Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Synthesis of 2-Aminopyridines *via* Ruthenium-Catalyzed [2+2+2] Cycloaddition of 1,6- and 1,7-Diynes with Cyanamides: Scope and Limitations

Fei Ye, Fatma Boukattaya, Mansour Haddad, Virginie Ratovelomanana-Vidal* and Véronique Michelet*

PSL Research University, Chimie ParisTech-CNRS, Institut de Recherche de Chimie Paris, 11 rue P. et M. Curie, 75005 Paris, France

Contents

I. Proposed Mechanism

Mechanistically, the metal-catalyzed [2+2+2] cycloaddition has been thoroughly studied in the presence of several metals. Nevertheless, as described in the Scheme below, one important feature concerns the regioselectivity of the ruthenium-catalyzed process, *e.g.,* the formation of the major isomer **D** versus **D'**. Following *in situ* ligand de-coordination and coordination of 1,6-diyne, the oxidative coupling of the two alkyne units leads to a ruthanacyclopentadiene **A'** or its canonical form **A**.[1,2] The next elemental step determines the regioselectivity of the reaction. Indeed, coordination of cyanamide gives intermediates **B** or **B'**. The origin of the observed regiochemistry can be reasonably explained by the steric hindrance of the amino part of the cyanamide and the steric bulkiness at α-positions of ruthenacyclopentadiene intermediate due to the Cp* ligand, leading to the favourable formation of **B**. Insertion of cyanamide at the less hindered position of the intermediate **B** gives rise to azaruthenacyclopentadiene intermediate **C**, which upon reductive elimination subsequently affords the 2-aminopyridine product **D**. When the 1,6-diyne is substituted by two very hindered groups (Table 1, entries 14-16), no reaction was observed. A hydrogen atom and/or methyl group as substituent of the alkynes are fully compatible with the cycloaddition process and favour the formation of the major intermediate B (Table 2). This mechanism is therefore in agreement with the experimental data.

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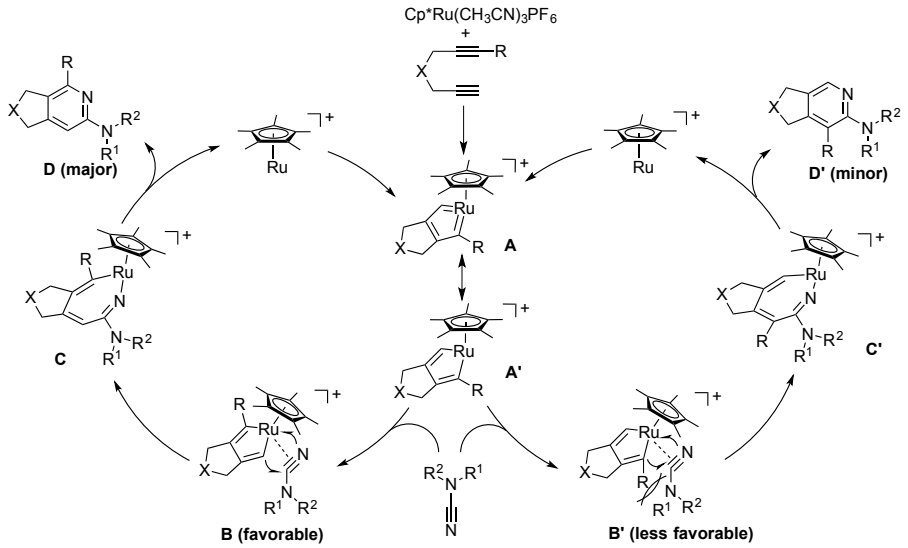
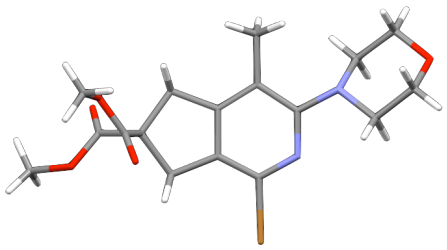
[1] For the intervention of Ru-biscarbenic intermediates, see: (a) M. O. Albers, D. J. A. de Waal, D. C. Liles, D. J. Robinson, E. Singleton and M. B. Wiege, *J. Chem. Soc. Chem. Commun.*, 1986, 1680; (b) Y. Yamamoto, T. Arakawa, R. Ogawa and K. Itoh, *J. Am. Chem. Soc.*, 2003, **125**, 12143; (c) J. Le Paih, F. Monnier, S. Dérien, P. H. Dixneuf, E. Clot and O. Eisenstein, *J. Am. Chem. Soc.*, 2003, **125**, 11964; (d) Y. Yamamoto, K. Hata, T. Arakawa and K. Itoh, *Chem. Commun.*, 2003, 1290.

[2] Several attempts to support the mechanism by isolating the active biscarbenic species did not succeed.



II. ORTEP diagram for the structure of compounds 5a and 10



X-ray structure of **5a** (CCDC 1559302)

Bond precision: C-C = 0.0018 A Wavelength=0.71073

Cell: a=27.4912(7) b=11.5671(3) c=11.9907(3)
alpha=90 beta=110.344(2) gamma=90
Temperature: 200 K

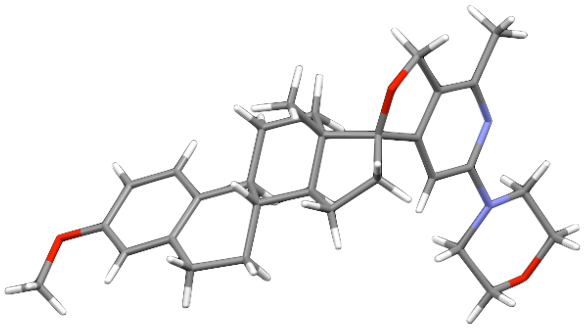
	Calculated	Reported
Volume	3575.12(16)	3575.12(16)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C17 H21 Br N2 O5	C17 H21 Br N2 O5
Sum formula	C17 H21 Br N2 O5	C17 H21 Br N2 O5
Mr	413.26	413.27
Dx,g cm-3	1.536	1.536
Z	8	8
Mu (mm-1)	2.330	2.330
F000	1696.0	1696.0
F000'	1694.49	
h,k,lmax	39,16,17	39,16,17
Nref	5498	5484
Tmin,Tmax	0.391,0.628	0.401,0.674
Tmin'	0.188	

Correction method= # Reported T Limits: Tmin=0.401 Tmax=0.674
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 30.570

R(reflections)= 0.0236(4763) wR2(reflections)= 0.0611(5484)

S = 1.029 Npar= 229

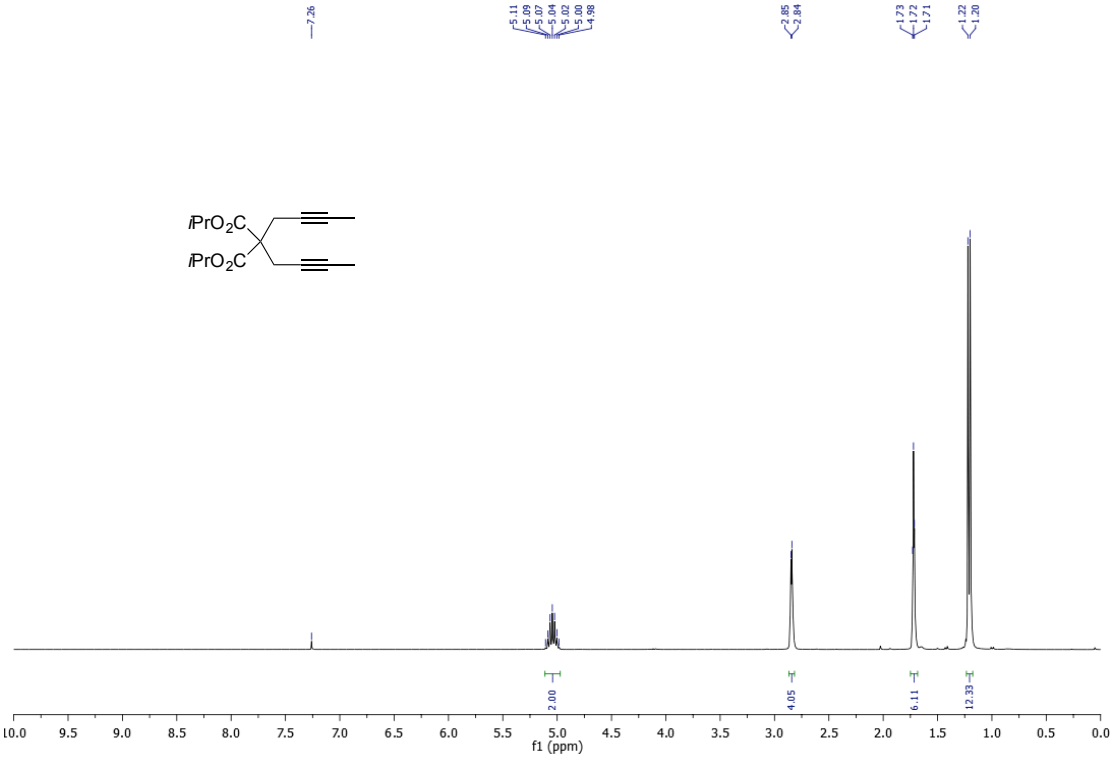


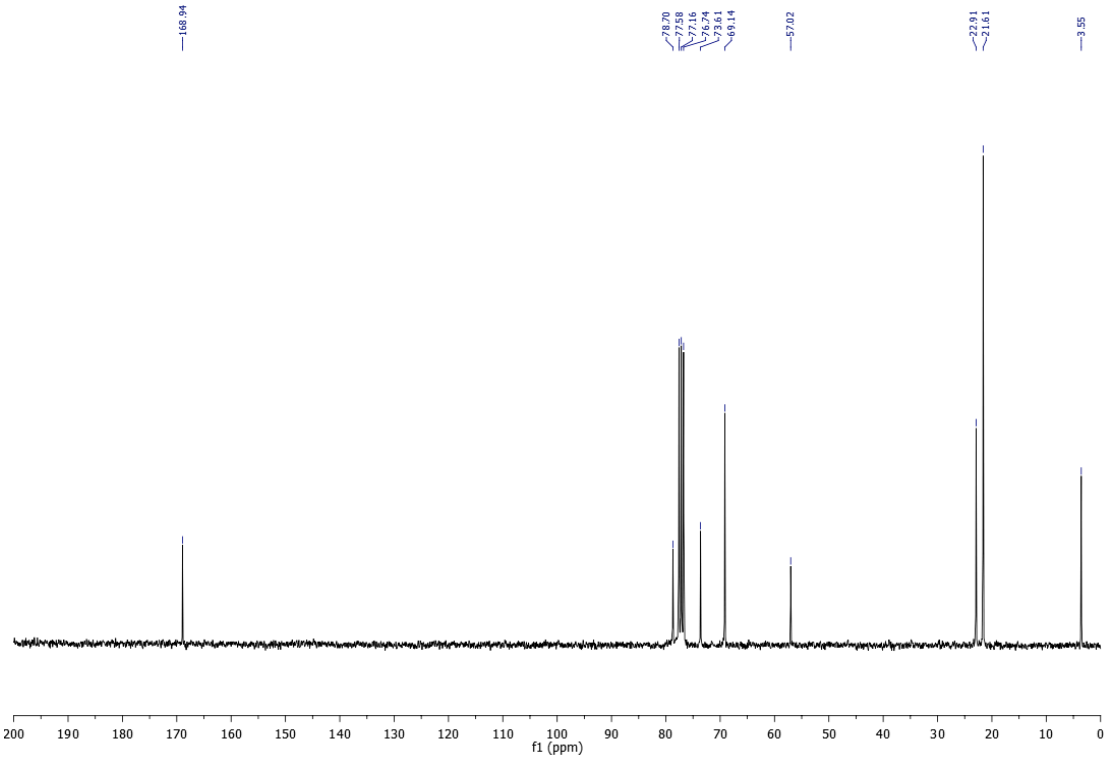
X-ray structure of **10** (CCDC 1559303)

```
Bond precision:  C-C = 0.0031 A          Wavelength=1.54178

Cell:            a=7.1178(2)     b=17.9132(5)     c=19.8302(6)
                 alpha=90        beta=90          gamma=90
Temperature:     200 K

                 Calculated                Reported
Volume           2528.40(13)               2528.40(13)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C30 H38 N2 O3             C30 H38 N2 O3
Sum formula      C30 H38 N2 O3             C30 H38 N2 O3
Mr               474.62                    474.62
Dx,g cm-3        1.247                     1.247
Z                4                         4
Mu (mm-1)        0.630                     0.630
F000             1024.0                    1024.0
F000'            1026.86
h,k,lmax         8,21,23                   8,21,23
Nref             4481[ 2575]               4468
Tmin,Tmax        0.927,0.981               0.788,1.000
Tmin'            0.685

Correction method= # Reported T Limits: Tmin=0.788 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.74/1.00      Theta(max)= 66.669

R(reflections)= 0.0405( 4282)     wR2(reflections)= 0.0998( 4468)

S = 1.062                 Npar= 318
```

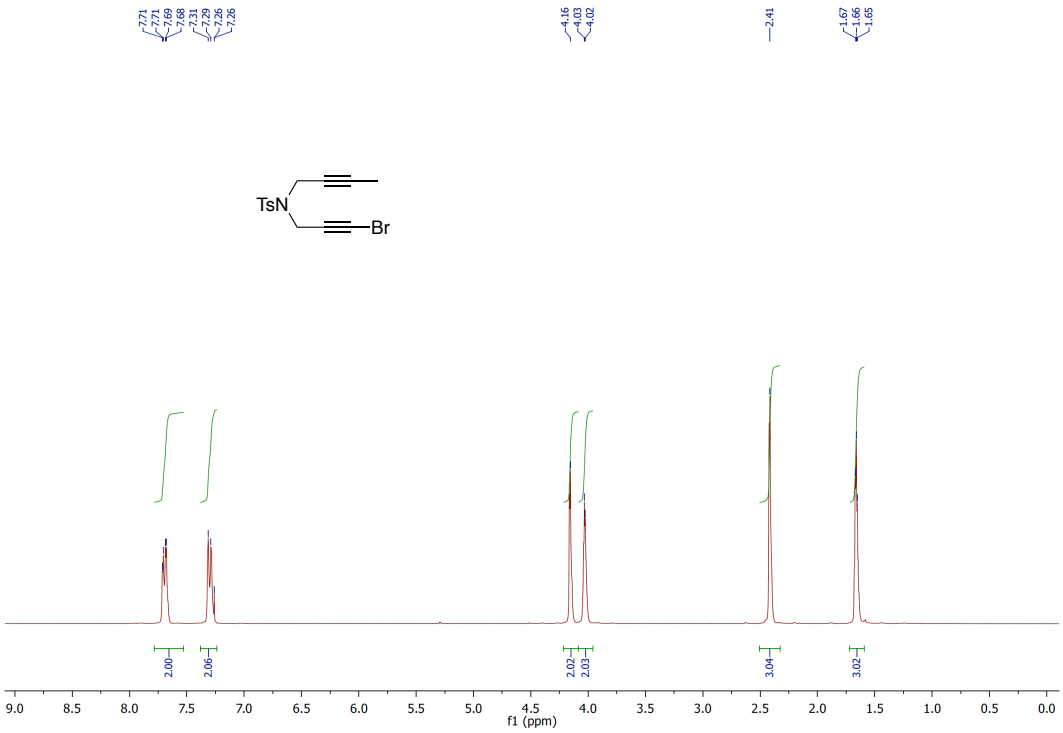
III. NMR spectra for compounds

1g





4b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7.68
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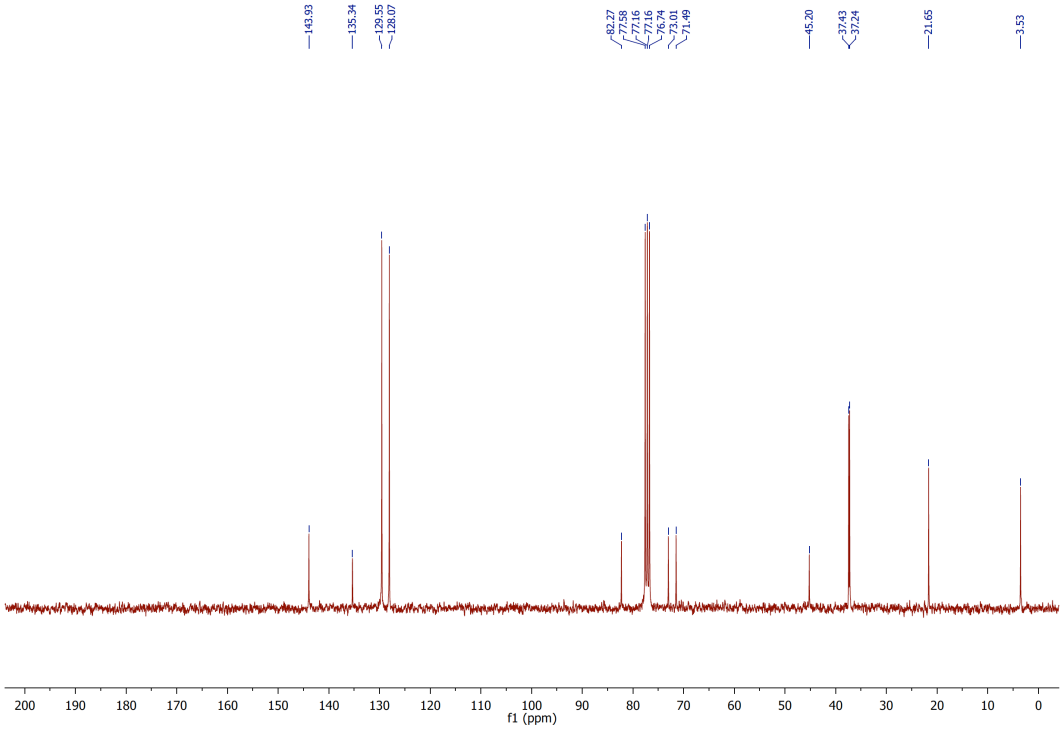
7.26
7.26
4.16
4.03
4.02
2.41
1.67
1.66
1.65
TsN
Br
2.00
2.06
2.02
2.03
3.04
3.02
f1 (ppm)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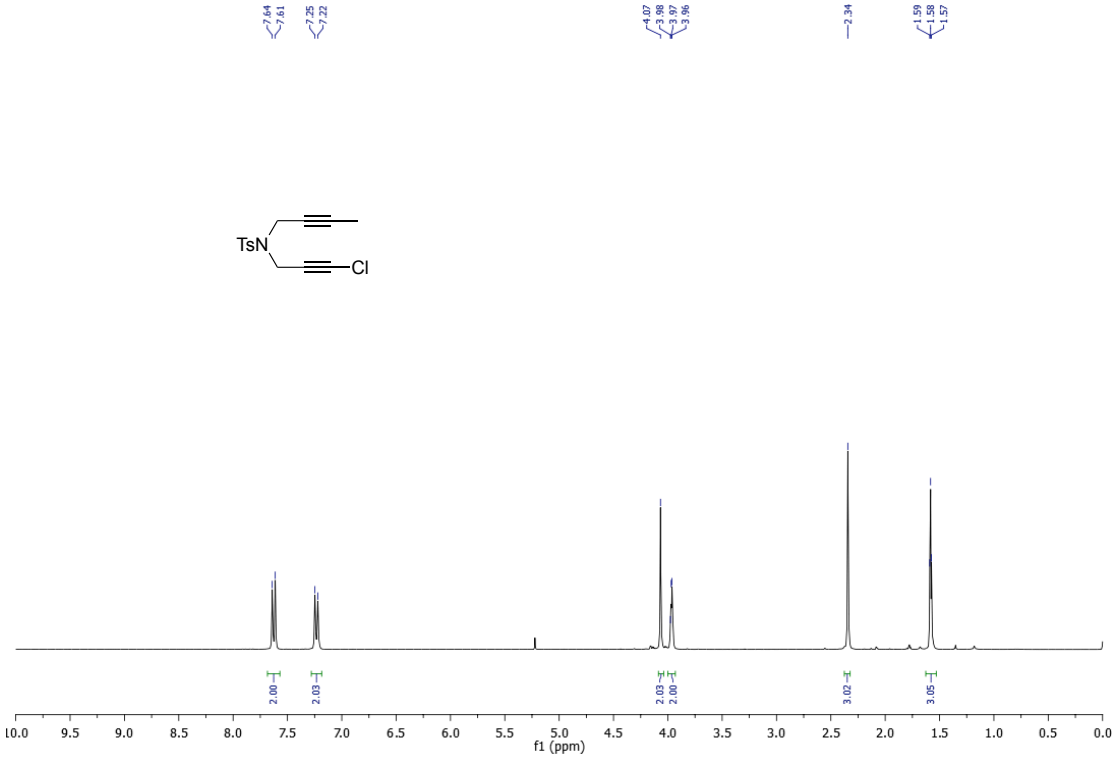
135.34
129.55
128.07
82.27
77.58
77.16
77.16
76.74
73.01
71.49
45.20
37.43
37.24
21.65
3.53
f1 (ppm)

4c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7.25
7.22
4.07
3.98
3.97
3.96
2.34
1.59
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Cl
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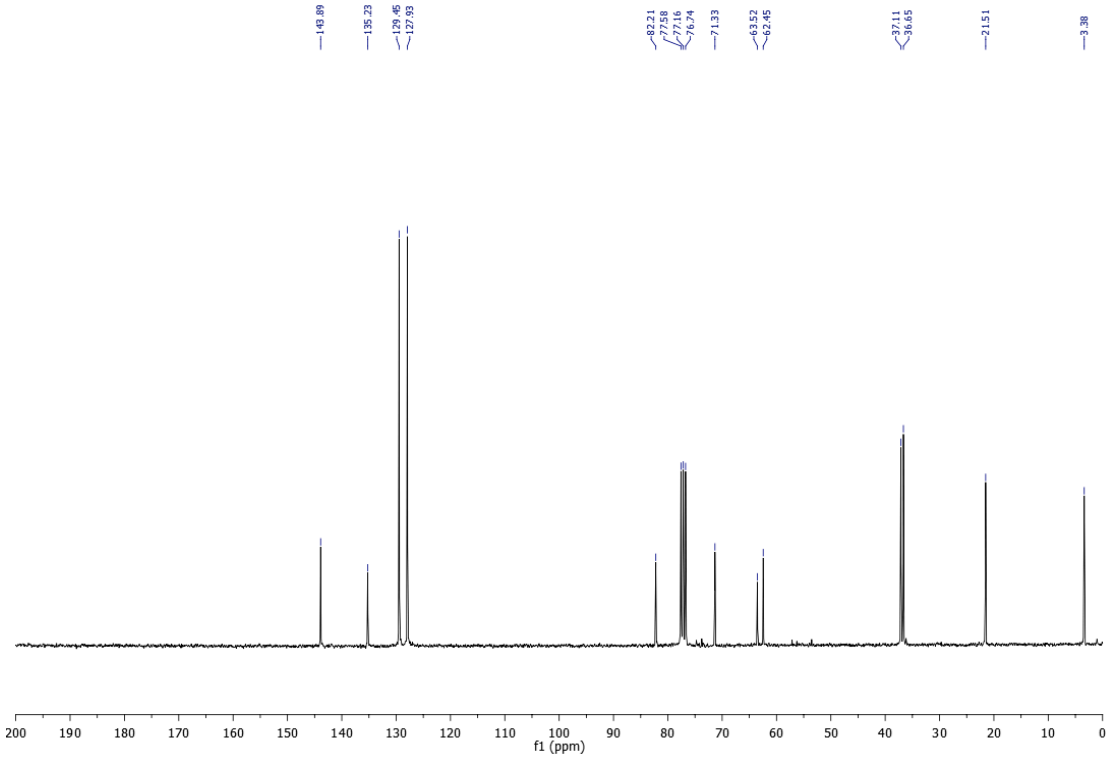
2.03
2.03
2.00
3.02
3.05
f1 (ppm)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127.93
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76.74
71.33
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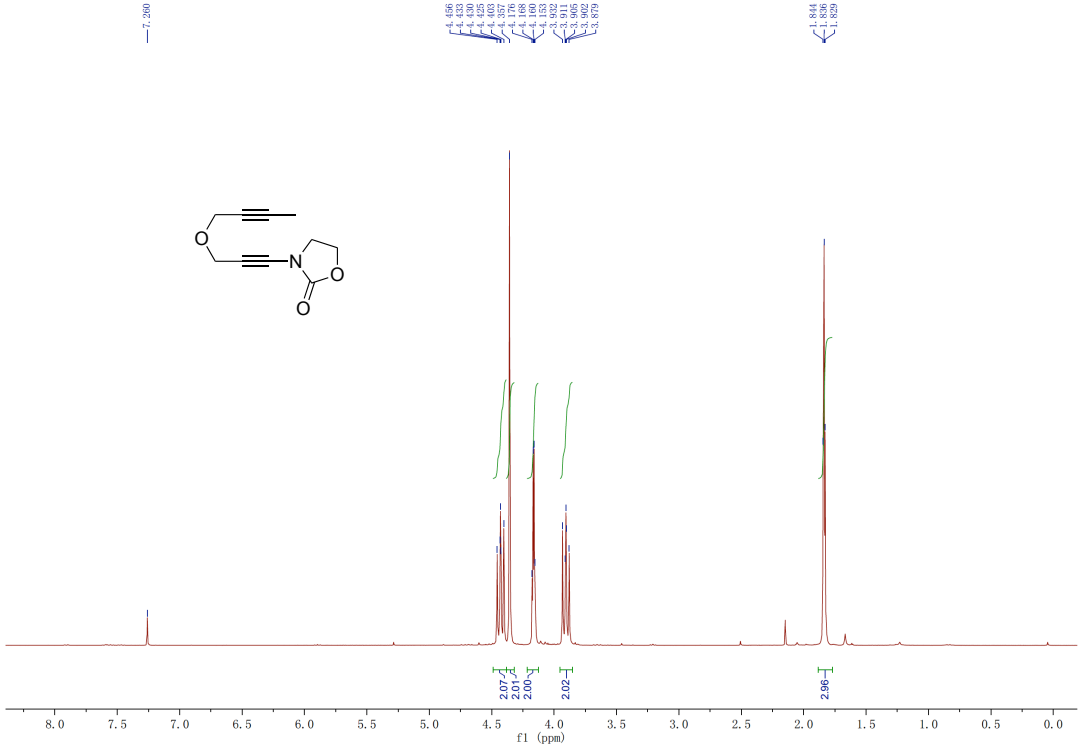
21.51
3.38
f1 (ppm)

4e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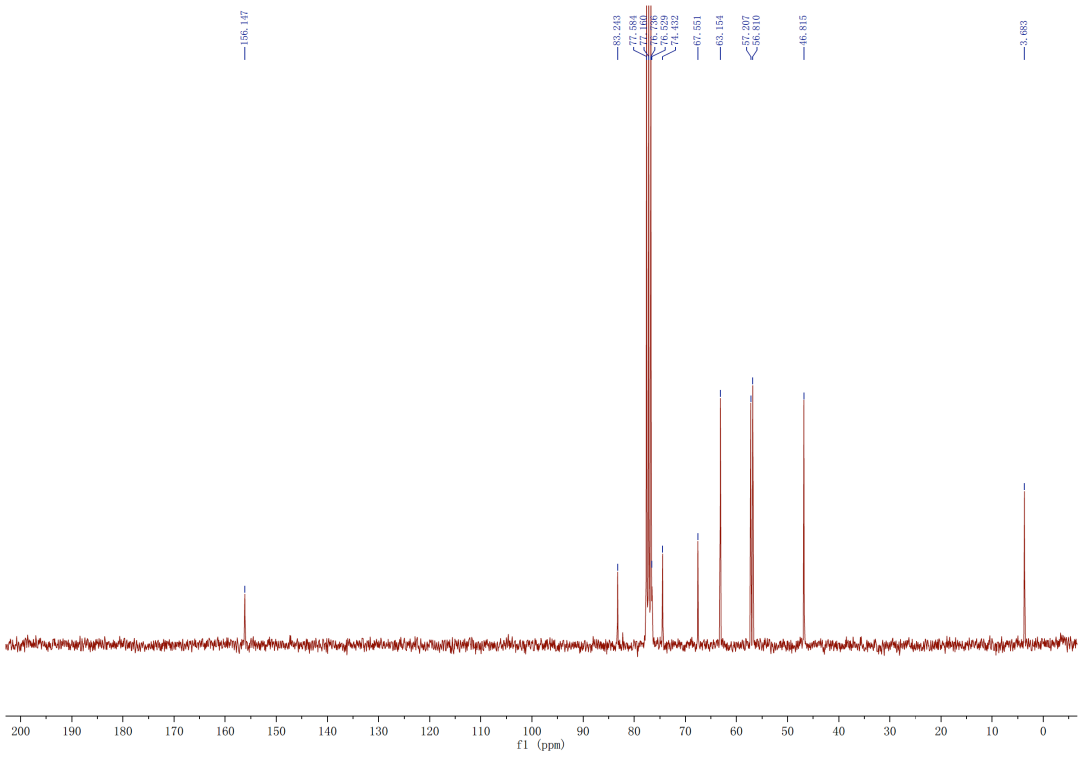
4.403
4.357
4.176
4.168
4.160
4.155
3.932
3.911
3.905
3.902
3.879
1.844
1.836
1.829
2.07
2.01
2.00
2.02
2.96
f1 (ppm)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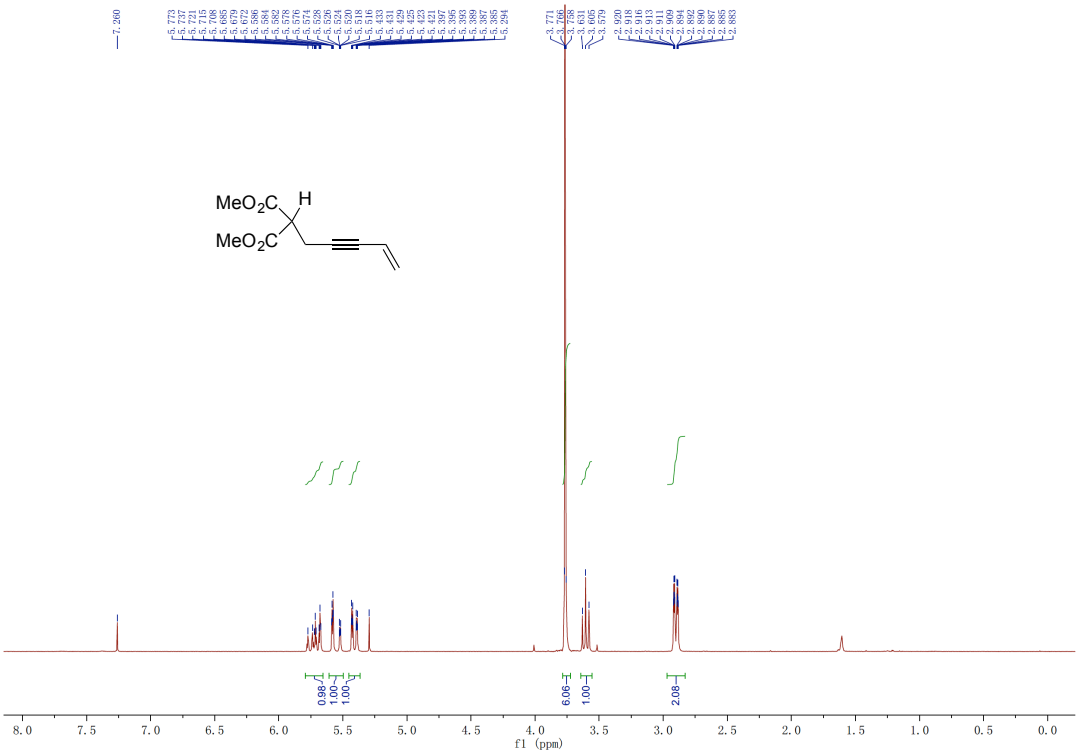
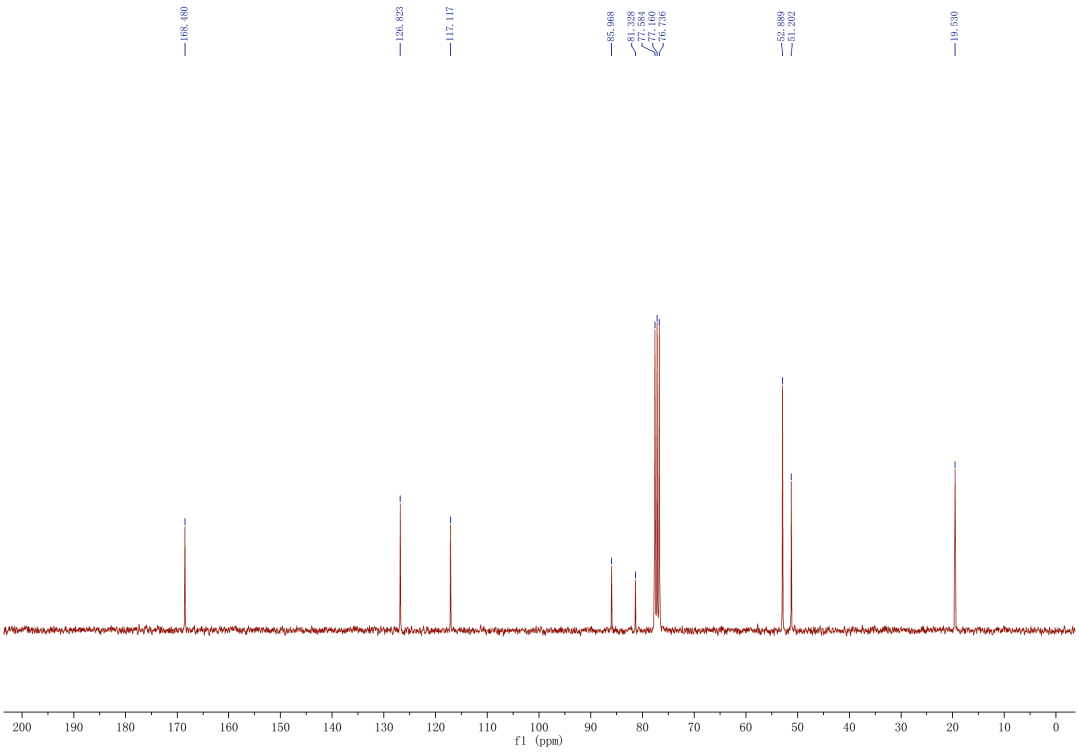
46.815
3.683
f1 (ppm)

