Electronic Supplementary Material (ESI) for ChemComm.

Regioselective differentiation of vicinal methylene C-H bonds enabled by silver-catalysed nitrene transfer

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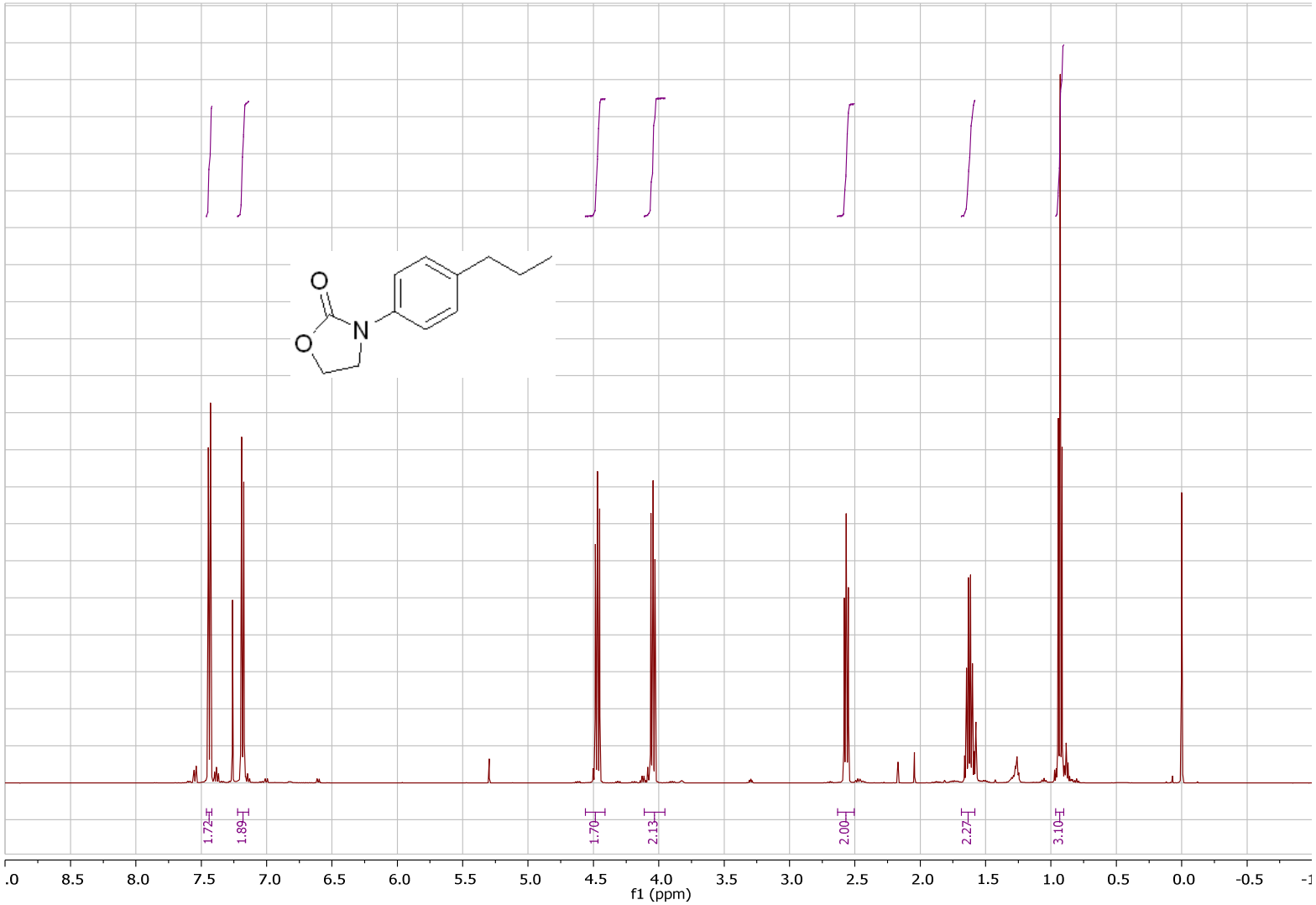
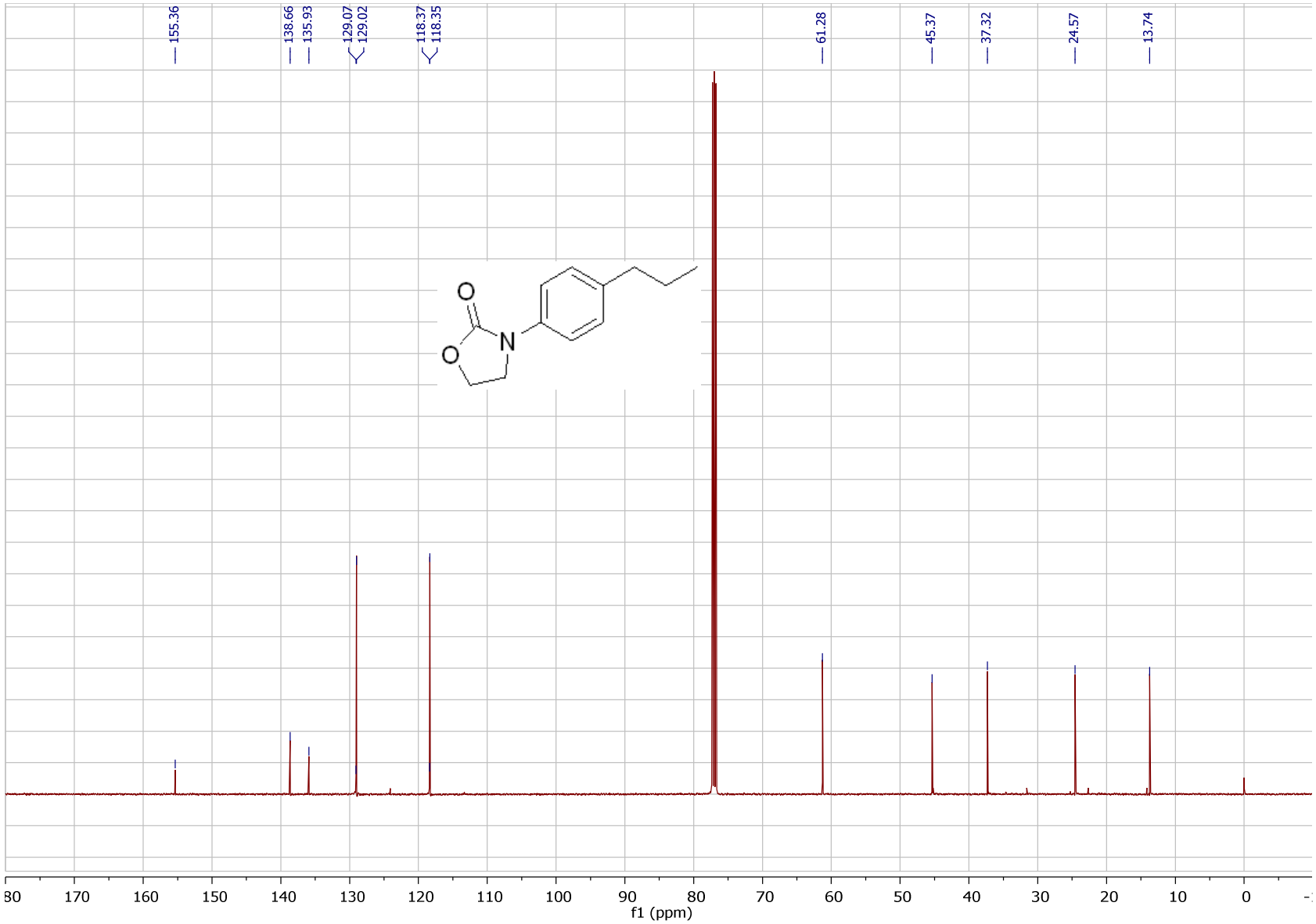
I. NMR Data of New Compounds and Reaction Products

Arene 5-P

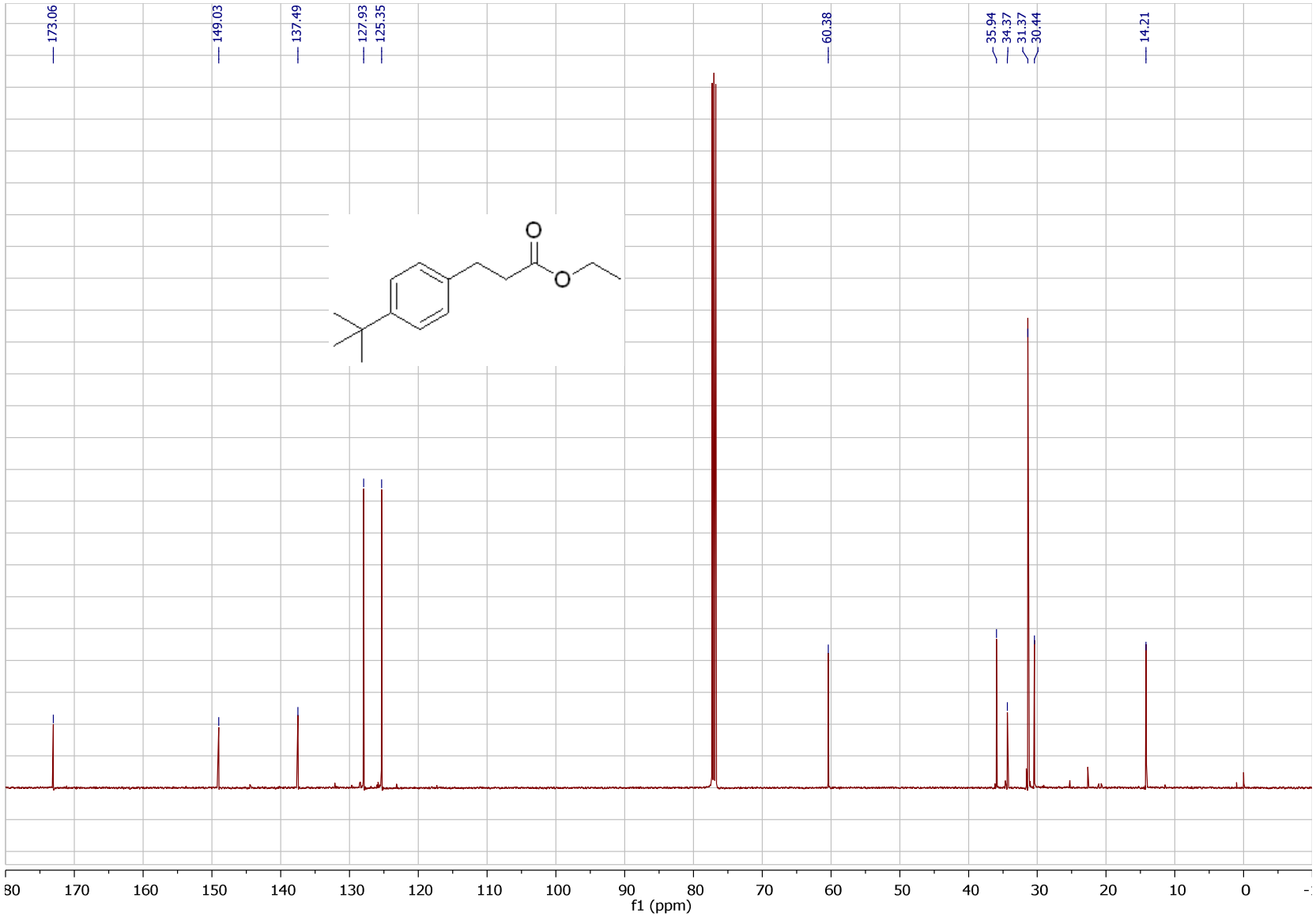


Arene 5-P

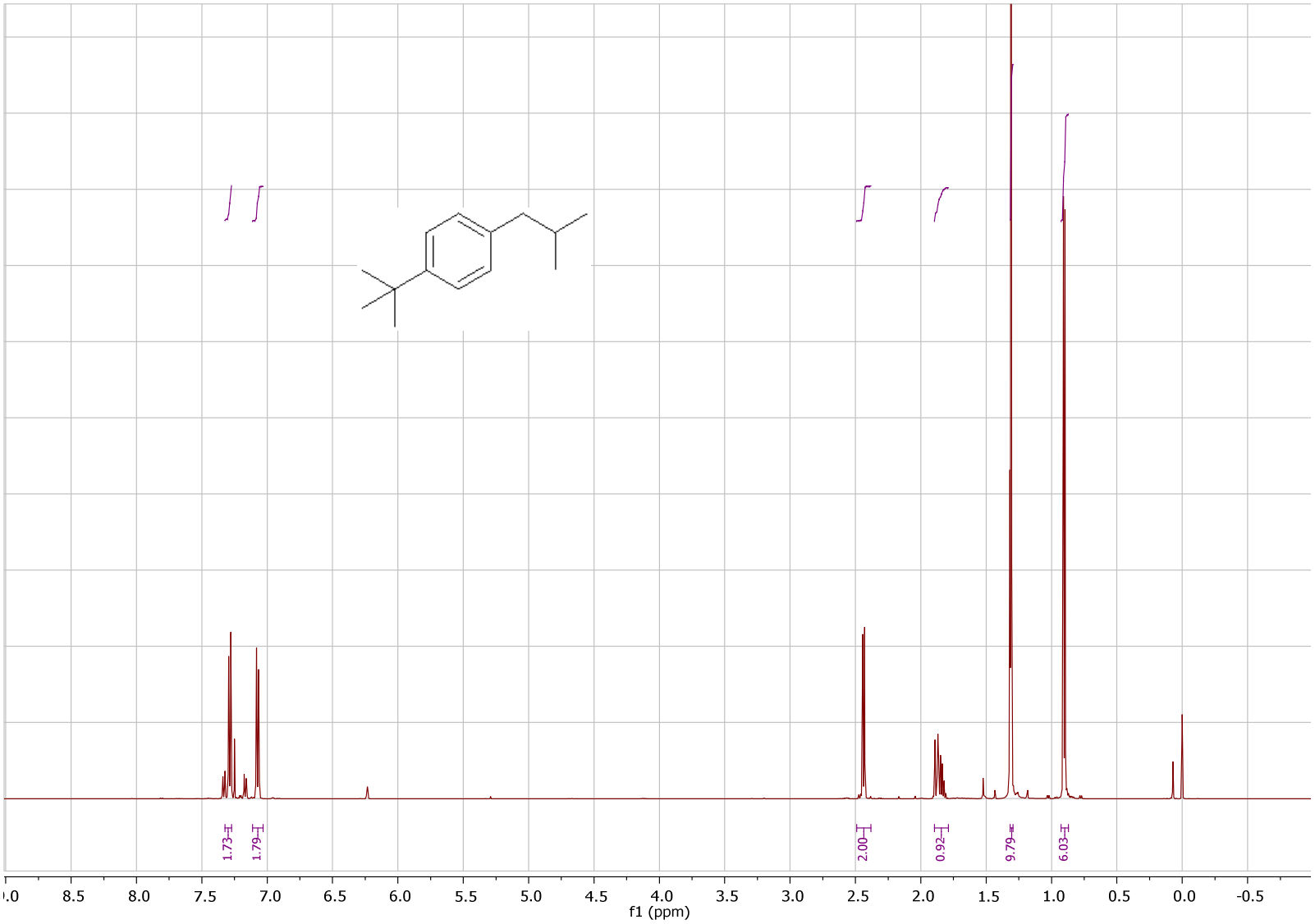

155.36
138.66
135.93
129.07
129.02
118.37
118.35
61.28
45.37
37.32
24.57
13.74
O
O
N
f1 (ppm)

Arene 7-P

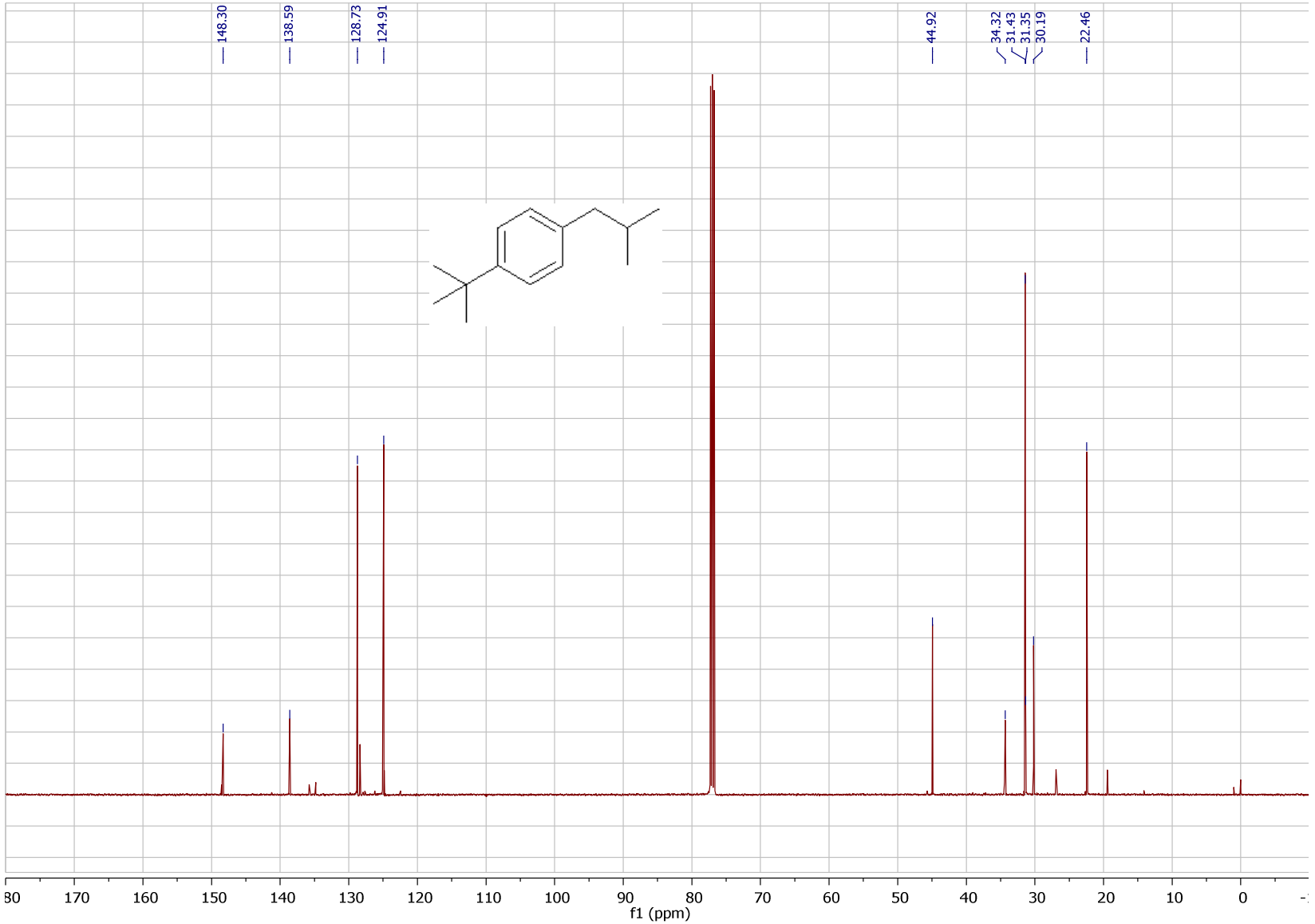
Arene 7-P


173.06
149.03
137.49
127.93
125.35
60.38
35.94
34.37
31.37
30.44
14.21
O
O
f1 (ppm)

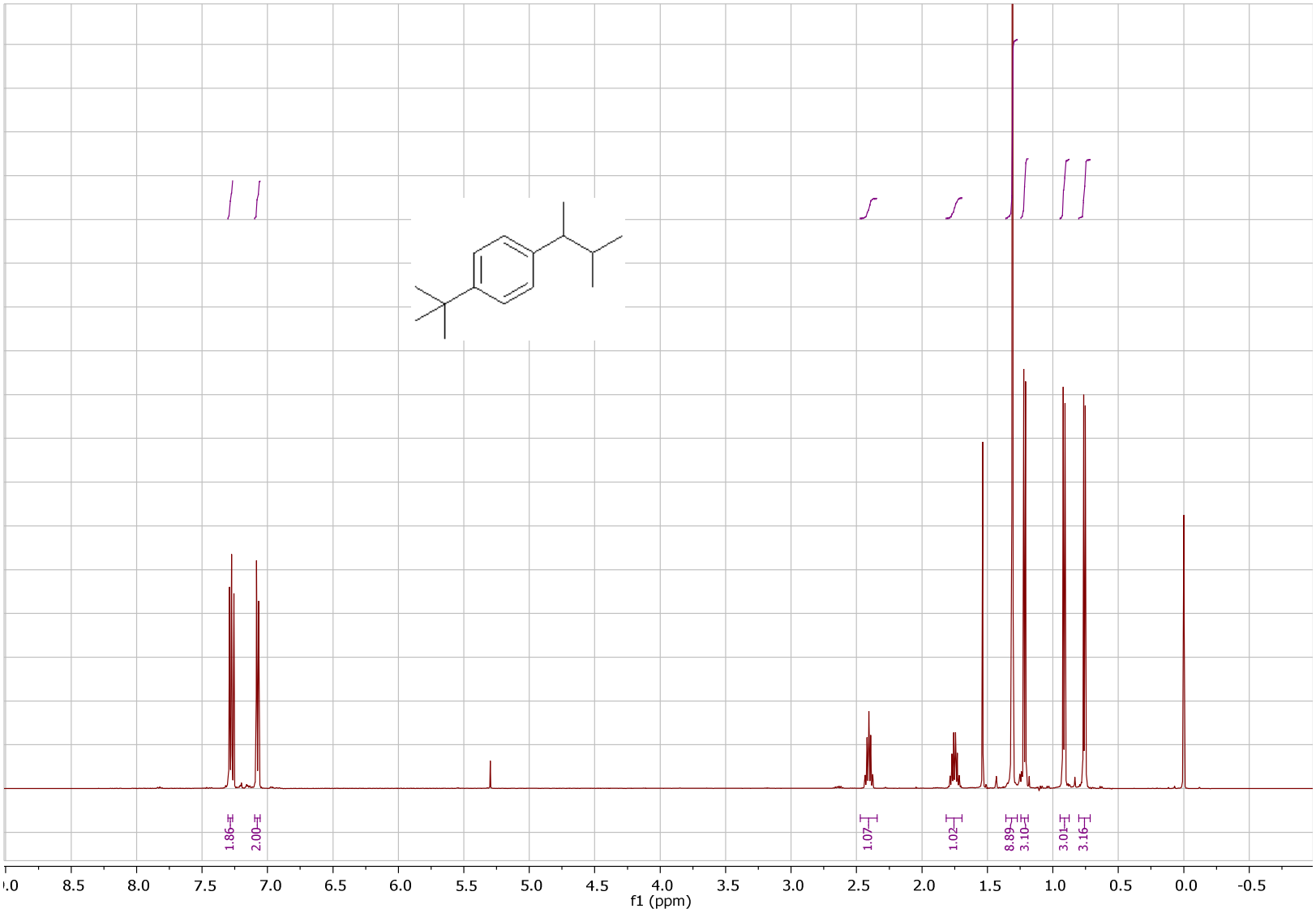
Arene 9-P


1.73
1.79
2.00
0.92
9.79
6.03
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
-0.5
f1 (ppm)

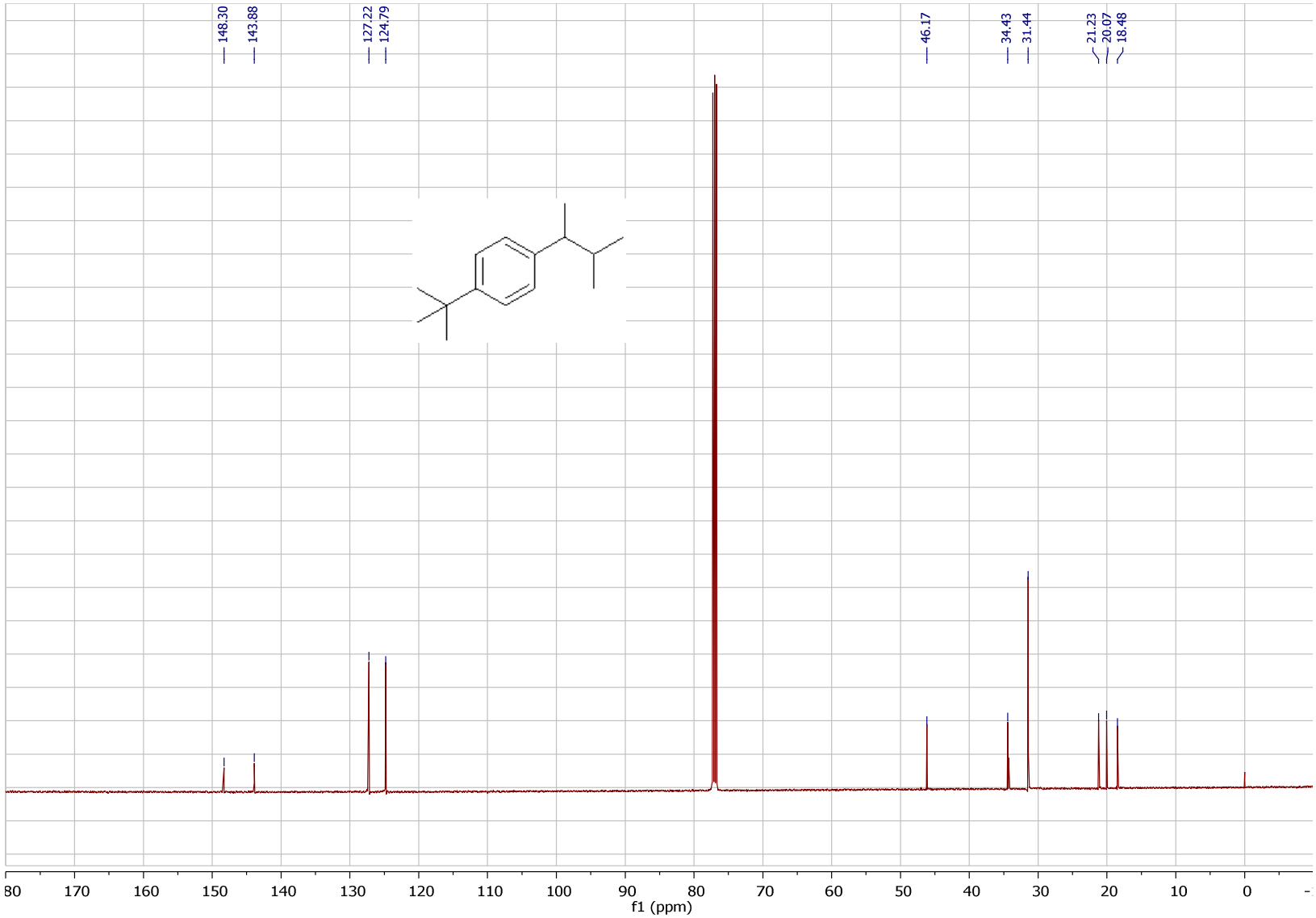
Arene 9-P



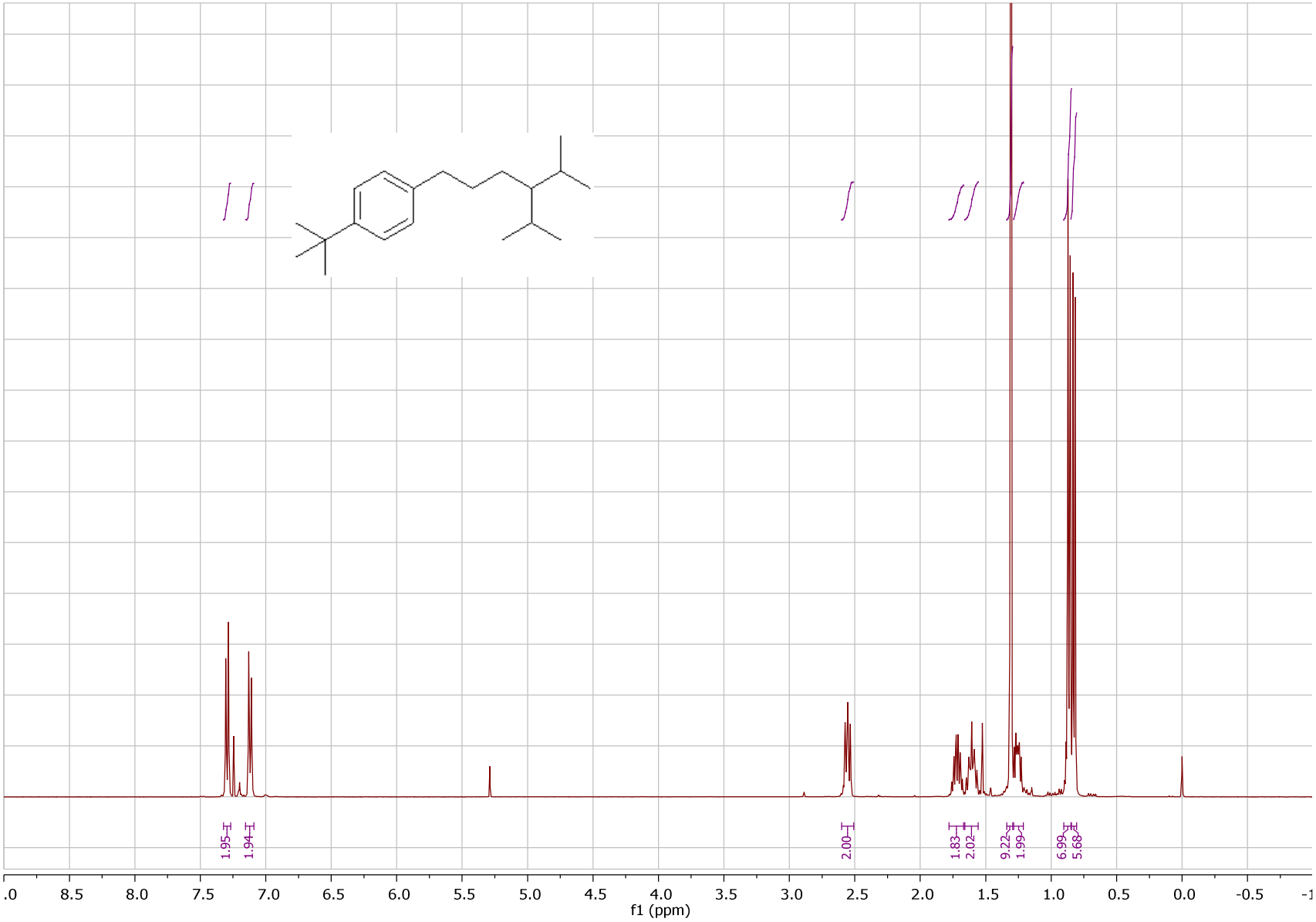
Arene 10-P


1.86
2.00
1.07
1.02
8.89
3.10
3.01
3.16
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
-0.5
f1 (ppm)

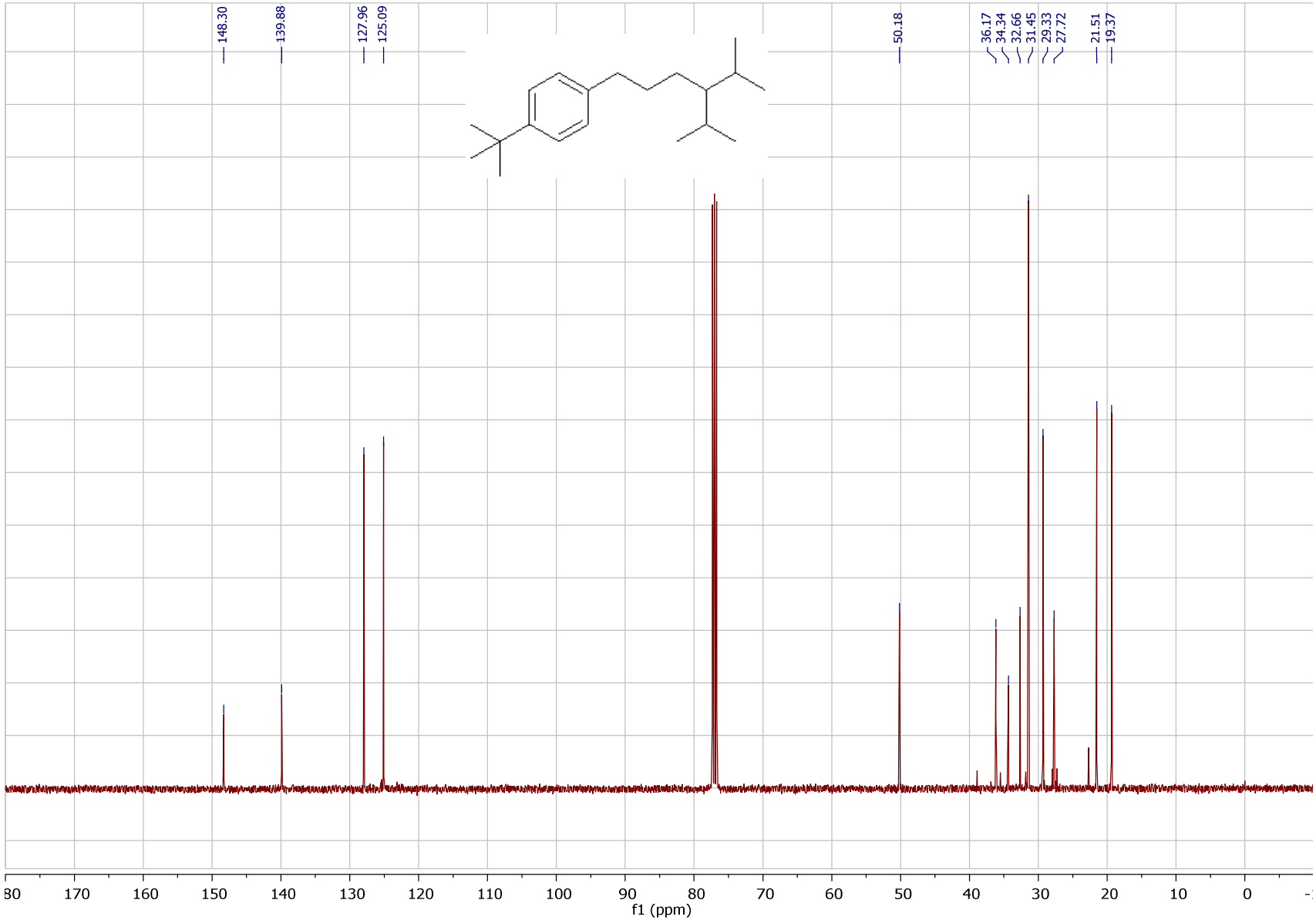
Arene 10-P



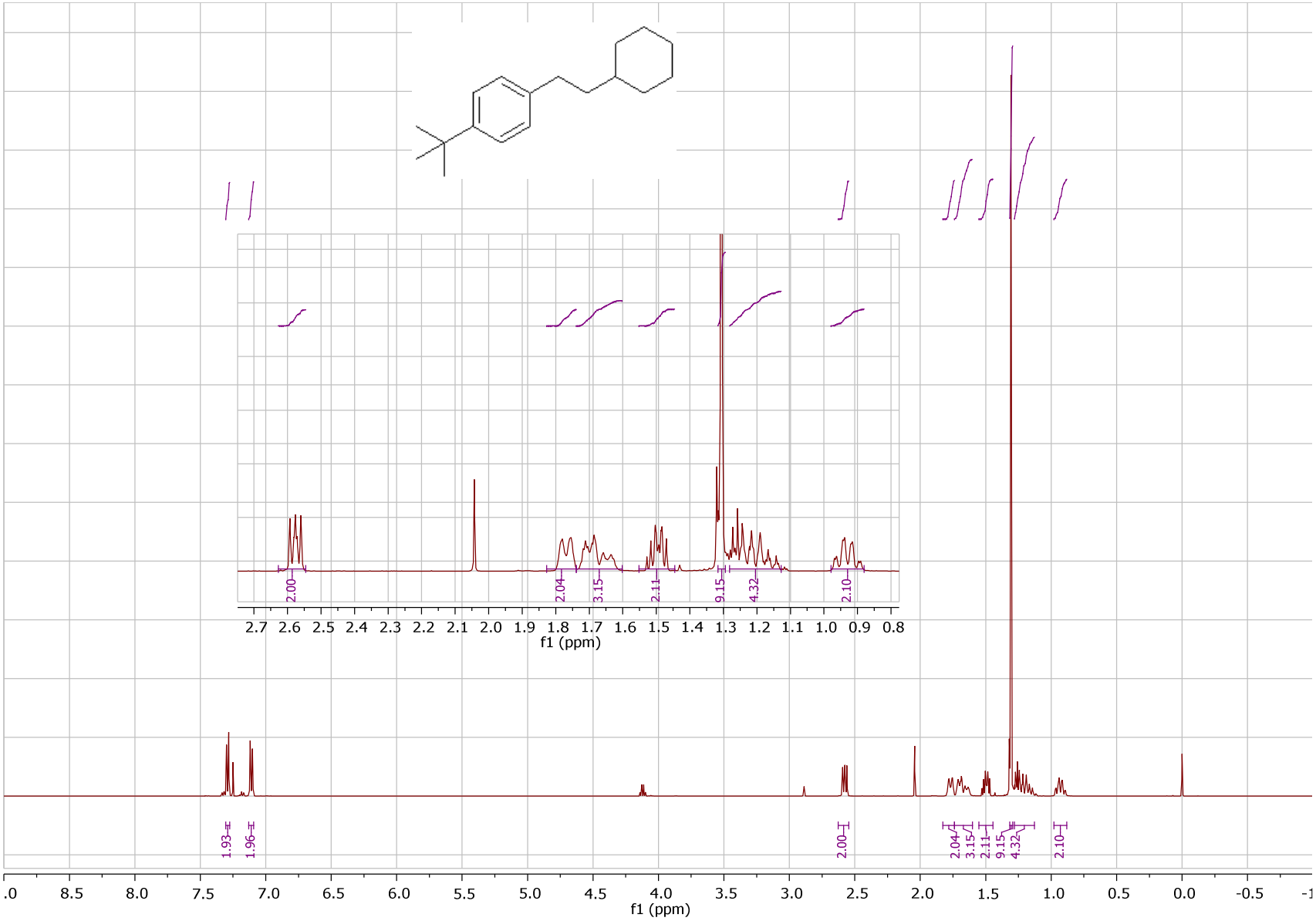
Arene 11-P


1.95
1.94
2.00
1.83
2.02
9.22
1.99
6.99
5.68
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
-0.5
f1 (ppm)

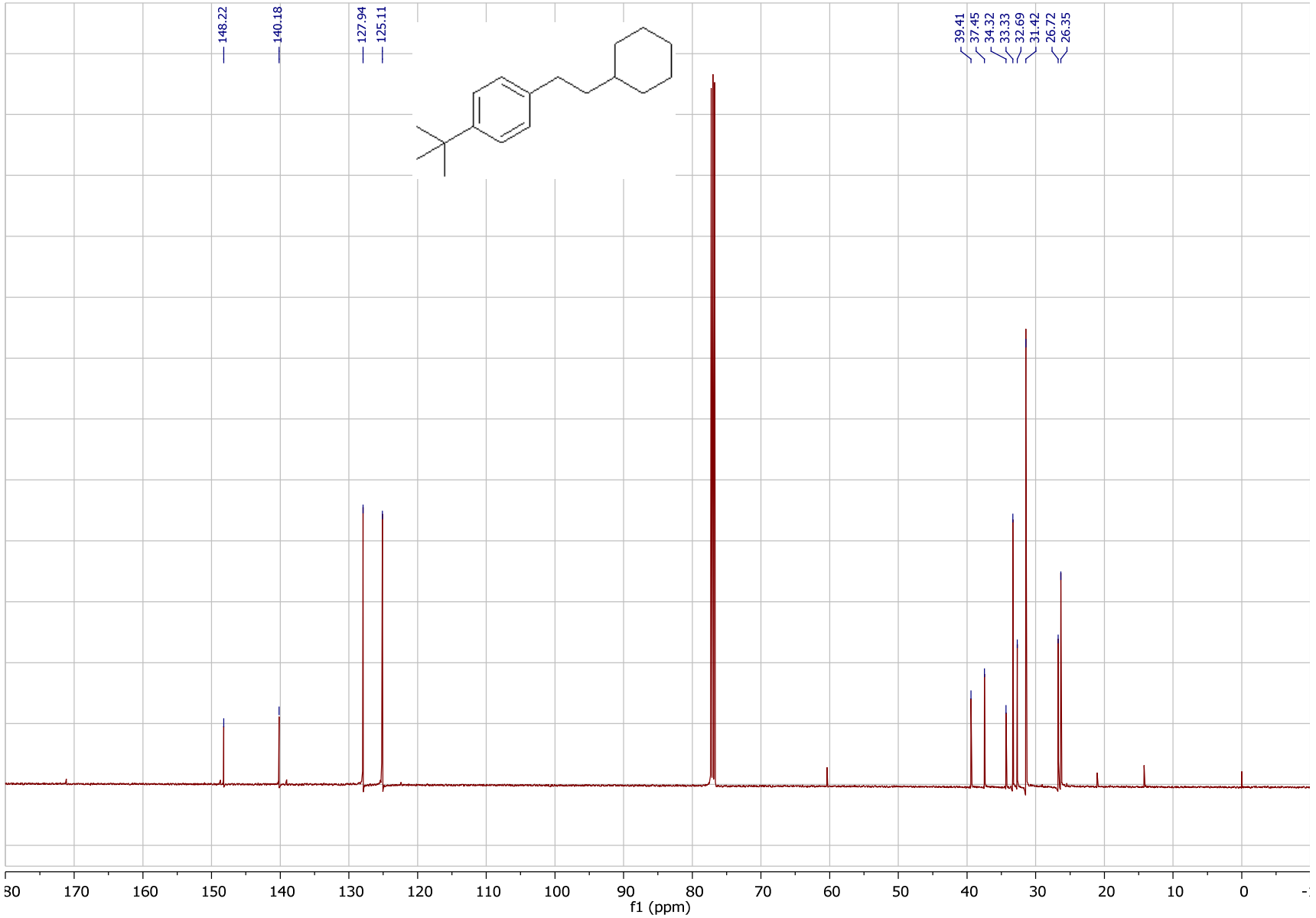
Arene 11-P


148.30
139.88
127.96
125.09
50.18
36.17
34.34
32.66
31.45
29.33
27.72
21.51
19.37
f1 (ppm)

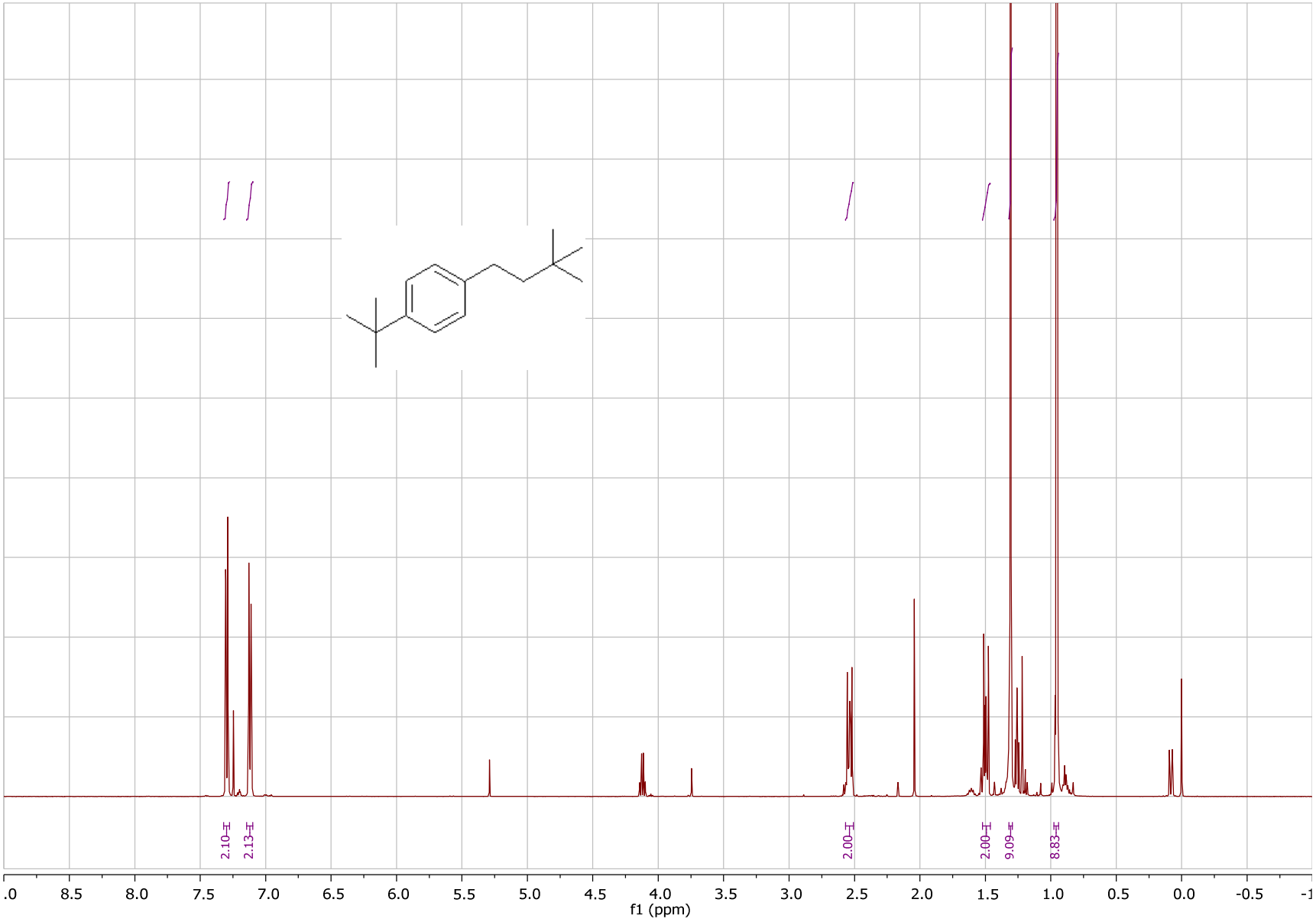
Arene 13-P


2.00
2.04
3.15
2.11
9.15
4.32
2.10
2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8
f1 (ppm)
1.93
1.96
2.00
2.04
3.15
2.11
9.15
4.32
2.10
.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 -0.5
f1 (ppm)

