Acetylation of anilines, amines, and alcohols using 5%MoO_3–SiO_2 and 5%WO_3–ZrO_2 as mesoporous acid catalysts

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Supplementary information

1. GC-FID Calculations

Conversion percentage $= \left[1 - \frac{A_t}{I_t} \Big/ \frac{A_0}{I_o}\right] \times 100$ Equation S1.

Selectivity percentage $= \frac{Product_{\,a}}{product_{\,a} + product_{\,b} + product_{\,\ldots}} \times 100$ Equation S2.

Yield percentage $= \left[\frac{conversion}{100}\right] \times \left[\frac{selectivity}{100}\right] \times 100$ Equation S3.

Where A_0 and A_t are areas of the substrate at 0 min and at a given time, respectively, and I_0 and I_t are areas of internal standard at 0 min and at a given time, respectively.

2. NH_3-TPD profiles of MMOs

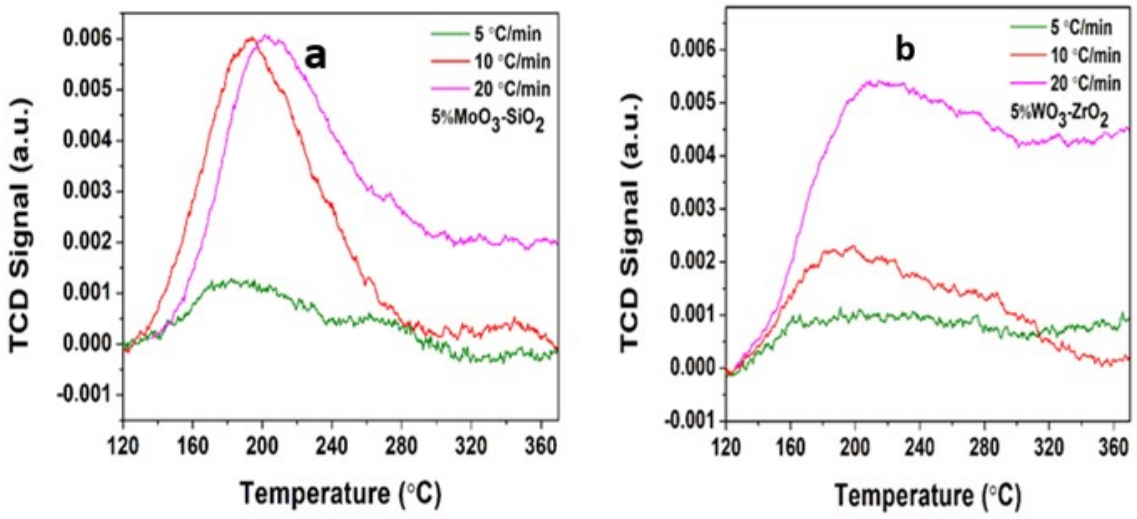
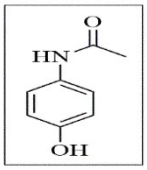


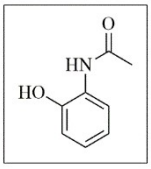
Figure S1: NH_3-TPD profiles of (a) 5%MoO_3-SiO_2, and (b) 5%WO_3-ZrO_2.

3. ^{1}H NMR and ^{13}C NMR of Acetylation products



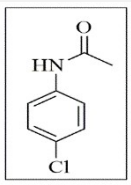
***N*-(4-Hydroxyphenyl)acetamide (Paracetamol)**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.37 (2H, d, J = 8.4.0 Hz), 6.72 (2H, d, J = 8.5 Hz), 2.00 (3H, s), 1.91 (1H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.28, 153.72, 131.36, 121.54, 115.51, 24.07.



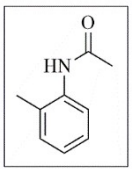
***N*-(2-Hydroxyphenyl)acetamide**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.91 (1H, s), 7.37 (1H, t, J = 8.0 Hz), 6.84 – 6.57 (3H, m), 1.98 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 169.76, 147.71, 126.42, 125.28, 121.60, 119.55, 117.37, 23.63.



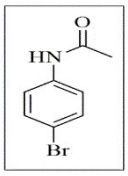
***N*-(4-Chlorophenyl)acetamide**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.29 (2H, d, J = 8.2 Hz), 6.94 (2H, d, J = 8.5 Hz), 1.83 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.81, 137.62, 128.30, 127.71, 120.79, 24.00.



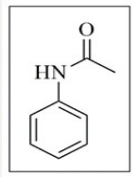
***N*-(o-Tolyl)acetamide**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.73 (1H, d, J = 8.0 Hz), 7.29 – 7.09 (6H, m), 2.26 (3H, s), 2.20 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.48, 135.63, 130.47, 129.60, 129.55, 126.69, 125.40, 123.65, 24.17, 17.77.



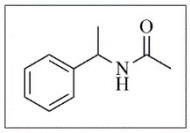
***N*-(4-Bromophenyl)acetamide**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.27 (1H, s), 7.33 (2H, d, J = 8.0 Hz), 7.17 (2H, d, J = 8.4 Hz), 1.93 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.87, 138.11, 131.35, 121.22, 115.54, 24.13.



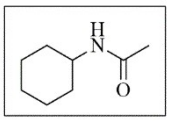
***N*-Phenylacetamide**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.48 (1H, s), 7.56 (2H, d, J = 8.0 Hz), 7.31 (2H, t, J = 9.2 Hz), 7.12 (2H, t, J = 9.4 Hz), 2.15 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 169.19, 138.15, 128.85, 124.27, 120.28, 24.31.



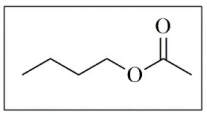
***N*-(1-Phenylethyl)acetamide**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.32 – 7.24 (5H, m), 6.79 (1H, s), 5.10-5.05 (1H, m), 1.96 (3H, s), 1.45 (3H, d, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 175.83, 170.47, 143.07, 128.57, 127.28, 126.15, 49.02, 22.89, 21.68, 20.83.



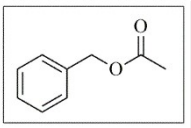
***N*-Cyclohexylacetamine**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.41 (1H, s), 3.49 (1H, s), 1.73 – 0.94 (12H, m) 1.96 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 169.10, 47.98, 32.85, 25.38, 24.78, 23.10.



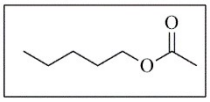
Butyl acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.61 (2H, t, *J* = 9.0 Hz), 2.00 (3H, s), 1.53 – 1.47 (1H, m), 1.36 – 1.28 (1H, m), 0.89 (3H, t, *J* = 9.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 176.46, 62.27, 34.28, 20.59, 18.75, 13.64.



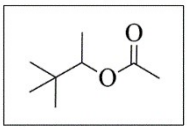
Benzyl acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.39 – 7.31 (5H, m), 5.65 (2H, s), 2.07 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 176.37, 140.59, 128.49, 127.58, 127.08, 64.90, 20.72.



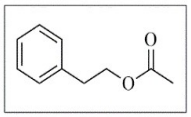
Pentyl Acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.02 (3H, s), 1.45 – 1.22 (5H, m), 1.14 (3H, d, *J* = 8.5 Hz), 0.89 (3H, t, *J* = 9.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 175.80, 67.94, 41.11, 22.89, 18.78, 13.90.



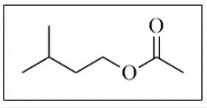
3,3-Dimethylbutan-2-yl acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.45 – 3.42 (1H, m), 1.99 (3H, s), 1.06 (3H, d, *J* = 8.5 Hz), 0.82 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 175.74, 75.66, 34.68, 25.26, 20.50, 17.37.



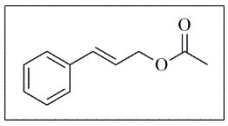
2-Phenylethyl acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.36 – 7.26 (5H, m), 3.88 (2H, t, *J* = 9.2 Hz), 2.91 (2H, t, *J* = 9.5 Hz), 2.08 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 175.88, 138.62,129.02, 128.47, 126.34, 63.42, 38.94, 20.62.



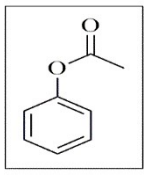
***iso*-Butyl acetate**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.33 (1H, d, *J* = 8.1 Hz), 3.88 (2H, t, *J* = 8.5 Hz), 1.98 (3H, s), 1.72-1.64 (1H, m), 0.82 (3H, d, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 176.31, 69.13, 30.30, 20.39, 18.58.



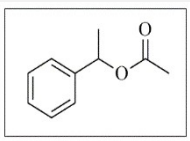
Cinnamyl acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.33 (1H, d, *J* = 8.4 Hz), 7.37 – 7.25 (5H, m), 4.33 (1H, d, *J* = 8.2 Hz), 3.86 (1H, t, *J* = 9.5 Hz), 2.97 – 2.90 (2H, m), 2.01(3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 129.08, 128.93, 128.57, 128.46, 126.62, 126.28, 65.02, 63.42, 39.29, 35.08, 20.73.



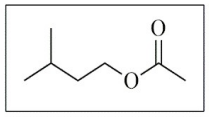
Phenyl acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.28 (2H, t, *J* = 9.2 Hz), 6.97 (1H, t, *J* = 9.4 Hz), 6.90 (2H, d, *J* = 7.5 Hz), 2.14 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 177.43, 155.57, 129.67, 120.68, 115.43, 20.74.



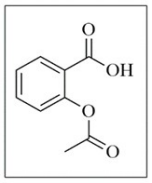
1-Phenyethyl acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.37 – 7.28 (5H, m), 4.90 – 4.86 (1H, q, *J* = 7.2 Hz), 2.05 (3H, s), 1.50 (3H, d, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 176.05, 145.59, 128.42, 127.38, 125.46, 70.33, 24.92, 20.66.



***iso*-Pentyl acetate**

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.68 (2H, t, *J* = 7.5 Hz), 2.07 (3H, s), 1.73 – 1.66 (1H, m), 1.48 – 1.44 (2H, q), 0.91 (6H, d, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 176.19, 61.13, 41.42, 24.65, 22.51, 20.67.

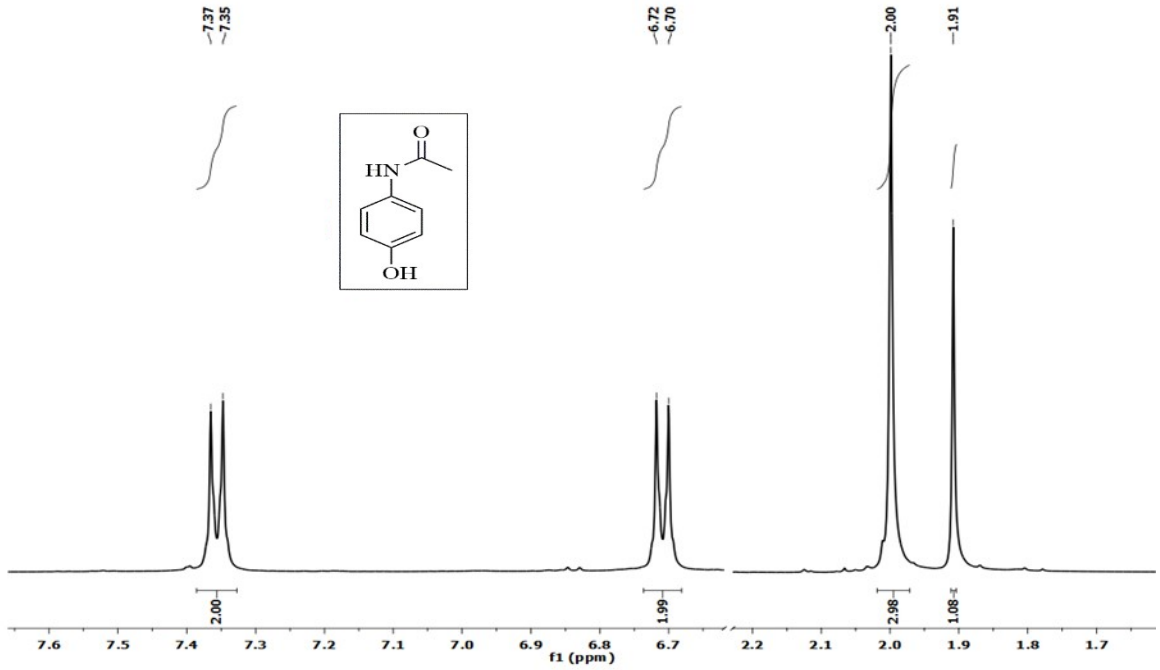


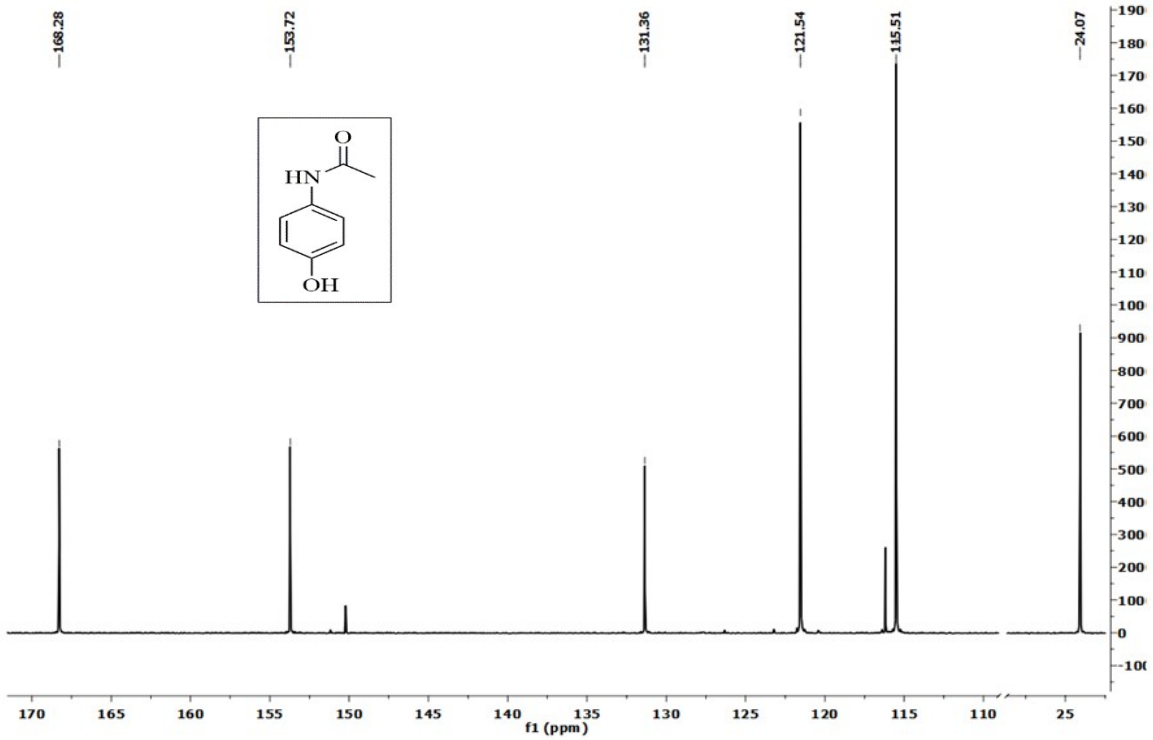
2-Acetoxybenzoic acid (Aspirin)

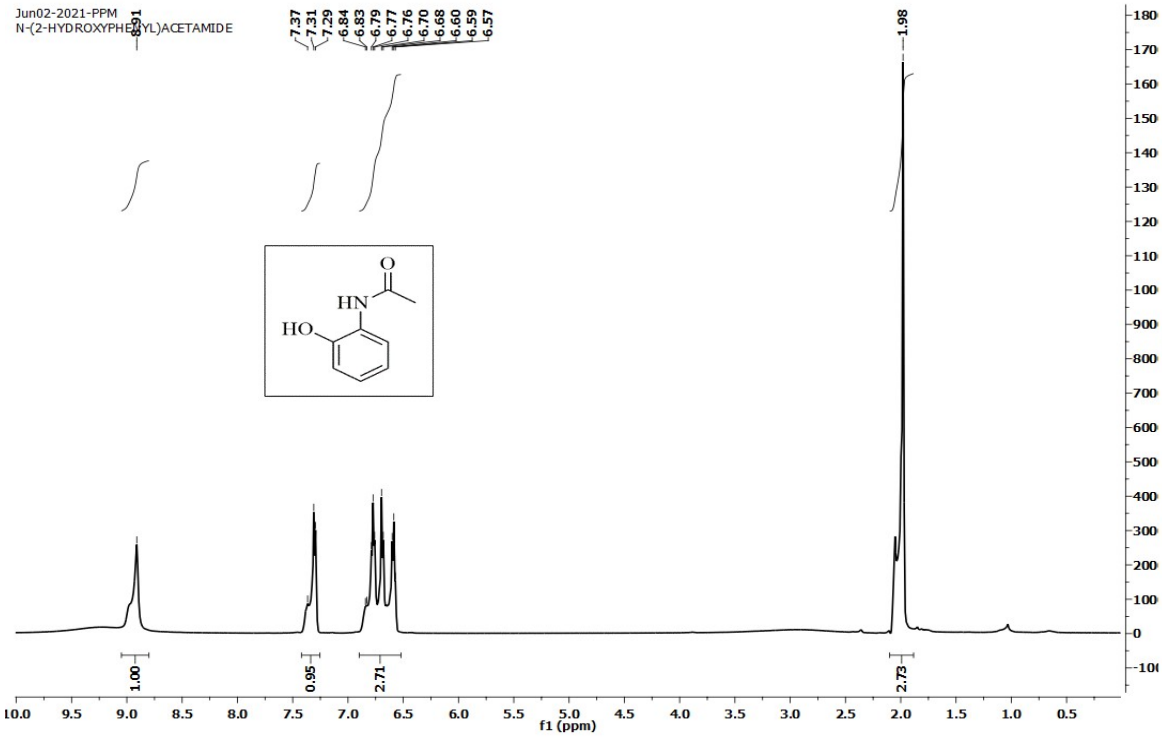
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.77 – 7.75 (2H, m), 7.45 (2H, t, *J* = 10.0 Hz), 6.30-6.87 (3H, m), 1.89 (1H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 172.46, 161.74, 135.84, 130.67, 119.38, 117.43, 113.33.

