Copper(II)-Catalyzed Reactions of α-Keto Thioesters with Azides via C-C and C-S Bond Cleavages: Synthesis of *N*-Acylureas and Amides

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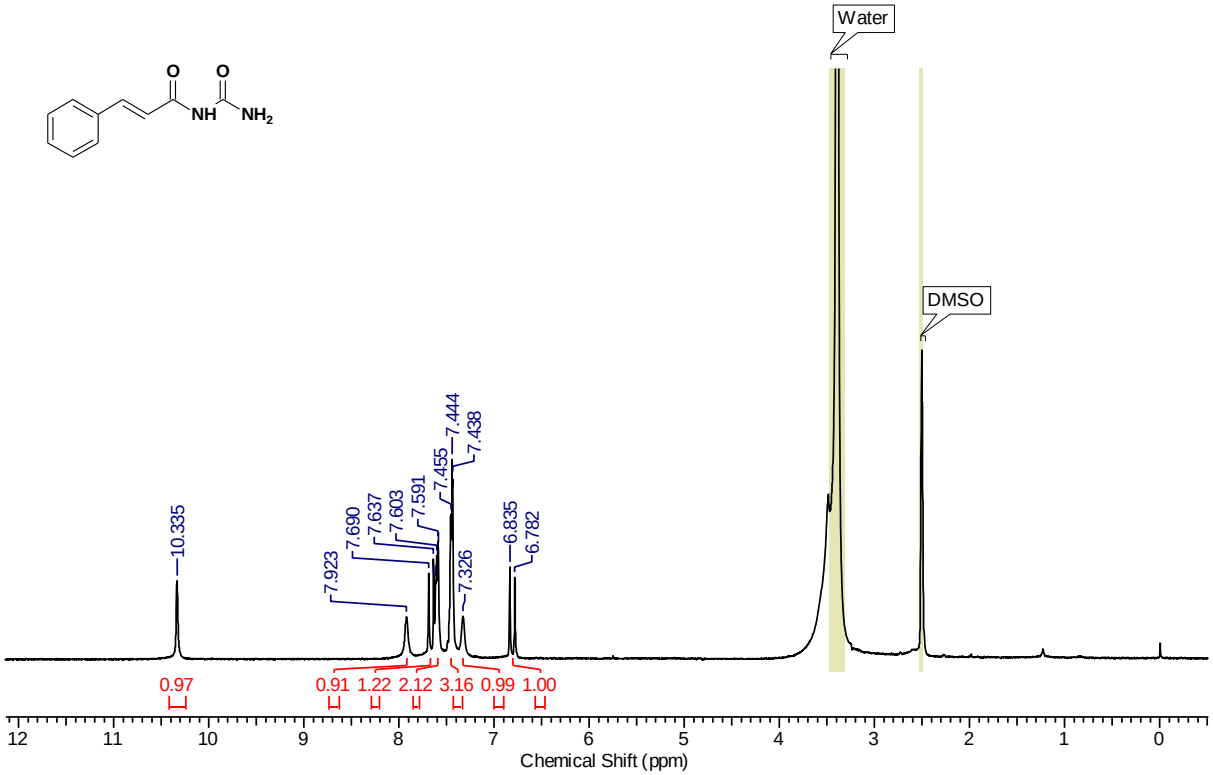
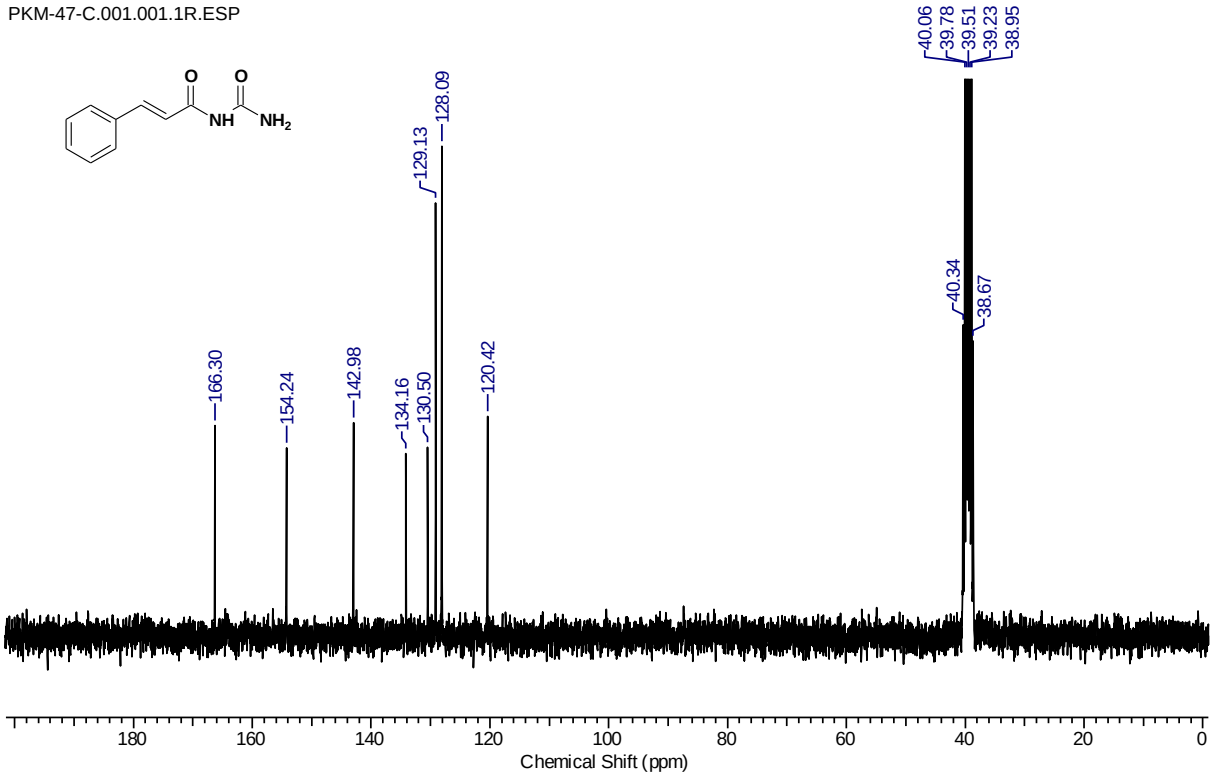
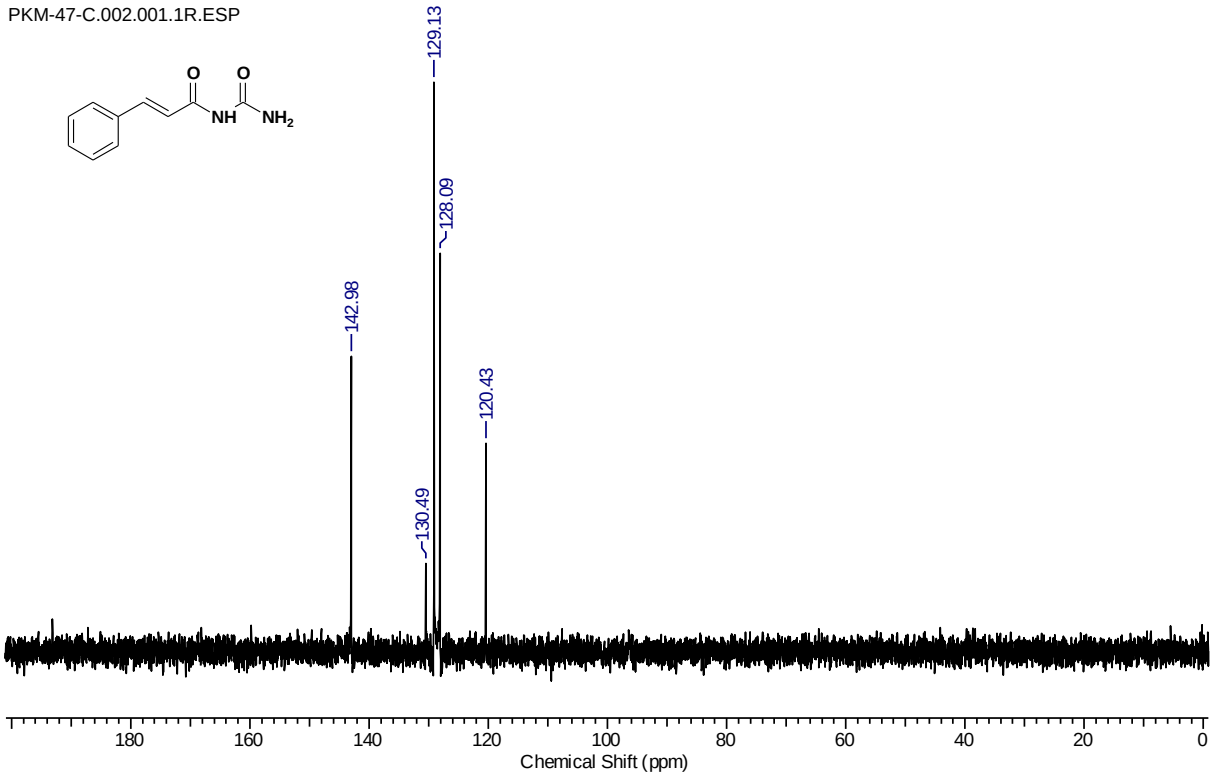
1. Copy of 1D NMR Spectra

^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3a:**







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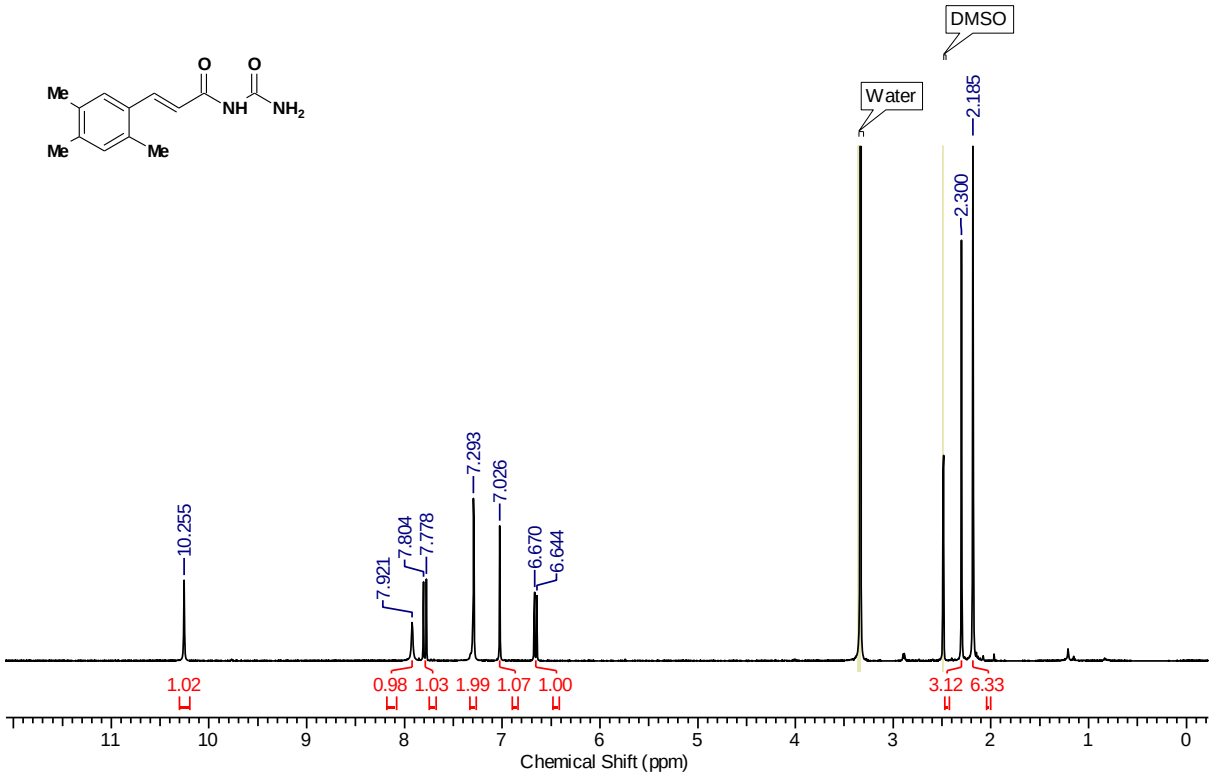

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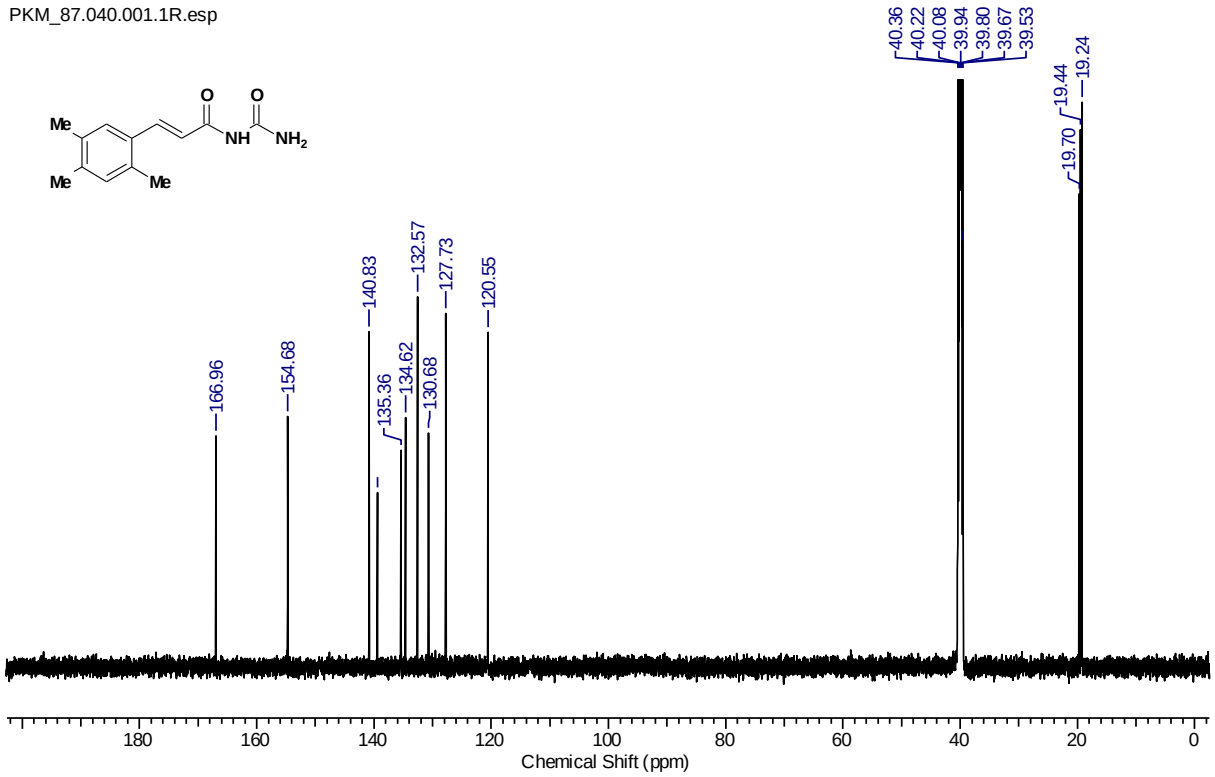

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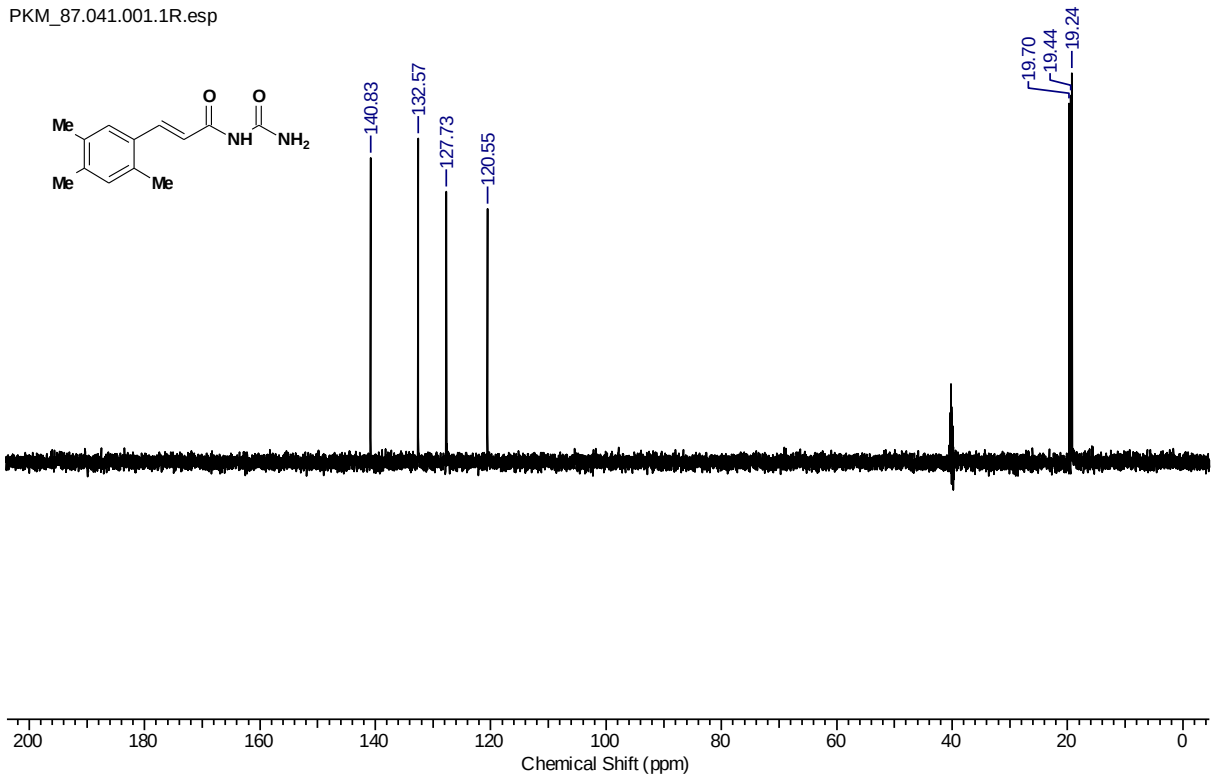

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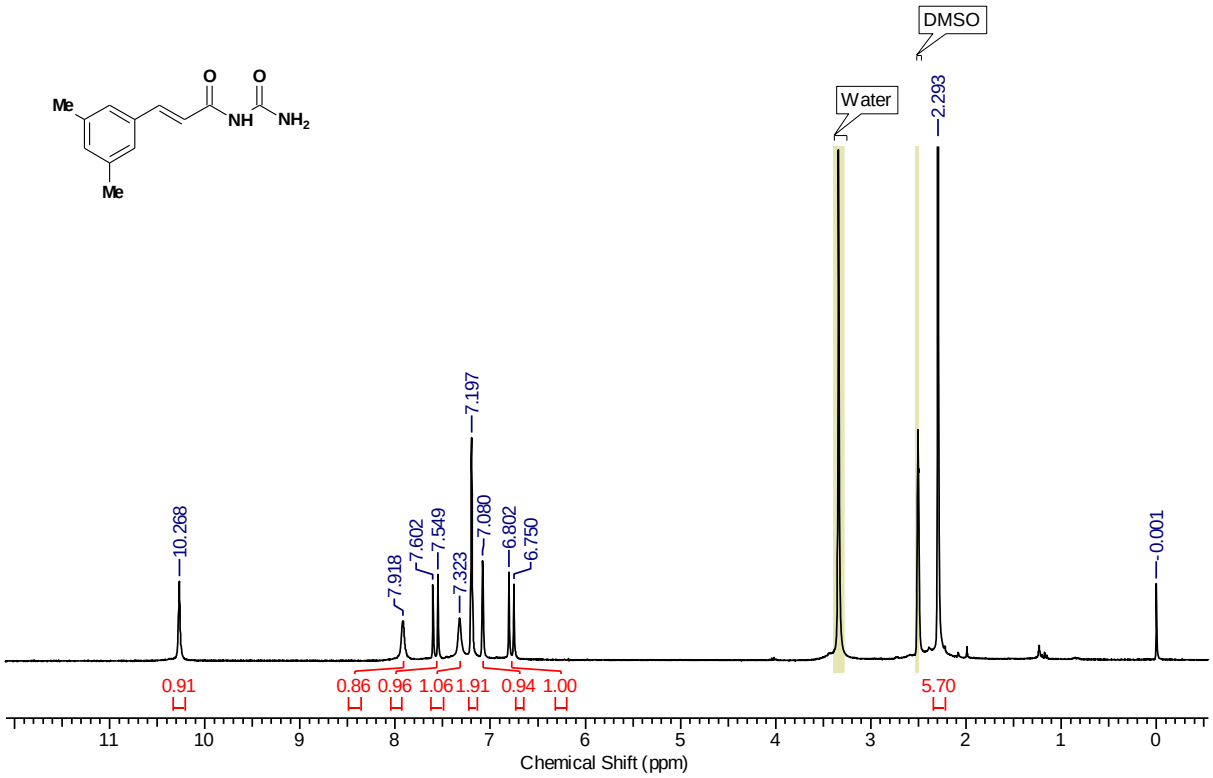

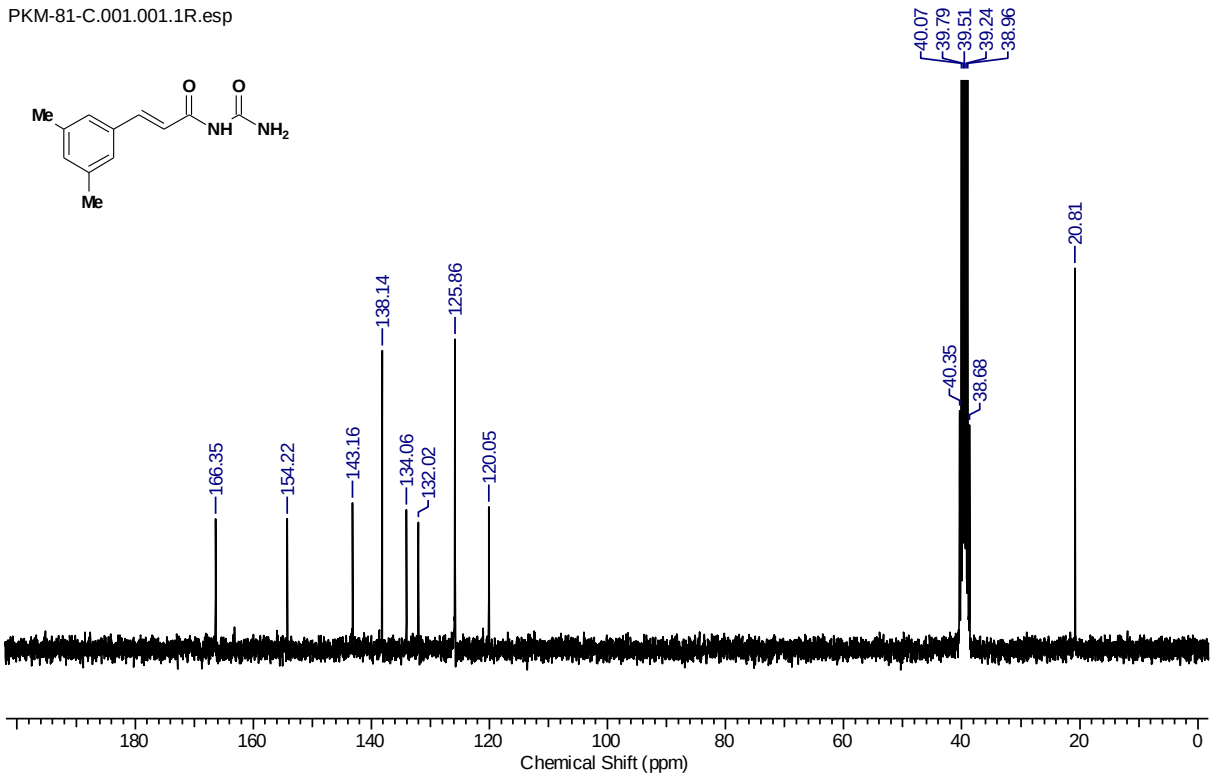

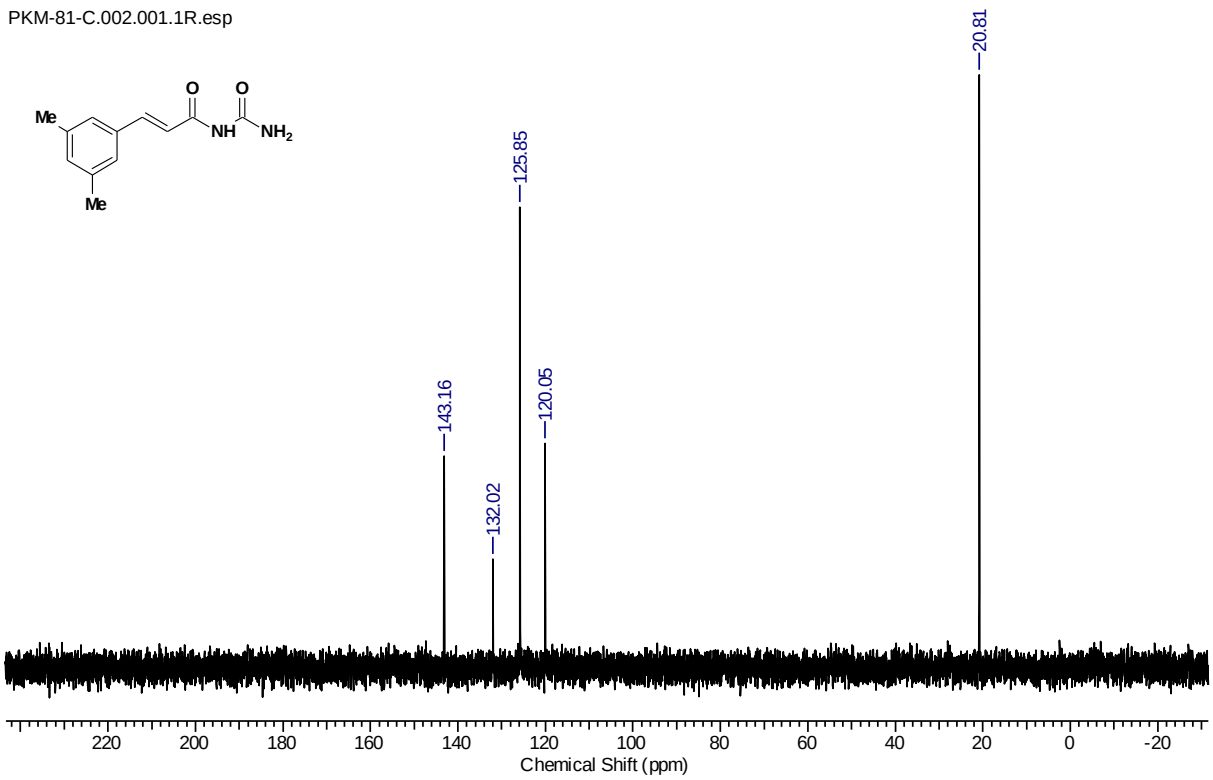

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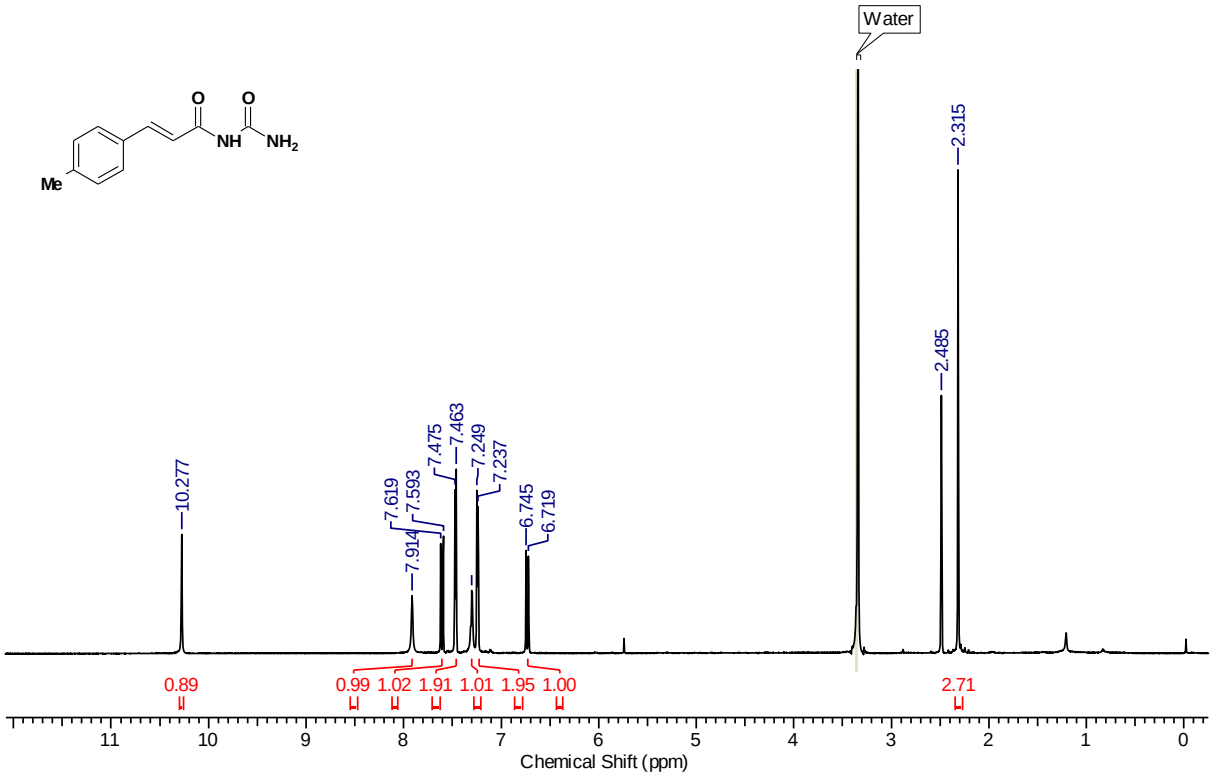

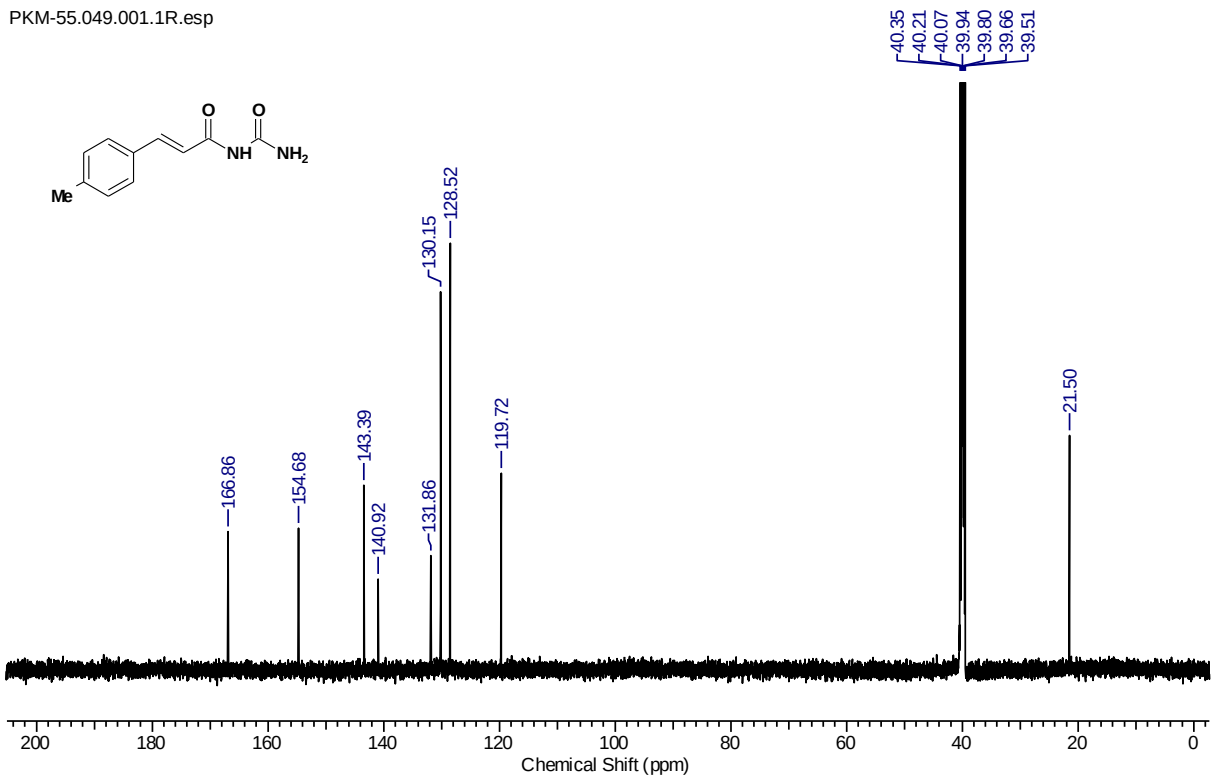
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154.68
143.39
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21.50
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20
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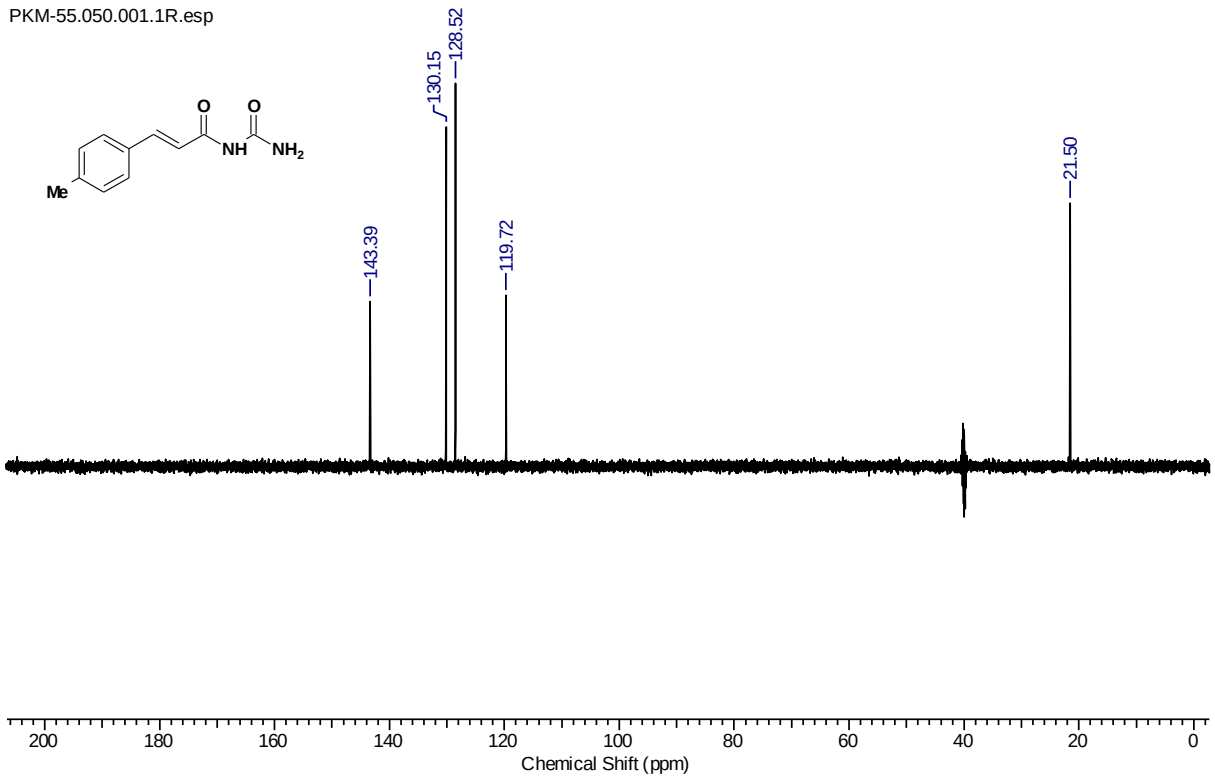
Chemical Shift (ppm)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20
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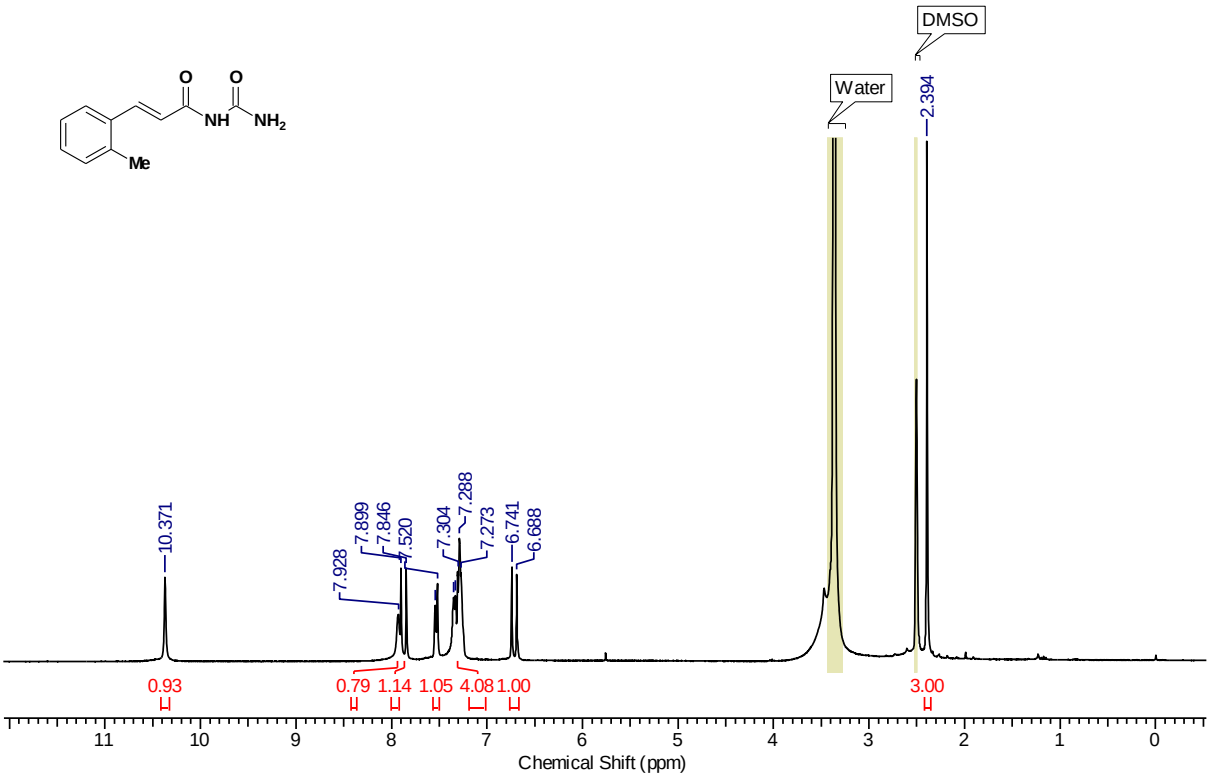
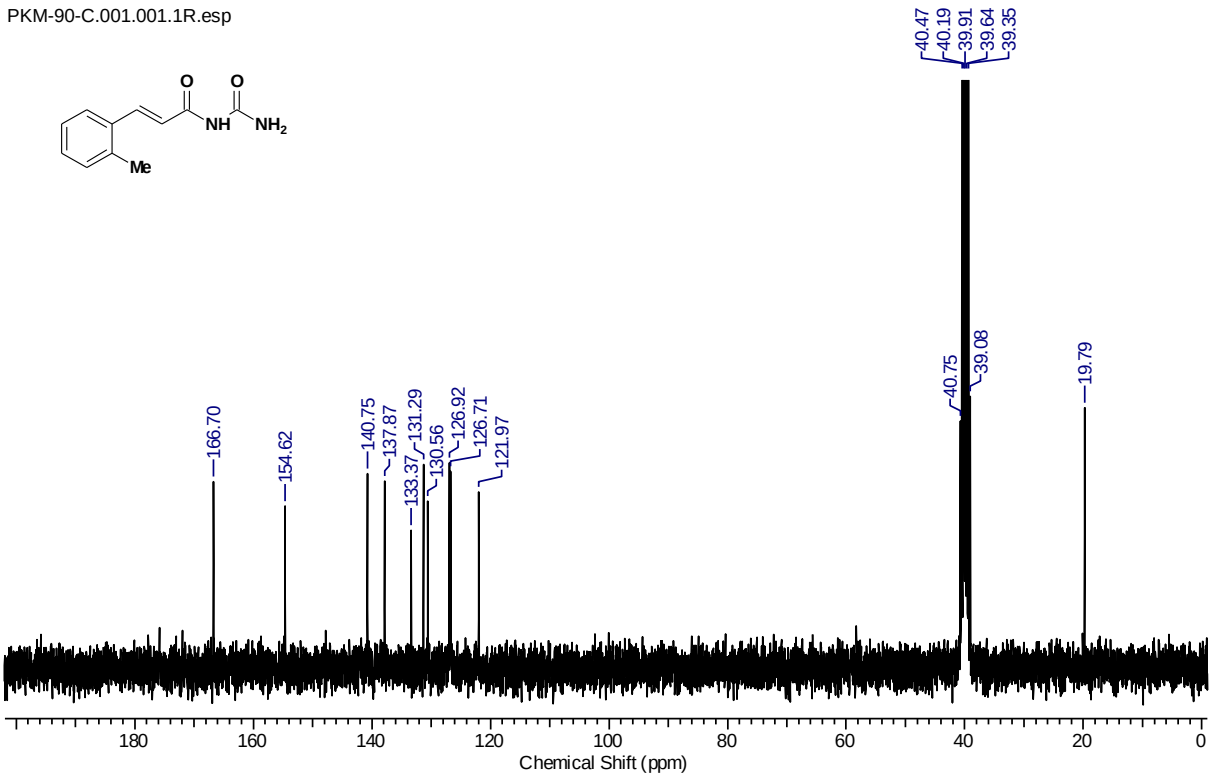
Chemical Shift (ppm)

^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3e:**





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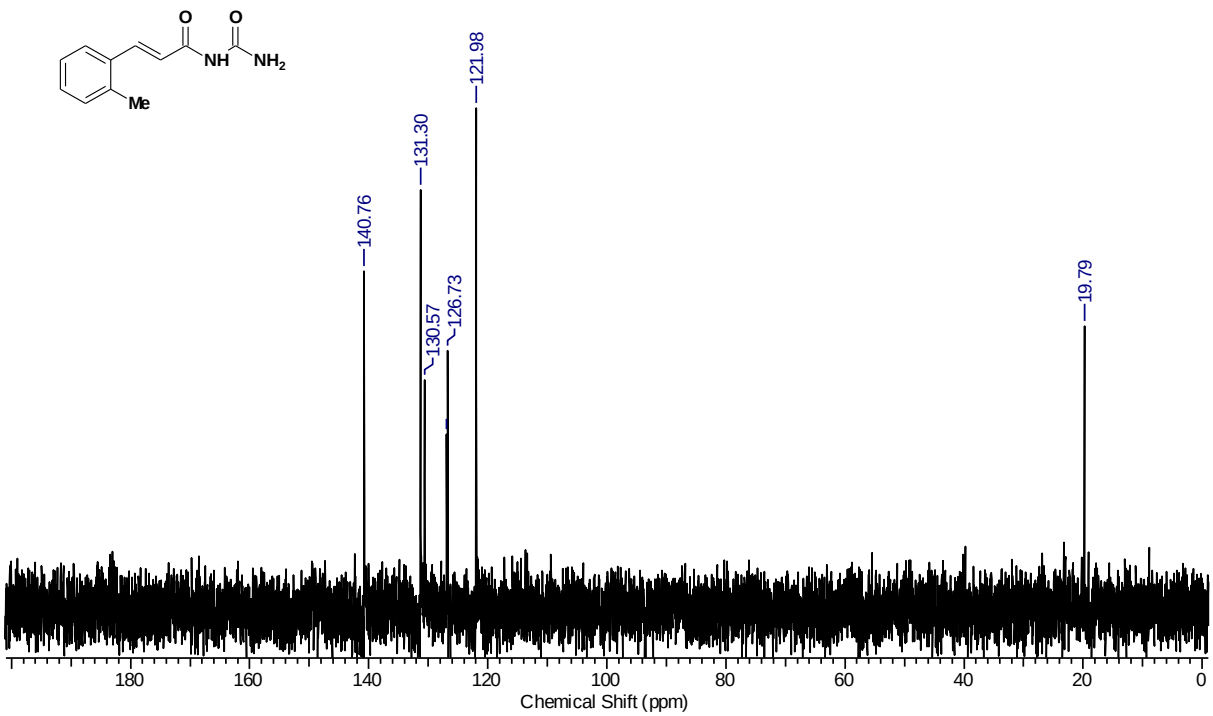

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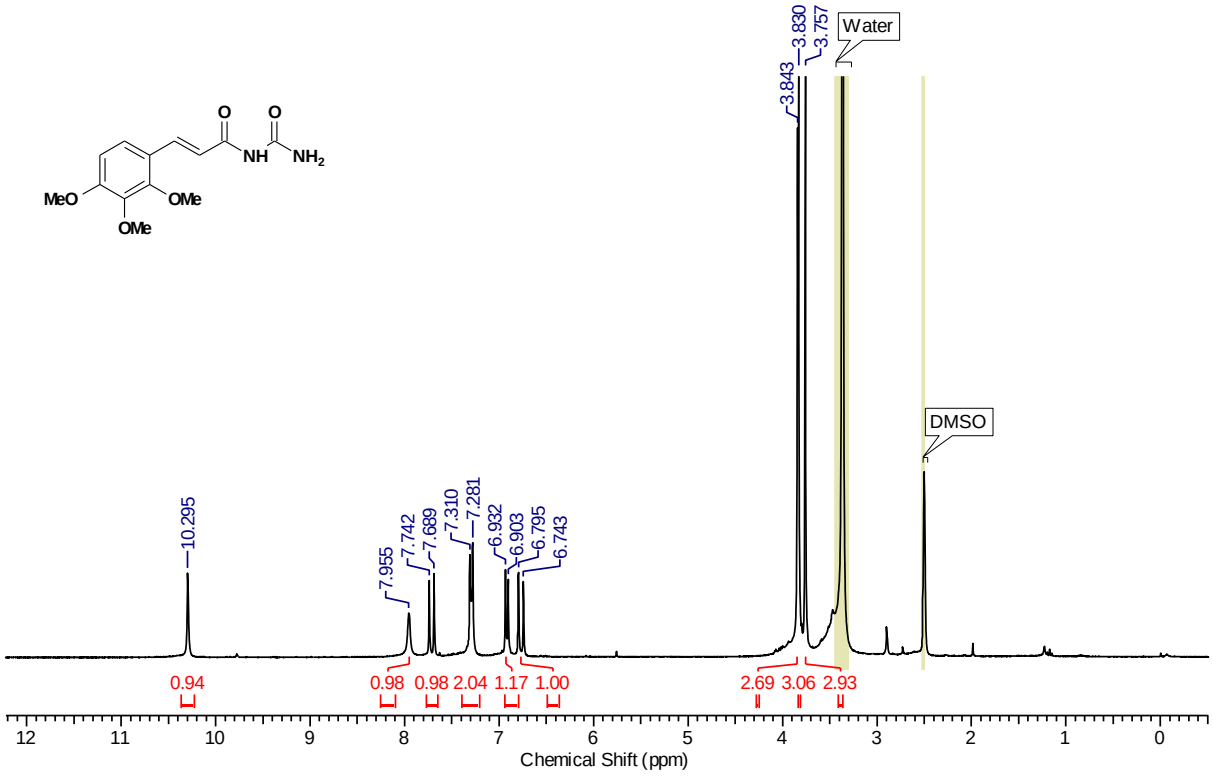

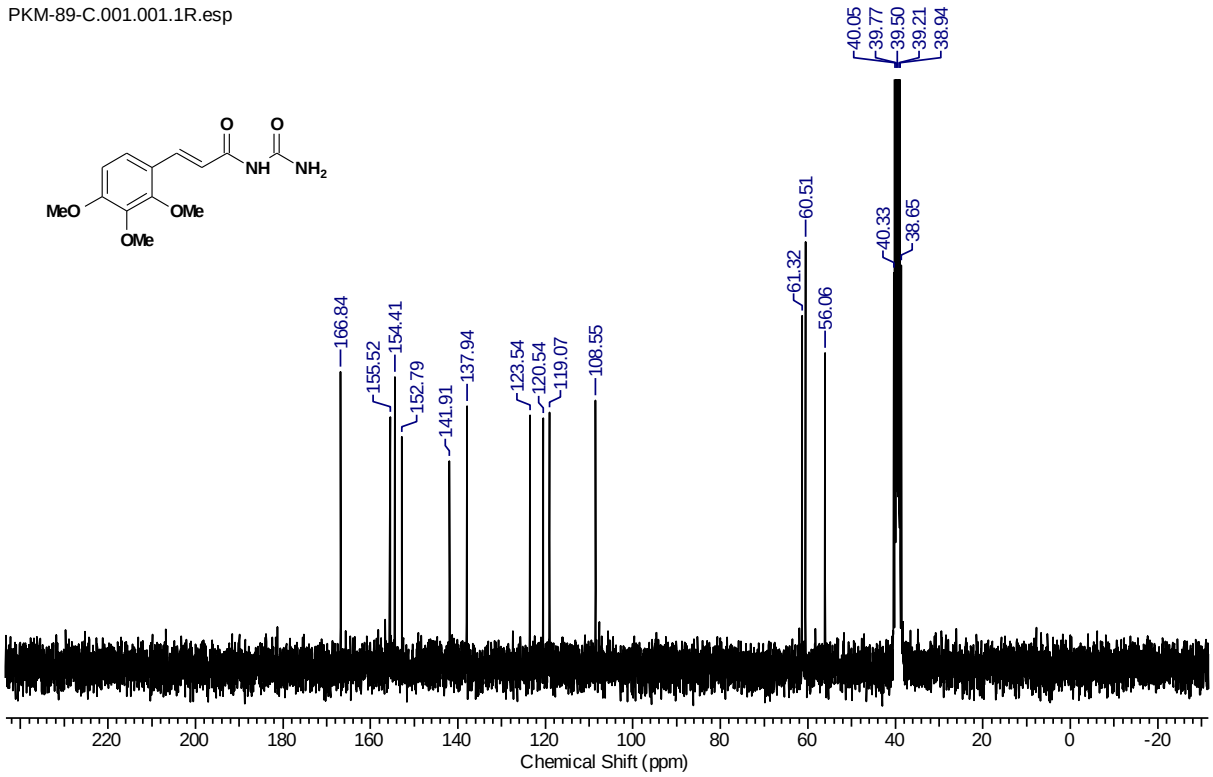

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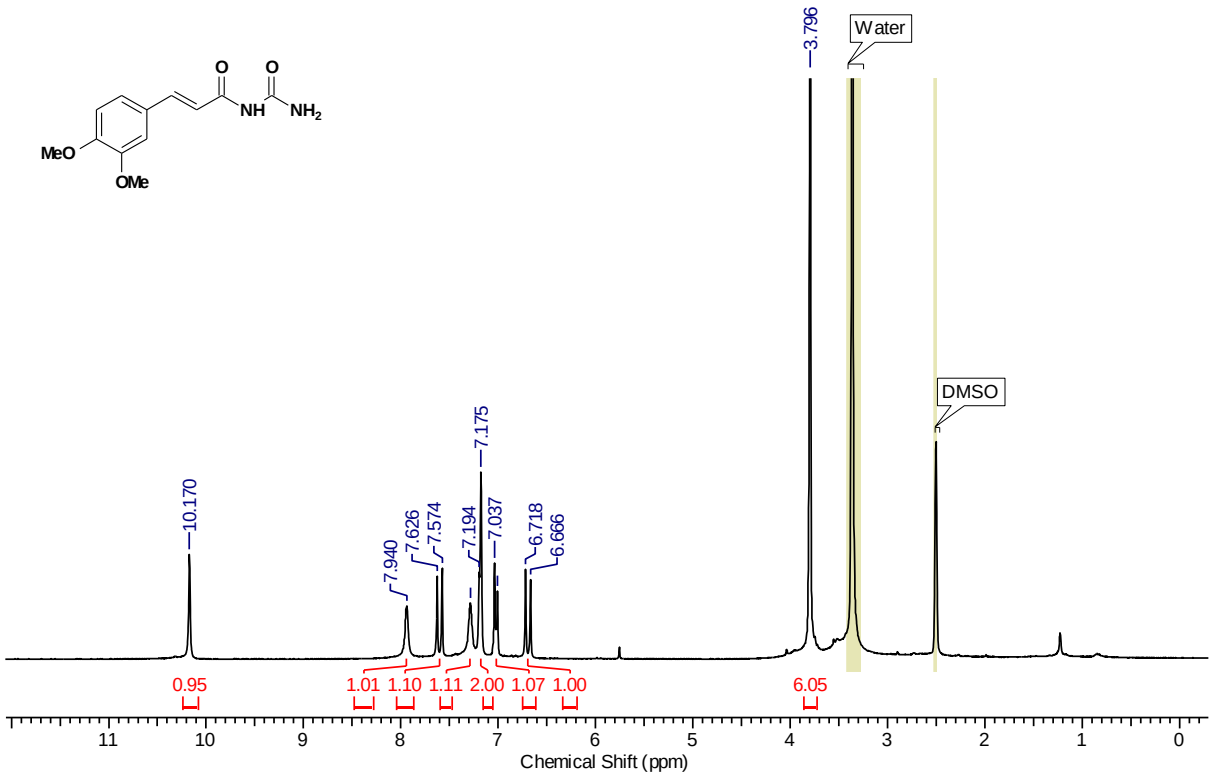

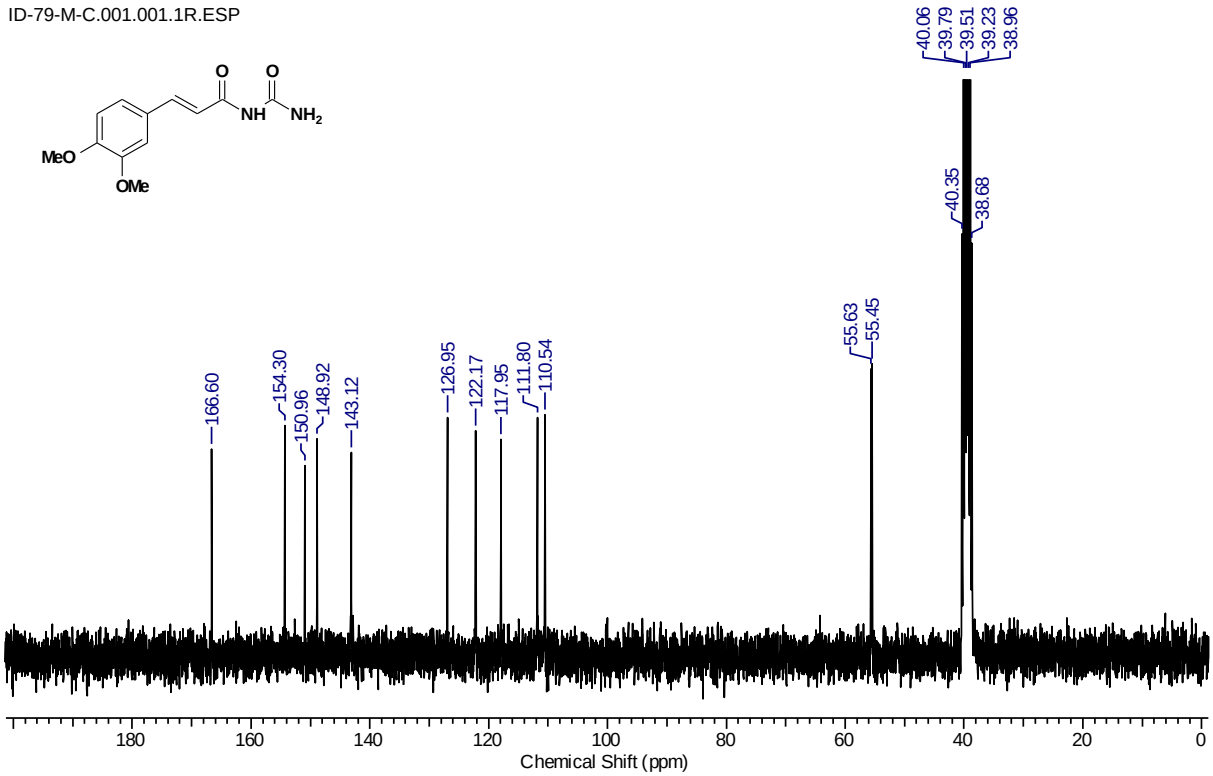

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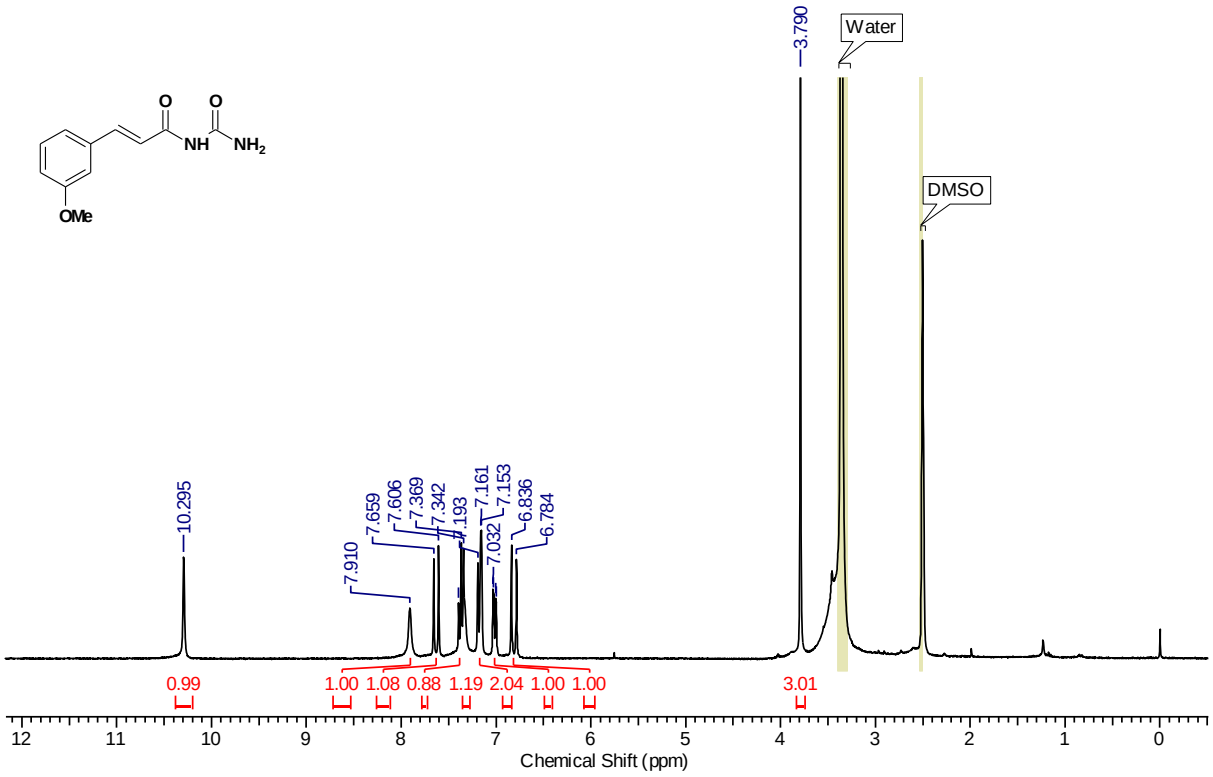

