Metal-free TEMPO Promoted C(sp^3)-H Amination to Afford Multisubstituted Benzimidazoles

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Supporting Information

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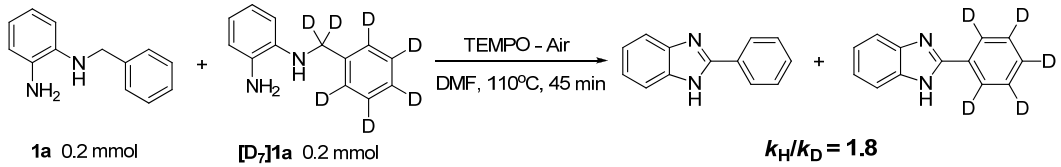
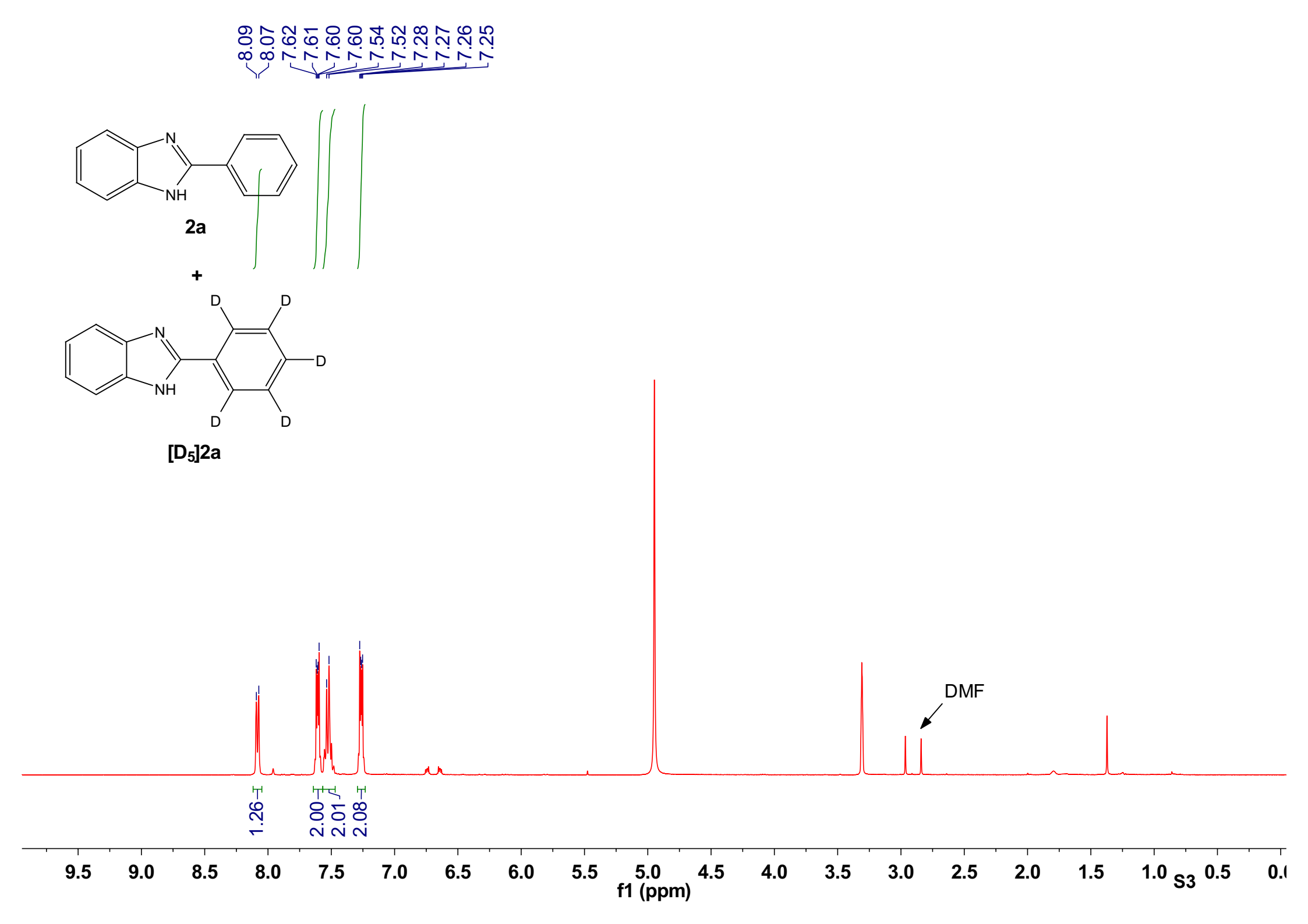
Studies on the kinetic isotope effects



To a solution of **1a** (40 mg, 0.2 mmol) and **[D_7]1a** (41 mg, 0.2 mmol) in DMF (4 mL) was added TEMPO (125 mg, 0.8 mmol), and the mixture was stirred at 110 °C for 45 min. The mixture was then diluted with AcOEt, washed with water and saturated NaCl aq. solution, then dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography and subsequently washed by n-hexane. The pure mixture of products was characterized by ^{1}H NMR. Kinetic isotope effect k_H/k_D = 1.8 was determined by taking the difference in the integration of protons from the 2-phenyl group of the benzimidazole product. The integration of the peak at 8.07-8.09 ppm was 1.26 instead of 1.99 and the peak at 7.48-7.55 ppm was 2.01 instead of 3.09.[1,2]

References:

(1) Matcha, K.; Antonchick, A. P. *Angew Chem Int Edit* **2013**, *52*, 2082.
(2) Yan, Y. Z.; Zhang, Y. H.; Feng, C. T.; Zha, Z. G.; Wang, Z. Y. *Angew Chem Int Edit* **2012**, *51*, 8077.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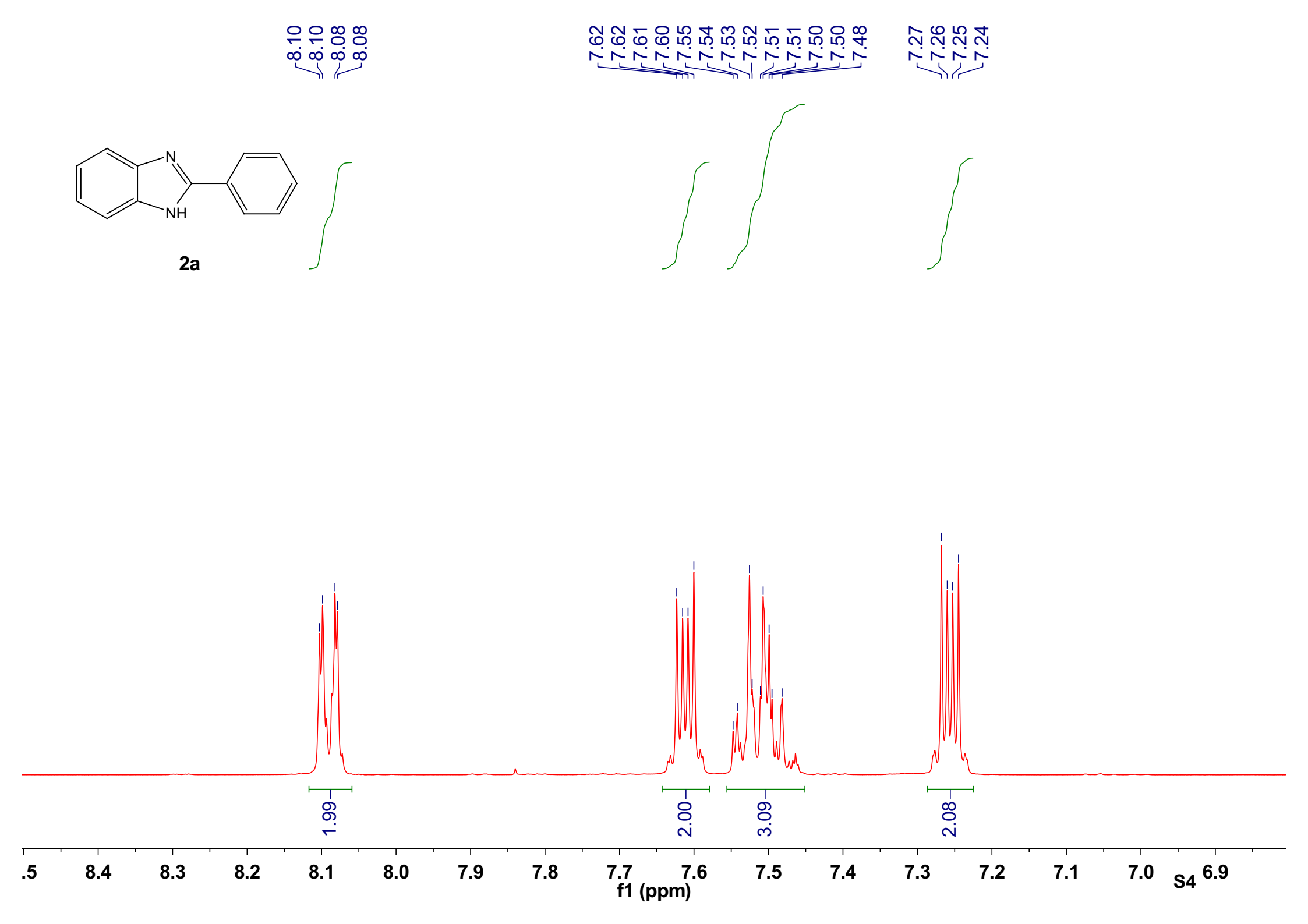
8.07
7.62
7.61
7.60
7.60
7.54
7.52
7.28
7.27
7.26
7.25
N
NH
2a
+
D
D
D
D
D
N
NH
[D5]2a
DMF
1.26
2.00
2.01
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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8.10
8.08
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7.62
7.61
7.60
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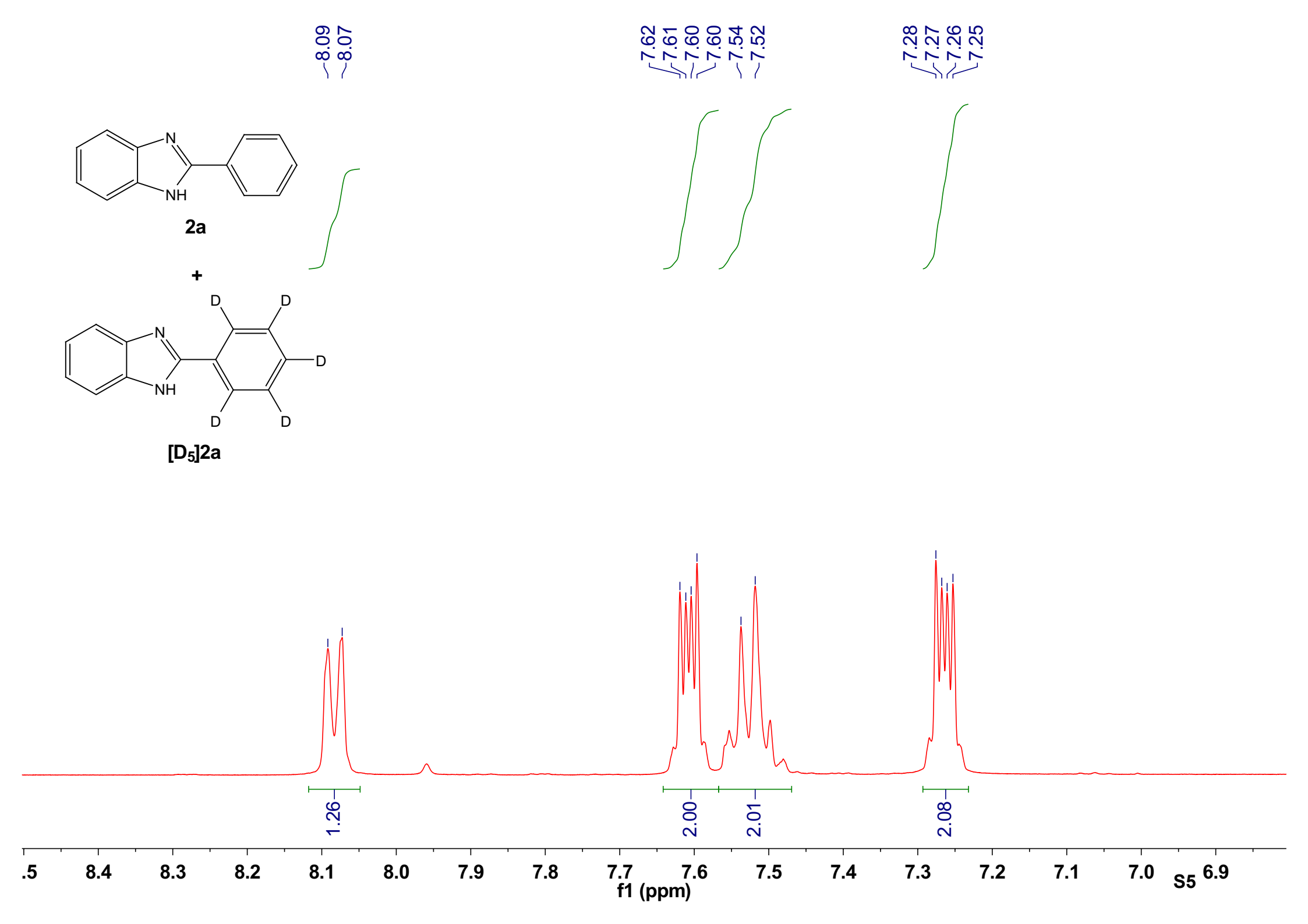
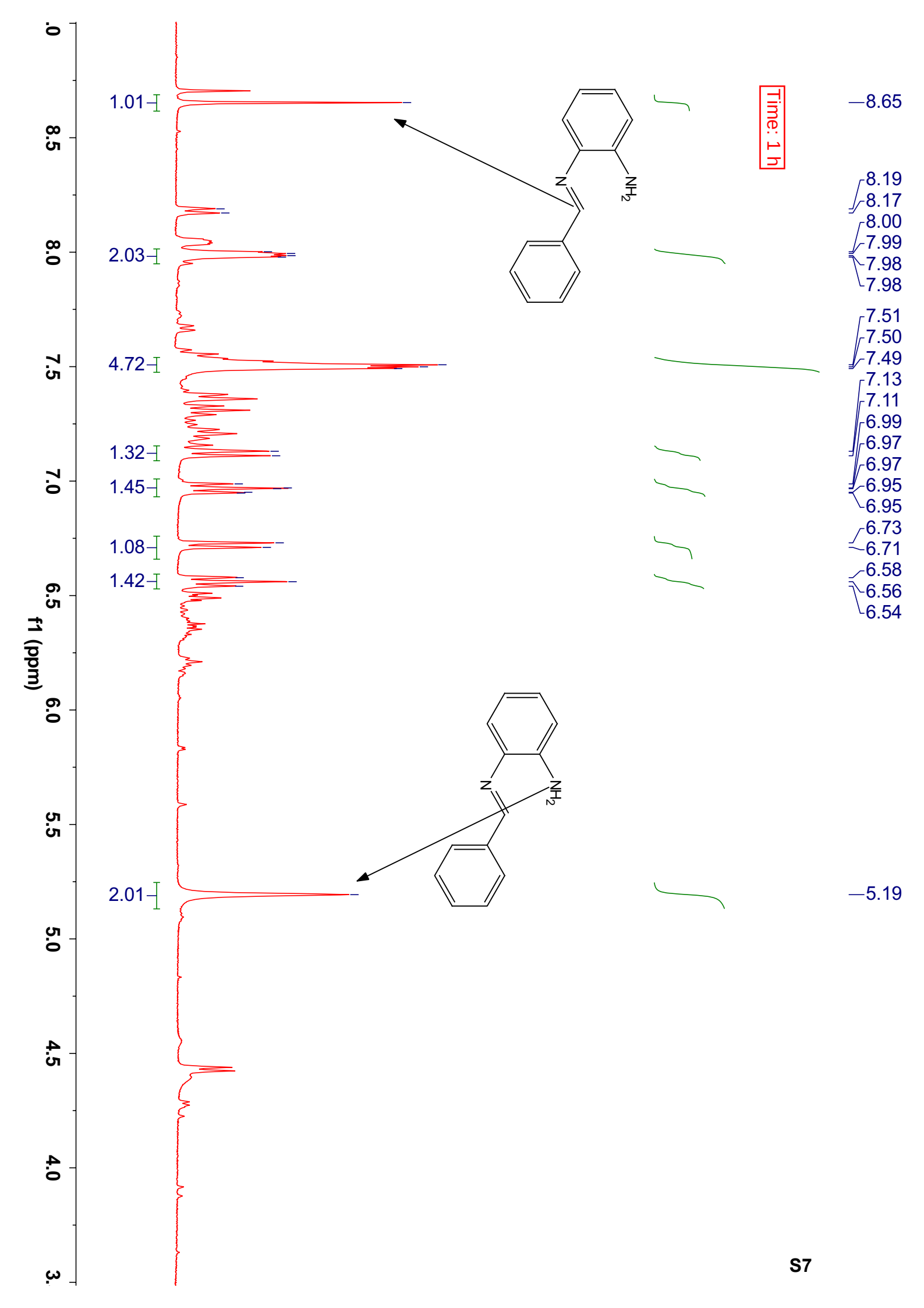
7.54
7.53
7.52
7.51
7.51
7.50
7.50
7.48
7.27
7.26
7.25
7.24
N
NH
2a
1.99
2.00
3.09
2.08
.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)


8.09
8.07
7.62
7.61
7.60
7.60
7.54
7.52
7.28
7.27
7.26
7.25
N
NH
2a
+
D
D
D
D
D
N
NH
[D5]2a
1.26
2.00
2.01
2.08
.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
S5

Time: 0 h
DMF
7.95
7.38
7.36
7.33
7.31
7.23
7.22
6.55
6.39
6.33
5.10
4.56
4.29
4.28
5.18
1.11
3.13
1.00
1.97
2.05
NH
NH2
1a
f1 (ppm)
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.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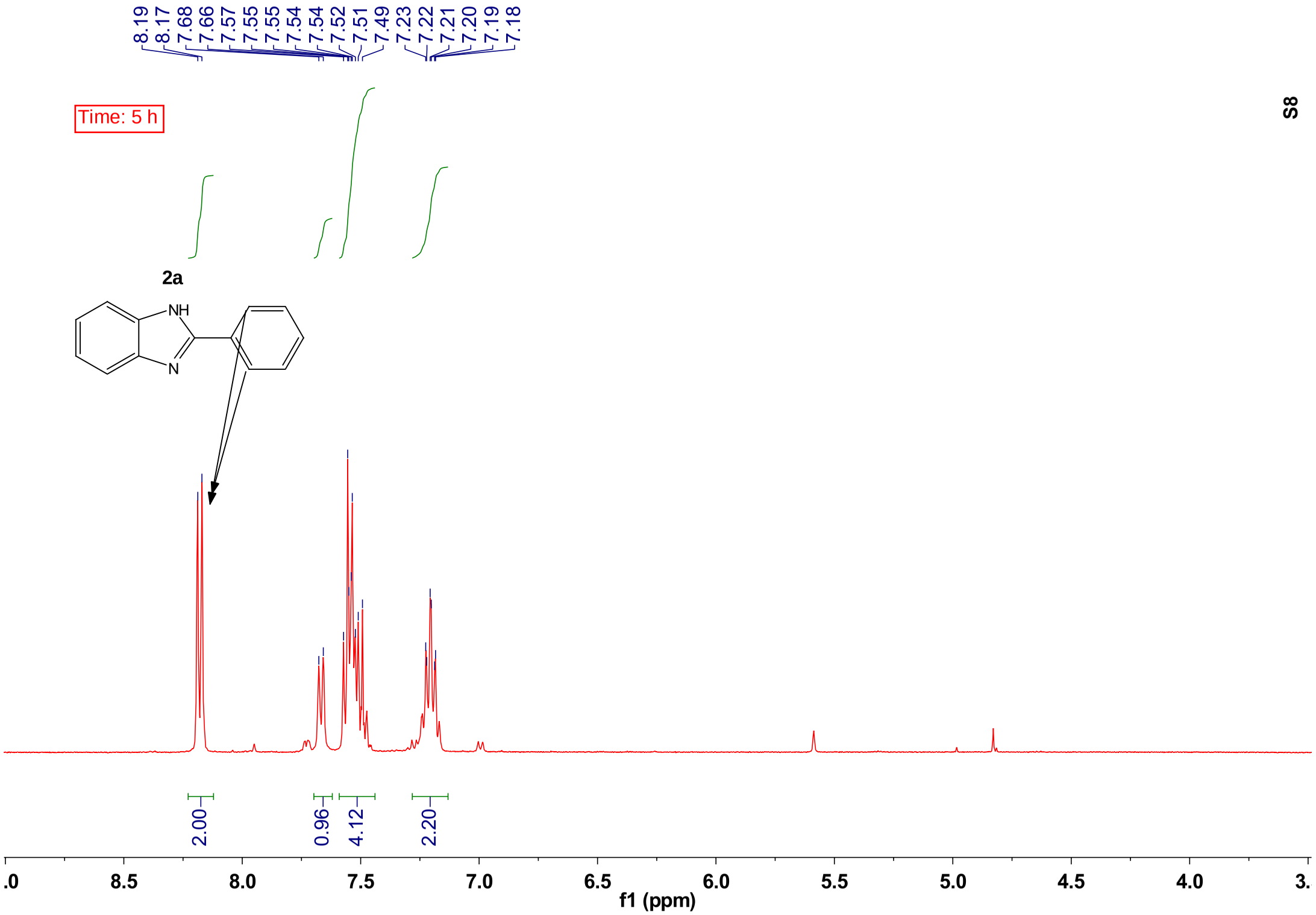
1.01
2.03
4.72
1.32
1.45
1.08
1.42
2.01
8.65
8.19
8.17
8.00
7.99
7.98
7.98
7.51
7.50
7.49
7.13
7.11
6.99
6.97
6.97
6.95
6.95
6.73
6.71
6.58
6.56
6.54
5.19
N
NH2
N
NH2
f1 (ppm)

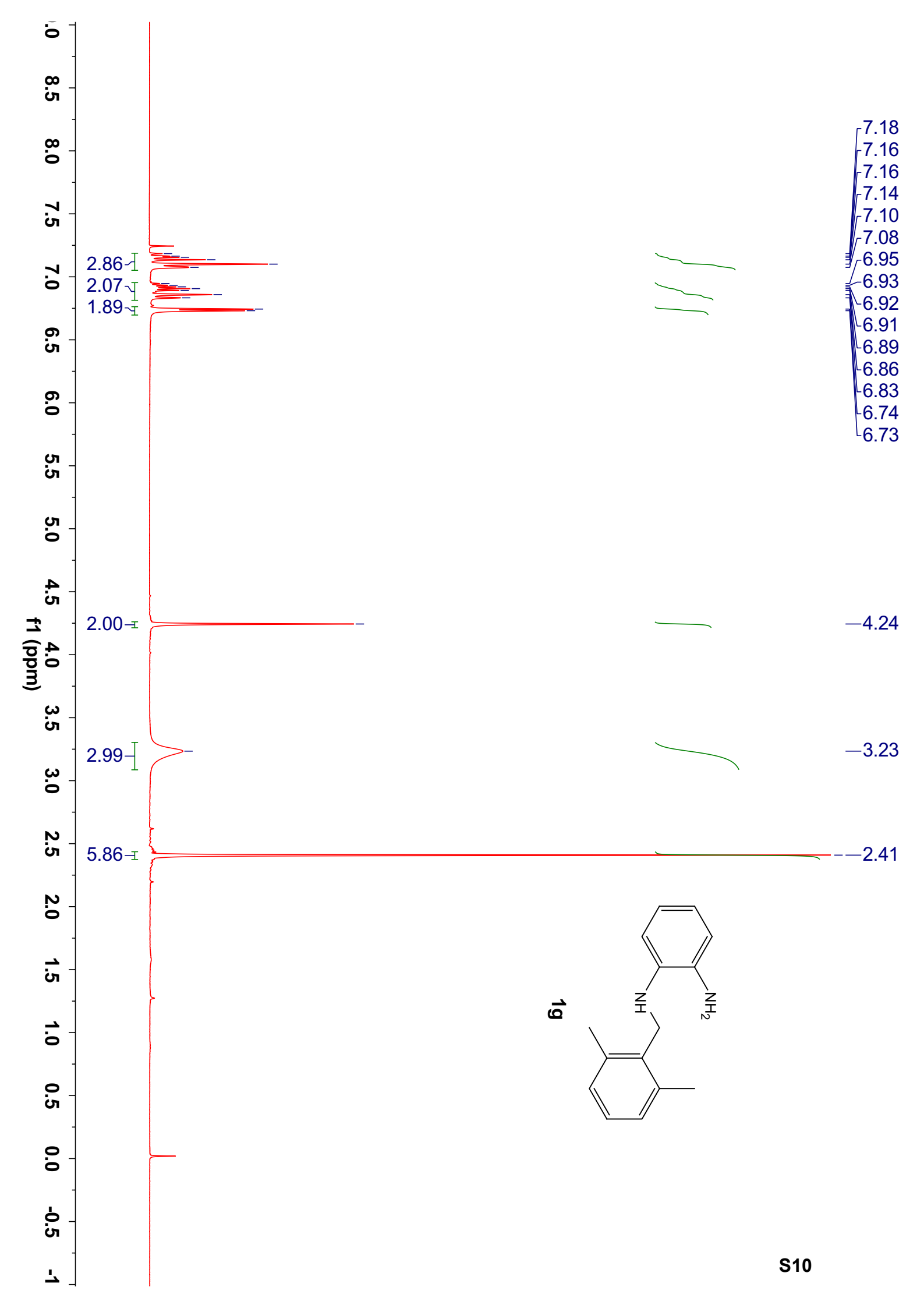

8.19
8.17
7.68
7.66
7.57
7.55
7.55
7.54
7.54
7.52
7.51
7.49
7.23
7.22
7.21
7.20
7.19
7.18
Time: 5 h
2a
NH
N
2.00
0.96
4.12
2.20
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.
f1 (ppm)

Notes:

a. The reaction was carried out using method B (cat. TEMPO-O_2 condition) for the sufficient transformation of the starting material (**1a**) to the imine intermediate before the generation of benzimidazole product (**2a**).

b. ^{1}H NMR Spectra were collected before the reaction started (0 h), when the starting material was completely converted to the intermediate determined by TLC (1 h) and when the reaction completed (5h).

c. 300 μ l of the reaction solution was directly evaporated to dryness and rapidly redissolved by DMSO-d6 for the ^{1}H NMR detection at specific time.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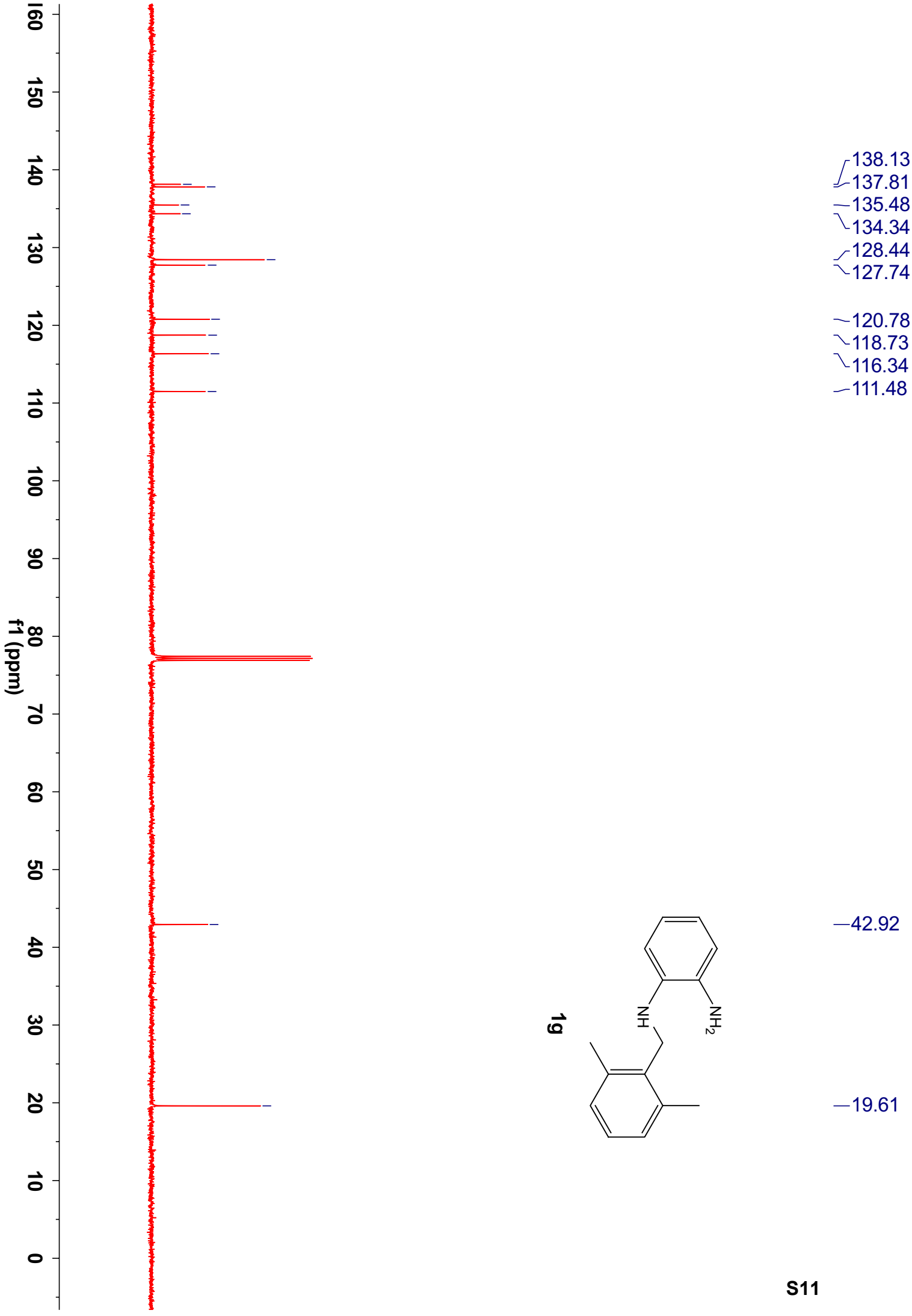
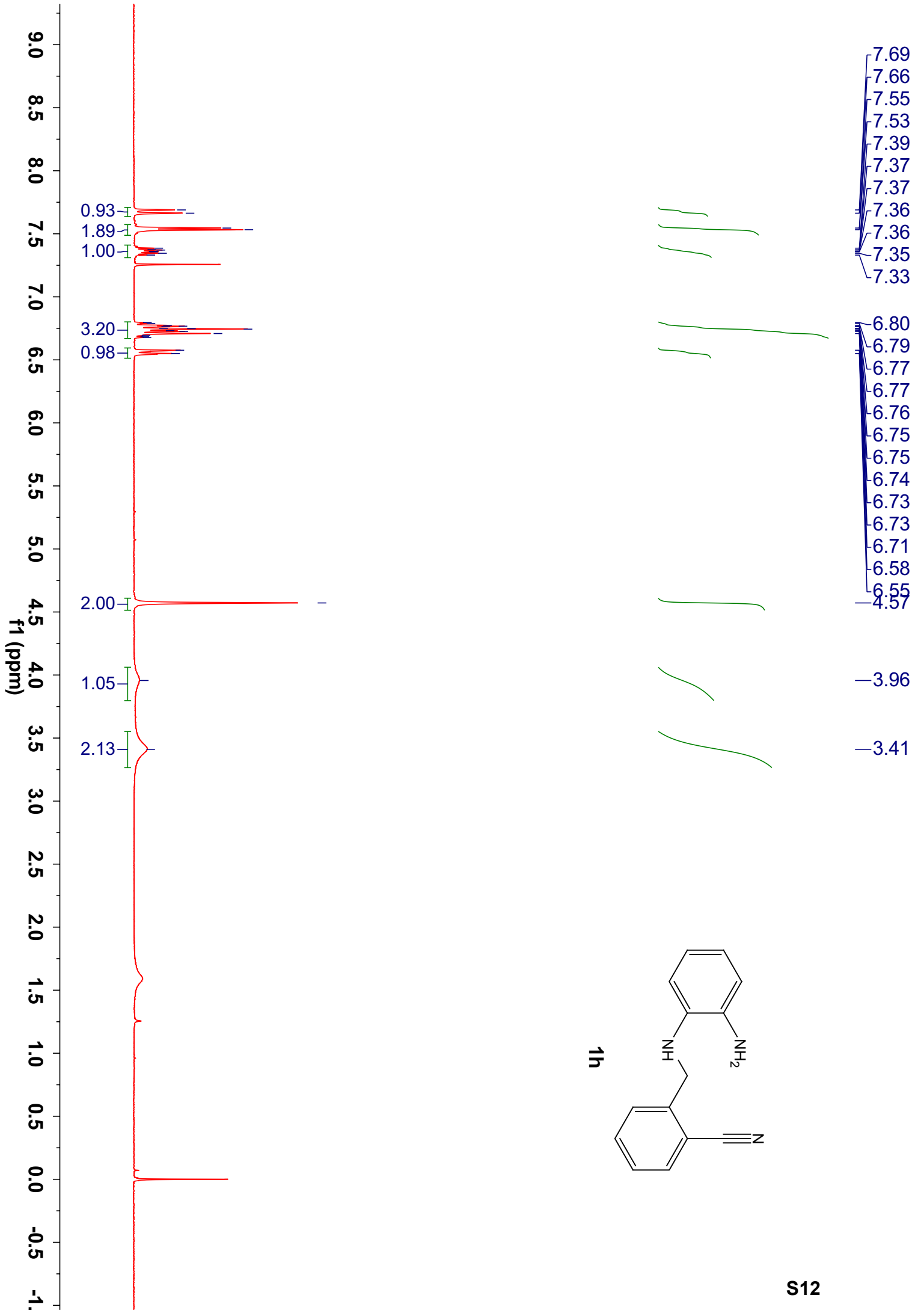
1.89
2.00
2.99
5.86
7.18
7.16
7.16
7.14
7.10
7.08
6.95
6.93
6.92
6.91
6.89
6.86
6.83
6.74
6.73
4.24
3.23
2.41
NH
NH2

