Supporting information

Introduction of Fe_3O_4@MCM-41/Zr@Piperazine as an efficient catalyst for the protection of alcohols and amines

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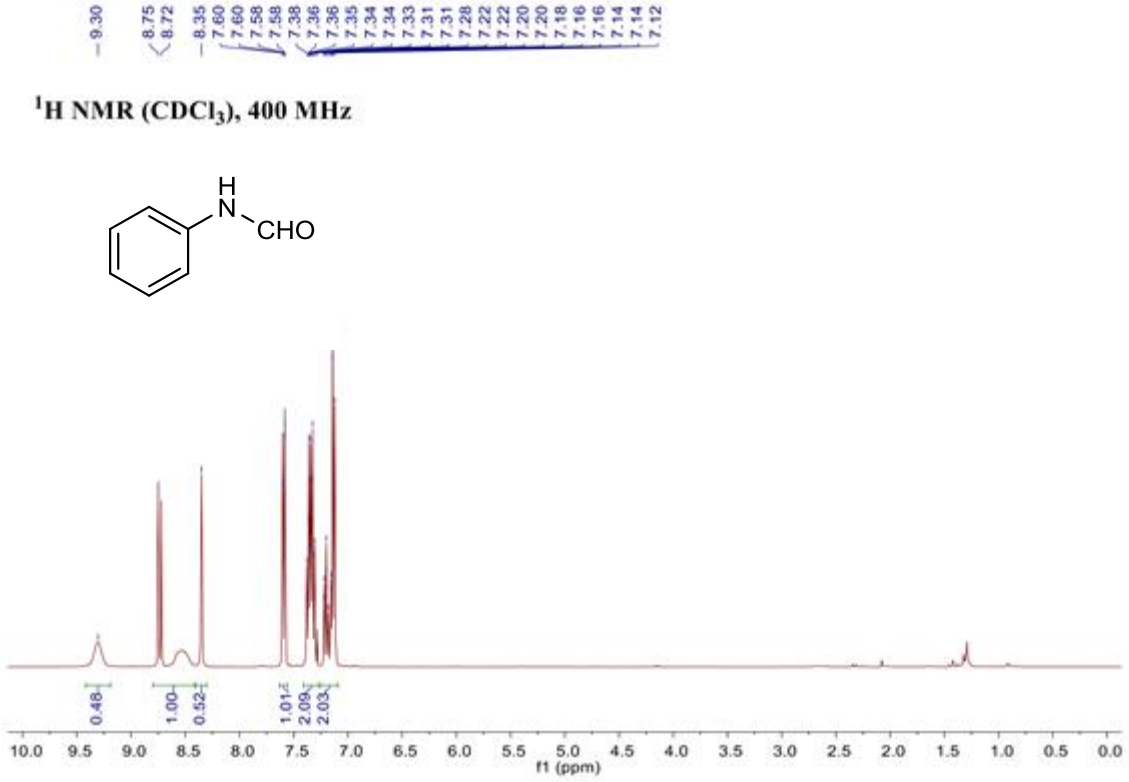
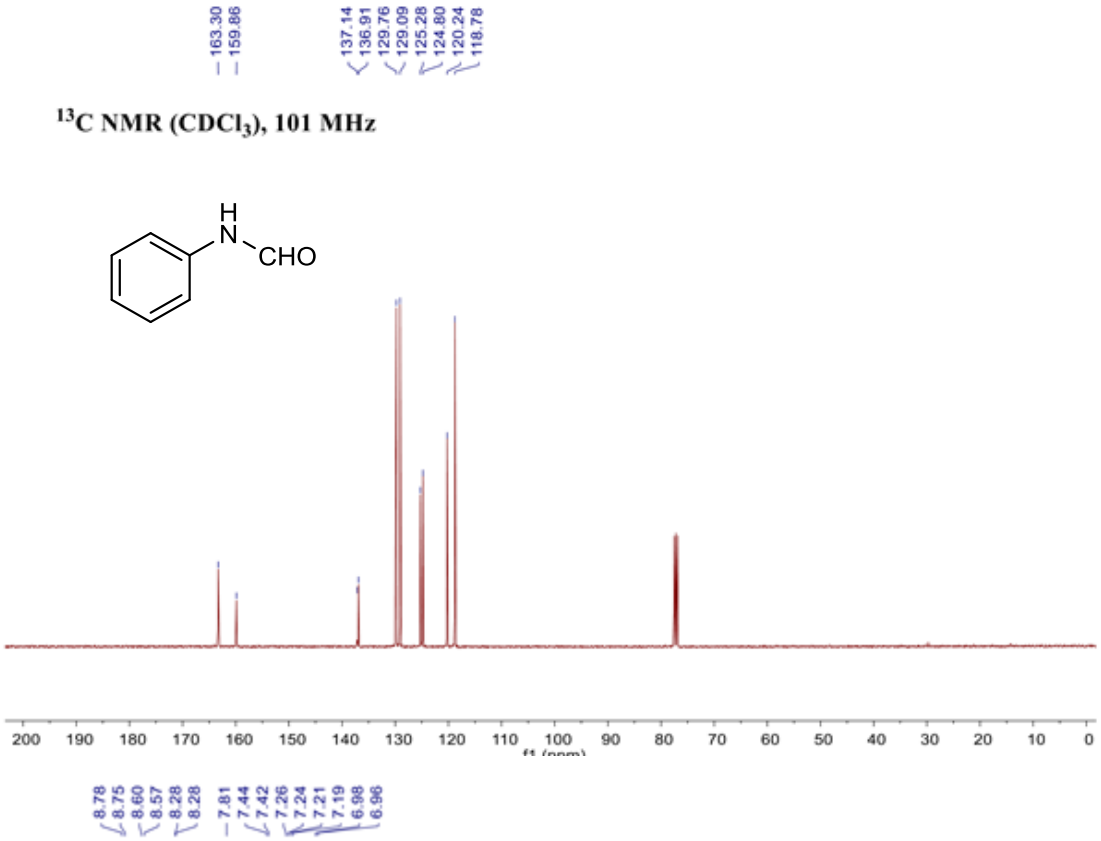
Supplemental Materials

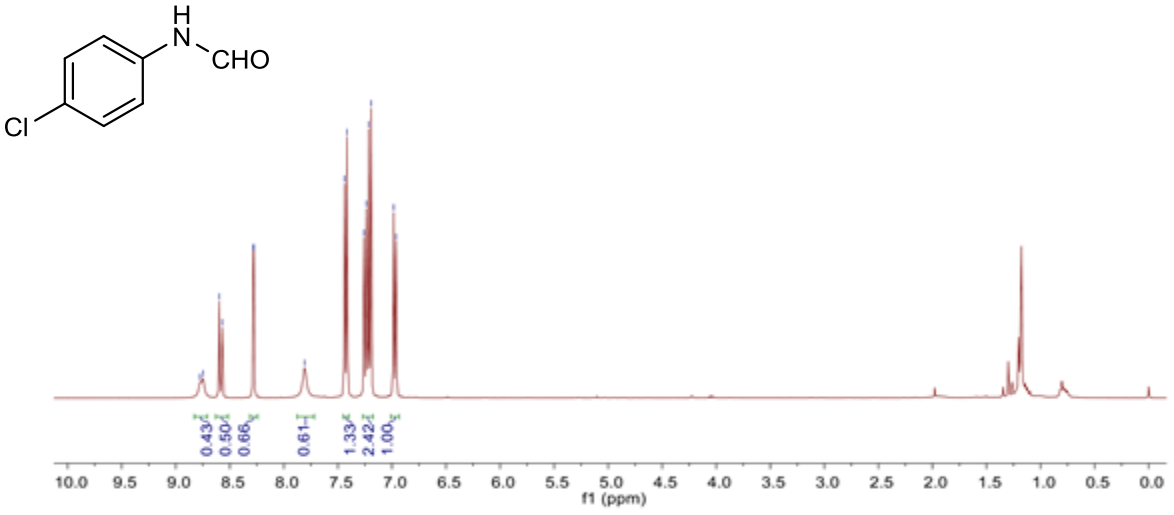
Table 2. Formylation of amines

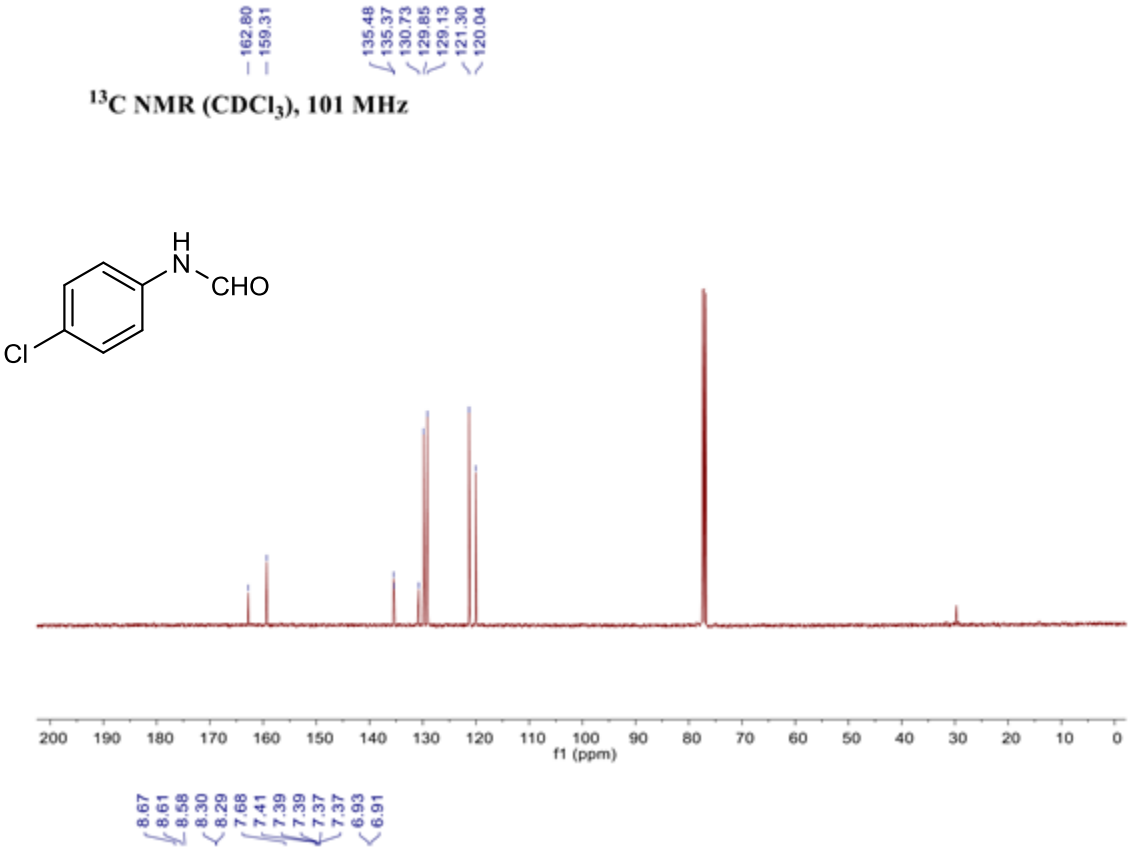




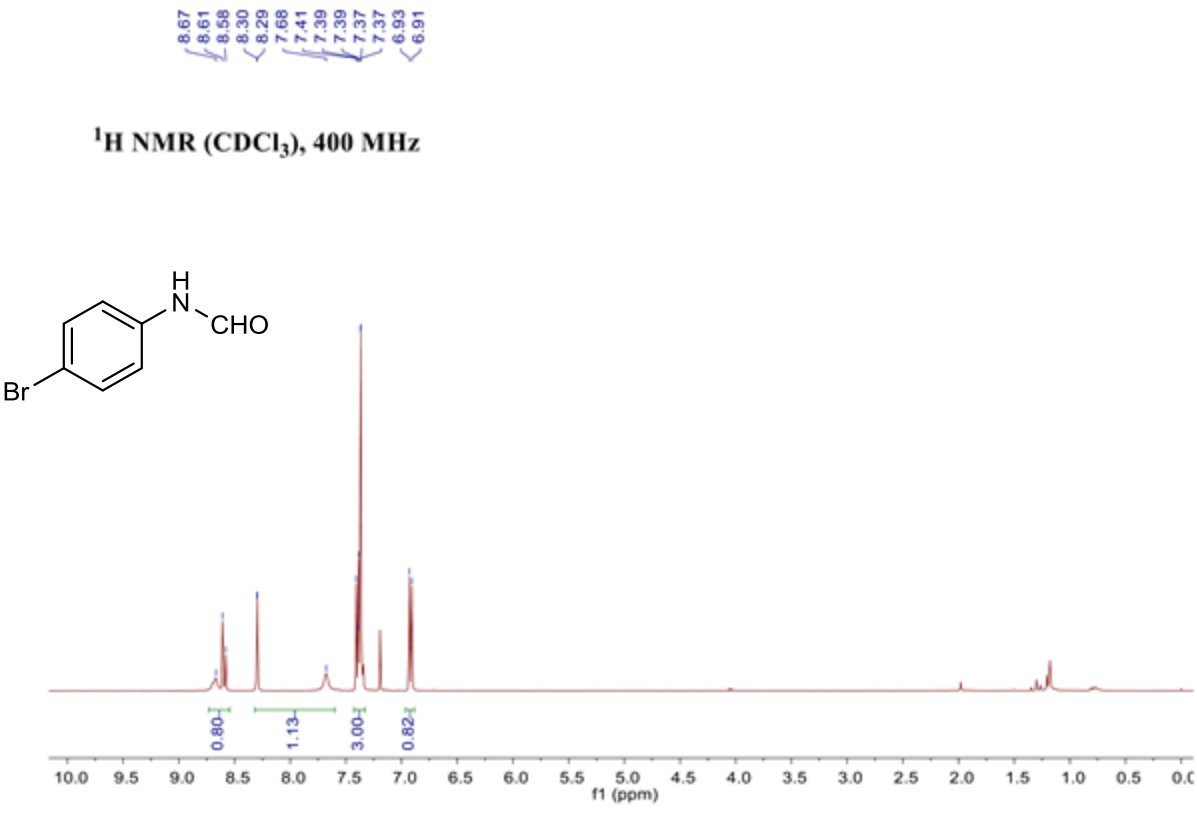
^{13}C NMR ($CDCl_3$), 101 MHz

^{1}H NMR ($CDCl_3$), 400 MHz



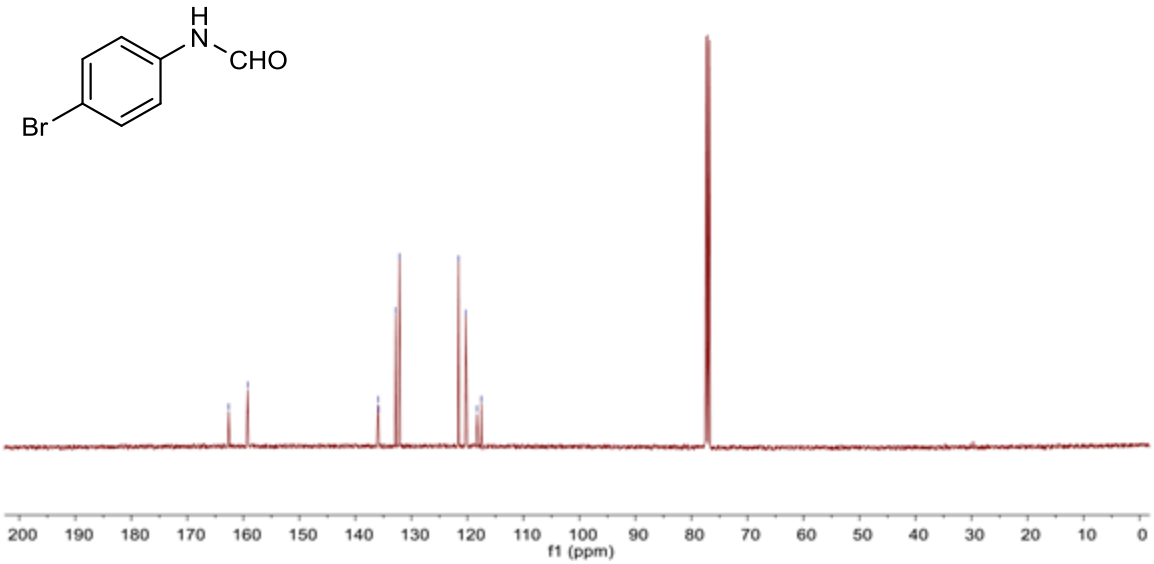


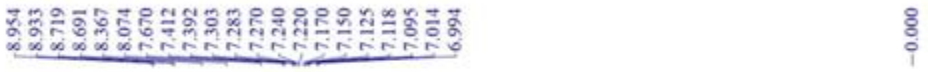
^{13}C NMR ($CDCl_3$), 101 MHz



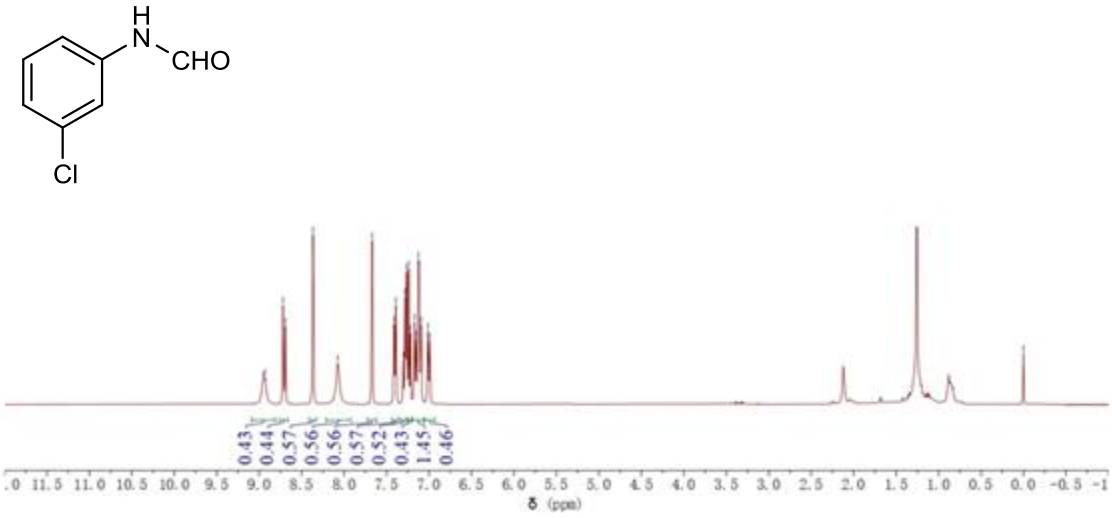
^{1}H NMR ($CDCl_3$), 400 MHz

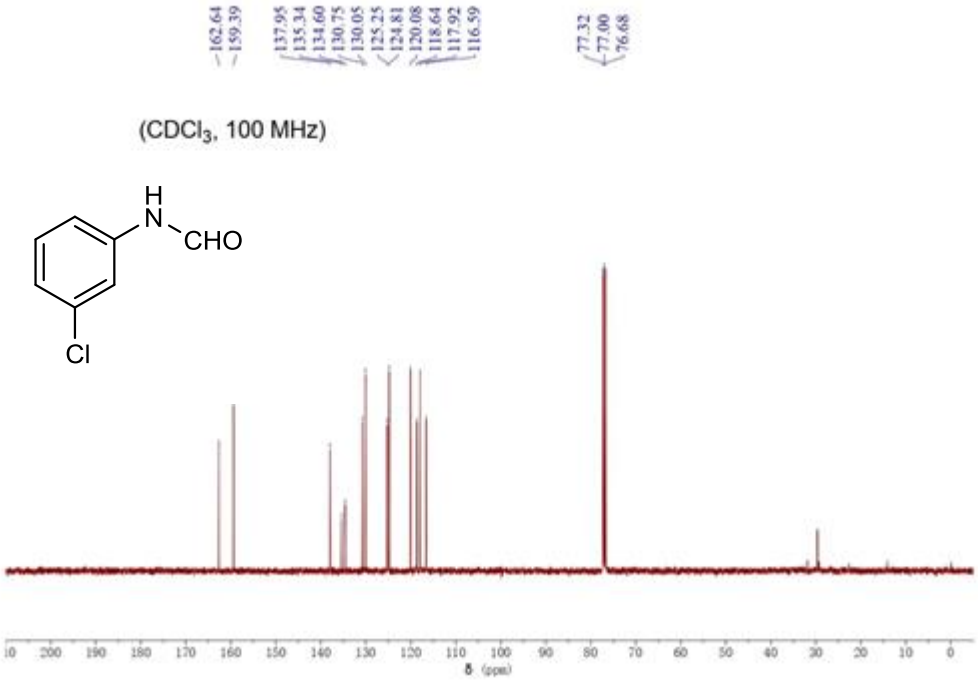
^{13}C NMR ($CDCl_3$), 101 MHz



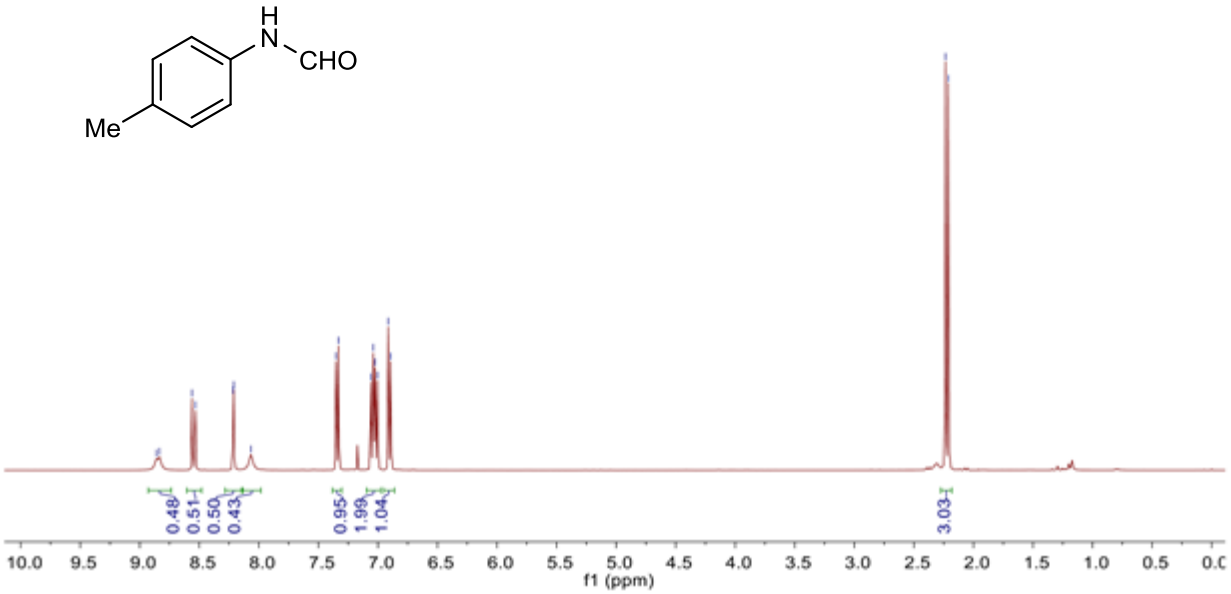


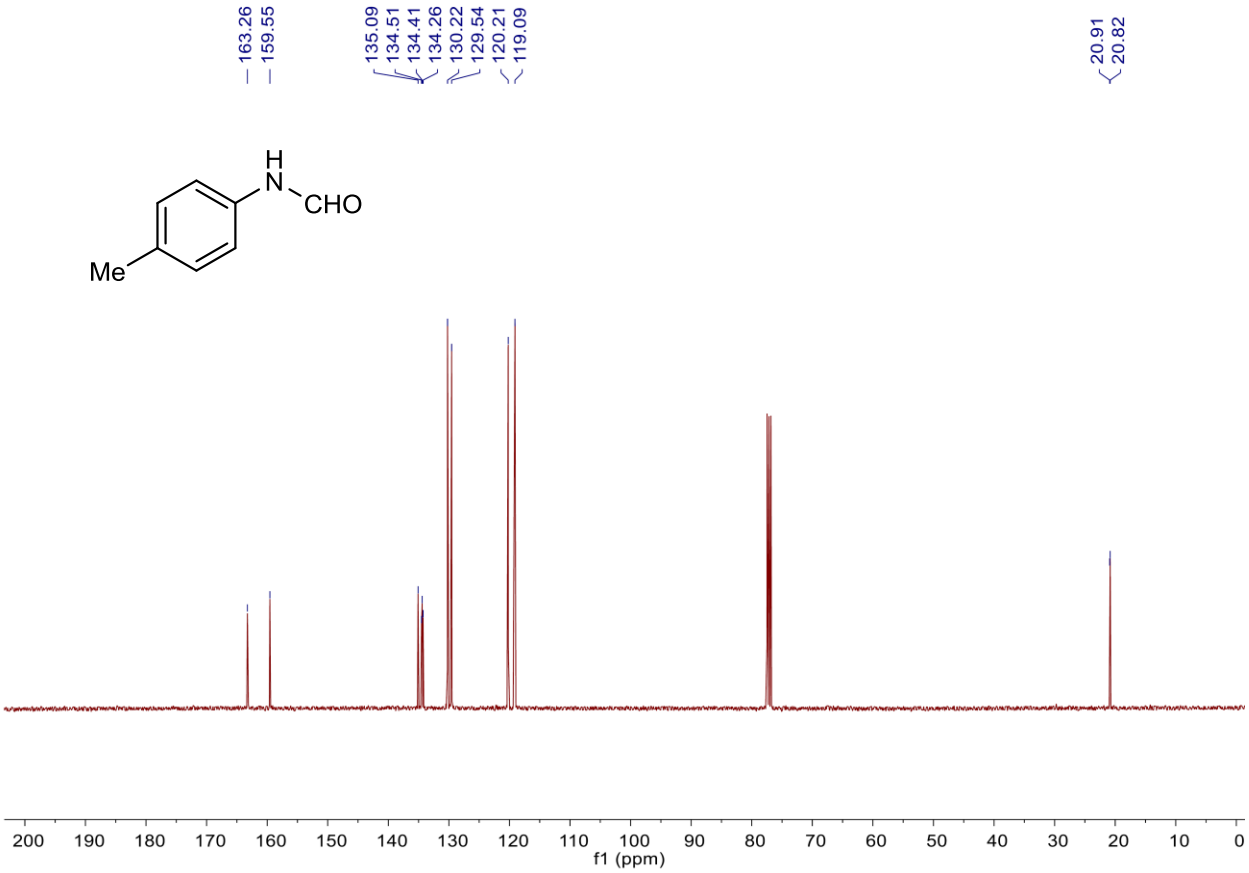
($CDCl_3$, 400 MHz)



