Supporting Information for

[4+3] Cycloaddition of Phthalazinium Dicyanomethanides with Azoalkenes Formed *in situ*: Synthesis of Triazepine Derivatives

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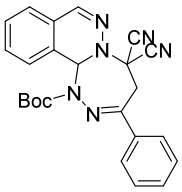
X-Ray Crystallographic Data of **4aa** S28

NMR Spectra of the Products 3, 4, 6 and 8



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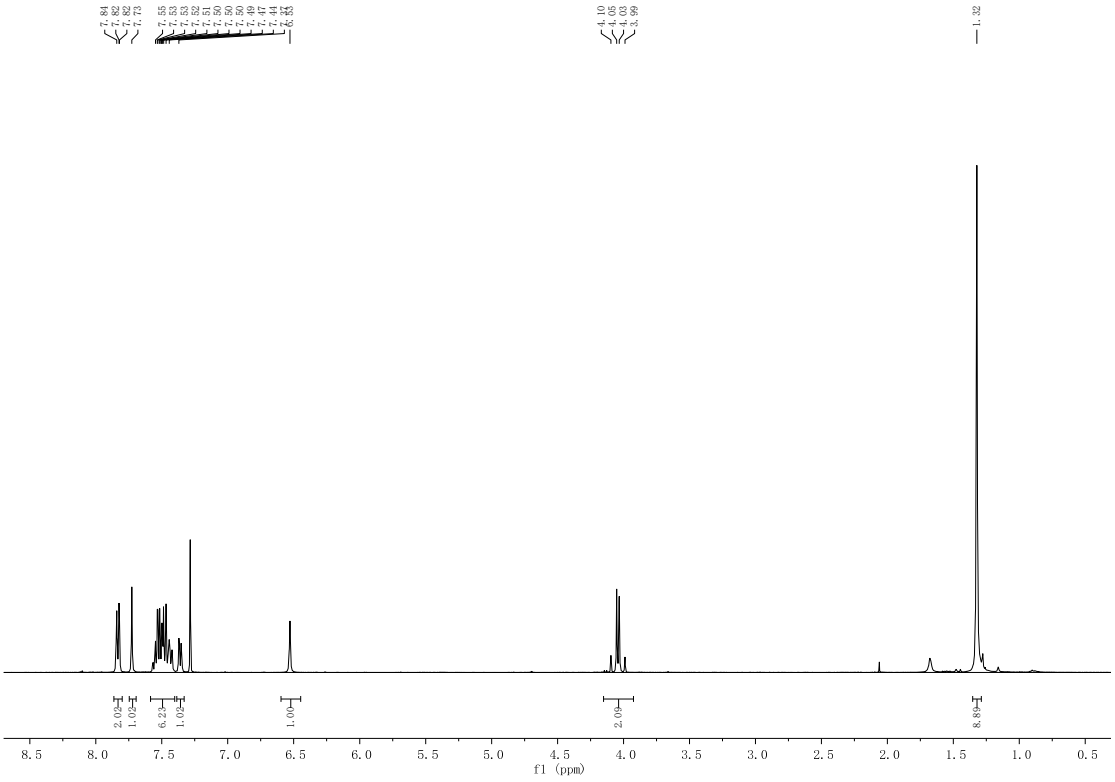

