SUPPORTING INFORMATION

[3+2] Cycloaddition and Subsequent Oxidative Dehydrogenation between Alkenes and Diazo Compounds: A Simple and Direct Approach to Pyrazoles Using TBAI/TBHP*

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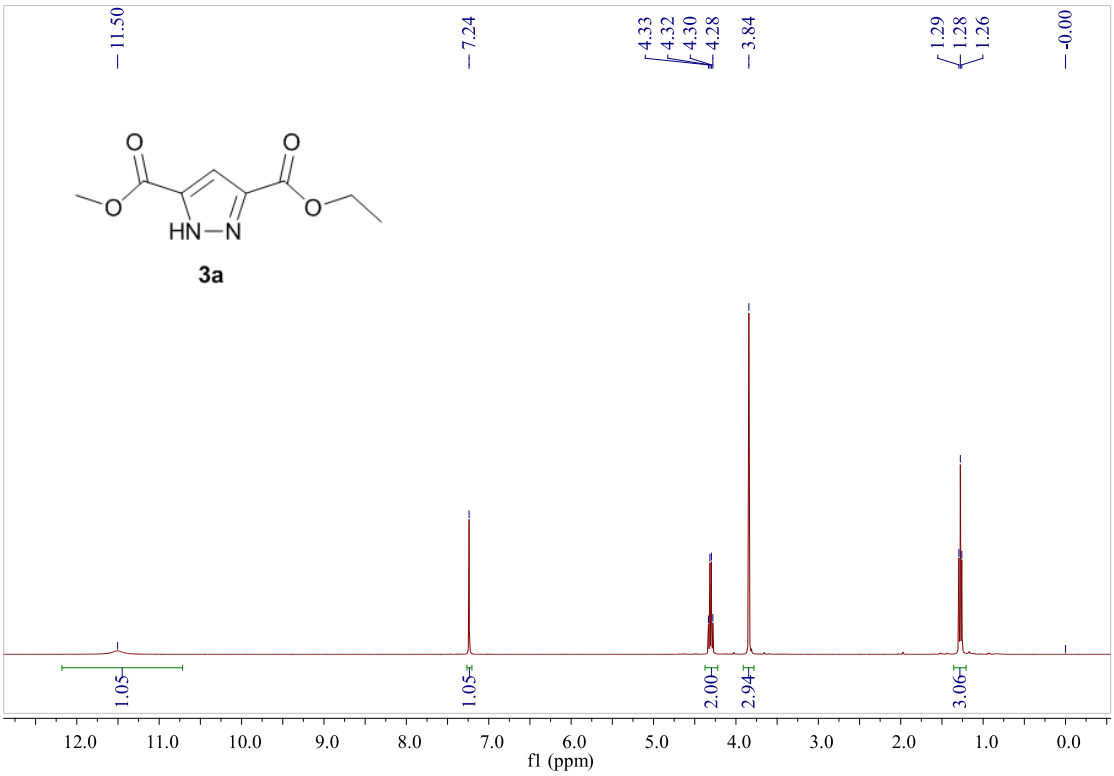
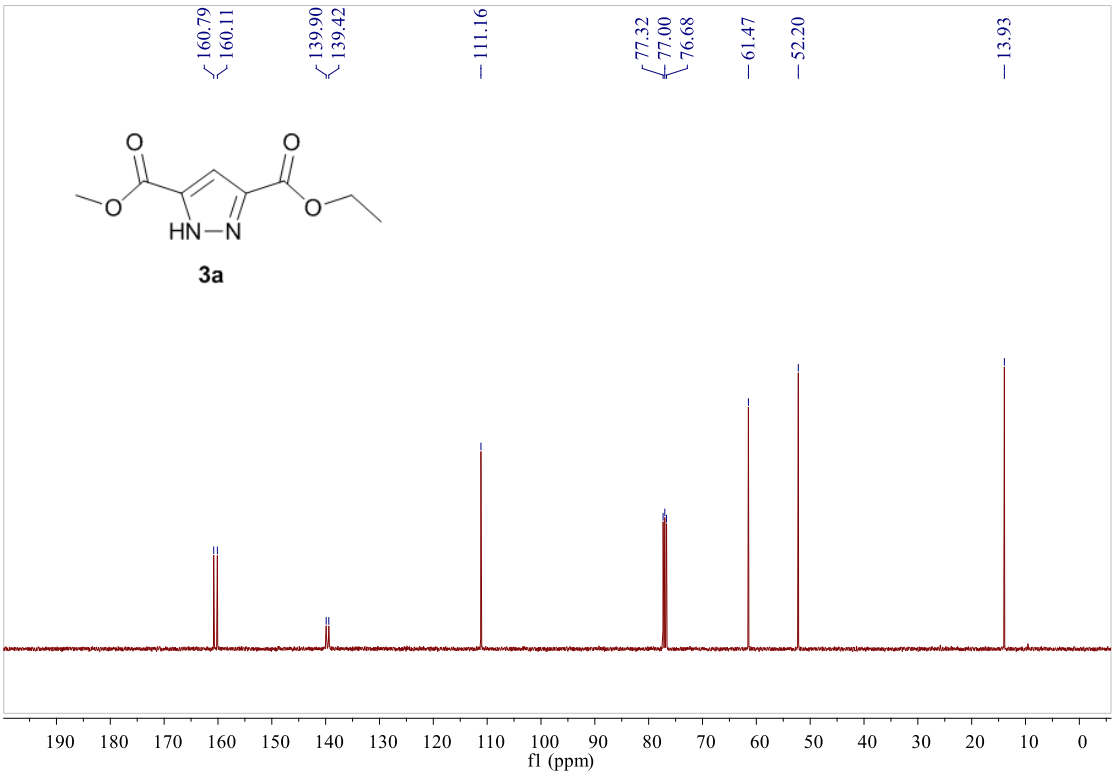
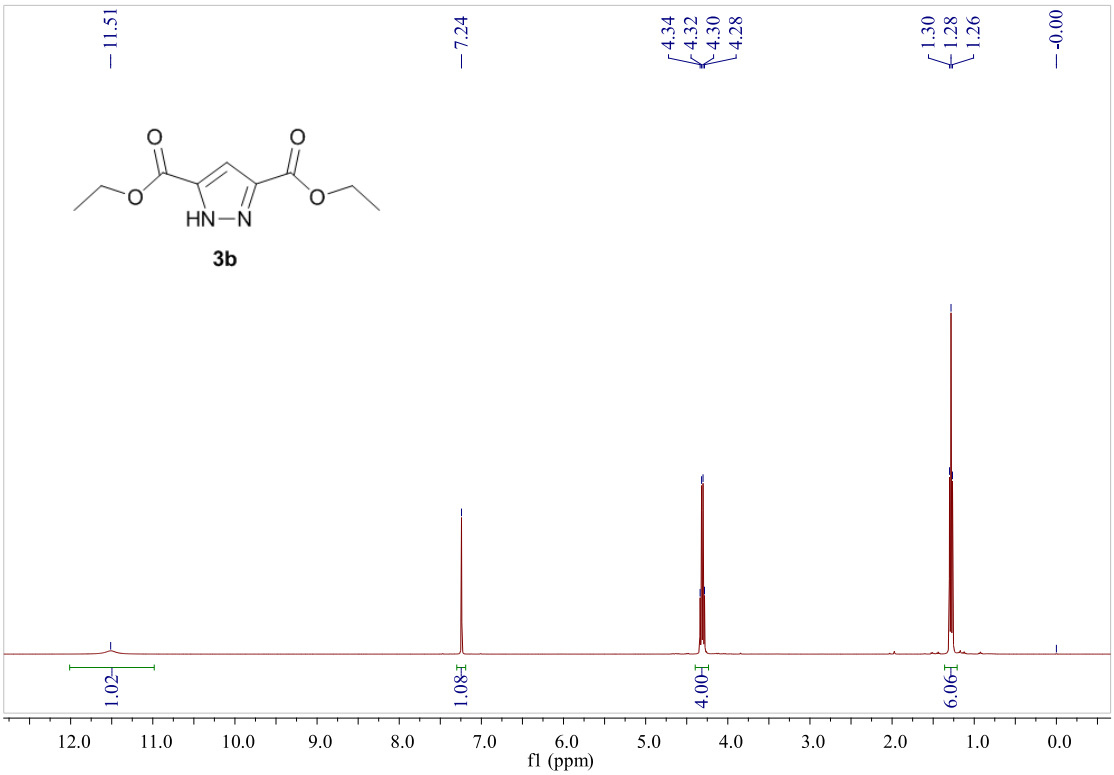
Spectroscopic Data for Products