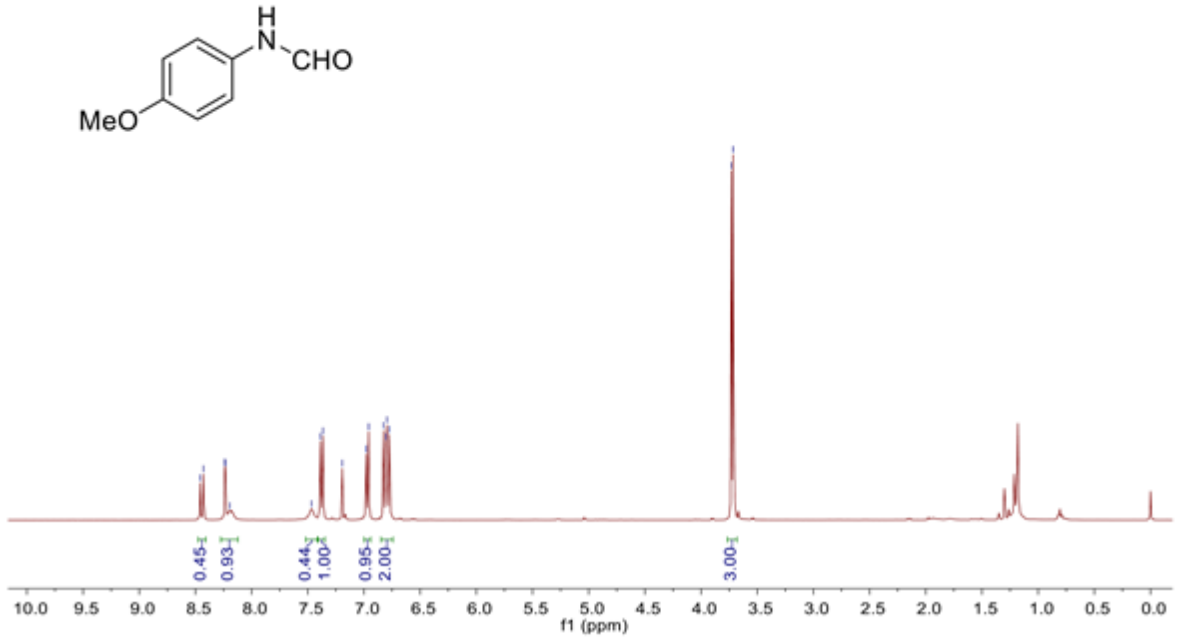


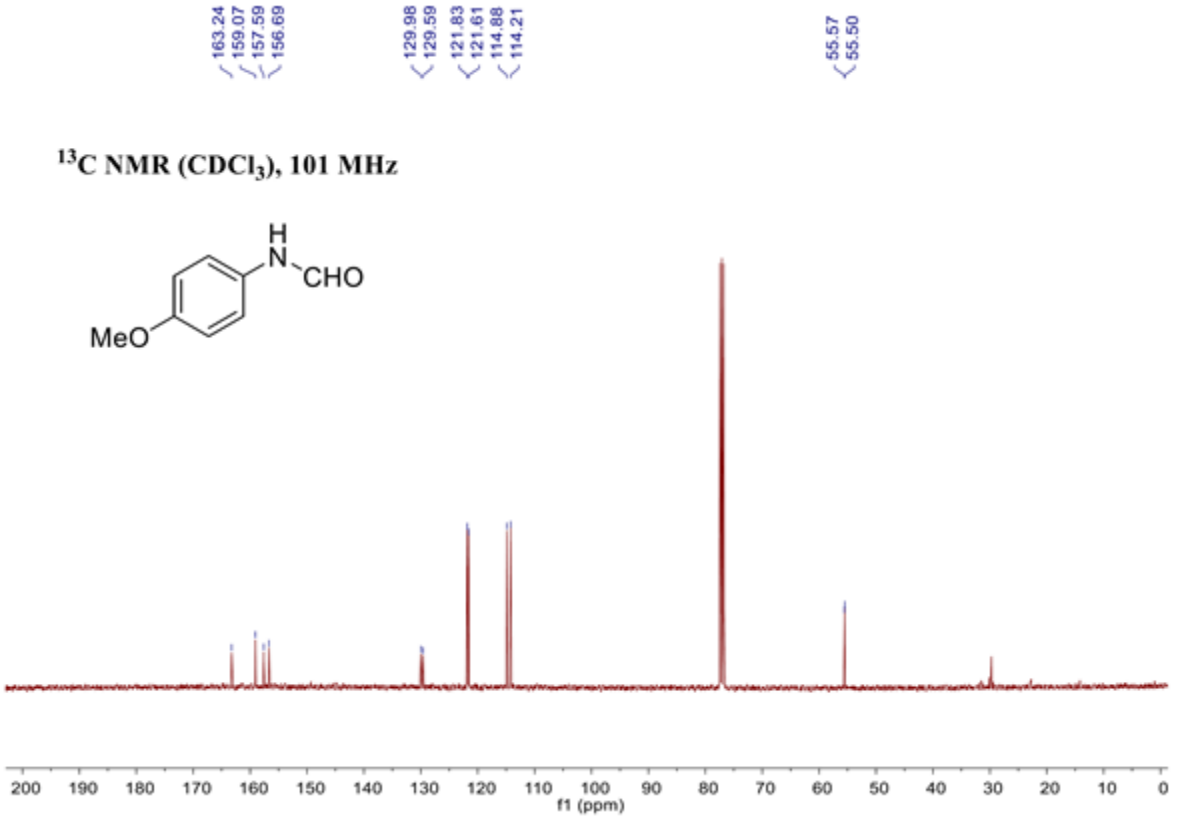
^{1}H NMR ($CDCl_3$), 400 MHz



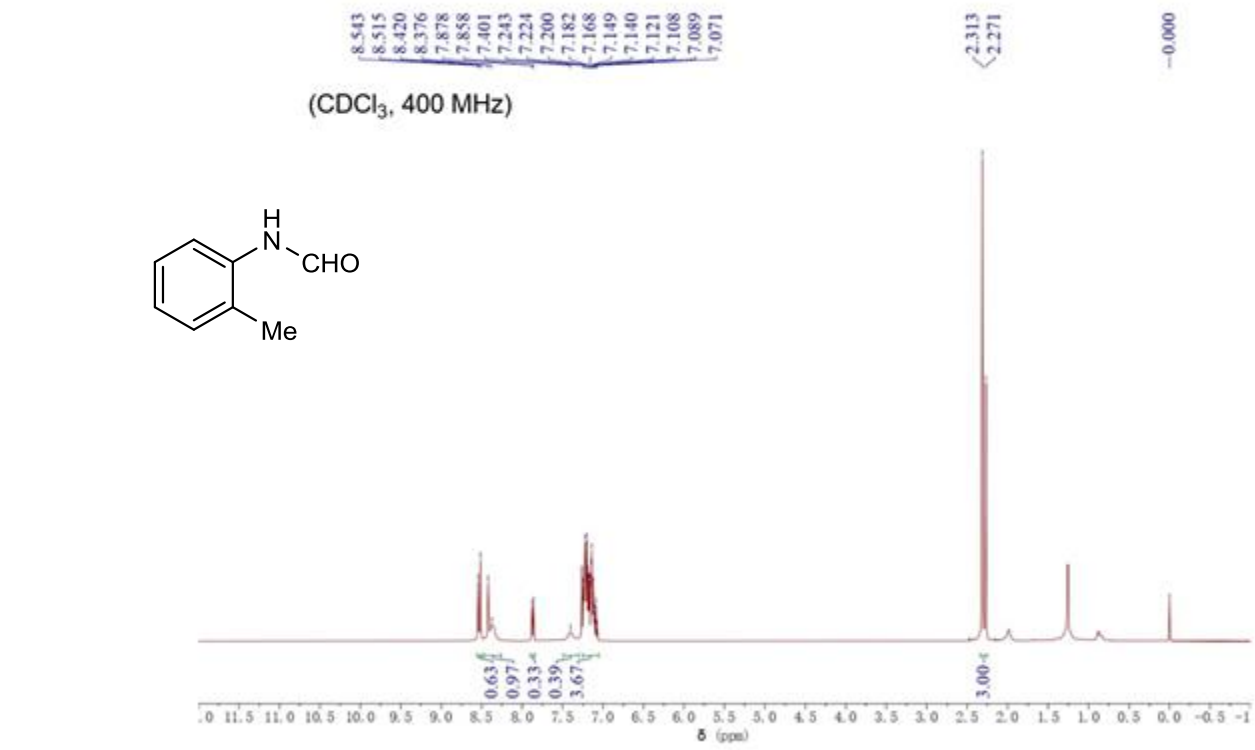


^{1}H NMR ($CDCl_3$), 400 MHz

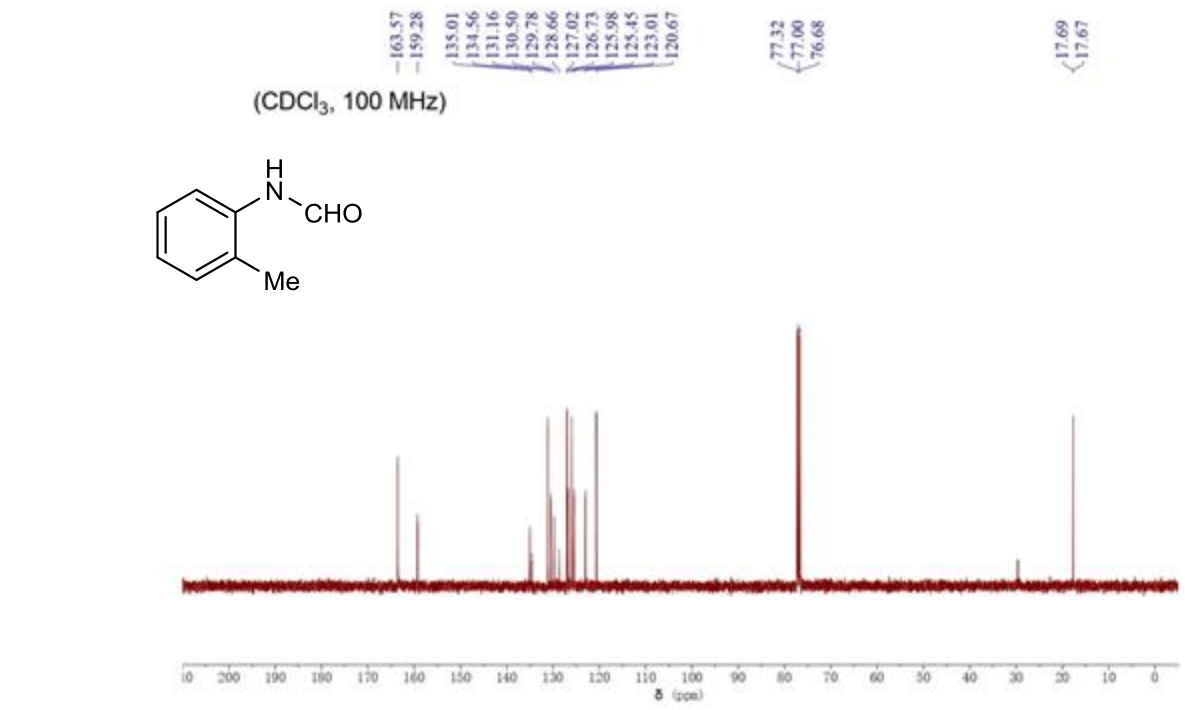




^{13}C NMR ($CDCl_3$), 101 MHz



($CDCl_3$, 400 MHz)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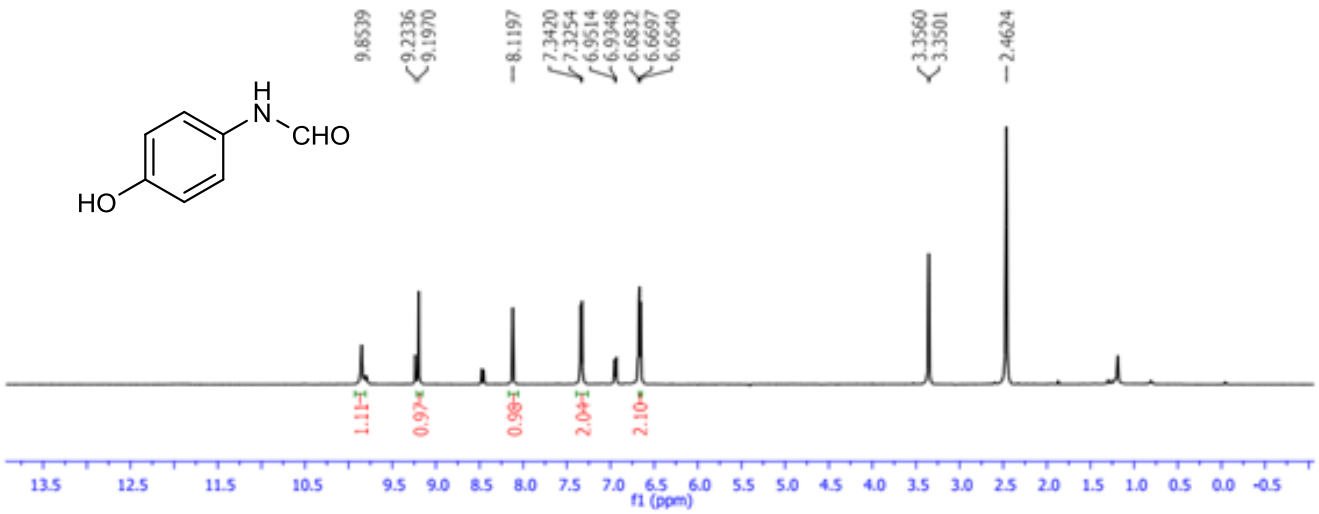
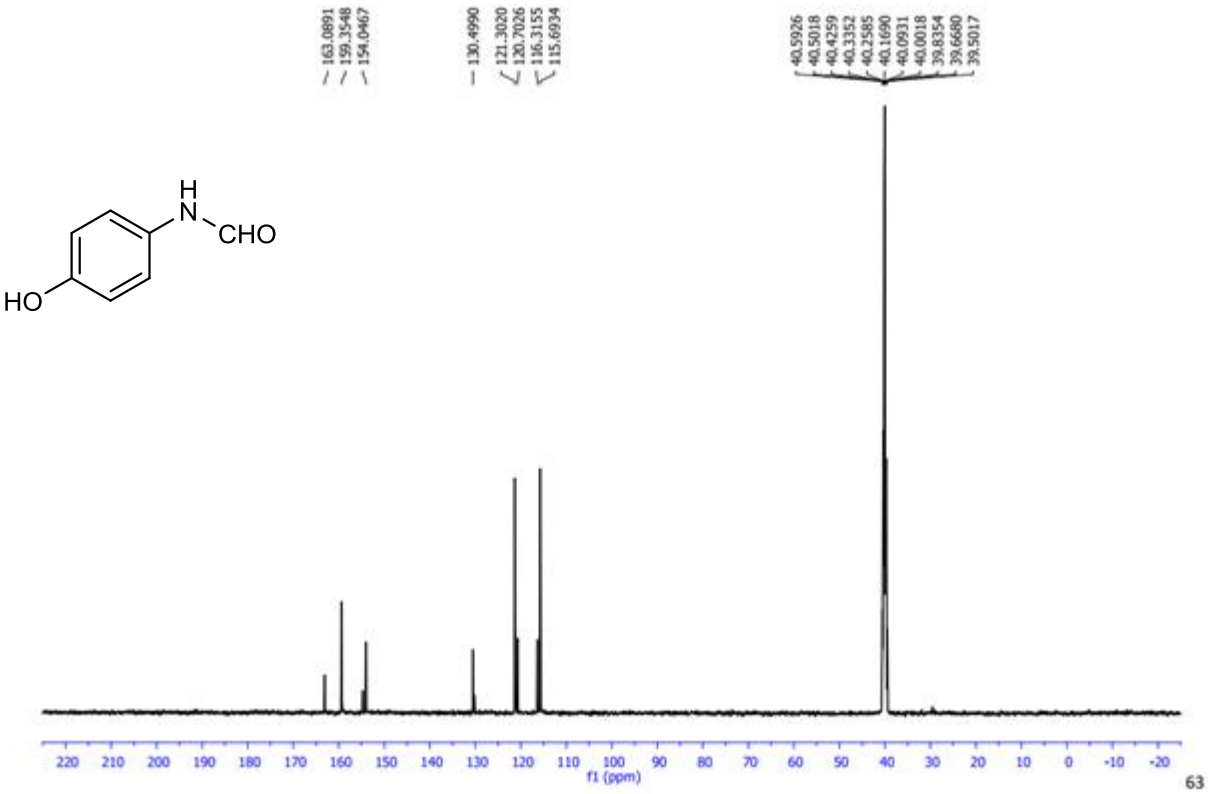
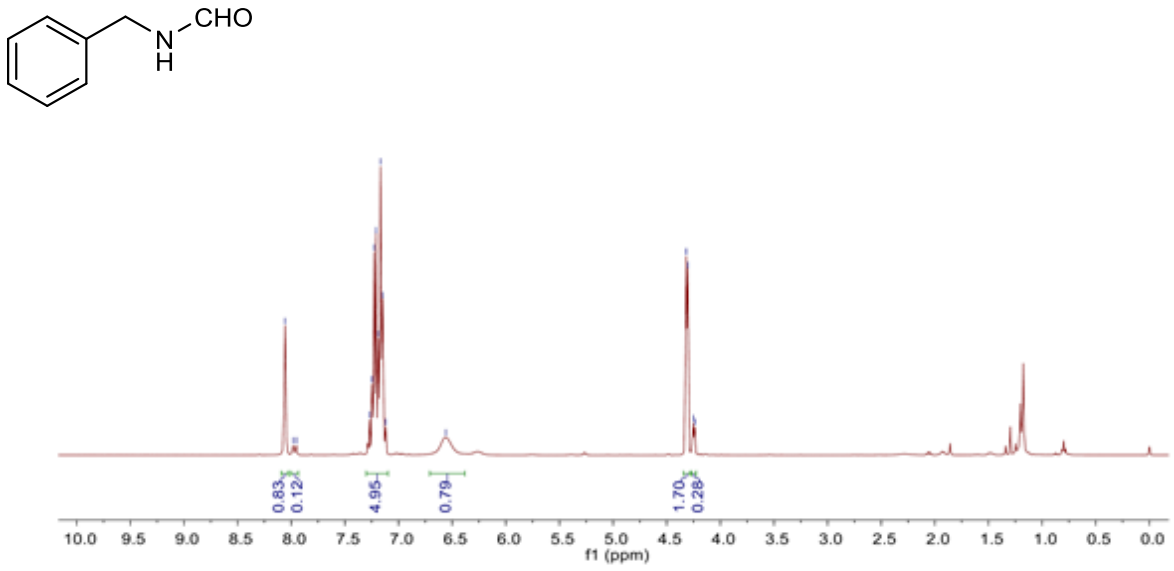
159.28
135.01
134.56
131.16
130.50
129.78
128.66
127.02
126.73
125.98
125.45
123.01
120.67
77.32
77.00
76.68
17.69
17.67
(CDCl3, 100 MHz)
H
N
CHO
Me
δ (ppm)


9.8539
9.2336
9.1970
8.1197
7.3420
7.3254
6.9514
6.9348
6.6832
6.6697
6.6540
3.3560
3.3501
2.4624
H
N
CHO
HO
1.11
0.97
0.98
2.04
2.10
f1 (ppm)

