Supporting information

Solvent- and catalyst-free synthesis of Nitrogen-Containing Bicyclic derivatives through hemiaminal formation/ diastereoselective hetero Diels-Alder Reaction with Diazenes

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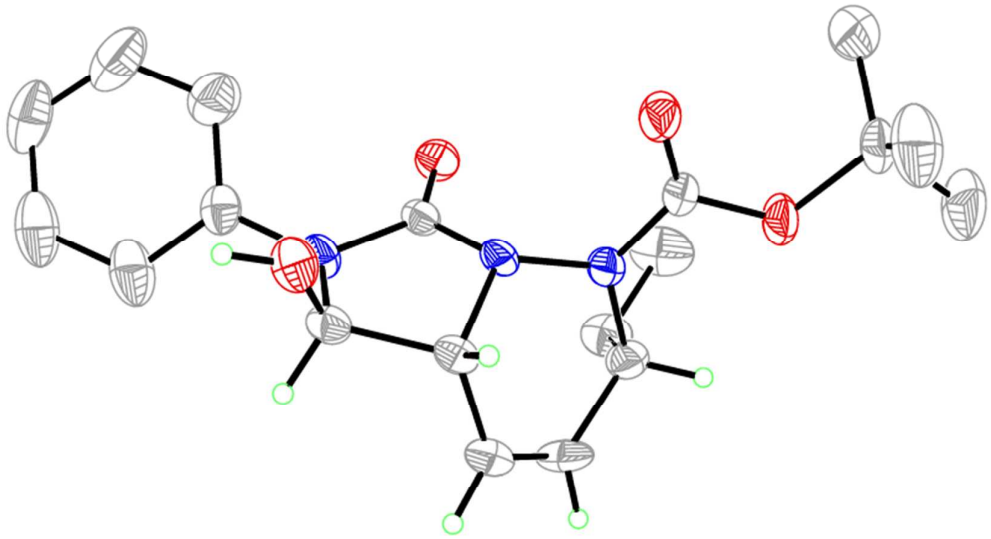
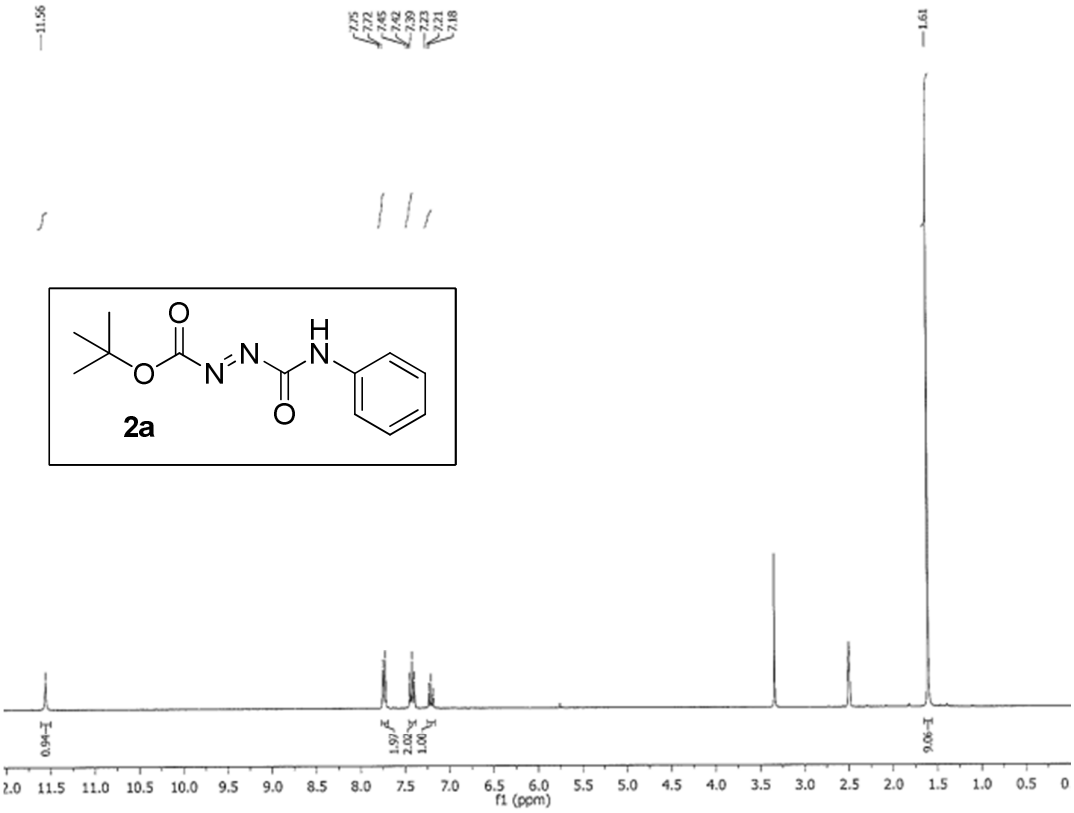
Contents

Crystal Structure of 4

Crystals suitable for X-ray analysis were grown by slow evaporation at room temperature of a solution of **4** in chloroform. $C_{19}H_{25}N_3O_4$, M_w = 359.42, orthorhombic, space group $P2_12_12_1$; dimensions: a = 6.9301(5) Å, b = 15.6506(12) Å, c = 22.8010(18) Å, V = 2473.0(3) $Å^3$; Z = 4; μ = 0.07 mm^{-1}; 107991 reflections measured at room temperature; independent reflections: 7213 [4661 Fo > 4σ(Fo)]; data were collected up to a 2Θmax value of 60.1° (99.7 % coverage). Number of variables: 240; R_1 = 0.087, wR_2 = 0.266, S = 1.08; highest residual electron density 0.29 e.$Å^{-3}$; CCDC = 1036052.

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O
N
N
O
O
2a
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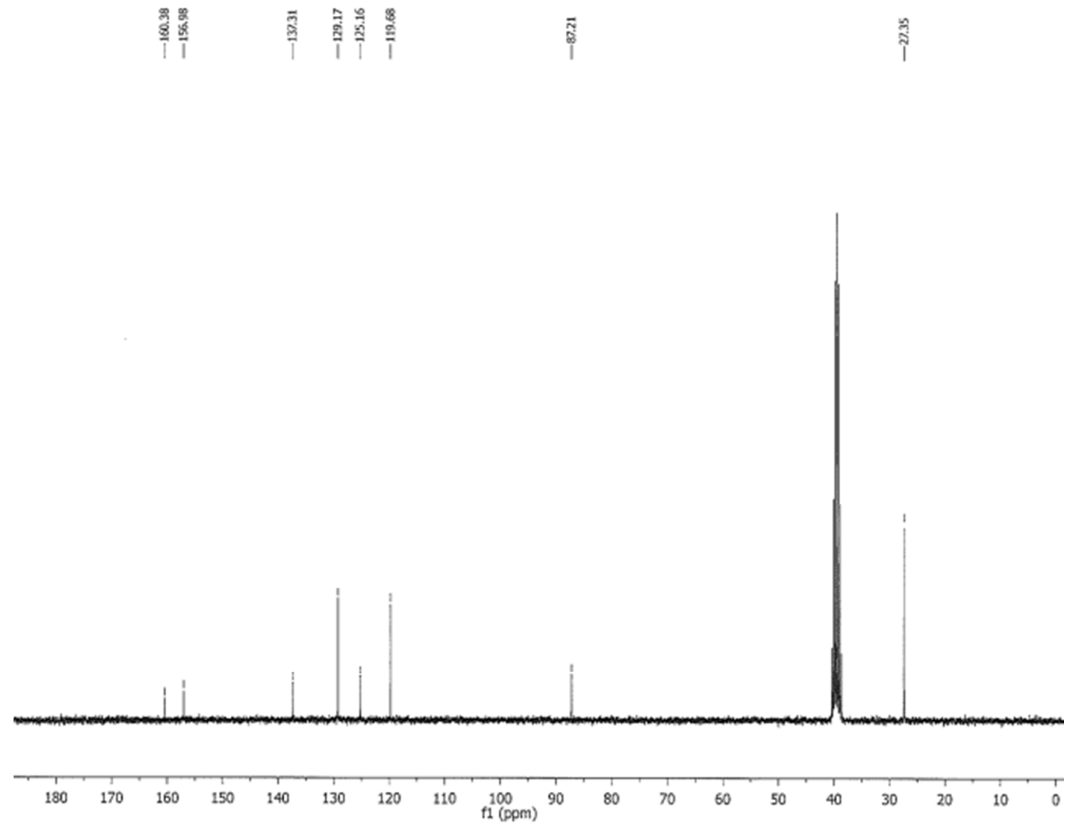
2.02
1.00
9.06
f1 (ppm)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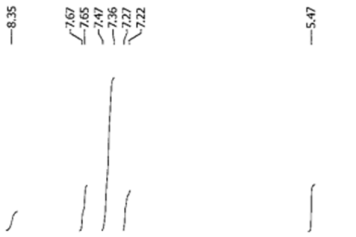
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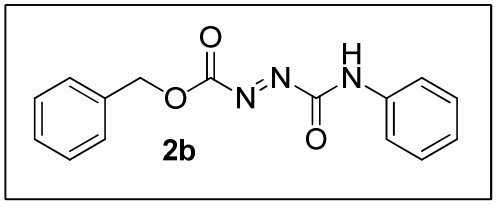
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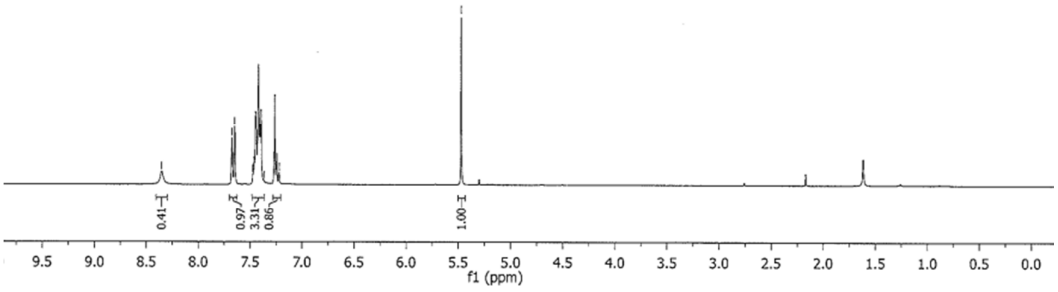
O
N
N
O
2b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119.78
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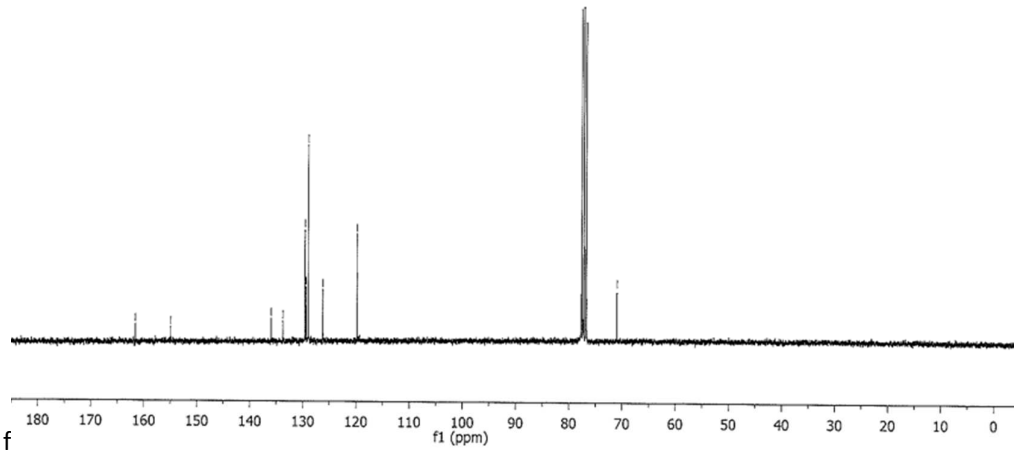
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f


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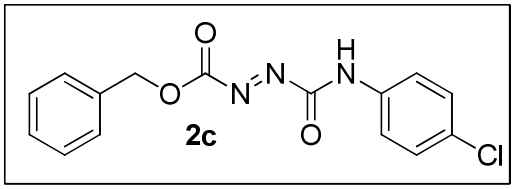
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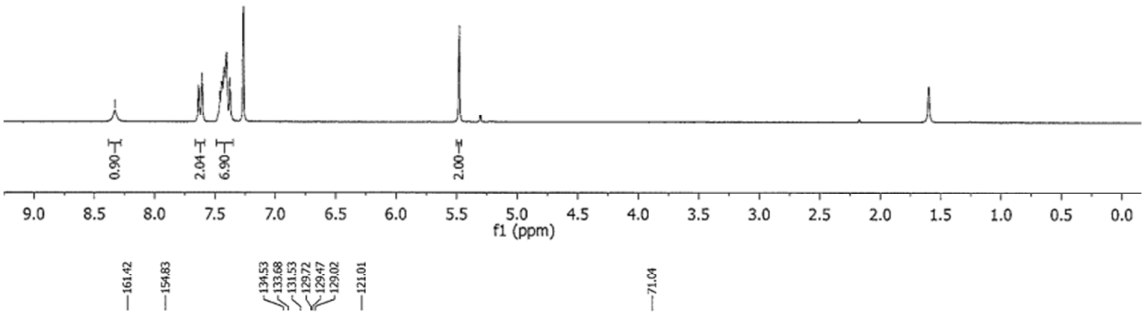
O
N
N
O
O
Cl