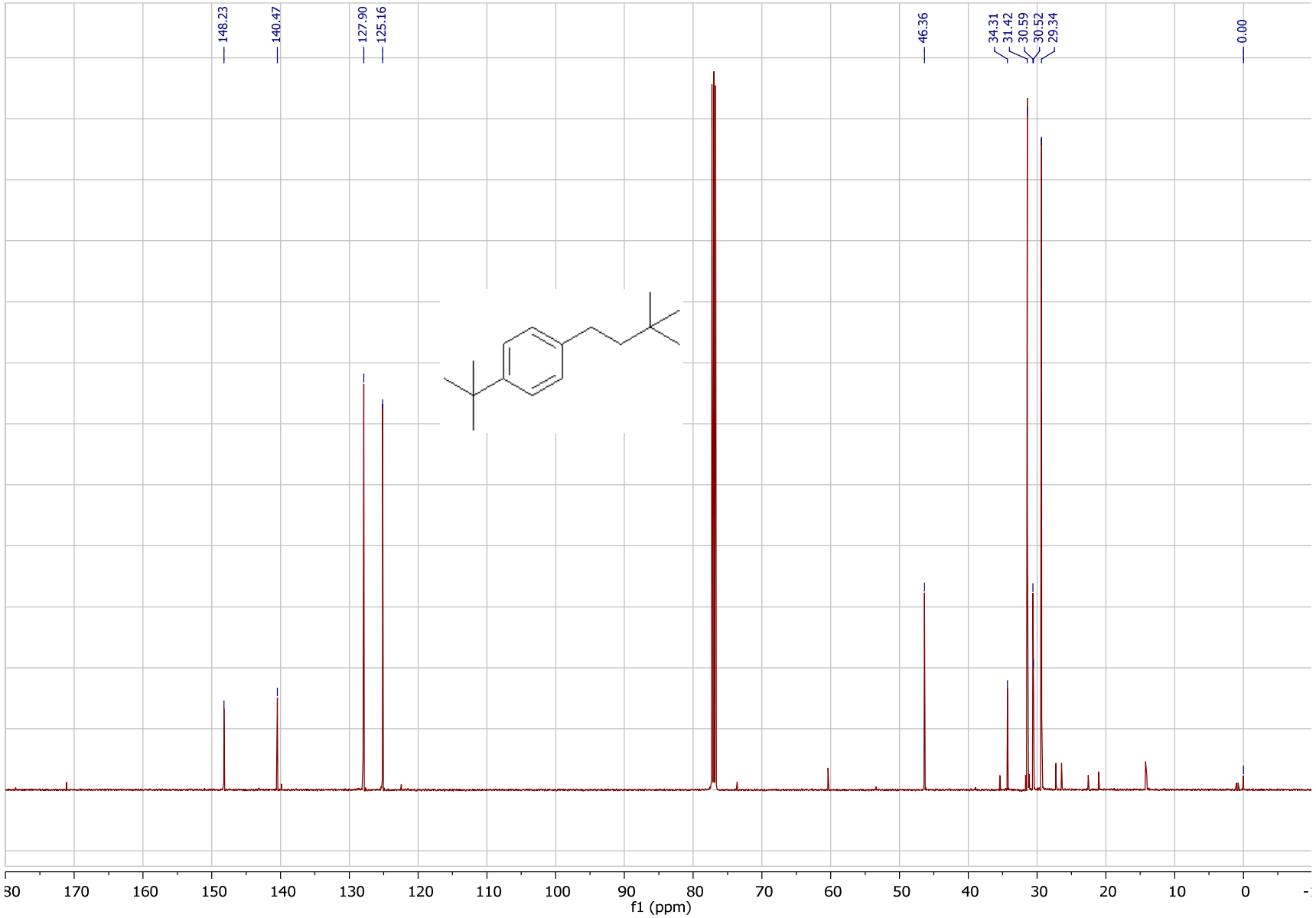
Arene 13-P


148.22
140.18
127.94
125.11
39.41
37.45
34.32
33.33
32.69
31.42
26.72
26.35
f1 (ppm)

Arene 14-P



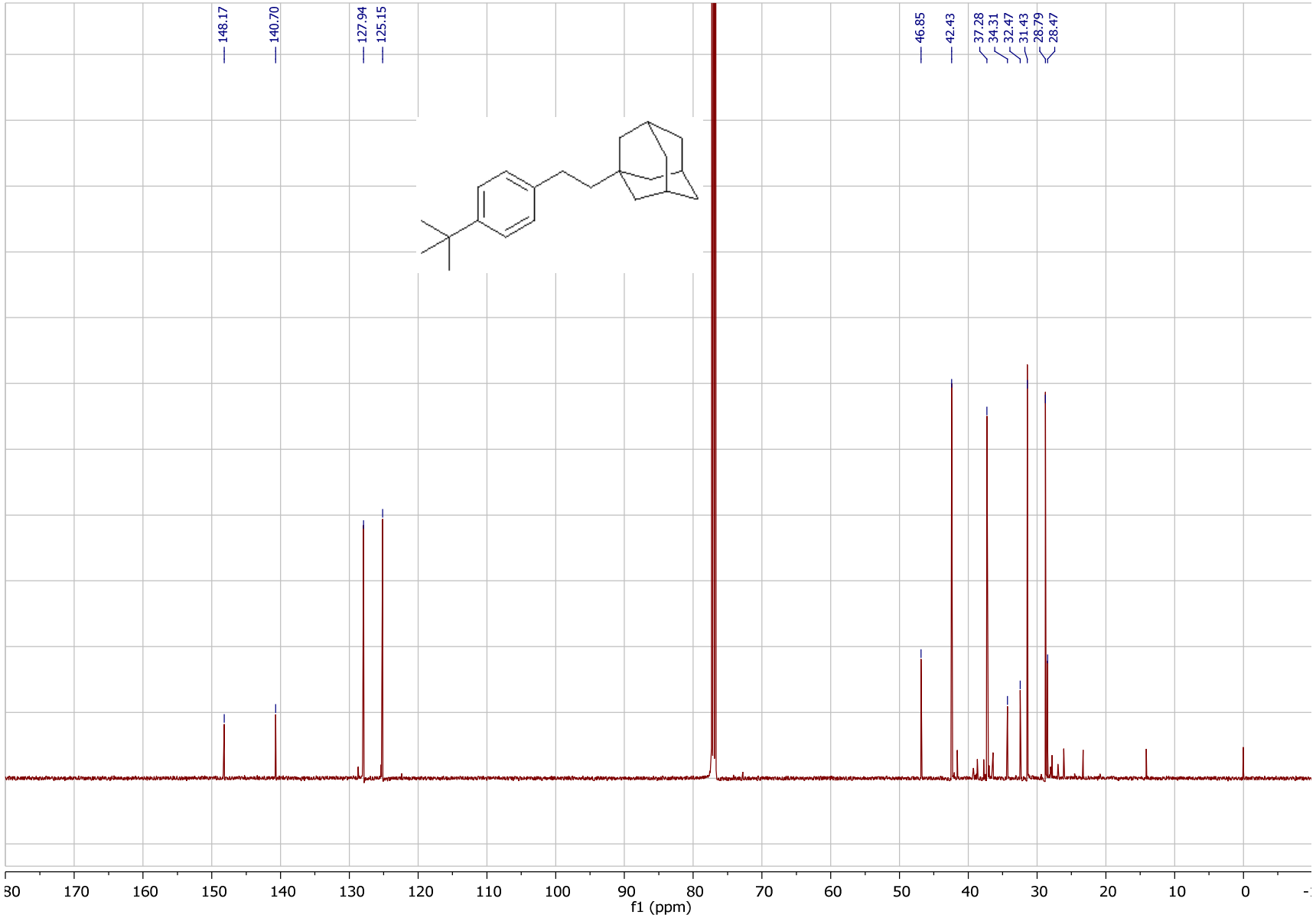
Arene 14-P


148.23
140.47
127.90
125.16
46.36
34.31
31.42
30.59
30.52
29.34
0.00
f1 (ppm)

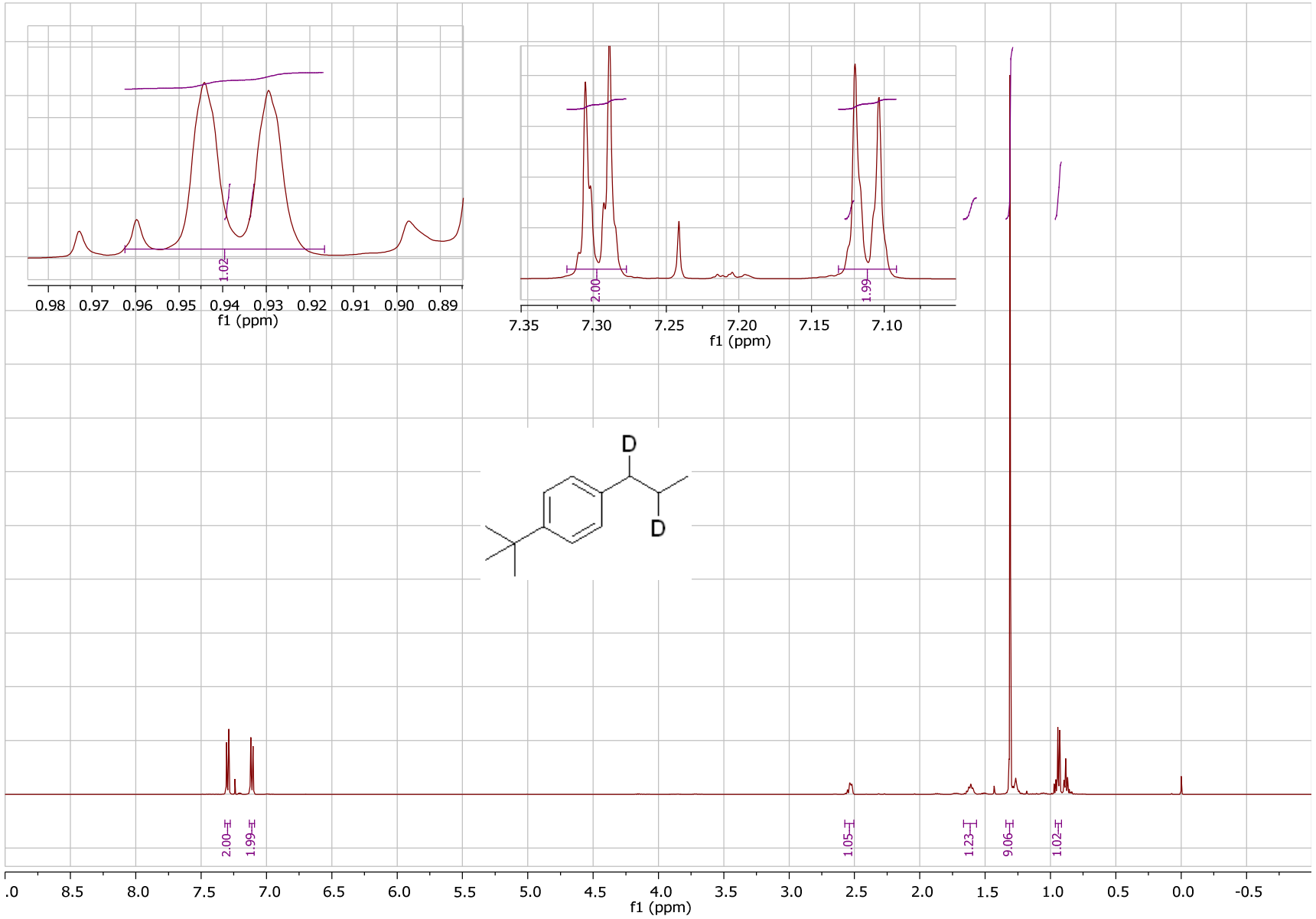
Arene 15-P


1.91
1.89
1.77
3.00
3.36
3.13
6.09
2.03
9.55
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
-0.5
f1 (ppm)

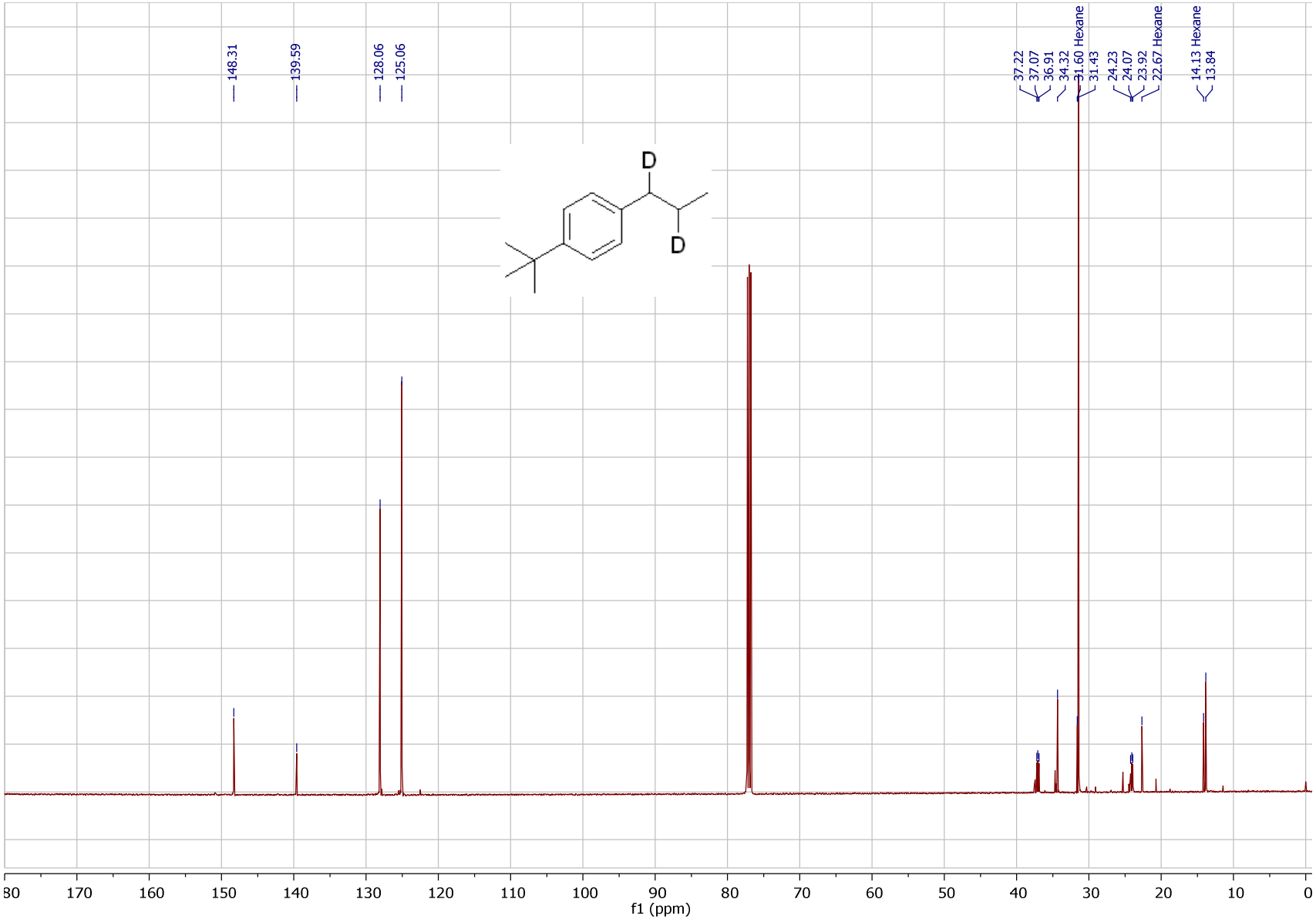
Arene 15-P


148.17
140.70
127.94
125.15
46.85
42.43
37.28
34.31
32.47
31.43
28.79
28.47
f1 (ppm)

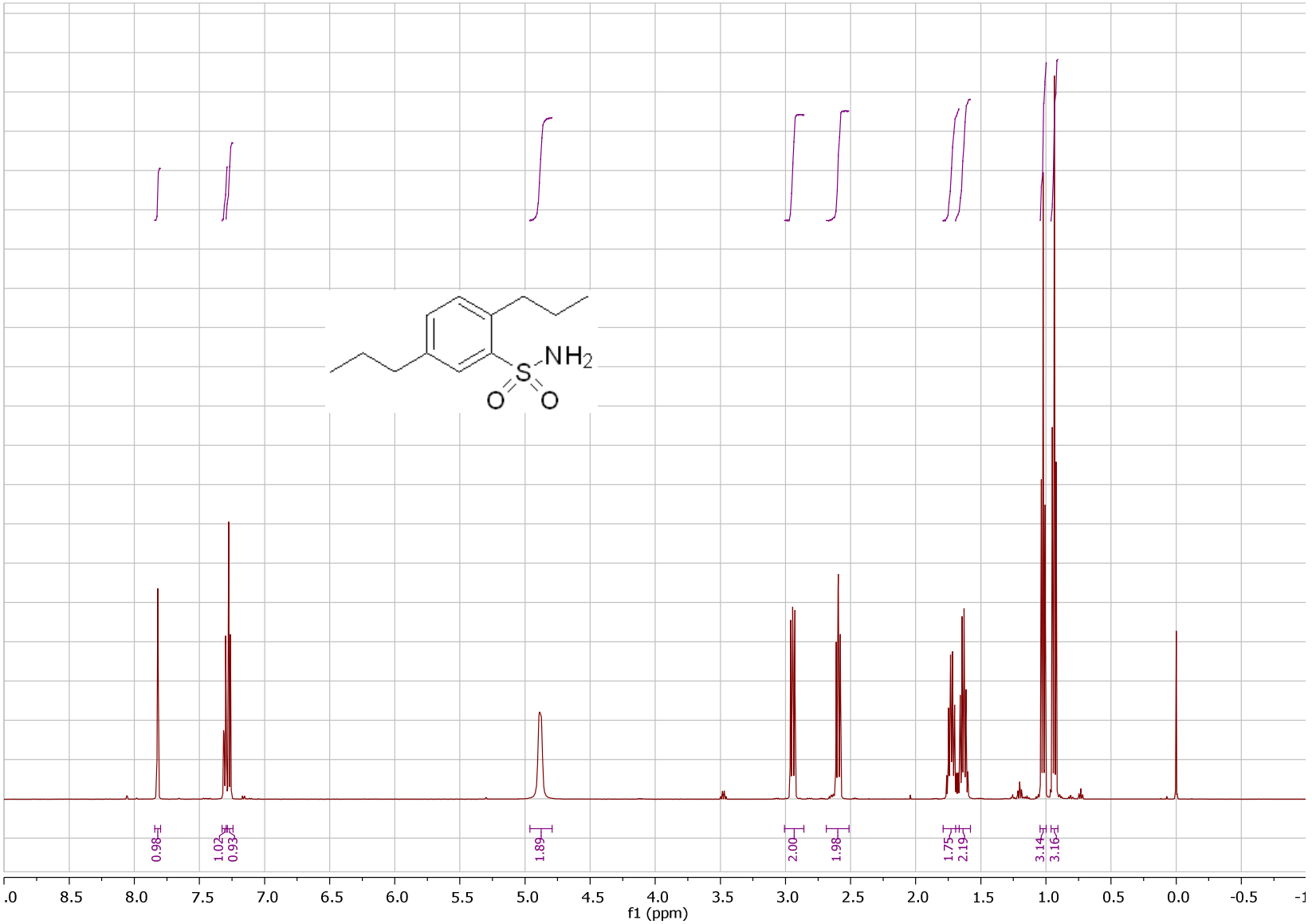
Arene 16-P


1.02
0.98 0.97 0.96 0.95 0.94 0.93 0.92 0.91 0.90 0.89
f1 (ppm)
2.00
1.99
7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
D
D
2.00
1.99
1.05
1.23
9.06
1.02
.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 -0.5
f1 (ppm)

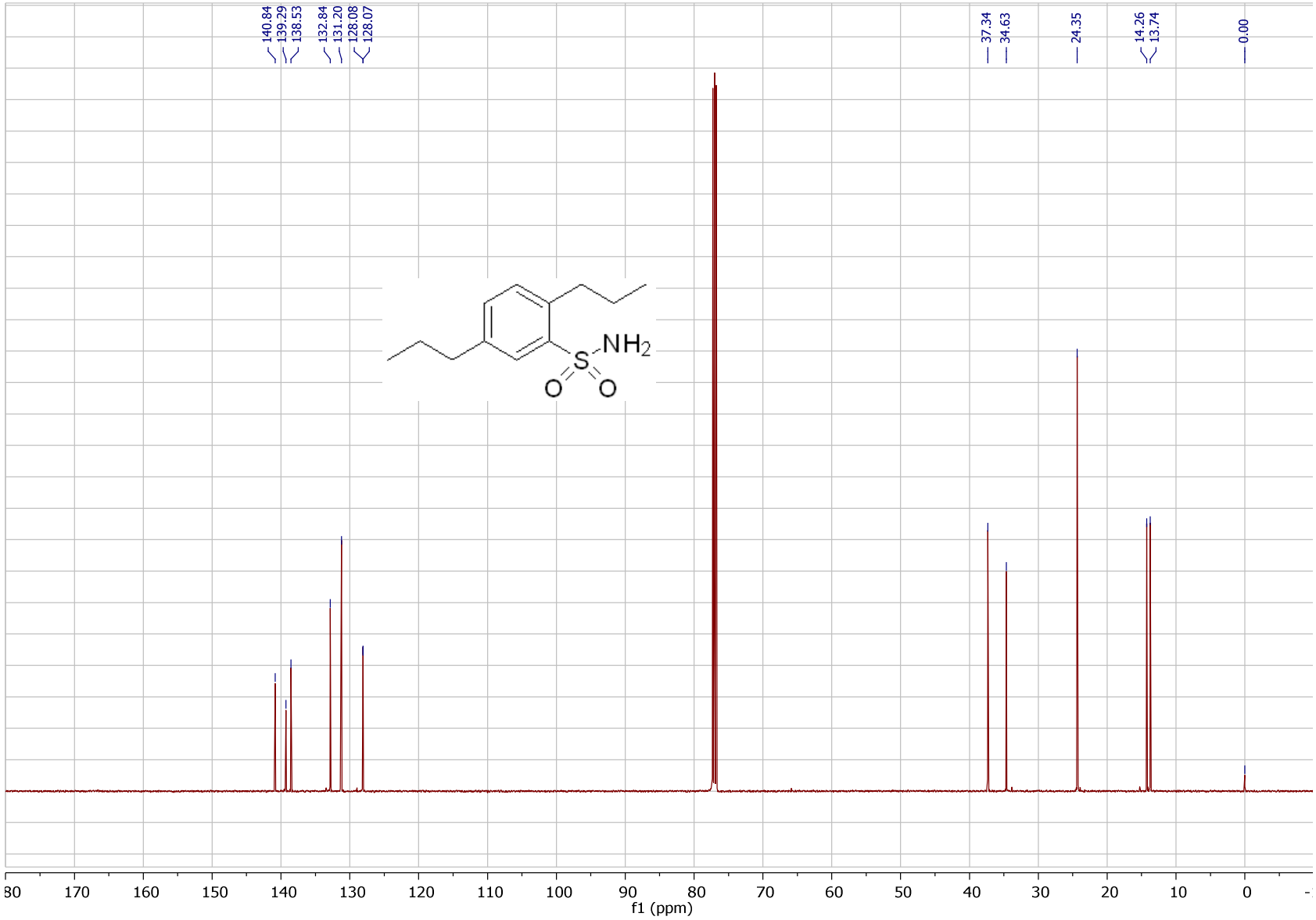
Arene 16-P


148.31
139.59
128.06
125.06
37.22
37.07
36.91
34.32
31.60 Hexane
31.43
24.23
24.07
23.92
22.67 Hexane
14.13 Hexane
13.84
D
D
f1 (ppm)

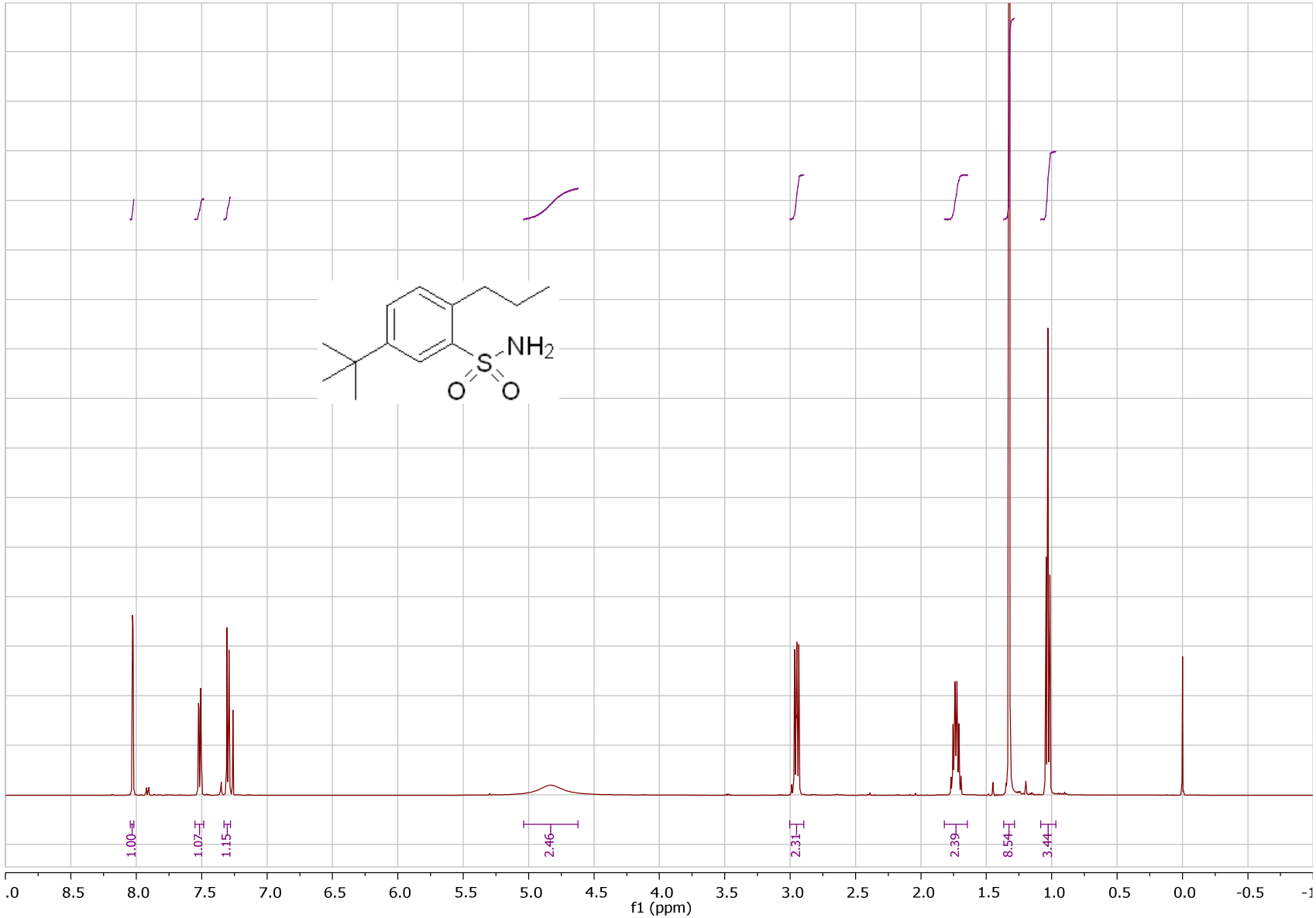
Compound 1


NH2
S
O
O
0.98
1.02
0.93
1.89
2.00
1.98
1.75
2.19
3.14
3.16
.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
-0.5
f1 (ppm)

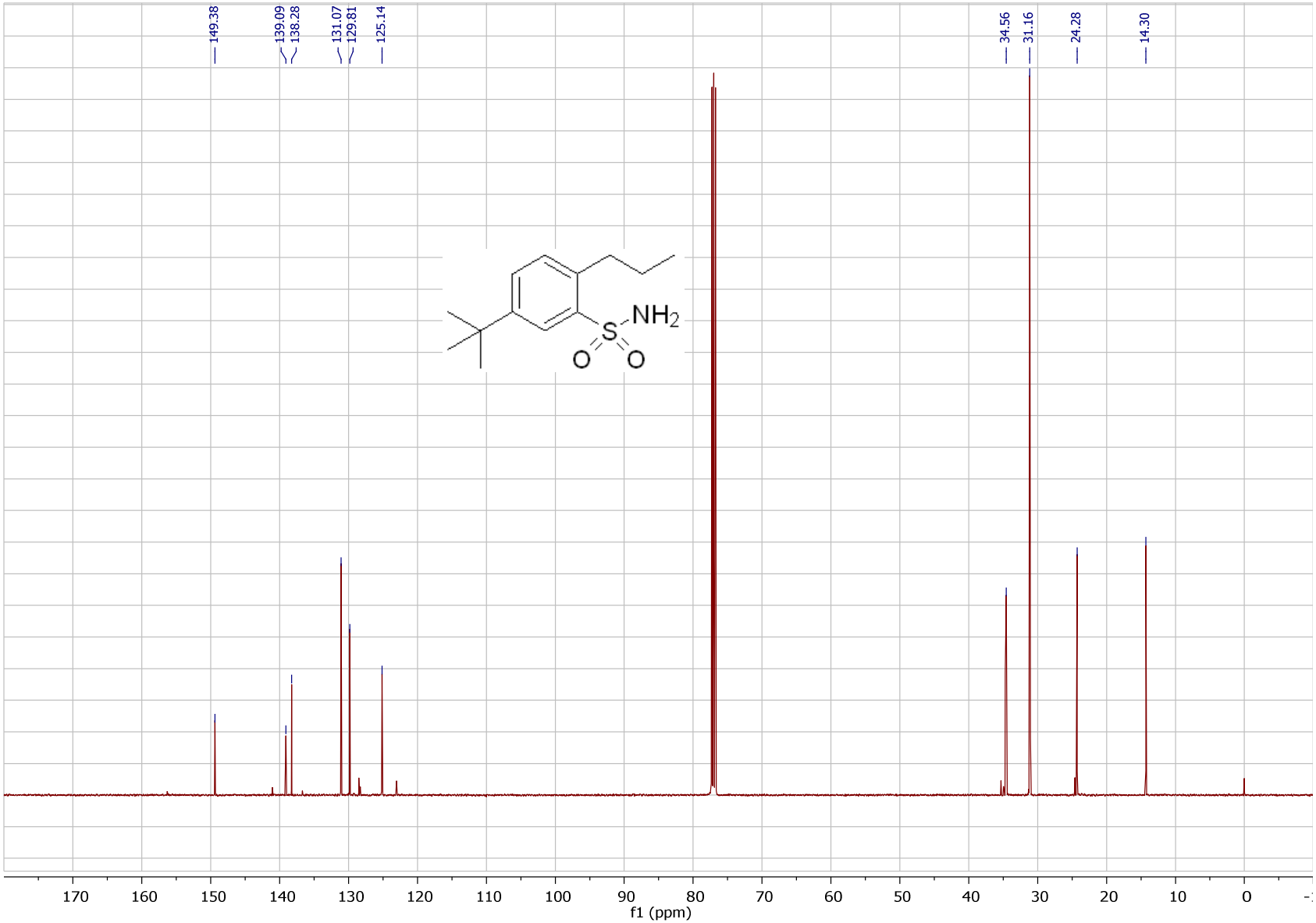
Compound 1


140.84
139.29
138.53
132.84
131.20
128.08
128.07
37.34
34.63
24.35
14.26
13.74
0.00
NH2
S
O
O
f1 (ppm)

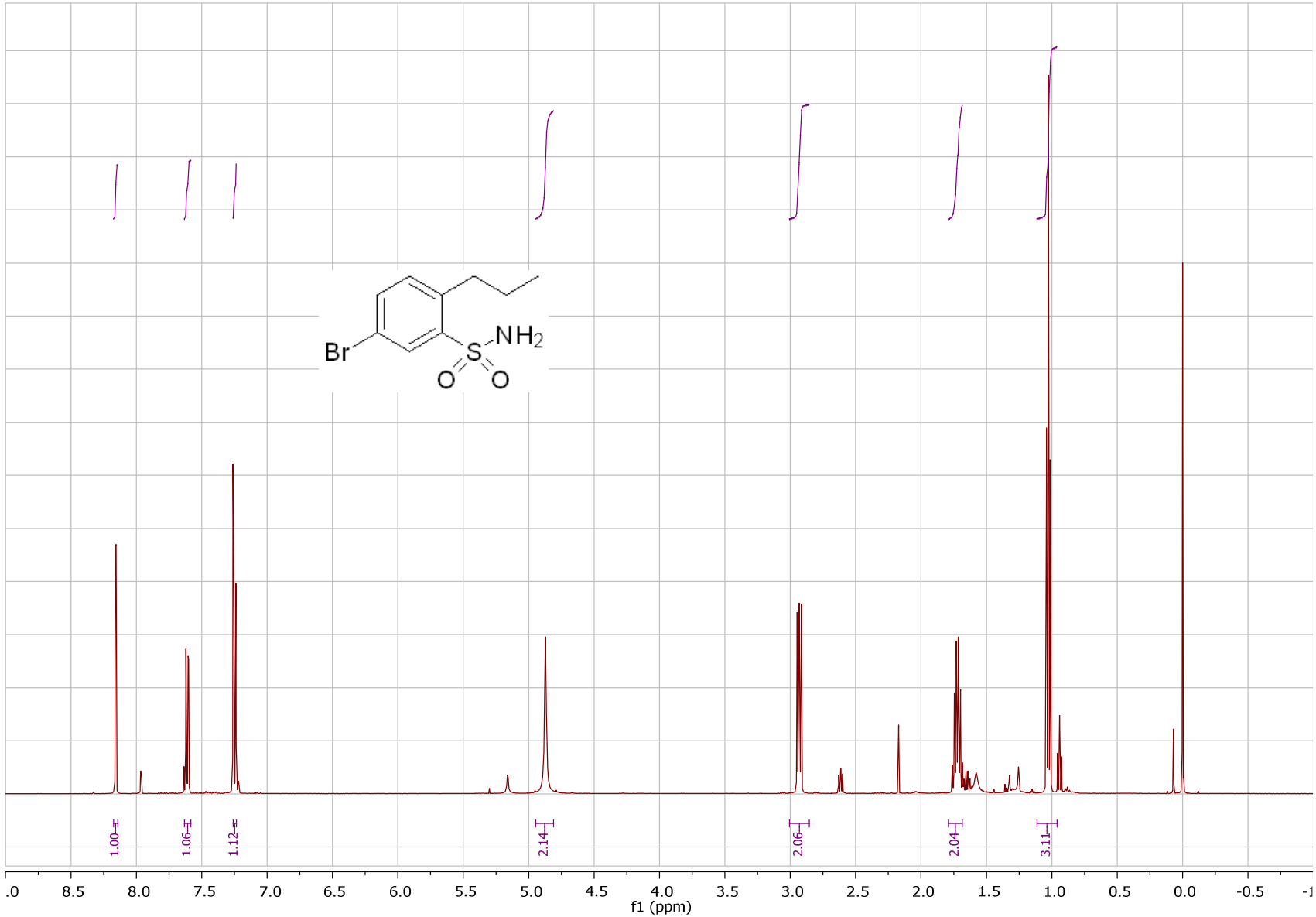
Compound 2



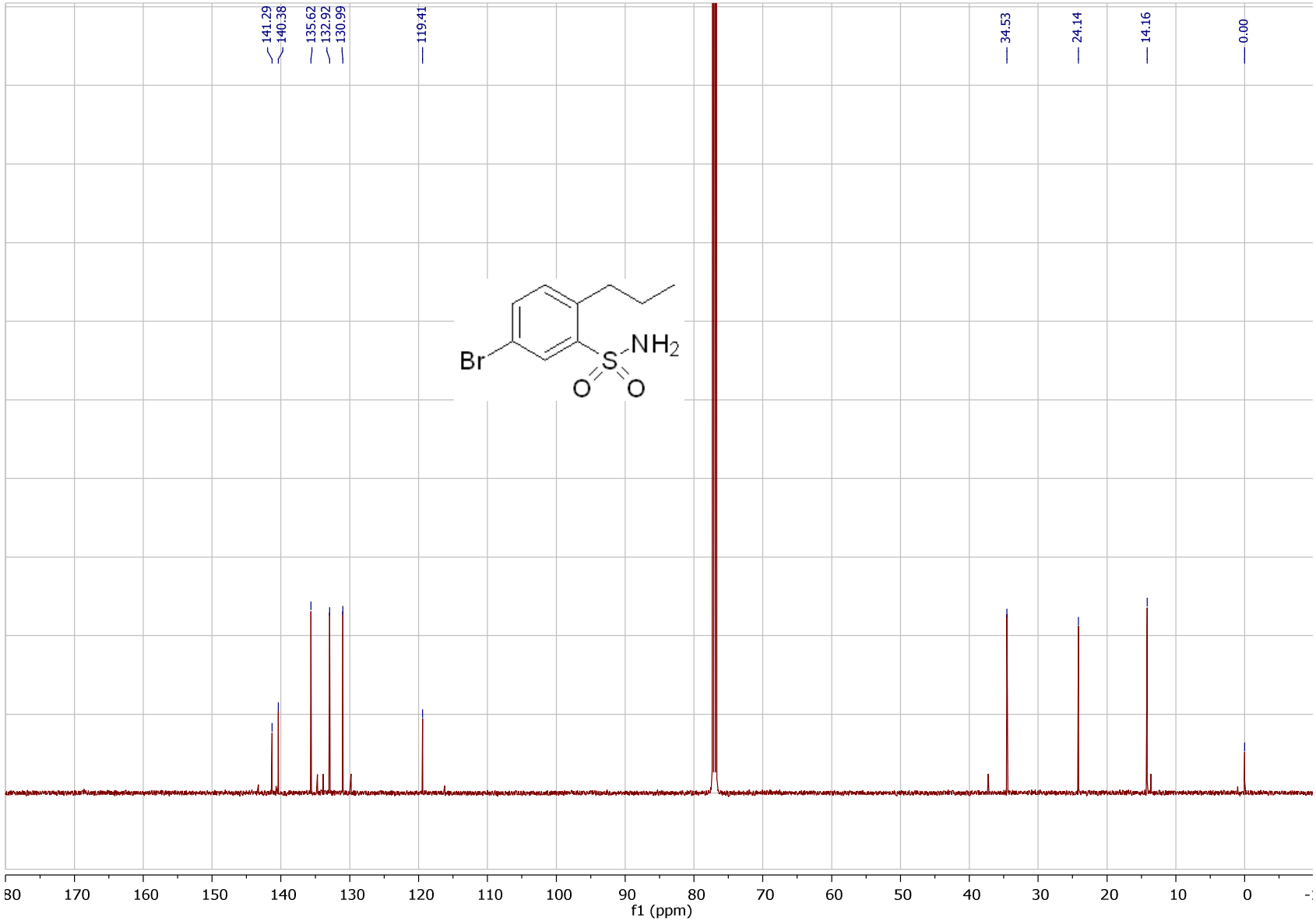
Compound 2


149.38
139.09
138.28
131.07
129.81
125.14
34.56
31.16
24.28
14.30
NH2
S
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

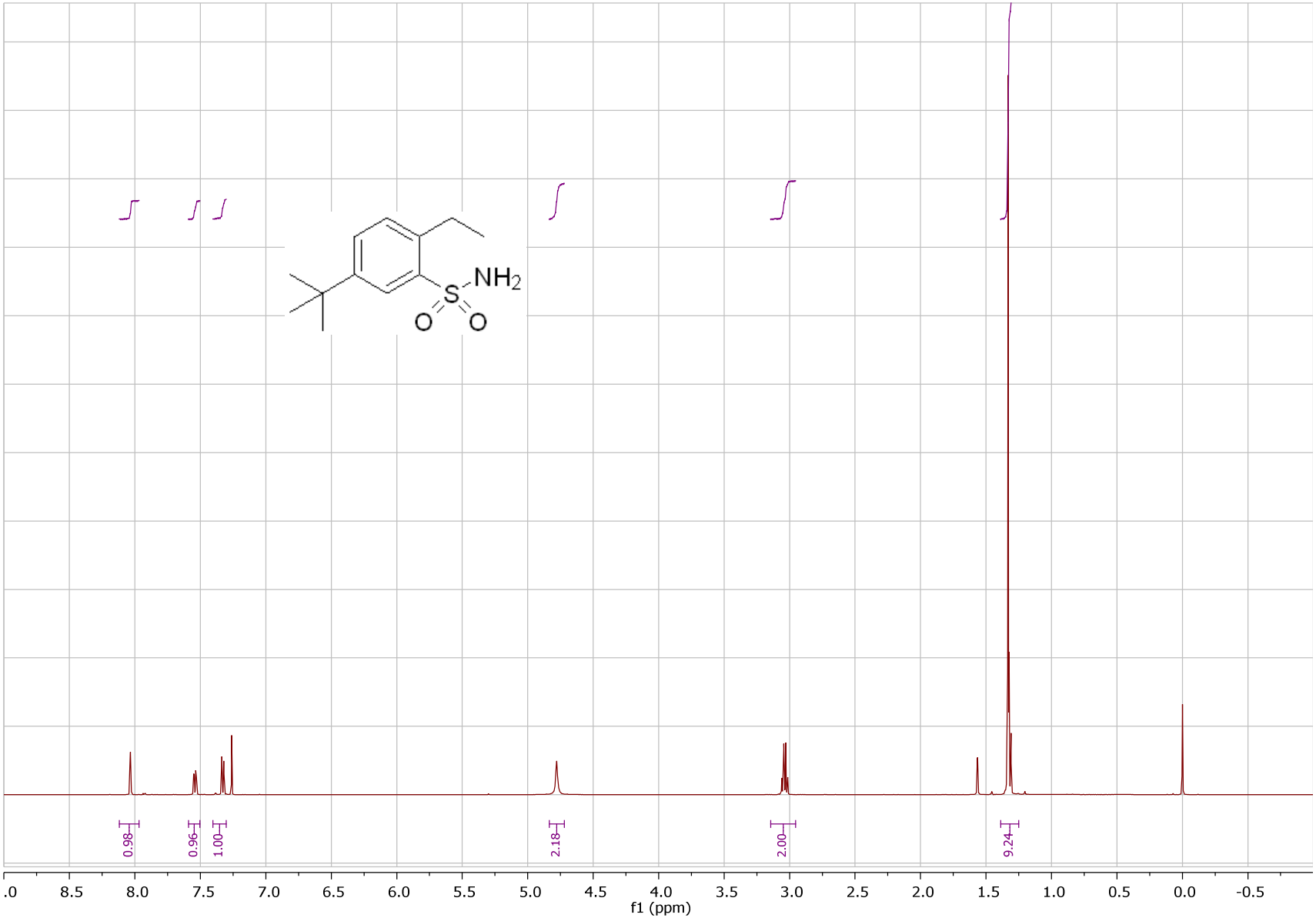
Compound 3



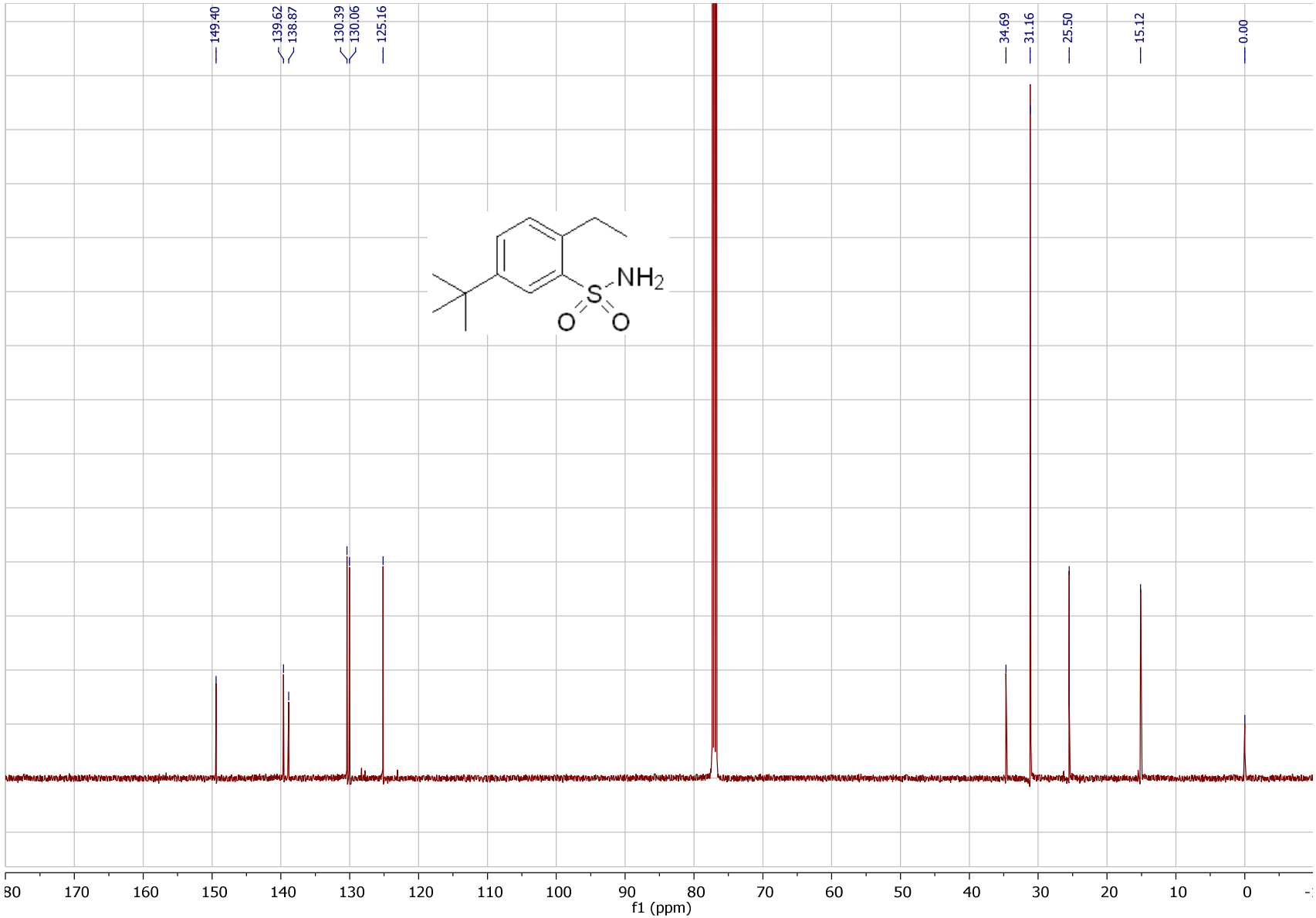
Compound 3


141.29
140.38
135.62
132.92
130.99
119.41
34.53
24.14
14.16
0.00
Br
S
NH2
O
O
f1 (ppm)

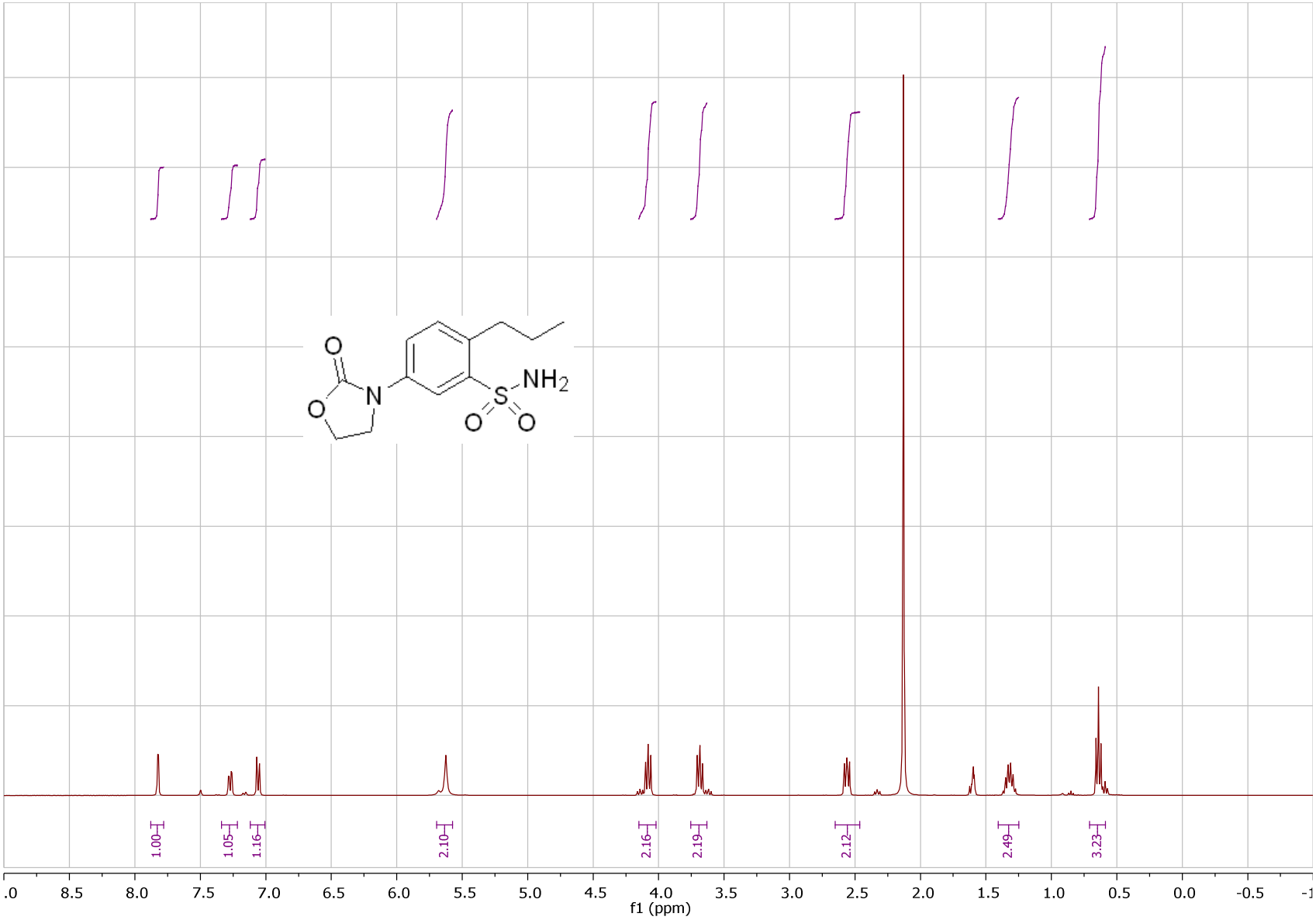
Compound 4


NH2
S
O
O
0.98
0.96
1.00
2.18
2.00
9.24
.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
-0.5
f1 (ppm)

