Supporting Information

for

Copper-Catalyzed Hydroxylation of Aryl Halides: Efficient Synthesis of Phenols, Alkyl Aryl Ethers and Benzofuran Derivatives in Neat Water

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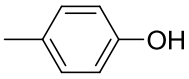
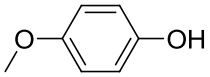
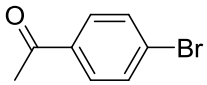
NMR data



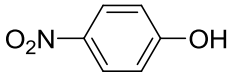
p-cresol[1]: ^{1}H NMR (400 MHz, [D$_1$]CDCl$_3$): δ 7.08 (d, *J*= 8.2 Hz, 2H), 6.78 (d, *J*= 8.3 Hz, 2H), 5.29 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, [D$_1$]CDCl$_3$): δ 153.1, 130.1, 130.0, 115.2, 20.5.



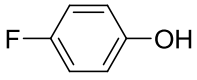
p-methoxyphenol[2]: ^{1}H NMR (400 MHz, [D$_1$]CDCl$_3$): δ 6.83~6.78 (m, 4H), 5.10 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, [D$_1$]CDCl$_3$): δ 155.4, 139.9, 129.5, 121.7, 116.7, 112.3, 21.3.



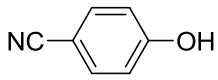
1-(4-hydroxyphenyl)ethanone[1]: ^{1}H NMR (400 MHz, [D$_1$]CDCl$_3$): δ 7.93 (d, J= 8.8 Hz, 2H), 6.97 (d, J= 8.7 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, [D$_1$]CDCl$_3$): δ 198.6, 161.4, 131.2, 129.6, 115.6, 26.3.



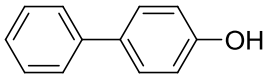
p-nitrophenol[3]: ^{1}H NMR (400 MHz, [D$_1$]CDCl$_3$): δ 8.20 (d, *J*= 9.0 Hz, 2H), 6.96 (d, *J*= 9.0 Hz, 2H), 6.24 (s, 1H); ^{13}C NMR (100 MHz, [D$_1$]CDCl$_3$): δ 161.5, 141.6, 126.3, 115.8.



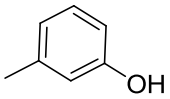
p-fluorophenol[1]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 6.97~6.92 (m, 2H), 6.81~6.78 (m, 2H), 5.00 (br, 1H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 158.6, 156.3, 151.2, 116.3.



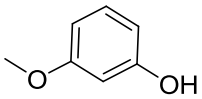
p-hydroxybenzonitrile[4]: ^{1}H NMR (400 MHz, [D_6]DMSO): δ 10.40 (s, 1H), 7.79 (d, *J*= 8.4 Hz, 2H), 6.82 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR (100 MHz, [D_6]DMSO): δ 167.6, 162.0, 132.0, 121.8, 115.6.



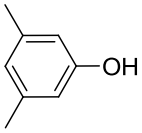
biphenyl-4-ol[1]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.57 (d, *J*= 8.0 Hz, 2H), 7.51 (d, *J*= 7.6 Hz, 2H), 7.44 (t, *J*= 7.1 Hz, 2H), 7.34 (t, *J*= 6.8 Hz, 1H), 6.94 (d, *J*= 7.6, 2H), 4.78 (s, 1H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 155.0, 140.8, 134.1, 128.7, 128.4, 126.7, 115.7.



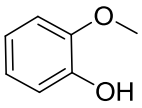
m-cresol[2]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.16 (t, *J*= 7.7 Hz, 1H), 6.80 (d, *J*= 7.5 Hz, 1H), 6.70~6.68 (m, 2H), 5.12 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 155.4, 139.9, 129.5, 121.7, 116.1, 112.3, 21.3.



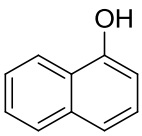
m-methoxyphenol[1]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.16 (t, *J*= 8.2 Hz, 1H), 6.52 (m, 1H), 6.45 (m, 2H), 5.00 (s, 3H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 160.9, 156.7, 130.2, 107.9, 106.5, 101.6, 55.3.



3,5-dimethylphenol[3]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 6.60 (s, 1H), 6.49 (s, 2H), 3.98 (s, 1H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 155.5, 139.5, 122.5, 113.1, 21.2.

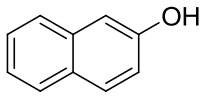


o-methoxyphenol: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 6.93 (m, 4H), 5.63 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 146.6, 145.7, 121.5, 120.1, 114.5, 110.7, 55.9.

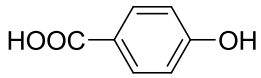


naphthalen-1-ol[1]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 8.25~8.27 (m, 1H), 7.87~7.90

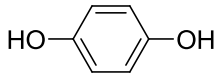
(m, 1H), 7.51~7.58 (m, 3H), 7.36 (t, *J*= 7.7 Hz, 1H), 6.85 (d, *J*= 7.4 Hz, 1H), 5.48 (s, 1H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 151.4, 134.8, 127.8, 126.5, 125.9, 125.4, 124.4, 121.6, 120.8, 108.8.



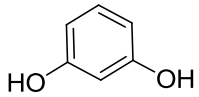
naphthalen-2-ol[3]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.79 (t, *J*= 7.2 Hz, 2H), 7.71 (d, *J*= 8.2 Hz, 1H), 7.46 (t, *J*= 7.4 Hz, 1H), 7.36 (t, *J*= 7.7 Hz, 1H), 7.17 (s, 1H), 7.13 (d, *J*= 8.8 Hz, 1H), 4.96 (s, 1H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 153.3, 134.6, 129.9, 129.0, 127.8, 126.4, 123.8, 123.5, 117.7, 109.5



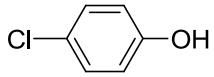
p-hydroxybenzoic acid[3]: ^{1}H NMR (400 MHz, [D_6]DMSO): δ 12.39 (s, 1H), 10.19 (s, 1H), 7.79 (d, *J*= 8.6 Hz, 2H), 6.82 (d, *J*= 8.6 Hz, 2H); ^{13}C NMR (100 MHz, [D_6]DMSO): δ 167.6, 162.0, 132.0, 121.8, 115.6.



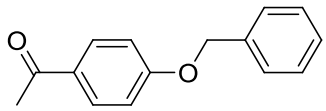
Hydroquinone[5]: ^{1}H NMR (400 MHz, [D_6]DMSO): δ 8.60 (s, 2H), 6.56 (s, 4H); ^{13}C NMR (100 MHz, [D_6]DMSO): δ 150.2, 116.1.



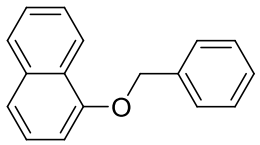
Resorcinol[6]: ^{1}H NMR (400 MHz, [D_6]DMSO): δ 9.12 (s, 2H), 6.94~6.90 (m, 1H), 6.20~6.18 (m, 3H); ^{13}C NMR (100 MHz, [D_6]DMSO): δ 158.9, 130.1, 106.7, 103.0.



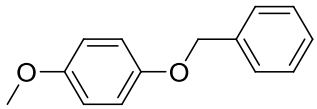
p-chlorophenol[3]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.22 (d, *J*= 8.8 Hz, 2H), 6.79 (d, *J*= 8.8 Hz, 2H), 5.00 (s, 1H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 154.1, 129.5, 125.7, 116.7.



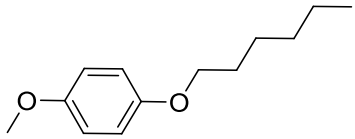
1-(4-(benzyloxy)phenyl)ethanone[7]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.96 (d, *J*= 8.7 Hz, 2H), 7.46~7.37 (m, 5H), 7.03 (d, *J*= 8.7 Hz, 2H), 5.16 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 196.7, 162.6, 136.2, 130.6, 128.7, 128.2, 127.5, 114.6, 70.2, 26.3.



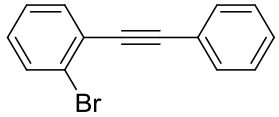
1-(benzyloxy)naphthalene[8]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.81~7.75 (m, 3H), 7.53~7.35 (m, 7H), 7.28~7.26 (m, 2H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 156.8, 136.9, 134.5, 129.5, 129.1, 128.6, 128.0, 127.7, 127.6, 126.8, 126.4, 123.7, 119.1, 107.2, 70.1.



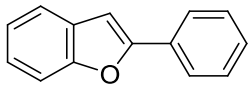
1-(benzyloxy)-4-methoxybenzene[8]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.47~7.33 (m, 5H), 6.96~6.86 (m, 4H), 5.05 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 154.0, 153.0, 137.4, 128.6, 127.9, 127.5, 115.9, 114.7, 70.8, 55.8.



1-(hexyloxy)-4-methoxybenzene[9]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 6.86 (s, 4H), 3.93 (t, J= 6.6 Hz, 2H), 3.79 (s, 3H), 1.82~1.75 (m, 2H), 1.50~1.46 (m, 2H), 1.38~1.36 (m, 4H), 0.96~0.92 (m, 3H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 153.7, 153.4, 115.5, 114.6, 68.7, 55.7, 31.6, 29.4, 25.8, 22.6, 14.0.

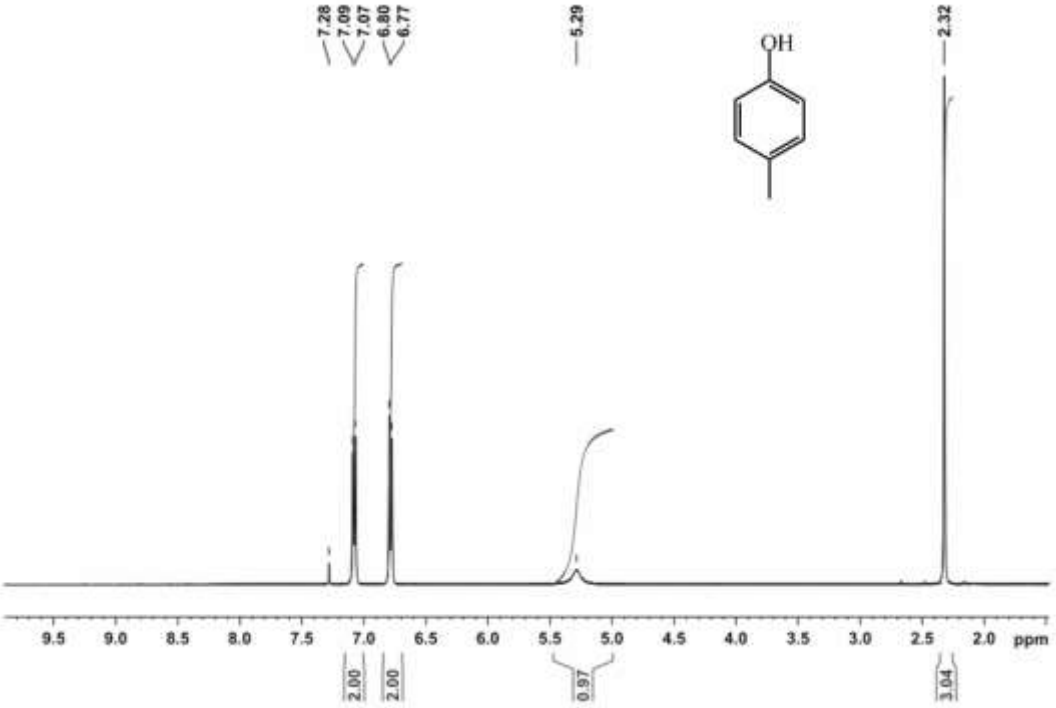


1-bromo-2-(phenylethynyl)benzene[10]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.66~7.58 (m, 4H), 7.40~7.38 (m, 3H), 7.34~7.30 (m, 1H), 7.29~7.19 (m, 1H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 133.2, 132.5, 131.7, 129.4, 128.7, 128.4, 127.0, 125.7, 125.4, 123.0, 94.0, 88.0.



2-phenylbenzofuran[11]: ^{1}H NMR (400 MHz, [D_1]$CDCl_3$): δ 7.92~7.90 (m, 2H), 7.62~7.61 (m, 1H), 7.57~7.55 (m, 1H), 7.50~7.46 (m, 2H), 7.40~7.37 (m, 1H), 7.30~7.24 (m, 2H), 7.06 (d, J= 0.7, 1H); ^{13}C NMR (100 MHz, [D_1]$CDCl_3$): δ 155.9, 154.9, 130.5, 129.2, 128.8, 128.6, 125.0, 124.3, 122.9, 120.9, 111.2, 101.3.

NMR Spectra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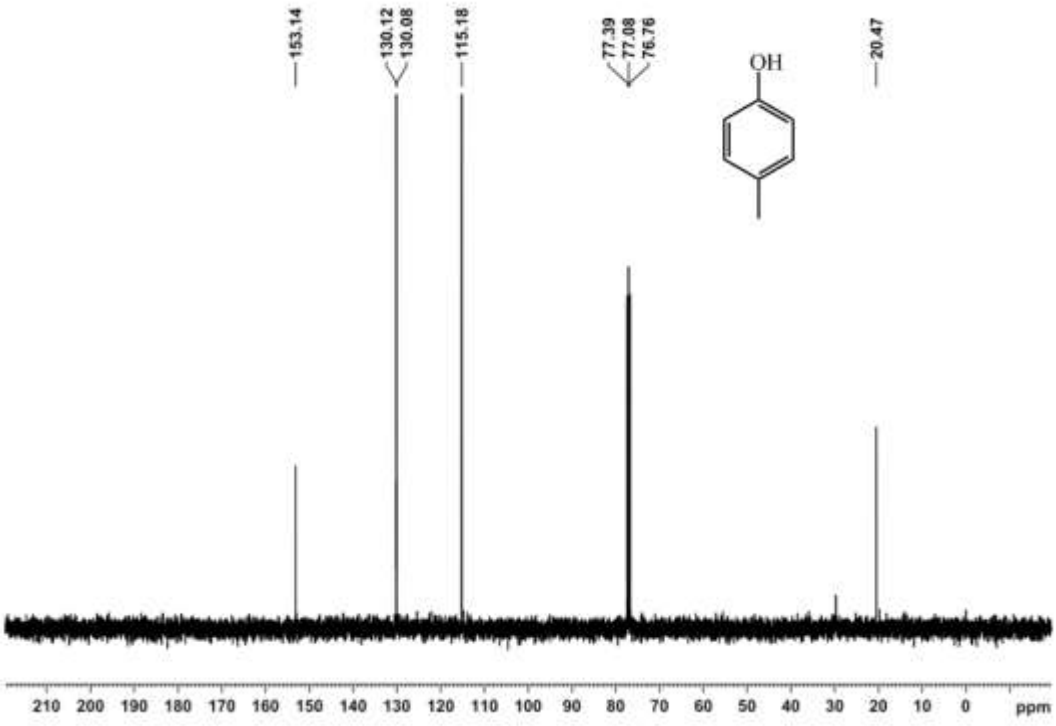
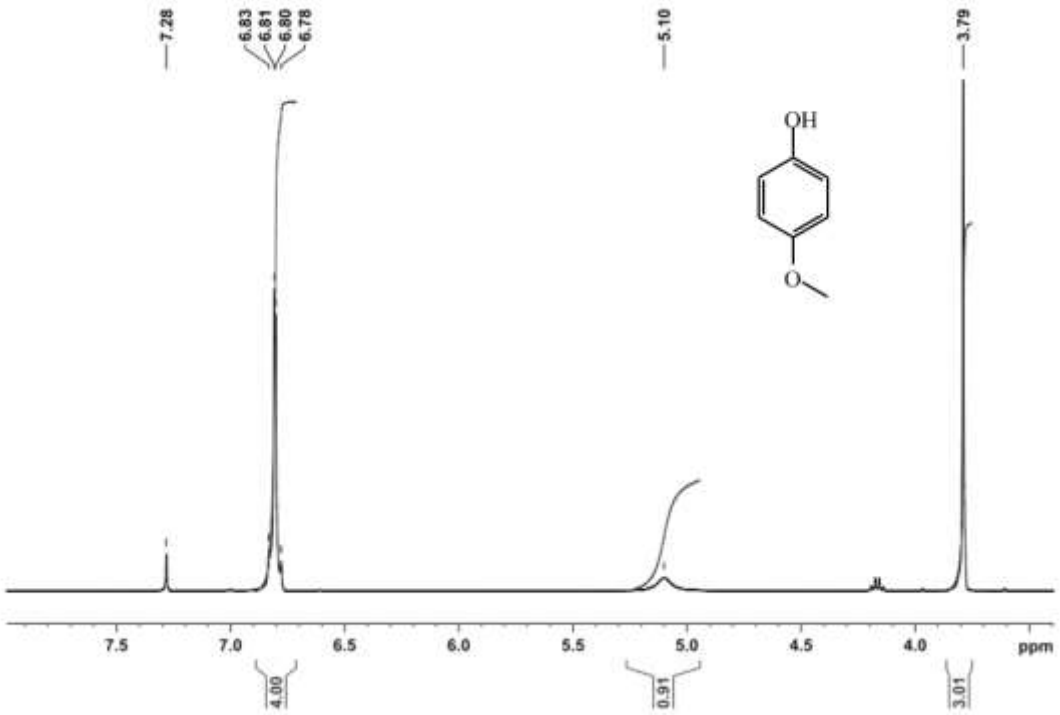
7.09
7.07
6.80
6.77
5.29
2.32
OH
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
2.00
2.00
0.97
3.04