1g


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
138.13
137.81
135.48
134.34
128.44
127.74
120.78
118.73
116.34
111.48
42.92
19.61
NH
NH2

1g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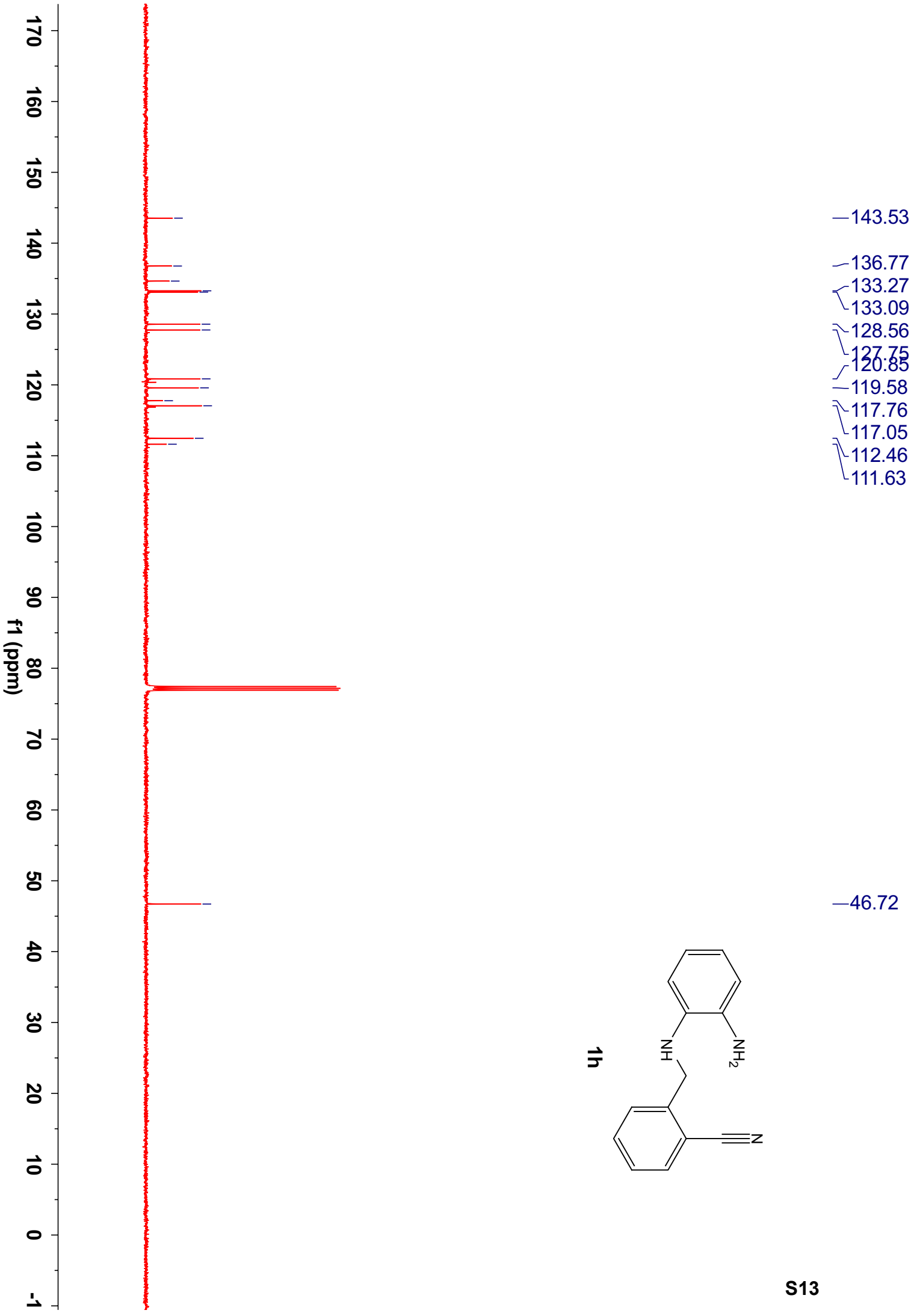
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)
0.93
1.89
1.00
3.20
0.98
2.00
1.05
2.13
7.69
7.66
7.55
7.53
7.39
7.37
7.37
7.36
7.36
7.35
7.33
6.80
6.79
6.77
6.77
6.76
6.75
6.75
6.74
6.73
6.73
6.71
6.58
6.55
4.57
3.96
3.41
NH
NH2
N

1h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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)
143.53
136.77
133.27
133.09
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119.58
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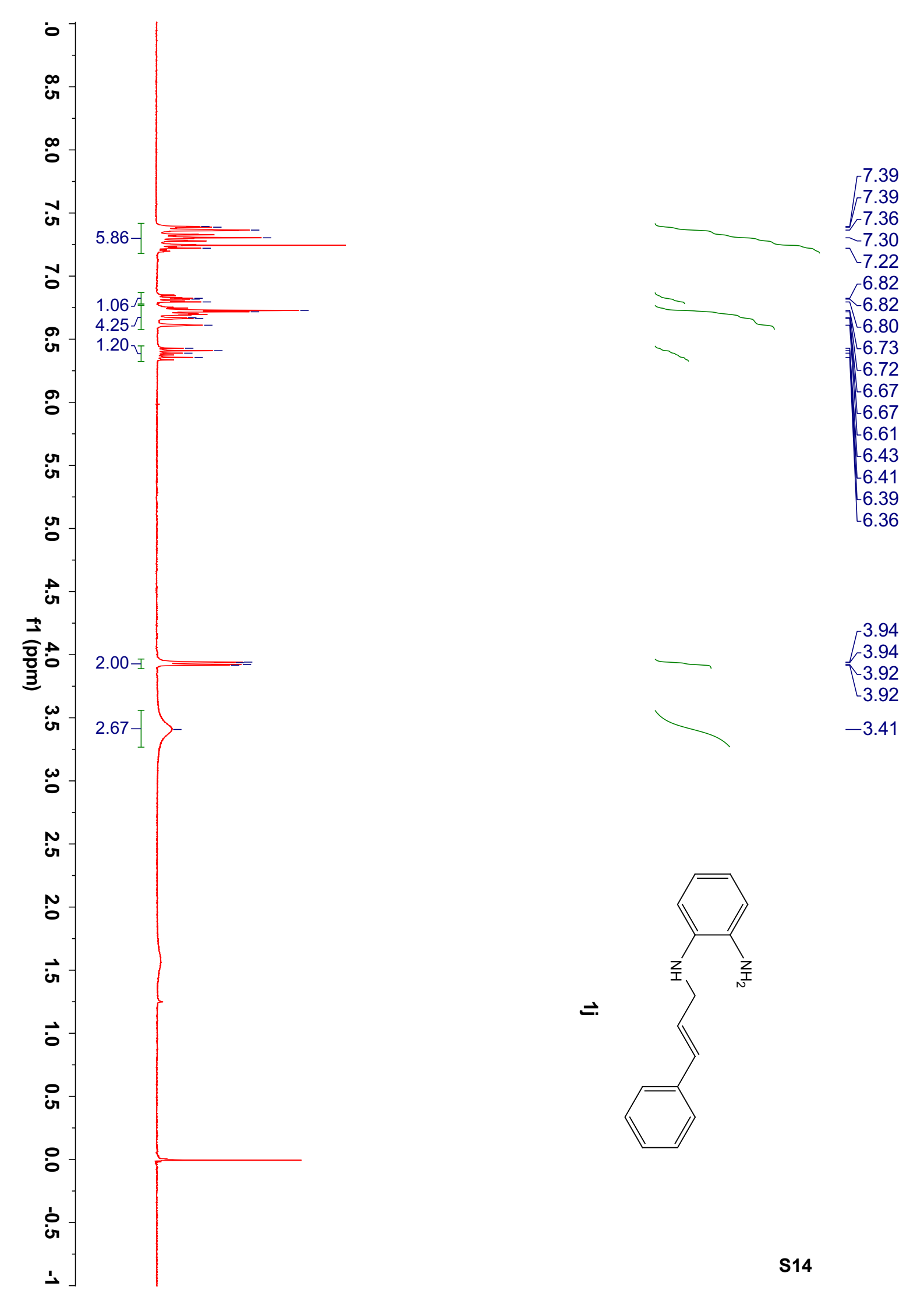
117.05
112.46
111.63
46.72
NH
NH2
N

1h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6.72
6.67
6.67
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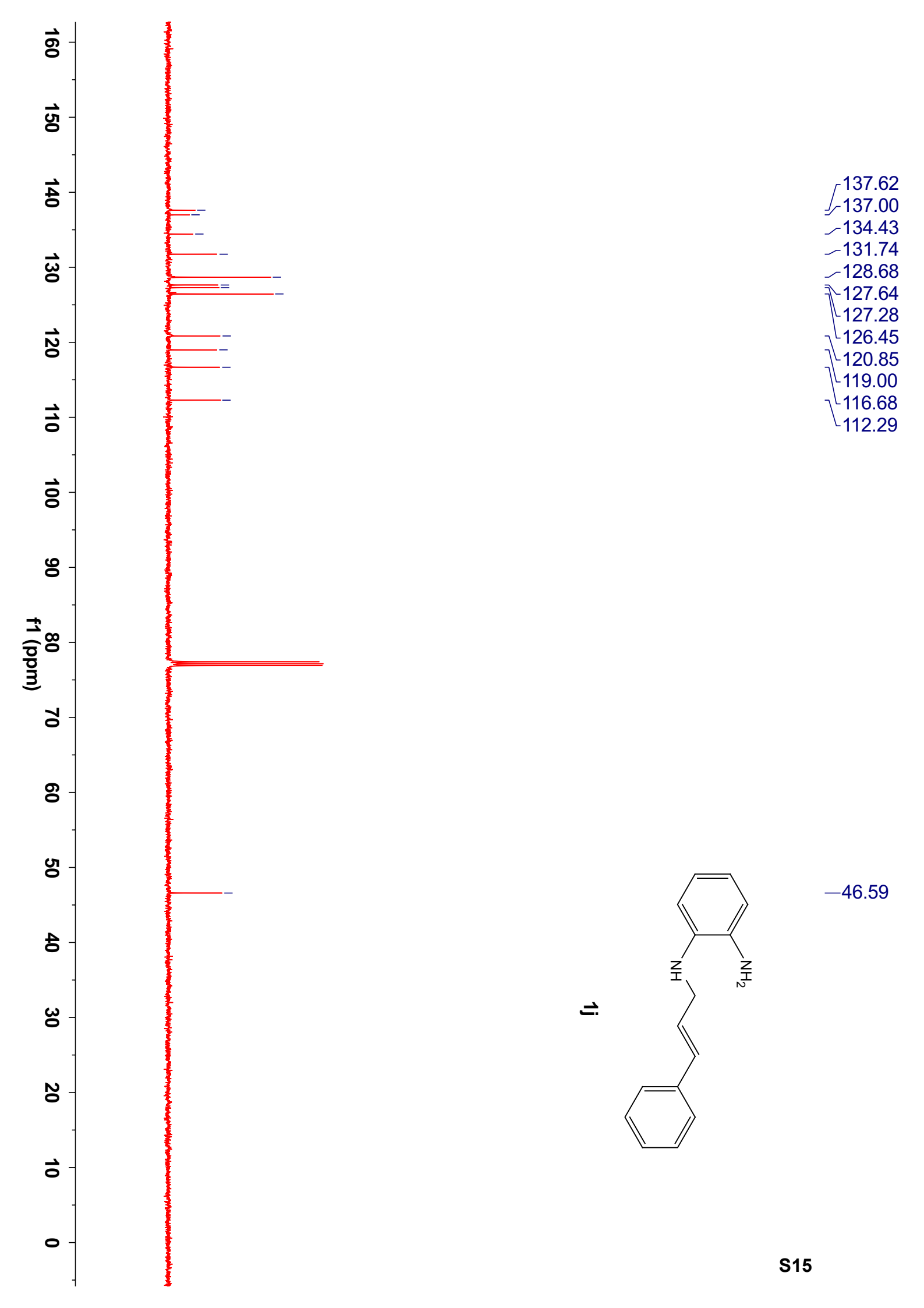
3.92
3.41
NH
NH2

1j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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
137.62
137.00
134.43
131.74
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127.28
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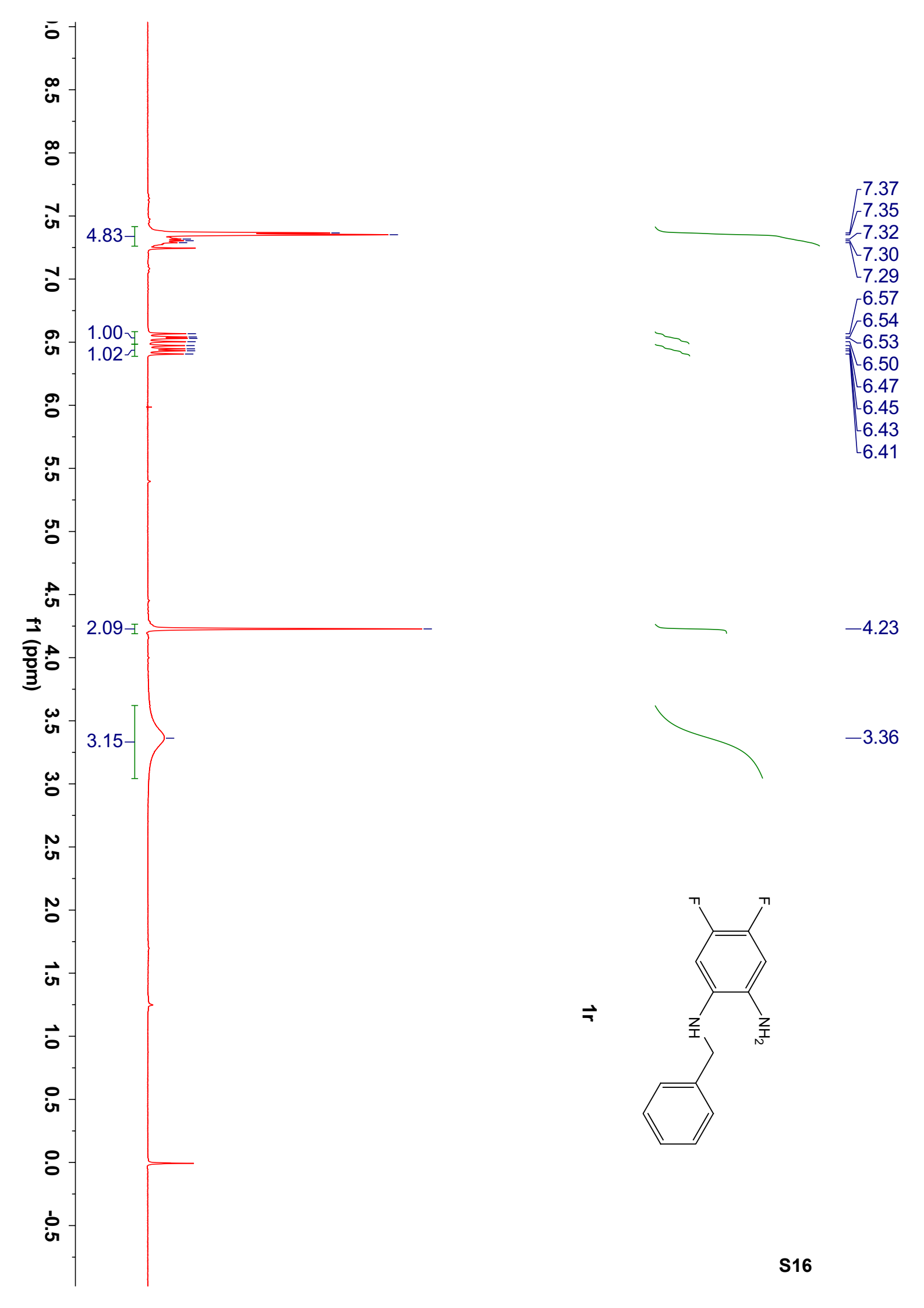
116.68
112.29
46.59
NH
NH2

1j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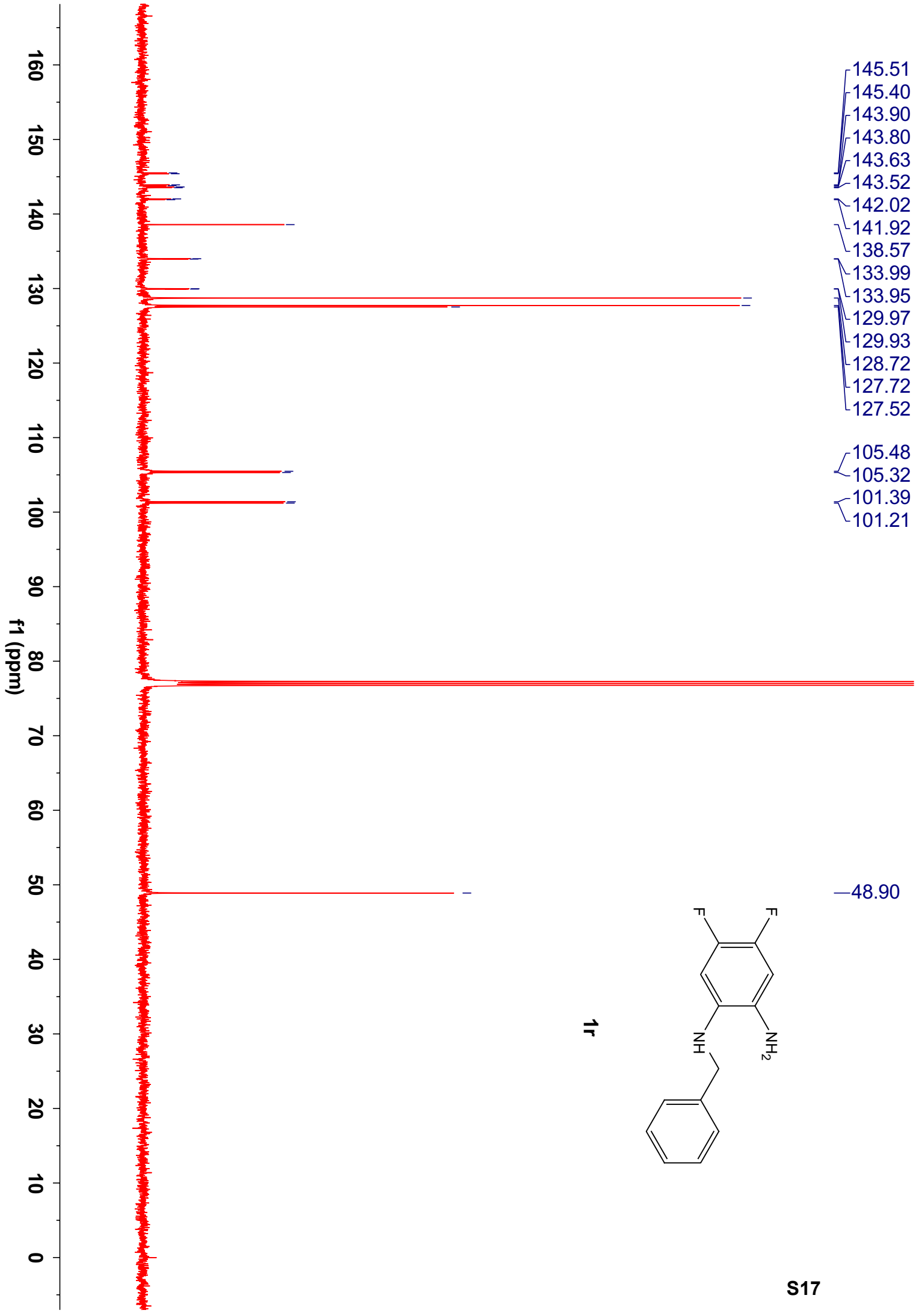
3.36
F
F
NH
NH2

1r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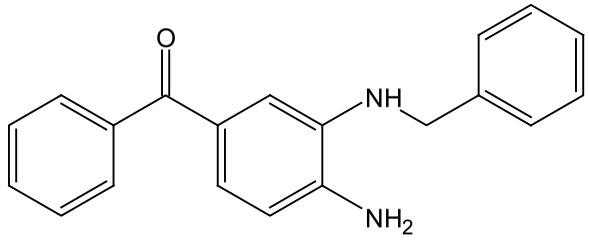
143.63
143.52
142.02
141.92
138.57
133.99
133.95
129.97
129.93
128.72
127.72
127.52
105.48
105.32
101.39
101.21
48.90
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
F
F
NH
NH2

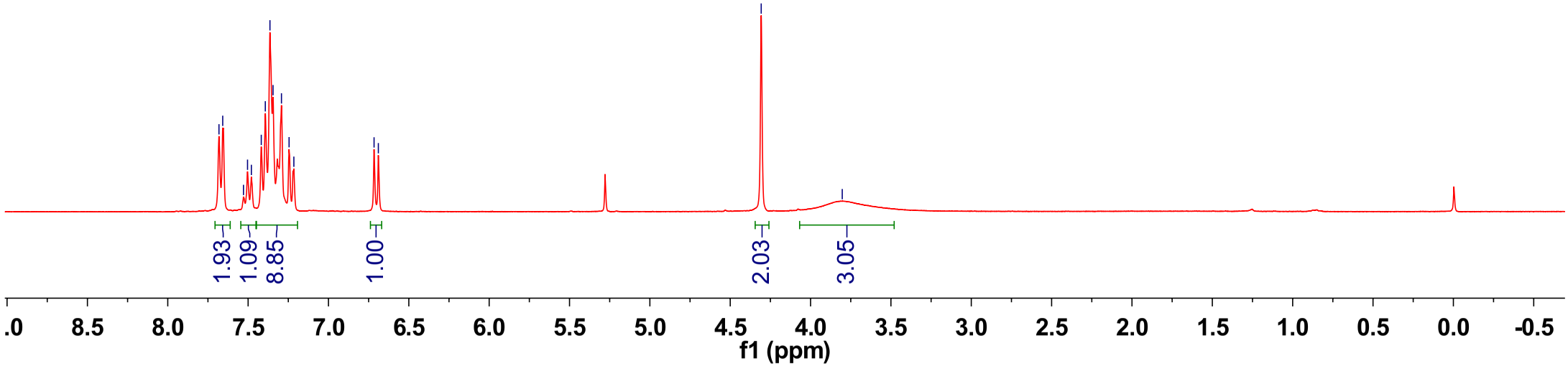
1r


7.68
7.66
7.53
7.50
7.48
7.42
7.39
7.36
7.34
7.29
7.25
7.22
6.72
6.69


4.31
3.80


O
NH
NH2

1t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6.0
5.5
5.0
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3.5
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1.0
0.5
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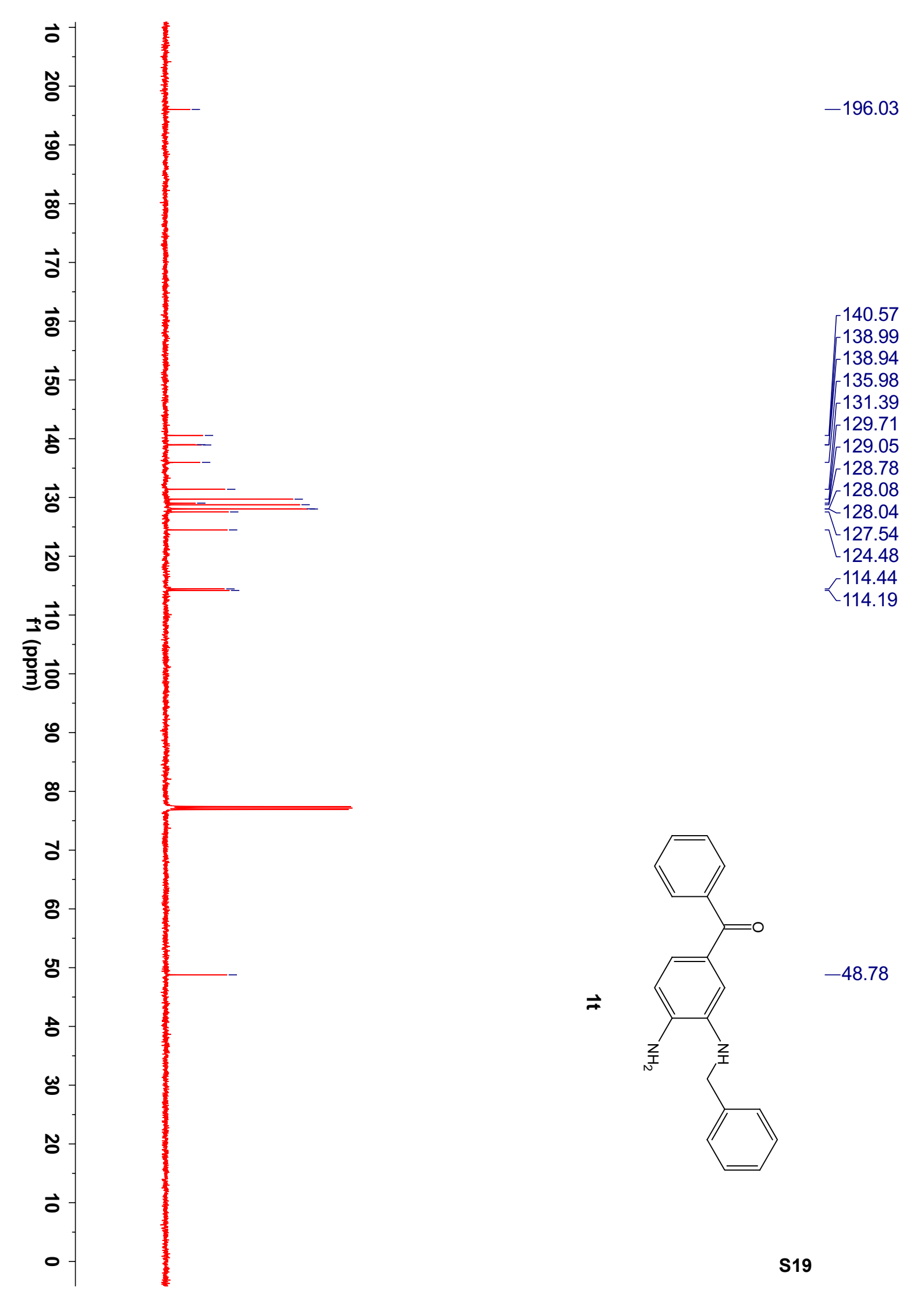
f1 (ppm)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114.44
114.19
48.78
f1 (ppm)
10
200
190
180
170
160
150
140
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20
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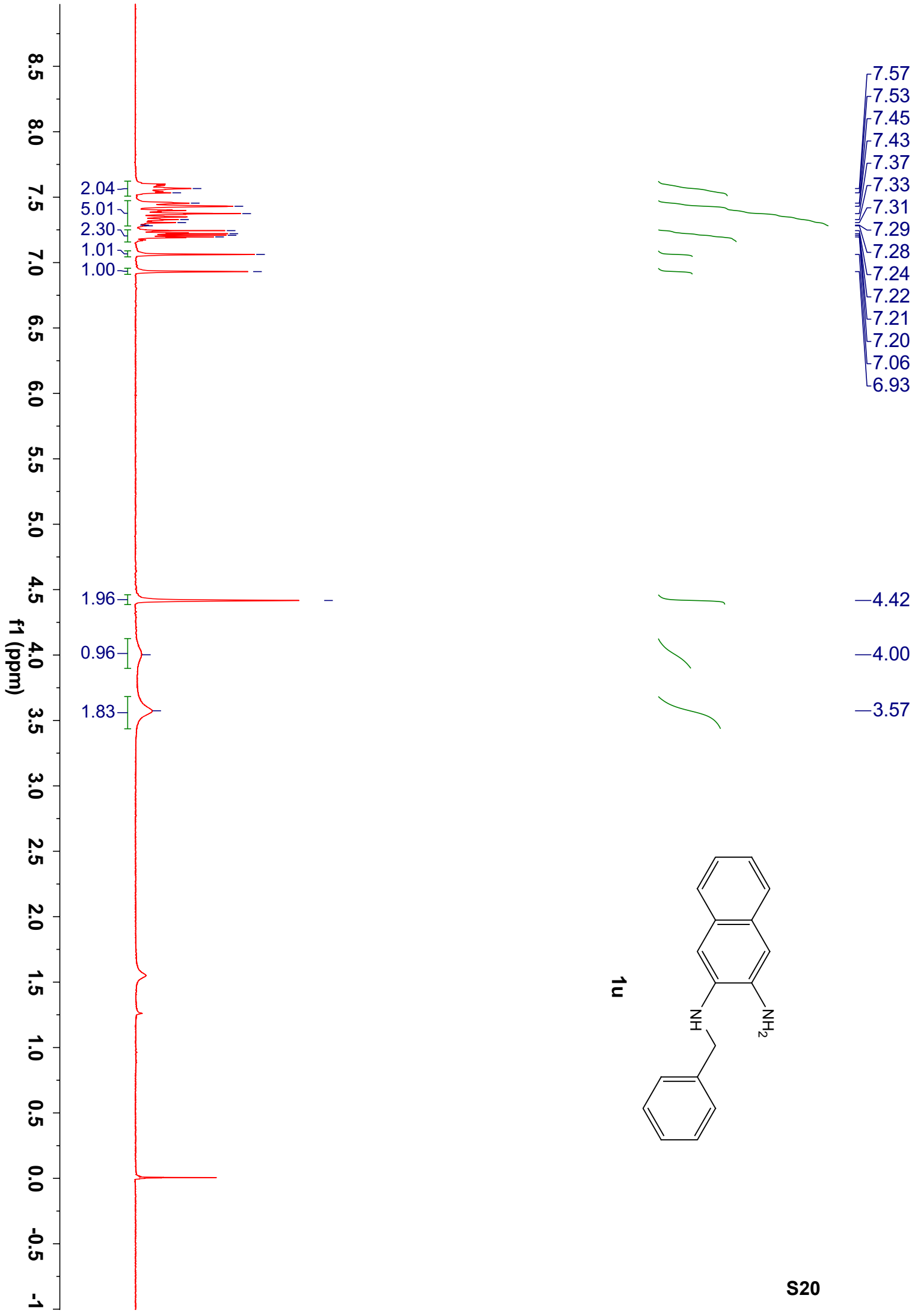
O
NH2
NH

1t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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
2.04
5.01
2.30
1.01
1.00
1.96
0.96
1.83
7.57
7.53
7.45
7.43
7.37
7.33
7.31
7.29
7.28
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4.42
4.00
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NH
NH2