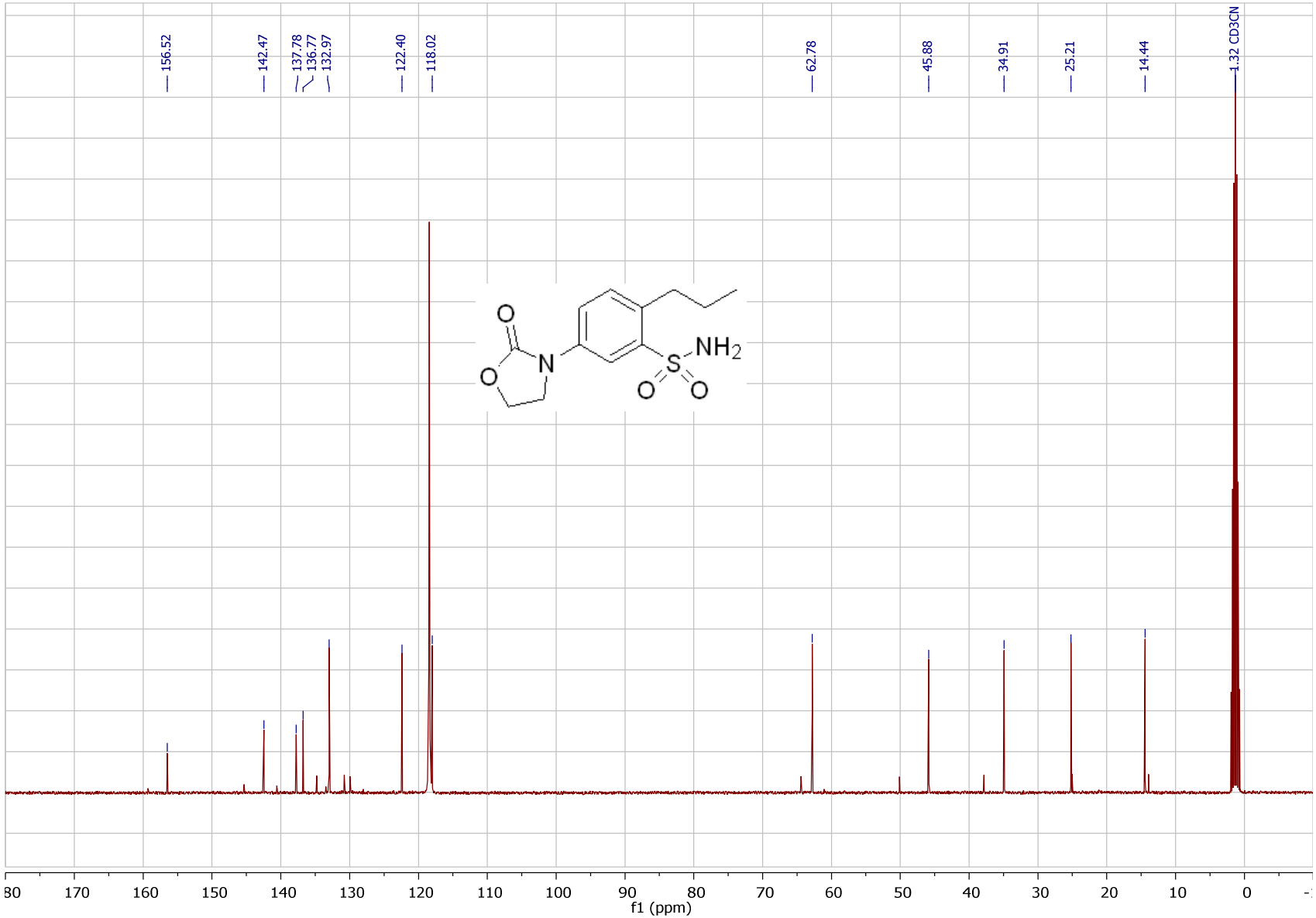
Compound 4


149.40
139.62
138.87
130.39
130.06
125.16
34.69
31.16
25.50
15.12
0.00
NH2
S
O
O
f1 (ppm)

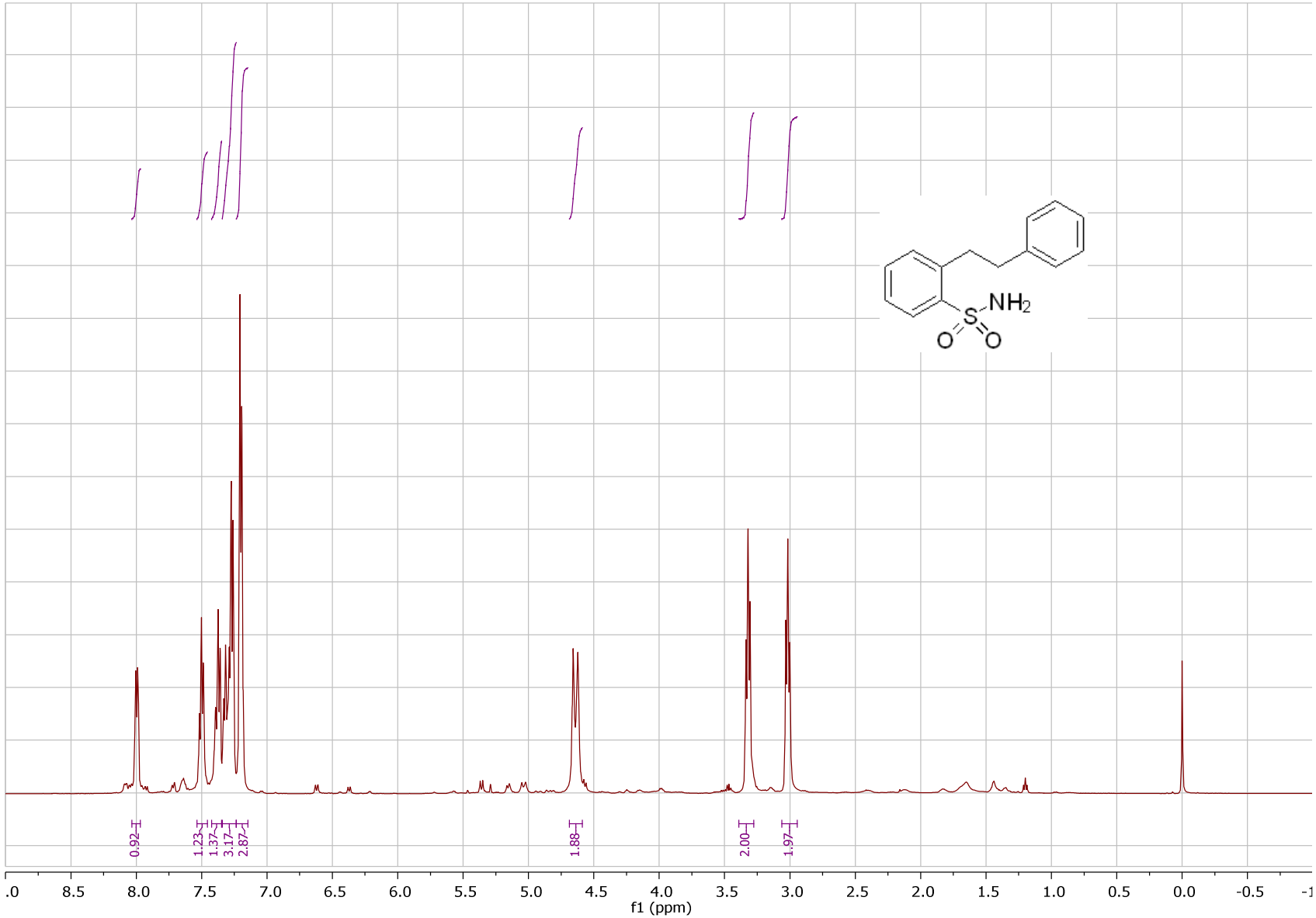
Compound 5


O
O
N
S
NH2
O
O
1.00
1.05
1.16
2.10
2.16
2.19
2.12
2.49
3.23
.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
-0.5
f1 (ppm)

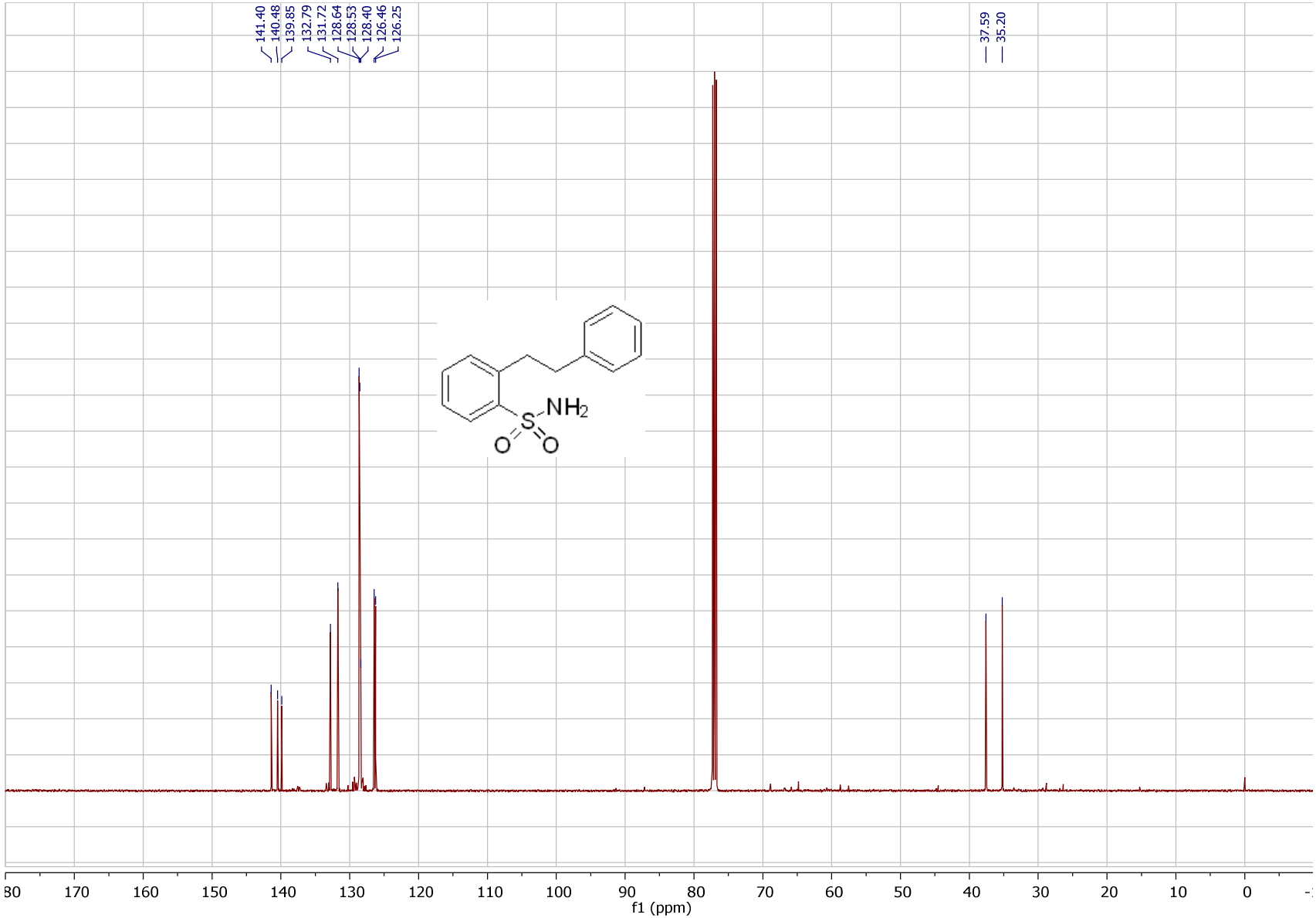
Compound 5


156.52
142.47
137.78
136.77
132.97
122.40
118.02
62.78
45.88
34.91
25.21
14.44
1.32 CD3CN
O
N
O
S
NH2
O
O
f1 (ppm)

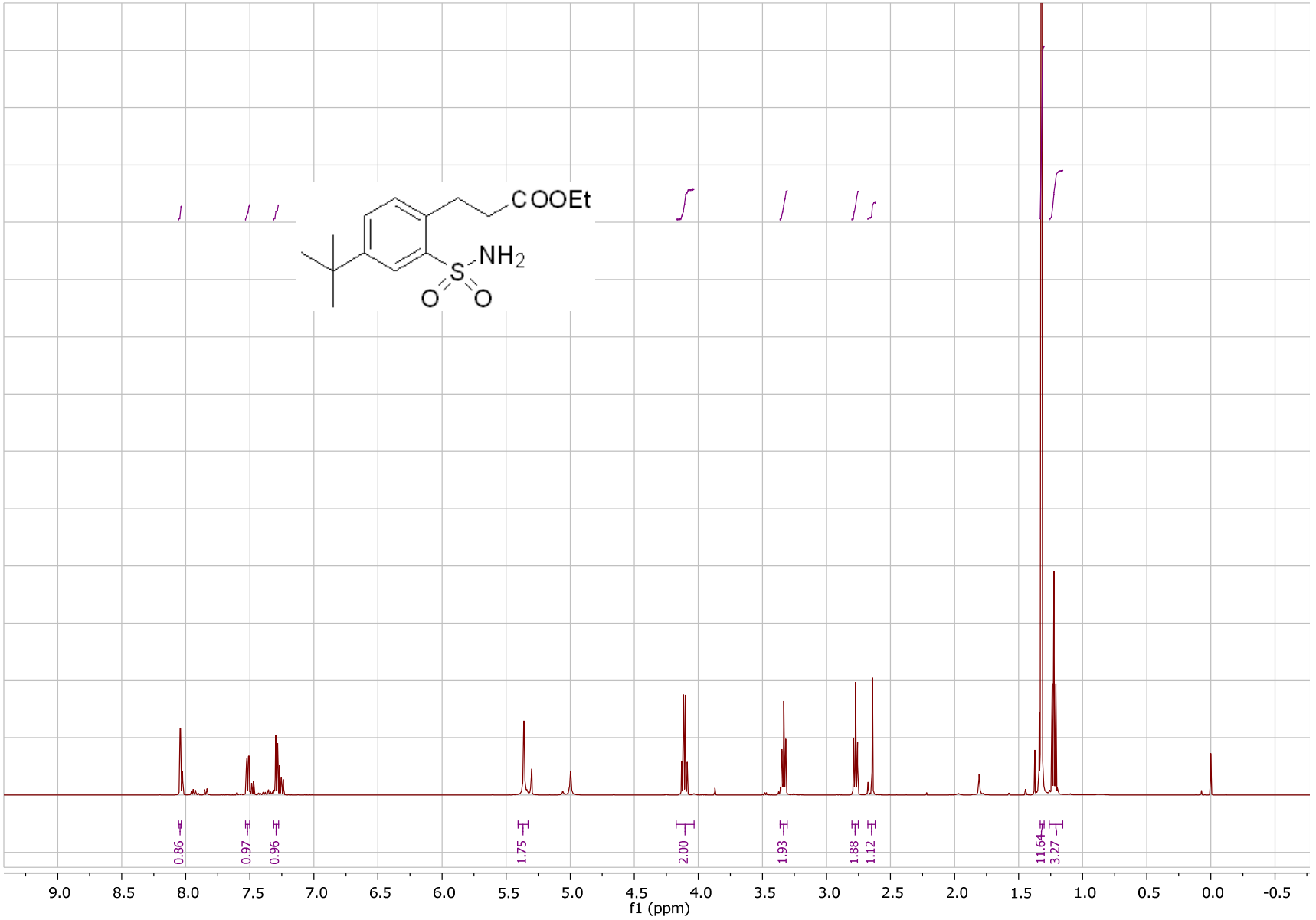
Compound 6


NH2
S
O
O
0.92
1.23
1.37
3.17
2.87
1.88
2.00
1.97
.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
-0.5
f1 (ppm)

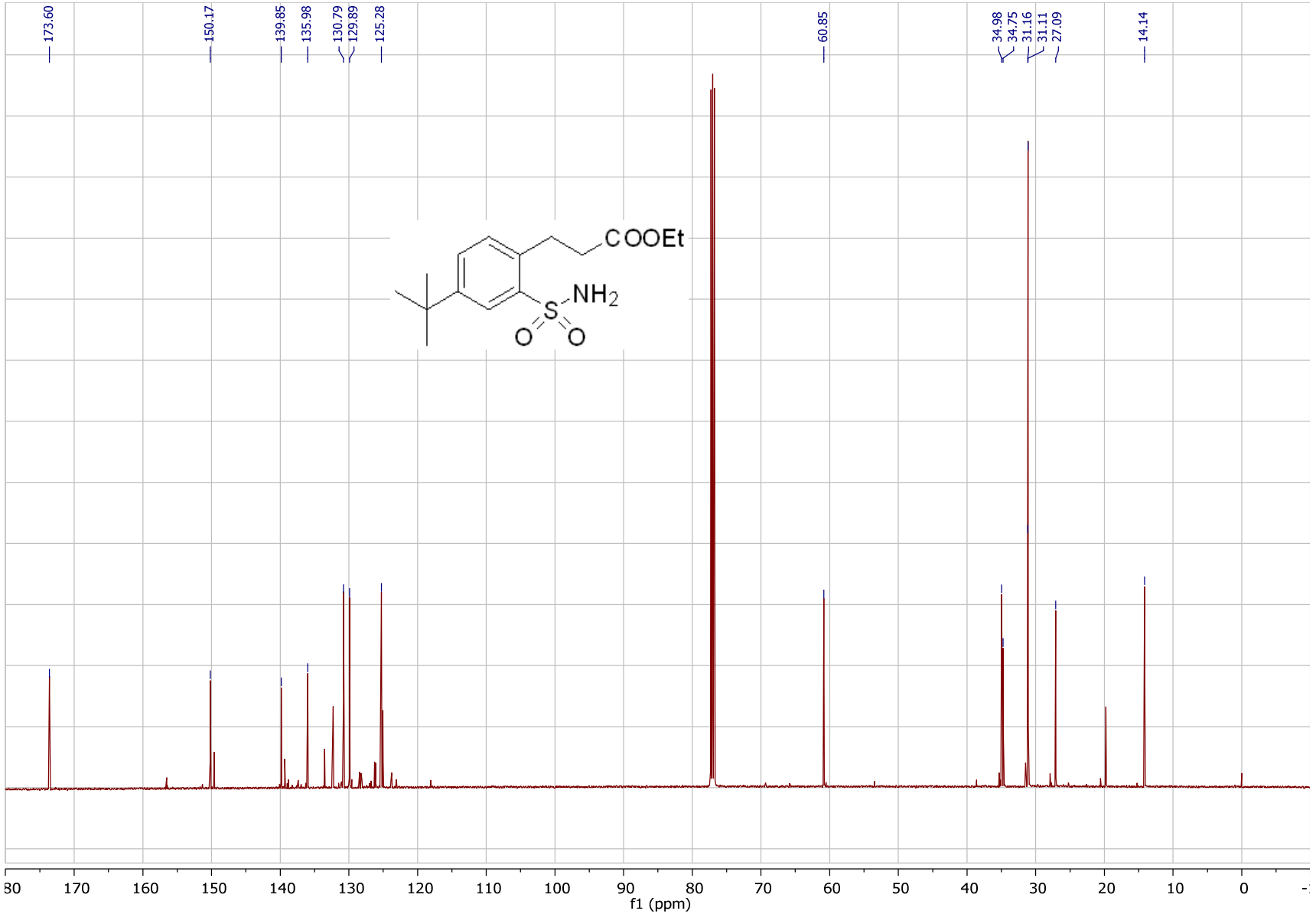
Compound 6


141.40
140.48
139.85
132.79
131.72
128.64
128.53
128.40
126.46
126.25
37.59
35.20
NH2
S
O
O
f1 (ppm)

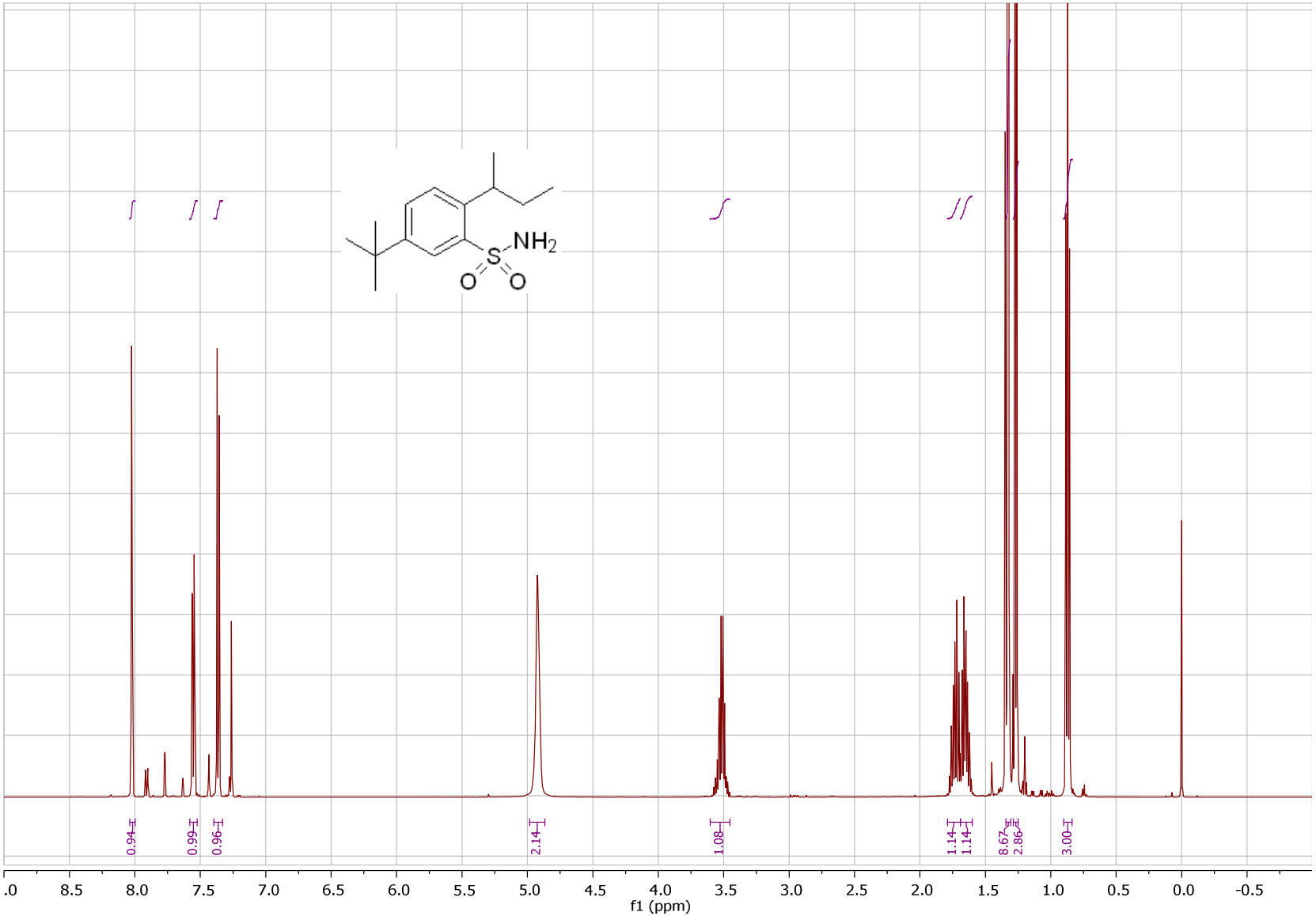
Compound 7


COOEt
NH2
S
O
O
0.86
0.97
0.96
1.75
2.00
1.93
1.88
1.12
11.64
3.27
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
-0.5
f1 (ppm)

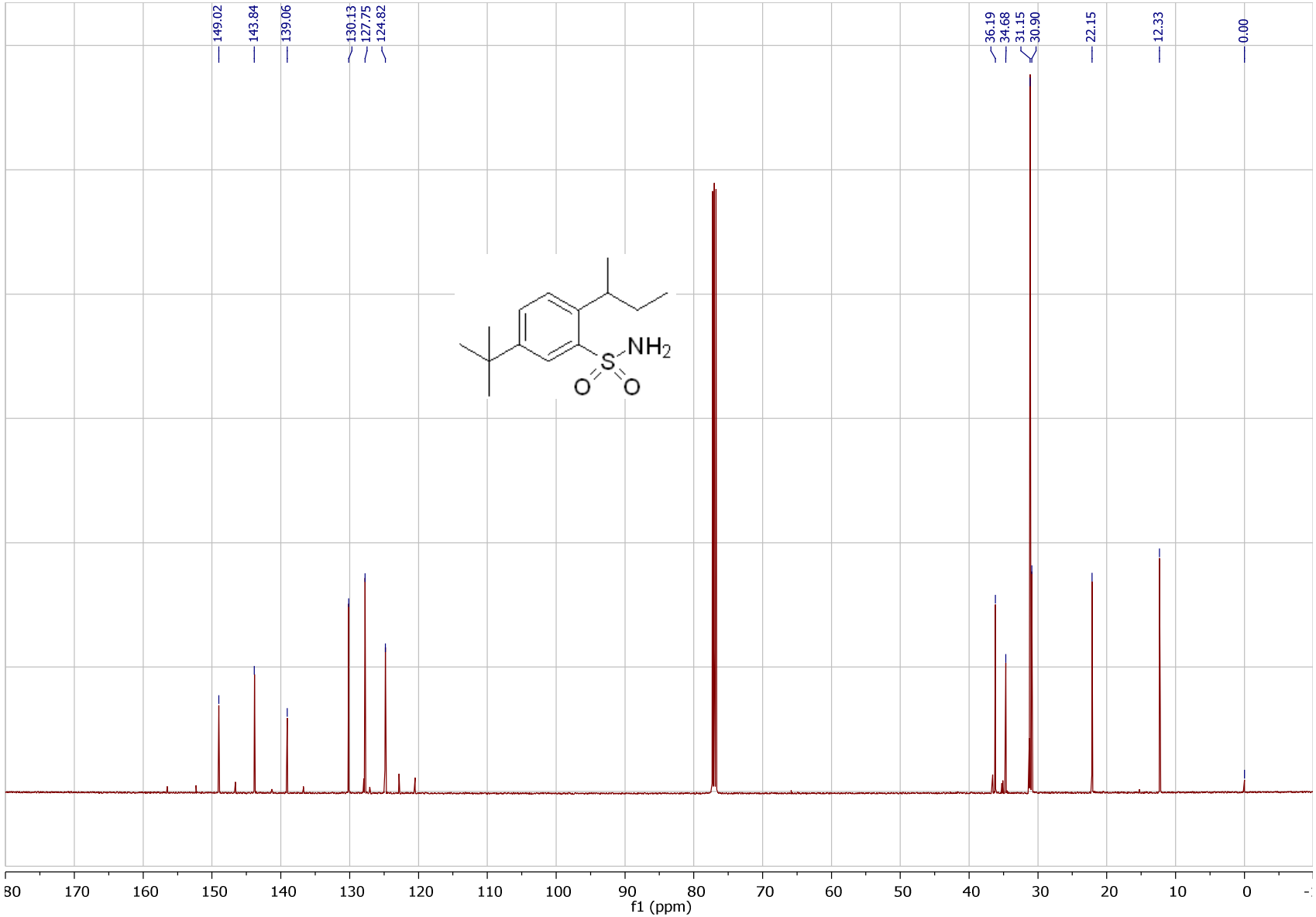
Compound 7


173.60
150.17
139.85
135.98
130.79
129.89
125.28
60.85
34.98
34.75
31.16
31.11
27.09
14.14
COOEt
NH2
S
O
O
f1 (ppm)

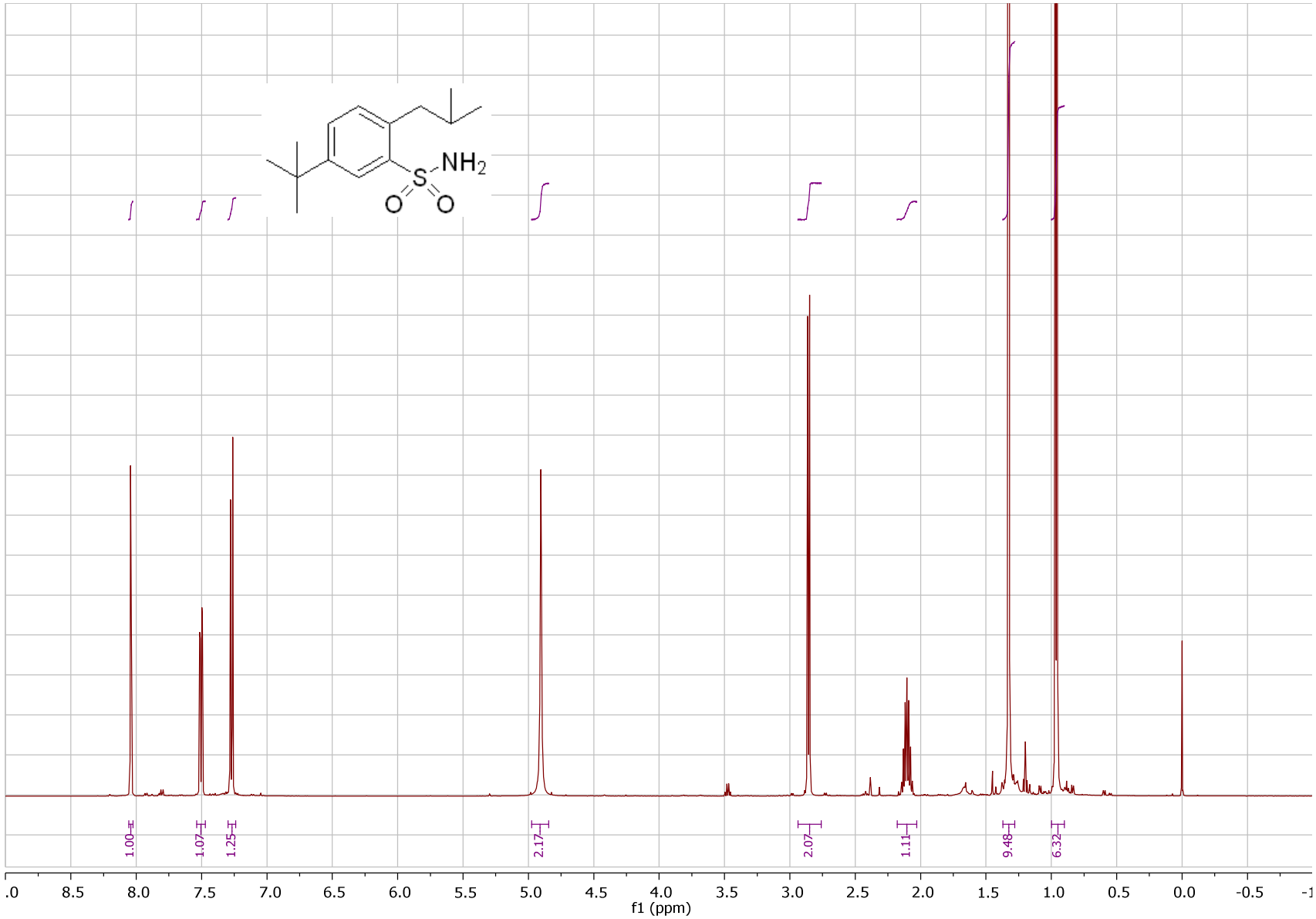
Compound 8



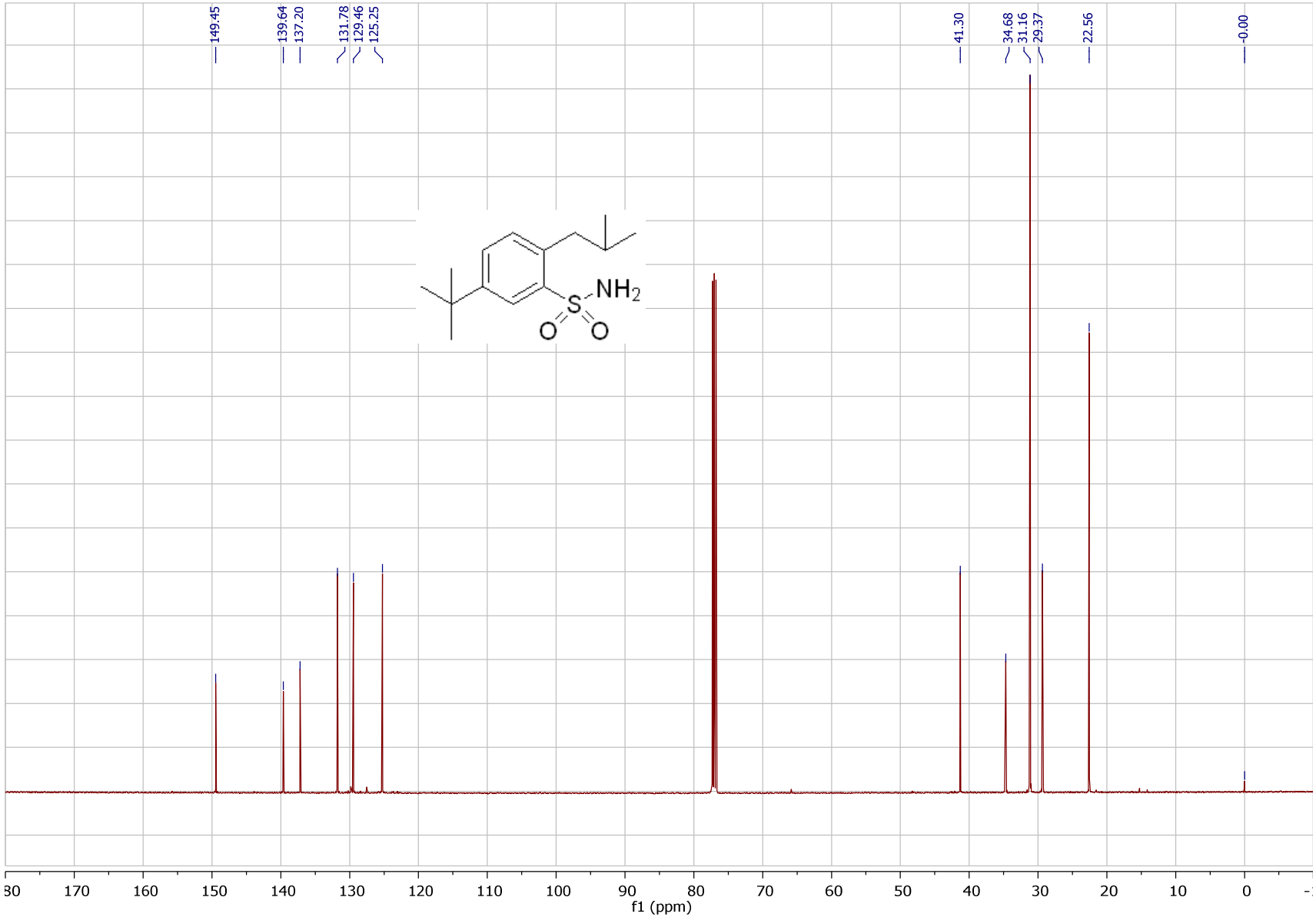
Compound 8


149.02
143.84
139.06
130.13
127.75
124.82
36.19
34.68
31.15
30.90
22.15
12.33
0.00
NH2
S
O
O
f1 (ppm)

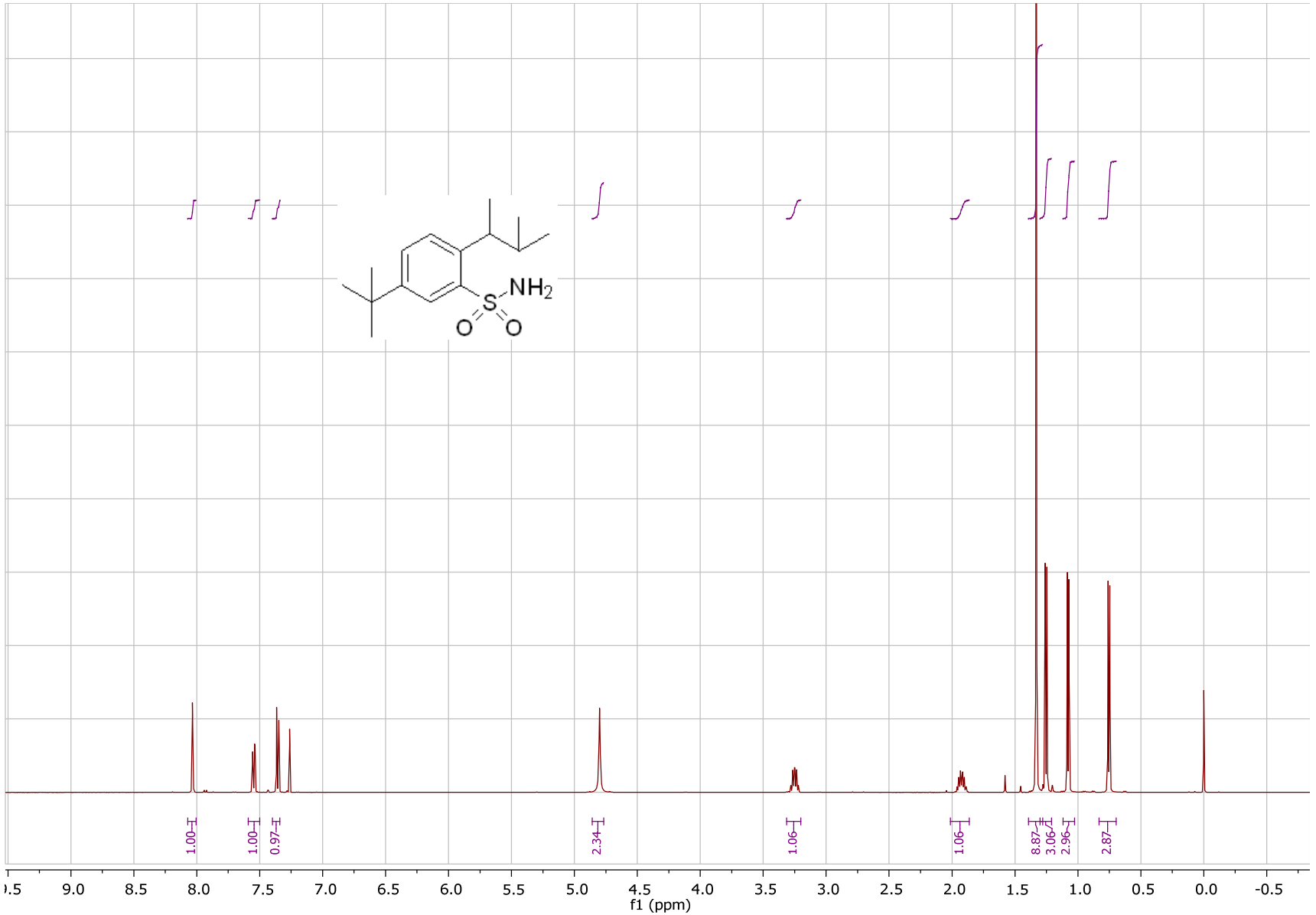
Compound 9


NH2
S
O
O
1.00
1.07
1.25
2.17
2.07
1.11
9.48
6.32
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
-0.5
f1 (ppm)

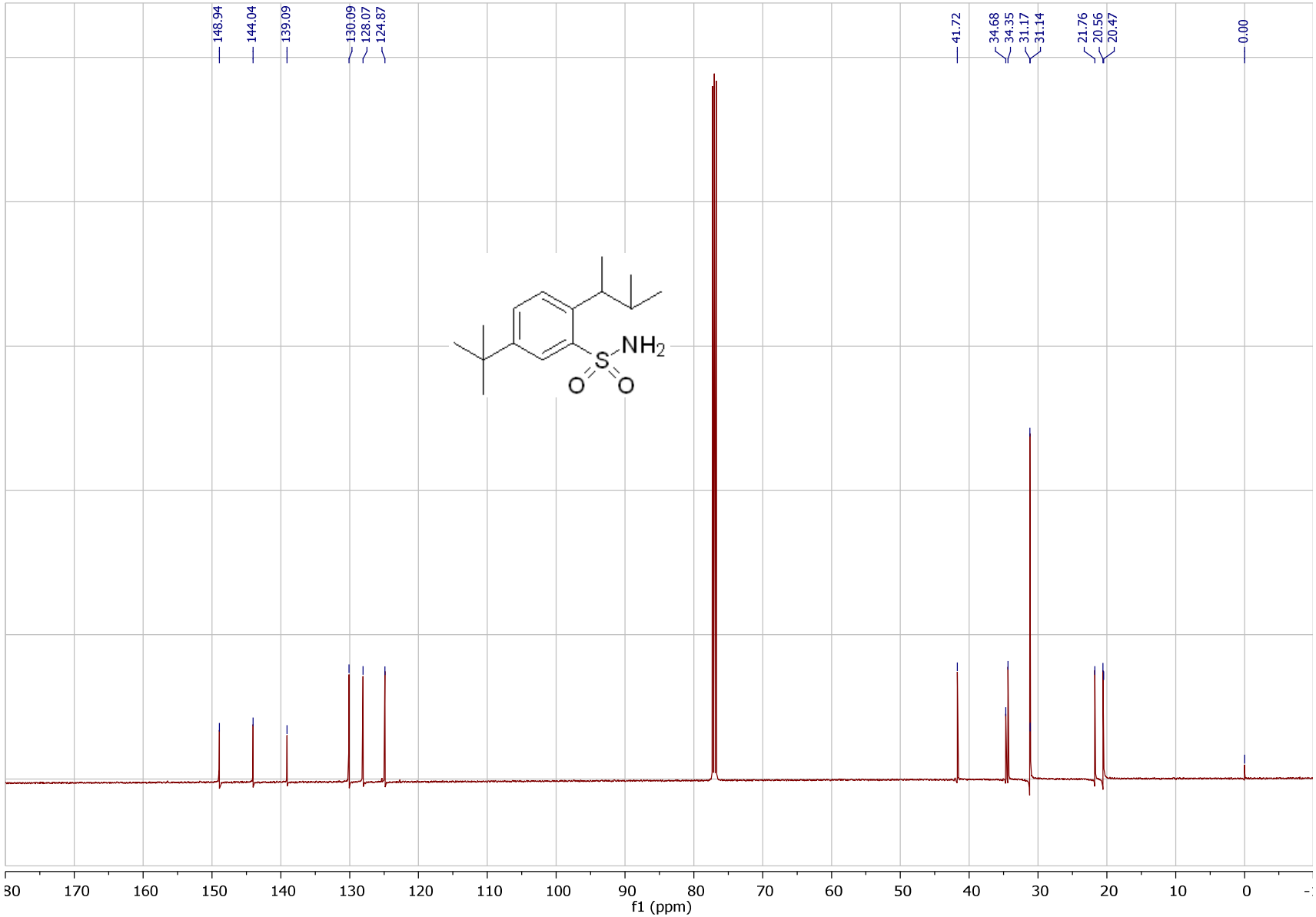
Compound 9


149.45
139.64
137.20
131.78
129.46
125.25
41.30
34.68
31.16
29.37
22.56
0.00
NH2
S
O
O
f1 (ppm)

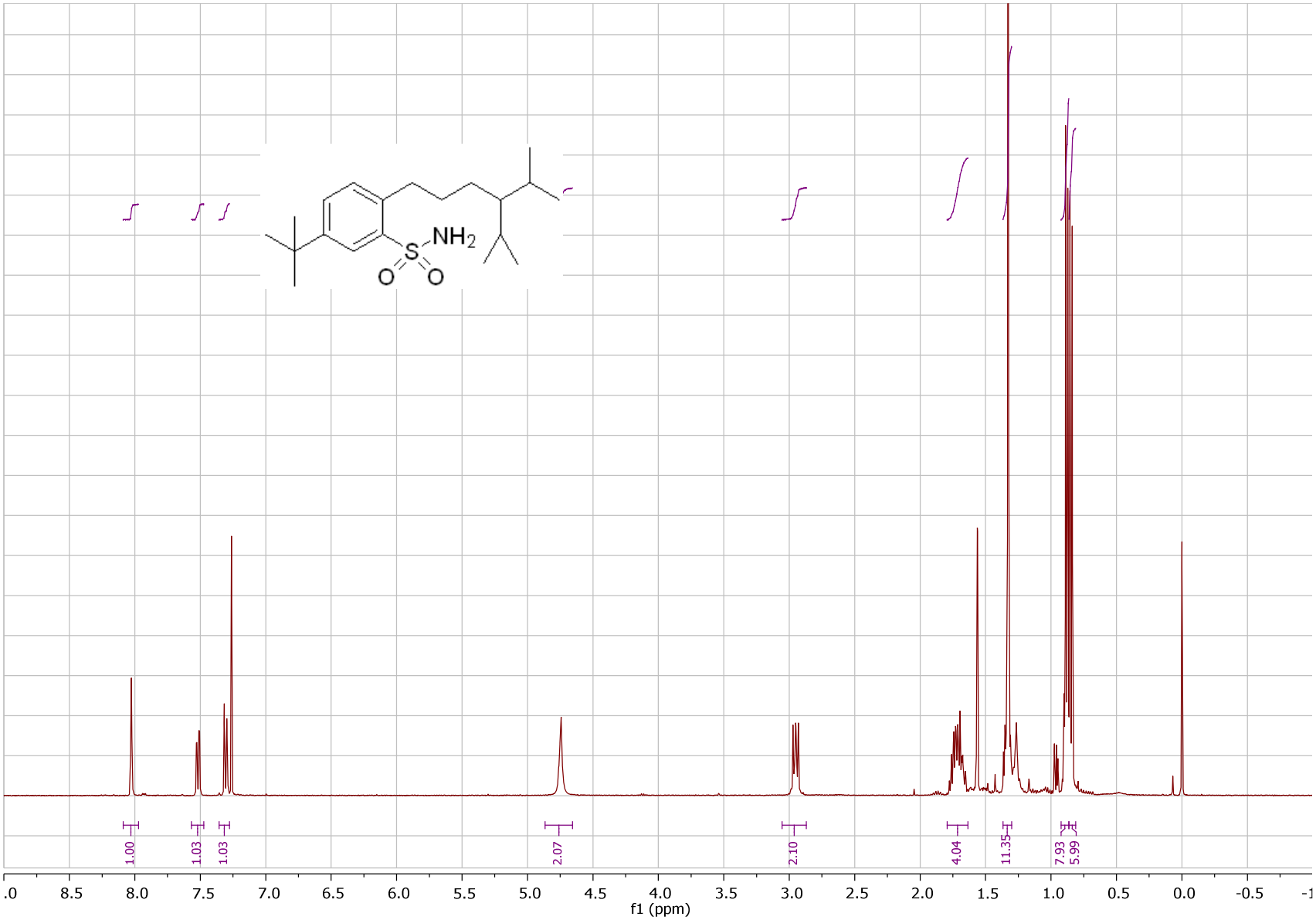
Compound 10


NH2
S
O
O
1.00
1.00
0.97
2.34
1.06
1.06
8.87
3.06
2.96
2.87
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
-0.5
f1 (ppm)