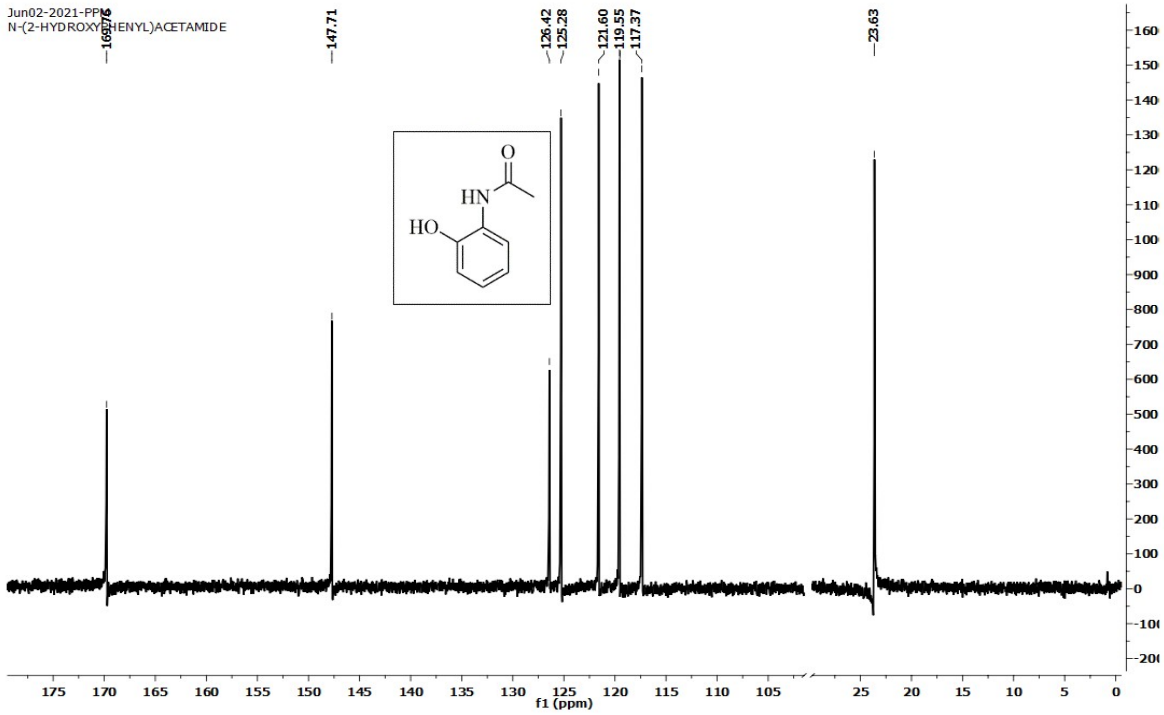
Figure S2. Acetylation products.

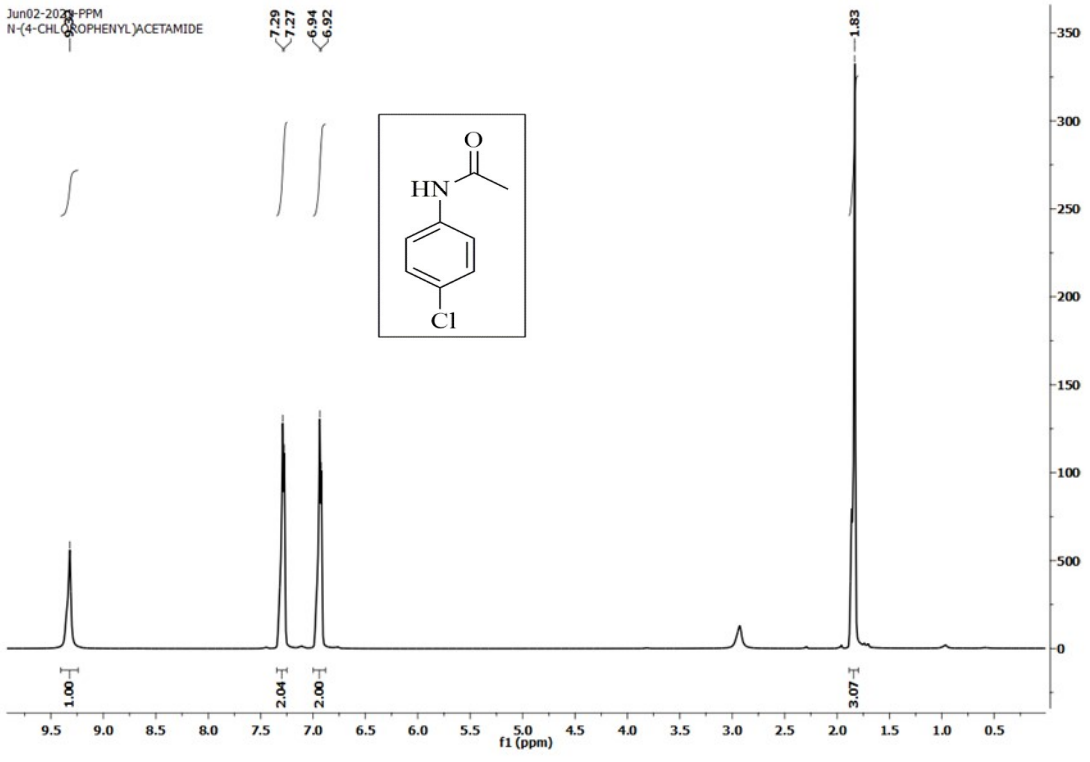
4. ^{1}H NMR and ^{13}C NMR Spectra




168.28
153.72
131.36
121.54
115.51
24.07
HN
O
OH
f1 (ppm)


Jun02-2021-PPM
N-(2-HYDROXYPHENYL)ACETAMIDE
8.91
7.37
7.31
7.29
6.84
6.83
6.79
6.77
6.76
6.70
6.68
6.60
6.59
6.57
1.98
HN
O
HO
1.00
0.95
2.71
2.73
f1 (ppm)


Jun02-2021-PPM
N-(2-HYDROXYPHENYL)ACETAMIDE
169.76
147.71
126.42
125.28
121.60
119.55
117.37
23.63
O
HN
HO
f1 (ppm)


Jun02-2021-PPM
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6.92
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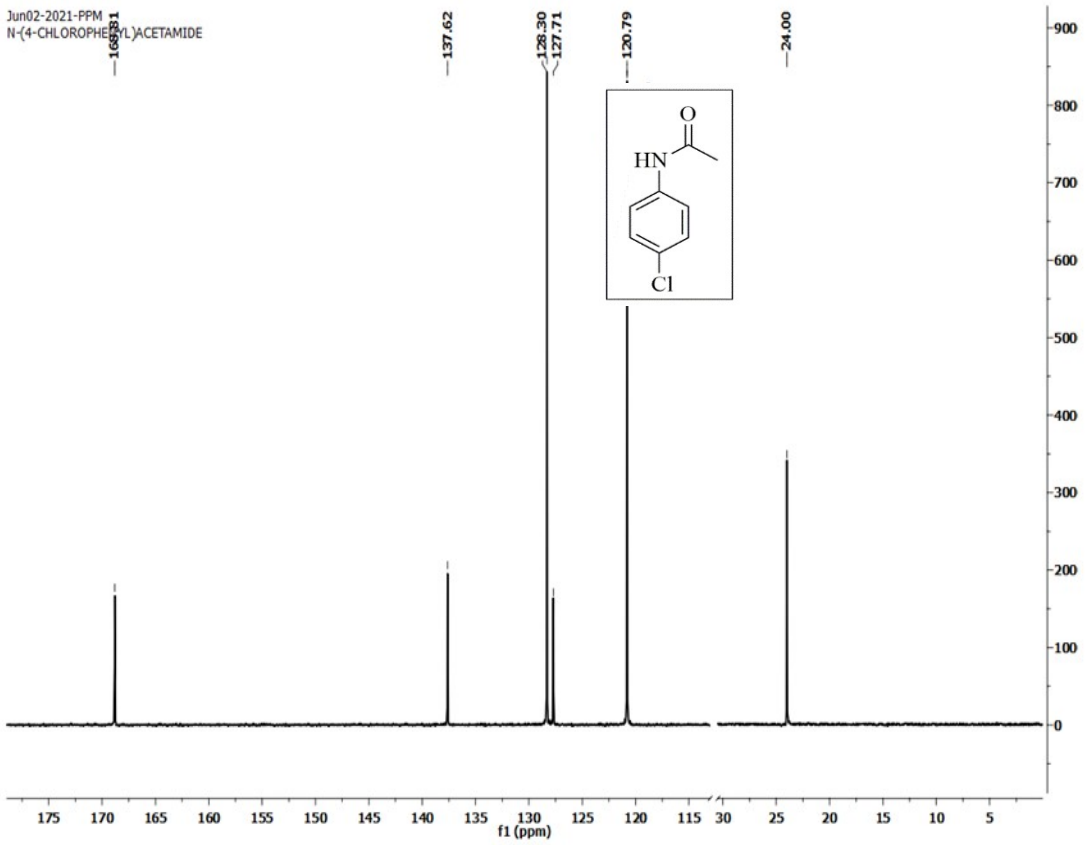
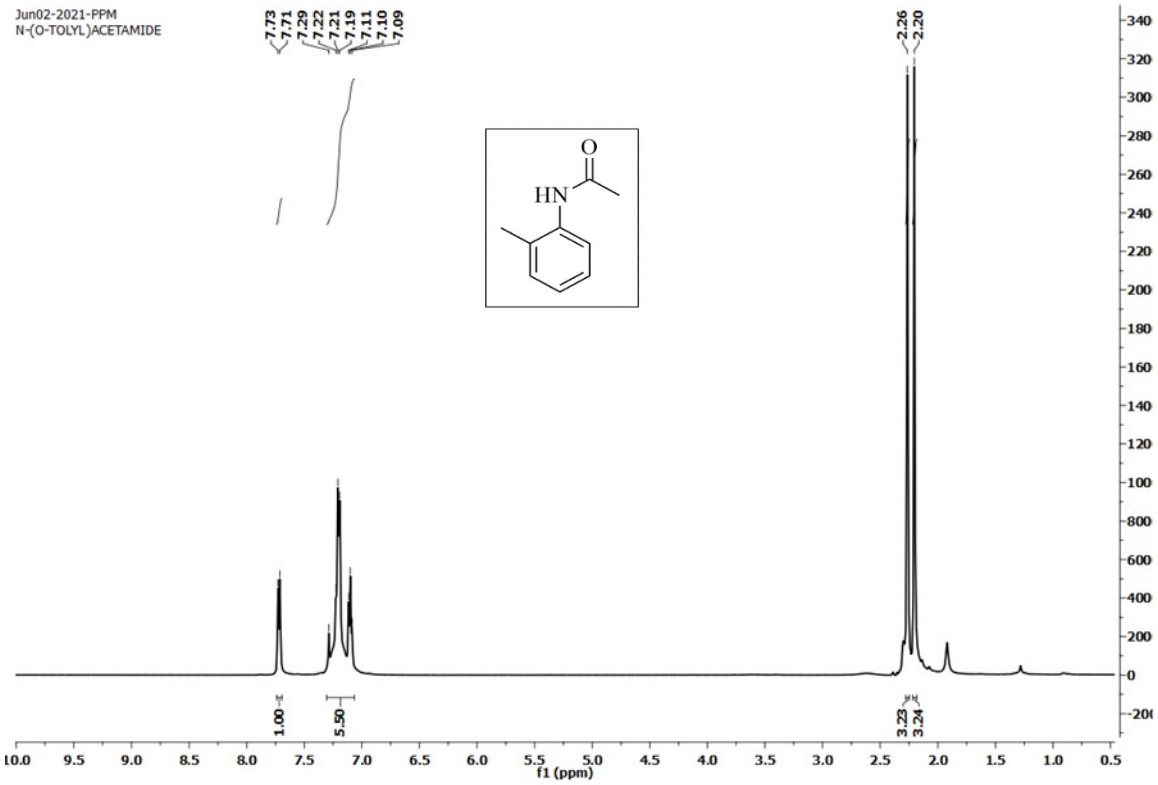
O
HN
Cl
1.00
2.04
2.00
3.07
f1 (ppm)