2c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3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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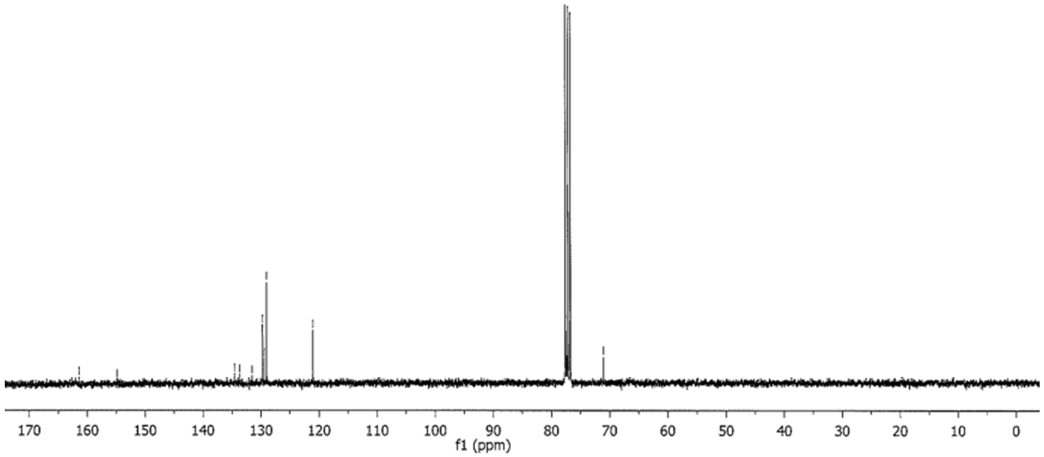
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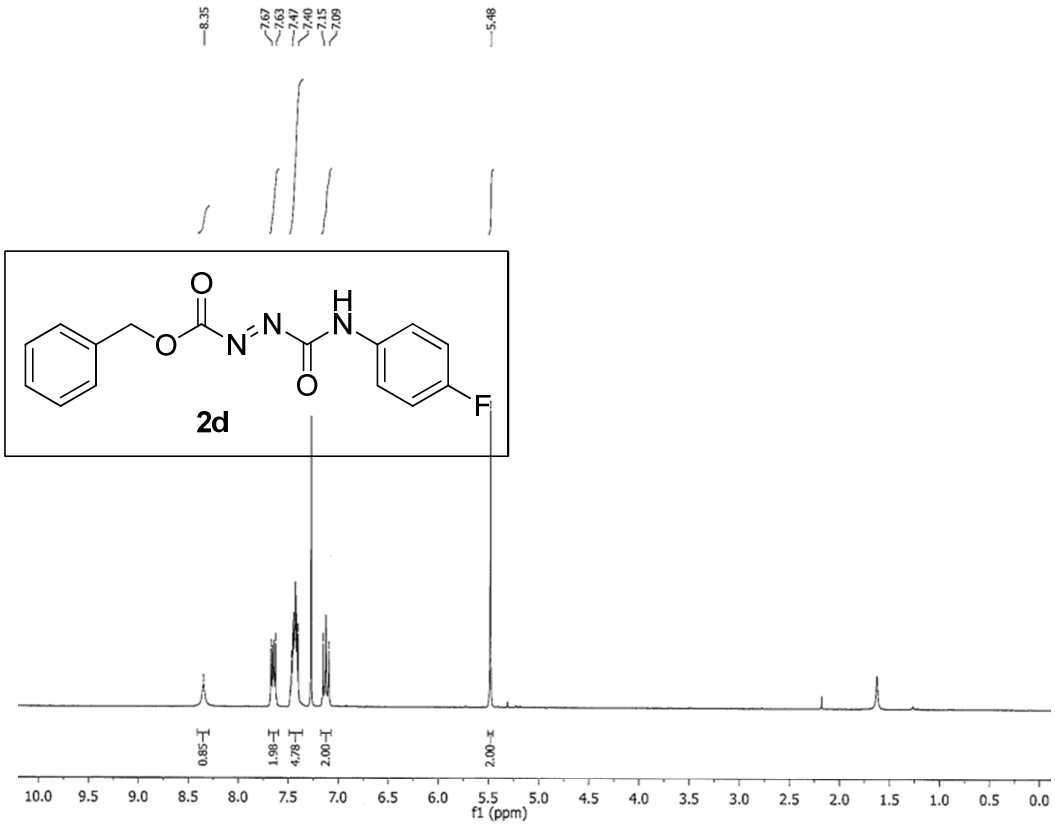
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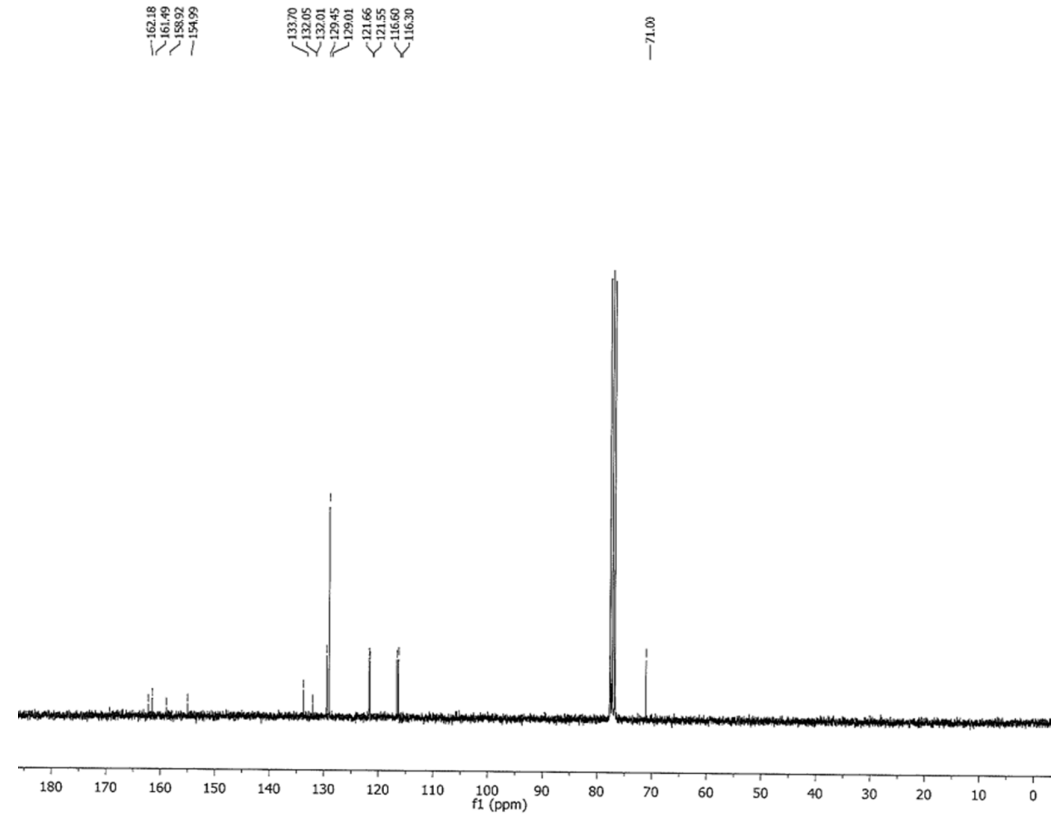
2.00
f1 (ppm)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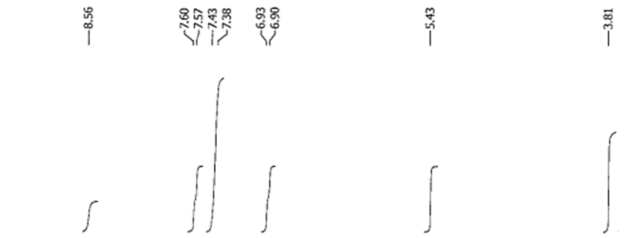
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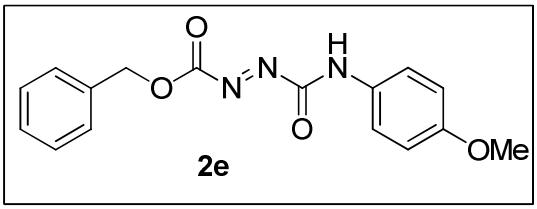
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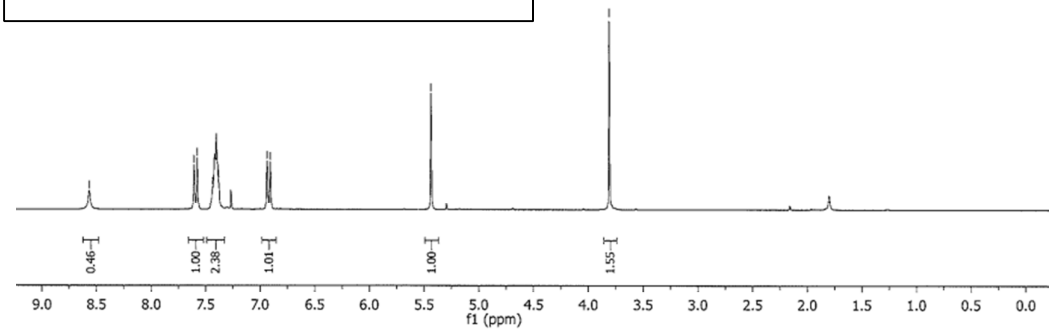
N
H
N
O
OMe

2e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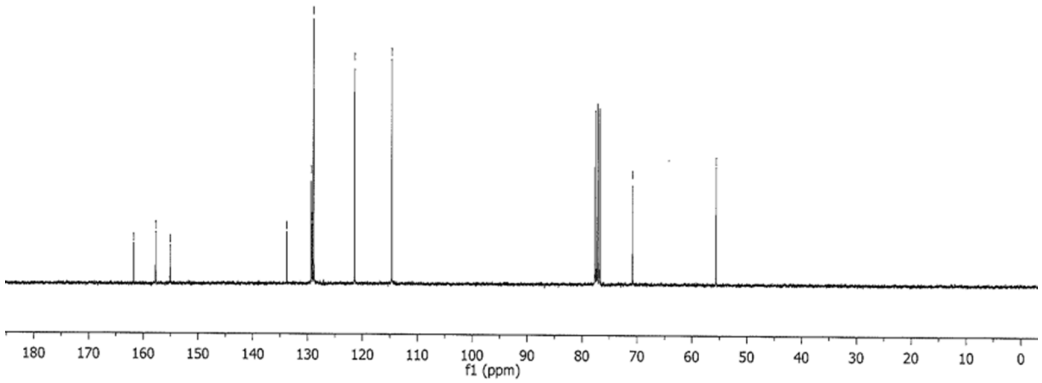
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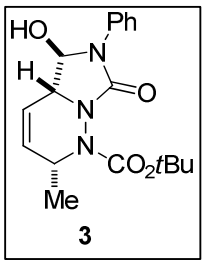
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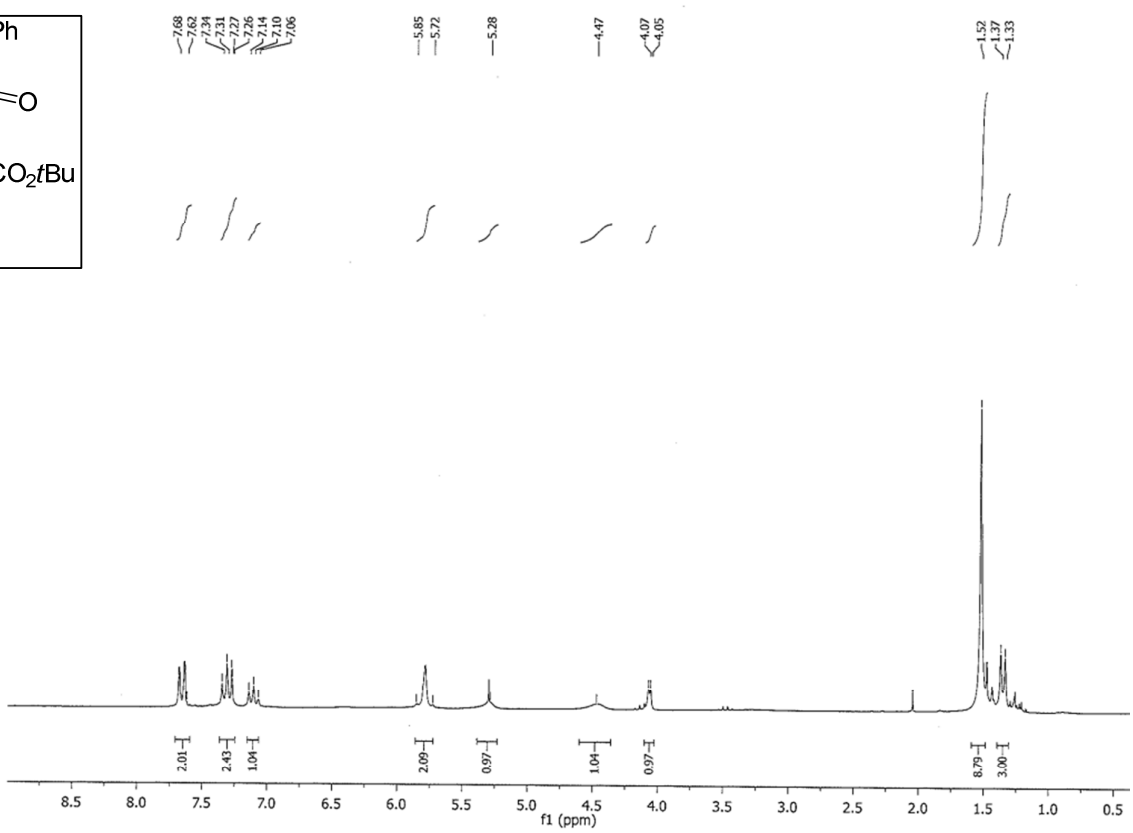
N
CO2tBu
Me

3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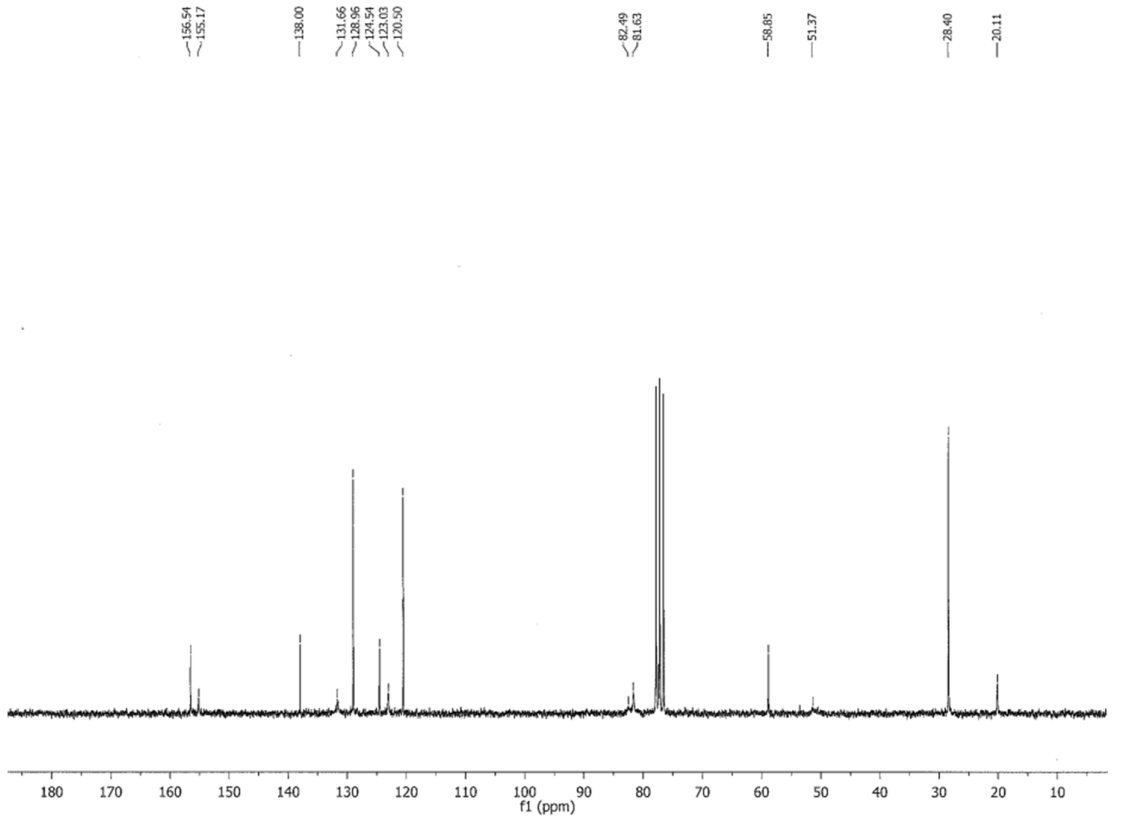
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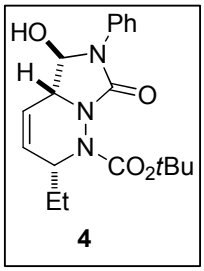
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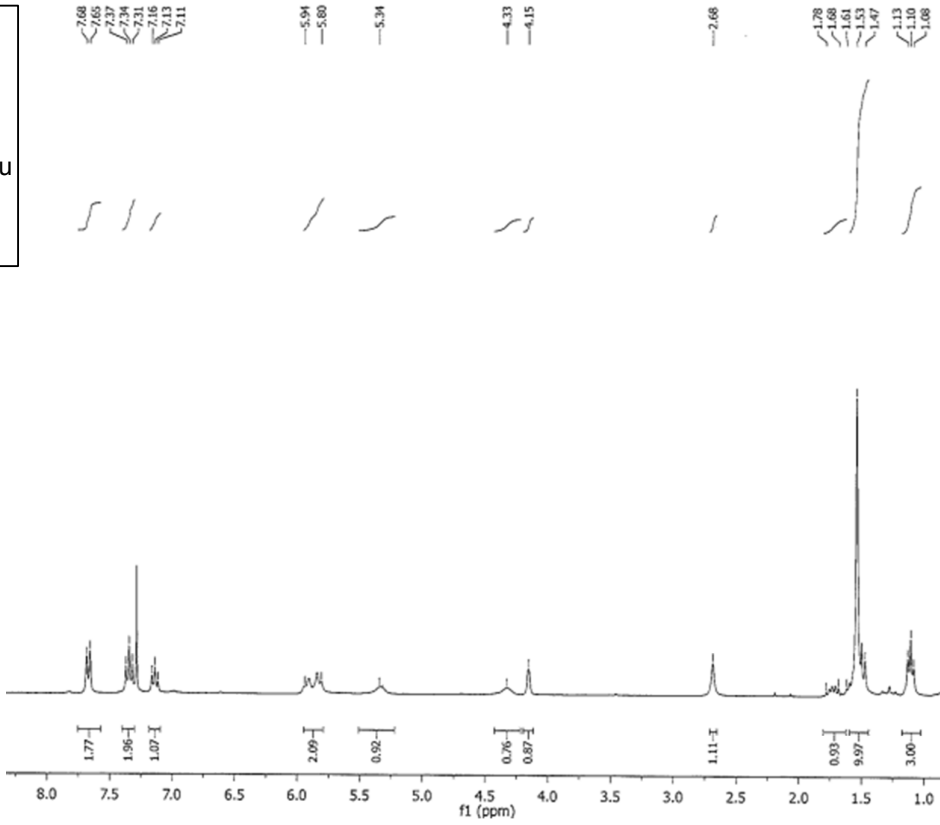
4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1.61
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1.47
1.13
1.10
1.08
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1.11
0.93
9.97
3.00
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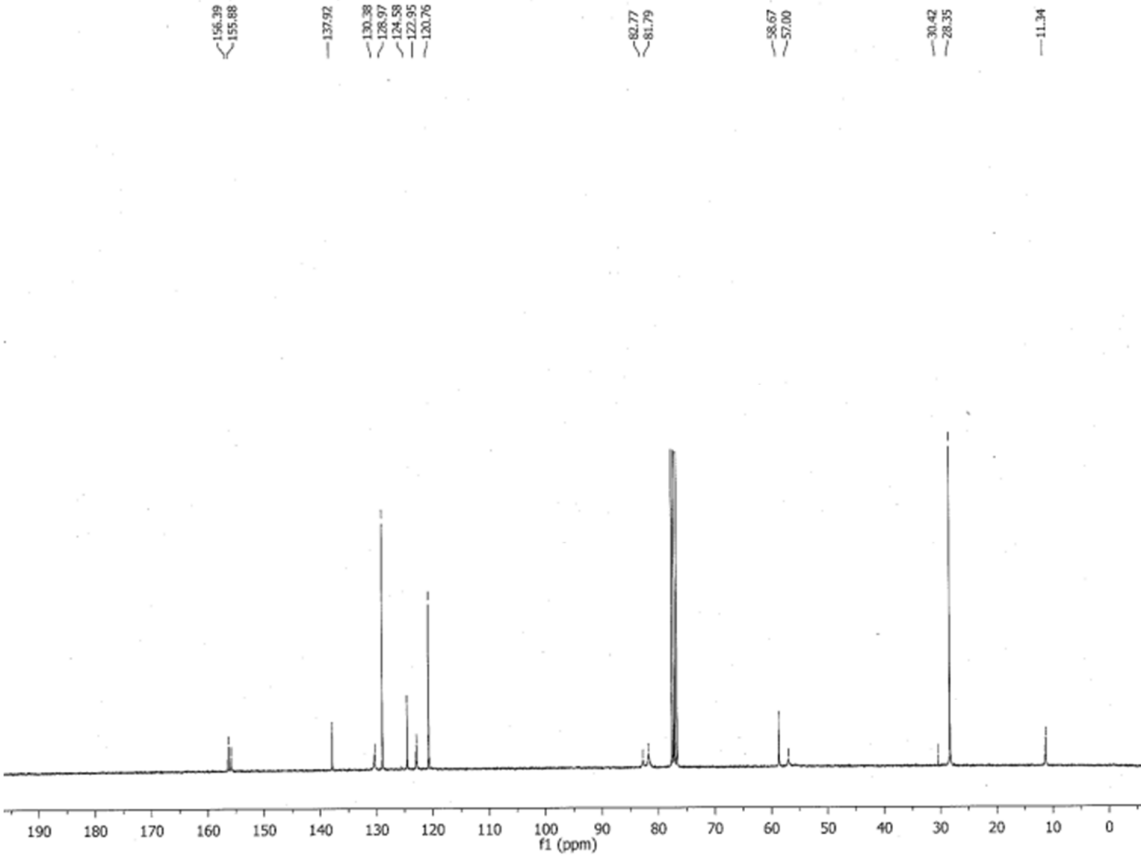
f1 (ppm)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11.34
190
180
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40
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0
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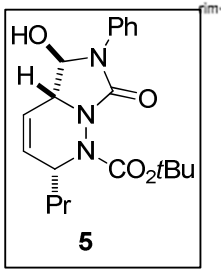
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CO2tBu
Pr

