Supporting Information for

Visible-Light-Induced, Base-Promoted Transition-Metal-Free Hydrogenation of Aryl Halides with *n*-Butanol

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Contents

I. General Information

All reagents and solvents utilized in this study were procured from commercial sources and employed without further purification, unless otherwise specified. Nuclear Magnetic Resonance (NMR) spectra were acquired using Bruker AV300, Bruker AV400, and Bruker AV500M spectrometers, and chemical shifts were reported in parts per million (δ) relative to the internal standard, tetramethylsilane (TMS), positioned at 0 ppm in $CDCl_3$. The determination of some chemicals was compared with the spectra reported in literature. The light sources employed were LED lamps with wavelengths ranging from 254 nm to 455 nm, providing an output power of 7W. Reaction progress was monitored by thin-layer chromatography (TLC). Column chromatography was performed using silica gel (200-300 mesh), and compounds were visualized under ultraviolet light. Elution during column chromatography was achieved using a mixture of ethyl acetate and petroleum ether as the eluent. High-performance liquid chromatography (HPLC) analyses were conducted using a Shimadzu LC-16 spectrometer. Gas chromatography-mass spectrometry (GC-MS) analyses were carried out utilizing a Thermo TRACE 1300 ISQ LT spectrometer.

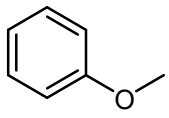
II. Procedure for the deiodination of 4-iodine-1,1’-biphenyl

A 35 mL thick-walled pressure vessel equipped with a Teflon cap was charged with a magnetic stir-bar, 4-iodine-1,1'-biphenyl (0.2 mmol), KOH (4 mmol), MeCN (2.5 mL), and *n*-Butanol (0.5 mL). Subsequently, the pressure vessel was immersed in an oil bath along with LED lamps (254 nm-455 nm, 7W×2) at temperatures of 30 °C, 40 °C, or 50 °C. To ensure light exclusion, the entire reaction system was carefully shielded with tinfoil film. The reaction mixture was stirred for 24, 48, or 96 hours. Following the designated reaction time, 0.2 mmol of 4-methylbiphenyl was introduced into the pressure vessel. Subsequently, 10 mL of water was added to terminate the reaction, and the resulting mixture was extracted using ethyl acetate (5 mL×4). The combined organic extracts were washed with brine, dried with sodium sulfate, and then subjected to filtration for subsequent HPLC analysis.

III. General procedure for the reduction of C−X bond

A 35 mL thick-walled pressure vessel, equipped with a Teflon cap and a magnetic stir bar, was charged with aryl halide (0.2 mmol), KOH (4 mmol), MeCN (2.5 mL), and *n*-Butanol (0.5 mL). The pressure vessel was then

positioned in an oil bath, accompanied by LED lamps emitting light at a wavelength of 405 nm and a power output of 7W×2, while maintaining a temperature of 30 °C. To ensure light exclusion, the entire reaction system was meticulously wrapped with tinfoil film. The mixture was stirred for 48 or 96 hours, as specified. Following the designated reaction time, 10 mL of water was added to quench the reaction, and the resulting mixture was extracted using ethyl acetate (5 mL×4). The combined organic extracts were subsequently washed with brine, dried with sodium sulfate, and concentrated under reduced pressure. The resulting residue was purified *via* preparative TLC on silica gel, using a gradient elution of petroleum ether and ethyl acetate (300:1-5:1) as the eluent, to afford the desired products. Confirmation of the products was accomplished by comparison with commercially available samples.



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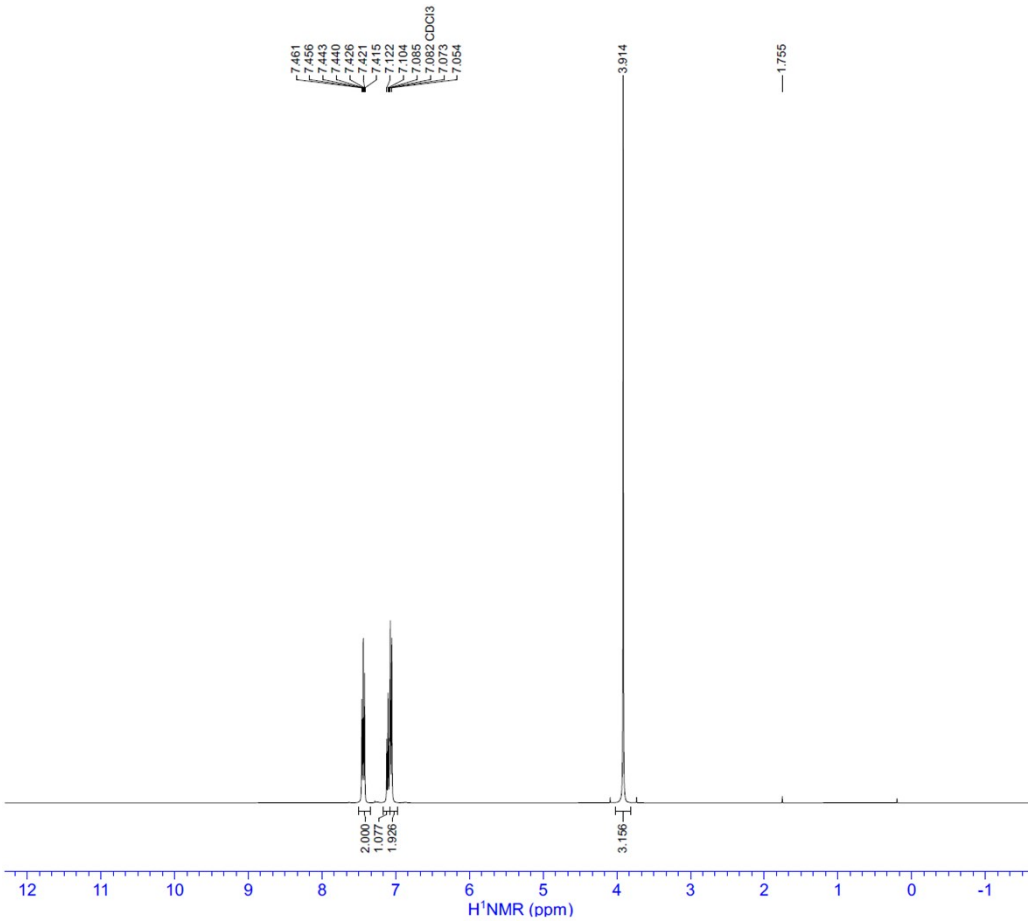
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7.054
3.914
1.755
2.000
1.077
1.928
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11
10
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2
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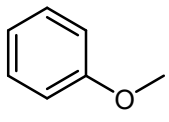
H1NMR (ppm)



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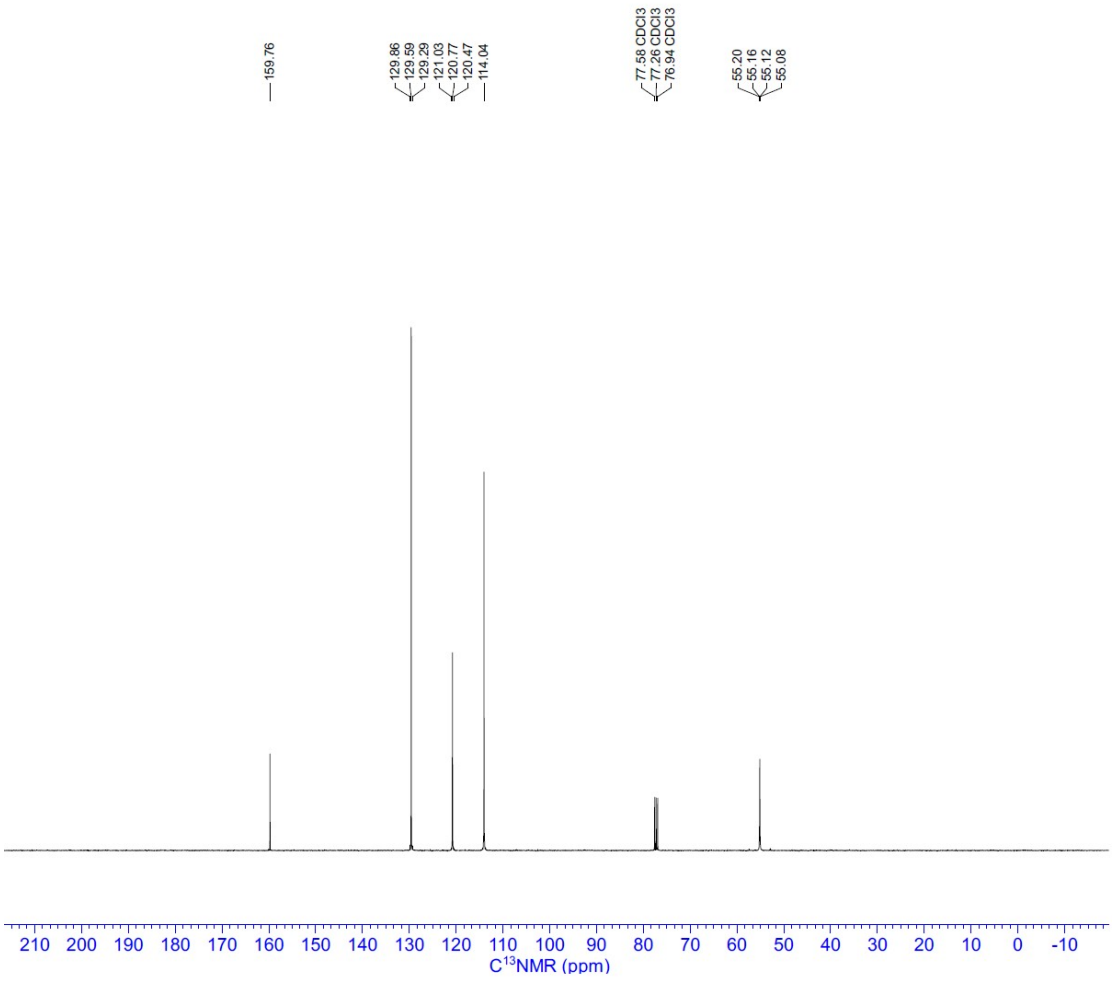
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114.04
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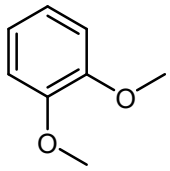