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4.32
4.30
4.28
1.30
1.28
1.26
-0.00
3b
1.02
1.08
4.00
6.06
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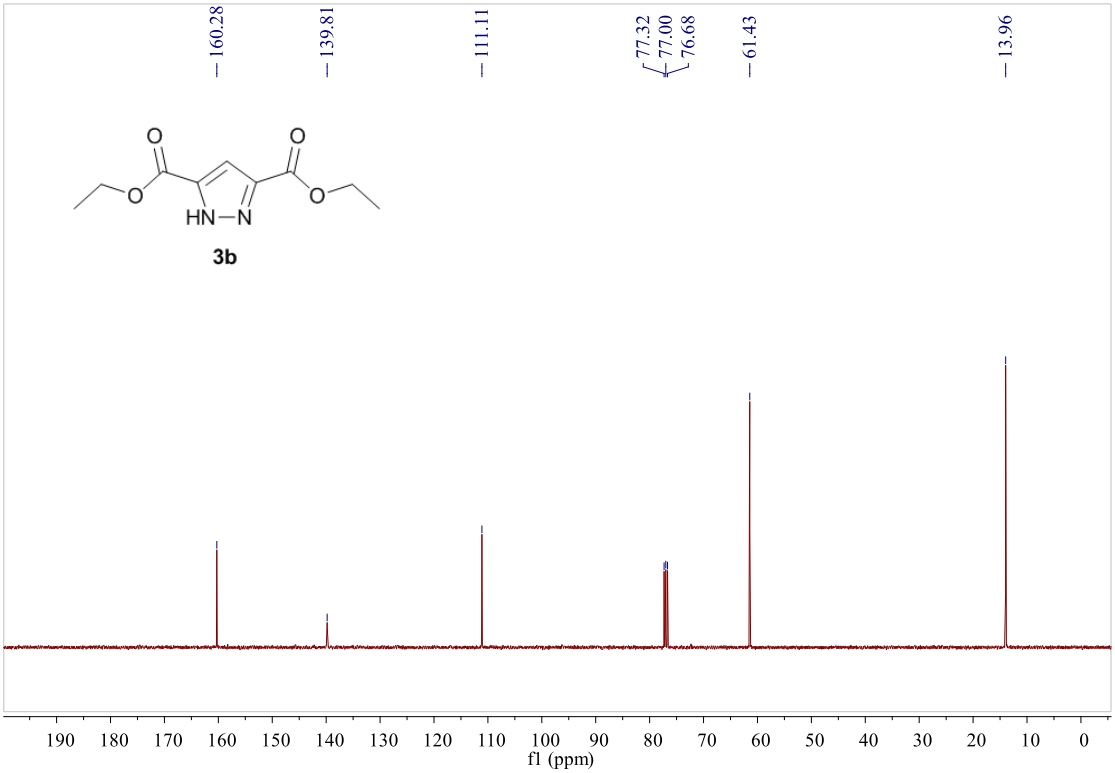
f1 (ppm)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3b
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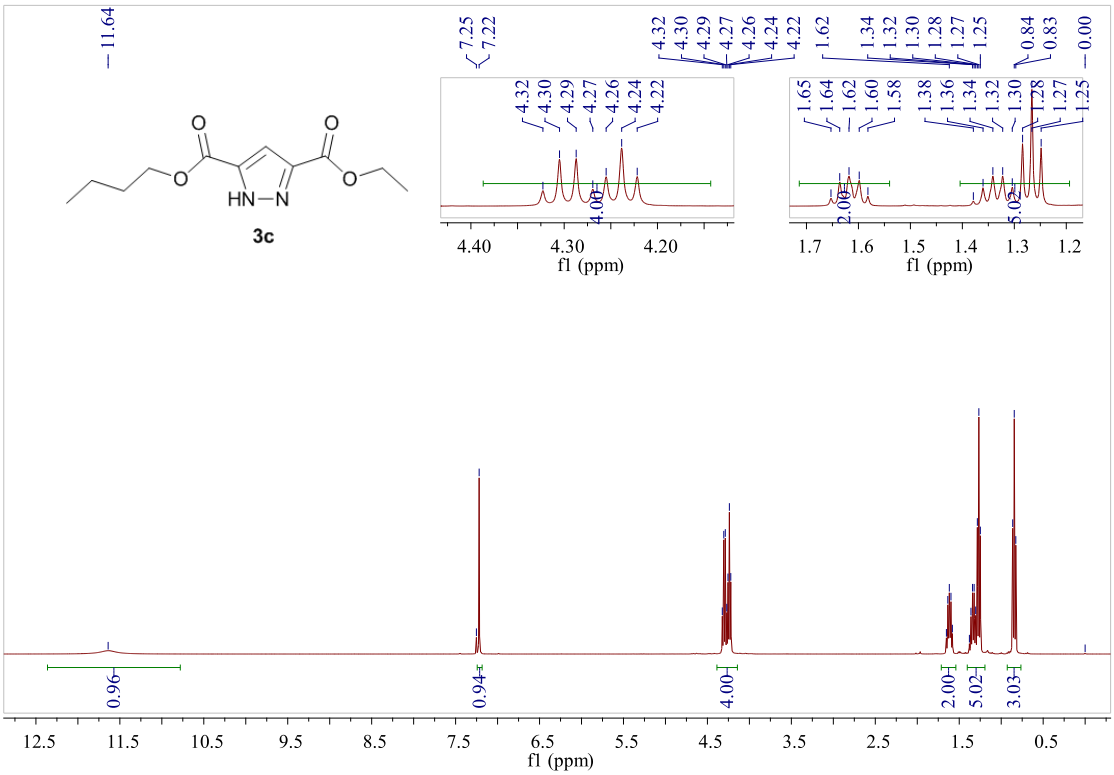
f1 (ppm)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4.29
4.27
4.26
4.24
4.22
1.62
1.34
1.32
1.30
1.28
1.27
1.25
0.84
0.83
0.00
1.65
1.64
1.62
1.60
1.58
1.38
1.36
1.34
1.32
1.30
1.28
1.27
1.25
O
O
O
O
HN—N
3c
4.00
2.00
5.02
4.40
4.30
4.20
1.7
1.6
1.5
1.4
1.3
1.2
f1 (ppm)
0.96
0.94
4.00
2.00
5.02
3.03
12.5
11.5
10.5
9.5
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7.5
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5.5
4.5
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2.5
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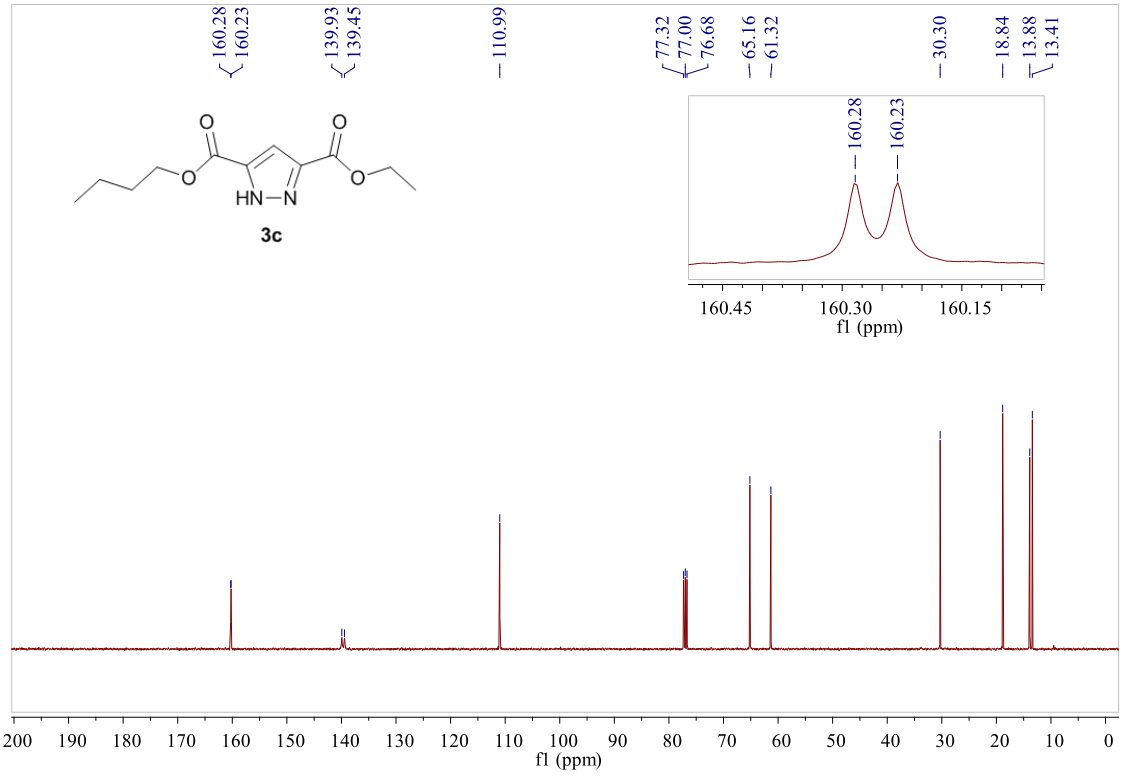
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77.00
76.68
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61.32
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18.84
13.88
13.41
O
O
O
O
HN—N
3c
160.28
160.23
160.45
160.30
160.15
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
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80
70
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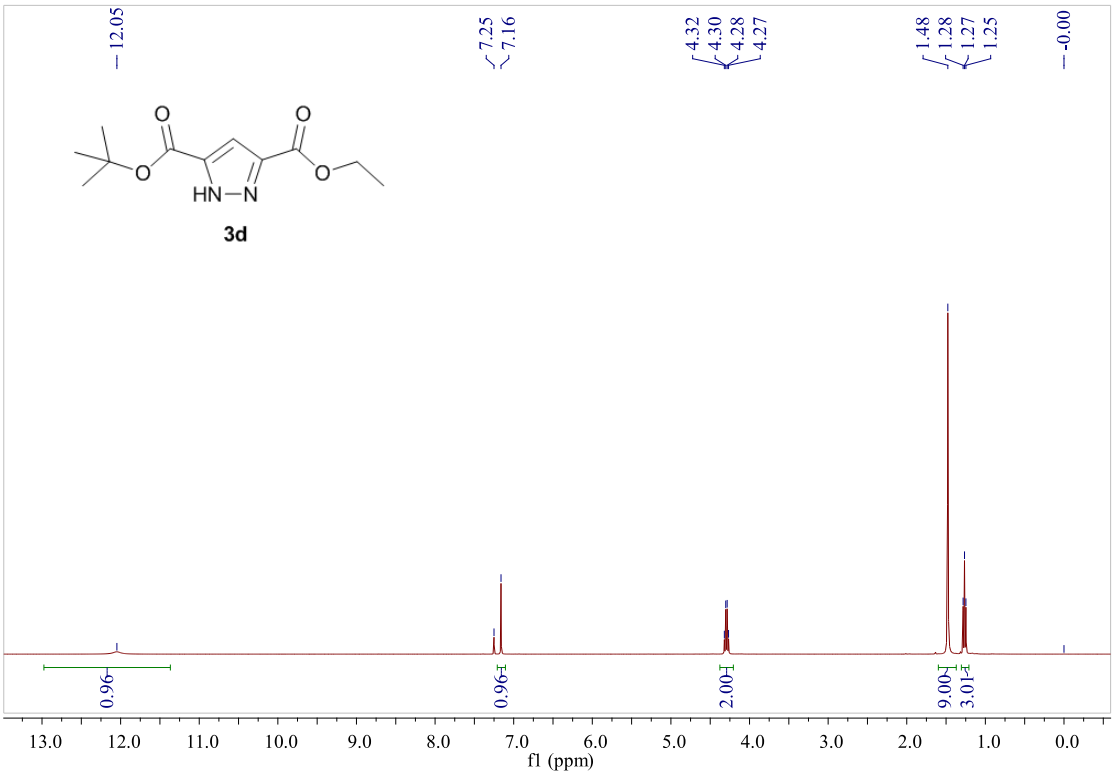
50
40
30
20
10
0
f1 (ppm)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7.16
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4.28
4.27
1.48
1.28
1.27
1.25
-0.00
3d
0.96
0.96
2.00
9.00
3.01
13.0
12.0
11.0
10.0
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6.0
5.0
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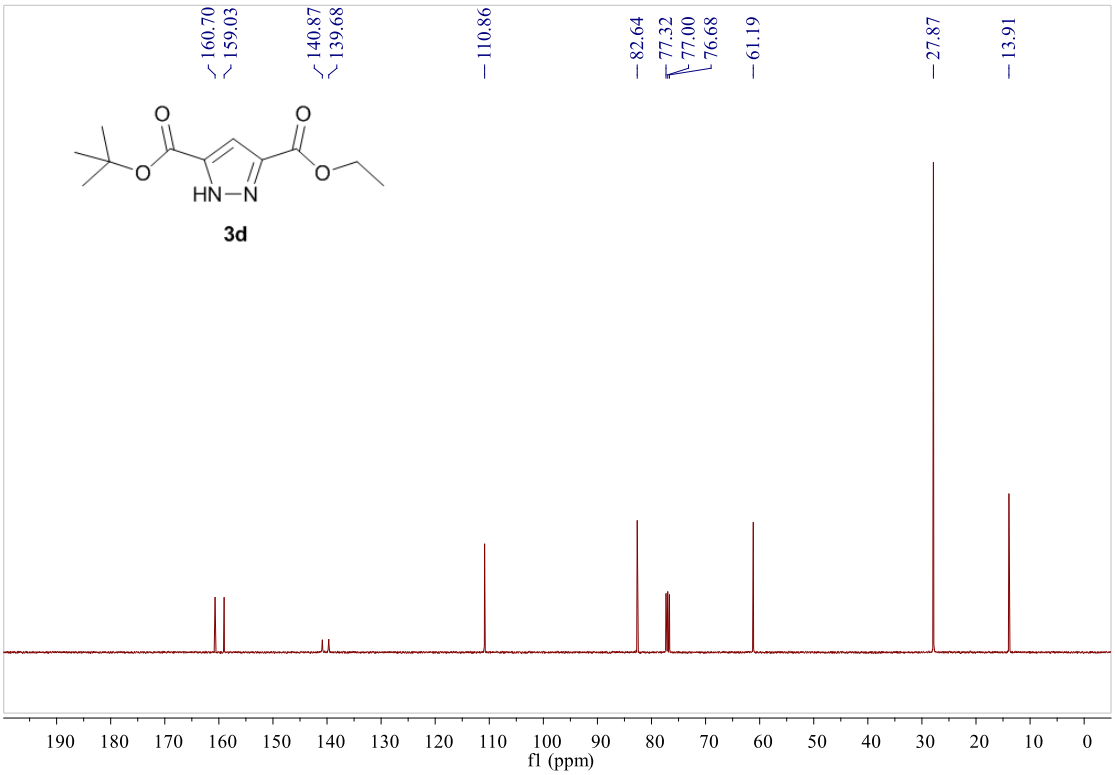
0.0
f1 (ppm)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76.68
61.19
27.87
13.91
3d
190
180
170
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150
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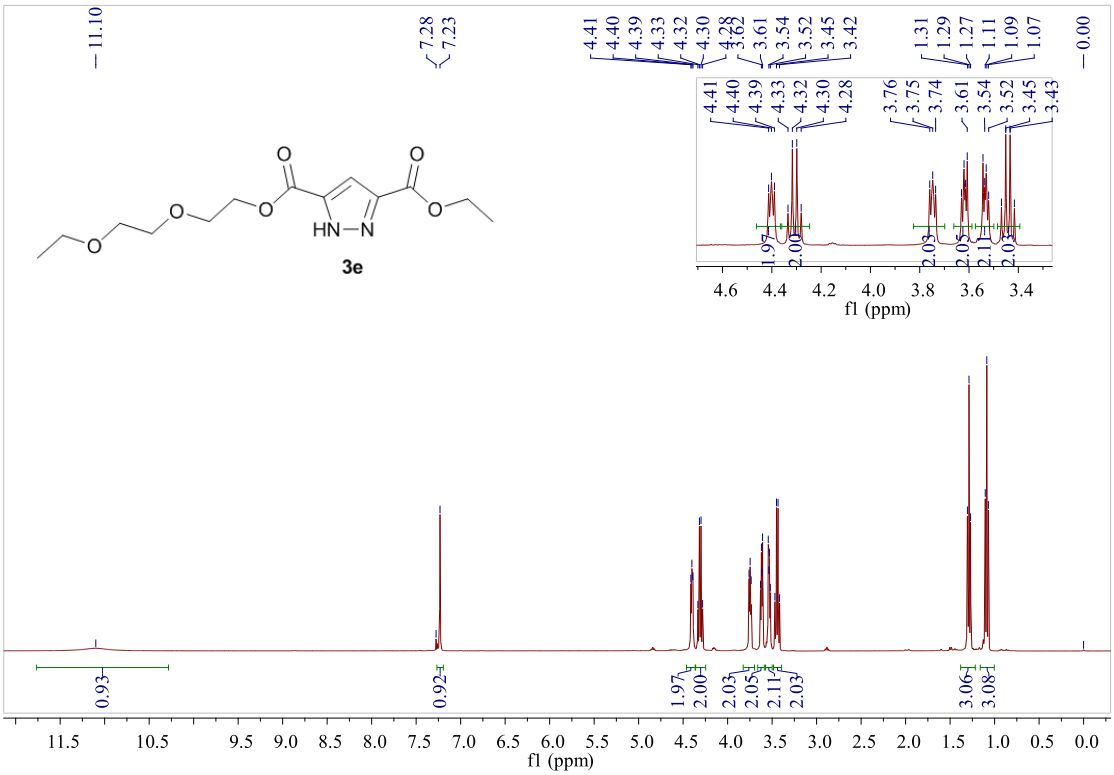
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.39
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3.62
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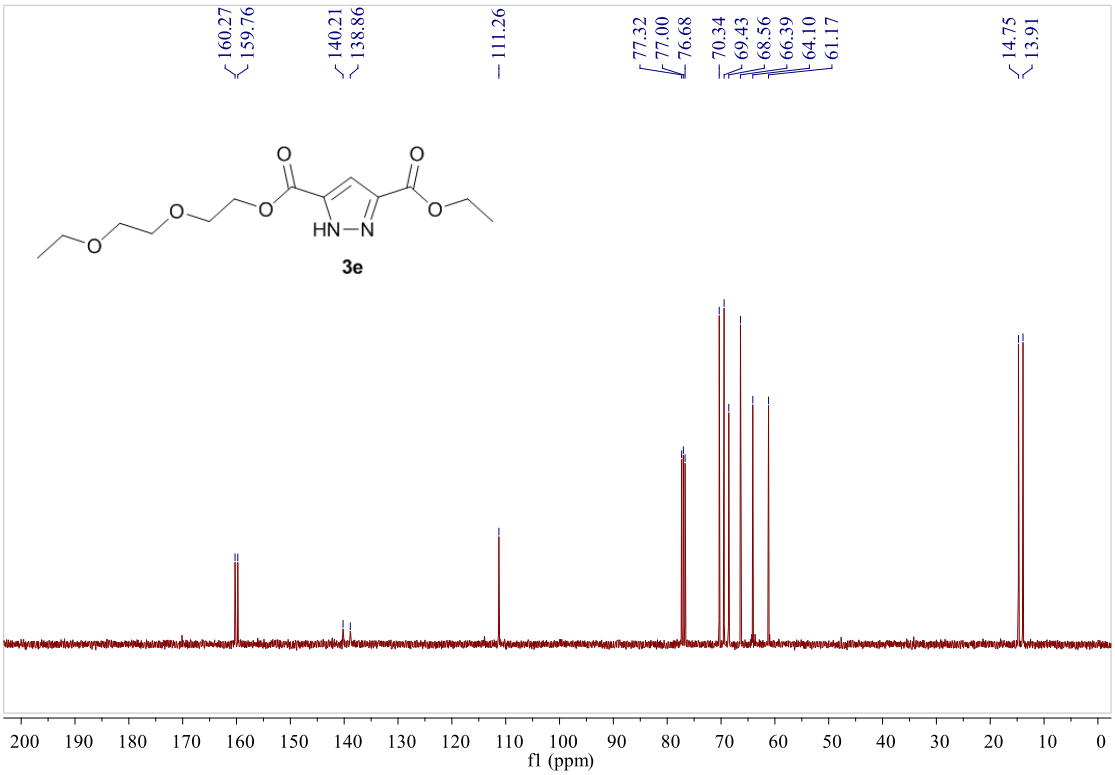
3.54
3.52
3.45
3.42
1.31
1.29
1.27
1.11
1.09
1.07
0.00
3.76
3.75
3.74
3.61
3.54
3.52
3.45
3.43
1.97
2.00
2.03
2.05
2.11
2.03
0.93
0.92
1.97
2.00
2.03
2.05
2.11
2.03
3.06
3.08
HN–N
3e
fl (ppm)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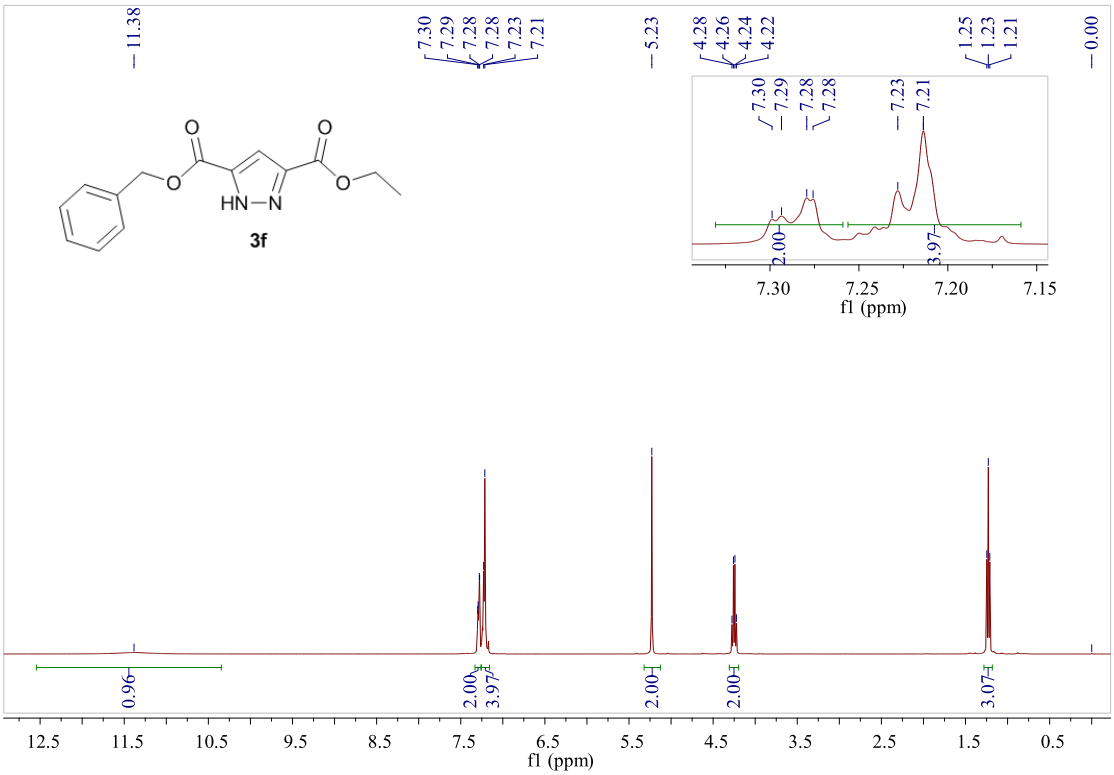
61.17
14.75
13.91
HN–N
3e
fl (ppm)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5.23
4.28
4.26
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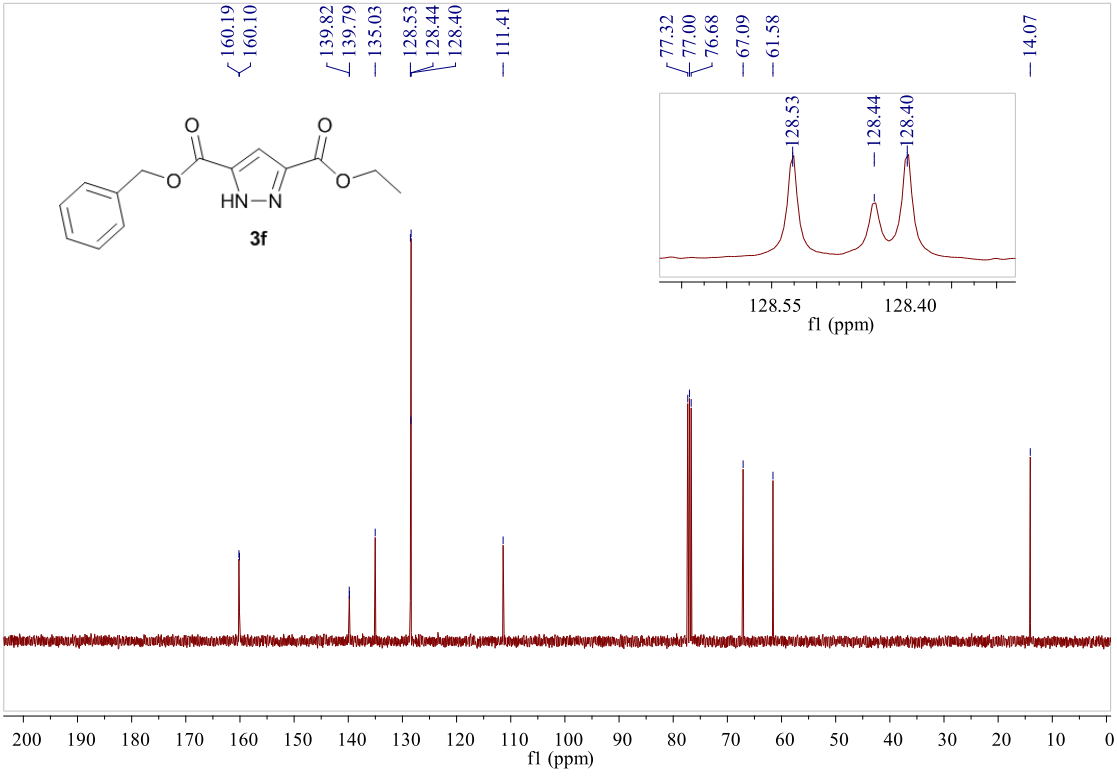
1.25
1.23
1.21
0.00
3f
7.30
7.29
7.28
7.28
7.23
7.21
2.00
3.97
7.30
7.25
7.20
7.15
f1 (ppm)
0.96
2.00
3.97
2.00
2.00
3.07
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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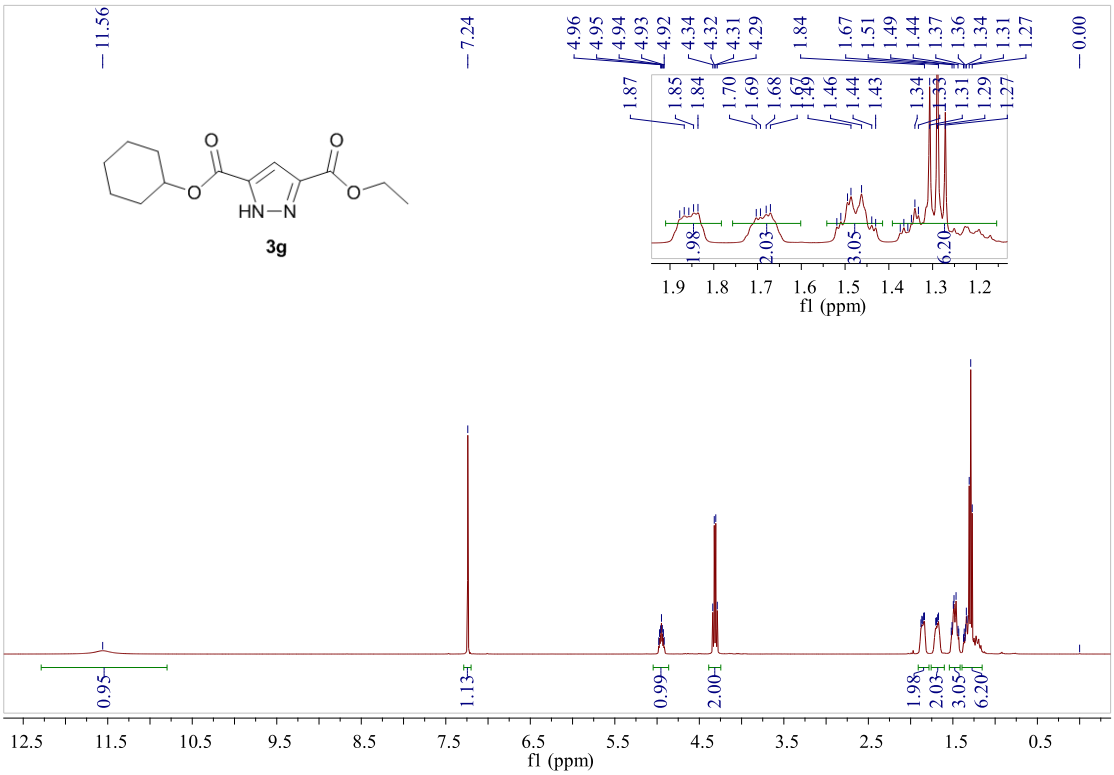
139.79
135.03
128.53
128.44
128.40
111.41
77.32
77.00
76.68
67.09
61.58
14.07
3f
128.53
128.44
128.40
128.55
128.40
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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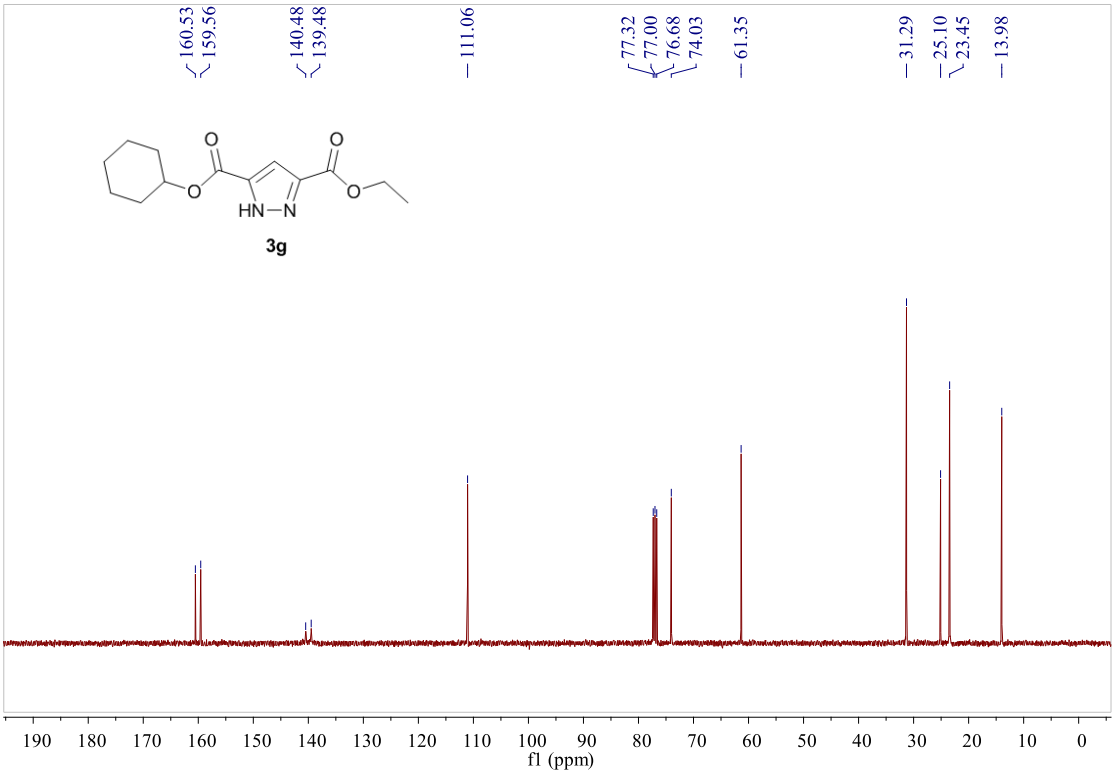
4.29
1.84
1.67
1.51
1.49
1.44
1.37
1.36
1.34
1.31
1.27
0.00
1.87
1.85
1.84
1.70
1.69
1.68
1.46
1.44
1.43
1.34
1.31
1.29
1.27
1.98