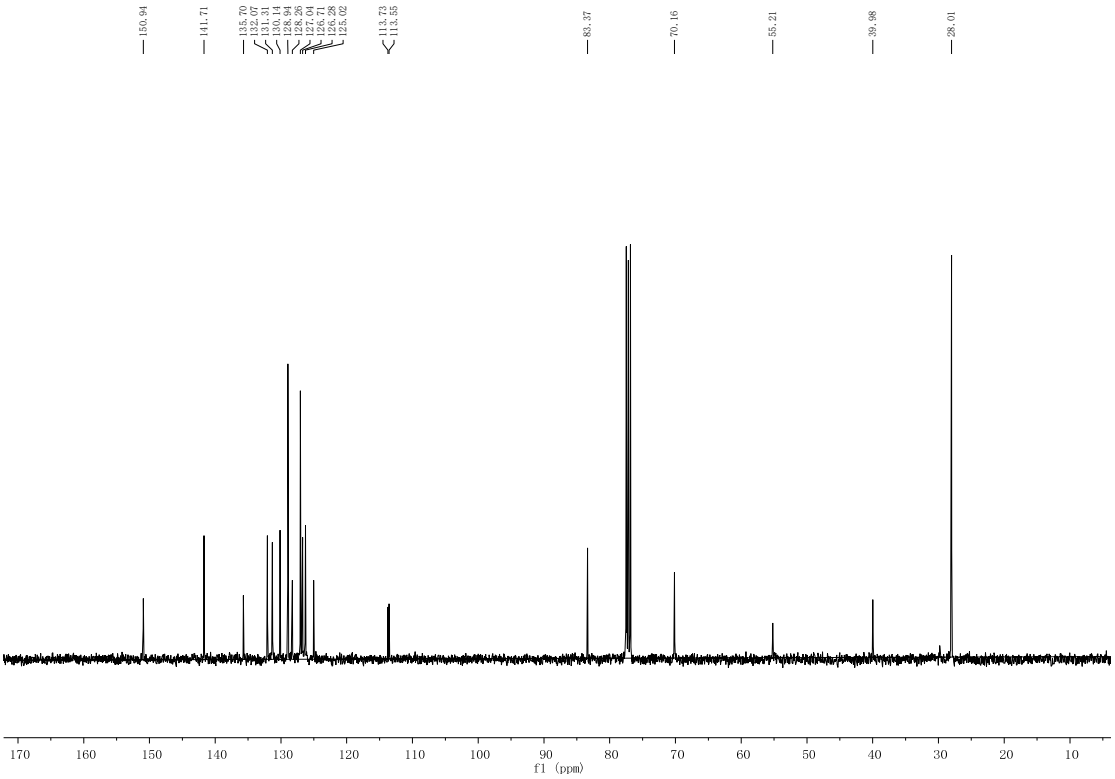

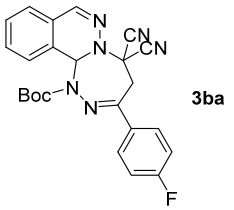
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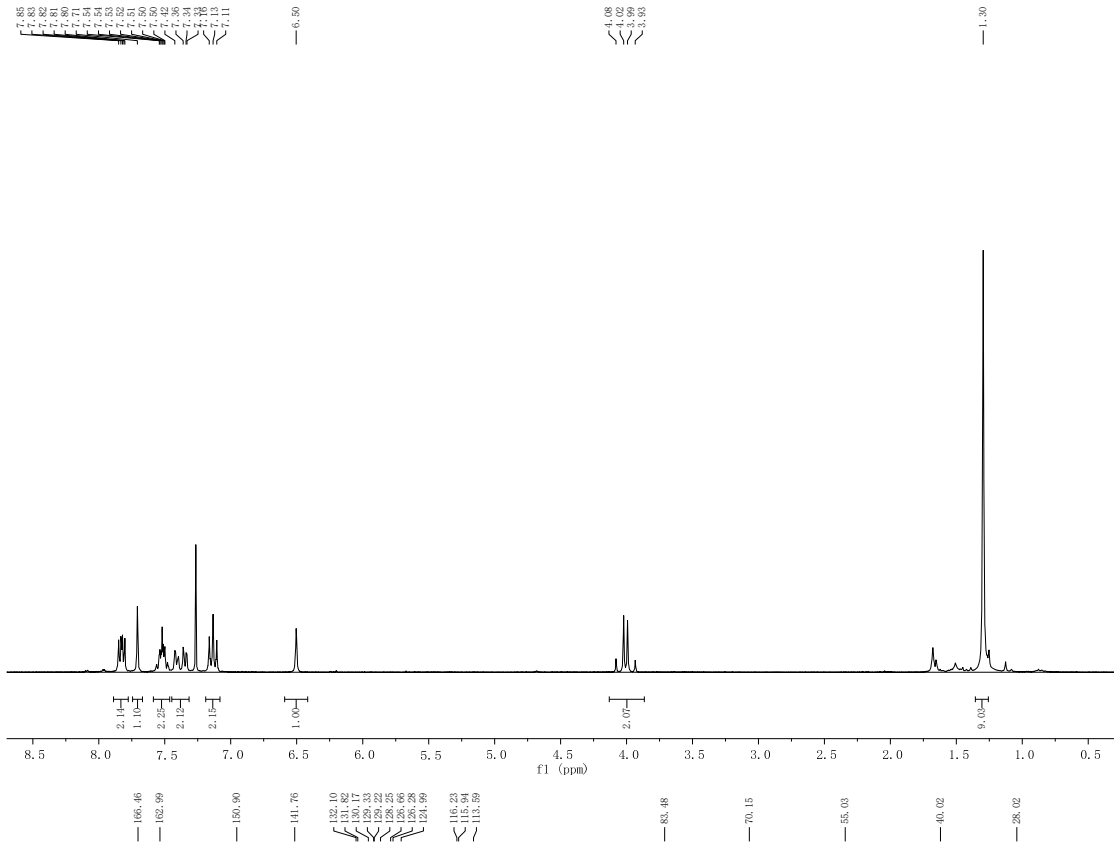
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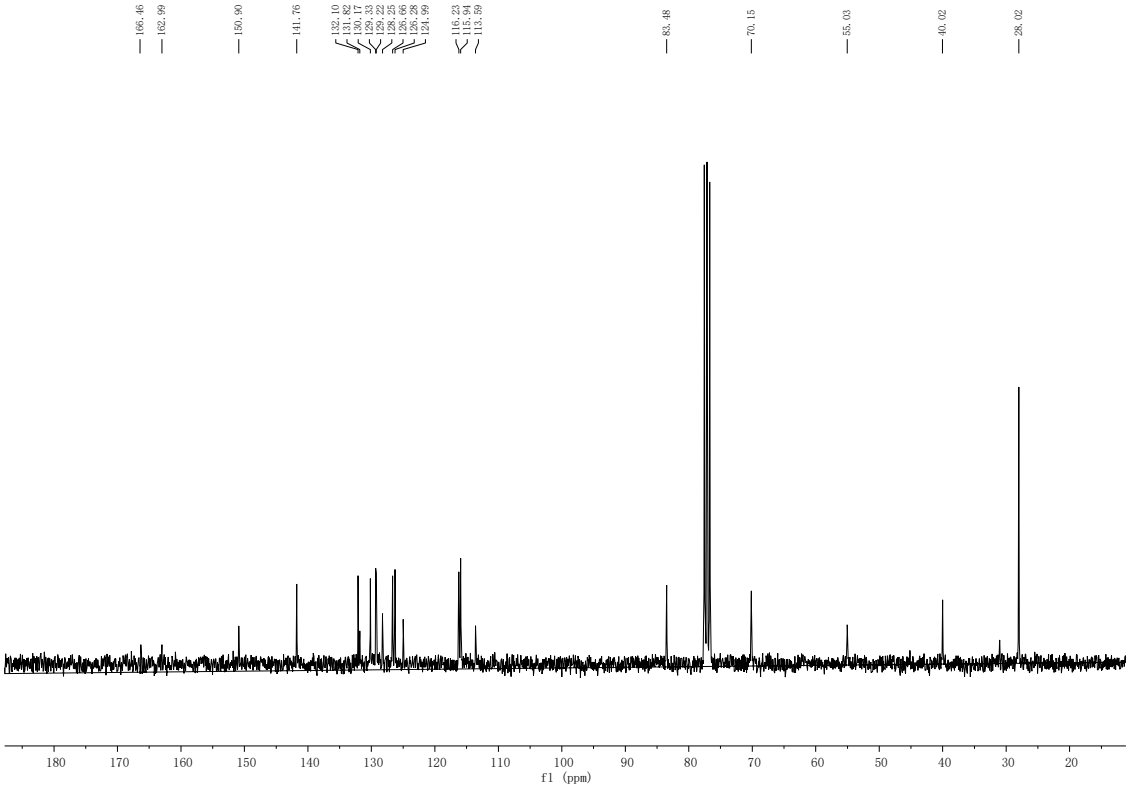
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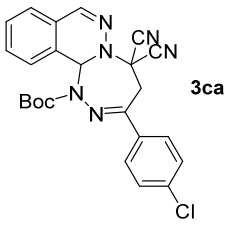
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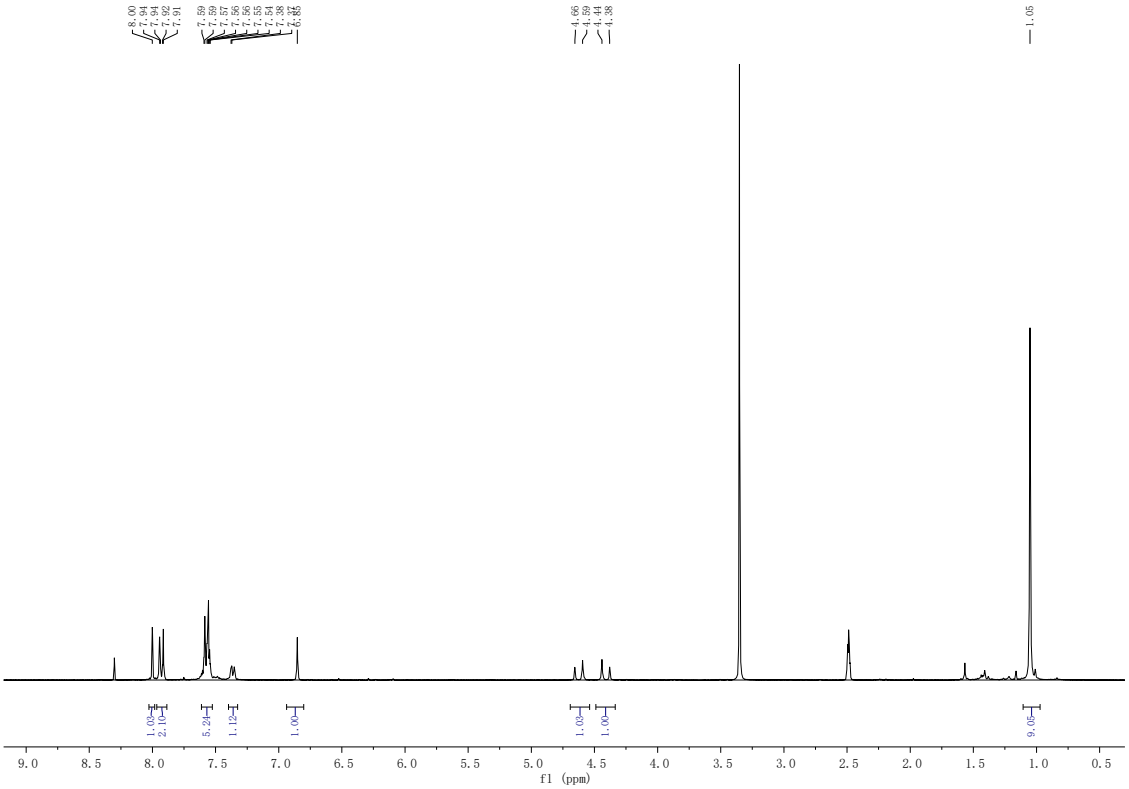
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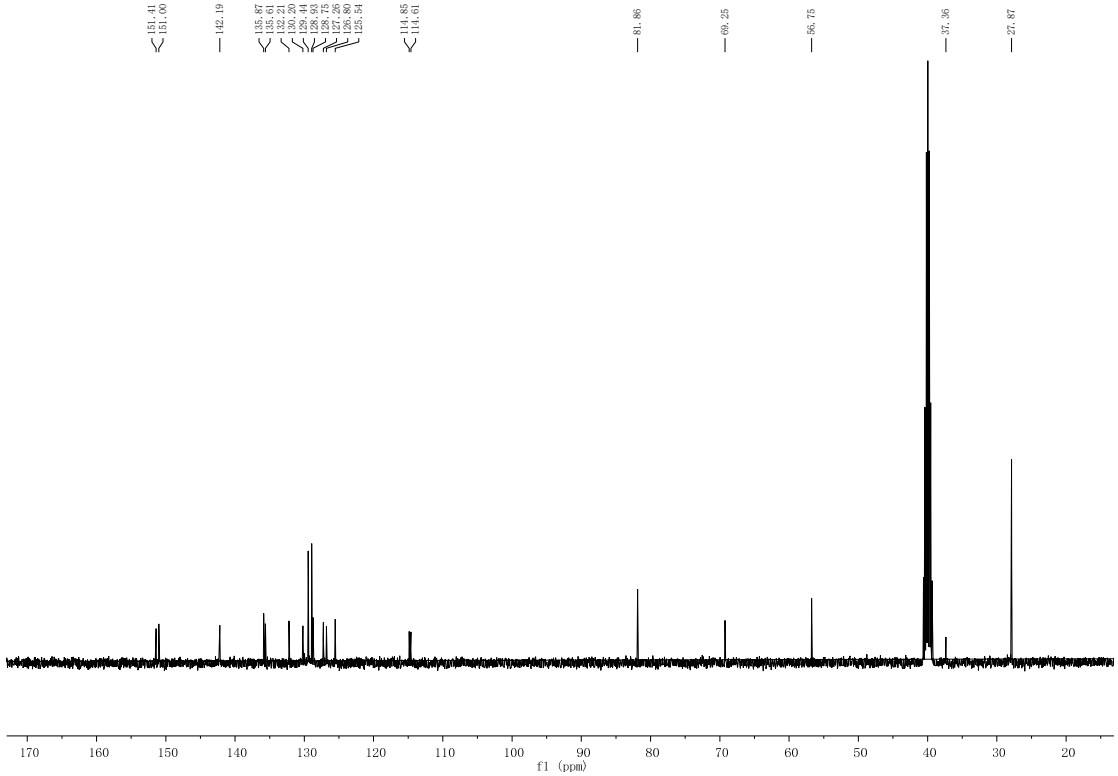
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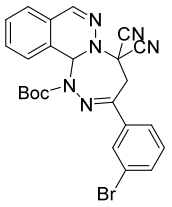
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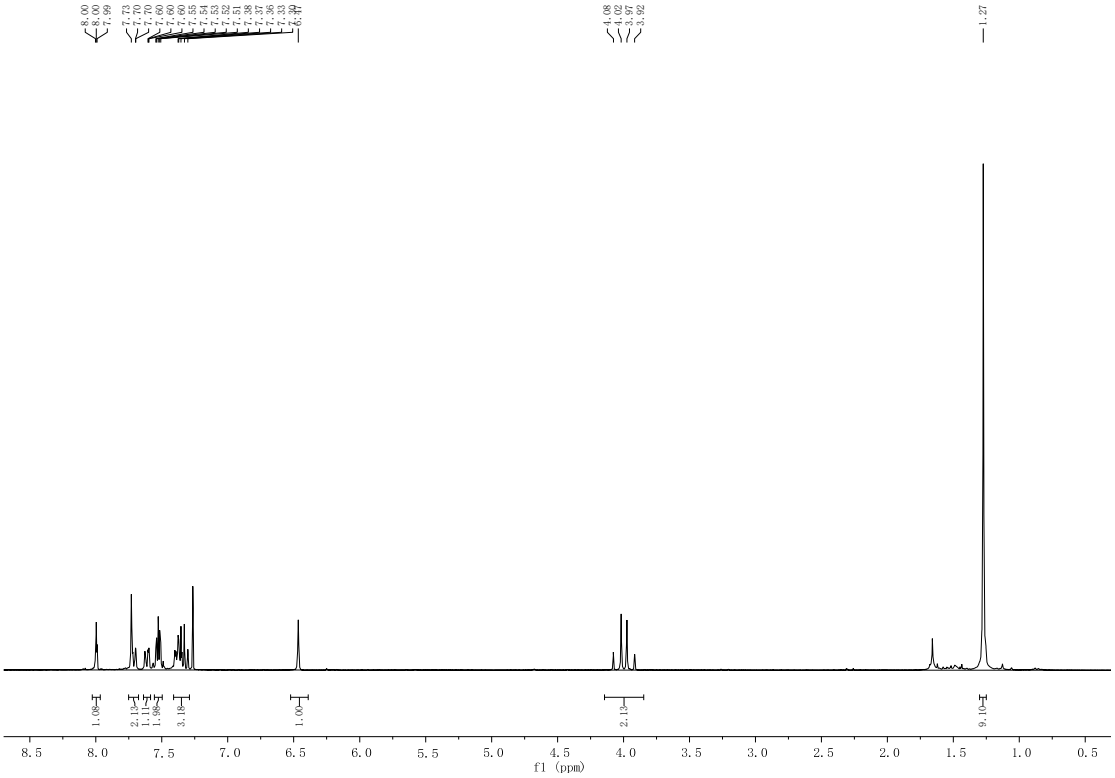
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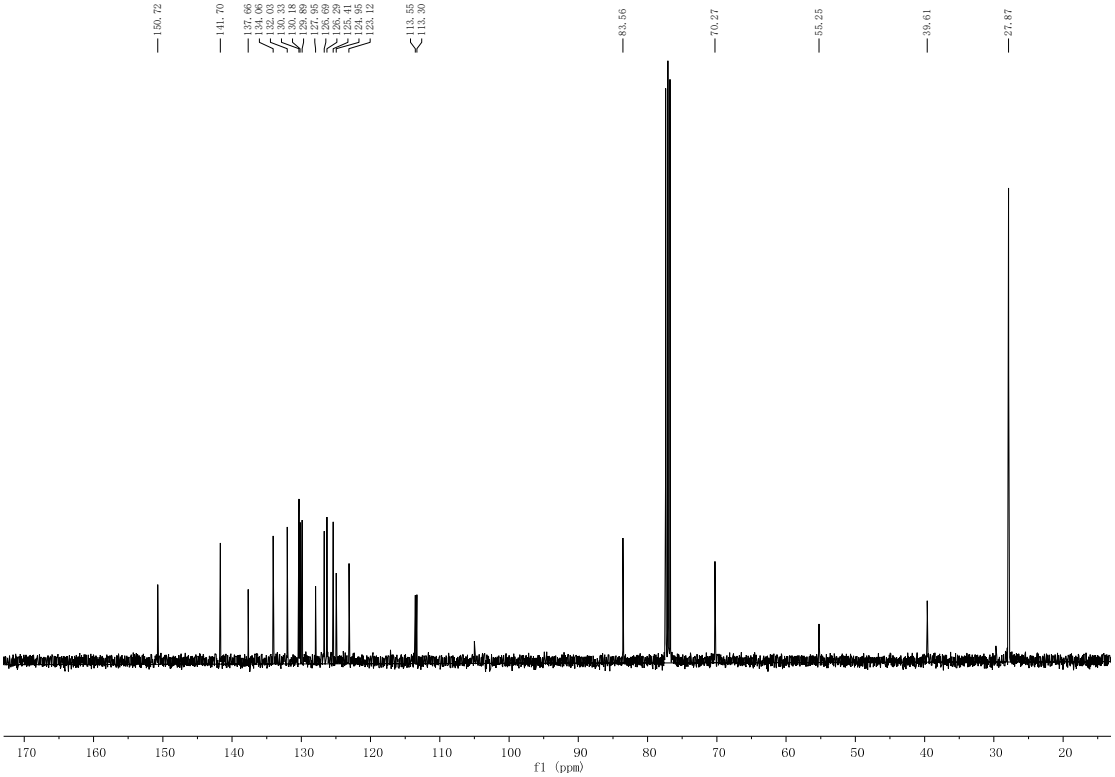
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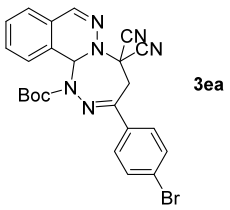
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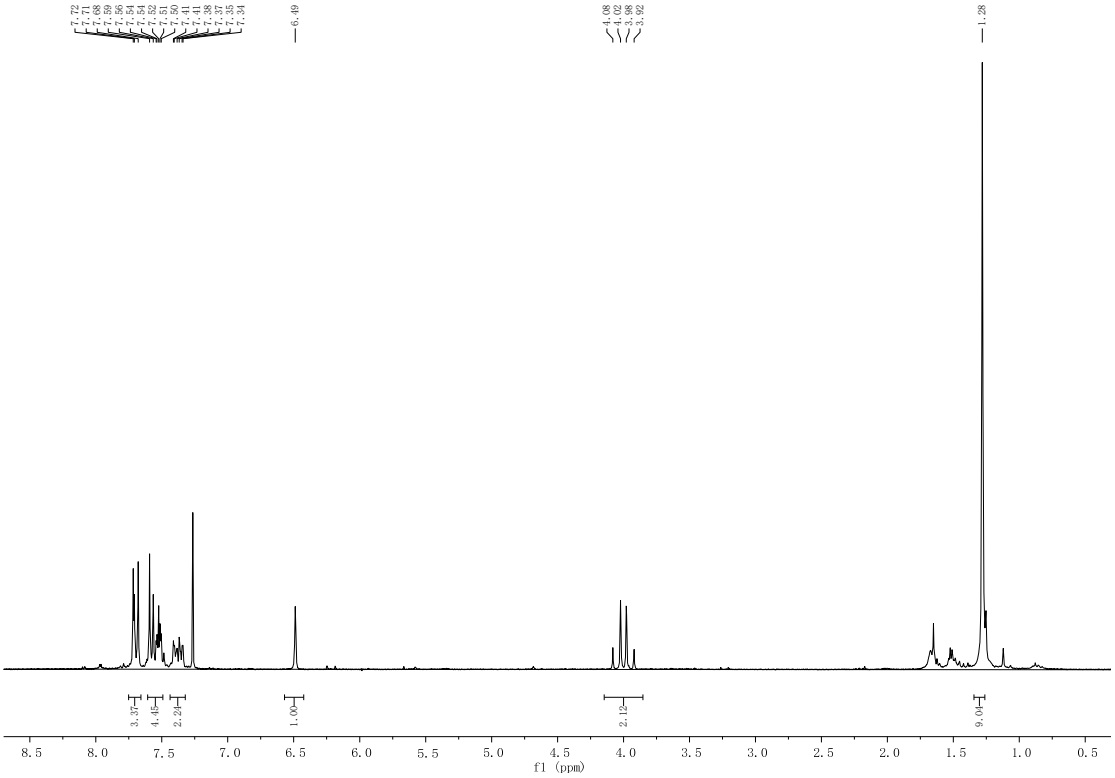
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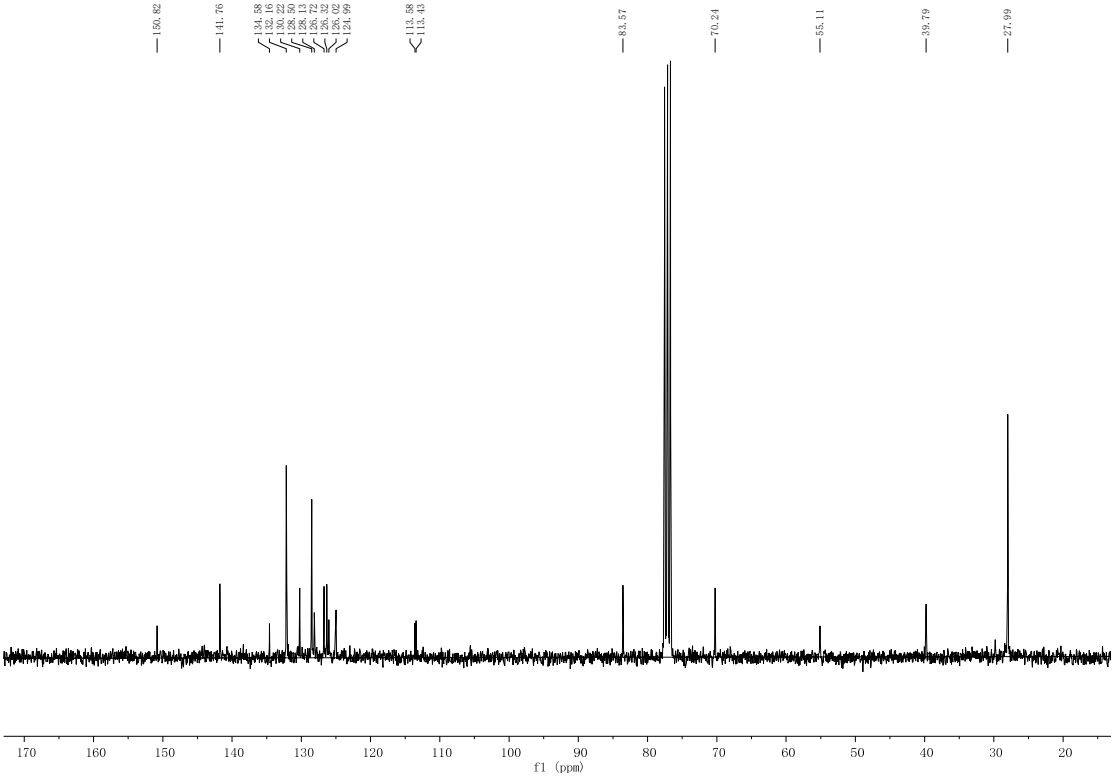
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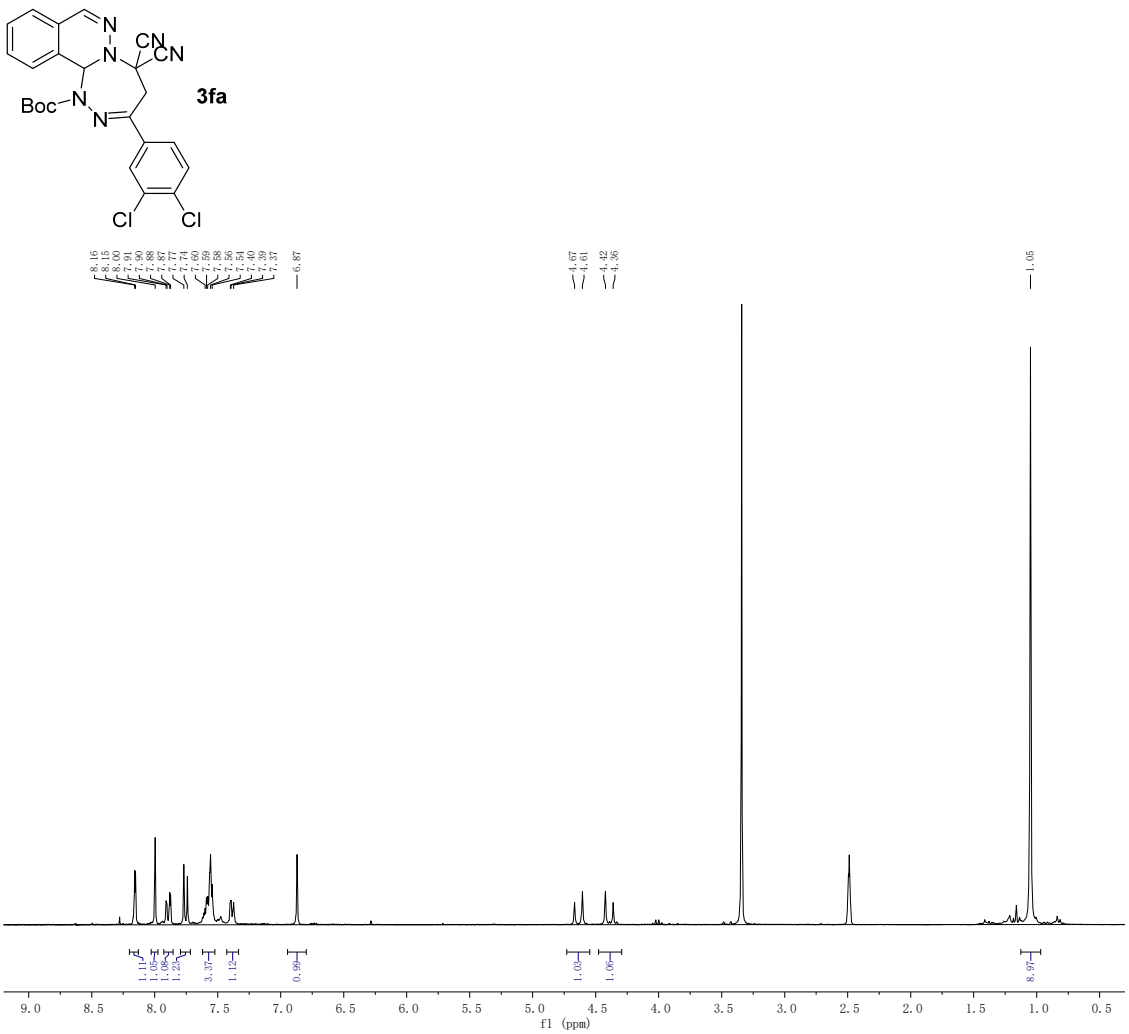
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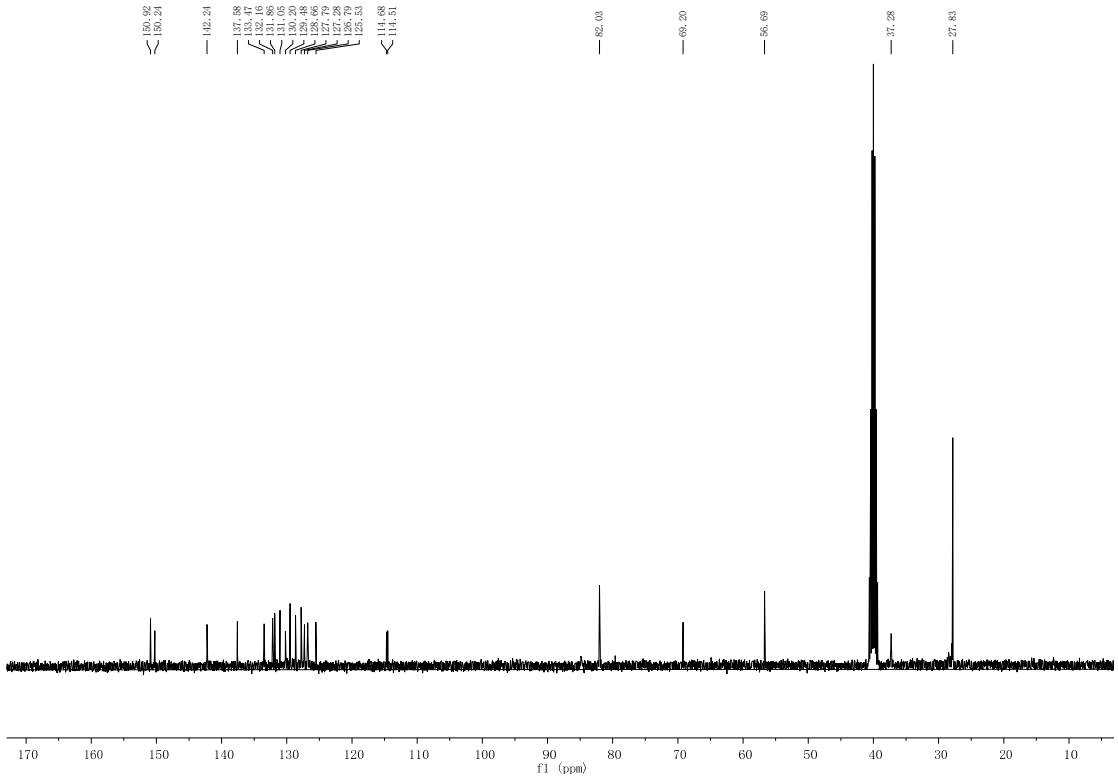
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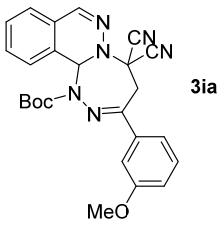
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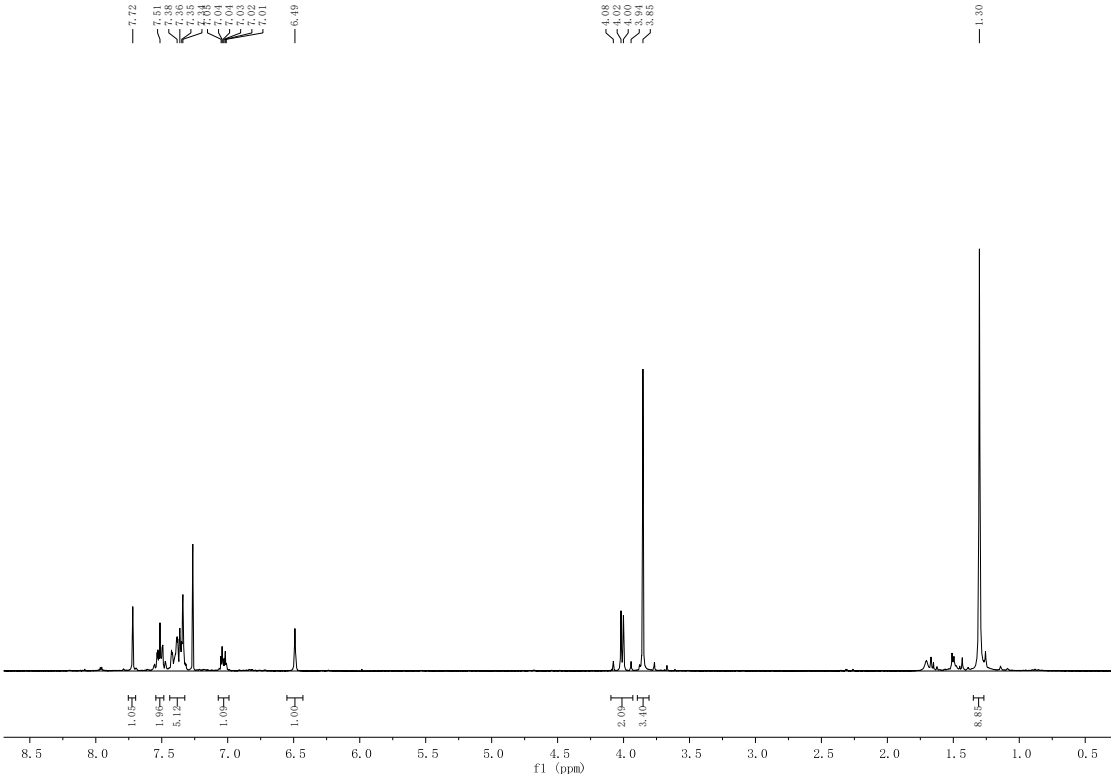
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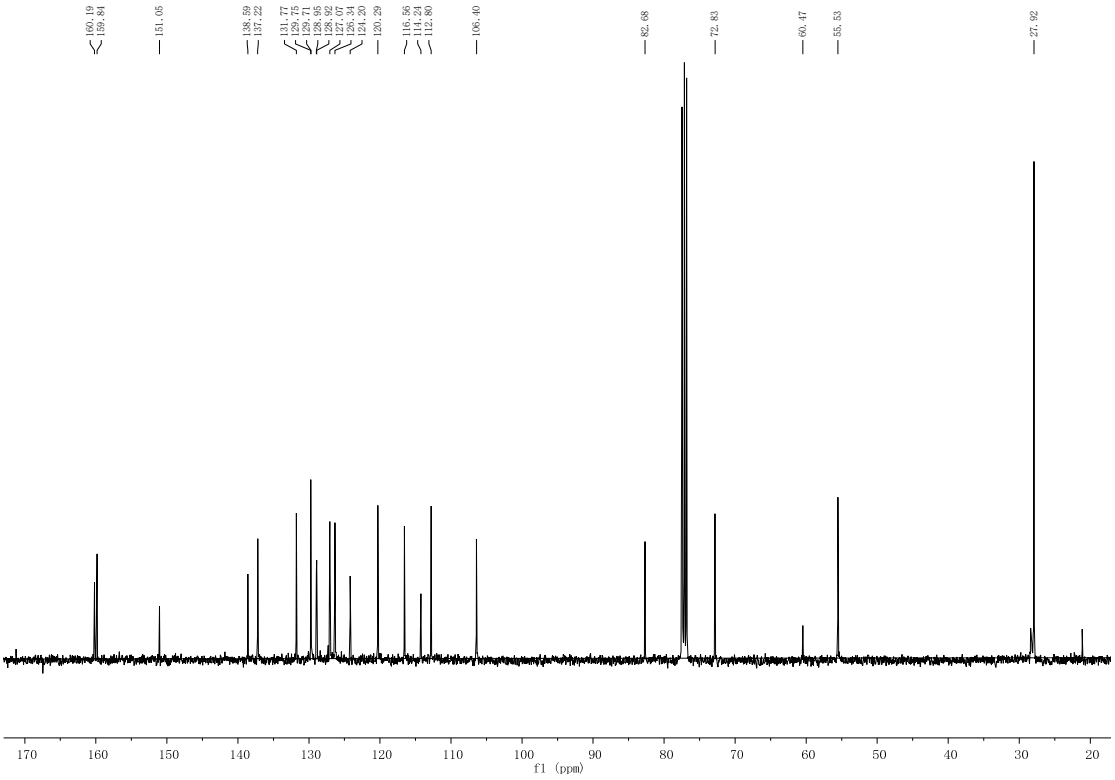
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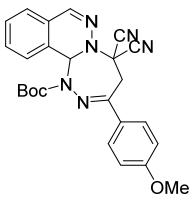
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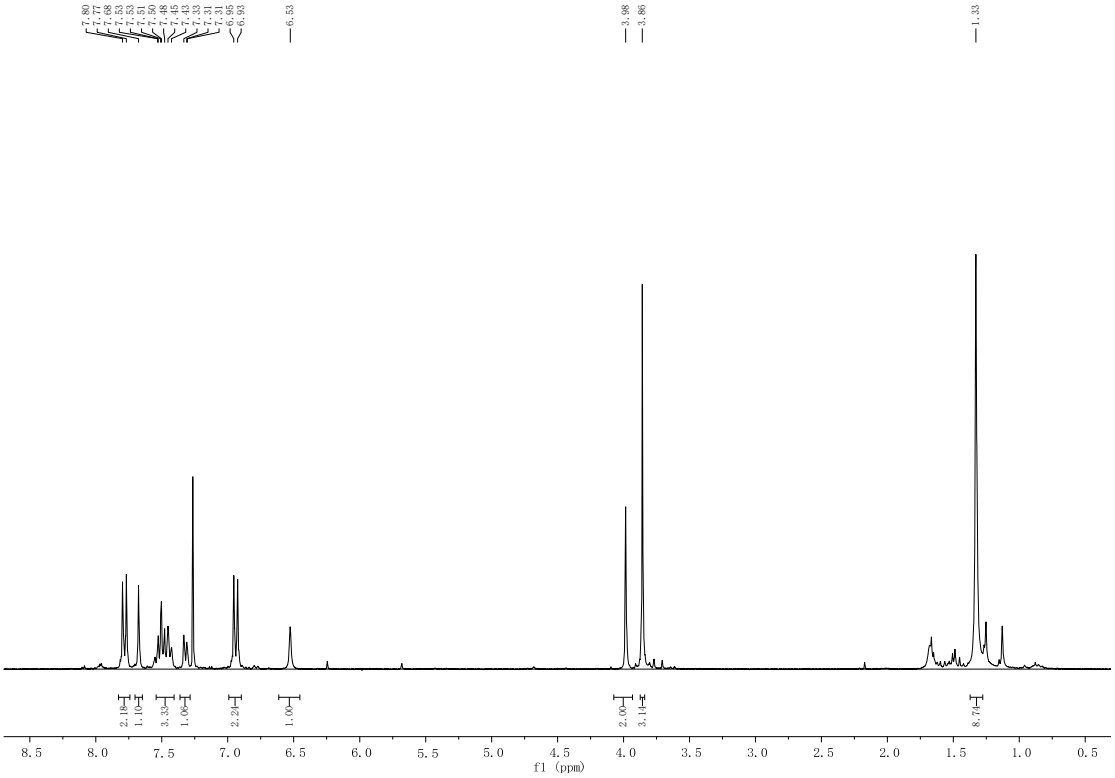
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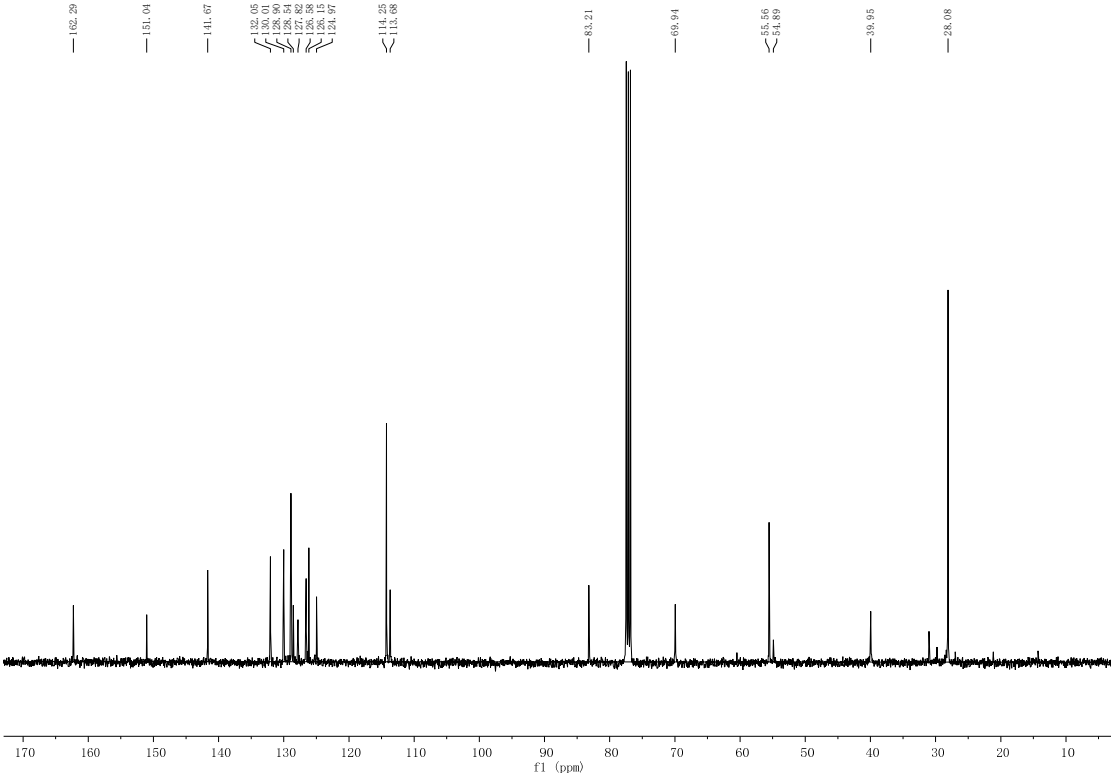
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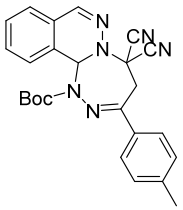
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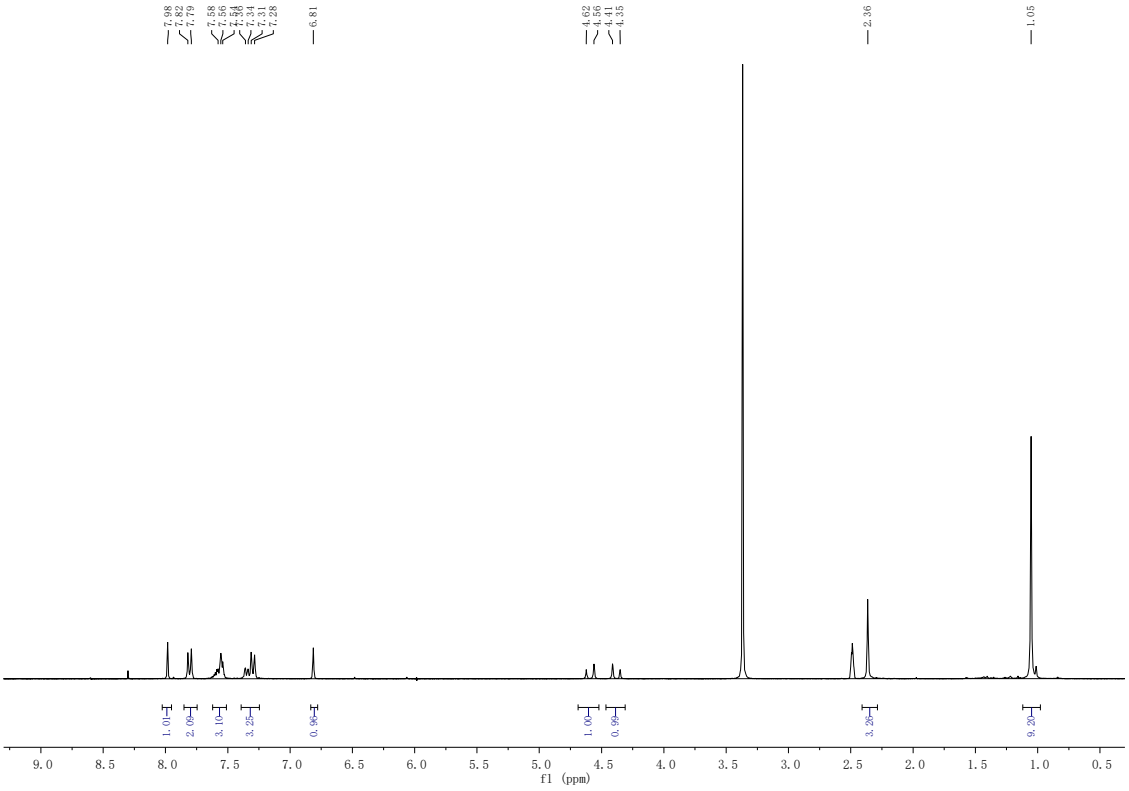
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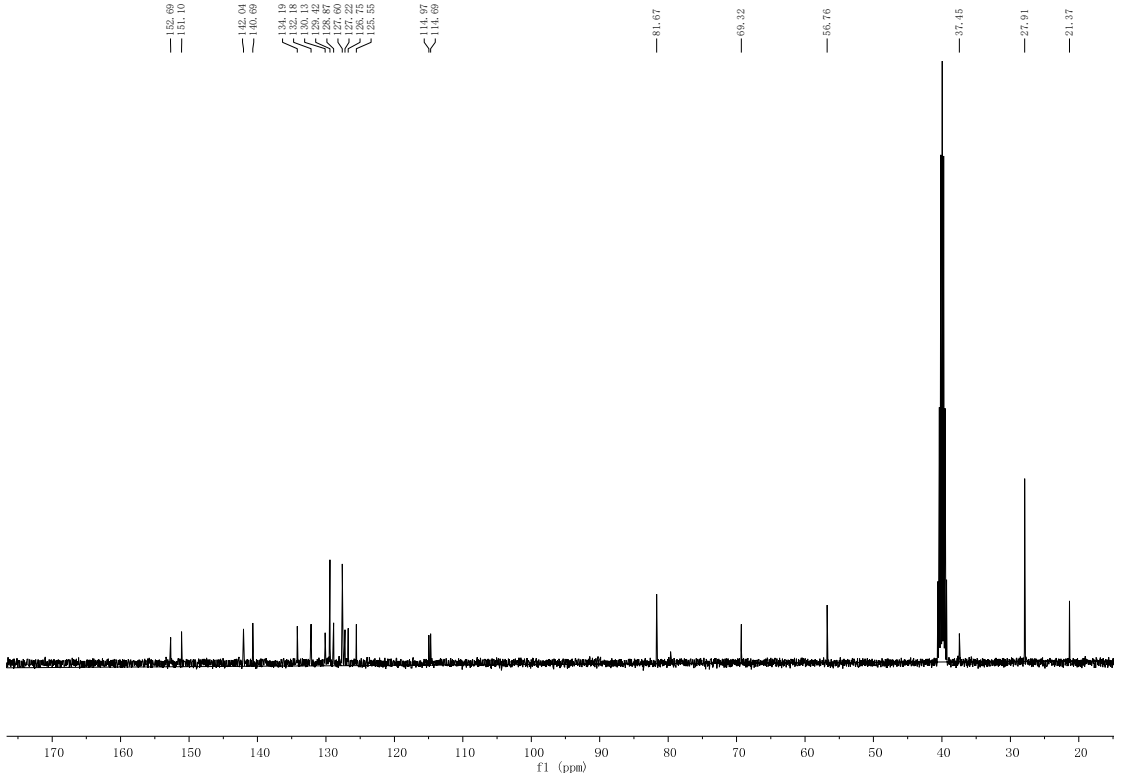
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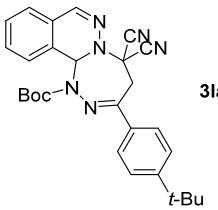
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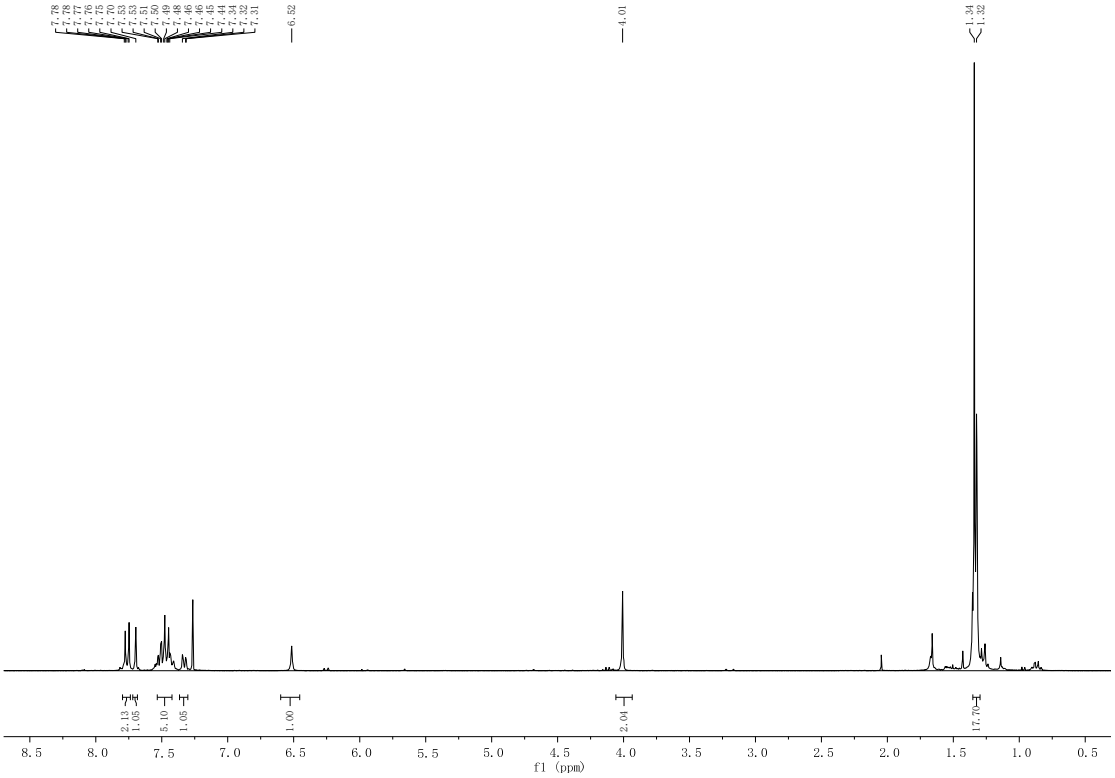
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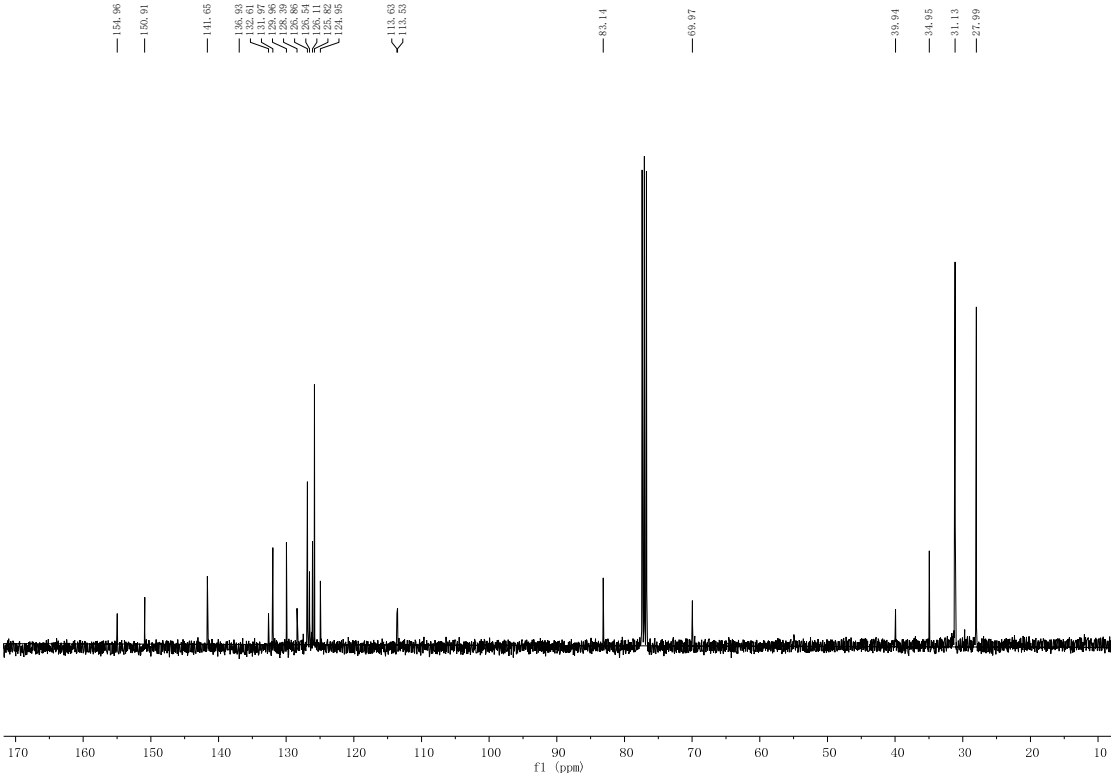
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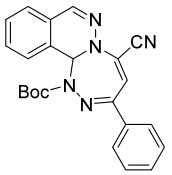
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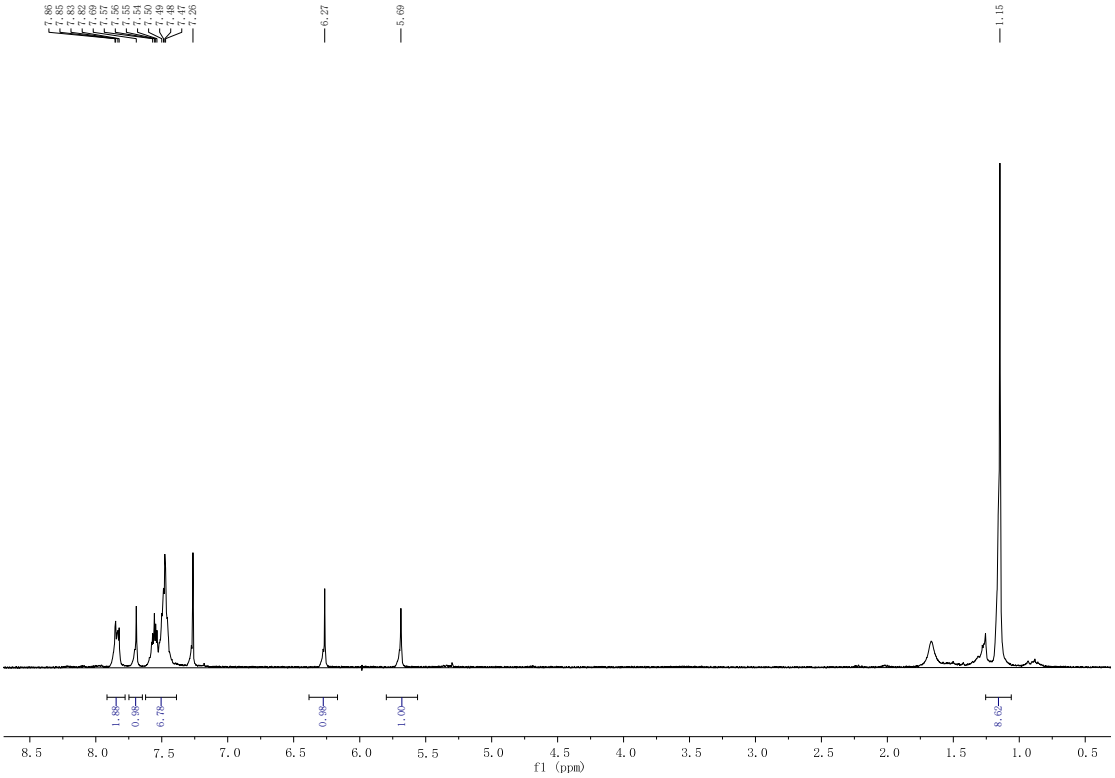
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7.49
7.48
7.47
7.25
6.27
5.69
1.15
1.88
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6.79
0.98
1.00
8.62
8.5
8.0
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7.0
6.5
6.0
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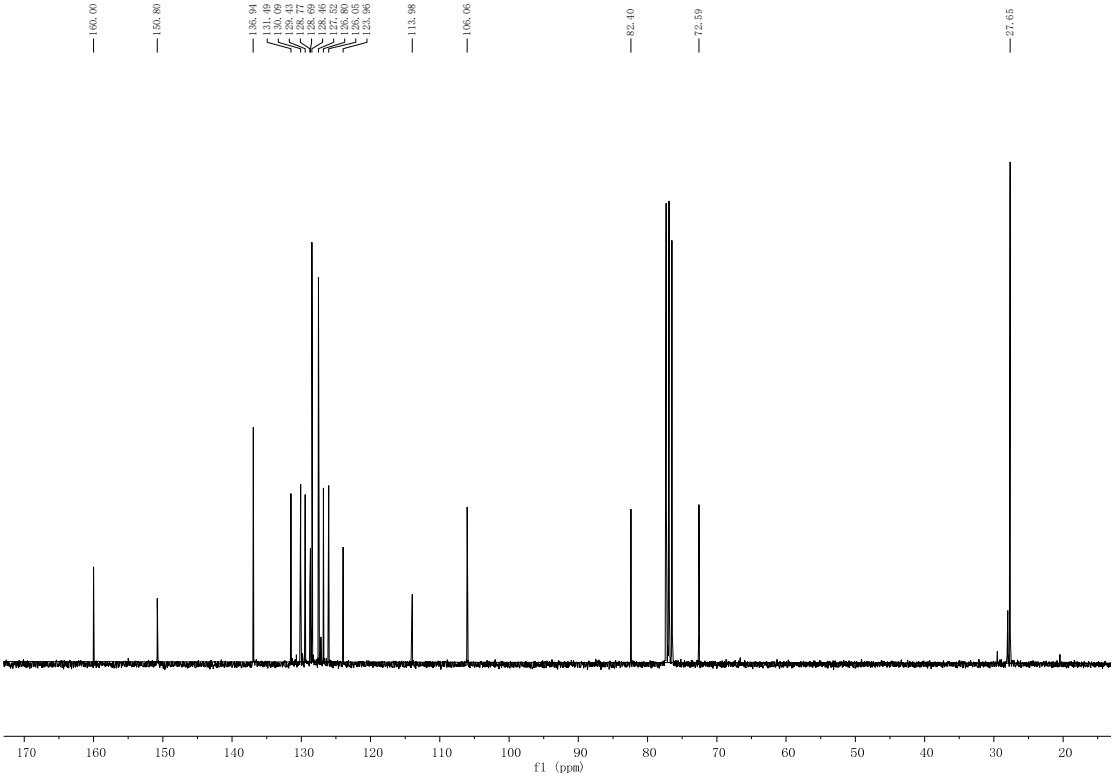
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125.05
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113.98
106.06
82.40
72.59
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150
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130
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110
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60
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30
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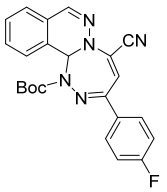
f1 (ppm)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Boc
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N
F

