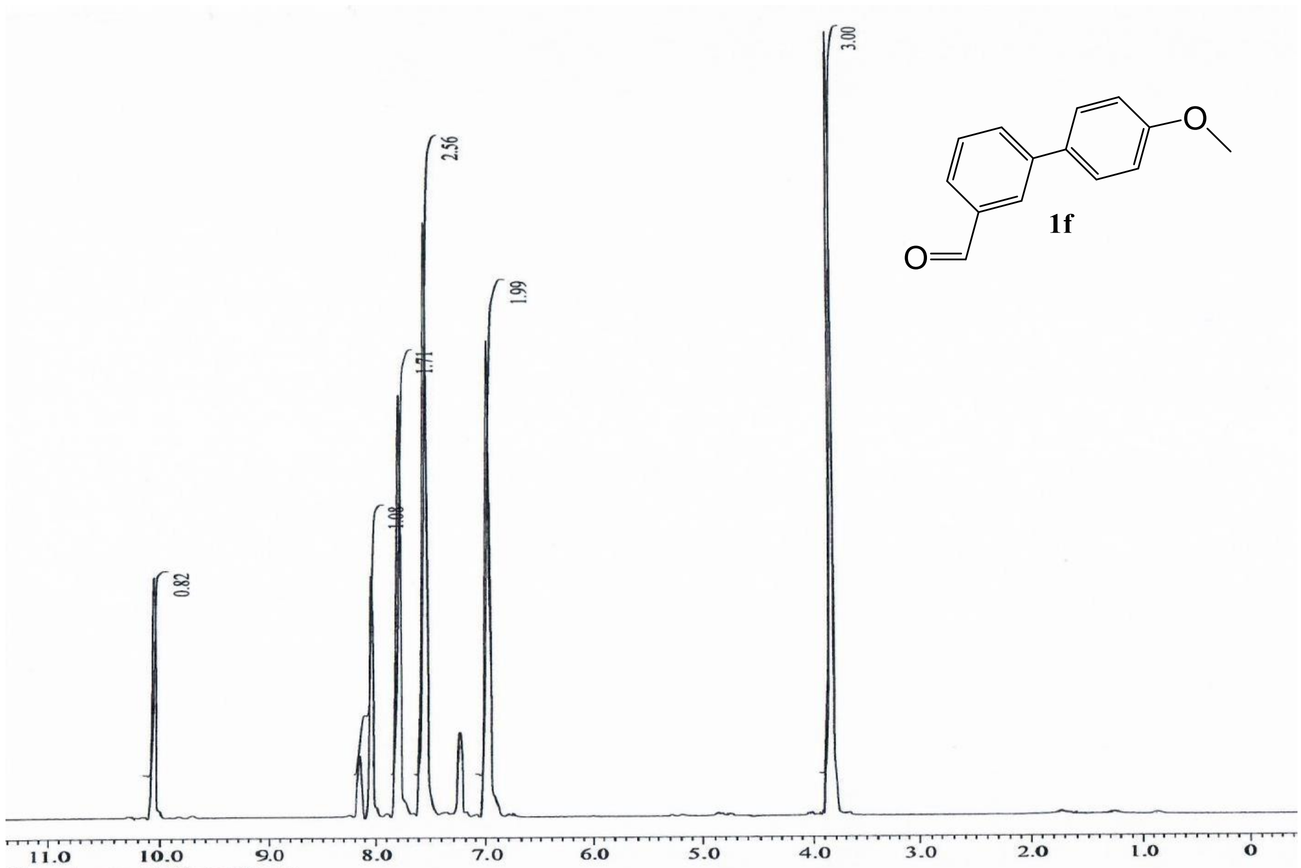
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1.0
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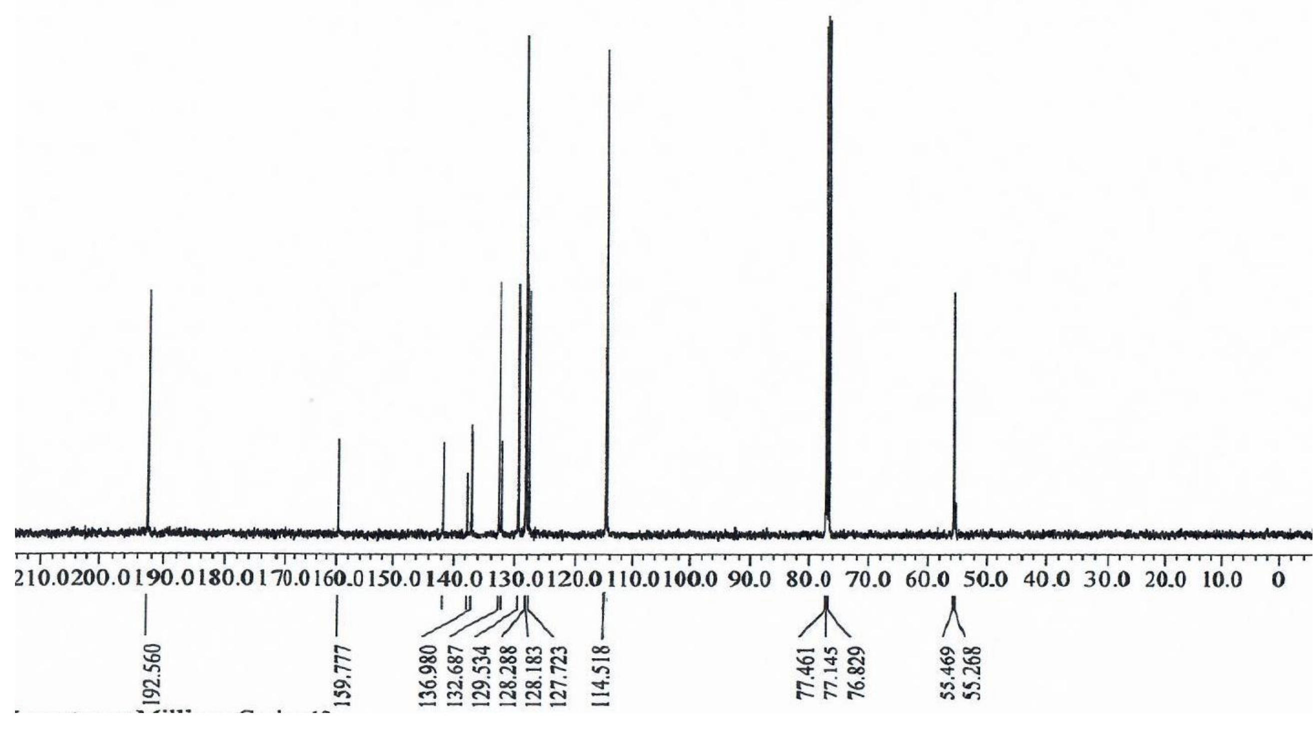