Jun02-2021-PPM
N-(4-CHLOROPHENYL)ACETAMIDE
168.31
137.62
128.30
127.71
120.79
24.00
O
HN
Cl
f1 (ppm)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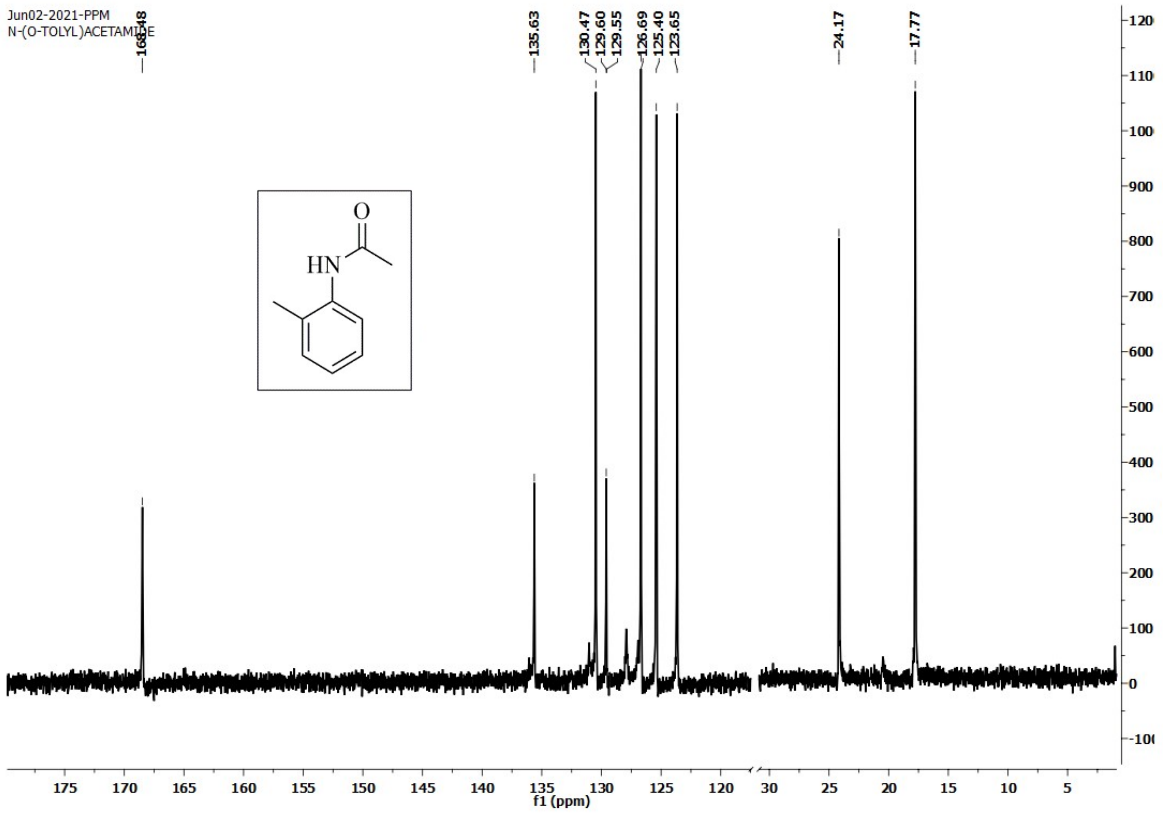
7.71
7.29
7.22
7.21
7.19
7.11
7.10
7.09
2.26
2.20
O
HN
1.00
5.50
3.23
3.24
f1 (ppm)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129.60
129.55
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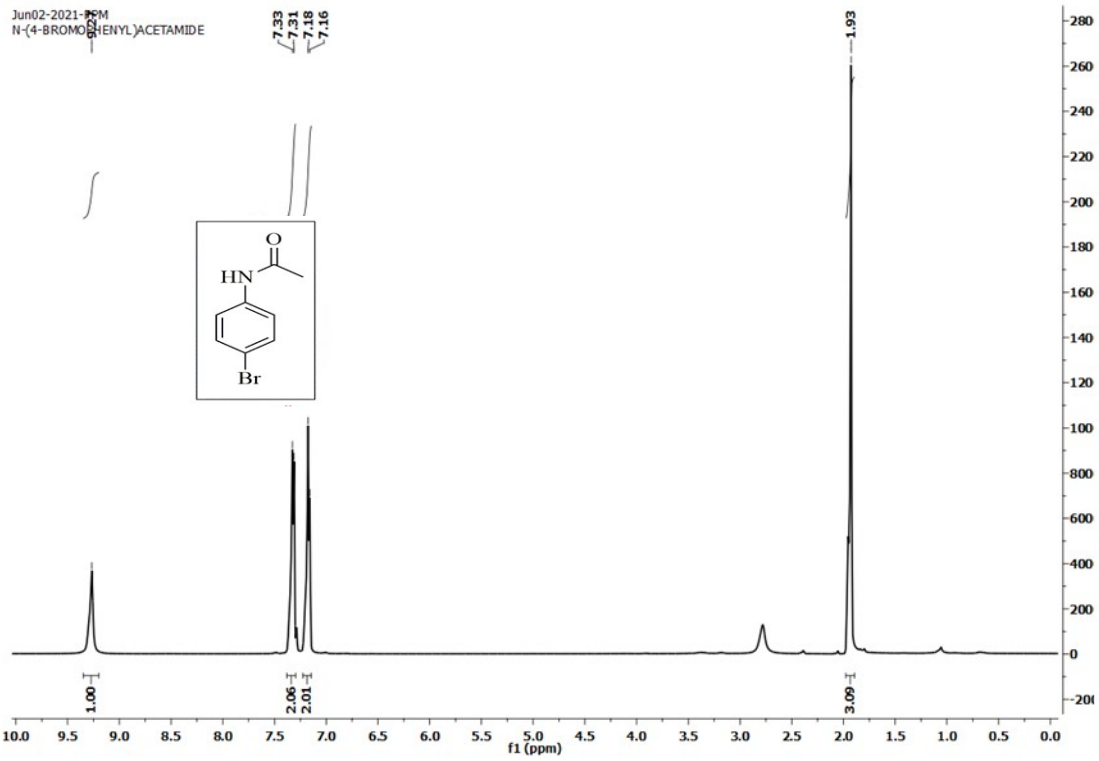
125.40
123.65
24.17
17.77
O
HN
f1 (ppm)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N-(4-BROMOPHENYL)ACETAMIDE
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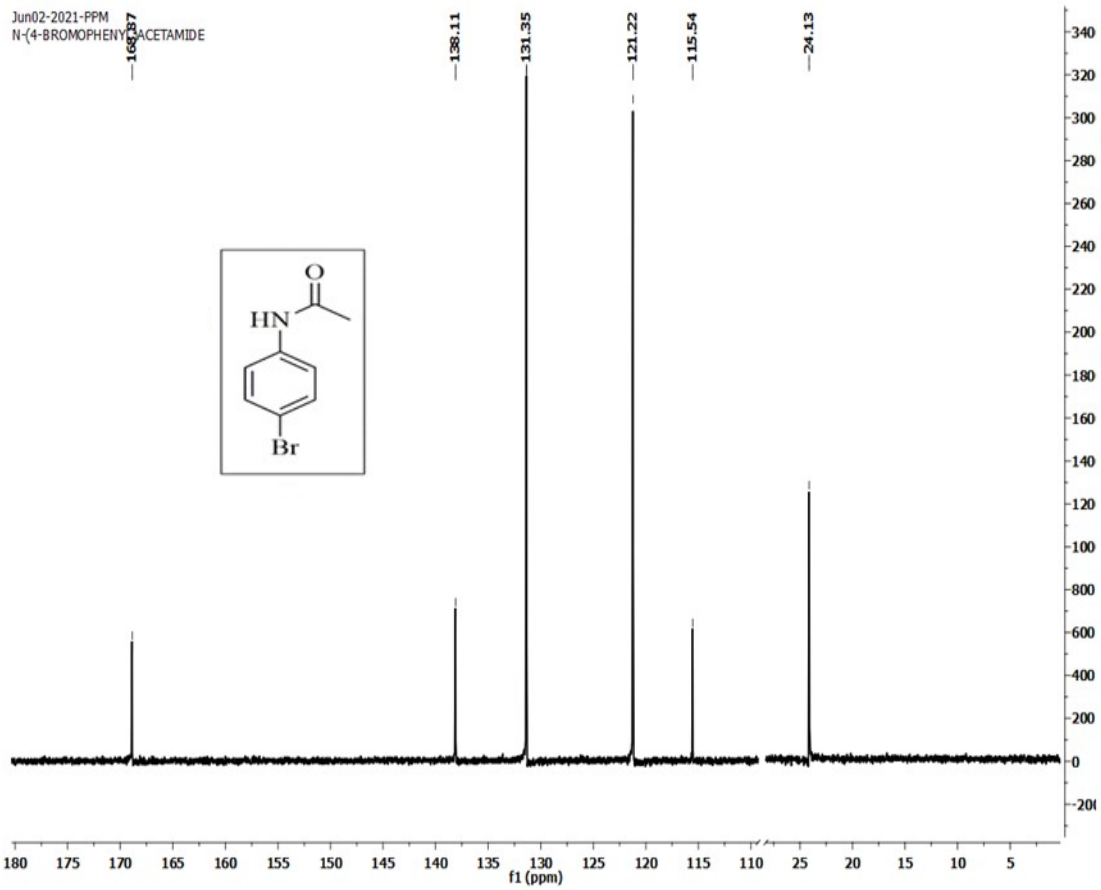
1.00
2.06
2.01
3.09
O
HN
Br
f1 (ppm)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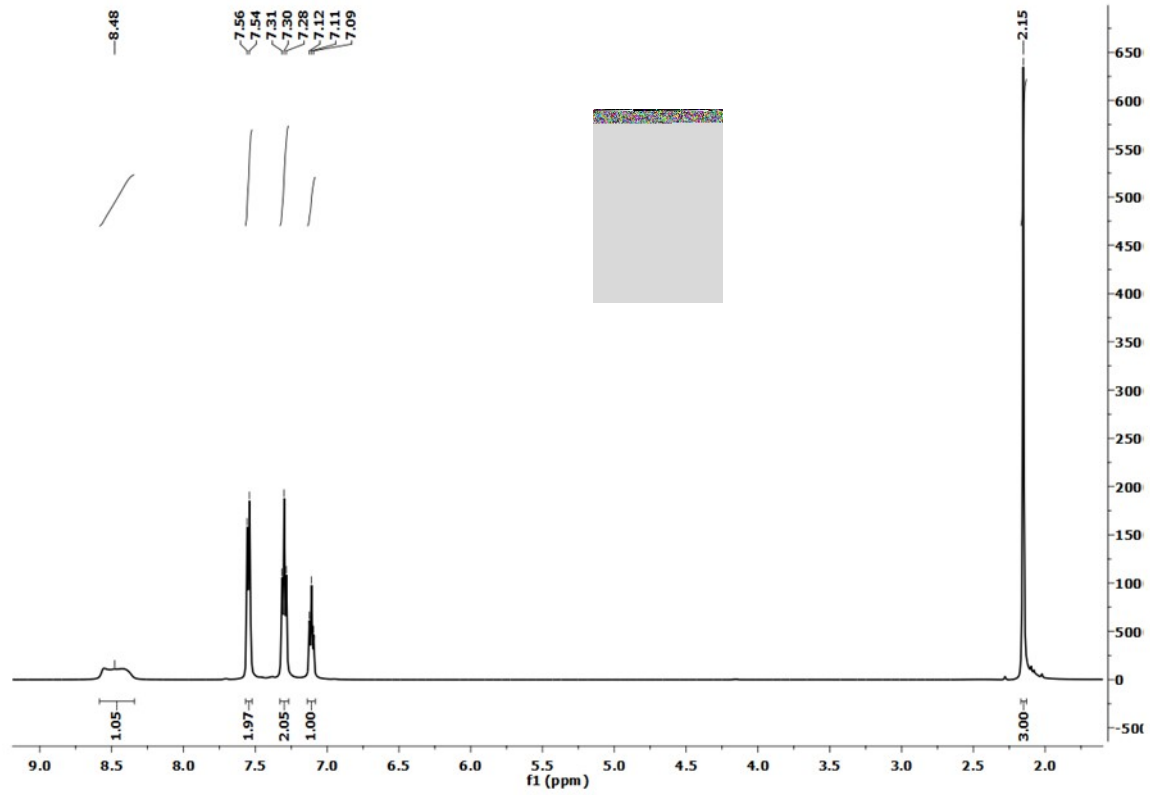
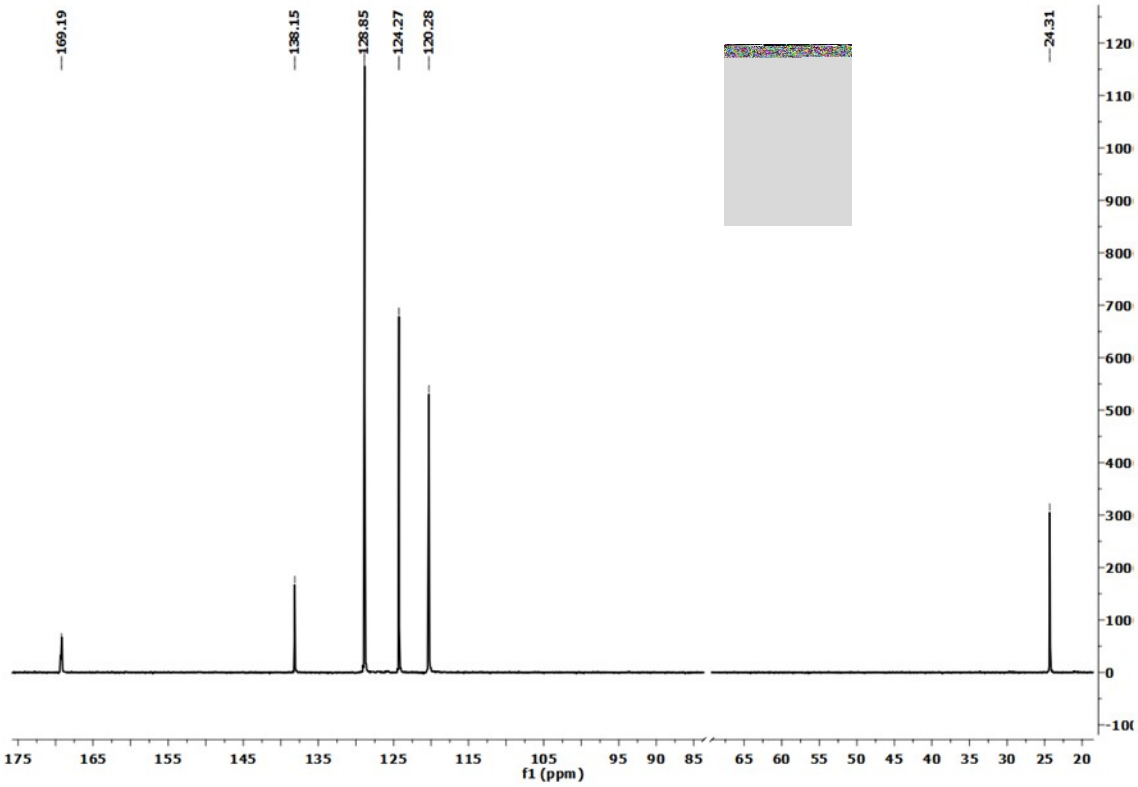
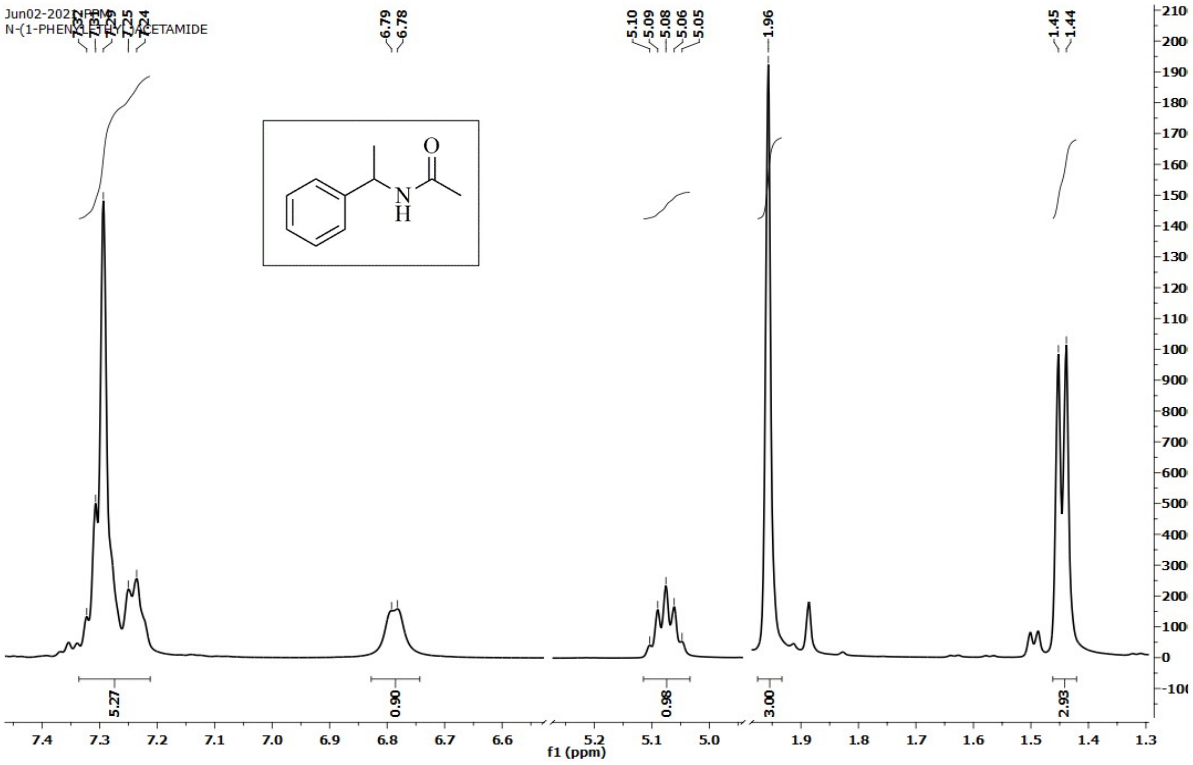
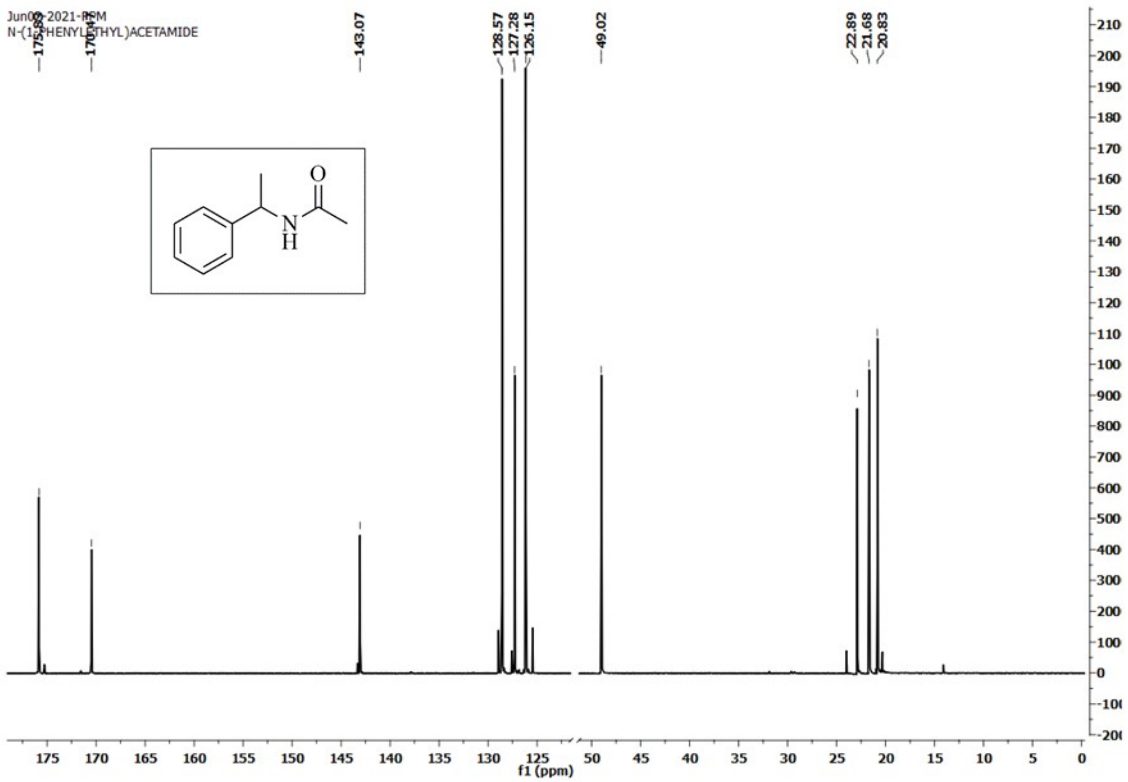
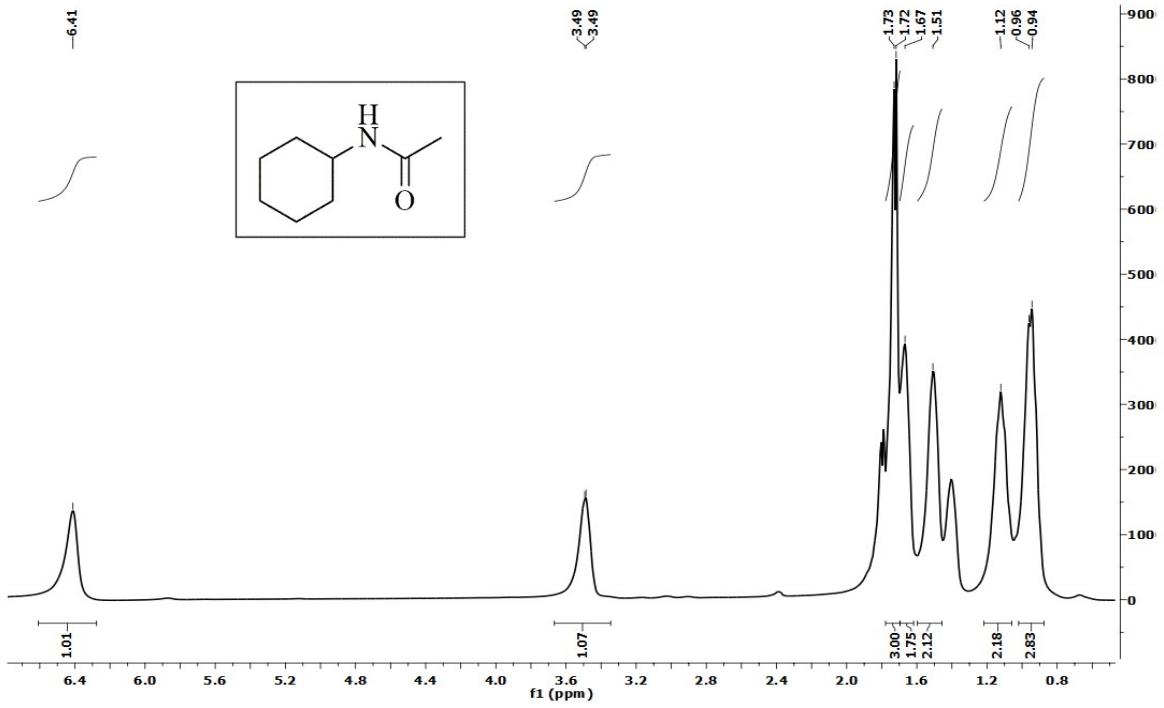
121.22
115.54
24.13
HN
O
Br
f1 (ppm)