2.03
3.05
6.20
1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2
f1 (ppm)
O
O
O
O
HN—N
3g
0.95
1.13
0.99
2.00
1.98
2.03
3.05
6.20
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)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159.56
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139.48
111.06
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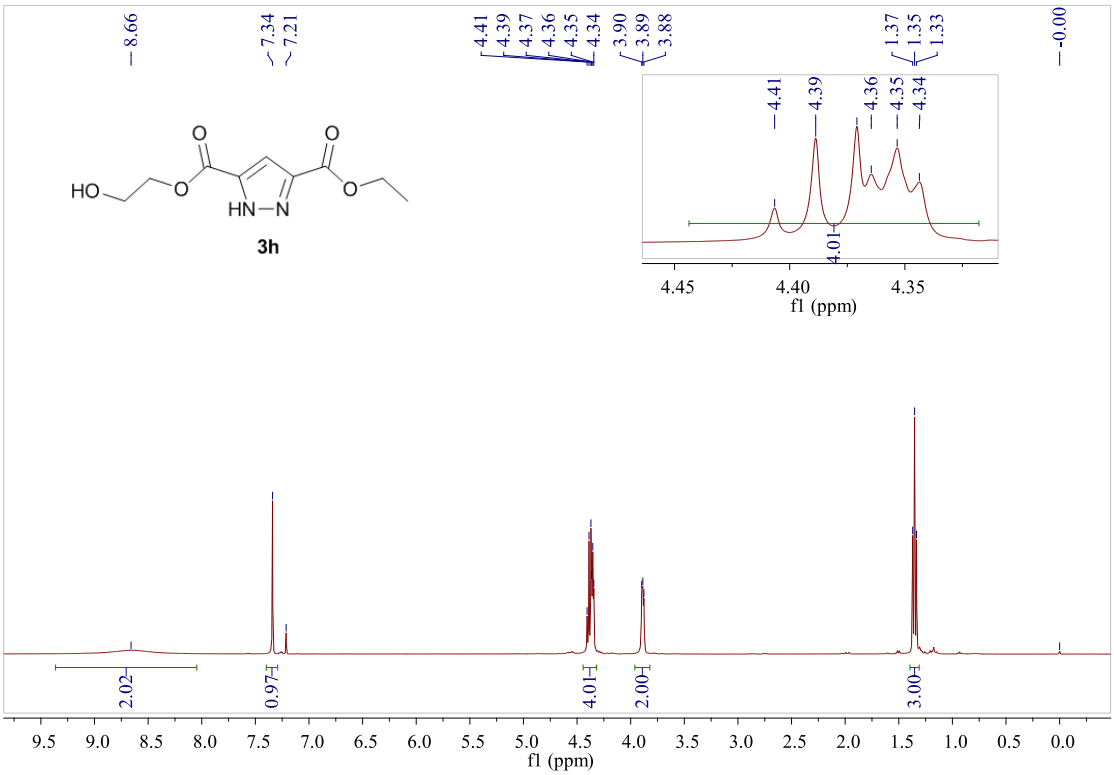
77.00
76.68
74.03
61.35
31.29
25.10
23.45
13.98
O
O
O
O
HN—N
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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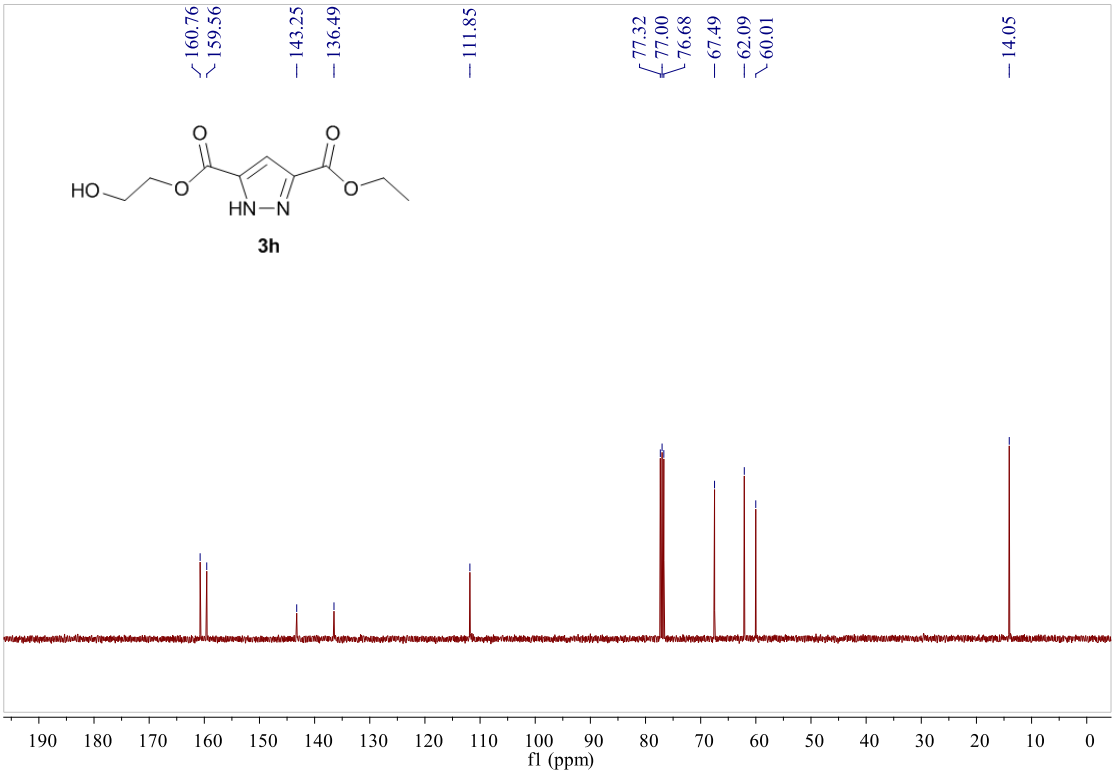
7.21
4.41
4.39
4.37
4.36
4.35
4.34
3.90
3.89
3.88
1.37
1.35
1.33
-0.00
HO
O
O
O
O
HN—N
3h
4.01
fl (ppm)
2.02
0.97
4.01
2.00
3.00
fl (ppm)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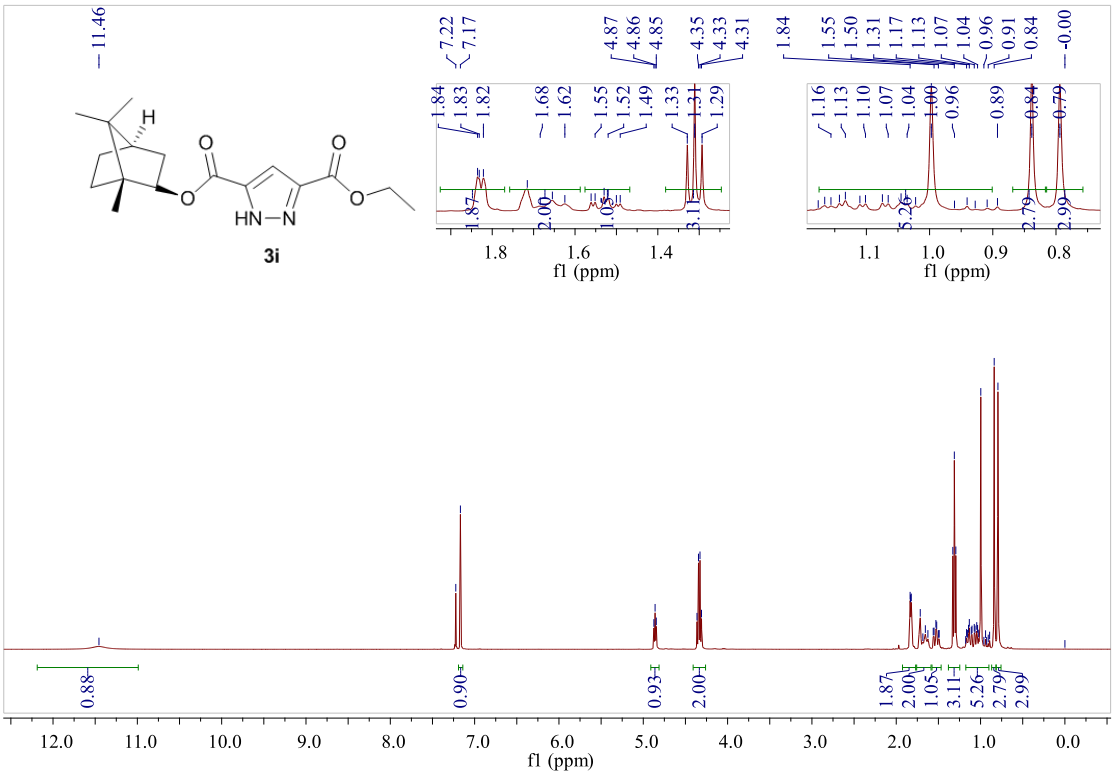
159.56
143.25
136.49
111.85
77.32
77.00
76.68
67.49
62.09
60.01
14.05
HO
O
O
O
O
HN—N
3h
fl (ppm)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4.85
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4.33
4.31
1.84
1.55
1.50
1.31
1.17
1.13
1.07
1.04
0.96
0.91
0.84
-0.00
1.84
1.83
1.82
1.68
1.62
1.55
1.52
1.49
1.33
1.31
1.29
1.16
1.13
1.10
1.07
1.04
1.00
0.96
0.89
0.84
0.79
H
O
O
O
O
HN—N
3i
1.8
1.6
1.4
f1 (ppm)
1.1
1.0
0.9
0.8
f1 (ppm)
0.88
0.90
0.93
2.00
1.87
2.00
1.05
3.11
5.26
2.79
2.99
12.0
11.0
10.0
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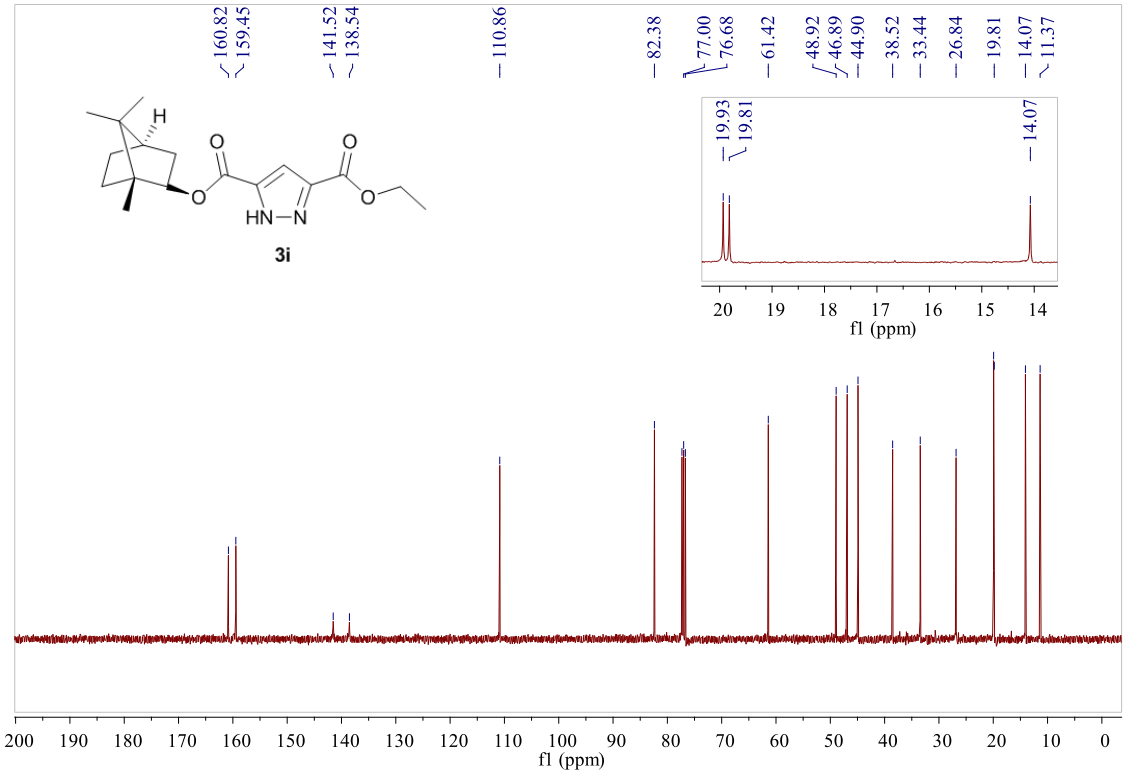
0.0
f1 (ppm)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46.89
44.90
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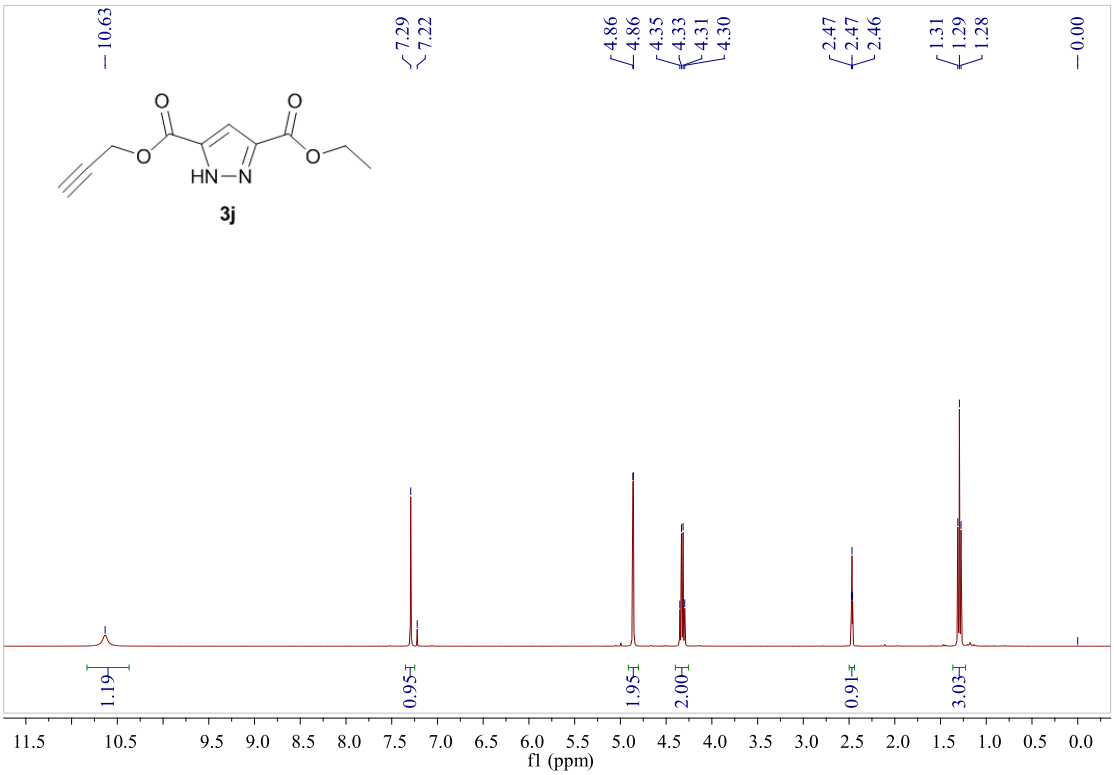
33.44
26.84
19.81
14.07
11.37
19.93
19.81
14.07
H
O
O
O
O
HN—N
3i
20
19
18
17
16
15
14
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.86
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2.47
2.46
1.31
1.29
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3j
1.19
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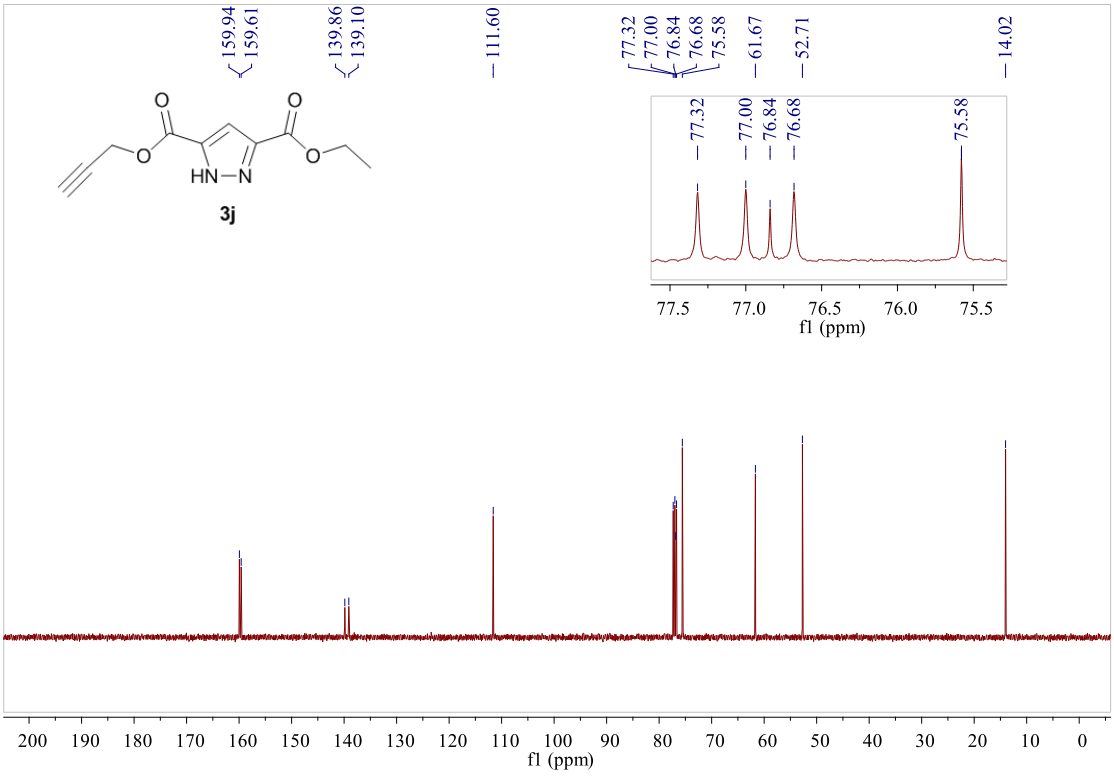
1.95
2.00
0.91
3.03
f1 (ppm)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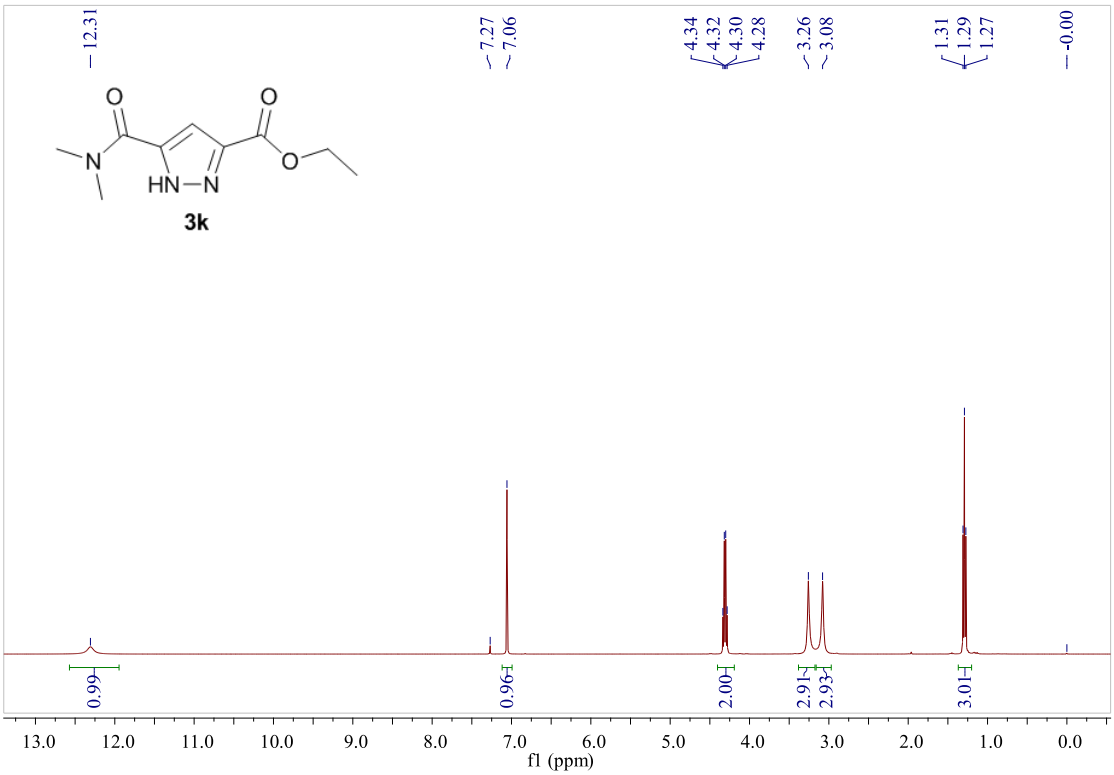
61.67
52.71
14.02
3j
f1 (ppm)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7.27
7.06
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4.30
4.28
3.26
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1.31
1.29
1.27
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3k
0.99
0.96
2.00
2.91
2.93
3.01
13.0
12.0
11.0
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2.0
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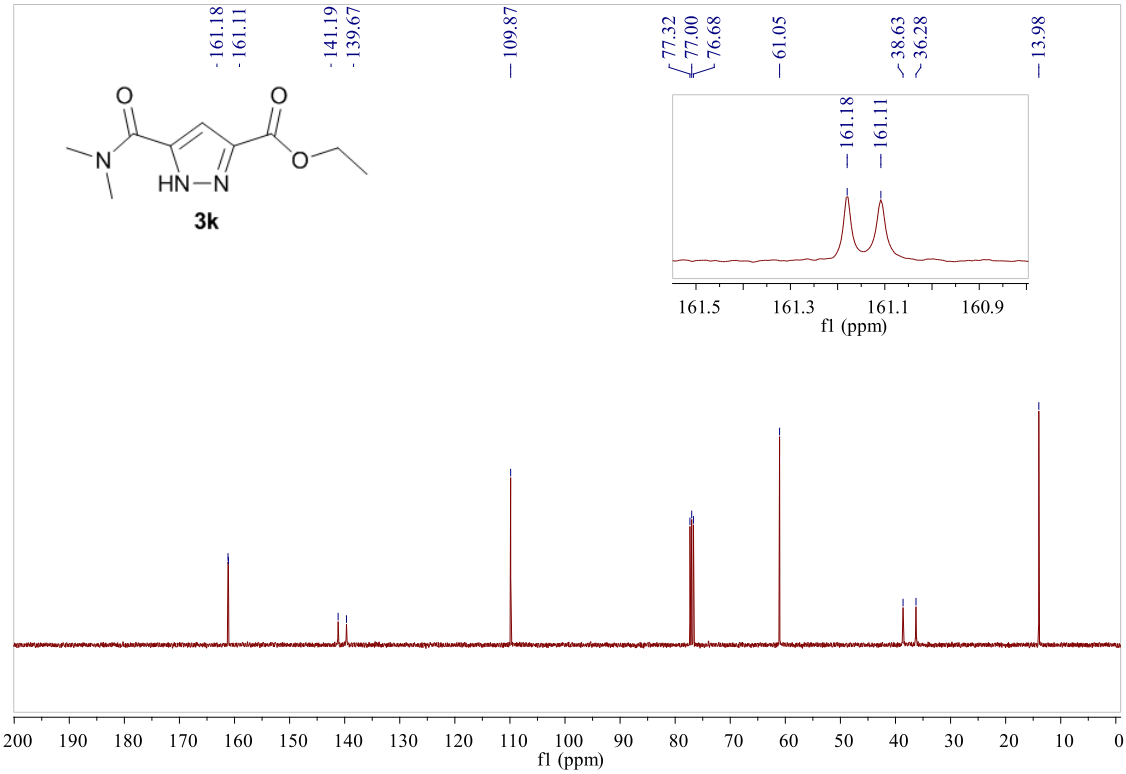
0.0
f1 (ppm)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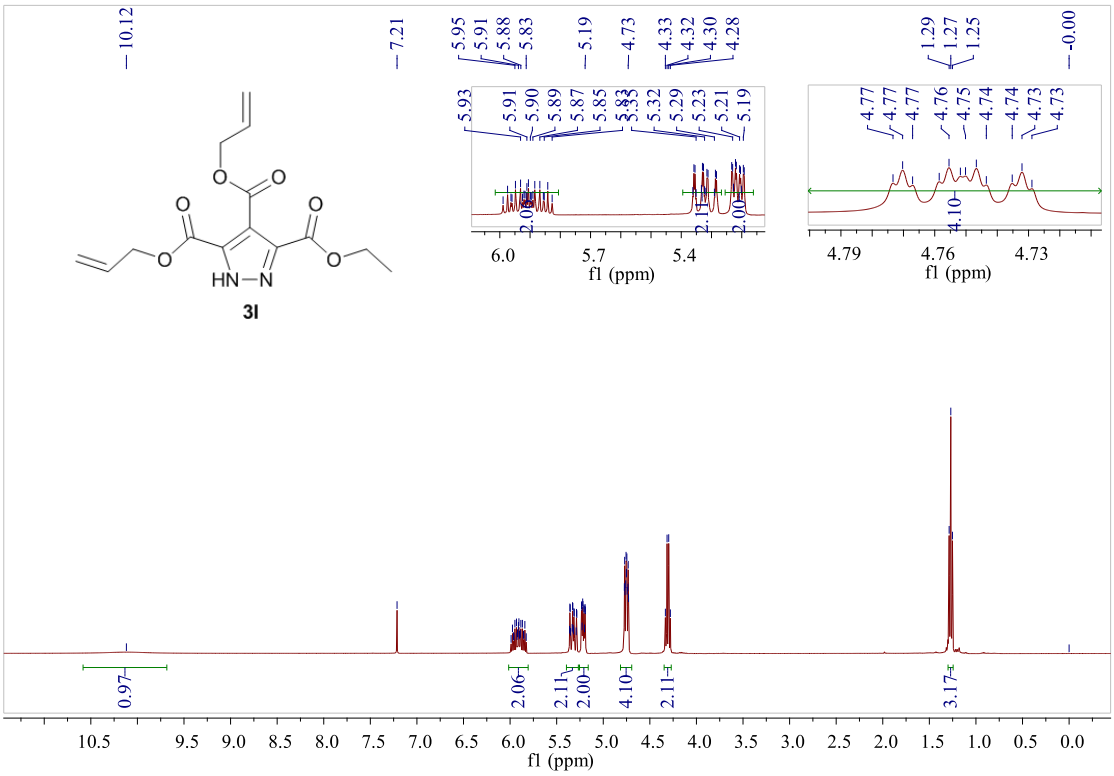
139.67
109.87
77.32
77.00
76.68
61.05
38.63
36.28
13.98
3k
161.18
161.11
161.5
161.3
161.1
160.9
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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5.83
5.19
4.73
4.33
4.32
4.30
4.28
1.29
1.27
1.25
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3l
fl (ppm)
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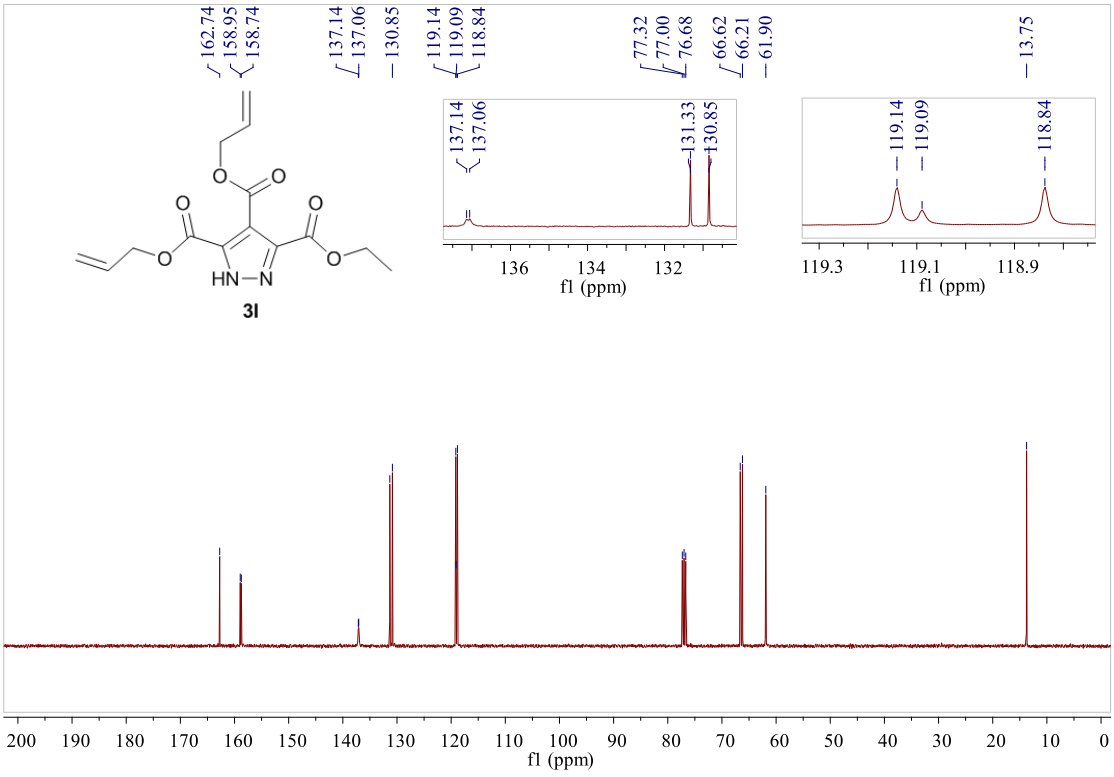
2.06
2.11
2.00
4.10
2.11
3.17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158.74
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66.62
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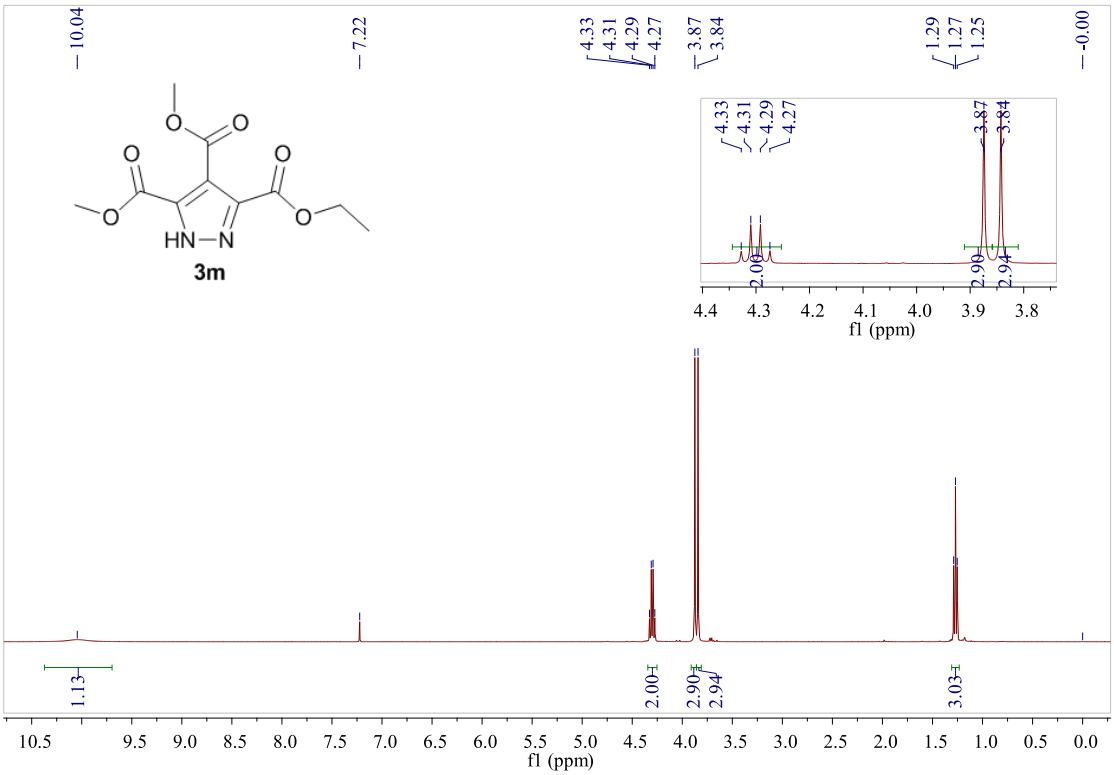
61.90
13.75
3l
fl (ppm)