S3





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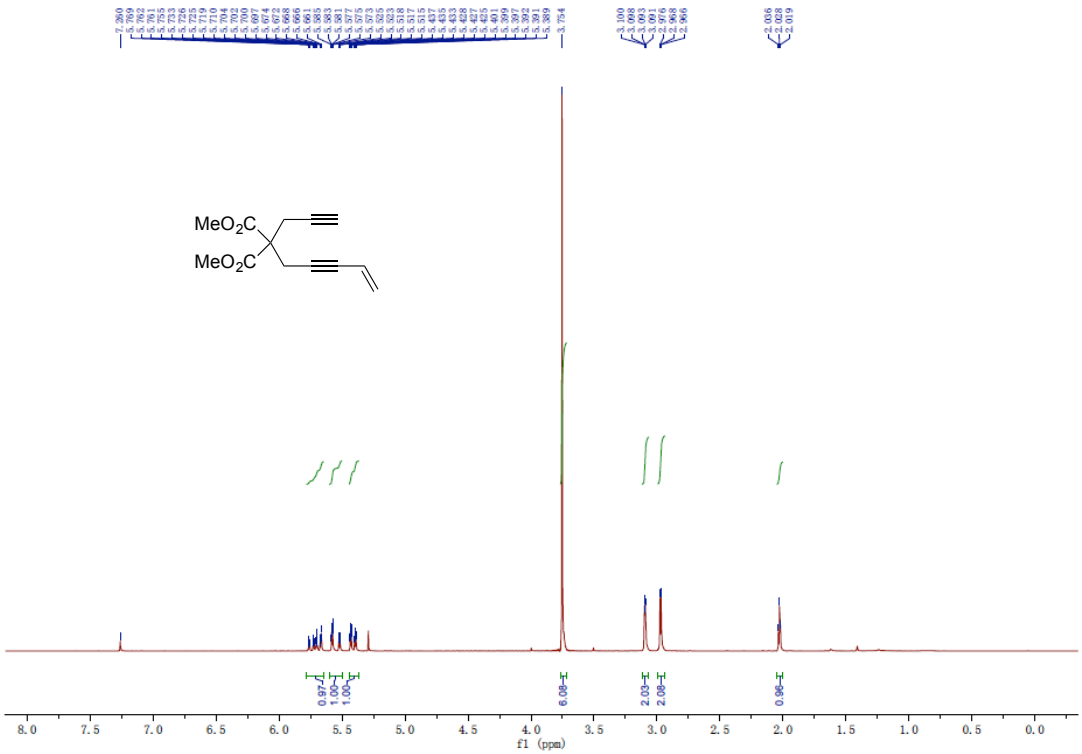
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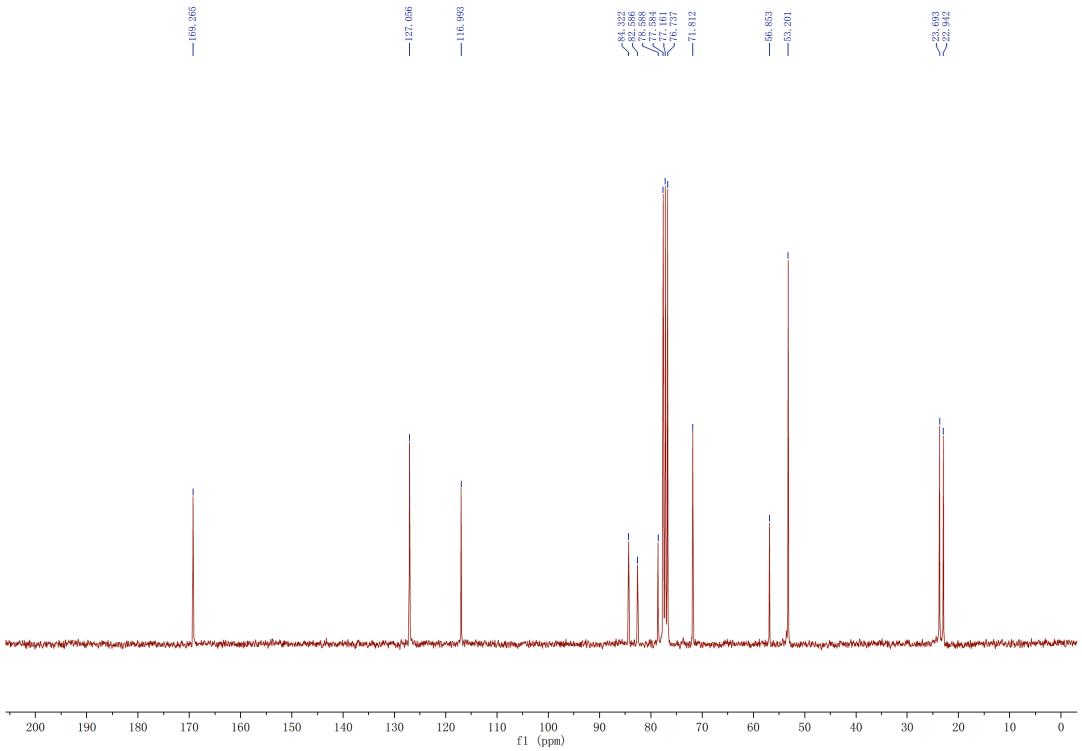
MeO2C
f1 (ppm)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84.322
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71.812
56.853
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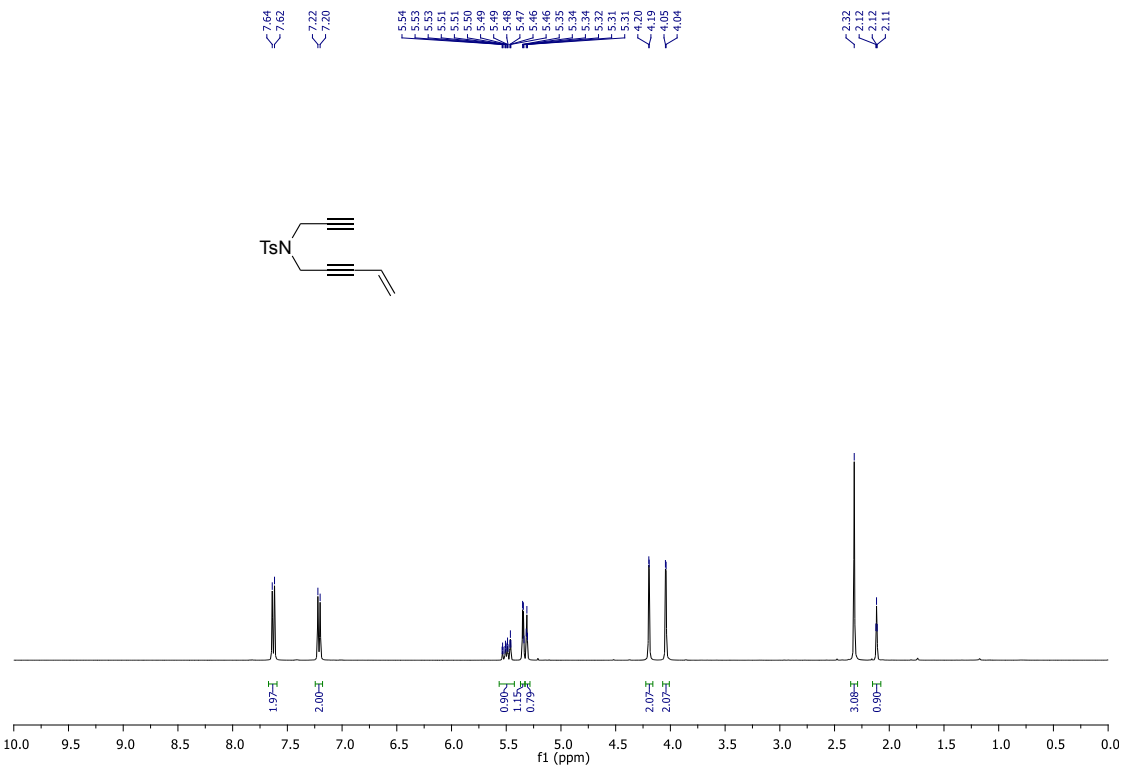
23.693
22.942
f1 (ppm)

4g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5.46
5.46
5.35
5.34
5.34
5.32
5.31
5.31
4.20
4.19
4.05
4.04
2.32
2.12
2.12
2.11
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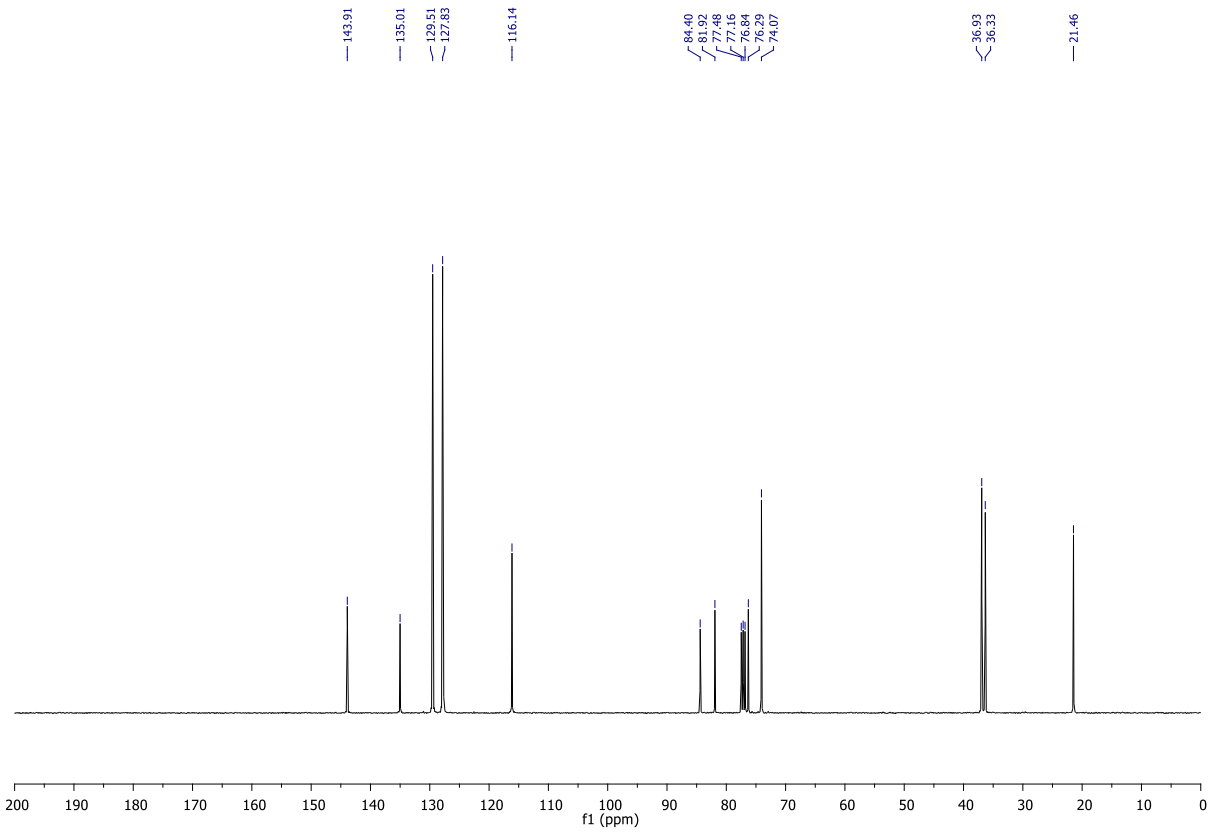
0.90
f1 (ppm)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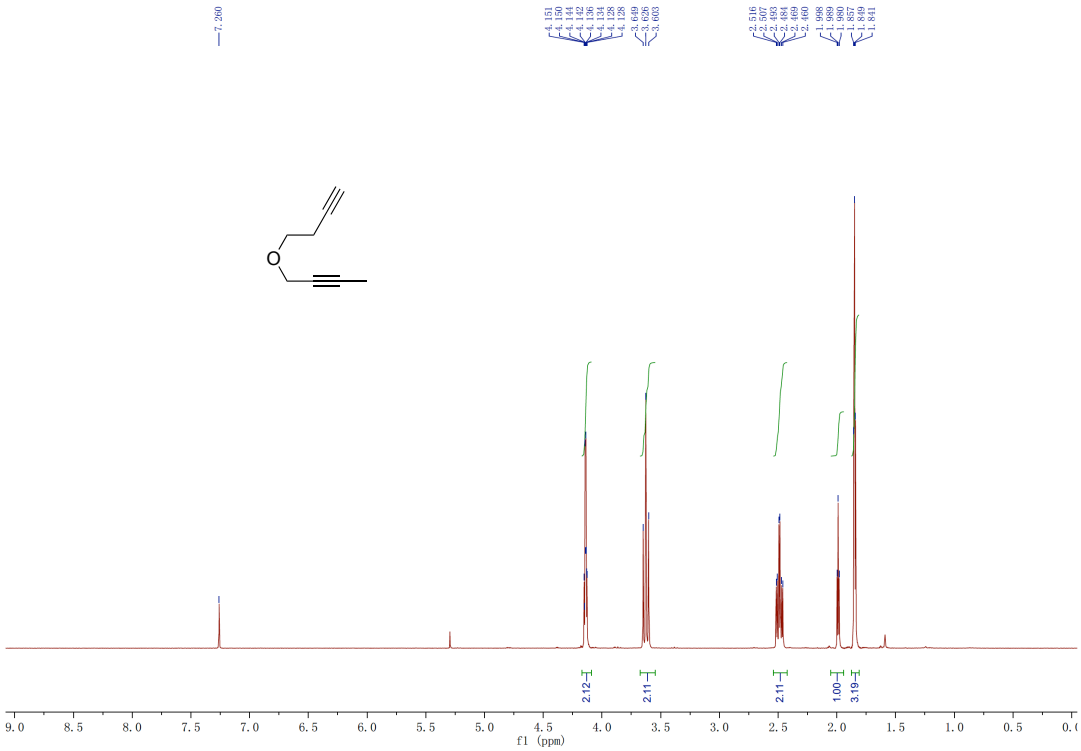
36.93
36.33
21.46
f1 (ppm)

6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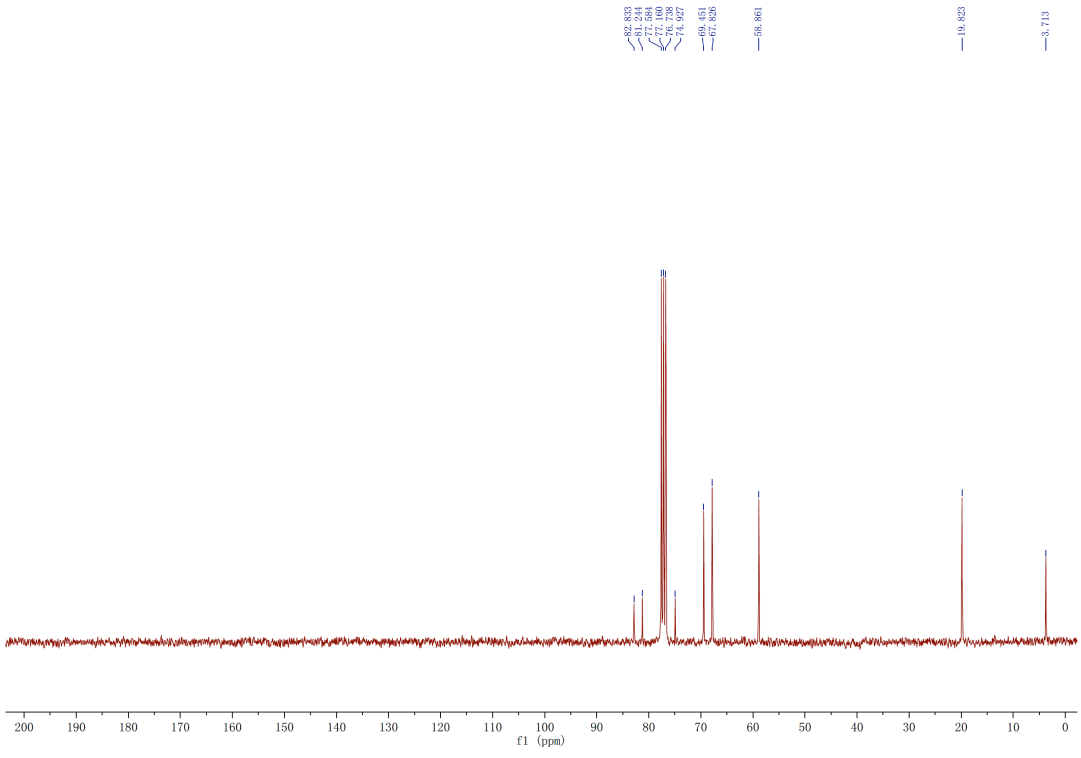
4.150
4.144
4.142
4.136
4.134
4.128
4.126
3.649
3.626
3.603
2.516
2.507
2.493
2.484
2.469
2.460
1.998
1.989
1.980
1.957
1.849
1.841
O
2.12
2.11
2.11
1.00
3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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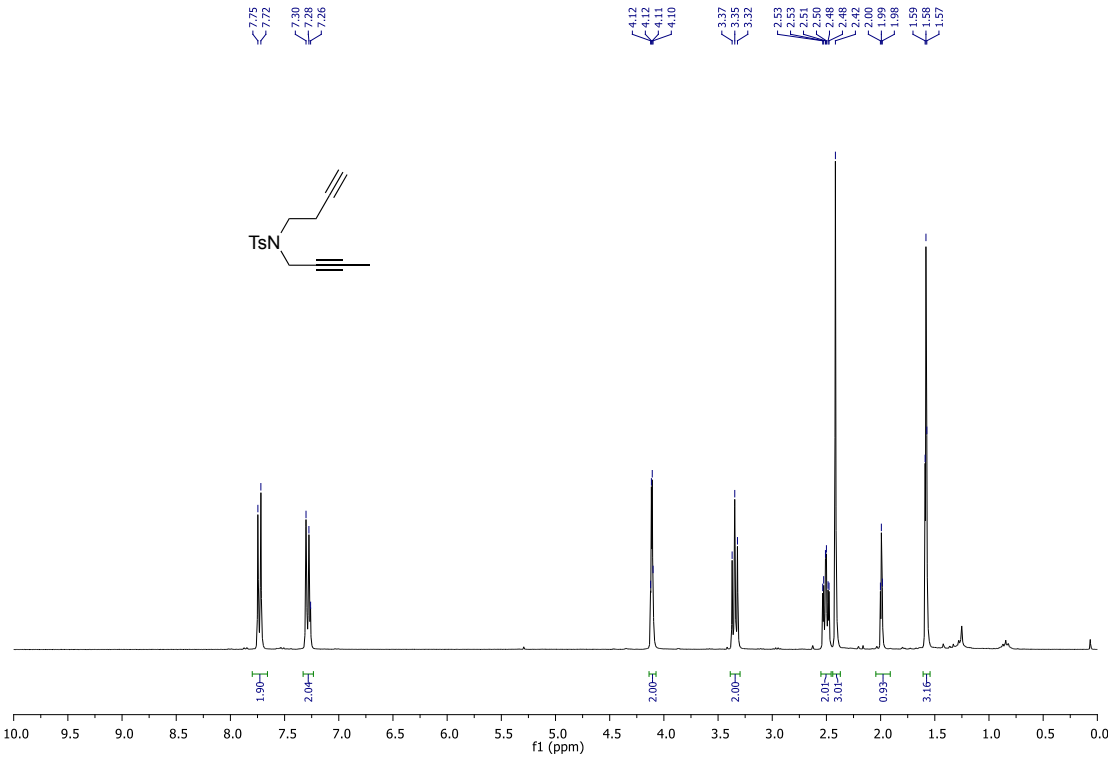
f1 (ppm)

7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7.26
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4.11
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2.53
2.53
2.51
2.50
2.48
2.48
2.42
2.00
1.99
1.98
1.59
1.58
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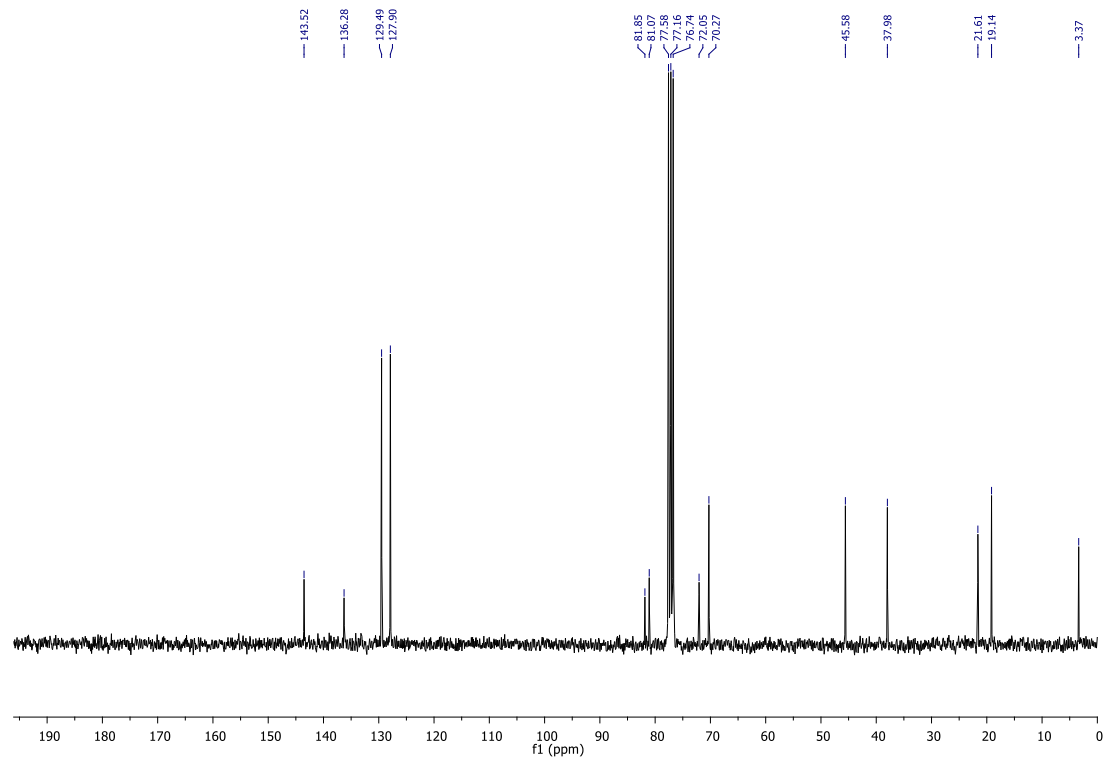
f1 (ppm)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81.07
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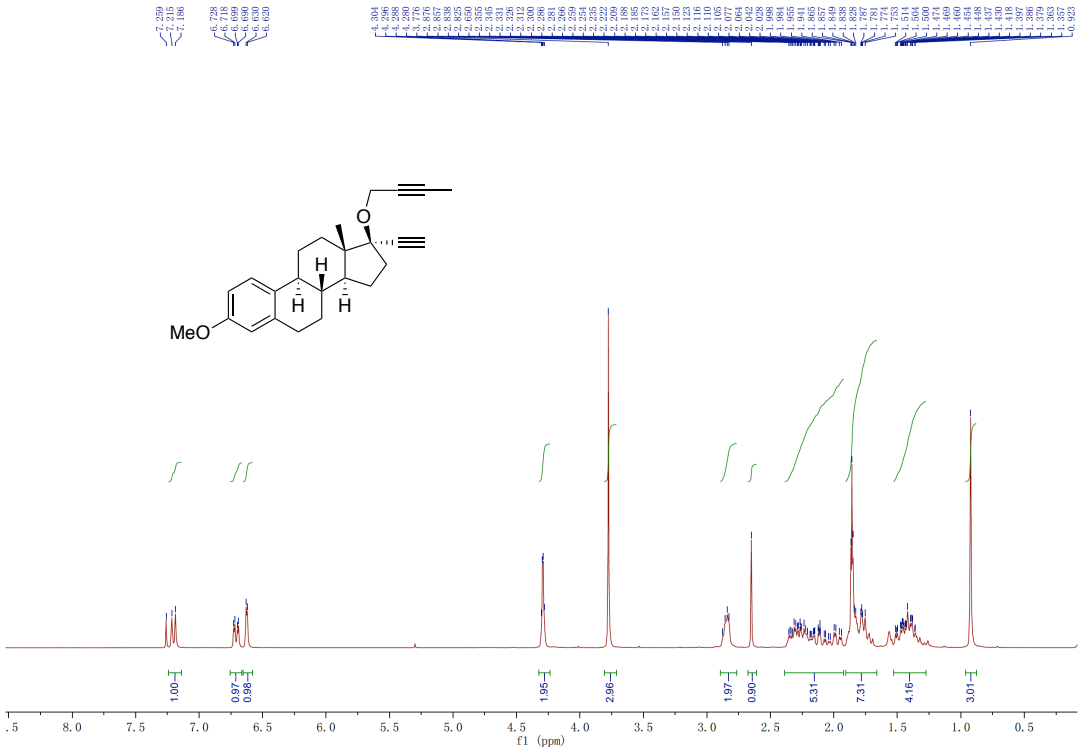
3.37
f1 (ppm)

9


MeO
H
H
H
O
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7.31
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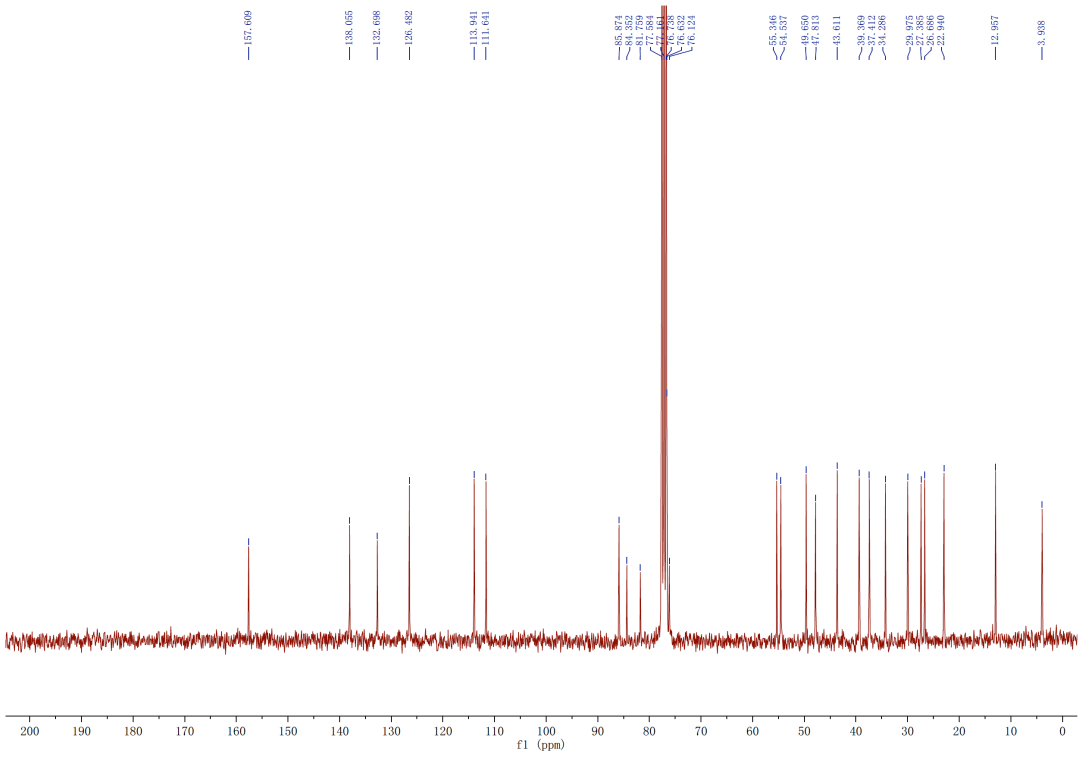
f1 (ppm)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76.738
76.652
76.124
55.346
54.537
49.650
47.813
43.611
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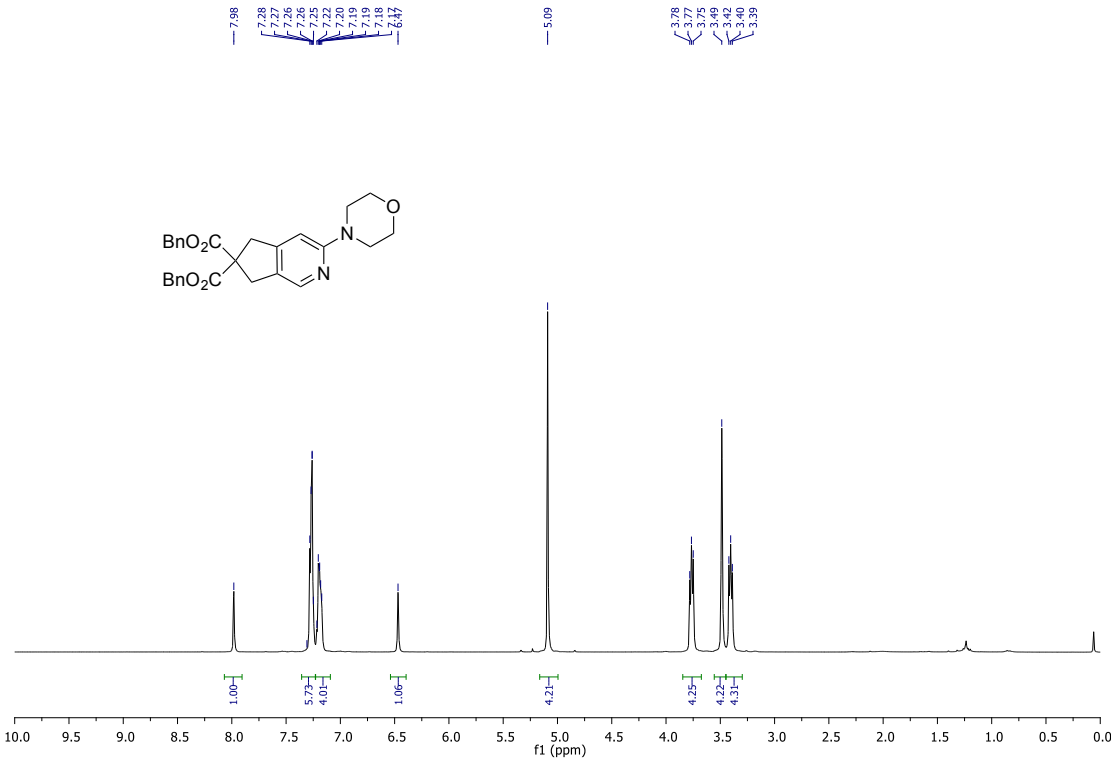
3.938
f1 (ppm)

3a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7.27
7.26
7.26
7.25
7.22
7.20
7.19
7.19
7.18
6.47
5.09
3.78
3.77
3.75
3.49
3.42
3.40
3.39
BnO2C
BnO2C
O
N
N
1.00
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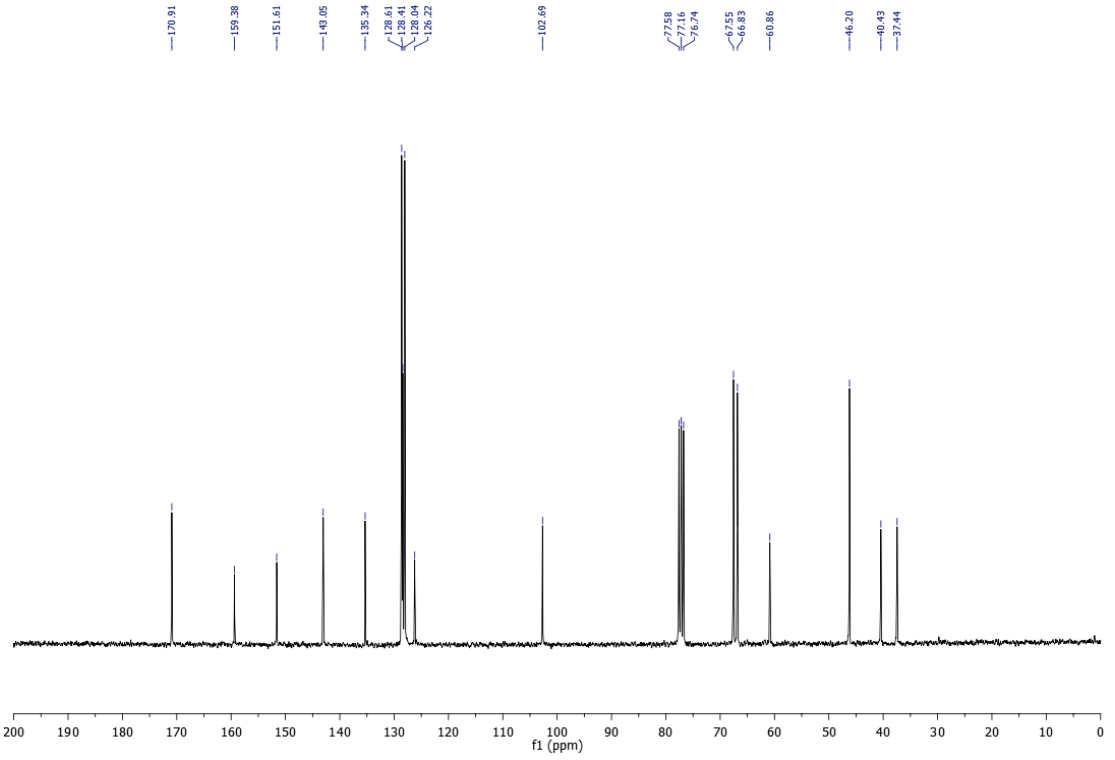
4.21
4.25
4.22
4.31
f1 (ppm)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151.61
143.05
135.34
128.61
128.41
128.04
126.22
102.69
77.58
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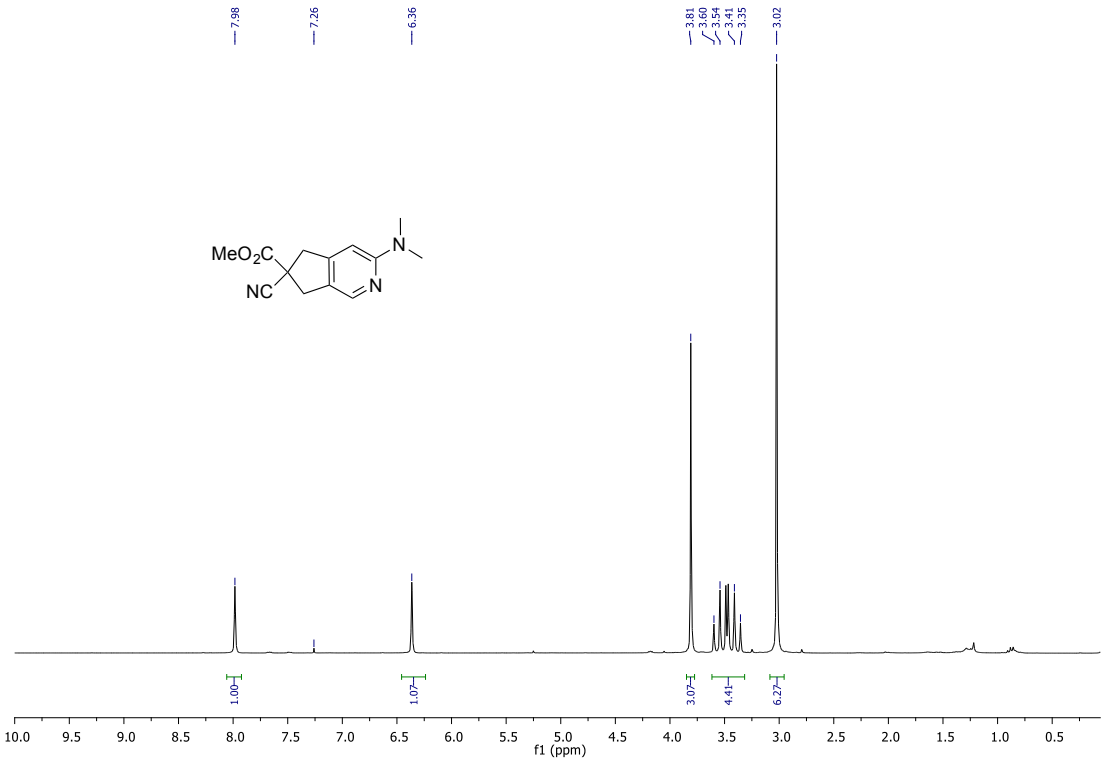
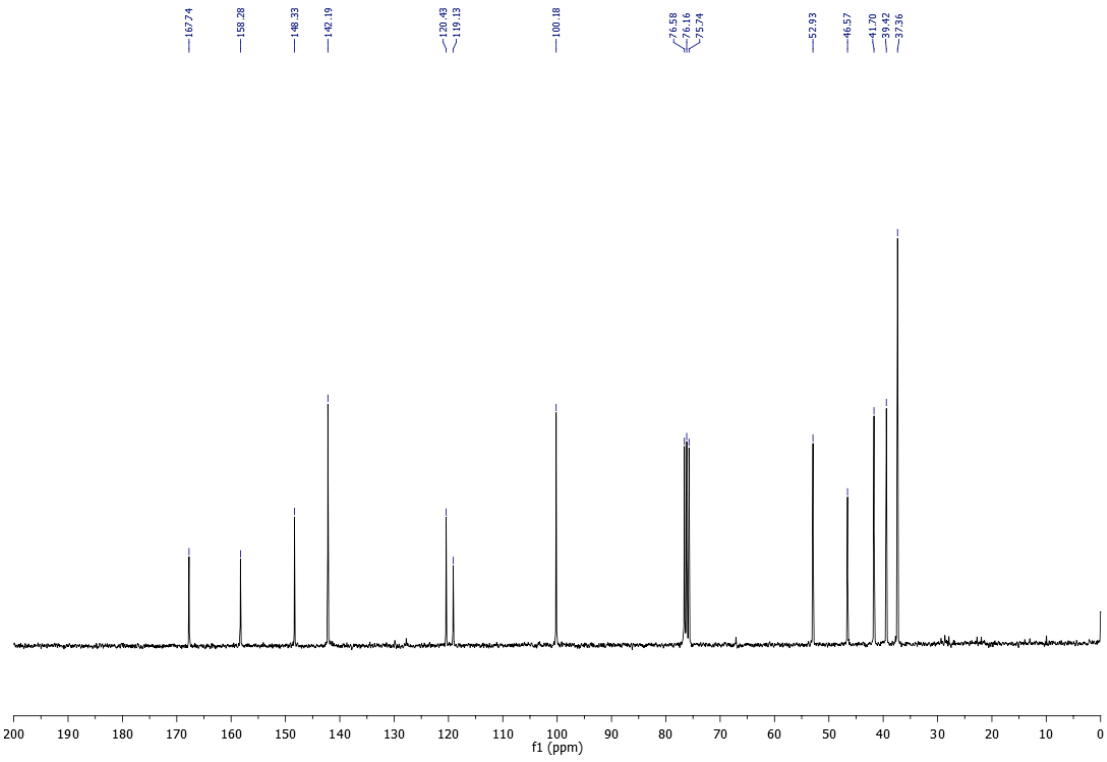
76.74
67.55
66.83
60.86
46.20
40.43
37.44
f1 (ppm)