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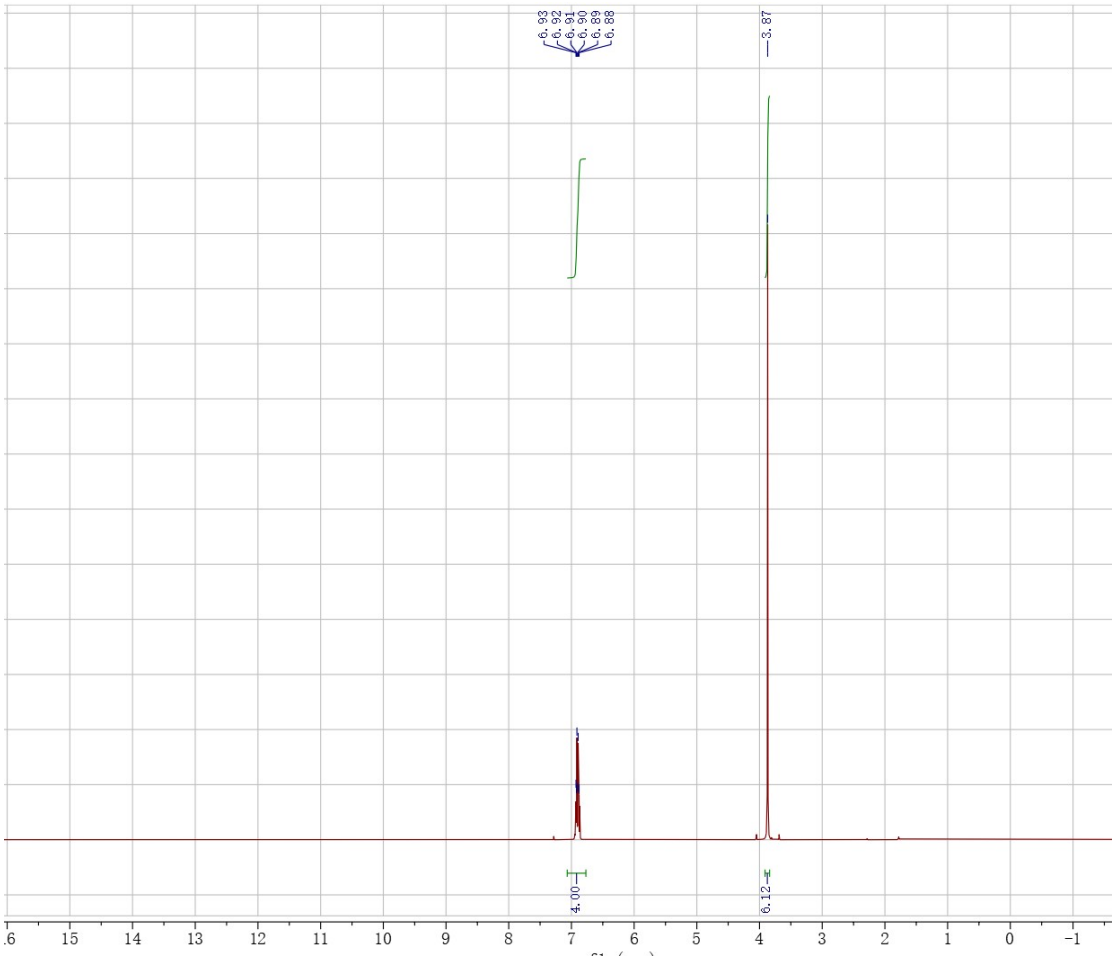
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2
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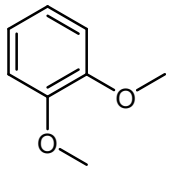
0
-1



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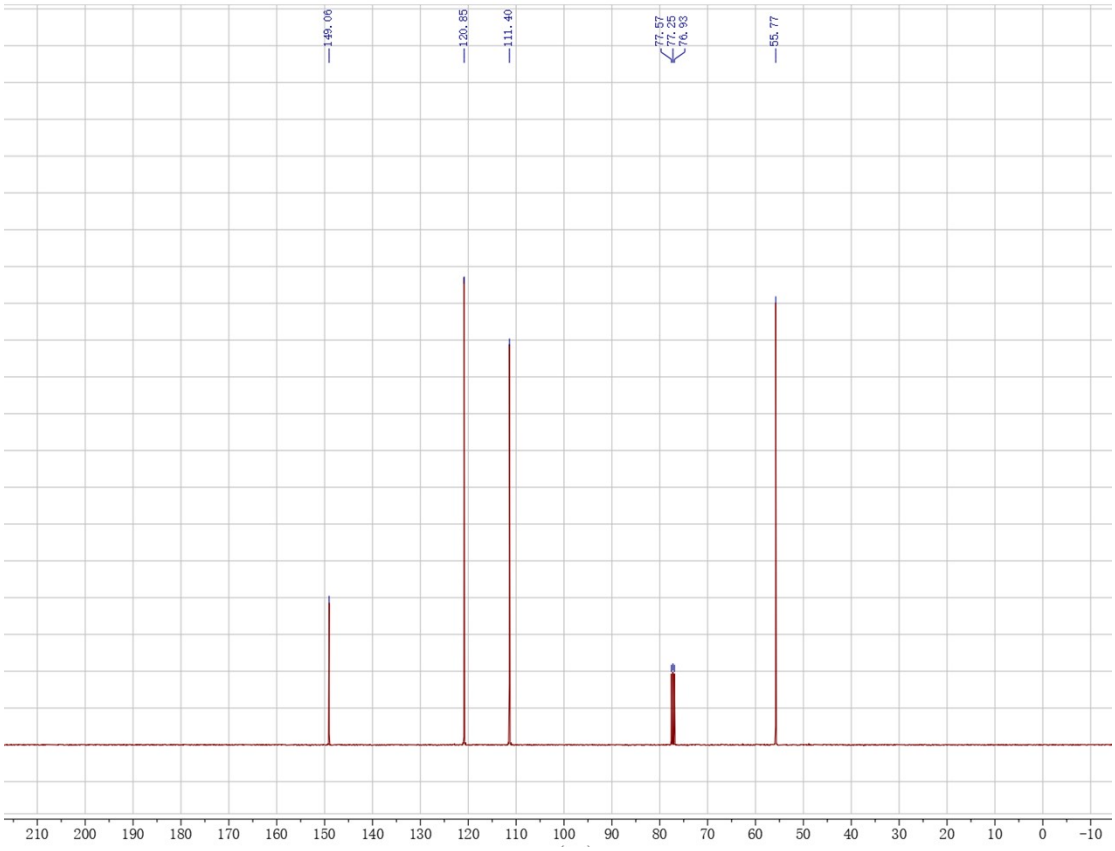
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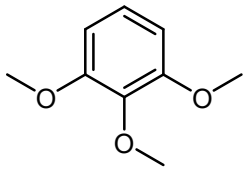

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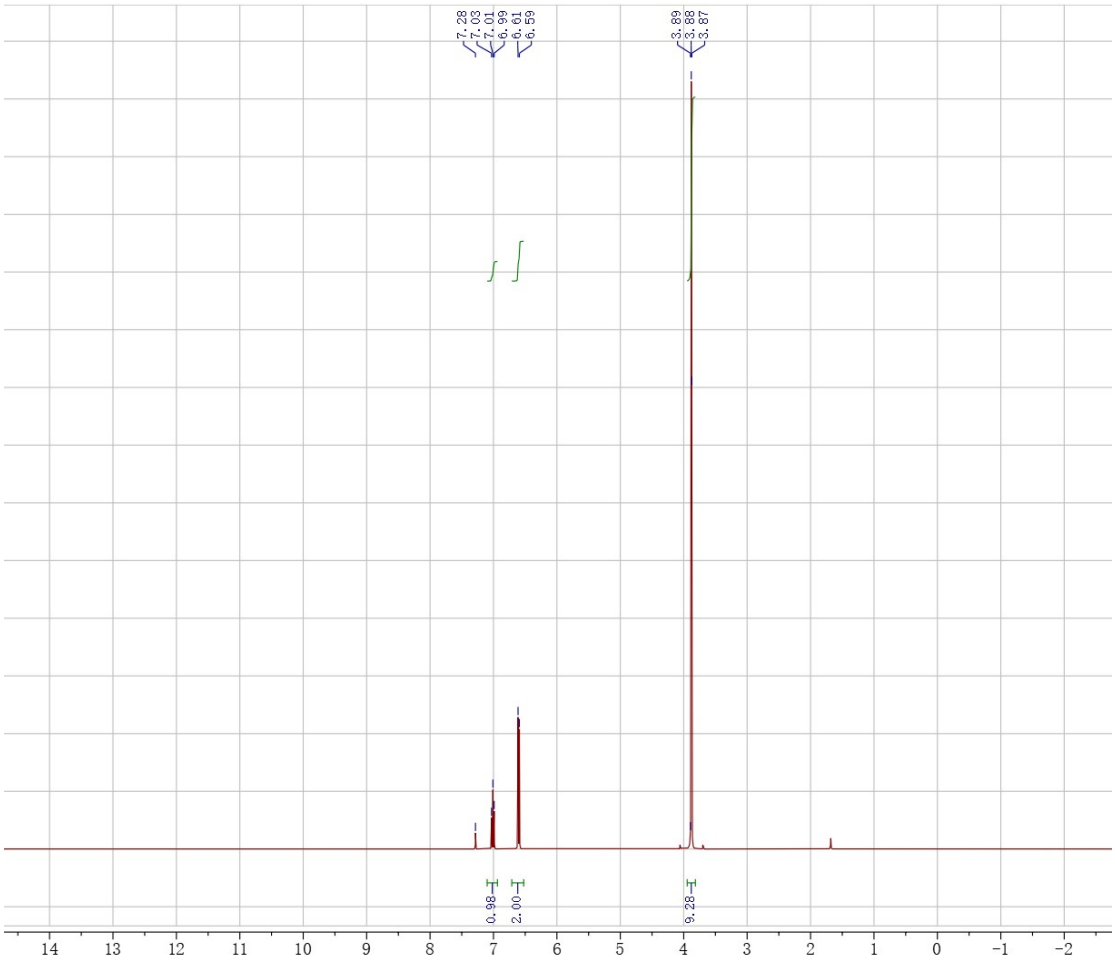
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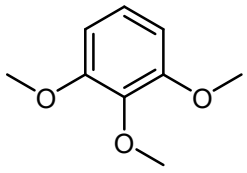