10.04
7.22
4.33
4.31
4.29
4.27
3.87
3.84
1.29
1.27
1.25
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3m
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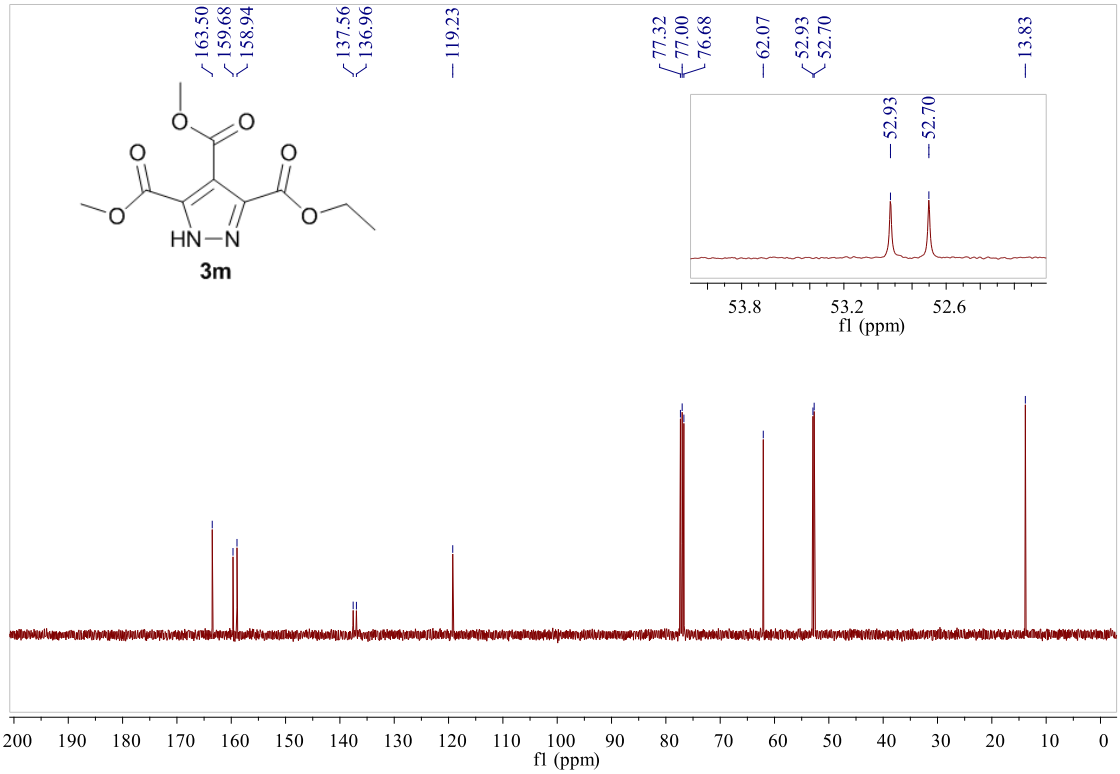
2.90
2.94
3.03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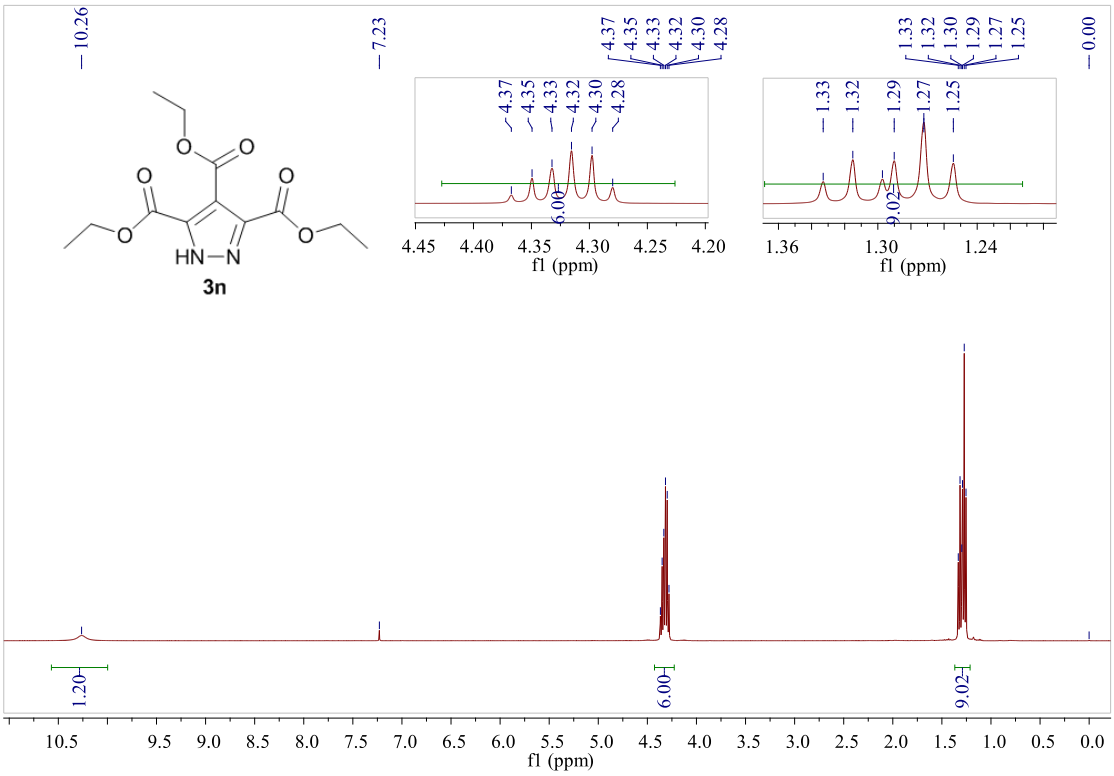
76.68
62.07
52.93
52.70
13.83
HN—N
3m
fl (ppm)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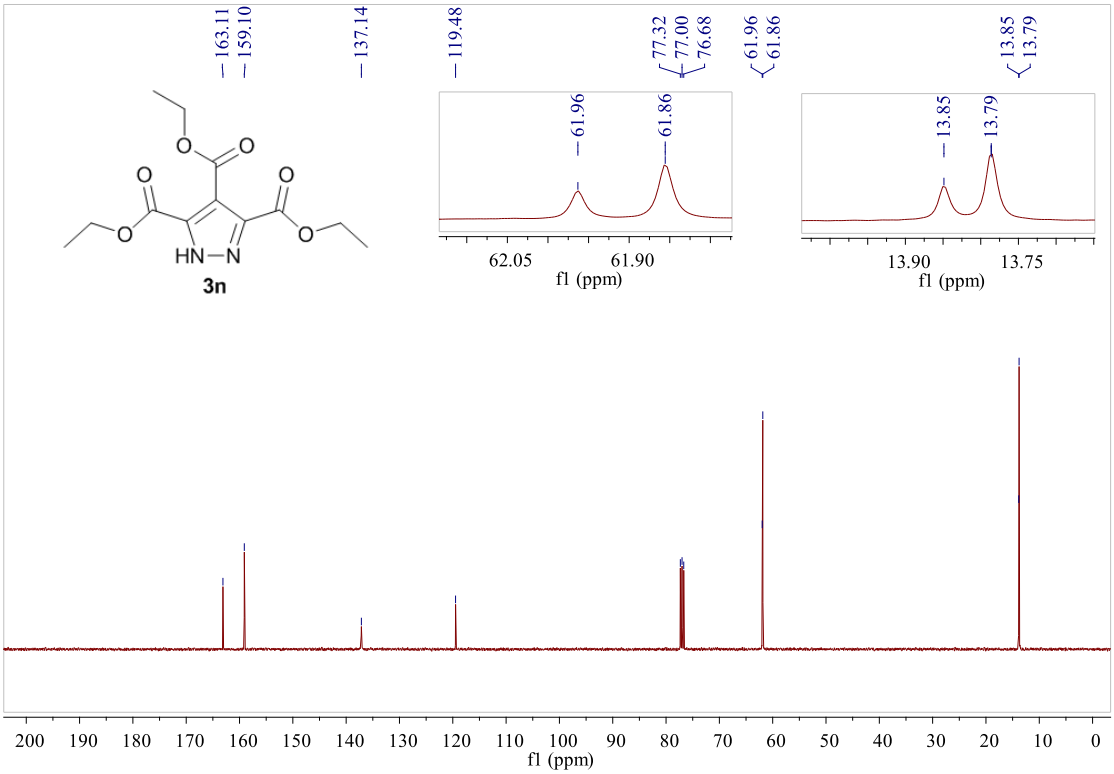
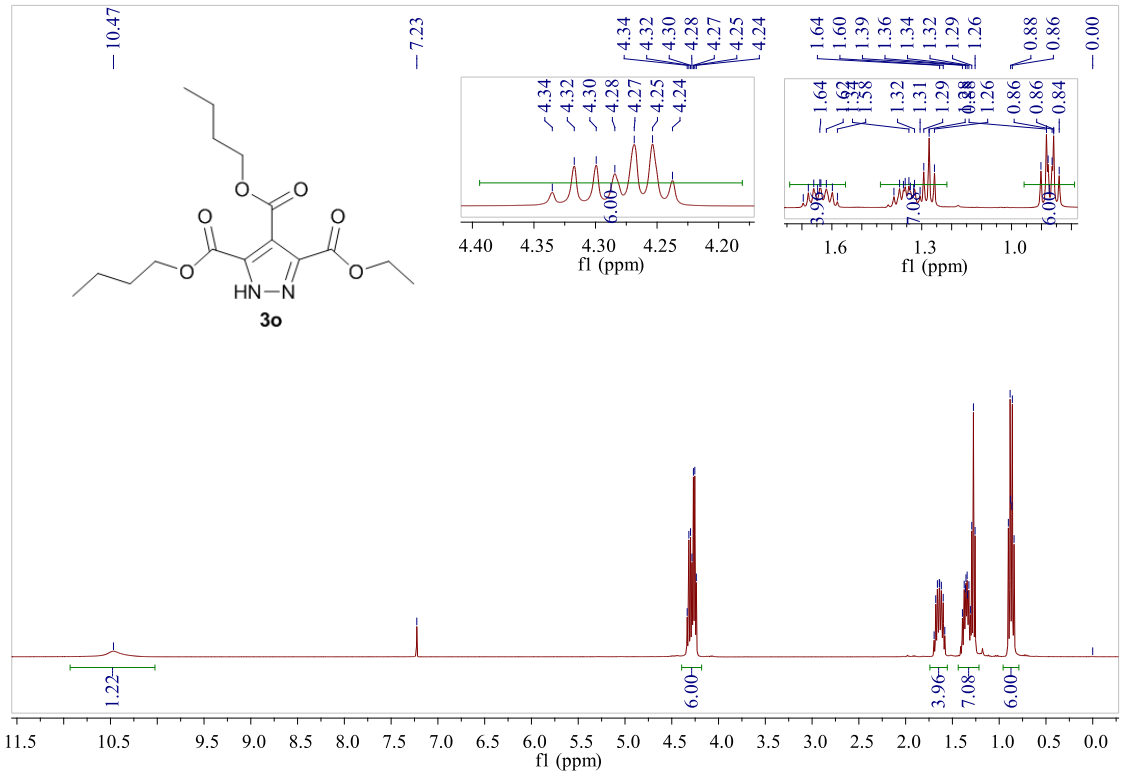
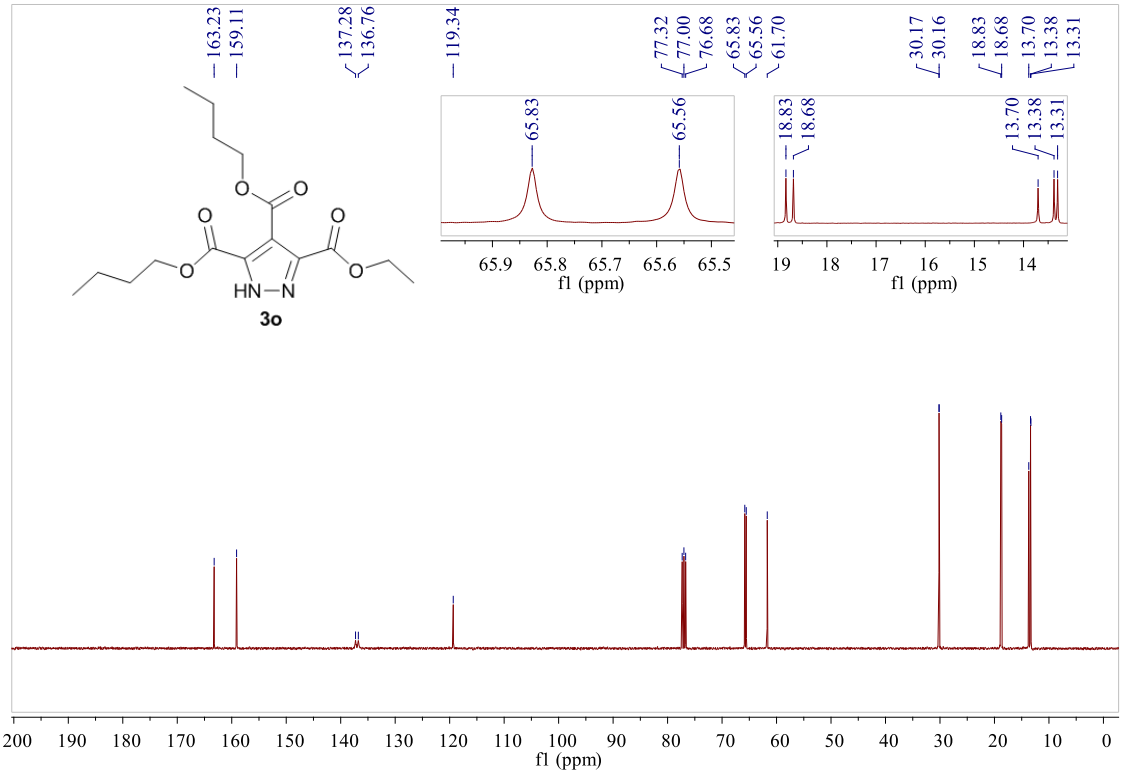
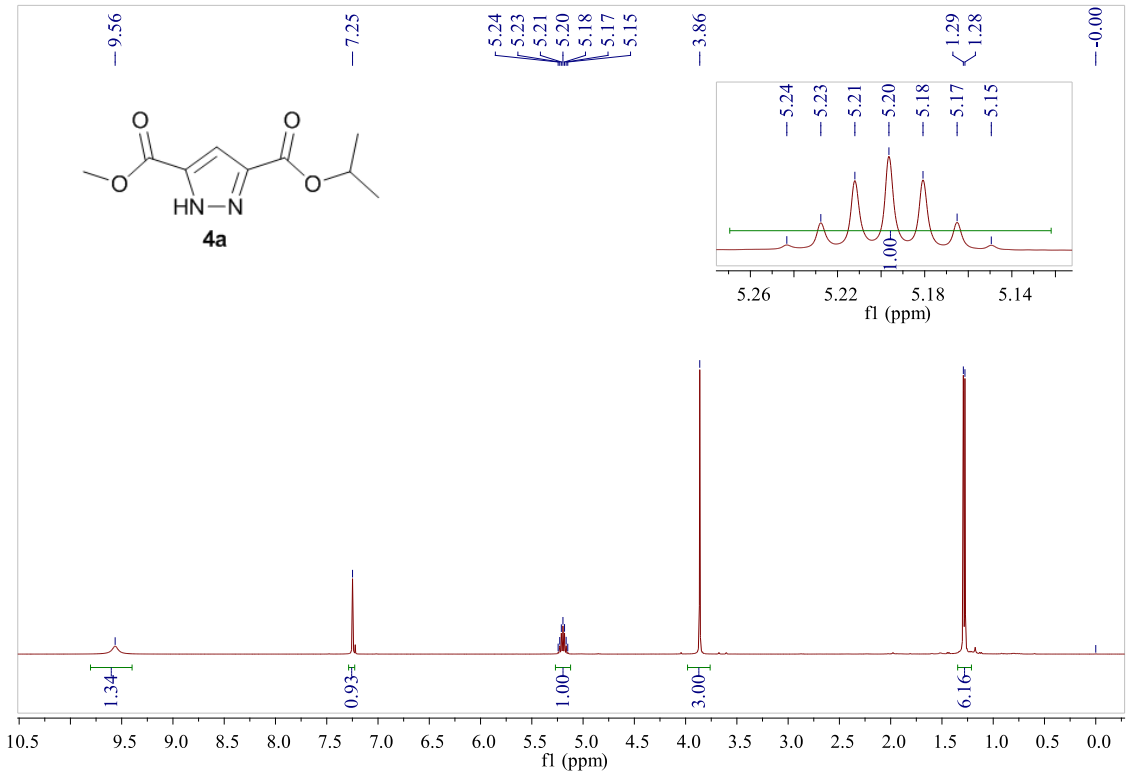
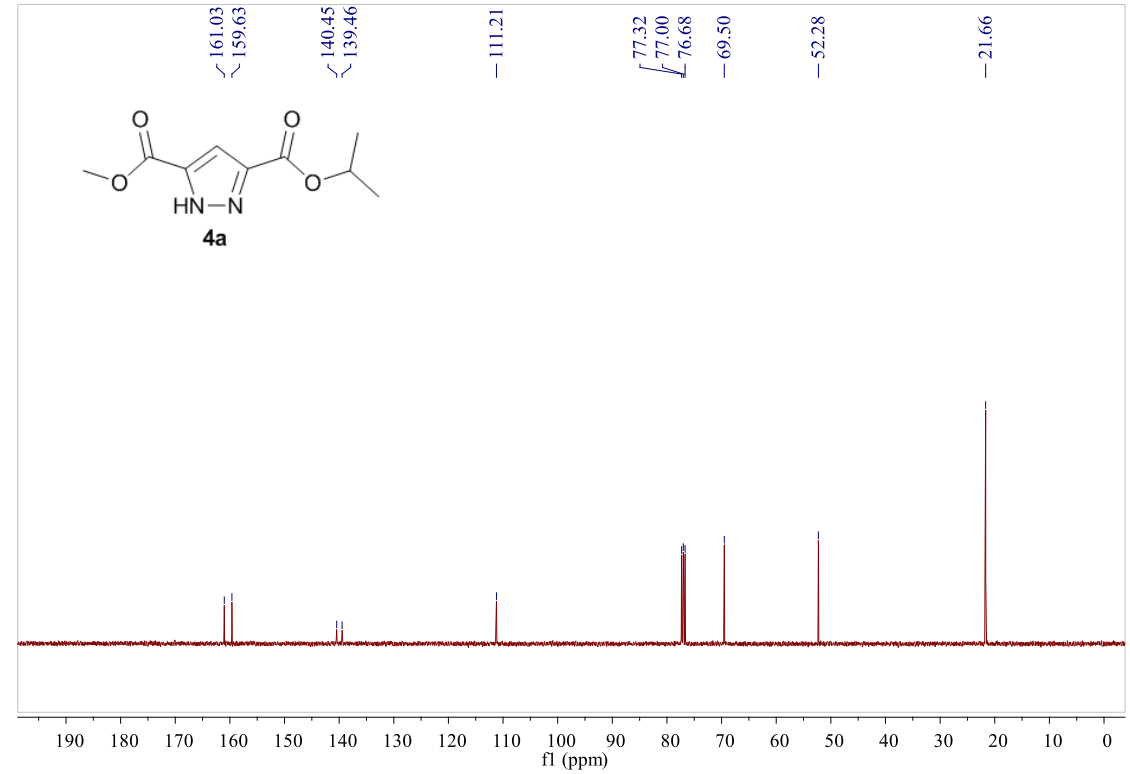
4.35
4.33
4.32
4.30
4.28
1.33
1.32
1.30
1.29
1.27
1.25
0.00
3n
6.00
9.02
1.20
6.00
9.02
fl (ppm)