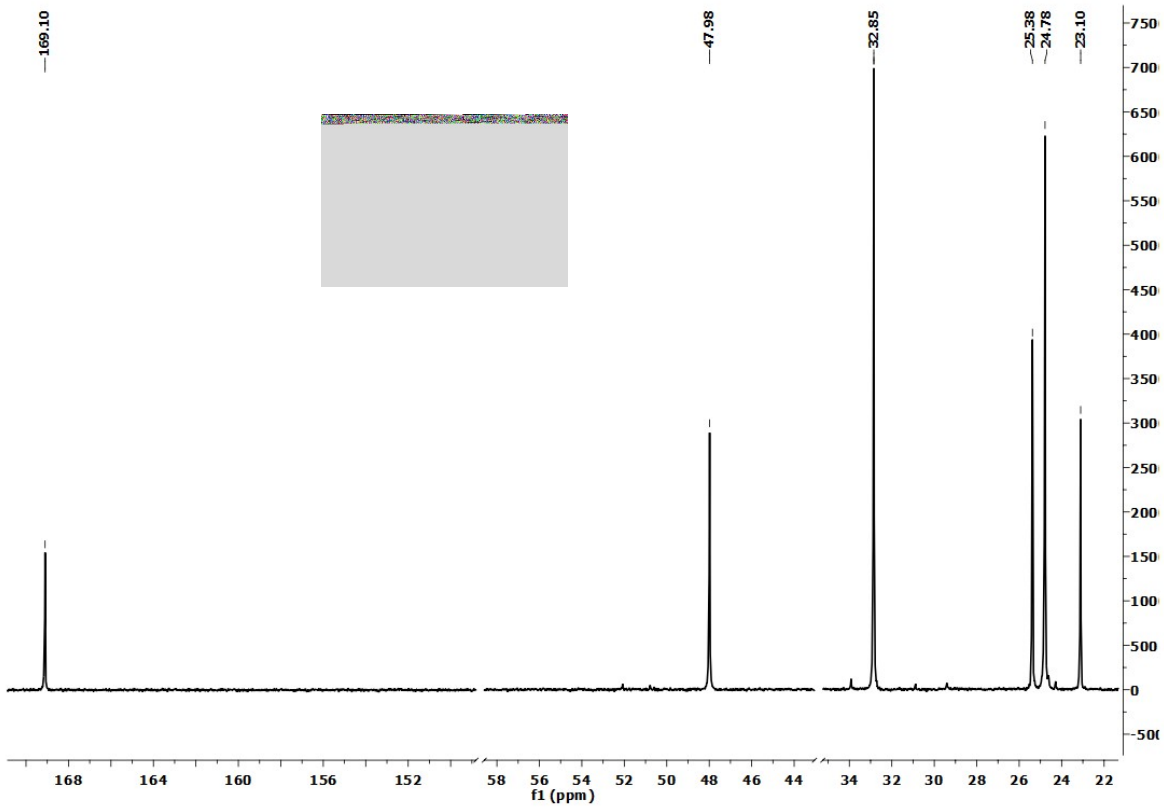

8.48
7.56
7.54
7.31
7.30
7.28
7.12
7.11
7.09
2.15
1.05
1.97
2.05
1.00
3.00
f1 (ppm)

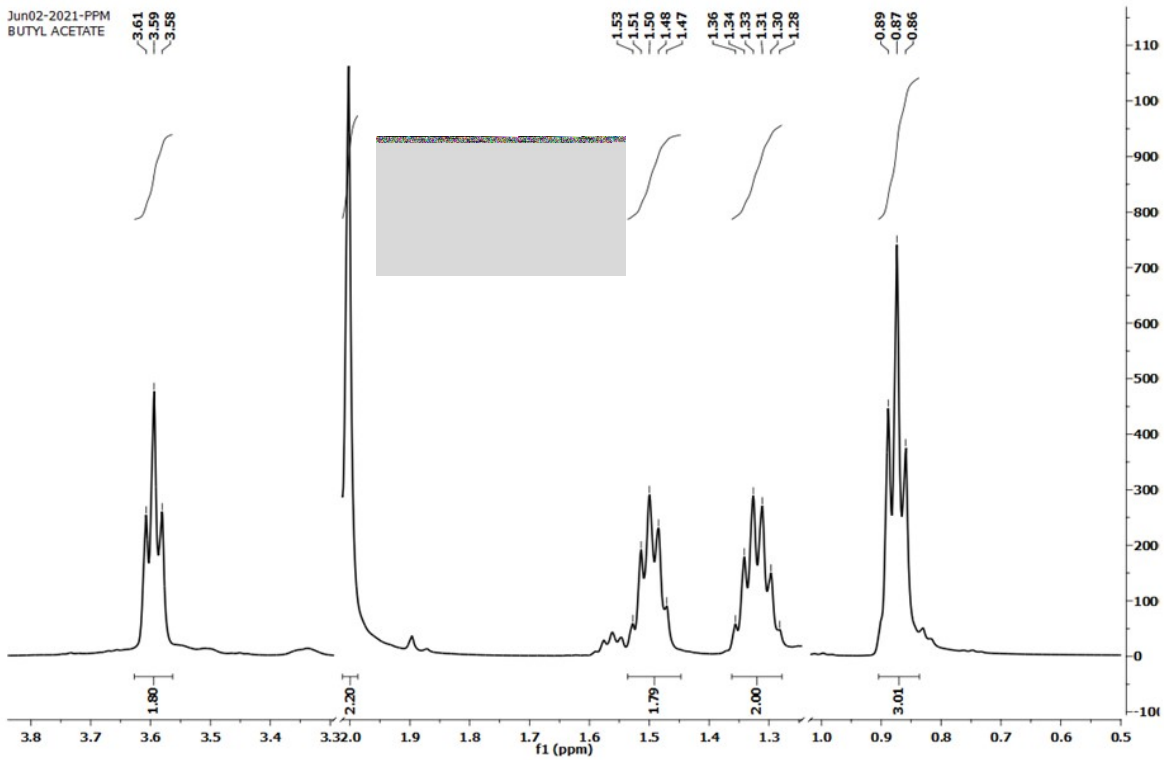

169.19
138.15
128.85
124.27
120.28
24.31
f1 (ppm)

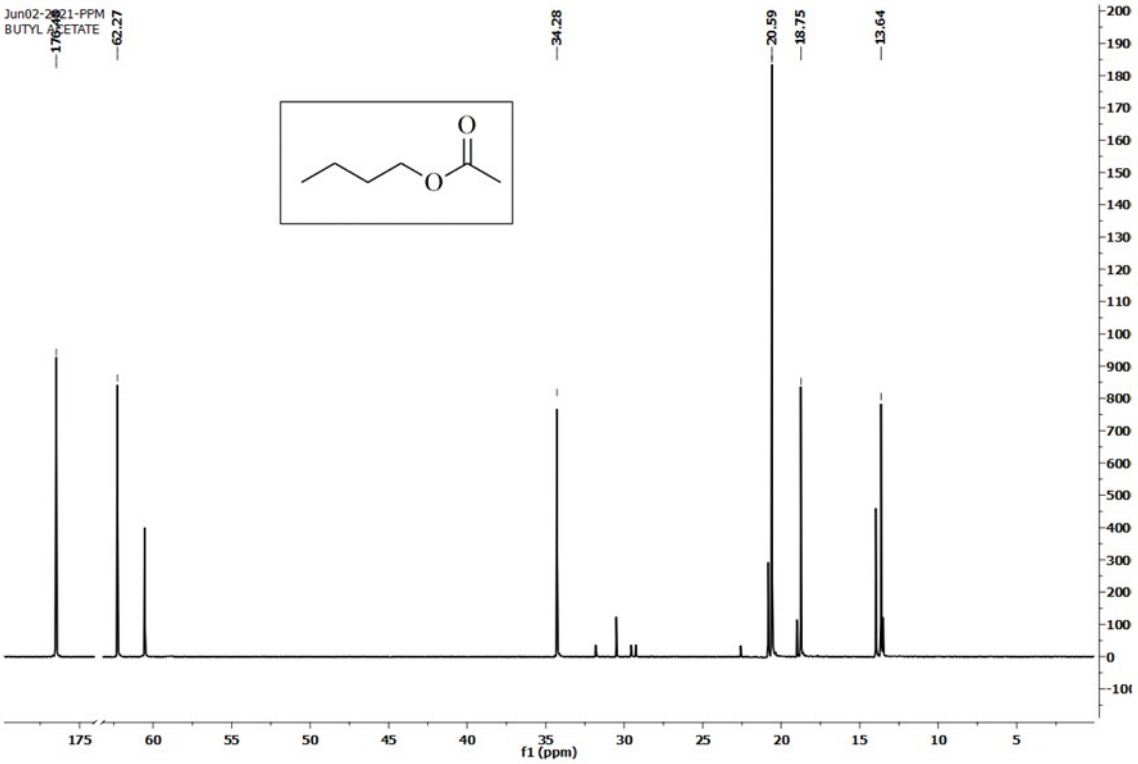

6.79
6.78
5.10
5.09
5.08
5.06
5.05
1.96
1.45
1.44
5.27
0.90
0.98
3.00
2.93
f1 (ppm)

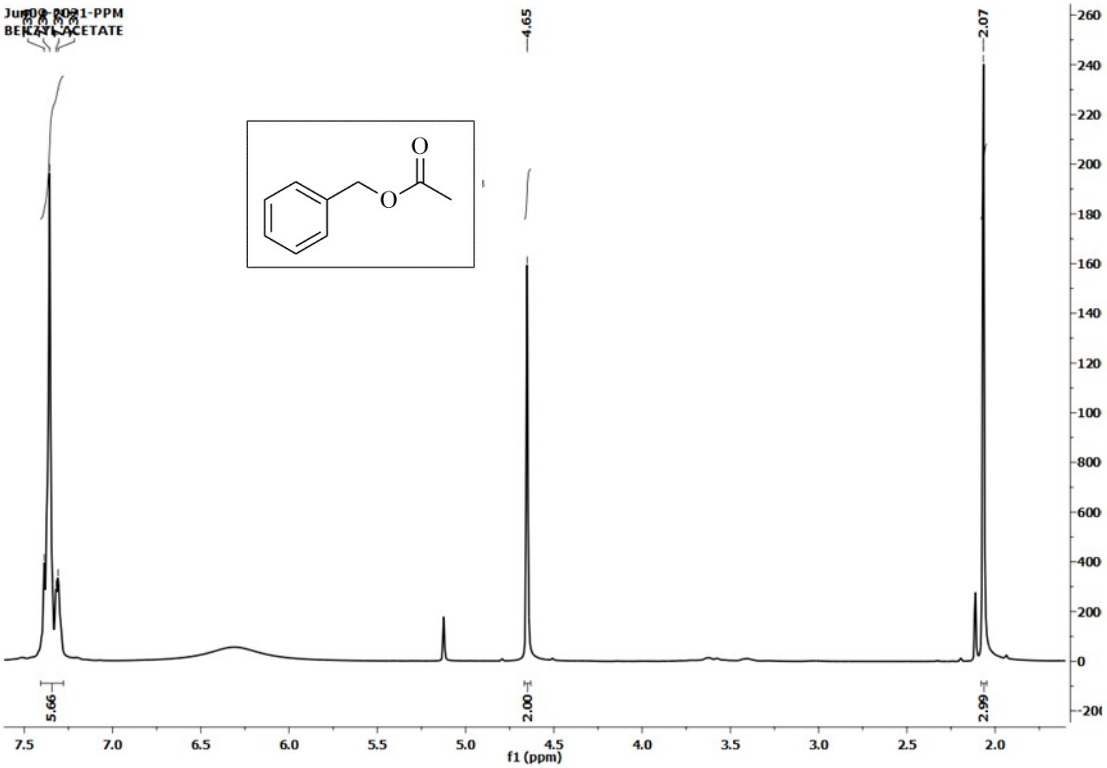

Jun09-2021-PSM
N-(1-PHENYLETHYL)ACETAMIDE
175.89
170.07
143.07
128.57
127.28
126.15
49.02
22.89
21.68
20.83
O
N
H
f1 (ppm)

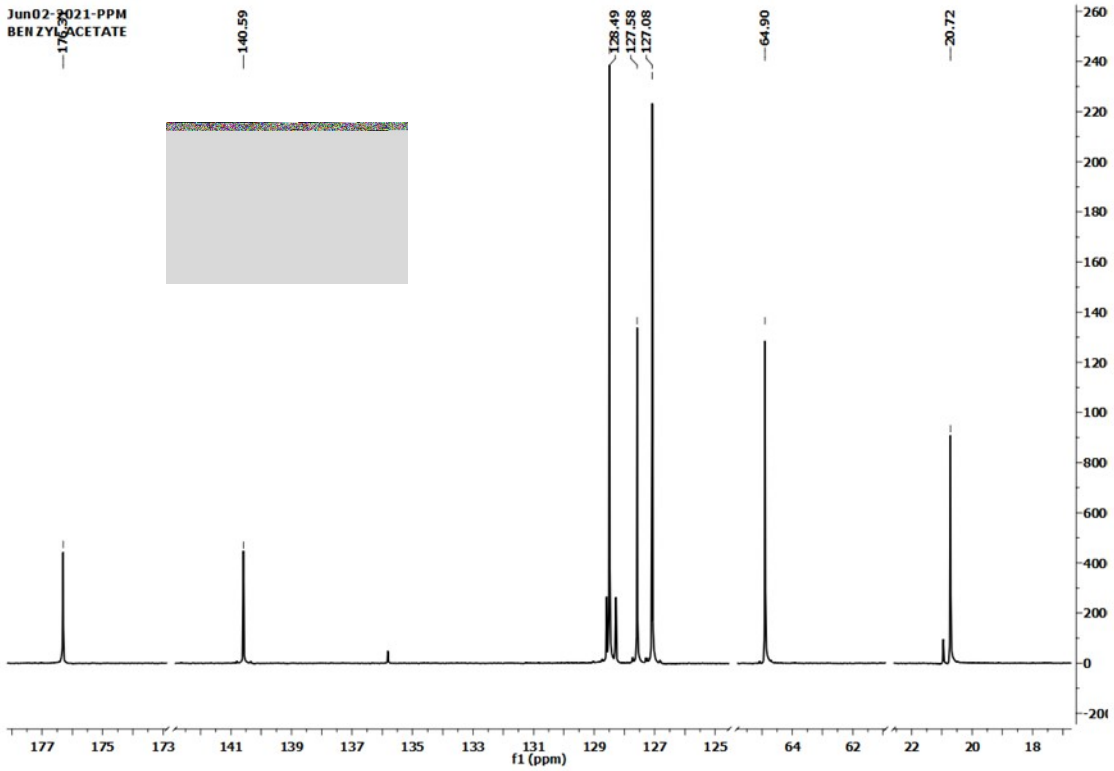

6.41
3.49
3.49
1.73
1.72
1.67
1.51
1.12
0.96
0.94
H
N
O
1.01
1.07
3.00
1.75
2.12
2.18
2.83
f1 (ppm)

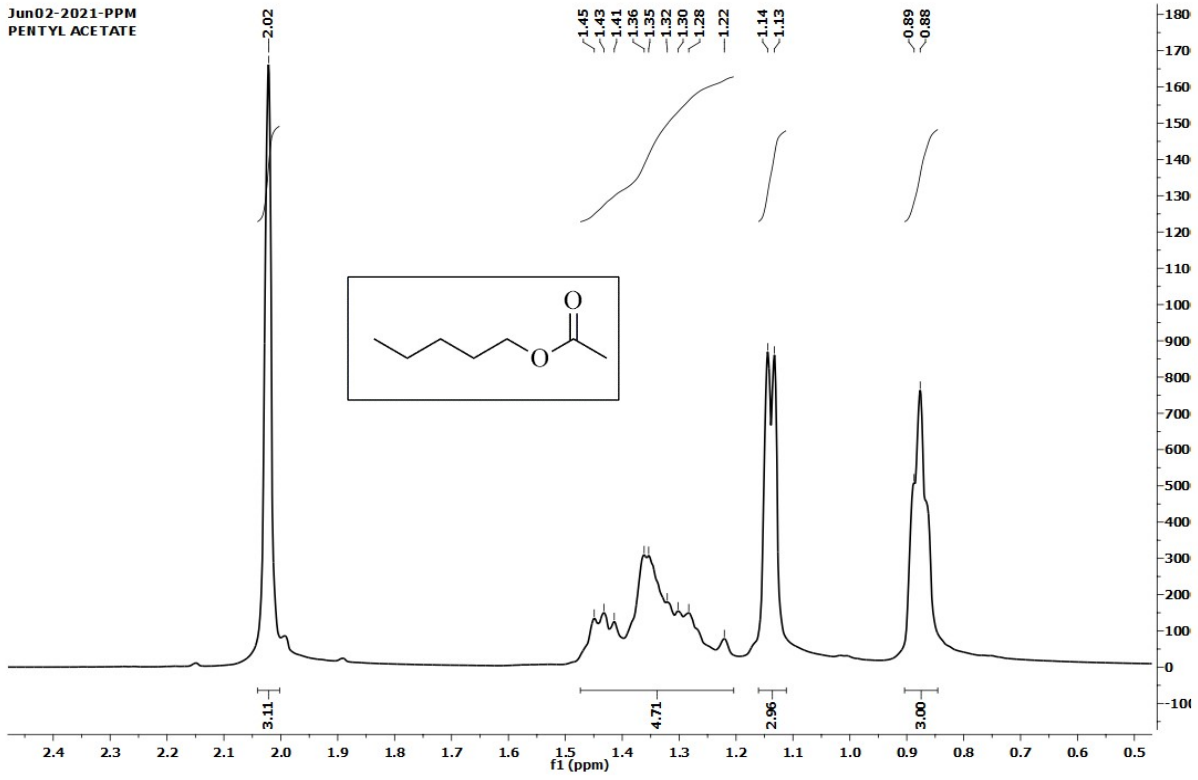

169.10
47.98
32.85
25.38
24.78
23.10
f1 (ppm)