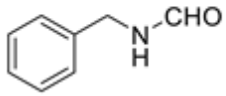


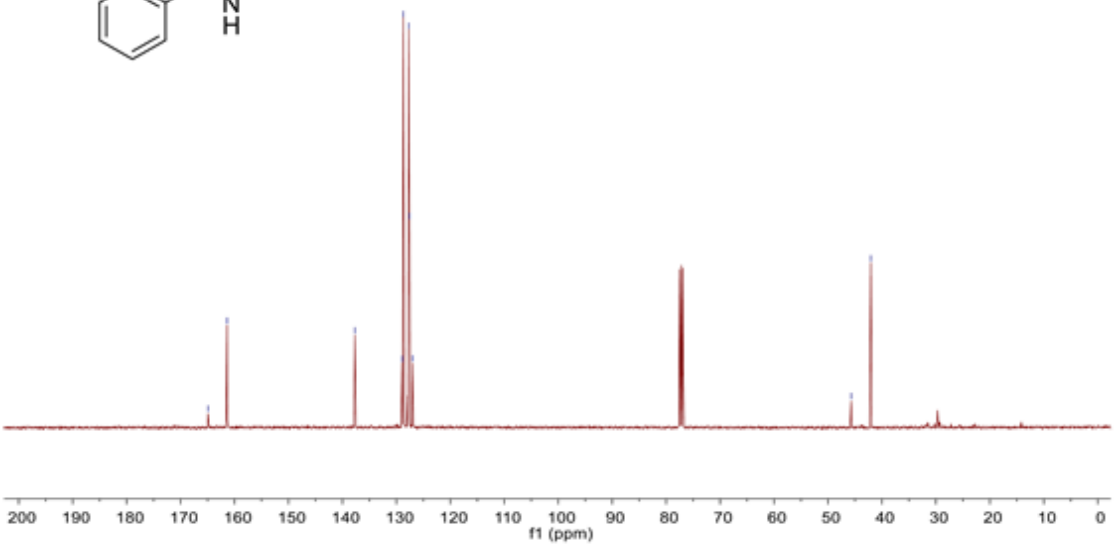
63

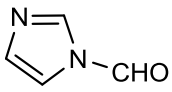
^{1}H NMR ($CDCl_3$), 400 MHz

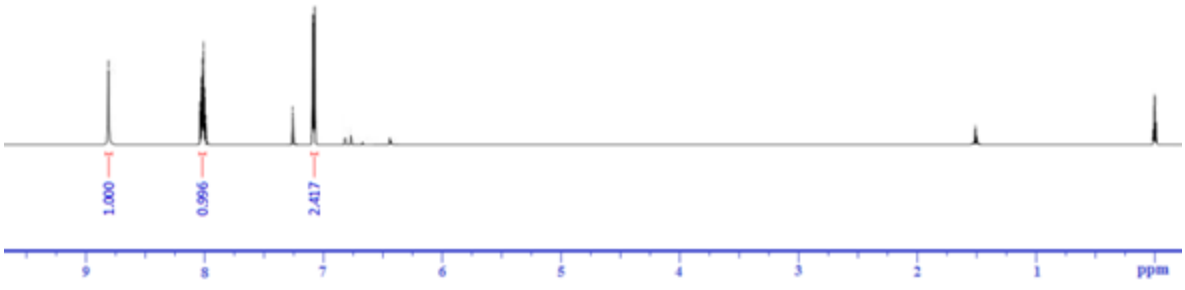


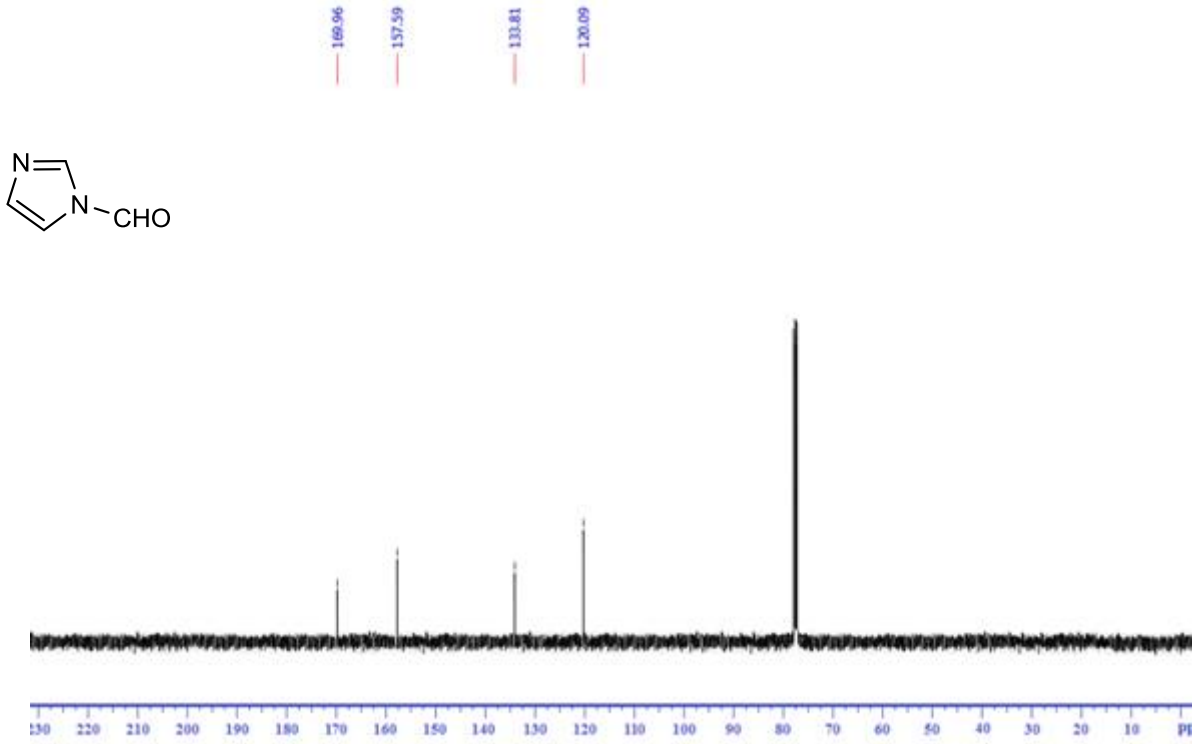
^{13}C NMR ($CDCl_3$), 101 MHz







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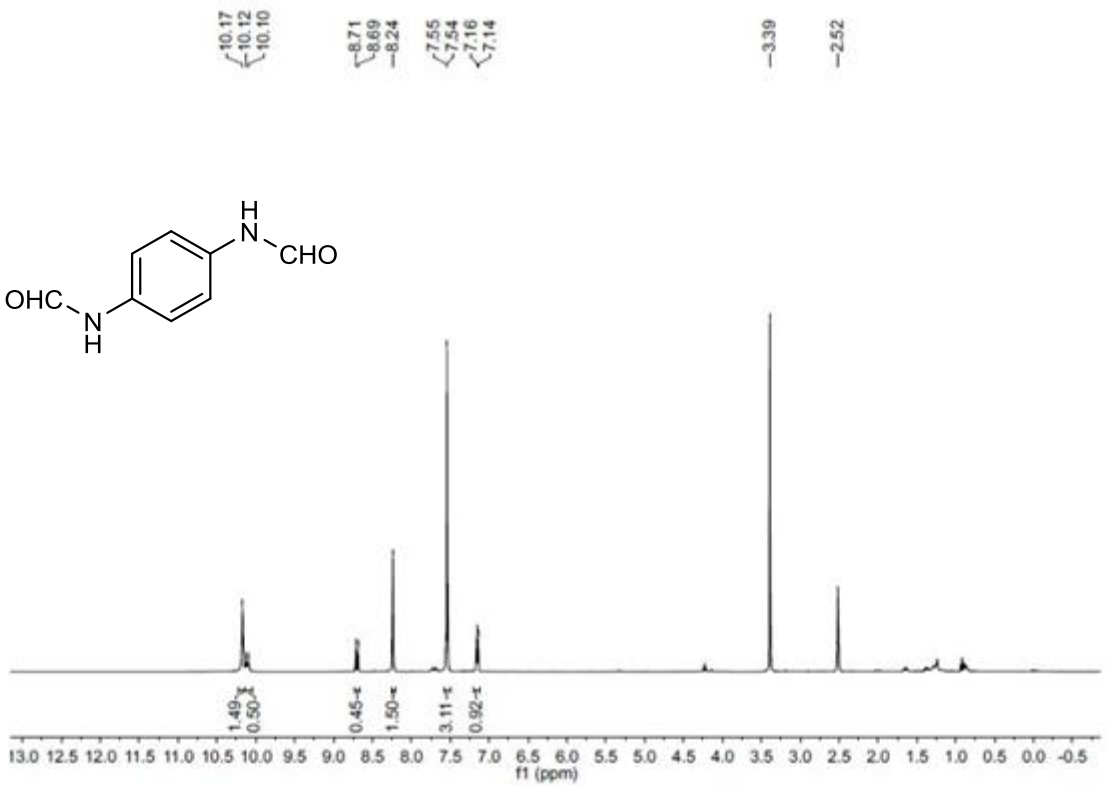
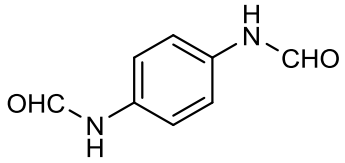
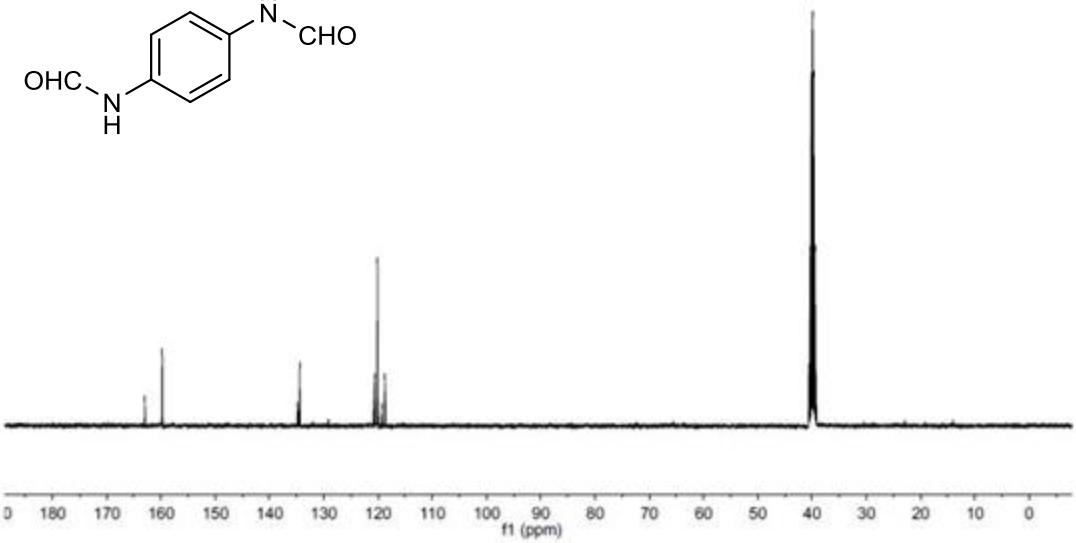
157.59
133.81
120.09
N
N
CHO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

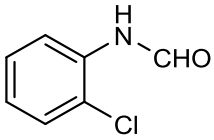

10.17
10.12
10.10
8.71
8.69
8.24
7.55
7.54
7.16
7.14
3.39
2.52
H
N
CHO
OHC
N
H
1.49
0.50
0.45
1.50
3.11
0.92
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

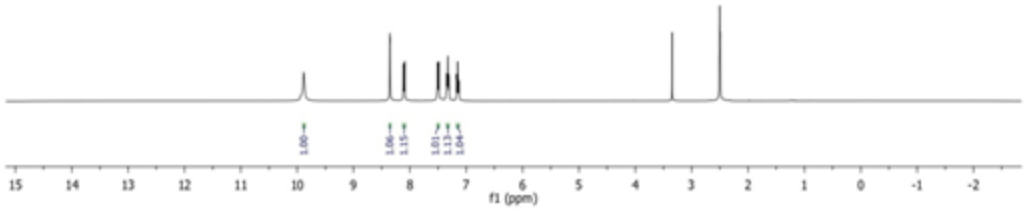

162.94
159.76
134.82
134.46
120.62
120.05
119.30
118.70
40.56
40.35
40.14
39.93
39.72
39.52
39.31


H
N
CHO
OHC
N
H


0 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


20062022-peptide
fa-5


H
N
CHO
Cl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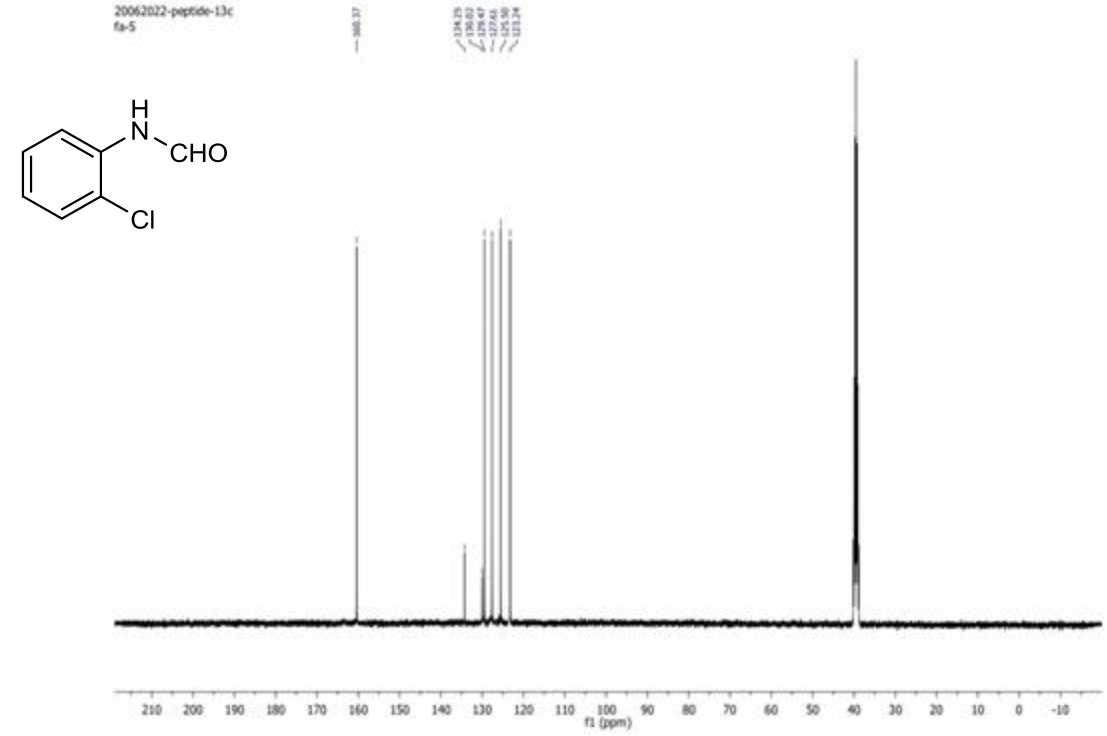
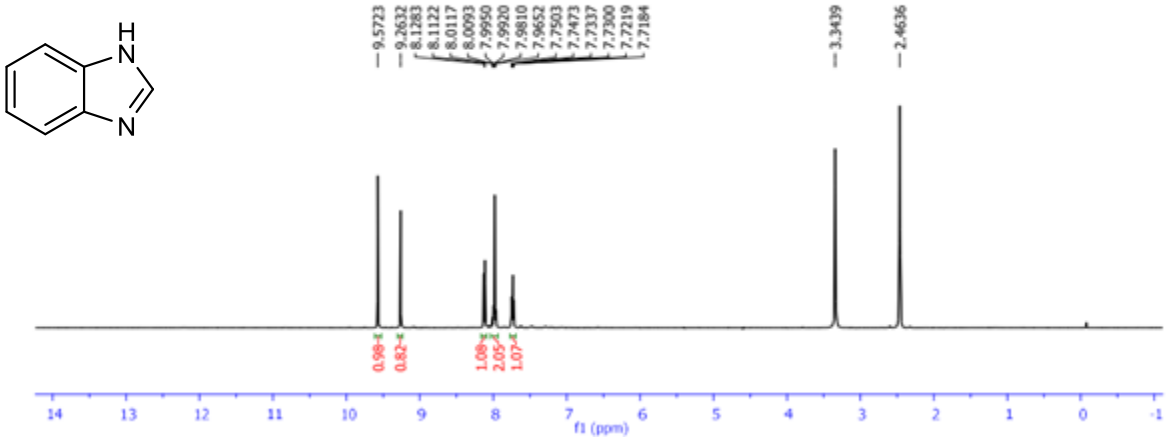
f1 (ppm)


20062022-peptide-13c
fa-5
H
N
CHO
Cl
160.37
134.35
130.03
129.47
127.61
125.50
123.24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
N
N
9.5723
9.2632
8.1283
8.1122
8.0117
8.0093
7.9950
7.9920
7.9810
7.9652
7.7503
7.7473
7.7337
7.7300
7.7219
7.7184
3.3439
2.4636
0.98
0.82
1.08
2.05
1.07
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

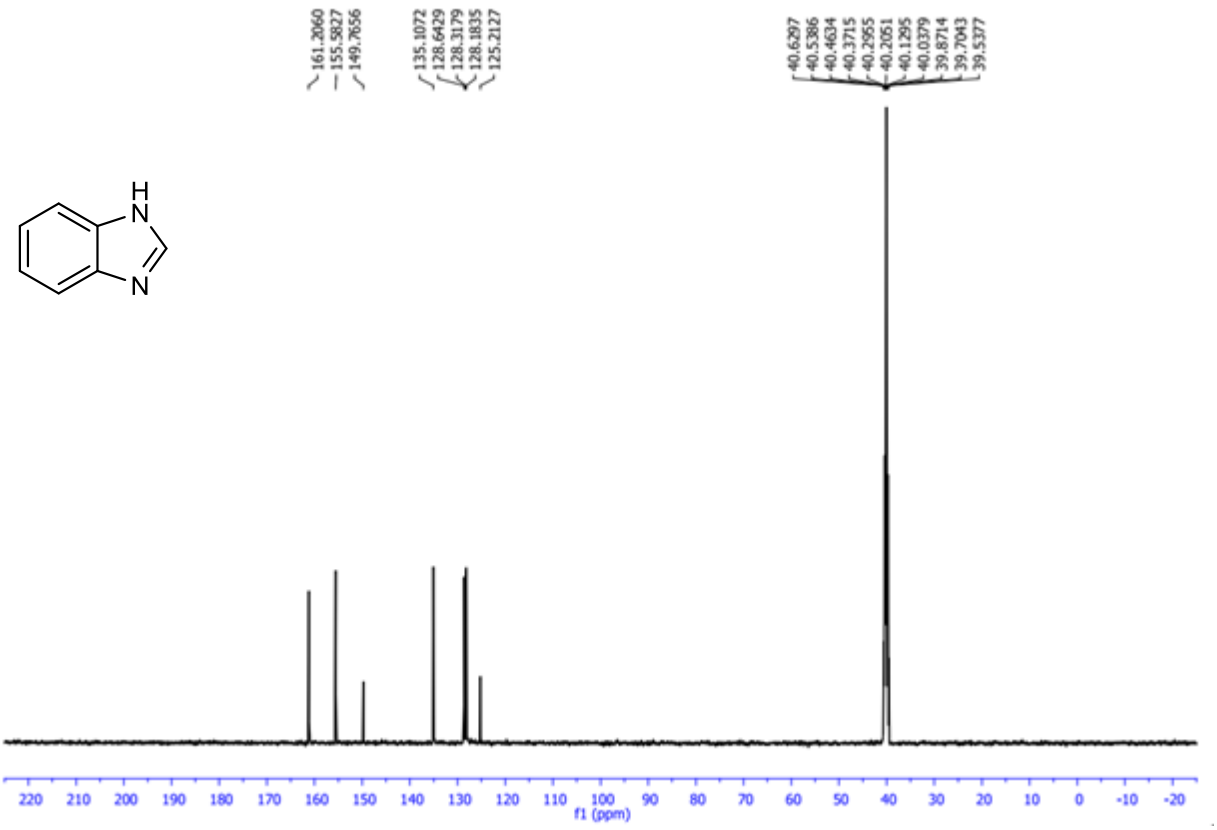
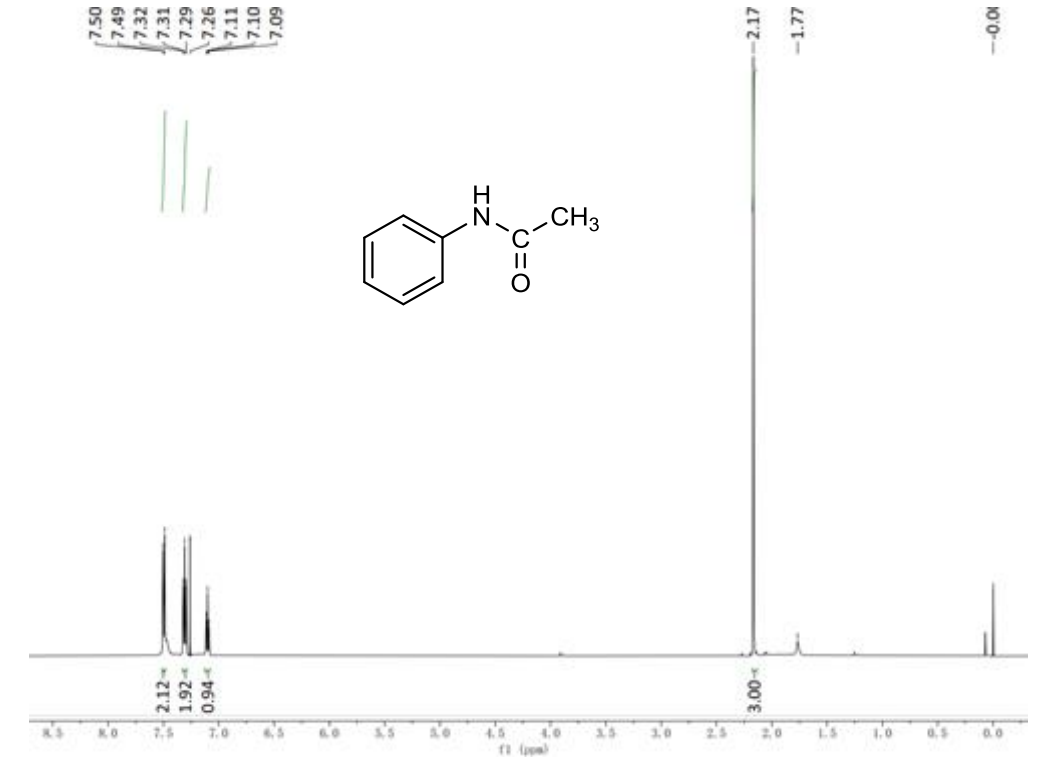
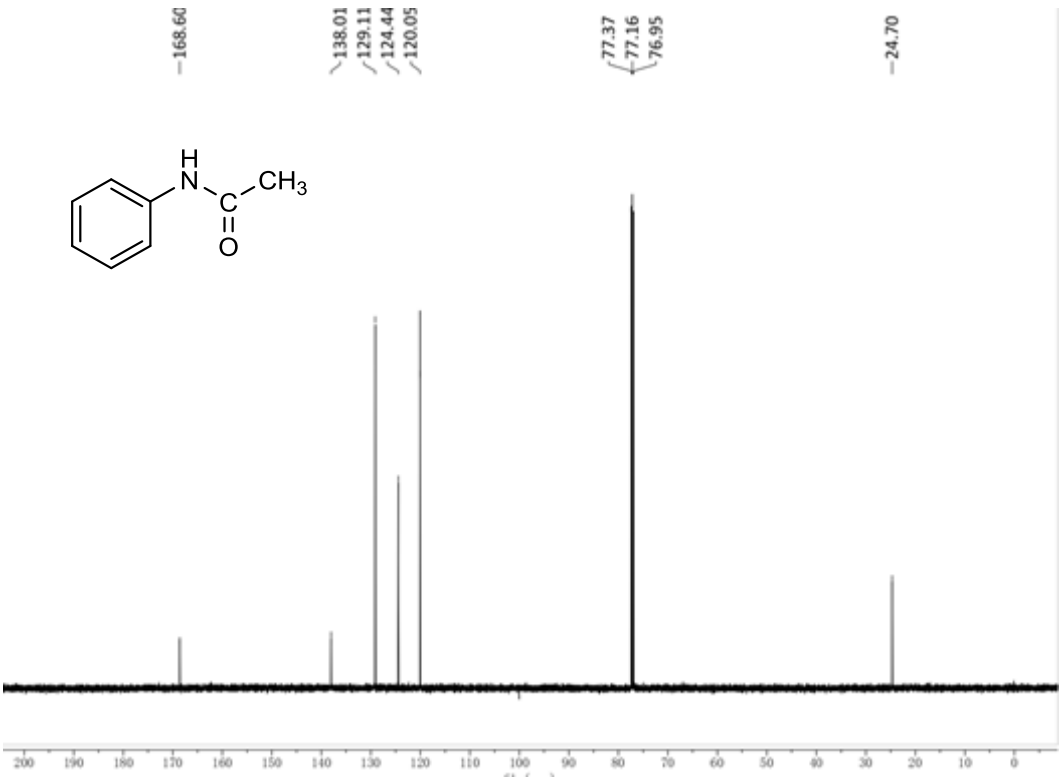
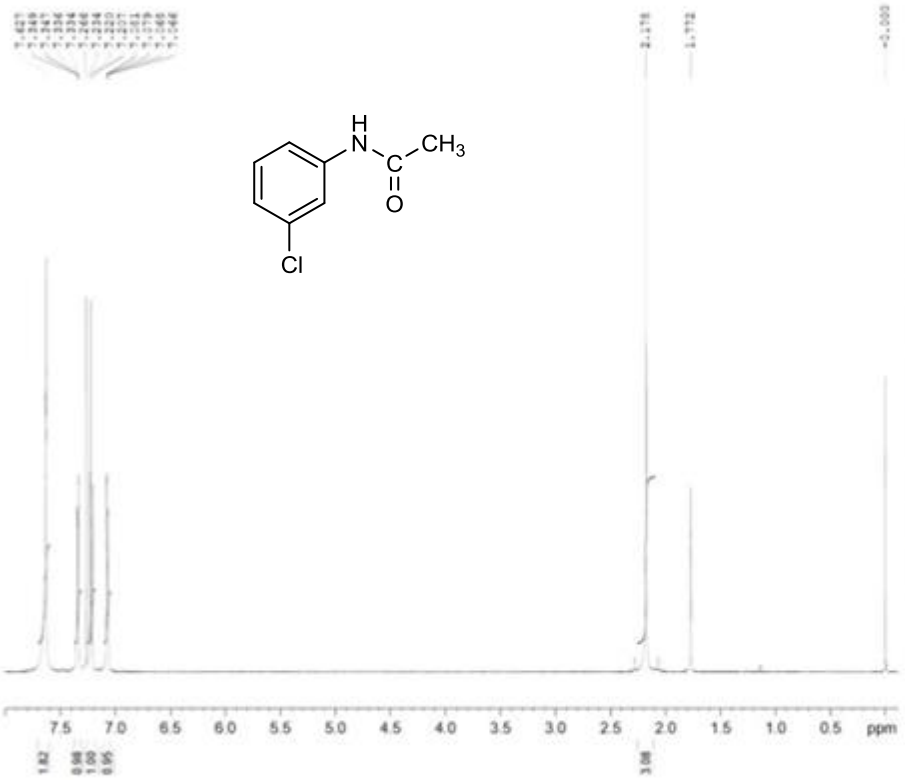


Table 5: Acetylation of mines and alcohols


7.50
7.49
7.32
7.31
7.29
7.26
7.11
7.10
7.09
2.17
1.77
0.00
H
N
C
O
CH3
2.12
1.92
0.94
3.00
f1 (ppm)


168.60
138.01
129.11
124.44
120.05
77.37
77.16
76.95
24.70
H
N
C
O
CH3

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134909
GYG0552_1
Gyorke Gabor
2020.10.09. (DA)

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EXPNO                     11
PROCNO                     1

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Time                  23.46 h
INSTRUM                spect
PROBHD   Z145856_0002 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               12019.230 Hz
FIDRES             0.366798 Hz
AQ                 2.7262976 sec
RG                    196.07
DW                   41.600 usec
DE                   25.00 usec
TE                   295.0 K
D1                1.00000000 sec
TD0                       1
SFO1          600.1037056 MHz
NUC1                     1H
P1                    11.50 usec
PLW1          28.00000000 W

F2 - Processing parameters
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SF            600.1000119 MHz
WDW                      EM
SSB                   0
LB                    0.10 Hz
GB                    0
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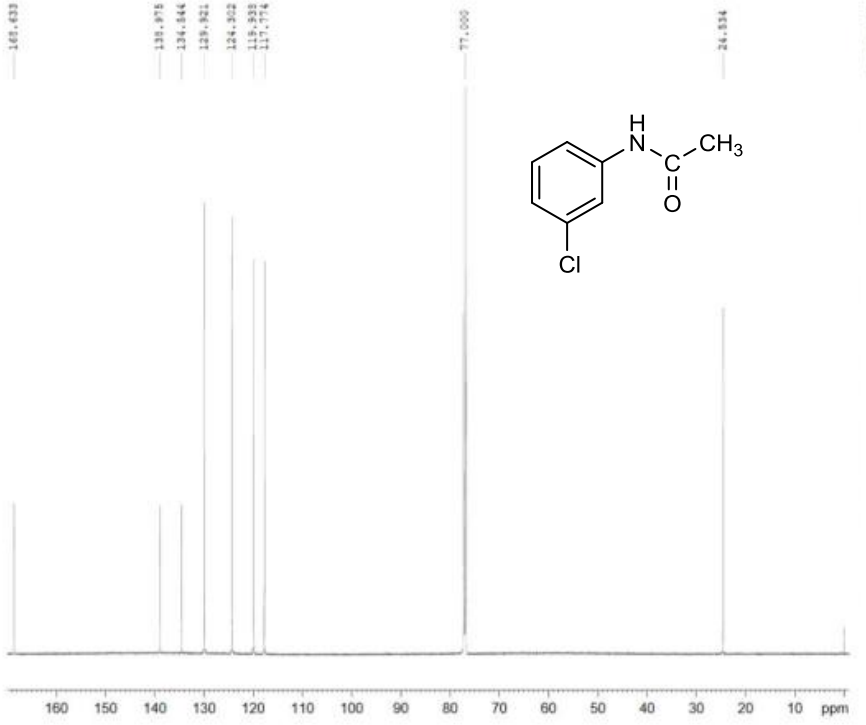


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Standard 13C
134909
GYG0552_1
Gyorke Gabor
2020.10.09. (DA)

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EXPNO                     12
PROCNO                     1

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Time                   0.55 h
INSTRUM                spect
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PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               36231.883 Hz
FIDRES             1.105709 Hz
AQ                 0.9043968 sec
RG                    196.07
DW                   13.800 usec
DE                   18.00 usec
TE                   295.0 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                       1
SFO1          150.9103545 MHz
NUC1                     13C
P1                   10.00 usec
PLW1          63.09999847 W
SFO2          600.1024004 MHz
NUC2                     1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2          30.48800087 W
PLW12          0.63000000 W
PLW13          0.31637999 W