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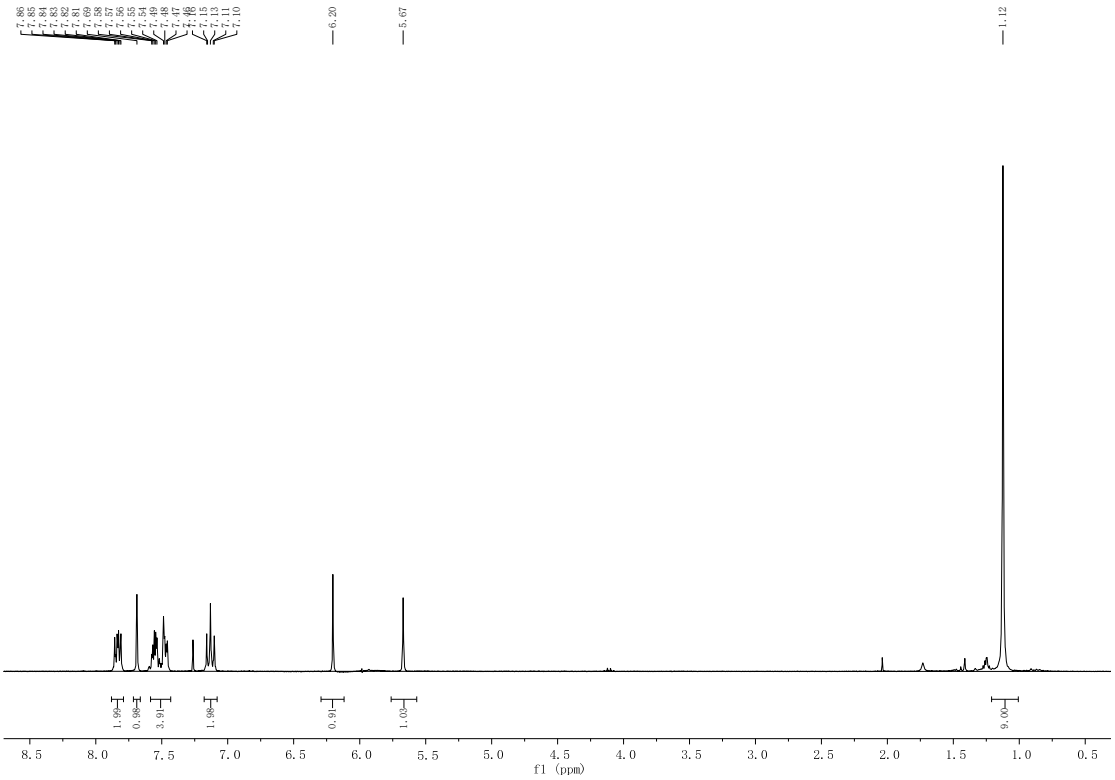
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7.49
7.48
7.47
7.46
7.15
7.13
7.11
7.10
6.20
5.67
1.12
1.99
0.98
3.91
1.98
0.91
1.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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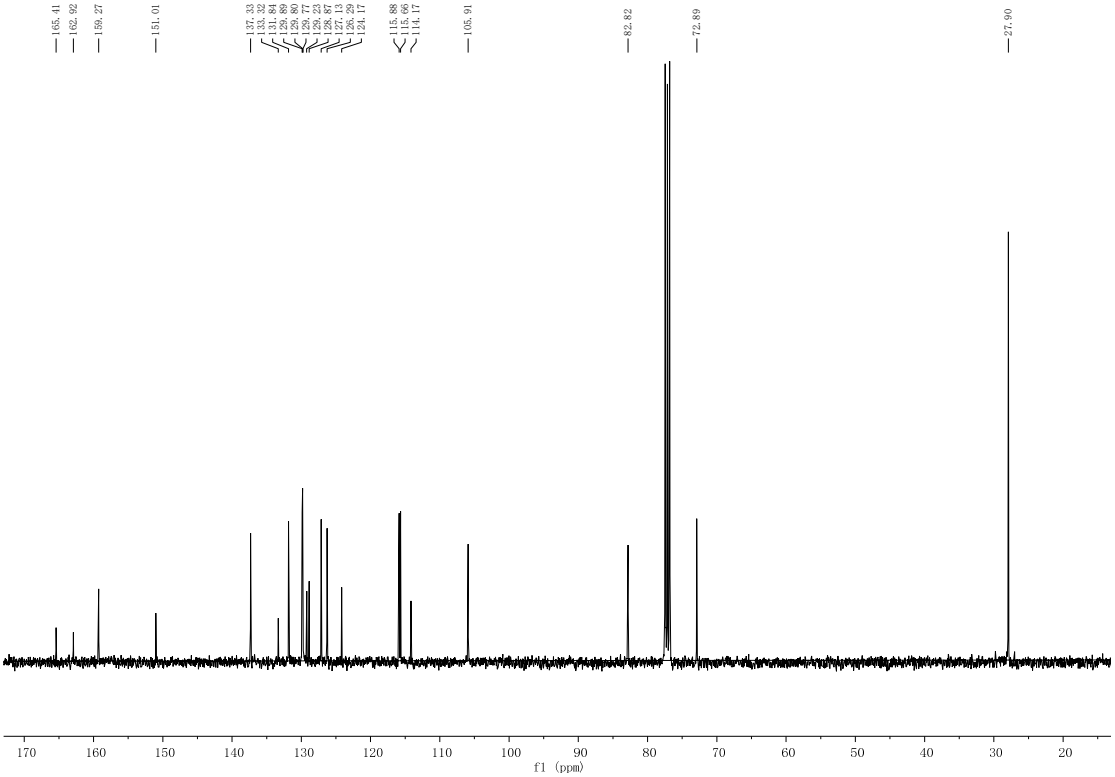
1.5
1.0
0.5
f1 (ppm)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129.27
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127.13
126.29
124.17
115.88
115.66
114.17
105.91
82.82
72.89
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150
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130
120
110
100
90
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70
60
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30
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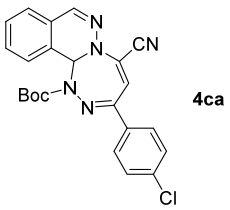
f1 (ppm)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Boc
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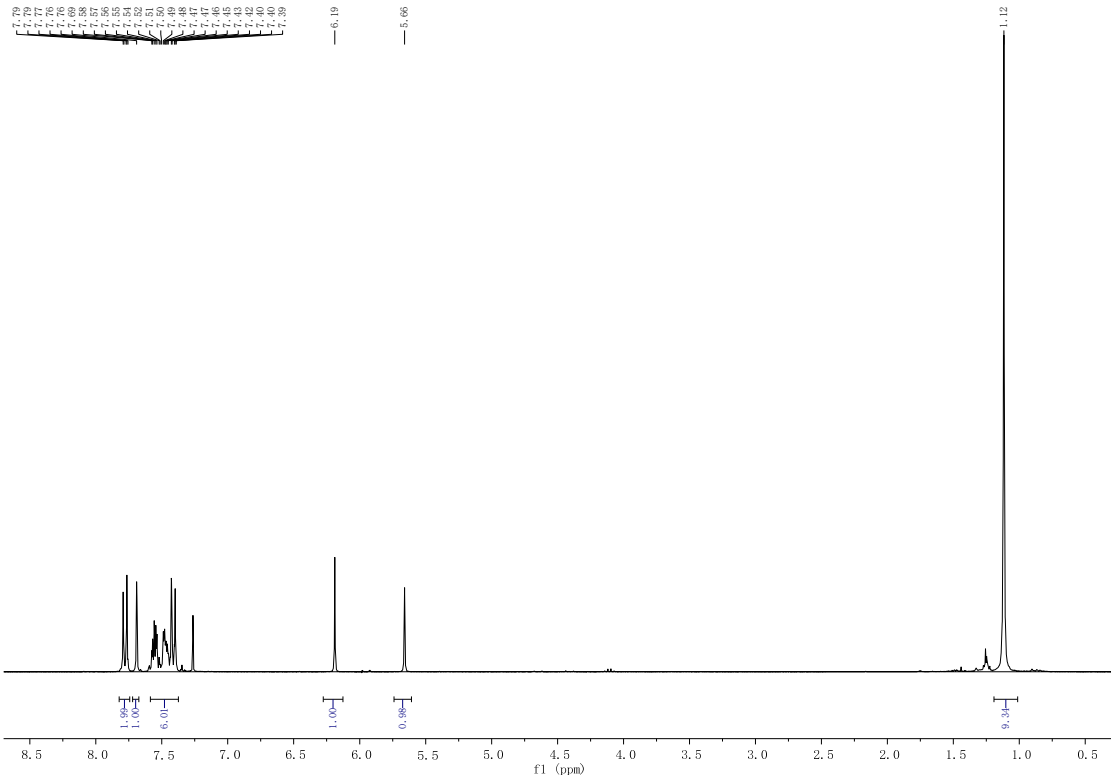
Cl