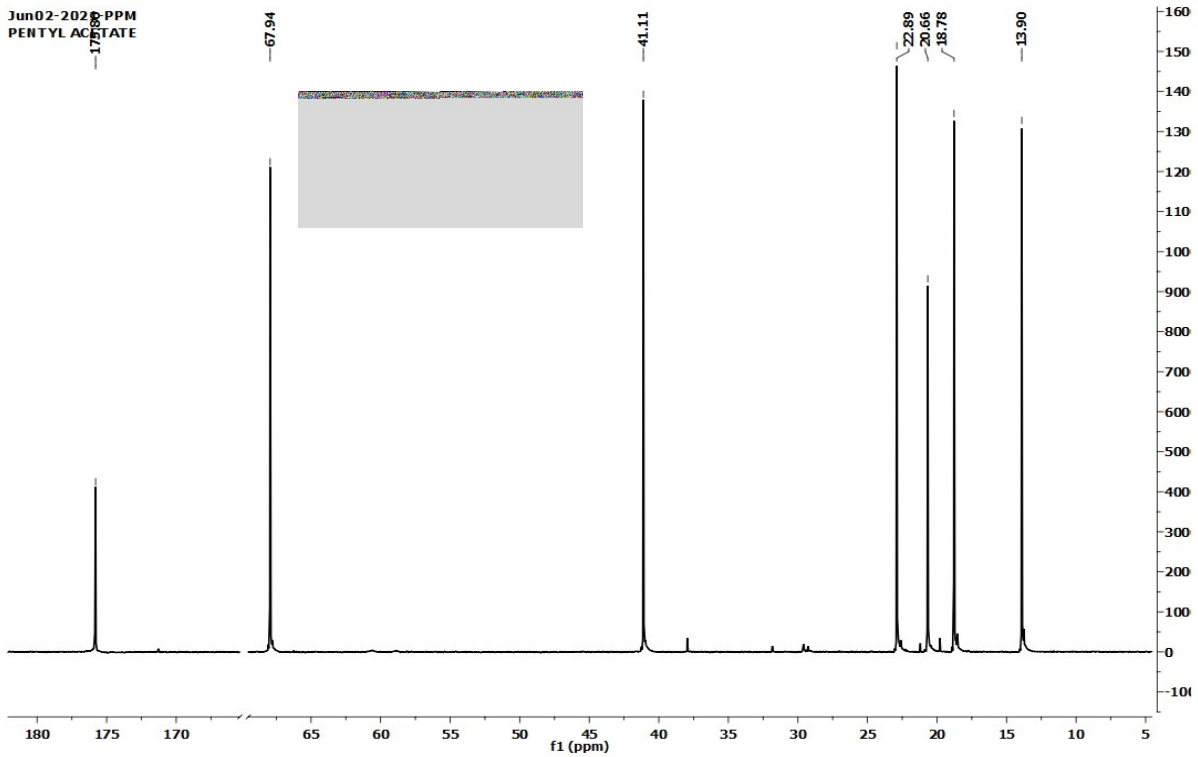

Jun02-2021-PPM
BUTYL ACETATE
3.61
3.59
3.58
1.53
1.51
1.50
1.48
1.47
1.36
1.34
1.33
1.31
1.30
1.28
0.89
0.87
0.86
1.80
2.20
1.79
2.00
3.01
f1 (ppm)

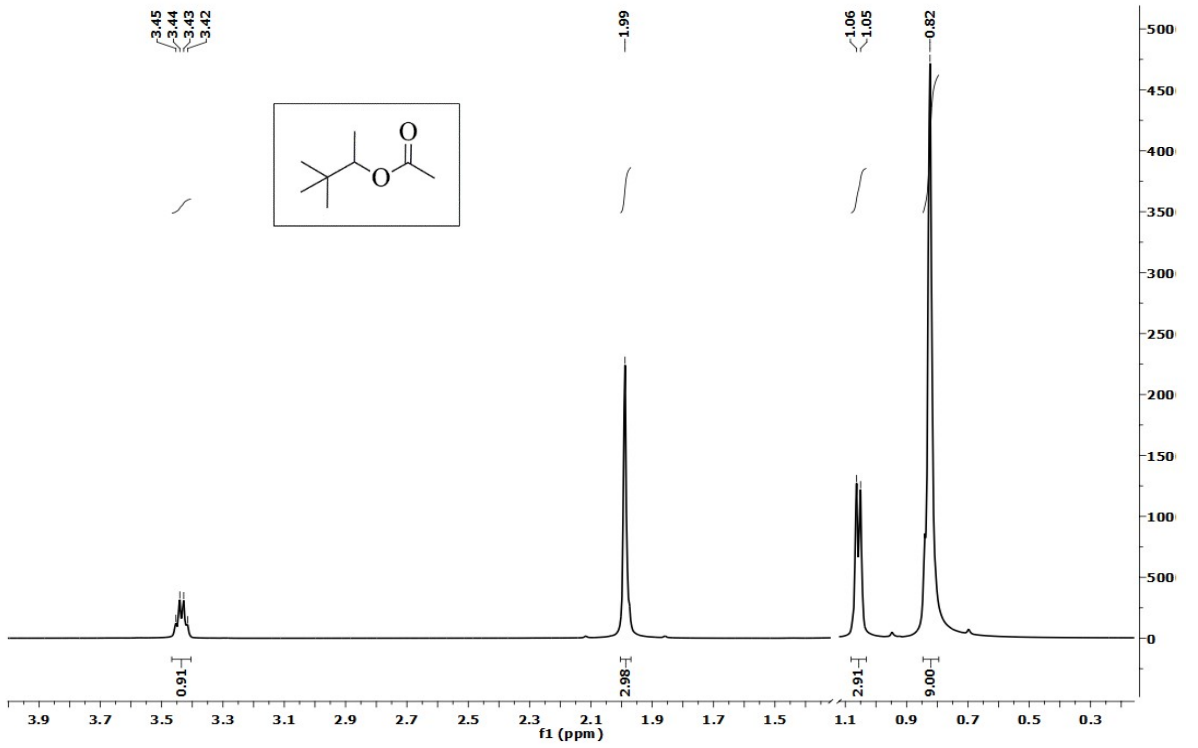

Jun02-2021-PPM
BUTYL ACETATE
170.49
62.27
34.28
20.59
18.75
13.64
O
O
f1 (ppm)

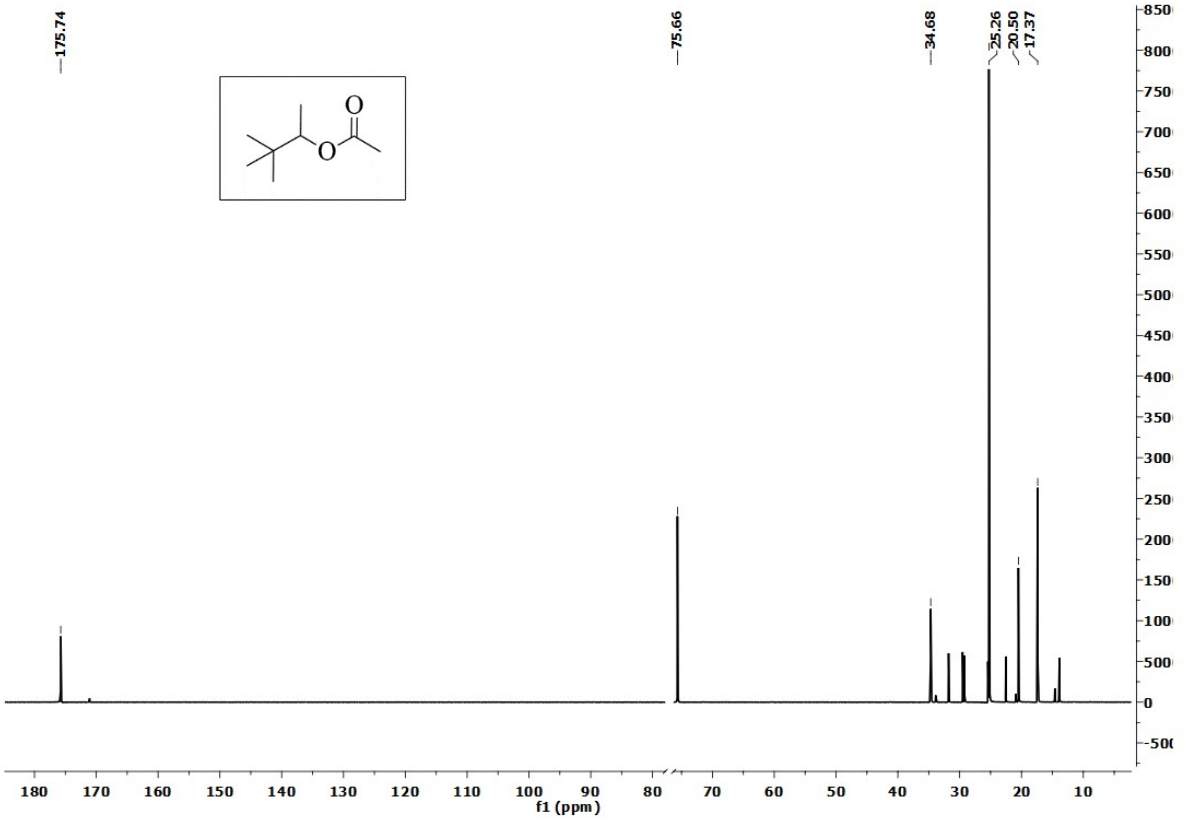

Jun09-2021-PPM
BENZYL ACETATE
4.65
2.07
O
O
5.66
2.00
2.99
f1 (ppm)

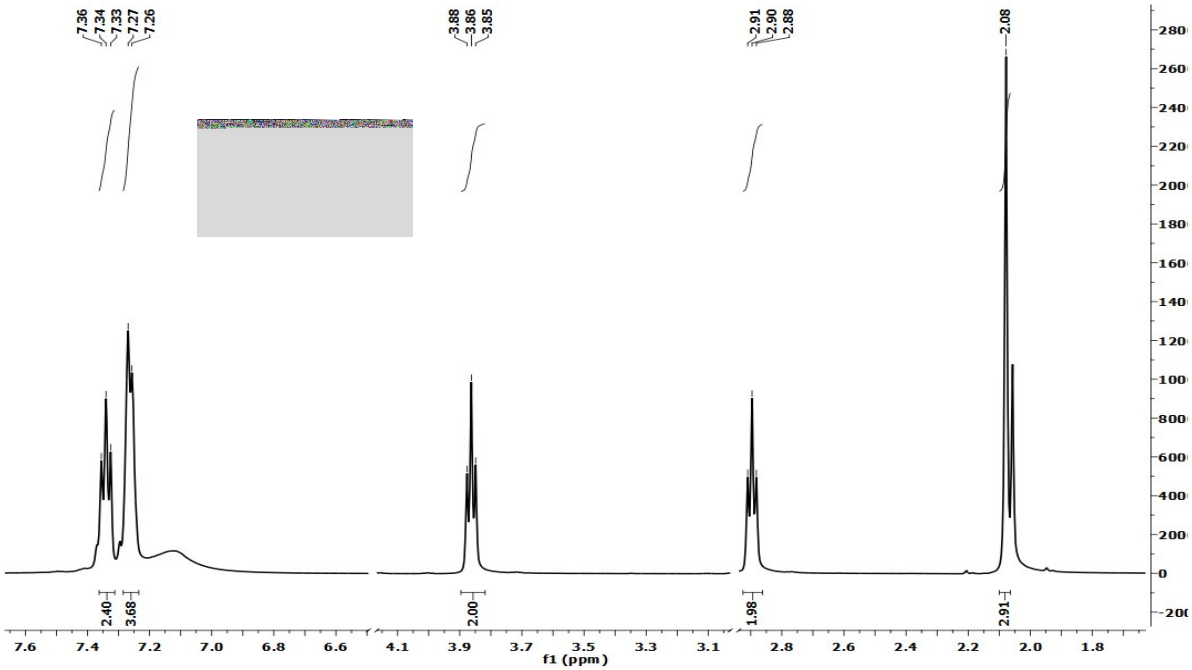

Jun02-2021-PPM
BENZYL ACETATE
170.39
140.59
128.49
127.58
127.08
64.90
20.72
f1 (ppm)

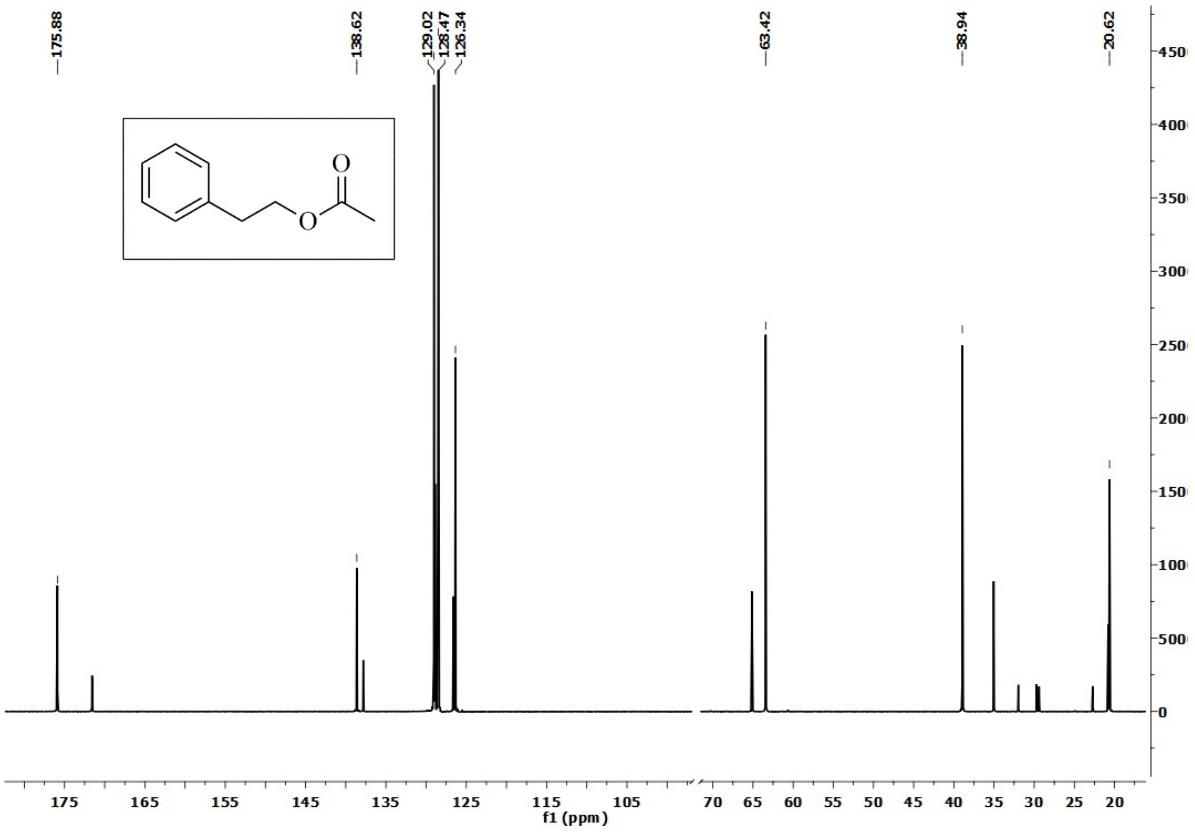

Jun02-2021-PPM
PENTYL ACETATE
2.02
1.45
1.43
1.41
1.36
1.35
1.32
1.30
1.28
1.22
1.14
1.13
0.89
0.88
3.11
4.71
2.96
3.00
f1 (ppm)

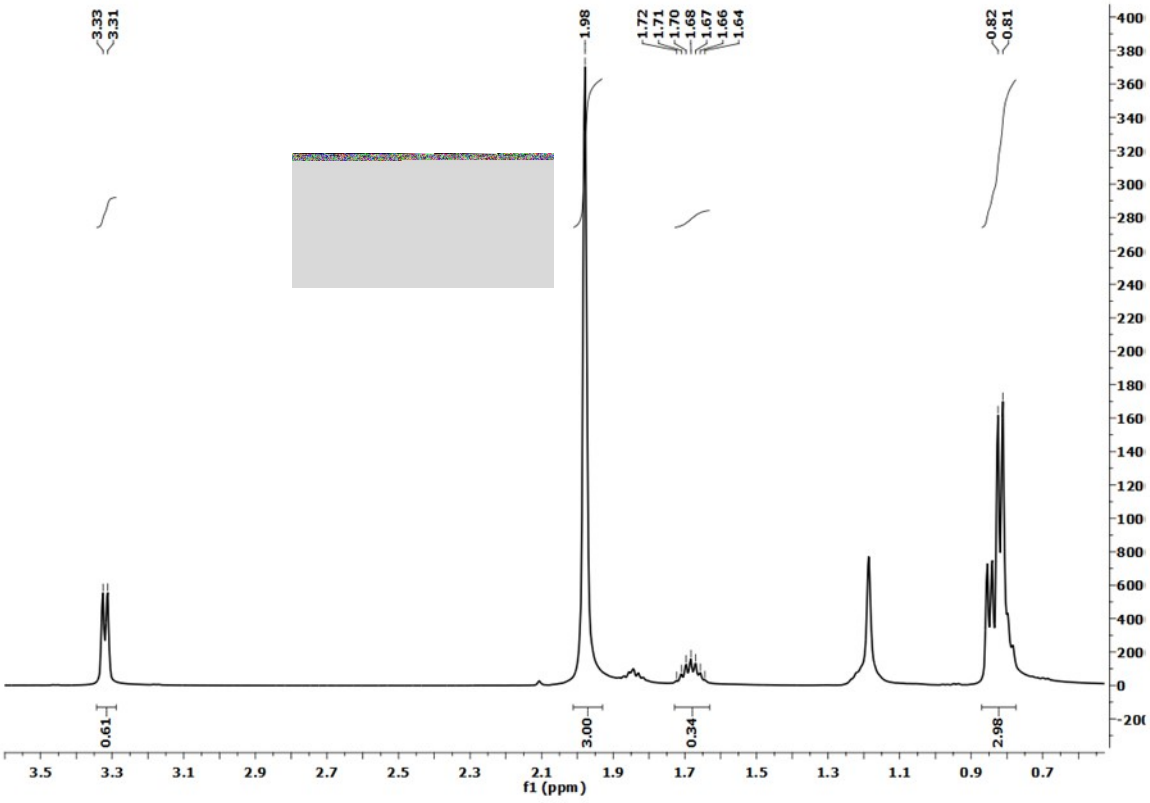

Jun02-2020-PPM
PENTYL ACETATE
175.89
67.94
41.11
22.89
20.66
18.78
13.90
f1 (ppm)