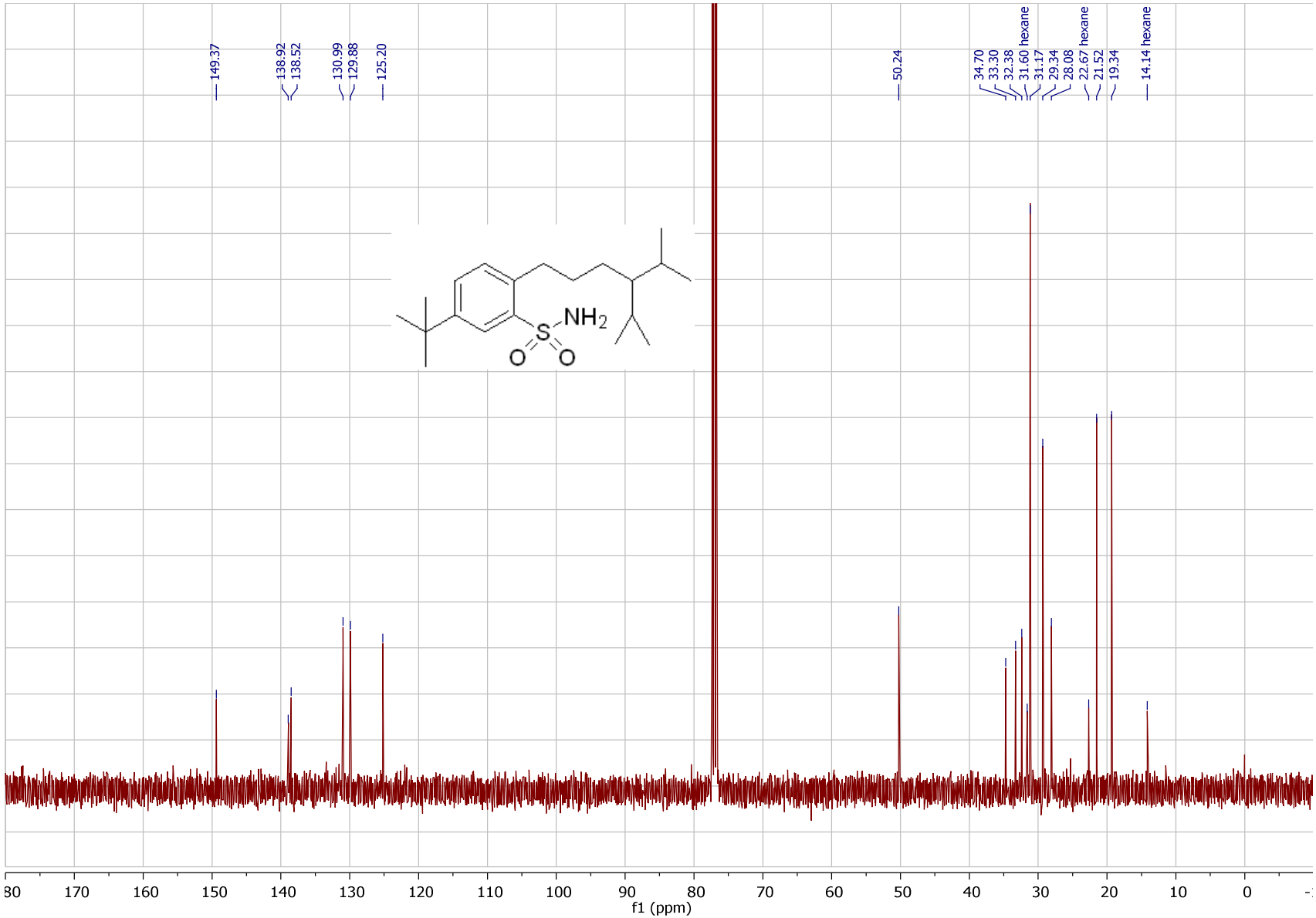
Compound 10


148.94
144.04
139.09
130.09
128.07
124.87
41.72
34.68
34.35
31.17
31.14
21.76
20.56
20.47
0.00
NH2
S
O
O
f1 (ppm)

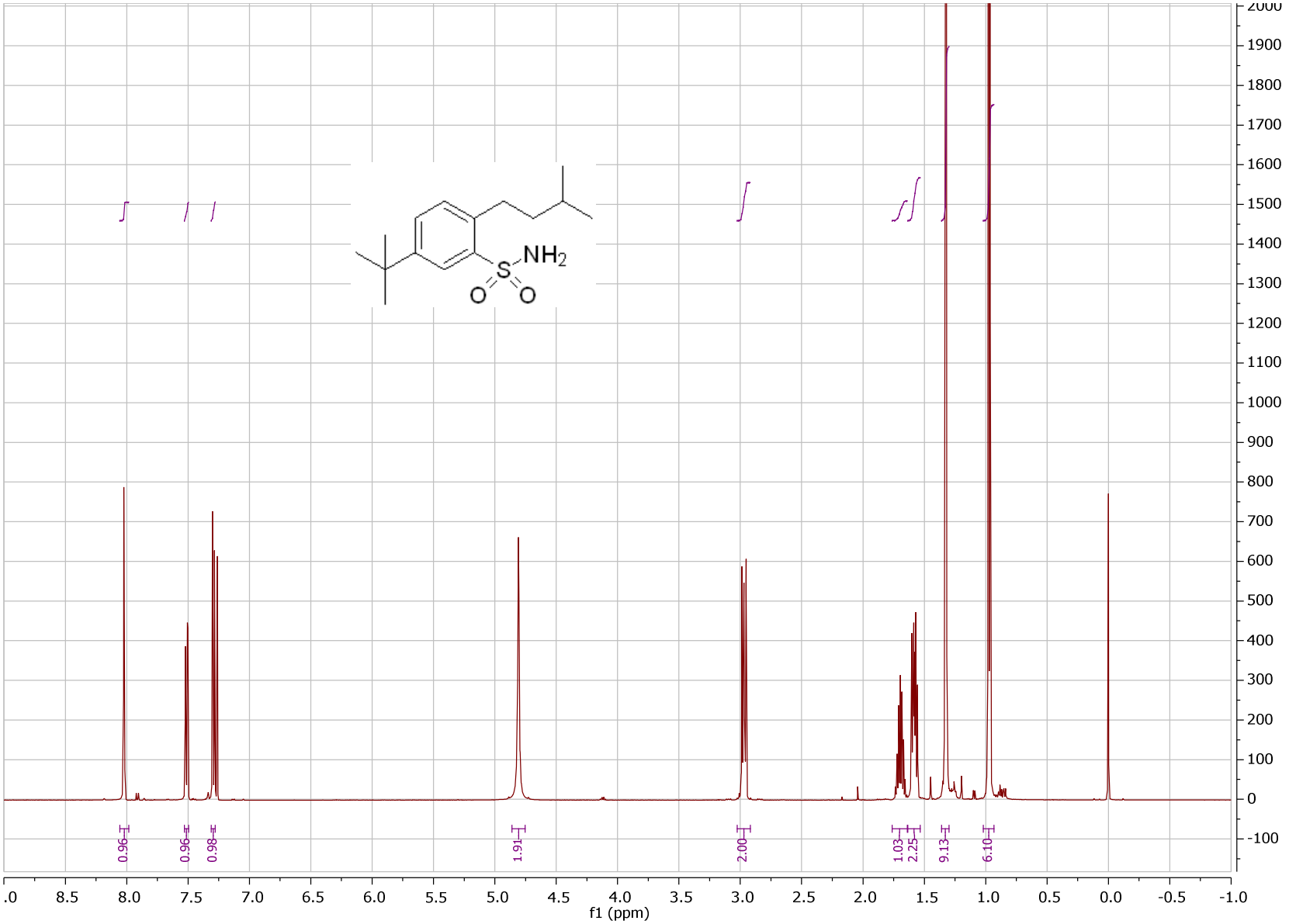
Compound 11


NH2
S
O
O
1.00
1.03
1.03
2.07
2.10
4.04
11.35
7.93
5.99
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
-0.5
f1 (ppm)

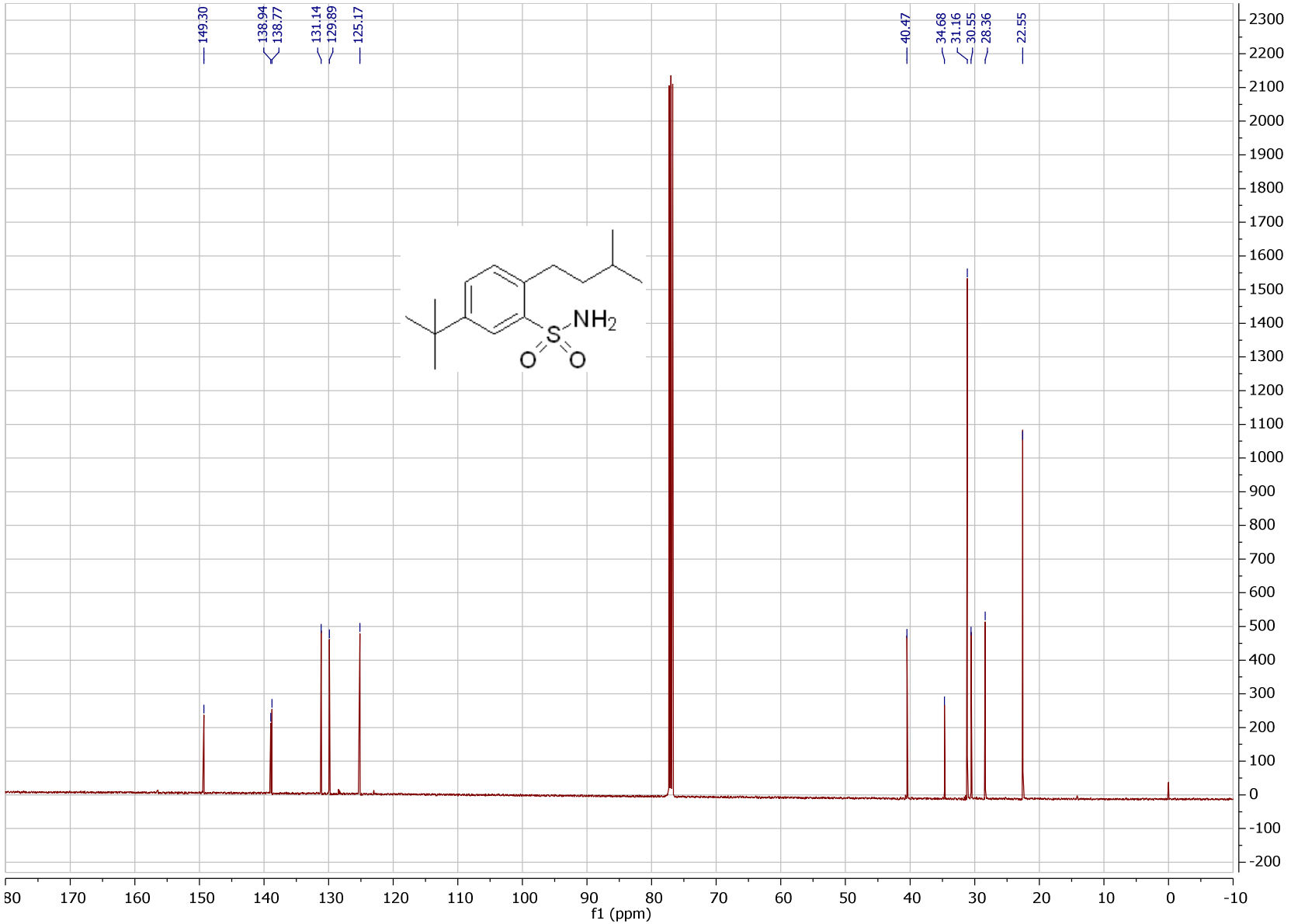
Compound 11


149.37
138.92
138.52
130.99
129.88
125.20
50.24
34.70
33.30
32.38
31.60 hexane
31.17
29.34
28.08
22.67 hexane
21.52
19.34
14.14 hexane
NH2
S
O
O
f1 (ppm)

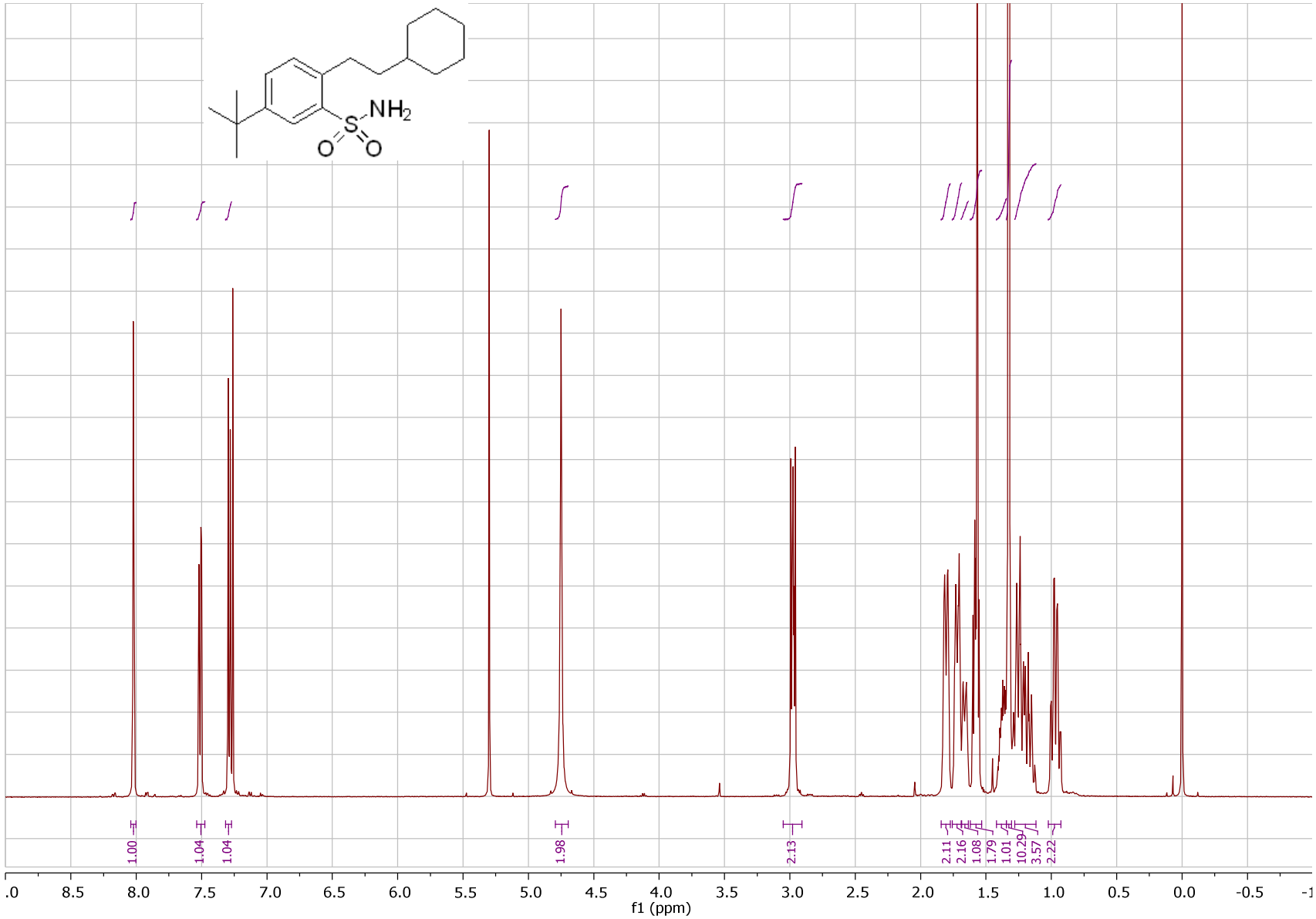
Compound 12



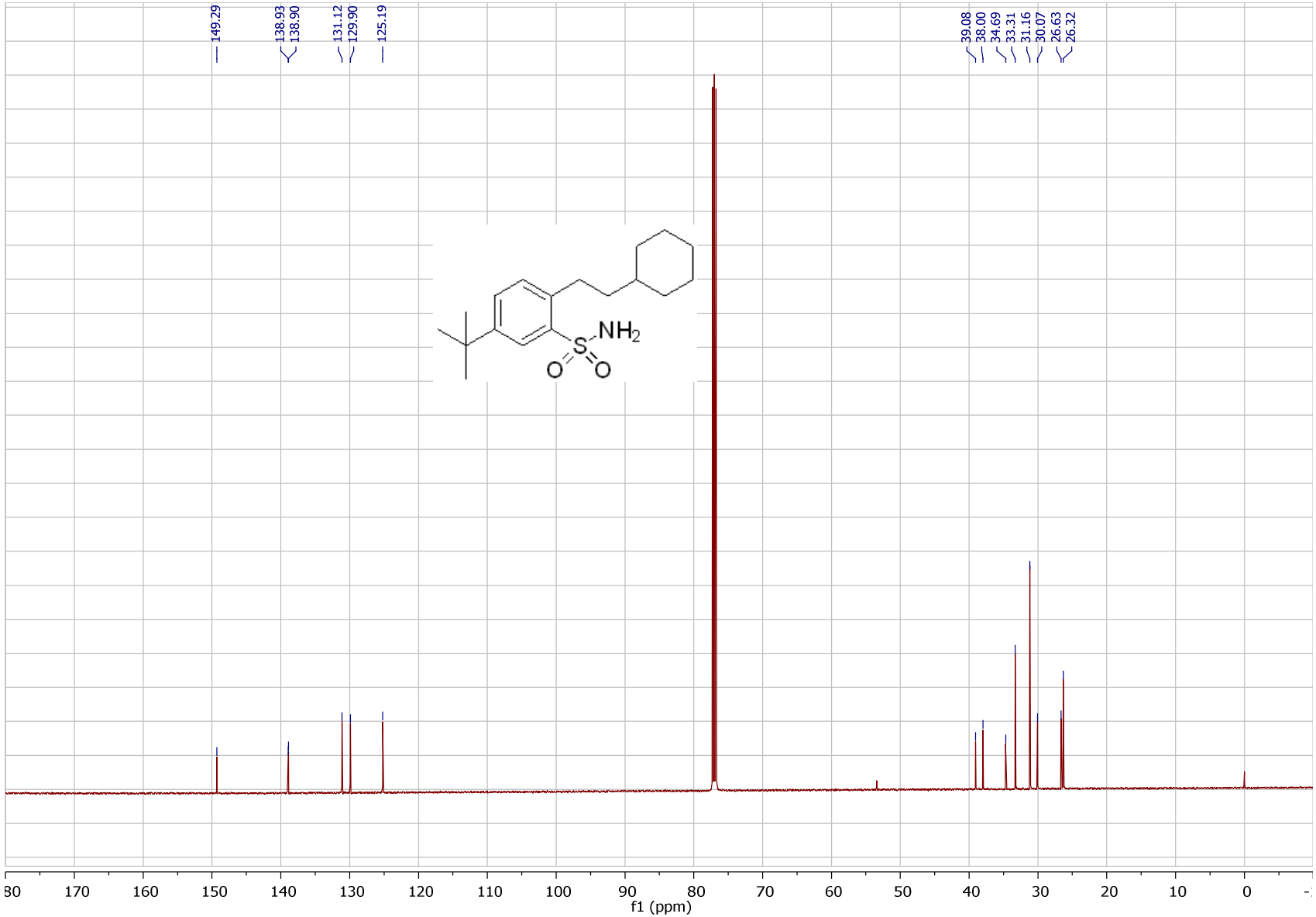
Compound 12


149.30
138.94
138.77
131.14
129.89
125.17
40.47
34.68
31.16
30.55
28.36
22.55
NH2
S
O
O
f1 (ppm)

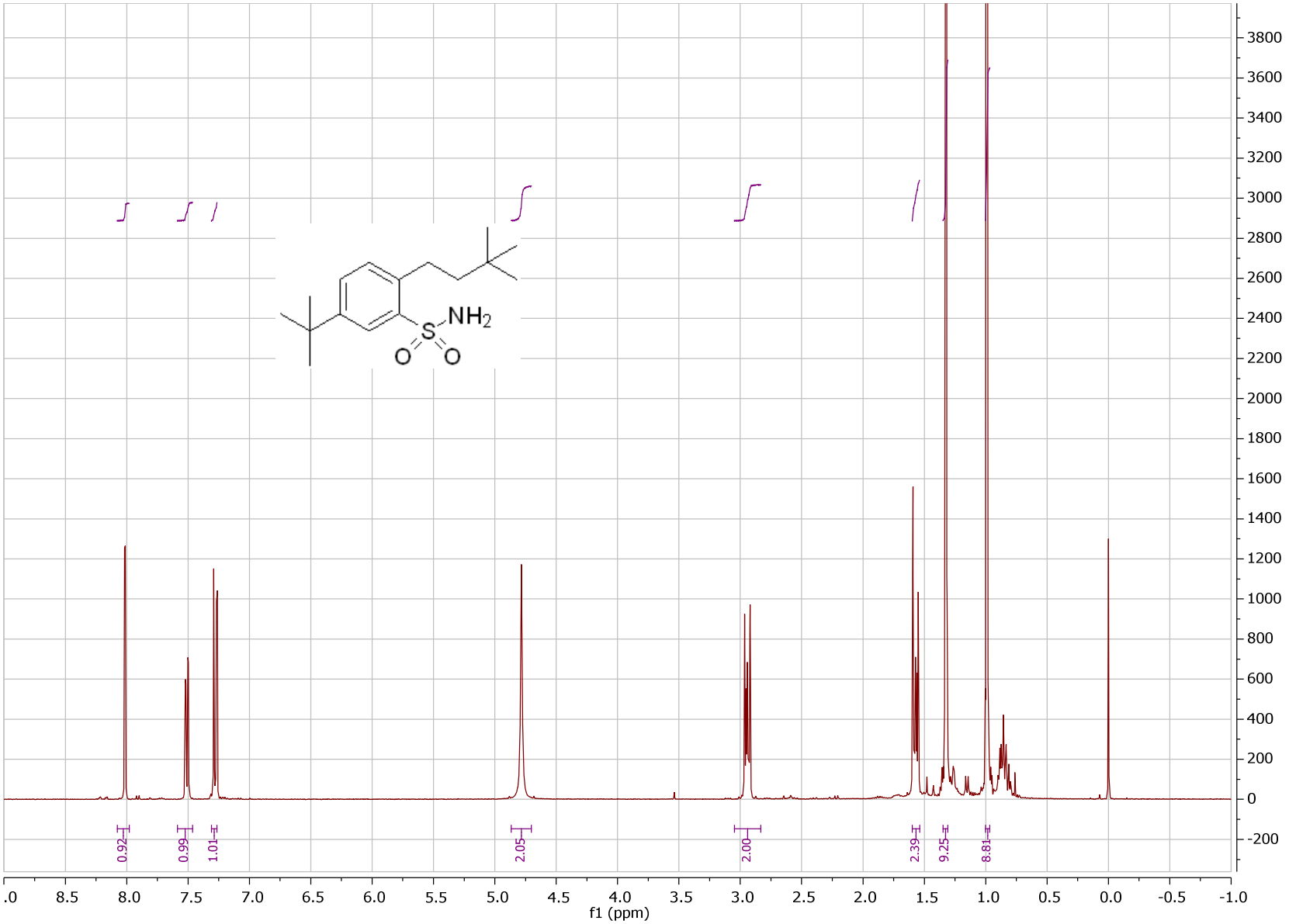
Compound 13


NH2
S
O
O
1.00
1.04
1.04
1.98
2.13
2.11
2.16
1.08
1.79
1.01
10.29
3.57
2.22
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
-0.5
f1 (ppm)

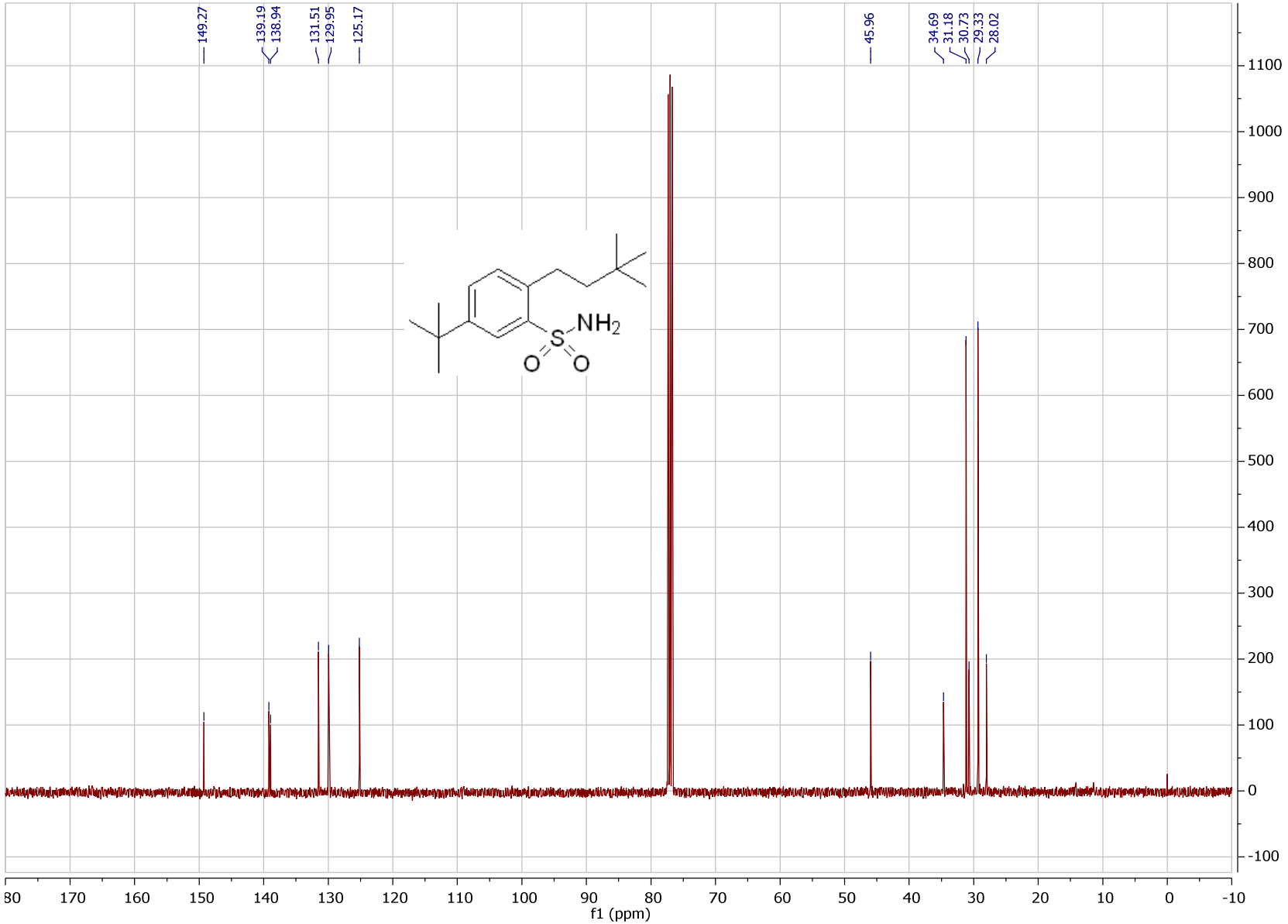
Compound 13


149.29
138.93
138.90
131.12
129.90
125.19
39.08
38.00
34.69
33.31
31.16
30.07
26.63
26.32
NH2
S
O
O
f1 (ppm)

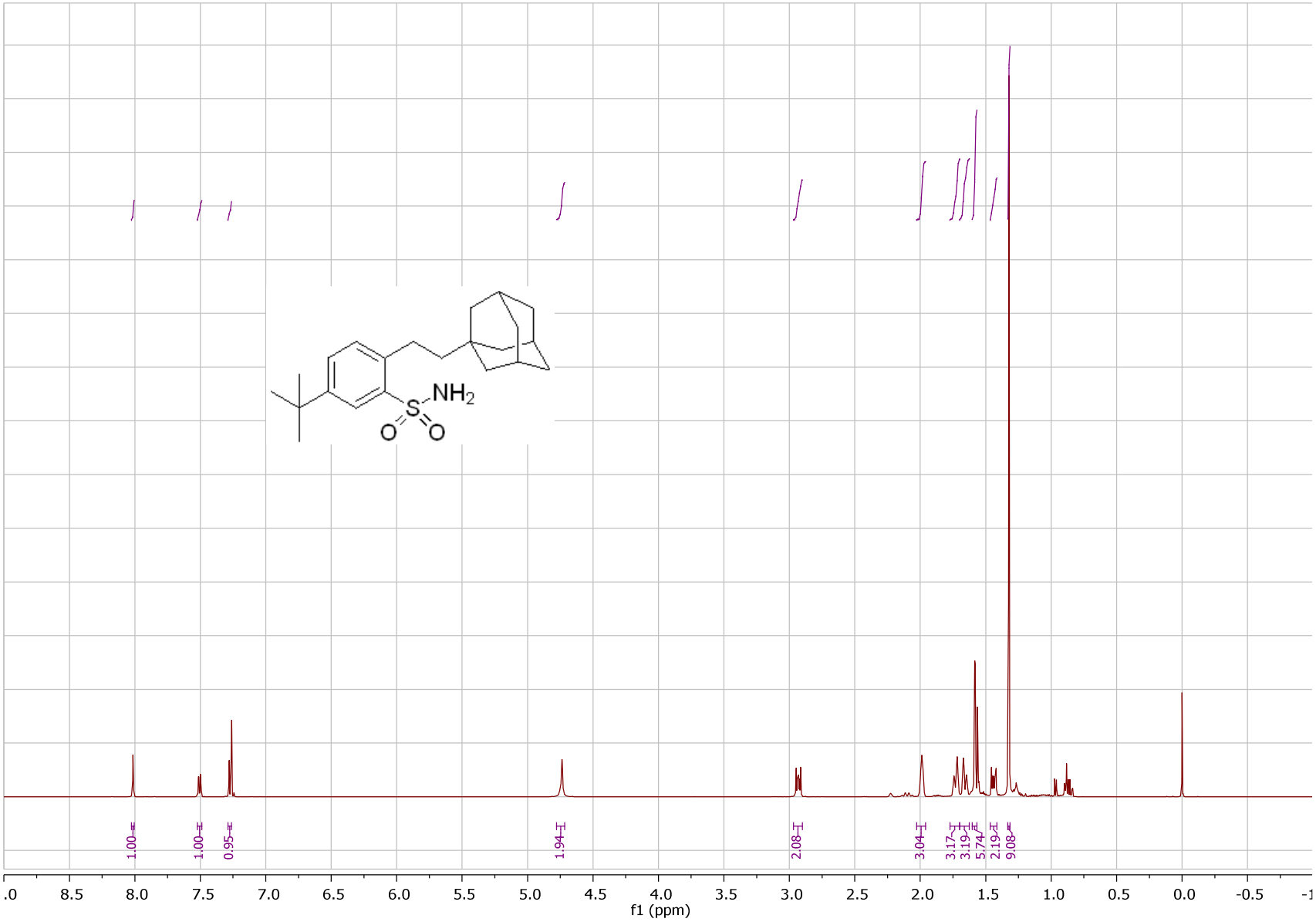
Compound 14



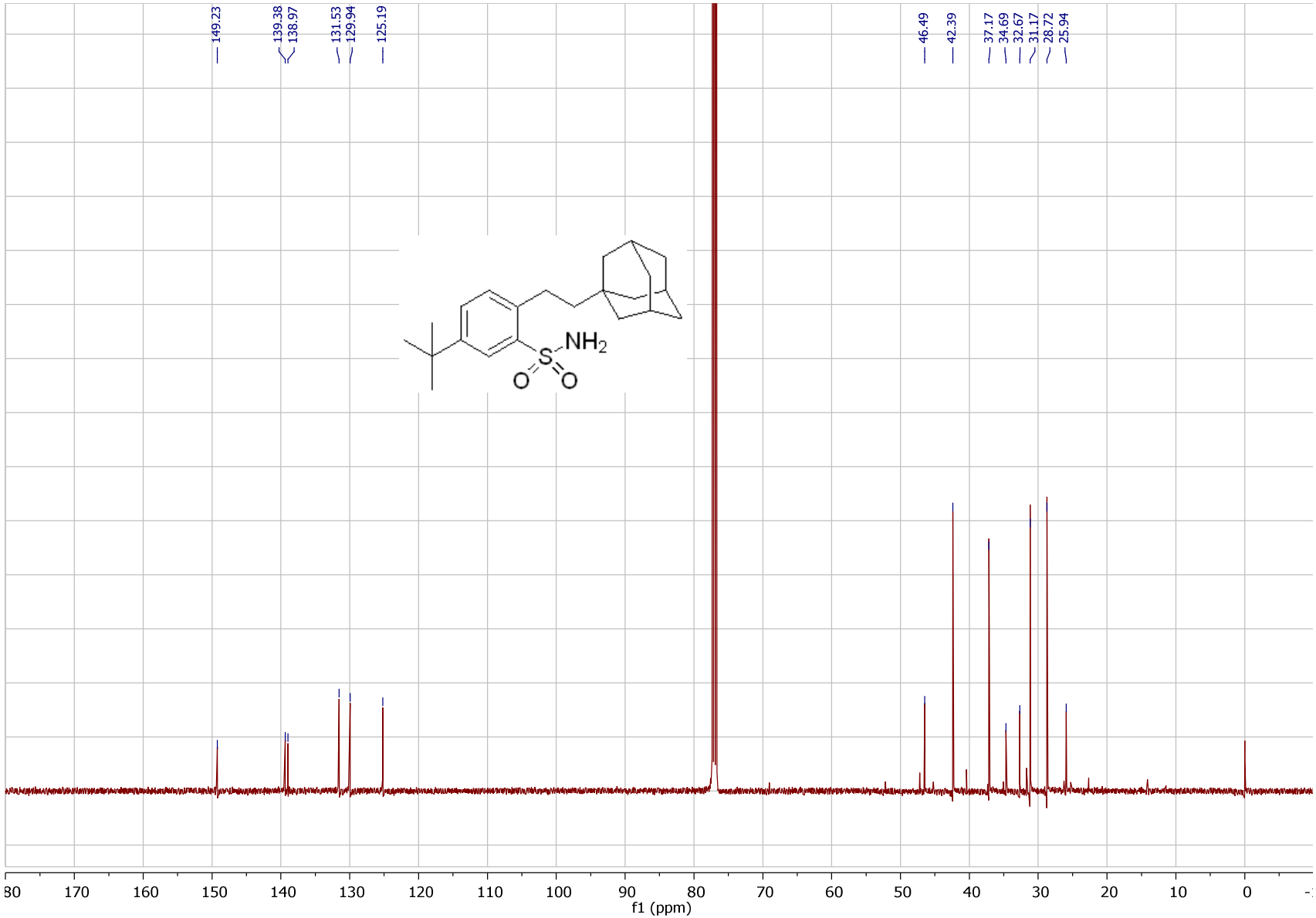
Compound 14


149.27
139.19
138.94
131.51
129.95
125.17
45.96
34.69
31.18
30.73
29.33
28.02
NH2
S
O
O
f1 (ppm)

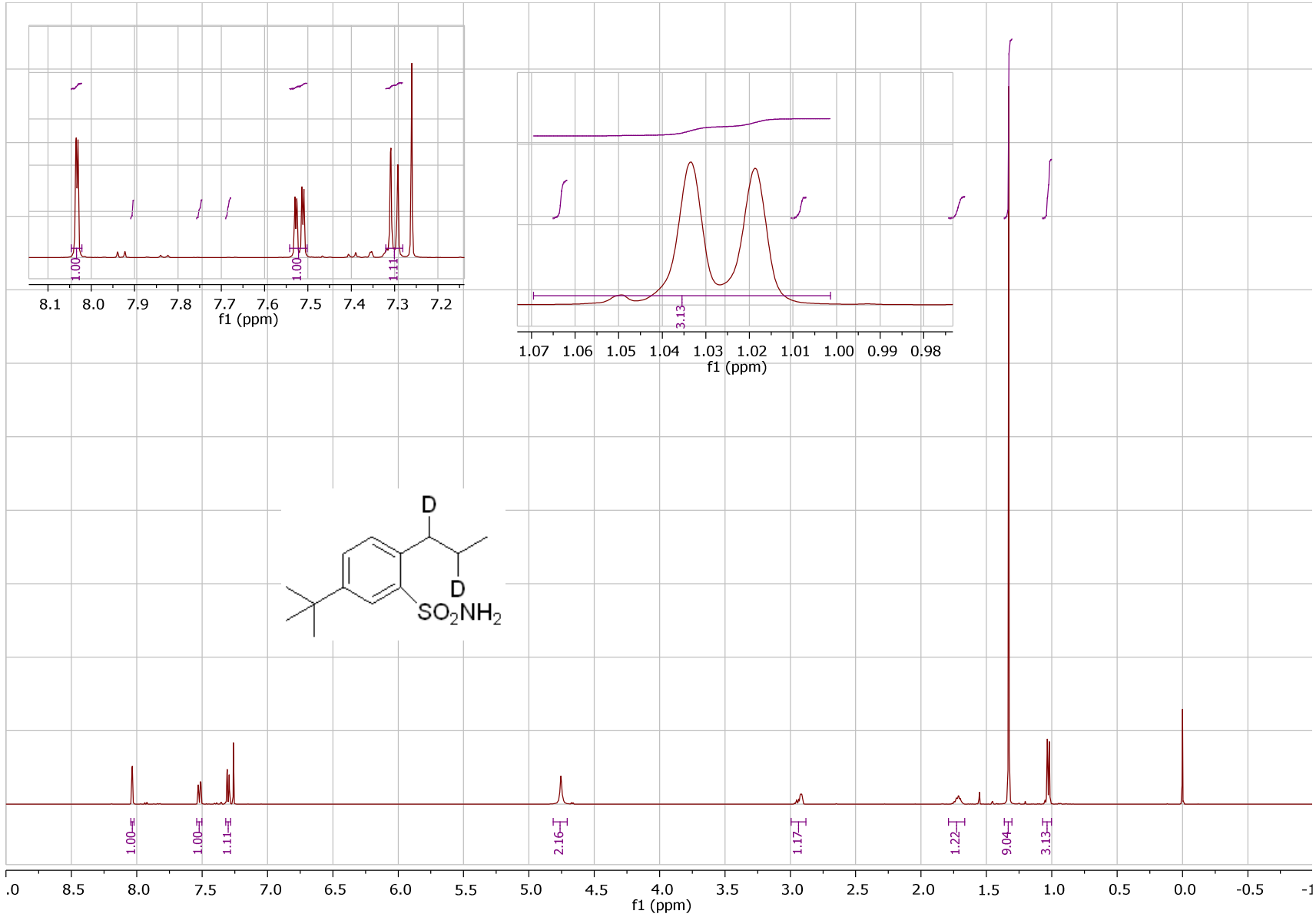
Compound 15



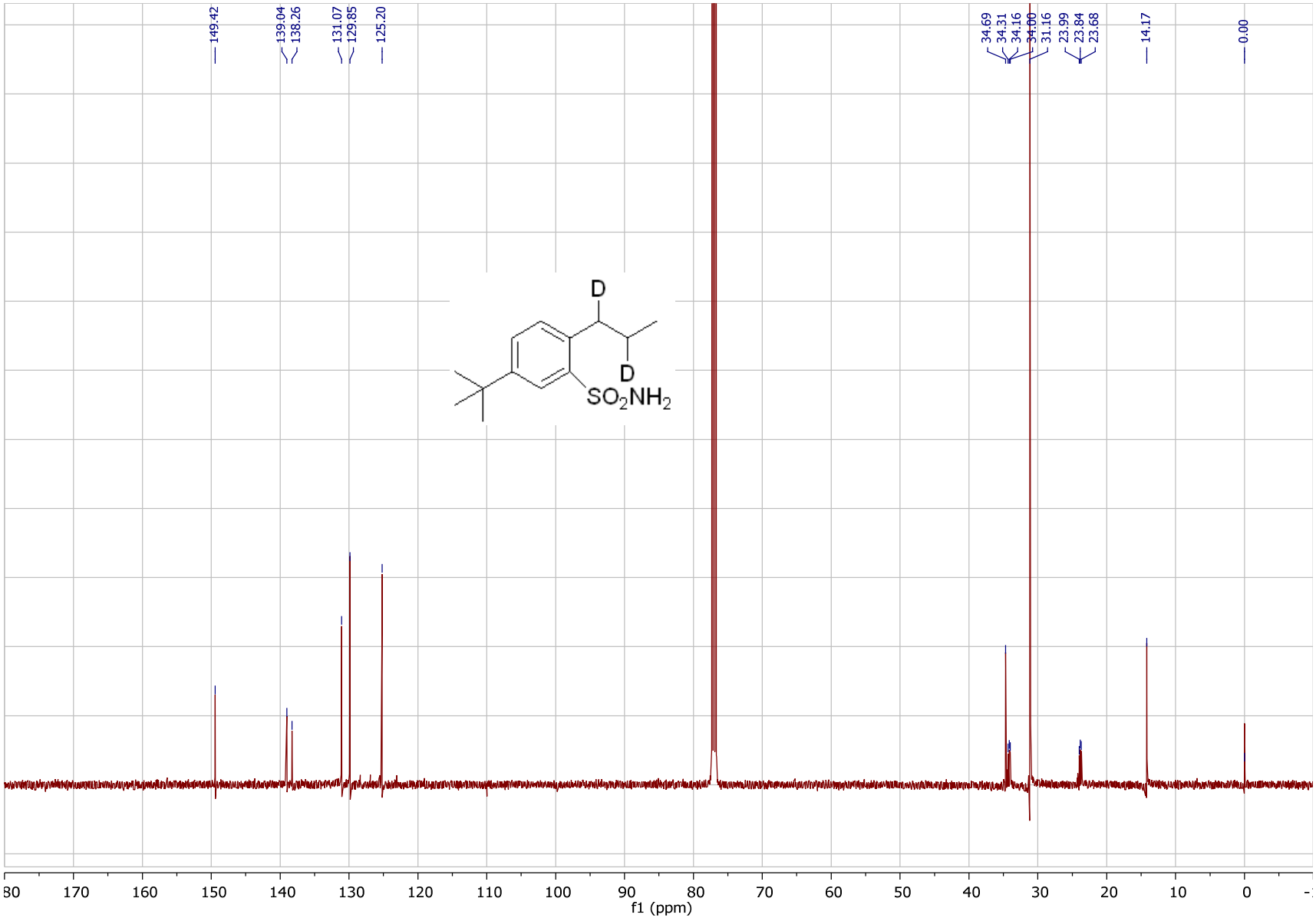
Compound 15


149.23
139.38
138.97
131.53
129.94
125.19
46.49
42.39
37.17
34.69
32.67
31.17
28.72
25.94
NH2
S
O
O
f1 (ppm)

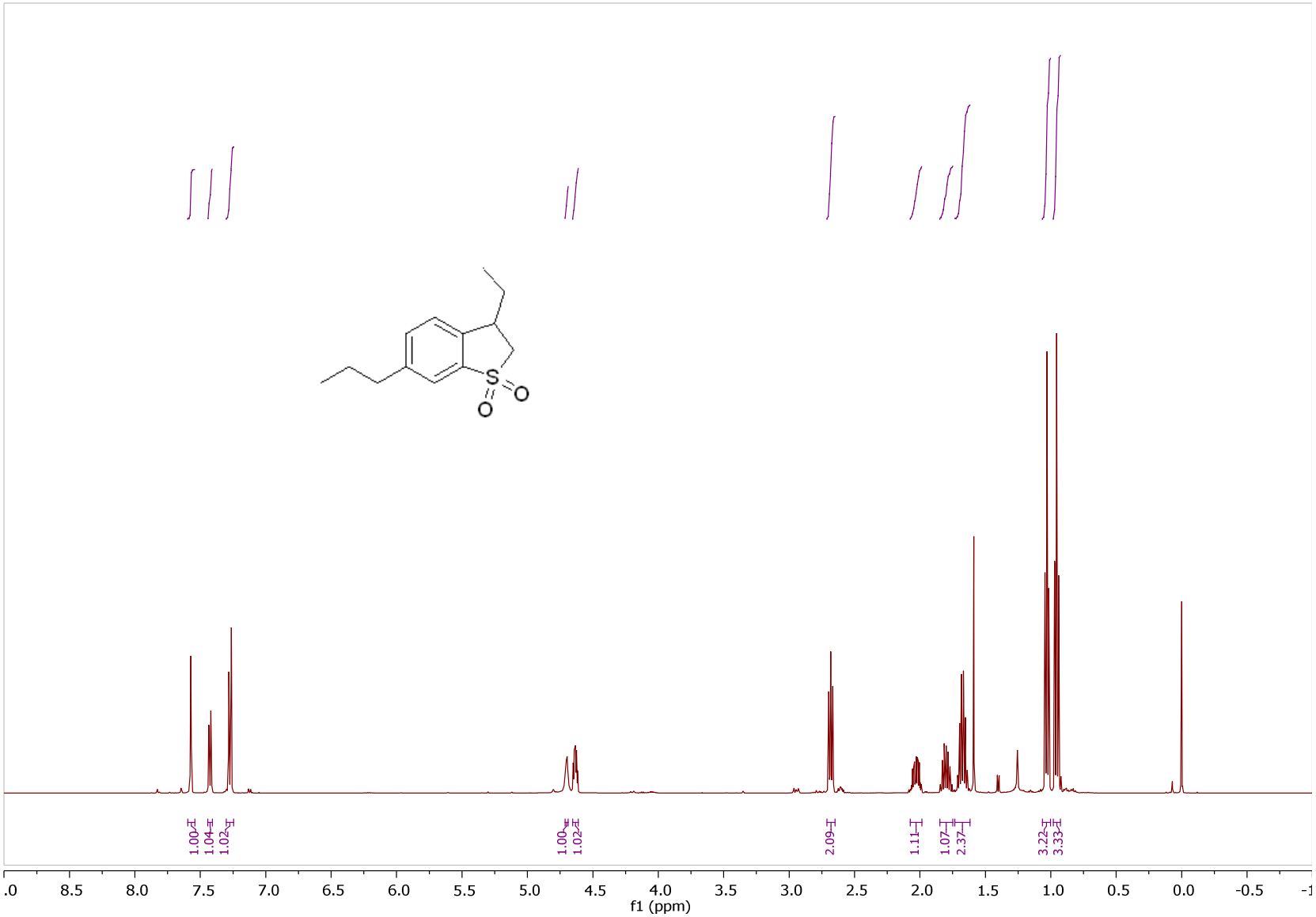
Compound 16


1.00
1.00
1.11
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
3.13
1.07 1.06 1.05 1.04 1.03 1.02 1.01 1.00 0.99 0.98
f1 (ppm)
D
D
SO2NH2
1.00
1.00
1.11
2.16
1.17
1.22
9.04
3.13
.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 -0.5 -1
f1 (ppm)