4ca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7.49
7.48
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7.47
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7.45
7.43
7.42
7.40
7.40
7.39
6.19
5.66
1.12
1.90
1.00
6.01
1.00
0.98
9.31
8.5
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7.0
6.5
6.0
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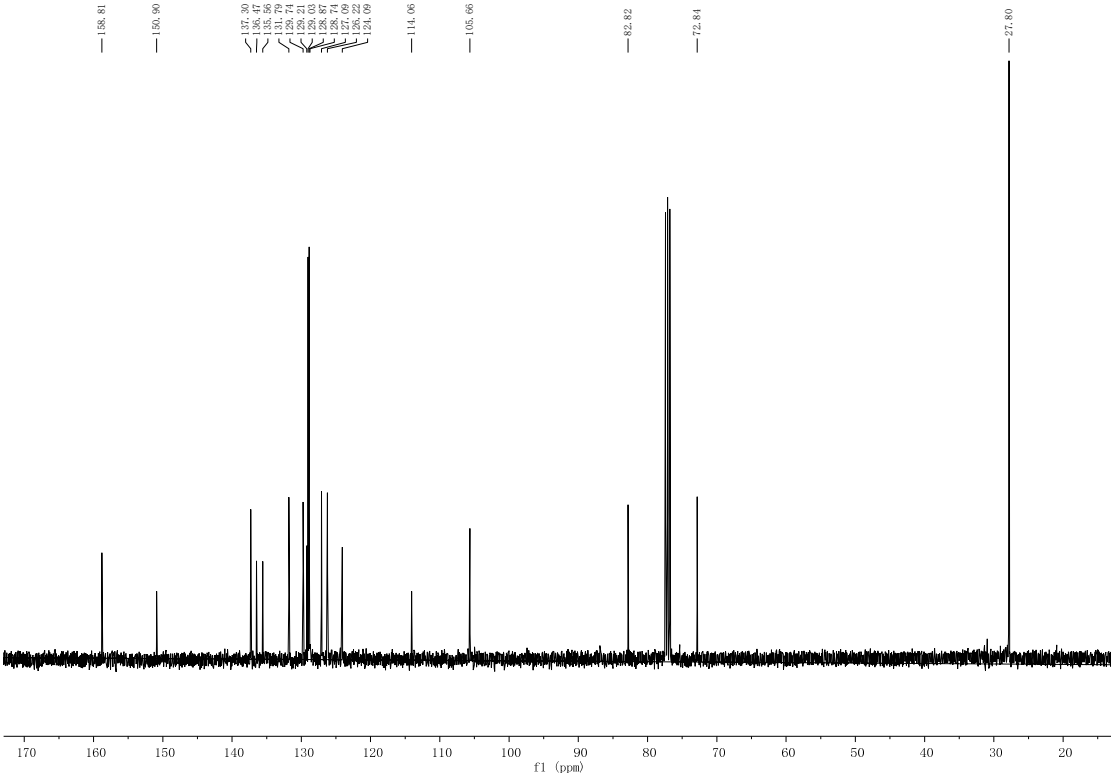
f1 (ppm)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129.21
129.03
128.87
128.71
128.09
127.69
125.22
124.09
114.06
105.66
82.82
72.84
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150
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130
120
110
100
90
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70
60
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30
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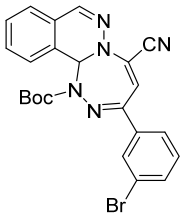
f1 (ppm)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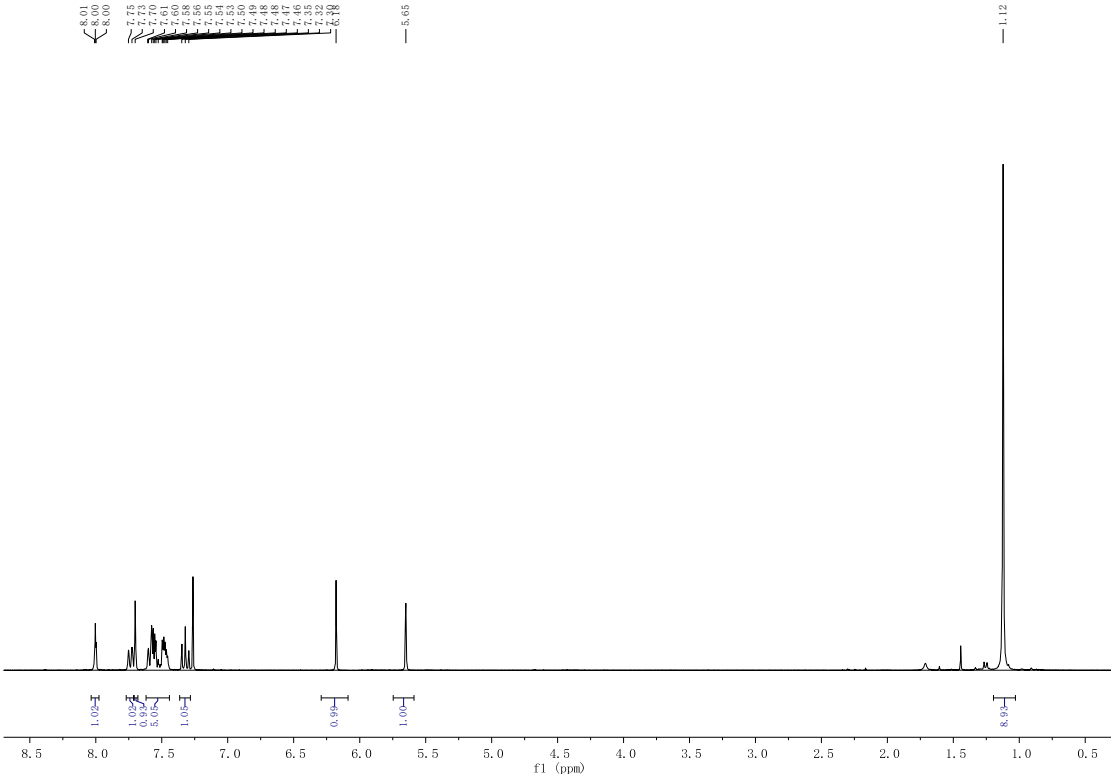
Boc
N
N
Br

4da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7.54
7.53
7.50
7.49
7.48
7.46
7.47
7.46
7.35
7.32
7.29
6.18
5.65
1.12
1.02
1.02
0.93
5.05
1.05
0.99
1.00
8.93
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7.0
6.5
6.0
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1.5
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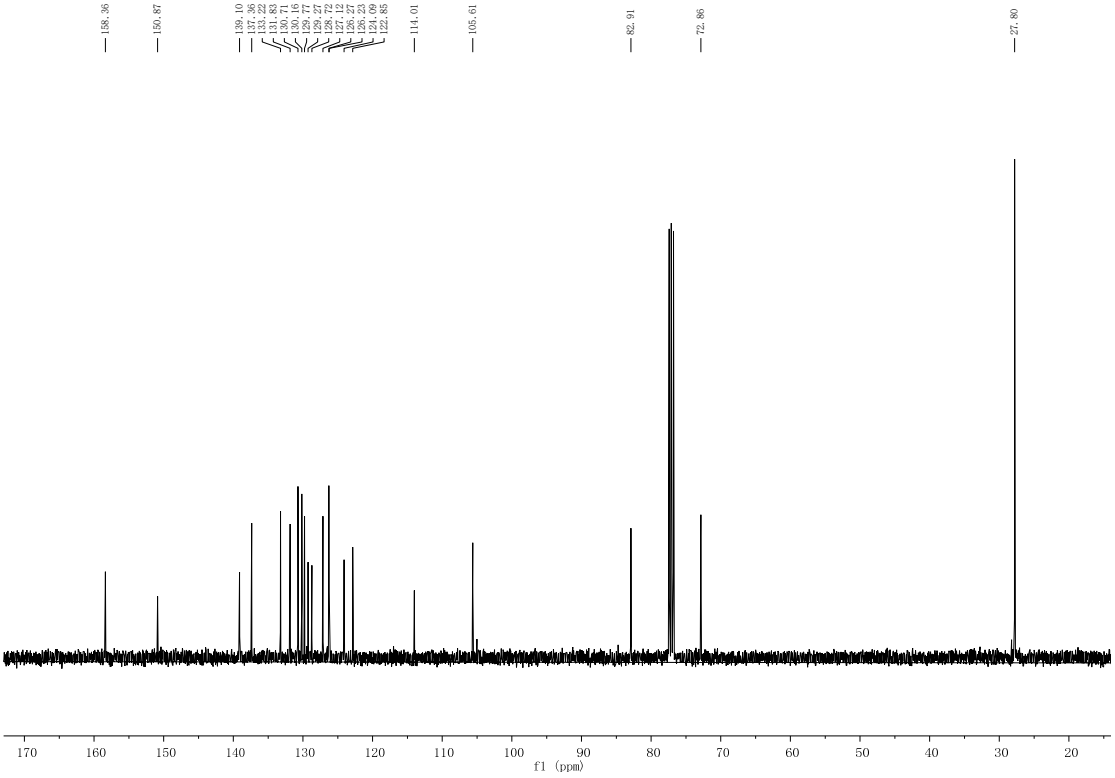
0.5
f1 (ppm)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129.37
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126.27
126.23
124.09
122.85
114.01
105.61
82.91
72.86
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90
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70
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30
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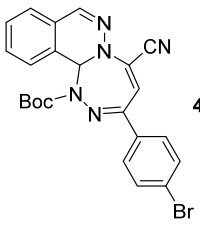
f1 (ppm)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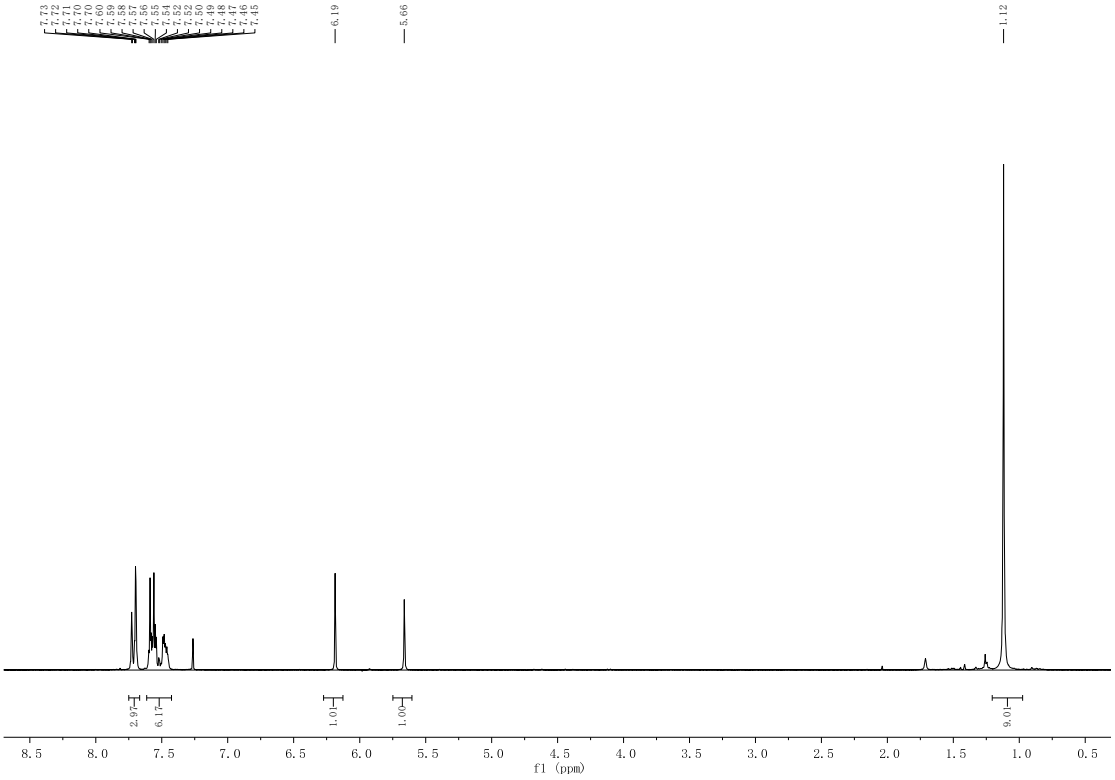
CN
Boc
N
N
Br

4ea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7.47
7.46
7.45
6.19
5.66
1.12
2.97
6.17
1.01
1.00
9.01
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6.5
6.0
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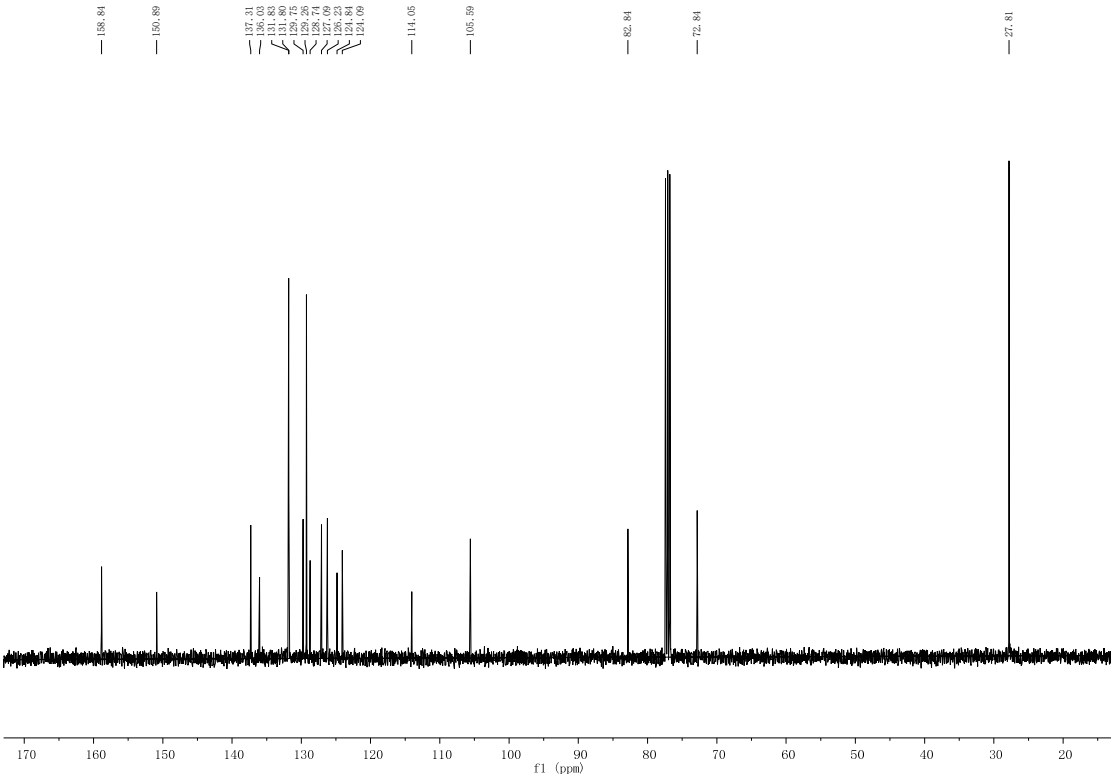
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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124.09
114.05
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82.84
72.84
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30
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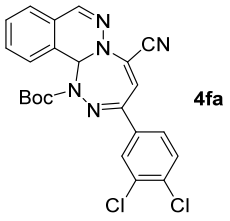
f1 (ppm)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Boc
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N
Cl
Cl