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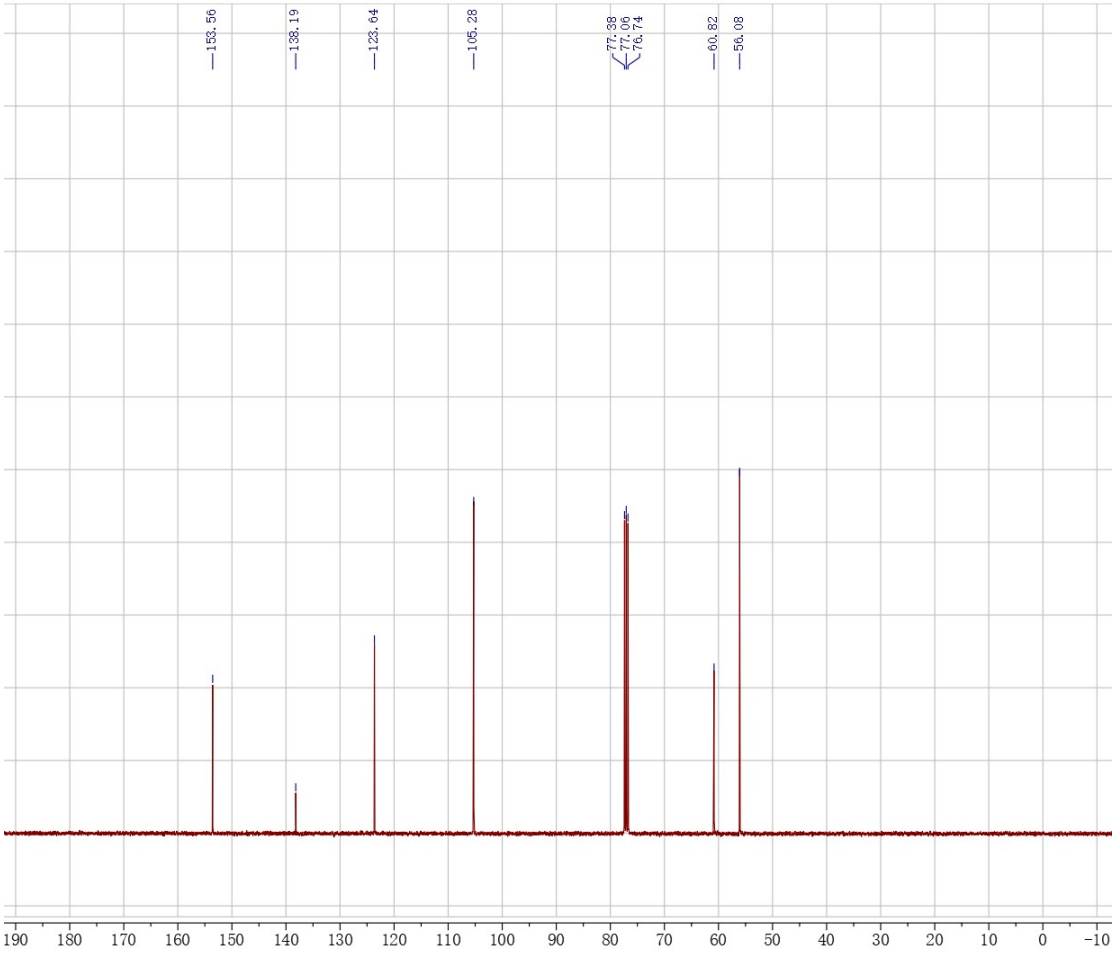
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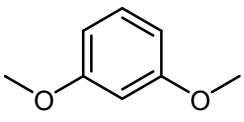

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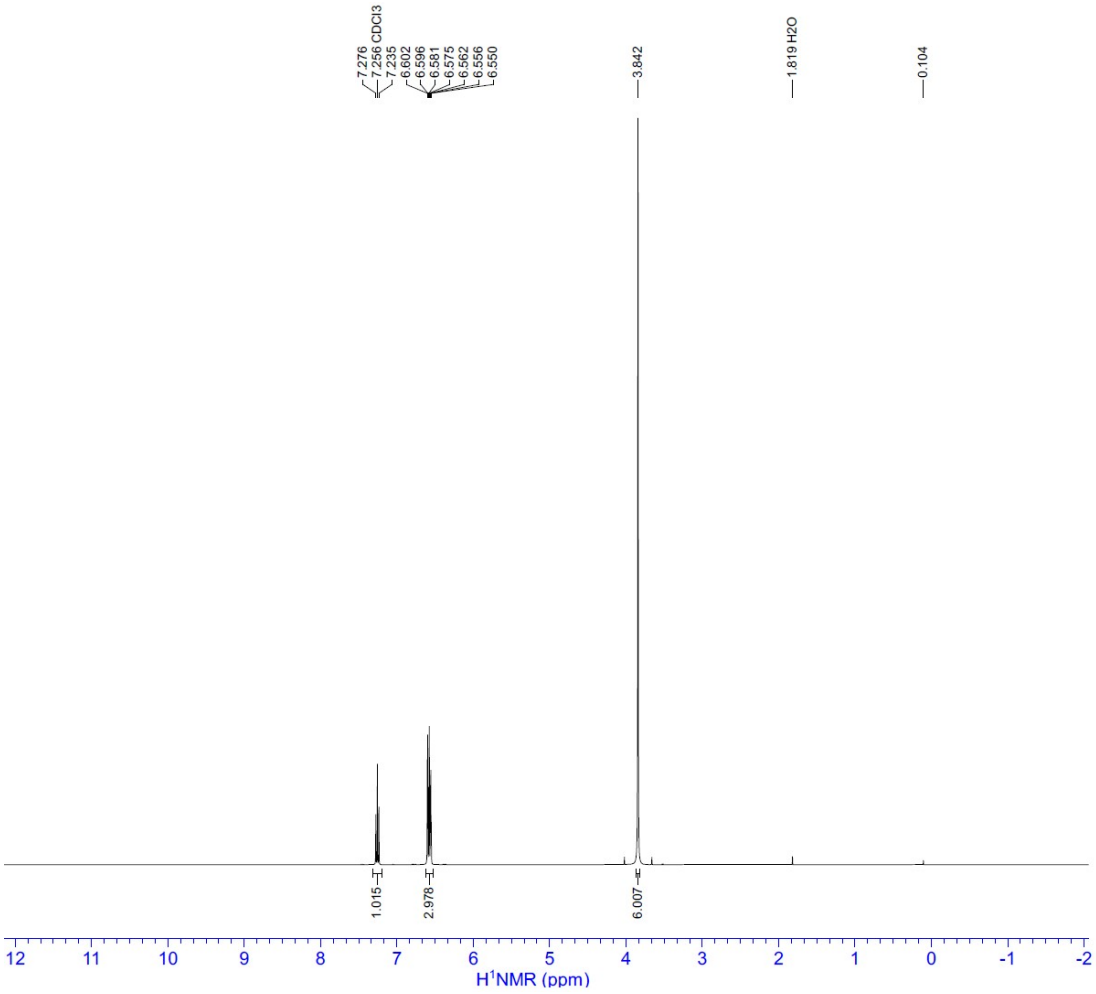
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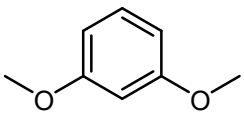
H1NMR (ppm)



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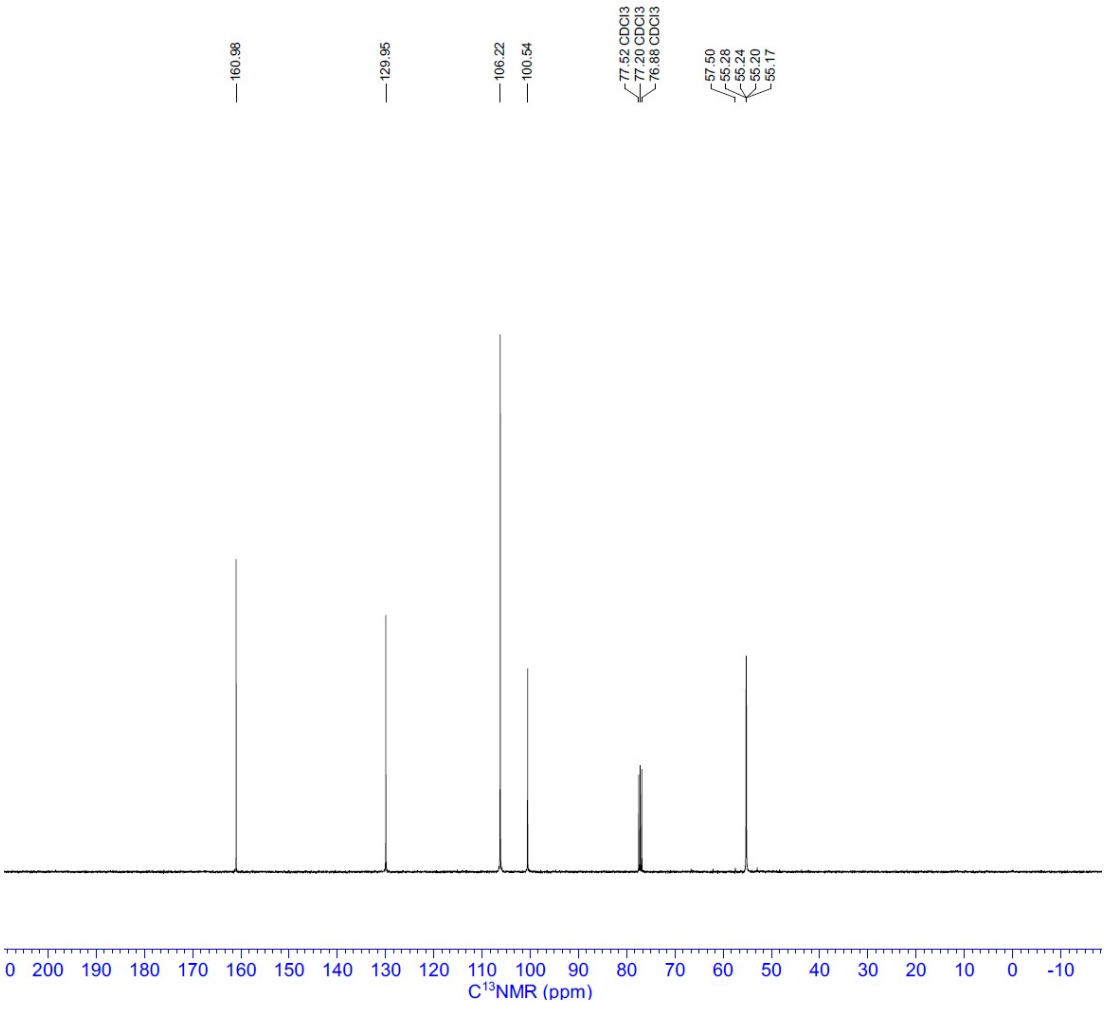
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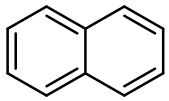