F2 - Processing parameters
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WDW                      EM
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LB                    1.00 Hz
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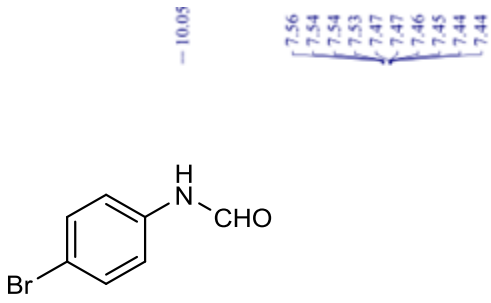
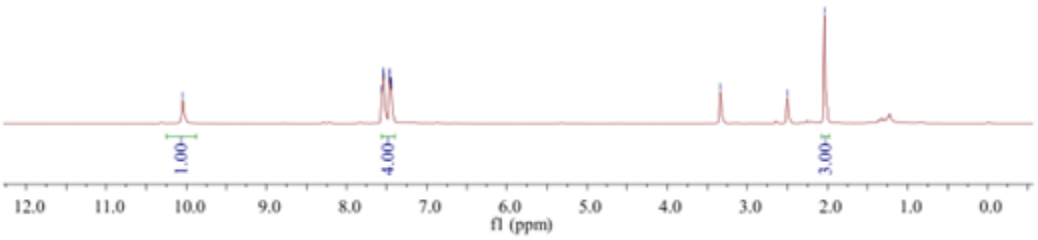
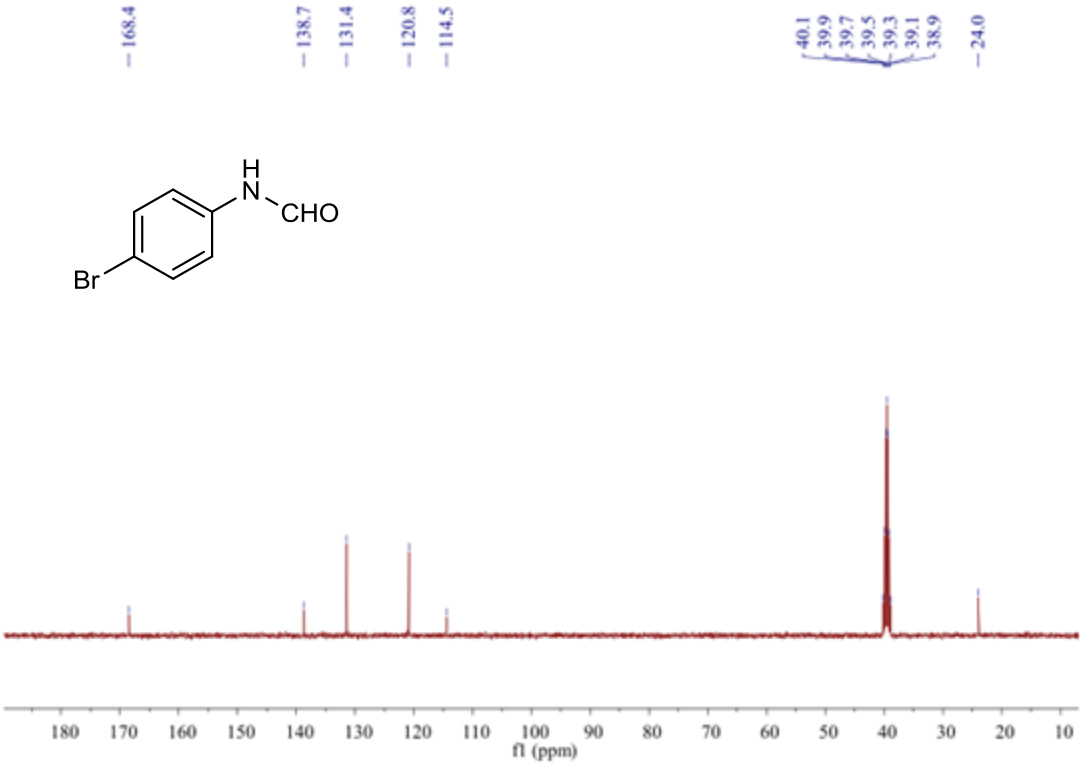
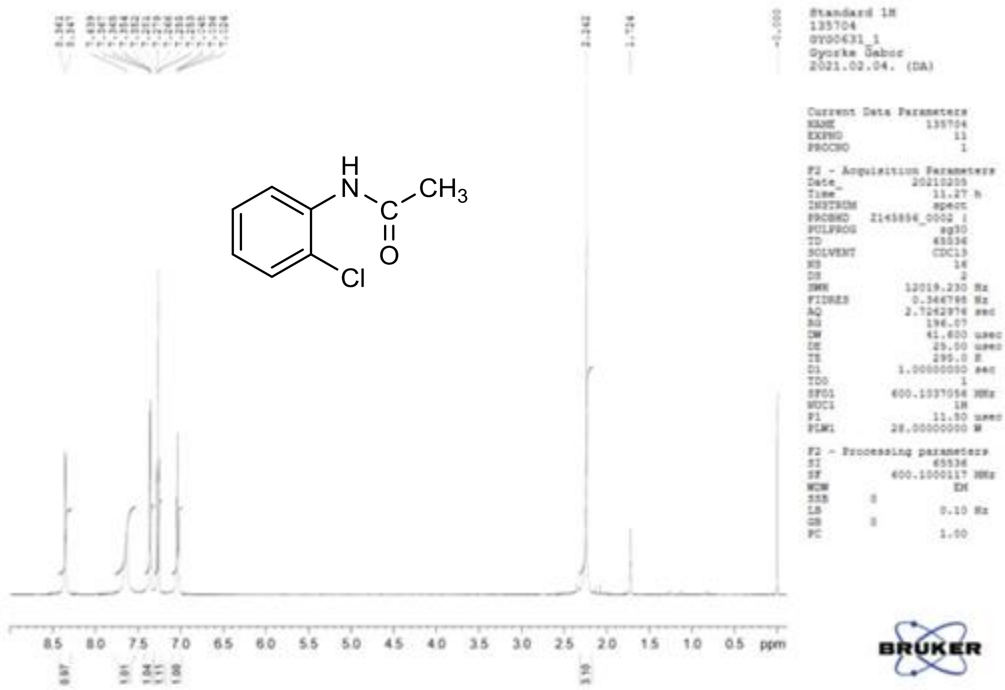
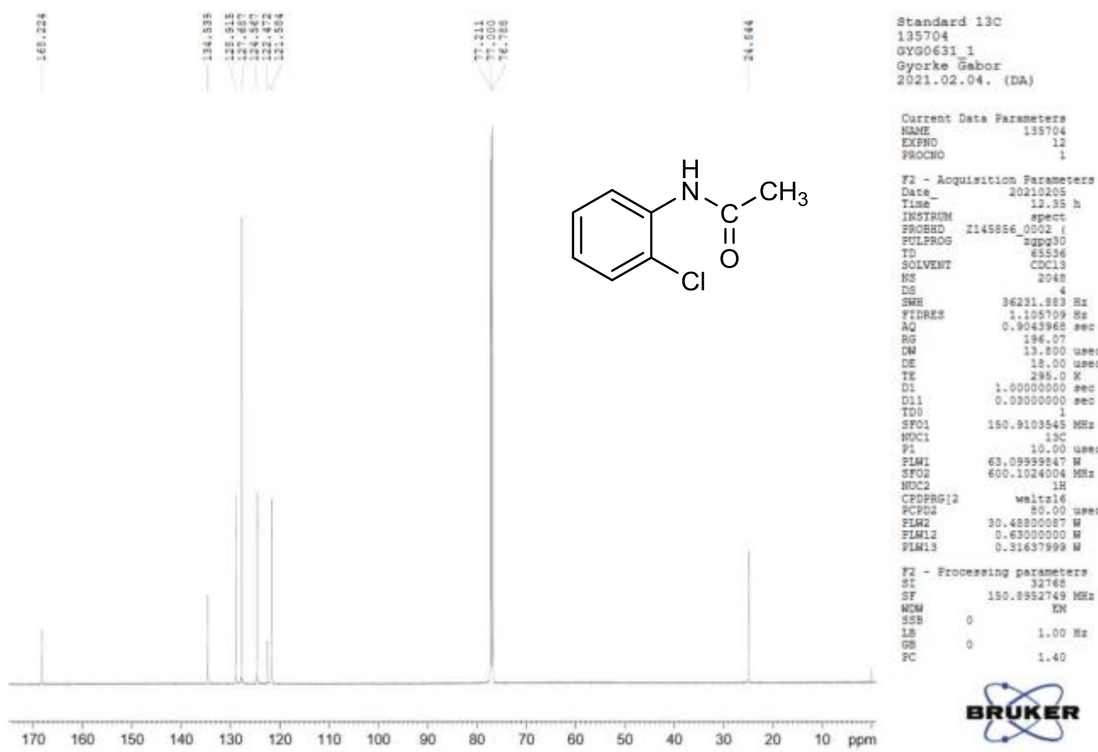

10.05
7.56
7.54
7.54
7.53
7.47
7.47
7.46
7.45
7.44
7.44
3.34
2.50
2.04
H
N
CHO
Br


1.00
4.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

H
N
CHO
Br


168.4
138.7
131.4
120.8
114.5
40.1
39.9
39.7
39.5
39.3
39.1
38.9
24.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Standard 1H
135704
GYG0631_1
Gyorke Gabor
2021.02.04. (DA)
Current Data Parameters
F2 - Acquisition Parameters
F2 - Processing parameters
BRUKER
ppm
Cl
CH3


Standard 13C
135704
GYG0631_1
Gyorke Gabor
2021.02.04. (DA)
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PROCNO 1
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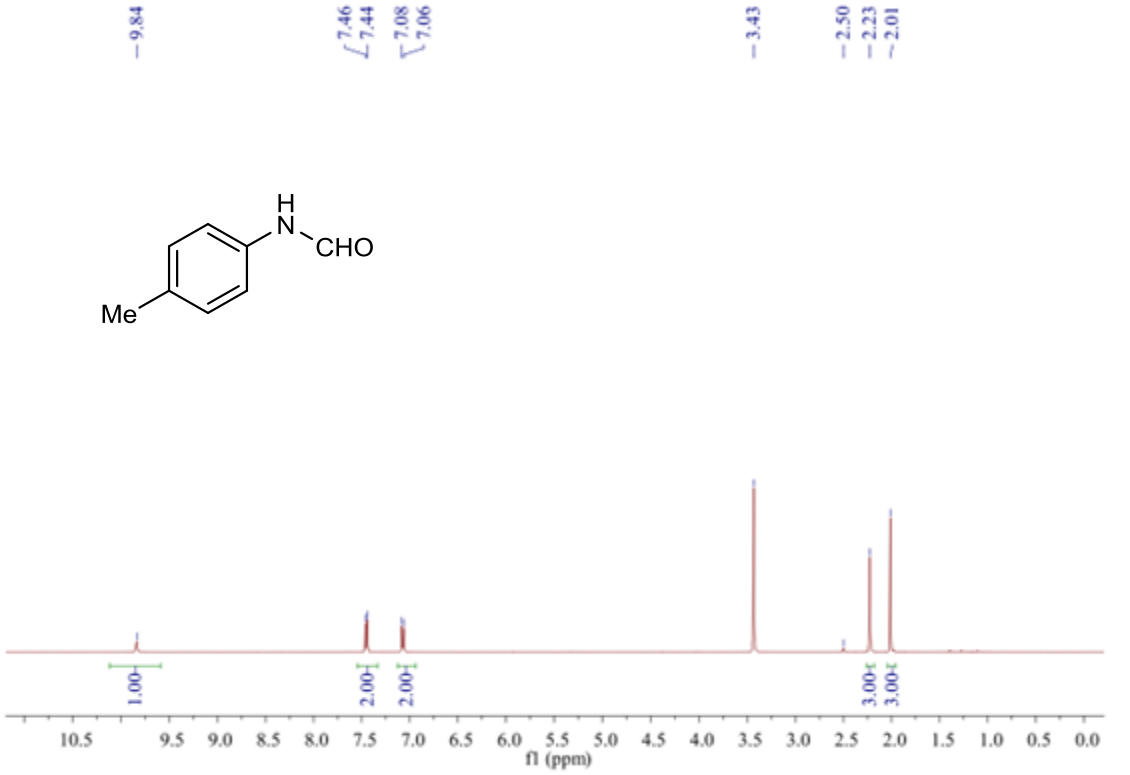
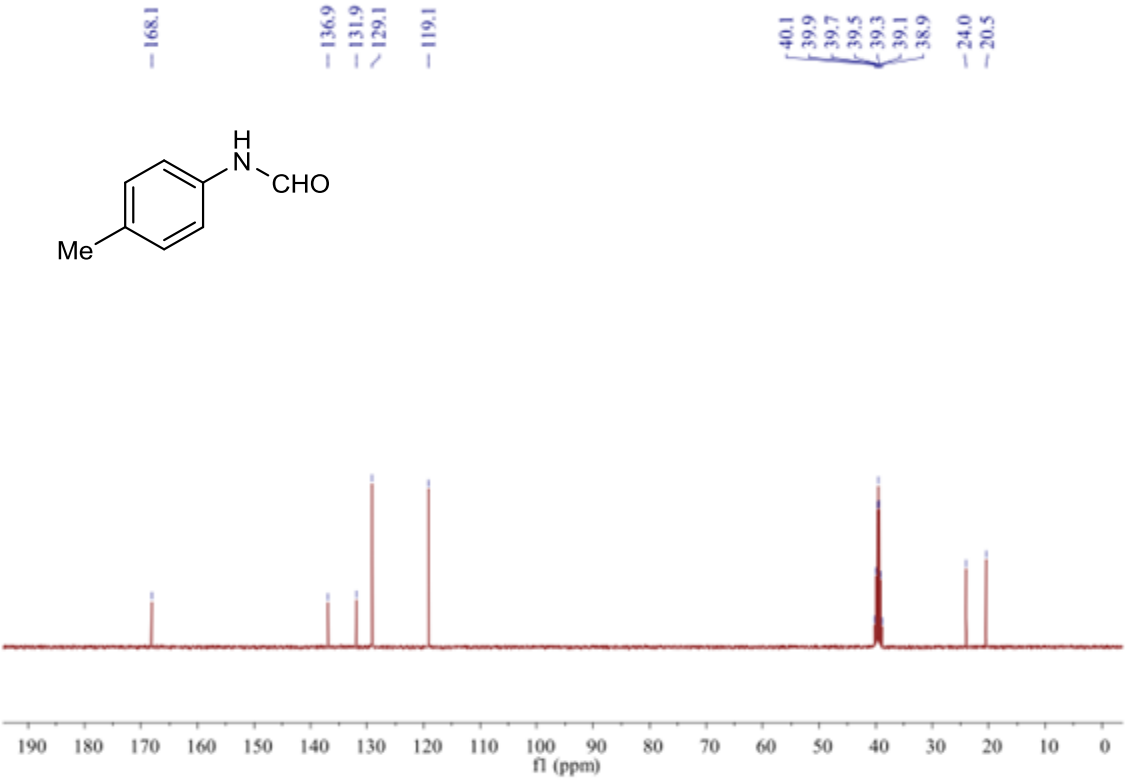
SOLVENT CDCl3
NS 2048
DS 4
SWH 36231.883 Hz
FIDRES 1.105709 Hz
AQ 0.9043968 sec
RG 196.07
DW 13.800 usec
DE 18.00 usec
TE 295.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9103545 MHz
NUC1 13C
P1 10.00 usec
PLW1 63.09999847 W
SFO2 600.1024004 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 30.48800087 W
PLW12 0.63000000 W
PLW13 0.31637999 W
F2 - Processing parameters
SI 32768
SF 150.8952749 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
BRUKER
ppm
Cl
CH3


9.84
7.46
7.44
7.08
7.06
3.43
2.50
2.23
2.01
H
N
CHO
Me
1.00
2.00
2.00
3.00
3.00
10.5 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
f1 (ppm)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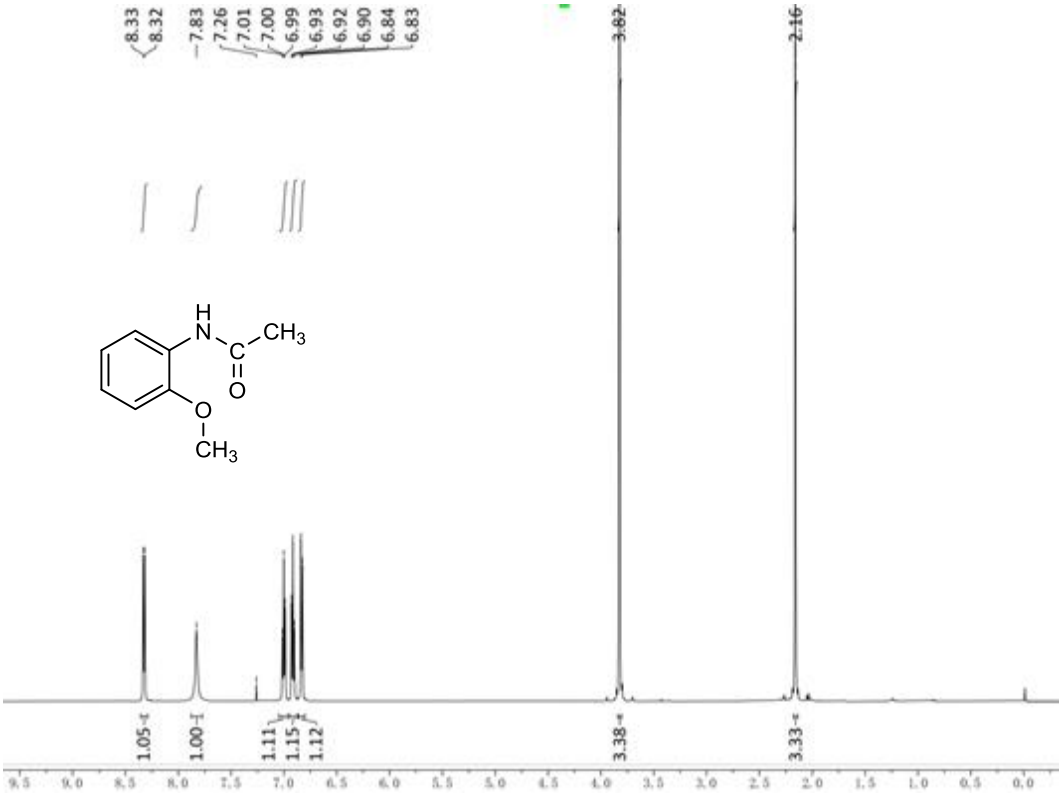
136.9
131.9
129.1
119.1
40.1
39.9
39.7
39.5
39.3
39.1
38.9
24.0
20.5
H
N
CHO
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.33
8.32
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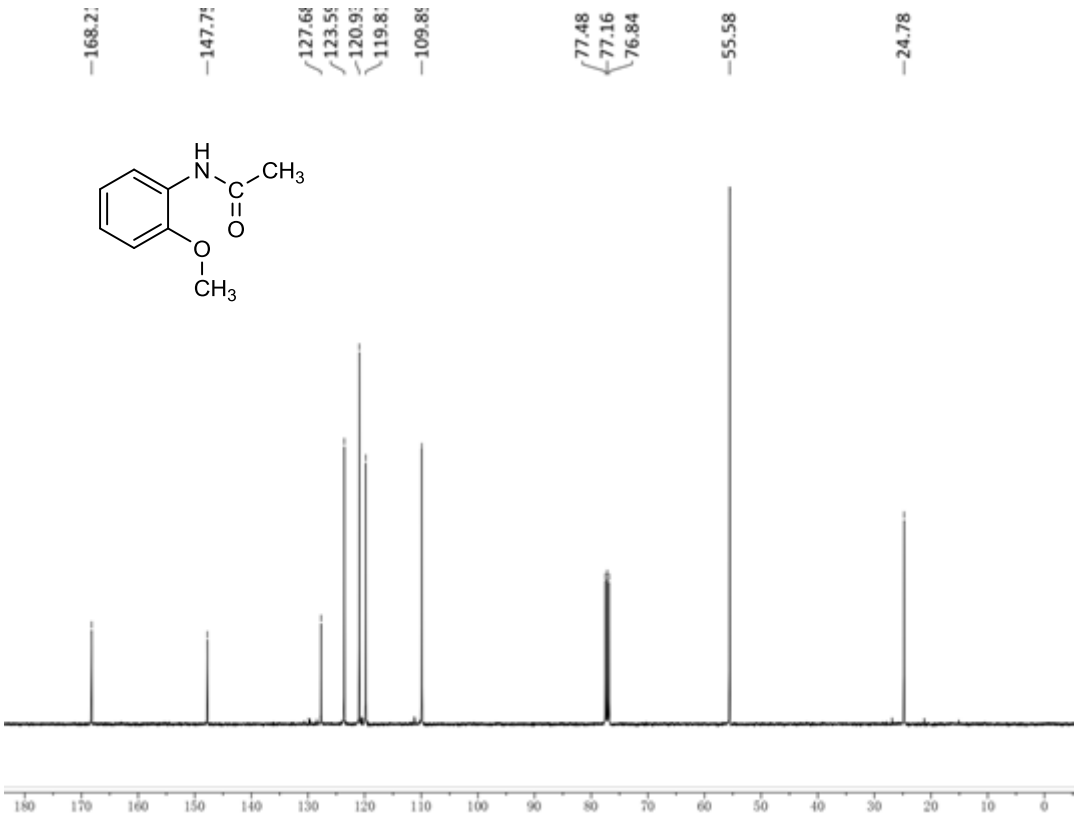
7.26
7.01
7.00
6.99
6.93
6.92
6.90
6.84
6.83
3.82
2.16
H
N
C
CH3
O
O
CH3
1.05
1.00
1.11
1.15
1.12
3.38
3.33
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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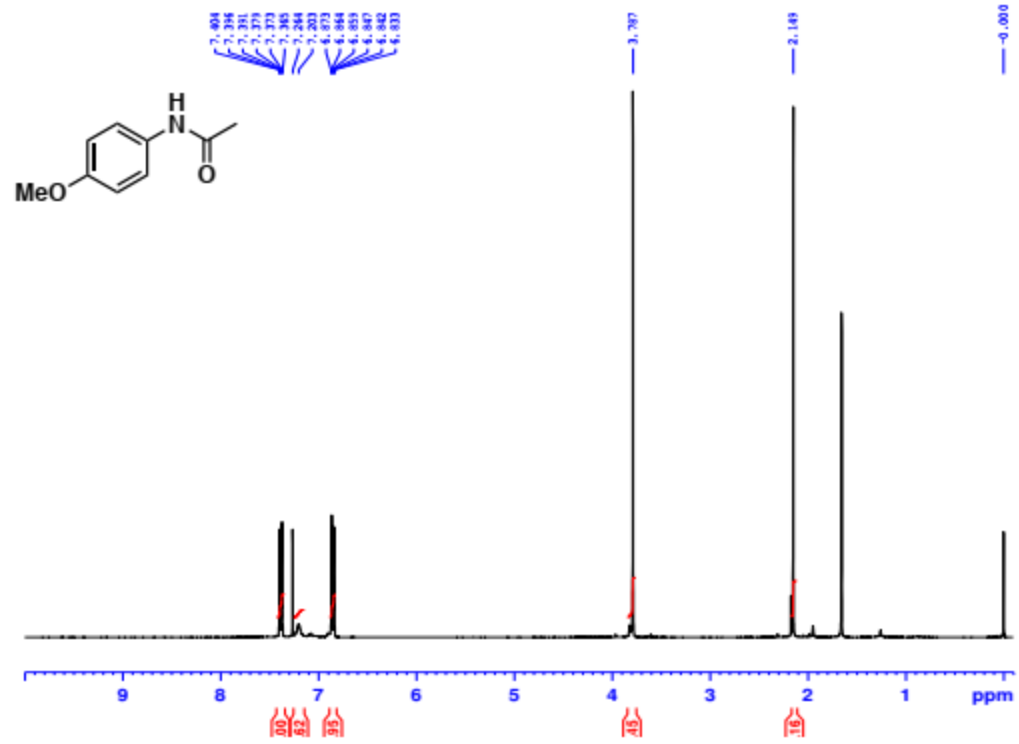
147.7
127.6
123.5
120.9
119.8
109.8
77.48
77.16
76.84
55.58
24.78
H
N
C
CH3
O
O
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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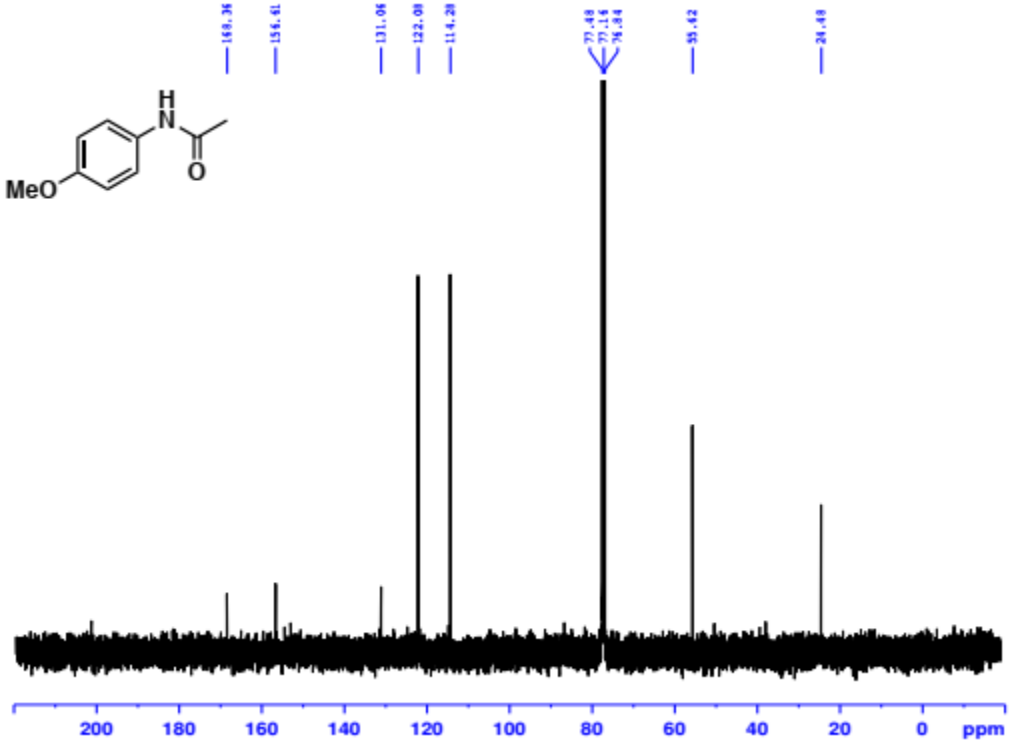
7.391
7.373
7.365
7.264
7.203
6.873
6.864
6.853
6.847
6.842
6.833
3.797
2.149
-0.000
MeO
H
N
O
9
8
7
6
5
4
3
2
1
ppm
00
62
35
45
16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156.61
131.06
122.08
114.20
77.48
77.16
76.84
55.42
24.48
MeO
H
N
O
200
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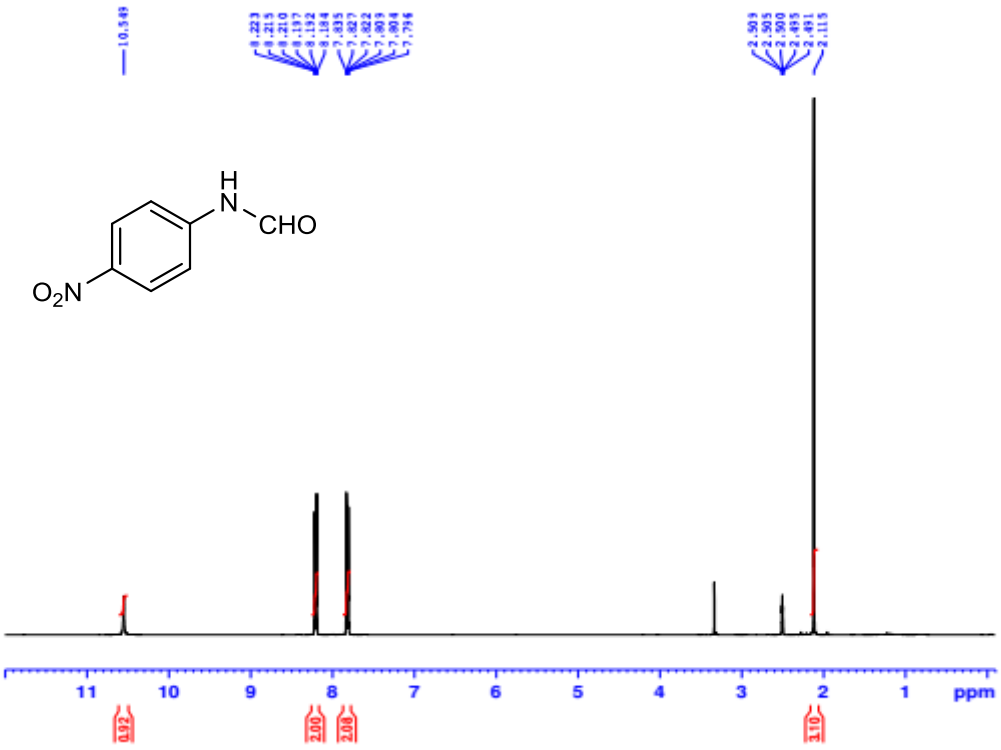
160
140
120
100
80
60
40
20
0
ppm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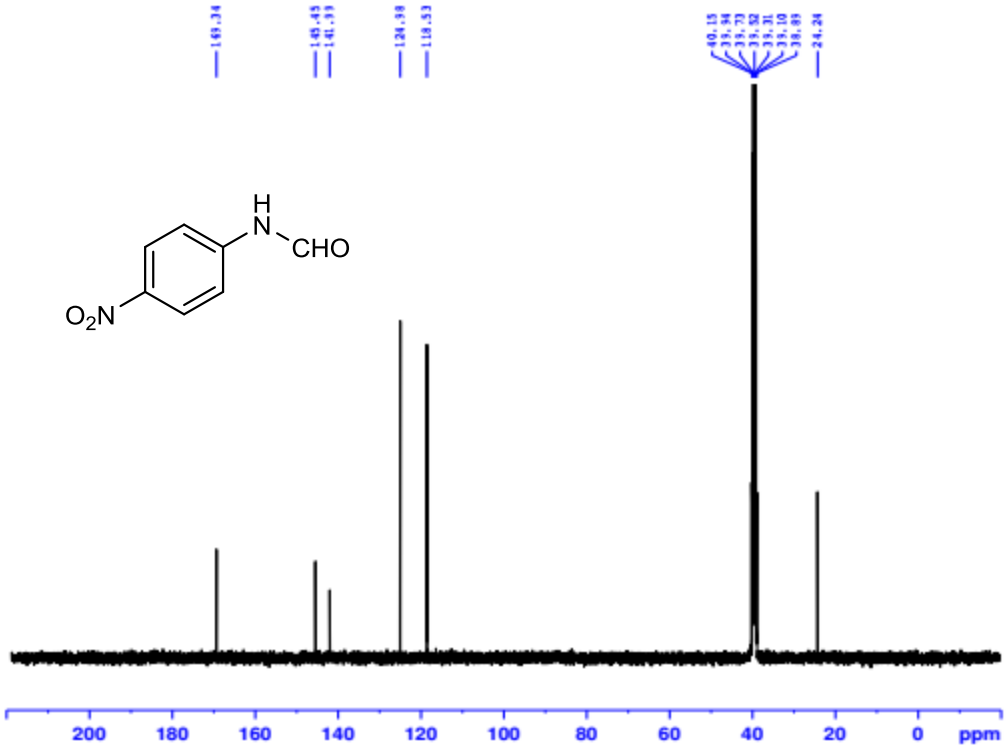
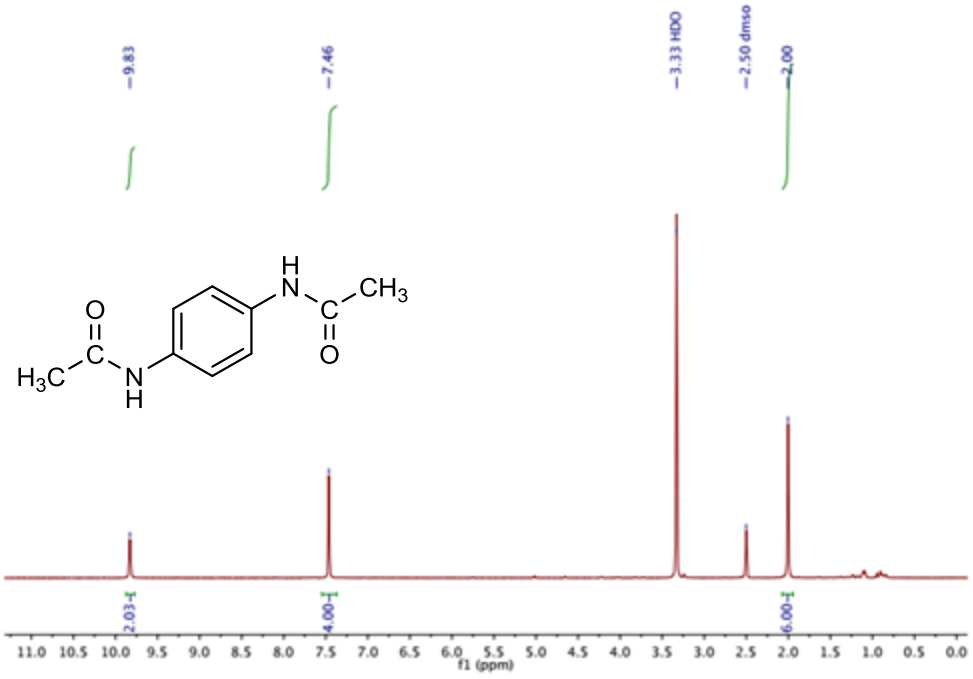
8.215
8.210
8.197
8.192
8.184
7.835
7.827
7.822
7.809
7.804
7.794
2.509
2.505
2.500
2.495
2.491
2.113
H
N
CHO
O2N
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
2.00
2.08
3.10