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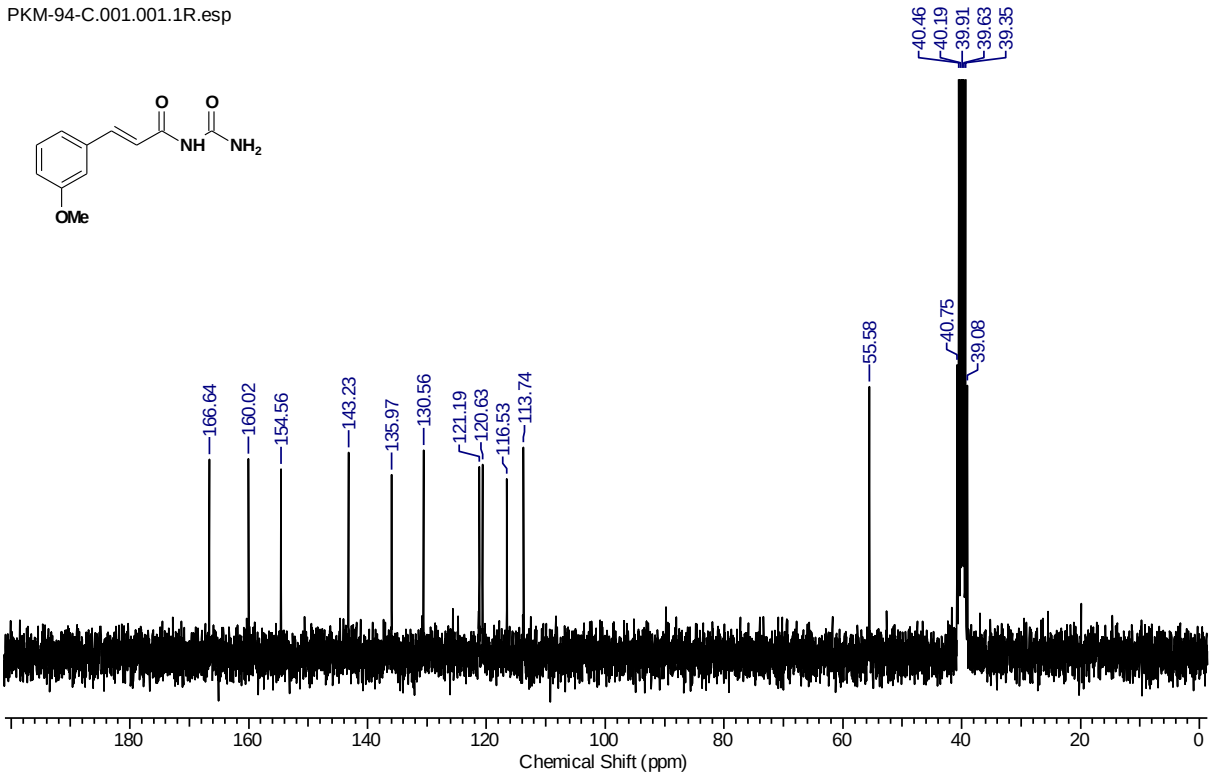

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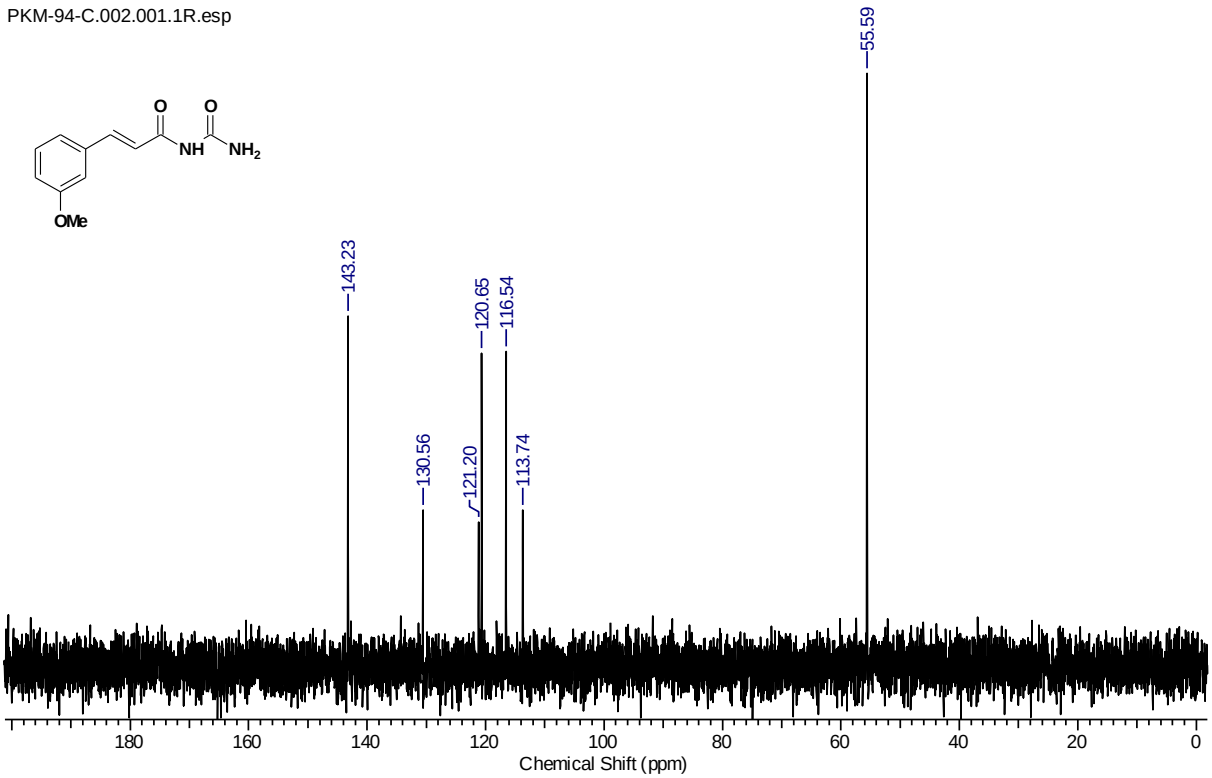

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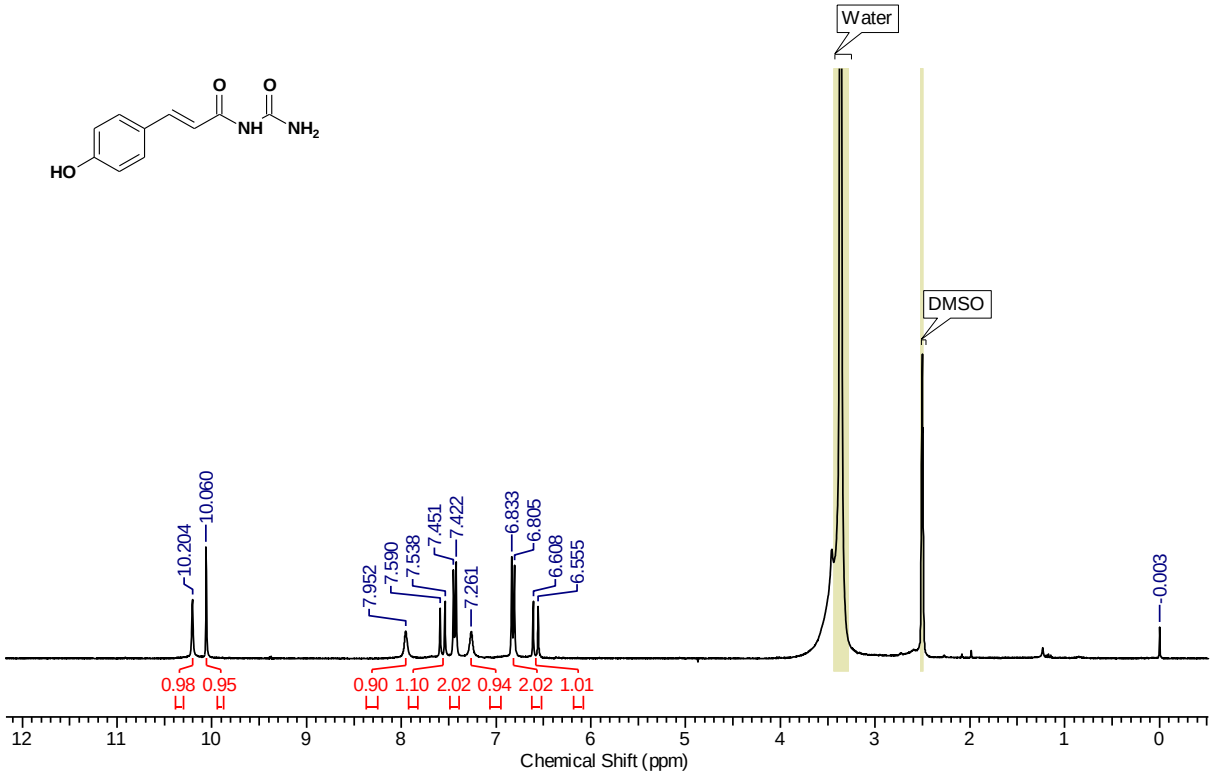

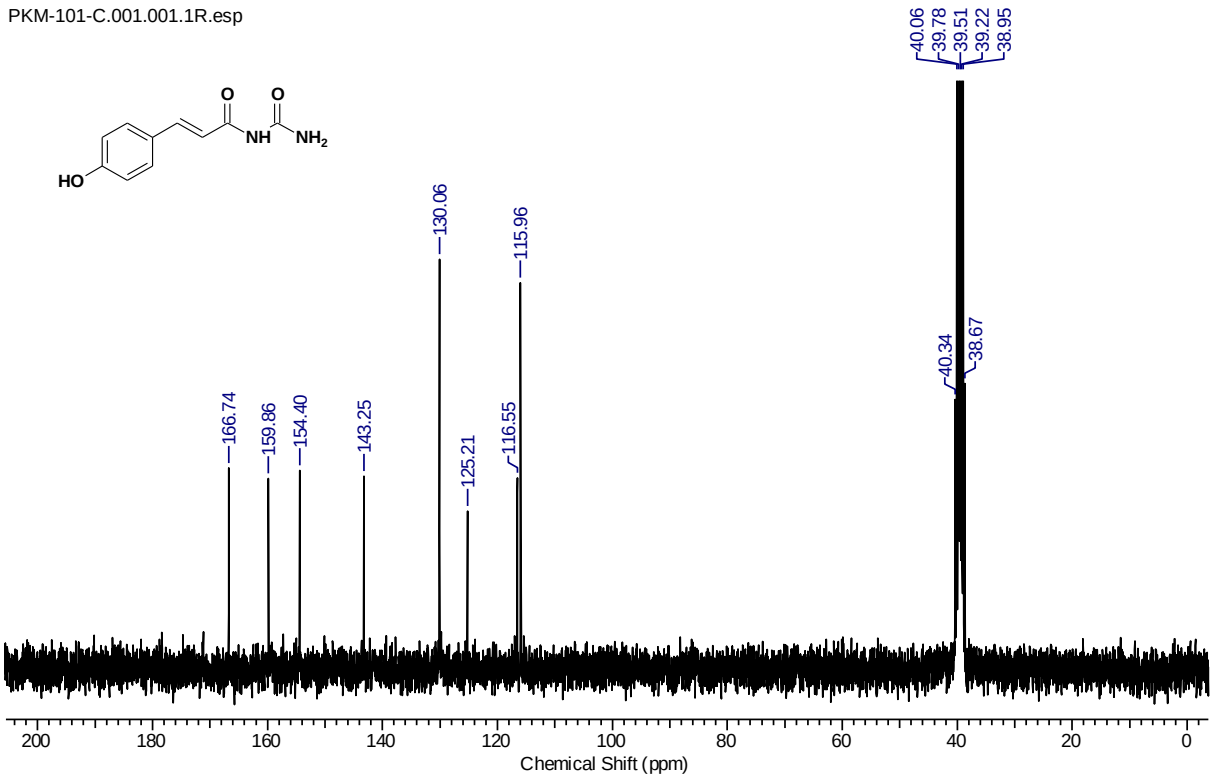

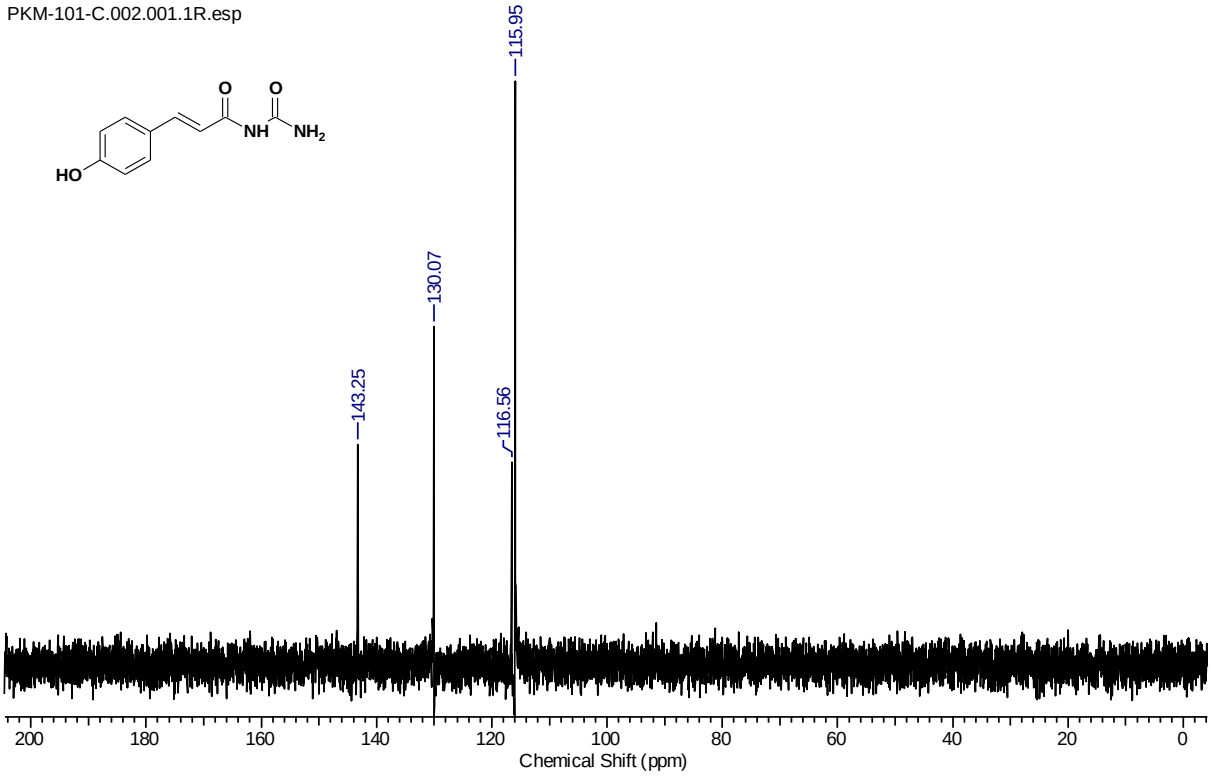

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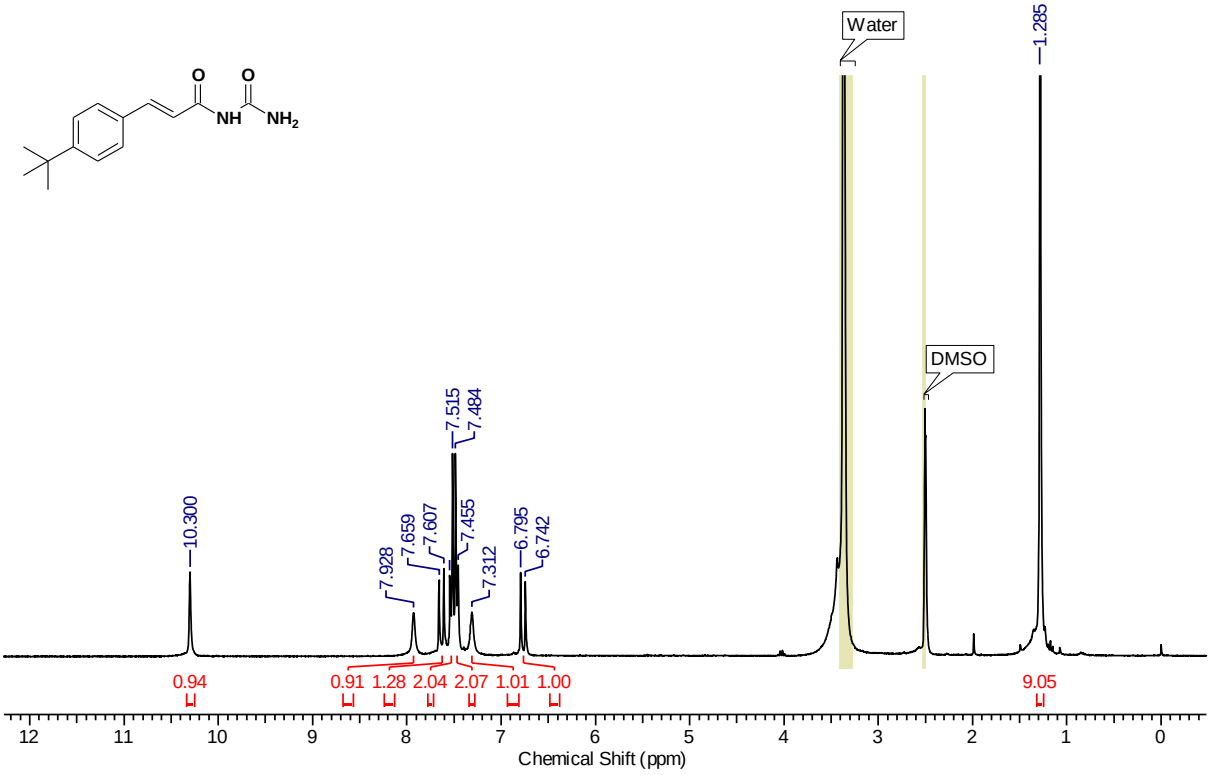

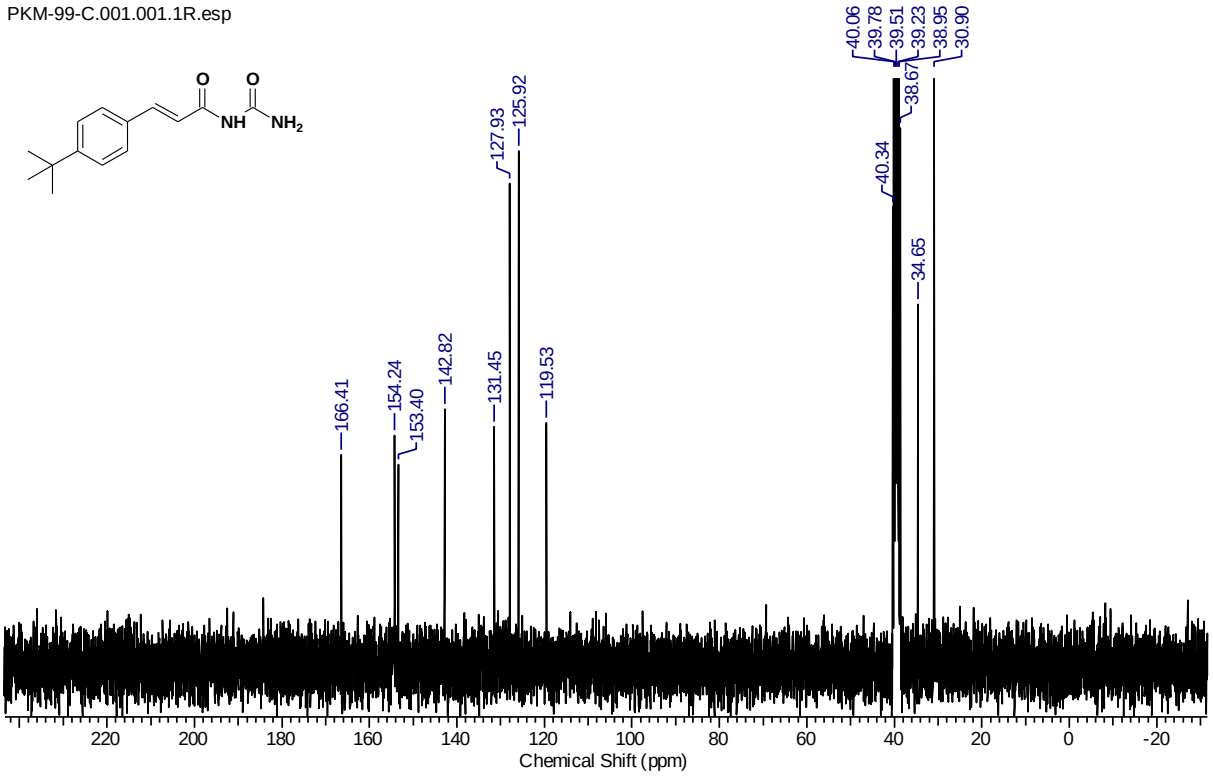
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38.95
38.67
40.34
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140
120
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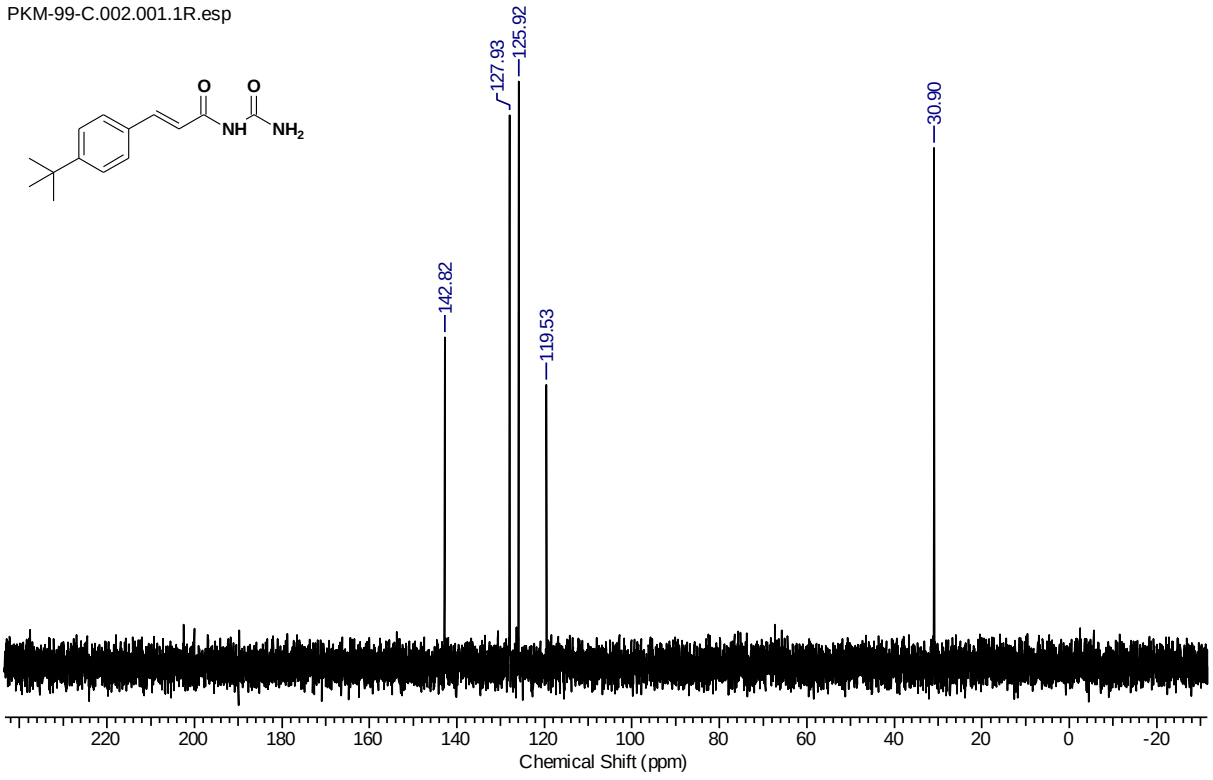
40
20
0
-20
Chemical Shift (ppm)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NH2
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119.53
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140
120
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80
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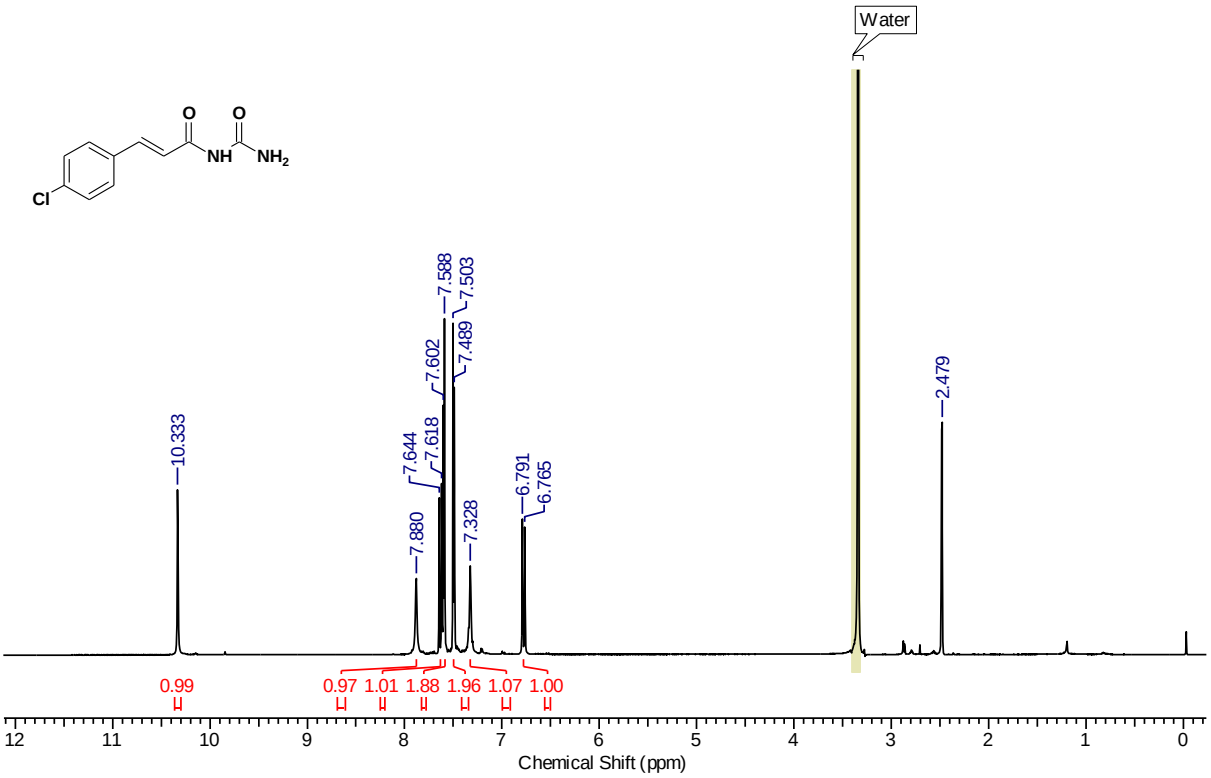
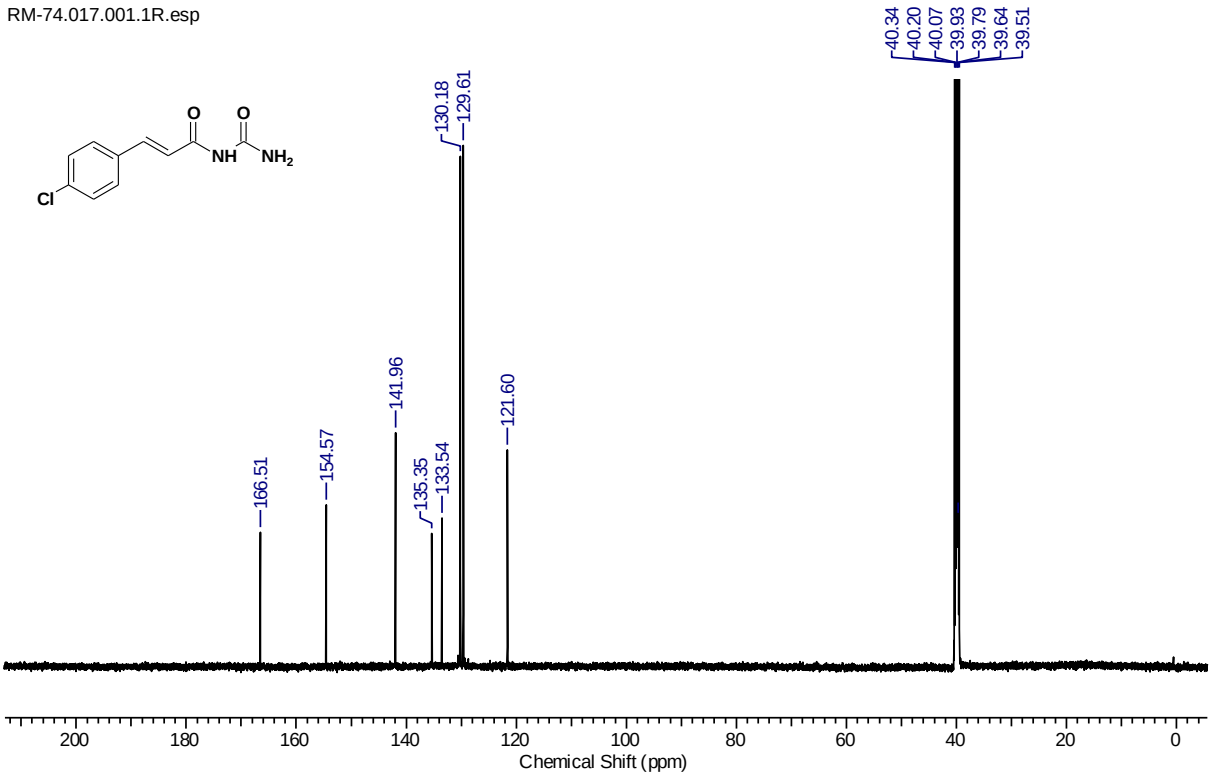
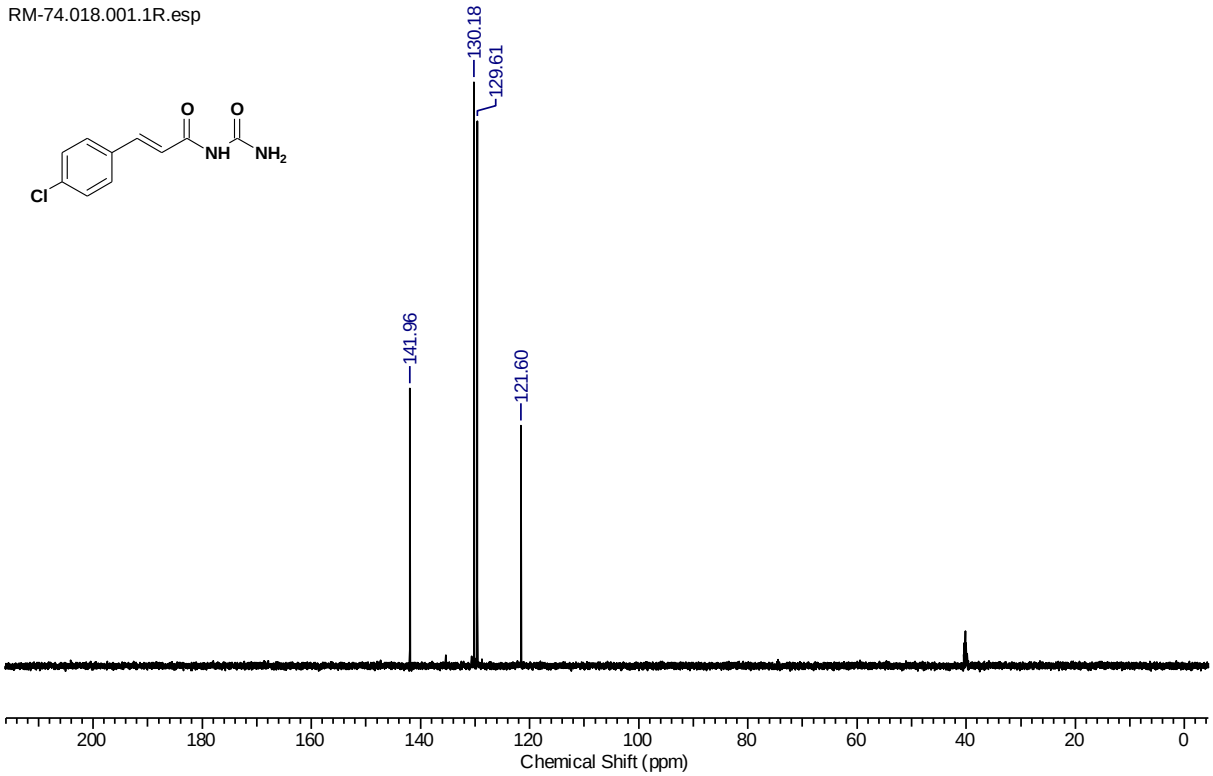
40
20
0
-20
Chemical Shift (ppm)

^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3k:**







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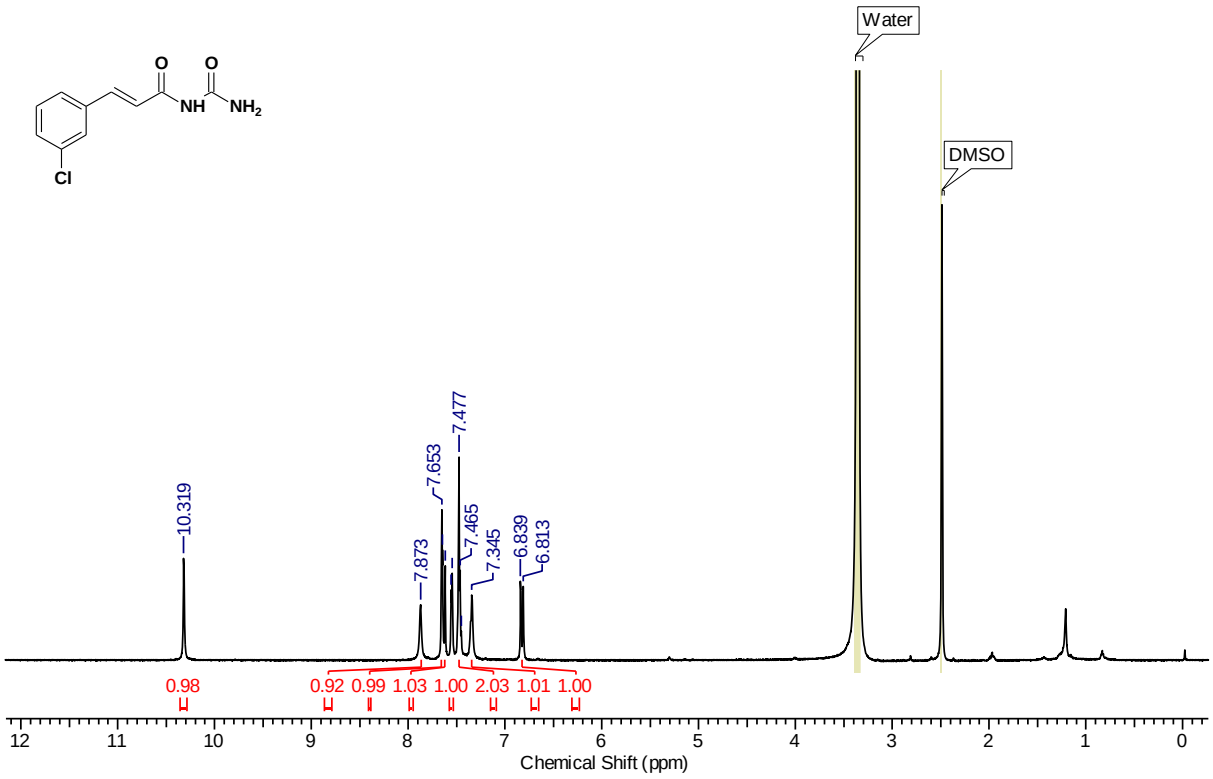

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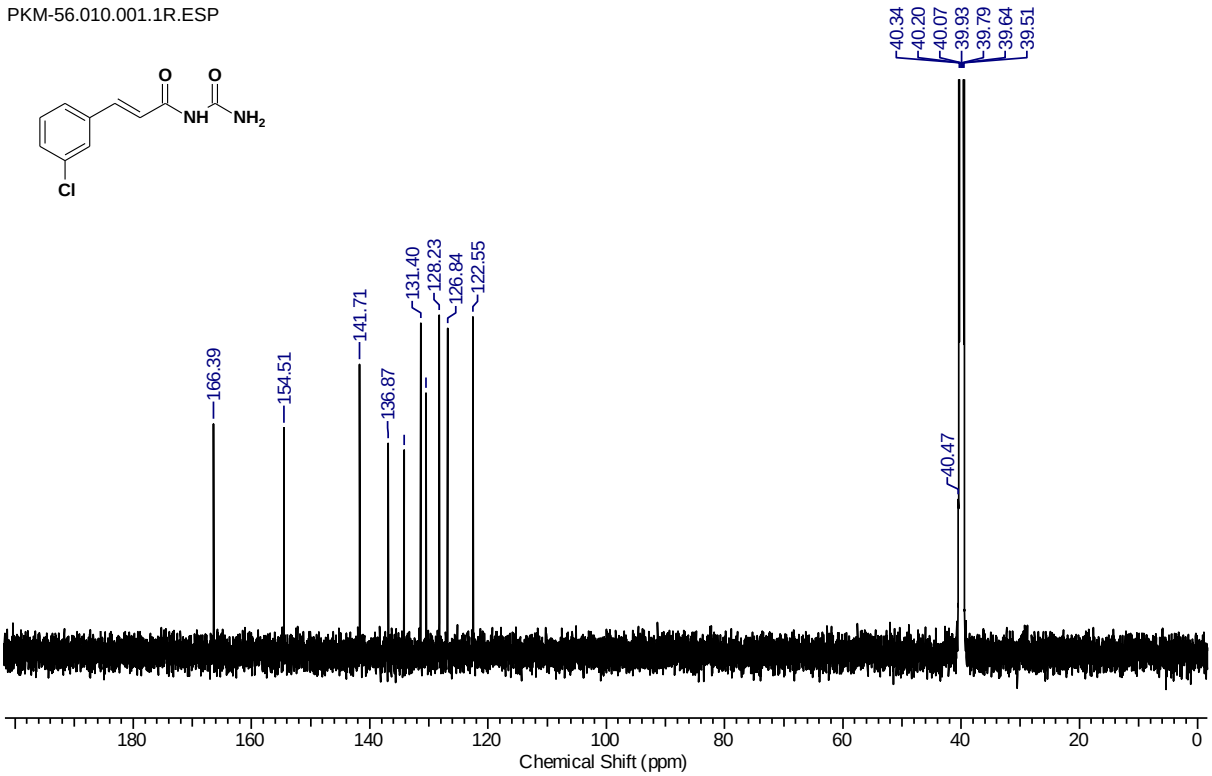

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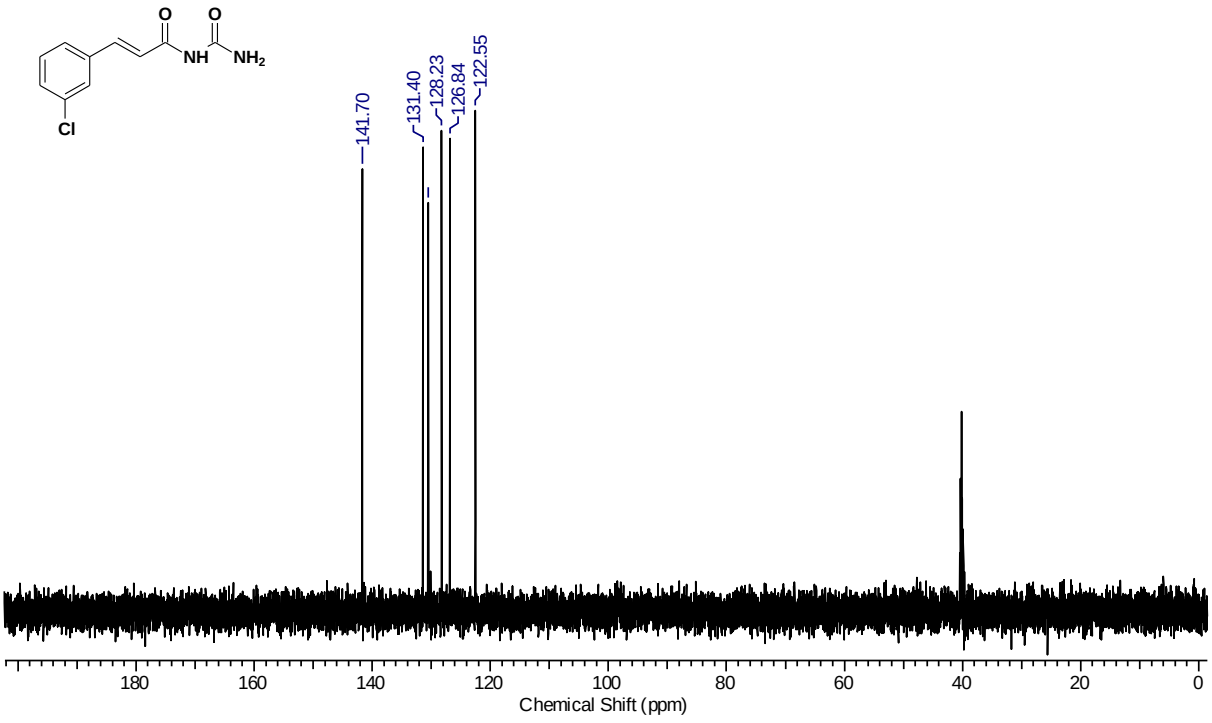

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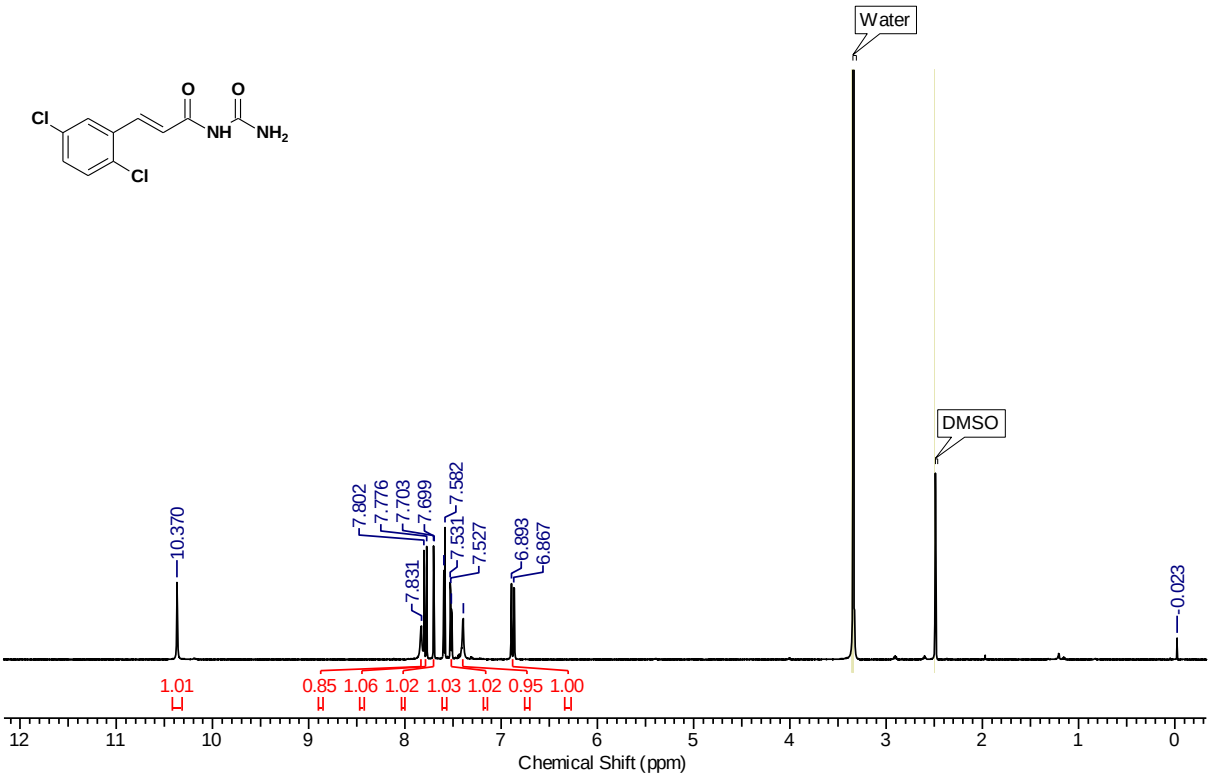

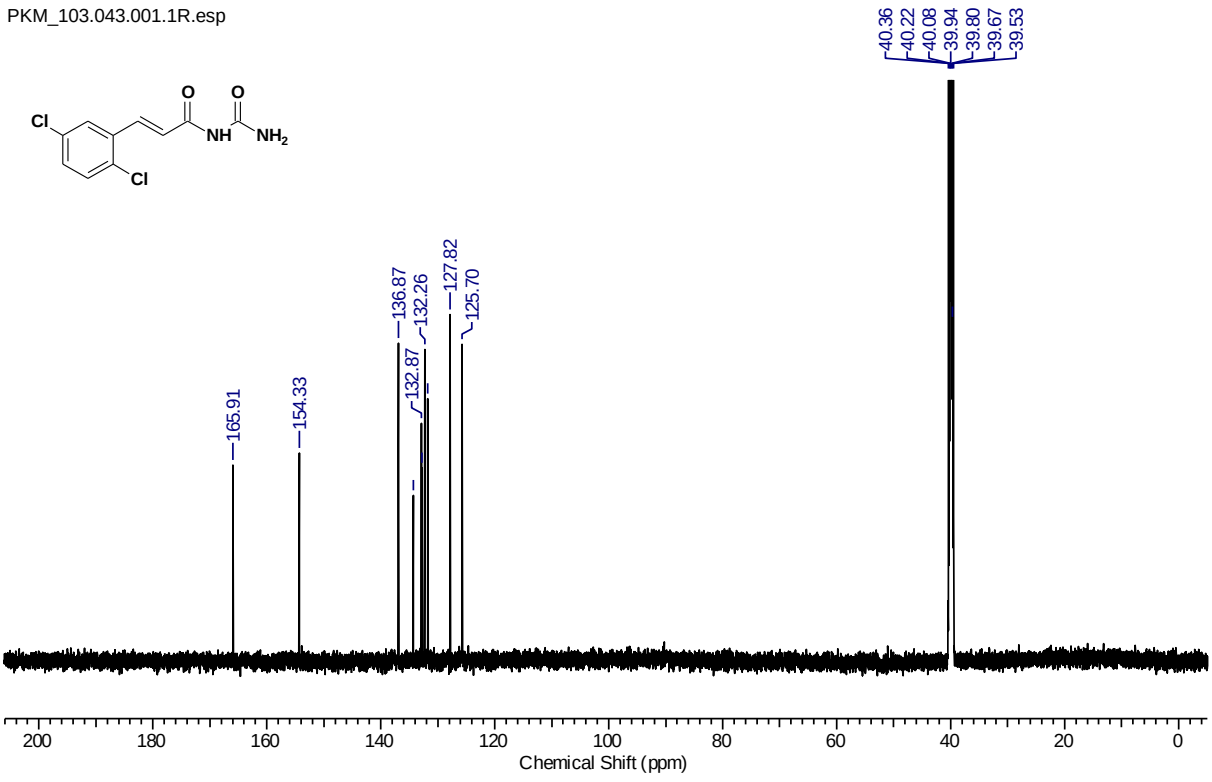

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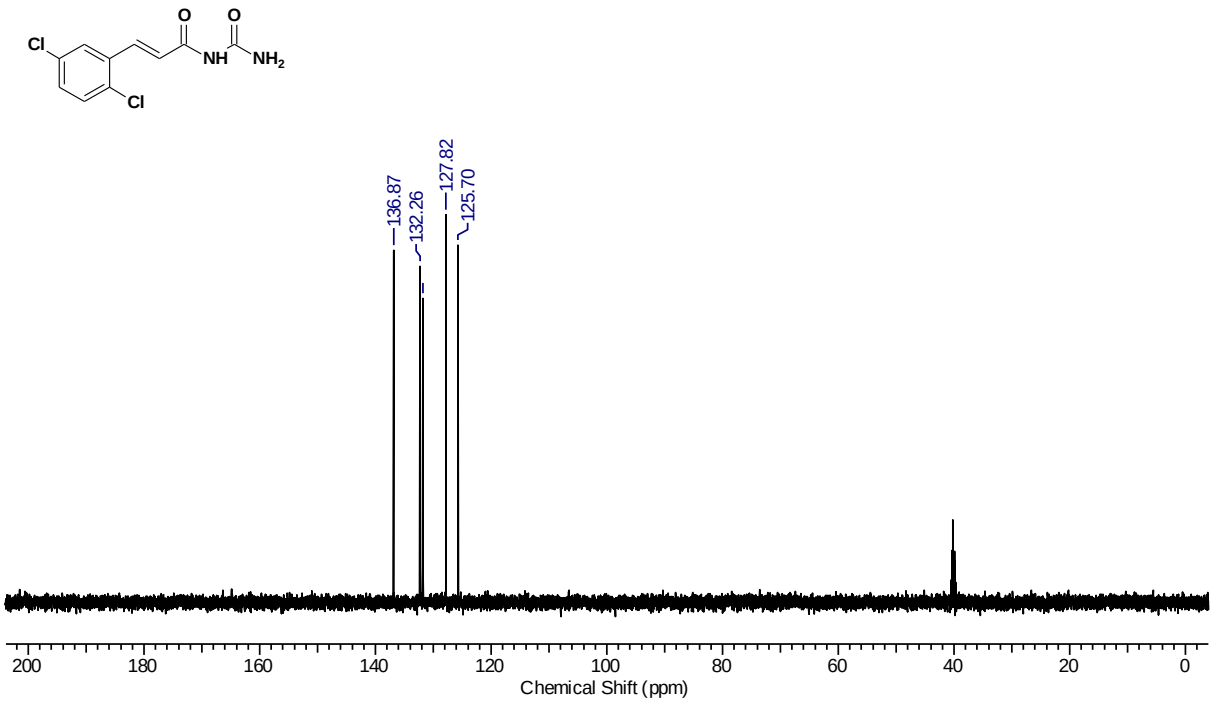

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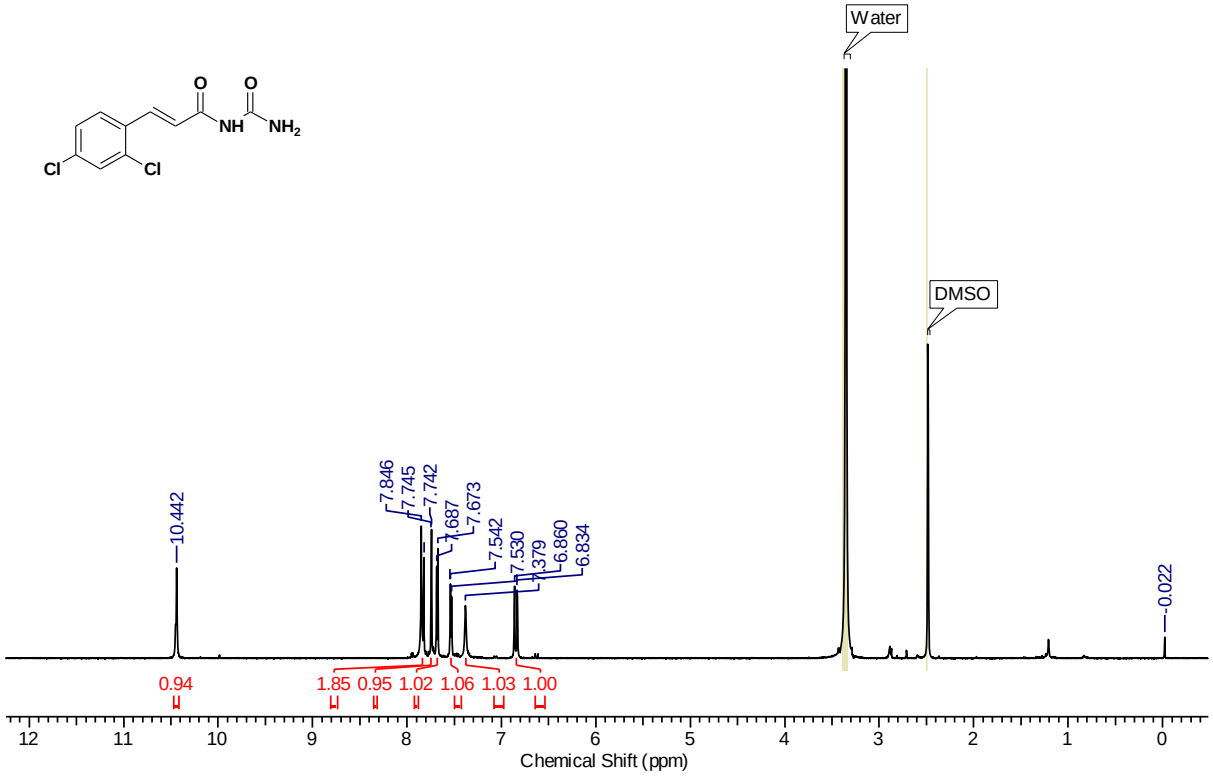

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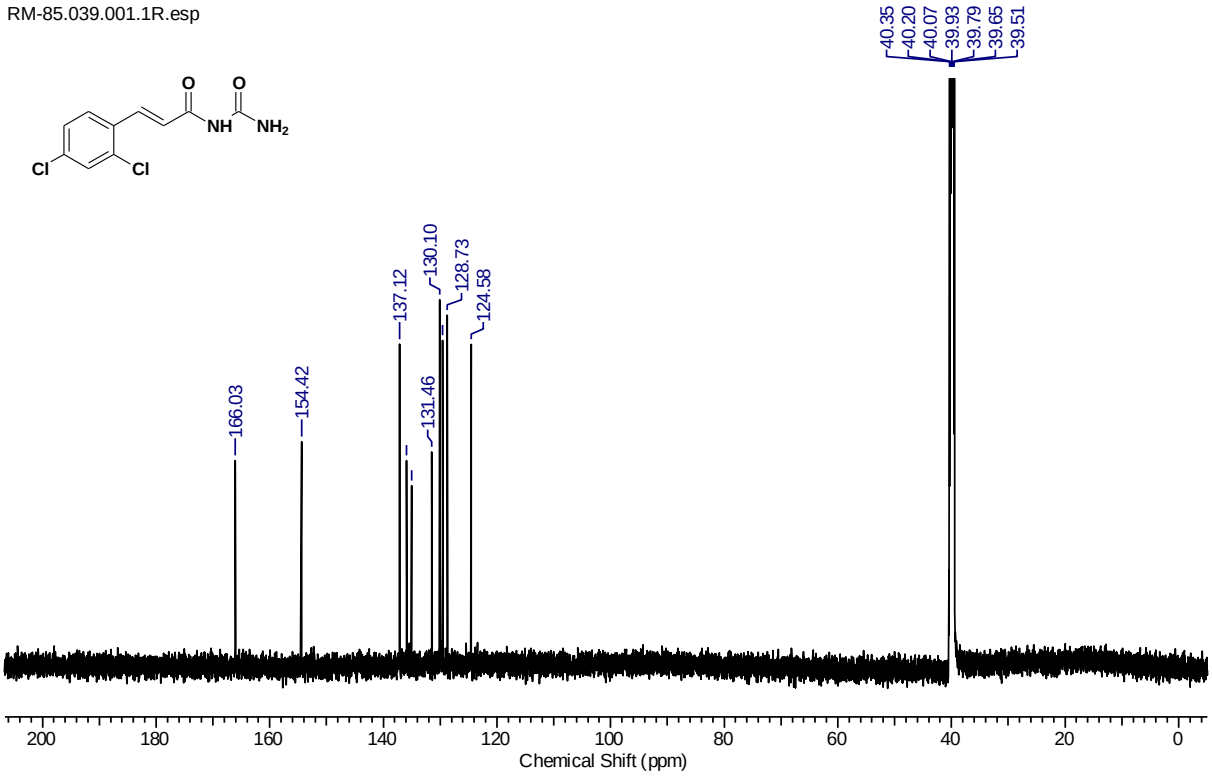

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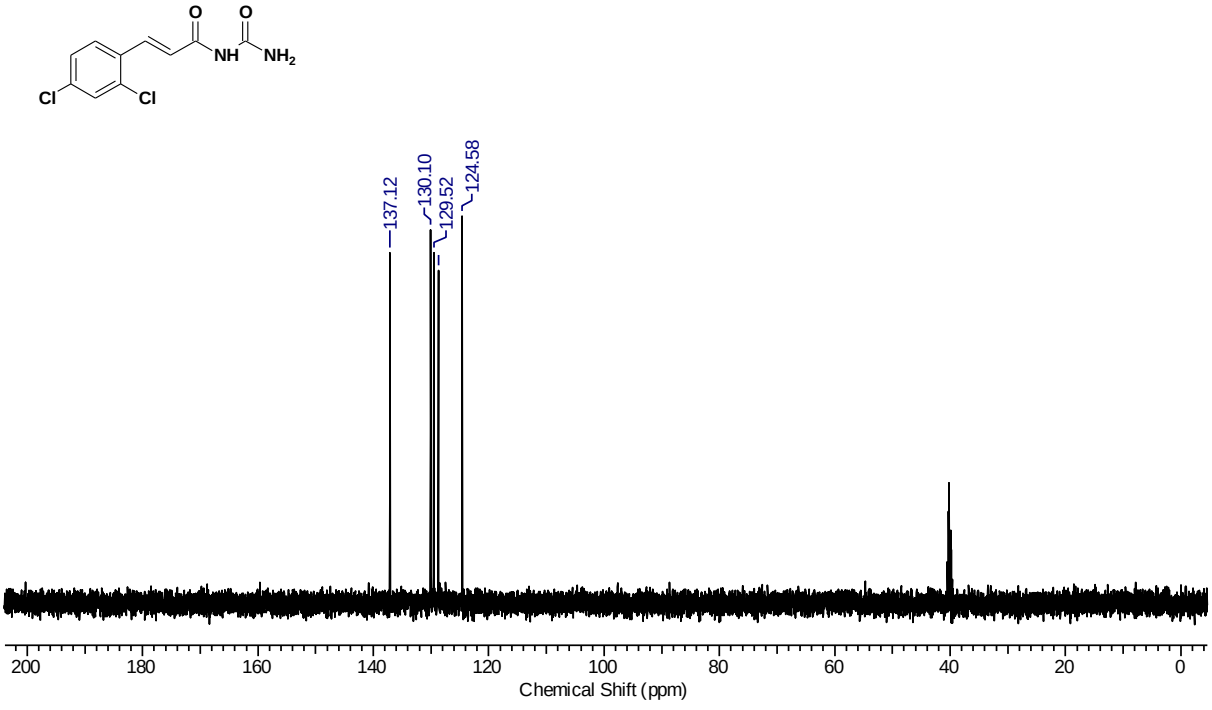