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192.560
159.777
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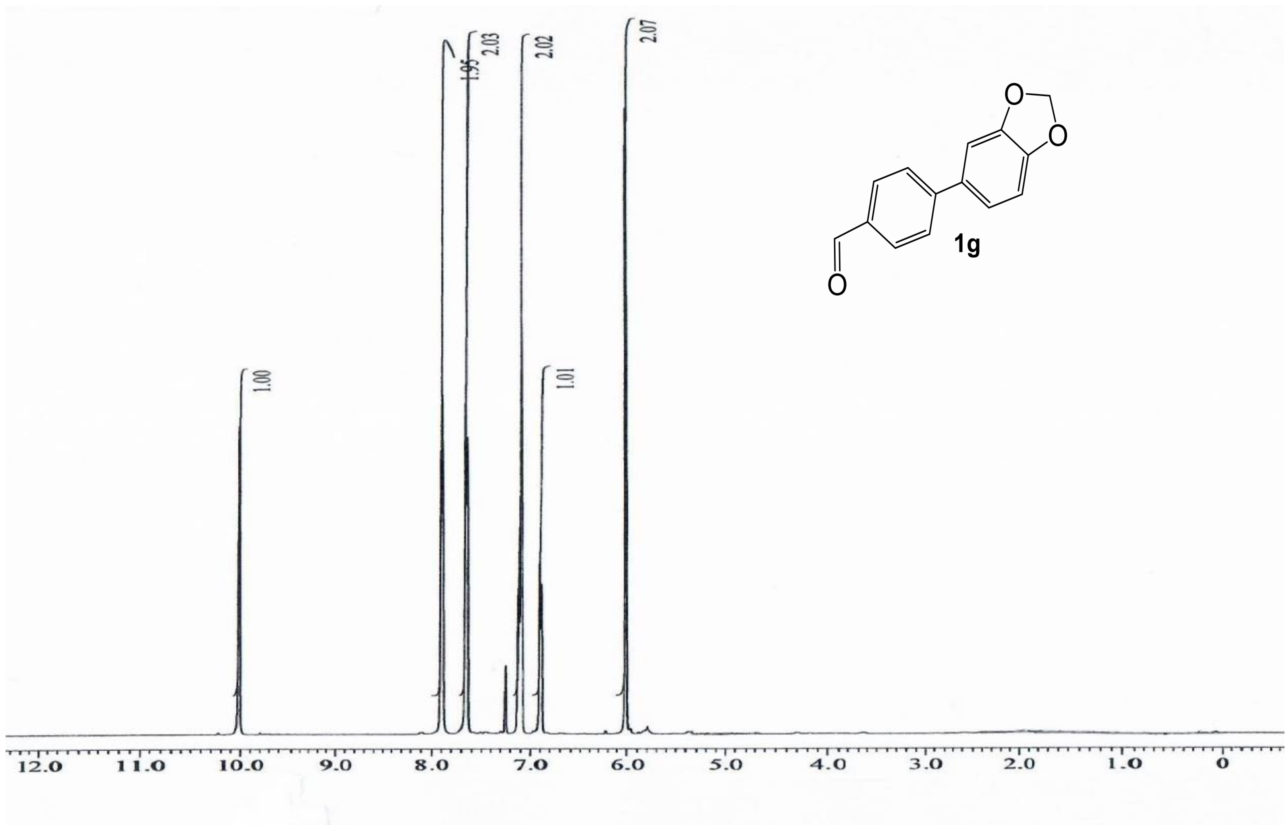