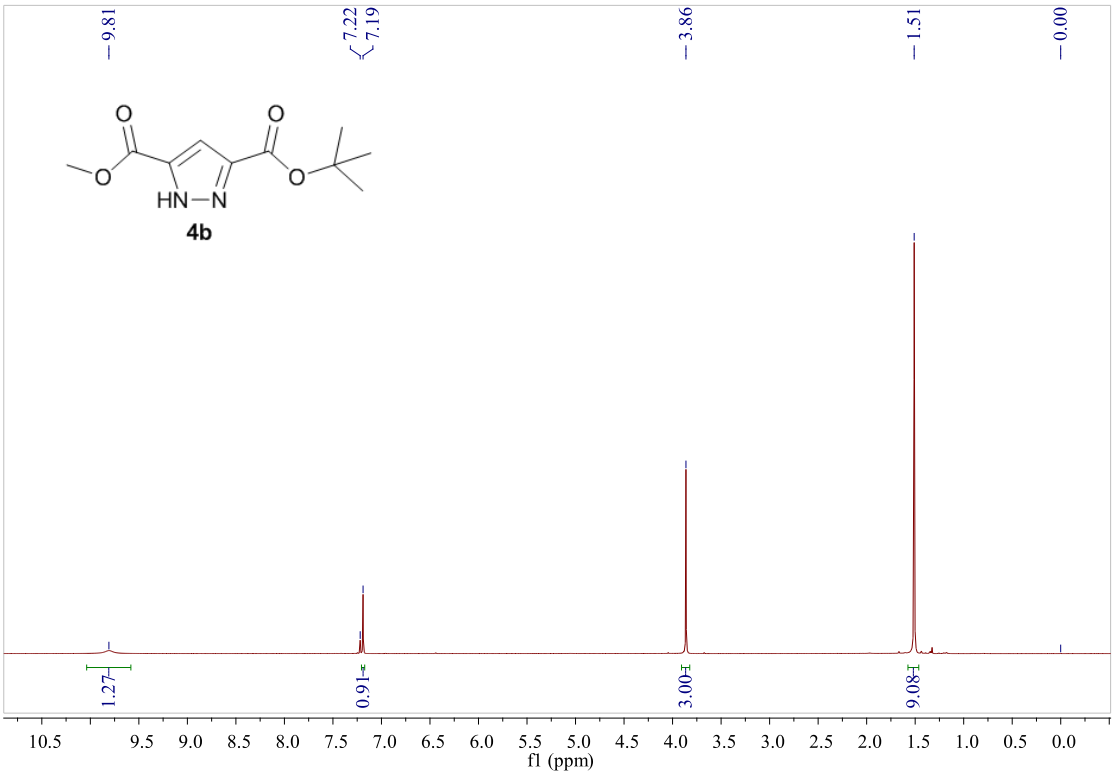

163.11
159.10
137.14
119.48
77.32
77.00
76.68
61.96
61.86
13.85
13.79
3n
fl (ppm)

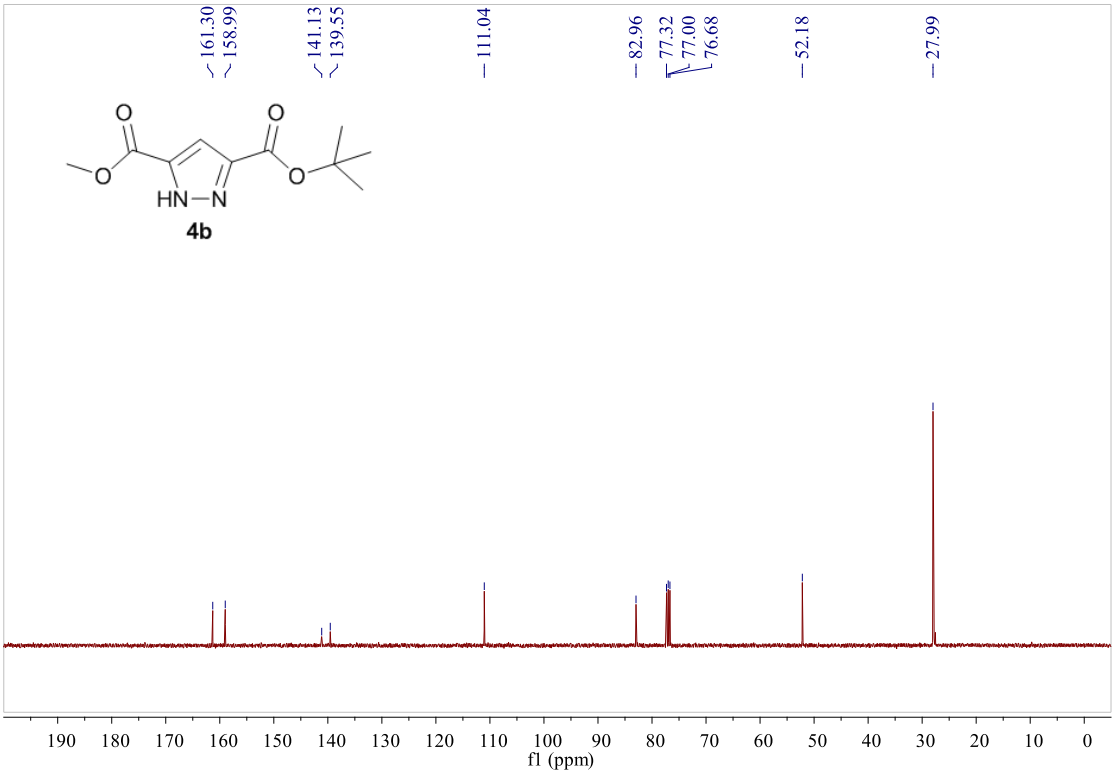

10.47
7.23
4.34
4.32
4.30
4.28
4.27
4.25
4.24
1.64
1.60
1.39
1.36
1.34
1.32
1.29
1.26
0.88
0.86
0.00
HN—N
3o
fl (ppm)
1.22
6.00
3.96
7.08
6.00

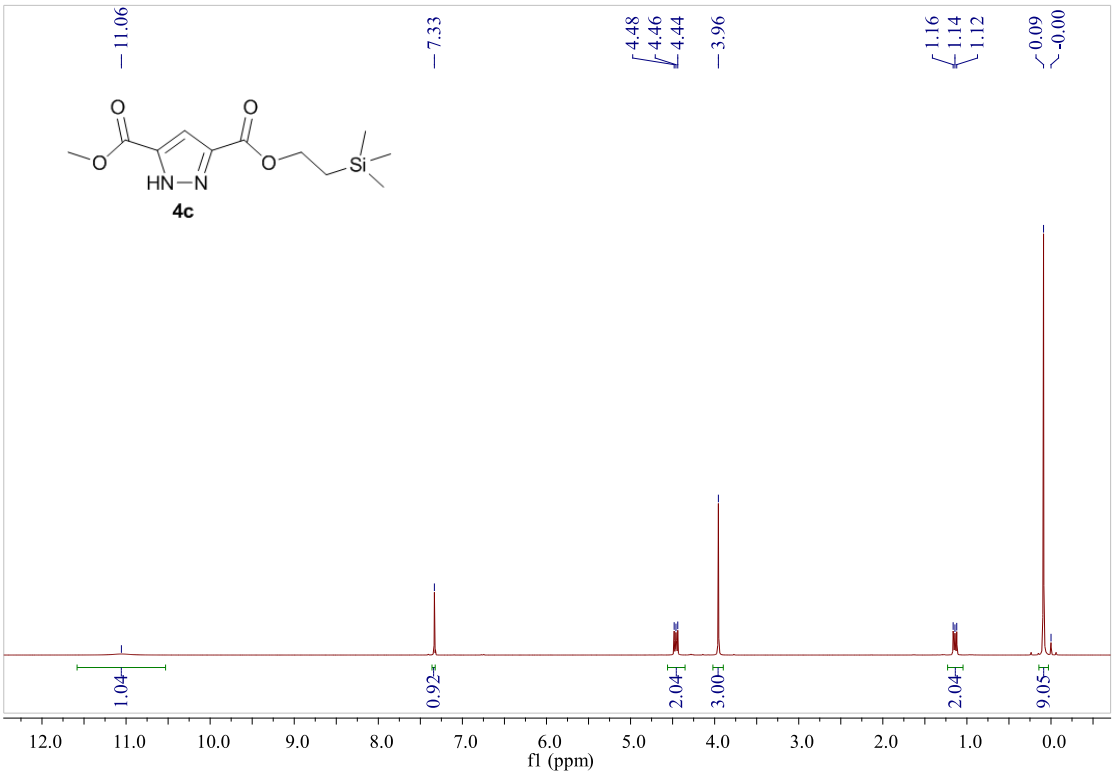

163.23
159.11
137.28
136.76
119.34
77.32
77.00
76.68
65.83
65.56
61.70
30.17
30.16
18.83
18.68
13.70
13.38
13.31
HN—N
3o
fl (ppm)

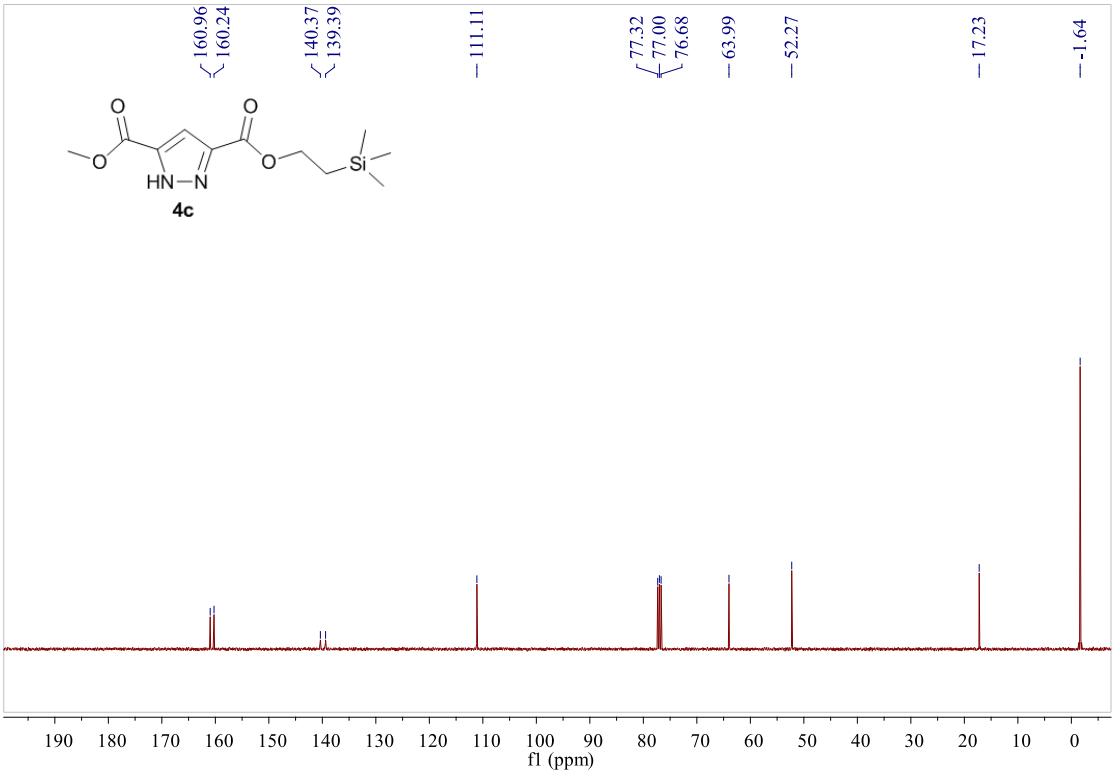

9.56
7.25
5.24
5.23
5.21
5.20
5.18
5.17
5.15
3.86
1.29
1.28
-0.00
HN—N
4a
1.00
f1 (ppm)
1.34
0.93
1.00
3.00
6.16
f1 (ppm)