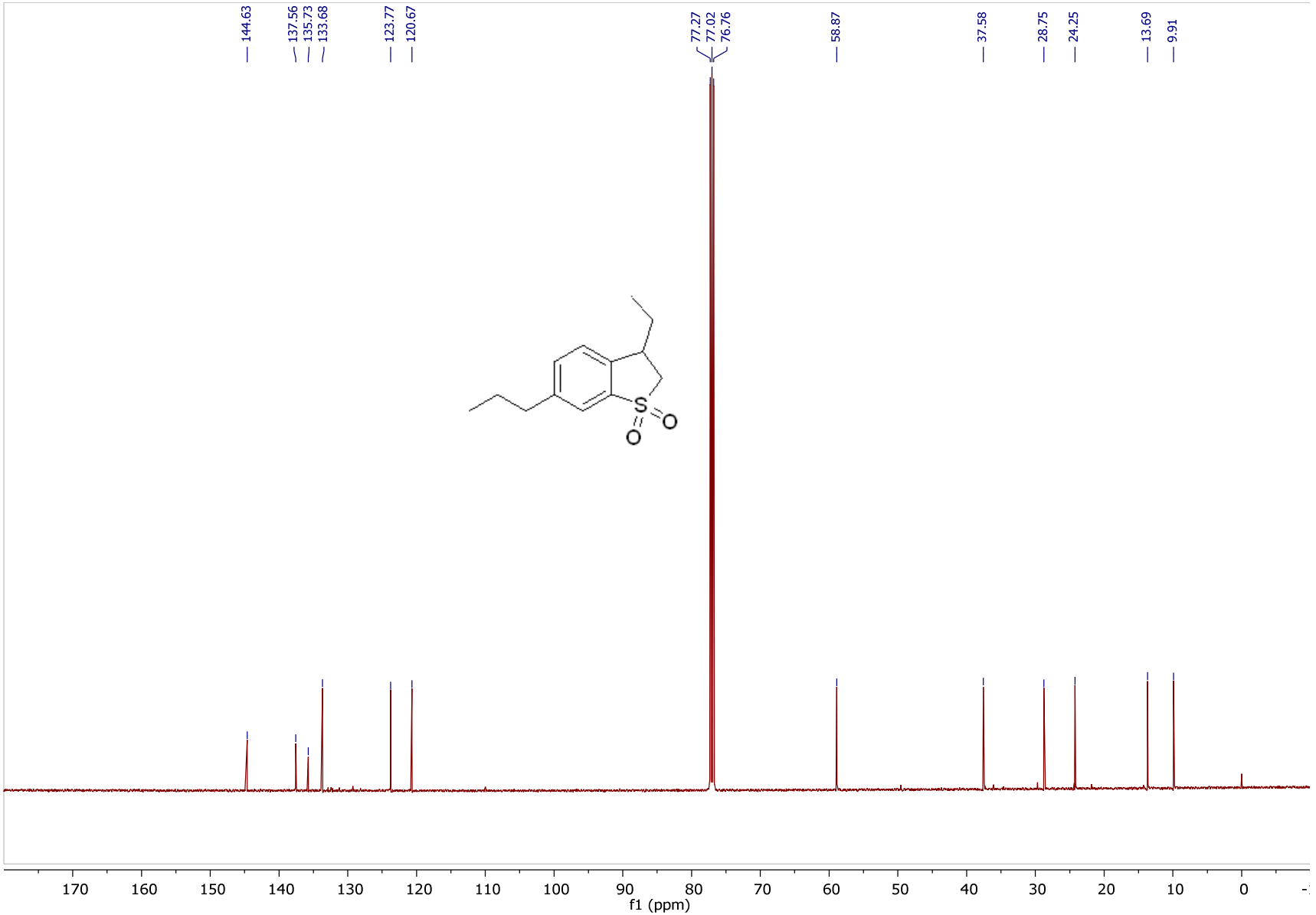
Compound 16


149.42
139.04
138.26
131.07
129.85
125.20
34.69
34.31
34.16
34.00
31.16
23.99
23.84
23.68
14.17
0.00
D
D
SO2NH2
f1 (ppm)

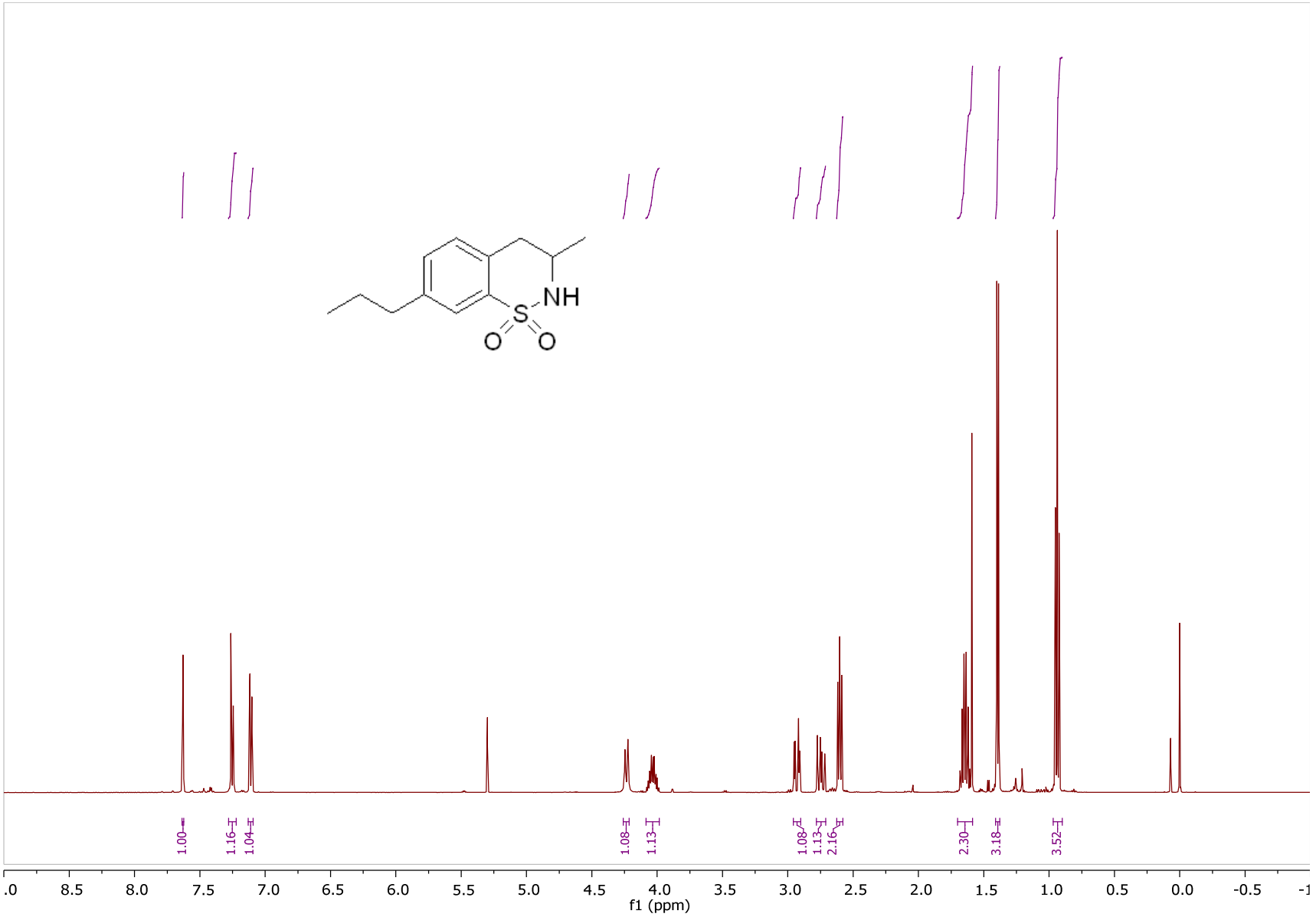
Compound 1a



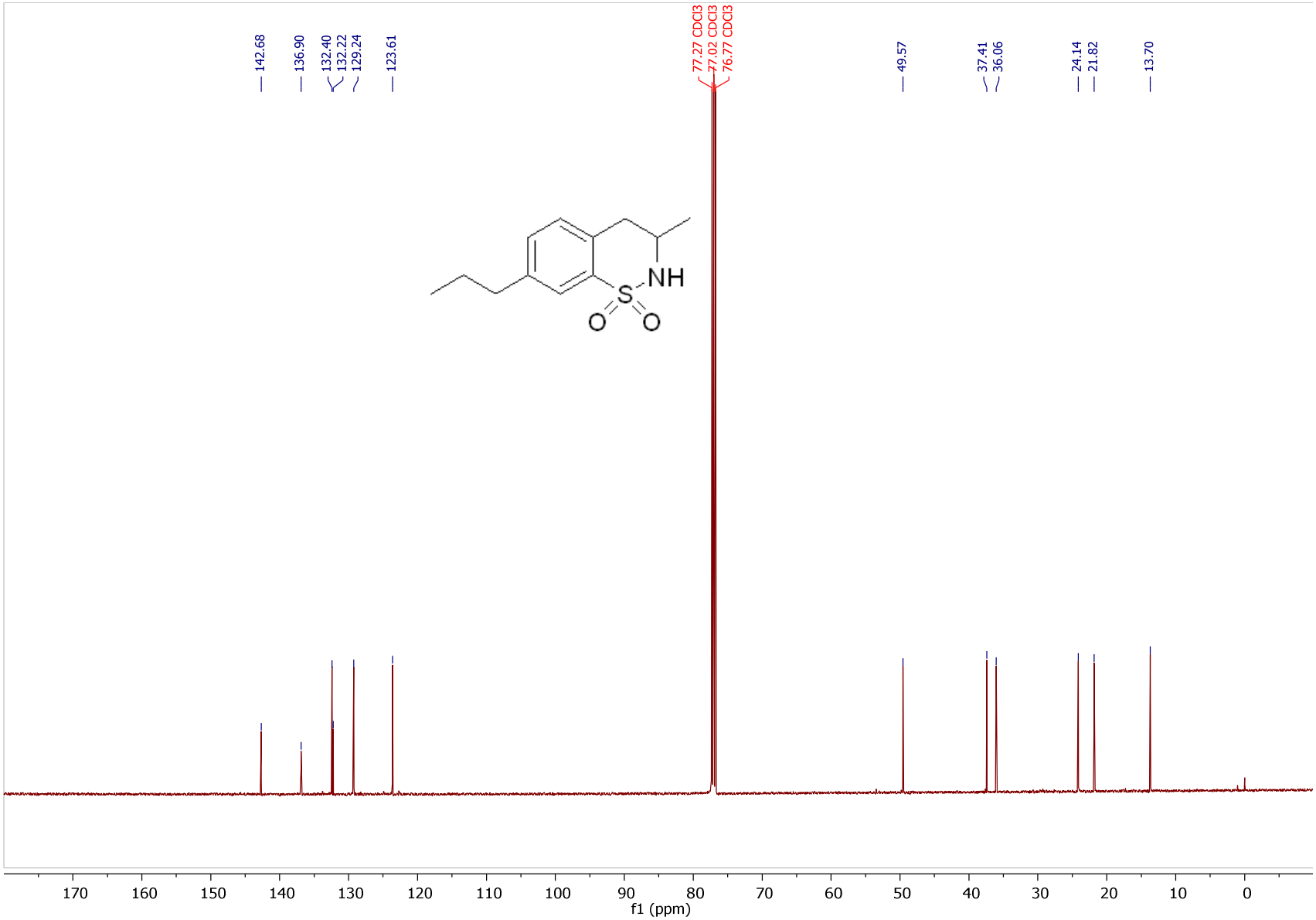
Compound 1a


144.63
137.56
135.73
133.68
123.77
120.67
77.27
77.02
76.76
58.87
37.58
28.75
24.25
13.69
9.91
S
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

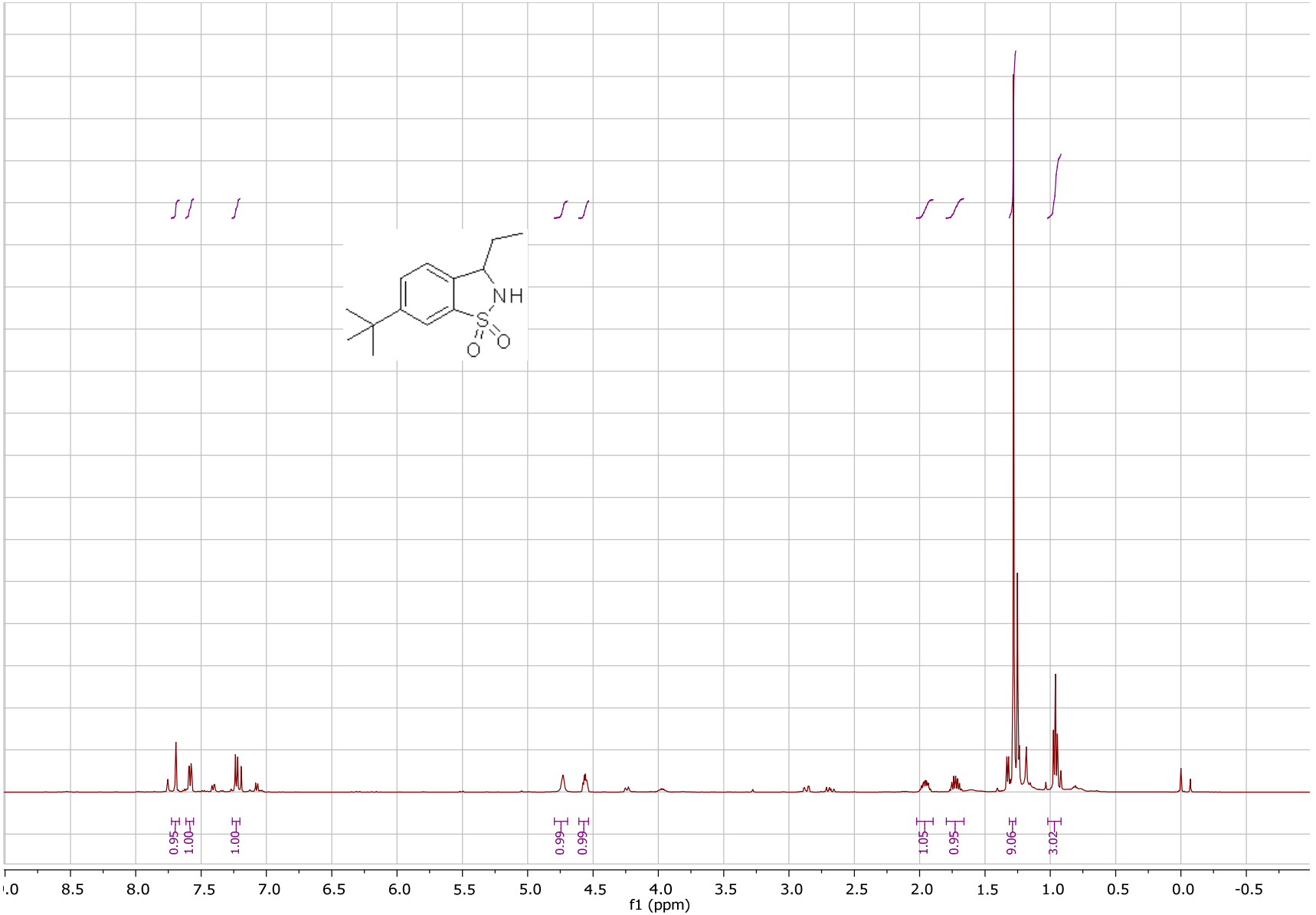
Compound 1b


NH
S
O
O
1.00
1.16
1.04
1.08
1.13
1.08
1.13
2.16
2.30
3.18
3.52
.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
-0.5
-1
f1 (ppm)

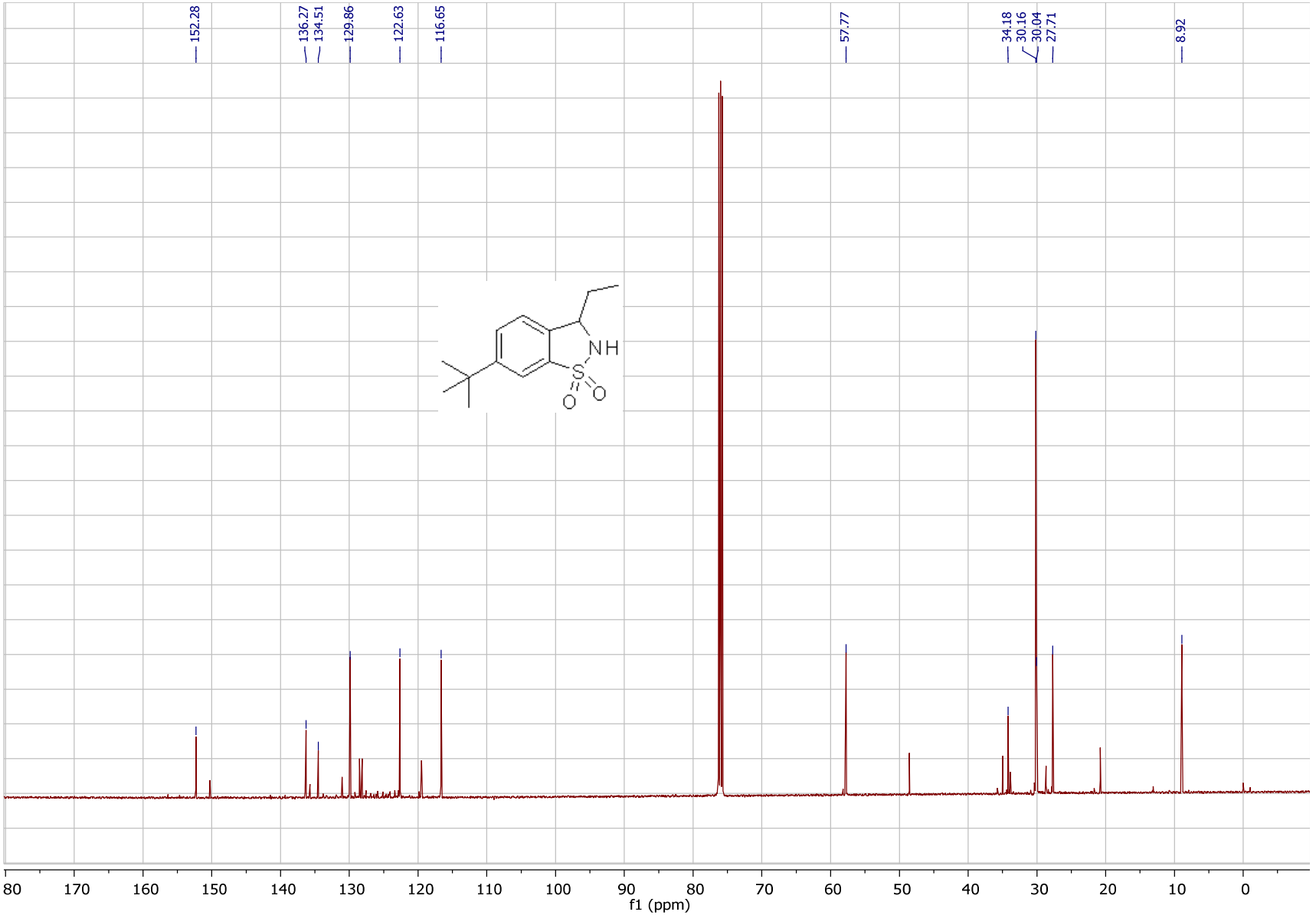
Compound 1b


142.68
136.90
132.40
132.22
129.24
123.61
77.27 CDCl3
77.02 CDCl3
76.77 CDCl3
49.57
37.41
36.06
24.14
21.82
13.70
NH
S
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

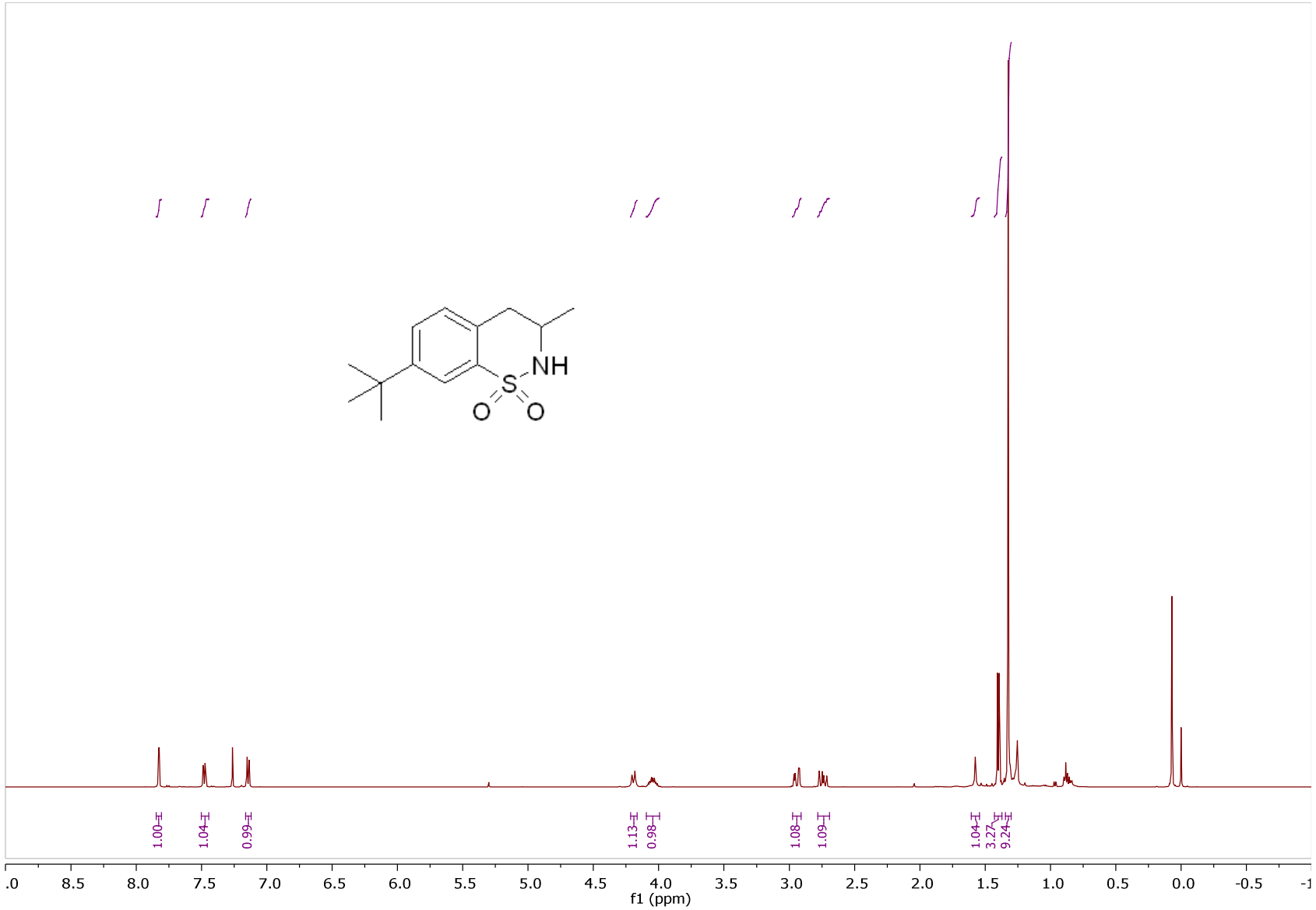
Compound 2a



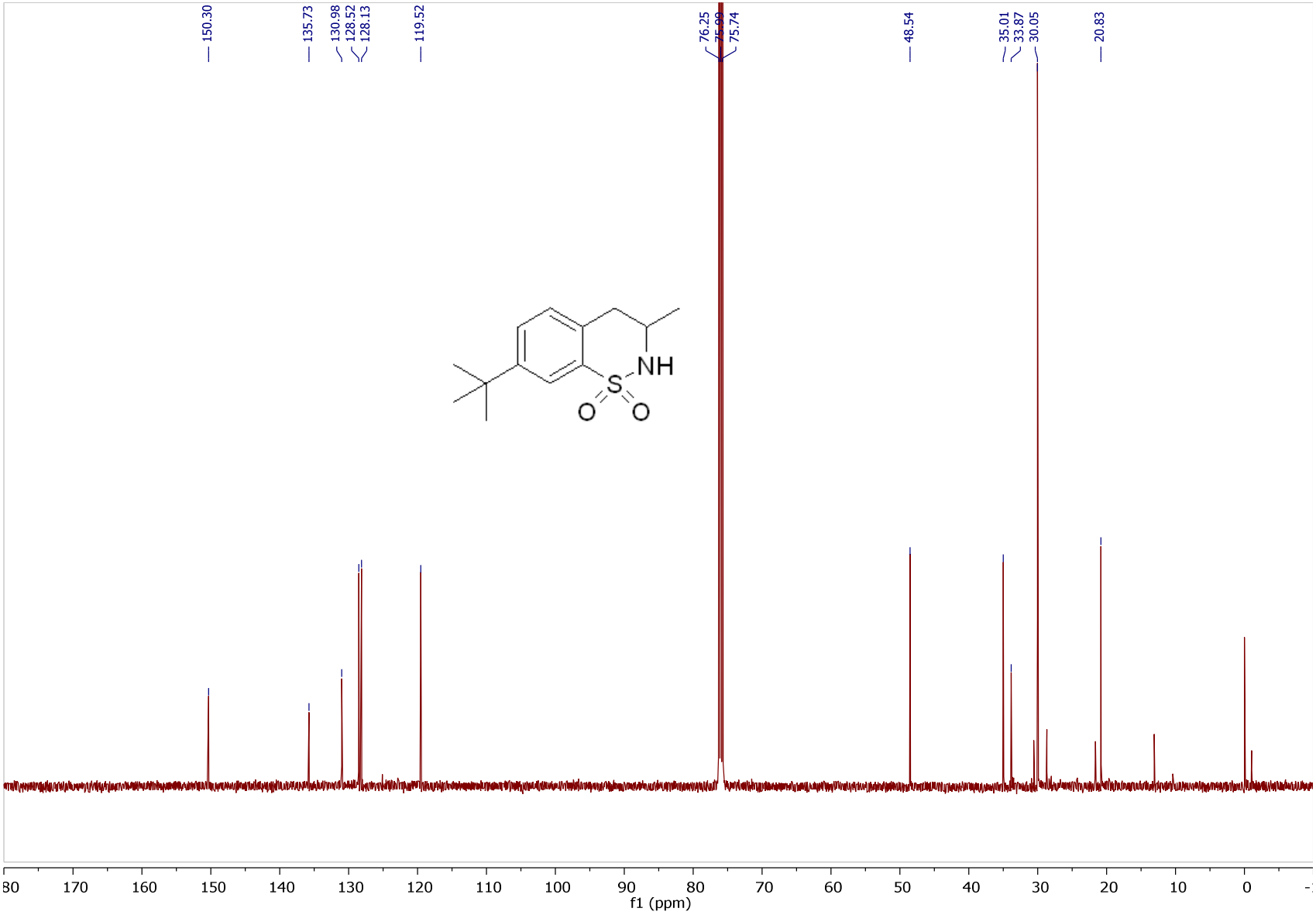
Compound 2a


152.28
136.27
134.51
129.86
122.63
116.65
57.77
34.18
30.16
30.04
27.71
8.92
NH
S
O
O
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

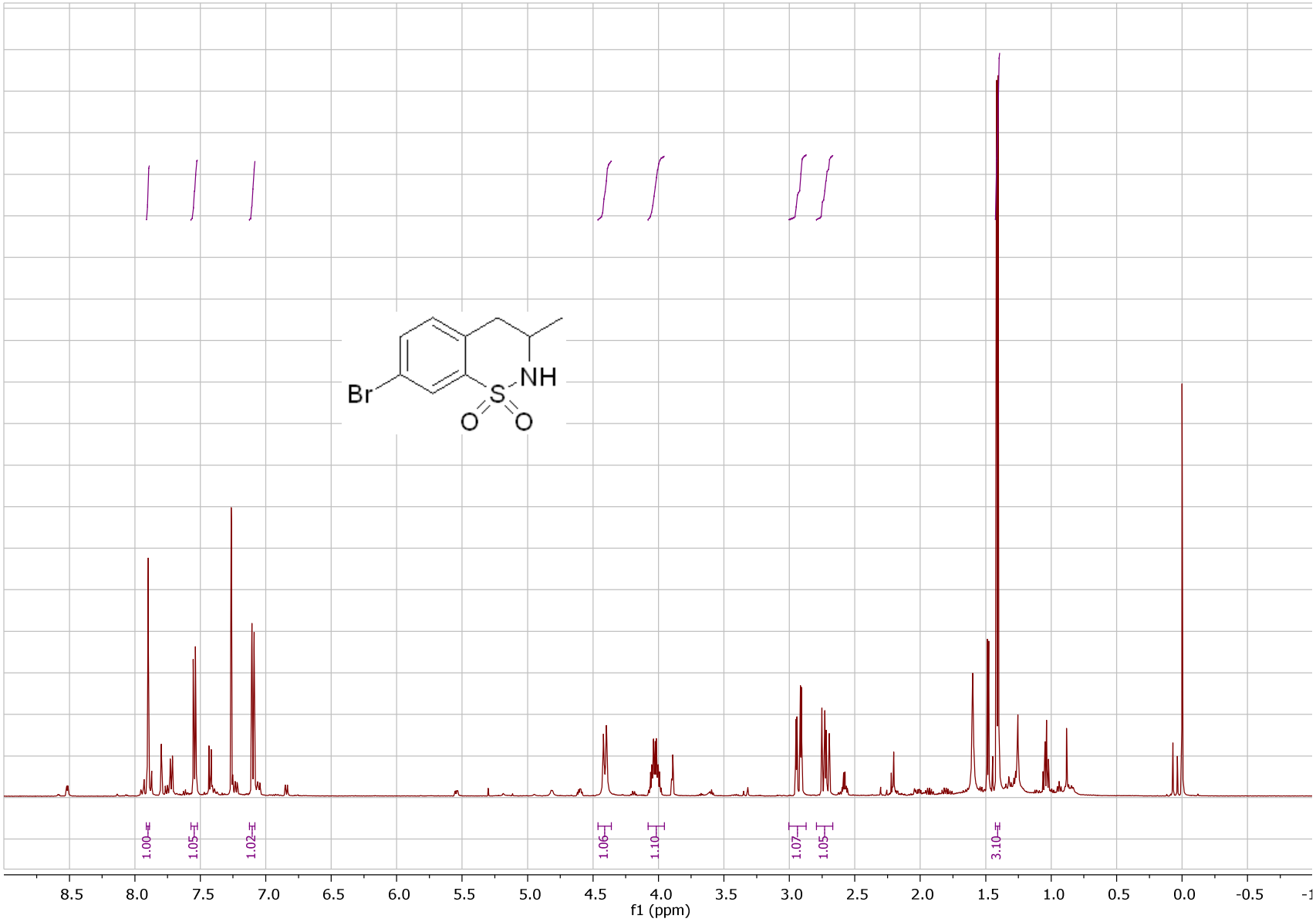
Compound 2b



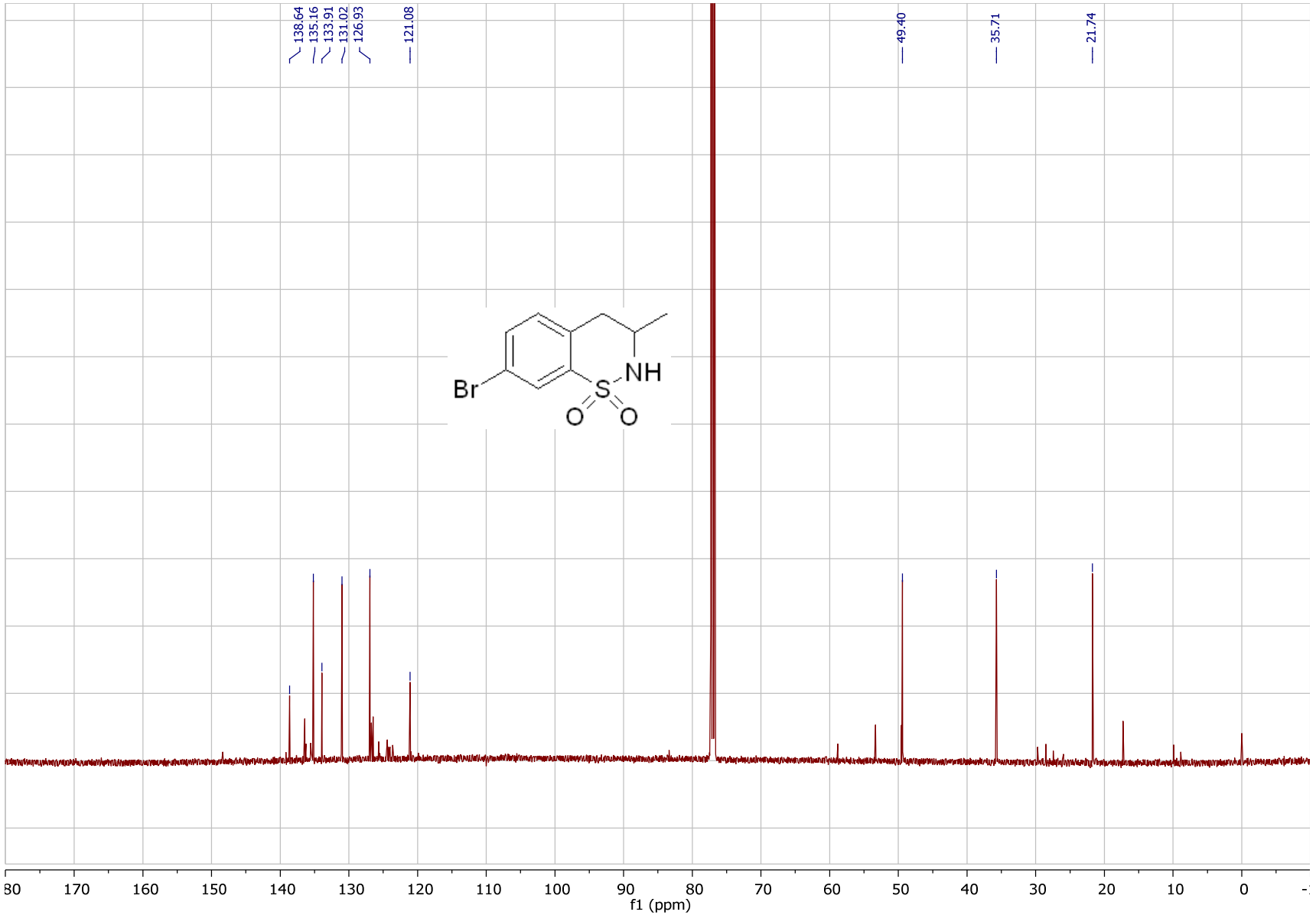
Compound 2b


150.30
135.73
130.98
128.52
128.13
119.52
76.25
75.99
75.74
48.54
35.01
33.87
30.05
20.83
NH
S
O
O
f1 (ppm)

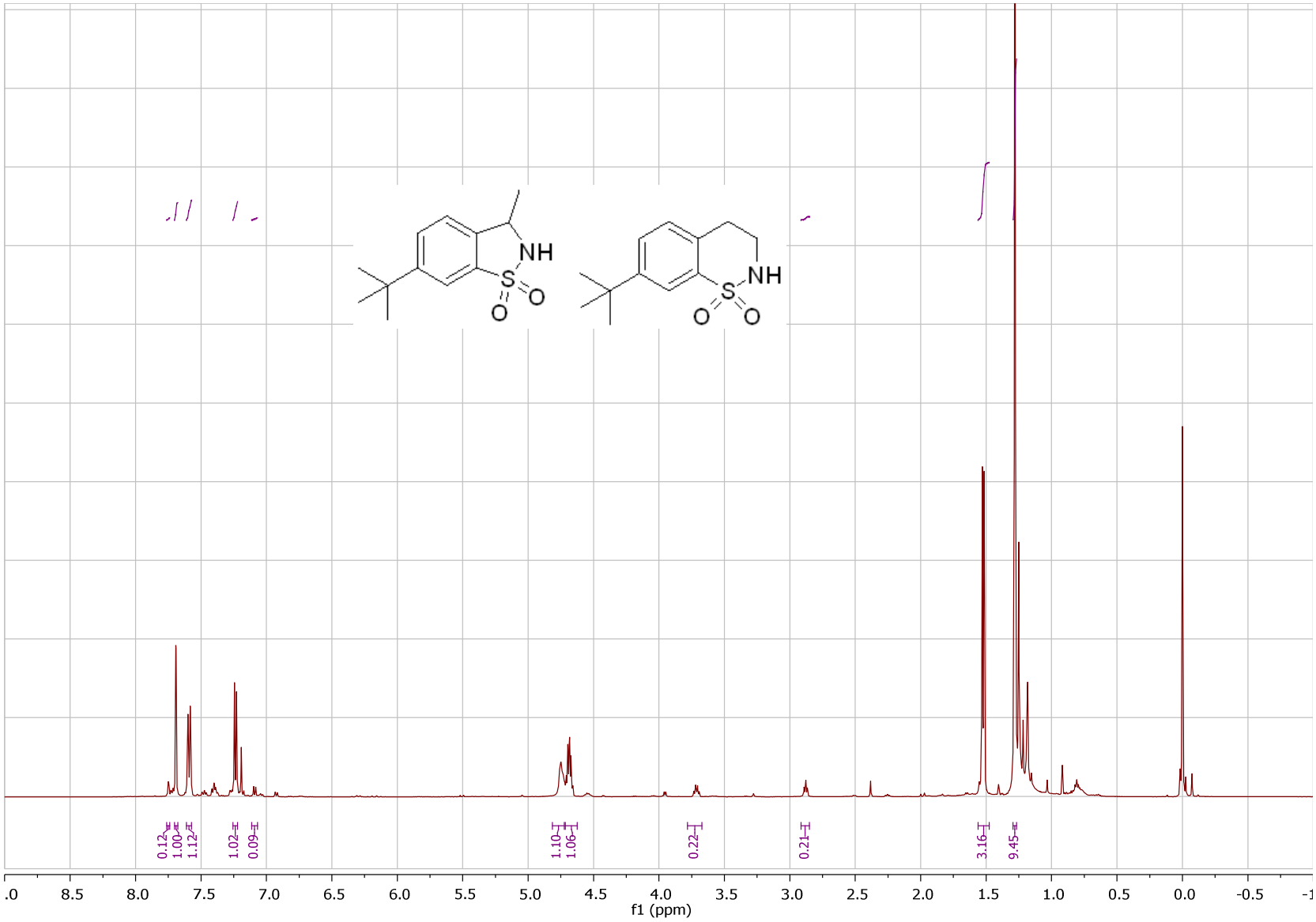
Compound 3a


Br
NH
S
O
O
1.00
1.05
1.02
1.06
1.10
1.07
1.05
3.10
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
-0.5
f1 (ppm)

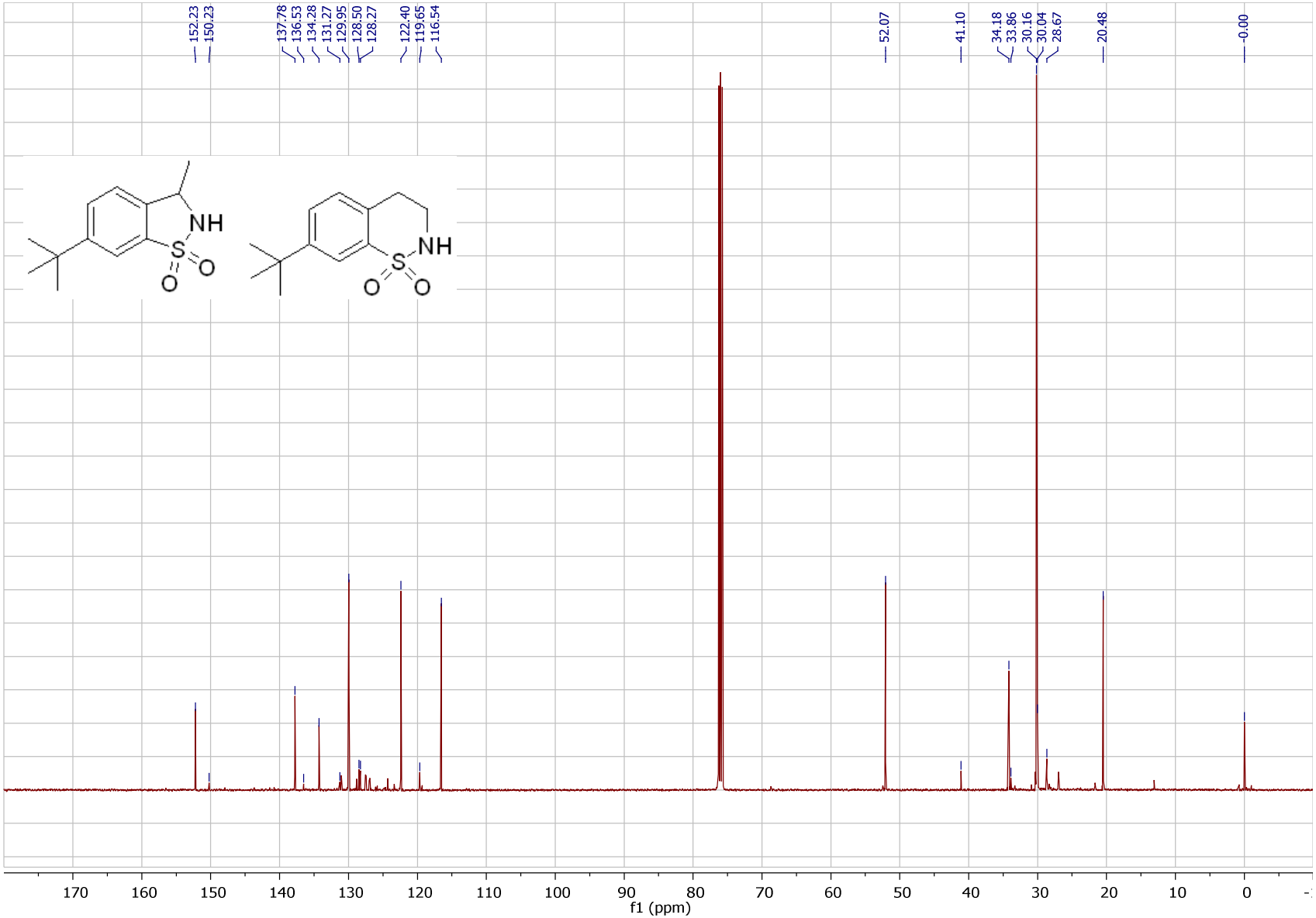
Compound 3a


138.64
135.16
133.91
131.02
126.93
121.08
49.40
35.71
21.74
Br
NH
S
O
O
f1 (ppm)