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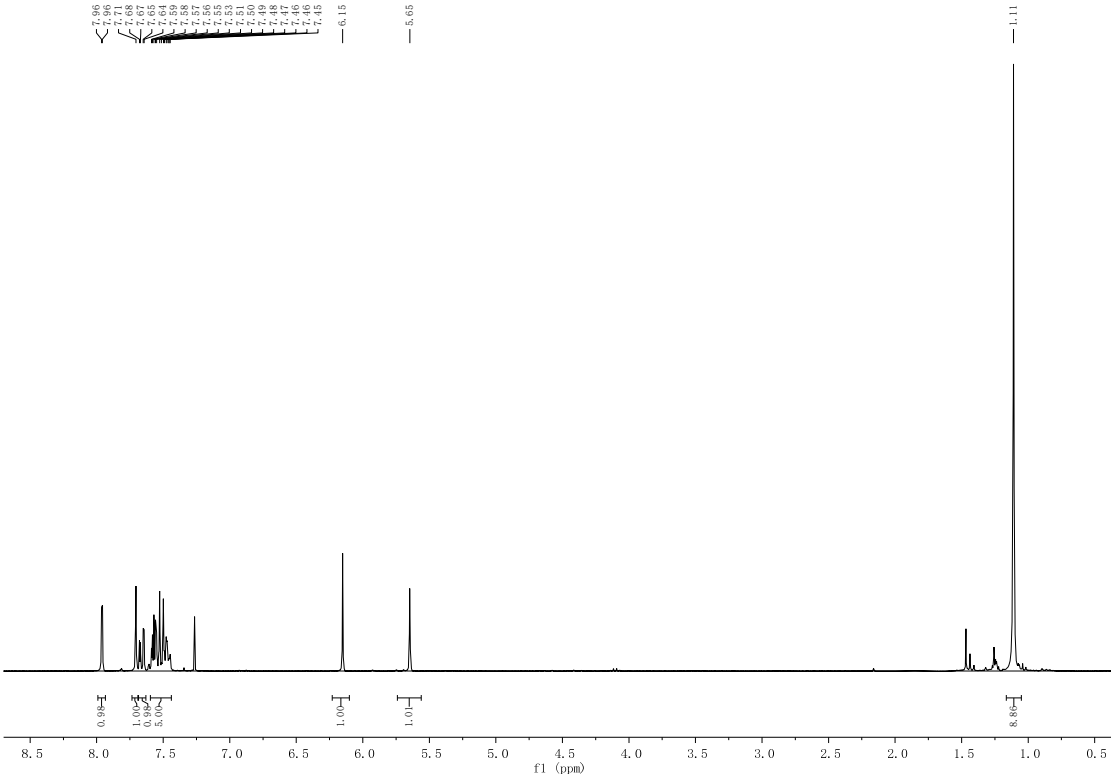
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7.51
7.50
7.49
7.48
7.47
7.46
7.46
7.45
6.15
5.65
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1.00
0.99
5.00
1.00
1.01
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6.0
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2.0
1.5
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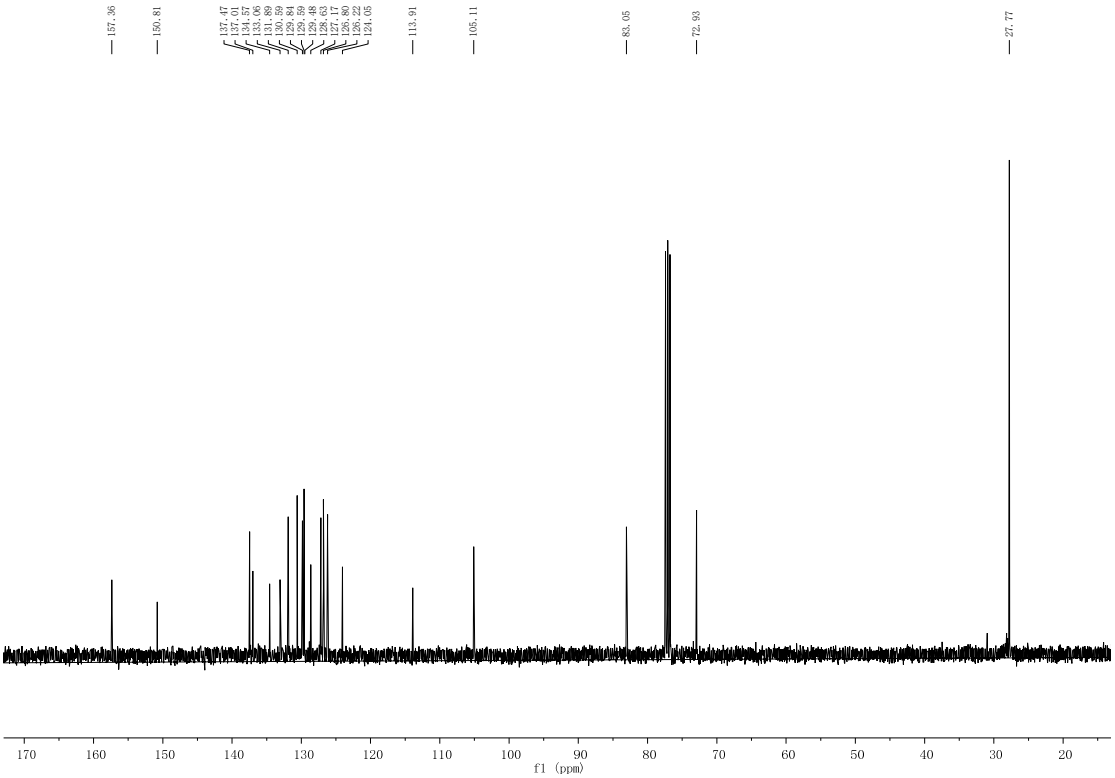
0.5
f1 (ppm)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129.48
128.63
127.17
126.89
126.22
124.05
113.91
105.11
83.05
72.93
27.77
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150
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130
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110
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90
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70
60
50
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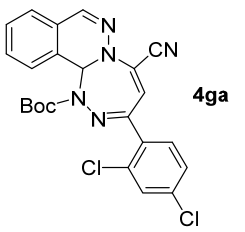
30
20
f1 (ppm)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Cl
Cl

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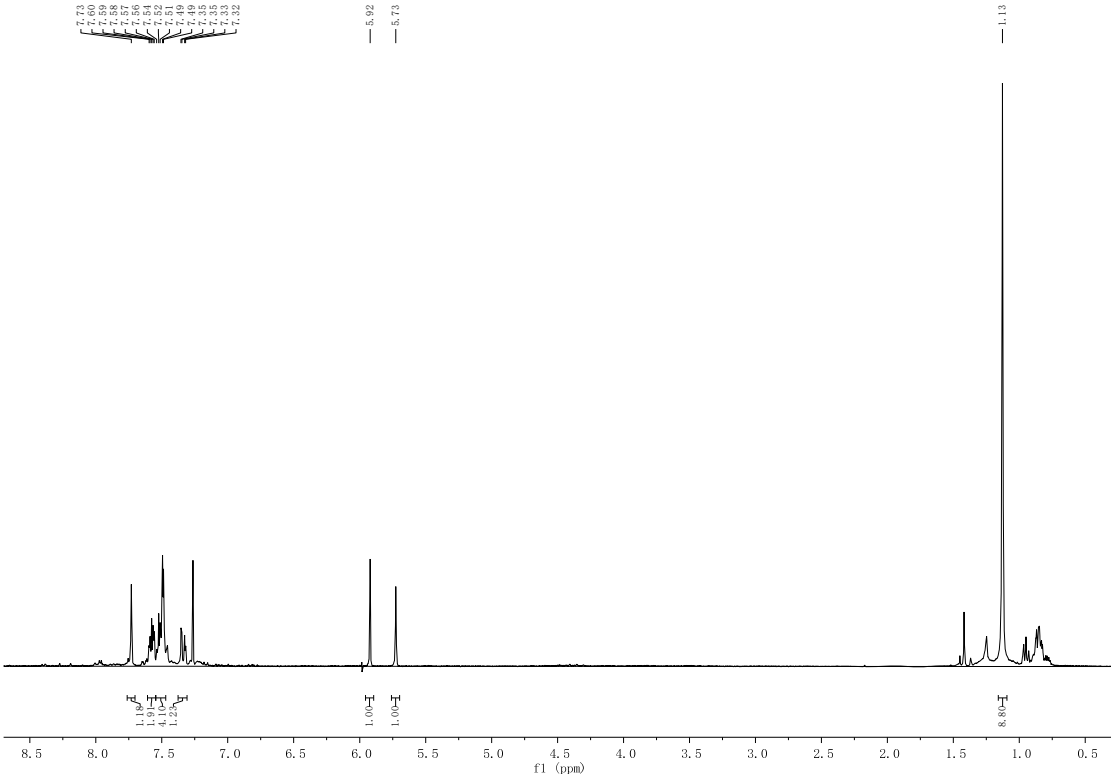
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7.33
7.32
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1.19
1.91
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1.00
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2.5
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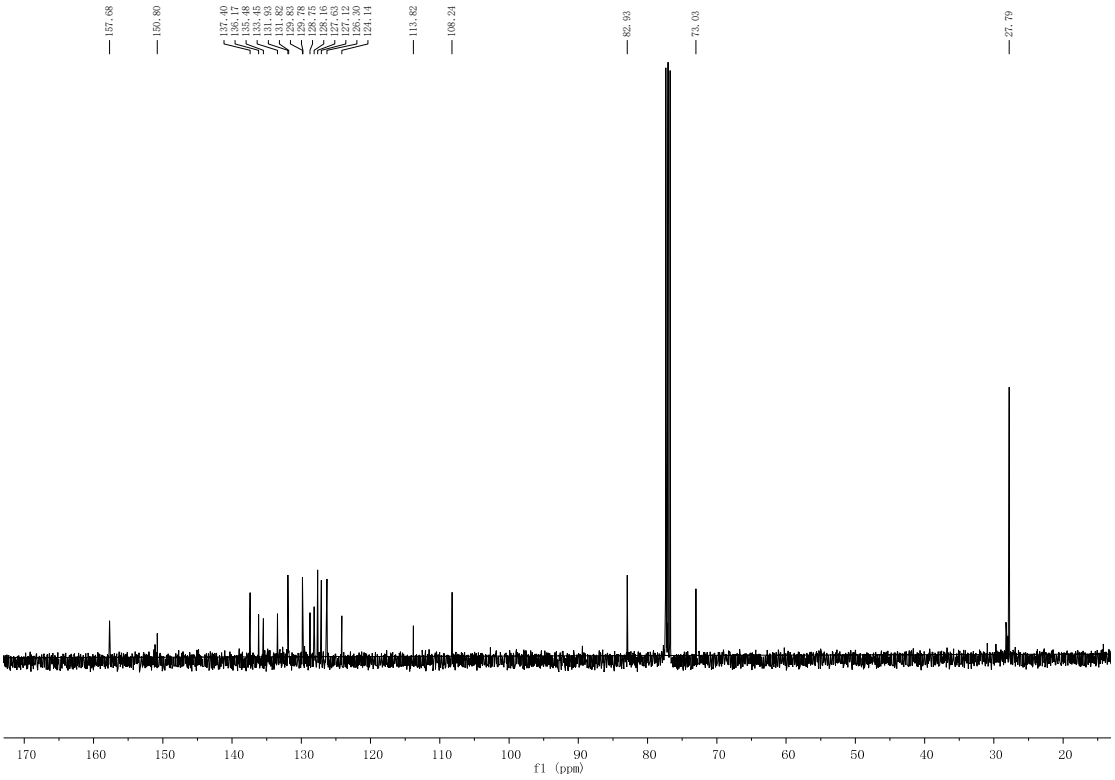
0.5
f1 (ppm)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127.12
127.12
126.30
124.14
113.82
108.24
82.93
73.03
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110
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30
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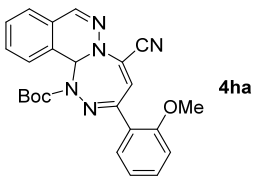
f1 (ppm)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Boc
N
N
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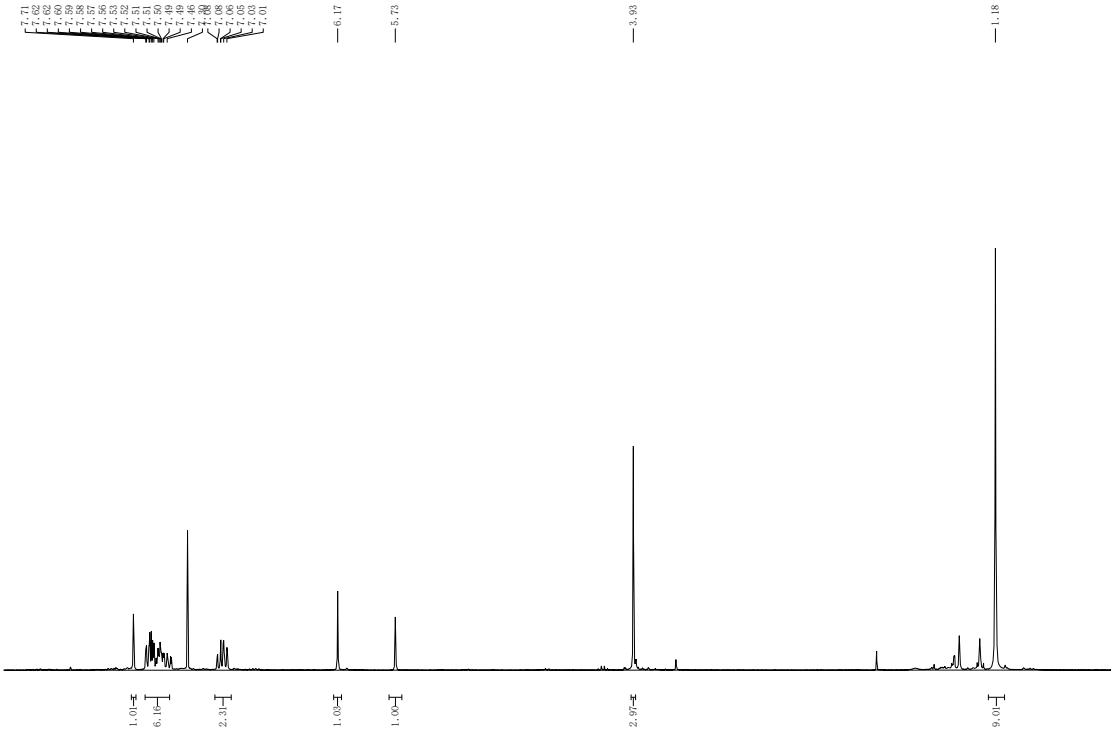
4ha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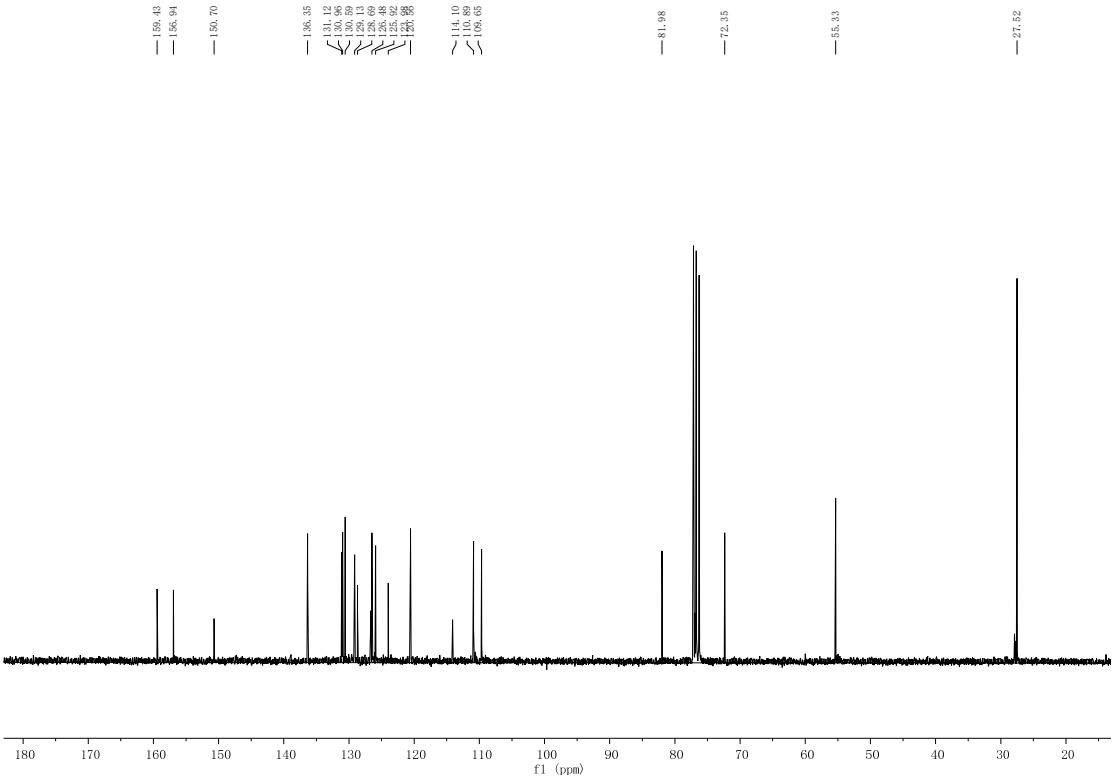
f1 (ppm)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123.88
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81.98
72.35
55.33
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120
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100
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60
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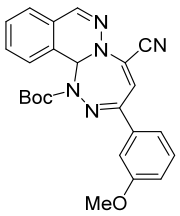
30
20
f1 (ppm)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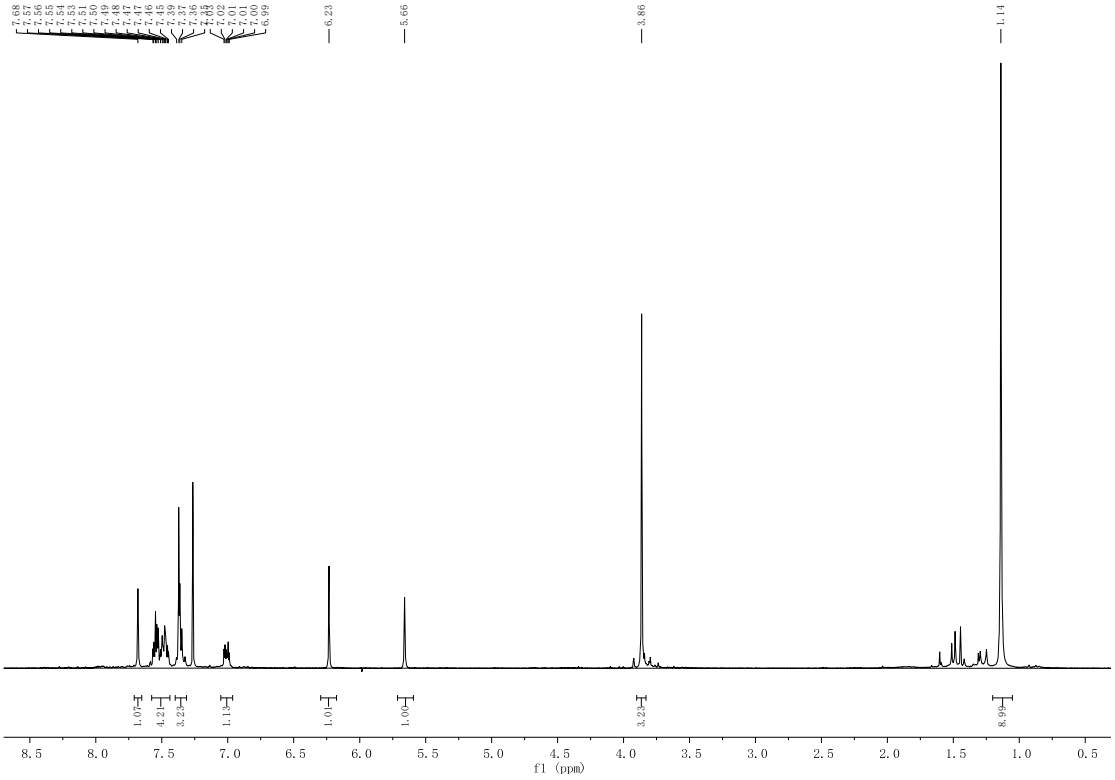
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7.35
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1.07
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1.13
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6.5
6.0
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3.0
2.5
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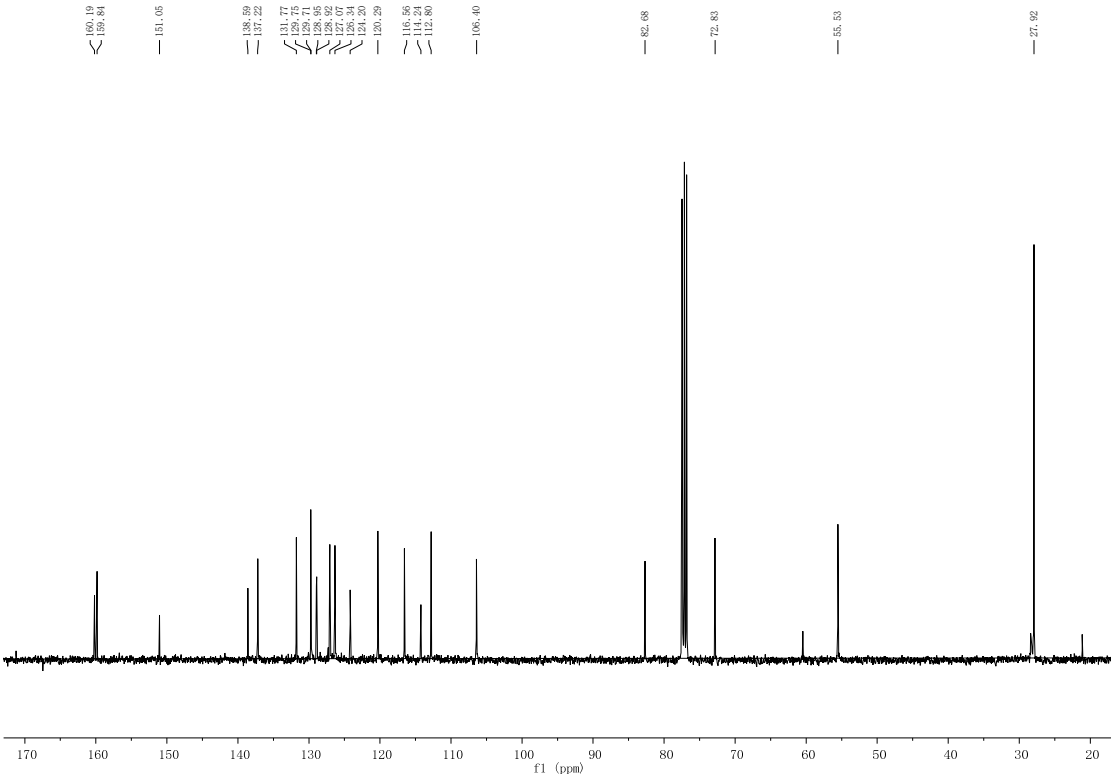
1.5
1.0
0.5
f1 (ppm)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128.92
127.07
126.34
124.20
120.29
116.56
114.24
112.80
106.40
82.68
72.83
55.53
27.92
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150
140
130
120
110
100
90
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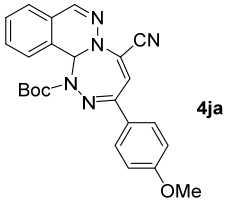
60
50
40
30
20
f1 (ppm)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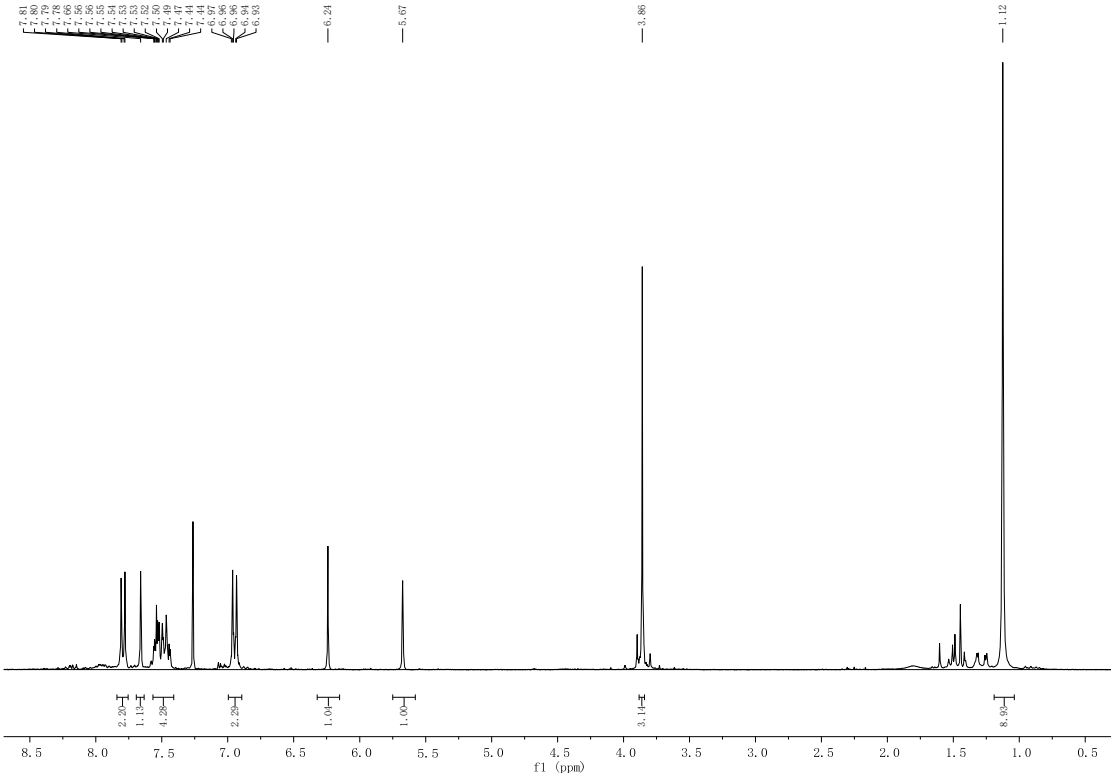
Boc
N
N
OMe