153.14
130.12
130.08
115.18
77.39
77.08
76.76
20.47
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.83
6.81
6.80
6.78
5.10
3.79
OH
O
7.5
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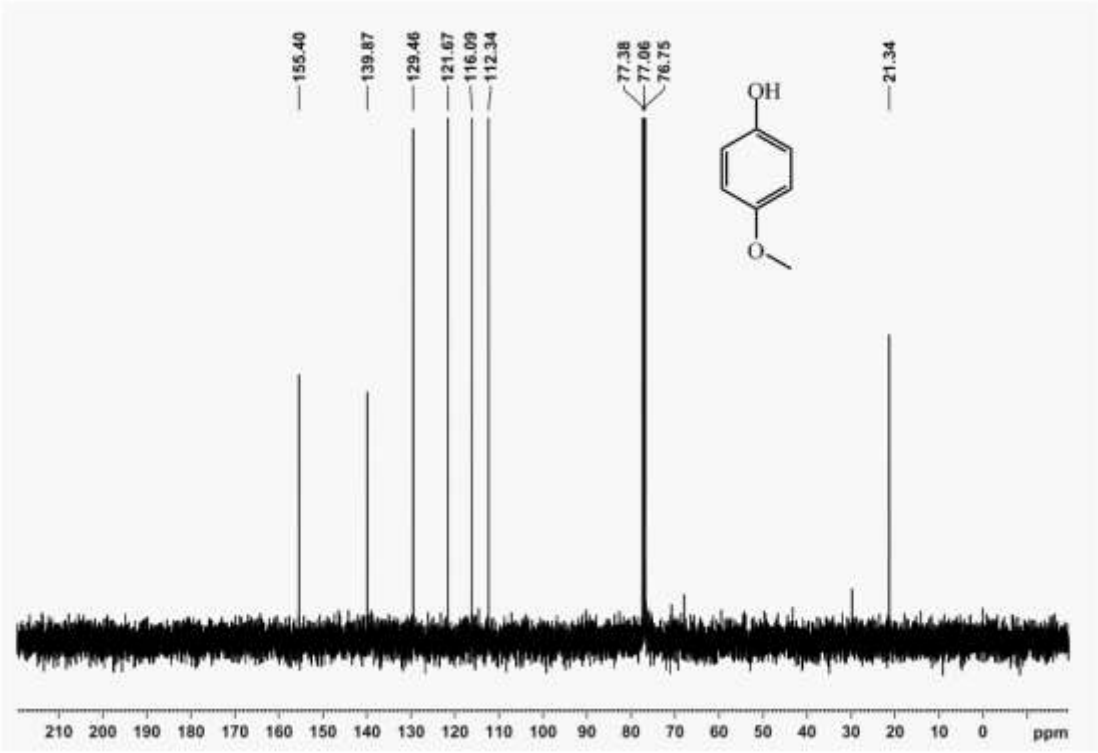
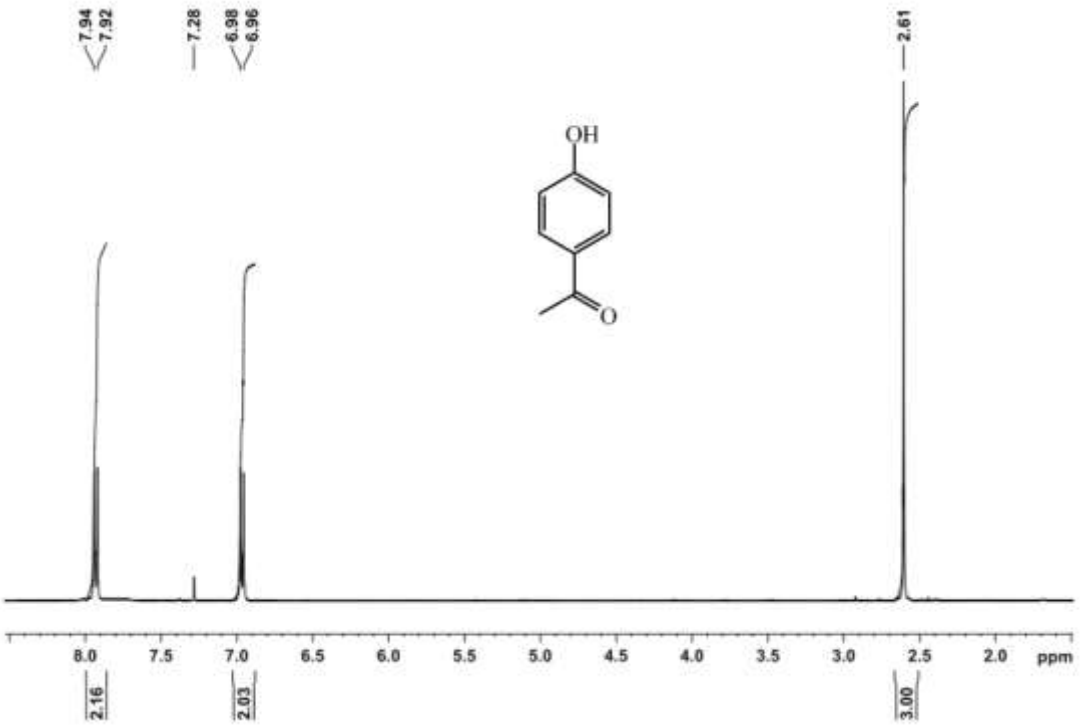
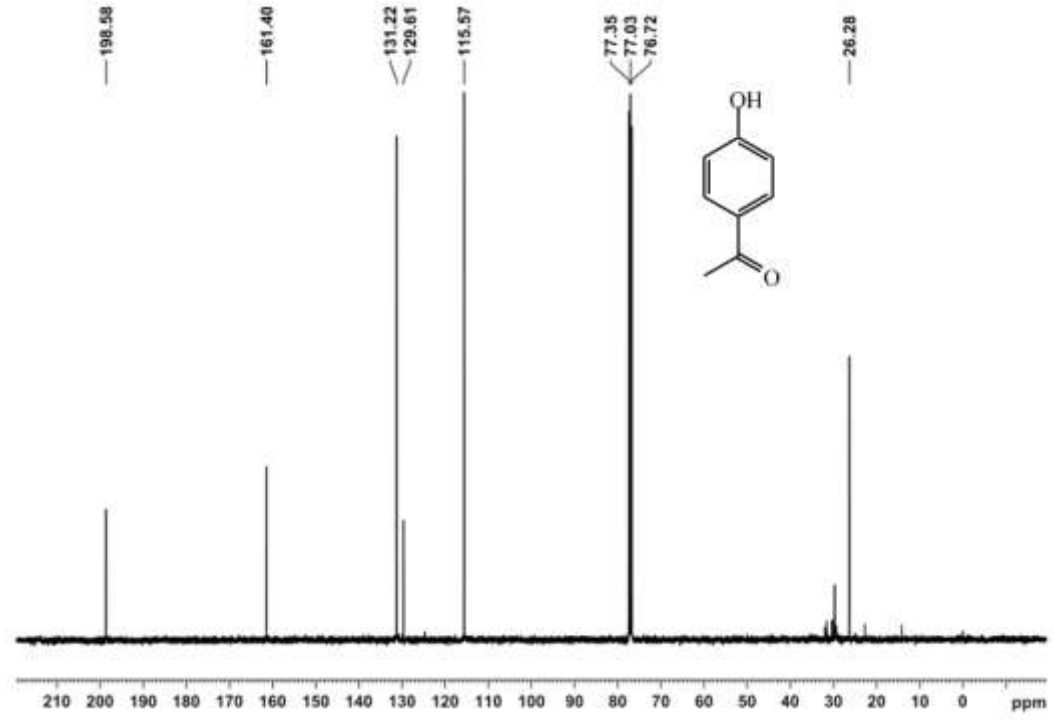
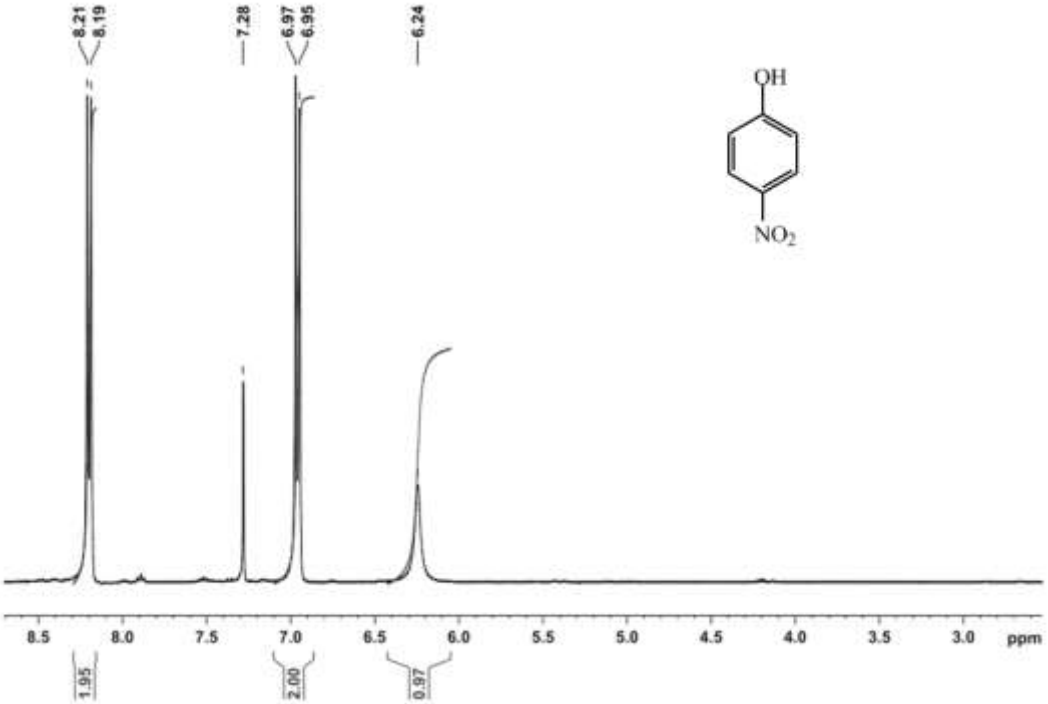
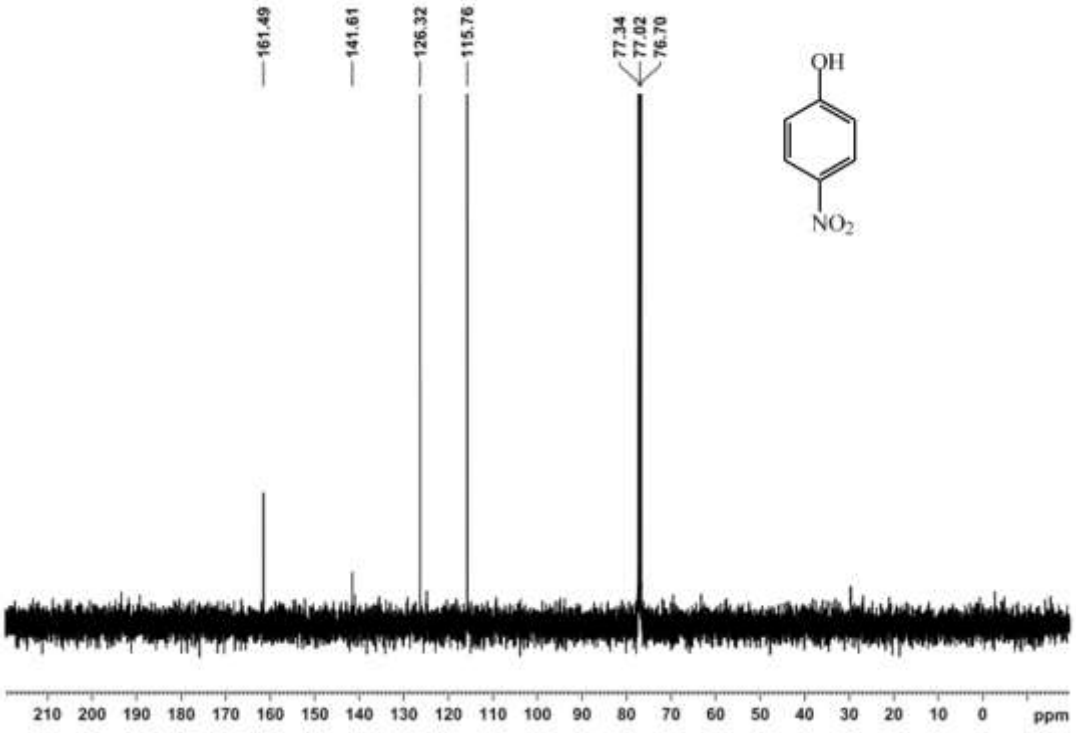
6.5
6.0
5.5
5.0
4.5
4.0
ppm
4.00
0.91
3.01

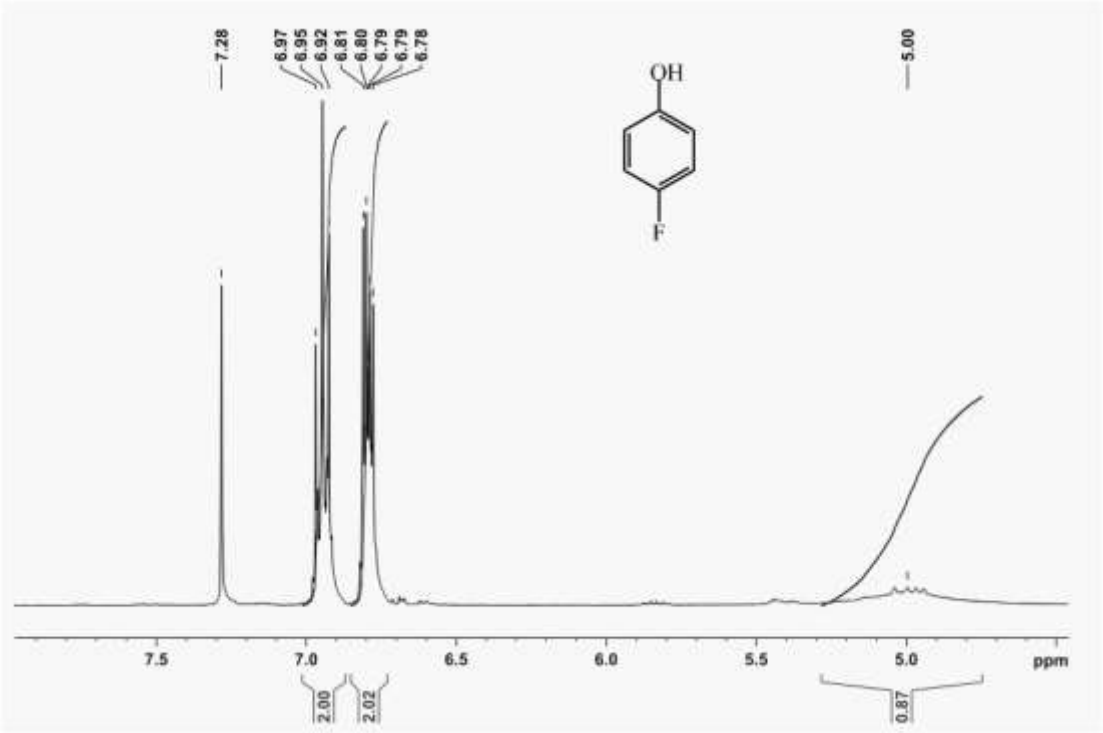

155.40
139.87
129.46
121.67
116.09
112.34
77.38
77.06
76.75
21.34
OH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.94
7.92
7.28
6.98
6.96
2.61
OH
O
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
ppm
2.16
2.03
3.00


198.58
161.40
131.22
129.61
115.57
77.35
77.03
76.72
26.28
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.21
8.19
7.28
6.97
6.95
6.24
OH
NO2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.95
2.00
0.97