3b


7.98
7.26
6.36
3.81
3.60
3.54
3.41
3.35
3.02
MeO2C
NC
N
N
1.00
1.07
3.07
4.41
6.27
f1 (ppm)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158.28
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142.19
120.43
119.13
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75.74
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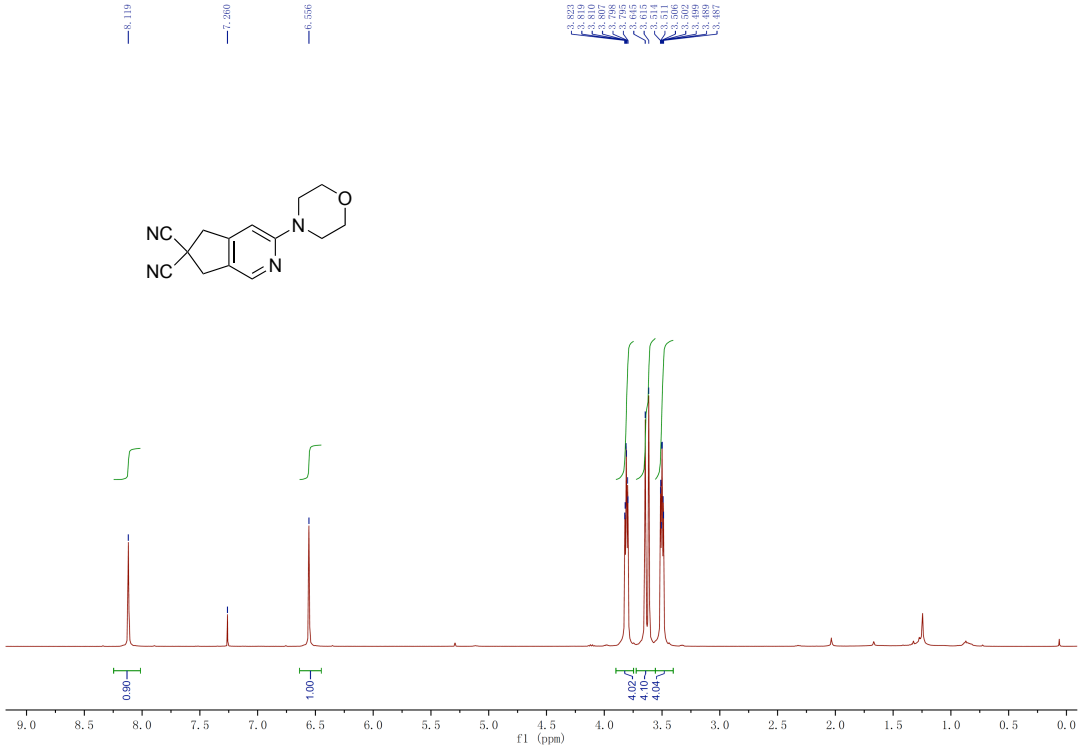
46.57
41.70
39.42
37.36
f1 (ppm)

3c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6.556
3.823
3.819
3.810
3.807
3.798
3.795
3.645
3.615
3.514
3.511
3.506
3.502
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NC
NC
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O
N
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4.10
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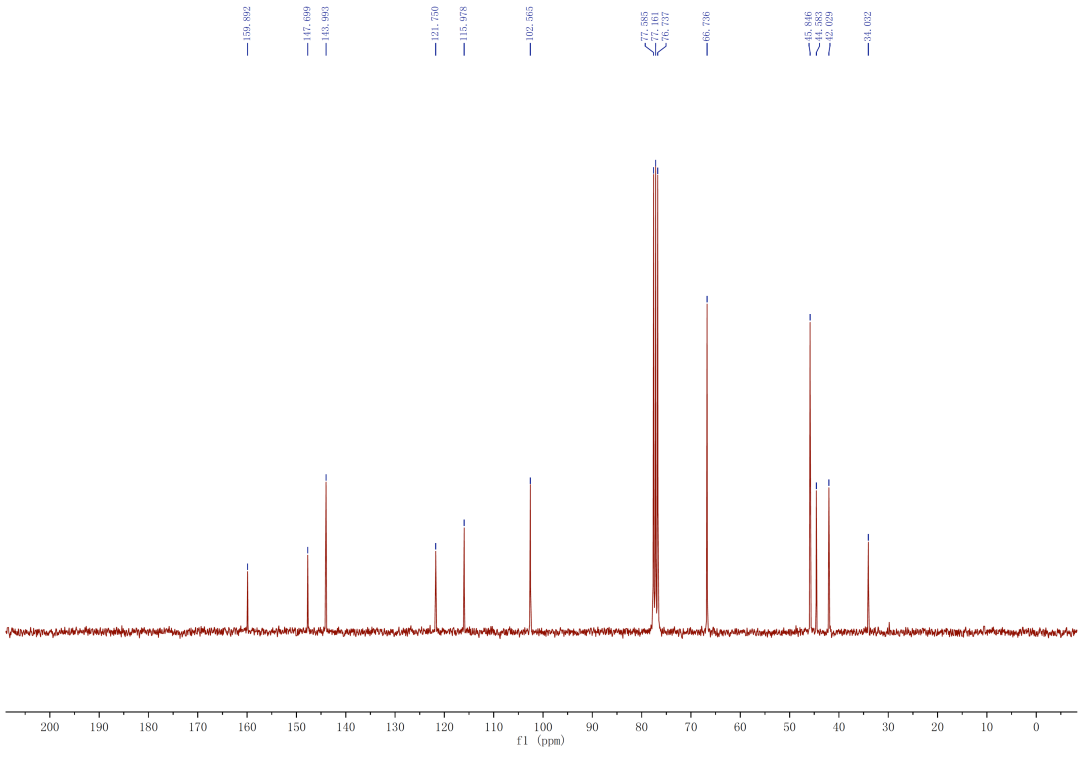
f1 (ppm)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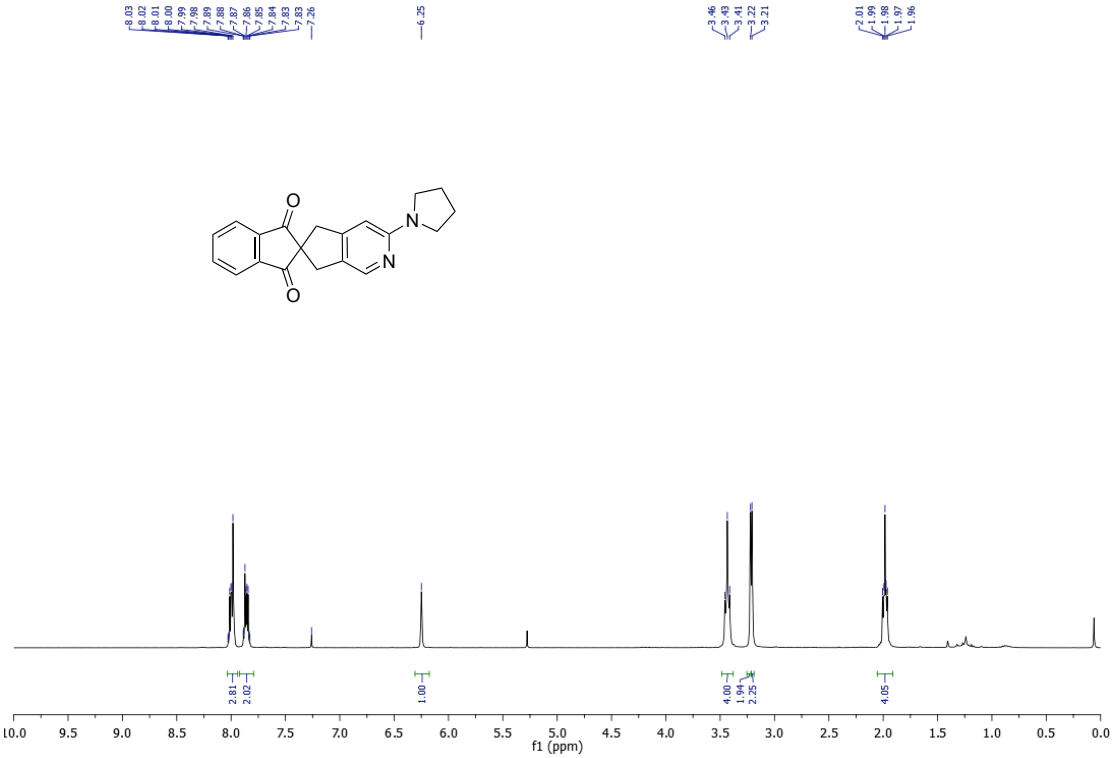
34.032
f1 (ppm)

3d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8.01
8.00
7.99
7.98
7.89
7.88
7.87
7.86
7.85
7.84
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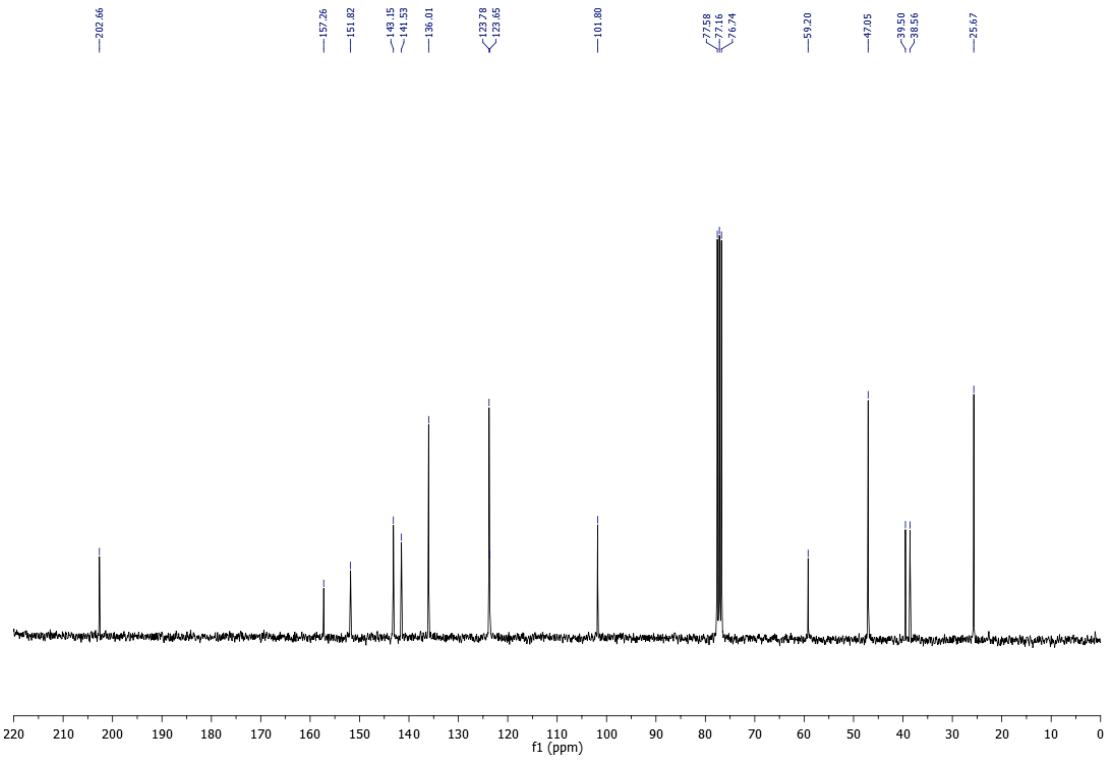
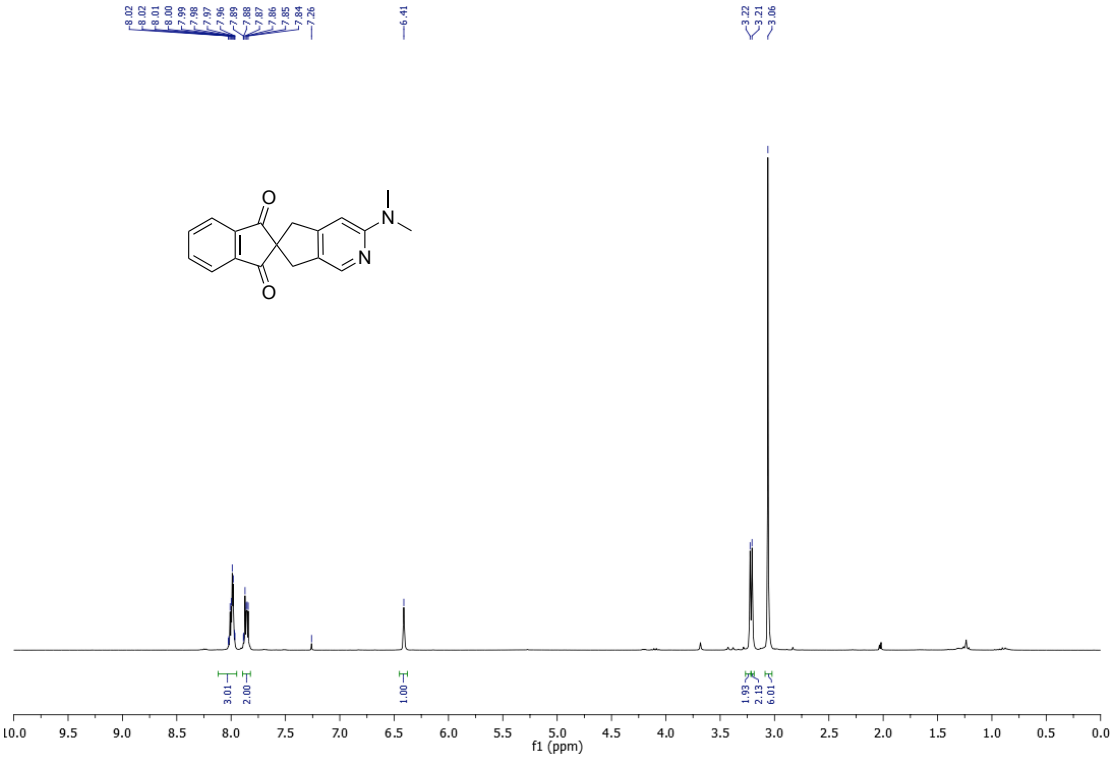
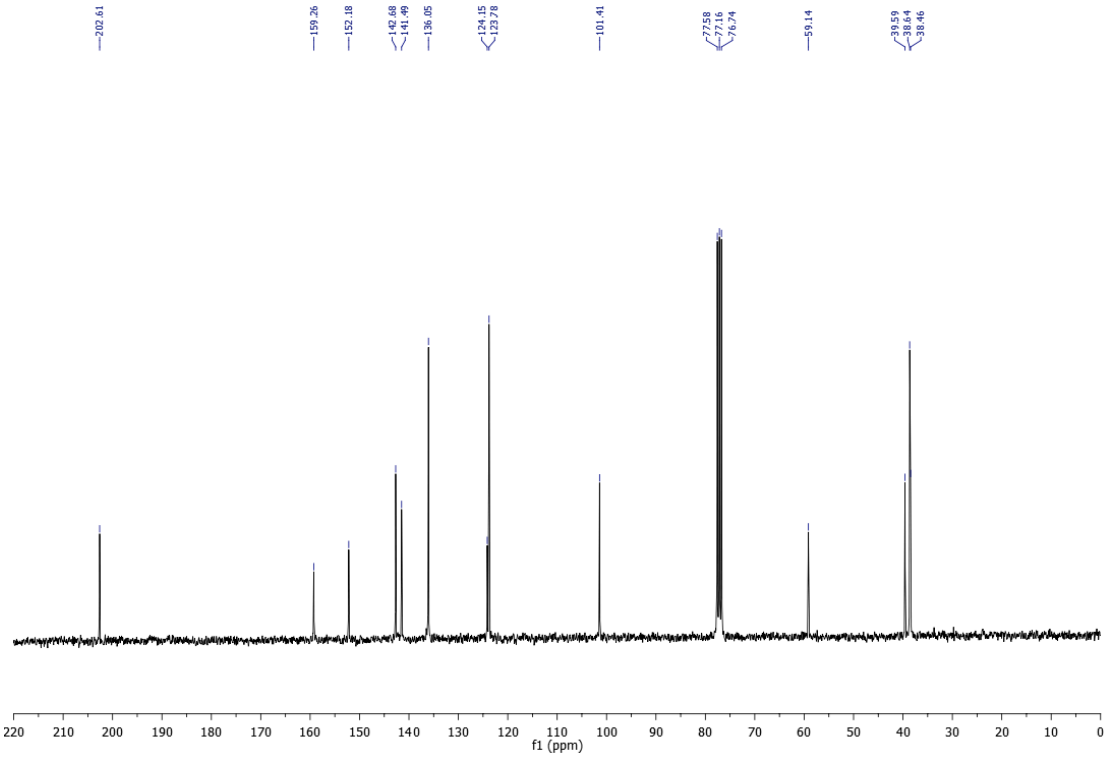
7.83
7.26
6.25
3.46
3.43
3.41
3.22
3.21
2.01
1.99
1.98
1.97
1.96
O
O
N
N
2.81
2.02
1.00
4.00
1.94
2.25
4.05
f1 (ppm)

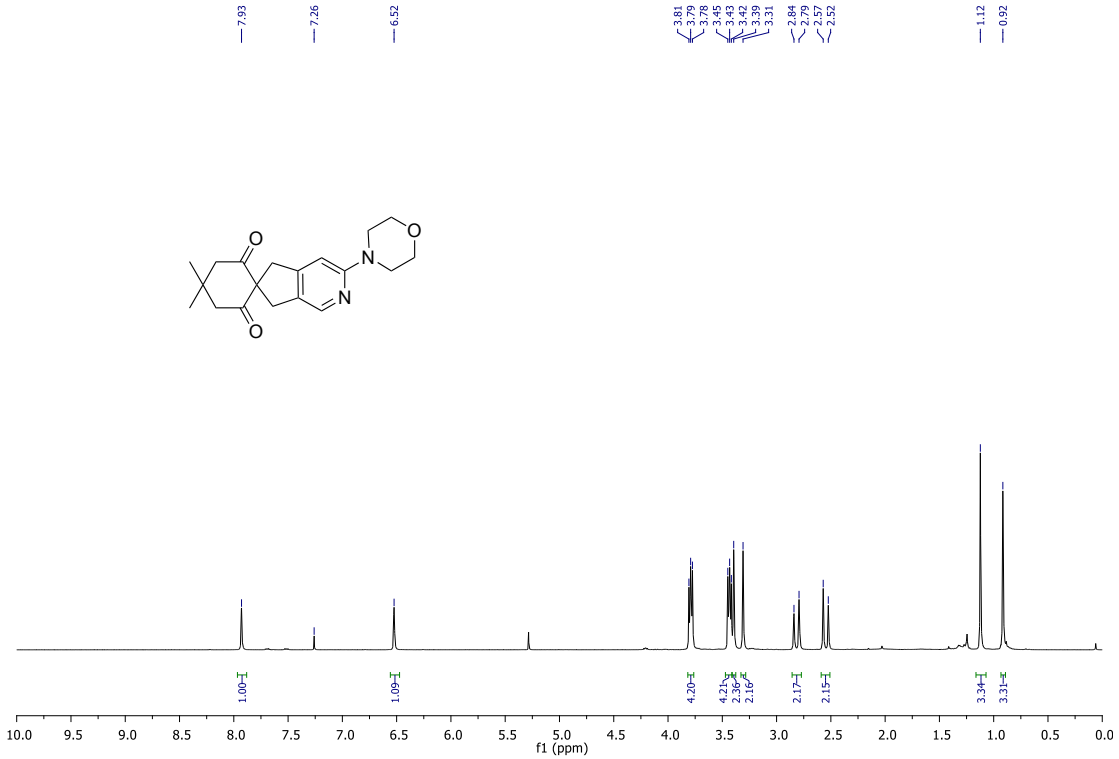

202.66
157.26
151.82
143.15
141.53
136.01
123.78
123.65
101.80
77.58
77.16
76.74
59.20
47.05
39.50
38.56
25.67
f1 (ppm)

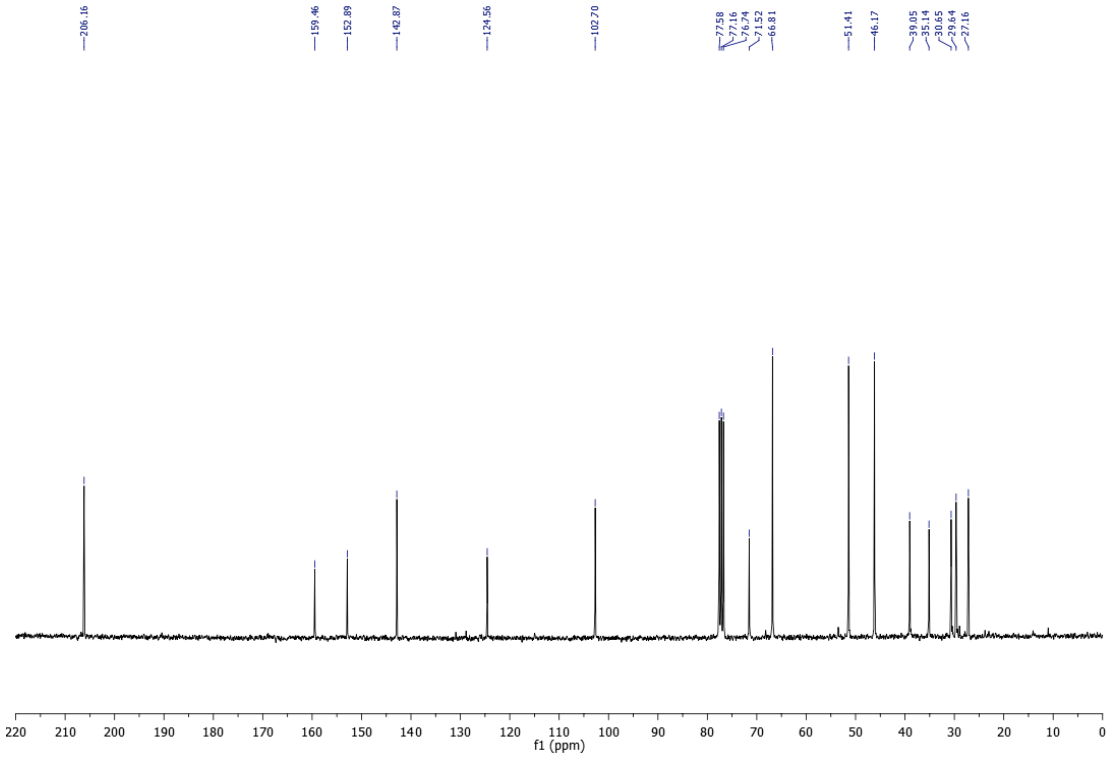
3e


8.02
8.02
8.01
8.00
7.99
7.98
7.97
7.96
7.89
7.88
7.87
7.86
7.85
7.84
7.26
6.41
3.22
3.21
3.06
O
O
N
N
3.01
2.00
1.00
1.93
2.13
6.01
f1 (ppm)

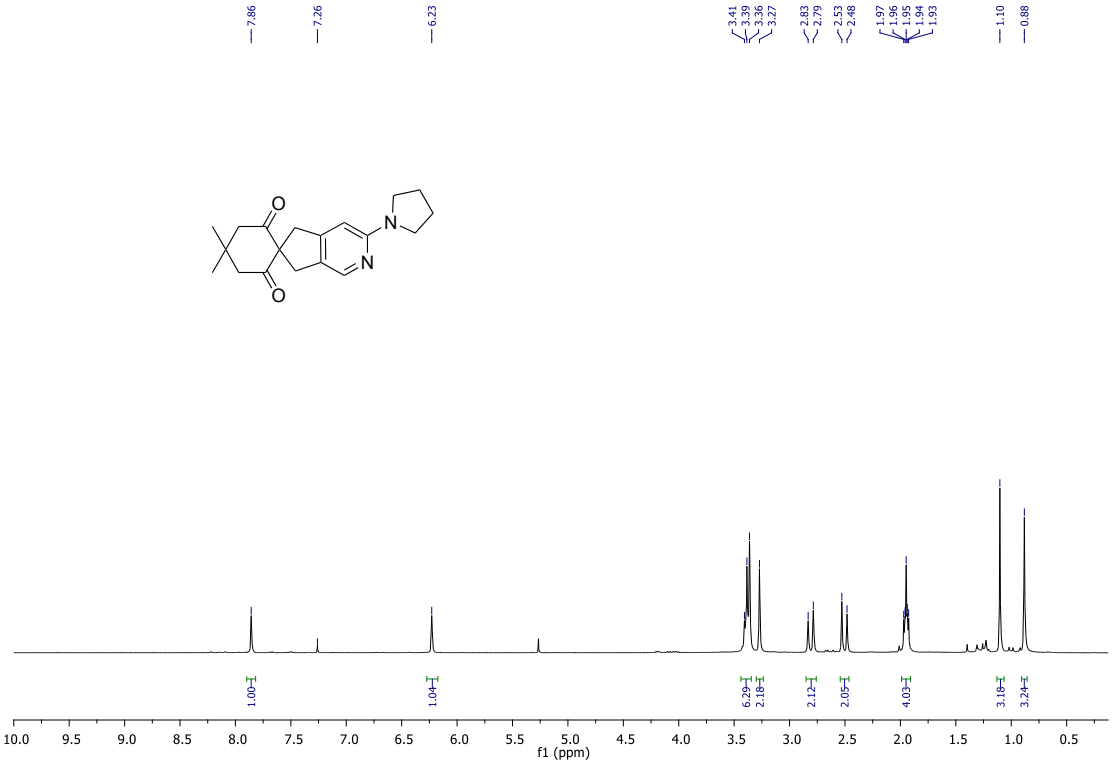

202.61
159.26
152.18
142.68
141.49
136.05
124.15
123.78
101.41
77.58
77.16
76.74
59.14
39.59
38.64
38.46
f1 (ppm)

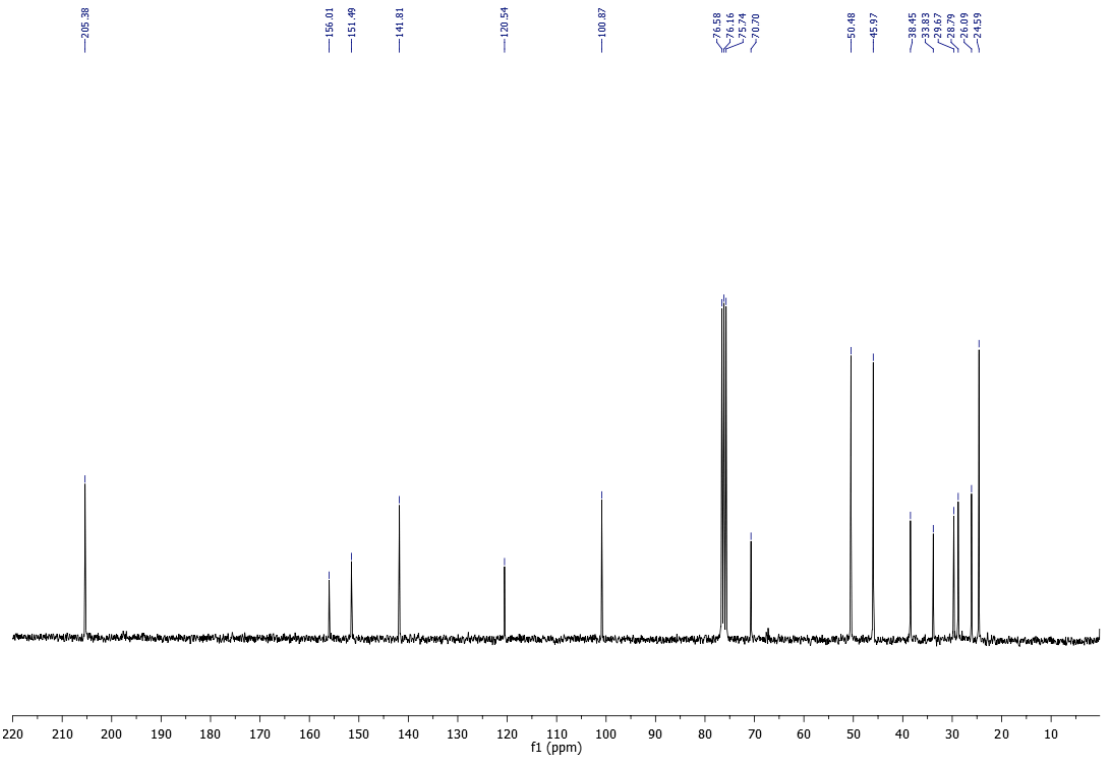
3f


7.93
7.26
6.52
3.81
3.79
3.78
3.45
3.43
3.42
3.39
3.31
2.84
2.79
2.57
2.52
1.12
0.92
O
O
N
O
N
1.00
1.09
4.20
4.21
2.36
2.16
2.17
2.15
3.34
3.31
f1 (ppm)

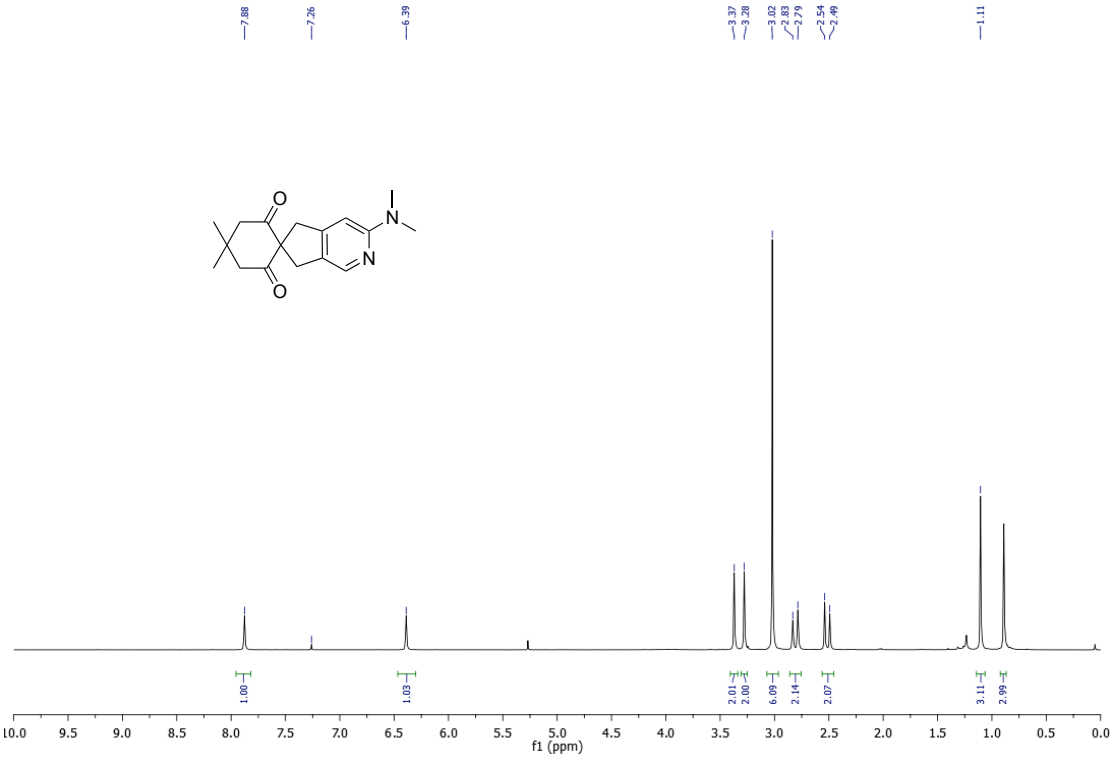

206.16
159.46
152.89
142.87
124.56
102.70
77.58
77.16
76.74
71.52
66.81
51.41
46.17
39.05
35.14
30.65
29.64
27.16
f1 (ppm)