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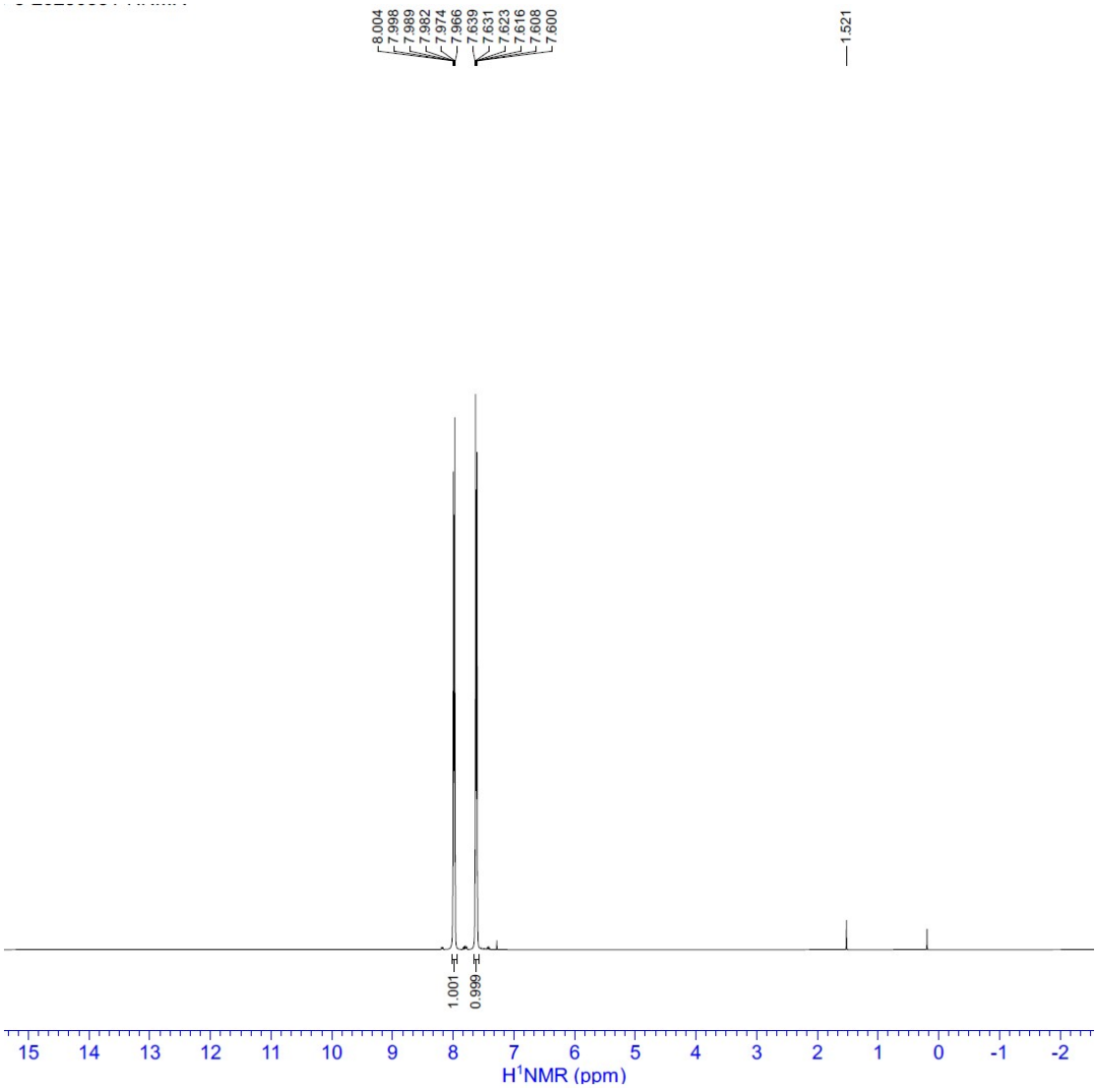
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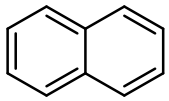

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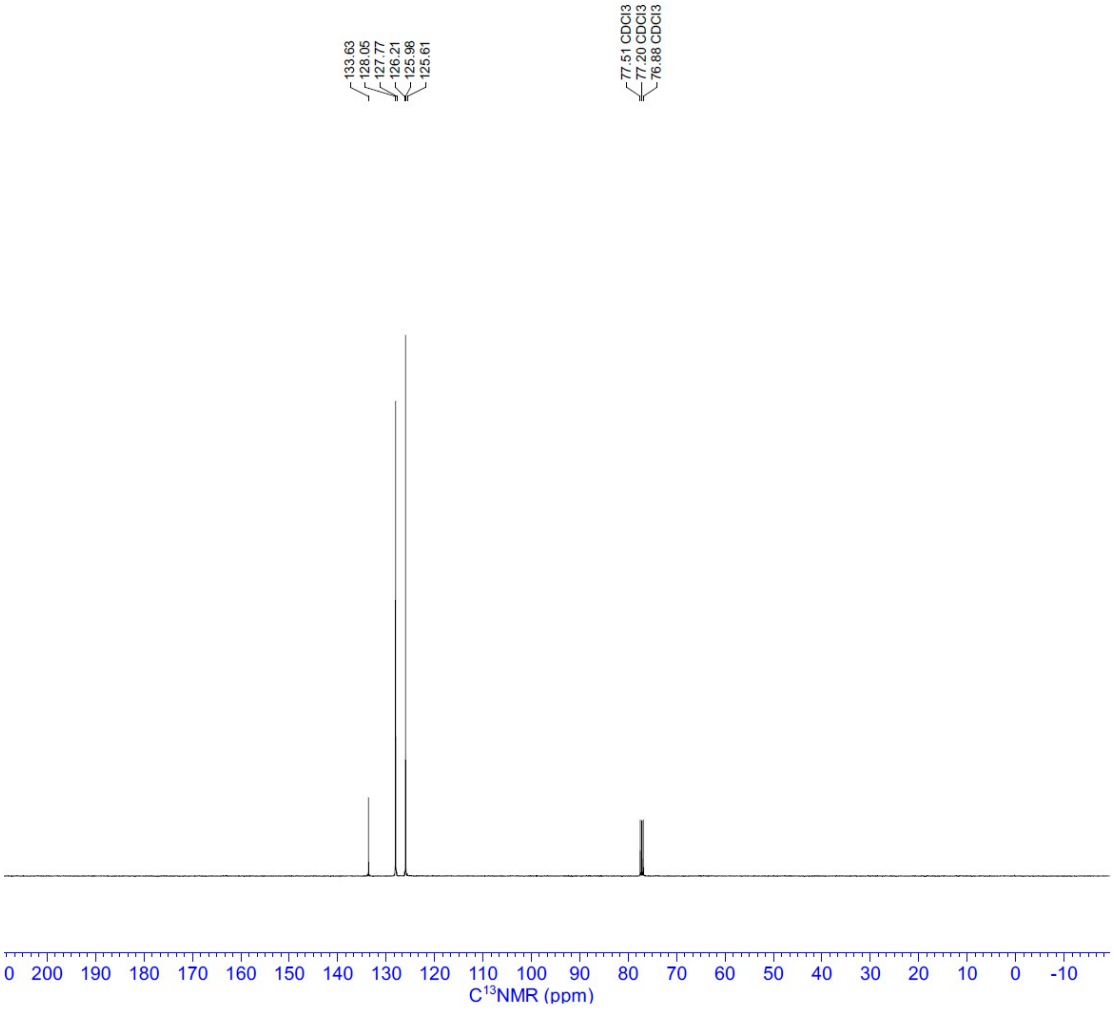
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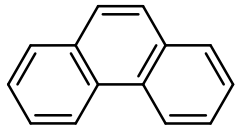

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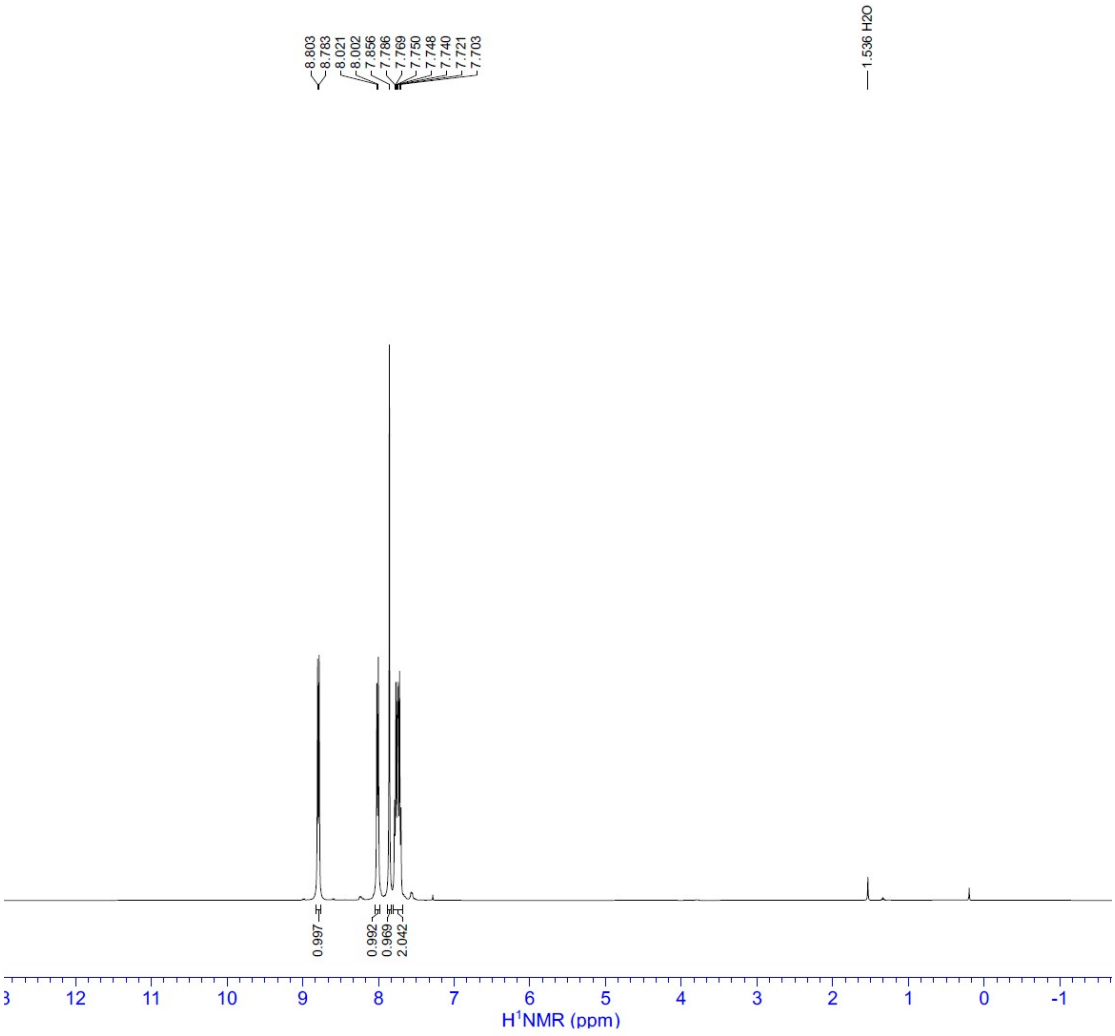
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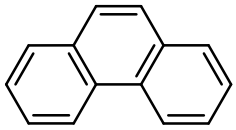