169.34
145.45
141.55
124.98
118.53
40.15
39.94
39.73
39.52
39.31
39.10
38.89
24.24
H
N
CHO
O2N
200
180
160
140
120
100
80
60
40
20
0
ppm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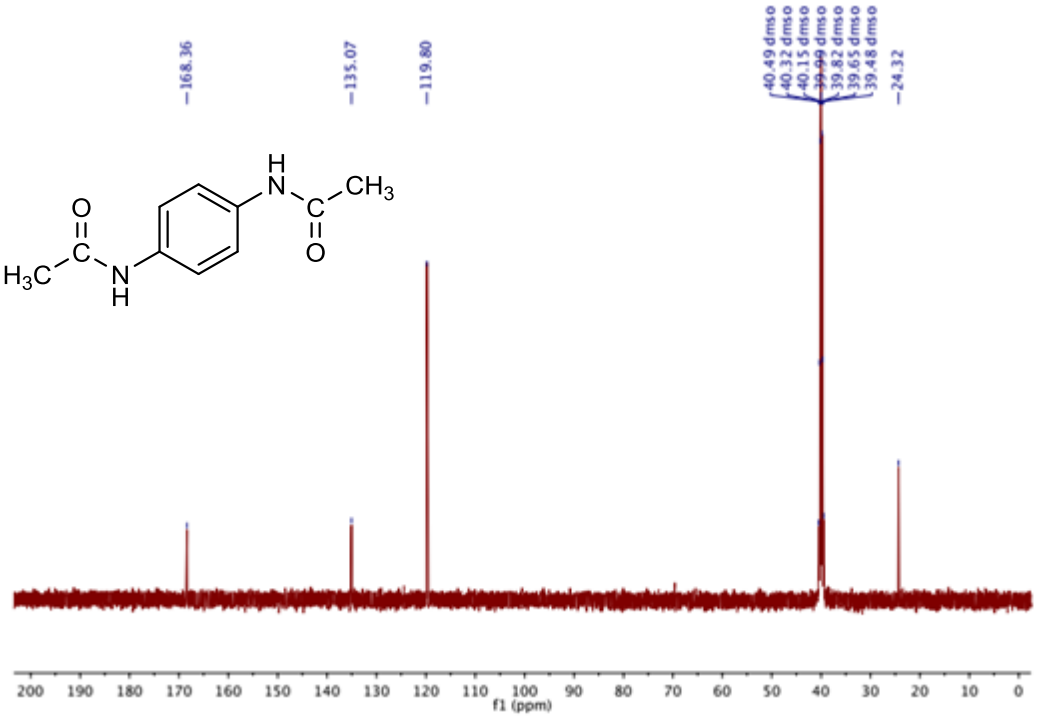
7.46
3.33 HDO
2.50 dmso
2.00
2.03
4.00
6.00
f1 (ppm)


168.36
135.07
119.80
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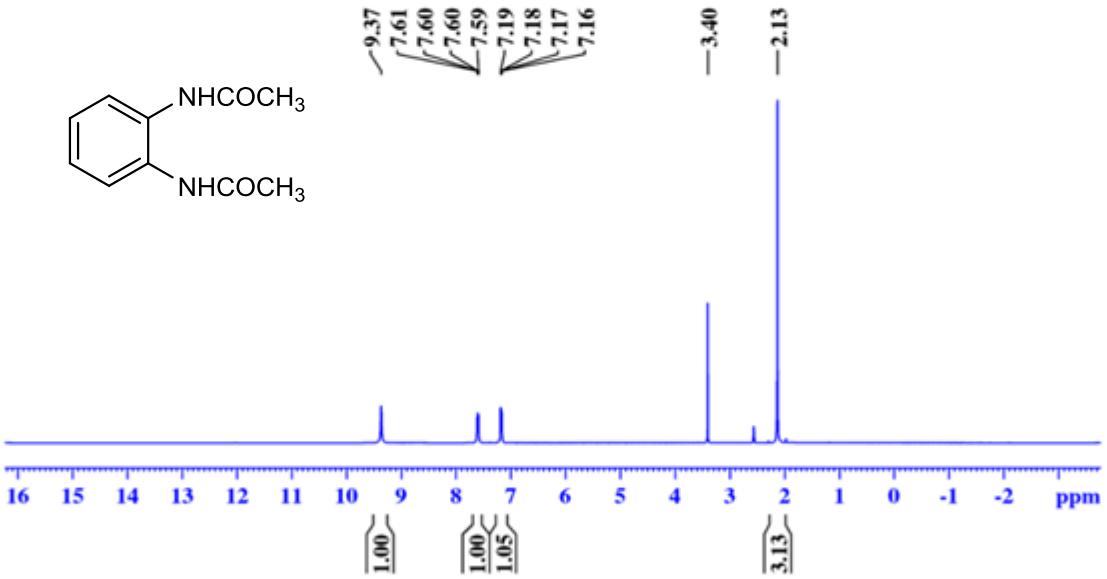
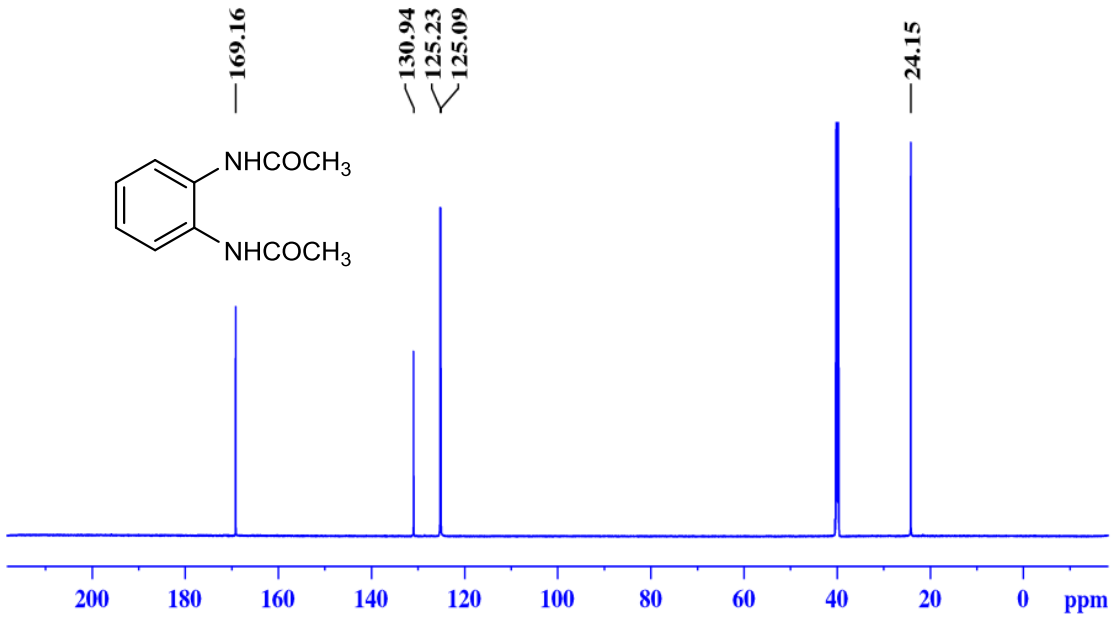
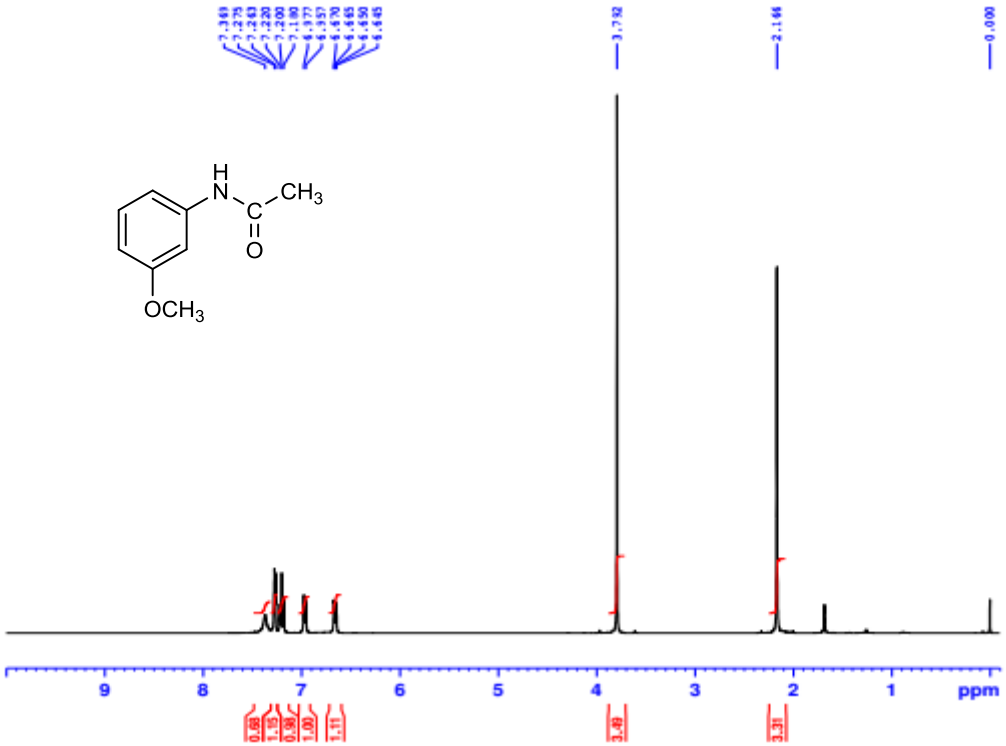
40.32 dmso
40.15 dmso
39.99 dmso
39.82 dmso
39.65 dmso
39.48 dmso
24.32
f1 (ppm)


9.37
7.61
7.60
7.60
7.59
7.19
7.18
7.17
7.16
3.40
2.13
NHCOCH3
NHCOCH3
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
1.00
1.00
1.05
3.13


169.16
130.94
125.23
125.09
24.15
NHCOCH3
NHCOCH3
200 180 160 140 120 100 80 60 40 20 0 ppm


H
N
C
O
CH3
OCH3
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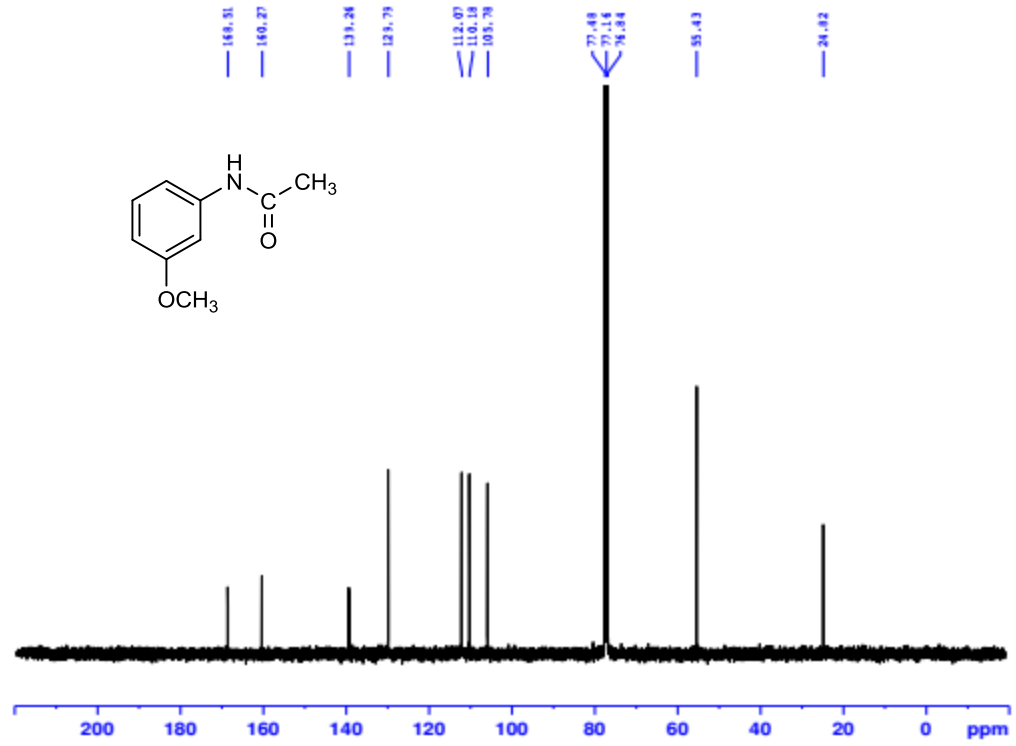
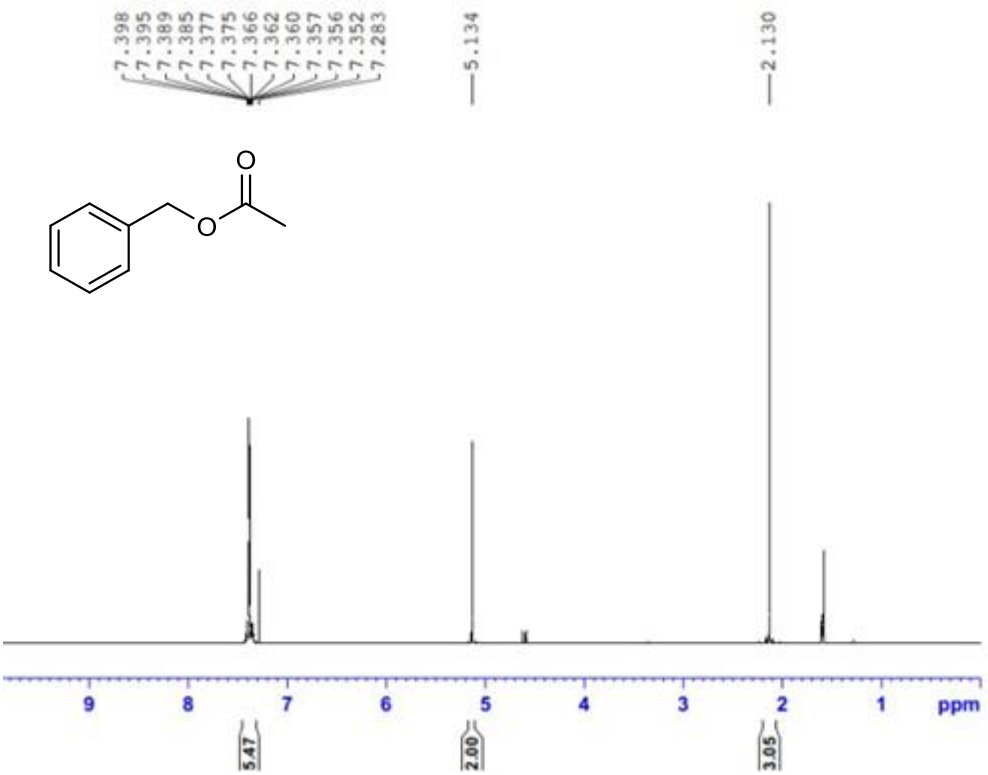
0.000
9
8
7
6
5
4
3
2
1
ppm


H
N
C
O
CH3
OCH3
168.31
160.27
131.24
129.79
112.07
110.18
105.70
77.48
77.16
76.84
55.43
24.02
200
180
160
140
120
100
80
60
40
20
0
ppm

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Current Data Parameters
NAME      Jun29-2022-nmrsu
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20220629
Time              15.57 h
INSTRUM   AvanceNeo 600
PROBHD   Z114607_0330 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           11904.762 Hz
FIDRES         0.363304 Hz
AQ             2.7525120 sec
RG                   101
DW                42.000 use
DE                 8.79 use
TE               298.3 K
D1            1.00000000 sec
TD0                    1
SFO1         600.4037075 MHz
NUC1                  1H
P0                  3.33 use
P1                 10.00 use
PLW1         27.65399933 W

F2 - Processing parameters
SI                 65536
SF          600.4000000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