3g


7.86
7.26
6.23
3.41
3.39
3.36
3.27
2.83
2.79
2.53
2.48
1.97
1.96
1.95
1.94
1.93
1.10
0.88
O
O
N
N
1.00
1.04
6.29
2.18
2.12
2.05
4.03
3.18
3.24
f1 (ppm)


205.38
156.01
151.49
141.81
120.54
100.87
76.58
76.16
75.74
70.70
50.48
45.97
38.45
33.83
29.67
28.79
26.09
24.59
f1 (ppm)

3h


7.88
7.26
6.39
3.37
3.28
3.02
2.83
2.79
2.54
2.49
1.11
O
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1.03
2.01
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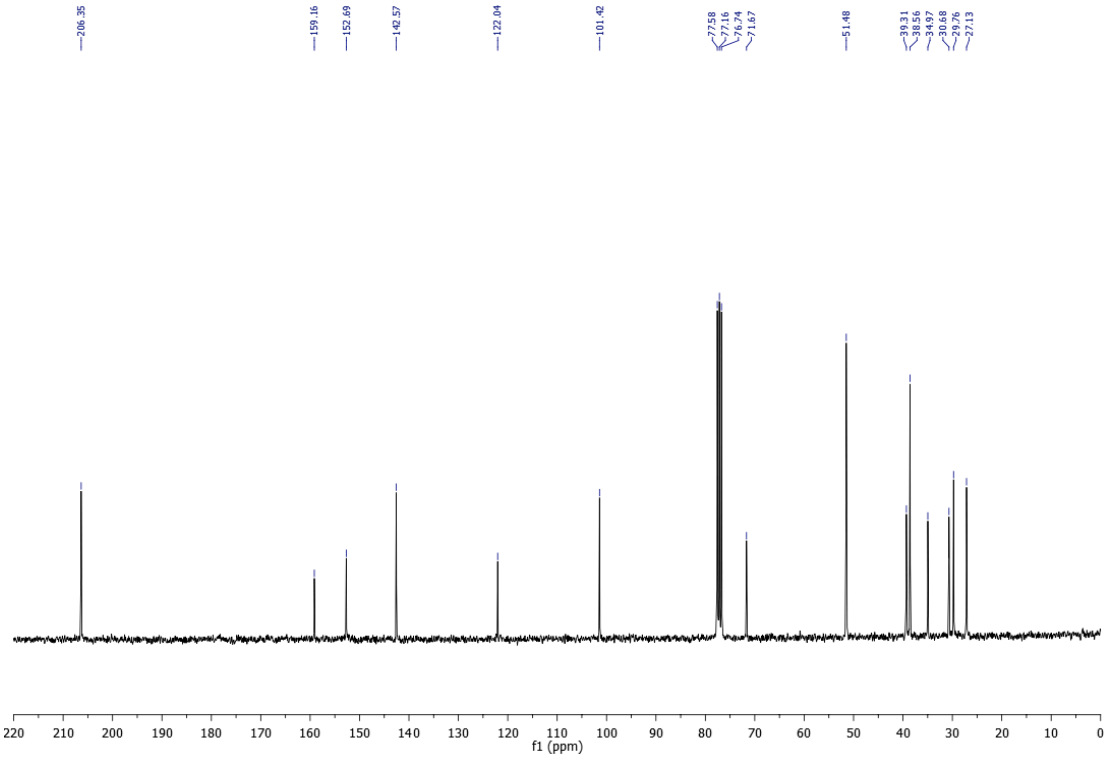
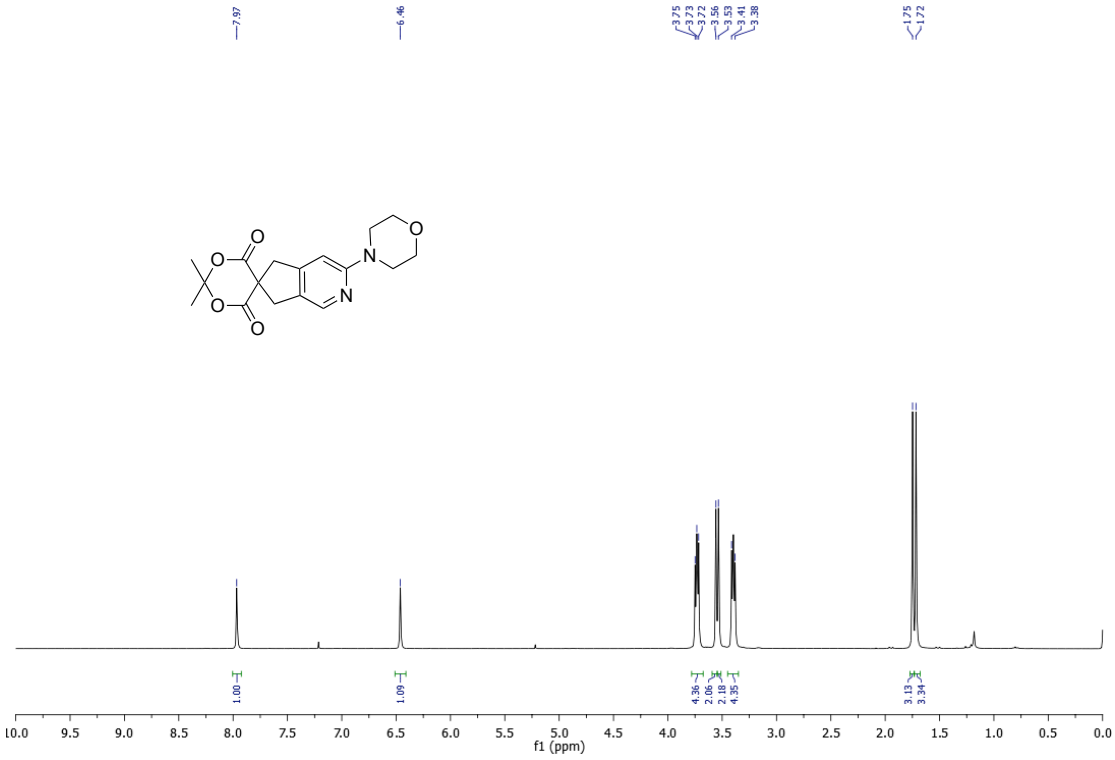
6.09
2.14
2.07
3.11
2.99
f1 (ppm)


206.35
159.16
152.69
142.57
122.04
101.42
77.58
77.16
76.74
71.67
51.48
39.31
38.56
34.97
30.68
29.76
27.13
f1 (ppm)

3i


7.97
6.46
3.75
3.73
3.72
3.56
3.55
3.41
3.38
1.75
1.72
O
O
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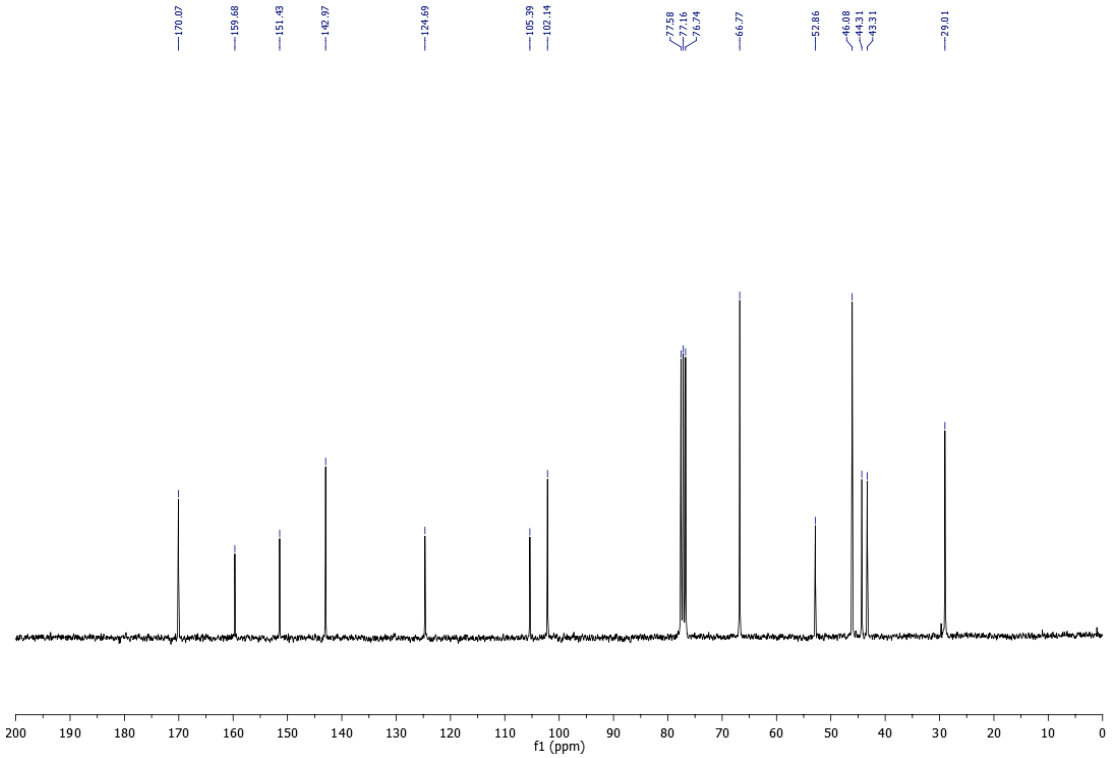
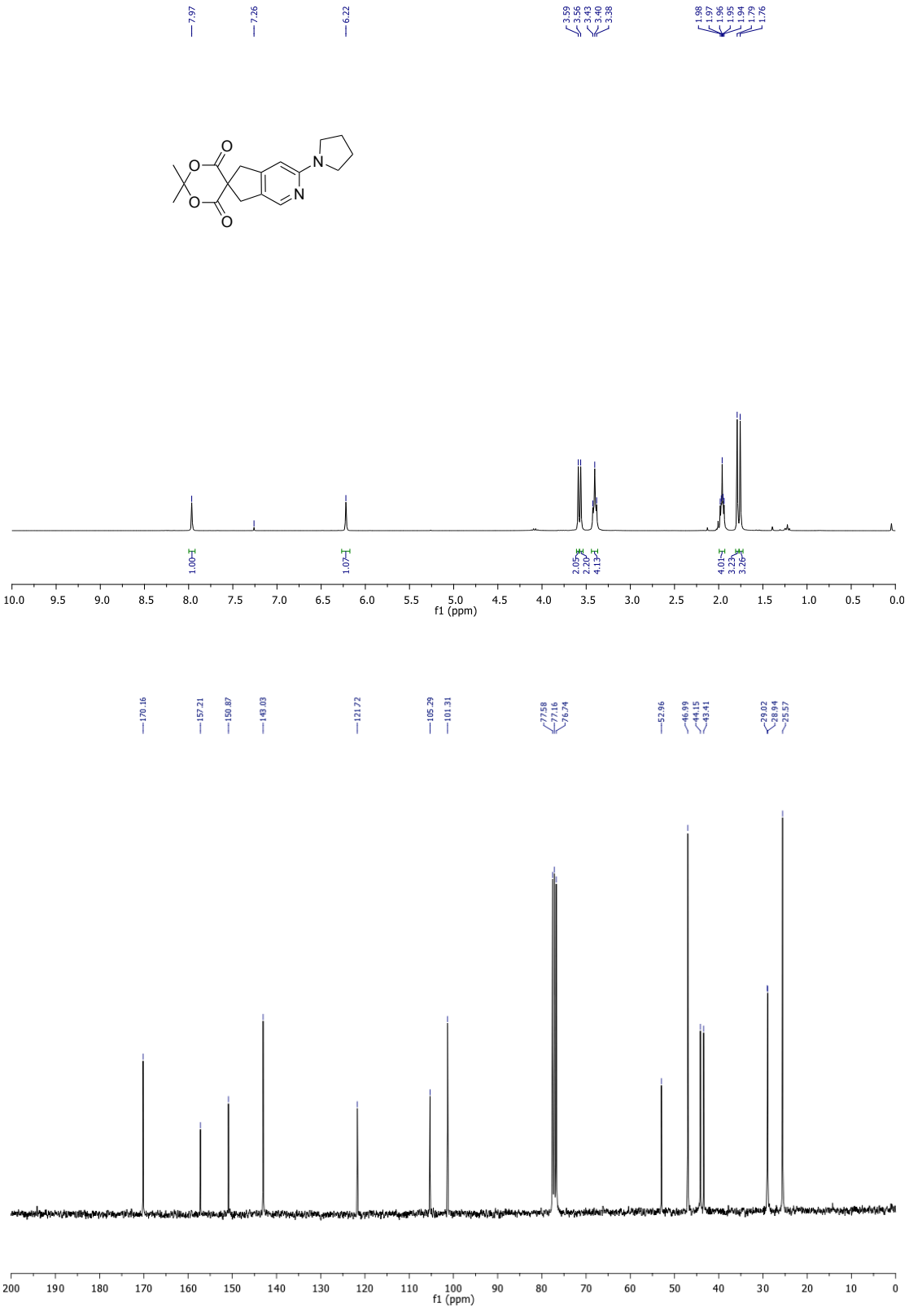
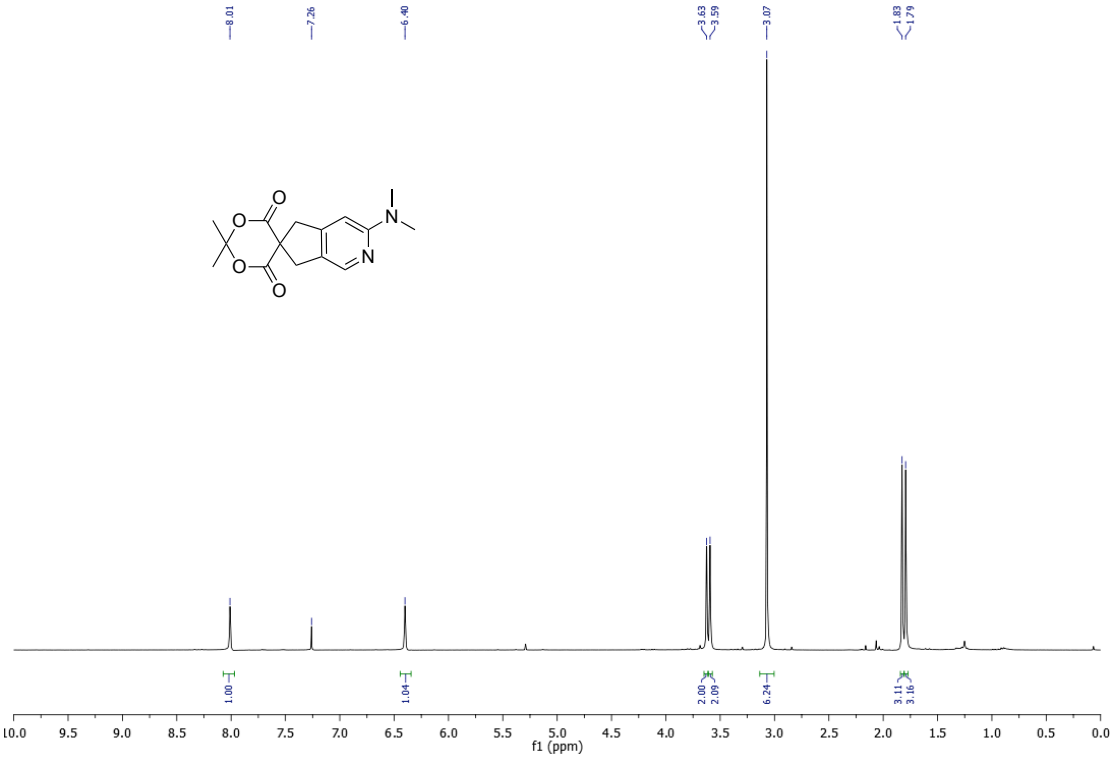
1.09
4.36
2.06
2.18
4.35
3.13
3.34
f1 (ppm)

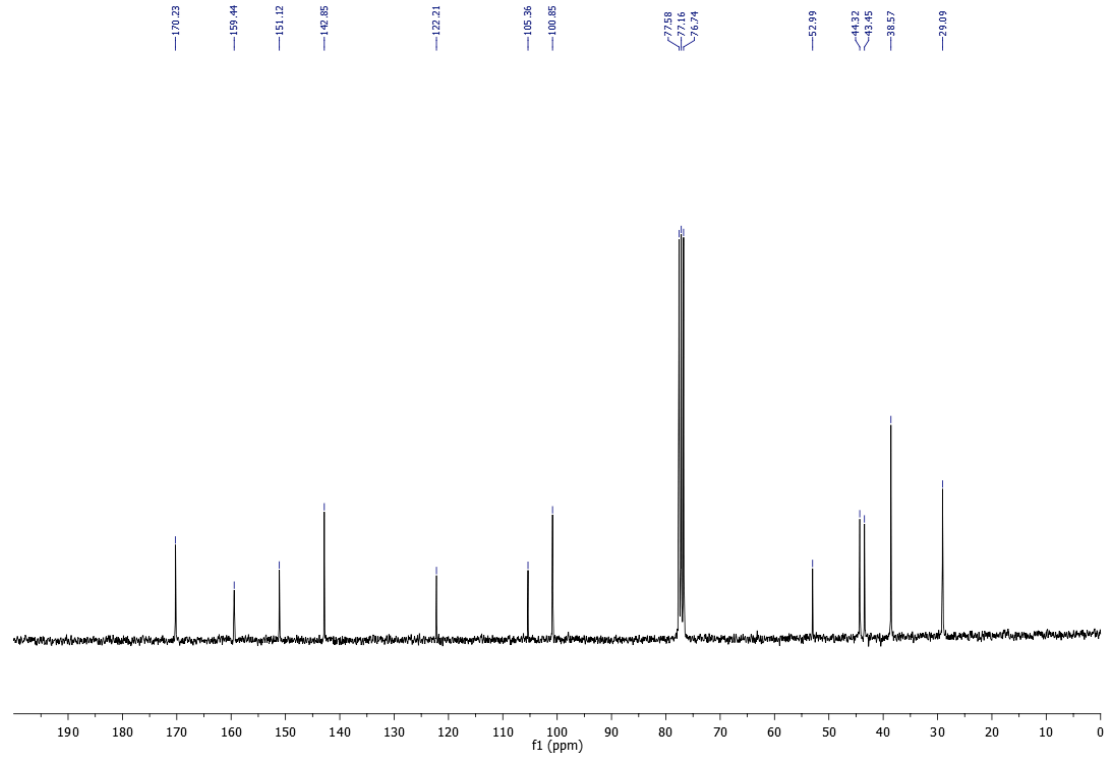

170.07
159.68
151.43
142.97
124.69
105.39
102.14
77.58
77.16
76.74
66.77
52.86
46.08
44.31
43.31
29.01
f1 (ppm)

3j

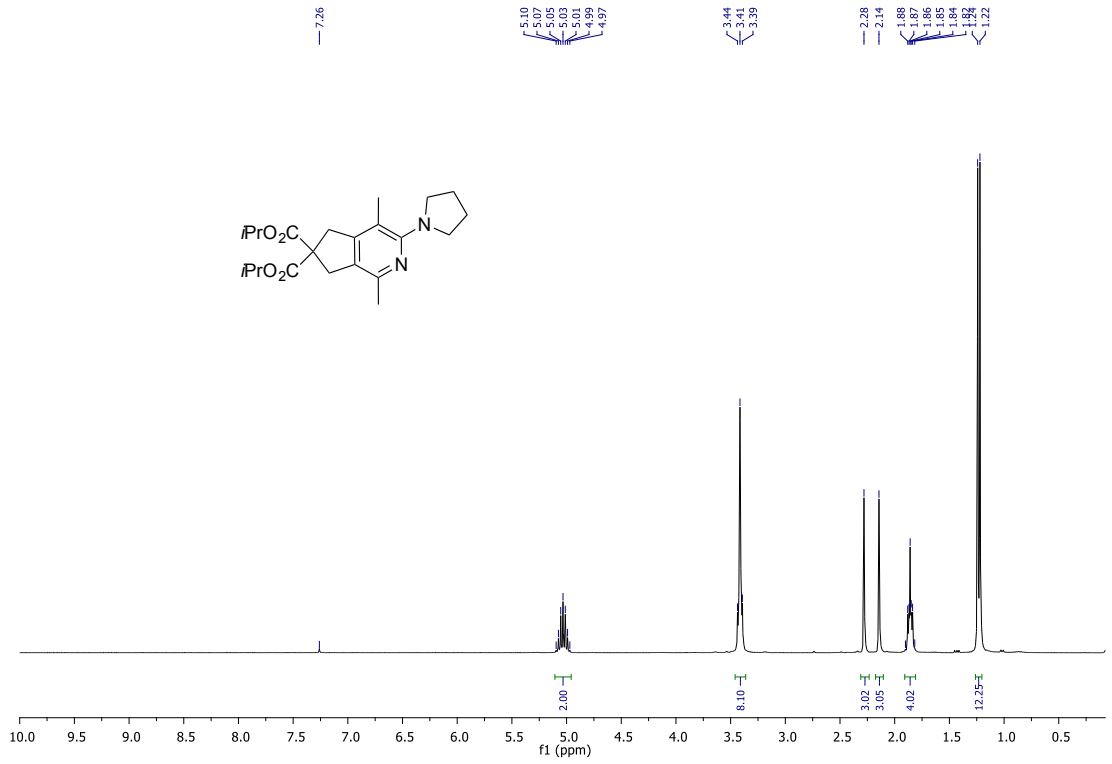

7.97
7.26
6.22
3.59
3.56
3.43
3.40
3.38
1.98
1.97
1.96
1.95
1.94
1.79
1.76
O
O
O
O
N
N
1.00
1.07
2.05
2.20
4.13
4.01
3.23
3.26
f1 (ppm)
170.16
157.21
150.87
143.03
121.72
105.29
101.31
77.58
77.16
76.74
52.96
46.99
44.15
43.41
29.02
28.94
25.57
f1 (ppm)

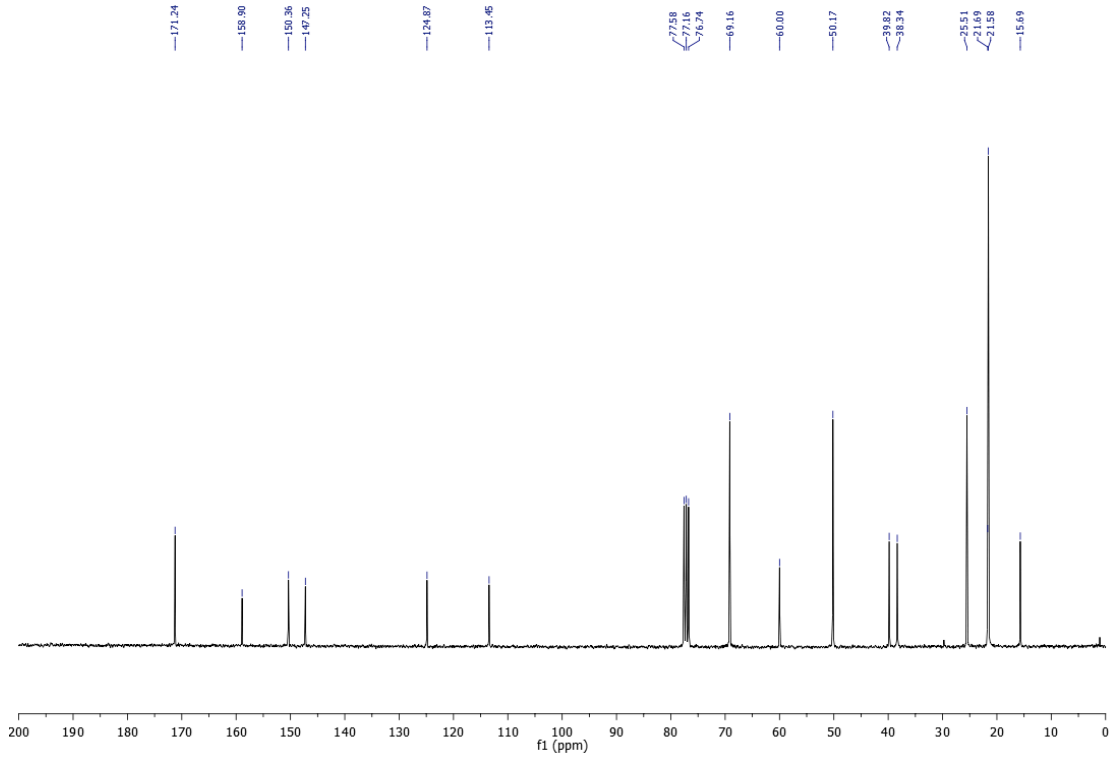
3k


8.01
7.26
6.40
3.63
3.59
3.07
1.83
1.79
1.00
1.04
2.00
2.09
6.24
3.11
3.16
f1 (ppm)

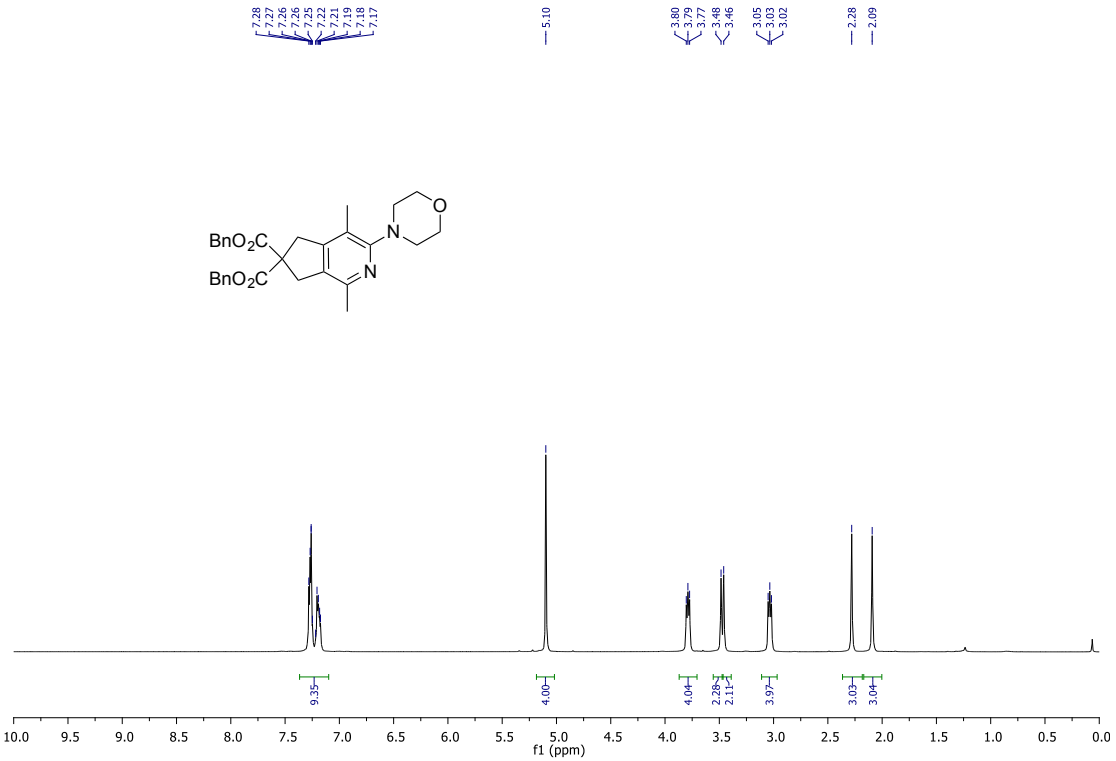

170.23
159.44
151.12
142.85
122.21
105.36
100.85
77.58
77.16
76.74
52.99
44.32
43.45
38.57
29.09
f1 (ppm)

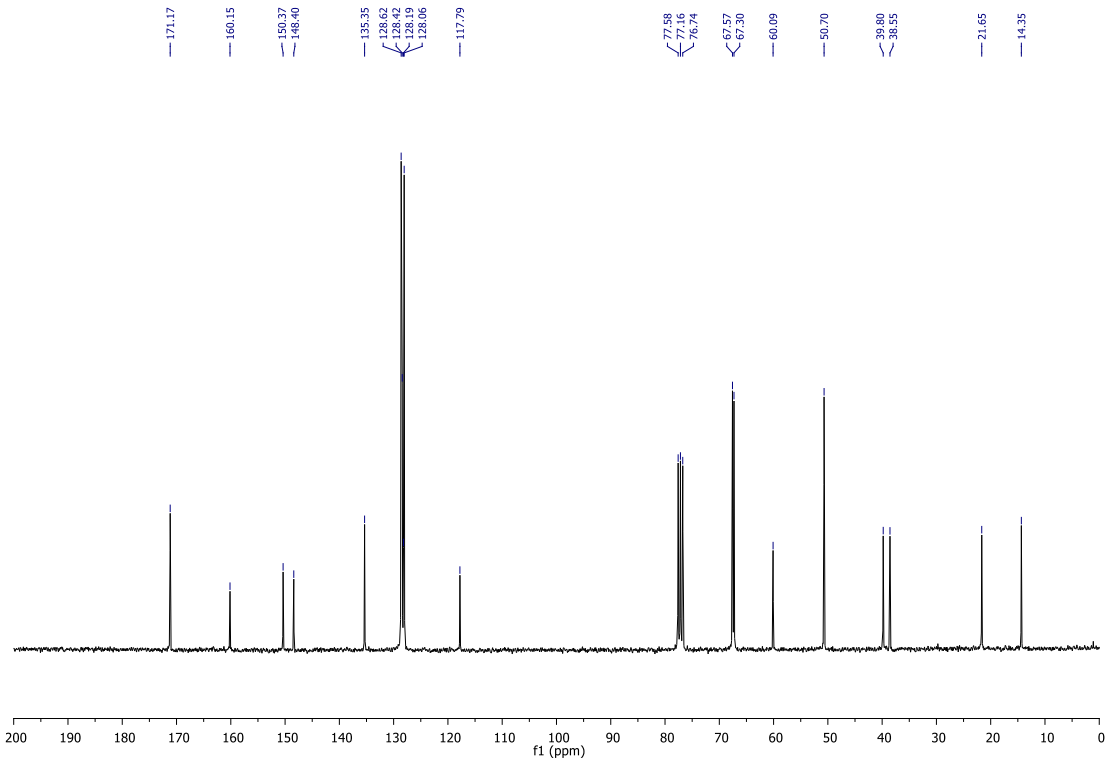
3l


7.26
5.10
5.07
5.05
5.03
5.01
4.99
4.97
3.44
3.41
3.39
2.28
2.14
1.88
1.87
1.86
1.85
1.84
1.82
1.24
1.22
iPrO2C
iPrO2C
N
N
2.00
8.10
3.02
3.05
4.02
12.25
f1 (ppm)

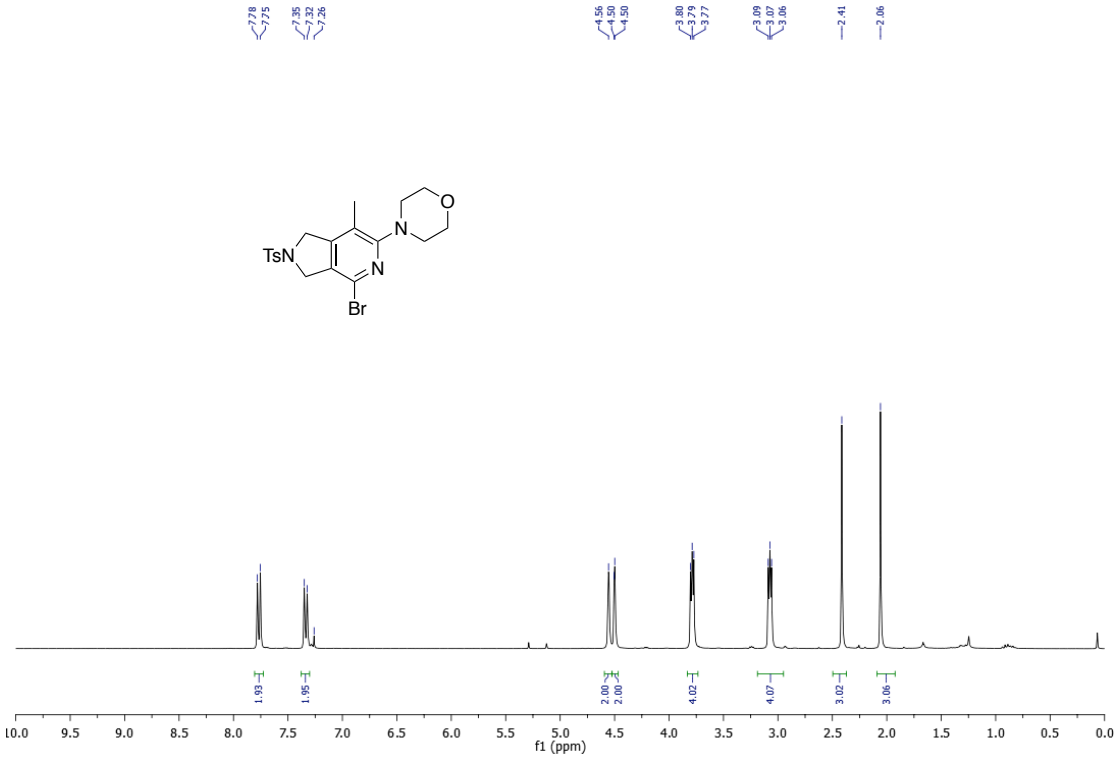

171.24
158.90
150.36
147.25
124.87
113.45
77.58
77.16
76.74
69.16
60.00
50.17
39.82
38.34
25.51
21.69
21.58
15.69
f1 (ppm)

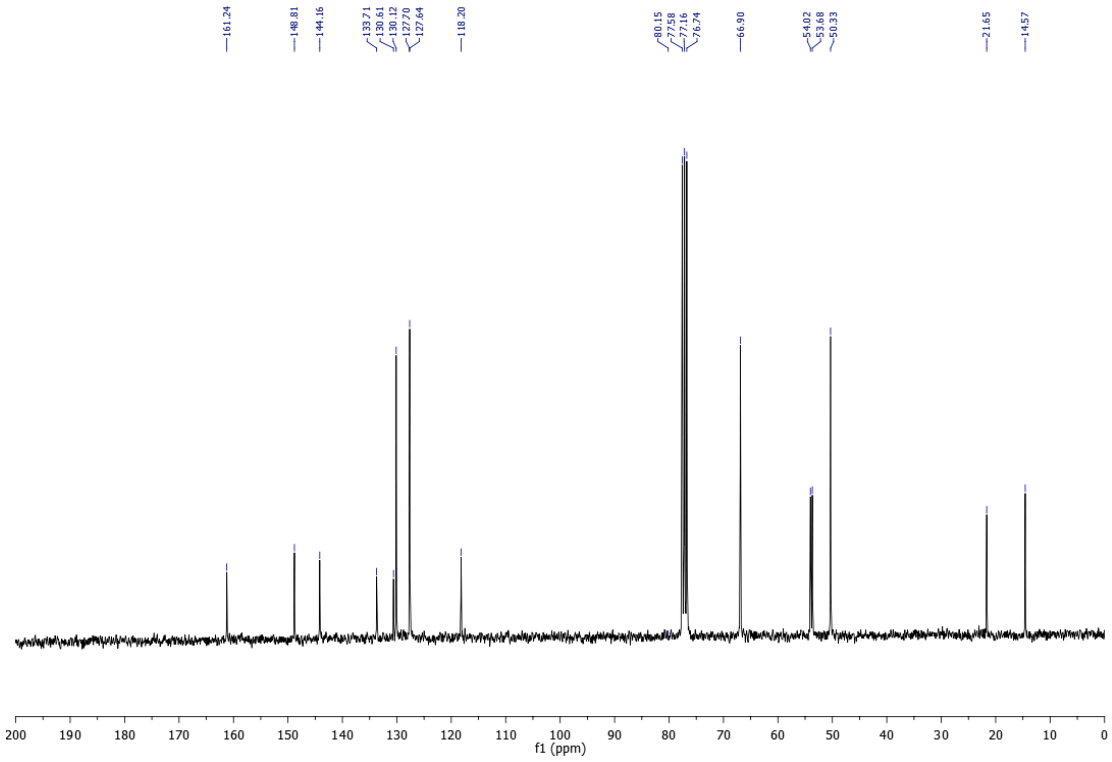
3m


7.28
7.27
7.26
7.26
7.25
7.22
7.21
7.19
7.18
7.17
5.10
3.80
3.79
3.77
3.48
3.46
3.05
3.03
3.02
2.38
2.09
BnO2C
BnO2C
N
O
N
9.35
4.00
4.04
2.28
2.11
3.97
3.03
3.04
f1 (ppm)