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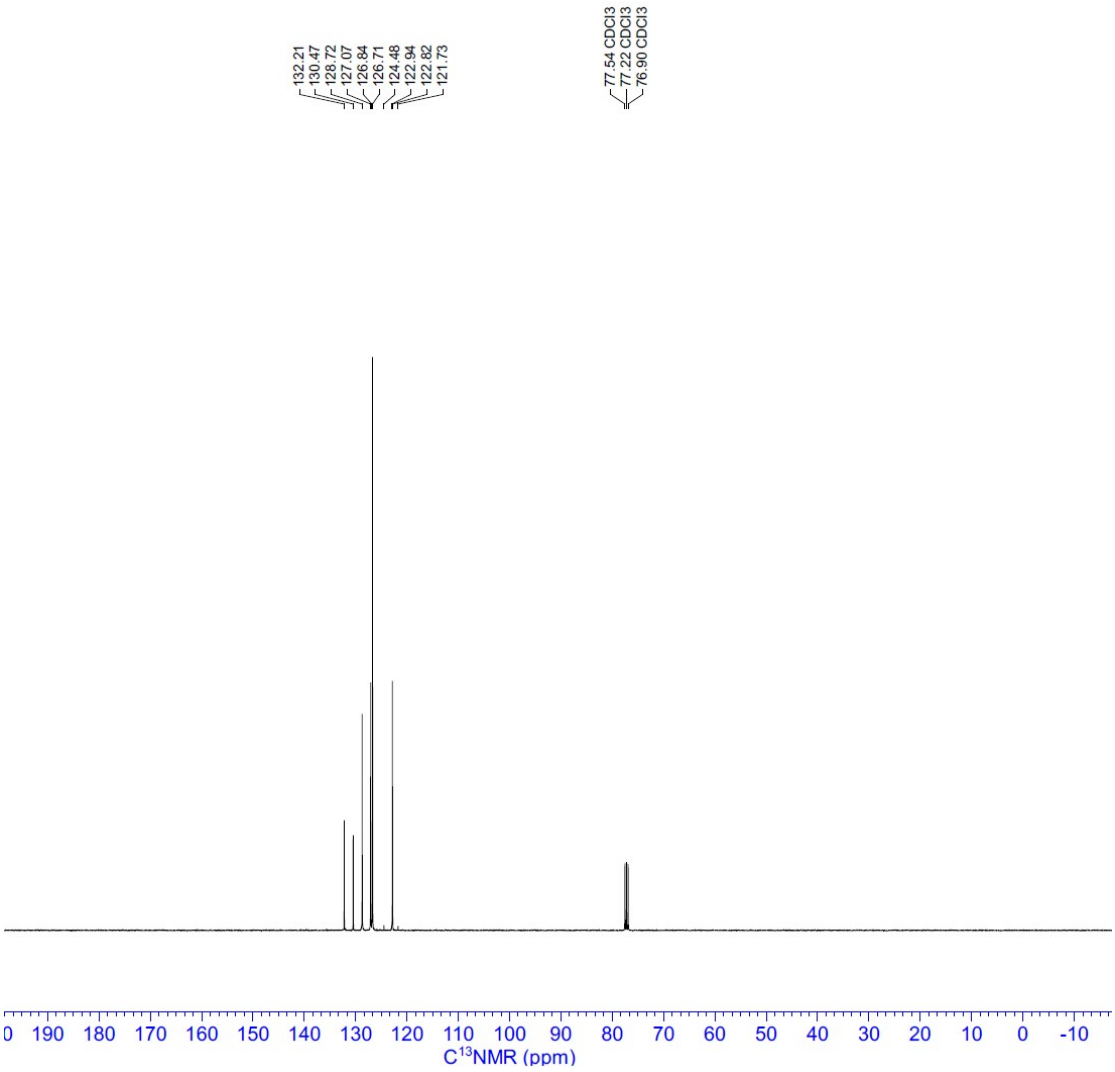
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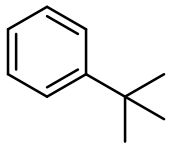

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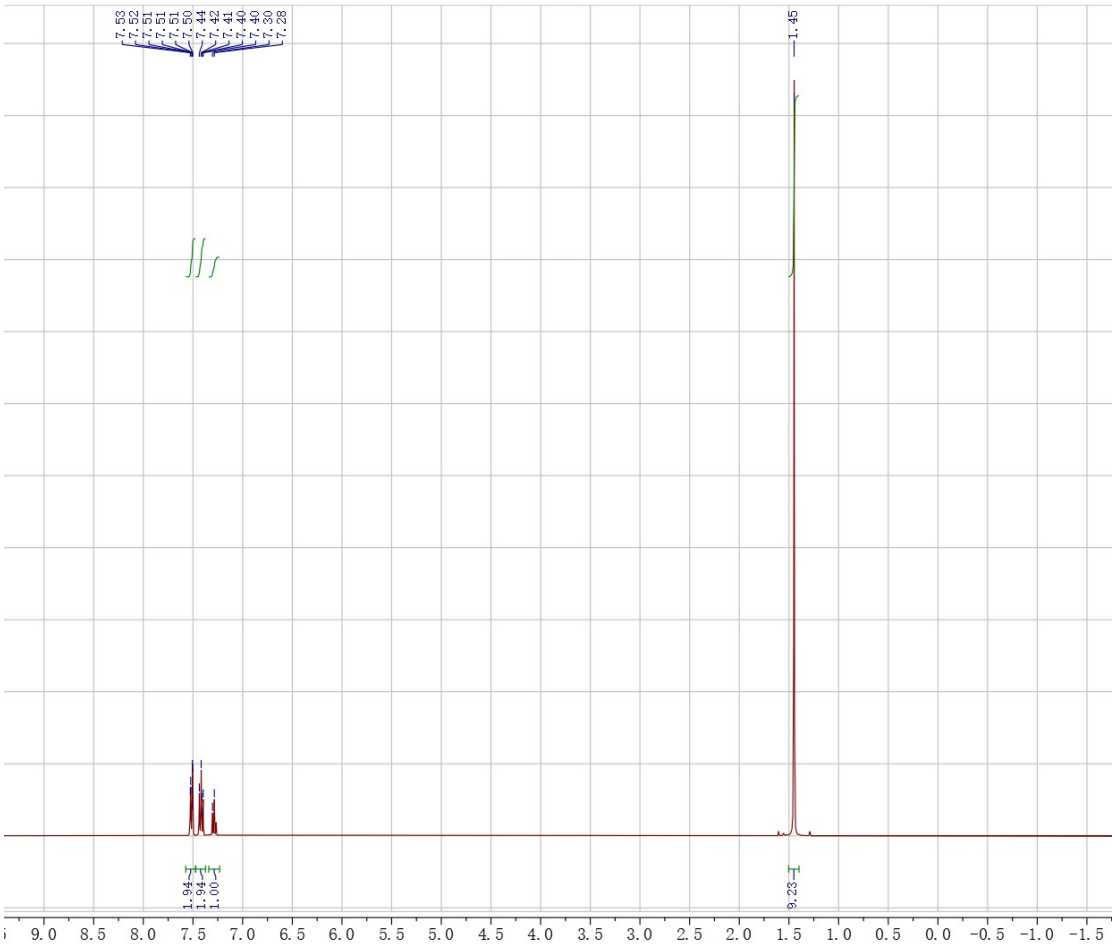
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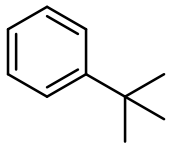