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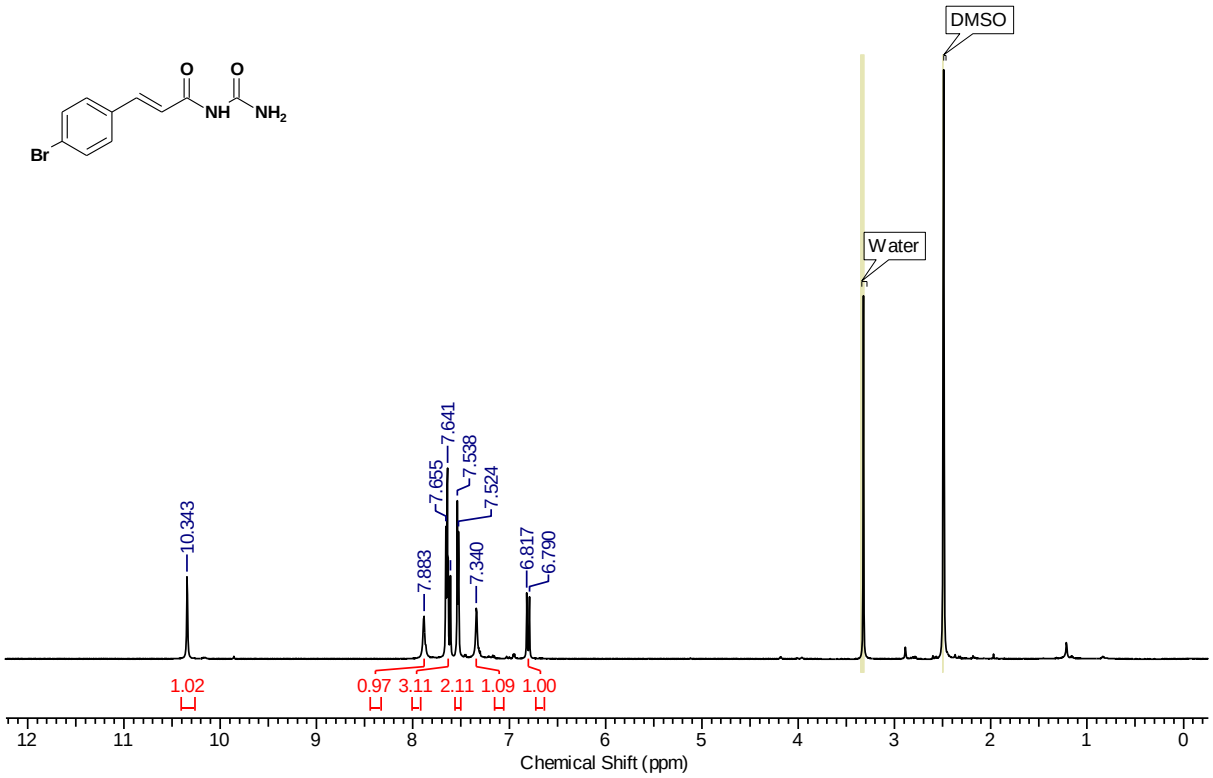

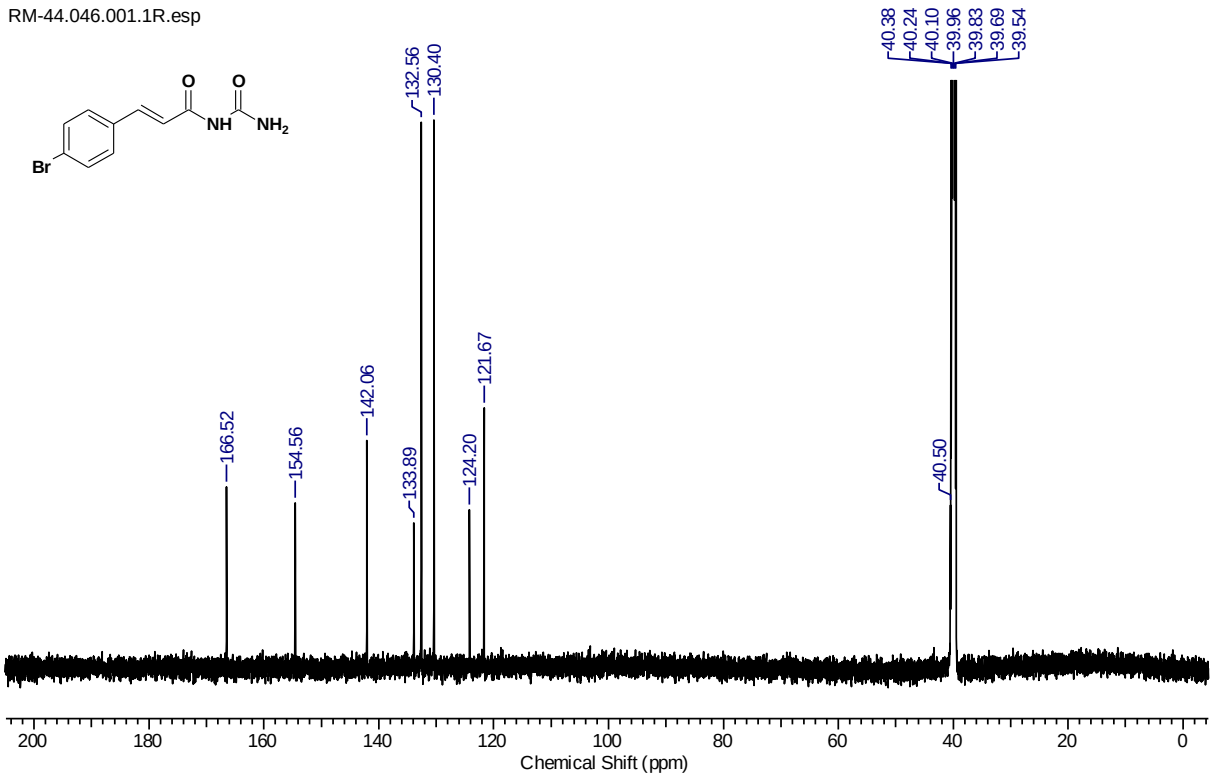

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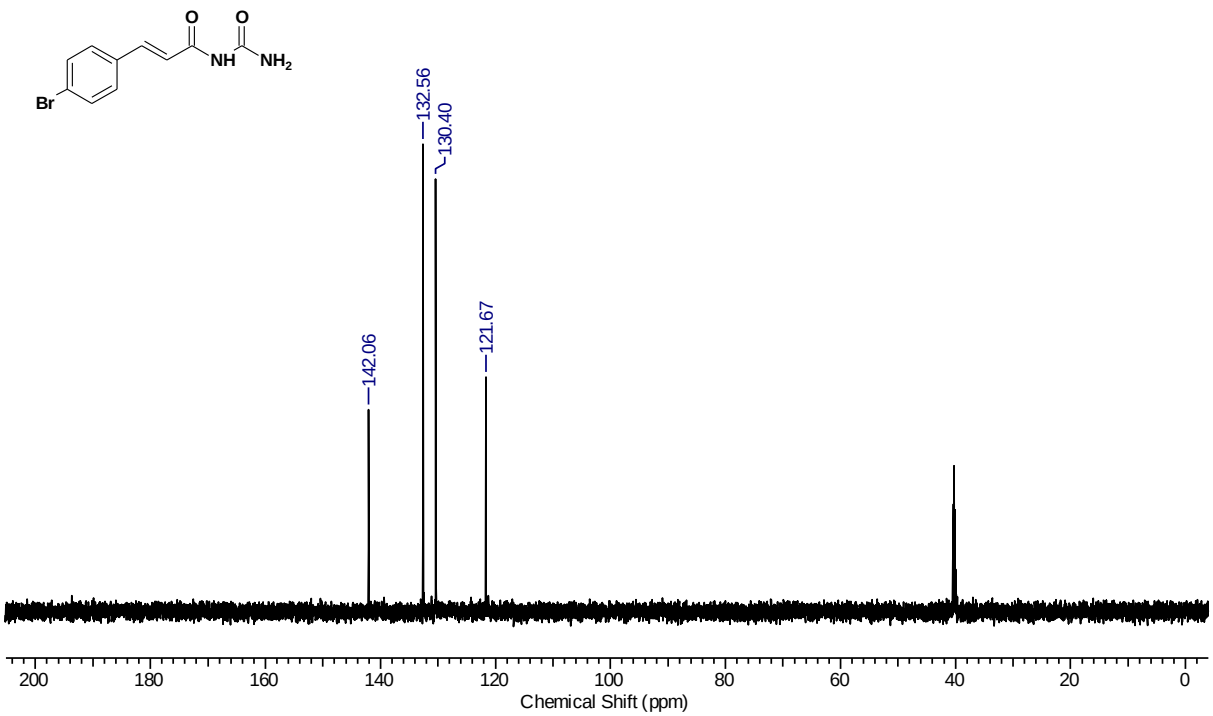

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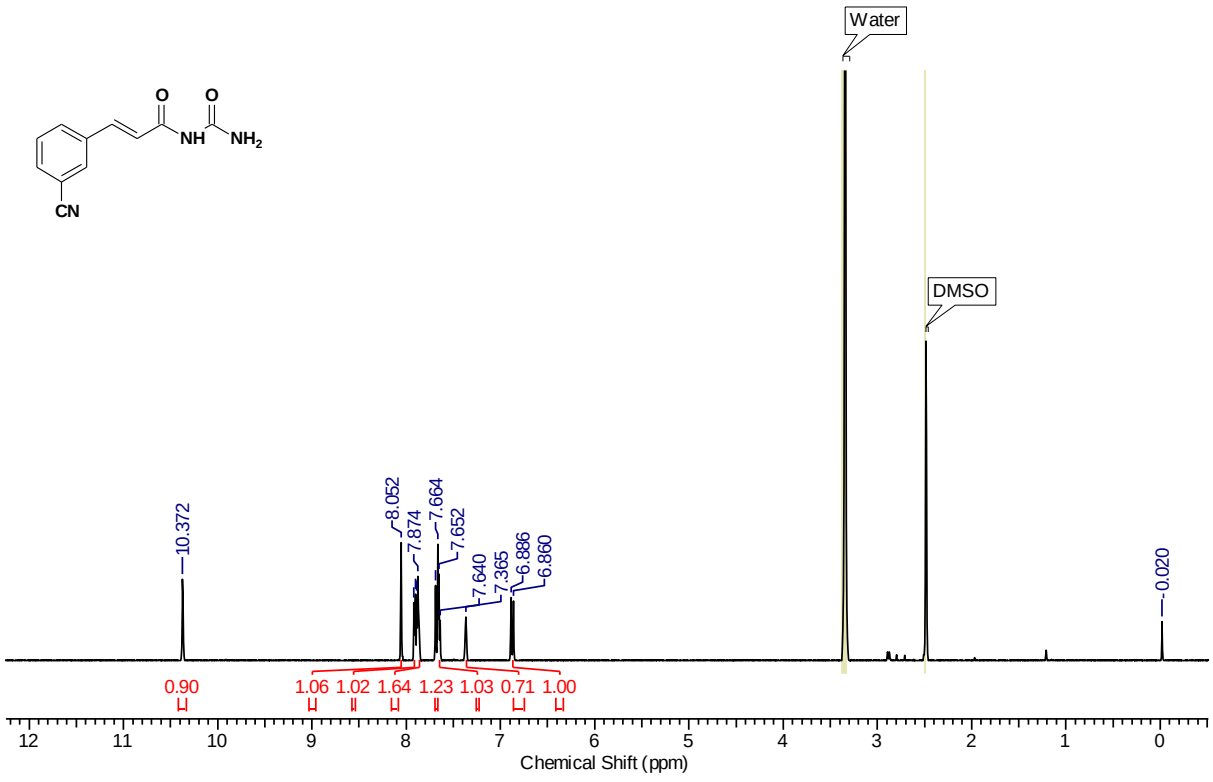

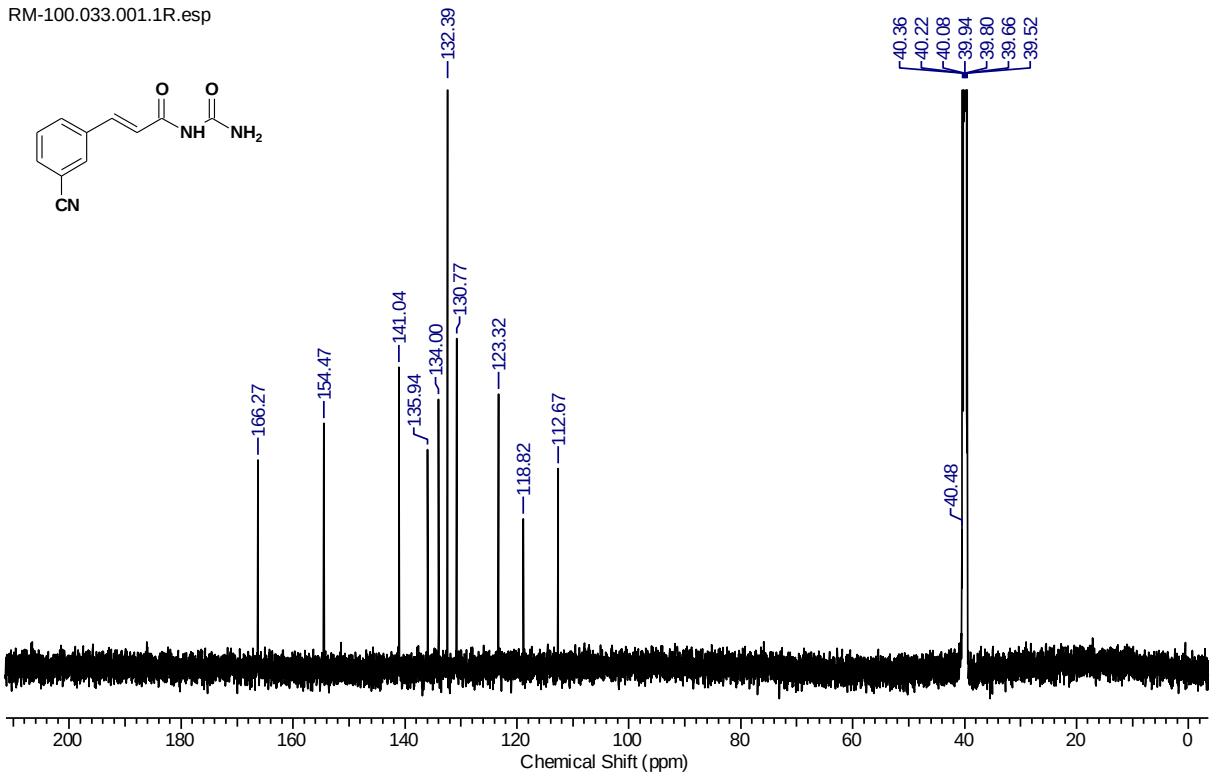
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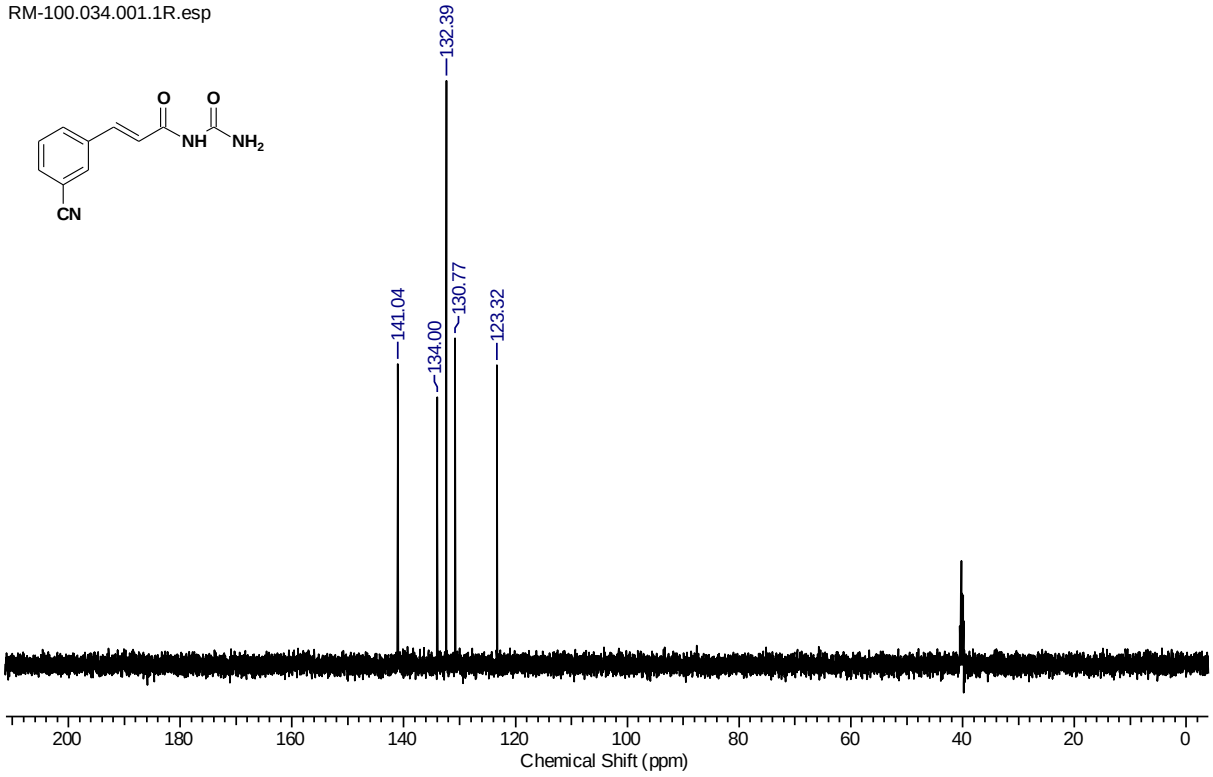
154.47
141.04
135.94
134.00
130.77
123.32
118.82
112.67
40.48
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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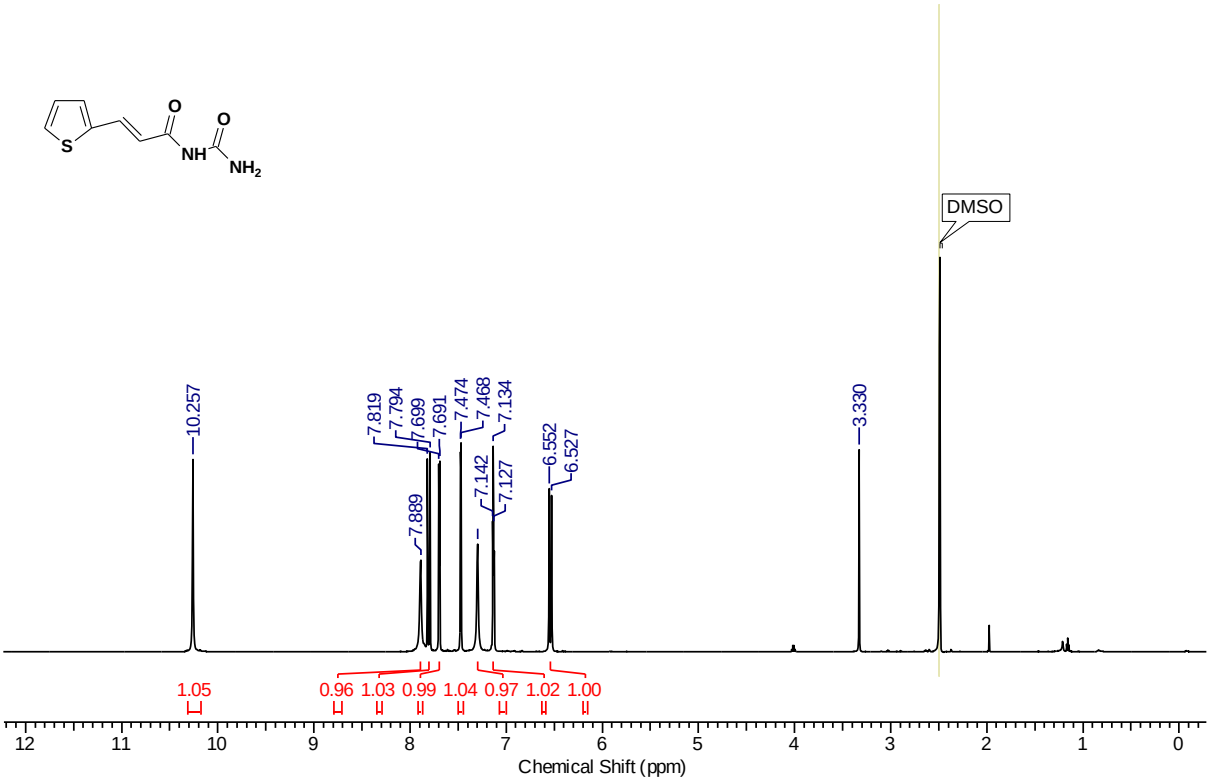
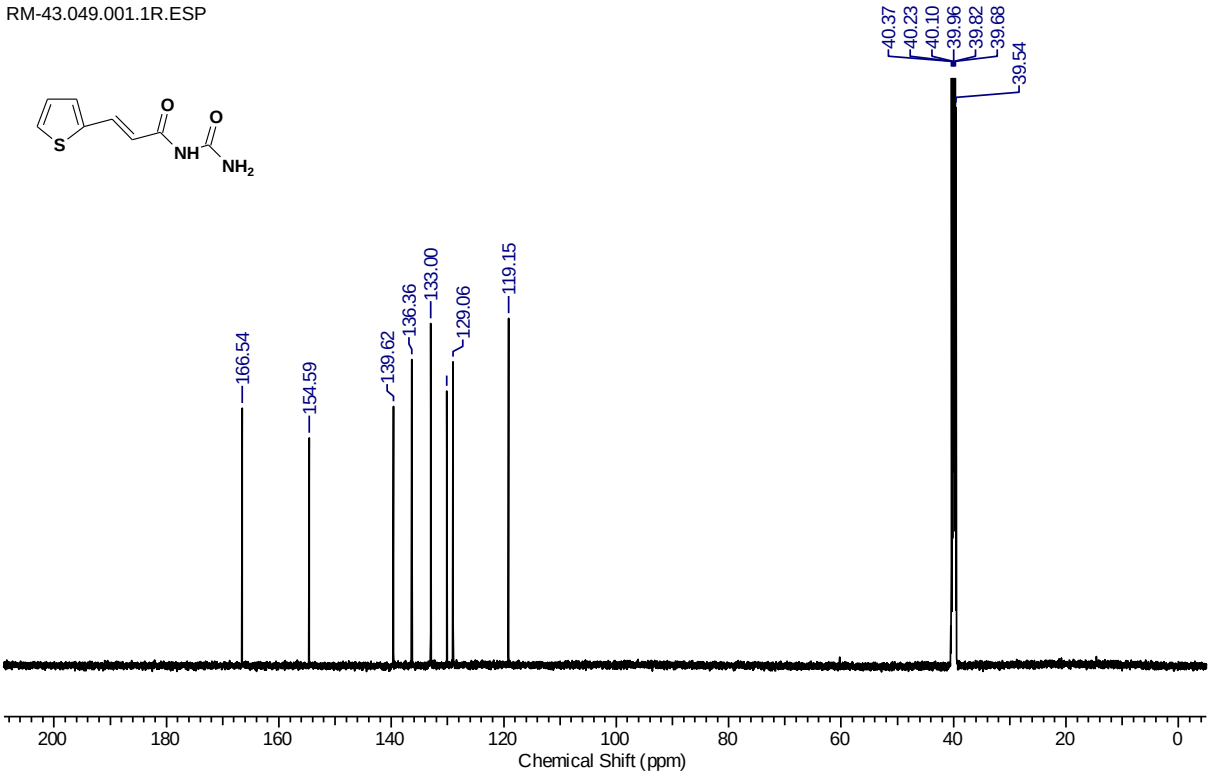
Chemical Shift (ppm)

^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3q:**





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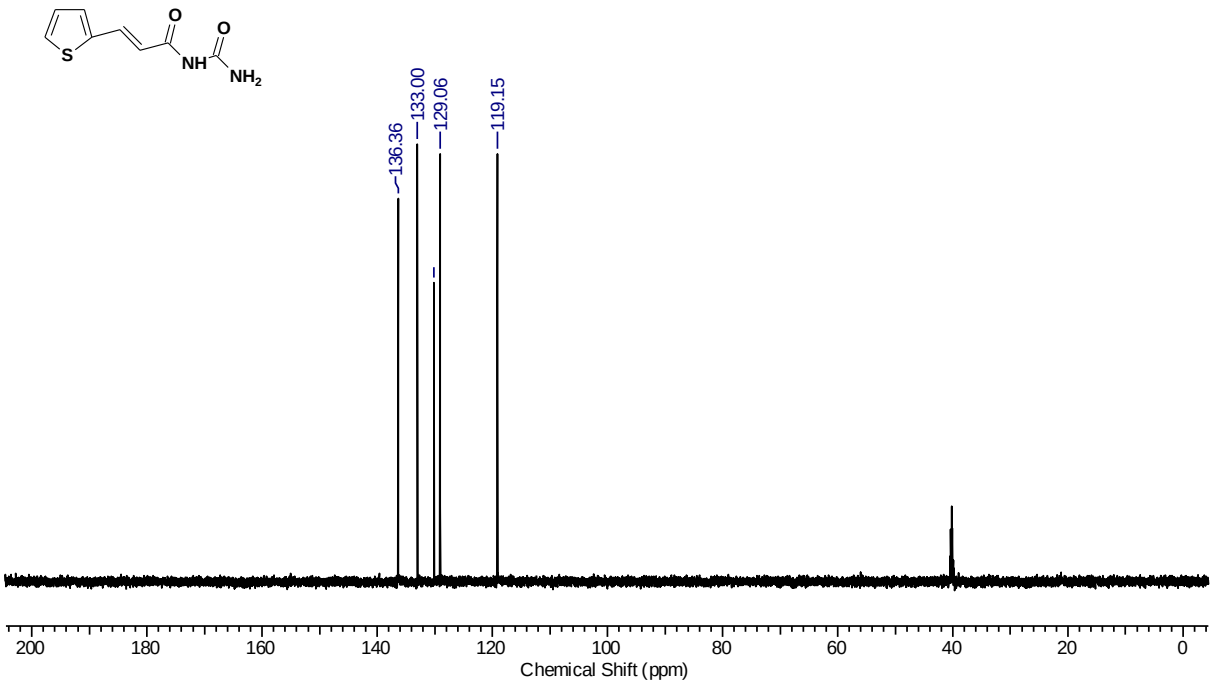
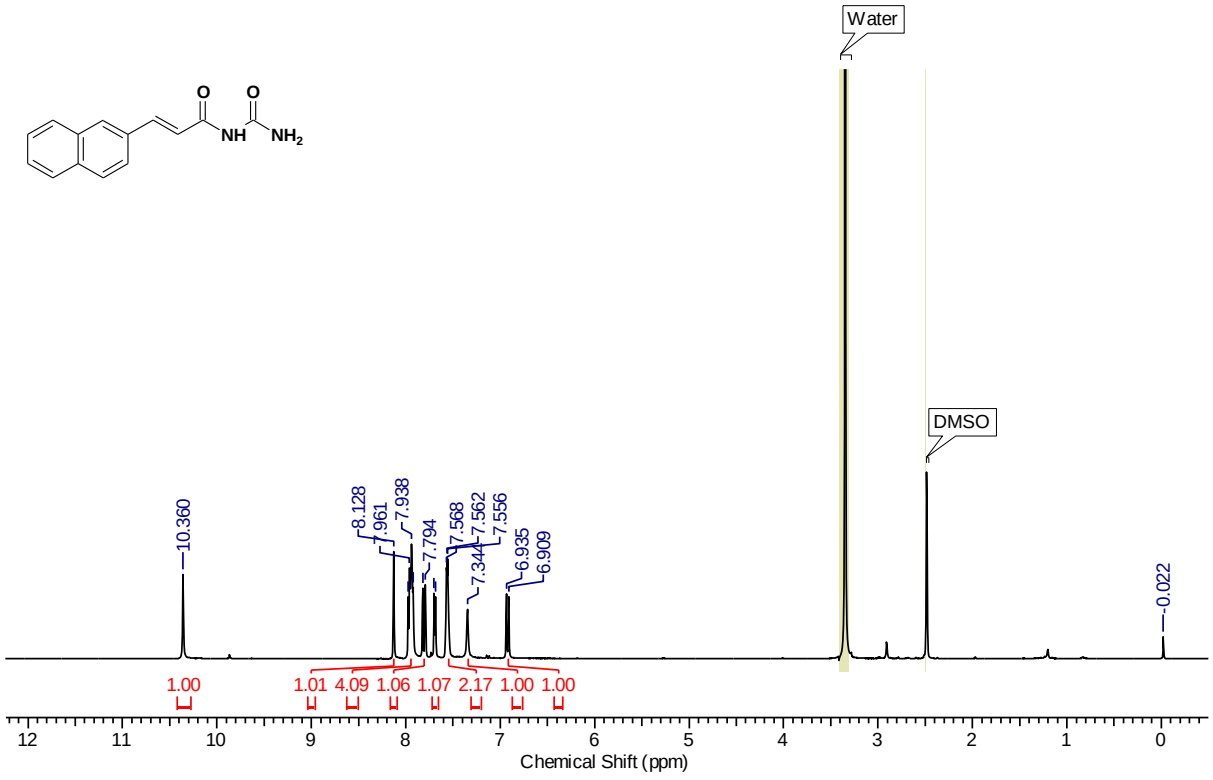
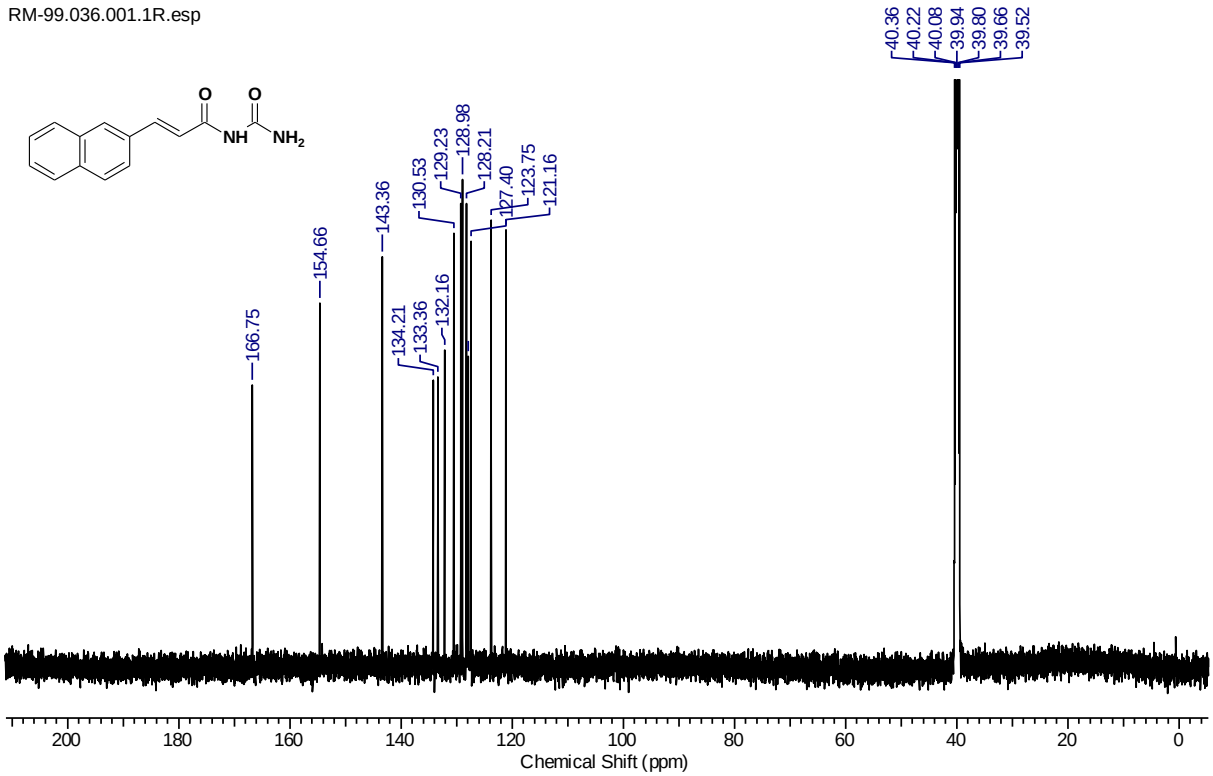


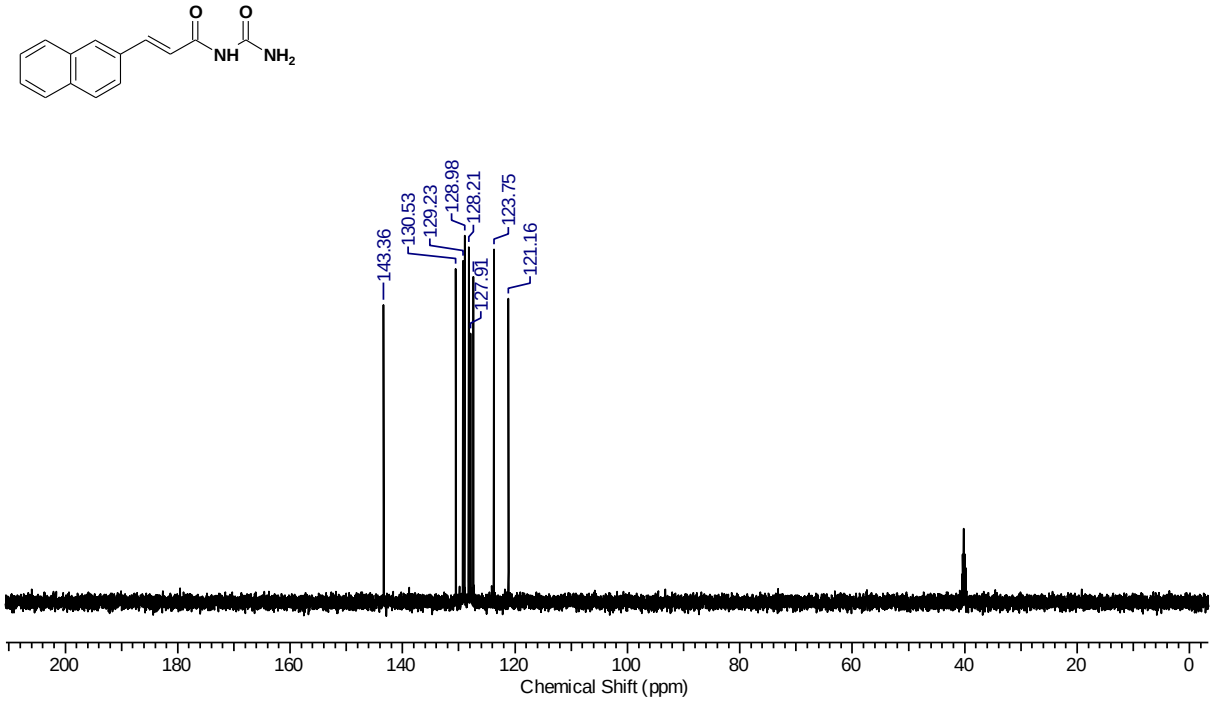
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3r:**



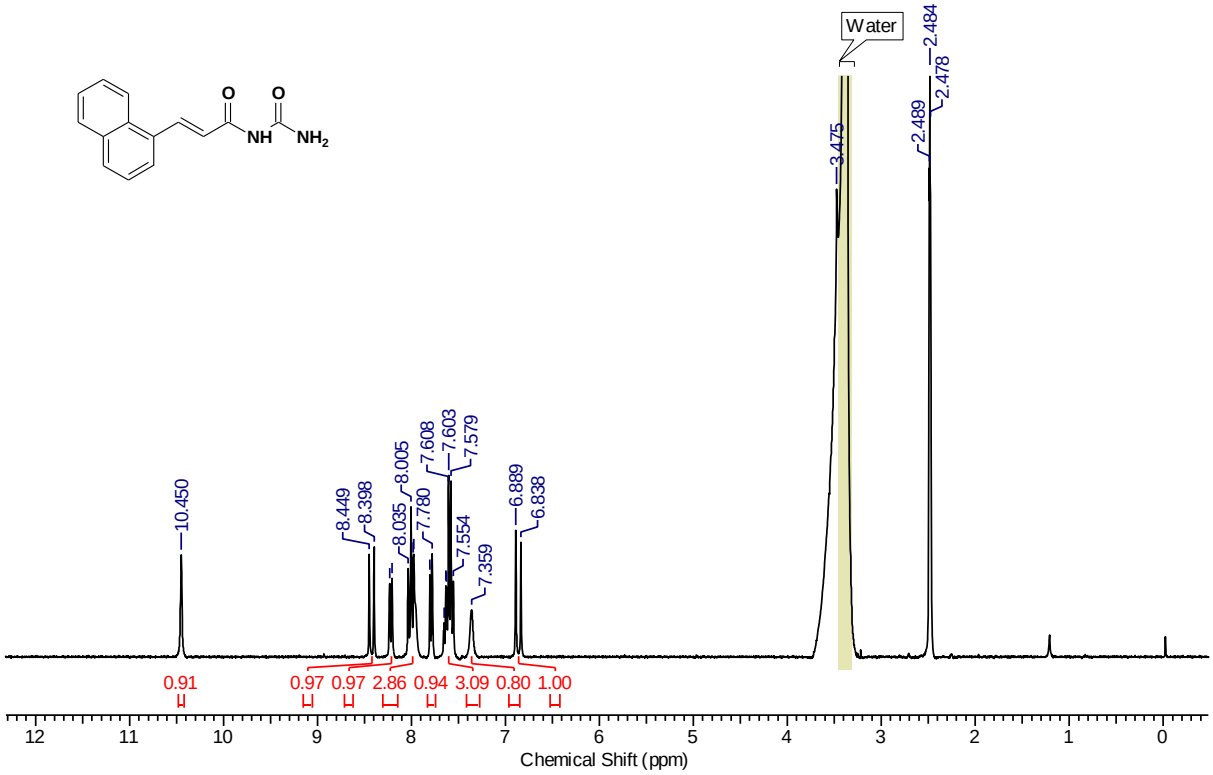
RM-99.036.001.1R.esp

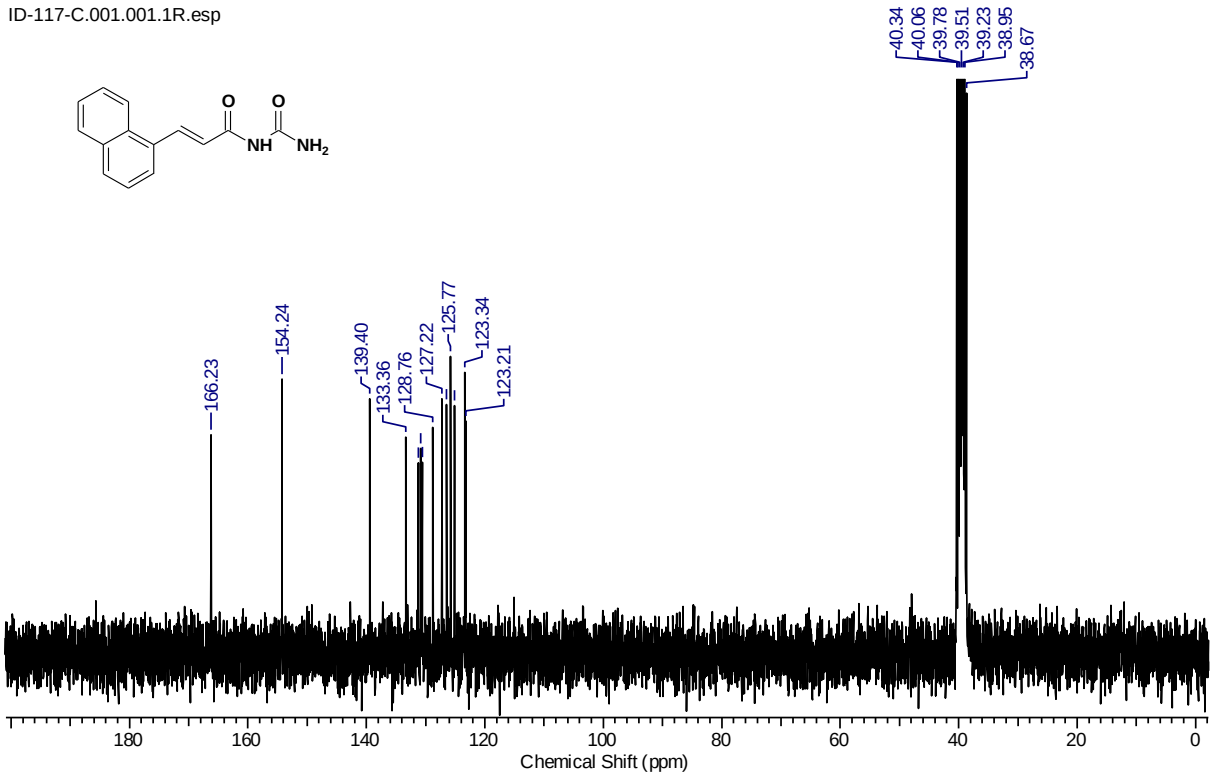


RM-99.037.001.1R.esp

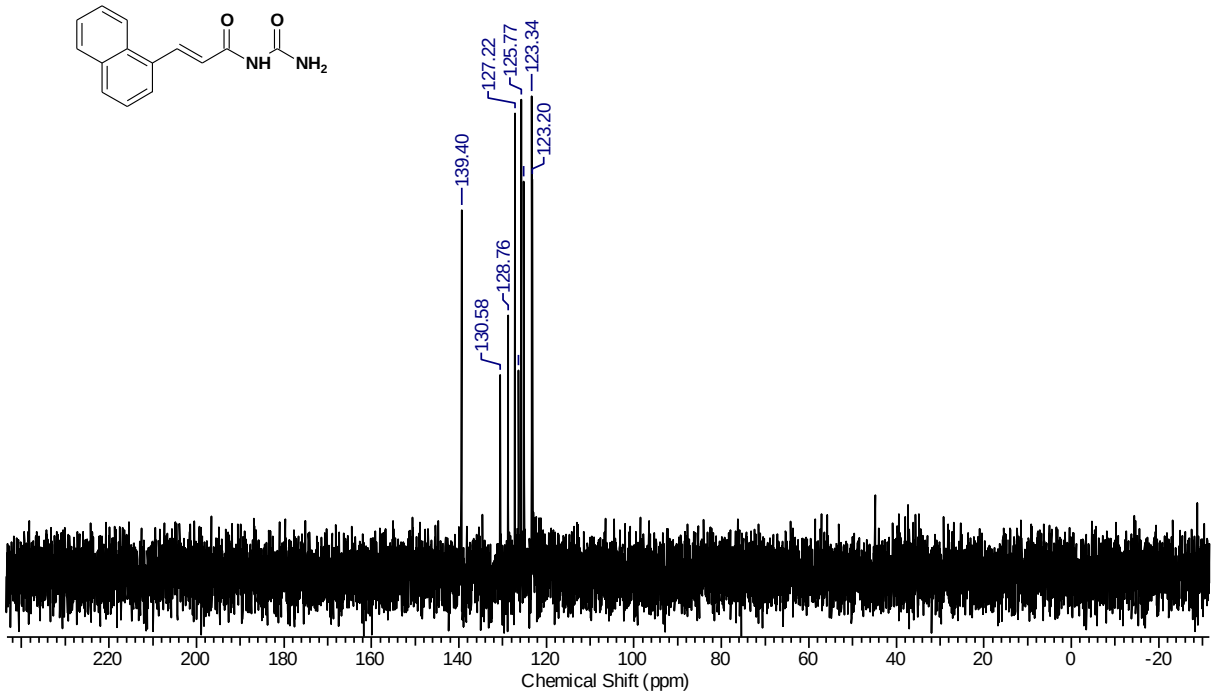


^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3s:**

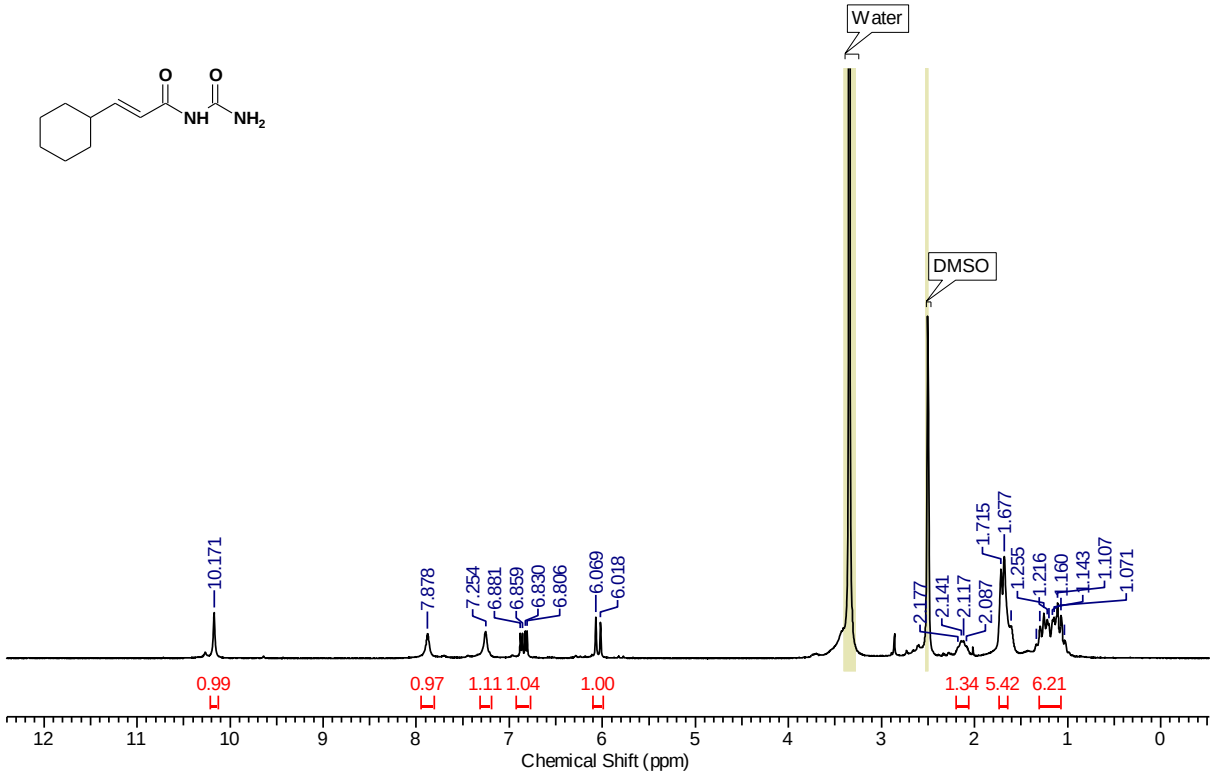




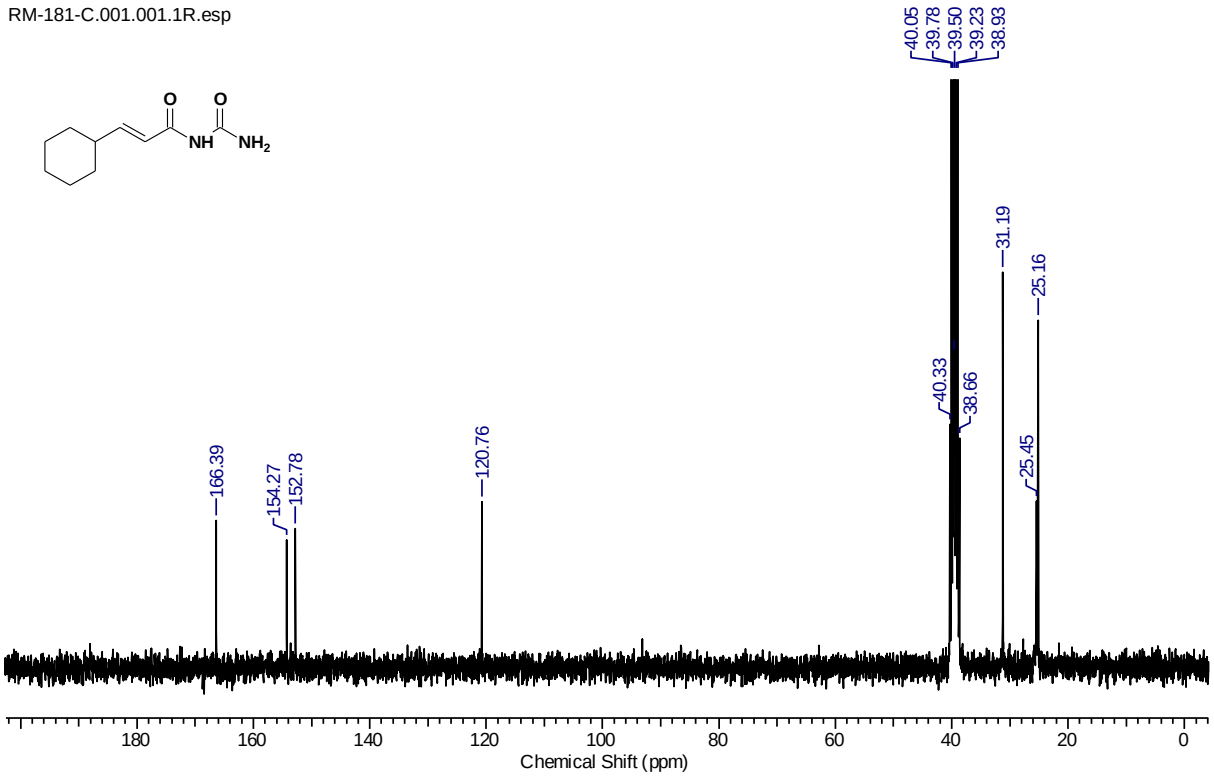
ID-117-C.002.001.1R.esp



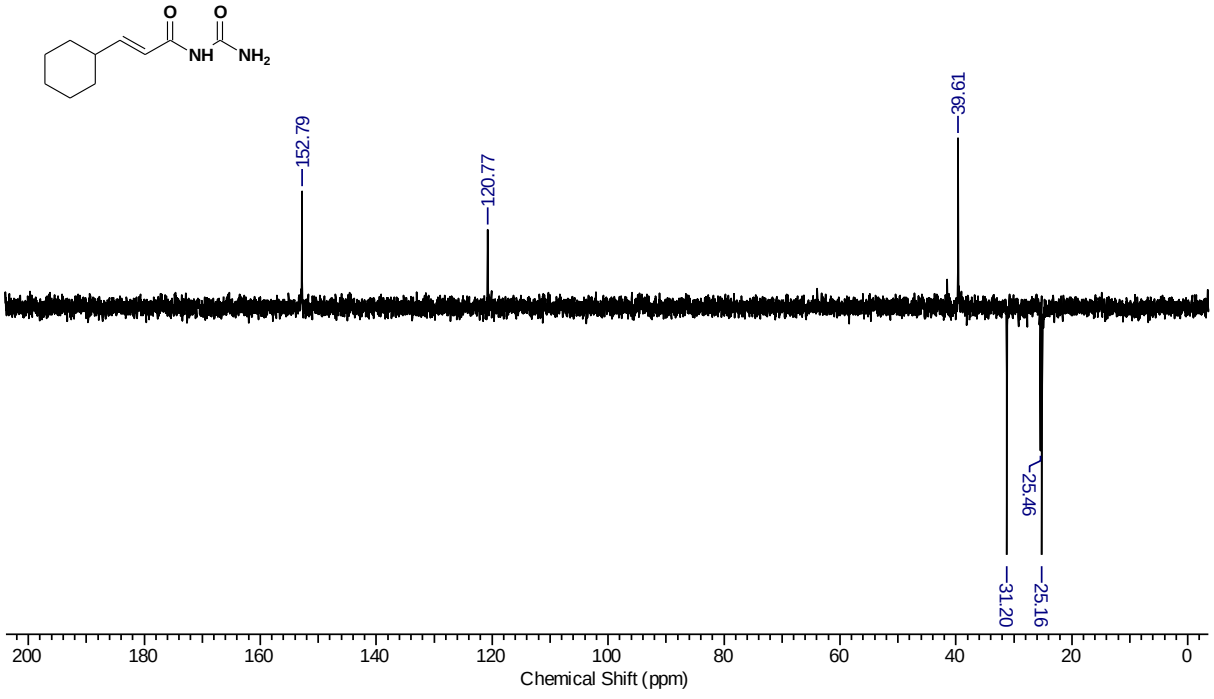
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3t:**



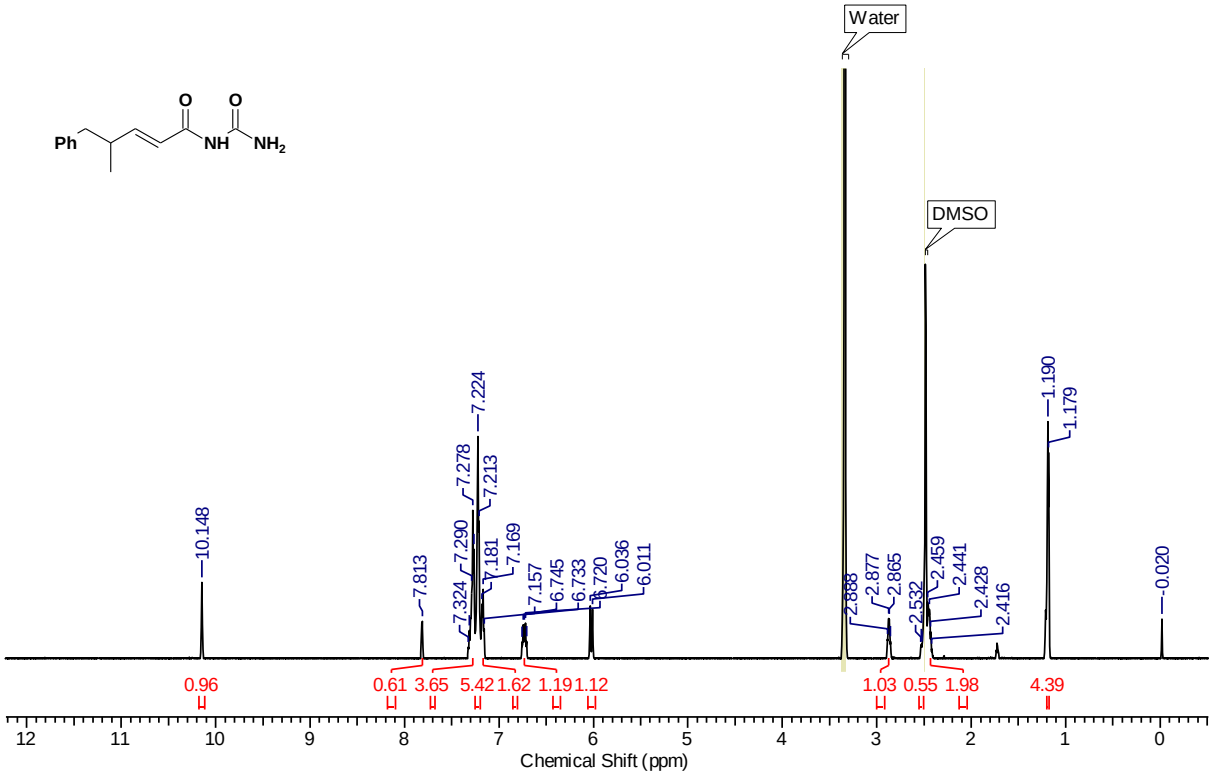
RM-181-C.001.001.1R.esp

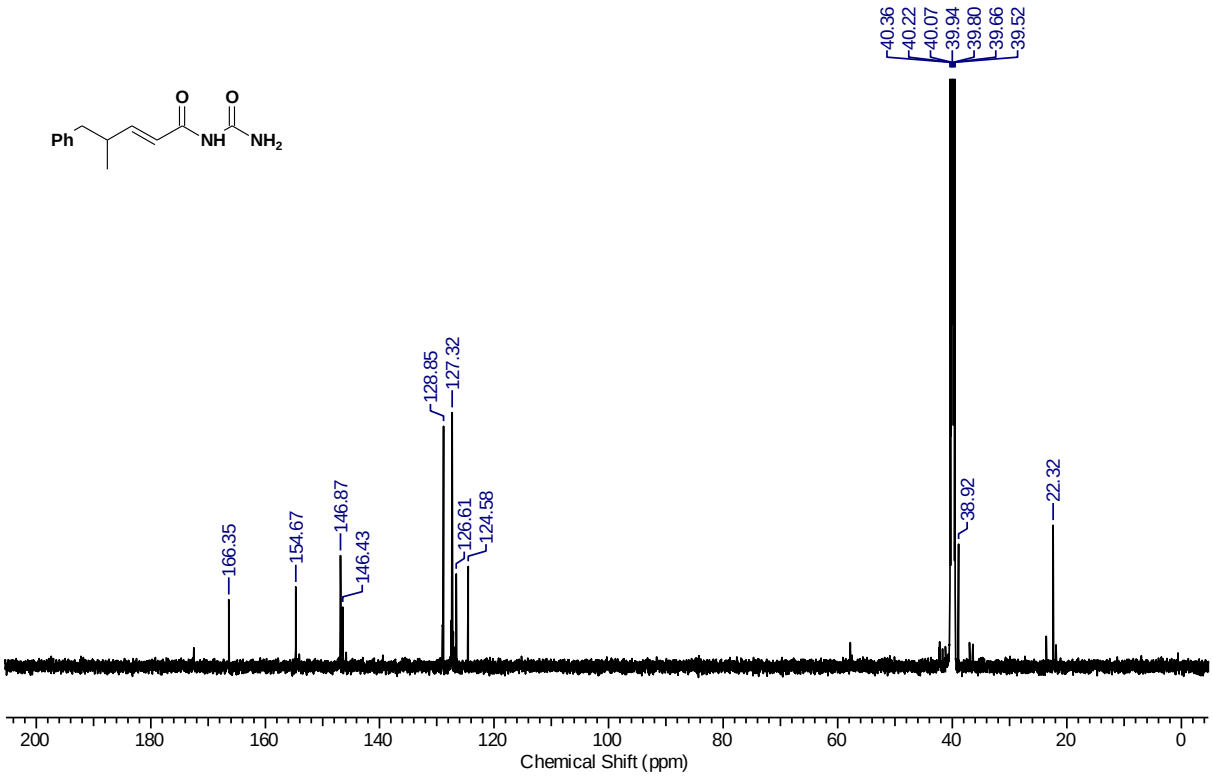


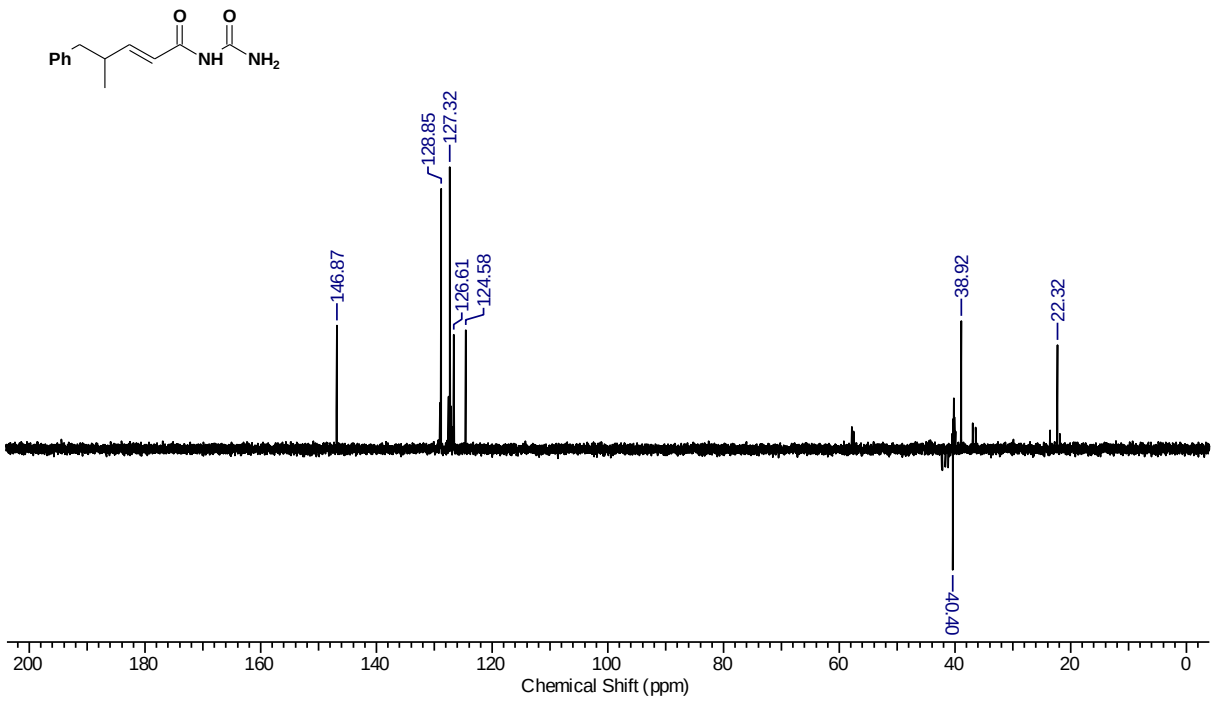
RM-181-C.002.001.1R.esp



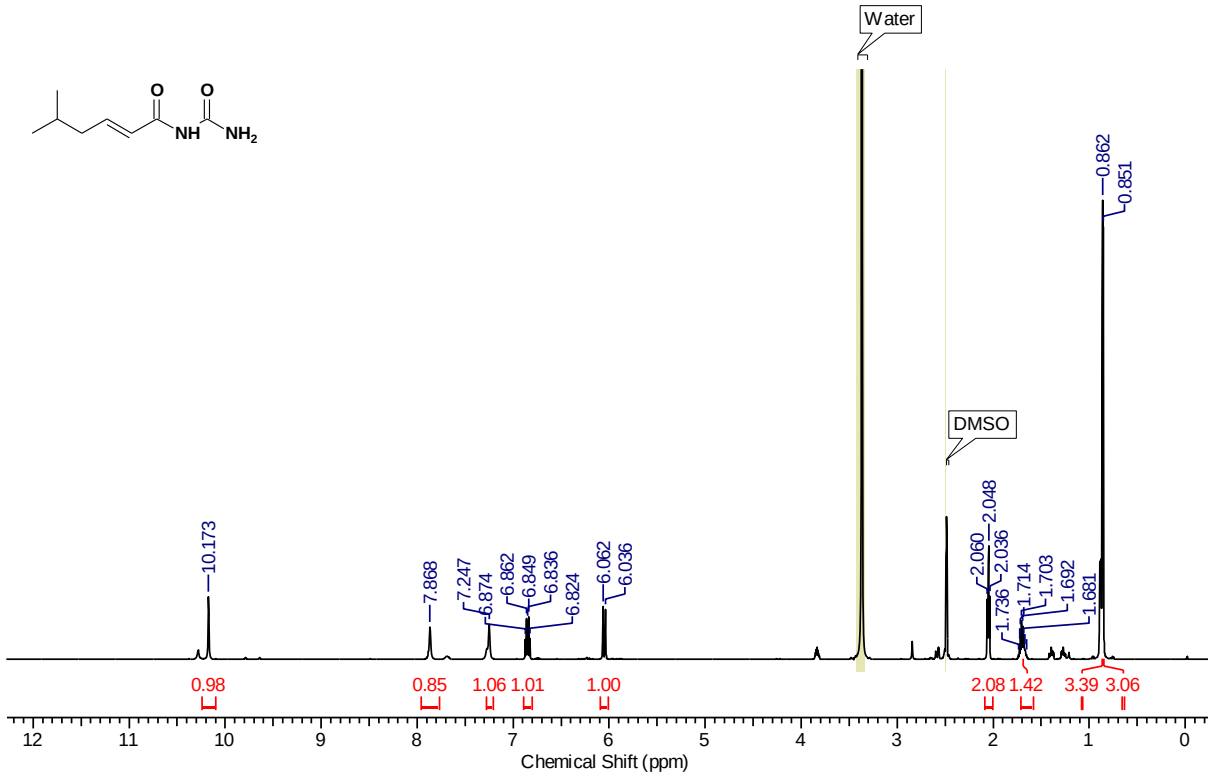
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3u:**