161.49
141.61
126.32
115.76
77.34
77.02
76.70
OH
NO2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.97
6.95
6.92
6.81
6.80
6.79
6.79
6.78
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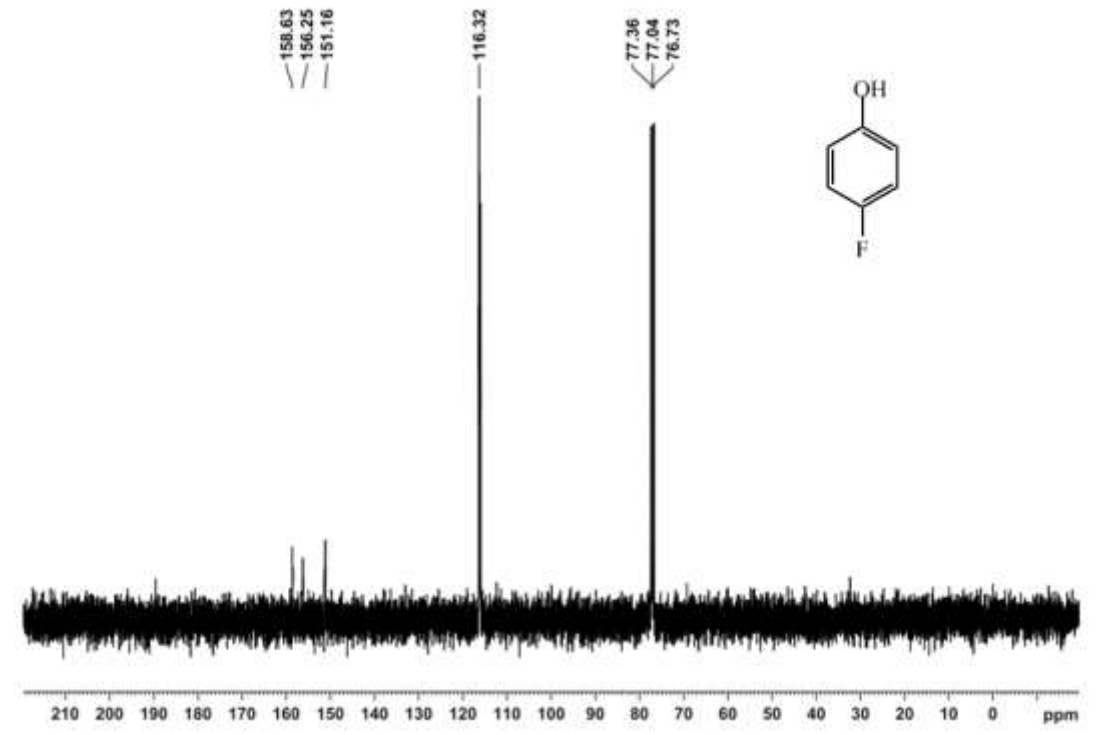
OH
F
7.5
7.0
6.5
6.0
5.5
5.0
ppm
2.00
2.02
0.87


158.63
156.25
151.16
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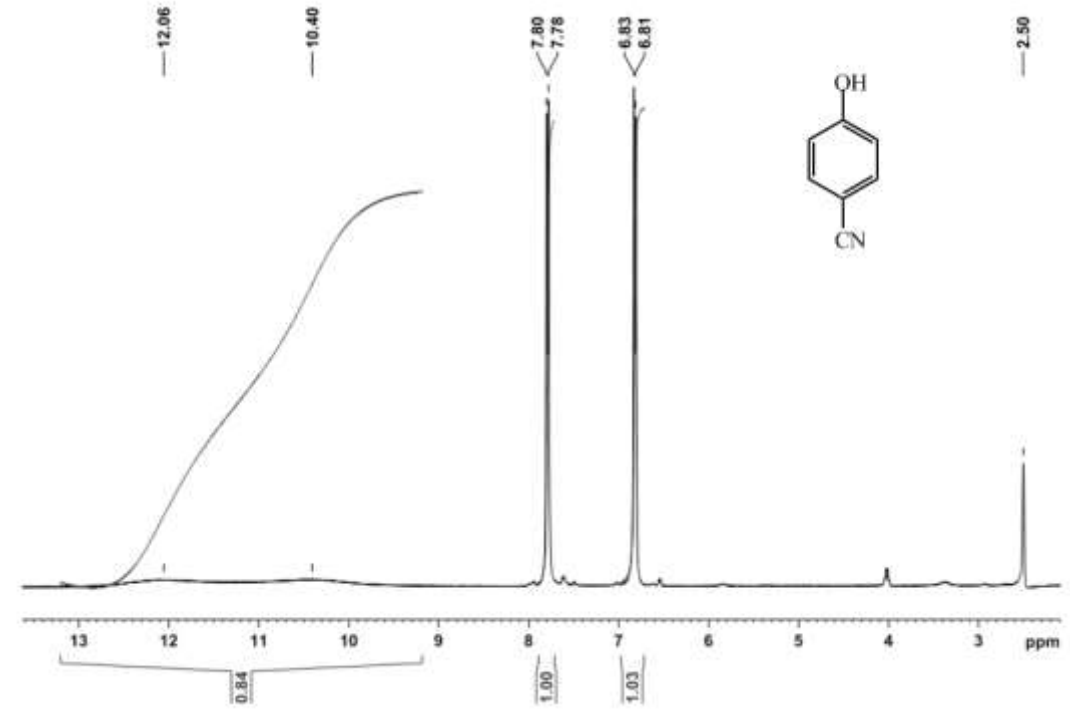
77.36
77.04
76.73
OH
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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10.40
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7.78
6.83
6.81
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OH
CN
13
12
11
10
9
8
7
6
5
4
3
ppm
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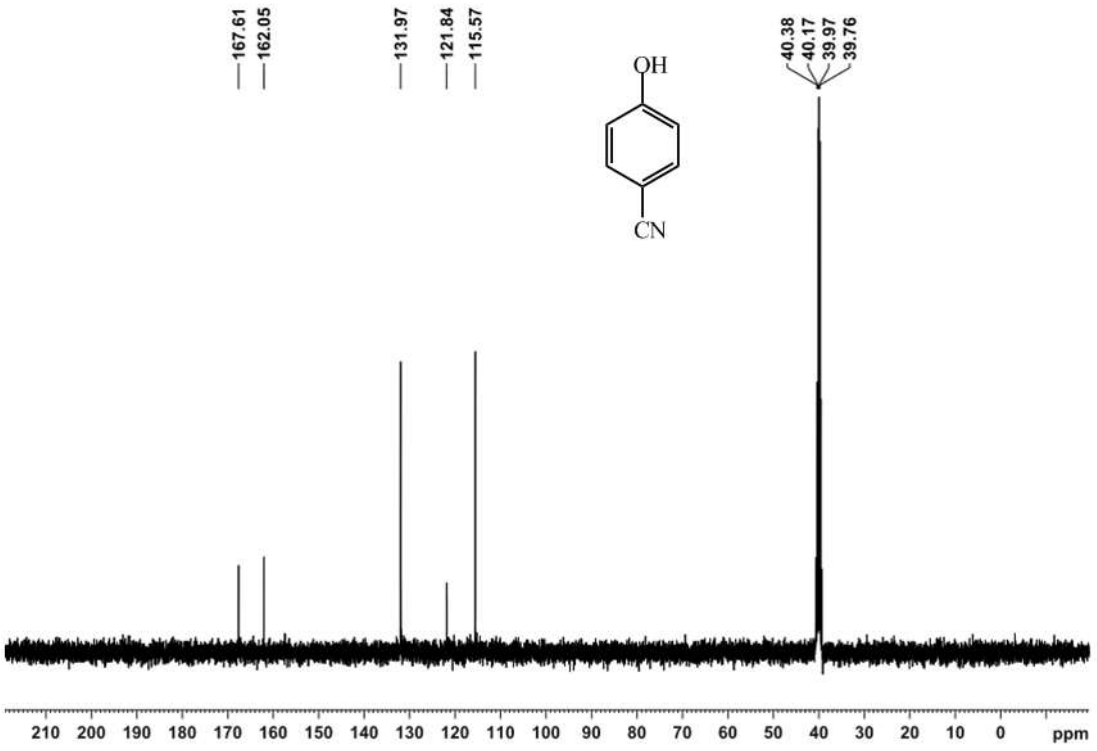
1.00
1.03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162.05
131.97
121.84
115.57
40.38
40.17
39.97
39.76
OH
CN
210
200
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180
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140
130
120
110
100
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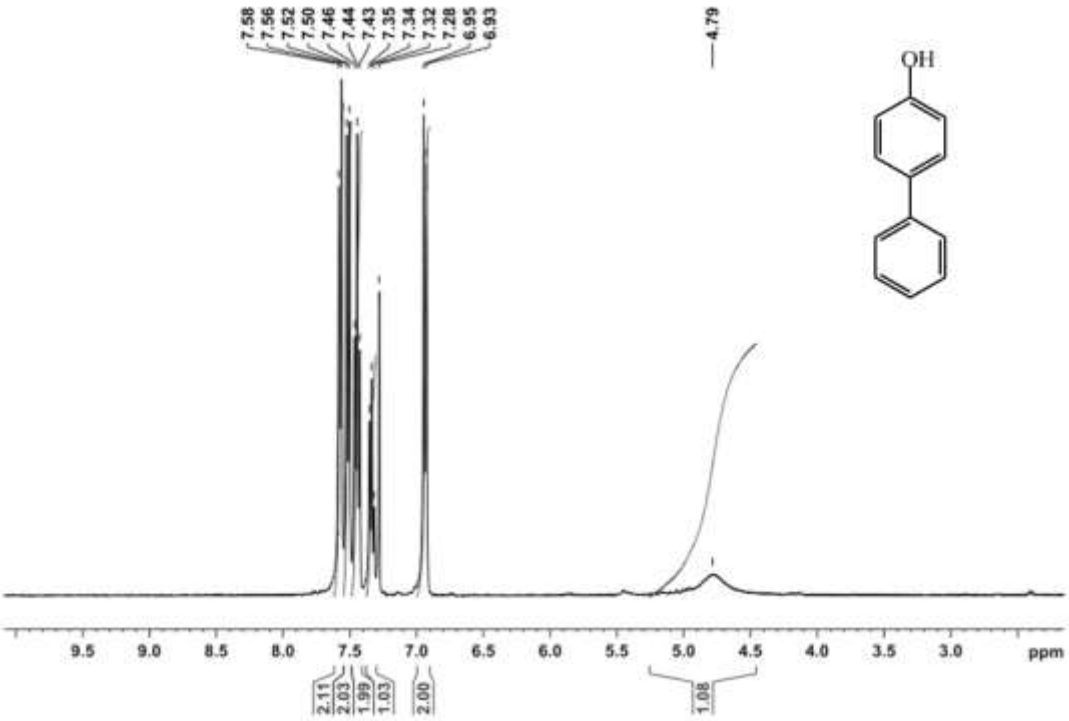
80
70
60
50
40
30
20
10
0
ppm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7.56
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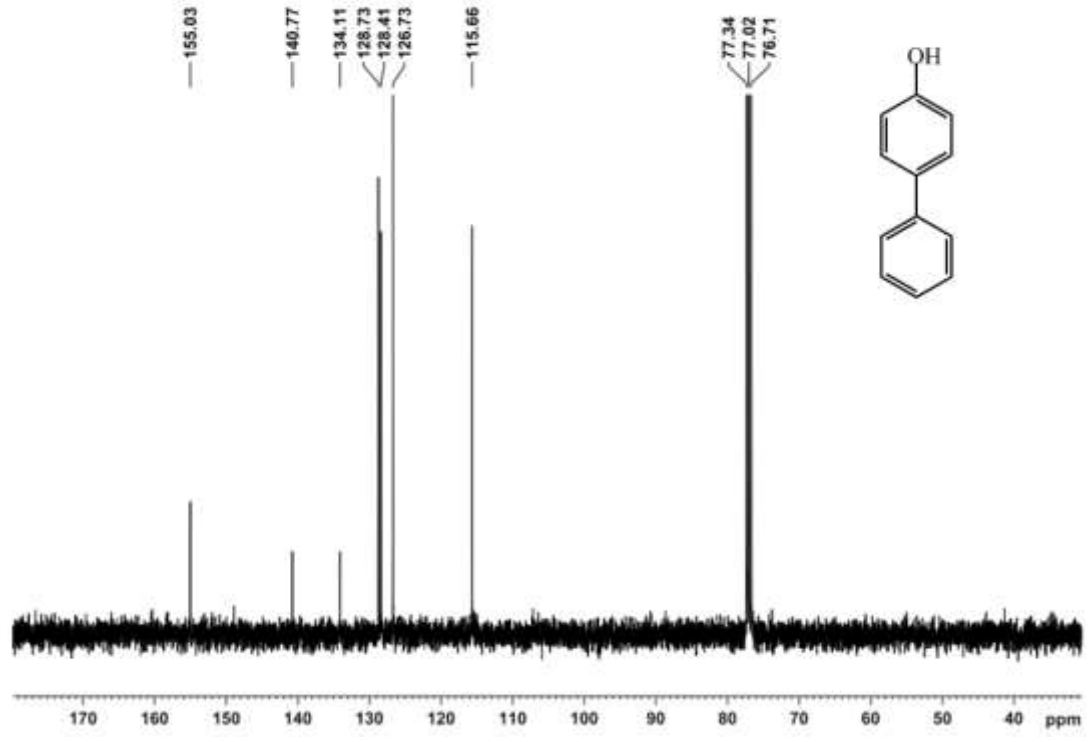
7.44
7.43
7.35
7.34
7.32
7.28
6.95
6.93
4.79
OH
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
2.11
2.03
1.99
1.03
2.00
1.08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140.77
134.11
128.73
128.41
126.73
115.66
77.34
77.02
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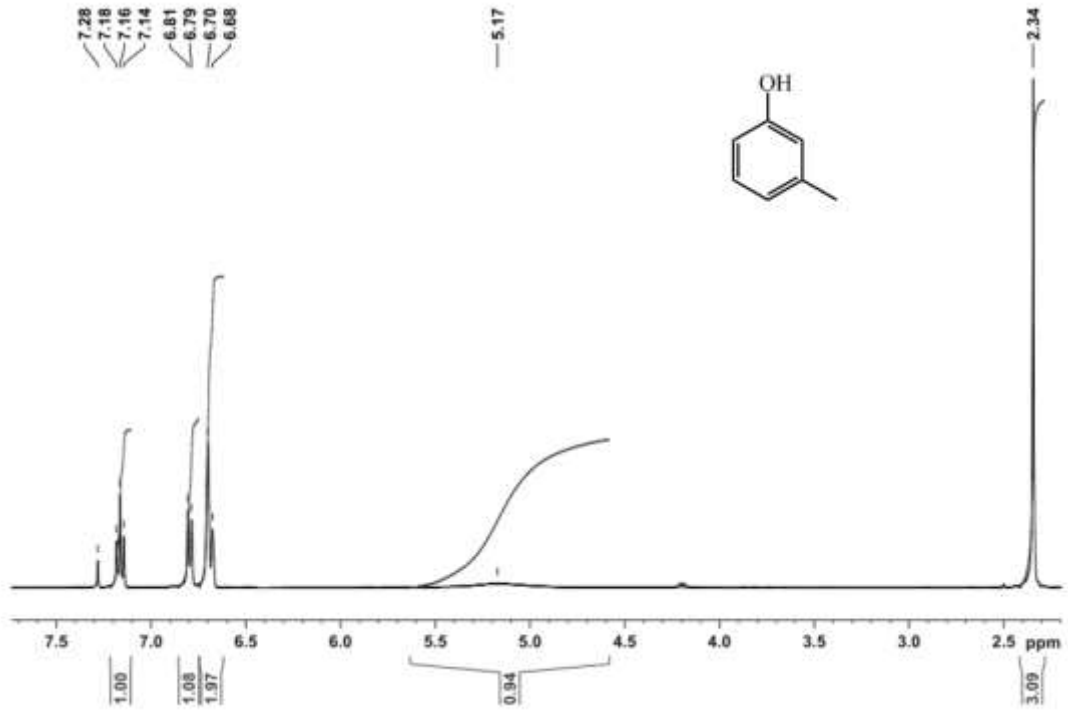
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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7.18
7.16
7.14
6.81
6.79
6.70
6.68
5.17
2.34
OH
7.5
7.0
6.5
6.0
5.5
5.0
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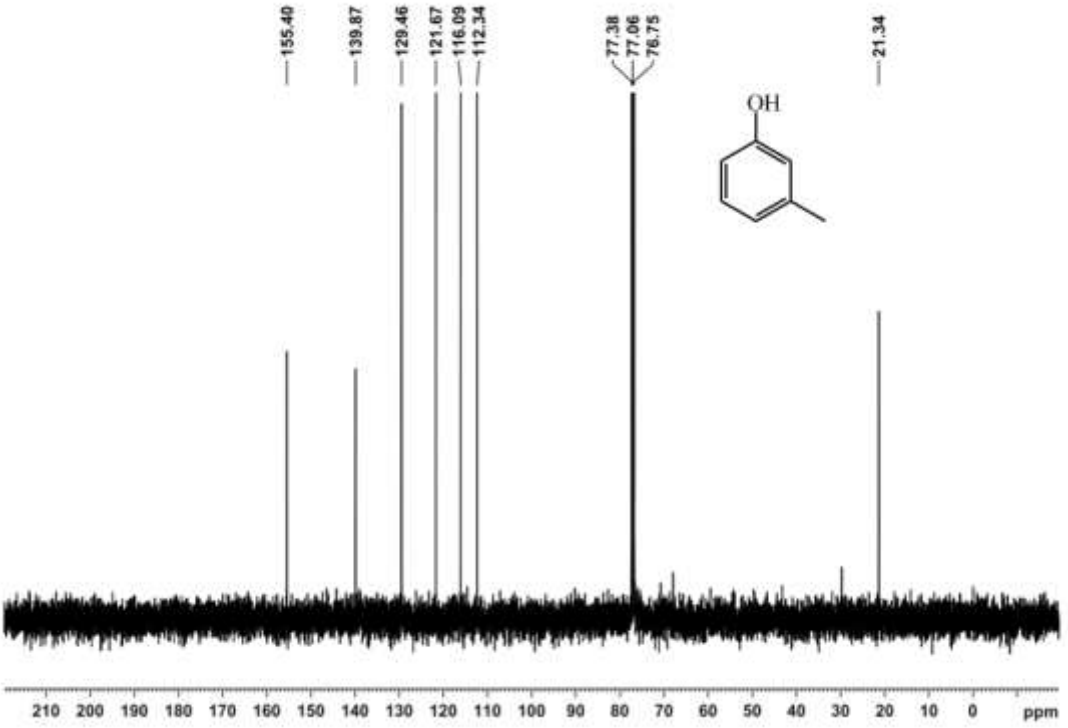
4.0
3.5
3.0
2.5
ppm
1.00
1.08
1.97
0.94
3.09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139.87
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116.09
112.34
77.38
77.06
76.75
21.34
OH
210
200
190
180
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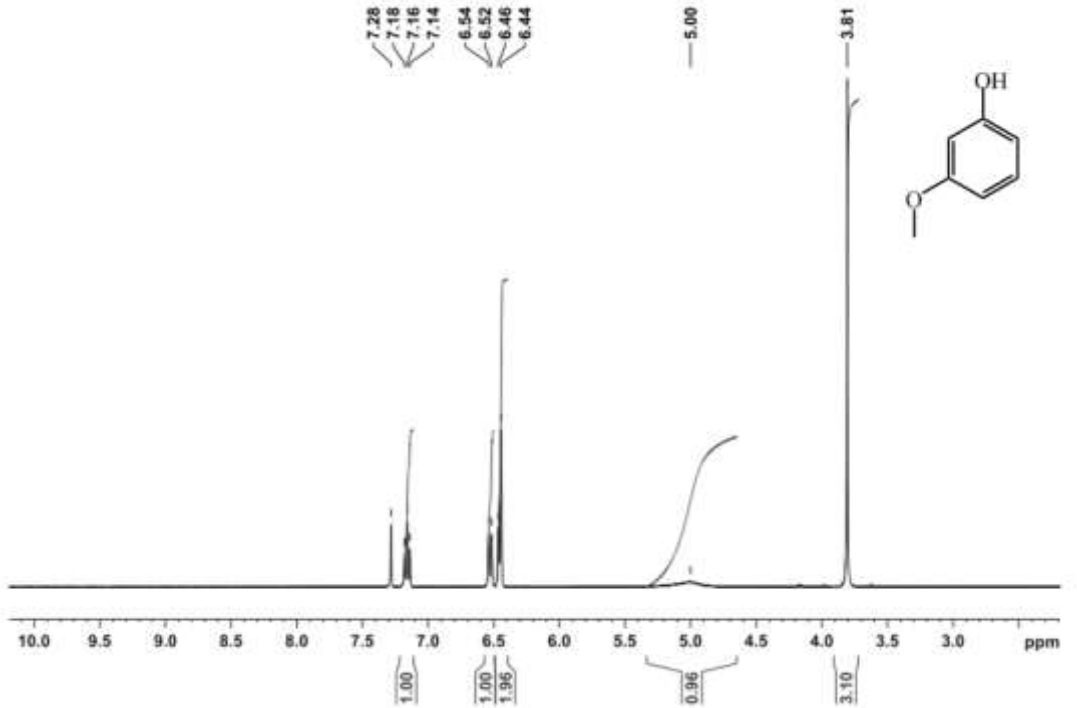
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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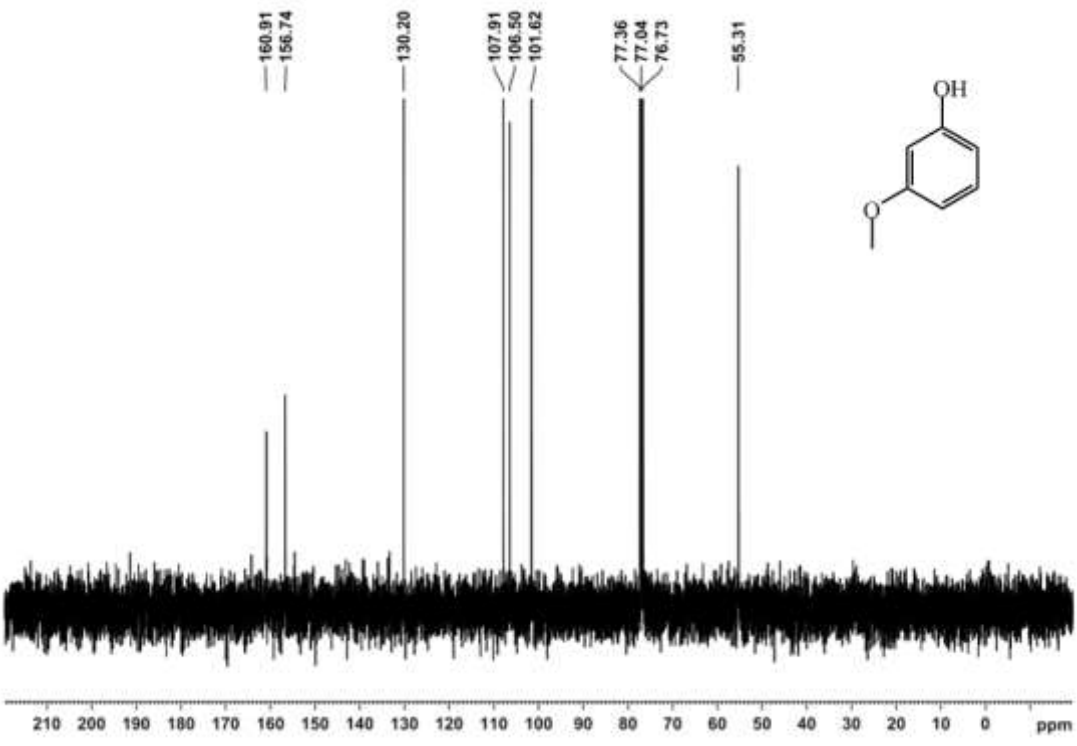
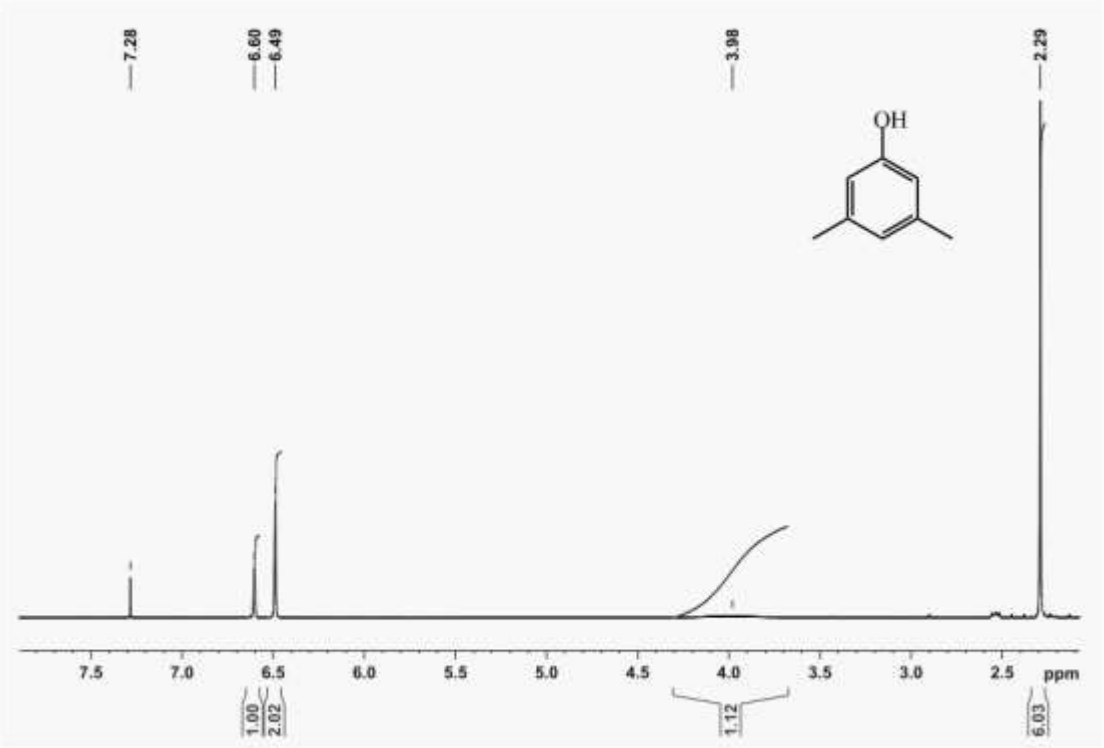
7.18
7.16
7.14
6.54
6.52
6.46
6.44
5.00
3.81
OH
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.00
1.00
1.96
0.96
3.10