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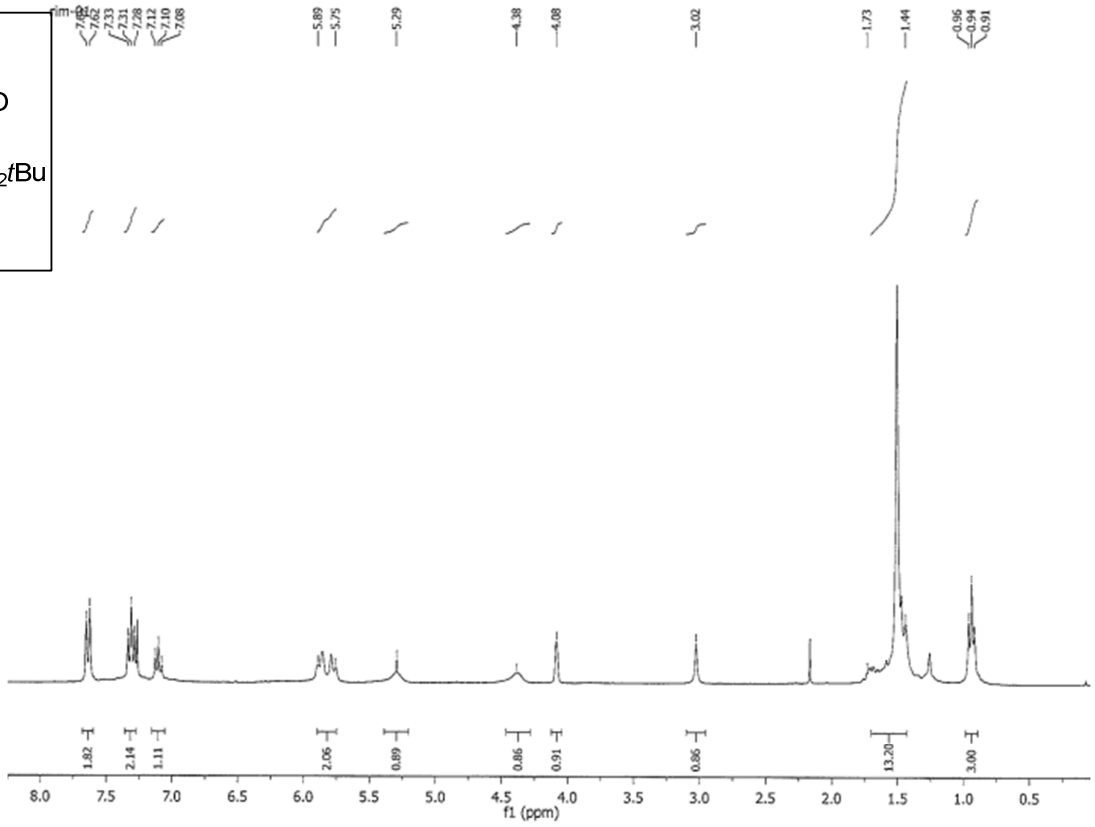
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0.96
0.94
0.91
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2.14
1.11
2.06
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0.91
0.86
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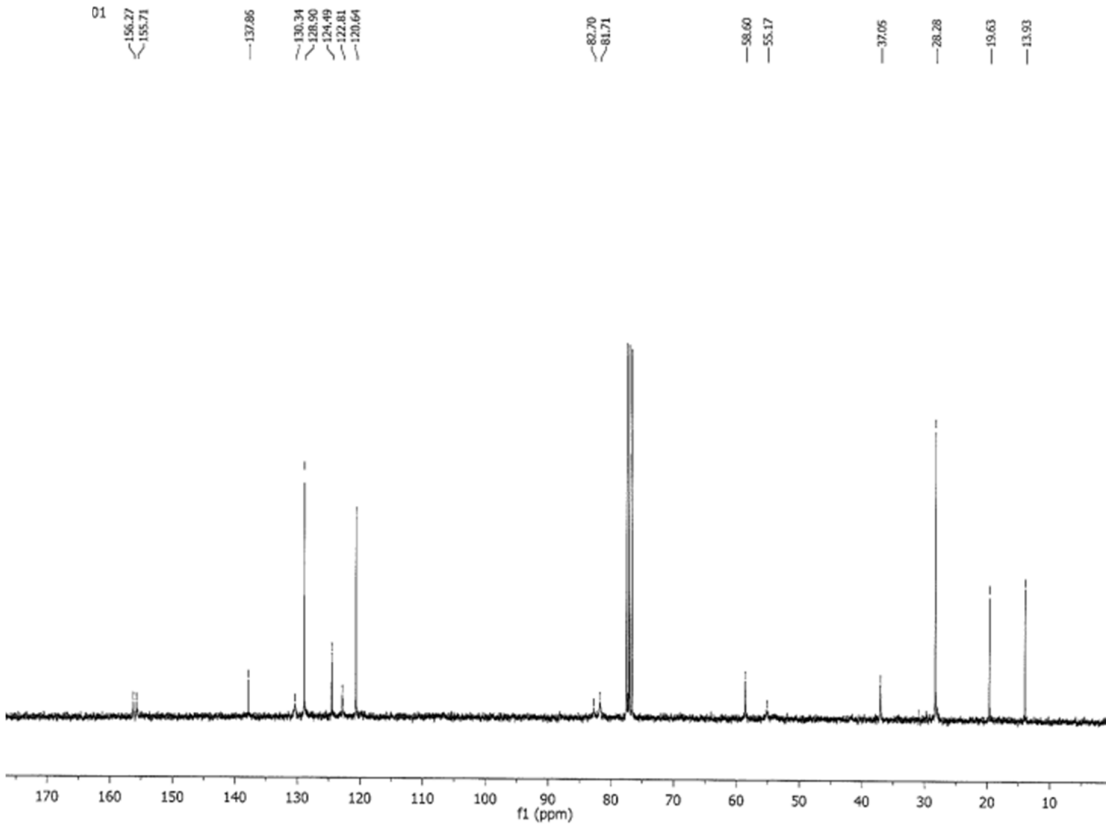
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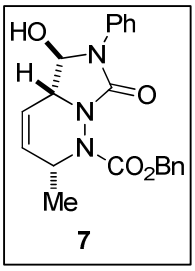
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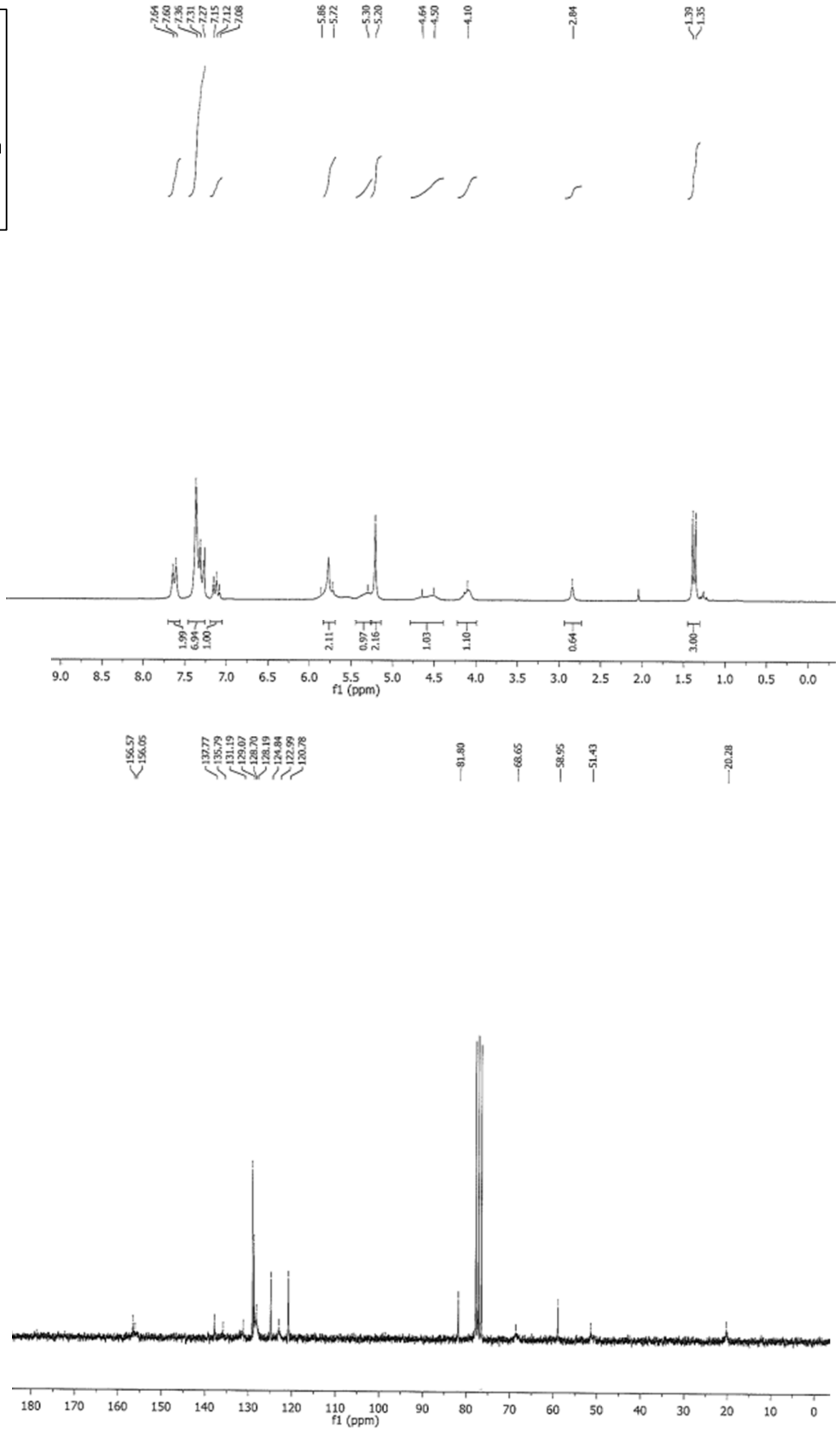
CO2Bn
Me

7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4.10
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1.35
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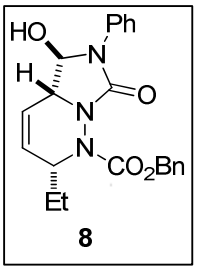
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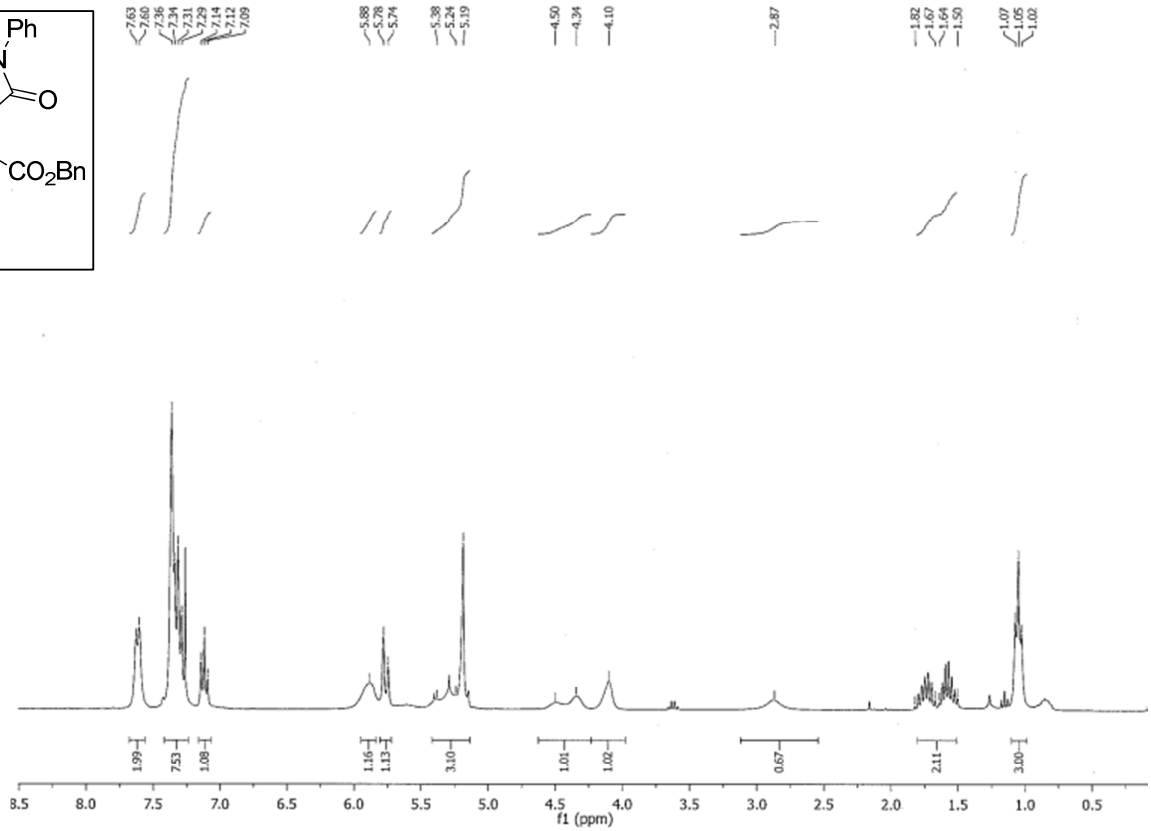
Et