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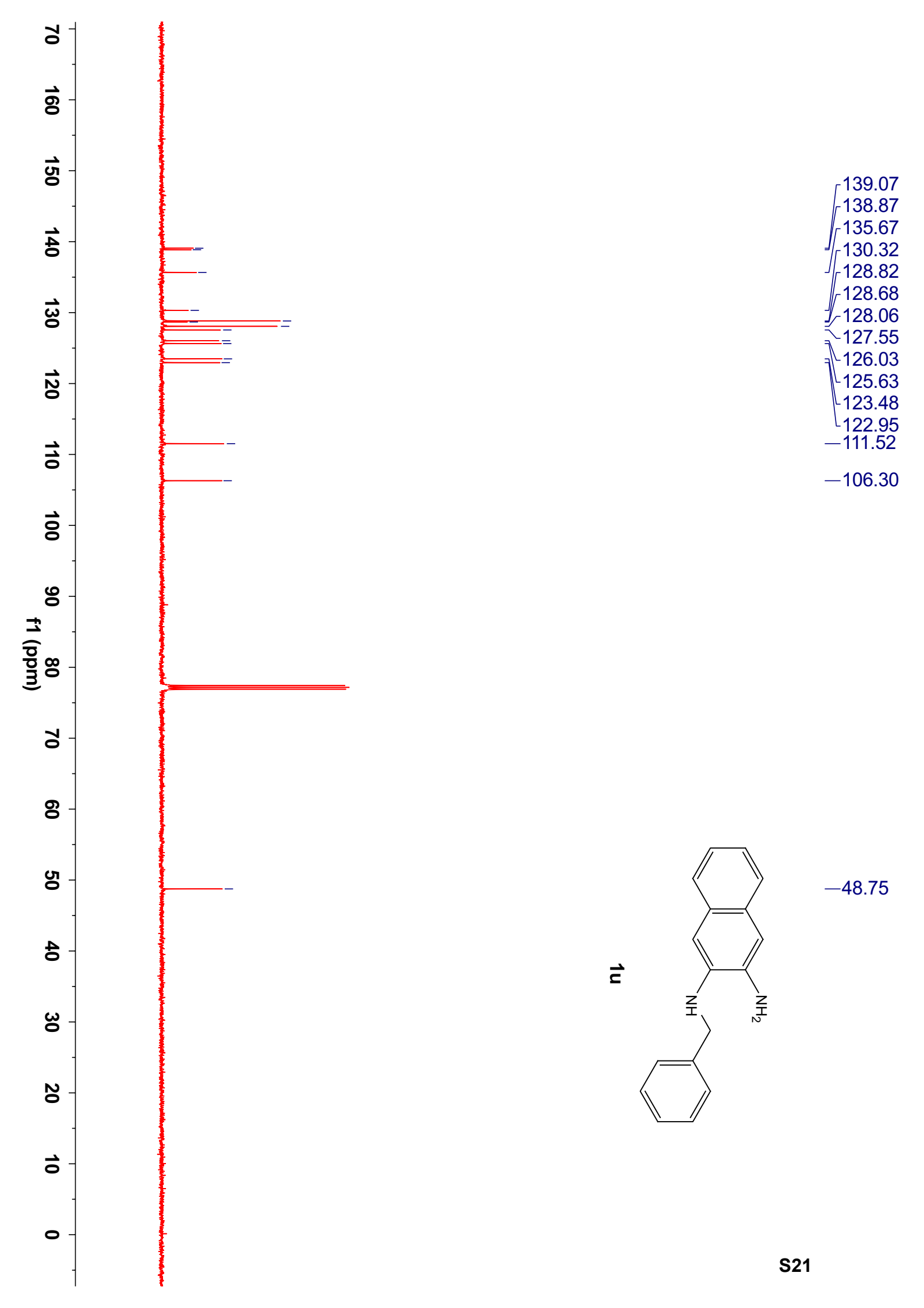
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138.87
135.67
130.32
128.82
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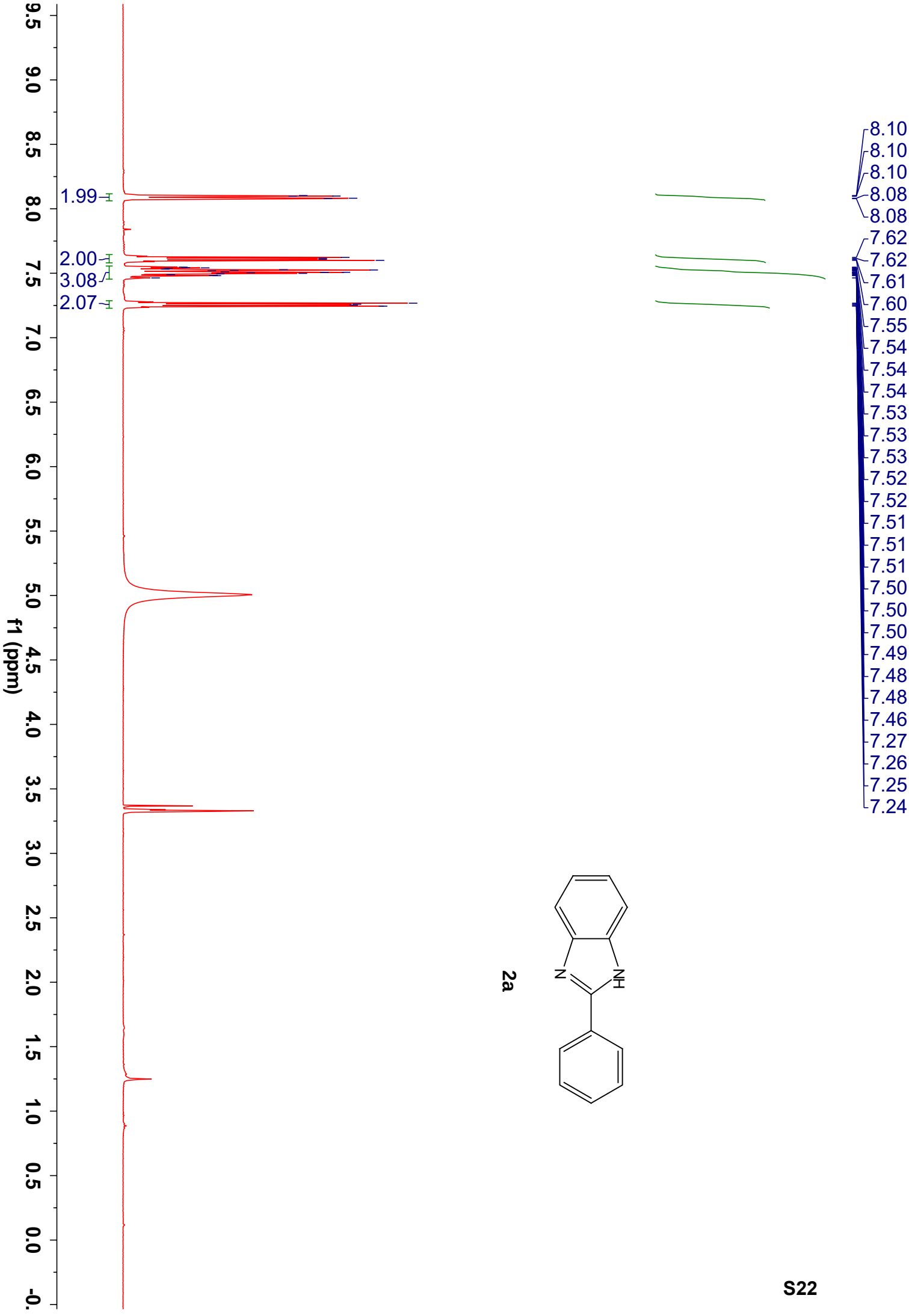
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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1.99
2.00
3.08
2.07
8.10
8.10
8.10
8.08
8.08
7.62
7.62
7.61
7.60
7.55
7.54
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
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7.51
7.50
7.50
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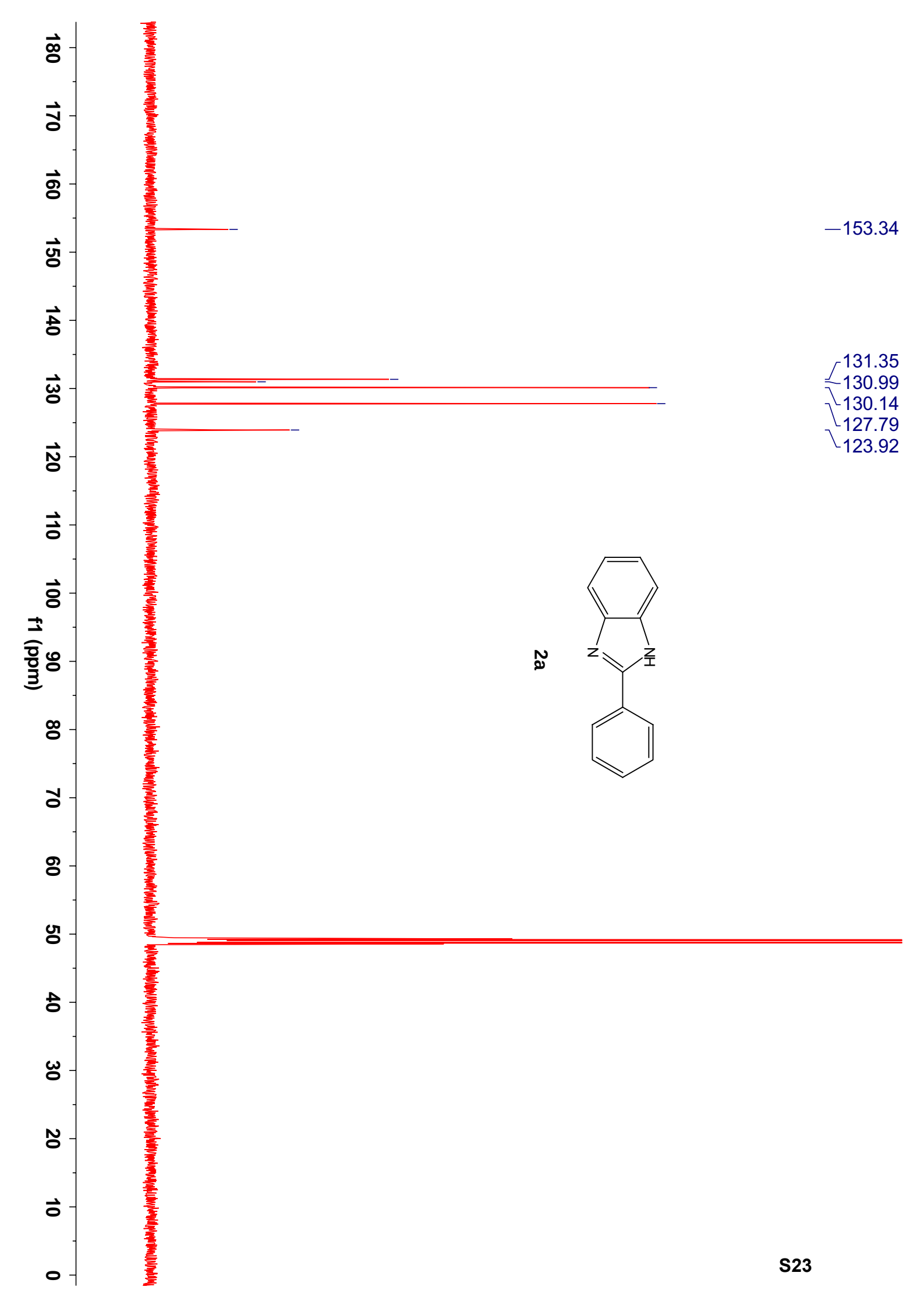
7.48
7.46
7.27
7.26
7.25
7.24
N
NH

2a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127.79
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f1 (ppm)
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170
160
150
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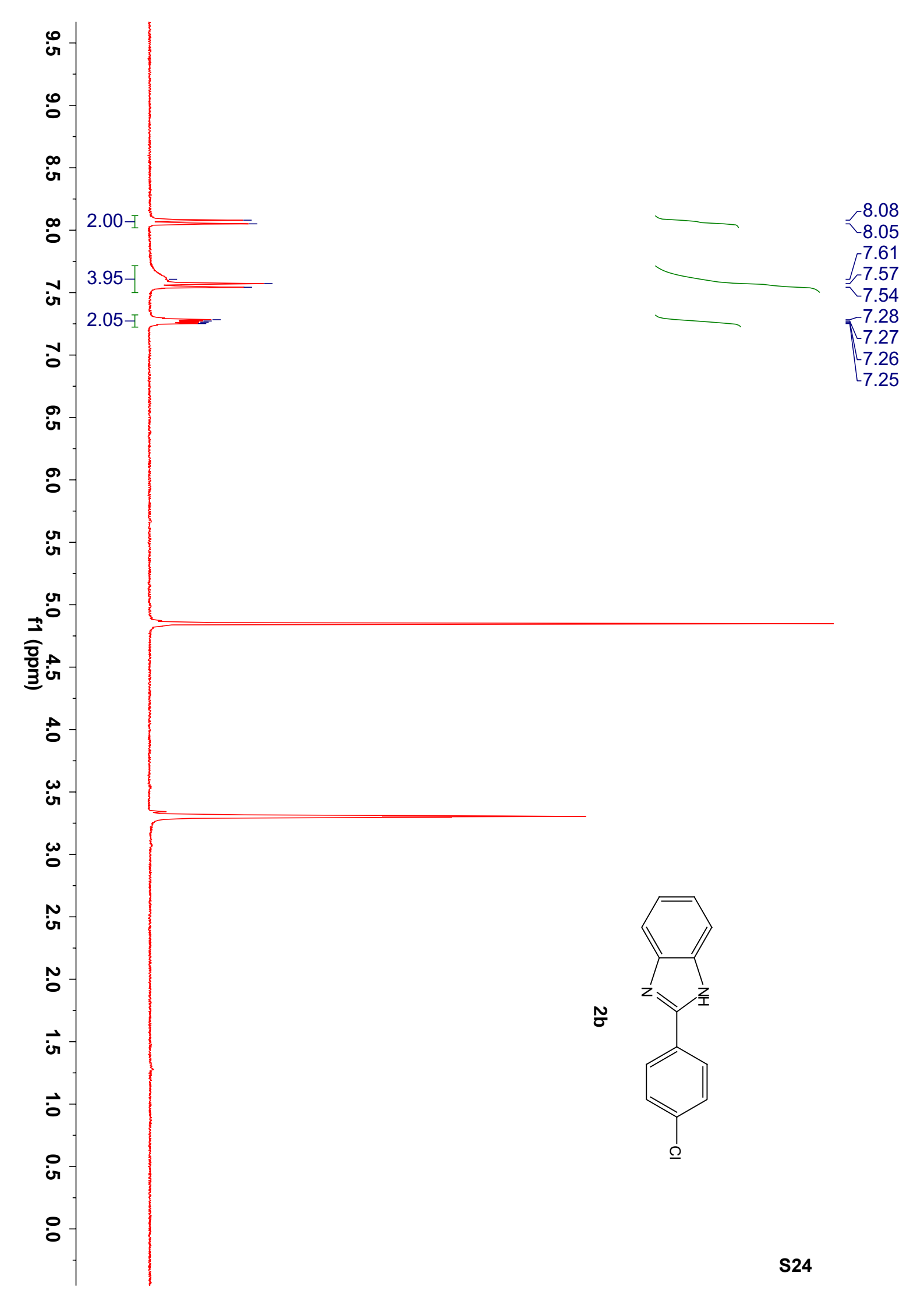
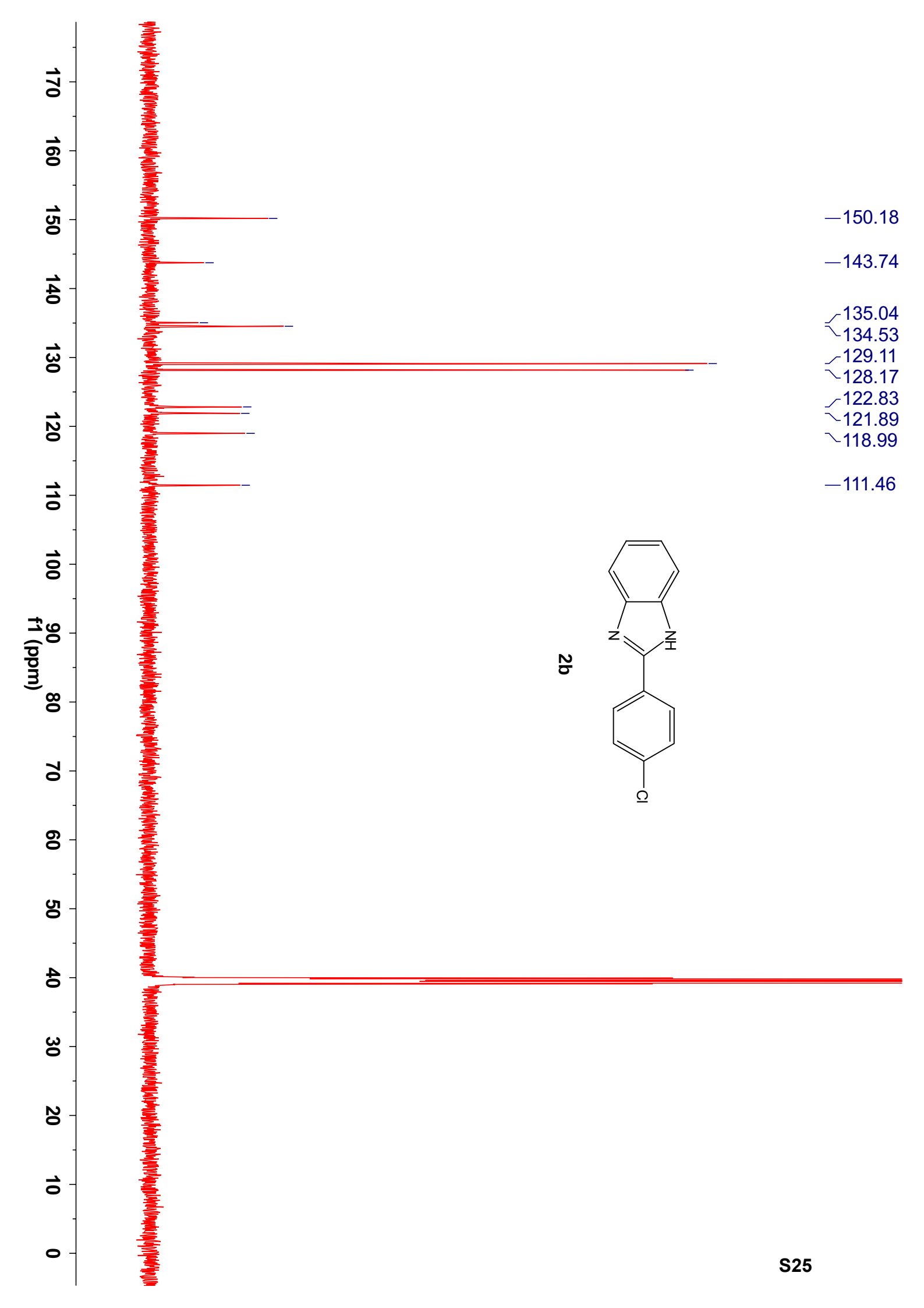
120
110
100
90
80
70
60
50
40
30
20
10
0
N
NH
2a


2.00
3.95
2.05
8.08
8.05
7.61
7.57
7.54
7.28
7.27
7.26
7.25
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
NH
Cl

2b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143.74
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f1 (ppm)
170
160
150
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110
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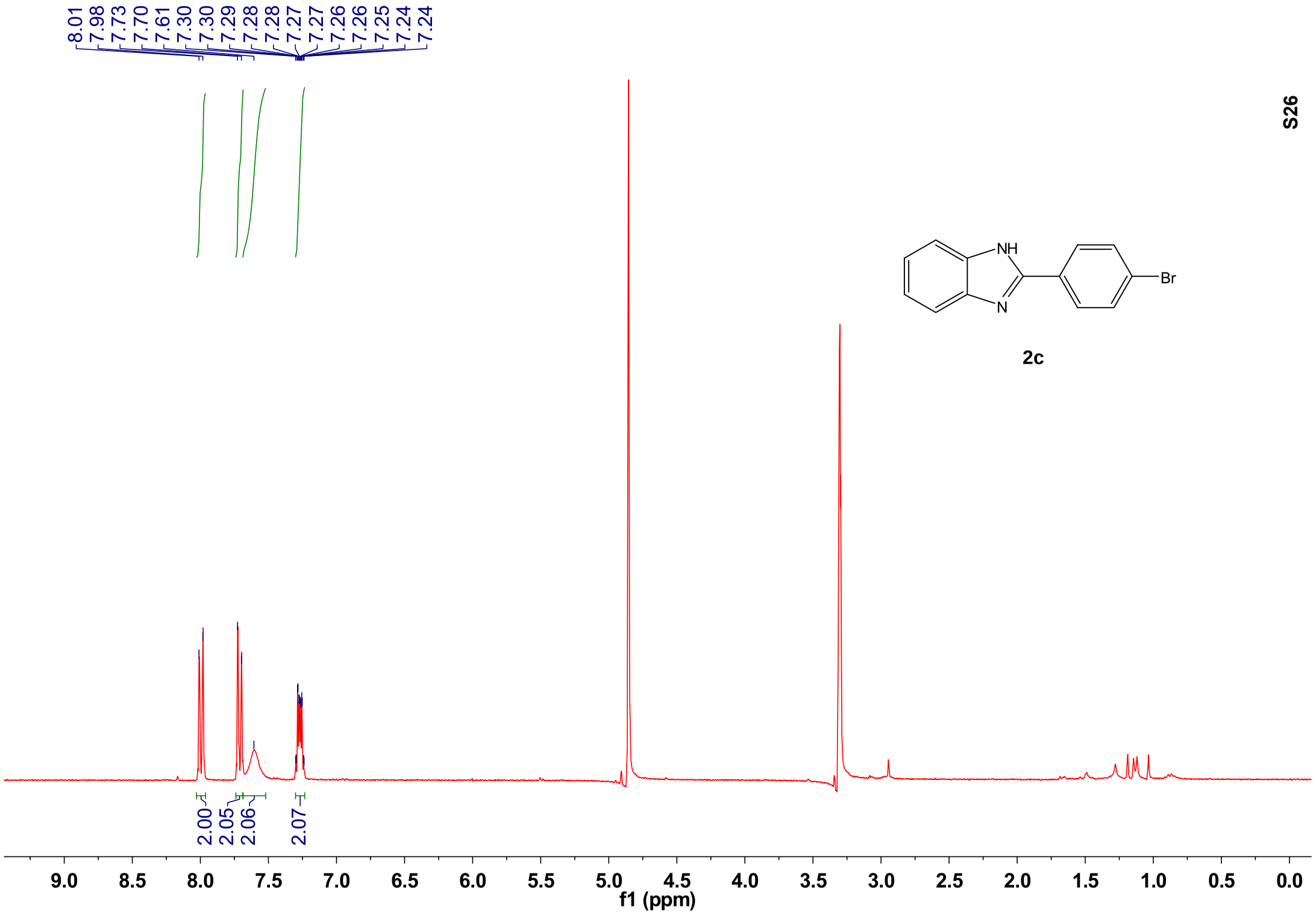
NH
Cl

2b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7.98
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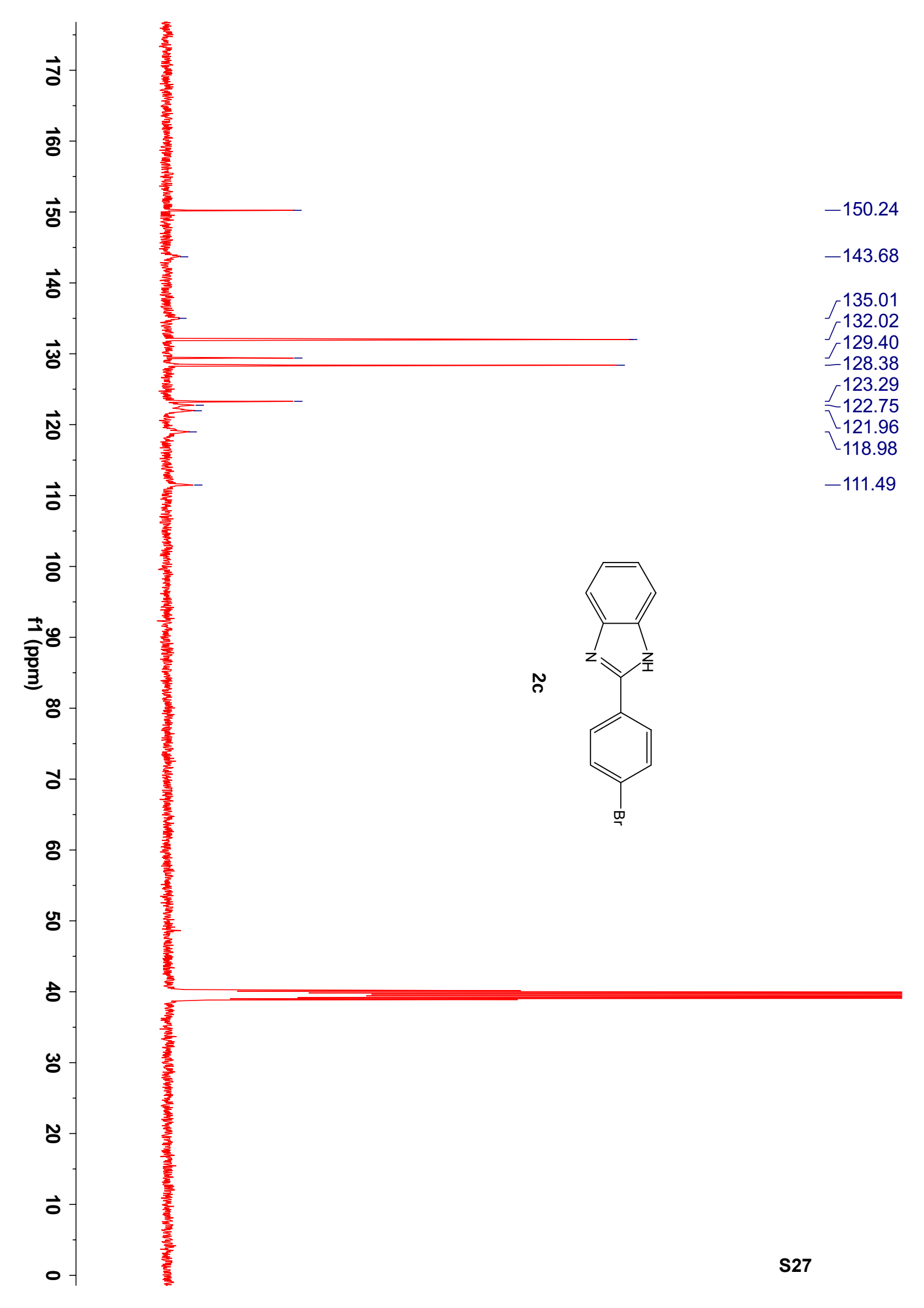
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
NH
N
Br
2c
2.00
2.05
2.06
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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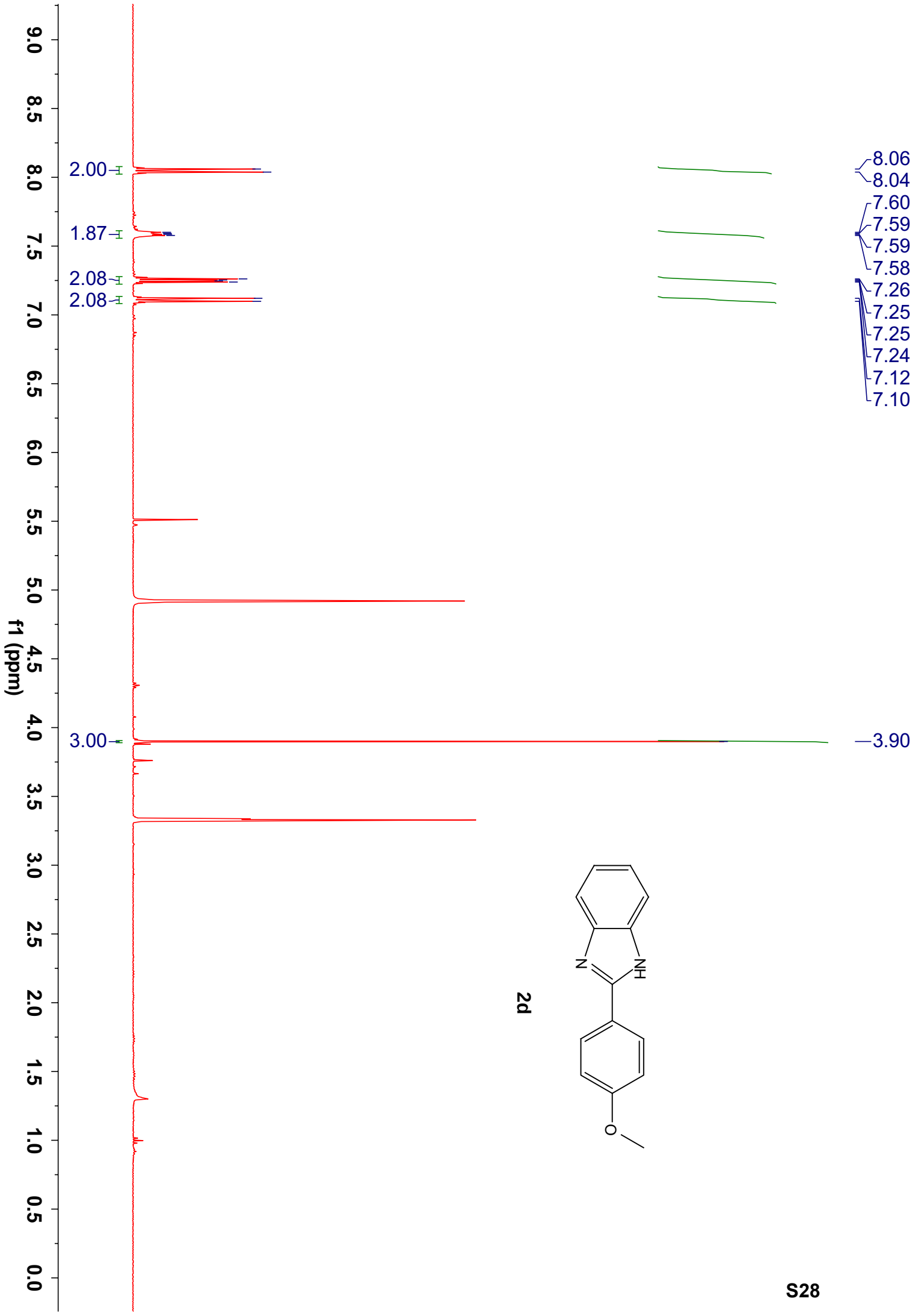
132.02
129.40
128.38
123.29
122.75
121.96
118.98
111.49
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
NH
Br
2c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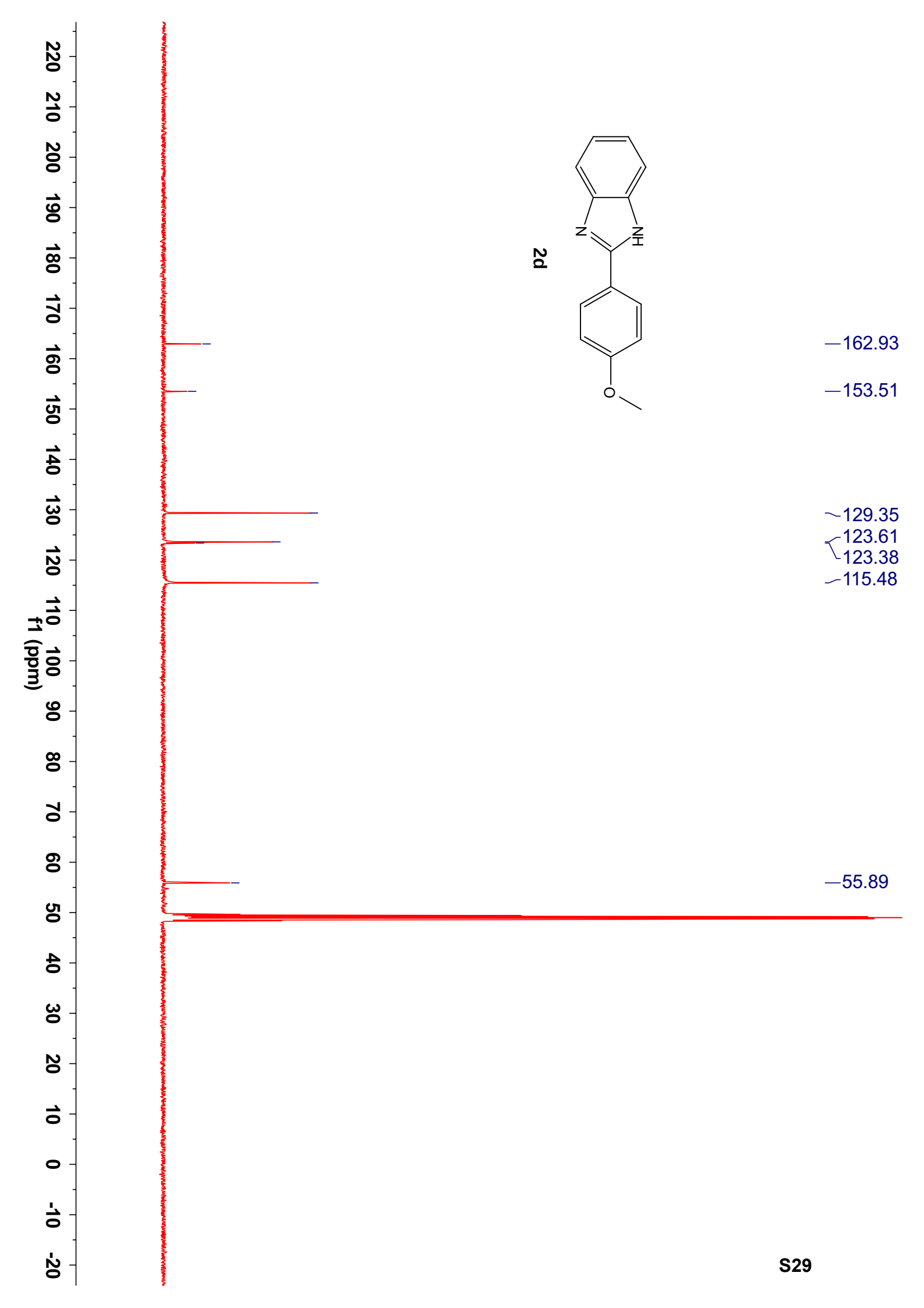
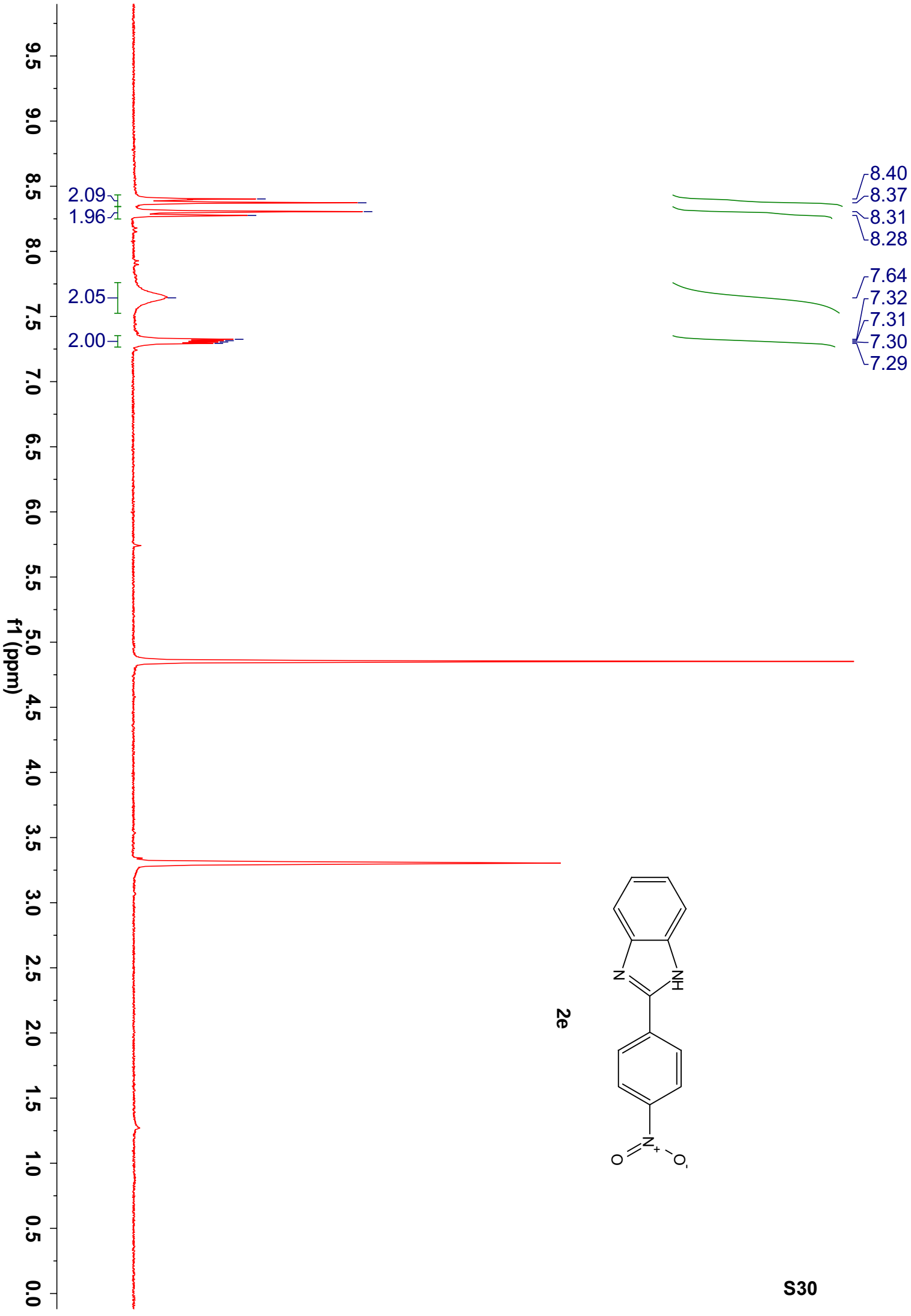
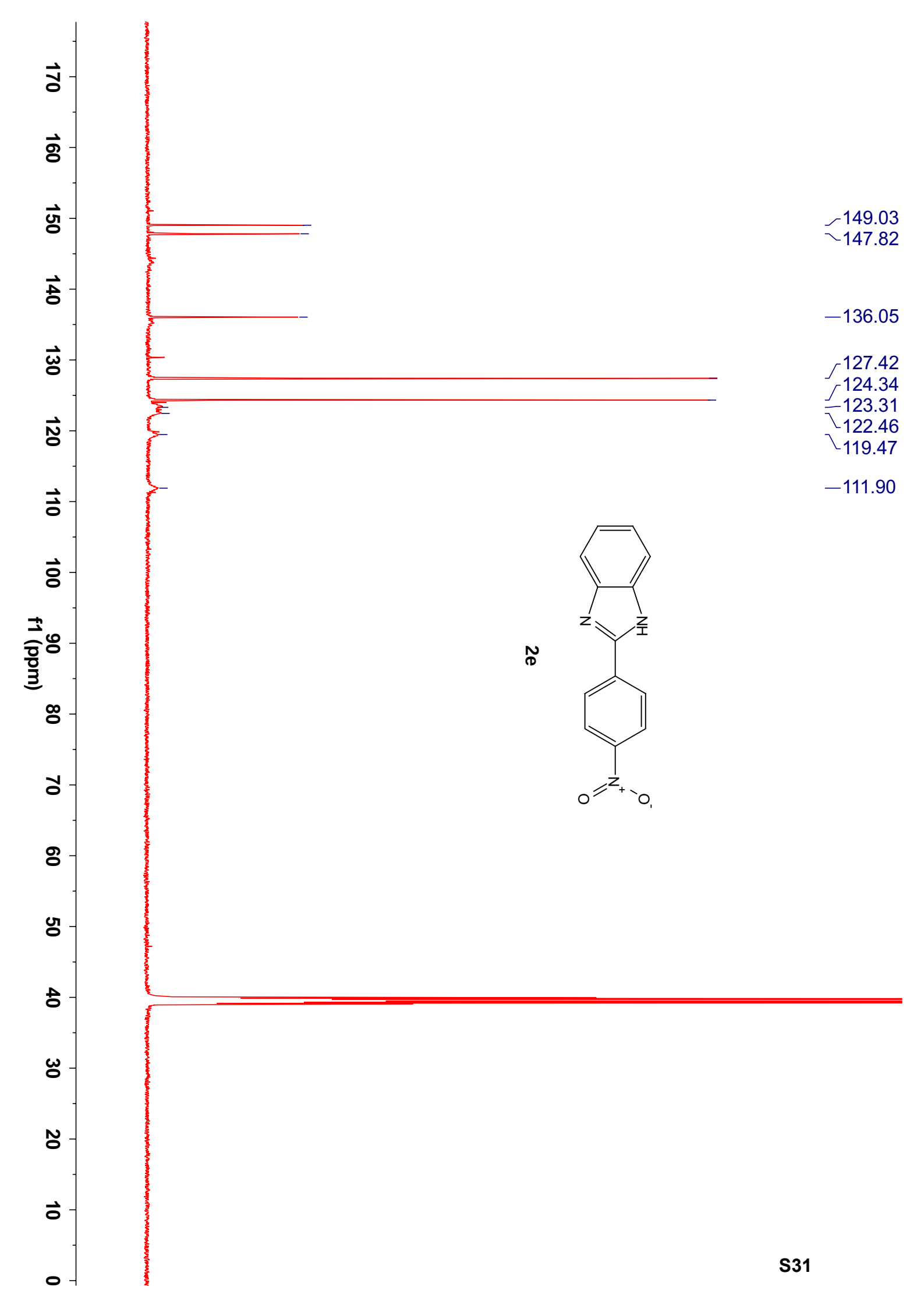
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2.00
1.87
2.08
2.08
3.00
8.06
8.04
7.60
7.59
7.59
7.58
7.26
7.25
7.25
7.24
7.12
7.10
3.90
N
NH
O