160.91
156.74
130.20
107.91
106.50
101.62
77.36
77.04
76.73
55.31
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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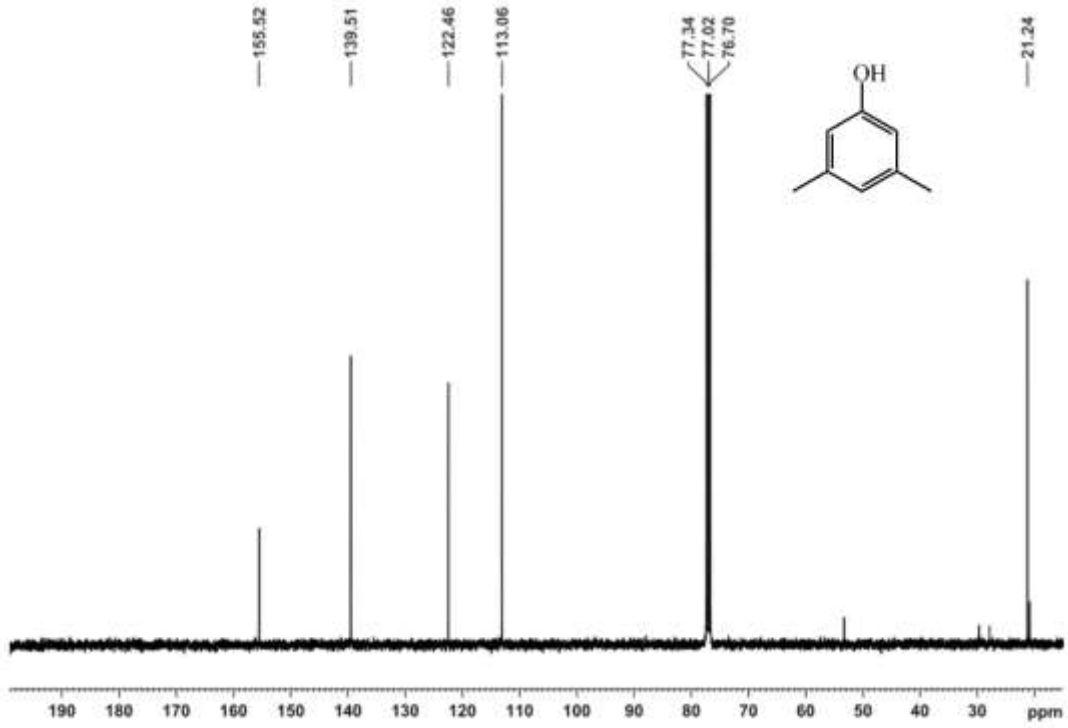
6.60
6.49
3.98
2.29
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.00
2.02
1.12
6.03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139.51
122.46
113.06
77.34
77.02
76.70
21.24
OH
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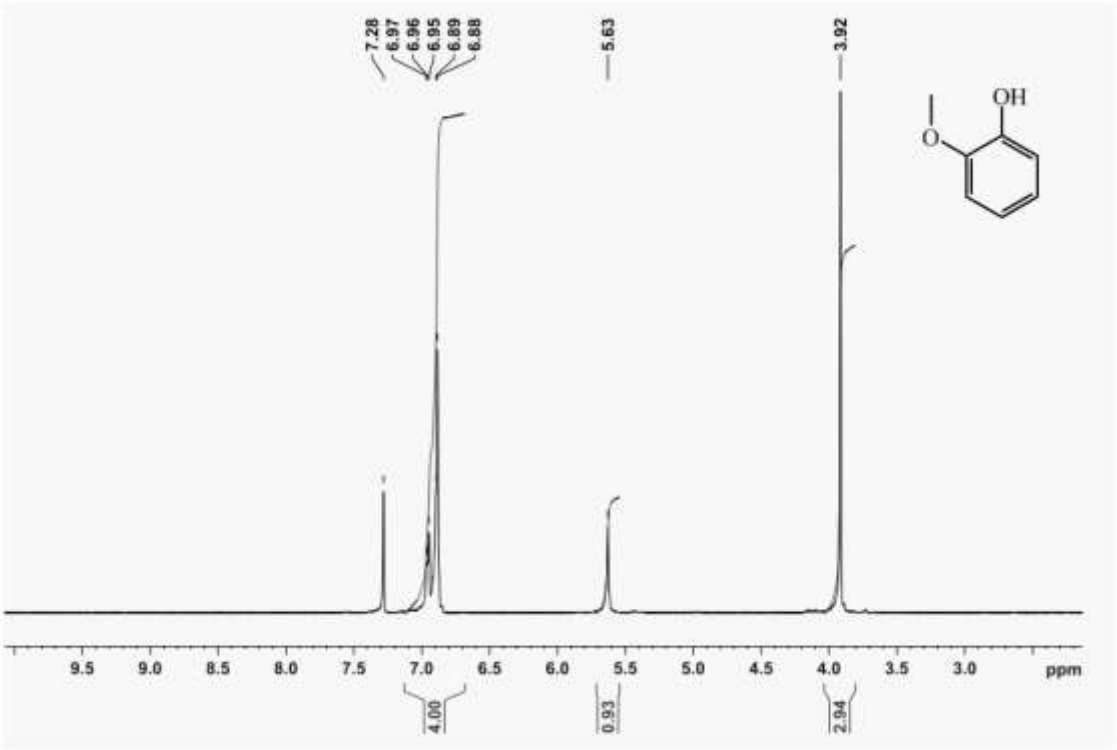
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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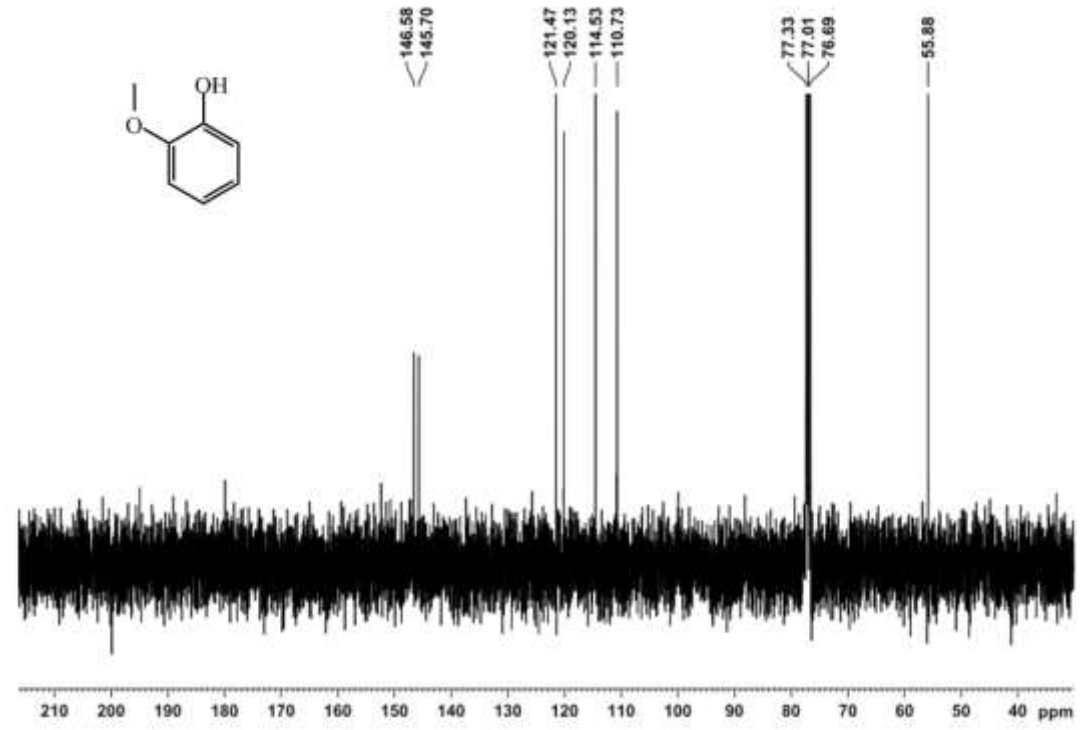
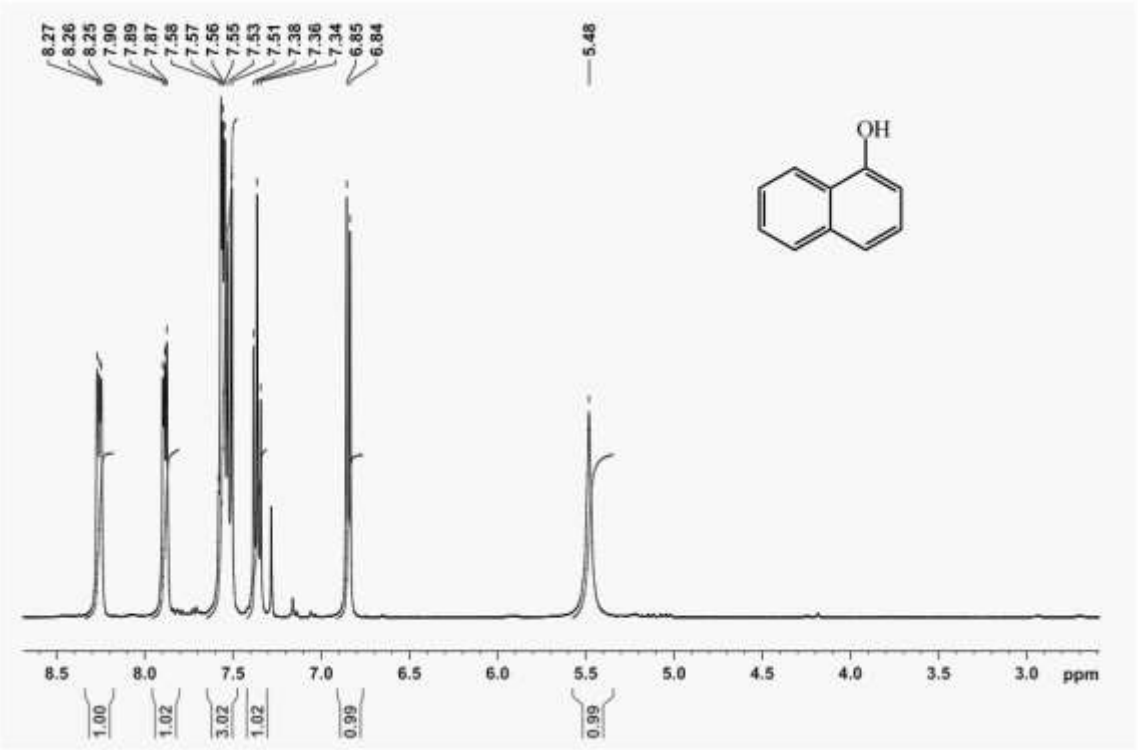
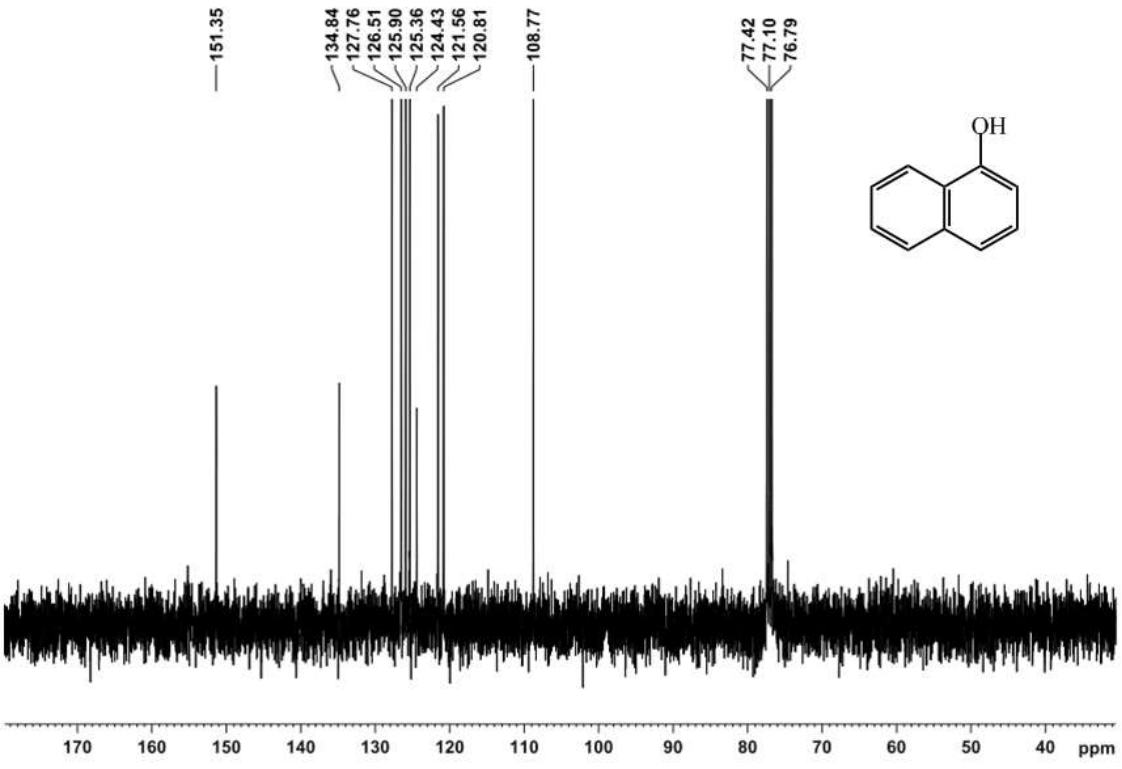
6.97
6.96
6.95
6.89
6.88
5.63
3.92
OH
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
4.00
0.93
2.94