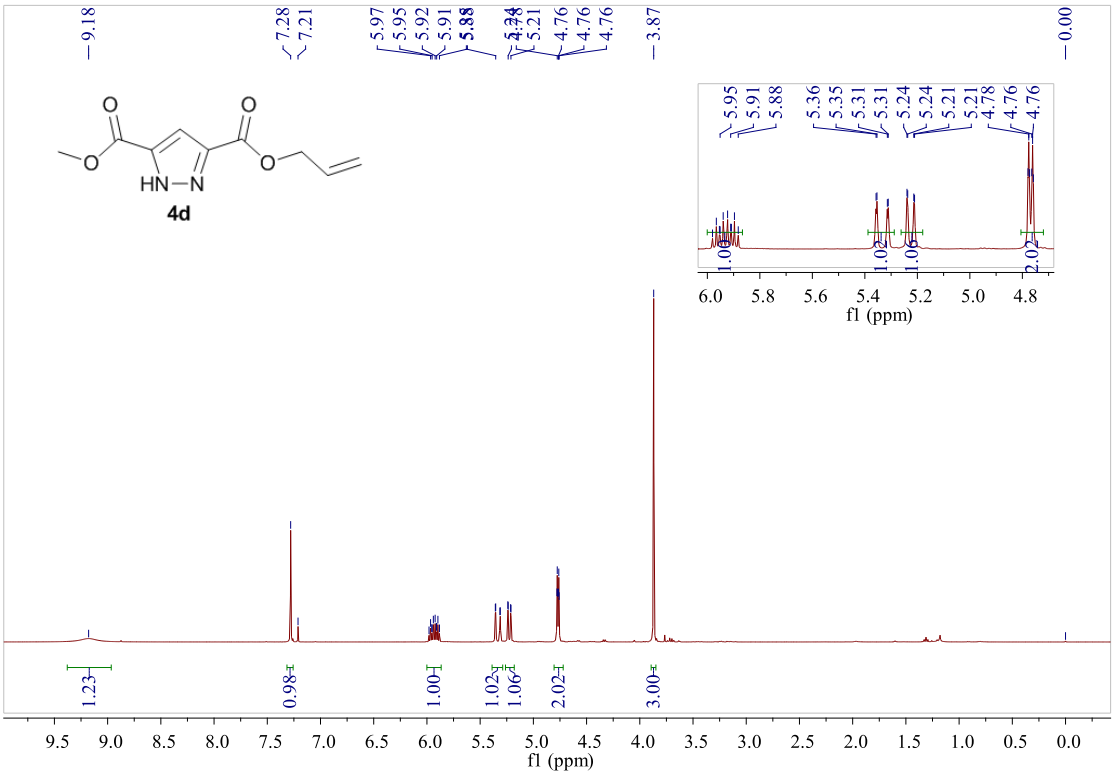

161.03
159.63
140.45
139.46
111.21
77.32
77.00
76.68
69.50
52.28
21.66
HN—N
4a
f1 (ppm)

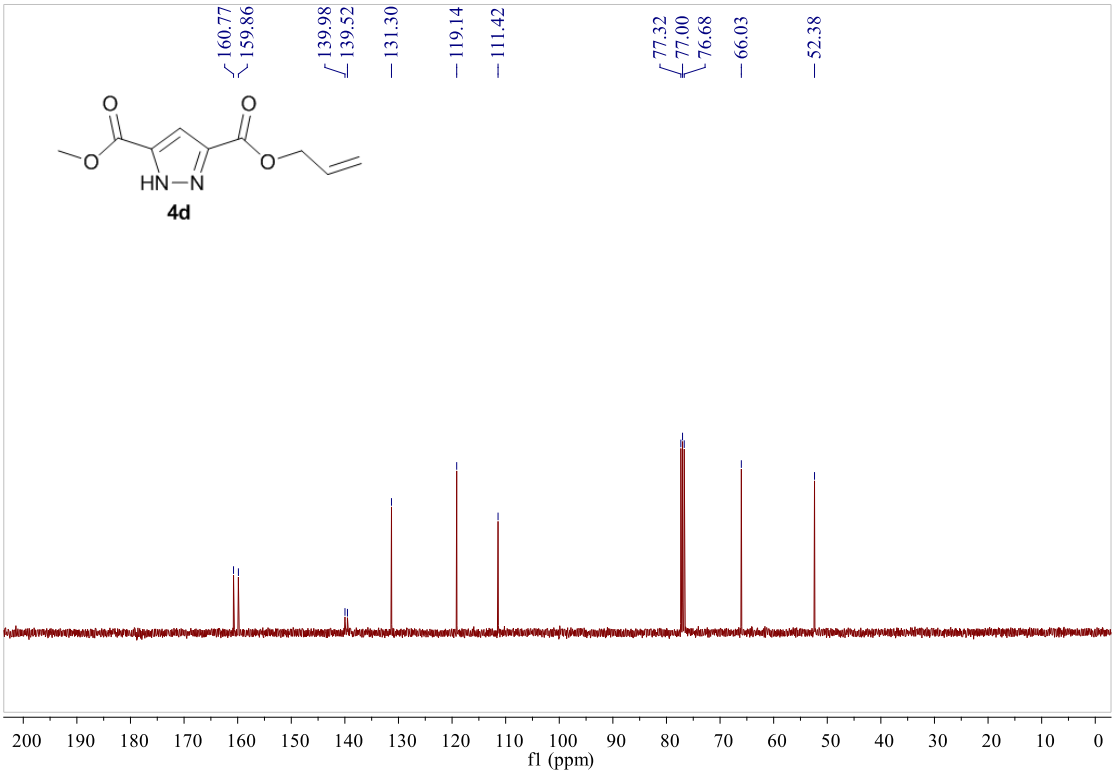

9.81
7.22
7.19
3.86
1.51
0.00
4b
1.27
0.91
3.00
9.08
fl (ppm)

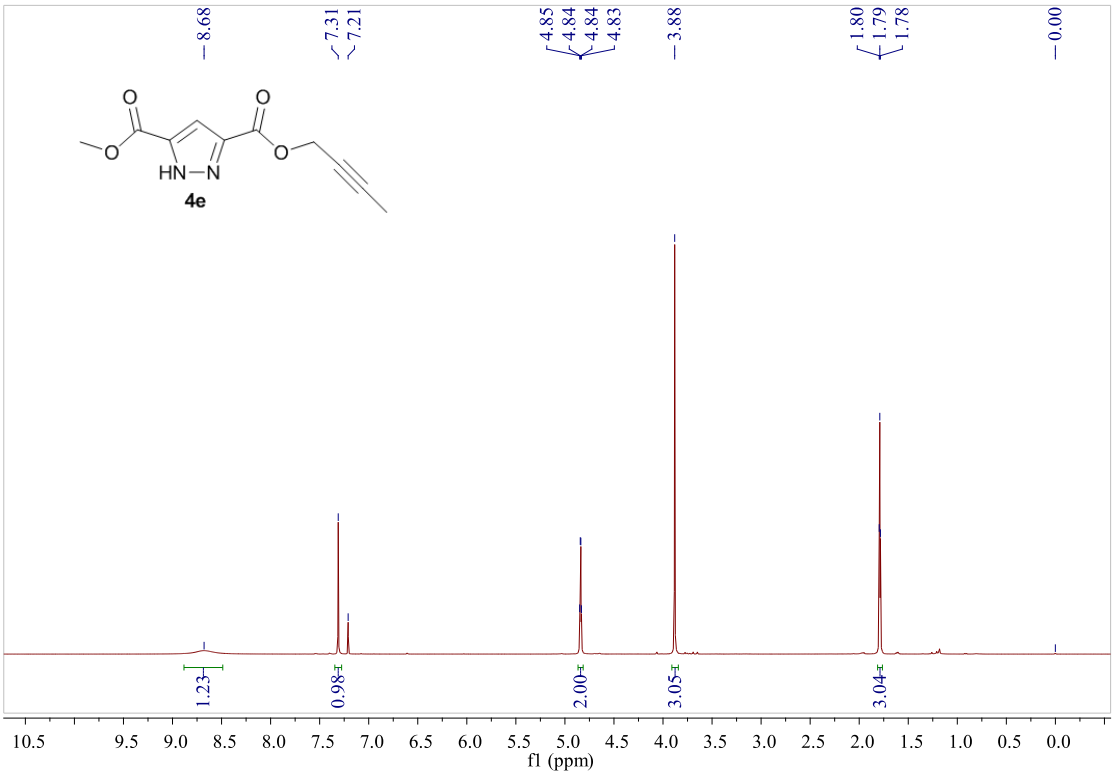

161.30
158.99
141.13
139.55
111.04
82.96
77.32
77.00
76.68
52.18
27.99
4b
fl (ppm)

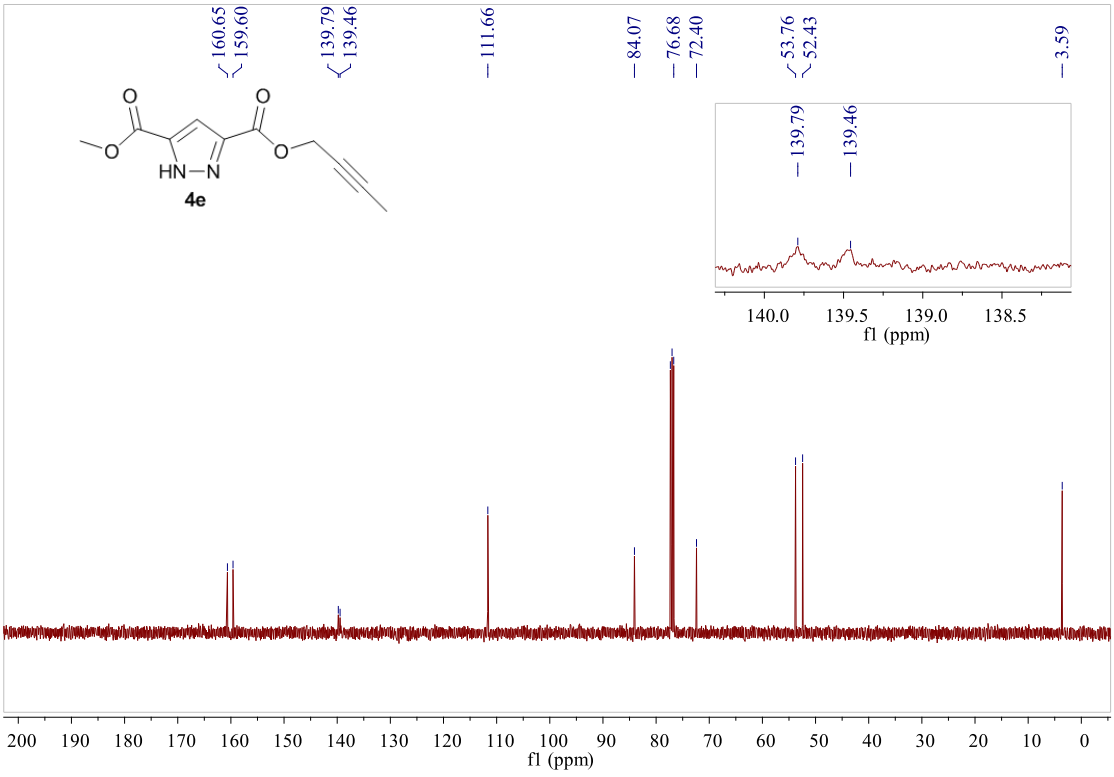

11.06
7.33
4.48
4.46
4.44
3.96
1.16
1.14
1.12
0.09
-0.00
4c
1.04
0.92
2.04
3.00
2.04
9.05
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

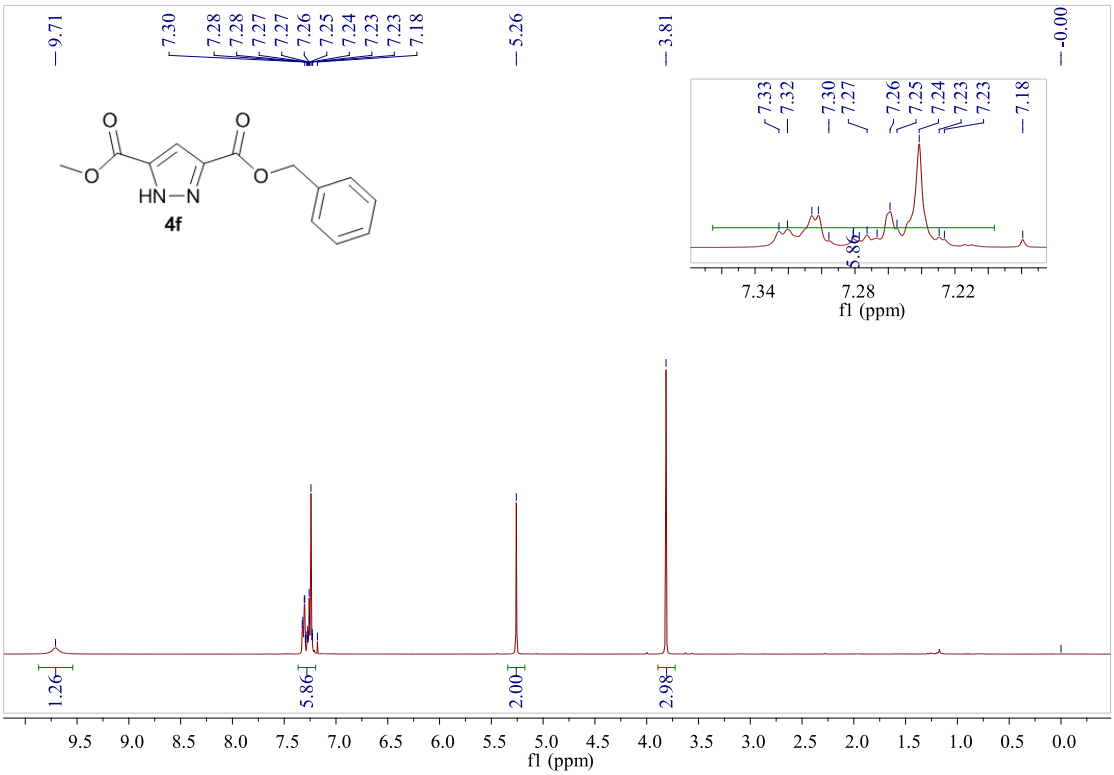

160.96
160.24
140.37
139.39
111.11
77.32
77.00
76.68
63.99
52.27
17.23
-1.64
4c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

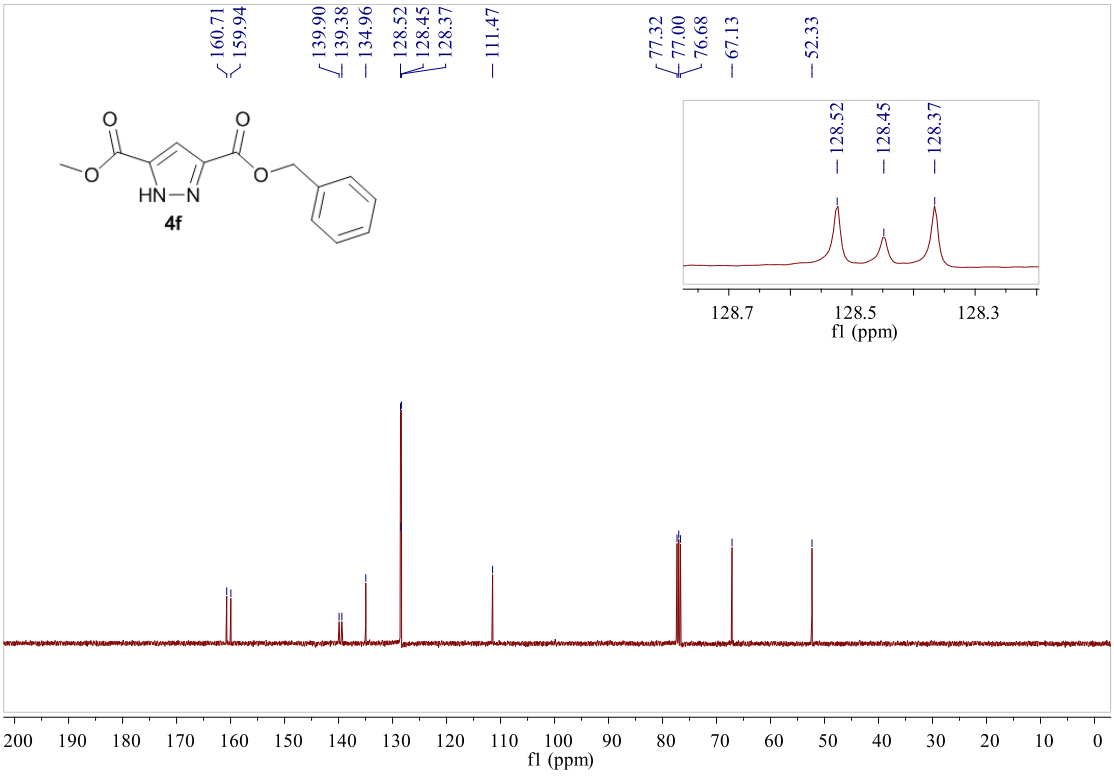

9.18
7.28
7.21
5.97
5.95
5.92
5.91
5.88
5.36
5.35
5.31
5.31
5.24
5.24
5.21
5.21
4.78
4.76
4.76
3.87
0.00
HN—N
4d
1.23
0.98
1.00
1.02
1.06
2.02
3.00
fl (ppm)

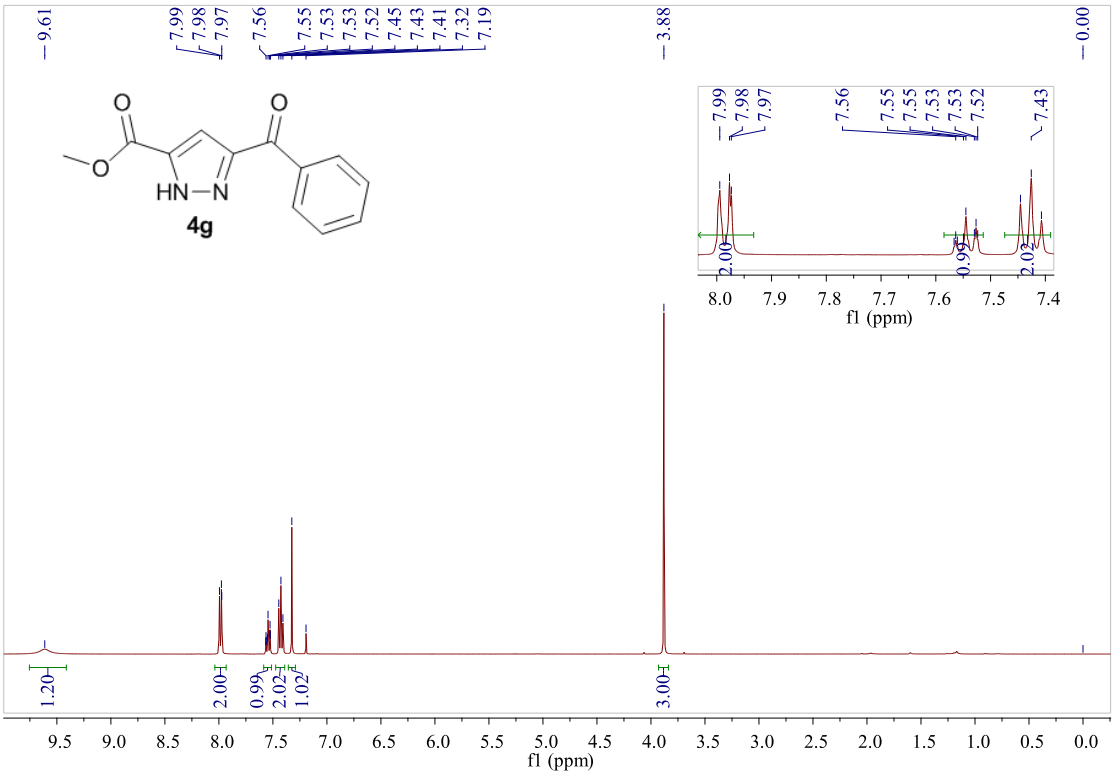

160.77
159.86
139.98
139.52
131.30
119.14
111.42
77.32
77.00
76.68
66.03
52.38
HN—N
4d
fl (ppm)

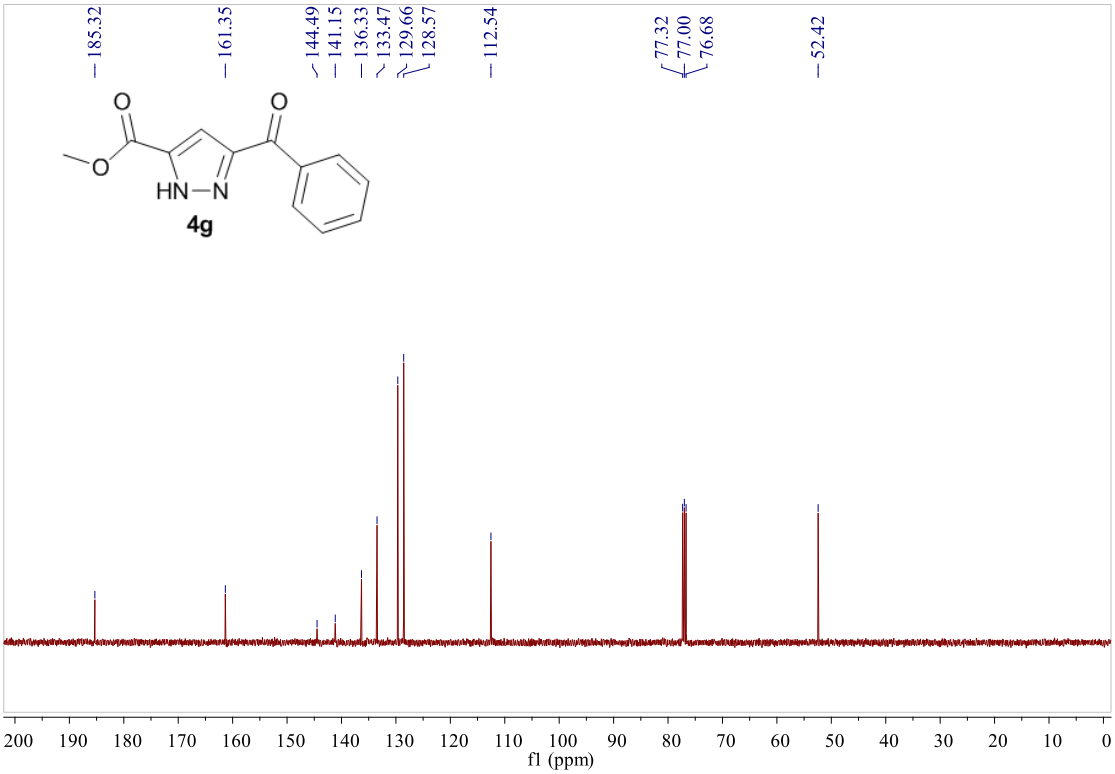

8.68
7.31
7.21
4.85
4.84
4.84
4.83
3.88
1.80
1.79
1.78
0.00
4e
1.23
0.98
2.00
3.05
3.04
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