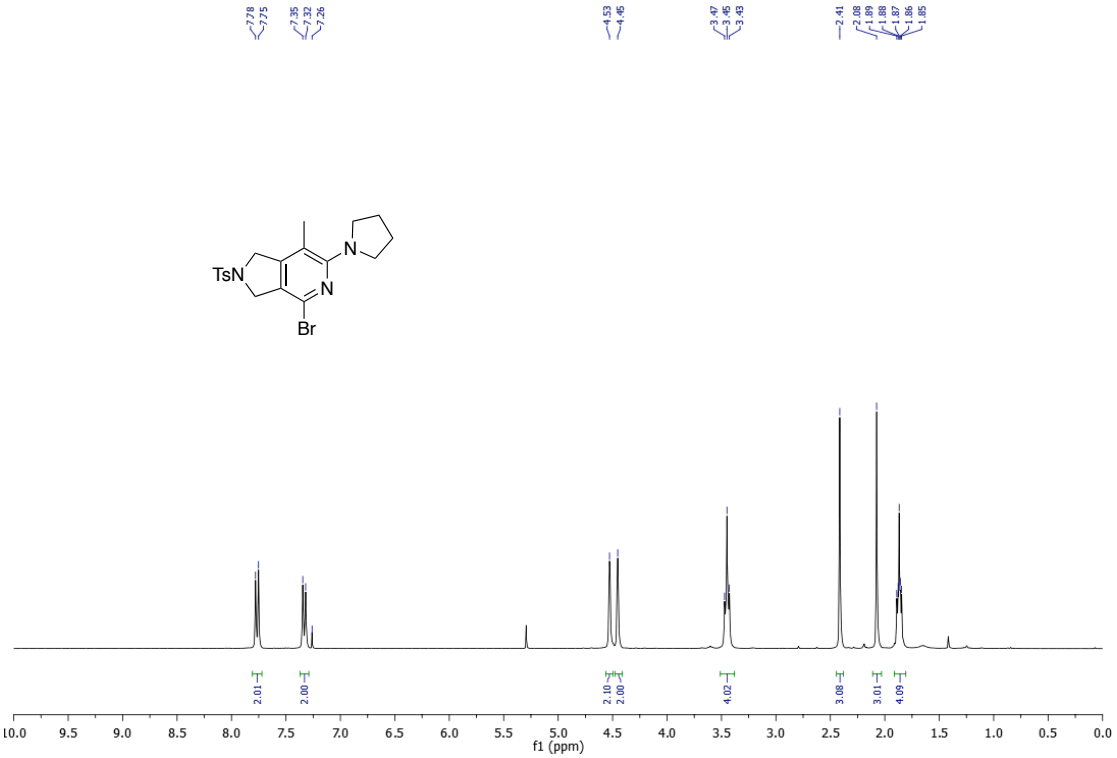

171.17
160.15
150.37
148.40
135.35
128.62
128.42
128.19
128.06
117.79
77.58
77.16
76.74
67.57
67.30
60.09
50.70
39.80
38.55
21.65
14.35
f1 (ppm)

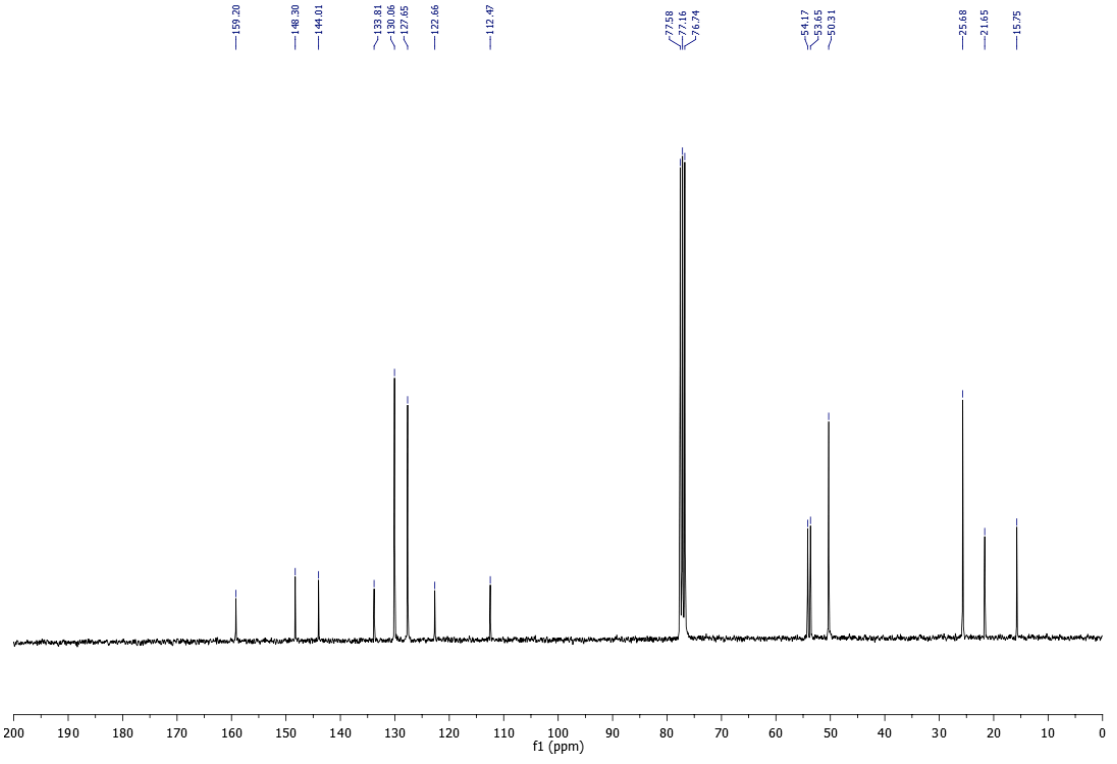
5b


7.78
7.75
7.35
7.32
7.26
4.56
4.50
4.50
3.80
3.79
3.77
3.09
3.07
3.06
2.41
2.06
TsN
N
O
N
Br
1.93
1.95
2.00
2.00
4.02
4.07
3.02
3.06
f1 (ppm)

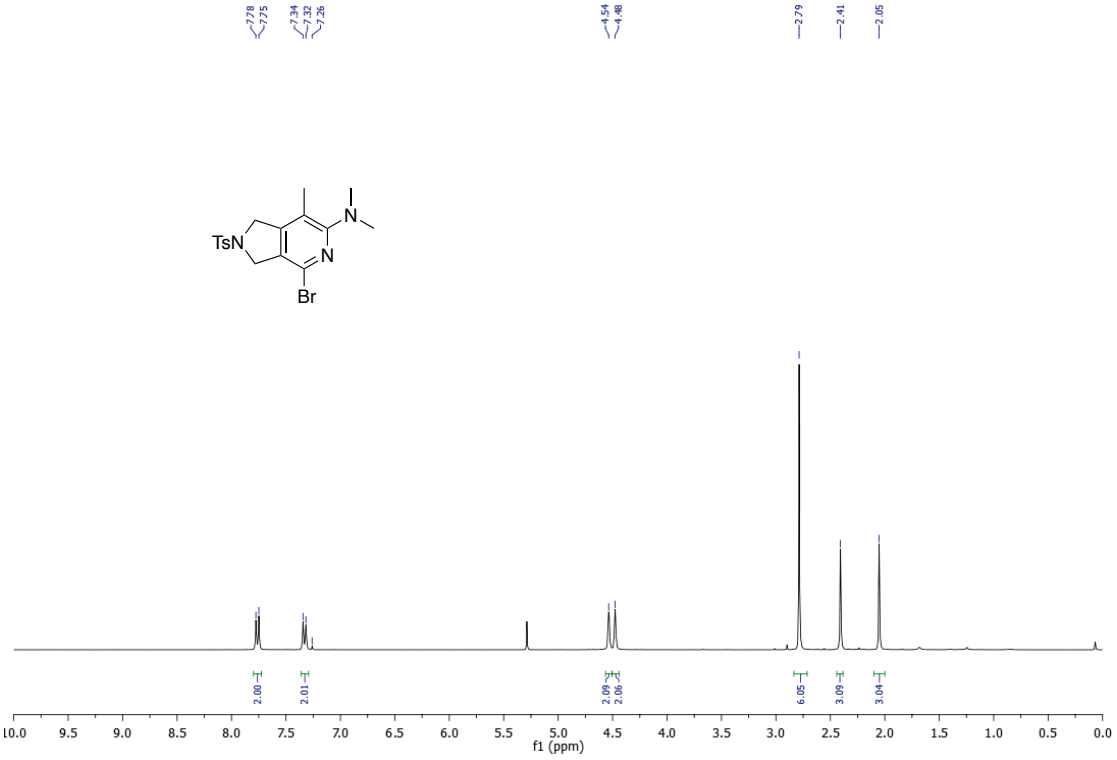

161.24
148.81
144.16
133.71
130.61
130.12
127.70
127.64
118.20
80.15
77.58
77.16
76.74
66.90
54.02
53.68
50.33
21.65
14.57
f1 (ppm)

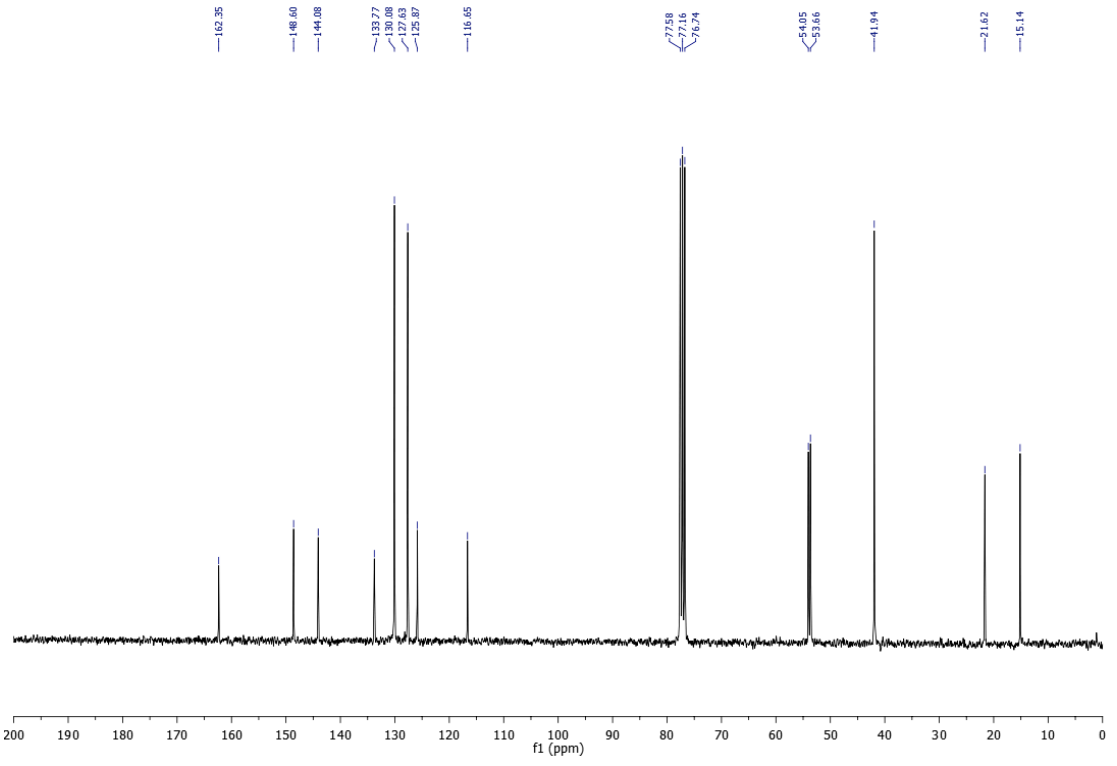
5c


7.78
7.75
7.35
7.32
7.26
4.53
4.45
3.47
3.46
3.43
2.41
2.08
1.89
1.88
1.87
1.86
1.85
TsN
N
N
Br
2.01
2.00
2.10
2.00
4.02
3.08
3.01
4.09
f1 (ppm)

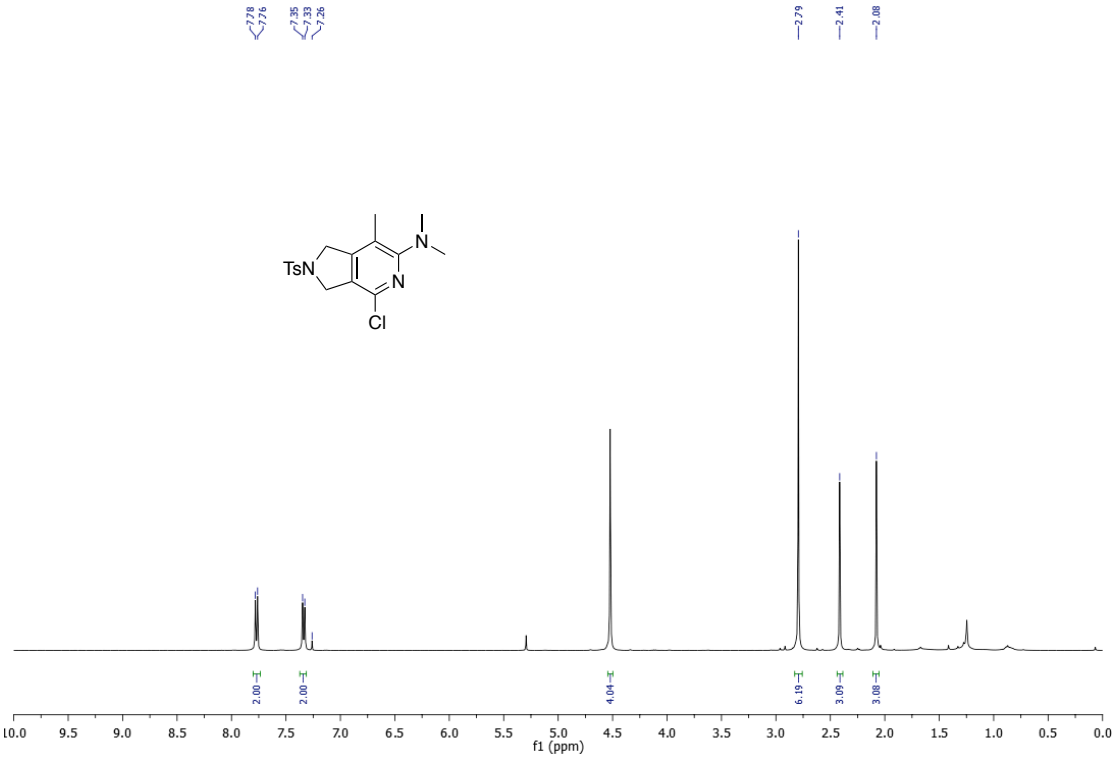

159.20
148.30
144.01
133.81
130.06
127.65
122.66
112.47
77.58
77.16
76.74
54.17
53.65
50.31
25.68
21.65
15.75
f1 (ppm)

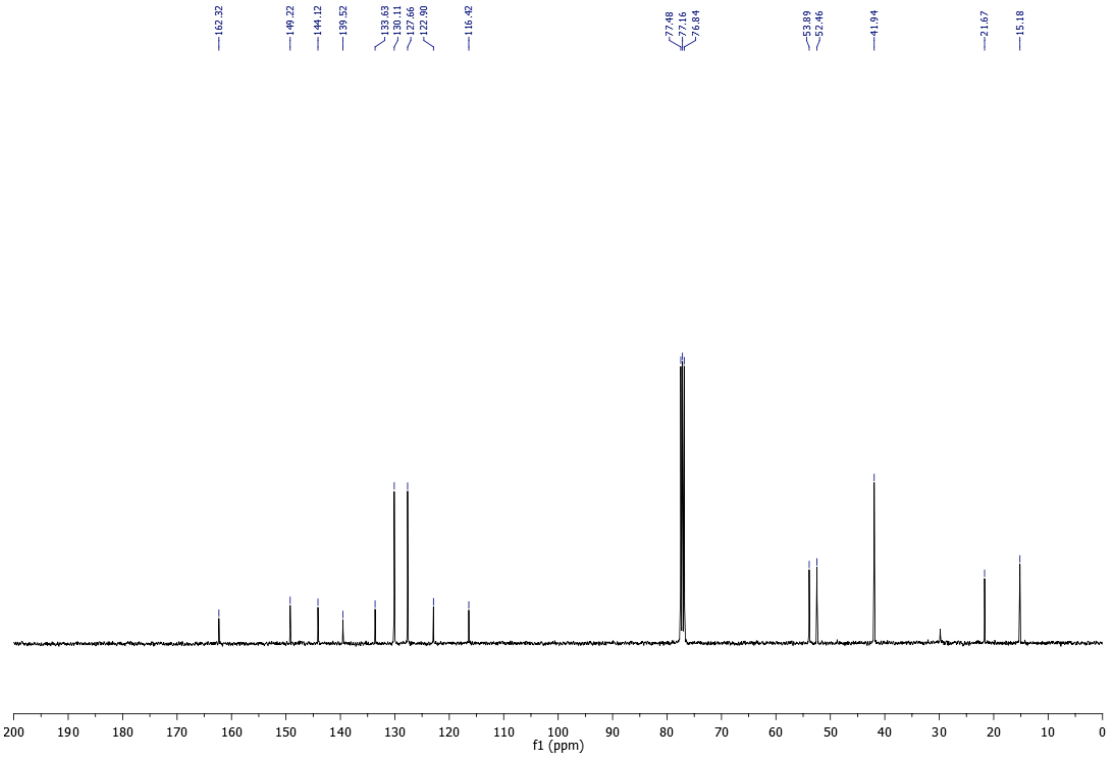
5d


7.78
7.75
7.34
7.32
7.26
4.54
4.48
2.79
2.41
2.05
TsN
N
N
Br
2.00
2.01
2.09
2.06
6.05
3.09
3.04
f1 (ppm)

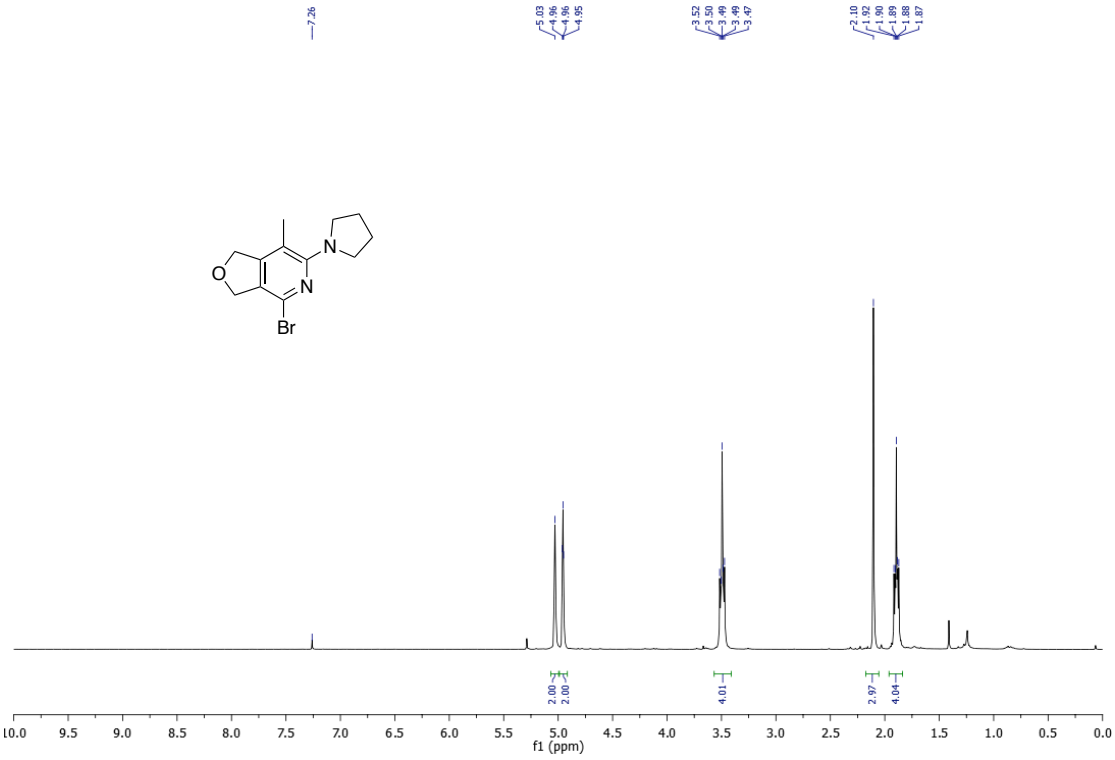

162.35
148.60
144.08
133.77
130.08
127.63
125.87
116.65
77.58
77.16
76.74
54.05
53.66
41.94
21.62
15.14
f1 (ppm)

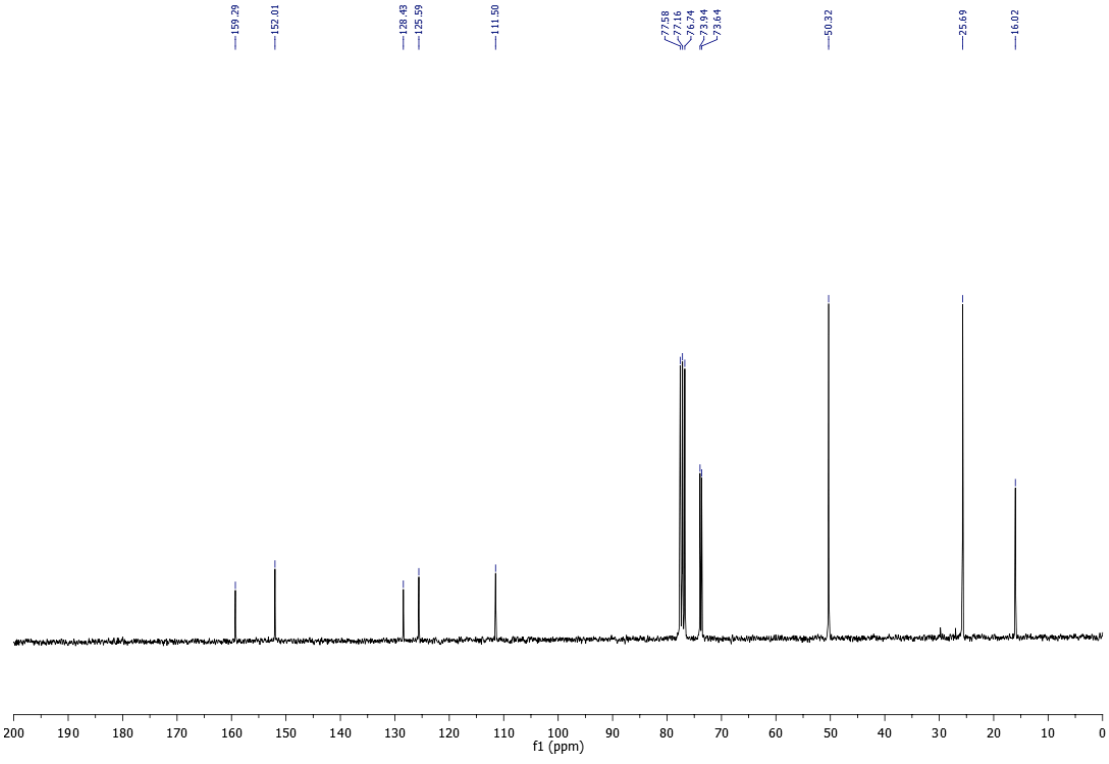
5e


7.78
7.76
7.35
7.33
7.26
2.79
2.41
2.08
TsN
N
N
Cl
2.00
2.00
4.04
6.19
3.09
3.08
f1 (ppm)

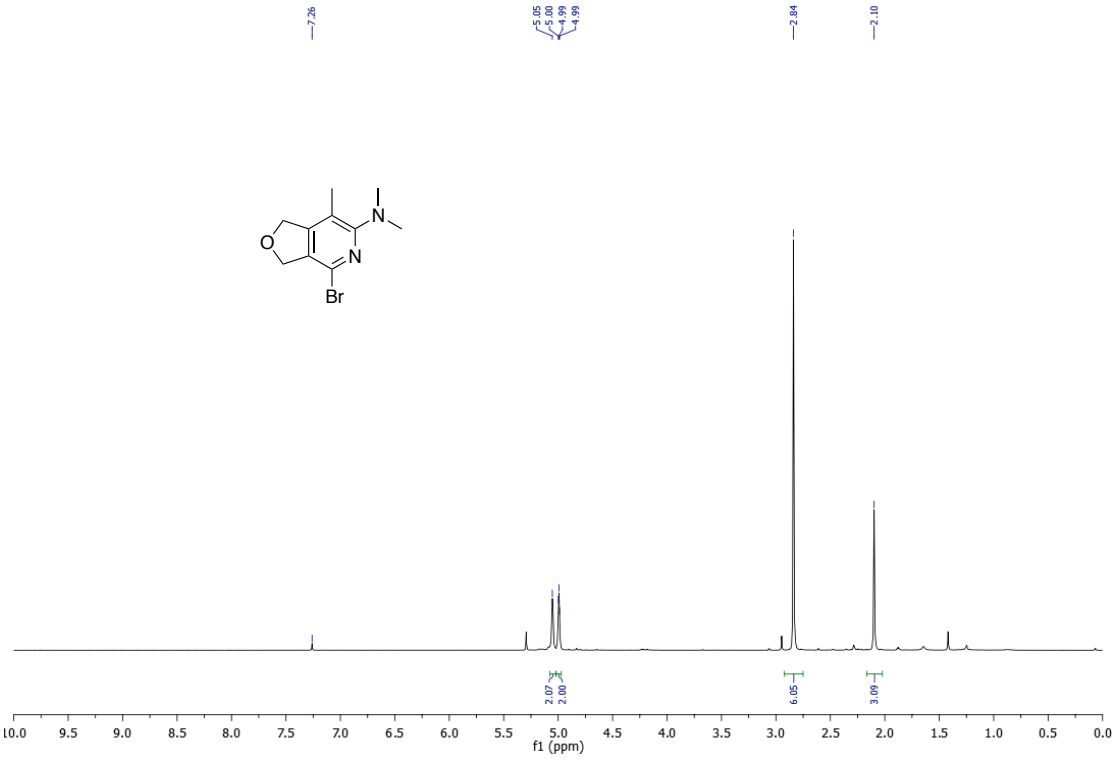

162.32
149.22
144.12
139.52
133.63
130.11
127.66
122.90
116.42
77.48
77.16
76.84
53.89
52.46
41.94
21.67
15.18
f1 (ppm)

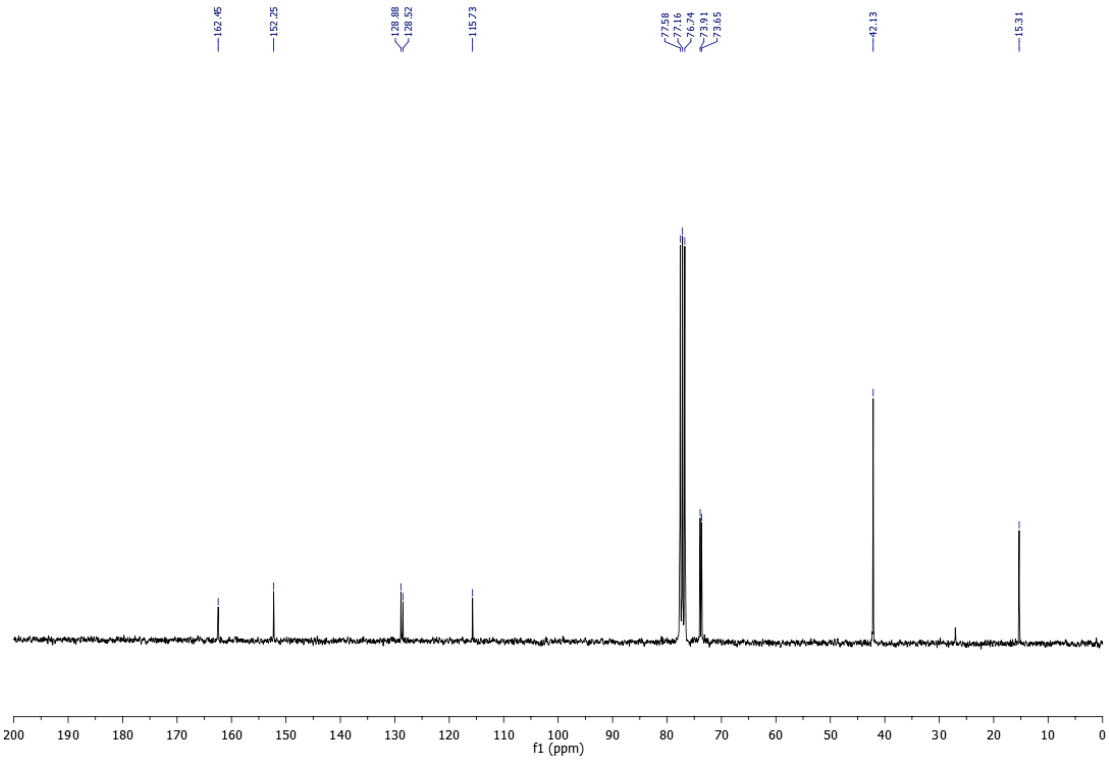
5f


7.26
5.03
4.96
4.96
4.95
3.52
3.50
3.49
3.49
3.47
2.10
1.92
1.90
1.89
1.88
1.87
O
N
N
Br
2.00
2.00
4.01
2.97
4.04
f1 (ppm)

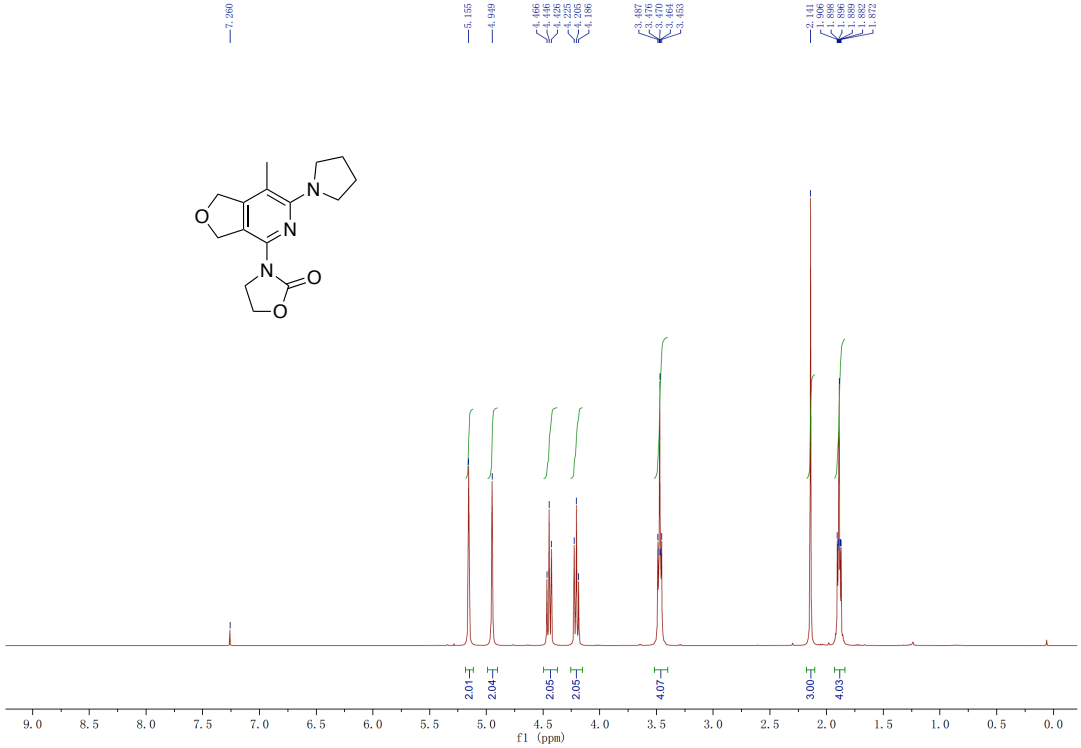

159.29
152.01
128.43
125.59
111.50
77.58
77.16
76.74
73.94
73.64
50.32
25.69
16.02
f1 (ppm)

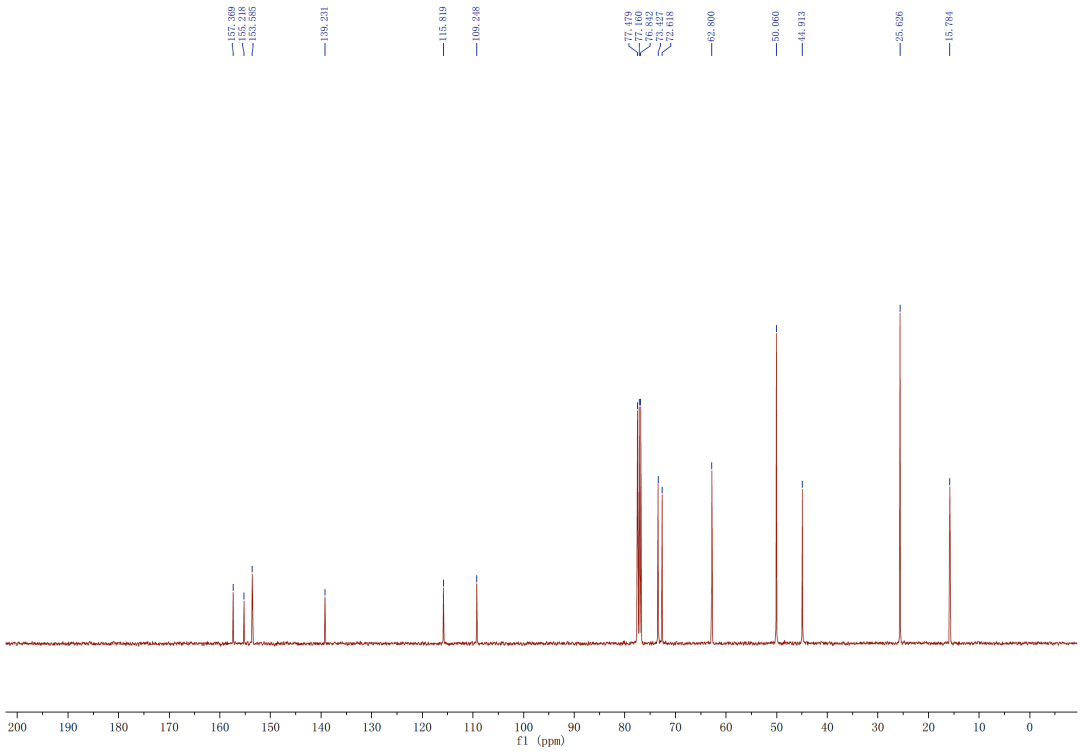
5g


7.26
5.05
5.00
4.99
4.99
2.84
2.10
O
N
N
Br
2.07
2.00
6.05
3.09
f1 (ppm)