4ja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5.67
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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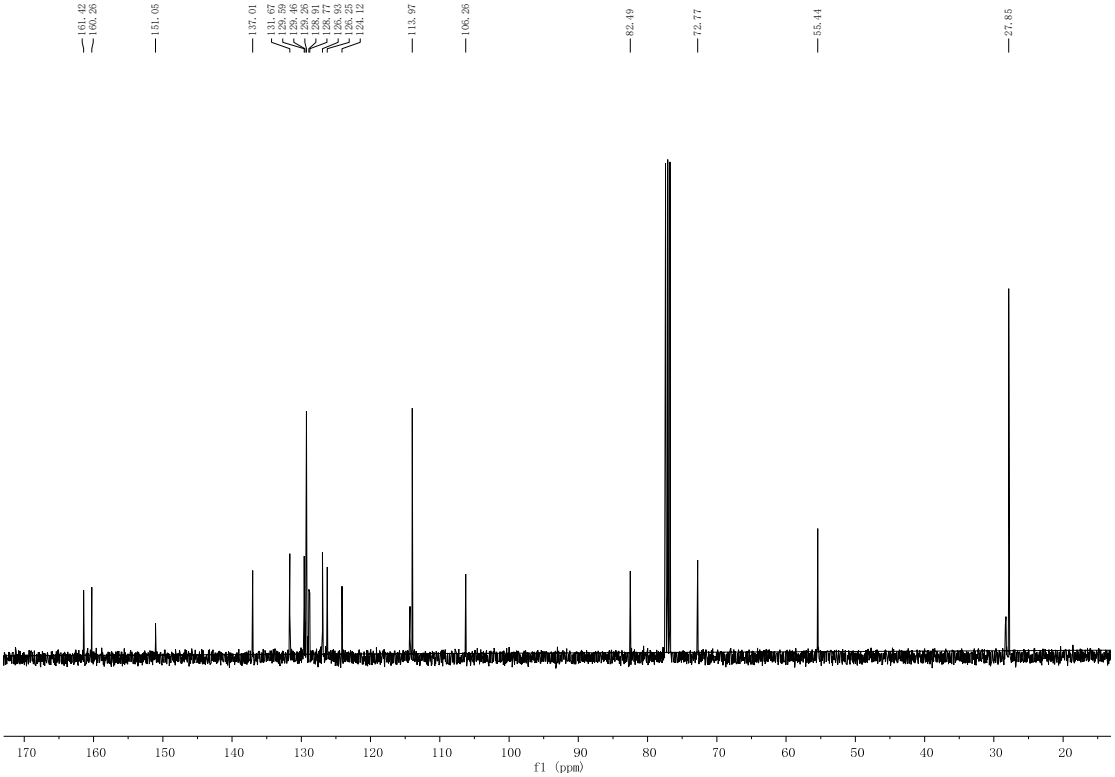
f1 (ppm)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113.97
106.26
82.49
72.77
55.44
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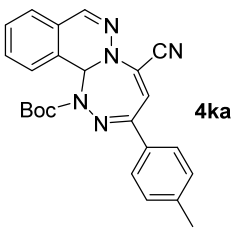
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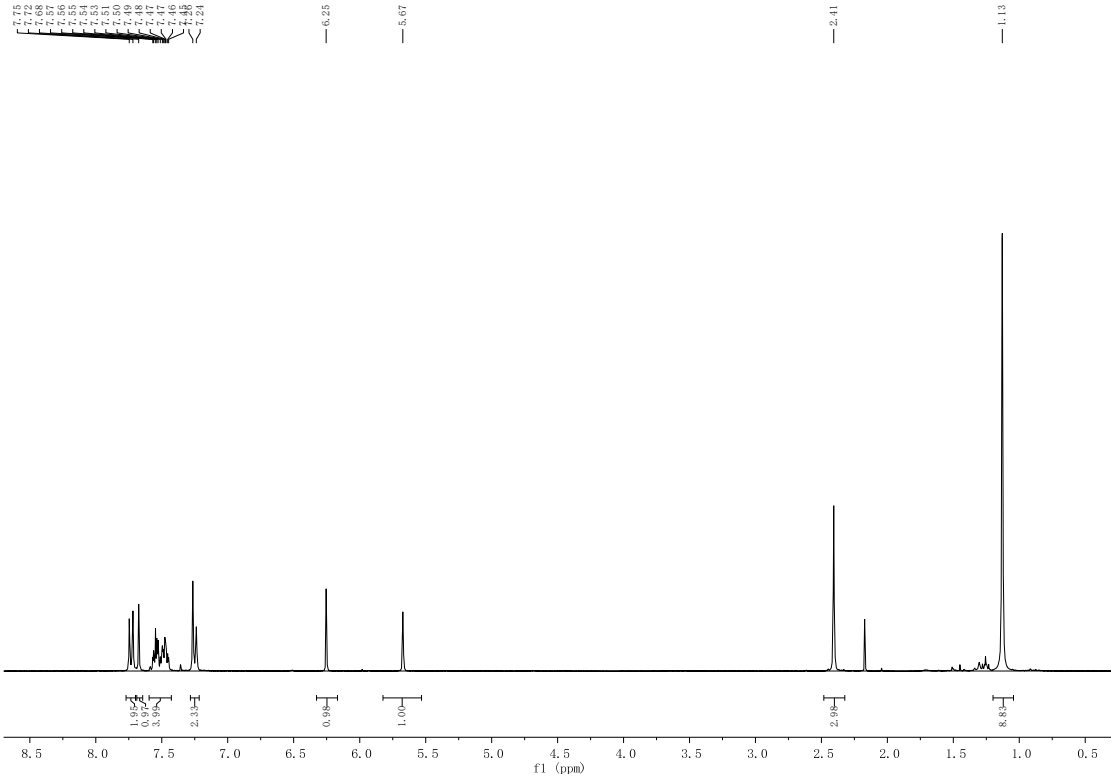
Boc
N
N

4ka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7.45
7.45
7.24
6.25
5.67
2.41
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1.95
0.97
3.99
2.39
0.98
1.00
2.98
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8.0
7.5
7.0
6.5
6.0
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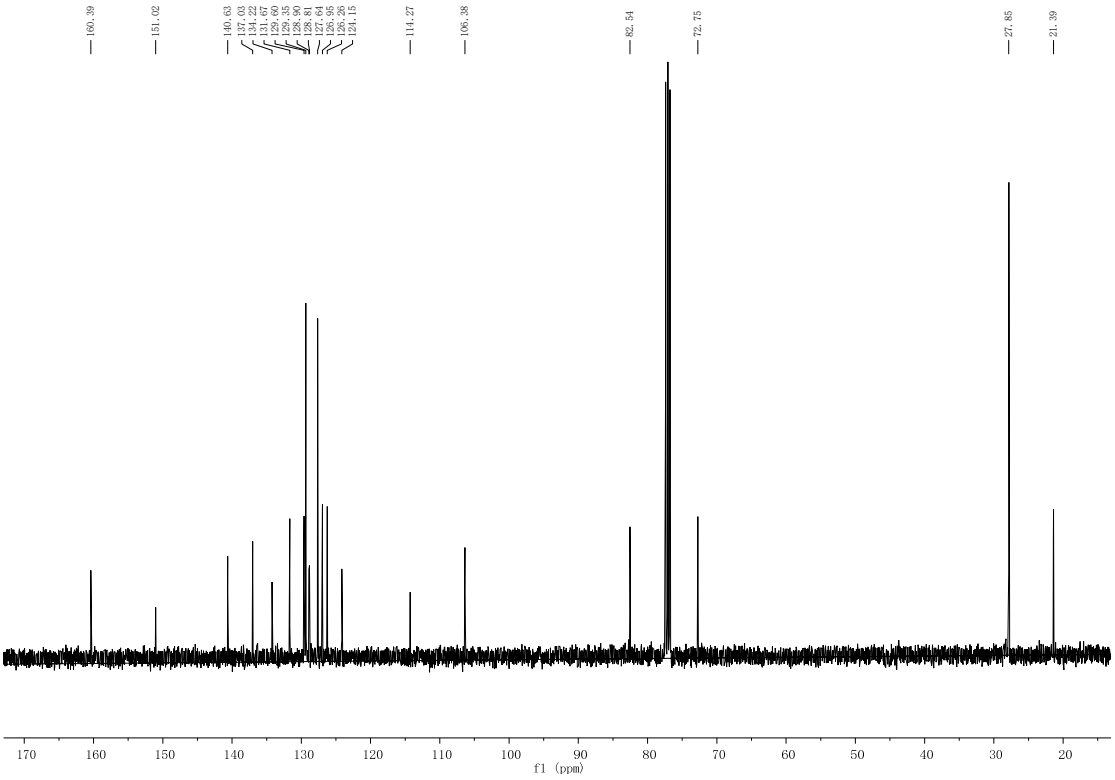
f1 (ppm)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124.15
114.27
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72.75
27.85
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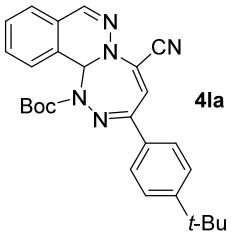
f1 (ppm)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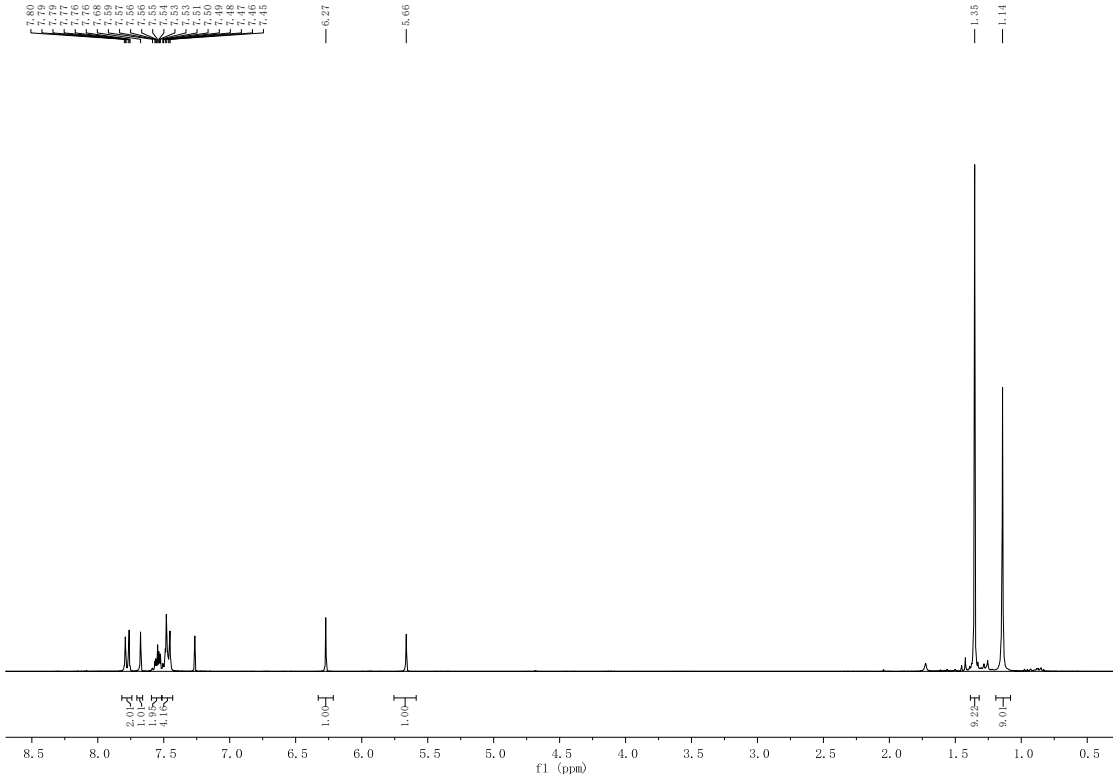
CN
Boc
N
N
t-Bu

4Ia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7.53
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7.51
7.50
7.49
7.48
7.47
7.46
7.45
6.27
5.66
1.35
1.14
2.01
1.01
1.95
4.16
1.00
1.00
9.22
9.01
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7.5
7.0
6.5
6.0
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1.5
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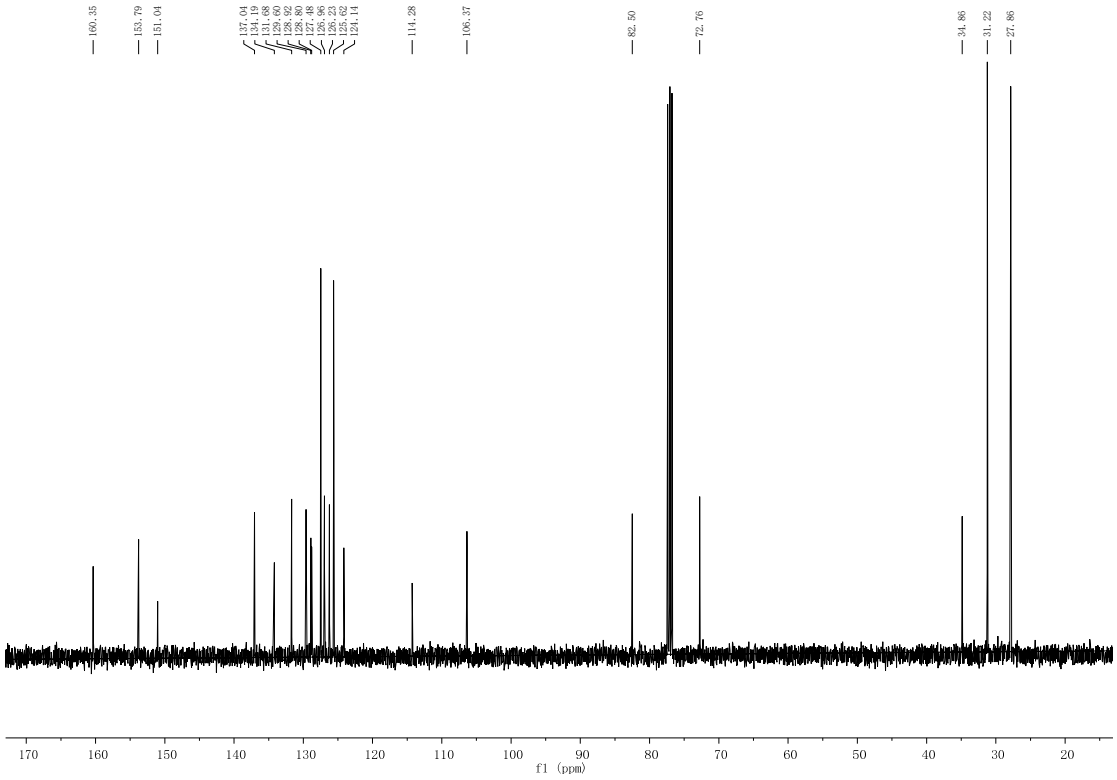
f1 (ppm)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126.23
125.62
124.14
114.28
106.37
82.50
72.76
34.86
31.22
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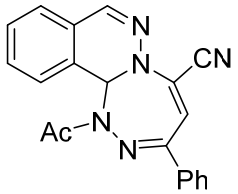
50
40
30
20
f1 (ppm)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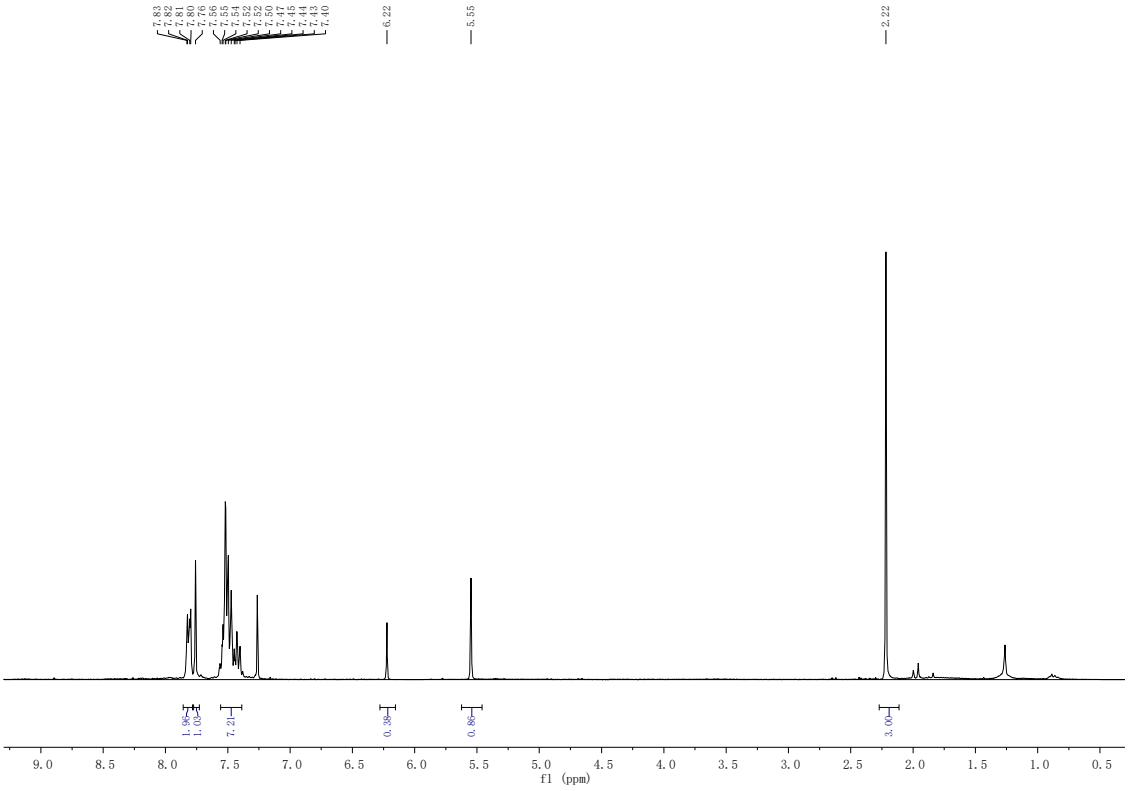
Ac
N
N
Ph