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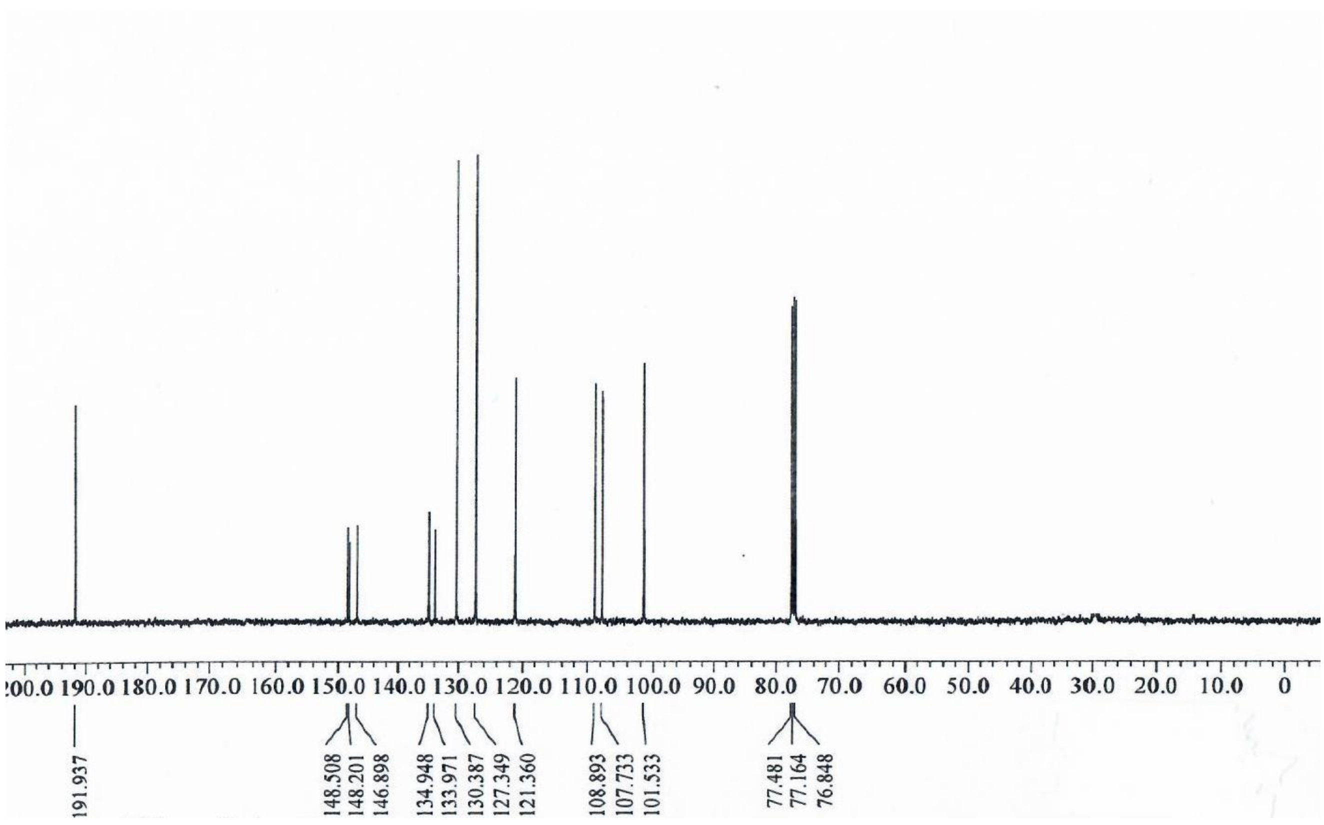
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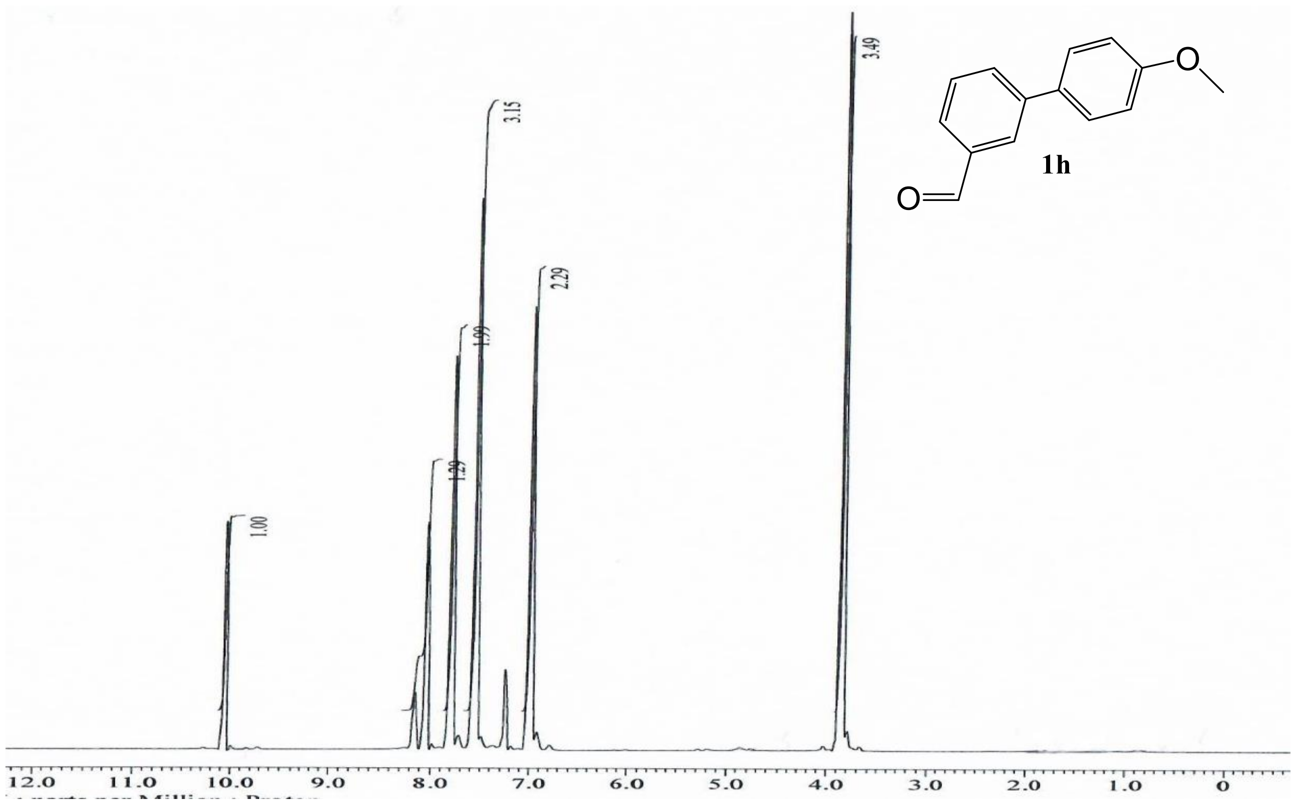