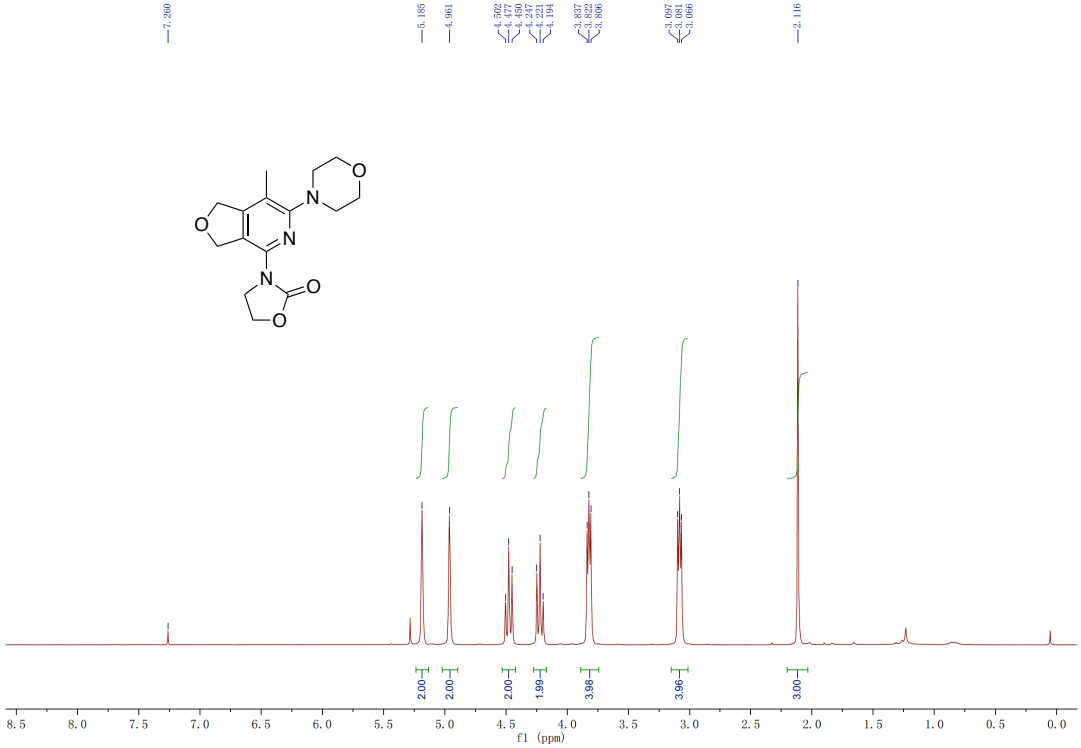

162.45
152.25
128.88
128.52
115.73
77.58
77.16
76.74
73.91
73.65
42.13
15.31
f1 (ppm)

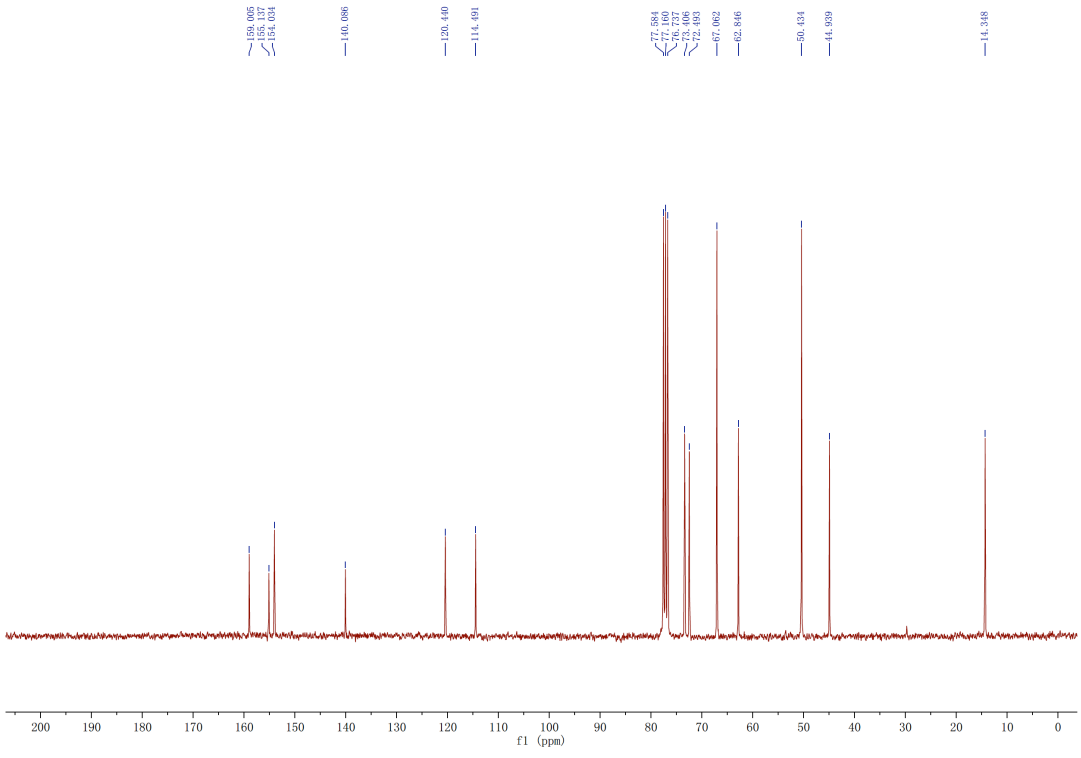
5h


7.260
5.155
4.949
4.466
4.446
4.436
4.225
4.205
4.186
3.487
3.476
3.470
3.464
3.453
2.141
2.096
1.898
1.896
1.889
1.882
1.872
O
N
N
N
O
O
2.01
2.04
2.05
2.05
4.07
3.00
4.03
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)

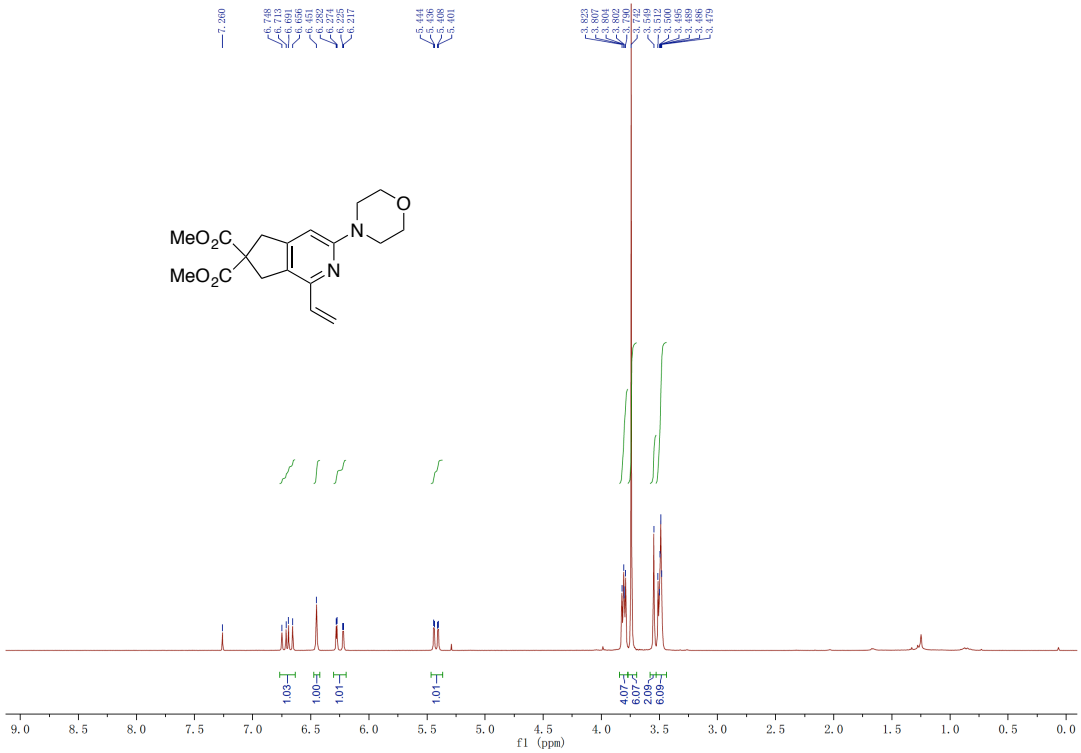

157.369
155.218
153.585
139.231
115.819
109.248
77.479
77.160
76.842
73.427
72.618
62.800
50.060
44.913
25.626
15.784
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

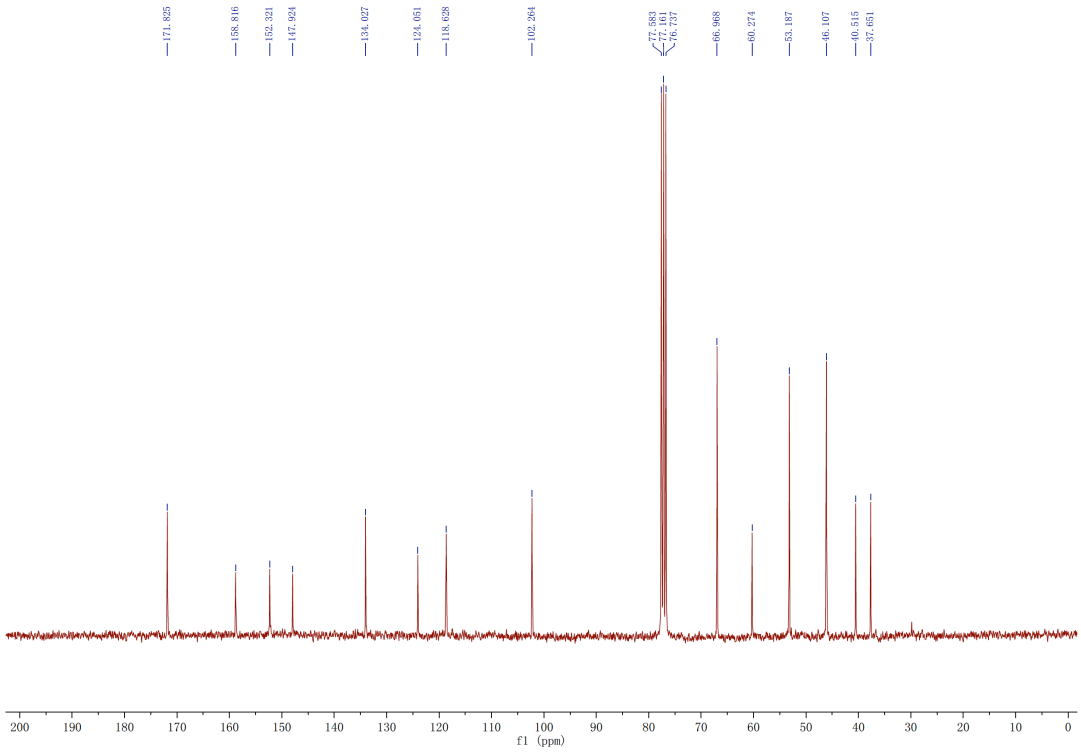
5i


7.260
5.185
4.961
4.502
4.477
4.490
4.457
4.221
4.194
3.837
3.822
3.806
3.097
3.081
3.066
2.116
2.00
2.00
2.00
1.99
3.98
3.96
3.00
f1 (ppm)

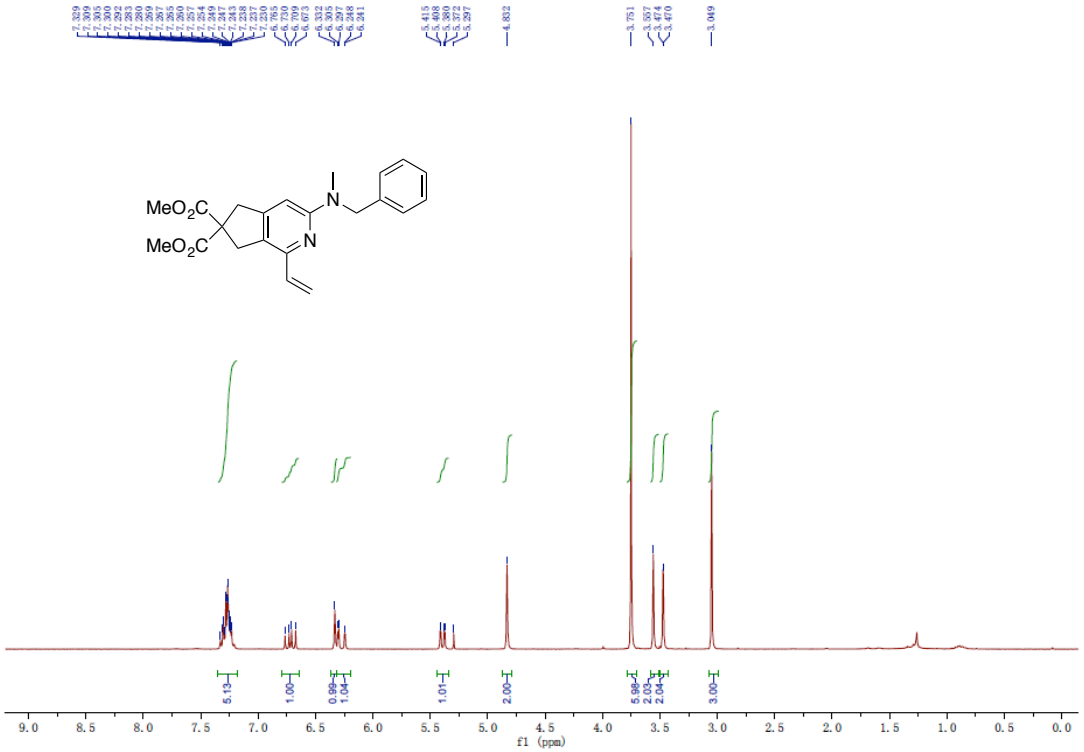

159.005
155.037
154.034
140.086
120.440
114.491
77.584
77.160
76.737
73.406
72.493
67.062
62.846
50.434
44.939
14.348
f1 (ppm)

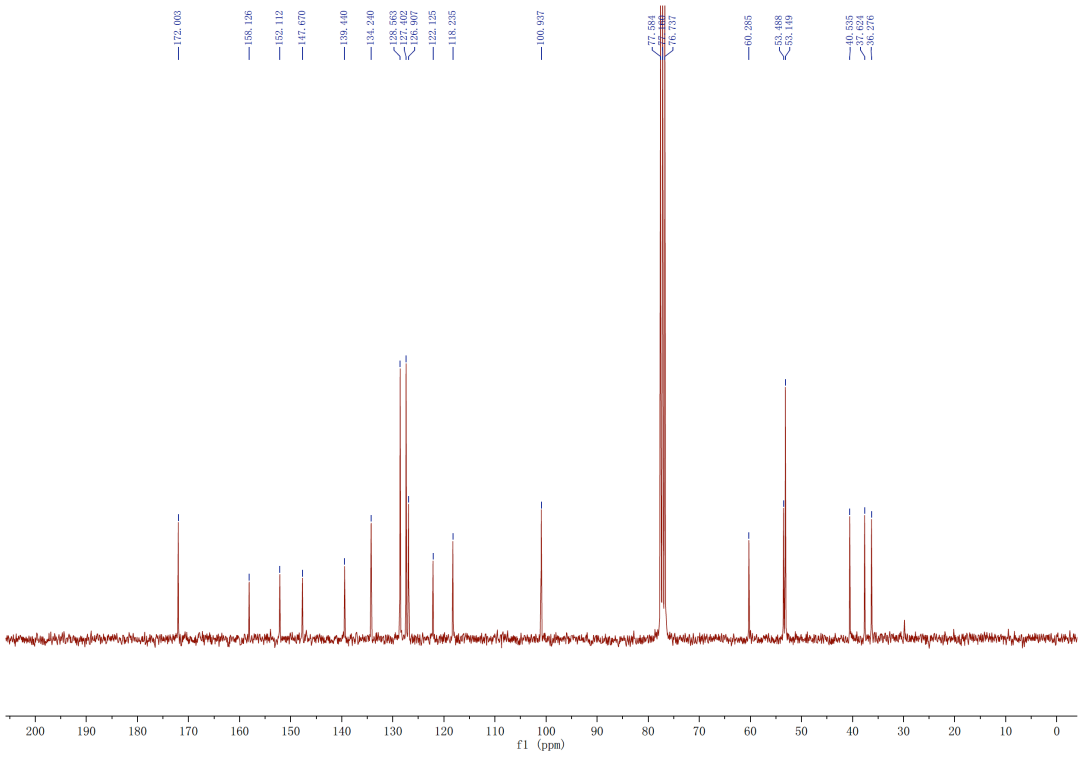
5j


7.260
6.748
6.733
6.691
6.656
6.451
6.392
6.274
6.225
6.217
5.444
5.436
5.408
5.401
3.823
3.807
3.804
3.802
3.790
3.742
3.549
3.512
3.500
3.495
3.489
3.486
3.479
MeO2C
MeO2C
N
O
N
1.03
1.00
1.01
1.01
4.07
6.07
2.09
6.09
f1 (ppm)

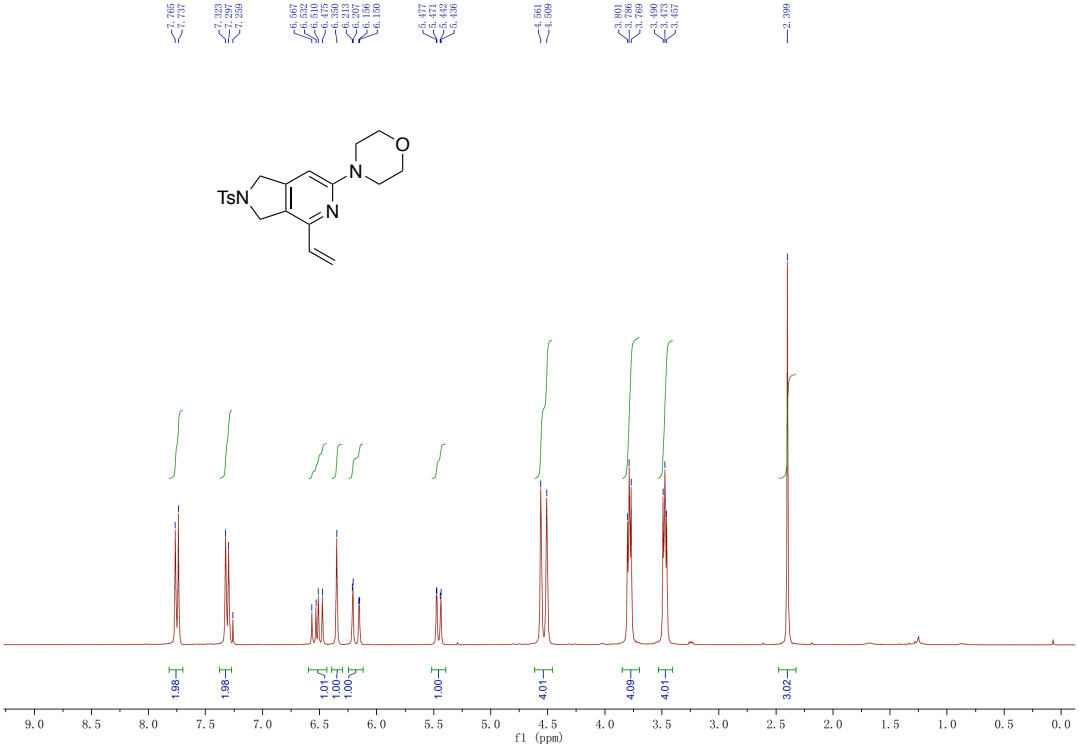

171.825
158.816
152.321
147.924
134.027
124.051
118.628
102.264
77.583
77.161
76.737
66.968
60.274
53.187
46.107
40.515
37.651
f1 (ppm)

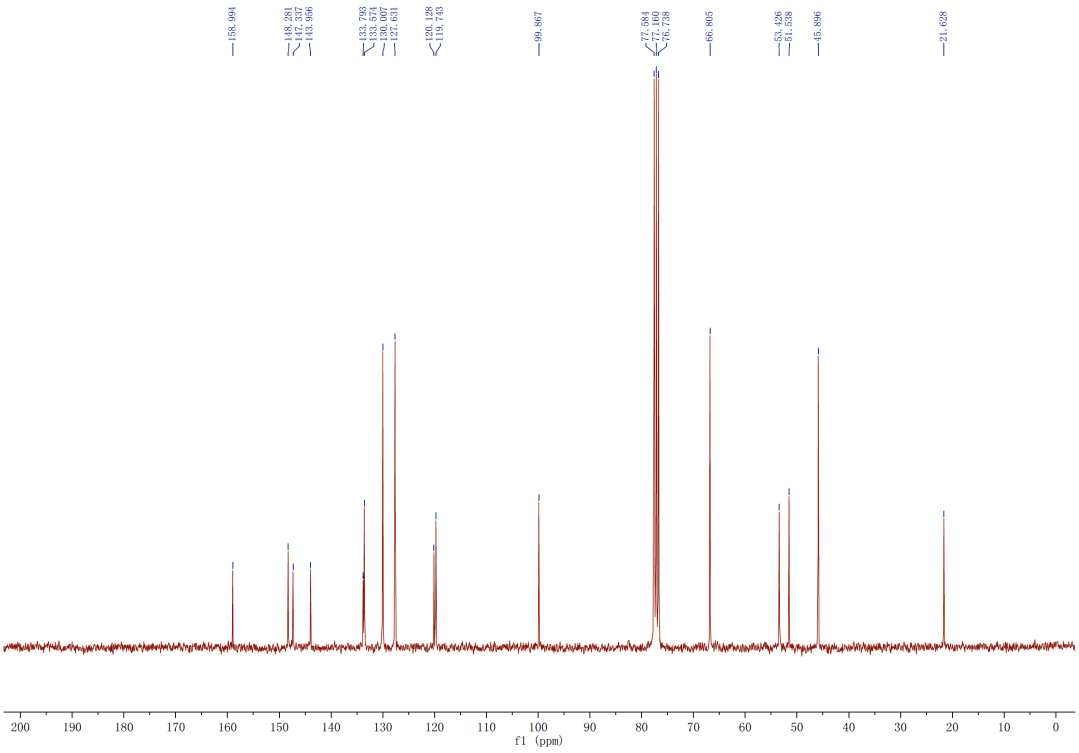
5k



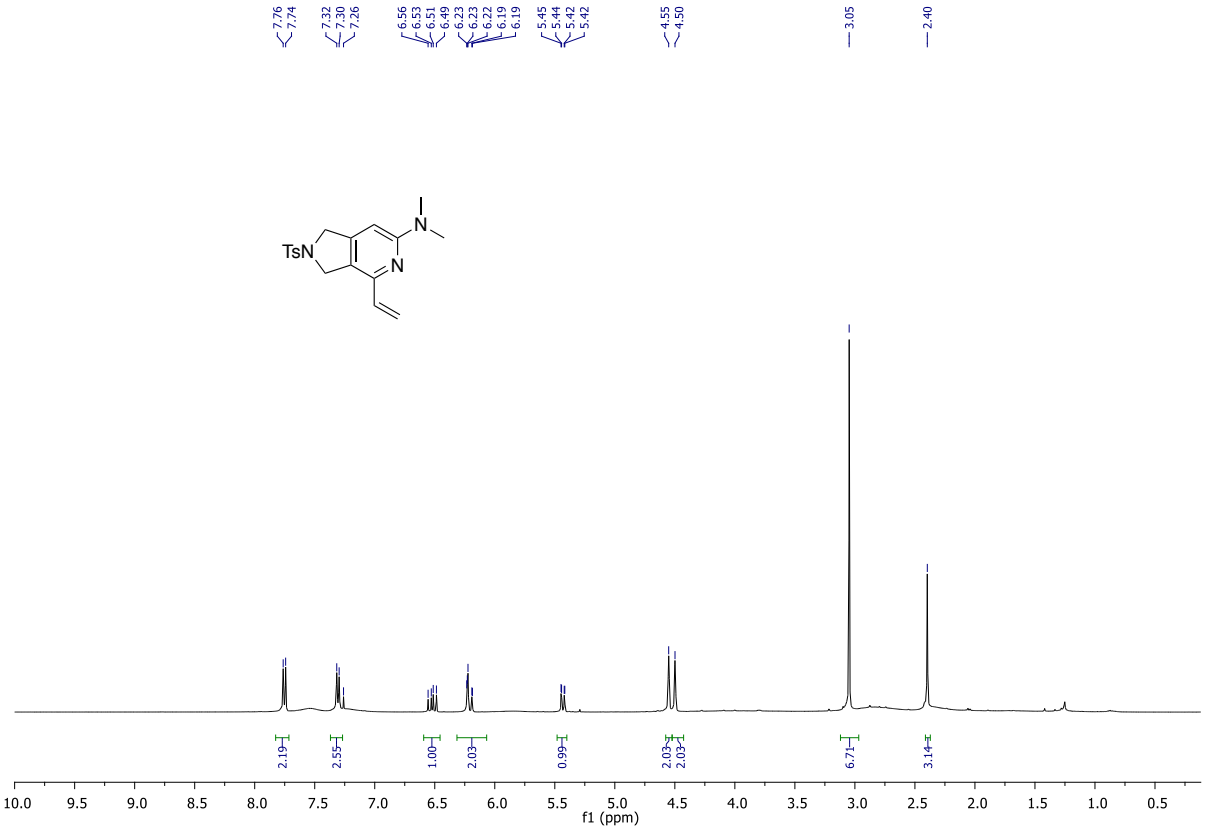


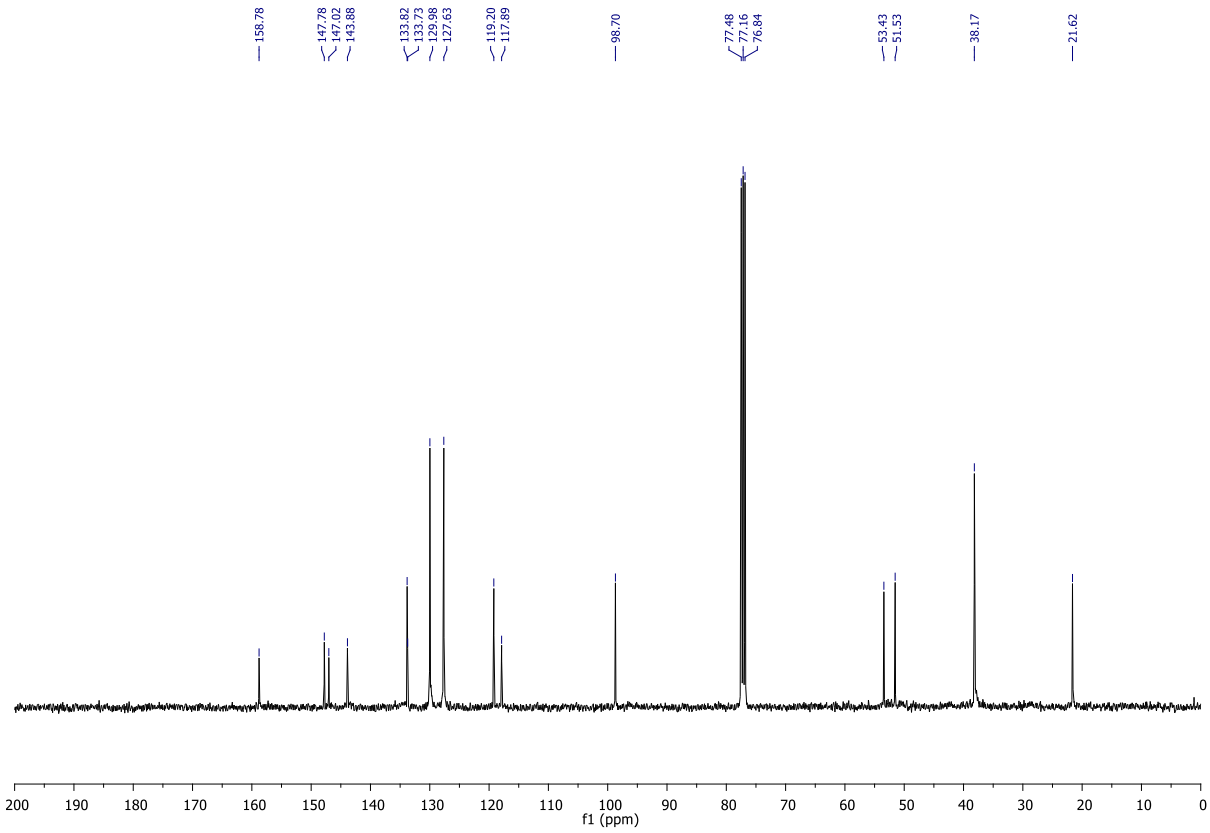
5l


7.765
7.737
7.323
7.297
7.259
6.567
6.532
6.510
6.475
6.350
6.313
6.207
6.156
6.150
5.477
5.471
5.462
5.436
4.561
4.509
3.801
3.786
3.769
3.460
3.443
3.457
2.399
TsN
N
O
N
1.98
1.98
1.01
1.00
1.00
4.01
4.09
4.01
3.02
f1 (ppm)

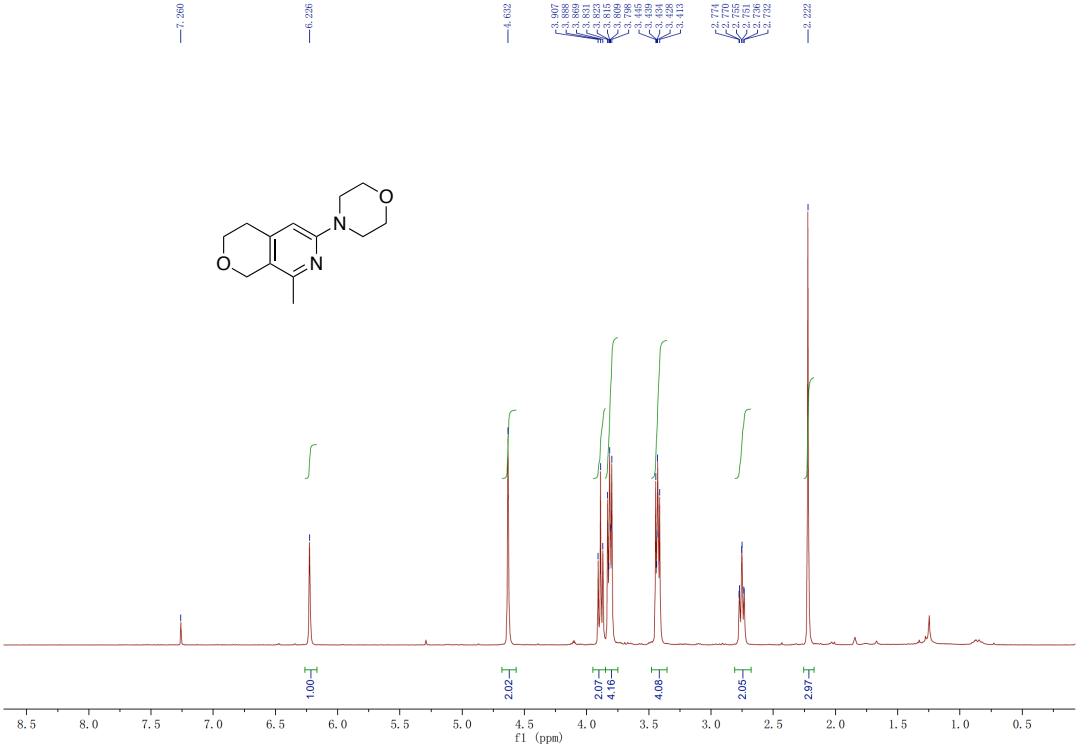

158.994
148.281
147.337
143.956
133.793
132.574
130.007
127.631
120.138
119.743
99.867
77.584
77.160
76.798
66.805
52.426
51.538
45.896
21.628
f1 (ppm)

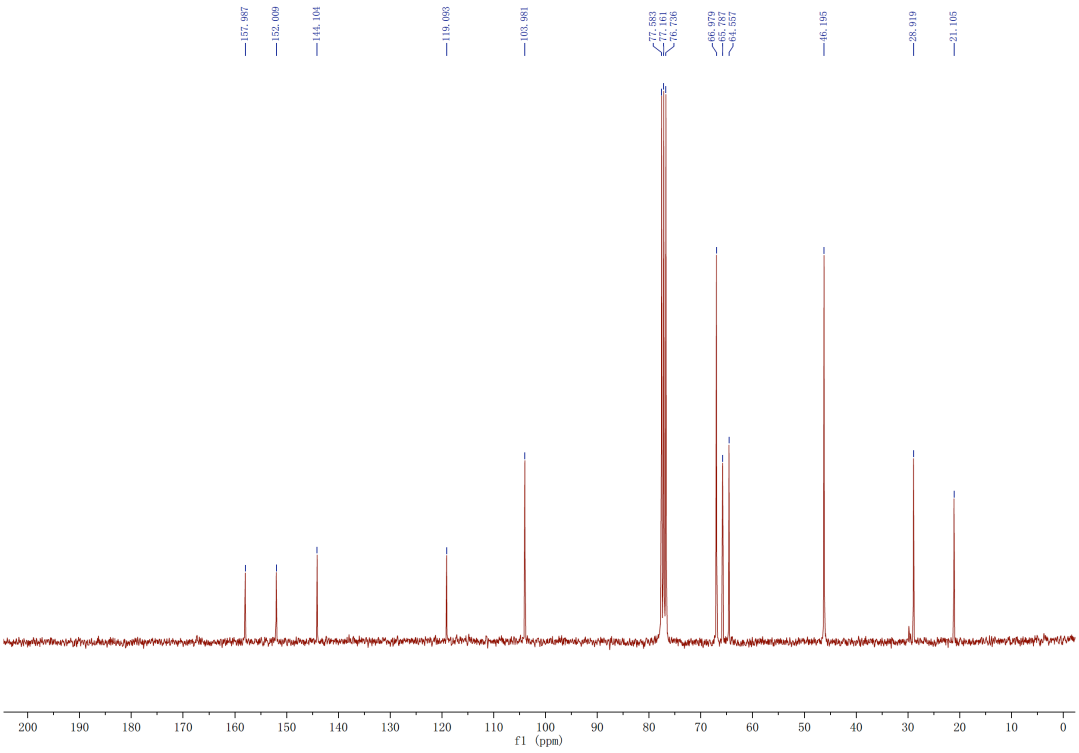
5m


7.76
7.74
7.32
7.30
7.26
6.56
6.53
6.51
6.49
6.23
6.23
6.22
6.19
6.19
5.45
5.44
5.42
5.42
4.55
4.50
3.05
2.40
TsN
N
N
2.19
2.55
1.00
2.03
0.99
2.03
2.03
6.71
3.14
f1 (ppm)