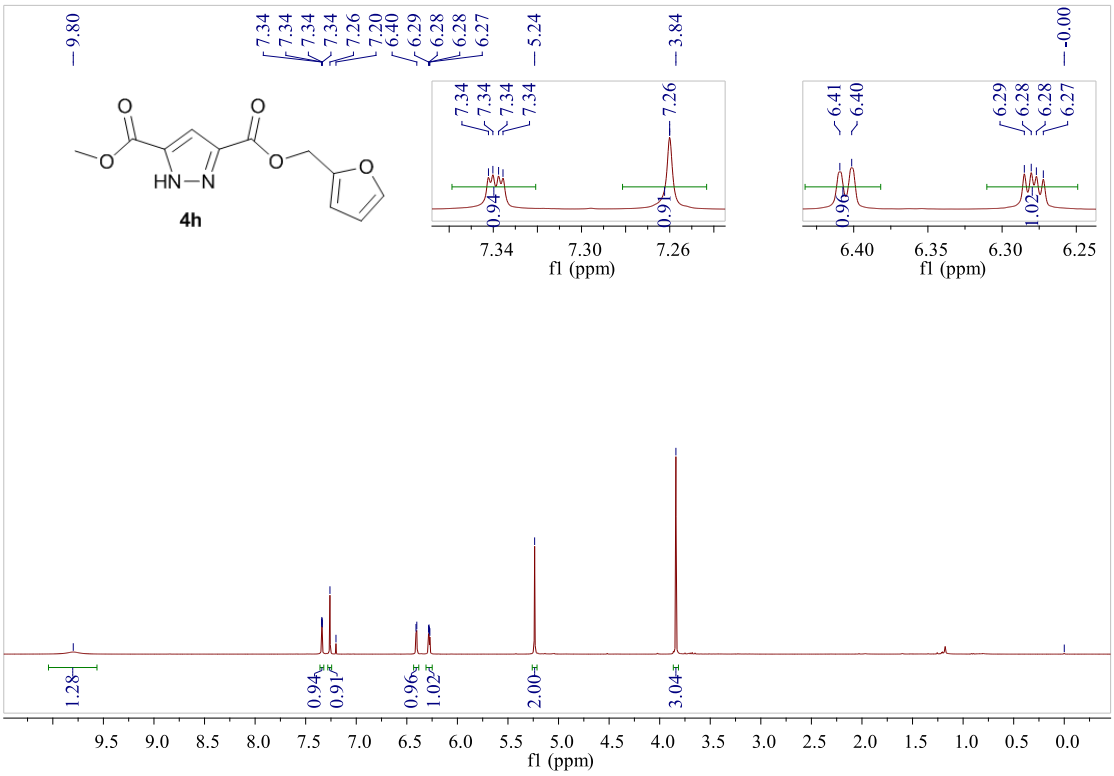

160.65
159.60
139.79
139.46
111.66
84.07
76.68
72.40
53.76
52.43
3.59
4e
139.79
139.46
140.0 139.5 139.0 138.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

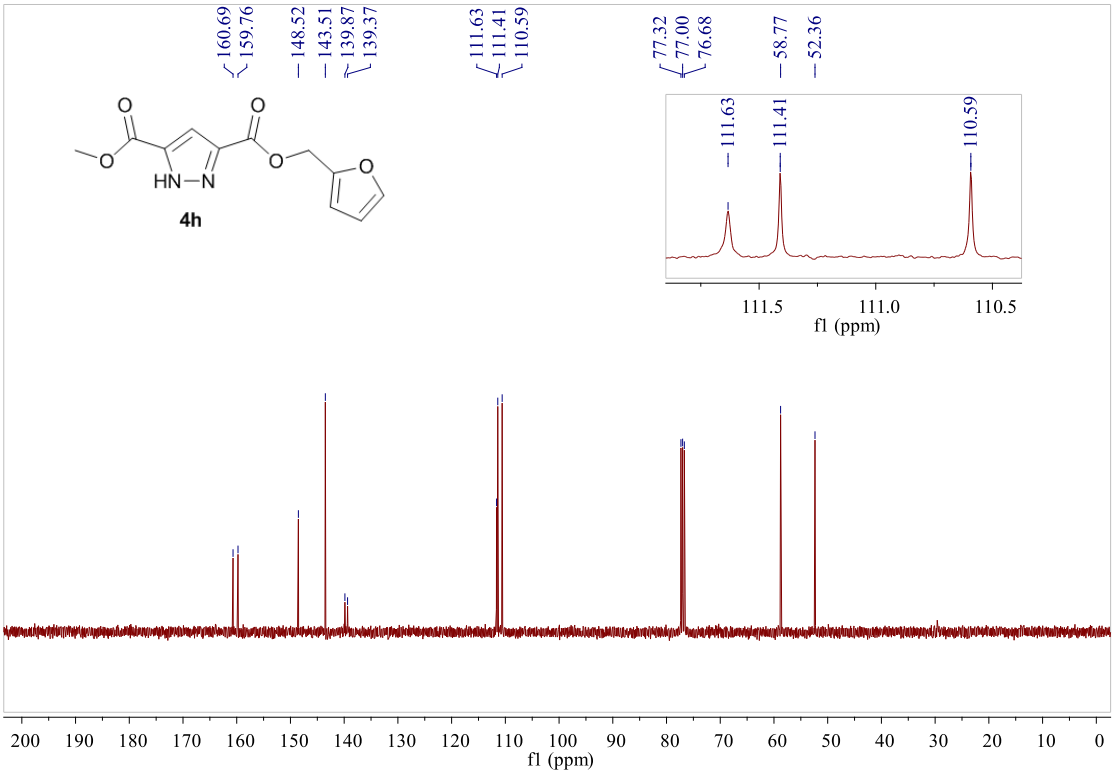

9.71
7.30
7.28
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.23
7.18
5.26
3.81
-0.00
HN—N
4f
7.33
7.32
7.30
7.27
7.26
7.25
7.24
7.23
7.23
7.18
5.86
7.34
7.28
7.22
f1 (ppm)
1.26
5.86
2.00
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

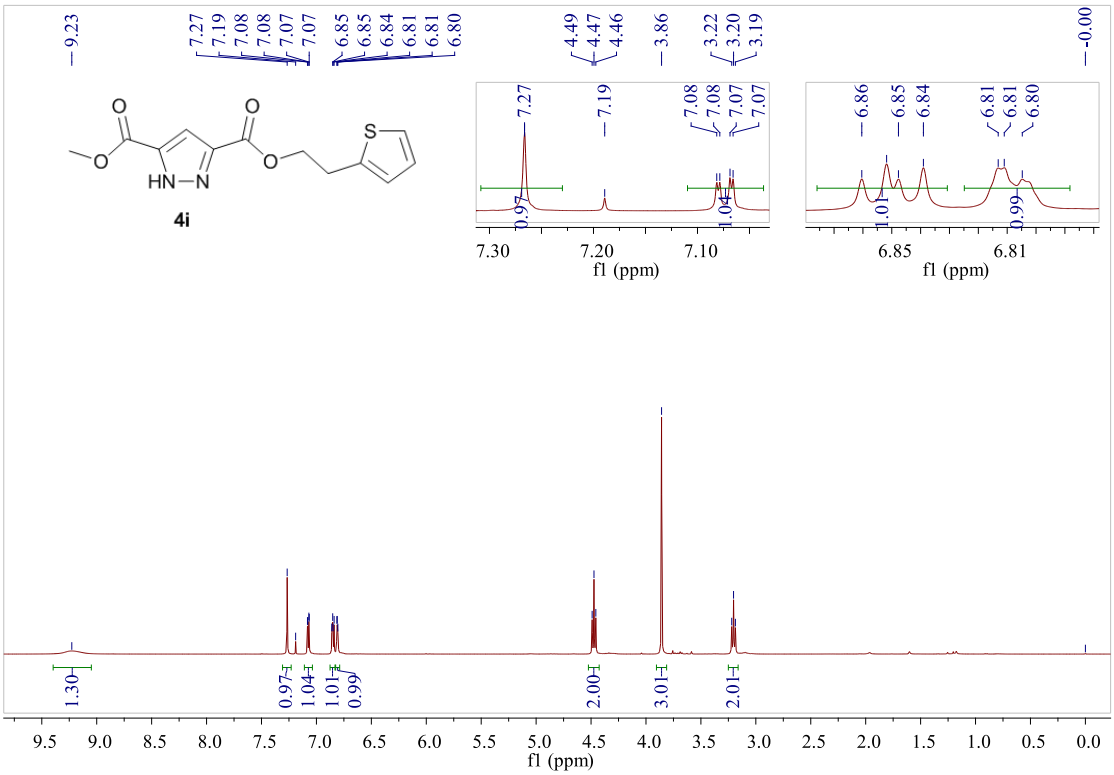

160.71
159.94
139.90
139.38
134.96
128.52
128.45
128.37
111.47
77.32
77.00
76.68
67.13
52.33
HN—N
4f
128.52
128.45
128.37
128.7
128.5
128.3
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

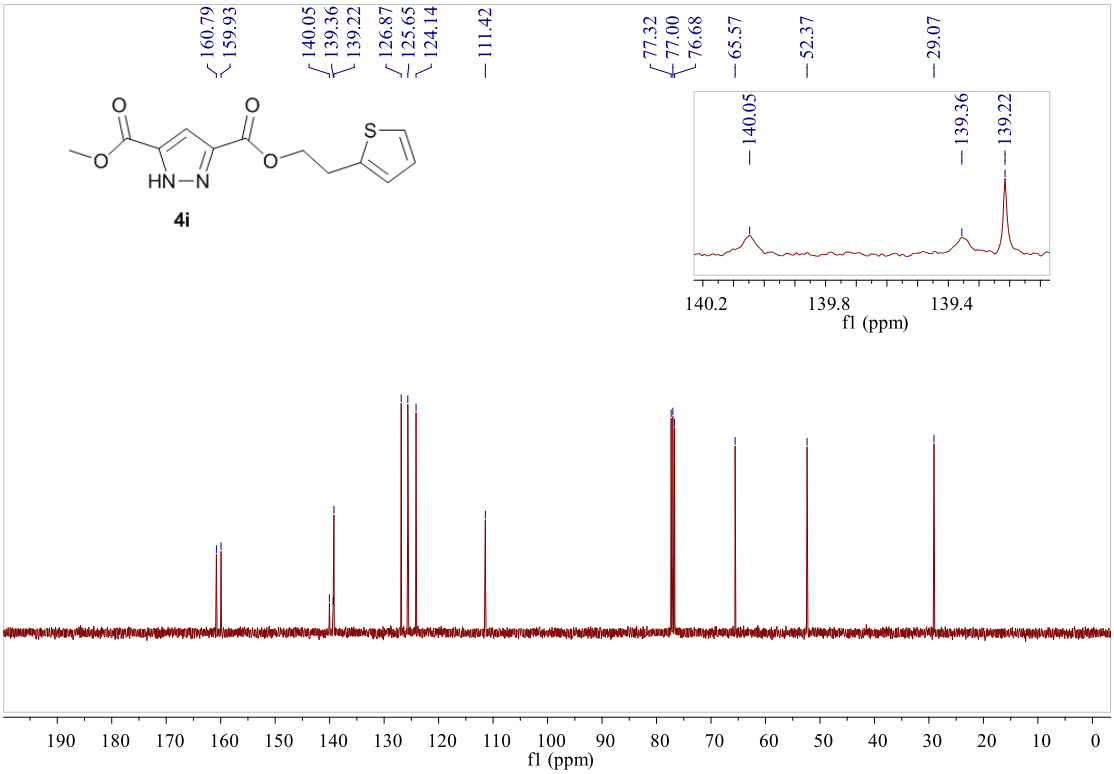

9.61
7.99
7.98
7.97
7.56
7.55
7.53
7.53
7.52
7.45
7.43
7.41
7.32
7.19
3.88
0.00
4g
1.20
2.00
0.99
2.02
1.02
3.00
fl (ppm)

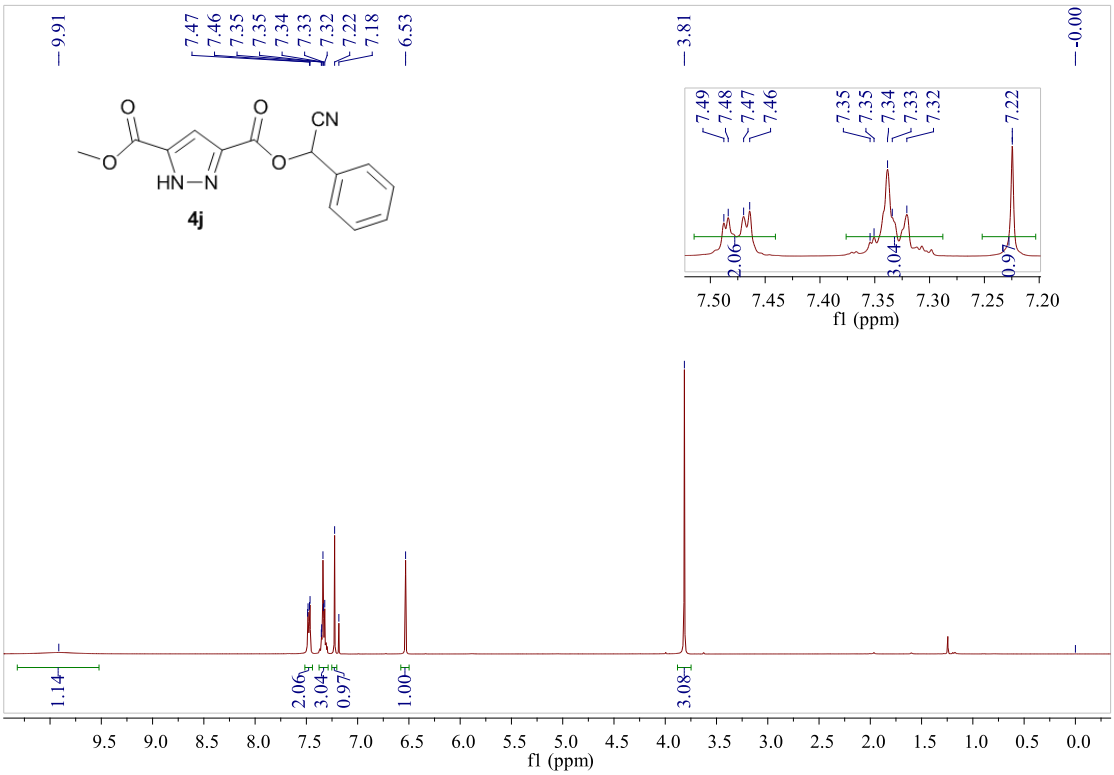

185.32
161.35
144.49
141.15
136.33
133.47
129.66
128.57
112.54
77.32
77.00
76.68
52.42
4g
fl (ppm)

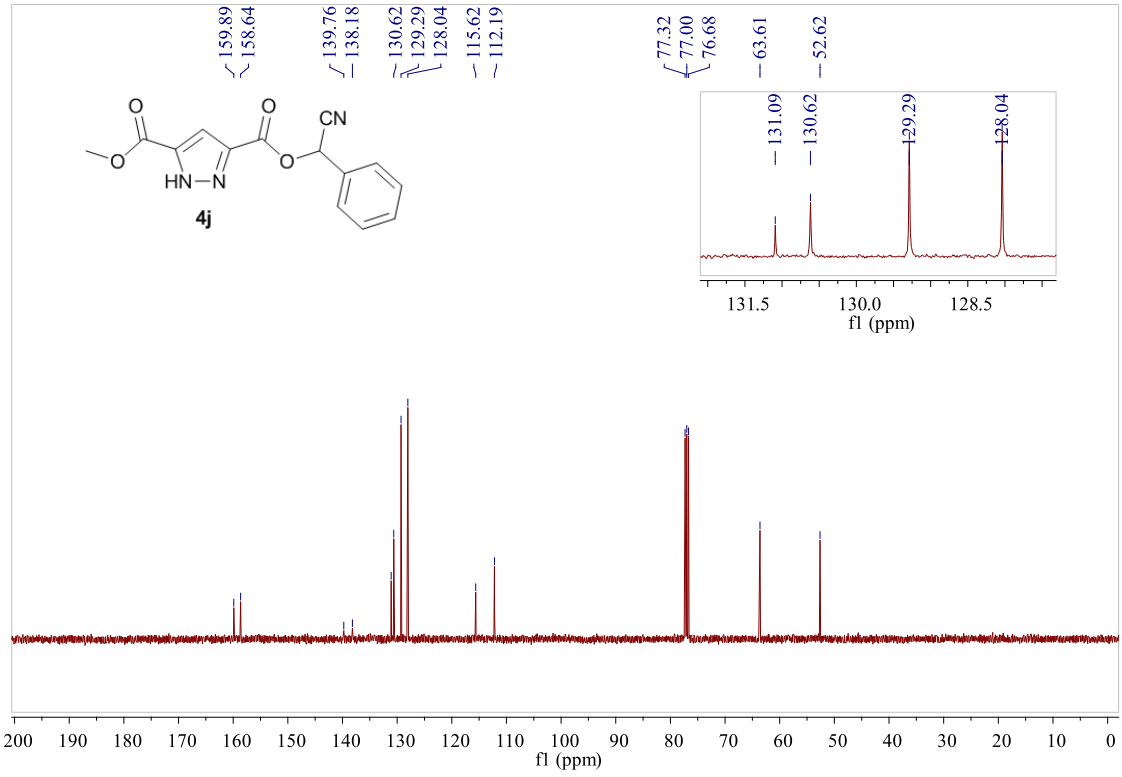

9.80
7.34
7.34
7.34
7.34
7.26
7.20
6.40
6.29
6.28
6.28
6.27
5.24
3.84
-0.00
HN—N
4h
7.34
7.34
7.34
7.34
7.26
0.94
0.91
7.34
7.30
7.26
fl (ppm)
6.41
6.40
6.29
6.28
6.28
6.27
0.96
1.02
6.40
6.35
6.30
6.25
fl (ppm)
1.28
0.94
0.91
0.96
1.02
2.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
fl (ppm)

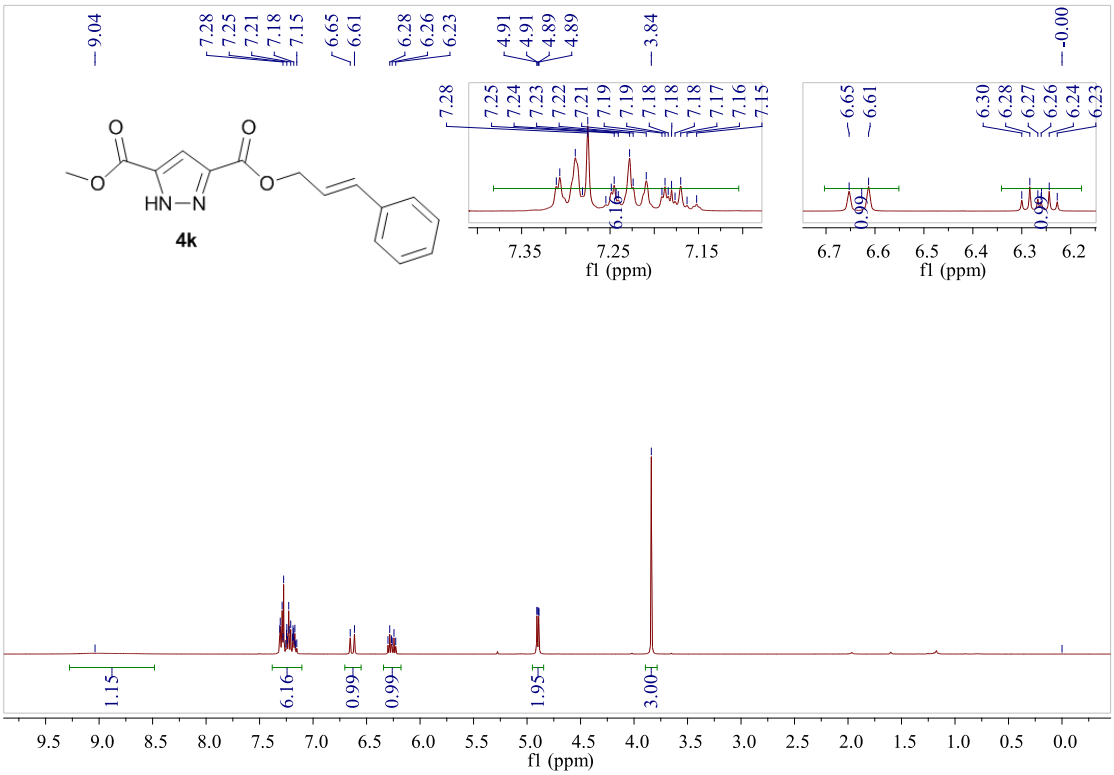

160.69
159.76
148.52
143.51
139.87
139.37
111.63
111.41
110.59
77.32
77.00
76.68
58.77
52.36
HN—N
4h
111.63
111.41
110.59
111.5
111.0
110.5
fl (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
fl (ppm)