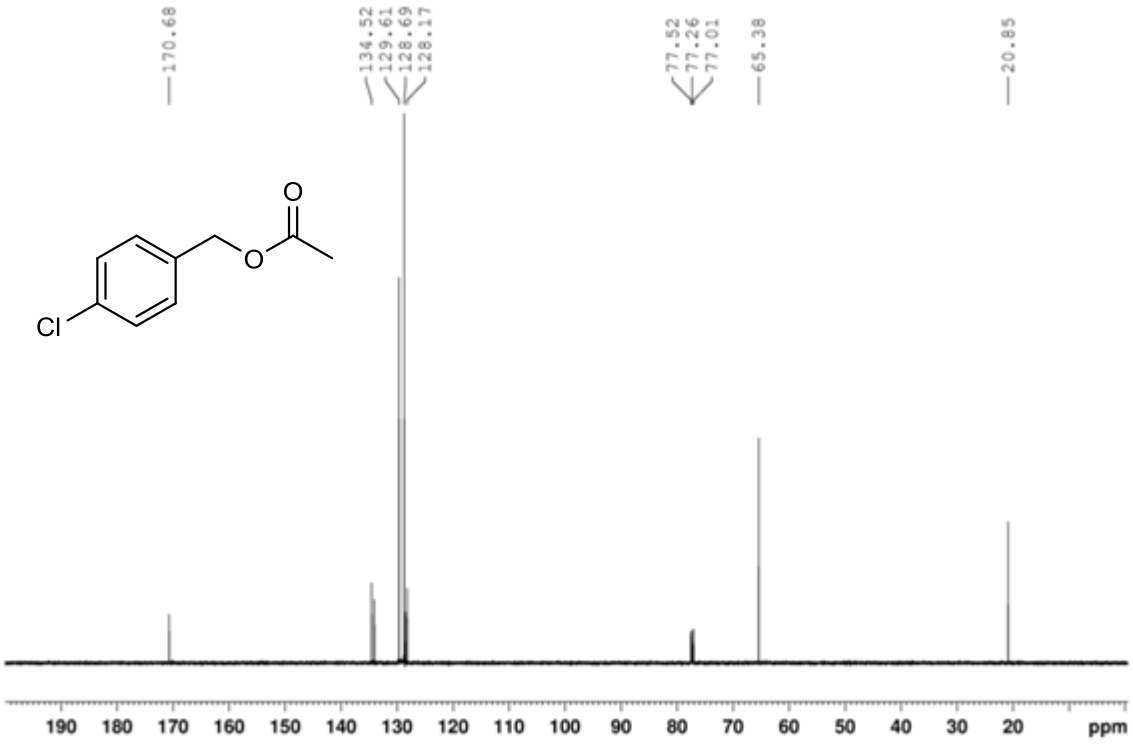

BRUKER

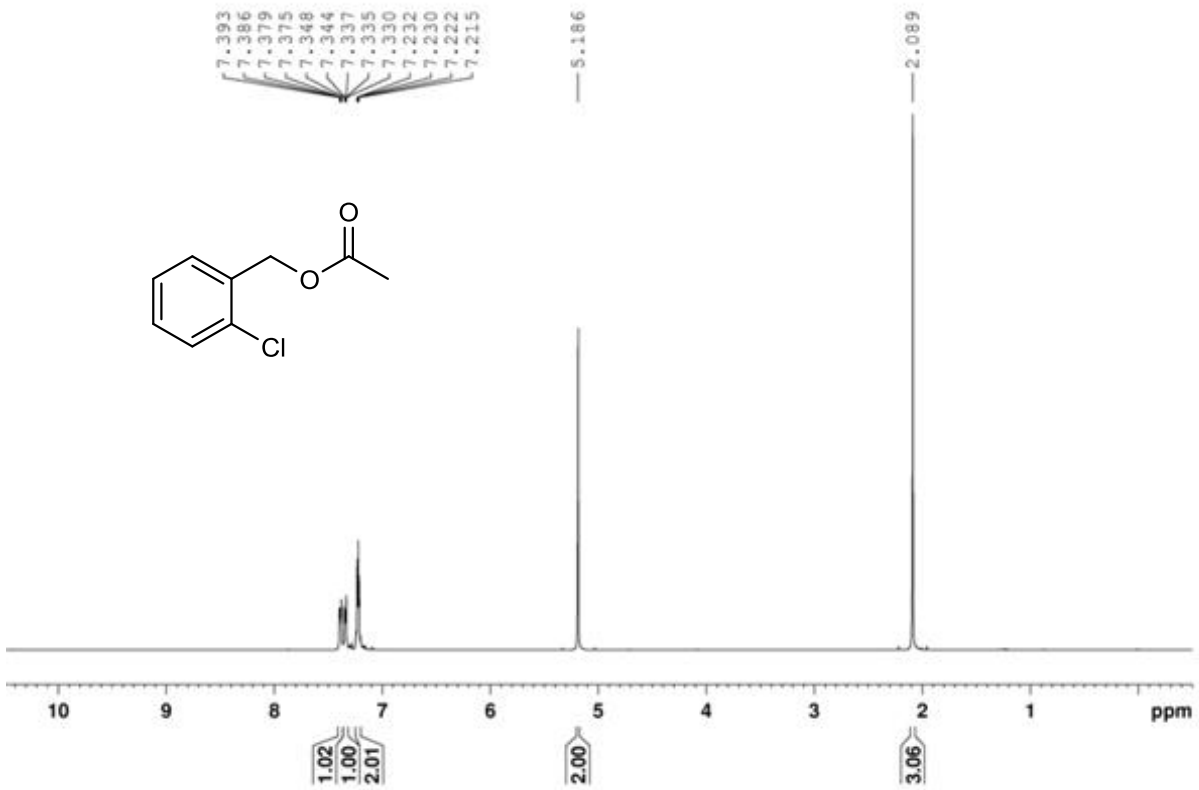
```
Current Data Parameters
NAME      Jun29-2022-nmrsu
EXPNO                   11
PROCNO                   1

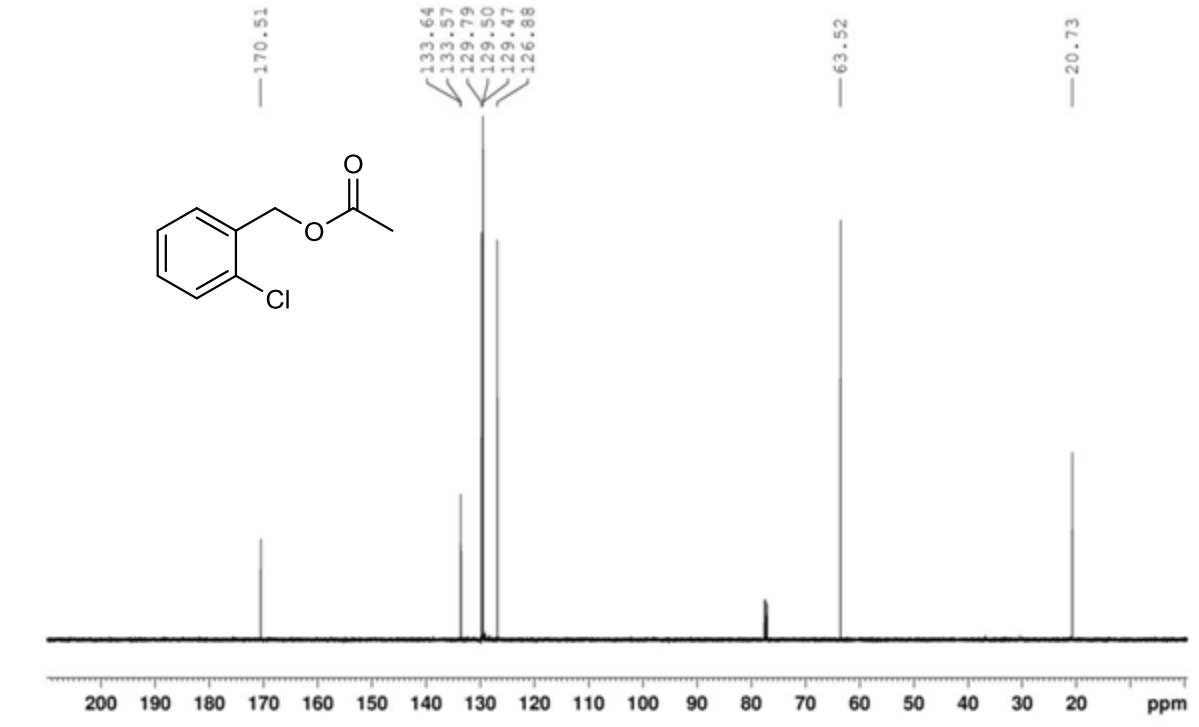
F2 - Acquisition Parameters
Date_           20220629
Time              16.32 h
INSTRUM   AvanceNeo 600
PROBHD   Z114607_0330 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   608
DS                     4
SWH           35714.285 Hz
FIDRES         1.089913 Hz
AQ             0.9175040 sec
RG                   101
DW                14.000 usec
DE                 6.50 usec
TE               299.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         150.9857971 MHz
NUC1                  13C
P0                 4.00 usec
P1                12.00 usec
PLW1         82.27400208 W
SFO2         600.4024016 MHz
NUC2                  1H
CPDPRG[2          waltz65
PCPD2             70.00 usec
PLW2         27.65399933 W
PLW12         0.56436002 W
PLW13         0.28387001 W

F2 - Processing parameters
SI                 32768
SF          150.9707001 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

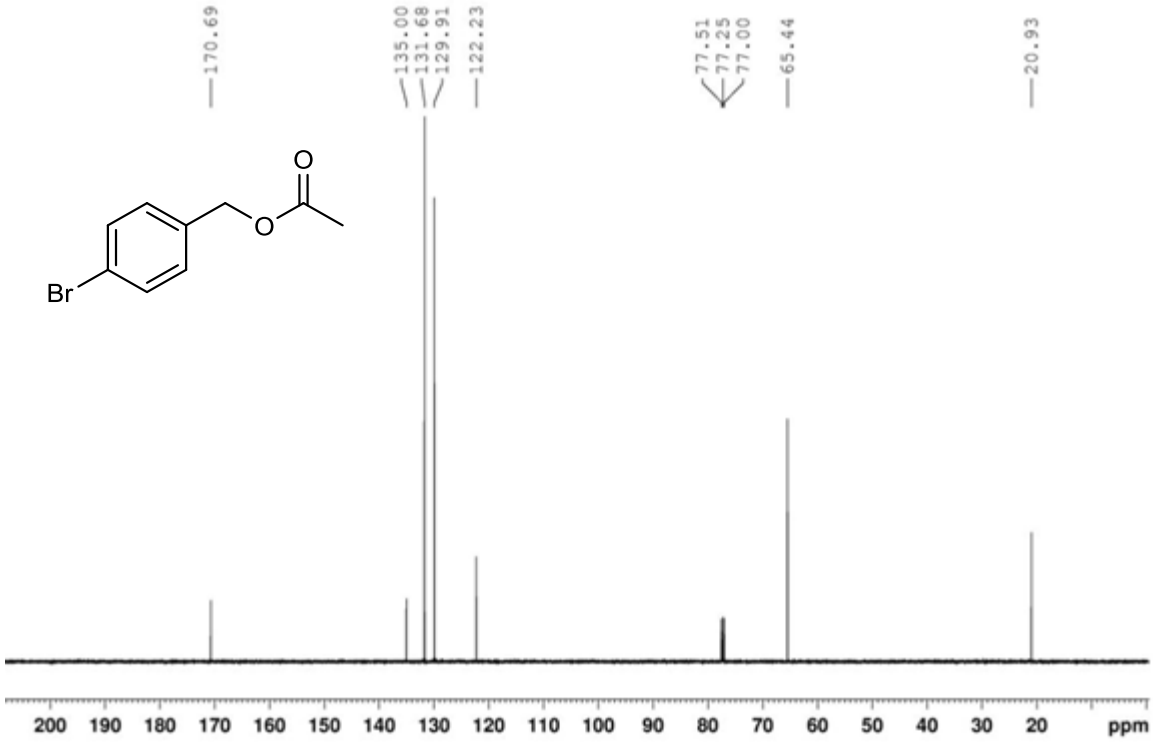

7.307
7.290
7.269
7.252
5.040
2.070
O
O
Cl
10
9
8
7
6
5
4
3
2
1
ppm
4.10
2.00
3.03


170.68
134.52
129.61
128.69
128.17
77.52
77.26
77.01
65.38
20.85
O
O
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.393
7.386
7.379
7.375
7.348
7.344
7.337
7.335
7.330
7.232
7.230
7.222
7.215
5.186
2.089
O
O
Cl
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.00
2.01
2.00
3.06


170.51
133.64
133.57
129.79
129.50
129.47
126.88
63.52
20.73
O
O
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.471
7.455
7.220
7.204
5.034
2.084
O
O
Br
10
9
8
7
6
5
4
3
2
1
ppm
2.01
2.10
2.06
3.00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135.00
131.68
129.91
122.23
77.51
77.25
77.00
65.44
20.93
O
O
Br
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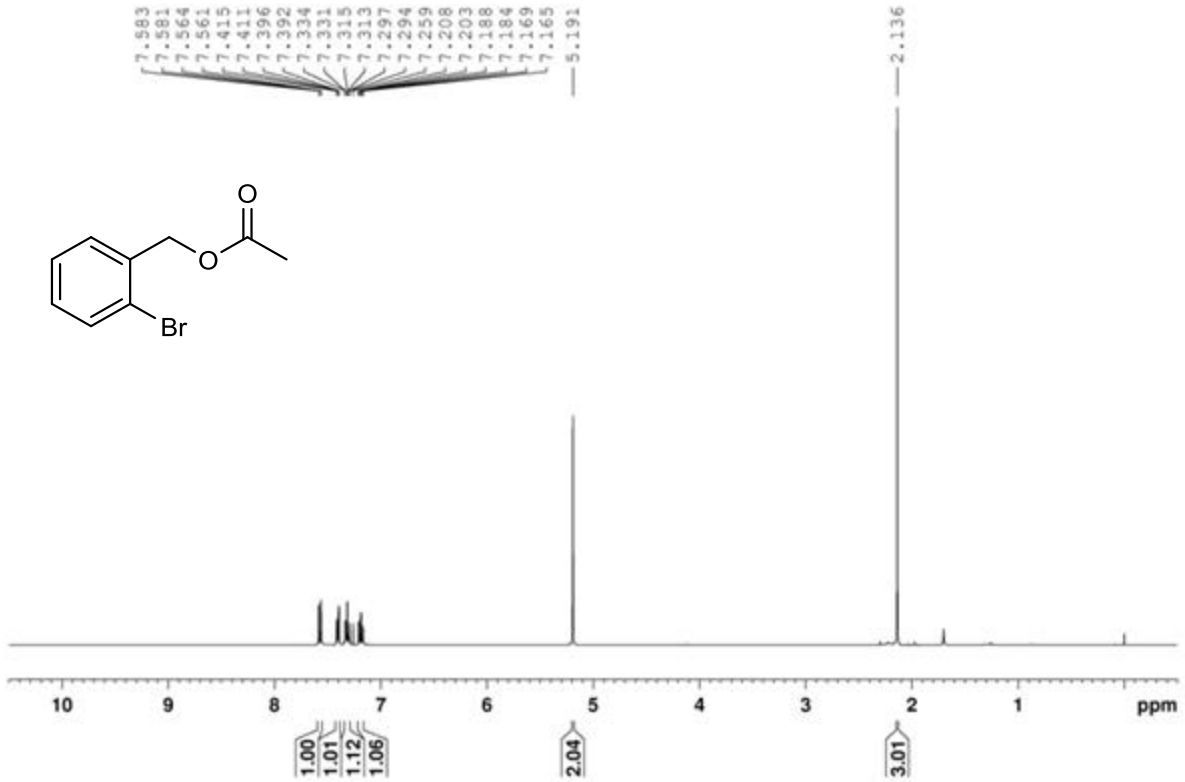
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.561
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7.411
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7.392
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7.331
7.315
7.313
7.297
7.294
7.259
7.208
7.203
7.188
7.184
7.169
7.165
5.191
2.136
O
O
Br
10
9
8
7
6
5
4
3
2
1
ppm
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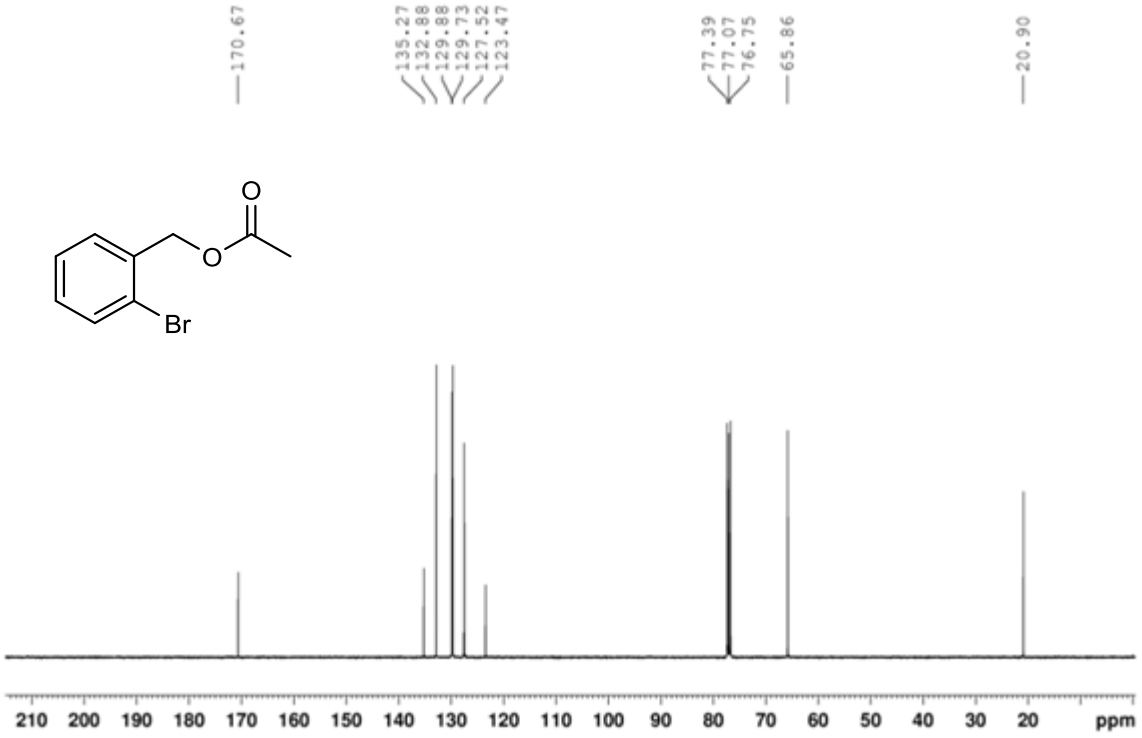