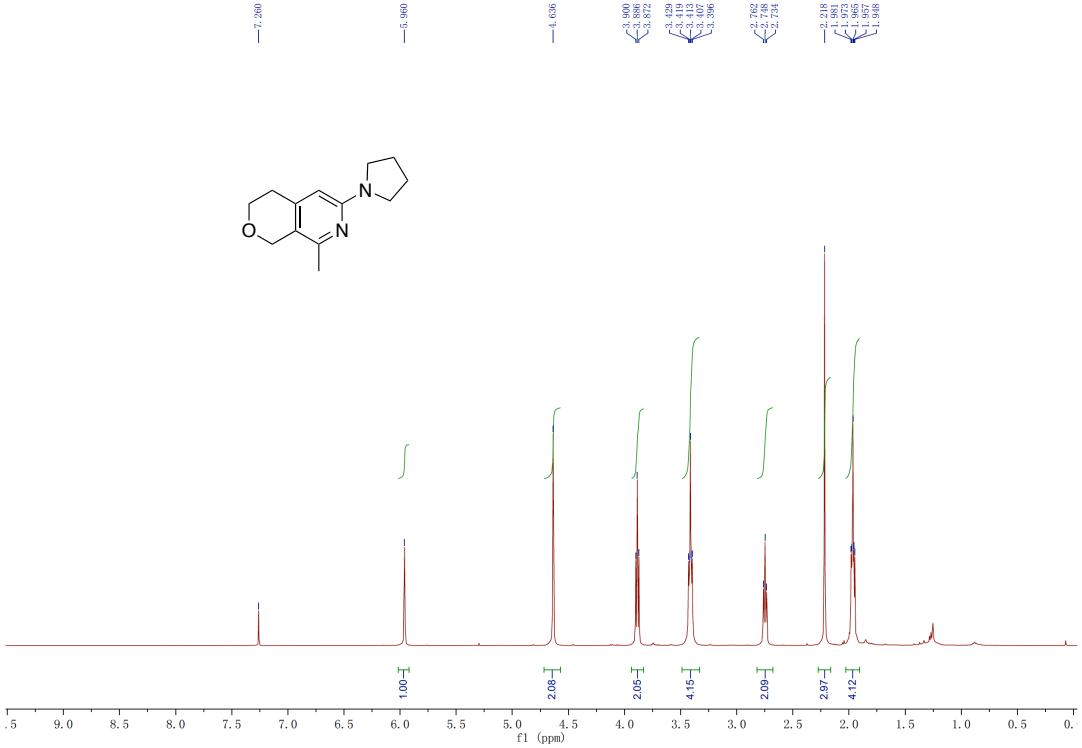

158.78
147.78
147.02
143.88
133.82
133.73
129.98
127.63
119.20
117.89
98.70
77.48
77.16
76.84
53.43
51.53
38.17
21.62
f1 (ppm)

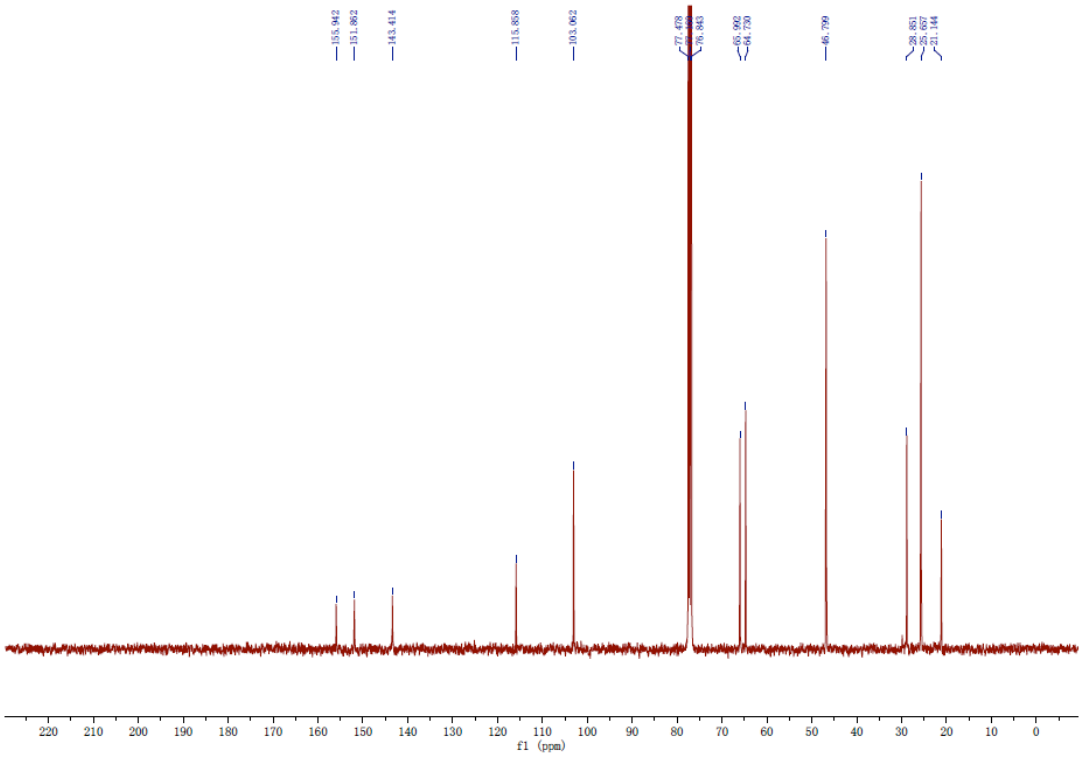
8a


7.260
6.226
4.632
3.907
3.888
3.869
3.831
3.822
3.815
3.809
3.798
3.445
3.439
3.434
3.428
3.413
2.774
2.770
2.755
2.751
2.736
2.732
2.222
O
N
O
N
1.00
2.02
2.07
4.16
4.08
2.05
2.97
f1 (ppm)

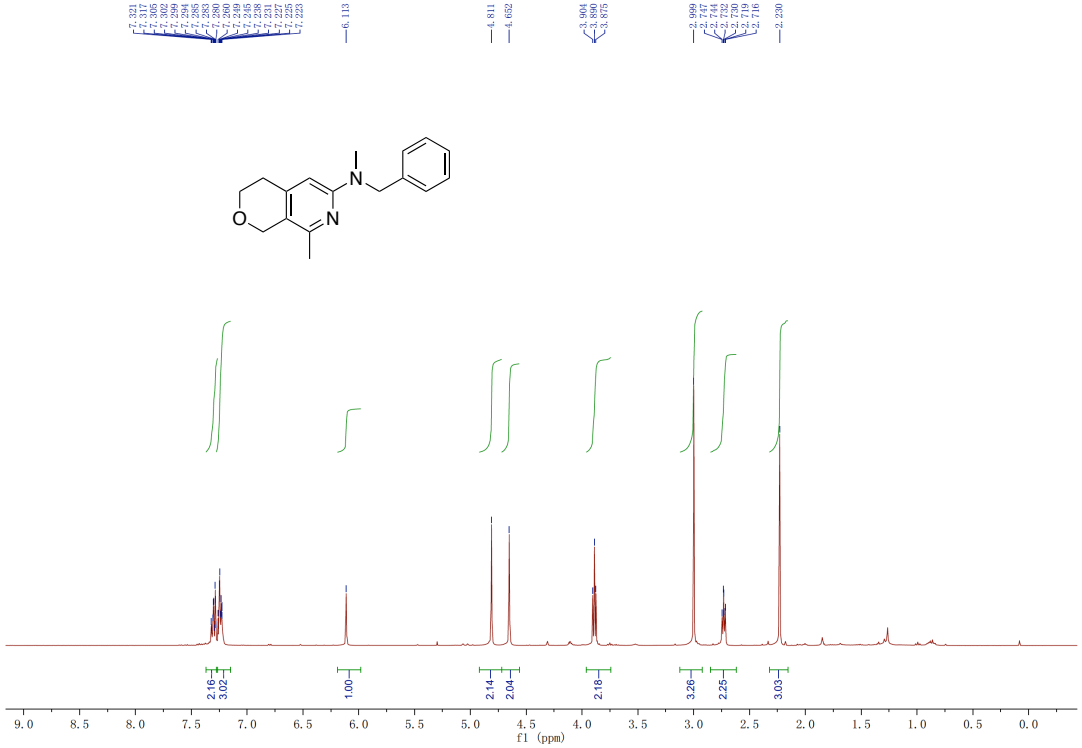

157.987
152.009
144.104
119.083
103.981
77.583
77.161
76.736
66.979
65.787
64.557
46.195
28.919
21.105
f1 (ppm)

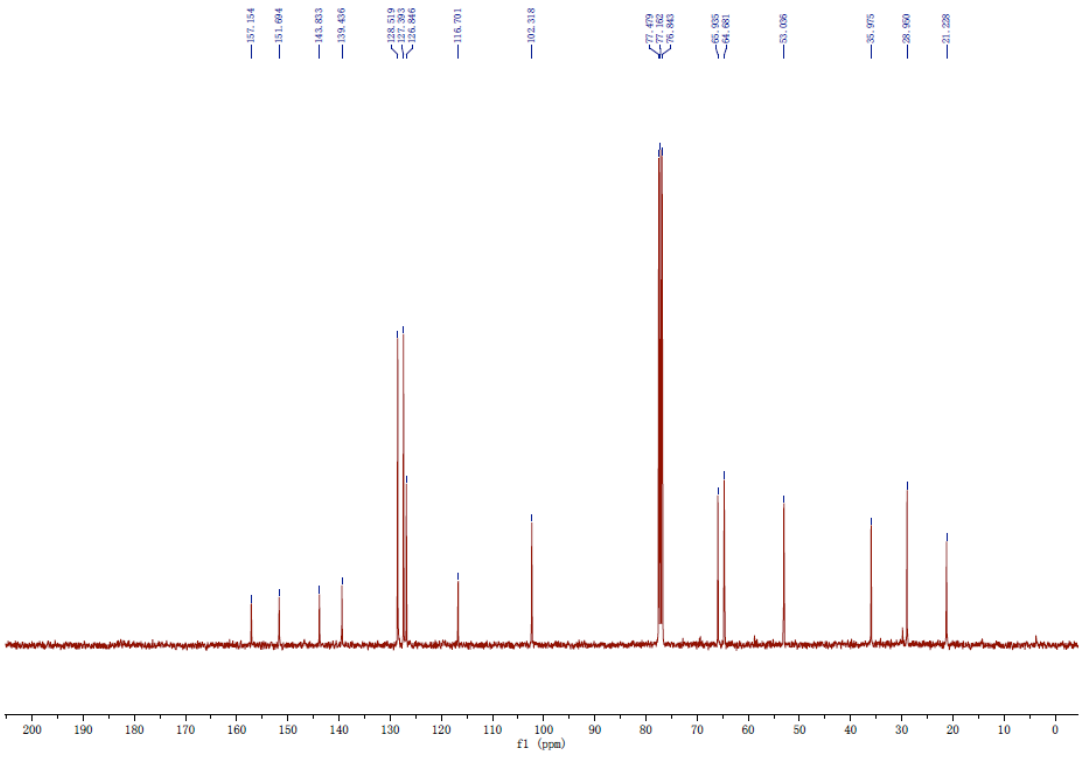
8b


7.260
5.960
4.636
3.900
3.886
3.872
3.429
3.419
3.413
3.407
3.396
2.762
2.748
2.734
2.218
1.981
1.973
1.965
1.957
1.948
O
N
N
1.00
2.08
2.05
4.15
2.09
2.97
4.12
f1 (ppm)

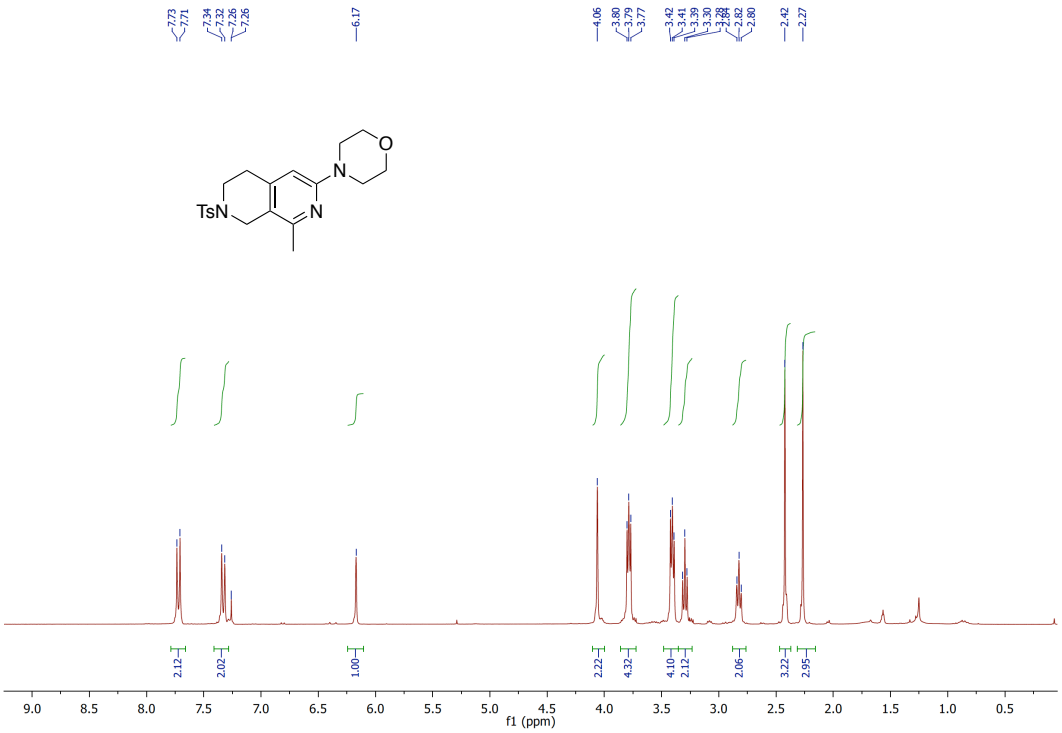

155.942
151.862
143.414
115.858
103.062
77.478
76.843
65.992
64.730
46.799
28.851
25.657
21.144
f1 (ppm)

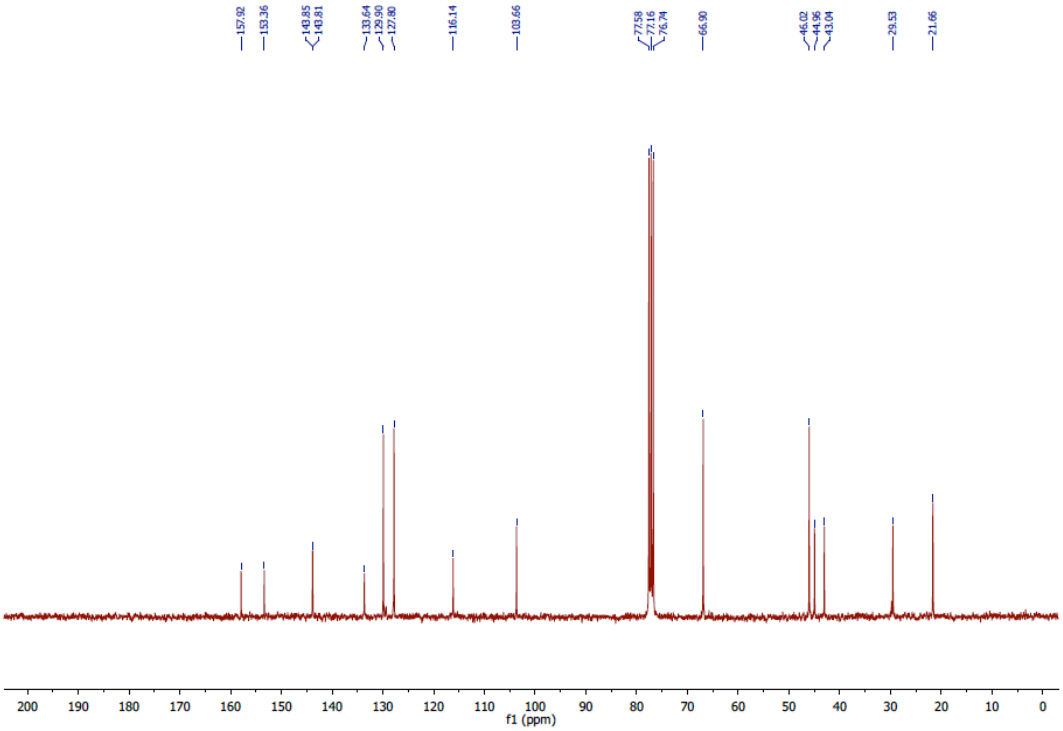
8c



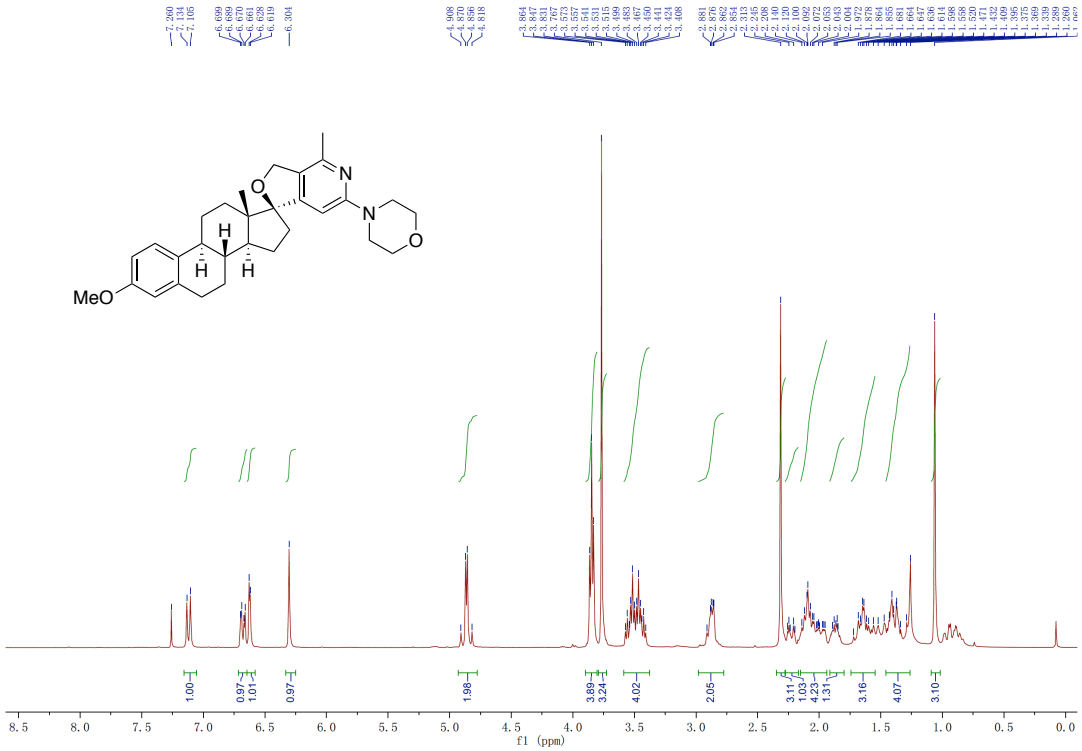


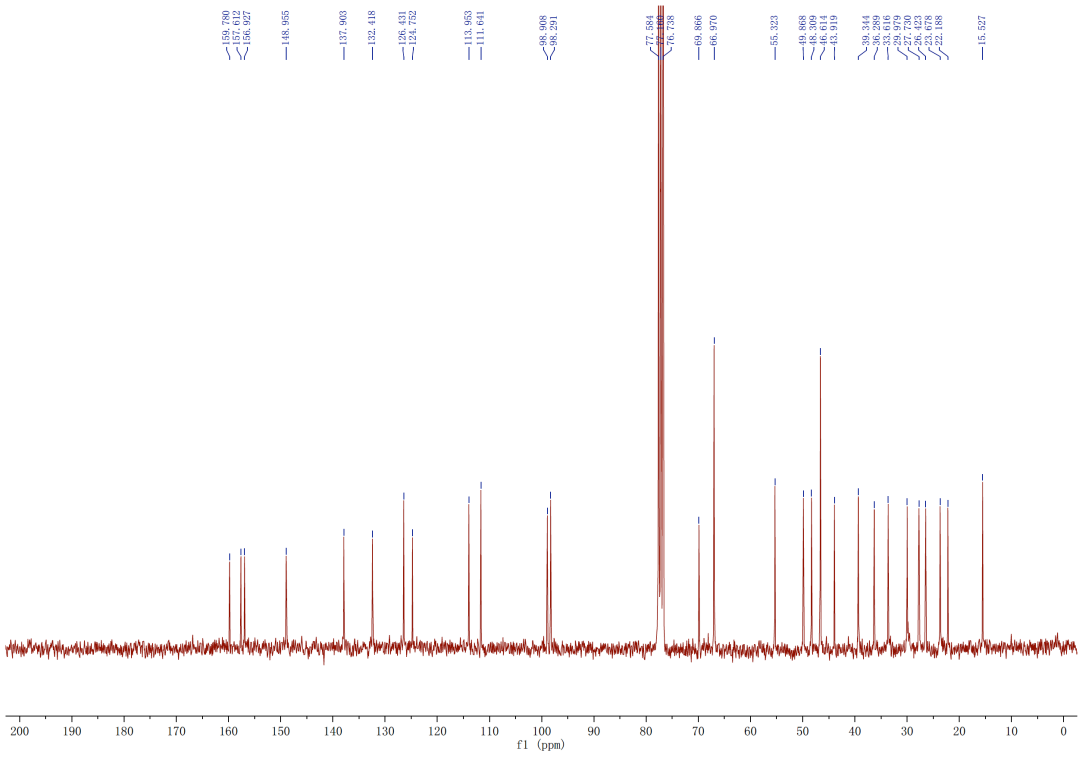
8d


7.73
7.71
7.34
7.32
7.26
7.26
6.17
4.06
3.80
3.79
3.77
3.42
3.41
3.39
3.30
2.82
2.80
2.42
2.27
TsN
N
O
N
2.12
2.02
1.00
2.22
4.32
4.10
2.12
2.06
3.22
2.95
f1 (ppm)

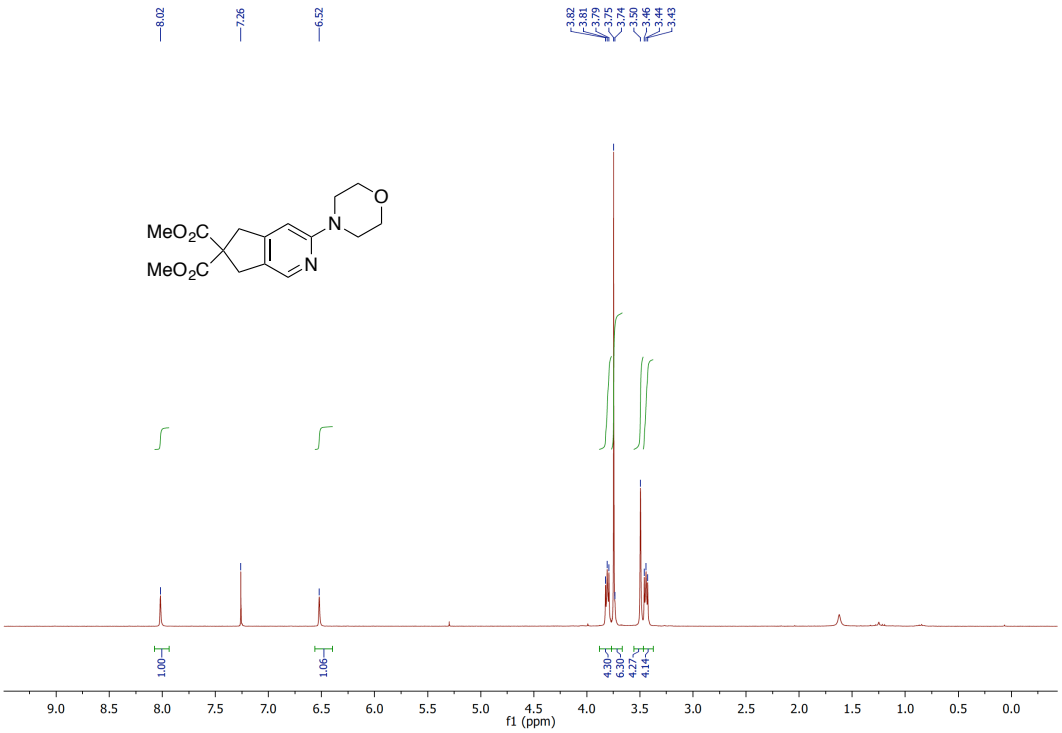

157.92
153.36
143.85
143.81
133.64
129.90
127.80
116.14
103.66
77.58
77.16
76.74
66.90
46.02
44.96
43.04
29.53
21.66
f1 (ppm)

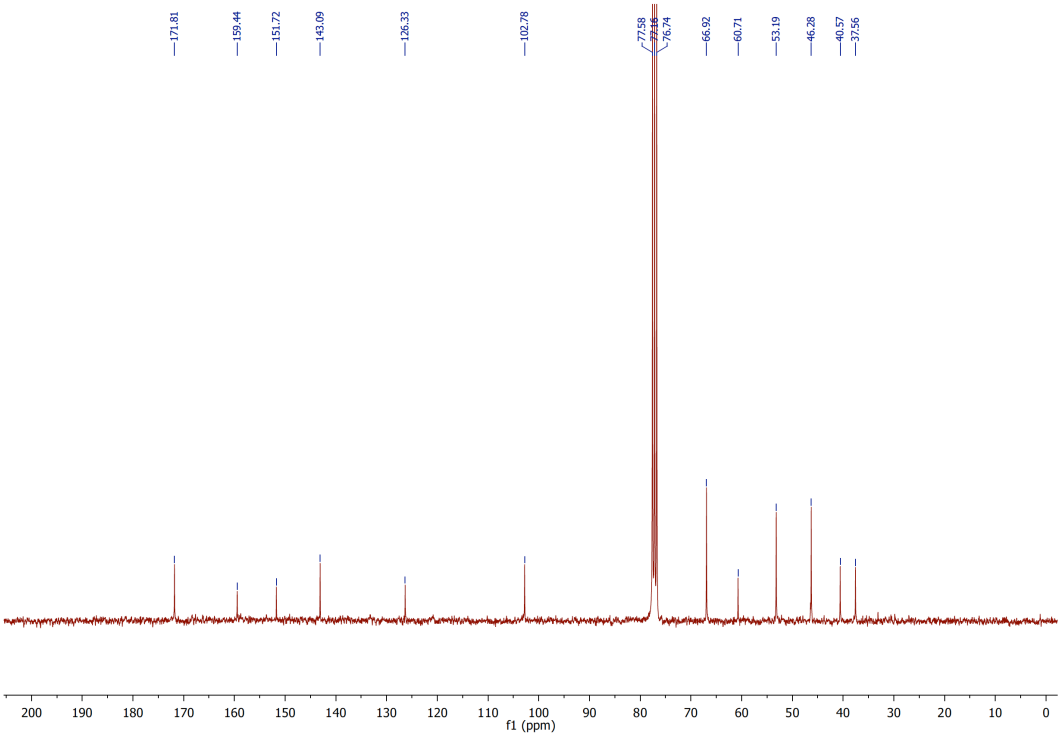
10


MeO
O
N
N
O
H
H
H
1.00
0.97
1.01
0.97
1.98
3.89
3.24
4.02
2.05
3.11
1.03
4.23
1.31
3.16
4.07
3.10
f1 (ppm)

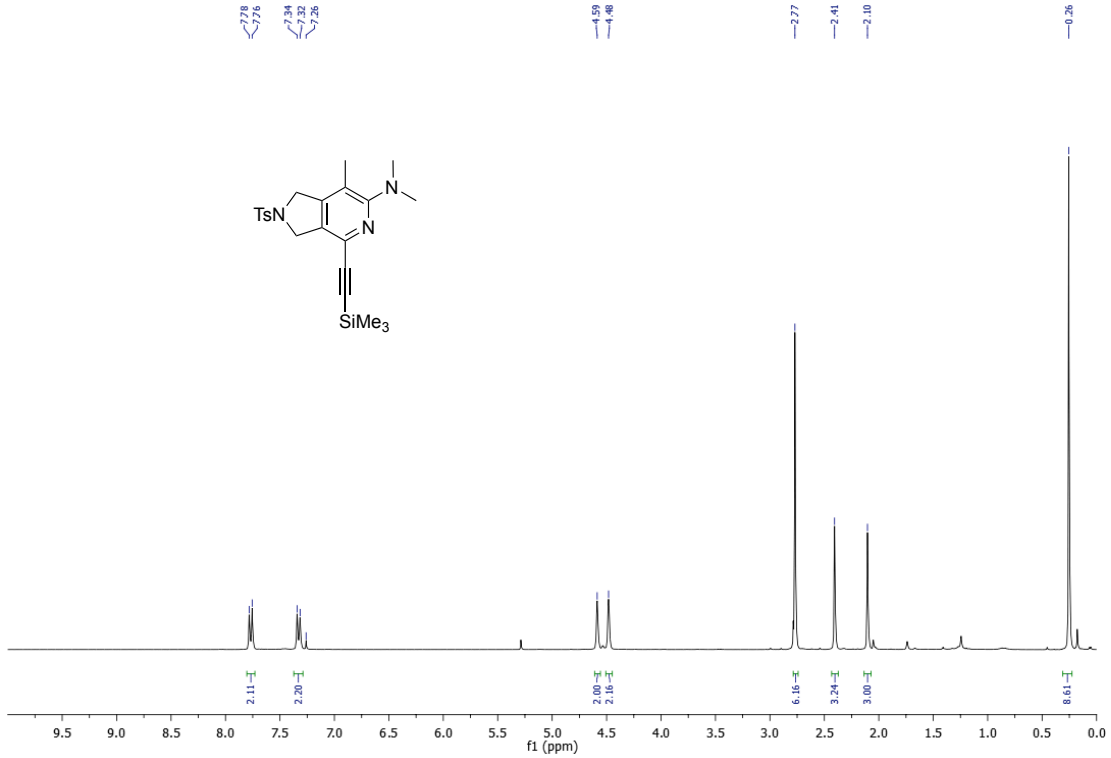

159.780
157.612
148.927
148.955
137.903
132.418
126.431
124.752
113.953
111.641
98.908
98.291
77.584
77.162
76.738
69.866
66.970
55.323
49.868
48.309
46.614
43.919
39.344
36.289
33.616
29.979
27.720
26.423
23.678
22.188
15.527
f1 (ppm)

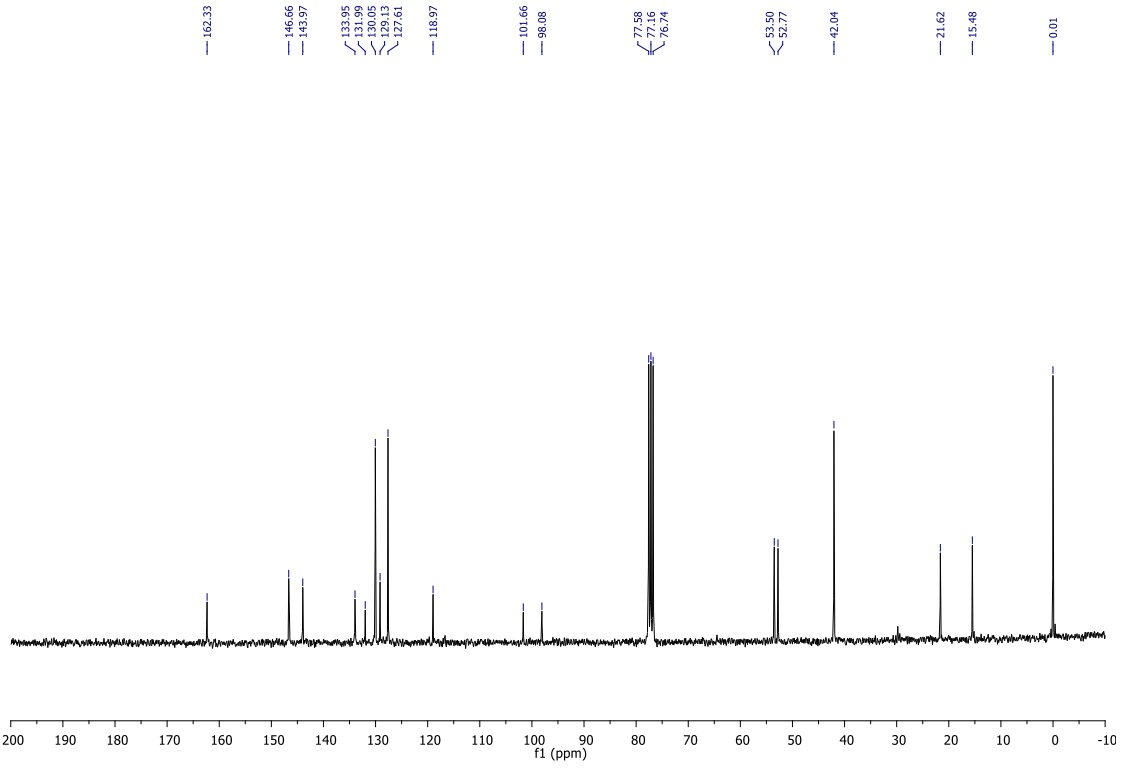
12


8.02
7.26
6.52
3.82
3.81
3.79
3.75
3.74
3.50
3.46
3.44
3.43
MeO2C
MeO2C
N
O
N
1.00
1.06
4.30
6.30
4.27
4.14
f1 (ppm)