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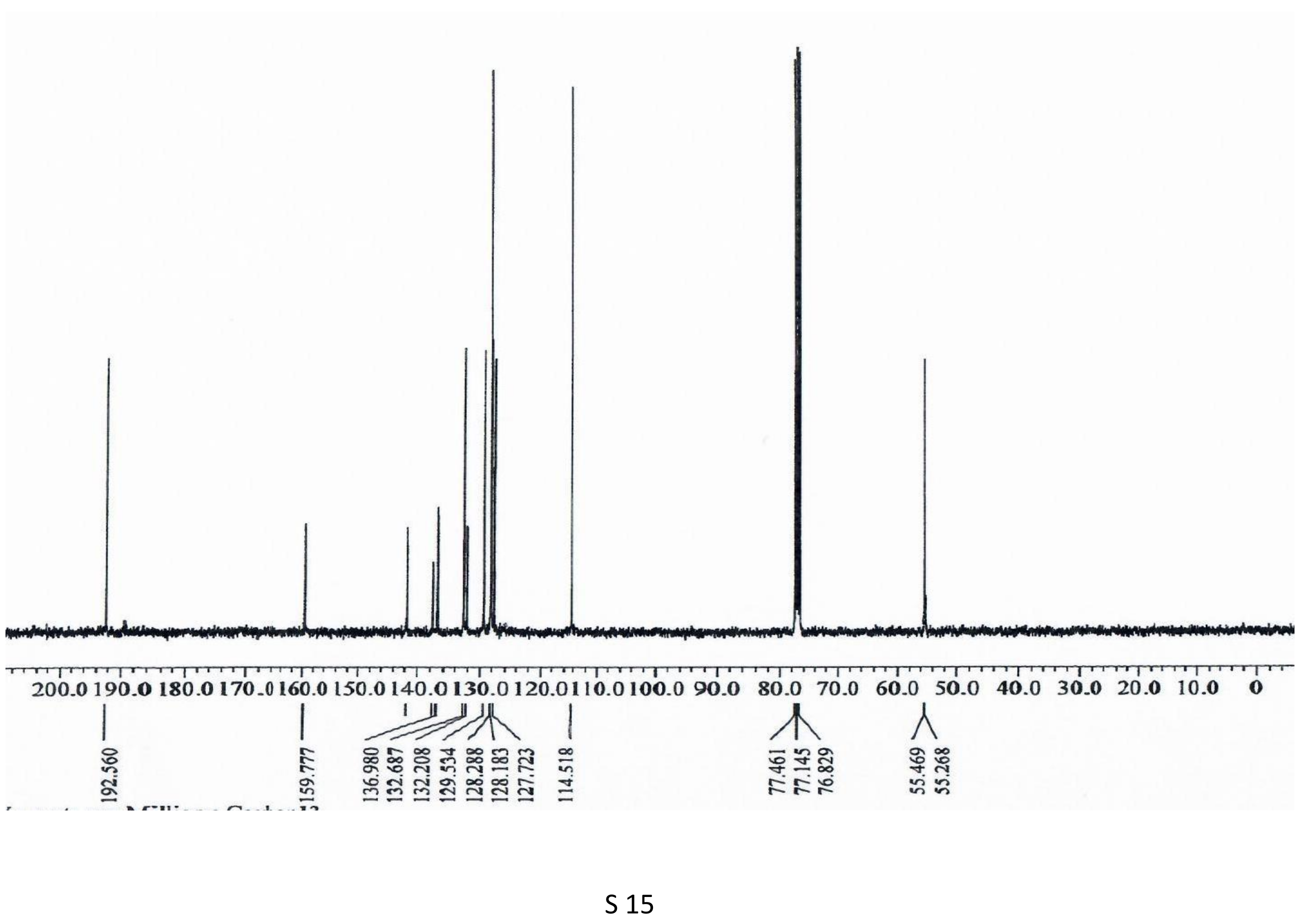
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192.560