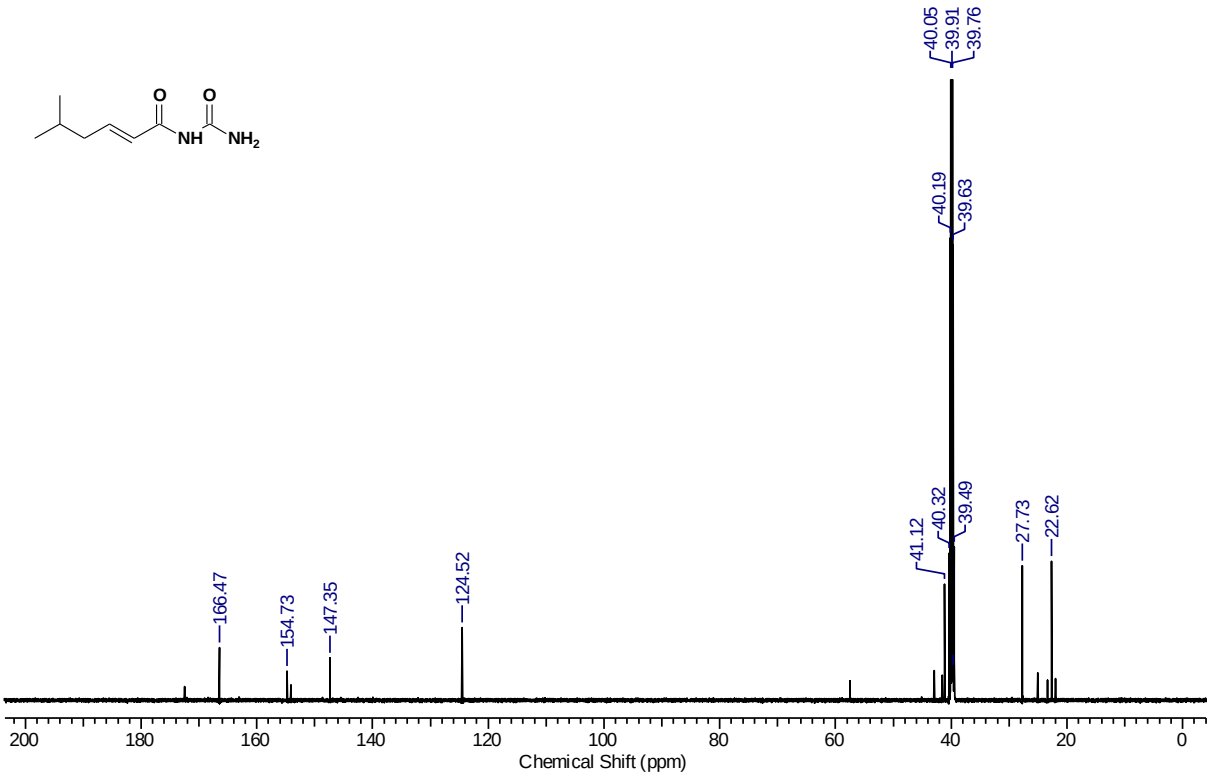


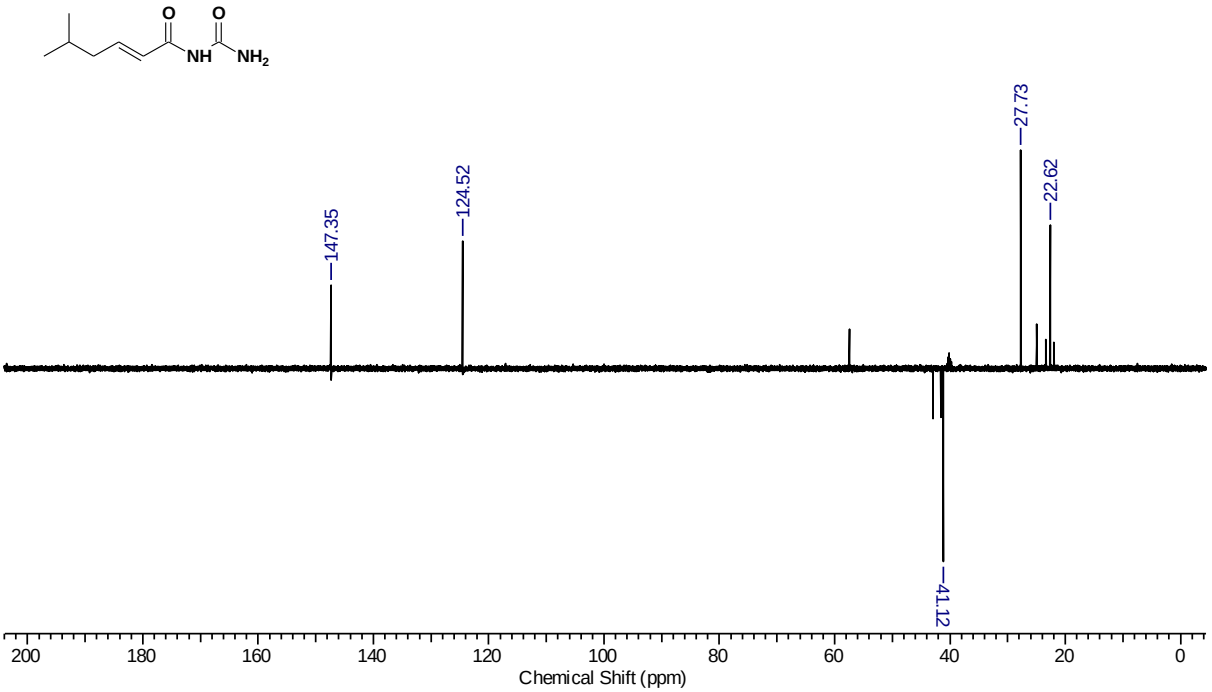




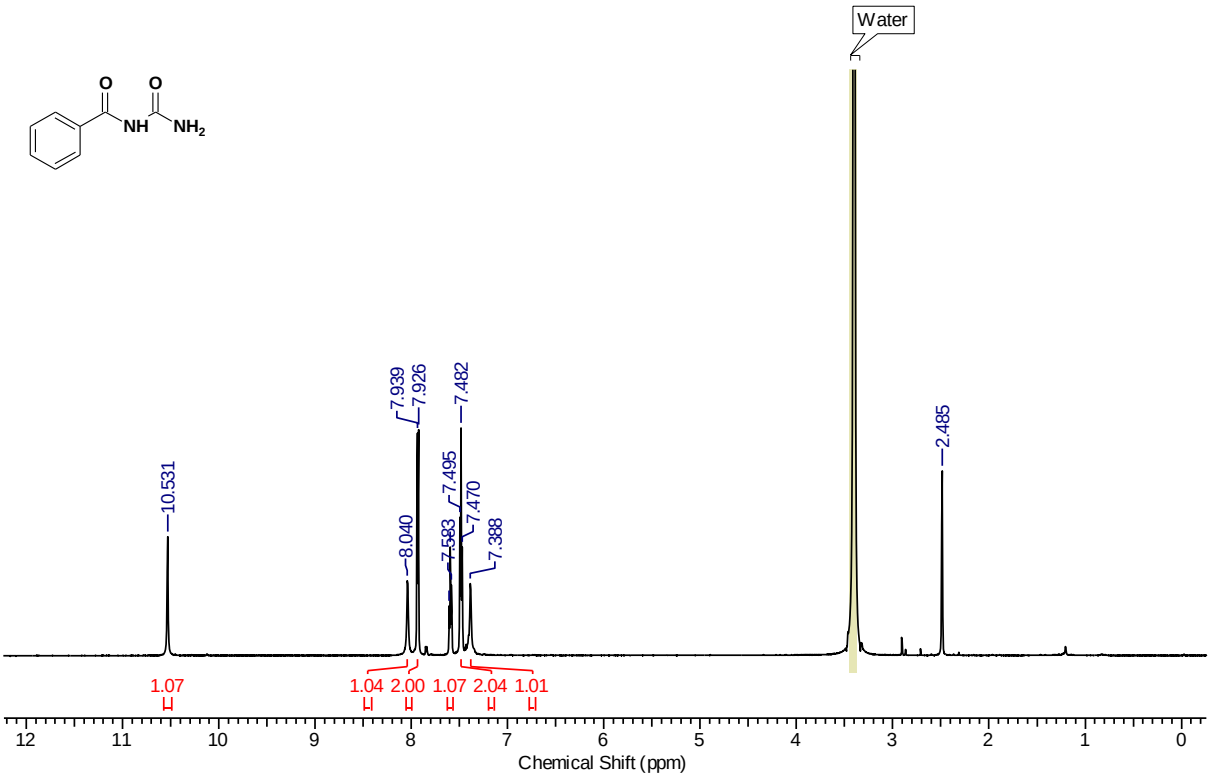
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3v:**

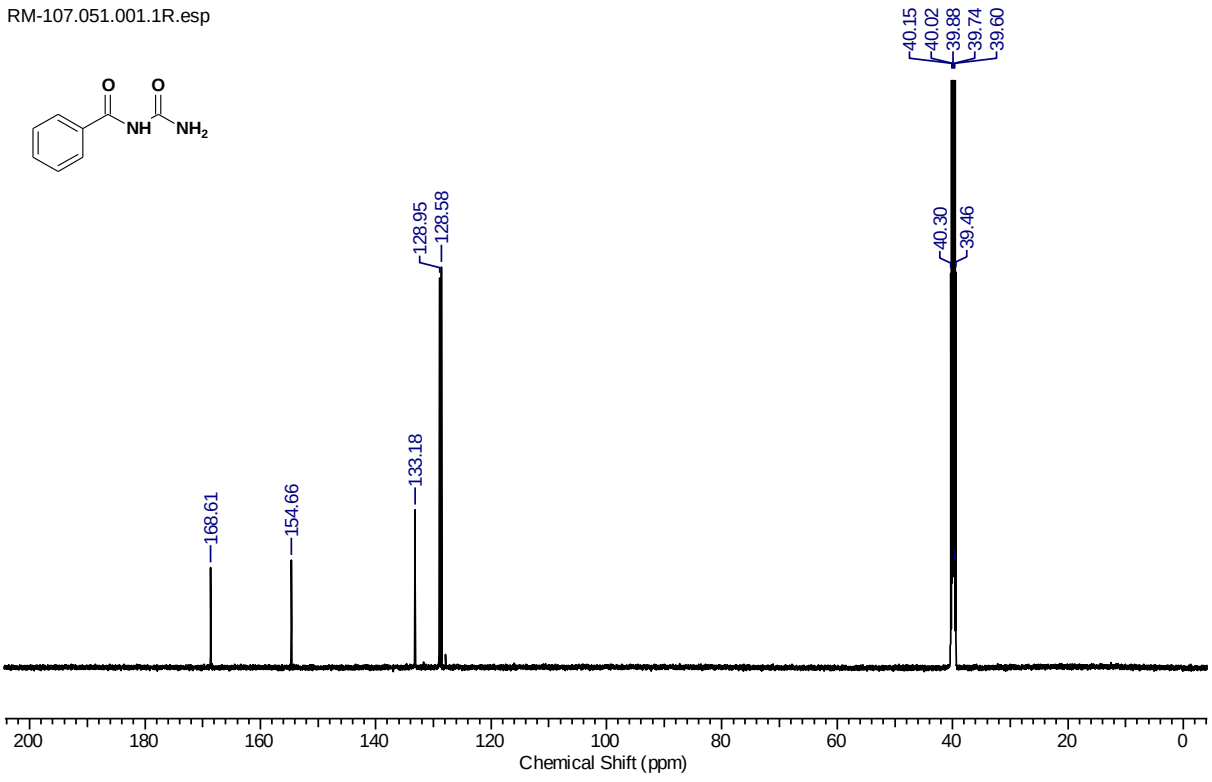



O
O
NH
NH2
40.05
39.91
39.76
40.19
39.63
41.12
40.32
39.49
27.73
22.62
166.47
154.73
147.35
124.52
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

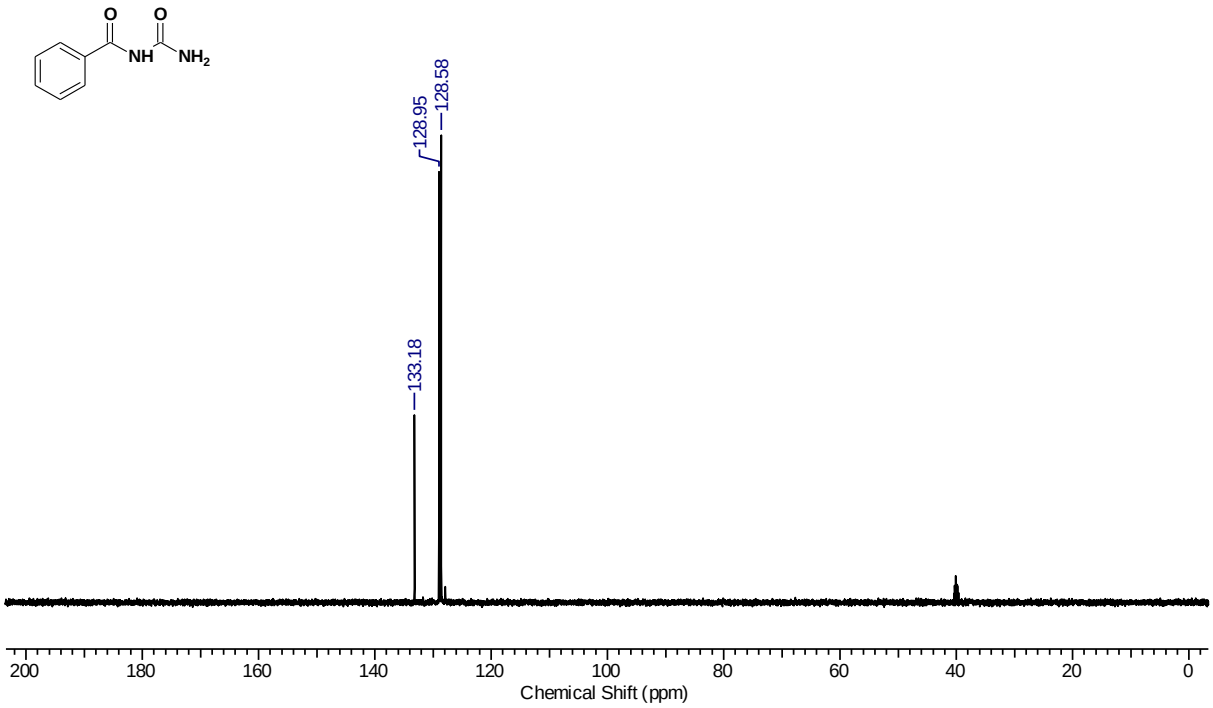

O
O
NH
NH2
27.73
22.62
147.35
124.52
41.12
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3aa:**

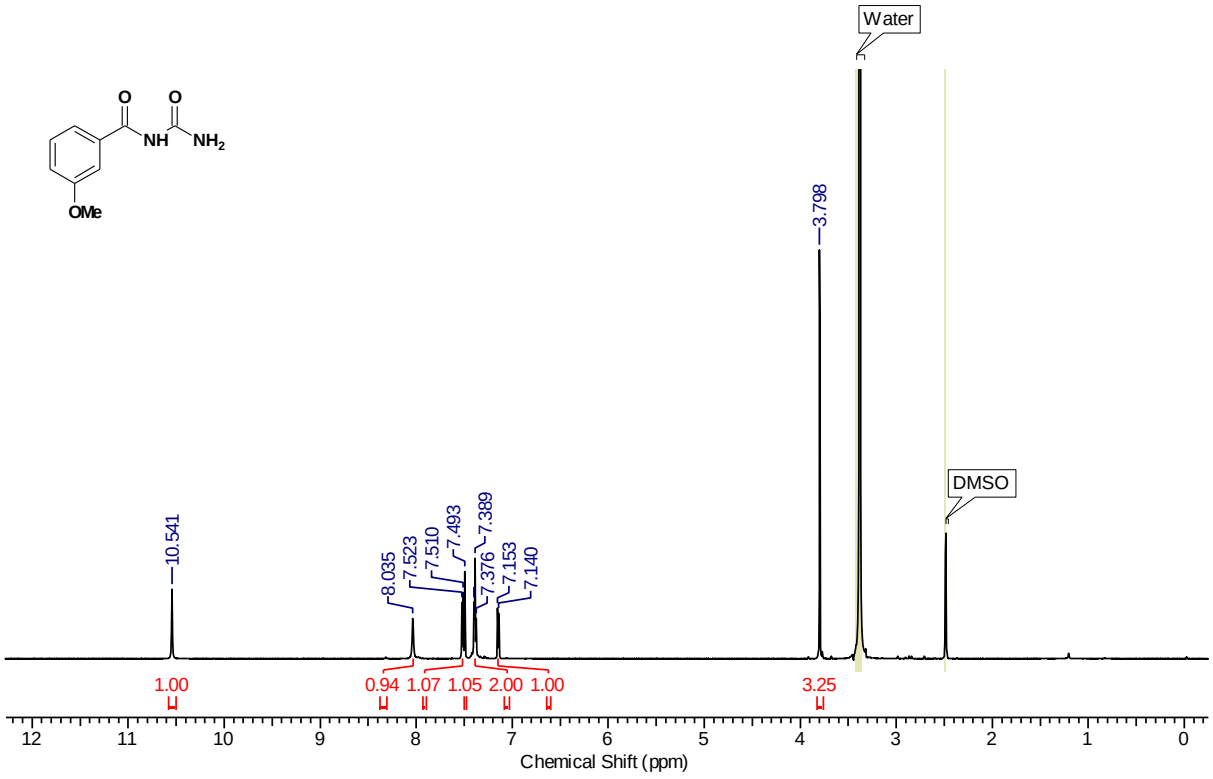




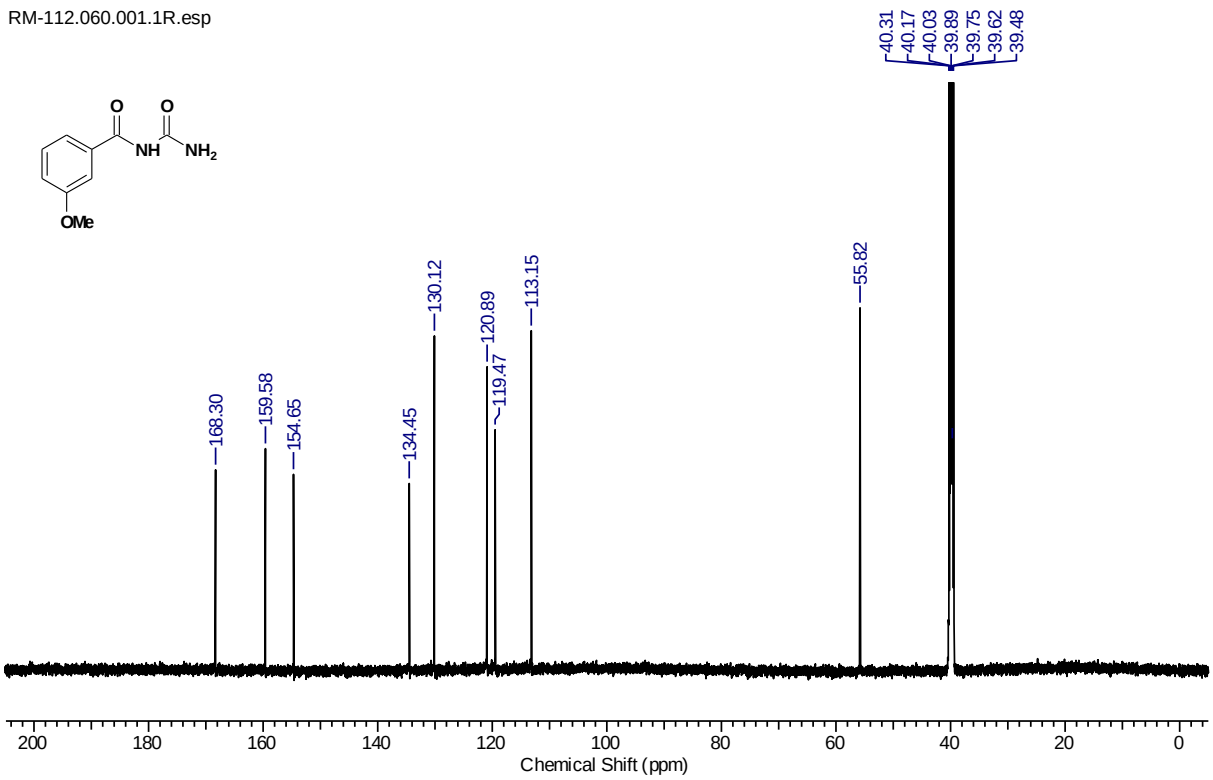
RM-107.052.001.1R.esp



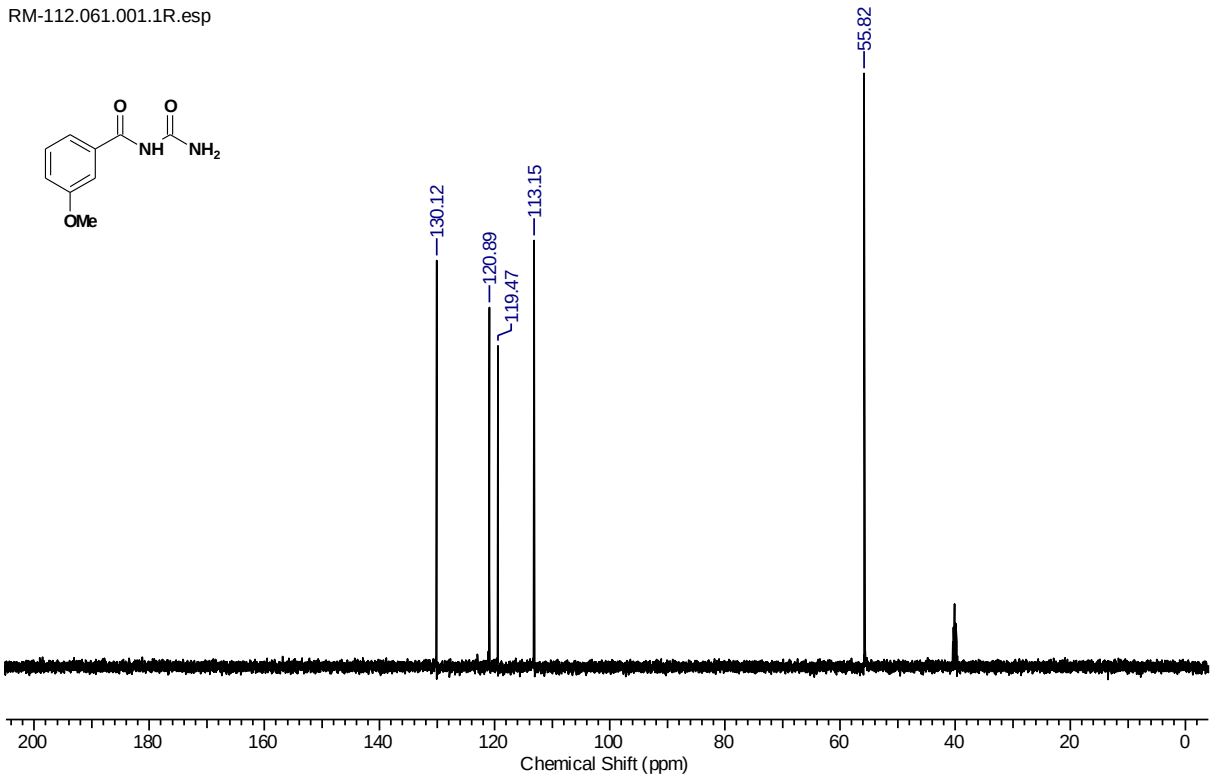
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3ab:**



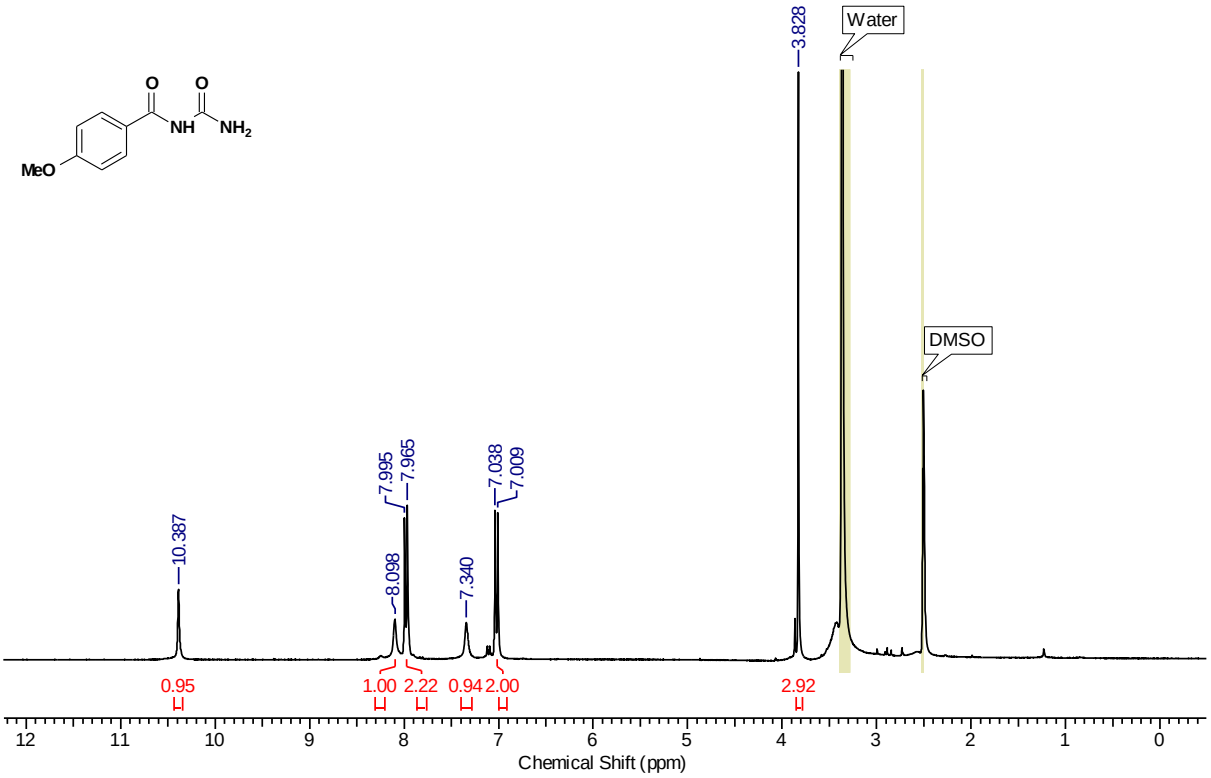
RM-112.060.001.1R.esp

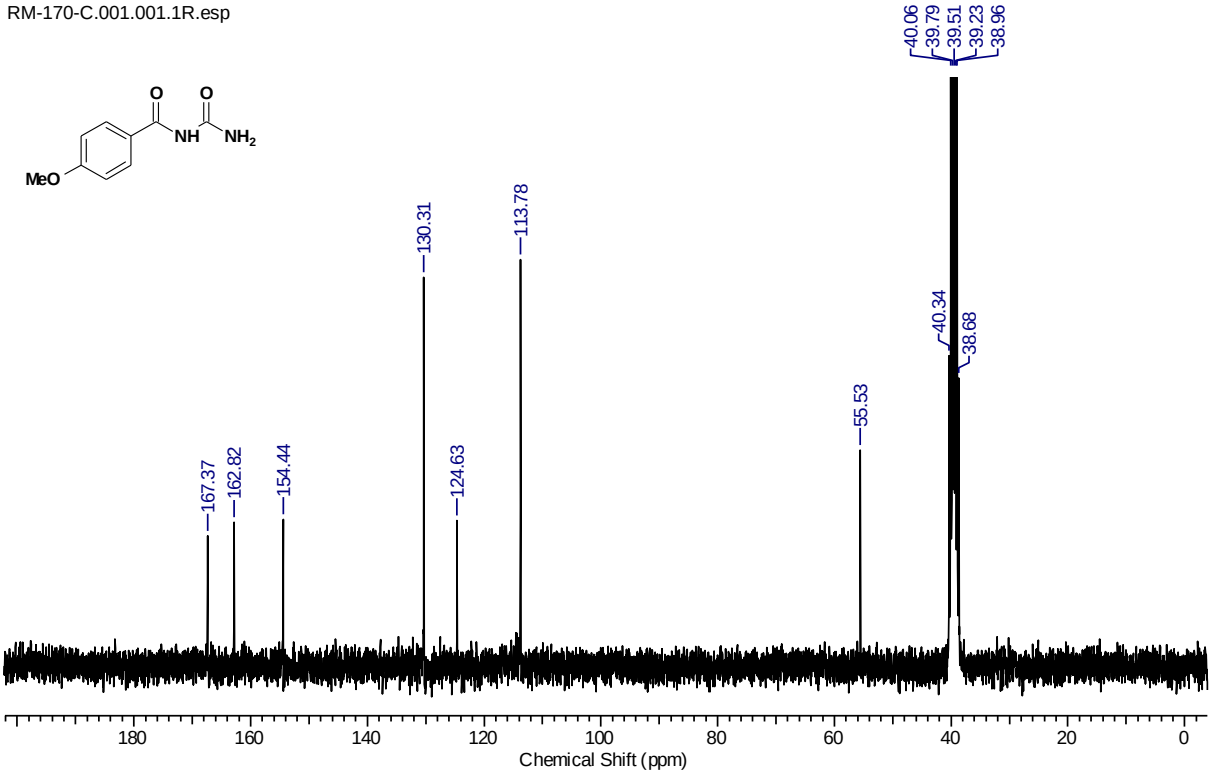


RM-112.061.001.1R.esp

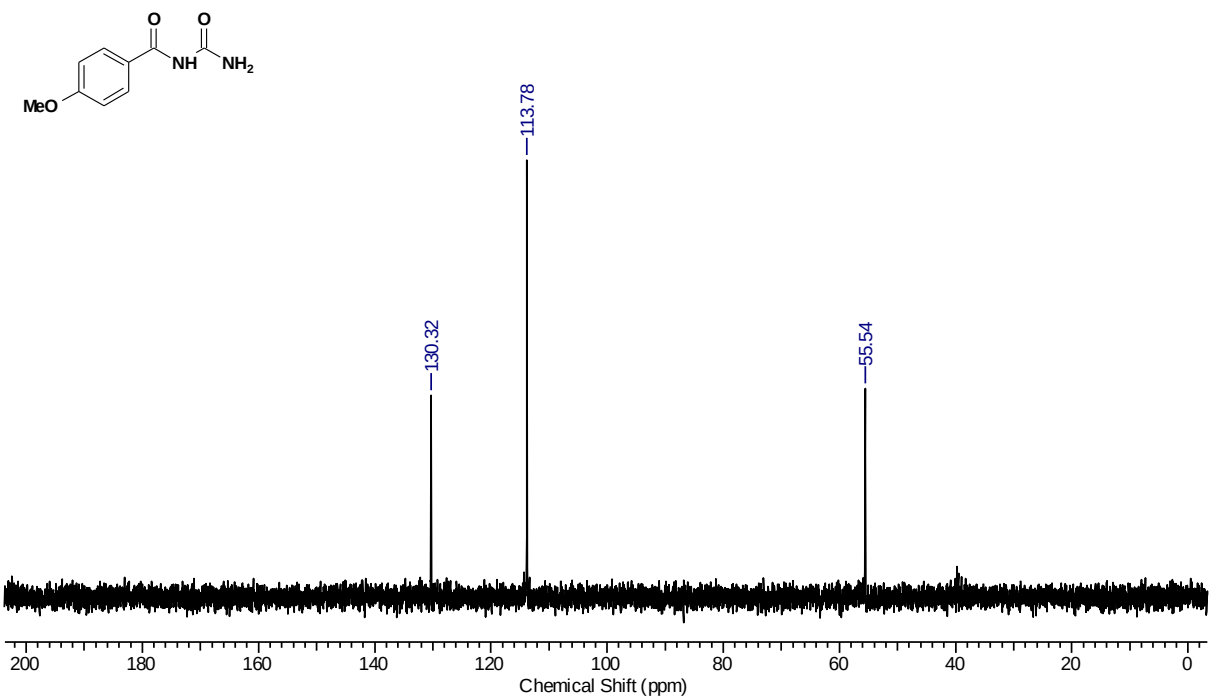


^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3ac:**

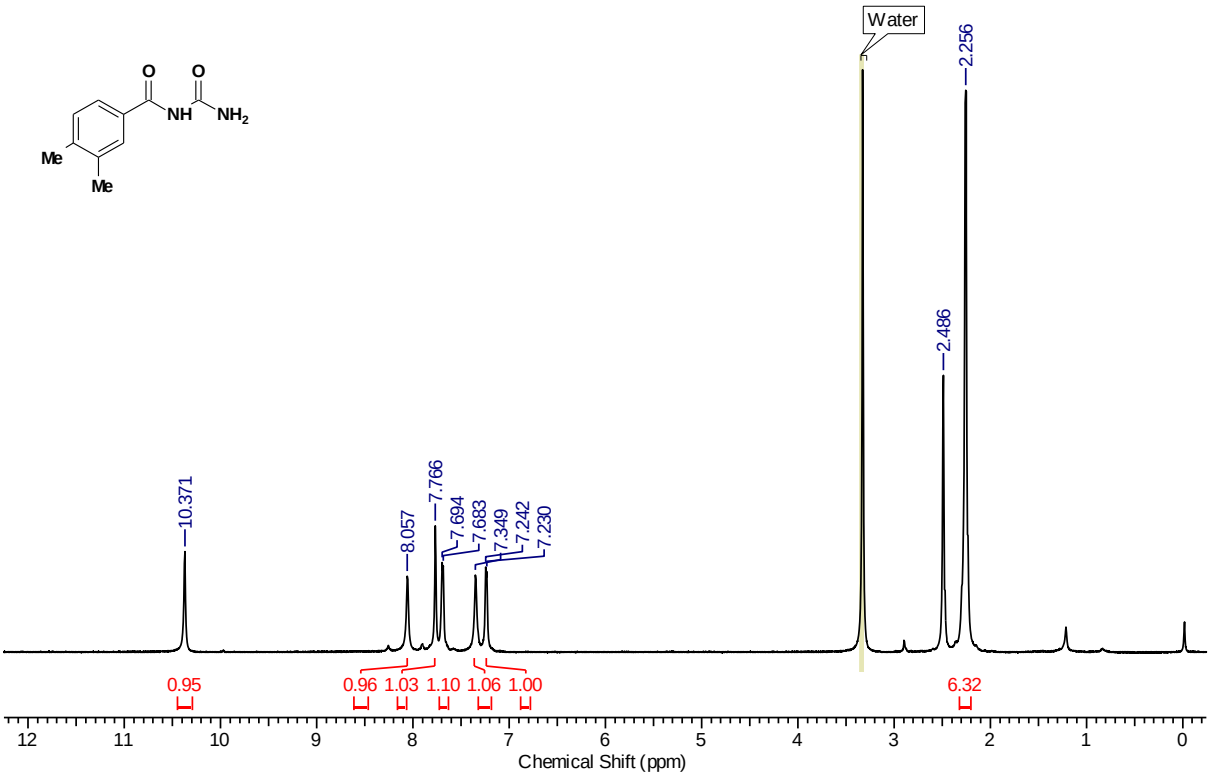




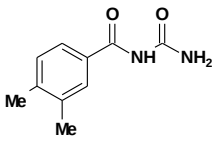
RM-170-C.002.001.1R.esp



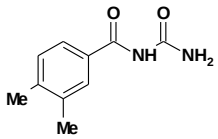
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3ad:**

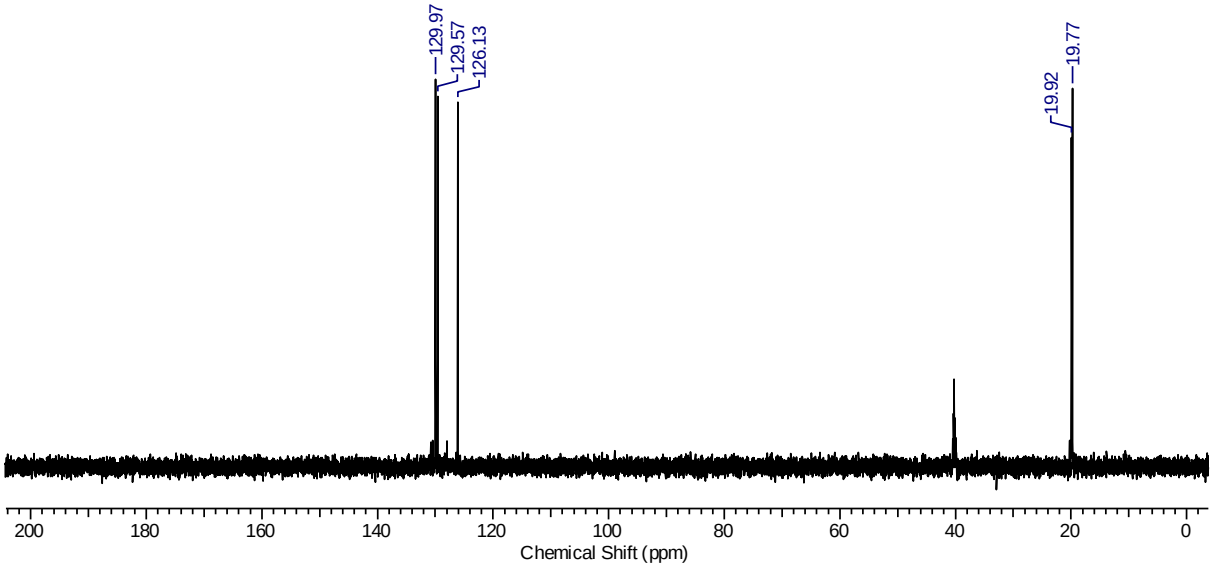


ID-117-MR.069.001.1R.esp

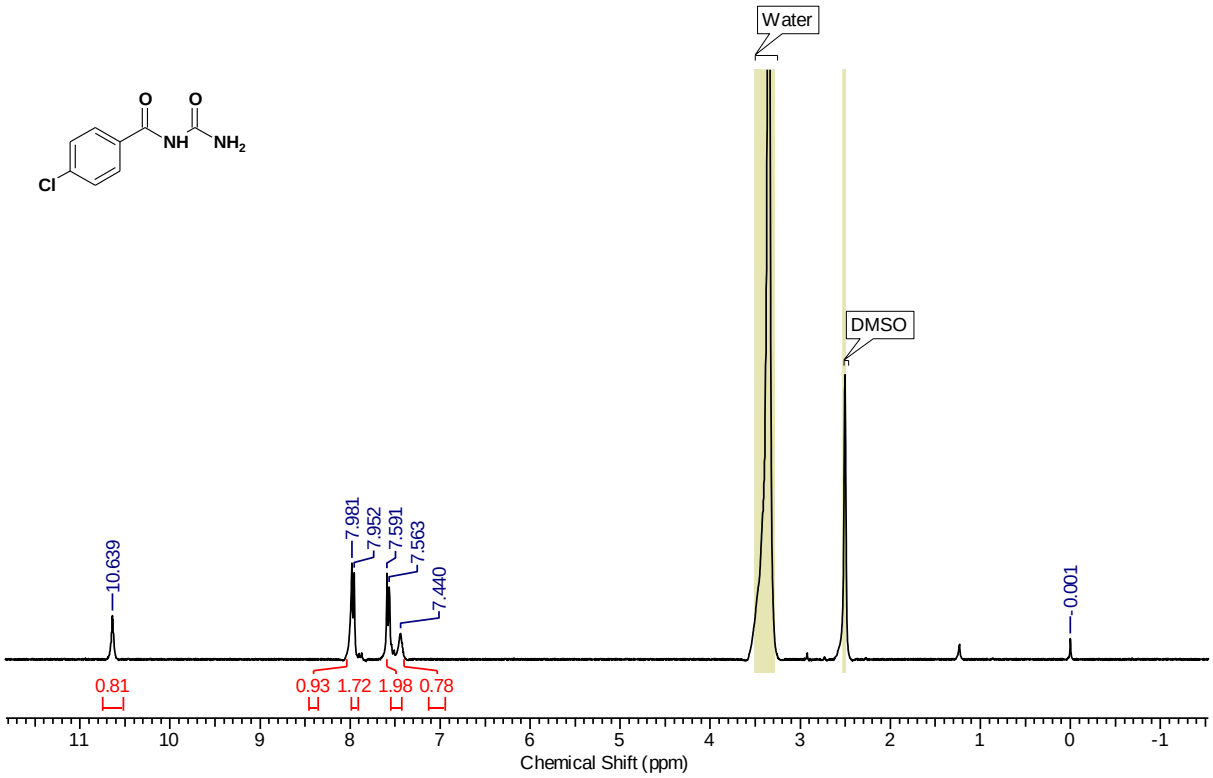


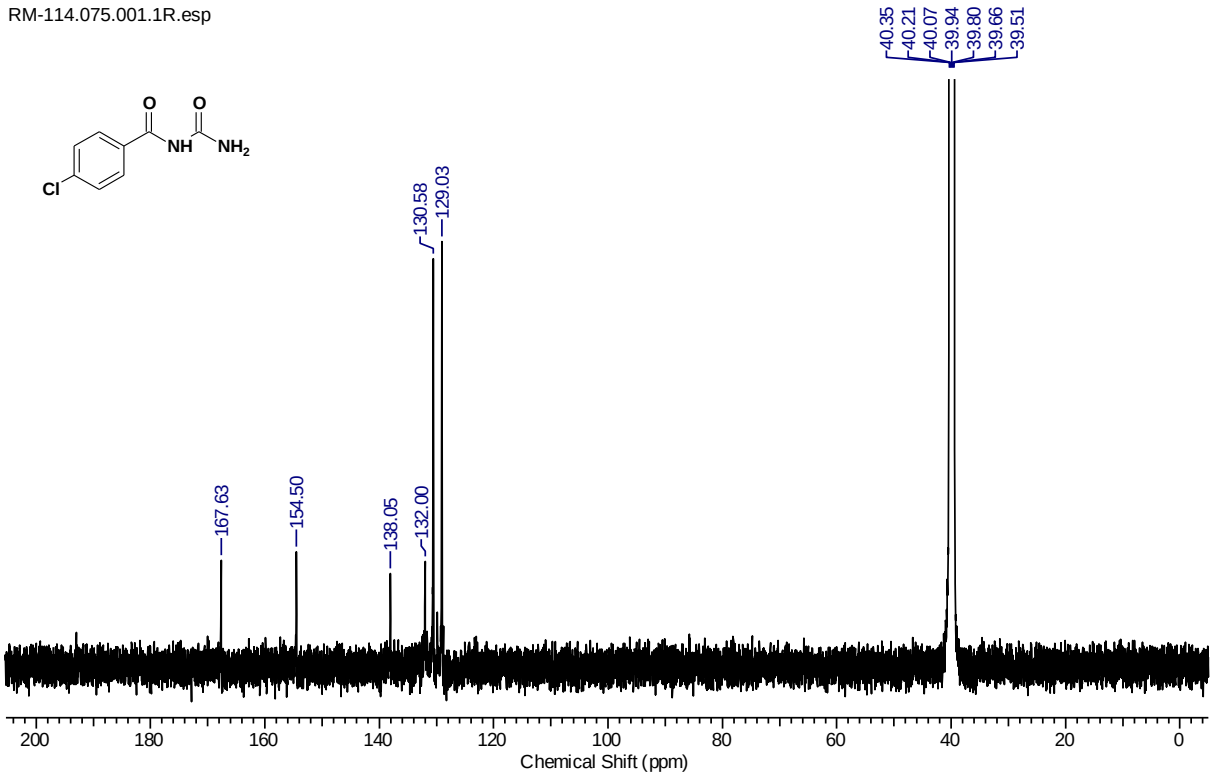
ID-117-MR.070.001.1R.esp



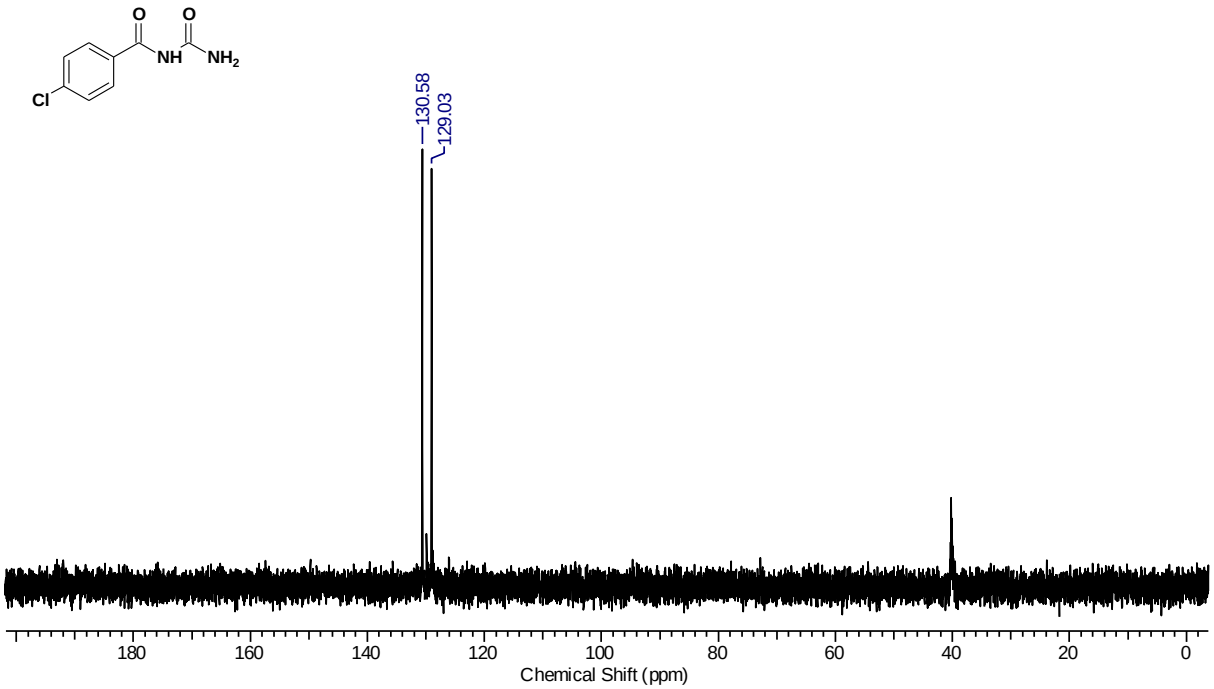


^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3ae:**

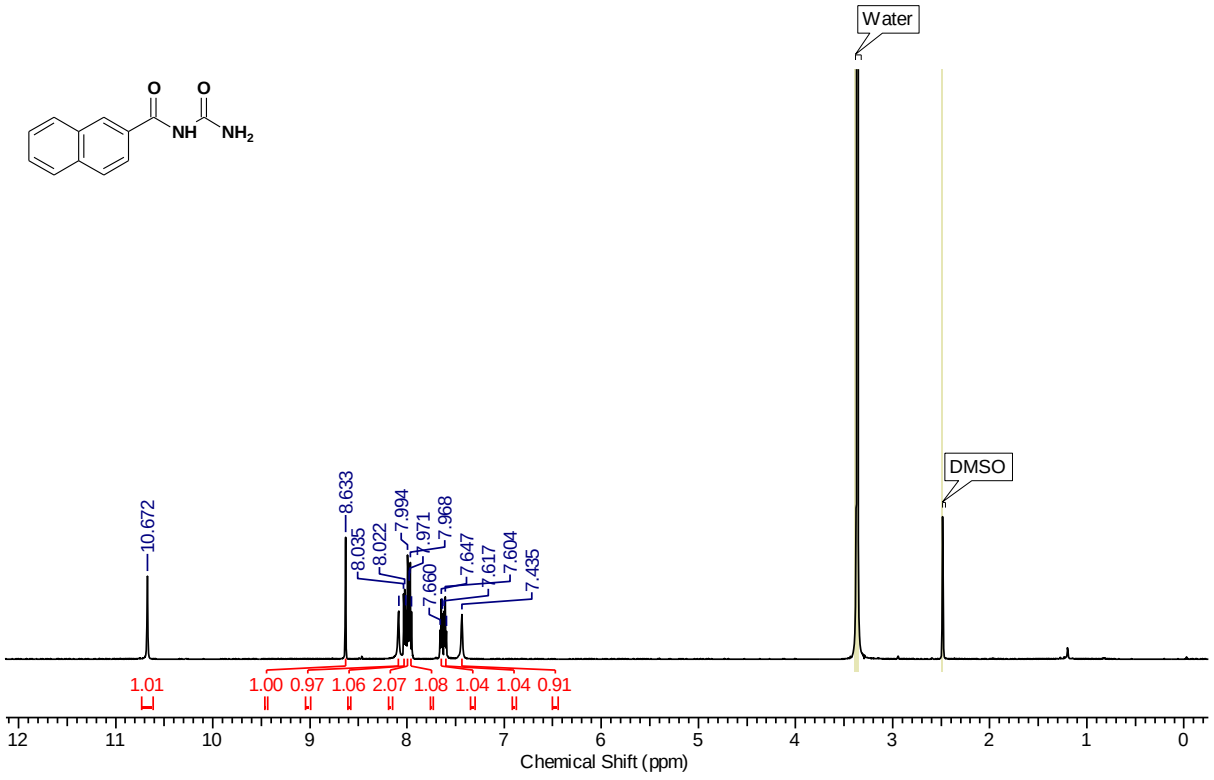




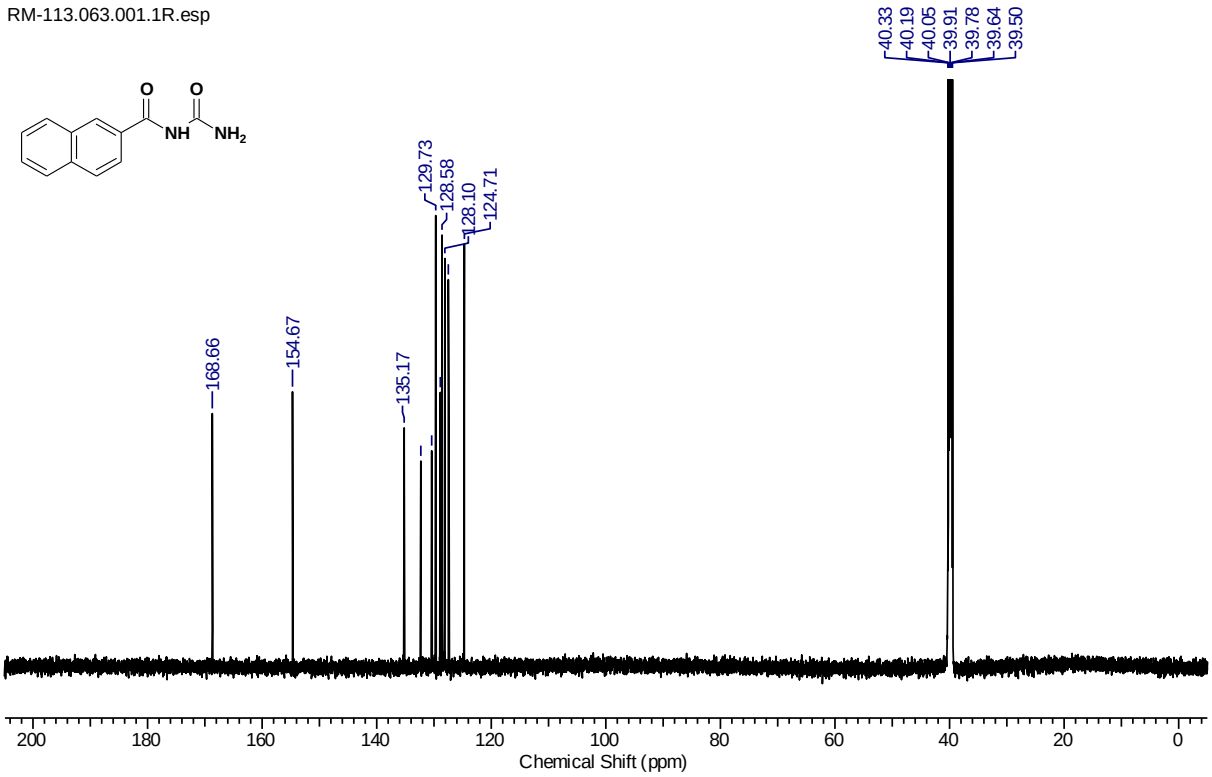
RM-114.076.001.1R.esp



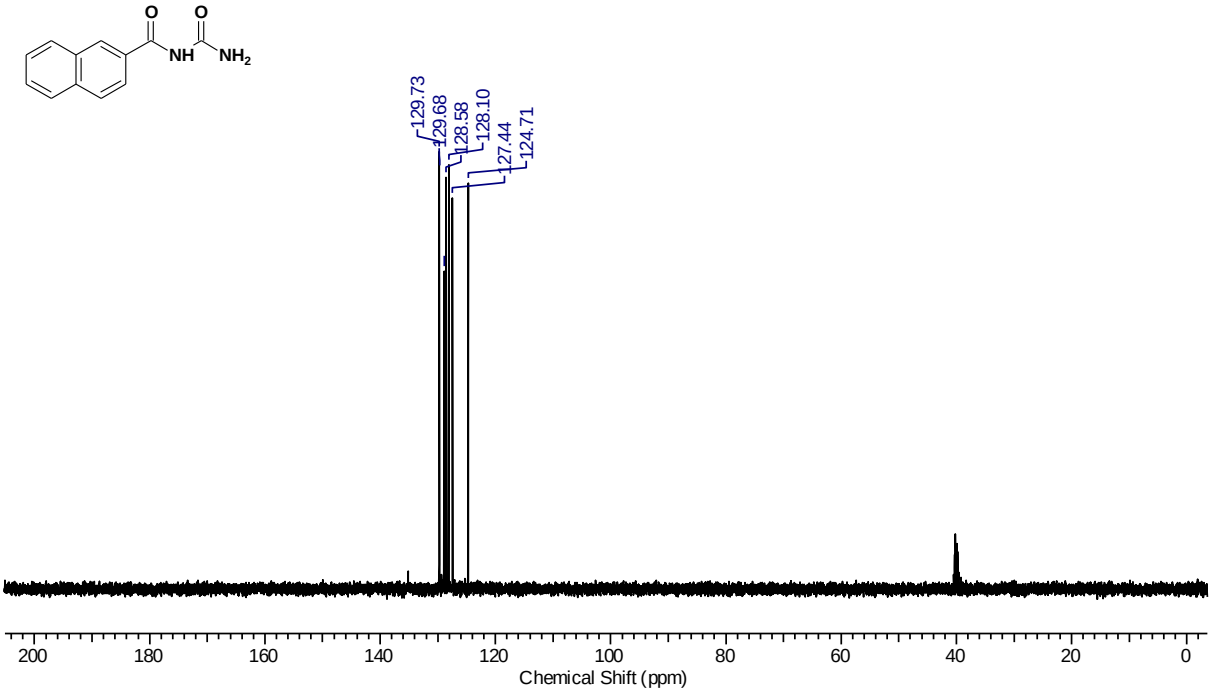
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3af:**