146.58
145.70
121.47
120.13
114.53
110.73
77.33
77.01
76.69
55.88
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


8.27
8.26
8.25
7.90
7.89
7.87
7.58
7.57
7.56
7.55
7.53
7.51
7.38
7.36
7.34
6.85
6.84
5.48
OH
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.00
1.02
3.02
1.02
0.99
0.99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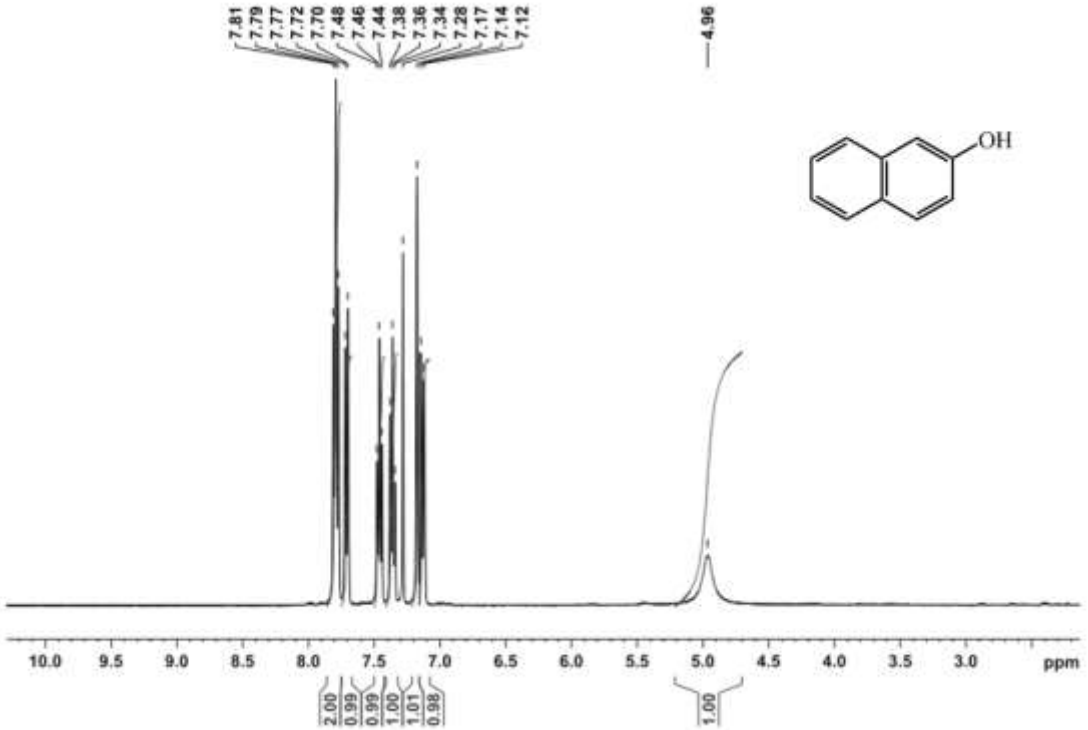
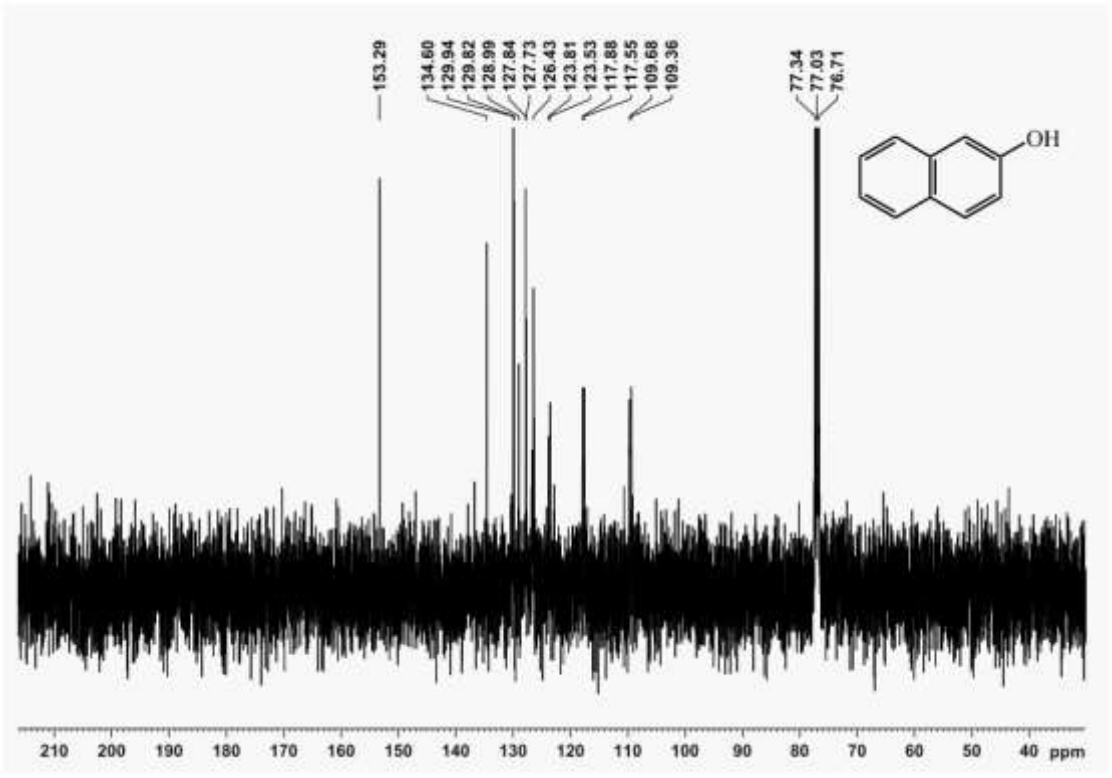
134.84
127.76
126.51
125.90
125.36
124.43
121.56
120.81
108.77
77.42
77.10
76.79
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