8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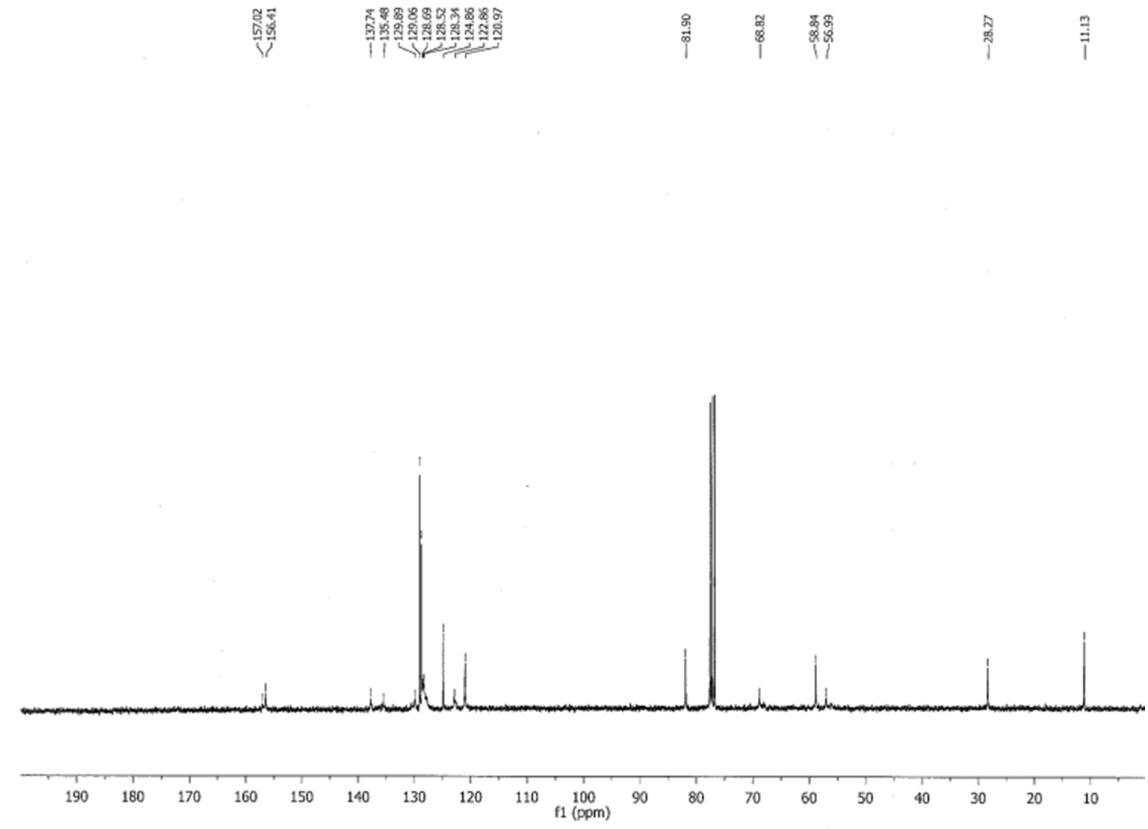
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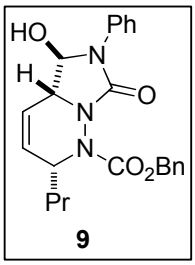

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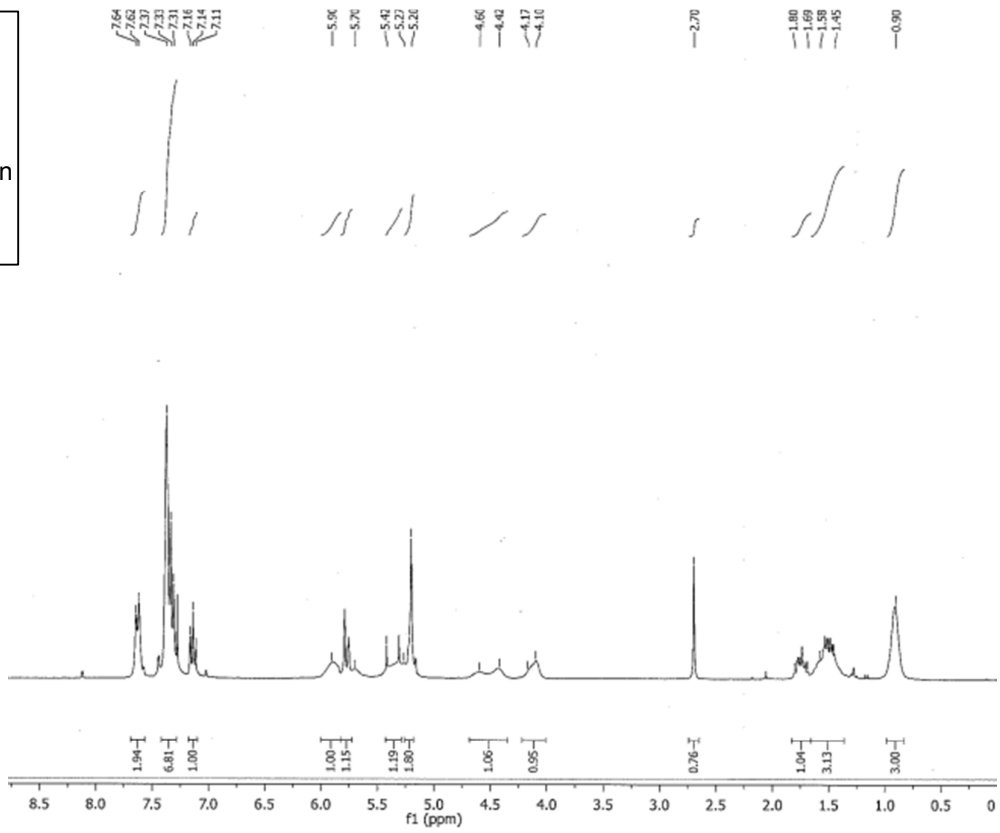

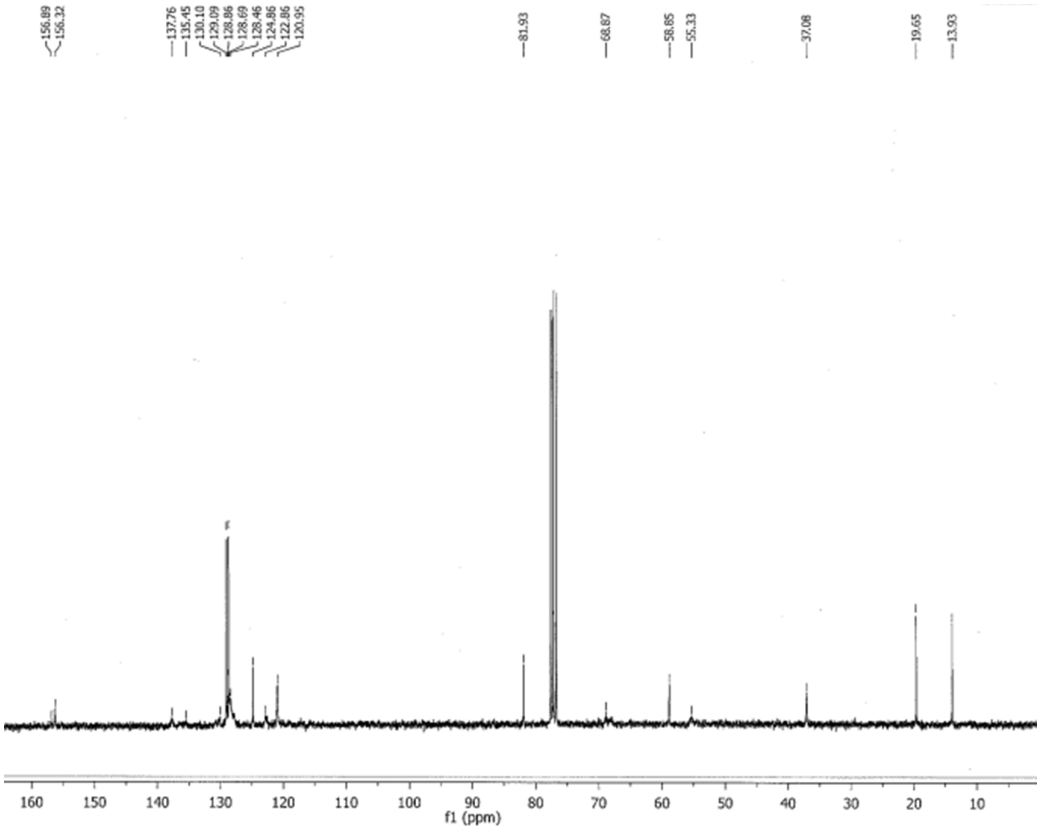

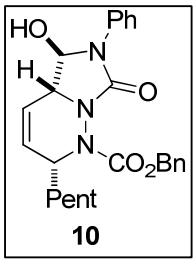
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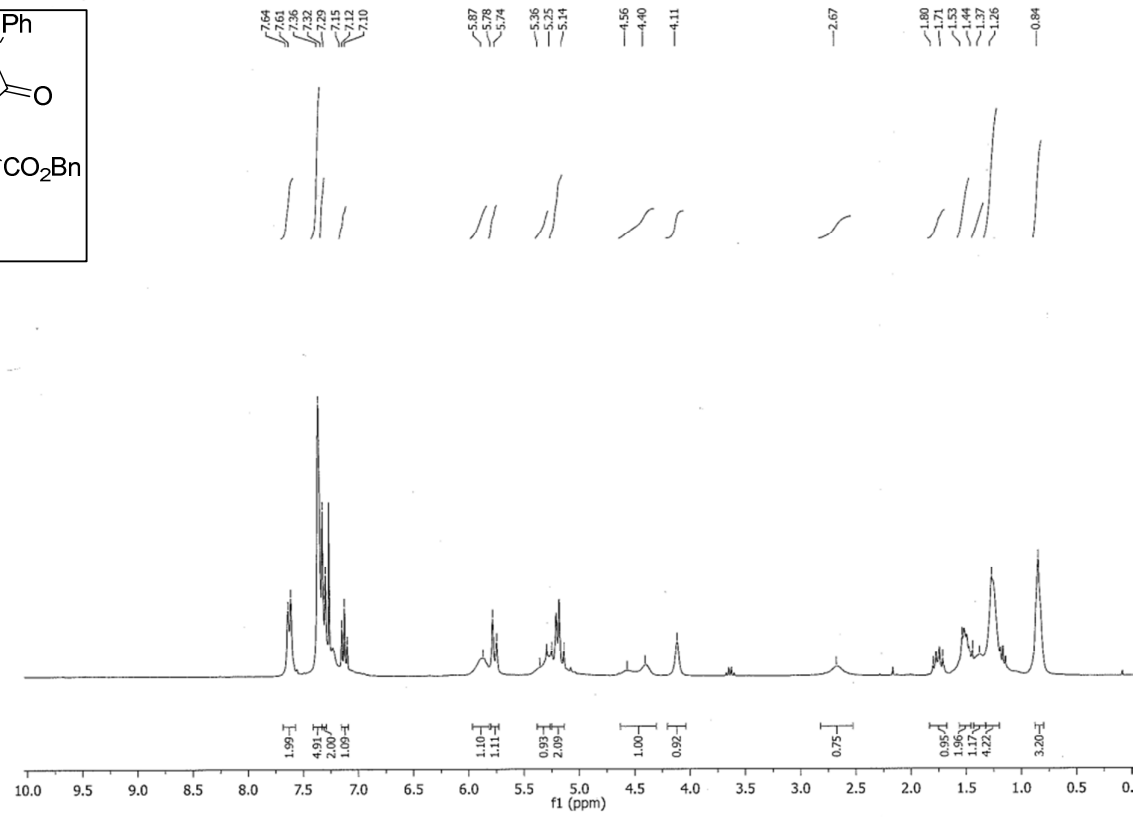
H
O
N
N
CO2Bn
Pent

10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7.32
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7.15
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7.10
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5.78
5.74
5.36
5.25
5.14
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4.40
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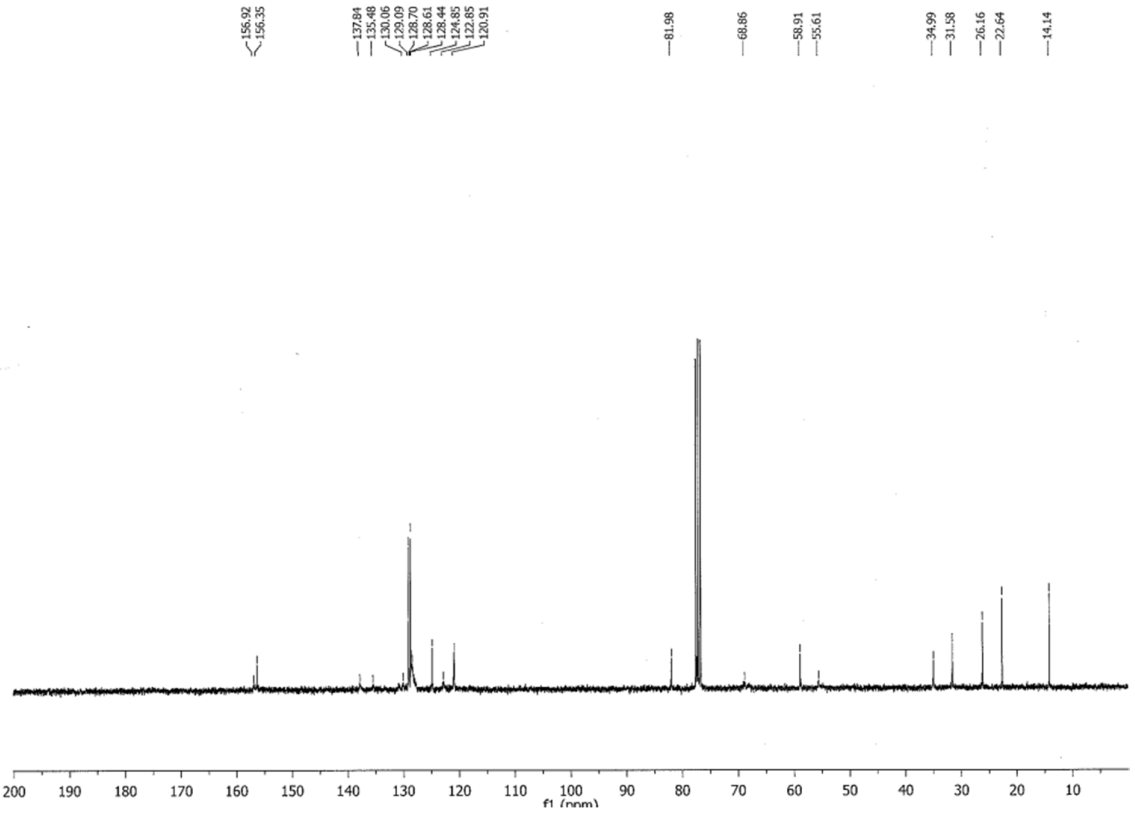
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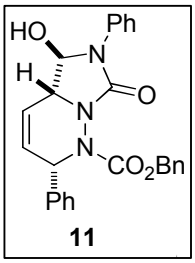
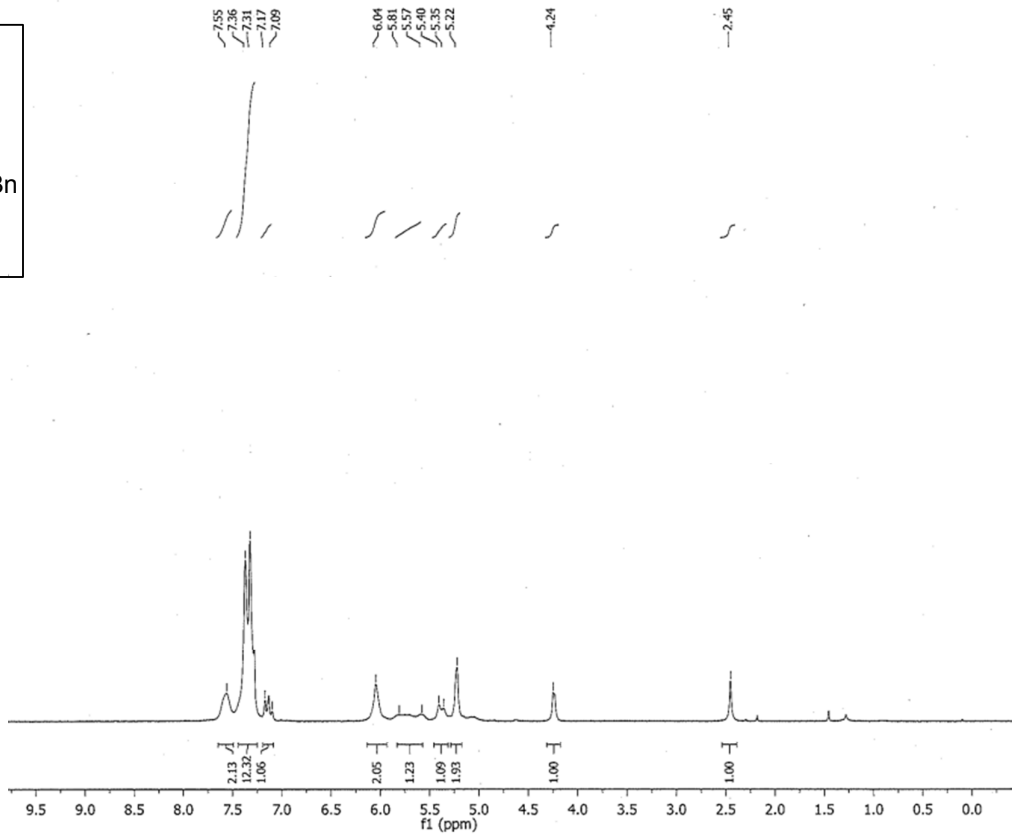
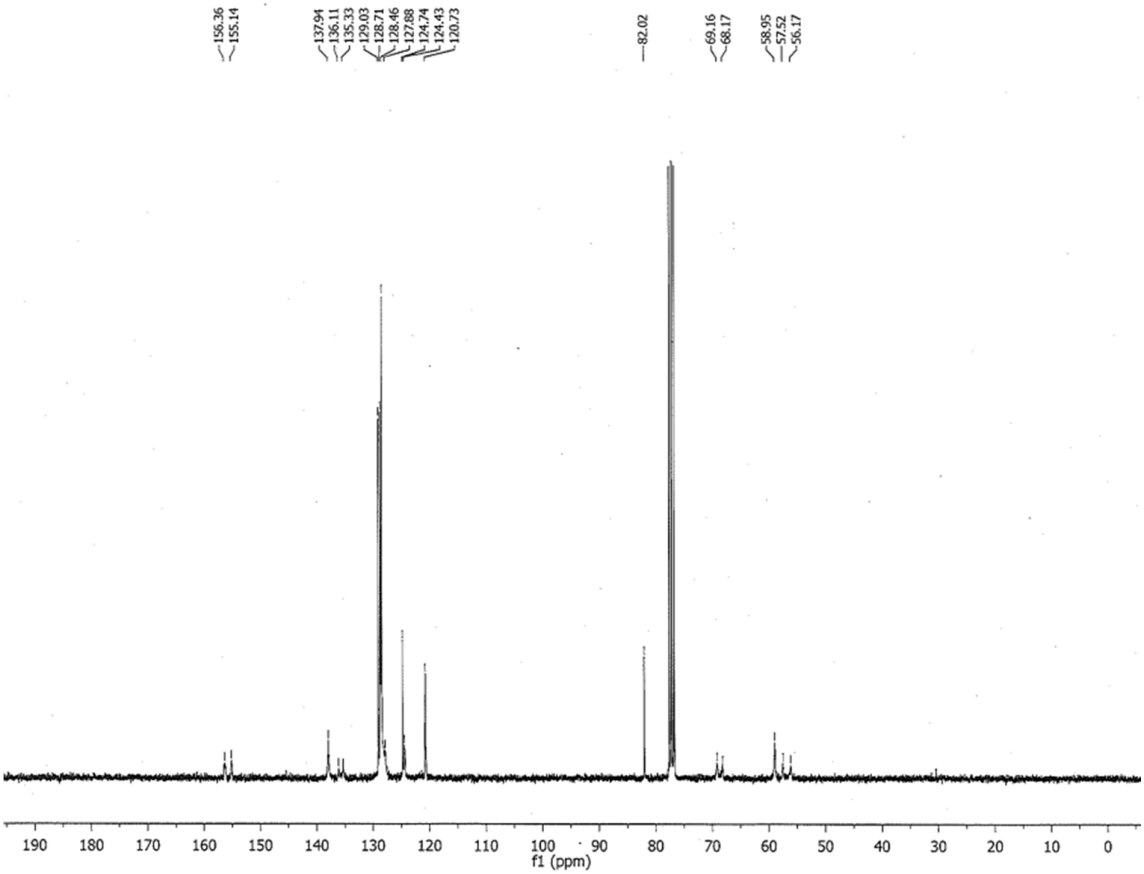
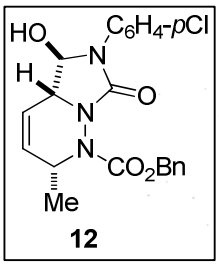
31.58
26.16
22.64
14.14
f1 (ppm)