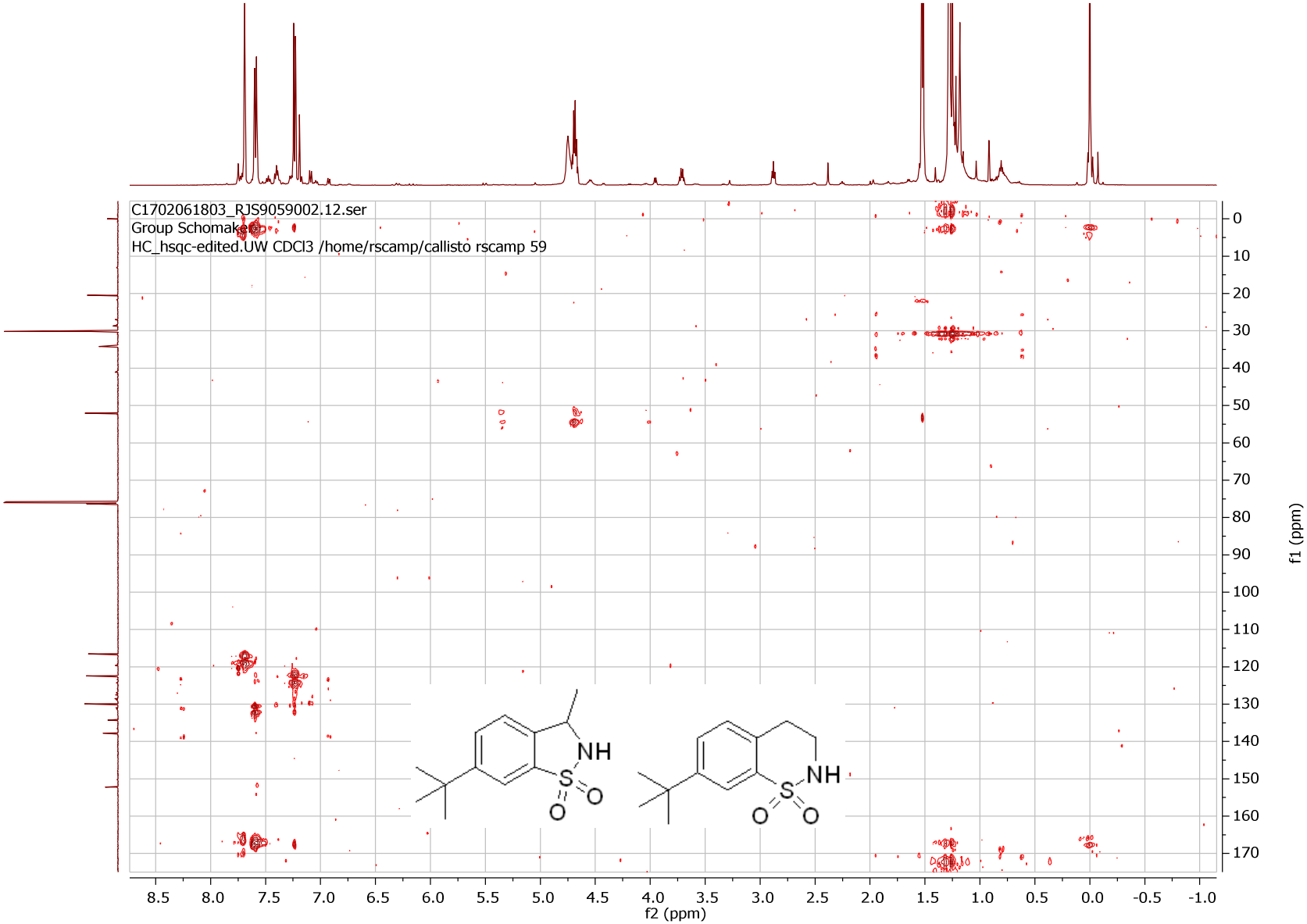
Compound 4a/4b



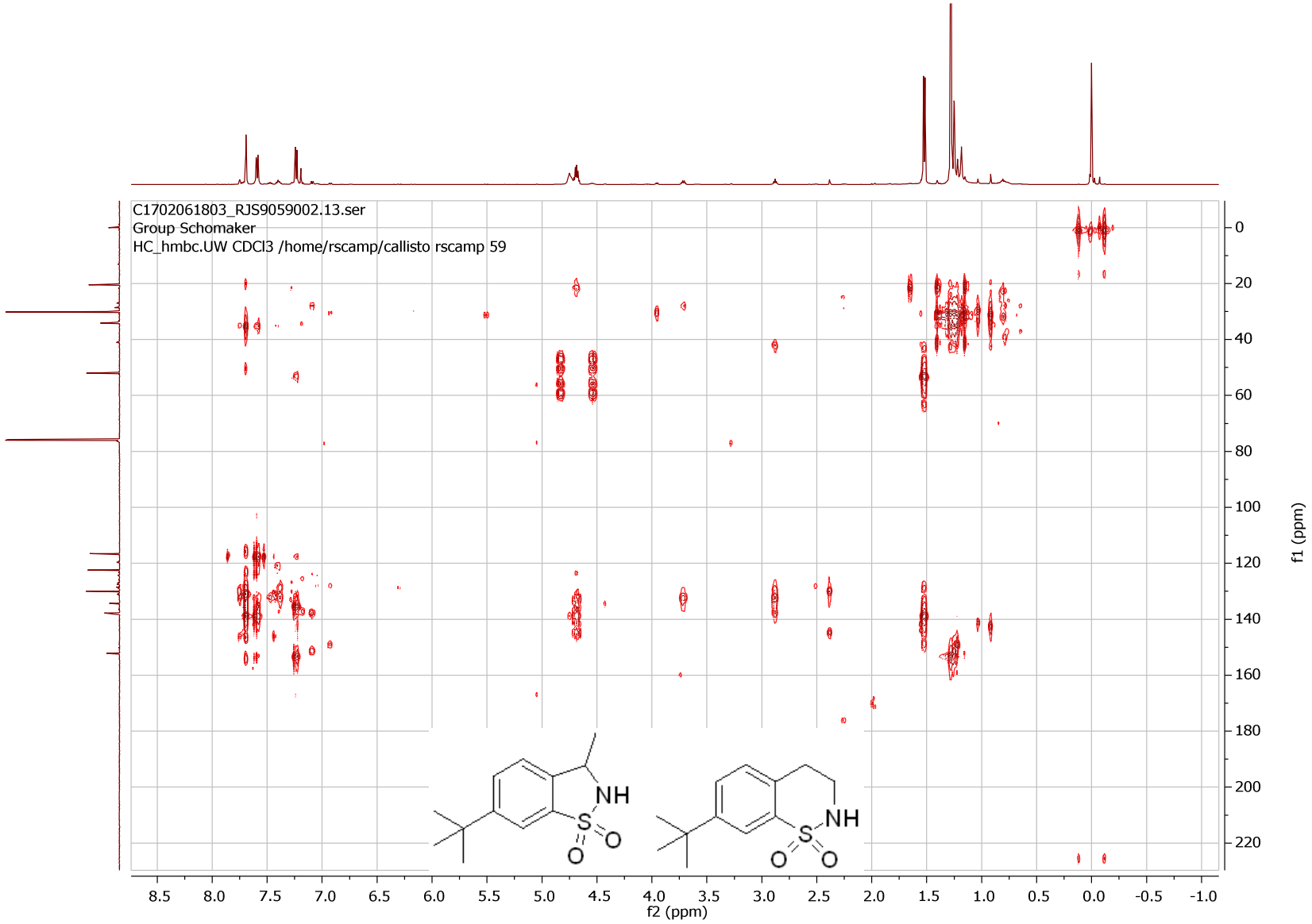
Compound 4a/4b



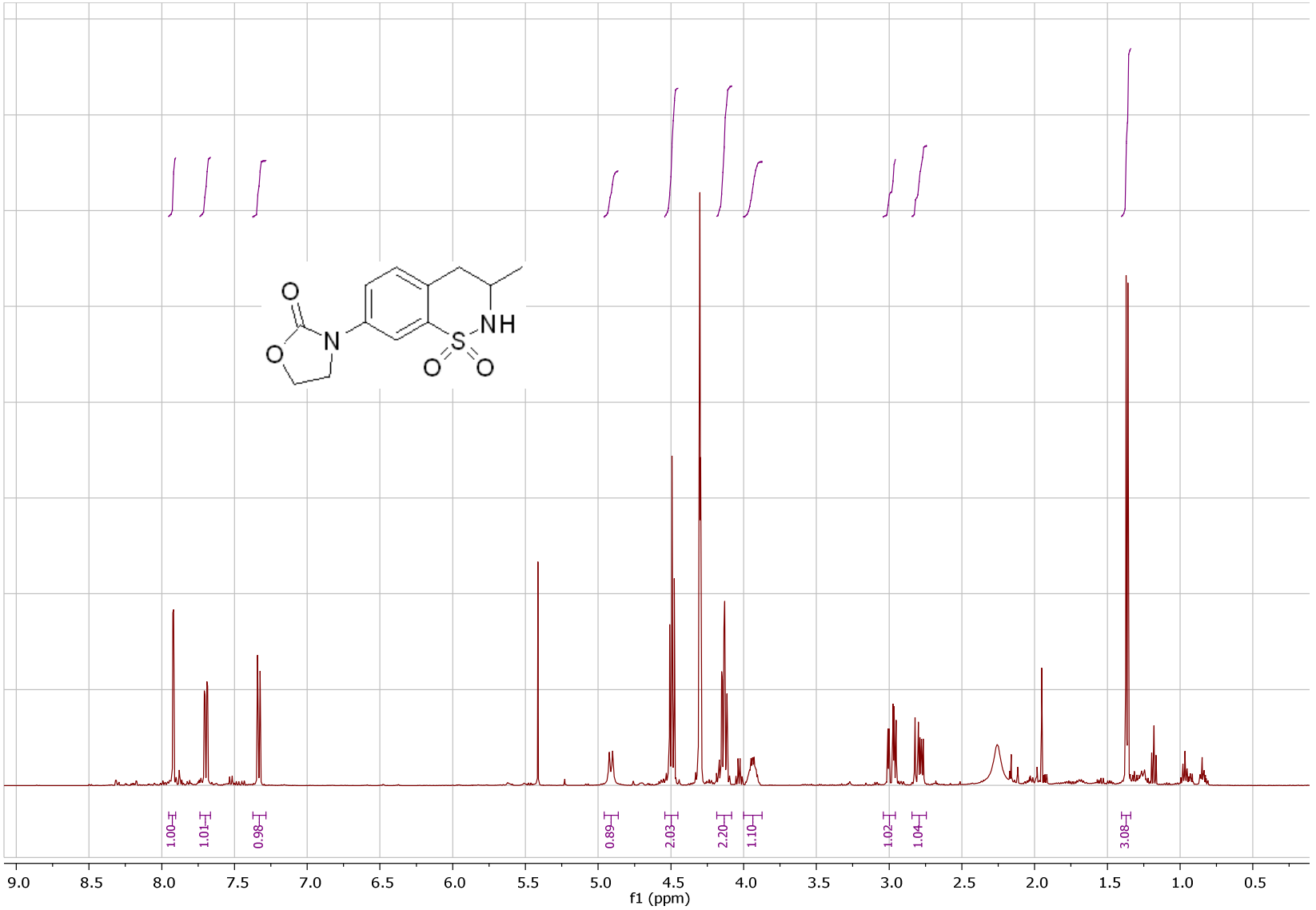
Compound 4a/4b



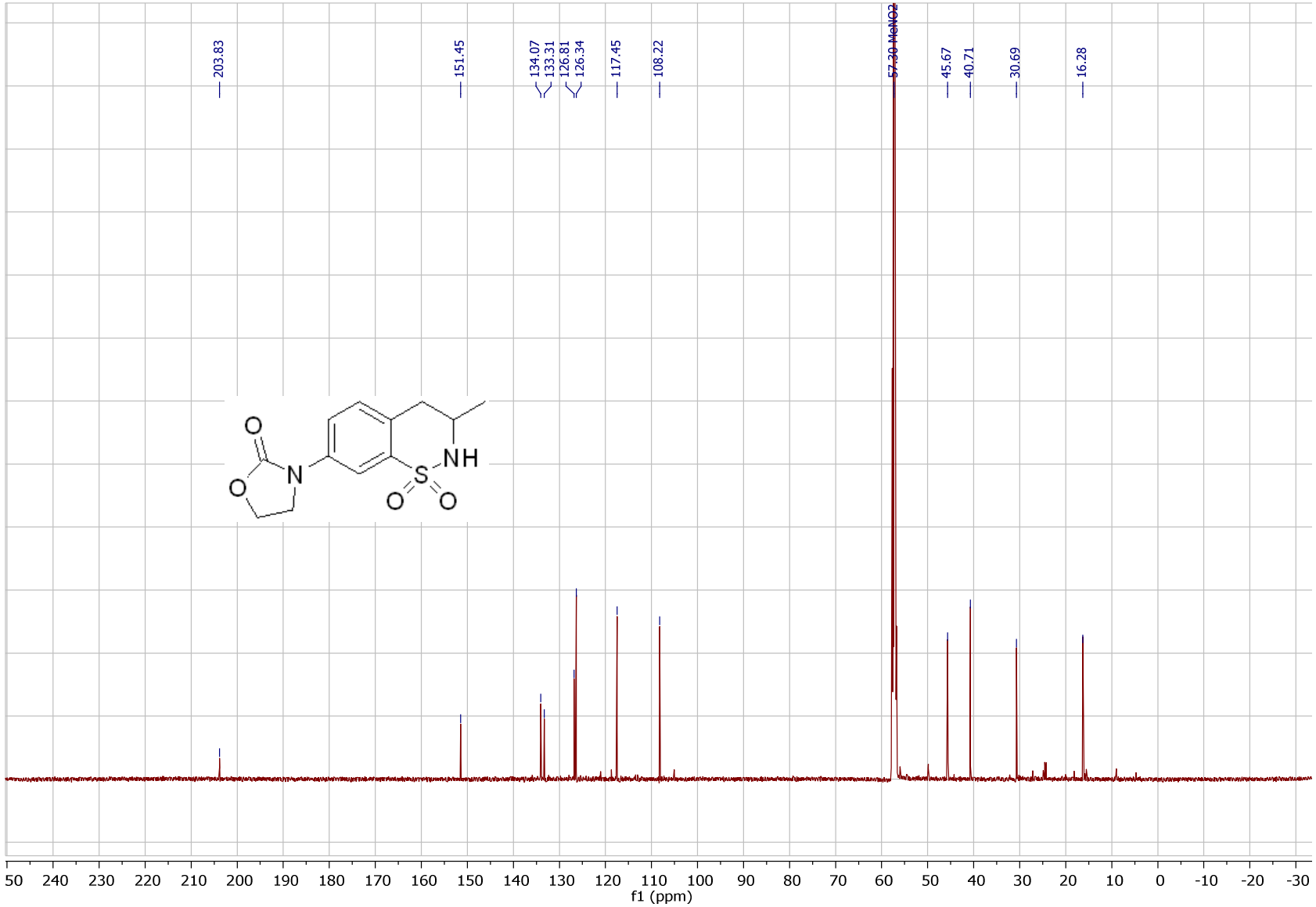
Compound 4a/4b



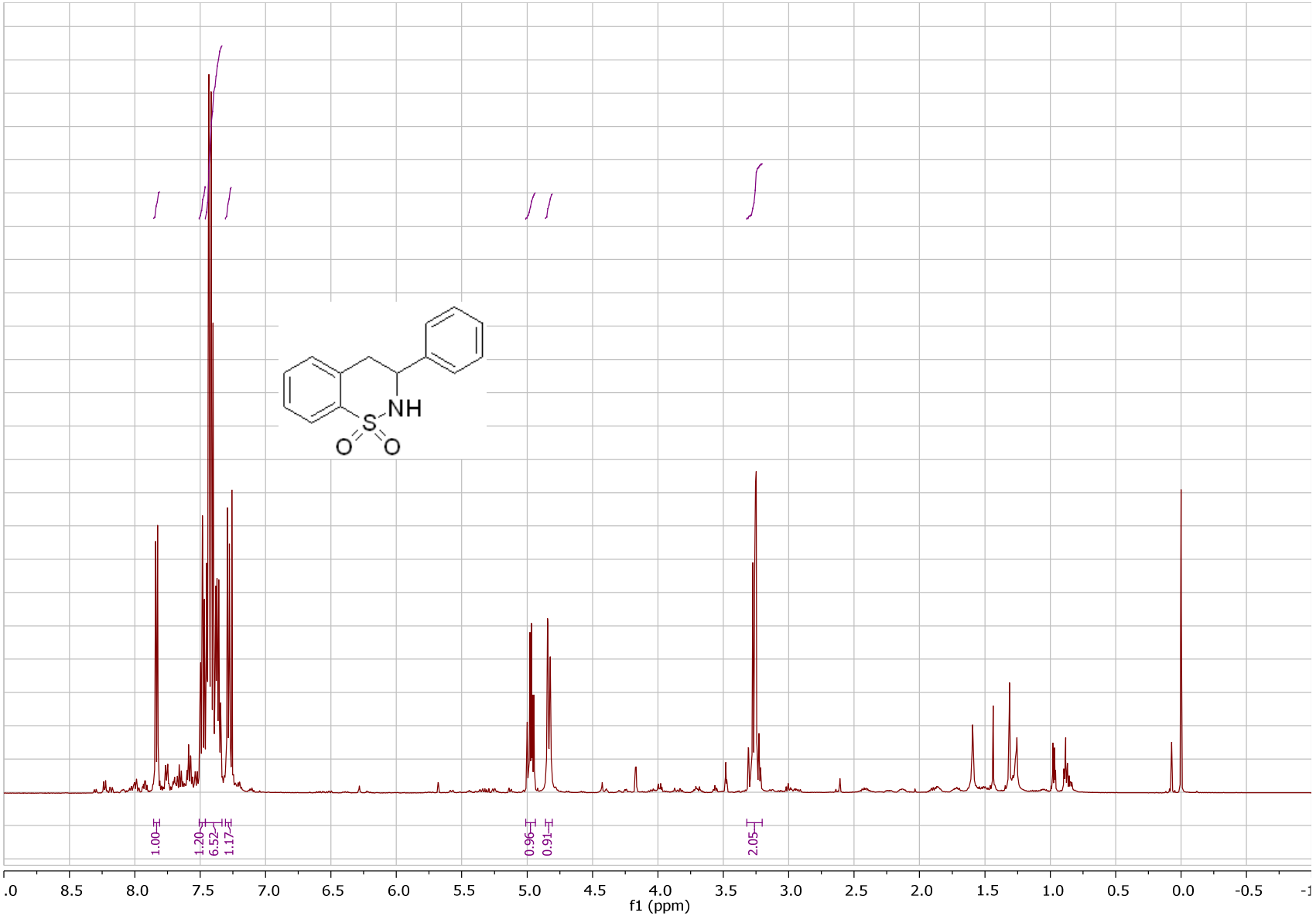
Compound 5a


O
N
O
NH
S
O
O
1.00
1.01
0.98
0.89
2.03
2.20
1.10
1.02
1.04
3.08
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)

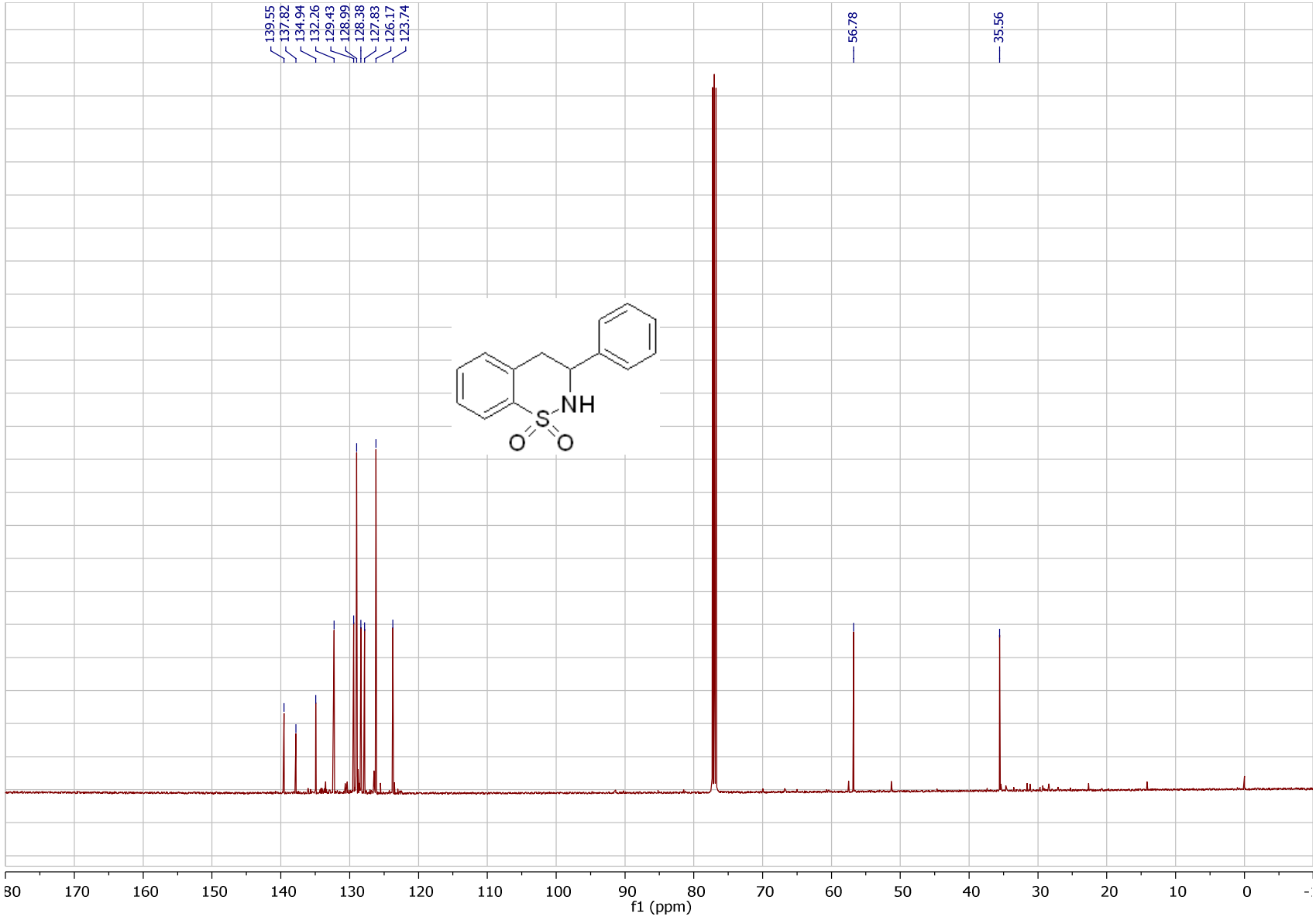
Compound 5a


203.83
151.45
134.07
133.31
126.81
126.34
117.45
108.22
57.30 MeNO2
45.67
40.71
30.69
16.28
O
N
O
S
NH
O
O
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

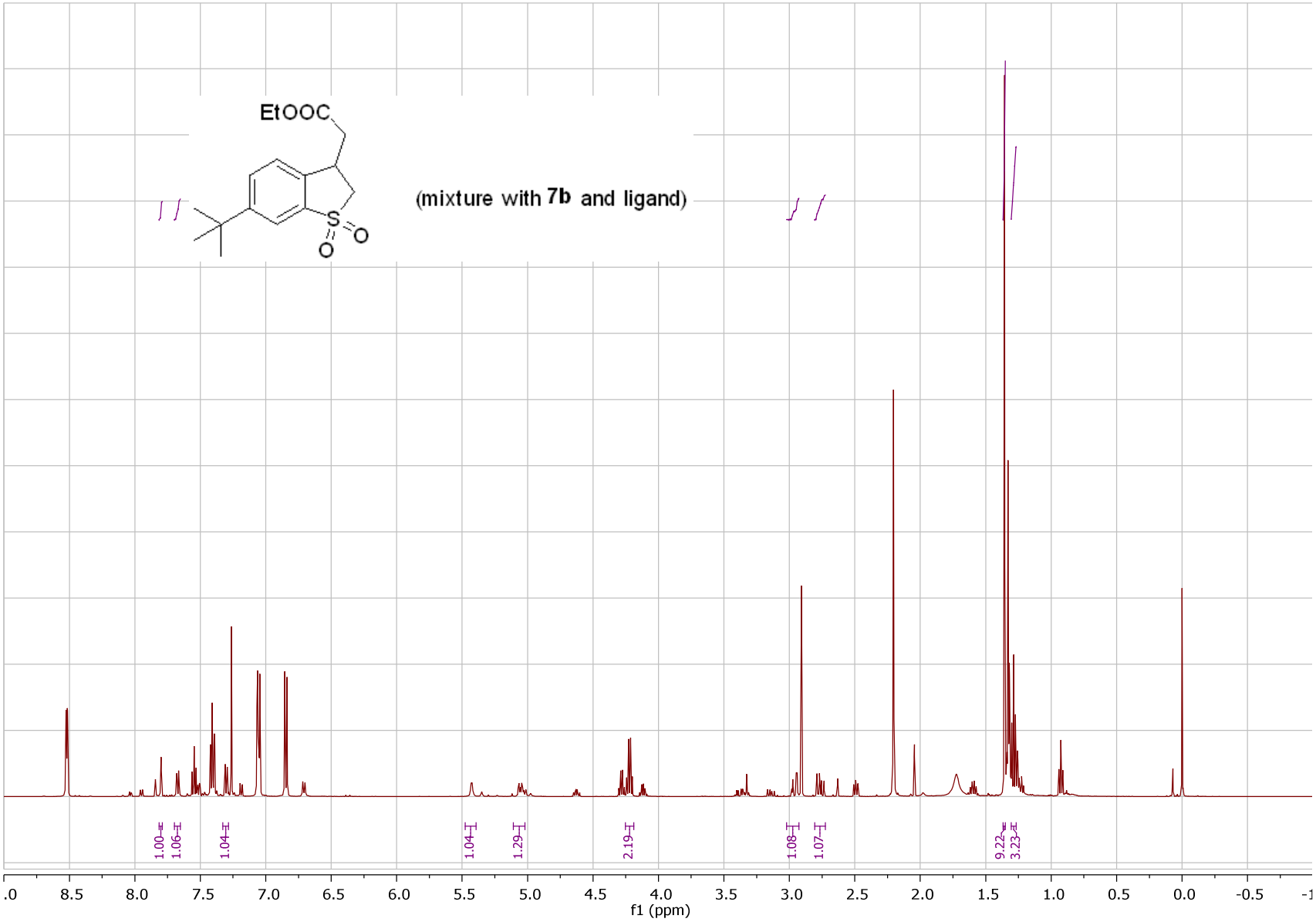
Compound 6a



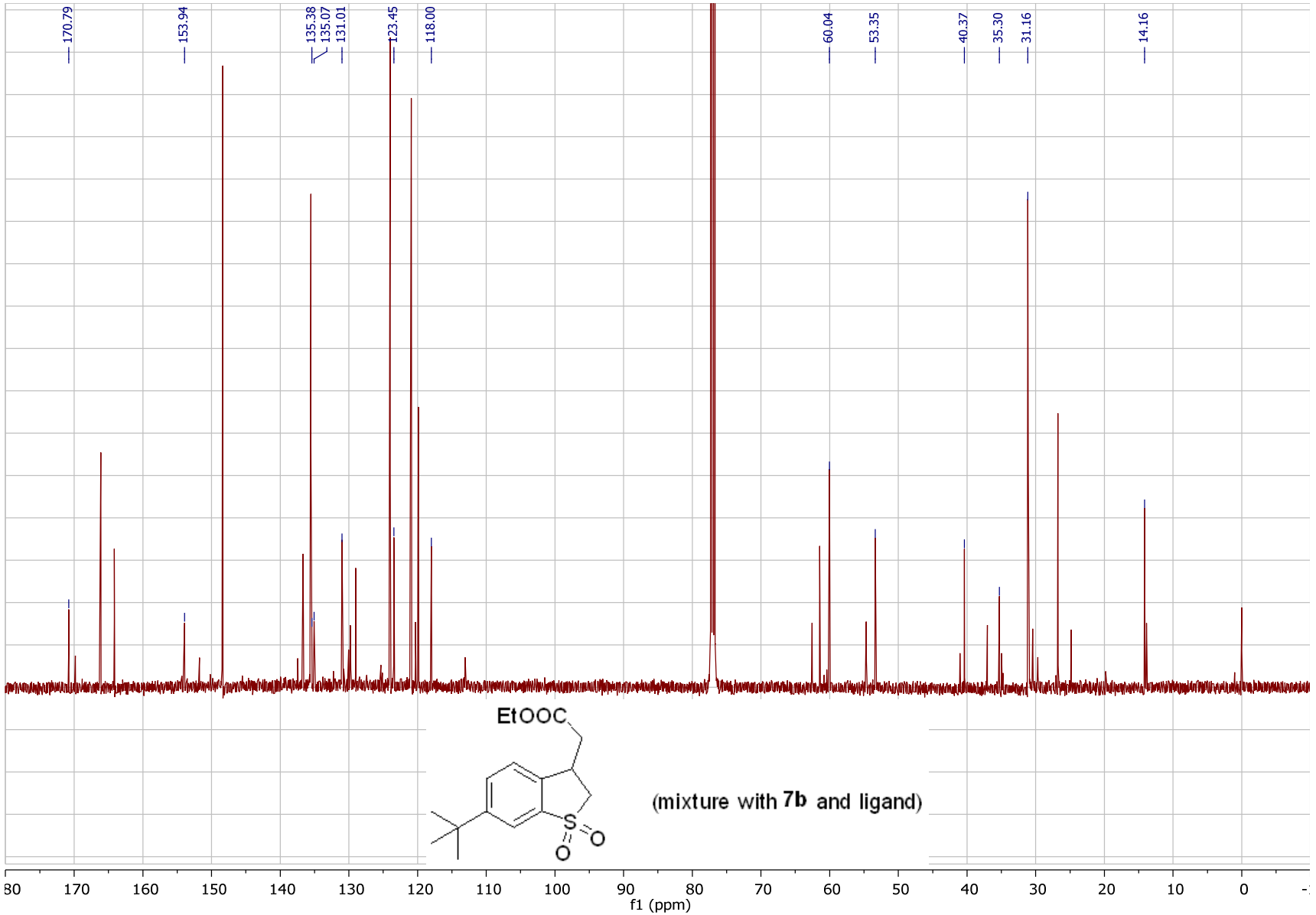
Compound 6a


139.55
137.82
134.94
132.26
129.43
128.99
128.38
127.83
126.17
123.74
56.78
35.56
NH
S
O
O
f1 (ppm)

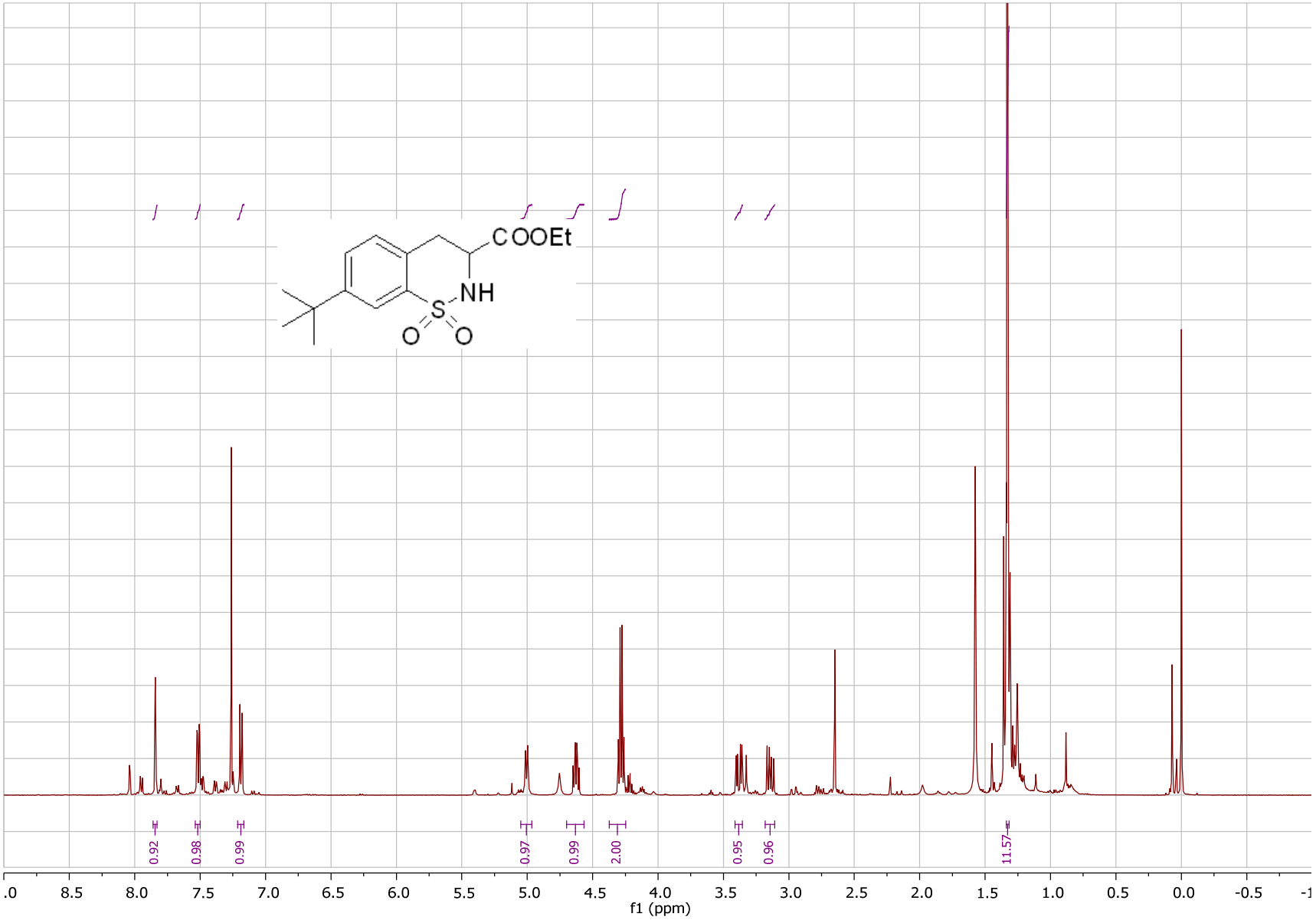
Compound 7a (isolated as mixture)



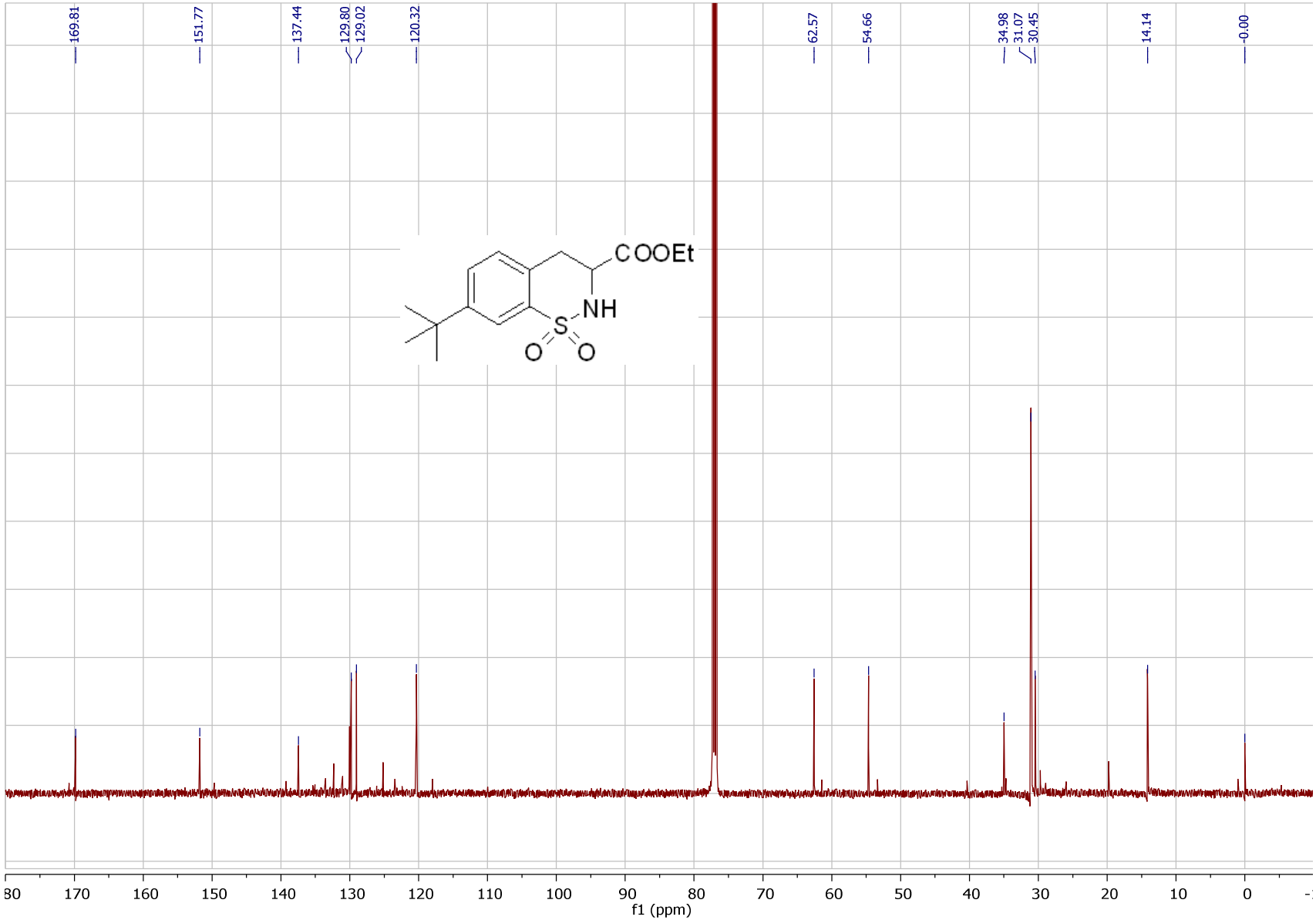
Compound 7a (isolated as mixture)



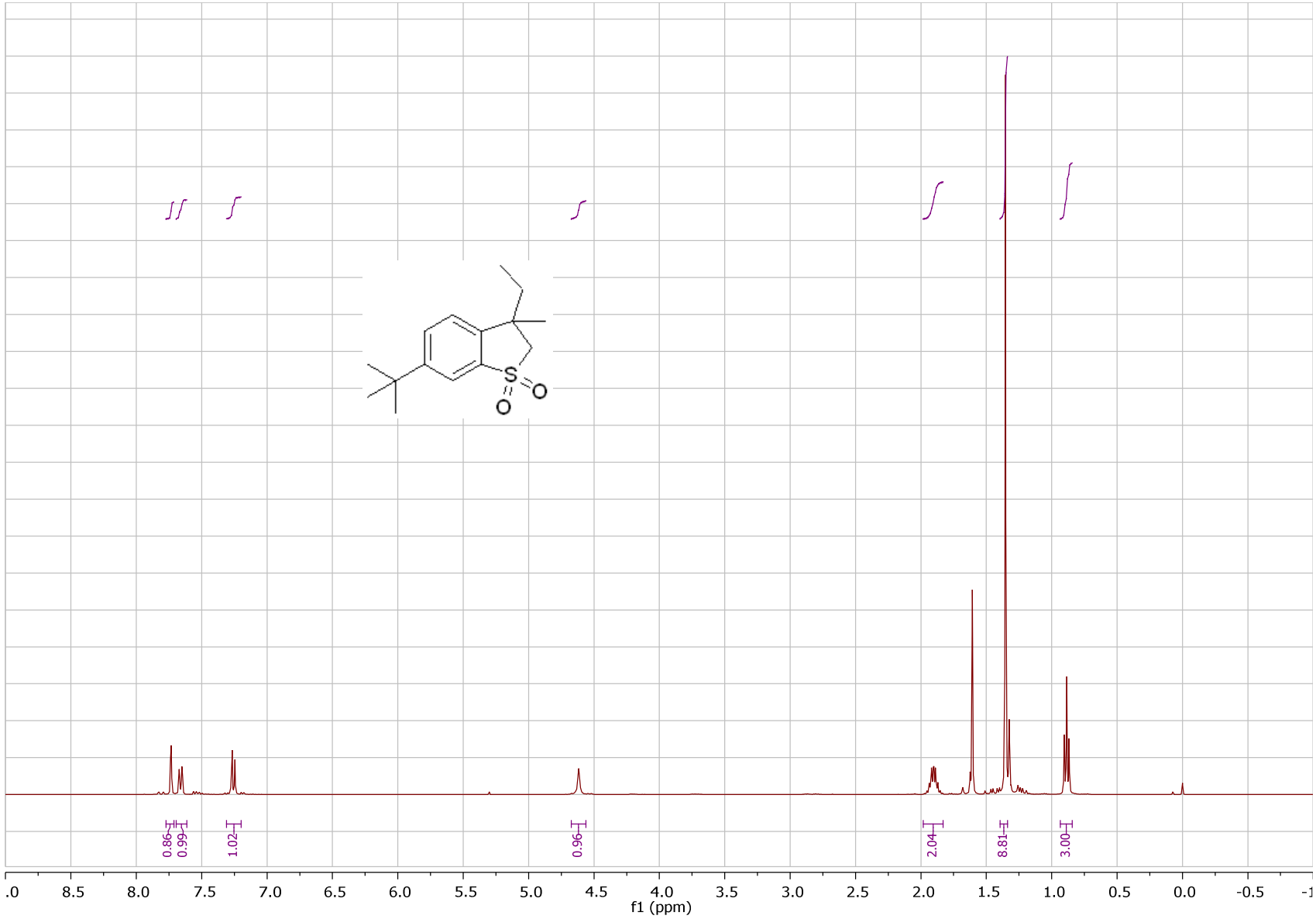
Compound 7b



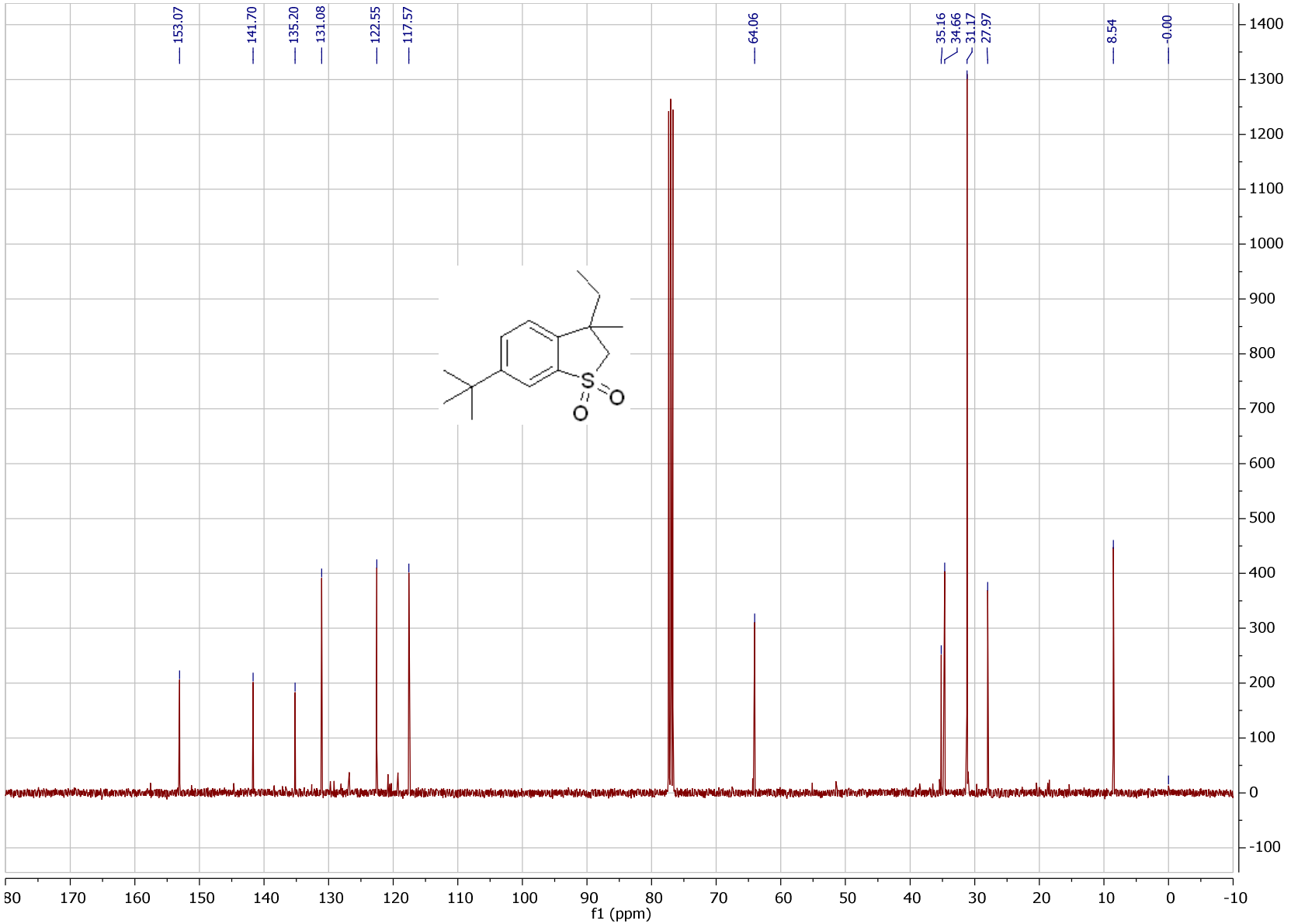
Compound 7b


169.81
151.77
137.44
129.80
129.02
120.32
62.57
54.66
34.98
31.07
30.45
14.14
0.00
COOEt
NH
S
O
O
f1 (ppm)

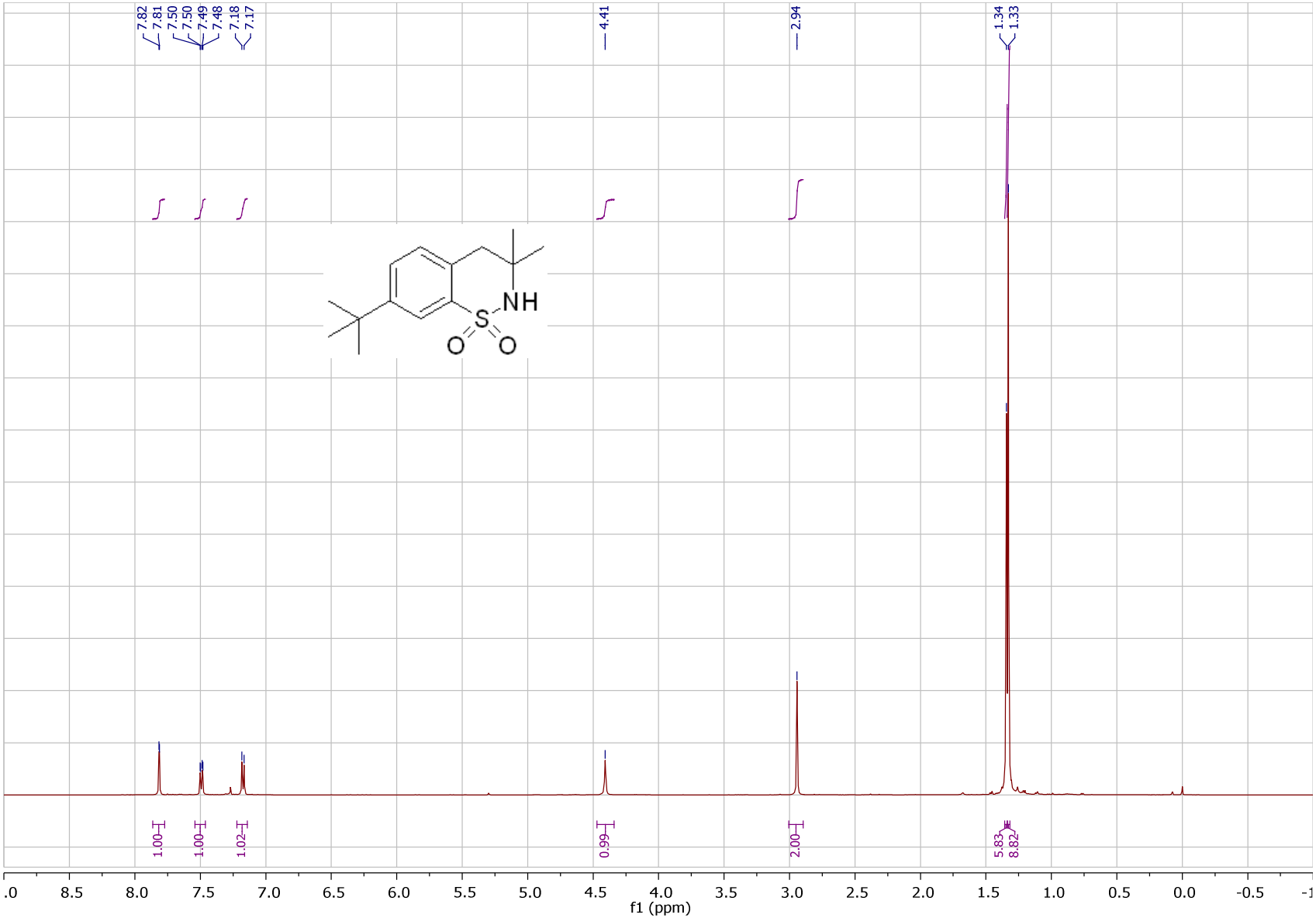
Compound 8a



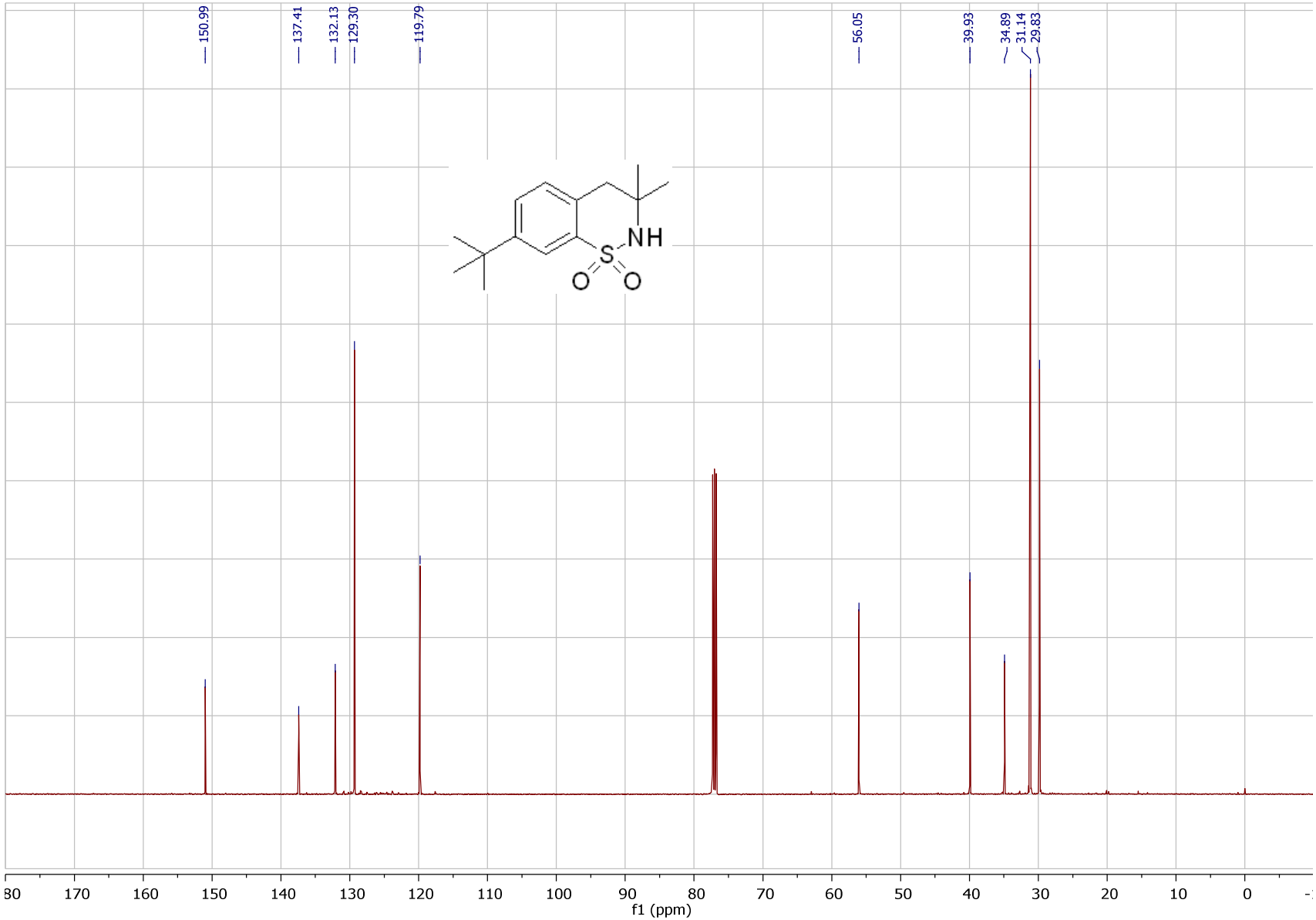
Compound 8a


153.07
141.70
135.20
131.08
122.55
117.57
64.06
35.16
34.66
31.17
27.97
8.54
-0.00
f1 (ppm)