159.777
136.980
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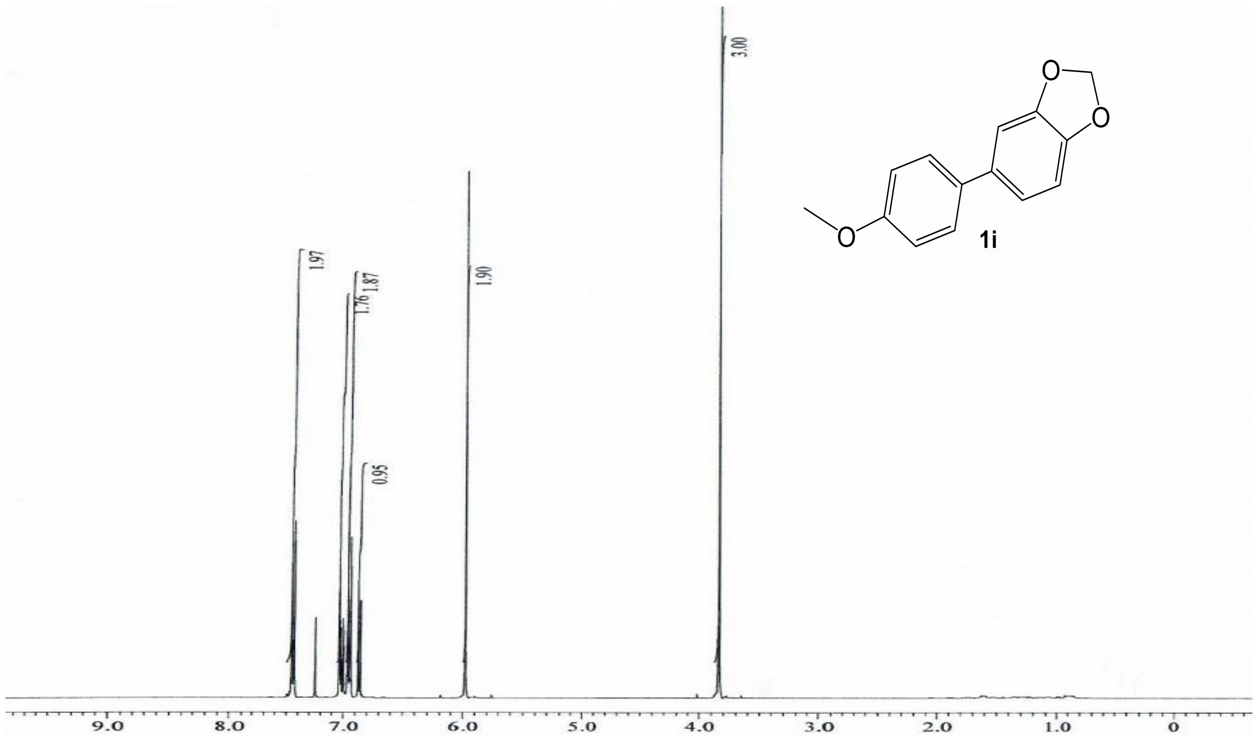
55.268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