7.81
7.79
7.77
7.72
7.70
7.48
7.46
7.44
7.38
7.36
7.34
7.28
7.17
7.14
7.12
4.96
OH
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
ppm
2.00
0.99
0.99
1.00
1.01
0.98
1.00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134.60
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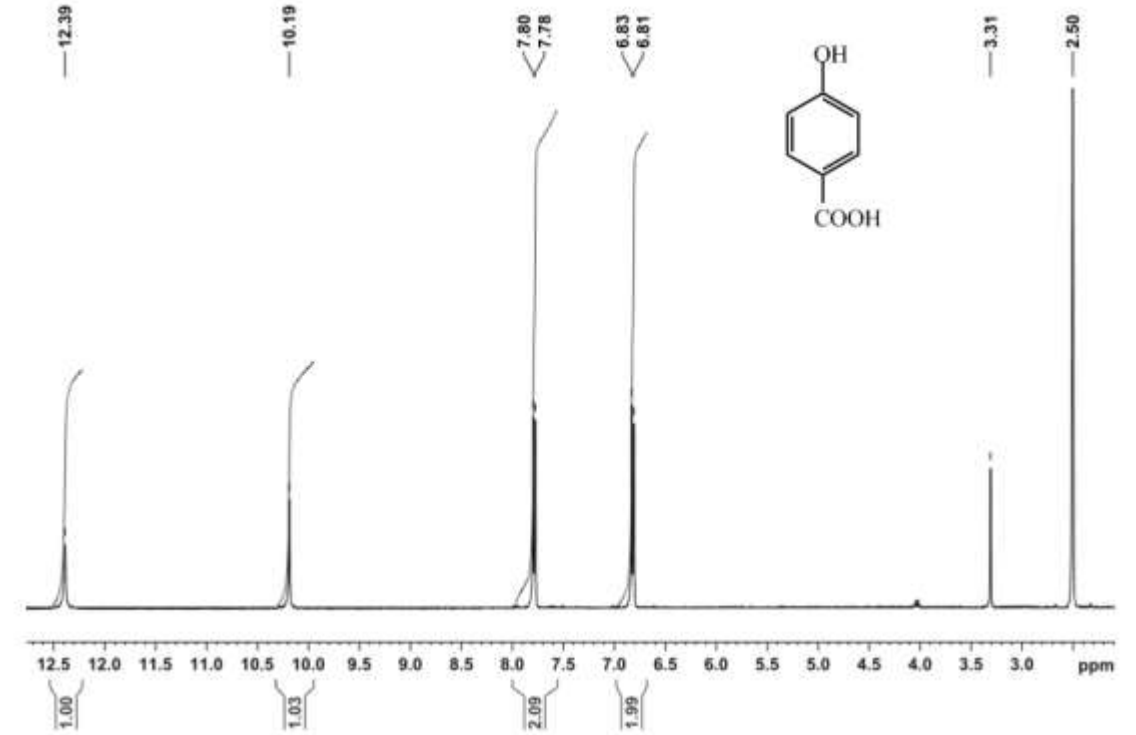
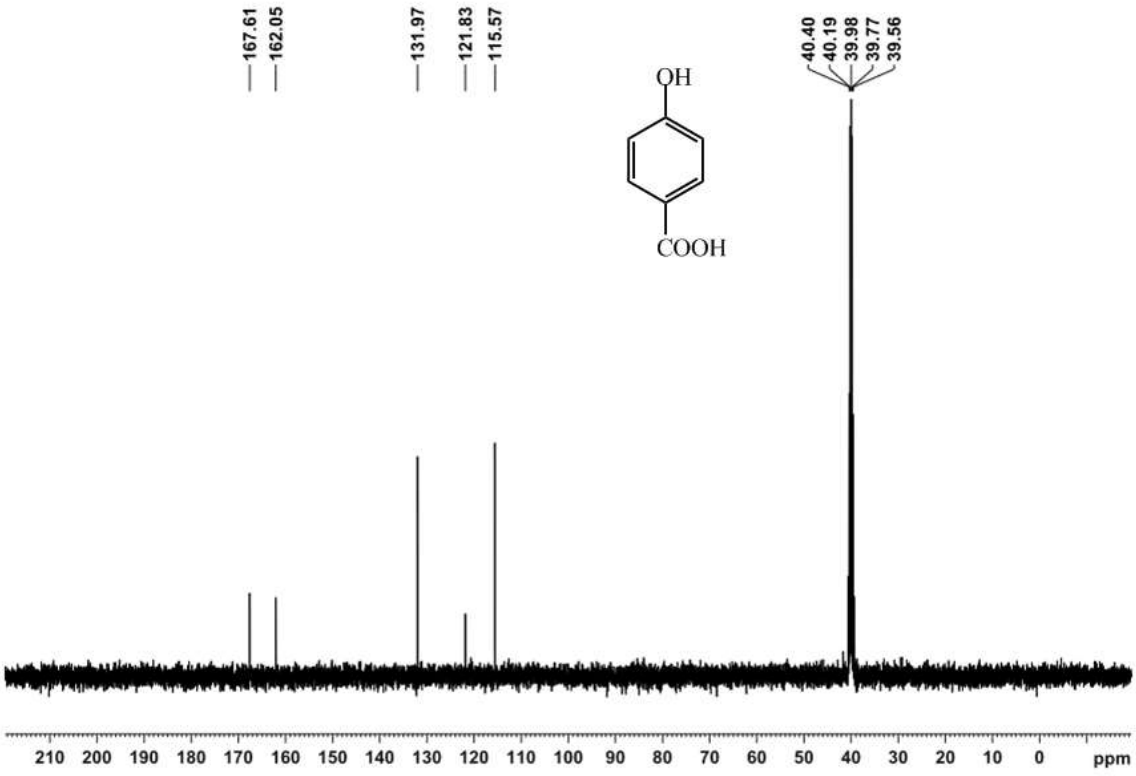
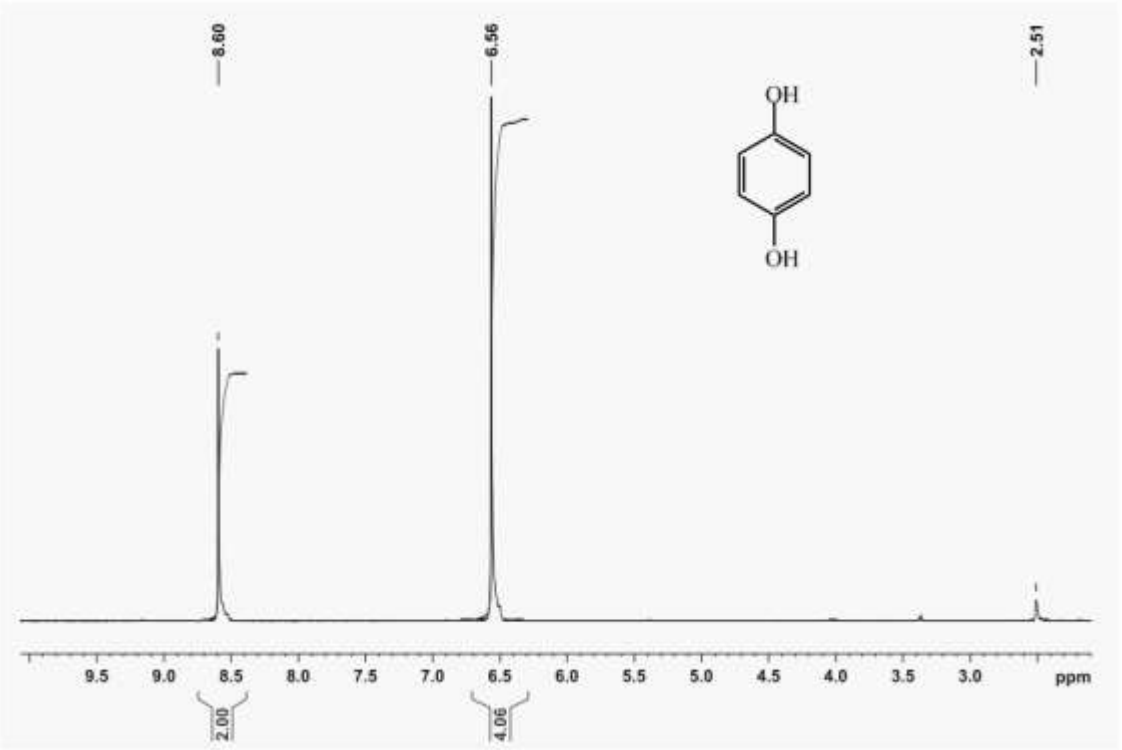
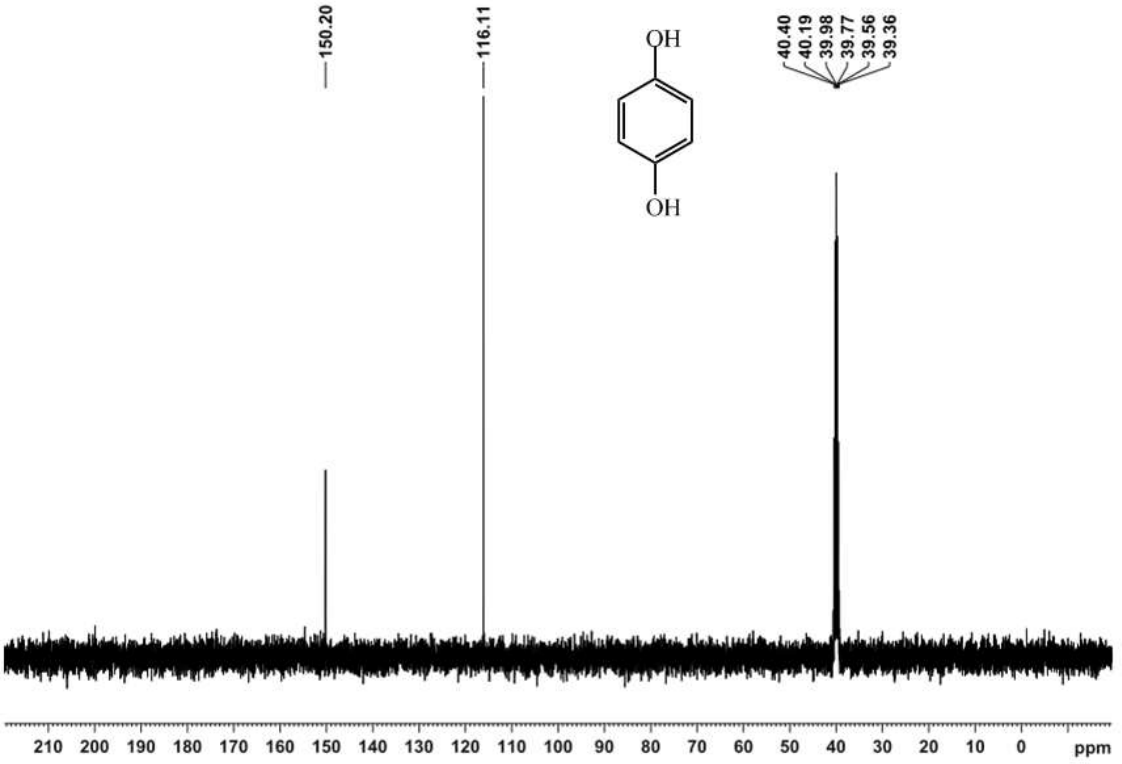
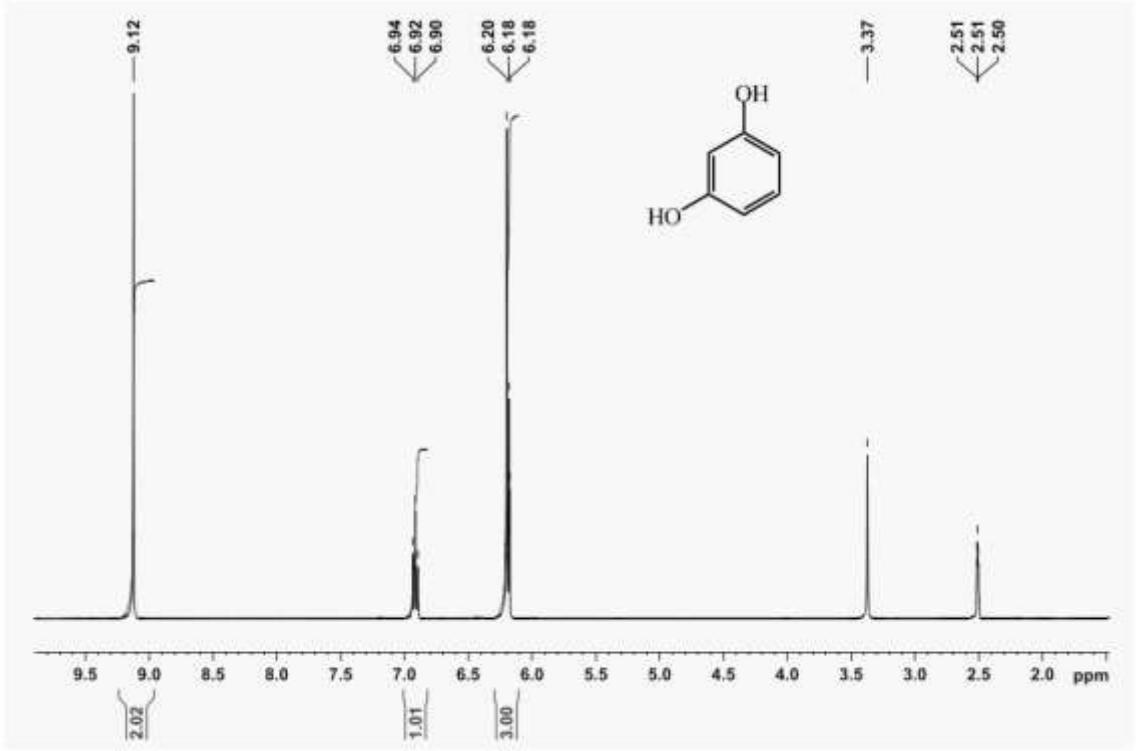
129.82
128.99
127.84
127.73
126.43
123.81
123.53
117.88
117.55
109.68
109.36
77.34
77.03
76.71
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

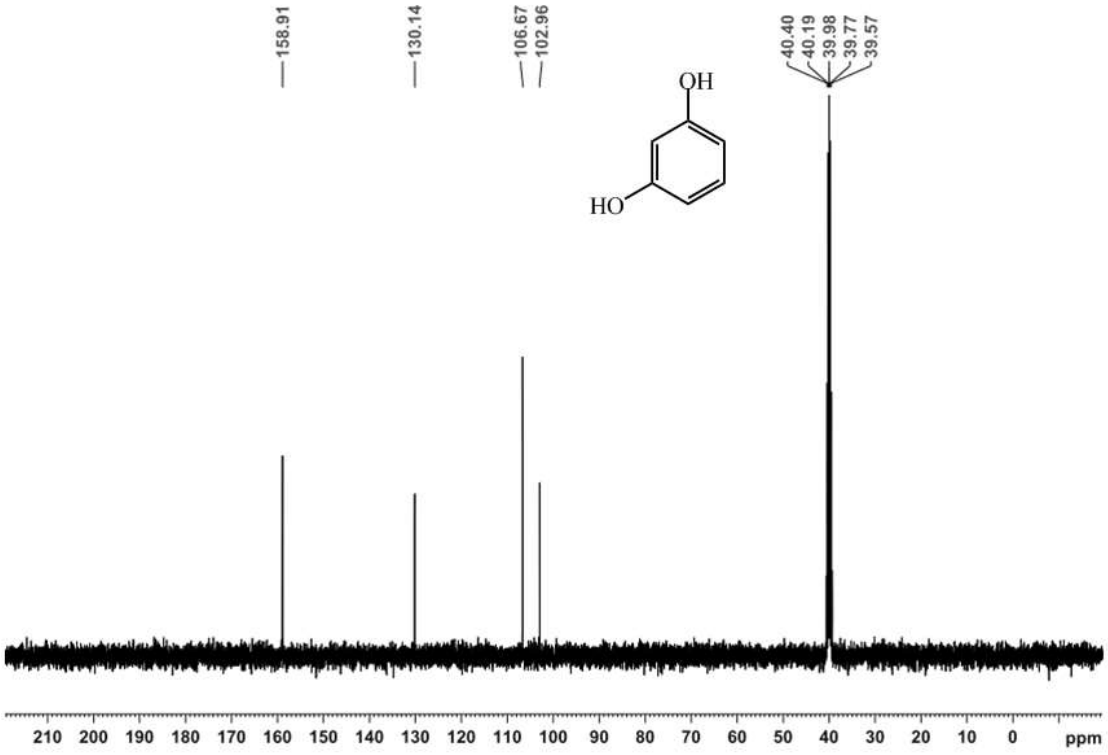

12.39
10.19
7.80
7.78
6.83
6.81
3.31
2.50
OH
COOH
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm
1.00
1.03
2.09
1.99

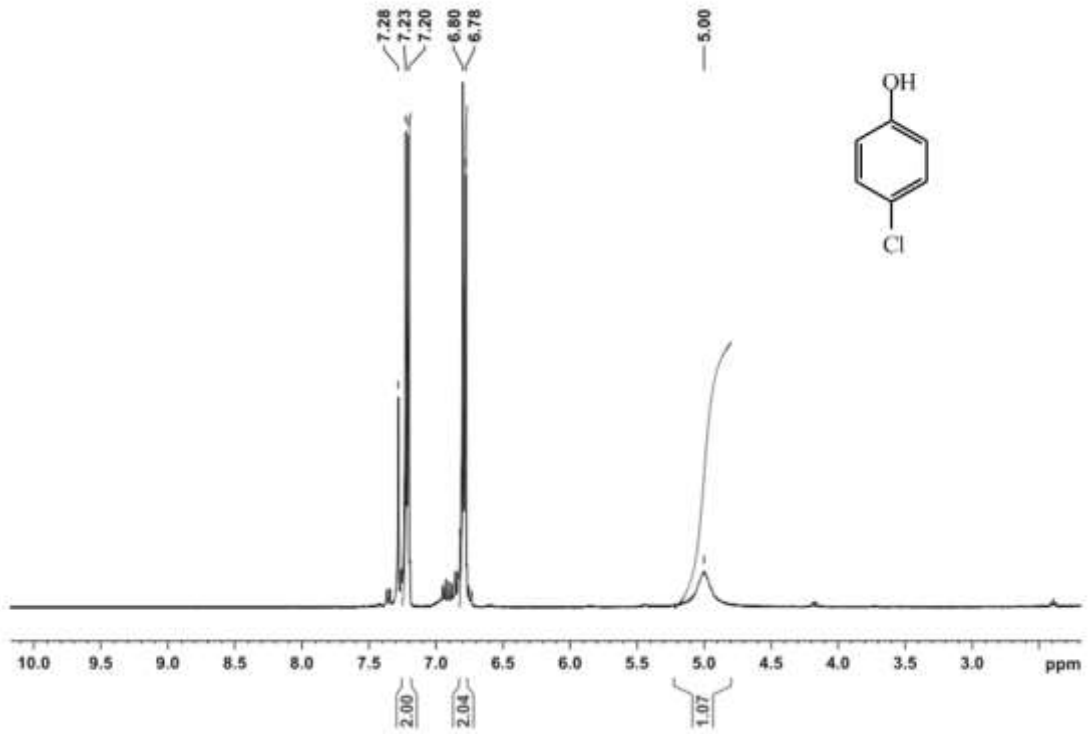

167.61
162.05
131.97
121.83
115.57
40.40
40.19
39.98
39.77
39.56
OH
COOH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.60
6.56
2.51
OH
OH
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
ppm
2.00
4.06


150.20
116.11
40.40
40.19
39.98
39.77
39.56
39.36
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.12
6.94
6.92
6.90
6.20
6.18
6.18
3.37
2.51
2.51
2.50
OH
HO
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 ppm
2.02
1.01
3.00