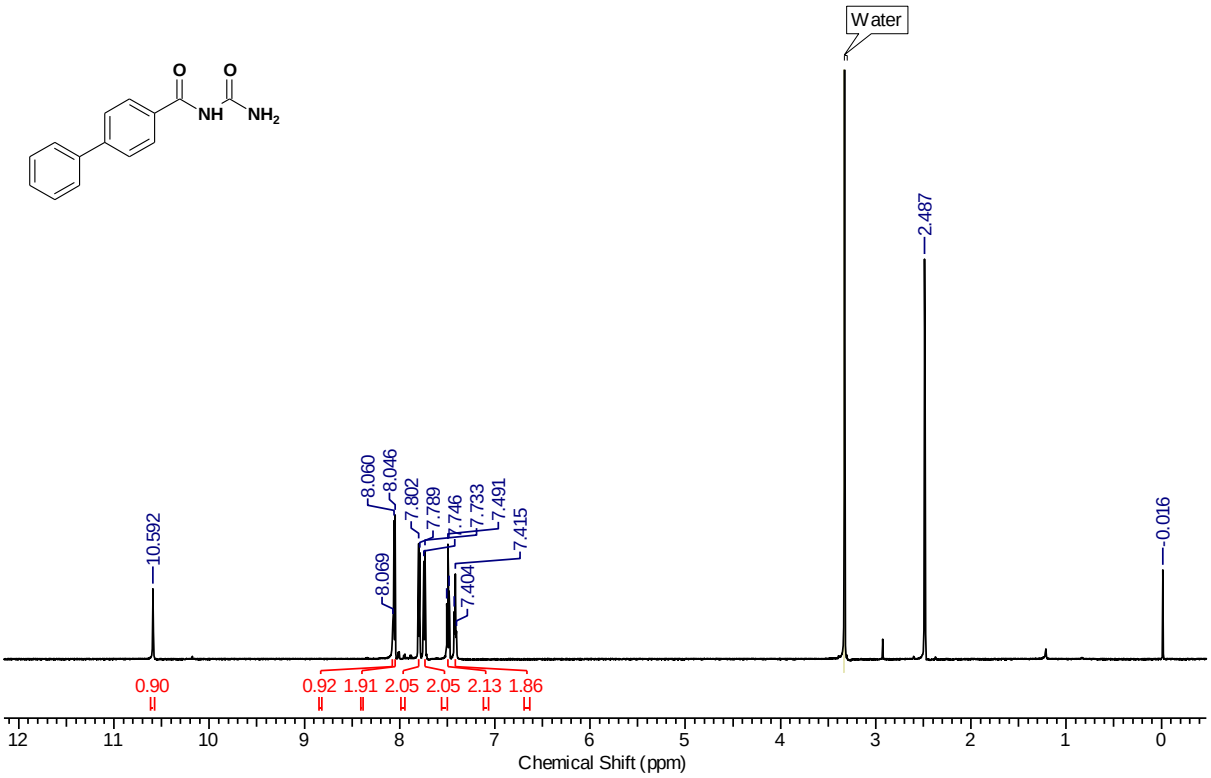
RM-113.063.001.1R.esp

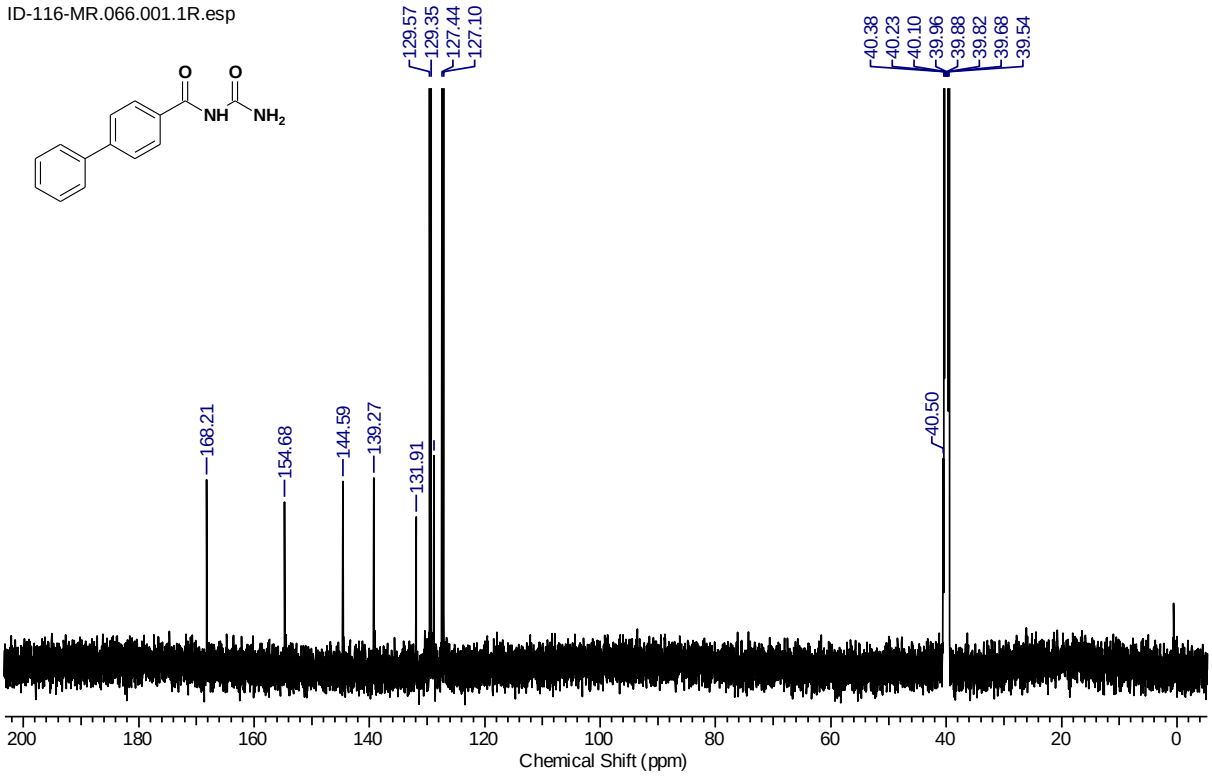


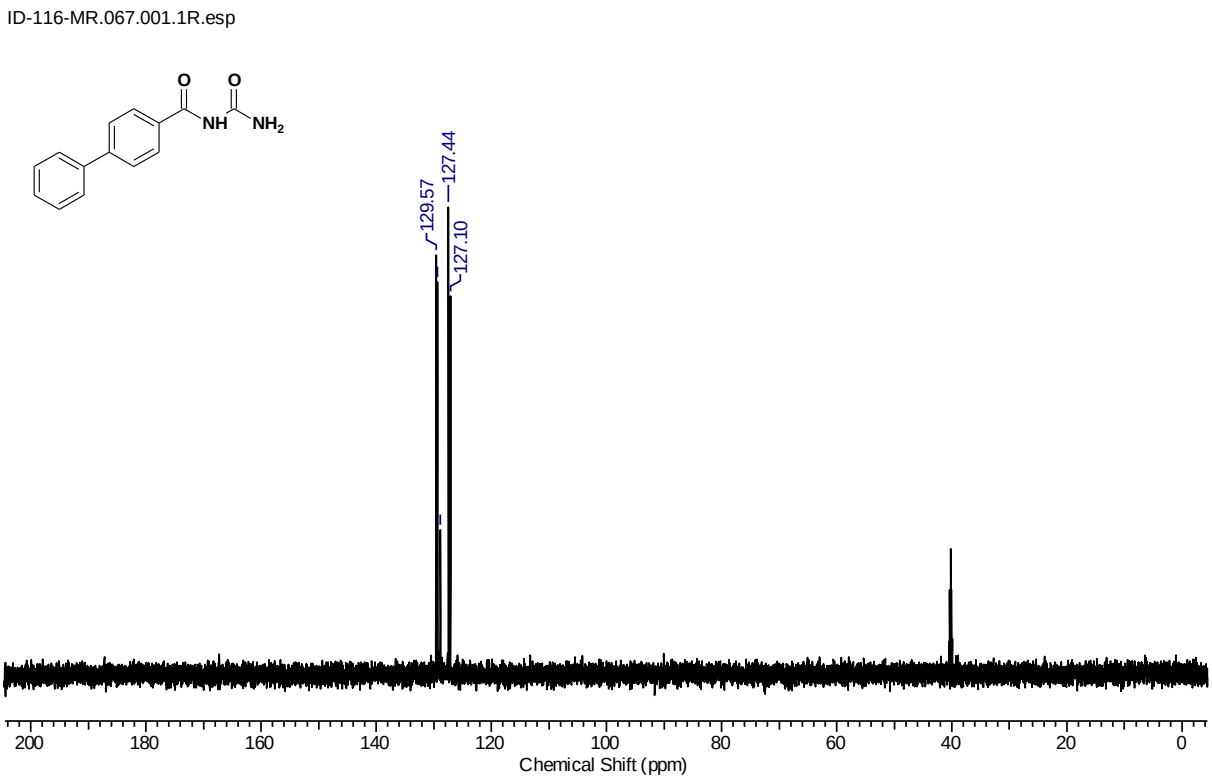
RM-113.064.001.1R.esp



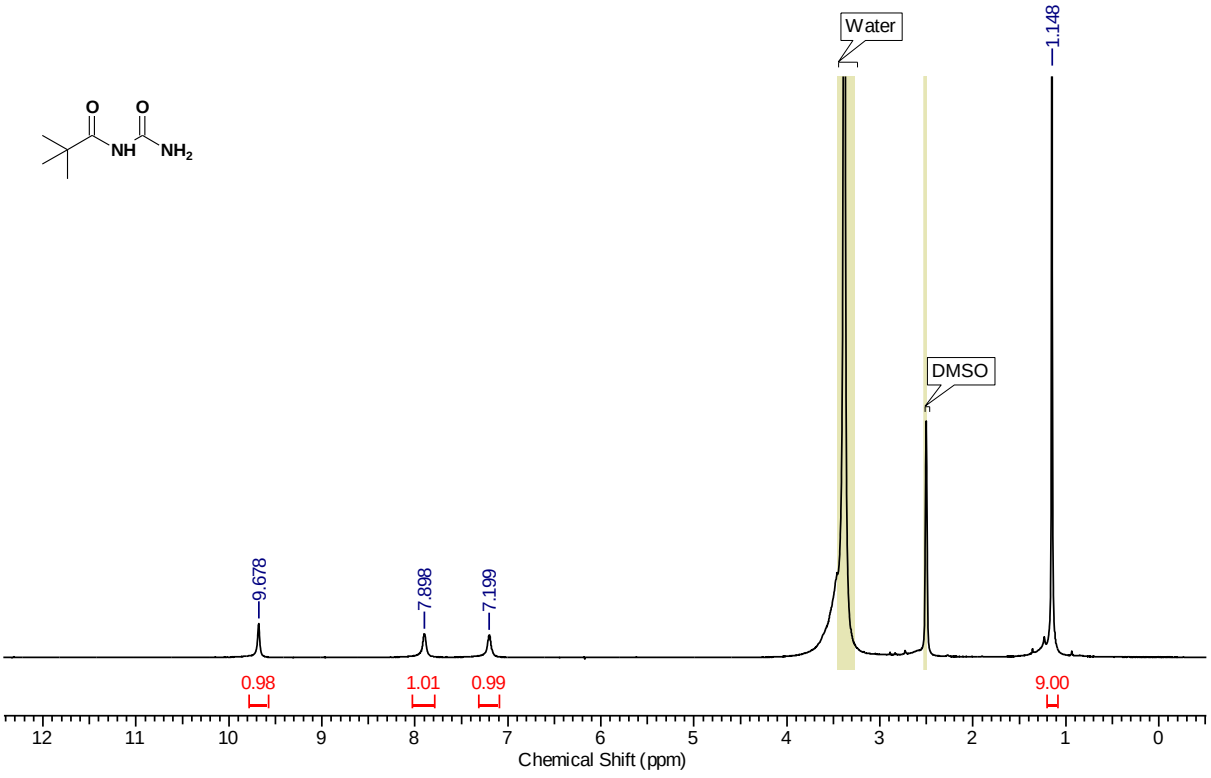
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3ag:**



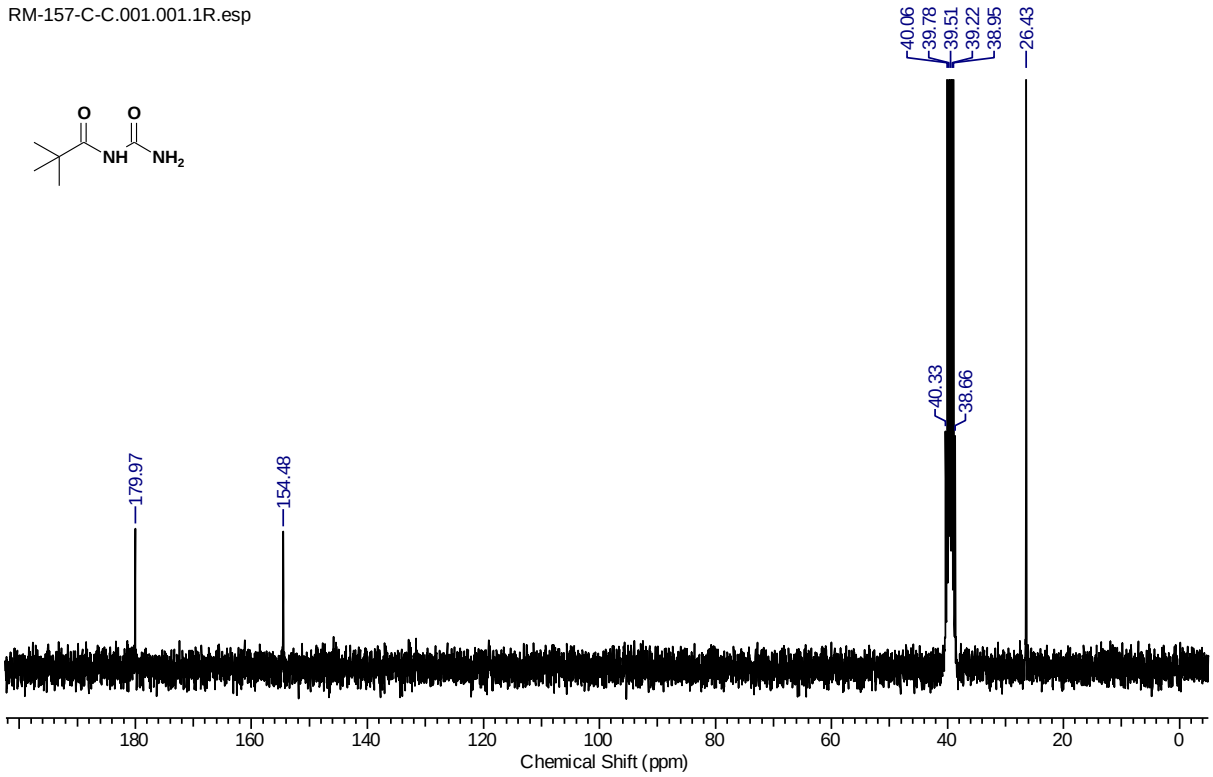




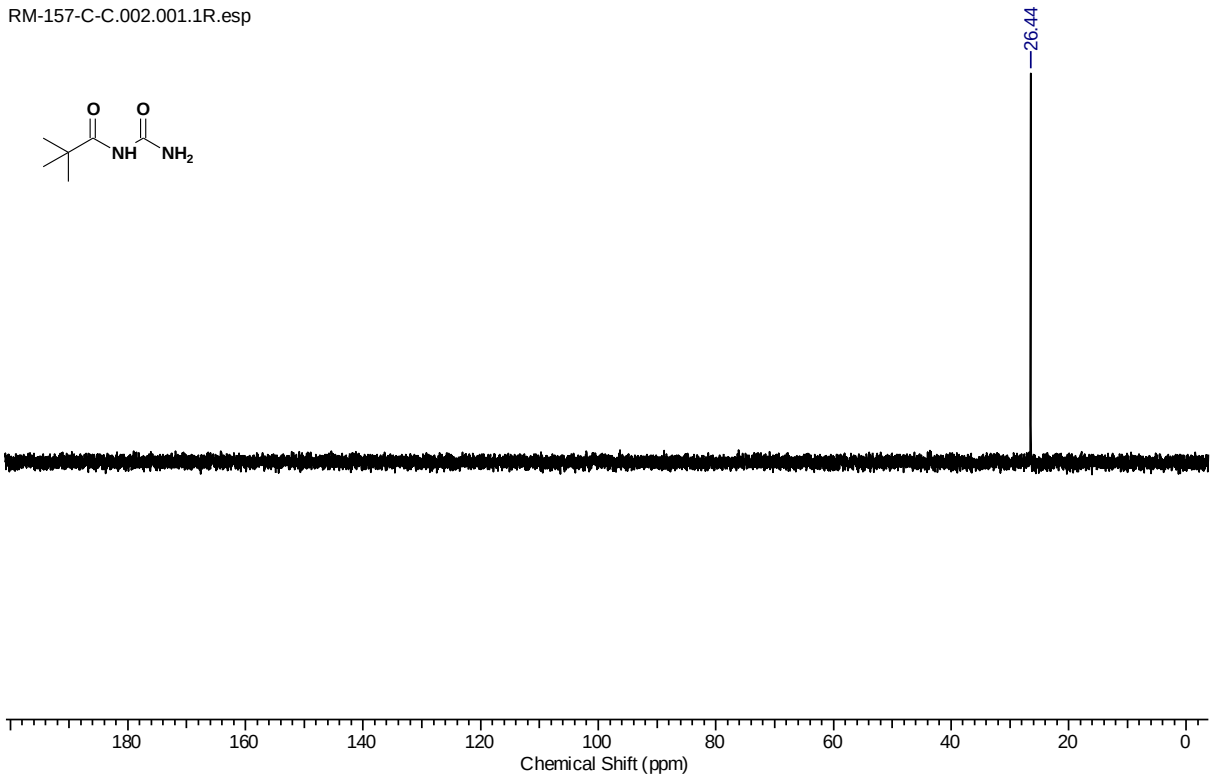
^{1}H, ^{13}C{^{1}H}, DEPT-135 NMR spectra of **3ah:**



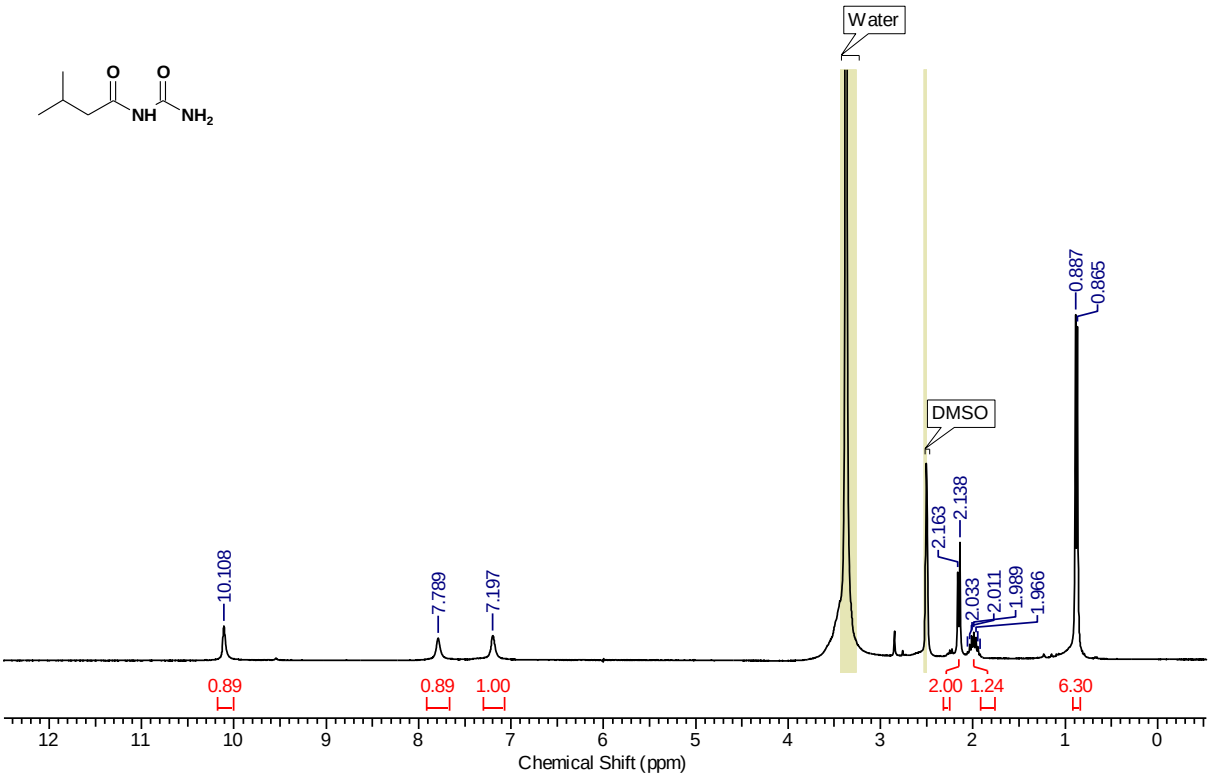
RM-157-C-C.001.001.1R.esp

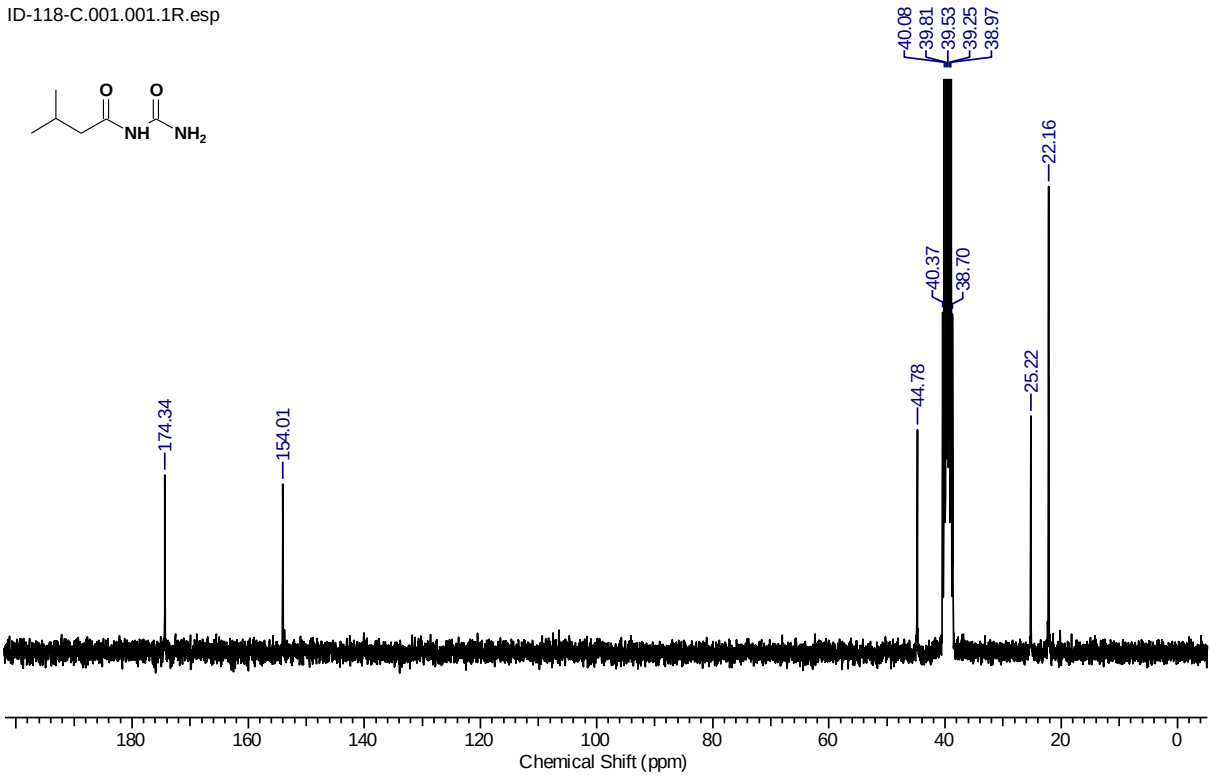


RM-157-C-C.002.001.1R.esp

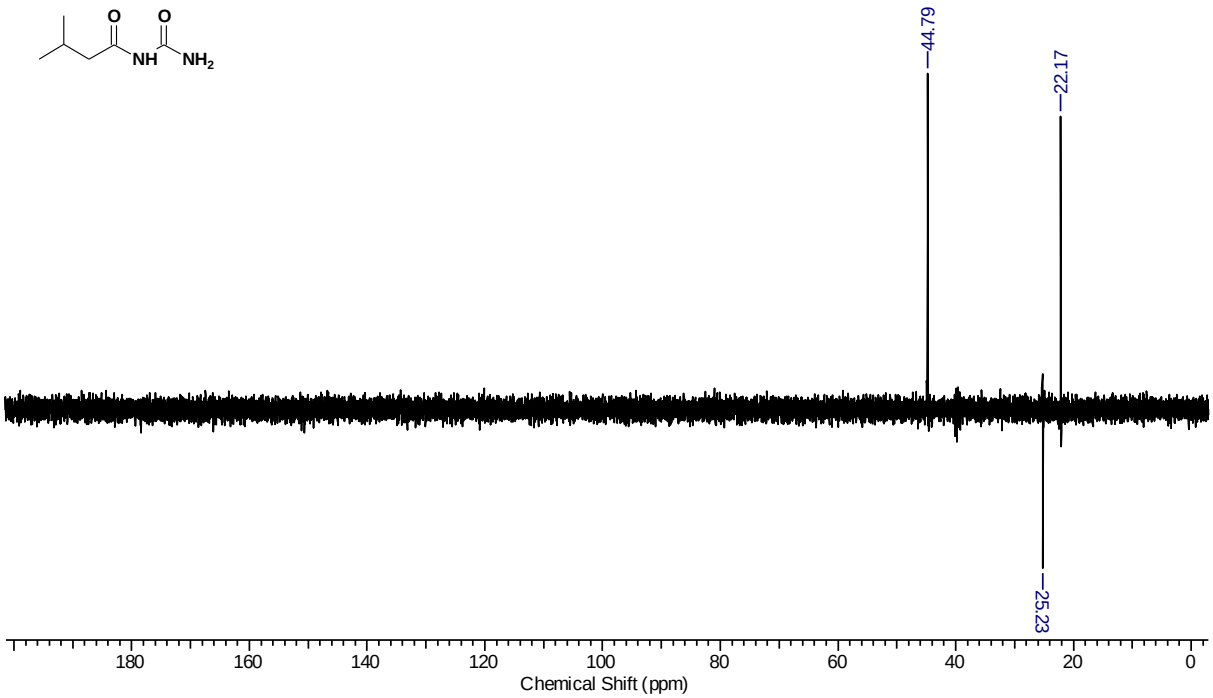


^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3ai:**

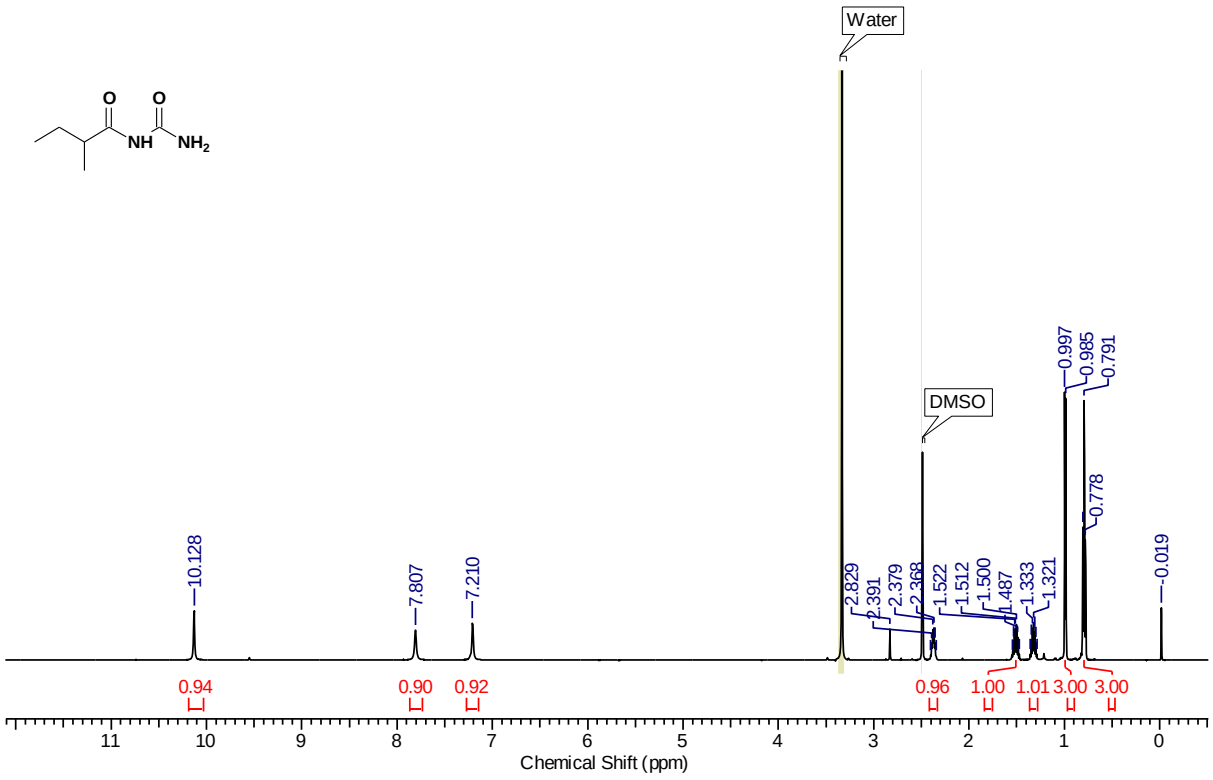


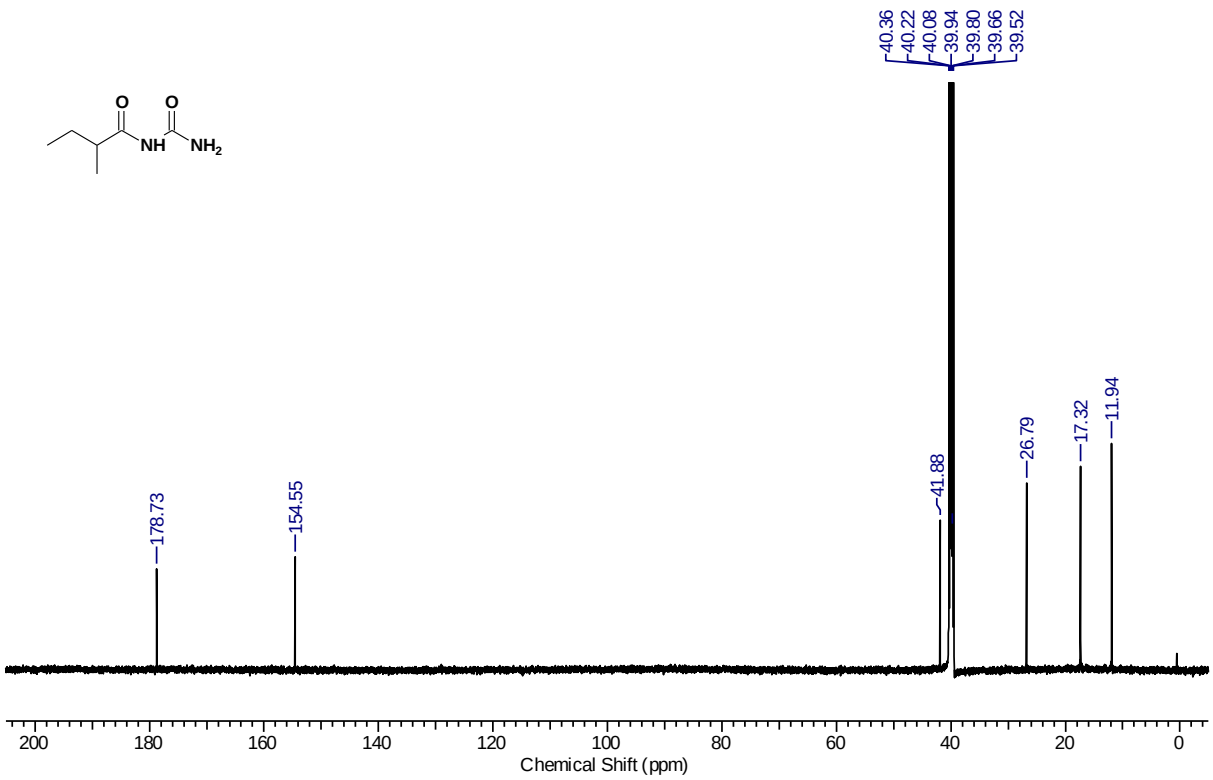


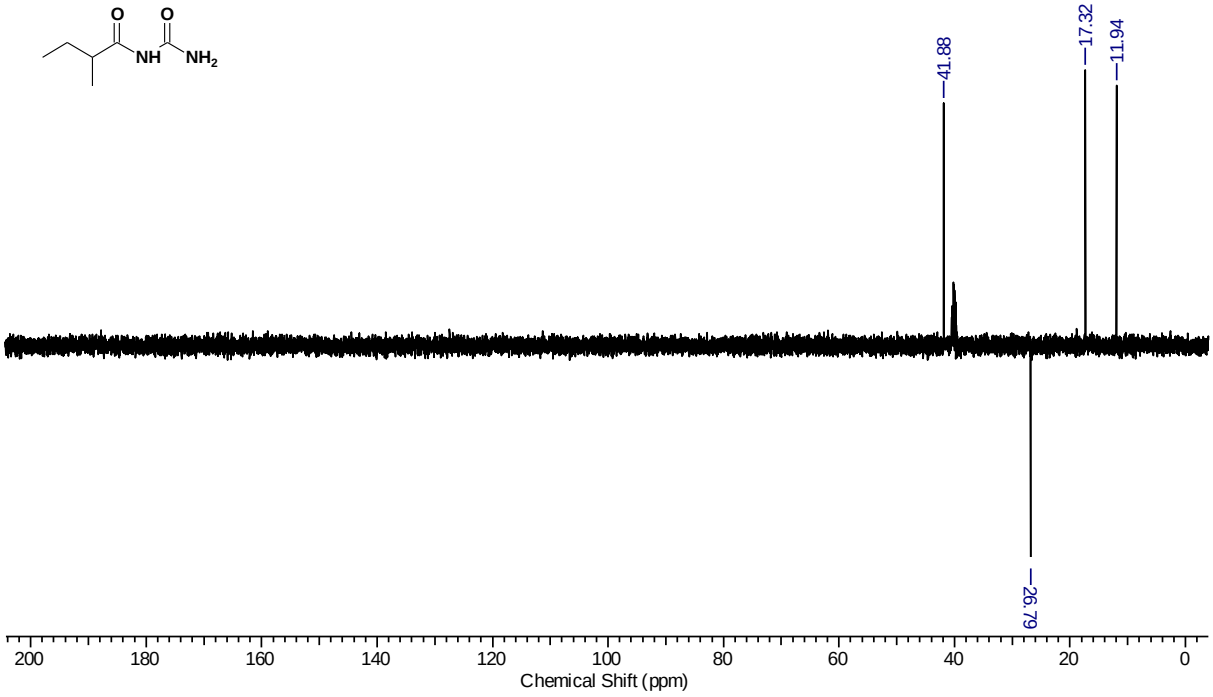
ID-118-C.002.001.1R.esp



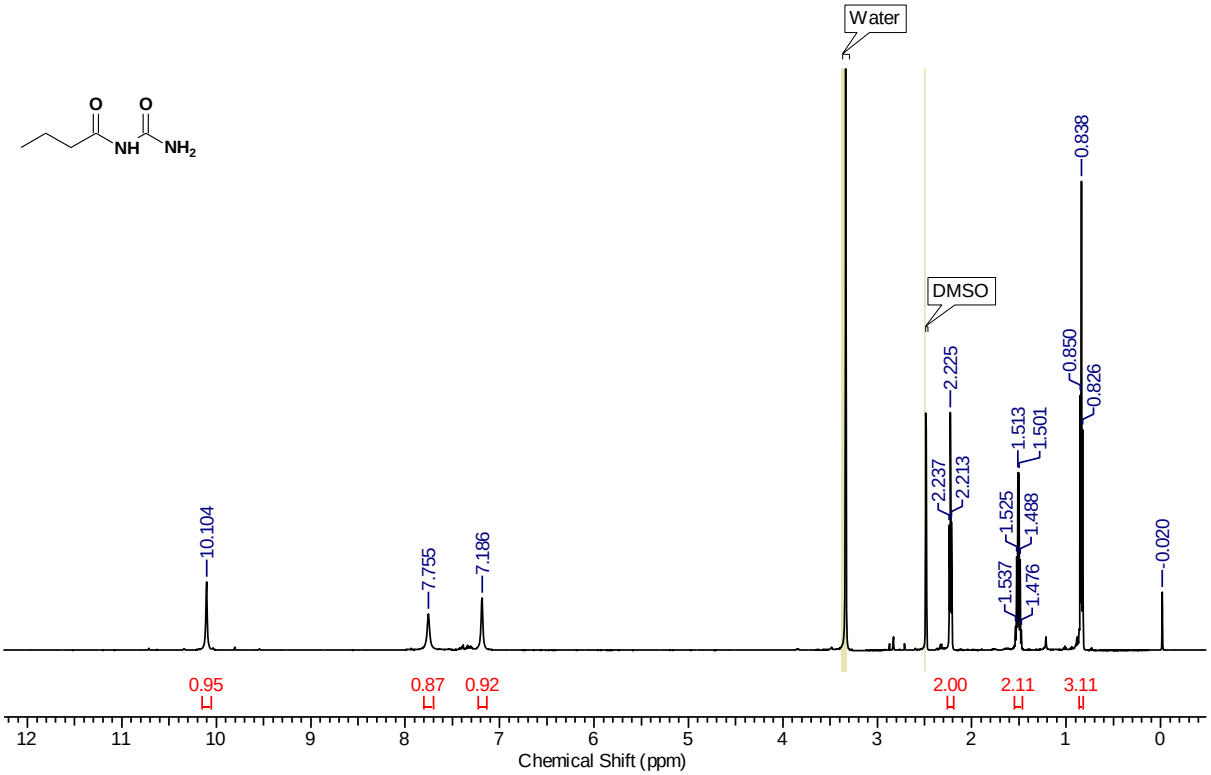
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3aj:**

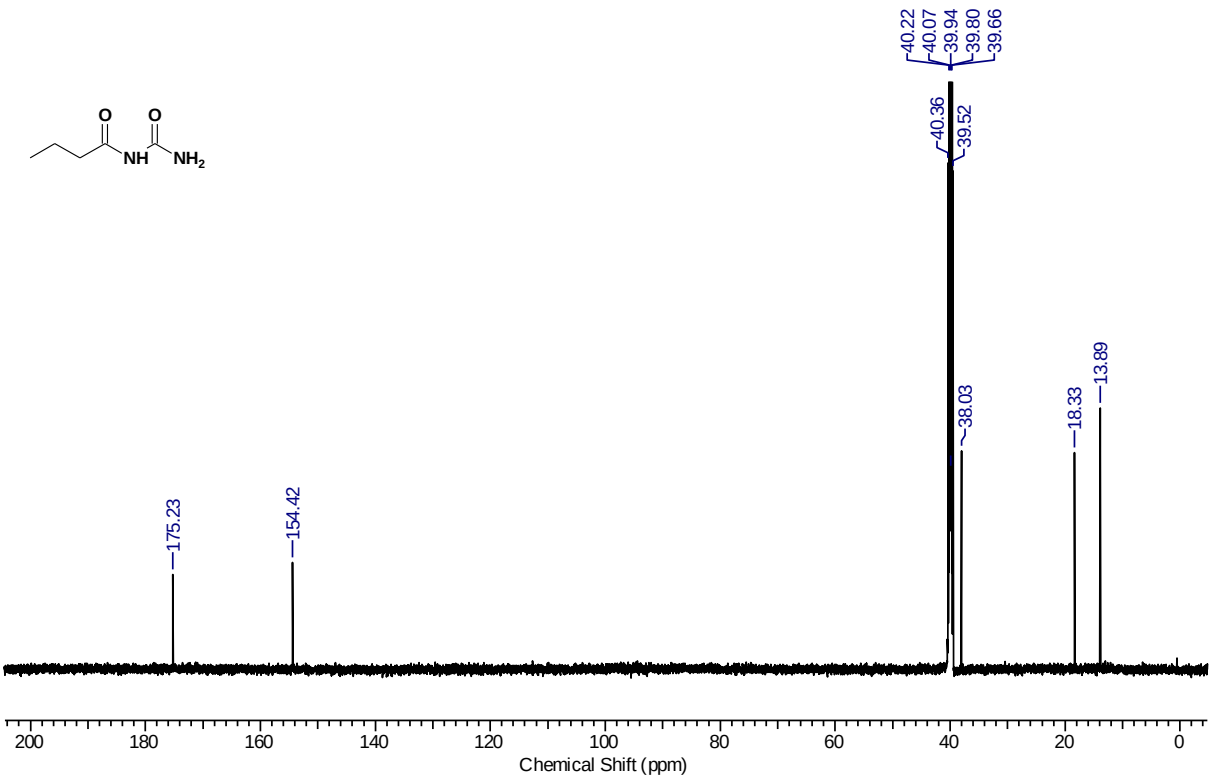


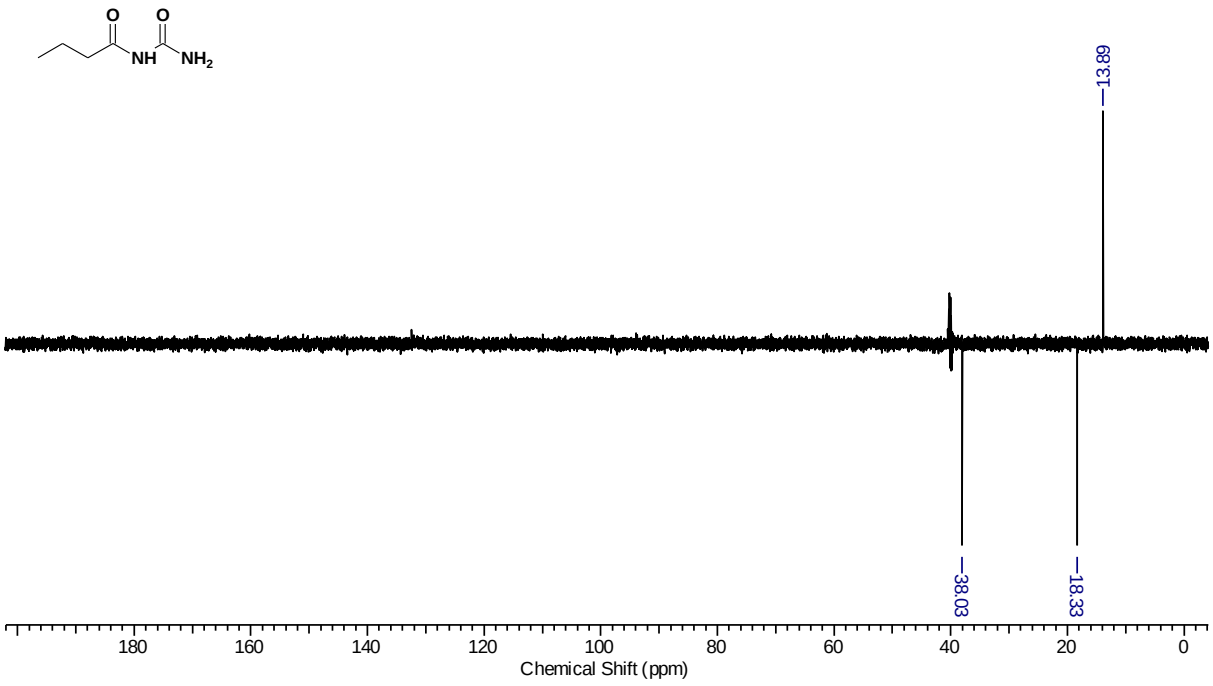

O
O
NH
NH2
40.36
40.22
40.08
39.94
39.80
39.66
39.52
178.73
154.55
41.88
26.79
17.32
11.94
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


O
O
NH
NH2
41.88
17.32
11.94
26.79
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

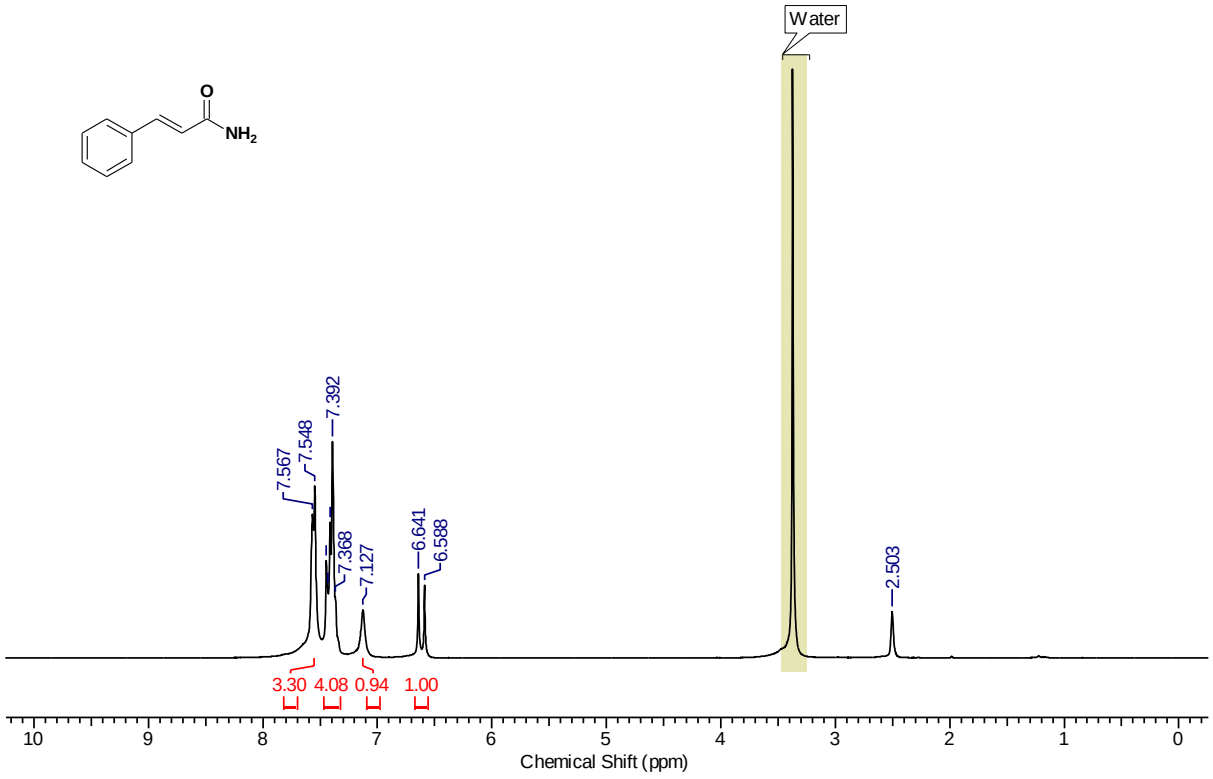
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **3ak**:



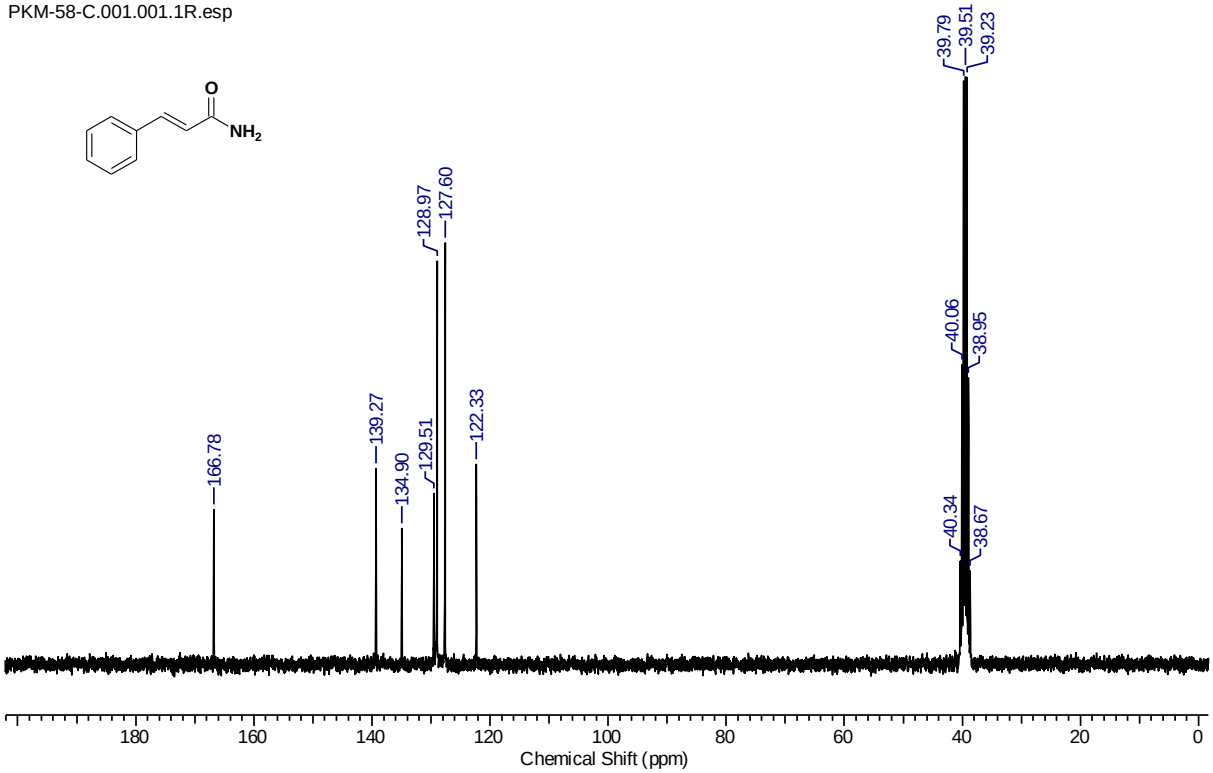




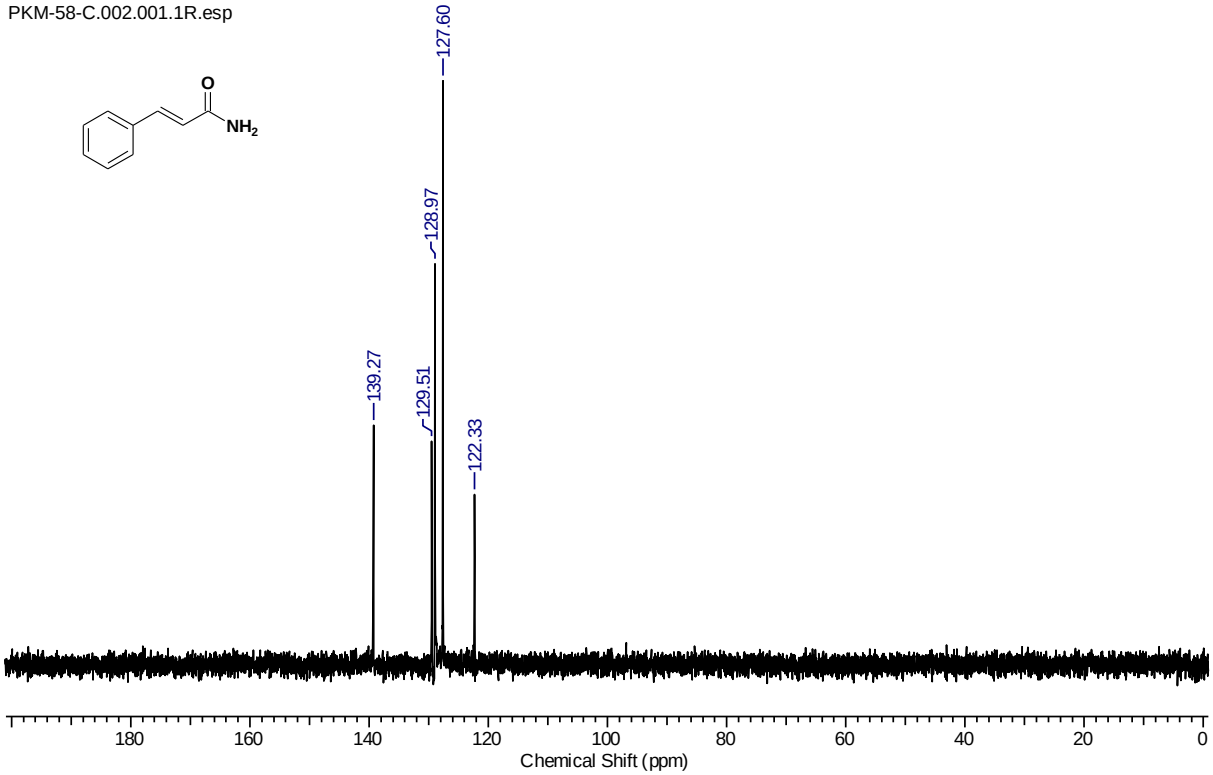
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4a:**