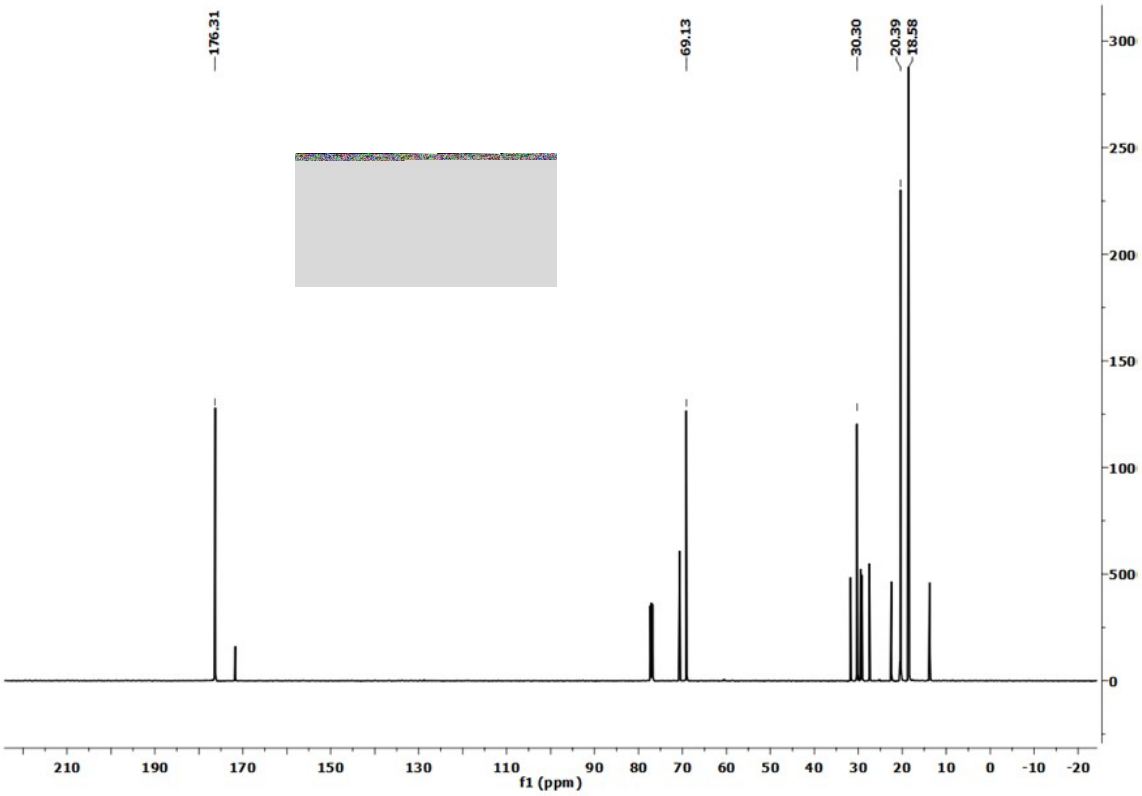

3.45
3.44
3.43
3.42
1.99
1.06
1.05
0.82
O
O
0.91
2.98
2.91
9.00
f1 (ppm)

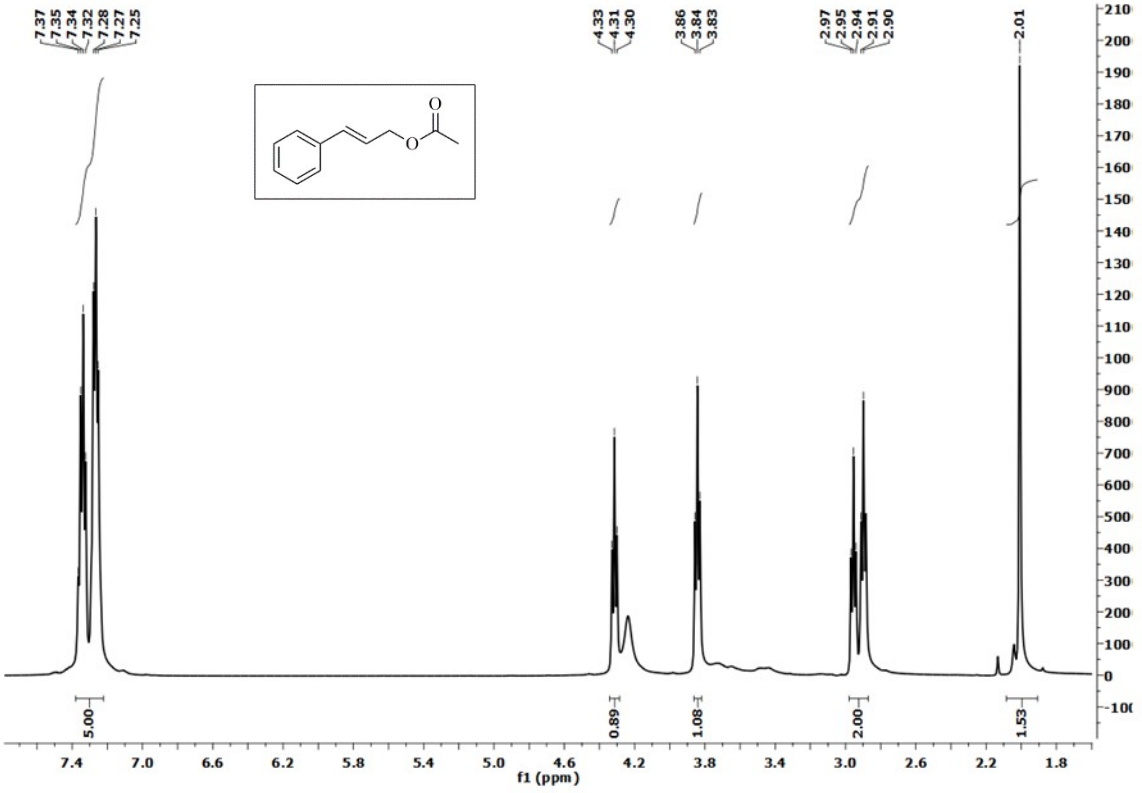

175.74
75.66
34.68
25.26
20.50
17.37
O
O
f1 (ppm)

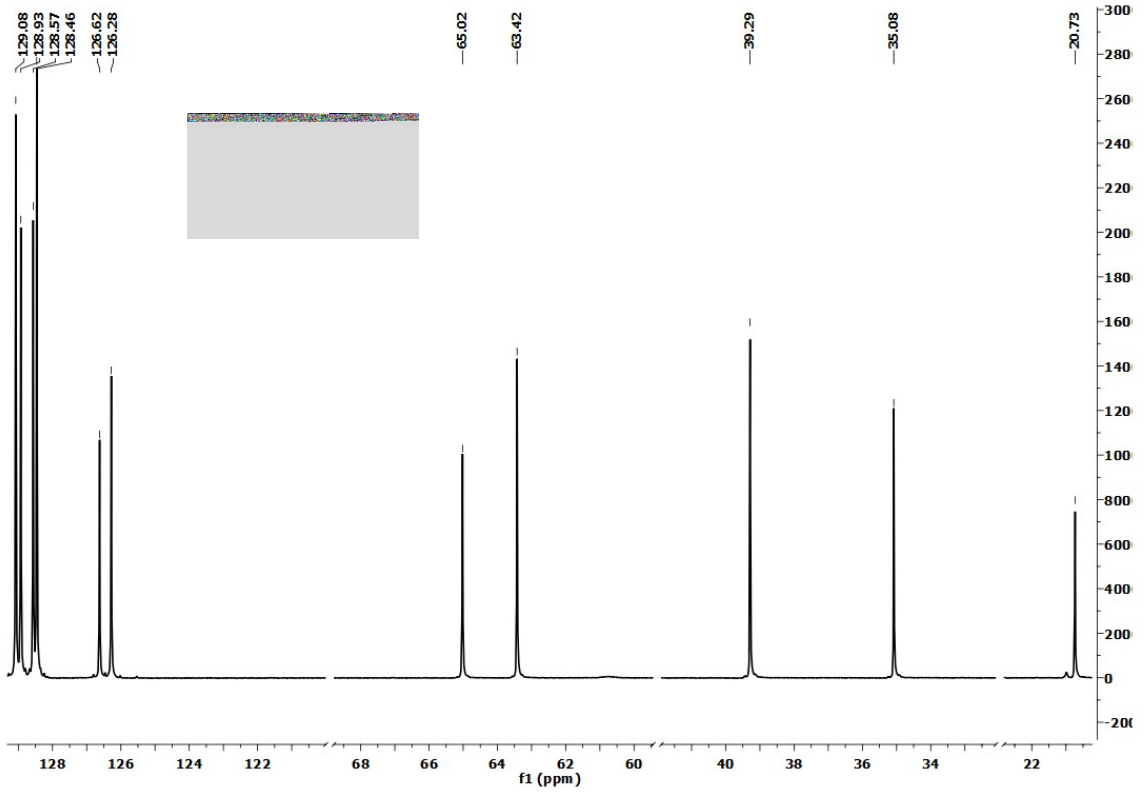

7.36
7.34
7.33
7.27
7.26
3.88
3.86
3.85
2.91
2.90
2.88
2.08
2.40
3.68
2.00
1.98
2.91
f1 (ppm)

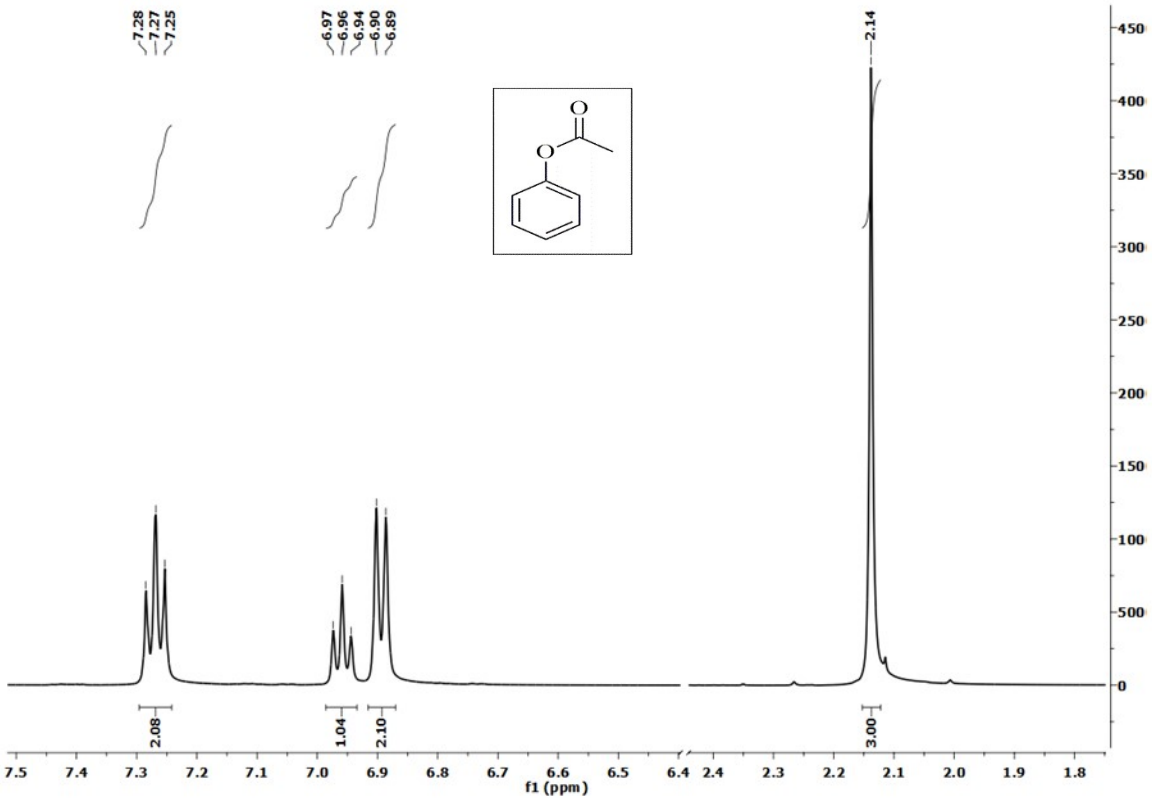

175.88
138.62
129.02
128.47
126.34
63.42
38.94
20.62
O
O
f1 (ppm)

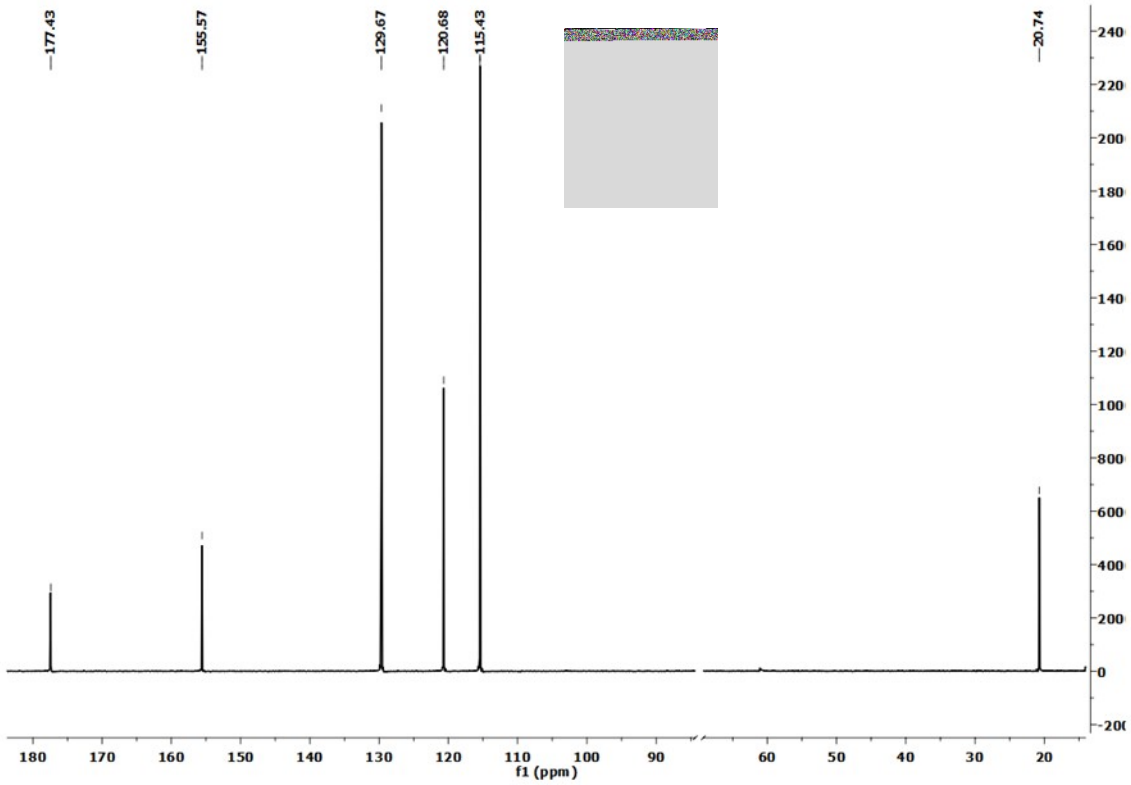

3.33
3.31
1.98
1.72
1.71
1.70
1.68
1.67
1.66
1.64
0.82
0.81
0.61
3.00
0.34
2.98
f1 (ppm)

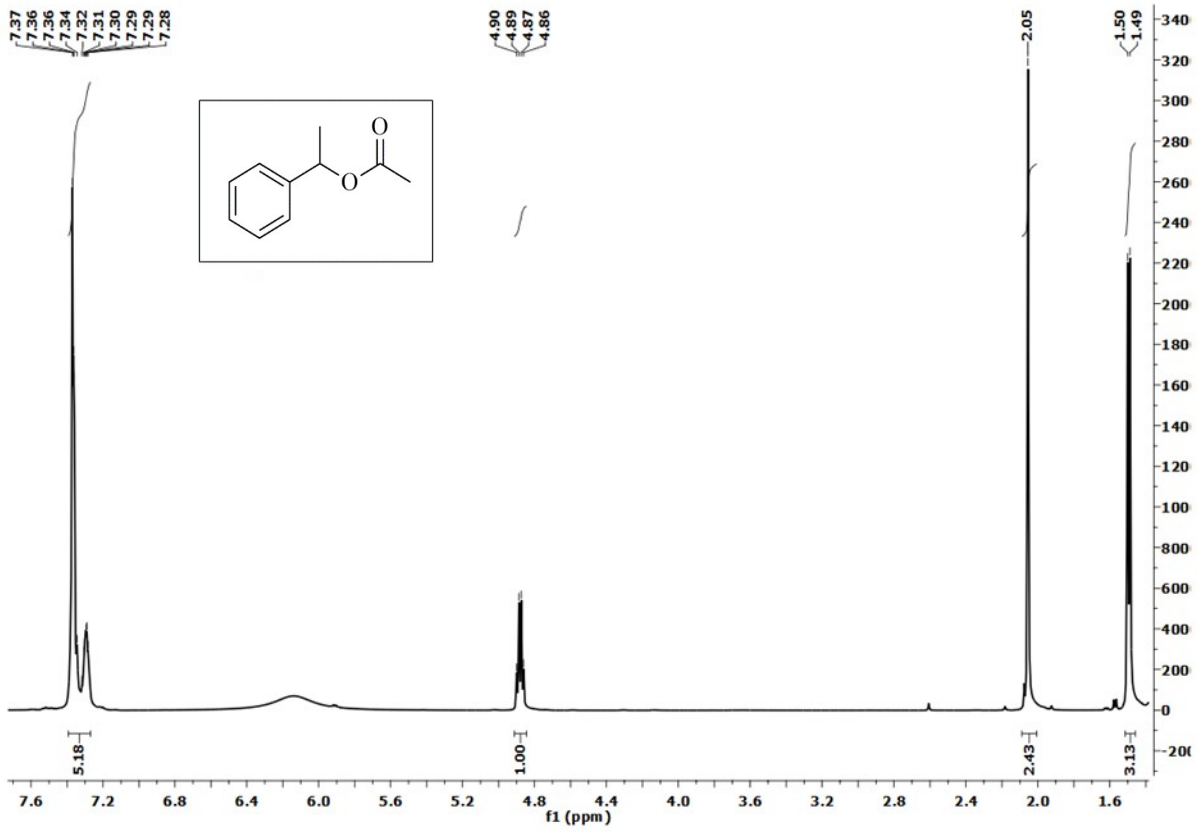

176.31
69.13
30.30
20.39
18.58
f1 (ppm)