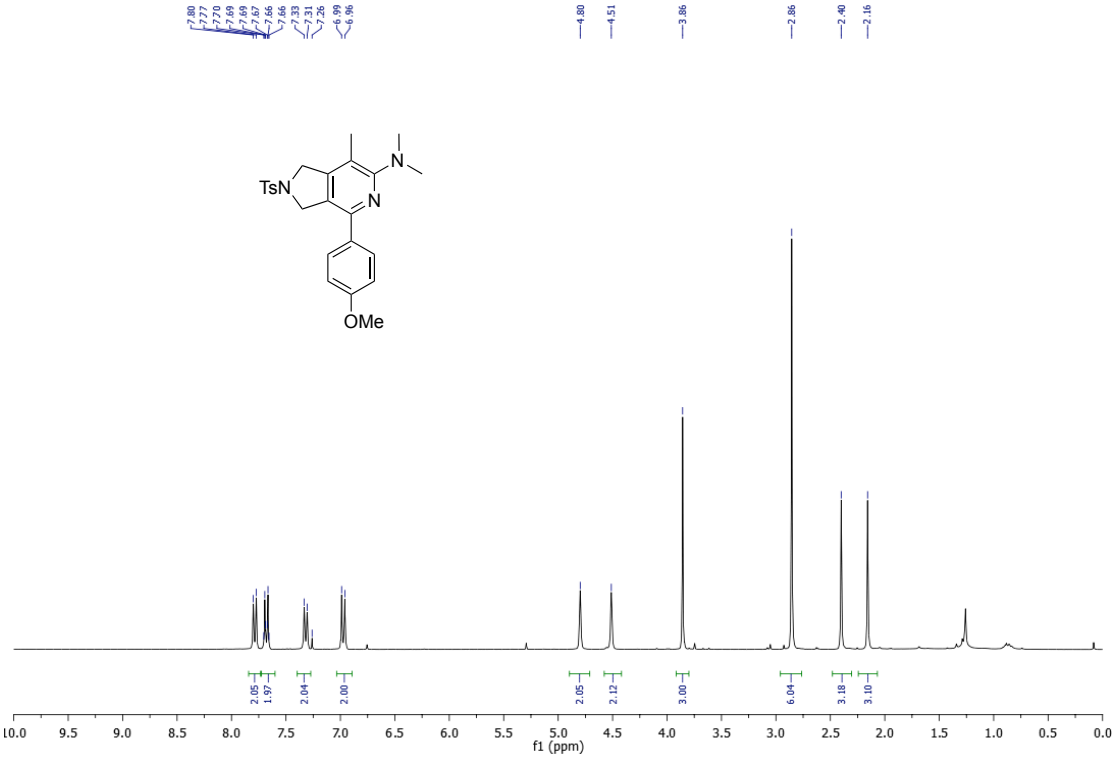

171.81
159.44
151.72
143.09
126.33
102.78
77.58
77.16
76.74
66.92
60.71
53.19
46.28
40.57
37.56
f1 (ppm)

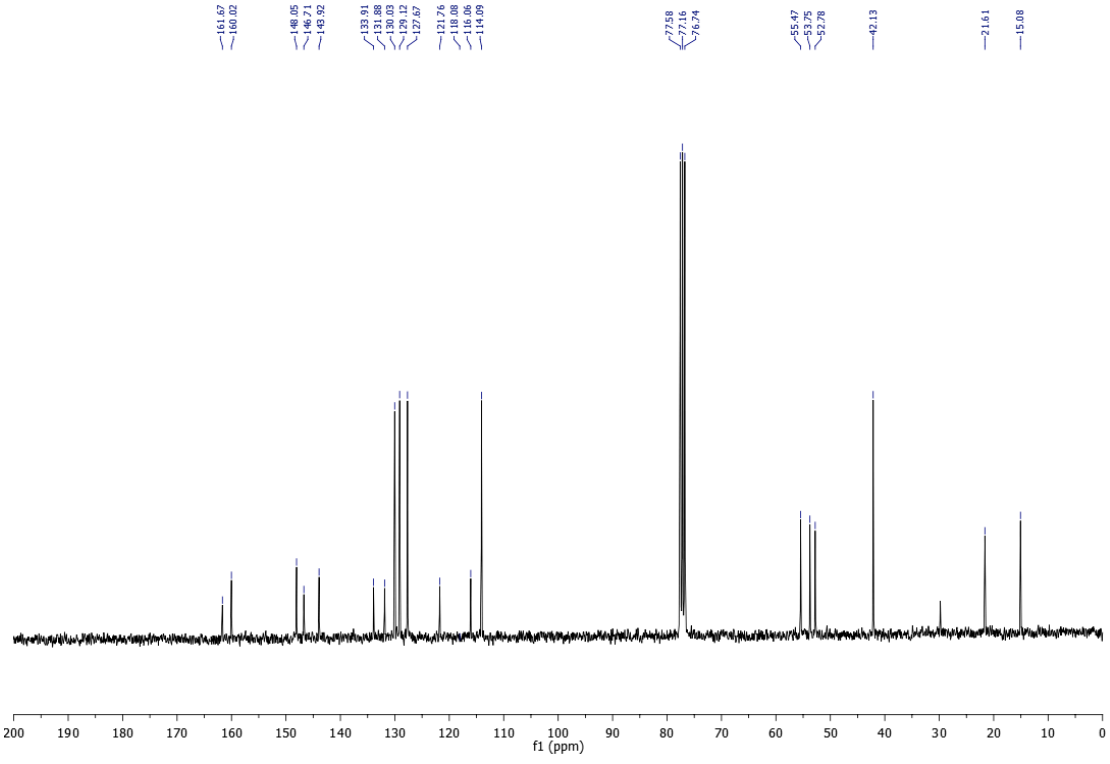
13


7.78
7.76
7.34
7.32
7.26
4.59
4.48
2.77
2.41
2.10
0.26
TsN
N
N
SiMe3
2.11
2.20
2.00
2.16
6.16
3.24
3.00
8.61
f1 (ppm)


162.33
146.66
143.97
133.95
131.99
130.05
129.13
127.61
118.97
101.66
98.08
77.58
77.16
76.74
53.50
52.77
42.04
21.62
15.48
0.01
f1 (ppm)

14


7.80
7.77
7.70
7.69
7.69
7.67
7.66
7.66
7.33
7.31
7.26
6.99
6.96
4.80
4.51
3.86
2.86
2.40
2.16
TsN
N
N
OMe
2.05
1.97
2.04
2.00
2.05
2.12
3.00
6.04
3.18
3.10
f1 (ppm)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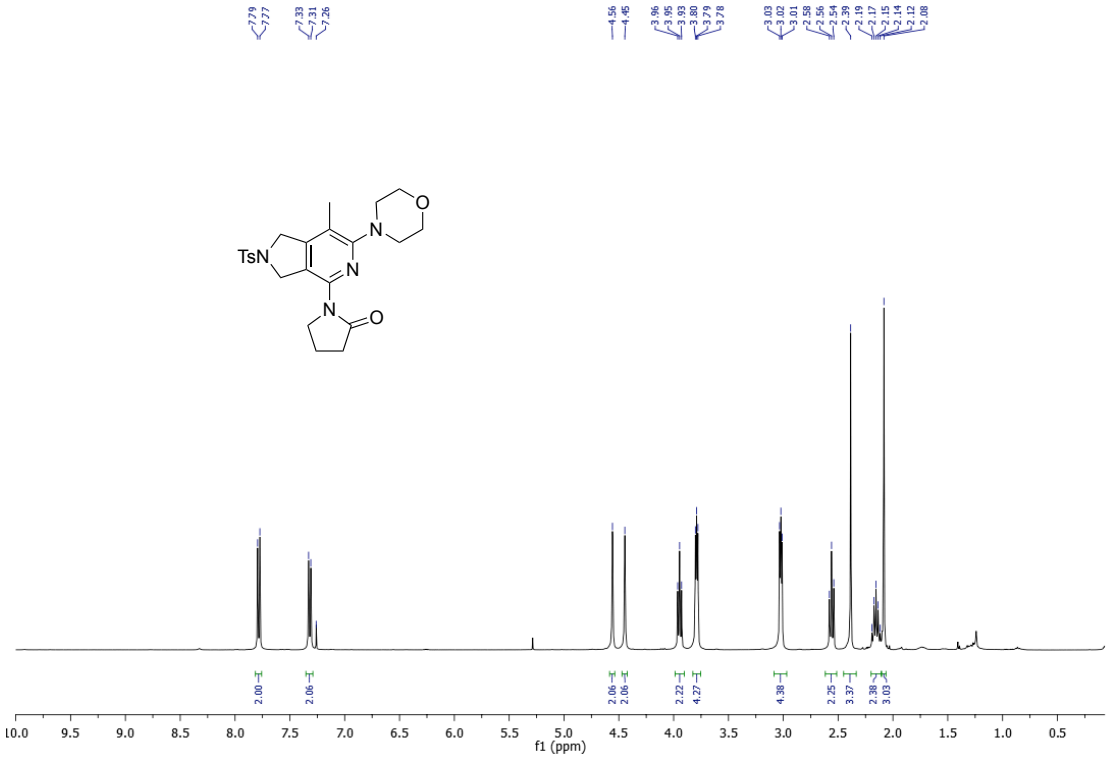
160.02
148.05
146.71
143.92
133.91
131.88
130.03
129.12
127.67
121.76
118.08
116.06
114.09
77.58
77.16
76.74
55.47
53.75
52.78
42.13
21.61
15.08
f1 (ppm)

15


7.79
7.77
7.33
7.31
7.26
4.56
4.45
3.96
3.95
3.93
3.80
3.79
3.78
3.03
3.02
3.01
2.58
2.56
2.54
2.39
2.19
2.17
2.15
2.14
2.12
2.08
TsN
N
O
N
N
O
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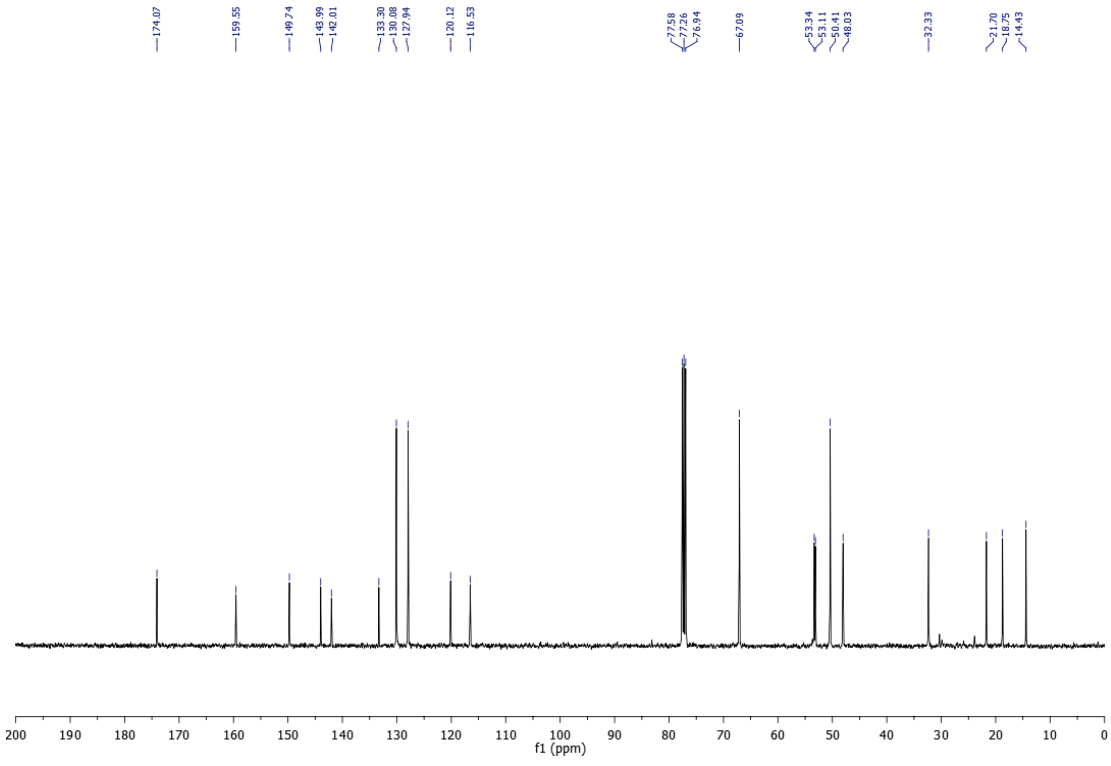
2.25
3.37
2.38
3.03
f1 (ppm)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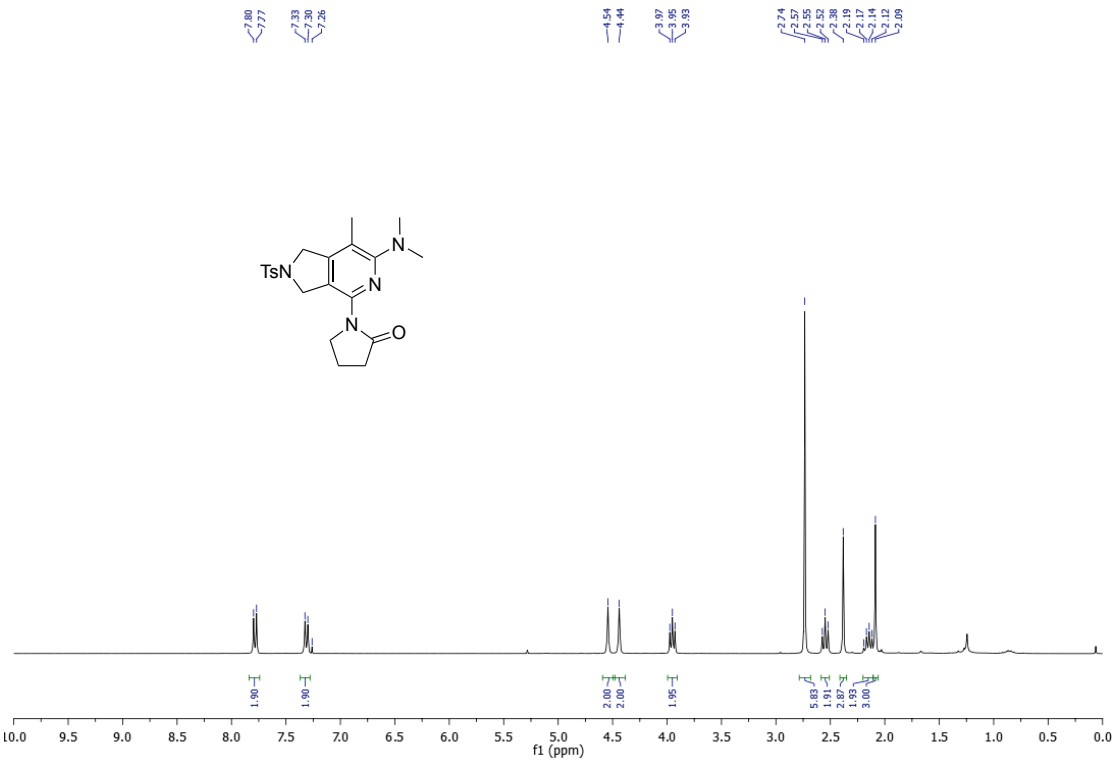
143.99
142.01
133.30
130.08
127.94
120.12
116.53
77.58
77.26
76.94
67.09
53.34
53.11
50.41
48.03
32.33
21.70
18.75
14.43
f1 (ppm)

16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7.77
7.33
7.30
7.26
4.54
4.44
3.97
3.95
3.93
2.74
2.57
2.55
2.52
2.38
2.19
2.17
2.14
2.12
2.09
TsN
N
N
O
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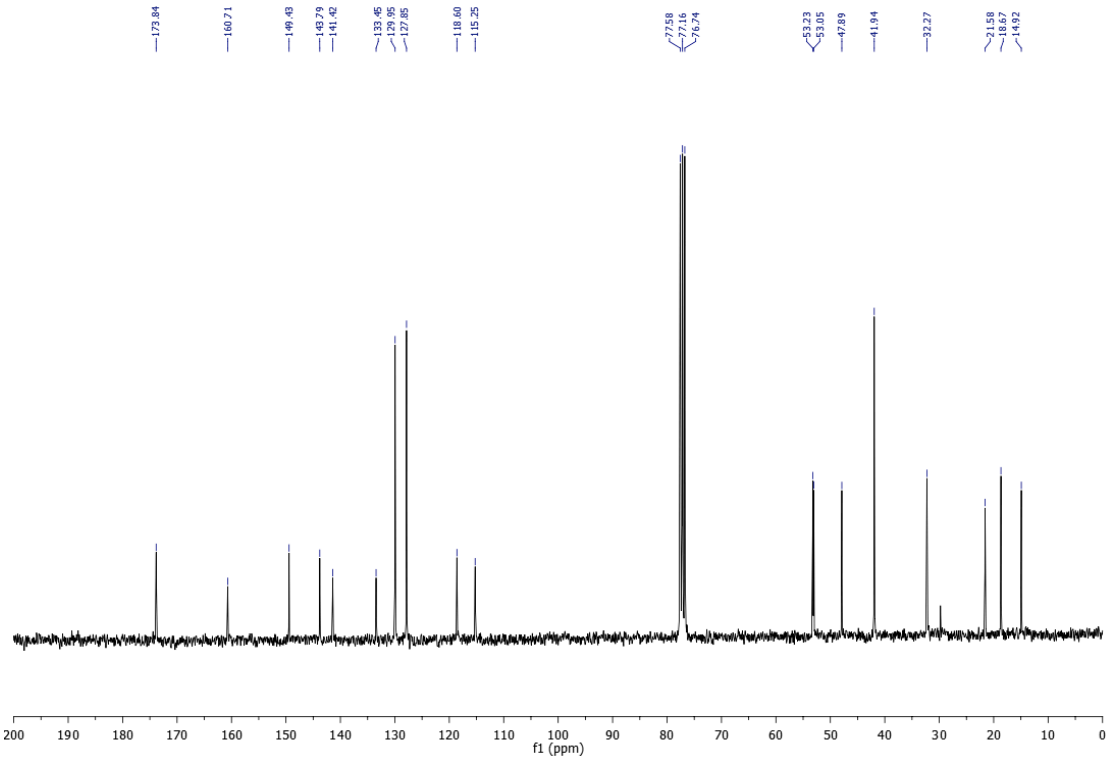
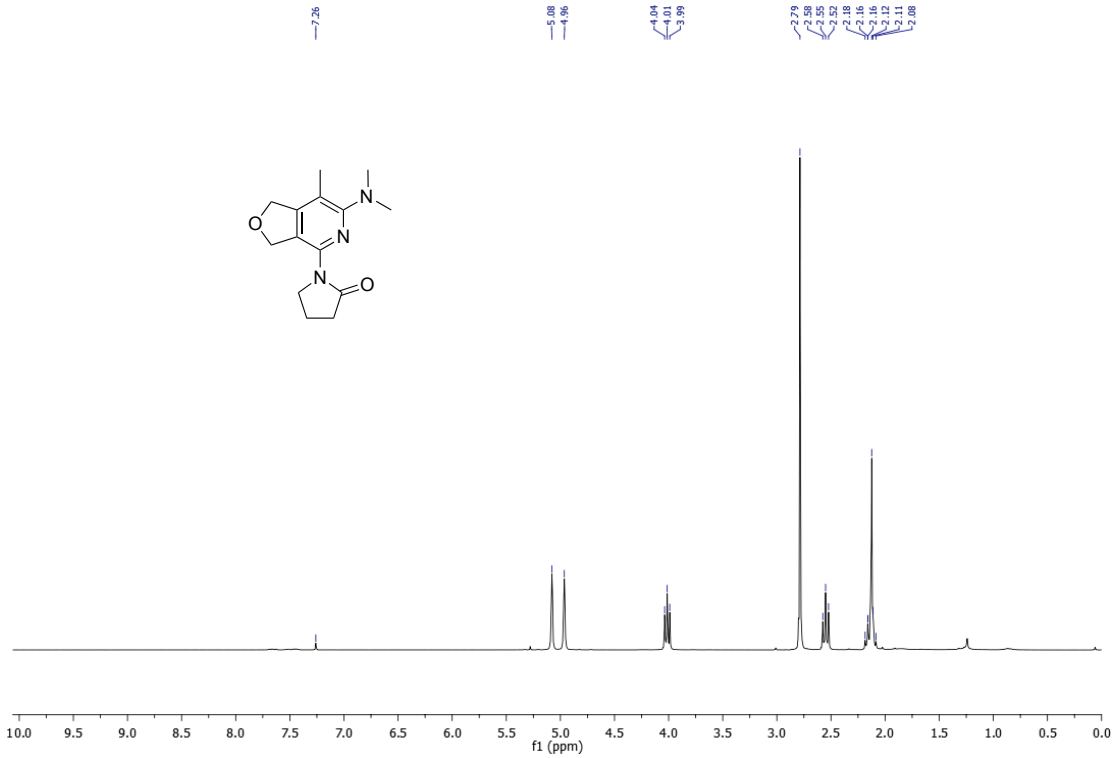
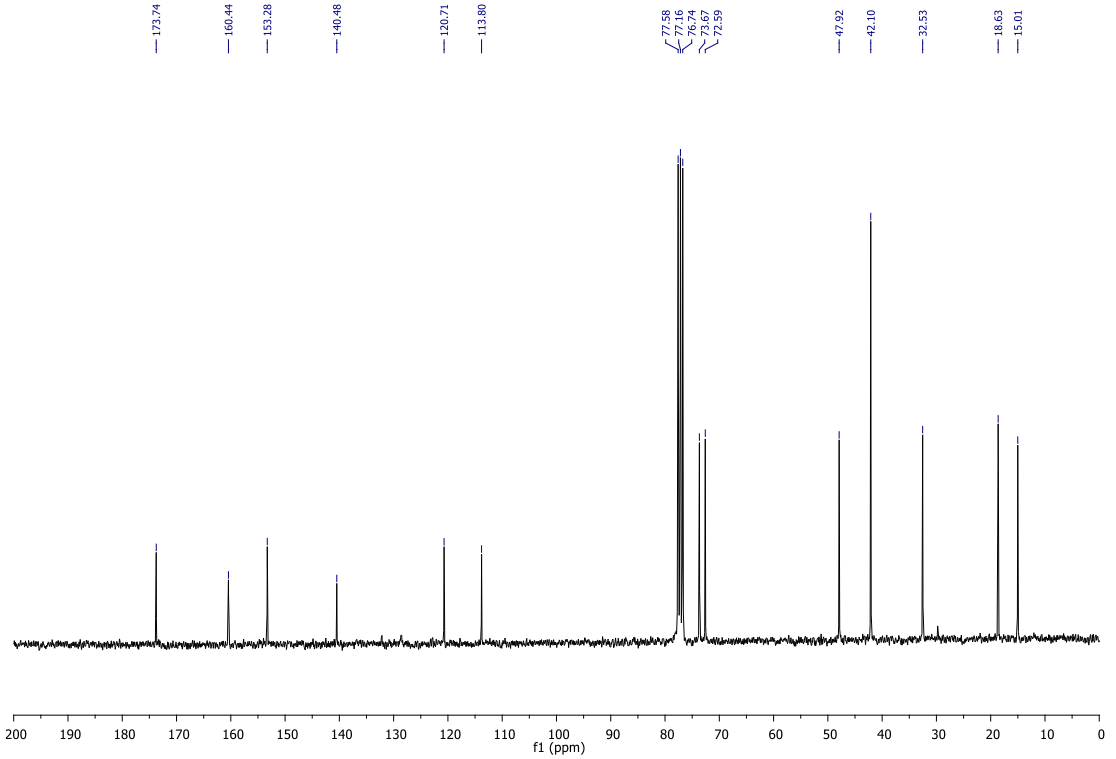
1.90
2.00
2.00
1.95
5.83
1.91
2.07
1.93
3.00
f1 (ppm)


173.84
160.71
149.43
143.79
141.42
133.45
129.95
127.85
118.60
115.25
77.58
77.16
76.74
53.23
53.05
47.89
41.94
32.27
21.58
18.67
14.92
f1 (ppm)

17


7.26
5.08
4.96
4.04
4.01
3.99
2.79
2.58
2.55
2.52
2.18
2.16
2.16
2.12
2.11
2.08
O
N
N
N
O
f1 (ppm)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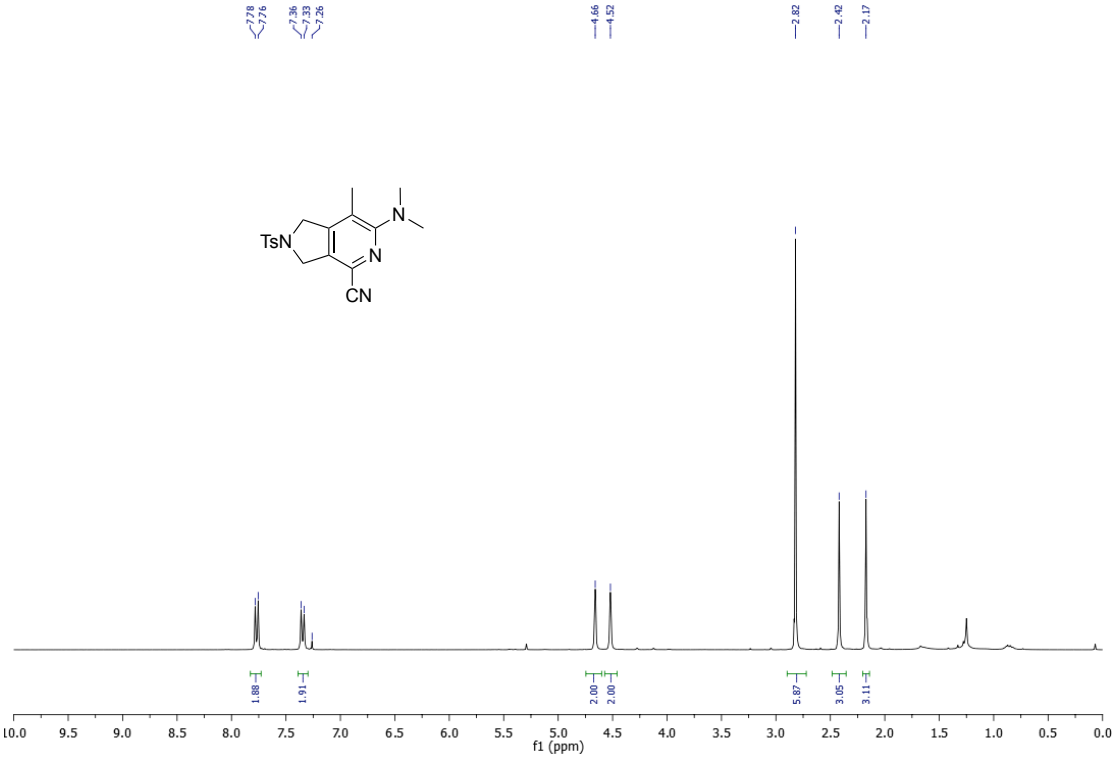
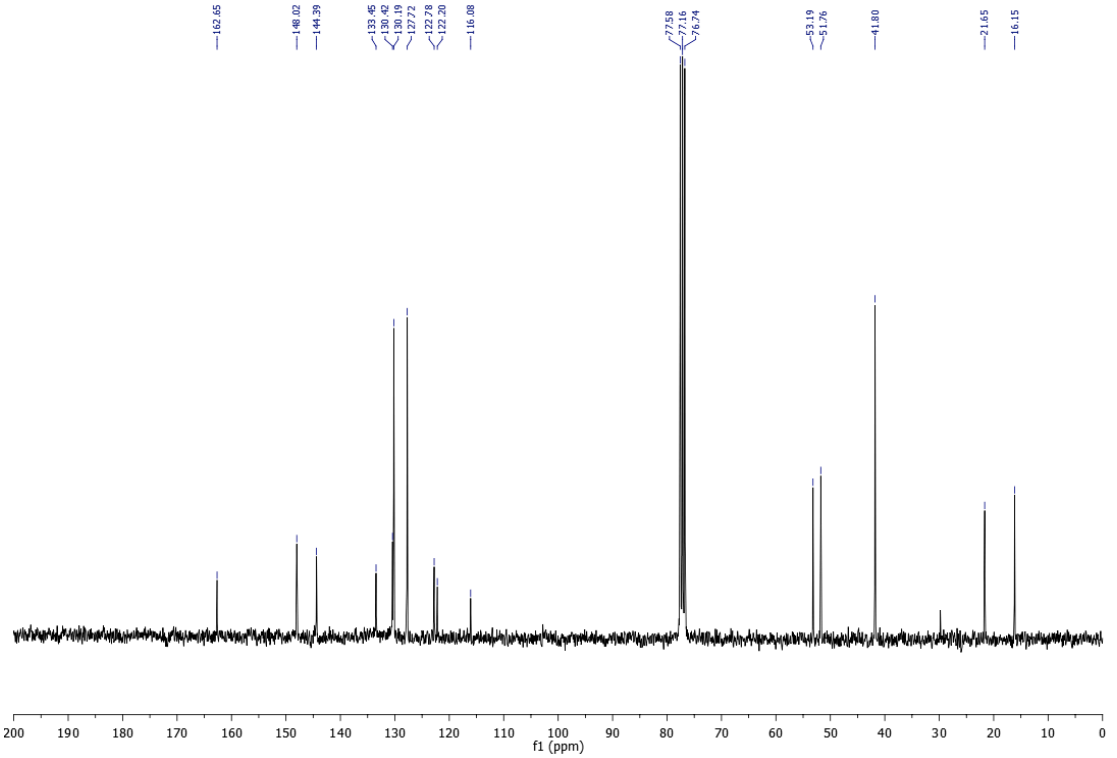
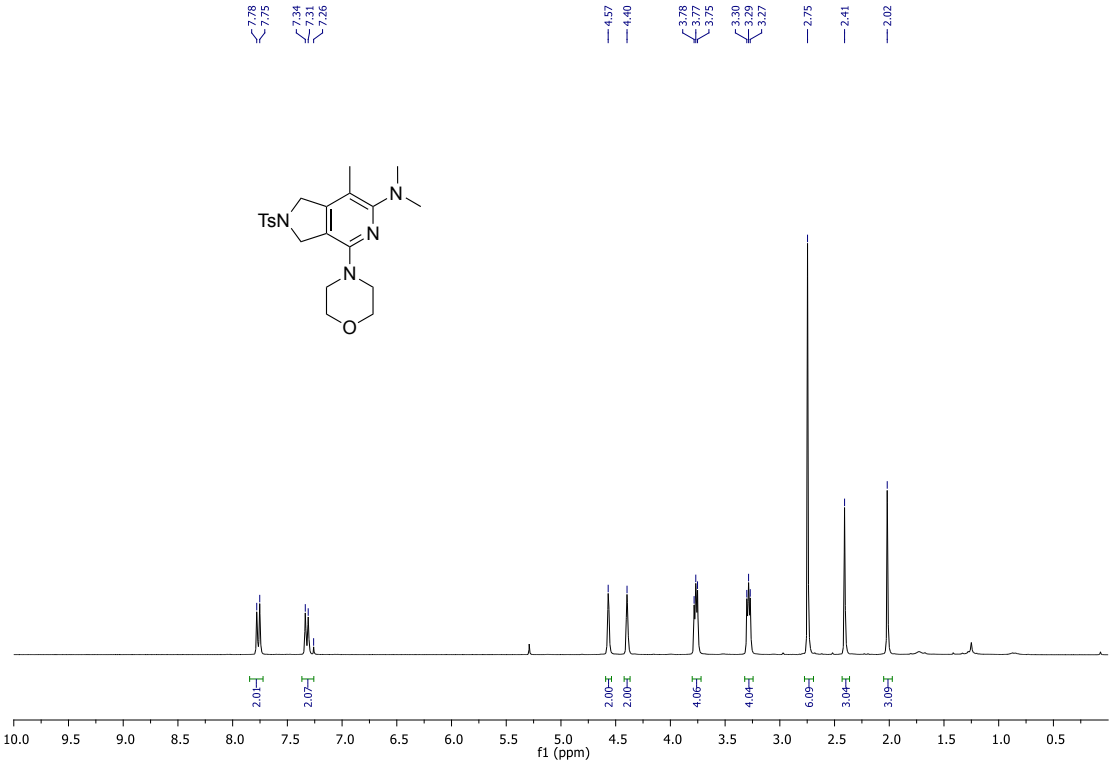
160.44
153.28
140.48
120.71
113.80
77.58
77.16
76.74
73.67
72.59
47.92
42.10
32.53
18.63
15.01
f1 (ppm)

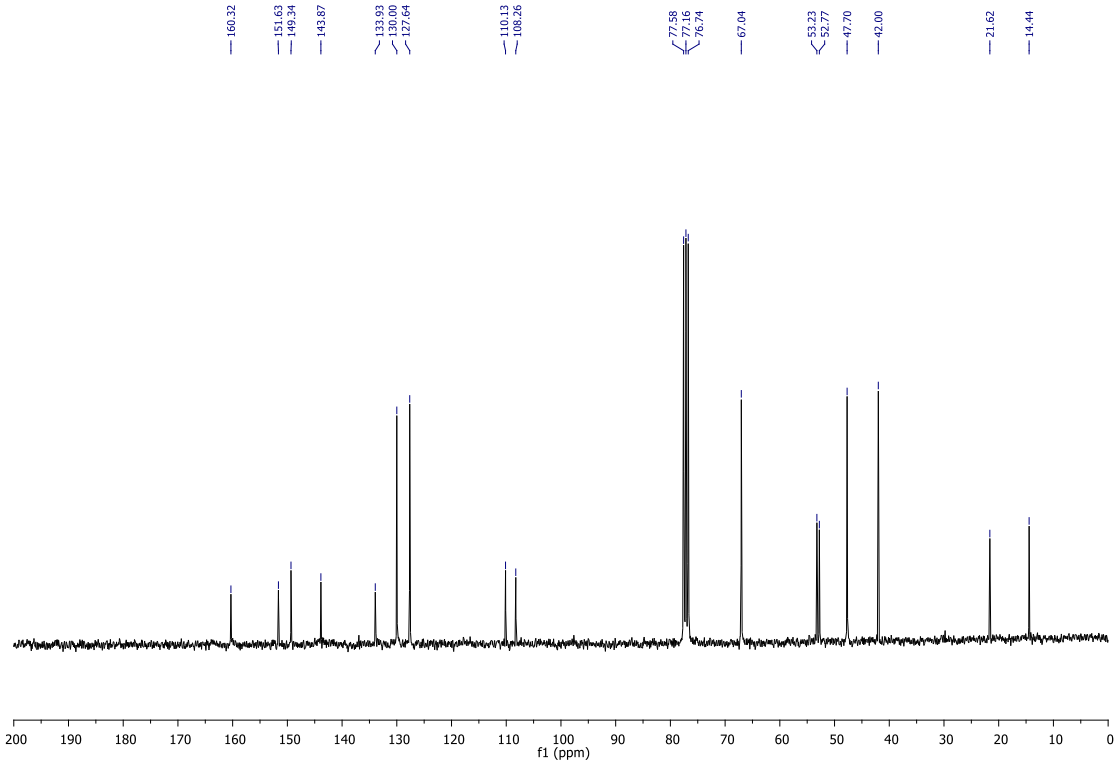
18


7.78
7.76
7.36
7.33
7.26
4.66
4.52
2.82
2.42
2.17
TsN
N
N
CN
1.88
1.91
2.00
2.00
5.87
3.05
3.11
f1 (ppm)


162.65
148.02
144.39
133.45
130.42
130.19
127.72
122.78
122.20
116.08
77.58
77.16
76.74
53.19
51.76
41.80
21.65
16.15
f1 (ppm)

19


7.78
7.75
7.34
7.31
7.26
4.57
4.40
3.78
3.77
3.75
3.30
3.29
3.27
2.75
2.41
2.02
TsN
N
N
O
2.01
2.07
2.00
2.00
4.06
4.04
6.09
3.04
3.09
f1 (ppm)


160.32
151.63
149.34
143.87
133.93
130.00
127.64
110.13
108.26
77.58
77.16
76.74
67.04
53.23
52.77
47.70
42.00
21.62
14.44
f1 (ppm)