158.91
130.14
106.67
102.96
40.40
40.19
39.98
39.77
39.57
OH
HO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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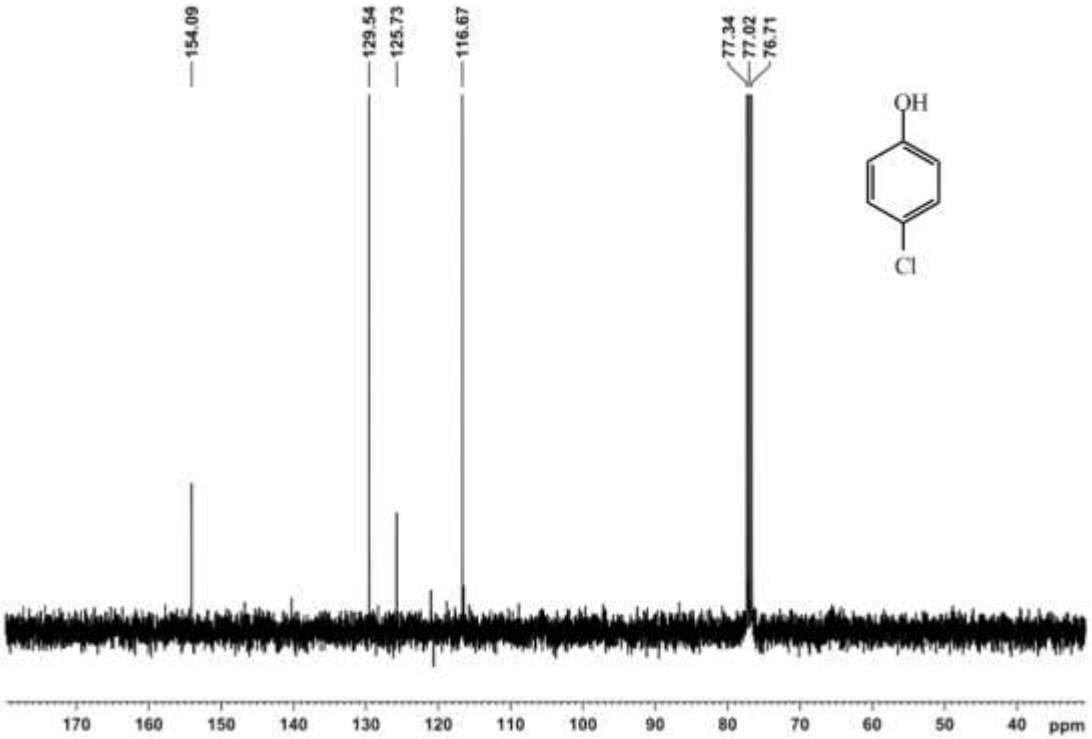
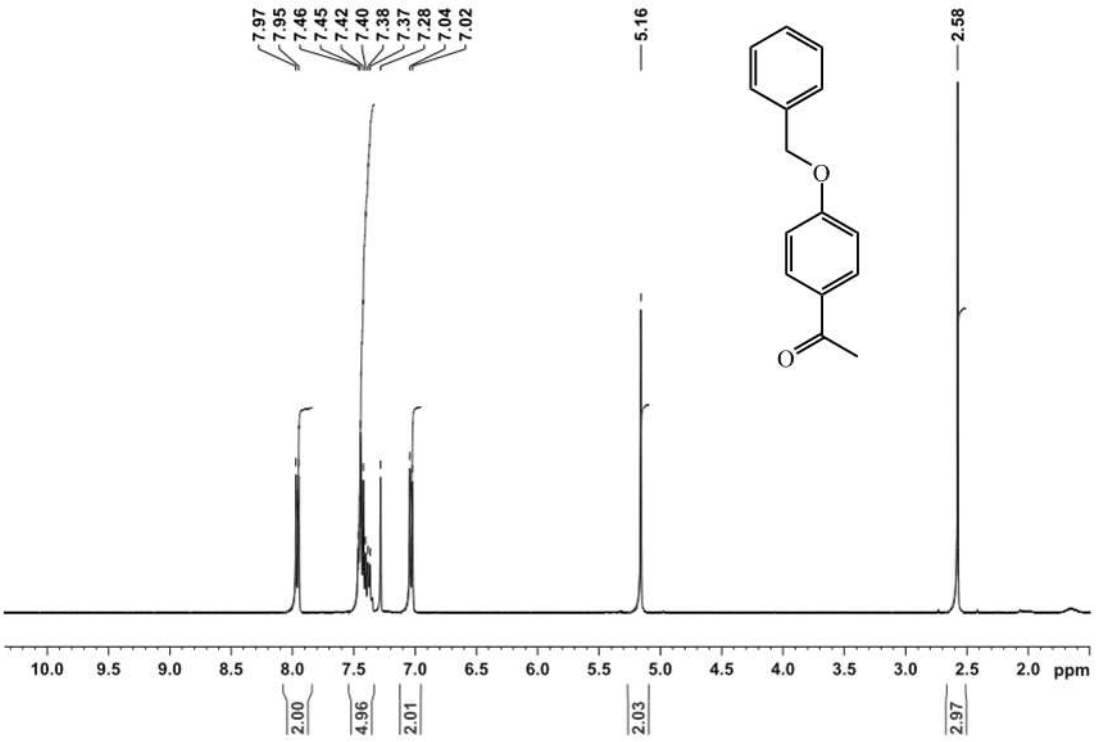
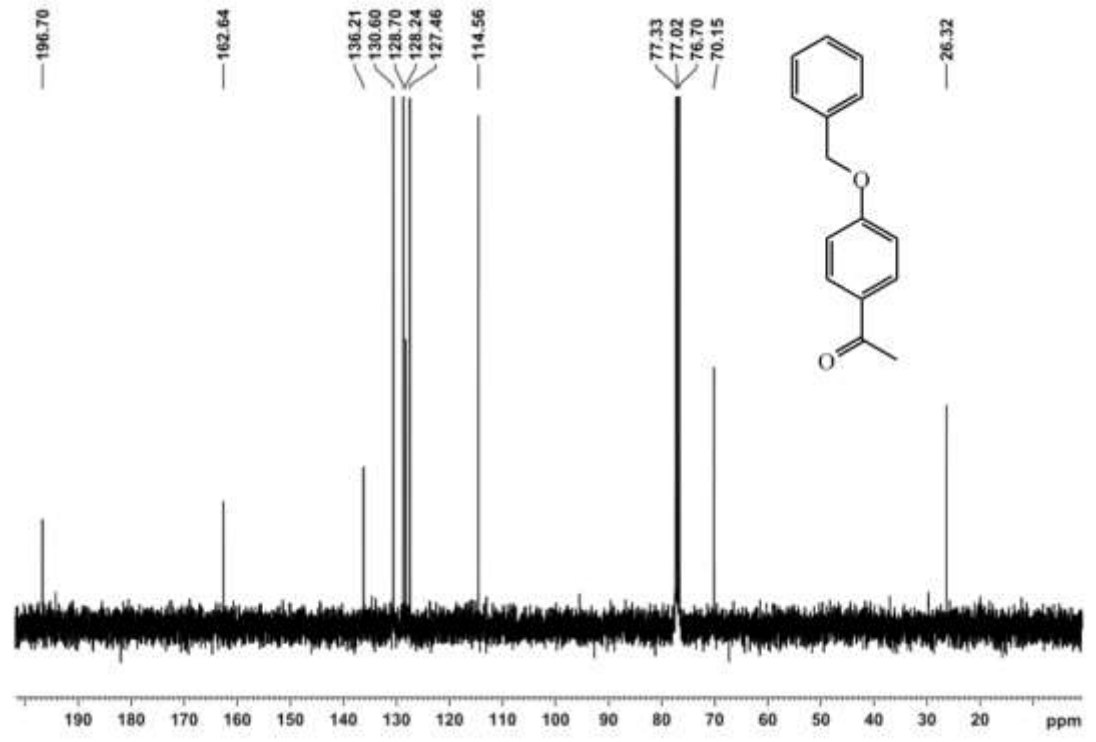
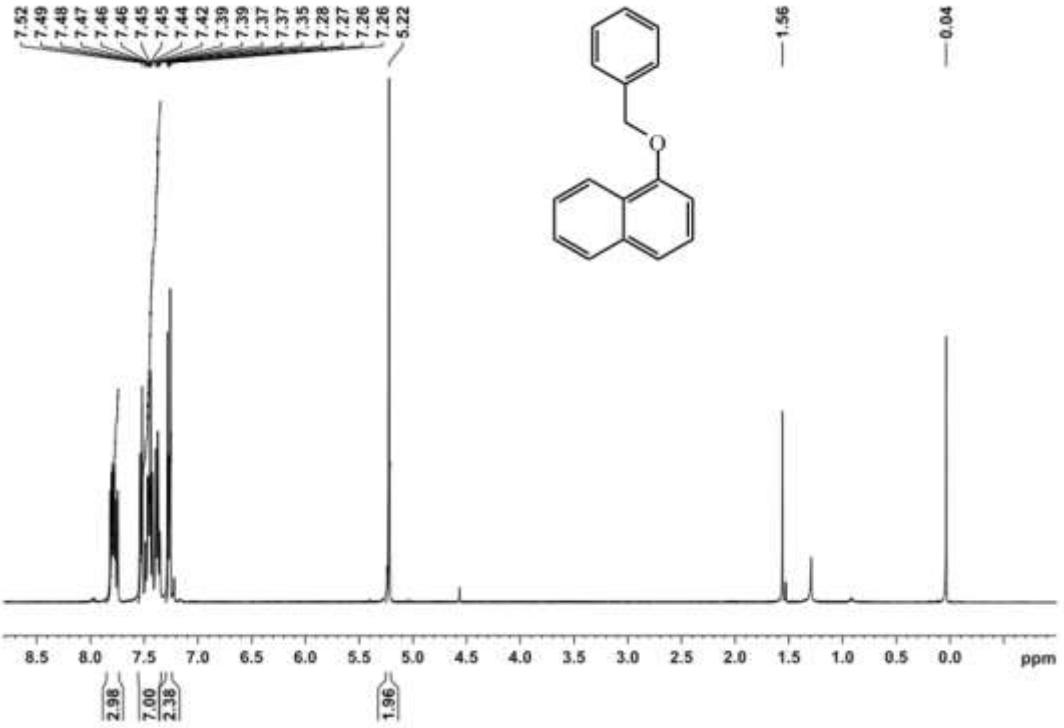
7.23
7.20
6.80
6.78
5.00
OH
Cl
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
2.00
2.04
1.07


154.09
129.54
125.73
116.67
77.34
77.02
76.71
OH
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


7.97
7.95
7.46
7.45
7.42
7.40
7.38
7.37
7.28
7.04
7.02
5.16
2.58
O
O
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 ppm
2.00
4.96
2.01
2.03
2.97