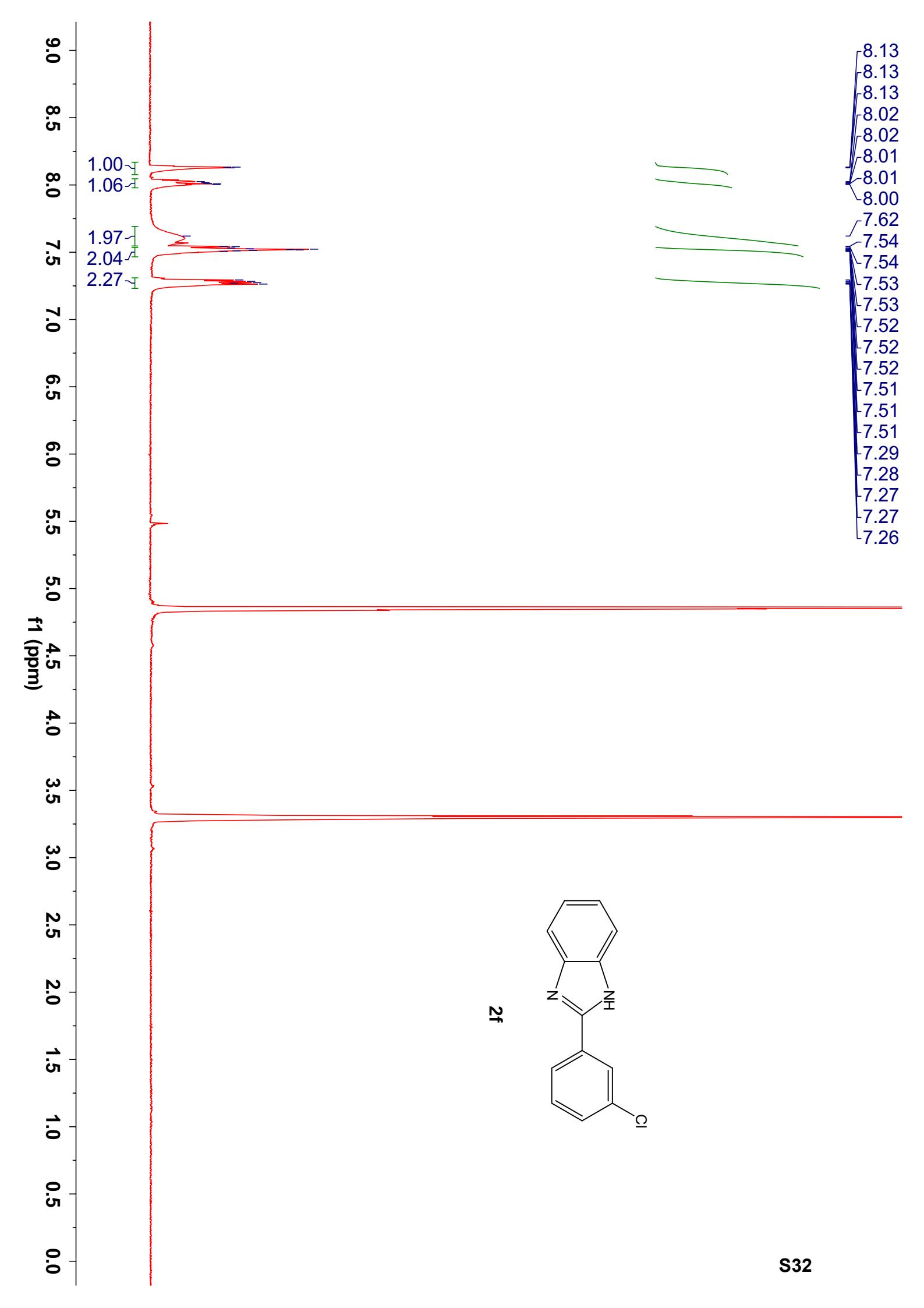
2d


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
2d
N
NH
O
162.93
153.51
129.35
123.61
123.38
115.48
55.89

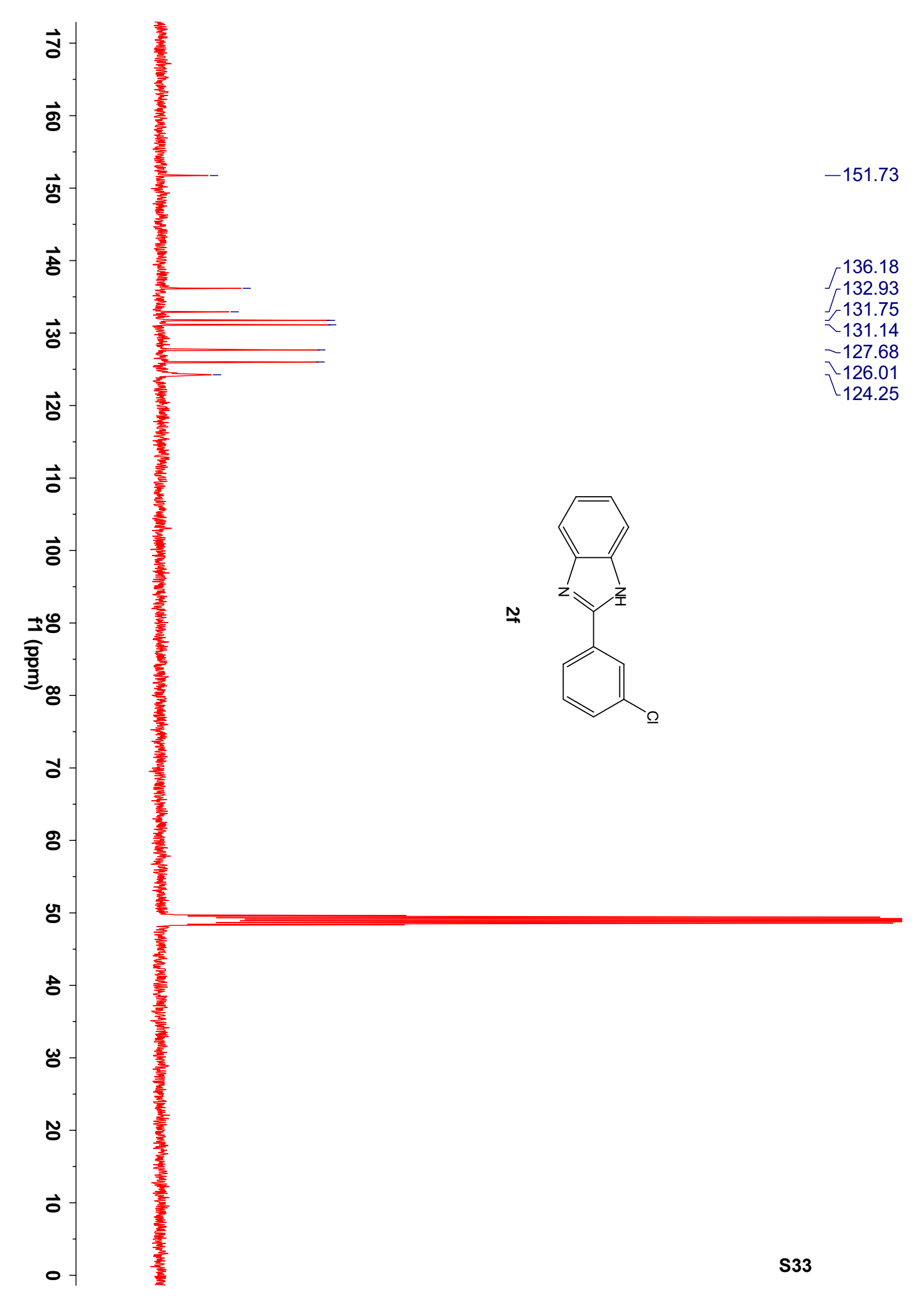

2.09
1.96
2.05
2.00
8.40
8.37
8.31
8.28
7.64
7.32
7.31
7.30
7.29
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
NH
O
N+
O-

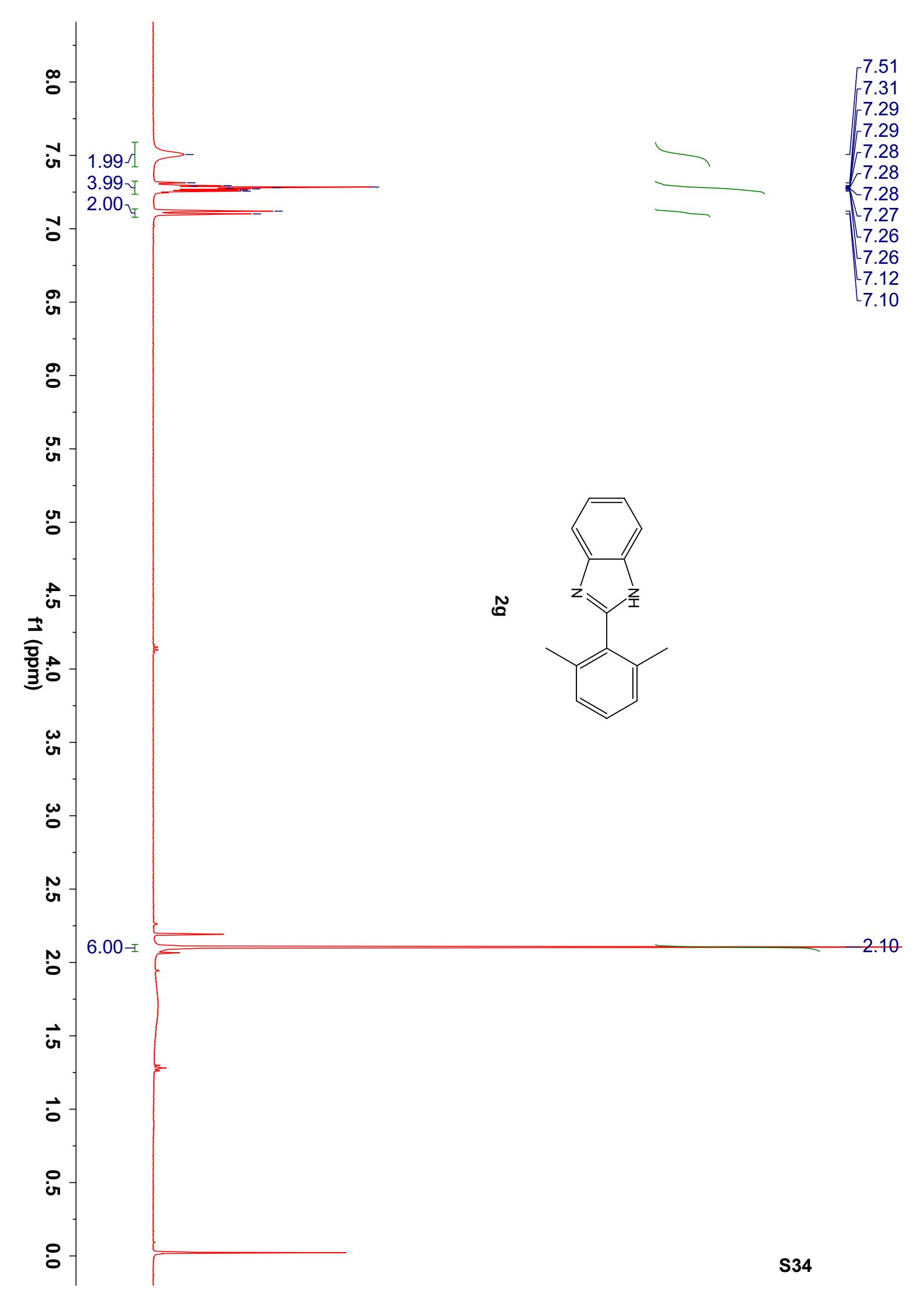
2e

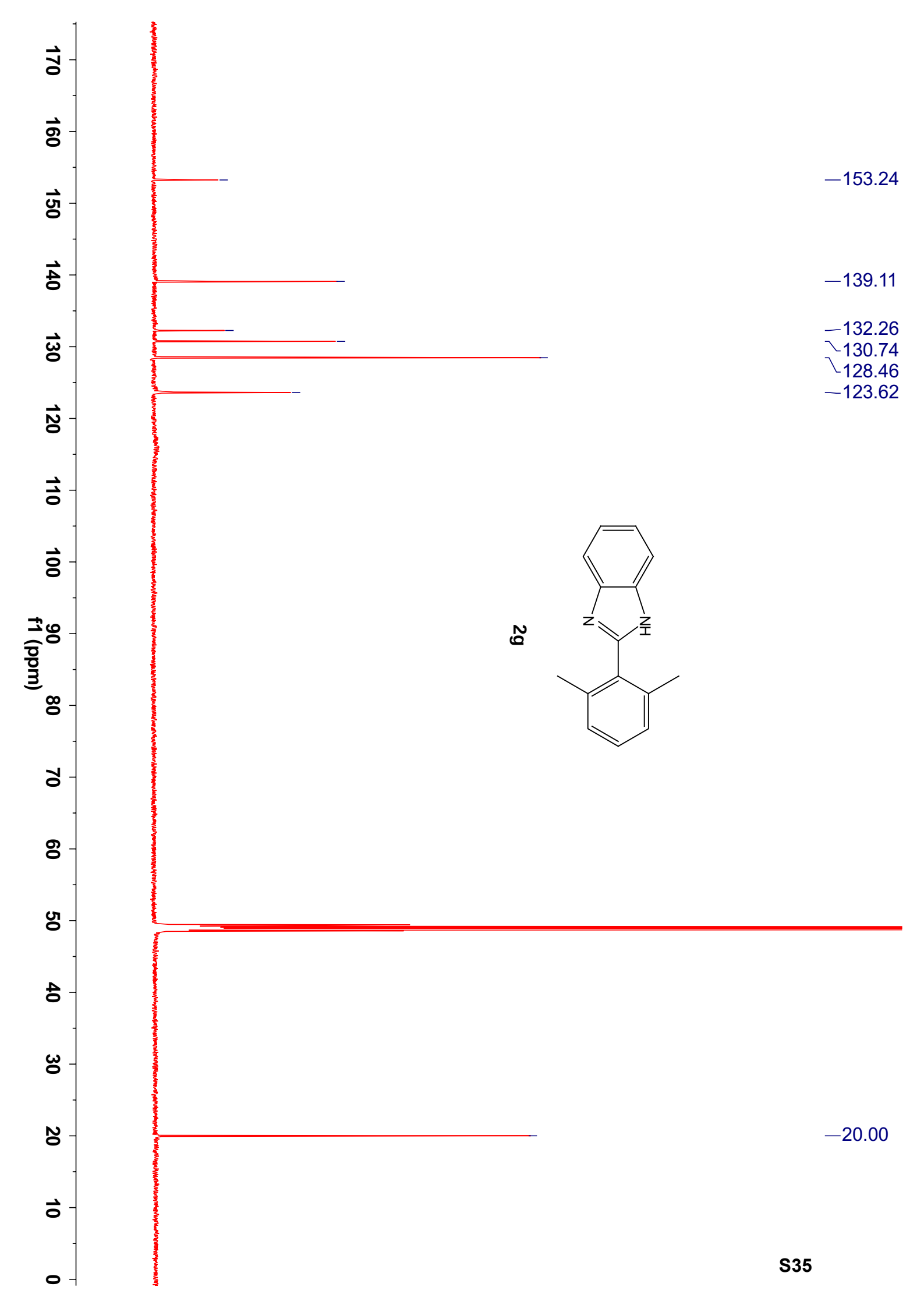

149.03
147.82
136.05
127.42
124.34
123.31
122.46
119.47
111.90
f1 (ppm)
2e

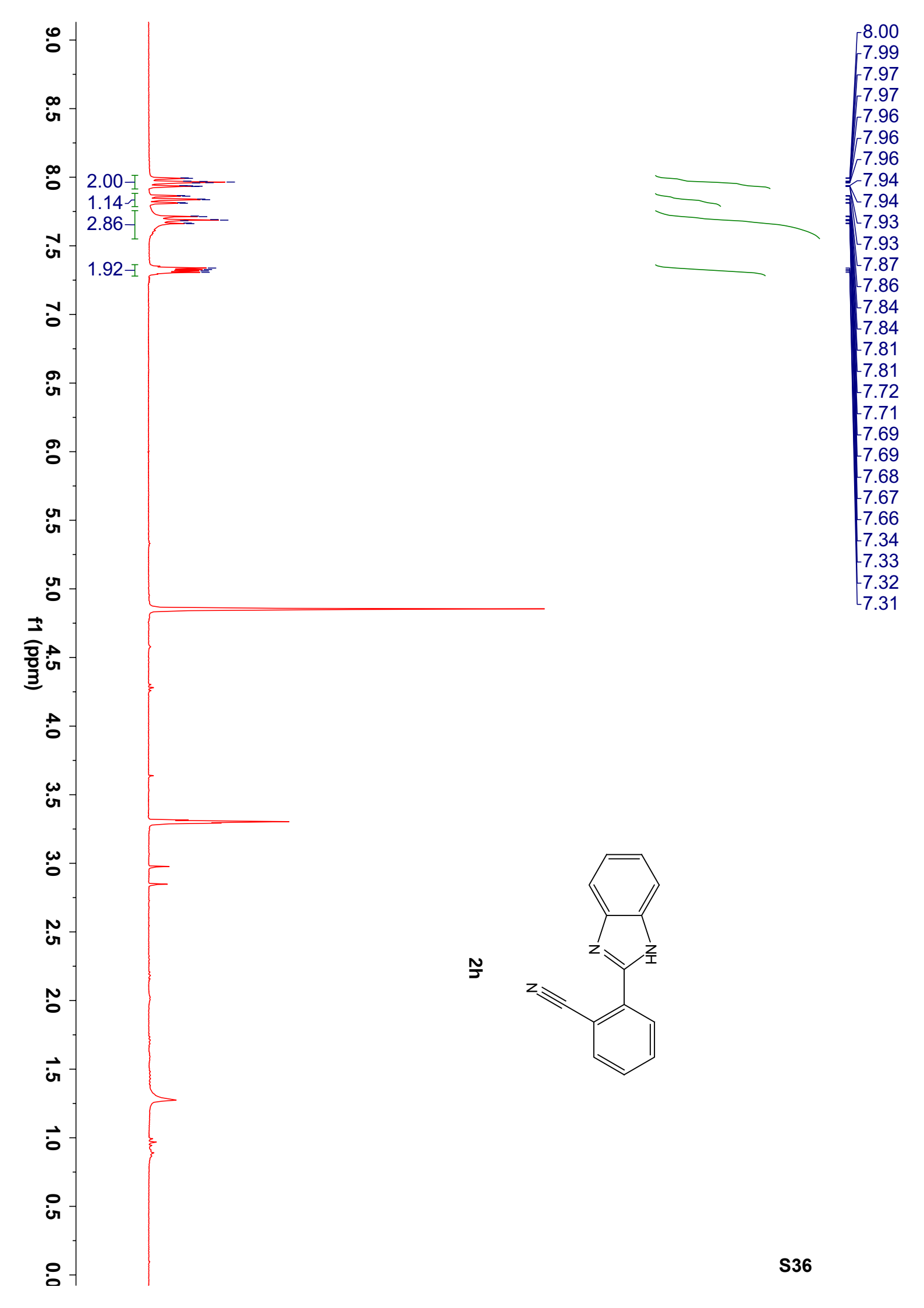

8.13
8.13
8.13
8.02
8.02
8.01
8.01
8.00
7.62
7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.51
7.29
7.28
7.27
7.27
7.26
1.00
1.06
1.97
2.04
2.27
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
NH
Cl

2f

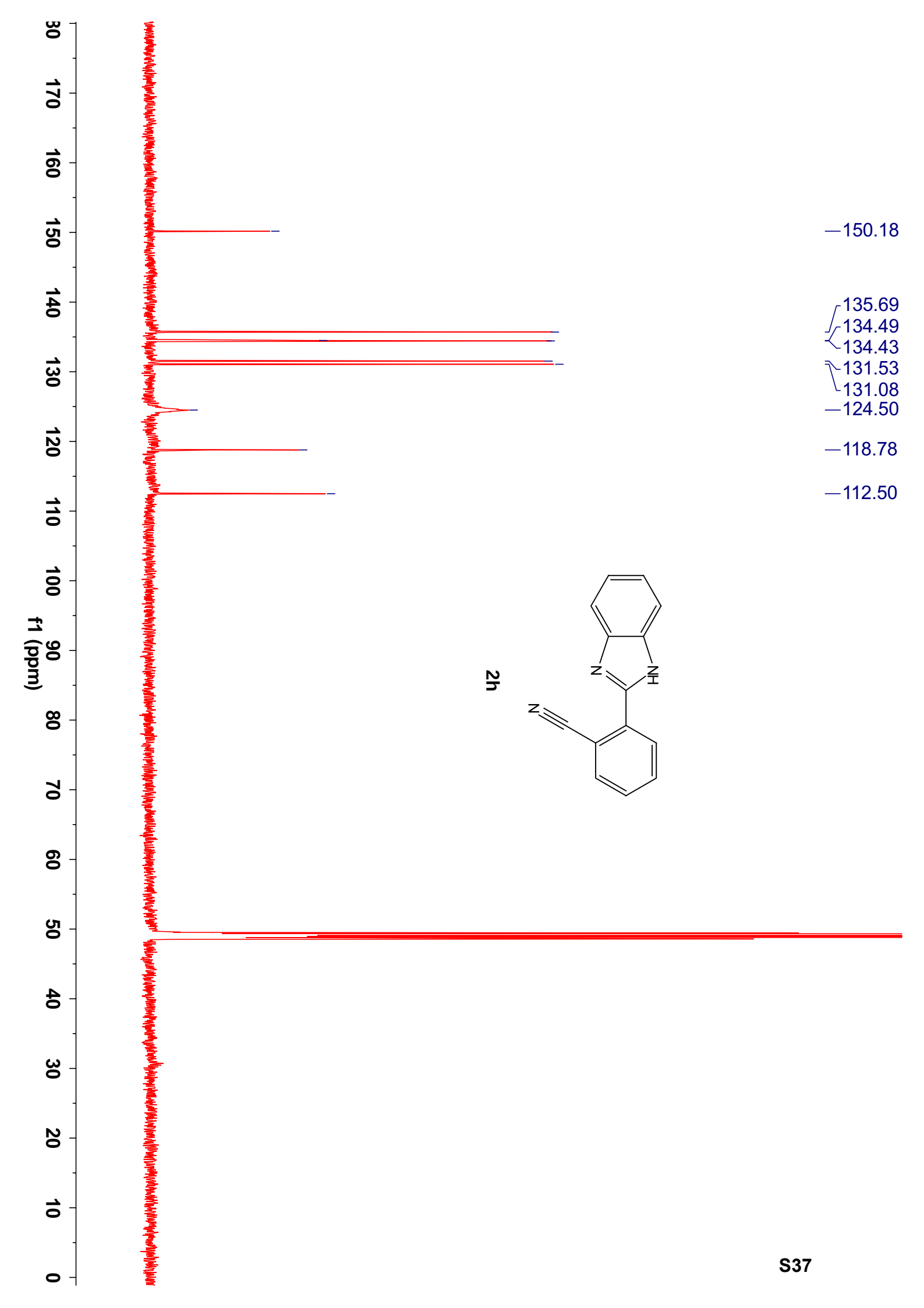

151.73
136.18
132.93
131.75
131.14
127.68
126.01
124.25
2f
N
NH
Cl
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

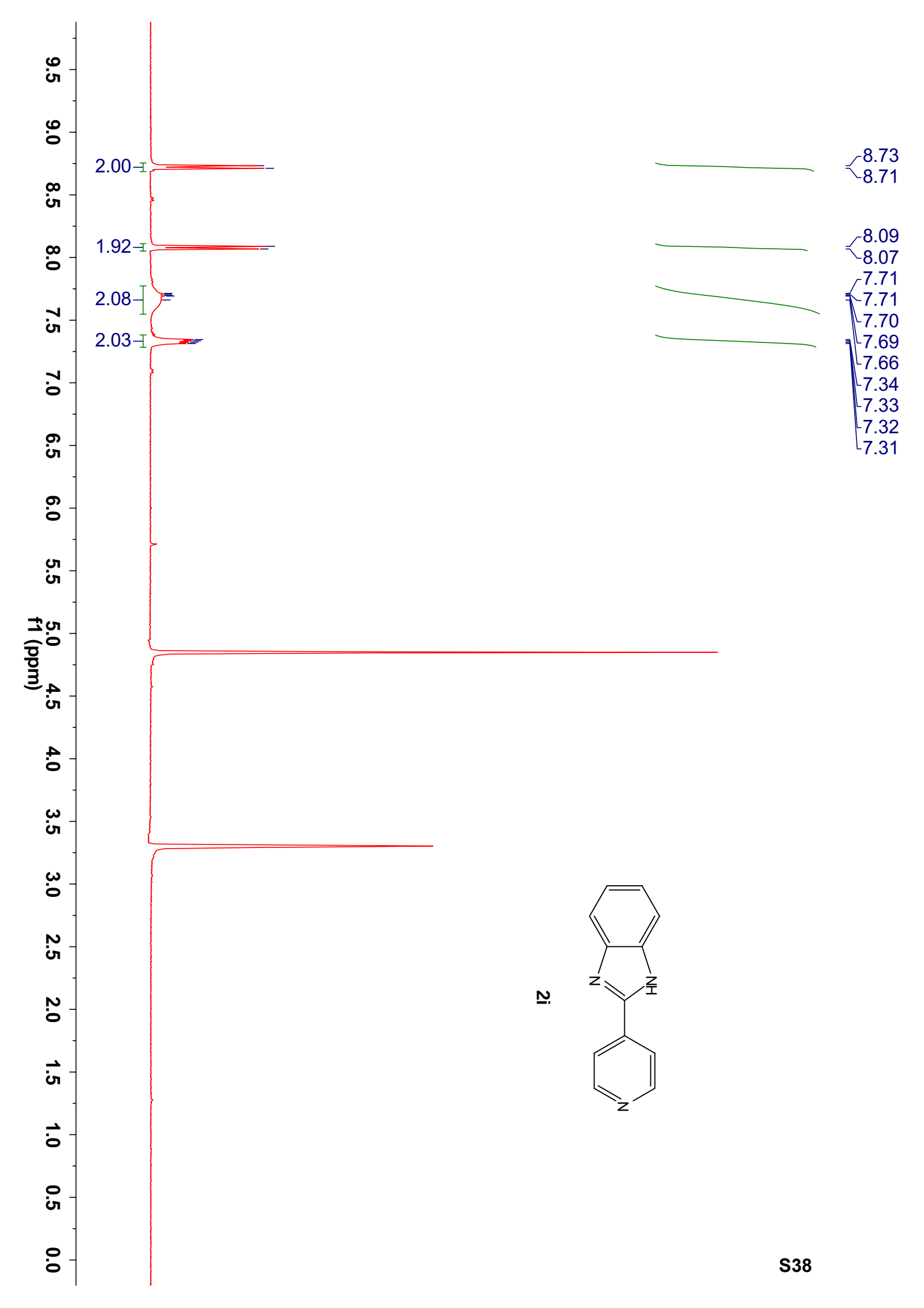

7.51
7.31
7.29
7.29
7.28
7.28
7.28
7.27
7.26
7.26
7.12
7.10
1.99
3.99
2.00
6.00
2.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
N
NH
2g


153.24
139.11
132.26
130.74
128.46
123.62
20.00
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
NH
2g

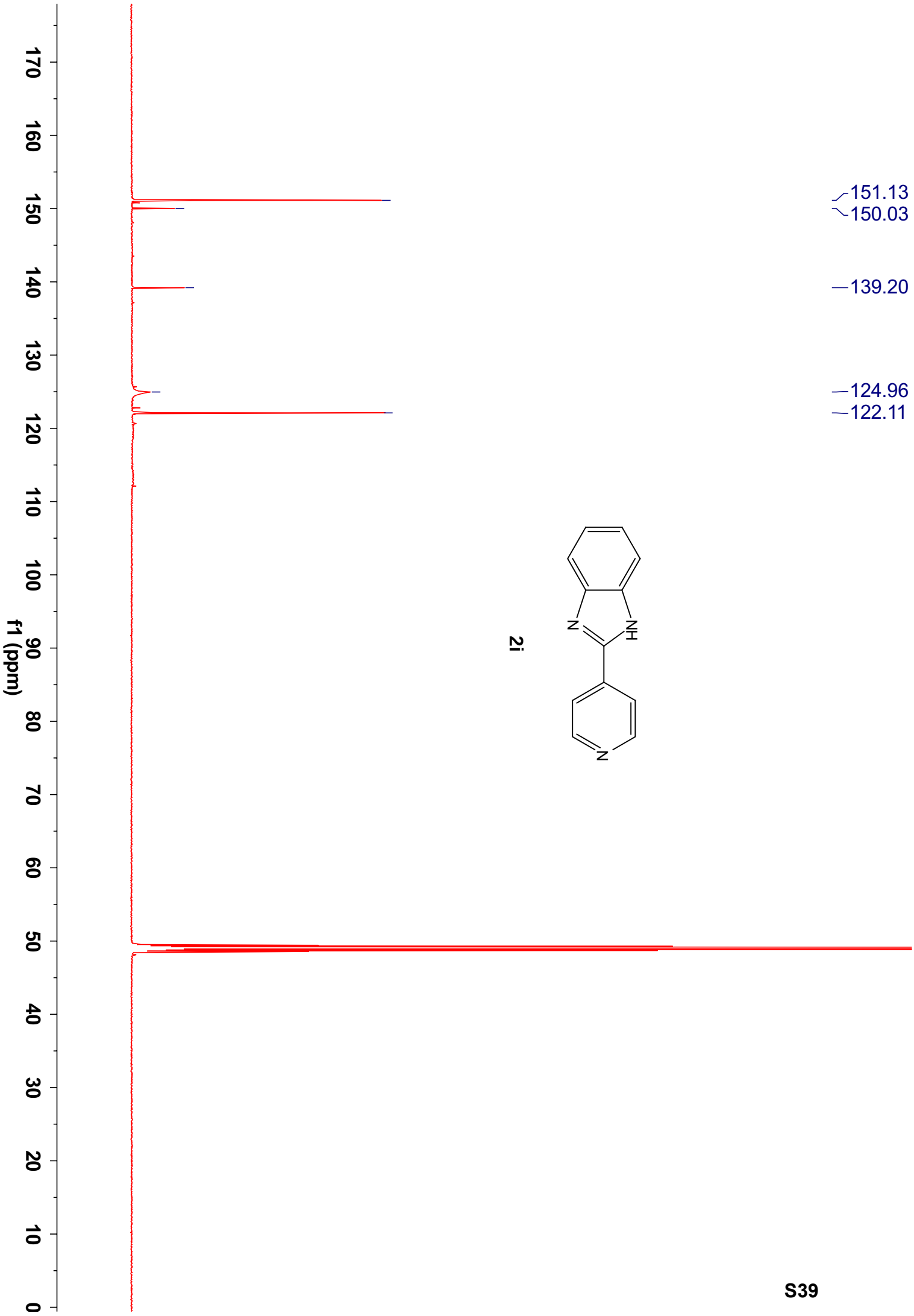

f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.00
1.14
2.86
1.92
8.00
7.99
7.97
7.97
7.96
7.96
7.96
7.94
7.94
7.93
7.93
7.87
7.86
7.84
7.84
7.81
7.81
7.72
7.71
7.69
7.69
7.68
7.67
7.66
7.34
7.33
7.32
7.31
N
NH
N