4na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7.45
7.44
7.43
7.40
6.22
5.55
2.22
1.96
1.03
7.21
0.38
0.86
3.00
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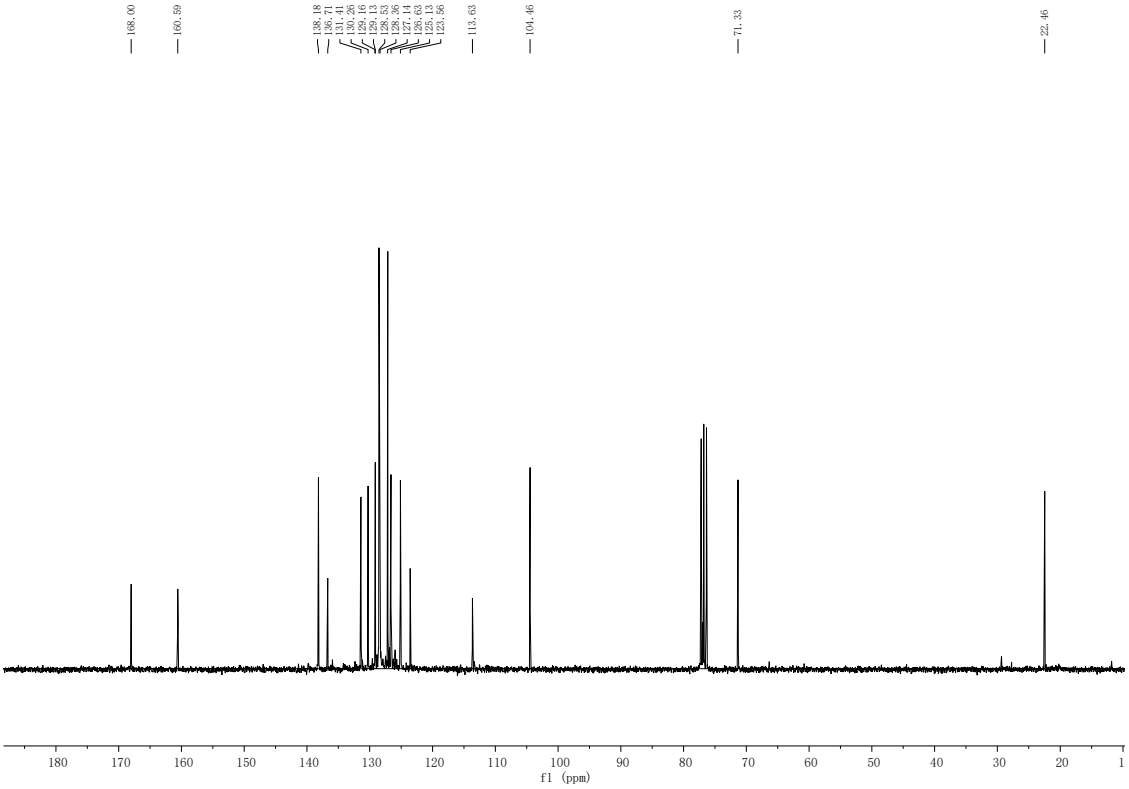
f1 (ppm)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130.26
129.15
129.13
128.53
128.36
127.14
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113.63
104.46
71.33
22.46
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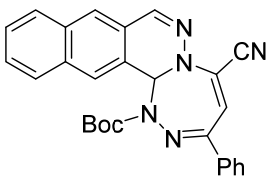
f1 (ppm)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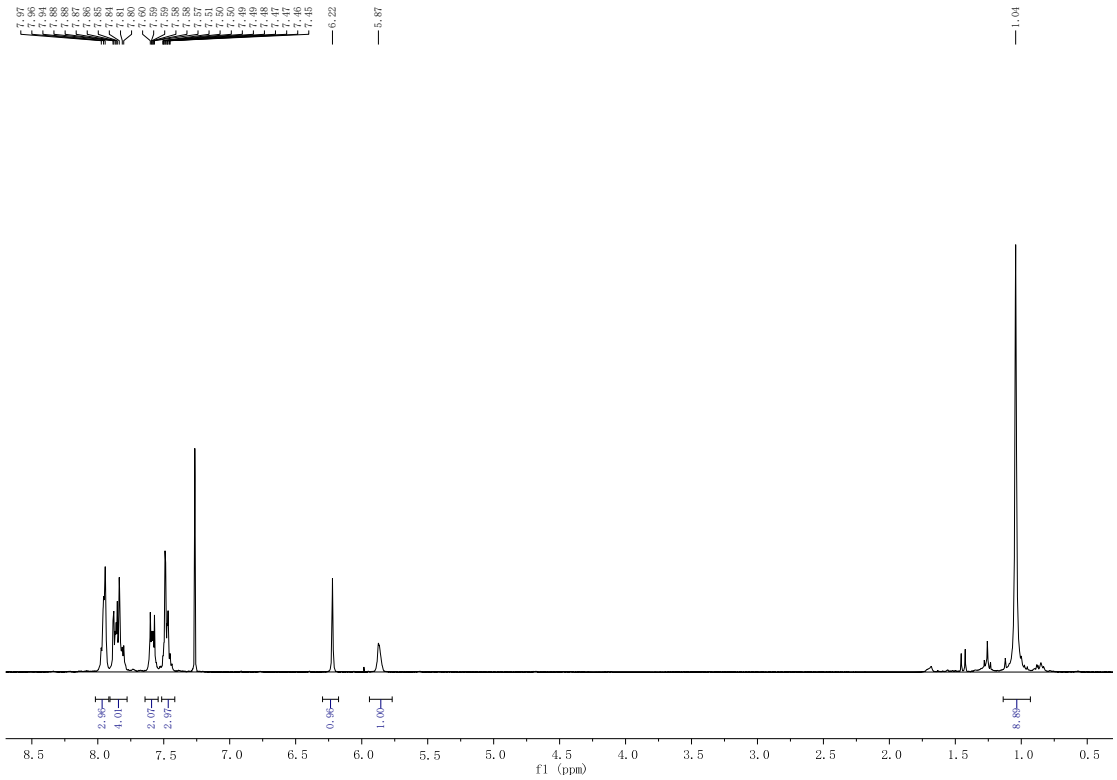
N
CN
Boc
N
N
Ph

4ab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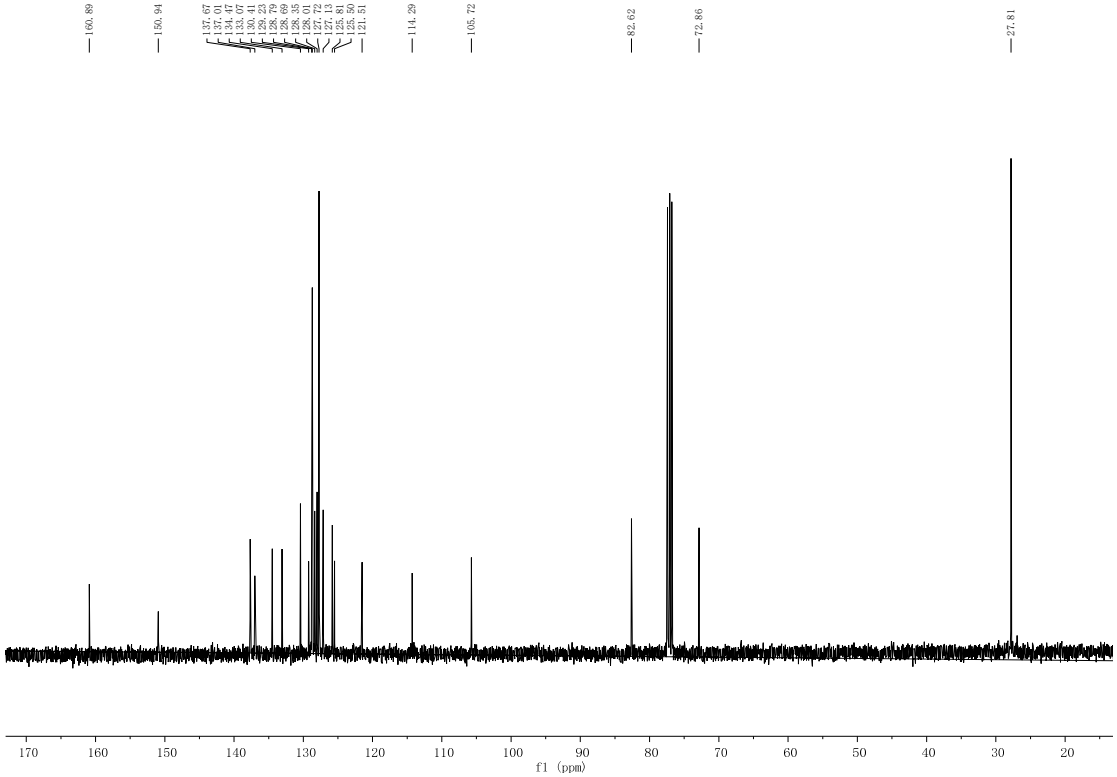
7.48
7.47
7.47
7.46
7.45
6.22
5.87
1.04
2.96
4.01
2.07
2.97
0.96
1.00
8.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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128.69
128.35
128.01
127.72
127.13
125.81
125.50
121.51
114.29
105.72
82.62
72.86
27.81
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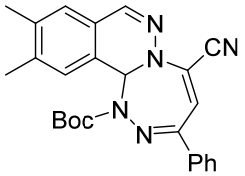
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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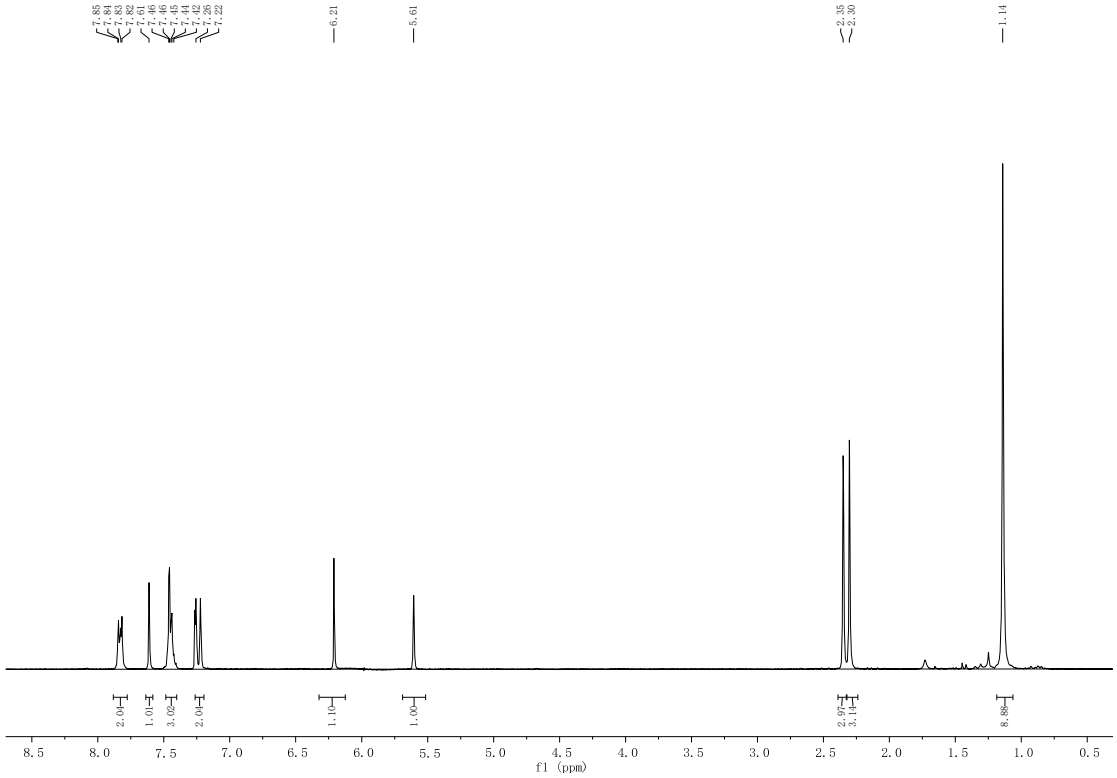
CN
Boc
N
N
Ph

4ac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5.61
2.35
2.30
1.14
2.04
1.01
3.02
2.04
1.10
1.00
2.97
3.14
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8.5
8.0
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7.0
6.5
6.0
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5.0
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4.0
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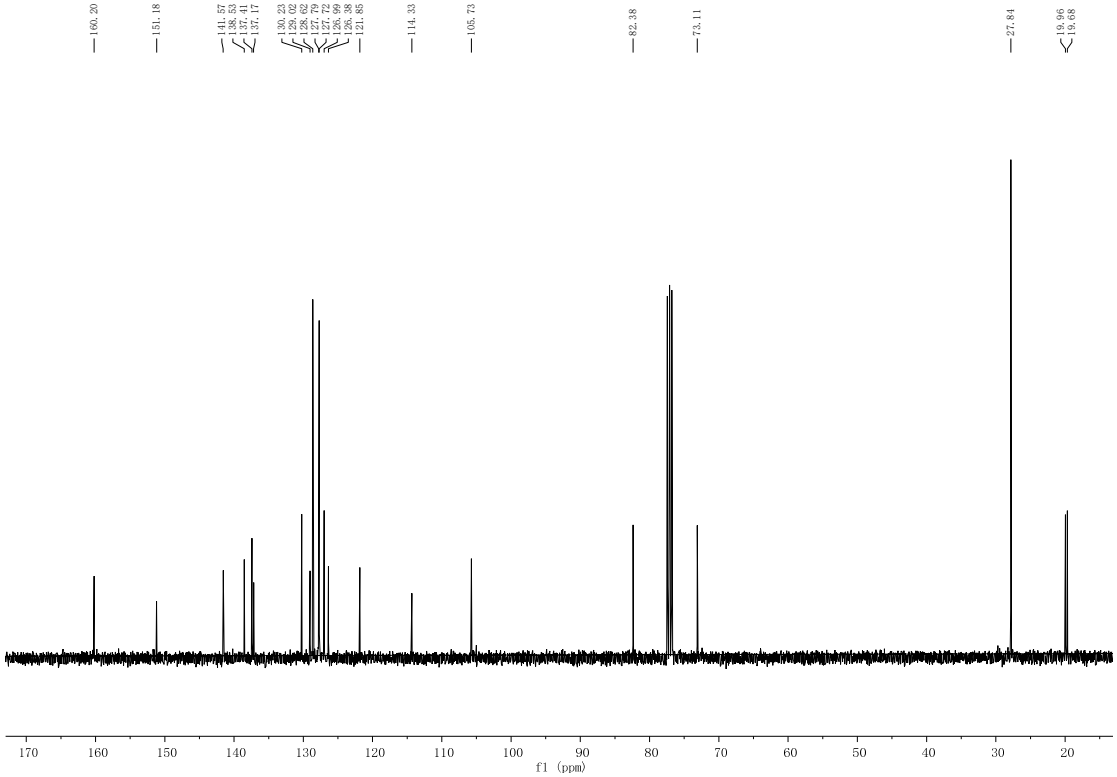
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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127.79
127.72
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126.38
121.85
114.33
105.73
82.38
73.11
27.84
19.96
19.68
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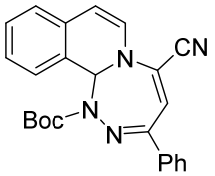
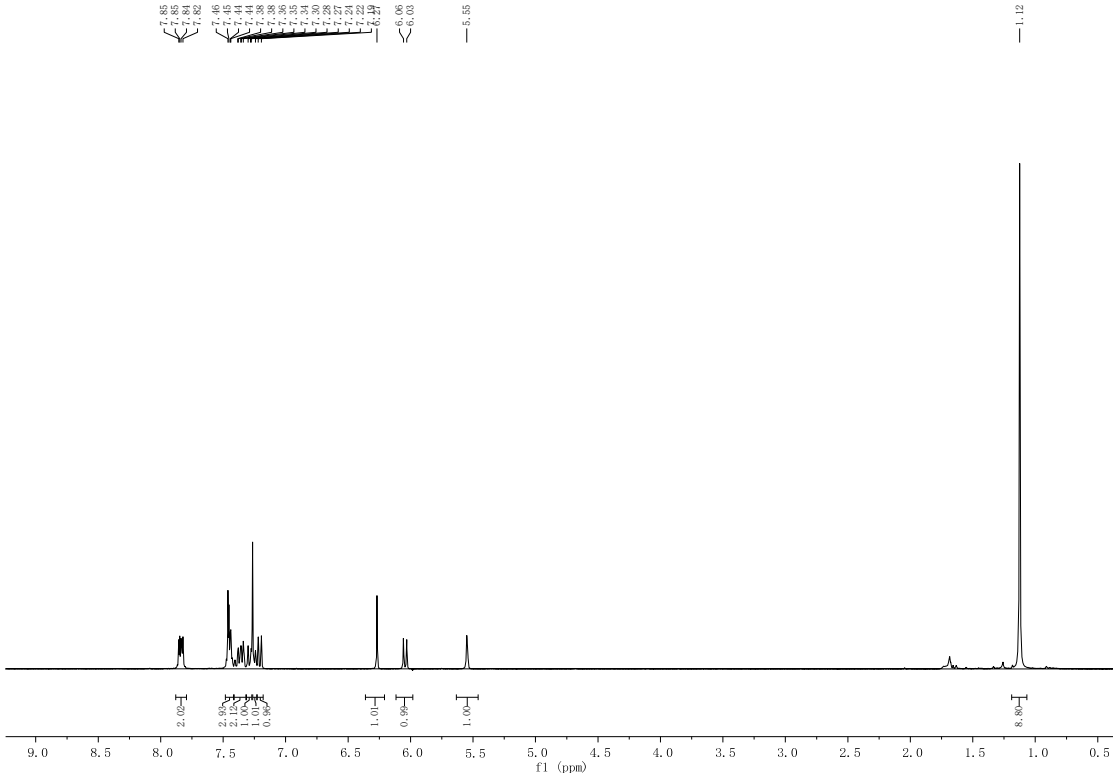
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


CN
N
Boc
N
N
Ph

6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7.44
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7.38
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7.34
7.30
7.28
7.27
7.24
7.24
7.22
7.19
6.27
6.06
6.03
5.55
1.12
2.00
2.90
2.15
1.06
1.01
0.96
1.01
0.90
1.00
8.80
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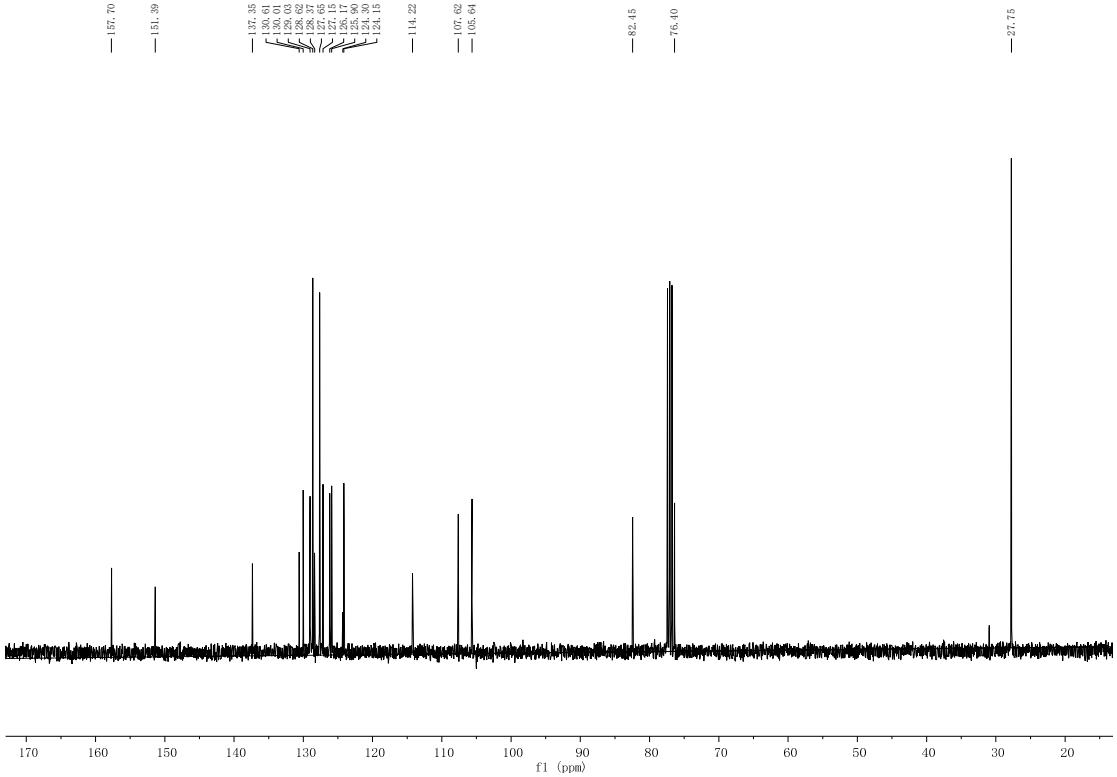
f1 (ppm)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125.90
124.30
124.15
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76.40
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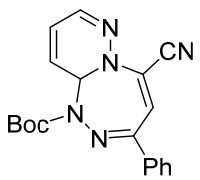
f1 (ppm)