HO
Ph
H
N
O
N
N
CO2Bn
Ph

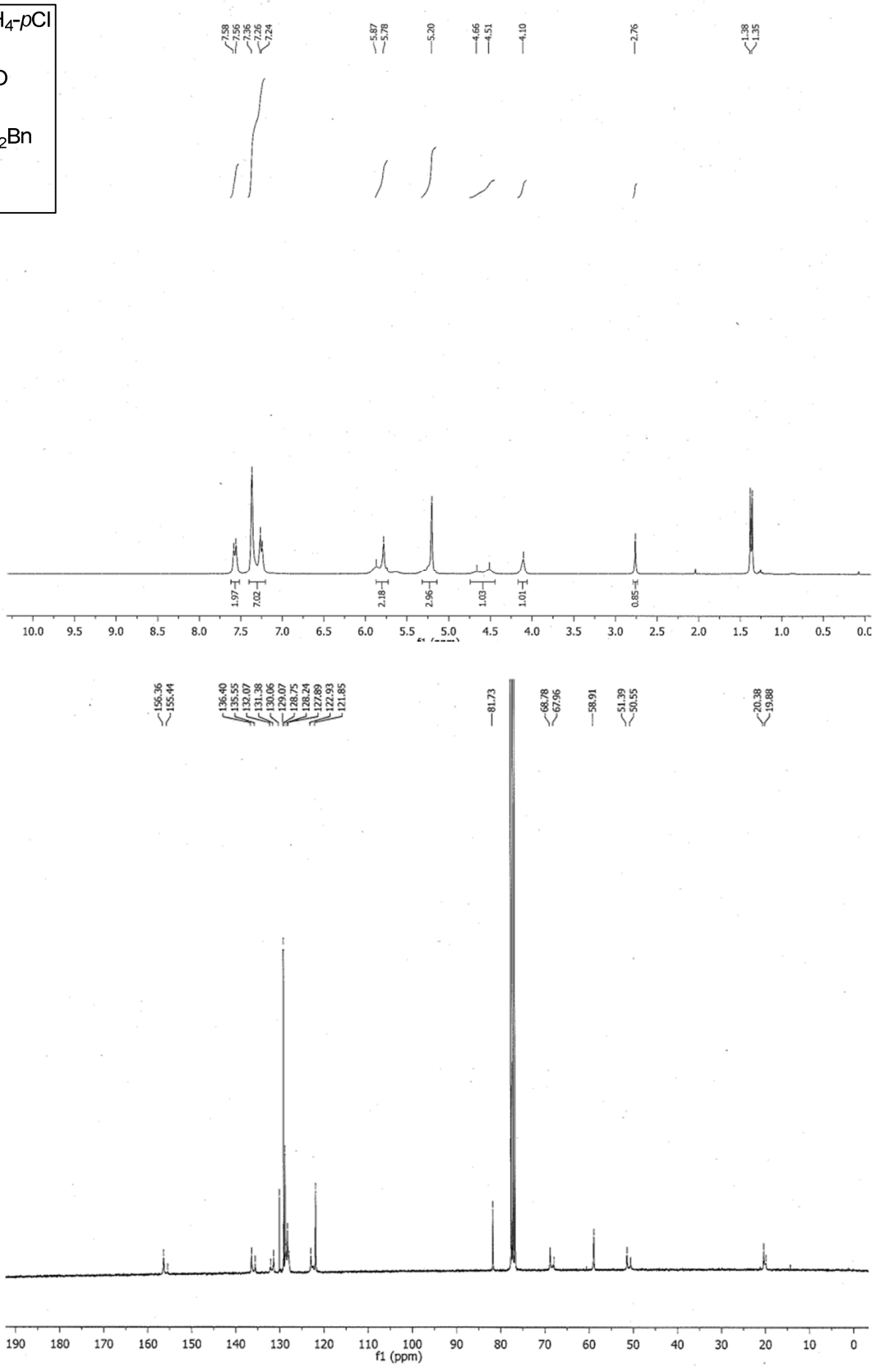
11

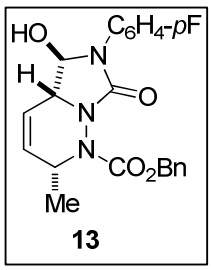

7.55
7.36
7.31
7.17
7.09
6.04
5.81
5.57
5.40
5.35
5.22
4.24
2.45
2.13
12.32
1.06
2.05
1.23
1.09
1.93
1.00
1.00
f1 (ppm)


156.36
155.14
137.94
136.11
135.33
129.03
128.71
128.46
127.88
124.74
124.43
120.73
82.02
69.16
68.17
58.95
57.52
56.17
f1 (ppm)

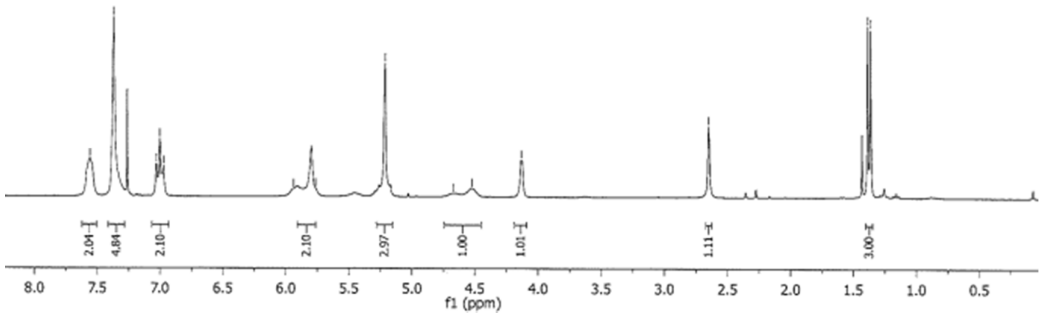

HO
C_6H_4-*p*Cl
H
N
O
N
N
CO_2Bn
Me

12

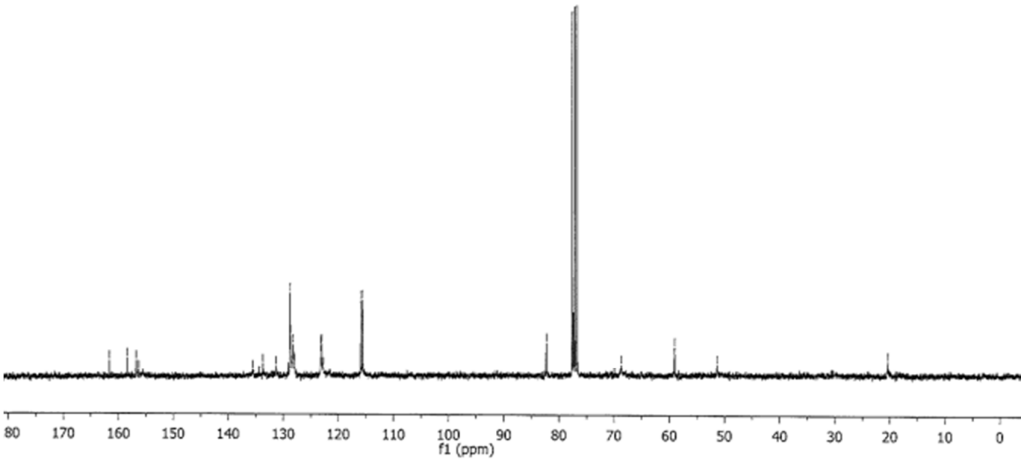

7.58
7.56
7.36
7.26
7.24
5.87
5.78
5.20
4.66
4.51
4.10
2.76
1.38
1.35
1.97
7.02
2.18
2.96
1.03
1.01
0.85
156.36
155.44
136.40
135.55
132.07
131.38
130.06
129.07
128.75
128.24
127.89
122.93
121.85
81.73
68.78
67.96
58.91
51.39
50.55
20.38
19.88
f1 (ppm)

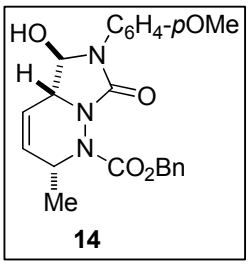

HO
C6H4-pF
H
N
O
N
N
CO2Bn
Me
13

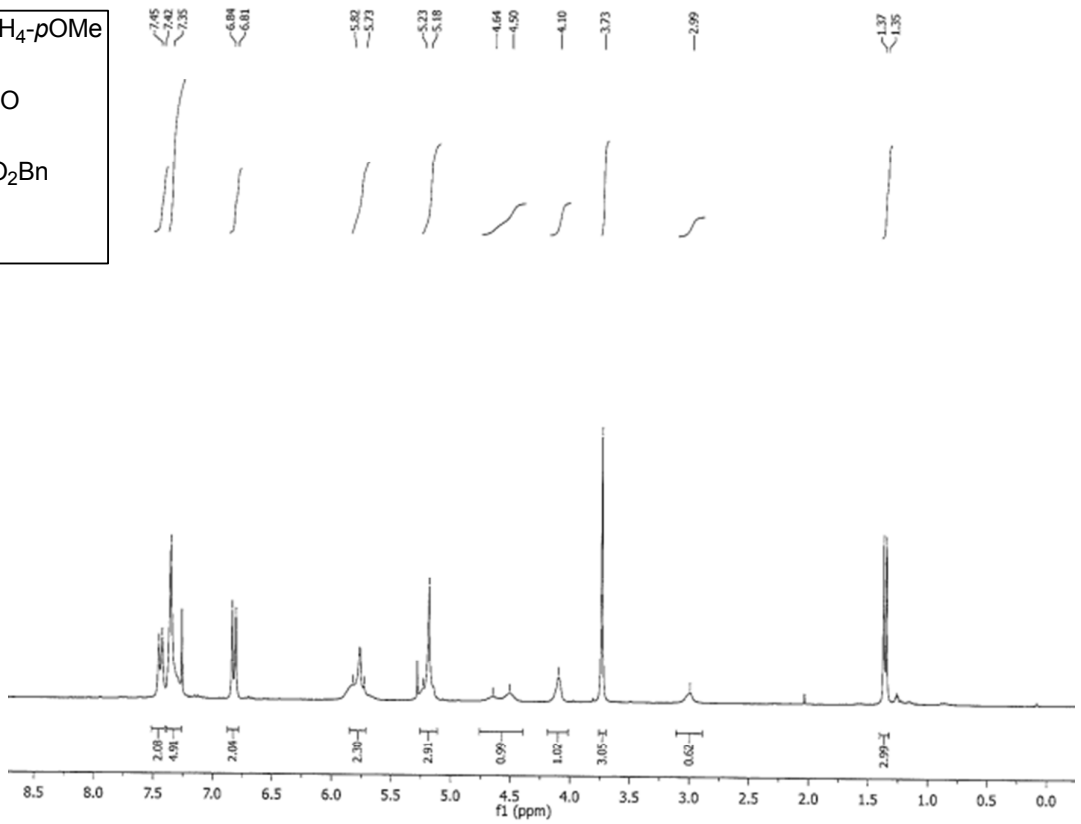

7.56
7.37
7.03
7.00
6.97
5.94
5.76
5.21
4.67
4.52
4.13
2.65
1.39
1.36

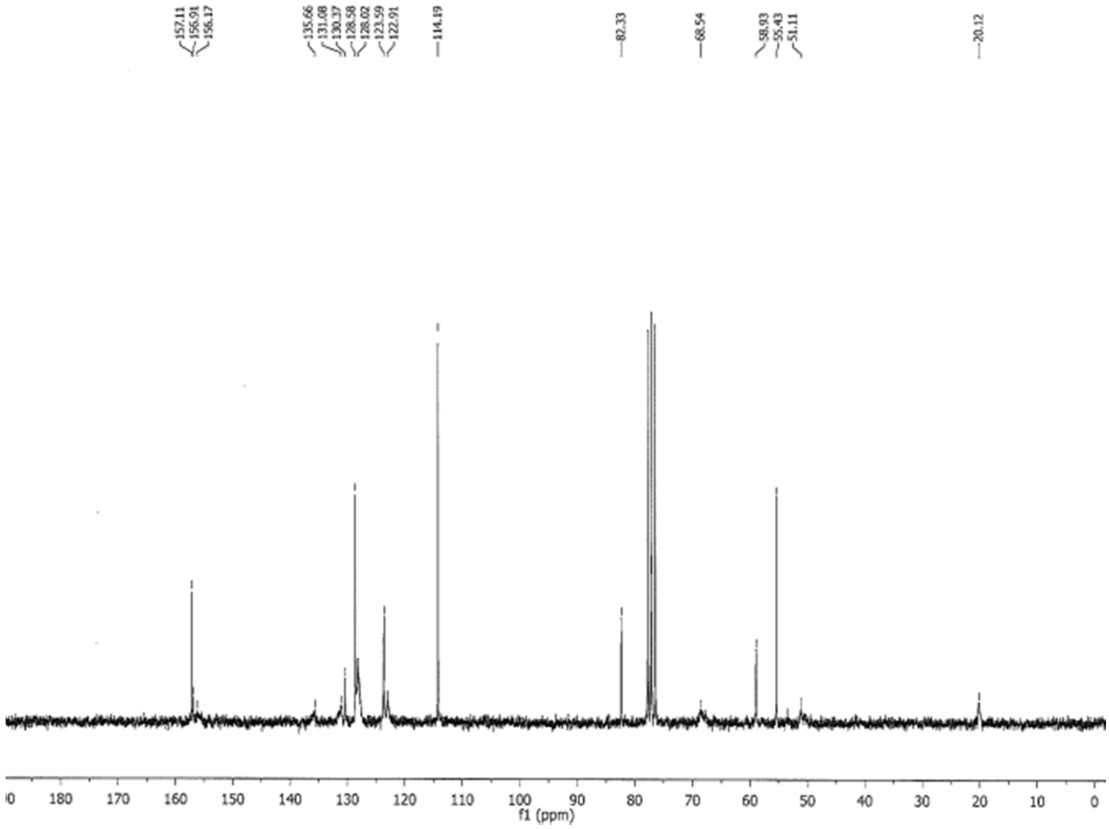

2.04
4.84
2.10
2.10
2.97
1.00
1.01
1.11
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