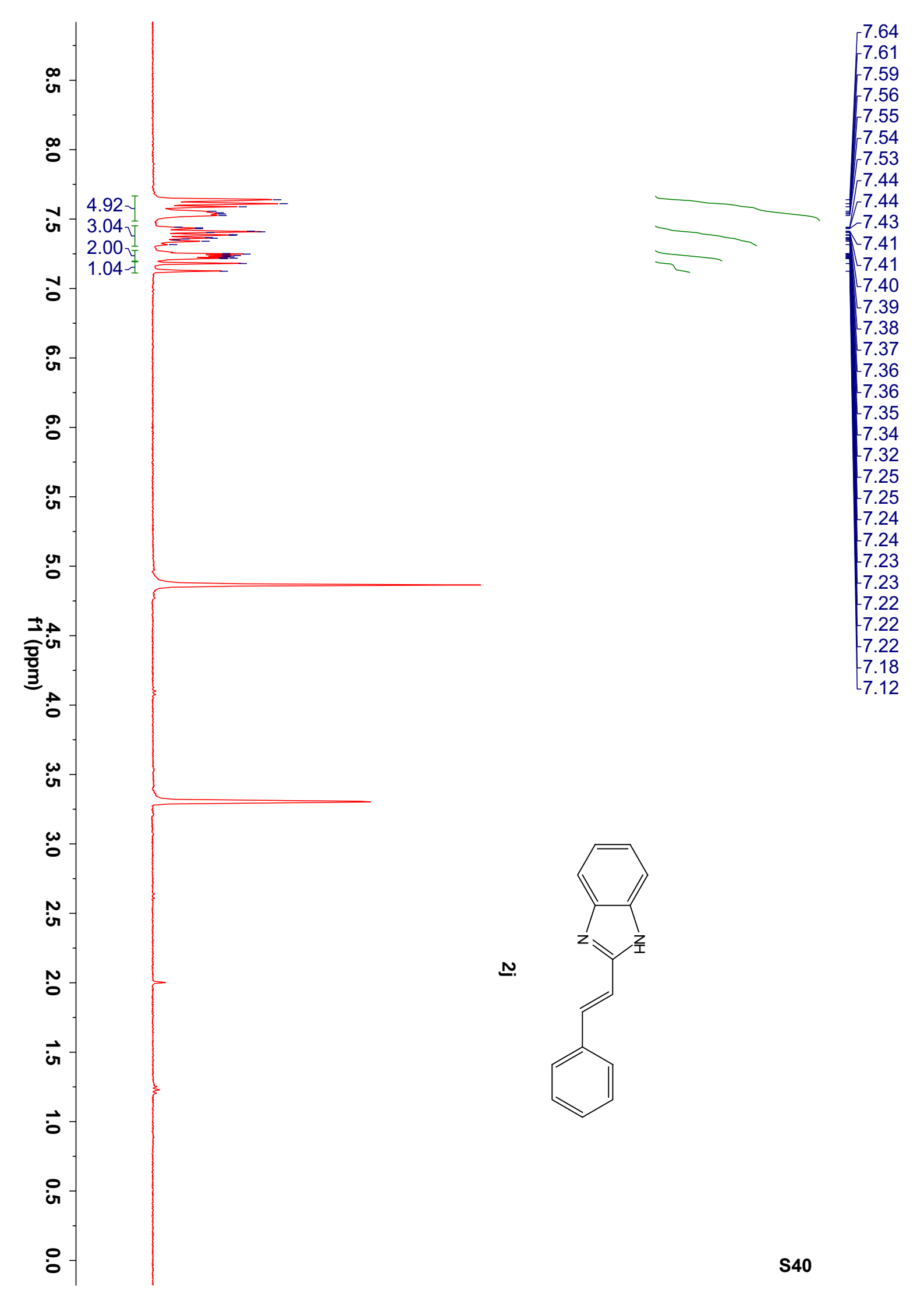
2h


150.18
135.69
134.49
134.43
131.53
131.08
124.50
118.78
112.50
f1 (ppm)
2h
N
NH
N

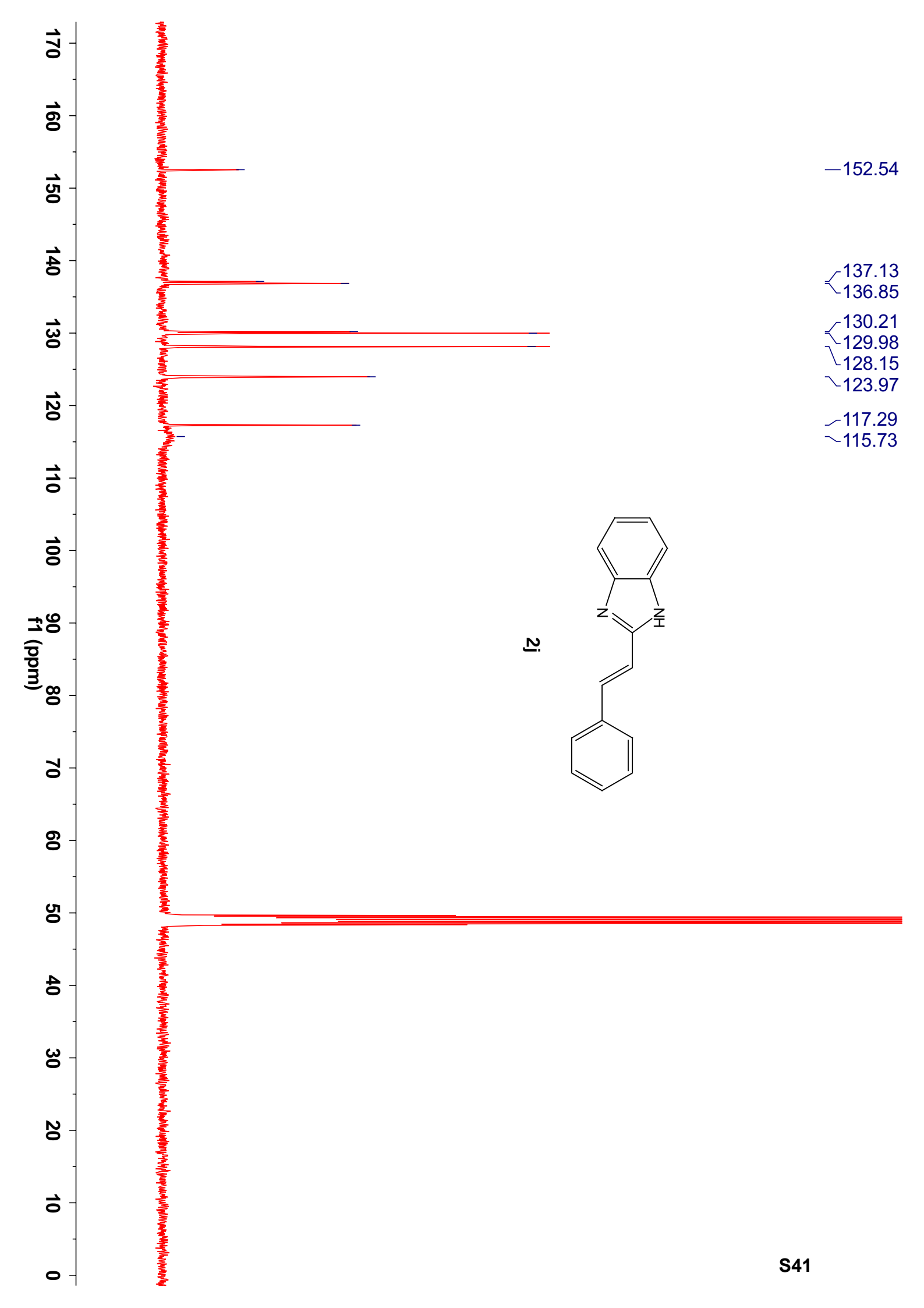

2.00
1.92
2.08
2.03
8.73
8.71
8.09
8.07
7.71
7.71
7.70
7.69
7.66
7.34
7.33
7.32
7.31
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
NH
N

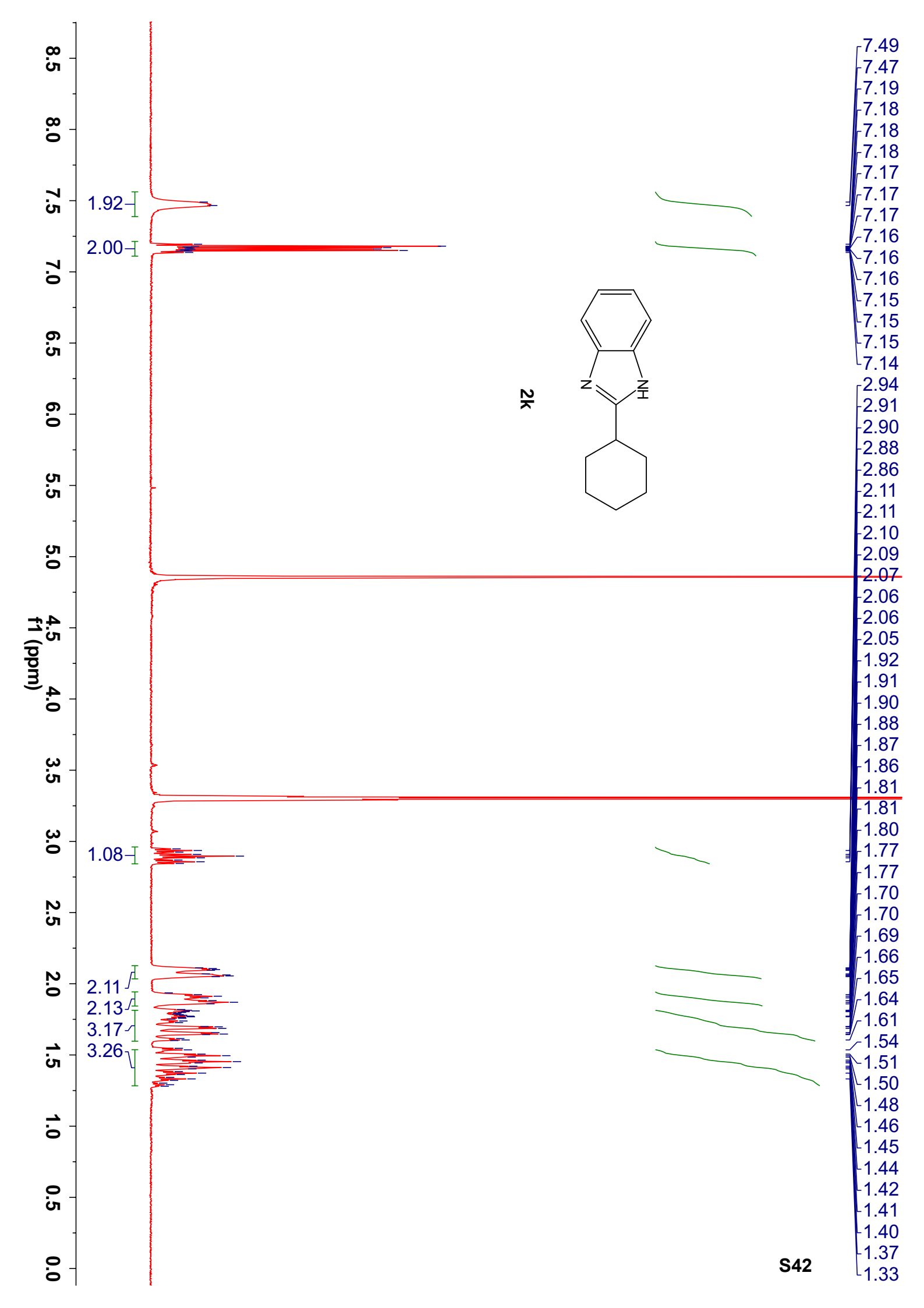
2i

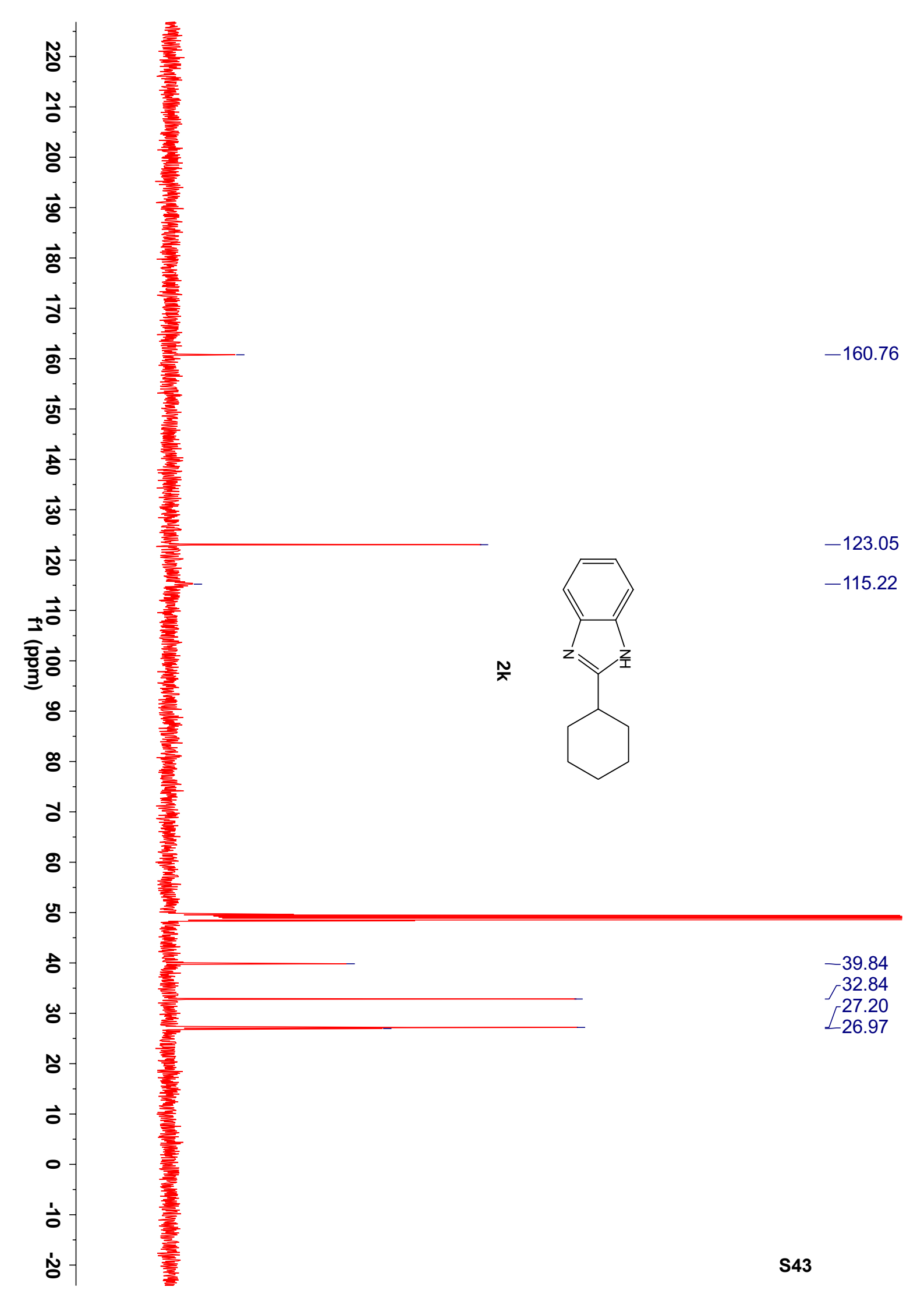

151.13
150.03
139.20
124.96
122.11
2i
N
NH
N
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

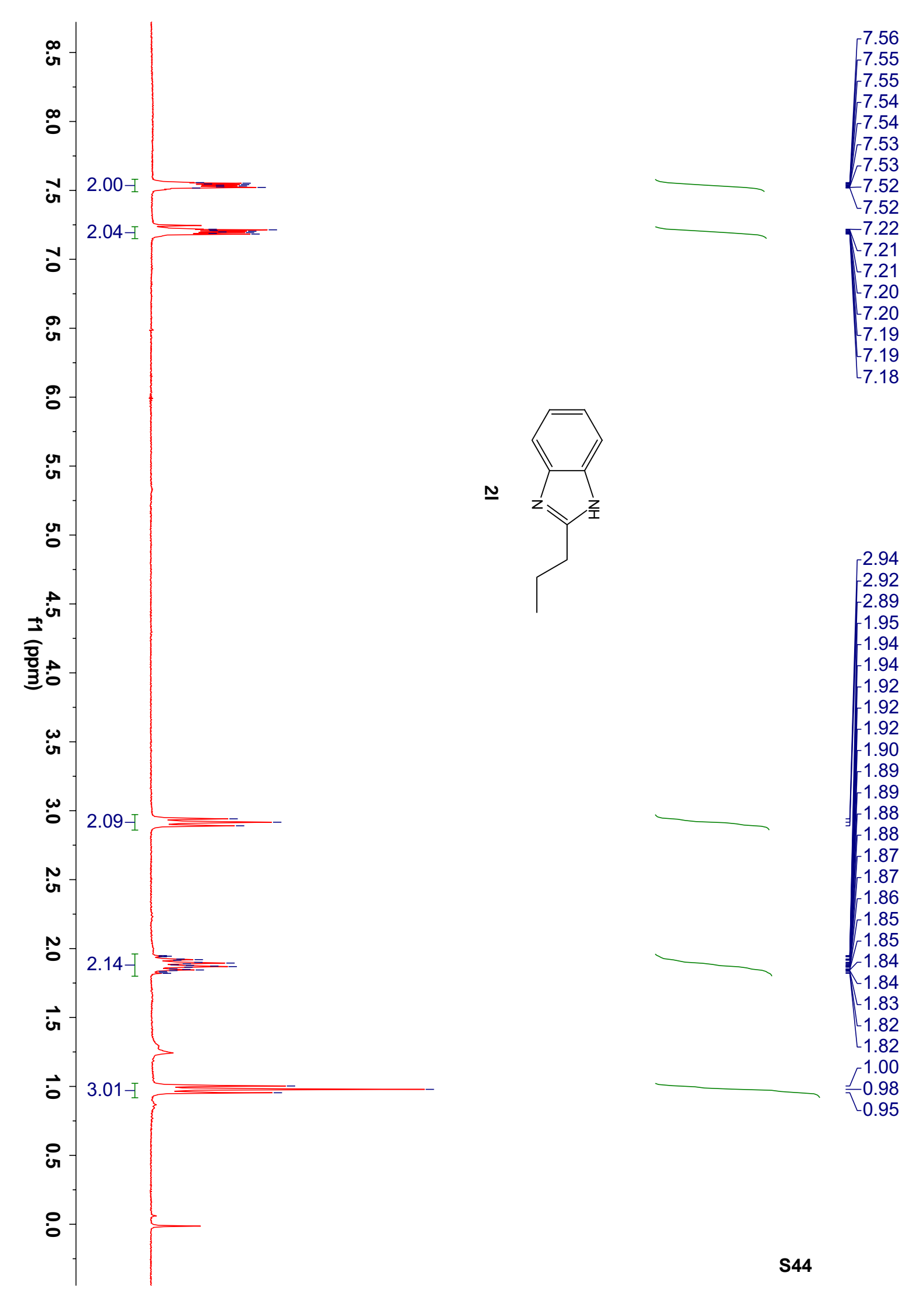

4.92
3.04
2.00
1.04
7.64
7.61
7.59
7.56
7.55
7.54
7.53
7.44
7.44
7.43
7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.32
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.18
7.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
N
NH

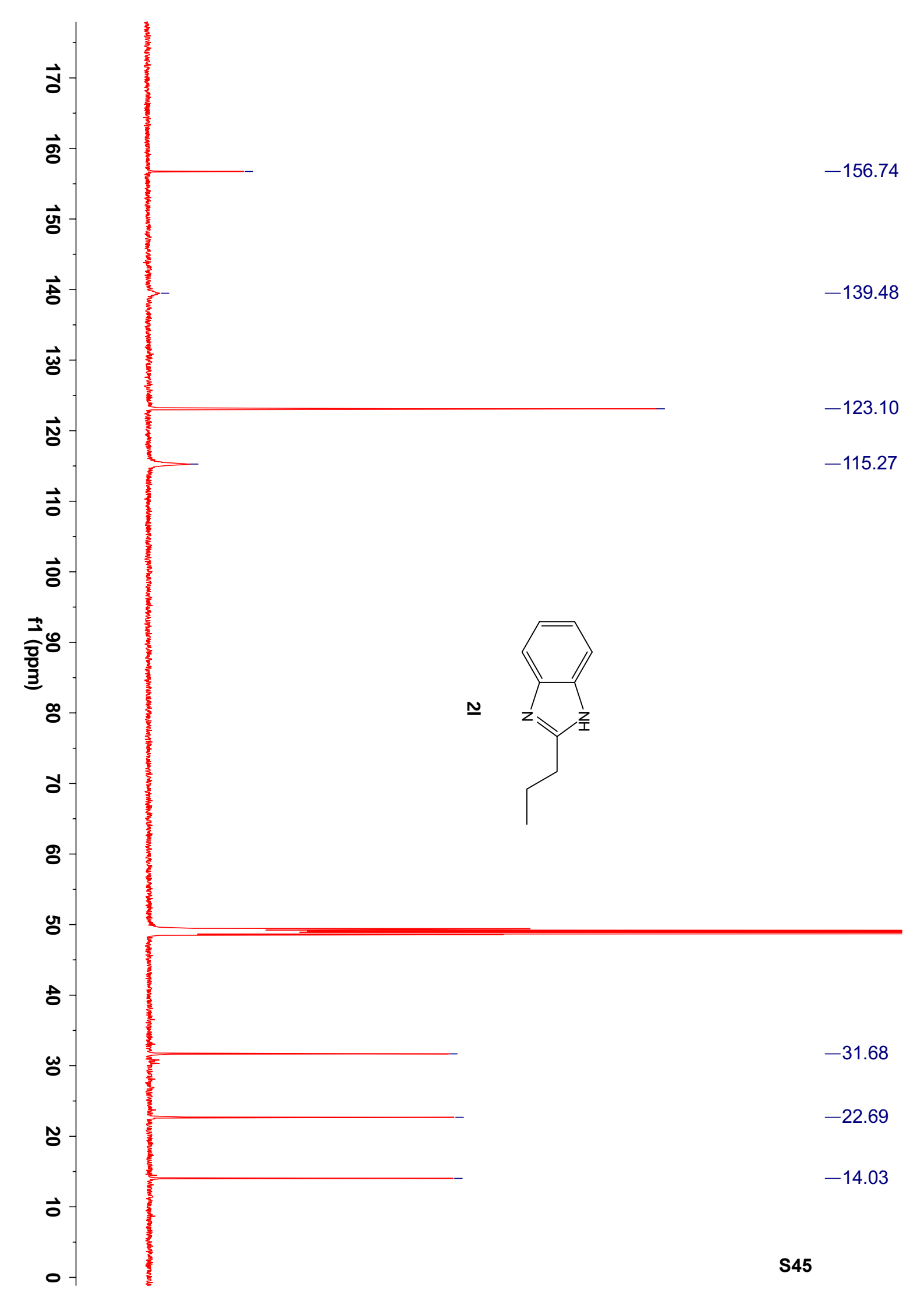
2j

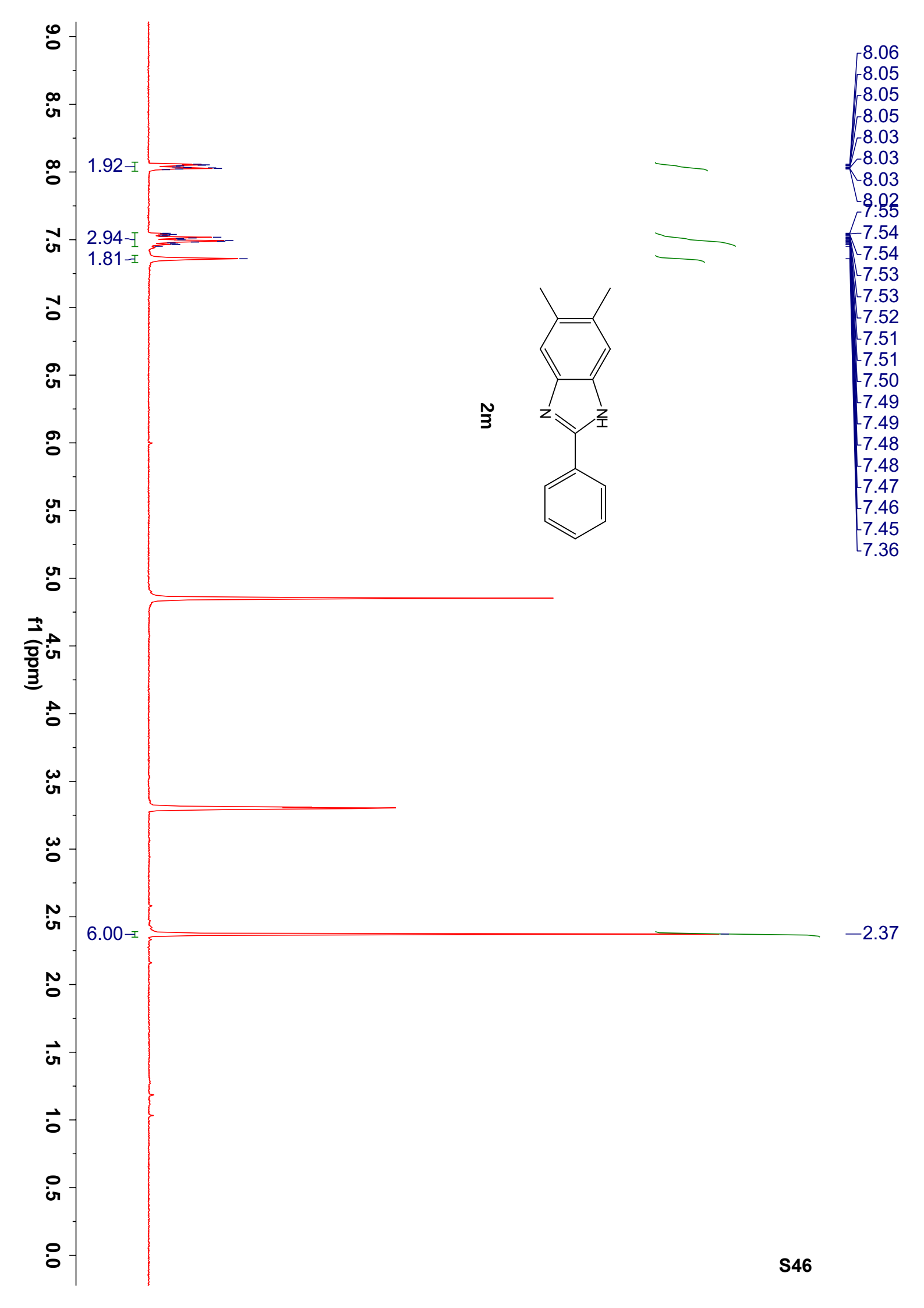

152.54
137.13
136.85
130.21
129.98
128.15
123.97
117.29
115.73
N
NH
2j
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

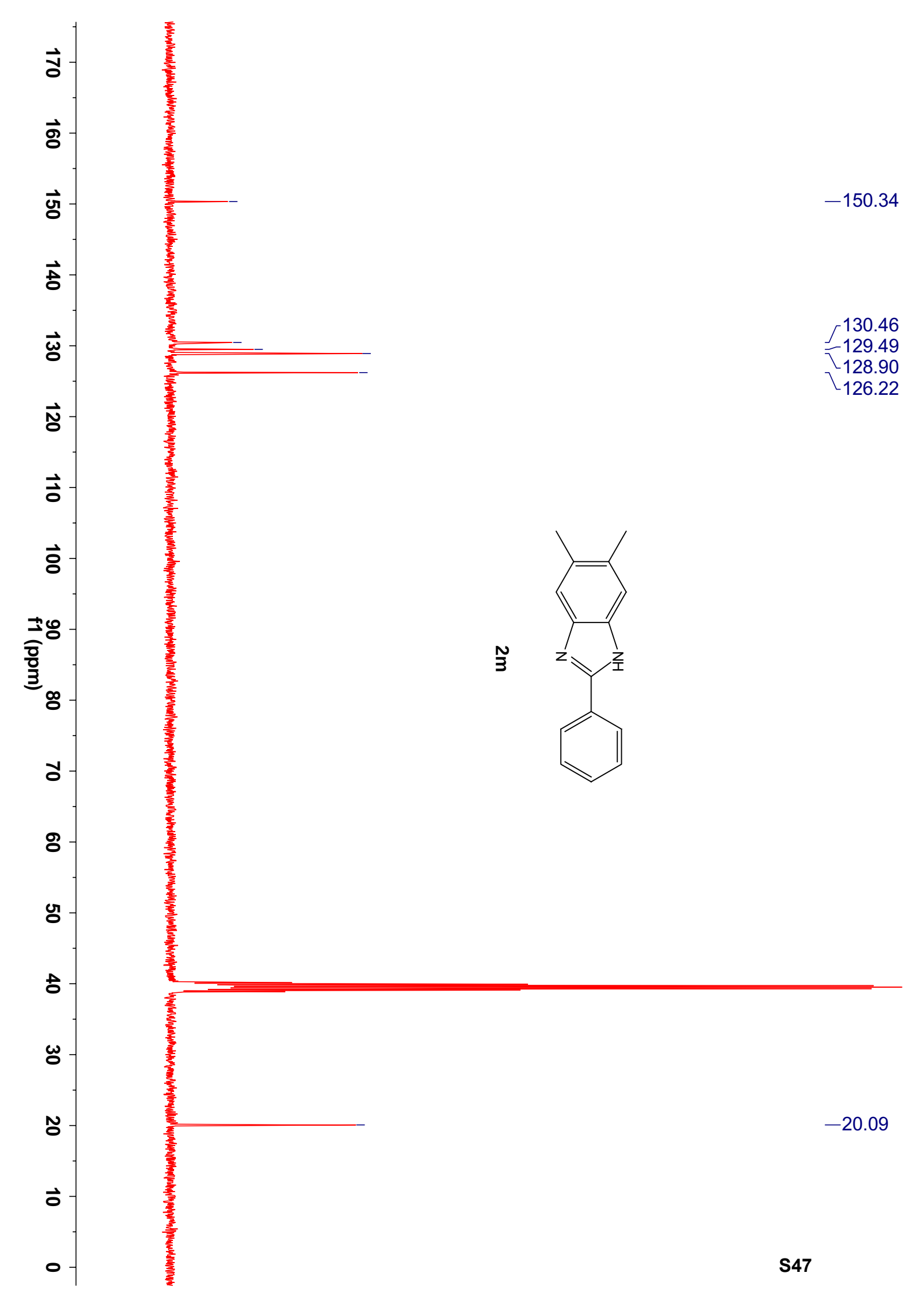

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.92
2.00
1.08
2.11
2.13
3.17
3.26
2k
N
NH
7.49
7.47
7.19
7.18
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.15
7.14
2.94
2.91
2.90
2.88
2.86
2.11
2.11
2.10
2.09
2.07
2.06
2.06
2.05
1.92
1.91
1.90
1.88
1.87
1.86
1.81
1.81
1.80
1.77
1.77
1.70
1.70
1.69
1.66
1.65
1.64
1.61
1.54
1.51
1.50
1.48
1.46
1.45
1.44
1.42
1.41
1.40
1.37
1.33