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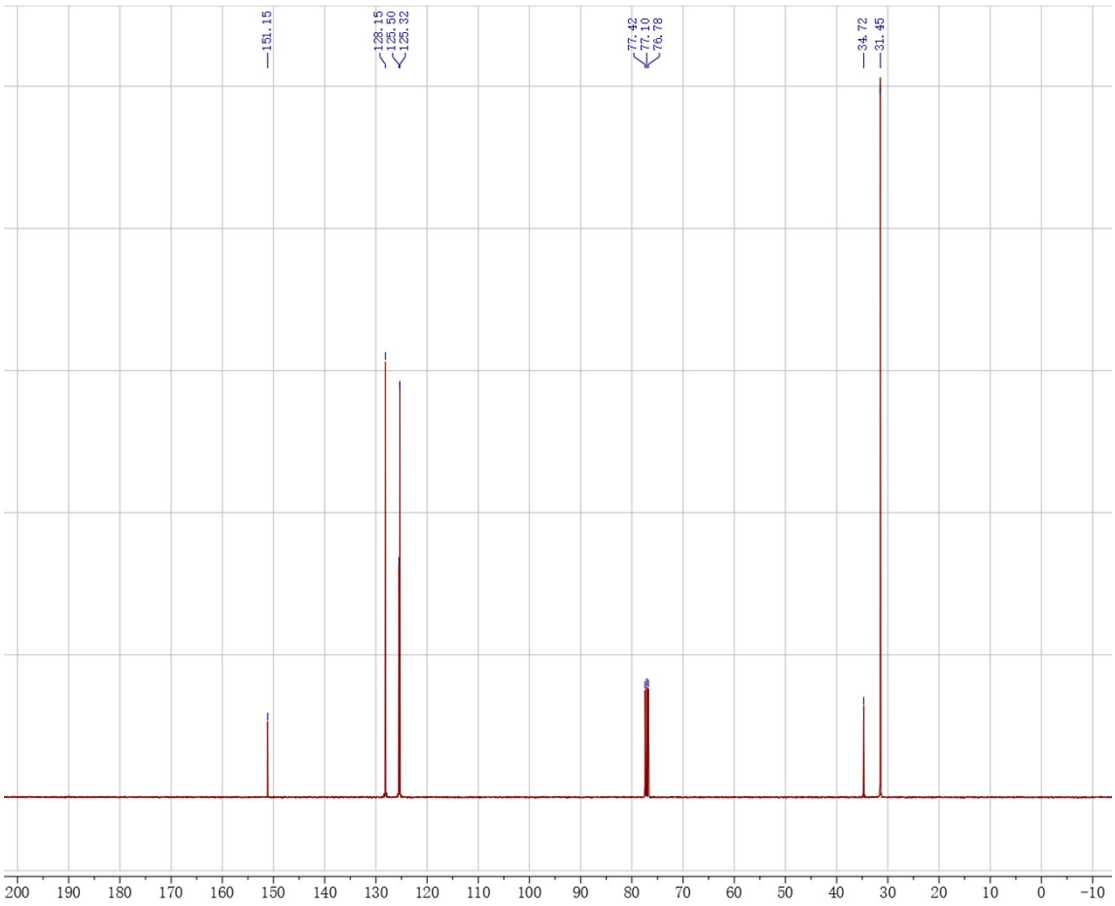
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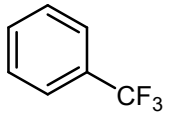
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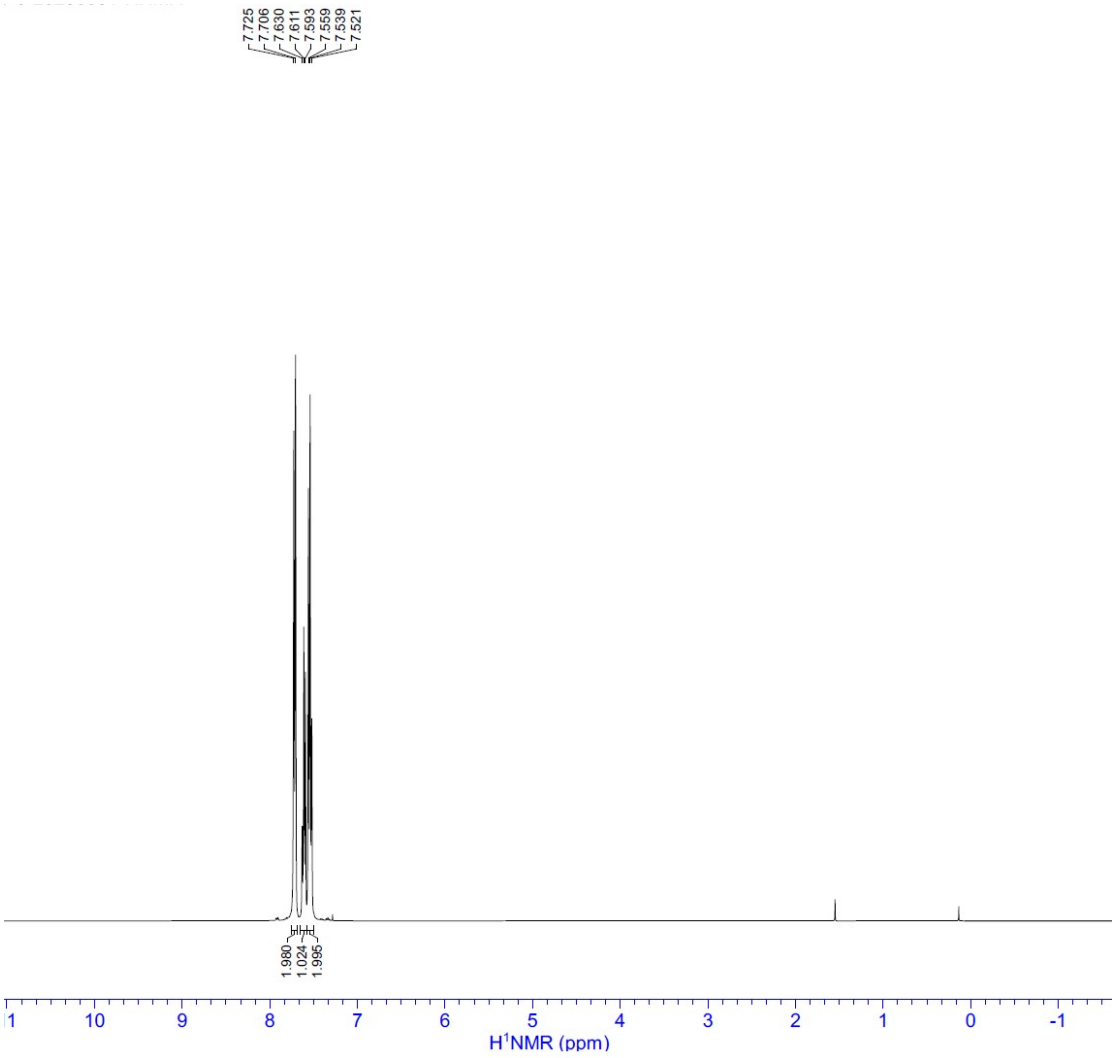
^{1}H NMR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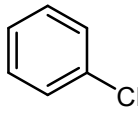
H1NMR (ppm)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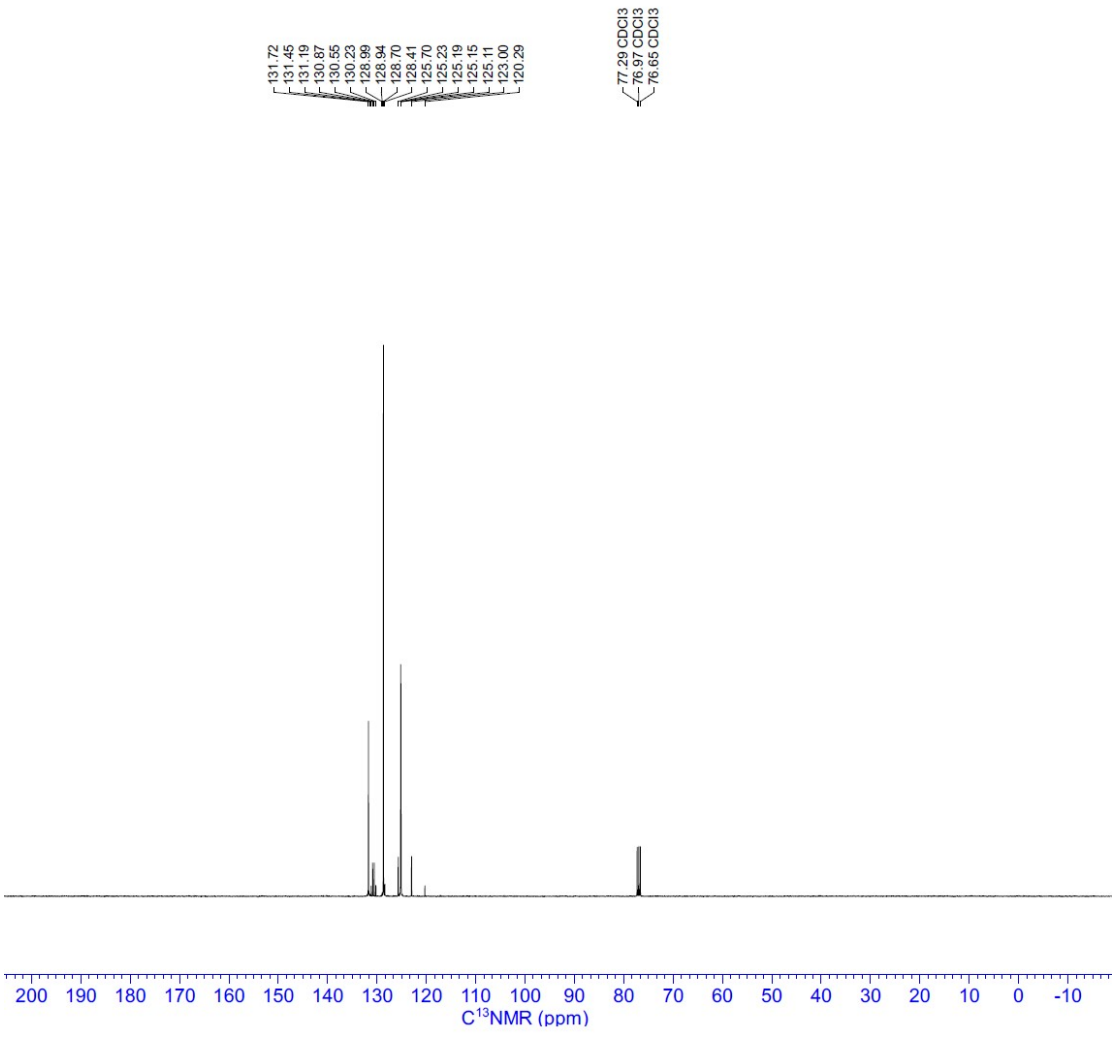
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125.11
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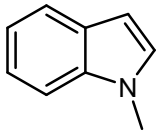

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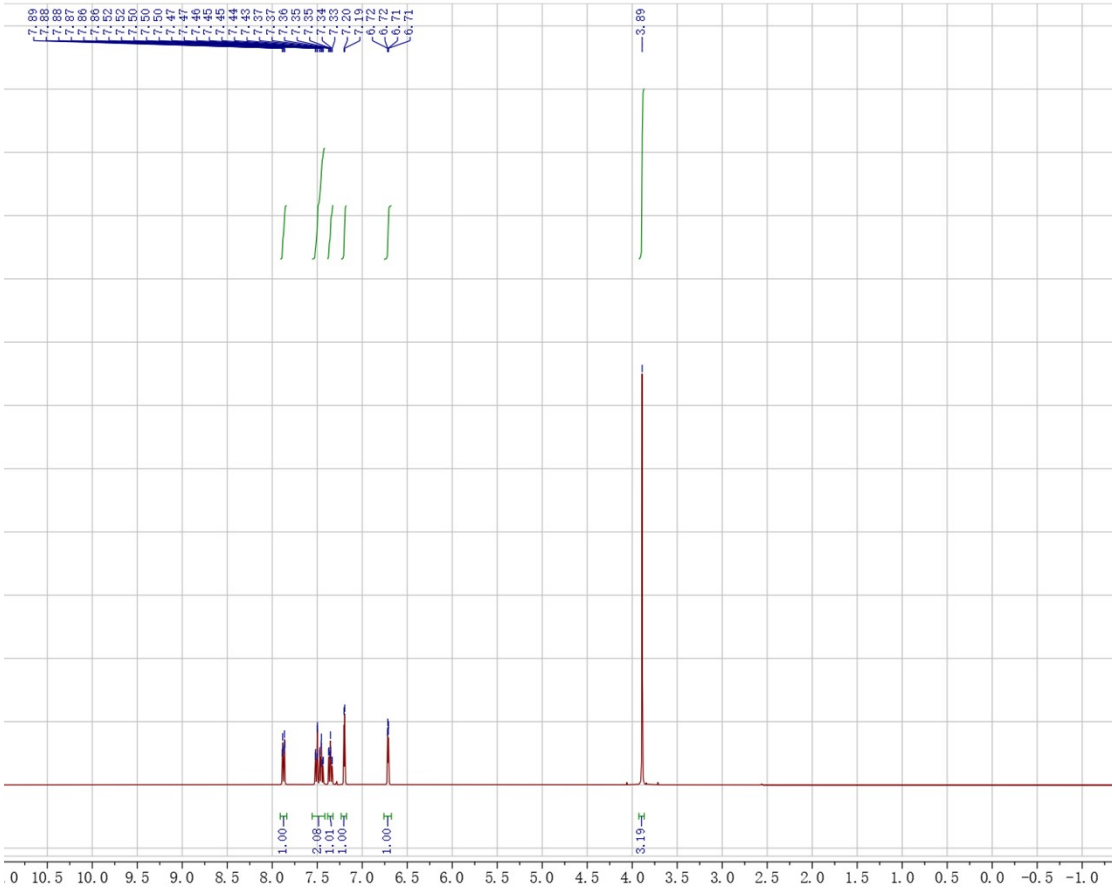
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7.19
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6.72
6.71
6.71
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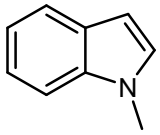
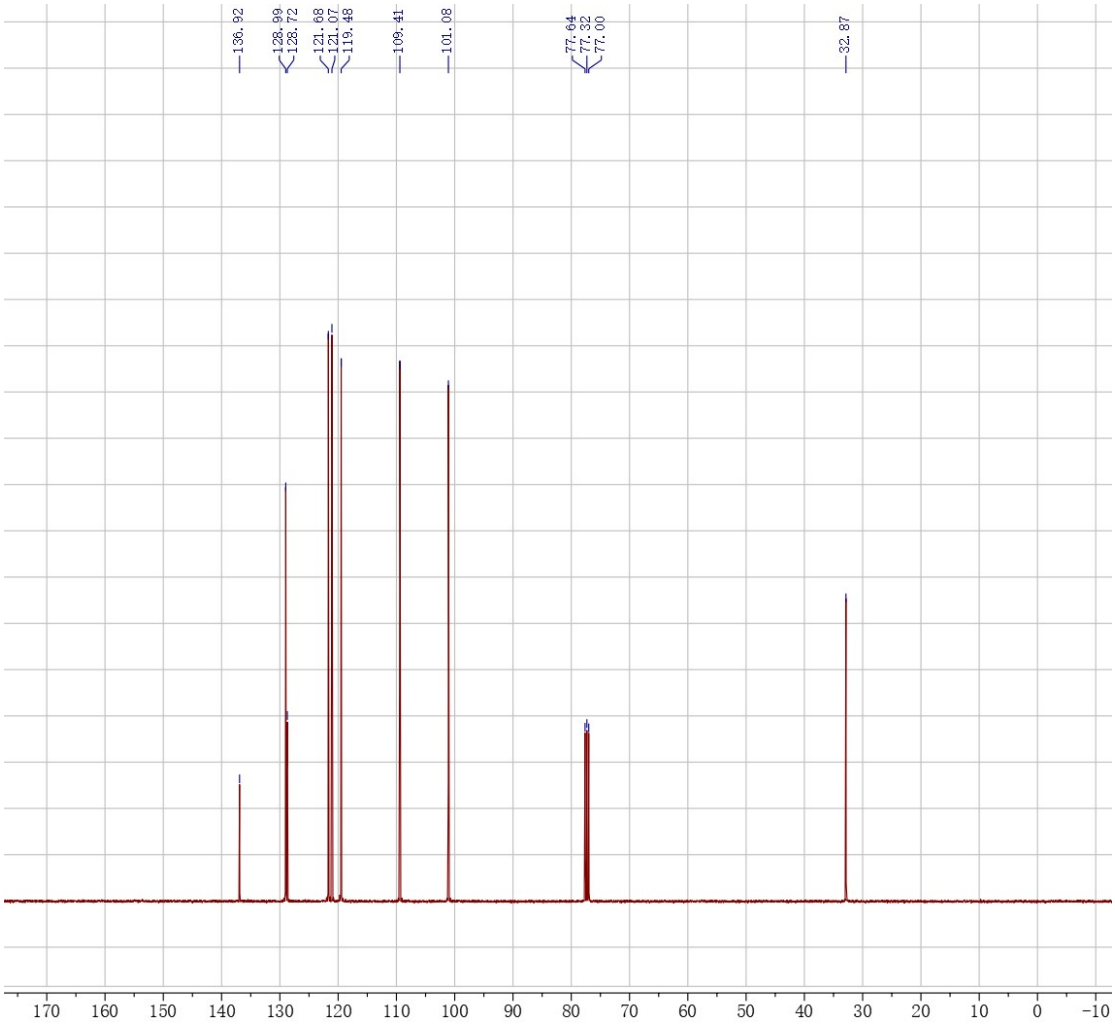
1.00
2.08
1.01
1.00
1.00
3.19
0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0