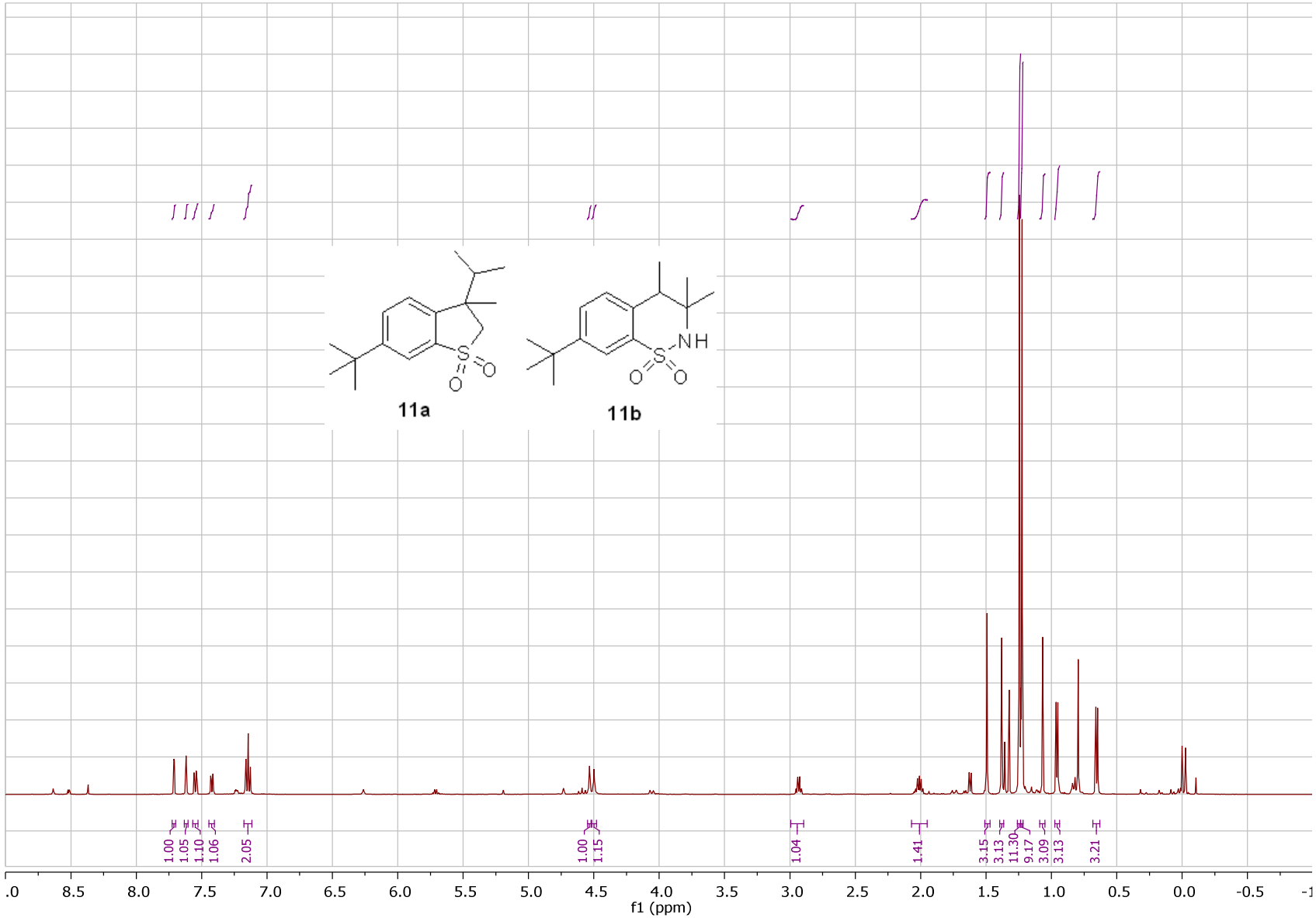
Compound 9a


7.82
7.81
7.50
7.50
7.49
7.48
7.18
7.17
4.41
2.94
1.34
1.33
NH
S
O
O
1.00
1.00
1.02
0.99
2.00
5.83
8.82
f1 (ppm)

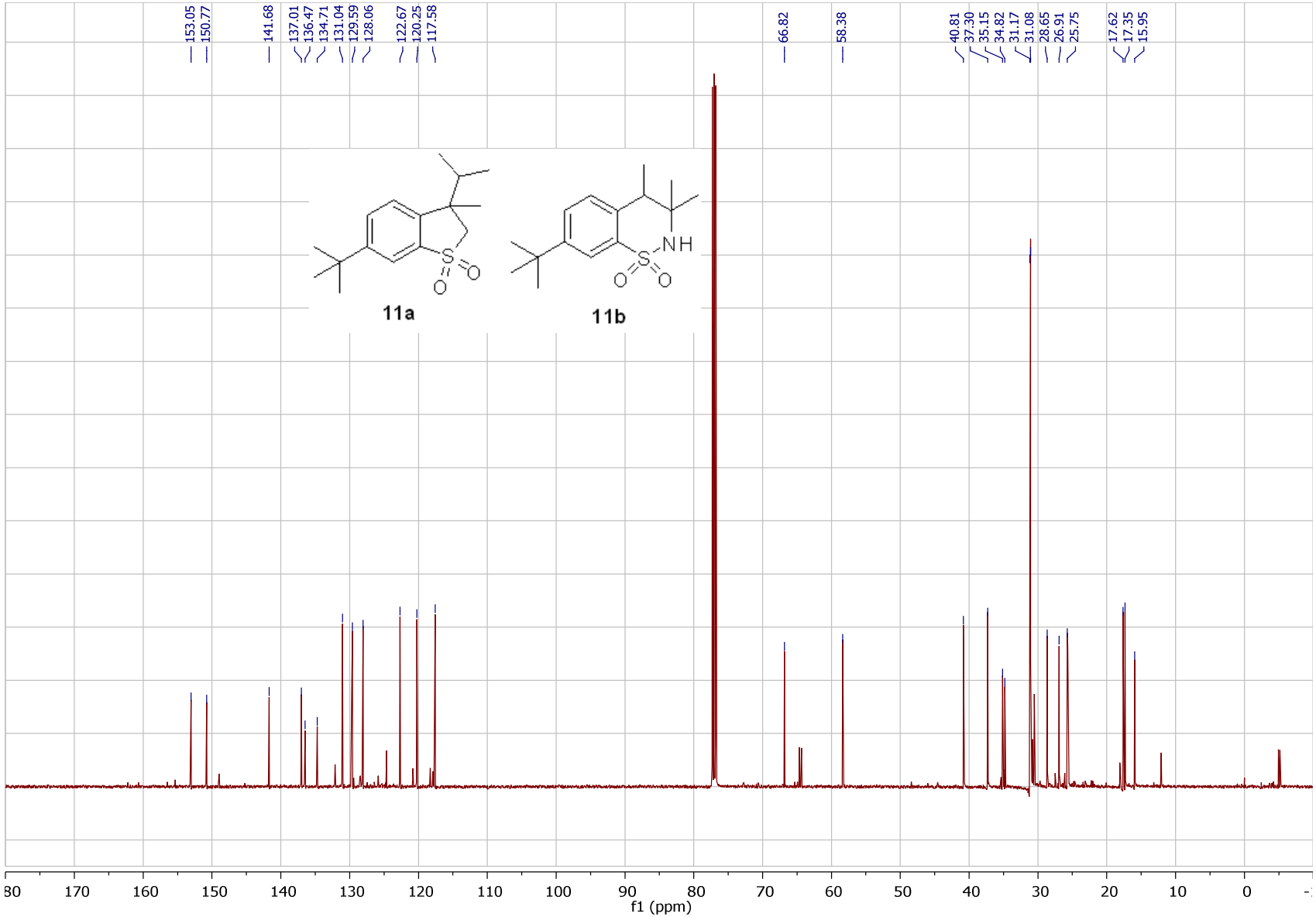
Compound 9a


150.99
137.41
132.13
129.30
119.79
56.05
39.93
34.89
31.14
29.83
NH
S
O
O
f1 (ppm)