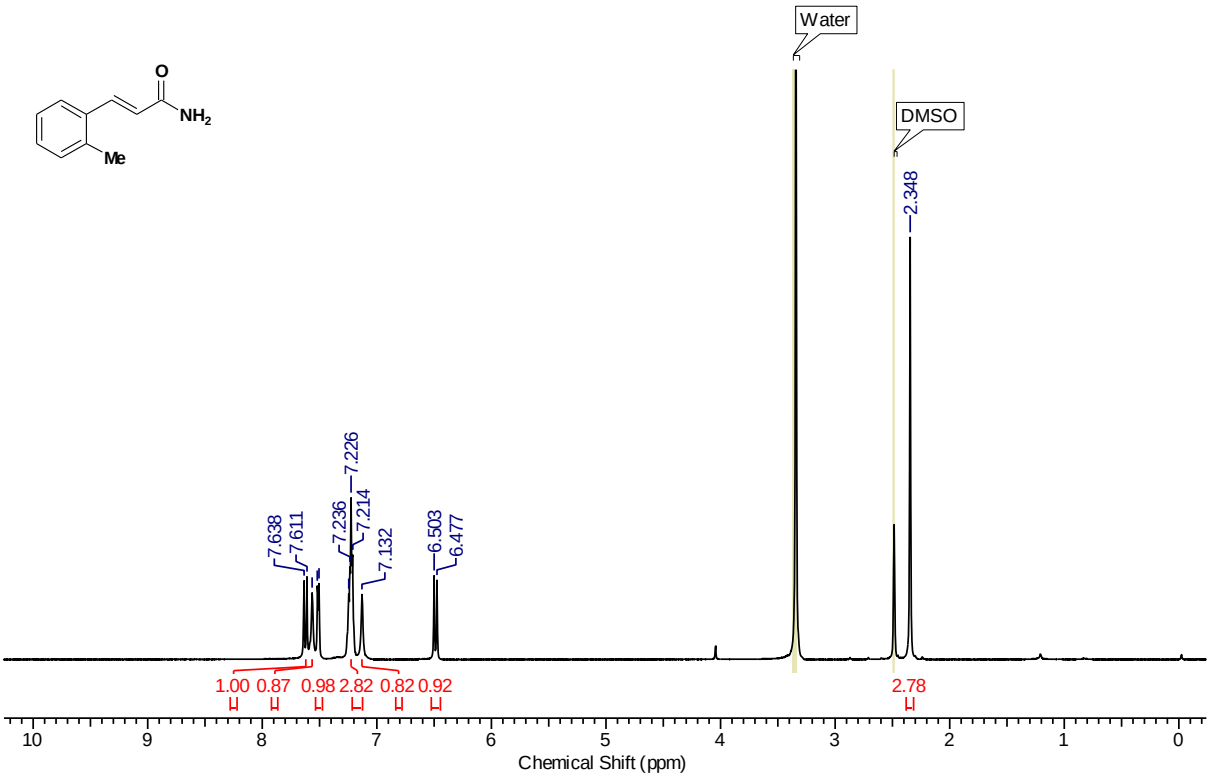
PKM-58-C.001.001.1R.esp

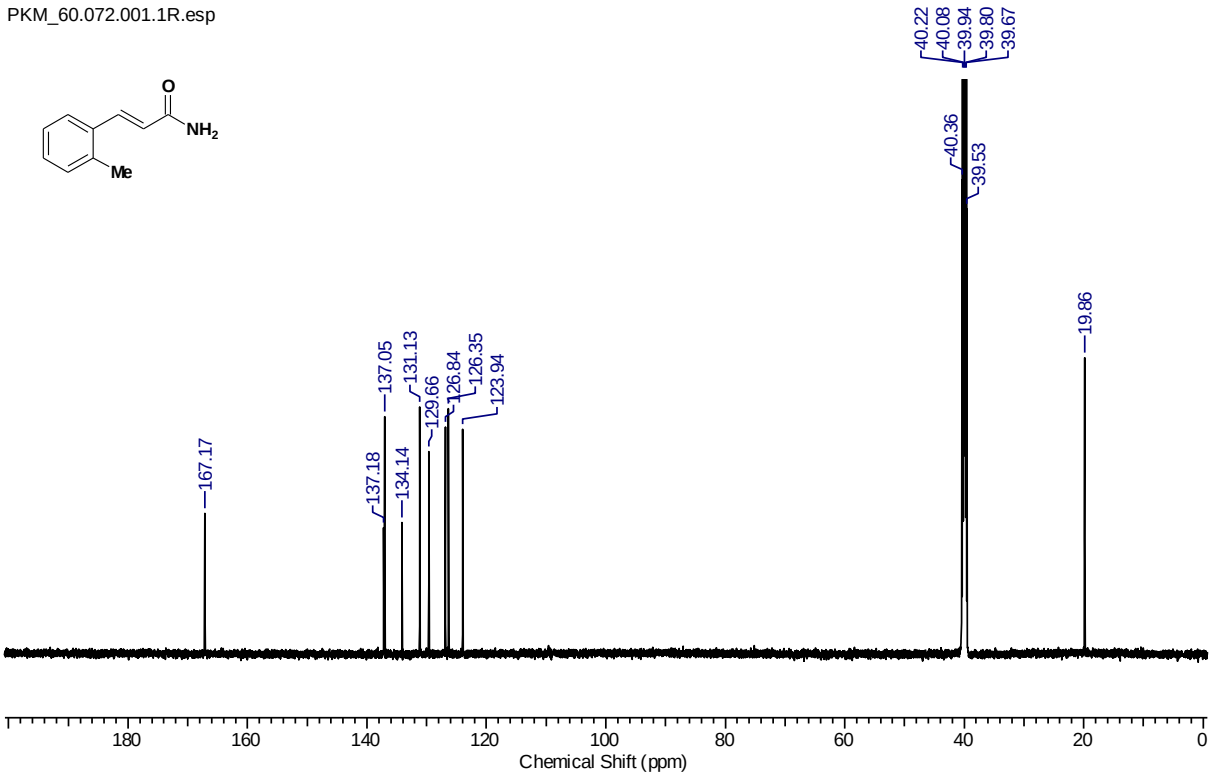


PKM-58-C.002.001.1R.esp

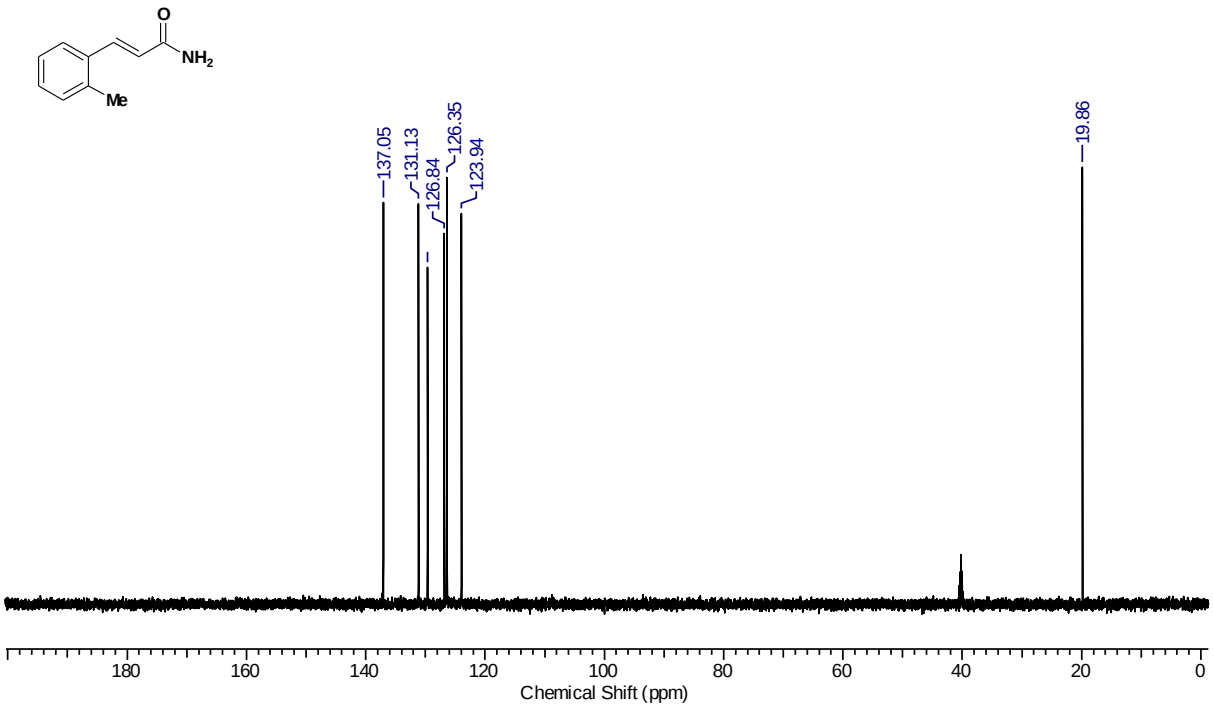


^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4b:**

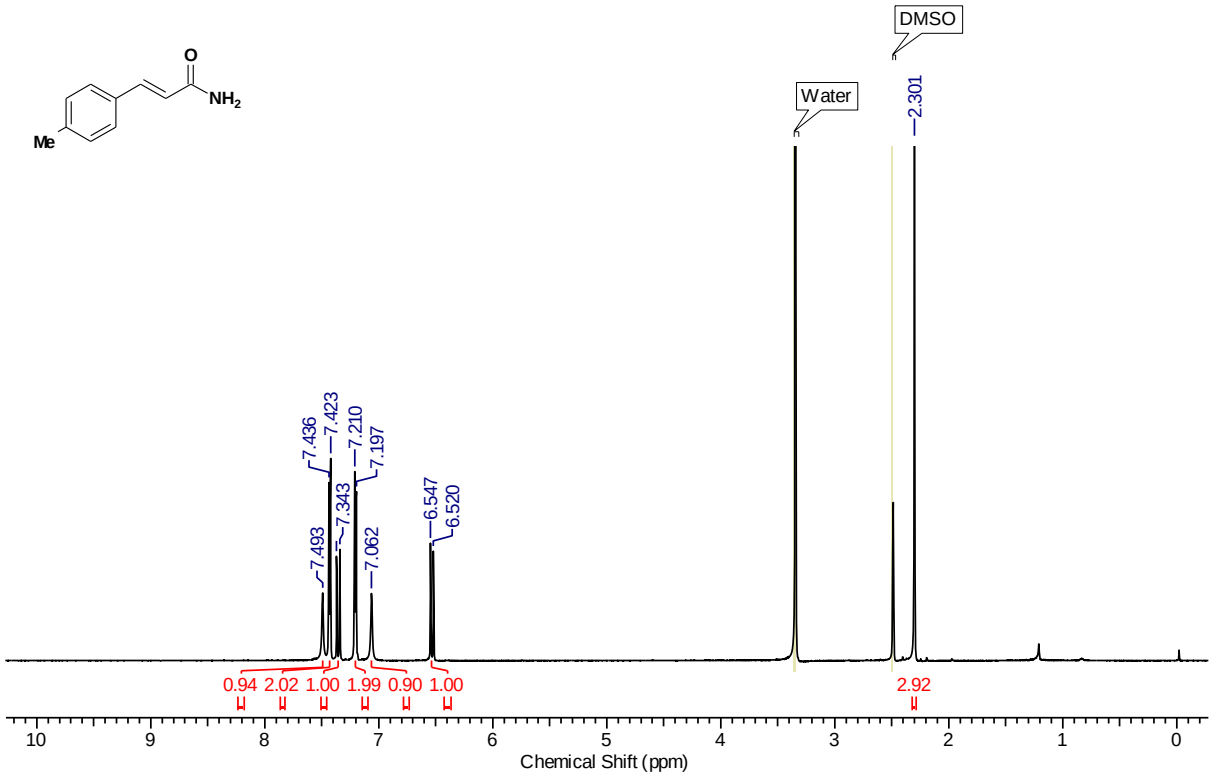


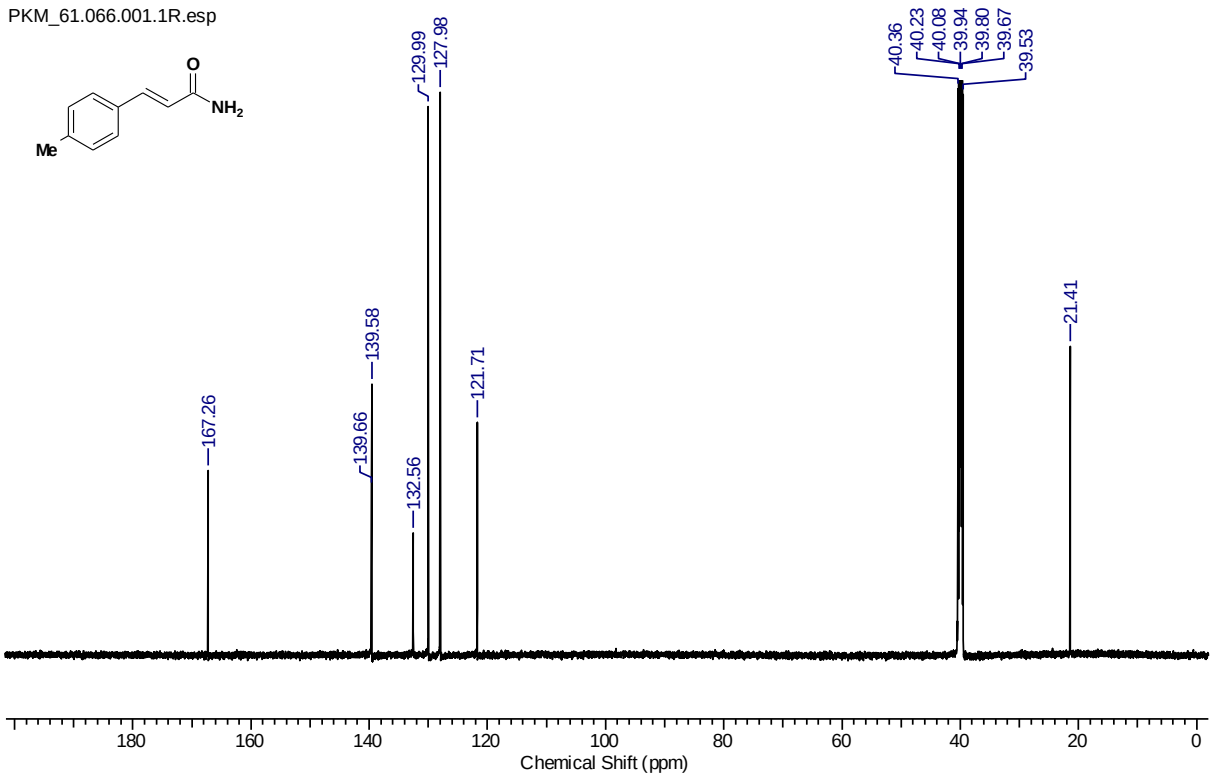


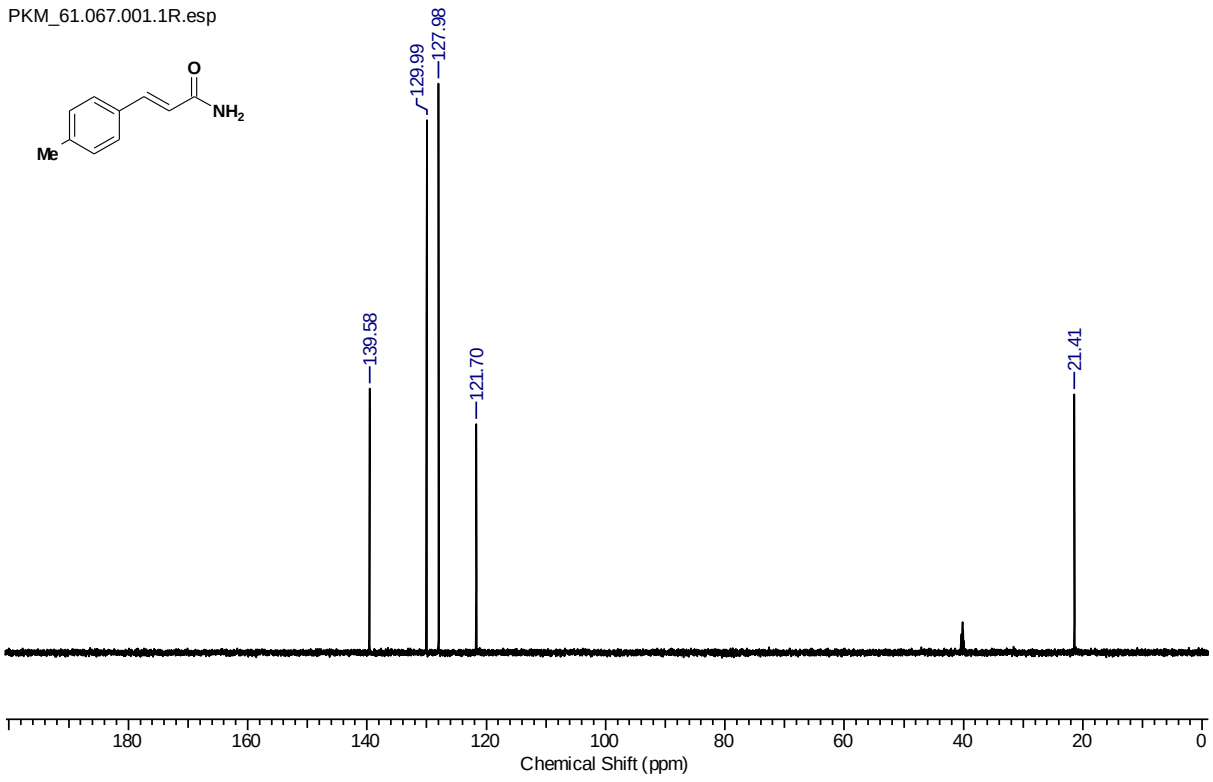
PKM_60.073.001.1R.esp



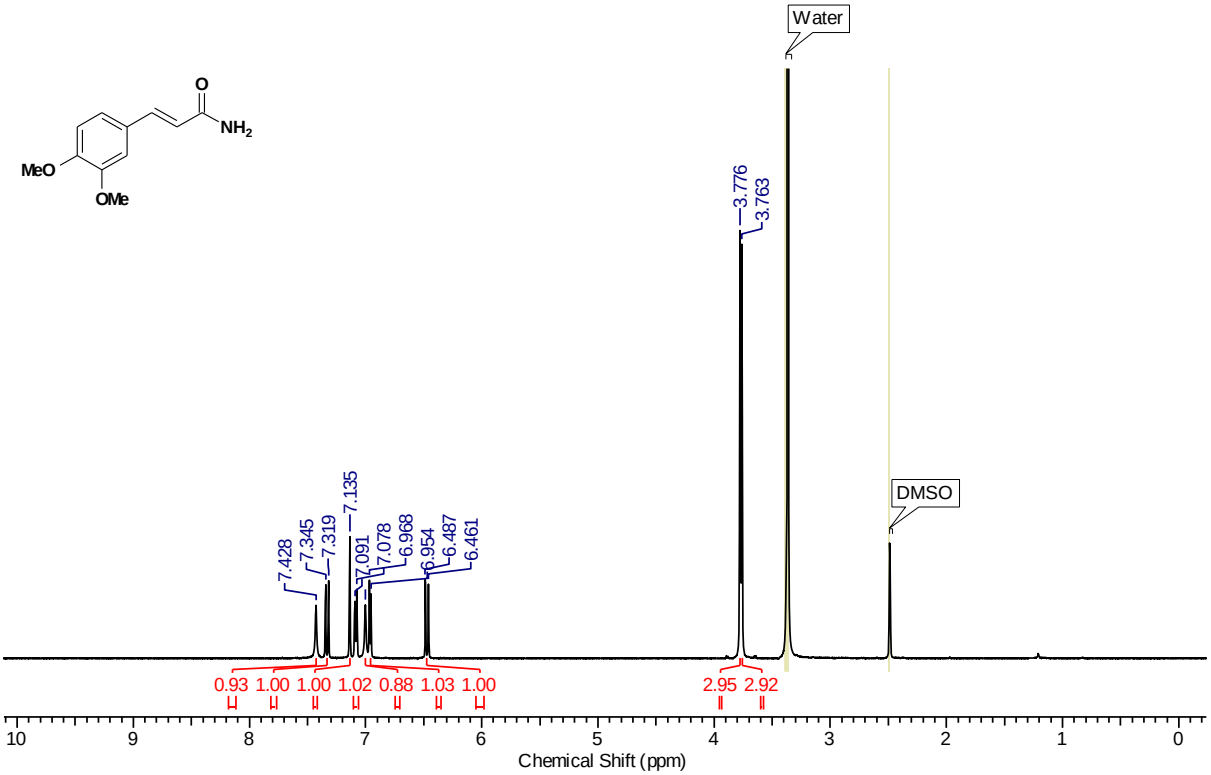
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4c:**

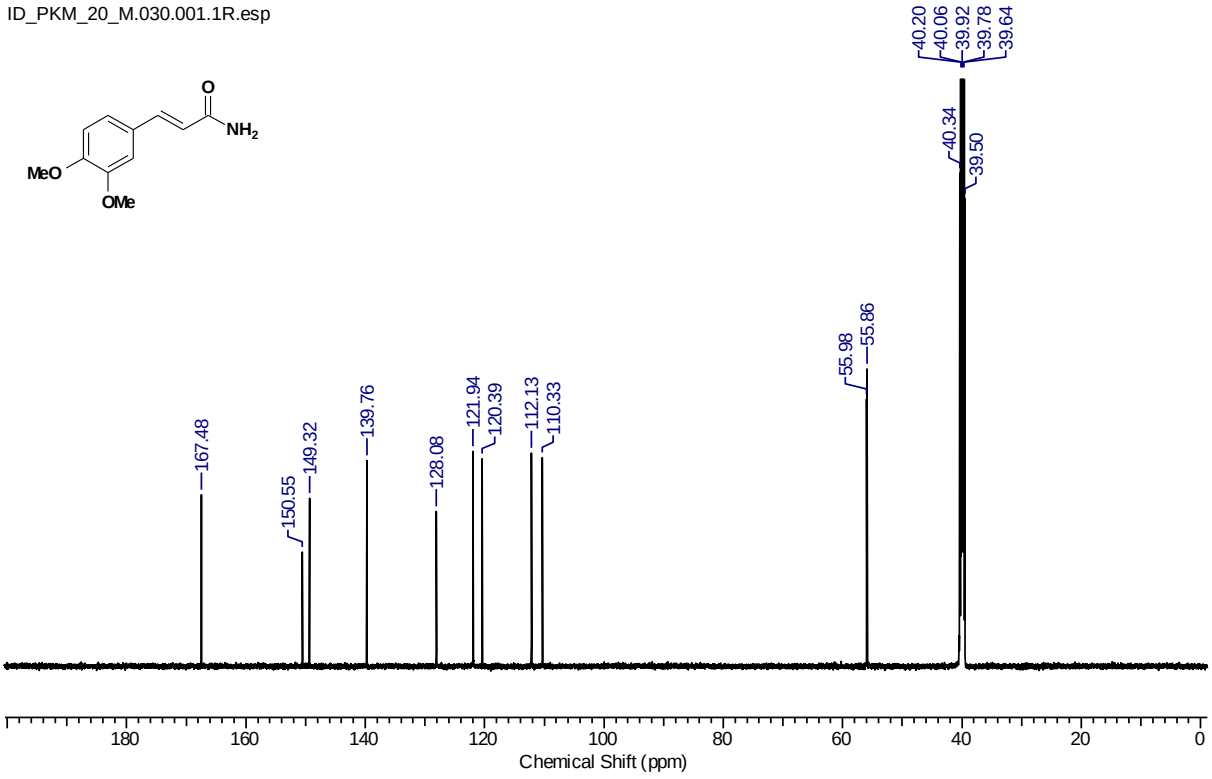


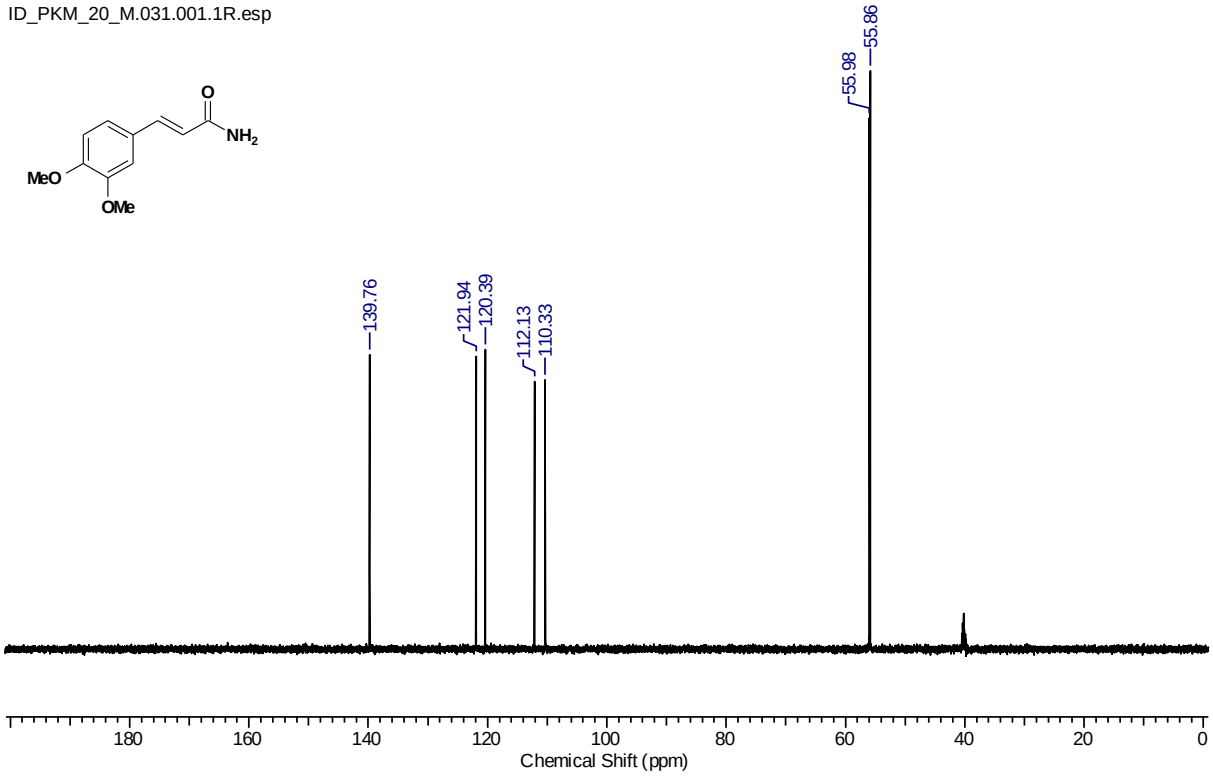

PKM_61.066.001.1R.esp
O
NH2
Me
167.26
139.66
139.58
132.56
129.99
127.98
121.71
40.36
40.23
40.08
39.94
39.80
39.67
39.53
21.41
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


PKM_61.067.001.1R.esp
O
NH2
Me
139.58
129.99
127.98
121.70
21.41
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

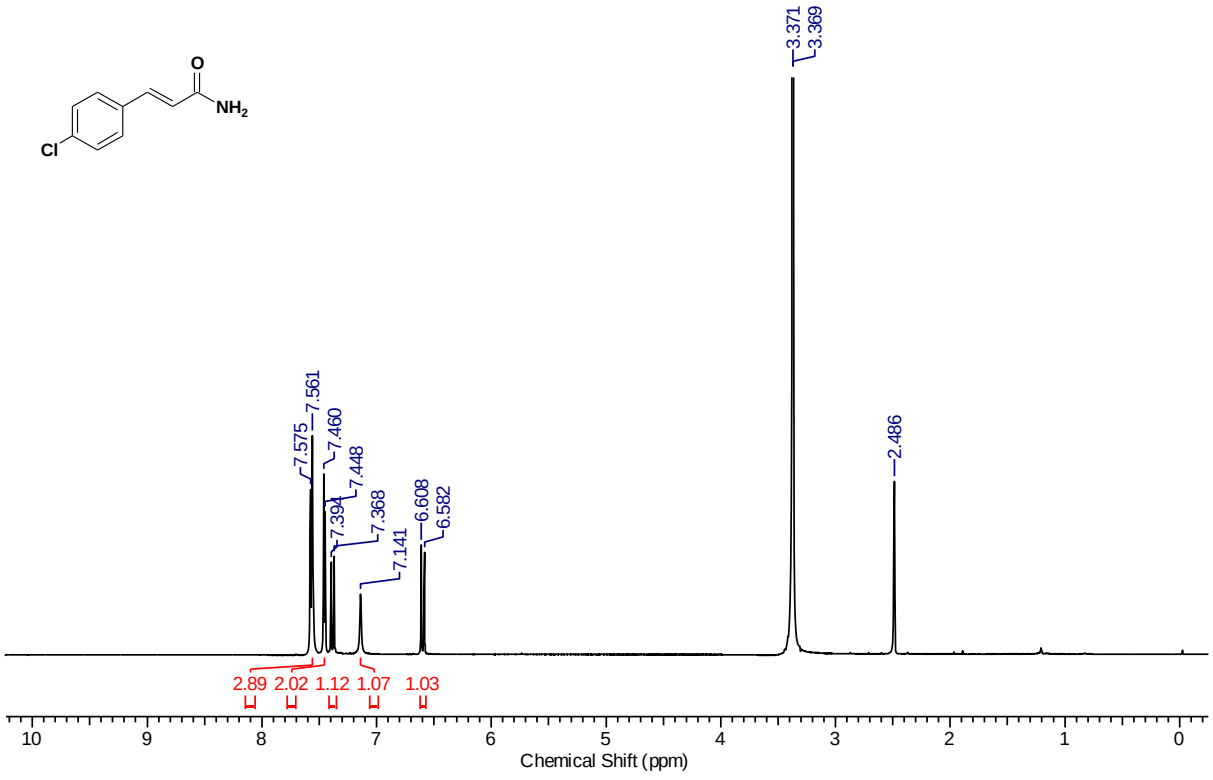
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4d:**

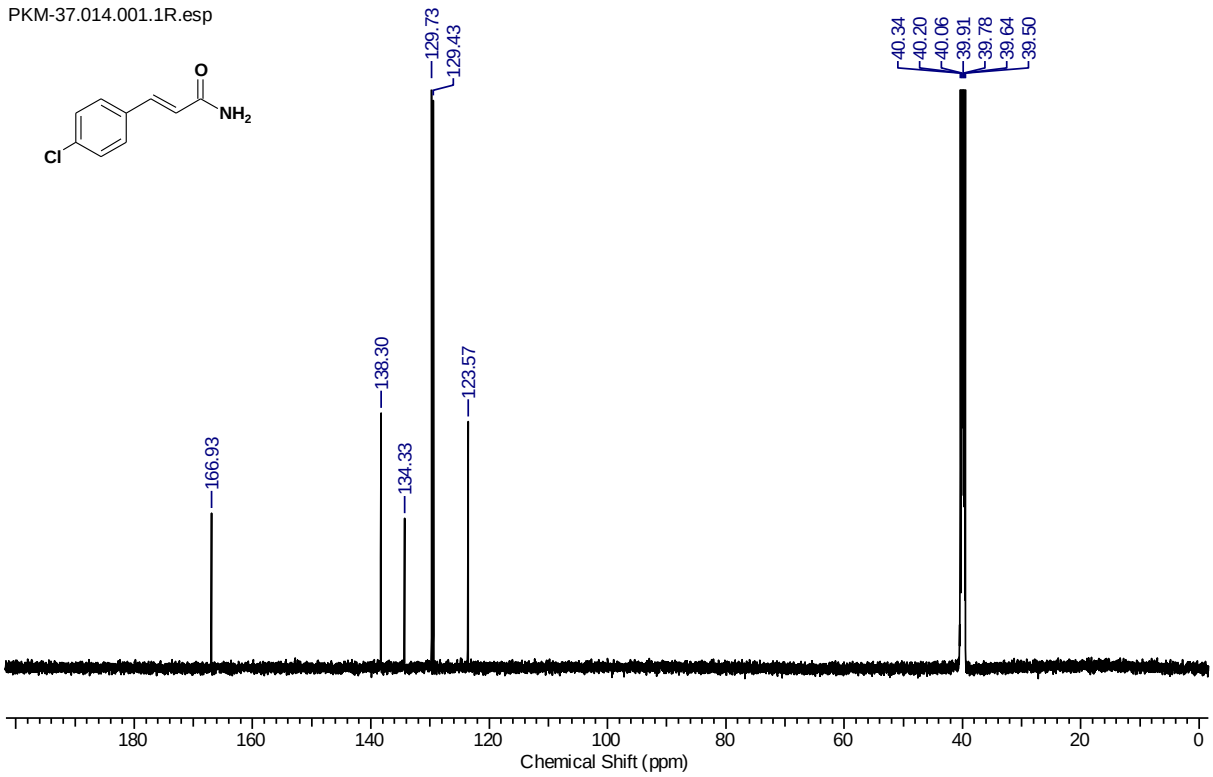


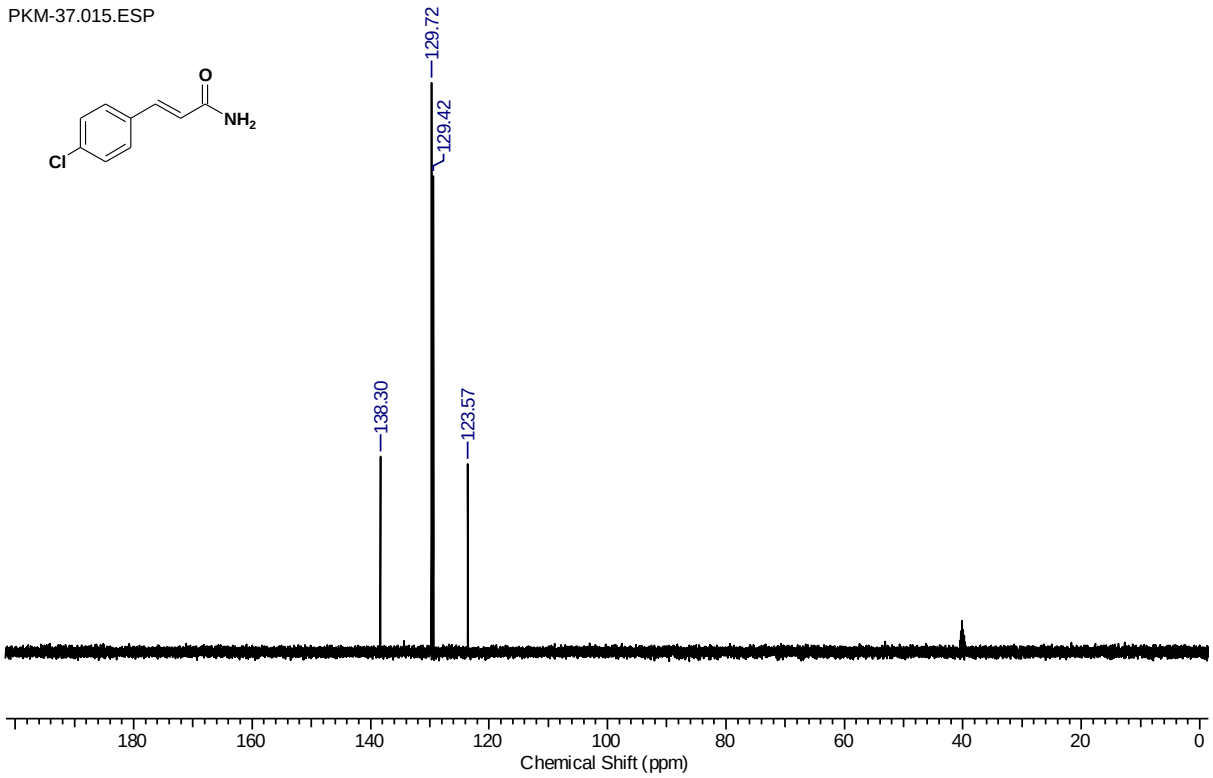




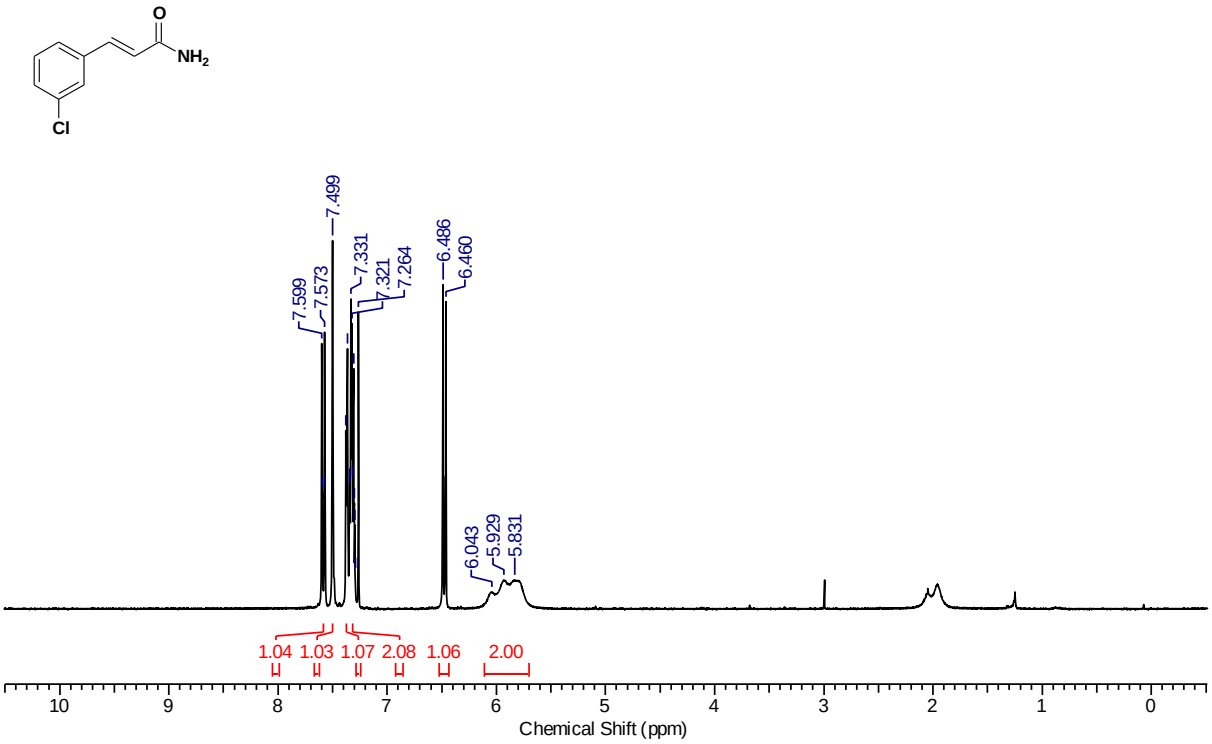
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4e:**

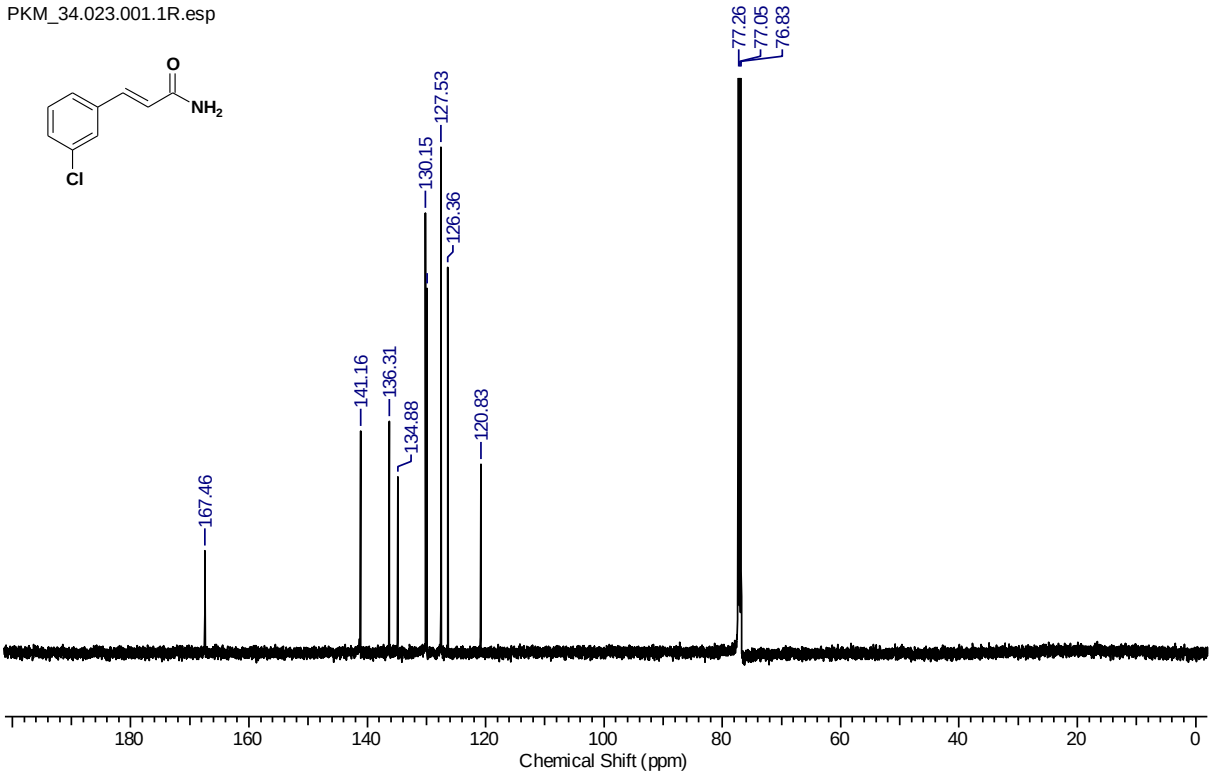


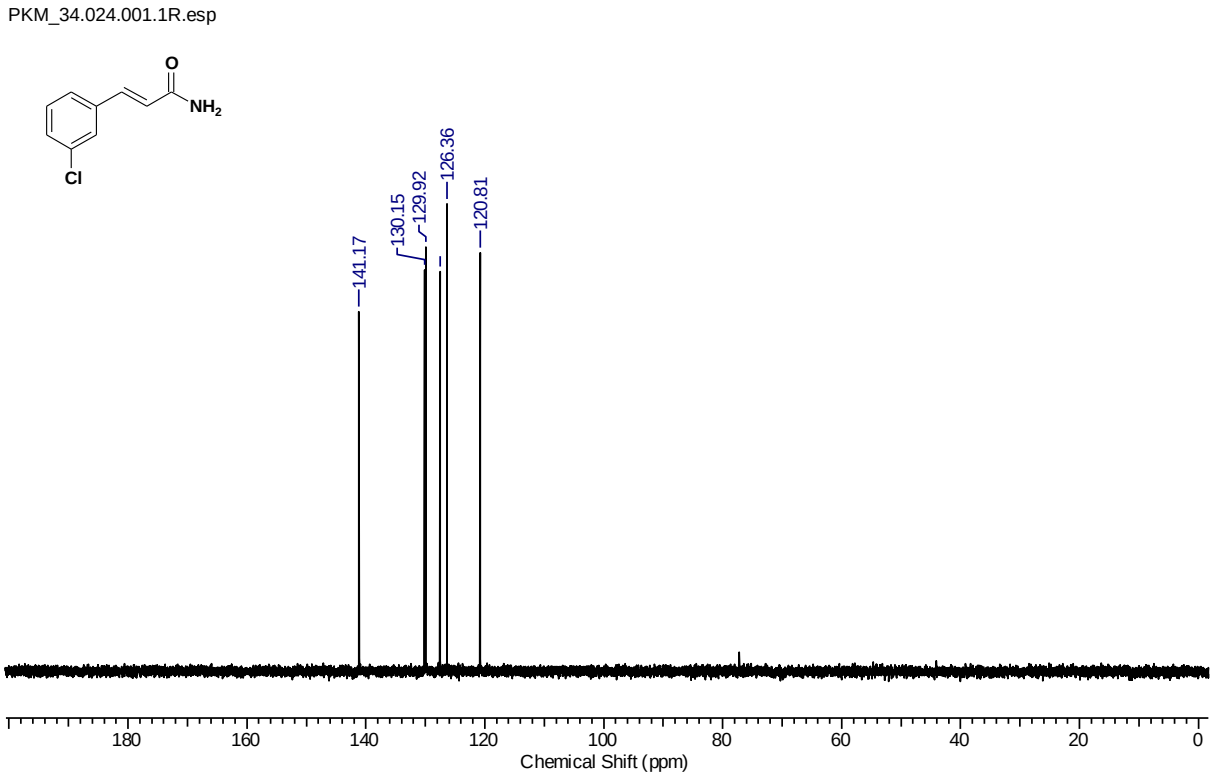

PKM-37.014.001.1R.esp
O
NH2
Cl
129.73
129.43
40.34
40.20
40.06
39.91
39.78
39.64
39.50
138.30
123.57
166.93
134.33
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


PKM-37.015.ESP
O
NH2
Cl
129.72
129.42
138.30
123.57
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

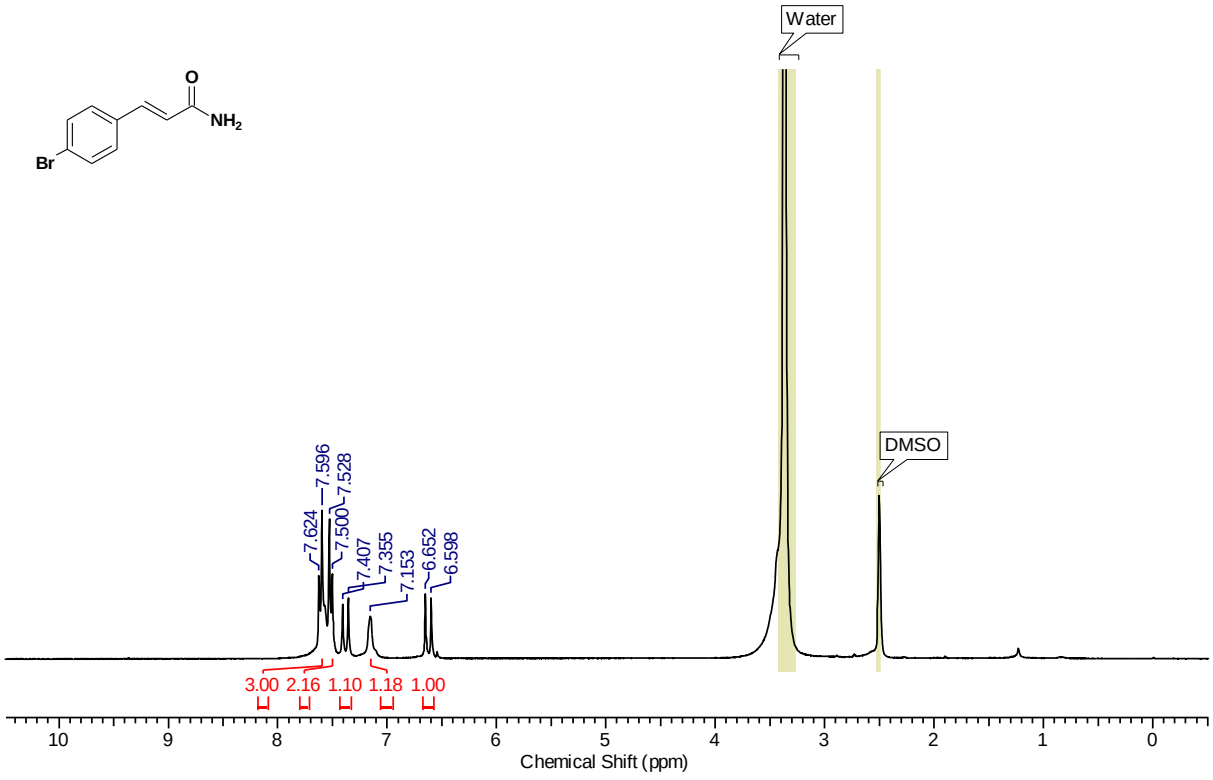
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4f:**

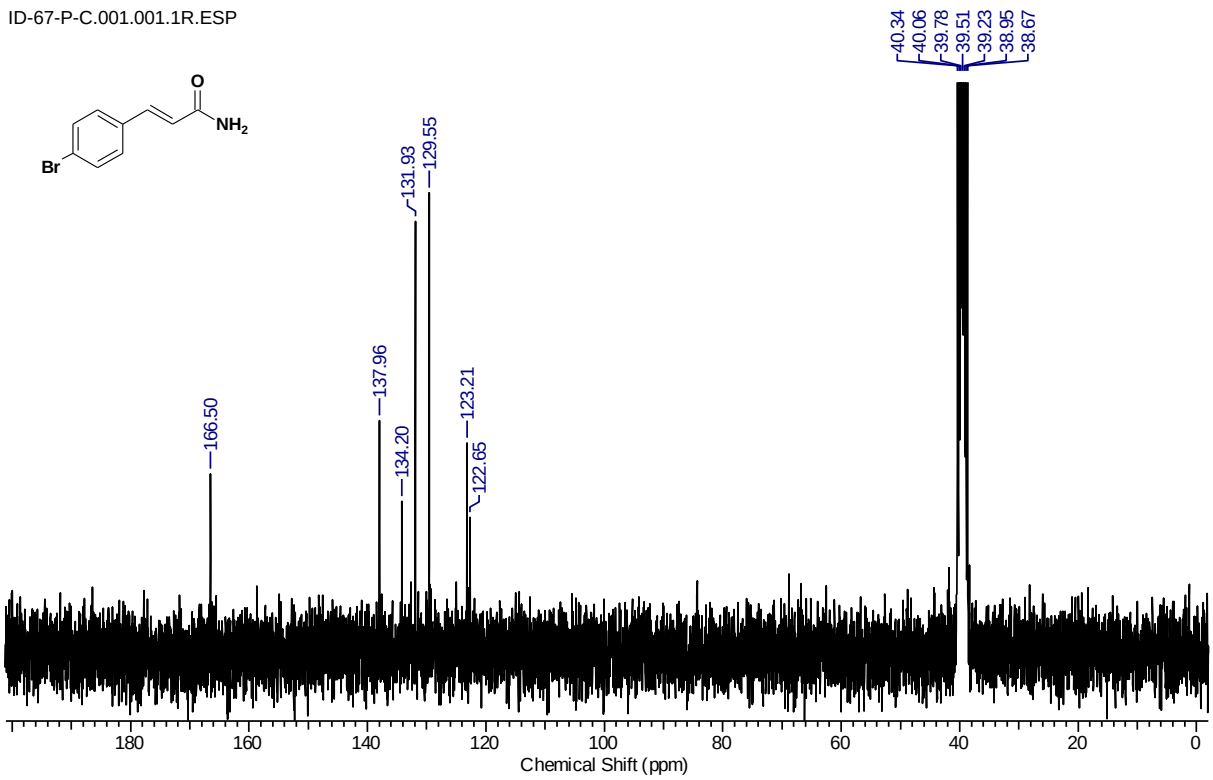




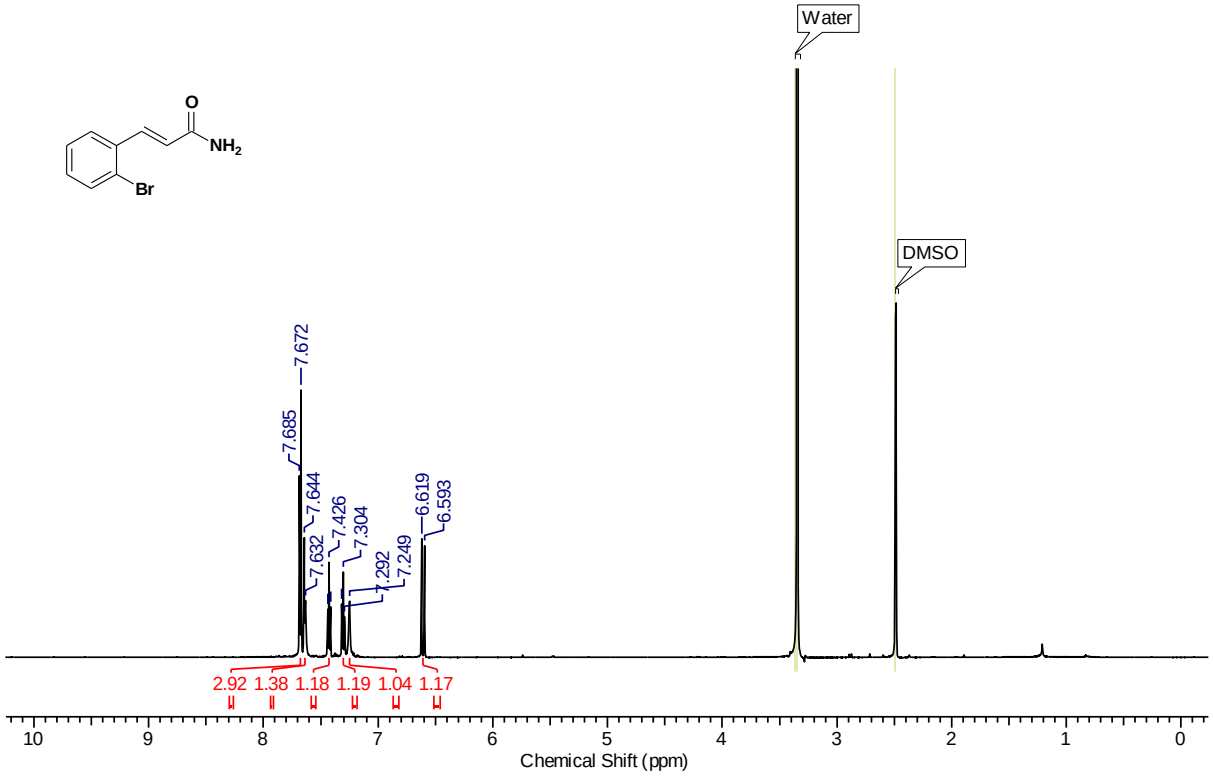


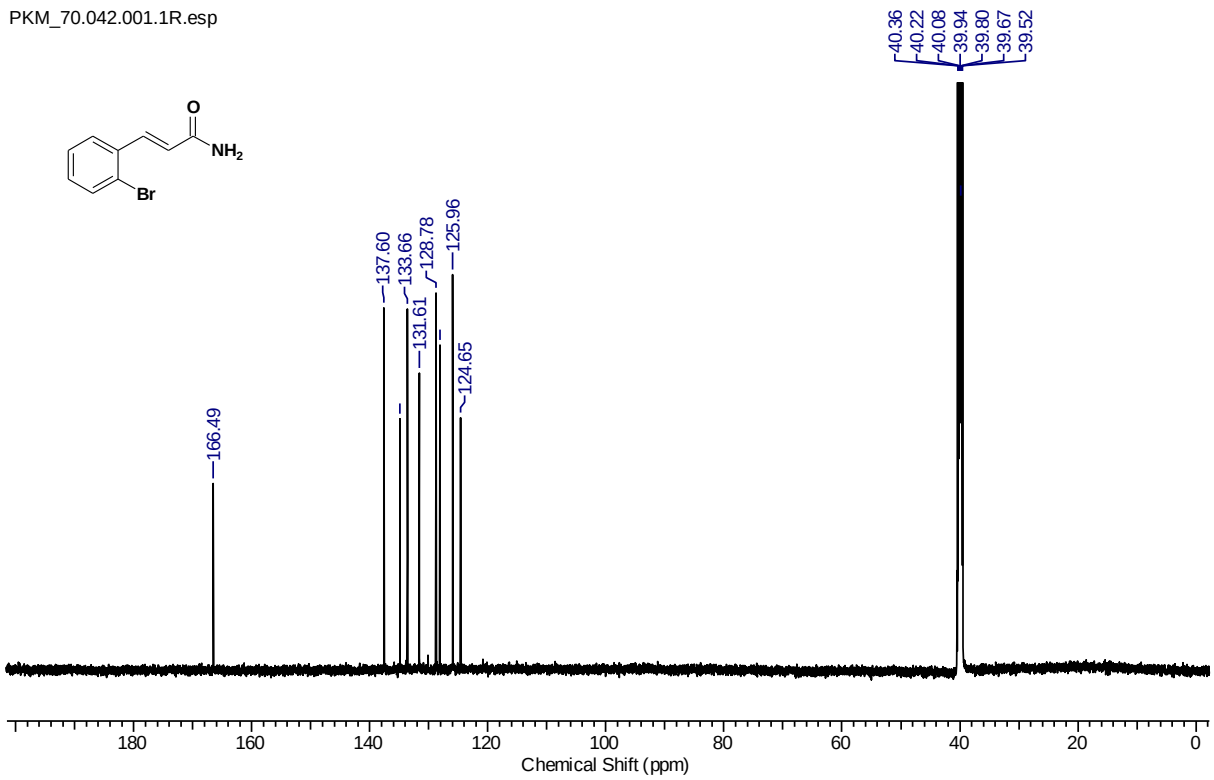
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4g:**



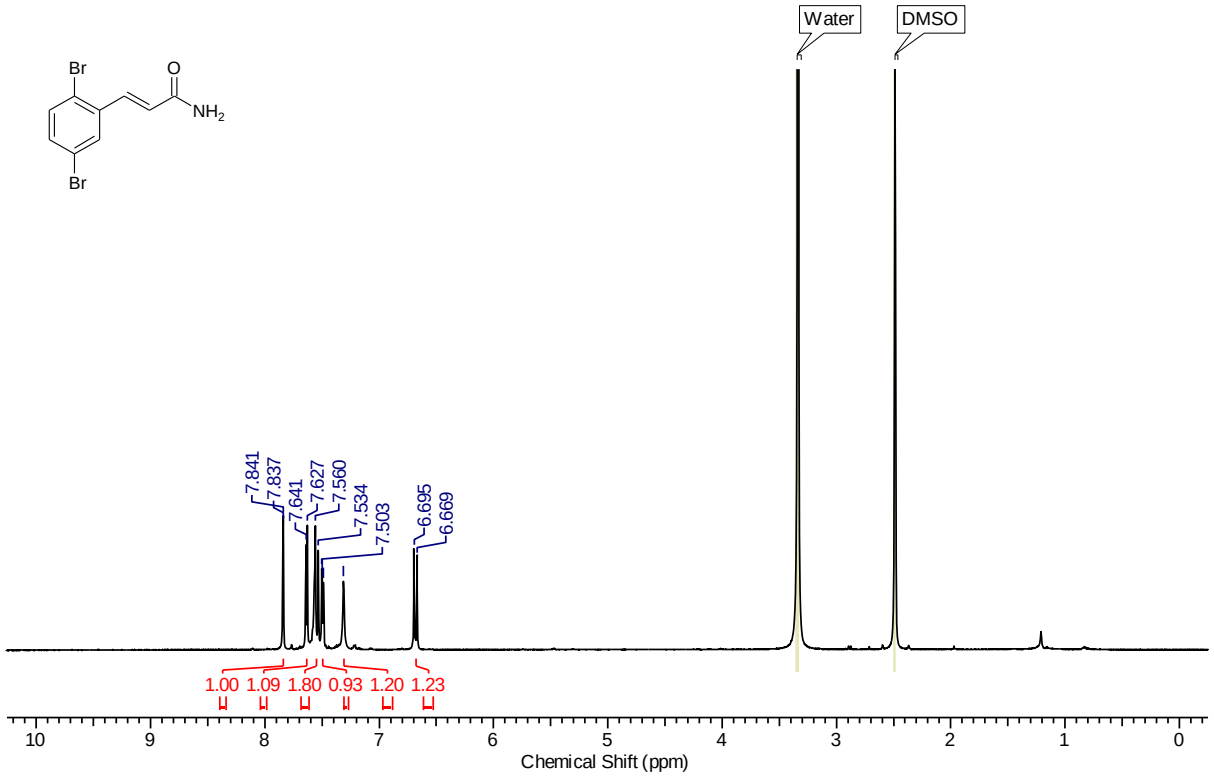


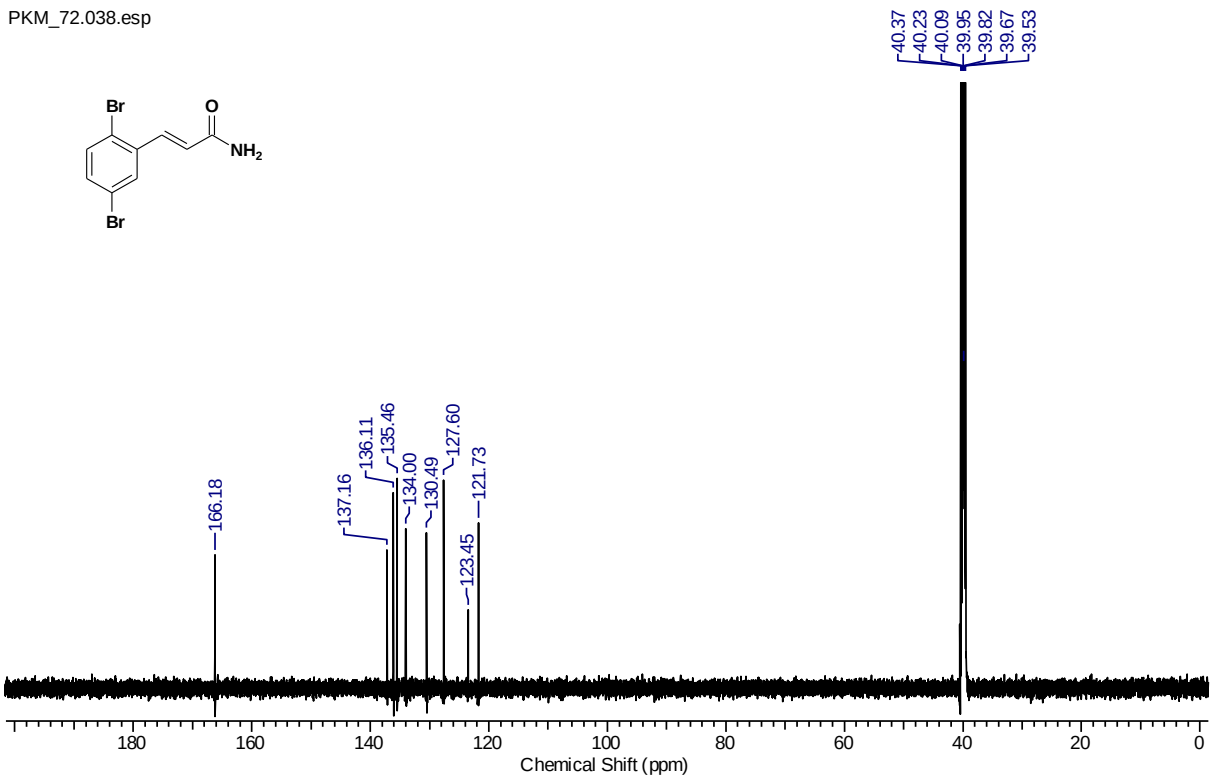
^{1}H and ^{13}C{^{1}H} NMR spectra of **4h:**



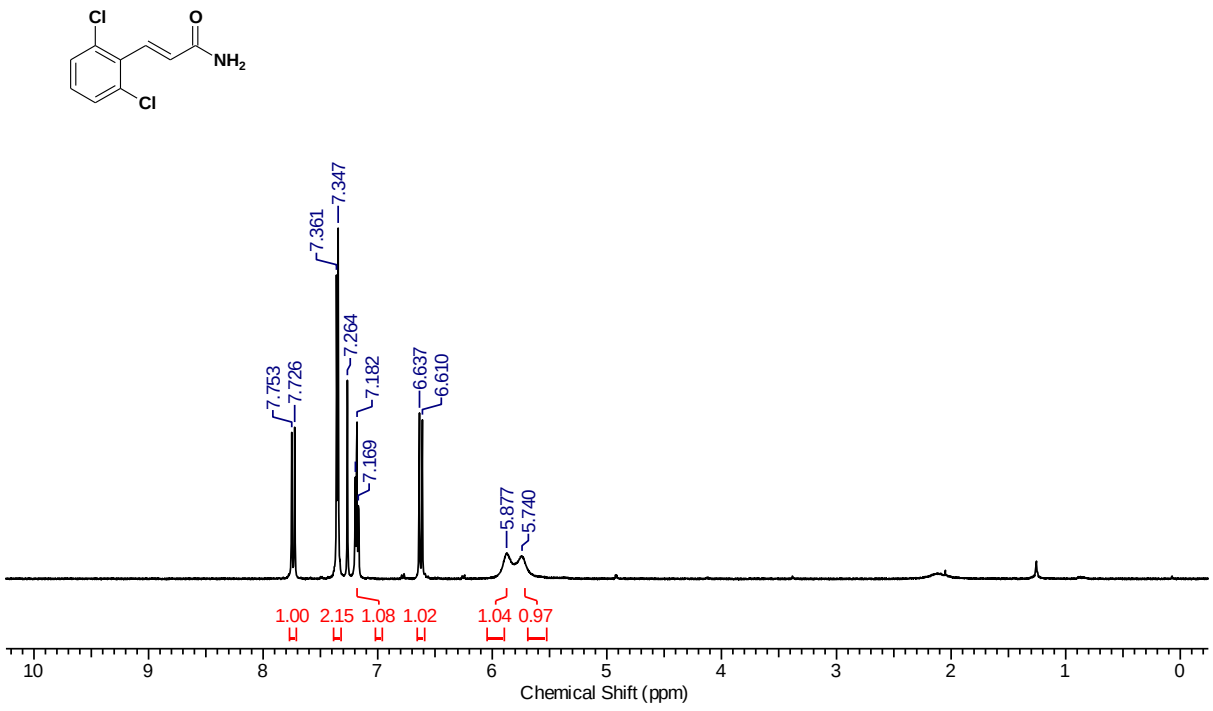


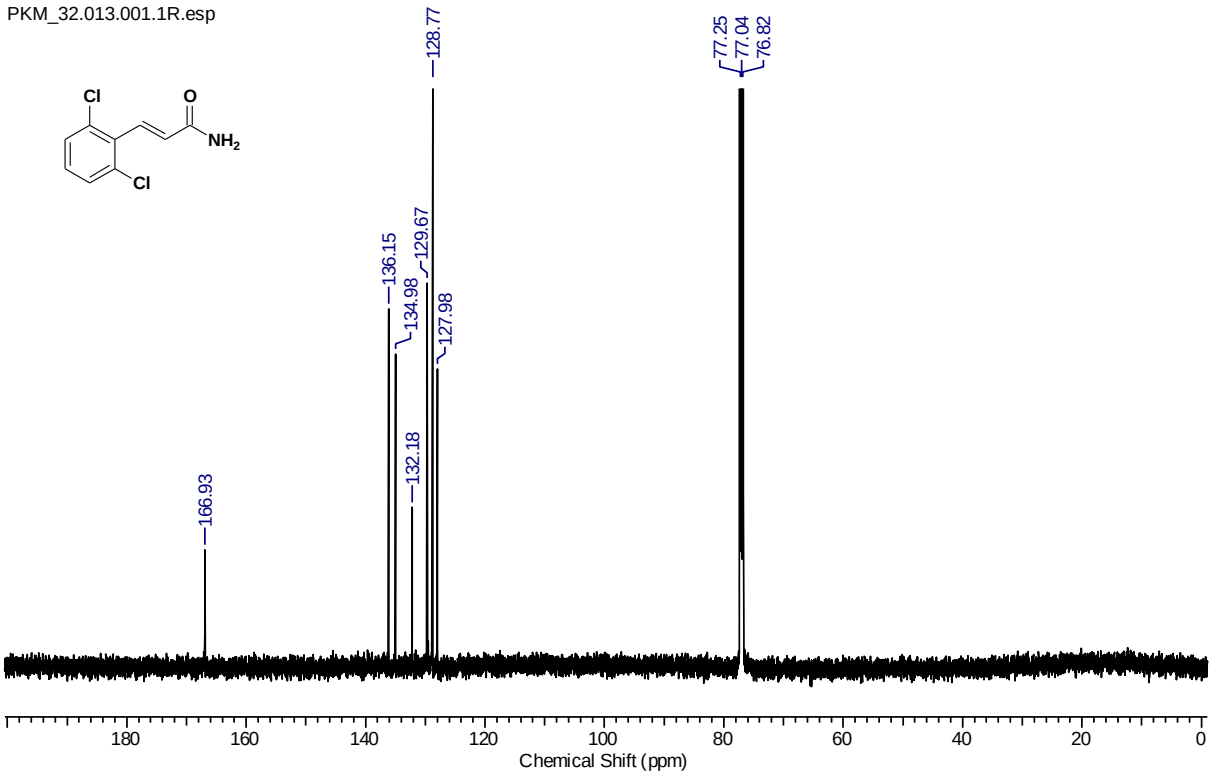
^{1}H and ^{13}C{^{1}H} NMR spectra of **4i:**