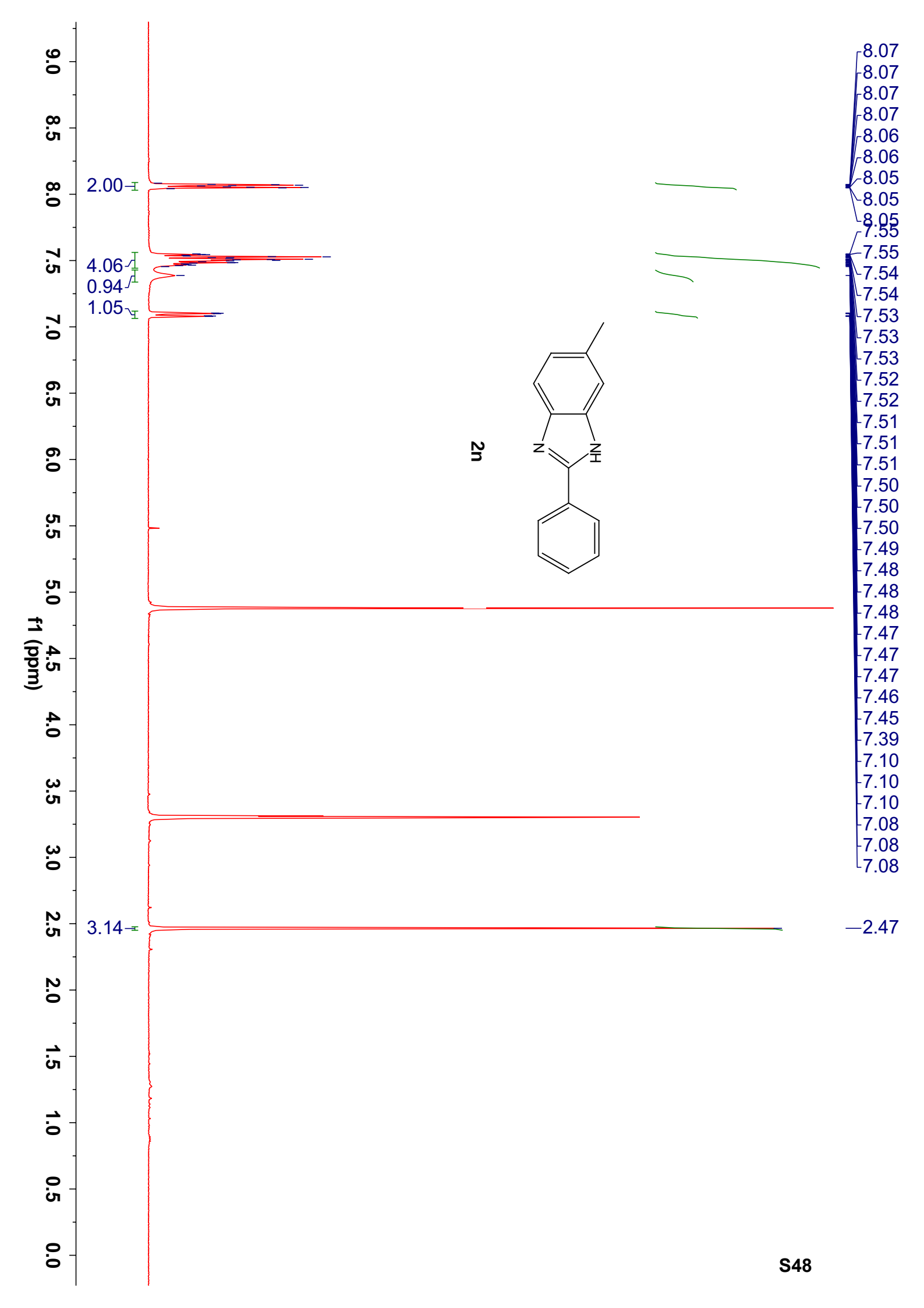

160.76
123.05
115.22
39.84
32.84
27.20
26.97
2k
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

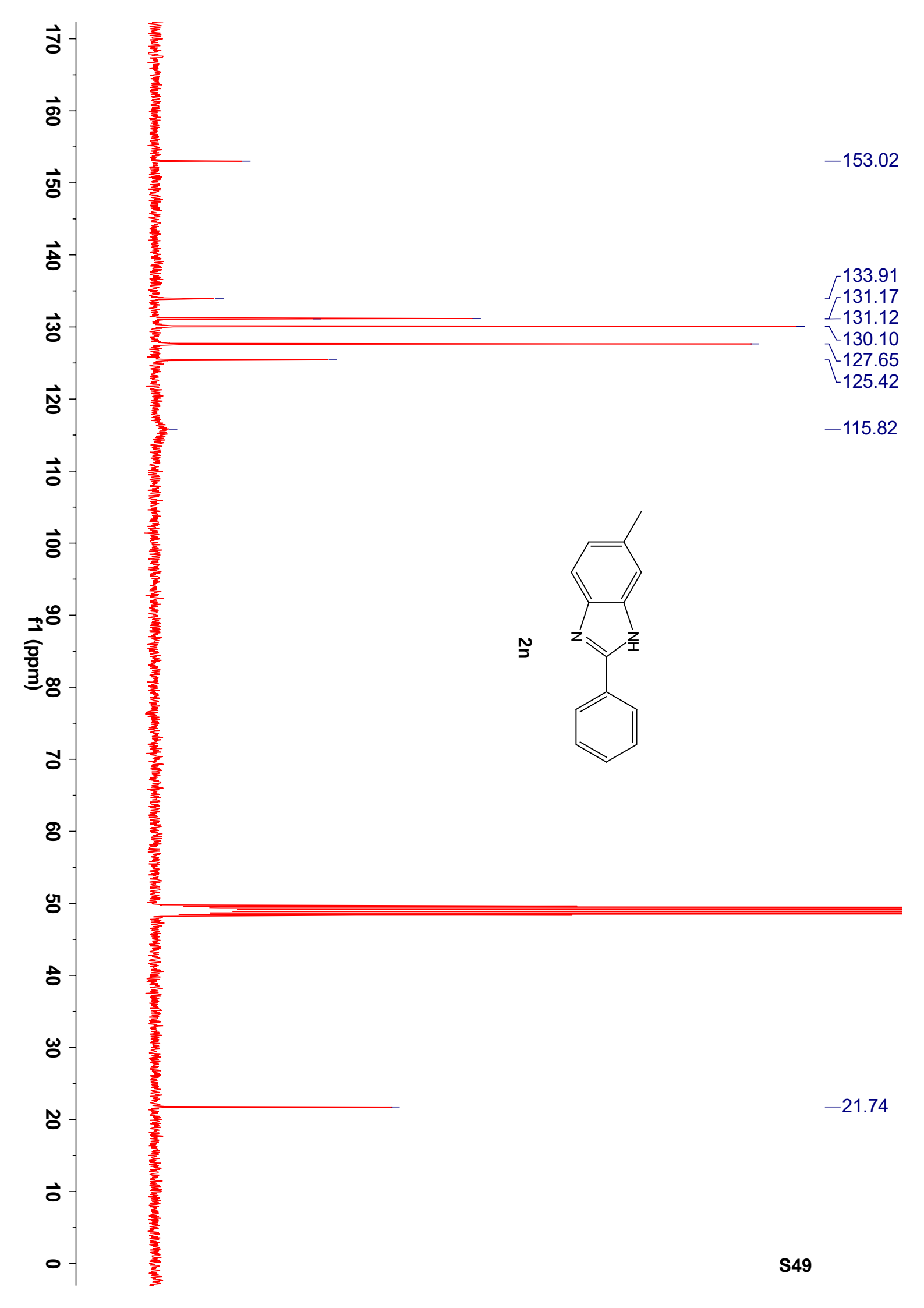

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.00
2.04
2.09
2.14
3.01
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
2.94
2.92
2.89
1.95
1.94
1.94
1.92
1.92
1.92
1.90
1.89
1.89
1.88
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.82
1.82
1.00
0.98
0.95
2l
N
NH

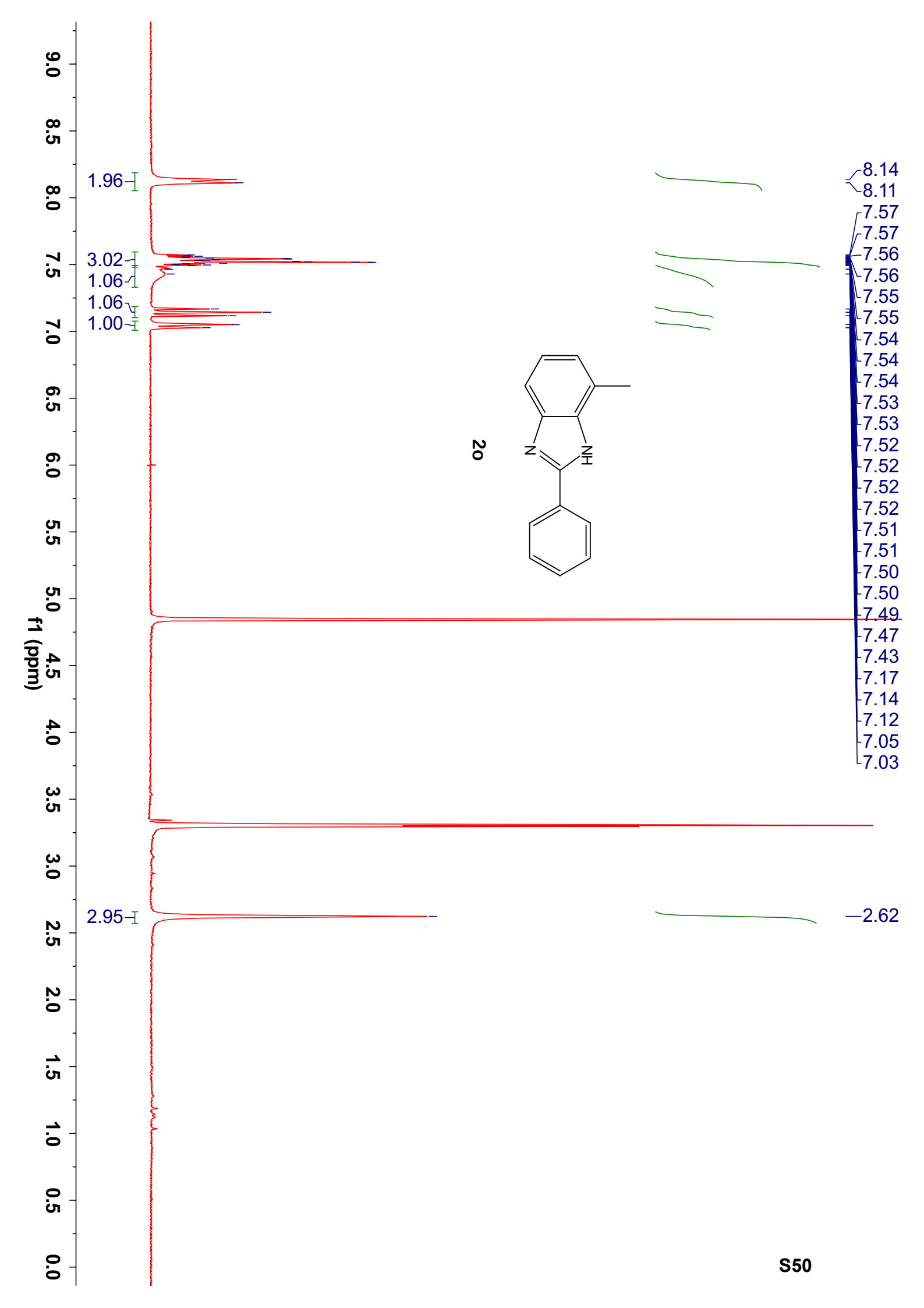

156.74
139.48
123.10
115.27
31.68
22.69
14.03
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
2l
N
NH

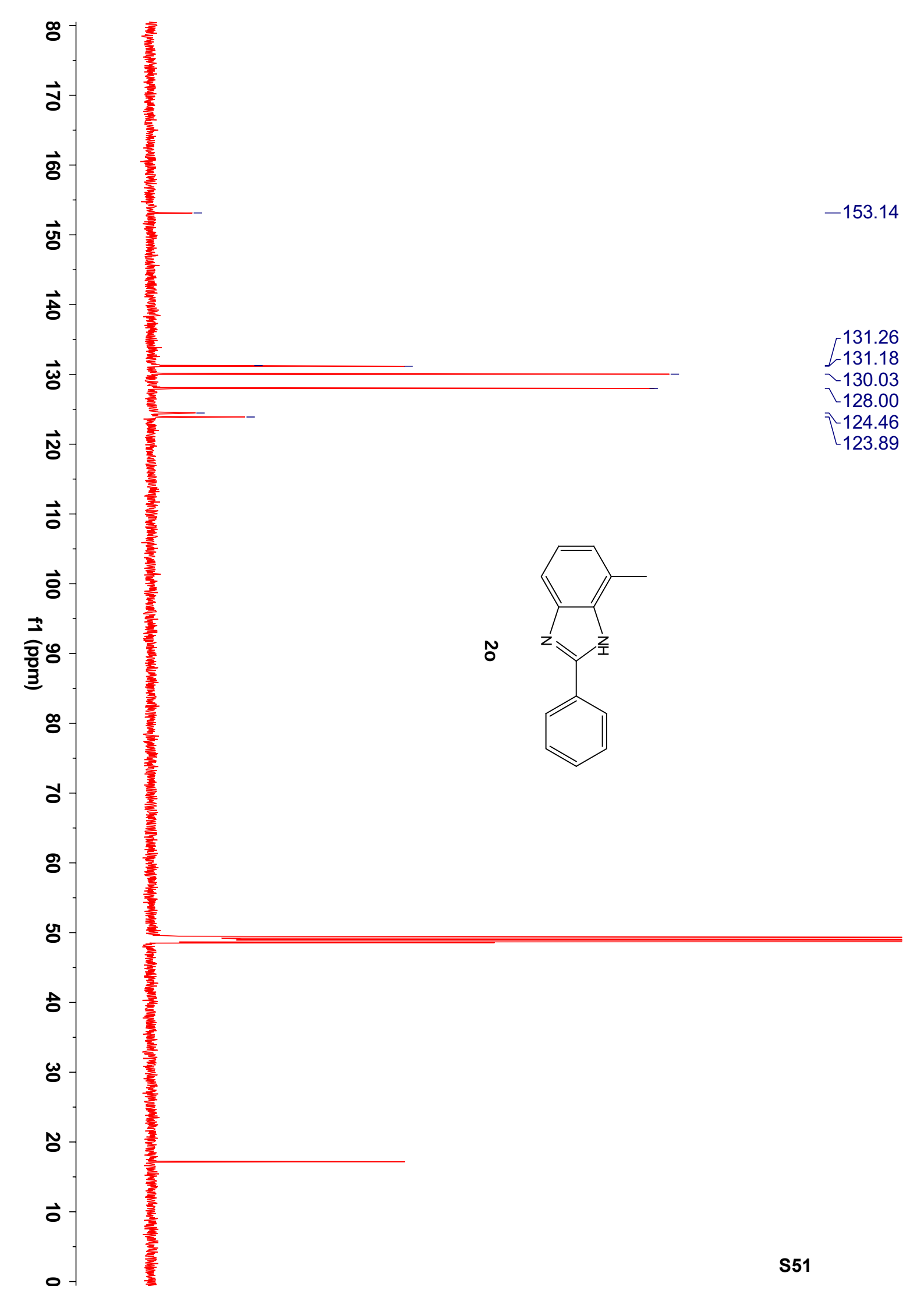

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.92
2.94
1.81
6.00
2m
N
NH
8.06
8.05
8.05
8.05
8.03
8.03
8.03
8.02
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.36
2.37


150.34
130.46
129.49
128.90
126.22
20.09
2m
N
NH
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

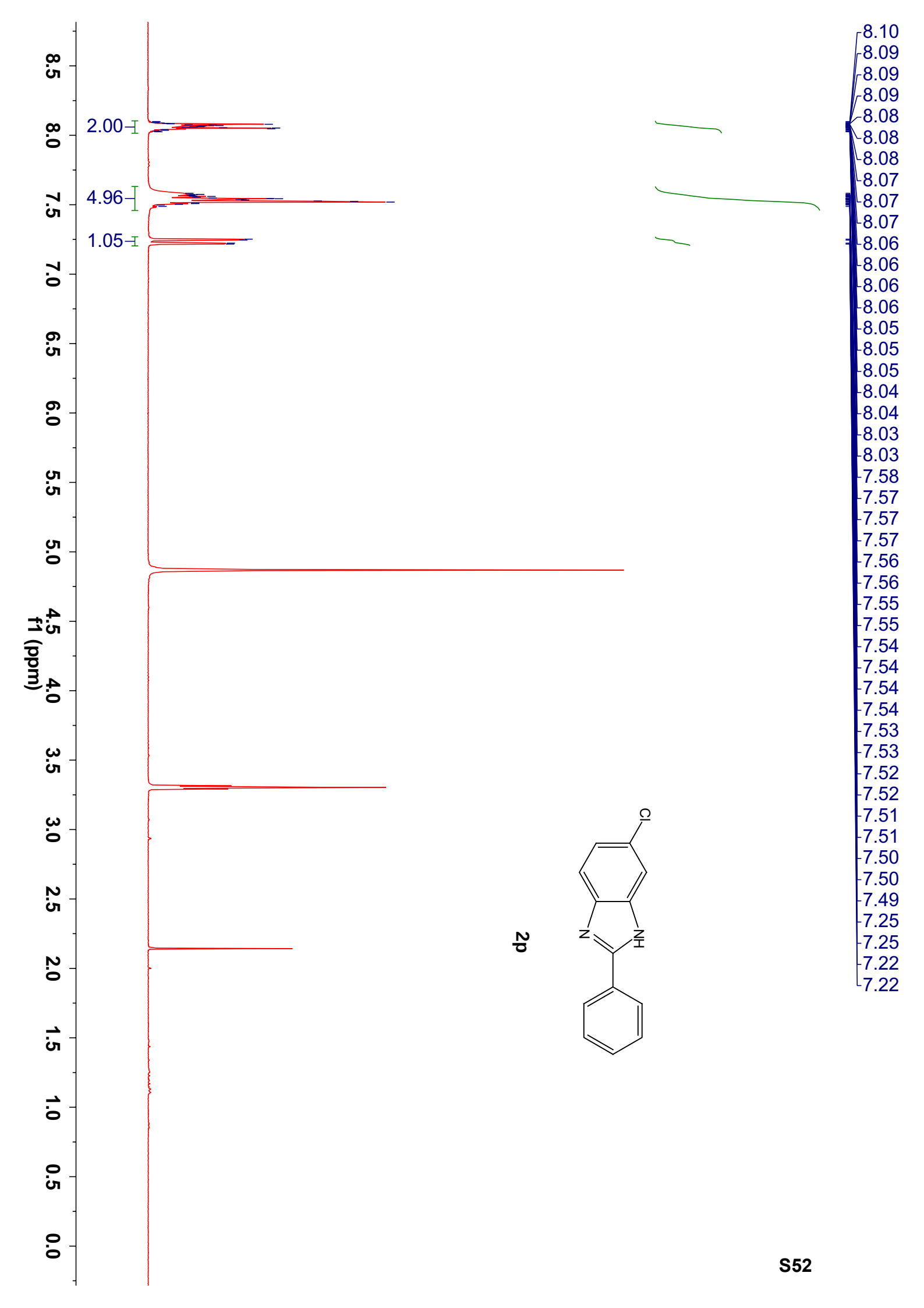

f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.00
4.06
0.94
1.05
3.14
2.47
8.07
8.07
8.07
8.07
8.06
8.06
8.05
8.05
8.05
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.46
7.45
7.39
7.10
7.10
7.10
7.08
7.08
7.08
2n
N
NH

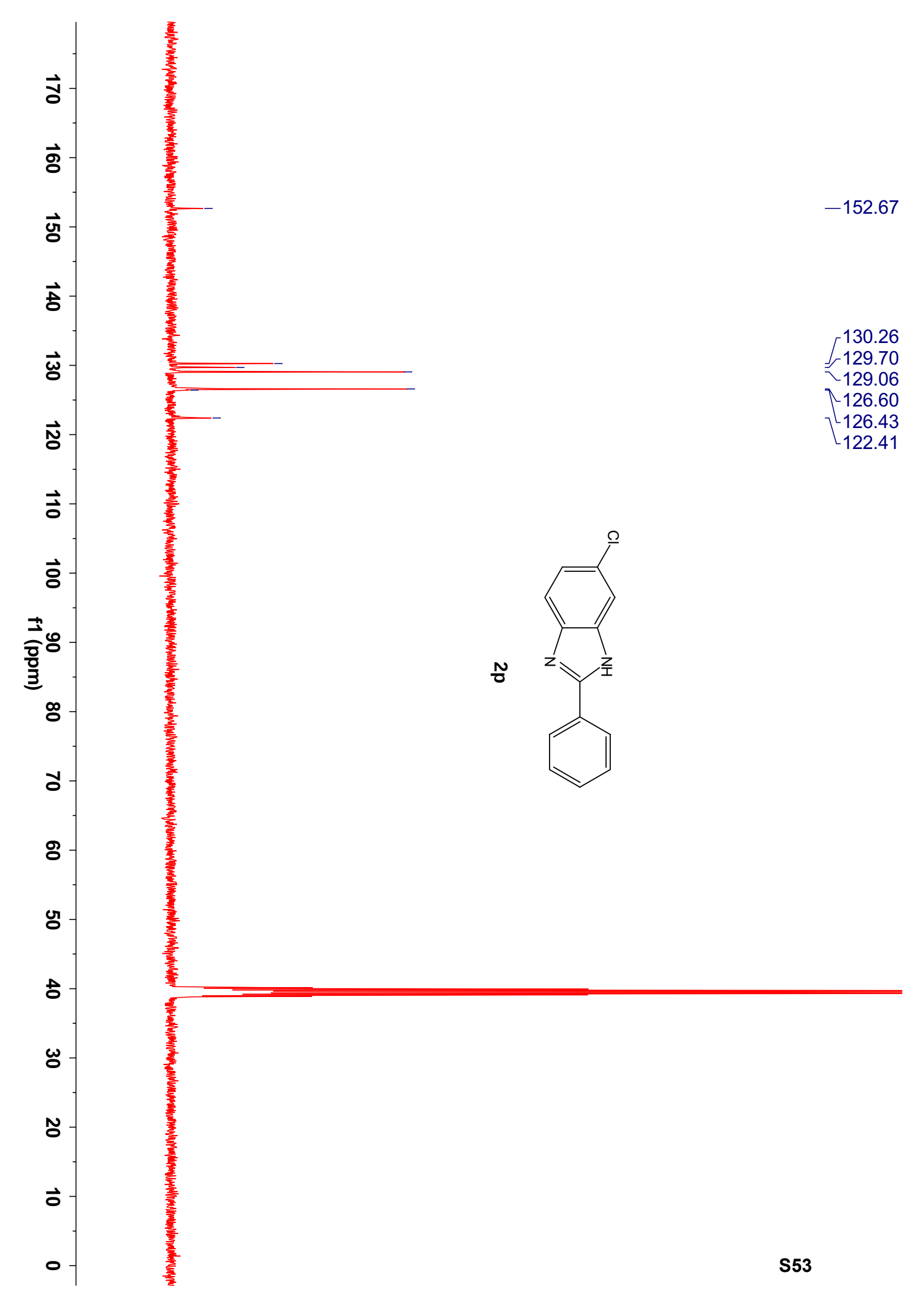

153.02
133.91
131.17
131.12
130.10
127.65
125.42
115.82
21.74
2n
N
NH
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

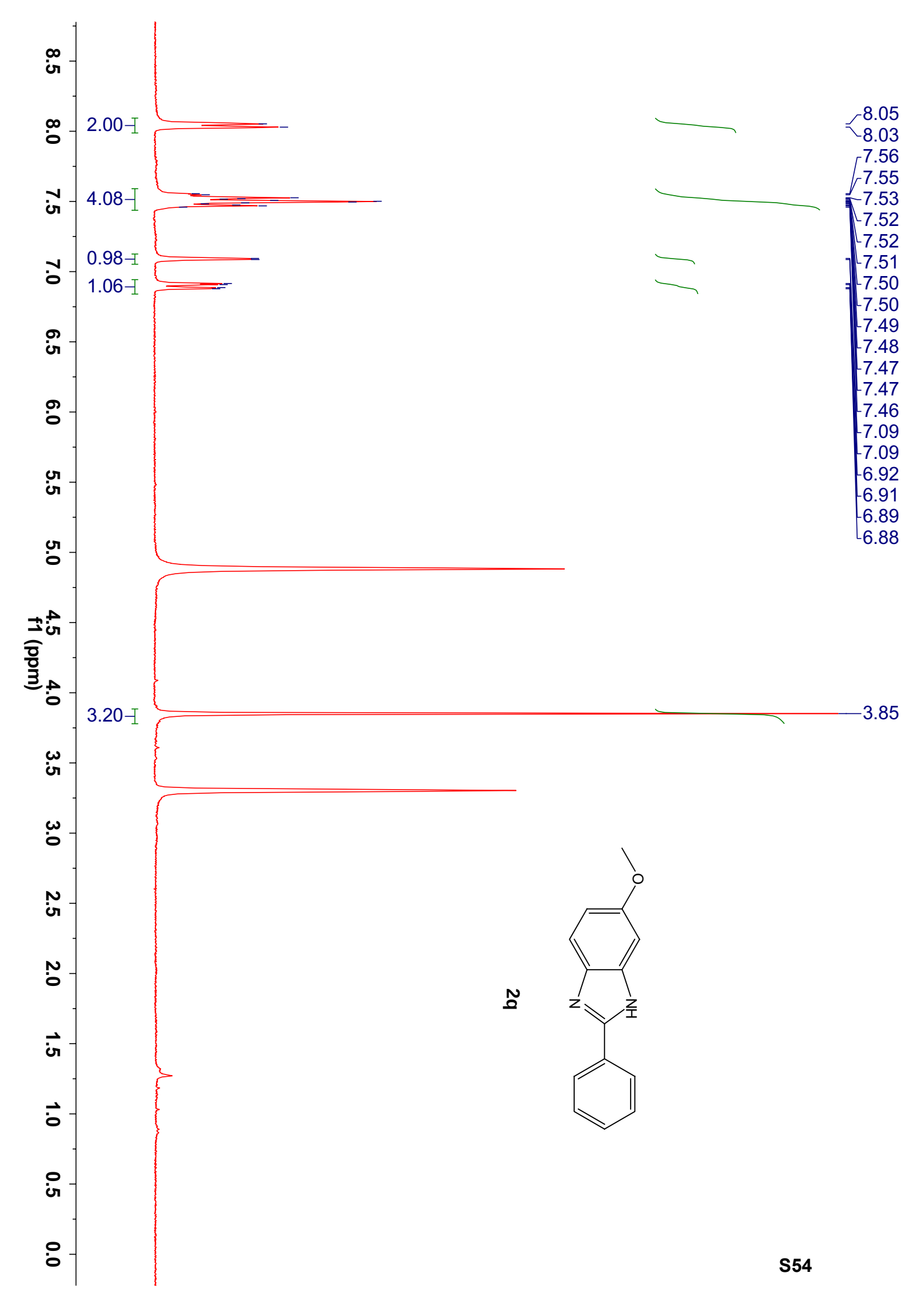

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.96
3.02
1.06
1.06
1.00
2.95
8.14
8.11
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.47
7.43
7.17
7.14
7.12
7.05
7.03
2.62
2o
N
NH

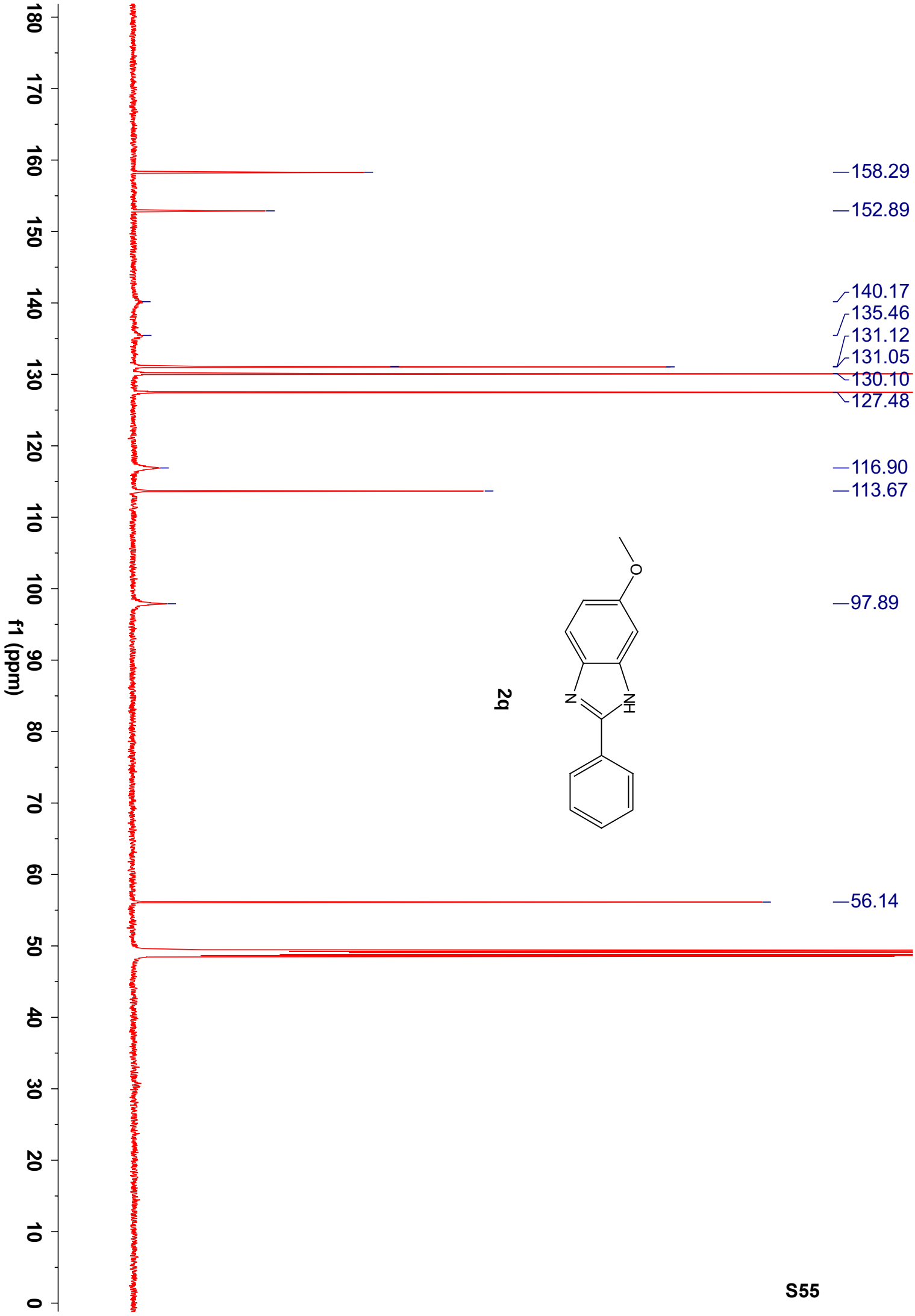

153.14
131.26
131.18
130.03
128.00
124.46
123.89
f1 (ppm)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
NH

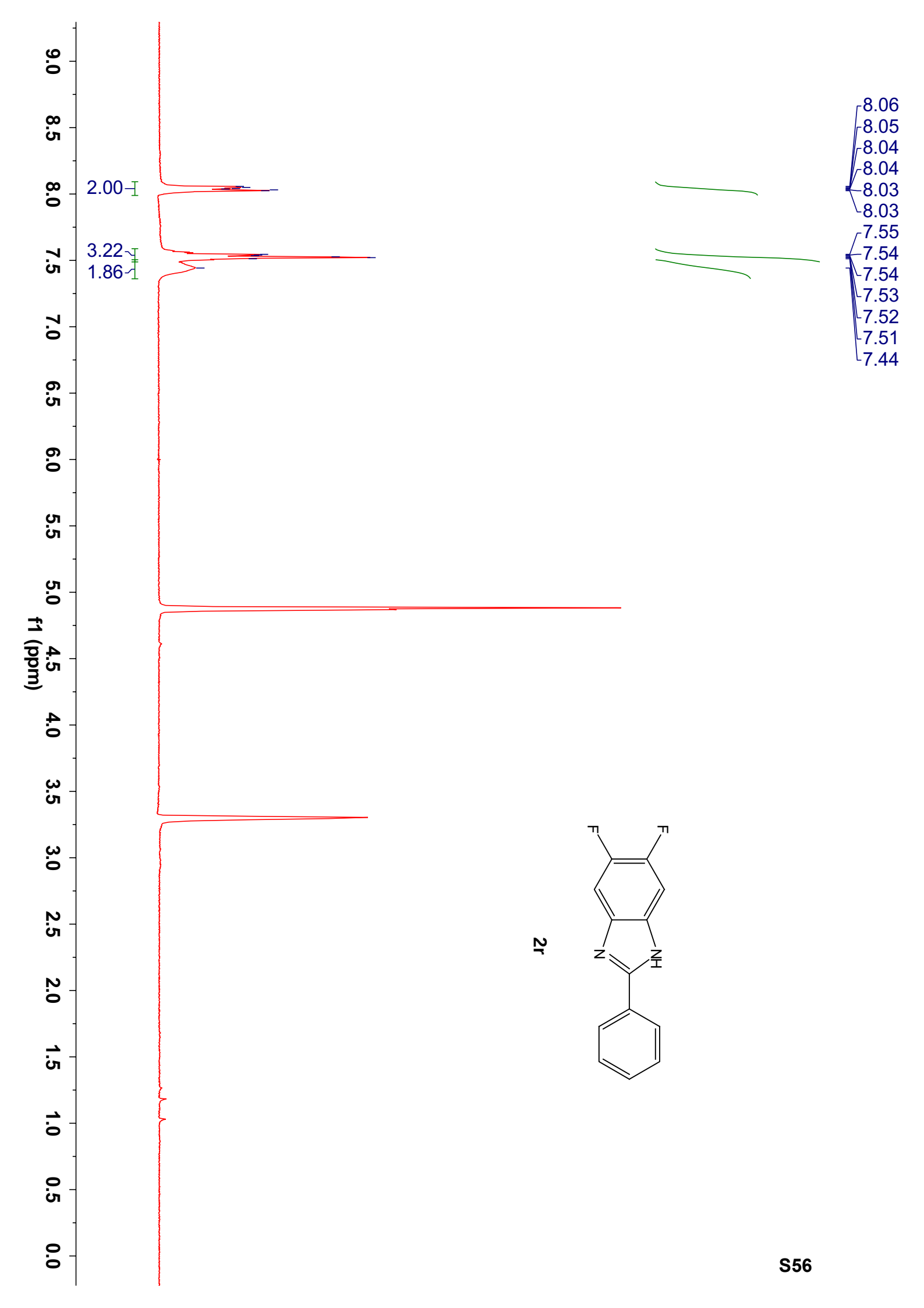
2o

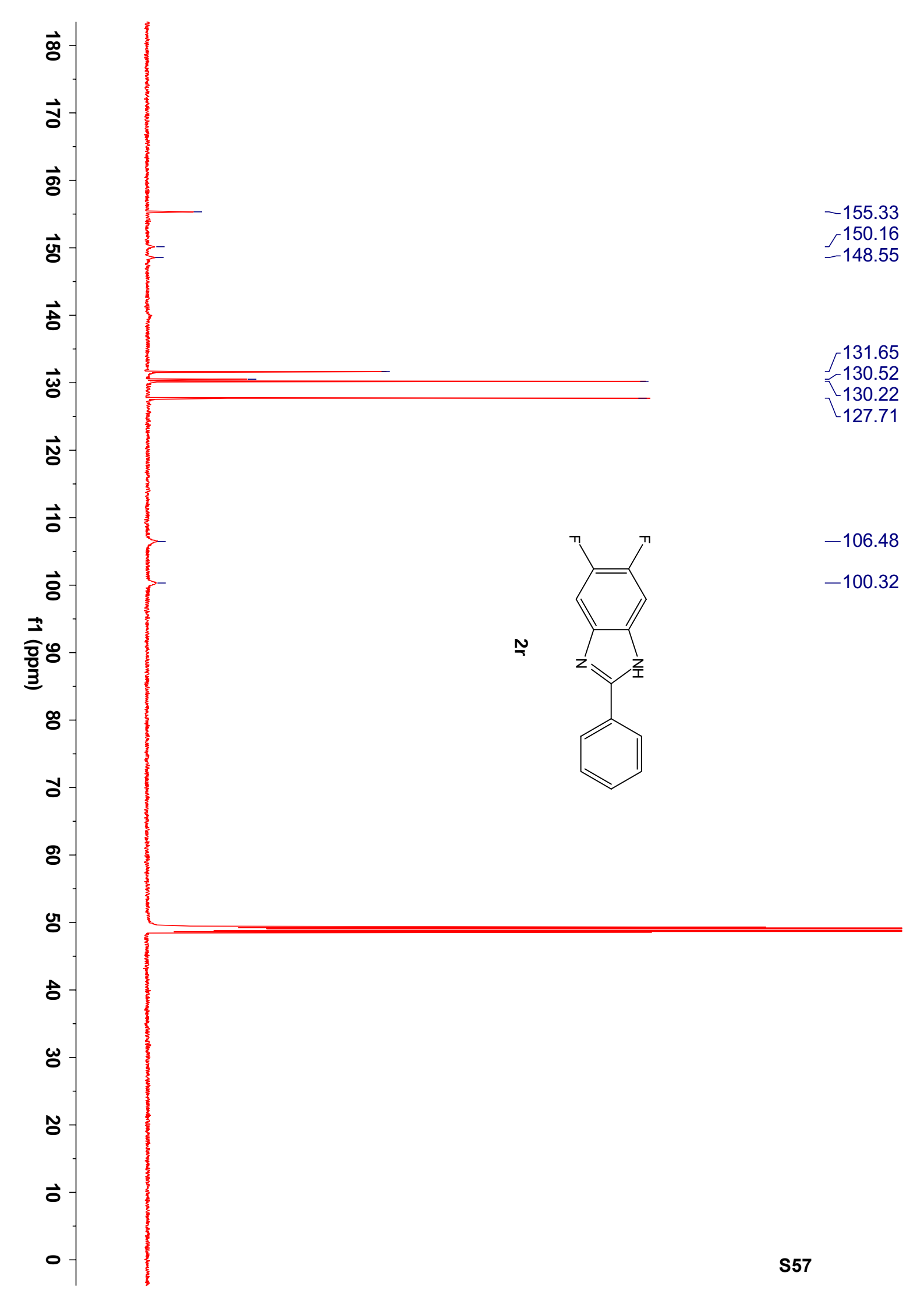

2.00
4.96
1.05
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
8.10
8.09
8.09
8.09
8.08
8.08
8.08
8.07
8.07
8.07
8.06
8.06
8.06
8.06
8.05
8.05
8.05
8.04
8.04
8.03
8.03
7.58
7.57
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.25
7.25
7.22
7.22
Cl
N
NH
2p