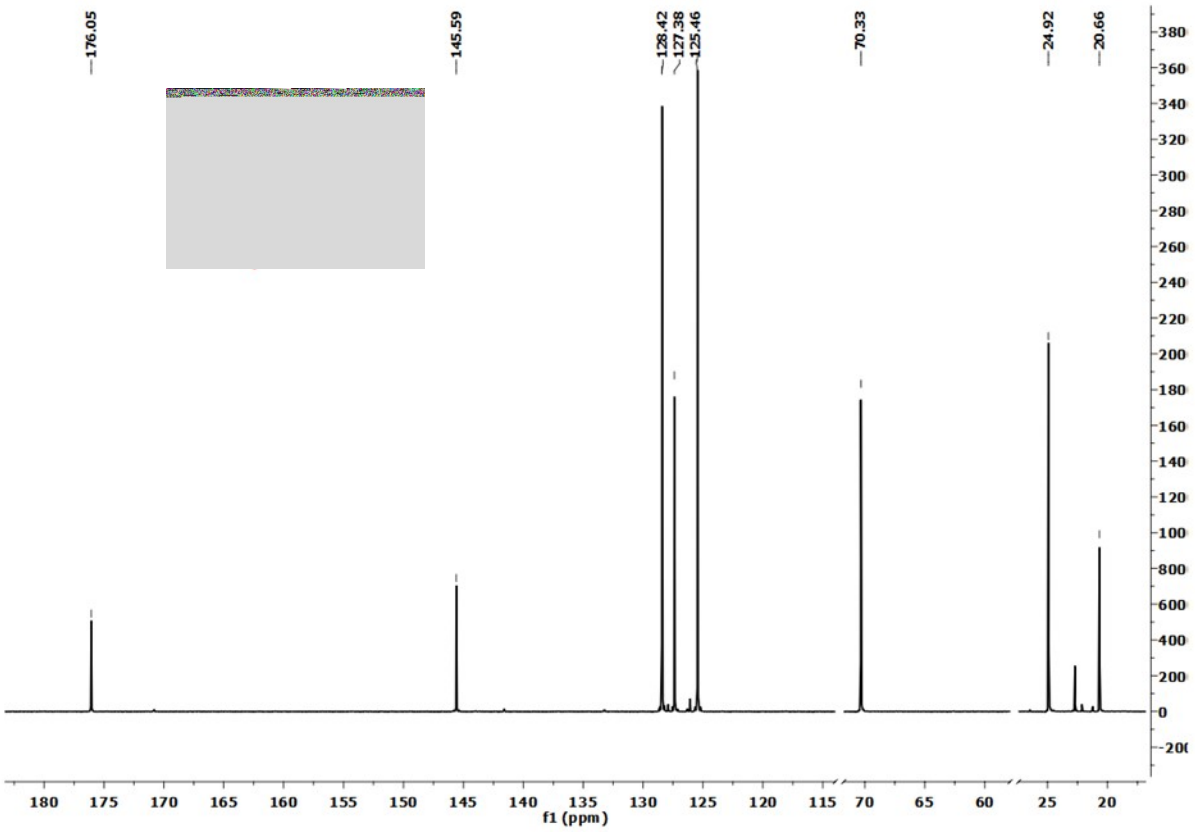

7.37
7.35
7.34
7.32
7.28
7.27
7.25
4.33
4.31
4.30
3.86
3.84
3.83
2.97
2.95
2.94
2.91
2.90
2.01
O
O
5.00
0.89
1.08
2.00
1.53
f1 (ppm)

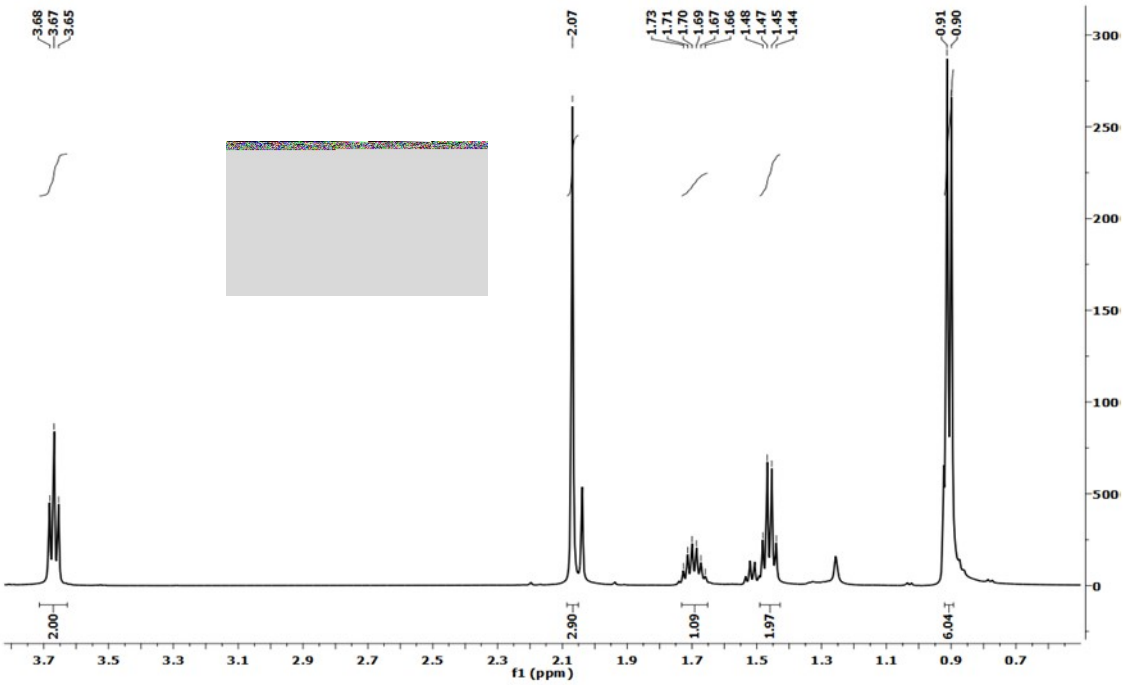

129.08
128.93
128.57
128.46
126.62
126.28
65.02
63.42
39.29
35.08
20.73
f1 (ppm)

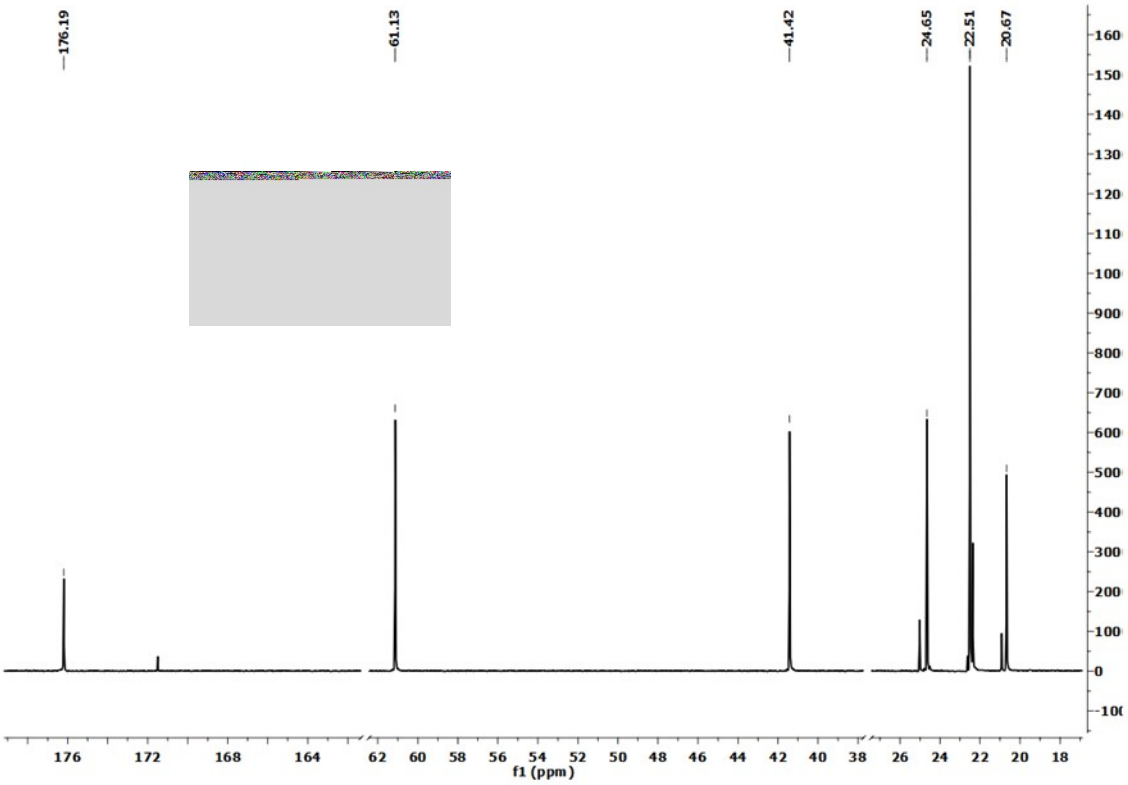

7.28
7.27
7.25
6.97
6.96
6.94
6.90
6.89
2.14
2.08
1.04
2.10
3.00
f1 (ppm)

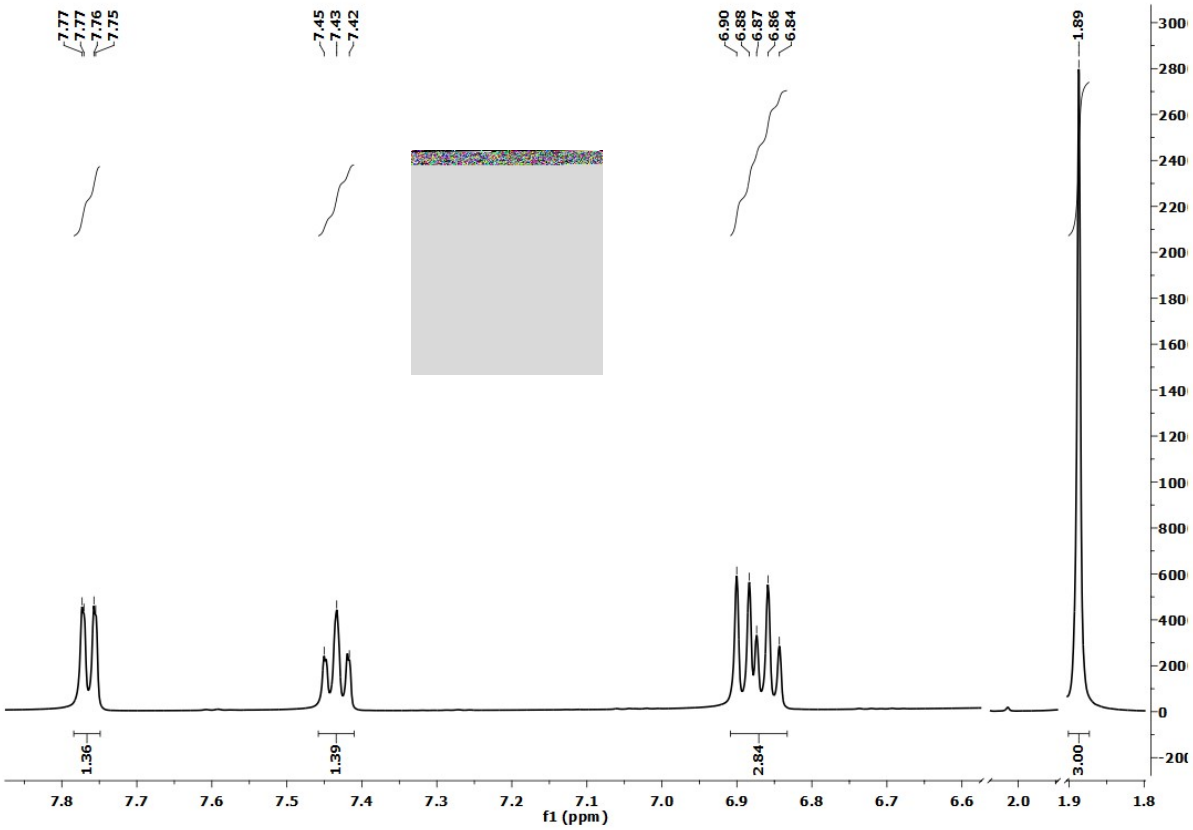

177.43
155.57
129.67
120.68
115.43
20.74
f1 (ppm)


7.37
7.36
7.36
7.34
7.32
7.31
7.30
7.29
7.29
7.28
4.90
4.89
4.87
4.86
2.05
1.50
1.49
O
O
5.18
1.00
2.43
3.13
f1 (ppm)


176.05
145.59
128.42
127.38
125.46
70.33
24.92
20.66
f1 (ppm)


3.68
3.67
3.65
2.07
1.73
1.71
1.70
1.69
1.67
1.66
1.48
1.47
1.45
1.44
0.91
0.90
2.00
2.90
1.09
1.97
6.04
f1 (ppm)


176.19
61.13
41.42
24.65
22.51
20.67
f1 (ppm)


7.77
7.77
7.76
7.75
7.45
7.43
7.42
6.90
6.88
6.87
6.86
6.84
1.89
1.36
1.39
2.84
3.00
f1 (ppm)

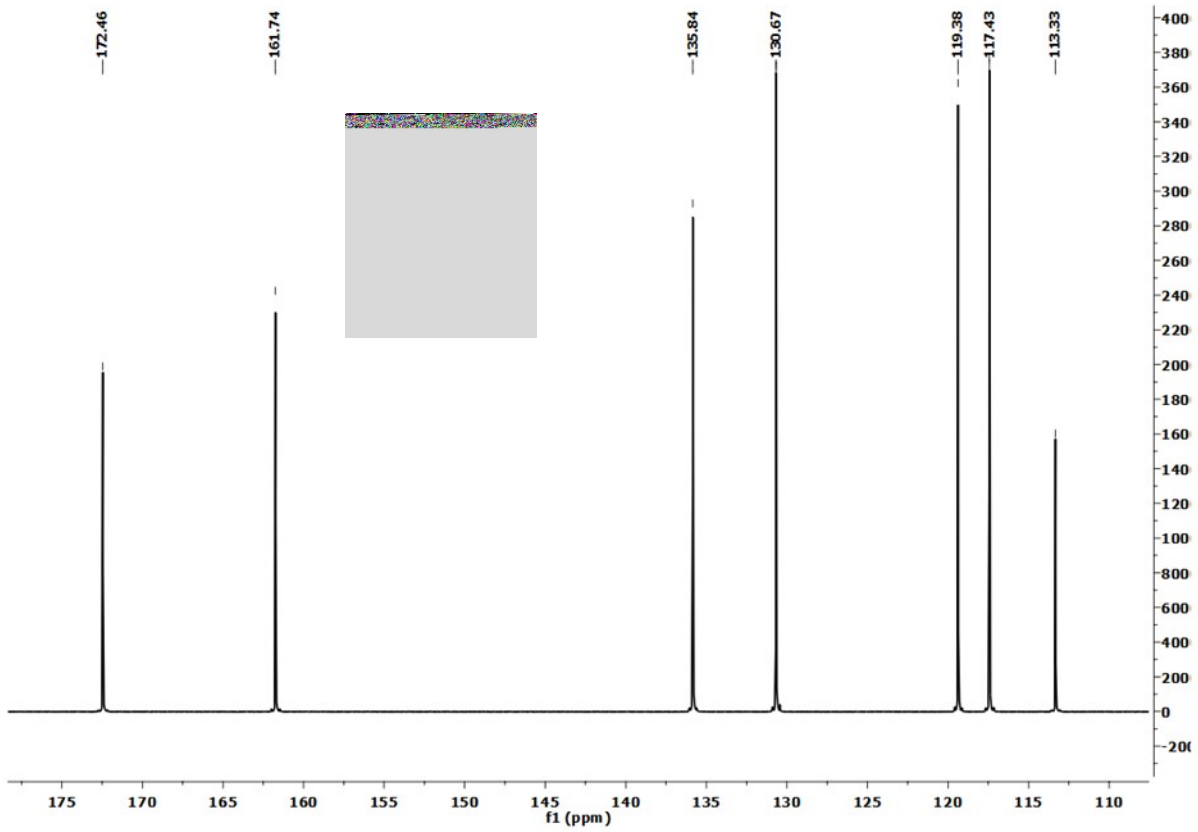
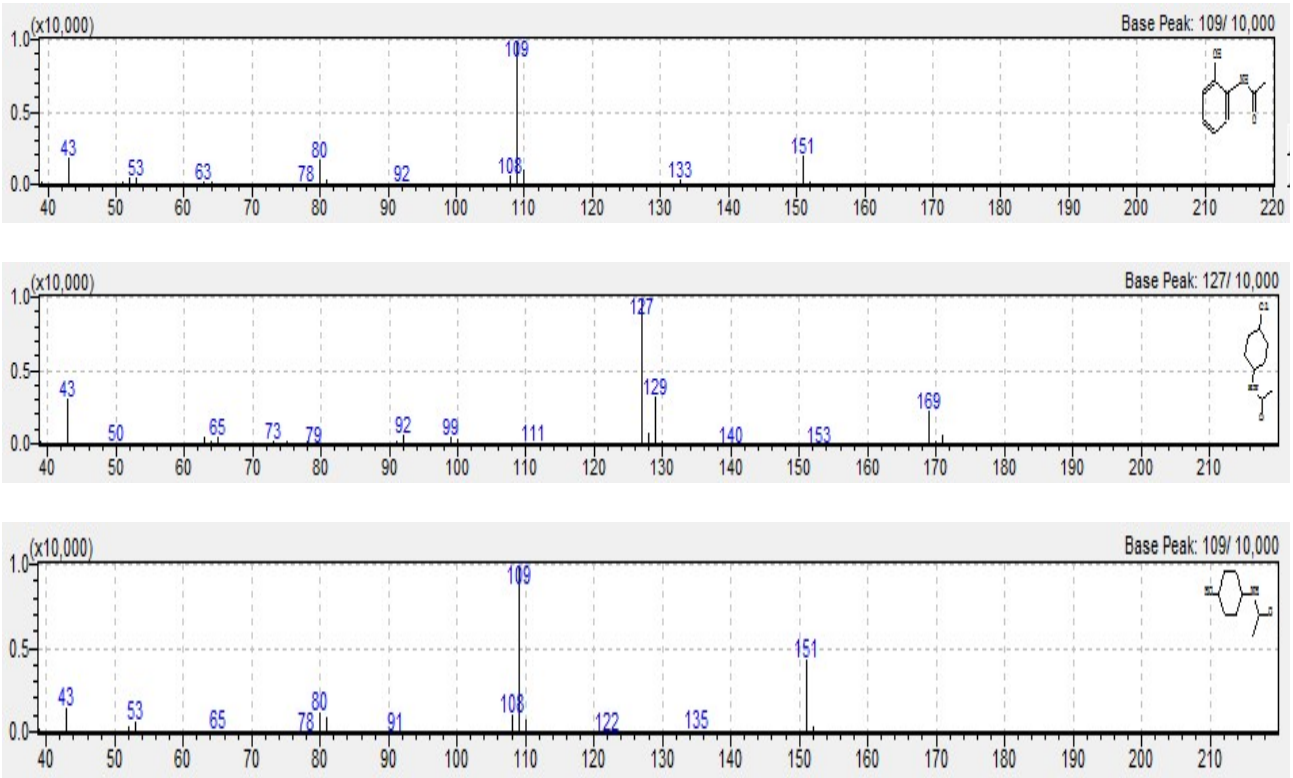
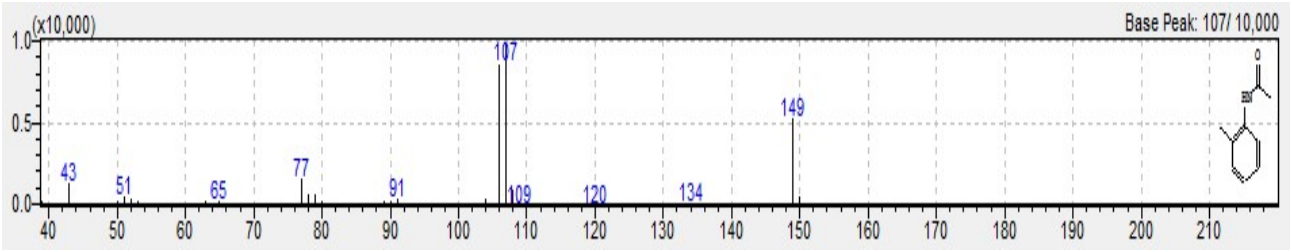
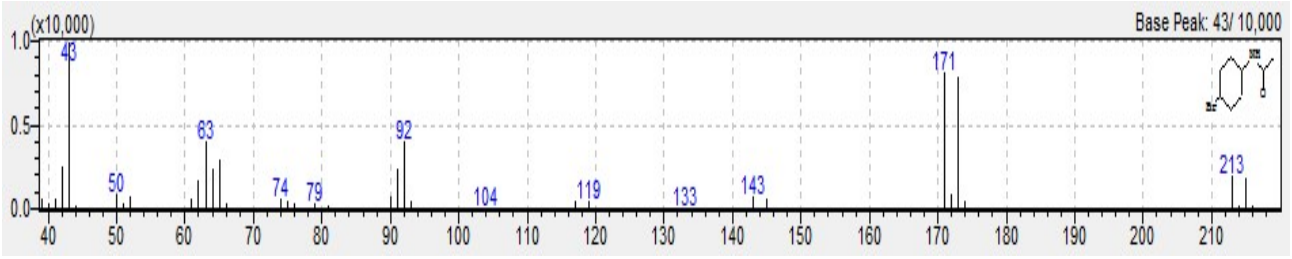