N
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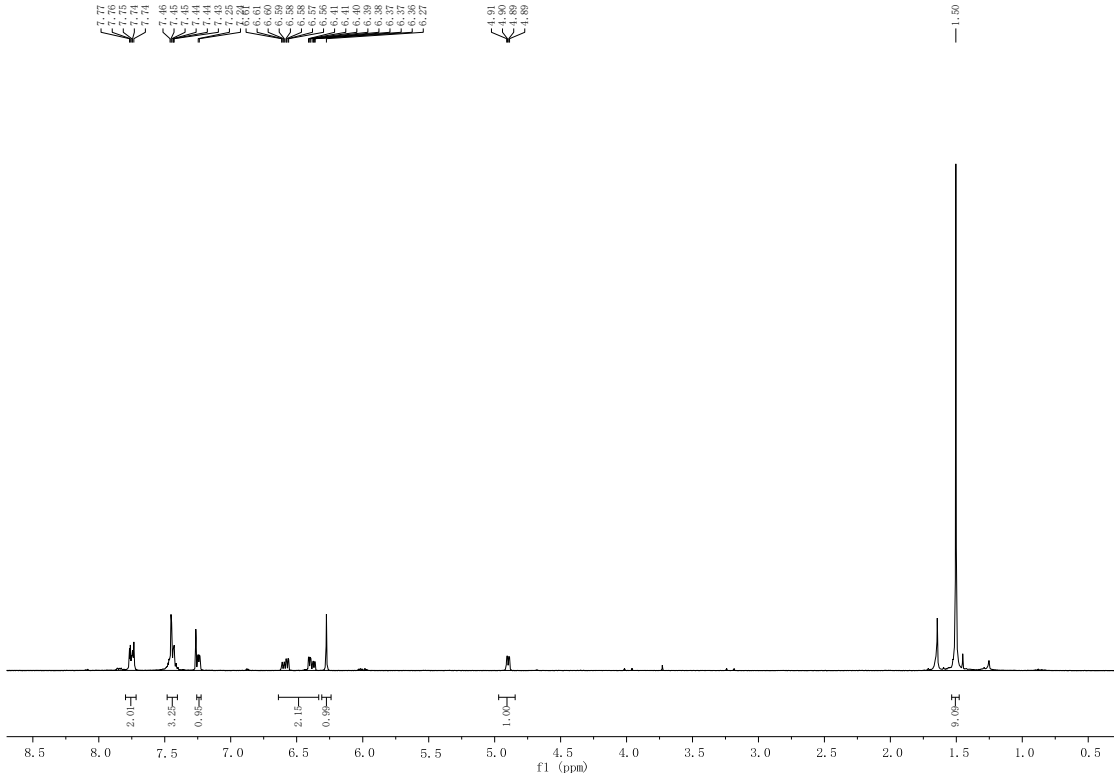
Boc
N
N
Ph

8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7.45
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7.44
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7.24
6.61
6.60
6.59
6.58
6.58
6.57
6.56
6.55
6.41
6.40
6.39
6.38
6.37
6.37
6.36
6.27
4.91
4.90
4.89
4.89
1.50
2.01
3.25
0.95
2.15
0.99
1.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
3.5
3.0
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2.0
1.5
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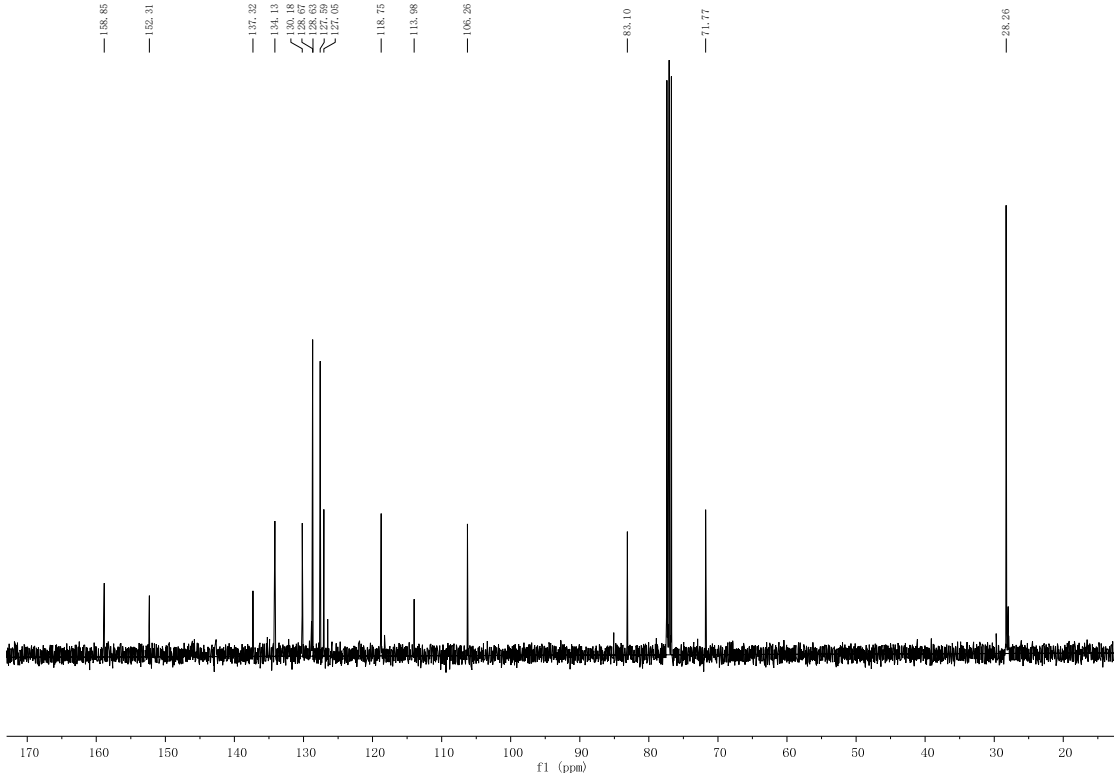
0.5
f1 (ppm)


158.85
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113.98
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71.77
28.26
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

X-ray Crystallography data

Crystallographic data for **4aa** have been deposited with the Cambridge Crystallographic Data Centre as supplementary numbers CCDC 1482368. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. The ellipsoid contour percent probability level is 30%.

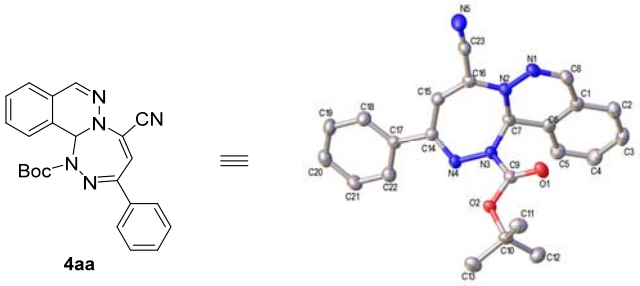

Table 1. Crystal data and structure refinement for **4aa**.

Identification code	**4aa**	
Empirical formula	C23 H21 N5 O2	
Formula weight	399.45	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 5.458(2) Å	α= 90°.
	b = 17.775(7) Å	β= 94.070(7)°.
	c = 20.714(8) Å	γ = 90°.
Volume	2004.6(14) $Å^3$	
Z	4	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	840	
Crystal size	0.42 x 0.2 x 0.06 mm^3	
Theta range for data collection	1.511 to 27.476°.	
Index ranges	-4<=h<=7, -23<=k<=22, -26<=l<=26	
Reflections collected	15519	
Independent reflections	4554 [R(int) = 0.0597]	
Completeness to theta = 26.000°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8614	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4554 / 0 / 274	
Goodness-of-fit on F^2	1.210	
Final R indices [I>2sigma(I)]	R1 = 0.0837, wR2 = 0.1336	
R indices (all data)	R1 = 0.1044, wR2 = 0.1445	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.234 and -0.264 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	-36(3)	4478(1)	3458(1)	33(1)
O2	1564(3)	3400(1)	3067(1)	25(1)
N1	-951(4)	6112(1)	2425(1)	28(1)
N2	922(4)	5644(1)	2259(1)	25(1)
N3	2718(4)	4512(1)	2691(1)	25(1)
N4	4232(4)	4108(1)	2298(1)	26(1)
N5	-2318(5)	6002(2)	809(1)	43(1)
C1	1188(5)	6209(2)	3496(1)	27(1)
C2	1263(5)	6523(2)	4114(1)	34(1)
C3	3113(5)	6327(2)	4571(1)	37(1)
C4	4937(5)	5828(2)	4415(1)	36(1)
C5	4904(5)	5514(2)	3806(1)	31(1)
C6	3013(5)	5693(1)	3348(1)	26(1)
C7	2897(4)	5338(1)	2689(1)	24(1)
C8	-765(5)	6374(2)	3006(1)	29(1)
C9	1300(4)	4143(1)	3114(1)	24(1)
C10	412(5)	2891(1)	3521(1)	26(1)
C11	-2367(5)	2960(2)	3461(2)	35(1)
C12	1459(5)	3051(2)	4204(1)	36(1)
C13	1213(5)	2128(2)	3289(2)	34(1)
C14	4120(4)	4331(1)	1699(1)	24(1)
C15	2347(5)	4862(2)	1394(1)	27(1)
C16	844(5)	5383(1)	1636(1)	25(1)
C17	5891(5)	3950(1)	1288(1)	25(1)
C18	5813(5)	4036(2)	621(1)	32(1)
C19	7527(6)	3679(2)	264(1)	38(1)
C20	9342(5)	3241(2)	558(1)	35(1)
C21	9438(5)	3144(2)	1223(1)	35(1)
C22	7737(5)	3499(2)	1586(1)	31(1)
C23	-954(5)	5744(2)	1187(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **4aa**.

O1-C9	1.211(3)
O2-C9	1.333(3)
O2-C10	1.478(3)
N1-N2	1.381(3)
N1-C8	1.288(3)
N2-C7	1.454(3)
N2-C16	1.369(3)
N3-N4	1.400(3)
N3-C7	1.471(3)
N3-C9	1.376(3)
N4-C14	1.298(3)
N5-C23	1.138(3)
C1-C2	1.396(4)
C1-C6	1.403(4)
C1-C8	1.448(4)
C2-H2	0.9300
C2-C3	1.379(4)
C3-H3	0.9300
C3-C4	1.389(4)
C4-H4	0.9300
C4-C5	1.377(4)
C5-H5	0.9300
C5-C6	1.389(4)
C6-C7	1.502(4)
C7-H7	0.9800
C8-H8	0.9300
C10-C11	1.518(3)
C10-C12	1.515(4)
C10-C13	1.512(4)
C11-H11A	0.9600
C11-H11B	0.9600
C11-H11C	0.9600
C12-H12A	0.9600
C12-H12B	0.9600
C12-H12C	0.9600
C13-H13A	0.9600

C13-H13B	0.9600
C13-H13C	0.9600
C14-C15	1.463(4)
C14-C17	1.495(3)
C15-H15	0.9300
C15-C16	1.356(4)
C16-C23	1.452(4)
C17-C18	1.388(4)
C17-C22	1.396(4)
C18-H18	0.9300
C18-C19	1.387(4)
C19-H19	0.9300
C19-C20	1.370(4)
C20-H20	0.9300
C20-C21	1.384(4)
C21-H21	0.9300
C21-C22	1.387(4)
C22-H22	0.9300

C9-O2-C10	120.49(19)
C8-N1-N2	116.2(2)
N1-N2-C7	127.0(2)
C16-N2-N1	117.7(2)
C16-N2-C7	115.1(2)
N4-N3-C7	117.91(19)
C9-N3-N4	120.5(2)
C9-N3-C7	121.2(2)
C14-N4-N3	114.2(2)
C2-C1-C6	119.1(3)
C2-C1-C8	122.2(2)
C6-C1-C8	118.6(2)
C1-C2-H2	120.0
C3-C2-C1	120.0(3)
C3-C2-H2	120.0
C2-C3-H3	119.9
C2-C3-C4	120.3(3)
C4-C3-H3	119.9
C3-C4-H4	119.7

C5-C4-C3	120.6(3)
C5-C4-H4	119.7
C4-C5-H5	120.2
C4-C5-C6	119.5(3)
C6-C5-H5	120.2
C1-C6-C7	119.2(2)
C5-C6-C1	120.4(2)
C5-C6-C7	120.4(2)
N2-C7-N3	109.1(2)
N2-C7-C6	112.5(2)
N2-C7-H7	106.7
N3-C7-C6	114.5(2)
N3-C7-H7	106.7
C6-C7-H7	106.7
N1-C8-C1	125.9(2)
N1-C8-H8	117.1
C1-C8-H8	117.1
O1-C9-O2	127.1(2)
O1-C9-N3	122.0(2)
O2-C9-N3	110.9(2)
O2-C10-C11	111.4(2)
O2-C10-C12	109.2(2)
O2-C10-C13	101.6(2)
C12-C10-C11	111.7(2)
C13-C10-C11	110.9(2)
C13-C10-C12	111.5(2)
C10-C11-H11A	109.5
C10-C11-H11B	109.5
C10-C11-H11C	109.5
H11A-C11-H11B	109.5
H11A-C11-H11C	109.5
H11B-C11-H11C	109.5
C10-C12-H12A	109.5
C10-C12-H12B	109.5
C10-C12-H12C	109.5
H12A-C12-H12B	109.5
H12A-C12-H12C	109.5
H12B-C12-H12C	109.5

C10-C13-H13A	109.5
C10-C13-H13B	109.5
C10-C13-H13C	109.5
H13A-C13-H13B	109.5
H13A-C13-H13C	109.5
H13B-C13-H13C	109.5
N4-C14-C15	126.5(2)
N4-C14-C17	114.6(2)
C15-C14-C17	118.8(2)
C14-C15-H15	113.6
C16-C15-C14	132.8(2)
C16-C15-H15	113.6
N2-C16-C23	115.4(2)
C15-C16-N2	126.9(2)
C15-C16-C23	117.6(2)
C18-C17-C14	122.8(2)
C18-C17-C22	118.2(2)
C22-C17-C14	119.0(2)
C17-C18-H18	119.7
C19-C18-C17	120.5(3)
C19-C18-H18	119.7
C18-C19-H19	119.5
C20-C19-C18	121.0(3)
C20-C19-H19	119.5
C19-C20-H20	120.4
C19-C20-C21	119.3(3)
C21-C20-H20	120.4
C20-C21-H21	119.9
C20-C21-C22	120.2(3)
C22-C21-H21	119.9
C17-C22-H22	119.6
C21-C22-C17	120.8(3)
C21-C22-H22	119.6
N5-C23-C16	176.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	30(1)	27(1)	44(1)	-3(1)	15(1)	1(1)
O2	25(1)	20(1)	30(1)	2(1)	8(1)	0(1)
N1	24(1)	26(1)	36(1)	1(1)	6(1)	5(1)
N2	22(1)	25(1)	28(1)	-1(1)	2(1)	3(1)
N3	27(1)	21(1)	28(1)	0(1)	10(1)	4(1)
N4	26(1)	25(1)	28(1)	-1(1)	7(1)	3(1)
N5	42(2)	52(2)	34(1)	-3(1)	-4(1)	18(1)
C1	26(1)	27(1)	30(1)	-1(1)	6(1)	-5(1)
C2	32(2)	34(2)	37(2)	-7(1)	8(1)	-2(1)
C3	38(2)	43(2)	31(2)	-10(1)	7(1)	-6(1)
C4	33(2)	43(2)	33(2)	-3(1)	-2(1)	-4(1)
C5	24(1)	36(2)	34(2)	-2(1)	2(1)	-2(1)
C6	24(1)	24(1)	29(1)	-1(1)	6(1)	-4(1)
C7	20(1)	23(1)	28(1)	1(1)	5(1)	0(1)
C8	24(1)	28(1)	36(2)	-4(1)	7(1)	4(1)
C9	20(1)	24(1)	28(1)	0(1)	2(1)	1(1)
C10	22(1)	24(1)	31(1)	5(1)	5(1)	-1(1)
C11	22(1)	38(2)	45(2)	8(1)	4(1)	-1(1)
C12	32(2)	45(2)	32(2)	3(1)	3(1)	3(1)
C13	27(1)	27(1)	48(2)	3(1)	7(1)	-4(1)
C14	22(1)	24(1)	26(1)	-1(1)	3(1)	-2(1)
C15	25(1)	30(1)	25(1)	1(1)	1(1)	2(1)
C16	22(1)	25(1)	28(1)	1(1)	2(1)	-2(1)
C17	22(1)	24(1)	29(1)	-2(1)	3(1)	-1(1)
C18	30(1)	38(2)	30(2)	1(1)	4(1)	7(1)
C19	40(2)	45(2)	30(2)	-5(1)	10(1)	7(1)
C20	29(1)	36(2)	41(2)	-7(1)	11(1)	1(1)
C21	31(2)	34(2)	40(2)	1(1)	6(1)	9(1)
C22	27(1)	33(2)	34(2)	1(1)	6(1)	4(1)
C23	29(1)	31(1)	30(1)	-4(1)	4(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4aa**.

	x	y	z	U(eq)
H2	64	6866	4218	41
H3	3140	6529	4985	44
H4	6193	5704	4724	44
H5	6138	5183	3703	38
H7	4438	5464	2499	28
H8	-1996	6699	3122	35
H11A	-2831	3453	3596	52
H11B	-3067	2589	3730	52
H11C	-2959	2881	3018	52
H12A	3220	3033	4219	54
H12B	873	2681	4493	54
H12C	947	3542	4333	54
H13A	575	2052	2850	51
H13B	599	1743	3560	51
H13C	2975	2106	3311	51
H15	2227	4838	944	32
H18	4602	4334	413	39
H19	7442	3739	-184	45
H20	10499	3011	315	42
H21	10646	2840	1426	42
H22	7828	3436	2032	37

Table 6. Torsion angles [°] for **4aa**.

N1-N2-C7-N3	117.9(2)
N1-N2-C7-C6	-10.4(3)
N1-N2-C16-C15	-172.8(2)
N1-N2-C16-C23	11.3(3)
N2-N1-C8-C1	-1.3(4)
N3-N4-C14-C15	-10.0(4)
N3-N4-C14-C17	174.8(2)
N4-N3-C7-N2	98.5(2)

N4-N3-C7-C6	-134.4(2)
N4-N3-C9-O1	-179.6(2)
N4-N3-C9-O2	-1.7(3)
N4-C14-C15-C16	18.5(5)
N4-C14-C17-C18	170.7(3)
N4-C14-C17-C22	-10.5(3)
C1-C2-C3-C4	1.3(4)
C1-C6-C7-N2	5.1(3)
C1-C6-C7-N3	-120.3(3)
C2-C1-C6-C5	-1.7(4)
C2-C1-C6-C7	178.4(2)
C2-C1-C8-N1	179.4(3)
C2-C3-C4-C5	-1.0(5)
C3-C4-C5-C6	-0.6(4)
C4-C5-C6-C1	2.0(4)
C4-C5-C6-C7	-178.0(2)
C5-C6-C7-N2	-174.9(2)
C5-C6-C7-N3	59.8(3)
C6-C1-C2-C3	0.0(4)
C6-C1-C8-N1	-3.0(4)
C7-N2-C16-C15	2.2(4)
C7-N2-C16-C23	-173.7(2)
C7-N3-N4-C14	-51.6(3)
C7-N3-C9-O1	7.1(4)
C7-N3-C9-O2	-175.0(2)
C8-N1-N2-C7	8.7(4)
C8-N1-N2-C16	-177.0(2)
C8-C1-C2-C3	177.6(3)
C8-C1-C6-C5	-179.3(2)
C8-C1-C6-C7	0.7(4)
C9-O2-C10-C11	62.3(3)
C9-O2-C10-C12	-61.6(3)
C9-O2-C10-C13	-179.5(2)
C9-N3-N4-C14	134.9(2)
C9-N3-C7-N2	-88.0(3)
C9-N3-C7-C6	39.1(3)
C10-O2-C9-O1	-8.5(4)
C10-O2-C9-N3	173.8(2)

C14-C15-C16-N2	12.8(5)
C14-C15-C16-C23	-171.3(3)
C14-C17-C18-C19	178.9(3)
C14-C17-C22-C21	-179.1(2)
C15-C14-C17-C18	-4.8(4)
C15-C14-C17-C22	173.9(2)
C16-N2-C7-N3	-56.6(3)
C16-N2-C7-C6	175.2(2)
C17-C14-C15-C16	-166.5(3)
C17-C18-C19-C20	-0.5(5)
C18-C17-C22-C21	-0.3(4)
C18-C19-C20-C21	1.0(5)
C19-C20-C21-C22	-1.2(4)
C20-C21-C22-C17	0.8(4)
C22-C17-C18-C19	0.2(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **4aa** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)