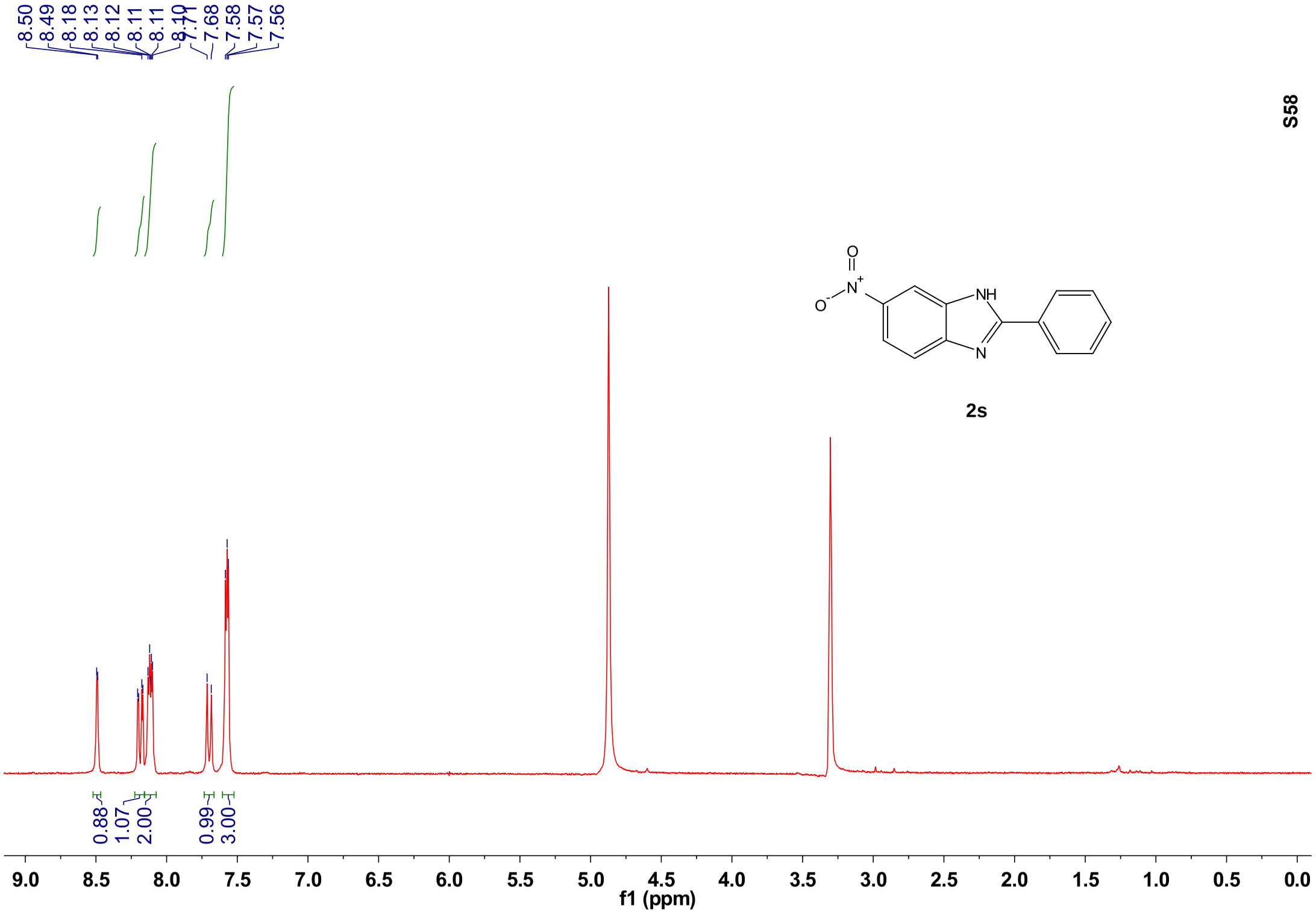

152.67
130.26
129.70
129.06
126.60
126.43
122.41
Cl
N
NH
2p
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.05
8.03
7.56
7.55
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.09
7.09
6.92
6.91
6.89
6.88
3.85
2.00
4.08
0.98
1.06
3.20
f1 (ppm)
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
O
N
NH
2q


158.29
152.89
140.17
135.46
131.12
131.05
130.10
127.48
116.90
113.67
97.89
56.14
f1 (ppm)
2q
O
N
NH

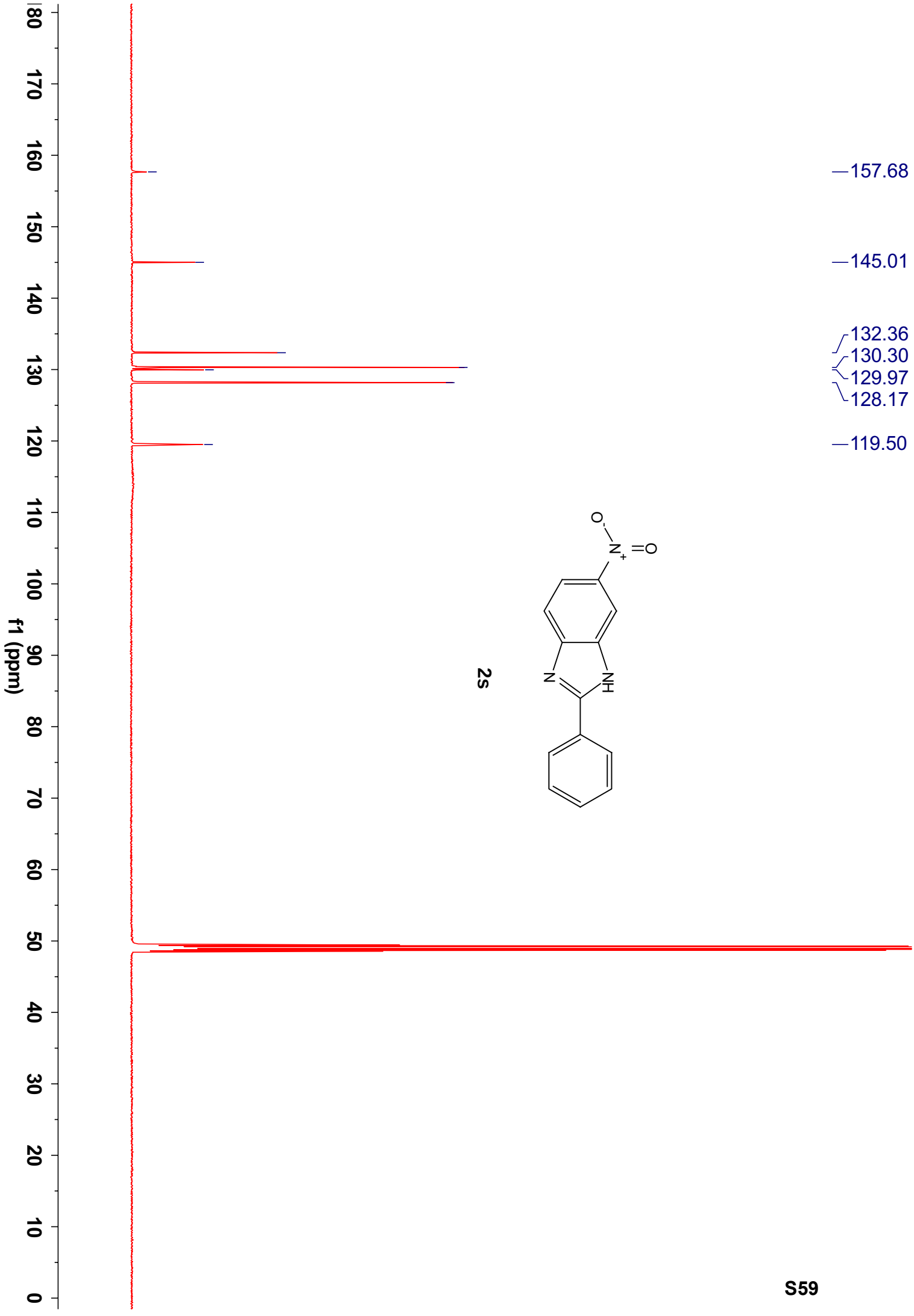

8.06
8.05
8.04
8.04
8.03
8.03
7.55
7.54
7.54
7.53
7.52
7.51
7.44
2.00
3.22
1.86
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
F
F
N
NH
2r

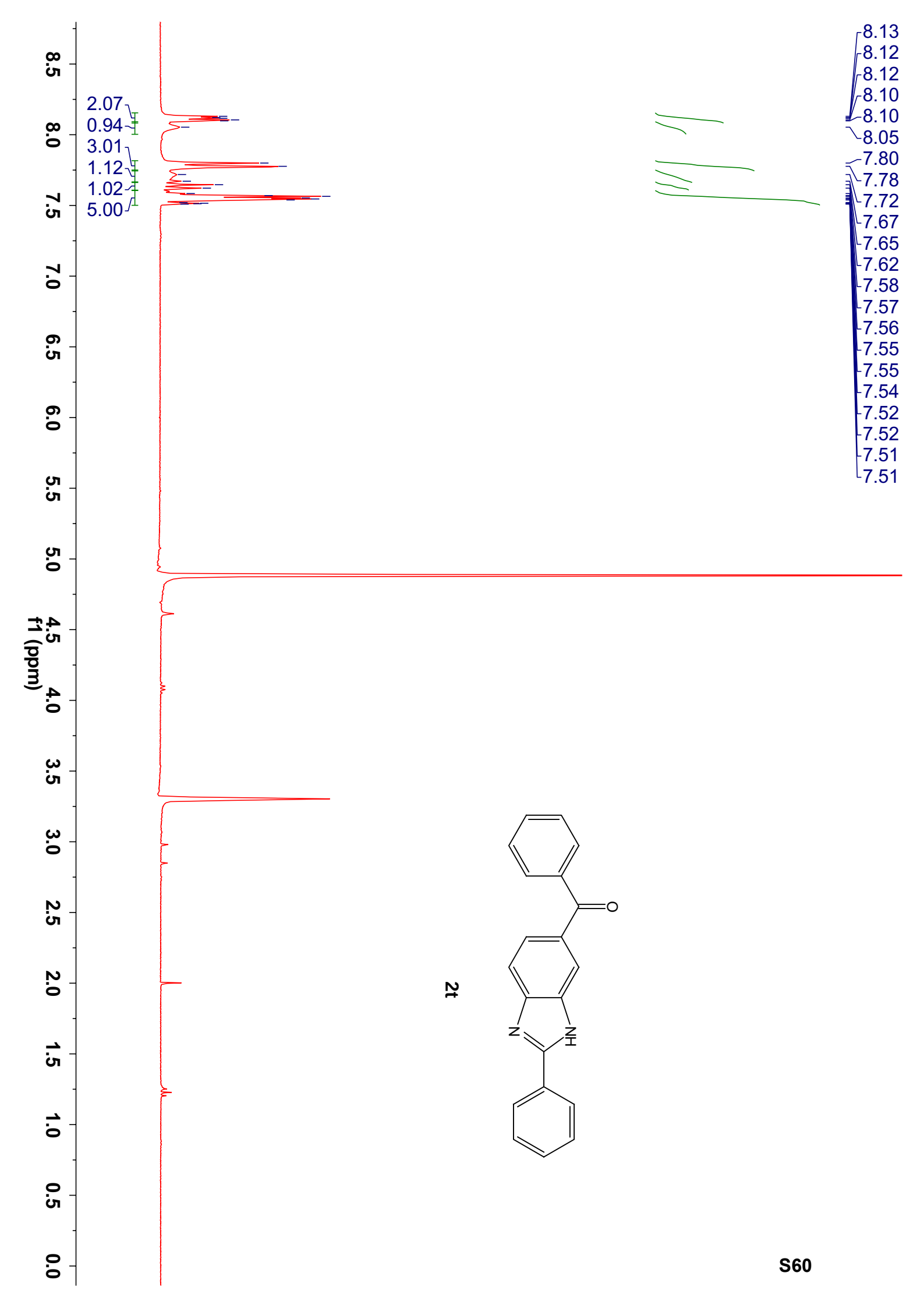

155.33
150.16
148.55
131.65
130.52
130.22
127.71
106.48
100.32
F
F
N
NH
2r
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

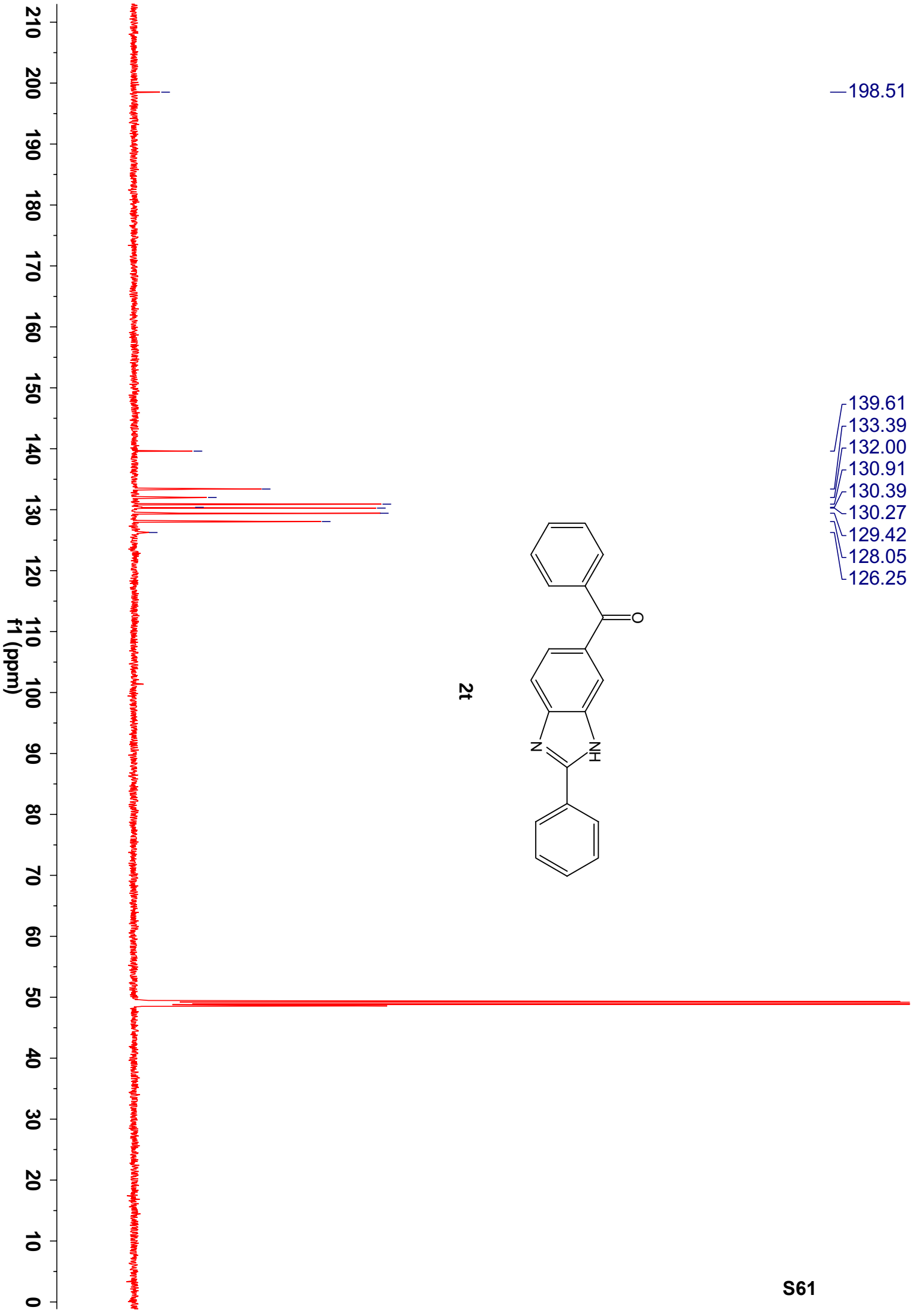

8.50
8.49
8.18
8.13
8.12
8.11
8.11
8.10
7.71
7.68
7.58
7.57
7.56
0.88
1.07
2.00
0.99
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

O
N+
O-
NH
N

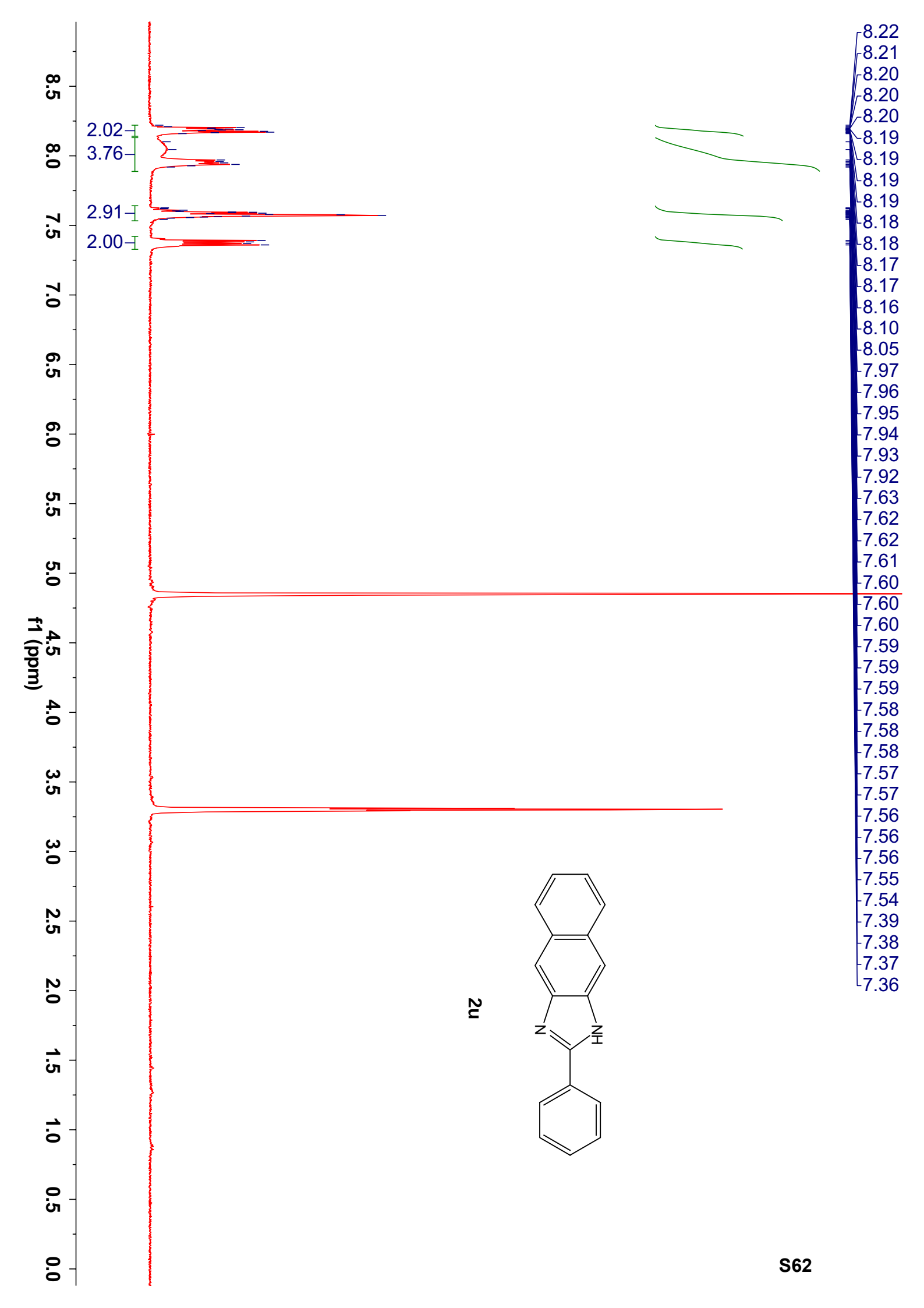
2s

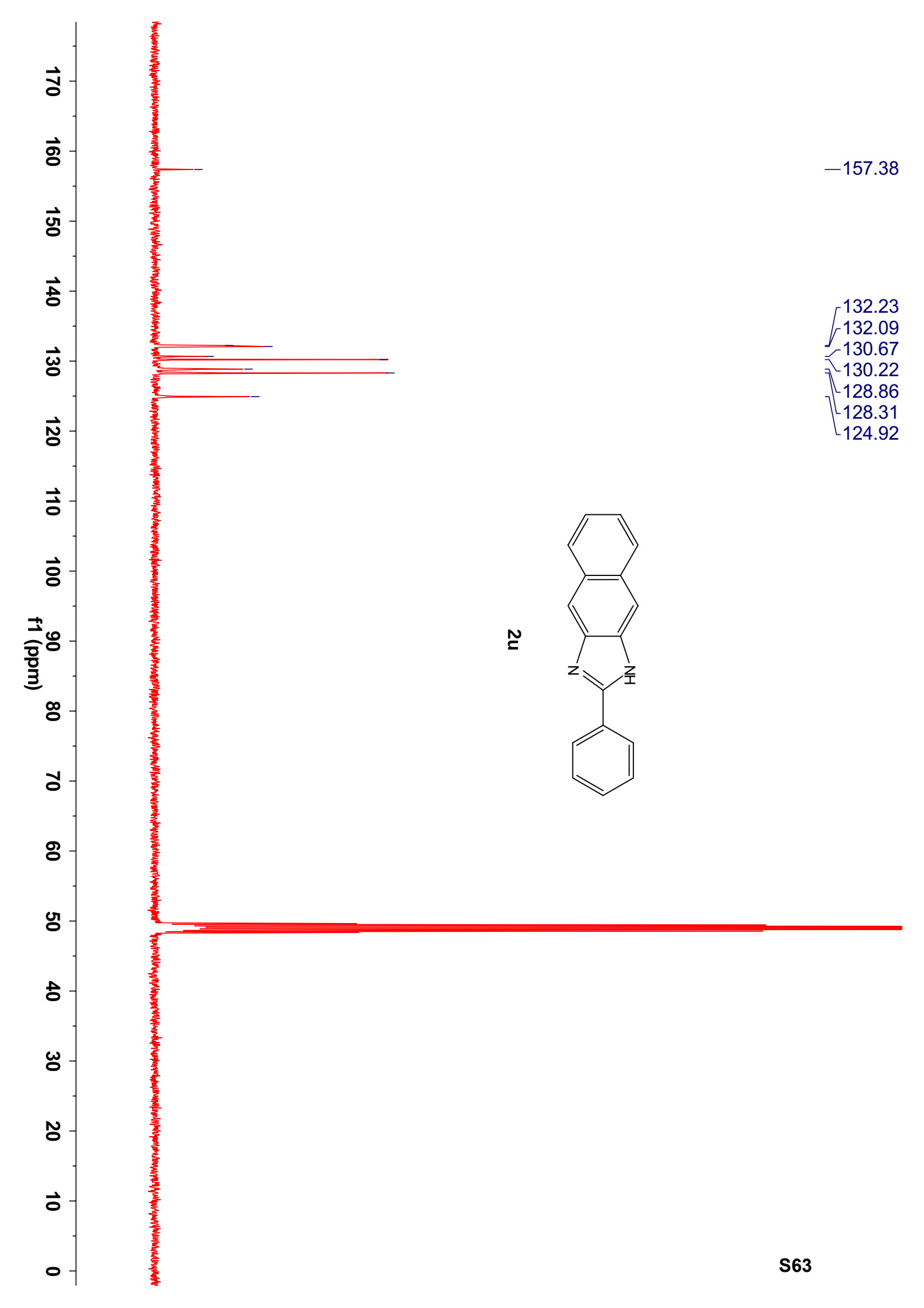

157.68
145.01
132.36
130.30
129.97
128.17
119.50
f1 (ppm)
2s

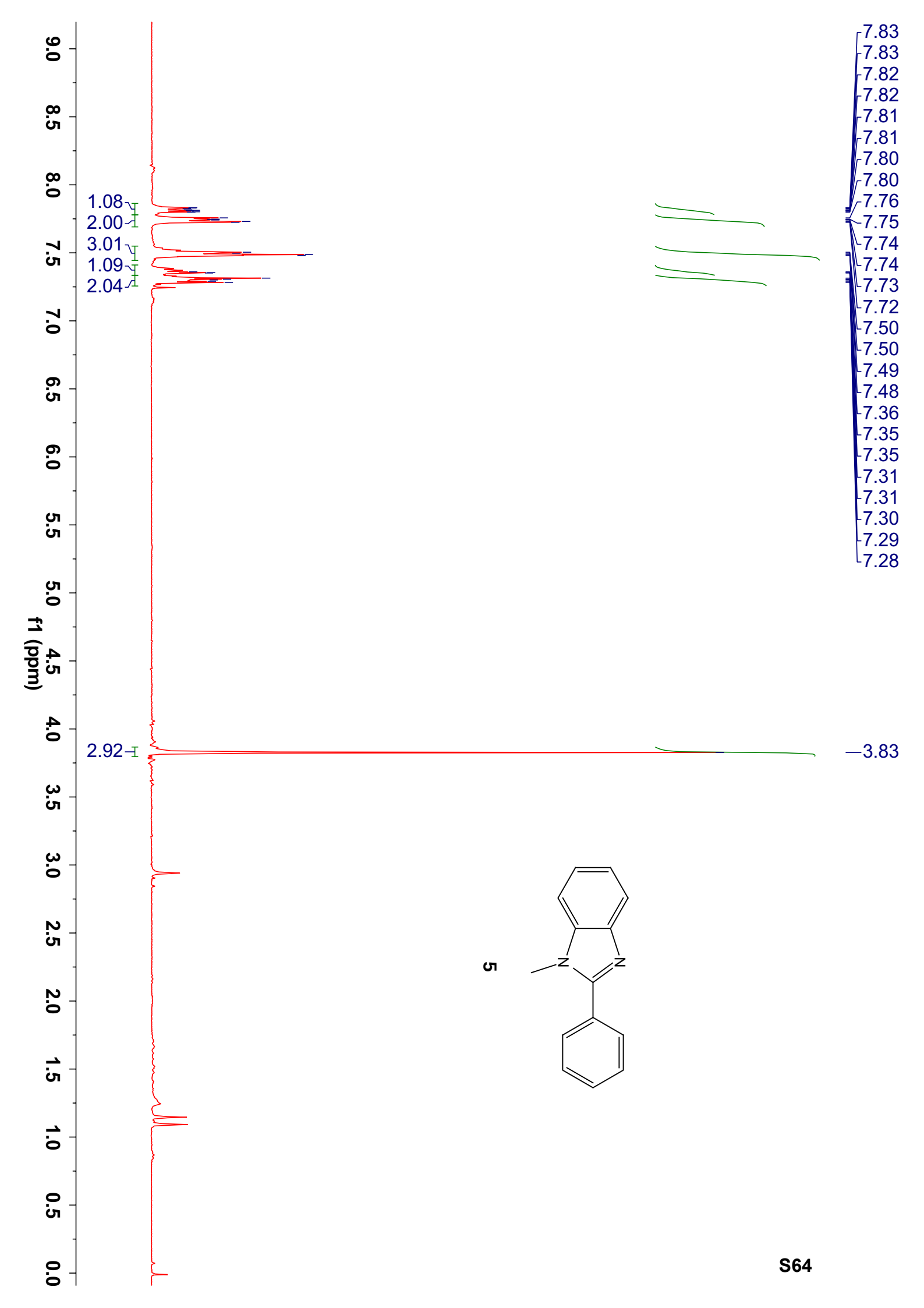

8.13
8.12
8.12
8.10
8.10
8.05
7.80
7.78
7.72
7.67
7.65
7.62
7.58
7.57
7.56
7.55
7.55
7.54
7.52
7.52
7.51
7.51
2.07
0.94
3.01
1.12
1.02
5.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
N
NH
2t

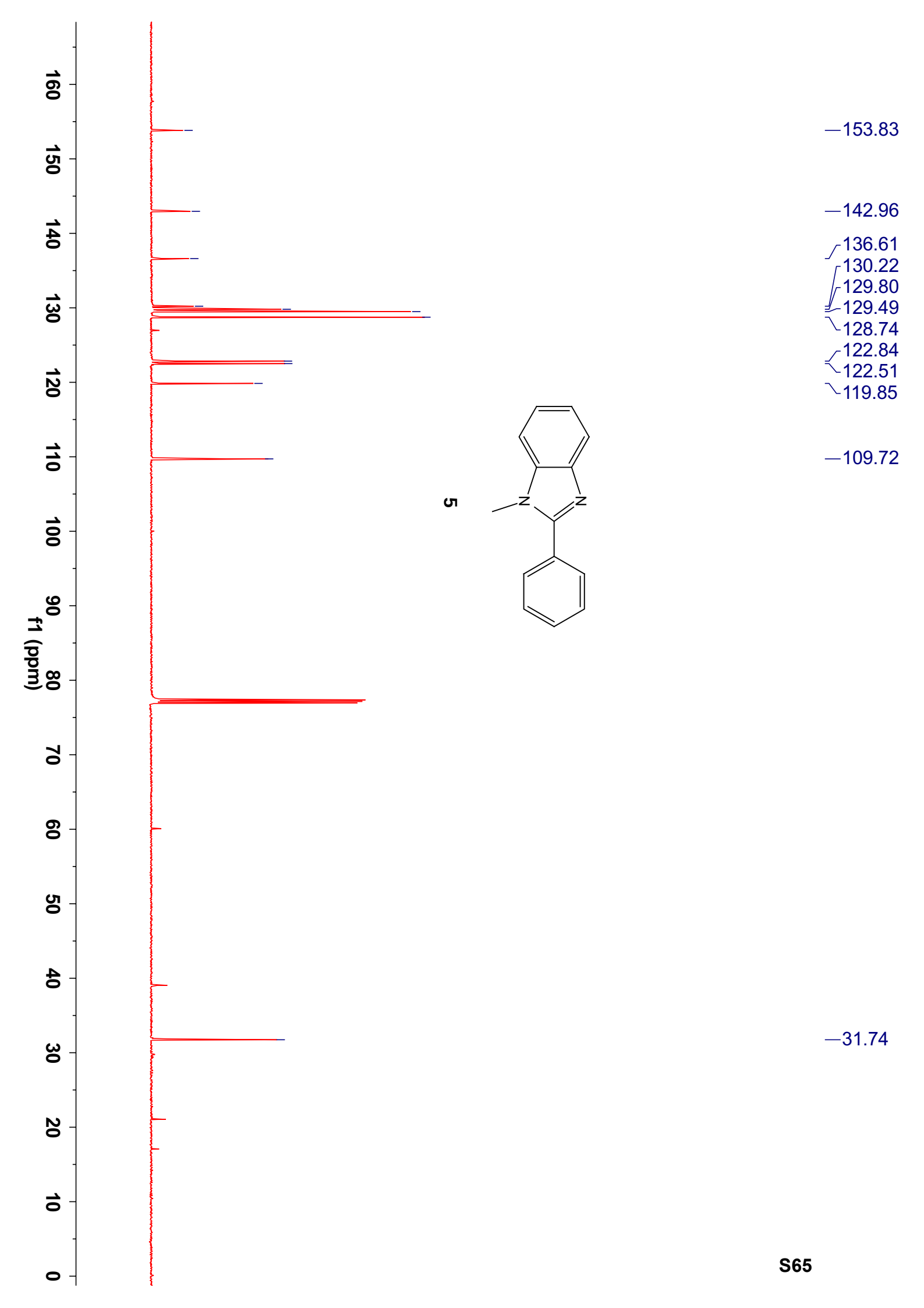

198.51
139.61
133.39
132.00
130.91
130.39
130.27
129.42
128.05
126.25
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
N
NH