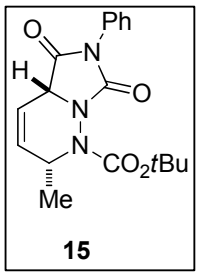

161.64
158.41
155.75
150.28
135.58
133.69
131.28
128.74
128.64
128.15
123.15
123.04
122.95
115.91
115.62
82.26
68.67
59.06
51.39
20.36


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

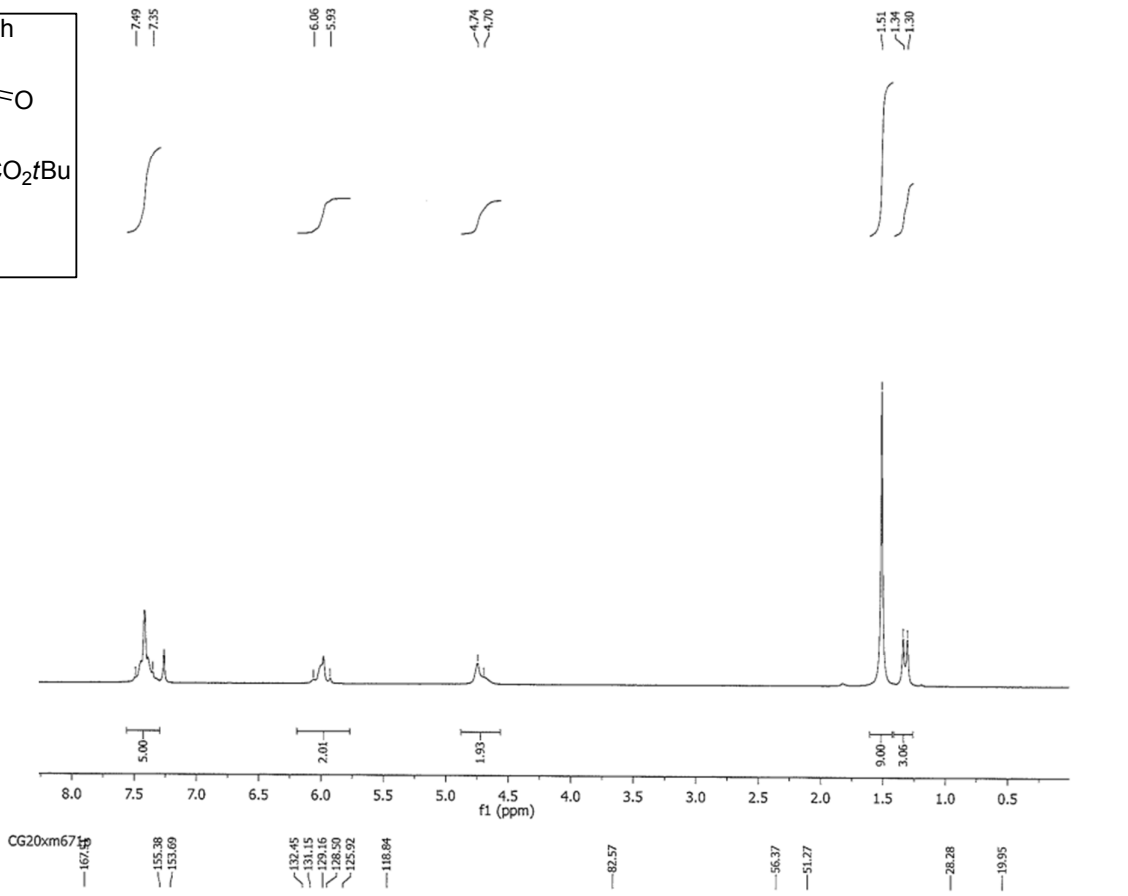

HO
C6H4-pOMe
N
H
O
N
N
CO2Bn
Me
14

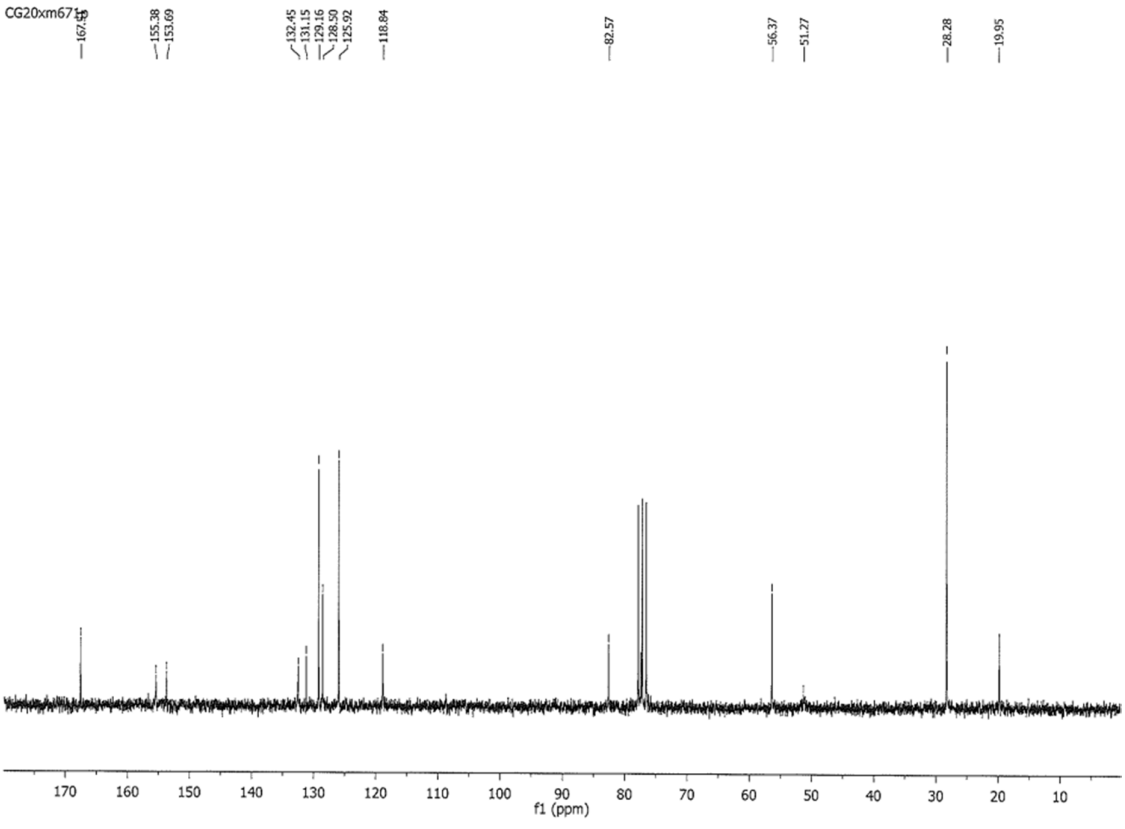

7.45
7.42
7.35
6.84
6.81
5.82
5.73
5.23
5.18
4.64
4.50
4.10
3.73
2.99
1.37
1.35
2.08
4.91
2.04
2.30
2.91
0.99
1.02
3.05
0.62
2.99
f1 (ppm)

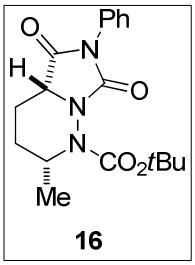

157.11
156.91
156.17
135.66
131.08
130.37
128.58
128.02
123.59
122.91
114.19
82.33
68.54
58.93
55.43
51.11
20.12
f1 (ppm)


O
Ph
N
H
O
N
N
CO2tBu
Me

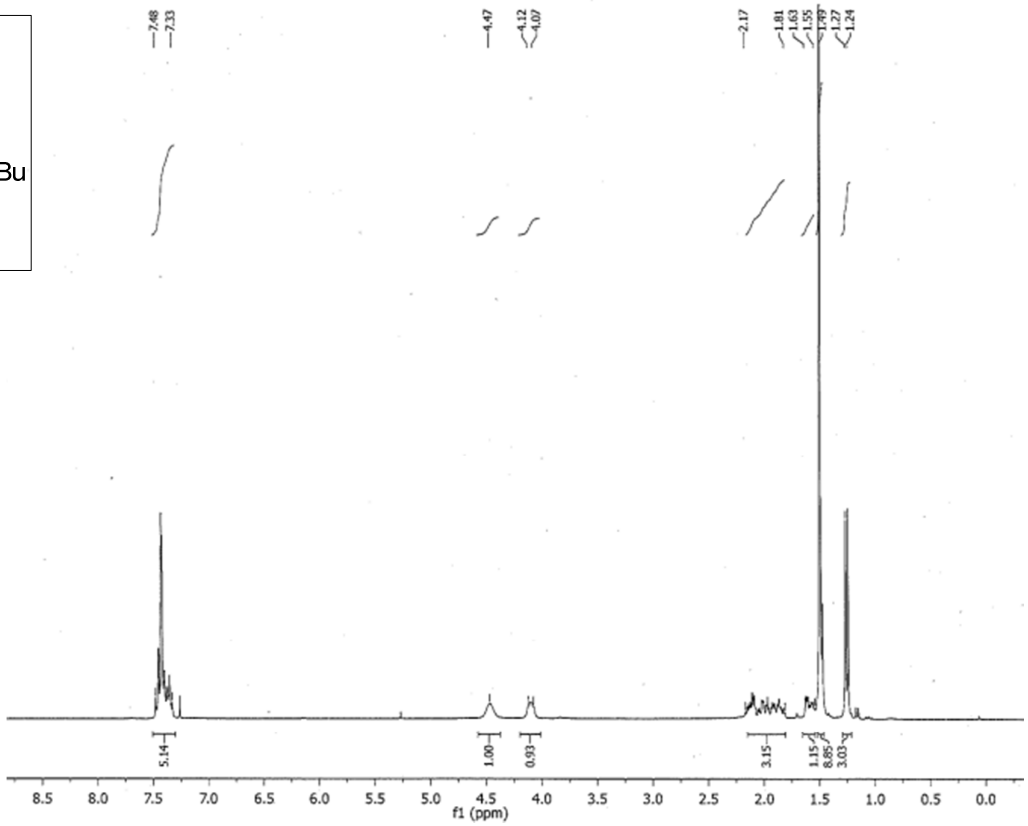
15

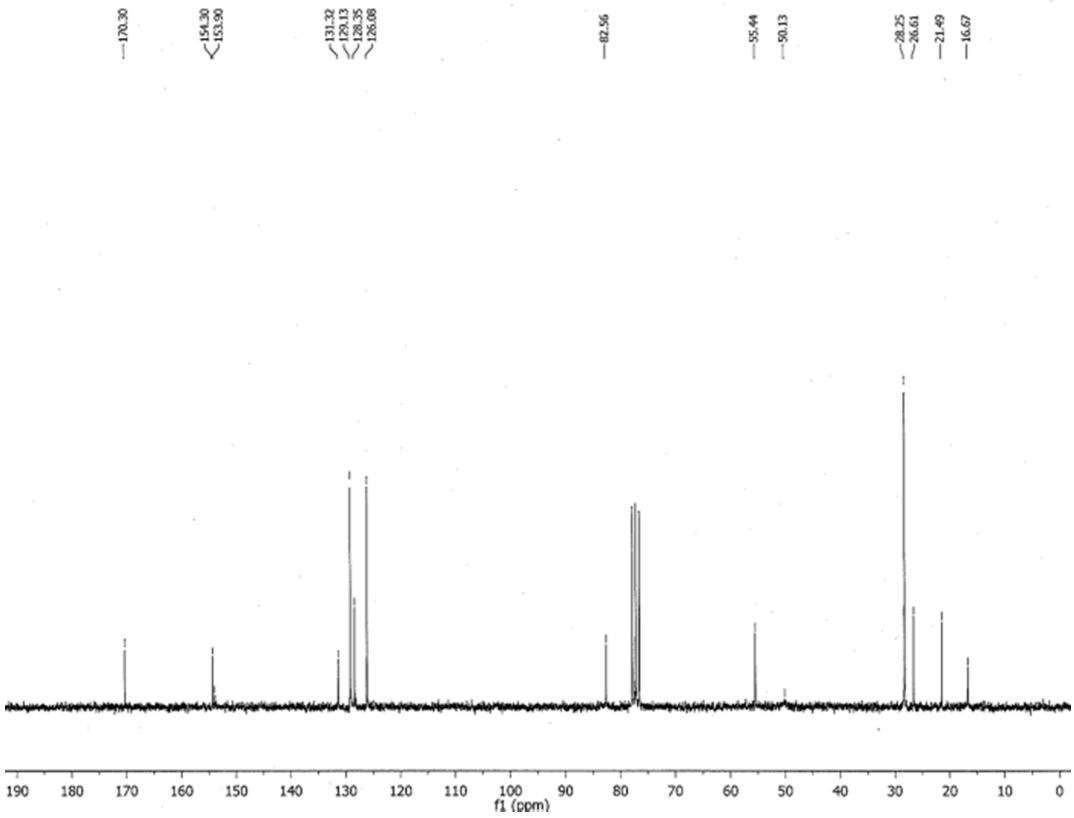

7.49
7.35
6.06
5.93
4.74
4.70
1.51
1.34
1.30
5.00
2.01
1.93
9.00
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

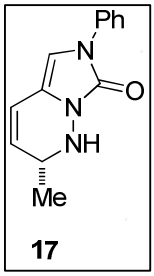

CG20xm671-1
167.49
155.38
153.69
132.45
131.15
129.16
128.50
125.92
118.84
82.57
56.37
51.27
28.28
19.95
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
O
N
H
O
N
N
CO2tBu
Me