196.70
162.64
136.21
130.60
128.70
128.24
127.46
114.56
77.33
77.02
76.70
70.15
26.32
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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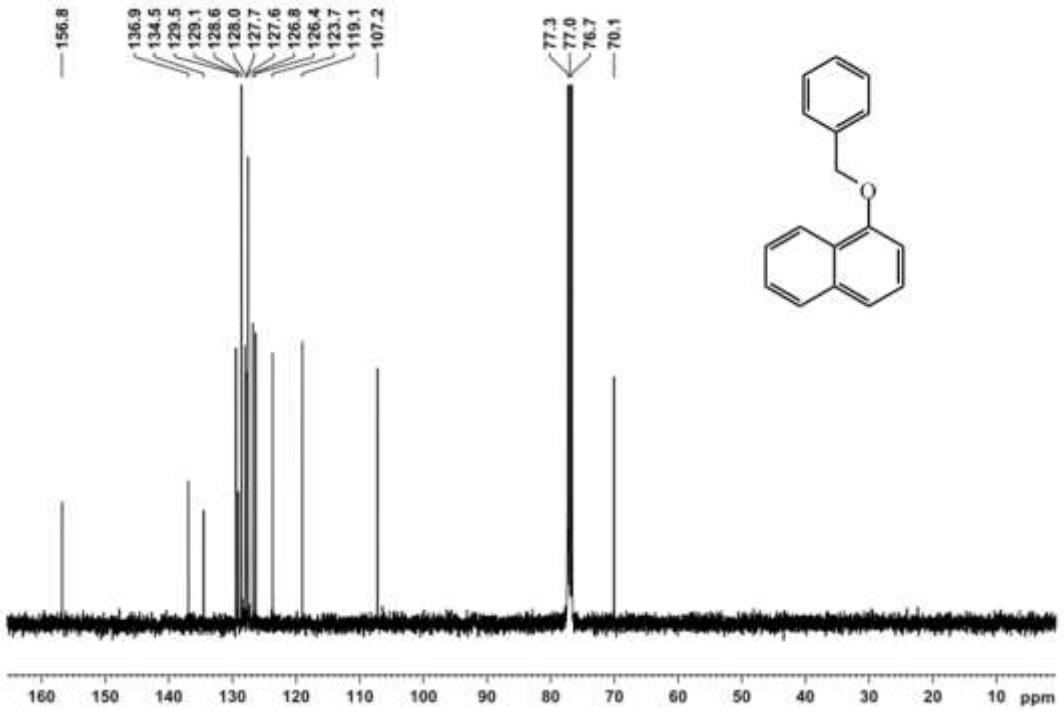
7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.42
7.39
7.39
7.37
7.37
7.35
7.28
7.27
7.26
7.26
5.22
1.56
0.04
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.98
7.00
2.38
1.96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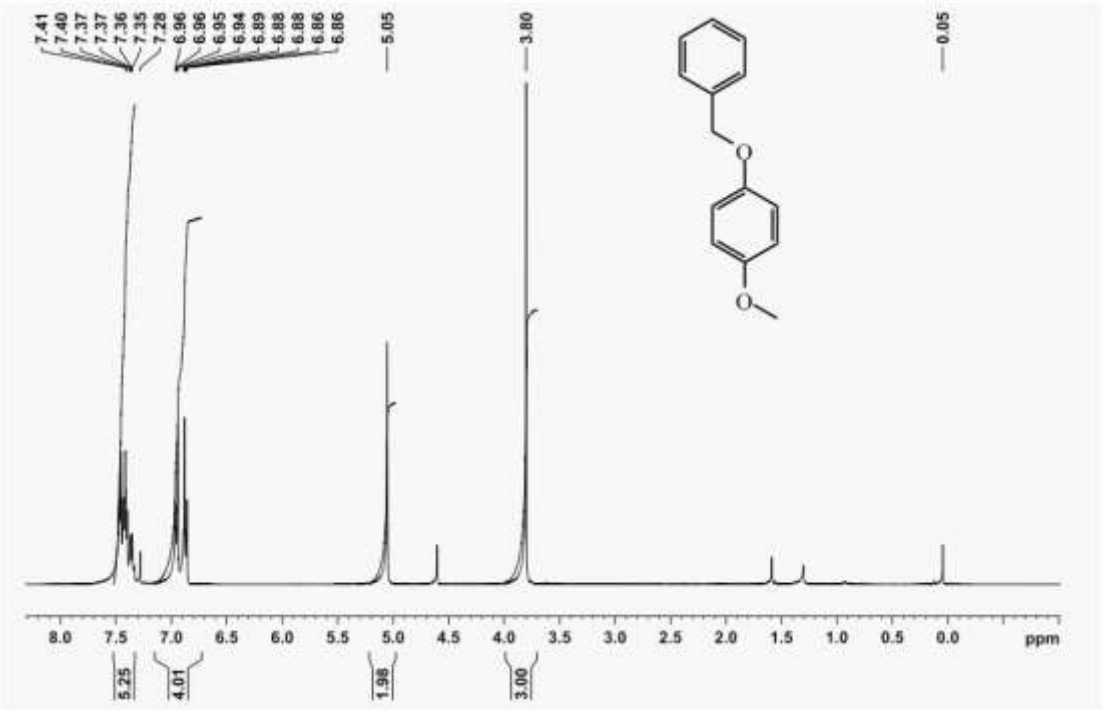
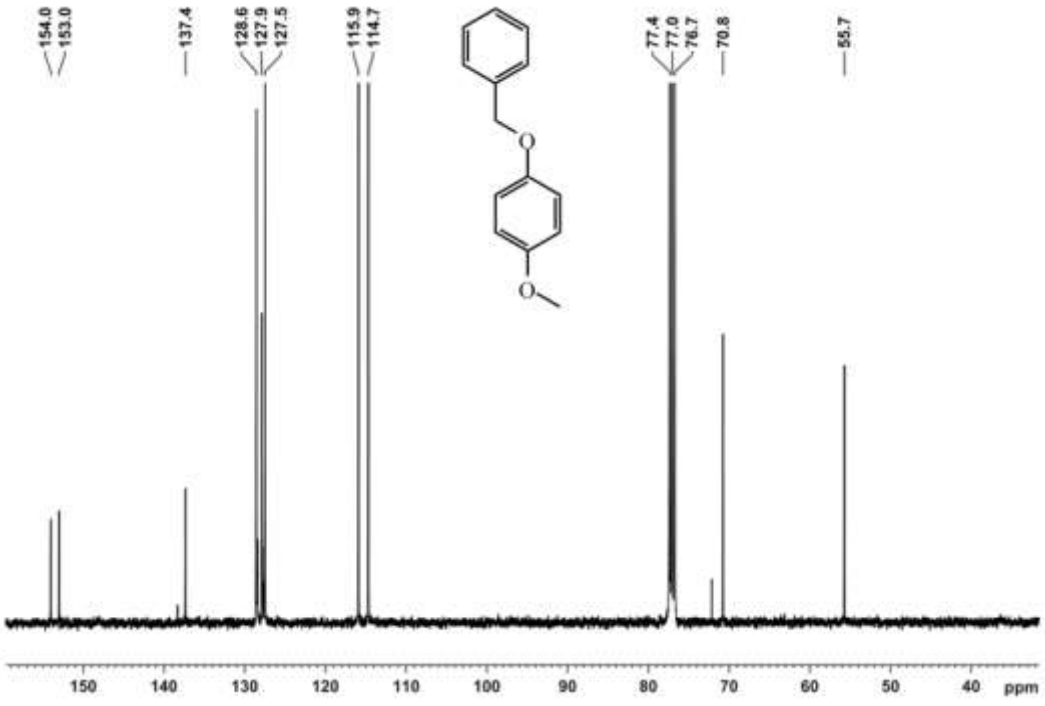
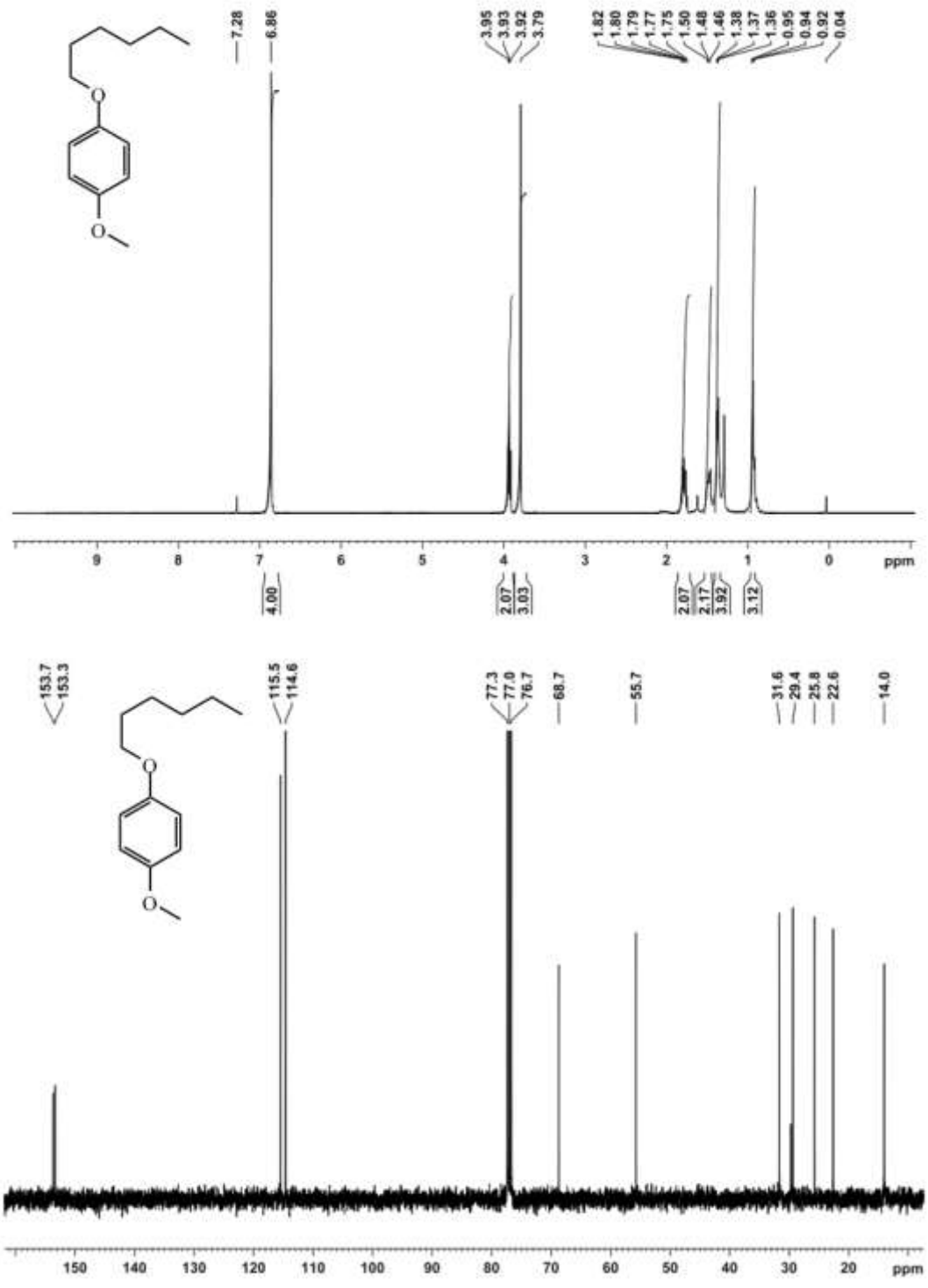
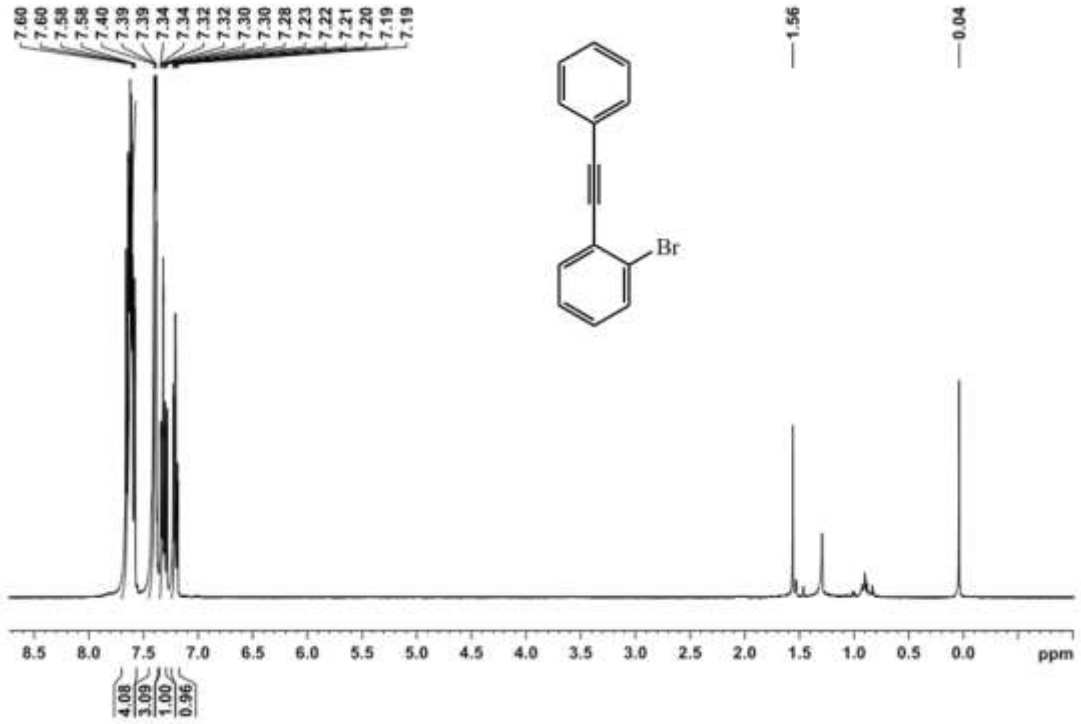
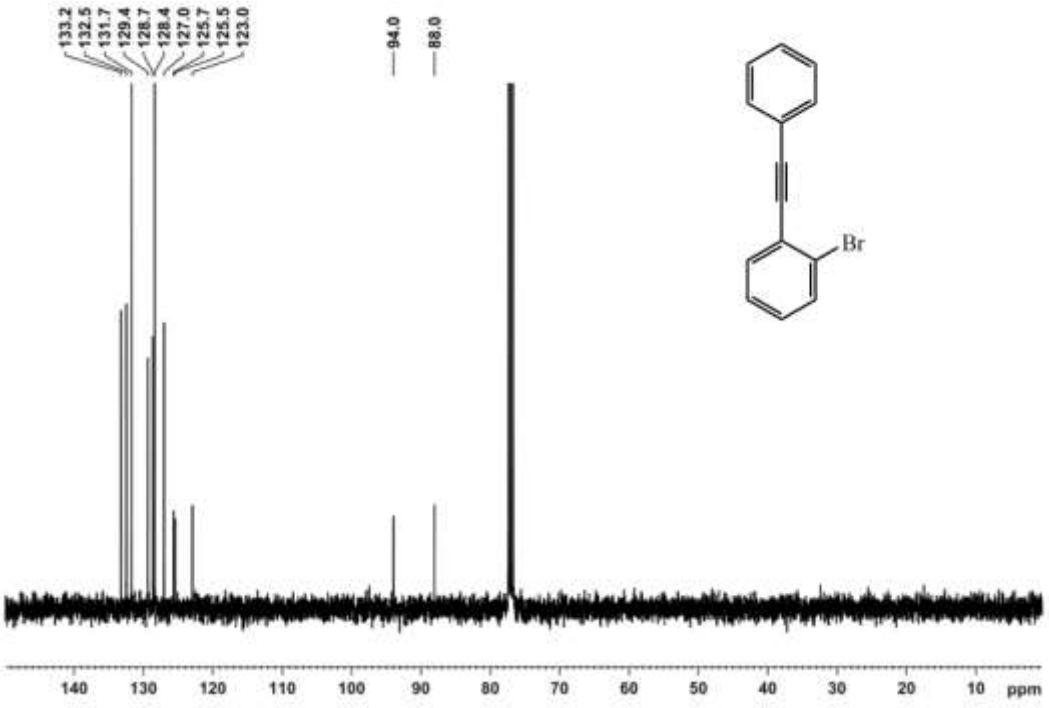
136.9
134.5
129.5
129.1
128.6
128.0
127.7
127.6
126.8
126.4
123.7
119.1
107.2
77.3
77.0
76.7
70.1
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

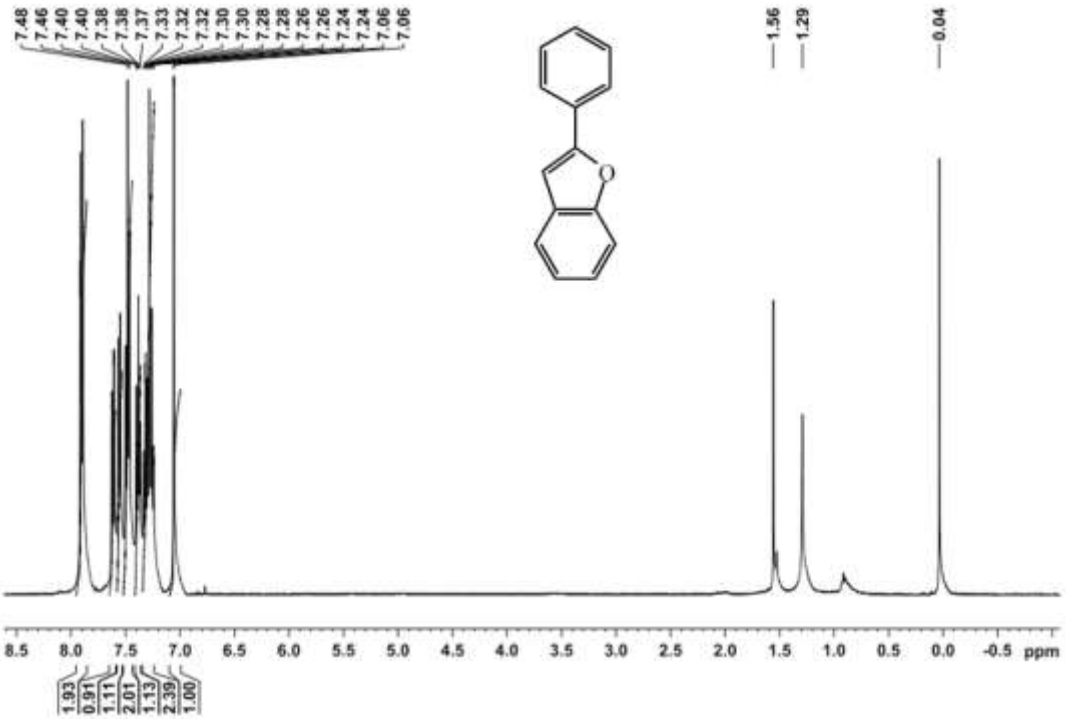

7.41
7.40
7.37
7.37
7.36
7.35
7.28
6.96
6.96
6.95
6.94
6.89
6.88
6.88
6.86
6.86
5.05
3.80
0.05
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.25
4.01
1.98
3.00

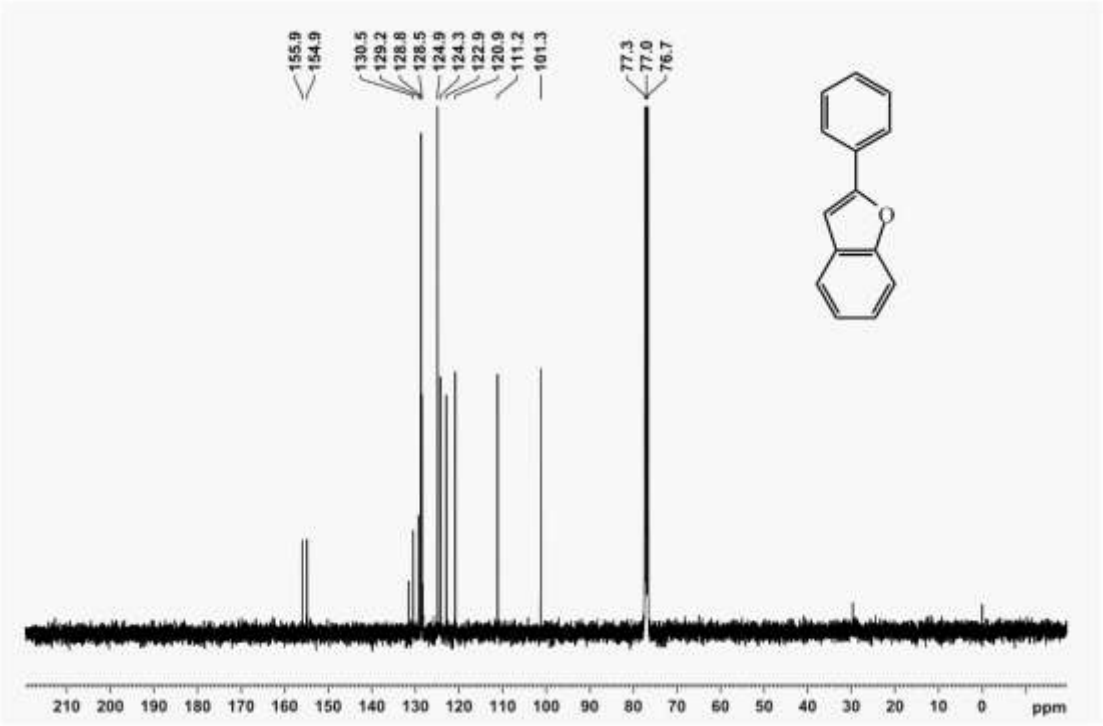

154.0
153.0
137.4
128.6
127.9
127.5
115.9
114.7
77.4
77.0
76.7
70.8
55.7
O
O
150
140
130
120
110
100
90
80
70
60
50
40
ppm


7.28
6.86
3.95
3.93
3.92
3.79
1.82
1.80
1.79
1.77
1.75
1.50
1.48
1.46
1.38
1.37
1.36
0.95
0.94
0.92
0.04
ppm
4.00
2.07
3.03
2.07
2.17
3.92
3.12
153.7
153.3
115.5
114.6
77.3
77.0
76.7
68.7
55.7
31.6
29.4
25.8
22.6
14.0
ppm


7.60
7.60
7.58
7.58
7.40
7.39
7.39
7.34
7.34
7.32
7.32
7.30
7.30
7.28
7.23
7.22
7.21
7.20
7.19
7.19
1.56
0.04
Br
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
ppm
4.08
3.09
1.00
0.96


133.2
132.5
131.7
129.4
128.7
128.4
127.0
125.7
125.5
123.0
94.0
88.0
Br
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.48
7.46
7.40
7.40
7.38
7.38
7.37
7.33
7.32
7.32
7.30
7.30
7.28
7.28
7.26
7.26
7.24
7.24
7.06
7.06
1.56
1.29
0.04
O
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 ppm
1.93
0.91
1.11
2.01
1.13
2.39
1.00


155.9
154.9
130.5
129.2
128.8
128.5
124.9
124.3
122.9
120.9
111.2
101.3
77.3
77.0
76.7
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

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