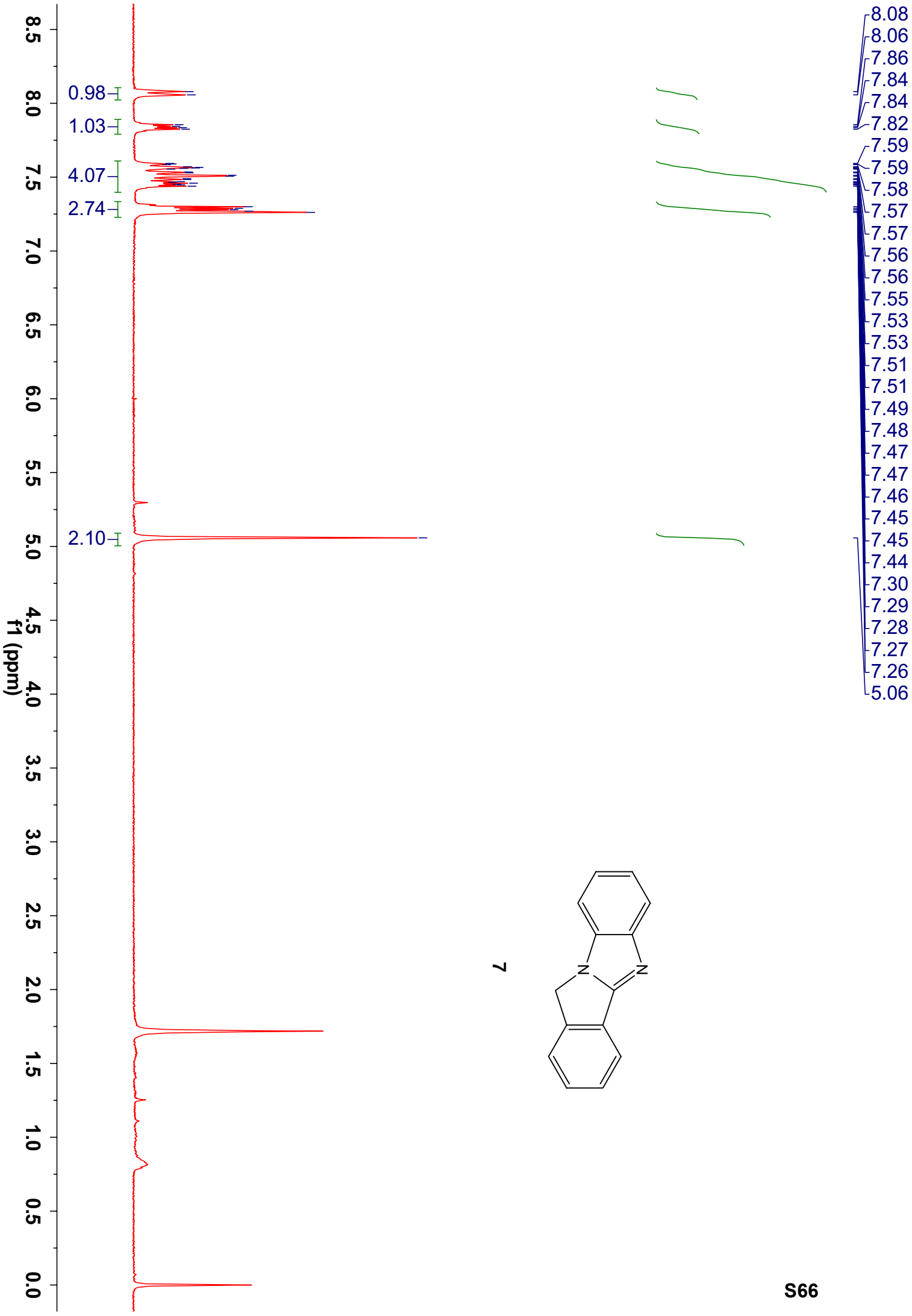
2t


8.22
8.21
8.20
8.20
8.20
8.19
8.19
8.19
8.19
8.18
8.18
8.17
8.17
8.16
8.10
8.05
7.97
7.96
7.95
7.94
7.93
7.92
7.63
7.62
7.62
7.61
7.60
7.60
7.60
7.59
7.59
7.59
7.58
7.58
7.58
7.57
7.57
7.56
7.56
7.56
7.56
7.55
7.54
7.39
7.38
7.37
7.36
2.02
3.76
2.91
2.00
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)
2u
N
NH

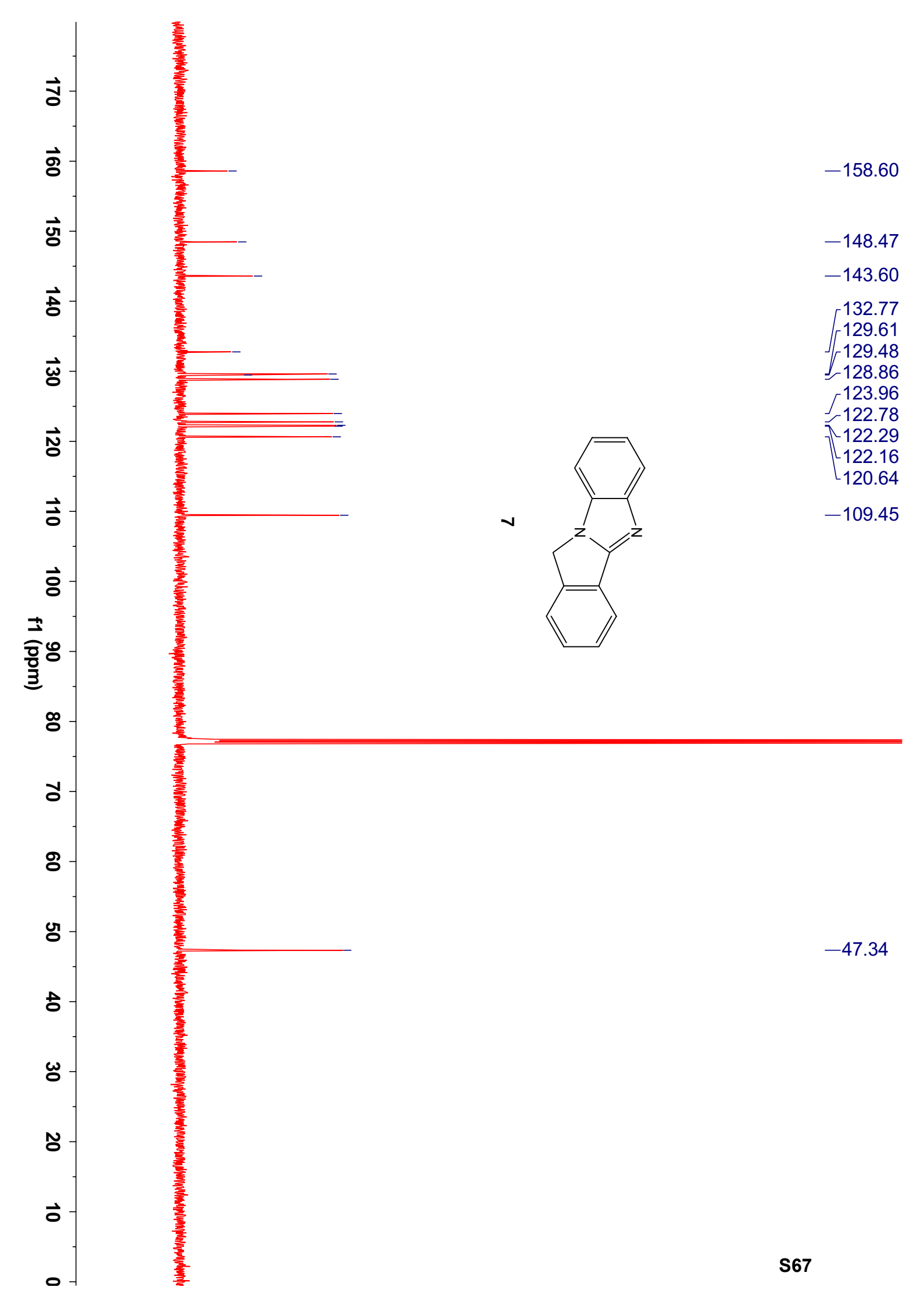

157.38
132.23
132.09
130.67
130.22
128.86
128.31
124.92
2u
N
NH
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

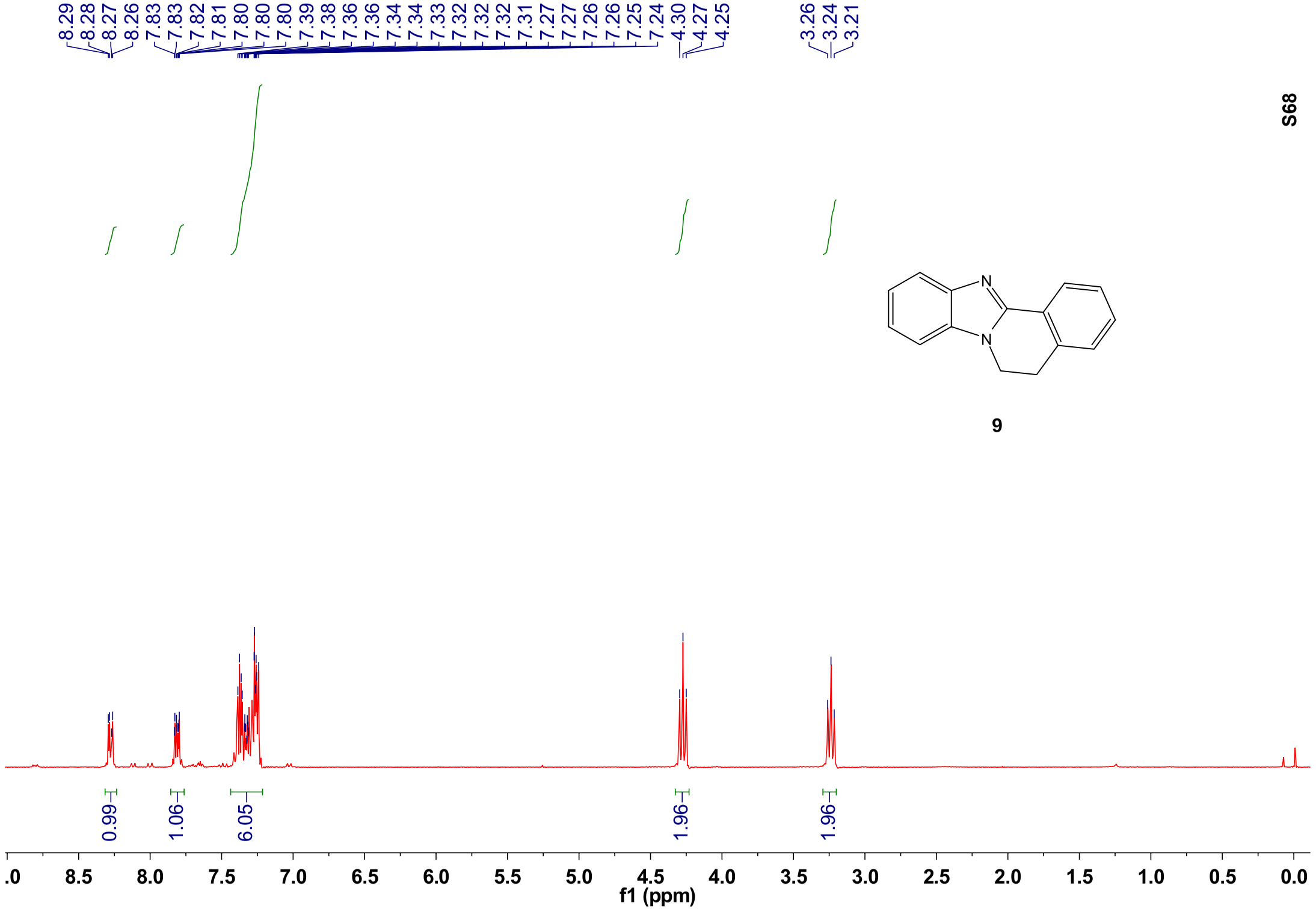

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.08
2.00
3.01
1.09
2.04
2.92
7.83
7.83
7.82
7.82
7.81
7.81
7.80
7.80
7.76
7.75
7.74
7.74
7.73
7.72
7.50
7.50
7.49
7.48
7.36
7.35
7.35
7.31
7.31
7.30
7.29
7.28
3.83
5
N
N


153.83
142.96
136.61
130.22
129.80
129.49
128.74
122.84
122.51
119.85
109.72
31.74
5
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

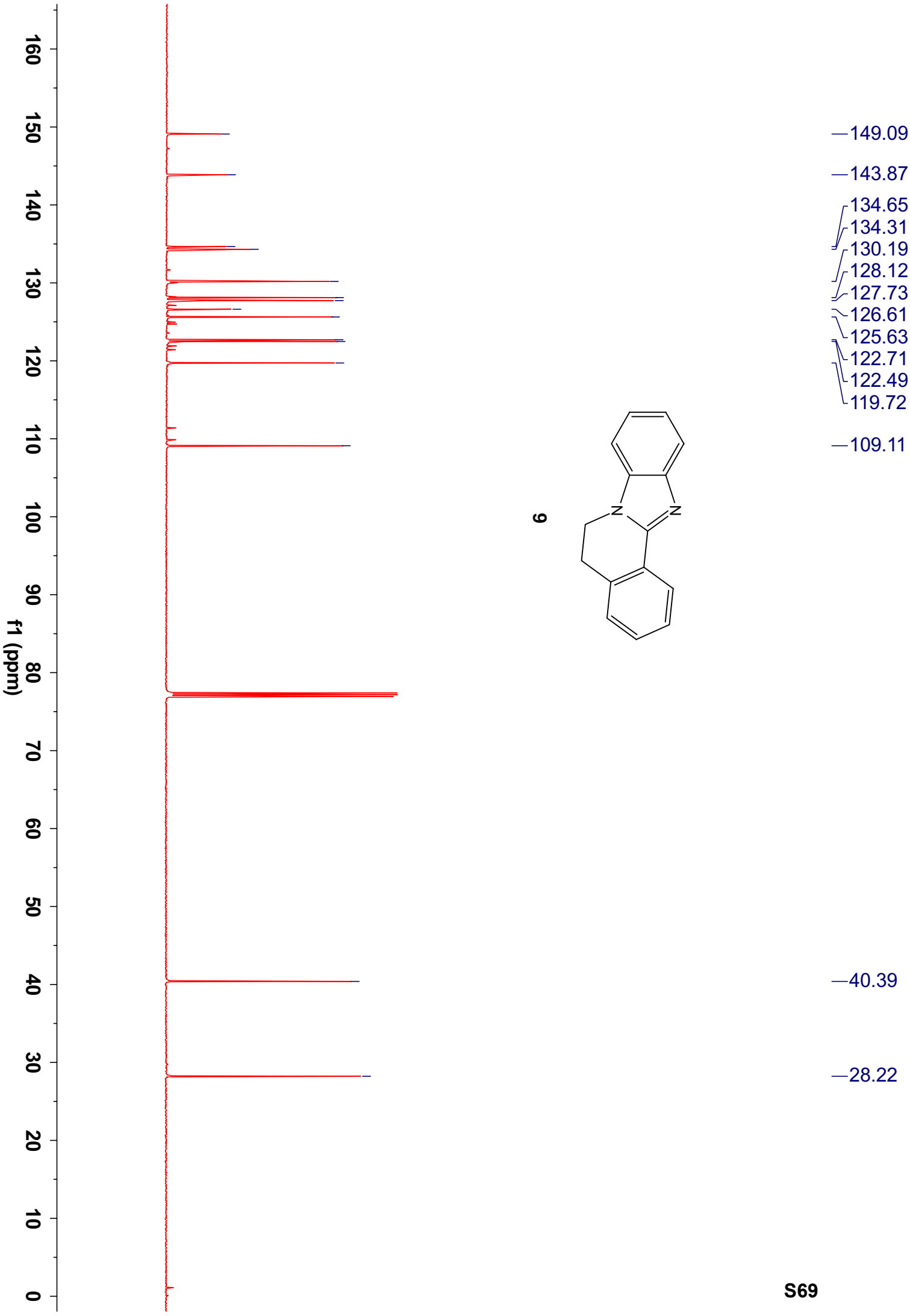

8.08
8.06
7.86
7.84
7.84
7.82
7.59
7.59
7.58
7.57
7.57
7.56
7.56
7.55
7.53
7.53
7.51
7.51
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.30
7.29
7.28
7.27
7.26
5.06
0.98
1.03
4.07
2.74
2.10
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

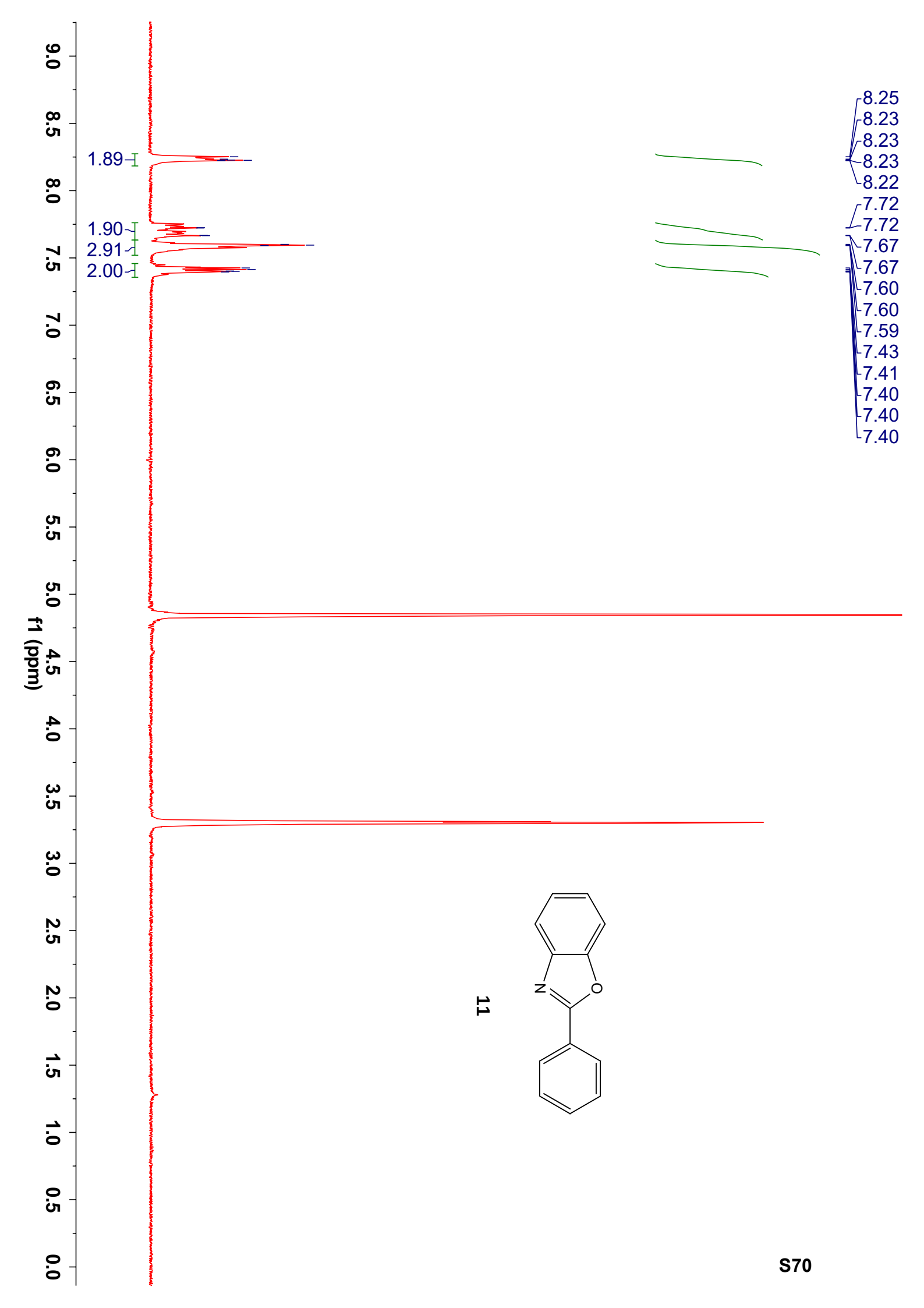
7


158.60
148.47
143.60
132.77
129.61
129.48
128.86
123.96
122.78
122.29
122.16
120.64
109.45
47.34
7
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

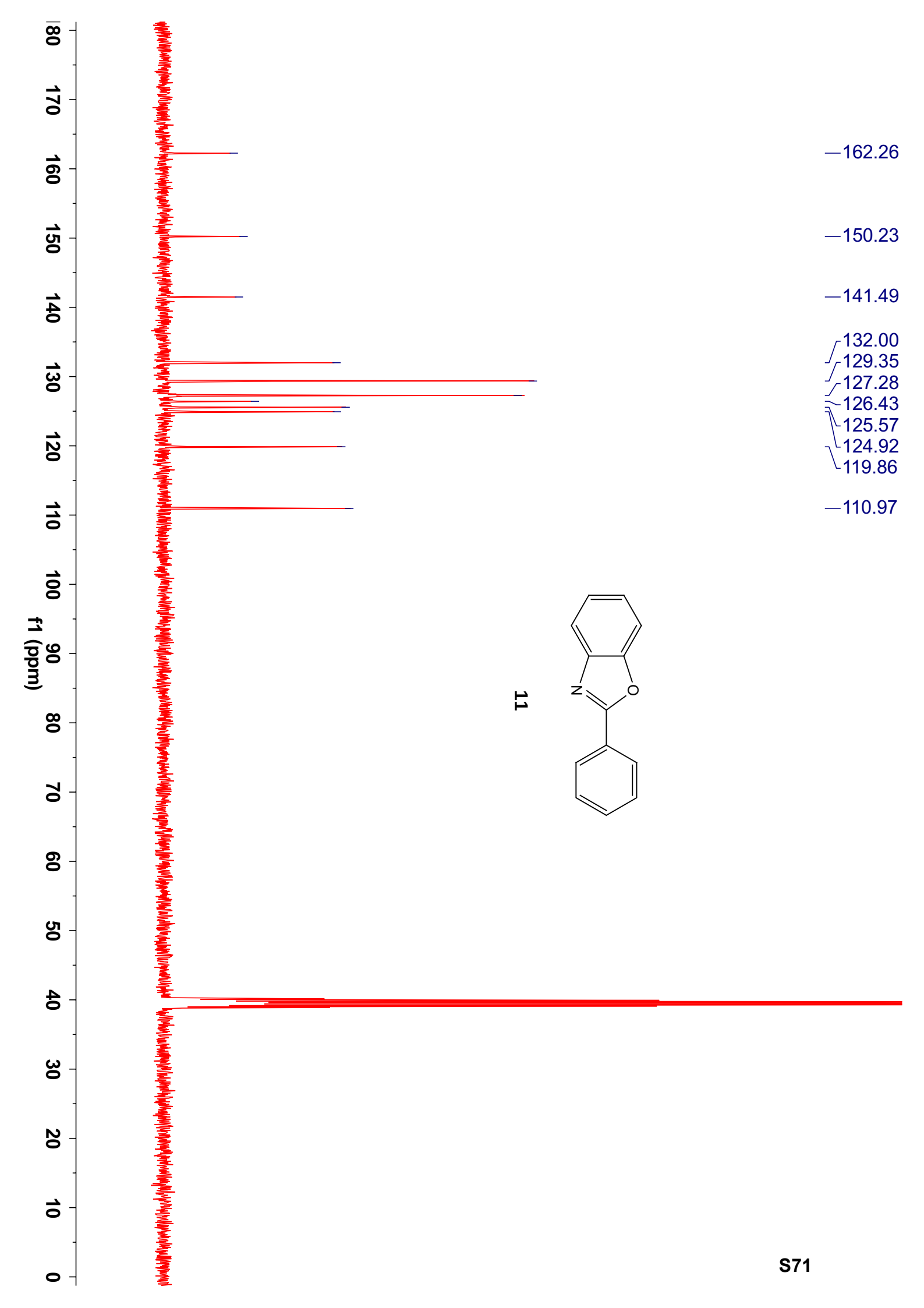

8.29
8.28
8.27
8.26
7.83
7.83
7.82
7.81
7.80
7.80
7.80
7.39
7.38
7.36
7.36
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.27
7.27
7.26
7.26
7.25
7.24
4.30
4.27
4.25
3.26
3.24
3.21
N
N
0.99
1.06
6.05
1.96
1.96
f1 (ppm)

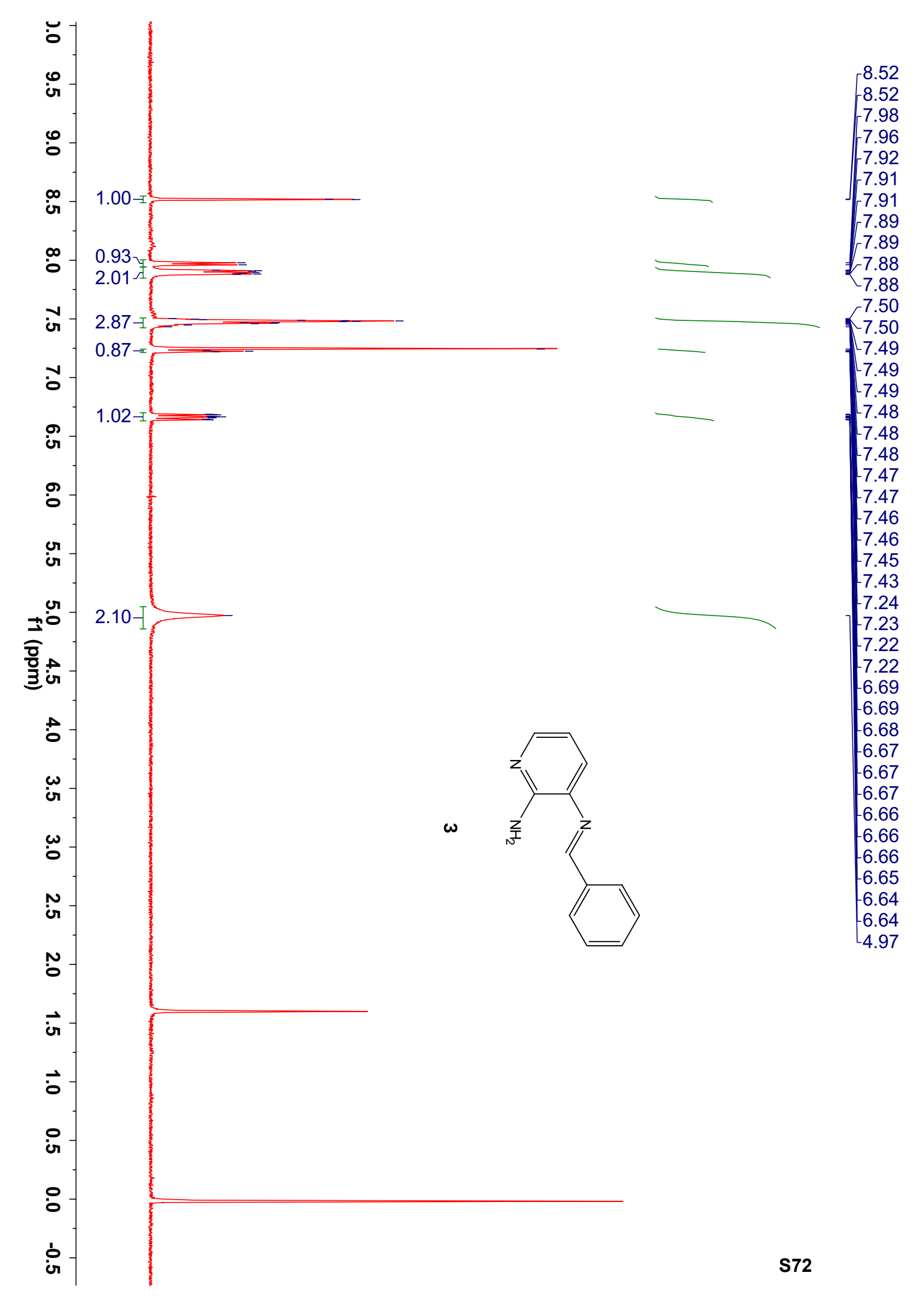
9

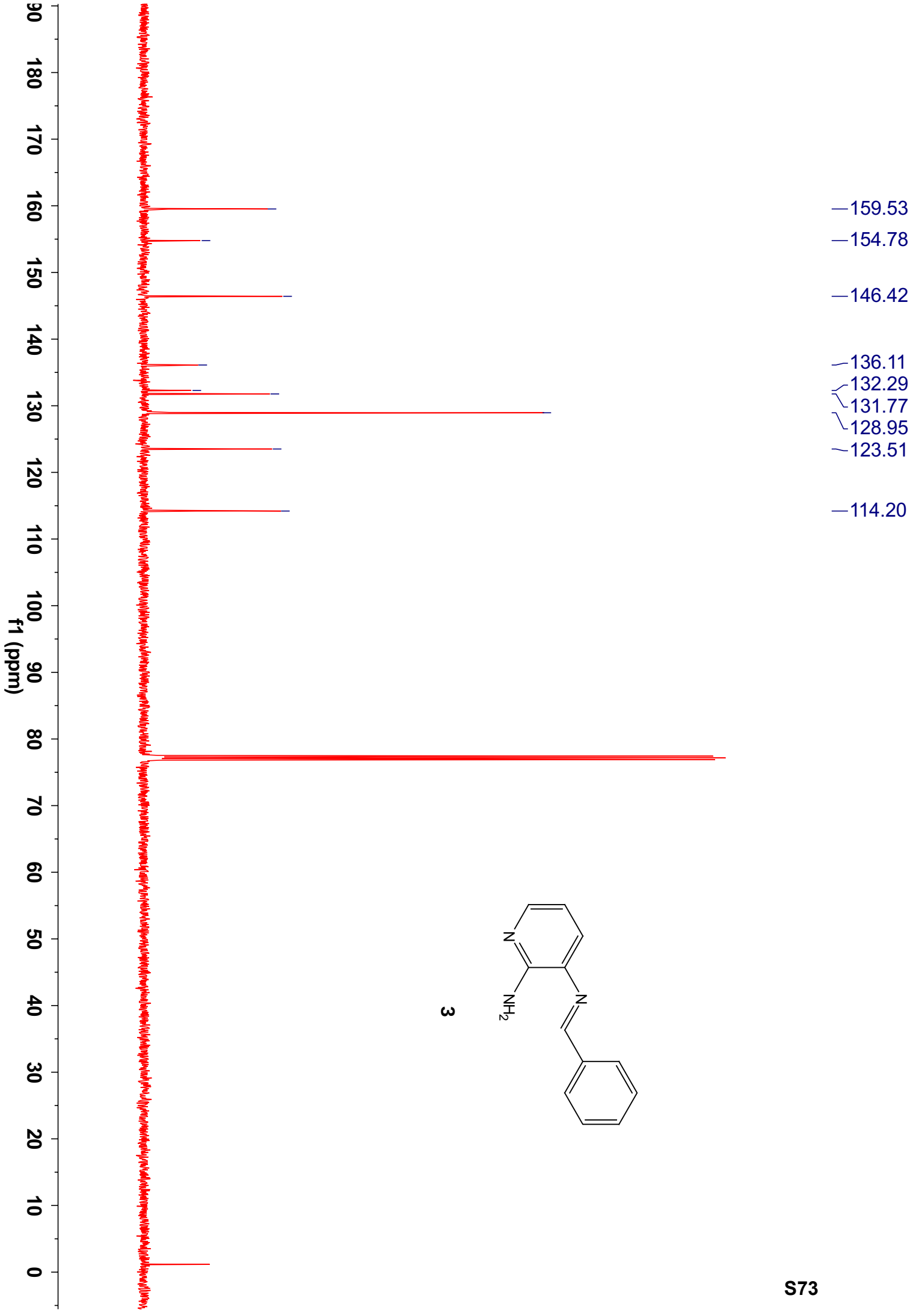

f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
149.09
143.87
134.65
134.31
130.19
128.12
127.73
126.61
125.63
122.71
122.49
119.72
109.11
40.39
28.22
9
N
N


8.25
8.23
8.23
8.23
8.22
7.72
7.72
7.67
7.67
7.60
7.60
7.59
7.43
7.41
7.40
7.40
7.40
1.89
1.90
2.91
2.00
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)
N
O

11


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
162.26
150.23
141.49
132.00
129.35
127.28
126.43
125.57
124.92
119.86
110.97
N
O
11


1.00
0.93
2.01
2.87
0.87
1.02
2.10
f1 (ppm)
3
NH2
N
N
8.52
8.52
7.98
7.96
7.92
7.91
7.91
7.89
7.89
7.88
7.88
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.43
7.24
7.23
7.22
7.22
6.69
6.69
6.68
6.67
6.67
6.67
6.66
6.66
6.66
6.65
6.64
6.64
4.97


f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
159.53
154.78
146.42
136.11
132.29
131.77
128.95
123.51
114.20
N
NH2
N
3