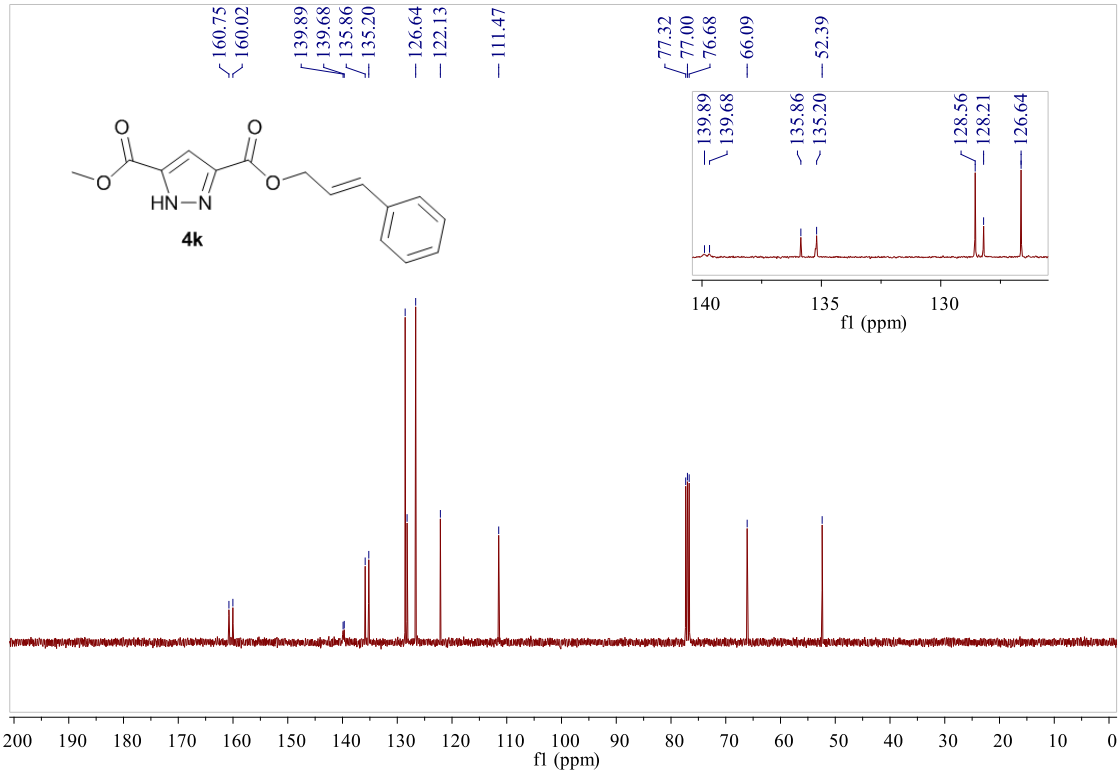

9.23
7.27
7.19
7.08
7.08
7.07
7.07
6.85
6.85
6.84
6.81
6.81
6.80
4.49
4.47
4.46
3.86
3.22
3.20
3.19
-0.00
4i
7.27
7.19
7.08
7.08
7.07
7.07
0.97
1.04
7.30
7.20
7.10
f1 (ppm)
6.86
6.85
6.84
6.81
6.81
6.80
1.01
0.99
6.85
6.81
f1 (ppm)
1.30
0.97
1.04
1.01
0.99
2.00
3.01
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

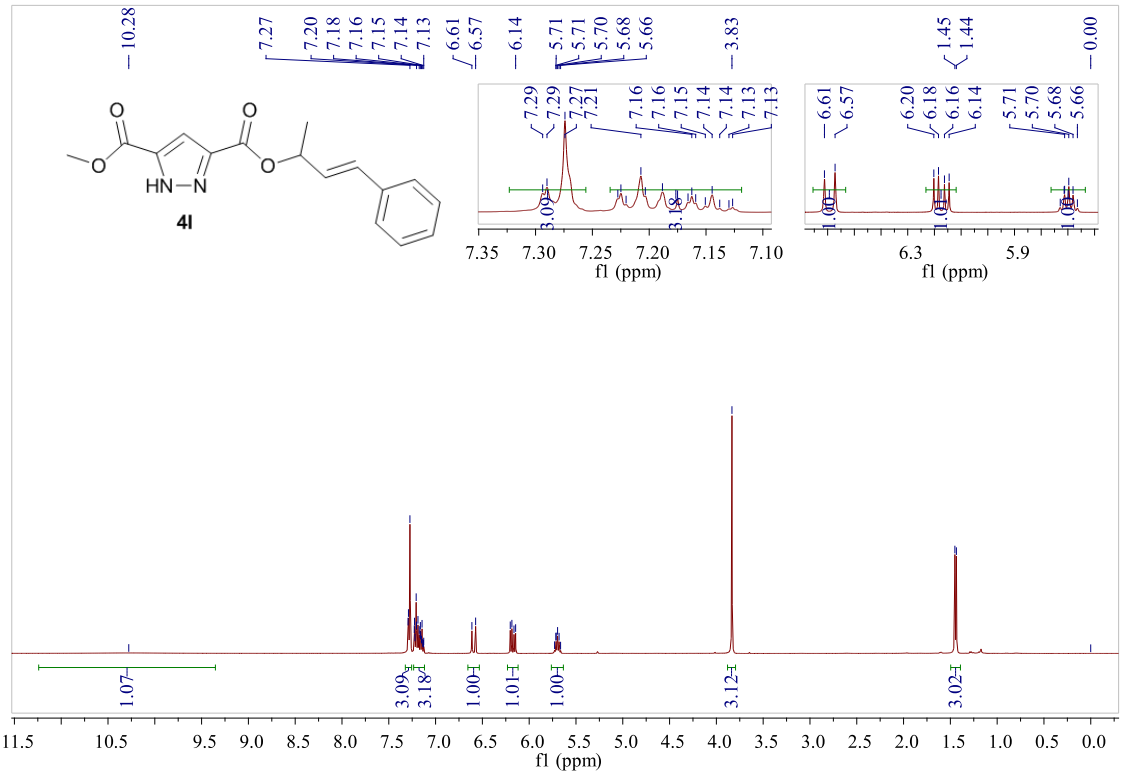

160.79
159.93
140.05
139.36
139.22
126.87
125.65
124.14
111.42
77.32
77.00
76.68
65.57
52.37
29.07
4i
140.05
139.36
139.22
140.2
139.8
139.4
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

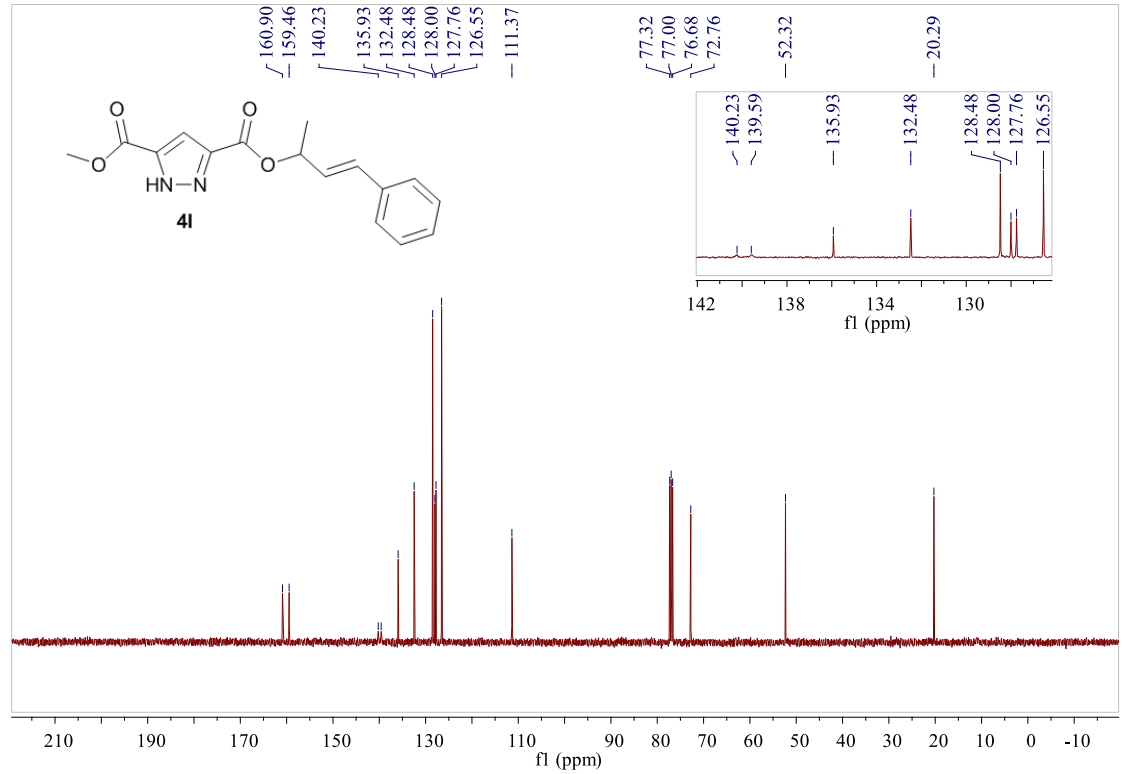

9.91
7.47
7.46
7.35
7.35
7.34
7.33
7.32
7.22
7.18
6.53
3.81
-0.00
O
O
CN
O
O
HN—N
4j
7.49
7.48
7.47
7.46
7.35
7.35
7.34
7.33
7.32
7.22
2.06
3.04
0.97
7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
1.14
2.06
3.04
0.97
1.00
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

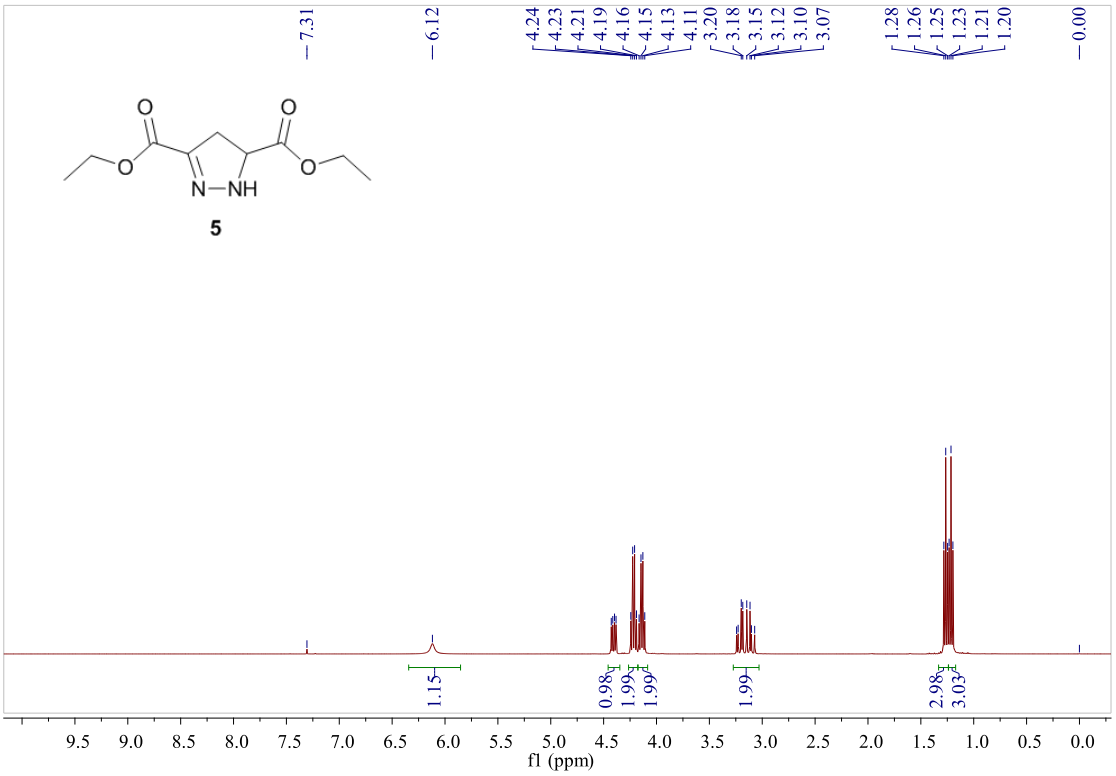

159.89
158.64
139.76
138.18
130.62
129.29
128.04
115.62
112.19
77.32
77.00
76.68
63.61
52.62
O
O
CN
O
O
HN—N
4j
131.09
130.62
129.29
128.04
131.5 130.0 128.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

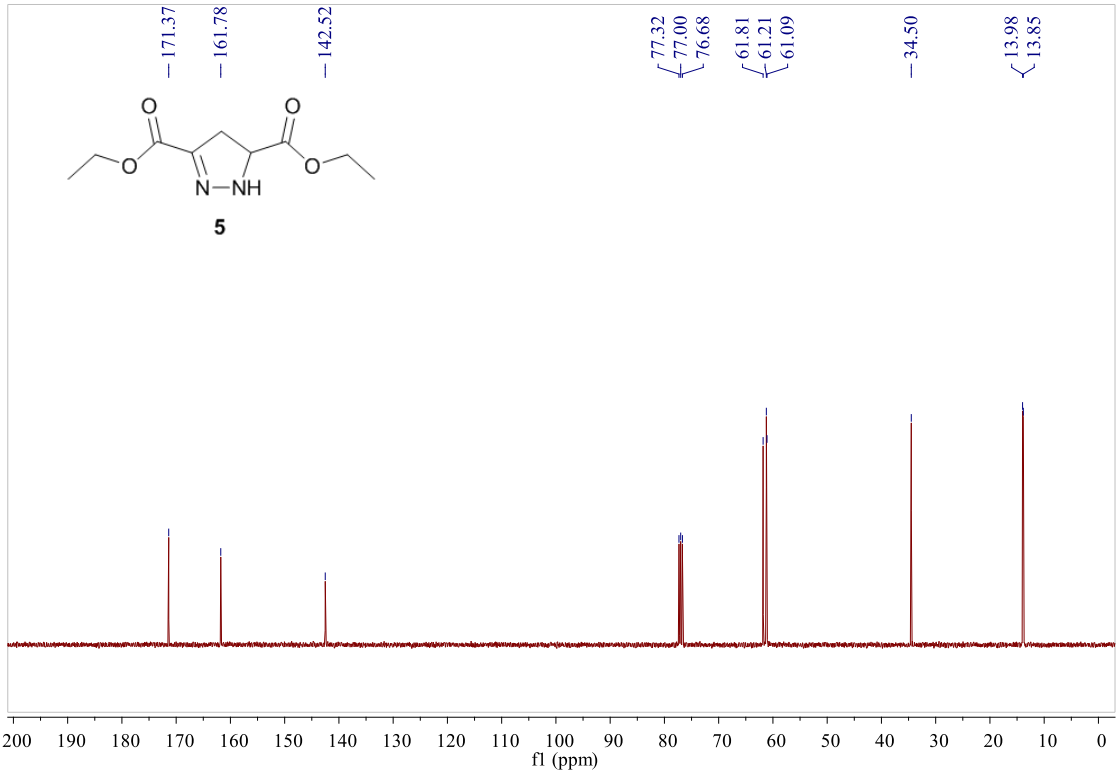

9.04
7.28
7.25
7.21
7.18
7.15
6.65
6.61
6.28
6.26
6.23
4.91
4.91
4.89
4.89
3.84
-0.00
4k
fl (ppm)
1.15
6.16
0.99
0.99
1.95
3.00


160.75
160.02
139.89
139.68
135.86
135.20
126.64
122.13
111.47
77.32
77.00
76.68
66.09
52.39
4k
128.56
128.21
126.64
fl (ppm)


4l
fl (ppm)


4l
fl (ppm)


7.31
6.12
4.24
4.23
4.21
4.19
4.16
4.15
4.13
4.11
3.20
3.18
3.15
3.12
3.10
3.07
1.28
1.26
1.25
1.23
1.21
1.20
0.00
O
O
O
O
N—NH
5
1.15
0.98
1.99
1.99
1.99
2.98
3.03
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)


171.37
161.78
142.52
77.32
77.00
76.68
61.81
61.21
61.09
34.50
13.98
13.85
O
O
O
O
N—NH
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

XRD Data of the Compound 3k.

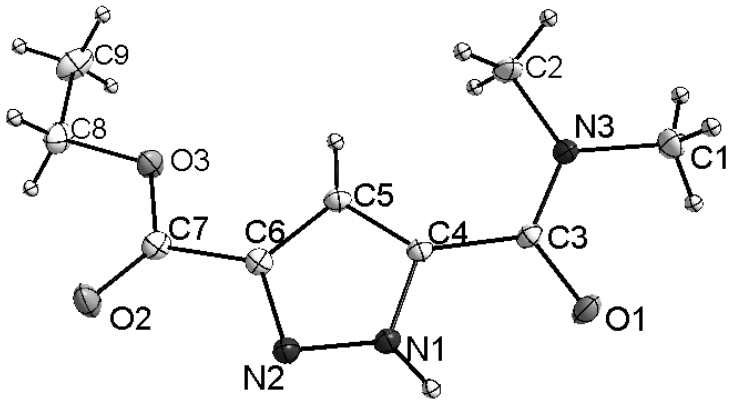


Figure S1. ORTEP structural drawing of **3k**. (CCDC: 1486515)

Table S1. Crystallography data for **3k**

complex	**3k**
Empirical formula	$C_9H_{13}N_3O_3$
Formula weight(g mol^{-1})	211.22
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	C2/c
Unit cell dimensions	a = 26.518(14) Å b = 6.018(3) Å c = 18.911(8) Å α = 90 ° β = 134.50(2) ° γ = 90 °
Volume ($Å^3$)	2152.5(19)
Z	8
ρ(g cm^{-3})	1.304
F(000)	896
Crystal size(mm^3)	0.44 x 0.32 x 0.30
Theta range for data collection	2.15 °to 25.50 °
Limiting indices	-30<=h<=32 -6<=k<=7 -22<=l<=22

Reflections collected / unique	4250 / 1992
Data / restraints / parameters	1992 / 0 / 139
GOF	0.982
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0656 *wR2* = 0.1744
R1,*wR2*(all data)	*R1* = 0.1052 *wR2* = 0.2175
Largest diff. peak and hole(e Å^3)	0.476 and -0.391

Table S2. Bond lengths [Å] and angles [°] for **3k**

N1-N2 1.340(3)	N1-C4 1.361(4)	N1-H1 0.9000	N2-C6 1.345(4)
N3-C3 1.341(4)	N3-C2 1.460(4)	N3-C1 1.469(4)	C1-H1A 0.9600
C1-H1B 0.9600	C1-H1C 0.9600	C2-H2A 0.9600	C2-H2B 0.9600
C2-H2C 0.9600	C3-O1 1.248(4)	C3-C4 1.497(4)	C4-C5 1.387(4)
C5-C6 1.404(4)	C5-H5 0.9300	C6-C7 1.479(4)	C7-O2 1.203(4)
C7-O3 1.346(4)	C8-O3 1.456(4)	C8-C9 1.511(5)	C8-H8A 0.9700
C8-H8B 0.9700	C9-H9A 0.9600	C9-H9B 0.9600	C9-H9C 0.9600
N2-N1-C4 113.9(2)	N2-N1-H1 124.5	C4-N1-H1 120.8	N1-N2-C6 103.5(2)
C3-N3-C2 124.8(2)	C3-N3-C1 118.3(2)	C2-N3-C1 116.9(2)	N3-C1-H1A 109.5
N3-C1-H1B 109.5	H1A-C1-H1B 109.5	N3-C1-H1C 109.5	H1A-C1-H1C 109.5
H1B-C1-H1C 109.5	N3-C2-H2A 109.5	N3-C2-H2B 109.5	H2A-C2-H2B 109.5
N3-C2-H2C 109.5	H2A-C2-H2C 109.5	H2B-C2-H2C 109.5	O1-C3-N3 121.6(3)
O1-C3-C4 117.4(3)	N3-C3-C4 121.1(3)	N1-C4-C5 105.7(2)	N1-C4-C3 115.9(2)
C5-C4-C3 138.5(3)	C4-C5-C6 104.6(2)	C4-C5-H5 127.7	C6-C5-H5 127.7
N2-C6-C5 112.2(3)	N2-C6-C7 119.1(3)	C5-C6-C7 128.7(3)	O2-C7-O3 124.2(3)
O2-C7-C6 125.8(3)	O3-C7-C6 110.0(2)	O3-C8-C9 106.7(3)	O3-C8-H8A 110.4
C9-C8-H8A 110.4	O3-C8-H8B 110.4	C9-C8-H8B 110.4	H8A-C8-H8B 108.6
C8-C9-H9A 109.5	C8-C9-H9B 109.5	H9A-C9-H9B 109.5	C8-C9-H9C 109.5
H9A-C9-H9C 109.5	H9B-C9-H9C 109.5	C7-O3-C8 116.3(2)	