1.01
1.12
1.06
2.04
3.01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129.88
129.73
127.52
123.47
77.39
77.07
76.75
65.86
20.90
O
O
Br
210
200
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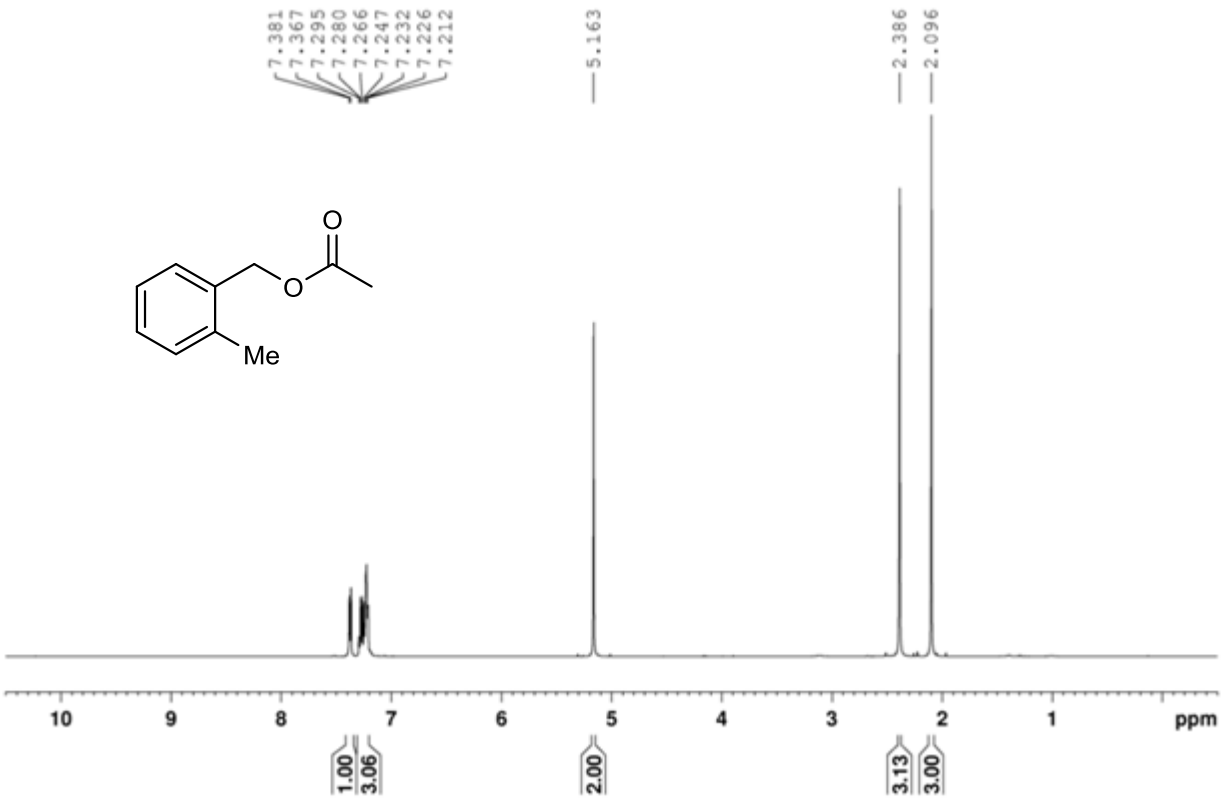
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.367
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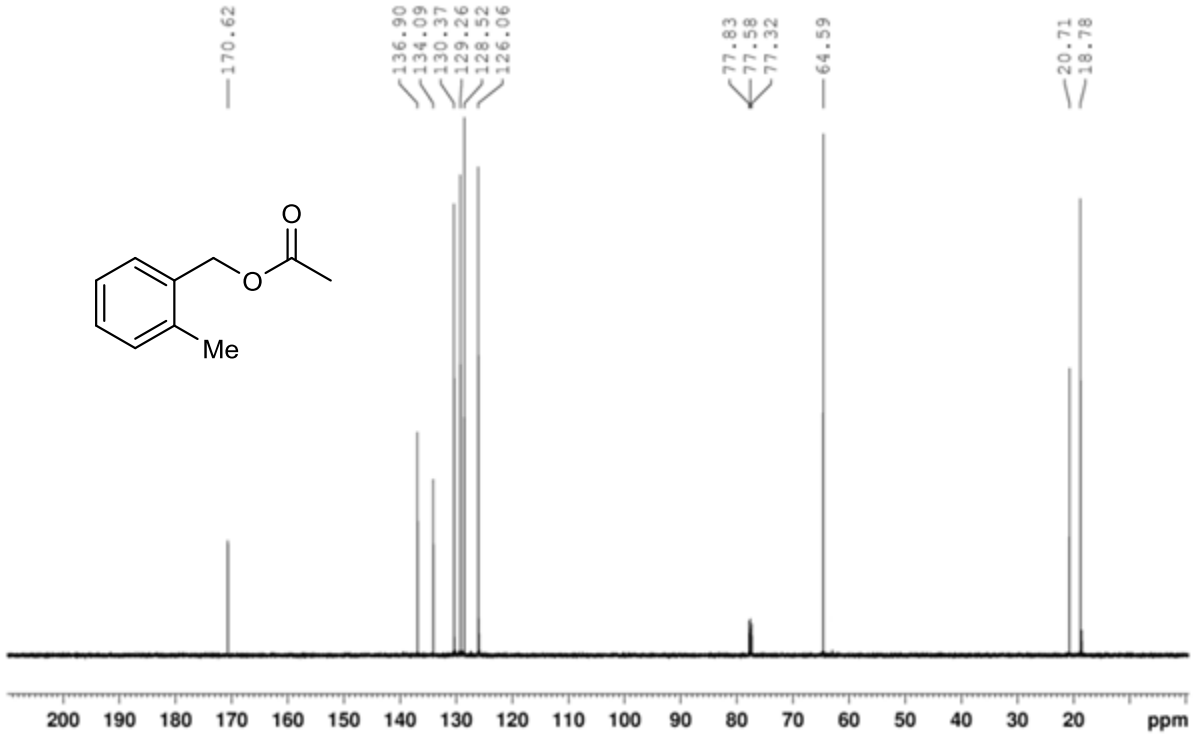
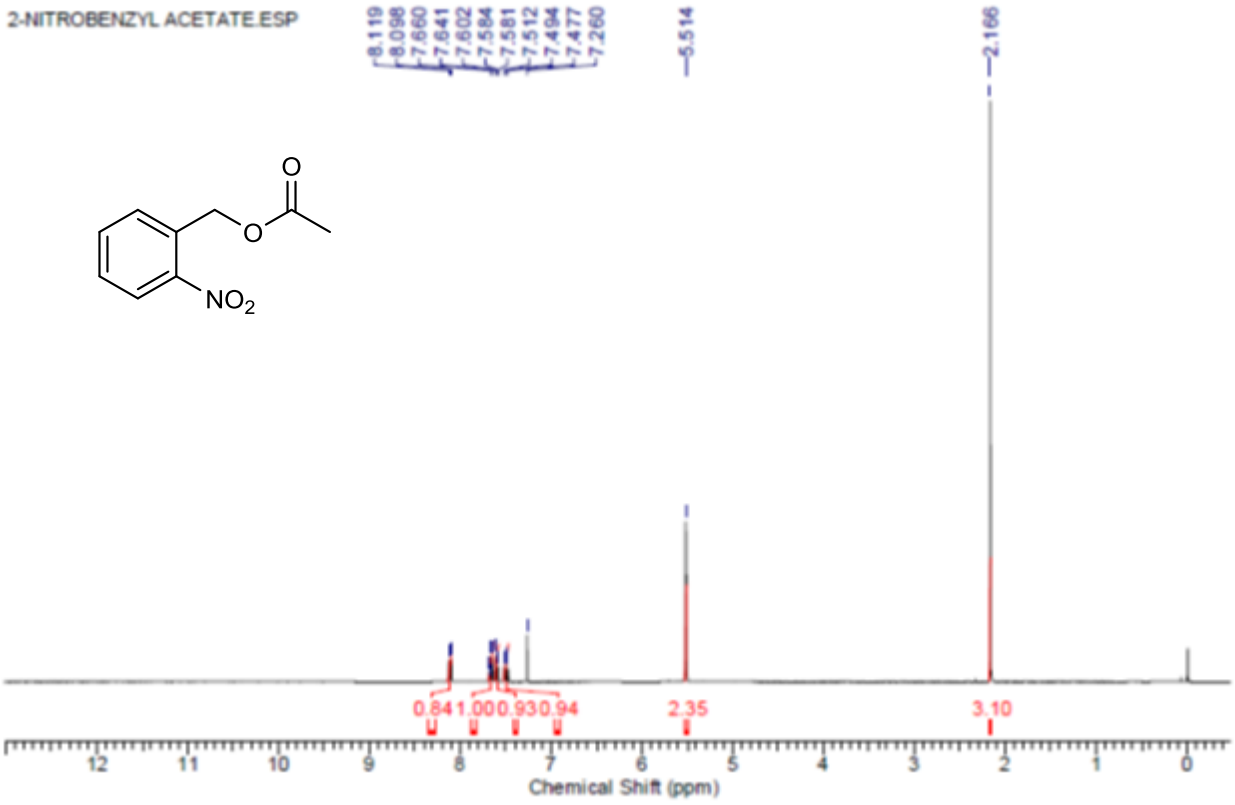
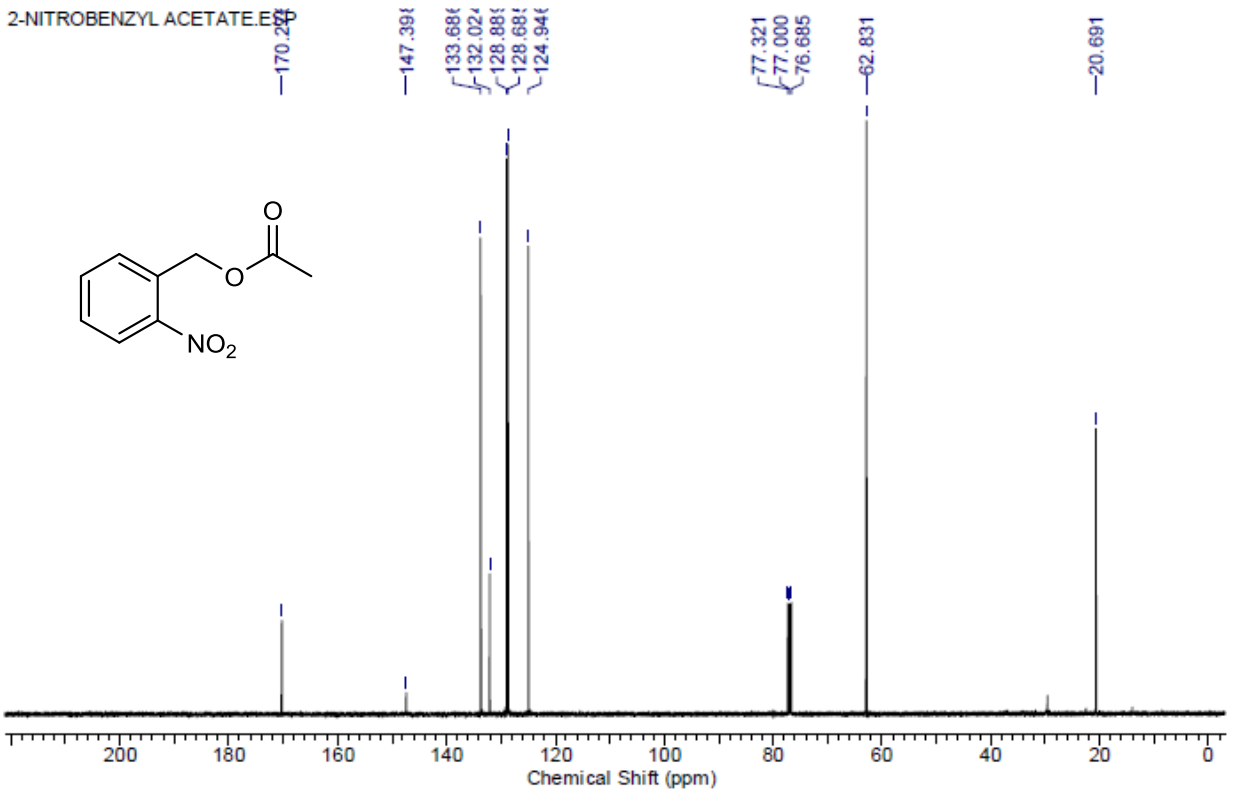
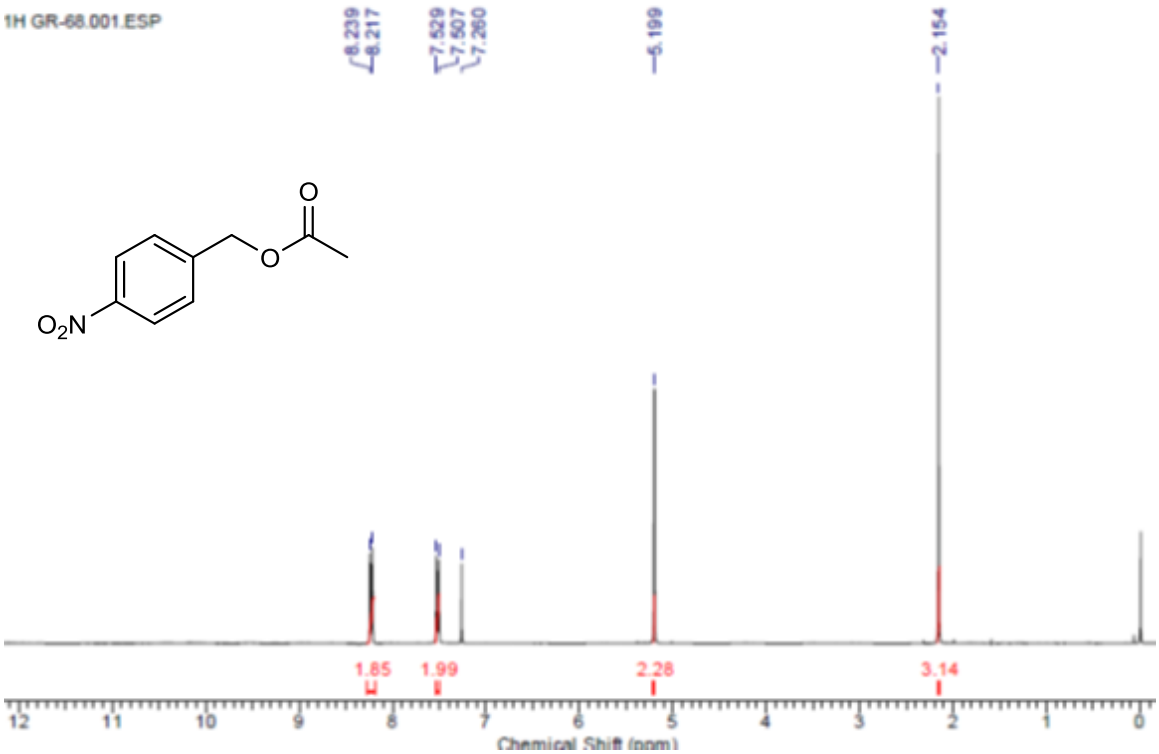
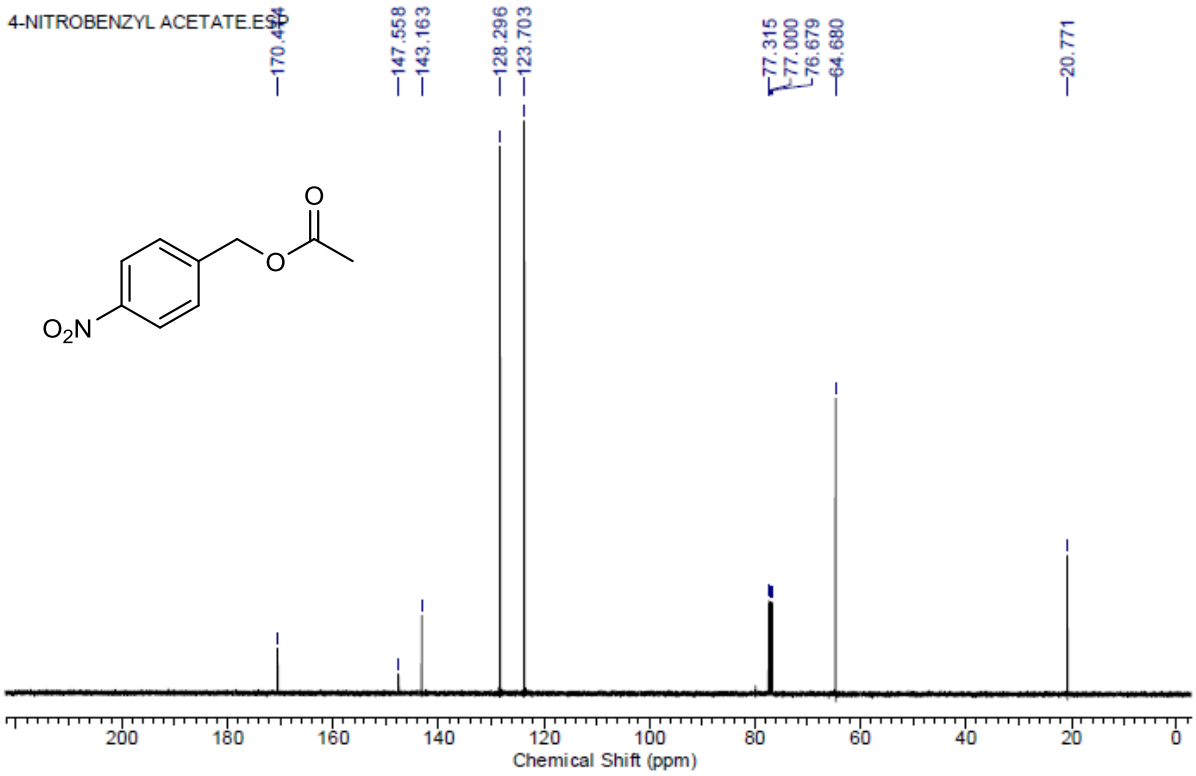
7.280
7.266
7.247
7.232
7.226
7.212
5.163
2.386
2.096
O
O
Me
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.06
2.00
3.13
3.00


170.62
136.90
134.09
130.37
129.26
128.52
126.06
77.83
77.58
77.32
64.59
20.71
18.78
O
O
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


2-NITROBENZYL ACETATE.ESP
8.119
8.098
7.660
7.641
7.602
7.584
7.581
7.512
7.494
7.477
7.260
5.514
2.166
O
O
NO2
0.84
1.00
0.93
0.94
2.35
3.10
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


2-NITROBENZYL ACETATE.ESP
170.27
147.39
133.68
132.02
128.88
128.68
124.94
77.321
77.000
76.685
62.831
20.691
O
O
NO2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


1H GR-68.001.ESP
8.239
8.217
7.529
7.507
7.260
5.199
2.154
O
O
O2N
1.85
1.99
2.28
3.14
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


4-NITROBENZYL ACETATE.ESP
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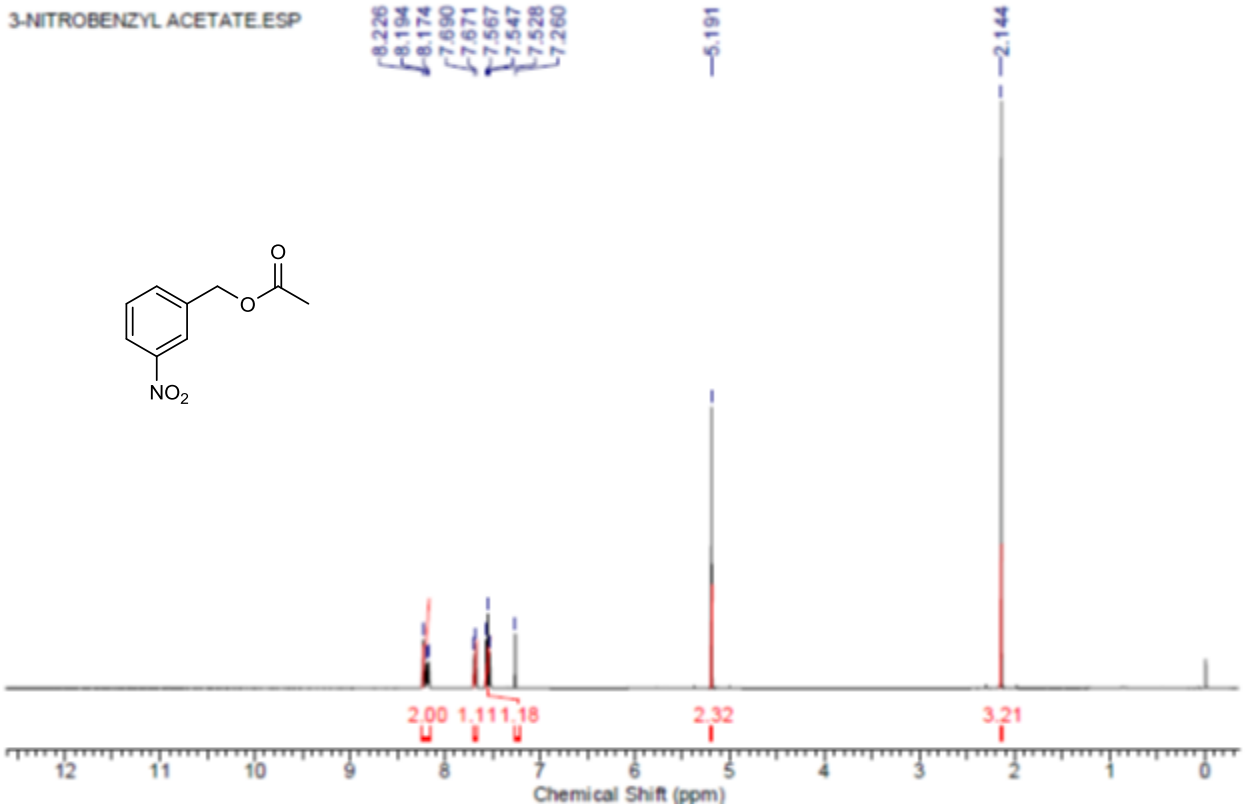
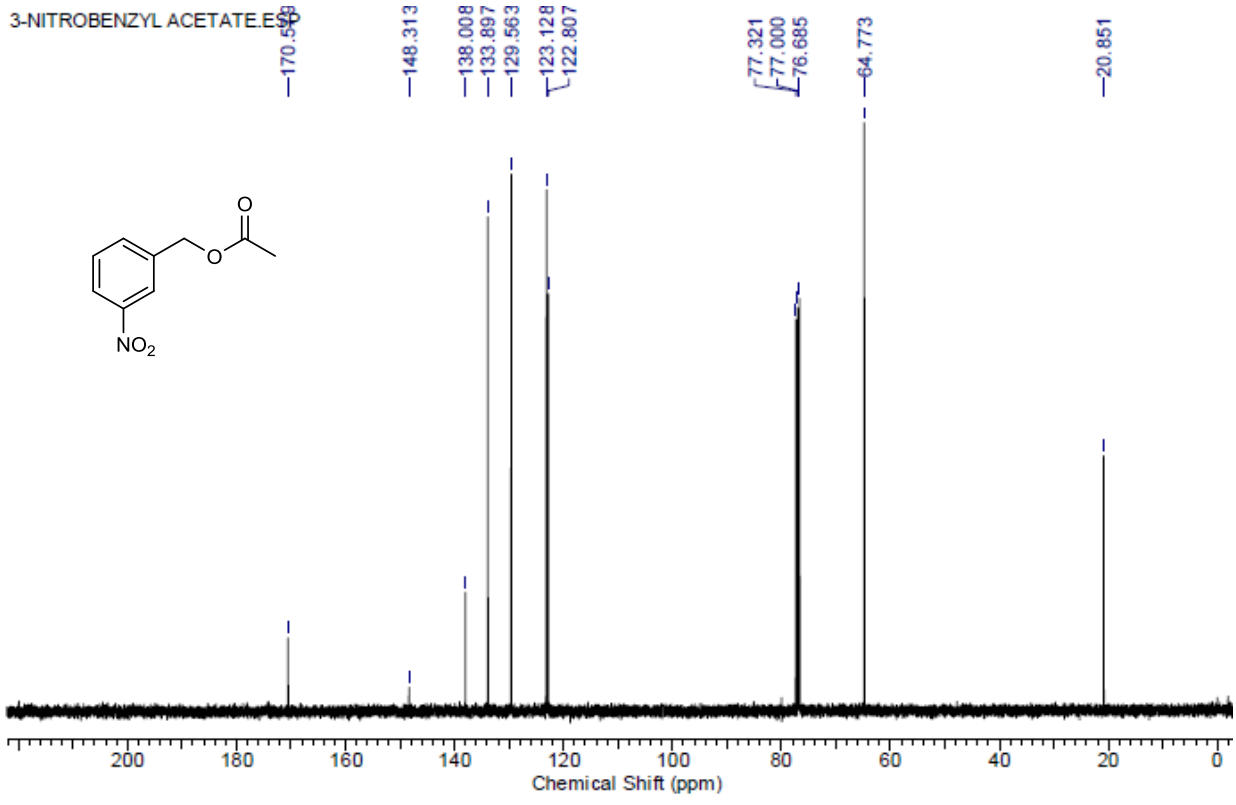
147.558
143.163
128.296
123.703
77.315
77.000
76.679
64.680
20.771
O
O
O2N
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

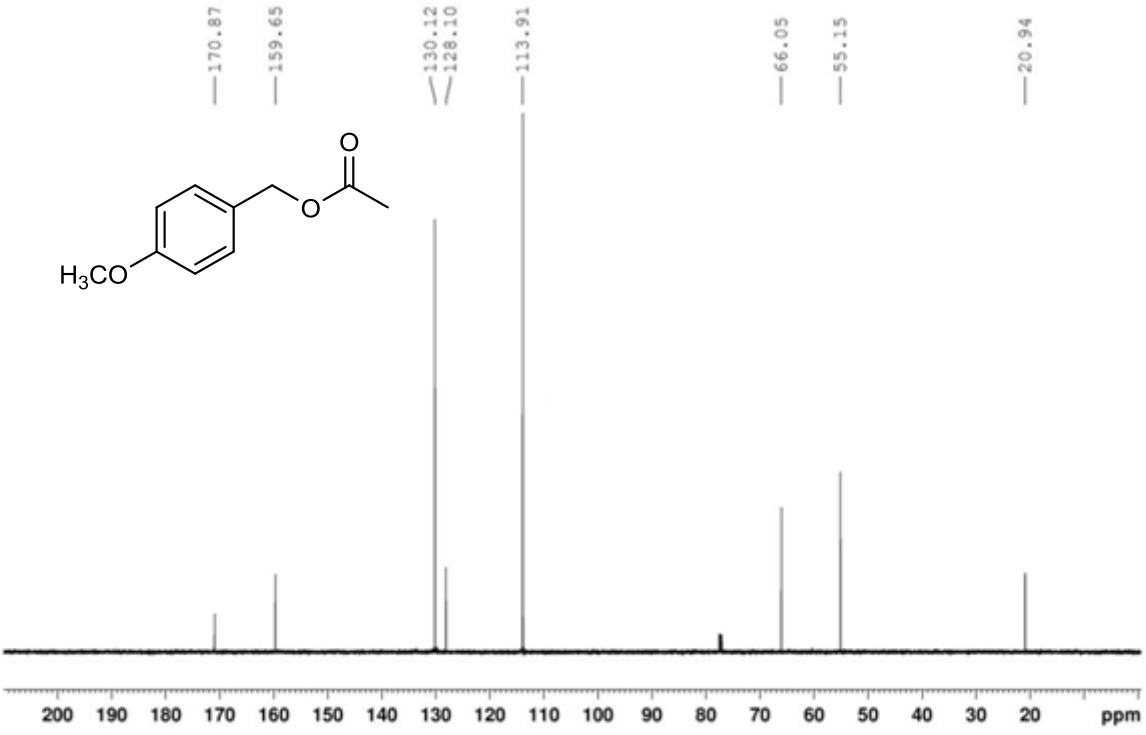
3-NITROBENZYL ACETATE.ESP

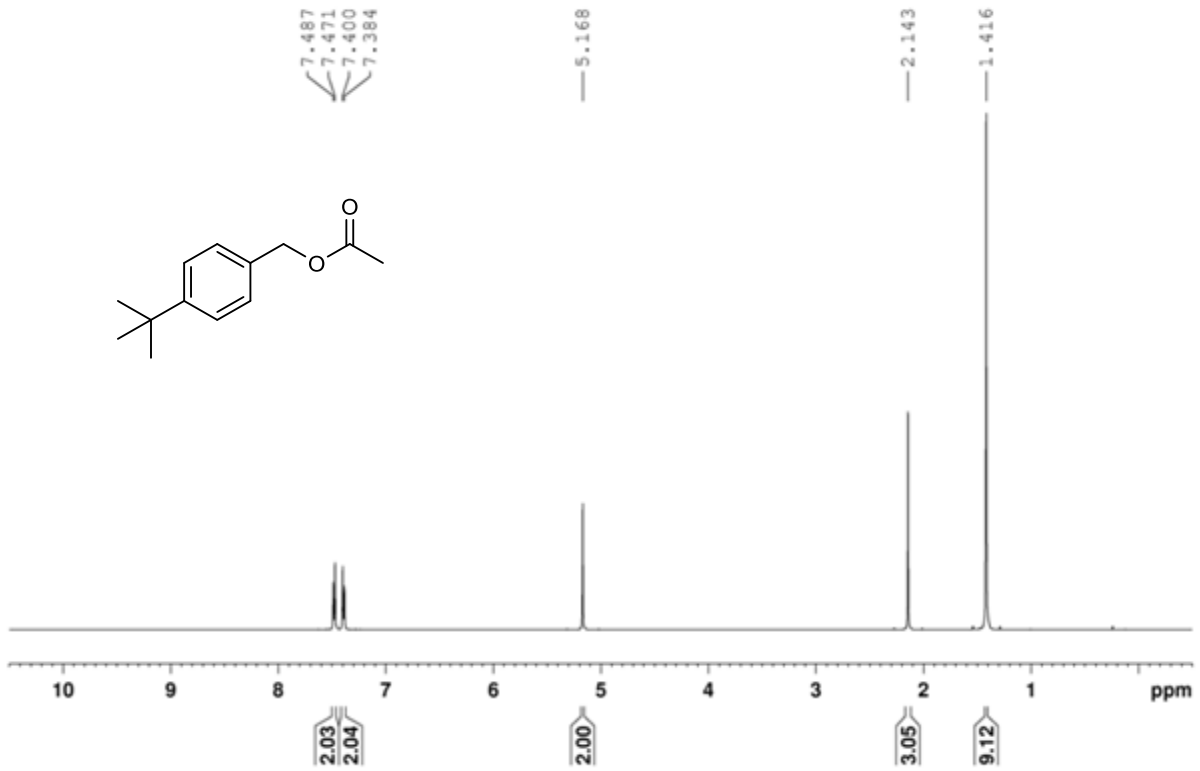


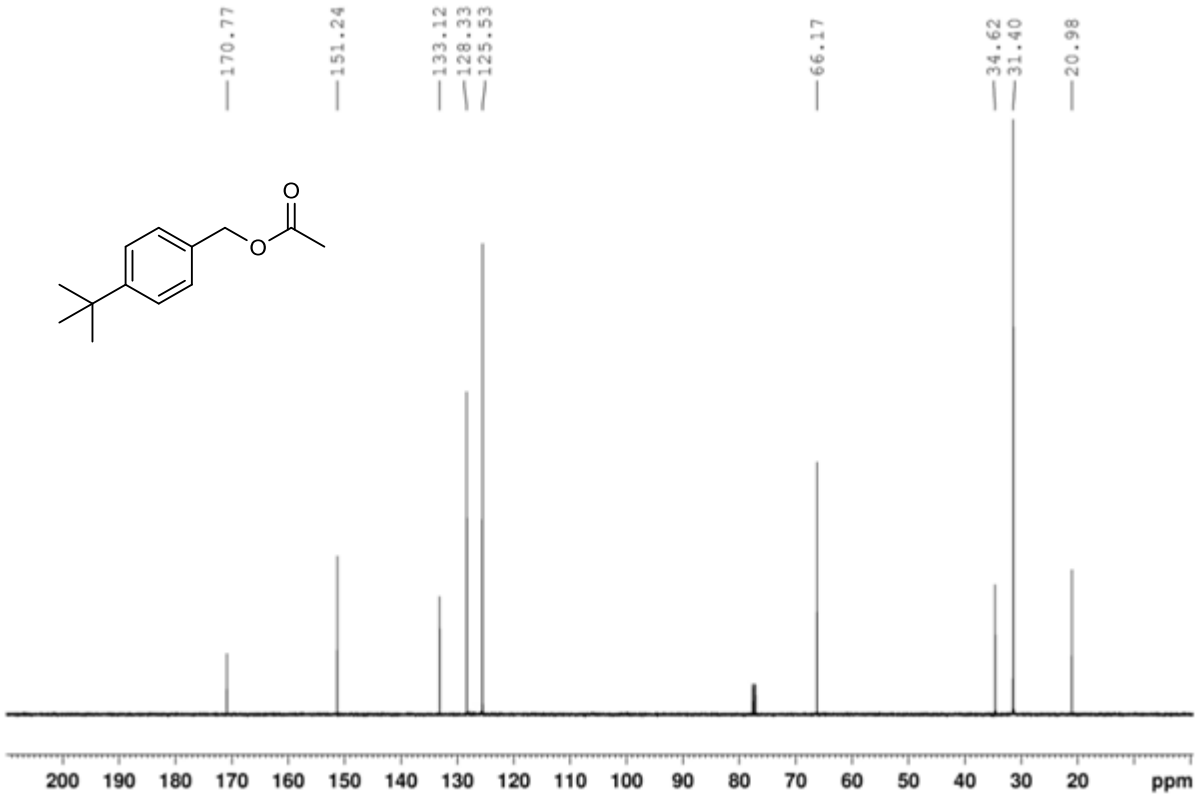
3-NITROBENZYL ACETATE.ESP

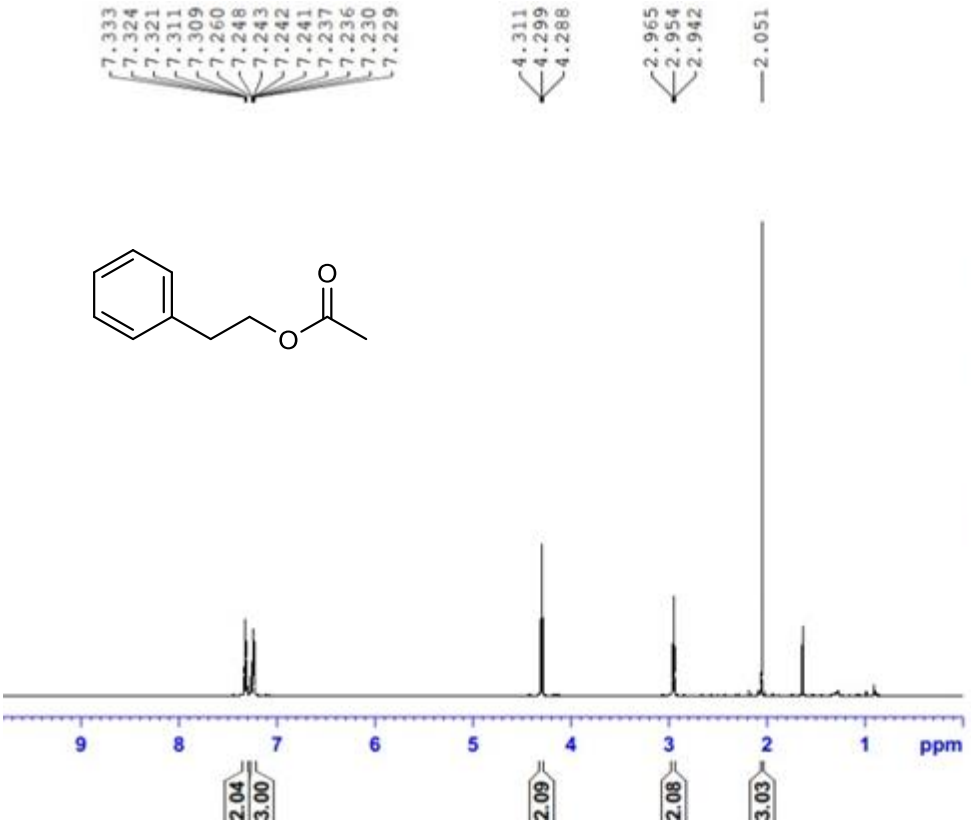



7.298
7.282
6.891
6.877
6.873
5.032
3.772
2.053
O
O
H3CO
10
9
8
7
6
5
4
3
2
1
ppm
2.20
2.17
2.00
3.19
3.09


170.87
159.65
130.12
128.10
113.91
66.05
55.15
20.94
O
O
H3CO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.487
7.471
7.400
7.384
5.168
2.143
1.416
O
O
10
9
8
7
6
5
4
3
2
1
ppm
2.03
2.04
2.00
3.05
9.12


170.77
151.24
133.12
128.33
125.53
66.17
34.62
31.40
20.98
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

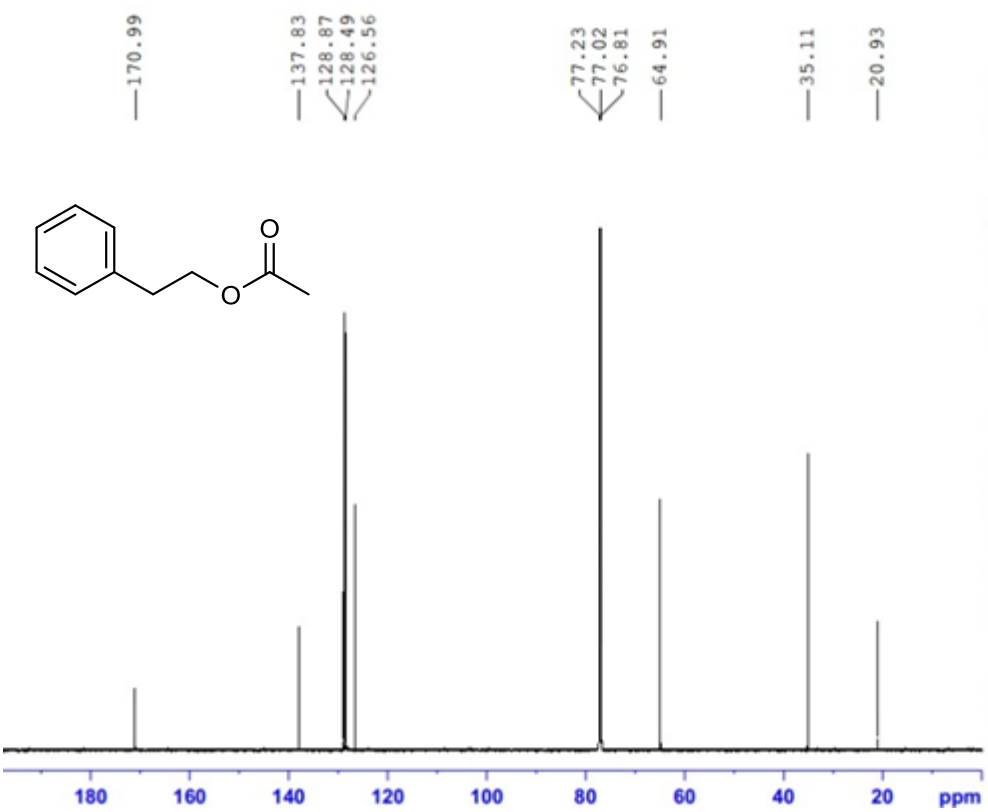


BRUKER