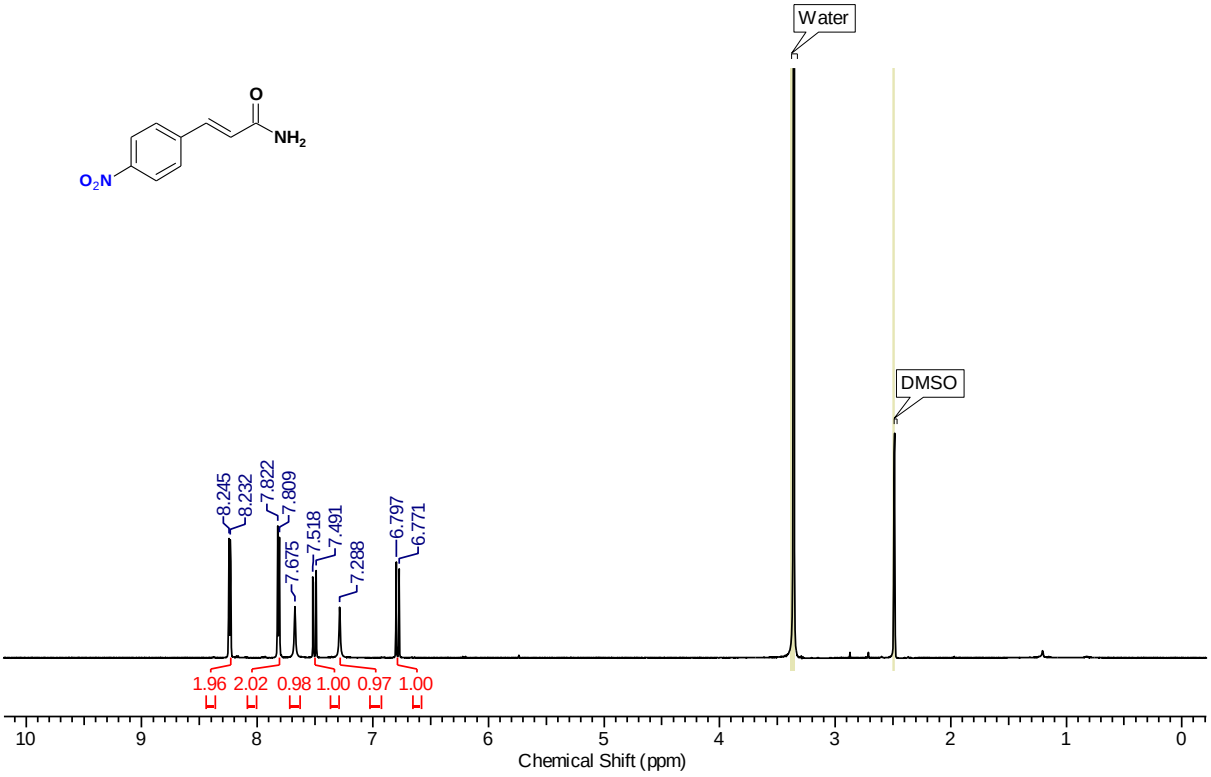


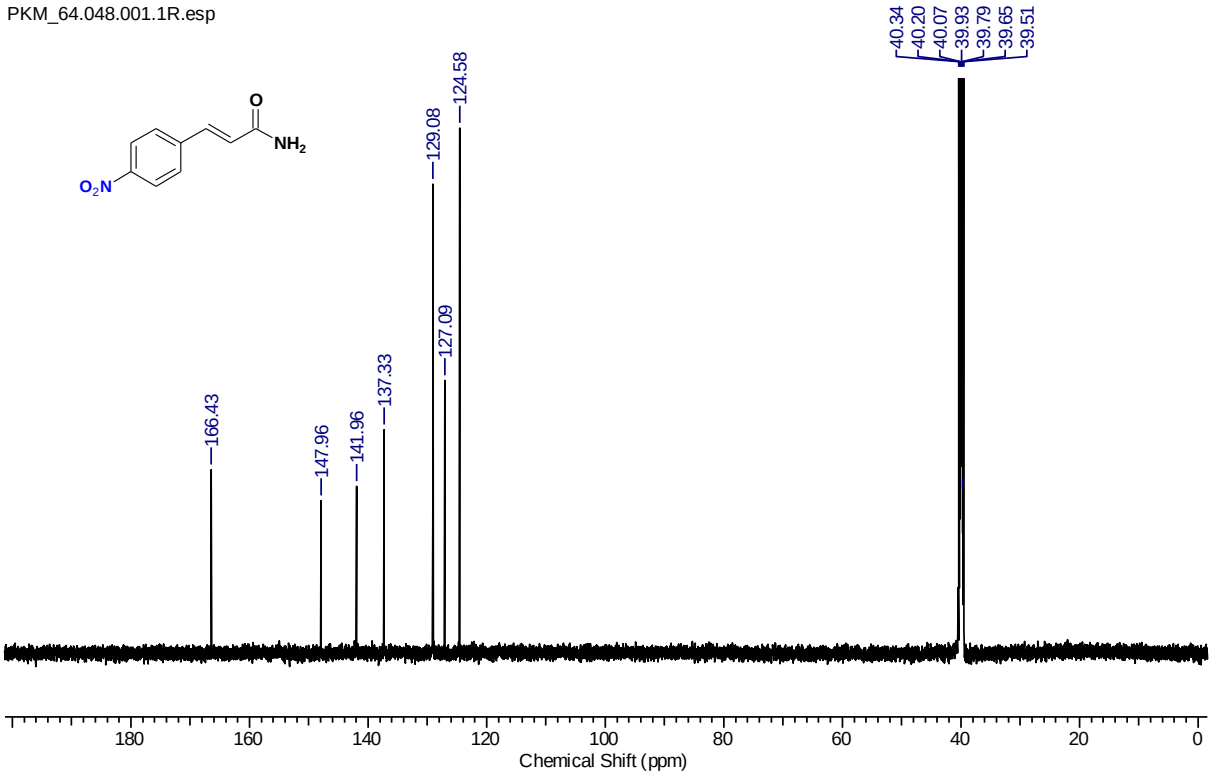
^{1}H and ^{13}C{^{1}H} NMR spectra of **4j:**

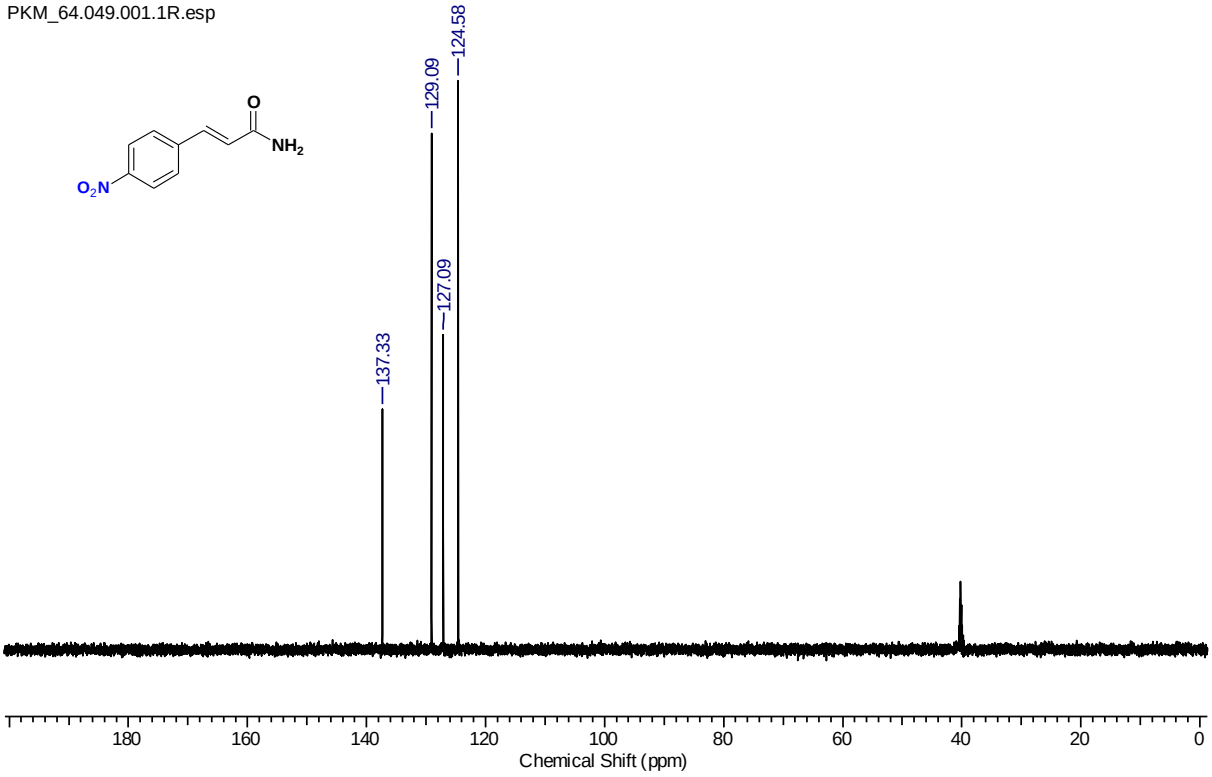




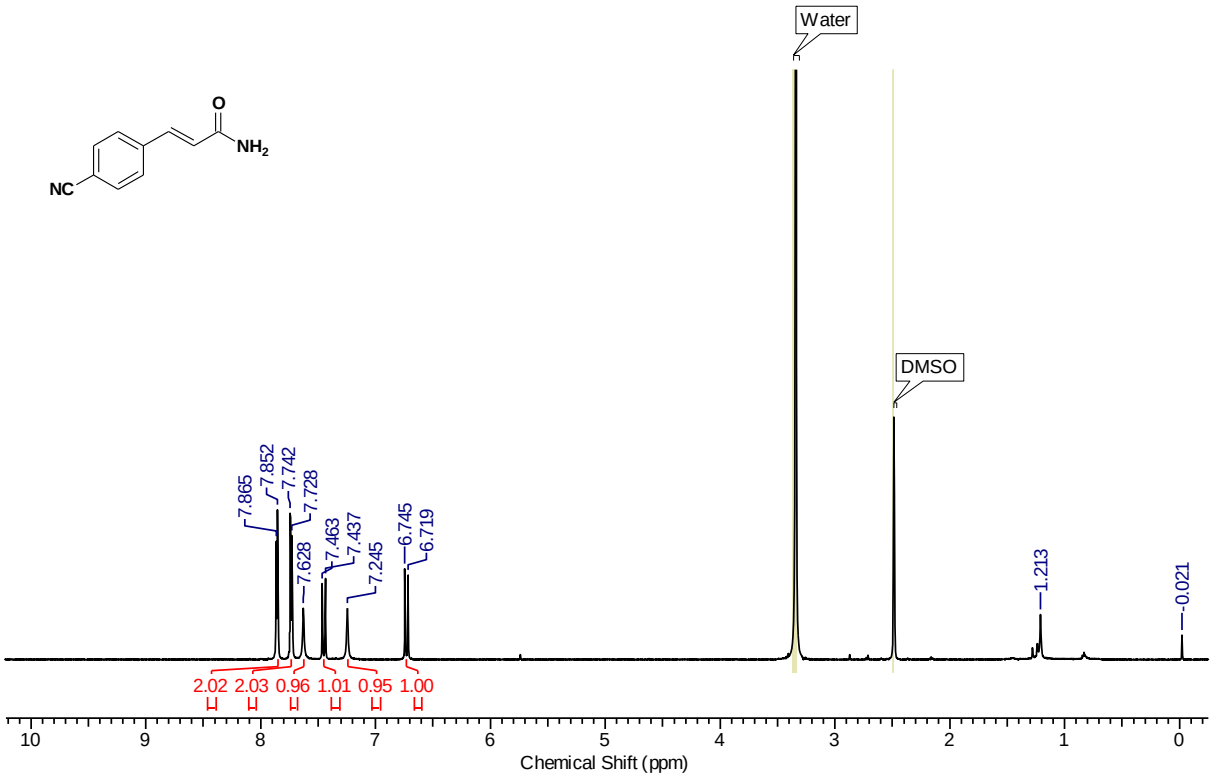
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4k:**

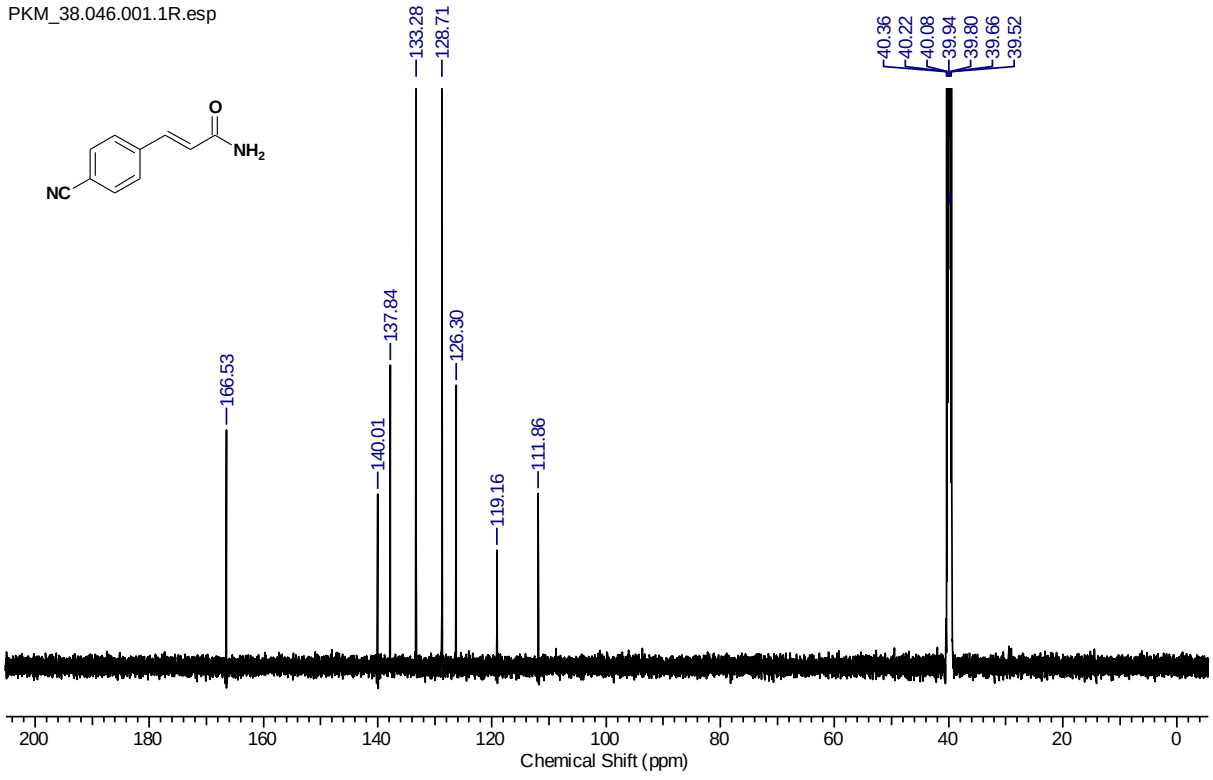


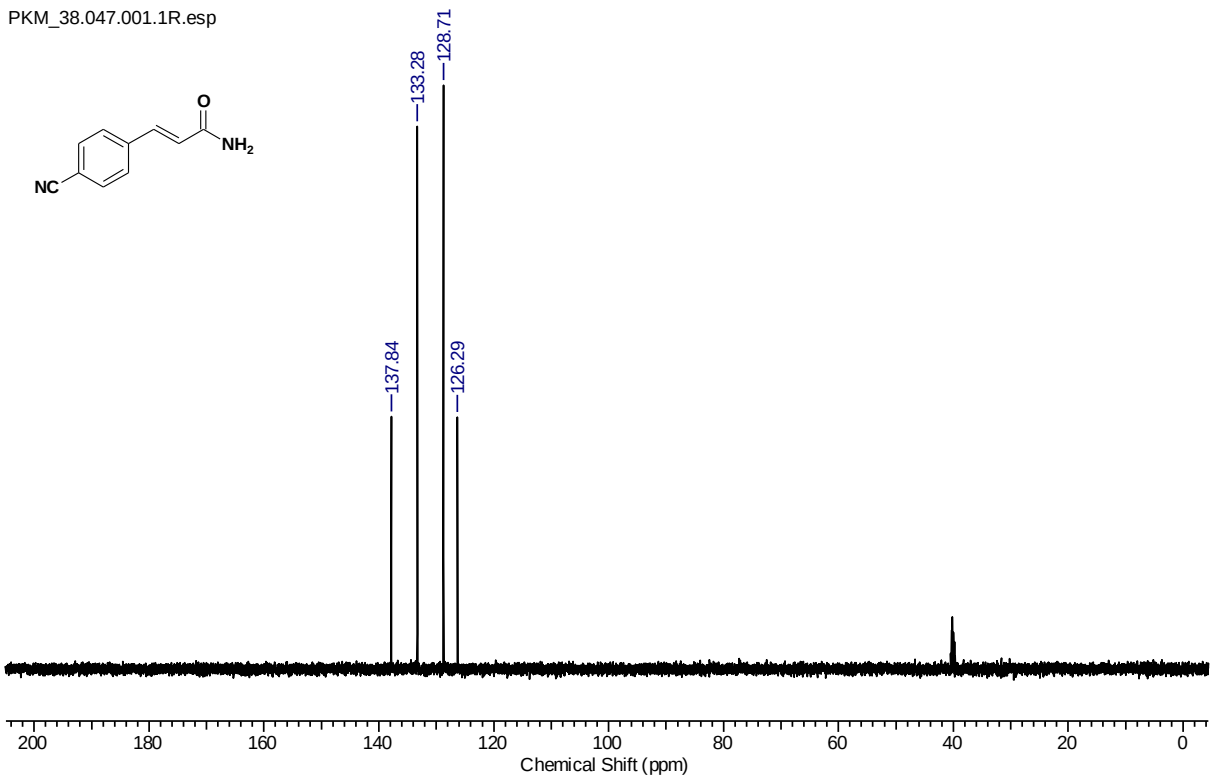

PKM_64.048.001.1R.esp
O
NH2
O2N
166.43
147.96
141.96
137.33
129.08
127.09
124.58
40.34
40.20
40.07
39.93
39.79
39.65
39.51
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


PKM_64.049.001.1R.esp
O
NH2
O2N
137.33
129.09
127.09
124.58
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

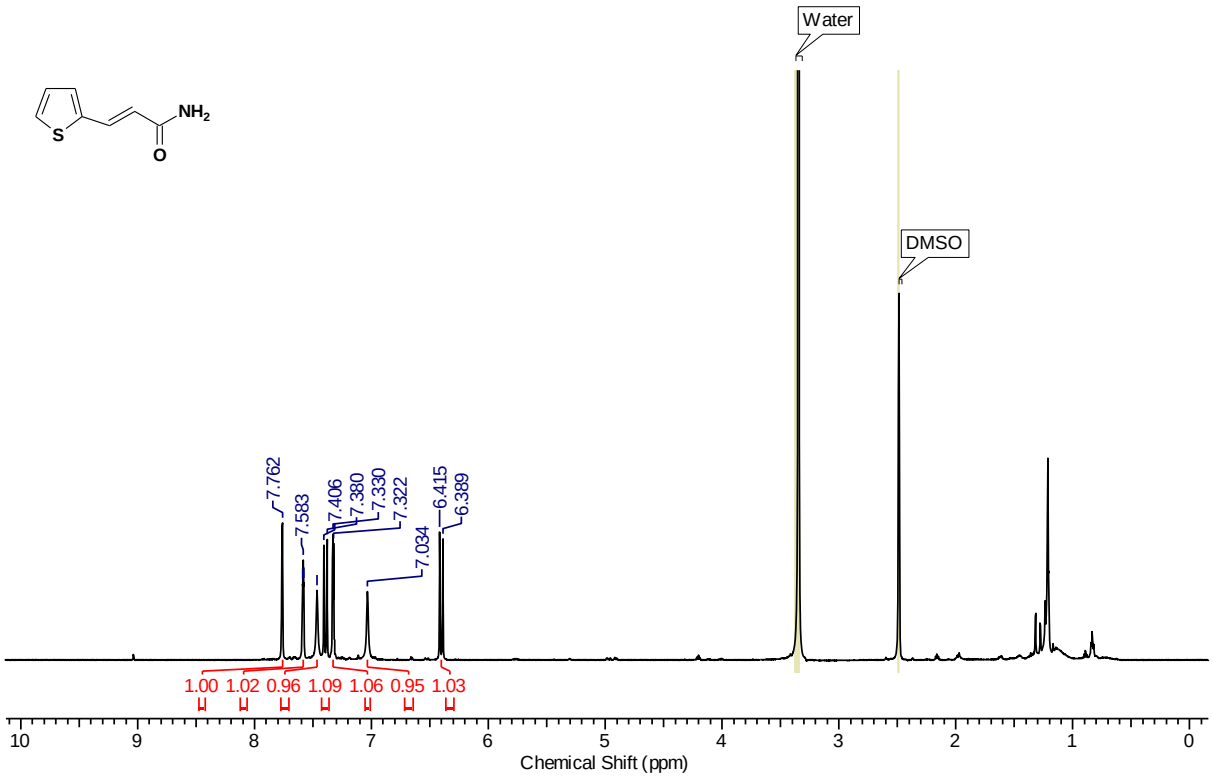
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4l:**

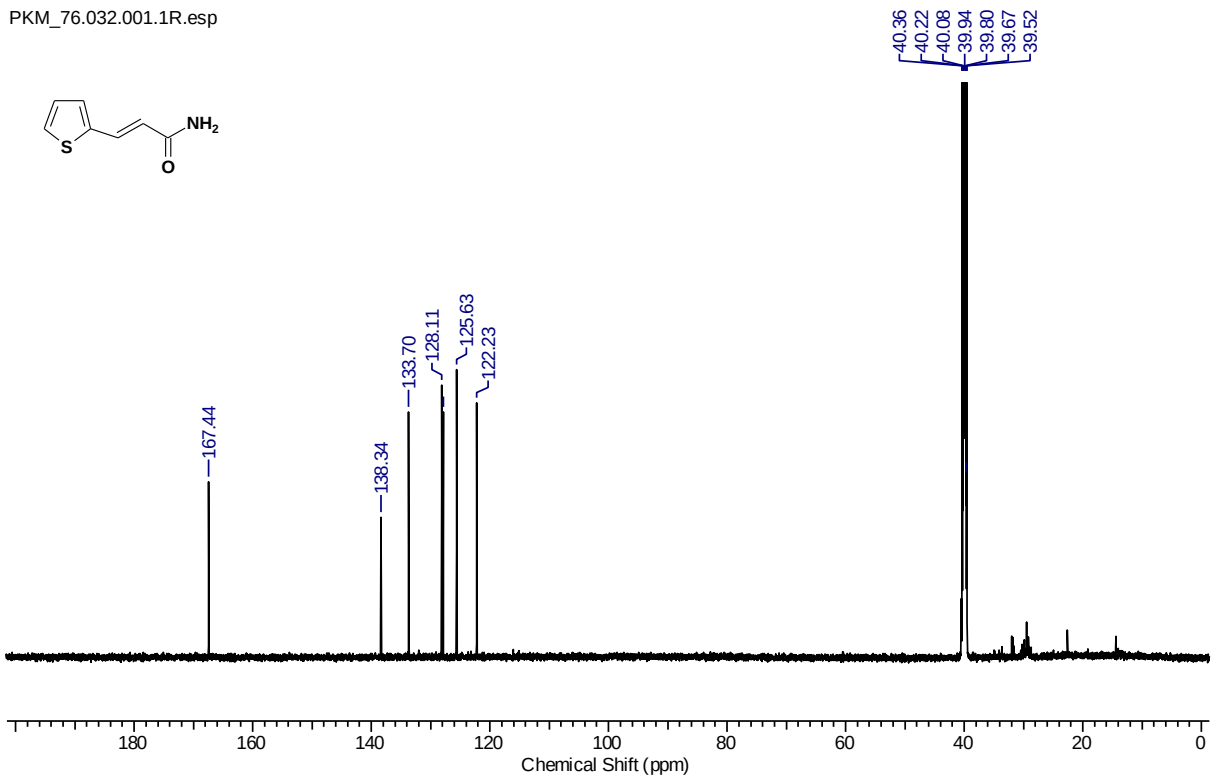




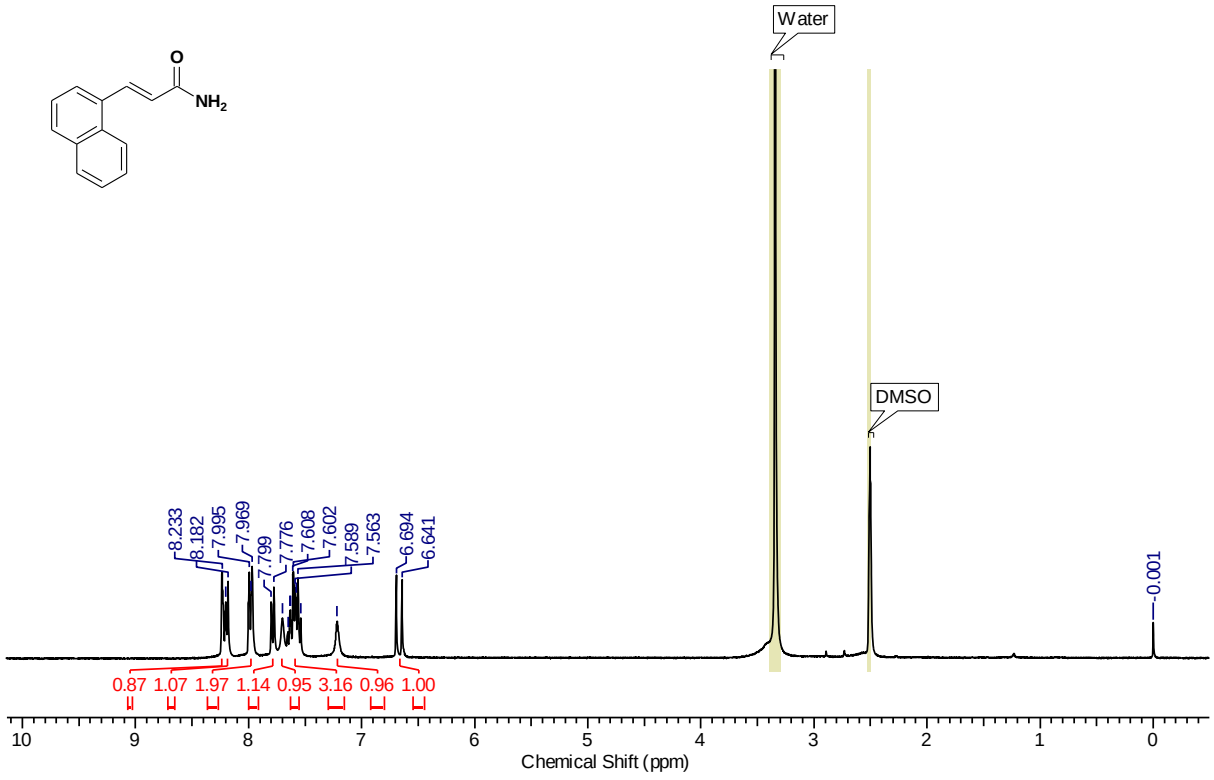


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4m:**

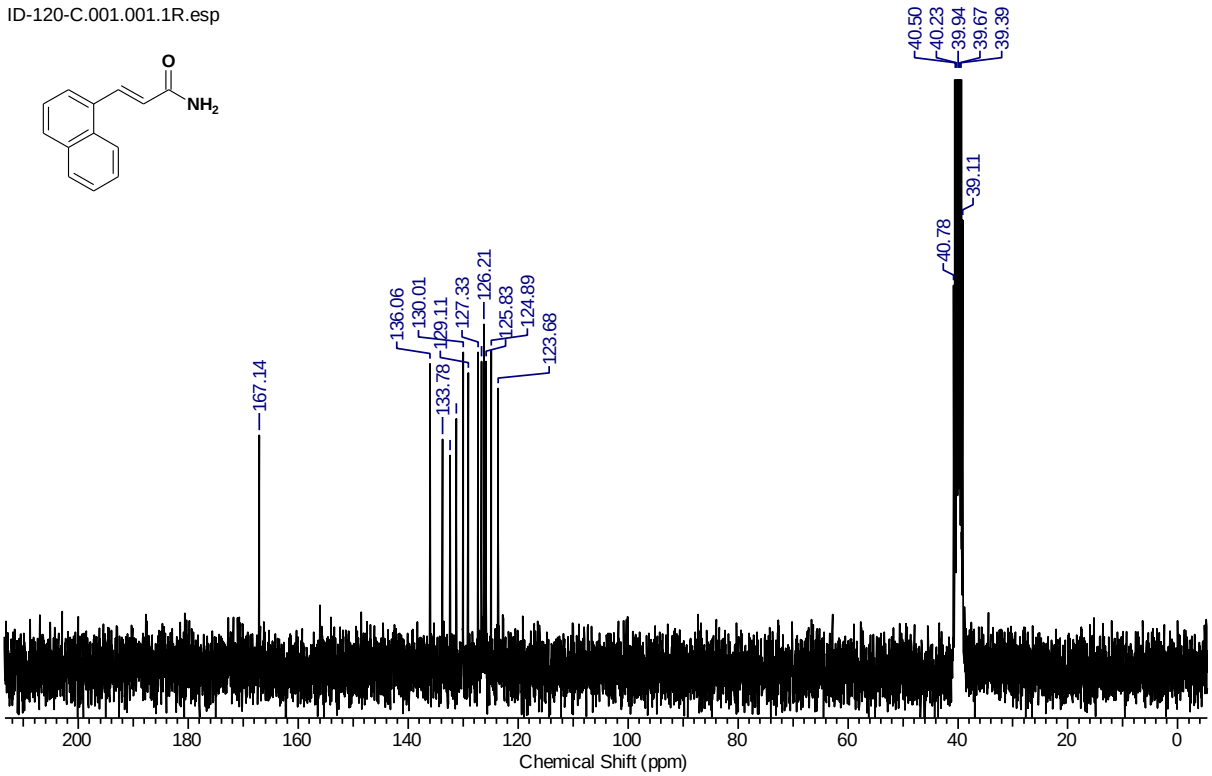




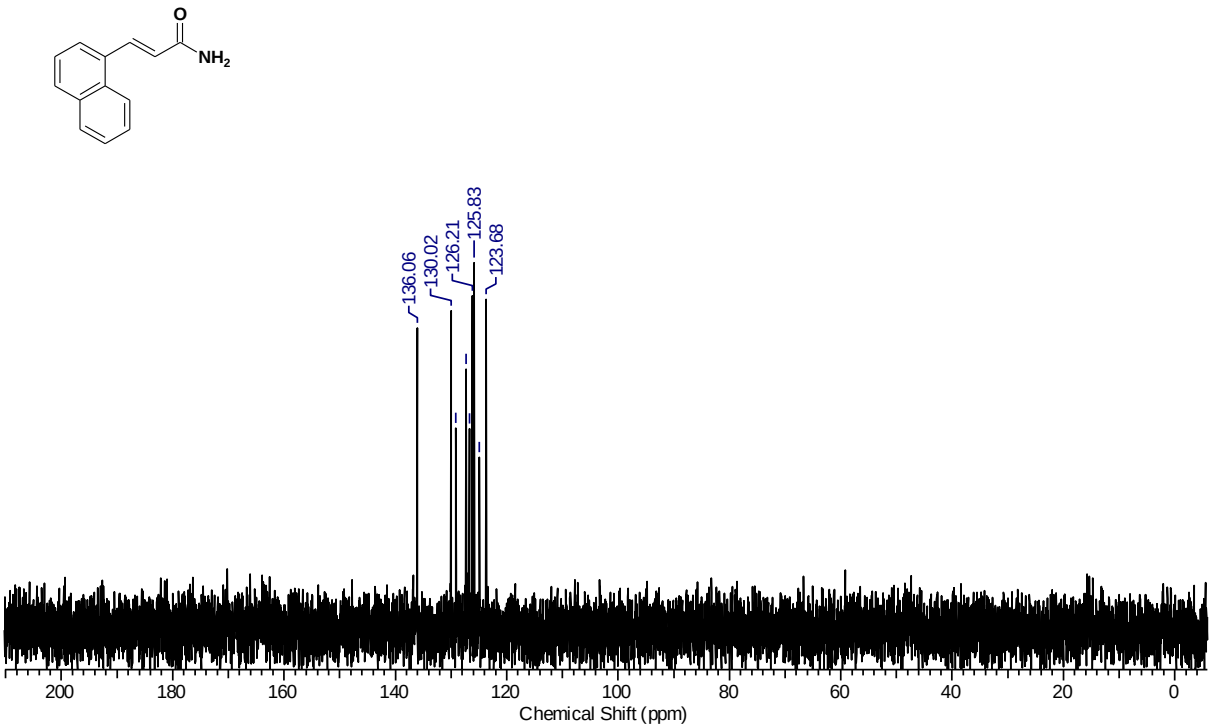
^{1}H, ^{13}C{^{1}H}, DEPT-135 NMR spectra of **4n:**



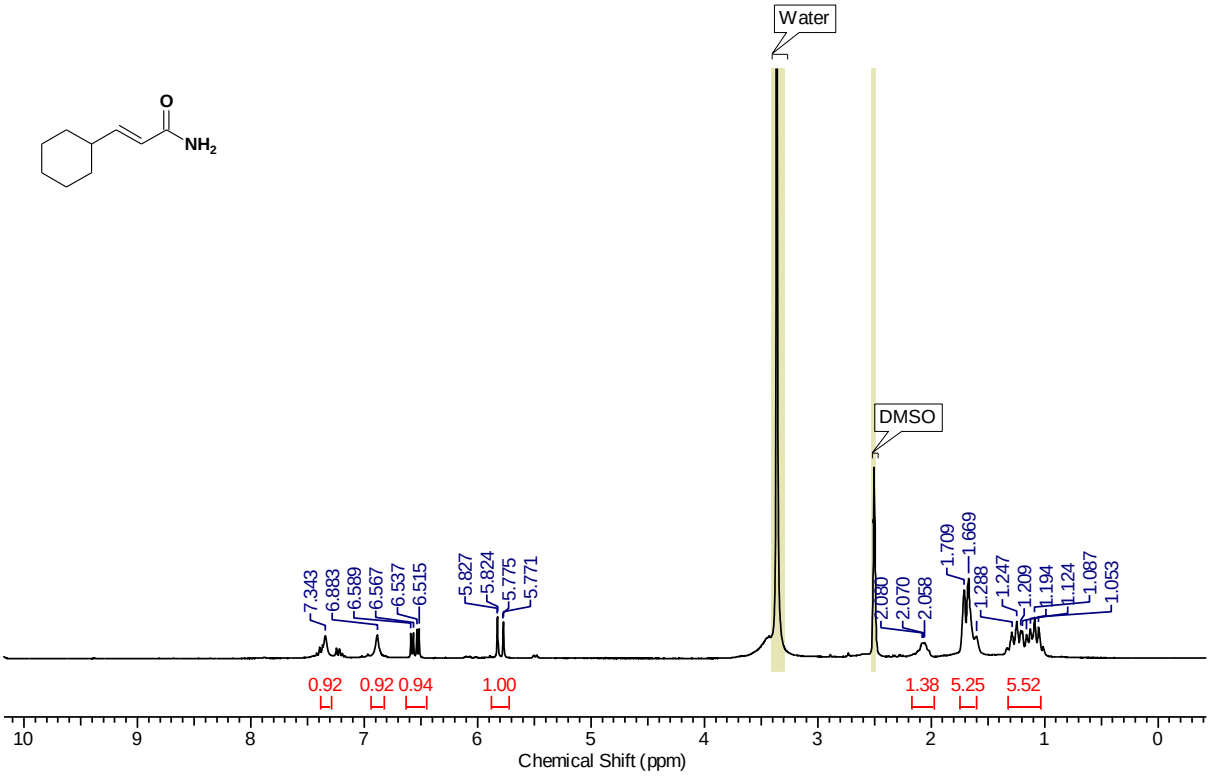
ID-120-C.001.001.1R.esp

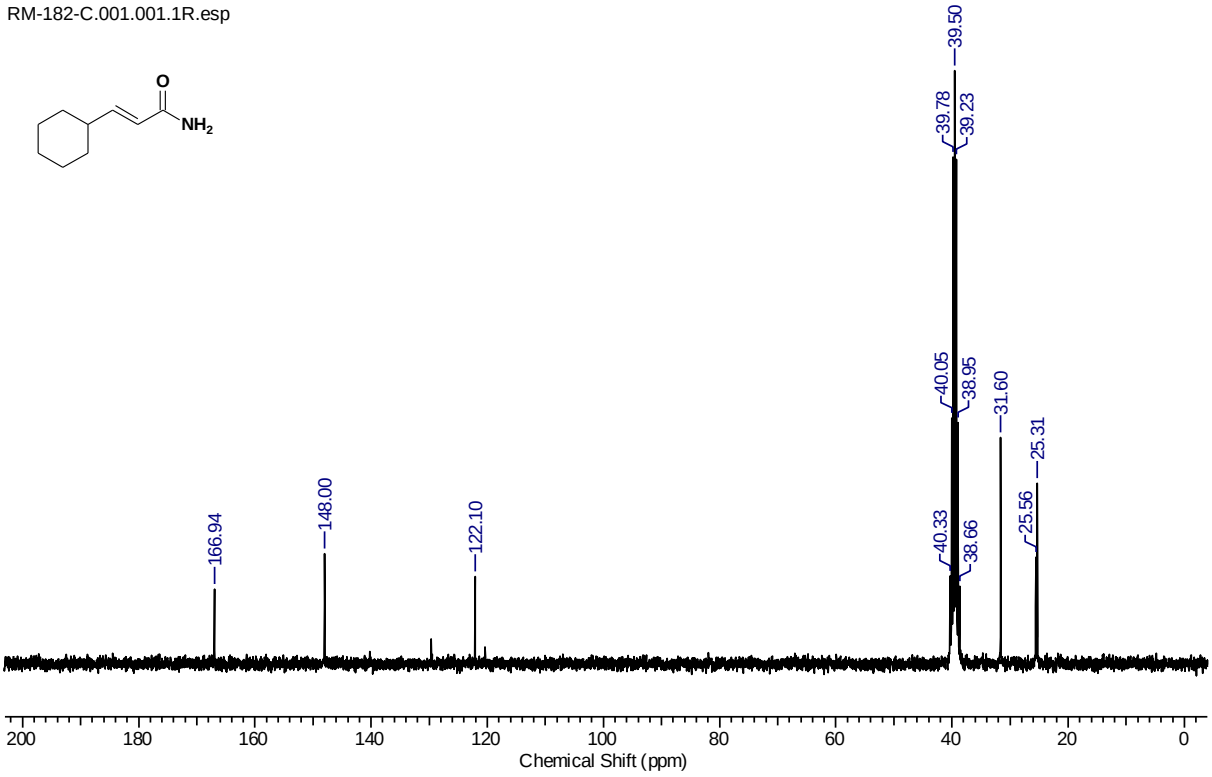


ID-120-C.002.001.1R.esp

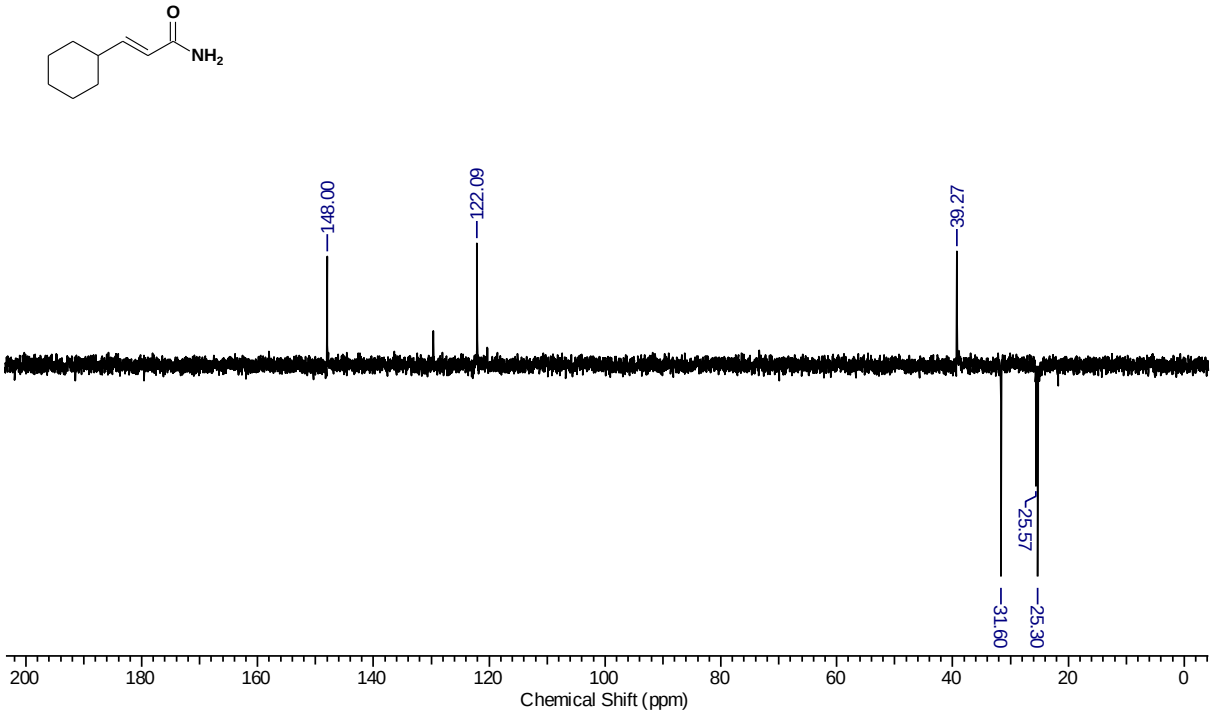


^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4o:**

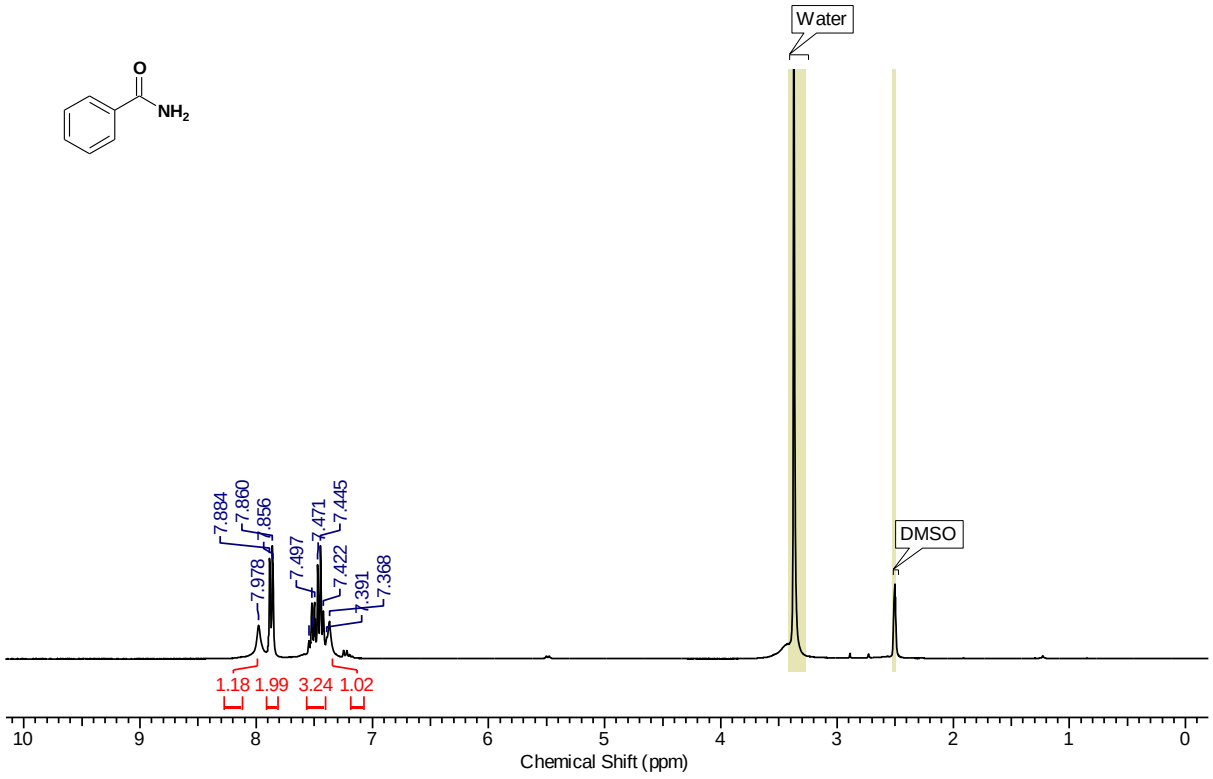




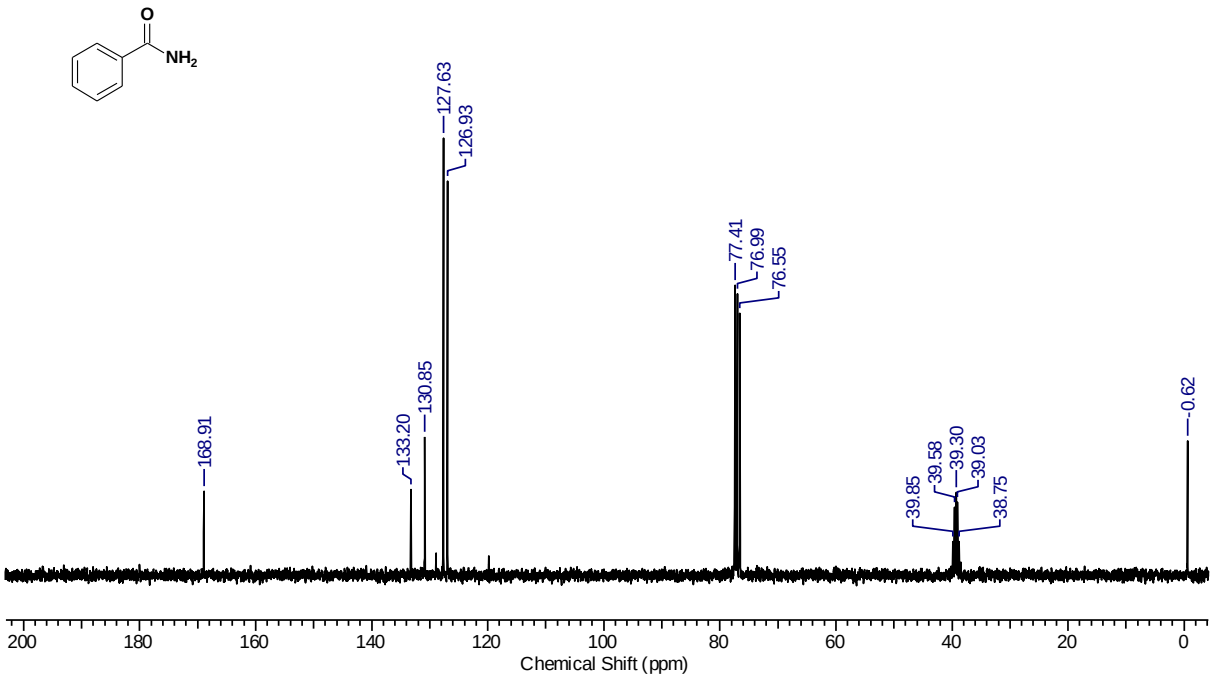
RM-182-C.002.001.1R.esp



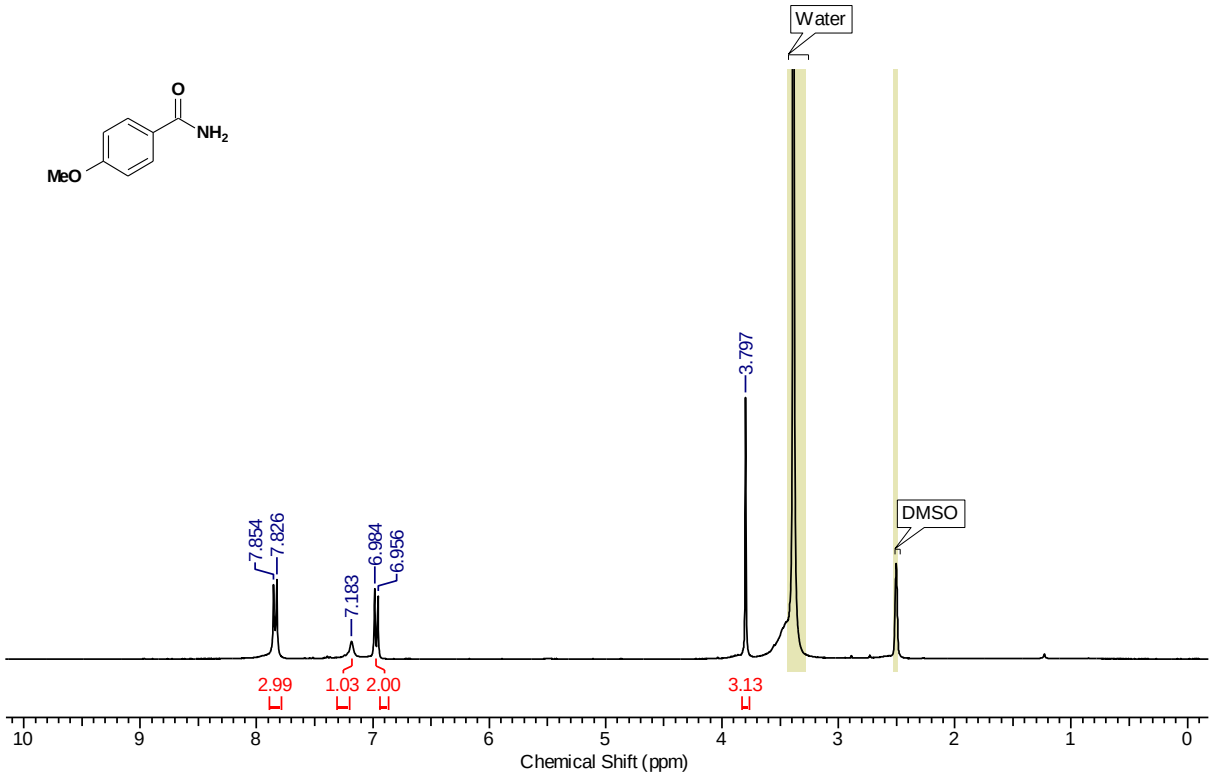
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4p:**



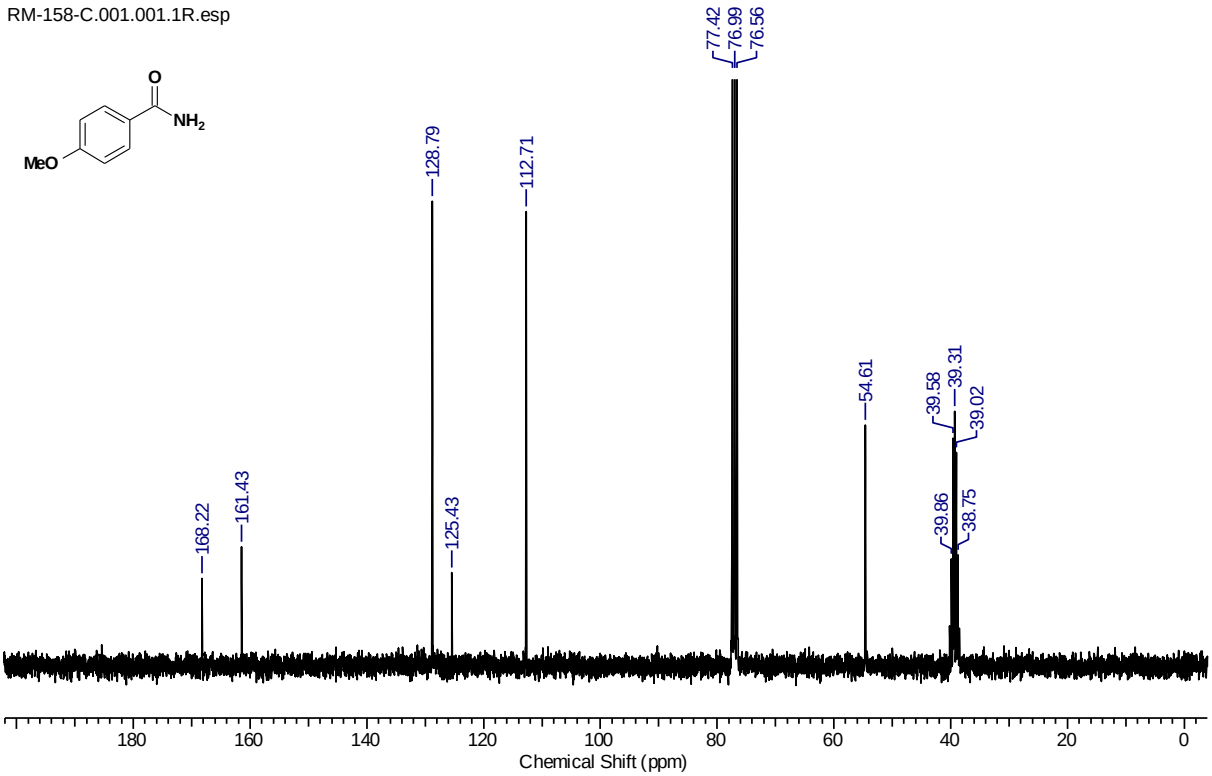
RM-165-C.001.001.1R.esp



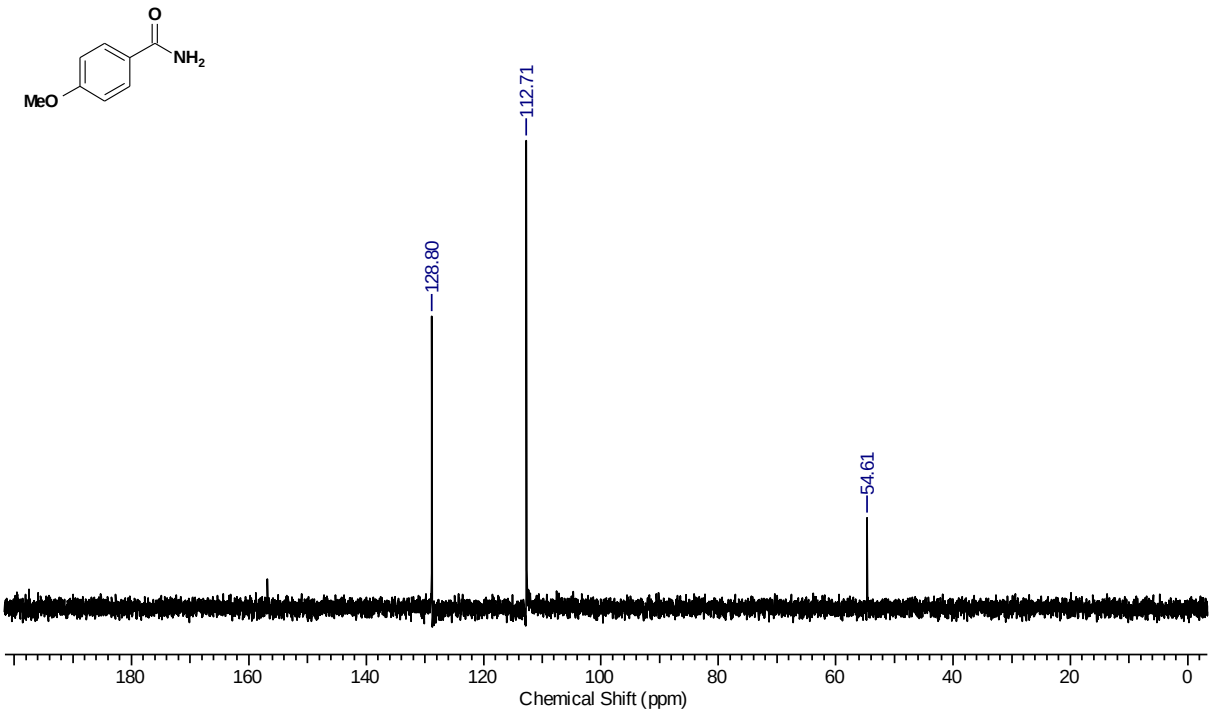
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4q:**