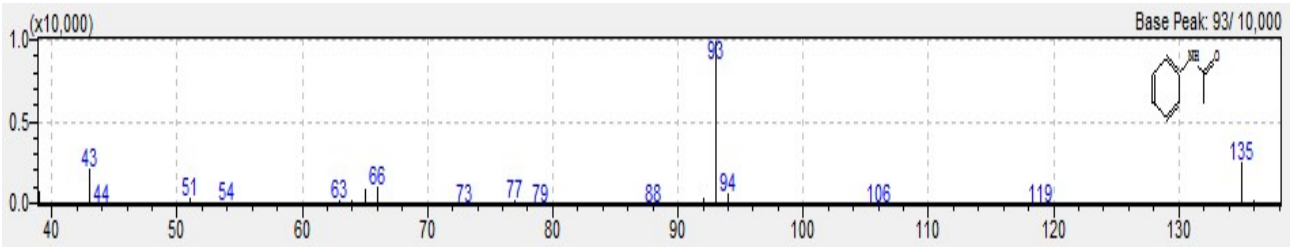
Figure S3: NMR spectra of the products of acetylation.

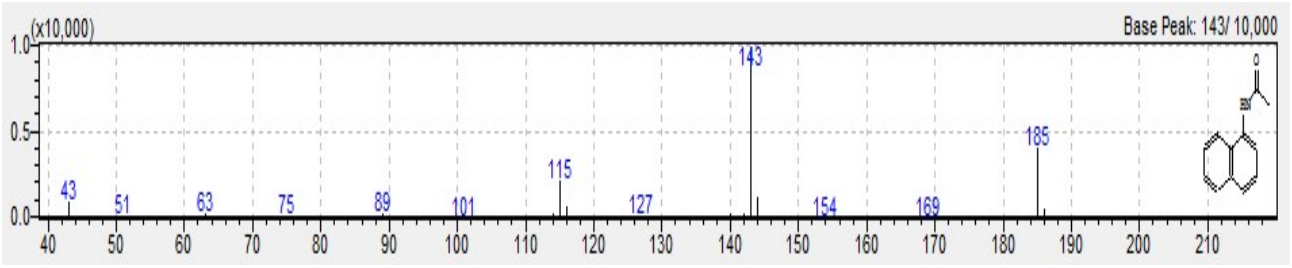
5. GC-MS results

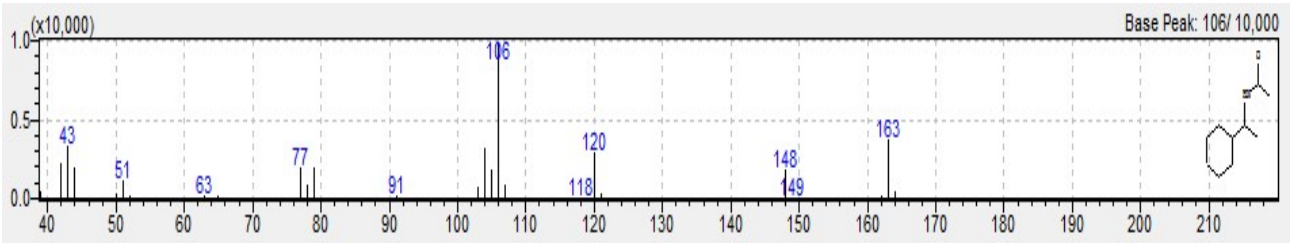


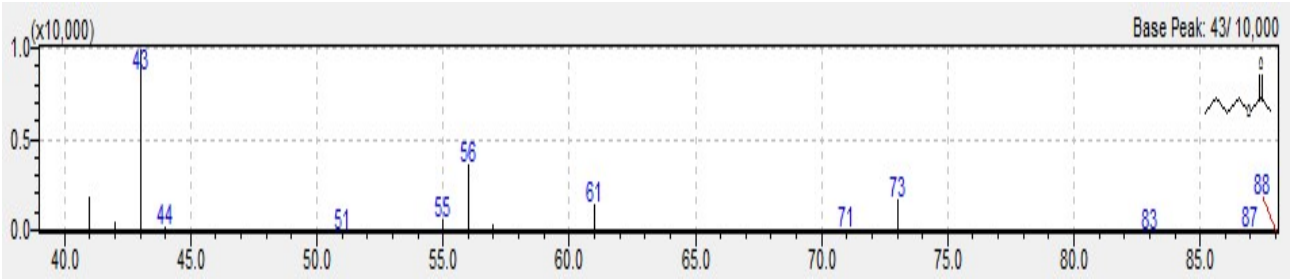

(x10,000)
Base Peak: 107/ 10,000
1.0
0.5
0.0
107
149
43
51
65
77
91
109
120
134
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210

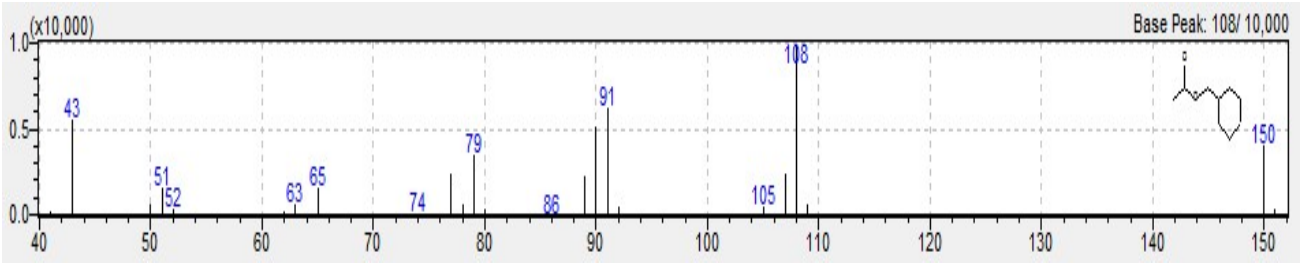

(x10,000)
Base Peak: 43/ 10,000
1.0
0.5
0.0
43
171
63
92
213
50
74
79
104
119
133
143
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210

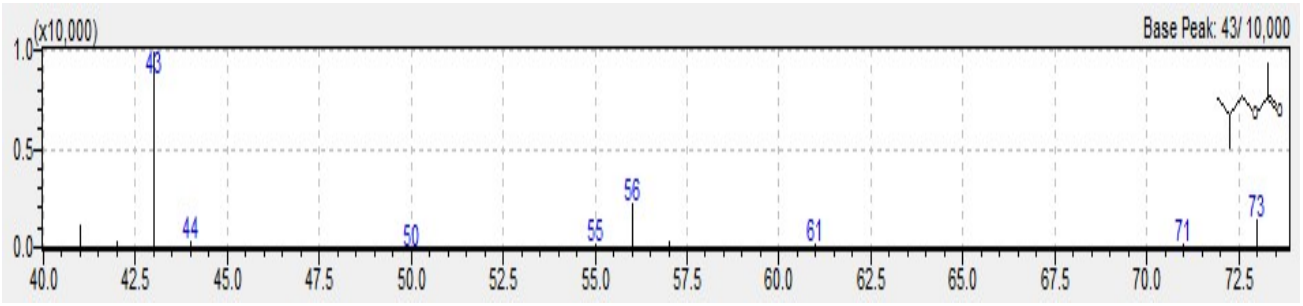

(x10,000)
Base Peak: 93/ 10,000
1.0
0.5
0.0
93
135
43
44
51
54
63
66
73
77
79
88
94
106
119
40 50 60 70 80 90 100 110 120 130

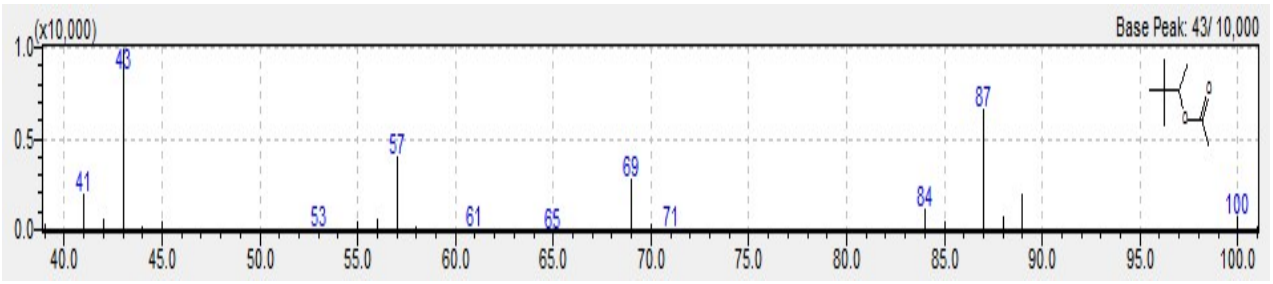

(x10,000)
Base Peak: 143/ 10,000
1.0
0.5
0.0
143
185
115
43
51
63
75
89
101
127
154
169
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210

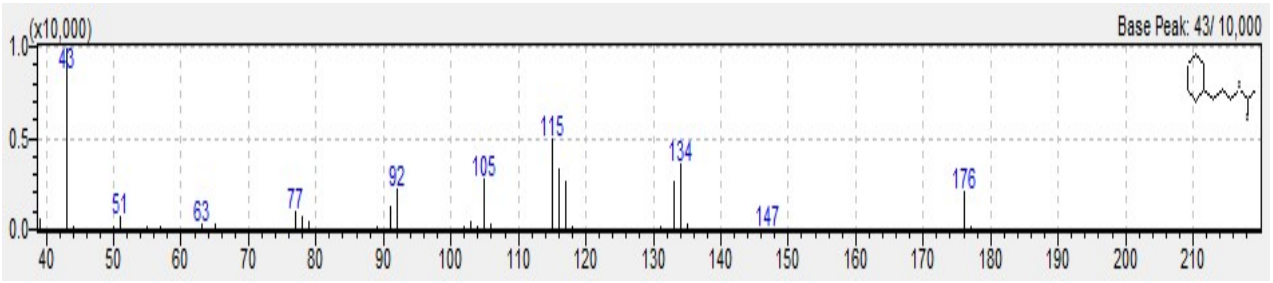

(x10,000)
Base Peak: 106/ 10,000
1.0
0.5
0.0
106
43
120
163
51
77
148
63
91
118
149
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210

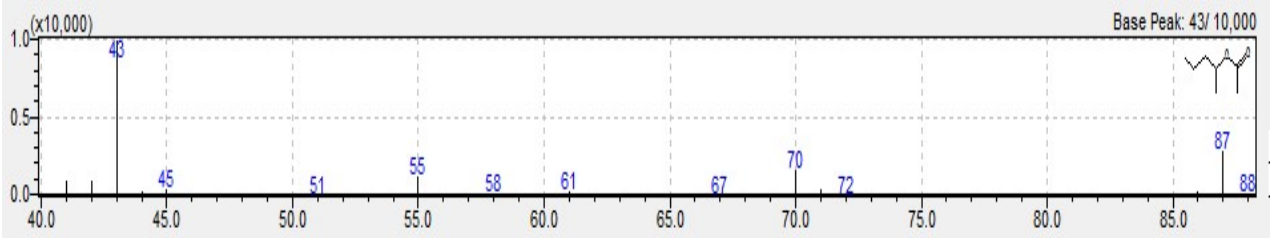

(x10,000)
Base Peak: 43/ 10,000
1.0
0.5
0.0
43
56
73
88
44
51
55
61
71
83
87
40.0 45.0 50.0 55.0 60.0 65.0 70.0 75.0 80.0 85.0

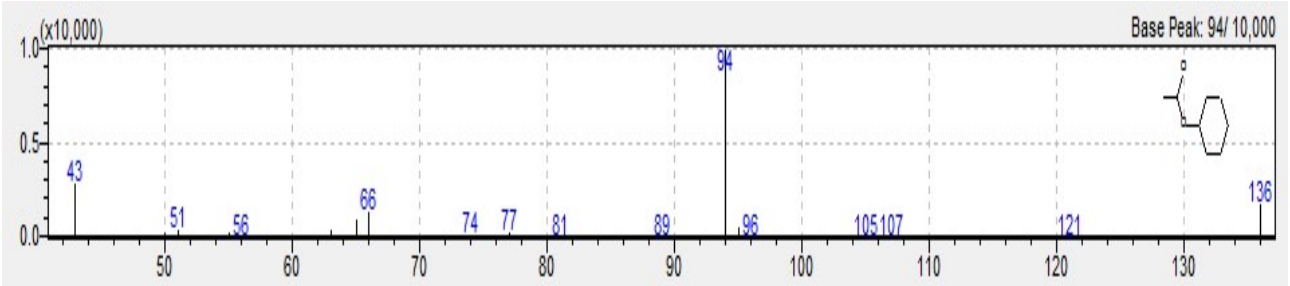

(x10,000)
Base Peak: 108/ 10,000
43
51
52
63
65
74
79
86
91
105
108
150


(x10,000)
Base Peak: 43/ 10,000
43
44
50
55
56
61
71
73


(x10,000)
Base Peak: 43/ 10,000
41
43
53
57
61
65
69
71
84
87
100


(x10,000)
Base Peak: 43/ 10,000
43
51
63
77
92
105
115
134
147
176


(x10,000)
Base Peak: 43/ 10,000
43
45
51
55
58
61
67
70
72
87
88


(x10,000)
Base Peak: 94/ 10,000
43
51
56
66
74
77
81
89
94
96
105
107
121
136

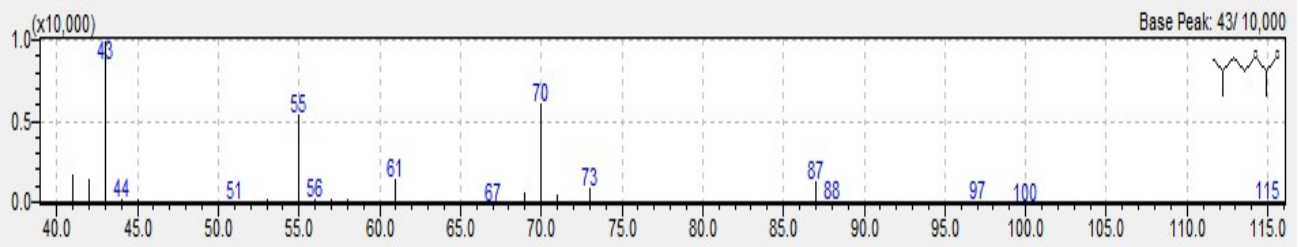


Figure S4: The GC-MS spectra of the plausible products obtain during acetylation.