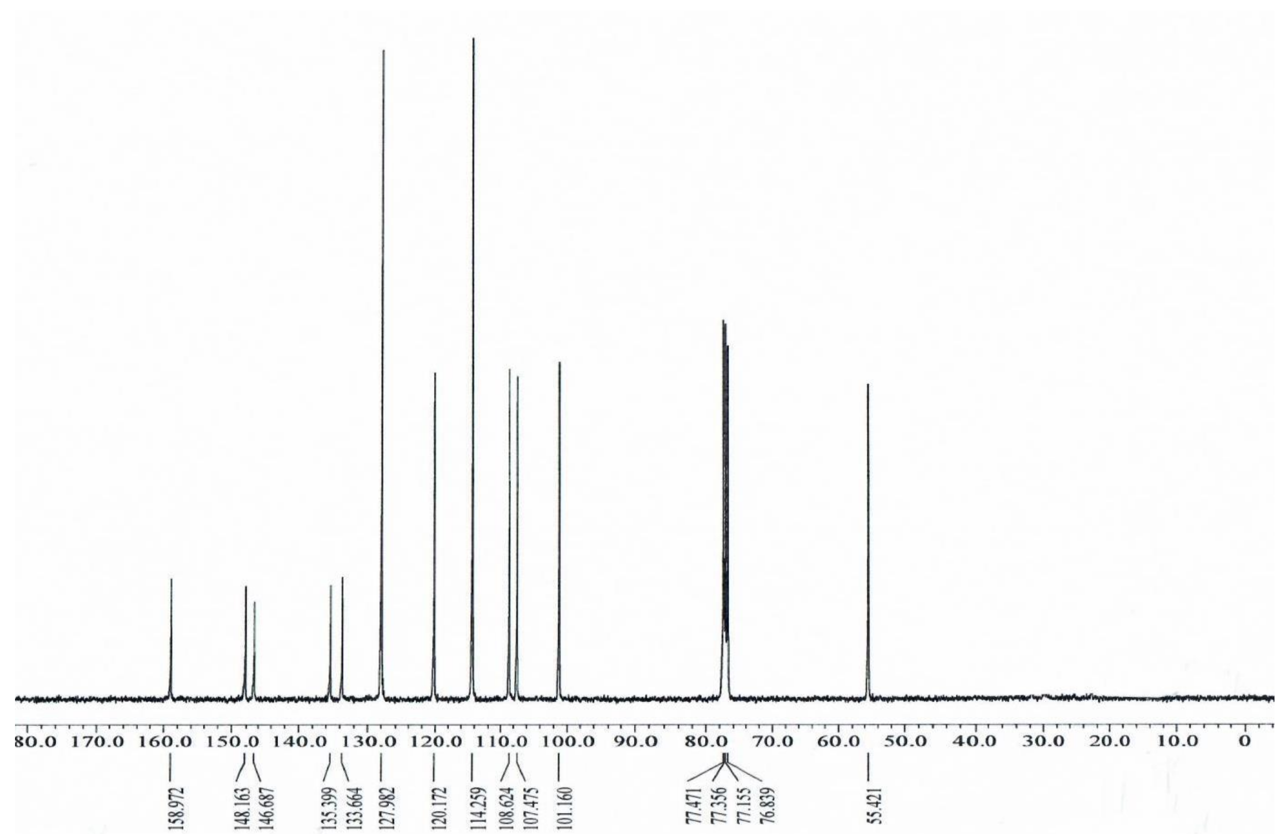
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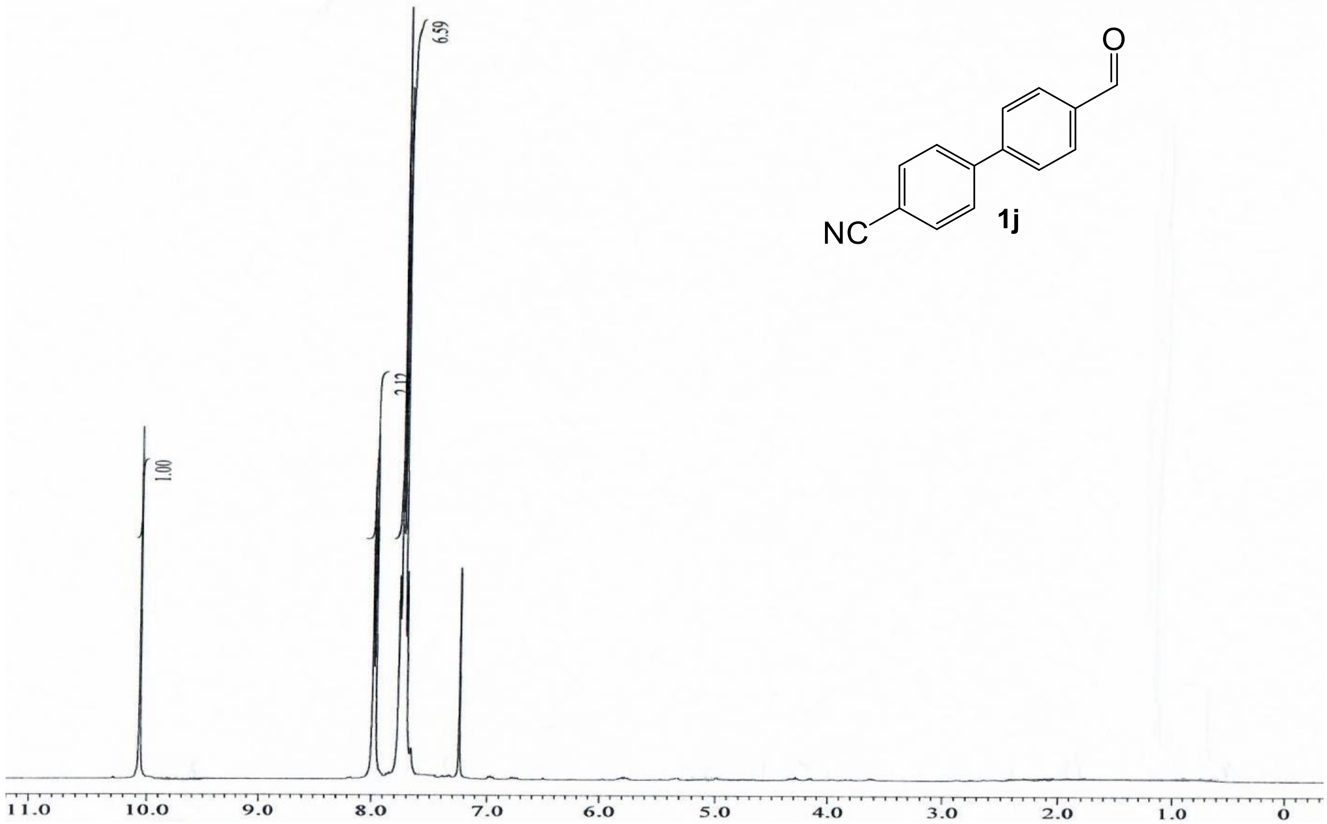
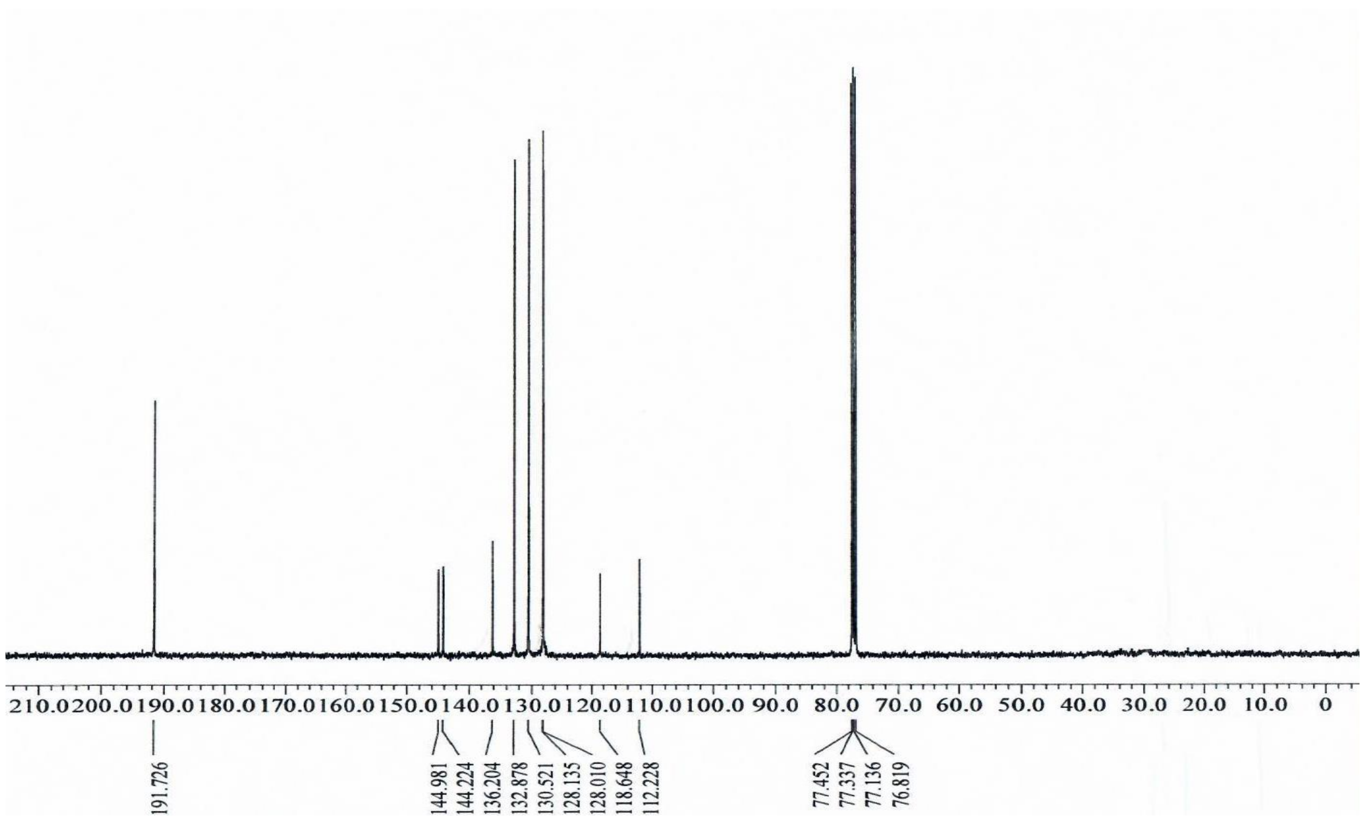
148.163
146.687
135.399
133.664
127.982
120.172
114.259
108.624
107.475
101.160
77.471
77.356
77.155
76.839
55.421


O
NC
1j
6.59
2.12
1.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0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191.726
144.981
144.224
136.204
132.878
130.521
128.135
128.010
118.648
112.228
77.452
77.337
77.136
76.819