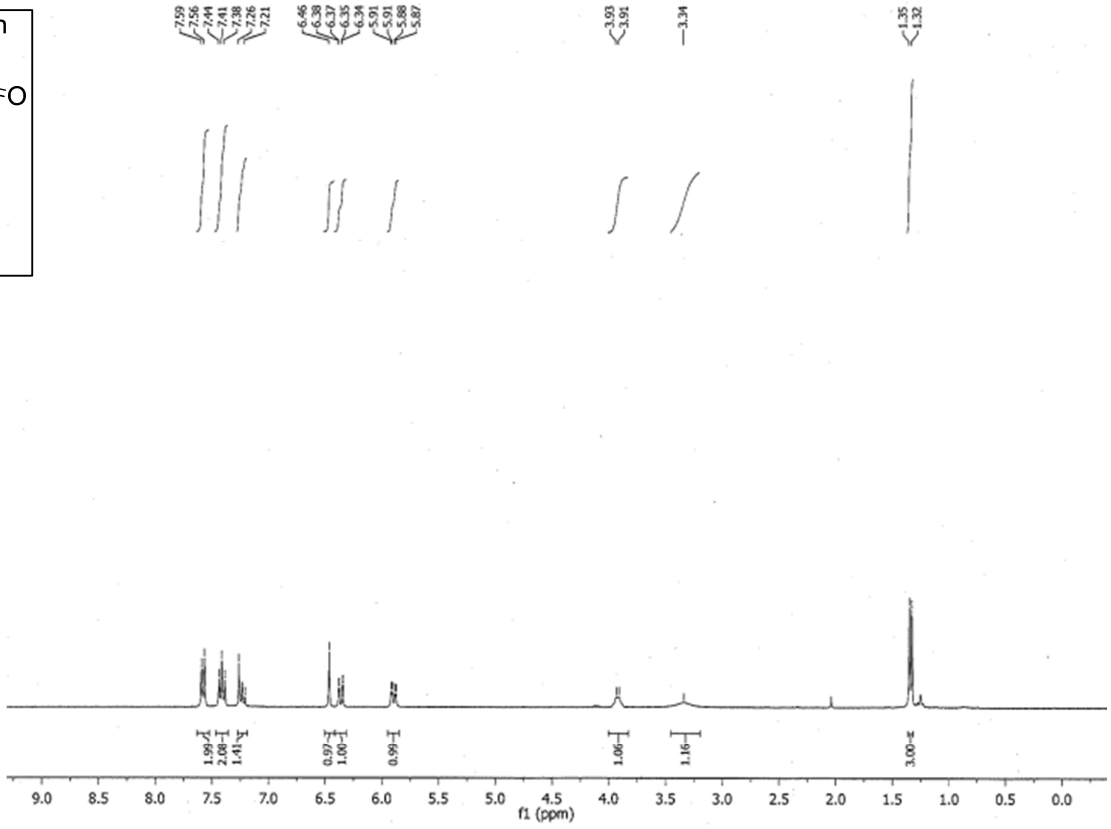
16

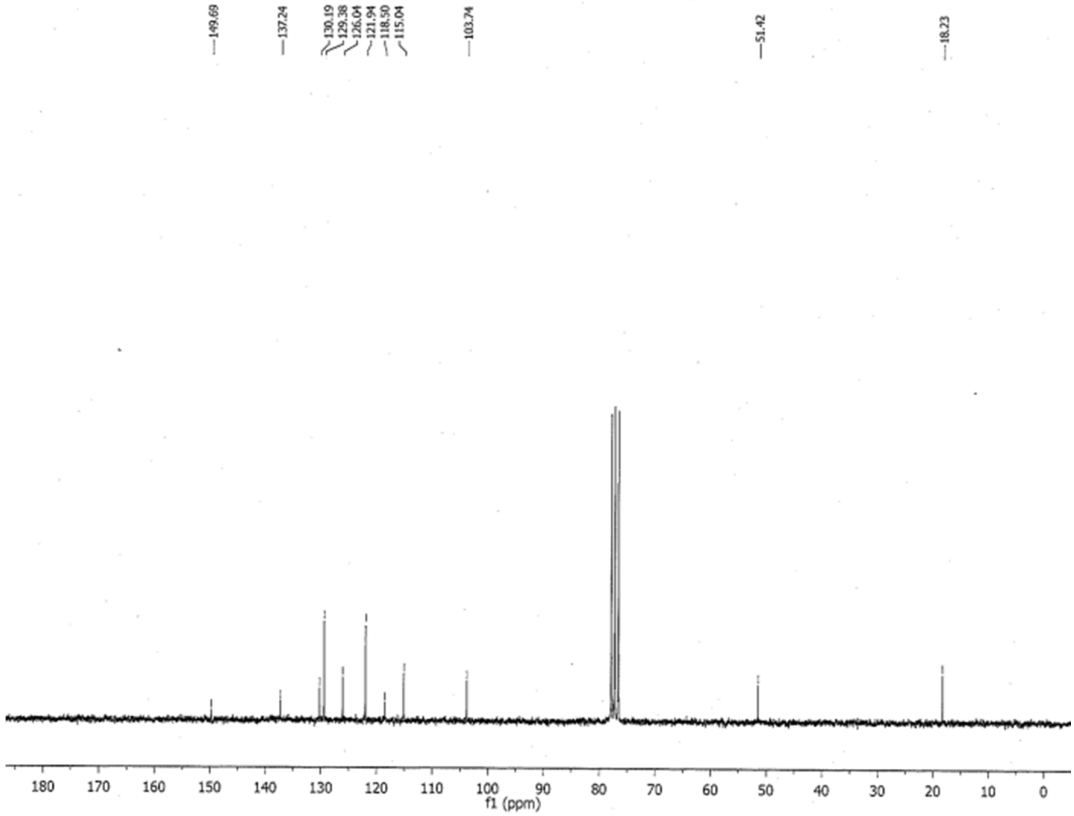

7.48
7.33
4.47
4.12
4.07
2.17
1.81
1.63
1.55
1.27
1.24
5.14
1.00
0.93
3.15
1.15
8.85
3.03
f1 (ppm)

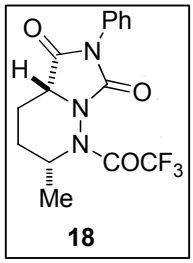

170.30
154.30
153.90
131.32
129.13
128.35
126.08
82.56
55.44
50.13
28.25
26.61
21.49
16.67
f1 (ppm)


Ph
N
O
N
NH
Me

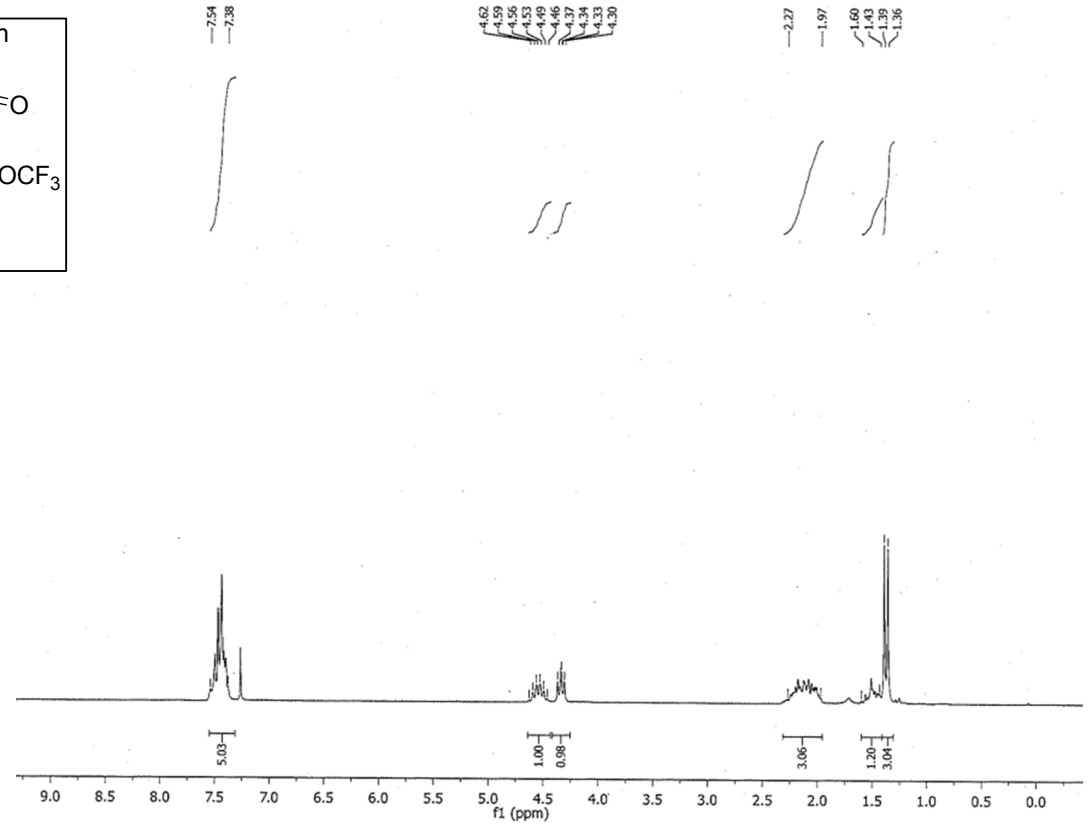
17

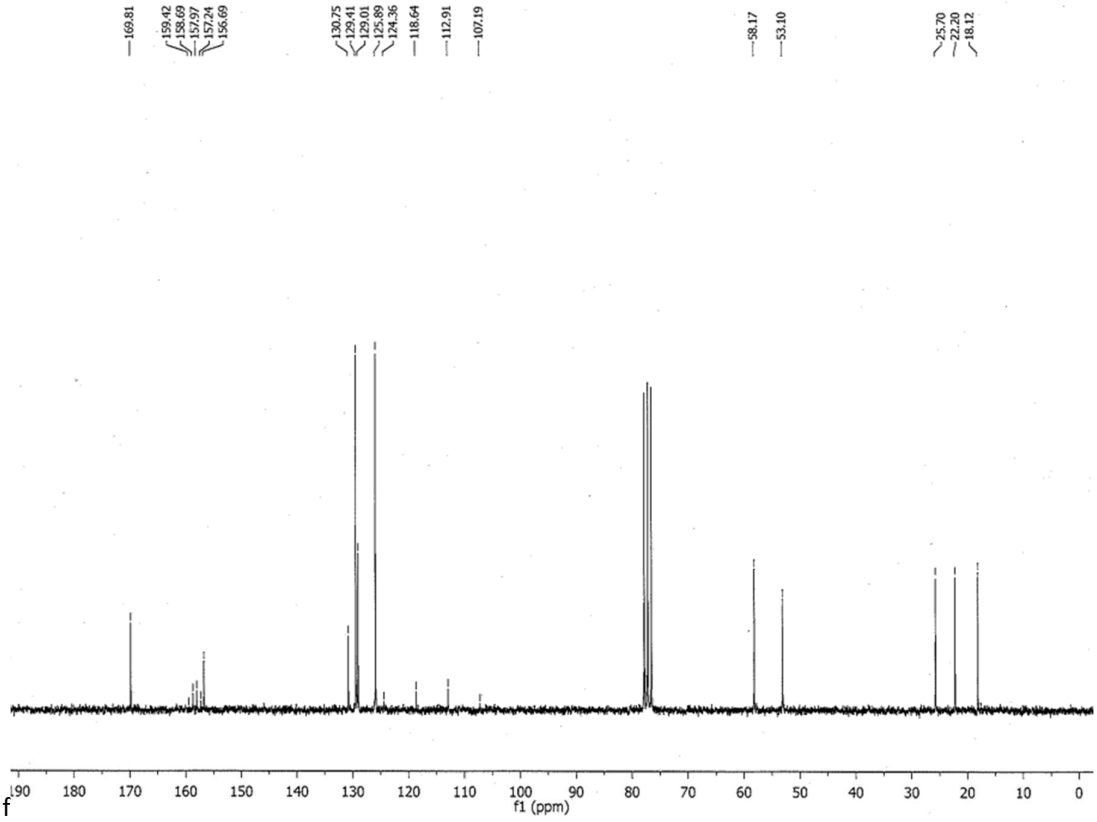

7.59
7.56
7.44
7.41
7.38
7.26
7.21
6.46
6.38
6.37
6.35
6.34
5.91
5.91
5.88
5.87
3.93
3.91
3.34
1.35
1.32
1.99
2.08
1.41
0.97
1.00
0.99
1.06
1.16
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.69
137.24
130.19
129.38
126.04
121.94
118.50
115.04
103.74
51.42
18.23
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

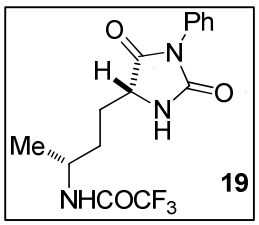

O
Ph
N
H
O
N
N
COCF3
Me

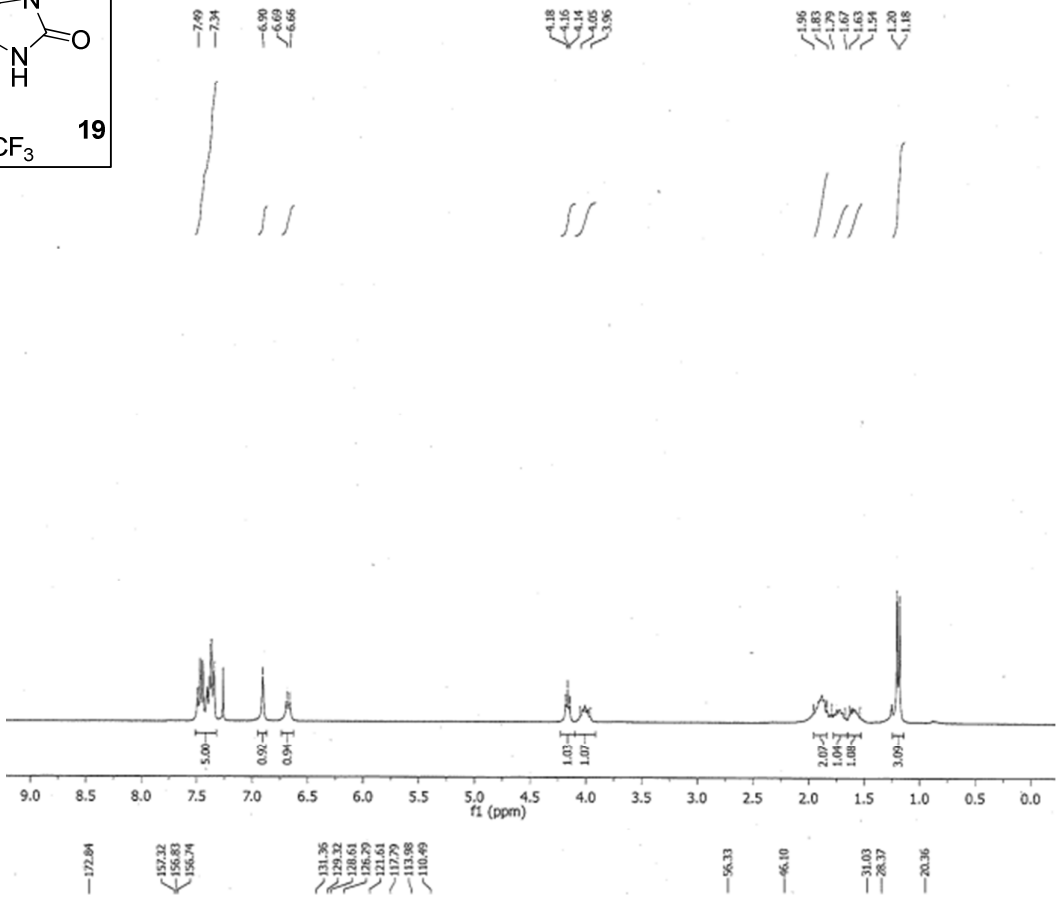
18

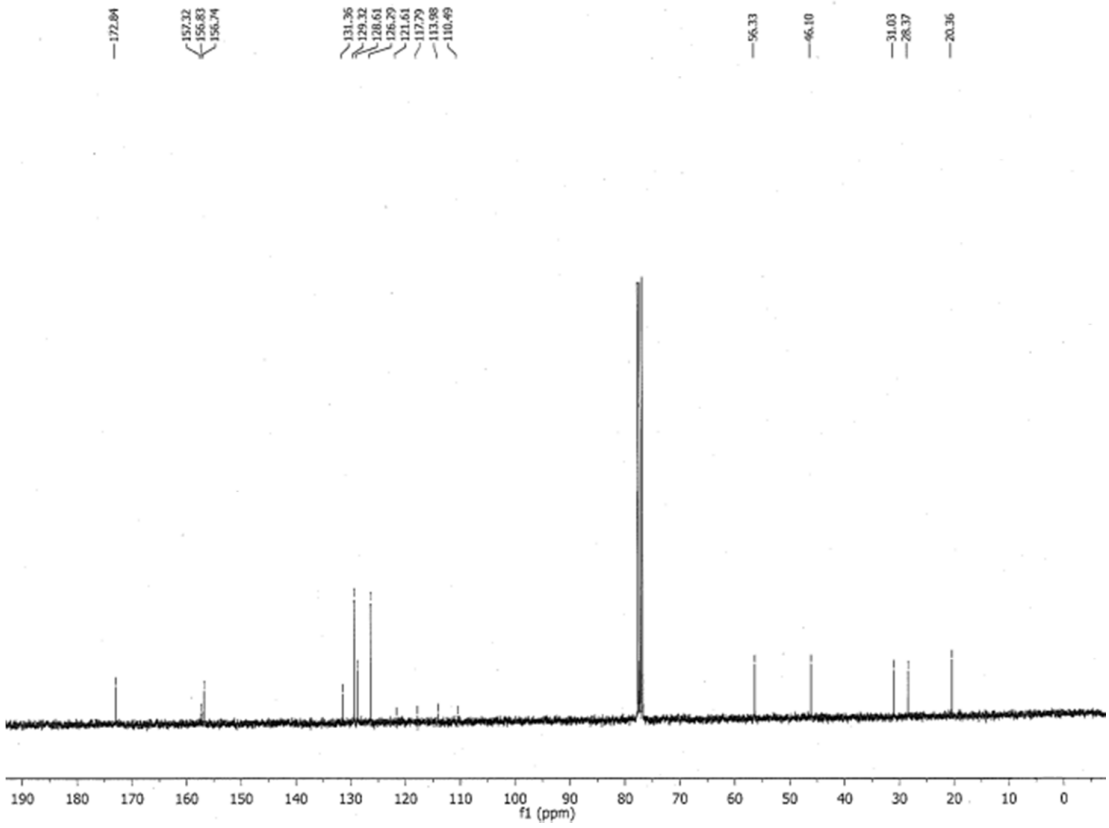

7.54
7.38
4.62
4.59
4.56
4.53
4.49
4.46
4.37
4.34
4.33
4.30
2.27
1.97
1.60
1.43
1.39
1.36
5.03
1.00
0.98
3.06
1.20
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