^{13}C NMR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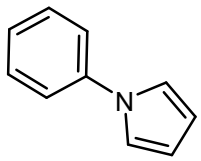

^{1}H NMR


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7.34
7.34
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7.30
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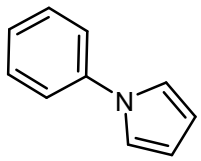
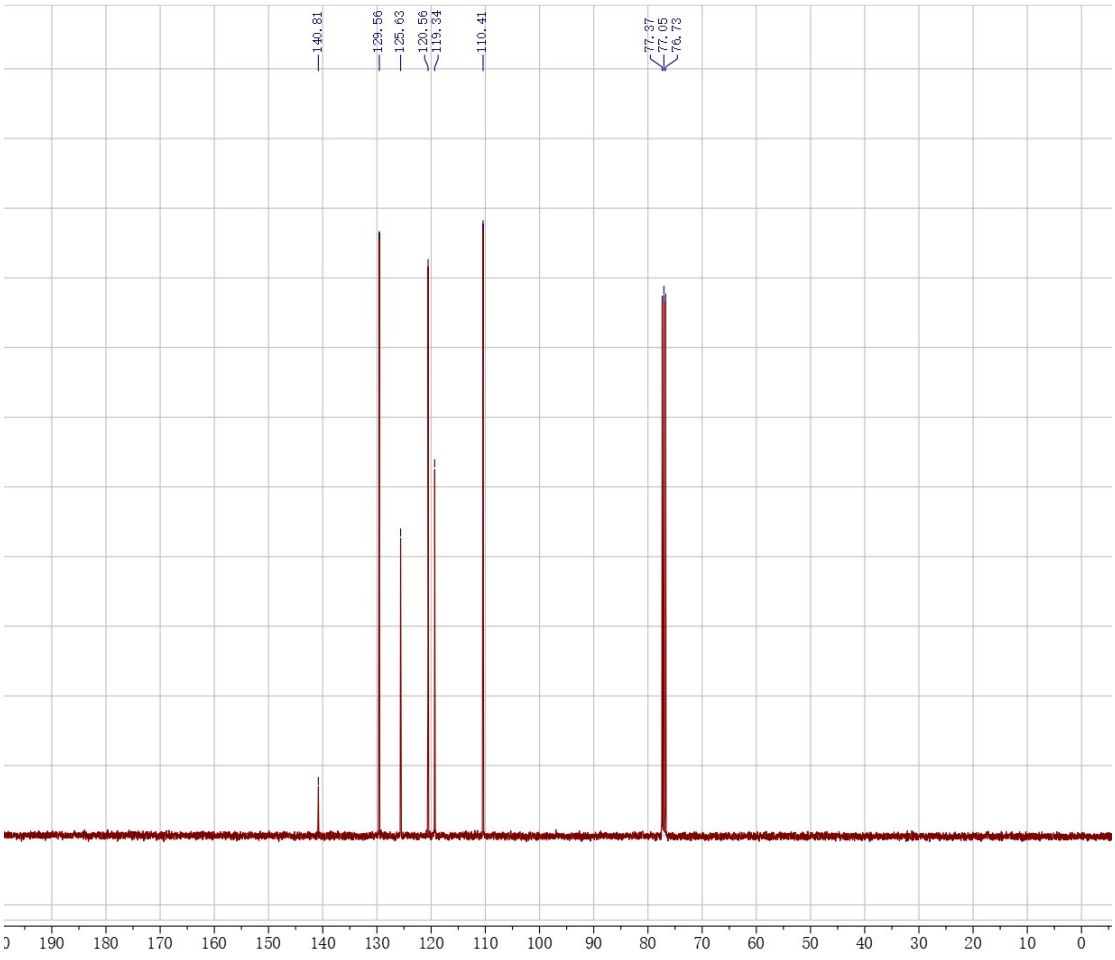
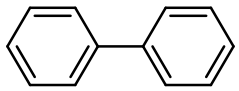
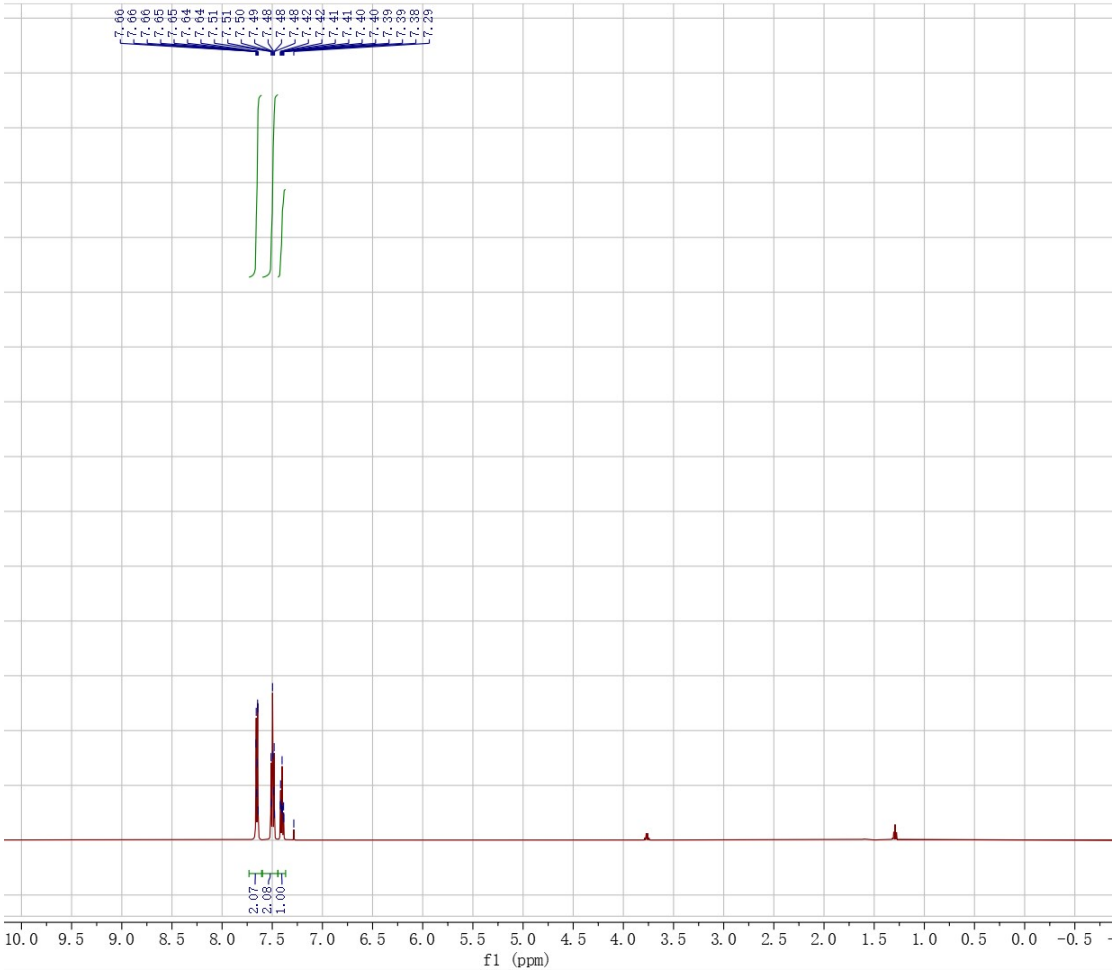


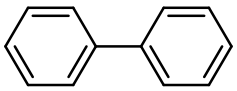
^{13}C NMR


140.81
129.56
125.63
120.56
119.34
110.41
77.37
77.05
76.73
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