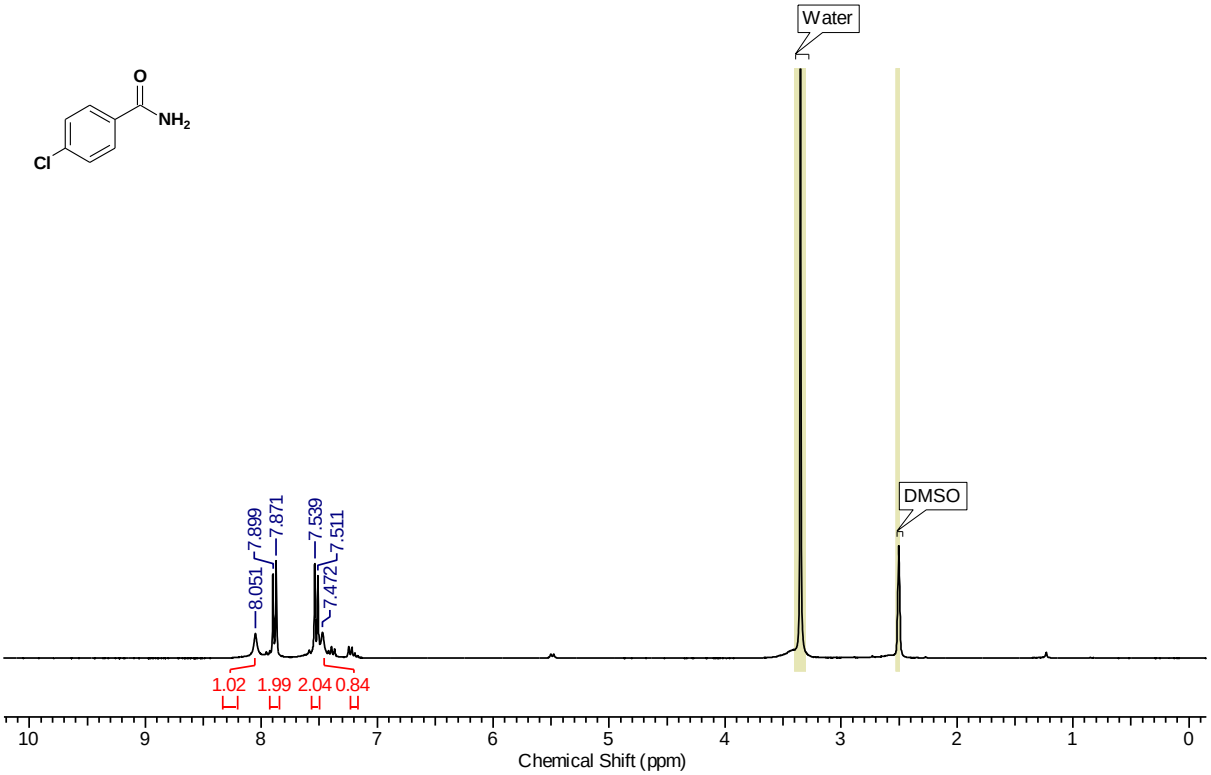
RM-158-C.001.001.1R.esp



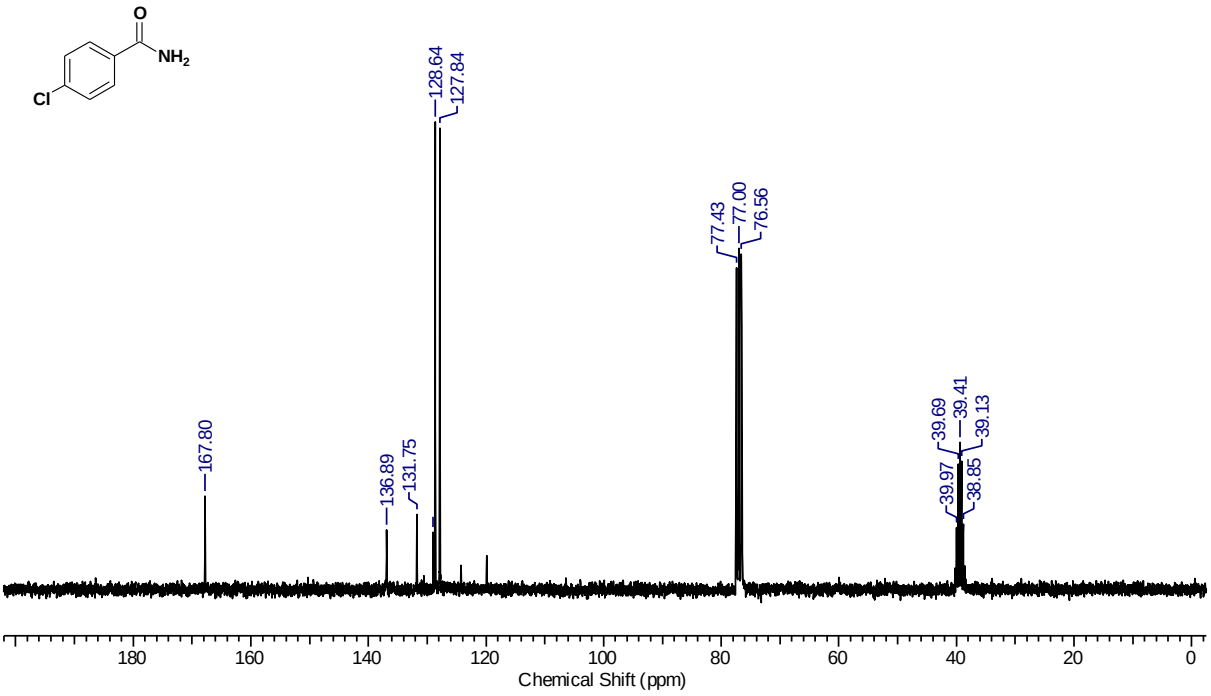
RM-158-C.002.001.1R.esp



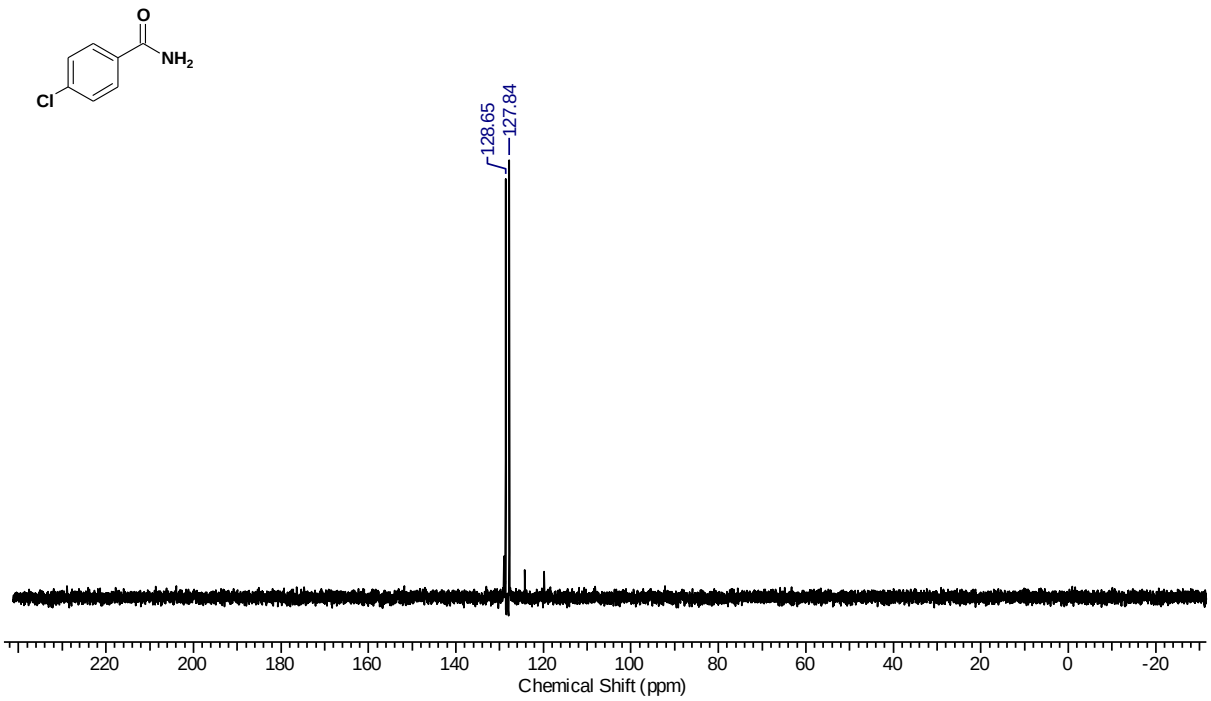
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4r:**



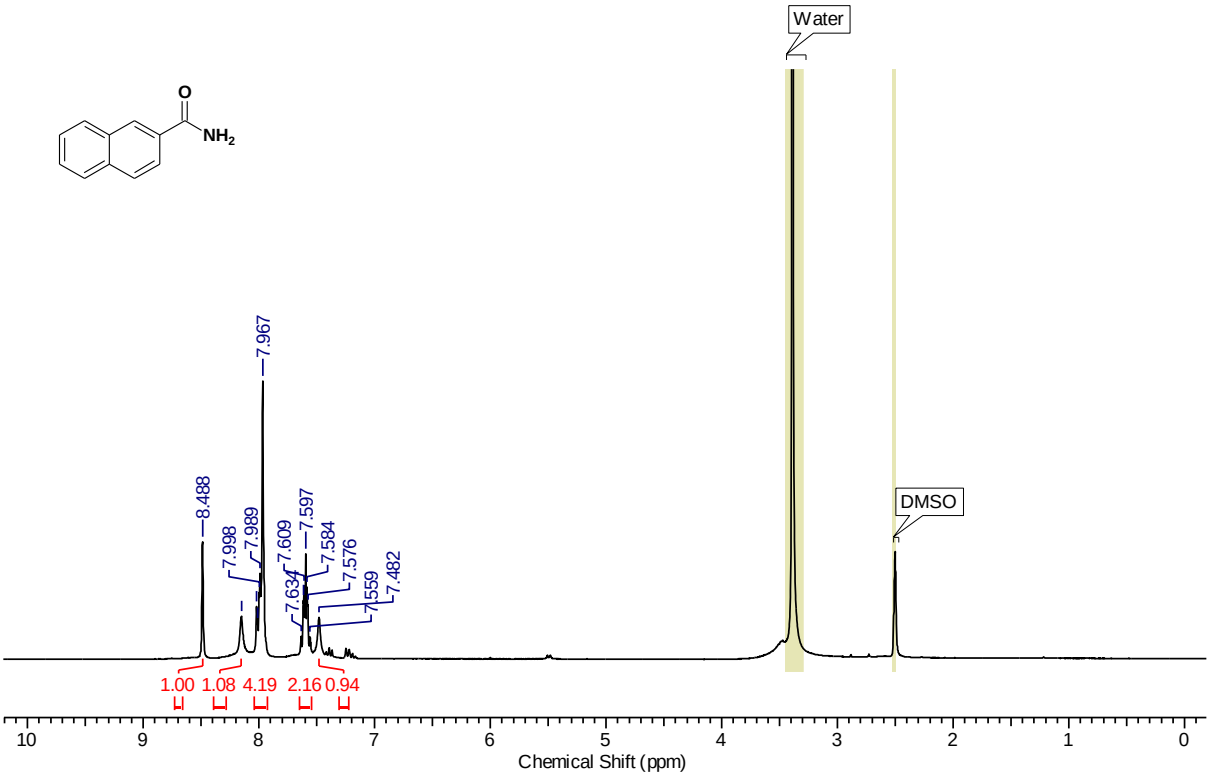
SN-220B-C.001.001.1R.esp



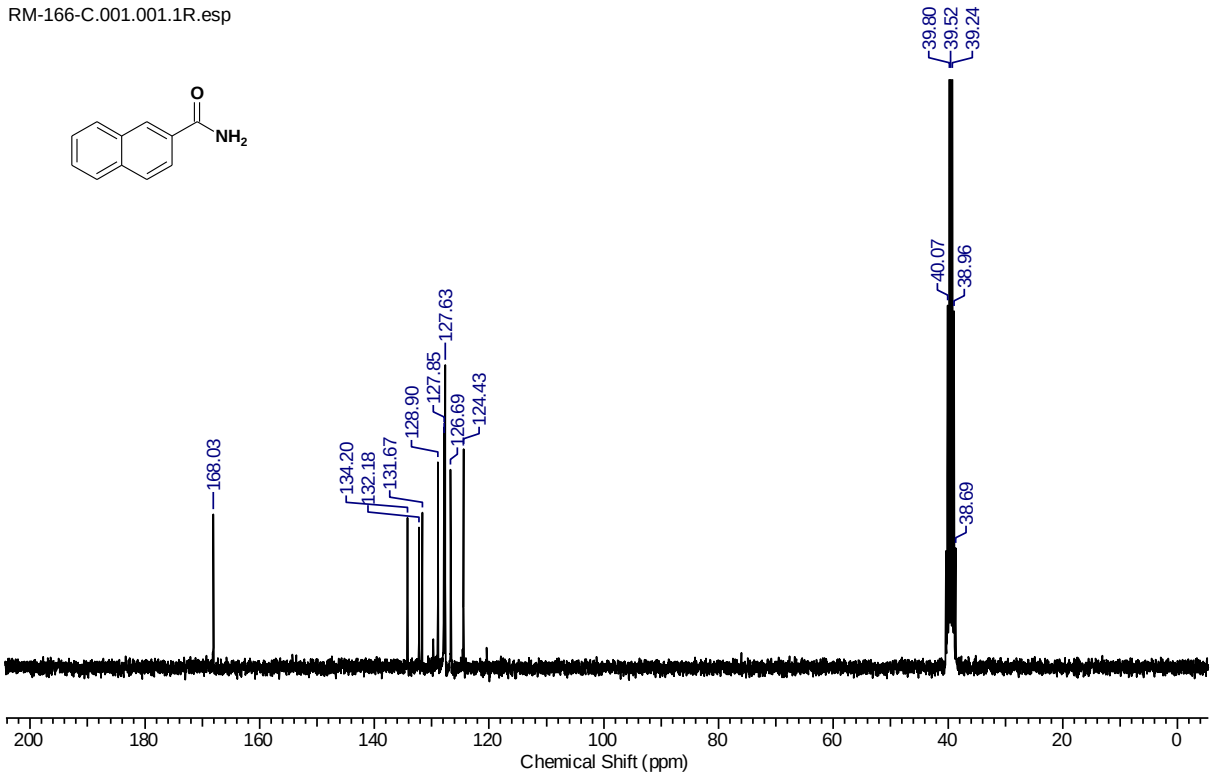
SN-220B-C.002.001.1R.esp



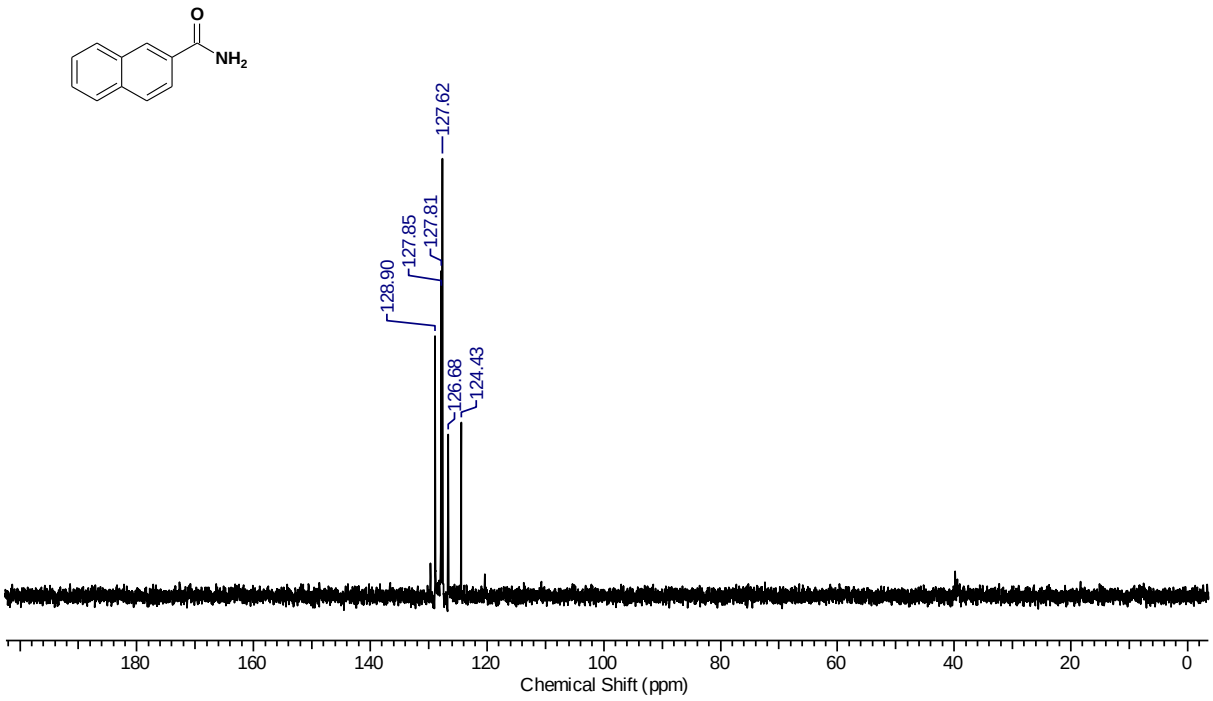
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4s:**



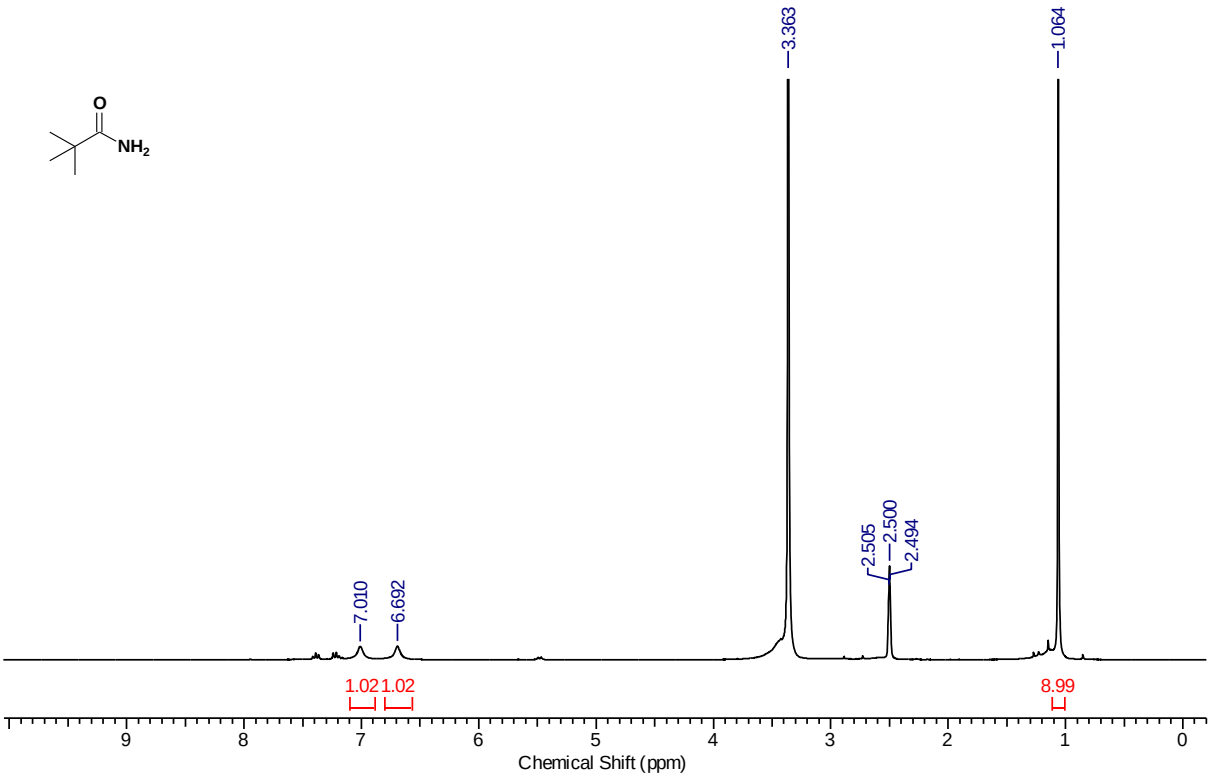
RM-166-C.001.001.1R.esp

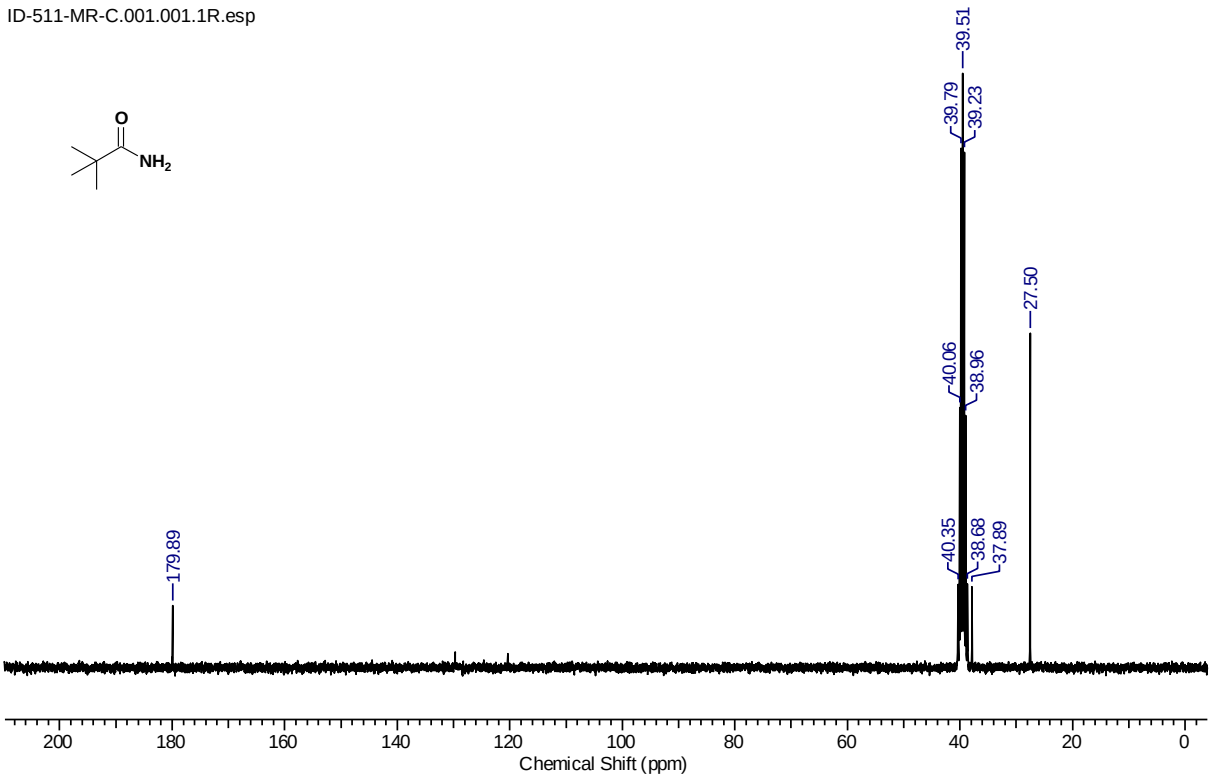


RM-166-C.002.001.1R.esp

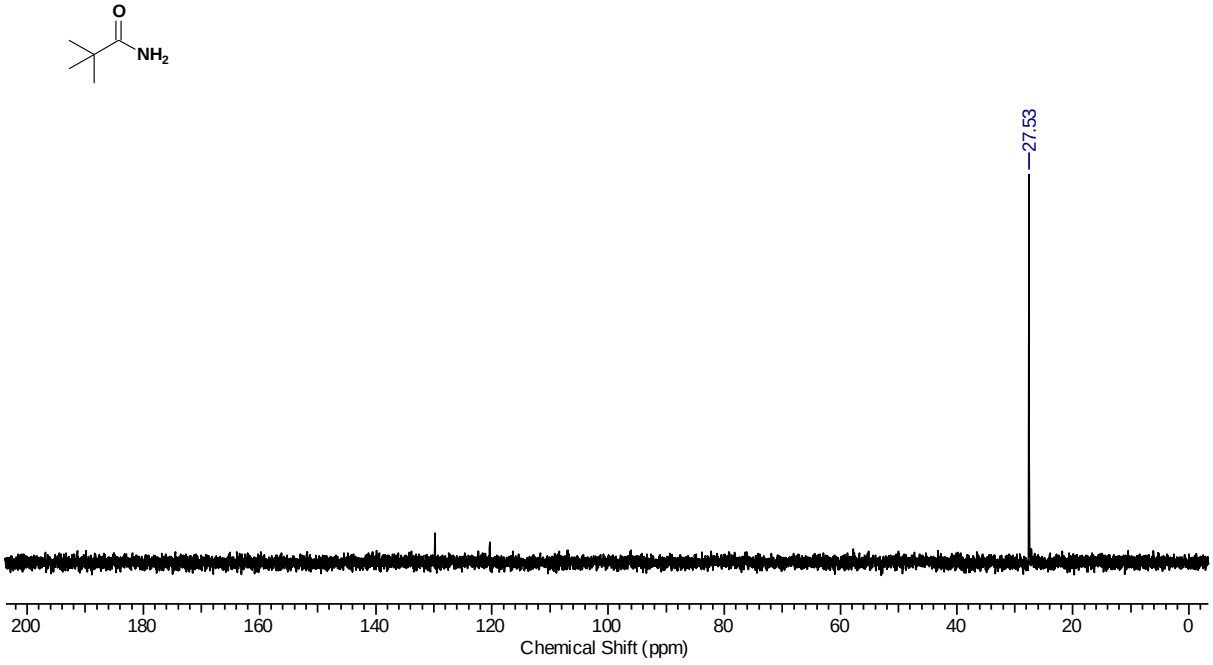


^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **4t:**

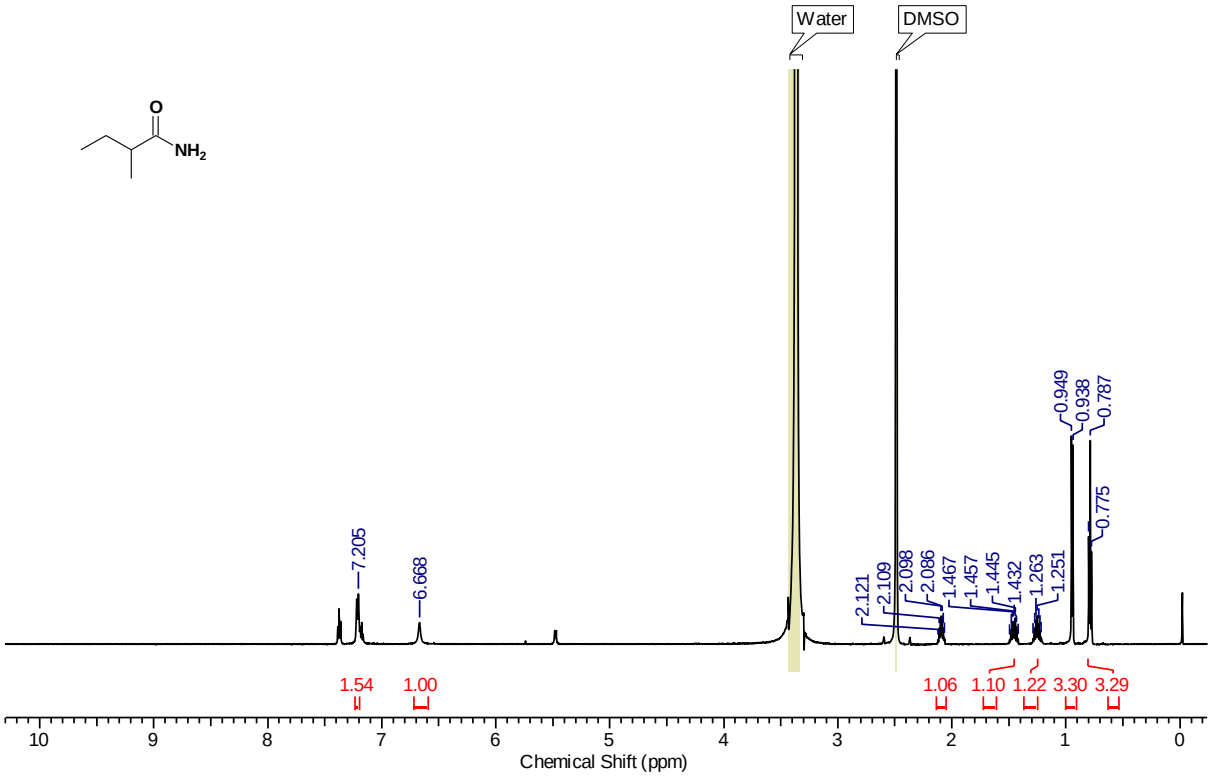


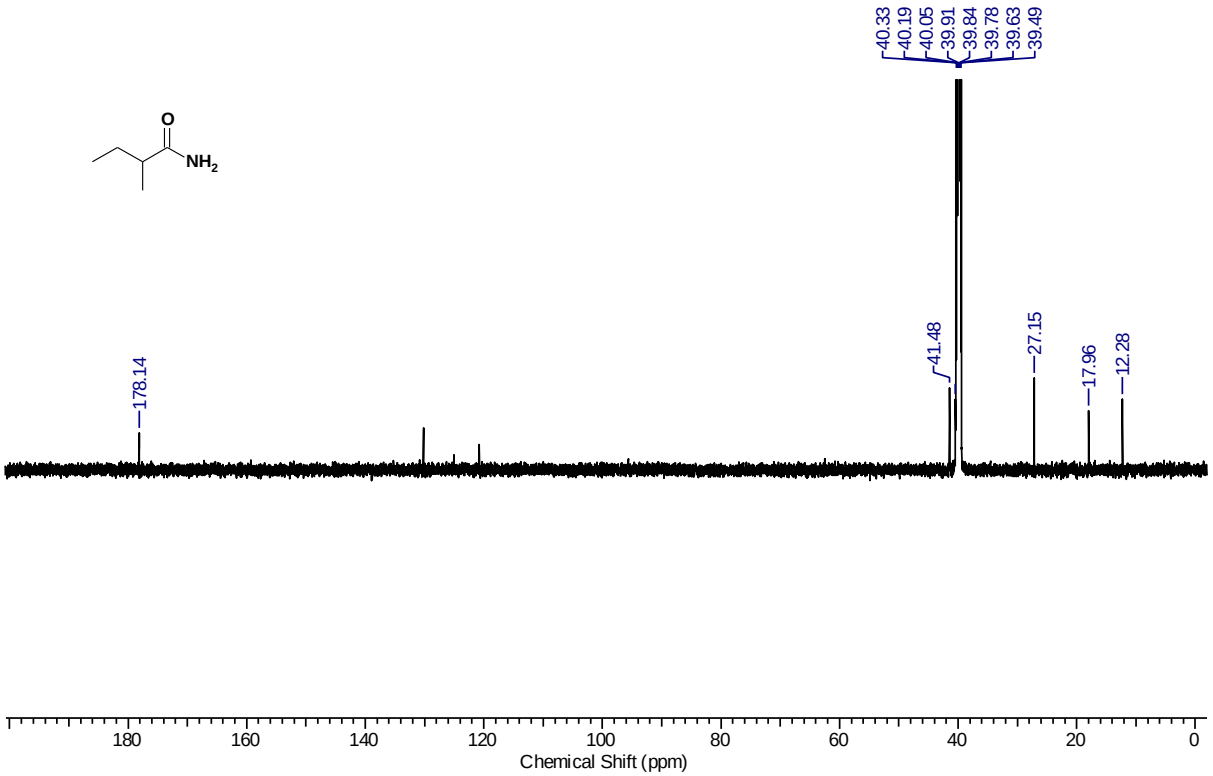


ID-511-MR-C.002.001.1R.esp

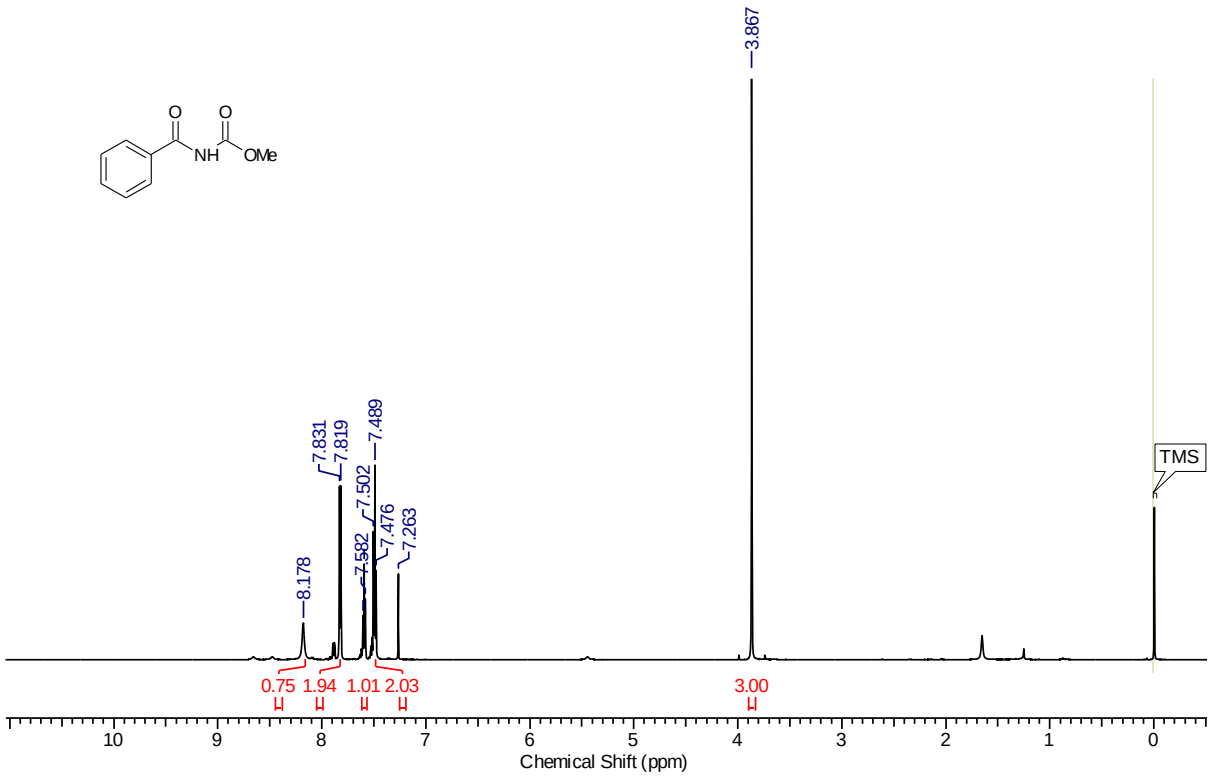


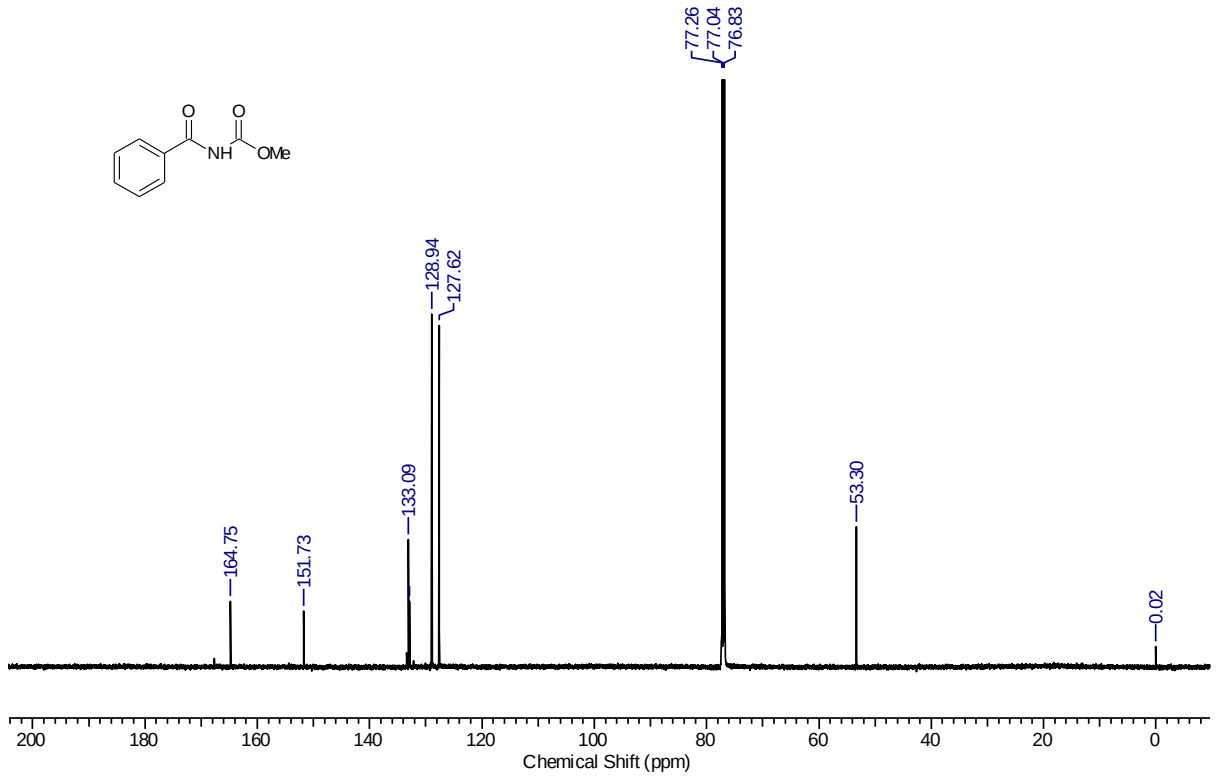
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4u:**

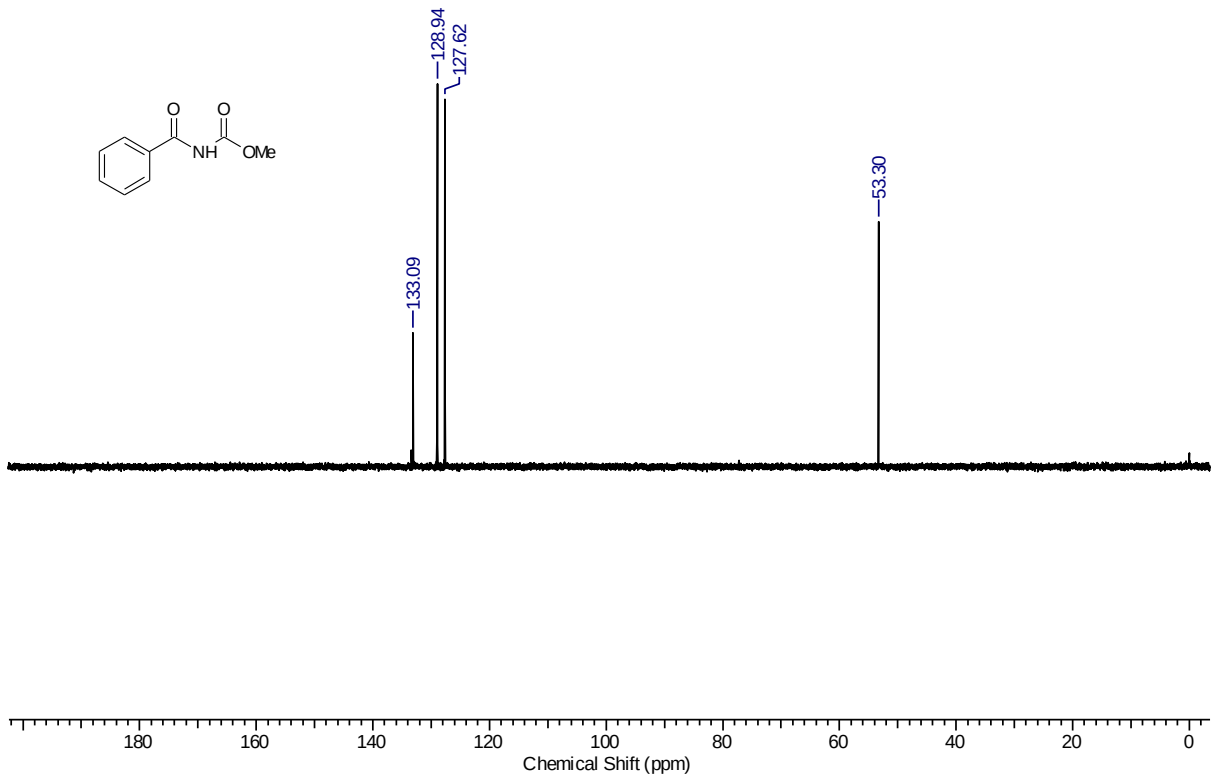




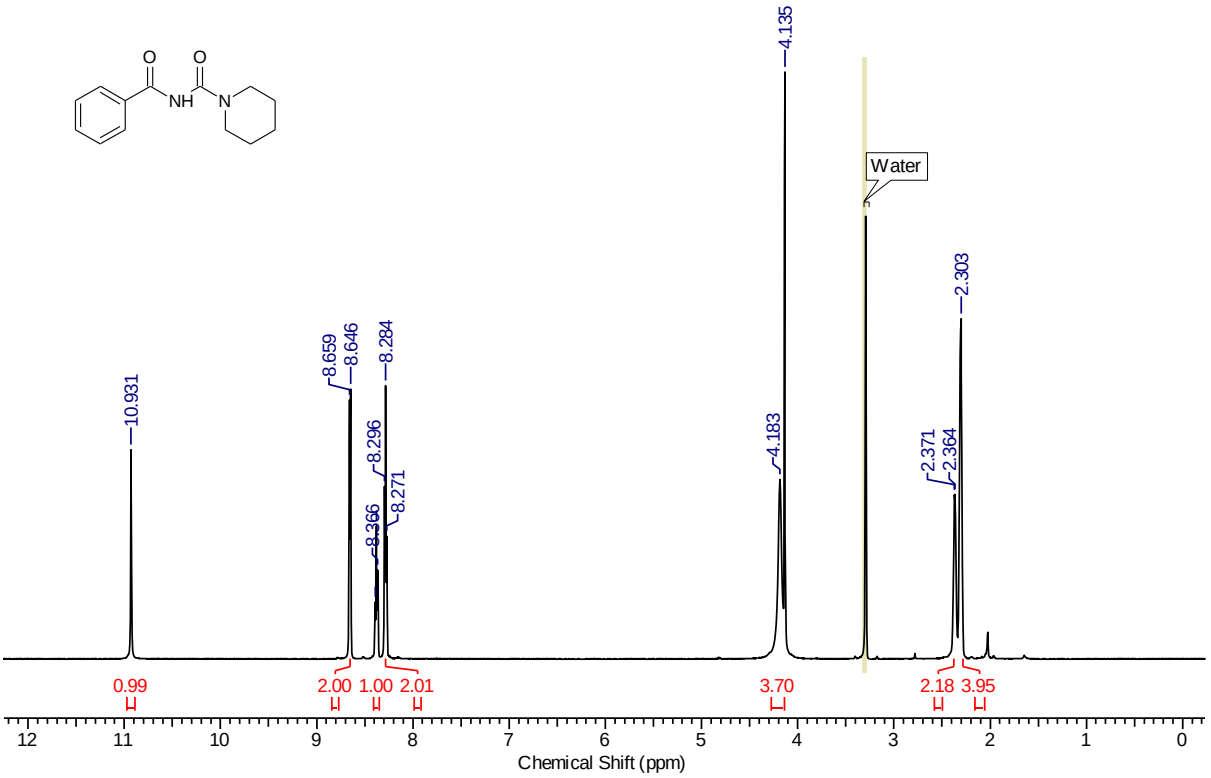
^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **5a:**

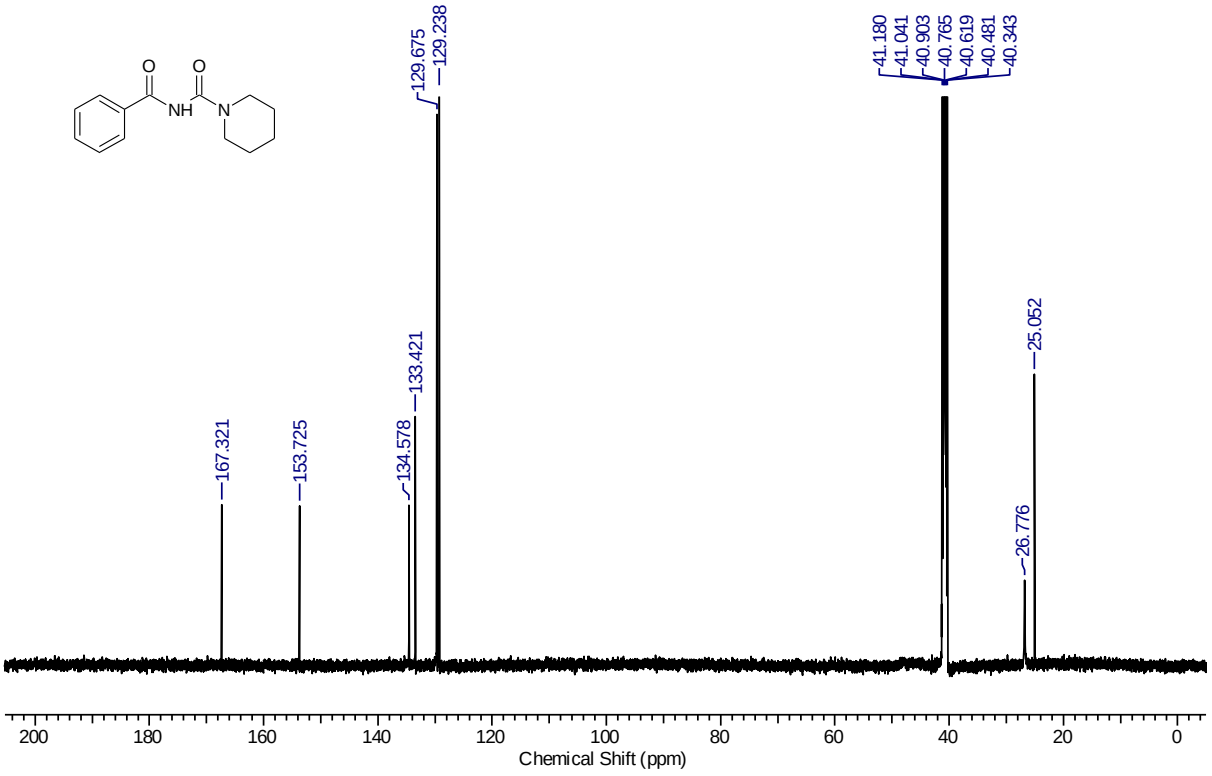


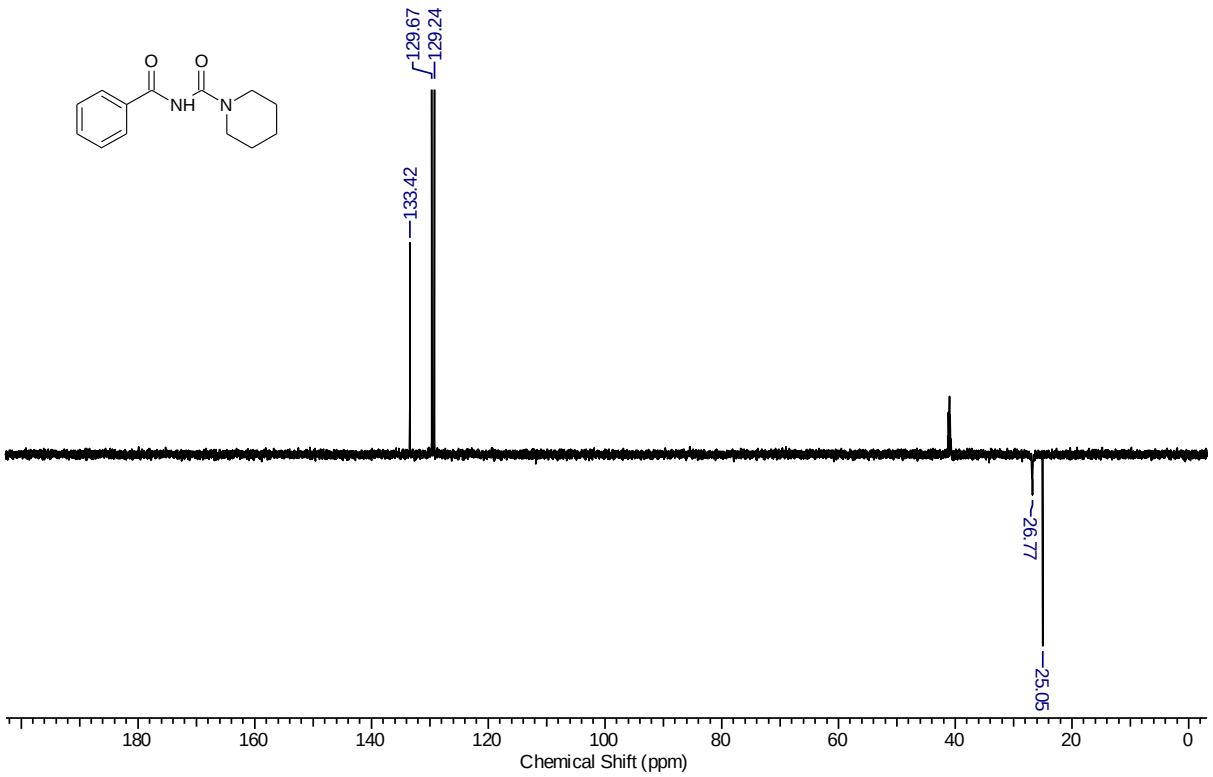

O
O
NH
OMe
77.26
77.04
76.83
128.94
127.62
133.09
164.75
151.73
53.30
0.02
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


O
O
NH
OMe
128.94
127.62
133.09
53.30
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

^{1}H, $^{13}C\{^{1}H\}$, DEPT-135 NMR spectra of **5b:**






O
O
NH
N
129.67
129.24
133.42
26.77
25.05
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

2. X-ray Crystal Structure:

ORTEP Diagram

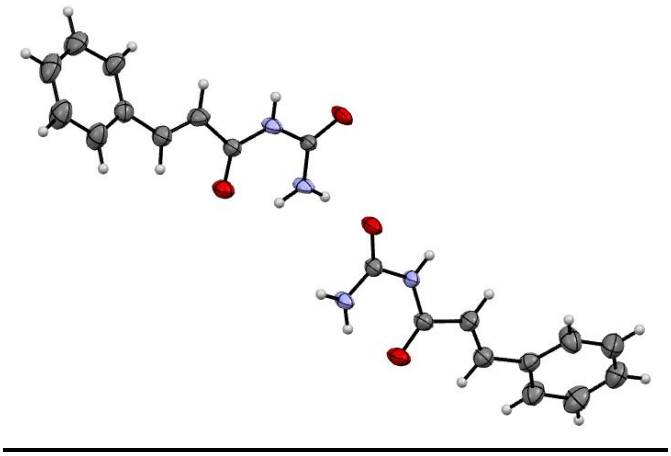


Figure S1. X-ray determined molecular structure of **3a** (CCDC 1581884). The thermal ellipsoids are shown in 50% probability level.

Datablock: 3a

```
Bond precision:      C-C = 0.0092 A              Wavelength=0.71073
Cell:        a=13.755(4)    b=5.1325(15)   c=25.638(8)
             alpha=90       beta=90        gamma=90
Temperature: 296 K
                    Calculated                      Reported
Volume              1810.0(9)                       1810.0(9)
Space group         P c a 21                        P c a 21
Hall group          P 2c -2ac                       P 2c -2ac
Moiety formula      C10 H10 N2 O2                   C10 H10 N2 O2
Sum formula         C10 H10 N2 O2                   C10 H10 N2 O2
Mr                  190.20                          190.20
Dx,g cm-3           1.396                           1.396
Z                   8                               8
Mu (mm-1)           0.100                           0.100
F000                800.0                           800.0
F000'               800.37
h,k,lmax            17,6,31                         16,6,31
Nref                3665[ 1877]                     3473
Tmin,Tmax           0.938,0.990                     0.556,0.745
Tmin'               0.925
Correction method= # Reported T Limits: Tmin=0.556
Tmax=0.745 AbsCorr = MULTI-SCAN
Data completeness= 1.85/0.95   Theta(max)= 26.245
R(reflections)= 0.0766( 3021)      wR2(reflections)= 0.2041( 3473)
S = 1.093             Npar= 253
```

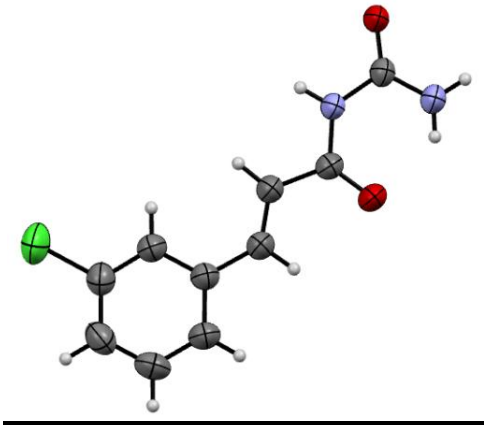


Figure S2. X-ray determined molecular structure of **3l** (CCDC 1581885). The thermal ellipsoids are shown in 50% probability level.

Datablock: 3l

```
Bond precision:      C-C = 0.0048 A              Wavelength=0.71073
Cell:        a=19.224(10)   b=10.624(6)    c=14.616(8)
             alpha=90       beta=136.066(4) gamma=90
Temperature: 296 K
                    Calculated                    Reported
Volume              2071(2)                       2071.3(19)
Space group         C 2/c                         C 1 2/c 1
Hall group          -C 2yc                        -C 2yc
Moiety formula      C10 H9 Cl N2 O2               C10 H9 Cl N2 O2
Sum formula         C10 H9 Cl N2 O2               C10 H9 Cl N2 O2
Mr                  224.64                        224.64
Dx,g cm-3           1.441                         1.441
Z                   8                             8
Mu (mm-1)           0.349                         0.349
F000                928.0                         928.0
F000'               929.56
h,k,lmax            24,13,18                      24,13,18
Nref                2294                          2254
Tmin,Tmax           0.931,0.972                   0.651,0.746
Tmin'               0.926
Correction method= # Reported T Limits: Tmin=0.651
Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.983       Theta(max)= 27.154
R(reflections)= 0.0471( 1374)     wR2(reflections)= 0.1350( 2254)
S = 1.032             Npar= 136
```

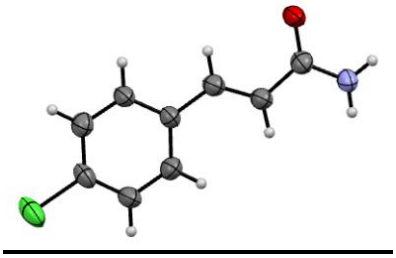


Figure S3. X-ray determined molecular structure of **4e** (CCDC 1581886). The thermal ellipsoids are shown in 50% probability level.

Datablock: 4e

```
Bond precision:      C-C = 0.0048 A              Wavelength=0.71073
Cell:         a=11.029(15)   b=9.057(12)    c=9.072(12)
              alpha=90       beta=108.10(2) gamma=90
Temperature: 296 K
                    Calculated                    Reported
Volume              861(2)                        861(2)
Space group         P 21/c                        P 1 21/c 1
Hall group          -P 2ybc                       -P 2ybc
Moiety formula      C9 H8 Cl N O                  C9 H8 Cl N O
Sum formula         C9 H8 Cl N O                  C9 H8 Cl N O
Mr                  181.61                        181.61
Dx,g cm-3           1.401                         1.400
Z                   4                             4
Mu (mm-1)           0.390                         0.389
F000                376.0                         376.0
F000'               376.73
h,k,lmax            14,11,11                      14,11,9
Nref                1973                          1324
Tmin,Tmax           0.822,0.977                   0.553,0.746
Tmin'               0.789
Correction method= # Reported T Limits: Tmin=0.553
Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.671        Theta(max)= 27.471
R(reflections)= 0.0457( 888)       wR2(reflections)= 0.1453( 1324)
S = 1.059             Npar= 109
```

3. Copy of HRMS-ESI Spectrum of the Crude Reaction Mixtures:

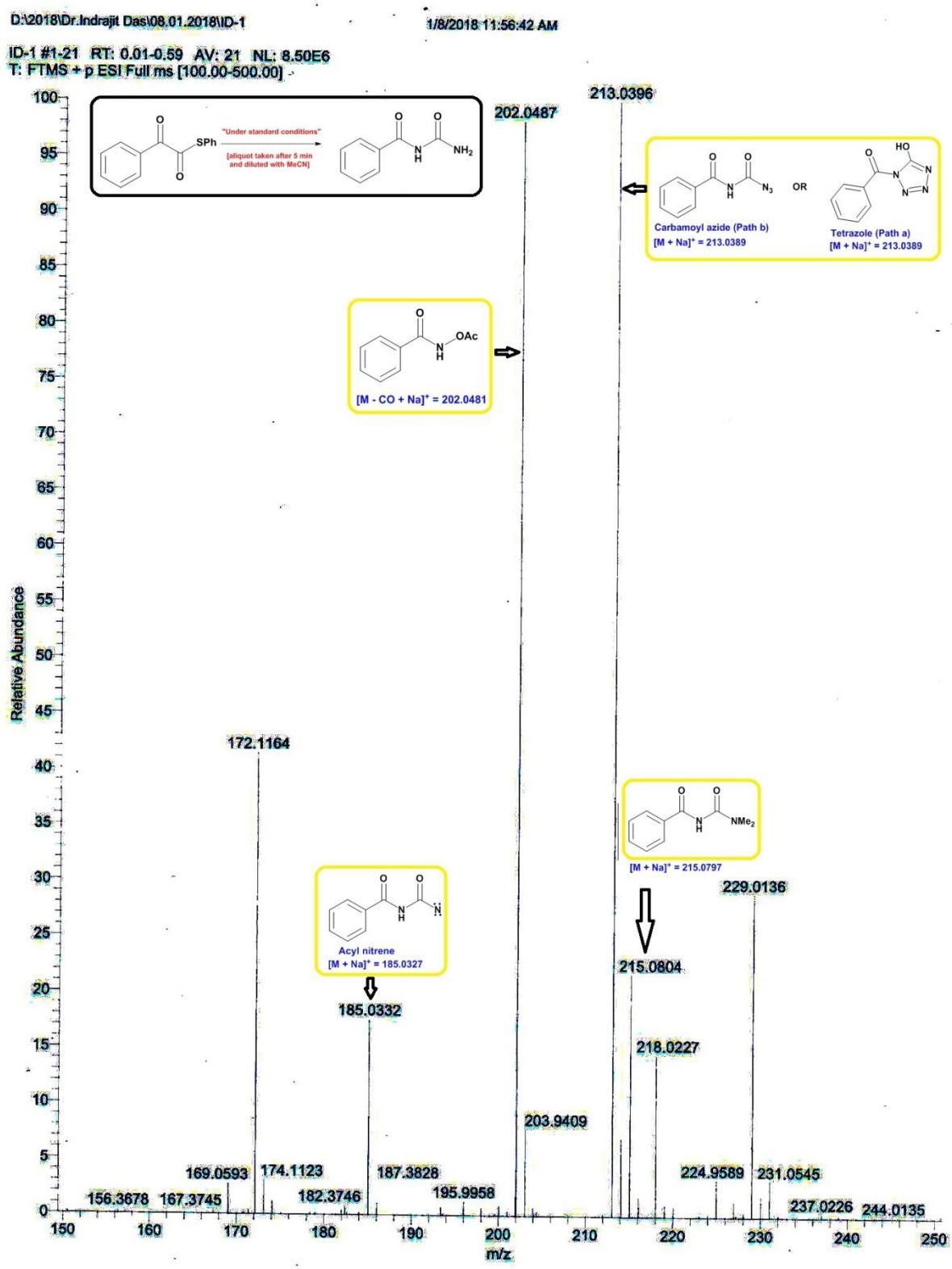


Figure S1. ESI-HRMS spectrum of the crude reaction mixture after five min (*m/z* 150-250).

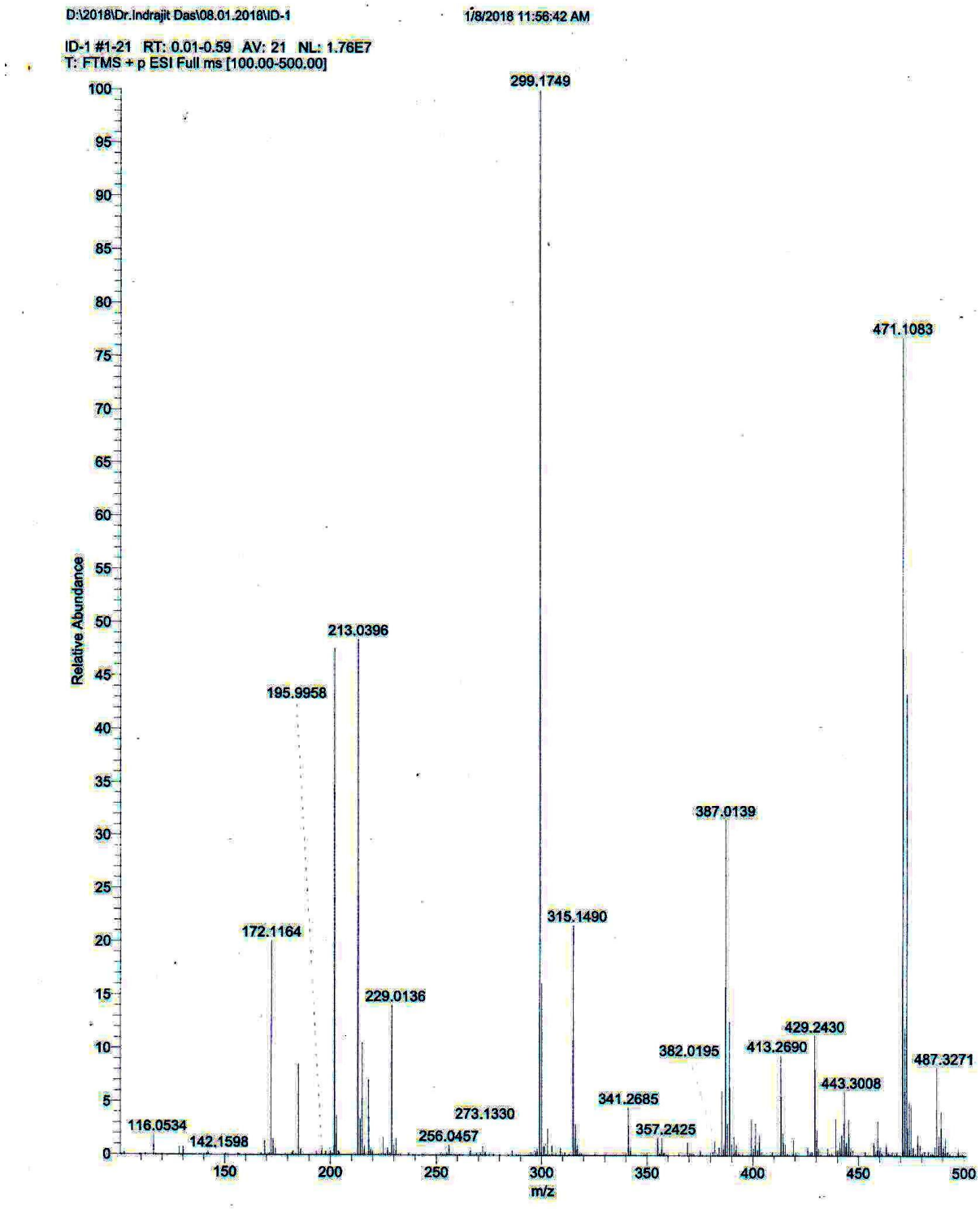


Figure S2. ESI-HRMS spectrum of the crude reaction mixture after five min (*m/z* 150-500).