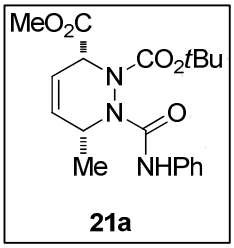

169.81
159.42
158.69
157.97
157.24
156.69
130.75
129.41
129.01
125.89
124.36
118.64
112.91
107.19
58.17
53.10
25.70
22.20
18.12
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

f

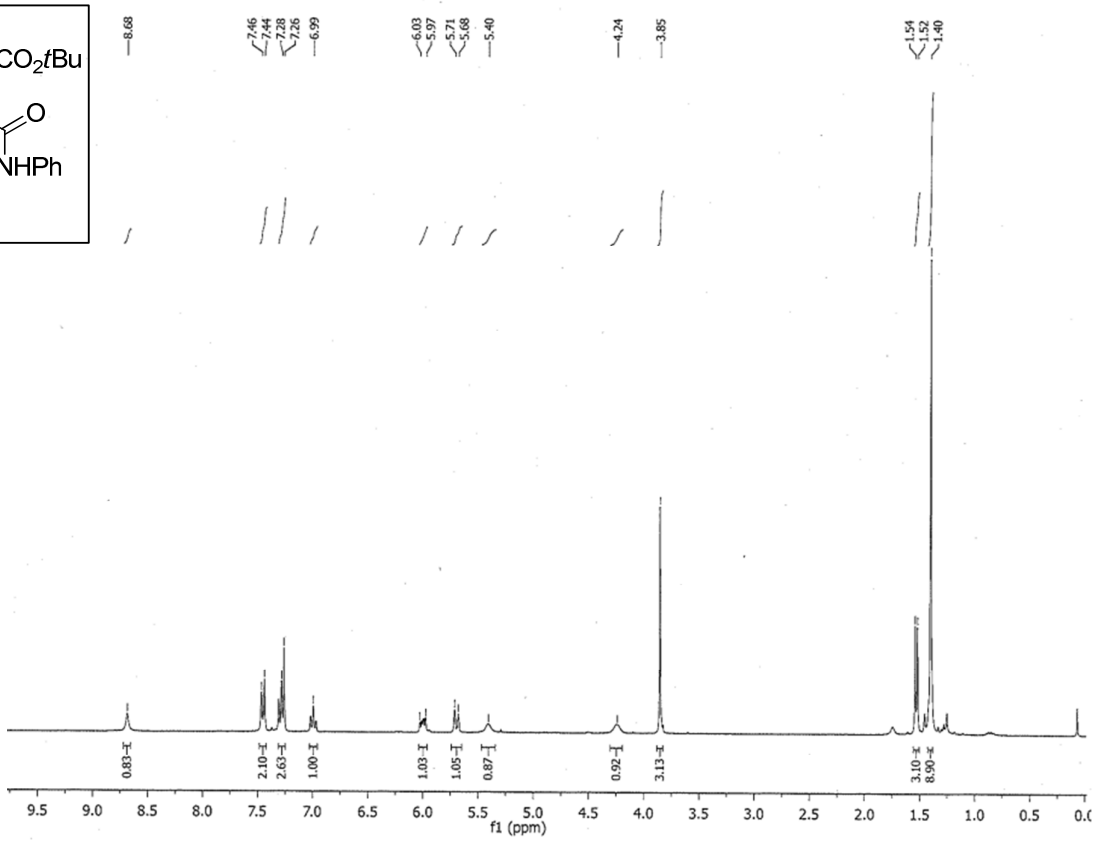

O
Ph
N
H
O
N
H
Me
NHCOCF3
19

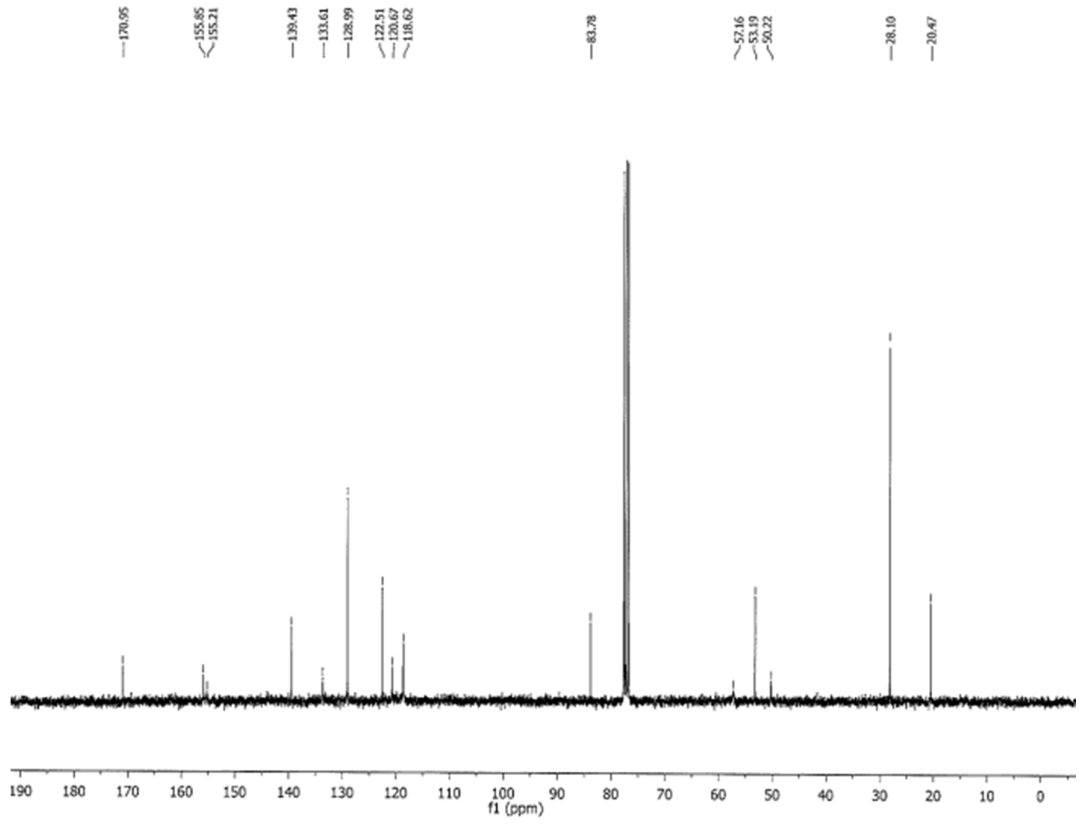

7.49
7.34
6.90
6.69
6.66
4.18
4.16
4.14
4.05
3.96
1.96
1.83
1.79
1.67
1.63
1.54
1.20
1.18
5.00
0.92
0.94
1.03
1.07
2.07
1.04
1.08
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

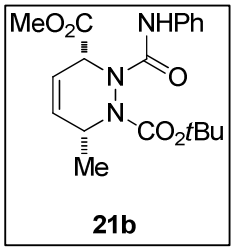

172.84
157.32
156.83
156.74
131.36
129.32
128.61
126.29
121.61
117.79
113.98
110.49
56.33
46.10
31.03
28.37
20.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO2C
CO2tBu
N
N
O
Me
NHPh

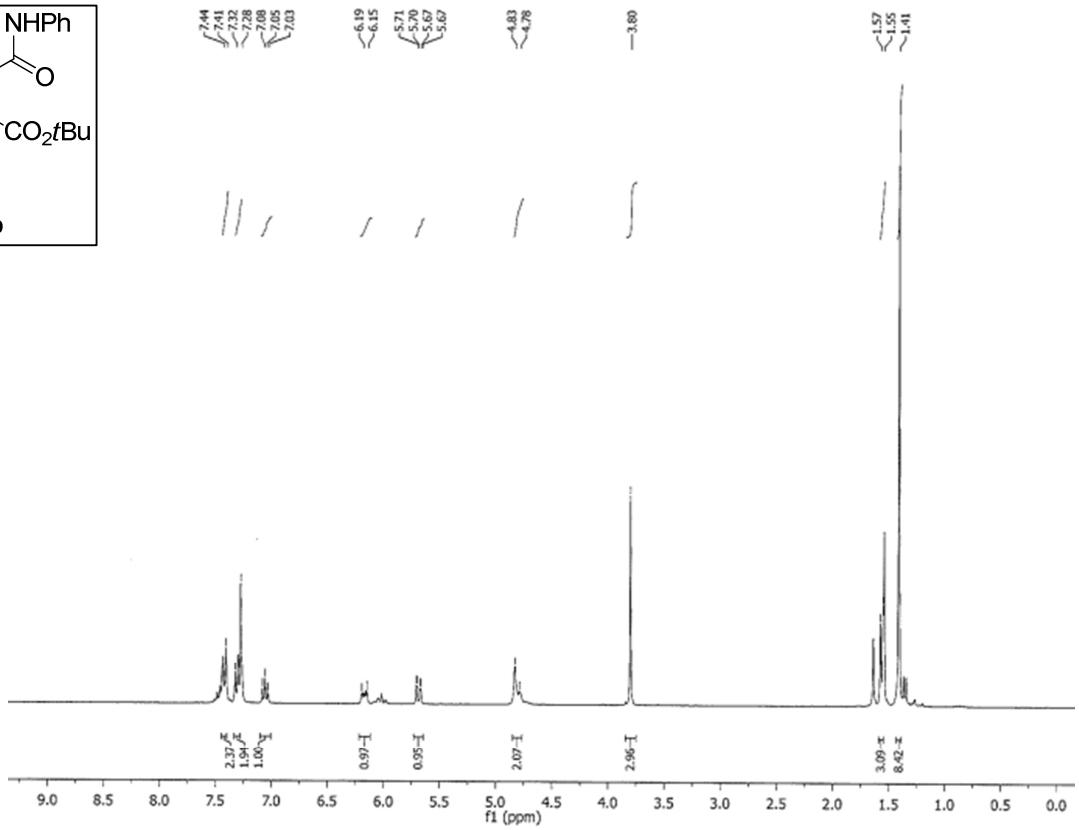
21a


8.68
7.46
7.44
7.28
7.26
6.99
6.03
5.97
5.71
5.68
5.40
4.24
3.85
1.54
1.52
1.40
0.83
2.10
2.63
1.00
1.03
1.05
0.87
0.92
3.13
3.10
8.90
f1 (ppm)

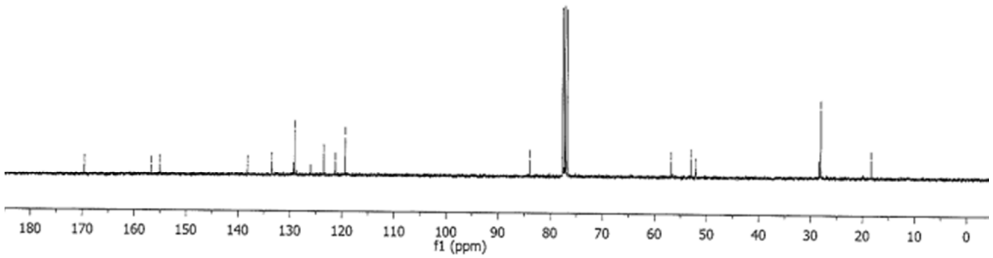

170.95
155.85
155.21
139.43
133.61
128.99
122.51
120.67
118.62
83.78
57.16
53.19
50.22
28.10
20.47
f1 (ppm)

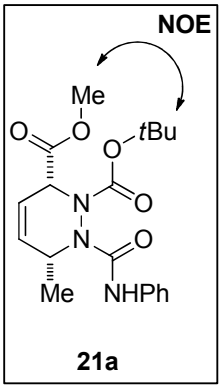

MeO2C
NHPh
O
N
N
CO2tBu
Me

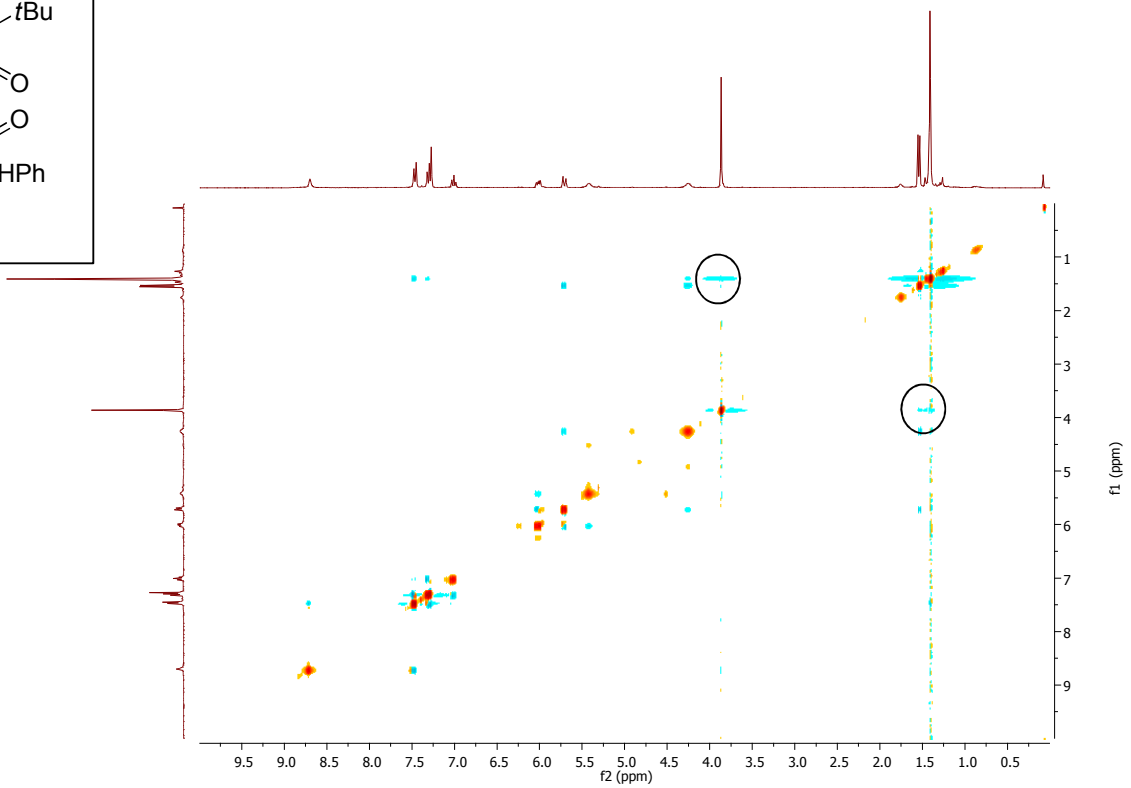
21b

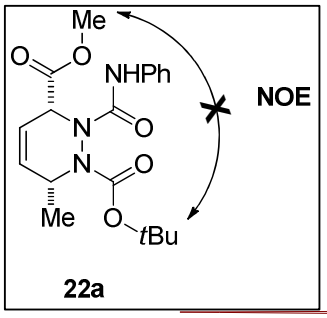

7.44
7.41
7.32
7.28
7.08
7.05
7.03
6.19
6.15
5.71
5.70
5.67
5.67
4.83
4.78
3.80
1.57
1.55
1.41
2.37
1.94
1.00
0.97
0.95
2.07
2.96
3.09
8.42
f1 (ppm)


169.56
156.67
155.03
138.12
133.47
129.09
123.45
121.25
119.34
83.91
56.78
52.98
52.08
28.05
18.35


f1 (ppm)







See a zoom below