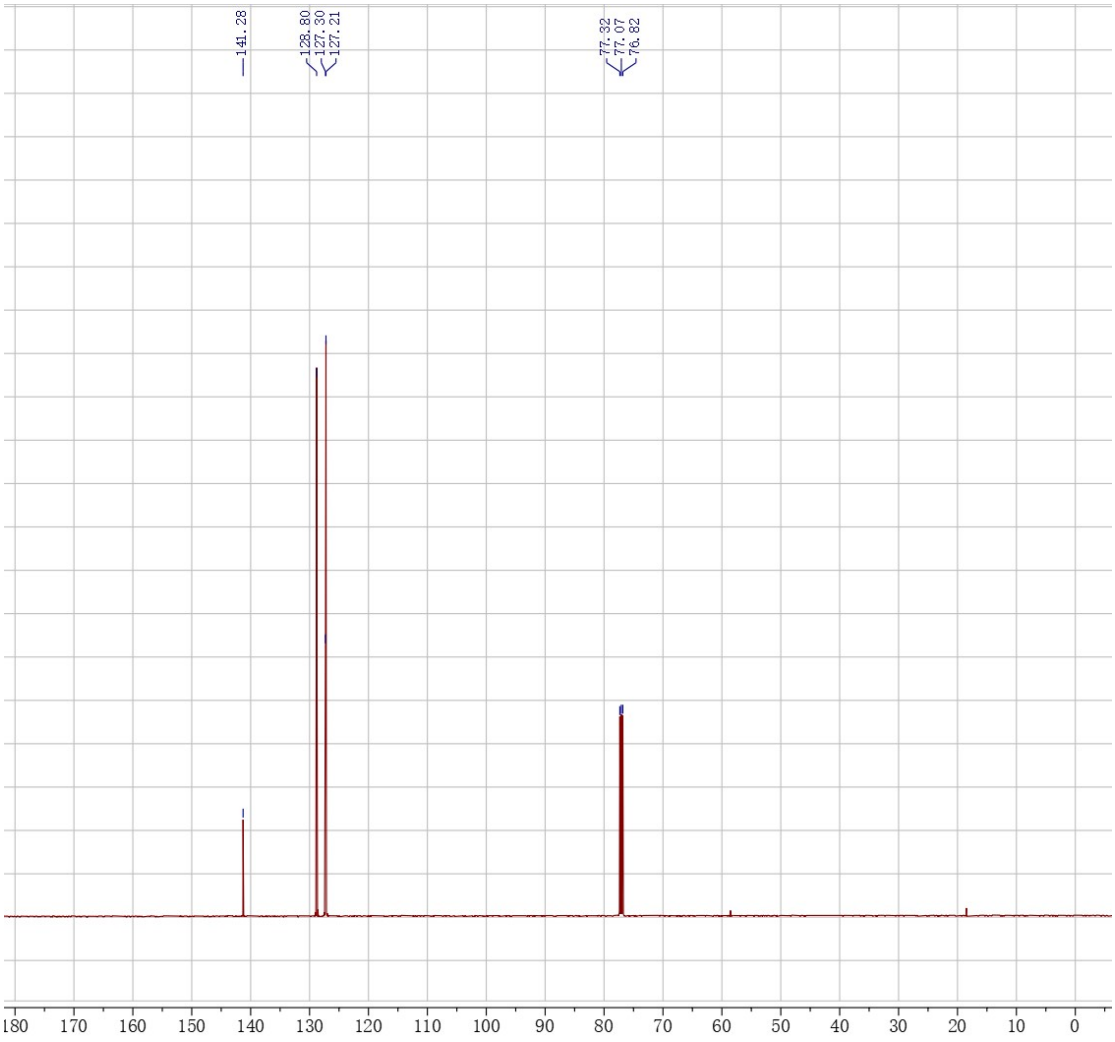


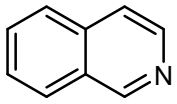
^{1}H NMR


7.66
7.66
7.66
7.65
7.65
7.64
7.64
7.51
7.50
7.49
7.48
7.48
7.42
7.41
7.41
7.40
7.39
7.38
7.29
2.07
2.08
1.00
10.0 9.5 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 -0.5
f1 (ppm)

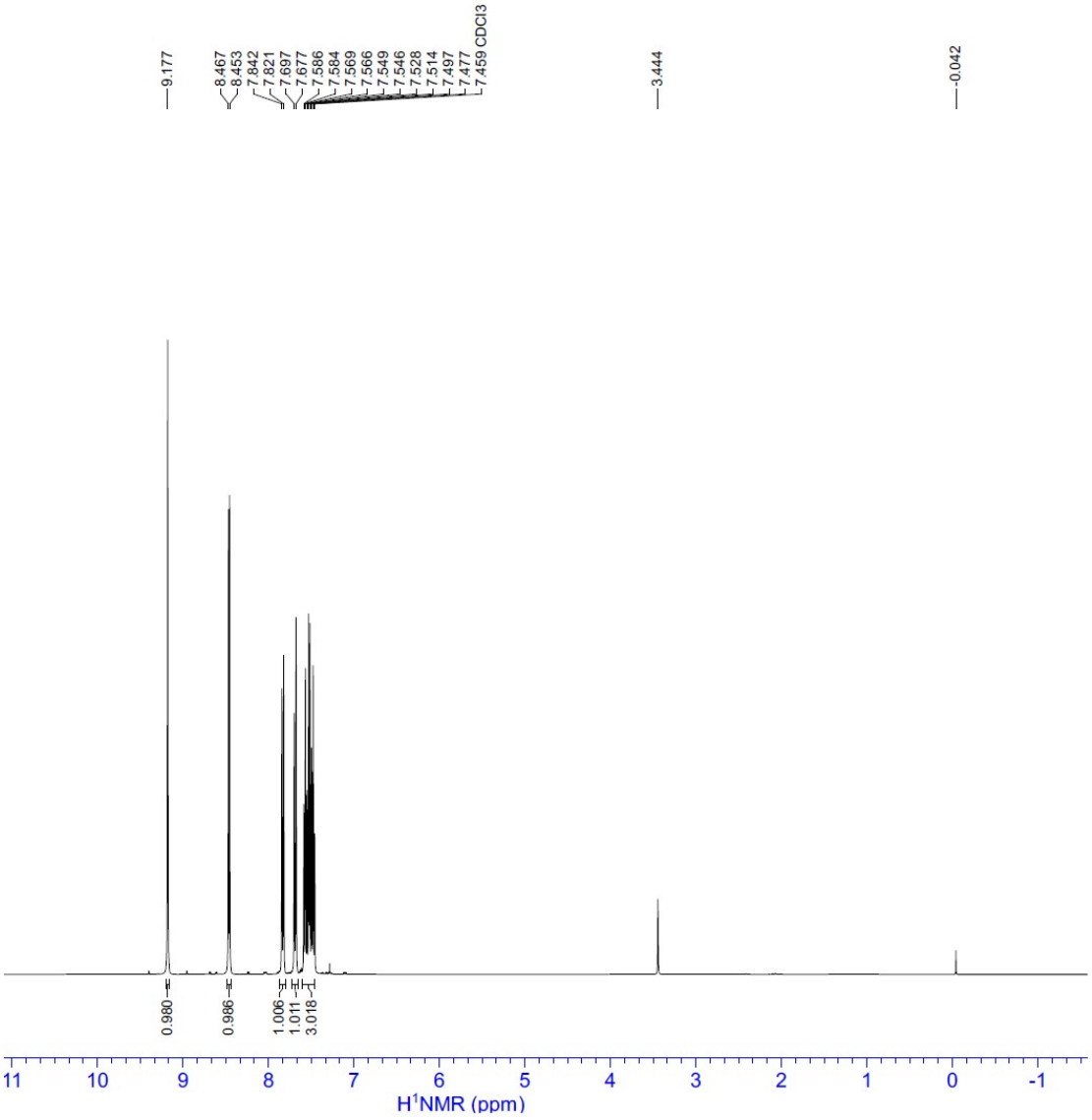


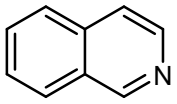
^{13}C NMR


141.28
128.80
127.30
127.21
77.32
77.07
76.82
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

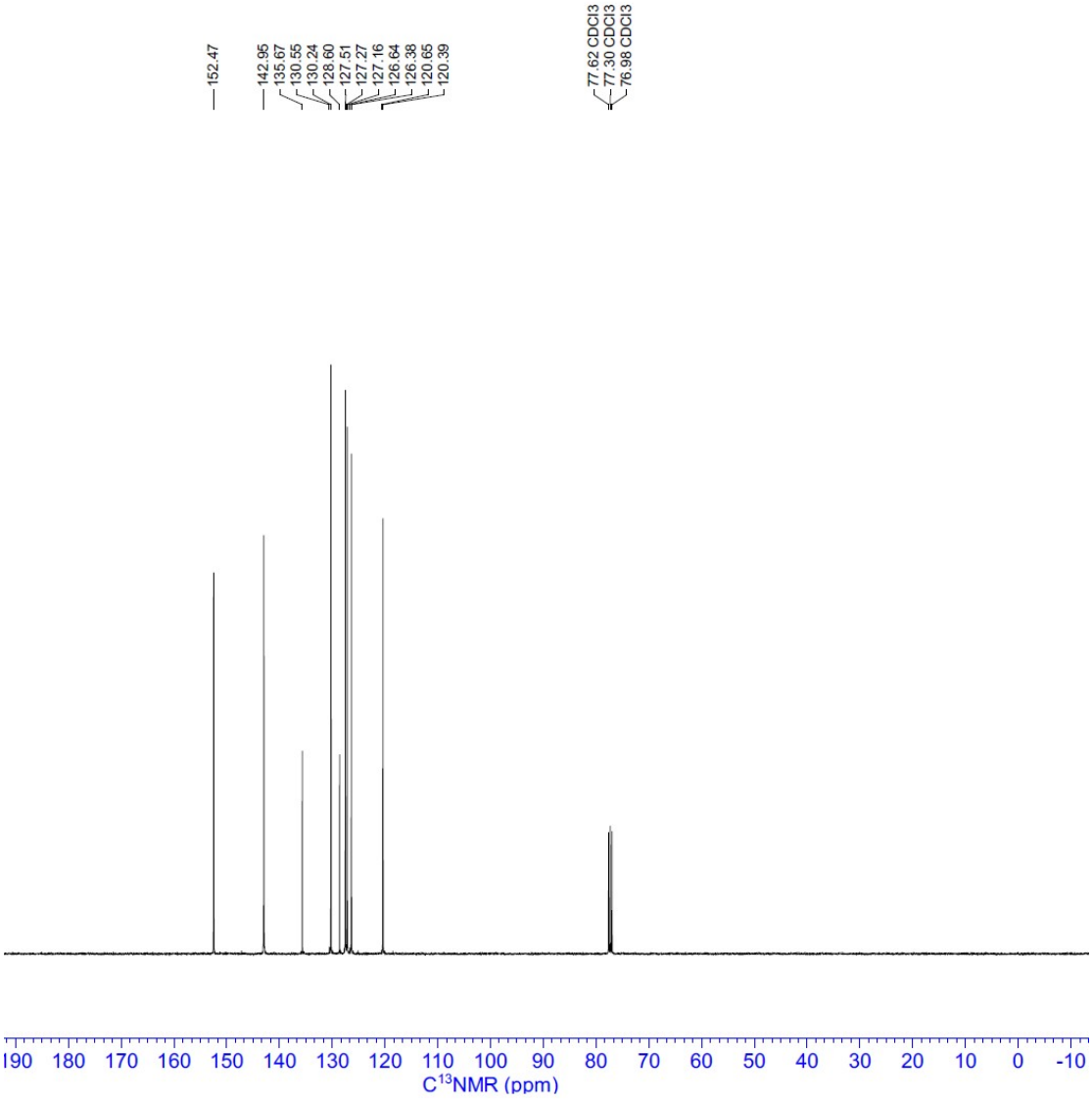

N

^{1}H NMR


9.177
8.467
8.453
7.842
7.821
7.697
7.677
7.586
7.584
7.569
7.566
7.549
7.546
7.528
7.514
7.497
7.477
7.459 CDCl3
3.444
-0.042
0.980
0.986
1.006
1.011
3.018
11
10
9
8
7
6
5
4
3
2
1
0
-1
H1NMR (ppm)



^{13}C NMR


152.47
142.95
135.67
130.55
130.24
128.60
127.51
127.27
127.16
126.64
126.38
120.65
120.39
77.62 CDCl3
77.30 CDCl3
76.98 CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
C13NMR (ppm)