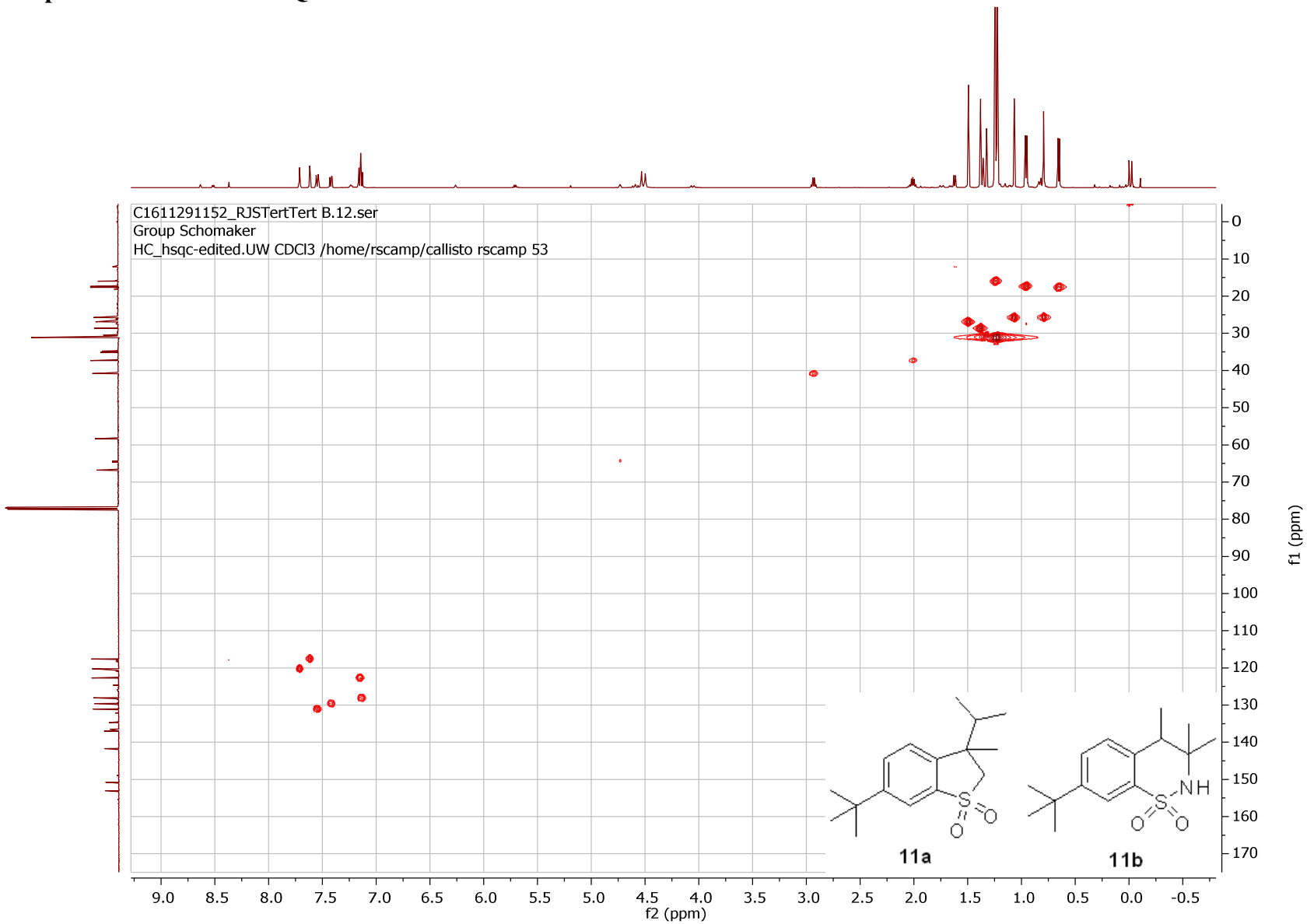
Compound 10a and 10b



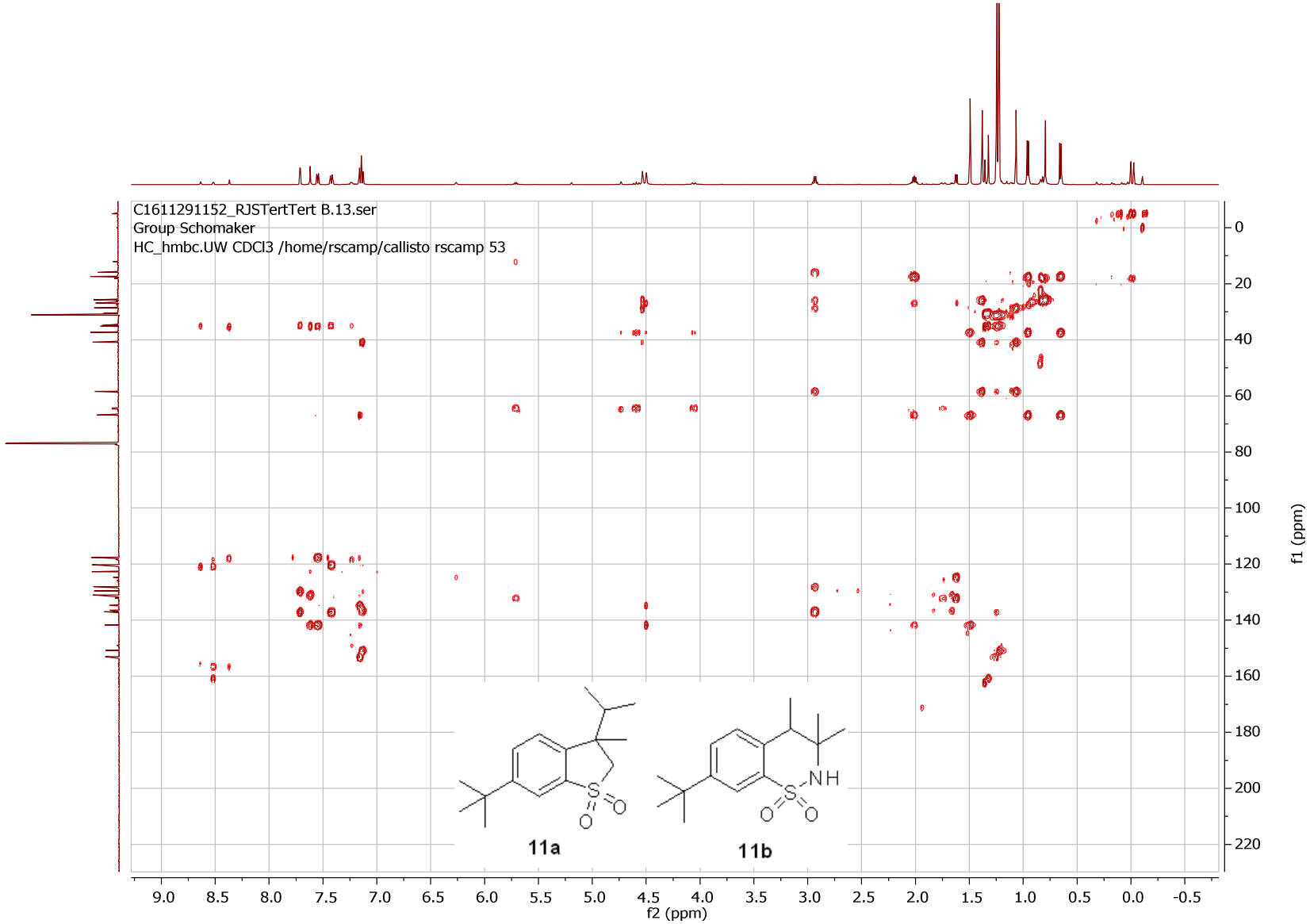
Compound 10a and 10b



Compound 10a and 10b-HSQC

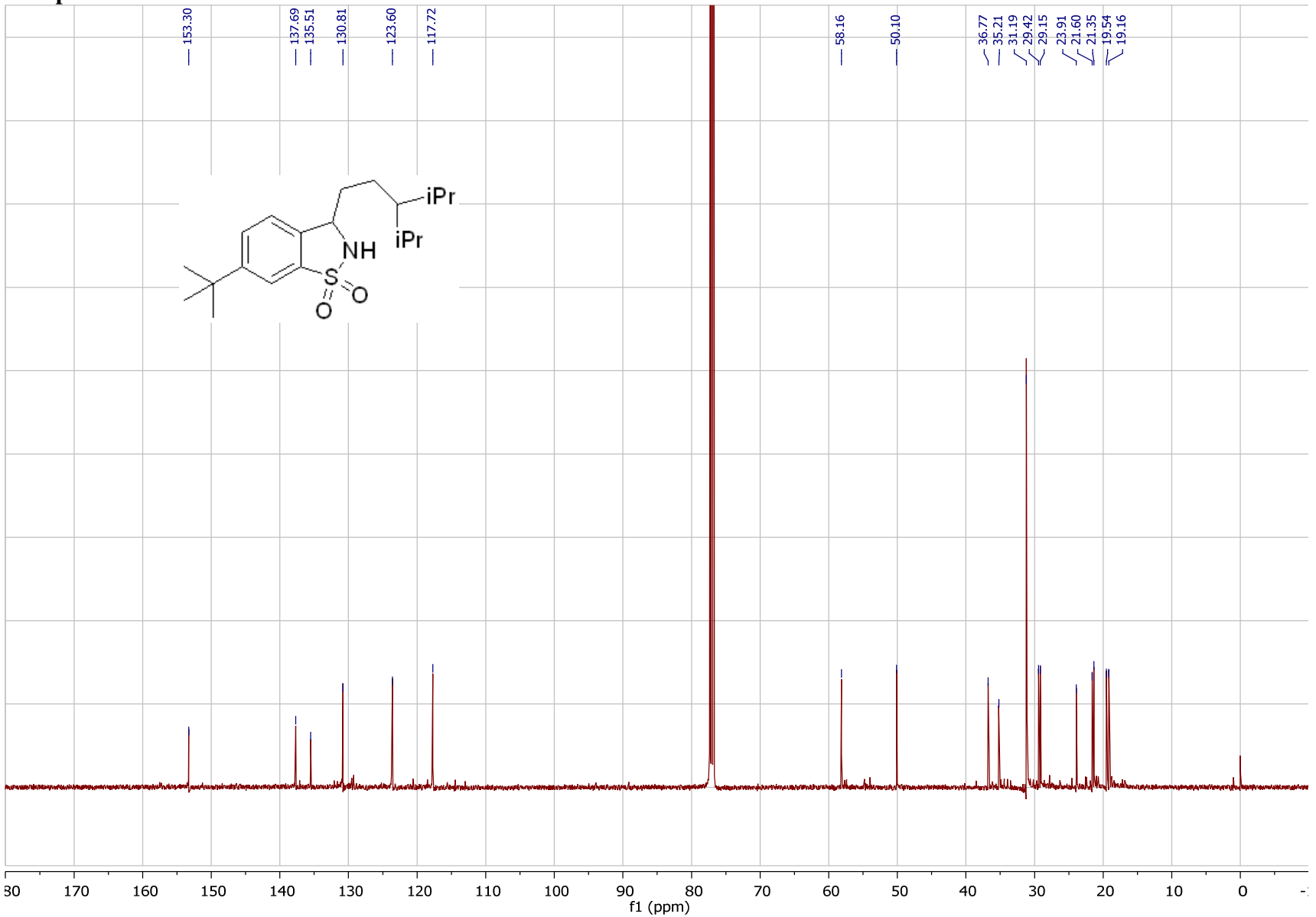


Compound 10a and 10b-HMBC

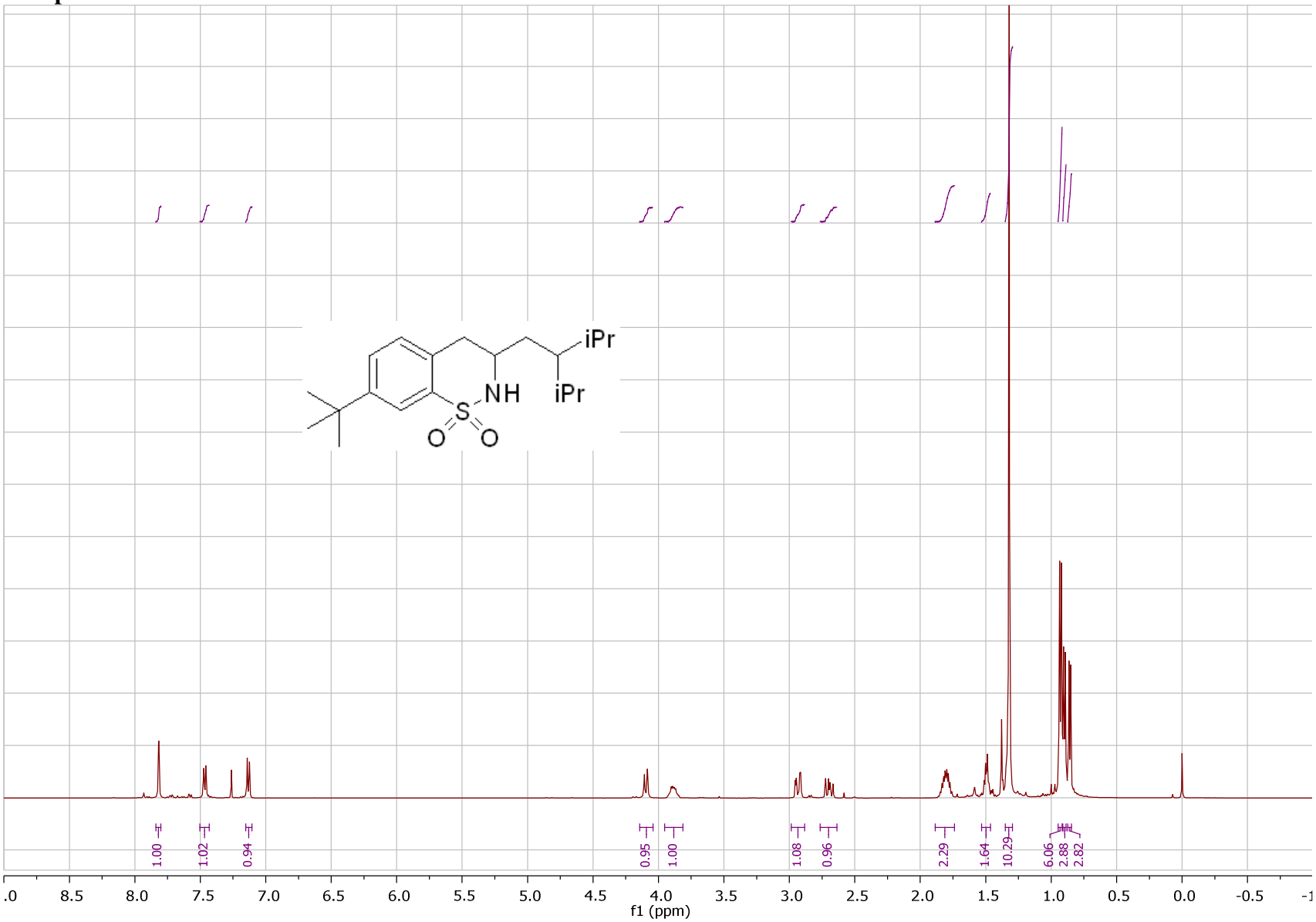


Compound 11a

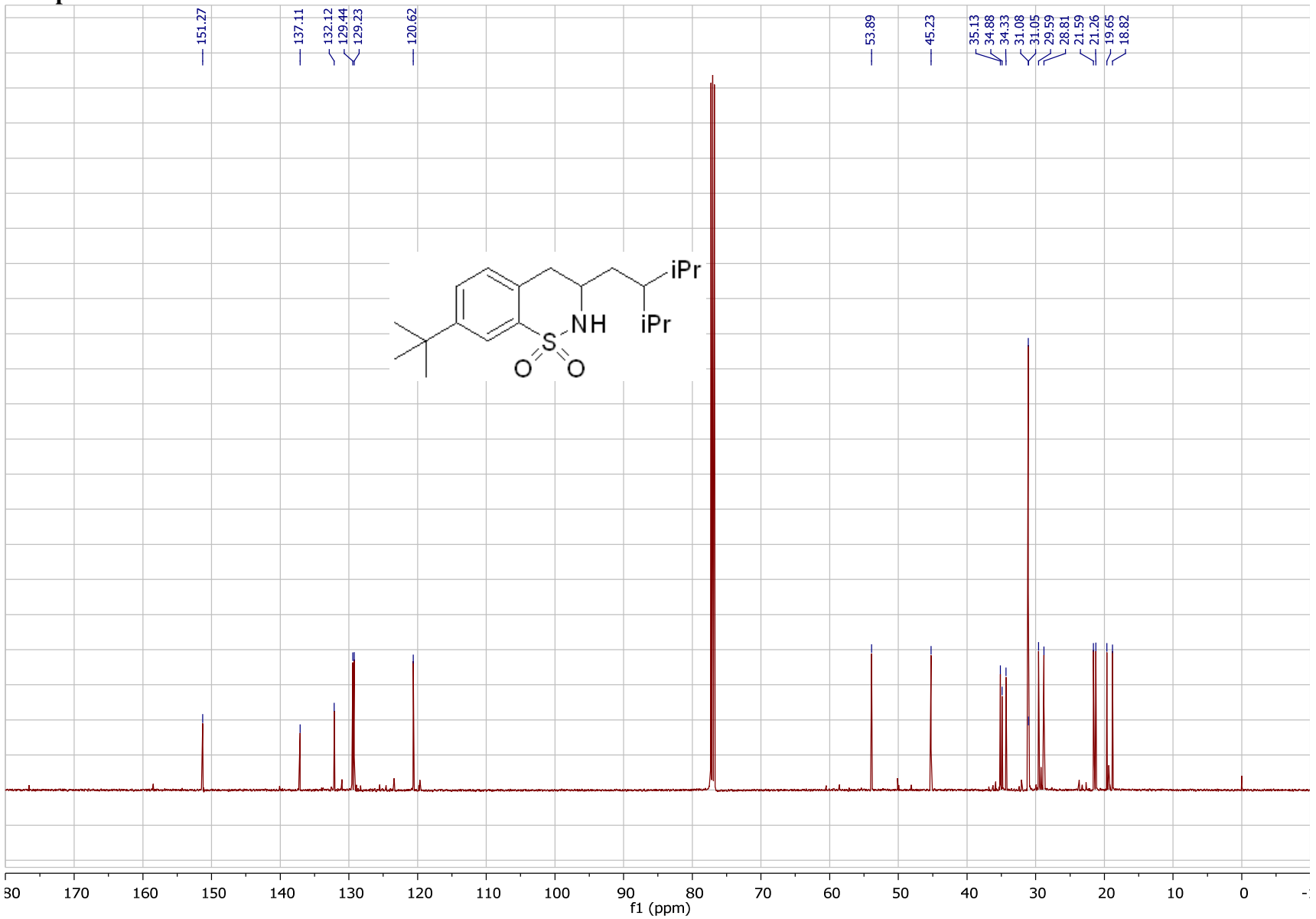
Compound 11a



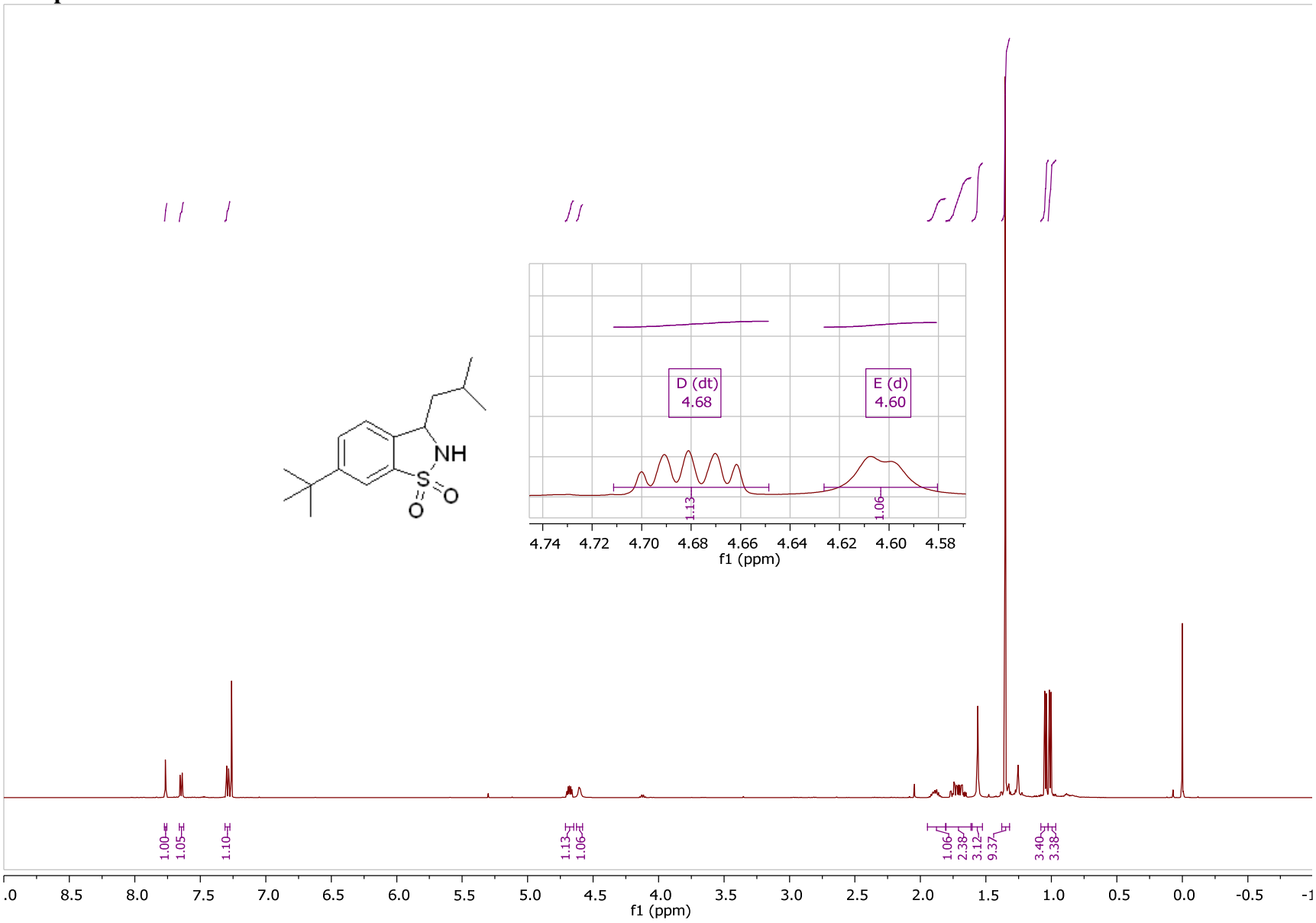
Compound 11b



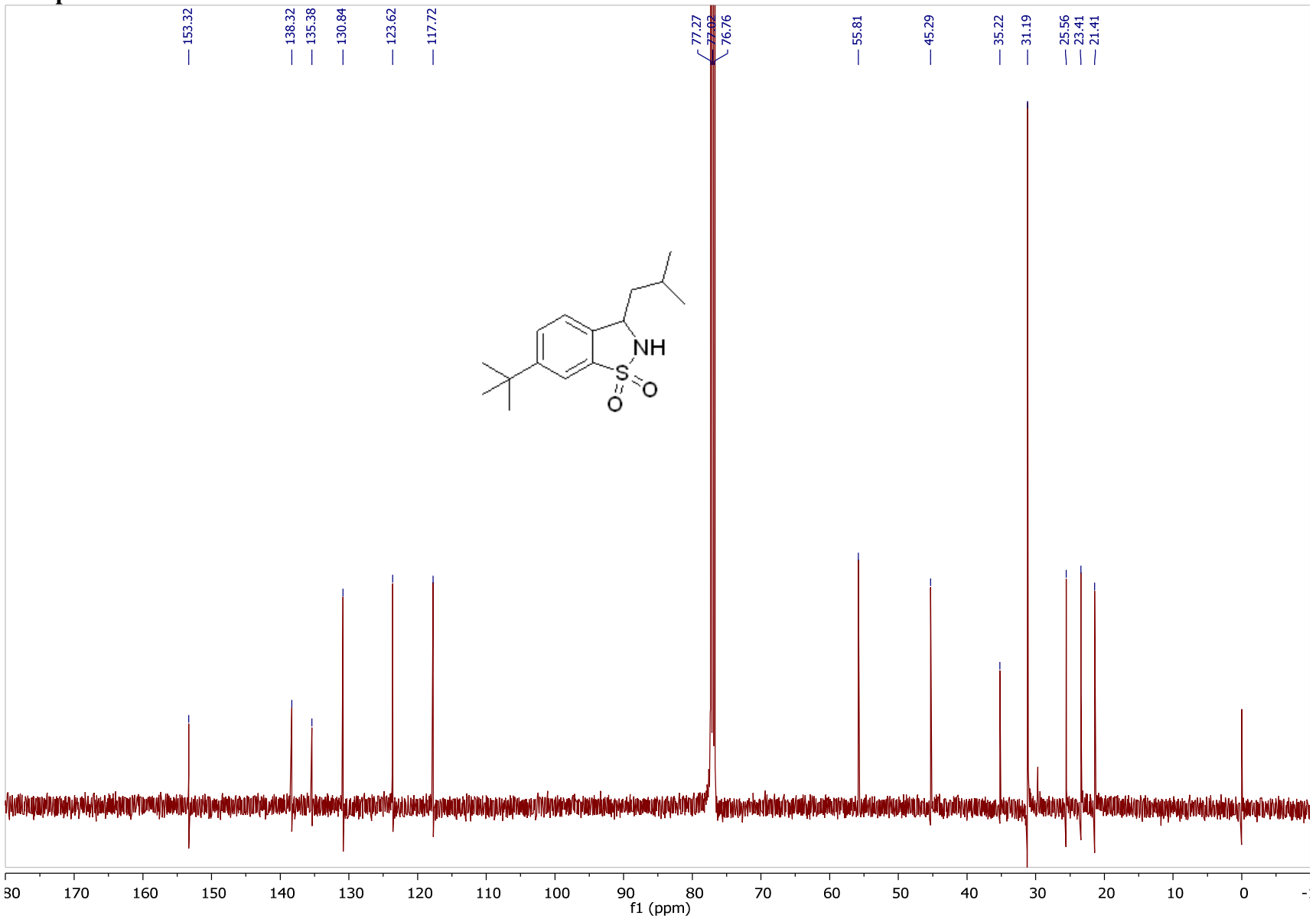
Compound 11b



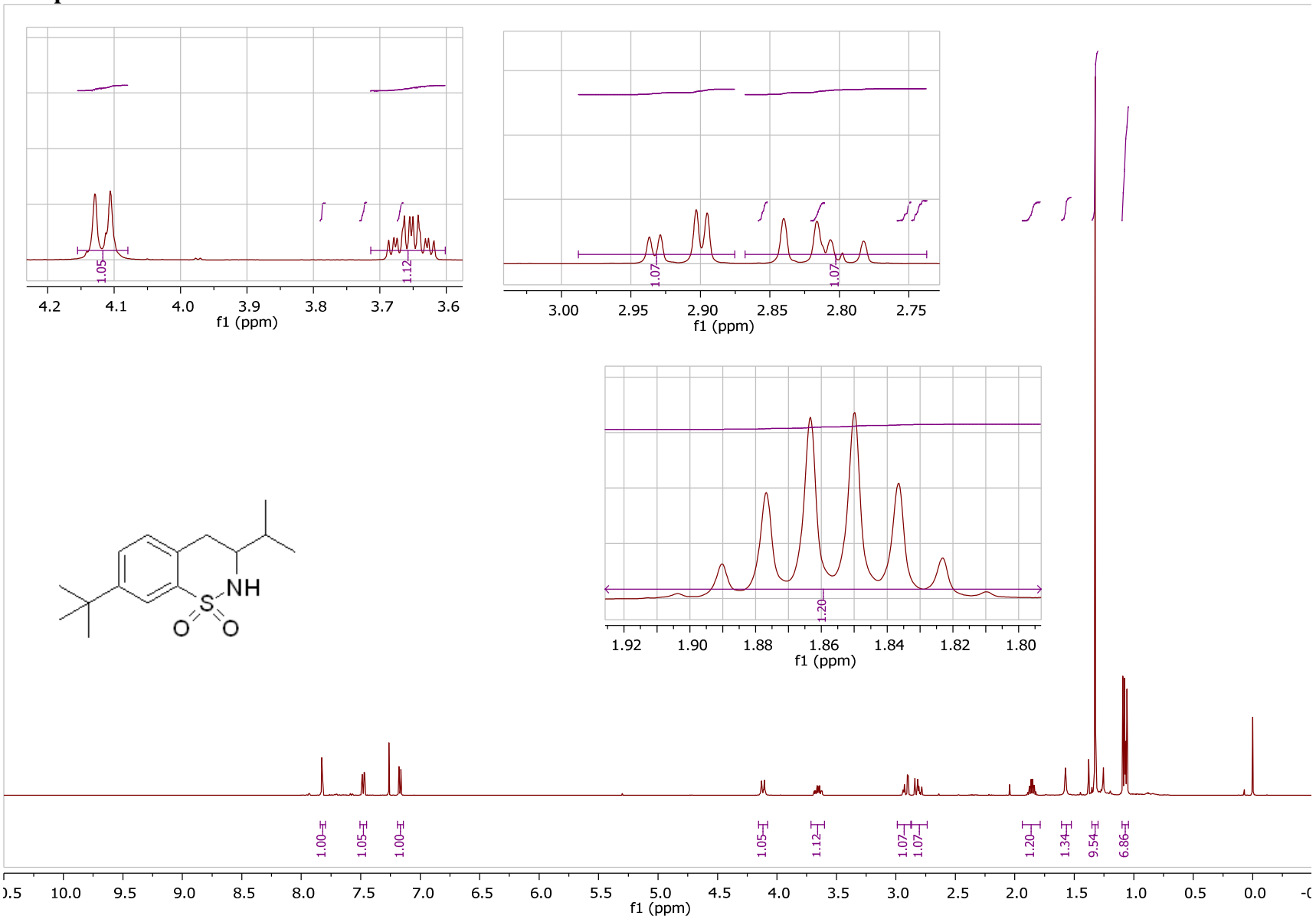
Compound 12a



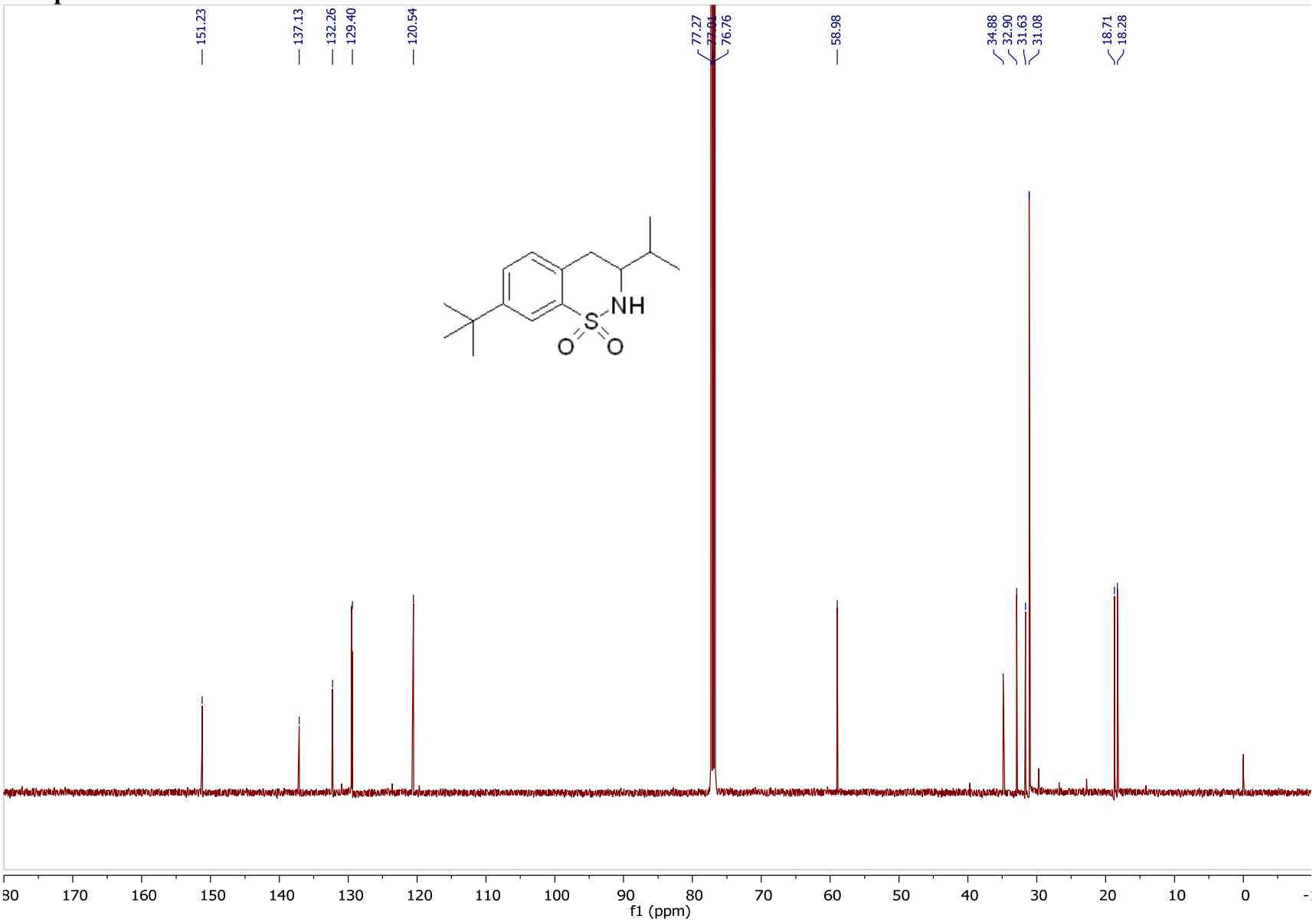
Compound 12a



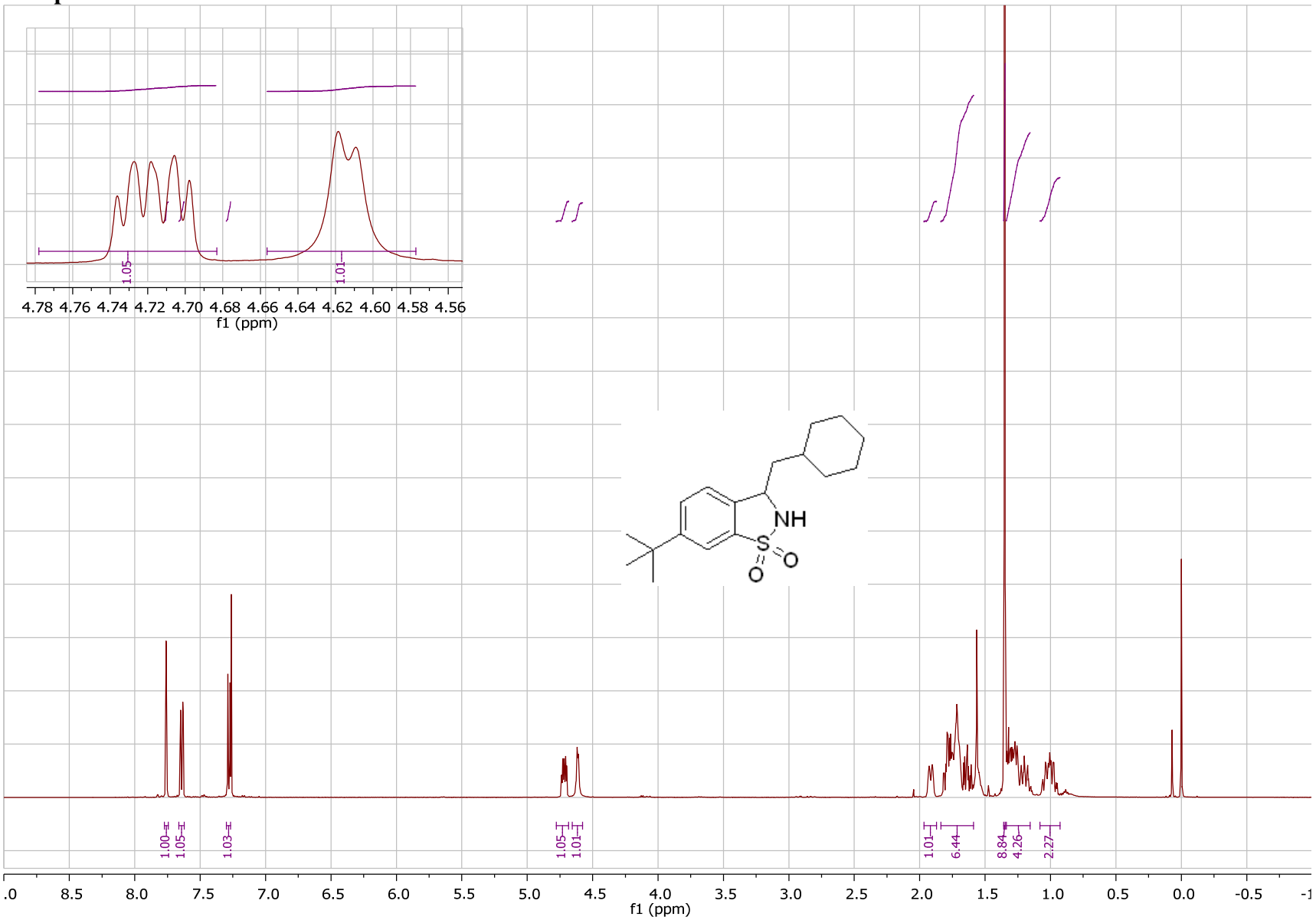
Compound 12b



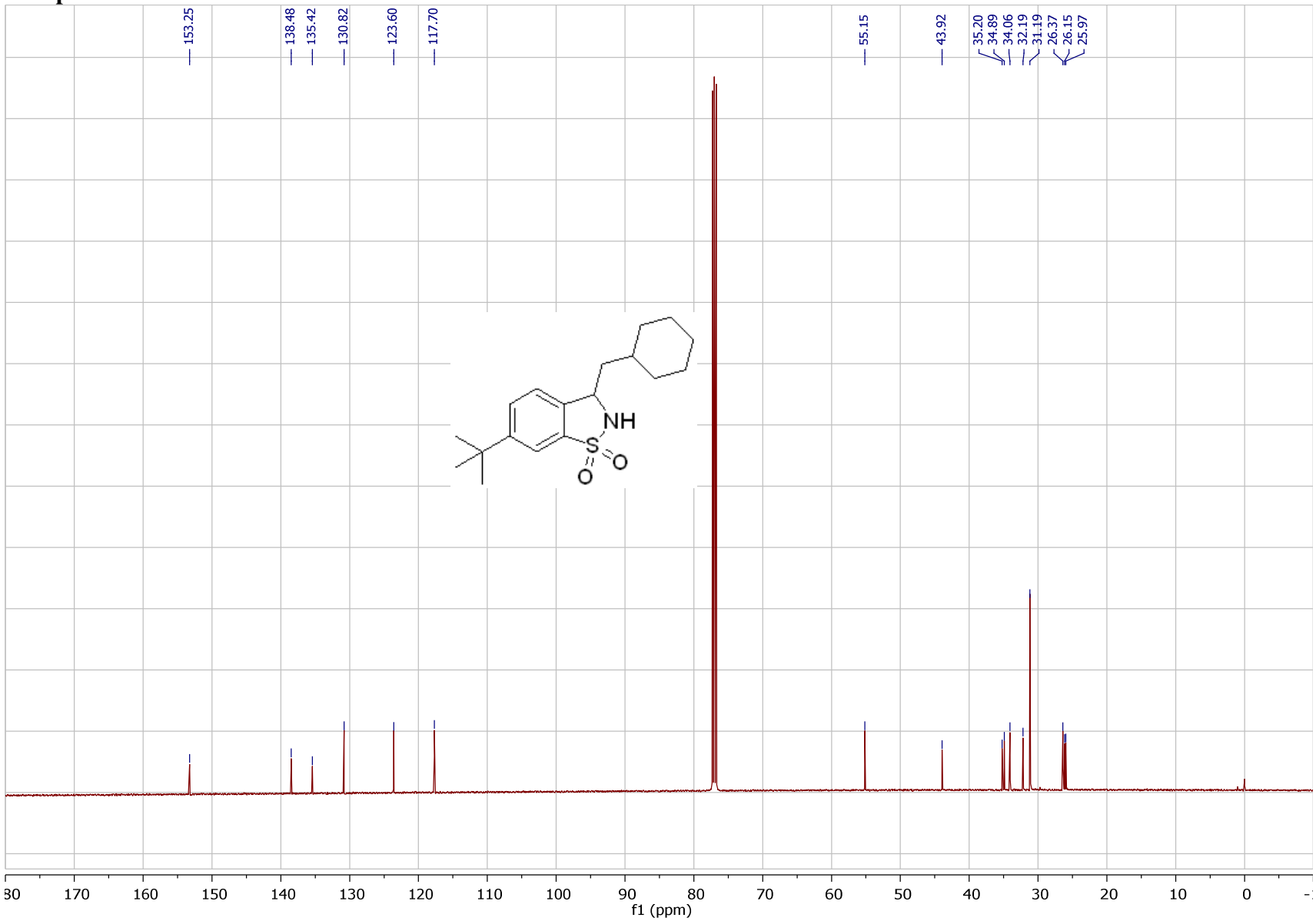
Compound 12b



Compound 13a



Compound 13a



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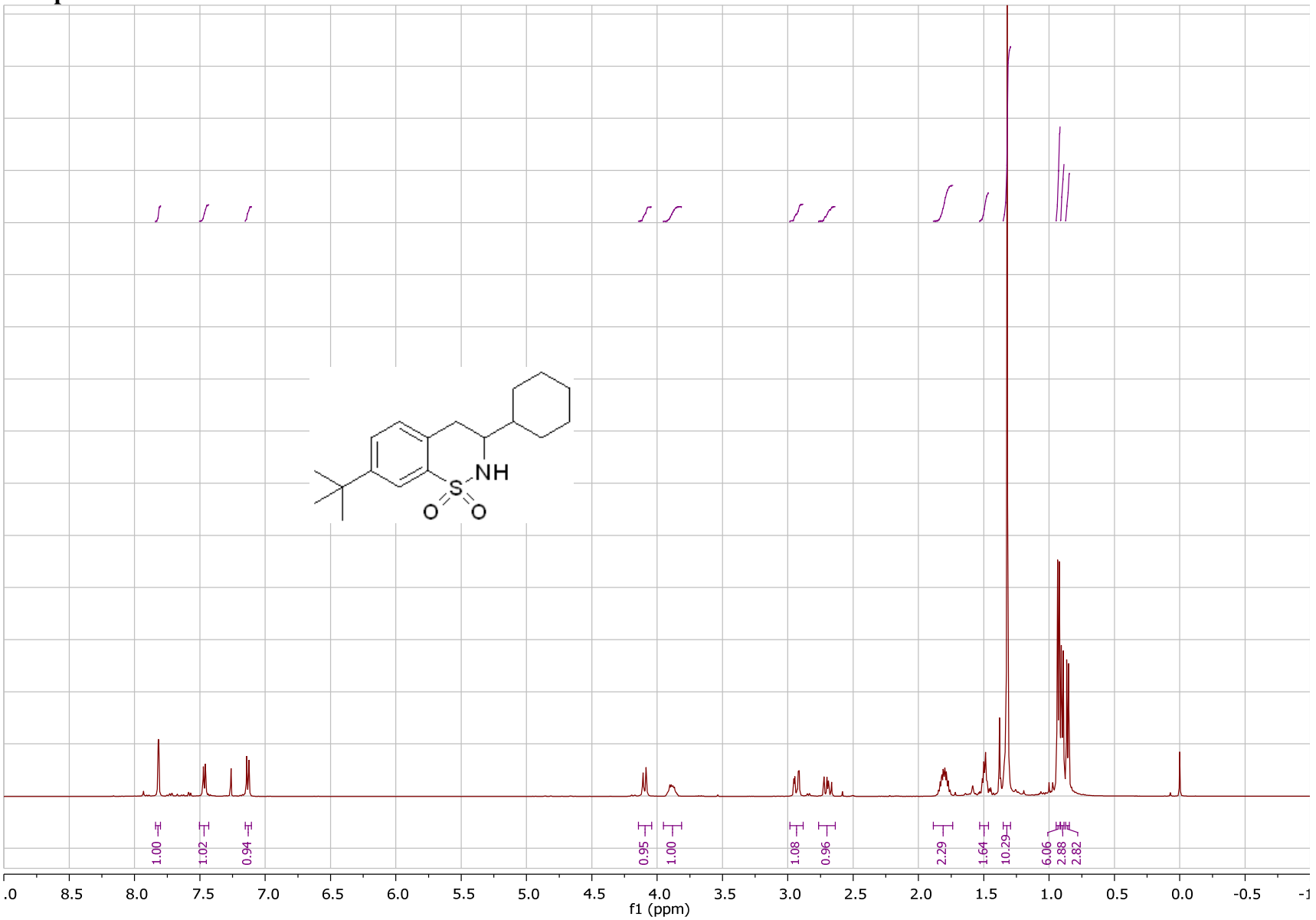
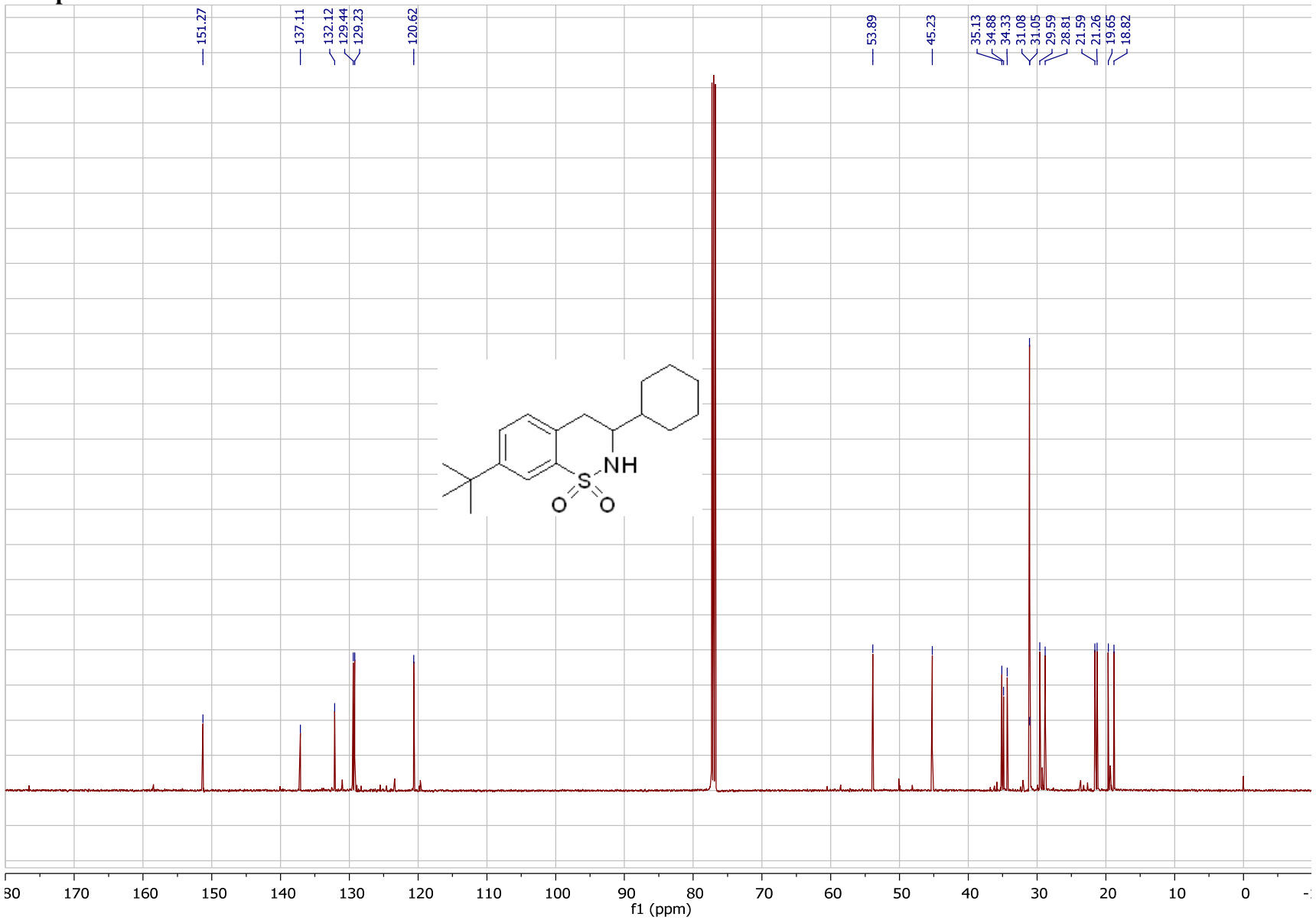
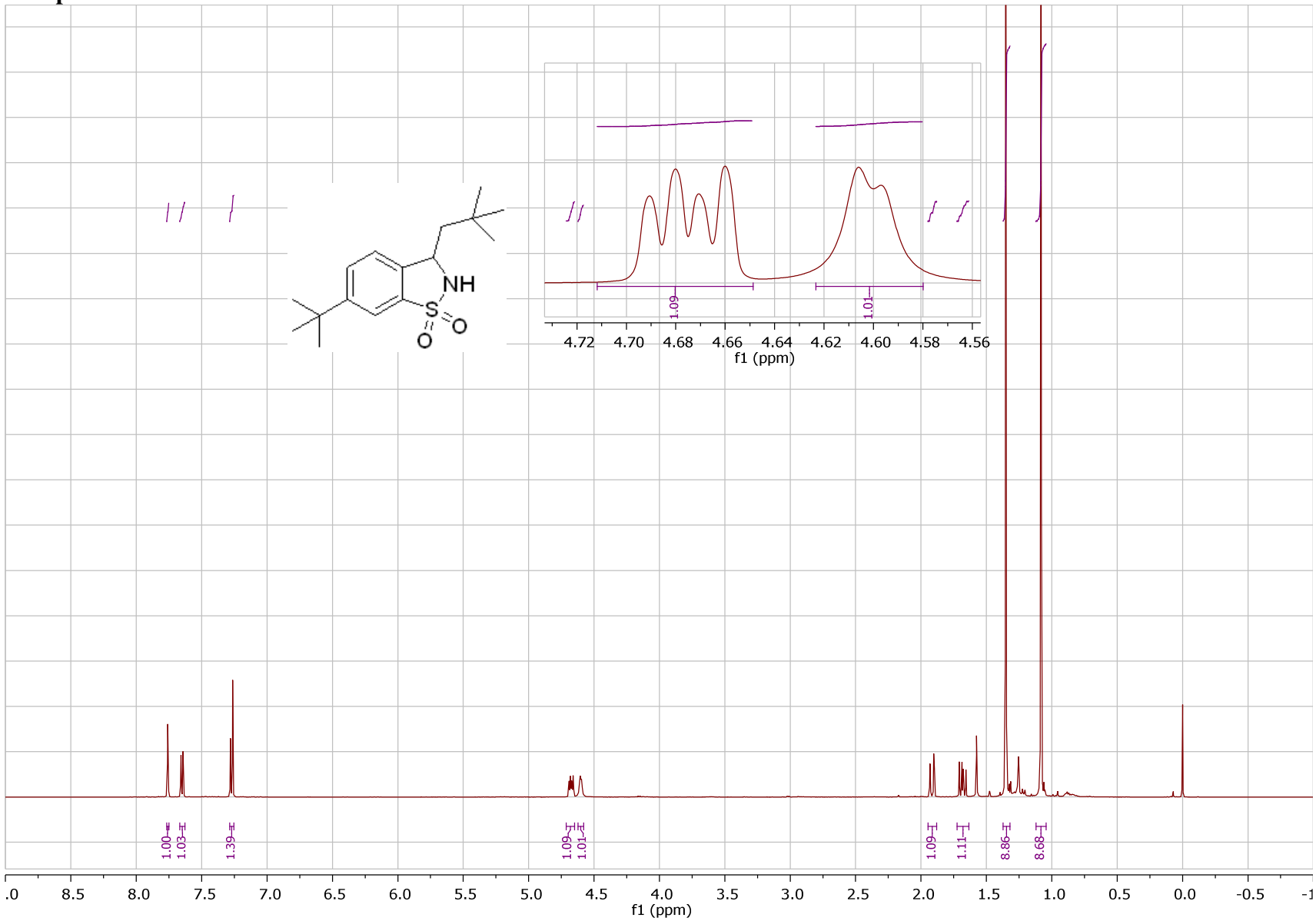


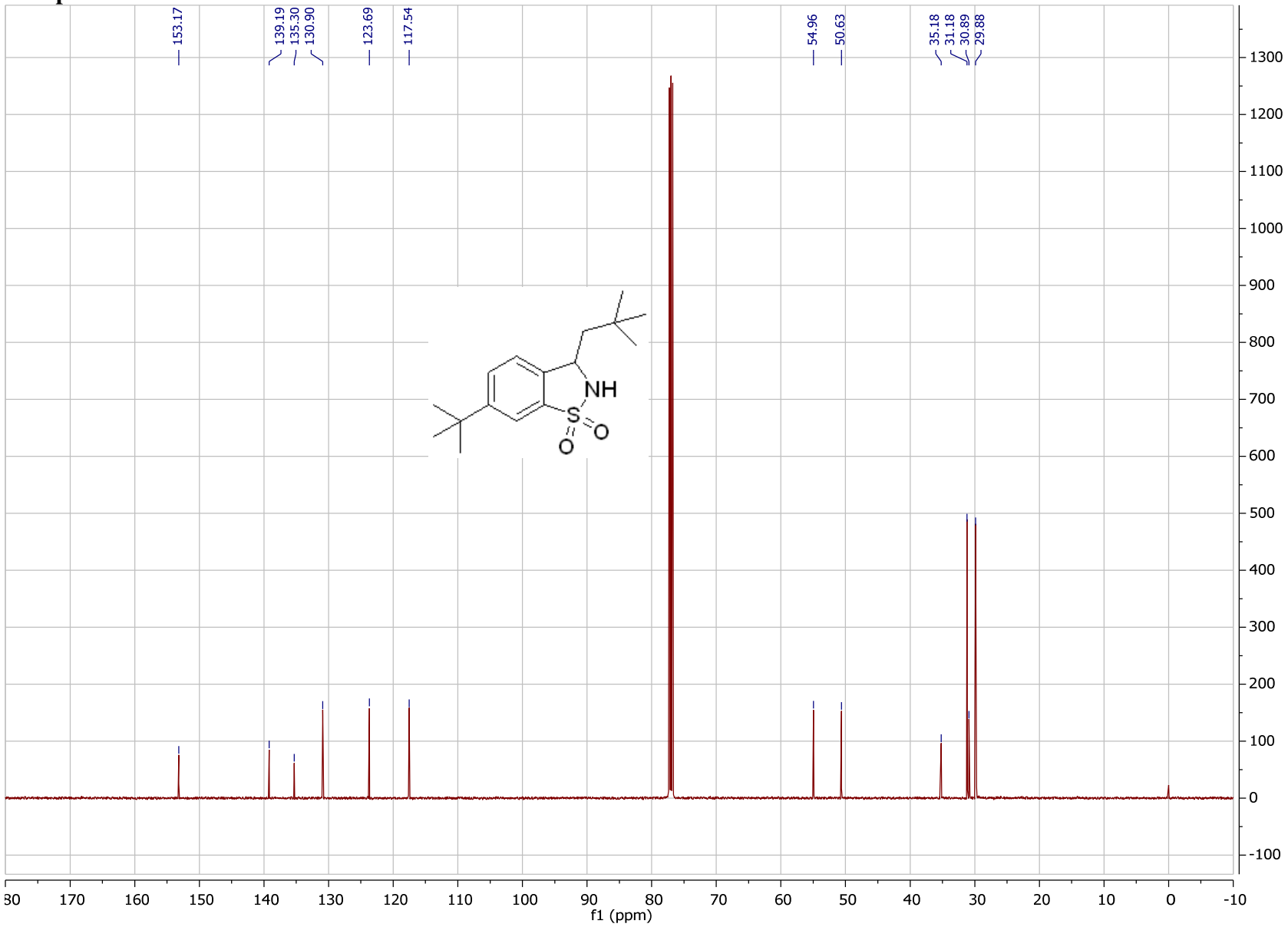
Compound 13b



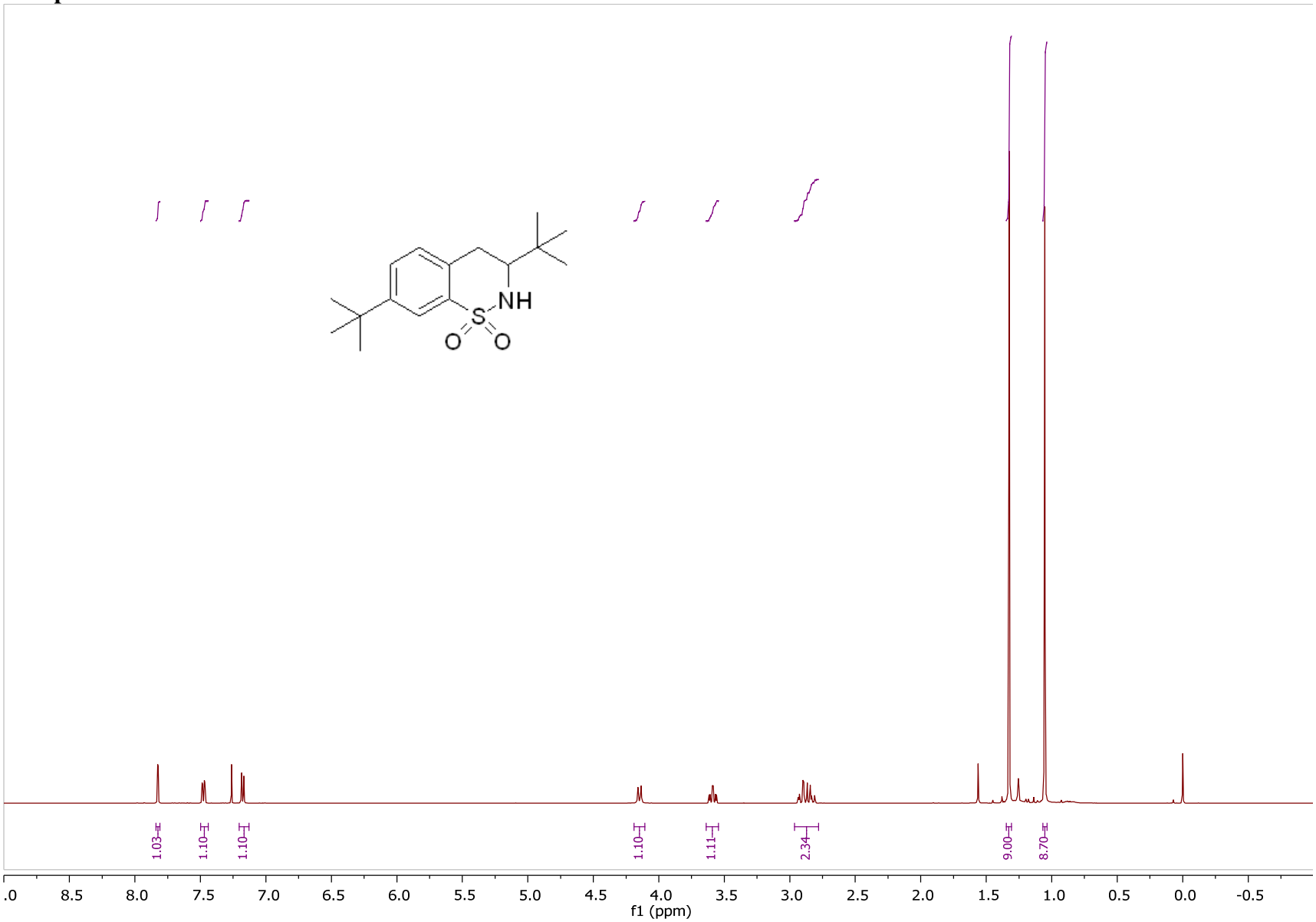
Compound 14a



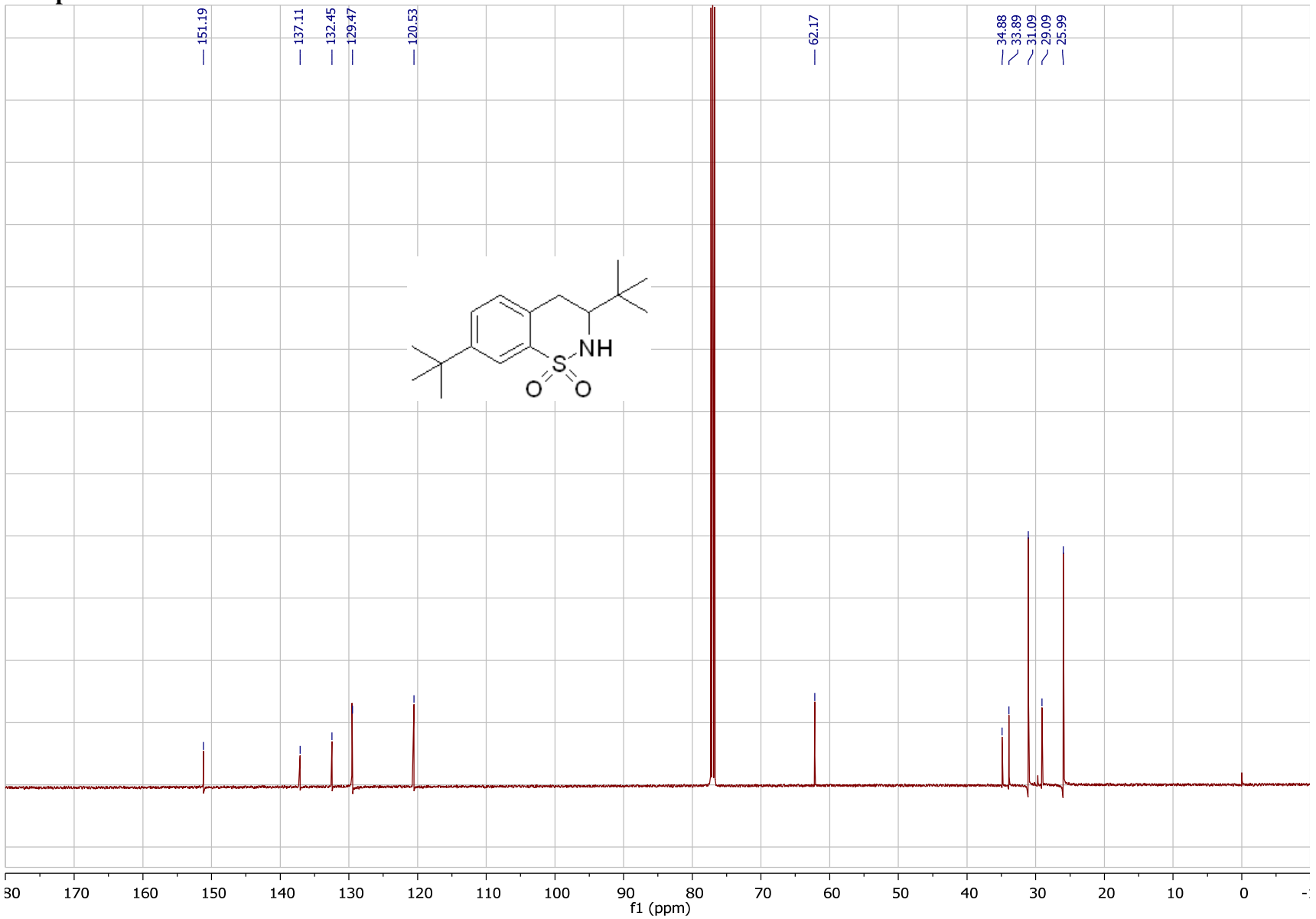
Compound 14a



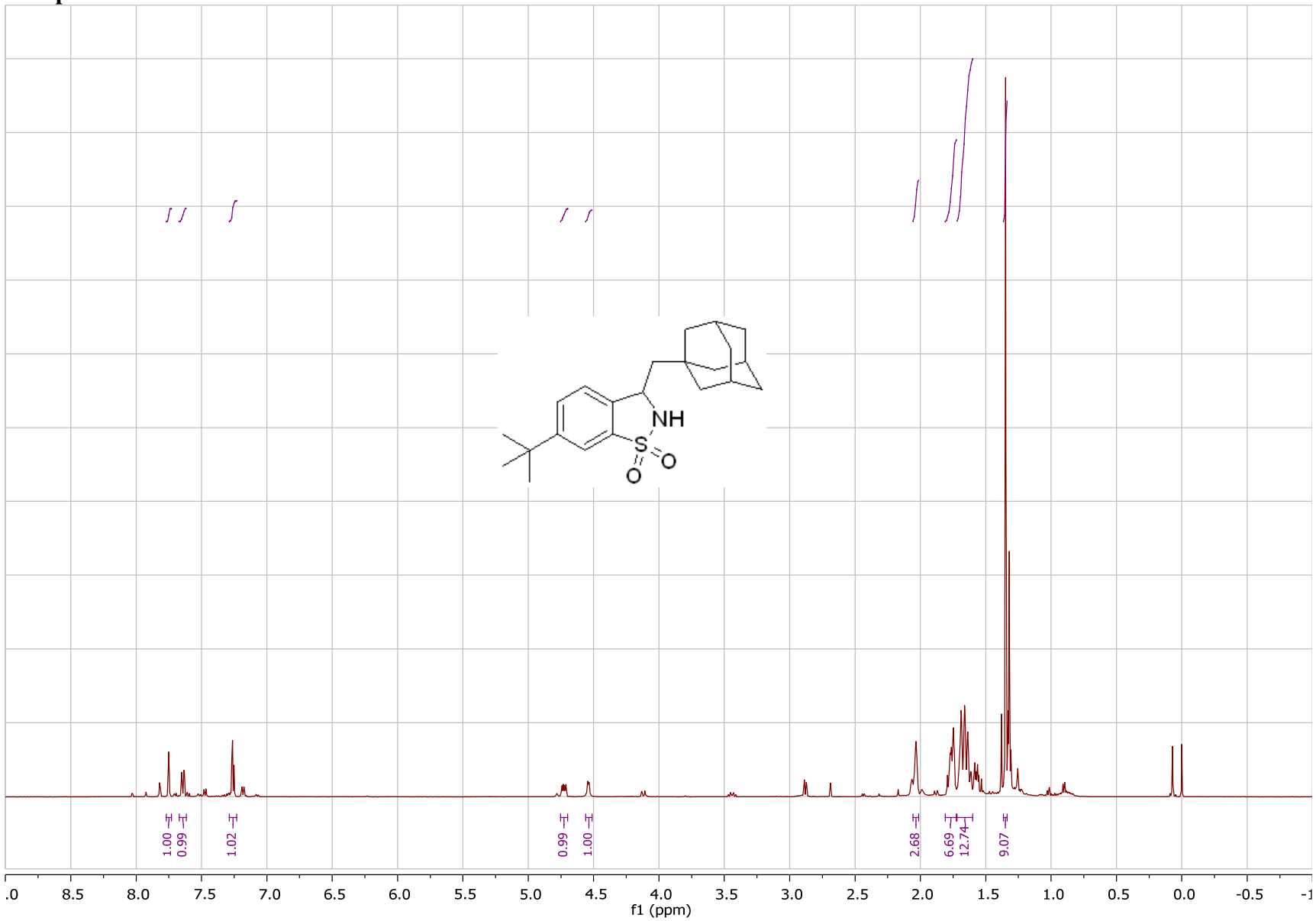
Compound 14b



Compound 14b



Compound 15a



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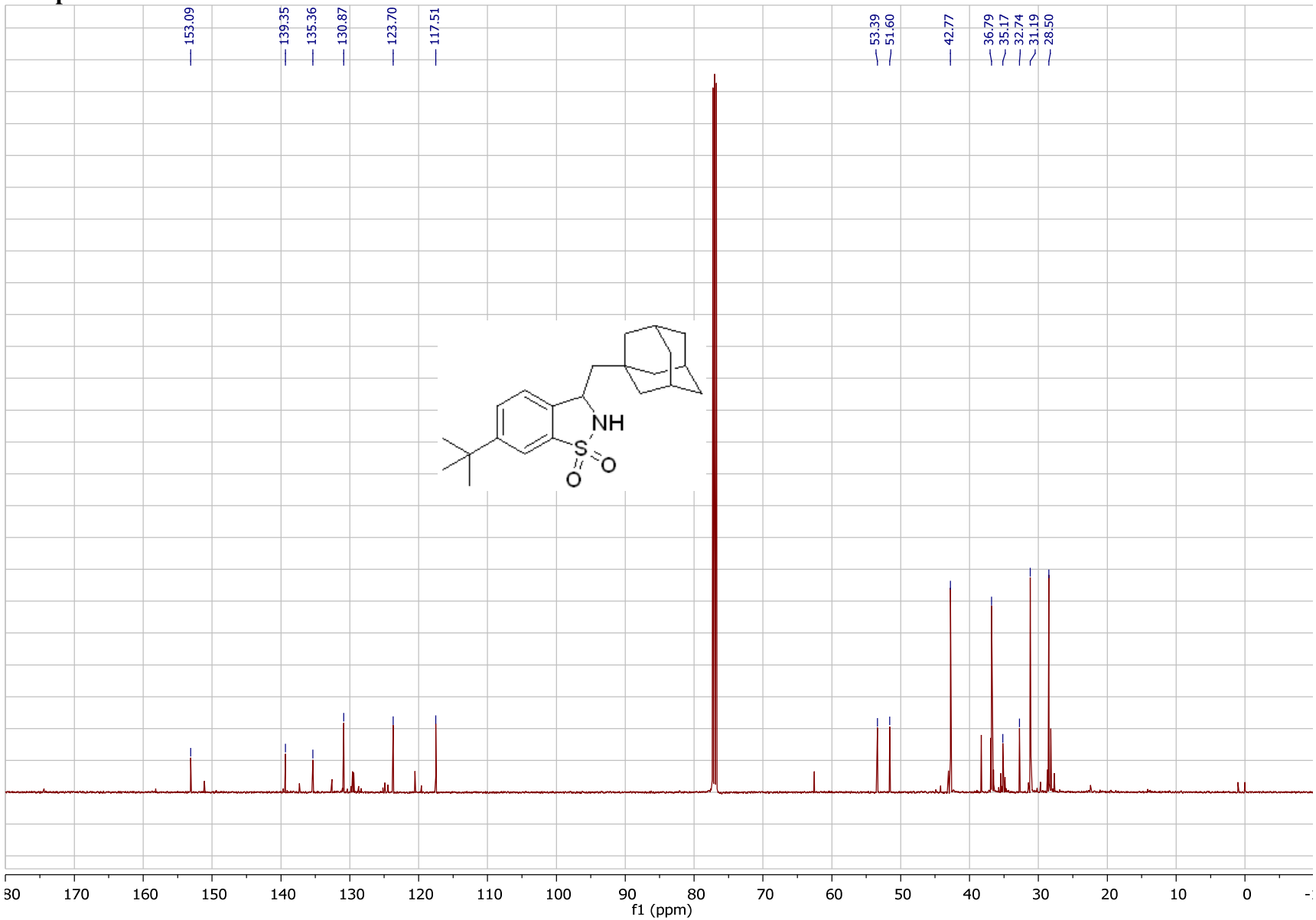

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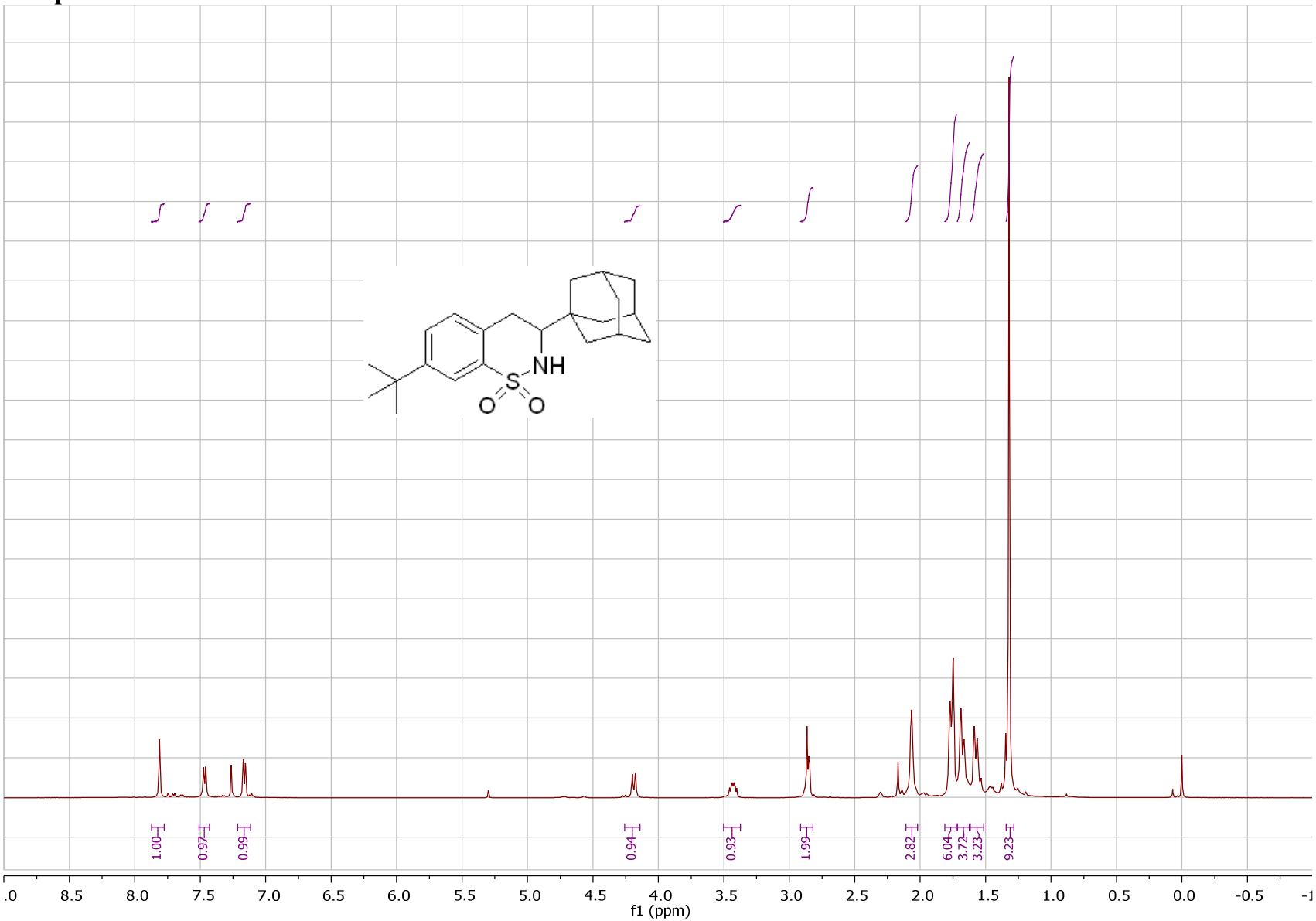

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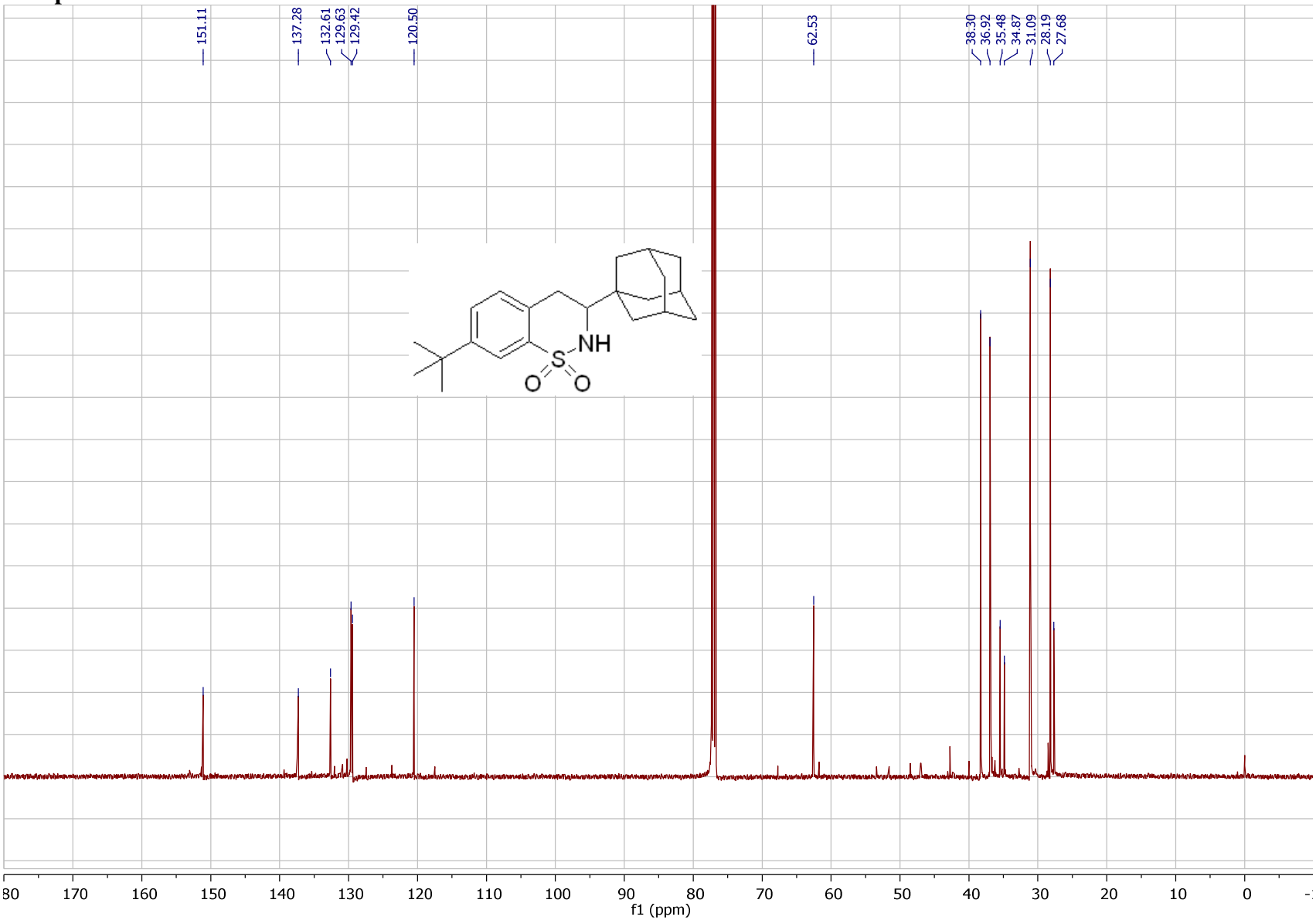
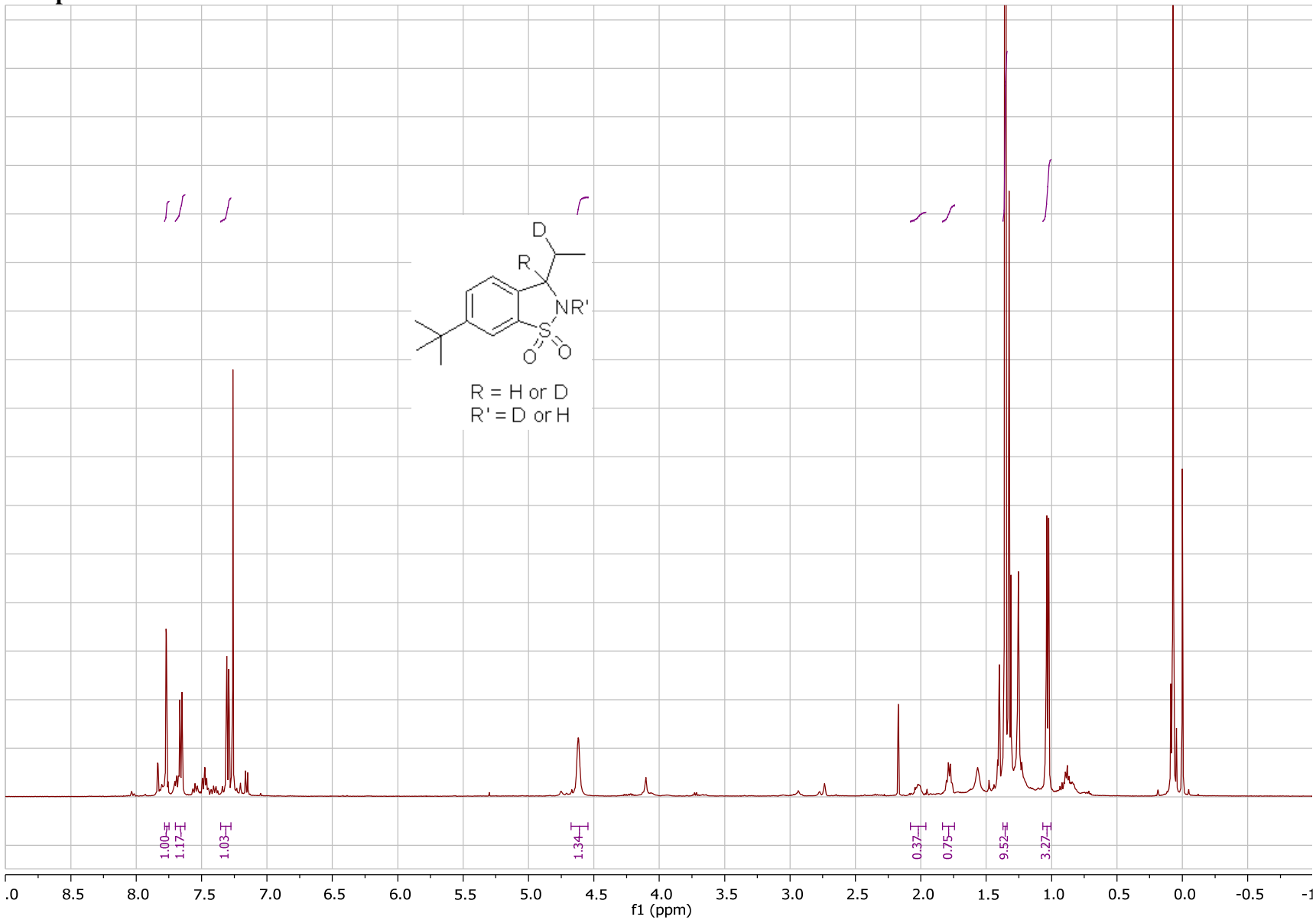
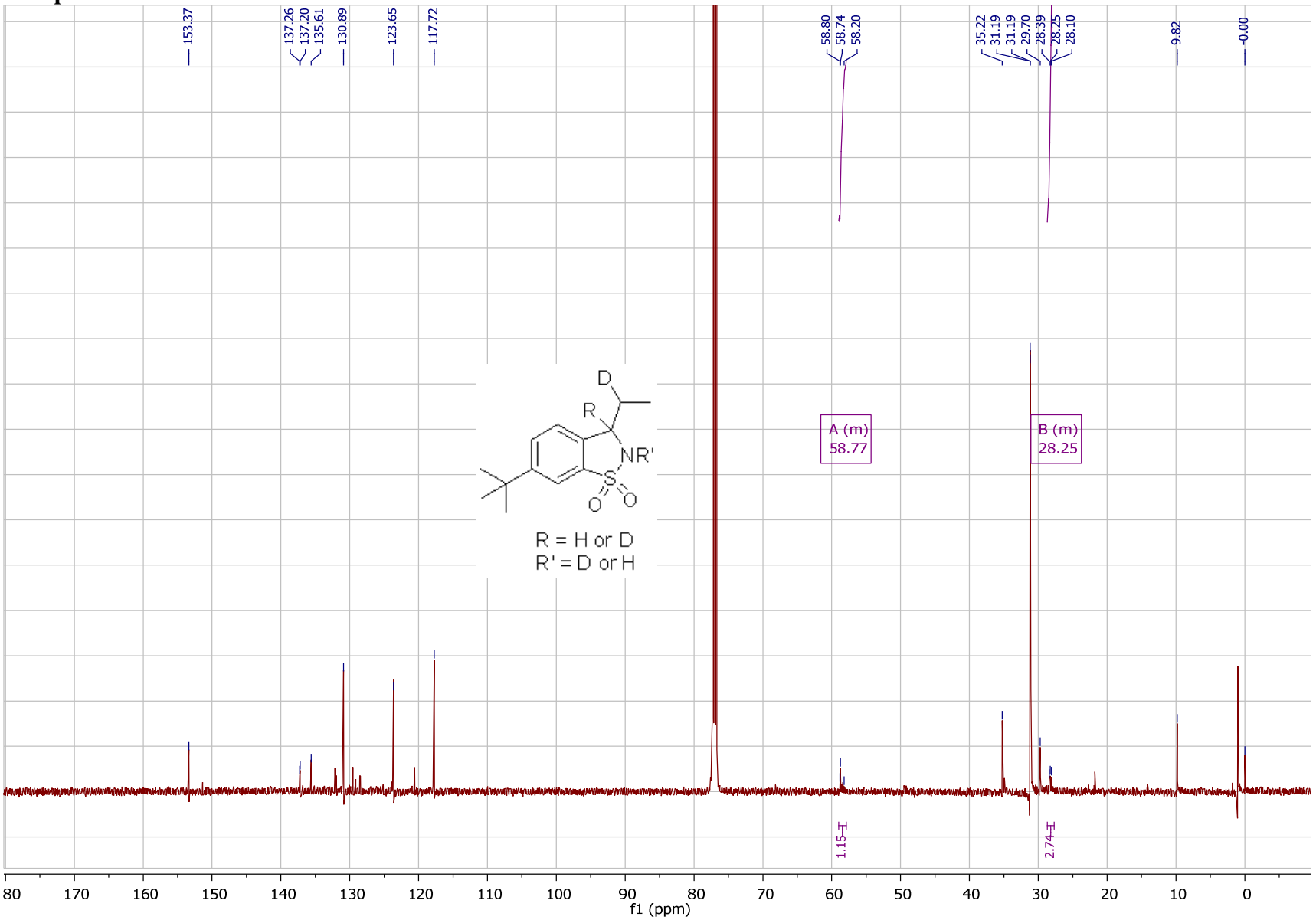


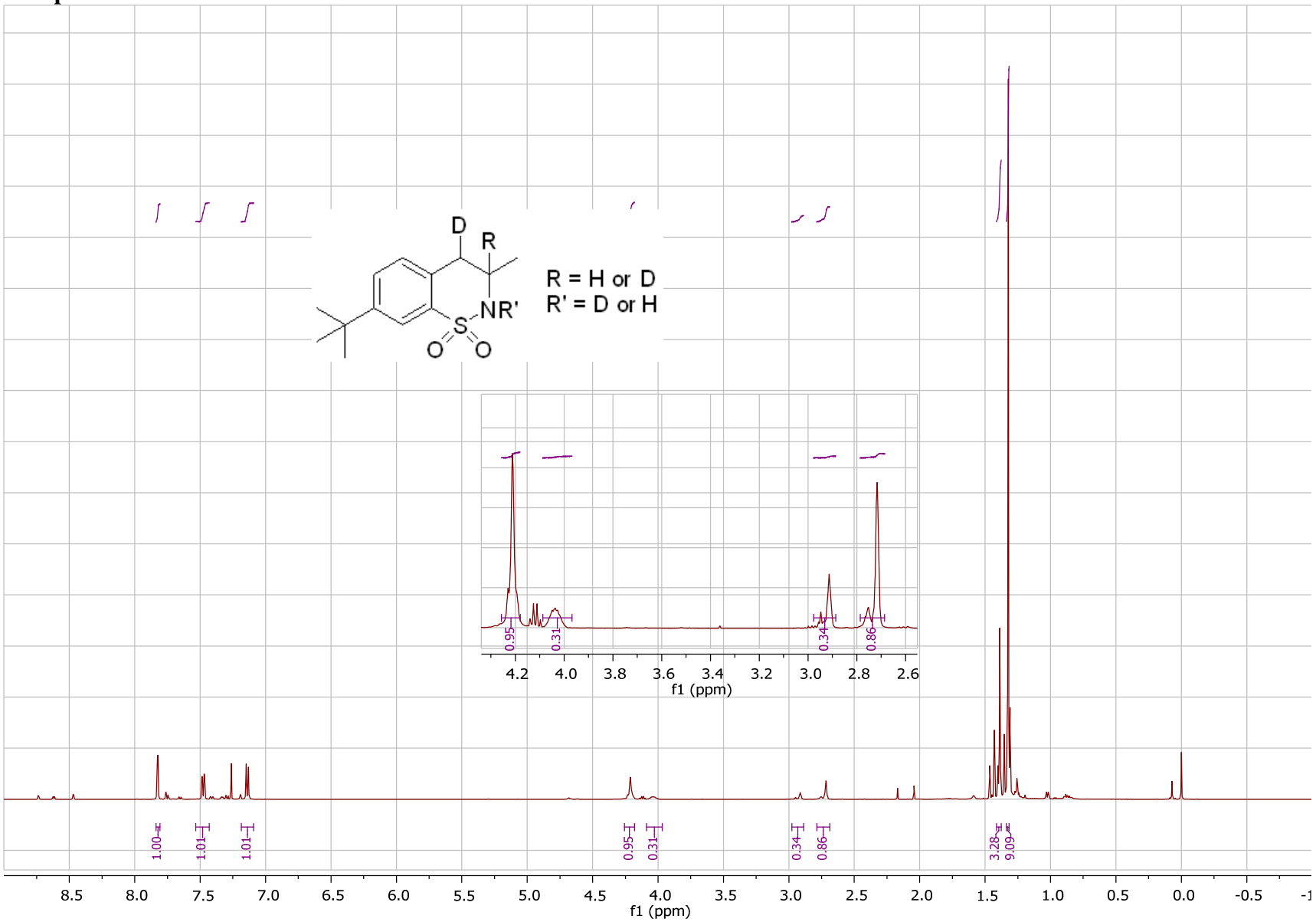
Compound 16a



Compound 16a



Compound 16b



Compound 16b