```
Current Data Parameters
NAME      Aug02-2022-nmrsu
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20220802
Time                14.06 h
INSTRUM   AvanceNeo 600
PROBHD   Z114607_0330 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             11904.762 Hz
FIDRES              0.363304 Hz
AQ              2.7525120 sec
RG                    101
DW                 42.000 usec
DE                  8.79 usec
TE                 299.3 K
D1              1.00000000 sec
TD0                     1
SFO1           600.4037075 MHz
NUC1                   1H
P0                  3.33 usec
P1                 10.00 usec
PLW1           27.65399933 W

F2 - Processing parameters
SI                  65536
SF             600.4000078 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

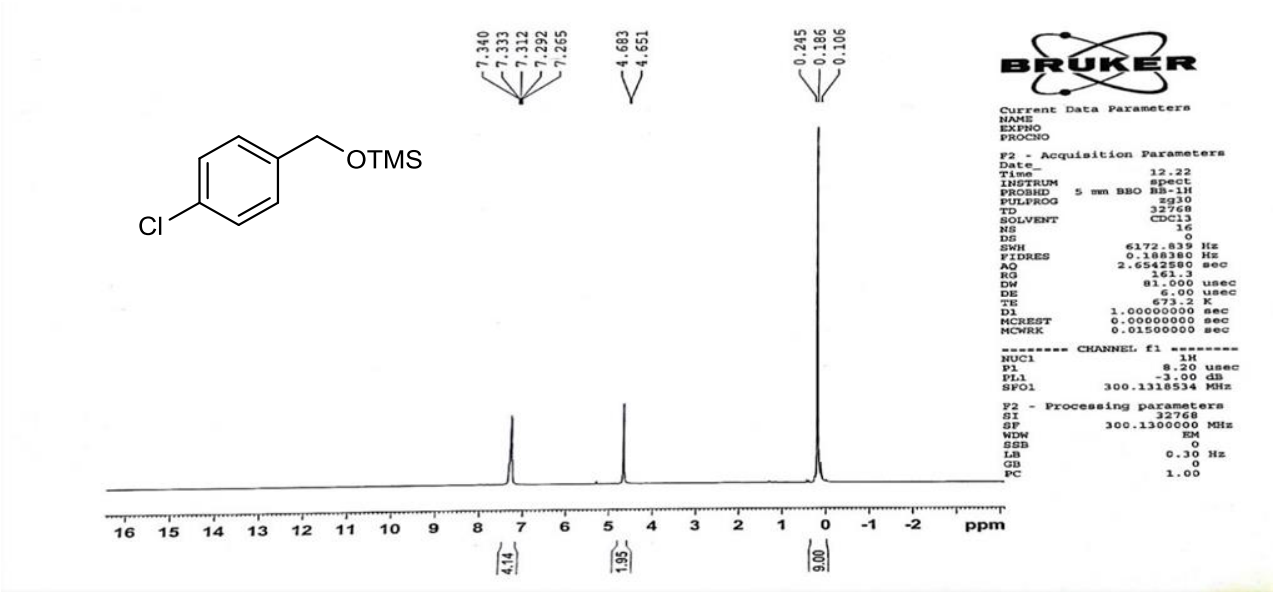
BRUKER

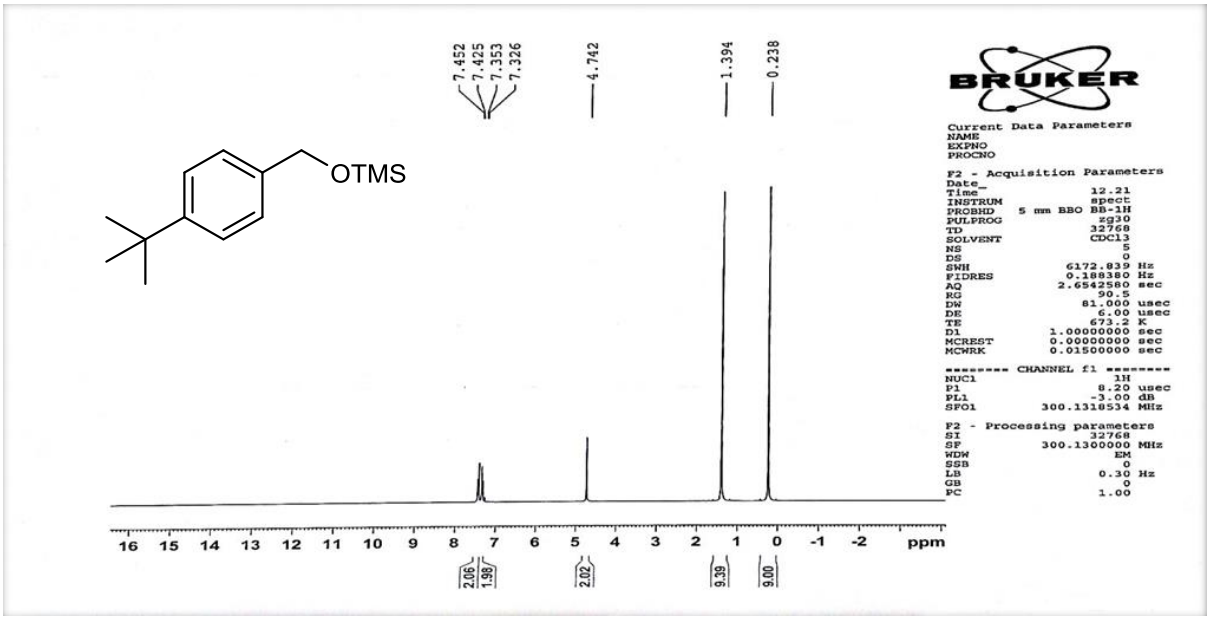
```
Current Data Parameters
NAME      Aug03-2022-nmrsu
EXPNO                   40
PROCNO                   1

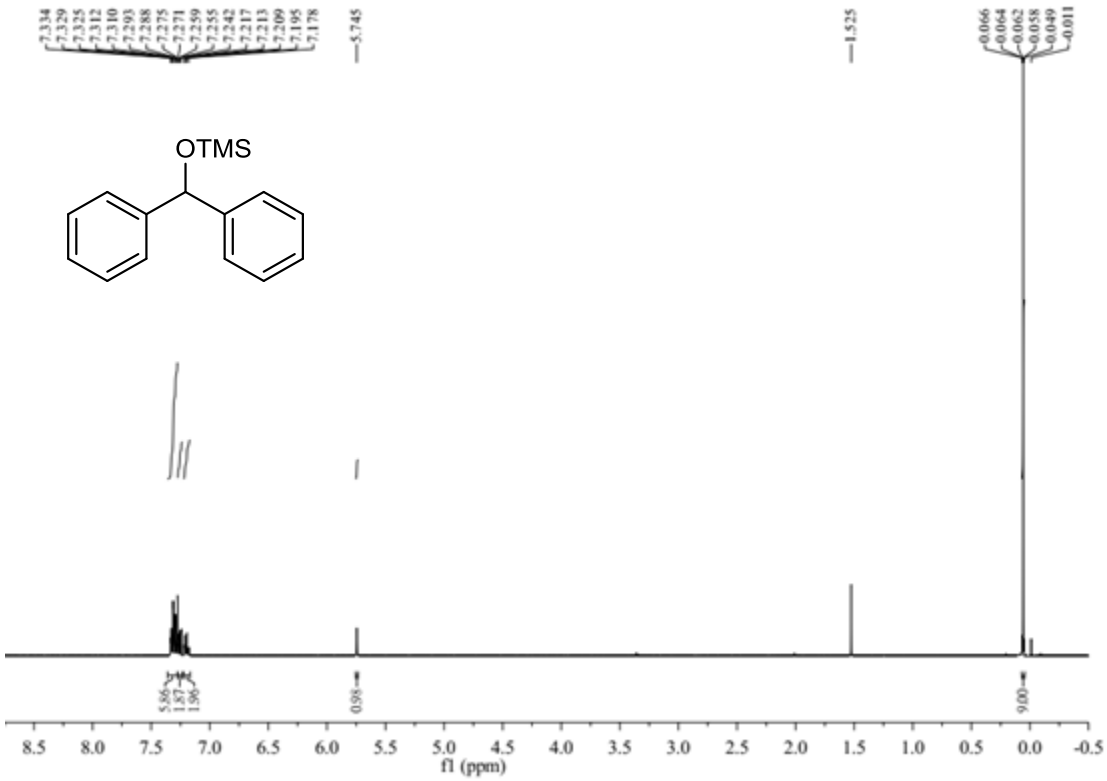
F2 - Acquisition Parameters
Date_           20220803
Time                12.52 h
INSTRUM   AvanceNeo 600
PROBHD   Z114607_0330 (
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             35714.285 Hz
FIDRES              1.089913 Hz
AQ              0.9175040 sec
RG                    101
DW                 14.000 usec
DE                  6.50 usec
TE                 300.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1
SFO1           150.9857971 MHz
NUC1                   13C
P0                  4.00 usec
P1                 12.00 usec
PLW1           82.27400208 W
SFO2           600.4024016 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2              70.00 usec
PLW2           27.65399933 W
PLW12           0.56436002 W
PLW13           0.28387001 W

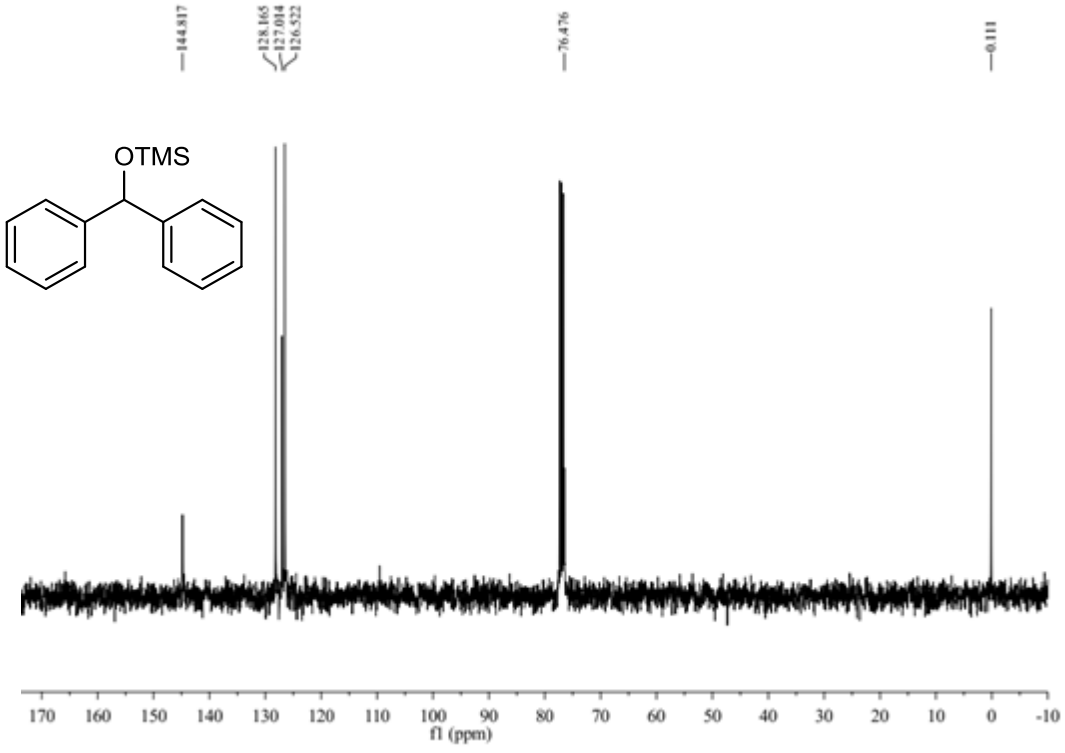
F2 - Processing parameters
SI                  32768
SF             150.9707001 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

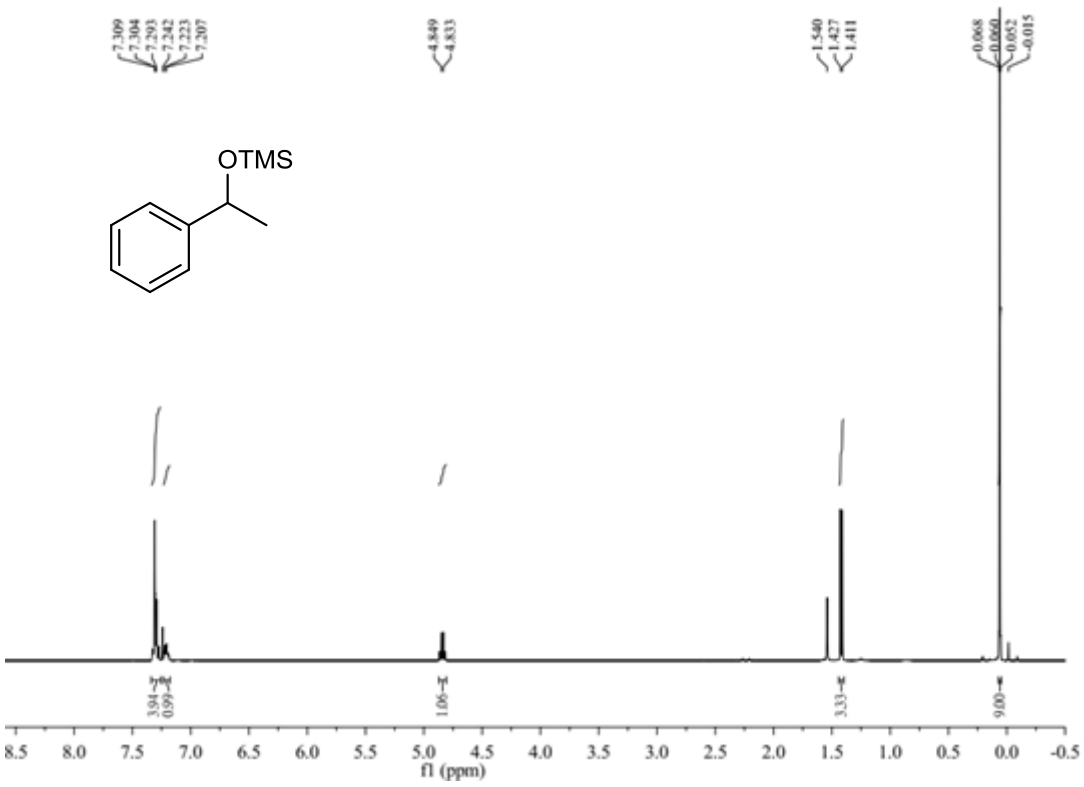
Table 9. Trimethylsilylation of alcohols

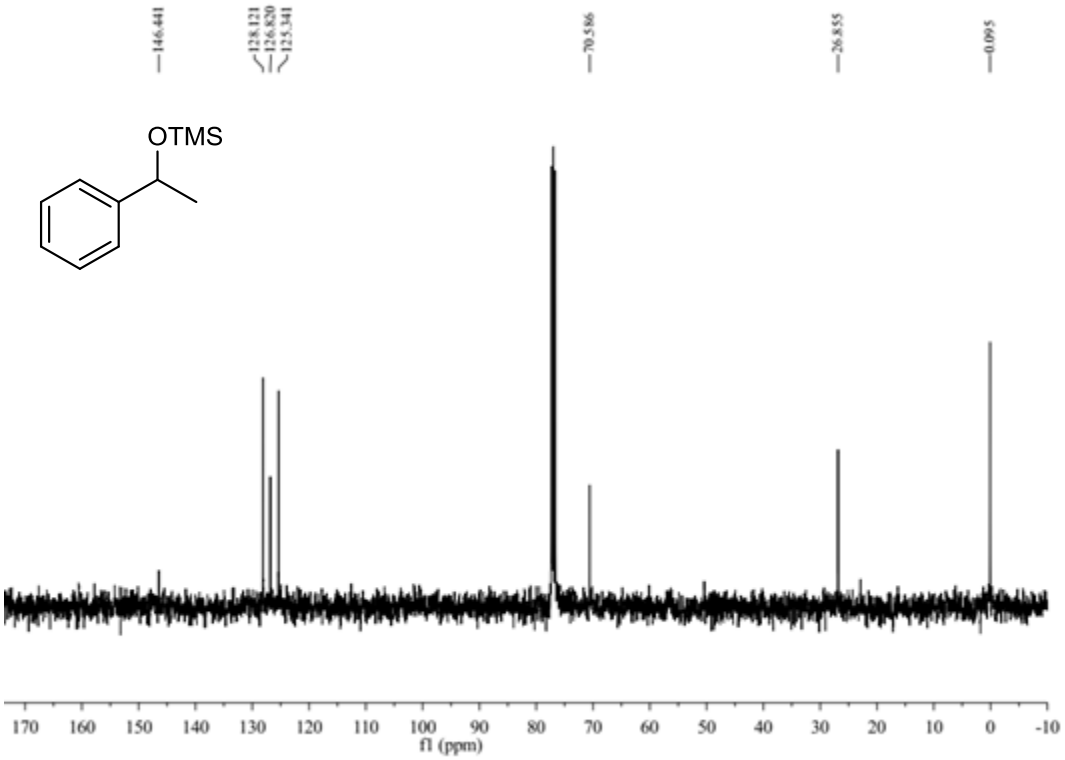


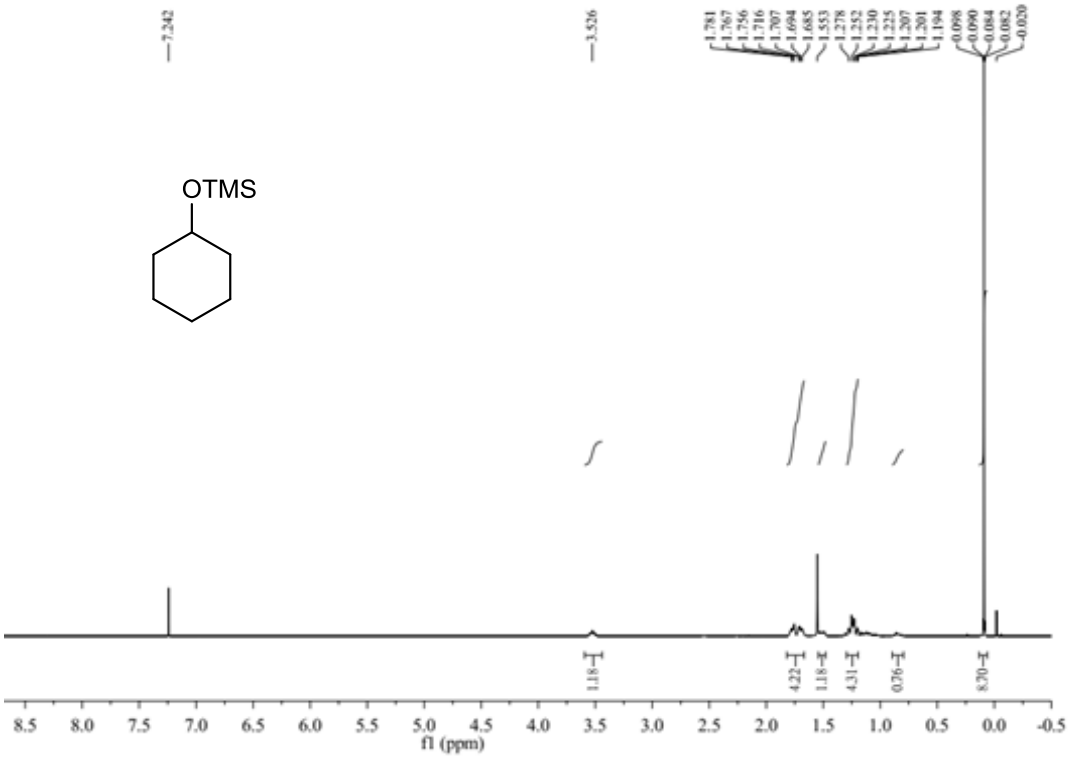


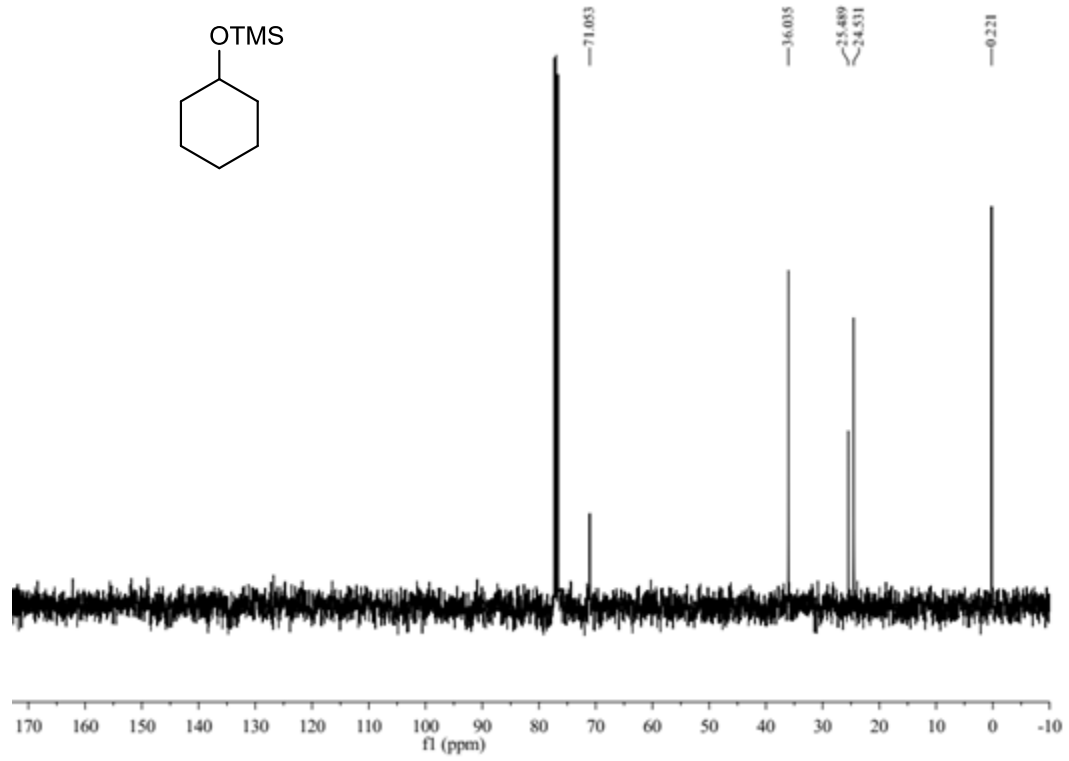

7.334
7.329
7.325
7.312
7.310
7.293
7.288
7.275
7.271
7.259
7.255
7.242
7.217
7.213
7.209
7.195
7.178
5.745
1.525
0.066
0.064
0.062
0.058
0.049
0.011
OTMS
5.85
1.87
1.96
0.98
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


144.817
128.165
127.014
126.522
76.476
0.111
OTMS
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.309
7.304
7.293
7.242
7.223
7.207
4.849
4.833
1.540
1.427
1.411
0.068
0.060
0.052
-0.015
OTMS
3.94
0.99
1.06
3.33
9.00
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)


146.441
128.121
126.820
125.341
70.586
26.855
0.095
OTMS
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OTMS
7.242
3.526
1.781
1.767
1.756
1.716
1.707
1.694
1.685
1.553
1.278
1.252
1.230
1.225
1.207
1.201
1.194
0.098
0.090
0.084
0.082
0.020
1.18
4.22
1.18
4.31
0.76
8.70
f1 (ppm)


OTMS
71.053
36.035
25.489
24.531
0.221
f1 (ppm)